Introduction to Density Functional Theory and Exchange-Correlation Energy Functionals

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Introduction to Density Functional Theory and Exchange-Correlation Energy Functionals

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Density functional calculations of cohesive and structural properties of molecules and solids can be performed with less computational effort than by using other methods of comparable accuracy. We outline the theory and discuss the local density approximations basic to most applications, and we discuss ways to modify these approximations to yield improved results.

1 Foreword

The NIC Winter School 2006 focuses on Computational Nanoscience, particularly on understanding the properties of materials so that we can “tailor” new ones with novel properties. A glance at the program shows the dominant role played by the density functional (DF) formalism in this area. I have been asked to present an introduction to this theory and, in a second lecture, to discuss approximations to the exchange and correlation energy. These lecture notes cover these topics, but the first lecture will follow a more historical (and more lively) approach to DF theory. The theory now plays a ubiquitous role in condensed matter calculations *and* in chemistry, but its general acceptance was slow in coming, and there has been much rewriting of history since its arrival. The following notes are derived in part from earlier articles[1] and provide a background for other talks in this School.

2 Introduction

The description of many-particle systems covers much of physics and chemistry. In computational nanoscience we focus on atoms, molecules, and solids, on their structural and cohesive properties, and on how they interact with each other. We usually emphasize the properties of specific materials rather than universal properties of all, and our interest on structural and binding means that the total energy E of a system and its components is very important. The density functional (DF) formalism is our main theme here, but we shall note how its perspective differs from that of other methods used to discuss many-particle systems.

If we wish to discuss the properties of an interacting system, such as the electrons in a molecule or solid, it is natural to consider the many-electron wave function, $\Psi(\vec{r}_1, \vec{r}_2, ...\vec{r}_N)$, where the $\vec{r}_i$ denote the particle coordinates and spins. This has been discussed in this School by Prof. V. Staemmler. Hartree[2] made one of the earliest approximations for Ψ in writing the many-electron wave function as a product of single-particle functions, i.e.

$$\Psi(\vec{r}_1, \vec{r}_2, ...) = \psi_1(\vec{r}_1).......\psi_N(\vec{r}_N) \tag{1}$$

Each of the functions $\psi_i(\vec{r}_i)$ satisfies a one-electron Schrödinger equation with a potential term arising from the average field of the other electrons, i.e.

$$(-\frac{\hbar^2}{2m}\nabla^2 + V_{\text{ext}} + \Phi_i)\;\psi_i(\vec{r}) = \epsilon_i\psi_i(\vec{r}), \tag{2}$$

where the Coulomb potential Φ_i is given by Poisson's equation,

$$\nabla^2\Phi_i = 4\pi e^2 \sum_{\substack{j=1\\ i\neq j}}^{N} |\psi_j|^2, \tag{3}$$

and V_{ext} is the potential due to the nuclei. Fermi statistics can be incorporated by replacing the product wave function by a single determinantal function.[3,4] This "Hartree-Fock" (HF) approximation leads to an additional, nonlocal exchange term in the Schrödinger equation, but does not change the single-particle picture, with the wave function described in terms of orbitals with particular spins and occupation numbers. The inclusion of "exchange" effects improves the total energy, and the HF approximation remains an indispensable benchmark in molecular physics.

In 1960 Coulson,[5] however, noted that "it is now perfectly clear that a single configuration (Slater determinant) wave function must inevitably lead to a poor energy". A linear combination of such determinants would be better, and the inclusion of "correlation effects" by this approach ("configuration interaction", CI) improves the many-particle wave function, from which most properties of interest can be calculated. Some such approaches will be discussed in this School by Dr. C. Hättig. The explosive increase in the number of configurations with increasing electron number means, however, that only systems with relatively few electrons can be calculated with high accuracy. The complexity of the resulting solutions can also hinder a simple interpretation of the results.

Thomas[6] and Fermi[7] had proposed much earlier a scheme based on the density of electrons in the system, $n(\vec{r})$. The Thomas-Fermi (TF) scheme assumes that the motions of the electrons are uncorrelated, and that the corresponding kinetic energy can be described by a local approximation based on the results for free electrons, $[n(\vec{r})]^{\frac{5}{3}}$. The potential of the system can be determined from solving Poisson's equation, and the requirement of constant chemical potential leads to the TF equation for $n(\vec{r})$. This approach gives a poor description of real systems, but in its focus on the *density* it is a forerunner of later DF theories, and its mathematical properties have received much attention.[8] In general, the integrated quantity $n(\vec{r}) = N\int d\vec{r}_2 .. \int d\vec{r}_N \Psi^*(\vec{r}, r_2 ... \vec{r}_N)\Psi(\vec{r}, r_2 ... \vec{r}_N)$ should be easier to describe than the precise details of the wave function, Ψ.

Shortly after the original work, Dirac[9] proposed that exchange effects be included by incorporating a term derived from the exchange energy density in a homogeneous system,

$$\varepsilon_{\text{x}}^{\text{Dirac}} = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}} n^{\frac{1}{3}} = \frac{0.458}{r_s}\ \text{a.u.}, \tag{4}$$

where $r_s = (3/(4\pi n))^{1/3}$ is a measure of the average interelectronic distance. The use of an approximate exchange potential in addition to the Hartree term in Eq. (2) was suggested by Slater,[10] who showed that the exchange potential in a system of variable density could be approximated by a term with the same density dependence. However, it is *crucial* to appreciate that the argument of Slater does not depend on the exchange energy in a homogeneous system. The exchange interaction means that an electron of a given spin will be surrounded by a region where the density of electrons with the same spin (say, spin up) is reduced. The effect of the "exchange hole" can be estimated by replacing it by a uniform density inside a sphere of radius r_0, and zero elsewhere. Since the hole contains a single electron,[10] $r_0 = (3/(4\pi n_\uparrow))^{1/3}$, and we obtain an exchange energy with the same density dependence as that of Dirac.

Gáspár[11] adopted the Dirac approximation to the exchange energy, and derived a slightly different exchange potential by using a variational approach. This method reproduced the HF eigenfunctions and eigenvalues for the Cu^+ ion very well, showing that an approximation based on results for a homogeneous system could give a satisfactory description even if the density is very far from uniform.

The above work has been essential to the development of modern DF theory. As an approximation to the (nonlocal) exchange potential, the simple local density (LD) approximation provided the basis for much of the work on the electronic structure of solids in the 1950's and early 1960's. The calculation of electronic band structures and related quantities is, of course, one of the success stories of modern condensed matter physics. The experience obtained in solving Schrödinger-like equations with local effective potentials and the improvement in numerical methods and computers during the past decades have been decisive in carrying out density functional calculations in recent years.

Hohenberg and Kohn[12] showed that ground state properties, particularly the total energy E, of a system of interacting particles could be related to the density distribution. For a nonmagnetic, nondegenerate ground state of a system of electrons in the presence of a scalar field V_{ext}, they showed that the density uniquely determines the potential, up to an arbitrary additive constant. Their proof has been simplified and extended by Levy,[13] and the TF equation may be derived from this formalism as an approximation. Its application to the total energy of the interacting system results in a minimum principle, and the determination of the energy of the ground state can be found by the solution of single-particle equations.[14] In practice, total energy calculations require approximations to be made for the exchange-correlation energy, E_{xc}, and Kohn and Sham[14] showed that the local density (LD) approximation,

$$E_{\mathrm{xc}}^{\mathrm{LD}} = \int d\vec{r}\, n(\vec{r})\, \varepsilon_{\mathrm{xc}}[n(\vec{r})], \tag{5}$$

could be applied to the limiting cases of a slowly varying density and very high densities. Here $\varepsilon_{\mathrm{xc}}[n]$ is the exchange and correlation energy per particle of a homogeneous electron gas with density n. The exchange contribution, ε_{x}, has the same form as that of Gáspár, and a variety of approximations exist for the correlation term, ε_c.

The limiting cases noted above are not realized in atoms, molecules or solids, and Kohn and Sham commented that "we do not expect an accurate description of chemical bonding" with the LD approximation.[14] A decade passed before the first attempts were made to test its ability to describe the bonds in molecules, and it is remarkable that these showed that the LD approximation could generally reproduce ground state geometries, vibration and phonon frequencies, and moments of the density very well. The DF formalism remains the basis of most of the parameter-free calculations in extended systems, and has found widespread application to molecules and clusters. Most calculations have used the local density approximation [Eq. (5)] or modifications of it.

The practical necessity of approximating E_{xc} leads to an essential difference in perspective between the density functional and CI approaches. The goal of the latter is an exact numerical solution of the Schrödinger equation, which would yield exact answers for most quantities of interest, whereas even an exact solution of the density functional equations will only reflect the accuracy of the approximation for E_{xc}. We shall discuss some of the many approximations that have been developed. In order to appreciate some qualitative features of the density in a real system, we show in Figure 1 the spherically averaged density in the ground state of the carbon atom. The density falls monotonically from the nucleus, with the radial oscillations often expected. The charge density in small molecules also tends to be relatively featureless, with maxima at the nuclei, saddle points along the bonds and a generally monotonic decay away from both. Furthermore, the electron density in a molecule or solid shows relatively small departures from the overlapped densities of its atomic constituents. Energy differences result from subtle changes in relatively featureless density distributions, and it is not surprising that it is difficult to find simple prescriptions for determining them.

