

180 Topics in Current Chemistry

Density Functional Theory I

Functionals and Effective Potentials

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With 34 Figures and 16 Tables



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Foreword

Density functional theory (DFT) is an entrancing subject. It is entrancing to chemists and physicists alike, and it is entrancing for those who like to work on mathematical physical aspects of problems, for those who relish computing observable properties from theory and for those who most enjoy developing correct qualitative descriptions of phenomena in the service of the broader scientific community.

DFT brings all these people together, and DFT needs all of these people, because it is an immature subject, with much research yet to be done. And yet, it has already proved itself to be highly useful both for the calculation of molecular electronic ground states and for the qualitative description of molecular behavior. It is already competitive with the best conventional methods, and it is particularly promising in the applications of quantum chemistry to problems in molecular biology which are just now beginning. This is in spite of the lack of complete development of DFT itself. In the basic researches in DFT that must go on, there are a multitude of problems to be solved, and several different points of view to find full expression.

Thousands of papers on DFT have been published, but most of them will become out of date in the future. Even collections of works such as those in the present volumes, presentations by masters, will soon be of mainly historic interest. Such collections are all the more important, however, when a subject is changing so fast as DFT. Active workers need the discipline imposed on them by being exposed to the works of each other. New workers can lean heavily on these sources to learn the different viewpoints and the new discoveries. They help allay the difficulties associated with the fact that the literature is in both physics journals and chemistry journals. [For the first two-thirds of my own scientific career, for example, I felt confident that I would miss nothing important if I very closely followed the *Journal of Chemical Physics*. Most physicists, I would guess, never felt the need to consult JCP. What inorganic or organic chemist in the old days took the time to browse in the physics journals?] The literature of DFT is half-divided, and DFT applications are ramping into chemical and physical journals, pure and applied. Watch JCP, *Physical Review A* and *Physical Review B*, and watch even *Physical Review Letters*, if you are a chemist interested in applying DFT. Or ponder the edited volumes, including the present four. Then you will not be surprised by the next round of improvements in DFT methods. Improvements are coming.

The applications of quantum mechanics to molecular electronic structure may be regarded as beginning with Pauling's *Nature of the Chemical Bond*, simple

molecular orbital ideas, and the Hückel and Extended Hückel Methods. The molecular orbital method then was systematically quantified in the Hartree-Fock SCF Method; at about the same time, its appropriateness for chemical description reached its most elegant manifestation in the analysis by Charles Coulson of the Hückel method. Chemists interested in structure learned and taught the nature of the Hartree-Fock orbital description and the importance of electron correlation in it. The Hartree-Fock single determinant is only an approximation. Configurations must be mixed to achieve high accuracy. Finally, sophisticated computational programs were developed by the professional theoreticians that enabled one to compute anything. Some good methods involve empirical elements, some do not, but the road ahead to higher and higher accuracy seemed clear: Hartree-Fock plus correction for electron correlation. Simple concepts in the everyday language of non theoretical chemists can be analyzed (and of course have been much analyzed) in this context.

Then, however, something new came along, density functional theory. This is, of course, what the present volumes are about. DFT involves a profound change in the theory. We do not have merely a new computational gimmick that improves accuracy of calculation. We have rather a big shift of emphasis. The basic variable is the electron density, not the many-body wavefunction. The single determinant of interest is the single determinant that is the exact wavefunction for a noninteracting (electron-electron repulsion-less) system corresponding to our particular system of interest, and has the same electron density as our system of interest. This single determinant, called the Kohn-Sham single determinant, replaces the Hartree-Fock determinant as the wavefunction of paramount interest, with electron correlation now playing a lesser role than before. It affects the potential which occurs in the equation which determines the Kohn-Sham orbitals, but once that potential is determined, there is no configurational mixing or the like required to determine the accurate electron density and the accurate total electronic energy. Hartree-Fock orbitals and Kohn-Sham orbitals are quantitatively very similar, it has turned out. Of the two determinants, the one of Kohn-Sham orbitals is mathematically more simple than the one of Hartree-Fock orbitals. Thus, each KS orbital has its own characteristic asymptotic decay; HF orbitals all share in the same asymptotic decay. The highest KS eigenvalue is the exact first ionization potential; the highest HF eigenvalue is an approximation to the first ionization potential. The KS effective potential is a local multiplicative potential; the HF potential is nonlocal and nonmultiplicative. And so on. When at the Kraków meeting I mentioned to a physicist that I thought that chemists and physicists all should be urged to adopt the KS determinant as the basic descriptor for electronic structure, he quickly replied that the physicists had already done so. So, I now offer that suggestion to the chemistry community.

On the conceptual side, the powers of DFT have been shown to be considerable. Without going into detail, I mention only that the Coulson work referred to above anticipated in large part the formal manner in which DFT describes molecular changes, and that the ideas of electronegativity and hardness fall into place, as do Ralph Pearson's HSAB and Maximum Hardness Principles.

It was Mel Levy, I think who first called density functional theory a charming subject. Charming it certainly is to me. Charming it should be revealed to you as you read the diverse papers in these volumes.

Chapel Hill, 1996

Robert G. Parr

Foreword

Thirty years after Hohenberg and myself realized the simple but important fact that the theory of electronic structure of matter can be rigorously based on the electronic density distribution $n(r)$ a most lively conference was convened by Professor R. Nalewajski and his colleagues at the Jagiellonian University in Poland's historic capital city, Krakow. The present series of volumes is an outgrowth of this conference.

Significantly, attendees were about equally divided between theoretical physicists and chemists. Ten years earlier such a meeting would not have had much response from the chemical community, most of whom, I believe, deep down still felt that density functional theory (DFT) was a kind of mirage. Firmly rooted in a tradition based on Hartree Fock wavefunctions and their refinements, many regarded the notion that the many electron function, $\Psi(r_1 \dots r_N)$ could, so to speak, be traded in for the density $n(r)$, as some kind of not very serious slight-of-hand. However, by the time of this meeting, an attitudinal transformation had taken place and both chemists and physicists, while clearly reflecting their different upbringings, had picked up DFT as both a fruitful viewpoint and a practical method of calculation, and had done all kinds of wonderful things with it.

When I was a young man, Eugene Wigner once said to me that understanding in science requires understanding from *several different points of view*. DFT brings such a new point of view to the table, to wit that, in the ground state of a chemical or physical system, the electrons may be regarded as a *fluid* which is fully characterized by its density distribution, $n(r)$. I would like to think that this viewpoint has enriched the theory of electronic structure, including (via potential energy surfaces) molecular structure; the chemical bond; nuclear vibrations; and chemical reactions.

The original emphasis on electronic ground states of non-magnetic systems has evolved in many different directions, such as thermal ensembles, magnetic systems, time-dependent phenomena, excited states, and superconductivity. While the abstract underpinning is exact, implementation is necessarily approximate. As this conference clearly demonstrated, the field is vigorously evolving in many directions: rigorous sum rules and scaling laws; better understanding and description of correlation effects; better understanding of chemical principles and phenomena in terms of $n(r)$; application to systems consisting of thousands of atoms; long range polarization energies; excited states.

Here is my personal wish lists for the next decade: (1) An improvement of the accuracy of the exchange-correlation energy $E_{xc}[n(r)]$ by a factor of 3-5. (2) A practical, systematic scheme which, starting from the popular local density approach, can – with sufficient effort – yield electronic energies with any specified accuracy. (3) A sound DFT of excited states with an accuracy and practicality comparable to present DFT for ground states. (4) A practical scheme for calculating electronic properties of systems of 10^3 - 10^5 atoms with "chemical accuracy". The great progress of the last several years made by many individuals, as mirrored in these volumes, makes me an optimist.

Santa Barbara, 1996

Walter Kohn

Preface

Density functional methods emerged in the early days of quantum mechanics; however, the foundations of the modern density functional theory (DFT) were established in the mid 1960s with the classical papers by Hohenberg and Kohn (1964) and Kohn and Sham (1965). Since then impressive progress in extending both the theory formalism and basic principles, as well as in developing the DFT computer software has been reported. At the same time, a substantial insight into the theory structure and a deeper understanding of reasons for its successes and limitations has been reached. The recent advances, including new approaches to the classical Kohn-Sham problem and constructions of more reliable functionals, have made the ground-state DFT investigations feasible also for very large molecular and solid-state systems (of the order of 10^3 atoms), for which conventional CI calculations of comparable accuracy are still prohibitively expensive. The DFT is not free from difficulties and controversies but these are typical in a case of a healthy, robust discipline, still in a stage of fast development. The growing number of monographs devoted to this novel treatment of the quantum mechanical many body problem is an additional measure of its vigor, good health and the growing interest it has attracted.

In addition to a traditional, solid-state domain of applications, the density functional approach also has great appeal to chemists due to both computational and conceptual reasons. The theory has already become an important tool within quantum chemistry, with the modern density functionals allowing one to tackle problems involving large molecular systems of great interest to experimental chemists. This great computational potential of DFT is matched by its already demonstrated capacity to both rationalize and quantify basic classical ideas and rules of chemistry, e.g., the electronegativity and hardness/softness characteristics of the molecular electron distribution, bringing about a deeper understanding of the nature of the chemical bond and various reactivity preferences. The DFT description also effects progress in the theory of chemical reactivity and catalysis, by offering a "thermodynamic-like" perspective on the electron cloud reorganization due to the reactant/catalyst presence at various intermediate stages of a reaction, e.g. allowing one to examine the relative importance of the polarization and charge transfer components in the resultant reaction mechanism, to study the influence of the infinite surface reminder of cluster models of heterogeneous catalytic systems, etc.

The 30th anniversary of the modern DFT was celebrated in June 1994 in Cracow,

where about two hundred scientists gathered at the ancient Jagiellonian University during the International Symposium: "Thirty Years of Density Functional Theory: Concepts and Applications", Satellite Meeting of the 8th International Congress of Quantum Chemistry in Prague. Professors Walter Kohn, Norman H. March and Robert G. Parr were the honorary chairmen of the conference. Most of the reviewers of these four volumes include the plenary lecturers of this symposium; other leading contributors to the field, physicists and chemists, were also invited to take part in this DFT survey. The fifteen chapters of this DFT series cover both the basic theory (Parts I, II, and the first article of Part III), applications to atoms, molecules and clusters (Part III), as well as the chemical reactions and the DFT rooted theory of chemical reactivity (Part IV). This arrangement has emerged as a compromise between the volume size limitations and the requirements of the maximum thematic unity of each part.

In these four DFT volumes of the *Topics in Current Chemistry* series, a real effort has been made to combine the authoritative reviews by both chemists and physicists, to keep in touch with a wider spectrum of current developments. The Editor deeply appreciates a fruitful collaboration with Dr. R. Stumpe, Dr. M. Hertel and Ms B. Kollmar-Thoni of the Springer-Verlag Heidelberg Office, and the very considerable labour of the Authors in preparing these interesting and informative monographic chapters.

Cracow, 1996

Roman F. Nalewajski

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Gradient-corrected or semi-local functionals (GGA's) have achieved the accuracy required to make density functional theory a useful tool in quantum chemistry. We show that local (LSD) and semi-local functionals work because they usefully model the exchange-correlation hole around an average electron, rather than by yielding accurate results at all electron positions. We discuss the system-averaged hole at small interelectronic separations, where such functionals are extremely accurate, and at large interelectronic separations, where the local approximation is incorrect for finite systems. We argue that the "on-top" hole density provides the missing link between real atoms and molecules and the uniform electron gas. We show how exchange-correlation potentials can be related to energies. We also discuss how the degree of nonlocality, i.e., the error made by LSD, is related to the spatial extent of the hole. Decomposing the energy by coupling-constant and spin, we find that the deeper the on-top hole is, the smaller the error in the local approximation to the energy. We use this insight to demonstrate that Hartree-Fock hybrid functionals do not consistently improve on GGA. A different hybrid invokes wavefunction methods for exchange and parallel-spin correlation, but we show that configuration interaction wavefunction calculations with limited basis sets for the Ne atom make the same relative errors in the antiparallel- and parallel-spin correlation energies, despite the lack of a Coulomb cusp in the parallel-spin correlation hole. Finally, we review a recent reinterpretation of spin density functional theory, which is preferable to the standard interpretation in certain cases of extreme nonlocality.

1 Density Functionals in Quantum Chemistry and Solid-State Physics: Introduction and Summary

Most practical electronic structure calculations using density functional theory [1] involve solving the Kohn-Sham equations [2]. The only unknown quantity in a Kohn-Sham spin-density functional calculation is the exchange-correlation energy (and its functional derivative) [2]

$$E_{xc} = T - T_s + V_{ee} - U, \quad (1)$$

where T is the interacting kinetic energy, T_s is the non-interacting kinetic energy, V_{ee} is the exact Coulomb repulsion, and $U = \int d^3r \int d^3r' n(\mathbf{r})n(\mathbf{r}')/2|\mathbf{r} - \mathbf{r}'|$ is the classical Coulomb energy associated with the density $n(\mathbf{r})$. Modern density functional calculations are based on some approximate form of E_{xc} . For example, the local spin density (LSD) approximation [2] is:

$$E_{xc}^{\text{LSD}}[n_{\uparrow}, n_{\downarrow}] = \int d^3r n(\mathbf{r}) \epsilon_{xc}^{\text{unif}}(n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r})), \quad (2)$$

where $\epsilon_{xc}^{\text{unif}}(n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r}))$ is the exchange-correlation energy per particle of a uniform electron gas (jellium) [3, 4]. Eq. (2) is exact for an electron gas of uniform (jellium) or slowly-varying spin densities.

For many years, LSD has been very popular with solid-state physicists [1], and quite unpopular with quantum chemists [5]. LSD achieves a remarkable moderate accuracy for the energies and densities of almost all systems, no matter how rapidly their densities vary. In fact, LSD solid-state calculations are often called *ab initio*. However, this moderate accuracy is insufficient for chemical purposes, and no way was known to improve the approximation systematically.

Recently, a new class of functionals, called generalized gradient approximations (GGA's) [6–14], has been developed. These take the general form

$$E_{xc}^{GGA}[n_{\uparrow}, n_{\downarrow}] = \int d^3r f(n_{\uparrow}(r), n_{\downarrow}(r), \nabla n_{\uparrow}, \nabla n_{\downarrow}), \quad (3)$$

where the function f is chosen by some set of criteria. The idea is that, by including information about the gradient, one should be able to improve the accuracy of the functional. Several forms for f are currently in use in the literature [7–11], but we focus on the Perdew-Wang 1991 (PW91) form [11–14], because it is derived without semiempirical parameters and is the ‘best’ functional on formal grounds [12]. Results of calculations with this form show that it typically reduces exchange energy errors from 10% in LSD to 1% and correlation energy errors from 100% to about 10% [13]. PW91 corrects the LSD overestimate of atomization energies for molecules and solids in almost all cases, it enlarges equilibrium bond lengths and lattice spacings, usually correctly, and reduces vibrational frequencies and bulk moduli, again usually correctly [14]. PW91 also generally improves activation barriers [15] and yields an improved description of the phase diagram of Fe under normal or high pressure [16]. In almost all cases where PW91 has been carefully tested, it significantly improves on LSD. Thus PW91 and similar GGA's have become popular in quantum chemistry.

The success of PW91 can be understood in terms of its construction as a systematic, parameter-free refinement of LSD. While LSD does not typically work well at all points in the system (Sect. 2.1), it does remarkably well for system-averaged quantities, such as the energy, because the average electron lives in a region of moderate density variation and because the LSD exchange-correlation hole satisfies many conditions satisfied by the exact hole. A straightforward gradient expansion violates these conditions, but a real-space cutoff procedure restores them [8, 11], leading to an improved description of system-averaged quantities, as shown in Sect. 2.2. The PW91 functional is a parametrization of the result of this procedure. In particular, we study the system-averaged exchange-correlation hole, a function of the separation between any two points in the system, and demonstrate that LSD gives a remarkably accurate description of this quantity [17], which is improved by PW91 [17].

The LSD and PW91-GGA system-averaged holes agree at zero interelectronic separation, where both are nearly exact. In Sect. 2.3, we discuss how the near-universality of this “on-top” hole density provides the missing link between real atoms and molecules and the uniform electron gas. Except very close to the nucleus, the *local* on-top hole density is also accurately represented by LSD, even in the classically-forbidden tail region of the electron density [18].

In Ref. [12], Perdew and Burke made a graphical comparison of various GGA's. The popular functionals for exchange (Perdew-Wang 86 [8], Becke 88 [9], and Perdew-Wang 91 [11–14]) are similar for practical purposes, but the popular functionals for correlation are not. In particular, the Lee-Yang-Parr 88 [10] functional is rather different from the Perdew-Wang 1986 [7], and 1991 [11–14] correlation functionals. In fact, the LYP correlation energy is in error

by about a factor of two in the important uniform-gas limit [18]. We discuss this difference further in Sect. 2.4, as we believe it has important consequences for the description of delocalized electrons in carbon clusters and metals, and for spin-magnetized systems. Indeed, because PW91 is the “most local” [12] of the GGA’s for exchange and correlation, as defined in Sect. 3, it is the least likely to overcorrect the subtle LSD errors for solids.

While the LSD exchange-correlation hole is accurate for small interelectronic separations (Sect. 2.3), it is less satisfactory at large separations, as discussed in Sect. 2.5. For example, consider the hole for an electron which has wandered out into the classically-forbidden tail region around an atom (or molecule). The exact hole remains localized around the nucleus, and in Sect. 2.5 we give explicit results for its limiting form as the electron moves far away [19]. The LSD hole, however, becomes more and more diffuse as the density at the electron’s position gets smaller, and so is quite incorrect. The weighted density approximation (WDA) and the self-interaction correction (SIC) both yield more accurate (but not exact) descriptions of this phenomenon.

PW91 and other GGA’s significantly improve the exchange-correlation energy, but the corresponding potential $v_{xc} = \delta E_{xc}/\delta n(\mathbf{r})$ is *not* much improved over LSD, and is in some respects worse [20–22]. We address this point in detail in Sect. 2.6. From our perspective, this is neither a surprising nor disturbing result. We are fitting a “square peg” (the exact $E_{xc}[n_{\uparrow}, n_{\downarrow}]$ with its derivative discontinuities [23, 24]) into a “round hole” (the simple continuum approximation of Eq. (3)). The areas (integrated properties) of a square and circle can be matched, but their perimeters (differential properties) remain stubbornly different. (For completeness, we note that the potential $v_{xc}(\mathbf{r})$, a functional derivative, can also be constructed from a more physical perspective [25–29].)

While PW91 and other GGA’s are more accurate than LSD, another factor-of-five reduction in error is needed to reach chemical accuracy. This might be achieved by isolating those aspects of the exchange-correlation problem that local and semi-local approximations treat well, and using more non-local approaches for the remainder. To do this, we must first understand the origin of nonlocal effects, i.e., corrections to LSD, in the energy (Sect. 3). Because LSD works best in the vicinity of the electron, the shorter the range of the hole, the better it is described by local and semi-local approximations [18]. Furthermore, because of sum-rules satisfied by both the exact hole and its functional approximation, the deeper the on-top hole is, the shorter is its range. Thus the depth of the on-top hole is strongly related to how accurate LSD (and, by extension, PW91) energies are.

This kind of analysis is relevant to the hybrid functionals which mix exact Hartree-Fock with semi-local functionals and are currently popular [30, 31]. The exchange on-top hole is shallower than the exchange-correlation hole, and so the exchange energy is less local than exchange and correlation together. Thus GGA’s might be improved by mixing some exact Hartree-Fock exchange. However, we show in Sect. 3.2 that the optimum amount of mixing is far from universal.

Another possible hybrid approach combines a density functional for antiparallel-spin correlation with conventional wavefunction methods for exchange and parallel-spin correlation. The parallel-spin correlation has no on-top hole density, and so is less local than the entire correlation energy, as we show in Sect. 3.3. This hybrid approach thus relies on the fact that the antiparallel-spin correlation can be accurately described by a local or semilocal density functional, and on the hope that the parallel-spin correlation contribution can be easily calculated within a finite basis-set approach such as the coupled-cluster (CC) or configuration-interaction (CI) techniques. Finite basis-set methods are known to be inefficient in describing the antiparallel-spin Coulomb cusp (see, e.g., [32–34]), and are believed to be efficient in the description of the more long-ranged parallel-spin correlation hole [35]. However, we show that, within the range of computationally-tractable basis sets, the convergence rates of the parallel and antiparallel-spin contributions to the correlation energy are comparable.

So far we have not distinguished between the self-consistent spin densities and the exact ones, because in most systems the difference is slight. In Sect. 4, we discuss ‘abnormal’ systems, where the self-consistent spin magnetization density, $m(\mathbf{r}) = n_{\uparrow}(\mathbf{r}) - n_{\downarrow}(\mathbf{r})$, is very different from the exact spin density. In such systems LSD (and PW91) functionals, evaluated on the exact spin densities, give very poor energies, but these functionals perform much better self-consistently. A stereotypical example is the stretched H_2 molecule, which has $m(\mathbf{r}) = 0$ everywhere. The LSD self-consistent solution makes the molecule (incorrectly) magnetized, with an $\uparrow$ electron on one nucleus, and a $\downarrow$ electron on the other. We review a re-interpretation of the standard theory [36], which shows that in such systems, it is in fact the on-top pair density which is well-approximated (i.e., differs little from its exact value) in LSD and GGA calculations for these systems, rather than $m(\mathbf{r})$. In the absence of an external magnetic field, the spin magnetization density is therefore *not* as robust a prediction as the energy and the density itself.

We use atomic units throughout ($e^2 = \hbar = m = 1$), unless otherwise stated.

2 Exchange-Correlation Hole

In order to understand why approximate functionals yield accurate exchange-correlation energies, we decompose the exchange-correlation energy as follows [37]. We define the pair density of the inhomogeneous system as

$$P_{\lambda}(\mathbf{r}, \mathbf{r}') = N(N-1) \sum_{\sigma_1, \dots, \sigma_N} \int d^3\mathbf{r}_3 \dots \int d^3\mathbf{r}_N \times |\Psi_{\lambda}(\mathbf{r}, \sigma_1, \mathbf{r}', \sigma_2, \dots, \mathbf{r}_N, \sigma_N)|^2, \quad (4)$$

where N is the number of electrons in the system, $\mathbf{r}_i, \sigma_i$ are the spatial and spin

coordinates of the i th electron, and Ψ_λ is the ground-state wavefunction of the system in which the strength of the Coulomb repulsion is given by λe^2 , where $0 \leq \lambda \leq 1$, and in which the external potential varies with λ , $v_{\sigma,\lambda}(\mathbf{r})$, in such a way as to keep the spin densities $n_\sigma(\mathbf{r})$ fixed [38]. The expectation value of the electron-electron repulsion operator is defined here as

$$V_{ee,\lambda} = \int d^3r \int d^3r' \frac{P_\lambda(\mathbf{r}, \mathbf{r}')}{2|\mathbf{r} - \mathbf{r}'|}. \quad (5)$$

The exchange-correlation hole density at $\mathbf{r}'$ around an electron at $\mathbf{r}$ for coupling strength λ , $n_{xc,\lambda}(\mathbf{r}, \mathbf{r}')$, is then defined by the relation

$$P_\lambda(\mathbf{r}, \mathbf{r}') = n(\mathbf{r})(n(\mathbf{r}') + n_{xc,\lambda}(\mathbf{r}, \mathbf{r}')), \quad (6)$$

where $n(\mathbf{r})$ is the density at $\mathbf{r}$. We may define an exchange-correlation energy as a function of coupling strength λ as simply 1/2 the Coulomb attraction between the λ -dependent hole density and the density of the electron it surrounds, i.e.,

$$\begin{aligned} E_{xc,\lambda} &= V_{ee,\lambda} - U \\ &= \frac{1}{2} \int d^3r \int d^3r' \frac{n(\mathbf{r})n_{xc,\lambda}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \end{aligned} \quad (7)$$

Note that this definition of $E_{xc,\lambda}$ differs from others, e.g. Ref. [39], but is convenient for the present purpose.

By defining all these quantities as explicit functions of λ , we can relate the density functional quantities to those more familiar from quantum chemistry. The exchange-correlation energy of density functional theory can be shown, via the Hellmann-Feynman theorem [38, 37], to be given by a coupling-constant average, i.e.,

$$E_{xc} = \int_0^1 d\lambda E_{xc,\lambda}. \quad (8)$$

(Note that, in the absence of explicit λ -dependence, our notation implies the coupling-constant averaged quantity.) On the other hand, at full coupling strength, $\lambda = 1$, we return to the fully-interacting system, so that, from Eqs. (6) and (7),

$$E_{xc,\lambda=1} = V_{ee,\lambda=1} - U = E_{xc} - T_c, \quad (9)$$

where $T_c = T - T_s$ is the correlation contribution to the kinetic energy. At zero coupling strength ($\lambda = 0$), the system is the non-interacting Kohn-Sham system, i.e., $v_{\sigma,\lambda=0}$ is the Kohn-Sham potential, and only exchange effects remain,

$$E_{xc,\lambda=0} = E_x. \quad (10)$$

We do not distinguish here this density functional definition of exchange energy from that of Hartree-Fock (HF). This simplification is well-justified, if the HF electron density and the exact electron density differ only slightly [40]. Similarly, the coupling-constant averaged exchange-correlation hole is the usual

one referred to in density functional theory, while the full coupling-strength hole can be extracted from the exact interacting wavefunction, via Eqs. (4) and (6), and the exchange hole is that of the non-interacting Kohn-Sham wavefunction $\Psi_{\lambda=0}$. For purposes of comparison between exact quantities calculated with more accurate methods and density functional quantities, we typically use the $\lambda = 0$ and $\lambda = 1$ contributions, which can be extracted directly from the Hartree-Fock and accurate interacting wavefunctions, respectively, whose details are given in Appendix A. We obtain the density functional approximations to such quantities by undoing the coupling-constant integration in the functional definitions.

The approach that we take to the question of how local and semilocal density functionals work for systems with large density gradients was pioneered by Gunnarsson, Jonson, and Lundqvist [41, 42]. Define $\mathbf{u} = \mathbf{r}' - \mathbf{r}$, the separation of two points in the system. Then the spherically-averaged hole is

$$n_{xc,\lambda}(\mathbf{r}, \mathbf{u}) = \int \frac{d\Omega_u}{4\pi} n_{xc,\lambda}(\mathbf{r}, \mathbf{r} + \mathbf{u}). \quad (11)$$

By studying the exchange (i.e., $\lambda = 0$) hole in Ne, Gunnarsson et al. pointed out that the LSD approximation to this quantity was far better than the LSD approximation to the exchange hole prior to spherical-averaging. Then, from Eq. (7), the energy depends only on this spherically-averaged hole, i.e.,

$$E_{xc,\lambda} = \int_0^\infty du \, 2\pi u \int d^3r \, n(\mathbf{r}) n_{xc,\lambda}(\mathbf{r}, \mathbf{u}). \quad (12)$$

In the subsections below, we show how this idea has been refined by further study of the exchange-correlation hole since that work.

2.1 Pointwise Decomposition of Energy

A natural way to decompose the exchange-correlation energy is in terms of the exchange-correlation energy per particle. Half the electrostatic potential at $\mathbf{r}$ due to the density of the hole surrounding an electron at $\mathbf{r}$ is

$$\begin{aligned} \varepsilon_{xc,\lambda}(\mathbf{r}) &= \int d^3r' \frac{n_{xc,\lambda}(\mathbf{r}, \mathbf{r}')}{2|\mathbf{r} - \mathbf{r}'|} \\ &= \int_0^\infty du \, 2\pi u n_{xc,\lambda}(\mathbf{r}, \mathbf{u}), \end{aligned} \quad (13)$$

and we take this as our definition of the exchange-correlation energy per particle. While other definitions are also possible, this definition is unambiguous, since $n_{xc,\lambda}(\mathbf{r}, \mathbf{r}')$ is defined in terms of the pair density, Eq. (6). Then LSD may be considered as making the approximation $\varepsilon_{xc,\lambda}(\mathbf{r}) = \varepsilon_{xc,\lambda}^{\text{unif}}(n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r}))$. In Figs. 1 and 2, we plot $\varepsilon_x(\mathbf{r}) = \varepsilon_{xc,\lambda=0}(\mathbf{r})$ and $\varepsilon_c(\mathbf{r}) = \varepsilon_{xc,\lambda=1}(\mathbf{r}) - \varepsilon_x(\mathbf{r})$ for the He atom, both exactly and in LSD. We see that the LSD curves are not very

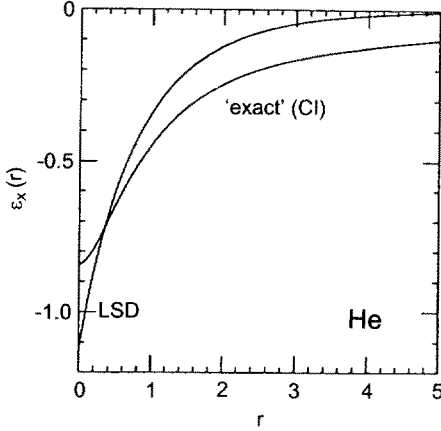


Fig. 1. Exchange energy per electron in the He atom, both exactly (CI) and in LSD. The nucleus is at $r = 0$

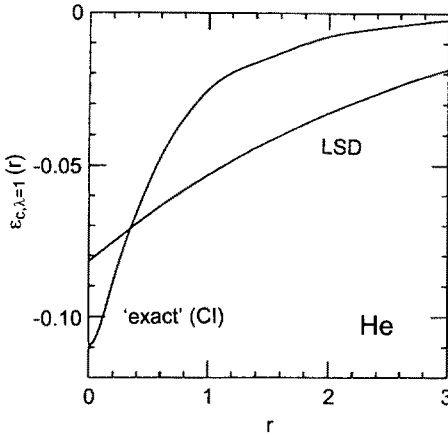


Fig. 2. Correlation energy per electron at full coupling-strength in the He atom, both exactly (CI) and in LSD. The nucleus is at $r = 0$

accurate. LSD yields the wrong value at $r = 0$ (where $\nabla^2 n/n^{5/3}$ diverges), has an incorrect cusp at $r = 0$, and decays exponentially as $r \rightarrow \infty$ (where $|\nabla n|/n^{4/3}$ diverges). The He atom is particularly difficult for LSD, because of the relative importance of the “rapidly-varying” regions $r \rightarrow 0$ and $r \rightarrow \infty$. However, the radial density-weighted curve, shown for the exchange energy in Fig. 3, looks much better. The LSD errors at small and large r are given little weight. The LSD approximation to the density-weighted integral of these curves, $E_{xc,\lambda} = \int d^3r n(r) \epsilon_{xc,\lambda}(r)$, is only in error by 16% at $\lambda = 0$ and by 6% at $\lambda = 1$, as can be seen in Table 1. (Note that we do not plot any PW91 curves, because PW91 invokes an integration by parts over r , and so makes meaningful predictions only for system-averaged quantities.) We conclude that, while the spherically-averaged hole is better in LSD than the unaveraged hole, it is vital to

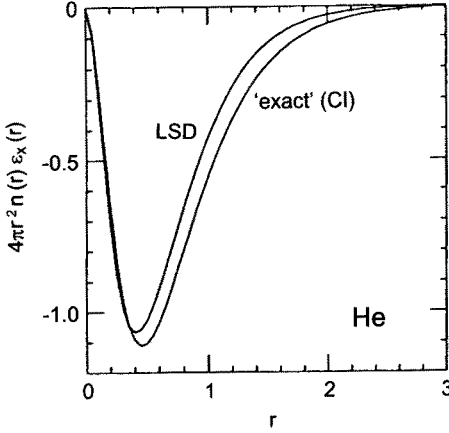


Fig. 3. Exchange energy per electron times the radial density in the He atom, both exactly (CI) and in LSD. The area under each curve is the exchange energy

Table 1. Various energies of the He atom (in eV). The approximate energies were evaluated on the self-consistent densities, and their errors measured relative to the exact energies. All numbers taken from Table 3 of Ref. [19]. (1 hartree = 27.2116 eV.)

Energy	LSD	Error (%)	PW91	Error (%)	Exact
E_x	-23.449	(-16)	-27.470	(-1)	-27.880
E_c	-3.023	(164)	-1.224	(7)	-1.146
T_c	1.825	(83)	1.010	(1)	0.997
E_{xc}	-26.472	(-9)	-28.693	(-1)	-29.026
$E_{xc, \lambda=1}$	-28.297	(-6)	-29.704	(-1)	-30.023
$E_c + T_c$	-1.198	(705)	-0.213	(43)	-0.149

consider density-weighted quantities to understand their effect on the corresponding total energy.

Similar remarks may be made about the exchange-correlation potential, $v_{xc}(\mathbf{r}) = \delta E_{xc} / \delta n(\mathbf{r})$, which, for the He atom, is shown very accurately in Figs. 10 and 11 of Ref. [21]. An important piece of $v_{xc}(\mathbf{r})$ is $2\varepsilon_{xc}(\mathbf{r})$. Again, LSD is inaccurate at small r and large r . In fact, PW91 is even worse, having a divergence at small r . It has been pointed out that the PW91 correlation potential would look closer to the exact potential if its sign were reversed! But, as in the case of the energy per particle, it is unclear what the effect of a poor-looking potential is on the quality of the energy. We show in Sect. 2.6 how a different decomposition yields more insight into which properties are being well-approximated by LSD and PW91.

2.2 Real-Space Decomposition of Energy

The real-space decomposition of the energy is in terms of $\mathbf{u} = \mathbf{r}' - \mathbf{r}$, the separation between points in the system [43]. We define the system- and

angle-averaged hole as

$$\begin{aligned}\langle n_{xc,\lambda}(u) \rangle &= \int \frac{d\Omega_u}{4\pi} \frac{1}{N} \int d^3r n(\mathbf{r}) n_{xc,\lambda}(\mathbf{r}, \mathbf{r} + \mathbf{u}) \\ &= \frac{1}{N} \int d^3r n(\mathbf{r}) n_{xc,\lambda}(\mathbf{r}, u),\end{aligned}\quad (14)$$

where Ω_u represents the solid angle of $\mathbf{u}$, and N is the number of electrons in the system. Thus, for any given system, $\langle n_{xc,\lambda}(u) \rangle$ is a function of one variable, u . The relation between this averaged hole and the exchange-correlation energy is immediate, from Eq. (7),

$$E_{xc,\lambda} = N \int_0^\infty du \, 2\pi u \langle n_{xc,\lambda}(u) \rangle. \quad (15)$$

Thus any good approximation to $\langle n_{xc,\lambda}(u) \rangle$ will yield a good approximation to $E_{xc,\lambda}$.

In Figs. 4 and 5, we plot the system-averaged exchange and correlation holes at full coupling strength in the He atom, taken from our configuration-interaction calculation. We also plot the LSD holes, and the numerical GGA holes (NGGA, defined below) which underlie the construction of PW91. Accurate analytic expressions for the uniform-gas hole are known [44], and were used to construct the LSD hole. We immediately see that LSD is doing a good job of modelling the hole, and GGA does even better.

We can easily understand why LSD does such a good job. The exact system-averaged hole obeys many conditions which have been derived over the years [14, 42, 45]. Amongst the most important for our purposes [1] are sum rules on the exchange and correlation contributions:

$$\int_0^\infty du \, 4\pi u^2 \langle n_x(u) \rangle = -1, \quad (16)$$

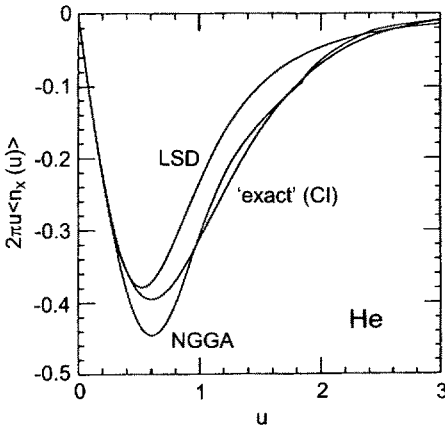


Fig. 4. System-averaged exchange hole density (in atomic units) in the He atom, in LSD, numerical GGA, and exactly (CI). The area under each curve is the exchange energy

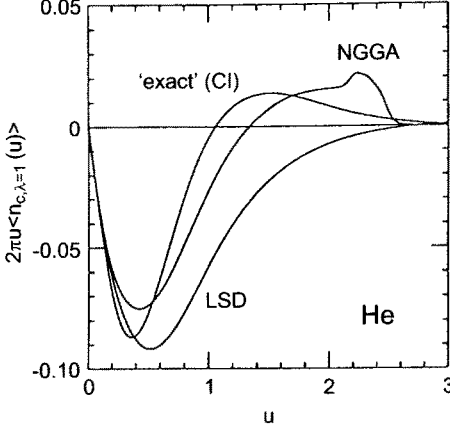


Fig. 5. System-averaged correlation hole density at full coupling strength (in atomic units) in the He atom, in LSD, numerical GGA, and exactly (CI). The area under each curve is the full coupling-strength correlation energy

$$\int_0^{\infty} du 4\pi u^2 \langle n_c(u) \rangle = 0, \quad (17)$$

the non-positivity of the exchange hole:

$$\langle n_x(u) \rangle \leq 0, \quad (18)$$

and the cusp condition [46, 47] at $u = 0$,

$$\left. \frac{\partial \langle n_{xc,\lambda}(u) \rangle}{\partial u} \right|_{u=0} = \lambda [\langle n_{xc,\lambda}(0) \rangle + \langle n(0) \rangle], \quad (19)$$

where

$$\langle n(u) \rangle = \frac{1}{N} \int \frac{d\Omega_u}{4\pi} \int d^3r n(r) n(r+u). \quad (20)$$

Now, since LSD replaces the exact hole of the inhomogeneous system by that of another physical system, namely the uniform gas, the LSD hole satisfies all these conditions. Furthermore, the on-top exchange hole, $\langle n_x(0) \rangle$, is exact in LSD [48–50] (for systems whose exchange wavefunction consists of a single Slater determinant – see Sect. 4 below), while the on-top correlation contribution is very accurate [51], although not exact [52]. From the cusp condition, this implies high accuracy for all u close to 0, while the sum rules then constrain LSD from doing too badly as u becomes large. These features can be seen in the plots, and explain why the LSD curves so closely match the exact ones.

To understand the origin of the NGGA curves, consider the construction of PW91 [11, 53]. Kohn and Sham [2] already recognized that a simple improvement on LSD might be provided by treating LSD as the zeroth-order term in a Taylor series in the gradients of the density, and therefore including the next higher terms. This defines the gradient expansion approximation (GEA), which includes terms up to $|\nabla n|^2$. Such an expansion works well to improve on the

local approximation to the kinetic energy [54]. However, while GEA moderately improves exchange energies, it produces very poor correlation energies. The reason for this failure is clear from our above analysis. In making this extension, we are no longer approximating $\langle n_{xc}(u) \rangle$ by the hole of another physical system, so that the sum rules and non-positivity constraints are violated. Thus the hole is no longer constrained by these conditions, and a poor approximation results.

The real-space cutoff procedure is designed to cure these problems in the gradient expansion [43]. At each point $\mathbf{r}$ in space, all positive portions of the gradient-expanded exchange hole are simply thrown away. Furthermore, beyond a given value of u , the rest of the hole is set to zero, with that point chosen to recover the exchange sum rule, Eq. (16). A similar procedure chops off the spurious long-range part of the correlation hole to make it respect Eq. (17). This recipe defines a no-parameter procedure for constructing what we call the numerical generalized gradient approximation to $\langle n_{xc,\lambda}(u) \rangle$ [17], which in turn yields a numerically-defined semilocal functional which obeys the exact conditions given above. The form of the correlation hole in this procedure was chosen [11] to restore LSD as $u \rightarrow 0$, so GGA retains the accuracy of LSD at small u . The PW91 functional was constructed to mimic the numerical GGA for moderate values of the gradient, while also incorporating further exact conditions for small and large gradients. The kink at $u \approx 1.8$ in the NGGA exchange hole of Fig. 4 and the bump at $u \approx 2.3$ in the NGGA correlation hole of Fig. 5 are both artifacts of the sharp cut-offs in this procedure [17]. The figures demonstrate that by using the gradient expansion, while still satisfying the exact conditions, the numerical GGA holes are indeed better approximations to the exact ones than LSD, thus demonstrating why PW91 yields better energies than LSD.

2.3 On-Top Exchange-Correlation Hole

As mentioned above, LSD yields a reasonable description of the exchange-correlation hole, because it satisfies several exact conditions. However, since the correlation hole satisfies a zero sum rule, the scale of the hole must be set by its value at some value of u . The local approximation is most accurate at points near the electron. In fact, while not exact at $u = 0$, LSD is highly accurate there. Thus the on-top hole provides the “missing link” between the uniform electron gas and real atoms and molecules [18].

To see this in more detail, consider the ratio of the system-averaged on-top exchange-correlation hole to the system-average of the density itself, $\langle n(0) \rangle$, as defined in Eq. (20). This ratio satisfies the inequalities

$$-1 \leq \frac{\langle n_{xc,\lambda}(0) \rangle}{\langle n(0) \rangle} \leq 0, \quad (21)$$

for all systems, both exactly and in LSD. Furthermore, for either fully spin-polarized systems or extremely low density, the on-top pair density vanishes,

making this ratio -1 , both exactly and in LSD. LSD also becomes exact in the high density $r_s \rightarrow 0$ or non-interacting $\lambda \rightarrow 0$ limits, where this ratio equals $-1/2$ for spin-unpolarized systems, and the approach to this limit is also highly accurate (but not exact). We can see this very clearly in the universal curve plotted in Fig. 6, which is this ratio as a function of the average r_s value in the system, defined for spin-unpolarized systems as

$$\langle r_s \rangle = \frac{\int d^3r n^2(\mathbf{r}) r_s(\mathbf{r})}{\int d^3r n^2(\mathbf{r})}, \quad (22)$$

where

$$r_s(\mathbf{r}) = \left(\frac{3}{4\pi n(\mathbf{r})} \right)^{1/3}. \quad (23)$$

The solid curve was obtained from Yasuhara's expression for the on-top hole for a uniform electron gas [55]. The circles indicate the LSD values of $\langle n_{xc,\lambda}(0) \rangle / \langle n(0) \rangle$. Their proximity to the uniform-gas curve indicates that the approximation

$$\langle n_{xc,\lambda}^{\text{LSD}}(0) \rangle \approx n_{xc,\lambda}^{\text{unif}}(\langle r_s \rangle; u = 0) \quad (24)$$

is highly accurate. The crosses represent either almost-exact numerical calculations [36] or exact analytic results for Hooke's atom [56], which consists of two electrons bound to a center by a spring of force constant k . The pluses represent CI results, which tend to underestimate the depth of the on-top hole, because of the difficulty in representing the cusp in a finite basis set (see Sect. 3.4).

The importance of the accuracy of the on-top hole in LSD cannot be over-stressed. This accuracy is not just in the system-average, but is also there on a point-wise basis. In Fig. 7, we plot the ratio of the full-coupling strength

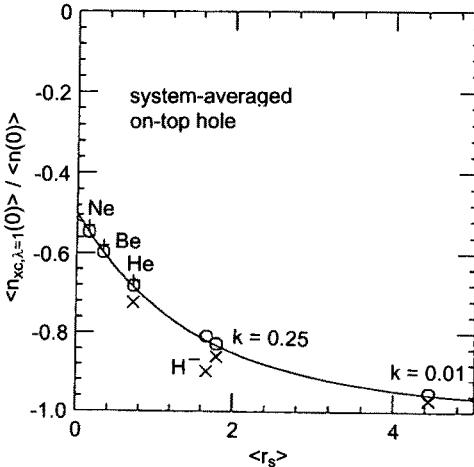


Fig. 6. Universal curve for the system-averaged on-top hole density in spin-unpolarized systems. The solid curve is for the uniform gas. The circles indicate values calculated within LSD, while the crosses indicate essentially exact results, and the plus signs indicate less accurate CI results. The high-density ($r_s \rightarrow 0$) and low-density ($r_s \rightarrow \infty$) limits behave respectively like the weak-coupling ($\lambda \rightarrow 0$) and strong-coupling ($\lambda \rightarrow \infty$) limits

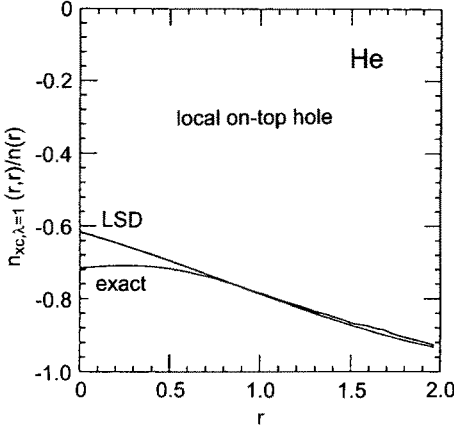


Fig. 7. Local on-top exchange-correlation hole at full coupling strength divided by density as a function of r in the He atom. The nuclear cusp produces greater LSD error for $r \rightarrow 0$

on-top exchange-correlation hole to the density as a function of r in the He atom, both exactly, using a very accurate wavefunction [36], and in LSD. We see that already for $r \geq 1$ ($r_s \geq 1.33$), the LSD on-top hole is extremely accurate. Thus, even in the tail region of the density, which is vital to understanding chemistry, the *on-top* LSD hole is highly accurate.

Successful density functional approximations such as the PW91 GGA or the self-interaction correction (SIC) [57] to LSD recover [19] LSD values for the on-top hole density and cusp. The weighted density approximation (WDA) [41, 42], which recovers the LSD exchange hole density but not the LSD correlation hole density [19] in the limit $u \rightarrow 0$, needs improvement in this respect.

2.4 Importance of the Uniform Gas Limit

The accuracy of the on-top hole density has a crucial bearing on the validity of GGA functionals. LSD and GGA are limited-form approximations to $E_{xc,\lambda}$. These limited forms can only be exact for uniform densities. Thus any GGA ought to be correct, i.e., reduce to LSD, in this limit. Otherwise, it will miss the vital link between the uniform gas and the real system, namely the on-top hole density, as shown in Figs. 6 and 7. Moreover, certain real systems (e.g., close-packed crystals of simple metals) closely resemble a uniform electron gas. However, a very popular GGA in use in quantum chemistry, the Lee-Yang-Parr (LYP) correlation functional [10], does not satisfy this condition. In Table 2, we compare the correlation energy in LYP for a uniform gas, as a function of r_s , and compare it with the essentially exact value [3, 4, 57], using the parametrization of Perdew and Wang [4]. We see that LYP does badly for the uniform gas, and therefore does not contain the information about the on-top hole found in functionals which reproduce this limit, such as PW91.

Table 2. Correlation energy of the uniform electron gas, comparing the highly-accurate parametrization of Perdew and Wang [4] with the LYP functional [10]

r_s	LYP	Accurate	Error (%)
0.01	− 0.0674	− 0.1902	− 65
0.05	− 0.0656	− 0.1413	− 54
0.1	− 0.0635	− 0.1209	− 47
0.5	− 0.0502	− 0.0766	− 34
1.0	− 0.0394	− 0.0598	− 34
2.0	− 0.0270	− 0.0448	− 40
5.0	− 0.0135	− 0.0282	− 52
10.0	− 0.0075	− 0.0186	− 60

For the spin-unpolarized uniform electron gas, the LYP correlation energy functional reduces to that of Colle and Salvetti [58], on which LYP is based. McWeeny’s work [59] may have contributed to the widespread misimpression that the Colle-Salvetti functional is accurate in this limit. Note however the McWeeny tested Eq. (9) of Ref. [58], and not the further-approximated Eq. (19) of Ref. [58], which is the basis of LYP and other Colle-Salvetti applications, and which is shown in Table 2.

A second observation about the LYP functional is that it predicts *no* correlation energy for a fully spin-polarized system of electrons. Yet, in the uniform-density limit, the correlation energy at full spin-polarization is about half that of the unpolarized system [3, 4, 57]. Even in the Ne atom, the parallel-spin contribution accounts for about 24% of the total correlation energy (Sect. 3.4).

A recent and much-discussed system with delocalized electrons illustrates the importance of a GGA recapturing the uniform and slowly-varying density limits. Three basic structures have been proposed for the ground state of C_{20} : a ring, a bowl, and a cage. Recent accurate calculations using diffusion Monte Carlo [60] place the bowl as the lowest energy structure. These structures differ only very slightly in their correlation energies per carbon atom, and so provide a very sensitive test of approximate treatments. Hartree-Fock calculations make the cage the highest energy and the ring the lowest, while LSD reverses this ordering. Various GGA functional forms, including BLYP, were tested, but only PW91, which does satisfy the slowly-varying constraint, yields the correct energy ordering, at a level of accuracy comparable to variational Monte Carlo. Note that the claim by the authors of Ref. [60], that no GGA works because several GGA forms yielded different answers, is overdrawn.

2.5 Long-Range Asymptotics of the Hole

We have recently discovered [19] a new exact formula for the asymptotic behavior of the wavefunction of an atom or molecule, when one coordinate

becomes large, namely

$$\begin{aligned} \lim_{r \rightarrow \infty} \Psi_\lambda(\mathbf{r}, \sigma, \mathbf{r}_2, \sigma_2, \dots, \mathbf{r}_N, \sigma_N) \\ = \sqrt{n_\sigma(\hat{\mathbf{r}})/N} \Psi_\lambda^{(+)}(\mathbf{r}_2, \sigma_2, \dots, \mathbf{r}_N, \sigma_N) \{\hat{\mathbf{r}}, \sigma\}. \end{aligned} \quad (25)$$

Here $\Psi_\lambda^{(+)}$ is (typically [19]) a ground-state wavefunction of the positive ion (assuming the N -electron system is neutral) which remains when one electron has been removed, and the notation $\{\hat{\mathbf{r}}, \sigma\}$ indicates a parametric dependence on the coordinates of the departing electron. If the remaining ion is non-degenerate, e.g., for He, then $\Psi_\lambda^{(+)}$ becomes independent of $\hat{\mathbf{r}}$ as $r \rightarrow \infty$. However, in the common case when the ion is degenerate, e.g., for Ne, Ar, Kr, Xe, which have non-spherical ions, the ionic wavefunction appearing in Eq. (25) is oriented relative to the direction of the departing electron, no matter how far from the nucleus that electron is.

This long-range correlation effect shows up in both the first-order density matrix and the exchange-correlation hole for finite systems [19]. We concentrate here on the exchange-correlation hole. The general asymptotic form of the pair density is then

$$\lim_{r \rightarrow \infty} P_\lambda(\mathbf{r}, \mathbf{r}') = n_\lambda^{(+)}(\mathbf{r}') \{\hat{\mathbf{r}}\} n(\mathbf{r}), \quad (26)$$

where

$$\begin{aligned} n_\lambda^{(+)}(\mathbf{r}') \{\hat{\mathbf{r}}\} = (N-1) \sum_{\sigma_1, \dots, \sigma_{N-1}} \int d^3r_2 \dots \int d^3r_{N-1} \\ \times |\Psi_\lambda^{(+)}(\mathbf{r}', \sigma', \mathbf{r}_2, \sigma_2, \dots, \mathbf{r}_{N-1}, \sigma_{N-1}) \{\hat{\mathbf{r}}, \sigma\}|^2, \end{aligned} \quad (27)$$

i.e., it is the density of the ion with coupling strength λ , oriented along the direction $\hat{\mathbf{r}}$. (Note that in the case of a non-degenerate ion, there is no orientation dependence.) Eq. (26) implies that the pair correlation function, $g_\lambda(\mathbf{r}, \mathbf{r}') = P_\lambda(\mathbf{r}, \mathbf{r}')/n(\mathbf{r})n(\mathbf{r}')$, does *not* typically tend to unity in the limit of large separations, contrary to intuitive expectations [1]. Only for $N \rightarrow \infty$, i.e., a solid, will $n_\lambda^{(+)}(\mathbf{r}') \{\hat{\mathbf{r}}\} \rightarrow n(\mathbf{r}')$, the uncorrelated case. In terms of the exchange-correlation hole density, we find

$$\lim_{r \rightarrow \infty} n_{\text{xc}, \lambda}(\mathbf{r}, \mathbf{r}') = n_\lambda^{(+)}(\mathbf{r}') \{\hat{\mathbf{r}}\} - n(\mathbf{r}'), \quad (28)$$

i.e., the hole remaining behind an electron at large distances is determined by the λ -dependent density of the degenerate ion, oriented relative to the departing electron.

We may also decompose the exchange and correlation contributions to this hole. At $\lambda = 0$, the ion density is that of the Kohn-Sham potential with $N-1$ electrons, so Eq. (28) becomes

$$\lim_{r \rightarrow \infty} n_{\text{x}}(\mathbf{r}, \mathbf{r}') = -|\phi_{\text{HO}}^{\text{KS}}(\mathbf{r}') \{\mathbf{r}\}|^2, \quad (29)$$

where $\phi_{\text{HO}}^{\text{KS}}$ is the highest-occupied Kohn-Sham orbital, oriented in the general direction $\hat{r}$. Thus the contribution of exchange to the exchange-correlation hole in the asymptotic limit $r \rightarrow \infty$ will typically be some finite fraction which varies with r' .

In the case where the degeneracy is due to symmetry, symmetry arguments may be used to determine $n_{\lambda}^{(+)}(r')\{\hat{r}\}$. For example, the Ne ion has an electron missing in a $2p$ orbital. For the ion density appearing in Eq. (28), the $2p$ hole points in the direction of the distant electron [19]. To illustrate these effects, we plot the radial exchange-correlation hole density $4\pi r'^2 n_{\text{xc},\lambda=1}(r, r')$ in the Ne atom, for several large values of r , for $r \parallel r'$, and $r \perp r'$. In Fig. 8, we look along the direction of departure of the electron. The hole for $r \rightarrow \infty$ has the shape of the radial density of a p orbital, oriented along the plot axis. For finite values of r , we observe a deformation of the hole, since the remaining electron in the p orbital moves away from the electron at position r to the other side of the atom. This deformation occurs even in the exchange (i.e., $\lambda = 0$) hole. For any finite value of r , there is a finite probability that the electron at r is either a $1s$ or a $2s$ electron, instead of a $2p$ electron, so that the exchange hole is a hybrid between a hole in an s -shell and a hole in a p -shell [61]. In Fig. 9, we plot the Hartree-Fock hole perpendicular to the direction of departure, for several values of the electron position. The p -orbital hole in the ion density vanishes for all x' , so, from Eq. (29), the exchange hole also vanishes for all x' as $r \rightarrow \infty$. However, correlation causes the ion density to relax as the electron leaves, and the density moves in toward the nucleus, becoming more compact, to partially fill the hole left behind. This effect is greatest when the electron is furthest, i.e., as $r \rightarrow \infty$. In Fig. 10, we plot the full coupling-strength exchange-correlation hole perpendicular to the direction of departure, for the same values of the electron position. Comparison with Fig. 9 shows that correlation dominates the shape of this hole.

In the limit $r \rightarrow \infty$, the LSD hole incorrectly spreads out over all space, while the SIC and WDA holes behave [19] exactly or approximately like Eq. (29). The

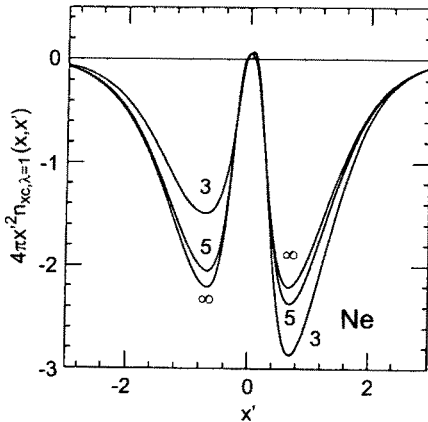


Fig. 8. Full coupling-strength radial exchange-correlation hole density around an electron at $x = 3, 5, \infty$, plotted along the direction of the departing electron

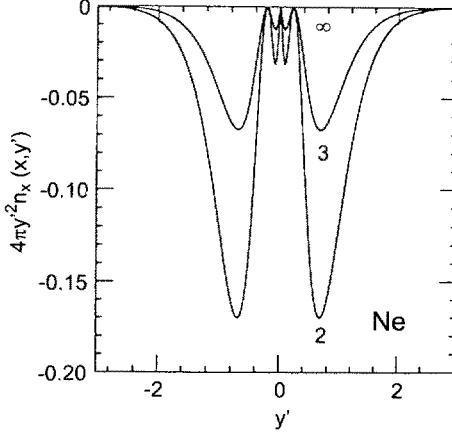


Fig. 9. Hartree-Fock radial hole density around an electron at $x = 2, 3, \infty$, plotted perpendicular to the direction of the departing electron

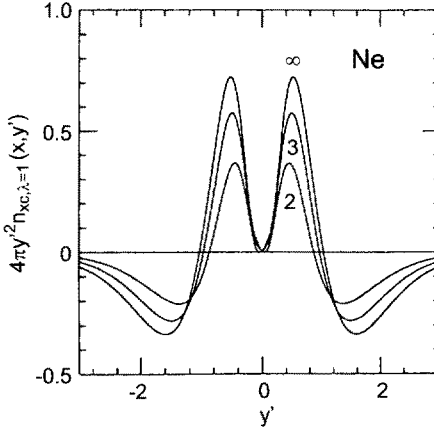


Fig. 10. Full coupling-strength radial exchange-correlation hole density around an electron at $x = 2, 3, \infty$, plotted perpendicular to the direction of the departing electron

LSD system-averaged hole decays as the uniform-gas hole decays: both exchange and correlation decay as u^{-4} , but these long tails cancel in their sum, to yield an exchange-correlation hole which vanishes as u^{-5} . This power law decay is quite incorrect in a finite system, when compared with the exponential decay of the hole due to that of $n(r)$. However, the cancellation of exchange and correlation reduces the error due to this tail, and so accounts, to some extent, for the cancellation of errors between the LSD exchange and correlation energies. The GGA behavior, on the other hand, provides an exponential decay for large values of u , because of the real-space cut-offs [17].

2.6 Relevance of the Exchange-Correlation Potential

In this subsection, we make a simple and direct connection between point-wise quantities and system-averaged quantities. In Sect. 2.1, we noted several papers

which detail the idiosyncrasies of the approximate exchange-correlation potentials, and their considerable deviation from the exact potential. We then showed in Sect. 2.2 how system-averaged quantities were much better approximated by the density functionals. This then raises the question: can we relate the potentials to some more physically meaningful system-averaged quantities, to see how significant the LSD and PW91 errors in the potentials are?

The answer is yes, in a very general way, as has been discussed before [62, 63]. Consider any parameter in the external potential, called γ . For definiteness, we choose the internuclear separation in a diatomic molecule. Then the exchange-correlation energy depends parametrically on this quantity. Now imagine making an infinitesimal change in γ . The differential change in E_{xc} is

$$\frac{dE_{xc}}{d\gamma} = \int d^3r v_{xc}(\mathbf{r}) \frac{dn(\mathbf{r})}{d\gamma}, \quad (30)$$

i.e., this change is determined by a system-average of the exchange-correlation potential. Thus one may relate system-averages of the potential to differential changes in the energy. Note that, since the particle number does not change with γ , there are no difficulties associated with derivative discontinuities. In the specific case we have chosen, the quantity $dE_{xc}/d\gamma$ has direct physical significance, as it goes into the equation determining the equilibrium bond length. Note that, within a fully self-consistent calculation, the equilibrium value of the bond length can be determined directly from the density and external potential alone, but that approximate functionals are usually tested on the exact density, to determine their accuracy. Thus calculations of such quantities might prove very useful in studying the efficacy of functionals.

We have applied a slight variation of this general idea to the exchange-correlation potential of the He atom [18]. The virial theorem applied to the Kohn-Sham system yields [39]:

$$E_x = - \int d^3r n(\mathbf{r}) \mathbf{r} \cdot \nabla v_x(\mathbf{r}) \quad (31)$$

and

$$E_c + T_c = - \int d^3r n(\mathbf{r}) \mathbf{r} \cdot \nabla v_c(\mathbf{r}). \quad (32)$$

Thus, just as in the case of the energy densities, the small- and large- r behaviors of the potential receive very little weight in the energy integrals, leading to the dramatic results of row 6 of Table 1. These results indicate that the potential in PW91 is far better than that of LSD in terms of energies (and is also the right way up).

3 Understanding Nonlocality

In this section, we examine the concept of nonlocality, in the sense of how much error LSD makes. We have seen in the previous section that LSD is most

accurate near $u = 0$, and least accurate at large u . Thus the deeper the hole is at the origin, and therefore, from the sum rule, the shorter its range in u , the better approximated it should be in LSD.

3.1 Coupling-Constant Decomposition

We tested this idea [18] by examining the holes and corresponding energies of three different coupling constants: $\lambda = 0$ (exchange), $\lambda = 1$ (full coupling strength), and averaged over λ (as in the actual E_{xc}). Since the on-top correlation hole is negative, the shallowest of these holes is the exchange hole, followed by the coupling-constant averaged hole, and the deepest is the full coupling-strength hole. This behavior is illustrated for the uniform electron gas in Fig. 6 of Ref. [18], and these qualitative features should be shared by the system-averaged holes of most inhomogeneous systems. This is borne out by the results of Table 2 of Ref. [18], in which the error in LSD atomic energies, measured relative to their PW91 counterparts, was tabulated for the energies of the three different holes. This error is largest for exchange and least for full coupling strength, and this effect becomes less significant as we approach the high-density limit. This is consistent with our idea that the deeper the on-top hole is, the more local is the corresponding energy.

An alternative way to see this effect is to consider the enhancement factor over local exchange in PW91. We may write any GGA energy, for spin-unpolarized systems, as

$$E_{xc,\lambda}^{GGA} = \int d^3r n(r) \epsilon_x(r_s) F_{xc,\lambda}(r_s, s), \quad (33)$$

where

$$s = |\nabla n|/2k_F n, \quad (34)$$

$k_F = (3\pi^2 n)^{1/3}$ is the Fermi wavevector, and

$$F_{xc,\lambda}(r_s, s) = \left(1 + r_s \frac{\partial}{\partial r_s}\right) F_{xc}(\lambda r_s, s), \quad (35)$$

where the differentiation with respect to r_s undoes the coupling-constant integral implicit in $F_{xc}(r_s, s)$. Eq. (35) at $\lambda = 1$ was found in Ref. [64], and used to calculate T_c in Ref. [65]. Then the enhancement factors for exchange, exchange-correlation, and exchange-correlation at full coupling strength are $F_x(s) = F_{xc,\lambda=0}(r_s, s) = F_{xc,\lambda}(r_s = 0, s)$, $F_{xc}(r_s, s) = \int_0^1 d\lambda F_{xc,\lambda}(r_s, s)$, and $F_{xc,\lambda=1} \times (r_s, s)$, respectively. In Figs. 11 and 12 we plot $F_{xc}(r_s, s)$ and $F_{xc,\lambda=1}(r_s, s)$ for PW91. At the LSD level, we would have $F_{xc,\lambda}(r_s, s) = F_{xc,\lambda}(r_s, s = 0)$, i.e., horizontal lines. Since the full coupling-strength curves change far less as a function of s , the full coupling-strength functional of Fig. 12 is more local than its coupling-constant averaged counterpart of Fig. 11. Furthermore, the greatest nonlocality occurs at $r_s = 0$, which is the exchange curve. These results further confirm our intuitive idea that the degree of nonlocality is strongly related to the spatial extent of the hole.

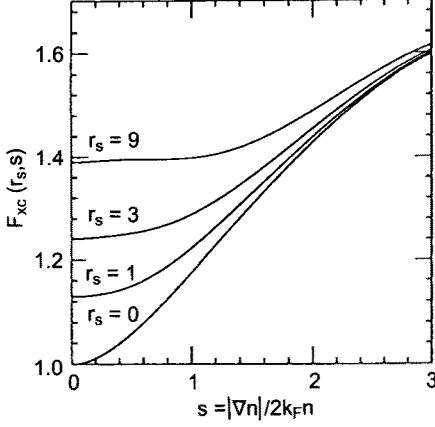


Fig. 11. Enhancement factor over local exchange, $F_{xc}(r_s, s)$, for spin-unpolarized systems in the PW91 GGA

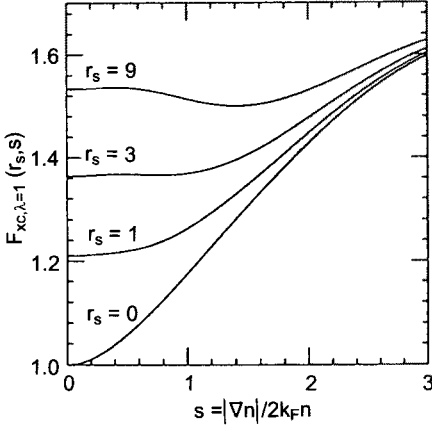


Fig. 12. Full coupling-strength enhancement factor over local exchange, $F_{xc, \lambda=1}(r_s, s)$, for spin-unpolarized systems in the PW91 GGA

3.2 Hybrid Functionals

Following the “B3” proposal of Becke [30], several schemes for mixing Hartree-Fock into density functional treatments have appeared in the literature [30, 31]. To get the correct energy for the slowly-varying electron gas, this hybrid functional must simplify to [18]

$$E_{xc} \approx (1 - a)E_x^{GGA} + aE_x^{HF} + E_c^{GGA}. \quad (36)$$

This “B1” form has recently been proposed independently by Becke [66], to reduce the number of empirical parameters in the original “B3” form.

To determine how much HF is needed, we consider systems where s is significantly greater than 1, but where GGA still works reasonably well. In Ref. [18], we examined the ionization potentials, electron affinities, and electronegativities of a variety of atoms, as well as the atomization energies of several

closed-shell hydrocarbon molecules. By examining root-mean-square errors in the energies, we found results consistent with those of Becke [30], namely that $a \approx 0.2$ slightly improved the PW91 results. However, in Table 3, we list a variety of root-mean-square energy errors Δ_a for some other systems, for several values of the mixing parameter a : $a = 0$ corresponds to no mixing (PW91), $a = 0.2$ corresponds to the amount of mixing recommended by Becke (B1), $a = 1$ corresponds to Hartree-Fock exchange and PW91 correlation, while $\Delta_{\min}$ is the minimum root-mean-square error, achieved at $a = a_{\min}$. The first row reports the electronegativity errors calculated over a subset of atoms, namely those in which the ground-state term of the negative ion is the same as that of the positive ion [13], the two ionic configurations differing by $(ns)^2$. Now $a = 0$ is clearly better than $a = 0.2$, and only marginally worse than the optimum value $a = 0.03$. These results are consistent with the suggestion that local (and semilocal) approximations to ionization potentials and electron affinities suffer from interterm and interconfigurational errors in their treatment of exchange [1]. These 12 term-conserving s -process electronegativities should not suffer from this error, and indeed need far less mixing with Hartree-Fock. However, this row also shows that $a = 0.2$ is not optimal for these processes.

The last row of Table 3 lists the error in the atomization energy of a single hydrocarbon molecule, C_2 . This molecule is “abnormal”, in the sense that no single determinant dominates its wavefunction [67]. It has low-lying excited states close to its ground-state. The HF atomization energy is seriously in error [13]. Hence the $a = 0.2$ error is far greater than the PW91 ($a = 0$) error.

Although the adiabatic connection formula of Eq. (8) justifies a certain amount of Hartree-Fock mixing, there are situations in which a should vanish. In a spin-restricted description of the molecule H_2 at infinite bond length (Sect. 4) the Hartree-Fock or $\lambda = 0$ hole is equally distributed over both atoms, and is independent of the electron’s position. But the hole for any finite λ , however small, is entirely localized on the electron’s atom, so no amount of Hartree-Fock mixing is acceptable in this case.

Thus we have argued that the only hybrid form which is correct for the slowly-varying densities is that of Eq. (36), with a value of a between 0 and 0.2. Note that the approximation $a = 1$, which reproduces exact exchange, ignores the cancellation of nonlocalities between the exchange and correlation energies, and the fourth column of Table 3 shows how poor the latter approximation is.

Table 3. Various properties evaluated using the hybrid functional of Eq. (36). We report root-mean-square errors in energies Δ_a (in eV) as a function of the mixing parameter a , and the optimum value of a . The properties and data sets on which they are evaluated are described in the text. All results were extracted from Tables V and VII of Ref. [13]. (1 eV = 23.06 kcal/mole.)

Energy	Δ_0	$\Delta_{0.2}$	Δ_1	$\Delta_{\min}$	$a_{\min}$
χ (term-conserving)	0.08	0.11	0.51	0.07	0.03
E_{atom} (open-shell)	0.19	0.66	4.08	0.02	0.04

As discussed in the previous sections, LSD works well, and GGA does better, by modelling the system-averaged hole in a way which respects the sum rules, amongst other things. A much better way to construct a hybrid functional [54, 68] would be to construct a hybrid hole, in which the small-separation contributions would be modelled in LSD (or GGA), which works well here, and the large-separation contributions would be modelled by some approximation designed to work at large distances, e.g., the random phase approximation [35], or the correct asymptotic limit [19].

3.3 Spin Decomposition

Another way to separate short- and long-range effects is via the spin decomposition. We may decompose Eq. (4) by writing

$$P_\lambda(r\sigma, r'\sigma') = N(N-1) \sum_{\sigma_3, \dots, \sigma_N} \int d^3r_3 \dots \int d^3r_N \times |\Psi_\lambda(r, \sigma, r', \sigma', \dots, r_N, \sigma_N)|^2, \quad (37)$$

where $\sigma = \uparrow$ or $\downarrow$, which in turn leads to a spin-decomposed hole:

$$P_\lambda(r\sigma, r'\sigma') = n_\sigma(r)(n_{\sigma'}(r') + n_{xc,\lambda}(r\sigma, r'\sigma')), \quad (38)$$

where $n_\sigma(r)$ is the density of spin σ , and to a spin-decomposed energy:

$$E_{xc,\lambda}^{\sigma,\sigma} = \frac{1}{2} \int d^3r \int d^3r' \frac{P_\lambda(r\sigma, r'\sigma) - n_\sigma(r)n_\sigma(r')}{|\mathbf{r} - \mathbf{r}'|},$$

$$E_{xc,\lambda}^{\uparrow\downarrow} = \int d^3r \int d^3r' \frac{P_\lambda(r\uparrow, r'\downarrow) - n_\uparrow(r)n_\downarrow(r')}{|\mathbf{r} - \mathbf{r}'|}. \quad (39)$$

Note that both antiparallel holes ($\uparrow\downarrow$ and $\downarrow\uparrow$) give the same contribution to the energy, and are conventionally added together into one antiparallel contribution, $E_{xc,\lambda}^{\uparrow\downarrow}$ as defined here.

We focus on the correlation energy only, as all the exchange energy is in the parallel-spin channels. Before we consider the question of locality of the different spin contributions, we first note that, contrary to assumptions in the literature [69, 70], while the antiparallel contribution is typically most of the correlation energy, the parallel contribution is often not negligible. For spin-unpolarized systems, if $N = 2$, *all* the correlation is antiparallel, while for $N \rightarrow \infty$ in the uniform gas, only 60% is antiparallel. As far as we know, all other spin-unpolarized systems fall between these two extremes. As we report below, for Ne, a full 24% of the correlation energy is in the parallel-spin channels.

We now consider the locality of the antiparallel-spin contribution to the correlation energy, relative to the total correlation energy. The holes corresponding to both these contributions obey the zero sum rule, Eq. (17). However, the parallel-spin on-top correlation hole vanishes, suggesting that this hole will

extend further out from the electron’s position, and therefore be less well-approximated by LSD. In Table 4 we compare the full correlation energy with just the antiparallel-spin contribution. We used the approximate GGA for antiparallel spin described in Ref. [35], which predicts that 20% of the correlation energy of Ne is from antiparallel spin. Clearly, the antiparallel contribution is much more local than the total.

3.4 Hybrid Density Functional-Wavefunction Methods

The results of the previous section suggest that a good hybrid method might treat antiparallel spin using a GGA, while using a wavefunction treatment for parallel-spin [54]. Since the parallel-spin hole has no cusp and is of greater spatial extent, this contribution should be more accessible to a wavefunction method beginning from one-particle wave functions, such as CI.

To test this idea, we performed Møller-Plesset (MP2) [71] perturbation calculation for the Ne atom, in which we spin-decomposed the correlation energy. The details of the calculation are given in Appendix B. These results are very close to values which may be extracted from Ref. [72], which we discovered after completing this work. We chose Ne because it is well known that MP2 gives an accurate account of the correlation energy of this atom. The parallel- and antiparallel-spin contribution to the MP2 correlation energy (E_2) for a number of different gaussian basis sets are given in Table 5. As expected, the MP2 correlation energy is very close in almost all cases to the correlation energy obtained from multireference configuration-interaction (CI) calculations. We assume that the MP2 spin-decomposed correlation contributions are as close to the spin-decomposed correlation energies of the elaborated CI calculations as the total correlation energies are. Comparison of the parallel- and antiparallel-spin correlation contributions obtained with the 14s9p4d3f1g basis set (which gives a CI correlation energy close to the exact value of -0.3917

Table 4. Errors in LSD correlation energies, relative to PW91, for several atoms (%). The results were calculated from the entries in Table III of Ref. [35]

Atom	ΔE_c	$\Delta E_c^{\uparrow\downarrow}$
H	236	0
He	145	58
Li	162	60
N	114	37
Ne	94	42
Ar	85	37
Kr	71	32
Xe	64	30

Table 5. Gaussian basis sets and corresponding spin-decomposed correlation energies (in hartree) for the Ne atom

Basis set	E_c^{CI}	E_2	$E^{\uparrow\uparrow} + E^{\downarrow\downarrow}$	$E^{\uparrow\downarrow}$	$\frac{E_2^{\uparrow\uparrow} + E_2^{\downarrow\downarrow}}{E_2}$
4s2p	− 0.12204	− 0.12390	− 0.03127	− 0.09263	0.25
3s2p1d	− 0.14852	− 0.14892	− 0.04231	− 0.10661	0.28
5s3p1d	− 0.22420	− 0.22795	− 0.05998	− 0.16797	0.26
14s9p4d3f	− 0.34936	− 0.34556	− 0.08297	− 0.26258	0.24
14s9p4d3f1g	− 0.35822	− 0.35476	− 0.08365	− 0.27111	0.24

(hartree) [73]) shows that the parallel-spin contribution is a significant fraction (24%) of the total correlation energy.

From the last column of the table, we see that the ratio of the parallel-spin to the total correlation energy is remarkably independent of the size of the basis set. Contrary to expectation, the parallel-spin correlation contribution appears to be about as difficult to account for within a finite basis-set approach as the antiparallel-spin correlation. Our investigation does not provide a careful study of the basis-set saturation behavior in MP2 calculations, such as is given in Refs. [74, 72, 75, 33]. However, our results show that, with small- and moderate-sized basis sets which are sufficiently flexible for most purposes and computationally tractable in calculations on larger systems, there is no evidence that the parallel-spin correlation contribution converges more rapidly than the antiparallel-spin contribution. A plausible explanation for this effect is that, for small interelectronic separations, the wavefunction becomes a function of the separation, which is difficult to represent in a finite basis-set approach for either spin channel. The cusp condition of Eq. (19) is a noticeable manifestation of this dependence, but does not imply that the antiparallel-spin channel is more difficult to describe with a moderate-sized basis set than the parallel channel. In fact, in the parallel correlation hole, there is a higher-order cusp condition, relating the second and third derivatives with respect to u [76].

It is also clear from Table 5 that the *absolute* basis-set truncation error in Ne is about three times bigger for the antiparallel-spin correlation energy than for parallel. Thus the proposed spin-analysis hybrid of Ref. [35] may yet have some (limited) utility.

4 Abnormal Systems and Extreme Nonlocality

We define a “normal” system as one in which the hole density at the weakly-interacting end of the coupling-constant integration is close to that of a single Slater determinant. In such a system, the local and gradient-corrected holes, evaluated for the exact spin-densities, are nearly exact near the position of the

electron they surround. As a result, the exchange-correlation energy is approximately a local functional of the exact spin densities. In this section, we show that accurate on-top hole densities in “abnormal” systems like stretched H_2 are found for a quite different reason: the self-consistent spin magnetization density goes wrong, in order to make the on-top hole density (and the associated energy) right [36].

At the equilibrium bond length of H_2 , the LSD or GGA equations have a single self-consistent ground-state solution with $m(r) = 0$. But, at a larger internuclear separation, this solution bifurcates and a second solution of “broken symmetry” and lower energy appears. In the limit of infinite separation, this second solution describes one hydrogen atom with an electron of spin up on the left, and another with an electron of spin down on the right. The molecular dissociation energies calculated for these two solutions pose a dilemma: The LSD or GGA energy is nearly exact for the broken-symmetry solution with qualitatively incorrect spin densities, and seriously in error if the correct physical spin symmetry (singlet [77]) is imposed on the spin densities, as shown in Table 1 of Ref. [36]. (This symmetry-breaking also occurs in Hartree-Fock theory.)

Evidently, the LSD and GGA approximations are working, but not in the way the standard spin-density functional theory would lead us to expect. In Ref. [36], a nearly-exact alternative theory, to which LSD and GGA are also approximations, is constructed, which yields an alternative physical interpretation in the absence of a strong external magnetic field. In this theory, $n_\uparrow(r)$ and $n_\downarrow(r)$ are not the physical spin densities, but are only intermediate objects (like the Kohn-Sham orbitals or Fermi surface) used to construct two physical predictions: the total electron density $n(r)$ from

$$\tilde{n}(r) = n_\uparrow(r) + n_\downarrow(r), \quad (40)$$

and the full-coupling strength on-top electron pair density $P_{\lambda=1}(r, r)$ from its LSD or GGA approximation

$$\tilde{P}_{\lambda=1}(r, r) = P_{\lambda=1}^{\text{unif}}(n_\uparrow(r), n_\downarrow(r); u = 0), \quad (41)$$

where $P_{\lambda=1}^{\text{unif}}(n_\uparrow, n_\downarrow; u = 0)$ is the full coupling-strength on-top pair density for an electron gas with uniform spin densities $n_\uparrow$ and $n_\downarrow$.

Since (for fixed $n_\uparrow + n_\downarrow$) $P_{\lambda=1}^{\text{unif}}(n_\uparrow, n_\downarrow; u = 0)$ is an *even* function of $n_\uparrow - n_\downarrow$, this alternative interpretation encounters no LSD or GGA spin-symmetry dilemma. In the separated-atom limit for H_2 , it correctly makes $P_{\lambda=1}(r, r) = 0$ for r in the vicinity of either atom, since (by the Pauli exclusion principle) $P_{\lambda=1}^{\text{unif}}(n_\uparrow, n_\downarrow; u = 0)$ vanishes when either $n_\uparrow$ or $n_\downarrow$ vanishes.

The two physical interpretations of LSD and GGA are about equally plausible in a “normal” system. But, especially in “abnormal” systems, these approximations may be more faithful to the alternative theory, because of the close relationship between $P_{\lambda=1}(r, r)$ and the electron-electron potential energy of Eq. (5). Thus, accurate total energies are expected to accompany accurate

on-top pair densities. Indeed, the new interpretation helps to explain why LSD and GGA yield accurate total energies, and why in practice spin-density functional calculations of the energy are more accurate than total-density ones even in the absence of an external magnetic field, where *formally* $n(\mathbf{r})$ by itself suffices. Of course, when there is a strong external magnetic field coupled to the physical spin magnetization density $m(\mathbf{r})$, the alternative interpretation (which makes no prediction for $m(\mathbf{r})$) is inappropriate.

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Note added in proof: Since this article was written, a method for improving the energy of semilocal functionals, using the ideas of Section 3.1, has appeared [83], and further examples of abnormal systems have been identified [84].

5 Appendices

5.1 Details of Configuration Interaction (CI) Calculations

The wave functions for the Ne and Be atoms which we used in this work are described in detail in Ref. [19].

The CI wave function for the He atom was calculated with the COLUMBUS program system [78, 79], which contains a program for the generation of the one- and two-particle density matrix of multireference single- and double-excited CI wave functions [79]. The gaussian basis set used for this calculation was an uncontracted 9s4p3d basis, as contained in the MOLCAS basis set library [80]. The correlation energy obtained with this basis set was -0.04014 hartree. To generate the data used in Fig. 2 the gaussian basis set was further augmented with two f functions with exponents 1.5 and 0.6. The resulting wave function gives a correlation energy of -0.04101 hartree.

