Density Functional Theory — a brief introduction

Nathan Argaman

Institute for Theoretical Physics, University of California, Santa Barbara, CA 93106, USA

Guy Makov

Physics Department, NRCN, P.O. Box 9001, Beer Sheva 84190, Israel

Abstract

Density Functional Theory (DFT) is one of the most widely used methods for “ab initio” calculations of the structure of atoms, molecules, crystals, surfaces, and their interactions. A brief undergraduate-level introduction to DFT is presented here — an alternative to the customary introduction, which is often considered too lengthy to be included in various curricula. The central theme of DFT, i.e. the notion that it is possible and beneficial to replace the dependence on the external potential $v(r)$ by a dependence on the density distribution $n(r)$, is considered here to be a generalization of the idea of switching between different independent variables in thermodynamics. Specifically, it is a direct extension of the familiar Legendre transform from the chemical potential $\mu$ to the number of particles $N$. This is used to obtain the Hohenberg–Kohn theorem and to derive the Kohn–Sham equations. The exchange–correlation energy and the local density approximation to it are then discussed, followed by a very brief survey of various applications and extensions.
A. Introduction

The predominant theoretical picture of solid-state and/or molecular systems involves
the inhomogeneous electron gas: a set of interacting point electrons moving quantum-
mechanically in the field of a set of atomic nuclei, which are considered to be static (the
Born–Oppenheimer approximation). Solution of such models generally requires the use of
approximation schemes, of which the most basic — the independent electron approximation,
the Hartree theory and Hartree–Fock theory — are routinely taught to undergraduates in
Physics and Chemistry courses. However, there is another approach which over the last
thirty years or so has become increasingly the method of choice for the solution of such
problems (see Fig. 1.) — Density Functional Theory (DFT). This method has the double
advantage of being able to treat many problems to high accuracy, as well as being computa-
tionally simple (involving only a slight modification of the Hartree scheme). Despite these
advantages it is absent from most undergraduate curricula with which we are familiar.

We believe that this omission stems in part from the apparent absence of a brief in-
troduction to density functional theory. While several excellent books and review papers
on this subject are available, e.g. Refs. [1–3], they all tend to follow the historical path of
development of the theory, which unnecessarily prolongs the introduction and grapples with
problems which are not directly relevant to the practitioner. It is our purpose here to give
a brief and self-contained introduction to density functional theory, assuming only a first
course in quantum mechanics and in thermostatistics. We break with the traditional ap-
proach by relying on the analogy with thermodynamics [4] — in this formulation, concepts
such as the exchange–correlation hole or generalized compressibilities, which are central to
recent developments in the theory [5], appear naturally from the outset. The discussion is
sufficiently detailed to provide a useful overview for the beginning practitioner, and can also
serve as the basis for a one or two hour class on DFT, to be included in courses on quantum
mechanics, atomic or molecular physics, solid state physics, or materials science.

The primary characteristics of density functional theory are the role played by the elec-
tron density, \( n(\mathbf{r}) \) and the absence of many–body wavefunctions. The density distribution can be introduced by a Legendre transform, as the variable conjugate to the external potential, as we shall show in detail below. This transform makes no reference to the quantum nature of electronic systems, and in fact density–functional methods have been developed in other fields as well, e.g., in the classical description of liquids [6]. We begin by recalling (in Sec. B) some salient facts about the Legendre transform in thermodynamics, and then proceed to obtain the Hohenberg–Kohn theorems from such a transform (Sec. C). We then relate the interacting electron problem to the non–interacting problem with the same \( n(\mathbf{r}) \) distribution, thus deriving the Kohn–Sham equations (Sec. D). Practical applications of DFT rest upon uncontrolled approximations to the so–called exchange–correlation energy, of which the local density approximation is the most widely applied. Accordingly, we present this approximation and discuss some recent improvements on it (Sec. E). Finally we attempt to place the present introduction in the context of current research in DFT (Sec. F).

B. Thermodynamics: a reminder

In this section, we recall some facts which are well–known from thermodynamics [7], and show that an analogue of the Hohenberg–Kohn theorem is already implied by them.

