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Density Functional Theory: Past, present, ... future?

R. O. Jones[1]

Peter-Grünberg-Institut PGI-1 and German Research School for Simulation Sciences,
Forschungszentrum Jülich, D-52425 Jülich, Germany.

Abstract

In little more than 20 years, the number of applications of the density functional (DF) formalism in chemistry and materials science has grown in astonishing fashion. The number of publications alone shows that DF calculations are a huge success story, and many younger colleagues are surprised to learn that the real breakthrough of density functional methods, particularly in chemistry, began only after 1990. This is indeed unexpected, because the origins are usually traced to the papers of Hohenberg, Kohn, and Sham more than a quarter of a century earlier. Olle Gunnarsson and I reviewed the DF formalism, its applications, and prospects for this journal as we saw them in 1989, and I argued shortly afterwards in *Angewandte Chemie* that combining such calculations with molecular dynamics should lead to an efficient way of finding molecular structures. Here I take that time (1990) as fixed point, review the development of density related methods back to the early years of quantum mechanics and follow their breakthrough after 1990. The two examples from biochemistry and materials science are among the many current applications that were simply beyond our dreams in 1990. I discuss the reasons why - after two decades of rapid expansion - some of the best-known practitioners in the field are concerned about its future.

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[1] r.jones@fz-juelich.de

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R. O. Jones*

Peter-Grünberg-Institut PGI-1 and German Research School for Simulation Sciences,
Forschungszentrum Jülich, D-52425 Jülich,
Germany.

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In little more than 20 years, the number of applications of the density functional (DF) formalism in chemistry and materials science has grown in astonishing fashion. The number of publications alone shows that DF calculations are a huge success story, and many younger colleagues are surprised to learn that the real breakthrough of density functional methods, particularly in chemistry, began only after 1990. This is indeed unexpected, because the origins are usually traced to the papers of Hohenberg, Kohn, and Sham more than a quarter of a century earlier. Olle Gunnarsson and I reviewed the DF formalism, its applications, and prospects for this journal as we saw them in 1989, and I argued shortly afterwards in *Angewandte Chemie* that combining such calculations with molecular dynamics should lead to an efficient way of finding molecular structures. Here I take that time (1990) as fixed point, review the development of density related methods back to the early years of quantum mechanics and follow their breakthrough after 1990. The two examples from biochemistry and materials science are among the many current applications that were simply beyond our dreams in 1990. I discuss the reasons why – after two decades of rapid expansion – some of the best-known practitioners in the field are concerned about its future.

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I. INTRODUCTION

The density functional (DF) formalism shows that ground state properties of a system of electrons in an external field can be determined from a knowledge of the *electron density distribution* $n(\mathbf{r})$ alone. Thomas (Thomas, 1927) and Fermi (Fermi, 1928) recognized the basic nature of the electron density, and Dirac (Dirac, 1930) noted already in 1930 that the state of an atom is determined completely by its density; one does not need to know the much more complicated many-electron wave function. This remarkable result was found in the context of "self-consistent field" (Hartree-Fock) theory.

My main focus here is on a property for which DF calculations are particularly valuable in chemistry and materials science: the total energy E of a system of electrons in the presence of ions located at R_{I}. Accurate calculations of the entire energy surface $E(R_{\mathrm{I}})$ are possible with traditional (wave function based) methods only for systems with very few atoms, and $E(R_{\mathrm{I}})$ 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 energies. The observation of Francis Crick in his autobiography (Crick, 1988):

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* Electronic address: r.jones@fz-juelich.de

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

may be self-evident to anyone interested in biology or molecules in general, but it is 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.

Olle Gunnarsson and I reviewed the DF formalism, its history, and its prospects in 1989 (Jones and Gunnarsson, 1989), and I took a similar perspective in numerous seminars. A more careful reading of the original literature some years ago caused me to change the format, and I trace DF history here from the first years after the development of quantum mechanics. It is a fascinating story with many players, and I quote in several places from the original texts.

Density functional calculations are well established *now* in condensed matter physics and chemistry, but they did not (and do not) find universal acceptance. The choice of 1990 as fixed point coincides with the publication of the review (Jones and Gunnarsson, 1989) and my article in *Angewandte Chemie* (Jones, 1991), where I advocated DF calculations in the context of molecular studies, particularly when combined with molecular dynamics (Car and Parrinello, 1985). As shown in Fig. 1 (Mavropoulos, 2014), it also marks the dramatic increase in the number of publications on density functional topics in recent years.[1] Figure 1 shows clearly two other features: there were *three times* as many publications in 1991 than in 1990, and there was almost no published work claiming to be "density functional" or "DFT" beforehand. In 1985, twenty years after its modern formulation and in the year that the combined DF/MD approach (Car and Parrinello, 1985) was formulated, there were just 77 publications! In this article, I revisit the period before 1990 and focus on aspects of the development since then. Recent perspectives on density functional theory have been given by Kieron Burke (Burke, 2012) and Axel Becke (Becke, 2014), and much more detailed information is available in monographs and review articles cited there. A recent issue of the Journal of Chemical Physics celebrates fifty years of density functional theory, and the articles range across many topics of current interest (Yang, 2014). A recent review of solid state applications of DF theory is provided by (Hasnip *et al.*, 2014). I have used numerous citations of participants in (and observers of) this story to illustrate how perspectives of the approach have changed over time. The two applications I discuss are DF simulations of systems that were unimaginable only a few years ago.

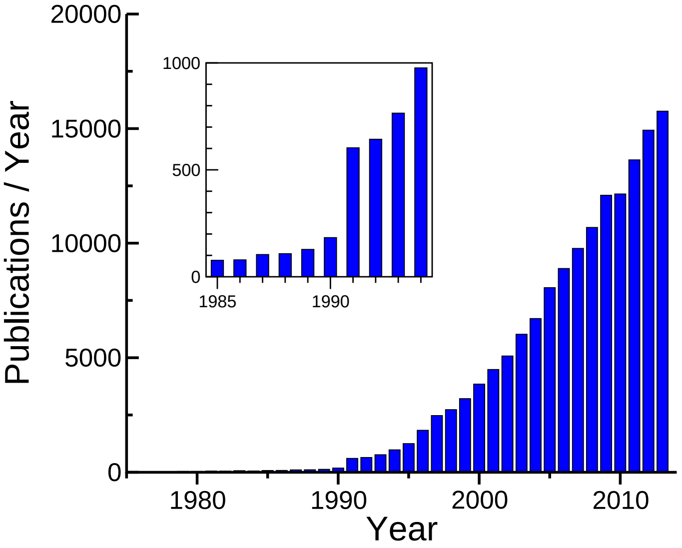

FIG. 1 (Color online) Number of publications per year (1975-2013) on topics "density functional" or "DFT", according to Web of Knowledge (July 2014). Inset shows data near 1990 on an expanded scale (Mavropoulos, 2014).

I have several goals in writing this review. The huge growth in the DF literature is only possible if many newcomers are entering the field. This review is written for them and for those in other areas of science who are curious about the DF world. I hope that all share my fascination with the formalism and its history. However, personal contacts over the years have shown that not only newcomers are unfamiliar with the past or the reaction of different scientific communities as the theory developed. Density related methods are also important in other areas, including classical systems and nuclei, and I encourage readers to look beyond the horizons of their particular interest. Finally, I note that both Burke (Burke, 2012) and Becke (Becke, 2014) are uneasy about some recent developments, and I shall raise my own questions about the future.

II. THE DENSITY AS BASIC VARIABLE

The recent books by Gino Segrè (Segrè, 2007) and Graham Farmelo (Farmelo, 2009) give fascinating accounts of the development of quantum mechanics in the years following 1926. Methods for finding approximate solutions of the Schrödinger equation followed soon after the equations were published and have had a profound effect on chemistry and condensed matter physics ever since.