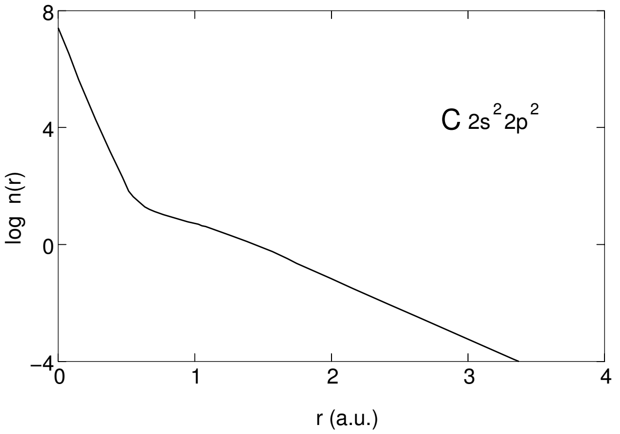

Figure 1. Spherical average of density in ground state of C atom

3 Density Functional Formalism

3.1 The Density as Basic Variable

Ground state (GS) properties of a system, including the energy E, can be expressed as functionals of the GS electron density, i.e. they are determined by a knowledge of the density alone. We show that $E[n]$ satisfies a variational principle. The Thomas-Fermi (TF) is a special case of this formalism.

The basic theorems of the density functional formalism were derived by Hohenberg and Kohn,[12] and Levy[13] provided a simpler and more general derivation. We consider N

electrons moving in an external potential, $V_{ext}(\vec{r})$, i.e. the Hamiltonian is

$$H = T + V_{\rm ee} + \sum_{i=1}^{N} V_{\rm ext}(\vec{r}_i), \tag{6}$$

where T and $V_{\rm ee}$ are the kinetic and electron-electron interaction operators, respectively. For all "N-representable" densities, $n(\vec{r})$,[a] i.e. those obtainable from some antisymmetric wave function, $\psi(\vec{r}_1, \vec{r}_2, ...\vec{r}_N)$, Levy defined the functional,

$$F[n] = \min_{\psi \to n} \langle \psi | T + V_{\rm ee} | \psi \rangle, \tag{7}$$

where the minimum is taken over all ψ that give the density n. $F[n]$ is universal in the sense that it refers neither to a specific system nor to the external potential $V_{\rm ext}(\vec{r})$. If we denote $E_{\rm GS}$, $\psi_{\rm GS}$, and $n_{\rm GS}(\vec{r})$ to be the ground state energy, wave function and density, respectively, then the two basic theorems of DF theory are:

$$E[n] \equiv \int d\vec{r}\, V_{\rm ext}(\vec{r}) n(\vec{r}) + F[n] \geq E_{\rm GS} \tag{8}$$

for all N-representable $n(\vec{r})$, and

$$\int d\vec{r}\, v(\vec{r}) n_{\rm GS}(\vec{r}) + F[n_{\rm GS}] = E_{\rm GS} \tag{9}$$

To prove the variational principle [Eq. (8)] we introduce the notation $\psi^n_{\rm min}(\vec{r})$ for a wave function that minimizes $F[n]$ in Eq. (7), so that

$$F[n] = \langle \psi^n_{\rm min} | T + V_{\rm ee} | \psi^n_{\rm min} \rangle \tag{10}$$

Writing $V = \sum_i V_{\rm ext}(\vec{r}_i)$, we have

$$\int d\vec{r}\, V_{\rm ext}(\vec{r}) n(\vec{r}) + F[n] = \langle \psi^n_{\rm min} | V + T + V_{\rm ee} | \psi^n_{\rm min} \rangle \geq E_{\rm GS}, \tag{11}$$

according to the minimum property of the GS. This proves the inequality (8). Using the minimum property once more we find

$$E_{\rm GS} = \langle \psi_{\rm GS} | V + T + V_{\rm ee} | \psi_{\rm GS} \rangle \leq \langle \psi^{n_{\rm GS}}_{\rm min} | V + T + V_{\rm ee} | \psi^{n_{\rm GS}}_{\rm min} \rangle. \tag{12}$$

We subtract the interaction with the external potential and obtain

$$\langle \psi_{\rm GS} | T + V_{\rm ee} | \psi_{\rm GS} \rangle \leq \langle \psi^{n_{\rm GS}}_{\rm min} | T + V_{\rm ee} | \psi^{n_{\rm GS}}_{\rm min} \rangle. \tag{13}$$

On the other hand, the definition of $\psi^{n_{\rm GS}}_{\rm min}$ yields the reverse relation between the two sides of Eq. (13). This is possible only if

$$\langle \psi_{\rm GS} | T + V_{\rm ee} | \psi_{\rm GS} \rangle = \langle \psi^{n_{\rm GS}}_{\rm min} | T + V_{\rm ee} | \psi^{n_{\rm GS}}_{\rm min} \rangle. \tag{14}$$

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[a] Hohenberg and Kohn[12] worked in the space of V-representable densities, i.e. those that can be realized for some external potential, $V_{\rm ext}(\vec{r})$. This space is a subspace of N-representable densities.

Then we have

$$\begin{aligned} E_{\rm GS} &= \int d\vec{r}\, V_{\rm ext}(\vec{r}) n_{\rm GS}(\vec{r}) + \langle \psi_{\rm GS} | T + V_{\rm ee} | \psi_{\rm GS} \rangle \\ &= \int d\vec{r}\, V_{\rm ext}(\vec{r}) n_{\rm GS}(\vec{r}) + \langle \psi_{\rm min}^{n_{\rm GS}} | T + V_{\rm ee} | \psi_{\rm min}^{n_{\rm GS}} \rangle \\ &= \int d\vec{r}\, V_{\rm ext}(\vec{r}) n_{\rm GS}(\vec{r}) + F[n_{\rm GS}] \end{aligned} \tag{15}$$

These are the basic theorems. An important result also follows from Eq. (14). If the ground state GS is nondegenerate, $\psi_{\rm min}^{n_{\rm GS}} = \psi_{\rm GS}$. If the ground state is degenerate, $\psi_{\rm min}^{n_{\rm GS}}$ is equal to one of the GS wave functions, and the others can also be obtained. The GS charge density then determines the GS wave function(s), from which all GS properties can be calculated. These properties are therefore functionals of the density.

It has been said that Wilson[15] gave a shorter, if less general, proof of the definitive role of the electron density shortly after the DF formalism was first published. It is based on the "cusp condition"[16] satisfied by the density at the nucleus

$$Z_\alpha = \frac{-1}{2\langle n(0)\rangle} \left[\frac{\partial \langle n(r_\alpha)\rangle}{\partial r_\alpha} \right]_{r_\alpha = 0}, \tag{16}$$

where the brackets $\langle \ldots \rangle$ denote a spherical average. The density n then determines uniquely the charges Z_α as well as the positions of the nuclei and hence the Hamiltonian.

These theorems provide a general method for calculating GS properties. If an approximation can be found for $F[n]$, we need to minimize $E[n]$ in Eq. (13) for the potential $v(\vec{r})$ of interest. This leads to corresponding approximations for $E_{\rm GS}$ and $n_{\rm GS}(\vec{r})$. The same procedure applies to a ground state property X if we have an approximation for the functional $X[n]$.

3.2 Thomas-Fermi (TF) Approximation

Here the electrons are treated as independent particles, and the electron-electron interaction energy arises solely from the electrostatic energy,

$$E_{\rm es}[n] = \frac{e^2}{2} \int d\vec{r} \int d\vec{r'}\, \frac{n(\vec{r}) n(\vec{r'})}{|\vec{r} - \vec{r'}|}. \tag{17}$$

Furthermore, we assume that the kinetic energy is given by

$$T[n] = \int d\vec{r}\, t[n(\vec{r})], \tag{18}$$

where $t[n]$ is the kinetic energy density for a system of noninteracting electrons with density n. We have

$$t[n] = 2 \frac{1}{(2\pi)^3} \int_{|k| \le k_F} d\vec{k}\, \frac{\hbar^2 k^2}{2m}, \tag{19}$$

where $2(4\pi/3){k_F}^3/(2\pi)^3 = n$. This gives

$$T_0[n] = C_k \int d\vec{r}\, \{n(\vec{r})\}^{\frac{5}{3}}, \tag{20}$$

where $C_k = 3\hbar^2(3\pi^2)^{\frac{2}{3}}/10m$.

