DFT in a nutshell - v1.1

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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 (DFT), 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. To check you've followed the essay, you should certainly try the conceptual questions at the end. If you wish to master the material, you should work through the problems.

CONTENTS

ELECTRONIC STRUCTURE PROBLEM

For the present purposes, we define the modern electronic structure problem as finding the ground-state energy of non-relativistic 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.
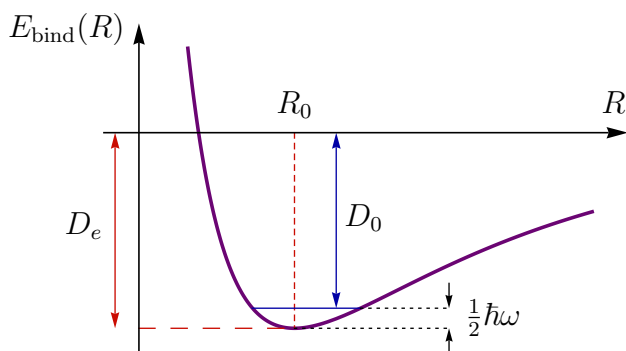

FIG. 1. Generic binding energy curve. For N_2, values for R_0 and D_e are given in table I.

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

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

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_e), corrected by zero-point energy ($\hbar\omega/2$), gives us the dissociation energy (D_0).

The Hamiltonian for the N electrons is

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

where the kinetic energy operator is

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

the electron-electron repulsion operator is

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

and the one-body operator is

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

In our Fig. 1, $v(\mathbf{r}) = -Z_A/r - Z_B/|\mathbf{r} - \mathbf{R}|$. We use atomic units unless otherwise stated, setting $e^2 = \hbar = m_e = 1$, so energies are in Hartrees (1 Ha = 27.2 eV or 628 kcal/mol) and distances in Bohr radii (1 a_0 = 0.529 Å). The ground-state energy satisfies the variational principle:

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

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 Ψ 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 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 $\phi(\mathbf{r})$, it is simply $|\phi(\mathbf{r})|^2$. In density functional theory (DFT), we write the ground-state energy in terms of $n(\mathbf{r})$ instead of Ψ. The first DFT was formulated by Thomas[6]. The kinetic energy density at any point is approximated by that of a uniform electron gas of non-interacting electrons of density $n(\mathbf{r})$, which for a spin-unpolarized system is:

$$T^{\mathrm{TF}} = a_{\mathrm{s}} \int d^3r\, n^{5/3}(\mathbf{r}), \qquad a_{\mathrm{s}} = 3(3\pi^2)^{2/3}/10. \quad (7)$$

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

$$U = \frac{1}{2} \int d^3r \int d^3r'\, \frac{n(\mathbf{r})\,n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (8)$$

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

$$V = \langle \hat{V} \rangle = \int d^3r\, n(\mathbf{r})\,v(\mathbf{r}). \quad (9)$$

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

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

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[7]). For same-spin, non-interacting fermions in 1d, the corresponding kinetic energy is

$$T^{\mathrm{TF\ 1d}}[n] = \frac{\pi^2}{6} \int dx\, n^3(x) \quad (11)$$

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, and noting what happens, especially for more than one particle.

But modern DFT began with the proof that the *exact* 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 minimze over all wavefunctions yielding a certain density, and then minimize over all densities. Because the one-body potential depends only on the density, we can define separately[8, 9]

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

where the minimization is over all antisymmetric wavefunctions yielding a given density $n(\mathbf{r})$. This is transparently a *functional* of the density, meaning it assigns a number to each density, as was first proven by Hohenberg and Kohn[10]. Then

$$E = \min_{n} \left\{ F[n] + \int d^3r\, n(\mathbf{r})\,v(\mathbf{r}) \right\}, \quad (13)$$