5.2 Details of MP2 Calculation of Spin-Decomposition

The total correlation energy, as obtained from a second-order Møller-Plesset (MP2) [71] calculation, can easily be split into parallel- and antiparallel-spin contributions. The MP2 correlation energy E_2 is given by [81]

$$E_2 = -\frac{1}{2} \sum_{\tilde{i}\tilde{j}\tilde{a}\tilde{b}} \frac{\langle \tilde{i}\tilde{j} | V | \tilde{a}\tilde{b} \rangle (\langle \tilde{i}\tilde{j} | V | \tilde{a}\tilde{b} \rangle - \langle \tilde{i}\tilde{j} | V | \tilde{b}\tilde{a} \rangle)}{\epsilon_{\tilde{a}} + \epsilon_{\tilde{b}} - \epsilon_{\tilde{i}} - \epsilon_{\tilde{j}}}, \quad (\text{B1})$$

where $\tilde{i}$ and $\tilde{j}$ are the indices of the spin orbitals which are occupied at the Hartree-Fock level, and $\tilde{a}$ and $\tilde{b}$ are indices of unoccupied spin orbitals. The

orbitals φ_i are obtained from a Hartree-Fock calculation and the ε_i denote the orbital energies. The expectation values $\langle \tilde{i}\tilde{j} | V | \tilde{a}\tilde{b} \rangle$ are given by $\langle \tilde{i}\tilde{j} | V | \tilde{a}\tilde{b} \rangle = \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \varphi_{\tilde{i}}(\mathbf{r}_1) \varphi_{\tilde{a}}(\mathbf{r}_1) \frac{\langle \sigma_{\tilde{i}} | \sigma_{\tilde{a}} \rangle \langle \sigma_{\tilde{j}} | \sigma_{\tilde{b}} \rangle}{|\mathbf{r}_1 - \mathbf{r}_2|} \varphi_{\tilde{j}}(\mathbf{r}_2) \varphi_{\tilde{b}}(\mathbf{r}_2)$. The sum in Eq. (B1) will now be decomposed into sums over all possible spin combinations. With this aim in view we split off the spin component $\uparrow$ or $\downarrow$ of the spin orbitals and obtain

$$\sum_{\tilde{i}\tilde{j}\tilde{a}\tilde{b}} = \sum_{a\uparrow b\uparrow i\uparrow j\uparrow} + \sum_{a\downarrow b\downarrow i\downarrow j\downarrow} + \sum_{a\uparrow b\downarrow i\uparrow j\downarrow} + \sum_{a\downarrow b\uparrow i\downarrow j\uparrow} + \sum_{a\uparrow b\downarrow i\downarrow j\uparrow} + \sum_{a\downarrow b\uparrow i\uparrow j\downarrow} . \quad (\text{B2})$$

The first two terms on the right hand side of this equation involve only parallel-spin electrons and therefore give rise to parallel-spin correlation contributions of the form

$$E_2^{\uparrow\uparrow} + E_2^{\downarrow\downarrow} = - \sum_{ijab} \frac{\langle ij | V | ab \rangle (\langle ij | V | ab \rangle - \langle ij | V | ba \rangle)}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}, \quad (\text{B3})$$

with

$\langle ij | V | ab \rangle = \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \varphi_i(\mathbf{r}_1) \varphi_a(\mathbf{r}_1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \varphi_j(\mathbf{r}_2) \varphi_b(\mathbf{r}_2)$. The third and fourth terms describe the interaction of electrons with antiparallel spin. The contribution from these terms is given by

$$E_2^{\uparrow\downarrow} = - \sum_{ijab} \frac{|\langle ij | V | ab \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}. \quad (\text{B4})$$

Note that the exchange integral $\langle i\downarrow j\uparrow | V | b\uparrow a\downarrow \rangle$ vanishes in this case. The last two terms of Eq. (B2) show a spin flip of the electrons as they are excited from orbital i to orbital a and from orbital j to orbital b . This contribution vanishes, since the Coulomb interaction between the particles does not cause a spin flip.

The contracted 4s2p, 3s2p1d, and 5s3p1d basis sets in Table 4 are the double-zeta, double-zeta plus polarization, and triple-zeta plus polarization basis sets from the TURBOMOLE [82] basis-set library. The CI calculations with these gaussian basis-sets were of single-reference single- and double-excited CI type. The multireference CI calculation for the Ne atom with the uncontracted 14s9p4d3f basis is described in Ref. [19]. This calculation was repeated with an additional g function with the exponent 2.88 leading to the results for the 14s9p4d3f1g basis set reported in Table 4.

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Nonlocal Energy Functionals: Gradient Expansions and Beyond

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1 Introduction

The determination of the ground state energy and the ground state electron density distribution of a many-electron system in a fixed external potential is a problem of major importance in chemistry and physics. For a given Hamiltonian and for specified boundary conditions, it is possible in principle to obtain directly numerical solutions of the Schrödinger equation. Even with current generations of computers, this is not feasible in practice for systems of large total number of electrons. Of course, a variety of alternative methods, such as self-consistent mean field theories, also exist. However, these are approximate.

The publication in 1964 of the seminal paper by Hohenberg and Kohn on the theory of the inhomogeneous electron gas marked a major advance in the rigorous description of many-electron systems and laid the foundation for extensive developments which have resulted in a wealth of new insights and successful applications [1]. The results of their paper are summarized in two theorems. The first theorem establishes a one-to-one correspondence between a given nondegenerate ground state density function $n(\mathbf{r})$ and (to within a constant) the external potential $V(\mathbf{r})$ in which the interacting electrons are situated. As a consequence, the ground state energy can be expressed as the functional

$$E[n] = \int d^3r V(\mathbf{r})n(\mathbf{r}) + F[n] \quad (1)$$

where explicit reference to $V(\mathbf{r})$ is not required for $F[n]$. The second theorem states that when $E[n]$ is varied over the allowed class of ground state density functions, for a given $V(\mathbf{r})$, the minimum value obtained is the true ground state energy and this minimum occurs when the density function is the true ground state density. The original theorems of Hohenberg and Kohn have been extended to multicomponent systems, to electronic systems in magnetic fields, to superconductors, to quantum field theoretic systems, and other areas. The generalizations to various ensembles include thermal ensembles at finite temperature. Discussions of these important extensions, together with appropriate references are given elsewhere in this volume.

The theorems of Hohenberg and Kohn are truly remarkable. The formulation of the theorems is conceptually very nontrivial, but their proofs are simple once the ideas have been formulated; there are no large-scale manipulations of equations. A rigorous logical framework is established for the treatment of inhomogeneous many-electron systems, with the case of a homogeneous system being tautological. The possibility of a logical description of inhomogeneous systems in terms of $F[n]$ is established, but information about the properties of this functional must be obtained by other means (such as explicit studies as described in the following). In generalized formulations, there is even freedom concerning the choice of the variable functions to be used in describing the basic functional, although some choices will be better than others. At the same time, these powerful ideas have had immensely important practical consequences. The density functional procedures which have developed from them, coupled with

the representation of Kohn and Sham [2] for the kinetic energy contribution to $F[n]$, have become the current state of the art techniques for obtaining accurate numerical results for the properties of atoms, molecules, clusters, and many condensed matter systems.

There is no doubt that further extensions and adaptations of density functional theory to new materials and new physical properties will be made in the near future and that important applications will follow. The continuing development of energy functionals which accurately describe an ever wider variety of physically different situations is essential. Systems of reduced dimensionality (such as heterojunctions) or of restricted geometry, strongly correlated electron systems, the low density regions of electronic systems, phase diagrams and all of thermodynamic properties at finite temperature, and complex liquids are a few examples. The universal functional applies to all of these cases, of course, but what is the most effective way to gain understanding of the various aspects of its structure?

I believe that progress in achieving a full density functional description of such a wide variety of systems will be enhanced if attention is focused at this point on features of energy functionals which distinguish between different physical situations. Sometimes the differences may be sufficiently fundamental as to warrant descriptions in terms of “universality subclasses”. Understanding gained from systematic study of different, well defined types of such functionals will be useful for extending our understanding of the universal aspects of density functional theory, for developing increasingly better approximate energy functionals which span wider ranges of physical systems, and also for practical applications.

In this contribution, I will first discuss some general properties and classifications of physical systems and their functionals $F[n]$ according to their global symmetries and global boundary conditions. The role of gradient expansions in systematic exploration of the structure of energy functionals in the case of slowly varying density distributions is then discussed. Convergence properties of such expansions are considered. Technical details are given in an Appendix. Important differences between finite systems and the thermodynamic limit of extended systems are pointed out. The development of new structure in the low density regime is emphasized. Results of recent calculations of the leading exchange gradient contributions to the free energy at finite temperature are summarized. The status of exchange-correlation gradient contributions, and of their generalizations, to the ground state energy is discussed.

2 Constructing the Energy Functional

It is clear that the functional $F[n]$, which plays such a prominent role in the theory of Hohenberg and Kohn, must be a quantity of unusual complexity. It is

useful to consider an explicit algorithm for its construction. The discussion will be pedestrian, but hopefully will also be clear.

In order to generate information about the functional $F[n]$ consider an electrically neutral system containing a strictly finite number N of electrons, interacting via Coulomb interactions, moving in a fixed one-body potential $V(\mathbf{r})$ in a space of D dimensions. For this $V(\mathbf{r})$, evaluate the appropriate ground state expectation value of the Hamiltonian and of the density operator. The corresponding value of $F[n]$ is determined by using Eq. (1). Now repeat this process by varying $V(\mathbf{r})$ in ways allowed by the physically imposed symmetries and the global boundary conditions which were imposed. Again using Eq. (1), the procedure can be thought of as building up a vast catalogue of numerical results for $F[n]$ for this class of allowed density functions. It is sufficient to index the different values of $F[n]$ by the density function, $n(\mathbf{r})$, alone because of the one-to-one correspondence between the one-body potential and the ground state density. These values of $F[n]$ will depend on the type of interactions in the system (in this case, Coulombic), the dimensionality of the space, and on all of the parameters entering the Hamiltonian (such as the particle masses). The values of $F[n]$ will also depend on the global boundary conditions which have been assumed for exactly the same reason that the solutions of the original Schrödinger equation depend on the boundary conditions which are imposed. This procedure can be repeated for a variety of symmetries and global boundary conditions. Next, include spin and orbital magnetic interactions and external magnetic fields, in which case the catalogue of $F[n]$ values now contains important relativistic effects. Such studies can be extended to study the thermodynamics of finite systems in thermal equilibrium at a finite temperature [3, 4].

This discrete “case by case” study is a reasonably well defined and concrete, although pedestrian, approach to obtaining information about $F[n]$. Careful study of this collection of data sets can yield substantial insight into the structure of the functional. There are now two issues. How “complete” is this information and how can this information be used? The information may be considered to be reasonably “complete” if a sufficiently representative set of density functions has been studied for each class of physical system of interest. Next, it is hoped that study of these representative data sets will result in sufficient insight and general understanding of the density function dependence that practical algorithms can be proposed for reliable approximations to $F[n]$ for the classes of systems which have been studied. The accuracy of suggested approximants when extrapolated to new situations can be tested and refinements introduced as appropriate.

The procedure which I have indicated proceeds by explicitly accumulating data on different types or classes of physical systems. Approximate functionals which have been developed for a given class of system need not automatically give adequate representations for different classes of systems. To describe this fact, it is useful to recognize explicit universality “subclasses”. Consider an example. It is feasible to imagine that the above procedures could result in the construction of functionals of the density which give highly accurate descrip-

tions of both simple Fermi-liquid-like systems and heavy fermion materials. It is also reasonable to expect that the description of the high temperature oxide superconductors, including the rich variety of their phase transitions, could also be incorporated, with some extensions of the functionals. These systems would thus belong to the same universality subclass and be explicitly described by the same functional. Other physical systems, of the same universality subclass, could be included as the theory is further extended and unified. On the other hand, physical systems which differ in more “global” ways, by virtue of symmetries, boundary conditions, geometrical constraints or topologies, or by certain types of limiting procedures, may require their own subclasses of the universal functional. Of course, the universal functional is defined by the totality of all of its subclasses.

3 Global Symmetries, Boundary Conditions and Universality Subclasses

It is natural in this constructive approach to focus attention on global symmetries and boundary conditions in the development of functionals for specific types of systems. One of the most important global effects concerns the effect of different boundary conditions on the density in strictly bounded geometries versus fully extended geometries. These considerations were implicit in all of the above discussion because the ground state energy on the left hand side of Eq. (1) requires that the boundary conditions on the ground state wave function be specified. This sharply distinguishes between finite, or bounded, systems and extended systems. Atoms and molecules are two examples of small systems with bounded geometries. Of course, there are also large systems having bounded geometry. The essentially bulk properties of a large system in thermodynamic limit can be described by the boundary conditions of an appropriate extended systems. Of course, it is only the interior of a macroscopic specimen, far away from all surfaces, that can be modeled as being a part or subvolume of an extended system. The density of electrons in such a case is more nearly “uniform” in that it never is essentially zero over a large portion of the space. Of course, the electronic density in the interior of any real metal or semiconductor, for example, is not uniform on truly microscopic distance scales. In fact, the range of variation may be very large, but the point is that the density does not vanish in the way characteristic of an isolated bounded system. This difference has very fundamental consequences.

The particle density in an isolated bounded system is required to be zero at the boundary point at infinity. This introduces gaps (or discreteness) in the excitation spectrum, at low energy, which are not present in extended systems. The presence of shell structure, and whether the shells are open or closed, is

a related global effect which is also particularly evident in small systems. In the case of strictly extended systems, periodic boundary conditions on the density are more suitable and the thermodynamic limit of large particle number, N , and large volume, Ω , is to be taken with finite average density, N/Ω . Of course, extended systems can also have subtle global effects. The interesting structure of functionals which can describe the band gap discontinuities in semiconductors, as a consequence of gaps in the single particle spectrum, is one example. Other examples could be given in which the structure of the low energy excitation spectrum is seen to play a major physical role. For the purpose of constructing approximate functionals for practical computations, it can be convenient to recognize these different types of physical systems as subclasses of the universal functional $F[n]$.

There is an important case which is intermediate between small bounded systems and macroscopic fully extended systems, namely the description of the surface region of a macroscopic metal. The correlation functions which describe density fluctuations in the surface region are extremely anisotropic and of long range, very unlike their counterparts in the bulk, and the thermodynamic limit must be taken with sufficient care. Consider the static structure factor for a large system of N particles contained within a volume Ω ,

$$NS(\mathbf{q}, \mathbf{q}) = \int_{\Omega} d^D r \int_{\Omega} d^D r' \exp[i\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}')] S(\mathbf{r}, \mathbf{r}'). \quad (2)$$

Both N and Ω are macroscopically large but strictly finite. (When the thermodynamic limit is taken later, their ratio is to be held fixed and finite.) There is no doubt that $S(\mathbf{q}, \mathbf{q})$ is exactly zero at $q = 0$ (due to particle number conservation) and that its limit as $q \rightarrow 0$ is also zero (since the volume and associated length scales, L , are strictly finite). However, the structure of Eq. (2) implies that the characteristic wavenumbers at which $S(\mathbf{q}, \mathbf{q})$ becomes dominated by the particle conservation sum rule are of order $1/L$, at large L . This wave number region disappears in the large N and Ω limit with the consequence that $S(\mathbf{q}, \mathbf{q})$ will tend, after the thermodynamic limit, to a nonuniversal (generally nonzero), geometry dependent limiting value.

The corresponding situation at finite temperature is also instructive. Suppose that density correlation functions have been calculated in a grand canonical ensemble, with particle number conserved on the average. It is fully expected that the static structure factor thus calculated will be in agreement with an experimental determination by neutron scattering, for example, in the accessible wave number range for a macroscopic sample. However, the $q \rightarrow 0$ limit of this grand canonical $S(\mathbf{q}, \mathbf{q})$ is fixed by the thermodynamic sum rule relating the mean square number fluctuations to the compressibility. The quantities in this sum rule, and therefore the limiting value in question, are material dependent, temperature dependent, generally nonzero, and certainly not universal. The point is again that taking the thermodynamic limit has removed from $S(\mathbf{q}, \mathbf{q})$ the structure which was important for ensuring the particle conservation sum rule for finite systems. Note that this nonuniversality of the small q limit of the grand

canonical static structure factor occurs even for a bulk system of uniform density, for which “perfect screening” considerations hold [5]. The differences between the grand canonical structure factor and its counterpart calculated with particle number strictly observed, which occur only at wavelengths of order the linear dimensions of the system, disappear when the thermodynamic limit is taken at fixed finite q .

It is therefore clear that particle number conservation considerations are not sufficient to determine $S(\mathbf{q}, q)$ at very small but finite q . In the case of broken translational symmetry, as certainly occurs in the vicinity of a surface, the perfect screening of density fluctuation matrix elements, which is characteristic of homogeneous systems, does not hold due to nonconservation of momentum, and the small q limit of $S(\mathbf{q}, q)$ is nonuniversal even in the zero temperature case.

Consequently, discontinuities in certain correlation functions are not uncommon in the thermodynamic limit. Other examples are known. For example, Kirzhnits made a similar point concerning the static dielectric function [6]. The mathematical reason why such discontinuities are not prohibited is that the commutation rule, $[N, H] = 0$, becomes meaningless in the thermodynamic limit. The reader is referred to the literature for additional discussion [7, 8].

This discussion has emphasized the fundamental differences between finite (whether small or large) and fully extended systems. An energy functional which describes, for example, 1 cm^3 of silicon or lead, contains a great deal of information about its surface properties as well as its bulk properties. However, all such surface information disappears from the functional when the thermodynamic limit is taken. I must emphasize that this process is irreversible! Information on physical quantities which are sensitive to the delicate correlations in the boundary regions cannot be found in energy functionals of the corresponding extended system. This is another example of the importance of the global boundary conditions and the related universality subclasses.

It is important to note that it is feasible, in principle, to postpone the strict thermodynamic limit and to consider energy functionals of very large but finite systems which have surface effects explicitly included. The same possibility applies to correlation functions, which exhibit long-range correlations in the vicinity of surfaces. It would be very desirable for applications to have representations which explicitly exhibit the “crossover” behaviour between large but finite and extended bulk systems. Analogous crossover behaviour is well known in large but finite systems which undergo second order phase transitions and exhibit long correlation lengths due to proximity to a critical point. In these cases, the corresponding “finite size scaling” representations, which also exhibit discontinuities in the infinite volume limit, have been found to be very powerful and are often indispensable in practice in the analysis of data. I emphasize again that information characterizing surface and finite size effects is irrevocably lost if the $1/L \rightarrow 0$ limit is taken. It is impossible to describe finite size features of the long wave-length structure factor in terms of elementary bulk ($1/L = 0$) properties just as it is impossible to describe correctly the finite temperature properties of a system in terms of ground state ($T = 0$) functionals.

Applications of density functional theory to practical computations of properties of physical systems at finite temperature will be increasingly important in the future. It is useful to consider how global symmetries and boundary conditions suggest universality subclasses in this situation. Suppose that in the finite temperature extension of density functional theory, a functional has become available which adequately describes the thermodynamic properties of materials of the $3d$ transition series and the $4f$ lanthanide series, many of which undergo magnetic phase transitions. This functional, denoted by $F[n, \mathbf{m}; T]$, will depend on the electron density $n(\mathbf{r})$, the density of magnetization $\mathbf{m}(\mathbf{r})$, and the temperature [4]. Now how does this functional lead to a prediction of the thermodynamic properties near a critical point? The order of the transition, critical exponents, and critical amplitude ratios must be correctly given, in principle. It is reasonable to expect that short distance details and “noncritical” degrees of freedom will be suppressed as T approaches T_c and that the predictions will be in agreement with those of a coarse grained Ginsburg-Landau-Wilson effective Hamiltonian or free energy [9].

It is well known that these effective Hamiltonians fall into Wilson’s “universality” classes which are defined by the number of degrees of freedom of the order parameter, the symmetries of the effective Hamiltonian, the dimensionality D of the space (which is related to a global boundary condition in the case of quasi- one-and-two-dimensional systems), with certain other features sometimes becoming relevant. All effective Hamiltonians within a given Wilson universality class have precisely the same critical characteristics, including critical exponents and critical amplitude ratios, near the critical point. Evidently, $F[n, \mathbf{m}; T]$ contains equivalent information, in addition to other features which are dominant in other domains of temperature or pressure. Free energy functionals, $F[n, \mathbf{m}; T]$, defined within density functional theory could then be categorized according to their properties near magnetic critical points, if desired. Of course, this is generally distinct from the classification into universality subclasses according to a global boundary condition, for example.

I now want to address the question of whether a description in terms of universality subclasses is useful. For orientation, consider the corresponding question in the case of the Wilson effective Hamiltonians near a critical point. Are the Wilson universality classes absolutely necessary? The answer is “no” in the sense that it could be argued that everything was already contained in the partition function defined in terms of the microscopic model Hamiltonian anyway and an explicit calculation based on a universally defined quantity would provide all of the results. Of course, this is obviously perverse and the time scale for making progress in this “straightforward” way is very long. The answer is unequivocally “yes” in several other senses. The overall level of understanding of critical phenomena advanced greatly by knowing which general features of a coarse-grained Hamiltonian are crucial and which are irrelevant. Also, on facing a new problem, it might happen that a general consideration of its order parameter and the symmetries of the associated effective Hamiltonian would lead to its identification in terms of a known Wilson

universality class. In this case, the critical properties of thermodynamic quantities in the new problem immediately become known since all members of a given class, irrespective of any differences in their microscopic origins, have the same critical behaviour. Further calculation is not needed. There is no need to turn to the (possibly insurmountable) task of evaluating the microscopically based partition function for the new problem. This is certainly useful!

Now return to finite temperature applications of density functional theory. There is the usual exact statistical mechanics algorithm for generating partition functions and the corresponding free energies in terms of thermodynamic variables. Of course, this is exactly the same fundamental algorithm which applies in critical phenomena. Now this “first principles” approach is sidestepped in critical phenomena by the functional integral representation for a coarse grained average effective partition function which emphasizes the long wavelength degrees of freedom and the symmetries of the order parameter. Explicit calculations in this representation are made possible by the renormalization group methods developed by Wilson [9]. Of course, these results are restricted in their validity to an appropriate vicinity of critical points. An essential goal of density functional theory is the development of suitable free energy functionals of the relevant particle densities such that practical, quantitatively reliable calculations of thermodynamic properties can similarly be performed without the need for returning to the microscopic partition function for each new application. In other words, the “first principles” approach is to be sidestepped by the concept of the universal free energy in a very general and rigorous way. It will be necessary to describe in density functional terms the fundamental differences which exist between physical systems, as well as the similar aspects which they share, in order to achieve the goal of a unified accurate approach to new classes of systems. Explicit recognition of universality subclasses can be useful for clarifying procedures in some aspects of this endeavour.

How are suitable approximations to the universal free energy functional to be obtained? It is necessary to make use of the fundamental partition function of statistical mechanics, of course. With this finite temperature algorithm, generate numerical data sets for free energies at temperature T for classes of physical systems. Following the same principles as for the ground state energy problem, extensive study of such collections of these data sets must provide the basis for constructing representations which express these free energies as functionals of the particle density (or densities in multicomponent cases). The proposed functionals are to be used in computations in fairly general circumstances, not just at critical points, and are to be subjected to extensive testing and updating, as new situations are described, just as was the case for the ground state problems.

It is evident that the task of producing high quality free energy functionals is challenging. All available guidance should be considered. In particular, there is no doubt that general considerations, such as global symmetries, will play a role and that different types of systems can be classified according to universality subclasses. Of course, their structure will be much richer than was the case for

ground state problems. In spite of this complexity, the prospects for progress are very good. A great deal is known about finite temperature many-body systems, ranging from low temperature expansions in dense systems to virial expansions for low density systems and to critical phenomena and systems which exhibit broken symmetries. This knowledge must be translated into density functional language.

The above discussion focused on fundamental differences which may exist between different physical systems of interest. There can also be important differences between different density regimes of a single physical system, provided the overall inhomogeneity in density is sufficiently strong.

4 Local Density Approximations and Gradient Expansions

In ground state applications of density functional theory, it is convenient to extract the Hartree energy from $F[n]$. The representation proposed by Kohn and Sham for the remainder has become the standard approach for most practical computations [2]. Their introduction of a noninteracting reference system described by orbitals explicitly recognizes the crucial nonlocality of the kinetic energy and also serves the important role of controlling the class of density functions which an approximate energy functional is allowed to sample. Having introduced this functional representation for the kinetic energy, the only remaining contribution to $F[n]$ is, by definition, the exchange-correlation contribution, $E_{xc}[n]$, to the ground state energy. Similar procedures apply to the free energy at finite temperature. It is the exchange-correlation contribution which contains the difficulties. The simplest approximation to E_{xc} is the local density approximation in which the exchange-correlation energy is approximated by its value in a locally uniform density system, with small corrections due to density gradients

$$E_{xc}[n] = \int d^3r n(r) \varepsilon_{xc}(n(r)) + 0((\nabla n(r))^2). \quad (3)$$

If the nonlocal gradient corrections are neglected altogether, the local density approximation for $E_{xc}[n]$ results. In many applications of density functional theory, it has been found to be important to extend the definition of the energy functionals to include spin polarization. The dependence of the exchange-correlation energy on spin $\uparrow$ and spin $\downarrow$ electrons separately can be determined. The local spin density approximation to the exchange correlation energy is then defined by

$$E_{xc}^{\text{local}}[n \uparrow, n \downarrow] = \int d^3r n(r) \varepsilon_{xc}(n^\uparrow(r), n^\downarrow(r)) \quad (4)$$

where $n(r) = n^\uparrow(r) + n^\downarrow(r)$.

Many density functional applications to atoms, molecules, clusters, and solid state systems have been made, based on the spin-polarized Kohn-Sham scheme

with Eq. (4) used for the exchange-correlation energy. The overall accuracy has been typically a few percent in many of these applications. Of course, whether or not this level of accuracy is sufficient depends on the objectives of the problem under consideration. There are cases where major contributions to the relevant energy, or energy differences, come from regions of space which are not well treated by local approximations. In such cases, errors will be more serious. Some examples are the total ionization energies of atoms, in particular the ionization energies of the innermost tightly bound electrons, *sp* and *sd* atomic transfer energies, the relative stability of electronic configurations and molecular bond energies. In general, substantial errors are expected if the quantities of interest are particularly sensitive to the electron densities either very near to or very far from nuclei.

Various reasons have been advanced for the relative accuracy of spin-polarized Kohn-Sham calculations based on local (spin) density approximations for E_{xc} . However, two very favourable aspects of this procedure are clearly operative. First, the Kohn-Sham orbitals control the physical class of density functions which are allowed (in contrast, for example, to simpler Thomas-Fermi theories). Second, local density approximations for $E_{xc}[n]$, are mild-mannered, unbiased, and everywhere finite and do not interfere with that controlling role. This applies near nuclei, in the low density regimes of atoms and molecules, and even far from a metallic surface.

There have been intense efforts to include corrections to Eq. (4) and thereby to increase the level of accuracy by addressing the inevitable nonlocal structure of $E_{xc}[n]$. Of course, accounting for nonlocality, particularly in sensitive regions of the electron density distribution, is very difficult due to the rather limited a priori knowledge of exchange and correlation in general inhomogeneous many-electron systems. In this contribution, insight will be generated by first studying limiting cases for which rigorous results can be obtained.

A systematic approach to learning something about $E_{xc}[n]$ in cases where the particle density is slowly varying in space was already indicated by Hohenberg and Kohn [1]. The local density approximation is taken as a starting point and corrections to it are generated by perturbation expansions taken to arbitrarily high order. The domain of validity of this approach is limited, of course, but the information gained is precise within that domain. From symmetry arguments, these nonlocal corrections are taken to be represented as an infinite series of terms involving integrals over gradients of the density

$$\begin{aligned}
 E_{xc}^g[n] = \int d^D r \{ & B_{xc}(n(\mathbf{r}))(\nabla n(\mathbf{r}))^2 + C_{xc}(n(\mathbf{r}))(\nabla^2 n(\mathbf{r}))^2 \\
 & + D_{xc}(n(\mathbf{r}))(\nabla^2 n(\mathbf{r}))(\nabla n(\mathbf{r}))^2 + E_{xc}(n(\mathbf{r}))((\nabla n(\mathbf{r}))^2)^2 \\
 & + \mathcal{O}(\nabla^6) + (\text{nonanalytic terms}) \}.
 \end{aligned} \tag{5}$$

The nonanalytic terms indicated in Eq. (5) are consequences of the singular logarithmic factors which contribute terms such as $k^2 \ln(k^2)$, $k^4 \ln(k^2)$ and so on to the long wavelength expansions of correlation functions describing interacting many-fermion systems in their ground states [7, 8]. These terms are not

artifacts of long range Coulomb interactions, but appear even for short range interaction systems. The singular character of these contributions can be circumvented by taking account of finite temperature [10, 11] but there are nevertheless implications for effective ion-ion interactions and spin-spin interactions [7, 8]. Derivations of the leading gradient coefficient, B_{xc} , were given by Ma and Brueckner [12] for the correlation component at high density and by Sham [13] for the first order exchange contribution. An exact self-consistent Hartree-Fock calculation of the exchange component [14, 15, 16] and an approximate calculation of the correlation component of B_{xc} in the range of metallic densities [17, 18] were then given. This was followed by a variety of extensions and applications to multicomponent spin-polarized systems [9] and to electron-hole liquids [20] and droplets [21]. The full derivation of the values of the coefficients, B_{xc} and so on, is somewhat technical. Extensive reviews with full references to the derivations and to applications of the results are available in the literature [7, 8]. An outline of the derivation is given in the Appendix. I want to focus here primarily on the meaning of the procedures and on the convergence properties of the results.

The most convenient and general way to derive Eq. (5) involves subjecting an otherwise uniform system to a very weak and slowly varying static external potential $V(\mathbf{r})$. The shift in the energy and the density are calculated to all orders in $V(\mathbf{r})$. A Lagrange inversion then gives $V(\mathbf{r})$ as a power series in the density shift and the result can be used to express the energy shift as an infinite series in powers of the density shift. The coefficients of this functional Taylor series involve not only the linear but also all of the higher order nonlinear density response functions of the uniform system at its density n_0 . These response functions are then expanded in powers of wavenumbers at long wavelength. The resulting series in powers of both wavenumbers and density shifts must then be rearranged and partially resummed to obtain two essential results. (1) The coefficients of the series expansion are now all evaluated at the local density $n(\mathbf{r})$. (2) The functional expansion parameters are now the entire set of all of the derivatives of the local density. The leading term of this expansion is the local density approximation and the rest of the series of gradient corrections is Eq. (5).

This rearrangement and partial resummation of the perturbation expansion is an extremely important step in the derivation of the gradient expansion series. Every term in Eq. (5) has contributions to all orders in powers of the external potential $V(\mathbf{r})$. As a consequence, the final result no longer has any reference to n_0 of the initial uniform system and so is of general validity within the universality subclass of slowly varying density systems, even though the overall variation of the density may be large throughout the system. The corresponding calculations at finite temperature for the gradient expansion for the contributions to the nonlocal free energy follow a similar path, although the technical details are more involved.

Now consider the convergence properties which might be expected for this method. There are four major points. (1) Each coefficient in Eq. (5) is based on a partial resummation of a perturbation expansion containing nonlinear re-

sponse functions to infinite order. No general conclusions about the convergence of the overall process can be drawn by study of only the lowest order linear response function. Instead, considerations of convergence must be based on the global functional structure of such expansions and are strongly dependent on the density profile. (2) The exact ground state linear and nonlinear response functions, for both particle number density and spin density, exhibit nonanalytic wavenumber dependence at long wavelength, as indicated in Eq. (5). This nonanalytic behaviour occurs even for very smooth applied potentials $V(\mathbf{r})$ and is due to the sharp Fermi surface. The convergence problem associated with this type of nonanalyticity is overcome by always working at finite temperature since thermal smearing removes the sharpness of the Fermi surface. At this point, the existence of all of the gradient coefficient functions in Eq. (5) can be taken as established. (3) The next step is to insert the density profile for the problem at hand into Eq. (5) and to carry out the integration over the space. For dimensional reasons, the terms with high powers of gradients must have high powers of $n(\mathbf{r})$ occurring in the denominators of the respective integrands. These terms give large contributions to the series. Note that this implies at once that the gradient series can have problems in low density situations, even if care has been taken with finite temperature and boundary conditions to ensure that the density does not actually vanish [22]. At this point, the existence of each of the integrals in Eq. (5) is assured. (4) Next, even if all expansion coefficients and all integrals exist, the actual sum of the series of gradient correction terms may be divergent. This corresponds to a global divergence of the gradient expansion. Provided the density profile is contained in the domain of slowly varying density variations, it is not unreasonable, based on experience with other perturbation expansions in many-body problems, to conjecture that the series may be asymptotic and that it might be usefully resummed (if actually required) by a suitable resummation procedure.

It is important to observe, however, that even if the series turns out to be only asymptotic, the use of an appropriate finite number of the low order terms of the series can still give accurate results, provided the density variation is slow enough. Important insight into the nonlocal energy and free energy and the correlation functions can be obtained in a controlled and precise way for this subclass of system.

5 Low Density Regimes

There are many problems of interest where the particle density becomes very small and may even vanish. Can the information obtained from the gradient expansions be of any use in such cases? First, note that an estimate of the nonlocal contributions to the energy can be given by Eq. (5), provided the series is truncated at an optimal point (certainly prior to the occurrence of any

extremely large contributions due to integrals over low density regions). This approach has been applied to a variety of situations, with results that are better than perhaps should be expected in view of its extreme simplicity. The importance of an optimal truncation of the gradient series is particularly striking in cases where applications are made to bounded systems where the particle density actually vanishes. Certainly, as was previously discussed, gradient expansions in the form of Eq. (5) do not treat correctly the low density regions of bounded systems.

If the elementary form of the gradient expansion for $E_{xc}[n]$ is of limited use for bounded systems, is there any possibility that the conjectured resummation of the asymptotic series could still be applicable? Information on this point is sparse but, as will be seen, the answer appears to be no. The utility of such a resummed asymptotic functional series, or of a convergent gradient series should that turn out to be the case, is limited to the universality subclass of sufficiently slowly varying density profiles. The conditions which are required to establish this functional series, and its convergence, cannot be satisfied in the case of an isolated bounded system. The character of the low density electron system, with high density gradients, is so different from the character of the low density gradient system, at high density, that it is to be expected that the gradient series, whether resummed or otherwise, will either diverge in an uncontrollable way or else “converge” to a result which has no relation to the physical problem at hand. In other words, the divergence of the gradient series, in this application, is physically real and unavoidable. Resummation and related devices can atone for bad mathematical behaviour engendered by awkward perturbation expansions carried out within a specific class of system, but they cannot bridge the gap between two universality subclasses which differ by global boundary conditions.

The treatment of the low density regions of electronic systems has traditionally posed problems for density functional theory and information is sparse. In order to appreciate more fully the fundamental character of the low density regime, it is instructive to reconsider the perturbation expansions which led to gradient expansions but to avoid the long wavelength approximations for the various density response functions. The exchange-correlation contribution to the ground state energy shift in the presence of an applied static external potential, $V(r)$, is given by standard second order perturbation theory in terms of the induced density shift, $\delta n(\mathbf{k})$, by Eq. (A.7) of the Appendix

$$\Delta E_{xc}[n] = -\frac{1}{2\Omega} \sum_{\mathbf{k}} |\delta n(\mathbf{k})|^2 v_{xc}(\mathbf{k}) \quad (6)$$

where the linear response function, $\pi(\mathbf{k})$, of the interacting many-electron system of uniform density, n_0 , has been expressed in terms of the residual, short range, attractive exchange-correlation interaction, $v_{xc}(\mathbf{k})$, thereby removing reference to the Lindhard function, $\pi_0(\mathbf{k})$, for the noninteracting electrons of the Kohn-Sham procedure. The previous approximation of replacing $v_{xc}(\mathbf{k})$ by its small

k expansion, which leads ultimately to gradient expansions, is appropriate only if the dominant contributions to Eq. (6) come from long wavelength Fourier components. This requires that $n(\mathbf{r})$ be slowly varying in space, which would be consistent. On the other hand, this approximation is certainly very poor when the density has rapid spatial variation.

What can be done to extract the rigorous information to order $\mathcal{O}(V^2)$ which is contained in Eq. (6) in cases where the weak external potential and the density profile have rapid variations in some regions of the physical system? Insight is obtained by considering the case of very low uniform density, n_0 . The contributions to Eq. (6) which are due to very rapid variation of the density come from large k Fourier components for which the wavenumbers are much larger than the fixed wavenumber scales of the problem, including the Fermi wavenumber, k_F , and the Thomas-Fermi screening length, k_{TF} . It is important to appreciate that, for essentially dimensional reasons, the limit of $v_{xc}(\mathbf{k})$ at large k and fixed finite density can also be achieved by the limit of low density at fixed finite k . Analysis of the perturbation expansions for the density response functions of the uniform density electron system confirms this expectation and shows that $v_{xc}(\mathbf{k})$ takes on a particularly revealing form. For $D = 3$ systems in the limit of large wavenumber, $v_{xc}(\mathbf{k}) \rightarrow -(4\pi e^2/k^2)\gamma_{xc}$ where γ_{xc} is a numerical constant ($\gamma_{xc} = 1/2$ in a self-consistent Hartree-Fock approximation) [23]. Note that there is no longer any reference to density scales! More detailed information for this large k and low density regime is generated by again considering a systematic expansion in powers of $V(\mathbf{r})$. The structure, for general D , of the rearranged series for the sum of the Hartree and the exchange-correlation energies in the low density regime is of the form [8, 24]

$$E_H[n] + E_{xc}[n] = \frac{1}{2} \int d^D r \int d^D r' n(\mathbf{r}) v(\mathbf{r} - \mathbf{r}') [1 - \gamma_{xc}(\mathbf{r}, \mathbf{r}')] n(\mathbf{r}') \quad (7)$$

This result has several important features which will be briefly discussed. An extremely large cancellation between the direct Coulomb (Hartree) energy and the exchange-correlation energy occurs in the low density regions of an electronic system. The same degree of cancellation occurs for the functional derivative of Eq. (7), which can also be constructed, so that the potentials which enter the Kohn-Sham equations have the correct behaviour in low density regimes. In particular, the regions of atoms and molecules which are far from nuclei are correctly represented. (The cancellation is complete in the case of the hydrogen atom, of course.) The physics of this cancellation is very important for a number of atomic and molecular problems, including self-interaction corrections, the ionization energies of few electron atoms, and molecular bond strengths. Conversely, insight into the character of energy functionals in low density regimes can be obtained by systematic study of properties of small molecules and clusters.

These considerations concerning low density regions apply not only to bounded systems but also to low density extended electron systems. A classic

example is given by the charge modulated states of the Wigner crystal in which the electron density may be very small but is nevertheless nonzero [8]. A precise treatment of low density regimes may also be relevant to an understanding of strongly inhomogeneous anisotropic extended many-electron systems which exhibit subtle charge and spin correlations due to regions of low carrier density. The cuprates and bismuthates of current interest are examples of this category.

I have emphasized that insight into energy functionals can be obtained by systematic procedures based on perturbative expansions, in powers of an external potential, for which various rearrangements and partial resummations are possible, leading to useful results. In the high density regions of a system, short range nonlocality can be included by gradient expansions. The nonlocal correlations in low density regions are of a very different, longer range, character. Both types of region will often occur in a single system of physical interest, of course, and the contributions of both types of region are included in the perturbation expansions. The simplest example of this is given by Eq. (6), in which the long wavelength contributions (leading to gradient expansions) are essentially disjoint from the large wavenumber contributions (leading to the low density nonlocal structures). Similar separations occur in higher order contributions. It is clearly not to be expected that any resummation of the long wavelength expansions could reproduce the structure of the short wavelength, low density regime. As previously concluded, the gradient expansion, however rearranged, must diverge when applied to a bounded system. Extended systems in the thermodynamic limit are in a different universality subclass and rearranged gradient expansions can be justified. However, a representation based on Eq. (7) will be more appropriate for the regions in which the density gradients are large. A functional which explicitly combines both the high and low density regimes, as well as the crossover between them, is required for general applications. Both Eq. (5) and Eq. (7) would then be contained as limiting cases. Such a functional is not yet available.

A number of suggestions have been made for semiempirical or otherwise approximate representations for the nonlocal contributions to $E_{xc}[n]$. A comprehensive review has been given in the monograph of Dreizler and Gross [25]. Information from the high density, low gradient regime required for application of Eq. (5) is incorporated into these representations in such a way that the approximations are correct in the domain of slowly varying density. The low density regions are controlled by explicit constraints imposed on the functional forms. In this manner, the two very different density regimes are incorporated into a simple energy functional in an approximate way. These approximate functionals are widely used and have been useful in a wide variety of situations. They are currently important components of state of the art computational algorithms.

6 Gradient Coefficients at Finite Temperature and Limiting Cases

I have emphasized the need to extend practical density functional computations to new areas of applications including systems of reduced dimensionality or restricted geometry and, especially, systems at finite temperature. The major problem is obtaining adequate approximations for the exchange-correlation contributions to the free energy. A systematic approach is required for the nonlocal contributions beyond the local density approximation and it is natural to consider gradient expansions. In this section, I will briefly discuss the results of a recent calculation [26] of $B_x(n_0; T)$ which determines the leading nontrivial nonlocal contribution to the free energy to first order in the interparticle two-body interaction, $v(\mathbf{r} - \mathbf{r})$, and to first order in $(\nabla n(\mathbf{r}))^2$. This provides the finite temperature exchange counterpart of $B_{xc}(n(\mathbf{r}))$ of Eq. (5). The corresponding correlation contributions will be required for practical applications but results are not yet available. Finite temperature calculations for reduced dimensional geometries have also been considered [27].

The procedures are similar to those used for the ground state energy. A general static external potential is treated in perturbation theory and the expansions are rearranged and resummed. The unperturbed system is of uniform density and fully extended and the thermodynamic limit is taken at the outset. Particular care is required to treat the chemical potential correctly. The result for $D = 3$ and arbitrary two-body interaction is [28, 29]

$$\begin{aligned}
 B_x(n_0; T) = \frac{\hbar^2}{m(n'_0)^2} \int d\mathbf{r} v(\mathbf{r}) \left\{ \frac{1}{6} \left[\left(\frac{n''_0}{n'_0} \right)^2 - \frac{n''_0}{2n'_0} \right] F_0 F'_0 + \frac{1}{6} F_0 F''_0 \right. \\
 + \frac{1}{2} F'_0 F''_0 - \frac{1}{6} \frac{n''_0}{n'_0} [F_0 F''_0 + (F'_0)^2] + \frac{\hbar^2}{2m} \left[\frac{1}{18} F_0 \nabla^2 F_0^{(iv)} \right. \\
 \left. \left. + \frac{2}{9} F'_0 \nabla^2 F''_0 - \frac{1}{6} \nabla F''_0 \cdot \nabla F''_0 \right] \right\} \quad (8)
 \end{aligned}$$

where primes and superscripts denote derivatives with respect to the chemical potential $\mu_0(T)$ of an extended system of uniform density $n_0 = n_0(\mu_0(T))$, and $F_0 = F_0(\mathbf{r}; T)$ is the Fourier transform of the Fermi distribution function at temperature T .

The case of bare Coulomb interactions, $v(\mathbf{r}) = e^2/r$, is of particular interest [29]. In this case, Eq. (8) can be evaluated analytically and expressed in closed form, after lengthy calculations, in terms of standard Fermi-Dirac integrals

$$B_x(n_0; T) = - \frac{\pi e^2 \hbar^4}{72 m^2} \beta^2 \left[\left(\frac{\mathcal{F}'_{-1/2}(\eta)}{\mathcal{F}_{-1/2}(\eta)} \right)^2 - 3 \left(\frac{\mathcal{F}''_{-1/2}(\eta)}{\mathcal{F}_{-1/2}(\eta)} \right) \right] \quad (9)$$

where $\eta = \mu_0(T)/k_B T$ and the Fermi-Dirac integral is defined by

$$\mathcal{F}_p(\eta) = \frac{1}{\Gamma(1+p)} \int_0^\infty \frac{x^p dx}{1 + e^{x-\eta}}, \quad (p > -1). \quad (10)$$

The limiting values in the degenerate (low T) and the classical (high T) limits are easily obtained from Eq. (9). It is interesting that $B_x(n_0; T)$ changes sign in the intermediate temperature region [29]. The low temperature limiting value is of special interest, as will be discussed in the following. This limit is given by $B_x^{th} = -\pi e^2/18k_F^4$ and will be referred to as the “thermal limit”.

The case of a Yukawa interaction, $v(r) = (e^2/r)\exp(-\lambda r)$, where λ may be thought of as simulating static screening, is also of interest. The previously used method of analysis is not suitable in this case and so results were obtained numerically after expressing Eq. (8) in wavenumber space [30]. In order to make contact with previous studies of ground state properties, special attention was given to low temperatures, $T/T_F \ll 1$ where T_F is the Fermi temperature, and to weak static screening, $\lambda/k_F \ll 1$. The limiting behaviour of $B_x(n_0; T, \lambda)$ is not uniform when both T and λ are both small. The temperature controls the limit if λ is taken to zero before the temperature; that is, $B_x(n_0; T, \lambda = 0) \rightarrow B_x^{th}$ as $T \rightarrow 0$. On the other hand, the static screening controls the limit if the temperature is taken to zero before λ ; that is, $B_x(n_0; T = 0, \lambda) \rightarrow B_x^{sc} = (7/8) B_x^{th} = -7\pi e^2/144k_F^4$ as $\lambda \rightarrow 0$. This latter value, which will be referred to as the “static screening” limit had been deduced by Sham in his study of the exchange gradient coefficient for the electron gas in its ground state [13].

The fact that there are two different limiting values for a single physical object is due to the potentially singular contributions to Eq. (8) from large interparticle separations. A regularization procedure is required. The static screening regularization of the physical bare Coulomb case introduces a factor of $\exp(-\lambda r)$ into the integrand of Eq. (8). It can be shown that the effect of finite temperature is to introduce into the integrand of Eq. (8) a factor of $[kr/\sinh(\kappa r)]^2$ at large distance and low temperature, where $\kappa = \pi k_B T/\hbar v_F$ describes how the ballistic motion of an electron of velocity v_F is damped by purely thermal fluctuations. It is the fact that thermal damping changes the power of r at large r in Eq. (8) in addition to introducing an exponential damping factor that leads to different limiting results for these two procedures.

In addition to these two different limiting values, there is yet another theoretical value of $B_x(n_0)$, for the ground state. The leading exchange corrections to the density response function, or equivalently $v_{xc}(k)$ of Eq. (6), were computed numerically for a wide range of k by Geldart and Taylor [23]. The curvature of the exchange contribution as a function of k in the long wavelength expansion determines $B_x(n_0)$. It was observed by Sham (see his Table I) that the data of Geldart and Taylor [23] implied an exchange gradient coefficient close to $(10/7)B_x^{sc}(n_0) = B_x^{gs}(n_0)$ [13]. We will refer to this value as the “ground state limit”.

It must be emphasized that the computation of $v_{xc}(k)$ at small k is very delicate, and must not be crudely pursued. There is a great deal of structure in the integrand of the multiple wavenumber integrals due to incipient singularities of the bare Coulomb potential and of the repeated energy denominators which are characteristic of perturbation expansions. In fact, the contributions of the individual Feynman graphs had already been calculated analytically in the

($k \rightarrow 0$) limit and shown to be logarithmically divergent at small wavenumber [31]. Geldart and Taylor took advantage of the explicit Pauli principle restrictions, and carried out a sequence of transformations and rescalings in such a way that absolutely all of the possible irregular behaviour was removed analytically. The resulting integrand was smooth in the new variables and the numerical multiple integration was relatively straightforward. Consequently, the accuracy obtained (at the level of fractions of 1%) was not only reasonable, particularly in view of limitations of computers of the late 1960s vintage, but was also even superior to some of the much later work on the same problem. It should be emphasized that the goal of the entire procedure of transforming and rescaling had been to obtain numerical stability by ensuring analytical cancellation of the singularities which were known to exist in the individual Feynman graphs at small k . For this reason, extensive testing of the integration routines was carried out in the regime of small k , much smaller than the step size of $0.1 k_F$ of the published table which was available to Sham. The numerical results were very close to the value surmised by Sham, which led to $B_x^{gs}(n_0)$.

The same Feynman graphs for the leading exchange contributions have been studied subsequently by various groups, some of which were apparently unaware of the earlier work of Geldart and Taylor [23]. The most accurate numerical work has been done by Chevary and Vosko who also emphasized the need to take care with the Pauli principle restrictions [32]. This paper also contains references to other numerical work. An analytical evaluation of $v_{xc}(\mathbf{k})$ has also been given by Engel and Vosko [33] and this treatment was completed by Glasser [34]. The most recent numerical work, and especially the exact small k expansion of the analytical result confirm completely the “ground state limit”, $B_x^{gs}(n_0)$ and confirm that the numerical results of Geldart and Taylor [23] are accurate to a fraction of 1%. Note that in this ground state case ($T \rightarrow 0$) with bare Coulomb interactions ($\lambda = 0$), it is k itself which controls the limiting value.

What is to be done with this plethora of values for what would have seemed to be a single physical quantity? The first point is that physically meaningful applications of gradient expansions to extended systems with continuous spectra demands that exchange and correlation contributions be treated together. Of course, it is often convenient to separate these two types of contributions. This is permissible provided a regularization procedure is consistently used with exactly the same procedures for both the exchange and the correlation components. Thus, the procedure of Sham is perfectly acceptable for treating exchange provided the same limiting procedure is used for correlation in the ground state, subject to the clear understanding that it is always the sum of the exchange and the correlation contributions which is physically meaningful for these extended systems. In this situation, the “static screening” parameter λ is merely a convenient device. For applications at finite temperature, the temperature automatically provides a regularization, which is also physically real rather than a device. In fact, there are never any divergent integrals even for bare Coulomb interactions! After calculations of the corresponding correlation

components are completed, the full $B_{xc}(n_0; T)$ will be available for physical applications. I emphasize that these comments apply only to extended systems.

Finally, I am unaware of reasons why any of the above possible candidates for the exchange gradient coefficient should be correct when applied to a bounded system. The semiempirical procedures based on fitting to the non-local exchange energies of atoms are more appropriate in this situation, even though they lack a complete, theoretical foundation at present [35, 36, 37, 38].

7 Summary

The theorems of Hohenberg and Kohn established a rigorous foundation for the description of inhomogeneous systems using the particle density as the natural variable. Based on their powerful ideas, modern density functional theory has not only provided a theoretical framework for discussing general inhomogeneous many-particle systems but also has developed into a highly effective computational tool for state of the art computations in practical chemical and condensed matter systems. Extensions of density functional methods to ever wider varieties of new physical situations (phenomena in reduced dimensionality, strongly correlated localized electronic materials, phase diagrams of materials, complex liquids, and all of finite temperature phenomena are some examples) will become increasingly important. The identification of the key features of the subtle exchange-correlation contributions to the energy functionals in these new situations will continue to be challenging and rewarding.

The universal functional $F[n]$ of Eq. (1) is a very special quantity. Its existence as the logical cornerstone of density functional theory may be taken as assured by the Hohenberg and Kohn theorems [1] and their extensions. However, explicit properties of $F[n]$ are not available, a priori, and it is necessary to construct procedures, based on Eq. (1) or its generalizations, to discover the essential properties. I have emphasized that this constructive approach to generating practical approximants to the universal energy functional focuses attention on global symmetries and boundary conditions and their natural role in classifying systems according to universality subclasses. I have discussed in some detail the fundamental differences which exist between finite, bounded systems and fully extended systems in their thermodynamic limit as well as the differences between high density, low gradient regions and low density, high gradient regions of a single system. I have described a systematic approach to studying the exchange-correlation energy functional of these inhomogeneous systems, based on rearrangements and partial resummations of perturbation expansions. The convergence properties of the long wavelength gradient expansions have been examined. An alternative nonlocal structure, which is characteristic of the low density regime, has also been indicated. Both the long wavelength

expansions and the short wavelength expansions are contained in the same perturbatively constructed exchange-correlation functional. The gradient expansion for the free energy of an extended system at finite temperature was discussed. Results were given for the leading contribution, of first order in the two-body interaction and of second order in density gradients, to the exchange gradient coefficient.

In closing, I want to stress again the essential importance of understanding in a fundamental way the nonlocal structure of exchange-correlation contributions to energy functionals. I believe that a full appreciation of the variety of ways that this nonlocal structure manifests itself, according to the different physical circumstances, will be vital for the construction of improved representations of $F[n]$ as the domain of applications of density functional theory continues to be extended into exciting new areas.

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8 Appendix: Energy of Inhomogeneous Electron Gas

Local (spin) density approximations provide instructive starting points for the discussion of energy functionals. Provided the space of density functions is appropriately constrained, their numerical results may be even surprisingly accurate. This suggests that it would be useful to study systematically the gradient corrections to local approximations. A simple model for doing so is the weakly inhomogeneous electron gas which is formed by imposing a weak external potential $V(r)$ on an otherwise uniform neutral system. The external potential is taken to be sufficiently weak that perturbative expansion can be freely utilized, provided the external potential does not promote any change of overall symmetry or instability. This can be assumed for the present discussion (a case to the contrary is given by the analysis of band gap discontinuities in semiconductors [8]). In this way, we have a tractable model system to study not only the nonlocal contributions to E_{xc} but also the effect of inhomogeneities on some subtle quantities, such as the structure factor.

In the presence of the static imposed external potential, which couples to the total charge density, the energy of the electron gas is shifted by an amount

$$\Delta E = \frac{1}{2\Omega} \sum_{\mathbf{k}} \chi(\mathbf{k}) |V_{\text{ext}}(\mathbf{k})|^2 + O(V_{\text{ext}}^3) \quad (\text{A.1})$$

where $\chi(\mathbf{k})$ is the static (zero frequency, $\omega = 0$) wave number dependent density-density correlation function of the uniform interacting electron gas.

$$\chi(\mathbf{k}) = -\pi(\mathbf{k})/[1 + v(\mathbf{k})\pi(\mathbf{k})] \quad (\text{A.2})$$

where $v(\mathbf{k})$ and $\pi(\mathbf{k})$ denote the Coulomb interaction and the static irreducible screening function, respectively. In order to identify the exchange-correlation contributions, we introduce the Fourier components of $n(\mathbf{r}) - n_0 = \delta n(\mathbf{r})$. From linear response,

$$\delta n(\mathbf{k}) = \chi(\mathbf{k}) V_{\text{ext}}(\mathbf{k}) \quad (\text{A.3})$$

and we rewrite (A.1) as

$$\begin{aligned} \Delta E &= \Delta E[n] = \frac{1}{2\Omega} \sum_{\mathbf{k}} \delta n(\mathbf{k})^2 / \chi(\mathbf{k}) + \dots \\ &= \frac{1}{2\Omega} \sum_{\mathbf{k}} V_{\text{ext}}(\mathbf{k}) \delta n(\mathbf{k}) + \Delta F[n] \end{aligned} \quad (\text{A.4})$$

The Hartree contribution is next removed from $\Delta F[n]$ by

$$\begin{aligned} \Delta F[n] &= -\frac{1}{2\Omega} \sum_{\mathbf{k}} \delta n(\mathbf{k})^2 / \chi(\mathbf{k}) + \dots \\ &= \frac{1}{2\Omega} \sum_{\mathbf{k}} \delta n(\mathbf{k}) [v(\mathbf{k}) + 1/\pi(\mathbf{k})] \delta n(-\mathbf{k}) + \dots \\ &= \Delta E_H[n] + \Delta G[n] \end{aligned} \quad (\text{A.5})$$

The kinetic energy of the Kohn-Sham reference system, also to second order in V_{ext} , is

$$\Delta E_K[n] = \frac{1}{2\Omega} \sum_{\mathbf{k}} |\delta n(\mathbf{k})|^2 / \pi_0(\mathbf{k}) + \dots \quad (\text{A.6})$$

where $\pi_0(\mathbf{k})$ is the Lindhard function. Thus the exchange-correlation energy shift is extracted from (A.5) as

$$\Delta E_{\text{xc}}[n] = \frac{1}{2\Omega} \sum_{\mathbf{k}} \delta n(\mathbf{k})^2 [\pi(\mathbf{k})^{-1} - \pi_0(\mathbf{k})^{-1}] + \dots \quad (\text{A.7})$$

which is rigorous to order V_{ext}^2 and is useful provided $\pi(\mathbf{k})$ is known for all $\mathbf{k}$ for which $\delta n(\mathbf{k})$ is significant in the sum (A.4).

The calculation of $\pi(\mathbf{k})$ is an important and very nontrivial many-body problem and requires the approximate solution of a Bethe-Salpeter equation. Our present objective is to generate gradient corrections to the LDA so (A.7) can be simplified by assuming that $\delta n(\mathbf{r})$ is so slowly varying in space (in addition to being of small magnitude) that $\delta n(\mathbf{k})$ is essentially zero except for very small k . A small k expansion of $\pi(\mathbf{k}) = a^{-1} - bk^2 + \dots$ (similarly for $\pi_0(\mathbf{k})$) then yields the small k expansion for $K_{\text{xc}}(\mathbf{k}) \equiv \pi(\mathbf{k})^{-1} - \pi_0(\mathbf{k})^{-1} \equiv K_{\text{xc}} + \frac{1}{2}k^2 K''_{\text{xc}}(0) + \dots$.

The exchange-correlation functional is then obtained as

$$\begin{aligned} E_{xc}[n] &= E_{xc}(n_0) + \Delta E_{xc}[n] \\ &= E_{xc}(n_0) + \int d^3 r \left[\frac{1}{2} K_{xc}(0) (\delta n(\mathbf{r}))^2 + \frac{1}{4} K_{xc}''(0) (\nabla \delta n(\mathbf{r}))^2 + \dots \right]. \end{aligned} \quad (\text{A.8})$$

Making use of $\delta n(\mathbf{k} = 0) = 0$, $\partial E / \partial N = \mu$ and a Ward identity $\partial \mu / \partial n_0 = \pi(0)^{-1} = a$, the first two terms of (A.8) provide the first two terms (only) of the expansion in powers of δn of

$$E_{xc}^{LDA} = \int d^3 r \left[A_{xc}(n_0) + \frac{1}{2} A_{xc}''(n_0) (\delta n(\mathbf{r}))^2 + \dots \right] \quad (\text{A.9})$$

where $A_{xc}(n(\mathbf{r})) = n(\mathbf{r}) \varepsilon_{xc}(n(\mathbf{r}))$. The third term of (A.8) gives the leading gradient correction

$$E_{xc}^g[n] = \int d^3 r B_{xc}(n_0) (\nabla n(\mathbf{r}))^2 + \dots \quad (\text{A.10})$$

on using $\nabla \delta n(\mathbf{r}) = \nabla n(\mathbf{r})$ with $B_{xc}(n_0) \equiv \frac{1}{4} K_{xc}''(0)$. Taken together, (A.9) and (A.10) give the leading inhomogeneity corrections to $E_{xc}[n]$ for a many-electron system having a density which is almost constant and also very slowly varying in space. Its range of validity is therefore very limited. However, rigorous applications can be given within this domain.

Explicit calculations of $B_{xc}(n_0)$ were first carried out by Ma and Brueckner [12] and by Sham [13] for the correlation and exchange contributions, respectively, in the high density limit ($r_s \ll 1$). The evaluation of the required Feynman graphs in the metallic and intermediate density range and the extension to include iterations of the scattering processes was given in a self-consistent random phase approximation [17, 18]. The results can be expressed as

$$B_{xc}(n_0) = e^2 n_0^{-4/3} C_{xc}(r_s) \quad (\text{A.11})$$

For convenience of applications, numerical results for $C_{xc}(r_s)$ can be presented as [39]

$$C_{xc}(r_s) = \frac{10^{-3} (2.568 + ar_s + br_s^2)}{1 + cr_s + dr_s^2 + 10br_s^3} \quad (\text{A.12})$$

where $C_{xc}(0) = 2.568 \times 10^{-3}$ is the value in the high density limit. The coefficients in (A.12) were obtained by fitting to data for $r_s \lesssim 10$ as $a = 23.266$, $b = 7.389 \times 10^{-3}$, $c = 8.723$ and $d = 0.472$. The Pade form (A.12) can also be used to extrapolate to lower density. The above discussion applies to a unpolarized (one component, essentially) electron gas. Ground state results are also available for the spin-polarized (two components) electron gas [19] and multicomponent electron-hole droplets [20, 21] in the high density limit. Results for finite temperature gradient corrections to the first order exchange free energy, via the coefficient $B_{xc}(n_0, T)$, are also known [26] although the corresponding correlation contributions are not known.

We will not describe here any details of the calculation of $B_{xc}(n_0)$ but refer to the literature and particularly to a fairly comprehensive recent review [7]. The

basic technical problem is that a Bethe-Salpeter equation must be solved to $\mathcal{O}(k^2)$. The first and probably the simplest general procedure for obtaining such exact solutions was given by Geldart and Rasolt [14]. It is well known that Ward identities (also often referred to as Ward-Pitayevski identities in the present context) determine the structure of solutions of integral equations for four-point scattering functions, three-point vertex functions, and two-point correlation functions in the $k \rightarrow 0$ limit. By purely algebraic matrix manipulations of these integral equations, it is also possible to extract the leading k dependence. This method yields a formal, but exact, result for $B_{xc}(n_0)$ for arbitrary static two-body interaction within a self-consistent Hartree-Fock approximation. Explicit results were given for a Yukawa static screened Coulomb interaction $v(r) = (e^2/r) \exp(-\lambda r)$ and the $\lambda \rightarrow 0^+$ limiting case was considered to simulate bare Coulomb interactions. This work was submitted as a report to the National Research Council of Canada in 1972. Response from seminars on the subject and apparent interest prompted us to submit the paper for publication [16]. The same conclusion was reached, using other methods, by Kleinman [15]. Only the procedures based on Ward identities and integral equations have been extended to the case of dynamically screened electron-electron interactions [17, 18].

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Exchange and Correlation in Density Functional Theory of Atoms and Molecules

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List of General Abbreviations

DFT	density functional theory
DM	density matrix
DS	Dirac-Slater
GS	ground-state
HF	Hartree-Fock
HK	Hohenberg-Kohn
KS	Kohn-Sham
OP	optimized potential
QM	quantum mechanical
SCS	spin compensated system
TFD	Thomas-Fermi-Dirac

List of Specific Subscript/Superscript Abbreviations

app	approximate
c	correlation

D	determinantal
ee	electron-electron (interaction)
eff	effective
ens	ensemble
es	electrostatic
ext	external
ferro	ferromagnetic
ncf	non-classical
para	paramagnetic
s	single-particle (noninteracting)
x	exchange
xc	exchange-correlation

The exchange and correlation energies and potentials, occurring in various density functional theory approaches and schemes are reviewed and their definitions compared. The ways of their determination and their long-range properties are discussed. General expressions for the exchange and correlation energy and the long-range asymptotic form of the exchange potential are obtained for mixed-state systems. Line-integral expressions for the exchange and correlation potentials, valid both for pure-state and mixed-state systems are derived. Approximation to the electrostatic-plus-exchange energy and corresponding potential for arbitrary mixed-state systems and approximation to the correlation energy and potential for a specific class of mixed-state systems are proposed. They are expressible in terms of any approximate functional of the density for the exchange energy and correlation energy, respectively, known for pure-state systems.

1 Background and Outline

The origins of density functional theory (DFT) are to be found in the statistical theory of atoms proposed independently by Thomas in 1926 [1] and Fermi in 1928 [2]. The inclusion of exchange in this theory was proposed by Dirac in 1930 [3]. In his paper, Dirac introduced the idempotent first-order density matrix which now carries his name and is the result of a total wave function which is approximated by a single Slater determinant. The total energy underlying the Thomas-Fermi-Dirac (TFD) theory can be written (see, e.g. March [4], [5]) as

$$\begin{aligned} \mathcal{E}_{\text{TFD}}[n] = & c_k \int d^3r \{n(\mathbf{r})\}^{5/3} + \int d^3r n(\mathbf{r}) v_{\text{en}}(\mathbf{r}) + \frac{1}{2} \int d^3r n(\mathbf{r}) v_{\text{es}}(\mathbf{r}) \\ & - c_x \int d^3r \{n(\mathbf{r})\}^{4/3} + E_{\text{nn}}. \end{aligned} \quad (1)$$

In Eq. (1) the individual terms on the r.h.s. are in order (i) the TF kinetic energy with $c_k = [3h^2/(10m)][3/(8\pi)]^{2/3}$, (ii) the electron-nuclear potential energy with $v_{\text{en}}(\mathbf{r})$ the bare nuclear one-body potential energy (in an atom having nuclear charge Ze , $v_{\text{en}} = -Ze^2/r$), (iii) the classical electrostatic energy of the charge

cloud of density $n(\mathbf{r})$, $v_{\text{es}}(\mathbf{r})$ being the electrostatic potential created by n , (iv) the Dirac exchange energy, with $c_x = (3/4)e^2(3/\pi)^{1/3}$ and (v) the nuclear-nuclear potential energy in multicentre system: either molecule or solid.

The variational principle

$$\delta(\mathcal{E}_{\text{TFD}} - \mu_{\text{TFD}}\mathcal{N}) = 0 \quad (2)$$

with the variation δ with respect to $n(\mathbf{r})$ subject to the constraint

$$\mathcal{N}[n] \equiv \int d^3r n(\mathbf{r}) = N \quad (3)$$

with N the total number of electrons, yields from Eq. (1)

$$\mu_{\text{TFD}} = \frac{5}{3}c_k\{n(\mathbf{r})\}^{2/3} + v_{\text{en}}(\mathbf{r}) + v_{\text{es}}(\mathbf{r}) - \frac{4}{3}c_x\{n(\mathbf{r})\}^{1/3}. \quad (4)$$

In Eq. (2), μ_{TFD} is the Lagrange multiplier taking care of the normalization constraint (3). It has the interpretation of the chemical potential of the electronic cloud and is written explicitly in Eq. (4) in the TFD approximation. It is seen from that equation that μ_{TFD} can be viewed as built up from the sum of three different pieces:

- (i) a kinetic part, $\frac{5}{3}c_k\{n(\mathbf{r})\}^{2/3}$,
- (ii) a ‘‘Hartree’’ potential $v_{\text{H}}(\mathbf{r}) = v_{\text{en}}(\mathbf{r}) + v_{\text{es}}(\mathbf{r})$,
- (iii) an exchange contribution $-\frac{4}{3}c_x\{n(\mathbf{r})\}^{1/3}$.

While Dirac [3] chose to solve Eq. (4) as a quadratic equation for $n^{1/3}$ in terms of the Hartree potential $v_{\text{H}}(\mathbf{r})$, it was Slater in 1951 ([6]; see also [4]) who chose an alternative, and more fruitful, route by regarding Eq. (4) as demonstrating that it could be viewed as a ‘‘modified Hartree’’ equation, with the Hartree potential $v_{\text{H}}(\mathbf{r})$ now supplemented by the exchange $n^{1/3}$ -potential (the so-called Dirac-Slater (DS) exchange potential), to yield a total one-body potential energy

$$v_{\text{TFD}}(\mathbf{r}) = v_{\text{H}}(\mathbf{r}) + v_{\text{x}}^{\text{DS}}(\mathbf{r}) \quad (5)$$

where the DS exchange (x) potential is given by

$$v_{\text{x}}^{\text{DS}}(\mathbf{r}) = -\frac{4}{3}c_x\{n(\mathbf{r})\}^{1/3}; \quad c_x = (3/4)e^2(3/\pi)^{1/3}. \quad (6)$$

Slater then proposed returning to one-electron Schrödinger equations (and therefore one-electron wave functions ϕ_i and corresponding eigenvalues ε_i) but now using not the Hartree-Fock (non-local) potential in these equations but the simplified potential

$$v_{\text{s}}(\mathbf{r}; [n]) = v_{\text{en}}(\mathbf{r}) + v_{\text{es}}(\mathbf{r}; [n]) + v_{\text{x}}^{\text{DS}}(\mathbf{r}; [n]). \quad (7)$$

Here it is now understood that $v_{\text{H}} = v_{\text{en}} + v_{\text{es}}$ and v_{x}^{DS} are no longer to be calculated from the approximate TFD Euler equation (4) but rather using a density $n(\mathbf{r})$ given by the ground-state sum

$$n(\mathbf{r}) = \sum_{i=1}^N \phi_i(\mathbf{r})\phi_i^*(\mathbf{r}), \quad (8)$$

where $\phi_i(\mathbf{r})$ are one-electron wave functions generated (self-consistently) by the

one-body potential energy $v_s(\mathbf{r}; [n])$ in Eq. (7), with $v_x^{\text{DS}}(\mathbf{r}; [n])$ given in terms of n in (8) by Eq. (6).

As will be developed in more detail below, the paper by Hohenberg and Kohn (1964) [7], which proved the existence theorem that the ground state energy is a functional of $n(\mathbf{r})$, but now without the approximations (valid for large N) in the explicit energy functional (1), formally completed the TFD theory. The work of Kohn and Sham (1965) [8] similarly gave the formal completion of Slater's 1951 proposal.

Since the terms exchange energy and correlation energy (and corresponding potentials) are used in various contexts with a slightly different meaning, we shall discuss this problem in detail in Sect. 2 for some well known approaches. In Sect. 3 various ways of reconstruction of the exchange and correlation potentials from accurate many-body wave functions are reviewed shortly. Section 4 is devoted to long-range properties of potentials and Kohn-Sham orbitals. Finally, in Sect. 5, a line-integral form of exchange and correlation potentials is presented, applicable to all types of mixed-state systems, together with analysis of expressions for corresponding energies.

2 Various Approaches to the Ground-State Problem

2.1 The Hohenberg-Kohn Theory

Our object of interest is a many electron finite system (such as an atom, molecule, cluster etc.), having, by assumption, a nondegenerate ground state (GS) (this assumption will be removed in Sects. 4.4 and 5). The number of electrons N and the electron-nuclei potential energy $v(\mathbf{r}) \equiv v_{\text{en}}(\mathbf{r})$ (the so-called external potential) are given and common for all schemes to be discussed. The GS energy E_{GS} and the GS wave function Ψ_{GS} of the system can be found from a variational principle as

$$E_{\text{GS}} = \min_{\Psi} \langle \Psi | \hat{\mathcal{T}} + \hat{\mathcal{U}} + \hat{\mathcal{V}} | \Psi \rangle = \langle \Psi_{\text{GS}} | \hat{\mathcal{T}} + \hat{\mathcal{U}} + \hat{\mathcal{V}} | \Psi_{\text{GS}} \rangle, \quad (9)$$

where the variational wave function $\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$ here and other wave functions elsewhere are assumed to be normalized. The notation $\mathbf{x}_i = (\mathbf{r}_i, s_i)$ for the i -th space and spin coordinate is adopted. The kinetic, electron-electron (ee) repulsion, and electron-nuclei attraction (external) energy operators, respectively, are defined as

$$\hat{\mathcal{T}} = \sum_{i=1}^N \hat{t}_i; \quad \hat{t}_i = -\frac{1}{2} \nabla_i^2, \quad (10)$$

$$\hat{\mathcal{U}} = \sum_{i=1}^{N-1} \sum_{j=i}^N u(\mathbf{r}_i, \mathbf{r}_j); \quad u(\mathbf{r}_i, \mathbf{r}_j) = 1/|\mathbf{r}_i - \mathbf{r}_j|, \quad (11)$$

$$\hat{\mathcal{V}} = \sum_{i=1}^N v(\mathbf{r}_i). \quad (12)$$

Atomic units are used throughout.

Following Levy's constrained-search formulation [9] (see also [10]) we can perform the minimization in Eq. (9) in two steps, namely

$$E_{\text{GS}} = \min_n \left\{ \min_{\Psi \rightarrow n} \langle \Psi | \hat{\mathcal{T}} + \hat{\mathcal{U}} + \hat{\mathcal{V}} | \Psi \rangle \right\}, \quad (13)$$

where by $\Psi \rightarrow n$ we denote such Ψ which integrates to the given electron density $n(\mathbf{r})$ (see Appendix A). The variational density $n(\mathbf{r})$ here and elsewhere is assumed to be constrained to the given number of electrons, Eq. (3). Finally, Eq. (13) can be rewritten as

$$E_{\text{GS}} = \min_n \mathcal{E}[n] = \min_n \{F^{\text{HK}}[n] + E_{\text{ext}}[n]\} = F^{\text{HK}}[n_{\text{GS}}] + E_{\text{ext}}[n_{\text{GS}}], \quad (14)$$

where the Hohenberg-Kohn (HK) functional is

$$F^{\text{HK}}[n] = \min_{\Psi \rightarrow n} \langle \Psi | \hat{\mathcal{T}} + \hat{\mathcal{U}} | \Psi \rangle = \langle \Psi^{\text{HK}}[n] | \hat{\mathcal{T}} + \hat{\mathcal{U}} | \Psi^{\text{HK}}[n] \rangle, \quad (15)$$

the external (ext) energy functional is

$$E_{\text{ext}}[n] = \int d^3r n(\mathbf{r}) v(\mathbf{r}), \quad (16)$$

and the GS density $n_{\text{GS}}(\mathbf{r})$ corresponds to the integrated Ψ_{GS} of Eq. (9). Formulation of the GS problem as minimization in terms of the density, Eq. (14), and existence theorem for $F^{\text{HK}}[n]$ were given first by Hohenberg and Kohn [7].

Owing to the wave function symmetry and operators structure, the expectation values of $\hat{\mathcal{T}}$ and $\hat{\mathcal{U}}$ can be written in terms of $\gamma = \gamma[\Psi]$ and $\xi_2 = \xi_2[\Psi]$ or $\rho = \rho[\Psi]$ and $n_2 = n_2[\Psi]$ – the reduced density matrices (DM) or spinless reduced DMs, generated from Ψ (see Appendix A):

$$\begin{aligned} \langle \Psi | \hat{\mathcal{T}} | \Psi \rangle &= \tilde{T}[\gamma] = \int d\mathbf{x} (-\tfrac{1}{2}) \nabla_1^2 \gamma(\mathbf{x}_1; \mathbf{x}_2)_{|\mathbf{x}_1 = \mathbf{x}_2 = \mathbf{x}} \\ &= \int d\mathbf{x} \tfrac{1}{2} \nabla_1 \nabla_2 \gamma(\mathbf{x}_1; \mathbf{x}_2)_{|\mathbf{x}_1 = \mathbf{x}_2 = \mathbf{x}} \\ &= \tilde{T}[\rho] = \int d^3r (-\tfrac{1}{2}) \nabla_1^2 \rho(\mathbf{r}_1; \mathbf{r}_2)_{|\mathbf{r}_1 = \mathbf{r}_2 = \mathbf{r}} \\ &= \int d^3r \tfrac{1}{2} \nabla_1 \nabla_2 \rho(\mathbf{r}_1; \mathbf{r}_2)_{|\mathbf{r}_1 = \mathbf{r}_2 = \mathbf{r}}, \end{aligned} \quad (17)$$

$$\begin{aligned} \langle \Psi | \hat{\mathcal{U}} | \Psi \rangle &= \tilde{E}_{\text{ee}}[\xi_2] = \int d\mathbf{x} d\mathbf{x}' \xi_2(\mathbf{x}, \mathbf{x}') u(\mathbf{r}, \mathbf{r}') \\ &= \tilde{E}_{\text{ee}}[n_2] = \int d^3r d^3r' n_2(\mathbf{r}, \mathbf{r}') u(\mathbf{r}, \mathbf{r}'). \end{aligned} \quad (18)$$

The diagonal second-order DM n_2 in Eq. (18) can be divided into its uncorrelated and correlated parts, Eq. (284), which leads to

$$\tilde{E}_{\text{ee}}[n_2] = E_{\text{es}}[n] + \tilde{E}_{\text{ncl}}[n, h_2], \quad (19)$$

where

$$E_{\text{es}}[n] = \tfrac{1}{2} \int d^3r d^3r' n(\mathbf{r}) n(\mathbf{r}') u(\mathbf{r}, \mathbf{r}') \quad (20)$$

is the classical electrostatic (es) energy of the electronic cloud of density $n(\mathbf{r})$, and

$$\tilde{E}_{\text{ncl}}[n, h_2] = \frac{1}{2} \int d^3r d^3r' n(\mathbf{r}) n(\mathbf{r}') h_2(\mathbf{r}, \mathbf{r}') u(\mathbf{r}, \mathbf{r}') \quad (21)$$

is the non-classical (ncl) part of the electron-electron interaction energy; $h_2(\mathbf{r}, \mathbf{r}')$ is known as the pair-correlation function.

It will be convenient to split the result of minimization in Eq. (15) into the kinetic and interaction energy terms according to Eqs. (17)–(19)

$$F^{\text{HK}}[n] = T^{\text{HK}}[n] + E_{\text{ce}}^{\text{HK}}[n] = T^{\text{HK}}[n] + E_{\text{es}}[n] + E_{\text{ncl}}^{\text{HK}}[n]. \quad (22)$$

where

$$T^{\text{HK}}[n] = \tilde{T}[\rho^{\text{HK}}[n]]; \quad E_{\text{ncl}}^{\text{HK}}[n] = \tilde{E}_{\text{ncl}}[n, h_2^{\text{HK}}[n]]. \quad (23)$$

Here $\rho^{\text{HK}}[n]$ and $h_2^{\text{HK}}[n]$ are DMs generated by $\Psi^{\text{HK}}[n]$.

2.2 The Hartree-Fock Method

In a well known practical but approximate method to solve the GS problem, known as the Hartree-Fock (HF) approximation (see e.g. [10]), the domain of variational functions Ψ in Eq. (9) is narrowed to those that are a single Slater determinant (D) Ψ_{D} , constructed out of orthonormal spin orbitals $\psi_i(\mathbf{x})$:

$$\Psi_{\text{D}} = \Psi_{\text{D}}[\psi_1, \dots, \psi_N] = (N!)^{-1/2} \det\{\psi_i(\mathbf{x}_j)\}_{\{i, j=1, \dots, N\}}, \quad (24)$$

so

$$E_{\text{GS}}^{\text{HF}} = \min_{\Psi_{\text{D}}} \langle \Psi_{\text{D}} | \hat{\mathcal{T}} + \hat{\mathcal{U}} + \hat{\mathcal{V}} | \Psi_{\text{D}} \rangle = \langle \Psi_{\text{GS}}^{\text{HF}} | \hat{\mathcal{T}} + \hat{\mathcal{U}} + \hat{\mathcal{V}} | \Psi_{\text{GS}}^{\text{HF}} \rangle. \quad (25)$$

Because the functional space of Ψ_{D} is narrower than the space of Ψ , the “upper bound” property holds

$$E_{\text{GS}} \leq E_{\text{GS}}^{\text{HF}}. \quad (26)$$

The difference between these two energies

$$E_{\text{c}}^{\text{QM}} = E_{\text{GS}} - E_{\text{GS}}^{\text{HF}} \leq 0. \quad (27)$$

is the conventional quantum mechanical (QM) correlation (c) energy. Here it is a single number characterizing the $\{N, v\}$ system, but in Sect. 2.5 it will be considered also as a functional of the density, and its value will be estimated.

Owing to Eq. (24), the minimization (25) can be rewritten as

$$E_{\text{GS}}^{\text{HF}} = \min_{\Psi_1, \dots, \Psi_N} \{ \tilde{F}^{\text{HF}}[\psi_1, \dots, \psi_N] + E_{\text{ext}}[n^{\text{D}}[\psi_1, \dots, \psi_N]] \}, \quad (28)$$

where

$$n^{\text{D}}(\mathbf{r}; [\psi_1, \dots, \psi_N]) = \sum_{i=1}^N \sum_s |\psi_i(\mathbf{r}, s)|^2 \quad (29)$$

is a density corresponding to the Ψ_D in Eq. (24), while $\tilde{F}^{\text{HF}}$, using Eqs. (17)–(21), equals

$$\begin{aligned}\tilde{F}^{\text{HF}}[\psi_1, \dots, \psi_N] &= \tilde{T}^{\text{HF}}[\psi_1, \dots, \psi_N] + E_{\text{es}}[n^D[\psi_1, \dots, \psi_N]] \\ &\quad + \tilde{E}_x^{\text{HF}}[\psi_1, \dots, \psi_N],\end{aligned}\tag{30}$$

thus it is a sum of the kinetic energy

$$\tilde{T}^{\text{HF}}[\psi_1, \dots, \psi_N] = \tilde{T}[\rho^D] = \sum_{i=1}^N \langle \psi_i | -\frac{1}{2} \nabla^2 | \psi_i \rangle,\tag{31}$$

the electrostatic energy (20), and the exchange (x) energy

$$\tilde{E}_x^{\text{HF}}[\psi_1, \dots, \psi_N] = \tilde{E}_{\text{ncI}}[n^D, h_2^D].\tag{32}$$

The 1-st order DM ρ^D and the pair-correlation function h_2^D , occurring in the above equations, are functionals of $\psi_1, \dots, \psi_N$, being generated by Ψ_D , Eq. (24), according to rules given in the Appendix A.

The conventional exchange energy $\tilde{E}_x^{\text{HF}}[\psi_1, \dots, \psi_N]$ of the HF method should not be confused with the exchange energy functionals of density, discussed in the following sections.

Minimization in Eq. (28), subject to normalization conditions for ψ_i , gives the HF differential eigenequations (see, e.g. [10])

$$(-\frac{1}{2} \nabla^2 + v + v_{\text{es}} + \hat{v}_x^{\text{HF}}) \psi_i = \varepsilon_i \psi_i, \quad i = 1, \dots, N,\tag{33}$$

where, besides the kinetic energy operator, there are two (multiplicative) potentials: external and electrostatic, the last in a form

$$v_{\text{es}}(\mathbf{r}; [n]) = \frac{\delta E_{\text{es}}[n]}{\delta n(\mathbf{r})} = \int d^3 r' n(\mathbf{r}') u(\mathbf{r}', \mathbf{r}),\tag{34}$$

to be taken in Eq. (33) with $n = n^D[\psi_1, \dots, \psi_N]$, and an integral operator $\hat{v}_x^{\text{HF}}$, a functional of $\psi_1, \dots, \psi_N$, called the ‘nonlocal’ exchange HF potential (see Appendix B); it should not be confused with exchange (multiplicative) potentials, discussed in the following sections.

Equations (33) can be solved numerically in an iterative manner, leading finally to self-consistency. In this way the energy $E_{\text{GS}}^{\text{HF}}$ and the determinantal wave function at minimum $\Psi_{\text{GS}}^{\text{HF}}$ are obtained and available for many systems: from simple atoms to large molecules, neutral or ionized.

2.3 The Kohn-Sham Approach

The success of a determinantal approach, leading to one-electron equations in the HF approximation, served as inspiration for applying it to the exact GS problem. Stemming from the ideas of Slater [6], the method was formally completed in the work of Kohn and Sham (KS) [8], and is traditionally known as KS approach. We recall it now using again a Levy’s constrained-search

formalism. The basic quantity of the KS approach is the noninteracting kinetic energy functional

$$T_s[n] \equiv T^{\text{KS}}[n] = \min_{\Phi_D \rightarrow n} \langle \Phi_D | \hat{\mathcal{T}} | \Phi_D \rangle = \langle \Phi_D^{\text{KS}}[n] | \hat{\mathcal{T}} | \Phi_D^{\text{KS}}[n] \rangle. \quad (35)$$

Here it is assumed that the density $n(\mathbf{r})$ possesses a property of being “non-interacting v -representable”, which is true for most of systems [for general densities, the restriction that a variational wave function should be determinantal must be removed in Eq. (35)].