We now minimize $E(n)$ under the condition that the number of electrons is kept constant,

$$\int d\vec{r}\, n(\vec{r}) = N. \tag{21}$$

Using the method of Lagrange multipliers, we require that

$$E[n] + \lambda N = T[n] + E_{\mathrm{es}}[n] + \int d\vec{r}\, n(\vec{r})\{V_{\mathrm{ext}}(\vec{r}) + \lambda\} \tag{22}$$

has a minimum. The corresponding Euler equation is the TF equation,

$$\frac{5}{3} C_k n(\vec{r})^{\frac{2}{3}} + e^2 \int d\vec{r'}\, \frac{n(\vec{r'})}{|\vec{r} - \vec{r'}|} + V_{\mathrm{ext}}(\vec{r}) + \lambda = 0. \tag{23}$$

Decades of study have shown that the TF model provides a rough description of, for example, the charge density and the electrostatic potential, but it has severe deficiencies. The charge density is infinite at the nucleus, and it does not decay exponentially far from the nucleus of an atom, but as r^{-6}. It has also been shown that TF theory does not result in atoms binding to form molecules or solids. The absence of shell structure in the TF atom means that the observed periodic variation of many properties with changing atomic number cannot be reproduced. In fact, the atoms *shrink* with increasing atomic number Z (as $Z^{-1/3}$),[17] and the model never predicts ferromagnetism.[18]

3.3 Single-particle Description of a Many-particle System

Many of the drawbacks of the Thomas-Fermi approach can be traced to the approximate treatment of the kinetic energy. The task of finding good approximations to the energy functional is greatly simplified by using a different separation introduced by Kohn and Sham,[14]

$$E[n] = T_0[n] + \int d\vec{r}\, n(\vec{r}) \Big(V_{\mathrm{ext}}(\vec{r}) + \frac{1}{2}\Phi(\vec{r}) \Big) + E_{\mathrm{xc}}[n]. \tag{24}$$

T_0 is the kinetic energy of a system with density n in the absence of electron-electron interactions, Φ is the classical Coulomb potential for electrons, and the remainder E_{xc} defines the exchange-correlation energy. T_0 differs from the true kinetic energy T, but it is of comparable magnitude and is treated *exactly* in this approach. This removes many of the deficiencies of the Thomas-Fermi approximation, such as the lack of a shell structure of atoms or the absence of chemical bonding in molecules and solids. All terms in Eq. (24) but the exchange-correlation energy E_{xc} can be evaluated exactly, so that the (unavoidable) approximations for E_{xc} play a central role in the following discussion.

The variational principle applied to Eq. (24) yields

$$\frac{\delta E[n]}{\delta n(\vec{r})} = \frac{\delta T_0}{\delta n(\vec{r})} + V_{\mathrm{ext}}(\vec{r}) + \Phi(\vec{r}) + \frac{\delta E_{\mathrm{xc}}[n]}{\delta n(\vec{r})} = \mu, \tag{25}$$

where μ is the Lagrange multiplier associated with the requirement of constant particle number.[b] If we compare this with the corresponding equation for a system with an effective potential $V(\vec{r})$ but *without* electron-electron interactions,

$$\frac{\delta E[n]}{\delta n(\vec{r})} = \frac{\delta T_0}{\delta n(\vec{r})} + V(\vec{r}) = \mu, \tag{26}$$

we see that the mathematical problems are identical, provided that

$$V(\vec{r}) = V_{\rm ext} + \Phi(\vec{r}) + \frac{\delta E_{\rm xc}[n]}{\delta n(\vec{r})}, \tag{27}$$

Where the last term is referred to as the exchange-correlation potential $V_{\rm xc}$. The solution of Eqs. (26), (27) can be found by solving the Schrödinger equation for noninteracting particles,

$$\left(-\frac{1}{2}\nabla^2 + V(\vec{r})\right)\ \psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r}), \tag{28}$$

yielding

$$n(\vec{r}) = \sum_{i=1}^{N} |\psi_i(\vec{r})|^2. \tag{29}$$

The condition (27) can be satisfied in a self-consistent procedure.

The solution of this system of equations leads then to the energy and density of the lowest state, and all quantities derivable from them. The formalism has also been generalized to the lowest state with a given set of quantum numbers.[19] In this case $E_{\rm xc}$ depends on the values of the quantum numbers, and the density variations must remain within the space corresponding to the given quantum numbers. Instead of seeking these quantities by determining the wave function of the system of interacting electrons, the density functional method reduces the problem to the solution of a single-particle equation of Hartree form. In contrast to the HF potential,

$$V_{\rm HF}\ \psi(\vec{r}) = \int d\vec{r'}\ V_{\rm HF}(\vec{r},\vec{r'})\psi(\vec{r'}), \tag{30}$$

the effective potential, $V(\vec{r})$ is *local*, and the equations are no more complicated to solve than Hartree's. The kinetic energy, the electrostatic interaction between core and valence electrons, and between valence electrons are treated exactly. Only the exchange energy, $E_{\rm x}$, and the even smaller correlation contribution require approximation. This is in marked contrast to the Thomas-Fermi and related methods, where the large kinetic energy term is approximated.

We note here the problem of the "self-interaction correction" (SIC), where the Coulomb energy of interaction of an electron with itself must be cancelled by a contribution to $E_{\rm xc}$.

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[b] The functional derivative $\delta F[n]/\delta n(\vec{r})$ is defined so that the first order change in the functional due to a change in its argument $n(\vec{r})$ is:

$$\delta F = \int d\vec{r} \frac{\delta F}{\delta n(\vec{r})} \delta n(\vec{r})$$

The importance of SIC is obvious immediately if we consider a single-electron system such as the hydrogen atom. We also note the scaling condition on the exchange energy[20]

$$E_{\rm x}\left[\lambda^3 n(\lambda\vec{r})\right] = \lambda E_{\rm x}\left[n(\vec{r})\right], \tag{31}$$

which has proved to be useful in constructing functional approximations.

3.4 Spin Systems

The generalization of the single-particle equations to spin systems or an external magnetic field requires the consideration of the spin indices, α, of the one-electron operators $\psi_\alpha(\vec{r})$. In general, this requires the replacement of $V_{\rm ext}$ by a spin-dependent potential, $V_{\rm ext}^{\alpha\beta}(\vec{r})$, and the charge density $n(\vec{r})$ by the density matrix

$$n_{\alpha\beta}(\vec{r}) = \langle\Psi|\psi_\beta^+(\vec{r})\psi_\alpha(\vec{r})|\Psi\rangle \tag{32}$$

All ground state properties are functionals of the density matrix $n_{\alpha\beta}$, and E is stationary with respect to variations in $n_{\alpha\beta}$, provided[21]

$$\sum_\alpha \int d\vec{r}\, n_{\alpha\alpha} = N. \tag{33}$$

The application of the variational principle requires that $n_{\alpha\beta}$ is N-representable, which is guaranteed for all non-negative, differentiable $n_{\alpha\beta}$ that satisfy Eq. (33).[22] The effective spin-dependent potential in the single-particle equations is

$$V_{\rm xc}^{\alpha\beta} = \frac{\delta E_{\rm xc}}{\delta n_{\alpha\beta}(\vec{r})}. \tag{34}$$

The original derivation of the Hohenberg-Kohn theorem leads to analytical problems in the case of spin systems. These authors showed that the ground state density $n(\vec{r})$ determined the ground state wave function $\Psi(\vec{r}_1, \vec{r}_2, ...)$ uniquely, which determines the potential $V(\vec{r})$ up to an additive constant. For spin DF theory, however, von Barth and Hedin[21] showed that the uniqueness of the potential is not guaranteed, and Capelle and Vignale[23] found that this is true in general. A similar result was found by Eschrig and Pickett.[24] Kohn et al.[25] estimate that the practical consequences for spin DF calculations are not significant. Since the potential and magnetic field are unambiguous, and the kinetic, Coulomb, and exchange-correlation energies are defined in terms of Ψ, but independently of $n(\vec{r})$ and the spin density. A result that is useful in constructing functional approximations is "spin scaling",[26] which applies to the exchange energy in spin DF theory,

$$E_{\rm x}^{\rm SDF}[n_\uparrow, n\downarrow] = \frac{1}{2}\left(E_{\rm x}^{\rm DF}[2n_\uparrow] + E_{\rm x}^{\rm DF}[2n_\downarrow]\right). \tag{35}$$

The approximation used most widely in total energy calculations of spin systems is the local spin density (LSD) approximation,

$$E_{\rm xc}^{\rm LSD} = \int d\vec{r}\, n(\vec{r})\; \varepsilon_{\rm xc}\left[n_\uparrow(\vec{r}), n_\downarrow(\vec{r})\right], \tag{36}$$

where $\varepsilon_{\rm xc}[n_\uparrow, n_\downarrow]$ is the exchange and correlation energy per particle of a homogeneous, spin-polarized electron gas with spin-up and spin-down densities $n_\uparrow$ and $n_\downarrow$, respectively.

Numerous electron gas calculations have been performed over the years, and some parameterizations of $\varepsilon_{\mathrm{xc}}[n_\uparrow, n_\downarrow]$ will be discussed below. Different calculations lead to somewhat different results, but all are free of adjustable parameters. The Xα-approximation is obtained if $\varepsilon_{\mathrm{xc}}$ in Eq. (5) is replaced by the exchange energy per electron and multiplied by $3\alpha/2$, i.e.

$$E_{\mathrm{x}}^{\mathrm{X}\alpha} = -\frac{3}{2}\alpha C \int d\vec{r} \, \left\{ (n_\uparrow(\vec{r}))^{4/3} + (n_\downarrow(\vec{r}))^{4/3} \right\}, \tag{37}$$

where $C = 3(3/4\pi)^{1/3}$. The α-dependence of energy differences for a given atom or molecule is weak for values near $2/3$, the exchange energy value (LSDX). There are systematic differences between the two sets of calculations, with the latter approximation leading to overestimates of the relative stability of states with larger spin densities.

3.5 Exchange-Correlation Energy, E_{xc}

The numerical advantages of the approach described are obvious. Efficient methods exist for solving single-particle Schrödinger equations with a local effective potential, and there is no restriction to small systems. We have noted, however, that E_{xc}, is defined as the difference between the exact energy and other contributions that may be evaluated numerically exactly. In practice, it is necessary to make approximations for this term, and we now examine it in detail.