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 $v(\mathbf{r})$, and (iii) the exact density satisfies

$$\frac{\delta F}{\delta n(\mathbf{r})} = -v(\mathbf{r}), \quad (14)$$

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[11], 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[12] vastly improved the accuracy of DFT by imagining a fictitious set of *non-interacting* 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, $\phi_{j\sigma}(\mathbf{r})$, $j = 1, ..., N, \sigma = \uparrow, \downarrow$. These KS electrons satisfy a non-interacting Schrödinger equation:

$$\left\{ -\frac{1}{2}\nabla^2 + v_{\mathrm{s},\sigma}(\mathbf{r}) \right\} \phi_{j\sigma}(\mathbf{r}) = \epsilon_{j,\sigma}\phi_{j,\sigma}(\mathbf{r}), \quad (15)$$

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

$$T_{\mathrm{s}} = -\frac{1}{2} \sum_{\sigma=\uparrow,\downarrow} \sum_{j=1}^{N} \int d^3r\, \phi_{j,\sigma}^*(\mathbf{r})\nabla^2\phi_{j,\sigma}(\mathbf{r}). \quad (16)$$

If we write the energy in terms of KS quantites:

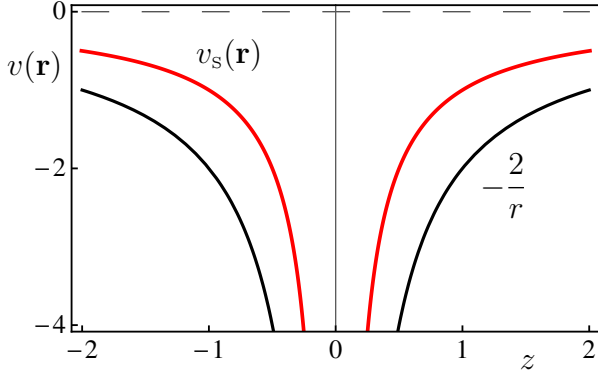$$E = T_{\mathrm{s}} + U + V + E_{\mathrm{xc}}, \quad (17)$$

FIG. 2. *Exact* KS potential of He atom along z axis. Thanks to Cyrus Umrigar[13].

E_{XC} is defined by Eq. (17) and called the exchange-correlation (XC) energy. 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

$$v_{\mathrm{H}}(\mathbf{r}) = \frac{\delta U}{\delta n(\mathbf{r})} = \int d^3 r' \, \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \qquad (18)$$

then

$$v_{\mathrm{S},\sigma}(\mathbf{r}) = v_{\sigma}(\mathbf{r}) + v_{\mathrm{H}}(\mathbf{r}) + v_{\mathrm{XC},\sigma}(\mathbf{r}), \qquad (19)$$

where

$$v_{\mathrm{XC},\sigma}(\mathbf{r}) = \frac{\delta E_{\mathrm{XC}}}{\delta n_{\sigma}(\mathbf{r})}. \qquad (20)$$

This is a formally exact scheme for finding the ground-state energy and density for any electronic problem. In Fig. 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[13]): Two non-interacting 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 $v_{\mathrm{XC}}(\mathbf{r})$.

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

$$E_{\mathrm{XC}} = E_{\mathrm{X}} + E_{\mathrm{C}}. \qquad (21)$$

The exchange energy is $\hat{V}_{\mathrm{ee}}$ evaluated on the KS Slater determinant minus the Hartree energy, and typically dominates. In terms of the orbitals:

$$E_{\mathrm{X}} = -\frac{1}{2} \sum_{\substack{\sigma,i,j \\ occ}} \int d^3 r \int d^3 r' \, \frac{\phi_{i\sigma}^*(\mathbf{r}) \, \phi_{j\sigma}^*(\mathbf{r}') \, \phi_{i\sigma}(\mathbf{r}') \, \phi_{j\sigma}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}, \qquad (22)$$

This is precisely the same orbital expression given in HF. Then the correlation energy is everything else, i.e., defined

to make Eq. (17) exact.[1]

REAL CALCULATIONS

Practical calculations use some simple approximation to $E_{\mathrm{XC}}[n_{\uparrow}, n_{\downarrow}]$. The KS equations are started with some initial guess for the density, yielding a KS potential via Eq. (20). The KS equations are then solved and a new density is found. This cycle is repeated until changes become negligible, i.e., this a self-consistent field (SCF) calculation.

