

I. THE ELECTRON GAS

We have defined the exchange and correlation energy before as the difference between the exact total energy of a system and the classical Hartree energy. Except in very simple cases it is impossible to treat exchange and correlation exactly and an approximation is in order. The quality of a DFT calculation is determined by how close the approximate exchange and correlation comes to the exact value. In this section, we shall get a glimpse of the -by now- huge literature on different methods of dealing with exchange and correlation in atomistic systems.

Before going into exchange and correlation in real systems, it's important to understand the behavior of a much simpler system, the interacting electron gas not only because it is the system that can be dealt with analytically the most easily but also due to the fact that approximations to exchange and correlation are built upon this simple system.

Let us first start with the noninteracting electron gas in order to to familiarize ourselves with concepts and establish some terminology.

A. The noninteracting electron gas

A noninteraction electron gas is homogeneous and is completely characterized by its density, $n = N/V$ where N is the total number of electrons and V is the volume of the system. An alternative way of characterizing such a system is through an operational parameter r_s , which is defined as the radius of a sphere containing a single electron

$$\frac{4\pi}{3}r_s^3 = \frac{1}{N/V} = \frac{1}{n} \Rightarrow r_s = \left(\frac{3}{4\pi n}\right)^{1/3} \quad (1)$$

The density or equivalently r_s in a real system is of course strongly position-dependent.

The Hamiltonian of the noninteracting electron gas is composed solely of the kinetic energy term and the total energy is just the sum of the kinetic energy of the first N planewave eigenstates. The *Fermi energy* is defined as the energy of the highest filled planewave state. It is characterized by the *Fermi wavevector* through the simple relation

$$E_F^\sigma = \frac{1}{2}k_F^\sigma \quad (2)$$

where the spin dependence is kept explicitly. The total energy is then just the integral over all the states having wavevectors up to \vec{k}_F . To simplify the measure, we do not calculate the total kinetic energy but the energy per electron for each spin.

$$\frac{T_{tot}^\sigma}{N} = \frac{\frac{1}{2} \int d\vec{k} k^2}{\int d\vec{k}} = \frac{1}{2} \frac{4\pi \int_0^{k_F^\sigma} k^4}{4\pi \int_0^{k_F^\sigma} k^2} = \frac{1}{2} \frac{(k_F^\sigma)^5/5}{(k_F^\sigma)^3/3} = \frac{3}{5} E_F^\sigma \quad (3)$$

where the last equality is taken from Eq. 2. As seen in the equations above, all the relevant properties of the noninteracting electron system may be determined by its density, which is in turn determined by the total number of electrons.

B. Interacting electrons

When the interaction between the electrons is turned on, the Hamiltonian becomes

$$\hat{H} = -\frac{1}{2} \sum_i \nabla^2 + \frac{1}{2} \left[\sum_{i \neq j} \frac{1}{|\vec{r}_i - \vec{r}_j|} - \int d\vec{r} d\vec{r}' \frac{n^2}{|\vec{r} - \vec{r}'|} \right] \quad (4)$$

where the last term has been substituted in place of the potential of the ions simulating the presence of a uniform positive background. It is necessary to include this term in order to cancel the divergence in the electron-electron interaction term. The total energy is then given as

$$E = \langle \hat{H} \rangle = \langle \hat{T} \rangle + \langle \hat{V}_{int} \rangle - \frac{1}{2} \int d\vec{r} d\vec{r}' \frac{n^2}{|\vec{r} - \vec{r}'|} \quad (5)$$

where the difference between the two last terms is precisely the exchange-correlation energy mentioned above.

In the Hartree-Fock method that we have seen before, only the exchange part of the interaction energy is taken into account. Since the problem of the interacting electron gas may be treated analytically at the Hartree-Fock level, we may calculate the exchange energy exactly. We first remind ourselves of the Hartree-Fock equations