The reason for calling $T_s[n]$ the noninteracting kinetic energy functional is recognized immediately when the GS problem of a system of N noninteracting electrons, moving in an external potential $v_s(\mathbf{r})$, is considered. In analogy with Eq. (9) we write

$$E_{\text{GS}}^s = \min_{\Phi_D} \langle \Phi_D | \hat{\mathcal{T}} + \hat{\mathcal{V}}_s | \Phi_D \rangle = \langle \Phi_{\text{GS}}^s | \hat{\mathcal{T}} + \hat{\mathcal{V}}_s | \Phi_{\text{GS}}^s \rangle. \quad (36)$$

Here, by definition, there is no electron-electron interaction operator $\hat{\mathcal{U}}$, while $\hat{\mathcal{V}}_s$ is defined similarly to $\hat{\mathcal{V}}$ in Eq. (12), but with $v(\mathbf{r})$ replaced by $v_s(\mathbf{r})$. The variational function can be chosen to be determinantal, because such a function describes a noninteracting system. By performing the minimization in two steps: external over n and internal over $\Phi_D \rightarrow n$ [compare Eqs. (13)–(16)] we arrive at

$$E_{\text{GS}}^s = \min_n \left\{ \min_{\Phi_D \rightarrow n} \langle \Phi_D | \hat{\mathcal{T}} | \Phi_D \rangle + \int d^3r n(\mathbf{r}) v_s(\mathbf{r}) \right\}, \quad (37)$$

i.e., using Eq. (35) and an analogue of Eq. (16)

$$E_{\text{ext}}^s[n] = \int d^3r n(\mathbf{r}) v_s(\mathbf{r}), \quad (38)$$

at

$$\begin{aligned} E_{\text{GS}}^s &= \min_n \mathcal{E}^s[n] = \min_n \{ T_s[n] + E_{\text{ext}}^s[n] \} \\ &= T_s[n_{\text{GS}}^s] + E_{\text{ext}}^s[n_{\text{GS}}^s]. \end{aligned} \quad (39)$$

But the noninteracting GS problem may be solved alternatively by varying in Eq. (35) the N spin orbitals $\phi_i(\mathbf{x})$ comprising the determinantal Φ_D [compare Eq. (24)]. With an imposed normalization condition on $\phi_i(\mathbf{x})$ this leads obviously to one-electron Schrödinger equations

$$(-\tfrac{1}{2} \nabla^2 + v_s) \phi_i = \varepsilon_i^s \phi_i. \quad (40)$$

The GS wave function Φ_{GS}^s in Eq. (36) is a determinant of N lowest-energy eigenfunctions $\phi_i(\mathbf{x})$ of Eq. (40). Then for the GS density and kinetic energy of Eq. (39) we have

$$n_{\text{GS}}^s(\mathbf{r}) = \sum_s \sum_{i=1}^N |\phi_i(\mathbf{r}, s)|^2, \quad (41)$$

$$T_s[n_{\text{GS}}^s] = \int d^3r t_s(\mathbf{r}; [n_{\text{GS}}^s]), \quad (42)$$

where the noninteracting kinetic energy density is

$$t_s(\mathbf{r}; [n_{\text{GS}}^s]) = \frac{1}{2} \sum_s \sum_{i=1}^N |\nabla \phi_i(\mathbf{r}, s)|^2. \quad (43)$$

We are ready now to present the KS method for solving the GS problem of the original—interacting electron system. By adding and subtracting $T_s[n] \equiv T^{\text{KS}}[n]$ in Eq. (22), the functional $F^{\text{HK}}[n]$ is rewritten as

$$F^{\text{HK}}[n] = T_s[n] + E_{\text{es}}[n] + E_{\text{xc}}[n], \quad (44)$$

with

$$\begin{aligned} E_{\text{xc}}[n] &= F^{\text{HK}}[n] - E_{\text{es}}[n] - T^{\text{KS}}[n] \\ &= \{T^{\text{HK}}[n] - T^{\text{KS}}[n]\} + E_{\text{ncl}}^{\text{HK}}[n]. \end{aligned} \quad (45)$$

The exchange-correlation (xc) energy functional defined above is shown to consist of two contributions: a difference between the interacting and noninteracting kinetic energy functionals and the nonclassical part of the electron-electron interaction energy functional. Using Eq. (44) we rewrite Eq. (14) as

$$E_{\text{GS}} = \min_n \mathcal{E}[n] = \min_n \{T_s[n] + V^{\text{KS}}[n]\} = T_s[n_{\text{GS}}] + V^{\text{KS}}[n_{\text{GS}}], \quad (46)$$

where the KS effective potential energy functional is

$$V^{\text{KS}}[n] = E_{\text{ext}}[n] + E_{\text{es}}[n] + E_{\text{xc}}[n]. \quad (47)$$

In order to see that the minimization in Eq. (46) can be performed using methods developed for the noninteracting problem (39), we compare the variation of the interacting system energy functional $\mathcal{E}[n]$ in (46)

$$\delta \mathcal{E}[n] = \int d^3r \left(\frac{\delta T_s[n]}{\delta n(\mathbf{r})} + \frac{\delta V^{\text{KS}}[n]}{\delta n(\mathbf{r})} \right) \delta n(\mathbf{r}) \quad (48)$$

with the variation of the noninteracting system energy functional $\mathcal{E}^s[n]$ in (39)

$$\delta \mathcal{E}^s[n] = \int d^3r \left(\frac{\delta T_s[n]}{\delta n(\mathbf{r})} + v_s(\mathbf{r}) \right) \delta n(\mathbf{r}). \quad (49)$$

These two variations can become equivalent if the role of the noninteracting potential is played by the functional derivative of $V^{\text{KS}}[n]$. Thus, the GS density $n_{\text{GS}}(\mathbf{r})$ and, consequently, $T_s[n_{\text{GS}}]$ can be calculated from the solutions of the so-called KS equations [compare Eq. (40)]:

$$(-\frac{1}{2} \nabla^2 + v_{\text{KS}}) \phi_i^{\text{KS}} = \epsilon_i^{\text{KS}} \phi_i^{\text{KS}}, \quad (50)$$

where the effective KS potential is [see Eq. (47)]

$$v_{\text{KS}}(\mathbf{r}; [n]) = \frac{\delta V^{\text{KS}}[n]}{\delta n(\mathbf{r})} = v(\mathbf{r}) + v_{\text{es}}(\mathbf{r}; [n]) + v_{\text{xc}}(\mathbf{r}; [n]). \quad (51)$$

Here v_{es} is given in (34), while the exchange-correlation potential of the KS approach is obviously

$$v_{\text{xc}}(\mathbf{r}; [n]) = \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})}. \quad (52)$$

At self-consistency, $v_{\text{KS}}(\mathbf{r}; [n])$ should be evaluated with $n = n_{\text{GS}}(\mathbf{r})$. This density is calculated from $\phi_i^{\text{KS}}(\mathbf{x})$ in a similar way as $n_{\text{GS}}^s(\mathbf{r})$ in Eq. (41) from $\phi_i(\mathbf{x})$.

The KS exchange-correlation energy is customarily partitioned into the exchange and correlation contributions:

$$E_{\text{xc}}[n] = E_{\text{x}}[n] + E_{\text{c}}[n], \quad (53)$$

of which the exchange-only part $E_{\text{x}}[n]$ is defined (see e.g. in [10]) as a nonclassical part of the KS electron-electron interaction energy:

$$E_{\text{x}}[n] \equiv E_{\text{x}}^{\text{KS}}[n] \equiv E_{\text{ncI}}^{\text{KS}}[n] = \langle \Phi_{\text{D}}^{\text{KS}}[n] | \hat{\mathcal{U}} | \Phi_{\text{D}}^{\text{KS}}[n] \rangle - E_{\text{es}}[n], \quad (54)$$

where $\Phi_{\text{D}}^{\text{KS}}[n]$ is the minimizer in (35). This definition can be also rewritten in a form

$$E_{\text{x}}[n] = \tilde{E}_{\text{ncI}}[n, h_2^{\text{KS}}[n]], \quad (55)$$

[see Eq. (21)], where the KS pair-correlation function $h_2^{\text{KS}}[n]$ is given in terms of the spin orbitals $\phi_i(\mathbf{x})$ comprising $\Phi_{\text{D}}^{\text{KS}}[n]$ [see Appendix A, Eq. (281) or (283) together with (278) and (279)].

The correlation contribution is obviously a difference between E_{xc} and E_{x} . From the partition (53) follows the partition of the potential (52) as

$$v_{\text{xc}}(\mathbf{r}; [n]) = v_{\text{x}}(\mathbf{r}; [n]) + v_{\text{c}}(\mathbf{r}; [n]). \quad (56)$$

However, there is no explicit expression known for calculating in practice [e.g. in terms of occupied $\phi_i(\mathbf{x})$ or $n(\mathbf{r})$] the exchange potential defined formally as

$$v_{\text{x}}(\mathbf{r}; [n]) = \frac{\delta E_{\text{x}}[n]}{\delta n(\mathbf{r})}. \quad (57)$$

With the help of Eqs. (45), (54), (35), (22) and (15) we can calculate the correlation energy from Eq. (53) as

$$\begin{aligned} E_{\text{c}}[n] &\equiv E_{\text{c}}^{\text{KS}}[n] = \langle \Psi^{\text{HK}}[n] | \hat{\mathcal{T}} + \hat{\mathcal{U}} | \Psi^{\text{HK}}[n] \rangle \\ &\quad - \langle \Phi_{\text{D}}^{\text{KS}}[n] | \hat{\mathcal{T}} + \hat{\mathcal{U}} | \Phi_{\text{D}}^{\text{KS}}[n] \rangle \\ &= (T^{\text{HK}}[n] - T^{\text{KS}}[n]) + (E_{\text{ee}}^{\text{HK}}[n] - E_{\text{ee}}^{\text{KS}}[n]) \\ &= T_{\text{c}}^{\text{KS}}[n] + U_{\text{c}}^{\text{KS}}[n], \end{aligned} \quad (58)$$

showing two sources of the correlation energy: from the differences in (i) kinetic energies, and (ii) electron-electron interaction energies, due to differences between the HK and KS wave functions.

It is obvious from Eq. (58) that

$$E_{\text{c}}[n] \leq 0, \quad (59)$$

because $\Psi^{\text{HK}}[n]$ is a minimizer of $\langle \hat{\mathcal{T}} + \hat{\mathcal{U}} \rangle$, Eq. (15). The next inequality

$$T_c^{\text{KS}}[n] \equiv \langle \Psi^{\text{HK}}[n] | \hat{\mathcal{T}} | \Psi^{\text{HK}}[n] \rangle - \langle \Phi_D^{\text{KS}}[n] | \hat{\mathcal{T}} | \Phi_D^{\text{KS}}[n] \rangle \geq 0 \quad (60)$$

holds because $\Phi_D^{\text{KS}}[n]$ is a minimizer of $\langle \hat{\mathcal{T}} \rangle$ [see Eq. (35) and a comment below it]. Finally

$$U_c^{\text{KS}}[n] \leq 0 \quad (61)$$

as a difference of inequalities (59) and (60).

It proves convenient for further considerations to rewrite Eq. (46) for the exact GS problem in a form

$$E_{\text{GS}} = \min_n \{ F^{\text{KS}}[n] + E_{\text{ext}}[n] + E_c[n] \}, \quad (62)$$

i.e. in terms of the KS functional [an analogue of the HK functional, Eq. (15)] defined as

$$F^{\text{KS}}[n] = \langle \Phi_D^{\text{KS}}[n] | \hat{\mathcal{T}} + \hat{\mathcal{U}} | \Phi_D^{\text{KS}}[n] \rangle = T_s[n] + E_{\text{es}}[n] + E_x[n], \quad (63)$$

with $\Phi_D^{\text{KS}}[n]$ defined in Eq. (35).

2.4 The Hartree-Fock Method Posed as a Density Functional Theory

Since the HF approximation plays so important a role in understanding various atomic and molecular systems, it is interesting to analyze it in terms of a DFT (see [11]). For that reason we apply to Eq. (25) the two-step minimization, as in Eq. (13), and obtain

$$\begin{aligned} E_{\text{GS}}^{\text{HF}} &= \min_n \mathcal{E}^{\text{HF}}[n] = \min_n \{ F^{\text{HF}}[n] + E_{\text{ext}}[n] \} \\ &= F^{\text{HF}}[n_{\text{GS}}^{\text{HF}}] + E_{\text{ext}}[n_{\text{GS}}^{\text{HF}}], \end{aligned} \quad (64)$$

where $E_{\text{ext}}[n]$ was already defined in Eq. (16) while the specific HF functional is

$$F^{\text{HF}}[n] = \min_{\Psi_D \rightarrow n} \langle \Psi_D | \hat{\mathcal{T}} + \hat{\mathcal{U}} | \Psi_D \rangle = \langle \Psi_D^{\text{HF}}[n] | \hat{\mathcal{T}} + \hat{\mathcal{U}} | \Psi_D^{\text{HF}}[n] \rangle. \quad (65)$$

It can be conveniently partitioned:

$$F^{\text{HF}}[n] = T^{\text{HF}}[n] + E_{\text{ee}}^{\text{HF}}[n] = T^{\text{HF}}[n] + E_{\text{es}}[n] + E_x^{\text{HF}}[n], \quad (66)$$

with

$$\begin{aligned} T^{\text{HF}}[n] &= \langle \Psi_D^{\text{HF}}[n] | \hat{\mathcal{T}} | \Psi_D^{\text{HF}}[n] \rangle, \\ E_{\text{ee}}^{\text{HF}}[n] &= \langle \Psi_D^{\text{HF}}[n] | \hat{\mathcal{U}} | \Psi_D^{\text{HF}}[n] \rangle. \end{aligned} \quad (67)$$

The HF GS density $n_{\text{GS}}^{\text{HF}}(\mathbf{r})$, occurring in Eq. (64), coincides with the density calculated according to Eq. (29) from ψ_i [the solutions of the HF equations (33)], because the two ways of calculation of $E_{\text{GS}}^{\text{HF}}$ are equivalent. By adding and subtracting the noninteracting kinetic energy functional to HF functional in

Eq. (66), similarly as in the case of HK functional in Eq. (44), and using the definition (63), we obtain

$$F^{\text{HF}}[n] = T_s[n] + E_{\text{es}}[n] + E_x[n] + E_c^{\text{HF}}[n], \quad (68)$$

where

$$\begin{aligned} E_c^{\text{HF}}[n] &= F^{\text{HF}}[n] - F^{\text{KS}}[n] \\ &= (T^{\text{HF}}[n] - T^{\text{KS}}[n]) + (E_x^{\text{HF}}[n] - E_x^{\text{KS}}[n]). \end{aligned} \quad (69)$$

Thus, the minimization in Eq. (64) can be performed alternatively as a solution of an equivalent noninteracting electron problem, leading to equations

$$(-\frac{1}{2}\nabla^2 + v + v_{\text{es}} + v_x + v_c^{\text{HF}})\phi_i^{\text{HF}} = \varepsilon_i^{\text{HF}}\phi_i^{\text{HF}}, \quad (70)$$

with

$$v_c^{\text{HF}}(\mathbf{r}; [n]) = \frac{\delta E_c^{\text{HF}}[n]}{\delta n(\mathbf{r})}, \quad (71)$$

analogously as minimization (46) led to KS equations (50). Here, at self-consistency, the density occurring in $v_{\text{es}}(\mathbf{r}; [n])$, $v_x(\mathbf{r}; [n])$, and $v_c^{\text{HF}}(\mathbf{r}; [n])$ is $n(\mathbf{r}) = n_{\text{GS}}^{\text{HF}}(\mathbf{r})$, while the corresponding $T_s[n_{\text{GS}}^{\text{HF}}]$ and $E_x[n_{\text{GS}}^{\text{HF}}]$ can be calculated as expectation values [see Eqs. (35) and (54)] with the determinantal wave function $\Phi_{\text{D}}^{\text{KS}}[n_{\text{GS}}^{\text{HF}}]$, constructed from the HF-KS spin orbitals ϕ_i^{HF} – the solutions of (70). These orbitals are different from ψ_i [the solutions of the original HF equations (33)] because the sum of the *local* potentials ($v_x + v_c^{\text{HF}}$) in Eq. (70) replaces the *nonlocal*, integral operator potential $\hat{v}_x^{\text{HF}}$ present in Eq. (33). The differences between ϕ_i^{HF} and ψ_i are discussed in detail in [11], using the Be atom system as an example.

Interesting inequalities can be obtained [12]:

$$\Delta T[n] \equiv T^{\text{HF}}[n] - T^{\text{KS}}[n] \geq 0 \quad (72)$$

and [see Eq. (69)]

$$\Delta F[n] \equiv E_c^{\text{HF}}[n] \leq 0. \quad (73)$$

They follow immediately from

$$\langle \Psi_{\text{D}}^{\text{HF}}[n] | \hat{\mathcal{T}} | \Psi_{\text{D}}^{\text{HF}}[n] \rangle \geq \langle \Phi_{\text{D}}^{\text{KS}}[n] | \hat{\mathcal{T}} | \Phi_{\text{D}}^{\text{KS}}[n] \rangle, \quad (74)$$

and from [see Eqs. (65) and (63)]

$$\langle \Psi_{\text{D}}^{\text{HF}}[n] | \hat{\mathcal{T}} + \hat{\mathcal{U}} | \Psi_{\text{D}}^{\text{HF}}[n] \rangle \leq \langle \Phi_{\text{D}}^{\text{KS}}[n] | \hat{\mathcal{T}} + \hat{\mathcal{U}} | \Phi_{\text{D}}^{\text{KS}}[n] \rangle, \quad (75)$$

because minimizations in Eq. (35) and (65) are performed in the same space, and $\Phi_{\text{D}}^{\text{KS}}$ is the minimizer of $\langle \hat{\mathcal{T}} \rangle$ whereas $\Psi_{\text{D}}^{\text{HF}}$ is that of $\langle \hat{\mathcal{T}} + \hat{\mathcal{U}} \rangle$. By subtracting the inequality (72) from (73) one obtains [12]

$$\Delta E_x[n] \equiv E_x^{\text{HF}}[n] - E_x^{\text{KS}}[n] \leq 0. \quad (76)$$

To avoid confusion, let us note that the notation $\Delta E_c[n]$ and $E_c^{\text{HF}}[n]$ is used in [12] for the objects denoted here as $E_c^{\text{HF}}[n]$ and $(E_c^{\text{KS}}[n] - E_c^{\text{HF}}[n])$, respectively.

It should be noted that in the case of the helium isoelectronic series (singlet GS of a two-electron system), because only one orbital $\psi(\mathbf{r})$ is sufficient to construct the determinantal wave function and to obtain the density as $n(\mathbf{r}) = 2[\psi(\mathbf{r})]^2$, the minimization over n in Eq. (64) is equivalent to the minimization over ψ in Eq. (28). Therefore the HF-KS and HF equations and their eigenfunctions are the same, $\psi(\mathbf{r}) = \phi^{\text{HF}}(\mathbf{r})$, and consequently $\Delta T[n] = \Delta E_x[n] = E_c^{\text{HF}}[n] = 0$.

Görling and Ernzerhof [12] performed quantitative investigation of $\Delta T[n]$ and $\Delta E_x[n]$ at $n(\mathbf{r}) = n_{\text{GS}}^{\text{HF}}(\mathbf{r})$ for some closed-shell atomic systems: Be, Ne, Mg, Ar, Ca. For that reason they solved HF equations (33), using Gaussian basis sets [13] for ψ_i , and in terms of these functions they calculated $n_{\text{GS}}^{\text{HF}}(\mathbf{r}) = n^{\text{D}}(\mathbf{r}; [\psi_1, \dots, \psi_N])$, Eq. (29), $T^{\text{HF}}[n_{\text{GS}}^{\text{HF}}] = \tilde{T}^{\text{HF}}[\psi_1, \dots, \psi_N]$, Eq. (31), and $E_x^{\text{HF}}[n_{\text{GS}}^{\text{HF}}] = E_x^{\text{HF}}[\psi_1, \dots, \psi_N]$, Eq. (32). Next, in order to find $T^{\text{KS}}[n_{\text{GS}}^{\text{HF}}]$ and $E_x^{\text{KS}}[n_{\text{GS}}^{\text{HF}}]$, these authors used a procedure of Ref. [14] to find such a single-particle potential $v_s(\mathbf{r})$, which, when substituted in Eqs. (40), results in $n_{\text{GS}}^s(\mathbf{r})$, Eq. (41), identical with the given $n_{\text{GS}}^{\text{HF}}(\mathbf{r})$. The calculated spin orbitals ϕ_i^s [solutions of (40)] are next used to obtain $T^{\text{KS}}[n_{\text{GS}}^{\text{HF}}] \equiv T_s[n_{\text{GS}}^{\text{HF}}]$ and $E_x^{\text{KS}}[n_{\text{GS}}^{\text{HF}}] \equiv E_x[n_{\text{GS}}^{\text{HF}}]$ according to definitions (42) and (54).

The results obtained in [12] show

$$\Delta T/T^{\text{HF}} < 4 \times 10^{-5} \quad (77)$$

and

$$\Delta E_x/E_x^{\text{HF}} < 4.4 \times 10^{-4} \quad (78)$$

for the systems considered.

It is interesting that the following approximate relation can be noted (although it was not mentioned in [12]) from these results

$$\Delta E_x[n_{\text{GS}}^{\text{HF}}] \approx -2\Delta T[n_{\text{GS}}^{\text{HF}}], \quad (79)$$

satisfied with an accuracy better than 3%. This can be explained in terms of the virial theorem relation for atoms: $\langle \hat{\mathcal{U}} + \hat{\mathcal{V}} \rangle = -2\langle \hat{\mathcal{T}} \rangle$, valid both for the GS in the HF approximation [see Eqs. (64) and (66)]

$$E_{\text{es}}[n_{\text{GS}}^{\text{HF}}] + E_x^{\text{HF}}[n_{\text{GS}}^{\text{HF}}] + E_{\text{ext}}[n_{\text{GS}}^{\text{HF}}] = -2T^{\text{HF}}[n_{\text{GS}}^{\text{HF}}], \quad (80)$$

and for the exact GS problem in the HK formulation [see Eqs. (14) and (22)]

$$E_{\text{ec}}^{\text{HK}}[n_{\text{GS}}] + E_{\text{ext}}[n_{\text{GS}}] = -2T^{\text{HK}}[n_{\text{GS}}]. \quad (81)$$

The last relation can be rewritten in terms of the KS functionals [see Eqs. (58), (63) and (54)]

$$\begin{aligned} E_{\text{es}}[n_{\text{GS}}] + E_x^{\text{KS}}[n_{\text{GS}}] + U_c^{\text{KS}}[n_{\text{GS}}] + E_{\text{ext}}[n_{\text{GS}}] \\ = -2(T^{\text{KS}}[n_{\text{GS}}] + T_c^{\text{KS}}[n_{\text{GS}}]). \end{aligned} \quad (82)$$

By neglecting in Eq. (82) the small terms: $O([n_{\text{GS}} - n_{\text{GS}}^{\text{HF}}])$, T_c^{KS} , and U_c^{KS} , an approximate relation is obtained

$$E_{\text{es}}[n_{\text{GS}}^{\text{HF}}] + E_x^{\text{KS}}[n_{\text{GS}}^{\text{HF}}] + E_{\text{ext}}[n_{\text{GS}}^{\text{HF}}] \approx -2T_c^{\text{KS}}[n_{\text{GS}}^{\text{HF}}]. \quad (83)$$

The difference between relations (80) and (83) gives (79).

It follows from the relation (79) that both contributions to the HF correlation energy $\Delta T + \Delta E_x = E_c^{\text{HF}}$ are of comparable magnitude and partially cancel out, leading to

$$E_c^{\text{HF}} \approx -\Delta T \approx \frac{1}{2}\Delta E_x. \quad (84)$$

In combination with the results (77) and (78) it gives

$$E_c^{\text{HF}}/E_{\text{GS}}^{\text{HF}} = |E_c^{\text{HF}}|/T^{\text{HF}} < 4 \times 10^{-5}; \quad E_c^{\text{HF}}/E_x^{\text{HF}} < 2.2 \times 10^{-4}. \quad (85)$$

We see that the HF correlation energy E_c^{HF} is a very small quantity indeed – four orders of magnitude smaller than the exchange energy. When compared with the known results for the KS correlation energy $E_c^{\text{KS}} \equiv E_c$ or the QM one [Eq. (27)], it happens to be two orders of magnitude smaller.

A small value of $|\Delta E_x|$ demonstrates that the total exchange energy, calculated in the HF method, quite accurately represents the exchange energy of KS method. Although this and all previous conclusions are drawn for $n = n_{\text{GS}}^{\text{HF}}$, one may expect them to be valid also for $n = n_{\text{GS}} \equiv n_{\text{GS}}^{\text{KS}}$, because these two densities (for a given system) are quite close.

2.5 The Exact Ground State Problem Posed as the Hartree-Fock Method

Taking into account the fact established in the previous section that E_x^{HF} is close to $E_x^{\text{KS}} \equiv E_x$ and, on the other hand, that an exact expression for the exchange potential $v_x = \delta E_x / \delta n$ is not known, one may wish to modify the HF method in such a way that it would lead to the exact GS energy and density (Baroni and Tuncel [15]). This can be easily obtained from Eq. (68) rewritten as

$$T_s[n] + E_{\text{es}}[n] + E_x[n] = F^{\text{HF}}[n] - E_c^{\text{HF}}[n], \quad (86)$$

and substituted into Eqs. (46), (47) and (53) to obtain

$$E_{\text{GS}} = \min_n \{F^{\text{HF}}[n] + E_{\text{ext}}^{\text{HF}}[n]\} = F^{\text{HF}}[n_{\text{GS}}] + E_{\text{ext}}^{\text{HF}}[n_{\text{GS}}], \quad (87)$$

where the effective external potential energy in this “corrected HF method” is defined to be

$$E_{\text{ext}}^{\text{HF}}[n] = E_{\text{ext}}[n] + E_c[n] - E_c^{\text{HF}}[n], \quad (88)$$

i.e. the bare external potential energy E_{ext} , Eq. (16), corrected by the difference between the KS and HF correlation energy functionals. The exact GS problem, formulated as minimization in Eq. (87), can be solved, however, as a traditional HF method, via HF equations similar to (33), but with the bare external

potential $v(\mathbf{r})$ replaced there by the HF “effective” one

$$v_{\text{ext}}^{\text{HF}}(\mathbf{r}; [n]) = \frac{\delta E_{\text{ext}}^{\text{HF}}[n]}{\delta n(\mathbf{r})} = v(\mathbf{r}) + \frac{\delta(E_c[n] - E_c^{\text{HF}}[n])}{\delta n(\mathbf{r})}. \quad (89)$$

One can be easily convinced that this “prescription” is correct, if one compares the variation of the functionals minimized in Eqs. (87) and (64); the last minimization being equivalent to that in Eq. (28), solved via Eq. (33). Because the effective external potential (89) depends functionally on $n(\mathbf{r})$, an iterative method, leading to self-consistency, must be employed.

The corrected HF method described above for the exact GS problem was discussed earlier, among others, by Parr and Yang [10] and termed by them the HF-KS method. However, the contribution of $v_c^{\text{HF}} = \delta E_c^{\text{HF}}/\delta n$ to the effective external potential (89) was not included there. The consequences of such neglect are discussed below, see the paragraph starting a few lines after Eq. (94).

It should be noted that the “correction” to $E_{\text{ext}}[n]$ in Eq. (88) is nonpositive:

$$E_c[n] - E_c^{\text{HF}}[n] \leq 0. \quad (90)$$

This follows from [see definitions (58) and (69)]

$$\begin{aligned} E_c[n] - E_c^{\text{HF}}[n] &= (F^{\text{HK}}[n] - F^{\text{KS}}[n]) - (F^{\text{HF}}[n] - F^{\text{KS}}[n]) \\ &= \langle \Psi^{\text{HK}}[n] | \hat{\mathcal{T}} + \hat{\mathcal{U}} | \Psi^{\text{HK}}[n] \rangle \\ &\quad - \langle \Psi_{\text{D}}^{\text{HF}}[n] | \hat{\mathcal{T}} + \hat{\mathcal{U}} | \Psi_{\text{D}}^{\text{HF}}[n] \rangle \end{aligned} \quad (91)$$

and the fact that both $\Psi_{\text{D}}^{\text{HF}}[n]$ and $\Psi^{\text{HK}}[n]$ are the minimizers of $\langle \hat{\mathcal{T}} + \hat{\mathcal{U}} \rangle$, the function $\Psi_{\text{D}}^{\text{HF}}[n]$ in a “narrower” space, see Eqs. (65) and (15).

We are ready now to estimate the conventional quantum mechanical correlation energy E_c^{QM} defined in Eq. (27). Using Eqs. (87) and (64), we rewrite it as

$$\begin{aligned} E_c^{\text{QM}} &= (F^{\text{HF}}[n_{\text{GS}}] + E_{\text{ext}}^{\text{HF}}[n_{\text{GS}}]) - (F^{\text{HF}}[n_{\text{GS}}^{\text{HF}}] + E_{\text{ext}}[n_{\text{GS}}^{\text{HF}}]) \\ &= E_{\text{ext}}^{\text{HF}}[n_{\text{GS}}^{\text{HF}}] - E_{\text{ext}}[n_{\text{GS}}^{\text{HF}}] + O([\delta n_{\text{GS}}^{\text{HF}}]^2) \\ &= E_c[n_{\text{GS}}^{\text{HF}}] - E_c^{\text{HF}}[n_{\text{GS}}^{\text{HF}}] + O([\delta n_{\text{GS}}^{\text{HF}}]^2). \end{aligned} \quad (92)$$

Functional Taylor series expansion of the functional minimized in Eq. (87), in powers of $\delta n_{\text{GS}}^{\text{HF}}(\mathbf{r}) = [n_{\text{GS}}^{\text{HF}}(\mathbf{r}) - n_{\text{GS}}(\mathbf{r})]$ has been employed first, and Eq. (88) used in the last step. So E_c^{QM} is close to KS correlation energy functional taken for the GS density of HF approximation, corrected by the (much smaller) HF correlation energy, and a small remainder of the second order in the density difference. The last quantity gives an estimate to the “large parentheses” term of Eq. (28) in [12].

By taking into account that E_c^{QM} characterizes the $\{N, v\}$ system, while N and v (within a trivial additive constant) are determined by the HF GS density $n_{\text{GS}}^{\text{HF}}$ (an analogue of HK theorem), the QM correlation energy can be considered a functional of $n_{\text{GS}}^{\text{HF}}$ (see Harris and Pratt [16])

$$E_c^{\text{QM}} = E_c^{\text{QM}}[n_{\text{GS}}^{\text{HF}}]. \quad (93)$$

Thus Eq. (92) gives an approximation to this functional in terms of KS and HF correlation energy functionals. Rewriting Eq. (27) with the help of (93) and (64) we obtain

$$E_{\text{GS}} = \mathcal{E}^{\text{HF}}[n_{\text{GS}}^{\text{HF}}] + E_{\text{c}}^{\text{QM}}[n_{\text{GS}}^{\text{HF}}], \quad (94)$$

which demonstrates that if the functional $E_{\text{c}}^{\text{QM}}[n]$ is known, the exact GS energy for the given system can be obtained by performing a single HF calculation. Unfortunately, the true GS density cannot be obtained in this way, contrary to the corrected HF method in Eq. (87), which, however, requires a few iterations of the HF calculations to gain the self-consistency.

Let us note that if the exact GS problem in the corrected HF form, Eq. (87), is approximated by a similar problem in which $E_{\text{c}}^{\text{HF}}[n]$ is neglected in Eq. (88), and its solution for the energy and density is denoted by $\tilde{E}_{\text{GS}}$ and $\tilde{n}_{\text{GS}}$, then

$$\tilde{E}_{\text{GS}} = E_{\text{GS}} + E_{\text{c}}^{\text{HF}}[\tilde{n}_{\text{GS}}] + O[(\tilde{n}_{\text{GS}} - n_{\text{GS}})^2] \quad (95)$$

holds, as obtained via the functional Taylor expansion of the functional minimized in Eq. (87), in powers of $[\tilde{n}_{\text{GS}}(\mathbf{r}) - n_{\text{GS}}(\mathbf{r})]$. So, because of the inequality (73), the considered approximation possesses a “lower-bound”-like property

$$\tilde{E}_{\text{GS}} \lesssim E_{\text{GS}}, \quad (96)$$

and the above inequality should in practice be “sharp”, because the second-order terms in Eq. (95) are expected to be small, as compared with the magnitude of the leading negative term E_{c}^{HF} . Unfortunately, the considered approximation belongs to “formal” ones, because the exact KS correlation energy functional $E_{\text{c}}[n]$ is not known. A practical and accurate approximation can be obtained, however, if besides the neglect of $E_{\text{c}}^{\text{HF}}[n]$, the best modern approximation, say $E_{\text{c}}^{\text{APP}}[n]$, for $E_{\text{c}}[n]$ is used in Eq. (88). As pointed out in [12] (see also Sect. 2.4), the neglect of E_{c}^{HF} leads to a small error (about 0.02% of E_{x}), so the main error is now due to the difference $E_{\text{c}}^{\text{APP}}[n] - E_{\text{c}}[n]$. Therefore the total error of such approximation may be expected to be significantly smaller than an error of analogous approximate use of the KS scheme, in which, besides the same approximation $E_{\text{c}}^{\text{APP}}[n]$ for $E_{\text{c}}[n]$, some approximation $E_{\text{x}}^{\text{APP}}[n]$ for the exchange energy functional $E_{\text{x}}[n]$ must be applied, in order to have an explicit approximate expression for $v_{\text{x}}(\mathbf{r}; [n])$, Eq. (57).

2.6 The Optimized Potential Method

This method is usually thought as an approach allowing one to find the exact exchange potential. It may be considered [17] as an approximation to the exact GS problem, similar to the HF approximation: namely, the solution of the optimized potential (OP) approximation – the energy $E_{\text{GS}}^{\text{OP}}$ and the wave function $\Phi_{\text{GS}}^{\text{OP}}$ – stems from the following minimization problem

$$E_{\text{GS}}^{\text{OP}} = \min_{\Phi_{\text{D}}^{\text{s}}} \langle \Phi_{\text{D}}^{\text{s}} | \hat{\mathcal{T}} + \hat{\mathcal{U}} + \hat{\mathcal{V}} | \Phi_{\text{D}}^{\text{s}} \rangle = \langle \Phi_{\text{GS}}^{\text{OP}} | \hat{\mathcal{T}} + \hat{\mathcal{U}} + \hat{\mathcal{V}} | \Phi_{\text{GS}}^{\text{OP}} \rangle. \quad (97)$$

Here Φ_D^s means such determinantal wave function, which is the GS function to a noninteracting N -electron system with some local potential $v_s(\mathbf{r})$ [see Eqs. (36) and (40)]. Obviously, spin orbitals $\phi_i^s(\mathbf{x})$ – the solutions of Eq. (40) – and Φ_D^s constructed of them, are functionals of the potential $v_s(\mathbf{r})$: $\Phi_D^s = \Phi_D^s[v_s]$. So Eq. (97) can be rewritten as

$$\begin{aligned} E_{GS}^{OP} &= \min_{v_s} \langle \Phi_D^s[v_s] | \hat{\mathcal{T}} + \hat{\mathcal{U}} + \hat{\mathcal{V}} | \Phi_D^s[v_s] \rangle \\ &= \langle \Phi_D^s[v_{GS}^{OP}] | \hat{\mathcal{T}} + \hat{\mathcal{U}} + \hat{\mathcal{V}} | \Phi_D^s[v_{GS}^{OP}] \rangle. \end{aligned} \quad (98)$$

There are algorithms allowing one, for the given external potential $v(\mathbf{r})$, to find the OP $v_{GS}^{OP}(\mathbf{r})$ [i.e. the minimizer in Eq. (98)] via solution of an integral equation, and, subsequently to get $\Phi_{GS}^{OP} = \Phi_D^s[v_{GS}^{OP}]$ and E_{GS}^{OP} . Actually, in the case of spherical spin-polarized and general spin-unpolarized atoms, an algorithm is known (see e.g. [18]), which leads to accurate results, whereas for remaining systems, an algorithm yielding an approximate solution only is available (see e.g. in [19] and [20]).

Owing to the HK theorem, applied now to a noninteracting problem, we know that the potential $v_s(\mathbf{r})$ is determined (within a trivial additive constant) by the GS density of the system [compare Eqs. (36), (37), and (35)]. So Eq. (98) can be further transformed to the form

$$E_{GS}^{OP} = \min_n \langle \Phi_D^{KS}[n] | \hat{\mathcal{T}} + \hat{\mathcal{U}} + \hat{\mathcal{V}} | \Phi_D^{KS}[n] \rangle. \quad (99)$$

This can be finally expressed in terms of the following functional [see definitions (63) and (16)]

$$\mathcal{E}^{KS}[n] = \langle \Phi_D^{KS}[n] | \hat{\mathcal{T}} + \hat{\mathcal{U}} + \hat{\mathcal{V}} | \Phi_D^{KS}[n] \rangle = F^{KS}[n] + E_{ext}[n]. \quad (100)$$

Therefore

$$E_{GS}^{OP} = \min_n \{ F^{KS}[n] + E_{ext}[n] \}, \quad (101)$$

or

$$E_{GS}^{OP} = \min_n \mathcal{E}^{KS}[n] = \mathcal{E}^{KS}[n_{GS}^{OP}]. \quad (102)$$

Two inequalities, connected with the OP-GS and HF-GS quantities are known [12]:

$$E_{GS}^{OP} \leq \mathcal{E}^{KS}[n_{GS}^{HF}], \quad (103)$$

$$E_{GS}^{HF} \leq E_{GS}^{OP}. \quad (104)$$

The first inequality follows immediately from minimization (102), while the second one holds due to the fact that the variational functional space involved in minimization (97) is narrower than in (25).

By expanding $\mathcal{E}^{KS}[n_{GS}^{HF}]$ in a functional Taylor series in powers of $[n_{GS}^{HF}(\mathbf{r}) - n_{GS}^{OP}(\mathbf{r})]$ around $n_{GS}^{OP}(\mathbf{r})$ we obtain from Eq. (102)

$$\mathcal{E}^{KS}[n_{GS}^{HF}] - E_{GS}^{OP} = O([n_{GS}^{HF} - n_{GS}^{OP}]^2). \quad (105)$$

This gives an explanation to the finding of Görling and Ernzerhof in their calculations [12] that “the equal sign practically holds for the relation (103)”.

Let us calculate now the variation of $\mathcal{E}^{\text{KS}}[n]$, Eq. (100), using (63) with (34) and (57),

$$\delta \mathcal{E}^{\text{KS}}[n] = \int d^3r \left(\frac{\delta T_s[n]}{\delta n(\mathbf{r})} + v(\mathbf{r}) + v_{\text{es}}(\mathbf{r}) + v_{\text{x}}(\mathbf{r}) \right) \delta n(\mathbf{r}) \quad (106)$$

and compare it with the variation (49) of the noninteracting system energy functional (39). We conclude, that at minimum (i.e. at self-consistency), when (98) and (102) are equivalent, the following equality holds

$$v_{\text{GS}}^{\text{OP}}(\mathbf{r}; [v]) = v(\mathbf{r}) + v_{\text{es}}(\mathbf{r}; [n_{\text{GS}}^{\text{OP}}]) + v_{\text{x}}(\mathbf{r}; [n_{\text{GS}}^{\text{OP}}]). \quad (107)$$

Because $v(\mathbf{r})$ is given and $v_{\text{es}}(\mathbf{r})$ easily calculable from the known density, Eq. (34), the KS exchange potential $v_{\text{x}}(\mathbf{r})$ is readily available from the OP solution $-v_{\text{GS}}^{\text{OP}}(\mathbf{r})$. It should be noticed, however, that this exchange potential $v_{\text{x}}(\mathbf{r}; [n_{\text{GS}}^{\text{OP}}])$ differs slightly from the exchange potential $v_{\text{x}}(\mathbf{r}; [n_{\text{GS}}])$ occurring in the exact GS problem solved by the KS method [see Eqs. (50), (51) and (56)], because the densities $n_{\text{GS}}^{\text{OP}}(\mathbf{r})$ and $n_{\text{GS}}(\mathbf{r})$ are slightly different.

2.7 The Exact Ground-State Problem Posed as the Optimized Potential Method

Let us rewrite the exact GS problem in Eq. (62) in a form

$$E_{\text{GS}} = \min_n \{ F^{\text{KS}}[n] + E_{\text{ext}}^{\text{OP}}[n] \}, \quad (108)$$

where

$$E_{\text{ext}}^{\text{OP}}[n] = E_{\text{ext}}[n] + E_{\text{c}}[n]. \quad (109)$$

Next, when we compare the variation of the functional minimized in Eq. (108) with that in Eq. (101), we conclude that the exact GS problem can be solved by algorithms of the OP method, if an OP “effective” external potential

$$v_{\text{ext}}^{\text{OP}}(\mathbf{r}; [n]) = \frac{\delta E_{\text{ext}}^{\text{OP}}[n]}{\delta n(\mathbf{r})} = v(\mathbf{r}) + v_{\text{c}}(\mathbf{r}; [n]) \quad (110)$$

is used instead of the bare external potential $v(\mathbf{r})$ in the original OP approximation. Since this potential is a functional of the density (and, therefore, of the optimized noninteracting system potential v_{s}), an iterative procedure, leading to self-consistency, must be applied. Such scheme is implicitly present in [20].

At self-consistency, the optimum potential of this “corrected OP method” equals

$$v_{\text{GS}}^{\text{COP}}(\mathbf{r}; [v]) = \{v(\mathbf{r}) + v_{\text{c}}(\mathbf{r}; [n_{\text{GS}}])\} + v_{\text{es}}(\mathbf{r}; [n_{\text{GS}}]) + v_{\text{x}}(\mathbf{r}; [n_{\text{GS}}]), \quad (111)$$

[see Eq. (107) with (110)], i.e. it coincides with the effective one-body potential of the KS method, Eq. (51), at its self-consistency.

It is worth noticing that a practical and accurate approximate scheme may be obtained from the formally exact corrected OP method described above, if the best modern approximations $E_c^{\text{APP}}[n]$ and $v_c^{\text{APP}}[n] = \delta E_c^{\text{APP}} / \delta n$ for $E_c[n]$ and $v_c[n]$ are used in Eqs. (108) and (109). Such an approach to the exact GS problem should be more accurate than a similar approach to the KS method, because for the last, besides the correlation energy and potential, also the exchange energy and potential must be somehow approximated.

3 Determination of the Exchange and Correlation Potentials from Accurate Many-Body Wave Functions

As discussed in previous sections, reliable approximate expressions for exchange and correlation energies and potentials (as functionals of the density) are necessary to perform DFT calculations in practice. In order to check the accuracy of such expressions, one needs exact results for comparison. As an input for this program, some accurate many-electron wave function may be used, obtained from e.g. configuration interaction or Hylleraas-type calculations for a particular system. Having accurate GS density $n_{\text{GS}}(\mathbf{r})$ determined from such a function, the effective KS potential, Eq. (51), leading to this density, can be established numerically by various methods (see e.g. [21], [14], [22], [23], [24] and references therein). After subtracting the external and electrostatic potentials, the remaining $v_{\text{xc}}(\mathbf{r}; [n_{\text{GS}}])$ is obtained with high accuracy. Next, methods leading to its separation into the exchange and correlation contributions will be discussed.

For the helium isoelectronic series, the exact exchange potential is known to be $v_{\text{x}}(\mathbf{r}; [n_{\text{GS}}]) = -\frac{1}{2}v_{\text{es}}(\mathbf{r}; [n_{\text{GS}}])$, so, after subtracting it from v_{xc} , an accurate $v_{\text{c}}(\mathbf{r}; [n_{\text{GS}}])$ is available in this case, see Umrigar and Gonze [25].

For more complicated systems, the exact $v_{\text{x}}(\mathbf{r}; [n_{\text{GS}}])$ may be estimated by applying the above discussed scheme to the density $n_{\text{GS}}^{\text{HF}}(\mathbf{r})$ obtained from the HF calculations (see e.g. in [21]). In this way the potential

$$v_{\text{xc}}^{\text{HF}}(\mathbf{r}) = v_{\text{x}}(\mathbf{r}; [n_{\text{GS}}^{\text{HF}}]) + v_{\text{c}}^{\text{HF}}(\mathbf{r}; [n_{\text{GS}}^{\text{HF}}]) \quad (112)$$

is determined [see Eq. (70)]. In view of the very small value of $E_{\text{c}}^{\text{HF}}[n_{\text{GS}}^{\text{HF}}]$ as compared with E_{x} [see Eq. (85)], the corresponding potential v_{c}^{HF} may be also expected to be very small as compared to v_{x} ; further, the densities $n_{\text{GS}}^{\text{HF}}(\mathbf{r})$ and $n_{\text{GS}}(\mathbf{r})$ (for a given system) are quite close. Therefore $v_{\text{xc}}^{\text{HF}}(\mathbf{r})$ may be considered a good estimate of $v_{\text{x}}(\mathbf{r}; [n_{\text{GS}}])$. A quantitative estimate for the difference $v_{\text{x}}(\mathbf{r}; [n_{\text{GS}}^{\text{HF}}]) - v_{\text{x}}(\mathbf{r}; [n_{\text{GS}}])$ exists for helium: it corresponds to a gap between the solid and dotted lines on Fig. 11 of [25]. Its value amounts to a few percent of $v_{\text{c}}(\mathbf{r}; [n_{\text{GS}}])$. Yet another way to estimate $v_{\text{x}}(\mathbf{r}; [n_{\text{GS}}])$ from the results of HF calculations is offered by Eq. (219) of Sect. 5.5 below. The potential $v_{\text{x}}(\mathbf{r}; [n_{\text{GS}}])$ may be also estimated via OP calculations for a given system. From the

determined optimum potential, Eq. (107), one immediately obtains $v_x(\mathbf{r}; [n_{\text{GS}}^{\text{OP}}])$ (see e.g. [20] and [18]), which may differ only slightly from $v_x(\mathbf{r}; [n_{\text{GS}}])$ due to a small remainder $O([n_{\text{GS}}^{\text{OP}}(\mathbf{r}) - n_{\text{GS}}(\mathbf{r})])$.

Finally, an exact $v_x(\mathbf{r}; [n_{\text{GS}}])$ may be determined in practice by applying the corrected OP method iteratively. In this case the correlation potential, determining the effective external potential in Eq. (110) during $(\ell + 1)$ -th iteration, is defined as

$$v_c^{(\ell+1)}(\mathbf{r}) = v_{xc}(\mathbf{r}; [n_{\text{GS}}]) - v_x^{(\ell)}(\mathbf{r}), \quad (113)$$

where $v_x^{(\ell)}(\mathbf{r})$ is the exchange part of the optimum potential $v_{\ell}^{\text{OP}}(\mathbf{r})$ obtained in the ℓ -th iteration:

$$v_x^{(\ell)}(\mathbf{r}) = v_{\ell}^{\text{OP}}(\mathbf{r}) - \{v(\mathbf{r}) + v_c^{(\ell)}(\mathbf{r})\} - v_{\text{es}}(\mathbf{r}; [n_{\text{GS}}^{(\ell)}]) \equiv v_x(\mathbf{r}; [n_{\text{GS}}^{(\ell)}]) \quad (114)$$

[compare Eq. (111)]. Here $n_{\text{GS}}^{(\ell)}(\mathbf{r})$ is the density obtained in the ℓ -th iteration. As initial conditions,

$$n_{\text{GS}}^{(0)}(\mathbf{r}) = n_{\text{GS}}^{\text{OP}}(\mathbf{r}) \quad \text{and} \quad v_x^{(0)}(\mathbf{r}) = v_x(\mathbf{r}; [n_{\text{GS}}^{\text{OP}}]) \quad (115)$$

should be taken. At convergence, $n_{\text{GS}}^{(\ell)}(\mathbf{r}) \rightarrow n_{\text{GS}}(\mathbf{r})$ and $v_x^{(\ell)}(\mathbf{r}) \rightarrow v_x(\mathbf{r}; [n_{\text{GS}}])$ – compare Eq. (114) and (111).

4 Long-Range Asymptotic Form of Potentials

4.1 Kohn-Sham Potential

Knowledge of all terms of the KS potential in Eq. (51) for a large distance from an atomic or molecular center is interesting both for setting the proper asymptotic behavior for the solutions of the KS equations (50), and for checking the accuracy of approximations for $v_x(\mathbf{r})$ and $v_c(\mathbf{r})$ in this region.

The external potential of a molecule having, as its framework, M nuclei of the charges Z_J , fixed at positions $\mathbf{R}_J$, is obviously

$$v(\mathbf{r}) = \sum_{J=1}^M -\frac{Z_J}{|\mathbf{r} - \mathbf{R}_J|}. \quad (116)$$

So its large- r expansion is

$$v(\mathbf{r}) = -\frac{Z}{r} + O\left(\frac{1}{r^2}\right); \quad Z = \sum_{J=1}^M Z_J. \quad (117)$$

The same expansion for the electrostatic potential (34) [u defined in (11)] is

$$v_{\text{es}}(\mathbf{r}; [n]) = \frac{1}{r} \int d^3r' n(\mathbf{r}') \left\{ 1 + O\left(\frac{r'}{r}\right) \right\} = \frac{N}{r} + O\left(\frac{1}{r^2}\right), \quad (118)$$

where in the second step the constraint (3) was applied. According to Almbladh

and von Barth [26], the exchange-correlation potential behaves as

$$v_{xc}(r; [n]) = -\frac{1}{r} + O\left(\frac{1}{r^p}\right), \quad (119)$$

where the exponent of the second term is $p = 4$ for a nondegenerate spin-unpolarized GS or for the spin-up potential of a spin-polarized GS, otherwise $p = 3$.

It should be noted that potentials $v_{es}(r)$ and $v_{xc}(r)$, being defined as a functional derivatives with respect to the density constrained by Eq. (3), are determined with accuracy to arbitrary additive constant only. In each case this constant is fixed traditionally by requiring the potential to be zero at infinity, similarly as in the case of the Coulomb potential due to the nuclei, Eq. (116).

The sum of the results (117)–(119) – the asymptotic expression for the total KS potential

$$v_{KS}(r) = v(r) + v_{es}(r) + v_{xc}(r) = -\frac{Z_{\text{eff}}}{r} + O\left(\frac{1}{r^2}\right), \quad (120)$$

where

$$Z_{\text{eff}} = Z - N + 1, \quad (121)$$

– shows a spherical symmetry of its leading term, so any eigenfunction of the KS equation (50) possesses also this property and equals

$$\phi_{i\sigma}^{\text{KS}}(r) = C_{i\sigma} \varphi_{i\sigma}(r) \{1 + O(r^{-1})\}, \quad \varphi_{i\sigma}(r) = r^{\beta_{i\sigma}} \exp(-\kappa_{i\sigma} r), \quad (122)$$

with

$$\kappa_{i\sigma} = (-2\varepsilon_{i\sigma}^{\text{KS}})^{1/2}, \quad \beta_{i\sigma} = Z_{\text{eff}}/\kappa_{i\sigma} - 1, \quad (123)$$

where $\varepsilon_{i\sigma}^{\text{KS}}$ is an eigenvalue corresponding to $\phi_{i\sigma}^{\text{KS}}$, while $C_{i\sigma}$ is a normalization constant.

As proven in [26], the KS eigenvalue corresponding to the uppermost occupied KS orbital equals the negative of the exact ionization potential I . Therefore the density (41), in the large- r region, behaves as

$$n(r) \propto r^{2\beta_0} \exp(-2\kappa_0 r) \{1 + O(r^{-1})\} \quad (124)$$

with

$$\kappa_0 = (2I)^{1/2}, \quad \beta_0 = Z_{\text{eff}}/\kappa_0 - 1. \quad (125)$$

4.2 Exchange Potential for a Pure-State System in the Conventional DFT

The long-range asymptotic form of the exchange potential, a constituent of the exchange-correlation potential (56), will be discussed in this and the remaining subsections. Since the known derivations of this form are very complicated and involve an analysis of an integral equation of the OP method (see, e.g. [17], [27],

[19]), it may be interesting to re-derive this form here in a simple and direct way. The most common case of a system having a nondegenerate GS (a pure-state system) is considered in the current subsection.

As a starting point we take the formula (54) for the exchange energy E_x expressed in terms of the first-order DM $\gamma(\mathbf{x}; \mathbf{x}') \equiv \gamma^{\text{KS}}(\mathbf{x}; \mathbf{x}')$ [see Eq. (272), where the KS spin orbitals should be employed: $\phi_j(\mathbf{x}) \equiv \phi_j^{\text{KS}}(\mathbf{x}; [n])$]. With the help of Eqs. (18) and (268) with (273) for $p = 2$ we have

$$\begin{aligned} E_x[n] &= \tilde{E}_{\text{ee}}[\zeta_2[n]] - E_{\text{es}}[n] \\ &= -\frac{1}{2} \int d\mathbf{x} d\mathbf{x}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \gamma(\mathbf{x}; \mathbf{x}') \gamma(\mathbf{x}'; \mathbf{x}), \end{aligned} \quad (126)$$

with

$$\gamma(\mathbf{x}; \mathbf{x}') = \sum_{i=1}^N \phi_i(\mathbf{x}) \phi_i^*(\mathbf{x}') \quad (127)$$

and

$$n(\mathbf{r}) = \sum_s \gamma(\mathbf{r}s; \mathbf{r}s) = \sum_s \sum_{i=1}^N |\phi_i(\mathbf{x})|^2. \quad (128)$$

The variation of the electron density (128) equals

$$\delta n(\mathbf{r}) = \sum_s \sum_{i=1}^N (\phi_i(\mathbf{x}) \delta \phi_i^*(\mathbf{x}) + \text{c.c.}), \quad (129)$$

where variations $\delta \phi_j$ of spin orbitals may be thought as induced by a variation of an effective single-particle potential, generating these KS orbitals (but this detail does not play any role in the further considerations). The variation of the exchange energy (126) can be calculated in a similar way to be

$$\begin{aligned} \delta E_x &= -\frac{1}{2} \int d\mathbf{x} d\mathbf{x}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \{ \gamma(\mathbf{x}; \mathbf{x}') \delta \gamma(\mathbf{x}'; \mathbf{x}) + \delta \gamma(\mathbf{x}; \mathbf{x}') \gamma(\mathbf{x}'; \mathbf{x}) \} \\ &= -\frac{1}{2} \int d\mathbf{x} d\mathbf{x}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \sum_{j=1}^N \sum_{i=1}^N 2 \left(\phi_i(\mathbf{x}') \phi_j^*(\mathbf{x}') \phi_j(\mathbf{x}) \delta \phi_i^*(\mathbf{x}) + \text{c.c.} \right). \end{aligned} \quad (130)$$

In the second step, after substituting the expression (127) for $\gamma(\mathbf{x}; \mathbf{x}')$, four terms were obtained in the integrand, reduced subsequently to two terms only by renaming integration variables $\mathbf{x} \leftrightarrow \mathbf{x}'$, in two of four terms. Next, the Coulomb potential is expanded formally in a power series of r'/r :

$$\delta E_x = - \int d\mathbf{x} \frac{1}{r} \sum_{ij} \left(\phi_j(\mathbf{x}) \delta \phi_i^*(\mathbf{x}) \int d\mathbf{x}' \phi_i(\mathbf{x}') \phi_j^*(\mathbf{x}') \left\{ 1 + O\left(\frac{r'}{r}\right) \right\} + \text{c.c.} \right) \quad (131)$$

Owing to the exponential decay of KS orbitals, Eq. (122), integrations over $d\mathbf{x}'$

are convergent for all terms of this series. The result of these integrations represents thus an asymptotic series in powers of $1/r$. Its leading term, due to orthonormality of KS orbitals, is simply δ_{ij} , so

$$\delta E_x = - \int d^3r \frac{1}{r} \left\{ \sum_s \sum_{j=1}^N \left(\phi_j(\mathbf{x}) \delta \phi_j^*(\mathbf{x}) + c.c. \right) + O\left(\frac{1}{r}\right) \right\}. \quad (132)$$

This variation can be rewritten with the help of Eq. (129) as

$$\delta E_x = - \int d^3r \frac{1}{r} \left\{ \delta n(\mathbf{r}) + O\left(\frac{1}{r}\right) \right\}, \quad (133)$$

which means that

$$v_x(\mathbf{r}) = \frac{\delta E_x[n]}{\delta n(\mathbf{r})} = -\frac{1}{r} + O\left(\frac{1}{r^2}\right) \quad (134)$$

– the same result as obtained in a different way in [17] or [27]. Let us note that, contrary to the papers mentioned, our derivation does not rely on a special role of the uppermost occupied orbital or on the presence (or absence) of a degeneracy of the uppermost KS eigenvalue.

What is remarkable for the leading term of the result (134) is that its form is universal – the same for all possible finite systems, regardless of their number of electrons or the nature of their nuclear framework. It coincides with the leading term of the asymptotic expansion for $v_{xc}(\mathbf{r})$, Eq. (119), which means that the correlation potential $v_c(\mathbf{r})$ does not play any role in the asymptotic region. Owing to its universal form $-1/r$, $v_x(\mathbf{r})$ provides just the term $+1$ in the expression (121) for the effective charge Z_{eff} of the leading term of the KS potential in Eq. (120), thus allowing for an interpretation as the following simple physical picture: if one places one electron far away from nuclei and other electrons near nuclei, then the electron “sees” an effective charge $Z_{\text{eff}}e$, which is a sum of the total nuclear charge $+Ze$ and the charge of all remaining electrons $-(N-1)e$.

4.3 Exchange Potential for a Pure-state System in the Spin DFT

The spin DFT is formulated in terms of two electron densities: $n_\uparrow(\mathbf{r})$ and $n_\downarrow(\mathbf{r})$, corresponding to the spin-up and spin-down subsystems [see Eqs. (274)–(279), in which the KS orbitals should be employed $\phi_{i\sigma}(\mathbf{r}) \equiv \phi_{i\sigma}^{\text{KS}}(\mathbf{r}; [n])$]. The exchange energy can be calculated according to Eqs. (55) and (21) with the pair correlation function h_2^{KS} given in Eq. (281), namely

$$E_x[n_\uparrow, n_\downarrow] = \sum_{\sigma} E_x^{\text{ferro}}[n_{\sigma}]; \quad \sigma = \uparrow, \downarrow, \quad (135)$$

where

$$E_x^{\text{ferro}}[n_{\sigma}] = \tilde{E}_x^{\text{ferro}}[\rho_{\sigma}] = -\frac{1}{2} \int d^3r d^3r' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \rho_{\sigma}(\mathbf{r}; \mathbf{r}') \rho_{\sigma}(\mathbf{r}'; \mathbf{r}), \quad (136)$$

with

$$\rho_\sigma(\mathbf{r}; \mathbf{r}') = \sum_{i=1}^{N_\sigma} \phi_{i\sigma}(\mathbf{r}) \phi_{i\sigma}^*(\mathbf{r}'), \quad (137)$$

and

$$n_\sigma(\mathbf{r}) = \rho_\sigma(\mathbf{r}; \mathbf{r}) = \sum_{i=1}^{N_\sigma} |\phi_{i\sigma}(\mathbf{r})|^2. \quad (138)$$

Since Eqs. (136)–(138) for a particular subsystem σ , in terms of orbitals $\phi_{i\sigma}(\mathbf{r})$, look the same as Eqs. (126)–(128) in terms of spin orbitals $\phi_j(\mathbf{x})$, all steps leading to the previous result (134) can be repeated again, leading now to the spin-polarized exchange potential

$$v_{x\sigma}(\mathbf{r}) = \frac{\delta E_x[n_\uparrow, n_\downarrow]}{\delta n_\sigma(\mathbf{r})} = \frac{\delta E_x^{\text{ferro}}[n_\sigma]}{\delta n_\sigma(\mathbf{r})} = -\frac{1}{r} + O\left(\frac{1}{r^2}\right). \quad (139)$$

This result should be, of course, consistent with the result for the conventional DFT of a spin-compensated (paramagnetic) system characterized by $n_\uparrow(\mathbf{r}) = n_\downarrow(\mathbf{r}) = \frac{1}{2}n(\mathbf{r})$. From Eq. (135) its exchange energy can be written as

$$E_x^{\text{para}}[n] = E_x^{\text{ferro}}[\tfrac{1}{2}n] + E_x^{\text{ferro}}[\tfrac{1}{2}n] = 2E_x^{\text{ferro}}[\tfrac{1}{2}n], \quad (140)$$

while the exchange potential calculated in Eq. (134) is

$$v_x(\mathbf{r}) = \frac{\delta E_x^{\text{para}}[n]}{\delta n(\mathbf{r})} = \frac{\delta E_x[n]}{\delta n(\mathbf{r})} = -\frac{1}{r} + O\left(\frac{1}{r^2}\right). \quad (141)$$

On the other hand, differentiating Eq. (140) we obtain

$$v_x(\mathbf{r}) = 2 \int d^3r' \left\{ \frac{\delta E_x^{\text{ferro}}[\bar{n}]}{\delta \bar{n}(\mathbf{r}')} \frac{\delta \bar{n}(\mathbf{r}')}{\delta n(\mathbf{r})} \right\}_{|\bar{n}=\frac{1}{2}n} = \frac{\delta E_x^{\text{ferro}}[\bar{n}]}{\delta \bar{n}(\mathbf{r})} = -\frac{1}{r} + O\left(\frac{1}{r^2}\right), \quad (142)$$

where, in the last step, the result (139) was employed. As expected, the results (141) and (142) are identical.

4.4 Exchange Potential for a Mixed-State System

A mixed-state description of a given system (see e.g. in [10] or [28]) is necessary in such situations, among others, when the GS is degenerate and/or when a non-integer average number of electrons is of interest. The first-order spinless ensemble DM and the ensemble electron density, characterizing this system, are in a form

$$\rho(\mathbf{r}; \mathbf{r}') = \rho_\uparrow^{\text{ens}}(\mathbf{r}; \mathbf{r}') + \rho_\downarrow^{\text{ens}}(\mathbf{r}; \mathbf{r}'), \quad (143)$$

$$n(\mathbf{r}) = n_\uparrow^{\text{ens}}(\mathbf{r}) + n_\downarrow^{\text{ens}}(\mathbf{r}), \quad (144)$$

where

$$\rho_{\sigma}^{\text{ens}}(\mathbf{r}; \mathbf{r}') = \sum_j f_{j\sigma} \phi_{j\sigma}(\mathbf{r}) \phi_{j\sigma}^*(\mathbf{r}'), \quad (145)$$

$$n_{\sigma}^{\text{ens}}(\mathbf{r}) = \sum_j f_{j\sigma} |\phi_{j\sigma}(\mathbf{r})|^2, \quad (146)$$

with

$$0 \leq f_{j\sigma} \leq 1; \quad \sum_j f_{j\sigma} = N_{\sigma}; \quad N = N_{\uparrow} + N_{\downarrow}, \quad (147)$$

[comp. Eqs. (137) and (138) for pure-state system]. The subsystem and total-system electron numbers N_{σ} and N are allowed to be noninteger. It will be convenient to number the KS orbitals $\phi_{j\sigma}(\mathbf{r})$ in each spin subsystem according to the following order of the corresponding eigenvalues

$$\varepsilon_{j\sigma} \leq \varepsilon_{j+1, \sigma}, \quad j = 1, 2, \dots \quad (148)$$

The expression for the exchange energy in terms of $\phi_{j\sigma}$ and $f_{j\sigma}$, used by Krieger et al. [19] can be neatly rewritten in a form

$$E_x = \sum_{\sigma} \tilde{E}_x^{\text{ferro}}[\rho_{\sigma}^{\text{ens}}] \quad (149)$$

[see definitions (145) and (136) for $\rho_{\sigma}^{\text{ens}}$ and $\tilde{E}_x^{\text{ferro}}$].

For the variation of the density (keeping the occupation numbers fixed) we obtain from Eqs. (144) and (146)

$$\delta n(\mathbf{r}) = \sum_{\sigma} \delta n_{\sigma}^{\text{ens}}(\mathbf{r}) = \sum_{j\sigma} f_{j\sigma} \left(\phi_{j\sigma}(\mathbf{r}) \delta \phi_{j\sigma}^*(\mathbf{r} + c.c.) \right), \quad (150)$$

[comp. Eq. (129)], while for the variation of the exchange energy, from Eqs. (149), (136) and (145), we find

$$\begin{aligned} \delta E_x = & -\frac{1}{2} \sum_{\sigma} \int d\mathbf{x} d\mathbf{x}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \sum_{ij} f_{i\sigma} f_{j\sigma} 2 \\ & \times \left(\phi_{i\sigma}(\mathbf{r}') \phi_{j\sigma}^*(\mathbf{r}') \phi_{j\sigma}(\mathbf{r}) \delta \phi_{i\sigma}^*(\mathbf{r}) + c.c. \right) \end{aligned} \quad (151)$$

in a way similar to that leading from Eq. (126) to (130). Repeating next the same steps as done in Eq. (131) and below it, we arrive at the following analogue of Eq. (132)

$$\delta E_x = - \sum_{\sigma} \int d^3r \frac{1}{r} \left\{ \sum_j f_{j\sigma}^2 \left(\phi_{j\sigma}(\mathbf{r}) \delta \phi_{j\sigma}^*(\mathbf{r}) + c.c. \right) + O\left(\frac{1}{r}\right) \right\}. \quad (152)$$

Contrary to the pure-state case, now δE_x in Eq. (152) cannot be directly written in terms of δn_{σ} in Eq. (150), because, for fractional occupation numbers, the inequality $f_{j\sigma}^2 \neq f_{j\sigma}$ holds. However, due to the exponential decay of KS orbitals, Eq. (122), for r large enough (say $r > R_{\sigma}$), the density $n_{\sigma}^{\text{ens}}(\mathbf{r})$ in Eq. (146) is composed solely of contributions due to g_{σ} orbitals of the highest occupied

degenerate energy level $\varepsilon_{m\sigma}$:

$$n_{\sigma}^{\text{ens}}(\mathbf{r}) = \sum_{m' = m - g_{\sigma} + 1, m - g_{\sigma} + 2, \dots, m} f_{m'\sigma} |\phi_{m'\sigma}(\mathbf{r})|^2, \quad \text{for } r > R_{\sigma}, \quad (153)$$

where

$$\varepsilon_{m - g_{\sigma}, \sigma} < \varepsilon_{m'\sigma} < \varepsilon_{m + 1, \sigma} \quad \text{and} \quad f_{j\sigma} = 0 \quad \text{for } j > m. \quad (154)$$

For the variation of the KS orbital in the large- r form (122) we have

$$\delta\phi_{i\sigma}(\mathbf{r})/\phi_{i\sigma}(\mathbf{r}) = \delta C_{i\sigma}/C_{i\sigma} + \ln(r)\delta\beta_{i\sigma} - r\delta\kappa_{i\sigma} \xrightarrow{r \rightarrow \infty} -r\delta\kappa_{i\sigma}, \quad (155)$$

so

$$\delta\phi_{i\sigma}(\mathbf{r}) = C_{i\sigma}\delta\varphi_{i\sigma}, \quad \text{for large } r. \quad (156)$$

Therefore the variation of the density (153) in the large- r region is

$$\delta n_{\sigma}^{\text{ens}}(\mathbf{r}) = \left[\sum_{m'} f_{m'\sigma} |C_{m'\sigma}|^2 \right] 2\varphi_{m\sigma}(r)\delta\varphi_{m\sigma}(r), \quad (157)$$

because the radial part $\varphi_{m\sigma}(r)$ is common for all $\phi_{m'\sigma}(\mathbf{r})$. Similarly, Eq. (152) can be rewritten as

$$\begin{aligned} \delta E_x = & - \sum_{\sigma} \int_{\{\text{larger-}r\}} d^3r \frac{1}{r} \left\{ \left[\sum_{m'} f_{m'\sigma}^2 |C_{m'\sigma}|^2 \right] 2\varphi_{m\sigma}(r)\delta\varphi_{m\sigma}(r) \right. \\ & \left. + O\left(\frac{1}{r}\right) \right\} + \int_{\{\text{remaining}\}} d^3r \{ \dots \}. \end{aligned} \quad (158)$$

By comparing Eqs. (157) and (158) we obtain finally

$$v_{x\sigma}^{\text{ens}}(\mathbf{r}) = \frac{\delta E_x}{\delta n_{\sigma}^{\text{ens}}(\mathbf{r})} = -\frac{a_{\sigma}}{r}, \quad \text{for large } r, \quad (159)$$

with

$$a_{\sigma} = \frac{\sum_{m'} f_{m'\sigma}^2 |C_{m'\sigma}|^2}{\sum_{m'} f_{m'\sigma} |C_{m'\sigma}|^2}. \quad (160)$$

It should be noted that the large- r region, where the result (159) is valid, may happen to be very distant when the energy level $\varepsilon_{m - g_{\sigma}, \sigma}$ is close to the highest occupied level $\varepsilon_{m\sigma}$ [see Eq. (154)].

For nondegenerate $\varepsilon_{m\sigma}$ level ($g_{\sigma} = 1$) the expression (160) simplifies to

$$a_{\sigma} = f_{m\sigma}, \quad (161)$$

giving thus in Eq. (159) the same result as obtained by Krieger et al. in [19] in a different way, while our result (160) allows for a generalization of their result to a degenerate situation.

Concluding this subsection, we remark that the expression (149) for the KS exchange energy of a mixed-state system is only approximate. The exact expression (204) is obtained in Sect. 5.4 and compared with the approximate one (149). The exact expression (236) for asymptotic $v_{x\sigma}^{\text{ens}}$ is obtained in Sect. 5.6.

However, expression (149) may be viewed as a definition of a specific exchange energy, say E_x^{APP} , (being thus somehow different from the KS exchange energy $E_x[n] = E_{ee}^{\text{KS}}[n] - E_{es}[n]$, where E_{ee}^{KS} in terms of KS DM n_2 is given in Eq. (18) as $\tilde{E}_{ee}[n_2]$). Then the difference $E_x[n] - E_x^{\text{APP}}[n]$ can be absorbed into the corresponding correlation energy contribution, because, actually, a total exchange-correlation energy only is defined for mixed-state functionals (see e.g. in [28]).

Although Krieger et al. [19] quote Perdew's paper [29] as a source for the expression (149), but this expression happens to be an infinite-size system limit of a more general formula (Eqs. (115)–(117) of [29]) obtained by Perdew for a finite system. But even that formula is not exact, because contributions due to electrostatic interactions inside pure subsystems were not balanced there with the global electrostatic energy (see Sect. 5.4 for details).

5 Exchange and Correlation Potentials in a Line-Integral Form

5.1 Differential Virial Theorems

A differential virial theorem represents an exact, local (at space point $\mathbf{r}$) relation involving the external potential $v(\mathbf{r})$, the (ee) interaction potential $u(\mathbf{r}, \mathbf{r}')$, the diagonal elements of the 1st and 2nd order DMs, $n(\mathbf{r})$ and $n_2(\mathbf{r}, \mathbf{r}')$, and the 1st order DM $\rho(\mathbf{r}_1; \mathbf{r}_2)$ 'close to diagonal', for a particular system. As it will be shown, it is a very useful tool for establishing various exact relations for a many electron systems. The mentioned dependence on ρ may be written in terms of the kinetic energy density tensor, defined as

$$t_{\alpha\beta}(\mathbf{r}; [\rho]) = \frac{1}{4} \left(\frac{\partial^2}{\partial r'_\alpha \partial r''_\beta} + \frac{\partial^2}{\partial r'_\beta \partial r''_\alpha} \right) \rho(\mathbf{r} + \mathbf{r}'; \mathbf{r} + \mathbf{r}'')|_{\mathbf{r}' = \mathbf{r} = \mathbf{0}}. \quad (162)$$

This is a real, symmetric tensor, the trace of which is the non-negative kinetic energy density (scalar)

$$t(\mathbf{r}; [\rho]) = \sum_{\alpha=1}^3 t_{\alpha\alpha}(\mathbf{r}; [\rho]) \geq 0, \quad (163)$$

leading to the global kinetic energy

$$T = \langle \Psi | \hat{T} | \Psi \rangle = \tilde{T}[\rho] = \int d^3r t(\mathbf{r}; [\rho]), \quad (164)$$

[comp. Eq. (17), its last form].

The differential virial theorem, obtained by us in [30], has the form of the following identity

$$\begin{aligned}
 n(\mathbf{r}) \frac{\partial}{\partial r_\alpha} v(\mathbf{r}) + 2 \int d^3 r' n_2(\mathbf{r}, \mathbf{r}') \frac{\partial}{\partial r_\alpha} u(\mathbf{r}, \mathbf{r}') - \frac{1}{4} \nabla^2 \frac{\partial}{\partial r_\alpha} n(\mathbf{r}) \\
 + 2 \sum_\beta \frac{\partial}{\partial r_\beta} t_{\alpha\beta}(\mathbf{r}; [\rho]) = 0.
 \end{aligned} \tag{165}$$

No assumptions concerning potentials $u(\mathbf{r}, \mathbf{r}')$ and $v(\mathbf{r})$ (like Coulombic character), unless they lead to bounded solutions Ψ of the Schrödinger equation [see Eqs. (10)–(12)]

$$(\hat{\mathcal{T}} + \hat{\mathcal{U}} + \hat{\mathcal{V}})\Psi = E\Psi, \tag{166}$$

were involved in obtaining the relation (165). The reduced DMs occurring in Eq. (165): $n_2(\mathbf{r}, \mathbf{r}')$, $\rho(\mathbf{r}; \mathbf{r}')$ and $n(\mathbf{r})$ are generated from the normalized Ψ by applying a reduction of $\gamma_N = \Psi\Psi^*$ [see Appendix A, Eqs. (265)–(270)]. It should be mentioned also, that no assumption concerning the nature (as GS or excited-state) of the solution Ψ or a degeneracy of its energy level E were invoked. The number N of the system electrons does not appear explicitly in Eq. (165). Furthermore, this equation is linear in DMs. All together, this leads to the conclusion, that the theorem remains true if each DM ρ_ℓ is replaced by a “mixture” of pure-state matrices $\rho_\ell^{(N\lambda)}$:

$$\rho_\ell = \sum_{N\lambda} p_{N\lambda} \rho_\ell^{(N\lambda)} \tag{167}$$

where the probabilities $p_{N\lambda}$ satisfy conditions

$$0 \leq p_{N\lambda} \leq 1, \quad \sum_{N\lambda} p_{N\lambda} = 1, \tag{168}$$

and where the index N denotes the (integer) number of electrons in a pure system, while λ denotes a set of quantum numbers, characterizing its particular eigenstate. In this way Eq. (165) may be applied to ensembles with a noninteger average number of electrons, with a degenerate GS and in many other circumstances.

From the differential virial theorem (165) for interacting electron systems one can obtain immediately an analogous theorem for noninteracting systems, just by putting $u \equiv 0$ and replacing the external potential $v(\mathbf{r})$ with $v_s(\mathbf{r})$:

$$n^s(\mathbf{r}) \frac{\partial}{\partial r_\alpha} v_s(\mathbf{r}) - \frac{1}{4} \nabla^2 \frac{\partial}{\partial r_\alpha} n^s(\mathbf{r}) + 2 \sum_\beta \frac{\partial}{\partial r_\beta} t_{\alpha\beta}(\mathbf{r}; [\rho^s]) = 0. \tag{169}$$

This equation relates the single-particle external potential $v_s(\mathbf{r})$, the 1st order DM $\rho^s(\mathbf{r}_1; \mathbf{r}_2)$ and its diagonal element $n^s(\mathbf{r})$ for a noninteracting system. As previously, this matrix can describe a mixed-state system also, thus having the ensemble DM form (143) with (145) in terms of single-particle (e.g. KS) orbitals $\phi_{j\sigma}(\mathbf{r})$ and occupation numbers $f_{j\sigma}$ [Eq. (147)].

The differential virial theorem (169) for noninteracting systems can alternatively be obtained [31], [32] by summing (with the weights $f_{j\sigma}$) similar relations obtained for separate eigenfunctions $\phi_{j\sigma}(\mathbf{r})$ of the one-electron Schrödinger equation (40) [in particular the KS equation (50)]. Just in that way one can obtain, from the one-electron HF equations (33), the differential virial theorem for the HF (approximate) solution of the GS problem, as is shown in Appendix B, Eq. (302), in a form:

$$\begin{aligned} n^{\text{HF}}(\mathbf{r}) \frac{\partial}{\partial r_\alpha} v(\mathbf{r}) + 2 \int d^3 r' n_2^{\text{HF}}(\mathbf{r}, \mathbf{r}') \frac{\partial}{\partial r_\alpha} u(\mathbf{r}, \mathbf{r}') - \frac{1}{4} \nabla^2 \frac{\partial}{\partial r_\alpha} n^{\text{HF}}(\mathbf{r}) \\ + 2 \sum_\beta \frac{\partial}{\partial r_\beta} t_{\alpha\beta}(\mathbf{r}; [\rho^{\text{HF}}]) = 0. \end{aligned} \quad (170)$$

Here $n_2^{\text{HF}}(\mathbf{r}, \mathbf{r}')$, $\rho^{\text{HF}}(\mathbf{r}; \mathbf{r}')$ and $n^{\text{HF}}(\mathbf{r})$ denote the reduced DMs generated from the GS HF determinantal wave function $\Psi_{\text{GS}}^{\text{HF}}$, Eq. (25), in terms of the self-consistent solutions $\psi_j(\mathbf{x})$ of the HF equations (33) (see appendix A for details). It is surprising that, despite the approximate (in the sense of the HF method) character of these DMs n_2^{HF} , ρ^{HF} and n^{HF} for a given system, they satisfy the same relation with $v(\mathbf{r})$ and $u(\mathbf{r}, \mathbf{r}')$ as the exact DMs n_2 , ρ and n do [compare Eq. (170) with Eq. (165)].

Many interesting integral relations may be deduced from the differential virial theorem, allowing us to check the accuracy of various characteristics and functionals concerning a particular system (for noninteracting systems see e.g. in [31] and [32]). As an example, let us derive here the global virial theorem. Applying the operation $\int d^3 r \sum_\alpha r_\alpha$ to Eq. (165), we obtain

$$2T = \int d^3 r n(\mathbf{r}) \mathbf{r} \cdot \nabla v(\mathbf{r}) + 2 \int d^3 r d^3 r' n_2(\mathbf{r}, \mathbf{r}') \mathbf{r} \cdot \nabla u(\mathbf{r}, \mathbf{r}') \quad (171)$$

[Eqs. (163) and (164) have been used]. Eq. (171) represents the virial theorem in its most general form (see e.g. in Levy and Perdew [33]). In the case of Coulombic $u(\mathbf{r}, \mathbf{r}')$, Eq. (11), the second integral in Eq. (171) can be evaluated, using the symmetry of n_2 , to be $-E_{ee}$. So, in this case, Eq. (171) gives

$$2T + E_{ee} = \int d^3 r n(\mathbf{r}) \mathbf{r} \cdot \nabla v(\mathbf{r}) \quad (172)$$

– the familiar virial theorem for a Coulombically interacting system.

5.2 Force Equations

The differential virial theorems (165), (170) and (169), can be rewritten as

$$\nabla v(\mathbf{r}) = -\mathbf{f}(\mathbf{r}; [u, n, \rho, n_2]), \quad (173)$$

$$\nabla v(\mathbf{r}) = -\mathbf{f}(\mathbf{r}; [u, n^{\text{HF}}, \rho^{\text{HF}}, n_2^{\text{HF}}]), \quad (174)$$

$$\nabla v_s(\mathbf{r}) = -\mathbf{f}_s(\mathbf{r}; [n^s, \rho^s]), \quad (175)$$

where the following “force” fields are introduced

$$f(\mathbf{r}; [u, n, \rho, n_2]) = \left\{ -\frac{1}{4} \nabla \nabla^2 n(\mathbf{r}) + \mathbf{z}(\mathbf{r}; [\rho]) + 2 \int d^3 r' n_2(\mathbf{r}, \mathbf{r}') \nabla u(\mathbf{r}, \mathbf{r}') \right\} / n(\mathbf{r}), \quad (176)$$

$$f_s(\mathbf{r}; [n^s, \rho^s]) = f(\mathbf{r}; [0, n^s, \rho^s, 0]) = \left\{ -\frac{1}{4} \nabla \nabla^2 n^s(\mathbf{r}) + \mathbf{z}(\mathbf{r}; [\rho^s]) \right\} / n^s(\mathbf{r}), \quad (177)$$

with the vector field [see Eq. (162)]

$$z_\alpha(\mathbf{r}; [\rho]) = 2 \sum_\beta \frac{\partial}{\partial r_\beta} t_{\alpha\beta}(\mathbf{r}; [\rho]). \quad (178)$$

Eqs. (173)–(175) offer an interesting possibility to analyze in 3 dimensions only (instead of $3N$ dimensions) the inaccuracies of any approximate solution for the N -electron eigenfunction Ψ by asking, what is the actual external potential which would lead to Ψ as its exact solution. The gradient of this potential may be calculated in terms of the low-order DMs, generated from this Ψ , as the left hand side of Eqs. (173)–(175) and compared then with the gradient of the original external potential used for calculations. In particular, the quality of a solution in sensitive regions, such as those close to nuclei, at interatomic bonds or at large distances, is easy to visualize. The analysis discussed may be applied to full interacting problem solutions, Eq. (173), (e.g. from configuration interaction or Hylleraas type calculations), to HF method solutions, Eq. (174), and to KS or OP method solutions, Eq. (175).