The standard approximations are very simple. The local (spin) density approximation (often just called LDA) is[12]:

$$E_{\mathrm{XC}}^{\mathrm{LDA}} = \int d^3 r \, e_{\mathrm{XC}}^{\mathrm{unif}}(n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r})) \qquad (23)$$

where $e_{\mathrm{XC}}^{\mathrm{unif}}(n_{\uparrow}, n_{\downarrow})$ is the XC energy density of a uniform gas of spin densities $n_{\uparrow}$ and $n_{\downarrow}$. The X contribution was first written by Dirac[14], and is found by inserting plane waves (the KS orbitals of a uniform gas) into Eq. (22). In the unpolarized case, the result is

$$e_{\mathrm{X}}^{\mathrm{unif}}(n) = -a_{\mathrm{X}} \, n^{4/3}, \qquad a_{\mathrm{X}} = 3(3\pi^2)^{1/3}/(4\pi) \qquad (24)$$

while $e_{\mathrm{C}}^{\mathrm{unif}}(n_{\uparrow}, n_{\downarrow})$ has been calculated and accurately parametrized[15]. More accurate energetics are usually obtained with a generalized gradient approximation (GGA), which includes dependence on the gradient of the density

$$E_{\mathrm{XC}}^{\mathrm{GGA}} = \int d^3 r \, e_{\mathrm{XC}}^{\mathrm{GGA}}(n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r}), |\nabla n_{\uparrow}(\mathbf{r})|, |\nabla n_{\downarrow}(\mathbf{r})|), \qquad (25)$$

where now the energy density is given by some approximate form. The third standard form of approximation is a hybrid, which mixes in a fixed fraction of the exact exchange energy

$$E_{\mathrm{XC}}^{\mathrm{hyb}} = a \left(E_{\mathrm{X}} - E_{\mathrm{X}}^{\mathrm{GGA}} \right) + E_{\mathrm{XC}}^{\mathrm{GGA}}, \qquad (26)$$

where a is a universal parameter (often about 1/4) and E_{X} is the exact exchange defined in Eq. (22).

While 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[16], while the hybrid is PBE0, mixing 25% exact exchange[17]. Of the empirical type, B88 is the standard GGA for exchange[18], LYP for correlation[19], combining to form BLYP. The most commonly used functional today is a hybrid called B3LYP[20].

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

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[1] This definition differs slightly from that of quantum chemistry.

	$\Delta = \text{calc} - \text{expt}$						expt
	HF	LDA	PBE	BLYP	PBE0	B3LYP	
D_e	−110	40.4	16.2	13.0	−1.73	1.06	227.0
R_0	−3.2	−0.33	0.41	0.40	−0.93	−0.80	109.8

TABLE I. Differences in calculated (using Turbomole[a][21]) versus experimental values (from [22]) for well depth (D_e) in kcal/mol and equilibrium distance (R_0) in pm of N_2.

[a] http://www.turbomole.com/

chemistry. GGA's reduce this error to about 0.3 eV/bond, and hybrids reduce it another factor of 2. Table I shows typical results. Empirical parametrized functionals are usually about a factor of 2 better than non-empirical ones, but with less systematic errors. While hybrids are popular in chemistry, where Hartree-Fock codes have been including exact exchange for decades, they are much less popular for solids, due to the singularities in HF for metals.

On the other hand, 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 (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[23].

There are many suggestions on how to improve these standards. Presently, meta-GGAs, which use KS kinetic energy densities to approximate E_{XC}, can produce accurate energetics without using HF exchange[24]. Alternatively, including only the short-ranged contribution to exchange can also avoid the difficulties of applying HF to solids[25]. But so far, none of these is even close to replacing the standard functionals in amount of use.

Computer codes also need some basis set to represent the KS orbitals. Basis functions localized on atoms are used for molecular systems in quantum chemistry. Most codes now use Gaussians, but some use Slater-type orbitals (exponentials centered on atoms) and localized basis sets. In solids and materials, periodic boundary conditions are convenient for extended systems, making plane-waves a natural choice. Core electrons are often treated as frozen or by pseudopotentials, saving calculational effort. A few codes use numerical grids[26].

