1 Density Functional Theory for Emergents

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1 Introduction

The "reductionist" view of science implies focus on simpler and simpler causes and finally on the ultimate constituents of matter. This belief—that our understanding of Nature will follow if we solve this "fundamental" problem—has a vigorous opponent in Philip Anderson, who has emphasized the "emergent" view over many years [1, 2]:

> "What really is the problem is called 'broken symmetry': the underlying laws have a certain symmetry and simplicity that is not manifest in the consequences of these laws. To put it crudely, a simple atom of gold cannot be shiny and yellow and conduct electricity: Metallicity is a property with meaning only for a macroscopic sample. ..."

Qualitatively different phenomena can occur as the level of complexity increases, and this school is devoted to understanding some of them, particularly new features that arise in "strongly correlated" systems.

A practical definition of "strongly correlated" systems covers those that are not described well by density functional (DF) theory. Many seminars and publications on "strongly correlated" mention at the outset the widespread use of density functional (DF) theory in materials science and chemistry and the physical insight that often results. The second sentence, however, often lists the systems where DF results are disastrous (an insulator is found to conduct, almost anything to do with rare earth elements, ...), emphasizing the importance of describing strongly correlated materials correctly.[1] DF theory is nevertheless an essential part of this workshop. The approach is used widely in materials science and chemistry and provides useful results for many systems for which the exact wave function cannot be computed. We should have a feel for the areas where physical insight can be obtained and *why* approximations used in DF calculations can give sensible answers far from their regions of obvious validity.

The origins of DF theory go back to the early years of quantum mechanics in the late 1920's. 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 by its density; it is not necessary to specify the wave function. We follow here the history of density-related methods to the single-particle equations of Kohn and Sham in 1965 and beyond. In its modern form, the DF formalism shows that ground state properties of a system of electrons in an external field can be determined from a knowledge of the *density distribution* $n(r)$ alone. Much of the work in materials science and chemistry focuses 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 R_I, which determines structural and cohesive properties.

Accurate calculations of the entire energy surface $E(R_I)$ 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

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[1] An example can be found in the Preface of the 2012 Autumn School [3]: "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."

between minima are essential to our studies of chemical reactions, including their activation energies. When I read the autobiography of Francis Crick [7], I was taken by his observation

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

This may be self-evident to molecular biologists, but it is also true in many other areas. The DF approach allows us to calculate $E(R_I)$, 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.

Olle Gunnarsson and I reviewed the density functional formalism, its history, and its prospects in 1989 [8], and I reread the original literature some years ago. My changed perspective is reflected here, where I trace DF history from the late 1920's to the present day.

2   The density as basic variable

The recent books by Gino Segrè [9] and Graham Farmelo [10] give fascinating accounts of the development of quantum mechanics in the years following 1926. Methods for finding approximate solutions of the Schrödinger equations followed soon after the equations were published 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 [11],

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

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 [11] introduced the idea of a "self-consistent field", with specific reference to the core and valence electrons, but his papers do not mention the approximation (1). Slater [12] and Fock [13] recognized immediately 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 [12, 13] 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 [14] and ferromagnetism [15], 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 [16]:

"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 systems.

Dirac [16] 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:

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

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 [16], and he included these effects in the "Thomas atom" [6] by means of the potential

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

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 and its extensions give rough descriptions of the charge density and the electrostatic potential of atoms, and its mathematical properties have attracted considerable attention [17, 18]. However, it has severe deficiencies. The charge density is infinite at the nucleus and decays as r^{-6}, not exponentially, far from it. Teller [19] 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 periodic variation of many properties with changing atomic number Z cannot be reproduced, nor can ferromagnetism [8]. Moreover, atoms *shrink* with increasing Z (as $Z^{-1/3}$) [20].

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."

