The purpose of this short essay is to introduce students and other newcomers to the basic ideas and uses of modern electronic density functional theory, including what kinds of approximations are in current use, and how well they work (or not). The complete newcomer should find it orients them well, while even longtime users and aficionados might find something new outside their area. Important questions varying in difficulty and effort are posed in the text, and are answered in the Supporting Information. © 2012 Wiley Periodicals, Inc.

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DFT in a Nutshell
Kieron Burke$^{[a,b]}$ and Lucas O. Wagner$^{*[a,b]}

Electronic Structure Problem

For the present purposes, we define the modern electronic structure problem as finding the ground-state energy of nonrelativistic electrons for arbitrary positions of nuclei within the Born-Oppenheimer approximation.\[1]\] If this can be done sufficiently accurately and rapidly on a modern computer, many properties can be predicted, such as bond energies and bond lengths of molecules, and lattice structures and parameters of solids.

Consider a diatomic molecule, whose binding energy curve is illustrated in Figure 1. The binding energy is given by

$$E_{\text{bind}}(R) = E_0(R) + \frac{Z_A Z_B}{R} - E_A - E_B \quad (1)$$

where $E_0(R)$ is the ground-state energy of the electrons with nuclei separated by $R$, and $E_A$ and $Z_A$ are the atomic energy and charge of atom $A$ and similarly for $B$. The minimum tells us the bond length ($R_0$) and the well-depth ($D_0$), corrected by zero-point energy ($\hbar \omega/2$), gives us the dissociation energy ($D_e$).

The Hamiltonian for the $N$ electrons is

$$\hat{H} = \hat{T} + \hat{V}_{\text{ee}} + \hat{V}, \quad (2)$$

where the kinetic energy operator is

$$\hat{T} = \frac{1}{2} \sum_{j=1}^{N} \nabla_j^2, \quad (3)$$

the electron–electron repulsion operator is

$$\hat{V}_{\text{ee}} = \frac{1}{2} \sum_{i<j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad (4)$$

and the one-body operator is

$$\hat{V} = \sum_{j=1}^{N} v(\mathbf{r}_j). \quad (5)$$

For instance, in a diatomic molecule, $v(\mathbf{r}) = -Z_A/\mathbf{r} - Z_B/|\mathbf{r} - \mathbf{R}|$.

The ground-state energy satisfies the variational principle:

$$E = \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle, \quad (6)$$

where the minimization is over all antisymmetric $N$-particle wavefunctions. This $E$ was called $E_0(R)$ in Eq. (1).

Many traditional approaches to solving this difficult many-body problem begin with the Hartree–Fock (HF) approximation, in which $\Psi$ is approximated by a single Slater determinant (an antisymmetrized product) of orbitals (single-particle wavefunctions)\[2]\] and the energy is minimized.\[3]\] These include configuration interaction, coupled cluster, and Møller-Plesset perturbation theory, and are mostly used for finite systems, such as molecules in the gas phase.\[4]\] Other approaches use reduced descriptions, such as the density matrix or Green’s function, but leading to an infinite set of coupled equations that must somehow be truncated, and these are more common in applications to solids.\[5]\]

More accurate methods usually require more sophisticated calculation, which takes longer on a computer. Thus, there is a compelling need to solve ground-state electronic structure problems reasonably accurately, but with a cost in

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*Explain why a vibrational frequency is a property of the ground-state of the electrons in a molecule.

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computer time that does not become prohibitive as the number of atoms (and therefore electrons) becomes large.

