Introduction to Computational Chemistry

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October 11, 2012
Density functional theory (DFT) is a quantum mechanical theory used in physics and chemistry to investigate the electronic structure (principally the ground state) of many-body systems, in particular atoms, molecules, and the condensed phases.

- With this theory, the properties of a many-electron system can be determined by using functionals, i.e. functions of another function, which in this case is the spatially dependent electron density.

- The multiple determinant calculations require very large basis sets due to the poor convergence of the correlation energy when the inter-electronic distance becomes very small. However, DFT can produce accurate results with relatively small basis sets.

- DFT has become the most popular and versatile method in computational chemistry, accounting for approximately 90% of all calculations today. The reason for this preference is that DFT scales with the same order as HF theory.
DFT avoids the expense of the more traditional methods, deriving the energy directly from the electron probability density, rather than the molecular wavefunction, thus drastically reducing the dimensionality of the problem.

Some history:
DFT has been very popular for calculations in solid state physics since the 1970s. DFT calculations agreed quite satisfactorily with experimental data. Also, the computational costs were relatively low when compared to Hartree-Fock theory and its descendants. However, DFT was not considered accurate enough for calculations in quantum chemistry until the 1990s, when the approximations used in the theory were greatly refined to better model the exchange and correlation interactions. DFT is now a leading method for electronic structure calculations in chemistry and solid-state physics.
Problems with DFT methods:

Despite the improvements in DFT, there are still difficulties in using density functional theory to properly describe intermolecular interactions, especially:

- van der Waals forces (dispersion)
- charge transfer excitations
- transition states
- global potential energy surfaces and some other strongly correlated systems
- calculations of the band gap in semiconductors.

Its poor treatment of dispersion renders DFT unsuitable (at least when used alone) for the treatment of systems which are dominated by dispersion (e.g., interacting noble gas atoms) or where dispersion competes significantly with other effects (e.g., in biomolecules). The development of new DFT methods designed to overcome this problem, by alterations to the functional or by the inclusion of additive terms, is a current research topic.
DFT is based on the two Hohenberg-Kohn theorems

The first H-K theorem demonstrates that the ground state properties of a many-electron system are uniquely determined by an electron density that depends on only 3 spatial coordinates.

- It lays the groundwork for reducing the many-body problem of \( N \) electrons with \( 3N \) spatial coordinates to 3 spatial coordinates, through the use of functionals of the electron density.

- This theorem can be extended to the time-dependent domain to develop time-dependent density functional theory (TDDFT), which can be used to describe excited states.

The second H-K theorem defines an energy functional for the system and proves that the correct ground state electron density minimizes this energy functional.

- The second Hohenberg-Kohn theorem has two drawbacks. Firstly, it assumes that there is no degeneracy in the ground state, and secondly the density has unknown form.
There is no systematic way to find or improve a density functional. The most appealing way forward is to find the exact solution for a model system, and then assume that the system of interest behaves similarly to the model.

The first density functionals were due to Thomas, Fermi, and Dirac, all of which used the uniform electron gas as their model.

The uniform electron gas is defined as a large number of electrons \( N \) in a cube of volume \( V \), throughout which there is a uniform spread of positive charge sufficient to make the system neutral. The uniform gas is then defined as the limit \( N \to \infty, V \to \infty \), with the density \( \rho = N/V \) remaining finite.

Although it does bear some resemblance to electrons in metals, its widespread use is due to its simplicity – it is completely defined by one variable, the electron density \( \rho \). Using the uniform electron gas, an expression for the kinetic energy (the Thomas-Fermi kinetic functional) can be derived

\[
T_{TF}^{27}[\rho_{\sigma}] = \frac{3}{10} (6\pi^2)^{2/3} \int \rho_{\sigma}^{5/3}(\mathbf{r}) \, d\mathbf{r}
\]

where \( \sigma \) can take the values of \( \alpha \) or \( \beta \).
When applied to atoms and molecules the Thomas-Fermi functional yields kinetic energies that are about 10% too small. Similarly, an expression for the exchange energy of the uniform electron gas can be calculated (the Dirac exchange functional)

\[
E_{x}^{D30}[\rho_{\sigma}] = -\frac{3}{2} \left( \frac{3}{4\pi} \right)^{1/3} \int \rho_{\sigma}^{4/3}(r) \, dr
\]  

(1)

