1 Density Functional Theory for the Correlated

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Contents

1   Introduction

A practical definition of "strongly correlated" systems covers those that are not described well by electron density functional (DF) theory. Most seminars and many publications on the subject mention in the first sentence the widespread use of density functional (DF) theory in materials, often quoting Walter Kohn: "For periodic solids it is sometimes referred to as the standard model" [1]. The second sentence, however, lists the systems where DF results with standard approximations are disastrous (a "metallic" transition metal oxide insulator, almost anything to do with rare earth or actinide elements, ...), emphasizing the importance of describing such "strongly correlated" materials correctly [2].[1] DF theory is nevertheless an essential part of this school. It is used widely in materials science and chemistry and provides useful results for countless systems for which the exact wave function cannot be computed. The organizers have asked me to provide you with 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 1920s. Thomas [3] and Fermi [4] recognized the electron density as a basic variable, and Dirac [5] showed already in 1930 that the state of an atom can be determined completely within Hartree-Fock theory by its one-particle density matrix; 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 the *structure* and cohesive energies and 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.

Accurate calculations of the entire energy surface $E(R_\mathrm{I})$ are possible only for systems with very few atoms, and this function generally has vast numbers of maxima and minima at unknown locations. The lowest energy, however, corresponds to the ground state *structure*, and paths between minima are essential to our studies of chemical reactions, including their activation barriers. When I read the autobiography of Francis Crick [6], I was taken by his observation

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

and have used it ever since. This relationship may be self-evident to molecular biologists and most chemists, but it is also true in many other areas. The DF approach allows us to calculate $E(R_\mathrm{I})$, 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.

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

Olle Gunnarsson and I reviewed the density functional formalism, its history, and its prospects in 1989 [7], and I returned to the subject and its literature again recently [8]. I have drawn on this article for some of the present content, and I refer you to it for a much wider discussion and more extensive literature. The focus here is on *electron* density functional theory, and I comment in [8] on DF methods in classical systems and nuclei. My final remarks in [8] discussed the concern that prominent DF practitioners express about the future of the field, and I return to this point below. A second review article covers my view of the fascinating history of the chemical "bond", starting from the first use of this word in the mid nineteenth century [9]. This is perhaps peripheral to the main interests of the "strongly correlated" community, but the reader will be surprised at how much he or she did not know. Have you ever really thought about why atoms usually like being close together and not infinitely far apart?

In my lecture at the Autumn School 2020, I plan to cover much of the ground presented in these notes. Participants at the school, however, should not be surprised if I make some less than standard remarks about DF theory and its relationship to other areas of many-electron physics and chemistry, as well as on some of the personalities involved.

2 The electron density as basic variable

The books by Gino Segrè [10] and Graham Farmelo [11] give fascinating accounts of the very rapid development of quantum mechanics in the years following 1925. Methods for finding approximate solutions of the Schrödinger equation followed soon after it was published in 1926 and have had a profound effect on chemistry and condensed matter physics ever since.

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

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

where each $\psi_i(\mathbf{r}_i)$ satisfies a one-electron Schrödinger equation with a potential term arising from the average field of the other electrons. Hartree [12] indeed 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). However, Slater [13] and Fock [14] 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 [13, 14] 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 [15] and ferromagnetism [16], 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 [17]:

> "The general theory of quantum mechanics is now almost complete, ... The underlying
> physical laws necessary for the mathematical theory of a large part of physics and the whole
> of chemistry are thus completely known, and the difficulty is only that the exact application

> of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation."

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

Dirac [17] also sought to improve the model of Thomas [3] and Fermi [4] 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 [17], and he included these effects in the "Thomas atom" [5] 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 [18, 19]. However, it has severe deficiencies. The charge density is infinite at the nucleus and decays as r^{-6}, not exponentially, far from it. Teller [20] 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, no ferromagnetism [7], and atoms *shrink* with increasing Z (as $Z^{-1/3}$) [21]. Nevertheless, it may be useful in the context of very dense matter [8].