Consider a system of many electrons, interacting with each other and with the nuclei of the corresponding atoms. The many–body Hamiltonian can be written as:

\[
\hat{H}_{MB} = \hat{T} + \hat{V} + \Lambda \hat{U},
\]

where \( \hat{T}, \hat{V}, \) and \( \hat{U} \) are respectively the kinetic, potential, and Coulomb–interaction energies of the electrons, and \( \Lambda = 1 \) is a parameter introduced for later convenience. Explicitly, the potential energy operator is \( \hat{V} = \int d\mathbf{r} \hat{n}(\mathbf{r}) v(\mathbf{r}) \), with \( \hat{n}(\mathbf{r}) \) the local density operator and \( v(\mathbf{r}) \) the potential energy due to the atomic nuclei; and the Coulomb–interaction operator is

\[
\hat{U} = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \hat{n}(\mathbf{r}) \left( \hat{n}(\mathbf{r}') - \delta(\mathbf{r}-\mathbf{r}') \right),
\]

where the second term in the bracket excludes the interaction of each electron with itself (we are using first quantized notation). The electron
density operator is defined as \( \hat{n}(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r} - \hat{\mathbf{r}}_i) \), where \( \hat{\mathbf{r}}_i \) is the position of the \( i \)th electron, and \( N \) is the number of electrons in the system. Depending on \( \nu(\mathbf{r}) \), this Hamiltonian may describe an atom with only a few electrons, a molecule, or a piece of solid material (in the latter case, periodic boundary conditions are usually implied).

The starting point for our discussion is the grand–canonical ensemble, in which the system is assumed to be in contact with a reservoir of finite temperature \( T \) and chemical potential \( \mu \). This differs from most uses of DFT which address the ground–state properties of a system of \( N \) electrons — we will recover this case below by taking the \( T \to 0 \) limit. The grand potential, which is the free energy in this case, is given by:

\[
\Omega = -T \log \text{Tr} \exp \left( \frac{\hat{H}_{MB} - \mu \hat{N}}{T} \right),
\]

where \( \hat{N} \) is the overall electron number operator, and the temperature is in energy units (i.e. \( k_B = 1 \)). The trace here sums over all possible electron numbers \( N \), and over all the states in the Hilbert space of the many–body Hamiltonian for each \( N \). The expectation value of the number of electrons in the system is given by a derivative of the grand potential, \( N = -\frac{\partial \Omega}{\partial \mu} \) (note that from here on, \( N \) denotes an expectation value and not a given number). Other partial derivatives give the values of additional physical quantities, such as the electronic Coulomb–interaction energy, \( \langle \hat{U} \rangle = \frac{\partial \Omega}{\partial \Lambda} \) or the entropy, \( S = -\frac{\partial \Omega}{\partial T} \).

A basic lesson of thermodynamics is that in different contexts it is advantageous to use different ensembles. The Helmholtz free energy [8], for example, can be obtained from \( \Omega \) by a Legendre transform: \( F(N, T) = \Omega(\mu, T) + \mu N \), where \( \mu \) on the right hand side is a function of \( N \), obtained by inverting the relationship \( N = -\frac{\partial \Omega}{\partial \mu} \) mentioned above. This inversion requires a one–to–one relationship between \( \mu \) and \( N \), a condition which is guaranteed by the convexity of the thermodynamic potentials (the condition of convexity may fail for infinite systems at a phase transition, but such exceptions will not concern us here). Note that the other partial derivatives are unchanged by the Legendre transform, in the sense that \( \frac{\partial \Omega}{\partial X} = \frac{\partial F}{\partial X} \) for \( X = \Lambda, T, \ldots \), where the derivatives of \( \Omega \) are taken at constant \( \mu \) and the derivatives of \( F \) are taken at constant \( N \).
For the purpose of comparison with DFT, it is useful to define the following grand potential function, which depends explicitly on both \( \mu \) and \( N \):

\[
\Omega_\mu(N,T) \equiv F(N,T) - \mu N .
\]  

(3)

This function gives the original grand potential of Eq. (2) when minimized with respect to \( N \), i.e. when the derivative \( \frac{\partial F}{\partial N} - \mu \) vanishes, which is the same as the condition \( N = N(\mu,T) \).

For other values of \( N \) it describes the “cost” in free energy of having a configuration with the “wrong” number of electrons. Since \( \mu(N) \) is monotonous, the minimum of Eq. (3) is unique.

C. The Hohenberg–Kohn theorem

The discussion above can be generalized in a quite straightforward manner to the treatment of the density distribution of the electrons, \( n(r) \), instead of their total number, \( N \). Recalling that the grand potential is a functional [9] of the external potential, \( v(r) \), one finds that the expectation value of the local density of electrons is given by the functional derivative:

\[
n(r) = \langle \hat{n}(r) \rangle = \frac{\delta \Omega}{\delta v(r)} \quad \text{this can be seen directly from Eq. (2), or equivalently from first order perturbation theory}.
\]

The Hohenberg–Kohn free energy can be defined via a functional Legendre transform:

\[
F_{HK}[n(r)] = \Omega[v(r) - \mu] - \int dr \, n(r) (v(r) - \mu),
\]

(4)

where \( v(r) - \mu \) on the right hand side is chosen to correspond to the given \( n(r) \) (the explicit temperature variable is omitted). Note that we are treating the difference \( v(r) - \mu \) as a single functional variable, rather than treating \( v(r) \) and \( \mu \) as independent variables [10] (which are defined only up to a constant) — this follows naturally from the definition of \( \Omega \), Eq. (2), and corresponds to the fact that \( N \) is not independent of \( n(r) \).

