Density Functional Theory - I

1 Density and Density Functional Theory

The density functional theory seeks to determine all the properties of atoms, molecules with many electrons in terms of an electron density function $\rho(\vec{r})$ in the three dimensional space and certain functionals of $\rho(\vec{r})$. The spin-less one electron density is related to the N-electron anti symmetrized wave function $\psi(x_1, x_2, ..., x_N)$ by the following definition ($x_i : r_i s_i$)

$$\rho(\vec{r}) = N\int \psi(x_1, x_2, ..., x_N)\psi^*(x_1, x_2, ..., x_N)dr_2...dr_N ds_1...ds_N \tag{1}$$

where $x_k \equiv (r_k s_k)$ represents the product of spatial (r_k) and spin (s_k) coordinates of the k^{th} electron of the system.

Note 1. Why does the factor N appear in the definition of $\rho(\vec{r})$?

Since $\rho(\vec{r})$ represents the probability of finding one electron at the space point $\vec{r}$, and there are N identical electrons in the system, we could have chosen to leave any one of the N number of electron coordinates **<u>unintegrated/nonintegrated</u>** instead of r_1 in equation (1).

Equation (1) defines the probability of finding one electron at any point $\vec{r}$, irrespective of its spin and where the remaining $N-1$ electrons are. The central theme of DFT is that the knowledge of $\rho(\vec{r})$ alone is sufficient to compute all the properties of the non-degenerate ground state of an atom or a molecule. Let us note that $\rho(\vec{r})$ of equation (1) has two evidently simple properties

$$\int \rho(\vec{r})dr = N \text{ (the number of electrons)} \tag{2}$$

$$\rho(\vec{r}) \geq 0 \text{ (non-negative at any point in space)} \tag{3}$$

Note 2. What is the N-representability Problem? Does any function $\rho(\vec{r})$ whatsoever represent electron density derivable from an N-electron anti-symmetric wave function? Are equations (2) and (3) sufficient to guarantee that?

These questions have been debated, analyzed and partially answered over many years and constitutes important elements of the N-representability problem. Since one plans to work with a single particle density function $\rho(\vec{r})$ in the DFT, it is in the fitness of things that one builds up the theory in the framework of a single-particle like Schrodinger equation for atoms and molecules. For a molecule with M-nuclei of charges $z_k e\,(k=1,2,...,M)$ located at space points $\{R_k\}$, the equation may be assumed to take the following form:

$$\left\{\frac{-\hbar^2}{2m}\nabla^2(\vec{r})-\sum_{k=1}^{M}\frac{z_k e^2}{|r-R_k|}+\frac{1}{2}\int_{r'}\rho(r')\frac{e^2}{|r-r'|}dr'+V_{xc}\right\}\phi_i(\vec{r})=\varepsilon_i\phi_i(\vec{r}) \tag{4}$$

where $\phi_i(\vec{r})$s are effective (space) orbital like entities which can be occupied by a pair of electrons of opposite spins. In equation (4) the electron in orbital $\phi_i(\vec{r})$ experiences the attraction due to all the M nuclei having positive charges $z_1e,...,z_Me$, the repulsive Coulomb interaction with all the electronic charges described by the electronic charge density $e\rho(\vec{r})$ (note here that the third term within the curly bracket incorrectly includes self-interaction of the electrons, for in an N electron system each electron would interact with the remaining N-1 and not N electrons) and in addition feels the so called exchange correlation potential $[V_{xc}]$. The exchange correlation potential seeks to take care of the fact that any two electrons having the same spin would strongly tend to avoid the same region of space (equivalent to feeling an ‘exchange repulsion’) and that even two electrons of opposite spins would tend to avoid being too close to each other (equivalent to feeling Coulomb correlation). Inclusion of $V_{xc}(\vec{r})$ would therefore eliminate self-interaction term and account for electron correlation. What gives legitimacy to this idea of introducing $V_{xc}(\vec{r})$? The legitimacy is provided by the famous Hohenberg-Kohn theorem which asserts that the ground state electron density $\rho(\vec{r})$ describing an N-electron system uniquely determines the external potential $V(\vec{r})$ in the atomic/molecular Hamiltonian

$$H=\sum_i\left\{\frac{-\hbar^2}{2m}\nabla_i^2+V(\vec{r}_i)\right\}+\frac{1}{2}\sum_{i\neq j}\frac{e^2}{|r_i-r_j|} \tag{5}$$