One point made by Dirac [5], 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

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[2]The exchange energy in a homogeneous (spin-polarized!) electron gas had been derived by Bloch [16] in 1929.
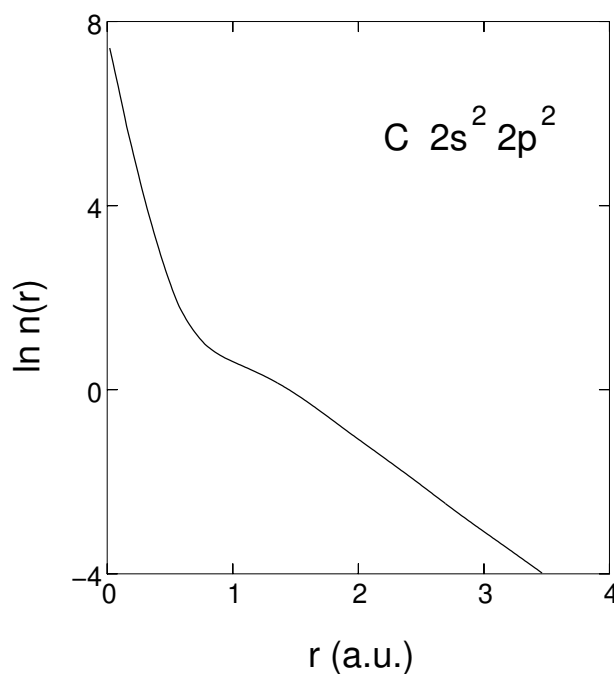
Fig. 1: *Logarithm of spherical average of density in ground state of C atom as a function of the distance from the nucleus (atomic units) [7].*

> exchange, then this total electric density (the matrix) has one important property, namely, if the value of the total electric density at any time is given, then its value at any later time is determined by the equations of motion. This means that *the whole state of the atom is completely determined by this electric density; it is not necessary to specify the individual three-dimensional wave functions that make up the total electric density.* Thus one can deal with any number of electrons by working with just one matrix density function."

The italics are in the original. The derivation is based on the "self-consistent field" or Hartree-Fock approximation, and the "matrix density function" is known today as the one-particle density matrix, but the observation that the density follows the equations of motion is much in the spirit of Ehrenfest's theorem [22], 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 know what it looks like 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 rather featureless, with maxima at the nuclei, saddle points along the bonds, and a generally monotonic decay from both. The electron density in molecules and solids also shows relatively small departures from the overlapped densities of the constituent atoms. Energy differences, including binding, ionization, and cohesive energies, are the focus of much DF work and result from subtle changes in relatively featureless density distributions. It is amazing that this is sufficient 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 approximations are essential. Furthermore, numerical techniques for solving the Schrödinger equation in extended systems were still to be developed.

Wigner and Seitz [23] 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-centered 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 [23]. 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 [24].

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 one unit charge and is referred to as the "Fermi" [23] or "exchange" hole [25]. In the Hartree-Fock scheme, the exchange hole is different for each electronic function, but Slater [25] developed a simplified "exchange potential" that depended only on the density

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

The Slater approximation (4) was proposed at the time that electronic computers were becoming available for electronic structure calculations and proved to be very useful in practice. Methods for solving the Schrödinger equation had been developed—but not implemented—somewhat earlier, including the augmented plane wave (APW) [26] and Korringa-Kohn-Rostoker approaches [27, 28].

The exchange potential of Slater (4) is 3/2 times that derived by Dirac and Bloch (3) for a homogeneous electron gas, but Slater [29] 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 [25]. The exchange hole discussed above for a spin up electron contains a single electron. If we assume
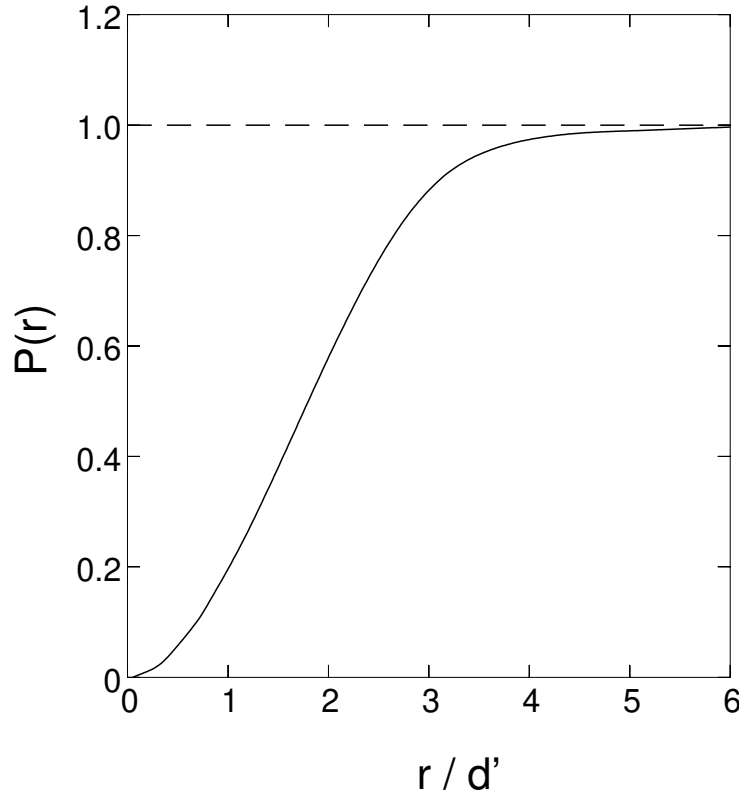
Fig. 2: *Probability that electrons in Na metal with parallel spins are r/d' apart $(d'^3 = V_0/(3\pi^2)$, where V_0 is the atomic volume). After Wigner and Seitz [23].*

