VIII. Approximate correlation energy functionals

While the correlation energy in atoms and molecules is only a small fraction of the total electronic energy, it is found that it is in fact a very large percentage when one computes energy differences, such as energy of atomization (i.e. the difference between the energy of the atomic constituents to the energy of the molecule) or relative energies of different conformations, as those determining the shape of the Born-Oppenheimer potential surface. In essence, the exchange correlation energy is the chemical bonding energy. It is therefore crucial to model this energy accurately. We describe below some of the basic approximations for density functional theory.

A. The local density approximation (LDA)

The mapping of the interacting electron system onto the non-interacting system, encapsulated in Eq. XX, is of formal interest only, unless we devise a way to approximate the correlation potential. One way is to consider the correlation energy per electron $\epsilon_C(n)$ in the homogeneous electron gas of density n. This energy can be computed with relatively high precision using Monte Carlo methods. Under this approximation we can write the correlation energy as $\int \epsilon_C\big(n(\boldsymbol{r})\big)\, n(\boldsymbol{r}) d^3r$. However, this does not yield in practice good enough results and is thus seldom used. A more successful ways was devised by Kohn and Sham. They considered both the exchange and correlation per an electron in the homogeneous gas, $\epsilon_{XC}(n)$. In this case the correlation energy comes out:

$$E_{XC}^{LDA}[n] = \int \epsilon_{XC}\big(n(\boldsymbol{r})\big) n(\boldsymbol{r}) d^3r - E_X[n] \tag{8.1.1}$$

This approximation is called the local density approximation (LDA)[2]. The functional $E_{XC}^{LDA}[n]$. It leads to the following LDA approximation for the energy functional:

$$E_v^{LDA}[n] = T_S[n] + \int v(\boldsymbol{r})n(\boldsymbol{r})d^3r + E_H[n] + \int \epsilon_{XC}\big(n(\boldsymbol{r})\big)n(\boldsymbol{r})d^3r \qquad (8.1.2)$$

The minimization of this functional, by the Kohn-Sham approach leads to the LDA approximation of DFT. This approach is highly successful and is considered in DFT as the basis for most of the developments of other functionals.

Note however that in LDA the correlation energy is extremely awkward looking because of the term $-E_X[n]$. The presence of this term has detrimental effects which harm some of the predictions of DFT.

i. The exchange energy per electron in the HEG

In section XXX we discussed in some detail the Hartree-Fock theory of the homogeneous electron gas. We defined a Jellium as a smeared positive background of Volume V at density $n = \frac{N_e}{V}$ together with N_e electrons. We showed that the Jellium self energy, the Jellium-electron attraction energy and the electron Hartree energy all cancel exactly in the HEG. Thus, the energy per particle is given by:

$$\epsilon(n) = t_S(n) + \epsilon_{XC}(n) = t_S(n) + \epsilon_X(n) + \epsilon_C(n) \qquad (8.1.3)$$

We already calculate exchange energy, using a Hartree-Fock treatment of the HEG and we saw that $\epsilon_X = -C_X n^{1/3}$ (see Eq. **Error! Reference source not found.**) with $C_X = \frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} E_h a_0$. In terms of the Wigner-Sietz radius, which is a dimensionless quantity given by:

$$r_s = \left(\frac{3}{4\pi n}\right)^{1/3} a_0 \tag{8.1.4}$$

is the radius of a Jellium sphere containing the charge of an electron. Thus:

$$\epsilon_X = -\left(\frac{243}{256\pi^2}\right)^{1/3} \frac{E_h}{r_s} = -\frac{0.45817}{r_s} E_h \tag{8.1.5}$$

If we have a way of computing $\epsilon(n)$ and $t(n)$, we can then find $\epsilon_{XC}(n)$ from Eq. (8.1.3). We can then also compute $\epsilon_C(n)$ from Eqs. (8.1.5).