A method for calculating the wave function of an atom was developed by Hartree (Hartree, 1928a,b). The "Hartree approximation" to the many-electron wave function is a product of single-particle functions,

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

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[1] A similar plot is given by Burke (Burke, 2012) for two popular approximations used in DF calculations.

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 (Hartree, 1928a) introduced the idea of a "self-consistent field", with specific reference to the core and valence electrons, but neither paper mentions the approximation (1). Slater (Slater, 1930) and Fock (Fock, 1930) recognized soon afterwards 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 (Fock, 1930; Slater, 1930) 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 (Slater, 1929) and ferromagnetism (Bloch, 1929), 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 (Dirac, 1929):

> "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."

Dirac emphasizes the difficulty of solving the equations of quantum mechanics and the desirability of developing "approximate practical methods of applying quantum mechanics" to explain complex systems. I cannot think of a better short description of density functional theory.

Dirac (Dirac, 1930) also sought to improve the model of Thomas (Thomas, 1927) and Fermi (Fermi, 1928) for calculating atomic properties based purely on the electron density $n(\mathbf{r})$.[2] 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 $n(\mathbf{r})$. The TF equations are:

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

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 (Dirac, 1929), and he included these effects in the "Thomas atom" (Dirac, 1930) by means of the potential

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

This term was derived for a homogeneous electron gas of density n and should be valid for weak spatial variations of $n(\mathbf{r})$.[3]. 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 (Lieb, 1981; Schwinger, 1980; Spruch, 1991) However, it has severe deficiencies. The charge density is infinite at the nucleus and decays as r^{-6}, not exponentially, far from it. Teller (Teller, 1962) also showed that TF theory does not bind neutral atoms or (with some restrictions) ions 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, and no ferromagnetism (Jones and Gunnarsson, 1989). Moreover, atoms *shrink* with increasing Z (as $Z^{-1/3}$) (Lieb and Simon, 1973).

One point made by Dirac (Dirac, 1930), 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

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[2] Fermi later extended the model to positive ions and spectroscopic energy levels. It has been pointed out recently (Guerra and Robotti, 2008) that the extension to positive ions and to Rydberg corrections was described by Majorana already in 1928 (an English translation is provided in (Guerra and Robotti, 2008)).

[3] The exchange energy in a homogeneous electron gas had been derived by Bloch (Bloch, 1929) already in 1929.

> 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, but the observation that the density follows the equations of motion is much in the spirit of Ehrenfest's theorem (Ehrenfest, 1927), which has wider validity. Ehrenfest had proved in 1927 what has been termed the "time-dependent Hellmann-Feynman theorem" (Hayes and Parr, 1965), 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 have a clear picture of its nature in real systems. In Fig. 2, we show the spherically averaged density in the ground state of the carbon atom. The density 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. We must also recognize that the electron density in molecules and solids 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 astonishing that this suffices to determine ground state properties.

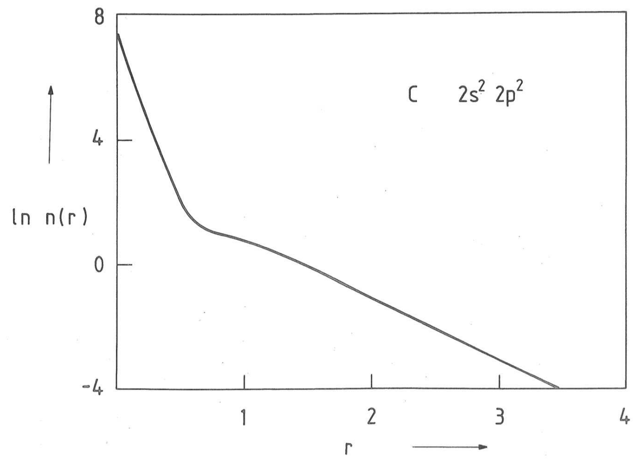

FIG. 2 Logarithm of spherical average of density in ground state of C atom as a function of the distance from the nucleus (atomic units) (Jones and Gunnarsson, 1989)

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

Wigner and Seitz (Wigner and Seitz, 1933, 1934) 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 replaced the nucleus and core electrons by an effective (pseudo-) potential, 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 spin components a distance r apart (Fig. 3). 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" $(\frac{3}{8\pi})^{\frac{1}{3}}\,d = 0.492\,d$. The exclusion principle means then that two electrons with parallel spin components will usually be associated with different ions (Wigner and Seitz, 1933). 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 (Slater, 1934). Similar views of electrons in metals have been given by Brillouin (Brillouin, 1934) and Wigner (Wigner, E., 1934).

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" (Wigner and Seitz, 1933) or "exchange" hole (Slater, 1951). The hole is of crucial importance to DF theory and plays a central role in the discussion below. In the Hartree-Fock scheme, the exchange hole is different for each electronic function, but Slater (Slater, 1951) developed a simplified

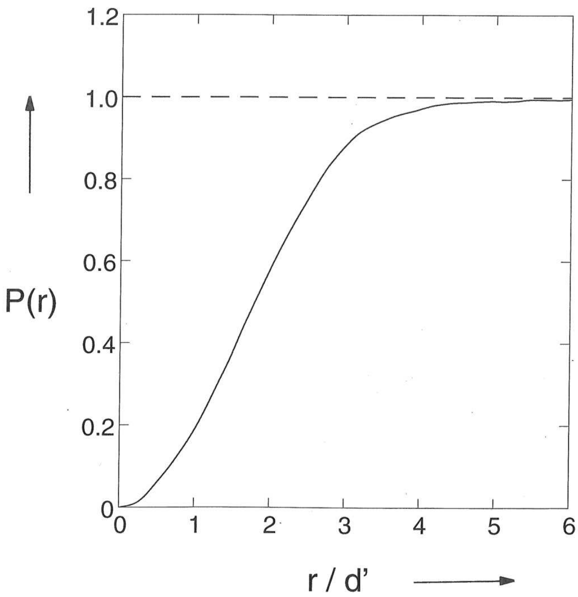

FIG. 3 Probability that electrons with parallel spins are r/d' apart in Na metal ($d'^3 = V_0/(3\pi^2)$, V_0 is the atomic volume). Adapted from Wigner and Seitz (Wigner and Seitz, 1933)

"exchange potential" that depended only on the density[4]

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

Sharp and Horton (Sharp and Horton, 1953) noted the advantages of an effective potential that is the same for all electrons and constructed an "optimized effective potential" (OEP) by varying the potential to optimize the energy. A Slater determinant constructed from the one-electron functions was used as the wave function of the system. Talman and Shadwick (Talman and Shadwick, 1976) showed that this effective potential has the correct asymptote far from an atom. The OEP is often discussed in the context of DF calculations, but it is an independent development.

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) (Slater, 1937) and Korringa-Kohn-Rostoker (KKR) approaches (Kohn and Rostoker, 1954; Korringa, 1947).

The exchange potential of Slater (4) is 3/2 times that derived by Dirac and Bloch (3) for a homogeneous electron gas, but Slater (Slater, 1968) 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 homogeneous electron gas arguments used in the original derivation (Slater, 1951). 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 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 (Slater, 1972b) to counter a (still widespread) misconception that local density approximations are only valid if the electron density is nearly homogeneous.

In 1954, Gáspár (Gáspár, 1954) 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" (Slater, 1974), and he adopted the procedure in his later work (Slater, 1972a):

> "There are important advantages in the Gáspár-Kohn-Sham procedure of using a statistical expression for total energy and varying the orbital to minimize the energy, and we shall henceforth adopt this approach."

However, he preferred to multiply this contribution to the energy with an adjustable parameter α ($\alpha = 2/3$ gives the exchange energy of a homogeneous electron gas), and the approximation was known as the "$X\alpha$ method" (see Sec. IV.B).