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 to counter a misconception (unfortunately still widespread) that local density approximations based on the homogeneous electron gas are only appropriate if the electron density is nearly homogeneous.

In 1954, Gáspár [30] 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" [31], but the larger value was used in most calculations in the following years.

4   Electron density functional formalism

The variational principle on the energy was the basis of the derivation of the density functional formalism given by Hohenberg and Kohn (HK) [32]. First, they showed that there is a one-to-one relationship between the external potential $V_{\text{ext}}(\mathbf{r})$ and the (nondegenerate) ground state (GS) wave function Ψ, and then that there is a one-to-one relationship between Ψ and the ground state density $n(\mathbf{r})$ of an N-electron system,

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

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

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

$$F[n] = \langle \Psi_n | T + V_{\text{ee}} | \Psi_n \rangle, \tag{7}$$

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

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

where

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

The minimization is performed in HK over all non-degenerate densities that can be derived from the ground state of some external potential ("V-representable"). Levy [33] generalized this to a minimization over all densities, including degeneracies.

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],

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

T_0 is the kinetic energy that a system with density n would have if there were no electron-electron interactions, 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 (10) 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 (10) yields

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

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,

$$\frac{\delta E[n]}{\delta n(\mathbf{r})} = \frac{\delta T_0}{\delta n(\mathbf{r})} + V(\mathbf{r}) = \mu, \tag{12}$$

we see that the mathematical problems are identical, provided that

$$V(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + \Phi(\mathbf{r}) + \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})}. \tag{13}$$

The solution of Eq. (12) can be found by solving the Schrödinger equation for *non-interacting* particles,

$$\left(-\frac{1}{2}\nabla^2 + V(\mathbf{r}) \right) \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}), \tag{14}$$

yielding

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2 \tag{15}$$

The condition (13) 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,

$$V_{\text{HF}} \, \psi(\mathbf{r}) = \int d\mathbf{r}' \, V_{\text{HF}}(\mathbf{r}, \mathbf{r}')\psi(\mathbf{r}'), \tag{16}$$

the effective potential, $V(\mathbf{r})$ is a *local* (i.e. multiplicative) operator.

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"

$$E_{\mathrm{xc}}^{\mathrm{LD}} = \int d\mathbf{r}\, n(\mathbf{r})\, \varepsilon_{\mathrm{xc}}[n(\mathbf{r})], \tag{17}$$

where $\varepsilon_{\mathrm{xc}}[n]$ is the exchange and correlation energy per particle of a homogeneous electron gas with density n. This approximation is exact in the limits of slowly varying densities and very high densities. The 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

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

where $\varepsilon_{\mathrm{xc}}[n_\uparrow, n_\downarrow]$ is the exchange and correlation energy per particle of a homogeneous, spin-polarized electron gas with spin-up and spin-down densities $n_\uparrow$ and $n_\downarrow$, respectively.[3] The "Xα" approximation

$$E_{\mathrm{x}}^{\mathrm{X}\alpha} = -\frac{3}{2}\alpha C \int d\mathbf{r}\left((n_\uparrow(\mathbf{r}))^{4/3} + (n_\downarrow(\mathbf{r}))^{4/3} \right), \tag{19}$$

where $C = 3(3/4\pi)^{1/3}$ was used in numerous calculations in the late 1960s and 1970s. The α-dependence of energy differences for a given atom or molecule is weak for values near $2/3$, the value of Bloch [16], Dirac [5], Gáspár [30] 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 [23] and Slater [25, 29].