**Basic DFT**

The electronic density \( n(\mathbf{r}) \) is defined by the requirement that \( n(\mathbf{r}) \ d^3r \) is the probability of finding any electron in the volume \( d^3r \) around \( \mathbf{r} \). For a single electron with wavefunction \( \psi(\mathbf{r}) \), it is simply \( |\psi(\mathbf{r})|^2 \). In density functional theory (DFT), we write the ground-state energy in terms of \( n(\mathbf{r}) \) instead of \( \Psi \). The first DFT was formulated by Thomas\cite{6} and Fermi.\cite{7} The kinetic energy density at any point is approximated by that of a uniform electron gas of noninteracting electrons of density \( n(\mathbf{r}) \), which for a spin-unpolarized system is:\footnote{Evaluate the TF kinetic energy of the H atom and deduce the % error. Repeat using spin-DFT.}

\[
T^{\text{TF}} = a_5 \int d^3r \ n^{5/3}(\mathbf{r}), \quad a_5 = 3(3\pi^2)^{2/3}/10. \tag{7}
\]

The interelectron repulsion is approximated by the classical electrostatic self-energy of the charge density, called the Hartree energy:

\[
U = \frac{1}{2} \int d^3r \ \int d^3r' \ n(\mathbf{r}) n(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|}. \tag{8}
\]

Because the one-body potential couples only to the density,

\[
V = \langle \hat{V} \rangle = \int d^3r \ n(\mathbf{r}) \ v(\mathbf{r}). \tag{9}
\]

The sum of these three energies is then minimized, subject to the physical constraints:

\[
n(\mathbf{r}) \geq 0, \quad \int d^3r \ n(\mathbf{r}) = N. \tag{10}
\]

This absurdly crude theory gives roughly correct energies (errors about 10% for many systems) but is not nearly good enough for most properties of interest (for example, molecules do not bind\cite{8}). For same-spin, noninteracting fermions in 1d, the corresponding kinetic energy is

\[
T^{\text{TF}}_{1d}[n] = \frac{\pi^2}{6} \int dx \ n^3(x) \tag{11}
\]

and makes only a 25% error on the density of a single particle in a box. Hours of endless fun and many good and bad properties of functional approximations can be understood by applying Eq. (11) to standard text book problems in quantum mechanics,\cite{9} and noting what happens, especially for more than one particle.\cite{9}

But modern DFT began with the proof that the solution of the many-body problem can be found, in principle, from a density functional. To see this, we break the minimization of Eq. (6) into two steps. First minimize over all wavefunctions yielding a certain density, and then minimize over all densities. Because the one-body potential energy depends only on the density, we can define separately\cite{9,10}

\[
F[n] = \min_\Psi \langle \Psi | \left( \hat{T} + \hat{V}_{ee} \right) | \Psi \rangle, \tag{12}
\]

where the minimization is over all antisymmetric wavefunctions yielding a given density \( n(\mathbf{r}) \).\footnote{Calculate the TF kinetic energy for a 1d particle of mass \( m = 1 \) in (a) a harmonic well \( v(x) = x^2/2 \) and (b) in a delta-well \( v(x) = -\delta(x) \). Give the % errors.} This is transparently a functional of the density, meaning it assigns a number to each density, as was first proven by Hohenberg and Kohn.\footnote{Deduce \( F[n] \) for a single electron. It has no electron–electron interaction, and is known as the von Weizsäcker kinetic energy.} Then

\footnote{Technically, HK only proved fact this for \( \tau \)-representable densities, i.e. densities which are the ground-state of some external one-body potential.}
where the minimization is over all reasonable densities satisfying Eq. (10). Hohenberg and Kohn proved (i) that all properties are determined by \( n(\mathbf{r}) \), i.e., they are functionals of \( n(\mathbf{r}) \); (ii) \( F[n] \) is a universal functional, independent of \( \nu(\mathbf{r}) \), and (iii) the exact density satisfies

\[
\frac{\delta F}{\delta n(\mathbf{r})} = -\nu(\mathbf{r}),
\]

where \( \delta F/\delta n(\mathbf{r}) \) is the functional derivative of \( F \) with respect to \( n(\mathbf{r}) \). In fact, these days we use spin DFT\(^{12} \) in which all quantities are considered functionals of the up, \( n_\uparrow(\mathbf{r}) \), and down, \( n_\downarrow(\mathbf{r}) \), spin densities separately. This makes approximations more accurate for odd electron systems and allows treatment of collinear magnetic fields. All functionals written without spin dependence, such as the ones discussed thus far, are assumed to be referring to a spin-unpolarized system.