Since H determines the ground state energy E_o and the wave function $\psi(r_1...r_N)$, $\rho(\vec{r})$ by virtue of determining $V(\vec{r})$ uniquely determines all the ground state properties of the system. The importance of $\rho(\vec{r})$ determining $V(\vec{r})$ must be emphasized. The external potential $V(\vec{r})$ specifies the spatial position and identity of the nuclei of which the system is made. $\rho(\vec{r})$

therefore also determines the equilibrium geometry of the molecule. The proof of HK theorem proceeds along the following lines (for a non-degenerate ground state).

Let us note that the total number of electrons in the system is fixed uniquely by $\rho(\vec{r})$ as $\int \rho(\vec{r})\,\vec{dr} = N$ (equation 2). Let us suppose that $\rho(\vec{r})$ does not uniquely fix $V(\vec{r})$ so that we can have two distinct potentials $V(\vec{r})$ and $V^{'}(\vec{r})$ defining two Hamiltonians (equation 5) H and $H^{'}$ both having the same ground state density. Let the corresponding ground state wave functions be $\psi(\vec{r})$ and $\psi^{'}(\vec{r})$; then the ground state energies are $\left\langle \psi(\vec{r}) | H | \psi(\vec{r}) \right\rangle = E_o$ and $\left\langle \psi^{'}(\vec{r}) | H^{'} | \psi^{'}(\vec{r}) \right\rangle = E_o^{'}$, respectively. By our assumption that both $\psi(\vec{r})$ and $\psi^{'}(\vec{r})$ lead to the same ground state electron density function $\rho(\vec{r})$. Now variational principle asserts that with $\psi^{'}$ as the trial wave function for the Hamiltonian H, $\langle \psi' | H | \psi' \rangle$ is an upper bound to the exact ground state energy of the system. That implies

$$\begin{aligned} E_o &< \left\langle \psi^{'} | H | \psi^{'} \right\rangle \\ &= \left\langle \psi^{'} | H^{'} + (H - H^{'}) | \psi^{'} \right\rangle \\ &= \left\langle \psi^{'} | H^{'} | \psi^{'} \right\rangle + \left\langle \psi^{'} | H - H^{'} | \psi^{'} \right\rangle \\ &= E_0^{'} + \int \rho(\vec{r}) \left\{ V(\vec{r}) - V^{'}(r) \right\} dr \end{aligned} \tag{6}$$

If we use ψ as the trial function with the Hamiltonian $H^{'}(\vec{r})$ and follow similar steps we can also show that

$$E_o^{'} \le E_o + \int \rho(\vec{r}) \left\{ V^{'}(\vec{r}) - V(\vec{r}) \right\} dr \tag{7}$$

If we add 12.6 and 12.7, we have

$$E_o + E_o^{'} \le E_o^{'} + E_o \tag{8}$$

Equation (8) can not hold unless we are dealing with a degenerate ground state but that contradicts our assumption that we are dealing with non-degenerate ground state. The HK theorem therefore confirms that two different external potentials $V(\vec{r})$ and $V^{'}(\vec{r})$ can not yield the same ground state electron density $\rho(\vec{r})$ for a non-degenerate ground state. The mapping $\rho(\vec{r}) \to V(\vec{r})$ is one to one. Once this basic assertion has been established we can argue back that since the ground state density $\rho(\vec{r})$ determines N (the number of electrons) and $V(\vec{r})$