The definition of \( F_{HK}[n] \) through a Legendre transform assumes that for each choice of the function \( n(r) \) there corresponds one and only one \( v(r) - \mu \) which has this \( n(r) \) as its
equilibrium density distribution (given the other parameters in $\Omega$, i.e., $T$ and $\Lambda$). This assumption was first proven for non-degenerate ground states, and is known as the first Hohenberg–Kohn theorem [11]. Rather than engage in a mathematical discussion of the domain of validity of different definitions [12], we take the same approach as was taken for thermodynamics above: we assume a one-to-one relationship between $n(r)$ and $v(r) - \mu$ (generalized convexity), and we admit that exceptions may exist and will perhaps need to be studied separately. In practice, the need for such a separate discussion does not arise.

The direct generalization of the free energy function of Eq. (3) is the free energy functional:

$$
\Omega_{v-\mu}[n(r)] = F_{\text{HK}}[n(r)] + \int dr \, n(r) (v(r) - \mu),
$$

with $v(r)$ and $n(r)$ treated as independent functional variables. If we minimize this free energy functional with respect to $n(r)$ at constant $v(r)$ (and given $\mu$, $T$, etc.), we obtain the relation

$$
\frac{\delta F_{\text{HK}}}{\delta n(r)} = \mu - v(r),
$$

and for $n(r)$ and $v(r)$ obeying this physical relation, the free energy functional is equal to the grand potential by inspection. This procedure is analogous to that used in Sec. B for $\mu$ and $N$. The existence of a functional of $n(r)$ with this property is one of the basic tenets of DFT, and is the second Hohenberg–Kohn theorem [11].

As already mentioned, most applications of DFT are studies of ground-state properties, i.e. refer to situations in which the temperature is negligibly small, and the number of electrons is fixed. It it thus important to note that all of the above arguments are valid in the $T \to 0$ limit, except for the claim that the relationship between $\mu$ and $N$ is one-to-one. In fact, both $\Omega(\mu)$ and $F(N)$ become piecewise linear functions in this limit, with a whole linear segment in one of them corresponding to a point with discontinuous derivative in the other [13] (the difference between them continues to be the trivial $\mu N$ product). This is not a major obstacle, and from here on we proceed to discuss the situation for $T \to 0$. 

6
In principle, this requires that we replace statements such as Eq. (6) by \( \frac{\delta F_{HK}}{\delta n(r)} \) is equal to \( -v(r) \) up to a constant”, but instead we simply assume that an infinitesimal value of the temperature is restored whenever it becomes necessary to remove some ambiguity.

### D. The Kohn–Sham equations

An expression for the Hohenberg–Kohn free energy of Eq. (4) is now needed. For a given density \( n(r) \) one can start from the case of noninteracting electrons with energy \( F_{ni}[n] \), and gradually increase the interaction strength \( \Lambda \) from 0 to 1, while keeping the density distribution \( n(r) \) fixed [14]:

\[
F_{HK}[n] = F_{ni}[n] + \int_0^1 \frac{\partial F_{HK}[n]}{\partial \Lambda} d\Lambda .
\]  
(7)

From the general properties of Legendre transforms, we find that the derivative with respect to the interaction strength, \( \frac{\partial F_{HK}[n]}{\partial \Lambda} \), is equal to the interaction energy \( \frac{\partial \Omega}{\partial \Lambda} = \langle \tilde{U} \rangle \). As \( n(r) \) is given here (and independent of \( \Lambda \)) it is natural to approximate this by the Hartree electrostatic energy. The difference between this approximation and the actual value is included as an exchange–correlation term [15]:

\[
F_{HK}[n(r)] = F_{ni}[n(r)] + E_{es}[n(r)] + E_{xc}[n(r)] ,
\]  
(8)

with the electrostatic energy given by

\[
E_{es}[n(r)] = \frac{e^2}{2} \int \frac{dr \, dr'}{|r-r'|} \, n(r) \, n(r') ,
\]  
(9)

and the exchange–correlation energy given formally by

\[
E_{xc}[n(r)] = \int_0^1 d\Lambda \, \frac{e^2}{2} \int \frac{dr \, dr'}{|r-r'|} \, \rho_{xc}(r, r'; [n], \Lambda) ;
\]  
(10)

\[
n(r) \rho_{xc}(r, r'; [n], \Lambda) = \langle \hat{n}(r) [\hat{n}(r') - \delta(r - r')] \rangle_{n(r), \Lambda} - n(r) \, n(r') .
\]  
(11)