The next crucial step in developing the modern theory came from (re)-introducing orbitals. Kohn and Sham\(^{13} \) vastly improved the accuracy of DFT by imagining a fictitious set of noninteracting electrons that are defined to have the same density as the interacting problem. They are still spin-\( \frac{1}{2} \) fermions obeying the Pauli principle, so like in HF theory, their wavefunction is (usually) a Slater determinant, an antisymmetrized product of orbitals of each spin, \( \phi_{\sigma j}(\mathbf{r}) \), \( j = 1, \ldots N_\sigma \), \( \sigma = \uparrow, \downarrow \). These KS electrons satisfy a noninteracting Schrödinger equation:

\[
\left\{ \frac{1}{2} \nabla^2 + V_{S,\sigma}(\mathbf{r}) \right\} \phi_{\sigma j}(\mathbf{r}) = \epsilon_{\sigma j} \phi_{\sigma j}(\mathbf{r}),
\]

and the \( \epsilon_{\sigma j} \) are called KS eigenvalues and \( \phi_{\sigma j}(\mathbf{r}) \) are KS orbitals.\(^{18} \) By evaluating Eq. (3) on the KS Slater determinant, the KS kinetic energy is the sum of the orbital contributions:\(^{59} \)

\[
T_S = -\frac{1}{2} \sum_{\sigma=\uparrow,\downarrow} \sum_{j=1}^{N_\sigma} \int d^3r \ \phi_{\sigma j}(\mathbf{r})^* \nabla^2 \phi_{\sigma j}(\mathbf{r}).
\]

If we write the energy in terms of KS quantities:

\[
E = T_S + U + V + E_{XC},
\]

\( E_{XC} \) is defined by Eq. (17) and called the exchange-correlation (XC) energy.\(^{55} \) KS showed that one could extract the unknown KS potential if one only knew how the terms depend on the density. Writing the Hartree potential as

\[
\nu_H(\mathbf{r}) = \frac{\delta U}{\delta n(\mathbf{r})} = \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|},
\]

then

\[
\nu_{S,\sigma}(\mathbf{r}) = \nu_H(\mathbf{r}) + \nu_{\sigma}(\mathbf{r}) + \nu_{XC,\sigma}(\mathbf{r}),
\]

where

\[
\nu_{XC,\sigma}(\mathbf{r}) = \frac{\delta E_{XC}}{\delta n_\sigma(\mathbf{r})}.
\]

This is a formally exact scheme for finding the ground-state energy and density for any electronic problem.\(^{***} \) In Figure 2, we emphasize the exactness of the KS scheme by plotting the exact KS potential for a He atom (which is trivial to find, once the exact density is known from an accurate many-body calculation\(^{114} \),\(^{†††} \) Two noninteracting electrons, doubly occupying the 1s orbital of this potential, have a density that matches that of the interacting system exactly.\(^{†††} \) But in practical calculations, we always use approximations to \( E_{XC} \) and hence to \( \nu_{XC}(\mathbf{r}) \).

Traditionally, \( E_{XC} \) is broken up into exchange (X) and correlation contributions:\(^{555} \)

\[
E_{XC} = E_X + E_C.
\]

The exchange energy is \( \tilde{V}_{\text{ex}} \) evaluated on the KS Slater determinant minus the Hartree energy, and typically dominates.\(^{***} \) In terms of the orbitals:

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\(^{11} \)Again, HK proved this only for \( \nu \)-representable densities.

\(^{12} \)Is the sum of the KS eigenvalues equal to the total energy?

\(^{18} \)Apply Eq. (12) to the KS system to define \( T_S \) without ever mentioning \( \nu_H(\mathbf{r}) \). Then prove that \( T \geq T_S \) always.

