ELECTRONIC STRUCTURE OF MATTER – WAVE FUNCTIONS AND DENSITY FUNCTIONALS

Nobel Lecture, January 28, 1999

by

WALTER KOHN

Department of Physics, University of California, Santa Barbara, CA 93106-9530, USA

I. INTRODUCTION

The citation for my share of the 1998 Nobel Prize in chemistry refers to the "development of the density functional theory". The initial work on Density Functional Theory (DFT) was reported in two publications: the first with Pierre Hohenberg in 1964[1] and the next with Lu J. Sham[2] in 1965. This was almost 40 years after E. Schroedinger[3] published his first epoch-making paper marking the beginning of wave-mechanics. The Thomas-Fermi theory, the most rudimentary form of DFT, was put forward shortly afterwards[4, 5] and received only modest attention.

There is an oral tradition that, shortly after Schroedinger's equation for the electronic wave-function Ψ had been put forward and spectacularly validated for simple small systems like *He* and H_2, P.M. Dirac declared that chemistry had come to an end – its content was entirely contained in that powerful equation. Too bad, he is said to have added, that in almost all cases, this equation was far too complex to allow solution.

In the intervening more than six decades enormous progress has been made in finding approximate solutions of Schroedinger's wave equation for systems with several electrons, decisively aided by modern electronic computers. The outstanding contributions of my Nobel Prize co-winner John Pople are in this area. The main objective of the present account is to explicate DFT, which is an alternative approach to the theory of electronic structure, in which the electron density distribution $n(r)$, rather than the many electron wavefunction plays a central role. I felt that it would be useful to do this in a comparative context; hence the wording "Wavefunctions and Density Functionals" in the title.

In my view DFT makes two kinds of contribution to the science of multiparticle quantum systems, including problems of electronic structure of molecules and of condensed matter:

The first is in the area of fundamental *understanding*. Theoretical chemists and physicists, following the path of the Schroedinger equation, have become accustomed to think in a truncated *Hilbert space of single particle orbitals*. The spectacular advances achieved in this way attest to the fruitfulness of this perspective. However, when high accuracy is required, so many Slater deter-

minants are required (in some calculations up to ~ 10^9!) that *comprehension* becomes difficult. DFT provides a complementary perspective. It focuses on quantities in the real, 3-dimensional coordinate space, principally on the electron density $n(r)$ of the groundstate. Other quantities of great interest are: the exchange correlation hole density $n_{xc}(r,r')$ which describes how the presence of an electron at the point r depletes the total density of the other electrons at the point r'; and the linear response function, $\chi(r,r';\omega)$, which describes the change of total density at the point r due to a perturbing potential at the point r', with frequency ω. These quantities are *physical*, independent of representation, and easily *visualisable* even for very large systems. Their understanding provides transparent and complementary insight into the nature of multiparticle systems.

The second contribution is practical. Traditional multiparticle wavefunction methods when applied to systems of *many particles* encounter what I call an exponential wall when the number of atoms, N, exceeds a critical value which, for "chemical accuracy", currently is in the neighborhood of $N_0 \approx 10$ (to within a factor of about 2) for a system without symmetries. A major improvement along present lines in the analytical and/or computational aspects of these methods will lead to only modest increases in N_0. Consequently, problems requiring the simultaneous consideration of very many interacting atoms, $N/N_0 \gg 1$, such as large organic molecules, molecules in solution, drugs, DNA, etc. overtax these methods. On the other hand, in DFT, computing time T rises much more moderately with the number of atoms, currently as $T \sim N^\alpha$ with $\alpha \approx 2$–3, with ongoing progress in bringing α down towards $\alpha \approx 1$ (so-called linear scaling). The current state of the art of applied DFT can handle systems with up to $N_0' = O(10^2)$–$O(10^3)$ atoms.

The following figures and legends illustrate what can currently be achieved. In these examples the number of atoms is $O(10^2)$ and the number of electrons several times larger.

In Section 1, I shall talk about traditional wavefunction methods and contrast their great success for few-atom systems with their fundamental limitations in dealing with very-many-atom systems.

Section 2 deals with DFT against the backdrop of wavefunction methods. The basic theory is summarized: First the original Hohenberg-Kohn (HK) variational principle, where $n(r)$ is the variational variable, is described. This is followed by the Kohn-Sham (KS) self-consistent single-particle equations which involve the well-defined exchange – correlation functional, $E_{xc}[n(r)]$. In principle, when used with the exact E_{xc}, these single particle equations incorporate *all* many-body effects.[1]

Next the physics of $E_{xc}[n(r)]$ is discussed in terms of the concept of the exchange correlation hole $n_{xc}(r,r')$. I have found the concept of "nearsightedness" useful which, in the present context, says that the exchange correlation hole $n_{xc}(r,r')$ for an electron at the point r is largely determined by $\mu - v_{eff}(\tilde{r})$, where μ is the chemical potential and $v_{eff}(\tilde{r})$ is the effective single particle

[1] It is however known that for some density distributions $E_{xc}[n(r)]$ cannot be defined.

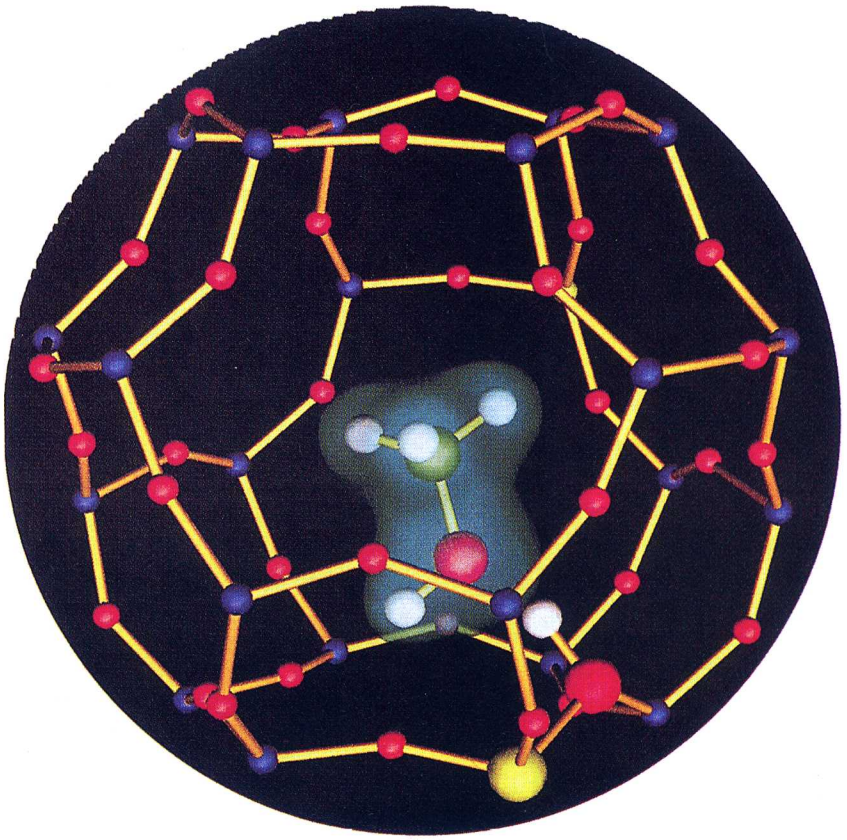

Figure 1. Methanol inside a cage of the zeolite sodalite. Zeolites are crystalline arrays of cages built of silicon (blue), aluminum (yellow), and oxygen (red) atoms. For each *Al* atom one must have a positive counter-ion (in this case H^+ (white)). A methanol molecule is inside the cage (carbon is green) where it can react with the proton. DFT calculations have assigned and clarified the IR spectra, have determined the binding sites of methanol, and have calculated the activation energy for the reaction. Acid catalysis in zeolites is widely used in the chemical industry. (After E. Nusterer, P. Bloechl and Karlheinz Schwarz, Angew. Chem. **35**, 175).

potential for $\tilde{r}$ *near* r. Although nearsightedness becomes a well defined concept only for metallic systems which are very large, it has been found to be useful also for systems as small as a single atom.

There follows a brief discussion of approximations for E_{xc}, which reflect nearsightedness, and other general principles.

Parts III-V discuss applications of DFT to electronic groundstates, as well as a host of generalizations to other electronic and non-electronic systems.

Finally a few concluding remarks and speculations are offered.