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. (14), (15). 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 [35], such that the ground state of the Hamiltonian

$$H_\lambda = -\frac{1}{2}\nabla^2 + V_{\mathrm{ext}}(\mathbf{r}) + V_\lambda + \lambda V_{\mathrm{ee}} \tag{20}$$

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 [36]

$$E_{\mathrm{xc}} = \frac{1}{2}\int d\mathbf{r}\, n(\mathbf{r}) \int d\mathbf{r}'\, \frac{1}{|\mathbf{r} - \mathbf{r}'|} n_{\mathrm{xc}}(\mathbf{r}, \mathbf{r}'-\mathbf{r}), \tag{21}$$

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[3]The calculation by Bloch [16] 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 $n_\downarrow^{4/3}$.

with

$$n_{xc}(\mathbf{r}, \mathbf{r}'-\mathbf{r}) \equiv n(\mathbf{r}') \int_0^1 d\lambda \left(g(\mathbf{r}, \mathbf{r}', \lambda) - 1 \right). \tag{22}$$

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 [23] and Slater [25] 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 (21) yields

$$E_{xc} = \frac{1}{2} \int d\mathbf{r} \, n(\mathbf{r}) \int_0^\infty dR \, R^2 \frac{1}{R} \int d\Omega \, n_{xc}(\mathbf{r}, \mathbf{R}). \tag{23}$$

Equation (23) shows that the xc-energy depends only on the spherical average of $n_{xc}(\mathbf{r}, \mathbf{R})$, so that approximations for E_{xc} can still give an *exact* value, even if the description of the non-spherical parts of n_{xc} is arbitrarily inaccurate. Third, the definition of the pair-correlation function leads to a sum-rule requiring that the xc-hole contains one electron, i.e., for all $\mathbf{r}$,

$$\int d\mathbf{r}' \, n_{xc}(\mathbf{r}, \mathbf{r}'-\mathbf{r}) = -1. \tag{24}$$

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

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

This leads to

$$E_{xc} = -\frac{1}{2} \int d\mathbf{r} \, n(\mathbf{r}) \left\langle \frac{1}{\mathbf{R}} \right\rangle_{\mathbf{r}}. \tag{26}$$
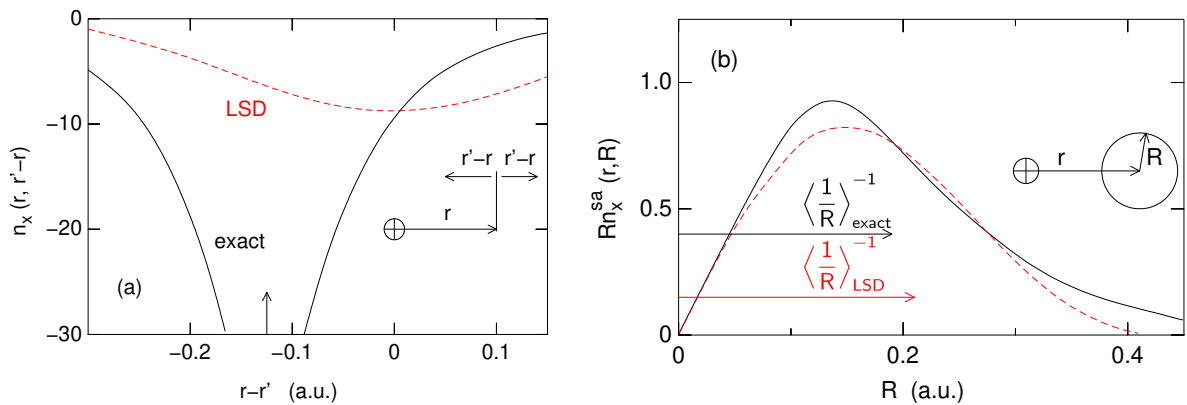

Fig. 3: *Magnitude of exact (solid) and LSD (red, dashed) exchange holes $n_{xc}(\mathbf{r}, \mathbf{r}'-\mathbf{r})$ for spin up electrons in an N atom for $\mathbf{r} = 0.13$ a.u. (a) Hole along line through nucleus (arrow) and electron ($\mathbf{r}-\mathbf{r}' = 0$). (b) spherical averages of holes, and $\langle 1/\mathbf{R} \rangle$ [Eq. (25)] [7].*

Provided Equation (24) 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]. Provided that the spherical average of the exchange-correlation hole is correct, approximations to E_{xc} can then lead to good total energies, even if other details are described very poorly. This is shown by the example 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 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 around 10%.