The expectation value in the last line describes the density of pairs of electrons at \( r \) and \( r' \), for a system with reduced interaction strength \( \Lambda \), and with the density distribution...
\( n(\mathbf{r}) \). In order to reproduce this distribution, the corresponding Hamiltonian must contain a \( \Lambda \)-dependent “external” potential \( v_\Lambda(\mathbf{r}) \). Clearly, \( v_1(\mathbf{r}) \) is just the external potential \( v(\mathbf{r}) \). On the other extreme is \( v_0(\mathbf{r}) \), which reproduces \( n(\mathbf{r}) \) for non-interacting electrons, and is also called the Kohn–Sham potential or the effective potential, \( v_{\text{eff}}(\mathbf{r}) \). The quantity \( \rho_{\text{xc}}(\mathbf{r}, \mathbf{r}'; [n], \Lambda) \) is the density of the so-called exchange–correlation hole — it describes the region in \( \mathbf{r}' \)-space from which an electron is “missing” if it is known to be at the point \( \mathbf{r} \).

Having written \( F_{\text{HK}}[n] \) as a sum of three terms in Eq. (8), we find that Eq. (6) gives a simple relationship between \( v_{\text{eff}}(\mathbf{r}) \) and \( v(\mathbf{r}) \):

\[
\mu - v_{\text{eff}}(\mathbf{r}) - e\varphi(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}) = \mu - v(\mathbf{r}),
\]

(12)

where the electrostatic potential is

\[
\varphi(\mathbf{r}) = -e \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|},
\]

(13)

and the exchange–correlation potential is defined as

\[
v_{\text{xc}}(\mathbf{r}) = \frac{\delta E_{\text{xc}}}{\delta n(\mathbf{r})}.
\]

(14)

Given a practical approximation for \( E_{\text{xc}}[n] \), and hence for \( v_{\text{xc}}(\mathbf{r}) \), one can thus find \( v_{\text{eff}}(\mathbf{r}) \) from \( n(\mathbf{r}) \) (the chemical potential \( \mu \) drops out of Eq. (12)). However, \( n(\mathbf{r}) \) can also be found from \( v_{\text{eff}}(\mathbf{r}) \) by solving the non-interacting problem,

\[
n(\mathbf{r}) = \sum_{i=1}^{N}\left|\psi_i(\mathbf{r})\right|^2; \quad \left( -\frac{\hbar^2}{2m} \nabla^2 + v_{\text{eff}}(\mathbf{r}) \right) \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}),
\]

(15)

i.e. by summing over the solutions of the single-particle Schrödinger equation (the states \( \psi_i \) here are ordered so that the energies \( \epsilon_i \) are non-decreasing, and the spin index is included in \( i \)). At finite temperatures, the Fermi–Dirac distribution is used for the occupations of the Kohn–Sham orbitals; fractional occupations are also implied when \( \epsilon_N \) is degenerate with \( \epsilon_{N+1} \), but if only spin-degeneracy is involved, this does not affect the expression for \( n(\mathbf{r}) \).

The set of equations (12)—(15) is called the Kohn–Sham equations of DFT [16], and must be solved self-consistently. It provides a scheme for finding \( n(\mathbf{r}) \) and the ground state
energy [17] for a system of $N$ interacting particles. Historically, additional properties [18] of the Kohn–Sham non–interacting system, e.g. the band structure for crystals, have also provided surprisingly accurate predictions when compared with experiment. In fact, the agreement between the calculated Kohn–Sham Fermi surface and the measured one was so remarkable for some systems [19], that it motivated analyses of simple soluble models for which the difference between the interacting and non–interacting Fermi surfaces could be calculated explicitly, and shown not to vanish [20]. Clearly, the accuracy of the DFT predictions for ground–state energetics and density distributions can be improved by finding better (but still practical) approximations for $E_{xc}[n]$, whereas improving the accuracy of such band–structure calculations may require “going back to the drawing board” and devising other, more appropriate, calculational schemes [21].

