2 Density Functional Theory for the Sceptical

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Contents

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1 Introduction

> Density Functional Theory:
> “Almost the right answer, for almost the right reason, at almost the right price,
> for almost all systems of interest”
> (J.P. Perdew) [1, p. 194]

There will be people in the audience who will say immediately that “strongly correlated” systems must be exceptions, since they are often viewed as those that are not described well by electron density functional theory (DFT) theory. Many seminars and publications on the subject mention at the outset the widespread use of DFT in materials, and they may even quote Walter Kohn: “For periodic solids it is sometimes referred to as the standard model” [2]. It is then a short step to listing the systems where DF results with standard approximations are unacceptable (a “metallic” transition metal oxide insulator, almost anything to do with rare earth or actinide elements, . . .), emphasizing the importance of describing such “strongly correlated” materials correctly [3].[1] DFT is nevertheless an essential part of this school. It is used widely in materials science and chemistry and provides useful results for countless systems for which the exact wave function cannot be computed. We shall see that physical insight can be obtained and *why* approximations used in DF calculations can give sensible answers far from their regions of obvious validity. Some features of the results, particularly the orbitals, are essential input for “strongly correlated” methods. We shall also see that improvements in the approximations needed in density functional calculations are now closing the distance to the strongly correlated world.

The origins of DF theory go back to the early years of quantum mechanics in the late 1920s. Thomas [4] and Fermi [5] recognized the electron density as a basic variable, and Dirac [6] showed already in 1930 that the state of an atom can be determined completely within Hartree-Fock theory by its one-particle reduced density matrix; we do not need to specify the wave function. We follow here the early history of density-related methods to the single-particle equations of Kohn and Sham in 1965. In its modern form, the DF formalism shows that ground state properties of a system of electrons in an external field can be determined, in principle, from a knowledge of the *density distribution* $n(\mathbf{r})$ alone. Much of the work in materials science and chemistry focuses on the *structure* and cohesive energies and on a property for which DF calculations are particularly valuable: the total energy E of a system of electrons in the presence of ions located at $\mathbf{R}_\mathrm{I}$.

Accurate calculations of the entire energy surface $E(\mathbf{R}_\mathrm{I})$ are possible only for systems with very few atoms, and this function generally has vast numbers of maxima and minima at unknown locations. The lowest energy, however, corresponds to the ground state *structure*, and paths between minima are essential to our studies of chemical reactions, including their activation

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[1] An example can be found in the Preface of the 2012 Autumn School: “Density functional theory (DFT) is considered the Standard Model of solid state physics. The state-of-the-art approximations to DFT, the local-density approximation (LDA) or its simple extensions, fail, however, even qualitatively, for strongly correlated systems.”

barriers. When I read the autobiography of Francis Crick [7], I was taken by his observation

> "If you want to understand *function*, study *structure*."

and have used it ever since. This relationship may be self-evident to molecular biologists and most chemists, but it is also true in other areas. The DF approach allows us to calculate $E(R_{\rm I})$, and hence the structure and many related properties, without using experimental input. If you are more interested in "real materials" than in mathematical models, this is a crucial advantage for strongly correlated materials as well.

Density functional theory is seen today as "the workhorse of quantum chemistry and materials science" [8], and it remains uncertain as to why it was resisted by the chemical community with great stubbornness for several decades. I have written about this matter elsewhere [9, 10] and shall not discuss it further here. However, a recent conference (Stockholm, 7–8 November 2024) was devoted to this question, and the seminars of leading DFT experts (Perdew, Baerends, Becke, Burke, Grimme, Head-Gordon, Savin,. . .) can be viewed online [11]. If you want to find out what really happened in the bleak years until DFT broke through in chemistry, watch [12].

There are many books and review articles on density functional theory, and I mention just two where I was involved [10, 13]. A long article with 70 authors, including many who played important roles in the development of DFT, surveys many important problems [8]. The focus in the present article is on *electron* density functional theory; DF methods in classical systems and nuclei are surveyed briefly in [10]. Symmetry breaking in density functional theory, in combination with the continuing improvement in approximate functional forms, may provide a direct link to the strongly correlated world and is discussed in Sec. 6.

2 The electron density as basic variable

The development of quantum mechanics after its introduction in 1925 was extremely rapid. Methods for finding approximate solutions of the Schrödinger equation followed soon after the equations were published in 1926 and have had a profound effect on chemistry and condensed matter physics ever since.

The "Hartree approximation" to the many-electron wave function is a product of single-particle functions,

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots) = \psi_1(\mathbf{r}_1) \cdots \psi_N(\mathbf{r}_N) \tag{1}$$

where each $\psi_i(\mathbf{r}_i)$ satisfies a one-electron Schrödinger equation with a potential term arising from the average field of the other electrons. Hartree [14] introduced the idea of a "self-consistent field", with specific reference to the core and valence electrons, but the approximation (1) is not mentioned in any of his papers. Slater [15] and Fock [16] recognized immediately, however, that the product wave function (1) in conjunction with the variational principle led to a generalization of the method that would apply to systems more complex than atoms. They showed that replacing (1) by a determinant of such functions [15, 16] led to equations that were not much more complicated than those of Hartree, while satisfying the Pauli exclusion principle. These determinantal functions, which had been used in discussions of atoms [17] and ferromagnetism [18], are known today as "Slater determinants", and the resulting "Hartree-Fock equations" have formed the basis of most discussions of atomic and molecular structure since.

In 1929 Dirac wrote [19]:

> "The general theory of quantum mechanics is now almost complete... The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation."

I cannot think of a better short description of density functional theory than an "approximate practical method of applying quantum mechanics" to explain "complex atomic systems". I was not the only one who ignored the point "without too much computation."

Dirac [19] also sought to improve the model of Thomas [4] and Fermi [5] for calculating atomic properties based purely on the electron density $n(r)$. In the first "density functional theory", Thomas and Fermi assumed that the electrons form a homogeneous electron gas satisfying Fermi statistics and the kinetic energy has a simple dependence on the density $n(r)$. The TF equations are:

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

where $C_k = 3\hbar^2(3\pi^2)^{\frac{2}{3}}/(10m)$, V_{ext} is the external potential, and λ is the Lagrange multiplier related to the constraint of constant particle number. Dirac noted the necessity of incorporating "exchange" phenomena, as in the Hartree-Fock approach [19], and he included these effects in the "Thomas atom" [6] by means of the potential

$$V_{\mathrm{x}}^{\mathrm{Dirac}} = -\left(\frac{1}{\pi}\right)\left(3\pi^2 n(\mathbf{r})\right)^{\frac{1}{3}}. \tag{3}$$

This term was derived for a homogeneous gas of density n and should be valid for weak spatial variations of $n(\mathbf{r})$.[2] The modified TF equation is often referred to as the "Thomas-Fermi-Dirac" equation.

The Thomas-Fermi method is a genuine "density functional" theory, in that the energy is related directly to the electron density. With its extensions, it provides a rough description of the charge density and the electrostatic potential of atoms, and its mathematical properties have attracted considerable attention [20,21]. However, it has severe deficiencies: The charge density is infinite at the nucleus and decays as r^{-6}, not exponentially, far from it. Teller [22] and others also showed that TF theory does not bind atoms to form molecules or solids, which rules out its use in chemistry or materials science. There is also no shell structure in the TF atom, so that the

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[2] The exchange energy in a homogeneous (spin-polarized!) electron gas had been derived by Bloch [18] in 1929.