ii. Correlation energy of the HEG: the high density limit

The calculation of ϵ_C can presently be done analytically in two limits. One is the high density limit $r_s \to 0$ where the kinetic energy dominates and the Coulomb interaction can be treated as a perturbation. In this limit the kinetic energy is that of non-interacting particles. Thus in the perturbative approach one can take $\hat{H}_0 = \sum_{n=1}^{N_e} -\frac{\hbar^2}{2m_e}\nabla_n^2$. The unperturbed wave function is the Slater wave functional wave function Ψ_0 composed of the plane wave orbitals $\frac{e^{i\boldsymbol{k}\cdot\boldsymbol{r}}}{\sqrt{V}}$ with $\boldsymbol{k}$ taking the N_e lowest momentum vectors $k < k_F$. The energy of the unperturbed state is $E_0 = \sum_{k<k_F} \frac{\hbar^2 k^2}{2m_e}$. The first order contribution of the the e-e Coulomb repulsions is $\langle\Psi_0|\hat{U}|\Psi_0\rangle$. This quantity is equal to the direct and exchange contribution (see Eq. **Error! Reference source not found.**). The direct part is nullified by the other electrostatic interactions, so the 1st order contribution is essentially the exchange energy of the HEG which we already included ϵ (see Eq. (8.1.3). Thus to continue and determine the interaction energy beyond exchange, i.e. the correlation energy, we must move to at least second order perturbation theory. When one does this, one finds that the usual second order perturbation theory yields infinite terms. These are associated with low wave length excitations where a pair of electrons having

the momentum statse$|\boldsymbol{k}_1\rangle$ and $|\boldsymbol{k}_2\rangle$, are excited by the Coulomb interaction $V_q = 4\pi/q^2$ to states $|\boldsymbol{k}_1 + \boldsymbol{q}\rangle$ and $|\boldsymbol{k}_2 - \boldsymbol{q}\rangle$ (such that $\frac{1}{2}(\boldsymbol{k}_1 + \boldsymbol{q})^2 > \epsilon_F$ and $\frac{1}{2}(\boldsymbol{k}_2 - \boldsymbol{q})^2 > \epsilon_F$). One can show that for small q this process gives a term proportional to $\ln q$ in the expression for the 2nd order perturbation energy. This term is singular at low q. A method of performing perturbation theory which is non-singular and goes beyond second order, was devised in 1957[5]. This theory is essentially exact at the high density limit and leads to the following relation:

$$\epsilon_C = A \ln r_s + C + O(r_s) \tag{8.1.6}$$

Where $r_s = \frac{1}{a_0}\left(\frac{3}{4\pi n}\right)^{-3}$ is the Wigner-Seitz radius, namely $a_0 r_s$ is the radius of a sphere in the Jelium which scoops an amount of charge equal to $1e$, where e is the elecmentary quantum of charge (the electron charge). $A = 0.0311E_h$ and $C = -0.048 \pm 0.001E_h$. Later work refined these constants: $A = 0.031091E_h$ and $C = -0.046644E_h$.

Exercise VIII-1

Using Eq. **Error! Reference source not found.** and the Hellman-Feynman theorem prove that

$$t_C \equiv t - t_S = 3v_{XC}^{HEG} - 4\epsilon_{XC}^{HEG} = 3v_C^{HEG} - 4\epsilon_C^{HEG} \tag{8.1.7}$$

Hints:

(a) Show that $e^2 \frac{\partial \epsilon^{HEG}}{\partial e^2} = u_{ee} - u_H$ where u_{ee} and u_H are, respectively, the total electronic repulsion energy per electron and the Hartree energy per electron.

(b) From the the fact that $\epsilon_X \propto n^{1/3}$ show that the last equality is correct.

iii. Correlation energy of the HEG: the low density limit and the Wigner crystal

The second limit is that of low density, where the electrons form a crystal. We give the development of this limit, originally proposed by Wigner[6] when he devised a theory for the electron density in metallic sodium.

Wigner assumed that at low energy the homogeneous electron gas forms a crystal. Now that may sound strange: how can the density be uniform and at the same time the electrons form a crystal? Thanks to Quantum Mechanics this is actually not a contradiction, as the following example shows.

Exercise: Show that for 2 particle in a 3D box of volume V with periodic boundary conditions, if the Hamiltonian is:

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 + u(\boldsymbol{r_1} - \boldsymbol{r}_2) \tag{8.1.8}$$

Then

1) The eigenstates have a homogeneous 1-particle density $n = \frac{2}{V}$
2) The pair correlation function has structure. ($g(x_1, x_2) = \frac{P(x_1|x_2)}{P_{class}(x_1|x_2)} = \frac{\Gamma(x_1,x_2)}{n(x_1)n(x_2)}$)