(external potential) uniquely it also determines H (cf equation (5)) completely. H in turn determines $\psi_o(\vec{r})$ and E_o. Since the properties of the system are uniquely determined by ψ_o, we come to conclude that the ground state density $\rho(\vec{r})$ determines all the properties uniquely. This result has important consequences. The first is that the kinetic energy T is fixed by the ground state density (T is a unique and universal functional $T[\rho]$ of ρ). The second is that the inter-electron interaction energy V_{ee} is also a universal functional of $V_{ee}[\rho]$ of ρ. The problem is that the forms of the universal functionals $V_{ee}[\rho]$ and $T[\rho]$ are unknown - HK theorem proves their existence without determining their forms. It has remained elusive, and will probably continue to remain so. The important point that HK theorem stresses is that the computational bottleneck that plagues the convential quantum chemical methods described in chapters 11-15 as they go on adding larger and larger number of configurations to represent the many-electron wave function, may be replaced by efforts to search for or design better and better functionals $T[\rho]$ and $V_{ee}[\rho]$ that can be used in equation (4) to determine $\rho(\vec{r})$ and all other properties with greater and greater accuracy.

2 *Approximations to* $T[\rho]$ *and* $V_{ee}[\rho]$

2.1 Forms of $T[\rho]$

We note that the kinetic energy operator involves second derivatives with respect to the spatial coordinates of electrons. It is difficult to see how the kinetic energy can be reduced to a functional $T[\rho]$ of ρ. One can try to understand and make some progress by making approximations.

Let us assume that we have a system of N non-interacting electrons moving in a cubic potential energy box of side 'L'. The energy states supported by this potential are characterized by the three quantum numbers n_x, n_y, n_z, and are given by the expression

$$E(n_x, n_y, n_z) = (n_x^2 + n_y^2 + n_z^2)\hbar^2 / 8mL^2 \tag{9}$$

$$= \frac{\hbar^2}{8mL^2}(R^2) \tag{10}$$

where n_x, n_y, n_z are positive non-zero integers (1,2,3,...etc.) and $R = \sqrt{(n_x^2 + n_y^2 + n_z^2)}$ defines the radius of a sphere in three dimensional space spanned by the quantum numbers n_x, n_y, n_z. We note that there is one state per unit volume of this space which immediately suggests that the volume Ω' accommodating all states with energy $E \leq \frac{\hbar^2}{8mL^2}(R^2)$ is given by

$$\Omega' = \frac{4}{3}\pi R^3 = \frac{4}{3}\pi(n_x^2 + n_y^2 + n_z^2)^{\frac{3}{2}} \tag{11}$$

But we must also note that, n_x, n_y, n_z can only be non-zero positive integers which immediately leads to the correct volume $\Omega(E)$ containing the states with $E \leq \frac{\hbar^2}{8mL^2}(R^2)$ where

$$\Omega(E) = \frac{1}{8}\Omega'(E) \tag{12}$$

$$= \frac{\pi}{6}(\frac{8mL^2E}{\hbar^2})^{\frac{3}{2}} \tag{13}$$

That there is only one state per unit volume of the designated space means $\Omega(E)$ also represents the number of states with energy $\leq E$. The number of states with energy lying between $E \leftrightarrow E + dE$ is therefore given by $d\Omega(E) = g(E)dE$ where

$$g(E) = \frac{d\Omega(E)}{dE} = \frac{\pi}{4}(\frac{8mL^2}{\hbar^2})^{\frac{3}{2}}E^{\frac{1}{2}} \tag{14}$$