5.3 Exact Expression for the Exchange-Correlation Potential, Applicable to Mixed-State Systems

Equation (173) may be viewed as a differential equation for the potential $v(\mathbf{r})$. Because $\mathbf{f}(\mathbf{r}) = -\nabla v(\mathbf{r})$, the force field $\mathbf{f}(\mathbf{r})$ is conservative. Therefore, it follows that the potential at point $\mathbf{r}_0$, say, is the work done in bringing an electron from infinity to $\mathbf{r}_0$ against the force field $\mathbf{f}(\mathbf{r})$:

$$v(\mathbf{r}_0) = - \int_{\infty}^{\mathbf{r}_0} d\mathbf{r} \cdot \mathbf{f}(\mathbf{r}). \quad (179)$$

Since $\mathbf{f}(\mathbf{r})$ is conservative, the value of the line integral in Eq. (179) does not depend on the path of integration chosen. Note that Eq. (179) has been written such that $v(\infty) = 0$: a standard choice of gauge for the potential. Eq. (179) may be used for the analysis, mentioned in the previous subsection, of approximate solutions, to be performed now in terms of the potential itself, rather than its gradient.

Using Eqs. (173) and (175), we are going to find an equation for the gradient of the exchange-correlation potential of the KS approach (the results of our investigation [30] will be recalled and generalized). Since these equations hold

for mixed-state systems (for interacting and noninteracting cases, respectively), it is worthwhile to extend the definition (45) of $E_{xc}[n]$ to mixed-state systems, by considering $F^{\text{HK}}[n]$ and $T^{\text{KS}}[n] \equiv T_s[n]$ to be defined for such systems. For that reason, minimizations (15) and (35) of $\langle \hat{\mathcal{T}} + \hat{\mathcal{U}} \rangle$ and $\langle \hat{\mathcal{T}} \rangle$ should be replaced by minimizations

$$F^{\text{HK}}[n] = \inf_{\hat{\mathcal{D}} \rightarrow n} \text{Tr} \{ \hat{\mathcal{D}} (\hat{\mathcal{T}} + \hat{\mathcal{U}}) \} = \text{Tr} \{ \hat{\mathcal{D}}^{\text{HK}}[n] (\hat{\mathcal{T}} + \hat{\mathcal{U}}) \}, \quad (180)$$

$$T^{\text{KS}}[n] = \inf_{\hat{\mathcal{D}} \rightarrow n} \text{Tr} \{ \hat{\mathcal{D}} \hat{\mathcal{T}} \} = \text{Tr} \{ \hat{\mathcal{D}}^{\text{KS}}[n] \hat{\mathcal{T}} \}, \quad (181)$$

over such ensemble density operators $\hat{\mathcal{D}}$, which yield the prescribed density $n(\mathbf{r})$ via

$$n(\mathbf{r}) = \text{Tr} \{ \hat{\mathcal{D}} \hat{n}(\mathbf{r}) \}. \quad (182)$$

The operators $\hat{\mathcal{T}}, \hat{\mathcal{U}}, \hat{n}$, occurring above, should be taken in the second-quantization form, free of explicit dependence on particle number, and “Tr” means the trace in Fock space (see e.g. [10] for details). Problems of existence and functional differentiability of generalized functionals $F^{\text{HK}}[n]$ and $T^{\text{KS}}[n]$ are discussed in [28]; the functional $F^{\text{HK}}[n]$ is denoted there as $F_L[n]$ or $F_{\text{frac}}[n]$ or $\tilde{F}_{\text{frac}}[n]$ (depending on the scope of $\hat{\mathcal{D}}$), similarly for $T^{\text{KS}}[n]$. Note that DMs can be viewed as the coordinate representation of the density operators.

By requiring the density $n^{\text{KS}}(\mathbf{r})$ of the equivalent noninteracting system of the KS method to be the same as the density $n^{\text{HK}}(\mathbf{r})$ of the original interacting system described by the HK formalism: $n^{\text{KS}}(\mathbf{r}) = n^{\text{HK}}(\mathbf{r}) = n(\mathbf{r})$, the KS potential of the former system is given in Eq. (51), where $v_{xc}(\mathbf{r}; [n])$, defined in Eq. (52), corresponds to $E_{xc}[n]$, generalized above for mixed-state systems to be:

$$E_{xc}[n] = \text{Tr} \{ \hat{\mathcal{D}}^{\text{HK}}[n] (\hat{\mathcal{T}} + \hat{\mathcal{U}}) \} - \text{Tr} \{ \hat{\mathcal{D}}^{\text{KS}}[n] \hat{\mathcal{T}} \} - E_{\text{es}}[n]. \quad (183)$$

So, keeping in mind the decomposition (51) of $v_s(\mathbf{r}) \equiv v_{\text{KS}}(\mathbf{r}; [n])$, we subtract Eq. (173) from Eq. (175) to obtain

$$V(v_{\text{es}}(\mathbf{r}) + v_{xc}(\mathbf{r})) = f(\mathbf{r}; [u, n, \rho, n_2]) - f_s(\mathbf{r}; [n, \rho^{\text{KS}}]) \quad (184)$$

where $\rho^{\text{KS}}(\mathbf{r}; \mathbf{r}')$ is the first-order DM constructed, with the help of Eqs. (143) and (145), of KS orbitals $\phi_{j\sigma}^{\text{KS}}$ – the solutions of the KS equation (50), and the corresponding density $n(\mathbf{r}) = n^{\text{KS}}(\mathbf{r})$ – with the help of Eqs. (144) and (146). But, using Eq. (34), we have

$$\mathbf{V}v_{\text{es}}(\mathbf{r}) = \int d^3r' n(\mathbf{r}') \mathbf{V}u(\mathbf{r}, \mathbf{r}'). \quad (185)$$

After subtracting Eq. (185) from Eq. (184) we arrive finally at the result

$$\mathbf{V}v_{xc}(\mathbf{r}) = -f_{xc}(\mathbf{r}; [u, n, \rho^{\text{KS}}, \rho, n_2]) \quad (186)$$

with

$$\begin{aligned} f_{xc}(\mathbf{r}; [u, n, \rho^{\text{KS}}, \rho, n_2]) &= \{z(\mathbf{r}; [\rho^{\text{KS}}]) - z(\mathbf{r}; [\rho])\} + \int d^3r' \left(\mathbf{V}u(\mathbf{r}, \mathbf{r}') \right) \\ &\quad \times \left(n(\mathbf{r})n(\mathbf{r}') - 2n_2(\mathbf{r}, \mathbf{r}') \right) / n(\mathbf{r}) \end{aligned} \quad (187)$$

(see Eq. (178) for the definition of $\mathbf{z}$). The force field $\mathbf{f}_{\text{xc}}(\mathbf{r})$ is conservative because it stems from the potential $v_{\text{xc}}(\mathbf{r})$, i.e. $\mathbf{f}_{\text{xc}}(\mathbf{r}) = -\nabla v_{\text{xc}}(\mathbf{r})$. Therefore, in complete analogy with Eq. (179) we have

$$v_{\text{xc}}(\mathbf{r}_0) = v_{\text{xc}}(\mathbf{r}_0; [n]) = - \int_{\infty}^{\mathbf{r}_0} d\mathbf{r} \cdot \mathbf{f}_{\text{xc}}(\mathbf{r}; [u, n, \rho^{\text{KS}}, \rho, n_2]), \quad (188)$$

where again the above line integral is independent of the particular path chosen for integration. The DMs n_2 , ρ and ρ^{KS} are functionals of n , as obtained from the density operators $\hat{\mathcal{D}}^{\text{HK}}[n]$ and $\hat{\mathcal{D}}^{\text{KS}}[n]$, Eqs. (180) and (181), in the form $\text{Tr}\{\hat{\mathcal{D}}^{\text{HK}}\hat{n}_2\}$, $\text{Tr}\{\hat{\mathcal{D}}^{\text{HK}}\hat{\rho}_1\}$ and $\text{Tr}\{\hat{\mathcal{D}}^{\text{KS}}\hat{\rho}_1\}$.

Eq. (188) represents an exact expression for $v_{\text{xc}}(\mathbf{r})$ in terms of objects written explicitly as arguments of $\mathbf{f}_{\text{xc}}$. Our construction of v_{xc} covers such mixed-state situations as e.g. a degenerate GS, a fractional particle number, a mixture of the GS and excited states.

By applying all above considerations to the HF method posed as the DFT in Section 2.4, where the equivalent noninteracting electron problem leads to the HF-KS equations (70), we obtain from Eqs. (174) and (175)

$$\begin{aligned} v_{\text{xc}}^{\text{HF}}(\mathbf{r}_0; [n^{\text{HF}}]) &= v_{\text{x}}(\mathbf{r}_0; [n^{\text{HF}}]) + v_{\text{c}}^{\text{HF}}(\mathbf{r}_0; [n^{\text{HF}}]) \\ &= - \int_{\infty}^{\mathbf{r}_0} d\mathbf{r} \cdot \mathbf{f}_{\text{xc}}(\mathbf{r}; [u, n^{\text{HF}}, \rho_{\text{KS}}^{\text{HF}}, \rho^{\text{HF}}, n_2^{\text{HF}}]), \end{aligned} \quad (189)$$

where n^{HF} , ρ^{HF} and n_2^{HF} are constructed of the HF orbitals ψ_i [the solutions of the HF equations (33)] while $\rho_{\text{KS}}^{\text{HF}}$ is constructed of the HF-KS orbitals ϕ_i^{HF} [the solutions of the HF-KS equations (70)]; the densities are identical: $n_{\text{KS}}^{\text{HF}}(\mathbf{r}) = n^{\text{HF}}(\mathbf{r})$. Eq. (189) represents an exact expression for the exchange-correlation potential $v_{\text{xc}}^{\text{HF}}(\mathbf{r}; [n^{\text{HF}}])$, Eqs. (57) and (71), occurring in the HF-KS theory (Sect. 2.4).

5.4 Expressions for the Exchange and Correlation Energy of Mixed-State Systems

We can generalize the partitioning (53) of the exchange-correlation energy for a pure-state system to an analogous partitioning for a mixed-state system, by adopting the following generalization of Eq. (54) for the exchange energy

$$E_{\text{x}}[n] \equiv E_{\text{x}}^{\text{KS}}[n] = \text{Tr}\{\hat{\mathcal{D}}^{\text{KS}}[n]\hat{\mathcal{U}}\} - E_{\text{es}}[n] = E_{\text{ee}}^{\text{KS}}[n] - E_{\text{es}}[n], \quad (190)$$

where the ensemble density operator $\hat{\mathcal{D}}^{\text{KS}}[n]$ is a minimizer in Eq. (181). Then Eq. (58), defining the correlation energy, is generalized to

$$\begin{aligned} E_{\text{c}}[n] &\equiv E_{\text{c}}^{\text{KS}}[n] = E_{\text{xc}}[n] - E_{\text{x}}[n] \\ &= \text{Tr}\{(\hat{\mathcal{D}}^{\text{HK}}[n] - \hat{\mathcal{D}}^{\text{KS}}[n])\hat{\mathcal{T}}\} + \text{Tr}\{(\hat{\mathcal{D}}^{\text{HK}}[n] - \hat{\mathcal{D}}^{\text{KS}}[n])\hat{\mathcal{U}}\} \\ &= T_{\text{c}}^{\text{KS}}[n] + U_{\text{c}}^{\text{KS}}[n], \end{aligned} \quad (191)$$

where the ensemble density operator $\hat{\mathcal{D}}^{\text{HK}}[n]$ is a minimizer in Eq. (180).

The exchange energy $E_x[n]$ and the components $T_c^{\text{KS}}[n]$ and $U_c^{\text{KS}}[n]$ of the correlation energy written in terms of the ensemble DMs, corresponding to the above density operators, are

$$E_x[n] = \int d^3r d^3r' u(r, r') \{n_2^{\text{KS}}(r, r') - \frac{1}{2} n(r) n(r')\}, \quad (192)$$

$$\begin{aligned} T_c[n] &= T^{\text{HK}}[n] - T^{\text{KS}}[n] \\ &= \tilde{T}[\rho^{\text{HK}} - \rho^{\text{KS}}] = \int d^3r \sum_{\alpha} t_{\alpha\alpha}(r; [\rho^{\text{HK}} - \rho^{\text{KS}}]), \end{aligned} \quad (193)$$

$$U_c[n] = E_{\text{ee}}^{\text{HK}}[n] - E_{\text{ee}}^{\text{KS}}[n] = \int d^3r d^3r' u(r, r') \{n_2^{\text{HK}}(r, r') - n_2^{\text{KS}}(r, r')\}. \quad (194)$$

In order to have an expression for the mixed-system exchange energy (192) in terms of the single-particle KS orbitals $\phi_{j\sigma}(r)$, we need such an expression for the ensemble DM n_2^{KS} – the diagonal of ρ_2^{KS} . When the ensemble density operator $\hat{\mathcal{D}}^{\text{KS}}[n]$ is characterized by the following decomposition into its pure-state contributions

$$\hat{\mathcal{D}}^{\text{KS}}[n] = \sum_{N\lambda} p_{N\lambda}^{\text{KS}} \hat{\mathcal{D}}_{\text{KS}}^{(N\lambda)}[n], \quad (195)$$

then analogous decomposition holds for DMs. In particular

$$\rho_2^{\text{KS}}(r; r') = \sum_{N\lambda} p_{N\lambda}^{\text{KS}} \rho_{\text{KS}, 2}^{(N\lambda)}(r; r'), \quad (196)$$

[comp. Eqs. (167) and (168)]. Because $\rho_{\text{KS}, 2}^{(N\lambda)}$ of Eq. (196) is a pure-state second-order DM of a noninteracting system, it can be written (see Appendix A) in terms of the first-order spin-polarized idempotent DMs

$$\rho_{\sigma}^{(N\lambda)}(r; r') = \sum_j \theta_{j\sigma}^{(N\lambda)} \phi_{j\sigma}(r) \phi_{j\sigma}^*(r'), \quad (197)$$

with occupation numbers

$$\theta_{j\sigma}^{(N\lambda)} = 0 \text{ or } 1; \quad \sum_j \theta_{j\sigma}^{(N\lambda)} = N_{\sigma}^{(N\lambda)}; \quad N_{\uparrow}^{(N\lambda)} + N_{\downarrow}^{(N\lambda)} = N, \quad (198)$$

where $N_{\sigma}^{(N\lambda)}$ and N are integers. According to Eqs. (280) and (281) we have for the pure-state DM

$$\begin{aligned} n_{\text{KS}, 2}^{(N\lambda)}(r, r') &= \frac{1}{2} \left\{ \sum_{\sigma} \rho_{\sigma}^{(N\lambda)}(r; r) \right\} \left\{ \sum_{\sigma'} \rho_{\sigma'}^{(N\lambda)}(r'; r') \right\} \\ &\quad - \frac{1}{2} \{ |\rho_{\uparrow}^{(N\lambda)}(r; r')|^2 + |\rho_{\downarrow}^{(N\lambda)}(r; r')|^2 \}. \end{aligned} \quad (199)$$

Therefore the ensemble DMs n_2^{KS} and ρ^{KS} for a mixed system described by Eq. (195) are

$$n_2^{\text{KS}}(r, r') = \sum_{N\lambda} p_{N\lambda}^{\text{KS}} n_{\text{KS}, 2}^{(N\lambda)}(r, r'), \quad (200)$$

$$\rho^{\text{KS}}(r; r') = \sum_{N\lambda} p_{N\lambda}^{\text{KS}} \rho_{\text{KS}}^{(N\lambda)}(r; r'), \quad (201)$$

where [see (197)]

$$\rho_{\mathbf{KS}}^{(N\lambda)}(\mathbf{r}; \mathbf{r}') = \sum_{\sigma} \rho_{\sigma}^{(N\lambda)}(\mathbf{r}; \mathbf{r}'). \quad (202)$$

Alternative forms of the ensemble DMs $\rho^{\mathbf{KS}} \equiv \rho$ and $\rho_{\sigma}^{\mathbf{KS}} \equiv \rho_{\sigma}^{\text{ens}}$ are given by Eq. (143) and Eq. (145) with the occupations

$$f_{j\sigma} = \sum_{N\lambda} p_{N\lambda}^{\mathbf{KS}} \theta_{j\sigma}^{(N\lambda)}, \quad (203)$$

and of the ensemble density $n(\mathbf{r})$ by Eq. (144) with (146).

Thus, the mixed-state exchange energy (192) in terms of orbitals is

$$E_x = E_x^{\mathbf{KS}} = \int d^3r d^3r' u(\mathbf{r}, \mathbf{r}') \{q_{\uparrow}(\mathbf{r}, \mathbf{r}') + q_{\downarrow}(\mathbf{r}, \mathbf{r}') + q_{\uparrow\downarrow}(\mathbf{r}, \mathbf{r}')\}, \quad (204)$$

where

$$\begin{aligned} q_{\sigma}(\mathbf{r}, \mathbf{r}') &= -\frac{1}{2} \sum_{jj'} F_{\sigma jj'} \phi_{j\sigma}(\mathbf{r}) \phi_{j\sigma}^*(\mathbf{r}') \phi_{j'\sigma}(\mathbf{r}') \phi_{j'\sigma}^*(\mathbf{r}) \\ &\quad + \frac{1}{2} \sum_{jj'} G_{\sigma \sigma' jj'} |\phi_{j\sigma}(\mathbf{r})|^2 |\phi_{j'\sigma}(\mathbf{r}')|^2, \end{aligned} \quad (205)$$

$$q_{\uparrow\downarrow}(\mathbf{r}, \mathbf{r}') = \sum_{jj'} G_{\uparrow\downarrow jj'} |\phi_{j\uparrow}(\mathbf{r})|^2 |\phi_{j'\downarrow}(\mathbf{r}')|^2, \quad (206)$$

with

$$F_{\sigma jj'} = \sum_{N\lambda} p_{N\lambda}^{\mathbf{KS}} \theta_{j\sigma}^{(N\lambda)} \theta_{j'\sigma}^{(N\lambda)}, \quad (207)$$

$$G_{\sigma \sigma' jj'} = \sum_{N\lambda} p_{N\lambda}^{\mathbf{KS}} \theta_{j\sigma}^{(N\lambda)} \theta_{j'\sigma'}^{(N\lambda)} - f_{j\sigma} f_{j'\sigma'}, \quad (208)$$

[see Eq. (203) for $f_{j\sigma}$]. The contribution to E_x in (204), in a form of the sum of all terms having $G_{\sigma \sigma' jj'}$ as coefficients, represents a difference between the weighted sum of electrostatic-type energies of pure-state subsystems and the global electrostatic energy, present in the definition (190). We note that, contrary to the pure-state case in Eq. (135), the exchange between opposite spin electrons too takes place in the mixed-state system, due to the $q_{\uparrow\downarrow}$ term in Eq. (204). The approximate expression (149) for the mixed-state system exchange energy, discussed in Sect. 4.4, corresponds to $F_{\sigma jj'}$ replaced by $f_{j\sigma} f_{j'\sigma}$ and $G_{\sigma \sigma' jj'}$ replaced by 0 in Eqs. (205) and (206).

Concerning the separation of the exchange energy E_x from the total exchange-correlation energy

$$E_{xc}[n] = E_x[n] + (T_c^{\mathbf{KS}}[n] + U_c^{\mathbf{KS}}[n]), \quad (209)$$

we see that, in order to obtain E_x alone, it is enough to neglect the differences between the interacting-system DMs and corresponding KS (equivalent non-interacting-system) DMs in the expression for E_{xc} , i.e. to neglect $(\rho - \rho^{\mathbf{KS}})$ in the expression (193) for $T_c^{\mathbf{KS}}$, and $(n_2 - n_2^{\mathbf{KS}})$ in the expression (194) for $U_c^{\mathbf{KS}}$.

5.5 Approximate Expression for the Exchange Potential

Now we adopt the above observation, concerning E_{xc} and E_x , in order to split the exact expression for v_{xc} in Eq. (188) into the sum of v_x^{app} and v_c^{app} ; interpreting these terms as approximate exchange potential and approximate correlation potential, respectively. Thus

$$\begin{aligned} v_{xc}(\mathbf{r}_0; [n]) &= v_x^{app}(\mathbf{r}_0; [n]) + v_c^{app}(\mathbf{r}_0; [n]) \\ &= - \int_{\infty}^{r_0} d\mathbf{r} \cdot \mathbf{f}_x(\mathbf{r}) - \int_{\infty}^{r_0} d\mathbf{r} \cdot \mathbf{f}_c(\mathbf{r}), \end{aligned} \quad (210)$$

where the force fields are given by

$$\begin{aligned} \mathbf{f}_x(\mathbf{r}) &= \mathbf{f}_x(\mathbf{r}; [u, n, n_2^{KS}]) \\ &= - \{ 2 \int d^3r' [\nabla u(\mathbf{r}, \mathbf{r}')] [n_2^{KS}(\mathbf{r}, \mathbf{r}') - \frac{1}{2}n(\mathbf{r})n(\mathbf{r}')] \} / n(\mathbf{r}), \\ \mathbf{f}_c(\mathbf{r}) &= \mathbf{f}_c(\mathbf{r}; [u, n, \rho - \rho^{KS}, n_2 - n_2^{KS}]) \\ &= - \{ \mathbf{z}(\mathbf{r}; [\rho - \rho^{KS}]) + 2 \int d^3r' [\nabla u(\mathbf{r}, \mathbf{r}')] [n_2(\mathbf{r}, \mathbf{r}') - n_2^{KS}(\mathbf{r}, \mathbf{r}')] \} / n(\mathbf{r}). \end{aligned} \quad (211)$$

Although we know that the total force field $\mathbf{f}_{xc}$ is conservative, we lack such knowledge concerning the separate pieces $\mathbf{f}_x$ or $\mathbf{f}_c$. Therefore some specific path of integration must be chosen to complete the definition (210). Seemingly the most natural path is along the radius on which the point $\mathbf{r}_0$ lies. As the center of the coordinate system a position of the nucleus is chosen in the case of single-ion system, the center of symmetry for a symmetrical molecule, and some ‘inner’ point for molecule or cluster with lower symmetry. Then

$$v_x^{app}(\mathbf{r}_0; [n]) = \int_{r_0}^{\infty} d\mathbf{r} \cdot \mathbf{e} \cdot \mathbf{f}_x(\mathbf{r}\mathbf{e}); \quad \mathbf{e} = \mathbf{r}_0/r_0. \quad (213)$$

The same path must be used for the calculation of v_c^{app} in order to leave the sum v_{xc} unchanged.

Using the separation of the pair-distribution function n_2^{KS} into its uncorrelated and correlated parts, Eq. (284), and noting that the combination

$$\rho_x(\mathbf{r}_1, \mathbf{r}_2) = h_2^{KS}(\mathbf{r}_1, \mathbf{r}_2)n(\mathbf{r}_2) \quad (214)$$

is customarily called the exchange hole at $\mathbf{r}_2$ of an electron at $\mathbf{r}_1$, we rewrite Eq. (211) as

$$\mathbf{f}_x(\mathbf{r}) = - \int d^3r' \rho_x(\mathbf{r}, \mathbf{r}') \nabla u(\mathbf{r}, \mathbf{r}'). \quad (215)$$

For the case of Coulombic $u(\mathbf{r}, \mathbf{r}')$, as in Eq. (11), Eq. (215) leads to

$$\mathbf{f}_x(\mathbf{r}) = \int d^3r' \rho_x(\mathbf{r}, \mathbf{r}') \frac{(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3}. \quad (216)$$

We recognize $\mathbf{f}_x(\mathbf{r})$, given by Eq. (216), to be identical with the force field $\mathcal{E}_x(\mathbf{r})$

proposed by Harbola and Sahni [34] (in their exchange-only version). This means that our approximation $v_x^{\text{app}}(\mathbf{r})$ to the exact $v_x(\mathbf{r})$ coincides with the Harbola-Sahni approximation. Since these two approximations were derived by using completely different reasoning, their coincidence strongly enhances expectation that this function is very close to the exact $v_x(\mathbf{r})$. See [35] for the latest review of the Harbola-Sahni work formalism approach to the theory of electronic structure.

The line-integral approximation $v_x^{\text{app}}(\mathbf{r}; [n])$, Eq. (213) with (211) or (216), to the exact $v_x(\mathbf{r}; [n])$ seems to be especially accurate. First of all, its asymptotic behavior for pure-state systems is the same as the behavior of the exact v_x in Eq. (134), therefore guaranteeing the proper asymptotic form of KS orbitals. Next, it satisfies exactly the Levy-Perdew [33] identity

$$E_x[n] = - \int d^3r n(\mathbf{r}) \mathbf{r} \cdot \nabla v_x(\mathbf{r}; [n]), \quad (217)$$

and the scaling identity

$$v_x(\mathbf{r}; [n_\lambda]) = \lambda v_x(\lambda \mathbf{r}; [n]), \quad (218)$$

where the scaled density is defined as $n_\lambda(\mathbf{r}) = \lambda^3 n(\lambda \mathbf{r})$. All three issues were discussed in [30]. Extensive numerical investigations, for various atomic systems, of $v_x^{\text{app}}(\mathbf{r})$ understood as the Harbola-Sahni exchange-only potential (see [35] and references therein), demonstrate that it is very close to the exact $v_x(\mathbf{r})$, reconstructed by means of OP methods. Therefore this approximation for the exchange potential, when used within the KS equations together with some available approximation for the correlation potential, should lead to a very accurate GS density and energy. It is worth noting about such scheme that: (i) it may be applied for various mixed-state problems (see Sect. 5.4), (ii) both E_x and v_x^{app} are expressible [via $n_2^{\text{KS}}(\mathbf{r}, \mathbf{r}')$ and $n(\mathbf{r})$, Eqs. (192) and (211)] in terms of KS orbitals and their occupation numbers (see Sect. 5.4) (iii) the form of the expressions mentioned indicates, that there is no need for a Coulomb self-energy correction (a serious difficulty in the case of other approximations to the exchange potential and energy).

The line-integral expression (189), for the exchange-correlation potential of the HF-KS approach in Sect. 2.4, offers an interesting way to reconstruct the exchange potential for a given system, from the known HF solution for this system. Being alternative to schemes discussed in Sect. 3, this method provides an expression for the exchange potential solely in terms of the HF orbitals in the form

$$\begin{aligned} v_x(\mathbf{r}_0; [n]) &\approx v_{xc}^{\text{HF}}(\mathbf{r}_0 = \mathbf{r}_0 \mathbf{e}; [n^{\text{HF}}]) \\ &\approx \int_{\mathbf{r}_0}^{\infty} d\mathbf{r} \mathbf{e} \cdot \mathbf{f}_{xc}(re; [u, n^{\text{HF}}, \rho^{\text{HF}}, \rho^{\text{HF}}, n_2^{\text{HF}}]), \end{aligned} \quad (219)$$

[the path along the radius, as in Eq. (213), is chosen]. Besides neglect of small terms of the order of $O([n - n^{\text{HF}}])$ (what is done also in all other schemes), here the difference between DMs ρ^{HF} and $\rho_{\text{KS}}^{\text{HF}}$ has been neglected, as compared with

the exact expression (189). In order to interpret this approximation, let us consider such replacement of $\rho_{\text{KS}}^{\text{HF}}$ by ρ^{HF} applied to

$$E_{\text{xc}}^{\text{HF}}[n^{\text{HF}}] = E_{\text{x}}[n^{\text{HF}}] + E_{\text{c}}^{\text{HF}}[n^{\text{HF}}], \quad (220)$$

expressed also in terms of $u, n^{\text{HF}}, \rho_{\text{KS}}^{\text{HF}}, \rho^{\text{HF}}, n_2^{\text{HF}}$. It would mean neglecting ΔT [the kinetic energy term of the HF correlation energy, Eqs. (69) and (72)] but retaining ΔE_{x} [the interaction energy term, Eq. (76)]. Because both ΔT and ΔE_{x} are very small [see Eqs. (84) and (85)], therefore Eq. (220) in the approximation discussed results in $E_{\text{x}}[n^{\text{HF}}]$ with high accuracy. By analogy, the line integral (219) is expected to give $v_{\text{x}}(\mathbf{r}_0; [n^{\text{HF}}])$ with high accuracy.

5.6 Alternative Formulation of the Kohn-Sham Approach Generalized for Mixed-State Systems

The traditional partitioning of the KS electron-electron interaction energy into the sum of the electrostatic and exchange energy is rooted in the fact, that the DM $n_2^{\text{KS}}(\mathbf{r}_1, \mathbf{r}_2) \equiv n_2^{\text{D}}(\mathbf{r}_1, \mathbf{r}_2)$, giving the electrostatic plus exchange contributions [comp. Eqs. (192) and (190)], splits for pure-state systems into $\frac{1}{2}n(\mathbf{r}_1)n(\mathbf{r}_2)$ and $-\frac{1}{2}\{|\rho_1(\mathbf{r}_1; \mathbf{r}_2)|^2 + |\rho_1(\mathbf{r}_1; \mathbf{r}_2)|^2\}$ [as is given by Eqs. (280) and (281)]. But there is no such natural splitting for the ensemble DM n_2^{KS} of a mixed-state origin. The resulting expression (204) for the exchange energy is quite complicated. Therefore it seems worthwhile to consider an alternative formulation of the KS approach, in which a sum of these two contributions is treated as a whole [comp. Eq. (190)]:

$$E_{\text{ee}}^{\text{KS}}[n] = \text{Tr}\{\hat{\mathcal{D}}^{\text{KS}}[n]\hat{\mathcal{U}}\} = \{E_{\text{es}}[n] + E_{\text{x}}[n]\}, \quad (221)$$

and, accordingly,

$$v_{\text{ee}}^{\text{KS}}(\mathbf{r}; [n]) = \frac{\delta E_{\text{ee}}^{\text{KS}}[n]}{\delta n(\mathbf{r})} = \{v_{\text{es}}(\mathbf{r}; [n]) + v_{\text{x}}(\mathbf{r}; [n])\}. \quad (222)$$

In the coordinate representation, Eq. (221) takes the form

$$E_{\text{ee}}^{\text{KS}}[n] = \tilde{E}_{\text{ee}}[n_2^{\text{KS}}] = \int d^3r d^3r' u(\mathbf{r}, \mathbf{r}') n_2^{\text{KS}}(\mathbf{r}, \mathbf{r}'), \quad (223)$$

and, using Eq. (200), the form

$$E_{\text{ee}}^{\text{KS}}[n] = \sum_{N\lambda} p_{N\lambda}^{\text{KS}} \tilde{E}_{\text{ee}}[n_{\text{KS},2}^{(N\lambda)}], \quad (224)$$

where $n_{\text{KS},2}^{(N\lambda)}$ is given in Eq. (199). This form of $n_{\text{KS},2}^{(N\lambda)}$ demonstrates a cancellation of the self-interaction terms for each pure-state subsystem separately.

The decomposition (224) of $E_{\text{ee}}^{\text{KS}}$ into its pure-state contributions allows us to find the long-range expansion of its functional derivative, using previous results

(118) and (134) obtained for pure-state systems:

$$\begin{aligned}\delta E_{ee}^{\text{KS}}[n] &= \sum_{N\lambda} p_{N\lambda}^{\text{KS}} \int d^3r \delta n_{\text{KS}}^{(N\lambda)}(\mathbf{r}) \left\{ \frac{\delta E_{\text{es}}[\bar{n}]}{\delta \bar{n}(\mathbf{r})} + \frac{\delta E_{\text{x}}[\bar{n}]}{\delta \bar{n}(\mathbf{r})} \right\} \Big|_{\bar{n}=n_{\text{KS}}^{(N\lambda)}} \\ &= \int d^3r \left\{ \frac{1}{r} + O\left(\frac{1}{r^2}\right) \right\} \sum_N (N-1) \sum_{\lambda} p_{N\lambda}^{\text{KS}} \delta n_{\text{KS}}^{(N\lambda)}(\mathbf{r}).\end{aligned}\quad (225)$$

According to Eq. (201), the variation of the density $n(\mathbf{r}) = \rho^{\text{KS}}(\mathbf{r}; \mathbf{r})$ is

$$\delta n(\mathbf{r}) = \sum_{N\lambda} p_{N\lambda}^{\text{KS}} \delta n_{\text{KS}}^{(N\lambda)}(\mathbf{r}). \quad (226)$$

Let us consider first the case of a system which is a mixture of pure states, including both GS solutions (many, if the GS energy is degenerate) and excited-state solutions, but having the same (integral) number N of electrons. As the summation over N is absent now, we recognize $\delta n(\mathbf{r})$ to be present in Eq. (225) and therefore find

$$\frac{\delta E_{ee}^{\text{KS}}[n]}{\delta n(\mathbf{r})} = \frac{N-1}{r} + O\left(\frac{1}{r^2}\right); \quad \text{at } (p_{N'\lambda}^{\text{KS}} = 0 \text{ for } N' \neq N). \quad (227)$$

This result for the considered class of mixed-state systems happens to be identical with the result for a pure-state system with the same number of electrons.

In order to handle the case of a system which is a mixture of pure states corresponding to various numbers of electrons, we must consider such large- r region, where the density is predominantly composed of the contributions due to the orbitals of the highest occupied energy level [see Eqs. (153)–(157)] with the occupations given by (203) because of the decomposition (197). Thus

$$\delta n_{\text{KS}}^{(N\lambda)}(\mathbf{r}) = \sum_{\sigma} \left\{ \sum_{m'} \theta_{m'\sigma}^{(N\lambda)} |C_{m'\sigma}|^2 \right\} 2\varphi_{m\sigma}(r) \delta\varphi_{m\sigma}(r), \quad \text{for } r > R_{\sigma}. \quad (228)$$

After substituting this expression into Eqs. (226) and (225) [and separating in the last equation the large- r region of integration, similarly as in Eq. (158)] we arrive at the following results:

(i) for the spin DFT, where $\varphi_{m\uparrow}(\mathbf{r}) \neq \varphi_{m\downarrow}(\mathbf{r})$, because of a spin-dependent KS potential:

$$\frac{\delta E_{ee}[n_{\uparrow}, n_{\downarrow}]}{\delta n_{\sigma}(\mathbf{r})} = \frac{\langle N \rangle_{m\sigma} - 1}{r}, \quad \text{for large } r, \quad (229)$$

where

$$\langle N \rangle_{m\sigma} = \left\{ \sum_N N \bar{p}_{N\sigma}^{\text{KS}} \right\} / \left\{ \sum_N \bar{p}_{N\sigma}^{\text{KS}} \right\}, \quad (230)$$

$$\bar{p}_{N\sigma}^{\text{KS}} = \sum_{\lambda} p_{N\lambda}^{\text{KS}} \sum_{m'} \theta_{m'\sigma}^{(N\lambda)} |C_{m'\sigma}|^2, \quad (231)$$

(ii) for the conventional DFT, where $\varphi_{m\uparrow}(\mathbf{r}) = \varphi_{m\downarrow}(\mathbf{r}) = \varphi_m(\mathbf{r})$, because of a spin-independent KS potential:

$$\frac{\delta E_{ee}[n]}{\delta n(\mathbf{r})} = \frac{\langle N \rangle_m - 1}{r}, \quad \text{for large } r, \quad (232)$$

where

$$\langle N \rangle_m = \left\{ \sum_N N \sum_{\sigma} \bar{p}_{Nm\sigma}^{\text{KS}} \right\} / \left\{ \sum_N \sum_{\sigma} \bar{p}_{Nm\sigma}^{\text{KS}} \right\}. \quad (233)$$

Results (229) and (232) can be also represented as a sum of the total electrostatic and total exchange contributions. For the first contribution we have [comp. Eq. (118)]

$$\frac{\delta E_{es}}{\delta n(\mathbf{r})} = \frac{\delta E_{es}}{\delta n_{\sigma}(\mathbf{r})} = \frac{\bar{N}}{r} + O\left(\frac{1}{r^2}\right), \quad (234)$$

where

$$\bar{N} = \int d^3r' n(\mathbf{r}') = \sum_{N\lambda} p_{N\lambda}^{\text{KS}} \int d^3r' n_{\text{KS}}^{(N\lambda)}(\mathbf{r}') = \sum_N N \sum_{\lambda} p_{N\lambda}^{\text{KS}}. \quad (235)$$

So

$$(i) \quad \frac{\delta E_x}{\delta n_{\sigma}(\mathbf{r})} = -\frac{A_{\sigma}}{r}; \quad (ii) \quad \frac{\delta E_x}{\delta n(\mathbf{r})} = -\frac{A}{r}; \quad \text{for large } r, \quad (236)$$

with

$$A_{\sigma} = 1 + \bar{N} - \langle N \rangle_{m\sigma}; \quad A = 1 + \bar{N} - \langle N \rangle_m. \quad (237)$$

We see that the coefficient A_{σ} obtained from the exact expression (224) for $E_{ee} = E_{es} + E_x$ is different from a_{σ} , Eq. (160), obtained from the approximate expression (149) for E_x .

The effective KS potential $v_{\text{KS}}(\mathbf{r}; [n])$ in the present formulation is

$$v_{\text{KS}}(\mathbf{r}; [n]) = v(\mathbf{r}) + v_{ee}^{\text{KS}}(\mathbf{r}; [n]) + v_c(\mathbf{r}; [n]), \quad (238)$$

which follows directly from Eqs. (51), (56) and (222). Eq. (184) can be rewritten as

$$\nabla(v_{ee}^{\text{KS}}(\mathbf{r}) + v_c(\mathbf{r})) = -\{f_{ee}(\mathbf{r}) + f_c(\mathbf{r})\}, \quad (239)$$

where

$$f_{ee}(\mathbf{r}) = f_{ee}(\mathbf{r}; [u, n, n_2^{\text{KS}}]) = -2\left\{ \int d^3r' (\nabla u(\mathbf{r}, \mathbf{r}')) n_2^{\text{KS}}(\mathbf{r}, \mathbf{r}') \right\} / n(\mathbf{r}), \quad (240)$$

and f_c is given by Eq. (212). From Eq. (239) the following exact expression for the “internal” potential term of v_{KS} [i.e. due to all (ee) interactions] is obtained

$$v_{ee}^{\text{KS}}(\mathbf{r}_0; [n]) + v_c(\mathbf{r}_0; [n]) = - \int_{\infty}^{r_0} d\mathbf{r} \cdot \{f_{ee}(\mathbf{r}) + f_c(\mathbf{r})\}, \quad (241)$$

valid for an arbitrary path of integration. Repeating arguments of the previous

subsection, it may be regarded as a sum of two approximate terms

$$v_{ee}^{\text{KS}}(\mathbf{r}_0; [n]) + v_c(\mathbf{r}_0; [n]) = v_{ee}^{\text{app}}(\mathbf{r}_0; [n]) + v_c^{\text{app}}(\mathbf{r}_0; [n]), \quad (242)$$

where

$$v_{ee}^{\text{app}}(\mathbf{r}_0 = r_0 \mathbf{e}; [n]) = \int_{r_0}^{\infty} dr \mathbf{e} \cdot \mathbf{f}_{ee}(r\mathbf{e}; [u, n, n_2^{\text{KS}}]), \quad (243)$$

$$v_c^{\text{app}}(\mathbf{r}_0 = r_0 \mathbf{e}; [n]) = \int_{r_0}^{\infty} dr \mathbf{e} \cdot \mathbf{f}_c(r\mathbf{e}; [u, n, \rho^{\text{HK}} - \rho^{\text{KS}}, n_2^{\text{HK}} - n_2^{\text{KS}}]). \quad (244)$$

In terms of the previously defined approximation (213) we have

$$v_{ee}^{\text{app}}(\mathbf{r}; [n]) = v_{es}(\mathbf{r}; [n]) + v_x^{\text{app}}(\mathbf{r}; [n]), \quad (245)$$

because the integration of the electrostatic contribution gives an exact result on an arbitrary path.

Similarly as in the case of the energy E_{ee}^{KS} in Eq. (224), the potential v_{ee}^{app} can be written as a sum of contributions connected with pure states because, with the help of Eqs. (200) and (240), the force of Eq. (243) has the form

$$\mathbf{f}_{ee}(\mathbf{r}; [u, n, n_2^{\text{KS}}]) = \sum_{N\lambda} p_{N\lambda}^{\text{KS}} \frac{n_{\text{KS}}^{(N\lambda)}(\mathbf{r})}{n(\mathbf{r})} \mathbf{f}_{ee}^{(N\lambda)}(\mathbf{r}), \quad (246)$$

where

$$\mathbf{f}_{ee}^{(N\lambda)}(\mathbf{r}) = \mathbf{f}_{ee}(\mathbf{r}; [u, n_{\text{KS}}^{(N\lambda)}, n_{\text{KS},2}^{(N\lambda)}]) \quad (247)$$

is the KS (ee) force due to the pure $N\lambda$ state alone. It is interesting to note that the weighting factor, present in the decomposition (246) of the force $\mathbf{f}_{ee}$ into its pure-state components, is a product of the probability $p_{N\lambda}^{\text{KS}}$ and the $\mathbf{r}$ -dependent ratio of densities $n_{\text{KS}}^{(N\lambda)}(\mathbf{r})/n(\mathbf{r})$. Because of this $\mathbf{r}$ -dependent factor, the approximate potential $v_{ee}^{\text{app}}(\mathbf{r})$, Eq. (243), cannot be equal to a weighted sum of corresponding potentials generated by pure-state subsystems.

In practice, the majority of KS calculations for pure-state systems is performed with $E_{ee}^{\text{KS}}[n]$ of Eq. (221) and $v_{ee}^{\text{KS}}(\mathbf{r}; [n])$ of Eq. (222) approximated by $E_{es}[n] + E_x^{\text{app}}[n]$ and by $v_{es}(\mathbf{r}; [n]) + v_x^{\text{app}}(\mathbf{r}; [n])$, where $E_x^{\text{app}}[n]$ denotes here a particular approximation to the exchange energy functional, e.g. in the local density form [fourth term in the TFD energy functional (1)] or some form of more sophisticated generalized gradient approximations, and the corresponding potential is $v_x^{\text{app}}(\mathbf{r}; [n]) = \delta E_x^{\text{app}}[n]/\delta n(\mathbf{r})$. The decompositions (224) and (246) suggest the following approximations for mixed-state systems, as analogues of the above-mentioned approximations:

$$E_{ee}^{\text{KS}}[n] \approx \sum_{N\lambda} p_{N\lambda}^{\text{KS}} \{E_{es}[n_{\text{KS}}^{(N\lambda)}] + E_x^{\text{app}}[n_{\text{KS}}^{(N\lambda)}]\}, \quad (248)$$

$$v_{ee}^{\text{KS}}(\mathbf{r}_0 = r_0 \mathbf{e}; [n]) \approx \int_{r_0}^{\infty} dr \mathbf{e} \cdot \mathbf{f}_{ee}^{\text{app}}(r\mathbf{e}), \quad (249)$$

where

$$f_{ee}^{\text{App}}(\mathbf{r}) = \sum_{N\lambda} p_{N\lambda}^{\text{KS}} \frac{n_{\text{KS}}^{(N\lambda)}(\mathbf{r})}{n(\mathbf{r})} (-V) \{v_{\text{es}}(\mathbf{r}; [n_{\text{KS}}^{(N\lambda)}]) + v_x^{\text{App}}(\mathbf{r}; [n_{\text{KS}}^{(N\lambda)}])\}. \quad (250)$$

5.7 Approximate Correlation Energy and Potential of Some Mixed Systems

The correlation energy of a mixed-state system is given by Eq. (191) with (193) and (194), where ρ^{KS} and n_2^{KS} are given by Eqs. (201) and (200), while ρ^{HK} and n_2^{HK} are

$$\rho^{\text{HK}}(\mathbf{r}; \mathbf{r}') = \sum_{N\lambda} p_{N\lambda}^{\text{HK}} \rho_{\text{HK}}^{(N\lambda)}(\mathbf{r}; \mathbf{r}'), \quad (251)$$

$$n_2^{\text{HK}}(\mathbf{r}, \mathbf{r}') = \sum_{N\lambda} p_{N\lambda}^{\text{HK}} n_{\text{HK},2}^{(N\lambda)}(\mathbf{r}, \mathbf{r}'), \quad (252)$$

as corresponding to the density operator $\hat{\mathcal{D}}^{\text{HK}}[n]$ of Eq. (180) decomposed as

$$\hat{\mathcal{D}}^{\text{HK}}[n] = \sum_{N\lambda} p_{N\lambda}^{\text{HK}} \hat{\mathcal{D}}_{\text{HK}}^{(N\lambda)}[n], \quad (253)$$

where λ denotes a set of quantum numbers characterizing a particular eigenstate $\Psi_{N\lambda}(\mathbf{x}_1, \dots, \mathbf{x}_N)$ of the interacting N electron system. Then $\rho_{\text{HK}}^{(N\lambda)}$ and $n_{\text{HK},2}^{(N\lambda)}$ are obtained by reduction of the N -th order DM $\gamma_{\text{HK},N}^{(N\lambda)} = \gamma_N = \Psi_{N\lambda} \Psi_{N\lambda}^*$ [see Eqs. (265)–(269) of Appendix A].

In some applications, such mixed-state systems may be of interest, for which their interacting and equivalent non-interacting pure-state systems are described by the same sets of quantum numbers, $\{\lambda\} \equiv \{\lambda\}$, and they are decomposed in Eqs. (253) and (195) with the same probabilities:

$$p_{N\lambda}^{\text{HK}} = p_{N\lambda}^{\text{KS}} \quad \text{for all } N\lambda. \quad (254)$$

Then the exact correlation energy has a form similar to (224), namely

$$E_c[n] = \sum_{N\lambda} p_{N\lambda}^{\text{KS}} E_c^{(N\lambda)}, \quad (255)$$

where

$$E_c^{(N\lambda)} = \tilde{T}[\rho_{\text{HK}}^{(N\lambda)} - \rho_{\text{KS}}^{(N\lambda)}] + \tilde{E}_{ee}[n_{\text{HK},2}^{(N\lambda)} - n_{\text{KS},2}^{(N\lambda)}] \quad (256)$$

is the correlation energy due to the pure $N\lambda$ state alone.

The decomposition (255) of the correlation energy [for mixed-state systems satisfying Eq. (254)] into its pure-state components suggests the following approximation for these systems

$$E_c \approx \sum_{N\lambda} p_{N\lambda}^{\text{KS}} E_c^{\text{App}}[n_{\text{KS}}^{(N\lambda)}], \quad (257)$$

in terms of any available approximation $E_c^{\text{App}}[n]$ to the correlation energy functional known for pure-state systems.

Here the density of the $N\lambda$ state of the noninteracting system

$$n_{\text{KS}}^{(N\lambda)}(\mathbf{r}) = \rho_{\text{KS}}^{(N\lambda)}(\mathbf{r}; \mathbf{r}) = \sum_{\sigma} \rho_{\sigma}^{(N\lambda)}(\mathbf{r}; \mathbf{r}) \quad (258)$$

has been chosen to represent this state, because it is available within the KS approach. Another possible choice – the density $n_{\text{HK}}^{(N\lambda)}(\mathbf{r})$ of the $N\lambda$ state of the interacting system – cannot be determined within the KS scheme. These two densities may be different, in principle, although quite close. But the ensemble densities must be equal, according to the definition of the equivalent noninteracting system:

$$n(\mathbf{r}) = n^{\text{KS}}(\mathbf{r}) = \sum_{N\lambda} p_{N\lambda}^{\text{KS}} n_{\text{KS}}^{(N\lambda)}(\mathbf{r}) = n^{\text{HK}}(\mathbf{r}) = \sum_{N\lambda} p_{N\lambda}^{\text{HK}} n_{\text{HK}}^{(N\lambda)}(\mathbf{r}). \quad (259)$$

For mixed-state systems satisfying Eq. (254), the force (212) of the approximate correlation potential (244) can be rewritten with the help of Eqs. (251), (252), (201) and (200) as a weighted sum

$$f_c(\mathbf{r}; [u, n, \rho^{\text{HK}} - \rho^{\text{KS}}, n_2^{\text{HK}} - n_2^{\text{KS}}]) = \sum_{N\lambda} p_{N\lambda}^{\text{KS}} \frac{n_{\text{KS}}^{(N\lambda)}(\mathbf{r})}{n(\mathbf{r})} f_c^{(N\lambda)}(\mathbf{r}), \quad (260)$$

where

$$f_c^{(N\lambda)}(\mathbf{r}) = f_c(\mathbf{r}; [u, n_{\text{KS}}^{(N\lambda)}, \rho_{\text{HK}}^{(N\lambda)} - \rho_{\text{KS}}^{(N\lambda)}, n_{\text{HK},2}^{(N\lambda)} - n_{\text{KS},2}^{(N\lambda)}]) \quad (261)$$

is the correlation force due to the pure $N\lambda$ state alone. Due to Eqs. (246) and (260), the total force ($f_{\text{ee}} + f_c$) occurring in the expression (241) for the internal potential ($v_{\text{ee}}^{\text{KS}} + v_c$) of v_{KS} is decomposed into pure-state contributions as

$$f_{\text{ee}}(\mathbf{r}) + f_c(\mathbf{r}) = \sum_{N\lambda} p_{N\lambda}^{\text{KS}} \frac{n_{\text{KS}}^{(N\lambda)}(\mathbf{r})}{n(\mathbf{r})} \{ f_{\text{ee}}^{(N\lambda)}(\mathbf{r}) + f_c^{(N\lambda)}(\mathbf{r}) \}, \quad (262)$$

With the force (262) and its components (247) and (261), Eq. (241) represents an exact expression for the internal potential, applicable to the mixed-state systems satisfying Eq. (254).

The form (260) of the correlation force suggests the following approximation for it in terms of the approximation $E_c^{\text{APP}}[n]$ to the correlation energy functional for pure-state systems, used already in (257):

$$f_c(\mathbf{r}) \approx f_c^{\text{APP}}(\mathbf{r}) = \sum_{N\lambda} p_{N\lambda}^{\text{KS}} \frac{n_{\text{KS}}^{(N\lambda)}(\mathbf{r})}{n(\mathbf{r})} (-\nabla) \left(\frac{\delta E_c^{\text{APP}}[\bar{n}]}{\delta \bar{n}(\mathbf{r})} \right) \Big|_{\bar{n} = n_{\text{KS}}^{(N\lambda)}}, \quad (263)$$

which leads to the approximation for the correlation potential

$$v_c^{\text{APP}}(\mathbf{r}_0 = r_0 \mathbf{e}; [n]) = \int_{r_0}^{\infty} dr \, \mathbf{e} \cdot f_c^{\text{APP}}(r\mathbf{e}) \quad (264)$$

written in terms of the KS orbitals. If, besides the above approximation for the correlation potential, $v_{\text{ee}}^{\text{KS}}$ is also approximated in the form of (249), their sum can be evaluated as a common line integral involving the force ($f_{\text{ee}}^{\text{APP}} + f_c^{\text{APP}}$).

While there is no way to estimate a priori the accuracy of the propositions (257) and (264), it would be interesting to compare the quality of the results obtained in calculations using the correlation energy in the form of (257) and the correlation potential in the form of (264), including the force (263), with the results of analogous calculations using just $E_c^{\text{APP}}[n]$ and $\delta E_c^{\text{APP}}[n]/\delta n(\mathbf{r})$.

6 Summary

The notion of the exchange energy as the nonclassical part of the electron-electron interaction energy evaluated in the HF method [Eq. (32)] and of the correlation energy, as a difference between the exact GS energy and its HF approximation [Eq. (27)] evolved during the development of the DFT from a collection of separate numbers, characteristic for particular systems, to universal functionals of the density, $E_x[n]$ and $E_c[n]$, defined precisely within the KS approach [Eqs. (54) and (58) for pure-state systems, and (190) and (191) for mixed-state ones]. As discussed in Sect. 2, their meaning is, in general, retained, and their values [for $n(\mathbf{r}) = n_{\text{GS}}(\mathbf{r})$ – the density of a given system] are close to original ones. Their functional derivatives – potentials – are important ingredients of many calculational schemes leading to the solution of the GS problem. However, as demonstrated in Sects. 2 and 3, the potentials occurring in various approaches differ slightly due to (minute) differences in the densities determined there and due to the inherent approximations of these approaches.

Long-range asymptotic properties of KS orbitals were recalled in Sect. 4, as dictated by asymptotic properties of all potentials of KS equations. A new, simple and direct method was applied to obtain the asymptotic form of the exchange potential. For pure-state systems the known results were confirmed in Sects. 4.2 and 4.3, while for mixed-state systems a new, exact result was obtained in Sect. 5.6.

Many interesting results of the paper are based on differential virial theorems. The theorem (165), pertaining to the exact N -interacting electron systems, was taken from our previous work [30]; that (169), pertaining to the noninteracting electron systems, was obtained from the previous one by removing the interaction; while the theorem (170), concerning the HF solution, was obtained here in Appendix B. These theorems happen to be general enough to describe mixed systems of any complexity. The major result of the present study, obtained from these theorems, is the line-integral formula (188) for the exchange-correlation potential $v_{xc}(\mathbf{r})$ for mixed-state systems, in terms of the quantities directly derivable from the second-order DM of the interacting system, of the first-order DM of the noninteracting (KS) system, and of the electron-electron interaction potential. The simplification in which the interacting system DMs are replaced by the independent-particle KS equivalents (which means neglecting correlation) leads to the approximate exchange poten-

tial $v_x^{\text{app}}(\mathbf{r})$ in line-integral form (213) with the force (215). For the Coulombic (ee) interaction $u(\mathbf{r}, \mathbf{r}')$ [the force is (216)], this potential is then found to coincide with the Harbola-Sahni exchange-only potential of their work-formalism approach (see [34] and [35]).

The decompositions (224) and (246) of the electrostatic-plus-exchange energy and force for arbitrary mixed-state systems, into their pure-state components, suggest analogous decompositions (248) and (250) for approximations in terms of any approximate exchange energy functional known for pure-state systems. Similarly, the decompositions (255) and (260) for the correlation energy and force, for mixed-state systems satisfying (254), suggest approximations (257) and (263) in terms of any approximate correlation energy functional for pure-state systems. We expect that these approximations for the exchange and correlation energies and potentials may allow one to obtain better results than previously in the KS-type calculations for mixed-system problems.

7 Appendices

7.1 Some Properties of Density Matrices

The N -th order density matrix (DM) generated from a normalized wave function Ψ of a N -electron system is defined as

$$\gamma_N(\mathbf{x}_1, \dots, \mathbf{x}_N; \mathbf{x}'_1, \dots, \mathbf{x}'_N) = \Psi(\mathbf{x}_1, \dots, \mathbf{x}_N) \Psi^*(\mathbf{x}'_1, \dots, \mathbf{x}'_N). \quad (265)$$

The p -th order reduced DM (for $p < N$) is given in terms of it (see e.g. ref. [10]) as

$$\gamma_p(\mathbf{x}_1, \dots, \mathbf{x}_p; \mathbf{x}'_1, \dots, \mathbf{x}'_p) = \binom{N}{p} \int d\mathbf{x}_{p+1} \dots d\mathbf{x}_N \gamma_N, \quad (266)$$

where $\int d\mathbf{x}_i$ means integration $\int d^3r_i$ and summation over s_i together with the replacement of $\mathbf{x}'_i$ by $\mathbf{x}_i$ in the integrand. In many applications spinless DMs are sufficient

$$\rho_p(\mathbf{r}_1, \dots, \mathbf{r}_p; \mathbf{r}'_1, \dots, \mathbf{r}'_p) = \sum_{s_1, \dots, s_p} \gamma_p(\mathbf{x}_1, \dots, \mathbf{x}_p; \mathbf{x}'_1, \dots, \mathbf{x}'_p) \Big|_{s'_i = s_i}. \quad (267)$$

The diagonal elements of DMs are denoted by

$$\xi_p(\mathbf{x}_1, \dots, \mathbf{x}_p) = \gamma_p(\mathbf{x}_1, \dots, \mathbf{x}_p; \mathbf{x}_1, \dots, \mathbf{x}_p) > 0, \quad (268)$$

$$n_p(\mathbf{r}_1, \dots, \mathbf{r}_p) = \rho_p(\mathbf{r}_1, \dots, \mathbf{r}_p; \mathbf{r}_1, \dots, \mathbf{r}_p) > 0. \quad (269)$$

The subscript ‘1’ can be omitted. The basic quantity of DFT – the electron number density – is thus

$$n(\mathbf{r}) = \rho(\mathbf{r}; \mathbf{r}) = \sum_s \xi(rs) = \sum_s \gamma(rs; rs). \quad (270)$$

From the definition (266) of γ_p one finds the following property:

$$\int d\mathbf{x}_p \gamma_p(\mathbf{x}_1, \dots, \mathbf{x}_p; \mathbf{x}'_1, \dots, \mathbf{x}'_p) = \frac{N+1-p}{p} \gamma_{p-1}(\mathbf{x}_1, \dots, \mathbf{x}_{p-1}; \mathbf{x}'_1, \dots, \mathbf{x}'_{p-1}), \quad (271)$$

since $\binom{N}{p} \binom{N}{p-1}^{-1} = \frac{N+1-p}{p}$.

For density matrices generated from a determinantal wave function Ψ^D (which occurs, e.g., in the HF method or the KS approach), the p -th order matrix can be obtained from the 1-st order one

$$\gamma^D(\mathbf{x}; \mathbf{x}') = \gamma_1^D(\mathbf{x}; \mathbf{x}') = \sum_{j=1}^N \phi_j(\mathbf{x}) \phi_j^*(\mathbf{x}'), \quad (272)$$

as the following determinant (see e.g. [10]):

$$\gamma_p^D(\mathbf{x}_1, \dots, \mathbf{x}_p; \mathbf{x}'_1, \dots, \mathbf{x}'_p) = \frac{1}{p!} \begin{vmatrix} \gamma_1^D(\mathbf{x}_1; \mathbf{x}'_1) & \dots & \gamma_1^D(\mathbf{x}_1; \mathbf{x}'_p) \\ \vdots & \ddots & \vdots \\ \gamma_1^D(\mathbf{x}_p; \mathbf{x}'_1) & \dots & \gamma_1^D(\mathbf{x}_p; \mathbf{x}'_p) \end{vmatrix}. \quad (273)$$

The set $\{\phi_j(\mathbf{r}s), j = 1, \dots, N\}$ of orbitals used for the construction of Ψ^D can be split into two subsets

$$\{\phi_{i\uparrow}(\mathbf{r})\alpha(s), \quad i = 1, \dots, N_\uparrow\} \quad (274)$$

and

$$\{\phi_{i\downarrow}(\mathbf{r})\beta(s), \quad i = 1, \dots, N_\downarrow\} \quad (275)$$

where

$$N_\uparrow + N_\downarrow = N. \quad (276)$$

Then the corresponding 1st order matrix [see Eq. (272)] is

$$\gamma_1^D(\mathbf{x}; \mathbf{x}') = \rho_\uparrow^D(\mathbf{r}; \mathbf{r}')\alpha(s)\alpha(s') + \rho_\downarrow^D(\mathbf{r}; \mathbf{r}')\beta(s)\beta(s'), \quad (277)$$

where

$$\rho_\sigma^D(\mathbf{r}; \mathbf{r}') = \sum_{i=1}^{N_\sigma} \phi_{i\sigma}(\mathbf{r}) \phi_{i\sigma}^*(\mathbf{r}'); \quad \sigma = \uparrow, \downarrow. \quad (278)$$

The matrices $\rho_\uparrow^D(\mathbf{r}; \mathbf{r}')$ and $\rho_\downarrow^D(\mathbf{r}; \mathbf{r}')$ are idempotent with respect to indices $\mathbf{r}, \mathbf{r}'$, while $\gamma_1^D(\mathbf{x}; \mathbf{x}')$ is idempotent with respect to $\mathbf{x}, \mathbf{x}'$. From Eqs. (277) and (267) an expression for the spinless 1st order matrix and its diagonal elements follows, namely

$$\rho^D(\mathbf{r}; \mathbf{r}') = \rho_\uparrow^D(\mathbf{r}; \mathbf{r}') + \rho_\downarrow^D(\mathbf{r}; \mathbf{r}'); \quad n^D(\mathbf{r}) = n_\uparrow^D(\mathbf{r}) + n_\downarrow^D(\mathbf{r}). \quad (279)$$

The diagonal element of the 2nd order DM, calculated according to Eqs. (273) and (277), is known to be

$$n_2^D(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2} n^D(\mathbf{r}_1) n^D(\mathbf{r}_2) \{1 + h_2^D(\mathbf{r}_1, \mathbf{r}_2)\}, \quad (280)$$

where

$$h_2^D(\mathbf{r}_1, \mathbf{r}_2) = - \frac{\{|\rho_\uparrow^D(\mathbf{r}_1; \mathbf{r}_2)|^2 + |\rho_\downarrow^D(\mathbf{r}_1; \mathbf{r}_2)|^2\}}{n^D(\mathbf{r}_1)n^D(\mathbf{r}_2)} < 0. \quad (281)$$

For spin-compensated systems (SCS), i.e. when

$$\rho_\uparrow^D = \rho_\downarrow^D = \frac{1}{2}\rho^D, \quad (\text{SCS}), \quad (282)$$

Eq. (281) simplifies to

$$h_2^D(\mathbf{r}_1, \mathbf{r}_2) = - \frac{1}{2} \frac{|\rho^D(\mathbf{r}_1; \mathbf{r}_2)|^2}{n^D(\mathbf{r}_1)n^D(\mathbf{r}_2)}, \quad (\text{SCS}). \quad (283)$$

For DMs generated from a general wave function Ψ , relation analogous to Eq. (280), namely

$$n_2(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2}n(\mathbf{r}_1)n(\mathbf{r}_2)\{1 + h_2(\mathbf{r}_1, \mathbf{r}_2)\}, \quad (284)$$

serve as definition of $h_2(\mathbf{r}_1, \mathbf{r}_2)$ – the pair-correlation function. It should be noted that for the determinantal case the correlations take place between the same spins only [in Eq. (281), $|\rho_\uparrow^D(\mathbf{r}_1; \mathbf{r}_2)|^2$ is just $\rho_\uparrow^D(\mathbf{r}_1; \mathbf{r}_2)\rho_\uparrow^D(\mathbf{r}_2; \mathbf{r}_1)$].

The following sum rule [stemming from Eq. (271)] holds for h_2 :

$$\int d^3r_2 h_2(\mathbf{r}_1, \mathbf{r}_2)n(\mathbf{r}_2) = -1; \quad \text{for any } \mathbf{r}_1. \quad (285)$$

7.2 Differential Virial Theorem for the Hartree-Fock Solution

The so-called nonlocal exchange potential $\hat{v}_x^{\text{HF}}$, a component of the HF differential equation (33), is an integral operator (see e.g. [10]):

$$(\hat{v}_x^{\text{HF}}\psi)(\mathbf{x}) = \int d\mathbf{x}' w(\mathbf{x}, \mathbf{x}')\psi(\mathbf{x}'), \quad (286)$$

with the kernel

$$w(\mathbf{x}, \mathbf{x}') = -u(\mathbf{r}, \mathbf{r}')\gamma(\mathbf{x}; \mathbf{x}'), \quad (287)$$

where $u(\mathbf{r}, \mathbf{r}')$ is the (real and symmetric) electron–electron attraction potential, and

$$\gamma(\mathbf{x}; \mathbf{x}') = \sum_{j=1}^N \psi_j(\mathbf{x})\psi_j^*(\mathbf{x}') \quad (288)$$

is the first-order DM, generated by the determinantal HF wave function Ψ_D [Eq. (24)] in terms of N lowest-energy eigenfunctions $\psi_j(\mathbf{x})$ – the solutions of the HF equation (33). Using the above definition of $\hat{v}_x^{\text{HF}}$ and the notation for complex functions $f = f^{\text{re}} + if^{\text{im}}$ and for spatial derivatives $f_{/\alpha} = \partial f(\mathbf{r})/\partial r_\alpha$, $f_{/\alpha\beta} = \partial^2 f(\mathbf{r})/(\partial r_\alpha \partial r_\beta)$, etc., we can rewrite the HF equation (33), separated into

its real and imaginary components, as

$$v(r) + v_{\text{es}}(r) - \varepsilon_j = \left(\psi_j^{\Re}(x) \right)^{-1} \left\{ \frac{1}{2} \sum_{\beta} \psi_{j|\beta\beta}^{\Re}(x) - \int dx' \left(w^{\Re}(x, x') \psi_j^{\Re}(x') - w^{\Im}(x, x') \psi_j^{\Im}(x') \right) \right\}, \quad (289)$$

$$v(r) + v_{\text{es}}(r) - \varepsilon_j = \left(\psi_j^{\Im}(x) \right)^{-1} \left\{ \frac{1}{2} \sum_{\beta} \psi_{j|\beta\beta}^{\Im}(x) - \int dx' \left(w^{\Re}(x, x') \psi_j^{\Im}(x') + w^{\Im}(x, x') \psi_j^{\Re}(x') \right) \right\}, \quad (290)$$

where

$$\begin{aligned} w^{\Re}(x, x') &= -u(r, r') \gamma^{\Re}(x; x') \\ &= -u(r, r') \sum_{j=1}^N \{ \psi_j^{\Re}(x) \psi_j^{\Re}(x') + \psi_j^{\Im}(x) \psi_j^{\Im}(x') \}, \end{aligned} \quad (291)$$

$$\begin{aligned} w^{\Im}(x, x') &= -u(r, r') \gamma^{\Im}(x; x') \\ &= -u(r, r') \sum_{j=1}^N \{ \psi_j^{\Im}(x) \psi_j^{\Re}(x') - \psi_j^{\Re}(x) \psi_j^{\Im}(x') \}. \end{aligned} \quad (292)$$

Next, we differentiate both sides of Eqs. (289) and (290) with respect to r_α , afterwards we multiply the first equation by $(\psi_j^{\Re}(x))^2$ and the second one by $(\psi_j^{\Im}(x))^2$, and finally we add together these two equations and sum the result over j to obtain

$$\left(v(r) + v_{\text{es}}(r) \right)_\alpha \gamma(x; x) = \sum_{\beta s} K_{\alpha\beta\beta}(x) + \sum_s \int dx' W_\alpha(x, x'), \quad (293)$$

where

$$\begin{aligned} K_{\alpha\beta\beta}(x) &= \frac{1}{2} \sum_{j=1}^N \{ \psi_j^{\Re}(x) \psi_{j|\alpha\beta\beta}^{\Re}(x) + \psi_j^{\Im}(x) \psi_{j|\alpha\beta\beta}^{\Im}(x) \\ &\quad - \psi_{j|\alpha}^{\Re}(x) \psi_{j|\beta\beta}^{\Re}(x) - \psi_{j|\alpha}^{\Im}(x) \psi_{j|\beta\beta}^{\Im}(x) \}, \end{aligned} \quad (294)$$

$$\begin{aligned} W_\alpha(x, x') &= \sum_{j=1}^N \{ w^{\Re}(x, x') [\psi_{j|\alpha}^{\Re}(x) \psi_j^{\Re}(x') + \psi_{j|\alpha}^{\Im}(x) \psi_j^{\Im}(x')] \\ &\quad + w^{\Im}(x, x') [\psi_{j|\alpha}^{\Im}(x) \psi_j^{\Re}(x') - \psi_{j|\alpha}^{\Re}(x) \psi_j^{\Im}(x')] \\ &\quad - w_{j|\alpha}^{\Re}(x, x') [\psi_j^{\Re}(x) \psi_j^{\Re}(x') + \psi_j^{\Im}(x) \psi_j^{\Im}(x')] \\ &\quad - w_{j|\alpha}^{\Im}(x, x') [\psi_j^{\Im}(x) \psi_j^{\Re}(x') - \psi_j^{\Re}(x) \psi_j^{\Im}(x')] \}. \end{aligned} \quad (295)$$

Eq. (294) can be rewritten as

$$\begin{aligned} K_{\alpha\beta\beta}(x) &= \sum_{j=1}^N \left\{ \frac{1}{4} \left(\psi_j^{\Re}(x) \psi_j^{\Re}(x) + \psi_j^{\Im}(x) \psi_j^{\Im}(x) \right)_{|\alpha\beta\beta} \right. \\ &\quad \left. - \left(\psi_{j|\alpha}^{\Re}(x) \psi_{j|\beta\beta}^{\Re}(x) + \psi_{j|\alpha}^{\Im}(x) \psi_{j|\beta\beta}^{\Im}(x) \right)_{|\beta} \right\}. \end{aligned} \quad (296)$$

Therefore, using expression (270) for the density, reducing γ into ρ according to Eq. (267) and applying the definition (162) of the kinetic energy tensor, we obtain from Eq. (296)

$$\sum_s K_{\alpha\beta\beta}(\mathbf{x}) = \frac{1}{4} n_{/\alpha\beta\beta}(\mathbf{r}) - 2t_{\alpha\beta/\beta}(\mathbf{r}; [\rho]). \quad (297)$$

After substituting into Eq. (295) the differentiated $w(\mathbf{x}, \mathbf{x}')$ taken from Eqs. (291) and (292), we observe cancellation of all terms involving derivatives of wave functions, thus

$$\begin{aligned} W_\alpha(\mathbf{x}, \mathbf{x}') &= u_{/\alpha}(\mathbf{r}, \mathbf{r}') \{ [\gamma^{\mathfrak{A}}(\mathbf{x}; \mathbf{x}')]^2 + [\gamma^{\mathfrak{B}}(\mathbf{x}; \mathbf{x}')]^2 \} \\ &= u_{/\alpha}(\mathbf{r}, \mathbf{r}') \gamma(\mathbf{x}; \mathbf{x}') \gamma(\mathbf{x}'; \mathbf{x}). \end{aligned} \quad (298)$$

With the results (297) and (298) inserted, Eq. (293) takes the form

$$\begin{aligned} v_{/\alpha}(\mathbf{r}) \sum_s \gamma(\mathbf{x}; \mathbf{x}) + \sum_s \int d\mathbf{x}' u_{/\alpha}(\mathbf{r}, \mathbf{r}') \{ \gamma(\mathbf{x}; \mathbf{x}) \gamma(\mathbf{x}'; \mathbf{x}') - \gamma(\mathbf{x}; \mathbf{x}') \gamma(\mathbf{x}'; \mathbf{x}) \} \\ + \sum_\beta \{ -\frac{1}{4} n_{/\alpha\beta\beta} + 2t_{\alpha\beta/\beta}(\mathbf{r}; [\rho]) \} = 0. \end{aligned} \quad (299)$$

We have used $n(\mathbf{r}) = \sum_s \gamma(\mathbf{x}, \mathbf{x})$ to represent in terms of γ the contribution due to the differentiated $v_{\text{es}}(\mathbf{r}; [n])$ [Eq. (34)]. The integrand in Eq. (299) may be put in a concise form, if we use Eq. (273), for $p = 2$, valid for DMs of determinantal origin, therefore applicable to the HF case:

$$\gamma_2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2) = \frac{1}{2} \{ \gamma(\mathbf{x}_1; \mathbf{x}'_1) \gamma(\mathbf{x}_2; \mathbf{x}'_2) - \gamma(\mathbf{x}_1; \mathbf{x}'_2) \gamma(\mathbf{x}_2; \mathbf{x}'_1) \}, \quad (300)$$

and use Eqs. (269) and (267) to obtain

$$n_2(\mathbf{r}_1, \mathbf{r}_2) = \sum_{s_1 s_2} \gamma_2(\mathbf{r}_1 s_1, \mathbf{r}_2 s_2; \mathbf{r}_1 s_1, \mathbf{r}_2 s_2). \quad (301)$$

Thus, finally Eq. (299) can be rewritten as the following differential virial theorem for the HF solution of the GS problem

$$n(\mathbf{r}) v_{/\alpha}(\mathbf{r}) + 2 \int d^3 r' n_2(\mathbf{r}, \mathbf{r}') u_{/\alpha}(\mathbf{r}, \mathbf{r}') + \sum_\beta \{ -\frac{1}{4} n_{/\alpha\beta\beta}(\mathbf{r}) + 2t_{\alpha\beta/\beta}(\mathbf{r}; [\rho]) \} = 0, \quad (302)$$

where the reduced DMs $n_2(\mathbf{r}_1, \mathbf{r}_2)$, $\rho(\mathbf{r}; \mathbf{r}')$ and $n(\mathbf{r})$, occurring in this equation, are generated from $\psi_j(\mathbf{x})$ – the solutions of the HF equations.

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Analysis and Modelling of Atomic and Molecular Kohn–Sham Potentials

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The basic concepts of the one-electron Kohn–Sham theory have been presented and the structure, properties and approximations of the Kohn–Sham exchange-correlation potential v_{xc} have been overviewed. The discussion has been focused on the most recent developments in the theory, such as the construction of v_{xc} from the correlated densities, the methods to obtain total energy and energy differences from the potential, and the orbital dependent approximations to v_{xc} . The recent achievements in analysis of the atomic shell and molecular bond midpoint structure of v_{xc} have been summarized. The consistent formulation of the discontinuous dependence of v_{xc} on the particle number and its effect on the spatial form of v_{xc} and charge transfer within the system have been presented. The recently developed direct approximations of the long- and short-range components of v_{xc} have been overviewed.

List of Symbols and Abbreviations

DFT	density functional theory
GGA	generalized gradient approximation
LDA	local density approximation
OPM	optimized potential model
CI	configuration interaction method
BLYP	combination of the approximate exchange functional of Becke and the Coulomb correlation functional of Lee, Yang and Parr
PW91	approximation of the exchange-correlation functional by Perdew and Wang (1991)
SIC	self-interaction correction method
KLI	approximation for the exchange and exchange-correlation potentials of Krieger, Li and Iafrate
WDA	weighted density approximation
GEA	gradient expansion approximation
B88PW91C	combination of the approximate exchange functional of Becke (1988) and the Coulomb correlation functional of Perdew and Wang (1991)

1 Introduction

Density functional theory (DFT) [1] has become an important computational tool within quantum chemistry [2, 3]. As has been tested in several studies [4–7] DFT yields results for many molecular systems which are comparable in

accuracy to the results obtained with the more traditional methods of quantum chemistry. They are however obtained at much lower cost, making DFT an important tool in the study of large molecular systems, impossible with the more conventional methods of quantum chemistry.

The increase in accuracy of the density functional method in the past decade is mainly due to the introduction of the generalized gradient approximations (GGAs) for the exchange-correlation energy which give large improvements in energetics over the more conventional local density approximation (LDA).

The work on GGAs was initiated by Langreth, Perdew and Mehl [8–10] who proposed gradient functionals derived from momentum space cutoffs that were introduced to enforce known constraints to the exchange-correlation hole obtained from gradient expansions of slowly varying densities. In later work, Perdew et al. [11–14] obtained accurate gradient functionals for the exchange-correlation energy by similar cutoffs of the exchange-correlation hole in real space. A more phenomenological, but important, contribution has been made by Becke [6, 15] who obtained a widely used GGA for the exchange energy. The Perdew–Wang exchange-correlation functional [11, 13, 14] or the Becke exchange functional [15] in combination with the correlation functional of Perdew [10] or Lee et al. [16] have turned out to be very successful in the calculation of molecular bond energies and geometries (for a recent review of the Becke and Perdew–Wang approach see [17]).

Although the GGAs give large improvements in exchange-correlation energies, the corresponding exchange-correlation potential still has significant deficiencies. For instance, they do not reproduce the required asymptotic Coulombic $-1/r$ behavior [18–21] in finite systems such as molecules. As a result of this, a too low absolute value for the highest occupied Kohn–Sham orbital, which should be equal to the ionization energy of the system [18], is obtained. Furthermore the required atomic shell structure, characterized by peaks at the atomic shell boundaries [19–21], is not correctly reproduced with the LDA and GGA approximations [22]. Another serious deficiency is the erroneous (Coulombic) singularity of the GGA potentials near the atomic nucleus [20, 23]. These deficiencies, of course, demonstrate that the GGA density functionals for the exchange-correlation energy do not have the correct density dependence, even if they reproduce quite well experimental energies. This clearly indicates a need for improved Kohn–Sham potentials, especially for the calculation of properties that depend sensitively on the quality of the electron density, such as polarizabilities and other response properties.

In this review we will give an overview of the properties (asymptotics, shell-structure, bond midpoint peaks) of exact Kohn–Sham potentials in atomic and molecular systems. Reproduction of these properties is a much more severe test for approximate density functionals than the reproduction of global quantities such as energies. Moreover, as the local properties of the exchange-correlation potential such as the atomic shell structure and the molecular bond midpoint peaks are closely related to the behavior of the exchange-correlation hole in these shell and bond midpoint regions, one might be able to construct

better exchange-correlation functionals (which are usually based on exchange-correlation hole considerations) by studying the local properties of the exchange-correlation potential.