The crucial simplification in the density functional scheme is the relationship between the interacting system, whose energy and density we seek, and the fictitious, noninteracting system for which we solve Eqs. (28), (29). This can be studied by considering the interaction $\lambda/|\vec{r} - \vec{r'}|$ and varying λ from 0 (noninteracting system) to 1 (physical system). This is done in the presence of an external potential, V_λ,[27] such that the ground state of the Hamiltonian

$$H_\lambda = -\frac{1}{2}\nabla^2 + V_{\mathrm{ext}}(\vec{r}) + V_\lambda + \lambda V_{\mathrm{ee}} \tag{38}$$

has density $n(\vec{r})$ for all λ. The exchange-correlation energy of the interacting system can then be expressed in terms of an integral over the coupling constant λ.[19, 28]

$$E_{\mathrm{xc}} = \frac{1}{2} \int d\vec{r} \, n(\vec{r}) \int d\vec{r'} \, \frac{1}{|\vec{r} - \vec{r'}|} n_{\mathrm{xc}}(\vec{r}, \vec{r'} - \vec{r}), \tag{39}$$

with

$$n_{\mathrm{xc}}(\vec{r}, \vec{r'} - \vec{r}) \equiv n(\vec{r'}) \int_0^1 d\lambda \, \left(g(\vec{r}, \vec{r'}, \lambda) - 1 \right). \tag{40}$$

The function $g(\vec{r}, \vec{r'}, \lambda)$ is the pair-correlation function of the system with density $n(\vec{r})$ and Coulomb interaction λV_{ee}. The exchange-correlation hole, n_{xc}, describes the effect of the interelectronic repulsions, i.e. the fact that an electron present at the point $\vec{r}$ reduces the probability of finding one at $\vec{r'}$. The xc-energy may then be viewed as the energy resulting from the interaction between an electron and its exchange-correlation hole. This picture is, of course, the same as that used by Slater.[10]

We note three points: Firstly, since $g(\vec{r},\vec{r'})$ tends to unity as $|\vec{r}-\vec{r'}|\to\infty$, the above separation into electrostatic and exchange-correlation energies can be viewed as an approximate separation of the consequences of long- and short-range effects, respectively, of the Coulomb interaction. We may then expect that the total interaction energy will be less sensitive to changes in the density, since the long-range part can be calculated exactly.

The second observation[19] arises from the isotropic nature of the Coulomb interaction, $V_{\rm ee}$, and has important consequences. A variable substitution $\vec{R}\equiv\vec{r'}-\vec{r}$ in Eq. (39) yields

$$E_{\rm xc}=\frac{1}{2}\int d\vec{r}\,n(\vec{r})\int_0^\infty dR\,R^2\,\frac{1}{R}\int d\Omega\,n_{\rm xc}(\vec{r},R). \tag{41}$$

Eq. (41) shows that the xc-energy depends only on the spherical average of $n_{\rm xc}(\vec{r},R)$, so that approximations for $E_{\rm xc}$ can give an *exact* value, even if the description of the nonspherical parts of $n_{\rm xc}$ is quite inaccurate. Thirdly, from the definition of the pair-correlation function, there is a sum-rule that requires that the xc-hole contains one electron, i.e. for all $\vec{r}$,

$$\int d\vec{r'}\,n_{\rm xc}(\vec{r},\vec{r'}-\vec{r})=-1. \tag{42}$$

This means that we can consider $-n_{\rm xc}(\vec{r},\vec{r'}-\vec{r})$ as a normalized weight factor, and define locally the radius of the xc-hole,

$$\Big\langle\frac{1}{\vec{R}}\Big\rangle_{\vec{r}}=-\int d\vec{r}\,\frac{n_{\rm xc}(\vec{r},R)}{|\vec{R}|}. \tag{43}$$

This leads to

$$E_{\rm xc}=-\frac{1}{2}\int d\vec{r}\,n(\vec{r})\Big\langle\frac{1}{\vec{R}}\Big\rangle_{\vec{r}}. \tag{44}$$

showing that, provided the sum-rule [Eq. (42)] is satisfied, the exchange-correlation energy depends only weakly on the details of $n_{\rm xc}$.[19] In fact, we can say that it is determined by the first moment of a function whose second moment we know exactly. This argument simply makes more precise the ideas of Slater concerning the exchange hole and its consequences.

The spin analogy of the exact expression for $E_{\rm xc}$ [Eqs. (39), (40)] is

$$E_{\rm xc}=\frac{1}{2}\sum_{\alpha\beta}\int d\vec{r}\,n_\alpha(\vec{r})\int d\vec{r'}\,\frac{n_\beta(\vec{r'})}{|\vec{r}-\vec{r'}|}\int_0^1 d\lambda\,\left(g_{\alpha\beta}(\vec{r},\vec{r'};\lambda)-1\right). \tag{45}$$

The atomic density distribution shown in Figure 1 makes it clear that arguments based on small departures from homogeneity cannot be applied. However, we have seen that a partial cancellation of errors can be expected provided that the sum-rule [Eq. (42)] is satisfied. It is instructive to compare the form of the exchange hole found in LSD calculations with that determined exactly, i.e. in a Hartree-Fock calculation. This is shown in Figure 2 for two representative values of $\vec{r}$ in the nitrogen atom. The approximate and exact holes are qualitatively different; the approximate hole is spherically symmetric and centred on $\vec{r}$, while the exact hole is very asymmetric around its centre $\vec{r'}$. The spherical averages are, however, remarkably similar, and the values of the exchange energy differ by only a few percent. The large differences in the exchange holes arise almost completely from the nonspherical components, which contribute nothing to the exchange energy.

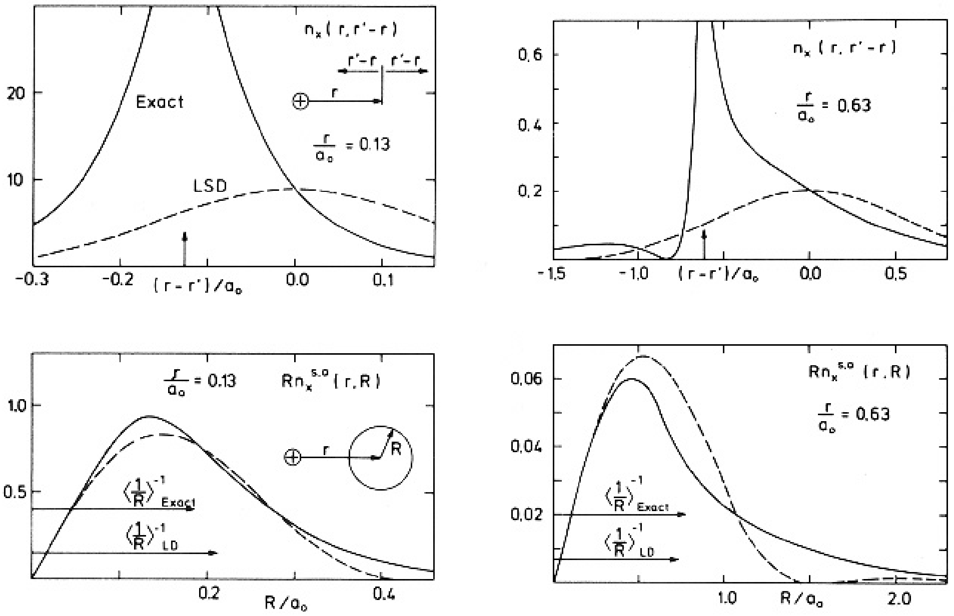


Figure 2. Exact (solid line) and approximate (broken line) exchange hole $n_{\mathrm{x}}(\vec{r}, \vec{r'} - \vec{r})$ [Eq. (40)] for a spin up electron in a nitrogen atom for $r = 0.13$ and 0.63 a.u. The top figure shows the hole along a line through the nucleus and the electron. The arrow indicates the nuclear position and $\vec{r} - \vec{r'} = 0$ gives the electron position. The exact hole has a large weight at the nucleus, while the approximate hole is centered on the electron. The lower figure shows the spherical average of the hole around the electron. The area under the curve is proportional to the exchange energy. The figure also shows the value of $\langle 1/\vec{R} \rangle_{\vec{r}}$ defined in Eq. (43).

4 Exchange-Correlation Energy Functionals

The local density (LD) and local spin density (LSD) approximations have played a continuing role in DF calculations, and most functional approximations in current use are based on them. In this section we discuss these approximations as used in actual calculations, the reasons for the errors that result, and some of the modifications introduced to correct for them.

4.1 LD and LSD Approximations

The LD approximation [Eq. (5)] has an exchange component ε_{x}, given by the Dirac formula [Eq. (4)], and a much more complicated correlation component ε_{c}. The latter is commonly based on the results of quantum Monte Carlo (MC) calculations for a homogeneous electron gas of different densities.[29,30] The LSD approximation [Eq. (36)] also requires results for a spin-polarized system and a means of interpolating for one with partial polarization.