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[2]The exchange energy in a homogeneous electron gas had been derived by Bloch [15] in 1929
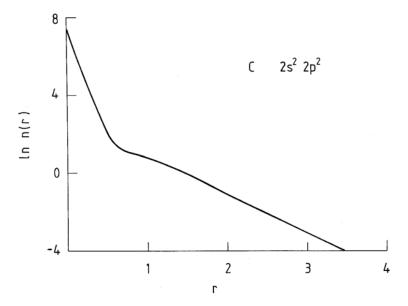
Fig. 1: *Logarithm of spherical average of density in ground state of C atom as a function of the distance from the nucleus (atomic units) [8].*

The italics are in the original. The derivation is based on the "self-consistent field" or Hartree-Fock approximation, but the observation that the density follows the equations of motion is much in the spirit of Ehrenfest's theorem [21], which has wider validity. Ehrenfest had proved in 1927 what I have seen referred to as the "time-dependent Hellmann-Feynman theorem", namely that the acceleration of a quantum wave packet that does not spread satisfied Newton's equations of motion.

The central role played by the density means that we must understand its nature in real systems. Figure 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 relatively 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. It really is amazing that this suffices to determine ground state properties.

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. 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
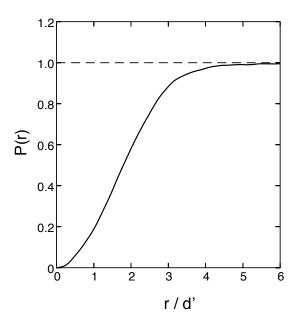
Fig. 2: *Probability that electrons in Na metal with parallel spins are r/d' apart ($d'^3 = V_0/(3\pi^2)$, V_0 is the atomic volume). After Wigner and Seitz [22].*

approximations are essential. Furthermore, numerical techniques for solving the Schrödinger equation in extended systems needed to be developed.

Wigner and Seitz [22] 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. 2). This function obtains its half-value for $r = 1.79\,d'$ or $0.460\,d$ for a body-centred cubic lattice with cube edge d, which is close to the radius of the "Wigner-Seitz sphere" $\left(\frac{3}{8\pi}\right)^{\frac{1}{3}} d = 0.492\,d$. 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 [22]. 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 [23].

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" [22] or "exchange" hole [24]. In the Hartree-Fock scheme, the exchange hole is different for each electronic function, but Slater [24] 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 around this time, including the augmented plane wave (APW) [25] and Korringa-Kohn-Rostoker approaches [26, 27].

The exchange potential of Slater (4) is 3/2 times that derived by Dirac and Bloch (3) for a homogeneous electron gas, but Slater [28] 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 [24]. 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

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

where $n_\uparrow$ is the density of spin up electrons. Since the electrostatic potential at the centre 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 (still widespread) misconception that local density approximations are only appropriate if the electron density is nearly homogeneous.

In 1954, Gáspár [29] 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" [30], but the larger value was used in most calculations in the following years.

4   Density functional formalism

The variational principle on the energy was the basis of the formulation of the density functional formalism given by Hohenberg and Kohn [31]. The ground state (GS) properties of a system of electrons in an external field can be expressed as functionals of the GS electron density, i.e. they are determined by a knowledge of the density alone. The total energy E can be expressed in terms of such a functional, and $E[n]$ satisfies a variational principle. These theorems were proved by Hohenberg and Kohn [31] for densities that can be derived from the ground state of some external potential V_{eff} ("V-representable"). A simpler and more general proof for ("N-representable") densities that can be derived from some antisymmetric wave function was given by Levy [32, 33]. Of course, these proofs do not provide practical prescriptions for writing the functional relationship between energy E and density n.

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 [34],

$$E[n] = T_0[n] + \int d\mathbf{r} \, n(\mathbf{r})\left(V_{\text{ext}}(\mathbf{r}) + \frac{1}{2}\Phi(\mathbf{r})\right) + E_{\text{xc}}[n] \ . \tag{6}$$

T_0 is the kinetic energy that a system with density n would have if there were no electron-electron interactions, Φ is the classical Coulomb potential for electrons, and E_{xc} *defines* the exchange-correlation energy. T_0 is not the true kinetic energy T, but it is of comparable magnitude and is treated here without approximation. This removes many of the 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 (6) all terms other than the exchange-correlation energy E_{xc} can be evaluated exactly, so that approximations for this term are crucial in density functional applications.