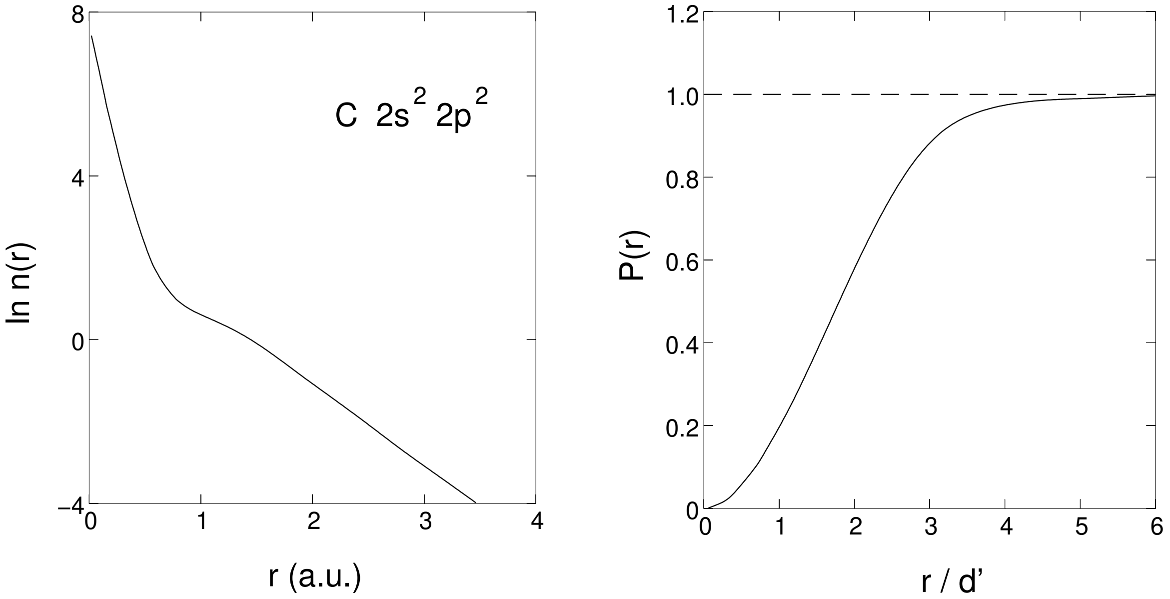


Fig. 1: *(left) Logarithm of spherical average of density in ground state of C atom as a function of the distance from the nucleus (atomic units [13]; (right) Probability that electrons in Na metal with parallel spins are* r/d' *apart (*$d'^3 = V_0/(3\pi^2)$*,* V_0 *is the atomic volume). After Wigner and Seitz [25].)*

periodic variation of many properties with changing atomic number Z cannot be reproduced, no ferromagnetism [13], and atoms *shrink* with increasing Z (as $Z^{-1/3}$) [23]. Nevertheless, it may be useful in the context of very dense matter [10].

One point made by Dirac [6], however, has been emphasized by many advocates of the DF method over the years, even if we were unaware of his words of over 80 years ago:

> "Each three-dimensional wave function will give rise to a certain electric density. This electric density is really a matrix, like all dynamical variables in the quantum theory. By adding the electric densities from all the wave functions we can obtain the total electric density for the atom. If we adopt the equations of the self-consistent field as amended for exchange, then this total electric density (the matrix) has one important property, namely, if the value of the total electric density at any time is given, then its value at any later time is determined by the equations of motion. This means that *the whole state of the atom is completely determined by this electric density; it is not necessary to specify the individual three-dimensional wave functions that make up the total electric density.* Thus one can deal with any number of electrons by working with just one matrix density function."

The italics are in the original. The derivation is based on the "self-consistent field" or Hartree-Fock approximation, and the "matrix density function" is known today as the one-particle reduced density matrix, but the observation that the density follows the equations of motion is much in the spirit of the theorem of Ehrenfest, who had proved in 1927 that the acceleration of a quantum wave packet that does not spread satisfied Newton's equations of motion [24].

The central role played by the density means that we must know what it looks like in real systems. Fig. 1 shows that the spherically averaged *density* in the ground state of the carbon atom falls monotonically from the nucleus and does not show the radial oscillations that occur if we plot $r^2 n(r)$. The charge density in small molecules is also rather featureless, with maxima at the nuclei, saddle points along the bonds, and a generally monotonic decay from both. The electron density in molecules and solids also shows relatively small departures from the overlapped densities of the constituent atoms. Energy differences, including binding, ionization, and cohesive energies, are the focus of much DF work and result from subtle changes in relatively featureless density distributions.

3 An "approximate practical method"

The basis of a quantum theory of atoms, molecules, and solids was in place at the beginning of the 1930's. Hans Bethe was another participant in this adventure and looked back on the time in this way:

> "The basic structure of quantum mechanics, quantum mechanics without relativity, that basic structure is finished … The understanding of atoms, molecules, the chemical bond, and so on, that was all complete by 1928." [26, p. 78]

Linear combinations of atomic orbitals formed molecular orbitals, from which determinantal functions could be constructed, and linear combinations of determinants ("configuration interaction") would provide approximations to the complete wave function. Dirac had noted already, however, that this procedure could not be implemented in practice, so that approximations are essential. Furthermore, numerical techniques for solving the Schrödinger equation in extended systems were still to be developed.

Wigner and Seitz [25] developed a method for treating the self-consistent problems in crystals, and the "Wigner-Seitz cell" is known to all condensed matter physicists. The first application to metallic sodium used a pseudopotential for the Na ion, and calculations of the lattice constant, cohesive energy, and compressibility gave satisfactory results. Of particular interest for our purposes, however, is the calculation of the probability of finding electrons with parallel spins a distance r apart (Fig. 1 (right)). This function obtains its half-value for $r = 1.79\, d'$ or $0.460\, d$ for a body-centered cubic lattice with cube edge d, which is close to the radius of the "Wigner-Seitz sphere" $(3/8\pi)^{\frac{1}{3}}\, d = 0.492\, d$. The exclusion principle means then that two electrons with parallel pins will very rarely be at the same ion. This argument does not depend significantly on the potential and should apply to a Fermi gas subject to periodic boundary conditions [25]. The corresponding curves for spin up and spin down electrons, as well as for both spins combined, were discussed in the 1934 review article of Slater [27].

The picture that results is simple and appealing: the exclusion principle means that an electron with a given spin produces a surrounding region where there is a deficiency of charge of the same spin. This region contains unit charge and is referred to as the "Fermi" [25] or "exchange" hole [28]. In the Hartree-Fock scheme, the exchange hole is different for each electronic function, but Slater [28] developed a simplified "exchange potential" that depended only on the density:

$$V_{\mathrm{x}}^{\mathrm{Slater}} = -\left(\frac{3}{2\pi}\right)\left(3\pi^2 n(r)\right)^{\frac{1}{3}}. \tag{4}$$

The Slater approximation (4) was proposed at the time that electronic computers were becoming available for electronic structure calculations and proved to be very useful in practice. Methods for solving the Schrödinger equation had been developed—but not implemented—somewhat earlier, including the augmented plane wave (APW) [29] and Korringa-Kohn-Rostoker approaches [30, 31].

The exchange potential of Slater (4) is 3/2 times that derived by Dirac and Bloch (3) for a homogeneous electron gas, but Slater [32] pointed out that an effective potential proportional to the cube root of the density could be obtained by arguments based on the exchange hole that do not depend on the free electron gas arguments used in the original derivation [28]. The exchange hole discussed above for a spin up electron contains a single electron. If we assume that it can be approximated by a sphere of radius $R_\uparrow$, then

$$\left(\frac{4\pi}{3}\right) R_\uparrow^3 n_\uparrow \overset{!}{=} 1 \;\rightsquigarrow\; R_\uparrow = \left(\frac{3}{4\pi n_\uparrow}\right)^{\frac{1}{3}} \tag{5}$$

where $n_\uparrow$ is the density of spin up electrons. Since the electrostatic potential at the center of such a spherical charge is proportional to $1/R_\uparrow$, the exchange potential will be proportional to $n_\uparrow^{\frac{1}{3}}$. This argument was used by Slater to counter a misconception (unfortunately still widespread) that local density approximations based on the homogeneous electron gas are only appropriate if the electron density is nearly homogeneous.

In 1954, Gáspár [33] questioned the prefactor of the effective exchange potential (Eq. 4). If one varies the spin orbitals to minimize the total energy in the Thomas-Fermi-Dirac form, one obtains a coefficient just $\frac{2}{3}$ as large. Gáspár applied this approximation to the Cu^+ ion and found good agreement with Hartree-Fock eigenfunctions and eigenvalues. Slater noted that Gáspár's method was "more reasonable than mine" [34], but the larger value was used in most calculations in the following years.

4 Electron density functional formalism

The variational principle on the energy was the basis of the derivation of the density functional formalism given by Hohenberg and Kohn (HK) [35]. First, they showed that there is a one-to-one relationship between the external potential $V_{\mathrm{ext}}(\mathbf{r})$ and the (nondegenerate) ground state (GS) wave function Ψ, and then that there is a one-to-one relationship between Ψ and the ground state density $n(\mathbf{r})$ of an N-electron system,

$$n(\mathbf{r}) = N\int d\mathbf{r}_2 \cdots d\mathbf{r}_N\, \Psi^*(\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_N)\,\Psi(\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_N)\,, \tag{6}$$

where the spin coordinates are not shown explicitly. Knowledge of the density then determines the external potential to within a constant, so that all terms in the Hamiltonian are known. Since the Hamiltonian operator determines completely all states of the system, $n(\mathbf{r})$ determines excited states as well as the ground state.