II. SCHROEDINGER WAVEFUNCTIONS – FEW VERSUS MANY ELECTRONS

The foundation of the theory of electronic structure of matter is the non-relativistic Schroedinger equation for the many-electron wavefunction Ψ,

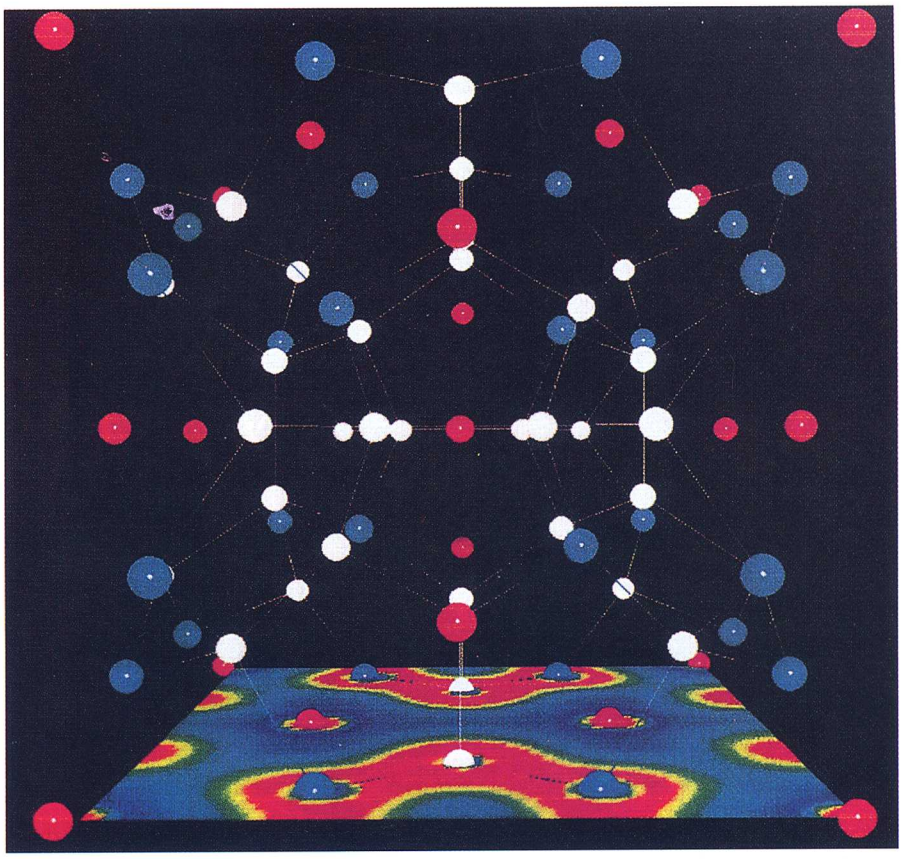

Figure 2. The geometric structure of the clathrate $Sr_8Ga_{16}Ge_{30}$ (Sr red, Ga blue, Ge white) and its charge density in a plane bisecting the centers of the cages. DFT calculations have shown that the Sr atoms are weakly bound and scatter phonons effectively, thereby, lowering thermal conductivity. However, contrary to intuitive expectations, the Sr atoms do not donate electrons to the frame and are practically neutral. Conductivity is due to electrons traveling through the frame, not through the one-dimensional Sr "wires" in the structure; there is thus little scattering of conduction electrons, by Sr vibrations. For these reasons, the compound is a metal with a large Seebeck coefficient (unlike ordinary metals). The calculation suggests that other compounds of this type may be even better thermoelectrics. (Theory by N.P. Blake and H. Metiu, submitted for publication).

$$\{-\frac{\hbar^2}{2m}\sum_j \nabla_j^2 - \sum_{j,\ell}\frac{Z_\ell e^2}{\mid r_j - R_\ell \mid} + \frac{1}{2}\sum_{j\neq j'}\frac{e^2}{\mid r_j - r'_j \mid} - E\}\Psi = 0\,, \quad (2.1)$$

where r_j are the positions of the electrons and R_l, Z_l the positions and atomic numbers of the nuclei; $\hbar$, m and e are the conventional fundamental constants; and E is the energy. This equation reflects the Born-Oppenheimer approximation, in which – for purposes of studying electron-dynamics – the much heavier nuclei are considered as fixed in space. This paper will deal largely with non-degenerate groundstates. The wavefunction Ψ depends on the positions and spins of the N electrons but in this paper spins will generally not be explicitly indicated. Thus

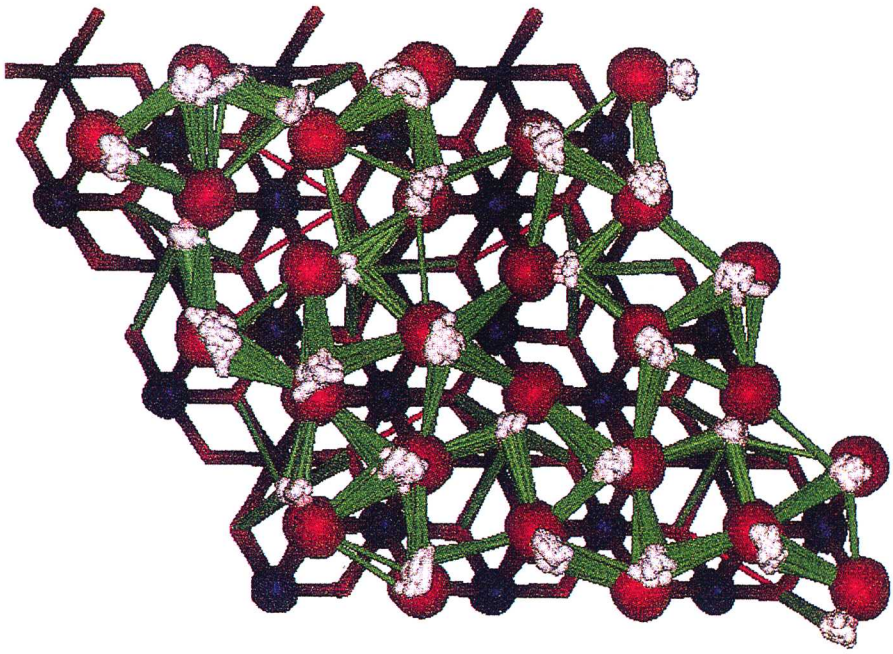

Figure 3. Fully Hydroxylated Aluminum (0001) Surface. (Red-O; blue-interior Al; grey-H-atoms; the green lines are H-bonds). Each surface Al-atom in Al_2O_3 has been replaced by 3 H-atoms. The figure represents a superposition of configurations in a molecular dynamics simulation at regular intervals of 1 ps. These calculations help to understand the complex dynamics of water adsorption on aluminum (K.C. Haas *et al.*, Science 282, 265 (1998)).

$$\Psi = \Psi(r_1, r_2, ...r_{\mathcal{N}}). \tag{2.2}$$

The Pauli principle requires that

$$P_{jj'}\Psi = -\Psi \ , \tag{2.3}$$

where $P_{jj'}$ permutes the space and spin coordinates of electrons j and j'. All physical properties of the electrons depend parametrically on the R_l, in particular the density $n(r)$ and total energy E which play key roles in this paper:

$$n(r) = n(r; R_1, ...R_{\mathcal{N}}) \ , \tag{2.4}$$

$$E = E(R_1, ...R_{\mathcal{N}}) \ , \tag{2.5}$$

where $\mathcal{N}$ is the number of nuclei.

A. Few Electron Systems–the H_2 Molecule

The first demonstrations of the power of the Schroedinger equation in chemistry were calculations of the properties of the simplest multielectron molecule, H_2: Its experimental binding energy[2] and internuclear separation are

[2] This is the observed dissociation energy plus the zero point energy of 0.27 eV.

$$E_{exp}: \; D = 4.75eV, \quad R = 0.740\,\text{Å}. \tag{2.6}$$

The earliest quantum theoretical estimate was made by Heitler and London in 1927[6], who used the Ansatz

$$\Psi_{HL} = A\,[\varphi_H(r_1 - R_1)\varphi_H(r_2 - R_2) + \varphi_H(r_1 - R_2)\varphi_H(r_2 - R_1)]\,\chi_0\,, \tag{2.7}$$

where $\varphi_H(r_1 - R_1)$ is the orbital wavefunction of electron 1 in its *atomic* groundstate around a proton located at R_1, etc; χ_0 denotes the spin singlet function; and A is the normalization. The components of this wavefunction describe two hydrogen atoms, at R_1 and R_2, with spins pointing in opposite directions. The combination satisfies the reflection symmetry of the molecule and the Pauli principle. The expectation value of the Hamiltonian as a function of $R = |R_1 - R_2|$ was calculated. Its minimum was found to occur at $R = 0.87$Å, and the calculated dissociation energy was $3.14eV$, in semiquantitative agreement with experiment. However the errors were far too great for the typical chemical requirements of $|\delta R| \leq 0.01$ Å and $|\delta D| \leq 0.1eV$.