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 (the names of some program packages also changed seamlessly). 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 valuable in some contexts, he continued:
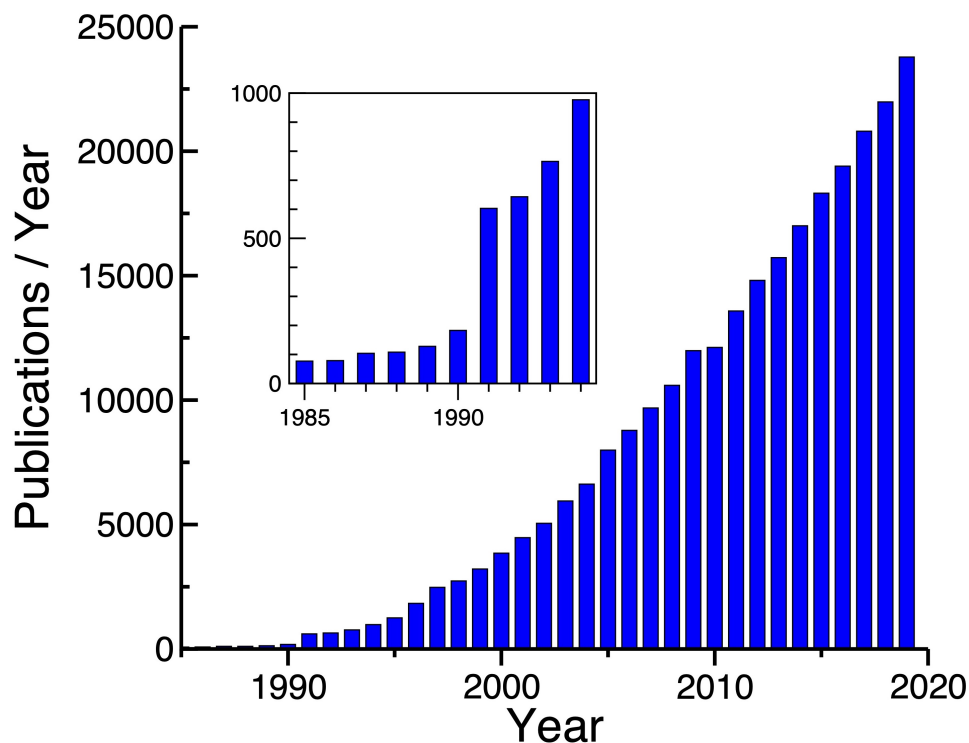
Fig. 4: *Number of publications per year (1980-2019) on topics "density functional" or "DFT", according to Web of Knowledge (June 2020). The inset shows data near 1990 on an expanded scale [39].*

> " . . . 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 are harsh words, and some DF practitioners are still angry about the damage that they caused. They did, however, apply to some electronic structure calculations at the time, and I return to them 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, 40], (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* (perhaps better described as "mechanical") way to approach the exact solution of the Schrödinger equation and, of course, the exact energy.

This last point was (and is) 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 an attractive proposition, and the dramatic improvements in computing power (three orders of magnitude per decade) might make the reservations of Dirac [17] 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 ($X\alpha$ calculations with $\alpha = 0.7$) on small molecules were carried out from 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, but we (with Olle) developed a full-potential LMTO code for small molecules and clusters [41]. 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 became 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 unexpected and exciting results, my own examples including the trends in the binding energies of group 2 dimers [42, 43] and the structures of small phosphorus clusters [44]. Most condensed matter physicists were neither surprised nor interested, but theoretical chemists remained sceptical or critical, or they ignored these developments entirely. This situation continued throughout the 1980s and into the 1990s.

The Seventh International Congress of Quantum Chemistry in Menton, France, from 2–5 July 1991, marked 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 [45], and this approximation was tested for the atomization energies of small molecules immediately after the meeting. Many—including the authors— were surprised by the results [46]:

> "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 [47]

> "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   Situation in 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, 48].