Perdew and Zunger[31] proposed the formula

$$\varepsilon_{\mathrm{c}}^{\mathrm{PZ}} = \begin{cases} A\ln r_s + B + C r_s \ln r_s + D r_s & r_s \leq 1, \\ \gamma/(1+\beta_1\sqrt{r_s} + \beta_2 r_s) & r_s > 1. \end{cases} \tag{46}$$

For dense electron systems ($r_s \leq 1$) the random phase approximation provides the parameters for the LD approximation, and the parameters for a fully polarized gas can be obtained by scaling arguments. Other parameters were obtained by fitting to the results of Ceperley and Alder.[29]

Another form that has find widespread use is due to Vosko et al.[32]

$$\begin{aligned} \frac{\varepsilon_{\mathrm{c}}^{\mathrm{VWN}}}{A} = \ln\left(\frac{r_s}{F(\sqrt{r_s})}\right) + \frac{2b}{\sqrt{4c-b^2}} \arctan\left(\frac{\sqrt{4c-b^2}}{2\sqrt{r_s}+b}\right) \\ - \frac{b x_0}{F(x_0)}\left[\ln\left(\frac{\sqrt{r_s}-x_0}{F(\sqrt{r_s})}\right) + \frac{2(b-2x_0)}{\sqrt{4c-b^2}} \arctan\left(\frac{\sqrt{4c-b^2}}{\sqrt{r_s}+b}\right)\right]. \end{aligned} \tag{47}$$

Here $F(x) = x^2 + bx + c$ and the fitting parameters, which differ for the polarized and unpolarized cases, are obtained from the data of Ceperley and Alder.[29]

Interpolation between unpolarized (U) and fully polarized (P) results is usually based on a formula involving the spin polarization ζ,

$$\varepsilon_{\mathrm{xc}}(n,\zeta) = f(\zeta)\varepsilon_{\mathrm{xc}}^{\mathrm{U}} + (1-f(\zeta))\,\varepsilon_{\mathrm{xc}}^{\mathrm{P}}(n) \tag{48}$$

where

$$\zeta = \frac{n_\uparrow(\vec{r}) - n_\downarrow(\vec{r})}{n_\uparrow(\vec{r}) + n_\downarrow(\vec{r})}. \tag{49}$$

Functional forms of $f(\zeta)$ based on the Hartree-Fock and random phase approximations have been suggested by von Barth and Hedin[21] and Vosko et al.,[32] respectively.

4.2 Results of LD and LSD Calculations – General Trends

We have noted above that the electron density in molecules and solids is generally close to a superposition of atomic densities. These are far from uniform and even have a cusp at the nucleus. The density is so far from uniform that the use of the LD and LSD approximations was treated initially by many with great reserve, particularly in the world of chemistry. We would not be discussing them today, however, if they did not have real value. In fact, they almost always lead to the correct *picture* of binding trends across and down the periodic table. Structures, bond lengths, and vibration frequencies in many systems are reproduced satisfactorily, and the deviations from measurements of these and other quantities are often quite systematic. We now discuss some of the deviations.

Binding energies of molecules and cohesive energies of solids are usually overestimated. In weakly bound systems, e.g. where closed-shell molecules bind, these overestimates are often large, and the bond lengths are too short. In finite systems (atoms, surfaces, ...)V_{XC} decays exponentially rather than with the inverse power of distance (the “image potential”). This is one of the consequences of the incomplete self-interaction correction. Negative ions (such as H$^-$) are often unbound, although it may be possible to estimate binding energies in some cases. In semiconductors the energy gap between valence and conduction bands is less than the measured values. This topic will be discussed in this school by Dr. A. Schindlmayr. The so-called strongly correlated systems, such as the insulating 3d-transition metal oxides, are not described well by LSD calculations, which predicts them to be metallic. Partially filled d- and f-bands, in general, require modifications of the LD and LSD approximations. Such problems will be discussed in this school by Dr. S. Kurth.[33] Some calculated energy differences are in spectacular disagreement with experiment and provide us with a way to understand the defects of the LD and LSD approximations. We now focus on promotion energies in atoms, i.e. different states of lowest symmetry of the same atom.

4.3 LSD Calculations – Sources of Error

The above arguments show that the LSD approximation can give a reasonable description of systems where the density is far from homogeneous. As experience with molecular calculations developed, however, it became clear that LSD calculations gave rise to some persistent, occasionally systematic errors for a variety of systems.[1] The binding energies of sp-bonded molecules, for example, is often overestimated by ~ 1 eV per bond, and discrepancies of this size are simply unacceptable.

When atoms bind to form a molecule or solid, there is generally a change in the relative s, p, d ... contributions to the wave function. Such energy transfers can be studied directly in atoms by calculating the energy required to change an s-electron into a p-electron, for example the ${}^4S$ $(2s^2 2p^3)$ ground state of N into the ${}^4P$ $(2s^1 2p^4)$ excited state. Since these are the lowest lying states of these symmetries, density functional calculations are justified.[19]

In Figure 3 we compare experimental sp-transfer energies for first row atoms and ions with the results of LSD calculations.[34] For atoms we define

$$\Delta_{sp} = E(1s^2 2s 2p^{n-1}) - E(1s^2 2s^2 2p^{n-2}) \tag{50}$$

with a similar definition for the ions. While the overall trends are given well, the absolute deviations in ΔE_{sp} are of variable quality, with particularly large deviations in the cases of O and N. Also shown are the HF[35,36] and LSDX (Xα) results. The trends are given fairly well by these calculations, but there are significant errors, and the comparison with experiment shows differences between the first and second halves of the row. To obtain insight into these problems we study some simple model systems, focusing on the exchange energy, where the presence of explicit formulas simplifies the discussion greatly.

The HF exchange energy can be expressed in terms of exchange integrals,[37]

$$I_{ij} = e^2 \int d\vec{r} \int d\vec{r'}\, \frac{\Phi_i^*(\vec{r})\Phi_j(\vec{r})\Phi_i(\vec{r'})\Phi_j^*(\vec{r'})}{\mid \vec{r} - \vec{r'} \mid} \ , \tag{51}$$

where Φ_i and Φ_j are HF orbitals. Such an integral depends strongly on the nodal structure of Φ_i and Φ_j. If Φ_i and Φ_j have different l- and m-quantum numbers, for example, the integrand oscillates and I_{ij} is reduced. Since the LSD approximations for exchange (referred to as LSDX) and correlation are expressed only in terms of the charge density, we cannot expect them to include effects of the nodal structure in a precise way.

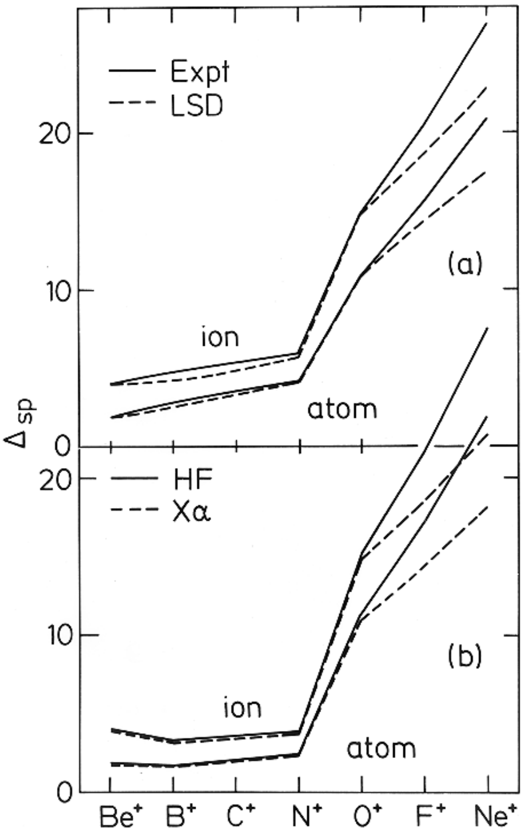


Figure 3. The sp transfer energies Δ_{sp} for the first row atoms and ions. (a) experimental and LSD results, (b) Hartree-Fock and LSDX (Xα) results. The energies are in eV.

As an example, we consider the sp-transfer in an F atom, where an $s_\downarrow$ electron is transferred to a $p_\downarrow$ orbital,[34]

$$1s^2 2s(\uparrow\downarrow)2p(\uparrow\uparrow\uparrow\downarrow\downarrow) \rightarrow 1s^2 2s(\uparrow)2p(\uparrow\uparrow\uparrow\downarrow\downarrow\downarrow)\ . \tag{52}$$

The change in the exchange energy due to this process is[37]

$$\Delta E_{\mathrm{x}} = -\frac{9}{25}G^2(2p,2p) + \frac{2}{3}G^1(2p,2s)\ , \tag{53}$$

where the Slater integrals G^k are defined by

$$G^k(i,j) = e^2 \int_0^\infty dr\, r^2 \int_0^\infty dr'(r')^2 \frac{r_<^k}{r_>^{k+1}} \phi_i(r)\phi_j(r)\phi_i(r')\phi_j(r')\ . \tag{54}$$

Here $r_<$ ($r_>$) is the smaller (larger) of r and r', and $\phi_i(r)$ is the radial part of $\Phi_i(\vec{r})$. The first term in Eq. (53) is the exchange interaction between a p-electron with $m = -1$ and two p-electrons with $m = 1$ and 0. The second term is the interaction between an s-electron and two p-electrons. The integrand of Eq. (51) corresponding to the p-p interaction has two nodal planes as a function of $\vec{r}$, while there is only a single nodal plane for the s-p interaction. The latter is larger as a result. Using realistic values for the Slater integrals, we find that $\Delta E_{\rm x} \sim 6$ eV. The LSDX calculation, however, gives similar radial extents for the s- and p-orbitals. If we assume that the radial parts are *identical* and neglect the small nonspherical corrections, the LSDX approximation predicts that the exchange energy is *unchanged* by the sp-transfer, and the LSDX value for Δ_{sp} differs from the HF result by 6 eV. The LSDX and LSD (both exchange and correlation) approximations show similar trends, although the deviation between the LSD result and experiment is reduced to 2.6 eV, since the large change in the exchange energy is compensated in part by a change in ΔE_c of opposite sign.

