VII. The Kohn-Sham method

Kohn and Sham noticed that the HK theory is valid for both interacting and non-interacting electrons. Now, they ask, what happens if for any system of interacting electrons, with density n there is a non-interacting system of the same density? It is clear that if such two systems exist they are unique. The non-interacting system has one advantage over the interacting system: we can find its ground-state rather easily, since the many-body wavefunction is a Slater wave function. So, the problem is: how to perform such a mapping.

A. Non-interacting electrons

If non-interacting electrons are tractable, let's study their density functionals. Given a density $n(\boldsymbol{r})$ we assume it is non-interacting v-representable, i.e that there exists a potential $v_s(\boldsymbol{r})$ such that the ground-state $\Phi_{gs}[n]$ of the non-interacting Hamiltonian $\hat{H}_s = \hat{T} + \hat{V}_s$ admits a ground-state having density $n(\boldsymbol{r})$. The Hohenberg-Kohn functional for non-interacting electrons is reduced to just the kinetic energy, i.e. we define:

$$T_S[n] = \langle \Phi_{gs}[n] | \hat{T} | \Phi_{gs}[n] \rangle \qquad (7.1.1)$$

As a private case of Eq. **Error! Reference source not found.** we have:

$$\Psi \to n \quad \Longrightarrow \quad T_S[n] \le \langle \Psi | \hat{T} | \Psi \rangle \qquad (7.1.2)$$

Thus, since our density is v-representable, $\Phi_{gs}[n]$ is the minimizer of $\langle \Psi | \hat{T} | \Psi \rangle$. In other words, the ground-state wave function of non-interacting particles associated with $n(\boldsymbol{r})$ minimizes the kinetic energy! Let us see some consequence this minimum principle.

A corollary, valid if the non-interacting system is non-degenerate, any function $\Phi[n]$ for which $\langle\Phi[n]|\hat{T}|\Phi[n]\rangle$ equals $T_S[n]$ must be the ground state of the non-interacting system with density n.

Let $\Phi_{gs}[n]$ be the ground state wave function of the system of non interacting electrons realizing the density $n(\boldsymbol{r})$. From the first equation in Eq. **Error! Reference source not found.** one sees that $\Phi_{gs}[n]_\gamma$ realizes $n_\gamma(\boldsymbol{r})$, thus one can plug it into the right hand side of Eq. (7.1.2), with $n_\gamma(\boldsymbol{r})$ plugged into T_S:

$$T_S[n_\gamma] = \langle\Phi_{gs}[n_\gamma]|\hat{T}|\Phi_{gs}[n_\gamma]\rangle \le \langle\Phi_{gs}[n]_\gamma|\hat{T}|\Phi_{gs}[n]_\gamma\rangle \tag{7.1.3}$$

Since now the right hand side is an expression of a scaled wave-function, one can use Eq. **Error! Reference source not found.** and obtain:

$$T_S[n_\gamma] \le \langle\Phi_{gs}[n]_\gamma|\hat{T}|\Phi_{gs}[n]_\gamma\rangle = \gamma^2\langle\Phi_{gs}[n]|\hat{T}|\Phi_{gs}[n]\rangle = \gamma^2 T_S[n] \tag{7.1.4}$$

And so $T_S[n_\gamma] \le \gamma^2 T_S[n]$. But we can also use this equation to scale n_γ back to n by dilating by $1/\gamma$, since: $(n_\gamma)_{1/\gamma} = n$. Then, the same rule applies and we get: $T_S[n] \le \gamma^{-2} T_S[n_\gamma]$, and so $T_S[n_\gamma] \ge \gamma^2 T_S[n]$. We obtained two contradicting equations which can agree only if both are reduced to equality. Thus:

$$T_S[n_\gamma] = \gamma^2 T_S[n]. \tag{7.1.5}$$

This should be compared with the analogous result of Eq. **Error! Reference source not found.** which is an inequality. The dilation effects for non-interacting electrons is obviously much simpler. One important corollary of (7.1.5) is that the non-interacting wave functions scale with the density. We saw that $\Phi_{gs}[n]_\gamma$ gives the correct kinetic energy of for the system with density n_γ, $T_S[n_\gamma]$, and therefore, necessarily:

$$\Phi_{gs}[n]_\gamma = \Phi_{gs}[n_\gamma]\,.\ (non-interacting\ particles) \tag{7.1.6}$$

Exercise

1) We can define a functional called the Hartree energy, which is the classical electrostatic energy associated with the charge distribution $n(\boldsymbol{r})$:

$$E_H[n]=\iint\frac{n(\boldsymbol{r})n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}d^3rd^3r' \tag{7.1.7}$$

Prove the following dilation relation:

$$E_H[n_\gamma]=\gamma E_H[n] \tag{7.1.8}$$

2) Now define the exchange energy functional (see also Eq. **Error! Reference source not found.** for a definition based on the orbitals):

$$K[n]\equiv\langle\Phi_{gs}[n]|\hat{U}|\Phi_{gs}[n]\rangle-E_H[n] \tag{7.1.9}$$

Use (7.1.6). Prove:

$$K[n_\gamma]=\gamma K[n] \tag{7.1.10}$$

What is the relation between the potential $v_S(\boldsymbol{r})$ for which $n(\boldsymbol{r})$ is a non-interacting ground state density and $v_{S,\gamma}(\boldsymbol{r})$ for which $n_\gamma(\boldsymbol{r})$ is a non-interacting ground state? We can use the basic DFT equation to answer this.