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[27]. But such calculations and calculators are also appearing in materials science, geology, and biochemical departments. Recent uses also include protein science, soil science, and astrophysics. Liquids can be simulated using ab initio molecular dynamics (AIMD)[28]. There is increasing interest in matter under high pressure and temperature (but not high enough to be pure plasma) and here DFT simulation is making a large impact[29].

In its original form, electronic 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 time-dependent one-body potentials[30]. In the linear response regime, this leads to a simple scheme for calculating transition frequencies which has become popular for molecules. The response scheme uses the ground-state KS orbitals as its starting point. In Fig. 2, the (doubly-occupied) $1s$ orbital is at -24.57 eV, precisely $-I$, the ionization potential for the system. The $2p$ orbital is at -3.429 eV, so the first allowed optical transition of the KS electrons has frequency 21.14 eV[31]. TDDFT corrects these transitions to the exact value 20.97 eV[32], but once again requires knowledge of an unknown functional, called the XC kernel, which depends on the perturbing frequency[33]. Present applications all use the adiabatic approximation, which ignores the frequency dependence and allows 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[34]. Dramatic failures of these approximations include double excitations, charge transfer, and a missing contribution to the optical response of solids[35].

USEFUL RESOURCES

Tables II and III give a list of acronyms and notation used in this essay. Perhaps the best pedagogical introduction of recent years is *A Primer in DFT*[36]. For physicists with some background in many-body theory, there's nothing better than Dreizler and Gross[37]. Analogously, if you are a chemist with knowledge of quantum chemical methods, try Parr and Yang[38]. A more pragmatic approach is that of Koch and Holthausen[39] who, in Part B, discuss the accuracy of different approximate functionals for different molecular properties. For time-dependent density functional theory, the standard reference is that edited by Marques[35].

The following questions are designed as a quick review to see if you digested the basic ideas above well-enough to make deductions on your own. Answers should be verbal or at most one equation.

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

TABLE II. Acronyms

abbr.	stands for
B88	Becke 88 E_X functional
BLYP	GGA using B88 and LYP
B3LYP	BLYP hybrid
DFT	Density functional theory
GGA	Generalized gradient approximation
HOMO	Highest-occupied molecular orbital
KS	Kohn-Sham
LDA	Local density approximation
LUMO	Lowest-unoccupied molecular orbital
LYP	Lee-Yang-Parr E_C functional[19]
PBE	Perdew-Burke-Ernzerhof GGA functional
PBE0	PBE hybrid
TF	Thomas-Fermi
X	Exchange
XC	Exchange-correlation

TABLE III. Notation of representative symbols

symbol	meaning
D_e	Electronic well-depth (see Fig. 1)
E_C	Correlation energy
E_X	Exchange energy (defined in Eq. (22))
$e_\mathrm{XC}^\mathrm{unif}$	Exchange-correlation energy density of uniform gas
$F[n]$	Hohenberg–Kohn universal functional (12)
$n_\uparrow(\mathbf{r})$	Density of spin $\uparrow$ electrons
R_0	Equilibrium bond length (see Fig. 1)
T	True kinetic energy (expectation of Eq. (3))
U	Hartree energy (defined in Eq. (8))
V_ee	Electron-electron repulsion (expectation of Eq. (4))
$v_\mathrm{S}(\mathbf{r})$	KS potential (20)
Z	Atomic charge

2. Why is a KS calculation much faster than direct solution of the Schrödinger equation?

3. Why is the KS potential less deep than the original potential in Fig. 2?

4. Is the sum of the KS eigenvalues equal to the total energy?

5. What is E_XC for a one-electron system?

6. Give the signs of E, T, V_ee, V, U, E_X, and E_C for real systems (i.e., atoms, molecules, and solids).

The next problems can all be done using the material presented, but each requires taking steps beyond what was explicitly shown in the chapter. They are designed to need only pencil and paper.

1. Apply Eq. (12) to the KS system to define T_S without ever mentioning $v_\mathrm{S}(\mathbf{r})$. Then prove that $T \geq T_\mathrm{S}$ always.

2. Derive $F[n]$ for a single electron. It has no electron-electron interaction, and is known as the von Weizsäcker kinetic energy.

3. Use dimensional analysis to explain the powers of the density in the local approximations of Eqs. (7), (11), and (24).