A simple model problem. In order to gain insight into these problems, Gunnarsson and Jones[34] performed extensive LSDX and LSD calculations for atoms and compared the results with HF calculations and experiment, respectively. The differences between the LSDX and HF results are reproduced remarkably well by model calculations where we isolate the effects of the l-dependence of the orbitals by assuming that the $s,\ p$ and d orbitals have the same *radial* dependence. With this assumption G^k only depends on k. For the $3s$ orbital in calcium, the numerical relations

$$G^0 = \frac{G^1}{0.680} = \frac{G^2}{0.516} = \frac{G^3}{0.414} = \frac{G^4}{0.344} \tag{55}$$

and

$$\int d\vec{r}\, \varepsilon_{\rm x}[n(\vec{r}), 0] = 0.451 G^0 \tag{56}$$

were found, where $n(\vec{r})$ is the charge density due to a Ca $3s$ electron. Similar coefficients were obtained for the orbitals of other elements of the iron series. Eq. (56) shows that the unphysical self-interaction, $-G^0/2$, is cancelled to within about 10%. In Figure 4(a) we compare the LSDX and HF exchange energies as a function of the number N of spin up electrons. In the HF case, the shells are filled in the order $s,\ p,\ d$ and within each shell in the order $m, m-1, .., -m$. In the LSDX case the small nonspherical contributions are neglected. The LSDX and HF results agree remarkably well.

Figure 4(b) shows results for the interelectronic exchange energy, for which the self-interaction has been subtracted. With the filling order $s,\ p,\ d$, the LSDX and HF results are in rather good agreement, with the magnitude of the LSDX results being somewhat larger. Figure 4(b) also shows results for occupations where a subshell is left empty. This does not influence the LSDX results in the present model, but it has a pronounced effect on the HF results. For instance, the curve “s-shell empty” is lower than the curve corresponding to the $s,\ p,\ d$ filling, since the p-p exchange interaction is smaller than the s-p interaction. It follows from the orthogonality of the HF orbitals that the exchange hole contains one electron, and a similar sum rule is also satisfied by the LSD and LSDX approximations.[19] Aspects of orthogonality and node formation are then included in all these schemes, although Figure 4(b) shows that the sum rule does not *guarantee* a good description.

This model calculation illustrates two important conclusions: (i) If we occupy the orbitals with the minimum number of nodal planes consistent with the Pauli principle, the trends in the interelectronic exchange energies are reproduced well by the LSDX approximation. The absolute value is overestimated in all systems considered by Gunnarsson and Jones.[34] (ii) The energy for the transfer from such a state to a state with one additional

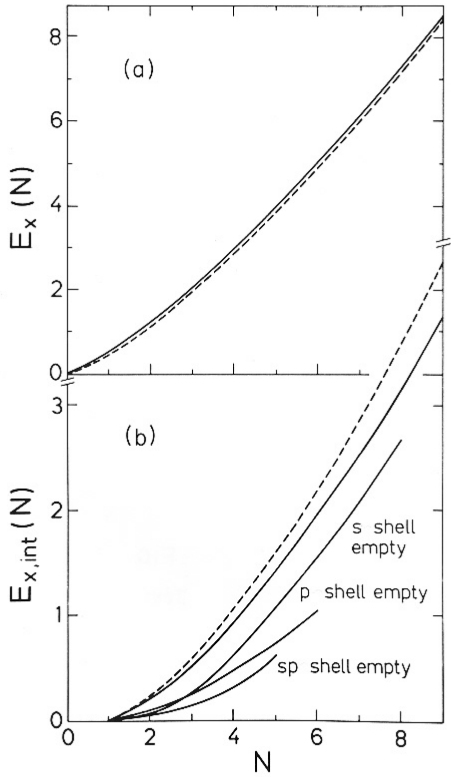


Figure 4. Exchange energies in model described in text. (a) E_x^{LSD} (dashed curve) and E_x^{HF} (solid curve) as a function of the number of electrons N (in units of $-G^0$); (b) the interelectronic exchange $E_{\mathrm{x,int}}$ for these two approximations. In the HF approximation, we show the dependence for different schemes of occupying the orbitals.

node is often underestimated substantially in the LSDX approximation. These results were derived from atomic calculations, but the arguments can be extended to small molecules.[34]

This shows that the nodal structure of the wave functions can greatly affect the accuracy of the LSD approximation, and we have identified classes of problems where the LSD results must be treated with caution. For states with the minimum number of nodal planes consistent with the orthogonality of the orbitals, the LSD approximation usually leads to a moderate overestimate of the exchange-correlation energy. For states with additional nodal planes the exchange-correlation energy is often greatly overestimated. In atoms, the depopulation of s-orbitals can lead to large errors, and similar effects may be expected in bonding situations where sp or sd hybridization reduces the s occupancy.

4.4 A Simplification of LD Calculations: Harris Functional

Before discussing some of the suggestions for overcoming problem with the LD and LSD approximations, we shall mention one way of *simplifying* LD calculations. In 1972, Kim and Gordon[38, 39] suggested the following extension of the Thomas-Fermi approach: The density of a system comprising closed-shell atoms or molecules is approximated by overlapping the HF densities of the free atoms (or molecules), and the energy is then calculated using the TF approximations for the electrostatic [Eq. (17)] and kinetic energy [Eq. (18)] terms and Eq. (5) for the exchange-correlation energy. The energies of the constituents are estimated in the same way, and the binding energies of rare gas molecules so obtained agree remarkably well with experiment.

The same approach has been studied in the DF context by Harris.[40] For systems where the density is close to the overlapped density of the constituents, one can derive an expression for the binding energy for a given geometry,

$$E_R \sim \sum_n a_n \tilde{\epsilon}_n - \int d\vec{r}\, n_f(\vec{r}) \left[\frac{1}{2}\phi_f(\vec{r}) + V_{\rm xc}^{n_f}(\vec{r})\right] + E_{\rm xc}[n_f] + E_N^R, \qquad (57)$$

where n_f is the sum of the densities of the fragments, ϕ_f and $V_{\rm xc}^{n_f}$ are the corresponding Coulomb and exchange-correlation potentials, and E_N is the internuclear repulsion. The $\tilde{\epsilon}_n$ are eigenvalues of the potential

$$\tilde{V}(\vec{r}) = \phi_f(\vec{r}) + V_{\rm xc}^{n_f}(\vec{r}) + V_{\rm ext}(\vec{r}), \qquad (58)$$

where $V_{\rm ext}$ is the external potential. This expression has the same form as that of Kim and Gordon, with the important difference that the change in kinetic energy (for bonding between atoms A and B with potentials V_A and V_B) is

$$\begin{aligned}\delta T_\epsilon &= 2\sum_n \delta\tilde{\epsilon}_n - \int d\vec{r}\, n(\vec{r}_1)\, [\tilde{V}(\vec{r}) - V_A(\vec{r}_1)] \\ &- \int d\vec{r}\, n(\vec{r}_2)[\tilde{V}(\vec{r}) - V_B(\vec{r}_2)],\end{aligned} \qquad (59)$$

instead of the corresponding Thomas-Fermi expression.

The results of this scheme agree satisfactorily with self-consistent DF calculations for He_2, Be_2, C_2, N_2, F_2 and Cu_2.[40] It provides a useful alternative in cases where more detailed calculations would be prohibitive, and it has been adopted in some molecular dynamics calculations, where more detailed calculations are performed at regular intervals to ensure that the trajectories are reliable. It is, however, not self-consistent, and spin plays no role.

4.5 Modifications of the LSD Approximation: Pair-correlation Functions

We have seen that the total energy of a system is insensitive to many details of the pair-correlation function $g(\vec{r}, \vec{r'})$, which occurs in Eq. (40). It is nevertheless tempting to modify the pair-correlation function to remove some of its more unpleasant features. The expression for the exchange-correlation energy [Eq. (41)] shows that the differences between the contributions of the exact and approximate exchange holes are largely due to the non-spherical components of the hole. Since these do not contribute to E_{xc}, total energies and total energy differences can be remarkably good, even in systems where the density distribution is far from uniform. In the LD approximation, we assume that the xc-hole $n_{\rm xc}(\vec{r}, \vec{r} - \vec{r'})$ depends only on the charge density at the electron. It would be more appropriate to assume[41] that n_{xc} depends on a suitable average $\overline{n(\vec{r})}$,

$$n_{\rm xc}(\vec{r},\vec{r'}-\vec{r}) = \overline{n(\vec{r})} \int d\lambda \, [g_h(\vec{r}-\vec{r'},\lambda,\overline{n(\vec{r})}) - 1]. \tag{60}$$

It is possible to choose the weight function which determines $\overline{n(\vec{r})}$ so that the functional reduces to the exact result in the limit of almost constant density. The approximation [Eq. (60)] satisfies the sum rule [Eq. (42)]. Other prescriptions for the weight function have been proposed.