From the basic definition of functional derivation:

$$\mu_\gamma-v_{S,\gamma}(\boldsymbol{r}')=\left.\frac{\delta T_S}{\delta n(\boldsymbol{r}')}\right|_{n_\gamma}=\lim_{\eta\to0}\frac{\left(T_S[n_\gamma(\boldsymbol{r})+\eta\delta(\boldsymbol{r}-\boldsymbol{r}')]-T_S[n_\gamma(\boldsymbol{r})]\right)}{\eta} \tag{7.1.11}$$

The 3D delta-function has the density dilation structure: $\delta(\boldsymbol{r}-\boldsymbol{r}')=\lambda^3\delta(\lambda\boldsymbol{r}-\lambda\boldsymbol{r}')$, so:

$$\mu_\gamma-v_{S,\gamma}(\boldsymbol{r}')=\lim_{\eta\to0}\frac{\left(T_S[\gamma^3(n(\gamma\boldsymbol{r})+\eta\delta(\gamma\boldsymbol{r}-\gamma\boldsymbol{r}'))]-T_S[\gamma^3n(\gamma\boldsymbol{r})]\right)}{\eta} \tag{7.1.12}$$

Then using Eq.:

$$\begin{aligned}\mu_\gamma - v_{S,\gamma}(\boldsymbol{r}') &= \lim_{\eta\to 0}\frac{\gamma^2(T_S[n(\boldsymbol{r})+\eta\delta(\boldsymbol{r}-\gamma\boldsymbol{r}')]-T_S[n(\boldsymbol{r})])}{\eta} \\ &= \gamma^2\left(\mu - v_S(\gamma\boldsymbol{r}')\right)\end{aligned} \quad (7.1.13)$$

By dilating in the reverse direction we can easily see that:

$$\begin{aligned}\mu_\gamma &= \gamma^2\,\mu \\ v_{S,\gamma}(\boldsymbol{r}') &= \gamma^2 v_S(\gamma\boldsymbol{r}')\end{aligned} \quad (7.1.14)$$

We could have obtained this result directly from the Schrödinger equation. Suppose $\Psi(\{\boldsymbol{r}\})$ is a many-body eigenfunction of Hamiltonian $\hat{H} = \hat{T} + V(\{\boldsymbol{r}\})$, i.e $\hat{T}\Psi = (E - V)\Psi$. Define a scaled wavefunction:

$$\Psi_\gamma(\boldsymbol{r}_1,\dots,\boldsymbol{r}_N) = \gamma^{-\frac{3N}{2}}\Psi(\gamma\boldsymbol{r}_1,\dots,\gamma\boldsymbol{r}_N) \quad (7.1.15)$$

Then clearly:

$$\hat{T}\Psi_\gamma(\{\boldsymbol{r}\}) = \gamma^2\gamma^{-\frac{3N}{2}}(\hat{T}\Psi)(\{\gamma\boldsymbol{r}\}) = \gamma^2\big(E - V(\{\gamma\boldsymbol{r}\})\big)\Psi_\gamma(\{\boldsymbol{r}\}) \quad (7.1.16)$$

And so Ψ_γ obeys the S.E. $\hat{T}\Psi_\gamma = \left(E_\gamma - V_\gamma\right)\Psi_\gamma$ with energy and potential given by:

$$\begin{aligned}V_\gamma(\{\boldsymbol{r}\}) &= \gamma^2 V(\{\gamma\boldsymbol{r}\}) \\ E_\gamma &= \gamma^2 E\end{aligned} \quad (7.1.17)$$

For a ground state of non-interacting the first equation means that $v_{s,\gamma}(\boldsymbol{r}) = \gamma^2 v_s(\gamma\boldsymbol{r})$ is the one-particle potential for the scaled determinant, and thus for the scaled density (since the scaled determinant realizes the scaled density).

B. Orbitals for the non-interacting electrons

Consider the ground state wave function for the non-interacting electrons $\Phi_{gs}[n]$. Suppose the non-interacting electrons reside in the potential v_S (the subscript S is in honor of Slater) then $(\hat{T}+\hat{V}_S)\Phi_{gs}[n]=E_S\Phi_{gs}[n]$. In most cases this wave function is a normalized Slater wave function. We introduce N_e orthormal spin-orbitals $\phi_q(\boldsymbol{x})$ $q=1\dots N_e$, from which $\Phi_{gs}[n]$ is built. These orbitals are excited states of the potential well in which the non-interacting electrons reside. Thus the orbitals must each obey the single-electron Schrödinger equation:

$$-\frac{\hbar^2}{2m_e}\nabla^2\phi_q(\boldsymbol{x})+v_S(\boldsymbol{r})\phi_q(\boldsymbol{x})=\epsilon_q\phi_q(\boldsymbol{x}) \tag{7.1.18}$$

The orbitals correspond to the N_e lowest eigenvalues ϵ_q. The fact that Φ_{gs} realizes the density $n(\boldsymbol{r})$ is expressed as :

$$n(\boldsymbol{r})=\sum_{q=1}^{N_e}\left|\phi_q(\boldsymbol{x})\right|^2 \tag{7.1.19}$$

The non-interacting kinetic energy $T_S[n]$ is then:

$$T_S[n]=\sum_{q=1}^{N_e}\int\phi_q(\boldsymbol{x})\left(-\frac{\hbar^2}{2m_e}\nabla^2\right)\phi_q(\boldsymbol{x})dx \tag{7.1.20}$$

When one wants to find the functional derivative of T_S with respect to $n(\boldsymbol{r})$ one can turn to basic equation, Eq. **Error! Reference source not found.** which in case of non-interacting electrons becomes:

$$\frac{\delta T_S[n]}{\delta n(\boldsymbol{r})}+v_S(\boldsymbol{r})=\mu \tag{7.1.21}$$

We will see that this equation is important for the method known as the Kohn-Sham method.