$$\epsilon_{\nu}\phi_{\nu}(\vec{r}) = \left[-\frac{1}{2}\nabla^2 + \sum_{\lambda} \int d\vec{r}' \phi_{\lambda}^*(\vec{r}')\phi_{\lambda}(\vec{r}') \frac{1}{|\vec{r}-\vec{r}'|} + V_{\text{ion}} \right] \phi_{\nu}(\vec{r}) - \sum_{\lambda} \delta_{\sigma_{\lambda}\sigma_{\nu}} \int d\vec{r}' \phi_{\lambda}^*(\vec{r}')\phi_{\nu}(\vec{r}')\phi_{\lambda}(\vec{r}) \frac{1}{|\vec{r}-\vec{r}'|} \quad (6)$$

for the electron system where λ and ν are the combined orbital/spin indices. The first term is the usual kinetic energy term, the second is the direct term and the final term is the exchange term. The ionic term, once again, has been substituted with the uniform background charge. Let us first consider the second (direct) term in isolation

$$V_d = \int d\vec{r}' \sum_{\lambda} |\phi_{\lambda}|^2 \frac{1}{|\vec{r}-\vec{r}'|} = \int d\vec{r}' \frac{n}{|\vec{r}-\vec{r}'|} \quad (7)$$

There are two things to notice about the result in Eq. 7 : one is that the density is still uniform even though the electrons are allowed to interact and the second is that the direct term is exactly canceled by the potential term due to the uniform background which replaces the ions,

$$V_{bg} = -\sum_I \frac{Z_I}{|\vec{r}-\vec{R}_I|} \longrightarrow -n \int \frac{d\vec{R}}{|\vec{r}-\vec{R}|}. \quad (8)$$

Then we are just left with the kinetic energy and the exchange terms. Surprisingly, the eigenstates of the system of equations in Eq. 6 are also planewaves. The eigenvalues are of course different with the usual free electron kinetic energy being augmented by the exchange term. We shall prove this by substituting directly planewaves in place of the wavefunctions.

$$\epsilon(\vec{k}) \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}} = \frac{k^2}{2} - \frac{1}{V} \frac{1}{\sqrt{V}} \sum_{\vec{k}'} e^{i\vec{k}'\cdot\vec{r}} \underbrace{\int d\vec{r}' \frac{e^{i(\vec{k}-\vec{k}')\cdot\vec{r}'}}{|\vec{r}-\vec{r}'|}}_I \quad (9)$$

Let's concentrate on the integral labeled I . This integral is simply the Fourier transform of the Coulombic potential, which is a problem we have dealt with before while we were learning about planewave representation of the Kohn-Sham equations. We shall therefore not go into details but just present the result once again after some rearrangements

$$I \equiv e^{i(\vec{k}-\vec{k}')\cdot\vec{r}} \int d\vec{u} \frac{e^{i(\vec{k}-\vec{k}')\cdot\vec{u}}}{u} = 4\pi \frac{e^{i(\vec{k}-\vec{k}')\cdot\vec{r}}}{|\vec{k}-\vec{k}'|^2}. \quad (10)$$

The last term in Eq. 9 then becomes

$$-\frac{4\pi}{V} \sum_j \frac{e^{i\vec{k}'\cdot\vec{r}} e^{i(\vec{k}-\vec{k}')\cdot\vec{r}}}{|\vec{k}-\vec{k}'|^2} = -\frac{4\pi}{V} \sum_{\vec{k}'} \frac{e^{i\vec{k}\cdot\vec{r}}}{|\vec{k}-\vec{k}'|^2}, \quad (11)$$

which completes the proof that planewaves are really eigenstates. Next we move on to find the eigenvalues. The sum over the wavevectors in Eq. 11 can be converted into an integral in the limit of large total volume. The conversion factor to be used is

$$\sum_j = \frac{V}{(2\pi)^3} \int d\vec{k} \quad (12)$$

Then the sum in Eq. 11 becomes

$$\frac{4\pi}{V} \sum_{\vec{k}'} \frac{1}{|\vec{k}-\vec{k}'|^2} \rightarrow \frac{2}{(2\pi)^2} \int d\phi (-d(\cos\theta)) \int_0^{k_F} \frac{k'^2 dk'}{k^2 - 2kk' \cos\theta + k'^2} \quad (13)$$

with the new choice of the variables for ease of notation. Now let's first evaluate the angular integration.