E. The Local Density Approximation

All the complicated physics of interacting electrons has thus been lumped into a formal expression for $E_{xc}$. For a slowly varying density of electrons $n(r)$, it makes sense to use properties of the homogeneous interacting electron gas, i.e. to assume that the exchange–correlation energy density at $r$ depends only on $n(r)$:

$$E_{xc}[n(r)] \simeq \int d\mathbf{r} \ n(\mathbf{r}) \ \epsilon_{xc}(n(\mathbf{r})) ,$$

(16)

where $\epsilon_{xc}(n)$ is the exchange–correlation energy per electron in a uniform electron gas of density $n$. This quantity is known exactly in the limit of high density, and can be computed accurately at densities of interest, using Monte Carlo techniques. In practice one employs interpolation formulas, e.g., that given by Gunnarson and Lundqvist (Ref. [23]): $\epsilon_{xc}(n) = -0.458/r_s - 0.0666G(r_s/11.4)$ Rydbergs, where the Wigner–Seitz radius $r_s = (3/4\pi n)^{-1/3}$ is in units of the Bohr radius, and $G(x) = \frac{1}{2}[(1+x^3) \log(1+x^{-1}) - x^2 + \frac{1}{2}x - \frac{1}{4}]$.

Note that the resulting approximation scheme is very similar to a Hartree calculation, with the only difference being the addition of a potential
\[ v_{xc}(r) = \left. \frac{d (n_\epsilon_{xc}(n))}{dn} \right|_{n=n(r)} \]  

(17)

to the electrostatic potential at the appropriate step in the self-consistency loop. This local density approximation (LDA) has been shown to give surprisingly good results for many atomic, molecular and crystalline interacting electron systems, even though in these systems the density of electrons is not slowly varying (see examples below).

Approximate models of many-electron systems which use the local density in a similar manner had already been in use when DFT was being developed. The best-known of these, the Thomas–Fermi model [22], is obtained in the present scheme by ignoring the exchange–correlation energy, \( E_{xc} \simeq 0 \), and using an LDA for the non–interacting problem \( F_{ni}[n] \simeq C \int n^{5/3}(r) \, dr \), with \( C = \frac{3}{10}(3\pi^2)^{2/3} \simeq 2.87 \) in atomic units, calculated for a uniform electron–gas of density \( n(r) \). Another well-known approximation scheme was the \( X\alpha \) method [24], in which an LDA was used for the exchange energy, and only the correlation energy was ignored, so that an accuracy comparable to that of the Hartree–Fock method could be obtained with a Hartree–like scheme. The advance made in introducing DFT was twofold: first, it promoted such calculation schemes from the status of “models” to that of a “theory”, by showing that in principle the density distribution \( n(r) \) contains all of the information about the system; and second, it pointed out the direction for improving the level of approximation: developing more and more accurate practical expressions for \( E_{xc}[n] \).

Indeed, improving upon the accuracy of the LDA is a goal which has been persistently pursued, with an important impetus coming from the very high degree of accuracy required by practical applications in chemistry. One improvement which is very often implemented is the local spin-density (LSD) approximation, which is motivated by the fact that the exchange–correlation hole is very different for electrons with parallel and with antiparallel spins. In this scheme, separate densities of spin–up and spin–down electrons are used as a pair of functional variables: \( n_\uparrow(r) \) and \( n_\downarrow(r) \). Correspondingly, the Hamiltonian contains separate potentials for spin up and spin down electrons — a Zeeman–energy magnetic field term is introduced. The exchange–correlation energy per particle is again taken from the
results of a homogeneous electron gas, $\epsilon_{xc}(n_\uparrow, n_\downarrow)$.

The next degree of sophistication is to allow $\epsilon_{xc}$ to depend not only on the local densities but also on the rate–of–change of the densities, i.e. to add gradient corrections. Unfortunately, it was found that such corrections do not necessarily improve the accuracy obtained. One way of explaining this is to note that the exchange–correlation hole of Eq. (10) obeys a simple sum–rule: if an electron is known to be at $r$, then exactly one electron (with the same spin) is missing from the surrounding space, $\int dr' \rho_{xc}(r, r') = -1$. Only the weighted inverse distance between $r$ and $r'$ affects the energy $E_{xc}[n]$, and approximating it with the inverse distance taken from a uniform electron gas at density $n(r)$ introduces only minor errors, which tend to further cancel out when the integration over $r$ is performed. In contrast, introducing gradient corrections in a straightforward and systematic manner, by expanding around the uniform electron gas, breaks this sum rule and is less accurate. This situation led to the development of various generalized gradient approximations (GGAs) [25,26], in which the spatial variations of $n(r)$ enter in a manner which conforms with the sum rule, and which have succeeded in reducing the errors of the LDA by a factor which is typically about 4.