Slater and Gáspár were not alone in their focus on the density. The "Hellmann-Feynman theorem" (Feynman, 1939; Hellmann, 1933, 1937) (see Appendix A)[5] considered forces in molecules, and Berlin (Berlin, 1951) developed this to separate space near a diatomic molecule into

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[4] Slater wrote in this paper: "The discussion of Wigner and Seitz was one of the first to show a proper understanding of the main points taken up in this paper, which must be understood to represent a generalization and extension of previously suggested ideas, rather than an entirely new approach. See also (Brillouin, 1934) for a discussion similar to the present one." Slater was more generous to his predecessors than some later authors were to him.

[5] An interesting account of the history of the Hellmann-Feynman theorem and its mathematical complexities is given in (Pupyshev, 2000).

"binding" and "antibinding" regions according to the electrostatic interaction between between the nuclei and the electron charge distribution. The Hellmann-Feynman equations apply only to the exact wave function of the system. In his "electrostatic method", however, Hurley (Hurley, 1954a,b,c) showed that force calculations could be performed with approximate wave functions if *all* variable parameters in the wave function for a molecule were chosen variationally. The procedure is simplified if the parameters do not depend on the nuclear configurations, and he described such functions as "floating functions". This approach has proved to be fruitful in many contexts, including dispersion interactions (Strømsheim, M. D. and Kumar, N. and Coriani, S. and Sagvolden, A. M. and Helgaker, T., 2011). It was around this time that Richard Bader began his studies of the topology of the density distribution that he pursued for many years (Bader, 1990).

A variant of the Hellmann-Feynman theorem with a variable nuclear charge Z was used by Wilson (Wilson, 1962) to show that the ground state energy of a system of electrons in the field of a set of fixed nuclei can be calculated if the electron density is known sufficiently accurately as a function of the spatial coordinates x, y, z *and* the parameter Z from 0 (non-interacting system) to 1 (physical system). He concluded with the question:

> "The important question remains: Does there exist some procedure for calculating (the density) ρ which avoids altogether the use of $3N$-dimensional space? Such a procedure might open the way to an enormous simplification of molecular calculations. For example, it would be tremendously simpler to expand a four dimensional function than a $3N$-dimensional wave function."

He did not have to wait long.[6]

IV. 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 (Hohenberg and Kohn, 1964). The ground state (GS) properties of a system of electrons in an external field $V_{\rm ext}$ 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 $E[n, V_{\rm ext}]$ satisfies a variational principle. These theorems were proved by Hohenberg and Kohn (Hohenberg and Kohn, 1964) for densities that can be derived from the ground state of some external potential $V_{\rm eff}$ ("V-representable"). In the spirit of the definition by Percus of a universal kinetic energy functional for non-interacting systems (Percus, 1978), Levy provided a simpler and more general proof for ("N-representable") densities that can be derived from some antisymmetric wave function (Levy, 1979). Lieb (Lieb, 1983) extended the "constrained search" arguments by introducing the Legendre transform of the energy as the universal functional. The use of the variational principle in these works goes beyond the insights of Dirac (Dirac, 1930) and Wilson (Wilson, 1962) in providing a method for determining the density. Of course, these proofs do not provide practical prescriptions for writing the functional relationship between energy E and density n.

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

The task of finding good approximations to the energy functional $E[n, V_{\rm ext}]$ is simplified greatly if we use the decomposition introduced by Kohn and Sham (Kohn and Sham, 1965),

$$E[n] = T_0[n] + \int d\mathbf{r}\; n(\mathbf{r})\Big(V_{\rm ext}(\mathbf{r}) + \frac{1}{2}\phi(\mathbf{r})\Big) + E_{\rm xc}[n]. \quad (6)$$

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 $E_{\rm xc}$ *defines* the exchange-correlation energy.[7] 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 $E_{\rm xc}$ can be evaluated exactly, so that approximations for this term are crucial in density functional applications.

The variational principle applied to (6) yields

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

where μ is the Lagrange multiplier associated with the requirement of constant particle number. If we compare

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[6] I understand that density functional theory came as no surprise to Wilson: If we know the density distribution, we can find its cusps, from which we can determine (from the electron-nucleus cusp condition, (Kato, 1957)) both the location of the nuclei and their atomic numbers. Integration over the electron density gives the total charge, so that we have all the terms in the Hamiltonian. This non-relativistic argument assumes point nuclei and the Born-Oppenheimer approximation. See also (Handy, 2009).

[7] In the world of wave functions, the "correlation energy" is defined as the difference between the *exact* and Hartree-Fock (single Slater determinant) energies.

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

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

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 functions ψ_i are single Slater determinants, and 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 (Gunnarsson and Lundqvist, 1976) and other systems with constraints (Dederichs *et al.*, 1984). 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,

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

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

The numerical advantages of solving the Kohn-Sham equations (Kohn and Sham, 1965) are obvious. Efficient methods exist for solving (self-consistently) single-particle Schrödinger-like equations with a local effective potential, and there is no restriction to small systems. With a local approximation to $E_{\rm xc}$, the equations can be solved as readily as the Hartree equations. Unlike the Thomas-Fermi method, where the large kinetic energy term is computed directly from the density, the kinetic energy term is computed from orbitals ψ_i in Eq. (10). The core-valence and valence-valence electrostatic interactions can be evaluated directly, but $E_{\rm xc}$ is the difference between the *exact* energy and terms we can evaluate accurately, and approximations are unavoidable.

B. Exchange-correlation energy $E_{\rm xc}$

Kohn and Sham (Kohn and Sham, 1965) proposed using the "local density (LD) approximation"

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

where $\varepsilon_{\rm xc}[n]$ 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 (Kohn and Sham, 1965):

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

Whether this is true or not depends, of course, on the definition of "accurate", but I sometimes feel that it set back chemical applications of DF theory by a decade or more.

Generalizations to spin-polarized systems were given by Barth and Hedin (von Barth and Hedin, 1972) and Rajagopal and Callaway (Rajagopal and Callaway, 1973). We write

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

where $\varepsilon_{\rm xc}[n_\uparrow, n_\downarrow]$ is the exchange and correlation energy per particle of a homogeneous, spin-polarized electron gas with spin-up and spin-down densities $n_\uparrow$ and $n_\downarrow$, respectively (von Barth and Hedin, 1972).[8] The "Xα" approximation

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

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 Bloch (Bloch, 1929), Dirac (Dirac, 1930), Gáspár (Gáspár, 1954), and Kohn and Sham (Kohn and Sham, 1965). 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 $E_{\rm xc}$ using arguments closely related to the "exchange hole" picture of Wigner and Seitz (Wigner and Seitz, 1933) and Slater (Slater, 1934, 1951, 1968).

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[8] The calculation by Bloch (Bloch, 1929) of ferromagnetism in a homogeneous, spin-polarized 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 $n_\downarrow^{4/3}$.

C. Exchange-correlation hole and E_{xc}

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).

Two equivalent ways of doing this have proved useful in the DF context. The first (Harris and Jones, 1974) considers the Hamiltonian

$$H_\lambda = T + V_{\mathrm{KS}} + \lambda(V_{\mathrm{ee}} + V_{\mathrm{ext}} - V_{\mathrm{KS}}), \tag{16}$$

where V_{KS} is the Kohn-Sham effective potential. This construction reduces the qualitative difference between the eigenfunctions ψ_0 and ψ_λ and guarantees that the densities of the non-interacting and interacting systems are the same. It leads to an expression for the total energy E and its components, including the exchange and correlation energies, in terms of integrals over λ.[9] One term can be related to the energy due to density fluctuations in the system and the density response function of a system of electrons described by H_λ, and all terms were evaluated for a model of a bounded electron gas (Harris and Jones, 1974).[10]

This approach, in which the density is constrained to be the physical density of the system for $\lambda = 0$ and 1, but not for intermediate values, can be implemented in standard program packages and provides detailed information about the density functional in small systems (Savin *et al.*, 1998). It is possible, however, to add an external potential V_λ such that the ground state of the Hamiltonian H_λ has density $n(\mathbf{r})$ for *all* λ (Gunnarsson and Lundqvist, 1976; Langreth and Perdew, 1975).[11] The exchange-correlation energy of the interacting system can then be expressed as an integral over the coupling constant λ (Gunnarsson and Lundqvist, 1976):

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

with

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

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 (Wigner and Seitz, 1933, 1934) and Slater (Slater, 1934, 1951) 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,

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

This leads to

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

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} (Gunnarsson and Lundqvist, 1976). 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 Fig. 4, 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 centered 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.