Note that the discussion of dilation in the previous subsection can be carried on to the orbitals. The only additional information to convey is that the orbitals scale as the density and each of the orbital energies scale as the total energy:

$$\epsilon_{q,\gamma} = \gamma^2 \epsilon_q \tag{7.1.22}$$

C. The correlation energy functional: definition and some formal properties

The ground state energy of the an system of electrons in density $n(\boldsymbol{r})$ can be written in terms of the non-interacting (Slater wave function) wave function $\Phi_{gs}[n]$:

$$E[n] = \langle \Phi_{gs}[n] | \hat{H} | \Phi_{gs}[n] \rangle + E_c[n] \tag{7.2.1}$$

This equation is actually a definition of a new density functional, the correlation energy functional $E_C[n]$. If we suppose for the time being that $E_C[n]$ is known, this expression can be used to define a working procedure for DFT known as the Kohn-Sham method. From our studies of the Hartree-Fock theory, we know that the expectation value of $\hat{H}$ within a determinant can be written as:

$$\langle \Phi_{gs}[n] | \hat{H} | \Phi_{gs}[n] \rangle = E_H[n] + K[n] \equiv U_S[n] \tag{7.2.2}$$

Where E_H is the Hartree energy:

$$E_H[n] = \frac{e^2}{2} \iint \frac{n(\boldsymbol{r}) n(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} d^3r d^3r' \tag{7.2.3}$$

And K is given in terms of the orbitals from which $\Phi_{gs}[n]$ is composed (Eq. **Error! Reference source not found.**):

$$K[n] = -\frac{e^2}{2} \iint \frac{|\rho(\boldsymbol{x}, \boldsymbol{x}')|^2}{|\boldsymbol{r} - \boldsymbol{r}'|} d^3x d^3x' \tag{7.2.4}$$

Based on this, we rewrite $F_{HK}[n]$ as:

$$F_{HK}[n]=\langle\Psi_{gs}[n]|\hat{F}|\Psi_{gs}[n]\rangle=\langle\Phi_{gs}[n]|\hat{F}|\Phi_{gs}[n]\rangle+E_C[n] \tag{7.2.5}$$

This allows us to write Eq. (7.2.5) compactly as:

$$F_{HK}[n]=T_S[n]+U_S[n]+E_C[n] \tag{7.2.6}$$

Clearly we have also the equivalent equation:

$$E_C[n]=T[n]-T_s[n]+U[n]-U_S[n] \tag{7.2.7}$$

Physical intuition concerning molecules and solids tells us that $E_C[n]$ is a small quantity when compared to $T_s[n]$ or $U_S[n]$. Thus, it is reasonable to look for approximations to this quantity. Approximation to the correlation energy functional is the most important issue in DFT. It is an open question, still being worked upon.

We shall deal with approximations later. Meanwhile, let us ask what can be safely said about the correlation functional. We prove here several important inequalities. First, consider the difference $T_C[n]\equiv T[n]-T_S[n]$, the correlation kinetic energy.

Exercise

Show $T_C[n]$ is a positive quantity. This is actually intuitively clear: the interacting electrons must have much more complicated "paths" in the interacting case because they want to avoid "bumping into" other electrons. Anything with more swirls must have higher kinetic energy.

Solution

Using the variational theorem:

$$\begin{aligned}T_S[n]+V_S[n]&=\langle\Phi_{gs}[n]|\hat{T}+\hat{V}_S|\Phi_{gs}[n]\rangle\le\langle\Psi_{gs}[n]|\hat{T}+\hat{V}_S|\Psi_{gs}[n]\rangle\\&=T[n]+V_S[n]\end{aligned} \tag{7.2.8}$$

Where $\Psi_{gs}[n]$ is the interacting ground-state wave function determined by n. Comparing the two sides we have:

$$T_S[n] \leq T[n] \tag{7.2.9}$$

Next, we can show that the exchange correlation energy is always negative. This comes about from our experience with expectation values of determinants:

$$F_{HK}[n] + V[n] = E_{gs} \leq \langle \Phi_{gs}[n] | \hat{H} | \Phi_{gs}[n] \rangle = T_S[n] + V[n] + U_S[n] \tag{7.2.10}$$

Using Eq. (7.2.6) we find:

$$E_C[n] < 0 \tag{7.2.11}$$

Furthermore $U_C[n] \equiv U[n] - U_S[n]$ is negative as can be seen from the fact that E_C is negative and T_C is positive:

$$U_C[n] = E_C[n] - T_C[n] \leq 0 \tag{7.2.12}$$

An additional property is the dilating relations. We have proved that $F_{HK}[n_\gamma] \leq \gamma^2 T[n] + \gamma U[n]$ and $T_S[n_\gamma] = \gamma^2 T_S[n]$, $U_S[n_\gamma] = \gamma U_S[n]$. Thus:

$$E_C[n_\gamma] = T_C[n_\gamma] + U_C[n_\gamma] \leq \gamma^2 T_C[n] + \gamma U_C[n] \tag{7.2.13}$$

One way to proceed is to substitute U_C with $E_C - T_C$. The other is to substitute T_C with $E_C - U_C$. We obtain from each possibility:

$$\begin{gathered} E_C[n_\gamma] \leq \gamma(\gamma - 1) T_C[n] + \gamma E_C[n] \\ E_C[n_\gamma] \leq \gamma^2 E_C[n] + \gamma(1 - \gamma) U_C[n] \end{gathered} \tag{7.2.14}$$

And, since T_C is always positive and U_C negative, we find that:

$$\begin{gathered} E_C[n_\gamma] \leq \gamma E_C[n] \qquad \gamma < 1 \\ E_C[n_\gamma] \leq \gamma^2 E_C[n] \qquad \gamma < 1 \end{gathered} \tag{7.2.15}$$

Obviously, the second relation is contained in the first (since $E_C < 0$) and so only the first relation is important; it can be used to derive complementary inequalities. Indeed, applying them for $\gamma \to \gamma^{-1}$ we find:

$$E_C\left[n_{1/\gamma}\right] \le \gamma^{-1} E_C[n] \qquad \gamma > 1 \tag{7.2.16}$$

This holds for any n, so we stick in (7.2.16) n_γ instead of n and using the fact that $\left(n_\gamma\right)_{1/\gamma} = n$ to obtain:

$$E_C\left[n_\gamma\right] \ge \gamma E_C[n] \qquad \gamma > 1 \tag{7.2.17}$$

In absolute values:

$$\left|E_C\left[n_\gamma\right]\right| \le \gamma \left|E_C[n]\right| \qquad \gamma > 1 \tag{7.2.18}$$

Intuitively, the larger $|E_C[n]|$ the more correlation we have. We see that compressing the density, say on the average by a factor 8 ($\gamma = 2$) does not necessarily raise the abs value of the correlation energy, certainly not by more than a factor 2.