The variational principle applied to (6) yields

$$\frac{\delta E[n]}{\delta n(\mathbf{r})} = \frac{\delta T_0}{\delta n(\mathbf{r})} + V_{ext}(\mathbf{r}) + \Phi(\mathbf{r}) + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} = \mu \ , \tag{7}$$

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

$$\frac{\delta E[n]}{\delta n(\mathbf{r})} = \frac{\delta T_0}{\delta n(\mathbf{r})} + V(\mathbf{r}) = \mu \ , \tag{8}$$

we see that the mathematical problems are identical, provided that

$$V(\mathbf{r}) = V_{ext}(\mathbf{r}) + \Phi(\mathbf{r}) + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} \ . \tag{9}$$

The solution of (Eq. 8) can be found by solving the Schrödinger equation for *non-interacting* particles,

$$\left(-\frac{1}{2}\nabla^2 + V(\mathbf{r}) \right) \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}) \ , \tag{10}$$

yielding

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2 \tag{11}$$

The condition (9) can be satisfied in a self-consistent procedure.

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 [35]. 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,

$$V_{HF} \ \psi(\mathbf{r}) = \int d\mathbf{r}' \ V_{HF}(\mathbf{r},\mathbf{r}')\psi(\mathbf{r}') \ , \tag{12}$$

the effective potential, $V(\mathbf{r})$ is *local*.

The numerical advantages of solving the Kohn-Sham equations [34] 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 [34] proposed using the "local density (LD) approximation"

$$E_{xc}^{LD} = \int d\mathbf{r}\, n(\mathbf{r})\, \varepsilon_{xc}[n(\mathbf{r})] \,, \tag{13}$$

where $\varepsilon_{xc}[n]$ 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 authors noted that this approximation "has no validity" at the "surface" of atoms and in the overlap regions of molecules and concluded [34]:

"We do not expect an accurate description of chemical bonding."

The generalization to spin-polarized systems is

$$E_{xc}^{LSD} = \int d\mathbf{r}\, n(\mathbf{r})\, \varepsilon_{xc}[n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r})] \,, \tag{14}$$

where $\varepsilon_{xc}[n_\uparrow, n_\downarrow]$ 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

$$E_x^{X\alpha} = -\frac{3}{2}\alpha C \int d\mathbf{r}\, \left((n_\uparrow(\mathbf{r}))^{4/3} + (n_\downarrow(\mathbf{r}))^{4/3} \right) \,, \tag{15}$$

where $C = 3(3/4\pi)^{1/3}$ was used in numerous calculations in the late 1960's and 1970's. The α-dependence of energy differences for a given atom or molecule is weak for values near $2/3$, the value of Dirac [6], Bloch [15], Gáspár [29] and Kohn and Sham [34]. We have noted that 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 [22] and Slater [24, 28].

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. 10, 11). 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, [36] such that the ground state of the Hamiltonian

$$H_\lambda = -\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}) + V_\lambda + \lambda V_{ee} \tag{16}$$

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[3]The calculation by Bloch [15] 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 $n_\downarrow^{4/3}$.

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 [35]:

$$E_{\mathrm{xc}} = \frac{1}{2} \int d\mathbf{r}\, n(\mathbf{r}) \int d\mathbf{r}'\, \frac{1}{|\mathbf{r} - \mathbf{r}'|}\, n_{\mathrm{xc}}(\mathbf{r}, \mathbf{r}' - \mathbf{r})\,, \tag{17}$$

with

$$n_{\mathrm{xc}}(\mathbf{r}, \mathbf{r}' - \mathbf{r}) \equiv n(\mathbf{r}') \int_0^1 d\lambda \left(g(\mathbf{r}, \mathbf{r}', \lambda) - 1 \right). \tag{18}$$

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 [22] and Slater [24] 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 (17) yields

$$E_{\mathrm{xc}} = \frac{1}{2} \int d\mathbf{r}\, n(\mathbf{r}) \int_0^\infty dR\, R^2\, \frac{1}{R} \int d\Omega\, n_{\mathrm{xc}}(\mathbf{r}, \mathbf{R})\,. \tag{19}$$