In the low density regime the electron kinetic energy (per electron) can be neglected since, as seen in XXX it is proportional to r_s^{-2} while the repulsion energy between the electrons per electron is proportional to r_s^{-1}. At lkow density the Pauli exclusion priniciple is non-operative, since electrons do not overlap. Thus the quantum nature of the electron is gone at this limit and we can think of the electron as a classical particle that localizes. This is because non-localization of particles in quantum mechanics arises only from their need to reduce kinetic energy. The electrons will arrange themselves in the lowest energy state by forming a close packed crystal. Each electron is then as far as possible from each other electron, while still filling 3D space with average density n. Let us calculate the energy of such a crystal. Consider one of the electrons in the crystal. We imagine it together with a cell containing 1 unit of positive charge. This cell shape depends on the crystal symmetry. Following Wigner, we neglect the crystal structure and assume each electron is surrounded by a *sphere* of positive charge completely neutralizing it. Our approximation then neglects the volume of the space between the spheres. The radius of the sphere is r_s and it is filled with smeared positive charge and with one negative charged point-electron at its center. The spheres do not interact since they are neutral and have no electric moments.

The total energy per electron is the energy $\epsilon_{sp}(r_s a_0)$ to assemble the Jellium sphere and the energy $\epsilon_{el}(r_s a_0)$ needed to bring the electron from infinity into the center of the sphere.

Let $\epsilon_{sp}(R)$ be the energy to assemble a sphere of charge density n and radius R. Suppose we now enlarge it by adding a shell of radius dR. The electric potential at distance $r > R$ outside the sphere is Q/r where $Q = \frac{4\pi}{3} enR^3$ is the charge in the sphere. The charge in the shell is $dq = n4\pi R^2 dR$ and bringing it from infinity, where the potential is zero to its place on top of the existing sphere involves the energy $d\epsilon_{sp} = dq\frac{Q}{R} = \frac{(4\pi)^2}{3} R^4 e^2 n^2 dR$. Thus, by integration from 0 to R, we find: $\epsilon_{sp}(R) = \left(\frac{4\pi n}{3}\right)^2 \frac{3}{5} R^5$. And so at $R = r_s a_0$:

$$\epsilon_{sp}(r_s) = \frac{3}{5}\frac{1}{r_s} E_h \qquad (8.1.9)$$

Next, we want to calculate the energy to bring an electron from infinity to the center of the sphere. This will be done in two stages, first bringing the electron from infinity to the rim of the sphere, a distance $a_0 r_s$ from its center and then from the rim to the center. Accordingly write $\epsilon_e = \epsilon_{rim} + \epsilon_{center}$. The first part is easy since we already know the potential, and it is negative since energy is released by this process, so:

$$\epsilon_{rim} = -\frac{1}{r_s}E_h \tag{8.1.10}$$

Inside the sphere, at a distance R from the center there exists an electric field due to the Jellium, which according to Gauss' is $\boldsymbol{E} = \frac{Q(R)\boldsymbol{R}}{R^3} = \frac{4\pi}{3}n\boldsymbol{R}$. This force is a Harmonic force, with force constant $k_H = \frac{4\pi}{3}n = \frac{1}{(a_0 r_s)^3}$. The work to move an electron in this field to the center is: $\epsilon_{center} = \int_{r_s}^{0}\boldsymbol{E}(R)\cdot d\boldsymbol{R} = -\frac{1}{2r_s}$. The energy for the second stage is therefore $\epsilon_{el}(r_s) = -\frac{3}{2}\frac{E_h}{r_s}$ and the total energy per electron in the crystal is:

$$\epsilon(r_s) = -\frac{9}{10}\frac{1}{r_s}E_h \tag{8.1.11}$$

This then is the exchange-correlation energy for low density. We neglected the volume between the spheres. The exchange energy we already know from (8.1.5), is $\epsilon_X(r_s) = -\frac{0.45817}{r_s}E_h$. Thus, Wigner's approximation for the correlation energy in the low density limit is:

$$\epsilon_C(r_s) = \epsilon(r_s) - \epsilon_X(r_s) = -\frac{0.44183}{r_s}E_h \quad (low\ density, r_s \to \infty) \tag{8.1.12}$$

Wigner also considered the correction due to the finite kinetic energy when r_s is finite. Since we saw that the electron inside the spherical Jellium drop is a Harmonic potential, one can reduce the correlation energy by the 3D Harmonic zero-point potential, $\frac{3}{2}\sqrt{k_H} = \frac{3}{2r_s^{3/2}}$. The correlation energy is then:

$$\epsilon_C(r_s) = -\frac{0.44183}{r_s}E_h + \frac{3}{2r_s^{3/2}} \quad (low\ density, r_s \to \infty) \tag{8.1.13}$$

iv. Monte-Carlo determination of the correlation energy for the HEG

Between these high and low limits there is no analytical theory, in general and a numerical computation can be made based on quantum Monte Carlo methods. The results of the calculation are then fitted to an analytical form which respects the limits

v. The polarized HEG; local spin-density approximation (LSDA)