Further improvements in practical expressions for $E_{xc}[n]$ are actively being pursued [27]. One direction which may achieve the accuracy needed for applications in chemistry [28], is to use the fact that the exact form of the exchange–correlation hole can be calculated for $\Lambda = 0$ relatively easily, directly from the non–interacting Kohn–Sham system. There is thus no need to use an approximation such as the LDA or the GGA for the low–$\Lambda$ portion of the integral in Eq. (10). Ultimately, one may hope that a systematic method of improving the approximation would be found, although the experience with the gradient expansion is not promising in this respect.
F. Discussion

We have outlined here the main ideas of DFT as they are commonly applied today. This efficient approximation scheme gives the electronic ground–state energy and density distribution as a function of the position of the atomic nuclei, which in turn determines molecular and crystal structure and gives the forces acting on the atomic nuclei when they are not at their equilibrium positions. DFT is being used routinely to solve problems in atomic and molecular physics, such as the calculation of ionization potentials [29] and vibration spectra, the study of chemical reactions, the structure of bio–molecules [30], and the nature of active sites in catalysts [31], as well as problems in condensed matter physics, such as lattice structures [32], phase transitions in solids [33], and liquid metals [34]. Furthermore these methods have made possible the development of accurate molecular dynamics schemes in which the forces are evaluated quantum mechanically “on the fly” [35].

It is important to stress that all practical applications of density functional theory rest on essentially uncontrolled approximations, such as the local density approximation discussed above. Thus the validity of the method is in practice established by its ability to reproduce experimental results. It is of interest to note some of the cases for which these approximations are known to fail. When considering a point \( r \) a short distance away from the surface of a metal, it is obvious that the exchange–correlation hole, \( \rho_{xc}(r, r') \), is concentrated at points \( r' \) inside or very near the surface of the metal, and this results in image forces, i.e. a \( 1/r \) behavior of \( v_{xc} \) (here \( r \) is the distance from the surface). This is not reproduced in local approximations. Likewise, van der Waals forces, which among other things are important for many biological molecules, are not reproduced. Both these examples are manifestations of the significance of non–local correlations — a non–locality which is by definition absent from the LDA and its immediate extensions. These examples of practical failure, together with the unattractiveness of uncontrolled approximations, spur research towards new and more exact exchange–correlation energy functionals.

A discussion of the role DFT plays in practice, compared to other alternative approaches,
necessarily depends very much on the specific applications one has in mind. For atoms and small molecules, the simplest version of the LDA already provides a very useful qualitative and semi–quantitative picture. It is of course a dramatic improvement over the Thomas–Fermi model, which fails to describe the shell structure of atoms and the very existence of chemical bonds. It even improves on the more labor–intensive Hartree–Fock method in many cases (for examples involving a few small atoms, see table 1), especially when one is calculating the strength of molecular bonds, which are severely overestimated in Hartree–Fock calculations. This can only be considered as a surprising success, keeping in mind that an isolated atom or molecule is as inhomogeneous an electronic system as possible, and therefore the last place where one might expect a local approximation to work. In other words, electronic correlations in such systems are in a sense weak, and are on average similar to those of a uniform electron gas (see the discussion of the sum–rule in Sec. E). However, the many–body quantum states of such relatively small systems can be solved for extremely accurately using well–known techniques of quantum chemistry. Furthermore, these techniques use controlled approximations, so that the accuracy can be improved indefinitely, given a powerful enough computer, and indeed impressive agreement with experiment is routinely achieved. For this reason, most quantum chemists did not embrace DFT methods at an early stage.

It is in studies of larger molecules that DFT becomes an indispensable tool [5]. The computational effort required in the conventional quantum chemistry approaches grows exponentially with the number of electrons involved, whereas in DFT it grows only as the second or third power of this number. In practice, this means that DFT can be applied to molecules with hundreds of atoms, whereas the conventional approaches are limited to systems with \( \sim 10 \) atoms, or less. It is appropriate to note here that simply solving the non–interacting problem for a complicated molecule may also be prohibitive, and various methods have been and are being developed in order to reduce the problem to a computationally manageable task. Of these, we mention the well–known pseudopotential method [37], which allows one to avoid recalculating the wavefunctions of the inert core electrons over
and over again, and the recent attempts to develop “order N” methods [36], which would make use of the fact that the behavior of the wavefunctions at each point is determined primarily by the atoms in its immediate vicinity rather than by the whole molecule. As implied already in Sec. E, it is for this problem that more and more accurate density functionals are most obviously needed. To illustrate this, we quote one sentence from Ref. [26]: “Accurate atomization energies are found [using the GGA] for seven hydrocarbon molecules, with a rms error per bond of 0.1 eV, compared with 0.7 eV for the LSD approximation and 2.4 eV for the Hartree–Fock approximation.”