4. Derive a formula for $E_\mathrm{X}[n_\uparrow, n_\downarrow]$ in terms of $E_\mathrm{X}[n]$, evaluated on various densities. Does the same formula apply to the KS kinetic energy, but with E_X replaced by T_S? How about for E_C?

5. What is the expectation value of the Hamiltonian of Eq. (2) evaluated on the KS Slater determinant? Use this to prove that the DFT definition of correlation energy is never positive.

6. Write the formula that extracts $v_\mathrm{S}(\mathbf{r})$ from $n(\mathbf{r})$ for the He atom calculation mentioned in Fig. 2. Can you explain why this does *not* tell us the vital $v_\mathrm{XC}[n](\mathbf{r})$ for *any* spin-unpolarized two-electron systems?

7. Show that if electrons repelled via a contact repulsion, $\delta(\mathbf{r} - \mathbf{r}')$, the exchange is given exactly by LDA, and give its expression, including spin-dependence.

Finally, we come to calculational problems. In solving these problems, one will greatly be aided by the use of a computer algebra system such as *Mathematica*.

1. 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.

2. Evaluate the TF kinetic energy of the H atom and deduce the % error. Repeat using spin-DFT.

3. Deduce the exact energy for N same-spin fermions in a flat box of width 1 bohr. Then evaluate the local approximation to the kinetic energy for $N = 1, 2$, and 3, and calculate the % error.

[1] M. Born and R. Oppenheimer, "Zur Quantentheorie der Molekeln," Annalen der Physik, **389**, 457 (1927).

[2] J. C. Slater, "The theory of complex spectra," Phys. Rev., **34**, 1293 (1929).

[3] D. R. Hartree and W. Hartree, "Self-Consistent Field, with Exchange, for Beryllium," Proceedings of the Royal Society of London. Series A - Mathematical and Physical Sciences, **150**, 9 (1935).

[4] A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry* (MacMillan, New York, 1982).

[5] E. K. U. Gross, E. Runge, and O. Heinonen, *Many-Particle Theory* (Adam Hilger, Bristol, 1991).

[6] L. H. Thomas, "The calculation of atomic fields," Mathematical Proceedings of the Cambridge Philosophical Society, **23**, 542 (1927).

[7] E. Teller, "On the stability of molecules in the Thomas-Fermi theory," Rev. Mod. Phys., **34**, 627 (1962).

[8] M. Levy, "Universal variational functionals of electron densities, first-order density matrices, and natural spin-orbitals and solution of the v-representability problem," Proceedings of the National Academy of Sciences of the United States of America, **76**, 6062 (1979).

[9] E. H. Lieb, "Density functionals for coulomb systems," International Journal of Quantum Chemistry, **24**, 243 (1983).

[10] P. Hohenberg and W. Kohn, "Inhomogeneous electron gas," Phys. Rev. B, **136**, 864 (1964).

[11] U. von Barth and L. Hedin, "A local exchange-correlation potential for the spin polarized case," Journal of Physics C: Solid State Physics, **5**, 1629 (1972).

[12] W. Kohn and L. J. Sham, "Self-consistent equations including exchange and correlation effects," Phys. Rev. A, **140**, 1133 (1965).

[13] C. J. Umrigar and X. Gonze, "Accurate exchange-correlation potentials and total-energy components for the helium isoelectronic series," Phys. Rev. A, **50**, 3827 (1994).

[14] P. A. M. Dirac, "Note on exchange phenomena in the Thomas atom," Mathematical Proceedings of the Cambridge Philosophical Society, **26**, 376 (1930).

[15] J. P. Perdew and Y. Wang, "Accurate and simple analytic representation of the electron-gas correlation energy," Phys. Rev. B, **45**, 13244 (1992).

[16] J. P. Perdew, K. Burke, and M. Ernzerhof, "Generalized gradient approximation made simple," Phys. Rev. Lett., **77**, 3865 (1996).

[17] K. Burke, M. Ernzerhof, and J. P. Perdew, "The adiabatic connection method: a non-empirical hybrid," Chemical Physics Letters, **265**, 115 (1997).