2 Key Concepts and Formulas

The basic quantity in density functional theory is the energy functional E_v which within constrained search [24, 25] is defined as

$$E_v[\{\rho_\sigma\}] = \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} + F_L[\{\rho_\sigma\}] \quad (1)$$

where ρ_σ are the spin densities and ρ is the total density which is given as the sum of the spin densities $\rho = \rho_\uparrow + \rho_\downarrow$. Here v is the external potential of the system (for instance for the case of a molecule it is the nuclear frame) and the functional F_L is defined as

$$F_L[\{\rho_\sigma\}] = \inf_{\hat{D} \rightarrow \{\rho_\sigma\}} \text{Tr} \hat{D}(\hat{T} + \hat{W}) . \quad (2)$$

In this functional the infimum of the expectation value of the kinetic energy operator $\hat{T}$ and the interparticle interaction operator $\hat{W}$ is searched over all N -particle density matrices which integrate to the prescribed spin densities $\{\rho_\sigma\}$. The energy functional E_v attains its minimum for the ground state densities $\{\rho_\sigma\}$ corresponding to the external potential v . The functional F_L is independent of v (as follows directly from its definition) and is in this sense universal. Once approximations for F_L are found it can be applied to a wide range of physical systems ranging from atoms and molecules to solids and surfaces. The functional F_L as defined above has the nice mathematical property that its functional differentiability can be proven [26, 27] at the ground state densities $\{\rho_\sigma\}$ corresponding to potential v of a certain class, providing a rigorous foundation for the variational equations in DFT. The functional F_L is usually split up as

$$F_L[\{\rho_\sigma\}] = T_L[\{\rho_\sigma\}] + \frac{1}{2} \int \frac{\rho(\mathbf{r}_1) \rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 + E_{xc}[\{\rho_\sigma\}] \quad (3)$$

where T_L is defined as

$$T_L[\{\rho_\sigma\}] = \inf_{\hat{D} \rightarrow \{\rho_\sigma\}} \text{Tr} \hat{D} \hat{T} . \quad (4)$$

As all functionals except the exchange-correlation functional E_{xc} are defined, Eq. (3) actually defines E_{xc} . As shown by Kohn and Sham [28] (for a rigorous

derivation see [26, 27]) the variational problem can be rewritten as

$$\left[-\frac{1}{2}\nabla^2 + v_{s\sigma}([\{\rho_\sigma\}]; \mathbf{r}) \right] \phi_{i\sigma}(\mathbf{r}) = \varepsilon_{i\sigma} \phi_{i\sigma}(\mathbf{r}) \quad (5)$$

$$\rho_\sigma(\mathbf{r}) = \sum_i f_{i\sigma} |\phi_{i\sigma}(\mathbf{r})|^2$$

$$v_{s\sigma}([\{\rho_\sigma\}]; \mathbf{r}) = v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc\sigma}([\{\rho_\sigma\}]; \mathbf{r})$$

$$v_{xc\sigma}([\{\rho_\sigma\}]; \mathbf{r}) = \frac{\delta E_{xc}[\{\rho_\sigma\}]}{\delta \rho_\sigma(\mathbf{r})}$$

where $f_{i\sigma}$ are the orbital occupation numbers. For the nondegenerate ground states $f_{i\sigma} = 1$ for the occupied orbitals $\phi_{i\sigma}$ and $f_{i\sigma} = 0$ for the unoccupied orbitals, so that T_L reduces to the kinetic energy functional of the noninteracting particles $T_s[\{\rho_\sigma\}]$:

$$T_s[\{\rho_\sigma\}] = \sum_\sigma \sum_i^{N_\sigma} \int \phi_{i\sigma}^*(\mathbf{r}) \left(-\frac{1}{2}\nabla^2 \right) \phi_{i\sigma}(\mathbf{r}) d\mathbf{r} . \quad (6)$$

Equations (5) will be referred to as the Kohn–Sham equations. The effective potential v_s is called the Kohn–Sham potential. By applying the Hohenberg–Kohn theorem [29] to a non-interacting system it can be uniquely determined (to within a constant) by the electron density. The quantity v_{xc} , the exchange–correlation potential, is equal to the functional derivative of E_{xc} . In practice it is usually calculated in the local density approximation (LDA) or using generalized gradient approximations (GGAs). The functional E_{xc} can be further split up into an exchange and a correlation part. The exchange functional is defined as

$$E_x[\{\rho_\sigma\}] = \langle \psi_s[\rho] | \hat{W} | \psi_s[\rho] \rangle - \frac{1}{2} \int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \quad (7)$$

where $\psi_s[\rho]$ is the Kohn–Sham determinant obtained from the solution of the Kohn–Sham equations. The correlation functional is defined as

$$E_c[\{\rho_\sigma\}] = E_{xc}[\{\rho_\sigma\}] - E_x[\{\rho_\sigma\}] . \quad (8)$$

The exchange and correlation potentials v_x and v_c are defined as the functional derivatives with respect to the electron density of the corresponding functionals:

$$v_{x\sigma}([\{\rho_\sigma\}]; \mathbf{r}) = \frac{\delta E_x[\{\rho_\sigma\}]}{\delta \rho_\sigma(\mathbf{r})} \quad (9)$$

$$v_{c\sigma}([\{\rho_\sigma\}]; \mathbf{r}) = \frac{\delta E_c[\{\rho_\sigma\}]}{\delta \rho_\sigma(\mathbf{r})} . \quad (10)$$

To study the structure of the exchange-correlation energy functional, it is useful to relate this quantity to the pair-correlation function. The pair-correlation function of a system of interacting particles is defined in terms of the diagonal two-particle density matrix $\Gamma_{\sigma_1\sigma_2}$ (for an extensive discussion of the properties of two-particle density matrices see [30]) as

$$g_{\sigma_1\sigma_2}(\mathbf{r}_1\mathbf{r}_2) = \frac{\Gamma_{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2)}{\rho_{\sigma_1}(\mathbf{r}_1) \rho_{\sigma_2}(\mathbf{r}_2)} . \quad (11)$$

We further define the coupling constant integrated pair correlation function [31, 32] by

$$\bar{g}_{\sigma_1\sigma_2}([\{\rho_\sigma\}]; \mathbf{r}_1, \mathbf{r}_2) = \int_0^1 g_{\sigma_1\sigma_2}^\lambda([\{\rho_\sigma\}]; \mathbf{r}_1, \mathbf{r}_2) d\lambda . \quad (12)$$

Here $g_{\sigma_1\sigma_2}^\lambda$ is the pair-correlation function corresponding to the ground state of the Hamiltonian

$$\hat{H}_\lambda = \hat{T} + \hat{V}_\lambda + \lambda \hat{W} \quad (13)$$

where the two-particle interaction $\hat{W}$ now has coupling strength λ and where the external potential $\hat{V}_\lambda$ is now chosen for each λ in such a way that the densities $\{\rho_\sigma\}$ remain constant as a function of λ . In this way the limit $\lambda = 1$ corresponds to the fully interacting system with external potential v and the limit $\lambda = 0$ corresponds to a noninteracting system with the Kohn–Sham potential v_s as an external potential. The exchange-correlation functional can now be written in terms of the coupling constant integrated pair-correlation function as

$$E_{xc}[\{\rho_\sigma\}] = \frac{1}{2} \sum_{\sigma_1\sigma_2} \int \frac{\rho_{\sigma_1}(\mathbf{r}_1) \rho_{\sigma_2}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} (\bar{g}_{\sigma_1\sigma_2}([\{\rho_\sigma\}]; \mathbf{r}_1, \mathbf{r}_2) - 1) d\mathbf{r}_1 d\mathbf{r}_2 . \quad (14)$$

This expression is very useful in the construction of approximate exchange-correlation functionals and in the analysis of the different long and short range properties of the exchange-correlation potential. Note that the exchange-correlation energy E_{xc} as defined here also contains the difference $T_c = T - T_s$ between the kinetic energy of the fully interacting system and the kinetic energy of the Kohn–Sham system. One can readily show that T_c is always a positive quantity [1]. In terms of the pair-correlation functions one has

$$T_c[\{\rho_\sigma\}] = \frac{1}{2} \sum_{\sigma_1\sigma_2} \int \frac{\rho_{\sigma_1}(\mathbf{r}_1) \rho_{\sigma_2}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} (\bar{g}_{\sigma_1\sigma_2}([\{\rho_\sigma\}]; \mathbf{r}_1, \mathbf{r}_2) - g_{\sigma_1\sigma_2}([\{\rho_\sigma\}]; \mathbf{r}_1, \mathbf{r}_2)) d\mathbf{r}_1 d\mathbf{r}_2 . \quad (15)$$

This expression shows explicitly how the coupling constant integration introduces the kinetic part of E_{xc} . We can further split up $\bar{g}$ into an exchange part g_x and a correlation part $\bar{g}_c$:

$$\bar{g}_{\sigma_1\sigma_2}([\rho]; \mathbf{r}_1\mathbf{r}_2) = g_{x\sigma_1\sigma_2}([\{\rho_\sigma\}]; \mathbf{r}_1, \mathbf{r}_2) + \bar{g}_{c\sigma_1\sigma_2}([\rho]; \mathbf{r}_1, \mathbf{r}_2) \quad (16)$$

where $g_{x\sigma_1\sigma_2}$ is defined by

$$g_{x\sigma_1\sigma_2}([\{\rho_\sigma\}]; \mathbf{r}_1, \mathbf{r}_2) = 1 - \delta_{\sigma_1\sigma_2} \frac{|\gamma_{s\sigma_1}(\mathbf{r}_1, \mathbf{r}_2)|^2}{\rho_{\sigma_1}(\mathbf{r}_1)\rho_{\sigma_1}(\mathbf{r}_2)} \quad (17)$$

where

$$\gamma_{s\sigma}(\mathbf{r}_1, \mathbf{r}_2) = \sum_i^{N_\sigma} f_{i\sigma} \phi_{i\sigma}(\mathbf{r}_1) \phi_{i\sigma}^*(\mathbf{r}_2) \quad (18)$$

is the one-particle density matrix for the Kohn–Sham system. The form of g_x shows that like spin electrons are uncorrelated in the exchange-only approximation. We further define

$$g_{s\sigma}([\{\rho_\sigma\}]; \mathbf{r}_1, \mathbf{r}_2) = g_{x\sigma\sigma}([\{\rho_\sigma\}]; \mathbf{r}_1, \mathbf{r}_2) \quad (19)$$

which we will call the pair-correlation function of the Kohn–Sham system. This allows us to write the exchange and correlation energy functionals as

$$\begin{aligned} E_x[\{\rho_\sigma\}] &= \frac{1}{2} \sum_\sigma \int \frac{\rho_\sigma(\mathbf{r}_1)\rho_\sigma(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} (g_{s\sigma}([\{\rho_\sigma\}]; \mathbf{r}_1, \mathbf{r}_2) - 1) d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \frac{1}{2} \sum_\sigma \int \frac{\rho_\sigma(\mathbf{r}_1)\rho_{x\sigma}(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \end{aligned} \quad (20)$$

$$\begin{aligned} E_c[\{\rho_\sigma\}] &= \frac{1}{2} \sum_{\sigma_1\sigma_2} \int \frac{\rho_{\sigma_1}(\mathbf{r}_1)\rho_{\sigma_2}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \bar{g}_{c\sigma_1\sigma_2}([\{\rho_\sigma\}]; \mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \frac{1}{2} \sum_{\sigma_1\sigma_2} \int \frac{\rho_{\sigma_1}(\mathbf{r}_1)\rho_{c\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \end{aligned} \quad (21)$$

where we defined the exchange or Fermi hole function as

$$\rho_{x\sigma}(\mathbf{r}_1, \mathbf{r}_2) = - \frac{|\gamma_{s\sigma}(\mathbf{r}_1, \mathbf{r}_2)|^2}{\rho_\sigma(\mathbf{r}_1)} \quad (22)$$

and the coupling constant integrated correlation hole or Coulomb hole function by

$$\rho_{c\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2) = \rho_{\sigma_2}(\mathbf{r}_2) \bar{g}_{c\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2) . \quad (23)$$

Note that the exchange hole is not affected by the coupling constant integration as the density and therefore the Kohn–Sham orbitals also remain the same during the integration. The exchange and correlation holes satisfy the important sum rule properties

$$\int \rho_{x\sigma}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = -1 \quad (24)$$

$$\sum_{\sigma_2} \int \rho_{c\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = 0 . \quad (25)$$

The exchange and correlation holes are important concepts in DFT as many approximate functionals are based on modelling of these functions [11, 32–34]. They also help to explain the success of DFT in chemical bonding situations [35, 36].

Finally we mention some basic relations which are essential in the discussion of explicitly orbital dependent functionals. Examples of such functionals are the Kohn–Sham kinetic energy T_s and the exchange energy E_x which are dependent on the density due to the fact that the Kohn–Sham orbitals are uniquely determined by the density. The functional dependence of the Kohn–Sham orbitals on the density is not explicitly known. However one can still obtain the functional derivative of orbital dependent functionals as a solution to an integral equation. Suppose we have an explicit orbital dependent approximation for E_{xc} in terms of the Kohn–Sham orbitals; then

$$\begin{aligned} v_{xc\sigma_1}([\rho_\sigma]; \mathbf{r}) &= \frac{\delta E_{xc}[\{\phi_{i\sigma_2}\}]}{\delta \rho_{\sigma_1}(\mathbf{r})} \\ &= \sum_i \sum_{\sigma_1 \sigma_2} \int \frac{\delta E_{xc}}{\delta \phi_{i\sigma_2}(\mathbf{r}_1)} \frac{\delta \phi_{i\sigma_2}(\mathbf{r}_1)}{\delta v_{\sigma_2}(\mathbf{r}_2)} \frac{\delta v_{\sigma_2}(\mathbf{r}_2)}{\delta \rho_{\sigma_1}(\mathbf{r})} d\mathbf{r}_1 d\mathbf{r}_2 + \text{c.c.} \end{aligned} \quad (26)$$

From this equation one finds that the exchange-correlation potential can alternatively be obtained as the solution to the integral equation [37, 38]

$$\int \chi_{s\sigma}(\mathbf{r}_1, \mathbf{r}_2) v_{xc\sigma}(\mathbf{r}_2) d\mathbf{r}_2 = Q_\sigma(\mathbf{r}_1) \quad (27)$$

where the function $\chi_{s\sigma}$ is the static density response function of the Kohn–Sham system

$$\chi_{s\sigma}(\mathbf{r}_1, \mathbf{r}_2) = \frac{\delta \rho_\sigma(\mathbf{r}_1)}{\delta v_{s\sigma}(\mathbf{r}_2)} = - \sum_i^N f_{i\sigma} \phi_{i\sigma}^*(\mathbf{r}_1) G_{i\sigma}(\mathbf{r}_1, \mathbf{r}_2) \phi_{i\sigma}(\mathbf{r}_2) + \text{c.c.} \quad (28)$$

where $G_{i\sigma}$ is the Greens function

$$G_{i\sigma}(\mathbf{r}_1, \mathbf{r}_2) = \sum_{j \neq i} \frac{\phi_{j\sigma}(\mathbf{r}_1) \phi_{j\sigma}^*(\mathbf{r}_2)}{\epsilon_{j\sigma} - \epsilon_{i\sigma}}. \quad (29)$$

The function Q_σ is defined as

$$Q_\sigma(\mathbf{r}_1) = \sum_i^N \int f_{i\sigma} \phi_{i\sigma}^*(\mathbf{r}_1) G_{i\sigma}(\mathbf{r}_1, \mathbf{r}_2) v_{xc, i\sigma}(\mathbf{r}_2) \phi_{i\sigma}(\mathbf{r}_2) d\mathbf{r}_2 + \text{c.c.} \quad (30)$$

where

$$v_{xc, i\sigma}(\mathbf{r}) = \frac{1}{\phi_{i\sigma}(\mathbf{r})} \frac{\delta E_{xc}}{\delta \phi_{i\sigma}^*(\mathbf{r})}. \quad (31)$$

The above equations are especially suitable for obtaining the exchange potential, as this potential is implicitly dependent on the density but explicitly on the Kohn–Sham orbitals. The above equations are, furthermore, very useful

for considering Kohn–Sham orbital dependent approximations to E_{xc} and v_{xc} . Neglect of correlation leads to the exchange-only optimized potential model (OPM) equations [21, 39–41]. Until now the OPM has been applied only to atomic systems, for which the Coulomb correlation has little effect on the electron density distribution. In this case the solution of the OPM equations leads to a very accurate exchange potential

$$v_{x\sigma}^{OPM}(\mathbf{r}) = \left. \frac{\delta E_x[\{\rho_\sigma\}]}{\delta \rho_\sigma(\mathbf{r})} \right|_{\rho^{OPM}} \quad (32)$$

which should be close to the exact exchange potential

$$v_{x\sigma}(\mathbf{r}) = \left. \frac{\delta E_x[\{\rho_\sigma\}]}{\delta \rho_\sigma(\mathbf{r})} \right|_{\rho^{exact}} \quad (33)$$

The importance of orbital dependent functionals for a correct representation of the atomic shell structure, the correct properties of v_{xc} for heteronuclear molecules, and the related particle number dependent properties will be discussed in Sect. 5.5.

3 Construction of Kohn–Sham Potentials from Electron Densities

As the exact form of the energy functional $E_{xc}[\rho]$ is unknown, approximations for this quantity must be introduced for practical applications. However the exact form of its functional derivative $v_{xc}(\mathbf{r}) = \delta E_{xc}/\delta \rho(\mathbf{r})$ can be studied once accurate ground state densities are available, as the Kohn–Sham potential v_s is uniquely (that is up to a constant) determined by the electron density. This observation follows immediately from the Hohenberg–Kohn theorem as applied to a non-interacting system of electrons. Therefore, having an accurate representation of the electron density ρ (for example from a configuration interaction calculation), one should (using the Kohn–Sham equations) be able to construct an accurate representation of the Kohn–Sham potential v_s . Knowledge of the external potential v then immediately yields v_{xc} . For the simple case of a spin unpolarized two-electron system this problem can be solved in a straightforward way, as the orbital density $|\phi|^2$ of the only doubly occupied Kohn–Sham orbital ϕ must be equal to the electron density. The Kohn–Sham equations then immediately yield

$$v_{xc}(\mathbf{r}) = \frac{1}{2} \frac{\nabla^2 \sqrt{\rho(\mathbf{r})}}{\sqrt{\rho(\mathbf{r})}} + \mu - \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' - v(\mathbf{r}). \quad (34)$$

In this way, accurate results for v_{xc} have been obtained for the helium atom and helium-like ions as well as for the hydrogen molecule [42–44]. However, for a system with more electrons the problem is less easily solved. The first

calculations of v_{xc} from a correlated electron density for a system with more than two electrons were carried out by Almbladh and Pedroza [45] for the three- and four-electron systems of the lithium and beryllium atoms. They used a method that had been applied before by von Barth [46] to construct the exchange potential v_x from the Hartree–Fock density for the case of the beryllium atom (see [47]). This method was based on an approximate expansion of the potential in some fit functions depending on parameters which can be optimized to yield a minimum density difference with the exact target density. Aryasetiawan and Stott [48] used a different method in which they needed to solve a set of coupled differential equations. However application of this method to other systems than spherically symmetric atoms (see [49, 50] for an application to a series of atoms) such as molecular systems seems to be quite involved.

Recently a few other methods for constructing v_{xc} have been proposed whose application to general molecular systems is feasible. Görling and Ernzerhof [51, 52] has revived an iterative method of Werden and Davidson [53] based on the relation

$$\delta v_s(\mathbf{r}) = \int \chi_s^{-1}(\mathbf{r}, \mathbf{r}') \delta \rho(\mathbf{r}') d\mathbf{r}' \quad (35)$$

where χ_s^{-1} is the inverse static density response function of the Kohn–Sham system which relates a change $\delta \rho$ in the electron density to a change δv_s in the Kohn–Sham potential. This relation has been used before [53] to construct the Kohn–Sham potential for a model problem. For the Kohn–Sham system the function χ_s^{-1} can be directly calculated from the Kohn–Sham orbitals and eigenvalues. At an iteration n , the density difference $\delta \rho = \rho_n - \rho$ between the density ρ_n at an iteration n and the exact density ρ determines, by the above relation, an updated Kohn–Sham potential $v_s + \delta v_s$. From this updated Kohn–Sham potential we can calculate new orbitals and eigenvalues and construct a new χ_s^{-1} . This procedure is then repeated until convergence is reached. The difficulty in this procedure originates from the fact that χ_s^{-1} is only determined up to a constant as, for a change of v_s by a constant, the density does not change. This implies that the constant function is an eigenfunction with eigenvalue 0 for the integral kernel χ_s . This has to be taken into account when defining χ_s^{-1} (see [53]).

A very different approach has been followed by Zhao et al. [54–57] who based their method on the constrained search definition of the Kohn–Sham kinetic energy. It follows from this definition that, from all Slater determinants which yield a given density, the Kohn–Sham determinant will minimize the kinetic energy. Suppose we have an exact density ρ_0 . If one minimizes the Kohn–Sham kinetic energy under the constraint

$$C[\rho, \rho_0] = \frac{1}{2} \int \frac{\Delta \rho(\mathbf{r}_1) \Delta \rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 = 0 \quad (36)$$

where $\Delta \rho(\mathbf{r}) = \rho(\mathbf{r}) - \rho_0(\mathbf{r})$ and where ρ_0 is the target density, one obtains the

Euler-Lagrange equations

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + \left(1 - \frac{1}{N}\right)v_H(\mathbf{r}) + \lambda \int \frac{\Delta\rho(\mathbf{r}_1)}{|\mathbf{r} - \mathbf{r}_1|} d\mathbf{r}_1 \right] \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}) \quad (37)$$

$$\rho(\mathbf{r}) = \sum_i^N |\phi_i(\mathbf{r})|^2 \quad (38)$$

where v and v_H are the external and the Hartree potentials (the latter being corrected with the Fermi-Amaldi self-interaction correction) and λ is a Lagrange multiplier. In the limit where $\Delta\rho(\mathbf{r})$ approaches zero, the orbitals ϕ_i will yield the exact density ρ_0 . As the Coulomb integral of $\Delta\rho$ then goes to zero the parameter λ must go to infinity at the solution point and the Kohn–Sham potential is given as

$$v_s(\mathbf{r}) = v(\mathbf{r}) + \lim_{\lambda \rightarrow \infty} \left[\lambda \int \frac{\Delta\rho(\mathbf{r}_1)}{|\mathbf{r} - \mathbf{r}_1|} d\mathbf{r}_1 - \frac{1}{N}v_H(\mathbf{r}) \right]. \quad (39)$$

The potential v_s can then be found by solving Eq. (37) for a number of values for λ which can then be extrapolated to infinity. The procedure also works for other constraints like

$$C[\rho, \rho_0] = \int \Delta\rho(\mathbf{r})^2 d\mathbf{r} = 0 \quad (40)$$

but the Coulombic constraint at Eq. (3b) leads to faster convergence in practical applications due to the built-in Coulombic asymptotics of the potential. Some recent applications of the procedure can be found in [56, 57] where the exchange-correlation potential is obtained for all the atoms He through Ar. The method is however straight-forwardly applicable to general systems such as molecules.

Another procedure has been devised by Wang and Parr [58] and yet another by van Leeuwen and Baerends [20]. As the procedures are similar in spirit we will only describe the procedure of the latter authors in some detail. Let us split up the Kohn–Sham potential into the external potential part $v(\mathbf{r})$ and the electronic part v_e :

$$v_s(\mathbf{r}) = v(\mathbf{r}) + v_e(\mathbf{r}) \quad (41)$$

where the electronic part is defined as

$$v_e(\mathbf{r}) = \int \frac{\rho(\mathbf{r}_1)}{|\mathbf{r} - \mathbf{r}_1|} d\mathbf{r}_1 + v_{xc}(\mathbf{r}) \quad (42)$$

which is a repulsive potential. Suppose the exact density is given by ρ_0 and we have a starting density ρ^0 and a starting potential v_e^0 (for instance from an LDA calculation). We then define an iterative procedure by

$$v_e^n(\mathbf{r}) = \frac{\rho^{n-1}(\mathbf{r})}{\rho_0(\mathbf{r})} v_e^{n-1}(\mathbf{r}) \quad (43)$$

where the potential v_e^n can be used to generate a new density from the solution of the Kohn–Sham equations. The procedure is then iterated until $|\rho^n(\mathbf{r}) - \rho_0(\mathbf{r})|$ becomes lower than some threshold. The way the procedure works can be understood intuitively. If the density at a point $\mathbf{r}$ is too low, $\rho^{n-1}(\mathbf{r}) < \rho_0(\mathbf{r})$, then $v_e^{n-1}(\mathbf{r})$ is multiplied by a factor smaller than one making the potential less repulsive at this point, which is a correction in the right direction. The opposite happens if $\rho^{n-1}(\mathbf{r}) > \rho_0(\mathbf{r})$, in which case $v_e^{n-1}(\mathbf{r})$ is multiplied by a factor larger than one making the potential more repulsive at this point, again yielding a correction in the right direction. Using similar arguments one can also devise alternative procedures of the form

$$v_e^n(\mathbf{r}) = f(\rho^{n-1}(\mathbf{r}) / \rho_0(\mathbf{r})) v_e^{n-1}(\mathbf{r}) \quad (44)$$

where f is a function satisfying $f(1) = 1$ or

$$v_e^n(\mathbf{r}) = v_e^{n-1}(\mathbf{r}) + g(\rho^{n-1}(\mathbf{r}) - \rho_0(\mathbf{r})) \quad (45)$$

where g is a function satisfying $g(0) = 0$. The procedure devised by Wang and Parr [58] is of the latter form. Recently Gritsenko et al. [59] obtained, by an iterative procedure of the form in Eq. (43), the exchange-correlation potentials of the molecules H_2 and LiH from the corresponding configuration interaction (CI) densities. The results for H_2 compare well with the results of Buijse et al. [43] who calculated the exchange-correlation potential of this two-electron system in a straightforward way. The work by Gritsenko et al. on LiH provides the first rather accurate results on the exchange-correlation potential for a molecular system with more than two electrons. The results for H_2 and LiH are displayed in Figs. 1 and 2. In Fig. 1 we plot the exchange and the exchange-correlation potential along the bond axis for the H_2 molecule at equilibrium distance. Note the difference in qualitative behavior between the exchange and the exchange-correlation potential in the bond midpoint region. Correlation effects build in a peak structure on top of the exchange potential. The origin of this structure is discussed in Sect. 5.4. In Fig. 2 the exchange-correlation potential for the LiH molecule at equilibrium distance is displayed along the bond

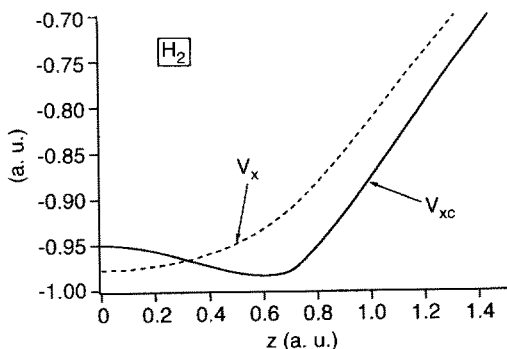


Fig. 1. Exchange and exchange-correlation potentials for H_2 . Potentials are plotted along the bond axis as functions of the distance z from the bond midpoint. The H nucleus is at $z = 0.7005$ a.u.

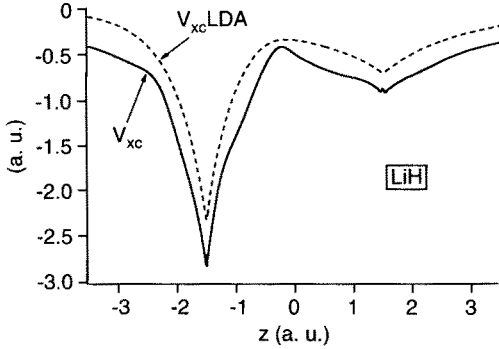


Fig. 2. Exchange-correlation potential and its LDA approximation along the bond axis of LiH as functions of the distance z from the bond midpoint. The Li nucleus is at $z = -1.508$ a.u. and H is at $z = 1.508$ a.u.

axis. Further insight in the properties of molecular Kohn–Sham potentials can be obtained if we apply the methods described above to more molecular systems. The study of accurate Kohn–Sham potentials in the case of molecular dissociation where correlation effects are large may give more insight into the successes and deficiencies of the presently used exchange-correlation functionals. Further analysis of exchange-correlation potentials for different molecular systems is in progress.

4 Energies from Potentials

In the previous section we have shown several ways of constructing nearly exact exchange-correlation potentials from a given electron density. As the exchange-correlation potential is equal to the functional derivative of the exchange-correlation functional E_{xc} taken at the exact ground state density we might ask whether we could obtain some information on the exchange-correlation energy from the constructed potentials (of course the density immediately fixes the value of E_{xc} from the constrained search definitions of the functionals F_L and T_L but this does not provide a practical method).

We will therefore look more closely into the relation between v_{xc} and E_{xc} . Suppose we have a parametrization of a set of electron densities $\gamma(t)$ starting at $\gamma(0) = \rho_0$ and ending in $\gamma(1) = \rho_1$. Then we have [60]

$$\begin{aligned} E_{xc}[\rho_1] - E_{xc}[\rho_0] &= \int_0^1 dt \frac{dE_{xc}}{dt} = \int_0^1 dt \int d\mathbf{r} \frac{\delta E_{xc}[\gamma(t)]}{\delta \rho(\mathbf{r})} \frac{d\gamma(t)}{dt} \\ &= \int_0^1 dt \int d\mathbf{r} v_{xc}([\gamma(t)]; \mathbf{r}) \frac{d\gamma(t)}{dt} \end{aligned} \quad (46)$$

where the outcome of the last integral is path-independent. In general, for

a given exchange-correlation potential v_{xc} , we can define the line integral of v_{xc} along a path from ρ_0 to ρ_1 as

$$\int_{\gamma} v_{xc} \equiv \int_0^1 dt \int d\mathbf{r} v_{xc}([\gamma(t)]; \mathbf{r}) \frac{d\gamma(t)}{dt}. \quad (47)$$

If we calculate the above line integral for an arbitrary approximate v_{xc} the result will, in general, be dependent on the path γ used. However path independence is guaranteed [60] if v_{xc} satisfies the condition

$$\frac{\delta v_{xc}(\mathbf{r})}{\delta \rho(\mathbf{r}')} - \frac{\delta v_{xc}(\mathbf{r}')}{\delta \rho(\mathbf{r})} = 0. \quad (48)$$

This is a vanishing curl condition implying (just as for ordinary vector fields) that v_{xc} is the functional derivative of some energy functional E_{xc} . In that case Eq. (46) is valid for any path γ from ρ_0 to ρ_1 . Let us first apply the above formulas to the calculation of exchange-correlation energy differences from a given exchange-correlation potential. The above equations clearly show that for this purpose it is not sufficient to know v_{xc} for one density, one needs to know v_{xc} along a line of densities. As an illustration we take the straight path from ρ_0 to ρ_1 given by $\gamma(t) = \rho_0 + t\Delta\rho$ with $\Delta\rho = \rho_1 - \rho_0$. In that case we obtain

$$E_{xc}[\rho_0 + \Delta\rho] - E_{xc}[\rho_0] = \int d\mathbf{r} \Delta\rho(\mathbf{r}) \int_0^1 dt v_{xc}([\rho_0 + t\Delta\rho]; \mathbf{r}). \quad (49)$$

When we use a simple Simpson rule for the t -integration we can approximate the above integral as

$$\begin{aligned} E_{xc}[\rho_0 + \Delta\rho] - E_{xc}[\rho_0] \\ = \int d\mathbf{r} \Delta\rho(\mathbf{r}) \left(\frac{1}{6} v_{xc}([\rho_0]; \mathbf{r}) + \frac{2}{3} v_{xc}\left([\rho_0 + \frac{1}{2}\Delta\rho]; \mathbf{r}\right) \right. \\ \left. + \frac{1}{6} v_{xc}([\rho_0 + \Delta\rho]; \mathbf{r}) \right) \end{aligned} \quad (50)$$

which requires the knowledge of v_{xc} for three different densities. The above procedure proves to be exactly equivalent to the transition state method for energy differences developed by Ziegler and Rauk [61] carried out to the third order in $\Delta\rho$. This method may easily be extended to higher order numerical quadrature in t which however requires the knowledge of v_{xc} for a larger set of densities. For molecular bond energies, where $\Delta\rho$ is given by the deformation density of the molecule, Eq. (50) is usually accurate enough for practical application [61].

We can also calculate the total exchange-correlation energy in the same way by integrating the density from 0 to ρ . To do this one could for instance choose the path $\gamma(t) = t\rho$. This path, however, has the disadvantage of not conserving the particle number which can therefore be fractional, giving theoretical problems if one wants to assign a potential to the corresponding density. A more

appealing path choice is the scaling path

$$\gamma(t) = \rho_t(\mathbf{r}) = t^3 \rho(t\mathbf{r}) \quad (51)$$

which is particle number conserving; thus

$$\int \gamma(t) d\mathbf{r} = \int \rho(\mathbf{r}) d\mathbf{r} = N \quad (52)$$

along the path. If we take an atomic or molecular density and let t approach zero, then the density $\gamma(t)$ becomes increasingly diffuse and approaches zero in every point of space. From the relations [62]

$$E_{xc}[\rho_t] = tE_x[\rho] + E_c[\rho_t] \quad (53)$$

and

$$\lim_{t \rightarrow 0} \frac{1}{t} E_c[\rho_t] = -b[\rho] \quad (54)$$

where $b[\rho]$ is a positive functional it follows that [62]

$$\lim_{t \rightarrow 0} E_{xc}[\rho_t] = 0 \quad (55)$$

and Eq. (46) yields

$$\begin{aligned} E_{xc}[\rho] &= \int_0^1 dt \int d\mathbf{r} v_{xc}([\rho_t]; \mathbf{r}) \frac{d\rho_t}{dt} \\ &= \int_0^1 dt \int d\mathbf{r} v_{xc}([\rho_t]; \mathbf{r}) [3t^2 \rho(t\mathbf{r}) + t^3 \mathbf{r} \times \nabla_{\mathbf{r}} \rho(t\mathbf{r})] \\ &= \int d\mathbf{r} \int_0^1 dt \frac{1}{t} v_{xc}\left([\rho_t]; \frac{1}{t} \mathbf{r}\right) [3\rho(\mathbf{r}) + \mathbf{r} \times \nabla \rho(\mathbf{r})] \end{aligned} \quad (56)$$

in which we performed the substitution $t\mathbf{r} \rightarrow \mathbf{r}$. This equation gives an explicit relation between the exchange-correlation energy and the exchange-correlation potential in terms of a line integral along a scaling path. The direct evaluation of the above line integral (for instance by means of numerical integration in the t -variable) requires the knowledge of v_{xc} for a number of scaled densities ρ_t . The exchange-correlation potentials corresponding to these scaled densities are not directly obtainable from accurate CI-densities, as the external potential v_i which generates ρ_t in the interacting system is in general not known. The explicit relation between v_i and $v_{xc}([\rho_t]; \mathbf{r})$ follows from the scaling property of the Kohn–Sham potential

$$v_s([\rho_t]; \mathbf{r}) = t^2 v_s([\rho]; t\mathbf{r}) \quad (57)$$

which together with

$$v_s([\rho_t]; \mathbf{r}) = v_i(\mathbf{r}) + t v_H([\rho]; t\mathbf{r}) + v_{xc}([\rho_t]; \mathbf{r}) \quad (58)$$

$$v_H([\rho]; \mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' \quad (59)$$

where v_H is the Hartree potential, yields

$$v_{xc}([\rho_t]; \mathbf{r}) = t^2 v_{xc}([\rho]; \mathbf{r}) + t^2 v(t\mathbf{r}) - v_t(\mathbf{r}) + t(t-1)v_H([\rho]; t\mathbf{r}) \quad (60)$$

where v is the external potential for $t = 1$. The unknown quantity v_t prevents the direct calculation of the line integral for E_{xc} . As a practical scheme one might be able to develop accurate approximations for $v_{xc}([\rho_t]; \mathbf{r})$ which are constructed to fit the $t = 1$ limit accurately and which are, furthermore, constructed to obey the known limits and inequalities [63] with respect to density scaling. Such approximations can be used directly in the line integral to determine the exchange-correlation energy.

Another path of densities for line integration has been proposed [64], which was parametrized by the Lagrange multiplier λ of Eq. (37). It starts with ρ corresponding to $\lambda = 0$ and terminates at the $\lambda = \infty$ solution.

5 Properties of Kohn–Sham Potentials

5.1 Invariance Properties with Respect to Symmetries

It follows from the definition of the functionals F_L and T_L that the exchange-correlation functional is invariant under the rotation and translation of the electron density. This follows directly from the fact that the kinetic energy operator $\hat{T}$ and the two-electron operator $\hat{W}$ are invariant with respect to these transformations. This also has implications for the exchange-correlation functional.

The formalism of line integrals as discussed in the previous section provides an easy way to obtain conditions on the energy functional in the case where the exchange-correlation potential has some invariance or symmetry property [60]. Suppose for instance that we vary the densities along our path γ by varying our path parameter t but that the potential v_{xc} has some symmetry property under such changes. Using Eq. (46) we then can deduce some properties of E_{xc} . In the following we will apply this idea to rotation, translation and scaling properties of E_{xc} .

If we define the path $\gamma(t)$ by

$$\gamma(t) = \rho(\mathbf{r} + t\mathbf{R}) \quad (61)$$

in which $\mathbf{R}$ is an arbitrary translation vector, and suppose that E_{xc} is a translational invariant, then we find that $E_{xc}[\gamma(t)] = E_{xc}[\rho]$ is constant as a function of

t and

$$\begin{aligned} 0 &= \frac{dE_{xc}[\gamma(t)]}{dt} \Big|_{t=1} = \int d\mathbf{r} \frac{\delta E_{xc}}{\delta \rho(\mathbf{r})} [\gamma(1)] \frac{d\gamma(t)}{dt} \Big|_{t=1} \\ &= \int d\mathbf{r} v_{xc}([\gamma(1)]; \mathbf{r}) \mathbf{R} \times \nabla \rho(\mathbf{r} + \mathbf{R}) . \end{aligned} \quad (62)$$

Similarly

$$\begin{aligned} 0 &= \frac{dE_{xc}[\gamma(t)]}{dt} \Big|_{t=0} = \int d\mathbf{r} v_{xc}([\rho]; \mathbf{r}) \mathbf{R} \times \nabla \rho(\mathbf{r}) \\ &= \int d\mathbf{r} v_{xc}([\rho]; \mathbf{r} + \mathbf{R}) \mathbf{R} \times \nabla \rho(\mathbf{r} + \mathbf{R}) . \end{aligned} \quad (63)$$

As the above Eqs. (62) and (63) yield the same result for all densities ρ and translation vectors $\mathbf{R}$ it follows that

$$v_{xc}([\rho(\mathbf{r} + \mathbf{R})]; \mathbf{r}) = v_{xc}([\rho(\mathbf{r})]; \mathbf{r} + \mathbf{R}) . \quad (64)$$

Thus v_{xc} with the translated density inserted yields the same value in point $\mathbf{r}$ as v_{xc} with the original density inserted in point $\mathbf{r} + \mathbf{R}$. Moreover we find from the above analysis that [60, 65]

$$0 = \int d\mathbf{r} v_{xc}([\rho]; \mathbf{r}) \nabla \rho(\mathbf{r}) . \quad (65)$$

We can derive a similar result from the rotational invariance if we define a path $\gamma(t)$ by

$$\gamma(t) = \rho(R(t)\mathbf{r}) \quad (66)$$

where $R(t)$ is a rotation in three dimensional space which rotates the vector $\mathbf{r}$ around a vector ω by an angle t . If the functional E_{xc} is invariant under rotations we find that $E_{xc}[\gamma(t)] = E_{xc}[\rho]$ is constant as a function of t and that [60]

$$v_{xc}([\rho(R(\theta)\mathbf{r})]; \mathbf{r}) = v_{xc}([\rho(\mathbf{r})]; R(\theta)\mathbf{r}) . \quad (67)$$

So if we insert in v_{xc} the rotated density, then we obtain the same value in point $\mathbf{r}$ as v_{xc} with the original density in the rotated point $R(\theta)\mathbf{r}$ [20, 60, 65]:

$$0 = \int d\mathbf{r} v_{xc}([\rho]; \mathbf{r}) \mathbf{r} \times \nabla \rho(\mathbf{r}) . \quad (68)$$

The constraints at Eqs. (65) and (68) are important checks on the accuracy of (non-variationally derived) approximate potentials, as they are usually not fulfilled by approximate potentials except in those cases where the fulfillment of these constraint is caused for symmetry reasons such as the spherical symmetry in atoms with a nondegenerate ground state. In the case of molecules these constraints will in general not be equal to zero for non-variationally derived potentials.

5.2 Long Range Asymptotics

The exchange-correlation potential possesses a natural splitup into a long range and a short range part. The division into these two different parts is based on Eq. (14) for the exchange-correlation energy in terms of the coupling constant integrated pair-correlation function. If we take the functional derivative of this equation we find that we can write v_{xc} as [66]

$$v_{xc\sigma}([\{\rho_\sigma\}]; \mathbf{r}_1) = \bar{v}_{xc,scr\sigma}([\{\rho_\sigma\}]; \mathbf{r}) + \bar{v}_{xc,scr\sigma}^{resp}([\{\rho_\sigma\}]; \mathbf{r}) \quad (69)$$

where the screening potentials is defined as

$$\bar{v}_{xc,scr\sigma_1}([\{\rho_\sigma\}]; \mathbf{r}_1) = \sum_{\sigma_2} \int \frac{\rho_{\sigma_1}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} (\bar{g}_{\sigma_1\sigma_2}([\{\rho_\sigma\}]; \mathbf{r}_1, \mathbf{r}_2) - 1) d\mathbf{r}_2 \quad (70)$$

and the screening response potential as

$$\bar{v}_{xc,scr\sigma_1}^{resp}([\{\rho_\sigma\}]; \mathbf{r}_1) = \frac{1}{2} \sum_{\sigma_2\sigma_3} \int \frac{\rho_{\sigma_2}(\mathbf{r}_2)\rho_{\sigma_3}(\mathbf{r}_3)}{|\mathbf{r}_2 - \mathbf{r}_3|} \frac{\delta \bar{g}_{\sigma_2\sigma_3}([\{\rho_\sigma\}]; \mathbf{r}_2, \mathbf{r}_3)}{\delta \rho_{\sigma_1}(\mathbf{r}_1)} d\mathbf{r}_2 d\mathbf{r}_3. \quad (71)$$

We will discuss in detail in the next section this potential, which incorporates the main features of the atomic shell structure. The screening potential is just the potential of the coupling constant integrated exchange-correlation hole. Due to the fact that this hole integrates to one electron, the screening potential has Coulombic long range asymptotics

$$\bar{v}_{xc,scr\sigma}([\{\rho_\sigma\}]; \mathbf{r}) \sim -\frac{1}{r} \quad (r \rightarrow \infty) \quad (72)$$

where $r = |\mathbf{r}|$ and the same asymptotics has been proven [18] for the total $v_{xc\sigma}$:

$$v_{xc\sigma}([\{\rho_\sigma\}]; \mathbf{r}) \sim -\frac{1}{r} \quad (r \rightarrow \infty). \quad (73)$$

From these formulas it follows that, being the difference of $v_{xc\sigma}$ and $\bar{v}_{xc,scr\sigma}$, the response potential $\bar{v}_{xc,scr\sigma_1}^{resp}$ has an asymptotic decay which is faster than Coulombic.

A quantity which is sensitively dependent on the asymptotic properties of the exchange-correlation potential is the value of the orbital energy of the highest occupied Kohn–Sham orbital. It can be shown [18, 67] that this quantity is equal to minus the ionization energy of the system. Reproduction of this quantity therefore represents a severe test for approximate density functionals. However, typical errors for the most widely used density functional, the local density approximation (LDA), are 5 eV. A related deficiency of the LDA is that it does not reproduce bound state solutions for negative ions. The origin of this error can be traced to the incorrect asymptotic decay of the LDA exchange-correlation potential. This potential has an exponential decay into the vacuum as can be seen directly from the exponential decay of the density itself. The LDA electron is therefore too weakly bound and, for negative ions, even unbound.

This breakdown of LDA in the outer region of the atom or molecule is also reflected in the exchange-correlation energy per particle $\varepsilon_{xc}(\mathbf{r})$ which can equivalently be seen as the potential due to the exchange-correlation hole and which has an asymptotic decay like $-1/2r$. The LDA in this case again gives an exponential decay. In the electron gas this quantity ε_{xc} is usually expressed in terms of the Wigner–Seitz radius r_s representing the mean electronic distance which is proportional to $\rho^{-1/3}$. If the local density approximation is applied to the outer regions of atoms and molecules, r_s grows exponentially and loses its meaning as a mean interelectronic distance which should grow linearly. The bad representation of this quantity by LDA explains the failure of LDA in this region.

One might now wonder if the current gradient corrections, which yield large improvements over the LDA in energetics, give any improvement for this asymptotic failure of LDA. This is however not the case as is immediately apparent from the fact that the GGAs give almost no improvement in the LDA eigenvalues, being generally also in error by 5–6 eV. We display some atomic results for some widely used GGAs in Table 1. The column VWN represents the LDA functional in the Vosko–Wilk–Nusair [68] parametrization of the electron gas data. The functional BLYP denotes the Becke exchange [15] in combination with the Lee–Yang–Parr [16] correlation functional and BP86 denotes the Becke exchange [15] with the Perdew 1986 [10] correlation functional. The functional PW91 represents the Perdew–Wang 1991 [11, 13, 14, 69] exchange–correlation functional (used together with Perdew’s parametrization of electron

Table 1. Ionization energies in atomic units from the highest occupied Kohn–Sham orbital. The mean absolute deviation from experiment is denoted by Δ

ATOM	VWN	BLYP	BP86	PW91	EXPT
He	0.570	0.585	0.584	0.583	0.903
Li	0.116	0.111	0.120	0.119	0.198
Be	0.206	0.201	0.209	0.207	0.343
B	0.151	0.143	0.151	0.149	0.305
C	0.228	0.218	0.228	0.226	0.414
N	0.309	0.297	0.309	0.308	0.534
O	0.272	0.266	0.267	0.267	0.446
F	0.384	0.376	0.379	0.379	0.640
Ne	0.498	0.491	0.494	0.494	0.792
Na	0.113	0.106	0.115	0.113	0.189
Mg	0.175	0.168	0.177	0.174	0.281
Al	0.111	0.102	0.114	0.112	0.220
Si	0.170	0.160	0.173	0.171	0.300
P	0.231	0.219	0.234	0.233	0.385
S	0.228	0.219	0.223	0.222	0.381
Cl	0.305	0.295	0.302	0.301	0.477
Ar	0.382	0.373	0.381	0.380	0.579
Δ	0.173	0.180	0.172	0.173	

gas data). The numbers for the BLYP functional were taken from [70], and the other data were calculated by a numerical atomic code [71]. Our self-consistent results for the eigenvalues of the PW91 functional are in excellent agreement with the results of [70]. From the table it follows that the GGAs hardly improve the LDA eigenvalues. The BLYP functional yields even worse eigenvalues than LDA.

5.3 Atomic Shell Structure

For the study of the atomic shell structure properties of the exchange-correlation potential, the division of v_{xc} in a long range and a short range part is particularly useful. One can split up the long range potential $v_{xc,scr}$ and the short range potential $v_{xc,scr}^{resp}$ further into an exchange and a correlation part. The exchange-correlation potential $v_{xc} = v_x + v_c$ can now be written as an exchange and a correlation part with corresponding screening and screening response potentials:

$$v_{x\sigma}([\{\rho_\sigma\}]; \mathbf{r}) = v_{x,scr\sigma}([\{\rho_\sigma\}]; \mathbf{r}) + v_{x,scr\sigma}^{resp}([\{\rho_\sigma\}]; \mathbf{r}) \quad (74)$$

and

$$\bar{v}_{c\sigma}([\{\rho_\sigma\}]; \mathbf{r}) = \bar{v}_{c,scr\sigma}([\{\rho_\sigma\}]; \mathbf{r}) + \bar{v}_{c,scr\sigma}^{resp}([\{\rho_\sigma\}]; \mathbf{r}) \quad (75)$$

where the potentials $v_{x,scr}$ and $\bar{v}_{c,scr}$ and their responses are defined as in Eqs. (70) and (71) with $\bar{g}$ replaced by g_s and $\bar{g}_c + 1$. The potential $v_{x,scr}$ has a Coulombic asymptotic behavior due to the fact that the exchange hole integrates to one electron. There is no Coulombic term in $\bar{v}_{c,scr}$ as the coupling constant integrated Coulomb hole integrates to zero electrons.

The exchange-correlation potential v_{xc} reflects the atomic shell structure (see below). The shell structure of v_{xc} arises from that of the pair-correlation function $\bar{g}$. The shell structure of the latter, in its turn, originates from the antisymmetry property of the wavefunction of the system and is mainly an exchange effect. We will therefore consider first the exchange-only case. The influence of correlation effects on the atomic shell structure will be discussed at the end of this section.

In Fig. 3 we plot the pair-correlation function of the OPM $g_{s\sigma}^{OPM}(r_1, r_2) - 1$ for the case of the beryllium atom. As in the Be atom only s shells are occupied, this function only depends on the radial distances $r_1 = |\mathbf{r}_1|$ and $r_2 = |\mathbf{r}_2|$ of electrons 1 and 2 from the atomic nucleus and not on the angle between vectors $\mathbf{r}_1$ and $\mathbf{r}_2$. This is a convenient feature for analysis. As Be is a closed shell atom, $g_{s\sigma}$ is equal for up and down spin, i.e., $g_{s\uparrow} = g_{s\downarrow}$. In the Be atom the boundary between the $1s$ shell and $2s$ shell is at a radial distance of about 1 bohr. From Fig. 3 we can see that $g_{s\sigma}(r_1, r_2) - 1$ is close to -1 along the diagonal where $r_1 \approx r_2$. This is an effect of the Pauli principle, the probability that two electrons of the same spin are at the same position is zero. A rather striking feature of $g_{s\sigma}(r_1, r_2) - 1$ is that it is close to -1 if r_1 and r_2 are in the same shell, but is close to zero if r_1 is in one shell and r_2 is in the other. This is in agreement with

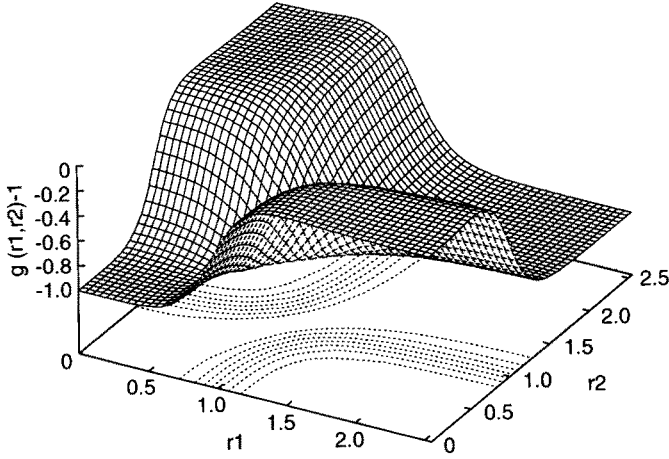


Fig. 3. The pair-correlation function of the OPM $g_s(r_1, r_2) - 1$ for Be as a function of the radial distances r_1 and r_2 of electrons 1 and 2

the well known fact that the exchange hole surrounding a reference electron at position r_1 has the shape of the shell in which the reference position is located. This holds irrespective of where the reference electron is located in that shell, which agrees for given r_1 with $g_{so}(r_1, r_2) - 1$ being approximately -1 for r_2 in the same shell but switching to zero when r_2 crosses the boundary region of the other shell. The plots demonstrate that this atomic shell structure of the pair-correlation function is very distinct.

The exchange-only potentials are given by

$$v_{x,scr\sigma}([\{\rho_\sigma\}]; \mathbf{r}_1) = \int \frac{\rho_\sigma(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} (g_{so}([\{\rho_\sigma\}]; \mathbf{r}_1, \mathbf{r}_2) - 1) d\mathbf{r}_2 \quad (76)$$

$$v_{x,scr\sigma}^{resp}([\{\rho_\sigma\}]; \mathbf{r}_3) = \frac{1}{2} \int \frac{\rho_\sigma(\mathbf{r}_1) \rho_\sigma(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \frac{\delta g_{so}([\{\rho_\sigma\}]; \mathbf{r}_1, \mathbf{r}_2)}{\delta \rho_\sigma(\mathbf{r}_3)} d\mathbf{r}_1 d\mathbf{r}_2 \quad (77)$$

the potential $v_{x,scr\sigma}$ being just the potential of the Kohn–Sham exchange hole. It is identical to the average Hartree–Fock potential introduced by Slater [39, 72] except for the fact that the orbitals involved are Kohn–Sham orbitals instead of Hartree–Fock orbitals. Due to fact that the exchange hole integrates to one electron, this potential (also denoted as Slater potential v_s) has long range Coulombic $-1/r$ asymptotics in finite systems. It is also a smooth function of the radial coordinate r in atoms. The other part of the exchange potential $v_{x,scr\sigma}^{resp}$ is short range and repulsive.

In order to better understand the structure of the $v_{x,scr\sigma}^{resp}$ potential we must calculate the functional derivative of the Kohn–Sham pair-correlation function. This function describes the sensitivity of the exchange screening between two electrons at $\mathbf{r}_1$ and $\mathbf{r}_2$ to density changes at point $\mathbf{r}_3$. One property of this

function is readily derived. As $g_{s\sigma}(\mathbf{r}_1, \mathbf{r}_1) = 0$ for any electron density it immediately follows that

$$\frac{\delta g_{s\sigma'}(\mathbf{r}_1, \mathbf{r}_1)}{\delta \rho_{\sigma}(\mathbf{r}_3)} = 0. \quad (78)$$

This puts a constraint on approximate functional derivatives of $g_{s\sigma}$. In general from the definition of $g_{s\sigma}$ it follows that

$$\begin{aligned} \frac{\delta g_{s\sigma'}(\mathbf{r}_1, \mathbf{r}_2)}{\delta \rho_{\sigma}(\mathbf{r}_3)} = & - \left(\gamma_{s\sigma'}^*(\mathbf{r}_1, \mathbf{r}_2) \frac{\delta \gamma_{s\sigma'}(\mathbf{r}_1, \mathbf{r}_2)}{\delta \rho_{\sigma}(\mathbf{r}_3)} + c.c. \right) \frac{1}{\rho_{\sigma'}(\mathbf{r}_1) \rho_{\sigma'}(\mathbf{r}_2)} \\ & - \left(\frac{\delta(\mathbf{r}_1 - \mathbf{r}_3)}{\rho_{\sigma}(\mathbf{r}_1)} + \frac{\delta(\mathbf{r}_2 - \mathbf{r}_3)}{\rho_{\sigma}(\mathbf{r}_2)} \right) (g_{s\sigma}(\mathbf{r}_1, \mathbf{r}_2) - 1) \delta_{\sigma\sigma'}. \end{aligned} \quad (79)$$

From the constraint at Eq. (78) it follows that the functional derivatives of $\gamma_{s\sigma}$ must contain delta functions in order to cancel the delta functions in the second part of the above equation for $\mathbf{r}_1$ equal to $\mathbf{r}_2$. As $\gamma_{s\sigma}$ depends explicitly on the orbitals we therefore have to calculate the functional derivative of the Kohn–Sham orbitals with respect to the density which is given by [66]

$$\frac{\delta \phi_{i\sigma'}(\mathbf{r}_1)}{\delta \rho_{\sigma}(\mathbf{r}_3)} = - \delta_{\sigma\sigma'} \int G_{i\sigma}(\mathbf{r}_1, \mathbf{r}_4) \phi_{i\sigma}(\mathbf{r}_4) \chi_{s\sigma}^{-1}(\mathbf{r}_4, \mathbf{r}_3) d\mathbf{r}_4. \quad (80)$$

From this equation it follows that $\delta g_{s\sigma}/\delta \rho_{\sigma'}$ is diagonal in the spin indices. We will therefore in the following put $\sigma = \sigma'$. Note that $\chi_{s\sigma}^{-1}$ is defined up to an arbitrary constant, as a density variation $\delta \rho_{\sigma}(\mathbf{r})$ determines the potential variation $\delta v_{s\sigma}(\mathbf{r})$ only up to a constant (see also [66]). To find an explicit expression for the above functional derivative we must find an expression for the inverse density response function $\chi_{s\sigma}^{-1}$. In order to do this we make the following approximation to the Greens function (see Sharp and Horton [39], Krieger et al. [21]):

$$G_{i\sigma}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\Delta \tilde{\epsilon}_{i\sigma}} (\delta(\mathbf{r}_1 - \mathbf{r}_2) - \phi_{i\sigma}(\mathbf{r}_1) \phi_{i\sigma}^*(\mathbf{r}_2)) \quad (81)$$

where $\Delta \tilde{\epsilon}_{i\sigma}$ is some mean energy difference. Just as the exact Greens function of Eq. (29), the above approximate Greens function projects orbital $\phi_{i\sigma}$ to zero. This approximate Greens function leads to a simplified expression for the density response function. The inverse of this function is derived in [66] using an approximation which fixes the arbitrary constant (i.e., the gauge of potential $v_{s\sigma}$) so that $v_{s\sigma} \rightarrow 0$ in infinity. It is given by

$$\chi_{s\sigma}^{-1}(\mathbf{r}_2, \mathbf{r}_3) = \frac{\delta(\mathbf{r}_2 - \mathbf{r}_3)}{a_{\sigma}(\mathbf{r}_2)} + \sum_{ik}^{N_e-1} \eta_{ik}^{\sigma} \frac{|\phi_{i\sigma}(\mathbf{r}_2)|^2 \phi_{k\sigma}(\mathbf{r}_3)}{a_{\sigma}(\mathbf{r}_2) a_{\sigma}(\mathbf{r}_3)} \quad (82)$$

where

$$a_{\sigma}(\mathbf{r}_1) = \sum_i^{N_e} - \frac{2f_{i\sigma}}{\Delta \tilde{\epsilon}_{i\sigma}} |\phi_{i\sigma}(\mathbf{r}_1)|^2 \quad (83)$$

and where the η_{ik}^σ are given by

$$\eta_{ik}^\sigma = -\frac{2f_{i\sigma}}{\Delta\tilde{\epsilon}_{i\sigma}}(\bar{I} - \bar{N}^\sigma)_{ik}^{-1} \quad (84)$$

for $i, k = 1, \dots, N_\sigma - 1$. Matrix $\bar{N}^\sigma$ is given by

$$\bar{N}_{ik}^\sigma = -\frac{2f_{k\sigma}}{\Delta\tilde{\epsilon}_{k\sigma}} \int \frac{|\phi_{i\sigma}(\mathbf{r})|^2 |\phi_{k\sigma}(\mathbf{r})|^2}{a_\sigma(\mathbf{r})} d\mathbf{r} \quad (85)$$

for $i, k = 1, \dots, N_\sigma - 1$. With this inverse density response function one obtains [66]

$$\frac{\delta g_{s\sigma}(\mathbf{r}_1, \mathbf{r}_2)}{\delta \rho_\sigma(\mathbf{r}_3)} = S_\sigma(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) + D_\sigma(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \quad (86)$$

where S_σ is a part we will call, for reasons to be explained, the steplike part. The steplike part S_σ and delta function part D_σ are in the additional approximation $\Delta\tilde{\epsilon}_{i\sigma} = \Delta\tilde{\epsilon}_\sigma$ explicitly given by

$$\begin{aligned} D_\sigma(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = & \delta(\mathbf{r}_1 - \mathbf{r}_3) \left(\frac{g_{s\sigma}(\mathbf{r}_1, \mathbf{r}_3) - g_{s\sigma}(\mathbf{r}_1, \mathbf{r}_2)}{\rho_\sigma(\mathbf{r}_1)} \right) \\ & + \delta(\mathbf{r}_2 - \mathbf{r}_3) \left(\frac{g_{s\sigma}(\mathbf{r}_2, \mathbf{r}_3) - g_{s\sigma}(\mathbf{r}_1, \mathbf{r}_2)}{\rho_\sigma(\mathbf{r}_2)} \right) \end{aligned} \quad (87)$$

and

$$\begin{aligned} S_\sigma(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = & \frac{\gamma_{s\sigma}(\mathbf{r}_1, \mathbf{r}_2)}{\rho_\sigma(\mathbf{r}_1)\rho_\sigma(\mathbf{r}_2)} \sum_i^{N_\sigma} \phi_{i\sigma}^*(\mathbf{r}_1) \phi_{i\sigma}(\mathbf{r}_2) \sum_k^{N_\sigma} 2\zeta_{ik}^\sigma \frac{|\phi_{k\sigma}(\mathbf{r}_3)|^2}{\rho_\sigma(\mathbf{r}_3)} \\ & - \frac{|\gamma_{s\sigma}(\mathbf{r}_1, \mathbf{r}_2)|^2}{\rho_\sigma(\mathbf{r}_1)\rho_\sigma(\mathbf{r}_2)} \sum_{kl}^{N_\sigma} \zeta_{kl}^\sigma \left[\frac{|\phi_{k\sigma}(\mathbf{r}_1)|^2}{\rho_\sigma(\mathbf{r}_1)} + \frac{|\phi_{k\sigma}(\mathbf{r}_2)|^2}{\rho_\sigma(\mathbf{r}_2)} \right] \\ & \times \frac{|\phi_{l\sigma}(\mathbf{r}_3)|^2}{\rho_\sigma(\mathbf{r}_3)} \end{aligned} \quad (88)$$

where

$$\zeta_{ik}^\sigma = (\bar{I} - \bar{M}^\sigma)^{-1} \quad (89)$$

for $i, k = 1, \dots, N_\sigma - 1$ and zero otherwise. Matrix $\bar{M}^\sigma$ is defined as

$$\bar{M}_{ik}^\sigma = f_{k\sigma} \int \frac{|\phi_{i\sigma}(\mathbf{r})|^2 |\phi_{k\sigma}(\mathbf{r})|^2}{\rho_\sigma(\mathbf{r})} d\mathbf{r} \quad (90)$$

for $i, k = 1, \dots, N_\sigma - 1$. Note that S_σ as given by Eq. (88) satisfies the relation $S_\sigma(\mathbf{r}_1, \mathbf{r}_1, \mathbf{r}_3) = 0$ in accordance with the constraint at Eq. (78). This constraint is not satisfied for this function S_σ if we take all the average orbital energies $\Delta\tilde{\epsilon}_{i\sigma}$ to be different [73]. The delta function part D_σ of Eq. (87) unlike S_σ , does not

satisfy $D_\sigma(\mathbf{r}_1, \mathbf{r}_1, \mathbf{r}_3) = 0$; however it satisfies this constraint in an integral sense:

$$\int D_\sigma(\mathbf{r}_1, \mathbf{r}_1, \mathbf{r}_3) d\mathbf{r}_1 = 0. \quad (91)$$

Some properties of the function S_σ are readily derived from Eq. (88) and they are illustrated in Fig. 4, where we plot the S_σ part of the functional derivative $\delta g_s(r_1, r_2)/\delta \rho(r_3)$ for the Be atom as a function of r_2 and r_3 with r_1 being fixed at 0.1 bohr which is well within the 1s shell. When electrons at $\mathbf{r}_1$ and $\mathbf{r}_2$ are well separated in different atomic shells, the one-particle density matrix $\gamma_{s\sigma}(\mathbf{r}_1, \mathbf{r}_2)$ is small and consequently the function S_σ should also be small. If on the other hand the two electrons are close to each other within the same atomic shell then, because S_σ is exactly zero for $\mathbf{r}_1 = \mathbf{r}_2$, the function S_σ will also be very small. Indeed, S_σ in Fig. 4 is small when the other electron at r_2 is situated either in the 1s shell or in the 2s shell. This function only becomes large when electron 2 crosses the boundary between the 1s and 2s shells at a radial distance of about 1 bohr. However, S_σ is then only large when r_3 is also located within 1s shell.

The step structure of S_σ as a function of $\mathbf{r}_3$ is determined by factors of the form $|\phi_{k\sigma}(\mathbf{r}_3)|^2/\rho_\sigma(\mathbf{r}_3)$ (see Eq. 88), each factor being approximately a constant if r_3 is within atomic shell k . The contribution of this factor to the total function S_σ is governed by the constants ζ_{ik}^a describing the coupling of the density perturbation in shell k with an electron in shell i . These constants are largest if $i = k$. Figure 4 clearly displays the step structure of S_σ as a function of r_3 in the region around $r_2 = 1$ bohr.

The discussed step structure of S_σ yields the corresponding structure of $v_{x,sc\sigma\sigma}^{resp}$, which follows from the insertion of Eqs. (86)–(88) into Eq. (77). After multiplication by the function $\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)/|\mathbf{r}_1 - \mathbf{r}_2|$ and integration over $\mathbf{r}_1$ and $\mathbf{r}_2$, the $\mathbf{r}_1, \mathbf{r}_2$ -dependent parts of S_σ yield coefficients in front of the abovementioned $\mathbf{r}_3$ -dependent functions $|\phi_{k\sigma}(\mathbf{r}_3)|^2/\rho_\sigma(\mathbf{r}_3)$. The latter are not involved in the integration, so that the step structure of S_σ is transferred to $v_{x,sc\sigma\sigma}^{resp}$. Carrying out

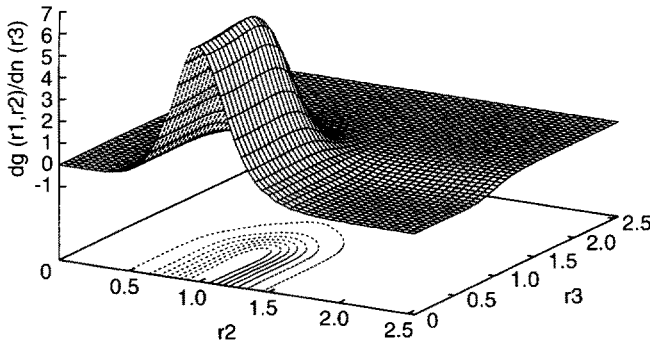


Fig. 4. The S_σ part of the functional derivative $\delta g_{s\sigma}(r_1, r_2)/\delta \rho_\sigma(r_3)$ as a function of the radial distances r_2 and r_3 . Electron 1 is located at $r_1 = 0.1$ bohr

this integration, one finds for $v_{x,scr\sigma}^{resp}$ [73] that

$$v_{x,scr\sigma}^{resp}(\mathbf{r}) = \frac{\sum_i^{N_\sigma-1} (\Delta\tilde{\epsilon}_{i\sigma})^{-1} (\bar{v}_{x\sigma i} - \bar{v}_{i\sigma}) \rho_{i\sigma}(\mathbf{r})}{\sum_i^{N_\sigma} (\Delta\tilde{\epsilon}_{i\sigma})^{-1} \rho_{i\sigma}(\mathbf{r})} + W_\sigma(\mathbf{r}) - v_{x,scr\sigma}(\mathbf{r}) \quad (92)$$

which yields for the exchange potential

$$v_{x\sigma}(\mathbf{r}) = v_{x,scr\sigma}(\mathbf{r}) + v_{x,scr\sigma}^{resp}(\mathbf{r}) = W_\sigma(\mathbf{r}) + \frac{\sum_i^{N_\sigma-1} (\Delta\tilde{\epsilon}_{i\sigma})^{-1} (\bar{v}_{x\sigma i} - \bar{v}_{i\sigma}) \rho_{i\sigma}(\mathbf{r})}{\sum_i^{N_\sigma} (\Delta\tilde{\epsilon}_{i\sigma})^{-1} \rho_{i\sigma}(\mathbf{r})} . \quad (93)$$

In the above expressions we defined [39]

$$W_\sigma(\mathbf{r}) = \frac{\sum_i^{N_\sigma} (\Delta\tilde{\epsilon}_{i\sigma})^{-1} v_{i\sigma}(\mathbf{r}) \rho_{i\sigma}(\mathbf{r})}{\sum_i^{N_\sigma} (\Delta\tilde{\epsilon}_{i\sigma})^{-1} \rho_{i\sigma}(\mathbf{r})} \quad (94)$$

where $\rho_{i\sigma} = f_{i\sigma} |\phi_{i\sigma}|^2$ and

$$v_{i\sigma}(\mathbf{r}_1) = - \frac{1}{\phi_{i\sigma}^*(\mathbf{r}_1)} \sum_k^{N_\sigma} \int f_{k\sigma} \frac{\phi_{i\sigma}^*(\mathbf{r}_2) \phi_{k\sigma}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2 \phi_{k\sigma}^*(\mathbf{r}_1) = \frac{1}{f_{i\sigma} \phi_{i\sigma}^*(\mathbf{r}_1)} \frac{\delta E_x}{\delta \phi_{i\sigma}(\mathbf{r}_1)} \quad (95)$$

which is equal to the orbital-dependent exchange potential within the Hartree–Fock approximation (except for the fact that we do not use Hartree–Fock orbitals). Note that W_σ is equal to the average exchange potential or Slater potential [72] except for the energies $\Delta\tilde{\epsilon}_{i\sigma}$. In fact this expression for the potential W_σ already appeared in the work of Sharp and Horton [39] in which they discuss the Slater potential. The constant $\bar{v}_{i\sigma}$ is defined as

$$\bar{v}_{i\sigma} = \int v_{i\sigma}(\mathbf{r}) |\phi_{i\sigma}(\mathbf{r})|^2 d\mathbf{r} \quad (96)$$

and $\bar{v}_{x\sigma i}$ is a similar average for the exchange potential v_x over the orbital density $|\phi_{i\sigma}|^2$. It is easily recognized that the first term in Eq. (92) represents a step function. If $\mathbf{r}$ is located in shell l , so that all other orbitals have small amplitude at $\mathbf{r}$, the function $\rho_{i\sigma}(\mathbf{r})/\rho_\sigma(\mathbf{r})$ will be almost equal to a constant of the order 1, which will be multiplied by the value of $\bar{v}_{i\sigma} - \bar{v}_{x\sigma i}$. The term $W_\sigma - v_{x,scr\sigma}$ in Eq. (92) represents the difference between two long range potentials both having a Coulombic $-1/r$ behavior and it therefore decays faster than Coulombic. In the approximation $\Delta\tilde{\epsilon}_{i\sigma} = \Delta\tilde{\epsilon}_\sigma$ the potential W_σ reduces to the Slater potential $v_{x,scr\sigma}$ and only the first term survives in Eq. (92). If we apply this same

approximation we obtain for the exchange potential the potential of Krieger et al. [21]:

$$v_{x\sigma}^{KLI}(\mathbf{r}) = \sum_i^{N_\sigma} \frac{v_{i\sigma}(\mathbf{r}) \rho_{i\sigma}(\mathbf{r})}{\rho_\sigma(\mathbf{r})} + \sum_i^{N_\sigma-1} \frac{(\bar{v}_{x\sigma i} - \bar{v}_{i\sigma}) \rho_{i\sigma}(\mathbf{r})}{\rho_\sigma(\mathbf{r})}. \quad (97)$$

We finally observe that if one multiplies Eq. (93) by $\sum_i^{N_\sigma} (\Delta \tilde{e}_{i\sigma})^{-1} \rho_{i\sigma}(\mathbf{r}_1)$ and integrates over $\mathbf{r}_1$ one can easily show that $v_{x\sigma}$ satisfies

$$\bar{v}_{x\sigma m} = \bar{v}_{m\sigma} \quad (98)$$

where $m = N_\sigma$ corresponds to the highest occupied Kohn–Sham orbital $\phi_{m\sigma}$. This equation is exactly valid within the so-called optimized potential model (OPM) [21, 40, 41] exchange potential and also, as observed by Krieger et al., for the approximate exchange potential $v_{x\sigma}^{KLI}$ [21].

In Fig. 5 we plot for the beryllium atom $v_{x,\text{scr}\sigma}^{OPM}$ and $v_{x,\text{scr}\sigma}^{\text{resp},OPM}$ and their sum, the exchange potential v_x^{OPM} . In an OPM calculation [40] the exchange potential and the orbitals ϕ_i are obtained directly. The screening potential $v_{x,\text{scr}\sigma}^{OPM}$ is then calculated from the OPM orbitals according to Eq. (70), using $g_{s\sigma}$ as defined in terms of the orbitals in Eqs. (18) and (19). The screening response potential is then simply the difference $v_x^{OPM} - v_{x,\text{scr}\sigma}^{OPM}$. We also display in Fig. 5 the

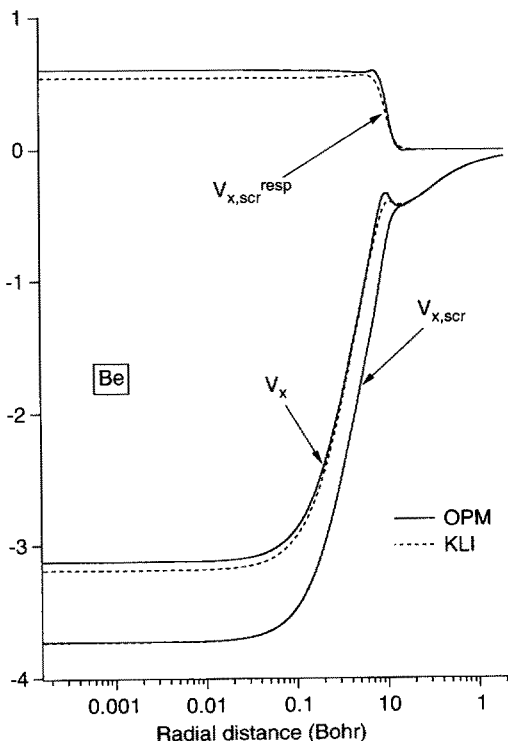


Fig. 5. The OPM and KLI exchange potentials with their components (in a.u.) for Be

potentials $v_{x,scr}^{KLI}$ and $v_{x,scr}^{resp,KLI}$. The orbitals used to calculate the KLI potentials are not the OPM orbitals but are obtained from a self-consistent solution of Eq. (97). In Fig. 6 we present the same quantities for the krypton atom. As we can see from these figures the $v_{x,scr}^{OPM}$ and $v_{x,scr}^{KLI}$ are so close that they cannot be distinguished on the scale presented. The step structure of the potential $v_{x,scr}^{resp,OPM}$ is approximated quite closely by $v_{x,scr}^{resp,KLI}$, the largest difference being a constant within the 1s shell. This testifies to the accuracy of the approximation to the Greens function used in the derivations. With respect to the accuracy of the KLI potential we observe that the only noteworthy difference with the OPM exchange potential is the smoothing of the intershell peak at the atomic shell boundaries in the KLI exchange potential.

Let us now discuss the correlation effects on the atomic shell structure. We plot in Fig. 7 some of the described potentials for the case of the beryllium atom. The exact exchange-correlation potential v_{xc} is calculated from an accurate CI (Configuration Interaction) density using the procedure described in [20]. The potentials v_x , $v_{x,scr}$ and $v_{x,scr}^{resp}$ are calculated within the optimized potential model (OPM) [21,40,41] and are probably very close to their exact values which can be obtained from the solution for v_x of the OPM integral equation [21,40,41] by insertion of the exact Kohn–Sham orbitals instead of the OPM

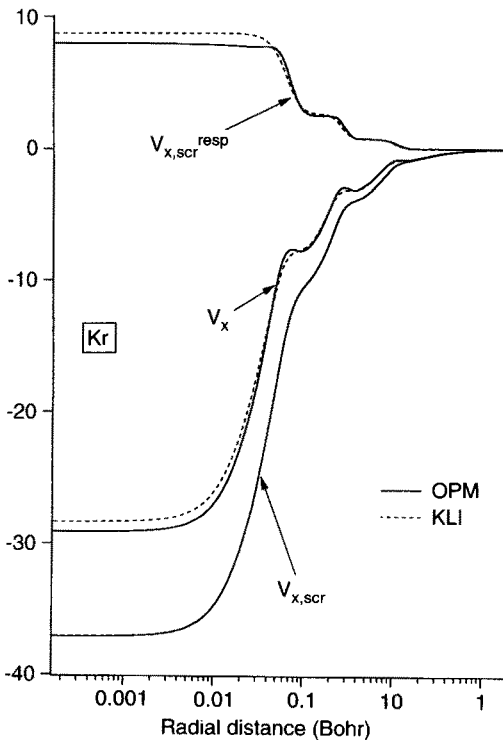


Fig. 6. The OPM and KLI exchange potentials with their components (in a.u.) for Kr

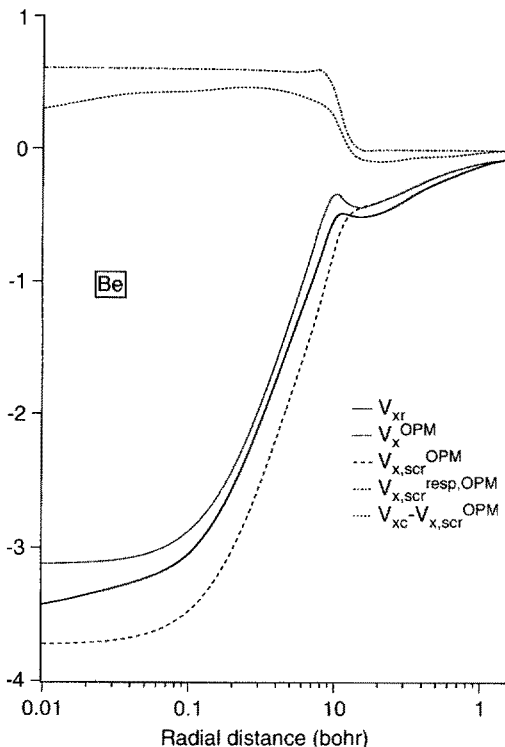


Fig. 7. The exchange-correlation potential and the OPM exchange potential with their components (in a.u.) for Be

orbitals. We further plotted $v_{xc} - v_{x,scr}^{OPM}$ which can be regarded as an approximation to $v_{xc,scr}^{resp} + v_{c,scr}$. Note the very clear step structure in $v_{xc,scr}^{resp}$. This potential is almost constant within the 1s-shell and drops rapidly to zero at the atomic shell boundary between the 1s and the 2s shell at a radial distance of about 1 bohr. As can be seen from the graph of $v_{xc} - v_{x,scr}^{OPM}$ this step structure is somewhat smoothed by correlation effects but, as these effects are less important than the exchange effects, the step structure is still clearly visible. So the effect of correlation is mainly a smoothing of the atomic shell structure due to the fact that the correlation potential has a dip at the atomic shell boundaries [48, 74]. This behavior of the correlation potential is related to the fact that at the atomic shell boundaries the exchange hole is not so strongly localized around the reference position as when the latter is within a shell. This makes the effect of the correlation hole more noticeable at the atomic shell boundaries. A more detailed discussion of these points for the case of the Be and Ne atoms is given in [74].

5.4 Molecular Bond Midpoint Properties

The number of studies on the exact exchange-correlation potential for molecular systems is very limited. Except for a thorough study by Buijse et al. [43] on the

hydrogen molecule and a recent work by Gritsenko et al. [59] on the hydrogen molecule and lithium hydride LiH, we are not aware of any study on molecular exchange-correlation potentials. Such a study is however of great interest to workers in quantum chemistry where the use of density functional methods has become commonplace, as it may help to explain the success of the presently used density functionals and also show their limitations.

In molecular systems new types of correlation come into play as compared to the atomic situation. In the case of molecular dissociation the so-called left-right correlation will cause a correct distribution of the electrons over the atomic fragments in the dissociation limit [75]. This correlation shows up as large changes in the molecular wavefunction in the bond region of dissociating molecules. How this influences the exchange-correlation potential we will discuss in the following.

For a spin restricted two-electron system such as the hydrogen molecule the occupied orbitals can explicitly be expressed in the electron density as $\psi_i = \sqrt{\rho/2}$. Substituting this in the Kohn–Sham equations then yields an explicit expression of the Kohn–Sham potential expressed in the exact ground state density. Buijse et al. [43] carried out a thorough investigation of this potential for the hydrogen molecule at various distances. The basic quantity in the analysis of Buijse et al. is the conditional probability amplitude $\Phi(\mathbf{r}_2, \dots, \mathbf{r}_N | \mathbf{r}_1)$ defined by [76, 77] as

$$\Phi(\mathbf{r}_2, \dots, \mathbf{r}_N | \mathbf{r}_1) = \frac{\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)}{\sqrt{\rho(\mathbf{r}_1)/N}} \quad (99)$$

where Ψ is the ground state wavefunction of the system. The amplitude gives a description of the $(N - 1)$ -electron system when one of the electrons is known to be at position $\mathbf{r}_1$. The amplitude squared gives the probability that the other electrons are at positions $\mathbf{r}_2, \dots, \mathbf{r}_N$ if one electron (the reference electron) is known to be at position $\mathbf{r}_1$. All the correlation effects of the system are contained in this quantity.

These correlation effects particularly show up in this case of the hydrogen molecule when we move the position of the reference electron along the bond axis from one atom to the other atom. Due to the Coulomb correlation of the electrons we have that, if one electron is known to be at a given atom, then the probability amplitude is large that the other electron will be at the other atom. This changes rapidly when the reference electron crosses the bond midpoint region because in that case the other electron has to switch quickly from one atom to the other atom. A quantity which measures this change in conditional amplitude (the so-called left-right correlation effect) as we move our reference electron is the so-called kinetic potential defined by

$$v_{kin}(\mathbf{r}_1) = \frac{1}{2} \int |\nabla_1 \Phi|^2 d\mathbf{r}_2 \cdots d\mathbf{r}_N . \quad (100)$$

This potential is clearly positive. The origin of the name of this potential stems

from the fact that it contributes to the kinetic energy of the system which is given by

$$T = \frac{1}{8} \int \frac{(\nabla \rho)^2}{\rho} d\mathbf{r} + \int \rho(\mathbf{r}) v_{kin}(\mathbf{r}) d\mathbf{r} . \quad (101)$$

This follows directly from the definition of the kinetic energy and the formula at Eq. (99). Note that the first term in the above formula is the von Weiszäcker kinetic energy $T_W[\rho]$ which for a two-electron system is equal to the Kohn-Sham kinetic energy $T_s[\rho]$. The term with v_{kin} therefore contributes to the correlation energy E_c of the system. For the general case of a multi-electron system E_c can be expressed as [74]

$$E_c[\rho] + \frac{1}{2} \int \rho(\mathbf{r}) v_{c,scr}(\mathbf{r}) d\mathbf{r} + T_c[\rho] \quad (102)$$

$$T_c[\rho] = \int \rho(\mathbf{r}) (v_{kin}(\mathbf{r}) - v_{s,kin}(\mathbf{r})) d\mathbf{r} = \int \rho(\mathbf{r}) v_{c,kin}(\mathbf{r}) d\mathbf{r} \quad (103)$$

where $v_{c,scr}$ is the potential of the Coulomb hole calculated at full strength of interaction $\lambda = 1$ and $v_{s,kin}$ is the kinetic potential corresponding to the Kohn-Sham Slater determinant wave function. From the functional differentiation of Eqs. (102) and (103) correlation potential v_c can be obtained as

$$v_c(\mathbf{r}) = v_{c,scr}(\mathbf{r}) + v_{c,scr}^{resp}(\mathbf{r}) + v_{c,kin}(\mathbf{r}) + v_{c,kin}^{resp}(\mathbf{r}) . \quad (104)$$

As the Kohn-Sham wave function has a delocalized exchange hole, and therefore lacks the left-right correlation, $v_{s,kin}$ is expected to display different bond midpoint features to v_{kin} . In fact, $v_{s,kin}$ is zero for two-electron systems, so that $T_c[\rho]$ and v_c reduce in this case to

$$T_c[\rho] = \int \rho(\mathbf{r}) v_{kin}(\mathbf{r}) d\mathbf{r} \quad (105)$$

$$v_c(\mathbf{r}) = v_{c,scr}(\mathbf{r}) + v_{c,scr}^{resp}(\mathbf{r}) + v_{kin}(\mathbf{r}) + v_{kin}^{resp}(\mathbf{r}) . \quad (106)$$

As has been shown in [43], v_{kin} is an important constituent of the Kohn-Sham correlation potential. In the dissociation limit v_{kin} even becomes equal to the correlation potential v_c in the bond midpoint region. By numerical calculation the following properties of the kinetic potential were observed [43, 78].

First of all this potential is peaked on the bond midpoint. As a result of this the total exchange-correlation potential is also peaked in this region. This peak in v_{kin} is not surprising from its definition. The changes in the conditional amplitude as we move our reference electron is the largest in the bond midpoint region as explained before. Secondly the peak in the kinetic potential gets higher when we dissociate the molecule. This is also what one expects since the left-right correlation effects grow stronger as we dissociate. This can also be seen from the well-known Hartree-Fock error for a dissociating system. The Hartree-Fock one-determinant wavefunction upon dissociation no longer gives an

accurate description of the division of the electrons over the atomic fragments by putting too much weight on ionic terms [79].

Let us discuss this property of the Hartree–Fock approximation in more detail in connection with the properties of the GGA exchange and correlation potentials in molecular systems, in particular the bond midpoint region. As has been discussed, the correlation potential exhibits a peak structure in dissociating molecules which is related to the left-right correlation effect. This left-right correlation effect consists mainly of the so-called near-degeneracy or non-dynamical correlation. The lack of this type of correlation is the main reason for the failure of the Hartree–Fock approximation in dissociating molecules. As is well-known to quantum chemists, this type of correlation is readily described by extending the Hartree–Fock wave function by a smaller number of proper dissociation Slater determinants. This has a considerable effect on the shape of the exchange-correlation hole. From a completely delocalized hole in the Hartree–Fock approximation (Fermi hole) it changes to a hole that is more or less localized around the reference electron [75]. This feature is illustrated in Fig. 8 (taken from [75] and [79]) for the dissociating hydrogen molecule. If we now turn to density functional theory we observe that the LDA and GGA *exchange* holes are always localized around the reference electron. This means that they not only give a pretty accurate description of the *exchange* hole in atoms but also describe the long range non-dynamical *correlation* in dissociating molecules. This explains the fact that the exchange functionals which are constructed to reproduce exchange energies of atoms yield reasonable binding energies for molecules, even when no gradient corrected correlation functionals are used in the calculation [6]. The additional correlation functionals such as the PW91 correlation functional yield correct correlation energies in atoms and have a correlation hole which is always located around the reference electron and may therefore be regarded as providing the remaining dynamical correlation (as well as part of the correlation energy contained in the kinetic energy functional).

From the above we can expect that, if the functional derivatives of the GGA functionals give a good representation of the properties of the exchange-correlation hole, the near-degeneracy correlation properties responsible for the bond midpoint peak will show up in the exchange potentials rather than the correlation potentials.

We illustrate the behavior of v_c and its components v_{kin} and $v_{c,scr}$ (denoted as $v_{cond} - v^{HF}$) for the hydrogen molecule in Figs. 9 and 10. Figure 9 displays v_{kin} and v_c (denoted as v_{corr}^{KS}) at an equilibrium distance of 1.4 bohr and Fig. 10 displays the same quantities at a bond distance of 5 bohr. The sum ($v_{c,scr}^{resp} + v_{kin}^{resp}$) denoted as v^{N-1} is also presented. The most noticeable features in Figs. 9 and 10 are the wells of $v_{c,scr}$ and v_c around the H nucleus and the peaks of v_{kin} and v_c at the bond midpoint. From these plots we can clearly see the growth of the peak structure at the bond midpoint upon dissociation of the molecule. v_c inherits the bond midpoint peak of v_{kin} and the well around the nucleus of $v_{c,scr}$, with the height of the peak and the depth of the well being very close (at the bond distance of 5 bohr) to those of v_{kin} and $v_{c,scr}$, respectively.