The remarkable usefulness of DFT for solid–state physics was apparent from the outset. For example, the lattice constants of simple crystals are obtained with an accuracy of about 1% already in the LDA. Admittedly, this method is inappropriate for treating some more complicated situations, such as antiferromagnets or systems with strong electronic correlations. In other cases, such as for the work–function of metals, the above–mentioned deficiency of the LDA in not accounting properly for image potentials can be corrected for “by hand”, yielding satisfactory results [38]. It is useful to note that, in contrast to approximations using free parameters which are empirically optimized to fit a certain set of data, the LDA and the GGA have proved to exhibit a consistent degree of accuracy or inaccuracy for various types of problems — when applied to a new problem, the results can thus be interpreted with some confidence.

Our discussion would not be complete without mentioning the existence of many other uses of density–functional methods, for electronic systems and for other physical systems. The former include time–dependent DFT, which relates interacting and non–interacting electronic systems moving in time–dependent potentials, and relativistic DFT, which uses the Dirac equation rather than the Schrodinger equation to calculate the Kohn–Sham states (these are reviewed in Ref. [2]). The latter include applications in nuclear physics, in which the densities of protons and neutrons and the resulting energies are studied [39], and in the theory of classical and quantum liquids, where the densities of atoms or of electrons and nuclei appear [6,40].
In summary, we have provided a brief introduction to density functional theory, based on an analogy with thermodynamics. Two of the advantages of this approach, as compared, e.g., with introducing DFT using Levy’s constrained–search method [12], are: (a) the introduction of $n(r)$ through a Legendre transform, as the variable conjugate to $v(r)$, makes it appear to be a natural variable, whereas in the conventional description of DFT the very existence of the functional $F[n]$ of Eq. (4) appears to be surprising and requires some digestion; and (b) using the standard properties of Legendre transforms, one immediately obtains the physical expression for the exchange–correlation energy in terms of the density of the exchange–correlation hole, an expression which serves as the basis for a discussion of the weaknesses and strengths of the approximations employed in practice. We hope that the availability of this type of introduction will help increase the awareness and understanding of DFT amongst potential users, and especially amongst the general audience of physicists and scientists.

Acknowledgments

The authors wish to express their gratitude to N.W. Ashcroft, W. Kohn, H. Metiu, Y. Rosenfeld, and G. Vignale for helpful discussions. N.A. acknowledges support under grants No. NSF PHY94-07194, and No. NSF DMR96-30452, and by QUEST, a National Science Foundation Science and Technology Center, (grant No. NSF DMR91–20007).
REFERENCES


[8] Note that $F(N)$ thus defined is not identical with that obtained by fixing the particle number — the equivalence of the canonical and grand–canonical ensembles is guaranteed only in the thermodynamic limit. This is not relevant for the present discussion, one reason being that we will focus on the $T \to 0$ limit, in which the equivalence is regained because the fluctuations of both the energy and the particle number vanish.
[9] Functionals and functional derivatives are not always familiar concepts to undergraduate students, and this is an excellent opportunity for them to be introduced. For our purposes one may simply regard the functional variables, \( n(r) \) and \( v(r) - \mu \) above, as defined on a dense lattice of \( M \) points \( r_i \), each point representing a small volume of space \( V_i \), with \( i = 1, 2, \ldots, M \) and with the limit \( M \to \infty \) in mind. In this picture the functionals such as \( F_{\text{HK}}[n] \) are simply functions of the \( M \) variables \( \{n_i\} \), where \( n_i = n(r_i) \). Integration over space is now expressed as a sum, e.g., \( \int d\mathbf{r} n(\mathbf{r})(v(\mathbf{r}) - \mu) \) becomes \( \sum_{i=1}^{M} V_i n_i (v_i - \mu) \), and correspondingly a \( \delta \) function near the point \( r_j \) is replaced by a Kronecker \( \delta_{i,j} \) divided by the volume \( V_j \). The functional derivative, which is conventionally defined as 
\[
\frac{\delta F}{\delta n(\mathbf{r})} = \lim_{\alpha \to 0} \frac{F[n(\mathbf{r}') + \alpha \delta(\mathbf{r}' - \mathbf{r})] - F[n]}{\alpha},
\]
then follows, and can be used in deriving, e.g., the relationship \( n(\mathbf{r}) = \frac{\delta \Omega}{\delta v(\mathbf{r})} \).


[12] Clearly, if for a certain potential \( v(\mathbf{r}) \) (and for a given value of \( N \) or \( \mu \)) there exist degenerate ground states \( \Psi_i \) with different density distributions \( n_i(\mathbf{r}) \), then the relationship between \( v(\mathbf{r}) \) and them is not one–to–one. In fact, there also exist density distributions \( n(\mathbf{r}) \), which do not correspond to any \( v(\mathbf{r}) \), (i.e. are not ground–state \( v \)–representable), e.g. those obtained by interpolating between degenerate \( n_i(\mathbf{r}) \) distributions, [see, e.g.,
M. Levy, “Electron densities in search of Hamiltonians,” Phys. Rev. A 26, 1200–1208 (1982)]. Here we are avoiding this problem by using a thermodynamic ensemble, for which \( n(r) \) is equal to the average of the \( n_i(r) \) in the \( T \to 0 \) limit, when a ground–state degeneracy occurs.