D. The Kohn Sham equations

i. The Kohn-Sham equation from a system of non-interacting problem

Let us now turn to the issue of determining $v_s(\boldsymbol{r})$, required for the mapping between the interacting non-interacting systems. Let us start form the basic equation Eq. **Error! Reference source not found.** which becomes, using Eq. (7.2.6):

$$\frac{\delta T_S[n]}{\delta n(\boldsymbol{r})} + v_{HX}(\boldsymbol{r}) + v_C(\boldsymbol{r}) + v(\boldsymbol{r}) = \mu \tag{7.3.1}$$

Where:

$$v_{HX}(\boldsymbol{r}) = \frac{\delta U_S[n]}{\delta n(\boldsymbol{r})} = v_H(\boldsymbol{r}) + v_X(\boldsymbol{r}) \tag{7.3.2}$$

is the Hartree-Exchange potential. Notice that:

$$v_H(\boldsymbol{r}) = \frac{\delta E_H[n]}{\delta n(\boldsymbol{r})} = \int \frac{n(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} d^3 r' \tag{7.3.3}$$

and:

$$v_X(\mathbf{r}) = \frac{\delta K[n]}{\delta n(\mathbf{r})} \tag{7.3.4}$$

Thus, from Eq. (7.1.21) and Eq. (7.3.1) (up to a constant):

$$v_S(\mathbf{r}) = v(\mathbf{r}) + v_{HX}(\mathbf{r}) + v_C(\mathbf{r}) \tag{7.3.5}$$

This equation gives us the potential of the non-interacting system. Thus, we have made a definite connection between the interacting and non-interacting systems.

Now, an important observation allows us to set up a simple method for obtaining the ground-state of an interacting system of electrons. We need to find a density that obeys two conditions:

a) It is the density of the non-interacting electrons so it is the sum of square orbitals (Eq. (7.1.19)) that obey the Schrödinger equations (7.1.18) with potential $v_S(\mathbf{r})$.

b) The potential $v_S(\mathbf{r})$ must be related to the interacting system by Eq. (7.3.5)

This leads to a simple SCF procedure, called "The Kohn-Sham method" reminiscent of the Hartree-Fock algorithm:

1. Guess $n(\mathbf{r})$.
Build $v_{HX}(\mathbf{r})$, $v_C(\mathbf{r})$ from $n(\mathbf{r})$ (Eq. (7.3.3) and (7.3.4)).
Obtain the orbitals $\phi_q(\mathbf{x})$ from the lowest N_e eigenvalues of Eq. (7.1.18).
Compute the density from Eq. (7.1.19)
Redo from step 2 using the new density until you converge – i.e. until the density changes no more.

When the process convergence, we have the exact ground-state density $n_v(\mathbf{r})$. It can be used to compute the ground-state energy by plugging it into the energy functional of Eq. **Error! Reference source not found.**:

$$E_v[n] = T_s[n] + \int v(\mathbf{r})n(\mathbf{r})d^3r + U_S[n] + E_C[n] \tag{7.3.6}$$

ii. Systems with partially occupied orbitals

Partially occupied orbitals arise in the realm of ensemble-DFT, i.e. when the density searched for is not "non-interacting v-representable". We still assume the density is a sum of orbital densities as follows:

$$n(\boldsymbol{r}) = \sum_q \left|\phi_q(\boldsymbol{x})\right|^2, \tag{7.3.7}$$

but unlike Eq. (7.1.19) we do not impose exactly N_e orbitals. The orbitals are almost completely unconstrained, except for the Fermionic condition, that their norm must be not be great than 1:

$$\langle\phi_q|\phi_q\rangle = n_q \leq 1, \tag{7.3.8}$$

but the total number of electrons is still N_e:

$$\int n(\boldsymbol{r}) d^3r = \sum_q n_q = N_e \tag{7.3.9}$$

And the kinetic energy is written similarly to Eq. (7.1.20):

$$T_S[n] = \sum_q \int \phi_q(\boldsymbol{x}) \left(-\frac{\hbar^2}{2m_e}\nabla^2\right) \phi_q(\boldsymbol{x}) dx \tag{7.3.10}$$

We generalized Eqs. (7.1.19) and (7.1.20) any number of orbitals leading to the following orbital Lagrangian:

$$\begin{aligned} L_{orb}\left[\{\phi_q\},\{n_q\}\right] \\ &= E_v\left[\sum_q \left|\phi_q(\boldsymbol{x})\right|^2\right] - \sum_q \epsilon_q\left(\langle\phi_q|\phi_q\rangle - n_q\right) \\ &- \mu\left(\sum_q n_q - N_e\right) \end{aligned} \tag{7.3.11}$$

ϵ_q $(q = 1,2,\dots)$ and μ are *Lagrange multipliers* assuring orbital normality and total number of particles. We minimize the Lagrangian with respect to the orbitals $\phi_q(\boldsymbol{r})$ and the occupation numbers (constraint to be non-negative and not greater than 1). The constraint minimum procedure thus requires that:

$$\frac{\delta L_{orb}}{\delta \phi_q(\boldsymbol{x})} = 0 \quad and \quad \frac{\delta L_{orb}}{\delta n_q} = 0 \tag{7.3.12}$$