$$\begin{aligned} \frac{1}{\pi} \int_0^{k_F} \left(-\frac{k'}{2k}\right) dk' \ln \left| k^2 - 2kk' + k'^2 \right|_{-1}^1 &= \frac{1}{2\pi} \int_0^{k_F} dk' \frac{k'}{k} \ln \left| \frac{k^2 + 2kk' + k'^2}{k^2 - 2kk' + k'^2} \right| \\ &= \frac{1}{\pi} \int_0^{k_F} dk' \frac{k'}{k} \ln \left| \frac{k+k'}{k-k'} \right| \end{aligned} \quad (14)$$

The logarithmic integral in Eq. 14 can be evaluated using integration by parts. We shall only present the result here. The \vec{k} -dependent energy eigenvalue is then

$$\epsilon(\vec{k}) = \frac{k^2}{2} - \frac{k_F}{\pi} f(x) \quad (15)$$

where $x = \frac{k}{k_F}$ and

$$f(x) = 1 + \frac{1-x^2}{2x} \ln \left| \frac{1+x}{1-x} \right| \quad (16)$$

Note here that the free electron kinetic energy has been augmented by the negative exchange energy. The exchange term then lowers the energy by keeping the electrons of the same spin away from each other thus reducing the Coulomb repulsion.

As we have done before, the total energy of the system in the Hartree-Fock approximation is given by the sum of the single-electron energies corrected by a half of the exchange term. Then

$$\begin{aligned} E_{HF} &= 2 \sum_{\vec{k}} \epsilon(\vec{k}) + \frac{1}{2} \sum_{\vec{k}} \epsilon_{exc}(\vec{k}) \\ &= \frac{2V}{(2\pi)^3} 4\pi \int_0^{k_F} k^2 \left(\frac{k^2}{2} + \frac{1}{2} \epsilon_{exc}(\vec{k}) \right) \end{aligned} \quad (17)$$

After some rather tedious calculus, we arrive at

$$\frac{E_{HF}}{N} = \left(\frac{2.21}{r_s^2} - \frac{0.916}{r_s} \right) \quad (18)$$

Eq. 18 is an important result which states that for the range of r_s that are relevant for metals, the exchange term has a very large effect on the total energy so it's an important component needed to describe the behavior of real systems. It has however been pointed out that the Hartree-Fock description has important shortcomings such as the divergence of the effective mass (due to the logarithmic term) and the severe underestimation of cohesive energies in metals. In the case of Li, a more extreme and absurd situation is observed where the Hartree-Fock approximation yields a positive cohesive energy. More surprisingly, it can be proven that the noninteracting picture does much better than Hartree-Fock theory in predicting cohesive energy if the ions are treated more accurately. It is thus evident that the inclusion of exchange by itself deteriorates the already existing result rather than improve it.

The *correlation* energy is defined as the difference between the total exact energy and the sum of kinetic and exchange energies. Correlations are a result of the collective behavior of electrons to screen and decrease the Coulombic interaction. Unlike the exchange term the correlations become more pronounced for opposite spins since they are more likely to occupy nearby locations.

Unfortunately, the correlation contribution cannot be calculated exactly analytically. There have been several propositions for correlation energy terms over the years :

- Wigner : Wigner solved the problem exactly in the limit of low r_s (the Wigner crystal), assumed the correlation energy would go to a constant in the high r_s limit and proposed a smooth interpolation inbetween.

$$\epsilon_c = -\frac{0.44}{r_s + 7.8} \quad (19)$$

- Gellman and Breuckner : G. and B. followed a diagrammatic approach where they summed an infinite series of Feynman diagrams and calculated exactly the high r_s limit.

$$\epsilon_c(r_s) = 0.311 \ln(r_s) - 0.048 + r_s(A \ln(r_s) + C) + \dots \quad (20)$$

The low r_s is retained and an interpolation is made in between as in Wigner's treatment.

- QMC calculations : Accurate quantum Monte Carlo calculations were made for a series of r_s values covering the entire relevant range, which was followed by several analytic fits made by different researchers. The most widely used correlation potentials are due the Perdew-Zunger (PZ) and Vosko-Wilkes-Nussair (VWN).