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[9] This appears to be the first use of "adiabatic connection" in the DF context. The derivative of the Hamiltonian with respect to a parameter and the integral form that follows are often attributed to Pauli (Pauli, 1933) [see (Musher, 1966) and references therein]. Pauli himself (Pauli, 1933) (p. 161) gives the credit to his student Paul Güttinger (Güttinger, 1931). See Appendix A.

[10] This calculation was motivated in part by our feeling that the LD approximation would not describe well the surface energy of a bounded electron gas. Our estimates of the exchange and correlation contributions were individually very different from the LD results, but the *sum* of the two components was very similar.

[11] It has been shown (Colonna and Savin, 1999) that results for the He and Be series atoms using the two schemes are very similar.

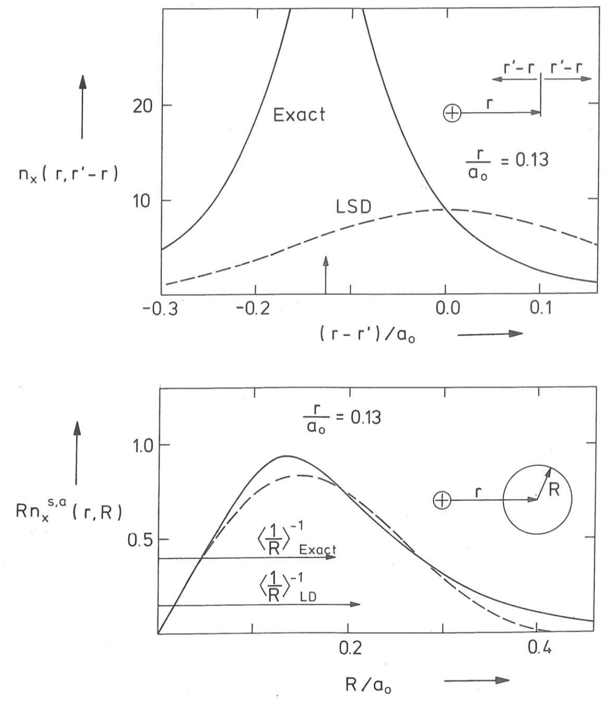

FIG. 4 Exact (solid) and LSD (dashed) exchange holes $n_{\rm xc}(\mathbf{r},\mathbf{r}'-\mathbf{r})$ for spin up electron in N atom for $\mathbf{r} = 0.13$ a.u. Upper: hole along line through nucleus (arrow) and electron ($\mathbf{r}-\mathbf{r}' = 0$). Lower: spherical averages of holes, and $\langle 1/\mathbf{R}\rangle$ (21) (Jones and Gunnarsson, 1989).

V. DF THEORY TO 1990

A. 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 "Xα" or "Hartree-Fock-Slater" calculations into the density functional world. I was so encouraged by our own results that I wrote an article in 1984 proposing the DF approach as *the* method for calculating bonding properties (Jones, 1984a). Nevertheless, Fig. 1 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 (Heine, 2002):

> "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 (Anderson, 1980):

> "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."

This article "never found a publisher" in the US (Anderson, 2011c), and the only version in print is in French (Anderson, 1980). Anderson associated the "Dream Machine" with the name of John Slater (Anderson, 2011c) 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" (Anderson, 1980). 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."

These comments may sound harsh to some,[12] but they did apply to some electronic structure calculations at the time. They may indeed have had prophetic character, as I discuss in Sec. IV.B. The increasing availability of computing resources allowed calculations that had previously been impossible, and not all users of the method were critical of the approximations involved.

B. Chemistry

It took many years for DF calculations to be taken seriously by most chemists,[13] and the reasons were often

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[12] He referred later to "the oxymoron 'computational physics'" (Anderson, 1999) and wrote that ". . . more recently 'theoretical chemistry' has become a service skill" (Anderson, 2011a)).

[13] Walter Kohn summarizes his own experiences, particularly with John Pople, in (Kohn and Sherrill, 2014). For some of my own,

convincing: (1) Unlike the TF theory, the Kohn-Sham expression for the energy is not an explicit "functional" of the density, since the kinetic energy term 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 (Levy, 1982; Lieb, 1983),[14] (3) approximations to the exchange-correlation energy are unavoidable, and their usefulness can be assessed only by trying them out. Approximations based on calculations for a homogeneous electron gas, in particular, were unfamiliar to users of atomic orbitals and the Hartree-Fock approximation.[15] (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 decade) might make the reservations of Dirac (Dirac, 1929) 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 [(Heijser *et al.*, 1976) and references therein]. The original motivation was to find a numerically efficient approximation to Hartree-Fock calculations, but it was found that $\alpha = 0.7$ gave better agreement with experiment, *if* the full potential was used, not just the "muffin-tin" component used in many "Xα" calculations at the time. Some of the first DF calculations on small molecules were performed by Olle Gunnarsson (Gunnarsson and Lundqvist, 1976). John Harris and I were sceptical that the local density approximations would give reasonable results for molecules, but we (with Olle) developed a full-potential LMTO code for small molecules and clusters (Gunnarsson *et al.*, 1977). 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 unprepared for so many exciting results, my own examples including the trends in the binding energies of group 2 dimers (Jones, 1979; Jones, R O, 2012), the energy surfaces of ozone (Jones, 1984b), and the structures of small phosphorus clusters (Jones and Hohl, 1990). Most condensed matter physicists were either not surprised or not interested, but theoretical chemists remained sceptical or critical, or they ignored the development completely. This situation continued throughout the 1980's and into the 1990's.

C. Menton, 1991

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, particularly in chemistry (Fig. 5). Density-related methods were discussed in detail, and communication between their proponents and the sceptics improved. When I asked John Pople why he did not like density functional methods, he replied that the total energies were not good enough. This cannot be denied, but I pointed out our focus on energy *differences*, such as binding energies, for which there is no variational principle. *All* such calculations rely on cancellation of errors.

FIG. 5 (Color online) Poster of Menton Congress, 1991

Axel Becke was awarded the Medal of the International Academy of Quantum Molecular Science for that year, and he described his development of an approximate functional that promised improvements over local density approximations (Becke, 1988). In his end-of-conference remarks, Pople maintained his distance from

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see (Jones, R O, 2012).

[14] However, all mathematically well-behaved densities can be obtained from an antisymmetric wave function (Harriman, 1981).

[15] Condensed matter physicists, on the other hand, were aware of the poor description of metals provided by the Hartree-Fock approximation, particularly the vanishing density of states at the Fermi energy.

density-related methods, but the comments of Roald Hoffmann immediately afterwards were more encouraging. It is certainly no coincidence that Pople and his coworkers tested this approximation on atomization energies of small molecules immediately after the meeting, but many will have been surprised by the results (Johnson *et al.*, 1992):

> "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 (Johnson *et al.*, 1993)

> "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.[16]

D. Progress to 1990

The number of citations to density functional theory and related topics was very small prior to 1990 and exploded thereafter (see Fig. 1). 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 (Dreizler and Gross, 1990; Jones and Gunnarsson, 1989).