These ideas can be applied to the total energy using the variational principle. For this purpose, HK defined the functional $F[n(\mathbf{r})]$, which is "universal" in the sense that it is valid for any external potential $V_{\rm ext}$,

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

and showed that the energy functional $E[n, V_{\rm ext}]$ satisfies a variational principle:

$$E_{\rm GS} = \min\nolimits_{n(\mathbf{r})} E[n, V_{\rm ext}], \tag{8}$$

where

$$E[n, V_{\rm ext}] = \int d\mathbf{r}\, V_{\rm ext}(\mathbf{r})\, n(\mathbf{r}) + F[n]. \tag{9}$$

The minimization is performed in HK over all non-degenerate densities that can be derived from the ground state of some external potential ("V-representable"). Levy [36] generalized this to a minimization over all densities, including degeneracies.

The generalization to finite temperatures was carried out soon after the work of Hohenberg and Kohn [35]. Mermin [37] showed that, in a grand canonical ensemble at given temperature T and chemical potential μ, the equilibrium density is determined by the external potential $V_{\rm ext}$, and the equilibrium density minimizes the grand potential. Single-particle equations can be derived for a fictitious system with kinetic energy T_0 and entropy S_0, with $E_{\rm xc}$ replaced by the exchange-correlation contribution to the free energy.

4.1 Single-particle description of a many-electron system.

The task of finding good approximations to the energy functional $E[n]$ is simplified greatly if we use the decomposition introduced by Kohn and Sham [38],

$$E[n] = T_0[n] + \int d\mathbf{r}\, n(\mathbf{r}) \Big(V_{\rm ext}(\mathbf{r}) + \frac{1}{2}\varPhi(\mathbf{r}) \Big) + E_{\rm xc}[n]. \tag{10}$$

T_0 is the kinetic energy that a system with density n would have if there were no electron-electron interactions, $\varPhi$ is the classical Coulomb potential for electrons, and $E_{\rm xc}$ *defines* the exchange-correlation energy. T_0 is not the true kinetic energy T, but it is of comparable magnitude. Its treatment without approximation removes many deficiencies of the Thomas-Fermi approach, such as the lack of a shell structure of atoms or the absence of chemical bonding in molecules and solids. In the expression (10) all terms other than the exchange-correlation energy $E_{\rm xc}$ can be evaluated exactly, so that approximations for this term are crucial in density functional applications.

The variational principle applied to (10) yields

$$\frac{\delta E[n]}{\delta n(\mathbf{r})} = \frac{\delta T_0}{\delta n(\mathbf{r})} + V_{\rm ext}(\mathbf{r}) + \varPhi(\mathbf{r}) + \frac{\delta E_{\rm xc}[n]}{\delta n(\mathbf{r})} = \mu, \tag{11}$$

where μ is the Lagrange multiplier associated with the requirement of constant particle number: $\int d\mathbf{r}\ \delta n(\mathbf{r}) = 0$, and the functional derivative is defined as

$$\delta F = \int d\mathbf{r} \left(\frac{\delta F}{\delta n(\mathbf{r})} \right) \delta n(\mathbf{r})\ . \tag{12}$$

If we compare this with the corresponding equation for a system with an effective potential $V(\mathbf{r})$ but *without* electron-electron interactions,

$$\frac{\delta E[n]}{\delta n(\mathbf{r})} = \frac{\delta T_0}{\delta n(\mathbf{r})} + V(\mathbf{r}) = \mu, \tag{13}$$

we see that the mathematical problems are identical, provided that

$$V(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + \Phi(\mathbf{r}) + \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})}. \tag{14}$$

The solution of (Eq. 13) can be found by solving the Schrödinger equation for *non-interacting* particles,

$$\left(-\frac{1}{2}\nabla^2 + V(\mathbf{r}) \right) \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}), \tag{15}$$

yielding

$$n(\mathbf{r}) = \sum_{i=1}^{N} f_i \left| \psi_i(\mathbf{r}) \right|^2 \tag{16}$$

where f_i are occupation numbers ($0 \leq f_i \leq 1$) corresponding to the relevant Slater determinant. We have mapped the original problem onto finding the solution of a *non-linear* equation, since the Hamiltonian in (15) is a function of its own eigenvectors. The equation must be solved iteratively (self-consistently) to satisfy the condition (14).

The solution of this system of equations leads to the energy and density of the lowest state, and all quantities derivable from them. The formalism can be generalized to the lowest state with a given symmetry [39]. Instead of seeking these quantities by determining the wave function of the system of interacting electrons, the DF method reduces the problem to the solution of a single-particle equation of Hartree form. In contrast to the Hartree-Fock potential,

$$V_{\text{HF}}\, \psi(\mathbf{r}) = \int d\mathbf{r}'\, V_{\text{HF}}(\mathbf{r}, \mathbf{r}')\, \psi(\mathbf{r}'), \tag{17}$$

the effective potential, $V(\mathbf{r})$ is a *local* (i.e., multiplicative) operator. It is worth noting that the non-interacting particles are still Fermions, and the Pauli principle must be satisfied.

The numerical advantages of solving the Kohn-Sham equations [38] are obvious. Efficient methods exist for solving single-particle Schrödinger-like equations with a local effective potential, and there is no restriction to small systems. With a local approximation to E_{xc}, the equations can be solved as readily as the Hartree equations. Unlike the Thomas-Fermi method, where the large kinetic energy term is approximated, the valence kinetic energy and the core-valence and valence-valence electrostatic interactions are treated exactly. However, E_{xc} is the difference between the *exact* energy and terms we can evaluate exactly, and approximations are unavoidable.

4.2 Exchange-correlation energy E_{xc} and the xc-hole

Kohn and Sham [38] proposed using the "local density (LD) approximation"

$$E_{\mathrm{xc}}^{\mathrm{LD}} = \int d\mathbf{r}\, n(\mathbf{r})\, \varepsilon_{\mathrm{xc}}[n(\mathbf{r})], \tag{18}$$

where $\varepsilon_{\mathrm{xc}}[n]$ is the exchange and correlation energy per particle of a homogeneous electron gas with density n. This approximation is exact in the limits of slowly varying densities and very high densities. The electron density in molecules and solids is generally far from that of a homogeneous electron gas, and the validity of calculations based on properties of a gas of constant density has often been questioned. We now discuss some general properties of E_{xc} using arguments closely related to the "exchange hole" picture of Wigner and Seitz [25] and Slater [28, 32].

The crucial simplification in the density functional scheme is the relationship between the interacting system, whose energy and density we seek, and the fictitious, non-interacting system for which we solve (Eq. 15, 16). This can be studied by considering the interaction $\lambda/|\mathbf{r}-\mathbf{r}'|$ and varying λ from 0 (non-interacting system) to 1 (physical system). This is done in the presence of an external potential V_λ [39], such that the ground state of the Hamiltonian

$$H_\lambda = -\frac{1}{2}\nabla^2 + V_{\mathrm{ext}}(\mathbf{r}) + V_\lambda + \lambda V_{\mathrm{ee}} \tag{19}$$

has density $n(\mathbf{r})$ for all λ. The exchange-correlation energy of the interacting system can then be expressed as an integral over the coupling constant λ [40]:

$$E_{\mathrm{xc}} = \frac{1}{2}\int d\mathbf{r}\, n(\mathbf{r}) \int d\mathbf{r}'\, \frac{1}{|\mathbf{r}-\mathbf{r}'|}\, n_{\mathrm{xc}}(\mathbf{r}, \mathbf{r}'-\mathbf{r}), \tag{20}$$

with

$$n_{\mathrm{xc}}(\mathbf{r}, \mathbf{r}'-\mathbf{r}) \equiv n(\mathbf{r}') \int_0^1 d\lambda\, \big(g(\mathbf{r}, \mathbf{r}', \lambda) - 1\big). \tag{21}$$

The function $g(\mathbf{r}, \mathbf{r}', \lambda)$ is the pair correlation function of the system with density $n(\mathbf{r})$ and Coulomb interaction λV_{ee}. The exchange-correlation hole n_{xc} describes the fact that an electron at point $\mathbf{r}$ reduces the probability of finding one at $\mathbf{r}'$, and E_{xc} is simply the energy resulting from the interaction between an electron and its exchange-correlation hole. This is a straightforward generalization of the work of Wigner and Seitz [25] and Slater [28] discussed above.