The Dirac functional also gives exchange energies that are roughly 10% smaller than those from HF theory. More worrying is that the spurious self-interaction of electrons is not exactly canceled.
The electron densities of atoms and molecules are often far from uniform, so functionals based on systems which include an inhomogeneous density should perform better. In 1935 von Weizsacker placed infinitesimally small ripples on the uniform electron gas and calculated the second order correction to the kinetic energy

\[ T^{W35}[\rho_\sigma] = T^{TF27}[\rho_\sigma] + \frac{1}{8} \int \rho^{5/3}_\sigma x^2 d\mathbf{r} \]  

(2)

where \( x(\mathbf{r}) \) is a dimensionless quantity, the reduced density gradient

\[ x(\mathbf{r}) = \frac{\left| \nabla \rho(\mathbf{r}) \right|}{\rho^{4/3}(\mathbf{r})}. \]  

(3)

Unfortunately the original derivation was flawed and the above functional is too large by a factor of nine. The corrected functional is a large improvement on \( T^{TF27}[\rho] \), yielding kinetic energies typically within 1% of HF theory.
A similar correction was made to the Dirac exchange functional by Sham and Kleinman. The second order correction to the exchange energy is

\[
E_{x}^{SK71}[\rho_{\sigma}] = E_{x}^{D30}[\rho_{\sigma}] - \frac{5}{(36\pi)^{5/3}} \int \rho_{\sigma}^{4/3} x_{\sigma}^{2} \, dr.
\]  

(4)

The corrected functional gives exchange energies that are typically within 3% of HF; however, it is not seen as an improvement over the Dirac functional, as the potential is unbounded in the Rydberg regions of atoms and molecules.
The kinetic energy has a large contribution to the total energy. Therefore even the 1% error in the kinetic energy of the Thomas-Fermi-Weizsacker model prevented DFT from being used as a quantitative predictive tool. Thus DFT was largely ignored until 1965 when Kohn and Sham introduced a method which treated the majority of the kinetic energy exactly.

**Key idea:** The intractable many-body problem of interacting electrons in a static external potential is reduced to a tractable problem of non-interacting electrons moving in an effective potential.

The theory begins by considering the noninteracting reference system: $N$ noninteracting electrons moving in external potential $v_s$, each in one of $N$ orbitals, $\psi_i$. Such a system will be defined by the Hamiltonian

$$\hat{H}_s = \sum_{i=1}^{N} \left( -\frac{1}{2} \nabla_i^2 \right) + \sum_{i=1}^{N} v_s(r_i)$$

(5)
which has an exact eigenfunction that is the single determinant constructed from the \( N \) lowest eigenstates of the one-electron equations

\[
\left[ -\frac{1}{2} \nabla^2 + v_s(r) \right] \psi_i = \varepsilon_i \psi_i.
\] (6)

We require that the ground state density be stationary. (In calculus of variations, the Euler–Lagrange equation, or Lagrange’s equation, is a differential equation whose solutions are the functions for which a given functional is stationary.) The corresponding Euler-Lagrange equation is

\[
\mu = v_s(r) + \frac{\delta T_s[\rho]}{\delta \rho(r)},
\] (7)

where the Lagrange multiplier is a familiar property to chemists, the chemical potential \( \mu \), has been introduced.
For this system the kinetic energy and electron density are given by

\[ T_s[\rho] = \sum_{i}^{N} \langle \psi_i | - \frac{1}{2} \nabla_i^2 | \psi_i \rangle \]  

\[ \rho(\mathbf{r}) = \sum_{i}^{N} |\psi_i(\mathbf{r})|^2 \]  

and the total energy is given by

\[ E[\rho] = T_s[\rho] + \int v_s(\mathbf{r}) \rho(\mathbf{r}) \, d\mathbf{r} \]  

The quantity \( T_s[\rho] \) is well-defined, but not the exact kinetic energy, \( T[\rho] \).
Kohn and Sham reformulated the interacting problem so that its kinetic component is defined to be $T_s[\rho]$ to give

$$E[\rho] = T_s[\rho] + J[\rho] + \int v_s(r)\rho(r)d\mathbf{r} + E_{xc}[\rho],$$  \hspace{1cm} (11)

where $J[\rho]$ is the Coulombic integral expressed in terms of electron density and $E_{xc}[\rho]$ is the exchange-correlation energy. The Euler–Lagrange equation now becomes

$$\mu = v_{eff}(r) + \frac{\delta T_s[\rho]}{\delta \rho(r)}$$  \hspace{1cm} (12)

where the Kohn-Sham (KS) effective potential, $v_{eff}$ is defined as

$$v_{eff}(r) = v_s(r) + \int \frac{\rho(r')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}(r)$$  \hspace{1cm} (13)

and the exchange-correlation potential, $v_{xc}$ is

$$v_{xc}(r) = \frac{\delta E_{xc}[\rho]}{\delta \rho(r)}.$$  \hspace{1cm} (14)
Kohn and Sham noticed that equation is the same as that for a **non-interacting system moving in the effective potential** \( v_{\text{eff}}(\mathbf{r}) \). Thus, the exact density can be obtained by solving the N one-electron equations (the restricted KS equations)

\[
\left[-\frac{1}{2} \nabla^2 + v_{\text{eff}}(\mathbf{r})\right] \psi_i = \varepsilon_i \psi_i. \tag{15}
\]