Equation (19) 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 give an *exact* value, even if the description of the non-spherical parts of n_{xc} is arbitrarily inaccurate. Thirdly, the definition of the pair-correlation function leads to a sum-rule requiring that the xc-hole contains one electron, i.e. for all $\mathbf{r}$,

$$\int d\mathbf{r}'\, n_{\mathrm{xc}}(\mathbf{r}, \mathbf{r}' - \mathbf{r}) = -1\,. \tag{20}$$

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

$$\left\langle \frac{1}{R} \right\rangle_{\mathbf{r}} = - \int d\mathbf{r}\, \frac{n_{\mathrm{xc}}(\mathbf{r}, \mathbf{R})}{|\mathbf{R}|}\,. \tag{21}$$

This leads to

$$E_{\mathrm{xc}} = -\frac{1}{2} \int d\mathbf{r}\, n(\mathbf{r}) \left\langle \frac{1}{R} \right\rangle_{\mathbf{r}}\,. \tag{22}$$

Provided Equation (20) is satisfied, E_{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_{xc} [35]. Approximations to E_{xc} can then lead to good total energies (and structures), even if the details of the exchange-correlation hole are described very poorly. This is shown in Figure 3, 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 a few percent.
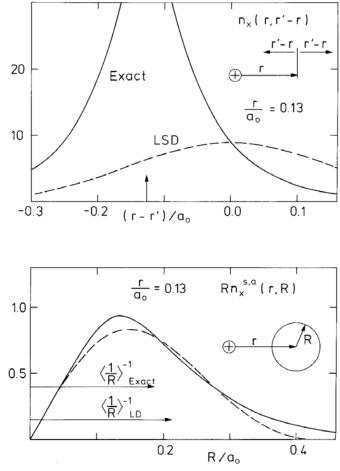
Fig. 3: *Exact (solid) and LSD (dashed) exchange holes $n_{xc}(\mathbf{r}, \mathbf{r}' - \mathbf{r})$ for spin up electron in N atom for $\mathbf{r} = 0.13$ a.u. Upper: hole along line through nucleus (arrow) and electron ($\mathbf{r} - \mathbf{r}' = 0$). Lower: spherical averages of holes, and $\langle 1/\mathbf{R}\rangle$ (21) [8].*

5 DF theory to 1990

5.1 Condensed matter

Condensed matter physicists were generally pleased to have justification for the "local density" calculations they had been performing for years, and numerous electronic structure theorists moved seamlessly from performing "$X\alpha$" or "Hartree-Fock-Slater" calculations into the density functional world. However, Fig. 4 shows that there was remarkably little impact of DF calculations prior to 1990. Volker Heine, a prominent condensed matter theorist, looked back on the 1960's in this way [37]:

> " Of course at the beginning of the 1960s the big event was the Kohn Hohenberg Sham reformulation of quantum mechanics in terms of density functional theory (DFT). Well, we recognize it now as a big event, but it did not seem so at the time. That was the second big mistake of my life, not to see its importance, but then neither did the authors judging from the talks they gave, nor anyone else. Did you ever wonder why they never did any calculations with it?"

There were also prominent critics of density functional and related computational techniques, and one of the best known solid state theoreticians, Philip Anderson, made devastating comments in 1980 [38]:

> " There is a school which essentially accepts the idea that nothing further is to be learned in terms of genuine fundamentals and all that is left for us to do is calculate. . . . One is left, in order to explain any phenomenon occurring in ordinary matter, only with the problem of doing sufficiently accurate calculations. This is then the idea that I call "The Great Solid State Physics Dream Machine" . . . This attitude is closely associated with work in a second field called quantum chemistry."

Anderson associated the "Dream Machine" with the name of John Slater and described the DF method as a "simplified rather mechanical kind of apparatus" that "shows disturbing signs of become a victim of the "Dream Machine" syndrome" [38]. While noting that DF calculations can be particularly valuable in some contexts, he continued:

> " . . . a great deal of the physics is concealed inside the machinery of the technique, and that very often once one has the answers that these techniques provide, one is not exactly clear what the source of these answers is. In other words the better the machinery, the more likely it is to conceal the workings of nature, in the sense that it simply gives you the experimental answer without telling you why the experimental answer is true."