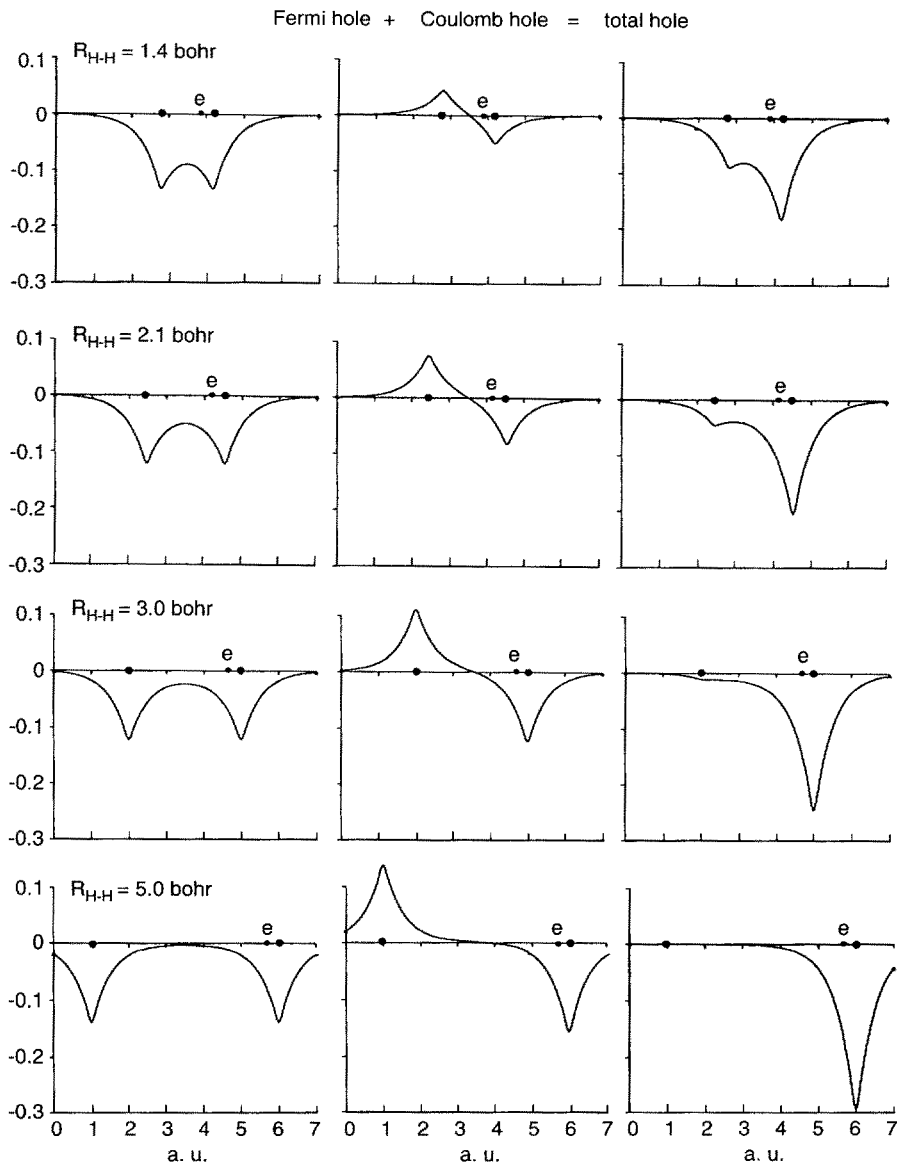


Fig. 8. Fermi hole, Coulomb hole and total hole in H_2 at various bond distances. In all plots the reference electron is placed at 0.3 bohr at the left of the right H atom

In the limit of infinite bond distance the width of the peak of the potential v_{kin} approaches zero and the height of the peak approaches a value equal to the ionization energy of the molecule [43, 78]. The asymptotic expression for $T_c = T - T_s$ can be obtained with T calculated with the Heitler-London

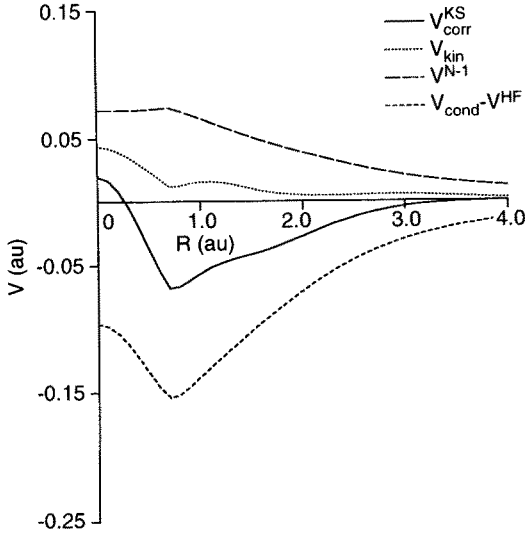


Fig. 9. Correlation potential $V_{\text{corr}}^{\text{KS}}$ and its components for H_2 at the equilibrium bond distance of 1.4 a.u. Potentials are plotted along the bond axis as functions of the distance R from the bond midpoint. The H nucleus is at $R = 0.7$ a.u.

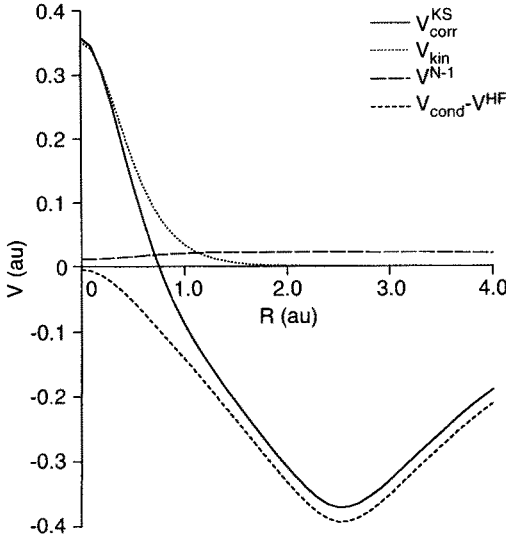


Fig. 10. Correlation potential $V_{\text{corr}}^{\text{KS}}$ and its components for H_2 at the bond distance of 5.0 a.u. Potentials are plotted along the bond axis as functions of the distance R from the bond midpoint. The H nucleus is at $R = 2.5$ a.u.

wavefunction [80] and T_s calculated with the minimal basis Slater determinant wavefunction, which yields

$$T_c = \frac{2(T_a S_{ab} - T_{ab})(1 - S_{ab})}{(1 + S_{ab})(1 + S_{ab}^2)}. \quad (107)$$

Here T_a, T_{ab} are the kinetic integrals

$$T_a = -\frac{1}{2} \int a^*(\mathbf{r}) \nabla^2 a(\mathbf{r}) d\mathbf{r} \quad (108)$$

$$T_{ab} = -\frac{1}{2} \int a^*(\mathbf{r}) \nabla^2 b(\mathbf{r}) d\mathbf{r} \quad (109)$$

and S_{ab} is the overlap integral

$$S_{ab} = \int a^*(\mathbf{r}) b(\mathbf{r}) d\mathbf{r} \quad (110)$$

of the 1s-type atomic orbitals $a(\mathbf{r})$ and $b(\mathbf{r})$ located on the H atoms A and B, respectively. T_c for the hydrogen molecule decreases with the decreasing S_{ab} and T_{ab} at longer bond distances and it becomes zero in the infinite separation limit, but the traditional correlation energy $T - T^{HF}$ is large (equal to minus the large correlation energy of -0.2565 a.u. [75]).

This can also be deduced from a coupling constant argument with the use of Eq. (15) [81]. In this equation T_c is expressed in terms of the coupling constant integrated pair-correlation function and the full ($\lambda = 1$) pair-correlation function. The Hamiltonian at coupling constant λ consists of a two-particle interaction term λ/r_{12} and an external potential v_λ which is defined in such a way that the density remains the same for all λ . Let us now consider the H_2 -molecule at large bond distance R . The interaction term λ/r_{12} for $\lambda > 0$ will favor wavefunction configurations in which the two electrons are residing on different atoms (i.e. the Heitler-London wavefunction). The density corresponding to this ground state wavefunction Ψ_λ will be exactly equal to the density corresponding to the wavefunction Ψ_1 at full coupling strength, which at large R is a wavefunction describing two weakly interacting hydrogen atoms. From these considerations it follows that

$$\lim_{R \rightarrow \infty} \Psi_\lambda = \Psi_1 \quad \text{if } \lambda > 0 \quad (111)$$

while the external potential v_λ in the infinite separation limit $R \rightarrow \infty$ approaches a value equal to its $\lambda = 1$ value v_1 around each hydrogen atom. Note that the above relation is not true for the $\lambda = 0$ wavefunction which will be just a Kohn-Sham determinant with a doubly occupied σ_g orbital. The $\lambda = 0$ region however becomes unimportant in the coupling constant integration for the pair-correlation function and we have

$$\begin{aligned} \lim_{R \rightarrow \infty} \int_0^1 g_{\sigma_1 \sigma_2}^2([\{\rho_\sigma\}]; \mathbf{r}_1, \mathbf{r}_2) d\lambda &= g_{\sigma_1 \sigma_2}^1([\{\rho_\sigma\}]; \mathbf{r}_1, \mathbf{r}_2) d\lambda \\ &= g_{\sigma_1, \sigma_2}^1([\{\rho_\sigma\}]; \mathbf{r}_1, \mathbf{r}_2) \end{aligned} \quad (112)$$

and it follows that T_c becomes zero in the infinite dissociation limit. As an illustration we plot in Fig. 11 several kinetic energy terms as a function of the bond distance corresponding to the dissociating H_2 -molecule. The quantity T^{CI} represents the nearly exact kinetic energy calculated from a full-CI wavefunction. The quantity T_s corresponds to the Kohn-Sham kinetic energy calculated from the CI-density. We further plotted the kinetic energy T^{HF} corres-

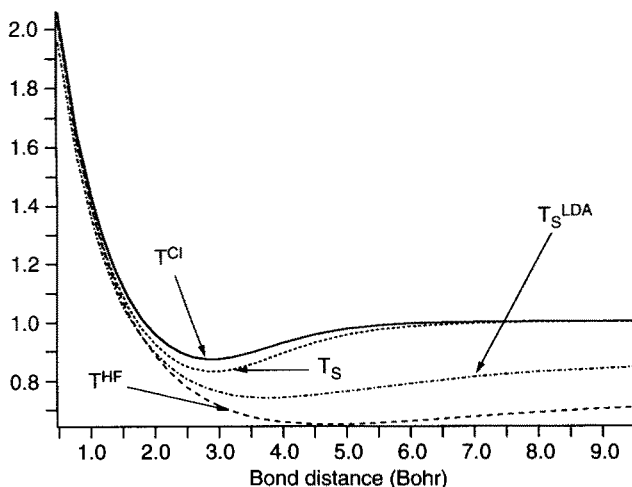


Fig. 11. The CI, HF, LDA and Kohn–Sham kinetic energies (in a.u.) for H_2 as functions of the bond distance

ponding to a Hartree–Fock wave-function and the LDA Kohn–Sham kinetic energy T_s^{LDA} . The difference $T^{CI} - T_s$ represents the quantity T_c . As can be deduced from this plot T_c becomes zero in the dissociation limit.

The conclusions reached here apply equally well to general multi-electron homonuclear molecules. In this case the value of T_c in the dissociation limit becomes equal to the sum of the T_c contributions of the atomic fragments. The λ -integrated exchange-correlation hole for a reference electron on one of the atomic fragments will then be equal to the λ -integrated hole of the atom itself. The properties of the exchange-correlation in heteronuclear molecules are discussed in the next section.

5.5 Derivative Discontinuities and Charge transfer

Up to now we have been discussing the local properties of the exchange-correlation potential as a function of the spatial coordinate $\mathbf{r}$. However there are also important properties of the exchange-correlation potential as a function of the particle number. In fact there are close connections between the properties as a function of the particle number and the local properties of the exchange-correlation potential. For instance the bumps in the exchange-correlation potential are closely related to the discontinuity properties of the potential as a function of the orbital occupation number [38]. For heteronuclear diatomic molecules for example there are also similar connections between the bond midpoint shape of the potential and the behavior of the potential as a function of the number of electrons transferred from one atomic fragment to another when

the two atoms are brought together [82, 83]. Another important physical process where the particle number is changed is ionization.

More insight into these processes is obtained by studying the particle number dependent properties of density functionals. This of course requires a suitable definition of these density functionals for fractional particle number. The most natural one is to consider an ensemble of states with different particle number (such an ensemble is for instance obtained by taking a zero temperature limit of temperature dependent density functional theory [84]). We consider a system of $N + \omega$ electrons where N is an integer and $0 \leq \omega \leq 1$. For the corresponding electron density we then have

$$\int \rho(\mathbf{r}) d\mathbf{r} = N + \omega . \quad (113)$$

This density can be obtained from the ensemble density matrix

$$\hat{D}_\omega = (1 - \omega) \hat{D}_N + \omega \hat{D}_{N+1} \quad (114)$$

where $\hat{D}_N$ and $\hat{D}_{N+1}$ are N and $N + 1$ -particle density matrices. We now extend our definition of the functional F_L to fractional particle number with

$$F^\omega[\rho] = \min_{\hat{D}_\omega \rightarrow \rho} \text{Tr} \hat{D}_\omega (\hat{T} + \hat{W}) \quad (115)$$

where the minimum is searched over all density matrices of the form of Eq. (114). The energy functional is then defined as

$$E_v^\omega[\rho] = F^\omega[\rho] + \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} . \quad (116)$$

The ground state energy of this fractional system is then obtained by

$$E_{N+\omega} = \min_{\rho} E_v^\omega[\rho] \quad (117)$$

where the minimum is searched over all densities integrating to $N + \omega$ electrons. It is however readily shown from the definition of E_v^ω that the ground state energy of the $N + \omega$ -electron system is given by [1]

$$E_{N+\omega} = (1 - \omega) E_N + \omega E_{N+1} \quad (118)$$

where E_N and E_{N+1} are the ground state energies of the N and $N + 1$ -electron system. The corresponding ground state density is given by

$$\rho_{N+\omega}(\mathbf{r}) = (1 - \omega) \rho_N(\mathbf{r}) + \omega \rho_{N+1}(\mathbf{r}) \quad (119)$$

where ρ_N and ρ_{N+1} are the ground state densities of the N - and $N + 1$ -electron system.

Corresponding to the interacting $N + \omega$ -electron system we now define a Kohn–Sham potential $v_s(\mathbf{r}; N + \omega)$. This is a local potential defined by the requirement that it must yield the same density $\rho_{N+\omega}$ in a fictitious noninteract-

ing Kohn–Sham system:

$$[-\frac{1}{2}\nabla^2 + v_s([\rho_{N+\omega}]; \mathbf{r})] \phi_i(\mathbf{r}) = \varepsilon_i(N + \omega) \phi_i(\mathbf{r}) \quad (120)$$

$$\rho_{N+\omega}(\mathbf{r}) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2 + \omega |\phi_{N+1}(\mathbf{r})|^2 . \quad (121)$$

So the highest occupied Kohn–Sham orbital has a fractional occupation number ω . The fact that v_s is uniquely defined by $\rho_{N+\omega}$ follows directly from the Hohenberg–Kohn theorem applied to the non-interacting system. The proof of the Hohenberg–Kohn theorem for systems with noninteger number of electrons proceeds along the same lines as for systems with integer particle number (alternatively it can be obtained from the zero temperature limit of temperature dependent density functional theory [82]). We further split up v_s as

$$v_s(\mathbf{r}; N + \omega) = v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}(\mathbf{r}; N + \omega) \quad (122)$$

(for convenience we use the notation $v_s(\mathbf{r}; N + \omega) = v_s([\rho_{N+\omega}]; \mathbf{r})$). This equation actually defines v_{xc} . One can, however, show that v_{xc} is obtained as the functional derivative of the exchange-correlation energy functional E_{xc}^ω defined by

$$E_{xc}^\omega[\rho] = F^\omega[\rho] - T_s^\omega[\rho] - \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' . \quad (123)$$

However we do not need this property in the following discussion. Now as v_s is defined up to a constant we are free to choose a suitable value. As usual this constant is fixed by requiring the potential to be zero at infinity:

$$\lim_{r \rightarrow \infty} v_s(\mathbf{r}; N + \omega) = 0 . \quad (124)$$

As the Hartree and external potential also vanish in this limit we have equivalently

$$\lim_{r \rightarrow \infty} v_{xc}(\mathbf{r}; N + \omega) = 0. \quad (125)$$

Using this equation we find the following asymptotic behavior of the Kohn–Sham orbital densities:

$$|\phi_i(\mathbf{r})|^2 \rightarrow e^{-2\sqrt{-2\varepsilon_i}r} \quad (r \rightarrow \infty) . \quad (126)$$

As the fractionally occupied orbital ϕ_{N+1} has the slowest decay, the asymptotic behavior of the density for $0 < \omega \leq 1$ is determined by this orbital and given by

$$\rho_{N+\omega}(\mathbf{r}) \rightarrow e^{-2\sqrt{2\varepsilon_{N+1}(N+\omega)}r} \quad (r \rightarrow \infty) . \quad (127)$$

On the other hand we know that $\rho_{N+\omega}$ is a linear combination of N - and $N + 1$ -particle densities for which the asymptotic behavior is determined by

the ionization energies I_N and I_{N+1} . One has

$$\rho_{N+1}(\mathbf{r}) \rightarrow e^{-2\sqrt{2I_{N+1}}r} \quad (r \rightarrow \infty) \quad (128)$$

with a similar equation for ρ_N . As the ionization energy for an $N+1$ -particle system is smaller than that of an N -particle system we have $I_{N+1} < I_N$. This means that ρ_{N+1} has a slower asymptotic decay. Therefore for $0 < \omega \leq 1$ we have

$$\rho_{N+\omega}(\mathbf{r}) \rightarrow e^{-2\sqrt{2I_{N+1}}r} \quad (r \rightarrow \infty) . \quad (129)$$

If we compare this with Eq. (127) we find

$$\varepsilon_{N+1}(N + \omega) = -I_{N+1} = \varepsilon_{N+1}(N + 1) \quad (0 < \omega \leq 1) \quad (130)$$

which means that the eigenvalue of the highest occupied Kohn–Sham orbital is independent of the occupation number ω for $0 < \omega \leq 1$. This interesting conclusion has been verified numerically in the exchange-only OPM model by Krieger et al. [21] (this conclusion has also interesting consequences for the Slater transition state method [85] for the calculation of excitation energies.)

Let us now turn to the properties of v_{xc} as a function of ω . We compare the potentials $v_{xc}(N + \omega)$ to the potential $v_{xc}(N)$ for small ω . The densities produced by these potentials are then similar in regions where the density ρ_N dominates $\rho_{N+\omega}$. For spherical systems one has for example a radius $R(\omega)$ for which $\rho_{N+\omega} \approx \rho_N$ for $r < R(\omega)$. An appropriate definition of such a radius is for example given by the equation

$$(1 - \omega)\rho_N(R(\omega)) = \omega\rho_{N+1}(R(\omega)) . \quad (131)$$

If we use the fact that ω is small and the asymptotic property

$$\rho_N(\mathbf{r}) \rightarrow A_N e^{-\alpha_N r} \quad (r \rightarrow \infty) \quad (132)$$

where $\alpha_N = 2\sqrt{2I_N}$, one finds

$$R(\omega) = (\alpha_N - \alpha_{N+1})^{-1} \ln \frac{A_N}{A_{N+1}} \frac{1}{\omega} \rightarrow -(\alpha_N - \alpha_{N+1})^{-1} \ln \omega \quad (\omega \downarrow 0) \quad (133)$$

which becomes infinite as expected when ω approaches zero. As $v_{xc}(N + \omega)$ and $v_{xc}(N)$ generate the same density in the region $r < R(\omega)$ they can at most differ by a constant Δ in this region. For $r \rightarrow \infty$ both $v_{xc}(N + \omega)$ and $v_{xc}(N)$ become zero by definition. Therefore one has [83]

$$v_{xc}(\mathbf{r}; N + \omega) - v_{xc}(\mathbf{r}; N) = \begin{cases} \Delta & \text{if } r < R(\omega) \\ 0 & \text{if } r \geq R(\omega) \end{cases} . \quad (134)$$

In the limit $\omega \downarrow 0$ the radius $R(\omega)$ becomes infinite and both potentials differ by a constant Δ everywhere. We will now show that Δ is unequal to zero. If we now insert $v_{xc}(N + \omega) = v_{xc}(N) + \Delta$ in the Kohn–Sham equations for the $N + \omega$ -particle system and use the fact that for small ω the orbitals in the region

$r < R(\omega)$ are equal to the orbitals of the N -particle system, we obtain

$$\varepsilon_i(N + \omega) = \varepsilon_i(N) + \Delta \quad (\omega \downarrow 0) . \quad (135)$$

In particular we have for $i = N + 1$ that

$$\Delta = \lim_{\omega \downarrow 0} (\varepsilon_{N+1}(N + \omega) - \varepsilon_{N+1}(N)) = -I_{N+1} - \varepsilon_{N+1}(N) \quad (136)$$

where we used the ω -independence of $\varepsilon_{N+1}(N + \omega)$ of Eq. (130). Therefore Δ is in general nonzero. Using $\varepsilon_{N+1}(N + 1) = -I_{N+1}$ one therefore finds the following discontinuity in v_{xc} :

$$\lim_{\omega \downarrow 0} v_{xc}(\mathbf{r}; N + \omega) - v_{xc}(\mathbf{r}; N) = \varepsilon_{N+1}(N + 1) - \varepsilon_{N+1}(N) . \quad (137)$$

Numerical results on Eq. (136) can be found in [82]. The reference also shows that the change from 0 to Δ in the difference $v_{xc}(N + \omega) - v_{xc}(N)$ is quite rapid and has a steplike behavior with the step moving to infinity as $\omega \downarrow 0$.

From the above considerations we can now also see how the atomic shell structure is related to the discontinuities in v_{xc} as a function of the orbital occupation. As a new shell is filled with fractional occupation ω a steplike function is added to the Kohn–Sham potential. This step function has value Δ for $r < R(\omega)$ and becomes zero for larger values of r . As ω increases and the shell gets filled the step moves inward. If the shell is finally completely filled the step function stabilizes at a value of r which is at the atomic shell boundary of the last two filled atomic shells [38]. The atomic shell structure is thus introduced by adding a series of step functions. This is perfectly consistent with our former results in which we showed that the short range part of v_{xc} which was responsible for the atomic shell structure consists of a superposition of steps. This conclusion, which has also been reached by Krieger et al. [38], shows that in order to obtain an accurate exchange–correlation potential correctly describing the atomic shell structure one must construct exchange–correlation functionals with the correct derivative discontinuities at integer particle number. This is however rather difficult using density functionals depending on the total density or its gradients. However, as shown by Krieger et al. [21], one can construct accurate exchange–correlation potentials possessing the integer discontinuity property by using orbital-dependent exchange–correlation functionals.

We will now consider the consequences of the integer discontinuity for the chemical bonding situation. For this purpose we consider a system of two well-separated atoms A and B with different ionization energies [83]. We study the energy change in the system when charge is transferred from one atom to the other. For each atom we therefore have to study the change in total energy when we change the number of electrons. From Eq. (118) we find

$$\lim_{\omega \downarrow 0} \frac{\partial E_{N+\omega}}{\partial \omega} = E_{N+1} - E_N = -A_N \quad (138)$$

where A_N is the electron affinity of the N -electron system. So the right derivative of $E_{N+\omega}$ yields minus the electron affinity. Let us now calculate the left derivative. If in Eq. (118) we make the replacements $N \rightarrow N - 1$ and $\omega \rightarrow 1 - \omega$ we obtain

$$E_{N-\omega} = \omega E_{N-1} + (1 - \omega) E_N . \quad (139)$$

From this equation we find

$$\lim_{\omega \downarrow 0} \frac{\partial E_{N-\omega}}{\partial \omega} = E_{N-1} - E_N = I_N \quad (140)$$

where I_N is the ionization energy of the N -electron system. This means that the left derivative of $E_{N+\omega}$ is given by minus the ionization energy of the system. We therefore have

$$\mu(N + \omega) = \frac{\partial E_{N+\omega}}{\partial \omega} = \begin{cases} -A_N & \text{if } 0 < \omega \leq 1 \\ -I_N & \text{if } -1 < \omega \leq 0 . \end{cases} \quad (141)$$

We thus find that the derivative of the total energy with respect to the particle number is a discontinuous function with discontinuities located at the integer particle numbers N . We now turn back to the problem of two different atoms at large distance from each other. In this system the discontinuity of μ is essential for keeping both atoms neutral. This is readily shown. Suppose μ is a continuous function of the particle number. Without restriction, we can assume that $\mu(A) > \mu(B)$. Then removing a positive number $\delta\omega$ of electrons from A to B yields the total energy change $\delta E = (\mu(B) - \mu(A))\delta\omega < 0$. This leads to the paradoxical result that the total energy is minimized with a net positive charge on A and a net negative charge on B [86]. However using Eq. (141) it is easily seen that the total energy

$$E = E_{A-\omega} + E_{B+\omega} \quad (142)$$

is minimized for $\omega = 0$. The discontinuous behavior of the energy as a function of the particle number is therefore essential for a correct division of charge over the atomic fragments. Functionals which lack this discontinuity, such as the LDA and GGA, will therefore lead to an incorrect division of charge over the atomic fragments. This can be explicitly shown for the local density approximation [38, 82] which gives for the NaCl molecule at large distance an energy minimum for $\text{Na}^{+0.4}\text{Cl}^{-0.4}$. Explicitly orbital dependent approaches such as the OPM approach, the Krieger–Li–Iafrate approach and the Perdew–Zunger self-interaction-correction (SIC) method [87] however yield correct neutral fragments.

Let us now take closer look at the relation of this charge transfer discontinuity and the shape of the exchange-correlation potential. We again take the example of two atoms A and B with ionization energies I_A and I_B at a large interatomic distance R_{AB} [83]. We assume that $I_A < I_B$. These ionization energies are equal to minus the highest occupied Kohn–Sham orbital energies of the

atomic fragments. We will now show that flow of charge from A to B is prevented by the formation of a region of an additional constant positive exchange-correlation potential of value $I_B - I_A$ around atom B . This shifts the orbital energies of atom B by a constant and makes the highest occupied orbital energy of atom B equal to the one of atom A .

Now the molecule $M = AB$ at large separation has an ionization energy I_M equal to the lowest ionization energy of one of the atomic fragments, in our case $I_M = I_A$. This means that the highest occupied molecular orbital ϕ_M satisfies

$$\left[-\frac{1}{2}\nabla^2 + v_s^M(\mathbf{r}) \right] \phi_M(\mathbf{r}) = -I_M \phi_M = -I_A \phi_M \quad (143)$$

where v_s^M is the molecular Kohn–Sham orbital. This further implies that the asymptotic decay of the density ρ_M of the molecule M is determined by the decay of atomic density ρ_A of atom A . The density of atom A will have a dominant contribution at distances from the molecular system large compared to the interatomic distance R_{AB} . Around atom A ϕ_M will be approximately equal to the highest atomic orbital ϕ_A of atom A and around atom B it will be approximately equal to the highest atomic orbital ϕ_B of atom B . We therefore have around A

$$\left[-\frac{1}{2}\nabla^2 + v_s^M(\mathbf{r}) \right] \phi_M(\mathbf{r}) = -I_M \phi_A = -I_A \phi_A \quad (144)$$

which means that v_s^M is close to the Kohn–Sham potential v_s^A of atom A which will go to zero at large distance from atom A . Around atom B we have however

$$\left[-\frac{1}{2}\nabla^2 + v_s^M(\mathbf{r}) \right] \phi_M(\mathbf{r}) = -I_M \phi_B = -I_A \phi_B . \quad (145)$$

Now we know that the asymptotic decay of the density far from atom B (but not so far that ρ_B still dominates the molecular density ρ_M) is determined by the ionization energy I_B . The asymptotic decay of the density ρ_B is however also determined by the highest occupied Kohn–Sham orbital ϕ_B . Then Eq. (145) implies that the Kohn–Sham potential cannot go to zero in the asymptotic region of atom B otherwise the density decay around atom B would be determined by I_A . As the Hartree and the external potential go to zero in the outer asymptotic region it follows from Eq. (145) that the only possibility is that the molecular exchange-correlation potential v_{xc}^M around atom B is given by

$$v_{xc}^M(\mathbf{r}) = v_{xc}^B(\mathbf{r}) + I_B - I_A \quad (146)$$

where v_{xc}^B is the exchange-correlation potential of atom B in the absence of atom A . We therefore see that the exchange-correlation potential around an isolated atom can change by a finite amount upon introduction of an atom with a different ionization energy at an arbitrarily large distance.

Density functionals without integer discontinuity such as the LDA or GGA functionals do not show this kind of behavior. Within these approximations

charge would flow from A to B until the highest occupied orbital energies of fragments A and B become equal and therefore no constant shift of the exchange-correlation potential arises. It may therefore well be possible to improve the current density functionals in chemical bonding situations by the inclusion of orbital-dependent terms.

6 Approximate Kohn–Sham Potentials

6.1 The Weighted Density Approximation

An important concept in DFT is the exchange-correlation hole ρ_{xc} and its coupling constant average. The importance follows immediately from the fact that the exchange-correlation energy E_{xc} can be directly expressed in terms of this hole function. Therefore a considerable amount of work has been carried out aiming to improve existing density functionals by direct approximations of the exchange and exchange-correlation hole [32–34]. The current GGAs of Perdew and Wang for instance are derived by putting exactly known constraints on the exchange-correlation hole obtained from the gradient expansion. This is a semi-local approach as the properties of GGA exchange-correlation holes depend mainly on the local density and the gradient of the density at the position of the reference electron. A completely nonlocal approach which also directly approximates the exchange-correlation hole is the weighted density approximation developed by Alonso and Girifalco [90,91] and Gunnarsson et al. [92,93]. The exchange-correlation hole ρ_{xc} is expressed in the coupling constant averaged pair-correlation function by

$$\rho_{xc\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2) = \rho_{\sigma_2}(\mathbf{r}_2)(\bar{g}_{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2) - 1). \quad (147)$$

In the WDA $\bar{g}$ is approximated (for a spin-unpolarized system) by

$$\bar{g}_{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2) = \tilde{g}_{\sigma_1\sigma_2}(|\mathbf{r}_1 - \mathbf{r}_2|; \bar{\rho}(\mathbf{r}_1)) \quad (148)$$

where $\bar{\rho}$ is a certain average density and $\tilde{g}$ a suitable approximation usually determined in order to satisfy known exact properties. The functional dependence of $\bar{\rho}$ on the spin densities ρ_σ is determined from the sum rule

$$\int \rho_{\sigma_2}(\mathbf{r}_2)(\tilde{g}_{\sigma_1\sigma_2}(|\mathbf{r}_1 - \mathbf{r}_2|; \bar{\rho}(\mathbf{r}_1)) - 1) d\mathbf{r}_2 = -\delta_{\sigma_1\sigma_2} \quad (149)$$

(in the case of a spin polarized system one has two average densities $\bar{\rho}_\uparrow$ and $\bar{\rho}_\downarrow$). The exchange-correlation functional now becomes

$$E_{xc}[\{\rho_\sigma\}] = \frac{1}{2} \sum_{\sigma_1\sigma_2} \int \frac{\rho_{\sigma_1}(\mathbf{r}_1)\rho_{\sigma_2}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} (\tilde{g}_{\sigma_1\sigma_2}(|\mathbf{r}_1 - \mathbf{r}_2|; \bar{\rho}(\mathbf{r}_1)) - 1) d\mathbf{r}_1 d\mathbf{r}_2. \quad (150)$$

From this expression one obtains the exchange-correlation potential by functional differentiation

$$\begin{aligned}
 v_{xc\sigma_1}(\mathbf{r}_1) = & \frac{1}{2} \sum_{\sigma_2} \int \frac{\rho_{\sigma_2}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} (\tilde{g}_{\sigma_1\sigma_2}(|\mathbf{r}_1 - \mathbf{r}_2|; \bar{\rho}(\mathbf{r}_1)) - 1) d\mathbf{r}_2 \\
 & + \frac{1}{2} \sum_{\sigma_2} \int \frac{\rho_{\sigma_2}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} (\tilde{g}_{\sigma_1\sigma_2}(|\mathbf{r}_1 - \mathbf{r}_2|; \bar{\rho}(\mathbf{r}_2)) - 1) d\mathbf{r}_2 \\
 & + \frac{1}{2} \sum_{\sigma_2\sigma_3} \int \frac{\rho_{\sigma_2}(\mathbf{r}_2)\rho_{\sigma_3}(\mathbf{r}_3)}{|\mathbf{r}_2 - \mathbf{r}_3|} \frac{\partial \tilde{g}_{\sigma_2\sigma_3}}{\partial \bar{\rho}}(|\mathbf{r}_2 - \mathbf{r}_3|; \bar{\rho}(\mathbf{r}_2)) \\
 & \times \frac{\delta \bar{\rho}(\mathbf{r}_2)}{\delta \rho_{\sigma_1}(\mathbf{r}_1)} d\mathbf{r}_2 d\mathbf{r}_3
 \end{aligned} \tag{151}$$

where the derivative $\delta \bar{\rho}/\delta \rho$ is obtained by differentiation of the sum rule [94, 95]. The first term in the above equation has a long range asymptotic behavior of $-1/2r$ in finite systems due to the fulfillment of the sum rule. However, due to the fact that the approximation at Eq. (148) does not exhibit the exact symmetry property $\tilde{g}(\mathbf{r}_1, \mathbf{r}_2) = \tilde{g}(\mathbf{r}_2, \mathbf{r}_1)$, the second term decays faster than Coulombic (for plots of these separate parts of v_{xc} in atoms see [94]). Such a behavior could be corrected using symmetric approximations to the pair-correlation function, for instance by using the argument $\bar{\rho}(\mathbf{r}_1) + \bar{\rho}(\mathbf{r}_2)$ instead of $\bar{\rho}(\mathbf{r}_1)$ [96]. Another way to correct the potential is to make the WDA approximation after functional differentiation. One then obtains [97, 98]

$$\begin{aligned}
 v_{xc\sigma_1}(\mathbf{r}_1) = & \sum_{\sigma_2} \int \frac{\rho_{\sigma_2}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} (\tilde{g}_{\sigma_1\sigma_2}(|\mathbf{r}_1 - \mathbf{r}_2|; \bar{\rho}(\mathbf{r}_1)) - 1) d\mathbf{r}_2 \\
 & + \frac{1}{2} \sum_{\sigma_2\sigma_3} \int \frac{\rho_{\sigma_2}(\mathbf{r}_2)\rho_{\sigma_3}(\mathbf{r}_3)}{|\mathbf{r}_2 - \mathbf{r}_3|} \frac{\partial \tilde{g}_{\sigma_2\sigma_3}}{\partial}(|\mathbf{r}_2 - \mathbf{r}_3|; \bar{\rho}(\mathbf{r}_2)) \frac{\delta \bar{\rho}(\mathbf{r}_2)}{\delta \rho_{\sigma_1}(\mathbf{r}_1)} d\mathbf{r}_2 d\mathbf{r}_3 .
 \end{aligned} \tag{152}$$

In this nonvariational approach for v_{xc} the first term represents the potential of the exchange-correlation hole which has long range $-1/r$ asymptotics. We recognize the previously introduced splitup into the screening and screening response part of Eq. (69). As discussed in the section on the atomic shell structure the correct properties of the atomic shell structure in v_{xc} arise from a steplike behavior of the functional derivative of the pair-correlation function. However the WDA pair-correlation function does not exhibit this step structure in atoms and decays too smoothly [94]. A related deficiency is that the intershell contributions to E_{xc} are overestimated. Both deficiencies arise from the fact that it is very difficult to represent the atomic shell structure in terms of the smooth function $\bar{\rho}$. Substantial improvement can be obtained however from a WDA scheme dependent on atomic shell densities [92, 93]. In this way the overestimated intershell contributions are much reduced. Although this orbital-depen-

dent WDA scheme has never been applied self-consistently (which requires the functional derivatives of the orbital densities) we can predict that the short range part of v_{xc} involving the derivatives $\delta\tilde{g}/\delta\bar{\rho}_i$ will be different in different atomic shells and reproduce the required step structure for this potential.

Although the WDA scheme improves v_{xc} compared to LDA and GGA and is based on appealing physical ideas, it has practical disadvantages. The most important problem in actual calculations is determination of the average $\bar{\rho}$ from the sum rule. This requires a three-dimensional integration for each point $\mathbf{r}_1$ of the density argument $\bar{\rho}(\mathbf{r}_1)$. This makes the WDA expensive for other than spherical systems, such as molecules. The method has however been applied to solids in the atomic sphere approximation where it has been shown to correct substantially the overbinding of the LDA for the cohesive energies [99]. An application to molecular systems has recently been announced [95]. The question as to whether the method can compete with the accurate GGA results in molecular systems remains to be answered. In this respect the application to solid state problems, where the GGAs have less improvement over the LDA [100], seems more promising.

6.2 Gradient Approximations for the Potential

Gradient corrections to the local density approximation for the exchange-correlation energy E_{xc} in the form of the GGAs have been very successful within quantum chemistry in the calculation of molecular binding energies. However the corresponding exchange-correlation potential v_{xc} still has serious deficiencies, which shows that the success of the present GGAs is based on cancellation of local errors. It is therefore useful for further improvement of DFT to study the local properties of the various gradient corrected exchange and exchange-correlation potentials and to compare them with exact ones. This enables us to identify local errors of the gradient approximations which clearly show up in v_{xc} but which can cancel in E_{xc} . A severe test of the gradient functionals for the exchange energy in this respect is the reproduction of the atomic shell structure and the Coulombic asymptotics. A corresponding severe test for the accuracy of the gradient functionals for the correlation energy is the correct description of molecular bond midpoint properties in dissociating molecules.

We will treat the case of the exchange functional first. The functionals for correlation will be dealt with at the end of this section. For the discussion of gradient functionals for the exchange we introduce some commonly used notation:

$$k_F(\mathbf{r}) = (3\pi^2 \rho(\mathbf{r}))^{1/3} \quad (153)$$

$$x(\mathbf{r}) = \frac{1}{2^3} \frac{|\nabla\rho(\mathbf{r})|}{\rho(\mathbf{r})^{4/3}} \quad s(\mathbf{r}) = \frac{|\nabla\rho(\mathbf{r})|}{2k_F(\mathbf{r})\rho(\mathbf{r})} \quad (154)$$

$$\begin{aligned}\xi(\mathbf{r}) &= \left(\frac{\nabla \rho(\mathbf{r})}{2k_F(\mathbf{r})\rho(\mathbf{r})} \right)^2 = s(\mathbf{r})^2 & \eta(\mathbf{r}) &= \frac{\nabla^2 \rho(\mathbf{r})}{4k_F^2(\mathbf{r})\rho(\mathbf{r})} \\ y(\mathbf{r}) &= 2^{\frac{2}{3}} \frac{\nabla^2 \rho(\mathbf{r})}{\rho^{\frac{5}{3}}}.\end{aligned}\quad (155)$$

These are all dimensionless combinations of the density and the density gradients and Laplacians. This enables one to obtain the correct scaling properties of the exchange functional. We plot the quantities x and y for the krypton atom in Fig. 12. The exchange energy density within the LDA is given by

$$e_x^{LDA}(\rho) = -\frac{3k_F(\mathbf{r})}{4\pi} \rho(\mathbf{r}). \quad (156)$$

The gradient expansion for the exchange has the form [101]

$$E_x[\rho] = \int d\mathbf{r} e_x^{LDA}(\rho) (1 + c_{x2}\xi + c_{x4}[\eta^2 + c_{\eta\xi}^x \eta\xi + c_{\xi^2}^x \xi^2] + \dots) \quad (157)$$

in which we have displayed the terms up to fourth order. In this expression the coefficients $c_{x2} = 10/81$ and $c_{x4} = 146/2025$ are known from linear response theory. The coefficients $c_{\eta\xi}^x$ and $c_{\xi^2}^x$ which are determined from nonlinear response theory are not known, although some estimates have been given [101, 102]. In the following we leave out the spin dependence. The spin polarized form of the exchange functional is however directly obtained from the above expression by

$$E_x[\rho_\uparrow, \rho_\downarrow] = \frac{1}{2}(E_x[2\rho_\uparrow] + E_x[2\rho_\downarrow]) \quad (158)$$

which yields for the corresponding exchange potential

$$v_{x\sigma}([\rho_\sigma]; \mathbf{r}) = \frac{\delta E_x[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\sigma(\mathbf{r})} = v_x([2\rho_\sigma]; \mathbf{r}) \quad (159)$$

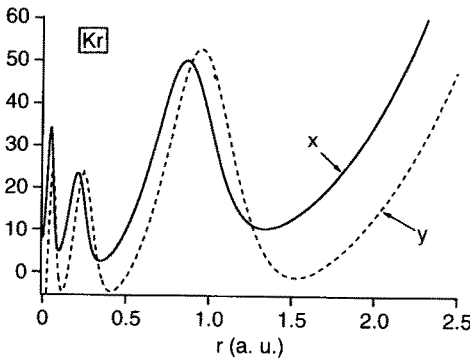


Fig. 12. Dimensionless arguments x and y for Kr

where

$$v_x([\rho]; \mathbf{r}) = \frac{\delta E_x[\rho]}{\delta \rho(\mathbf{r})} . \quad (160)$$

Approximating the exchange functional by a finite number of terms of the gradient expansion yields the gradient expansion approximation (GEA). However, when exponentially decaying densities are inserted, the GEA for the exchange yields infinite results for the fourth and higher order terms. This indicates that infinite summations must be carried out in order to yield sensible results for finite systems (note that this divergency does not occur for solids). The generalized gradient approximations can be considered as such partial resummations of the gradient series. For this reason the GGAs are often required to reproduce the known coefficients of the gradient expansion in the limit of slowly varying densities. The most widely used gradient functionals only depend on the first order derivative through the variable s or equivalent x and are of the form

$$E_x[\rho] = \int e_x^{LDA}(\rho) F(s(\mathbf{r})) d\mathbf{r} = \int e_x^{LDA}(\rho) g(x(\mathbf{r})) d\mathbf{r} . \quad (161)$$

In the widely used Becke functional [15] for the exchange, for instance, the function $g(x)$ is given by

$$g(x) = 1 + \frac{\beta}{c_x} \frac{x^2}{1 + 6\beta x \sinh^{-1} x} \quad c_x = \frac{3}{4} \left(\frac{3}{\pi} \right)^{\frac{1}{3}} . \quad (162)$$

Useful local quantities which can be investigated to test the local properties of the GEA and GGA approximations for the exchange functional are the exchange hole, the long-range screening potential which is equal to the potential of the exchange hole or the Slater potential, and the exchange-correlation potential. The gradient expansion of the exchange hole has been derived by Perdew et al. [12, 103, 104] on the basis of the Kirzhnits expansion for the Kohn–Sham one-particle density matrix [1]. This GEA expansion for the exchange-hole has been compared with exact exchange holes in atomic systems by Slamet and Sahni [105, 106]. Their analysis shows that the GEA hole is not negative definite and has spurious long range oscillations. The GGA holes due to Perdew and Wang cure these deficiencies by means of real-space cutoffs of the exchange hole which are determined from the sum rules. For an extensive discussion we refer to [14].

Related local quantity of interest is the potential of the exchange hole or the Slater potential v_s . This potential is given by the expression at Eq. (70) of the screening potential where one should replace the $\bar{g}$ by its exchange-only equivalent given at Eq. (19). If one calculates this potential from the gradient expansion of the exchange hole one finds that it diverges. This divergency is removed in the GGA. The corresponding Slater potential from the GGA exchange hole of [103] has been presented in [106]. The exchange energy is related to the Slater

potential by

$$E_x[\rho] = \frac{1}{2} \int \rho(\mathbf{r}) v_s(\mathbf{r}) d\mathbf{r}. \quad (163)$$

Noting the GGA expressions for E_x of Eq. (161) one is tempted to write

$$v_s^{GGA}(\mathbf{r}) = 2\rho^{\frac{1}{3}}(\mathbf{r}) F(s(\mathbf{r})) = 2\rho^{\frac{1}{3}}(\mathbf{r}) g(x(\mathbf{r})). \quad (164)$$

However this is in general not allowed as, in the construction of the GGA energy expression, partial integrations have been carried out [12] to remove the Laplacian terms (for instance the GEA v_s explicitly contains Laplacian terms [104] which can be removed in the energy expression by partial integration). However noting the similarity of the dimensionless gradient and Laplacian terms ξ and η for atoms, Eq. (164) can still be a rather good approximation for atoms (however ξ and η have quite different behavior in clusters calculated within the jellium model [101]). For the Becke functional it is legitimate to use Eq. (164) as this functional has been designed to reproduce v_s , and in particular its long range Coulombic asymptotics. If we use this equation for the second order GEA and for the Becke exchange we obtain the expressions

$$v_s^{GEA}(\mathbf{r}) = -3 \left(\frac{3}{8\pi} \right)^{\frac{1}{3}} \rho^{\frac{1}{3}}(\mathbf{r}) [1 + 2\beta_1 x^2(\mathbf{r})] \quad (165)$$

$$v_s^{GGA}(\mathbf{r}) = -\rho^{\frac{1}{3}}(\mathbf{r}) \left[3 \left(\frac{3}{8\pi} \right)^{\frac{1}{3}} + 2\beta_2 \frac{x^2(\mathbf{r})}{1 + 6\beta_2 x(\mathbf{r}) \sinh^{-1} x(\mathbf{r})} \right] \quad (166)$$

where $\beta_1 = 0.005$ is the GEA coefficient of Herman et al. [107, 108] which has been shown to be an optimal value for atomic systems and $\beta_2 = 0.0042$ is the GGA coefficient of Becke [15]. In Fig. 13 we plot the exact v_s , and the Slater potentials for the GEA and Becke GGA for the cadmium atom as a function of the radial coordinate. As one can see from this figure, the LDA potential decays too fast in the outer region of the atom whereas the GEA potential diverges in this region. The Slater potential of the GGA gives the best fit of the exact Slater potential and has, furthermore, the correct asymptotics. This is a general trend for atomic systems [22]. The GGA therefore, gives not only in the energy but also locally in the exchange hole potential, an improvement over the LDA.

We now turn to the corresponding exchange potentials. The GGA exchange potential is given by

$$v_x^{GGA}(\mathbf{r}) = \frac{4}{3} \rho^{\frac{1}{3}}(g(x) - xg'(x) + x^2g''(x)) + (g'(x) - xg''(x)) \sum_{i,j=1}^3 \frac{\partial_i \rho \partial_i \partial_j \rho \partial_j \rho}{|\nabla \rho|^3} - g'(x) \frac{\nabla^2 \rho}{|\nabla \rho|} \quad (167)$$

where g' and g'' are the first and second derivatives of g with respect to x . In the region near to the atomic nucleus and in the outer asymptotic region of an atom or molecule the density has an exponential decay $\rho(\mathbf{r}) = \text{Ne}^{-\alpha r}$. If we insert this

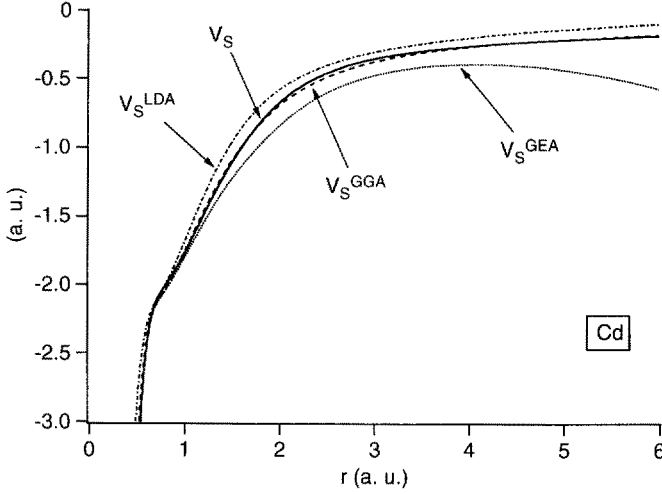


Fig. 13. Slater potentials of OPM, LDA, GEA and GGA for Cd

density in the above equation for v_x^{GGA} we obtain

$$v_x^{GGA}(\mathbf{r}) = \frac{4}{3} \rho^{\frac{1}{3}} \left(g(x) - xg'(x) + \frac{x^2}{4} g''(x) \right) + \frac{2}{r} g'(x) . \quad (168)$$

From this equation one finds that v_x^{GGA} has a Coulombic singularity near the atomic nucleus. Furthermore it follows that if the GGA reproduces the correct asymptotic behavior of the Slater potential

$$v_S \sim -\frac{1}{r} \quad (r \rightarrow \infty) \quad (169)$$

which requires

$$g(x) \sim -\frac{1}{6} \frac{x}{\ln(x)} \quad (x \rightarrow \infty) \quad (170)$$

then v_x^{GGA} has a r^{-2} behavior for $r \rightarrow \infty$, which is particularly true for the Becke functional [109]. Therefore the proper asymptotic behavior for the Slater potential v_S and the exchange potential v_x cannot be simultaneously satisfied for functionals of the form in Eq. (161). This was first shown by Engel et al. [19]. It is however possible to satisfy both constraints if one extends the GGA with Laplacian terms [110]. In order to improve the GGA exchange potential Engel and Vosko [111] used a Padé approximant of the form

$$E_x^{EV93}[\rho] = \int e_x^{LDA}(\rho) \frac{1 + a_1 \xi + a_2 \xi^2 + a_3 \xi^3}{1 + b_1 \xi + b_2 \xi^2 + b_3 \xi^3} d\mathbf{r} \quad (171)$$

in which a_1 and b_1 were restricted to yield the correct gradient coefficient

$c_{x2} = a_1 - b_1$. The coefficients were then determined to give an optimal local fit of the Levy–Perdew integrand by minimizing the expression

$$\Delta_2 = \sum_A \frac{1}{E_{x,A}} \int_0^\infty 4\pi r^2 |3\rho_A(\mathbf{r}) + \mathbf{r} \times \nabla \rho_A(\mathbf{r})| (v_{x,A}^{EV93}([\rho_A]; \mathbf{r}) - v_{x,A}([\rho_A]; \mathbf{r})) dr \quad (172)$$

where A runs over a number of atoms and ρ_A , $E_{x,A}$ and $v_{x,A}$ represent the density, exchange energy and potential of an exchange-only OPM calculation. This procedure improves the atomic shell structure of the exchange potential. The price that has to be paid for this improvement is a worsening of the exchange energy. More importantly the GGA deficiencies for small and large r are not cured by the above procedure. The deficiencies of the GGA exchange potential near the atomic nucleus and in the outer asymptotic region can however be cured using a nonvariational procedure by direct approximation of the exchange potential of the form

$$v_x^f([\rho]; \mathbf{r}) = v_x^{LDA}([\rho]; \mathbf{r}) + 2^{\frac{1}{3}} \rho^{\frac{1}{3}}(\mathbf{r}) f(x(\mathbf{r}), y(\mathbf{r})) . \quad (173)$$

This approximate form satisfies the required scaling properties of the exchange potential. The corresponding exchange energy can then be calculated using the Levy–Perdew relation. An appropriate choice which ensures finiteness at the atomic nucleus and correct long range asymptotics is given by a Padé type expression of the form [22]

$$f(x, y) = -\frac{a_0^x x^2}{1 + 3a_0^x x \sinh^{-1} x} + \frac{a_0^y y + a_1^y y^2}{1 + b_1^y y^2} . \quad (174)$$

The parameters in this expression can then be optimized by minimizing for a range of atomic systems the quantity

$$\Delta_1 = \sum_A \frac{1}{E_{x,A}^2} \int_0^\infty [4\pi r^2 \rho_A(\mathbf{r}) (v_{x,A}^f([\rho_A]; \mathbf{r}) - v_{x,A}([\rho_A]; \mathbf{r}))^2 dr \quad (175)$$

or, alternatively, the quantity

$$\Delta_2 = \sum_A \frac{1}{E_{x,A}^2} \int_0^\infty [4\pi r^2 (3\rho_A(\mathbf{r}) + \mathbf{r} \times \nabla \rho_A(\mathbf{r})) (v_{x,A}^f([\rho_A]; \mathbf{r}) - v_{x,A}([\rho_A]; \mathbf{r}))^2 dr \quad (176)$$

where A runs over a number of atoms and $E_{x,A}$ and $v_{x,A}$ represent the exchange energy and potential of an exchange-only OPM calculation. Both minimization procedures were carried out by Gritsenko et al. [22] and yielded corresponding approximate exchange potentials $v_{x^1}^f$ and $v_{x^2}^f$ with parameter sets $(a_0^x, a_0^y, a_1^y, b_1^y) = (0.0123, 0.0087, 0.0004, 0.0011)$ and $(0.0204, 0.0086, 0.0005, 0.0022)$. In Fig. 14 we plot for the cadmium atom the difference between the LDA potential and the exchange potential of OPM, GEA, Becke GGA and the Padé approximants $v_{x^1}^f$ and $v_{x^2}^f$ which therefore represents the nonlocal correction to

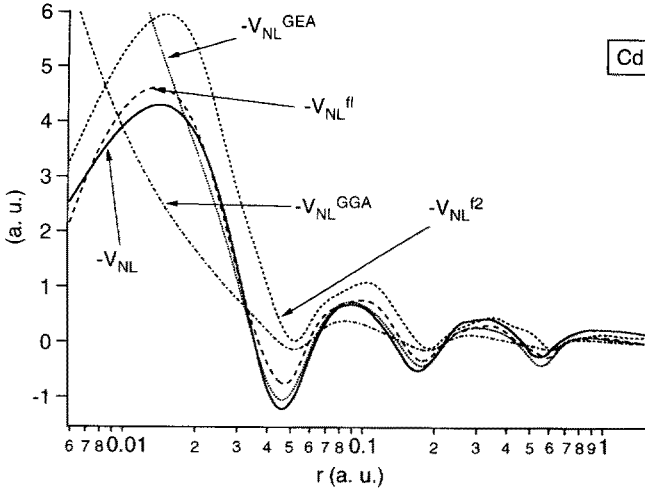


Fig. 14. Non-local corrections of OPM, GEA, GGA and of the fitting potentials to the LDA exchange potential for Cd

the LDA exchange potential. From this figure we can see that the GGA correction to the LDA exchange potential deviates considerably from its exact value. It diverges in the core region and its atomic shell structure is not pronounced enough. A better reproduction of the atomic shell structure is provided by the GEA potential (an even better reproduction of the shell structure is provided by the fourth order GEA [101]). This potential however diverges both in the core and the asymptotic outer region of the atom. The best overall fit is achieved by the potential $v_x^{f_1}$ obtained by minimization of quantity Δ_1 . It also yields better exchange energies as obtained from the Levy-Perdew relation at Eq. (196)]. The values of the exchange energies of the fitting potentials $v_x^{f_1}$ and $v_x^{f_2}$ are better than the LDA and GEA values, although worse than the GGA value. This shows the subtle cancellation of local errors for the GGA exchange potential in the Levy-Perdew energy expression also noted by Engel and Vosko [11]. The fit $v_x^{f_2}$ obtained by minimizing Δ_2 yields a better fit of the outer asymptotic region and gives better values for the highest occupied orbital energies [22]. The possibility of obtaining a better overall fit which incorporates both the advantages of $v_x^{f_1}$ and $v_x^{f_2}$ is however severely restricted due to the concerted behavior of the variables x and y (see Fig. 12). As a result a better fit for the inner part of v_x produces at the same time a worse fit for the outer region and vice versa. For further improvement of the current approximations one therefore needs other gradient parameters that should have distinctly different behavior in the core and valence regions.

A more difficult problem is to obtain the correct gradient approximation for the exchange-correlation potential. This is because the correlation potential has a more difficult spin dependence and must also describe the correlations be-

tween unlike spin electrons. One approach is to modify the exchange-correlation potentials of the GGA (which incorporate these spin correlations) in such a way that finiteness at the nucleus and the correct long-range asymptotics are obtained. However the current GGA correlation potentials seem to give large local errors in atomic systems [44]. A similar conclusion has been reached for the behavior of the GGA correlation potential in molecular systems [78]. A simple GGA for the exchange-correlation potential has been proposed in [20] which yielded much better values for the highest occupied Kohn–Sham eigenvalues (for an application of this potential in the calculation of photoionization cross sections see [112]). However, due to its too simple form, it lacks the correct spin dependence. The correct representation of the exchange-correlation potential remains a challenge for approximate DFT.

6.3 The Krieger-Li-Iafrate Approximation

As we discussed, approximate orbital dependent expressions for the exchange-correlation functional greatly improve the description of properties which are sensitive to the non-local effects of electron correlation, such as the atomic shell structure or the dependence of energy and potential on the particle number. It is therefore worthwhile to explore the advantages and limitations of approximate orbital dependent exchange-correlation functionals and potentials. Such orbital dependent expressions for exchange and correlation have been proposed by Colle and Salvetti [113–115], Becke and Roussel [34, 116] and Dobson [117]. Self-consistent OPM calculations using the Colle-Salvetti formula have recently been reported [70]. Also the successful combination of exact orbital dependent exchange and GGA exchange-correlation proposed by Becke [88, 118] using a coupling constant integration argument can be regarded as an orbital dependent exchange-correlation functional. Construction of the corresponding exchange-correlation potential requires the solution of the integral at Eq. (27) for v_{xc} . This is awkward for practical applications. However, Krieger, Li and Iafrate [21, 38] showed that it is possible to transform this integral equation into a manageable form. They obtain the following exact expression for v_{xc} :

$$v_{xc\sigma}(\mathbf{r}) = \sum_i \frac{v_{i\sigma}(\mathbf{r}) \rho_{i\sigma}(\mathbf{r})}{\rho_{\sigma}(\mathbf{r})} + \sum_i \frac{(\bar{v}_{xc\sigma i} - \bar{v}_{i\sigma}) \rho_{i\sigma}(\mathbf{r})}{\rho_{i\sigma}(\mathbf{r})} + \frac{1}{2} \sum_i \frac{\nabla \times (\mathbf{p}_{i\sigma}(\mathbf{r}) \nabla \rho_{i\sigma}(\mathbf{r}))}{\rho_{\sigma}(\mathbf{r})} \quad (177)$$

where $\rho_{i\sigma}$ are the orbital densities and $\bar{v}_{xc\sigma i}$ and $\bar{v}_{i\sigma}$ are defined by

$$\bar{v}_{xc\sigma i} = \int \rho_{i\sigma}(\mathbf{r}) v_{xc\sigma}(\mathbf{r}) d\mathbf{r} \quad (178)$$

$$\bar{v}_{i\sigma} = \int \rho_{i\sigma}(\mathbf{r}) v_{\sigma i}(\mathbf{r}) d\mathbf{r} . \quad (179)$$

The function $p_{i\sigma}$ is defined by

$$p_{i\sigma}(\mathbf{r}) = \frac{1}{\phi_{i\sigma}(\mathbf{r})} \int d\mathbf{r}' [v_{xc\sigma}(\mathbf{r}') - v_{i\sigma}(\mathbf{r}')] G_{i\sigma}(\mathbf{r}, \mathbf{r}') \phi_{i\sigma}^*(\mathbf{r}') \quad (180)$$

and $G_{i\sigma}$ is defined in Eq. (29). This set of equations must be solved self-consistently. This can however be done for any given approximation for any orbital dependent approximation $E_{xc}[\{\phi_{i\sigma}\}]$ without having to solve an integral equation. The function $p_{i\sigma}$ furthermore satisfies the condition

$$\int p_{i\sigma}(\mathbf{r}) \rho_{i\sigma}(\mathbf{r}) d\mathbf{r} = 0. \quad (181)$$

In practical applications the term in the exchange-correlation potential involving this function turns out to be very small for atomic systems. Its main effect is an improved description of the peaks at the atomic shell boundaries. Neglect of this term still leads to an accurate approximation for the atomic exchange-correlation potential.

The term $v_{i\sigma}$ in the above equation involves two-electron integrals over orbitals which can make the construction of v_{xc} rather expensive in molecular or solid state calculations. For an application of the KLI potential in bandstructure calculations Li et al. [119] approximated this term using the SIC functional of Perdew and Zunger [87] by

$$v_{i\sigma}(\mathbf{r}) = v_{xc}^{LSD}\left(\left[\frac{1}{2}\rho, \frac{1}{2}\rho\right]; \mathbf{r}\right) - \left(v_{xc}^{LSD}([\rho_i, 0]; \mathbf{r}) + \int \frac{\rho_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'\right) \quad (182)$$

where $v_{xc}^{LSD}([\rho_\uparrow, \rho_\downarrow]; \mathbf{r})$ is the exchange-correlation potential of the local spin density (LSD) formalism. Note that, in contrast to the Perdew-Zunger SIC formalism, the KLI potential is still local. In the above approximation the potential still preserves its desirable integer discontinuity, atomic shell structure and Coulombic asymptotics.

Let us consider some other approximations to the KLI potential. We consider subsequently the exchange and exchange-correlation versions of the KLI potential. In the exchange-only case one has

$$v_x^{KLI}(\mathbf{r}) = v_{x,scr}^{KLI}(\mathbf{r}) + v_{x,scr}^{KLI,resp}(\mathbf{r}) \quad (183)$$

written as the sum of a long and a short range part where

$$v_{x,scr}^{KLI}(\mathbf{r}) = \sum_i \frac{|\phi_i(\mathbf{r})|^2}{\rho(\mathbf{r})} u_{x,i}(\mathbf{r}) \quad (184)$$

$$v_{x,scr}^{KLI,resp}(\mathbf{r}) = \sum_i w_{x,i} \frac{|\phi_i(\mathbf{r})|^2}{\rho(\mathbf{r})} \quad (185)$$

and where the functions $u_{i,x}(\mathbf{r})$ and the constants $w_{x,i}$ are defined as

$$u_{i,x}(\mathbf{r}) = \frac{1}{\phi_i^*(\mathbf{r})} \frac{\delta E_x[\{\phi_i\}]}{\delta \phi_i(\mathbf{r})} \quad (186)$$

$$w_{x,i} = \int |\phi_i(\mathbf{r})|^2 (v_x^{KLI}(\mathbf{r}) - u_{i,x}(\mathbf{r})) d\mathbf{r} \quad (187)$$

where $v_{x,scr}$ is equal to the Slater potential v_s as calculated from Coulomb integrals over Kohn–Sham orbitals. In order to avoid the calculation of two-electron integrals, we propose a GGA-like approximation for v_s and derive some approximate orbital energy dependent expressions for the constants w_i [120]. For v_s we propose

$$v_s^{GGA}(\mathbf{r}) = 2\varepsilon_x^{GGA}(\mathbf{r}) . \quad (188)$$

If we use the Becke exchange energy density [15] then (for the spin unpolarized case) we have

$$\varepsilon_x^{GGA}(\mathbf{r}) = -\rho^{\frac{1}{3}} \left[\frac{3}{2} \left(\frac{3}{8\pi} \right)^{\frac{1}{3}} + \frac{\beta x^2}{1 + 6\beta x \sinh^{-1} x} \right] \quad (189)$$

where $x = \frac{1}{2^{\frac{1}{3}}} |\nabla \rho| / \rho^{\frac{4}{3}}$ and $\beta = 0.0042$. Our v_s^{GGA} exhibits the correct asymptotics

$$v_s^{GGA}(\mathbf{r}) \rightarrow -\frac{1}{r} \quad (r \rightarrow \infty) \quad (190)$$

and at the same time we have a rather accurate description of the exchange energies from our v_s^{GGA} as

$$E_x^{GGA}[\rho] = \frac{1}{2} \int \rho(\mathbf{r}) v_s^{GGS}(\mathbf{r}) d\mathbf{r} = \int \rho(\mathbf{r}) \varepsilon_x^{GGA}(\mathbf{r}) d\mathbf{r} \quad (191)$$

which is known to yield accurate exchange energies. For the constants $w_i = \bar{v}_{xi} - \bar{v}_i$ we propose an approximation in terms of the orbital energy ε_i . From gauge invariance requirements we can infer that w_i can only depend on an energy difference. We therefore make the following ansatz

$$w_i = f(\mu - \varepsilon_i) \quad (192)$$

where $\mu = \varepsilon_N$ is the highest occupied Kohn–Sham eigenvalue (equal to the ionization energy in the exact case). Scaling properties of the Kohn–Sham orbital energies and the exchange potential then determine the form of the function f and we obtain

$$w_i = K[\rho] \sqrt{\mu - \varepsilon_i} \quad (193)$$

where $K[\rho]$ is a functional satisfying

$$K[\rho_\lambda] = K[\rho] \quad (194)$$

where $\rho_\lambda(\mathbf{r}) = \lambda^3 \rho(\lambda \mathbf{r})$. Note that $w_N = 0$ as can also be proven for the KLI-potential. If we further approximate this functional by a constant and require our exchange potential to be exact for the homogeneous electron gas, we obtain

$K = 8\sqrt{2}/3\pi^2 \approx 0.382$ and the potential of the form [120]

$$v_x^{(1)}(\mathbf{r}) = v_s^{GGA}(\mathbf{r}) + \sum_i^N \frac{8\sqrt{2}}{3\pi^2} \sqrt{\mu - \varepsilon_i} \frac{|\phi_i(\mathbf{r})|^2}{\rho(\mathbf{r})}. \quad (195)$$

We can however also determine the functional form of the functional $K[\rho]$ by requiring v_x to satisfy the Levy-Perdew [121] relation

$$E_x[\rho] = \frac{1}{2} \int \rho(\mathbf{r}) v_s(\mathbf{r}) d\mathbf{r} = \int (3\rho(\mathbf{r}) + \mathbf{r} \times \nabla \rho(\mathbf{r})) v_x(\mathbf{r}) d\mathbf{r} \quad (196)$$

which yields

$$K[\rho] = - \frac{I_1[\rho]}{I_2[\rho]} \quad (197)$$

where

$$I_1[\rho] = \int \left(\frac{5}{2} \rho(\mathbf{r}) + \mathbf{r} \times \nabla \rho(\mathbf{r}) \right) v_s(\mathbf{r}) d\mathbf{r} \quad (198)$$

$$I_2[\rho] = \int (3\rho(\mathbf{r}) + \mathbf{r} \times \nabla \rho(\mathbf{r})) R(\mathbf{r}) d\mathbf{r} \quad (199)$$

$$R(\mathbf{r}) = \sum_i^N \sqrt{\mu - \varepsilon_i} \frac{|\phi_i(\mathbf{r})|^2}{\rho(\mathbf{r})}. \quad (200)$$

The functionals I_1 and I_2 both scale like $I[\rho_\lambda] = \lambda I[\rho]$ showing the correct scaling property of the functional $K[\rho]$. The above equations can be solved self-consistently and provide the more advanced approximation [120]

$$v_x^{(2)}(\mathbf{r}) = v_s^{GGA}(\mathbf{r}) + \sum_i^N - \frac{I_1}{I_2} \sqrt{\mu - \varepsilon_i} \frac{|\phi_i(\mathbf{r})|^2}{\rho(\mathbf{r})} \quad (201)$$

which also yields the exact exchange potential in the homogeneous electron gas limit.

In Table 2 we present some results for the highest occupied Kohn–Sham orbital obtained from the approximate potentials $v_x^{(1)}$ and $v_x^{(2)}$ denoted as GGA1 and GGA2. The approximations S1 and S2 are obtained by replacing the GGA approximation for the Slater potential by the exact self-consistently calculated Slater potential while retaining our approximations for the screening response potential. From this table we can see that the best value for the highest occupied Kohn–Sham orbital are obtained from the approximations S1 and S2 using the exact Slater potential indicating that the largest error is in the GGA approximation to the Slater potential. A more careful analysis shows that this is indeed the case. Local errors in the GGA v_s in the region close to the atomic nucleus lead to a considerable overestimation of the integral I_1 of Eq. (198) and the functional $K[\rho]$. For this reason the approximation GGA1 with the fixed constant K performs better than GGA2. The approximation GGA1 turns out to give an accurate local representation of the Kohn–Sham exchange potential which, due

Table 2. Orbital energies of the highest occupied Kohn–Sham orbital. The mean absolute deviation from OPM is denoted by Δ

ATOM	OPM	KLI	S2	S1	GGA2	GGA1
Be	0.309	0.309	0.308	0.303	0.280	0.301
Ne	0.851	0.849	0.830	0.821	0.723	0.753
Mg	0.253	0.252	0.248	0.248	0.234	0.247
Ar	0.591	0.589	0.573	0.570	0.534	0.548
Ca	0.196	0.195	0.186	0.186	0.181	0.190
Zn	0.293	0.292	0.307	0.307	0.312	0.318
Kr	0.523	0.522	0.503	0.503	0.481	0.490
Sr	0.179	0.178	0.167	0.169	0.167	0.174
Cd	0.265	0.265	0.263	0.264	0.271	0.278
Xe	0.456	0.455	0.433	0.434	0.421	0.428
Δ		0.001	0.013	0.014	0.036	0.027

to its simplicity, has the virtue of being applicable to large molecular systems and solids.

We will now study the problem of approximating the more general case of the exchange-correlation potential. We propose similar approximations as for the exchange-only case. For the screening part we take a GGA-like approximation

$$v_{xc,scr}^{GGA}(\mathbf{r}) = 2\varepsilon_{xc}^{GGA}(\mathbf{r}) = 2\varepsilon_x^B(\mathbf{r}) + 2\varepsilon_c^{PW91}(\mathbf{r}) \quad (202)$$

where ε_x^B denotes the exchange energy density due to Becke [15] as described in the previous section and ε_c^{PW91} denotes the correlation energy density of the Perdew-Wang (PW91) [11, 13, 14] correlation functional. In this way we obtain accurate exchange-correlation energies from

$$E_{xc}^{GGA}[\rho] = \frac{1}{2} \int \rho(\mathbf{r}) v_{xc,scr}^{GGA}(\mathbf{r}) d\mathbf{r} = E_x^B[\rho] + E_c^{PW91}[\rho] \quad (203)$$

and also obtain the correct asymptotics due to the correct asymptotic decay of the Becke exchange energy density

$$v_{xc,scr}^{GGA}(\mathbf{r}) \rightarrow -\frac{1}{r} \quad (r \rightarrow \infty). \quad (204)$$

For the constants $w_{xc,i}$ we assume a similar relation as for the exchange

$$w_{xc,i} = K_{xc}[\rho] \sqrt{\mu - \varepsilon_i}. \quad (205)$$

The only difference with the exchange case is that the functional $K_{xc}[\rho]$ does not obey a simple scaling relation in Eq. (197) as in the exchange case. We determine the functional form of K_{xc} by requiring our approximate v_{xc} to satisfy the relation due to Averill and Painter [122] and Levy and Perdew [121]

$$E_{xc}[\rho] = \frac{1}{2} \int \rho(\mathbf{r}) v_{xc,scr}(\mathbf{r}) d\mathbf{r} = \int v_{xc}(\mathbf{r}) (3\rho(\mathbf{r}) + \mathbf{r} \times \nabla \rho(\mathbf{r})) d\mathbf{r} - T_c[\rho] \quad (206)$$

where $T_c = T - T_s$ is the difference between the exact and Kohn–Sham kinetic energy which can be proven to be positive. We then obtain the following expression for K_{xc} :

$$K_{xc}[\rho] = - \frac{I_1[\rho]}{I_2[\rho]} \quad (207)$$

where

$$I_1[\rho] = \int \left(\frac{5}{2} \rho(\mathbf{r}) + \mathbf{r} \cdot \nabla \rho(\mathbf{r}) \right) v_{xc,scr}(\mathbf{r}) d\mathbf{r} - T_c[\rho] . \quad (208)$$

The integral I_2 has the same form as given by Eq. (199) in the previous section. Due to the appearance of the $T_c[\rho]$ term in the equation for $I_1[\rho]$ the functional $K_{xc}[\rho]$ lacks a scaling property as in Eq. (197). The quantity $T_c[\rho]$ is to be calculated within the GGA approximation from the relation

$$T_c[\rho] = \left. \frac{dE_c[\rho_\lambda]}{d\lambda} \right|_{\lambda=1} - E_c[\rho] . \quad (209)$$

In the PW91 approximation for the correlation energy this becomes

$$T_c[\rho] = \int \rho(\mathbf{r}) t_c(\mathbf{r}) d\mathbf{r} \quad (210)$$

where

$$t_c(\mathbf{r}) = - r_s(\mathbf{r}) \frac{\partial \varepsilon_c^{PW91}}{\partial r_s}(\mathbf{r}) - \varepsilon_c^{PW91}(\mathbf{r}) \quad (211)$$

where $r_s(\mathbf{r}) = (4\pi\rho/3)^{-1/3}$ is the Wigner-Seitz radius. The above relation follows from the fact that $r_s(\rho_\lambda(\mathbf{r})) = \lambda^{-1} r_s(\rho(\lambda\mathbf{r}))$ is the only non-dimensionless parameter in the PW91 correlation energy density. Our final exchange-correlation potential has a similar form as the one obtained in the exchange-only approximation

$$v_{xc}(\mathbf{r}) = v_{xc,scr}^{GGA}(\mathbf{r}) + \sum_i^N - \frac{I_1}{I_2} \sqrt{\mu - \varepsilon_i} \frac{|\phi_i(\mathbf{r})|^2}{\rho(\mathbf{r})} . \quad (212)$$

One can still use a simpler exchange-like expression for $w_{xc,i}$ with the constant K_{xc} . A possible option to determine this constant is to use the essentially accurate potentials v_{xc} constructed from the correlated densities as described in Sect. 3. One can insert v_{xc} and the model response potential into the expression for $v_{xc,scr}$:

$$v_{xc,scr}(\mathbf{r}) = v_{xc}(\mathbf{r}) - K_{xc} \sum_i^N \sqrt{\mu - \varepsilon_i} \frac{|\phi_i(\mathbf{r})|^2}{\rho(\mathbf{r})} . \quad (213)$$

With Eq. (213) K_{xc} can be fitted using the requirement that the integral of

Table 3. Orbital energies of the highest occupied Kohn–Sham orbital compared to the experimental ionization energy. The mean absolute deviation from experiment is denoted by Δ

ATOM	EXPT	OPM	B88PW91C	S2	S1	GGA2	GGA1
He	0.903	0.918	0.582	0.955	0.955	0.928	0.928
Be	0.343	0.309	0.206	0.330	0.329	0.302	0.330
N	0.534	0.571	0.310	0.577	0.568	0.516	0.529
Ne	0.792	0.851	0.491	0.858	0.839	0.749	0.772
Na	0.189	0.182	0.111	0.184	0.182	0.170	0.179
Mg	0.281	0.253	0.173	0.269	0.266	0.259	0.269
P	0.385	0.392	0.225	0.399	0.390	0.375	0.380
Ar	0.579	0.591	0.378	0.605	0.593	0.567	0.572
Δ		0.025	0.191	0.029	0.024	0.024	0.012

$v_{xc,scr}$ should reproduce $E_{xc}[\rho]$:

$$E_{xc}[\rho] = \frac{1}{2} \int \rho(\mathbf{r}) v_{xc,scr}(\mathbf{r}) d\mathbf{r} . \quad (214)$$

With v_{xc} and ϕ_i constructed via the procedure [20] for the *Ne* atom, we obtain the value $K_{xc} = 0.470$. In Table 3 we present some results for the highest occupied Kohn–Sham eigenvalue which should be equal to the ionization energy of the system. The approximation of Eq. (212) is denoted GGA2. If we replace in this equation the functional K_{xc} by the constant $K_{xc} = 0.470$ we obtain an approximation called GGA1. The potentials S1 and S2 denote the same potentials in which we replace the exchange part of the screening potential (that is two times the Becke energy density) by the exact exchange expression, which is the Slater potential v_s . The column B88PW91C denotes the eigenvalues from the exchange–correlation functional consisting of the Becke exchange and the Perdew–Wang 91 correlation energy. From this table we can see that the approximations S1 and S2 with the exact Slater potential yield results close to the exchange-only OPM results, indicating that the correlation correction to the potential is too small. However if we use the GGA approximation to the Slater potential then, due to the errors introduced in v_s , there is a fortuitous error cancellation which brings the highest occupied Kohn–Sham eigenvalues closer to the correlated ones. However, important local errors in the GGA approximation, especially in the core region, still prevent a uniformly accurate representation of the exchange–correlation potential. More work has to be done to correct these errors. The accurate approximation of the exchange–correlation potential and functional in molecules remains an even greater challenge.

7 Conclusions and Outlook

In this review we have given an overview of the properties of exact and approximate exchange–correlation potentials. We have shown how the local

properties of the pair-correlation function and the exchange-correlation hole show up in the various constituents of the exchange-correlation potential and determine the shape of v_{xc} , such as its atomic shell and the bond midpoint properties. The exchange-correlation hole determines not only the local properties of v_{xc} but also directly relates to the exchange-correlation energy E_{xc} . The exchange-correlation potential turns out to be a quantity which is incorrectly represented by most of the existing approximate density functionals. Presently the most widely used approximation in quantum chemistry in the calculation of molecular properties is the GGA approach. However the current GGAs have important deficiencies with respect to their exchange-correlation potentials, notably the incorrect long range asymptotics. A much better representation of the properties of the exchange-correlation potential is provided by the use of orbital dependent density functionals, such as the OPM and KLI schemes. The OPM and KLI approaches are the only approaches thus far which have been able to describe correctly the particle number dependent properties of E_{xc} and v_{xc} . Moreover the KLI approach does provide a simple and accurate approximation for v_{xc} which incorporates the correct atomic shell structure. A practical disadvantage of the orbital dependent approach however is that the calculation of E_{xc} and v_{xc} is just as expensive as a Hartree-Fock calculation, which prohibits the application to large molecular systems. The method is nevertheless still applicable to molecules of intermediate size. As shown by Becke [88, 116, 118], a combination of GGAs and orbital dependent density functionals turns out to be very successful in the accurate prediction of molecular bond energies. In view of the rapid developments in this field we can expect further improvements of the GGA and orbital dependent density functionals in the near future. This requires, among other things, a better understanding of the success of the current approaches. The study of local properties such as the exchange-correlation hole and the exchange-correlation potential in atomic and molecular systems can be of great help in this respect and can provide important guidance in the search for more accurate density functionals.

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Local-Scaling Transformation Version of Density Functional Theory: Generation of Density Functionals

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We review in the present work the *local-scaling transformation version of density functional theory* both for ground and excited states. The historical development of the concept of space-coordinate density-transformation and of its effect on the formulation of several versions of density functional theory is discussed. We then present the various steps in the elaboration of the local-transformation version and indicate some of its accomplishments with respect to the N -representability problem *for the energy functionals*. Examples are given showing how the application of these methods to atomic sample systems lead to Hartree–Fock energies that are undistinguishable from the SCF values. In addition, the explicit construction of analytic density functionals for the energy, via local-scaling transformations, is discussed and is exemplified for the particular case of the Hartree–Fock approximation for atoms. Finally, applications of local-scaling transformations to the direct solution of the Kohn–Sham equations are reviewed.

1 Introduction

The demands that materials science, fine chemistry, molecular biology, and condensed-matter physics exert on the quantum mechanical methods which have been developed throughout the years for the purpose of calculating the properties of many-particle systems, are really quite formidable. The point is that these disciplines have an exacting need for working methods that lead to

accurate results for “molecules” formed by thousands of electrons and hundreds of nuclei. As is well-known, straightforward tackling of such very large systems through variational or perturbation-theory methods stemming from the Schrödinger equation is not possible nowadays, as the computational difficulties that emerge defy even the most sophisticated supercomputers. It is in this respect that density functional theory – because it avoids the usual complexities of the standard treatments and leads at the same time to quite reasonable results – has become a very promising alternative for the calculation of many-particle systems, both at the quantal and semi-classical levels. [1–4].

Density functional theory was first formulated – albeit incipiently – by Thomas and Fermi in 1927 [5, 6] (for reviews on this theory see the already classic works of March [7] and Lieb [8]). Basically, the idea of this theory was to bypass the Schrödinger equation and to recast the many-body problem in terms of a “statistical approximation”, where the energy is expressed as a functional of the one-particle density. Notwithstanding the allure of this idea, its actual development proceeded rather slowly in the first four decades, during which a number of authors painstakingly added density-dependent terms, obtained through gradient expansions, to the original Thomas–Fermi energy expression, [9–15].

The turning point occurred in 1964 when Hohenberg and Kohn [17] advanced a theorem which states that the exact ground-state energy is a functional of the exact ground-state one-particle density. Although this is just an existence theorem, it lent support – in a formal sense – to the earlier generalizations of the Thomas–Fermi theory, and opened the gate to new searches of the energy as a functional of the one-particle density. The growth of density functional theory after 1964 has been exponential. Presently, density functional theory has undoubtedly attained, a prominent place among the theories that deal with the quantum many-particle problem [16]. But will it finally replace the more traditional variational and perturbational approaches based on the Schrödinger equation? Will it become the choice theory for calculations that demand an energy accuracy of the order of cm^{-1} ? Or is it doomed to remain a theory well suited for giving “fairly reasonable” results at a low price, but the results of which can be neither improved nor compared to the strict upper bounds yielded by conventional quantum mechanics (i.e., bond energies computed by taking the difference between a molecule and isolated atoms)?

Within the Hohenberg–Kohn approach [17, 18], the possibility of transforming density functional theory into a theory fully equivalent to the Schrödinger equation hinges on whether the elusive “universal” energy functional can ever be found. Unfortunately, the Hohenberg–Kohn theorem, being just an existence theorem, does not provide any indication of how one should proceed in order to find this functional. Moreover, the contention that such a functional should exist – and that it should be the same for systems that have neither the same number of particles nor the same symmetries (for an atom, for example, those symmetries are defined by $\hat{L}^2$, $\hat{L}_z$, $\hat{S}^2$, $\hat{S}_z$ and the parity operator $\hat{\Pi}$) – certainly opens the door to dubious speculation.