The first equation leads to the KS equations:

$$-\frac{\hbar^2}{2m_e}\nabla^2\phi_q(\boldsymbol{x}) + v_S(\boldsymbol{r})\phi_q(\boldsymbol{x}) = \epsilon_q\phi_q(\boldsymbol{x}) \tag{7.3.13}$$

For convenience, we order the indexing so that the series of orbital energies is ascending: $\epsilon_1 \le \epsilon_2 \le \cdots$ The orbitals are now eigenfunctions of a Hermitian Hamiltonian, and so we can assume they are orthogonal:

$$\langle \phi_q | \phi_{q'} \rangle = n_q \delta_{qq'}, \tag{7.3.14}$$

We define as a short-hand notation $v_S(\boldsymbol{r}) \equiv v(\boldsymbol{r}) + v_{HX}(\boldsymbol{r}) + v_C(\boldsymbol{r})$ (see Eq. (7.3.5)). By multiplying Eq. (7.3.13) by $\phi_q(\boldsymbol{x})$ integrating on $\boldsymbol{x}$ and summing on q we find:

$$T_S + \int v_s(\boldsymbol{r})n(\boldsymbol{r})d^3r = \sum_q \epsilon_q n_q \tag{7.3.15}$$

The second condition for minimum of L_{orb} holds only in cases that the minimum is attained with non-integer electron number, $n_q < 1$. The cases $n_q = 1$ or $n_q = 0$ are the boundary of the constraints and the derivative need not be zero there. From this second part of the equation, we have:

$$\epsilon_q = \mu, \quad 0 < n_q < 1 \tag{7.3.16}$$

This shows that all incompletely occupied orbitals have the same orbital energy equal to the chemical potential μ, the Lagrange multiplier imposing the number of particle constraint of the Hohenberg-Kohn theory (Eq. **Error! Reference source not found.**).

Typically, all orbitals with $\epsilon_q < \mu$ are fully occupied ($n_q = 1$) and those with $\epsilon_q > \mu$ are fully unoccupied ($n_q = 0$). The interacting electron energy is obtained using Eqs. (7.3.6) and (7.3.15) as

$$E_v = \sum_q \epsilon_q n_q + E_{HX}[n] + E_C[n] - \int n(\boldsymbol{r})\big(v_{HX}(\boldsymbol{r}) + v_C(\boldsymbol{r})\big) d^3 r \tag{7.3.17}$$

We should note that the development here assumed non-interacting v-representability. In cases where this is not valid other occupation rules may apply.

iii. Is the ground state wave function of non-interacting particles always a Slater wave function

The standard KS approach to the non-interacting kinetic energy is by defining the functional T_S as a minimum principle on the manifold of single determinants:

$$T_S[n] = \min_{\Phi \to n(\boldsymbol{r})} \langle \Phi | \hat{T} | \Phi \rangle \tag{7.3.18}$$

Setting up a Lagrangian and searching for the constrained minimum yields N occupied orbitals. If the density is not v-representable one or more of the low energy orbitals may have 0 occupation numbers.

Another way to define a non-interacting kinetic energy functional is by an extended minimum search over more general wave functions:

$$T_{NI}[n] = \min_{\Psi \to n(\boldsymbol{r})} \langle \Psi | \hat{T} | \Psi \rangle \tag{7.3.19}$$

Usually this search ends with Ψ being a single Slater wave function and for these case T_{NI} and T_S given are the same. Yet, this may not always be the case.

Let us assume that we are searching through all $\Psi = \cos\theta\,\Phi_A + \sin\theta\,\Phi_B$ where Φ_A or Φ_B are Slater wave functions. In general, the kinetic energy is then:

$$T_{NI}[n] = \min_{\Psi\to n(r)} \langle \Phi_\mathrm{A}|\hat{T}|\Phi_\mathrm{A}\rangle \cos^2\theta + \sin 2\theta\,\langle \Phi_\mathrm{A}|\hat{T}|\Phi_\mathrm{B}\rangle \\ + \langle \Phi_\mathrm{B}|\hat{T}|\Phi_\mathrm{B}\rangle \sin^2\theta \tag{7.3.20}$$

Now, if Φ_A and Φ_B differ by only one orbital (say $\phi_A^k = \phi_B^k$ for $k = 1, \dots, N-1$) then Ψ is actually a Slater wave function: its orbitals are the $N-1$ ϕ_A^k's and then a new orbital $\phi_N^{new} = \cos\theta\,\phi_A^N + \sin\theta\,\phi_B^N$ is added. Next, if Φ_A and Φ_B differ by two (or more) orbitals the cross term in (7.3.20) is zero and the kinetic energy is simply the sum of orbitals kinetic energies with occupation numbers given by $\cos^2\theta$ and $\sin^2\theta$. The orbitals shared by the two determinants will have unity occupation number (since $\cos^2\theta + \sin^2\theta = 1$) while orbitals in the A determinant but not in the B determinant will have occupation number $\cos^2\theta$ and those in the B determinant but not in the A determinant will have occupation number $\sin^2\theta$. The orbitals coming out from the minimization will all solve a Schrödinger equation with the same potential. The 4 odd orbitals (2 from each determinant) will all have the same orbital energy equal to μ. When there are more than 2 Slater wavefunctions a similar treatment will result and even more orbitals will be degenerate at the chemical potential. Even if n is v-representable this type of wave function can arise.