An alternative Ansatz, analogous to that adopted by Bloch for crystal electrons, was made by Mullikan in 1928[7]:

$$\Psi_{BM} = \varphi_{mol}(r_1)\varphi_{mol}(r_2) \cdot \chi_0\,, \tag{2.8}$$

where

$$\varphi_{mol}(r_1) = A'(\varphi_H(r_1 - R_1) + \varphi_H(r_1 - R_2))\,, \tag{2.9}$$

and A' is the appropriate normalization constant. In this function both electrons occupy the same molecular orbital $\varphi_{mol}(r)$. The spin function χ_0 is again the antisymmetric singlet function. The results obtained with this function were $R = 0.76$ Å, and $D = 2.65eV$, again in semiquantitative agreement with experiment.

The Mullikan Ansatz can be regarded as the simplest version of a more general, so-called Hartree-Fock Ansatz, the Slater determinant

$$\Psi_{HF} = \frac{1}{2^{1/2}} Det\,|\,\varphi_m(r_1)\alpha(1)\varphi_m(r_2)\beta(2)\,|\,, \tag{2.10}$$

where $\varphi_m(r)$ is a general molecular orbital and α and β denote up and down spin functions. For given $R \equiv |R_1 - R_2|$, minimization with respect to $\varphi_m(r)$ of the expectation value of H leads to the non-local Hartree Fock equations[8] for the molecular orbital $\varphi_m(r)$, whose solution gives the following results: $R = 0.74$ Å, D = $3.63eV$.

The most complete early study of H_2 was undertaken by James and Coolidge in 1933[9]. They made the very general variational Ansatz

$$\Psi_{JC} = \Psi(r_1, r_2)\chi_0\,, \tag{2.11}$$

where $\Psi(r_1,r_2)$ is a general, normalized function of r_1 and r_2, symmetric under interchange of r_1 and r_2 and respecting the spatial symmetries of the molecule. The trial function Ψ was written as depending on a number of parame-

ters, $p_1, p_2 \ldots p_M$, so that for given $|R_1 - R_2|$, the expectation value of the Schroedinger Hamiltonian in Ψ, an upper bound to the true groundstate energy, became a function of the parameters p_j, $E = E(p_1,\ldots,p_M)$. The calculations were made with M up to 13. Minimization of $E(p_1,\ldots,p_M)$ with respect to the p_j resulted in $R = 0.740$ $\mathring{A}$ and $D = 4.70$ *eV*, in very good agreement with experiment. More recent variational calculations of the same general character give theoretical results whose errors are estimated to be much smaller than experimental uncertainties, and other theoretical corrections.

Before leaving the variational calculation for H_2, we want to make a *very* rough "guesstimate" of the number of parameters M needed for a satisfactory result.

The number of continuous variables of $\Psi(r_1,r_2)$ is $6 - 1 = 5$, the reduction by 1 reflecting axial symmetry. Let us call the number of parameter per variable needed for the desired accuracy p. Since a fractional accuracy of $O(10^{-2})$ is needed for the energy, implying a fractional accuracy of $O(10^{-1})$ in Ψ, we guess that $3 \ll p \ll 10$. Hence $M = p^5 = 3^5 - 10^5 \approx 10^2 - 10^5$.

By using symmetries and chemical and mathematical insights, this number can be significantly reduced. Such relatively modest numbers are very managable on today's (and even yesterday's) computers.

It is thus not surprising that *for sufficiently small molecules, wavefunction methods give excellent results.*

B. Many Electrons – Encountering an Exponential Wall

In the same spirit as our last "guesstimates" for H_2, let us now consider a general molecule consisting of N atoms with a total of N interacting electrons, where $N \gg 10$ say. We ignore symmetries and spin, which will not affect our general conclusions. Reasoning as before, we see that the number M of parameter required is

$$M = p^{3N}, \quad 3 \leq p \leq 10. \tag{2.12}$$

The energy needs to be minimized in the space of these M parameters. Call $\bar{M}$ the maximum value feasible with the best available computer software and hardware; and $\bar{N}$ the corresponding maximum number of electrons. Then, from Eq. (2.12) we find

$$\bar{N} = \frac{1}{3}\frac{log\bar{M}}{logp} \cdot \tag{2.13}$$

Let us optimistically take $\bar{M} \approx 10^9$ and $p = 3$. This gives the shocking result

$$\bar{N} = \frac{1}{3}\,\frac{9}{0.48} = 6(!) \cdot \tag{2.14}$$

In practice, by being "clever", one can do better than this, perhaps by one half order of magnitude, up to say $\bar{N} \approx 20$. But the exponential in Eq. (2.12) represents a "wall" severely limiting $\bar{N}$.

Let us turn this question around and ask what is the needed M for $N = 100$. By Eq. (2.12) and taking $p = 3$ we find

$$M \approx 3^{300} \approx 10^{150}(!) \tag{2.15}$$

I cannot foresee an advance in computer science which can minimize a quantity in a space of 10^{150} dimensions. Of course, estimates like Eq. (2.15) are very rough and only their logarithm should be taken seriously. But the "exponential wall" is real and reflects the interconnectedness of $\Psi(r_1,...,r_N)$ in the $3N$ dimensional configuration space defined by the requirement that all r_j be inside the 3D region containing the molecule.

We conclude that traditional wavefunction methods, which provide the "required" chemical accuracy are generally limited to molecules with a small total number of chemically active electrons, $N \lesssim O(10)$.

C. Some Meta-physical-chemical Considerations

The following remarks are related to a very old paper by one of my teachers, J.H. Van Vleck,[11] in which he discusses a problem with many-body wavefunctions, later referred to as the Van Vleck catastrophy.

I begin with a provocative statement. *In general the many-electron wavefunction* $\Psi(r_1,...,r_N)$ *for a system of N electrons is not a legitimate scientific concept, when* $N \geq N_0$, *where* $N_0 \approx 10^3$.

I will use two criteria for defining "legitimacy": a) That Ψ can be calculated with sufficient accuracy and b) can be recorded with sufficient accuracy.

Construction of an accurate approximation to Ψ.

Without leaving the context of wavefunctions, I shall call the approximate wavefunction $\tilde{\Psi}$ sufficiently accurate if

$$|\,\tilde{\Psi}, \Psi)\,|^2 \gg 0.5\ , \tag{2.16}$$

a rather liberal requirement. (One could equally well choose 0.9 or 0.1).

Consider now the example of N' non-overlapping identical n-electron molecules with exact wave-functions $\psi_l(r_1,...,r_n)$, and approximate wave-functions $\tilde{\psi}_l(r_1,...,r_n)$. Let us take $n = 10$ and posit that a very accurate $\tilde{\psi}_l$ can be calculated with

$$|\,(\tilde{\psi}_\ell, \psi)\,| = 1 - \epsilon \ \textit{where}\ \epsilon = 10^{-2}\ , \tag{2.17}$$

again a liberal estimate.

Then, for an N'-molecule system with $N' \approx 10^2$, and thus $N = 10^3$ electrons $(\tilde{\Psi}, \Psi) = (1 - \varepsilon)^{N'} \approx e^{-N'\varepsilon} \approx e^{-1} \approx 0.37$, i.e., almost acceptable by the criterion (2.16). Note however, that for $N = 10^4$, $(\tilde{\Psi}, \Psi) \approx e^{-10} \approx 5 \times 10^{-5}$ so that $|\tilde{\Psi}, \Psi\ |^2 \sim 3 \times 10^{-9}(!)$ – the exponential wall is again there, in another form. For fully interacting systems the situation is much worse and our estimate of $N_0 \approx 10^3$ is probably much too high.

Can this problem ever be overcome along present lines of thought? I think not. Even if there were *no* computational limits, other physical effects, such as

relativistic or radiative corrections which may be minor for systems of small N exponentiate when N exceeds N_0.

(It is obvious that the estimates made above have only logarithmic validity).

Recording of $\Psi(r_1,r_2,...,r_N)$.

Let us now assume that somehow we have obtained an accurate approximation to $\tilde{\Psi}$, in the sense of Eq (2.16), and wish to record it so it can be reproduced at a later time. How many bits are needed? Let us take q bits per variable. Then the total number of bits is

$$B = q^{3N} \tag{2.18}$$

For $q = 3$, a very rough fit, and $N = 10^3$, $B = 10^{1500}$, a quite unrealistic number. (The total number of baryons in the accessible universe is estimated as $10^{80\pm}$).