$g(E)$ is called the density of states at energy E. The ground state energy of the system of N electrons which occupy the $\frac{N}{2}$ lowest single particle energy levels (the orbitals), each level (orbital) being occupied by a pair of electrons with opposite spins (electrons obey Fermi Dirac statistics), is given by

$$E_o = 2\int_0^{\varepsilon_F} g(E)EdE \tag{15}$$

$$= (\frac{8\pi}{5})(\frac{2m}{\hbar^2})^{\frac{3}{2}}L^3\varepsilon_F^{\frac{5}{2}} \tag{16}$$

where ε_F is the Fermi energy. The total number of electrons can be directly obtained by integrating $g(E)$ from 0 to ε_F and multiplying the result by 2,

$$N = 2\int_0^{\varepsilon_F} g(E)dE \tag{17}$$

$$= (\frac{8\pi}{3})(\frac{2m}{\hbar^2})^{\frac{3}{2}} L^3 \varepsilon_F^{\frac{3}{2}} \tag{18}$$

Equation (18) can be used to express ε_F in terms of N giving

$$\varepsilon_F = (\frac{N}{L^3})^{\frac{2}{3}} (\frac{1}{2})^{\frac{2}{3}} (\frac{3}{8\pi})^{\frac{2}{3}} 3^{\frac{2}{3}} (\frac{\hbar^2}{m}) \tag{19}$$

When used in equation (16), it leads to an expression for the ground state energy in terms of N, the total number of electrons in the system:

$$E_o = \frac{3\hbar^2}{10m}(\frac{3}{8\pi})^{\frac{2}{3}} L^3 (\frac{N}{L^3})^{\frac{5}{3}} \tag{20}$$

$\frac{N}{L^3} = \frac{N}{V}$ is nothing but the electron density $\rho(x, y, z)$ inside the box which in this case is a uniform density. Since the potential energy is zero everywhere inside the box, E_o is just the kinetic energy of the particles inside the box. The kinetic energy E_o can thus be related to electron density $\rho(\vec{r})$ ($E_k(\vec{r}) \propto [\rho(\vec{r})]^{\frac{5}{3}}$) at the 'local' level - i.e. at each point r. The kinetic energy density functional of N electron atoms and molecule that arises from the above treatment is known as Thomas-Fermi approximation $T_{TF}[\rho]$ to the elusive exact kinetic energy density functional $T[\rho]$. For each point in space one now assumes equation (19) to hold for the volume element dv around r and obtain the total kinetic energy by integrating the expression over all space:

$$T_{TF}[\rho] = \frac{3\hbar^2}{10m}(\frac{3}{8\pi})^{\frac{2}{3}} \int [\rho(\vec{r})]^{\frac{5}{3}} dv \tag{21}$$

$$= C_F \int [\rho(\vec{r})]^{\frac{5}{3}} d^3 r \tag{22}$$

If we asume for the time being that exchange-correlation contribution to the ground state energy can be neglected, we have the Thomas Fermi expression for the ground state energy

$$E_o^{TF}[\rho] = C_F \int [\rho(\vec{r})]^{\frac{5}{3}} d^3 \vec{r} + \int V(\vec{r})\rho(\vec{r}) d^3 \vec{r} + \frac{e^2}{2} \int \frac{\rho(\vec{r})\rho(\vec{r}^{\,'})}{|\vec{r} - \vec{r}^{\,'}|} d^3 \vec{r} \tag{23}$$

The second term in equation (23) represents the energy of interaction between the electrons and the nucleii while the third term represents the Coulombic energy arising out of $e-e$ repulsions. Equation (23) is what has been known as the simplest local density functional approximation to the ground state energy functional $E[\rho]$.

The simplest LDA description given above neglects exchange as well correlation energy contributions to $E_o[\rho]$. The exchange energy contribution can be estimated by using the exact expression for exchange energy of a uniform electron gas obtained by Dirac at the local level which suggests (R.G. Parr, W. Yang, DFT for atoms and molecules, Oxford University Press, 1989)

$$E_{Exch}^{Dirac}[\rho] = -C_x \int [\rho(\vec{r})]^{\frac{4}{3}} d^{r} \tag{24}$$

where $C_x = (\frac{3}{4})(\frac{3}{\pi})^{\frac{1}{3}}$.