An alternative approximation is obtained if we keep the proper prefactor $n(\vec{r'})$ in Eq. (40), leading to the so-called "weighted density" (WD) approximation,

$$n_{\rm xc}(\vec{r},\vec{r'}-\vec{r}) = n(\vec{r'}) \; G(|\vec{r}-\vec{r'})|,\tilde{n}(\vec{r})), \tag{61}$$

where $\tilde{n}(\vec{r})$ is chosen to satisfy the sum rule [Eq. (42)]. The WD models provide a link between ε_{xc}, the density-density correlation function, and the response function of a homogeneous system. As an example, we now discuss an analytic form[42] that is computationally simpler and can be chosen to give exact results in certain limits. We assume that

$$G(\vec{r},n) = C(n) \; \left(1 - \exp[-\lambda(n)/|r|^5]\right), \tag{62}$$

where C and λ are parameters to be determined. The functional G behaves as $|\vec{r}|^{-5}$ for large distances, which is needed to obtain an image potential. For a homogeneous system with density n, we require that the model functional should both fulfil the sum rule for $\tilde{n}(\vec{r}) = n$ and give the exact xc-energy. This leads to two equations

$$\int d\vec{r} \, G(|\vec{r}|,n) = -1 \tag{63}$$

$$\frac{e^2}{2} \int d\vec{r} \, \frac{1}{|\vec{r}|} \, G(|\vec{r}|,n) = \varepsilon_{xc}(n), \tag{64}$$

which are sufficient to determine the two parameters $C(n)$ and $\lambda(n)$.

This functional is exact in several limiting cases: (i) for a homogeneous system, (ii) for one-electron systems such as the hydrogen atom it gives an exact cancellation of the electron self-interaction, (iii) for an atom it gives the correct behaviour of the xc-energy density far from the nucleus. $\varepsilon_{\rm xc}(\vec{r}) = -e^2/2r$, (iv) far outside the surface it gives the image potential $\varepsilon_{\rm xc}(z) = -e^2/(4z)$. The LSD approximation gives qualitatively incorrect answers for (iii) and (iv), and the cancellation in (ii) is only approximate. Since (ii) is satisfied, this approximation provides a "self-interaction correction" in the sense we discuss below. The errors in the WD approximation for the total energy of atoms are about an order of magnitude smaller than those in the LSD approximation, but the sp- and sd-transfer energies are little improved over LSD results.[1]

4.6 Self-interaction Corrected (SIC) Approximations

In the DF formalism each electron interacts with itself via the Coulomb electrostatic energy, and this unphysical interaction would be exactly cancelled by a contribution from the xc-energy. In the LSD approximation this cancellation is imperfect, but numerically rather good. The incorrect treatment of the self-interaction in approximate functionals has led some workers to consider self-interaction corrected (SIC) functionals. Within the LSD approximation the SIC functional takes the form

$$E_{\mathrm{SIC}} = E_{\mathrm{LSD}}[n_{\uparrow}(\vec{r}), n_{\downarrow}(\vec{r})] - \sum_{i\sigma} \delta_{i\sigma}, \tag{65}$$

where E_{LSD} is the LSD energy functional and

$$\delta_{i\sigma} = \frac{e^2}{2} \int d\vec{r} \int d\vec{r'}\, \frac{n_{i\sigma}(\vec{r}) n_{i\sigma}(\vec{r'})}{|\vec{r} - \vec{r'}|} + E_{\mathrm{xc}}^{\mathrm{LSD}}(n_{i\sigma}, 0) \tag{66}$$

is the self-interaction correction (SIC) for the orbital i with spin σ and charge density $n_{i\sigma}(\vec{r})$. The first term in Eq. (66) is the self-interaction energy, and the second is the LSD approximation to the xc-energy of a fully spin-polarized system with density $n_{i\sigma}(\vec{r})$. This functional is exact for a one-electron system. It leads to the equation

$$[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) + V_{i\sigma}^{\mathrm{SIC}}(\vec{r})]\phi_{i\sigma} = \sum_{i} \lambda_{ij}^{\sigma} \phi_{j\sigma}, \tag{67}$$

where $V(\vec{r})$ is the effective potential (27) entering in a normal LSD calculation, and $V_{i\sigma}^{\mathrm{SIC}}(\vec{r})$ is additional potential resulting from the term Eq. (66). This potential is orbital-dependent and the Lagrange parameters λ_{ij}^{σ} are introduced to ensure that the solutions $\phi_i(\vec{r})$ (referred to as "local orbitals") are orthogonal. The SIC approximation is not invariant under a unitary transformation of the orbitals, and different basis sets lead to different total energies.

Unfortunately, ionization and transfer energies of atoms are not generally better in the LSD-SIC approximation, at least if non-spherical corrections are neglected. The improved total energies in SIC calculations can, in fact, be traced to a much better treatment of the innermost core electrons,[43] which play a relatively minor role in most chemical and physical processes of interest.

4.7 Modifications of the LSD Approximation: Gradient Expansions

Hohenberg and Kohn[12] introduced the local density approximation in the context of DF theory, but they also pointed out the need for modifications in systems where the density is not homogeneous. One such modification was the approximation

$$E_{\mathrm{xc}} = E_{\mathrm{xc}}^{\mathrm{LSD}} - \frac{1}{4} \int d\vec{r} \int d\vec{r'}\, K_{\mathrm{xc}} \left(\vec{r} - \vec{r'}, n(\frac{\vec{r} + \vec{r'}}{2}) \right) \left\{ n(\vec{r}) - n(\vec{r'}) \right\}^2, \tag{68}$$

where the kernel K_{xc} is related to the dielectric function of a homogeneous medium. This approximation is exact in the limit of weak density variations

$$n(\vec{r}) = n_0 + \Delta n(\vec{r}), \tag{69}$$

where $|\Delta n(\vec{r})| \ll n_0$, but the results for real systems were not encouraging. For free atoms the energy is infinite,[41] indicating that the sum-rule [Eq. (42)] is not satisfied. In spite of this, gradient expansions have played an extremely important role in DF theory and its applications. We shall now discuss some of the forms used.

4.7.1 Generalized Gradient Approximations (GGA)

The second-order generalized gradient approximation to the exchange-correlation energy is written

$$E_{\mathrm{xc}}^{\mathrm{GGA}}(n) = \int d\vec{r} \varepsilon_{\mathrm{xc}} \left(n, |\nabla n|, \nabla^2 n\right) . \tag{70}$$

Many forms of such functionals have been suggested, and some of the most important (and all their parameters) are given by Filippi et al.[44] These authors also compared these forms with the exact results for an exactly soluble system of two electrons in an external harmonic potential. We shall discuss some functionals that are widely used in actual calculations. We use some standard abbreviations:

$$k_F = (3\pi n)^{1/3};\ \ k_s = \left(\frac{4}{\pi}k_F\right)^{1/2};\ \ s = \frac{|\nabla n|}{2k_F n};\ \ t = \frac{|\nabla n|}{2k_s n};\ \ r_s = \left(\frac{3}{4\pi n}\right)^{1/3} \tag{71}$$

For the exchange contribution, Becke[45] suggested the following form:

$$\varepsilon_{\mathrm{x}} = \varepsilon_{\mathrm{x}}^{\mathrm{LD}} \left[1 - \frac{\beta}{2^{1/3}A_{\mathrm{x}}} \frac{x^2}{1 + 6\beta x \ \mathrm{arcsinh}(x)}\right] , \tag{72}$$

where $x = 2(6\pi^2)^{1/3}s = 2^{1/3}|\nabla n|/n^{4/3}, A_{\mathrm{x}} = \frac{3}{4}(3/\pi)^{1/3}$, and $\beta = 0.0042$. The parameter β was optimized to give exchange energies of noble gas atoms using Hartree-Fock orbitals). This functional has been coupled with the LYP functional for correlation:[46]

$$\varepsilon_{\mathrm{c}} = -a\frac{1}{1 + dn^{1/3}} \left\{n + bn^{-2/3}\left[C_F n^{5/3} - 2t_W + \frac{1}{9}\left(t_W + \frac{1}{2}\nabla^2 n\right)\right] \exp(-cn^{-1/3})\right\} , \tag{73}$$

where

$$t_W = \frac{1}{8}\left(\frac{|n|^2}{n} - \nabla^2 n\right) \tag{74}$$

and $C_F = 3/10(3\pi^2)^{2/3},\ a = 0.04918,\ b = 0.132,\ c = 0.2533,\ d = 0.349$. It surprised many that the combination of Becke exchange with either the VWN or LYP correlation functionals outperformed correlated *ab initio* methods (MP2 and QCSID) in calculations of atomization energies for 32 molecules.[47] The importance of using a non-local exchange has been underscored by many subsequent calculations.[48]

The question of ways to improve exchange-correlation functionals has led to a clear dichotomy of views. The first implies that the search for a functional is so difficult that we should develop a reasonable form and fit its adjustable parameters to experimental data. The BLYP and B3LYP functionals are of this type. From this standpoint, DF theory is then “of semi-empirical nature”.[49] Experimental data from up to 407 atomic and molecular systems have been used,[49] in this case with a functional with 15 adjustable parameters. The second approach seeks to build on the positive features of the LSD approximation by incorporating exact constraints and hoping that the added features will automatically improve the description of reality. We shall focus on functionals in the second category.