While some may find these words a little harsh, his comments did apply to some electronic structure calculations at the time. They may indeed have had prophetic character, as I discuss in Sec. 7. The increasing availability of computing resources made possible calculations that had previously been inaccessible, and not all users of the method were critical of the approximations involved.

5.2   Chemistry

It took many years for DF calculations to be taken seriously by most chemists, and the reasons were often convincing: (1) Unlike the TF theory, the Kohn-Sham expression for the energy is not really a "functional" of the density, since the kinetic energy term is treated exactly and is defined by an effective potential that leads to the density, (2) the original functional of Hohenberg and Kohn is not even *defined* for all n, because not all densities can be derived from the ground state of some single-particle potential [33], (3) approximations to the exchange-correlation energy are unavoidable, and their usefulness can be assessed only by trying them out, and (4) there is no *systematic* way to approach the exact solution of the Schrödinger equation and, of course, the exact energy.

This last point was emphasized by many. In principle, the Hartree-Fock method could be extended to multiple determinants ("configuration interaction") and, coupled with a large basis set, lead to the exact wave function and all properties obtainable from it. This is a very attractive proposition, and the dramatic improvements in computing power (three orders of magnitude per
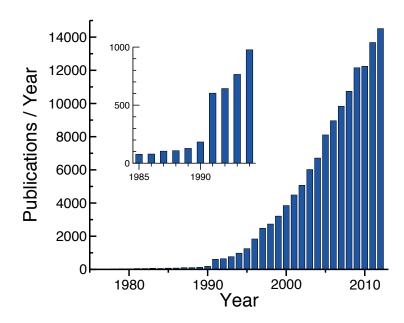
Fig. 4: *Number of publications per year (1975-2012) on topics "density functional" or "DFT", according to Web of Knowledge (May 2013). Inset shows data near 1990 on an expanded scale [39].*

decade) might make the reservations of Dirac [16] less formidable. It was often emphasized that solutions of the Schrödinger equation led to the "right answer for the right reason." Nevertheless, obtaining numerically exact total energies from calculations of the wave function remains a major challenge to this day, and it is not surprising that several groups looked at alternatives.

Hartree-Fock-Slater calculations on small molecules were carried out in the early 1970's, particularly by Evert Jan Baerends and collaborators in Amsterdam, and some of the first DF calculations on small molecules were performed by Olle Gunnarsson [35]. John Harris and I had not expected that the local density approximations would give reasonable results for molecules, and we (with Olle) developed a full-potential LMTO code for small molecules and clusters [40]. These calculations led to good geometries and reasonable binding energies in most cases. In spite of the shortcomings of the local density description of E_{xc}, it was now possible to perform calculations without adjustable parameters on families of molecules and small clusters that had previously been inaccessible. I was almost unprepared for so many really exciting results, my own examples including the trends in the binding energies of group 2 dimers [41, 42] and the structures of small phosphorus clusters [43]. Most condensed matter physicists were either not surprised or not interested, but theoretical chemists remained sceptical or critical, and this situation continued throughout the 1980's and into the 1990's.

The Seventh International Congress of Quantum Chemistry, held in Menton, France, from 2-5 July 1991, marks for me a major turning point in the fortunes of DF methods in chemistry. Density-related methods were discussed in detail, and communication between their proponents and the sceptics improved. Becke described his development of a non-local exchange functional that promised improvements over local approximations [44], and this approximation was tested

for the atomization energies of small molecules immediately after the meeting. Many will have been surprised by the results [45]:

> " In summary, these initial results indicate that DFT is a promising means of obtaining quantum mechanical atomization energies; here, the DFT methods B-VWN and B-LYP outperformed correlated ab initio methods, which are computationally more expensive."

and [46]

> " The density functional vibration frequencies compare favorably with the ab initio results, while for atomization energies two of the DFT methods give excellent agreement with experiment and are clearly superior to all other methods considered."