For small r_s values, which are relevant for metals, the correlation energy is a small contribution. However in the large r_s limit it becomes very important. So far we have dealt with systems that are unpolarized. For partially polarized systems $n^\uparrow \neq n^\downarrow$. For each spin channel, the total exchange energy per electron may be written in terms of the density in a given spin channel as

$$\epsilon_x^\sigma = \frac{E_x^\sigma}{N^\sigma} = -\frac{3}{4\pi} k_F^\sigma = -\frac{3}{4} \left(\frac{6}{\pi} n^\sigma \right)^{1/3} \quad (21)$$

The spin-polarized exchange and correlation energies are usually expressed in terms of the total density and the difference between densities of the two spin channels defined by

$$\xi = \frac{n^\uparrow - n^\downarrow}{n} \quad (22)$$

The total energy of the spin-polarized system is the sum of the exchange energy of the two spin channels. Exchange energy as a function of this difference and the total density is given by

$$\epsilon_x(n, \xi) = \epsilon_x(n, 0) + [\epsilon_x(n, 1) - \epsilon_x(n, 0)] f_x(\xi) \quad (23)$$

where

$$f_x(\xi) = \frac{1}{2} \frac{(1 + \xi)^{4/3} + (1 - \xi)^{4/3} - 2}{2^{1/3} - 1} \quad (24)$$

The polarization dependence of the correlation energy was taken to be the same as that of the exchange energy by PZ while a slightly more accurate treatment was introduced by VWN.

II. EXCHANGE AND CORRELATION — RULES THAT NEED TO BE OBEYED

A. The exchange-correlation hole

The fact that exchange and correlation both tend to keep electrons apart gave way to the description of the exchange and correlation contribution in terms of a hole surrounding each electron and keeping other electrons from approaching it. The exchange-correlation hole can be interpreted in relation to the joint probability of finding an electron at point \vec{r} given that there exists another electrons at point \vec{r}' . It may be written in terms of a quantity familiar from probabilistic considerations, namely the pair correlation function. The pair-correlation function is determined as the part of the joint probability after the uncorrelated probability has been subtracted away

$$\begin{aligned} n(\vec{r}, \sigma; \vec{r}', \sigma') &= \left\langle \sum_{i \neq j} \delta(\vec{r} - \vec{r}_i) \delta(\sigma - \sigma_i) \delta(\vec{r}' - \vec{r}_j) \delta(\sigma' - \sigma_j) \right\rangle \\ &= N(N-1) \sum_{\sigma_3, \sigma_4, \dots} \int d\vec{r}_3 \dots d\vec{r}_N |\Psi(\vec{r}, \sigma; \vec{r}', \sigma'; \vec{r}_3, \sigma_3; \dots; \vec{r}_N, \sigma_N)|^2 \\ n(\vec{r}, \sigma; \vec{r}', \sigma') &= n(\vec{r}, \sigma) n(\vec{r}', \sigma') + \Delta n(\vec{r}, \sigma; \vec{r}', \sigma') \\ g(\vec{r}, \sigma; \vec{r}', \sigma') &= \frac{n(\vec{r}, \sigma; \vec{r}', \sigma')}{n(\vec{r}, \sigma) n(\vec{r}', \sigma')} = 1 + \frac{\Delta n(\vec{r}, \sigma; \vec{r}', \sigma')}{n(\vec{r}, \sigma) n(\vec{r}', \sigma')} \end{aligned} \quad (25)$$

Defining the density of this hole as $n_{xc}(\vec{r}, \vec{r}')$, the exchange-correlation energy may be written using the adiabatic connection formula set forth by Harris (*Physical Review A*, **29**, 1648). The many-particle Hamiltonian may be written in a way to make a connection between noninteracting electrons and the fully interacting case by means of a coupling constant, λ :

$$\hat{H}_\lambda = \hat{T} + \lambda \hat{V}_{ee} + \lambda \hat{V}_{ext}^\lambda \quad (26)$$

where $\lambda = 0$ corresponds to the noninteracting case and $\lambda = 1$ to full interaction. The exchange and correlation energy may be written in terms of an average over this coupling constant

$$E_{xc}[n] = \int_0^1 d\lambda \frac{d\langle \Psi_\lambda | V_{ee} | \Psi_\lambda \rangle}{d\lambda} - E_H \quad (27)$$