A third way to define the kinetic energy is as an ensemble average. Instead of a wave function, one uses a mixed density matrix $D = \sum_n c_n |\Phi_n\rangle\langle\Phi_n|$. The constants c_n are positive and sum to 1. The density is the convex sum $\sum_n c_n n_n(\boldsymbol{r})$ of densities from each participating determinant. A similar expression will arise for the kinetic energy. This approach is designed to solve the problems of non-interacting v-representability emanating from convex sums of degenerate wave functions (see section XXX).

iv. Janak's Theorem

A very general theorem was noted by Janak [5], based on earlier work of Slater and Wood[6] concerning the meaning of orbital energies. Let us return to the functional of Eq. (7.3.11) and assume now that the occupation numbers n_q are given and they are all non-negative and not larger than 1 and that they sum up to the number of electrons. Thus, for a given set of occupation numbers we can search for the orbitals that minimize the following functional:

$$L[\{\phi_q\}] = E_v\left[\sum_q \left|\phi_q(\boldsymbol{x})\right|^2\right] - \sum_q \epsilon_q\left(\langle\phi_q|\phi_q\rangle - n_q\right) \qquad (7.3.21)$$

The equations that the orbitals must obey are still derived from Eq. (7.3.12) leading to the same equations as in (7.3.13), the KS equation. Now, let us ask: what happens to the energy when we change the occupation number of one of the orbitals n_q by an infinitesimal amount δn_q? When we do this the "total number of electrons" N_e changes by this amount as well. This is not a physical change (since electrons cannot change by non-intereger amounts) but still mathematically speaking the change can be studied. Since n_q are the constraints and ϵ_q the Lagrange multipliers in a minimization problem we can use the general result of Eq. **Error! Reference source not found.** that the rate at which the minimized function changes when the constraints change is equal to the Lagrange multiplier:

$$\frac{\partial E_v}{\partial n_q} = \epsilon_q \qquad (7.3.22)$$

This relation, giving some meaning to the orbital energies is called Janak's theorem. This theorem is quite general but relies on some analytical assumptions of the energy functional. For example, when the occupation number is 1 the change can only be by a negative amount and when it is zero – only positive. For approximate functionals, that are analytical with respect to any $n(\boldsymbol{r})$ and $\phi_q(\boldsymbol{r})$ this relation holds. Such is the case for the often used local, semilocal and even most hybrid functionals, including Hartree-Fock theorem.

In the conext of Hartree-Fock theory this result is a restatement of Koopmans' theorem, by which $-\epsilon_q$ is the unrelaxed ionization energy from orbital q. The orbital relaxation is a second order effect and thus negligible when occupation numbers change infinitesimally.

E. "Virial Theorem" related identities in DFT

The following development is inspired by the virial theorem treatment. It continues to consider dilation relations. Taking the derivative of $n_\gamma(\boldsymbol{r})$with respect to γ, we have $\frac{d}{d\gamma}n_\gamma(\boldsymbol{r}) = \gamma^3\boldsymbol{r}\cdot\nabla n(\gamma\boldsymbol{r}) + 3\gamma^2 n(\gamma\boldsymbol{r})$ and since, $\nabla\cdot\big(\boldsymbol{r}f(\boldsymbol{r})\big) = 3f(\boldsymbol{r}) + \boldsymbol{r}\cdot\nabla f(\boldsymbol{r})$, we find

$$\frac{d}{d\gamma}n_\gamma(\boldsymbol{r}) = \gamma^2\big[\nabla_{\mathbf{s}}\cdot\big(\boldsymbol{s}n(\boldsymbol{s})\big)\big]_{\boldsymbol{s}=\gamma\boldsymbol{r}} \tag{7.4.1}$$

For a general density functional, $A[n]$, we have, using the chain rule for derivatives, $a[n](\boldsymbol{r}) = \delta A[n]/\delta n(\boldsymbol{r})$ and Eq. (7.4.1)then:

$$\frac{d}{d\gamma}A[n_\gamma] = \int a[n_\gamma](\boldsymbol{r})\gamma^2\big[\nabla_{\mathbf{s}}\cdot\big(\boldsymbol{s}n(\boldsymbol{s})\big)\big]_{\boldsymbol{s}=\gamma\boldsymbol{r}}d^3r = \int \gamma^{-1}a[n_\gamma](\gamma^{-1}\boldsymbol{s})\nabla_{\mathbf{s}}\cdot\big(\boldsymbol{s}n(\boldsymbol{s})\big)d^3s$$

$$= -\gamma^{-1}\int\Big(\boldsymbol{r}\cdot\nabla_{\mathbf{r}}a[n_\gamma](\boldsymbol{r})\Big)_{\boldsymbol{r}=\gamma^{-1}\boldsymbol{s}}n(\boldsymbol{s})d^3s$$

From which a completely general virial-dilation relation holds for any functional:

$$\frac{dA[n_\gamma]}{d\gamma} + \gamma^2 \int \left(\boldsymbol{r}\cdot\nabla_{\mathbf{r}} a[n_\gamma](\boldsymbol{r})\right) n(\gamma\boldsymbol{r}) d^3r = 0 \tag{7.4.2}$$

We will be especially interested in the case of $\gamma = 1$. Thus the basic relation:

$$\left(\frac{dA[n_\gamma]}{d\gamma}\right)_{\gamma=1} + \int (\boldsymbol{r}\cdot\nabla a[n](\boldsymbol{r}))n(\boldsymbol{r})d^3r = 0 \tag{7.4.3}$$

We further find that

$$A[n] + \int (\boldsymbol{r}\cdot\nabla a[n](\boldsymbol{r}))n(\boldsymbol{r})d^3r = \left(\frac{d(\gamma A[n] - A[n_\gamma])}{d\gamma}\right)_{\gamma=1} \tag{7.4.4}$$

Let us apply this for the Hartree energy. From Eq. (7.1.8) we find the following relation, valid for any γ: $\gamma E_H[n] - E_H[n_\gamma] = 0$, so:

$$E_H[n] + \int \boldsymbol{r}\cdot\nabla v_H[n](\boldsymbol{r})\, n(\boldsymbol{r})d^3r = 0 \tag{7.4.5}$$

A similar relation, namely $\gamma K_X[n] - K_X[n_\gamma] = 0$ hold also for the exchange energy $K_X[n]$ (see Eq. (7.1.10)), and so:

$$K_X[n] + \int \boldsymbol{r}\cdot\nabla v_X[n](\boldsymbol{r})\, n(\boldsymbol{r})d^3r = 0 \tag{7.4.6}$$

Where $v_X[n](\boldsymbol{r}) = \delta K_X[n]/\delta n(\boldsymbol{r})$ is the exchange potential.