Second, the isotropic nature of the Coulomb interaction V_{ee} has important consequences. A variable substitution $\mathbf{R} \equiv \mathbf{r}'-\mathbf{r}$ in (20) yields

$$E_{\mathrm{xc}} = \frac{1}{2}\int d\mathbf{r}\, n(\mathbf{r}) \int_0^\infty dR\, R^2\, \frac{1}{R} \int d\Omega\, n_{\mathrm{xc}}(\mathbf{r}, \mathbf{R}). \tag{22}$$

Equation (22) shows that the xc-energy depends only on the spherical average of $n_{\mathrm{xc}}(\mathbf{r}, \mathbf{R})$, so that approximations for E_{xc} can still give an *exact* value, even if the description of the non-spherical parts of n_{xc} is quite inaccurate. The energy depends on certain averages over the hole, and this implies a systematic partial cancellation of errors in the LSD approximation. Third, the

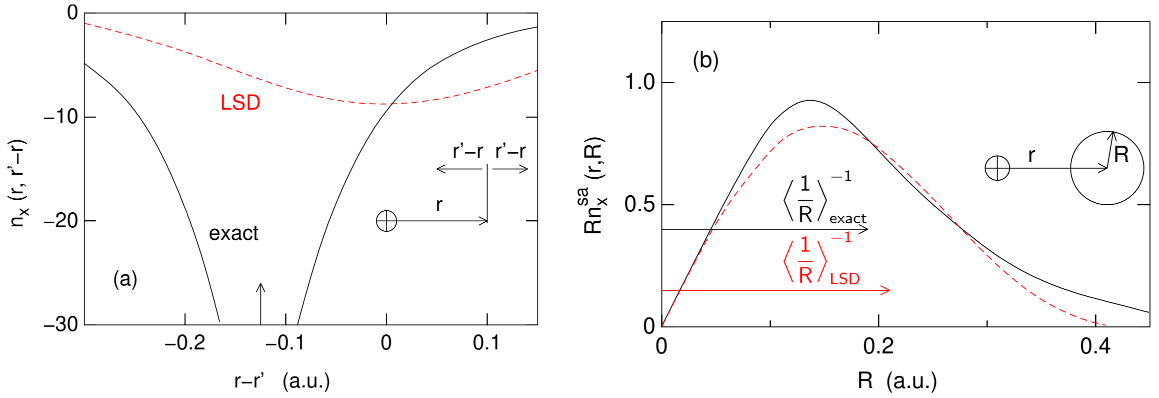


Fig. 2: *Magnitude of exact (solid) and LSD (red, dashed) exchange holes* $n_{\rm xc}(\mathbf{r},\mathbf{r}'{-}\mathbf{r})$ *for spin up electron in N atom for* $\mathbf{r} = 0.13$ *a.u. (a) Hole along line through nucleus (arrow) and electron* $(\mathbf{r}{-}\mathbf{r}' = 0)$*. (b) spherical averages of holes, and* $\langle 1/\mathbf{R} \rangle$ *[Eq. (24)] (from [13]).*

definition of the pair-correlation function leads to a sum-rule requiring that the xc-hole contains one electron, i.e. for all $\mathbf{r}$,

$$\int d\mathbf{r}'\, n_{\rm xc}(\mathbf{r},\mathbf{r}'{-}\mathbf{r}) = -1. \tag{23}$$

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

$$\left\langle \frac{1}{\mathbf{R}} \right\rangle_{\mathbf{r}} = -\int d\mathbf{R}\, \frac{n_{\rm xc}(\mathbf{r},\mathbf{R})}{|\mathbf{R}|}. \tag{24}$$

This leads to

$$E_{\rm xc} = -\frac{1}{2}\int d\mathbf{r}\, n(\mathbf{r}) \left\langle \frac{1}{\mathbf{R}} \right\rangle_{\mathbf{r}} . \tag{25}$$

Provided Equation (23) is satisfied, $E_{\rm xc}$ is determined by the first moment of a function whose second moment we know exactly and depends only weakly on the details of $n_{\rm xc}$ [39]. Provided that the spherical average of the exchange-correlation hole is correct, approximations to $E_{\rm xc}$ can then lead to good total energies, even if other details are described very poorly. This is shown by the example in Fig. 2, where the exchange hole in a nitrogen atom is shown for a representative value of $\mathbf{r}$ for both the local density and exact (Hartree-Fock) cases. The holes are qualitatively different: The LD hole is spherically symmetric and centred on the electron, while the exact hole has a large weight at the nucleus and is very asymmetric. Nevertheless, the spherical averages are very similar, and the exchange energies differ by only around 10%.

5 Local density approximation (LDA) and extensions

The early expectations of the LDA were very modest. John Perdew noted:

> "One of the authors (J.P.P.) was told by W. Kohn (personal communication) that he anticipated the LDA to be only slightly more accurate than the Hartree approximation ($E_{xc} = 0$) that was widely used in condensed matter physics in 1965." [1, p. 196]

In fact, the original paper of Kohn and Sham [38] found good reasons for this:

> “In atoms and molecules one can distinguish three regions: (1) . . . , (2) . . . (3) The ‘surface’ of atoms and the overlap regions in molecules. Here our approximation [LDA] has no validity and therefore we expect this region to be the main source of error. We do not expect an accurate description of chemical binding ” [38].

Hindsight is always much sharper, of course, but Kohn was certainly correct in noticing:

> “I believe that formal DFT would have been of very little interest if there had not been a simple and very practical approximation for E_{xc}, the LDA, which has yielded surprisingly accurate results” [41].

5.1 Three examples

We discuss here three cases where the LDA and a simple extension gave interesting and unexpected results.

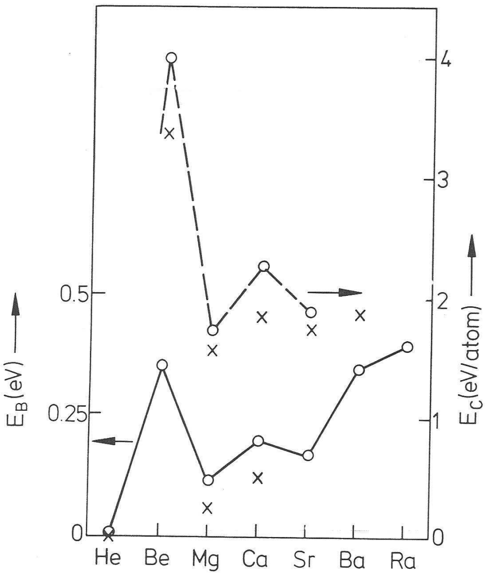
5.1.1 Group 2 dimers: He$_2$, Be$_2$, Mg$_2$, Ca$_2$, . . .

The group 2 elements have a particularly simple structure of the valence electrons: a closed shell of s-electrons, ns^2. When two such atoms approach each other, there is again a closed shell configuration $\sigma_g^2\sigma_u^2$, with an equal number of electrons in bonding an antibonding orbitals (“bond order” zero). Prior to the first DF calculations, the accepted picture was that binding was only possible in the presence of London dispersion forces, which increase as the atomic polarizability increases. This was consistent with available experimental data at the time, which showed an increase in binding energies from He$_2$ → Mg$_2$ → Ca$_2$, Be$_2$ having not yet been identified experimentally (Fig. 3). All Hartree-Fock and correlated wave function calculations on Be$_2$ to that time gave no binding or a weak minimum at large interatomic separation ($\sim$ 4.5 Å).

The prediction of DF calculations that the Be$_2$ dimer should not only exist, but should be more stable than Mg$_2$ [42], was treated by many in the “correlated wave function” world as evidence that DF calculations were unreliable. Nevertheless, the zigzag behavior in the binding energies is also present in the bulk cohesive energies (Fig. 3), and a calculation one year later using correlated wave functions [43] also gave a similar bond length, shorter than widely expected, and a larger binding energy than in Mg$_2$. The essential correctness of the DF prediction was finally confirmed experimentally five years later [44]. More details of this saga are provided in [9].