Up to now we have assumed that the electron gas is unpolarized, i.e. the total z component of spin S_z per electron is zero. However, S_z is a good quantum number and it can vary continuously from $-\frac{1}{2}$ to $\frac{1}{2}$. The extreme case is the fully polarized case. In general one may define the density of spin-up electron $n_\uparrow(\boldsymbol{r})$ and that of spin down $n_\downarrow(\boldsymbol{r})$. Then:

$$\begin{aligned} n(\boldsymbol{r}) &= n_\uparrow(\boldsymbol{r}) + n_\downarrow(\boldsymbol{r}) \\ \zeta(\boldsymbol{r}) &= \frac{n_\uparrow(\boldsymbol{r}) - n_\downarrow(\boldsymbol{r})}{n_\uparrow(\boldsymbol{r}) + n_\downarrow(\boldsymbol{r})} \end{aligned} \tag{8.1.14}$$

For a fully polarized gas $\zeta = 1$ and the difference is first of all in the Fermi energy. For the HEG, since every momentum state can populate only one electron, we find by a similar analysis as in the unpolarized case:

$$\begin{aligned} k_{F\uparrow\downarrow} &= k_F(1 \pm \zeta)^{1/3} \\ \epsilon_{F\uparrow\downarrow} &= \frac{\hbar^2 k_{F\uparrow\downarrow}^2}{2m_e} = \epsilon_F(1 \pm \zeta)^{2/3} \\ t_{\uparrow\downarrow} &= \frac{T_{\uparrow\downarrow}}{N_{\uparrow\downarrow}} = \frac{3}{5}\epsilon_{F\uparrow\downarrow} \end{aligned} \tag{8.1.15}$$

The total kinetic energy us the sum of up and down contributions: $t = \frac{n_\uparrow t_\uparrow + n_\downarrow t_\downarrow}{n}$, which is evaluated to be $t = \frac{3}{5}\frac{\epsilon_{F\uparrow} n_\uparrow + \epsilon_{F\downarrow} n_\downarrow}{n}$ using the expressions for $n_{\uparrow\downarrow}$ we obtain

$$t = \frac{3}{5}\epsilon_F \frac{(1+\zeta)^{5/3} + (1-\zeta)^{5/3}}{2} \tag{8.1.16}$$

As for exchange energy, since exchange interaction occurs only between like spins, we XXXXX

vi. Successes and failures of LSDA

vii. Plausible reasons for the success of LSDA

One of the uses of Eq. **Error! Reference source not found.** expression is to explain the success of a simple theory such as LDA[8]. TO see this, let us expand the XC hole in terms of moments around $\boldsymbol{r}$:

$$n_{XC}^{\lambda}(\boldsymbol{r}, \boldsymbol{r}+\boldsymbol{R}) = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} n_{lm}^{\lambda}(\boldsymbol{r}; R) Y_{lm}(\theta,\phi) \tag{8.1.17}$$

where: $\boldsymbol{R} = R\hat{\boldsymbol{u}} \equiv (R\sin\theta\cos\phi, R\sin\theta\sin\phi, R\cos\theta)$ and

$$n_{lm}^{\lambda}(\boldsymbol{r}; R) = \int_0^{\pi}\int_0^{2\pi} n_{XC}^{\lambda}(\boldsymbol{r}, \boldsymbol{r}+R\hat{\boldsymbol{u}})\, Y_{lm}(\theta,\phi)\sin\theta\, d\theta\, d\phi \tag{8.1.18}$$

Then consider the XC energy, it can be written as:

$$\begin{aligned} E_{XC}[n] &= \frac{1}{2}\iint \frac{n(\boldsymbol{r})\bar{n}_{XC}(\boldsymbol{r},\boldsymbol{r}+\boldsymbol{R})}{R} d^3R d^3r \\ &= \frac{1}{2\sqrt{4\pi}}\iint \frac{n(\boldsymbol{r})\bar{n}_{00}(\boldsymbol{r},R)}{R} d^3r R^2 dR \end{aligned} \tag{8.1.19}$$

Were:

$$\bar{n}_{00}(\boldsymbol{r}, R) = \int_0^1 n_{00}^{\lambda}(\boldsymbol{r}, R)\, d\lambda \tag{8.1.20}$$

And:

$$\sqrt{4\pi}\int_0^\infty \bar{n}_{00}(\boldsymbol{r},R)R^2dR=-1 \tag{8.1.21}$$

Thus, only the 00 moment of the λ dependent XC holes enters the expression. Therefore, in a sense the angular shape of the average XC hole gets averaged over and only the radial dependence affects the XC energy. This is used to explain some of the success of LDA.