In Eq. 27, it is important to keep the density constant as λ is varied. If this is satisfied, all energy terms except the electron-electron interaction term will remain unchanged. By the Hellman-Feynman theorem that we have seen earlier, the expression in Eq. 27 reduces to

$$E_{xc}[n] = \int_0^1 d\lambda \langle \Psi_\lambda | \frac{dV_{ee}}{d\lambda} | \Psi_\lambda \rangle - E_H. \quad (28)$$

The exchange and correlation energy defined in Eq. 28 may also be written in terms of the *average exchange-correlation hole density*, \bar{n}_{xc} as

$$E_{xc}[n] = \int d\vec{r} d\vec{r}' \frac{n(\vec{r}) \bar{n}_{xc}(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|} \quad (29)$$

B. Restrictions

Needless to mention, neither the exchange correlation hole density or the pair correlation function may be calculated exactly. The quality of a DFT calculation rests upon how well it approximated these quantities. Many successful approximations have so far been designed making DFT a practical and powerful tool to predict several properties of many systems. While devising such approximations there are many restrictions that need to be obeyed. These all stem from the definition of the exact exchange and correlation hole.

1. **Sum rule** : The exchange and correlation hole as defined in Eq. 25 integrates over space exactly to -1 per electron.

$$\begin{aligned} \sum_{\sigma\sigma'} \int d\vec{r} d\vec{r}' n_{xc}(\vec{r}, \vec{r}') &= N(N-1) \int d\vec{r} d\vec{r}' d\vec{r}_3 \cdots d\vec{r}_N |\psi(\vec{r}, \sigma, \vec{r}', \sigma', \vec{r}_3, \sigma_3 \cdots, \vec{r}_N \sigma_N)|^2 \\ &\quad - N^2 \sum_{\sigma, \sigma_2, \cdots, \sigma_N} \int d\vec{r} d\vec{r}_2 \cdots d\vec{r}_N |\psi(\vec{r}, \sigma, \vec{r}_2, \sigma_2 \cdots, \vec{r}_N \sigma_N)|^2 \\ &\quad \times \sum_{\sigma', \sigma_2, \cdots, \sigma_N} \int d\vec{r}' d\vec{r}_2 \cdots d\vec{r}_N |\psi(\vec{r}', \sigma', \vec{r}_2, \sigma_2 \cdots, \vec{r}_N \sigma_N)|^2 \\ &= N^2 - N - N^2 = -N \end{aligned} \quad (30)$$

The exchange-correlation hole may be split into separate exchange and correlation contributions. n_x is the part of the hole that describes the tendency of like spins to avoid each other. The exchange hole must also integrate to -1, a fact which comes from the fact that an electron cannot be at \vec{r}' if it is at \vec{r} . Because of this and Eq. 30 the remaining part of n_{xc} , a.k.a. the correlation hole must integrate to zero.

2. **Scaling properties** : Scaling properties (as many other exact constraints) for the exact functionals were obtained by Levy and Perdew (*Physical Review A*, **32**, 2010). We give them here without proof :

$$E_x[n_\lambda] = \lambda E_x[n] \quad (31)$$

$$E_c[n_\lambda] > \lambda E_c[n] \quad \text{for } \lambda > 1 \quad (32)$$

$$E_c[n_\lambda] < \lambda E_c[n] \quad \text{for } \lambda < 1 \quad (33)$$

3. **The one-electron limit** : In the one-electron limit, the exchange energy still exists due to the fact that the sum in the exchange term in any Slater determinant formalism is designed to contain the term $i = j$. Moreover, this term is exactly equal to the negative Hartree term and they cancel each other exactly. This just leaved the correlation term which should be equal to zero if we want to eliminate any spurious self-interaction terms. Thus if $n^{(1)}$ is the one-electron density,

$$E_c[n^{(1)}] = 0 \quad \text{and} \quad (34)$$

$$E_x[n^{(1)}] = -E_H[n^{(1)}] \quad (35)$$

$$(36)$$

4. **The Lieb-Oxford bound** : The exact exchange-correlation energy satisfies

$$E_{xc}[n] \geq -1.68 \int d\vec{r} n(\vec{r})^{4/3} \quad (37)$$

5. **The derivative discontinuity** : This property is very important in describing the gap in insulators. This so-called *fundamental gap* is defined to be the difference in energy of the same system with number of electrons differing by one :