The Dirac exchange energy corrected Thomas Fermi energy function results when $E_{Exch}^{Dirac}[\rho]$ is added to $E_o^{TF}[\rho]$. The corresponding energy functional has been known as Thomas-Fermi-Dirac energy functional $E_o^{TFD}[\rho]$ for the ground state and reads

$$\begin{aligned} E_o^{TFD}[\rho] &= C_F \int [\rho(\vec{r})]^{\frac{5}{3}} d^3r + \int V(\vec{r})\rho(\vec{r}) d^3r \\ &+ \frac{e^2}{2} \int \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} d^3r' d^3r - C_x \int [\rho(\vec{r})]^{\frac{4}{3}} d^3r \end{aligned} \tag{25}$$

It turns out that in the limit of very high or low densities the "uniform electron gas" model predicts that the Coulomb correlation energy of the gas per electron can be written as a function of the electron density $\rho(\vec{r})$ alone. At intermediate densities however, no such exact expression has so far been worked out. One has to be satisfied therefore with formula that interpolates between the known exact ones in the limits of high and low densities and works as best as possible at intermediate densities. Let us represent such an interpolation formula by $f_c(\rho)$ so that the Coulomb correlation energy of the $N-$electron system can be estimated as

$$E_c[\rho] = \int \rho(\vec{r}) f_c(\rho) d\vec{r} \tag{26}$$

A complete formula for the ground state energy functional assembled from bits and pieces now reads (under uniform electron gas approximation)

$$E_o[\rho] = C_F \int [\rho(\vec{r})]^{\frac{5}{3}} d^3 \vec{r} + \int V(\vec{r})\rho(\vec{r}) d^3 \vec{r} + \frac{e^2}{2} \int \frac{\rho(\vec{r})\rho(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|} d^3\vec{r}\,' d^3 \vec{r}$$

$$-C_x \int [\rho(\vec{r})]^{\frac{4}{3}} d^3\vec{r} + \int \rho(\vec{r}) f_c(\vec{r}) d^3 r \tag{27}$$

There are a number of deficiencies that the equation (27) suffers from. The root of these deficiencies lie in the fact that electron densities in atoms and molecule are not spatially uniform (there is shell structure), but they vary quite strongly, particularly near the nuclei. There are corrections arising from the spatial inhomogeneity of $\rho(\vec{r})$ manifested in the non-zero gradient of $\rho\,[i.e. \nabla\rho(\vec{r})]$. Gradient corrected expression for the kinetic energy functional was first obtained by Weizascker which turns out to be

$$T^W[\rho] = C_F \int \rho[\vec{r}]^{\frac{5}{3}} d^3\vec{r} + \frac{1}{7}\frac{\hbar}{m} \int \frac{|\nabla\rho(\vec{r})|^2}{\rho(\vec{r})} d^3\vec{r} \tag{28}$$

A gradient corrected expression for the exchange energy was obtained by Becke and the corresponding formula has become known as Becke 88 exchange energy functional $E^{Becke88}_{Exch}[\rho]$ where

$$E^{Becke88}_{Exch}[\rho] = -C_x \int [\rho(\vec{r})]^{\frac{4}{3}} d^3 r - \gamma \int x^2 \rho^{\frac{4}{3}} \left\{1 + 6\gamma x sinh^{-1} x\right\}^{-1} d^3 r \tag{29}$$

γ in equation 29 has been obtained by calibration against known exchange energies of inert gas atoms (Becke fixes it as $\gamma = 0.0042$) while $x = \rho^{-\frac{4}{3}} |\nabla\rho(\vec{r})|$. Various other formulae have been derived/ suggested from time to time. A basic breakthrough in DFT has been the Kohn-Shan approach in which the KE part is evaluated in an ingenious manner. WE examine the approach in the next chapter.