Notice that \( v_{\text{eff}} \) depends on \( \rho(\mathbf{r}) \), via equation (13), hence the KS equations must be solved iteratively.
The KS equations are very similar to the Hartree–Fock equations. In fact, setting the exchange-correlation potential to the HF exchange potential yields the HF equations. Drawing too many similarities to HF is dangerous, however. Firstly, the KS orbitals are simply a way of representing the density; they are not (as in HF) an approximation of the wavefunction. Also, HF theory is variational, providing an upper bound to the exact energy, yet DFT is only variational if the exact energy functional is used.

The above analysis is only appropriate for closed shell molecules. Because the KS equations so closely follow the restricted HF equations, both the restricted open shell and unrestricted methodologies are readily available. However, the KS equations are formally exact (given the exact $E_{xc}[\rho]$), so it must be able to produce an excess of $\beta$ electron density at points in the molecule, and therefore only the unrestricted formalism is appropriate.
Just as in HF theory, the KS equations are solved by expanding the orbitals over a basis set.

The major advantage of DFT is that the basis set requirements are far more modest than the more conventional correlated methods.

In DFT the basis set only needs to represent the one electron density – the inter-electron cusp is accounted for by the effective potential, $v_{\text{eff}}$. In the more traditional methods the basis set describes the entire N-electron wavefunction, requiring an accurate description of the cusp which is sensitive to the basis set.

The kinetic energy functional is known exactly.

The exchange-correlation part of the total-energy functional remains unknown and must be approximated.
In local-density approximation (LDA), the exchange-correlation energy functional $E_{xc}[^\rho]$ (see Eq.(11) depends only on the density at the coordinate where the functional is evaluated.

$$E_{xc}^{LDA}[\rho] = \int \epsilon_{xc}(\rho) \rho(r) \text{d}r,$$

(16)

where $\epsilon_{xc}(\rho)$ is the exchange-correlation energy density. The exchange-correlation energy is decomposed into exchange and correlation terms linearly

$$E_{xc} = E_x + E_c,$$

(17)

so that separate expressions for $E_x$ and $E_c$ are sought. The uniform electron gas functional is used for the $E_x$. Only limiting expressions for the correlation density are known exactly, leading to numerous different approximations for $E_c$. 
LDA treats all systems as homogeneous. However, real systems are inhomogeneous. Generalized gradient approximation (GGA) takes this into account by including the derivative information of the density into the exchange-correlation functionals.

$$E_{xc}^{GGA}[ho] = \int f(\rho(\textbf{r}), \nabla(\rho(\textbf{r})))d\textbf{r},$$  \hspace{1cm} (18)

- In comparison with LDA, GGA tend to improve total energies, atomization energies, energy barriers and structural energy differences.
- GGA expand and soften bonds, an effect that sometimes corrects and sometimes overcorrects the LDA prediction.
- Whereas the $\epsilon_{xc}(\rho)$ (in LDA) is well established, the best choice for $f(\rho(\textbf{r}), \nabla(\rho(\textbf{r})))$ is still a matter of debate.
In practice, Kohn-Sham theory can be applied in several distinct ways depending on what is being investigated.

- In solid state calculations, the local density approximations are still commonly used along with plane wave basis sets, as an electron gas approach is more appropriate for electrons delocalised through an infinite solid.

- In molecular calculations more sophisticated functionals are needed, and a huge variety of exchange-correlation functionals have been developed for chemical applications.

- In the chemistry community, one popular functional is known as BLYP (from the name Becke for the exchange part and Lee, Yang and Parr for the correlation part).

- Even more widely used is B3LYP which is a hybrid functional in which the exchange energy, in this case from Becke’s exchange functional, is combined with the exact energy from Hartree–Fock theory. The adjustable parameters in hybrid functionals are generally fitted to a 'training set' of molecules.
Unfortunately, although the results obtained with these functionals are usually sufficiently accurate for most applications, there is no systematic way of improving them (in contrast to methods like configuration interaction or coupled cluster theory).

Hence in the current DFT approach it is not possible to estimate the error of the calculations without comparing them to other methods or experiments.