Now, what about the correlation energy? Let us consider the KS DFT functional:

$$E_v[n] = T_S[n] + \int v(\boldsymbol{r})\, n(\boldsymbol{r})d^3r + U_S[n] + E_C[n] \tag{7.4.7}$$

Suppose $n(\boldsymbol{r})$ is the density minimizing minimizer of $E_v[n]$ and now plug into the latter the scaled density. This will give a γ dependent energy:

$$\tilde{E}(\gamma) = E_v[n_\gamma] \tag{7.4.8}$$

And clearly, the minimum is at $\gamma = 1$ so:

$$\tilde{E}'(1) = 0 \tag{7.4.9}$$

Now, let us evaluate $\tilde{E}'(\gamma)$ using Eq. (7.1.5):

$$\tilde{E}'(\gamma) = 2\gamma T_S[n] + \frac{d}{d\gamma}\left(\int v(\boldsymbol{r}) n_\gamma(\boldsymbol{r}) d^3r\right) + U_S[n] + \frac{d}{d\gamma} E_C[n_\gamma], \tag{7.4.10}$$

and plug in $\gamma = 1$. We obtain:

$$\frac{d}{d\gamma}\left\{E_C[n_\gamma] + \int v(\boldsymbol{r}) n_\gamma(\boldsymbol{r}) d^3r\right\}_{\gamma=1} = -2T_S[n] - U_S[n]. \tag{7.4.11}$$

or, using Eq. (7.4.3):

$$\int \left(\boldsymbol{r} \cdot \nabla_{\mathbf{r}}\left(v_C[n](\boldsymbol{r}) + v(\boldsymbol{r})\right)\right) n(\boldsymbol{r}) d^3r = -2T_S[n] - U_S[n] \tag{7.4.12}$$

The second term in the parenthesis can be related to the interacting system. Indeed we have, using Eqs. **Error! Reference source not found.**:

$$\begin{aligned} E[\Psi_\gamma] &= T[\Psi_\gamma] + U[\Psi_\gamma] + \int v(\boldsymbol{r})\, n_\gamma(\boldsymbol{r}) d^3r \\ &= \gamma^2 T[\Psi] + \gamma U[\Psi] + \int v(\boldsymbol{r})\, n_\gamma(\boldsymbol{r}) d^3r \end{aligned} \tag{7.4.13}$$

Taking the derivative with respect to γ, remembering that $E'[\Psi_\gamma]_{\gamma=1} = 0$ we find, for $\gamma = 1$:

$$0 = 2T[\Psi] + U[\Psi] + \frac{d}{d\gamma}\left(\int v(\boldsymbol{r})\, n_\gamma(\boldsymbol{r}) d^3r\right)_{\gamma=1} \tag{7.4.14}$$

(As a sidenote, you can see that substituting this relation in Eq. (7.4.1) gives after trivial manipulation the virial theorem $2T[\Psi] + U[\Psi] = \int \left(\boldsymbol{r} \cdot \nabla v(\boldsymbol{r})\right) n(\boldsymbol{r}) d^3r$). Continuing the above development, using Eqs. (7.4.11) and (7.4.14) we finally find:

$$\frac{d}{d\gamma}E_C[n_\gamma]|_{\gamma=1} = 2T_C + U_C, \tag{7.4.15}$$

which can be written equivalently as:

$$E_C[n] - \frac{d}{d\gamma}E_C[n_\gamma]|_{\gamma=1} = -T_C[n], \tag{7.4.16}$$

or, using Eq. (7.4.3):

$$E_C[n] + \int \big(\boldsymbol{r} \cdot \nabla_{\mathbf{r}} v_C[n](\boldsymbol{r})\big) n(\boldsymbol{r}) d^3r = -T_C[n] \leq 0. \tag{7.4.17}$$

The Hartree and exchange energies give zero while the correlation energy gives a negative quantity equal exactly to $-T_C[n]$.

This result shows that the correlation energy functional and the correlation potential are enough for determining the correlation kinetic energy (and from it, by $T = T_S + T_C$) the kinetic energy itself.

This latter result is related to the virial theorem of Slater, which shows that one can derive the kinetic energy of the electrons from the Born-Oppneheimer potential surface itself (Eq. **Error! Reference source not found.**). Since DFT gives, in principle the Born-Oppenheimer potential surface, one can access the kinetic energy (and the potential energy) from the DFT calculation.