Having attempted to discredit the very-many-electron wavefunction $\Psi(r_1,...,r_N)$, for *many* electrons I must, of course, recall two well-known facts: physically/chemically interesting quantities, like total energy E, density $n(r)$, pair correlation function $g(r,r')$, etc. depend on only very *few variables* and, formally, can be thought of as obtained by tracing over all other variables, e.g.

$$n(r) = N \int \Psi^*(r, r_2, ..., r_N)\Psi(r, r_2, ..., r_N)dr_2...dr_N \ ; \tag{2.19}$$

and that some $\tilde{\Psi}$'s which, by the criterion (1.16) are hopelessly "bad" for large N, give respectable and even very accurate results for these contracted quantities. Of course not *every* bad trial-$\tilde{\Psi}$ will give good results for these quantities, and the question of how one discriminates the useful "bad" $\tilde{\Psi}$, from the vast majority of useless "bad" $\tilde{\Psi}$'s requires much further thought. This issue is related, I believe, to the concept of "nearsightedness" which I have recently suggested[10].

In concluding this section I remark that DFT, while *derived* from the N-particle Schroedinger equation, is finally expressed entirely in terms of the density $n(r)$, in the Hohenberg-Kohn formulation,[1] and in terms of $n(r)$ and *single*-particle wavefunctions $\psi_j(r)$, in the Kohn-Sham formulation[2]. This is why it has been most useful for systems of very many electrons where wavefunction methods encounter and are stopped by the "exponential wall".

III. DENSITY FUNCTIONAL THEORY–BACKGROUND

In the fall of 1963, I was spending a sabbatical semester at the École Normale Supérieure in the spacious office of Philippe Nozières. A few weeks after my arrival Pierre Hohenberg, also a visitor from the US, joined forces with me. Ever since my period at the Carnegie Institute of Technology (1950-1959) I had been interested in disordered metallic alloys, partly because of the excellent metallurgy department and partly because of the interesting experimental program of Emerson Pugh, in Physics, on substitutional alloys of Cu with the adjacent elements in the periodic table, such as Cu_xZn_{1-x}. These alloys were viewed in two rather contradictory ways: As an *average* periodic crystal with

non-integral atomic number $\bar{Z} = xZ_1 + (1-x)Z_2 (Z_1 = 29,\ Z_2 = 30)$. This model nicely explained the linear dependence of the electronic specific heat on x. On the other hand the low temperature resistance is roughly proportional to $x(1-x)$, reflecting the degree of disorder among the two constituents. While isolated *Cu* and *Zn* atoms are, of course, neutral, in a *Cu–Zn* alloy there is transfer of charge between *Cu* and *Zn* unit cells on account of their chemical differences. The electrostatic interaction energy of these charges is an important part of the total energy. Thus in considering the energetics of this system there was a natural emphasis on the electron density distribution $n(r)$.

Now a very crude theory of electronic energy in terms of the electron density distribution, $n(r)$, the Thomas-Fermi (TF) theory, had existed since the 1920s[4] [5]. It was quite useful for describing some qualitative trends, e.g. for *total* energies of atoms, but for questions of chemistry and materials science, which involve valence electrons, it was of almost no use; for example it did not lead to any chemical binding. However the theory had one feature which interested me: It considered interacting electrons moving in an external potential $v(r)$, and provided a highly over-simplified one-to-one implicit relation between $v(r)$ and the density distribution $n(r)$:

$$n(r) = \gamma(\mu - v_{eff}(r))^{3/2} \qquad \left(\gamma = \frac{1}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\right), \tag{3.1}$$

$$v_{eff}(r) \equiv v(r) + \int \frac{n(r')}{|r - r'|} dr', \tag{3.2}$$

where μ is the r-independent chemical potential; Eq. (3.1) is based on the expression

$$n = \gamma(\mu - v)^{3/2} \tag{3.3}$$

for the density of a *uniform*, non-interacting, degenerate electron gas in a constant external potential v; and the second term in (3.2) is just the classically computed electrostatic potential times (–1), generated by the electron density distribution $n(r')$. Since Eq. (3.1) ignores gradients of $v_{eff}(r)$ it was clear that the theory would apply best for systems of slowly varying density.

In subsequent years various refinements (gradient-, exchange-and correlation corrections) were introduced, but the theory did not become significantly more useful for applications to the electronic structure of matter. It was clear that TF theory was a rough representation of the exact solution of the many-electron Schroedinger equation, but since TF theory was expressed in terms of $n(r)$ and Schroedinger theory in term of $\Psi(r_1,...,r_N)$, it was not clear how to establish a strict connection between them.

This raised a general question in my mind: Is a *complete, exact* description of groundstate electronic structure in terms of $n(r)$ possible in principle. A key question was whether the density $n(r)$ *completely* characterized the system. It was true in TF theory, where $n(r)$, substituted in Eq. (3.1) yields, $(v_{eff}(r) - \mu$ and, by (3.2), $(v(r) - \mu)$. In addition, $n(r)$ also yields the total number of elec-

trons by integration. Thus the physical system is completely specified by $n(r)$. It was also simple to check that the same was true for any 1-particle system, as well as for a weakly perturbed, interacting, uniform electron gas

$$v(r) = v_0 + \lambda v_1(r) \quad (\lambda \ll 1) \ , \tag{3.4}$$

$$n(r) = n_0 + \lambda n_1(r) + \dots \ , \tag{3.5}$$

for which $v_1(r)$ can be explicitly calculated in term of $n_1(r)$ by means of the wave-number-dependent susceptibility of the uniform gas. This suggested the hypothesis that *a knowledge of the groundstate density of $n(r)$ for any electronic system, (with or without interactions) uniquely determines the system.* This hypothesis became the starting point of modern DFT.

IV. THE HOHENBERG-KOHN FORMULATION OF DENSITY FUNCTIONAL THEORY

A. The Density n(r) as the Basic Variable

The Basic Lemma of HK. The groundstate density $n(r)$ of a bound system of interacting electrons in some external potential $v(r)$ determines this potential uniquely[1].

Remarks:

(1) The term "uniquely" means here up to an uninteresting additive constant.

(2) In the case of a degenerate groundstate, the lemma refers to *any* groundstate density $n(r)$.

(3) This lemma is mathematically rigorous.

The proof is very simple. We present it for a non-degenerate groundstate.

Let $n(r)$ be the non-degenerate groundstate density of N electrons in the potential $v_1(r)$, corresponding to the groundstate Ψ_1, and the energy E_1. Then,

$$E_1 = (\Psi_1, H_1\Psi_1) = \int v_1(r)n(r)dr + (\Psi_1, (T+U)\Psi_1) \ , \tag{4.1}$$

where H_1 is the total Hamiltonian corresponding to v_1, and T and U are the kinetic and interaction energy operators. Now assume that there exists a second potential $v_2(r)$, *not* equal to $v_1(r)$ + constant, with groundstate Ψ_2, necessarily $\neq e^{i\Theta}\Psi_1$, which gives rise to the same $n(r)$. Then

$$E_2 = \int v_2(r)n(r)dr + \int (\Psi_2, (T+U)\Psi_2). \tag{4.2}$$

Since Ψ_1 is assumed to be non-degenerate, the Rayleigh-Ritz minimal principle for Ψ_1 gives the inequality,

$$E_1 < (\Psi_2, H_1\Psi_2) = \int v_1(r)n(r)dr + (\Psi_2, (T+U)\Psi_2)$$
$$= E_2 + \int (v_1(r) - v_2(r))n(r)dr. \qquad (4.3)$$

Similarly

$$E_2 \leq (\Psi_1, H\Psi_1) = E_1 + \int (v_2(r) - v_1(r_1))n(r)dr \quad , \qquad (4.4)$$

where we use $\leq$ since the non-degeneracy of Ψ_2 was not assumed. Adding (4.3) and (4.4) leads to the contradiction

$$E_1 + E_2 < E_1 + E_2. \qquad (4.5)$$

We conclude by *reductivo ad absurdum* that the assumption of the existence of a second potential $v_2(r)$, which is unequal to $v_1(r)$ + constant and gives the same $n(r)$, must be wrong. The lemma is thus proved for a non-degenerate groundstate.

Since $n(r)$ determines both N and $v(r)$ (ignoring an irrelevant additive constant) it gives us the full H and N for the electronic system. Hence $n(r)$ determines implicitly *all* properties derivable from H through the solution of the time-independent or time-dependent Schroedinger equation (even in the presence of additional perturbations like electromagnetic fields), such as: the many-body eigenstates $\Psi^{(0)}(r_1,...,r_N)$, $\Psi^{(1)}(r_1,...,r_N)$, ... the 2-particle Green's function $G(r_1t_1, r_2t_2)$, the frequency dependent electric polarizability $\alpha(\omega)$, and so on. We repeat that all this information is implicit in $n(r)$, the groundstate density.