5.1.2 Phosphorus clusters: P$_n$

The combination of DF calculations with molecular dynamics (DF/MD, Car-Parrinello method [45] made simulations of bulk systems at elevated temperatures possible, and simulated annealing techniques could be used to study the energy surfaces of molecules and clusters. The use



Mg_2	Expt	HF	DF
R_e (Å)	3.89	–	3.81
ω_e (cm^{-1})	51.12	–	80
E_B (eV)	0.052	–	0.11

Ca_2	Expt	HF	DF
R_e (Å)	4.28	–	4.30
ω_e (cm^{-1})	64.93	–	80
E_B (eV)	0.13 ± 0.02	–	0.20

Be_2	Expt[a]	HF	ICF[b]	DF
R_e (Å)	2.45	–	2.49 ± 0.02	2.57
ω_e (cm^{-1})	~ 250	–	–	300
E_B (eV)	–	–	0.10 ± 0.01	0.35

[a] V.E. Bondybey and J.H. English, J. Chem. Phys. **80**, 568 (1984)

[b] B. Liu and A.D. McLean, J. Chem. Phys. **72**, 3418 (1980)

Fig. 3: *(left) binding energies of diatomic molecules (left scale, eV) and cohesive energies of bulk metals (right scale, eV per atom). Crosses: experimental values, as available ca. 1980. (right) spectroscopic constants of group 2 dimers [42].*

of molecular dynamics provides an element of randomness needed if one is to avoid biasing the search for cluster structures.

Four-atom clusters of phosphorus were among the first atomic clusters to be studied using gas-phase electron diffraction [46]. The most stable form of P_4 is tetrahedral, but a second, "butterfly" (C_{2v}) form has a much higher energy, but also a much larger region where it is the nearest local minimum to a given arrangement of four P atoms. The only larger cluster to have been studied in any detail was the cubic (O_h) form of P_8. This was an obvious choice for the valence configuration of P ($3s^2 3p^3$), with three p-orbitals at 90° to each other, but it was noted that the stability of this structure relative to two P_4 tetrahedra was remarkably low.

The reason became clear after DF calculations [47] showed that an unexpected C_{2v} structure had a much (1.7 eV) lower energy than the cube. Other structures were found for P_5 to P_8 that were confirmed by calculations with more traditional methods and by subsequent experiments. The "butterfly" form can be seen as a component of many larger clusters.

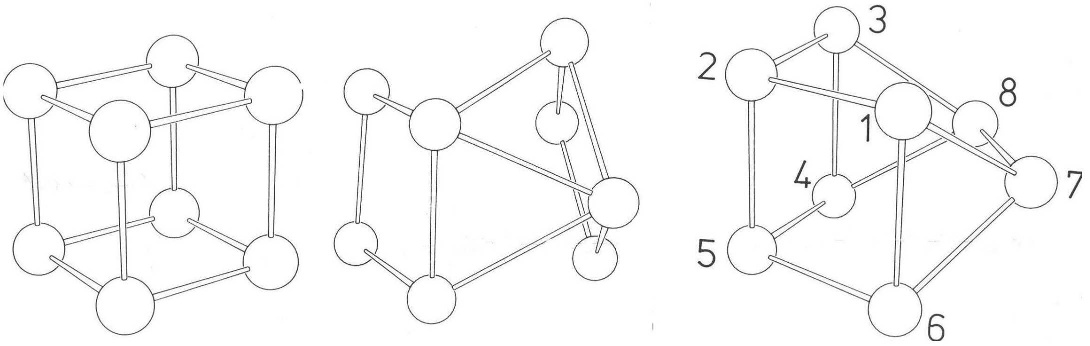


Fig. 4: *Molecular dynamics and simulated annealing of P_8 from the cubic (O_h) to a C_2 structure to the most stable (C_{2v}) form [47].*

5.1.3 Liquid bismuth

An example from the condensed matter world is provided by extensive DF/MD simulations using the PBEsol functional approximation [48] (over 500 atoms, up to 100 ps) of liquid bismuth at four temperatures between 573 K and 1023 K). These simulations have provided details of the dynamical structure factor, the dispersion of longitudinal and transverse collective modes, and related properties. Agreement with available inelastic x-ray and neutron scattering data and with previous simulations is remarkably good [49].

The density fluctuations in the liquid can be described by the intermediate scattering function

$$F(q,t) = \left\langle \mathrm{Re}\left(n(q,t{+}t_0)\, n(q,t_0)\right)\right\rangle, \tag{26}$$

where $\langle \ldots \rangle$ denote averages over all reference times t_0, and $n(q,t)$ is a Fourier component of the density,

$$n(q,t) = \frac{1}{\sqrt{N}} \sum_i \exp(i\vec{q}{\cdot}\vec{r}_i). \tag{27}$$

The index i runs over all particles, whose total number is N. The dynamical structure factor $S(q,\omega)$ is the Fourier transform of $F(q,t)$

$$S(q,\omega) = \frac{1}{2\pi} \int dt\, F(q,t) \exp(i\omega t). \tag{28}$$

Calculations of structure factors and related functions involve averages over all equivalent q vectors with q $= |q|$. In Fig. 5, we compare the calculated [49] and experimental [50] structure factors $S(q,\omega/S(q)$ for liquid Bi at 573 K.

The current autocorrelation function $C(q,t)$ can be calculated directly from the Fourier transform of the particle current $J(q,t)$, which has a longitudinal component

$$J_L(q,t) = \frac{1}{\sqrt{N}} \sum_i \vec{q}{\cdot}\vec{v}_i \, \exp(i\vec{q}{\cdot}\vec{r}_i) \tag{29}$$

and a transverse component

$$J_T(\vec{q},t) = \frac{1}{\sqrt{N}} \sum_i \vec{q}{\times}\vec{v}_i \, \exp(i\vec{q}{\cdot}\vec{r}_i). \tag{30}$$

The longitudinal component of the current autocorrelation function is

$$C_L(q,t) = \left\langle \mathrm{Re}\left(J_L(q,t{+}t_0)\, J_L(q,t_0)\right)\right\rangle \tag{31}$$

with a transverse component

$$C_T(q,t) = \frac{1}{2}\left\langle \mathrm{Re}\left(J_T(q,t{+}t_0)\, J_T(q,t_0)\right)\right\rangle. \tag{32}$$

A variety of experimental probes, including x-rays and neutrons, couple to longitudinal density fluctuations, but provide no direct information about transverse fluctuations. The shear viscosity η is a rare transport property that couples to the transverse momentum and can be calculated from $C_T(q,t)$ [49]. The results are 573 K: 1.86 (1.65) mPa s; 773 K: 1.42 (1.18) mPa s; 923 K: 1.11 (1.06) mPa s; 1023 K: 1.08 (0.94) mPa s, where the values in brackets are experimental values interpolated from the tables of Assael *et al.* [51]. Given the scatter in the experimental data of different groups, the agreement is very satisfactory.

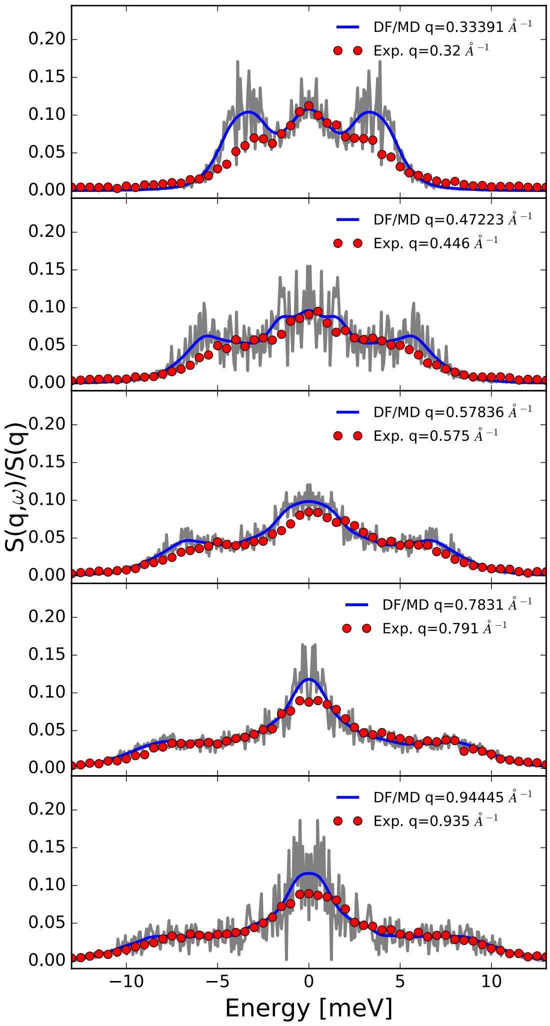


Fig. 5: *Ratio of dynamical to static structure factors, $S(q,\omega)/S(q)$, for selected q-values at 573 K [49]. Grey: DF/MD results, blue: DF/MD with 3 meV Gaussian broadening, red: experimental IXS [50].*

