Introduction To Density Functional Theory (DFT)

single particle

$$E[\Phi] = \langle \Phi | \hat{K} + \hat{V} + \hat{U}_{ee} | \Phi \rangle$$

$\hat{V} = \hat{V}_{NN} + \hat{V}_{Ne}$

$$\hat{U}_{ee} = \langle \Phi | \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i}^{N} \frac{1}{|\hat{r}_i - \hat{r}_j|} | \Phi \rangle$$

$$= \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i}^{N} \int dr_1 dr_2 \ldots dr_i \ldots dr_j \ldots dr_N \; \Phi^*(r_1, r_2, \ldots r_N) \frac{1}{|r_i - r_j|} \Phi(r_1, r_2, \ldots r_N)$$

($r_i \ldots r_j$ above the integrand)

↑ spin "eliminates" the 1/2

$$= \sum_{i=1}^{N} \sum_{j \neq i}^{N} \int dr_1 dr_2 \ldots dr_i \ldots dr_j \ldots dr_N \frac{|\Phi(r_1, r_2, \ldots r_i \ldots r_j \ldots r_N)|^2}{|r_i - r_j|}$$

Since the density is symmetric in the particle labels, the value of the integral cannot depend on the specific choice of i, j. The sum is then a sum of $\frac{N(N-1)}{2}$ identical terms:

$$\Rightarrow U_{ee} = \frac{1}{2} N(N-1) \int dr\, dr' \int dr_3 \ldots dr_N \frac{|\Phi(r, r', r_3, r_4 \ldots r_N)|^2}{|r - r'|}$$

$$\equiv \int dr\, dr' \frac{\rho_2(r, r')}{|r - r'|}$$

$\rho_2(r, r')$ is known as the two-body density matrix (in the coordinate representation)

$$\rho_2(r, r') = \frac{N(N-1)}{2} \int dr_3 \ldots dr_N \; |\Phi(r, r', r_3, \ldots r_N|^2$$

We can also define the one body density matrix in the same representation as

$$\rho_1(r, r') = N \int dr_2 \ldots dr_N \; \Phi^*(r, r_2, \ldots, r_N) \Phi(r', r_2, \ldots, r_N)$$

The diagonal elements of $\rho_1(r, r')$, $\rho(r) = \rho_1(r, r')$,

correspond to the electronic density. We introduce an auxiliary function, known as the two-body direct correlation function as

$$g_2(r,r') = 2\,\frac{\rho_2(r,r')}{\rho(r)\,\rho(r')}$$

With this notation

$$U_e = \frac{1}{2}\int dr\,dr'\,\frac{\rho(r)\,\rho(r')}{|r-r'|} + \frac{1}{2}\int dr\,dr'\,\frac{\rho(r)\,\rho(r')}{|r-r'|}\,[g_2(r,r')-1]$$

↑ classical el. energy (Coulomb term) $J[\rho]$

↑ correlations (exchange-correlation term). $E_{xc}[\rho]$

Let us recast the energy functional in light of the notation introduced. We have

$$E[\Phi] = \langle\Phi|\hat{K} + \hat{V}_{ne} + \hat{U}_{ee}|\Phi\rangle$$

$$= \langle\Phi|\hat{K}|\Phi\rangle + \langle\Phi|\hat{V}_{ne}|\Phi\rangle + \langle\Phi|\hat{U}_{ee}|\Phi\rangle$$

We have seen that the last term is in fact a functional of the one-body density $\rho(r) = \rho_1(r,r)$:

$$\langle\Phi|\hat{U}_{ee}|\Phi\rangle = J[\rho] + E_{xc}[\rho]$$

We also have

$$\langle\Phi|\hat{V}_{ne}|\Phi\rangle = \sum_i \sum_\alpha \int dr_1 \ldots dr_N\,\frac{|\Phi(r_1, r_2, \ldots r_i, \ldots r_N)|^2}{|r_i - R_\alpha|}$$

$$= \sum_\alpha \int dr\,\frac{\rho(r)}{|r-R_\alpha|}$$

Although less trivially, it can also be shown that the kinetic energy term is a functional of the (one-body) density. Its exact form is, however, unknown and different approximations are commonly employed. Typical examples are the