But there is a more basic difficulty in the Hohenberg–Kohn formulation [19–21], which has to do with the fact that the functional N -representability condition on the energy is not properly incorporated. This condition arises when the many-body problem is presented in terms of the reduced second-order density matrix; in that case it takes the form of the N -representability problem for the reduced 2-matrix [19, 22–24] (a problem that has not yet been solved). When this condition is not met, an energy functional is not in one-to-one correspondence with either the Schrödinger equation or its equivalent variational principle; therefore, it can lead to energy values lower than the experimental ones.

In the Hohenberg–Kohn formulation, the problem of the functional N -representability has not been adequately treated, as it has been assumed that the 2-matrix N -representability condition in density matrix theory only implies an N -representability condition on the one-particle density [21]. Because the latter can be trivially imposed [26, 27], the real problem has been effectively avoided.

It is in response to the questions posed above concerning the limitations of the Hohenberg–Kohn formulation of density functional theory that the *local-scaling transformation version of density functional theory* has been advanced [20, 25, 28–32, 94, 99, 108–112]. This new theory addresses precisely those fundamental aspects which are either ignored or treated superficially in former theories. It develops well-defined procedures for the construction of N -representable energy functionals expressed in terms of the one-particle density. It turns out, however, that in order to preserve a one-to-one correspondence between these functionals and the usual Schrödinger equation, i.e., in order to satisfy the functional N -representability condition, it is necessary that these functionals depend both on the number of particles N , and on the symmetry, which – in the case of an atom, for example – is described by the quantum numbers of a specific spectroscopic term. Thus, the energy functionals are specific to a particular system and do not refer solely to ground states.

In spite of the specificity evinced by energy functionals advanced in the context of the local-scaling version of density functional theory, these functionals do share some very basic forms regardless of the system under consideration, and it is in this sense that one can talk about a “universal form” of energy density functionals. One must bear in mind, however, that these expressions must be multiplied by specific correction factors in order to include the details pertaining to particular systems (see for details Sects. 5.1.1 and 5.1.2). Moreover, these forms are quite similar to those that appear in the approximate energy functionals constructed in the context of the Hohenberg–Kohn theory. Thus, the local-scaling version of density functional theory that is being reviewed here not only provides an adequate perspective from where to assess previous works, but it also furnishes systematic ways for constructing new energy functionals and improving already existing ones.

In Sect. 2, we discuss a class of transformations which we label as “space-coordinate (and also momentum-coordinate) density transformations” and

illustrate how they have already been used in quantum mechanics for a considerable number of years. Local-scaling transformations correspond to particular combinations of the former. We also review in this Section the application of these transformations to orbitals and their implications in density functional theory. In Sect. 3, we compare the local-scaling version of density functional theory with the density-driven version of Cioslowski and show that the latter is a finite-basis realization of the former. In Sect. 4, we deal with the construction of *implicit* energy-density functionals and summarily discuss the functional N -representability problem. We also discuss “intra-orbit” and “inter-orbit” energy-density optimizations. In Sect. 5, we deal with the analytic representation of the energy density functionals generated in the context of the local-scaling transformation version of density functional theory and discuss their relationship to the usual approximate expressions for Hohenberg–Kohn-based energy density functionals. In Sect. 6, we review applications of local-scaling transformations to the determination of Kohn–Sham potentials and energies.

2 Space Coordinate-Density Transformations

2.1 The Pioneers

Space-coordinate density transformations have been used by a number of authors in various contexts related to density functional theory [26, 27, 53–64, 85–87]. As the free-electron gas wavefunction is expressed in terms of plane waves associated with a constant density, these transformations were introduced by Macke in 1955 for the purpose of producing modified plane waves that incorporate the density as a variable. In this manner, the density could be then be regarded as the variational object [53, 54]. Thus, explicitly a set of plane waves (defined in the volume V in $\mathcal{R}^3$ and having uniform density $\rho_0 = N/V$):

$$\phi_{\vec{k}_j}(\vec{r}) = e^{i\vec{k}_j \cdot \vec{r}} \quad \text{for } j = 1, \dots, N \quad (1)$$

is carried into the new deformed plane waves:

$$\psi_{\vec{k}_j}(\vec{r}) \equiv \left[\frac{\rho(\vec{r})}{N} \right]^{1/2} e^{i\vec{k}_j \cdot \vec{R}(\vec{r})} \quad (2)$$

The space transformation implied in the above expressions carries a vector $\vec{r}$ into another vector $\vec{R}(\vec{r})$:

$$\vec{r} = (x, y, z) \xrightarrow{\hat{R}} \vec{R}(\vec{r}) = (R_1(\vec{r}), R_2(\vec{r}), R_3(\vec{r})) \quad (3)$$

and the transformation is defined by the condition:

$$\frac{\rho(\vec{r})}{N} = \det |\partial R_i(x, y, z)/\partial x_j| \quad (4)$$

where $x_1 = x$, $x_2 = y$ and $x_3 = z$. As this determinant is the Jacobian $J(\vec{R}; \vec{r})$ of the transformation, Macke actually introduced the following orbital transformation:

$$\psi_k(\vec{r}) = [J(\vec{R}; \vec{r})]^{1/2} \phi_k(\vec{R}(\vec{r})) \quad (5)$$

An extension of Macke's formulation to the 1-matrix was given by March and Young in 1958 [55]. These authors applied these generalized transformations to the free-electron gas 1-matrix $D_0^1(\vec{r}, \vec{r}')$ which is carried into the new 1-matrix $D^1(\vec{r}, \vec{r}')$:

$$D^1(\vec{r}, \vec{r}') = [J(\vec{R}; \vec{r})J(\vec{R}'; \vec{r}')]^{1/2} D_0^1(\vec{R}, \vec{R}') \quad (6)$$

where $J(\vec{R}; \vec{r})$ is the Jacobian of the transformation. Of course, when we take $\vec{r} = \vec{r}'$ this reduces to the Jacobian problem relating the density of the free electron gas $\rho_0(\vec{r})$ and a density $\rho(\vec{r})$:

$$\rho(\vec{r}) = J(\vec{R}; \vec{r}) \rho_0(\vec{R}(\vec{r})) \quad (7)$$

In illustration, March and Young [55] constructed an idempotent 1-matrix which, for example, for the one-dimensional case with N odd ($N = 2m + 1$, for m integer) is given by:

$$\rho_0(x', x) = \sum_{k=-m}^m \exp - 2\pi i k x' \exp 2\pi i k x \quad (8)$$

with a similar expression for N even, and showed that for both cases the 1-matrix could be written in compact form as:

$$\rho_0(x', x) = \frac{\sin N\pi(x' - x)}{\sin \pi(x' - x)} \quad (9)$$

Although they did not obtain a closed-form analytic expression for the three-dimensional case, they dealt with a trasformed one-matrix for the single Slater determinant constructed from plane waves, and rewrote the energy in terms of this transformed matrix. The conditions on the transformation were not imposed through the Jacobian but rather through the equations:

$$\rho(x, y, z) = \prod_{i=1}^3 f_i(x, y, z) \quad (10)$$

and

$$\begin{aligned} & \frac{\partial R_i(x, y, x)}{\partial x} \frac{\partial R_j(x, y, x)}{\partial x} + \frac{\partial R_i(x, y, x)}{\partial y} \frac{\partial R_j(x, y, x)}{\partial y} \\ & + \frac{\partial R_i(x, y, x)}{\partial z} \frac{\partial R_j(x, y, x)}{\partial z} = f_i^2(x, y, z) \delta_{ij} \end{aligned} \quad (11)$$

Equations (11) guarantee the orthogonality of the transformation.

Both in the work of Macke [53] and of March and Young [55], the orbital transformation is restricted to plane waves. A more general formulation, how-

ever, was advanced in 1960 by Hall [56]. This author discussed the unitary transformation that keeps the overlap between a pair of untransformed and transformed one-particle orbitals invariant. Consider, for example, the orthonormal set $\{\phi_i(r, \theta, \phi)\}$ from which one obtains transformed orbitals through the relation:

$$\psi_i(r, \theta, \phi) = \left(\frac{df(r)}{dr} \right)^{1/2} \frac{f(r)}{r} \phi_i(f(r), \theta, \phi) \quad (12)$$

The invariance of the overlap under this transformation is easily shown. Thus, for the untransformed orbitals, the overlap is:

$$S_{ij}(\phi) = \int dr r^2 \int d\theta \sin \theta \int d\phi \phi_i^*(r, \theta, \phi) \phi_j(r, \theta, \phi) \quad (13)$$

Similarly, for the transformed ones, we have:

$$\begin{aligned} S_{ij}(\psi) &= \int dr r^2 \int d\theta \sin \theta \int d\phi \psi_i^*(r, \theta, \phi) \psi_j(r, \theta, \phi) \\ &= \int dr r^2 \int d\theta \sin \theta \int d\phi \frac{df(r)}{dr} \frac{f(r)^2}{r^2} \phi_i^*(f(r), \theta, \phi) \phi_j(f(r), \theta, \phi) \\ &= \int df(r) f(r)^2 \int d\theta \sin \theta \int d\phi \phi_i^*(f(r), \theta, \phi) \phi_j(f(r), \theta, \phi) = S_{ij}(\phi) \end{aligned} \quad (14)$$

The general Jacobian problem associated with the transformation of a density $\rho_1(\vec{r})$ into a density $\rho_2(\vec{r})$ (where these densities differ from that of the free-electron gas) was discussed by Moser in 1965 [58]. This work was not performed in the framework of orbital transformations – which might have interested chemists, nor was it done in the context of density functional theory – which might have attracted the attention of physicists. It was a paper written for mathematicians and, as such, it remained unknown to the quantum chemistry community. In the discussion that follows, we use the more accessible reformulation of Bokanowski and Grebert (1995) [65] which relies heavily on the work of Zumbach and Maschke (1983) [61]. Let us define as $\mathcal{L}_N \equiv L_A^2(\mathcal{R}^{3N})$ the space of square-integrable antisymmetric complex functions (the subindex A denotes antisymmetry with respect to the spatial variables $\vec{r}_i$). Let us consider an arbitrary N -electron wavefunction $\Phi_1 \in \mathcal{L}_N$, from which we obtain the density $\rho_1 \equiv \rho_{\Phi_1}$ as follows:

$$\rho_1(\vec{r}) = N \int d^3\vec{r}_2 \cdots d^3\vec{r}_N |\Phi_1(\vec{r}, \vec{r}_2, \dots, \vec{r}_N)|^2 \quad (15)$$

Similarly, let us consider a wavefunction $\Phi_2 \in \mathcal{L}_N$, that yields the density $\rho_2 \equiv \rho_{\Phi_2}$. The set of all densities coming from N -particle functions in Hilbert space is denoted by $\mathcal{N}_{\Phi}$:

$$\mathcal{N}_{\Phi} = \{\rho(\vec{r}) | \rho \leftarrow \Phi \in \mathcal{L}_N\} \quad (16)$$

The Jacobian problem associated with these densities is that of finding the diffeomorphism $\vec{f}(\vec{r})$ for the density transformation [58, 65]:

$$\forall \vec{r}, \quad \rho_2(\vec{r}) = J(\vec{f}; \vec{r}) \rho_1(\vec{f}(\vec{r})) \quad (17)$$

In Moser's treatment [58], and more recently, in that of Bokanowski and Grébert [65, 66], the transformation vector $\vec{f}(\vec{r})$ in Eq. (17) is obtained by successive applications of the density transformations appearing in Eq. (7) (this is given explicitly in Eq. (27) below):

$$\forall \vec{r}, \quad \rho_2(\vec{r}) = J(\vec{R}_{\rho_2}; \vec{r}) \rho_0(\vec{R}_{\rho_2}(\vec{r})) \quad (18)$$

and

$$\forall \vec{r}, \quad \rho_1(\vec{r}) = J(\vec{R}_{\rho_1}; \vec{r}) \rho_0(\vec{R}_{\rho_1}(\vec{r})) \quad (19)$$

where in general, $\rho_0(\vec{r})$, comes from the integration of the N -particle function $\Phi_0 \in L_A^2(V^N)$ (where V is defined as the unit cube $V = [0, 1]^3$):

$$\rho_0(\vec{r}) = N \int_{V^{N-1}} d^3\vec{r}_2 \cdots d^3\vec{r}_N |\Phi_0(\vec{r}, \vec{r}_2, \dots, \vec{r}_N)|^2 \quad (20)$$

The N -particle function $\Phi_0 \in L_A^2(V^N)$ is given, in general as a linear combination of Slater determinants constructed from plane waves, thus extending the treatment of both Macke [53, 54] and of March and Young [55]. Thus, we have $\Phi_0 = \sum_K C_K \chi_K$, where χ_K is the Slater determinant $\chi_K = (N)^{-1/2} \det [\phi_{\vec{k}_1}, \dots, \phi_{\vec{k}_N}]$ and $\phi_{\vec{k}_i}(\vec{r})$ is the plane wave defined in Eq. (1), with momentum $\vec{k} \in Z^3$. Clearly, in view of this definition of $\Phi_0 \in L_A^2(V^N)$, the resulting density is $\rho_0(\vec{r}) = N/V$, provided that the expansion coefficients satisfy the equation:

$$\sum_{K=1} \sum_{L=1} C_K C_L \Delta_{KL}^{k_i k_j} = 0 \quad \text{for } K \neq L \quad \text{and } k_i \neq k_j \quad (21)$$

where according to Ref. [67]:

$$\Delta_{KL}^{k_i k_j} = (-1)^{i+j} \quad \text{when } \{K - k_i\} = \{L - k_j\} \quad (20)$$

and zero otherwise.

In order to determine explicitly the transformation vector $\vec{R}_\rho(\vec{r}) = (R_1, R_2, R_3)$ connecting densities $\rho(\vec{r})$ and $\rho_0(\vec{r})$, its components are defined, following Zumbach and Maschke [61], as:

$$\begin{aligned} R_1(x, y, z) &= \frac{\int_{-\infty}^x dx' \rho(x', y, z)}{\int_{-\infty}^{+\infty} dx' \rho(x', y, z)} \\ R_2(y, z) &= \frac{\int_{-\infty}^{+\infty} \int_{-\infty}^y dy' \rho(x', y', z)}{\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} dx' dy' \rho(x', y', z)} \\ R_3(z) &= \frac{\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^z dz' \rho(x', y', z')}{\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} dx' dy' dz' \rho(x', y', z')} \end{aligned} \quad (23)$$

It follows from this definition that:

$$\begin{aligned}
 \frac{\partial R_1(x, y, x)}{\partial x} &= \rho(x, y, z) \frac{1}{\int_{-\infty}^{\infty} dx' \rho(x', y, z)} \\
 \frac{\partial R_2(y, x)}{\partial y} &= \frac{\int_{-\infty}^{\infty} dx' \rho(x', y, z)}{\int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dy' \rho(x', y', z)} \\
 \frac{\partial R_2(x, y, x)}{\partial x} &= 0 \\
 \frac{\partial R_3(x, y, x)}{\partial z} &= \frac{1}{N} \int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dy' \rho(x', y', z) \\
 \frac{\partial R_3(x, y, x)}{\partial x} &= \frac{\partial R_3(x, y, x)}{\partial y} = 0
 \end{aligned} \tag{24}$$

In view of the above equations, the Jacobian of the transformation yields $\rho(x, y, z)/N$:

$$\begin{aligned}
 &\begin{bmatrix} \frac{\partial R_1(x, y, z)}{\partial x} & \frac{\partial R_2(x, y, z)}{\partial x} & \frac{\partial R_3(x, y, z)}{\partial x} \\ \frac{\partial R_1(x, y, z)}{\partial y} & \frac{\partial R_2(x, y, z)}{\partial y} & \frac{\partial R_3(x, y, z)}{\partial y} \\ \frac{\partial R_1(x, y, z)}{\partial z} & \frac{\partial R_2(x, y, z)}{\partial z} & \frac{\partial R_3(x, y, z)}{\partial z} \end{bmatrix} \\
 &= \frac{\partial R_1(x, y, z)}{\partial x} \frac{\partial R_2(x, y, z)}{\partial y} \frac{\partial R_3(x, y, z)}{\partial z} = \frac{1}{N} \rho(x, y, z)
 \end{aligned} \tag{25}$$

which we write in a more succinct form as [61]:

$$J(\vec{R}_\rho; \vec{r}) = \frac{\rho(\vec{r})}{N} \tag{26}$$

In terms of the transformations for the vector components given by Eqs. (23) and using the result of Eq. (26), the general transformation connecting densities ρ_1 and ρ_2 may now be expressed as [58, 65]:

$$\hat{f} = (\hat{R}_{\rho_1})^{-1} \circ \hat{R}_{\rho_2} \tag{27}$$

which leads to a Jacobian:

$$J(\vec{f}(\vec{r}); \vec{r}) = \frac{\rho_2(\vec{r})}{\rho_1(\vec{f}(\vec{r}))} \tag{28}$$

We show in Sect. 2.7 how Eq. (27) can be implemented for the calculation of the transformation function $\vec{f}(\vec{r})$.

Although we have employed Zumbach and Maschke's technique for producing the transformation vectors $\vec{R}_{\rho_1}$ and $\vec{R}_{\rho_2}$, these vectors have been used in a wider context for the purpose of finding the transformation that connects two arbitrary densities $\rho_1(\vec{r})$ and $\rho_2(\vec{r})$, associated to N -particle wavefunctions $\Phi_1 \in \mathcal{L}_N$ and $\Phi_2 \in \mathcal{L}_N$, respectively. In this important sense, the procedure advanced by Moser [58] frees us in principle from a plane-wave basis and allow us to search for general transformations between arbitrary one-particle orbital sets. This is precisely what is done through local-scaling transformations.

2.2 Local-Scaling Transformations

Local-scaling transformations, or point transformations, are generalizations of the well-known scaling transformations. The latter have been widely used in many domains of the physical sciences. Scaling transformations carry a vector $\vec{r} \in \mathcal{R}^3$ into $\vec{f}(\vec{r}) \equiv \lambda \vec{r}$, where λ is just a constant. In the case of local-scaling transformations, λ is a function (i.e., $\lambda \equiv \lambda(\vec{r})$). Notice that the transformed vector $\vec{f}(\vec{r}) \in \mathcal{R}^3$ conserves the same direction as the original one and is given by $\vec{f}(\vec{r}) \equiv \lambda(\vec{r})\vec{r}$. In terms of the operator $\hat{f}$ associated with this transformations, we can relate $\vec{r}$ and $\vec{f}(\vec{r})$ by:

$$\vec{r} \xrightarrow{\hat{f}} \vec{f}(\vec{r}) \quad (29)$$

In order to see that they correspond to the general transformations studied by Moser [58], consider the effect of applying a local-scaling transformation, denoted by the operator $\hat{f}$, to each of the coordinates appearing in the wavefunction $\Phi_1(\vec{r}_1, \dots, \vec{r}_N) \in \mathcal{L}_N$. Hence, the resulting wavefunction $\Phi_2(\vec{r}_1, \dots, \vec{r}_N) \in \mathcal{L}_N$ is given by:

$$\begin{aligned} \Phi_2(\vec{r}_1, \dots, \vec{r}_N) &\equiv \underbrace{\hat{f} \dots \hat{f}}_{N\text{-times}} \Phi_1(\vec{r}_1, \dots, \vec{r}_N) \\ &= \prod_{i=1}^N [J(\vec{f}(\vec{r}_i); \vec{r}_i)]^{1/2} \Phi_1(\vec{f}(\vec{r}_1), \dots, \vec{f}(\vec{r}_N)) \end{aligned} \quad (30)$$

where $J(\vec{f}(\vec{r}_i); \vec{r}_i)$ is the Jacobian of the transformation. In order to guarantee uniqueness, we restrict these transformations to those having positive definite Jacobians. It is clear that the transformed wavefunction maintains its normalization. Moreover, the following relation is obtained between the density $\rho_2 \equiv \rho_{\Phi_2}(\vec{r})$ of the transformed wavefunction and the density $\rho_1 \equiv \rho_{\Phi_1}(\vec{r})$ of the initial wavefunction:

$$\rho_2(\vec{r}) = J(\vec{f}(\vec{r}); \vec{r}) \rho_1(\vec{f}(\vec{r})) \quad (31)$$

This fundamental relation between the densities arises from:

$$\rho_2(\vec{r}_1) = N \int d^3\vec{r}_2 \dots \int d^3\vec{r}_N |\Phi_2(\vec{r}_1, \dots, \vec{r}_N)|^2$$

$$\begin{aligned}
 &= J(\vec{f}(\vec{r}_1); \vec{r}_1) N \int d^3 \vec{f}(\vec{r}_2) \cdots \int d^3 \vec{f}(\vec{r}_N) |\Phi_1(\vec{f}(\vec{r}_1), \dots, \vec{f}(\vec{r}_N))|^2 \quad (32) \\
 &= J(\vec{f}(\vec{r}); \vec{r}) \rho_1(\vec{f}(\vec{r}))
 \end{aligned}$$

where we have used Eq. (15) and the relation:

$$d^3 \vec{r} J(\vec{f}(\vec{r}_i); \vec{r}_i) = d^3 \vec{f}(\vec{r}_i) \quad (33)$$

The Jacobian $J(\vec{f}(\vec{r}); \vec{r}) = J(\lambda(\vec{r})\vec{r}; \vec{r})$ of the local-scaling transformation can be evaluated explicitly by calculating the determinant:

$$J(\lambda(\vec{r})\vec{r}; \vec{r}) = \begin{vmatrix} \frac{\partial \lambda(\vec{r})x}{\partial x} & \frac{\partial \lambda(\vec{r})y}{\partial x} & \frac{\partial \lambda(\vec{r})z}{\partial x} \\ \frac{\partial \lambda(\vec{r})x}{\partial y} & \frac{\partial \lambda(\vec{r})y}{\partial y} & \frac{\partial \lambda(\vec{r})z}{\partial y} \\ \frac{\partial \lambda(\vec{r})x}{\partial z} & \frac{\partial \lambda(\vec{r})y}{\partial z} & \frac{\partial \lambda(\vec{r})z}{\partial z} \end{vmatrix} = \lambda^3(\vec{r}) [1 + \vec{r} \cdot \nabla_{\vec{r}} \ln \lambda(\vec{r})] \quad (34)$$

It is also useful to express this Jacobian in terms of the function $f(\vec{r})$ of $\lambda(\vec{r}) = f(\vec{r})/r$:

$$J(\vec{f}(\vec{r}); \vec{r}) = \frac{\vec{r} \cdot \nabla_{\vec{r}} f^3(\vec{r})}{r^3} \quad (35)$$

Substituting Eq. (35) into Eq. (31), using polar coordinates (i.e., $\vec{r} = (r, \theta, \phi)$), and selecting a fixed ray at angles θ_o and ϕ_o , we obtain the following first order differential equation for the transformation function:

$$\frac{\partial f(r, \theta_o, \phi_o)}{\partial r} = \frac{r^2}{f^2(r, \theta_o, \phi_o)} \frac{\rho_2(r, \theta_o, \phi_o)}{\rho_1(f(r, \theta_o, \phi_o), \theta_o, \phi_o)} \quad (36)$$

The total transformation function $f(r, \theta, \phi)$ can be obtained by spanning over all values angular. The existence of a unique solution to Eq. (36) is guaranteed if the following condition is satisfied along each one of the rays:

$$\int_0^\infty dx x^2 \rho_1(x, \theta_o, \phi_o) = \int_0^\infty dy y^2 \rho_2(y, \theta_o, \phi_o) \quad (37)$$

For the spherically-symmetric case Eq. (36) becomes:

$$\frac{df(r)}{dr} = \frac{r^2}{f^2(r)} \frac{\rho_2(r)}{\rho_1(f(r))} \quad (38)$$

which is given in integrated form by:

$$\int_0^{f(r)} dx x^2 \rho_1(x) = \int_0^r dy y^2 \rho_2(y) \quad (39)$$

when we take the boundary condition at $r = 0$, or equivalently, by:

$$\int_{f(r)}^{\infty} dx x^2 \rho_1(x) = \int_r^{\infty} dy y^2 \rho_2(y) \quad (40)$$

when we take this condition at infinity.

The full-fledged introduction of local-scaling transformations into density functional theory took place in the works of Kryachko, Petkov and Stoitsov [28–30, 32, 34], and of Kryachko and Ludeña [1, 20, 31, 33, 35–37].

2.3 Local-Scaling Transformations and the Topology of the Density

Through extensive analyses of accurate one-particle densities, Bader et al. [89, 88] have been able to determine the topological properties that characterize these objects. Consider, for example, a one-electron density corresponding to the ground state of a molecule – whose nuclei are fixed by the vectors $\{\vec{R}_\alpha\}_{\alpha=1}^M$ – which we indicate by:

$$\rho(\vec{r}; \{\vec{R}_\alpha\}_{\alpha=1}^M) \equiv \rho(\vec{r}; Q) \quad (41)$$

where Q denotes the nuclear configuration which fixes the molecular geometry. The density has an associated vector field of gradient paths, i.e., paths of steepest descent, given by:

$$\frac{d\vec{r}(s)}{ds} = \nabla \rho(\vec{r}(s); Q) \quad (42)$$

In the neighborhood of a critical point, these gradient paths can be written as:

$$\frac{d\vec{r}(s)}{ds} = \mathbf{A}(\vec{r}(s); Q) \vec{r}(s) \quad (43)$$

where $\mathbf{A}(\vec{r}(s); Q)$ is the Hessian matrix ($\mathbf{A}_{ij} = \partial^2 \rho / \partial x_i \partial x_j$). The critical points are characterized by the eigenvalues λ_1 , λ_2 , and λ_3 of the Hessian matrix. When $\lambda_1, \lambda_2, \lambda_3 > 0$, the critical point corresponds to a minimum; when $\lambda_1, \lambda_2, \lambda_3 < 0$, to a maximum; the two kinds of saddle points are defined by $\lambda_1, \lambda_2 > 0, \lambda_3 < 0$ and $\lambda_1 > 0, \lambda_2, \lambda_3 < 0$. Some of these properties are depicted in Fig. 1 for the particular case of the diatomic molecule LiH.

In addition to the critical points an important feature appearing in one-electron densities are the closed contour curves corresponding to a given value of the density [20]. These closed equidensity curves envelop each one of the nuclei up to the bond critical point located along the bond path joining two nuclei. Other closed equidensity contours envelop both nuclei, etc. This is shown schematically in Fig. 2 for the LiH molecule.

Let us now show that when we apply a local-scaling transformation to a closed contour $S_1(\vec{r}; C)$ of ρ_1 (defined by $\rho_1(\vec{r}) - C = 0$), we obtain a closed

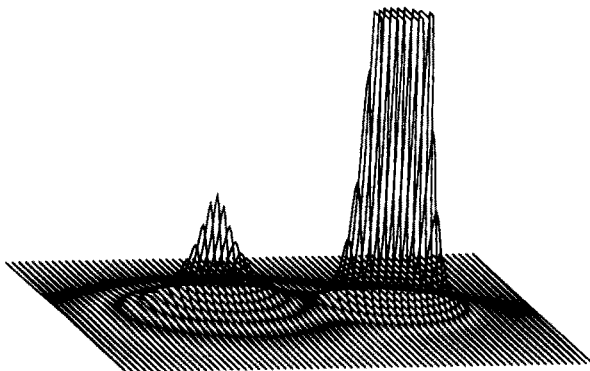


Fig. 1. Schematic representation of the one-electron density of LiH

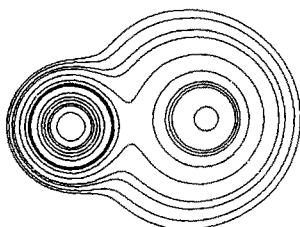


Fig. 2. Equidensity curves for LiH

contour of ρ_2 (see Fig. 3). The transformed contour is:

$$S_2(\vec{r}; C) = J(\vec{f}(\vec{r}); \vec{r}) S_1(\vec{f}(\vec{r}); C) = \left[\frac{\rho_2(\vec{r})}{\rho_1(\vec{f}(\vec{r}))} \right] S_1(\vec{f}(\vec{r}); C) \quad (44)$$

where, in the right-hand side of Eq. (44), we have used the explicit expression for the Jacobian given in Eq. (31). It is clear that the transformed contour has the same functional form as the initial one. At each point in $\mathcal{R}^3$, the Jacobian creates a positive and bounded factor multiplying $S_1(\vec{f}(\vec{r}); C)$, for all allowable values of C . The continuity, positivity and finiteness of the Jacobian guarantees that a set of closed equidensity contours in the initial density is mapped into a corresponding set of closed equidensity contours in the transformed density. In addition, it follows that local-scaling transformations map the topological features of the initial density into the transformed one.

It is clear that arbitrary one-particle densities of a molecular system need not have the same topology. In fact, only those belonging to the same “structural region” will share this property. To make these concepts clearer, consider two nuclear configurations X and Y belonging to the nuclear configuration space $\{\vec{R}_\alpha\}$ in the context of the Born–Oppenheimer approximation. The corresponding one-electron densities are $\rho(\vec{r}; X)$ and $\rho(\vec{r}; Y)$, respectively. Consider the

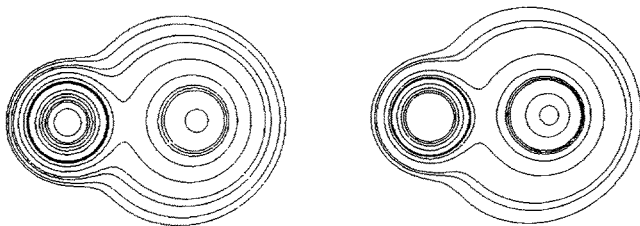


Fig. 3. Schematic representation of the transformation of a closed density contour curve of ρ_1 (dark contour on the left-hand side) into that of ρ_2 (dark contour right) by local-scaling transformations

two vector fields $\nabla\rho(\vec{r}; X)$ and $\nabla\rho(\vec{r}; Y)$. The nuclear configurations X and Y are equivalent if there exists a homeomorphism between the vector fields $\nabla\rho(\vec{r}; X)$ and $\nabla\rho(\vec{r}; Y)$. It is precisely this homeomorphism that guarantees that they have the same topological features, i.e., that they are contained in the equivalence class or “structural region” of the particular molecular graph or molecular structure. In plain words, if we stretch a molecule without either breaking the bonds or changing in any way the number and types of critical points, we can transform densities throughout the whole space of allowable “stretches” by application of local-scaling. In particular, for clamped nuclei we can transform densities of approximate wavefunctions into the exact density corresponding to the clamped nuclear positions. At this point let us introduce the set of one-particle densities

$$\mathcal{N}_B \equiv \{\rho(\vec{r}; Q) | \rho \text{ satisfying Bader's topological features}\} \quad (45)$$

Clearly, the set $\mathcal{N}_B$ is a subset of $\mathcal{N}_\Phi$ of Eq. (16), i.e., $\mathcal{N}_B \subset \mathcal{N}_\Phi$. The set $\mathcal{N}_B$ will be useful in the definition of “orbit” advanced in Sect. 4.1.

2.4 Density-Transformed One-Particle Orbitals and Their use in the Construction of Energy Functionals

Let us consider now the application of local-scaling transformations to sets of single-particle functions or orbitals. As it was shown in Sect. 2.1, a set of plane waves gives rise to the transformed orbitals described by Eq. (2). In particular, the application of this transformation to one-dimensional plane-waves leads to Harriman’s “equidensity orbitals” [27], which are given by:

$$\psi_k(a, b, c) = \sqrt{\frac{\rho(a, b, c)}{N}} \exp[i k f(a)] \quad (46)$$

where the one-dimensional phase factor is defined as:

$$f(a) = 2\pi \int_{a_0}^a \alpha(a') \bar{\rho}(a') da' \quad (47)$$

In this expression, a is one of the coordinates a, b and c in three-dimensions, whose volume element is $d^3\vec{r} = \alpha(a)\beta(b)\gamma(c)dadbdc$ and where:

$$\bar{\rho}(a) = \int_{b_0}^{b_1} \int_{c_0}^{c_1} \rho(a, b, c) \beta(b) \gamma(c) dbdc \quad (48)$$

Note that these orbitals satisfy the “equidensity” condition $\psi_k^*(a, b, c) \psi_k(a, b, c) = \rho(a, b, c)/N$; hence, a single Slater determinant constructed from these orbitals yields the density:

$$\rho(a, b, c) = \sum_{k=1}^N \psi_k^*(a, b, c) \psi_k(a, b, c) \quad (49)$$

In polar coordinates, we have the following explicit form for these “equidensity orbitals” [27]:

$$\psi_k(r, \theta, \phi) = \sqrt{\frac{\rho(r, \theta, \phi)}{N}} \exp \left[i \left(k - \frac{N+1}{2} \right) f(r) \right] \quad (50)$$

where an additional phase factor, $\exp[-i \frac{N+1}{2} f(r)]$, has been added for the purpose of minimizing the kinetic energy [61, 63, 64].

The density-transformed orbitals given by Eq. (50) can be used directly in the construction of closed analytic expressions for the 1-matrix in the single-determinantal case:

$$D_\rho^1(\vec{r}_1, \vec{r}_2) = \sum_{k=1}^N \psi_k^*(\vec{r}_1) \psi_k(\vec{r}_2) \quad (51)$$

Substituting the explicit form of Eq. (50) into Eq. (51) and carrying out the summation, one obtains [64]:

$$D_\rho^1(\vec{r}_1, \vec{r}_2) = \frac{1}{N} \sqrt{\rho(\vec{r}_1) \rho(\vec{r}_2)} \frac{\sin \frac{N}{2} F(r_1, r_2)}{\sin \frac{1}{2} F(r_1, r_2)} \quad (52)$$

where $F(r_1, r_2) \equiv f(r_1) - f(r_2)$. Note that in view of Eq. (47), the phase factor $f(r)$ depends upon the density $\rho(\vec{r})$:

$$f(r) \equiv f([\rho]; r). \quad (53)$$

Clearly then, the closed expression for the density-transformed 1-matrix in Eq. (52) (i.e., the 1-matrix constructed from transformed orbitals) is a function of the single-electron density $\rho(\vec{r})$. Hence, when we express the total energy of an N -particle system (in the single-determinantal approximation) in terms of the transformed one-matrix described by Eq. (52), one can readily obtain an energy functional which depends on ρ . This fact, which has been exploited by several authors [59–62, 85], is considered below with particular reference to the work of Ludeña [60].

Consider the N -electron Hamiltonian:

$$\hat{H}_v = \hat{T} + \hat{V}_{ext} + \hat{U} = \sum_{i=1}^N -\frac{1}{2} \nabla_{\vec{r}_i}^2 + \sum_{i=1}^N \hat{v}(\vec{r}_i) + \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{1}{|\vec{r}_i - \vec{r}_j|} \quad (54)$$

where $v(\vec{r}_i)$ is the external potential for coordinate $\vec{r}_i$. The energy, expressed as a functional of the normalized wavefunction $\Phi \in \mathcal{L}_N$, is:

$$E[\Phi] = \langle \Phi | \hat{H}_v | \Phi \rangle \quad (55)$$

When $\Phi \equiv \Phi_\rho$ adopts the form of a normalized single Slater determinant formed from density-transformed orbitals, the energy functional is:

$$\begin{aligned} E[\Phi_\rho] &= T[\Phi_\rho] + E_{ext}[\Phi_\rho] + U[\Phi_\rho] \\ &= T[\Phi_\rho] + E_{ext}[\Phi_\rho] + E_{Coulomb}[\Phi_\rho] + E_x[\Phi_\rho] \end{aligned} \quad (56)$$

where $T[\Phi_\rho]$ is the kinetic energy, $E_{ext}[\Phi_\rho]$ the energy contribution due to the external potential, $E_{Coulomb}[\Phi_\rho]$, the Coulomb (or Hartree) energy, and $E_x[\Phi_\rho]$ the exchange energy. The energy functional of Eq. (56) can be expressed exactly in terms of the 1-matrix $D_\rho^1(\vec{r}_1, \vec{r}_1')$, and the one particle density $\rho(\vec{r})$:

$$\begin{aligned} E[\Phi_\rho] &= \frac{1}{2} \int d^3\vec{r}_1 \nabla_{\vec{r}_1} \nabla_{\vec{r}_1'} D_\rho^1(\vec{r}_1, \vec{r}_1')|_{\vec{r}_1'=\vec{r}_1} + \int d^3\vec{r} \rho(\vec{r}) v(\vec{r}) \\ &\quad + \frac{1}{2} \int d^3\vec{r}_1 \int d^3\vec{r}_2 \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} \\ &\quad - \frac{1}{2} \int d^3\vec{r}_1 \int d^3\vec{r}_2 \frac{D_\rho^1(\vec{r}_1, \vec{r}_2) D_\rho^1(\vec{r}_2, \vec{r}_1)}{|\vec{r}_1 - \vec{r}_2|} \end{aligned} \quad (57)$$

Introducing the closed analytic expression for D_ρ^1 given by Eq. (52), we obtain for the kinetic energy term [64]:

$$\begin{aligned} T[\Phi_\rho] &= \frac{1}{2} \int d^3\vec{r}_1 \nabla_{\vec{r}_1} \nabla_{\vec{r}_1'} D_\rho^1(\vec{r}_1, \vec{r}_1')|_{\vec{r}_1'=\vec{r}_1} \\ &= \frac{1}{8} \int d^3\vec{r} \frac{[\nabla_{\vec{r}} \rho(\vec{r})]^2}{\rho(\vec{r})} + \frac{8}{3} \pi^4 \left(1 - \frac{1}{N^2}\right) \int d^3\vec{r} r^4 \rho^3(\vec{r}) \end{aligned} \quad (58)$$

Substituting for r the radius of the Fermi sphere $r_F = (3/4\pi\rho)^{-1/3}$, we can rewrite the kinetic energy as:

$$T[\Phi_\rho] = T_w[\Phi_\rho] + \left(\frac{3}{4\pi}\right)^{1/3} 2\pi^3 \left(1 - \frac{1}{N^2}\right) \int d^3\vec{r} \rho^{5/3}(\vec{r}) \quad (59)$$

where T_w is the Weiszäcker term. Note that the last term in Eq. (59) is just a corrected Thomas–Fermi kinetic energy expression.

The exchange energy contribution is also a functional of the one-particle density:

$$\begin{aligned} E_x[\Phi_\rho] &= -\frac{1}{2} \int d^3\vec{r}_1 \int d^3\vec{r}_2 \frac{D_\rho^1(\vec{r}_1, \vec{r}_2) D_\rho^1(\vec{r}_2, \vec{r}_1)}{|\vec{r}_1 - \vec{r}_2|} \\ &= -\frac{1}{2N^2} \int d^3\vec{r}_1 \int d^3\vec{r}_2 \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} \frac{\sin^2 \frac{N}{2}[f(r_1) - f(r_2)]}{\sin^2 \frac{1}{2}[f(r_1) - f(r_2)]}. \end{aligned} \quad (60)$$

In the particular case when ρ is spherically symmetric, the exchange energy can be rewritten in the simpler form [60]:

$$E_x[\Phi_\rho] = - \int_0^\infty dr_1 r_1^2 \bar{\rho}(r_1) v_x(f([\rho]; r_1)) \quad (61)$$

where (for example, for N even) [60]:

$$\begin{aligned} v_x(f([\rho]; r_1)) = & \sum_{i=1}^N \sum_{j=1}^N \sum_{k=0}^{\omega-k} (c_N^0)_i (c_N^0)_j c_k^{\omega-k} (-1)^k \\ & \times \frac{1}{r_1} \left[\cos^\omega \frac{f(r_1)}{2} \sin^\omega \frac{f(r_1)}{2} P_{\omega,k}(f(r_1)) \right. \\ & \left. + \sin^\omega \frac{f(r_1)}{2} \cos^k \frac{f(r_1)}{2} Q_{\omega,k}(f(r_1)) \right] \end{aligned} \quad (62)$$

In Eq. (62) $\omega = i - j + k$ and c_n^m is the binomial coefficient,

$$P_{\omega,k}(f(r_1)) = \frac{1}{2\pi} \int_0^{f(r_1)} \frac{df(r_2)}{2} \sin^\omega \frac{f(r_2)}{2} \cos^k \frac{f(r_2)}{2} \quad (63)$$

and

$$Q_{\omega,k}(f(r_1)) = \frac{1}{2\pi} \int_0^{f(r_1)} \frac{df(r_2)}{2} \cos^\omega \frac{f(r_2)}{2} \sin^k \frac{f(r_2)}{2} \quad (64)$$

Note again that because of Eq. (53), the exchange energy given by Eq. (61) is an implicit functional of ρ . (For a similar formulation of this problem, see [114].)

A generalization of Harriman's orbitals has been proposed by Gosh and Parr [63]; it is based on a description similar to that of Zumbach and Maschke [61] but uses polar spherical coordinates:

$$\begin{aligned} f_1(r, \theta, \phi) &= \frac{\int_0^\phi d\phi' \rho(r, \theta, \phi')}{\int_0^{2\pi} d\phi \rho(r, \theta, \phi)} \\ f_2(r, \theta) &= \frac{\int_0^\theta \int_0^{2\pi} d\theta' \sin \theta' d\phi' \rho(r, \theta', \phi')}{\int_0^\pi \int_0^{2\pi} d\theta \sin \theta d\phi \rho(r, \theta, \phi)} \\ f_3(r) &= \int_0^r \int_0^\pi \int_0^{2\pi} dr' r'^2 d\theta \sin \theta d\phi \rho(r', \theta, \phi). \end{aligned} \quad (65)$$

For the spherically symmetric case, this transformation leads to:

$$\begin{aligned} f_1 &= \phi/2\pi \\ f_2 &= (1 - \cos \theta)/2 \\ f_3 &= f(r) \end{aligned} \quad (66)$$

and the corresponding transformed three-dimensional plane wave can be

written as

$$\psi_{klm}(r, \theta, \phi) = \sqrt{\frac{\rho(r, \theta, \phi)}{N}} \exp i2\pi[kf(r) + (l/2)(1 - \cos \theta) + (m/2)\phi] \quad (67)$$

where k, l, m are quantum numbers. The kinetic energy term that ensues from these orbitals has been discussed by Gosh and Parr [63], but – as these authors point out – there appear singularities which might not lead to improved expressions for this functional.

2.5 Application of Space-Coordinate Density Transformations to Atomic Orbitals

We illustrate here a specific example of the application of local-scaling transformations to atomic orbitals [111]. Consider the $R_{1s}(r)$ and $R_{2s}(r)$ orbitals of the Raffennetti type for the beryllium atom [71]:

$$R_{ns}(r) = \sum_{j=1}^{12} C_{nsj} \chi_j(r) \quad (68)$$

expanded in terms of 1s Slater orbitals:

$$\chi_j(r) = (2\alpha_j)^{3/2}/2!^{1/2} \exp(-\alpha_j r) \quad (69)$$

with exponents $\alpha_j = \alpha\beta^j$ that depend only on the parameters α and β . The twelve-term expansion of Eq. (68) is sufficiently flexible to describe the Hartree–Fock wavefunction of the beryllium atom quite accurately [71].

The density associated with the Hartree–Fock–Raffennetti wavefunction is denoted by $\rho_{HF}^{R12}(r)$. We take this to be the initial density in our local-scaling transformation, i.e., $\rho_1(r) \equiv \rho_{HF}^{R12}(r)$. We take as the final density, that associated with the 650-term CI wavefunction of Esquivel and Bunge [73], which we call $\rho_2(r) \equiv \rho_{CI}(r)$. These two densities are practically about the same, as can be seen clearly in Fig. 4, where we have also plotted their difference. The transformed radial orbitals are given by:

$$R_{ns}^T(r) = \sqrt{J(f(r); r)} R_{ns}(f(r)) = \sqrt{\frac{\rho_{CI}(r)}{\rho_{HF}^{R12}(f(r))}} R_{ns}(f(r)) \quad (70)$$

The transformation function $f(r)$ is computed by solving either Eq. (39) or (40) numerically, depending on whether we take the boundary condition at zero or at infinity. In practical applications, Eq. (40) is preferred; thus, we rewrite the integrated equation as:

$$F(f(r)) = \int_{f(r)}^{\infty} dx x^2 \rho_1(x) - \int_r^{\infty} dy y^2 \rho_2(y) = 0 \quad (71)$$

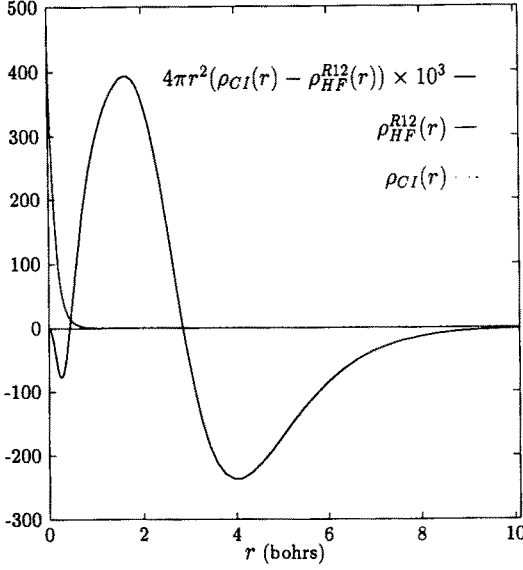


Fig. 4. Comparison of Raffenetti and Esquivel and Bunge densities for beryllium atom. [Reproduced with permission from Fig. 1 of Ludeña et al. [111]]

where both densities are normalized to N . In general, when the one-electron densities are selected to have the following form:

$$\rho(r) = \sum_{i=1}^K a_i r^{b_i} \exp(-c_i r) \quad (72)$$

(which, incidentally, is just the form of the Raffenetti and Bunge densities $\rho_{HF}^{R12}(r)$ and $\rho_{CI}(r)$, respectively), the integrals appearing in Eq. (71) can be obtained analytically in closed form. The transformation function $f(r)$ can then be calculated at each point r by the Newton method [48]:

$$f_{n+1}(r) = f_n(r) - F(f_n(r))/F'(f_n(r)) \quad (73)$$

where

$$F'(f) = f^2 \rho_2(f) \quad (74)$$

Although the method converges well, it is numerically unstable both for small values of r ($r < 10^{-4}$) and for large values of r ($r > 20$). The instability at the small r limit can be remedied by applying the McLaurin expansion to the densities appearing in Eq. (71):

$$\begin{aligned} \int_r^\infty dx x^2 \rho_1(x) &= \int_0^\infty dx x^2 \rho_1(x) - \int_0^r dx x^2 \rho_1(x) \\ &= \frac{N}{4\pi} - \left[\frac{\rho_1(0)}{3} \right] r^3, \quad r \ll 1, \end{aligned} \quad (75)$$

$$\int_{f(r)}^{\infty} dy y^2 \rho_2(y) = \frac{N}{4\pi} - \left[\frac{\rho_2(0)}{3} \right] f(r)^3, \quad f(r) \ll 1 \quad (76)$$

It follows, therefore, that when r (and $f(r)$) go to zero, an approximate solution to Eq. (71) is:

$$f(r) = \left[\frac{\rho_1(0)}{\rho_2(0)} \right]^{1/3} r \quad (77)$$

For large values of r , the dominant terms in the density expansions (see Eq. (72)) are those with the smallest exponents. Moreover, because the exponential term is the dominant one, we can approximate $F(f(r))$ in Eq. (71) by:

$$F(f(r)) = P(r) \exp(-Ar) - P(r) \exp(-Bf(r)) = 0 \quad (78)$$

with $A = \min \{c_i^1\}$ and $B = \min \{c_i^2\}$. When r is large, this leads to the approximate solution:

$$f(r) = \frac{A}{B} r \quad (79)$$

In Fig. 5, we present plots for the transformation function $f(r)$, for the Jacobian of the transformation $J(f(r); r)$, and for the derivative of the transformation function, $df(r)/dr$ corresponding to the example at hand. Selected values for the transformed orbitals are presented in Table 1, where we have also listed the corresponding values of the Hartree-Fock-Raffenetti orbitals, as well as the difference between untransformed and transformed orbitals for the sake of completeness.

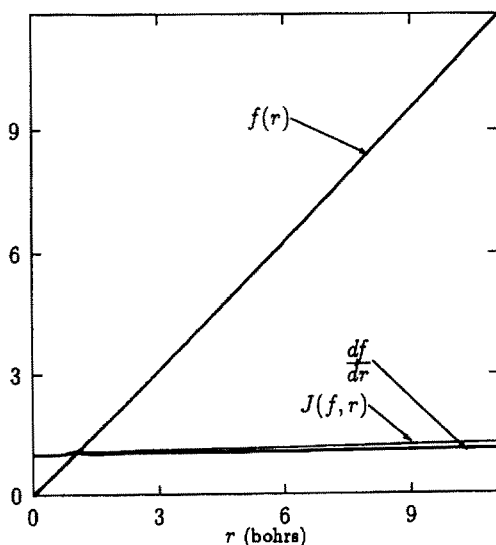


Fig. 5. Graph of the local-scaling transformation function $f(r)$ and related quantities

Table 1. Selected values of the Raffinetti–Hartree–Fock orbitals $1s_{HF}$ and $2s_{HF}$ for Be, of their locally-scaled transformed functions $1s_{HF}^T$ and $2s_{HF}^T$ and of their differences $\Delta_{1s} = (1s_{HF} - 1s_{HF}^T)$ and $\Delta_{2s} = (2s_{HF} - 2s_{HF}^T)$. [Reproduced with permission from Table 1 Ludeña et al. [111]]

$r(\text{bohrs})$	$1s_{HF}$	$1s_{HF}^T$	Δ_{1s}	$2s_{HF}$	$2s_{HF}^T$	Δ_{2s}
0.09735	2.816731	2.815507	0.001224	− 0.506750	− 0.506534	− 0.000216
0.21599	1.785544	1.784217	0.001327	− 0.301088	− 0.300898	− 0.000189
0.31426	1.235548	1.234669	0.000880	− 0.183859	− 0.183820	− 0.000039
0.41632	0.848934	0.848758	0.000176	− 0.096321	− 0.096472	0.000150
0.52628	0.570176	0.570811	− 0.000635	− 0.029220	− 0.029474	0.000254
0.60575	0.428996	0.430208	− 0.001212	0.006530	0.006387	0.000143
0.73067	0.275433	0.277403	− 0.001969	0.047078	0.047799	− 0.000721
0.92365	0.139958	0.141070	− 0.001112	0.083892	0.088085	− 0.004193
1.01443	0.102036	0.101597	0.000439	0.093826	0.099183	− 0.005357
1.22364	0.049491	0.047283	0.002209	0.105225	0.109704	− 0.004479
1.34391	0.032735	0.030793	0.001942	0.106814	0.110390	− 0.003576
1.40840	0.026245	0.024540	0.001705	0.106643	0.109848	− 0.003205
1.54683	0.016359	0.015138	0.001221	0.104514	0.107143	− 0.002629
1.62106	0.012706	0.011698	0.001008	0.102624	0.105028	− 0.002404
1.69886	0.009756	0.008933	0.000823	0.100237	0.102440	− 0.002203
1.78039	0.007401	0.006736	0.000665	0.097395	0.099413	− 0.002018
1.95537	0.004099	0.003677	0.000421	0.090538	0.092200	− 0.001662
2.14756	0.002148	0.001892	0.000257	0.082447	0.083736	− 0.001289
2.47182	0.000727	0.000617	0.000111	0.068895	0.069564	− 0.000669
2.84505	0.000211	0.000170	0.000041	0.054834	0.054858	− 0.000024
3.12468	0.000084	0.000065	0.000019	0.045767	0.045405	0.000362
3.59648	0.000018	0.000013	0.000005	0.033330	0.032546	0.000785
3.76908	0.000010	0.000007	0.000003	0.029598	0.028724	0.000874
4.13952	0.000003	0.000002	0.000001	0.022855	0.021883	0.000972
4.54638	0.000001	0.000000	0.000000	0.017130	0.016154	0.000976

2.6 The Transformation of N -Particle Wavefunctions

The uniqueness of the density transformation has an important implication: any two one-particle densities $\rho_1(\vec{r})$ and $\rho_2(\vec{r})$ having the same topology, i.e., $\rho_1(\vec{r}), \rho_2(\vec{r}) \in \mathcal{N}_B$ (see Eq. (45)) are uniquely connected by the local-scaling transformation which is a solution to Eq. (36). In Hilbert space we have an infinite number of N -particle wavefunctions that yield a given density. This means that if we apply this particular local-scaling transformation to an arbitrary wavefunction $\Phi_{\rho_1}^{[i]}$ that associates with the density $\rho_1(\vec{r})$ (where the superindex $[i]$ indicates a given wavefunction selected from the infinite set), then – according to Eq. (30) – the transformation yields a wavefunction $\Phi_{\rho_2}^{[i]}$. Note that we keep the same superindex in this transformed wavefunction, because it is uniquely generated from $\Phi_{\rho_1}^{[i]}$.

In order to exemplify these ideas, we construct three initial or generating wavefunctions for the ^1S state of the helium atom, and generate two types of

transformed wavefunctions by applying local-scaling transformations. These two cases are itemized below:

- All transformed wavefunctions yield the “exact” (Benesch [68]) one-particle density.
- All transformed wavefunctions yield the Hartree–Fock (Boyd [72]) one-particle density.

We take the initial wavefunctions to be very limited configuration-interaction expansions, containing only s orbitals. Thus, we take as the first wavefunction in the one formed by all single and double excitations generated from the basic configuration $[1s^2]$ by substitutions comprising the $2s$ orbital; for the second wavefunction, we span over the $2s$ and $3s$ orbitals; and for the third one, we use orbitals $1s'$, $2s'$ and $3s'$. Hence, are all these wavefunctions are “full CI” wavefunctions for such bases. Explicitly, these wavefunctions are

$$\Phi_a^{[1]} = C_{1s^2}[1s^2] + C_{1s2s}[1s2s] + C_{2s^2}[2s^2] \quad (80)$$

$$\begin{aligned} \Phi_b^{[2]} = & C_{1s^2}[1s^2] + C_{2s^2}[2s^2] + C_{3s^2}[3s^2] + C_{1s2s}[1s2s] \\ & + C_{1s3s}[1s3s] + C_{2s3s}[2s3s] \end{aligned} \quad (81)$$

and

$$\begin{aligned} \Phi_c^{[3]} = & C_{1s'^2}[1s'^2] + C_{2s'^2}[2s'^2] + C_{3s'^2}[3s'^2] + C_{1s'2s'}[1s'2s'] \\ & + C_{1s'3s'}[1s'3s'] + C_{2s'3s'}[2s'3s']. \end{aligned} \quad (82)$$

The orbitals ns and ns' are expanded in terms of Slater functions:

$$ns(r) = \sum_{j=1}^m c_{nsj} \chi_j(r) \quad (83)$$

with $\chi_j(r) = N_j r^{n_j-1} \exp(-\lambda_j r)$ and $\chi'_j(r) = N'_j r^{n'_j-1} \exp(-\lambda'_j r)$. In Table 2, we list the CI expansion coefficients of the generating wavefunctions. In Tables 3, 4 and 5, we list the values of the parameters for the orbitals entering in wavefunctions $\Phi_a^{[1]}$, $\Phi_b^{[2]}$ and $\Phi_c^{[3]}$, respectively.

The wavefunctions described by Eqs. (80), (81) and (82) are associated with the one-particle densities $\rho_a(r)$, $\rho_b(r)$, and $\rho_c(r)$, respectively. For example, the

Table 2. Configuration interaction expansion coefficients for the wavefunctions

	Φ_a	Φ_b	Φ_c
C_{1s^2}	-0.96861	0.96084	-0.98862
C_{2s^2}	0.03370	-0.02994	0.05557
C_{3s^2}		-0.00530	0.00763
C_{1s2s}	0.24628	-0.21596	-0.13717
C_{1s3s}		-0.17093	0.02252
C_{2s3s}		0.00184	-0.01268

Talbe 3. Orbital parameters for Φ_a function

i	c_{1s_i}	c_{2s_i}	n_i	λ_i
1	0.84347	− 1.08553	1	2.36923
2	0.21087	1.35844	2	1.67585

Table 4. Orbital parameters for Φ_b function

i	c_{1s_i}	c_{2s_i}	c_{3s_i}	n_i	λ_i
1	1.00000	− 2.11677	1.11180	1	2.00
2	0.00000	2.34109	− 1.77632	2	2.20
3	0.00000	0.00000	1.34909	3	1.30

Table 5. Orbital parameters for Φ_c function

i	c_{1s_i}	c_{2s_i}	c_{3s_i}	n_i	λ_i
1	1.00000	− 2.90019	5.38297	1	1.45987
2	0.00000	3.06775	− 13.16192	2	1.83110
3	0.00000	0.00000	8.32176	3	2.14871

explicit form of $\rho_a(r)$ is:

$$\rho_a(r) = n_{1s^2}(1s(r))^2 + n_{1s2s}(1s(r)2s(r)) + n_{2s^2}(2s(r))^2 \quad (84)$$

where

$$\begin{aligned} n_{1s^2} &= (2C_{1s^2}^2 + C_{1s2s}^2) \\ n_{1s2s} &= 2\sqrt{2}C_{1s2s}(C_{1s^2} + C_{2s^2}) \\ n_{2s^2} &= (C_{1s2s}^2 + 2C_{2s^2}^2) \end{aligned} \quad (85)$$

The “exact” one-particle density for the helium atom is assumed in this case to be that of Benesch [68]:

$$\rho_{exact}(r) = \sum_{n=1}^{14} a_n r^n e^{-kr} + \sum_{n=1}^7 b_n r^n e^{-2kr} \quad (86)$$

For the Hartree–Fock density, we take that of Boyd [72]:

$$\rho_{HF}(r) = \sum_{k=1}^{15} c_k r^{n_k} e^{-Z_k r} \quad (87)$$

The transformation functions $f(r)$ for the case considered here have been calculated by solving Eq. (36). Selected values of these transformations are listed in Table 6.

The superindices [1], [2] and [3] that label wavefunctions $\Phi_a^{[1]}$, $\Phi_b^{[2]}$ and $\Phi_c^{[3]}$, respectively, indicate the different subclasses of wavefunctions that can be generated from the initial ones by means of local-scaling transformations. Thus, although wavefunctions $\Phi_b^{[2]}$ and $\Phi_c^{[3]}$ have the same form, the fact that they contain different orbitals makes it impossible to transform one into the other by means of local-scaling transformations. The particular subclasses of wavefunctions that are generated from some given, but otherwise arbitrary, initial or generating wavefunctions are called “orbits”. Note that these “orbits” are sets of N -particle wavefunctions and have nothing in common with atomic or molecular “orbitals”.

Thus, for example, from wavefunction $\Phi_b^{[2]}$ we can generate an “orbit” which contains – among the infinite number of wavefunctions obtained through the application of local-scaling transformation, the particular wavefunctions $\Phi_{b, \rho_{HF}}^{[2]}$ and $\Phi_{b, \rho_{exact}}^{[2]}$. The important aspect of “orbits” is that the uniqueness of the local-scaling transformation associates a different one-particle density $\rho \in \mathcal{N}_B$ with each wavefunction in an “orbit”. In other words, for all wavefunctions within an “orbit”, there is a one-to-one correspondence between wavefunctions and one-particle densities. Moreover, all wavefunctions belonging to an “orbit” can be *constructively generated*.

To complete this section, we present in Table 7 some energy values for the initial, as well as for the transformed wavefunctions $\Phi_a^{[1]}$, $\Phi_b^{[2]}$ and $\Phi_c^{[3]}$ discussed above. The energies in the first column correspond to the expectation values of the untransformed wavefunctions. The second and third columns are those of

Table 6. Selected values for the transformation functions $f(r)$

r	$f_a^{exact}(r)$	$f_a^{HF}(r)$	$f_b^{exact}(r)$	$f_b^{HF}(r)$	$f_c^{exact}(r)$	$f_c^{HF}(r)$
0.00070	0.00070	0.00070	0.00071	0.00071	0.00070	0.00070
0.03895	0.03894	0.03884	0.03988	0.03978	0.03889	0.03879
0.13569	0.13565	0.13530	0.13782	0.13754	0.13554	0.13520
0.19679	0.19670	0.19623	0.19904	0.19857	0.19661	0.19613
0.26963	0.26949	0.26889	0.27132	0.27073	0.26945	0.26885
0.35796	0.35780	0.35780	0.35780	0.35780	0.35780	0.35780
0.46732	0.46723	0.46657	0.46481	0.46416	0.46740	0.46674
0.60622	0.60652	0.60612	0.59941	0.59903	0.60683	0.60643
0.78849	0.78999	0.79032	0.77604	0.77635	0.79037	0.79069
1.03822	1.04278	1.04466	1.02147	1.02332	1.04287	1.04474
1.40138	1.41248	1.41742	1.39573	1.40093	1.41128	1.41619
2.86944	2.89079	2.90968	3.37882	3.40908	2.88787	2.90695
3.88840	3.88391	3.90478	4.96967	5.00238	3.90333	3.92496
4.98703	4.98704	4.94333	6.55808	6.58243	4.99914	5.01661
6.24795	6.08257	6.10331	8.23826	8.26792	6.24235	6.26488

Table 7. Energy values for the initial and locally-scaled wavefunctions Φ_a , Φ_b and Φ_c (energies in hartrees)

	ρ_{initial}	ρ_{HF}	ρ_{Benesch}
$C_I^{\text{non-opt}}$			
$\Phi_a, \{1s2s\}$	-2.877415	-2.877220	-2.877396
$\Phi_b, \{1s2s3s\}$	-2.867977	-2.876634	-2.876793
$\Phi_c, \{1s2s3s\}^{\text{opt}}$	-2.878605	-2.878295	-2.878507
C_I^{opt}			
Φ_a		-2.877226	-2.877398
Φ_b		-2.877031	-2.876996
Φ_c		-2.878522	-2.878580

the transformed wavefunctions with final densities ρ_{HF} and ρ_{Benesch} , respectively. The coefficients in the first three lines are those that were originally chosen. Those in the last three lines have been optimized, keeping the final density fixed. It is of interest in the present context to note that although all six energy values in the last column correspond to wavefunctions that associate with the same exact one-particle density (we assume here that this exact density is approximated well by that of Benesch [68]), these values are quite different. This clearly illustrates the fact that the energy functional does not depend on the density alone, but it also depends on the form of the generating wavefunction, which – in turn – determines the shape of the exchange and correlation holes (see Sect. 4.2).

2.7 General Space-Coordinate Density Transformations

Let us now elaborate on the relation given by Eq. (27): $\hat{f} = (\hat{R}_{\rho_1})^{-1} \circ \hat{R}_{\rho_2}$. Clearly, from this relation we obtain:

$$\hat{R}_{\rho_1} \circ \hat{f} = \hat{R}_{\rho_2} \quad (88)$$

Now let us determine the effect of the operators on both sides of Eq. (88) on the vector $\vec{r} = (r, \theta, \phi)$. When we operate with $\hat{R}_{\rho_2}$ on the vector $\vec{r} = (r, \theta, \phi)$, we obtain:

$$\hat{R}_{\rho_2} \vec{r} \equiv \hat{R}_{\rho_2}(r, \theta, \phi) = (R_{\rho_2, r}(r, \theta, \phi), R_{\rho_2, \theta}(r, \theta, \phi), R_{\rho_2, \phi}(r, \theta, \phi)) \quad (89)$$

The effect of the operators on the left hand side of Eq. (88) on $\vec{r}$ is:

$$\begin{aligned} \hat{R}_{\rho_1} \circ \hat{f} \vec{r} &\equiv \hat{R}_{\rho_1} \circ \hat{f}(r, \theta, \phi) \\ &= \hat{R}_{\rho_1}(f_r(r, \theta, \phi), f_\theta(r, \theta, \phi), f_\phi(r, \theta, \phi)) \\ &= (R_{\rho_1, r}(f_r, f_\theta, f_\phi), R_{\rho_1, \theta}(f_r, f_\theta, f_\phi), R_{\rho_1, \phi}(f_r, f_\theta, f_\phi)) \end{aligned} \quad (90)$$

Equating the vector components of Eq. (89) with those of Eq. (90) we obtain the set of equations:

$$\begin{aligned} R_{\rho_2,r}(r, \theta, \phi) &= R_{\rho_1,r}(f_r, f_\theta, f_\phi) \\ R_{\rho_2,\theta}(r, \theta, \phi) &= R_{\rho_1,\theta}(f_r, f_\theta, f_\phi) \\ R_{\rho_2,\phi}(r, \theta, \phi) &= R_{\rho_1,\phi}(f_r, f_\theta, f_\phi) \end{aligned} \quad (91)$$

Introducing the measure:

$$\mu_\rho(r, \theta, \phi) = \rho(r, \theta, \phi) r^2 \sin \theta \quad (92)$$

we define the vector components in polar coordinates as (see Gosh and Parr [63], or Zumbach and Masche [61]):

$$R_{\rho,r}(r, \theta, \phi) = \frac{\int_0^r \int_0^\pi \int_0^{2\pi} dr' d\theta' d\phi' \mu(r', \theta', \phi')}{\int_0^{+\infty} \int_0^\pi \int_0^{2\pi} dr' d\theta' d\phi' \mu(r', \theta', \phi')} \quad (93)$$

$$R_{\rho,\theta}(r, \theta, \phi) = \frac{\int_0^\theta \int_0^\pi \int_0^{2\pi} d\theta' d\phi' \mu(r, \theta', \phi')}{\int_0^\pi \int_0^{2\pi} d\theta' d\phi' \mu(r, \theta', \phi')} \quad (94)$$

$$R_{\rho,\phi}(r, \theta, \phi) = \frac{\int_0^\phi d\phi' \mu(r, \theta, \phi')}{\int_0^{2\pi} d\phi' \mu(r, \theta, \phi')} \quad (95)$$

The equalities given by Eq. (91) can be now explicitly written. Thus, for the r component, we have:

$$\frac{\int_0^{f_r} \int_0^\pi \int_0^{2\pi} df'_r df'_\theta df'_\phi \mu_{\rho_1}(f'_r, f'_\theta, f'_\phi)}{\int_0^{+\infty} \int_0^\pi \int_0^{2\pi} df'_r df'_\theta df'_\phi \mu_{\rho_1}(f'_r, f'_\theta, f'_\phi)} = \frac{\int_0^r \int_0^\pi \int_0^{2\pi} dr' d\theta' d\phi' \mu_{\rho_2}(r', \theta', \phi')}{\int_0^{+\infty} \int_0^\pi \int_0^{2\pi} dr' d\theta' d\phi' \mu_{\rho_2}(r', \theta', \phi')} \quad (96)$$

For the θ component, we are led to the expression:

$$\frac{\int_0^{f_\theta} \int_0^\pi df'_\theta df'_\phi \mu_{\rho_1}(f_r, f'_\theta, f'_\phi)}{\int_0^\pi \int_0^{2\pi} df'_\theta df'_\phi \mu_{\rho_1}(f_r, f'_\theta, f'_\phi)} = \frac{\int_0^\theta \int_0^\pi d\theta' d\phi' \mu_{\rho_2}(r, \theta', \phi')}{\int_0^\pi \int_0^{2\pi} d\theta' d\phi' \mu_{\rho_2}(r, \theta', \phi')} \quad (97)$$

Finally, for the ϕ component, we have the result:

$$\frac{\int_0^{f_\phi} df'_\phi \mu_{\rho_1}(f_r, f_\theta, f'_\phi)}{\int_0^{2\pi} df'_\phi \mu_{\rho_1}(f_r, f_\theta, f'_\phi)} = \frac{\int_0^\phi d\phi' \mu_{\rho_2}(r, \theta, \phi')}{\int_0^{2\pi} d\phi' \mu_{\rho_2}(r, \theta, \phi')} \quad (98)$$

For spherically symmetric densities, Eqs. (96), (97), and (98) become:

$$\frac{4\pi}{N} \int_0^{f_r} df'_r f'^2_r \rho_1(f'_r) = \frac{4\pi}{N} \int_0^r dr' r'^2 \rho_2(r') \quad (99)$$

$$\frac{1 - \cos f_\theta}{2} = \frac{1 - \cos \theta}{2} \quad (100)$$

and

$$\frac{f_\phi}{2\pi} = \frac{\phi}{2\pi} \quad (101)$$

Equation (99) is completely equivalent to Eq. (39). Thus, the transformations discussed here and the local-scaling transformations coincide in this spherically symmetric case. It is clear however, that the procedure outlined in this Section is much more flexible than the one presented in Sect. 2.2.

Let us also consider the application of these transformations to diatomic molecules. We note that the density transformations carry the initial prolate spheroidal coordinates (ζ, η, ϕ) into the transformed coordinates $(\zeta_\rho, \eta_\rho, \phi)$. The equations that define these transformations are [119]:

$$\frac{\int_{-1}^{\eta} \rho(\eta', \zeta)(\zeta^2 - \eta'^2) d\eta'}{\int_{-1}^1 \rho(\eta', \zeta)(\zeta^2 - \eta'^2) d\eta'} = \frac{\int_{-1}^{\eta_\rho} \rho_1(\eta', \zeta_\rho)(\zeta_\rho^2 - \eta'^2) d\eta'}{\int_{-1}^1 \rho_1(\eta', \zeta_\rho)(\zeta_\rho^2 - \eta'^2) d\eta'} \quad (102)$$

and

$$\frac{\int_{-1}^1 \int_{-1}^{\zeta} \rho(\eta', \zeta')(\zeta'^2 - \eta'^2) d\eta' d\zeta'}{N/2\pi} = \frac{\int_{-1}^1 \int_{-1}^{\zeta_\rho} \rho_1(\eta', \zeta')(\zeta'^2 - \eta'^2) d\eta' d\zeta'}{N/2\pi} \quad (103)$$

2.8 Momentum-Coordinate Density Transformations

Let us consider an N -particle wavefunction $\Phi_{\rho_1}(\vec{r}_1, \dots, \vec{r}_N)$ (where for simplicity we disregard spin) associated with the one-particle density $\rho_1(\vec{r})$, and let us obtain the Fourier transform of this wavefunction by means of:

$$\Psi_{\gamma_1}(\vec{p}_1, \dots, \vec{p}_N) \equiv (2\pi)^{-3N/2} \int d^3\vec{r}_1 \dots \int d^3\vec{r}_N \exp\left(-i \sum_{k=1}^N \vec{p}_k \cdot \vec{r}_k\right) \times \Phi_{\rho_1}(\vec{r}_1, \dots, \vec{r}_N) \quad (104)$$

The momentum wavefunction is associated with the momentum density $\gamma_1(\vec{p})$ through the relation

$$\gamma_1(\vec{p}) = N \int d^3\vec{p}_2 \dots \int d^3\vec{p}_N |\Psi_{\gamma_1}(\vec{p}, \vec{p}_2, \dots, \vec{p}_N)|^2 \quad (105)$$

From the momentum density one can find the radial momentum density by integration over the angular variables $\Omega_{\vec{r}}$ in momentum space:

$$I(p) = \int d\Omega_{\vec{r}} p^2 \gamma(\vec{p}) \quad (106)$$

as well as the spherically symmetric isotropic Compton profile (within the impulse approximation):

$$J(q) = \frac{1}{2} \int_{|q|} p^{-1} I(p) \quad (107)$$

Note that the momentum density $\gamma(\vec{p})$ is *not* the Fourier transform of the position density $\rho(\vec{r})$.

Just as it was done in position space, we can introduce local-scaling transformations in momentum space, in view of the fact that the momentum densities satisfy the following conditions:

1. $\gamma(\vec{p})$ is nonnegative everywhere in $\mathcal{R}_p^3$.
2. $\int d^3\vec{p} \gamma(\vec{p}) = N$.
3. $\gamma(\vec{p})$ is a continuously differentiable function of $\vec{p} \in \mathcal{R}_p^3$, i.e., each component of $\nabla_{\vec{p}}\gamma(\vec{p})$ is a continuous function of $\vec{p}$.
4. Any equidensity path $\gamma(\vec{p}) = C$ is closed and continuous and the whole set of these paths covers the entire space of $\mathcal{R}_p^3$ when C ranges over the domain of values of a given $\gamma(\vec{p})$.

Thus, we can consider the following local-scaling transformation in momentum space:

$$\vec{p} \xrightarrow{\hat{T}} \vec{P}(\vec{p}) = \frac{P(\vec{p})}{p} \vec{p} \quad (108)$$

Given two momentum densities $\gamma_2(\vec{p})$ and $\gamma_1(\vec{p})$ satisfying the above constraints, we obtain as a result of this transformation:

$$\gamma_2(\vec{p}) = J(\vec{P}(\vec{p}); \vec{p}) \gamma_1(\vec{P}(\vec{p})) \quad (109)$$

where $J(\vec{P}(\vec{p}); \vec{p})$ is the Jacobian of the transformation. Again, as in the case of position space, we restrict these transformations to those having positive definite Jacobians, in order to guarantee uniqueness.

In analogy with the position-space treatment, we have the following explicit expression for the Jacobian:

$$J(\vec{P}(\vec{p}); \vec{p}) = \frac{\vec{p} \cdot \nabla_{\vec{p}} P^3(\vec{p})}{p^3} \quad (110)$$

For the spherically symmetric case we have:

$$\frac{dP(p)}{dp} = \frac{p^2}{P^2(p)} \frac{\gamma_2(p)}{\gamma_1(P(p))} \quad (111)$$

which in integrated form becomes:

$$\int_0^{P(p)} dx x^2 \gamma_1(x) = \int_0^p dy y^2 \gamma_2(y) \quad (112)$$

It follows from the above considerations that local-scaling transformations can be advanced in momentum space on an equal footing with those in position space. In particular, wavefunctions in momentum space can be transformed so as to generate new wavefunctions that have the property of belonging to an “orbit”.

Local-scaling transformations have been employed [39] in order to obtain a one-particle density in position space from the one-particle density in momentum space, and vice versa. This problem arises from example when we have a $\gamma(\vec{p})$, obtained from experimental Compton profiles, and wish to calculate the corresponding $\rho(\vec{r})$ [98].

3 Relationship Between “Density-Driven” and Local-Scaling Transformations

In a recent monograph (1990) on the “density driven” approach, Cioslowski [77] summarizes the development of density functional theory as follows:

First in their celebrated paper Hohenberg and Kohn [17] have shown that the electronic wavefunction of the ground state is entirely determined by the corresponding density. This provided a *nonconstructive proof* of the existence of the density functional for the electronic energy, $E[\rho]$. It had taken [*sic*] 15 years before the next step was reached. The constrained search approach [78, 84, 86] yielded an *implicit construction* for the functional $E[\rho]$. A rigorous prescription for $E[\rho]$ was given, but its algebraic form (either direct or indirect) remained unknown. Various approaches to this problem, often connected with the efforts to find a Schrödinger-like equation for the electron density, followed soon [62, 79–83, 92, 93]. However, an *explicit construction* of $E[\rho]$ has become only known recently [74–76]

The *explicit construction* to which Cioslowski refers is that provided by the “density-driven” approach, advanced in 1988. But, already in 1986, an alternative way for carrying out this explicit construction had been set forward by Kryachko, Petkov and Stoitsov [28]. This new approach – based on local-scaling transformations – was further developed by these same authors [29, 30, 32, 34], by Kryachko and Ludeña [1, 20, 31, 33, 35–37], and by Koga [51]. In this Section we show that Cioslowski’s “density-driven” method corresponds to a finite basis representation of the local-scaling transformation version of density functional theory [38].

It is instructive, however, in order to establish the connection between the usual methods in quantum chemistry – based on molecular orbitals – and the local-scaling transformation version of density functional theory, to discuss Cioslowski’s work in some detail.

Consider the orthonormal set of one-particle functions $\{\phi_{k_i}(\vec{r})\}$ for $k_i = 1, \dots, m$, with m greater than the number of particles N , from which an ordered set of $M \equiv \binom{m}{N}$ Slater determinants:

$$\Phi_K \equiv \frac{\det}{\sqrt{N!}} [\phi_{k_1}(\vec{r}_1) \cdots \phi_{k_N}(\vec{r}_N)] \quad (113)$$

is constructed (K denotes the ordered set of indexes $k_1 < k_2 < \cdots < k_N$). The N -electron wavefunction Ψ in this finite basis is given by:

$$\Phi = \sum_K^M C_K \Phi_K \equiv \vec{C} \vec{\Phi}^\dagger \quad (114)$$

and the 1-matrix takes the form:

$$D^1(\vec{r}, \vec{r}') = \sum_{k_i=1}^m \sum_{k_j=1}^m D_{k_i, k_j}^1 \phi_{k_i}(\vec{r}) \phi_{k_j}(\vec{r}') \quad (115)$$

where $D_{k_i, k_j}^1 \equiv D_{k_i, k_j}^1[\vec{C}]$ is the following function of the variational coefficients (see Eq. (22)):

$$D_{k_i, k_j}^1[\vec{C}] = \sum_{K=1}^M \sum_{L=1}^M C_K C_L \Delta_{KL}^{k_i k_j} \quad (116)$$

The total energy becomes a functional of $\vec{C}$ and $\vec{\Phi}$:

$$\begin{aligned} E[\vec{\Phi}, \vec{C}] = & \frac{1}{2} \sum_{k_i=1}^m \sum_{k_j=1}^m D_{k_i, k_j}^1[\vec{C}] \int d^3\vec{r} \int d^3\vec{r}' \nabla \phi_{k_i}(\vec{r}) \nabla \phi_{k_j}(\vec{r}') \\ & + \int d^3\vec{r} \rho(\vec{r}) v(\vec{r}) + \frac{1}{2} \int d^3\vec{r}_1 \int d^3\vec{r}_2 \frac{\rho(\vec{r}_1) \rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} \\ & - \sum_{k_i=1}^m \sum_{k_j=1}^m \sum_{k_k=1}^m \sum_{k_l=1}^m B_{k_i, k_j, k_k, k_l}[\vec{C}] \\ & \times \int d^3\vec{r}_1 \int d^3\vec{r}_2 \frac{\phi_{k_i}(\vec{r}_1) \phi_{k_j}(\vec{r}_1) \phi_{k_k}(\vec{r}_2) \phi_{k_l}(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} \end{aligned} \quad (117)$$

where the first term is the kinetic energy and the last term is the exchange-correlation energy. Note that the tensor $B_{k_i, k_j, k_k, k_l}[\vec{C}]$ in this last term takes specific forms, depending on the orbital approximation. Thus, in the Hartree–Fock case, it becomes the product of the 1-matrix expansion coefficients. Any variation of this energy expression must be constrained by the orthogonality conditions on the orbitals:

$$\int d^3\vec{r} \phi_{k_i}^*(\vec{r}) \phi_{k_j}(\vec{r}) = \delta_{k_i k_j} \quad (118)$$

The gist of Cioslowski's work is to set up an energy functional that depends on the density, in the context of the constrained-search approach of Levy [84]. This functional is, therefore, defined by:

$$E[\rho] = \min_{(\vec{\Phi}, \vec{C}) \rightarrow \rho} \{E[\vec{\Phi}, \vec{C}]\} \quad (119)$$

where ρ denotes a fixed density. The possibility of carrying out this constrained search hinges upon the construction of all wavefunctions that yield the fixed density. This problem is solved in Cioslowski's approach by introducing a density-dependent set of one particle functions or orbitals. These functions are given explicitly by:

$$\psi_{k_i}([\rho]; \vec{r}) = \beta^{-1/2}(\vec{r}) \rho(\vec{r}) \sum_{k_j=1}^m (S^{-1/2})_{k_i k_j}^* \phi_{k_j}(\vec{r}) \quad (120)$$

where:

$$\beta(\vec{r}) = \sum_{k_i=1}^m \sum_{k_j=1}^m \sum_{k_k=1}^m \sum_{k_l=1}^m D_{k_i, k_j}^1[\vec{C}](S^{-1/2})_{k_i k_k} (S^{-1/2})_{k_j k_l}^* \phi_{k_j}^*(\vec{r}) \phi_{k_l}(\vec{r}) \quad (121)$$

and the generalized overlap matrix S is a Hermitian positive-definite solution of the equation:

$$S_{k_i k_j} = \int d^3\vec{r} \phi_{k_j}^*(\vec{r}) \phi_{k_i}(\vec{r}) \beta^{-1}(\vec{r}) \rho(\vec{r}) \quad (122)$$

Clearly, the energy functional constructed with these transformed orbitals must satisfy

$$E[\tilde{\Psi}[\rho], \vec{C}] = E[\rho, \vec{\Phi}, \vec{C}] \quad (123)$$

as the transformed N -particle wavefunction becomes $\Psi = \sum_K C_K \Psi_K$, where the Slater determinants Ψ_K are constructed from the transformed orbitals. Thus, the energy functional $E[\rho, \vec{\Phi}, \vec{C}]$ can be minimized with respect to $\rho(\vec{r})$, to the vector $\vec{\Phi}$ formed by the initial Slater determinants, and also to the vector $\vec{C}$ comprising the expansion coefficients. Clearly, this functional attains its minimum at $\rho(\vec{r}) = \rho_0(\vec{r})$ (where $\rho_0(\vec{r})$ is the exact ground state density), provided that the space spanned by the initial Slater determinants is infinite and that the set of expansion coefficients is optimal.