5.2 Spin systems. LSD approximation

Spin plays a minor role in the systems we have just considered: the Be atom and the beryllium dimer are closed-shell systems, as are P_4 and P_8 clusters, and the lowest-lying state of liquid Bi with an even number of atoms is also spin-free. The extension to spin systems [52] or an external magnetic field requires the introduction of the spin indices α of the one-electron operators $\psi_\alpha(\mathbf{r})$ and replacing $V_{\rm ext}$ by $V_{\rm ext}^{\alpha\beta}(\mathbf{r})$, and the charge density $n(\mathbf{r})$ by the density matrix $n_{\alpha\beta}(\mathbf{r}) = \langle\Psi|\psi_\beta^\dagger(\mathbf{r})\psi_\alpha(\mathbf{r})|\Psi\rangle$. All ground state properties are functionals of $n_{\alpha\beta}$, and E is stationary with respect to variations in $n_{\alpha\beta}$. The expression for the energy $E_{\rm xc}$ is analogous to Equations (20,21).

The generalization of the LDA to spin-polarized systems is known as the local spin density (LSD) approximation:

$$E_{\rm xc}^{\rm LSD} = \int d\mathbf{r}\, n(\mathbf{r})\, \varepsilon_{\rm xc}[n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r})], \tag{33}$$

where $\varepsilon_{\mathrm{xc}}[n_\uparrow, n_\downarrow]$ 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.[3]
The "Xα" approximation

$$E_{\mathrm{x}}^{\mathrm{X}\alpha} = -\frac{3}{2}\alpha C \int d\mathbf{r}\, \Big(\big(n_\uparrow(\mathbf{r})\big)^{4/3} + \big(n_\downarrow(\mathbf{r})\big)^{4/3} \Big), \tag{34}$$

where $C = 3(3/4\pi)^{1/3}$, was used in numerous calculations in the late 1960s and 1970s. The α-dependence of energy differences for a given atom or molecule is weak for values near $2/3$, the value of Bloch [18], Dirac [6], Gáspár [33] and Kohn and Sham [38]. The usual physical interpretation of $n_\uparrow(\mathbf{r})$ and $n_\downarrow(\mathbf{r})$ is that $n_\uparrow(\mathbf{r})+n_\downarrow(\mathbf{r})$ is the total density $n(\mathbf{r})$, and $n_\uparrow(\mathbf{r})-n_\downarrow(\mathbf{r})$ is the spin magnetization density.

5.3 Shortcomings of LD/LSD approximations

5.3.1 Self-interaction correction

A particularly obvious defect of the LDA is evident when one considers a system containing only one electron, since the contribution to the total energy (Eq. 10) contains a spurious "self-interaction" of the electron with itself. If we knew the exact functional E_{xc}, it would cancel the direct Coulomb energy in (10). Perdew and Zunger [53] developed an approximation for correcting the SIC to the LSD or any approximation to the exchange-correlation energy

$$E_{xc}^{SIC} = E_{xc}^{LSD}(n_\uparrow, n_\downarrow) - \sum_{\alpha\sigma} \delta_{\alpha\sigma}\ , \tag{35}$$

where

$$\delta_{\alpha\sigma} = \frac{1}{2}\int d\mathbf{r} \int d\mathbf{r}'\, \frac{n_{\alpha\sigma}(\mathbf{r}) n_{\alpha\sigma}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_{xc}^{LSD}[n_{\alpha\sigma}, 0]\ , \tag{36}$$

where E_{xc}^{LSD} is the energy functional in the LSD approximation and $\delta_{\alpha\sigma}$ is the SIC correction for the orbital α with spin σ and charge density $n_{\alpha\sigma}$. The last term is the LSD approximation to the exchange and correlation energy of a fully spin polarized system with density $n_{\alpha\sigma}$. This functional is exact for a one-electron system, and it was shown that it led to much better total energies for atoms [53, 54]. However, energy differences, such as the sd-promotion energies in atoms, showed little improvement, and the substantial improvement in total energies was shown to result from a better description of the most tightly bound core electrons [54]. These are the least relevant for many problems, including chemical bonding.

5.3.2 Further problems

Most of the early DF calculations on small clusters and molecules used the LD (Eq. 18) and/or LSD (Eq. 33) approximations. The results were often encouraging and provided insight into interesting physical problems, but it was soon clear that local density calculations can lead to

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[3] The calculation by Bloch [18] in 1929 of ferromagnetism in a free-electron model of a metal was the first where the exchange energy was expressed as the sum of terms proportional to $n_\uparrow^{4/3}$ and $n_\downarrow^{4/3}$.

unacceptable results. Examples include the overbinding of many molecules, the exchange energy difference between states with different nodal structures, e.g. the sp-promotion energies in first-row atoms, particularly O and F, and the sd-promotion energies in transition element atoms [55]. The Kohn-Sham eigenvalues often underestimate measured optical band gaps significantly.

Better approximations were needed, and corrections involving density gradients were soon available for the correlation [56, 57] and exchange energies [58], where the semi-empirical approximation of Becke [58] had the correct asymptotic behavior for atoms. Hybrid functionals including exact exchange were introduced by Becke in 1993 [59]. This form of E_{x} has three parameters, and its combination with E_{c} of Lee, Yang, and Parr [57] (B3LYP) is still one of the most common approximations used in chemical applications.

Many other empirical and hybrid functionals have been developed since, with parameters usually fit to thermochemical data for particular groups of molecules. The use of experimental data for fitting functional forms provided additional parameters that led to improvement over LD and LSD results [60], and the use of "training sets" of atomic and molecular systems to optimize the parameters improved the calculated results for particular sets of molecules [61]. Caution is advised when applying "well-trained" functional forms to systems of a different nature.

Dispersion forces—the weak, non-local interactions between closed shells systems—are a particular problem for DF approximations (DFA). The long-range interaction between separated atoms or molecules is absent, and yet the LD approximation *overestimates* the binding energy in many such systems, e.g. He_2 and other group 2 dimers [42]. The development of a functional that changes seamlessly on going from weakly interacting units to a combined system remains an important goal. Langreth and coworkers [62], for example, developed a functional that incorporates results for electron gas slabs and the electron gas itself and is free of experimental input. Empirical corrections to DF results have been studied by Grimme and coworkers [63, 64, and references therein] and are very widely used.

"Strongly correlated" systems often involve transition element or rare earth atoms, and the potential energy can dominate over the kinetic energy. Local density approximations can lead to poor descriptions of these materials, and ways of avoiding these problems is the topic of this school. A common approach has been to add an on-site Coulomb repulsion ("Hubbard U") in the "LSD+U" scheme [65]. The parameter U can be estimated within a DF framework [66] or fit to experiment. We shall return to these systems below.

5.4 "Jacob's Ladder"

An alternative path has been followed by others, particular Perdew and collaborators, who developed a sequence ("Jacob's ladder") of approximations without experimental input, where each "rung" builds on the experience of lower levels and satisfies additional physical constraints (Fig. 6). This approach is systematic and not empirical [67]. Starting with a proof of the existence of a functional, one can derive formally exact relationships that can be used as constraints on approximate forms. If these forms are flexible enough, we can fit their free parameters to

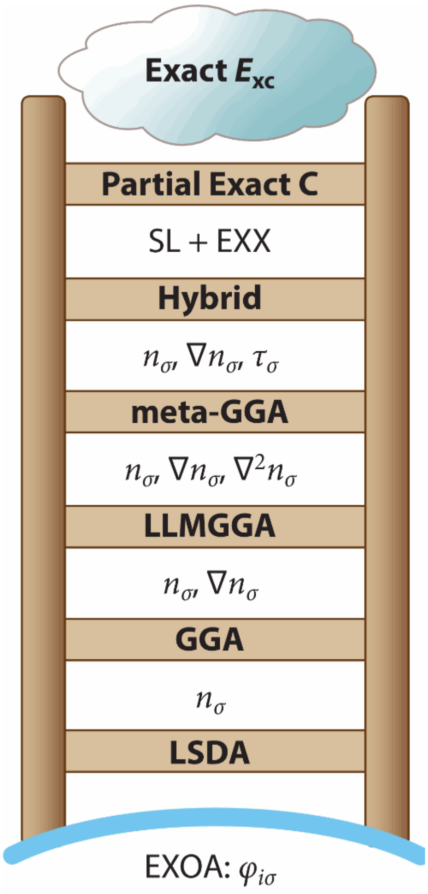

Fig. 6: *Jacob's ladder hierarchy of density functional approximations. For each quantity, the spin index* σ *equals* $\uparrow, \downarrow$. *Abbreviations: EXOA, exchange-only approximation; EXX, exact exchange; GGA, generalized gradient approximation; LLMGGA, Laplacian level meta-generalized gradient approximation; LSDA, local spin-density approximation; meta-GGA, meta-generalized gradient approximation; SL, semi-local; xc, exchange correlation. Reproduced from [1], ©2023 The Authors, published by Annual Reviews)*

appropriate norms of energies or densities. These should not include binding energies, which are always susceptible to error cancellation between exchange and correlation.