- Thomas-Fermi kinetic functional (homogeneous electron gas)

$$K_{TF}[\rho] = c \int dr\, \rho^{5/3}(r), \qquad c = 3.8738$$

- Thomas-Fermi-von Weizsäcker kinetic functional

$$K_{TFW}[\rho] = K_{TF}[\rho] + \lambda T_W[\rho]$$

("optimal value" $\lambda = 1/9$)

$$T_W[\rho] = \frac{\hbar^2}{8m} \int dr \frac{|\nabla \rho(r)|^2}{\rho(r)}$$

$\Rightarrow$ **Energy is a functional of the one-body density**

Theorem 1 (Hoenberg-Kohn 1964)

Every observable of a stationary quantum mechanical system can be calculated, in principle exactly, from the ground state density. I.e. there is a mapping of the form

$$v \xrightarrow{C} \Psi \xrightarrow{D} N$$

where v is the set of one-particle external potentials, Ψ the set of ground state wave functions, and N the set of one-particle densities. This mapping is

one-to-one and can therefore be inverted, so from the density one can reconstruct univocally the external potential.

$$\rho \xrightarrow{(\Phi)^{-1}} v$$

Since, for systems of nuclei and electrons, the kinetic energy and the interparticle interactions are specified, the density in fact determines the ground state energy univocally.

Observation

The ground state density can be computed, in principle exactly, using the variational method

$$E_0 = \min_{\rho \in N} E[\rho]$$

If $\rho_0(r)$ is the ground state density $E_0 = E[\rho_0]$.

Notation (for Hohenberg & Kohn)

(A) $E[\rho] = F_{HK}[\rho] + V_{ext}[\rho]$

$F_{HK} \hookrightarrow K[\rho] + U_{ee}[\rho]$

$V_{ext}[\rho] \hookrightarrow \int dr\, \rho(r) v(r)$ ↕ external potential

F_{HK} is a universal (i.e. system independent) potential

Formalization of the variational procedure

Assume a trial density $\tilde{\rho}(r)$ such that

$$\tilde{\rho}(r) \geq 0 \quad \forall r$$

and for which

$$\int dr\ \tilde{\rho}(r) = N$$

↑ number of electrons in the system

Then

$$E_0 \leq E[\tilde{\rho}]$$

⇒ If $\tilde{\rho}$ represents the correct number of electrons N, the total energy calculated via $\tilde{\rho}$ is an upper bound (or equal) to the ground state energy.

The second condition, $\int dr\ \tilde{\rho}(r) = N$, is known as N-representability. Its interpretation and impact are delicate (e.g. Trivially achievable by rescaling). However, the condition is automatically insured if $\tilde{\rho}(r)$ can be mapped to some wavefunction.

(*) Mathematical formulation of the minimum search

$$\delta E[\rho] = 0$$

But we must also impose $\int dr\ \rho(r) = N$

$\Leftrightarrow$ $\int dr\ \rho(r) - N = 0$ this imposes a constraint on the admissible $\rho(r)$. Math procedure: method of Lagrange multipliers. The simultaneous achievement of minimum + constraint is obtained by solving

$$\delta\left\{E[\rho] - \mu \int dr\ \rho(r) - N\right\} = 0$$

↑ undetermined parameter known as Lagrange multiplier (constant)

Thus

$$\delta E[\rho] - \mu \int dr \delta\rho(r) = 0 \qquad (*)$$

Now let's vary ρ to $\rho + \delta\rho$. To first order in the variation

$$\delta E[\rho] = E[\rho+\delta\rho] - E[\rho] = E[\rho] + \int dr \frac{\delta E[\rho]}{\delta\rho(r)} \delta\rho(r) - E[\rho]$$

$$= \int dr \frac{\delta E[\rho(r)]}{\delta \rho(r)} \delta\rho(r)$$

$$\Rightarrow (*) \Rightarrow \int dr \left[\frac{\delta E[\rho(r)]}{\delta\rho(r)} - \mu \right] \delta\rho(r) = 0$$

This is satisfied, for every variation $\delta\rho$, if

$$\frac{\delta E[\rho(r)]}{\delta \rho(r)} = \mu$$

which determines the parameter μ.