The generalizations to finite temperatures and to spin systems were carried out soon after the original work of Hohenberg and Kohn (Hohenberg and Kohn, 1964) The former was provided by Mermin (Mermin, 1965), 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 (von Barth and Hedin, 1972; Rajagopal and Callaway, 1973) 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 $V_{\mathrm{ext}}^{\alpha\beta}(\mathbf{r})$, 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 (Vignale and Rasolt, 1988). Time-dependent density functional theory, which has proved to be very valuable in discussing excited states, was described by Runge and Gross (Runge and Gross, 1984).

Most of the early DF calculations on small clusters and molecules used the LD and/or LSD approximations, often based on the quantum Monte Carlo calculations of the correlation energy in the homogeneous electron gas by Ceperley and Alder (Ceperley and Alder, 1980). Although the results were generally encouraging, it soon became clear that local density calculations can lead to unacceptable errors. Examples were the exchange energy difference between states with different nodal structures (Gunnarsson and Jones, 1985), including the $s-p$ promotion energies in first-row atoms, particularly O and F, $s-d$ promotion energies in transition element atoms, and $d-f$ promotion energies in rare earth atoms.

Dispersion forces, the weak, non-local interactions between closed shell 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 (Jones, 1979) and crystalline polyethylene (Montanari and Jones, 1997). It is not surprising that new approximations were developed, and corrections involving density gradients were soon available for the correlation (Lee *et al.*, 1988; Perdew, 1986) and exchange energies (Becke, 1988). The semi-empirical approximation of Becke (Becke, 1988) was constructed so that the exchange energy density had the correct asymptotic behavior ($\sim r^{-1}$) for atoms.[17]

The combination of DF calculations with molecular dynamics (Car-Parrinello method) (Car and Parrinello, 1985) made simulations of bulk systems at elevated temperatures possible, and simulated annealing techniques

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[16] Although one of the authors of these papers wrote an obituary on density functional theory not long afterwards (Gill, 2001), noting 1993 as the year of its death.

[17] Although the asymptotic form of the corresponding *potential* ($\sim r^{-2}$) did not (van Leeuwen and Baerends, 1994).

could be used to study the energy surfaces of molecules and clusters. My 1991 article (Jones, 1991) 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, as well as extended systems.

VI. AFTER THE BREAKTHROUGH

There have been 150,000 publications on the topics "density functional" and "DFT" between 1990 and June 2014 (Fig. 1). I leave detailed surveys of this vast and rapidly expanding literature to others and refer again to the very recent issue of the *Journal of Chemical Physics* (Yang, 2014). The aspects I have chosen should be of general interest, but not everyone will approve of my choice. I give two examples of the possibilities provided by the combination of DF calculations with molecular dynamics.

A. 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. Michael Frisch, first author of that package, seems to have been a willing convert. At the end of his 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?"

His answer was memorable, and I wrote it down immediately:

> "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 (Botti *et al.*, 2007; Isegawa *et al.*, 2012). The number of publications in a year that use the Car-Parrinello method[18] has grown nearly linearly from almost zero in 1990 to over 1900 in 2013 (Mavropoulos, 2014). Many applications now use Born-Oppenheimer molecular dynamics, which allow substantially longer time steps in the simulations. The optimized effective potential has been extended by Krieger, Li, and Iafrate (Krieger *et al.*, 1992) and many others, and there are lengthy reviews of orbital-dependent (and other) density functionals (Kümmel and Kronik, 2008) and constrained density functional theory (Dederichs *et al.*, 1984; Kaduk *et al.*, 2012). The random phase approximation (RPA) is a long-established method for studying correlations in the homogeneous electron gas, and it has become established in the DF world (Eshuis *et al.*, 2012; Ren *et al.*, 2012; Xiao *et al.*, 2013).

The combination of DF calculations for a chemically active region with classical molecular dynamics for the surrounds (the "QM/MM approach") (Carloni *et al.*, 2002) has found applications in many systems in biology, organic, and solid state chemistry (Lin and Truhlar, 2007). 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 (Behler and Parrinello, 2007). These and other developments are very welcome, but the proliferation of approximations to the exchange-correlation energy has become the source of confusion.

1. Approximations for $E_{\rm xc}$

The local density (LD) [Eq. (13)] and local spin density (LSD) [Eq. (14)] approximations lead to overbinding of many molecules, poor exchange energy differences if the nodal structures of the orbitals change, and the corresponding 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 clearer. However, if insight is not enough and reliable *numbers* are needed, improved approximations are essential.

The first generalized gradient approximations (Becke, 1988; Lee *et al.*, 1988; Perdew, 1986) did lead to better results, and "hybrid" functionals, which include a Hartree-Fock-like exchange component, were introduced by Becke in 1993 (Becke, 1993). This form of $E_{\rm x}$ has three parameters, and its combination with $E_{\rm c}$ of Lee, Yang, and Parr (Lee *et al.*, 1988) (B3LYP) is still the most common approximation used in chemical applications (Burke, 2012). Many other empirical and hybrid functionals have been developed since, with parameters

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[18] I use this term to cover methods where the electronic and ionic degrees of freedom are propagated.

often fit to thermochemical data for particular groups of molecules. The use of experimental data for fitting functional forms may be understandable (Boese and Handy, 2001), but the result was that DF theory was now viewed by some as "semi-empirical" in nature. 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 (Zhao and Truhlar, 2008).

There is no doubt that the increased focus on Hartree-Fock-like exchange and its role in "hybrid" functionals has been one of the most significant developments in recent years. The use of the standard technique of chemists has brought the world of "chemistry" and "materials science" closer, as the need for approximations that gave satisfactory results in both areas became obvious.[19] An example of recent studies of functionals that give broad accuracy in both fields is that of Peverati and Truhlar (Peverati, R. and Truhlar, D. G., 2012). The implementation of HF-like exchange usually comes with a high computational price, especially in calculations using very large plane-wave basis sets. However, new algorithms on massively parallel computers have reduced or even eliminated this drawback (Curioni, 2013).

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 (Perdew *et al.*, 1996) (PBE) incorporates the LSD form below it, and the "meta-GGA" form of Tao, Perdew, Staroverov, and Scuseria (TPSS) (Tao *et al.*, 2003), 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 computational demands increase) as one climbs the "ladder" (Furche and Perdew, 2006). Models of the exchange-correlation hole continue to provide a way of developing DF approximations [e.g. (Giesbertz *et al.*, 2013)], and *systematic* ways of correcting for the results of DF calculations are still being pursued. A recent example is the use of multi-determinant wave functions for hybrid functionals (Savin, 2014).

2. Dispersion interactions

Two areas have remained particular challenges for DF calculations, the first being the weak dispersion or van der Waals forces mentioned above. Crystalline polyethylene, where parallel chains of covalently bonded molecules are bound by such forces (see Fig. 6) provides an example of the problems that arise.

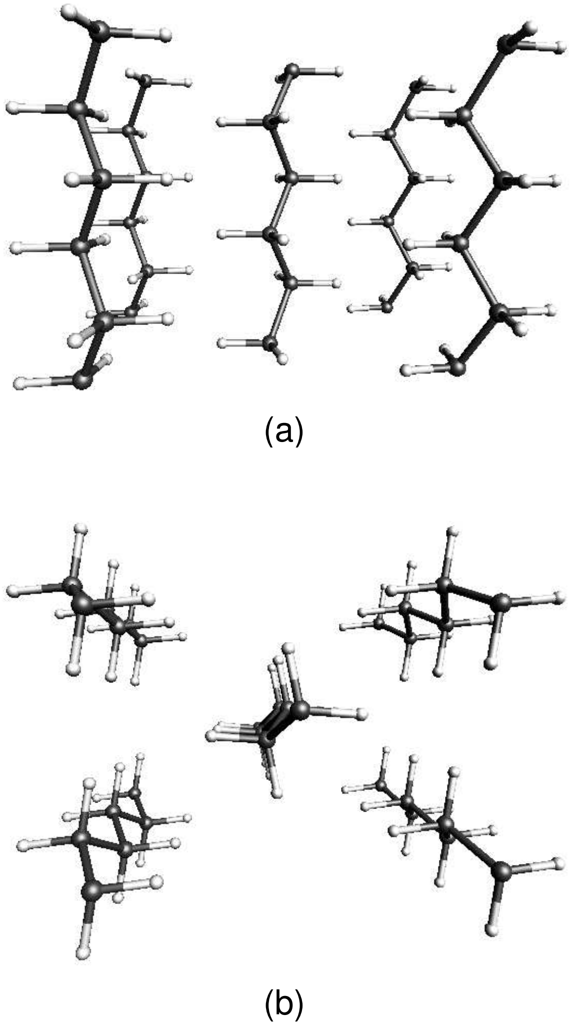

FIG. 6 View of the orthorhombic structure of polyethylene along (a) *b*-axis, (b) *c*-axis (the axis of the polymer chains) (Montanari and Jones, 1997).