\(^{55} \)Give the signs of \( E, T, \nu_{S,\sigma}, V, U, E_H \), and \( E_C \) for real systems (i.e., atoms, molecules, and solids).

\(^{***} \)Why is a KS calculation much faster than direct solution of the Schrödinger equation?

\(^{†††} \)Write the formula that extracts \( \nu_H(\mathbf{r}) \) from \( n(\mathbf{r}) \) for the helium atom. Can you explain why this does not tell us the vital \( \nu_{XC}[n(\mathbf{r})] \) for any spin-unpolarized two-electron systems?

\(^{††} \)Why is the helium KS potential less deep than the original potential, \( -2/\mathbf{r} \)?

\(^{†††} \)What is \( E_C \) for a one-electron system?

\(^{55} \)What is the expectation value of the Hamiltonian \( \langle \mathcal{H} = \mathcal{T} + \mathcal{V} + \mathcal{V}_{\text{ex}} \rangle \) evaluated on the KS Slater determinant? Use this to prove that the DFT definition of correlation energy is never positive.
Although LDA is uniquely defined, there are two basic flavors of the more sophisticated functionals. There are those that are derived without fitting to reference data on atoms and molecules, using information from only the slowly varying electron and known exact conditions on the functional. The standard GGA of this type is PBE\[18\] while the hybrid is PBE0, mixing 25% exact exchange.\[19\] Of the empirical type, B88 is the standard GGA for exchange,\[20\] LYP for correlation,\[21\] combining to form BLYP. The most commonly used functional today is a hybrid called B3LYP.\[22\]

The original LDA became a standard tool in solid-state physics, yielding excellent lattice parameters, and fairly good bulk moduli. But LDA typically overbinds by about 1 eV/bond, which is too large an error to be useful in quantum chemistry. GGAs reduce this error to about 0.3 eV/bond, and hybrids reduce it another factor of 2. Table 1 shows typical results. Empirical parametrized functionals are usually about a factor of 2 better than nonempirical ones, but with less systematic errors.\[25\] Although hybrids are popular in chemistry, where HF codes have been including exact exchange for decades, they are much less popular for solids, due to the singularities in HF for metals.

In contrast, many limitations of these functionals have been identified. Perhaps the most well-known is the gap problem. The fundamental gap is \( I - A \), the difference between the ionization potential and the electron affinity of a system. This is usually larger than the KS gap, the difference between the KS HOMO and LUMO energy eigenvalues. Calculations with LDA and GGA yield fundamental gaps of insulating solids close to the KS gap, and so are too small (by about a factor of 2). This is related to self-interaction error (that is, the functionals are incorrect for one electron). Hybrid functionals often do better. Other well known failures of these approximations include the lack of asymptotic van der Waals forces, which can be important for soft matter.\[26\]

<table>
<thead>
<tr>
<th>( \Delta = \text{calc} - \text{expt} )</th>
<th>HF</th>
<th>LDA</th>
<th>PBE</th>
<th>BLYP</th>
<th>PBE0</th>
<th>B3LYP</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D_0 )</td>
<td>-110</td>
<td>40.4</td>
<td>16.2</td>
<td>13.0</td>
<td>-1.73</td>
<td>1.06</td>
<td>227.0</td>
</tr>
<tr>
<td>( R_0 )</td>
<td>-3.2</td>
<td>-0.33</td>
<td>0.41</td>
<td>0.40</td>
<td>-0.93</td>
<td>-0.80</td>
<td>109.8</td>
</tr>
</tbody>
</table>
Electronic KS-DFT has been implemented in a huge variety of codes, and is being applied in many areas of science. Modern computers allow routine calculation of hundreds of atoms, far more than with traditional quantum chemical methods, but with a reasonable (not very high) degree of accuracy and reliability. In traditional areas of condensed-matter physics and quantum chemistry, many experimental groups run codes themselves, and many purely computational groups exist. For example, new catalysts have been found by calculation, then demonstrated in the lab, patented, and are being further developed for industrial production. But such calculations are often treated as frozen or by pseudo-potentials, saving calculational effort. A few codes use numerical grids. Electronic KS-DFT focused purely on the ground-state energy and density. Several approaches exist to tackle excited states, but the most popular is time-dependent density functional theory (TDDFT), based on a formal proof for the kernel to be extracted from a ground-state XC approximation. Typical results give moderate accuracy for transition frequencies (0.4 eV errors), but excellent results for the properties of molecules in excited states. Dramatic failures of these approximations include double excitations, charge transfer, and a missing contribution to the optical response of solids.