$$E_g = (E_{N+1} - E_N) - (E_N - E_{N-1}) \quad (38)$$

This together with Koopman's theorem says that the gap is equal to the difference between the HOMO (highest-occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) obtained from a Kohn-Sham calculation. In terms of the eigenvalues then the true gap should be given as

$$E_g = \epsilon_{N+1}(N+1) - \epsilon_N(N) \quad (39)$$

where what's usually available to us is the difference in HOMO and LUMO that we obtain in an N -electron calculation

$$\epsilon_g = \epsilon_{N+1}(N) - \epsilon_N(N). \quad (40)$$

We shall call the difference $\Delta_{xc} = E_g - \epsilon_g = \epsilon_{N+1}(N+1) - \epsilon_{N+1}(N)$ anticipating that the difference should arise from exchange and correlation.

The variational principle applied together with the constraint that the density integrates to the total number of electrons dictates that

$$\frac{\partial T_{s,M}}{\partial n} + V = \mu_M \quad (41)$$

where M is the total number of electrons. The chemical potential μ_M is the energy of the eigenenergy of the M th orbital for all M except N . Taking the difference of the two limits where M tends to N from above and to $N+1$ from below

$$\epsilon_g = \frac{\partial T_s}{\partial \delta n_+} - \frac{\partial T_s}{\partial \delta n_-} \quad (42)$$

Thus there is a discontinuity in the single-particle kinetic energy. A similar discontinuity exists in the exchange-correlation potential with

$$\Delta_{xc} = V_{xc}^+ - V_{xc}^- \quad (43)$$

where

$$V_{xc}^\mp = \frac{\partial E_{xc}}{\partial n_\mp} \quad (44)$$

This conclusion explain why *local density approximation* to exchange and correlation, the gap is severely underestimated. In LDA (besides the question of an accurate ϵ_g), Δ_{xc} is identically zero.

III. APPROXIMATIONS TO EXCHANGE AND CORRELATION

A. Local density approximation(LDA)

The oldest and the most popular of the exchange-correlation functional, LDA assumes a simple form which is a linear functional of the density

$$E_{xc}^{LDA} = \int d\vec{r} n(\vec{r}) \epsilon_{xc}^{hom}(n(\vec{r})) \quad (45)$$

where $\epsilon_{xc}^{hom}(n(\vec{r}))$ is the exchange correlation energy density of an interacting homogeneous electron gas at the density $n(\vec{r})$. Recall here that the exchange part of $\epsilon_{xc}^{hom}(n(\vec{r}))$ is calculated exactly in the Hartree-Fock sense whereas the correlation part is a result of a fit to accurate MC data. Although LDA is a very crude approximation for systems that are not as homogeneous as an electron gas, it has proven to be a huge success much to the surprise of the community. This is in part due to the cancellation of errors where LDA typically overestimates E_X while it underestimates E_c . This comes from the fact that while the LDA xc hole satisfies the sum rule described above, the individual exchange and correlation holes do

not. This can only occur if the integrated errors in the exchange hole cancels that in the correlation hole. LDA has a big drawback which is that it does not satisfy the one-electron limit. This may be fixed by augmenting it with what is called a *self-interaction correction (SIC)*. The correction

$$E_{xc}^{LDA,SIC} = E_{xc}^{LDA} - \sum_i (E_H[n_i] - E_{xc}[n_i]) \quad (46)$$

subtracts the error which would be made by the Hartree and xc functionals in the case of a single electron.

B. Generalized gradient approximations

LDA treats all systems as homogeneous. However, real systems are clearly inhomogeneous with spatially varying electric fields due to nuclei and screening. In order to take this into account, a step may be taken beyond the LDA by including the derivative information of the density into the exchange-correlation functionals. One way to do this is to try to include gradients $|\nabla n(\vec{r})|$, $|\nabla n(\vec{r})|^2$, $\nabla^2 n(\vec{r})$... into the approximation. However, what works better is to seek a more general functional

$$E_{xc}^{GGA} = \int d\vec{r} f(n(\vec{r}), \nabla n(\vec{r})). \quad (47)$$

Such functionals are referred to as generalized gradient approximations. There are different flavors of GGA, each making a different choice for the function f .