Remarks:

1. The requirement of non-degeneracy can easily be lifted[12].
2. Of course the lemma remains valid for the special case of non-interacting electrons.
3. Lastly we come to the question whether *any* well-behaved positive function $n(r)$, which integrates to a positive integer N, is a possible groundstate density corresponding to *some* $v(r)$. Such a density is called v-representable (VR). On the positive side it is easy to verify that, in powers of λ, any nearly uniform, real density of the form $n(r) = n_o + \lambda\Sigma\, n(q)e^{iq.r}$ is VR, and that for a single particle any normalized density $n(r) = |\psi(r)|^2$ is also VR. On the other hand Levy[13] and Lieb [14] have shown by an example which involves degenerate groundstates, that there do exist well-behaved densities which are *not* VR. The topology of the regions of v-representability in the abstract space of all $n(r)$ continues to be studied. But this issue has so far not appeared as a limitation in practical applications of DFT.

B. The Hohenberg-Kohn Variational Principle

The most important property of an electronic groundstate is its energy E. By wavefunction methods E could be calculated either by direct approximate

solution of the Schroedinger Equation $H\Psi = E\Psi$ or from the Rayleigh Ritz minimal principle,

$$E = min_{\tilde{\Psi}}(\tilde{\Psi}, H\tilde{\Psi}) \ , \tag{4.6}$$

where $\tilde{\Psi}$ is a normalized trial function for the given number of electrons, N.

The formulation of the minimal principle in terms of trial densities, $\tilde{n}(r)$, rather than trial wavefunctions $\tilde{\Psi}$ was first presented in ref. 1. Here we shall follow the more succinct derivation due to Levy[13] and Lieb[14], called the *constrained search method.*

Every trial function $\tilde{\Psi}$ corresponds to a trial density $\tilde{n}(r)$ obtained by integrating $\tilde{\Psi} * \tilde{\Psi}$ over all variables except the first and multiplying by N. One may carry out the minimization of (4.6) in two stages. First fix a trial $\tilde{n}(r)$ and denote by $\tilde{\Psi}^{\alpha}_{\tilde{n}}$ the class of trial functions with this $\tilde{n}$. We define the constrained energy minimum, with $\tilde{n}(r)$ fixed, as

$$\begin{aligned} E_v[\tilde{n}(r)] &\equiv \min_{\alpha}(\tilde{\Psi}^{\alpha}_{\tilde{n}}, H\tilde{\Psi}^{\alpha}_{\tilde{n}}) \\ &= \int v(r)\tilde{n}(r)dr + F[\tilde{n}(r)], \end{aligned} \tag{4.7}$$

where

$$F[\tilde{n}(r)] \equiv \min_{\alpha}(\tilde{\Psi}^{\alpha}_{\tilde{n}(r)}, (T+U)\Psi^{\alpha}_{\tilde{n}(r)}) \ . \tag{4.8}$$

$F[\tilde{n}(r)]$ requires no explicit knowledge of $v(r)$. It is a universal functional of the density $\tilde{n}(r)$, (whether the latter is VR or not). In the second step minimize (4.7) over all $\tilde{n}$,

$$E = min_{\tilde{n}(r)}E_v[\tilde{n}(r)] = min_{\tilde{n}(r)}\{\int v(r)\tilde{n}(r)dr + F[\tilde{n}(r)]\}. \tag{4.9}$$

For a non-degenerate groundstate, the minimum is attained when $\tilde{n}(r)$ is the groundstate density; and, for the case of a degenerate groundstate, when $\tilde{n}(r)$ is any one of the groundstate densities. The HK minimum principle (4.9) may be considered as the formal exactification of Thomas-Fermi theory.

The formidable problem of finding the minimum of $(\tilde{\Psi}, H\tilde{\Psi})$ with respect to the 3N-dimensional trial function $\tilde{\Psi}$ has been transformed into the *seemingly* trivial problem of finding the minimum of $E_v[\tilde{n}(r)]$ with respect to the 3-dimensional trial function $\tilde{n}(r)$.

Actually the definition (4.8) of $F[\tilde{n}(r)]$ leads us right back to minimization with respect to 3N-dimensional trial wavefunctions. Nevertheless, significant *formal* progress has been made: *the strict formulation* of the problem of groundstate densities and energies entirely in terms of the density distribution $\tilde{n}(r)$ and of a well-defined, though, not explicitly known, functional of the density, $F[\tilde{n}(r)]$, which represents the sum of kinetic energy and interaction energy $(T+U)$, associated with $\tilde{n}$ (see Eq. (4.8)).

One can now easily re-derive the Thomas-Fermi (TF) theory by making the approximations

$$T = \int n(r) \frac{3}{10} k_F^2(n(r)) dr, \tag{4.10}$$

$$U = \frac{1}{2} \int \frac{n(r)n(r')}{|r - r'|} dr dr', \tag{4.11}$$

where $k_F(n)$ is the Fermi wave-vector of a uniform electron gas of density n and $\frac{3}{10} k_F^2(n)$ is the mean kinetic energy per electron of such a gas. The expression for U is the classical (or mean field) approximation. Various previously known corrections, of TF theory for exchange, correlation and density gradients can also be easily re-derived.

The main remaining error is due to the seriously inadequate representation of the kinetic energy, T, by Eq.(4.10) or its gradient-corrected forms. This deficiency is largely remedied by the self-consistent, so-called Kohn-Sham equations, discussed in the following Section 4C.

A second interesting class of systems $n(r) = n_0 + n_1(r)$, where $n_1(r) \ll n_0$, could also be treated using the n_0-dependent density-density response function, $K(|r - r'|)$.

C. The Self Consistent Kohn-Sham Equations

Soon after the publication of the TF theory, Hartree[8] proposed a set of self-consistent single particle equations for the approximate description of the electronic structure of atoms[8]. The concept was physically very simple. Every electron was regarded as moving in an effective single particle potential

$$v_H(r) = -\frac{Z}{r} + \int \frac{n(r')}{|r - r'|} dr', \tag{4.12}$$

where the first term represents the potential due to a nucleus of atomic number Z and the second the potential due to the average density distribution $n(r)$. (The negative charge of the electron has been allowed for). Thus each electron obeys the single particle Schroedinger equation

$$\{-\frac{1}{2} \nabla^2 + v_H(r)\} \varphi_j(r) = \epsilon_j \varphi_j(r), \tag{4.13}$$

where j denotes both spatial as well as spin quantum numbers. The mean density is given by

$$n(r) = \sum_{j=1}^{N} |\varphi_j(r)|^2, \tag{4.14}$$

where, in the groundstate, the sum runs over the N lowest eigenvalues, to respect the Pauli exclusion principle. Equations (4.12)–(4.14) are called the

self-consistent Hartree equations. One may start from a first approximation for $n(r)$, (e.g. from TF theory), construct $v_H(r)$, solve (4.13) for the φj; and recalculate $n(r)$ from Eq. (4.14), which should be the same as the initial $n(r)$. If it is not one iterates appropriately until it is.

In the winter of 1964, I returned from France to San Diego, where I found my new post-doctoral fellow, Lu Sham. I knew that the Hartree equations described atomic groundstates much better than TF theory. The difference between them lay in the different treatments of the kinetic energy T (See Eqs. (4.10) and (4.13). I set ourselves the task of extracting the Hartree equations from the HK variational principle for the energy, Eqs. (4.9), (4.7), (4.8), which I knew to be formally *exact* and which therefore had to have the Hartree equations *and* improvements "in them". In fact it promised a Hartree-like formulation, which – like the HK minimal principle – would be formally exact.

The Hartree differential equation (4.13) had the *form* of the Schroedinger equation for *non-interacting* electrons moving in the external potential v_{eff}. Could we learn something useful from a DFT for non-interacting electrons moving in a given external potential $v(r)$?. For such a system, the HK variational principle takes the form

$$E_{v(r)}[\tilde{n}] \equiv \int v(r)\tilde{n}(r)dr + T_s[\tilde{n}(r)] \tag{4.15}$$

$$\geq E\,, \tag{4.16}$$

where (assuming that $\tilde{n}(r)$ is *VR* for non-interacting electrons),

$$T_s[\tilde{n}(r)] \equiv \text{kinetic energy of the groundstate of } \textit{non-interacting} \text{ electrons with density distribution } \tilde{n}(r). \tag{4.17}$$

The Euler-Lagrange equations, embodying the fact that the expression (4.14) is stationary with respect to variations of $\tilde{n}(r)$ which leave the total number of electrons unchanged, is

$$\delta E_v[\tilde{n}(r)] \equiv \int \delta\tilde{n}(r)\,\{v(r) + \frac{\delta}{\delta\tilde{n}(r)}T_s[\tilde{n}(r)]\;|_{\tilde{n}=n} - \epsilon\}dr = 0\;, \tag{4.18}$$

where $\tilde{n}(r)$ is the exact groundstate density for $v(r)$. Here ε is a Lagrange multiplyer to assure particle conservation. Now in this soluble, non-interacting case we know that the groundstate energy and density can be obtained by calculating the eigenfunctions $\varphi_j(r)$ and eigenvalues ε_j of non-interacting, single-particle equations

$$(-\frac{1}{2}\nabla^2 + v(r) - \epsilon_j)\varphi_j(r) = 0\,, \tag{4.19}$$

yielding

$$E = \sum_{j=1}^{N}\epsilon_j\;\;;\;\; n(r) = \sum_{j=1}^{N} |\,\varphi_j(r)\,|^2\,. \tag{4.20}$$

(Here j labels both orbital quantum numbers and spin indices, ± 1).