Perdew, Burke, and Ernzerhof[50] have described a functional form (PBE) that has several attractive features:

$$E_{\mathrm{xc}} = \int d\vec{r}\, n(\vec{r})\varepsilon_{\mathrm{x}}^{\mathrm{LD}}(n(\vec{r}))F_{\mathrm{xc}}(n, \zeta, s), \tag{75}$$

where

$$F_{\mathrm{x}}(s) = 1 + \kappa - \frac{\kappa}{1 + \mu^2/\kappa}, \tag{76}$$

$\mu = \beta(\pi^2/3) = 0.21951$, and $\beta = 0.066725$. The correlation energy has the form

$$E_{\mathrm{c}} = \int d\vec{r}\, n(\vec{r}) \left[\varepsilon_{\mathrm{c}}^{\mathrm{LSD}}(n,\zeta) + H(n,\zeta,t)\right] \tag{77}$$

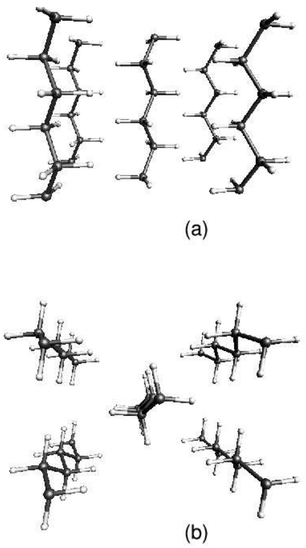
with

$$H(n,\zeta,t) = \left(\frac{e^2}{a_0}\right) \gamma\phi^3 \ln\left\{1 + \frac{\beta\gamma^2}{t}\left[\frac{1 + At^2}{1 + At^2 + A^2t^4}\right]\right\}. \tag{78}$$

The spin-scaling factor $\phi(\zeta) = \left[(1+\zeta)^{2/3} + (1-\zeta)^{2/3}\right]/2$, $\gamma = (1 - \ln 2)/\pi^2 = 0.031091$, and

$$A = \frac{\beta}{\gamma}\left[\exp\left(-\varepsilon_{\mathrm{c}}^{\mathrm{LD}}[n]/(\gamma\phi^3 e^2/a_0)\right) - 1\right]^{-1}. \tag{79}$$

The PBE form has several advantages, including: (1) In the slowly varying limit ($t \to 0$), H is given by the second-order gradient expansion, (2) In the rapidly varying limit ($t \to \infty$), $H \to -\varepsilon_{\mathrm{c}}^{\mathrm{LD}}$, and correlation vanishes, (3) It cancels the logarithmic singularity of $\varepsilon_{\mathrm{c}}^{\mathrm{LD}}$ in the high density limit. The accuracy of the PBE functional for atoms and molecules has been compared with results of LSD, BLYP, and B3LYP functions has been made by Ernzerhof and Scuseria.[51] The PBE functional performed as well as B3LYP for the properties considered by these authors.



	r_{CC}	r_{CH}	α_{CCC}	α_{HCH}
X-rays [a]	1.534±0.006	1.09*	112.0±0.3	109.5*
X-rays [b]	1.533±0.022	1.07±0.022	111.9±1.8	107.0±1.8
X-rays [c]	1.527±0.007	1.091*	112±0.8	–
LD	1.512	1.111	114.3	105.2
BP	1.536	1.111	113.8	105.6
PBE	1.523	1.110	113.0	105.8

[a] Ref. 52, monoclinic n-hexatriacontane $C_{36}H_{74}$
[b] Ref. 53, orthorhombic n-hexatriacontane $C_{36}H_{74}$
[c] Ref. 54.

Figure 5. Left: Structure of crystalline polyethylene: (a) normal to chain axis, (b) along chain axis. Right: Structural parameters of crystalline PE from x-ray diffraction, and calculated structures for a single chain. Bond lengths are in Å, angles in degrees. Values marked with an asterisk (*) were assumed, and not measured directly.

Generalized gradient approximations generally lead to improved bond angles, lengths, and energies. In particular, the strengths of hydrogen bonds and other weak bonds between closed shell systems are significantly better than local density results. However, the self-interaction problem remains, and some asymptotic requirements for isolated atoms are not satisfied ($V_{\rm xc}^{\rm GGA}$ vanishes exponentially far from the nucleus, $V_{\rm xc}^{\rm GGA}(\vec{r} \rightarrow 0) \rightarrow -\infty$).

An example of the differences between LSD and PBE calculations is shown in Figure 5.[55] Polyethylene crystallizes in a structure with parallel chains, and the table shows that the structure of the individual chains is described rather well, with the C-C bonds being slightly longer in PBE and BP[56] calculations than in those using LD. There are, however, striking differences in the *inter*chain separations. The LD calculations lead to a pronounced minimum with a shortest distance between C atoms in different chains (3.67 Å) less than the measured value (4.59 Å),[54] while PBE leads to a modest overestimate (4.66 Å).

4.7.2 Meta-GGA

The next step in the development of gradient approximations is to incorporate the kinetic energy density (or the Laplacian of the density). A version based on the PBE form was described by Perdew et al.,[57] who added the variables $\tau_\uparrow$ and $\tau_\downarrow$, where

$$\tau_\sigma(\vec{r}) = \sum_i^{\rm occ.} \frac{1}{2} |\nabla \psi_{i\sigma}(\vec{r})|^2 \tag{80}$$

is the kinetic energy density for the occupied Kohn-Sham orbitals. However, this and other forms initially developed included parameter(s) found by fitting to experimental data. This last feature was avoided in the recent work of TPSS,[58] whose form satisfied the requirement that the exchange potential be finite at the nucleus for ground state one- and two-electron densities. This is a constraint satisfied by LSD, but lost in GGA. Extensive numerical tests for atoms, molecules, solids, and jellium surfaces showed generally very good results.

4.7.3 Hybrid Schemes: Combination of HF and DF Schemes

In section (4.3) we saw just how poor the exchange energy differences could be between states whose wave functions have different nodal structures. It has also been noted for many years (see, for example, Ref. 27) that errors in the LD descriptions of exchange and correlation tend to balance. This suggests that a combination of Hartree-Fock exchange and DF calculations could be useful.

$$E_{\rm xc}^{\rm hybrid} = \alpha E_{\rm x}^{\rm HF} + E_{\rm c} \ , \tag{81}$$

where α can be chosen to satisfy particular criteria. A formal justification for such hybrid schemes was given by Görling and Levy.[59] The B3LYP functional,[48] which is widely used in the chemical community, is an example. Here three adjustable parameters are used to fit calculated values to a molecular data base.

4.7.4 Optimized Effective Potential (OEP)

In the Kohn-Sham implementation of DF theory we describe the kinetic energy functional for the system of non-interacting electrons in terms of the orbitals $\psi_{i\sigma}(\vec{r})$. The best *local* effective potential (a requirement of DF theory) can be determined variationally for each σ such that, when substituted into a stationary single-particle equation it leads to a set of eigenfunctions that minimize $E[\psi_{i\sigma}(\vec{r})]$. This was first suggested by Sharp and Horton[60] following the local density description of exchange,[10] and it is referred to as the optimized effective potential (OEP).[61] Its determination requires the solution of an integral equation for each $V_{\mathrm{xc},\sigma}(\vec{r})$, which is a demanding exercise. How this can be done, as well as possible simplifications, are discussed in this School by Dr. S. Kurth.

5 Concluding Remarks

The density functional theory is the basis of most of the calculations in computational nanoscience that are free of adjustable parameters. It is clear from the present discussion that "DF calculations" cover a colourful variety of functional approximations, and not all are "free of adjustable parameters". The development of approximations to the exchange-correlation functionals over the past 20 years has improved the performance of DF calculations, and John Perdew is no doubt not alone in thinking that progress up the "Jacob's ladder"[62] (Figure 6) will continue until energy differences can be determined to within $\sim$ 1 kcal/mol ("chemical accuracy"). The numerical cost increases as one climbs, and this may not necessarily bring more information. Most problems in "computational nanoscience" are performed part way up the ladder, and this situation will probably remain true for some time.

DF calculations should always be performed with all critical facilities intact. The familiar program "packages" will almost always lead to an answer, but it is easy to obtain

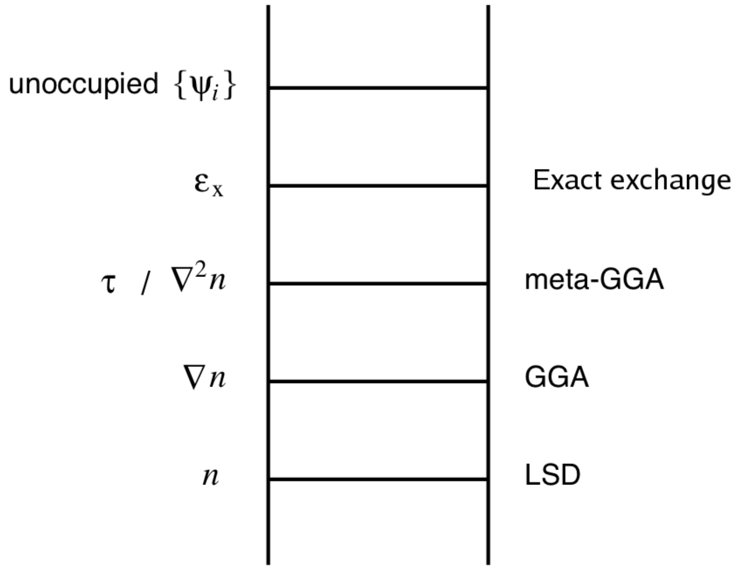


Figure 6. "Jacob's ladder" of DF schemes according to Perdew and collaborators.

answers void of physical content. It is odd to have to conclude this manuscript on such a note, but years of refereeing articles in the field suggest that it is necessary.

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