The structures obtained by complete relaxation of all atomic coordinates are representative for many similar systems. First, the bond lengths in the chains are reproduced well by the LDA, PBE (Perdew *et al.*, 1996), and Becke-Perdew (Becke, 1988; Perdew, 1986) approximations (Montanari *et al.*, 1998): The C-H bonds are slightly longer than the experimental values for orthorhombic hexatriacontane $C_{36}H_{74}$ (Teare, 1959), while the C-C bond lengths are reproduced within the experimental uncertainty. The LDA value is $\sim 1\%$ shorter than in the PBE and BP calculations, and the C-C-C bond angle is farthest from the measured value. The shortest distance between C atoms in *different* chains, however, depends strongly on the choice of functional. The value

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[19] Slater (Slater, 1974) noted that one characteristic of his work "was the use of the same techniques both for molecular and solid state problems."

for the LDA approximation (3.67 Å) is much less than the experimental value (4.15 Å), the PBE value (4.66 Å) is too large, and the Becke-Perdew functional results in no binding at all!

The poor results obtained for van der Waals bonds with "standard" approximations for $E_{\rm xc}$ led to a pronounced increase in dispersion-corrected DF studies in recent years [see Fig. 1 of (Klimeš and Michaelides, 2012)]. The progress that has resulted (DiStasio *et al.*, 2014; Dobson and Gould, 2012; Klimeš and Michaelides, 2012) is viewed by many as one of the success stories in recent DF research.

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 van der Waals interactions can be built into the electron gas picture in various ways (Berland *et al.*, 2014; Dobson and Dinte, 1996; Rapcewicz and Ashcroft, 1991). The functional of Langreth and coworkers (Dion *et al.*, 2004) is free of experimental input, involving results from electron gas slabs and the electron gas itself, and has been implemented in several program packages. We have seen above that the exchange and correlation energy can be expressed as an integral over the coupling constant $\lambda = e^2$, and this is the basis of several approximations for dispersion (Dion *et al.*, 2004; Dobson and Wang, 1999; Vydrov and Van Voorhis, 2009). An empirical correction to DF results (DFT-D2) has been proposed by Grimme (Grimme, 2006), and an alternative has been suggested by Tkatchenko and Scheffler (Tkatchenko and Scheffler, 2009). A more recent parametrization by Grimme and coworkers (DFT-D3) (Grimme *et al.*, 2010) provides a consistent description of dispersion forces for elements up to Pu that can be added to DF packages. It depends on the environment of the atoms involved, and has been applied in a range of contexts.

The failure of local density approximations to describe dispersion forces have led to numerous studies of the reasons. One approach has involved the accurate determination of the wave function and correlation effects in simple systems [e.g. He_2 (Allen and Tozer, 2002)], another uses the adiabatic connection theorem [(Tkatchenko *et al.*, 2013) and references therein]. Adiabatic connection is also the basis of the range separation approach, where short-range density functional and the long-range random phase approximations are combined (Toulouse *et al.*, 2009). This method describes the bonds in Be and Ne dimers well.

3. "Strongly correlated" systems

The term "strongly correlated" is often used in extended systems as a synonym for cases where "standard" approximations in DF calculations give poor answers. They are usually cases where the potential energy dominates over the kinetic energy and often involve transition element or rare earth atoms. The metal-insulator transition of Mott (Imada *et al.*, 1998; Mott, 1968) is a well-studied example. Local density approximations can give qualitatively incorrect descriptions of these materials, examples being a metallic DF band structure in insulating transition metal oxides.

The use of model Hamiltonians has been a popular way to avoid these problems, and a common way of modifying DF calculations is the addition of an on-site Coulomb repulsion ("Hubbard U") in the "LSD+U" scheme (Anisimov *et al.*, 1997). The parameter U can be estimated within a DF framework (Cococcioni and de Gironcoli, 2005), but it is often fit to experiment. The dynamical mean field theory (Georges *et al.*, 1996; Kotliar and Vollhardt, 2004) is a mapping of lattice models onto quantum impurity models subject to a self-consistency condition, and the "LDA+DMFT" method merges the DF theory with a modern many-body approach. It allows the modeling of structural, electronic, and magnetic properties of transition metals, their oxides, and other "strongly correlated" materials.

In the chemical context, "strong correlations" are present in systems that cannot be described well by single-determinant solutions to the Kohn-Sham equations. The basic DF theorems tell us that a *single* symmetry-restricted Slater determinant should be able to describe even molecular dissociation, which is a well-known deficiency of Hartree-Fock theory, but the development of appropriate functionals remains a challenge. The study of two-determinant mixing with a recently proposed functional is promising (Becke, 2013).

The adiabatic connection between non-interacting and interacting systems was used above [Eq. (17),(18)] to show that local density approximations can give reasonable results for systems that are far from uniform, but it can also be used to understand *why* local density approximations sometimes fail badly. The crucial point is the λ-dependence of the integrand that leads to $E_{\rm xc}$, and this has been studied in the context of hybrid functionals [see, for example, (Ernzerhof, 1996)] and in calculations for a variety of systems [see, for example, (Teale *et al.*, 2010)]. In "weakly correlated" systems, the integrand is only weakly λ-dependent, the "mapping" of the non-interacting to the interacting system presents few problems, and standard DF prescriptions provide a reasonable description. In cases where the nature of the system changes even for small values of λ, the linear dependence is a poor approximation (Teale *et al.*, 2010), and other ways of estimating the correlation energy must be used.

4. Developments related to QMC

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 (Shepherd *et al.*, 2012) and to simple solids (Booth *et al.*, 2013). 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 (Levy, 1979; Lieb, 1983) in terms of the density *and* the $(N-1)$-conditional probability density, which can be treated by ground state path integral QMC (Delle Site *et al.*, 2013). It remains to be seen whether the computational demands usually associated with QMC can be reduced.

5. Notation

The terms "ab initio" and "first principles" are used differently in the "chemical" and "materials" worlds. For most chemists, the expressions mean solutions of the Schrödinger equation for the system of interacting electrons (e.g. by QMC), for many materials scientists it can be a DF calculation without (or even *with*) adjustable parameters. I use the term "density functional" to describe my work and "ab initio" for solutions of the Schrödinger equation. I look forward to the day when I no longer hear that correct predictions of DF calculations are "right for the wrong reason."

B. Two applications

I shall describe briefly the results of one DF simulation in biology and one in materials science that indicate the scale of DF calculations that are possible. They are not "standard" applications by any means, requiring very large computing resources and substantial human effort. In the spirit of addressing newcomers to the field, I now mention some practical points about DF calculations.

The ready availability of DF programs does not mean that they are easy to use or that careful choices of input parameters can be avoided. Some methods of calculation consider *all* electrons, but many focus on the outermost valence electrons that dominate structural properties and replace the effect of inner "core" electrons by an effective potential (pseudopotential) or a frozen core density. A basis set must be chosen and its convergence checked, and the final results depend on the approximation adopted for the exchange-correlation energy functional. Both of the applications discussed here use the PBE functional (Perdew *et al.*, 1996).

