Density Functional Theory - II

3 Kohn-Sham Equation

Let us consider the energy functional of equation (27) or more realistic ones obtained after incorporating gradient correction (viz equation 28 or 29). There still remains the question: how does one get $\rho(\vec{r})$? One possibility is to guess a form for $\rho(\vec{r})$ containing several free parameters which are varied to obtain the lowest possible energy. A more general recipe for determining $\rho(\vec{r})$ at a particular level of approximation is to solve Kohn-Sham equation for the Kohn-Sham orbitals $\{\phi_k(\vec{r})\}$ and generating the density function $\rho(\vec{r})$ from them. In the conventional KS technique one expresses the density $\rho(r)$ and the total energy $E_{DFT}[\rho]$ in terms of the spin-orbitals of an N electron Hartree-Fock system which is equivalent to the many electron system under study in the sense that the Hartree Fock system has the same ground state density. Whether such an equivalent reference system exists is a debatable issue. However, the issue has been bypassed in the constrained search formalism of Mel Levy [Phys. Rev. A 26, 1200 (1982)]. The constrained-search constructs the KS-theory (may be exact /approximate) by simply introducing a set of orbitals and allowing them to vary. Under the assumption of static nuclei, the KS minimization procedure sets

$$\frac{\delta E_{DFT}}{\delta \rho} = 0 \tag{30}$$

subject to the constraint that

$$\rho(r) = \sum_i n_i \,|\, \phi_i(r) \,|^2 \tag{31}$$

n_i in equation (31) represents the occupation number of the KS-orbital ϕ_i. The variational procedure leads to a pseudo eigenvalue equation for the KS-orbitals (see note 8):

$$\left\{ \frac{-\hbar^2}{2m}\nabla^2 + V(\vec{r}) + \frac{e^2}{2}\int \frac{\rho(\vec{r}')d^3r'}{|\vec{r}-\vec{r}'|} + V_{xc}(\vec{r}) \right\} \phi_k(\vec{r}) = \varepsilon_k \phi_k(\vec{r}) \tag{32}$$

In equation (32), $V_{xc}(\vec{r})$ represents the so-called local exchange correlation potential which can be obtained by functionally differentiating the exchange correlation functional $E_{xc}[\rho]$, supposed to be known, with respect to $\rho(\vec{r})$ i.e.

$$V_{xc}(\vec{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\vec{r})} \tag{33}$$

We may note at this point that the exchange correlation energy $E_{xc}[\rho]$ in the KS theory absorbs in it the exchange-energy, Coulombic correlation energy, kinetic correlation energy as well as self-interaction energy; that way, it goes beyond the HF description.

Once equation (32) is solved for ϕ_k s, KS theory asserts that $\rho(\vec{r})$ can be constructed by weighted superposition of the KS orbitals $\{\phi_k(\vec{r})\phi_k^*(\vec{r})\}$ over the set of occupied KS orbitals, The occupancy level of each orbital in the given state represented by a weight factor n_k. That is,

$$\rho(\vec{r}) = \sum_k n(k)\phi_k(\vec{r})\phi_k^*(\vec{r})$$
$$= \sum_k n(k) \mid \phi_k(\vec{r}) \mid^2 \tag{34}$$

KS theory also simplifies the calculation of kinetic energy by directly using the KS orbitals $\{\phi_k(\vec{r})\}$ and the weight factors $\{n_k\}$ as follows

$$\langle T \rangle = \sum_k n(k) \left\langle \phi_k(\vec{r}) \left| \frac{-\hbar^2}{2m} \nabla^2 \right| \phi_k(\vec{r}) \right\rangle \tag{35}$$

With the KS theorem in place, the DFT becomes computationally well-defined and tractable.

The KS equation can be used with any suitable choice of exchange correlation energy functional and leads to the following self-consistent scheme for determining the ground state density and other properties of the atoms and molecules. One usually proceeds in the following steps.

1. A linearly independent atomic orbital basis $\{\chi_p^a\}$ set is chosen for expanding the KS orbitals $\{\phi_k\}$ as linear combinations of $\{\chi_p^a\}$s and a set of initial expansion coefficients as well as KS orbital occupation numbers are guessed (n_i) to start with.

2. The trial density is computed as

$$\rho^{(i)}(\vec{r}) = \sum_j n_j \mid \phi_j^{KS}(\vec{r}) \mid^2 \tag{36}$$

3. The density $\rho^{(i)}(\vec{r})$ is used to compute the Hamiltonian in the KS equation which is solved for a new set of Kohn-Shan orbitals $\left\{\phi_j^{i+1}(\vec{r})\right\}$ and the corresponding eigenvalues $\varepsilon_j^{(i+1)}(\vec{r})$.

4. $\left\{\phi_j^{i+1}(\vec{r})\right\}$ are used to determine the new density function

$$\rho^{(i+1)}(\vec{r}) = \sum_j n_j \mid \phi_j^{i+1}(\vec{r}) \mid^2 \tag{37}$$

5. The process [2-4] is continued till a self consistent density function emerges i.e. till the $\max_r \mid \rho^{(i+1)}(\vec{r}) - \rho^{(i)}(\vec{r}) \mid < \varepsilon$, ε being a predetermined small number.

6. Once the convergence is achieved, $E[\rho]$ is calculated from the energy expression $E[\rho] = \sum_j n_j \left\langle \phi_j(\vec{r}) \mid T \mid \phi_j(\vec{r}) \right\rangle + \int V(\vec{r})\rho(\vec{r})d^3r + \frac{e^2}{2}\int \frac{\rho(r')\rho(\vec{r})}{\mid \vec{r} - \vec{r}' \mid} drdr' + E_{xc}[\rho]$. Several points about the KS-theory are worth noting at this point. We just mention them without further elaborating these aspects here. The detailed may be found in references [?] .