Let us now consider the transformed orbitals from the perspective of local-scaling transformations. For a fixed set of single-particle functions $\{\phi_{k_i}(\vec{r})\}$ and a fixed set of expansion coefficients $\{C_K\}$, the wavefunction given by Eq. (114) is also fixed and yields a one-particle density $\rho_\Phi(\vec{r})$. We now consider the local-scaling transformation that carries this density into a density $\rho(\vec{r})$ and obtain the corresponding transformed orbitals:

$$\psi_{k_i}(\vec{r}) = [J(\vec{f}(\vec{r}); \vec{r})]^{1/2} \phi_{k_i}(\vec{f}(\vec{r})) = \left[\frac{\rho(\vec{r})}{\rho_\Phi(\vec{f}(\vec{r}))} \right]^{1/2} \phi_{k_i}(\vec{f}(\vec{r})) \quad (124)$$

Let us now expand the function $\phi_{k_i}(\vec{f}(\vec{r}))$ appearing in Eq. (124) in terms of the one particle set $\{\phi_{k_p}(\vec{r})\}_{k_p=1}^m$:

$$\phi_{k_i}(\vec{f}(\vec{r})) = \sum_{k_p=1}^m W_{k_i k_p} \phi_{k_p}(\vec{r}) \quad (125)$$

where the expansion coefficients $W_{k_i k_p}$ are – for the moment – undetermined. It follows from Eqs. (125) and (115) that the one-particle density ρ_Φ evaluated at the position vector $\vec{f}(\vec{r})$ becomes:

$$\rho_\Phi(\vec{f}(\vec{r})) = \sum_{k_i=1}^m \sum_{k_j=1}^m \sum_{k_p=1}^m \sum_{k_q=1}^m D_{k_p, k_i}^1 W_{k_j k_q}^* W_{k_i k_p} \phi_{k_p}(\vec{r}) \phi_{k_q}(\vec{r}) \quad (126)$$

The conditions that explicitly define the transformation matrix W can be obtained by noting that the overlap is not modified by local-scaling transforma-

tions:

$$\begin{aligned}
 S_{k_i k_j}(\psi) &\equiv \int d^3\vec{r} \psi_{k_i}^*(\vec{r}) \psi_{k_j}(\vec{r}) = \int d^3\vec{r} J(\vec{f}(\vec{r}); \vec{r}) \phi_{k_i}^*(\vec{f}(\vec{r})) \phi_{k_j}(\vec{f}(\vec{r})) \\
 &= \int d^3\vec{f} \phi_{k_i}^*(\vec{f}) \phi_{k_j}(\vec{f}) \equiv S_{k_i k_j}(\phi)
 \end{aligned}
 \tag{127}$$

Moreover, since we assume that the set $\{\phi_{k_i}(\vec{r})\}$ is orthonormal, it follows that $S_{k_i k_j}(\psi) = S_{k_i k_j}(\phi) = \delta_{k_i k_j}$. In order to establish the connection with Cioslowski's work, let us define the matrix element of the Jacobian of the transformation as:

$$\tilde{S}_{k_p k_q} \equiv \int d^3\vec{r} \frac{\rho(\vec{r})}{\rho_\phi(\vec{f}(\vec{r}))} \phi_{k_p}^*(\vec{r}) \phi_{k_q}(\vec{r})
 \tag{128}$$

Using Eqs. (128) and (125), we obtain from the first line of Eq. (127) the following condition on the matrix elements of W :

$$S_{k_i k_j}(\psi) = \delta_{k_i k_j} = \sum_{k_p=1}^m \sum_{k_q=1}^m W_{k_p k_i}^* W_{k_j k_q} \tilde{S}_{k_p k_q}
 \tag{129}$$

Making use of the property of a semi-definite one-body operator, say, $\hat{L}$:

$$\langle i | \hat{L} | j \rangle = \langle i | \hat{L}^{1/2} \hat{L}^{1/2} | j \rangle = \sum_k \langle i | \hat{L}^{1/2} | k \rangle \langle k | \hat{L}^{1/2} | j \rangle
 \tag{130}$$

it is easily seen that Eq. (129) is satisfied if:

$$W = \tilde{S}^{-1/2}
 \tag{131}$$

The identification with Cioslowski's work becomes evident if we let $\rho_\phi(\vec{f}(\vec{r})) = \beta(\vec{r})$.

It is clear, therefore, that Cioslowski's approach based on "density-driven" orbitals [74, 75, 77], corresponds to a finite orbital representation of the local-scaling transformation version of density functional theory [38].

4 The Construction of Approximate Energy Density Functionals by Means of Local-Scaling Transformations

4.1 Functional N -Representability and the Notion of "Orbits"

We have already introduced the notion of "orbit" in Sect. 2.6. Here we formalize this concept and show its implications for the *functional* N -representability problem.

Consider the class of N -particle wavefunctions $\{\Phi_g^{[i]}\}_{i=1}^\infty$ contain all wavefunctions in Hilbert space that yield the same (but arbitrary) generating density $\rho_g(\vec{r}) \in \mathcal{N}_B$. For any given final density $\rho(\vec{r}) \in \mathcal{N}_B$, there exists a unique coordinate transformation that carries $\rho_g(\vec{r})$ into $\rho(\vec{r})$. This transformation is given, in general, by Eq. (27). When we apply the operator $\hat{f}$ to each of the coordinates of a particular wavefunction $\Phi_g^{[k]}$ belonging to the above class, we obtain, in analogy with Eq. (30):

$$\begin{aligned} \Phi_\rho^{[k]}(\vec{r}_1, \dots, \vec{r}_N) &\equiv \underbrace{\hat{f} \dots \hat{f}}_{\text{N-times}} \Phi_g^{[k]}(\vec{r}_1, \dots, \vec{r}_N) \\ &= \prod_{i=1}^N [J(\vec{f}(\vec{r}_i); \vec{r}_i)]^{1/2} \Phi_g^{[k]}(\vec{f}(\vec{r}_1), \dots, \vec{f}(\vec{r}_N)) \end{aligned} \quad (132)$$

Thus, for any $\rho(\vec{r}) \in \mathcal{N}_B$ there exists a unique wavefunction $\Phi_\rho^{[k]}$, generated by means of local-scaling transformation from the arbitrary generating wavefunction $\Phi_g^{[k]}$. The set of all the wavefunctions thus generated, yielding densities $\rho(\vec{r})$ in $\mathcal{N}_B$, is called an “orbit” and is denoted by $\mathcal{O}_{\mathcal{G}}^{[k]}$:

$$\mathcal{O}_{\mathcal{G}}^{[k]} \equiv \{\Phi_\rho^{[k]} \mid \Phi_\rho^{[k]} \rightarrow \rho(\vec{r}); \quad \Phi_\rho^{[k]} \in \mathcal{L}_N; \quad \rho(\vec{r}) \in \mathcal{N}_B\} \quad (133)$$

We emphasize once more that the term “orbit” should not be confused with the word “orbital”, which, in its usual connotation in quantum chemistry, denotes a one-particle function.

The uniqueness of the local-scaling transformation guarantees that *within an orbit* $\mathcal{O}_{\mathcal{G}}^{[i]} \subset \mathcal{L}_N$ there exists a one-to-one correspondence between one particle densities, $\rho(\vec{r}) \in \mathcal{N}_B$ and N -particle wavefunctions, $\Phi_\rho^{[i]} \in \mathcal{O}_{\mathcal{G}}^{[i]} \subset \mathcal{L}_N$. Note, moreover, that Hilbert space corresponds to the union of all “orbits”:

$$\mathcal{L}_N = \bigcup_{i=1}^\infty \mathcal{O}_{\mathcal{G}}^{[i]} \quad (134)$$

Using the definition of the energy functional advanced in Eq. (55), we can state the variational problem leading to E_0^v as:

$$E_0^v = \inf_{\Phi \in \mathcal{L}_N} \{E_v[\Phi]\} \quad (135)$$

However, taking into account Eqs. (132) and (134), it clearly follows that the variational principle can be reformulated in terms of these “orbits” as [20] (see Fig. 6):

$$E_0^v = \inf_{\substack{\text{over all orbits} \\ \mathcal{O}_{\mathcal{G}}^{[i]} \subset \mathcal{L}_N}} \left\{ \inf_{\Phi_\rho^{[i]} \in \mathcal{O}_{\mathcal{G}}^{[i]}} \{E_v[\Phi_\rho^{[i]}]\} \right\} \quad (136)$$

where the inner variation is carried out within a particular “orbit” $\mathcal{O}_{\mathcal{G}}^{[i]}$, whereas the outer variation spans all orbits making up Hilbert space.

Because of the one-to-one correspondence between one-particle densities, $\rho(\vec{r}) \in \mathcal{N}_\phi$, and N -particle wavefunctions, $\Phi_\rho^{[i]} \in \mathcal{O}_{\mathcal{G}}^{[i]}$ within each one of the

$\mathcal{N}_B$	$\mathcal{O}_{\mathcal{L}}^{[1]}$	...	$\mathcal{O}_{\mathcal{L}}^{[2]}$	...	$\mathcal{O}_{\mathcal{L}}^{[i]}$	...	$\mathcal{O}_{\mathcal{L}}^{[HK]}$	...
ρ_1	$\Phi_{\rho_1}^{[1]}$	...	$\Phi_{\rho_1}^{[2]}$	...	$\Phi_{\rho_1}^{[i]}$	...	$\Phi_{\rho_1}^{[HK]}$	...
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$
ρ_{HF}	$\Phi_{\rho_{HF}}^{[1]}$	...	$\Phi_{\rho_{HF}}^{[2]}$	...	$\Phi_{\rho_{HF}}^{[i]}$	...	$\Phi_{\rho_{HF}}^{[HK]}$	...
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$
ρ	$\Phi_{\rho}^{[1]}$	...	$\Phi_{\rho}^{[2]}$	...	$\Phi_{\rho}^{[i]}$	...	$\Phi_{\rho}^{[HK]}$	...
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$
ρ_o^{exact}	$\Phi_{\rho_o^{exact}}^{[1]}$	...	$\Phi_{\rho_o^{exact}}^{[2]}$	...	$\Phi_{\rho_o^{exact}}^{[i]}$	...	$\Phi_{\rho_o^{exact}}^{[HK]} = \Phi_o^v$	...
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$

Fig. 6. Many-to-one correspondance between wavefunctions in $\mathcal{L}_N$ and one-particle densities; $\mathcal{O}_{\mathcal{L}}^{[HK]}$ is the Hohenberg–Kohn orbit, i.e., the orbit that contains the exact ground-state wavefunction Φ_o^v

“orbits”, we can formally write:

$$\begin{aligned}
 E_v[\Phi_{\rho}^{[i]}(\vec{r}_1, \dots, \vec{r}_N)] &= E_v \left[\prod_{i=1}^N \sqrt{\rho(\vec{r}_i)/\rho_g(\vec{f}_i)} \Phi_g^{[i]}(\vec{f}_1, \dots, \vec{f}_N) \right] \\
 &\equiv \mathcal{E}_v[\rho(\vec{r}); \Phi_g^{[i]}(\vec{f}_1, \dots, \vec{f}_N)]
 \end{aligned} \tag{137}$$

where since we assume that the orbit-generating wavefunction $\Phi_g^{[i]}$ is known we emphasize in the last line the fact that the functional depends solely (although implicitly through $\vec{f}([\rho]; \vec{r})$) on the object density, $\rho(\vec{r})$. The particular form in which the transformed vector depends on the object density can be obtained by solving Eq. (91). For this reason, the variational principle of Eq. (136) can be recast as [20]:

$$E_0^v = \inf_{\substack{\text{over all orbits} \\ \mathcal{O}_g^{[i]} \subset \mathcal{L}_N}} \left\{ \inf_{\substack{\rho(\vec{r}) \in \mathcal{N}_g \\ \Phi_g^{[i]} \in \mathcal{O}_g^{[i]} \subset \mathcal{L}_g}} \{ \mathcal{E}_v[\rho(\vec{r}); \Phi_g^{[i]}] \} \right\} \tag{138}$$

Notice too that in view of the one-to-one correspondance between densities and wavefunctions within an orbit, the variation of $\mathcal{E}_v[\rho(\vec{r}); \Phi_g^{[i]}]$ with respect to the one-particle density $\rho(\vec{r})$ is equivalent to the variation of $E_v[\Phi_{\rho}^{[i]}]$ with respect to the wavefunction $\Phi_{\rho}^{[i]} \in \mathcal{O}_{\mathcal{L}}^{[i]}$. This equivalence guarantees functional N -representability and illustrates the basic role of the notion of “orbit” in this respect. Note also that an approximate functional that does not satisfy Eq. (137) at all points of variation fails to comply with the unavoidable *functional* N -representability condition.

4.2 Construction of the Energy Density Functional Within an “Orbit”

Let us now show how one can proceed to the actual construction of the energy functional, $\mathcal{E}_v[\rho(\vec{r}); \Phi_\rho^{[i]}]$. We start from:

$$E[\Phi_\rho^{[i]}] = \frac{1}{2} \int d^3\vec{r}_1 \nabla_{\vec{r}_1} \nabla_{\vec{r}_1} D_\rho^{1[i]}(\vec{r}_1, \vec{r}_1)|_{\vec{r}_1 = \vec{r}_1} + \int d^3\vec{r} \rho(\vec{r}) v(\vec{r}) + \int d^3\vec{r}_1 \int d^3\vec{r}_2 \frac{D_\rho^{2[i]}(\vec{r}_1, \vec{r}_2; \vec{r}_1, \vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} \quad (139)$$

In order to rewrite this functional in terms of the generating 1- and 2-matrices, we use the following expressions [20]:

$$D_\rho^{1[i]}(\vec{r}_1, \vec{r}_1) = \sqrt{\frac{\rho(\vec{r}_1)}{\rho_g(\vec{f}(\vec{r}_1))}} \sqrt{\frac{\rho(\vec{r}_1')}{\rho_g(\vec{f}(\vec{r}_1'))}} D_g^{1[i]}(\vec{f}(\vec{r}_1), \vec{f}(\vec{r}_1')) \quad (140)$$

and

$$D_\rho^{2[i]}(\vec{r}_1, \vec{r}_2; \vec{r}_1, \vec{r}_2) = \frac{\rho(\vec{r}_1)}{\rho_g(\vec{f}(\vec{r}_1))} \frac{\rho(\vec{r}_2)}{\rho_g(\vec{f}(\vec{r}_2))} D_g^{2[i]}(\vec{f}(\vec{r}_1), \vec{f}(\vec{r}_2); \vec{f}(\vec{r}_1), \vec{f}(\vec{r}_2)) \quad (141)$$

In addition, we decompose the 1-matrix that appears in the right-hand side of Eq. (140) into its local and non-local components:

$$D_g^{1[i]}(\vec{f}(\vec{r}_1), \vec{f}(\vec{r}_1')) = [\rho_g(\vec{f}(\vec{r}_1))]^{1/2} [\rho_g(\vec{f}(\vec{r}_1'))]^{1/2} \tilde{D}_g^{1[i]}(\vec{f}(\vec{r}_1), \vec{f}(\vec{r}_1')) \quad (142)$$

where $\tilde{D}_g^{1[i]}$ is the non-local part of the 1-matrix. Similarly, for the 2-matrix in the right-hand side of Eq. (141), we have:

$$D_g^{2[i]}(\vec{f}(\vec{r}_1), \vec{f}(\vec{r}_2); \vec{f}(\vec{r}_1), \vec{f}(\vec{r}_2)) = \frac{1}{2} \rho_g(\vec{f}(\vec{r}_1)) \rho_g(\vec{f}(\vec{r}_2)) (1 + \mathcal{F}_{xc,g}^{[i]}(\vec{f}(\vec{r}_1), \vec{f}(\vec{r}_2))) \quad (143)$$

where $\mathcal{F}_{xc,g}^{[i]}$ is the non-local exchange-correlation factor. Substituting the expressions for the 1- and 2-matrices into Eq. (139), we obtain after some simple algebra [20]:

$$\begin{aligned} E[\Phi_\rho^{[i]}] &\equiv \mathcal{E}[\rho(\vec{r}); \Phi_\rho^{[i]}[\{\vec{f}_i\}]] \\ &= \frac{1}{8} \int d^3\vec{r} \frac{[\nabla_{\vec{r}} \rho(\vec{r})]^2}{\rho(\vec{r})} + \frac{1}{2} \int d^3\vec{r} \rho(\vec{r}) \nabla_{\vec{r}} \nabla_{\vec{r}} \tilde{D}_g^{1[i]}(\vec{f}(\vec{r}), \vec{f}(\vec{r}'))|_{\vec{r} = \vec{r}} \\ &\quad + \int d^3\vec{r} \rho(\vec{r}) v(\vec{r}) + \frac{1}{2} \int d^3\vec{r}_1 \\ &\quad \times \int d^3\vec{r}_2 \frac{\rho(\vec{r}_1) \rho(\vec{r}_2) (1 + \mathcal{F}_{xc,g}^{[i]}(\vec{f}(\vec{r}_1), \vec{f}(\vec{r}_2)))}{|\vec{r}_1 - \vec{r}_2|} \end{aligned} \quad (144)$$

Bearing in mind that the transformation vector is an implicit function of the density, namely:

$$\vec{f}(\vec{r}) = \vec{f}([\rho]; \vec{r}) \quad (145)$$

whose particular form can be obtained by solving Eq. (91), it is clear that Eq. (144) expresses the energy as a functional of the one-particle density $\rho(\vec{r})$ within an orbit $\mathcal{O}_{\mathcal{F}}^{[i]}$. Notice that in the present case the functional given by Eq. (144) is of a “dynamic type” as any change in the density $\rho(\vec{r})$ brings about the corresponding change *in the form* of the functional, through the introduction of $f([\rho(\vec{r})]; \vec{r})$ into the non-local parts of the energy expression. It is precisely this dynamical character that allows the functional to modify itself, so as to maintain the one-to-one correspondence with $E[\Phi_{\rho}^{[i]}]$ that is required by Eq. (137) in order to comply with functional N -representability.

In Fig. 7, we present a general scheme, comprising the intra- and inter-orbit optimizations appearing in the variational problem described by Eq. (138). We discuss this optimization process with reference to only three of the infinite number of orbits into which Hilbert space is decomposed. These orbits are $\mathcal{O}_{\mathcal{F}}^{[i]}$, $\mathcal{O}_{\mathcal{F}}^{[j]}$ and $\mathcal{O}_{\mathcal{F}}^{[HK]}$.

$\mathcal{O}_{\mathcal{F}}^{[i]}$ is an arbitrary initial orbit, which is selected by choosing an initial wavefunction. In order to make these ideas clearer, consider, for example, an *arbitrary* wavefunction $\Phi_g^{[i]} \in \mathcal{O}_{\mathcal{F}}^{[i]}$, that can be a configuration interaction wavefunction (or, in general, some trial wavefunction incorporating inter-particle coordinates [96, 97]). This wavefunction must allow for a proper representation of the important physical aspects of the problem at hand. Thus, if we wish to generate an energy density functional that describes exchange and correlation fairly well, we must select a configuration interaction wavefunction that contains the minimal set of configurations necessary for the description of electron correlation. For example, neither of the helium wavefunctions described by Eqs. (80), (81), and (82) would suit this purpose, because an adequate description of electron correlation demands that at least we add $[p^2]$, and $[d^2]$ configurations. However, it is not necessary that the configuration-interaction wavefunction selected as an orbit generating wavefunction should contain parameters that have been optimized in an actual calculation. We can just simply guess these values and proceed to improve the arbitrary initial wavefunction by means of local-scaling transformations [49, 50].

Orbit $\mathcal{O}_{\mathcal{F}}^{[j]}$ is reached by optimization of the energy density functional through inter-orbit jumping. This process, which is illustrated in Fig. 7 by means of a sequence of arrows, is discussed in detail below. The inter-orbit jumping process is repeated until one finally reaches orbit $\mathcal{O}_{\mathcal{F}}^{[HK]}$. This is the orbit where, by definition, one finds the exact ground state wavefunction Ψ_o^v that satisfies the Schrödinger equation $\hat{H}_v \Psi_o^v = E_o^v \Psi_o^v$. For this reason, we call this the Hohenberg-Kohn orbit. Clearly, within $\mathcal{O}_{\mathcal{F}}^{[HK]}$, the application of local-scaling transformations to any initial wavefunction leads to the exact ground-state wavefunction as well as to the exact ground-state density.

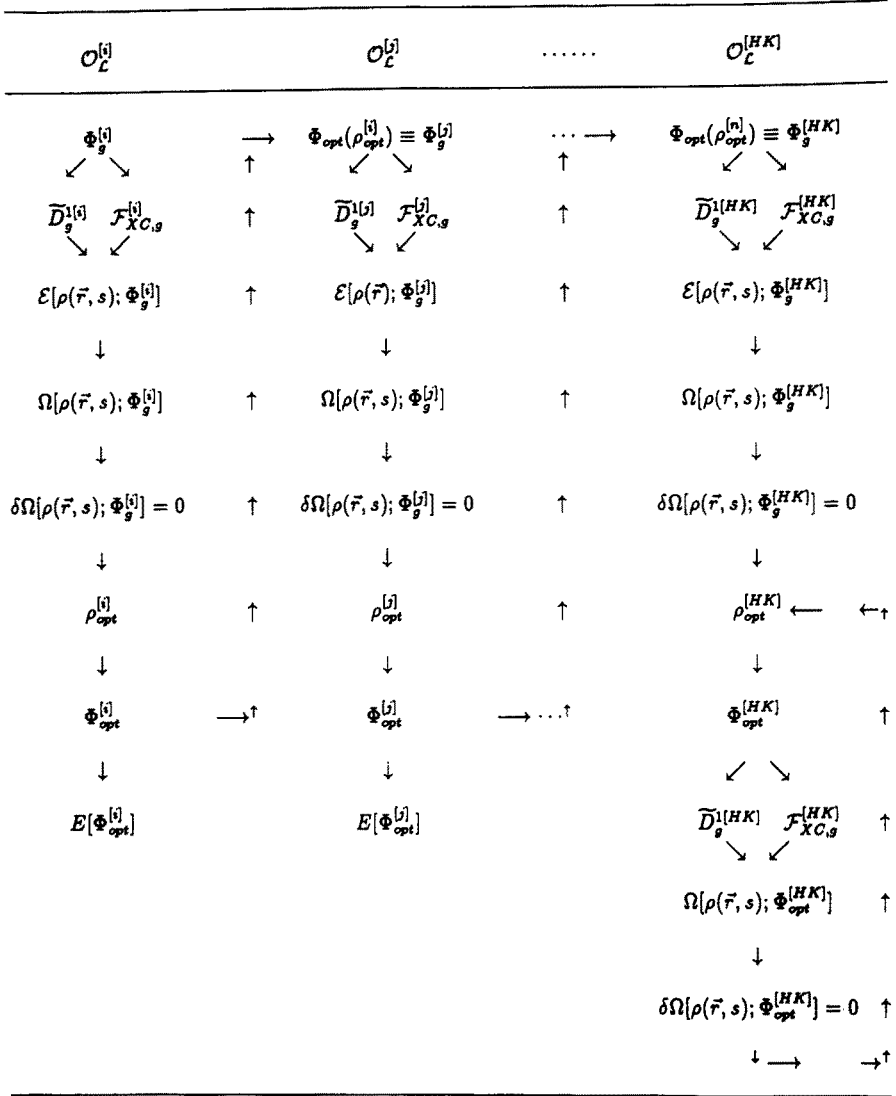


Fig. 7. Schematic representation of intra-orbit and inter-orbit optimizations

4.3 Intra-Orbit Optimization of Energy Density Functionals

The intra-orbit optimization process is shown schematically in each one of the columns of Fig. 7, underneath the orbit symbol. Thus, with particular reference to the column below $\mathcal{O}_L^{[j]}$, let us assume that the orbit-generating function $\Phi_g^{[j]}$ is chosen. Since this function is explicitly known, we can obtain explicit expres-

sions for the non-local part of the 1-matrix $\tilde{D}_g^{1[i]}(\vec{r}, \vec{r})$ as well as for the non-local part of the 2-matrix, that is, for the exchange-correlation factor $\mathcal{F}_{xc,g}^{[i]}(\vec{r}_1; \vec{r}_2)$. These quantities enter into the energy functional described by Eq. (144) as functions of the transformed vector $\tilde{f}(\vec{r})$, namely, as $\tilde{D}_g^{1[i]}(\tilde{f}([\rho]; \vec{r}), \tilde{f}([\rho]; \vec{r}))$ and $\mathcal{F}_{xc,g}^{[i]}(\tilde{f}([\rho]; \vec{r}_1), \tilde{f}([\rho]; \vec{r}_2))$. Now, if it were possible to obtain the transformed vector $\tilde{f}([\rho]; \vec{r})$ as an explicit function of the one-particle density $\rho(\vec{r})$, then we could also rewrite the energy functional of Eq. (144) as an explicit functional of $\rho(\vec{r})$. However, since $\tilde{f}([\rho]; \vec{r})$ is known through the solution of an equation, we cannot obtain the $\tilde{f}([\rho]; \vec{r})$ as an explicit function of the density in actual cases. In fact, in most cases, all we can obtain is a numerical solution for $\tilde{f}([\rho]; \vec{r})$.

Moreover, the construction of functionals for the energy that depend explicitly on the one-particle density is, of course, quite feasible, if one uses analytic approximations for the transformed vector $\tilde{f}([\rho]; \vec{r})$. Such an alternative is open if, for instance, one resorts to the use of Padé approximants. We discuss this way of dealing with this problem in Sect. 5.

As indicated in Fig. 7, the next step after either an explicit or an implicit energy density functional $\mathcal{E}[\rho(\vec{r}); \Phi_g^{[i]}]$ has been constructed is to devise an intra-orbit optimization procedure. For this purpose, one introduces the auxiliary functional $\Omega[\rho(\vec{r}); \Phi_g^{[i]}]$, made up of the energy functional $\mathcal{E}[\rho(\vec{r}); \Phi_g^{[i]}]$, plus the auxiliary conditions which must be imposed on the variational magnitudes. Notice that there are many ways of carrying out this variation, but that – in general – one obtains Euler–Lagrange equations by setting $\delta\Omega[\rho(\vec{r}); \Phi_g^{[i]}] = 0$. In Sections 4.4, and 4.5, we treat the intra-orbit variation with respect to $\rho(\vec{r})$, and to the set of N orthonormal orbitals $\{\phi_i(\vec{r})\}_{i=1}^N$, respectively.

4.4 Euler–Lagrange Equation for Intra-Orbit Optimization of $\rho(\vec{r})$

Assuming that the variational magnitude in the functional $\mathcal{E}[\rho(\vec{r}); \Phi_g^{[i]}]$ of Eq. (144) is the density $\rho(\vec{r})$, we can set up the following auxiliary functional:

$$\Omega[\rho(\vec{r}); \Phi_g^{[i]}] \equiv \mathcal{E}[\rho(\vec{r}); \Phi_g^{[i]}] - \mu^{[i]} \left(\int d^3\vec{r} \rho(\vec{r}) - N \right) \quad (146)$$

where $\mu^{[i]}$ is the Lagrange multiplier that accounts for the normalization of the density. Setting this variation equal to zero:

$$\frac{\delta\Omega[\rho(\vec{r}); \Phi_g^{[i]}]}{\delta\rho(\vec{r})} = 0 \quad (147)$$

we obtain, the Euler–Lagrange equation for the one-particle density [90, 91]:

$$\begin{aligned} \frac{1}{8} \left[\frac{V\rho(\vec{r})}{\rho(\vec{r})} \right]^2 - \frac{1}{4} \frac{V^2\rho(\vec{r})}{\rho(\vec{r})} + v_{T,g}^{[i]}([\rho(\vec{r}); \vec{r}]) + v(\vec{r}) + v_H([\rho(\vec{r}); \vec{r}]) \\ + v_{xc,g}^{[i]}([\rho(\vec{r}); \vec{r}]) = \mu^{[i]} \end{aligned} \quad (148)$$

In Eq. (148), $v(\vec{r})$ is the external potential and $v_H([\rho(\vec{r})]; \vec{r})$, the Hartree or Coulomb potential. In addition, we observe the presence of $v_{T,g}^{[i]}$, arising from the non-local part of the kinetic energy (see Eq. (144)):

$$v_{T,g}^{[i]}([\rho(\vec{r})]; \vec{r}) = \frac{1}{2} \left\{ [\nabla_{\vec{r}} \nabla_{\vec{r}'} \tilde{D}_g^{1[i]}(\vec{f}(\vec{r}); \vec{f}(\vec{r}'))]_{\vec{r}=\vec{r}, s'=s} + \rho(\vec{r}) \frac{\delta}{\delta \rho(\vec{r})} ([\nabla_{\vec{r}} \nabla_{\vec{r}'} \tilde{D}_g^{1[i]}(\vec{f}(\vec{r}); \vec{f}(\vec{r}'))]_{\vec{r}=\vec{r}, s'=s}) \right\} \quad (149)$$

and of $v_{XC,g}^{[i]}([\rho(\vec{r})]; \vec{r})$, the exchange-correlation potential, coming from the non-local part of the electron–electron interaction:

$$v_{XC,g}^{[i]}([\rho(\vec{r})]; \vec{r}) = \mathcal{E}_{XC,g}^{[i]}([\rho(\vec{r})]; \vec{r}) + \rho(\vec{r}) \frac{\delta \mathcal{E}_{XC,g}^{[i]}([\rho(\vec{r})]; \vec{r})}{\delta \rho(\vec{r})} \quad (150)$$

In Eq. (150), the exchange-correlation energy density is defined by (see Eq. (144)):

$$\mathcal{E}_{XC,g}^{[i]}([\rho(\vec{r}_1)]; \vec{r}_1) = \frac{1}{2} \int d^3\vec{r}_2 \frac{\rho(\vec{r}_2) \mathcal{F}_{XC,g}^{[i]}(\vec{f}(\vec{r}_1); \vec{f}(\vec{r}_2))}{|\vec{r}_1 - \vec{r}_2|} \quad (151)$$

The optimal energy for intra-orbit variation is attained at $\mathcal{E}[\rho_{opt}^{[i]}(\vec{r}); \Phi_g^{[i]}]$. Because the functional N -representability condition is fulfilled, this value is an upper bound to E_o^v (i.e., to the optimal energy within the Hohenberg–Kohn orbit as $\mathcal{E}[\rho_{opt}^{[HK]}(\vec{r}); \Phi_g^{[HK]}] = E_o^v$).

The question arises of why not to carry out this energy minimization for an energy functional that has been defined from the outset in the Hohenberg–Kohn orbit. The answer is that if we wish to construct the exact energy density functional $\mathcal{E}[\rho(\vec{r}); \Phi_g^{[HK]}]$, we must depart from some orbit-generating wavefunction $\Phi_g^{[HK]}$, which – upon local-scaling transformation of its coordinates – yields the exact wavefunction $\Phi_{\rho_o^v}^{[HK]} \equiv \Psi_o^v$. The problem is that, finding such an orbit-generating wavefunction would be as complicated as finding Ψ_o^v . The Hohenberg–Kohn orbit, nevertheless, is important from a conceptual point of view as the Kohn–Sham equations are realized within this orbit.

4.5 Euler–Lagrange Equations for the Intra-Orbit Optimization of N Orthonormal Orbitals: Kohn–Sham-Like Equations

Let us define the subclass $\mathcal{S}_N$ consisting of all single Slater determinants:

$$\Phi_{\rho}^{SD[i]}(\vec{r}_1, \dots, \vec{r}_N) \equiv \frac{\det}{\sqrt{N!}} [\phi_{\rho,1}^{[i]}(\vec{r}_1) \cdots \phi_{\rho,N}^{[i]}(\vec{r}_N)] \quad (152)$$

constructed from the transformed orbitals:

$$\phi_{\rho,k}^{[i]}(\vec{r}) = \hat{f} \phi_{g,k}^{[i]}(\vec{r}) = [J(\vec{f}(\vec{r}); \vec{r})]^{1/2} \phi_{g,k}^{[i]}(\vec{f}(\vec{r})) = \left[\frac{\rho(\vec{r})}{\rho_g(\vec{f}(\vec{r}))} \right]^{1/2} \phi_{g,k}^{[i]}(\vec{f}(\vec{r})). \quad (153)$$

where these orbitals are obtained by local-scaling transformations of the generating set $\{\phi_{g,k}^{[i]}\}_{k=1}^N$. Following Kohn and Sham [95], we assume that Eq. (152) describes a non-interacting system. It is clear that $\mathcal{S}_N$ is not a subspace of $\mathcal{L}_N$, since a linear combination of Slater determinants does not in general yield a single Slater determinant. Applying the same arguments as those of Section 4.1, we conclude that $\mathcal{S}_N$ can be decomposed into the orbits $\mathcal{O}_{\mathcal{S}}^{[i]}$:

$$\mathcal{O}_{\mathcal{S}}^{[i]} \equiv \{\Phi_p^{SD[i]} | \Phi_p^{SD[i]} \rightarrow \rho(\vec{r}); \quad \Phi_p^{SD[i]} \in \mathcal{S}_N; \quad \rho(\vec{r}) \in \mathcal{N}_B\} \quad (154)$$

The union of all orbits exhausts the subclass: $\mathcal{S}_N = \bigcup_{i=1}^{\infty} \mathcal{O}_{\mathcal{S}}^{[i]}$. The one-particle density associated with the single Slater determinant of Eq. (152) (i.e., the density of a non-interacting system) is:

$$\rho(\vec{r}) = \sum_{k=1}^N |\phi_{\rho,k}^{[i]}(\vec{r})|^2 \quad (155)$$

It is of interest to write down the kinetic energy for this wavefunction (i.e., the kinetic energy for a non-interacting system):

$$\begin{aligned} T_s[\{\phi_{\rho,k}^{[i]}(\vec{r})\}] &= \sum_{k=1}^N \frac{1}{2} \int d^3\vec{r} \nabla_{\vec{r}} \phi_{\rho,k}^{[i]}(\vec{r}) \nabla_{\vec{r}} \phi_{\rho,k}^{[i]}(\vec{r})|_{\vec{r}=\vec{r}} \\ &= \frac{1}{8} \int d^3\vec{r} \frac{[\nabla_{\vec{r}} \rho(\vec{r})]^2}{\rho(\vec{r})} \\ &\quad + \frac{1}{2} \int d^3\vec{r} \rho(\vec{r}) \nabla_{\vec{r}} \nabla_{\vec{r}} \tilde{D}_g^{1SD[i]}(\vec{f}(\vec{r}), \vec{f}(\vec{r}))|_{\vec{r}=\vec{r}} \end{aligned} \quad (156)$$

where $\tilde{D}_g^{1SD[i]}$ is the non-local part of the 1-matrix of the non interacting system.

Following Kohn and Sham [95], let us consider the energy density functional for the interacting system given by Eq. (157), but let us assume that the one-particle density for the interacting system appearing in $\mathcal{E}[\rho; \Phi_g^{[i]}]$ is given by Eq. (155). Under this assumption we can write this functional as $\mathcal{E}[\{\phi_{\rho,k}^{[i]}(\vec{r})\}; \Phi_g^{[i]}]$. Introducing the auxiliary functional:

$$\begin{aligned} \Omega[\{\phi_{\rho,k}^{[i]}(\vec{r})\}; \Phi_g^{[i]}] &\equiv \mathcal{E}[\{\phi_{\rho,k}^{[i]}(\vec{r})\}; \Phi_g^{[i]}] + T_s[\{\phi_{\rho,k}^{[i]}(\vec{r})\}] - T_s[\{\phi_{\rho,k}^{[i]}(\vec{r})\}] \\ &\quad - \sum_{k=1}^N \sum_{l=1}^N \lambda_{kl} \left(\int d^3\vec{r} \phi_{\rho,k}^{*[i]}(\vec{r}) \phi_{\rho,l}^{[i]}(\vec{r}) - \delta_{kl} \right) \end{aligned} \quad (157)$$

where the $\{\lambda_{kl}\}$ are the Lagrange multipliers that enforce orbital orthonormality, and explicitly decomposing the energy functional into its various contributions, we obtain:

$$\begin{aligned} \Omega[\{\phi_{\rho,k}^{[i]}(\vec{r})\}; \Phi_g^{[i]}] &= T_s[\{\phi_{\rho,k}^{[i]}(\vec{r})\}] + E_{ext}[\rho(\vec{r})] + E_{Coulomb}[\rho(\vec{r})] \\ &\quad + E_{XC,g}^{KS[i]}[\rho(\vec{r}); \Phi_g^{[i]}[\{\vec{f}_i\}]] \\ &\quad - \sum_{k=1}^N \sum_{l=1}^N \lambda_{kl} \left(\int d^3\vec{r} \phi_{\rho,k}^{*[i]}(\vec{r}) \phi_{\rho,l}^{[i]}(\vec{r}) - \delta_{kl} \right) \end{aligned} \quad (158)$$

where

$E_{\text{ext}}[\rho(\vec{r})] = \int d^3\vec{r} \rho(\vec{r}) v(\vec{r})$, $E_{\text{Coulomb}}[\rho(\vec{r})] = (1/2) \int d^3\vec{r}_1 \int d^3\vec{r}_2 \rho(\vec{r}_1) \rho(\vec{r}_2) |\vec{r}_1 - \vec{r}_2|^{-1}$ and

$$\begin{aligned} E_{\text{xc},g}^{\text{KS}[i]}[\rho(\vec{r}); \Phi_g^{[i]}[\{\vec{f}_i\}]] &= \frac{1}{2} \int d^3\vec{r} \rho(\vec{r}) \nabla_{\vec{r}} \nabla_{\vec{r}} [\tilde{D}_g^{1[i]}(\vec{f}(\vec{r}), \vec{f}(\vec{r}')) \\ &\quad - \tilde{D}_g^{1SD[i]}(\vec{f}(\vec{r}), \vec{f}(\vec{r}'))] |_{\vec{r}' = \vec{r}} \\ &\quad + \frac{1}{2} \int d^3\vec{r}_1 \int d^3\vec{r}_2 \frac{\rho(\vec{r}_1) \rho(\vec{r}_2) \mathcal{F}_{\text{xc},g}^{[i]}(\vec{f}(\vec{r}_1), \vec{f}(\vec{r}_2))}{|\vec{r}_1 - \vec{r}_2|} \end{aligned} \quad (159)$$

Explicitly, the variation of the functional $\Omega[\{\phi_{\rho,k}^{[i]}(\vec{r}); \Phi_g^{[i]}\}]$ with respect to one-particle orbitals is given by

$$\begin{aligned} &\frac{\delta T_s[\{\phi_{\rho,k}^{[i]}(\vec{r})\}]}{\delta \phi_{\rho,k}^{[i]}(\vec{r})} + \frac{\delta}{\delta \rho(\vec{r})} (E_{\text{ext}}[\rho(\vec{r})] + E_{\text{Coulomb}}[\rho(\vec{r})] \\ &\quad + E_{\text{xc},g}^{\text{KS}[i]}([\rho(\vec{r})]; \Phi_g^{[i]})) \frac{\delta \rho(\vec{r})}{\delta \phi_{\rho,k}^{[i]}(\vec{r})} - \sum_{k=1}^N \sum_{l=1}^N \lambda_{kl} \frac{\delta}{\delta \phi_{\rho,k}^{[i]}(\vec{r})} \\ &\quad \times \left(\int d^3\vec{r} \phi_{\rho,k}^{*[i]}(\vec{r}) \phi_{\rho,l}^{[i]}(\vec{r}) - \delta_{kl} \right) = 0 \end{aligned} \quad (160)$$

and leads to the following system of Kohn–Sham-like single particle equations:

$$\begin{aligned} &[-\frac{1}{2} \nabla^2 + v(\vec{r}) + v_H([\rho(\vec{r})]; \vec{r}) + v_{\text{xc},g}^{\text{KS}[i]}([\rho(\vec{r})]; \vec{r})] \phi_{\rho^{\text{opt}},k}^{[i]}(\vec{r}) \\ &= \sum_{l=1} \lambda_{kl} \phi_{\rho^{\text{opt}},l}^{[i]}(\vec{r}) \end{aligned} \quad (161)$$

The potentials $v(\vec{r})$, and $v_H([\rho(\vec{r})]; \vec{r})$ of Eq. (161) are precisely those of Eq. (148). The exchange correlation potential $v_{\text{xc},g}^{\text{KS}[i]}([\rho(\vec{r})]; \vec{r})$ is, nonetheless, quite different from the one described by Eq. (150). Note that the Kohn–Sham-like exchange-correlation potential contains a kinetic energy contribution arising from the difference between the interacting and non-interacting systems. This term is positive and thus lowers the negative contribution corresponding to the exchange-correlation energy proper.

Let us finish this Section by discussing the relationship between the Kohn–Sham-like equations advanced above and the actual Kohn–Sham equations. From the perspective of local-scaling transformations, we can analyze this relationship as follows. First of all, we assume that, for an interacting system, we are able to select an orbit-generating wavefunction $\Phi_g^{[HK]}$, belonging to the Hohenberg–Kohn orbit $\mathcal{O}_{\mathcal{L}}^{[HK]} \subset \mathcal{L}_N$. (Of course, it must be understood that this is possible only in a formal sense, since it is clearly as difficult to obtain $\Phi_g^{[HK]}$ as to solve the exact N -particle problem). Knowledge of this wavefunction allows us to calculate the non-local part of the 1-matrix, $\tilde{D}_g^{1[HK]}(\vec{r}_1, \vec{r}_1)$ and the exchange-correlation factor $\mathcal{F}_{\text{xc},g}^{[HK]}(\vec{r}_1, \vec{r}_2)$, which are needed for the construction of

$\mathcal{E}[\{\phi_{p,k}^{[i]}(\vec{r}); \Phi_g^{[i]}\}]$. In addition, since the non-local part of the 1-matrix for the single Slater determinant (for a non-interacting system) also appears in Eqs. (159) and (160), it is necessary that we select a generating function $\Phi_g^{SD[KS]}$ in a particular orbit $\mathcal{O}_{\mathcal{S}}^{[KS]} \subset \mathcal{S}_N$. This wavefunction satisfies the condition of minimizing the kinetic energy for the non-interacting system when $\rho(\vec{r}) = \rho_o^{exact}$, namely, for the exact ground-state density. For this reason we denote this orbit as the Kohn–Sham orbit and label it with the superscript $[KS]$.

The minimum of the Kohn–Sham functional is attained for the transformed wavefunctions $\Phi_{\rho_o^{exact}}^{[HK]} \in \mathcal{O}_{\mathcal{S}}^{[HK]} \subset \mathcal{S}_N$ and $\Phi_{\rho_o^{exact}}^{SD[KS]} \in \mathcal{O}_{\mathcal{S}}^{[KS]} \subset \mathcal{S}_N$, namely, when the variational density is equal to that of the exact ground-state: $\rho(\vec{r}) = \rho_o^{exact}(\vec{r})$. At this extremum, one obtains the Kohn–Sham equations, which – in canonical form – are given by [95]:

$$\begin{aligned} & \left[-\frac{1}{2} \nabla^2 + v(\vec{r}) + v_H([\rho_o^{exact}(\vec{r})]; \vec{r}) + v_{XC,g}^{KS[HK]}([\rho_o^{exact}(\vec{r})]; \vec{r}) \right] \psi_{\rho_o^{exact},k}^{[HK]}(\vec{r}) \\ &= \mathcal{E}_k^{KS} \psi_{\rho_o^{exact},k}^{[HK]}(\vec{r}). \end{aligned} \quad (162)$$

4.6 Inter-Orbit Optimization

Having examined the process of intra-orbit optimization in the previous Sections, let us turn our attention to “inter-orbit jumping”. This process is shown in Fig. 7 by means of steps indicated by arrows, each of which involves the transformation of a “density-optimal” wavefunction $\Phi_{opt}^{[i]} \in \mathcal{O}_{\mathcal{S}}^{[i]}$ into another wavefunction $\Phi_{opt}(\rho_{opt}^{[i]})$. We denote the latter as the orbit-generating wavefunction $\Phi_g^{[j]}$ for orbit $\mathcal{O}_{\mathcal{S}}^{[j]}$.

The possibility for “inter-orbit jumping” comes about from the fact that the energy functional $E[\Phi_{opt}^{[i]}] \equiv \mathcal{E}[\rho_{opt}^{[i]}(\vec{r}); \Phi_g^{[i]}[\{\vec{f}_i\}]]$ is a minimum just within $\mathcal{O}_{\mathcal{S}}^{[i]}$, but is not the global minimum, which occurs at the exact density and at the Hohenberg–Kohn orbit $\mathcal{O}_{\mathcal{S}}^{[HK]}$. Thus, variation of the energy functional $\mathcal{E}[\rho_{opt}^{[i]}(\vec{r}); \Phi_g^{[i]}[\{\vec{f}_i\}]]$ at fixed density $\rho_{opt}^{[i]}(\vec{r})$ – where the variational magnitude is the wavefunction $\Phi_g^{[i]}[\{\vec{f}_i\}]$ – can lead to a lower energy. This minimum is attained at the wavefunction $\Phi_{opt}(\rho_{opt}^{[i]})$. As this wavefunction yields an energy which is lower than the lowest possible one in orbit $\mathcal{O}_{\mathcal{S}}^{[i]}$, it is clear that the improved wavefunction cannot belong to this orbit. Hence, we take it to be the orbit-generating function for orbit $\mathcal{O}_{\mathcal{S}}^{[j]}$ and write $\Phi_{opt}(\rho_{opt}^{[i]}) \equiv \Phi_g^{[j]}$ [48, 50].

Let us note, however, that in spite of the fact that the “orbit jumping” optimization is carried out at fixed density, the resulting wavefunction, $\Phi_{opt}(\rho_{opt}^{[i]}) \equiv \Phi_g^{[j]}$, is not necessarily associated with the fixed density $\rho_{opt}^{[i]}(\vec{r})$. For this reason, it is then possible to apply a local-scaling transformation to it and produce an optimized wavefunction which, at the same time, is associated with the fixed density. We denote this wavefunction by $\Phi_{inh-opt}^{[j]}$. Moreover, we can optimize the density within orbit $\mathcal{O}_{\mathcal{S}}^{[j]}$ and obtain the new wavefunction $\Phi_{opt}^{[j]}$. The energy functionals associated with these wavefunctions satisfy the following inequalities:

$$E[\Phi_{opt}^{[j]}] \leq E[\Phi_{inh-opt}^{[j]}] \leq E[\Phi_{opt}^{[i]}] \leq E[\Phi_g^{[i]}], \quad i \neq j \quad (163)$$

4.7 An Application of Intra- and Inter-Orbit Optimization: Hartree–Fock Calculations for the Li and Be Atoms

We describe in this Subsection the application of local-scaling transformations to the calculation of the energy for the lithium and beryllium atoms at the Hartree–Fock level [113]. (For other reformulations of the Hartree–Fock problem see [114] and references therein.) The procedure described here involves three parts. The first part is orbital transformation already discussed in Sect. 2.5. The second is intra-orbit optimization described in Sect. 4.3 and the third is inter-orbit optimization discussed in Sect. 4.6.

In a way, the applications of the local-scaling-transformation version of density functional theory, which we have selected to discuss here, are not spectacular, in the sense that they refer to very small systems containing three and four electrons, respectively. Moreover, they are taken at the Hartree–Fock level, which means that electron correlation is not included. These applications might consequently, seem to be rather limited in terms of their accomplishments compared to those involving the calculation of exchange and correlation energies of very large molecular systems. There is, however, a basic difference that we would like to stress. Whereas Hohenberg–Kohn–Sham density functional theory calculations of large (and also small) electronic systems rely on the use of approximate energy density functionals (either at the Hartree–Fock or at the correlated levels), the Hartree–Fock energy density functionals constructed in the calculations that we review here lead, through a process of intra- and inter-orbit optimizations, to the Clementi–Roetti [69] SCF values for these atoms. In other words, the present examples, although they deal with small systems, illustrate the upper-bound character of the local-scaling-transformation version of density functional theory, and show how one can construct energy functionals that depend implicitly on the one-particle density and lead to values comparable to the usual quantum chemistry ones.

Although, in the present Subsection, we have chosen to discuss this problem from the point of view of locally-scaled one-particle orbitals, in Sect. 5 we reconsider this same problem with respect to the construction of explicit energy density functionals

Let us consider for the lithium atom the Raffenetti orbitals [71] described in Eqs. (68) and (69). However, in order to emphasize the presence of variational parameters in these orbitals, we rewrite them as follows:

$$R_{ns}([\alpha^{[i]}, \beta^{[i]}, \{C_{nsj}^{[i]}\}]; r) = \sum_{j=1}^M C_{nsj} (2\alpha\beta^j)^{3/2} / (2)^{1/2} \exp(-\alpha\beta^j r) \quad (164)$$

Note that a particular orbit, therefore, is determined by fixing the values of the parameters α , β and $\{C_{nsj}\}_{j=1}^M$. Thus, employing these orbitals, we can construct a single Slater determinant for the configuration $[1s^2 2s]$, that is the generating wavefunction of orbit $\mathcal{O}_{\rho}^{[i]}$:

$$\Phi_{\rho_g}^{[i]}(\vec{r}_1, s_1, \dots, \vec{r}_3, s_3) = \Phi_{\rho_g}^{[i]}([\alpha^{[i]}, \beta^{[i]}, \{C_{nsj}^{[i]}\}]; \vec{r}_1, s_1, \dots, \vec{r}_3, s_3) \quad (165)$$

where s_i is the spin coordinate and ρ_g is the density associated with this generating wavefunction. Again, as was discussed in Sect. 2.5, the locally scaled orbitals for a transformation connecting $\rho_g(r)$ and $\rho(r)$ are (cf. Eq. (70)):

$$R_{ns}^T([\alpha^{[i]}, \beta^{[i]}, \{C_{nsj}^{[i]}\}]; r) = \sqrt{\frac{\rho(r)}{\rho_g(f(r))}} R_{ns}([\alpha^{[i]}, \beta^{[i]}, \{C_{nsj}^{[i]}\}]; f(r)) \quad (166)$$

It follows, therefore, that the transformed Slater determinant $\Phi_\rho^{T[i]}$ also depends upon the parameters $\alpha^{[i]}, \beta^{[i]}, \{C_{nsj}^{[i]}\}$ that define the transformed orbitals. Moreover, if we select the following representation for the one-particle density:

$$\rho(\vec{r}) = \rho([\{a_i, b_i, c_i\}], \vec{r}) = \sum_{i=0} a_i r^{b_i} \exp(-c_i r) \quad (167)$$

we can rewrite the energy density functional as:

$$\mathcal{E}[\rho(r); \Phi_\rho^{[i]}] = \mathcal{E}[\{a_i, b_i, c_i\}; \alpha^{[i]}, \beta^{[i]}, \{C_{nsj}^{[i]}\}] \quad (168)$$

The intra-orbit optimization process is carried out by varying the density parameters $\{a_i, b_i, c_i\}$ while keeping the wavefunction (or orbital) parameters $\alpha^{[i]}, \beta^{[i]}, \{C_{nsj}^{[i]}\}$ fixed. Alternatively, inter-orbit optimization is accomplished by optimizing the wavefunction parameters for the energy functional

$$\mathcal{E}[\rho_{opt}^{[i]}(r); \Phi_\rho^{[i]}] = \mathcal{E}[\{a_i^{opt}, b_i^{opt}, c_i^{opt}\}; \alpha^{[i]}, \beta^{[i]}, \{C_{nsj}^{[i]}\}] \quad (169)$$

This procedure is carried out in subsequent steps until convergence is attained. At each step, however, new transformed orbitals are obtained as linear combinations of the old ones. In order to show that the choice of initial orbitals is not critical, the same procedure was carried out for the beryllium atom, using single- ζ orbitals in the configuration $[1s^2 2s^2]$:

$$\begin{aligned} R_{1s}^{[i]}(r) &= ((\zeta_1^{[i]})^3/\pi)^{1/2} \exp(-\zeta_1^{[i]} r) \\ R_{2s}^{[i]}(\vec{r}) &= ((\zeta_2^{[i]})^3/(\pi(3\lambda^2 - 3\lambda + 1)))^{1/2} (1 - \zeta_2^{[i]}\lambda r) \exp(-\zeta_2^{[i]} r) \end{aligned} \quad (170)$$

with $\lambda = (\zeta_1 + \zeta_2)/3\zeta_1$. In Fig. 8, some energy values corresponding to intra- and inter-orbit optimization for the beryllium atom are presented. The particular optimization path shown in Fig. 8 is one of the infinitely many paths available. In particular, the one presented in Fig. 8 starts from the single- ζ wavefunction with an energy of -14.556740 hartrees. Note that the converged energy is undistinguishable from the SCF value of Clementi and Roetti [69].

In Table VIII, we present the local-scaling- transformation-energy results for lithium and beryllium and compare them with results obtained with other methods. It is worth mentioning that the Hartree-Fock results for these atoms are a first instance of accurate energy values obtained within the context of a formalism based on density functional theory.

$\mathcal{O}_s^{[1]}$	$\mathcal{O}_s^{[2]}$	...	$\mathcal{O}_s^{[n]}$
$\mathcal{E}_g^{[1]} = -14.556740$			
$\downarrow$			
$\mathcal{E}_{opt}^{[1]} = -14.570001$	$\longrightarrow \mathcal{E}_g^{[2]} = -14.572215$		
	$\downarrow$		
	$\mathcal{E}_{opt}^{[2]} = -14.573011$	...	$\mathcal{E}_{opt}^{[n]} = -14.573021$
$\mathcal{E}_g^{[i]} = \mathcal{E}[\rho_g^{[i]}, \Phi_{\rho_g}^{[i]}]$	$\mathcal{E}_{opt}^{[i]} = \mathcal{E}[\rho_{opt}^{[i]}, \Phi_{\rho_g}^{[i]}]$		

Fig. 8. Intra- and inter-orbit energy convergence for an initial single- ζ wavefunction for the beryllium atom (energy in hartrees)

Table 8. Comparison of approximate Hartree–Fock energy values for Li and Be atoms (hartrees)

	Li	Be
SCF ^a	– 7.4327267	– 14.573021
Local-Scaling ^b	– 7.4327267	– 14.573021
H-F limit ^{c,d,e}	– 7.4327269	– 14.573023

^a Clementi – Roetti [69], ^b Ludeña et al. [113], ^c Froese-Fischer [117], ^d Bunge et al. [70], ^e Koga et al. [118]

4.8 Energy Density Functionals for Excited States

In conventional quantum mechanics, a wavefunction describing the ground or excited states of a many-particle system must be a simultaneous eigenfunction of the set of operators that commute with the Hamiltonian. Thus, for example, for an adequate description of an atom, one must introduce the angular momentum and spin operators $\hat{L}^2$, $\hat{S}^2$, $\hat{L}_z$, $\hat{S}_z$ and the parity operator $\hat{\Pi}$, in addition to the Hamiltonian operator.

In variational treatments of many-particle systems in the context of conventional quantum mechanics, these symmetry conditions are explicitly introduced, either in a direct constructive fashion or by resorting to projection operators. In the usual versions of density functional theory, however, little attention has been paid to this problem. In our opinion, the basic question has to do with how to incorporate these symmetry conditions – which must be fulfilled by either an exact or approximate wavefunction – into the energy density functional.

The symmetry problem is solved trivially in the local-scaling version of density functional theory, because the symmetry conditions can be included in

the choice of orbit-generating or initial wavefunction $\Phi_g^{[i]}$ [36]. Since it is from this initial wavefunction that we obtain $\tilde{D}_g^{1[i]}$ and $\mathcal{F}_{XC,g}^{[i]}$, namely, the non-local quantities appearing in the energy functional of Eq. (50), it follows that the symmetry properties of the parent wavefunction are transferred to the variational functional. Notice, therefore, that the symmetry of the wavefunction is carried into the symmetry of the non-local parts of the 1- and 2-matrices $\tilde{D}_g^{1[i]}$ and $\mathcal{F}_{XC,g}^{[i]}$, respectively, and hence into the Fermi and Coulomb holes.

In the constructive approach to density functional theory reviewed here, the extension to excited states is straightforward, provided that the orbit-generating wavefunction $\Phi_{n,g}^{[i]}(\{\vec{r}_i, s_i\}) \in \mathcal{O}_{\mathcal{L}}^{[i]}$ satisfies both wavefunction- and Hamiltonian orthonormalities: [51]:

$$\langle \Phi_{n,\rho}^{[i]} | \Phi_{m,\rho}^{[i]} \rangle = \delta_{n,m} \quad (171)$$

and

$$\langle \Phi_{n,\rho}^{[i]} | \hat{H} | \Phi_{m,\rho}^{[i]} \rangle = \mathcal{E}[\rho_n(\vec{r}); \Phi_{n,g}^{[i]}[\{\vec{f}(\vec{r}_i), s_i\}]] \delta_{n,m} \quad (172)$$

Eqs. (171) and (172) require that, in addition to $\Phi_{n,\rho}^{[i]}$, we generate all other lower-lying state functions $\{\Phi_{m,\rho}^{[i]}\}_{m=0}^{n-1}$, as it is with respect to them that the above conditions are to be fulfilled. We illustrate in what follows a possible – but certainly, not the only – course of action open to us.

Let us assume that the orbit-generating wavefunction for the n th state is given in the form of a configuration interaction wavefunction (i.e., a linear combination of configuration state functions):

$$\Phi_{n,g}^{[i]}(\{\vec{r}_i, s_i\}) = \sum_{I=1}^M C_{I,g}^n \psi_{I,g}^{CSF[i]}(\{\vec{r}_i, s_i\}) \equiv \tilde{C}_g^n \tilde{\psi}_g^{CSF[i]\dagger} \quad (173)$$

where $\tilde{C}_g^n = (C_{1,g}^n, \dots, C_{M,g}^n)$, $\tilde{\psi}_g^{CSF[i]} \equiv (\psi_{1,g}^{CSF[i]}, \dots, \psi_{M,g}^{CSF[i]})$ and $\tilde{\psi}_g^{CSF[i]\dagger}$ is its complex conjugate. In this case, wavefunction and Hamiltonian orthogonality are satisfied if the expansion coefficients are generated by solving the eigenvalue problem:

$$\mathbf{H} \tilde{C}_g^{n\dagger} = E_n \mathbf{S} \tilde{C}_g^{n\dagger} \quad (174)$$

where the matrix elements of $\mathbf{H}$ and $\mathbf{S}$ are

$$H_{IJ} = \langle \psi_{I,g}^{CSF[i]} | \hat{H} | \psi_{J,g}^{CSF[i]} \rangle, \quad S_{IJ} = \langle \psi_{I,g}^{CSF[i]} | \psi_{J,g}^{CSF[i]} \rangle \quad (175)$$

Considering a particular excited state n , we can obtain a local-scaling transformation function $f_n(\vec{r})$ connecting the initial density $\rho_{n,g}(\vec{r})$ with the object density $\rho_n(\vec{r})$, and generate the transformed wavefunctions:

$$\Phi_{m,\rho}^{[i]}(\{\vec{r}_i, s_i\}) = \sum_{I=1}^M C_{I,\rho}^m \psi_{I,\rho}^{CSF[i]}(\{\vec{r}_i, s_i\}) \equiv \tilde{C}_\rho^m \tilde{\psi}_\rho^{CSF[i]\dagger} \quad (176)$$

for all states $m = 0, \dots, n$.

However, although the locally scaled transformed wavefunctions preserve the orthonormality condition, they fail to comply with Hamiltonian orthogonality. Of course, one can recombine the transformed wavefunctions so as to satisfy the latter requirement, by solving once more the eigenvalue problem

given by Eq. (174) for the Hamiltonian matrix constructed from the transformed wavefunctions [51]:

$$\mathbf{H}[\rho_n, \tilde{C}_{\rho_n}] \tilde{C}_{\rho_n}^{\dagger} = E_n \mathbf{S}[\rho_n, \tilde{C}_{\rho_n}] \tilde{C}_{\rho_n}^{\dagger} \quad (177)$$

Note that in the present case the matrix elements depend on the final density ρ_n . Moreover, because this density is obtained from the transformed wavefunction, they also depend on the expansion coefficients. For this reason, Eq. (177) must be solved iteratively. Such a procedure has been applied – in a sample calculation – to the 2^1S excited state of the helium atom. The upper-bound character of the energy corresponding to the energy functional for the transformed wavefunction $\Phi_{n,\rho}^{[i]}(\{\tilde{r}_{ij}\})$ with respect to the exact energy $E_{n,exact}$ is guaranteed by the Hylleraas–Undheim–MacDonald theorem.

The procedure described above has been generalized by introducing a *concerted* local-scaling transformation that carries an initial density $\rho_g(\tilde{r}) \equiv \frac{1}{M} \sum_{j=0}^{M-1} \rho_{j,g}(\tilde{r})$ into a final density $\rho(\tilde{r}) \equiv \frac{1}{M} \sum_{j=0}^{M-1} \rho_j(\tilde{r})$. This generalization [52] corresponds to Katriel’s super-particle approach.

5 Approximate Explicit Energy Functionals Generated by Local-Scaling Transformations

We review in this Section some recent work by Ludeña, López–Boada and Pino [113] on the construction of energy functionals that depend explicitly upon the one-particle density, but which are generated in the context of the local-scaling-transformation version of density functional theory. This work does not consider the general case involving exchange and correlation, but restricts itself to the exchange-only Hartree–Fock approximation.

5.1 Explicit Hartree–Fock Functionals

For the Hartree–Fock case, the energy functional $E[\Phi_\rho^{SD[i]}]$ for the density-transformed single Slater determinant given by Eq. (152), may be rewritten as a functional of the one-particle density:

$$\begin{aligned} \mathcal{E}[\rho; \Phi_\rho^{SD[i]}] = & \frac{1}{2} \int d^3\tilde{r}_1 \nabla_{\tilde{r}_1} \nabla_{\tilde{r}_1} D_\rho^{1SD[i]}(\tilde{r}_1, \tilde{r}'_1)|_{\tilde{r}'_1=\tilde{r}_1} + \int d^3\tilde{r} \rho(\tilde{r}) v(\tilde{r}) \\ & + \frac{1}{2} \int d^3\tilde{r}_1 \int d^3\tilde{r}_2 \frac{\rho(\tilde{r}_1) \rho(\tilde{r}_2)}{|\tilde{r}_1 - \tilde{r}_2|} \\ & - \frac{1}{2} \int d^3\tilde{r}_1 \int d^3\tilde{r}_2 \frac{D_\rho^{1SD[i]}(\tilde{r}_1, \tilde{r}_2) D_\rho^{1SD[i]}(\tilde{r}_2, \tilde{r}_1)}{|\tilde{r}_1 - \tilde{r}_2|} \end{aligned} \quad (178)$$

Note that the non-local part of the kinetic energy as well as the exchange energy are implicit functionals of the one particle density. In this Section we discuss how one can rewrite and approximate these terms so as to express them as explicit functionals of $\rho(\vec{r})$.

5.1.1 Explicit Kinetic Energy Functional

The kinetic energy can be rewritten as a sum of the Weiszäcker term [10] (a local component which depends only on the density) plus a non-local one:

$$T[\Phi_\rho^{SD(i)}] = \frac{1}{8} \int d^3\vec{r} \frac{[\nabla_{\vec{r}}\rho(\vec{r})]^2}{\rho(\vec{r})} + \frac{1}{2} \int d^3\vec{r} \rho(\vec{r}) \nabla_{\vec{r}} \nabla_{\vec{r}'} \tilde{D}_g^{1SD(i)}(\vec{f}(\vec{r}), \vec{f}(\vec{r}'))|_{\vec{r}'=\vec{r}} \quad (179)$$

The non-local part of the 1-matrix is

$$\tilde{D}_g^{1(i)}(\vec{f}(\vec{r}_1), \vec{f}(\vec{r}_1)) = \frac{D_g^{1(i)}(\vec{f}(\vec{r}_1), \vec{f}(\vec{r}_1))}{[\rho_g(\vec{f}(\vec{r}_1))]^{1/2} [\rho_g(\vec{f}(\vec{r}_1))]^{1/2}} \quad (180)$$

We assume, furthermore, that the generating 1-matrix can be expressed as:

$$D_g^{1SD(i)}(\vec{f}(\vec{r}), \vec{f}(\vec{r}')) = \sum_{j=1}^N \phi_{g,j}^*(\vec{f}(\vec{r})) \phi_{g,j}(\vec{f}(\vec{r}')) \quad (181)$$

It has been shown elsewhere that when Eqs. (180) and (181) are substituted into Eq. (179), use is made of the chain rule $\nabla_{\vec{r}} = \nabla_{\vec{f}} \nabla_{\vec{f}} \vec{f}(\vec{r})$, and $\nabla_{\vec{r}} \vec{f}(\vec{r})$ is reformulated according to Eq. (36), one is led to:

$$T[\Phi_\rho^{SD(i)}] = T_W[\rho] + \frac{1}{2} \int d^3\vec{r} \rho^3(\vec{r}) \frac{r^4}{f^4(\vec{r}) \rho_g^3(\vec{f}(\vec{r}))} \left[\sum_{j=1}^N |\nabla_{\vec{f}} \phi_{g,j}(\vec{f}(\vec{r}))|^2 - \frac{1}{4} \frac{(\nabla_{\vec{f}} \rho_g(\vec{f}(\vec{r})))^2}{\rho_g(\vec{f}(\vec{r}))} \right] \quad (182)$$

Moreover, when the relation $\lambda(\vec{r}) = f(\vec{r})/r$ is introduced in Eq. (182) through the expression

$$\lambda(\vec{r}) = \left(\frac{\rho(\vec{r})}{\rho_g(\vec{f}(\vec{r}))} \frac{1}{(1 + \vec{r} \cdot \nabla_{\vec{f}} \ln \lambda(\vec{r}))} \right)^{1/3} \quad (183)$$

obtained from Eq. (34), the kinetic-energy functional adopts the more familiar form:

$$T[\Phi_\rho^{SD(i)}] = T_W[\rho] + \frac{1}{2} \int d^3\vec{r} \rho^{5/3}(\vec{r}) A_N([\rho(\vec{r})]; \vec{r}) \quad (184)$$

where

$$A_N([\rho(\vec{r})]; \vec{r}) = ((1 + \vec{r} \cdot \nabla_{\vec{f}} \ln \lambda(\vec{r}))^{4/3} t_N(\vec{f}(\vec{r})), \quad (185)$$

and

$$t_N(\vec{f}(\vec{r})) = \frac{1}{\rho_g^{5/3}(\vec{f}(\vec{r}))} \left[\sum_{j=1}^N |\nabla_{\vec{r}} \phi_{g,j}(\vec{f}(\vec{r}))|^2 - \frac{1}{4} \frac{(\nabla_{\vec{r}} \rho_g(\vec{f}(\vec{r})))^2}{\rho_g(\vec{f}(\vec{r}))} \right] \quad (186)$$

Note that $A_N([\rho(\vec{r}); \vec{r}])$ depends upon the number of particles N and, in this sense, is specific to the particular problem at hand, i.e., it is not universal. This, of course, is not surprising, as – within the constructive approach to energy density functional theory reviewed here (as well as in Cioslowski's density-driven method) – no such a “universal” functional arises. (The allegation concerning the existence of this functional, in the context of the Hohenberg–Kohn formalism, seems to us to be based on a misunderstanding.) We should remark, however, that if we take the first two terms in the non-local contribution to the kinetic energy expression, namely, $\rho^{5/3}(\vec{r})$ and $(1 + \vec{r} \cdot \nabla_{\vec{r}} \ln \lambda(\vec{r}))^{4/3}$, and introduce in the latter the first-order approximation to $\lambda(\vec{r})$ that is, $\lambda(\vec{r}) \simeq (\rho(\vec{r})/\rho_g(\vec{f}))^{1/3}$, (see discussion below) we get a general and “universal” part of the kinetic energy functional, that depends exclusively on the one-particle density $\rho(\vec{r})$:

$$\rho^{5/3}(\vec{r})(1 + \vec{r} \cdot \nabla_{\vec{r}} \ln(\rho(\vec{r})/\rho_g(\vec{f}))^{1/3})^{4/3} \quad (187)$$

Thus, in a very natural way, a “universal” factor arises in the kinetic energy functional which is modulated by the function $t_N(\vec{f})$, where the latter contains specific information pertaining to the N -electron system at hand.

For the elucidation of the specific nature of the N -particle modulating factor $t_N(\vec{f})$, we first have to know the explicit form of the vector function $\vec{f}(\vec{r}) = \vec{f}([\rho(\vec{r}); \vec{r}])$. This may be done by means of an iterative approximation, based on the following relation:

$$\lambda^{(i)}(\vec{r}) = \left[\frac{\rho(\vec{r})}{\rho_g(\lambda^{(i-1)}(\vec{r})\vec{r})(1 + \vec{r} \cdot \nabla_{\vec{r}} \ln \lambda^{(i-1)}(\vec{r})\vec{r})} \right]^{1/3} \quad (188)$$

where the initial value for the iteration is $\lambda^{(0)}(\vec{r}) = 1$. Another way to obtain analytic approximations to $\vec{f}(\vec{r})$ is to use Padé approximants. As has been shown elsewhere [113], we have, for the spherically symmetric case:

$$\lambda \simeq 1 + \frac{2\rho_g(r)\Delta Q(r)}{2\rho_g^2(r)r^3 + [rd\rho_g(r)/dr + 2\rho_g(r)]\Delta Q(r)} \quad (189)$$

where

$$\Delta Q(r) = \int_0^r dr' r'^2 \rho(r') - \int_0^r dr' r'^2 \rho_g(r') \quad (190)$$

Other Padé approximants are also studied in Ref. [113] and references therein.

5.1.2 Explicit Exchange-only Functional

Let us now consider the exchange energy. Starting from the definition:

$$E_x[\Phi_\rho^{SD(i)}] = -\frac{1}{2} \int d^3\vec{r} \int d^3\vec{r}' \frac{D_\rho^{1SD(i)}(\vec{r}, \vec{r}') D_\rho^{1SD(i)}(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|} \quad (191)$$

using Eqs. (140) and (181), and assuming that we have spherical symmetry, we can rewrite Eq. (191) as:

$$E_x[\Phi_\rho^{SD[i]}] = -\frac{1}{2} \sum_{j=1}^N \sum_{k=1}^N \int dr r \rho(r) \frac{(a_{jk}(f)P_{kj}(f) + a_{kj}(f)P_{jk}(f))}{\rho_g(f)} \quad (192)$$

where we have defined

$$a_{jk}(\vec{r}) = \phi_{g,j}^*(\vec{r}) \phi_{g,k}(\vec{r}) \quad (193)$$

and

$$P_{jk}(f) = \int_0^f df' f'^2 a_{jk}(f') \quad (194)$$

In order to compare expression (192) with the usual approximations to the exchange energy, we rewrite this Equation as:

$$E_x[\Phi_\rho^{SD[i]}] = -\frac{1}{2} \sum_{j=1}^N \sum_{k=1}^N \int dr r^2 \rho(r) \frac{1}{r} \frac{(a_{jk}(f)P_{kj}(f) + a_{kj}(f)P_{jk}(f))}{\rho_g(f)} \quad (195)$$

Bearing in mind that $1/r = \lambda(r)/f$ and, putting $\lambda(r)$ in the explicit form given by Eq. (183), we can rewrite Eq. (195) as follows:

$$E_x[\Phi_\rho^{SD[i]}] = -\frac{1}{2} \int dr r^2 \rho^{4/3}(r) B_N([\rho(r)]; r) \quad (196)$$

where

$$B_N([\rho(r)]; r) = \left[\frac{1}{(1 + \vec{r} \cdot \vec{\nabla}_r \ln \lambda(\vec{r}))} \right]^{1/3} \chi_N(f) \quad (197)$$

and

$$\chi_N(f) = \frac{1}{f \rho_g^{4/3}(f)} \left[\sum_{j=1}^N \sum_{k=1}^N (a_{jk}(f)P_{kj}(f) + a_{kj}(f)P_{jk}(f)) \right] \quad (198)$$

Again, as in the case of the kinetic energy, here too we can extract an approximate expression that is “universal” from the first two factors in the exchange energy density; this expression is approximate in the sense that we have replaced $\lambda(\vec{r})$ by the first-order term of Eq. (188):

$$\rho^{4/3}(r) \left[\frac{1}{(1 + \vec{r} \cdot \vec{\nabla}_r \ln \lambda(\vec{r}))} \right]^{1/3}. \quad (199)$$

We observe that the first factor is precisely Dirac’s expression for the exchange energy [9]. The role of the function $\chi_N(f)$ is again that of modulating the “universal” part of the exchange functional, so as to introduce the particularities of a given system. As was done for the kinetic energy functional, it is also possible in the case of the exchange functional to obtain an analytic expression

for the function $\chi_N(f)$ by resorting to the iterative solutions for $\lambda(r)$ (Eq. (188)), or else by employing Padé approximants (Eq. (189)).

5.1.3 Results of Explicit Analytic Energy Density Functionals for the Li and Be Atoms

Let us now incorporate the results of Eqs. (184) and (196) and rewrite the implicit energy density functional given by Eq. (179) as:

$$\begin{aligned}
 E[\Phi_\rho^{SD[i]}] \mathcal{E}[\rho; \Phi_\rho^{SD[i]}] = & \frac{1}{8} \int d^3\vec{r} \frac{[V_\tau \rho(\vec{r})]^2}{\rho(\vec{r})} + \frac{1}{2} \int d^3\vec{r} \rho(\vec{r})^{5/3} A_N([\rho(\vec{r})]; \vec{r}) \\
 & + \int d^3\vec{r} \rho(\vec{r}) v(\vec{r}) + \frac{1}{2} \int d^3\vec{r}_1 \int d^3\vec{r}_2 \frac{\rho(\vec{r}_1) \rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} \\
 & - \frac{1}{2} \int dr r^2 \rho^{4/3}(r) B_N([\rho(r)]; r) \quad (200)
 \end{aligned}$$

As discussed above, this still remains as an implicit functional of the one-particle density, in view of the fact that $f(r) = f([\rho]; r)$. Nevertheless, when we introduce the analytic Padé approximant for $f([\rho]; r)$ given by Eq. (189), we can transform Eq. (200) into an explicit functional of ρ .

The resulting functional has been evaluated for the initial orbitals of the lithium and beryllium atoms given in Section 4.6. Using the same process of intra- and inter-orbit optimization carried out in Section 4.6, but substituting, in each step, the value for $f(r)$ given by the Padé approximant obtained from Eq. (189), energy values were obtained for the Li and Be atoms that are indistinguishable from those previously calculated with the exact values of $f(r)$, namely, when Eq. (40) is solved.

These preliminary results indicate that the possibility of finding explicit functionals of the one-particle density for arbitrary systems is not too far away. Clearly, these *constructive functionals* are both symmetry as well as system-size dependent. In this sense, our constructive approach leads to energy density functionals which are not universal. Nevertheless, Eqs. (184) and (196) show (for the Hartree–Fock case) a remarkable structure for the kinetic energy and exchange functionals. A considerable part of these functionals is common to all systems, regardless of their symmetry or size. This property, can perhaps be favorably exploited in the construction of approximate energy density functionals.

6 Calculation of Kohn–Sham Orbitals and Potentials by Local-Scaling Transformations

It has been shown by Levy and Perdew [100] that it is possible to solve the Kohn–Sham equations by means of a density-constrained variation of the

kinetic energy of a non-interacting system. Since the density constraint is easily imposed by means of local-scaling transformations, it turns out that the local-scaling-transformation version of density functional theory may be successfully applied to solve the Kohn–Sham problem.

The difficulty of this problem can be appreciated by noticing that in order to solve the Kohn–Sham equations exactly, one must have the exact exchange-correlation potential v_{xc}^{KS} which, moreover, must be obtained from the *exact* exchange-correlation functional $E_{xc}^{KS}[\rho(\vec{r})]$ given by Eq. (160). As this functional is not known, the attempts to obtain a direct solution to the Kohn–Sham equations have had to rely on the use of approximate exchange-correlation functionals. This approximate direct method, however, does not satisfy the requirement of functional N -representability.

As opposed to the direct method, the “inverse method” (corresponding to the density constrained variation of the kinetic energy) does not require that we know the exact exchange-correlation functional $E_{xc}^{KS}[\rho(\vec{r})]$, but just the *exact* ground-state one-particle density $\rho(\vec{r})$. These densities can be obtained, in general, from experiment [98], although for the purpose of carrying out very precise calculations, it is customary to use densities obtained from highly accurate quantum mechanical wavefunctions.

We have reviewed here the implementation of the inverse method for going from densities to potentials, based on local-scaling transformations. For completeness, let us mention, however, that several other methods have also been advanced to deal with this inverse problem [101–111]. Consider the decomposition of $\mathcal{S}_N \subset \mathcal{L}_N$ into orbits $\{\mathcal{O}_{\mathcal{J}}^{[i]}\}$. Such orbits are characterized by the fact that there is a one to one correspondence between wavefunctions $\Phi_{\rho_j}^{[i]} \in \mathcal{O}_{\mathcal{J}}^{[i]}$ and one-particle densities $\rho_j \in \mathcal{N}_{\Phi}$. Hence, the minimization of the energy at fixed density clearly defines a process of “orbit-jumping”, where one searches for the optimal wavefunction associated with the fixed density. Observe that if this is the exact ground-state density ρ_o^{exact} , then, the energy minimum is attained at $\Phi_{\rho_o^{exact}}^{SD[KS]} = \Phi_{KS}^{SD}$, namely, at the single determinant Φ_{KS}^{SD} formed by Kohn–Sham orbitals. The interesting part of this whole procedure is that, in fact, one does not need to minimize the total energy, but just the kinetic energy corresponding to a non-interacting system. The reason is that, as has been shown by Lieb [87], the minimum of the kinetic energy T_s (see Eq. (157)) of a non-interacting system is attained at the solutions of the Kohn–Sham equation (Eq. (161)). In other words, it satisfies the following variational principle:

$$\begin{aligned} T_s[\{\psi_{\rho_o^{exact},k}^{[HK]}\}] &\equiv \langle \Phi_{\rho_o^{exact}}^{SD[HK]} | \hat{T} | \Phi_{\rho_o^{exact}}^{SD[HK]} \rangle \\ &= \min_{\substack{\Phi_{\rho_o^{exact}}^{SD[k]} \in \mathcal{S}_N \\ \Phi_{\rho_o^{exact}}^{SD[k]} \rightarrow \rho_o^{exact}(\vec{r}) \in \mathcal{N}_{\Phi}}} \{ \langle \Phi_{\rho_o^{exact}}^{SD[k]} | \hat{T} | \Phi_{\rho_o^{exact}}^{SD[k]} \rangle \} \end{aligned} \quad (201)$$

It is now easy to establish the equivalence between the variational principle given by Eq. (201) and the Kohn–Sham equations. For this purpose, let us

introduce the auxiliary functional:

$$\begin{aligned} \Omega[\{\phi_{\rho,k}^{[i]}(\vec{r})\}; \Phi_g^{[i]}] &= T_s[\{\phi_{\rho,k}^{[i]}(\vec{r})\}; \Phi_g^{[i]}] \\ &\quad - \int d^4x \omega(\vec{r}) \left(\sum_{k=1}^N \phi_{\rho,k}^{*[i]}(\vec{r}) \phi_{\rho,k}^{[i]}(\vec{r}) - \rho_o^{exact} \right) \\ &\quad - \sum_{k=1}^N \sum_{l=1}^N \mathcal{E}_{kl} \left(\int d^4x \phi_{\rho,k}^{*[i]}(\vec{r}) \phi_{\rho,l}^{[i]}(\vec{r}) - \delta_{kl} \right) \quad (202) \end{aligned}$$

where the generalized Lagrange multiplier $\omega(\vec{r})$ guarantees that the variational density $\rho(\vec{r})$ is equal at all stages of this variation to ρ_o^{exact} . Upon variation of this auxiliary functional with respect to the orthonormal orbitals $\phi_{\rho,k}^{*[i]}(\vec{r})$, one obtains a system of equations that, in diagonal form, are the canonical Kohn–Sham equations:

$$[-\frac{1}{2} \nabla^2 + \omega(\vec{r})] \psi_{\rho_o^{exact},k}^{[HK]}(\vec{r}) = \mathcal{E}_k \psi_{\rho_o^{exact},k}^{[HK]}(\vec{r}) \quad (203)$$

The presence of the Lagrange multiplier function $\omega(\vec{r})$ is fundamental in this variation, as it is this multiplier that assumes the role of the effective Kohn–Sham potential:

$$\begin{aligned} \omega(\vec{r}) &= v_{eff}^{KS[HK]}([\rho_o^{exact}(\vec{r})]; \vec{r}) = v(\vec{r}) + v_H([\rho_o^{exact}(\vec{r})]; \vec{r}) \\ &\quad + v_{XC,g}^{KS[HK]}([\rho_o^{exact}(\vec{r})]; \vec{r}) \quad (204) \end{aligned}$$

Thus, it is clearly equivalent to solving the Kohn–Sham equations or to dealing with the constrained variational principle for T_s .

The way in which local-scaling transformations have been used for the minimization of the kinetic energy functional is as follows [108–111]. An arbitrary Slater determinant $\Phi_g^{SD[i]}$ is selected to be the orbit-generating wavefunction for $\mathcal{O}_g^{[i]} \subset \mathcal{S}_N$. This wavefunction is constructed from orbitals $\{\phi_k([\{\alpha_j^{[i]}\}]; \vec{r})\}$ that depend on some variational parameters $\{\alpha_j^{[i]}\}$. For a particular choice of these parameters, say $\{\tilde{\alpha}_j^{[i]}\}$, we have a particular one-particle density $\rho_g([\{\tilde{\alpha}_j^{[i]}\}]; \vec{r})$. For a given fixed final density $\rho_o^{exact}(\vec{r})$ we have – according to Eq. (36) – a unique local-scaling transformation $f(\vec{r})$ from which we can generate the set of locally-scaled transformed orbitals $\{\phi_{\rho_o^{exact},k}^{[i]}(\vec{r})\}$ (see Eq. (70)). Every time the orbital parameters are changed, one produces a new wavefunction belonging to a different orbit. This follows from the one-to-one correspondence between N -representable densities and wavefunctions *within a given orbit*. As a result, optimization of these transformed orbitals in the kinetic energy expression leads to the minimum value $T_s[\{\phi_{\rho_o^{exact},k}^{[KS]}(\vec{r})\}]$ corresponding to the parameters $\{\tilde{\alpha}_k^{[KS]}\}$, since this minimum is attained at the Kohn–Sham orbit $\mathcal{O}_g^{[KS]}$. In consequence, one obtains the orbitals $\{\phi_{\rho_o^{exact},k}^{[KS]}(\vec{r})\}$, which are, in general, non-canonical Kohn–Sham orbitals. When we put these orbitals in canonical form, can be obtained from them the effective potential $v_{eff}^{KS[HK]}([\rho_o^{exact}(\vec{r})]; \vec{r})$ quite directly, by inversion of the canonical Kohn–Sham equations.

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