Using the definition in (A), the condition above becomes

$$\mu = V_{ext}(r) + \frac{\delta F_{HK}[\rho(r)]}{\delta \rho(r)} \qquad (**)$$

Recapping

$$E[\rho] = K[\rho] + \frac{1}{2} \int \frac{\rho(r)\,\rho(r')}{|r-r'|} dr\,dr' + E_{ex}[\rho]$$

$$+ \int dr\, V_{ext}(r)\, \rho(r)$$

Minimize wrt ρ, find μ from (**)

⇒ Problem $K[\rho]$ is not known and current approximations are not satisfactory. In fact $K[\rho]$ is easier to compute starting from wave functions

Kohn-Sham method (1965)

Consider an auxiliary (fictitious) non-interacting system.

The universal part of the energy functional becomes

$$F_{HK}[\rho] = K[\rho] + U_{ee}[\rho]$$

$U_{ee}[\rho] \to 0$

$\uparrow\ J[\rho] + E_{xc}[\rho]$

Coulomb interactions

$$\to F_0[\rho] = K_0[\rho]$$

Now let's impose that ρ is the the density of the (interacting) system that we are interested in. It can be shown that ρ can (almost always) be found via minimization of an energy functional of the form

$$E_{KS}[\rho] = K_0[\rho] + \int dr\, V_{eff}[\rho; r]\,\rho(r)$$

The key point here is that V_{eff} (single particle potential) must exist.

The minimum condition now is

$$\frac{\delta E_{KS}[\rho(r)]}{\delta \rho(r)} = 0 \iff \frac{\delta K_0[\rho]}{\delta \rho} = -V_{eff}[\rho; r)] \quad (11)$$

which formally defines V_{eff}

Now let's go back to

$$F_{HK}[\rho] = K[\rho] + J[\rho] + E_{xc}[\rho]$$

$$= K_0[\rho] + J[\rho] + \underbrace{E_{xc}[\rho] + (K[\rho] - K_0[\rho]}_{\text{exchange-correlation } E_{xc}[\rho]}$$

The minimum is obtained for

$$\frac{\delta F_{KH}}{\delta \rho} + v_{ex}(r) = 0$$

$$\Leftrightarrow \frac{\delta K_0}{\delta \rho} = -\frac{\delta J}{\delta \rho} - \frac{\delta E_{xc}}{\delta \rho} - v_{ex}(r) = 0$$

And, from (a)

$$V_{eff}[\rho; r] = \frac{\delta J}{\delta \rho} + \frac{\delta E_{xc}}{\delta \rho} + v_{ex}(r)$$

$\hookrightarrow V_H[\rho; r]$ $\quad$ $\hookrightarrow V_{xc}[\rho; r]$ (not known)

which gives us a more explicit form for V_{eff}.

Now: we said that minimizing $E_{KS}[\rho] = K_0[\rho] + \int dr\, V_{eff}[\rho; r]\,\rho(r)$ will give us ρ, i.e. the ground state density of the interacting system. This minimization is simpler than the original one because we know that for a non interacting system, the wavefunction (from which the density can be trivially obtained) is a Slater determinant.

Let's call ϕ_i the orbitals in the determinant.

Following the steps of the Hartree-Fock method, the minimum condition is equivalent to the system of (Kohn-Sham) equations (ρ is here)

$$\left[-\frac{1}{2}\nabla_i^2 + V_{eff}(r)\right]\phi_i(r) = \varepsilon_i \phi_i(r) \qquad (*)$$

As in Hartree-Fock, this can be solved self-consistently

- guess a set of $\phi_i(r)$
- compute density via $\rho(r) = \sum_i |\phi_i(r)|^2$
- compute a non interacting kinetic term

$$K_0 = -\frac{1}{2}\sum_i \langle \phi_i | \nabla_i^2 | \phi_i \rangle$$

- compute V_{eff}
- check (*)
- iterate if necessary

Note that

- V_{eff} is not just given by the nuclear potential
- The true wavefunction of the system is not a Slater determinant
- We do not know E_{xc} $\Rightarrow$ approximations
- The non-interacting reference system may not exist (carbon dimer)