The ab initio methods mentioned were Hartree-Fock, second order Møller-Plesset (MP2), and quadratic configuration interaction with single and double substitutions (QCISD). In addition to the growing body of results on molecules and clusters that were beyond the scope of calculations of correlated wave functions, this change in attitude by one of the most prominent theoretical chemists led to a dramatically new attitude towards the DF method in chemistry.

5.3   Progress to 1990

The number of citations to density functional theory and related topics was very small prior to 1990 and exploded thereafter (see Figure 4). However, work was already in place by 1990 that has proved to be crucial to the ultimate acceptance of the method, and I now outline some of it. More details can be found elsewhere [8, 47].

The generalizations to finite temperatures and to spin systems were carried out soon after the original work of Hohenberg and Kohn [31]. The former was provided by Mermin [48], who 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_{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_{xc} replaced by the exchange-correlation contribution to the free energy.

The extension to spin systems [49] 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_{ext} by $V_{\text{ext}}^{\alpha\beta}(\mathbf{r})$, and the charge density $n(\mathbf{r})$ by the density matrix $\rho_{\alpha\beta}(\mathbf{r}) = \langle \Psi | \psi_\beta^+(\mathbf{r})\psi_\alpha(\mathbf{r}) | \Psi \rangle$. All ground state properties are functionals of $\rho_{\alpha\beta}$, and E is stationary with respect to variations in $\rho_{\alpha\beta}$. The expression for the energy E_{xc} is analogous to Equations (17,18). A current- and spin density functional theory of electronic systems in strong magnetic fields was formulated by Vignale and Rasolt [50]. Time-dependent density functional theory, which has proved to be valuable in discussing excited states, was described by Runge and Gross [51].

Most of the early DF calculations on small clusters and molecules used the LD and/or LSD approximations. Although the results were generally encouraging, it was soon clear that local density calculations can lead to unacceptable errors. Examples were the exchange energy difference between states with different nodal structures [52], including the s-p promotion energies

in first-row atoms, particularly O and F. Dispersion forces – the weak, non-local interactions between closed shells systems – are a particular problem for such approximations. 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$_2$ [41]. It is not surprising that new approximations were developed, and corrections involving density gradients were soon available for the correlation [53, 54] and exchange energies [44]. The semi-empirical exchange energy approximation of Becke [44] had the correct asymptotic behaviour for atoms.

The combination of DF calculations with molecular dynamics (Car-Parrinello method) [55] 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. My 1991 article [56] showed that unexpected structures could result. An essential part of DF work prior to 1990 was, of course, the gradual generation of a data base of results for molecules and clusters.

6   After the breakthrough

There have been over 134,000 publications on the topics "density functional" and "DFT" between 1990 and May 2013 (Figure 4), and I leave detailed surveys of this vast literature to others. I mention here some aspects that should be of general interest and give an example of the possibilities provided by the combination of DF calculations with molecular dynamics.

6.1   Progress and problems

One of the first signs of growing acceptance of DF methods in chemistry was the incorporation of such calculations into popular ab initio program packages, with Gaussian leading the way. It seems that Michael Frisch, first author of that package, was a willing convert. At the end of a talk at the ACS National Meeting in San Francisco (13 April 1997) on "Ab initio calculations of vibrational circular dichroism and infrared spectra using SCF, MP2, and density functional theories for a series of molecules," an unknown (to me) member of the audience asked:

> " What about Hartree-Fock?"

I wrote his answer down without delay:

> " It does not matter what you want to calculate, and it does not matter what functional you
> use; density functional results are always better than Hartree-Fock."

The availability of such codes and the possibility of comparing the results of different types of calculation were important to establishing the credentials of DF calculations in chemistry.