If we consider the class of semilocal (SL) density functional approximations

$$E_{xc}^{SL}[n_\uparrow, n_\downarrow] = \int d\mathbf{r}\; \varepsilon_{xc}^{SL}(n_\uparrow, n_\downarrow, \ldots; \mathbf{r}) \;, \tag{37}$$

there are 17 known constraints that must be satisfied, with another four if we consider nonlocal approximations, which are typically two-point functionals [1]. A detailed explanation of these constraints is given in [1].

In this spirit, the gradient corrected form of Perdew, Burke, and Ernzerhof [68] (PBE) incorporates the LSD form below it, and the "meta-GGA" form of Tao, Perdew, Staroverov, and Scuseria (TPSS) [69], where $n_\uparrow$ and $n_\downarrow$ are joined by their gradients and the kinetic energy density of the occupied Kohn-Sham orbitals, builds on both. The complexity of the calculations increases as one climbs the "ladder" [70], while the physical content may well seem less transparent.

5.5 Functional approximations: current status

Hundreds of functional approximations have been developed over the years, although the number in widespread use is limited. The LDA is still used for its simplicity, PBE is used in many molecular calculations, PBEsol gives improved geometries in extended systems, and B3LYP is very widely used in chemistry. A broad survey of DFA in chemistry [71] came to the conclusion that "ultimately, today's state-of-the-art functionals are close to achieving the level of accuracy desired for a broad range of chemical applications, and the principal remaining limitations are associated with systems that exhibit significant self-interaction/delocalization errors and/or strong correlation effects" [71].

Geometrical arrangements are often the goal of DF calculations, but band gaps in the energy eigenvalue spectrum are also important. A database of 473 semiconductors and insulators has been used to benchmark over 30 exchange-correlation energy functionals according to the calculated band gaps. Meta-GGAs and hybrid functionals generally gave the best results [72].

The choice of functional approximation is not the only variable in a calculation; we must also write a program or use one of the many now available. The reproducibility in DF calculations in solids has been studied in some detail [73], with the reassuring conclusion that "most of the commonly used codes and methods are now found to predict essentially identical results."

The agreement with experiment generally improves, as we shall see in the case of the ladder from LDA $\rightarrow$ PBE $\rightarrow$ r^2SCAN [74], the most recent of the family of strongly constrained and appropriately normed ("SCAN" [75]) functionals of Perdew and coworkers. A rather thorough comparison of r^2SCAN results with other DFA [1] provides an encouraging picture, not only for the developers of the approximation. Formation enthalpies are improved, self-interaction errors are reduced,[4] and the Hubbard-U values needed to fit experimental data are lower. SCAN recognizes without adjustment that undoped $\mathrm{La_2CuO_4}$ is an antiferromagnetic insulator and its Sr-doped counterpart is metallic, which is not the case for most other DFA. r^2SCAN predicts an essentially constant magnetization as the structure of NiO is varied, which is consistent with experiment and an improvement over the GGA functionals PBE and PBEsol [77].

Density functional calculations also predict the electronic density distribution, and Medvedev *et al.* [67] noted some years ago that many (empirically fitted) functionals developed since the year 2000 lead to improved energies but *densities* that are further from the exact results. An extensive study of dipole moments of small molecules calculated using coupled-cluster theory with up to triple excitations showed that the best performing of the 88 DFA tested were of comparable accuracy [78]. Hybrid functionals performed best, although it is a little disconcerting that some modern DFA performed little better than LDA.

A very recent study of 26 molecules with up to four atoms compared the charge distribution in DF calculations with Hartree-Fock and with 12 widely-used DFA with the densities obtained from coupled-cluster (single and double excitations) calculations [79]. This work showed that modern DFA can provide highly accurate charge densities, particularly in the case of meta-GGA

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[4] Recent studies of the sd-promotion energies in transition metal atoms [76] suggest that the Perdew-Zunger [53] model for SIC induces a significant error in these atoms.

and hybrid functionals. These DFA outperform Hartree-Fock for simple, sp-bonded molecules near their equilibrium geometries. The only functional that was worse than Hartree-Fock was LDA. Particularly striking was the finding that “the functionals that adhere to theoretical constraints, such as SCAN and r^{2}SCAN, produced the most consistent results across all error measures. In contrast, empirically designed functionals exhibited a significantly larger spread in at least one error measure, emphasizing the importance of adhering to physically rigorous constraints for achieving consistently accurate charge densities” [79].

6 Broken symmetry. Connection to strong correlation?

> “We can now propose a definition of strong correlation: Strong correlation in a symmetry-constrained wave function is any correlation between electrons that results in an exceptionally structured electron-pair density, or is otherwise qualitatively different from the “normal” Coulomb correlation found in simple sp-bonded materials in their ground states near equilibrium nuclear geometries… This definition has little in common with “everything that DFT gets wrong.”
> J.P. Perdew *et al.* (2021) [80]
>
> “The focus on quantum materials has raised questions on the fitness of density functional theory for the description of the basic physics of such strongly correlated systems. Recent studies point to another possibility: the perceived limitations are often not a failure of the density functional theory per se, but rather a failure to break symmetry.”
> A. Zunger (2022) [81]

Can it really be true that a symmetry-broken version of density functional theory is able to handle some “strongly correlated” problems? We now look at simple examples of symmetry breaking in density functional calculations.

6.1 Broken symmetry in general

We have noted that the Hamiltonian in Eq. (15) is a function of its own eigenvectors, so must be solved iteratively to satisfy the condition (14). The non-linearity means that solutions may not be unique and may break essential symmetries of the system, often connected with phase transitions. Additional correlations may occur. Such considerations can suggest new physical processes or provide new insight, but the broken-symmetry wave functions do not have the symmetry of the original system, so that many results cannot be compared directly with experiment. General group-theoretical techniques that have been developed to restore the original symmetry are reviewed in [82] and apply also to the extension of the restricted Hartree-Fock (RHF) approach, where the single Slater determinant wave function is constrained to have the underlying molecular symmetry, to the unrestricted Hartree-Fock (UHF) approach, where it is not. A

