IX. Generalized Kohn-Sham approaches

A. The generalized Kohn-Sham framework

The Kohn-Sham approach is based on pure density functionals for the exchange correlation energy. This approach is based on the Hohenberg-Kohn universal density functional $F_{HK}[n]$ is written as:

$$F_{HK}[n] = T[n] + U[n]$$  \hspace{1cm} (9.1.1) 

We noted one problem with $F_{HK}$ is that it is not defined for all densities. This problem can be cured by the Levy-Lieb procedure, where the $F_{HK}$ is replaced by a functional based on a constrained minimum principle:

$$F_{LL}[n] = \min_{\Psi \rightarrow n} (\Psi|\hat{T} + \hat{U}|\Psi)$$  \hspace{1cm} (9.1.2) 

Similarly, for the non-interacting system, one finds:

$$T_S[n] = \min_{\Phi \rightarrow n} (\Phi|\hat{T}|\Phi) = \min_{\Phi \rightarrow n} S[\Phi]$$  \hspace{1cm} (9.1.3) 

Where here the search is over all determinants. Here we defined here a new determinantal functional $S[\Phi]$ with the intent of generalizing the KS approach, as we do now. Using the minimizing determinant $\Phi_S$, the Kohn-Sham correlation energy:

$$E_c[n] = F_{LL} - T_S - U_S$$  \hspace{1cm} (9.1.4) 

Is written using $T_S = (\Phi_S|\hat{T}|\Phi_S)$ and $U_S = (\Phi_S|\hat{U}|\Phi_S)$.

Since a Slater wave function is given in terms of orthonormal one-electron orbitals $\phi_n(x)$, it is best to view $S$ as a functional of the orbitals and we write $S[(\phi)]$. We can now generalize and demand that $S[(\phi)]$ not be just the kinetic energy but a more general functional of the Slater wave function. We denote the functional derivative of $S$ as follows:
\[
\frac{\delta S[\Phi]}{\delta \phi_n(r)} = \hat{O}_S \phi_n(r)
\]  
(9.1.5)

Where \(\hat{O}_S\) is some convenient operator.

We now define the energy functional for a given potential \(v_S(r)\) and determinant \(\Phi\):

\[
E_S[v_S, \Phi] = S[\Phi] + \int v_S(r)n[\Phi](r)d^3r
\]  
(9.1.6)

Where:

\[
n[\Phi](r) = \langle \Phi|\hat{n}(r)|\Phi \rangle
\]  
(9.1.7)

We then minimize with respect to the orbitals of \(\Phi\), keeping them normalized. This constrained minimization results in the orbital equations:

\[
\left(\hat{\delta}_S + v_S(r)\right)\phi_n = \epsilon_n \phi_n.
\]  
(9.1.8)

Furthermore, let us define the density functional \(F_S\) resulting from minimizing \(S\) with constrained of a given density:

\[
F_S[n] = \min_{\Phi} S[\Phi].
\]  
(9.1.9)

From this we further define the density functional \(R_S[n]\):

\[
F_{\text{LH}}[n] = F_S[n] + R_S[n]
\]  
(9.1.10)

In actual implementations the functional \(R_S\) must of course be approximated. Now we put all ingredients together. The HK DFT energy is developed as a train of equalities as follows:
In the last step we changed the order of the minimum procedure, assuming this is OK. Note that the final procedure is minimization with respect to orbitals instead of to density. The minimization, under normality of the orbitals \( \Phi \) from which the Slater wave function is built is gives the generalized Kohn-Sham equation:

\[
\left( \hat{\mathcal{H}} + v_R(\mathbf{r}) + v(\mathbf{r}) \right) \phi_n = \epsilon_n \phi_n
\]  

(9.1.12)

Where:

\[
v_R(\mathbf{r}) = \frac{\delta R}{\delta n(\mathbf{r})}
\]  

(9.1.13)

If we write:

\[
v_s(\mathbf{r}) = v_R(\mathbf{r}) + v(\mathbf{r})
\]  

(9.1.14)

we find that the orbitals also obey equations (9.1.8). Thus, the density \( n(\mathbf{r}) \) obtained from the orbitals of the GKS procedure is the minimizing density of the following density functional

\[
E_s[n] = \min_{n(\mathbf{r})} \left\{ F_s[n] + \int n(\mathbf{r}) d^3r \right\}
\]  

(9.1.15)

The strength of the GKS scheme is that it incorporates explicit orbital functionals. This greatly enlarges the scope of approximations for DFT.
B. Kohn–Sham from generalized KS

By choosing: \( O_5[\Phi] = \langle \Phi | \hat{T} + \hat{U} | \Phi \rangle \) one immediately obtained the usual KS theory, with \( R_5[n] = E_C[n] \).

C. The Hybrid functional of Becke

Let us return to the adiabatic connection formula Eq. Error! Reference source not found.: 

\[
E_C[n] = \int_0^1 \langle \Psi_\lambda | \hat{T} | \Psi_\lambda \rangle d\lambda - U_s[n] \quad (9.2.1)
\]

Becke \(^4\), suggested the following trapezoidal approximation for the integral:

\[
\int_0^1 \langle \Psi_\lambda | \hat{T} | \Psi_\lambda \rangle d\lambda \approx \frac{\langle \Psi_0 | \hat{T} | \Psi_0 \rangle + \langle \Psi_1 | \hat{T} | \Psi_1 \rangle}{2} \quad (9.2.2)
\]

Leading to the Becke’s Half & Half approximation:

\[
E_C[n] \approx \frac{1}{2} U_C^1 - \frac{1}{2} U_s = \frac{1}{2} (U_C^1 + E_H) - \frac{1}{2} K \quad (9.2.3)
\]

The function \( (U_C^1 + E_H)[n] \) is next approximated as a local density functional:

\[
(U_C^1 + E_H)[n] \approx \int u_{XC}(n(r)) n(r) d^3 r \quad (9.2.4)
\]

Where \( u_{XC}(n) = \epsilon_{XC}(n) - t(n) + t_s(n) \). the interaction energy per electron in a homogeneous electron gas is \( u_{XC}(n) \). This function can be computed using the Quantum Monte-Carlo results concerning the XC energy.