**Useful Resources**

Tables 2 and 3 give a list of acronyms and notation used in this essay. Perhaps the best pedagogical introduction of recent years is a Primer in DFT. For physicists with some background in many-body theory, there's nothing better than Dreizler and Gross, or the more recent Engel and Dreizler. Analogously, if you are a chemist with knowledge of quantum chemical methods, try Parr and Yang. A more pragmatic approach is that of Koch and Holthausen, who, in Part B, discuss the accuracy of different approximate functionals for different molecular properties. For TDDFT, the standard reference is that edited by Marques, and there is a new introduction by Ullrich.

**Keywords:** density functional theory, electronic structure, local density approximation

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**Table 2. Acronyms.**

<table>
<thead>
<tr>
<th>Abbr.</th>
<th>Expansion</th>
</tr>
</thead>
<tbody>
<tr>
<td>B88</td>
<td>Becke 88 E_x functional</td>
</tr>
<tr>
<td>BLYP</td>
<td>GGA using B88 and LYP</td>
</tr>
<tr>
<td>B3LYP</td>
<td>BLYP hybrid</td>
</tr>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>GGA</td>
<td>Generalized gradient approximation</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest-occupied molecular orbital</td>
</tr>
<tr>
<td>KS</td>
<td>Kohn-Sham</td>
</tr>
<tr>
<td>LDA</td>
<td>Local density approximation</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest-unoccupied molecular orbital</td>
</tr>
<tr>
<td>LYP</td>
<td>Lee-Yang-Parr E_x functional</td>
</tr>
<tr>
<td>PBE</td>
<td>Perdew-Burke-Ernzerhof GGA functional</td>
</tr>
<tr>
<td>PBE0</td>
<td>PBE hybrid</td>
</tr>
<tr>
<td>TF</td>
<td>Thomas-Fermi</td>
</tr>
<tr>
<td>X</td>
<td>Exchange</td>
</tr>
<tr>
<td>XC</td>
<td>Exchange-correlation</td>
</tr>
</tbody>
</table>

**Table 3. Notation of representative symbols.**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>D_e</td>
<td>Electronic well-depth (see Fig. 1)</td>
</tr>
<tr>
<td>E_C</td>
<td>Correlation energy</td>
</tr>
<tr>
<td>E_x</td>
<td>Exchange energy [defined in Eq. (22)]</td>
</tr>
<tr>
<td>(E_{xc}^{\text{TF}})</td>
<td>Exchange-correlation energy density of uniform gas</td>
</tr>
<tr>
<td>(F_{\text{H}})</td>
<td>Hohenberg–Kohn universal functional (12)</td>
</tr>
<tr>
<td>(n_i)</td>
<td>Density of spin – electrons</td>
</tr>
<tr>
<td>T</td>
<td>True kinetic energy [expectation of Eq. (3)]</td>
</tr>
<tr>
<td>U</td>
<td>Hartree energy [defined in Eq. (8)]</td>
</tr>
<tr>
<td>V_w</td>
<td>Electron–electron repulsion [expectation of Eq. (4)]</td>
</tr>
<tr>
<td>(v_z)</td>
<td>KS potential (20)</td>
</tr>
<tr>
<td>Z</td>
<td>Atomic charge</td>
</tr>
</tbody>
</table>

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