There has been progress in all the above areas. Time-dependent DF theory has become a standard way to calculate excited states and is an option in most DF program packages. The number of publications in a year that use the Car-Parrinello method has grown nearly linearly from

almost zero in 1990 to 1400 in 2012 [39]. The combination of DF calculations for a chemically active region with classical molecular dynamics for the surrounds (the "QM/MM approach") [57] has found applications in many systems in biology, as well as organic and solid state chemistry [58]. Classical force fields that lead to simulations with near-DF accuracy can be developed by a neural network representation of the results of (many) DF calculations on small systems [59]. There are lengthy reviews of orbital-dependent (and other) density functionals [60] and constrained density functional theory [61]. The random phase approximation (RPA) is being tested in various contexts [62, 63].

These and other developments are very welcome, but they do not hide the fact that the most contentious issue has been the development of approximations to the exchange-correlation energy that overcome the weaknesses of the local density approximations. The LD (Eq. (13)) and LSD (Eq. (14)) approximations lead to overbinding of many molecules, poor exchange energy differences if the nodal structures of the orbitals change, and the Kohn-Sham eigenvalues often underestimate measured optical band gaps. Nevertheless, calculations that used them provided insight into many physical problems, and the reasons for the errors (and ways to assess their magnitude) became clear. However, if insight is not enough and reliable *numbers* are needed, improved approximations are necessary.

The first generalized gradient approximations [44, 53, 54] did lead to better results, and hybrid functionals including exact exchange were introduced by Becke in 1993 [64]. This form of E_{x} has three parameters, and its combination with E_{c} of Lee, Yang, and Parr [54] (B3LYP) is still the most common approximation used in chemical applications [65]. 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 is understandable [66]. The additional parameters led to improvement over the LD and LSD results, and the use of "training sets" of atomic and molecular systems to optimize the parameters improved the calculated results for particular sets of molecules [67].

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" built on the experience of lower level and satisfies particular physical constraints. 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, built on both. The agreement with experiment improves (and the complexity of the calculations increases) as one climbs the "ladder" [70].

Two areas have remained particular challenges for DF calculations. The first are the weak dispersion or van der Waals forces mentioned above, where there has been substantial progress during recent years. The development of a functional that changes seamlessly on going from weakly interacting units to a combined system has been a goal of many, and one successful project has been that of Langreth and coworkers [71]. Their functional incorporates results for electron gas slabs and the electron gas itself, is free of experimental input, and has been implemented in several program packages. An empirical correction to DF results has been
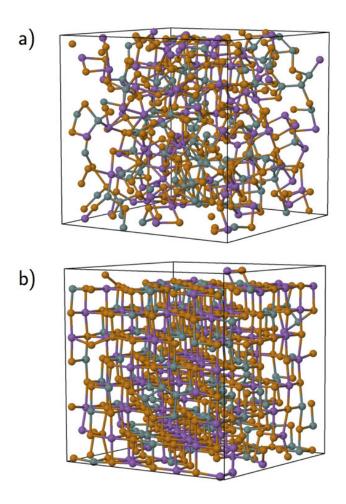
Fig. 5: *Crystallization in GST alloy at 600 K. (a) Amorphous structure after 215 ps, (b) crystalline structure after 1045 ps. Green: Ge, purple: Sb, Orange: Te.*

made by Grimme [72], and an alternative has been suggested by Tkatchenko and Scheffler [73].

"Strongly correlated" systems are those where the interaction energy dominates over the kinetic energy and often involve transition element or rare earth atoms. Local density approximations can give qualitatively incorrect descriptions of these materials, and the use of model Hamiltonians has been a popular way to avoid them. A common approach has been to add an on-site Coulomb repulsion ("Hubbard U") in the "LSD+U" scheme [74, 75]. The parameter U can be estimated within a DF framework [75, 76] or fit to experiment.

There are developments in the quantum Monte Carlo (QMC) studies of *interacting* electron systems that could be relevant for future DF work. The full configuration interaction (FCI) implementation of QMC has been applied recently to the homogeneous electron gas [77] and to simple solids [78]. Condensed matter scientists have much experience with periodic boundary conditions and plane wave orbital expansions, and this should aid the implementation of the method in extended systems. Another example is the reformulation of the constrained search approach in DF theory [32, 33] in terms of the density *and* the $(N-1)$-conditional probability density, which can be treated by ground state path integral QMC [79]. It remains to be seen

whether the computational demands usually associated with QMC can be reduced.