Becke showed that this half and half theory gives a big improvement over LDA and in some cases also over GGA functionals. This is because he has found a way to approximate Hartree-Fock theory and LDA.

The Becke Half & Half orbital (BH&H) was the first example of a hybrid theory, a theory which is a mixture of a Hartree-Fock functional of orbitals
and a DFT functional of density. Becke eventually wrote down a functional which contains 3 parameters:

\[ E_{B3LYP}[\phi_1, \ldots, \phi_{N_e}] \]

\[ \approx E_{XC}^{\text{LSDA}}[n] + a_0 \left( K - E_X^{\text{LSDA}}[n] \right) + a_x \left( E_X^{\text{B88}} - E_X^{\text{LSDA}}[n] \right) + a_C \left( E_C^{\text{PW91}}[n] - E_C^{\text{LSDA}}[n] \right) \] (9.2.5)

We see that the B3LYP functional starts from a LSDA functional and adds to it 3 corrections. One is a fraction of the explicit orbital exchange correction \( (K - E_X^{\text{LSDA}}[n]) \) then a correction \( (E_X^{\text{B88}} - E_X^{\text{LSDA}}[n]) \) to the LSDA exchange given by a GGA type functional called Becke88 \(^6\) and finally a GGA correction for the correlation energy, given by the PW91 functional \(^8\). The values of the 3 parameters \( a_0 = 0.20 \), \( a_x = 0.72 \) and \( a_C = 0.81 \) were found by optimizing the performance of the functional for 56 atomization energies, 42 ionization potentials (calculated by \( \Delta \text{SCF} \) method) and 8 proton affinities.

\[ D. \]

**E. Long-Range self-repulsion and lack of derivative discontinuity**

**F. Range separated hybrids**

**G. Orbital functionals and optimized effective potentials**

**H. Approximate correlation functionals and the Born-Oppenheimer force on nuclei**

The Kohn-Sham density functional theory method (KS-DFT), when applied for electrons of molecules makes sense only for frozen nuclei, because the external potential in DFT is assumed time-independent. However, the nuclei
in molecules are not in general motionless. How do we KS-DFT a useful approach for molecules? Here we use the Born-Oppenheimer approximation, which allows us to divide the electron-nuclear problem into 2 stages: first computing the electronic energy $E([R])$ for each nuclear configuration $\{R\}$ and then combining it with the nuclear repulsion energy $V_{rep}([R])$ to obtain an effective potential for the motion of the nuclei. The nuclear-electron potential is given by:

$$v_{\text{nuc}}(r, \{R\}) = -\sum_i \frac{Z_i e^2}{|r - R_i|} \quad (9.3.1)$$

In order to compute the electronic energy we first write down the functional:

$$E_{v([R])}[n] = T_s[n] + \int v_{\text{nuc}}(r, \{R\}) n(r) d^3r + E_{\text{HXC}}[n] \quad (9.3.2)$$

We then minimize it under the constraint for the number of electrons

$$\int n(r) d^3r = N.$$  This gives a minimizing density $n_*(r)$ and we have:

$$E([R]) = E_{v([R])}[n_*] = T_s[n_*] + \int v_{\text{nuc}}(r, \{R\}) n_*(r) d^3r + E_{\text{HXC}}[n_*] \quad (9.3.3)$$

Since in exact DFT $E([R])$ is the exact electronic energy, we are assured that:

$$F_I = \int -\nabla_I v_{\text{nuc}}(r, \{R\}) n_*(r) d^3r \quad (9.3.4)$$

Since this relation is true for the electronic Hamiltonian (as can be seen from Hellman-Feynamn theorem).

However, what happens when we use an approximation for $E_{\text{HXC}}$, as done in all applications of KSDFT? Does this relation still hold? We now show that indeed it does.

The density $n_*$ is determined by:
The electronic force on the nuclei is given by:

\[
F_i = -\nabla_i E = -\nabla_i E_v^R \left[ n_s \right]
\]

\[
= \int -\nabla_i v_{\text{nuc}}(r_c, \{R\}) n_s(r) d^3r - \int \left. \frac{\delta E_v^R[n]}{\delta n(r)} \right|_{n_s} \nabla_i n_s(r) d^3r \tag{9.3.6}
\]

The second integral is zero because:

\[
\int \left. \frac{\delta E_v^R[n]}{\delta n(r)} \right|_{n_s} \nabla_i n_s(r) d^3r = \int \mu \nabla_i n_s(r) d^3r = \mu \nabla_i \int n_s(r) d^3r = 0 \tag{9.3.7}
\]

Thus we find that the relation:

\[
F_i = \int -\nabla_i v_{\text{nuc}}(r_c, \{R\}) n_s(r) d^3r \tag{9.3.8}
\]

still holds. Even if the approximate XC functional does not yield the exact density, the formal relation between the force and the density is still valid.