One of the many possibilities for the evolution of life on Earth is the formation of protein molecules under extreme—prebiotic—conditions. Schreiner et al. (Nair *et al.*, 2008; Schreiner *et al.*, 2008, 2011) studied possible reactions of N-carboxy anhydrides (a form of activated amino acids) in water under high pressures and temperatures in the presence of pyrites FeS_2 (the "iron-sulfur world" of Wächtershäuser) (Wächtershäuser, 1988). The presence of an FeS_2 surface (Fig. 7) changes the free energetics of the steps of reactions carried out under different sets of conditions, and it stabilizes the peptide product against hydrolysis. The reactions studied are just possible scenarios for the production of molecules that are essential to life on Earth, but they demonstrate the value of simulations under conditions that are difficult to attain experimentally. They also show that simulations without adjustable parameters can be performed on biological systems that were unthinkable with earlier generations of computers. Of course, there are many biological systems for which the simulation sample sizes currently accessible with this method are simply inadequate. Classical force fields with appropriately chosen parameters are likely to remain the method of choice for such systems.

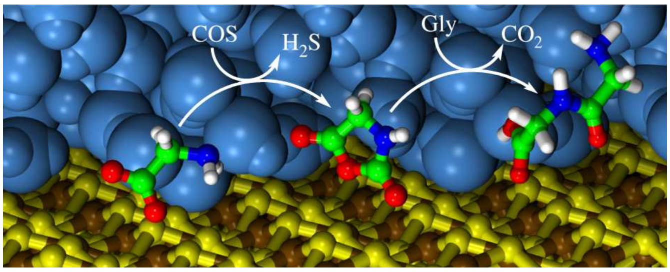

FIG. 7 (Color online, schematic) Glycine (left), activated glycine (center), and the glycine-glycine dipeptide (right) between an FeS_2 surface (below) and water (blue).

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 $Ge_2Sb_2Te_5$ (Kalikka *et al.*, 2012) (Fig. 8). 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. It is very unusual for a phase transition to be fast enough (here nanoseconds) that it is accessible to DF calculations under the actual physical conditions, and we are sure that the details of the structural change will shed light on the mechanism of other phase transitions. The steady (and essential) improvement in numerical algorithms has played an important role, but such calculations also require computers of the highest performance class.

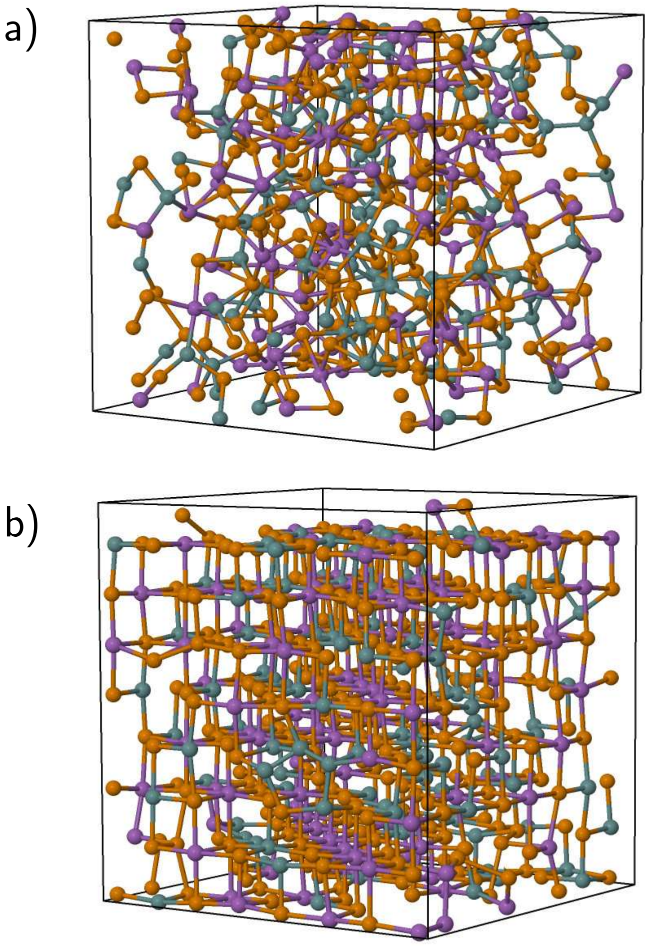

FIG. 8 (Color online) Crystallization in GST alloy at 600 K. (a) Amorphous structure after 215 ps, (b) crystalline structure after 1045 ps. Green: Ge, purple: Sb, Orange: Te

C. Other systems

The dominant role of the *electron* density functional theory in materials science and chemistry means that many of its practitioners identify the term solely with electrons. "DF calculations" are also performed in other contexts.

1. Classical density functional theory

Work in this area focuses on the thermodynamics of systems interacting with classical potentials and is based on the Hohenberg-Kohn-Mermin formulation at finite temperatures (Sec. V.D). The focus is on the Helmholtz free energy and its expression as a functional of the density. The systems considered are very large by electron density functional standards (I have read about particle numbers "up to Avogadro's number"), with particular emphasis on phase transitions, but surveys of the field show that we have much in common (Ashcroft, 1995; Baus, 1990; Evans, 1979, 1992; Haymet and Oxtoby, 1981; Wu and Li, 2007). Electron density functional theory needs approximations for the exchange-correlation energy, the classical counterpart an expression for the excess free energy arising from interactions in the system. The free energy is written as the sum of terms involving a reference system (e.g. a liquid) and a second system of interest (such as a solid), and the "coupling constant integration" technique can be used to switch from one density to the other or from a "non-interacting" to an "interacting" system.

Particularly familiar to me were the weighted density (WD) approximations for the excess free energy in an inhomogeneous liquid (Curtin and Ashcroft, 1985; Tarazona, 1984), where the free energy density at a given point is taken to be that of a homogeneous system with a density determined by weighting over a physically relevant region. This is precisely the motivation of the "WD approximation" in electronic systems (Gunnarsson and Jones, 1980; Gunnarsson *et al.*, 1979), where the "physically relevant region" is determined by the exchange-correlation hole [Eq. (18)]. In the WD approximation, this can be written

$$n_{\rm xc}^{\rm WD}(\mathbf{r},\mathbf{r}'-\mathbf{r}) \equiv n(\mathbf{r}')\; G^{\rm WD}\big(\mathbf{r},\mathbf{r}';\tilde{n}(r)\big), \tag{23}$$

where $G^{\rm WD}$ is a model pair-correlation function, and $\tilde{n}(r)$ is a non-local parameter chosen to satisfy the sum rule Eq. (20). $G^{\rm WD}$ can be chosen to satisfy additional requirements, such as reproducing the LD result in a homogeneous system. A particularly simple form has been tested for atoms with mixed success (Gunnarsson and Jones, 1980; Jones and Gunnarsson, 1989).

2. Nuclei

The number of nuclides (isotopes) that occur or can be synthesized on Earth is approximately 3000 and increases every year. Of these, less than 300 are considered stable (Erler *et al.*, 2012). The stability of a nuclide is determined by the amount of energy needed to remove a single neutron or proton or a pair of neutrons or protons, and it is natural that the limits of nuclear binding have received much attention. The microscopic method of choice in describing weakly bound complex nuclei is the nuclear density functional theory based on a self-consistent mean-field approach (Bender *et al.*, 2003). Nuclear many-body theories are not yet able to provide input for effective energy-density functionals, and experimental input is unavoidable. Many calculations are based on the functional form suggested by Skyrme (Skyrme, 1956, 1959), and the optimization of the parameters involved is an ongoing challenge (Klüpfel *et al.*, 2009; Kortelainen *et al.*, 2010). A detailed study of the "nuclear landscape" using a range of functionals concluded that the number of bound nuclides with between 2 and 120 protons is 6900±500 (Erler *et al.*, 2012).