Returning now to the problem of *interacting* electrons, which had previously been addressed approximately by the single-particle-like Hartree equations, we deliberately wrote the functional $F[\tilde{n}(r)]$ of Eq. (4.8) in the form

$$F[\tilde{n}(r)] \equiv T_s[\tilde{n}(r)] + \frac{1}{2}\int \frac{\tilde{n}(r)\tilde{n}(r')}{|\, r - r' \,|} dr dr' + E_{xc}[\tilde{n}(r)] \ , \qquad (4.21)$$

where $T_s[\tilde{n}(r)]$ is the kinetic energy functional for *non-interacting* electrons, Eq. (4.15). The last term, $E_{xc}[\tilde{n}(r)]$, the so-called exchange-correlation energy functional is then *defined* by Eq. (4.21). The HK variational principle for *interacting* electrons now takes the form,

$$E_v[\tilde{n}(r)] \equiv \int v(r)\tilde{n}(r)dr + T_s[\tilde{n}(r)] + \frac{1}{2}\int \frac{\tilde{n}(r)\tilde{n}(r')}{|\, r - r' \,|} dr dr' + E_{xc}[\tilde{n}(r)] \qquad (4.22)$$
$$\geq E \ .$$

The corresponding Euler-Lagrange equations, for a given total number of electrons has the form

$$\delta E_v[\tilde{n}(r)] = \int \delta\tilde{n}(r)\{v_{eff}(r) + \frac{\delta}{\delta\tilde{n}(r)} T_s[\tilde{n}(r)] \,|_{\tilde{n}(r)=n(r)} - \epsilon\}\, dr = 0, \qquad (4.23)$$

where

$$v_{eff}(r) \equiv v(r) + \int \frac{n(r')}{|\, r - r' \,|} dr' + v_{xc}(r) \qquad (4.24)$$

and

$$v_{xc}(r) \equiv \frac{\delta}{\delta\tilde{n}(r)} E_{xc}[\tilde{n}(r)] \,|_{\tilde{n}(r)=n(r)}. \qquad (4.25)$$

Now the *form* of Eq. (4.23) is identical to that of Eq. (4.18) for non-interacting particles moving in an effective external potential v_{eff} instead of $v(r)$, and so we conclude that the minimizing density $n(r)$ is given by solving the single-particle equation

$$(-\frac{1}{2}\nabla^2 + v_{eff}(r) - \epsilon_j)\, \varphi_j(r) = 0 \ , \qquad (4.26)$$

with

$$n(r) = \sum_{j=1}^{N} |\, \varphi_j(r) \,|^2 \ , \qquad (4.27)$$

$$v_{eff}(r) = v(r) + \int \frac{n(r')}{|\, r - r' \,|} dr' + v_{xc}(r), \qquad (4.28)$$

where $v_{xc}(r)$ is the *local* exchange-correlation potential, depending functionally on the entire density distribution $\tilde{n}(r)$, as given by Eq. (4.25). These self-consistant equations are now called the Kohn-Sham (KS) equations.

The groundstate *energy* is given by

$$E = \sum_j \epsilon_j + E_{xc}[n(r)] - \int v_{xc}(r)n(r)dv - \frac{1}{2}\int \frac{n(r)n(r')}{|r-r'|}. \quad (4.29)$$

If one neglects E_{xc} and v_{xc} altogether, the KS equations (4.26)-(4.29), reduce to the self-consistent Hartree equations.

The KS theory may be regarded as the formal exactification of Hartree theory. With the *exact* E_{xc} and v_{xc} all many body effects are in principle included. Clearly this directs attention to the functional $E_{xc}[\tilde{n}(r)]$. The practical usefulness of groundstate DFT depends entirely on whether approximations for the functional $E_{xc}[\tilde{n}(r)]$ could be found, which are at the same time sufficiently simple and sufficiently accurate. The next section V briefly describes the development and current status of such approximations.

Remarks:

1. The exact effective single particle potential $v_{eff}(r)$ of KS theory, Eq. (4.28) can be regarded as that unique, fictitious external potential which leads, for non-interacting particles, to the same physical density $n(r)$ as that of the interacting electrons in the physical external potential $v(r)$. Thus if the physical density $n(r)$ is independently known (from experiment or–for small systems–from accurate, wavefunction-based calculations) $v_{eff}(r)$ and hence also $v_{xc}(r)$ can be directly obtained from the density $n(r)$ [15].
2. Because of their linkage to the exact physical density $n(r)$, the KS single particle wavefunctions $\varphi_j(r)$ may be considered as "density-optimal", while, of course, the Hartree-Fock HF wavefunctions $\varphi_j^{HF}(r)$ are "total energy-optimal" in the sense that their normalized determinant leads to the lowest groundstate energy attainable with a single determinant. Since the advent of DFT the term "exchange energy" is often used for the exchange energy computed with the exact KS $\varphi_j(r)$, and not with the HF φ_j^{HF}. (For the uniform electron gas the two definitions agree; typically the differences are very small).
3. Neither the exact KS wavefunctions φ_j nor energies ε_j have any known, directly observable, strict meaning, except for a) the connection (4.27) between the φ_j and the true, physical density $n(r)$; and b) the fact that the magnitude of the highest occupied ε_j, relative to the vacuum equals the ionization energy [16].

In concluding this Section we remark that most practical application of DFT use the KS equations, rather than the generally less accurate HK formulation.

V. APPROXIMATION FOR $E_{xc}[n(r)]$: FROM MATHEMATICS TO PHYSICAL SCIENCE

So far DFT has been presented as a formal *mathematical framework* for viewing electronic structure from the perspective of the electron-density $n(r)$. This mathematical framework has been motivated by physical considerations, but

to make concrete use of it we require effective approximations for $F[n(r)]$ in the HK formulation, and for $E_{xc}[n(r)]$ in the KS formulation. *These approximations reflect the physics of electronic structure and come from outside of DFT.* In this account I limit myself to the much more extensively used functional E_{xc}.

The most important approximations for $E_{xc}[n(r)]$ have a quasi-local form. As will be discussed in Section 5B, $E_{xc}[n(r)]$ can be written in the form

$$E_{xc}[n(r)] = \int e_{xc}(r; [n(\tilde{r}])n(r)dr\,, \tag{5.1}$$

where $e_{xc}(r;[n(\tilde{r})])$ represents an exchange-correlation (xc) energy/particle at the point r, which is a functional of the density distribution $n(\tilde{r})$. It depends primarily on the density $n(\tilde{r})$ at points $\tilde{r}$ near r, where "near" is a microscopic distance such as the local Fermi wavelength $\lambda_F(r) \equiv [3\pi^2 n(r)]^{-1/3}$ or TF screening length, typically of similar magnitude. The general form of Eq. (5.1), representing the total E_{xc} as an integral over all space of a suitable integrand is similar to the treatment of kinetic energy in Thomas-Fermi theory, Eq. (4.10). All components of the KS energy, can be expressed in terms of the 1- and 2- particle density matrices of the interacting and non-interacting system $n_1(r_1;r_1')$, $n_2(r_1,r_2;r_1', r_2')$ and $n_1^0(r_1;r'_1)$, $n_2^0(r_1r_2;r'_1r'_2)$, all corresponding to and uniquely defined by the *same* physical $n(r)$; their calculation involves these Green's functions primarily for arguments, such as (r_1,r_1') and $(r_1,r_2;r_1'r_2')$, which are microscopically close to one another; furthermore, for given r_1, these Green's functions depend only on the form of $n(\tilde{r})$ for $\tilde{r}$ near r_1 – the property of "nearsightedness" previously mentioned[10]. This leads immediately to the form (5.1) for $E_{xc}[n(r)]$, where e_{xc} is a nearsighted functional of $n(\tilde{r})$.

We now briefly discuss several implementations of this quasi-local approach.