We see that the XC anisotropy of the XC hole around $\mathbf{r}$ is averaged over. Only this average enters the XC energy formula. In LDA we use the homogeneous electron gas to compute the HEG. Of course this leads to an isotropic XC hole. Yet, since only the spherical average of the hole enters into the XC energy, this drastic approximation gives a reasonably good XC energy.

Exercise: Calculate the spherically averaged X-hole for a 1-electron system (H atom for example)

Solution: The orbital is $\psi(\boldsymbol{r})$, the density is $n(\boldsymbol{r})=\psi(\boldsymbol{r})^2$ and the DM is $P(\boldsymbol{r},\boldsymbol{r}')=\psi(\boldsymbol{r})\psi(\boldsymbol{r}')$ thus:

$$n_X(\boldsymbol{r};\boldsymbol{r}')=-n(\boldsymbol{r}') \tag{8.1.22}$$

The hole is independent of the reference point $\boldsymbol{r}$.

One of the important results shown below is that only the spherically averaged hole enters the XC energy. Thus we only need the spherically averaged hole:

$$n_X^{SA}(\boldsymbol{r};s)=\frac{1}{4\pi}\int n_X(\boldsymbol{r};\boldsymbol{r}+\boldsymbol{s})d\Omega_s \tag{8.1.23}$$

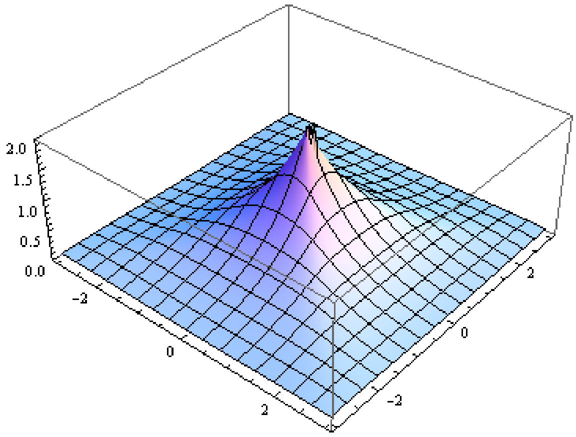
Which becomes:

$$n_X^{SA,1el}(\boldsymbol{r};s)=\frac{1}{4\pi}\int n(\boldsymbol{r}+\boldsymbol{s})d\Omega_s \tag{8.1.24}$$

For the H-atom $n(\boldsymbol{r})=A^2e^{-\alpha r}$, defining $\beta=\alpha\sqrt{r^2+s^2}$ $\gamma=\frac{2rs}{(r^2+s^2)}$ therefore $\beta\sqrt{1\pm\gamma}=\alpha|r\pm s|$ and $\gamma\beta^2=\alpha^2 2rs$:

$$\begin{aligned}
n_X^{SA,1el}(\boldsymbol{r};s) &= \frac{1}{4\pi}A^2\int e^{-\alpha|\boldsymbol{r}+\boldsymbol{s}|}d\Omega_s=\frac{1}{2}A^2\int_0^{\pi}e^{-\alpha\sqrt{r^2+s^2+2rs\cos\theta}}\,d\cos\theta \\
&= \frac{A^2}{2\gamma}\int_{-\gamma}^{\gamma}e^{-\beta\sqrt{1+y}}\,dy \\
&= \frac{A^2}{\alpha^2 2rs}\left[(1+\alpha|r-s|)e^{-\alpha|r-s|}\right. \\
&\quad \left.-(1+\alpha|r+s|)e^{-\alpha|r+s|}\right]
\end{aligned} \tag{8.1.25}$$

The form of this spherically averaged hole function as function of s and r is shown here:



The hole has a cusp at the r-s origin.

B. Semilocal functionals and the generalized gradient approximation