The generalizations to finite temperatures and to spin systems were carried out soon after the original work of Hohenberg and Kohn [32]. The former was provided by Mermin [49], 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 $E_{\text{x}c}$ replaced by the exchange-correlation contribution to the free energy.

The extension to spin systems [50] 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 $E_{\text{x}c}$ is analogous to Equations (21), (22). A current- and spin density functional theory of electronic systems in strong magnetic fields was formulated by Vignale and Rasolt [51]. Time-dependent density functional theory, which has proved to be invaluable in discussing excited states, was described by Runge and Gross [52].

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 [53], 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 [42]. It is not surprising that new approximations were developed, and corrections involving density gradients were soon available for the correlation [54, 55] and exchange energies [45]. The semi-empirical exchange energy approximation of Becke [45] had the correct asymptotic behavior for atoms.

The combination of DF calculations with molecular dynamics (Car-Parrinello method) [56] 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 [57] 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   1990–present

There have been over 200,000 publications on the topics "density functional" and "DFT" between 1990 and June 2020 (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?"

Michael Frisch answered:

> "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 combination of density functional calculations with molecular dynamics is likewise a part of many such packages. The combination of DF calculations for a chemically active region with classical molecular dynamics for the surrounds (the "QM/MM approach") [58] has found applications in many systems in biology, organic and solid state chemistry [59]. Classical force fields that lead to simulations with near-DF accuracy can be developed by a neural network or machine-learning representation of the results of (very many) DF calculations on small systems [60], and this has been an active field of research recently [61, 62]. Reviews of orbital-dependent functionals and constrained DF theory are provided in [8].
These and other developments are very welcome, but 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. (17)] and LSD [Eq. (18)] 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 significantly. 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 [45, 54, 55] did lead to better results, and hybrid functionals including exact exchange were introduced by Becke in 1993 [63]. This form of E_x has three parameters, and its combination with E_c of Lee, Yang, and Parr [55] (B3LYP) remains one of the most common approximations used in chemical applications [64]. 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 [65]. 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 [66].

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 [67] (PBE) incorporates the LSD form below it, and the "meta-GGA" form of Tao, Perdew, Staroverov, and Scuseria (TPSS) [68], 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" [69].

It should be emphasized that the Jacob's ladder approach is systematic and not empirical [70]. Starting with a proof of the existence of a functional, we can derive formally exact relationships that we can develop into constraints on approximate forms. If these forms are flexible enough, we can fit their free parameters to appropriate norms of energies or densities. These should not include binding energies, which are always susceptible to error cancellation between exchange and correlation. A recent member of the family is the "SCAN" (strongly constrained and appropriately normed) semilocal functional of Sun et al. [71]. Medvedev et al. [70] note that many (empirically fitted) functionals developed since the year 2000 lead to improved energies but *densities* that are more removed from the exact results.

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 [72]. 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 made by Grimme [73], an alternative has been suggested by Tkatchenko and Scheffler [74].

"Strongly correlated" systems often involve transition element or rare earth atoms, and the potential energy can dominate over the kinetic energy. Local density approximations can 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 [75]. The parameter U can be estimated within a DF framework [76] or fit to experiment.

There are developments in the quantum Monte Carlo (QMC) studies of *interacting* electron systems that are relevant for DF work. The full configuration interaction (FCI) implementation of QMC uses Monte Carlo sampling of Slater determinants and circumvents the Fermion sign problem. It has been applied to the homogeneous electron gas [77] and to simple solids [78]. For a recent application to the solid phases of hydrogen under pressure, see [79]. Condensed matter scientists have much experience with periodic boundary conditions and plane wave orbital expansions, and this has aided the implementation of the method in extended systems. Another example is the reformulation of the constrained search approach in DF theory [33, 40] in terms of the density *and* the $(N-1)$-conditional probability density, which can be treated by ground state path integral QMC [80]. 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

In 1871, Charles Darwin saw the formation of protein molecules under extreme—prebiotic— conditions as a possible path of evolution of life on Earth [81]:

> " . . . But if (and what a big if) we could conceive in some warm little pond with all sorts of ammonia and phosphoric salts,—light, heat, electricity, &c present, that a protein compound was chemically formed, ready to undergo still more complex changes, at the present day such matter would be instantly devoured, or absorbed, which would not have been the case before living creatures were formed."