The terms "ab initio" and "first principles" are used differently in the "chemical" and "materials" worlds. For most chemists, the expressions means solutions of the Schrödinger equation for the system of interacting electrons (e.g. by QMC), for materials scientists it can be a DF calculation without (or even with) adjustable parameters. I carry out "density functional" calculations and describe them as such, and I am happy to use the term "ab initio" for solutions of the Schrödinger equation, as done by chemists.

6.2   An application

The results of one DF simulation in materials science using the PBE functional [68] show the scale of DF simulations that are possible today. Phase change (PC) materials are alloys of chalcogens (group 16 elements) that are ubiquitous in the world of rewritable optical storage media, examples being the digital versatile disk (DVD-RW) and Blu-ray Disc. Nanosized bits in a thin polycrystalline layer are switched reversibly and extremely rapidly between amorphous and crystalline states, and the state can be identified by changes in resistivity or optical properties. Crystallization of the amorphous bit is the rate-limiting step in the write/erase cycle, and much attention has been focused on this process. Alloys of Ge, Sb, and Te are often used in PC materials, and 460-atom simulations have been carried out at 600 K on amorphous $Ge_2Sb_2Te_5$ [80] (Fig. 5). Crystallization takes place in just over 1 ns, and it is possible to monitor changes in the distribution of the cavities, the diffusion of atoms of the different elements, and percolation of crystalline units in the sample. These calculations involve over 400,000 (!) self-consistent DF calculations of structure, energies, and forces for a 460-atom sample. The steady (and essential) improvement in numerical algorithms has played an important role, but such calculations also require computers of the highest performance class.

7   Summary and outlook

The astonishing growth of density functional calculations since 1990 resulted in the award of the 1998 Nobel Prize for Chemistry to Walter Kohn. Although he noted that "very deep problems" remain, Philip Anderson felt that this award may indicate that [81]

> "the labours and controversies . . . in understanding the chemical binding in materials had finally come to a resolution in favour of 'LDA' and the modern computer",

The LD and LSD approximations have well documented drawbacks, and the resulting *numbers* (binding energies, band gaps, . . .) should be treated with caution. However, the approximations satisfy important physical criteria, such as the sum rule on the exchange-correlation hole, and our long experience with them helps us to judge when the results may be wrong and by how much. The bonding *patterns* are correct in most cases, which is no doubt one reason why LD approximations and their modifications are still in widespread use. They make possible the simultaneous study of numerous related systems, such as families of molecules or materials, with

the computational resources needed to determine the wave function of a single much smaller system.

This pragmatic approach seems to be giving way to the search for schemes that produce better *numbers* automatically, preferably without having to worry about the nature of the system or the bonding mechanism involved. The long and growing list of approximate functionals and countless publications comparing their predictions with each other and with experiment have led to a chaotic situation. A newcomer to the field must despair of understanding why one approximation should be favoured over another or the real physical reasons behind a particular result. Are DF calculations in chemistry now following the "Dream Machine" scenario foreseen for the solid state world by Anderson in 1980? [38]. Furthermore, a comparison of the band gaps in LiH and four alkali halides, four oxides, and solid Ne and Ar (gaps between 0.2 and 20 eV) with the predictions of many popular functionals [82] showed that the identification of the "best" functional depends on the choice of statistical measure (mean error, mean absolute error, variance, ...)!

Density functional theory deserves better than to be a background justification for empirical curve fitting, which clearly implies a lack of confidence in the theory, or the development of a never ending chain of approximations seeking the "right" numbers, with less concern for their physical origin. It is a wonderful development with a long and fascinating history involving some of the best known names in physics. It may not provide precise answers to some questions using simple descriptions of the exchange-correlation energy, but its ability to outperform methods that seek exact solutions of the Schrödinger equation is not threatened. We shall continue to obtain insight into all sorts of problems that we cannot imagine today.

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* (see, for example, Sec. 4.2) 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.

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