Numerous concepts that one encounters in the nuclear physics literature (such as "Skyrme-Hartree-Fock", "mean-field theory", "DFT", "Bardeen-Cooper-Schrieffer (BCS) wave function", superfluidity, spin-orbit coupling, even Thomas-Fermi) sound very familiar to many in the condensed matter world. It really is interesting to look outside one's own field.

VII. SUMMARY AND OUTLOOK

A. An "approximate practical method"

The astonishing growth of density functional calculations since 1990 was due in part to the relabeling of "electron band structure" and "Hartree-Fock-Slater" calculations (and the programs developed for them) with a more modern term. Few can doubt that such calculations would have continued with a variety of local density approximations, but the theoretical justification of the density functional was an essential step that resulted in Walter Kohn being awarded (with John Pople) the 1998 Nobel Prize for Chemistry. Anderson noted that this award may indicate that (Anderson, 2011b)

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

("Dream Machine ↑ Mott ↓") (Anderson, 2011c), but he emphasized that "very deep problems" remain with the former (Anderson, 2011b).

The recognition of the basic role of the electron density goes back to the earliest days of quantum mechanics. Thomas and Fermi developed the first density functional, and Dirac (1930) not only incorporated exchange effects into it, but observed that the density could determine completely the state of an atom. It is not necessary to specify the wave function. The self-consistent field of Hartree and the use of determinantal wave functions by Slater, Bloch, and Fock, were followed by the calculations of Wigner and Seitz, who showed that the exchange hole of an electron in Na metal was localized to a single ion. The exchange hole picture is a central concept in DF theory and was developed further by Slater in 1951. An effective exchange potential of the form of Bloch and Dirac was derived and tested by Gáspár in 1954. The work of Hohenberg, Kohn, and Sham (Hohenberg and Kohn, 1964; Kohn and Sham, 1965) is known to everyone.

Kohn and Sham (Kohn and Sham, 1965) did not expect the local density approximation for exchange and correlation to give "an accurate description of chemical binding", and this view was shared by most theoretical chemists for many years. Nevertheless, we now know that approximations to the exchange-correlation energy based on the homogeneous electron gas (LD, LSD) and their modifications provides a scheme that can give valuable information about large molecules and extended systems. It was shown *later* why approximations to E_{xc} could give good results for density distributions far from those where they are obviously valid (Jones and Gunnarsson, 1989). The approach does appear to satisfy the 80-year-old goal of Dirac (Dirac, 1930) to find "approximate practical methods of applying quantum mechanics to [explain] the main features of complex atomic systems without too much computation." Those involved in this activity know that few of us took the last point seriously.

B. Exchange-correlation approximations

The LD and LSD approximations have well documented drawbacks, and the resulting *numbers* (binding energies, band gaps, . . .) should always be treated with caution. However, the approximations and their further developments 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. After spending several years developing functional forms based on experimental data, Nicholas Handy noted that some simpler functionals allow us to separate different types of correlation in molecules and concluded (Handy, 2009; Handy, N C, 2002):

> "We are returning to the view that the simplest parameter-free GGA functionals are the best functionals to use with DFT, because they offer the simplest interpretation and have greater global predictive power."

In fact, 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. Is this pragmatic approach giving way to the search for schemes that produce better *numbers* automatically, as the long list of approximate functionals and publications comparing their predictions might suggest?

C. Quo vadis?

Figure 1 shows that density functional theory will be with us for the foreseeable future, and we can be sure that some exciting results lie ahead. Why then should two of the most cited workers in the field have serious reservations about the future of DF theory? Kieron Burke (Burke, 2012) wrote that "it is clearly both the best of times and the worst of times for DFT" and wondered whether it is time for a "paradigm shift". A newcomer to the field might indeed despair of understanding why one of the countless approximations for E_{xc}, even those with a sound physical basis, should be favored over another, or the real physical reasons behind a particular result. Are DF calculations now following the "Dream Machine" scenario foreseen by Anderson in 1980 (Anderson, 1980)? Furthermore, the identification of the "best" functional may be ambiguous. A recent 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 (Civalleri *et al.*, 2012) showed that finding the "best" functional also depends on the choice of statistical measure (mean error, mean absolute error, variance, . . .).

The concerns of Axel Becke (Becke, 2014) are just as real. It is obvious that great progress has been made in applying DF methods to systems that seemed beyond us only 10 or 15 years ago, and the use of Hartree-Fock-like exchange in many modern functionals has helped communication between the different fields where DF methods are used. However, Becke (and many others, including the author) have focused for years on on the "Kohn-Sham" version of DF theory ("occupied orbitals only"), which is a major reason for the popularity of the method. Will the inherent accuracy of wave function-based methods prove to be decisive as computational resources expand? Many years ago, a colleague predicted that DF methods would ultimately lose out to solutions of the Schrödinger equation as computer power increased. He was not impressed by my view that DF calculations would always be years ahead (I think I said $5-10$, but it is more) in the size of system we could calculate, and he moved on. I didn't.

Density functional theory has a long and fascinating history involving some of the best known names in physics. It deserves better than to be the basis for developing a vast array of approximations seeking the "right" numbers. It cannot be expected to provide precise answers to all questions when simple descriptions of the exchange-correlation energy are used, 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.

VIII. ACKNOWLEDGMENTS

Our density functional work in Jülich has involved many collaborators, but the contributions of Olle Gunnarsson and John Harris in the early years were essential. Also crucial were the support of Gert Eilenberger and his conviction that curiosity-driven research was not (yet) an outdated concept. I thank Dominik Marx for Fig. 7 and information about the work of his group, Jaakko Akola and Janne Kalikka for collaboration on GST crystallization, Phivos Mavropoulos for providing Fig. 1, numerous colleagues for comments on earlier versions of the manuscript, and Richard Jones for many discussions and suggestions.

Appendix A: ADIABATIC COUPLING

If we make infinitesimally slow changes to a parameter describing a system in a stationary state, the system remains in its original state. This *adiabatic principle* is familiar from the earlier quantum theory (Ehrenfest, 1916) and was shown already in 1926 to be valid in quantum mechanics (Born, 1926; Born and Fock, 1928). If the Hamiltonian H of a system depends on some parameters λ, Güttinger (Güttinger, 1931) showed that

$$\frac{\partial E_n}{\partial\lambda} = \left(\frac{\partial H}{\partial\lambda}\right)_{nn} \tag{A1}$$

for the diagonal terms, and

$$\int dr\; u_m^* \frac{\partial u_n}{\partial\lambda} = \frac{1}{E_n - E_m}\left(\frac{\partial H}{\partial\lambda}\right)_{mn} \tag{A2}$$

for $n \neq m$. E_n is the energy eigenvalue and u_n the eigenfunction of state n. These results are implicit in first-order Rayleigh-Schrödinger perturbation theory (Schrödinger, 1926) and in the proof of adiabaticity of Born and Fock (Born and Fock, 1928), who considered only off-diagonal terms (A2). If λ is a coordinate of an atom in a molecule, Eq. (A1) is familiar as the "Hellmann-Feynman theorem" for forces in a molecule (Feynman, 1939; Hellmann, 1933, 1937).

The integrated form of A1

$$E_n(\lambda) = \int_0^{\lambda_f} d\lambda \left(\frac{\partial H}{\partial\lambda}\right)_{nn} . \tag{A3}$$

is often attributed to Pauli (Musher, 1966) and described as the "Pauli trick". However, it is an intermediate result of Güttinger in the context of the adiabatic principle (λ is the time). The "integration over the coupling constant" method is an obvious choice in studies of the relationship between the *non-interacting* ($\lambda = 0$) and *interacting* ($\lambda = e^2$) electron systems.

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