[18] A. Becke, "Density-functional exchange-energy approximation with correct asymptotic behavior," Phys. Rev. A, **38**, 3098 (1988).

[19] C. Lee, W. Yang, and R. G. Parr, "Development of the colle-salvetti correlation-energy formula into a functional of the electron density," Phys. Rev. B, **37**, 785 (1988).

[20] A. D. Becke, "Density-functional thermochemistry. iii. the role of exact exchange," The Journal of Chemical Physics, **98**, 5648 (1993).

[21] R. Ahlrichs, M. Bär, M. Häser, H. Horn, and C. Kölmel, "Electronic structure calculations on workstation computers: The program system turbomole," Chemical Physics Letters, **162**, 165 (1989).

[22] M. Ernzerhof and G. E. Scuseria, "Assessment of the Perdew–Burke–Ernzerhof exchange-correlation functional," J. Chem. Phys, **110**, 5029 (1999).

[23] M. Dion, H. Rydberg, E. Schröder, D. C. Langreth, and B. I. Lundqvist, "Van der Waals density functional for general geometries," Phys. Rev. Lett., **92**, 246401 (2004).

[24] J. P. Perdew, A. Ruzsinszky, G. I. Csonka, L. A. Constantin, and J. Sun, "Workhorse semilocal density functional for condensed matter physics and quantum chemistry," Phys. Rev. Lett., **103**, 026403 (2009).

[25] J. Heyd and G. E. Scuseria, "Efficient hybrid density functional calculations in solids: Assessment of the Heyd–Scuseria–Ernzerhof screened coulomb hybrid functional," The Journal of Chemical Physics, **121**, 1187 (2004).

[26] R. M. Martin, *Electronic Structure: Basic Theory and Practical Methods* (Cambridge University Press, 2004).

[27] A. Nilsson, L. G. Pettersson, and J. Nørskov, eds., *Chemical Bonding at Surfaces and Interfaces* (Elsevier, Amsterdam, 2008).

[28] R. Car and M. Parrinello, "Unified approach for molecular dynamics and density-functional theory," Phys. Rev. Lett., **55**, 2471 (1985).

[29] S. Root, R. J. Magyar, J. H. Carpenter, D. L. Hanson, and T. R. Mattsson, "Shock compression of a fifth period element: Liquid xenon to 840 gpa," Phys. Rev. Lett., **105**, 085501 (2010).

[30] E. Runge and E. K. U. Gross, "Density-functional theory for time-dependent systems," Phys. Rev. Lett., **52**, 997 (1984).

[31] C. J. Umrigar, A. Savin, and X. Gonze, "Are unoccupied Kohn-Sham eigenvalues related to excitation energies?" in *Electronic Density Functional theory: Recent progress and new directions*, edited by J. F. Dobson, G. Vignale, and M. P. Das (Plenum, New York, 1997).

[32] A. Kono and S. Hattori, "Accurate oscillator strengths for neutral helium," Phys. Rev. A, **29**, 2981 (1984).

[33] K. Burke, J. Werschnik, and E. K. U. Gross, "Time-dependent density functional theory: Past, present, and future," The Journal of Chemical Physics, **123**, 062206 (2005).

[34] P. Elliott, F. Furche, and K. Burke, "Excited states from time-dependent density functional theory," in *Reviews of Computational Chemistry*, edited by K. B. Lipkowitz and T. R. Cundari (Wiley, Hoboken, NJ, 2009) pp. 91–165.

[35] M. Marques, C. A. Ullrich, F. Nogueira, A. Rubio, K. Burke, and E. K. U. Gross, eds., *Time-dependent density functional theory* (Springer, Heidelberg, 2006).

[36] C. Fiolhais, F. Nogueira, and M. Marques, eds., *A Primer in Density Functional Theory* (Springer-Verlag, NY, 2003).

[37] R. M. Dreizler and E. K. U. Gross, *Density Functional Theory: An Approach to the Quantum Many-Body Problem* (Springer–Verlag, 1990).

[38] R. G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules* (Oxford University Press, 1989).

[39] W. Koch and M. C. Holthausen, *A Chemist's Guide to Density Functional Theory*, 2nd ed. (Wiley-VCH, Weinheim, 2002).