A. The Local Density Approximation (LDA)

The simplest, and at the same time remarkably serviceable, approximation for $E_{xc}[n(r)]$ is the so-called local density approximation (LDA),

$$E_{xc}^{LDA} \equiv \int e_{xc}(n(r))\, n(r)dr, \tag{5.2}$$

where $e_{xc}(n)$ is the exchange-correlation energy of a *uniform* electron gas of density n[2]. The exchange part is elementary and given, in atomic units, by

$$e_x(n) \equiv -\frac{0.458}{r_s}\,, \tag{5.3}$$

where r_s, is the radius of a sphere containing one electron and given by $(4\pi/3)r_s^3 = n^{-1}$. The correlation part was first estimated by E.P. Wigner[17]

$$\epsilon_c(n) = -\frac{0.44}{r_s + 7.8}\,, \tag{5.4}$$

and more recently with a high precision of about ± 1 % by D.M. Ceperly[18] using Monte Carlo methods.

Remarks:

1. The LDA, obviously exact for a uniform electron gas, was a priori expected to be useful only for densities varying slowly on the scales of the local Fermi wavelength λ_F and TF wavelength, λ_{TF}. In atomic systems these conditions are rarely well satisfied and very often seriously violated. Nevertheless the LDA has been found to give extremely useful results for most applications. This has been at least partly rationalized by the observation that the LDA satisfies a sum rule which expresses the normalization of the exchange correlation hole. In other words, given that an electron is at r, the conditional electron density $n(r;r')$ of the other electrons is depleted near r in comparison with the average density $n(r')$ by the hole distribution $n_h(r';r)$ which integrates to 1.
2. The solution of the KS equation in the LDA is minimally more difficult than the solution of the Hartree equation and very much easier than the solution of the HF equations. Its accuracy for the exchange energy is typically within O(10 %), while the normally much smaller correlation energy is generally overestimated by up to a factor of 2. The two errors typically cancel partially.
3. Experience has shown that the LDA gives ionization energies of atoms, dissociation energies of molecules and cohesive energies with a fair accuracy of typically 10–20 %. However the LDA gives bond-lengths and thus the geometries of molecules and solids typically with an astonishing accuracy of ~ 1 %.
4. The LDA (and the LSDA, its extension to system with unpaired spins) can fail in systems, like heavy fermion systems, so dominated by electron-electron interaction effects that they lack any resemblance to non-interacting electron gases.

B. Beyond the Local Density Approximation

The LDA is the "mother" of almost all approximations currently in use in DFT. To discuss more accurate approximations we now introduce the concept of the *average xc hole* distribution around a given point r. The *physical xc hole* is given by

$$n_{xc}(r,r') = g(r,r') - n(r') \quad , \tag{5.5}$$

where $g(r,r')$ is the conditional density at r' given that one electron is at r. It describes the "hole" dug into the average density $n(r')$ by the electron at r. This hole is normalized

$$\int n_{xc}(r,r')dr' = -1 \quad , \tag{5.6}$$

which reflects a total "screening" of the electron at r, and generally is localized due to the combined effect of the Pauli principle and the electron-elec-

tron interaction. Of course, like everything else, it is a functional of the density distribution $n(\tilde{r})$. To define the *average xc* hole one introduces a fictitious, λ-depentent Hamiltonian, H_λ for the many body system, $0 \leq \lambda \leq 1$, which differs from the physical Hamiltonian, $H_{\lambda=1}$, by the two replacements

$$\frac{e^2}{|r_i - r_j|} \longrightarrow \frac{\lambda e^2}{|r_i - r_j|} \ , \tag{5.7}$$

$$v(r) \longrightarrow v_\lambda(r) \ , \tag{5.8}$$

where the fictitious $v_\lambda(r)$ is so chosen that for all λ in the interval (0,1) the corresponding density equals the physical density, $n(r)$:

$$n_\lambda(r) \equiv n_{\lambda=1}(r) = n(r) \ . \tag{5.9}$$

The procedure (5.2), (5.3) represents an interpolation between the KS system ($\lambda = 0$) and the physical system ($\lambda = 1$). The average *xc* hole density $\bar{n}(r,r')$ is then defined as

$$\bar{n}_{xc}(r,r') = \int_0^1 d\lambda n_{xc}(r,r';\lambda) \ . \tag{5.10}$$

Its importance stems from the exact result, proved independently in three important publications[19], that

$$E_{xc} = \frac{1}{2}\int dr dr' \frac{n(r)\bar{n}_{xc}(r,r')}{|r - r'|} \ . \tag{5.11}$$

An equivalent expression is[20]

$$E_{xc} = -\frac{1}{2}\int dr n(r)\bar{R}_{xc}^{-1}(r,[n(\tilde{r})] \ , \tag{5.12}$$

where

$$\bar{R}_{xc}^{-1}(r,n(\tilde{r})) \equiv \int dr' \frac{(-\bar{n}_{xc}(r,r'[n(\tilde{r})])}{|r - r'|} \ , \tag{5.13}$$

is the moment of degree (–1) of $\bar{n}_{xc}(r,r')$, i.e., minus the inverse radius of the λ-averaged *xc* hole. Comparison of Eqs. (5.12) and (5.1) gives the very physical, formally exact relation

$$e_{xc}(r;[n(\tilde{r})]) = -\frac{1}{2}R_{xc}^{-1}(r;[n(\tilde{r})]) . \tag{5.14}$$

Gradient Expansion and Generalized Gradient Approximation

Since $R_{xc}^{-1}(r)$ is a functional of $n(\tilde{r})$, expected to be (predominantly) short-sighted, we can formally expand $n(\tilde{r})$ around the point r which we take to be the origin:

$$n(\tilde{r}) = n + \sum n_i \tilde{r}_i + \frac{1}{2} \sum n_{ij} \tilde{r}_i \tilde{r}_j + \ldots, \tag{5.15}$$

where $n \equiv n(0)$, $n_i \equiv \nabla_i n(r) \mid_{r=0}$ etc., and then consider $R_{xc}(r)$ as a function of the coefficients $n, n_i, n_{ij}, \ldots$. Ordering in powers of the differential operators and respecting the scalar nature of R_{xc}^{-1} gives

$$\begin{aligned} R_{xc}^{-1}(r) = F_0(n(r)) + F_{21}(n(r))\, \nabla^2 n(r) + F_{22}(n(r)) \\ \times \sum (\nabla_i n(r))(\nabla_i (n(r)) + \ldots \end{aligned} \tag{5.16}$$

When this is substituted into Eq. (5.12) for E_{xc} it leads (after an integration by parts) to the gradient expansion

$$E_{xc} = E_{xc}^{LDA} + \int G_2(n)(\nabla n)^2 dr + \int [G_4(n)(\nabla^2 n)^2 + \ldots]\, dr + \ldots, \tag{5.17}$$

where $G_2(n)$ is a universal functional of n[2]. In application to real systems this expansion has generally been disappointing, indeed often worsened the results of the LDA.

The series (5.15) can however be formally resummed to result in the following sequence

$$E_{xc}^0 = \int \epsilon(n(r)) n(r) dr \quad (LDA), \tag{5.18}$$

$$E_{xc}^{(1)} = \int f^{(1)}(n(r), \mid \nabla n(r) \mid) n(r) dr \quad (GGA), \tag{5.19}$$

$$E_{xc}^{(2)} = \int f^{(2)}(n(r), \mid \nabla n(r) \mid \ \nabla^2 n(r))\, dr, \tag{5.20}$$

E_{xc}^0 is the (LDA), requiring the independently calculated function of one variable, $x \equiv n$. $E_{xc}^{(1)}$ the so-called generalized gradient approximation (GGA) requires the independently calculated function of two variables, $x \equiv n$, $y \equiv |\nabla n|$ etc.

Thanks to much thoughtful work important progress has been made in deriving successful GGA's of the form (5.19). Their contruction has made use of sum rules, general scaling properties, asymptotic behavior of effective potentials and densities in the tail regions of atoms and their aggregates. In addition, A. Becke in his work on GGAs, introduced some numerical fitting parameters which he determined by optimizing the accuracy of atomization

energies of standard sets of molecules. This subject was recently reviewed[21]. We mention here some of the leading contributors: A.D. Becke, D.C. Langreth, M. Levy, R.G. Parr, J.P. Perdew, C. Lee, W. Yang.

In another approach A. Becke introduced a successful *hybrid* method

$$E_{xc}^{hyb} = \alpha E_x^{KS} + (1-\alpha) E_{xc}^{GGA}, \tag{5.21}$$

where E_x^{KS} is the exchange energy calculated with the exact KS wavefunctions, E_{xc}^{GGA} is an appropriate GGA, and α is a fitting parameter[22]. The *form* of this linear interpolation can be rationalized by the λ-integration in Eq. (5.10), with the lower limit corresponding to pure exchange.