In the DFT literature, this problem is solved in a different manner: an alternative definition of \( F_{HK}[n] \), which does not explicitly use the potential \( v(r) \), but coincides with the definition of Ref. [11] for \( v \)–representable distributions, was suggested in M. Levy, “Universal variational functionals of electron densities, first–order density matrices, and natural spin–orbitals and solution of the \( v \)–representability problem,” Proc. Natl. Acad. Sci. (USA) 76, 6062–6065 (1979). As Levy’s formulation may also be very useful for a pedagogical introduction to DFT (see, e.g., Fig. 3.1 in Ref. [1]), we reproduce it briefly in this footnote. The ground state energy is known to be the minimal expectation value of \( \hat{H}_{MB} \), with respect to all wavefunctions \( \Psi \) in the Hilbert space of \( N \) particles. If we constrain the range of this search only to wavefunctions which produce a certain \( n(r) \) (denoted by \( \Psi \to n \)), we will necessarily find a higher energy, with the ground–state energy being obtained only if \( n(r) \) is the ground–state density. Thus, Levy defined a ground–state energy functional \( F_L[n] + \int dr \, n(r)v(r) \), with \( F_L[n] = \min_{\Psi \to n} \langle \Psi | \hat{T} + \hat{U} | \Psi \rangle \), a definition which is valid for any reasonable \( n(r) \). One advantage of the thermodynamic approach we are using here is that it clarifies the special role of the density distribution, \( n(r) \), whereas in Levy’s formulation one could equally well imagine other ways of constraining the search to other subspaces of the Hilbert space.


[15] Note that this definition differs from the conventional one for exchange–correlation energy.


[17] For completeness, we write the interacting ground–state energy $E_0$ explicitly in terms of the Kohn–Sham eigenvalues and the density distribution:

$$E_0 = \sum_{i=1}^{N} \epsilon_i - \int d\mathbf{r} \ n(\mathbf{r}) \left( v_{\text{eff}}(\mathbf{r}) - v(\mathbf{r}) \right) + E_{\text{es}}[n(\mathbf{r})] + E_{\text{xc}}[n(\mathbf{r})].$$

In the LDA, and using Eq. (12), this can be rewritten as

$$E_0 = \sum_{i=1}^{N} \epsilon_i + \int d\mathbf{r} \ n(\mathbf{r}) \left( \epsilon_{\text{xc}}(n(\mathbf{r})) - v_{\text{xc}}(n(\mathbf{r})) \right) - E_{\text{es}}[n(\mathbf{r})].$$

At finite temperatures, the free energy is obtained by including a term involving the entropy of the Kohn–Sham system, and using a temperature–dependent approximation for $\epsilon_{\text{xc}}(n)$.

[18] Interestingly, the work function of a metal surface is equal to that of the Kohn–Sham system. Using the fact that both $\varphi(\mathbf{r})$ and $v_{\text{xc}}(\mathbf{r})$ decay as $1/r$ at large distances away from the system, and taking $v(\mathbf{r})$ and $v_{\text{eff}}(\mathbf{r})$ to vanish at infinity by convention, one finds that Eq. (12) reduces to a statement of the equality of the chemical potentials for the interacting and the Kohn–Sham system.


FIG. 1. One indicator of the increasing use of DFT is the number of records retrieved from the INSPEC databases by searching for the keywords “density”, “functional” and “theory”. This is compared here with a similar search for keywords “Hartree” and “Fock”, which parallels the overall growth of the INSPEC databases (for any given year, approximately 0.3% of the records have the Hartree–Fock keywords).
Table 1: First ionization potentials of isolated atoms, calculated in the Hartree–Fock approximation, and using density functional theory with the LDA (Ref. [41]) and with the GGA (Ref. [26]), compared with experiment [42].

<table>
<thead>
<tr>
<th>Method</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>10.81</td>
<td>13.91</td>
<td>12.05</td>
<td>15.70</td>
</tr>
<tr>
<td>LDA</td>
<td>12.15</td>
<td>15.47</td>
<td>14.60</td>
<td>18.57</td>
</tr>
<tr>
<td>GGA</td>
<td>11.28</td>
<td>14.78</td>
<td>13.37</td>
<td>17.40</td>
</tr>
<tr>
<td>EXP</td>
<td>11.24</td>
<td>14.54</td>
<td>14.61</td>
<td>17.45</td>
</tr>
</tbody>
</table>