DF simulations can be used to test whether biological molecules can be produced by chemical processes that do not require biological synthesis machines like ribosomes. Schreiner et al. [82] 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 controversial "iron-sulfur world" of Wächtershäuser [83]). The presence of an FeS_2 surface changes the free energetics of the steps of the carbonyl sulfide (COS)-mediated polymerization of glycine carried out under different thermodynamic conditions (Fig. 5), and it stabilizes the peptide product against hydrolysis.

The reactions studied are just a few of many possible scenarios for the production of molecules that are essential to life on Earth, but they demonstrate the value of simulations under conditions
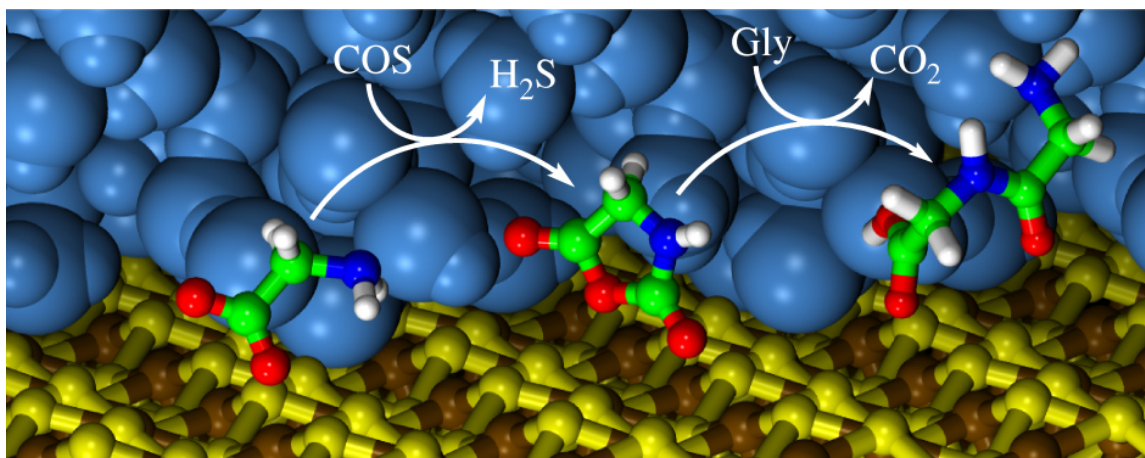
Fig. 5: *(Schematic) Glycine (left), activated glycine (center), and the glycine-glycine dipeptide (right) between an FeS_2 surface (below) and water (blue). COS: carbonyl sulfide.*

that are difficult to attain experimentally. They also show that simulations without adjustable parameters can be performed on biological systems that were absolutely out of the question with earlier generations of computers. Of course, there are many such systems for which the simulation sample sizes currently accessible with DF methods are simply inadequate. Classical force fields with appropriately chosen parameters are likely to remain the method of choice for such systems for some time yet.

7 Summary. Quo vadis?

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 [2]

> "the labours and controversies [. . .] in understanding the chemical binding in materials had finally come to a resolution in favor 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 used. 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.

Figure 4 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 [64] 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.

The concerns of Axel Becke [84] 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 me) have focused for years on the "Kohn-Sham" version of DF theory ("occupied orbitals only"), which is a major reason for the popularity of the method. Should we move our focus away from the relatively featureless electron density with its small and subtle changes? Can the combination with density matrix functional methods lead to a new breakthrough? Will the inherent accuracy of wave function-based methods prove to be decisive as computational resources expand?[4] 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 far ahead in the size of system we could calculate (I think I said 5–10 years, but it is more), and he moved on. I stayed.

The comments by Burke and Becke were made some years ago, but not everyone noticed them. The number of DF applications continues to rise (Fig. 4), and there are developments in important areas, such as functionals for use with "orbital-free" calculations [85] or understanding range-separated hybrid functionals [86]. Nevertheless, there is still much debate and little consensus on the "best" functional approximations, and the search for schemes that produce better *numbers* automatically continues. Comparisons of the results of calculations with those of other approximations and with experiment abound. Are DF calculations in chemistry and materials science now following the "Dream Machine" scenario foreseen for the solid state world by Anderson in 1980 [38]?

Density functional theory deserves better than to be a background justification for empirical curve fitting, which implies a lack of confidence in the theory, or the development of a chain of approximations seeking the "right" numbers, with less concern for their physical origin. Its long and fascinating history involves 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.

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