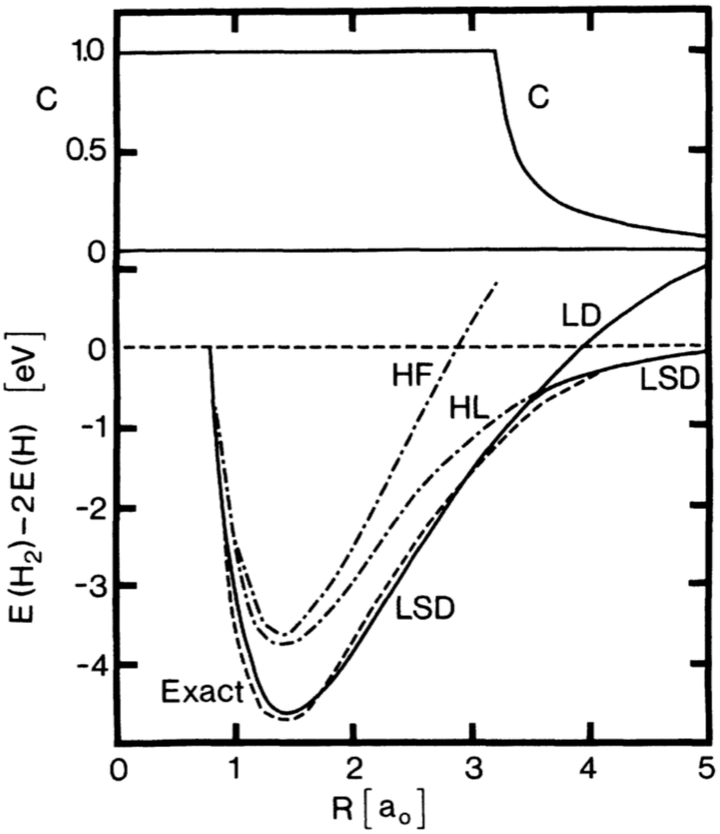

Fig. 7: *Energy of the hydrogen molecule as a function of the internuclear distance. The full curves show the results in the LD and LSD approximations, which differ for $R \geq 3.2$ The dashed curve gives the accurate result of Ref. [84]. The upper part of the figure shows the quantity c in Eq. (38), which gives the degree of spin polarization. For $c = 1$, the system is unpolarized. Reproduced with permission from [39]. ©1976 American Physical Society.*

single Slater determinant of different orbitals for different spins, for example, is not a satisfactory eigenfunction of the total spin operator $\langle S^2 \rangle$, and the ground state can be contaminated by excited states [83].

6.2 Symmetry-broken systems: H_2, Cr_2, Be_2 ...

One of the earliest DF calculations of a molecule, now 50 years ago, was the study of the ground state ($^1\Sigma_g^+$) of H_2 by Gunnarsson and Lundqvist [39]. The results for several approaches are shown in Fig. 7 and include the Hartree-Fock (HF), Heitler-London (HL), local density (LD), and the numerically exact result [84].

The LSD curve is obtained by assuming that the two orbitals contributing to the spin density are $\psi_{i\alpha} = \Phi_i \xi_\alpha$, where ξ_α is a spin function and

$$\Phi_i(\mathbf{r}) = [\phi_i(\mathbf{r}) + c\phi_j(\mathbf{r})]/(1 + 2cS + c^2)^{1/2}, \quad (i, j = a, b, i \neq j) \tag{38}$$

with $S = \int d\mathbf{r}\ \phi_a(\mathbf{r})\phi_b(\mathbf{r})$. This means that the spin polarization can be different for atoms a and b. The LSD curve follows the exact curve closely and allows dissociation into two neutral

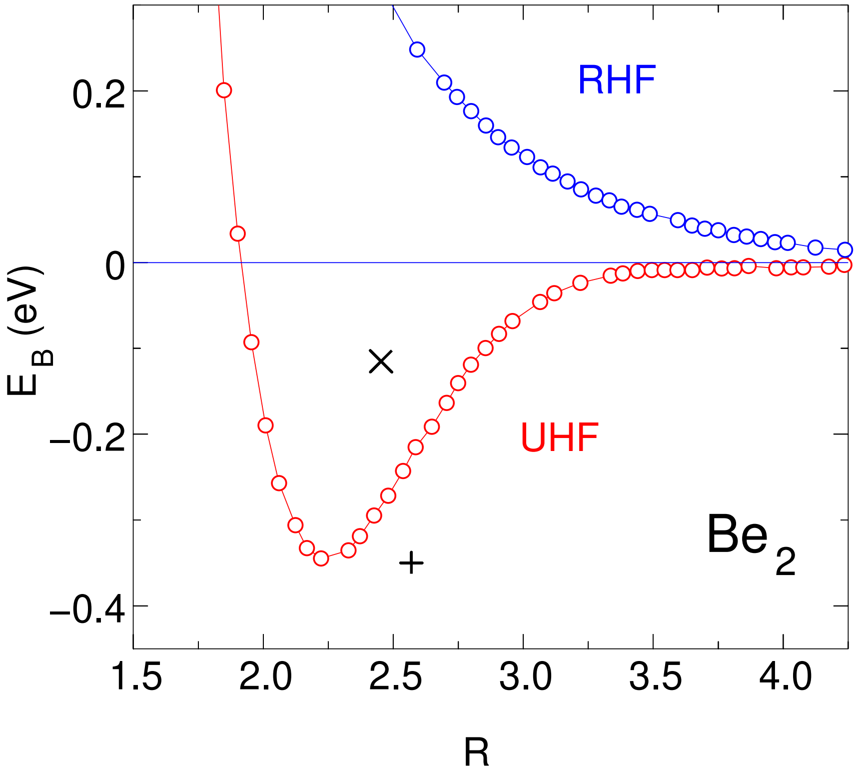

Fig. 8: *Restricted (blue) and unrestricted (red) Hartree-Fock calculations for* Be_2 *(after [93]).* $\times$*: correlated wave function results of [43],* $+$*: LDA results [42].*

H atoms with opposite spin. The degree of spin polarization is given by the value of c (Fig. 7, upper), and the symmetry-broken state has a lower energy than the LD calculation for $r > 3.2$ Å. The fact that a large part of correlation effects can be described by a single determinantal wave function with broken-symmetry orbitals and projection to an eigenstate of total spin was pointed out first by Coulson and Fischer [85].

The transition point depends on the DFA used, both for closed-shell [86] and open-shell molecules [87]. This electronic instability corresponds to the Mott transition in solids [88], where the broken-symmetry solutions are described as spin- or charge-density waves. Spin waves were identified much earlier by Bloch [89].

The first density functional calculations on transition metal dimers [90] considered only states with the full symmetry of the molecule, and it was difficult to make a clear prediction of the ground state of Cr_2, where the balance between favoring the occupation of bonding orbitals and having a high-spin state is delicate. This study overlooked the possibility of antiferromagnetic coupling in these systems [91, and references therein]. It is possible to describe a ladder of spin states by constructing states of mixed spin symmetry and lower space symmetry.

We have seen that DF calculations for the beryllium dimer [42] led to an unexpectedly short bond length (2.57 Å). Previous Hartree-Fock calculations had led to a repulsive curve and no binding, but these were restricted HF calculations that required the wave function to have the full molecular symmetry. Unrestricted HF calculations [92], however, showed a weak minimum (depth 0.26 eV, interatomic separation $\sim$ 2.3 Å). In Fig. 8, we show very recent (and much more accurate) RHF and UHF calculations for Be_2 [93], as well as the minimum energies and separations found in density functional [42] and correlated wave function calculations [43]. One can only speculate about the course of events if the UHF result had been known *before* the DF results.

The quotations at the beginning of this section suggest that the broken-symmetry ideas we have just discussed could be useful in addressing some long-running problems in the density functional description of strongly-correlated systems, e.g., transition metal monoxides such as FeO and NiO. It has now been shown [77, 94] that the antiferromagnetic, insulating phase in these materials can be described well if the unit cell is chosen to allow antiferromagnetic order. The smallest unit cell has a single transition element atom, so that the local magnetic moment is zero, not just the global magnetization. It should be noted that the energy eigenvalues in general and band gaps in particular do not agree with experiment. This can be improved by adding about 20 % "exact exchange" to the r^2-SCAN functional or by adding a Hubbard-U.

7 Concluding remarks

Density functional theory has a long and fascinating history involving some of the best known names in physics and has become, without dispute, the "workhorse of quantum chemistry and materials science" [8]. This is a remarkable result for a method that has experienced much opposition. The theoretical chemistry community took many years to be convinced of its usefulness, and its dismissal by a leading condensed matter theorist, Philip Anderson, as the "Great Solid State Physics Dream Machine" did little to help its establishment in the wider condensed matter community. Its difficulties in the past to describe "strongly correlated" materials led to their definition in terms of this failure.

I concluded my lecture at the 2013 School with the following lines:

> "I end with a note of caution for the 'strongly correlated' community, Few theoretical chemists thought that DF calculations were relevant to understanding the electronic structure of molecules, but local density approximations (and their modifications) have given far better results than *anyone* expected. It was shown *afterwards* why approximations to E_{xc} could give good results for density distributions far from those where they are obviously valid. Perhaps DF theory has some real surprises in store for the 'strongly correlated' world." [95]

Developments in the recent past seem to bear this out. The remarkable improvement in the results from DFA that satisfy increasing numbers of physical constraints has been accompanied by a new focus on broken symmetry wave functions as a way to study some of the problems involving strong correlations. I was not expecting either development, but I am optimistic about the future of both.

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