Use of GGAs and hybrid approximations instead of the LDA has reduced errors of atomization energies of standard sets of small molecules, consisting of light atoms, by factors of typically 3-5. The remaining errors are typically ± (2–3) kg moles per atom, about twice as high as for the best current wavefunction methods. This improved accuracy, the ease of calculation, together with the previously emphasized capability of DFT to deal with systems of very many atoms, has, over a period of relatively few years beginning about 1990, made DFT a significant component of quantum chemistry.

For other kinds of improvements of the LDA, including the weighted density approximation (WDA) and self-interaction corrections (SIC) we refer the reader to the literature, e.g.[21].

Before closing this section I remark that the treatments of *xc*-effects in the LDA and all of its improvements, mentioned above, is completely inappropriate for all those systems or subsystems for which the starting point of an electron gas of slowly varying density $n(r)$ is fundamentally incorrect. Examples are a) the electronic Wigner crystal; b) Van der Waals (or polarization) energies between non-overlapping subsystems; c) the electronic tails evanescing into the vacuum near the surfaces of bounded electronic systems. However this does not preclude that DFT with appropriate, *different* approximations could successfully deal with such problems (See Sec. VII).

VI. GENERALIZATIONS AND QUANTITATIVE APPLICATIONS

While DFT for non-degenerate, non-magnetic systems has continued to progress over the last several decades, the DFT paradigm was also greatly extended and generalized in several directions. The purpose of this section is to give the briefest mention of these developments. For further details we refer to two monographs[23], [24] and a recent set of lecture notes[21]

A. Generalizations

a. Spin DFT for spin polarized systems: $v(r)$, $B_z(r)$; $n(r)$, $(n_\uparrow(r) - n_\downarrow(r))$.
b. Degenerate groundstates: $v(r)$; $n_\nu(r)$ $\nu = 1,...M$; E_0.
c. Multicomponent systems (electron hole droplets, nuclei): $v_\alpha(r)$; $n_\alpha(r)$; E_0.
d. Ensemble DFT for M degenerate groundstates: $v(r)$; $n(r)$ $(\equiv M^{-1}(Tr\, n_\nu(r))$; E_0.

e. Free energy at finite temperatures T: $v(r)$; $n(r)$, Ω (grand potential).
f. Superconductors with electronic pairing mechanisms: $v(r)$, $\Delta(r)$ (gap function); $n_{norm}(r)$, $n_{super}(r)$, E_0.
g. M excited states equi-ensembles $v(r)$, $\bar{n}(r) \equiv M^{-1}\sum_1^M n_m(r))$, $\bar{E} \equiv M^{-1}\sum_1^M E_m$.
h. Relativistic electrons.
i. Current-density functional theory diamagnetism: $v(r)$, *curl* $A(r)$; $n(r)$, *curl* $j(r)$; E_0.
j. Time-dependent phenomena: $v(r,t)$; $n(r,t)$, and excited states $v(r)e^{-i\omega t}$; $n(r)e^{-i\omega t}$; $E_j - E_i = \omega$.
k. Bosons (instead of fermions) $v(r)$; $n(r)$; E_0.
l. Combination of DFT with molecular dynamics or Monte Carlo methods (especially for determinations of structures). (Car-Parrinello method).
m. Combination of the LDA with Hubbard on-site repulsion parameter U ("LDA + U").

This incomplete list is only intended to give a general sense of the great diversity of contexts in which the basic concept of DFT has been found useful.

B. Applications

To do any kind of justice to the many thousands of applications of DFT to physical and chemical systems is entirely impossible within the framework of this lecture. So I will, quite arbitrarily, choose one example, the spin susceptibility of the alkali metals (Table 1)[25].

Table I. Spin Susceptibility of the Alkali Metals

Metal	χ/χ_0 Variational Theory	Experiment
Li	2.66	2.57
Na	1.62	1.65
K	1.79	1.70
Rb	1.78	1.72
Cs	2.20	2.24

After S.H. Vosko *et al.*,[25]. χ_0 is the Pauli susceptibility of a free electron gas.

This is an early, completely parameter-free calculation. It uses only the independently calculated external pseudo-potential $v(r)$ and the exchange correlation energy of a spatially uniform, magnetized electron gas (the so-called local spin density approximation, LSDA). The only input specific to each metal is the atomic number Z. Note how accurately the theoretical results agree with the rather irregular sequence of experimental data. The deviations of the ratio (χ/χ_0) from 1, are due, in comparable degree, to the combination of the effects of the non-uniform, periodic potentials and the electron-electron interactions.

Of course these metals have, over most of space, fairly uniform densities, which makes them favorable test-cases for local spin density calculations. For other classes of systems and their properties the accuracies can be considerably poorer, with the exception of the already mentioned very accurate results for structures, with typically a 1 % error (which is still somewhat astonishing to me).

Inclusion of gradient corrections and/or hybrid schemes have improved calculated energies for large classes of chemical applications by typically almost an order of magnitude; in physical applications the improvement is usually less dramatic. Accuracies of geometric parameters remain at the 1 % level.

VII. CONCLUDING REMARKS

DFT has now been widely accepted by both physicists and chemists. For periodic solids it is sometimes referred to as the standard model. In chemistry DFT complements traditional wave-function based methods, particularly for systems with very many atoms($\gtrsim O(10)$).

In cases where DFT currently works still rather poorly (e.g. long range polarization energies; regions of evanescent electron densities; partially filled electronic shells; reaction barriers) it often provides clues of how our present understanding of electronic structure in *real space coordinates* needs to be modified.

Looking into the future I expect that wavefunction-based and density-based theories will, in complementary ways, continue not only to give us quantitatively more accurate results, but also contribute to a better physical/chemical understanding of the electronic structure of matter.

REFERENCES

[1] P. Hohenberg and W. Kohn, *Phys. Rev.*, **136**, B864 (1964).
[2] W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).
[3] E. Schroedinger, *Am. Physik* **79**, 361 (1926).
[4] L.H. Thomas, *Proc. Camb. Phil. Soc.* **23**, 542 (1927).
[5] E. Fermi, Atti. *Accad. Nazl. Lincei* **6**, 602 (1927).
[6] W. Heitler and F. London, Zs. f. Physics **44**, 455 (1927).
[7] R.S. Mullikan, *Phys. Rev.* **32**, 186 (1928).
[8] D.R. Hartree, *Proc. Camb. Phil. Soc.* **24**, 89 (1928), F. Fock, Zs. f. Phys., **61**, 126 (1930).
[9] H.M. James and A.S. Coolidge, *J. of Chem. Phys.* **1**, 825(1933).
[10] W. Kohn, *Phys. Rev.* **76**, 17 (1996).
[11] J.H. Van Vleck, *Phys. Rev.* **49**, 232 (1936).
[12] W. Kohn, *Proc. Int'l School of Physics*, Enrico Fermi, Course LXXXIX, p. 4 (1985).
[13] M. Levy, *Phys. Rev. A* **26**, 1200 (1982).
[14] E. Lieb, in Physics as Natural Philosophy: Essays in Honor of Laszlo Tisza on his 75th Birthday, Ed. by A. Shimony and H. Feshbach (Cambridge, Mass., 1982), p. 111.
[15] Y. Wang and R. Parr, *Phys. Rev. A* **47**, 1591 (1993).
[16] C.O. Almbladh and U. von Barth, *Phys. Rev. B* **31**, 3231 (1985).
[17] E.P. Wigner, *Trans. Faraday Soc.* **34**, 678 (1938).
[18] D.M. Ceperley, *Phys. Rev. B* **18**, 3126 (1978); D.M. Ceperly and B.J. Alder, *Phys. Rev. Lett.* **45**, 566 (1980).
[19] J. Harris and R.O. Jones, *J. Phys. F* **4**, 1170 (1974); D.C. Langreth and J.P. Perdew, *Sol. State Comm.* **17**, 1425 (1975); O. Gunnarsson and B.I. Lundquist, *Phys. Rev. B* **13**, 4274 (1976).
[20] W. Kohn and A.E. Mattsson, *Phys. Rev. Lett.* **81**, 16 (1998).
[21] J.P. Perdew and S. Kurth in Density Functionals: Theory and Applications, p. 8, D. Joubert (Ed.), Springer, Berlin (1998).

[22] A.D. Becke, *J. Chem. Phys.* **104**, 1040 (1996).
[23] R.G. Parr and W. Yang, Density Functional Theory of Atoms and Molecules, Oxford University Press, Oxford, 1989.
[24] R.M. Dreizler and E.K.V. Gross, Density Functional Theory, Springer, Berlin, 1990.
[25] S.H. Vosko *et al., Phys. Rev. Lett* **35**, 1725 (1975).