• The exchange correlation potential is strictly local and this local nature is independent of the local density approximation introduced. So

$$\frac{\delta E_{xc}}{\delta \rho_i} = V_{xc}(r_i) \tag{38}$$

where local density approximation is used.

• The KS-orbitals do not, in general correspond explicitly to a wave function or density matrix for the system of interest.

• KS-eigenvalues, in general, are not interpretable as ionization potentials, as done in Koopermans' theorem applied to Hartree-Fock eigenvalues.

Note 8.

Let us consider the differential equation for the Hartree orbitals (h=1, e=1,m=1) of an n-electron atom of nuclear charge z which read (i=1,2……n)

$$\left(-\frac{1}{2}\nabla^2 + V_H(\vec{r})\right).\phi_i(\vec{r}) = \varepsilon_i(\vec{r})\phi_i(\vec{r}) \quad \ldots\ldots(39)$$

It has the form of Schrodinger equation for n-non-interacting electrons moving in an effective potential $V_H(\vec{r})$ (the Hartree potential)

$$V_H(\vec{r}) = -\frac{Z}{r} + \int \frac{\rho(\vec{r})}{|\vec{r}-\vec{r}'|} d\vec{r}' \quad \ldots\ldots(40)$$

with $\rho(\vec{r}) = \sum_{i=1}^{n} n_i \left|\phi_i(\vec{r})\right|^2$ *and* $\int \rho(\vec{r})\, d\vec{r} = n$ (n_is are fixed orbital occupancy indices)

we can define an energy functional $E_{v_H}[\rho]$ for the effective potential $V_H(\vec{r})$ as follows.

$$E_{v_H}[\rho] = \int d\vec{r}\, V_H(\vec{r})\rho(\vec{r})\, d\vec{r} + T[\rho(\vec{r})] \quad \ldots\ldots(41)$$

$T[\rho(\vec{r})]$ is the Kinetic energy functional of the non-interacting electron. The HK variational principle assists

$$E_{v_H}[\rho] \geq E_0 \quad \ldots\ldots(42)$$

and suggests a means of finding the ground state density by making $E_{v_H}[\rho]$ stationary with respect to variations in $\rho(\vec{r})$ under the condition that $\int \rho(\vec{r})\, d\vec{r} = n$ which leads to the Euler-Lagrange equation (ε= Lagrange multiplier) for the constraint on ρ)

$$\delta E_{v_H}[\rho(\vec{r})] = \int \delta\rho(\vec{r}) \left(V_H(\vec{r}) + \frac{\delta T[\mathrm{P}]}{\delta\rho} - \varepsilon \right) d\vec{r} = 0 \quad \ldots\ldots(43)$$

If we use $T[\rho] = \sum_{i=1}^{n} \frac{1}{2} \left\langle \phi_i \left| \nabla^2 \right| \phi_i \right\rangle$ and express $\delta\rho(\vec{r})$ in terms of variations $\delta\phi_i(\vec{r})$ in $\phi_i(\vec{r})$, the stationary condition on $E_{v_H}[\rho]$ leads to equations determining the Hartree orbitals $\phi_i(\vec{r})$ (eq. 39).

For the n-interacting electron problem, the KS theory attempts to mach the non-intetacting description by defining the functional

$$E[\rho(\vec{r})] = T[\rho(\vec{r})] + \frac{1}{2}\int \frac{d\vec{r}\, d\vec{r}'\, \rho(\vec{r})\rho(\vec{r}')}{|r-r'|} + E_{xc}[\rho(\vec{r})]$$

$E_{xc}[\rho(\vec{r})]$ represents the exchange correlation functional (taking care of exchange, coulomb

correlation, self-interaction energy, kinetic correlation energies)

If the external potential is $V(\vec{r})$, the HK variational principle for the n-interacting electrons in the external potential $V(\vec{r})$ is

$$E_{v(\vec{r})}[\rho]=\int d\vec{r}\,V(\vec{r})\rho(\vec{r})+T[\rho(\vec{r})]+\frac{1}{2}\int\frac{d\vec{r}\,d\vec{r}\,'\rho(\vec{r})\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}+E_{xc}[\rho(\vec{r})]\geq E_0\text{'}$$

By making $E_{v(\vec{r})}$ stationary w.r.t. arbitrary variation in $\rho(\vec{r})$ subject to the condition $\int\rho(\vec{r})d\vec{r}=n$, we arrive at the Euler-Lagrange equation

$$\int\delta\rho(\vec{r})\left(V(\vec{r})+\frac{\delta T[\vec{\rho}]}{\delta\rho}+\int\frac{\delta\vec{r}\,\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}+\frac{\delta E_{xc}[\rho(\vec{r})]}{\delta\rho(\vec{r})}-\varepsilon\right)d\vec{r}=0$$

Let us define the exchange correlation potential $V_{xc}(\vec{r})=\frac{\delta E_{xc}[\rho(\vec{r})]}{\delta\rho(\vec{r})}$ and the kinetic energy functional $T[\rho]=\sum_{i=1}^{n}-\frac{1}{2}\langle\phi_i|\nabla^2|\phi_i\rangle$. Then expressing $\delta\rho(\vec{r})$ in terms of variations $\delta\phi_i(\vec{r})$ in the orbitals, the variational procedure leads to the KS equation (eqs.. 32 of this chapter).