F. Galilean invariance

A basic property of the electron-electron interaction is that if the coordinates of all electrons are shifted by a constant $\boldsymbol{L}$:

$$\boldsymbol{r}_n' = \boldsymbol{r}_n - \boldsymbol{L} \tag{7.5.1}$$

the e-e interaction enegy does not change

$$U' = \frac{1}{2}\sum_{n\neq m}\frac{1}{|\boldsymbol{r}_n' - \boldsymbol{r}_m'|} = \frac{1}{2}\sum_{n\neq m}\frac{1}{|\boldsymbol{r}_n - \boldsymbol{r}_m|} = U \tag{7.5.2}$$

This property is shows that the e-e interaction is translationally invariant. This property is also called Galilean invariance. The same property holds when the coordinates of each electron are rotated around some axis. This roatation can be described by a 3×3 orthogonal matrix O, where $O^T O = OO^T = I$:

$$\boldsymbol{r}_n'' = O\boldsymbol{r}_n \tag{7.5.3}$$

The lengths of vectors are preserved under a rotation:

$$|\boldsymbol{r}_n''|^2 = \boldsymbol{r}_n''^T \boldsymbol{r}_n'' = (O\boldsymbol{r}_n)^T O\boldsymbol{r}_n = \boldsymbol{r}_n^T O^T O\boldsymbol{r}_n = \boldsymbol{r}_n^T \boldsymbol{r}_n = |\boldsymbol{r}_n|^2 \tag{7.5.4}$$

Thus the e-e interaction enegy does not change

$$\begin{aligned} U'' &= \frac{1}{2}\sum_{n\neq m} \frac{1}{|\boldsymbol{r}_n'' - \boldsymbol{r}_m''|} = \frac{1}{2}\sum_{n\neq m} \frac{1}{|O\boldsymbol{r}_n - O\boldsymbol{r}_m|} = \frac{1}{2}\sum_{n\neq m} \frac{1}{|O(\boldsymbol{r}_n - \boldsymbol{r}_m)|} \\ &= \frac{1}{2}\sum_{n\neq m} \frac{1}{|\boldsymbol{r}_n - \boldsymbol{r}_m|} = U \end{aligned} \tag{7.5.5}$$

Thus the e-e energy is rotational invariant.

These relations indeed hold for the density functional $E_H[n]$ since it is a reflection of the e-e functional. Indeed, define the shifted density:

$$n'(\boldsymbol{r}') = n(\boldsymbol{r}) = n(\boldsymbol{r}' + \boldsymbol{L}) \tag{7.5.6}$$

Then:

$$\begin{aligned} E_H[n'] &= \frac{1}{2}\iint \frac{n'(\boldsymbol{r}_1')n'(\boldsymbol{r}_2')}{|\boldsymbol{r}_1' - \boldsymbol{r}_2'|} d^3r_1' d^3r_2' \\ &= \frac{1}{2}\iint \frac{n(\boldsymbol{r}_1' + \boldsymbol{L})n(\boldsymbol{r}_2' + \boldsymbol{L})}{|\boldsymbol{r}_1' - \boldsymbol{r}_2'|} d^3r_1' d^3r_2' \end{aligned} \tag{7.5.7}$$

We now make a variable replacement: $\boldsymbol{r}_n' \to \boldsymbol{r}_n - \boldsymbol{L}$ and obtain:

$$\begin{aligned}E_H[n'] &= \frac{1}{2}\iint \frac{n(\boldsymbol{r_1})n(\boldsymbol{r_2})}{|(\boldsymbol{r}_1-\boldsymbol{L})-(\boldsymbol{r}_2-\boldsymbol{L})|}d^3r_1d^3r_2 \\ &= \frac{1}{2}\iint \frac{n(\boldsymbol{r_1})n(\boldsymbol{r_2})}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}d^3r_1d^3r_2 = E_H[n]\end{aligned} \tag{7.5.8}$$

This condition, that $E_H[n]=E_H[n']$ is called Galilean invariance. It is easy to show that $E_H[n]$ functional is also rotational invariant.

The exchange energy is also Galilean invariant, since the translation of the density will cause a translation of the density matrix:

$$\rho[n'](\boldsymbol{r}_1',\boldsymbol{r}_2')=\rho[n](\boldsymbol{r}_1,\boldsymbol{r}_2) \tag{7.5.9}$$

It is easy based on this to show that $E_X[n]=E_X[n']$.

Finally, the same will hold for the kinetic energies $T[n]$, $T_S[n]$. All this shows that we must demand this invariance of the correlation energy:

$$E_C[n'']=E_C[n']=E_C[n] \tag{7.5.10}$$

One consequence is the property of Galilean covariance of the potentials for each of the above energy functionals. For example, for the correlation energy we have the following result. Suppose we shift the density by a small displacement:

$$n'(\boldsymbol{r})=n(\boldsymbol{r}'+\delta\boldsymbol{L})=n(\boldsymbol{r}')+\delta\boldsymbol{L}\cdot\boldsymbol{\nabla}n(\boldsymbol{r}')$$

Thus:

$$E_C[n']=E_C'[n+\delta\boldsymbol{L}\cdot\boldsymbol{\nabla}n]=E_C[n]+\delta\boldsymbol{L}\cdot\int\frac{\delta E_C}{\delta n(\boldsymbol{r}')}\boldsymbol{\nabla}n(\boldsymbol{r}')d^3r' \tag{7.5.11}$$

Since we demand Galilean invariance $E_C[n']=E_C[n]$ we find:

$$\delta\boldsymbol{L}\cdot\int\frac{\delta E_C}{\delta n(\boldsymbol{r}')}\boldsymbol{\nabla}n(\boldsymbol{r}')d^3r'=0 \tag{7.5.12}$$

Since $\frac{\delta E_C}{\delta n(\boldsymbol{r}')}=v_C[n](\boldsymbol{r})$ and $\delta\boldsymbol{L}$ is arbitrary:

$$\int v_C[n](\boldsymbol{r})\,\boldsymbol{\nabla}n(\boldsymbol{r})d^3r = 0 \tag{7.5.13}$$

For finite systemswhere the density drops to zero at infinity we can move the nabla sign to the potential:

$$\int -\boldsymbol{\nabla}v_C[n](\boldsymbol{r})\,n(\boldsymbol{r})d^3r = 0 \tag{7.5.14}$$

$-\boldsymbol{\nabla}v_C[n](\boldsymbol{r})$ is the force derived from the correlation potential. This shows that the total correlation force is always zero. Another consequence from Galilean invariance of the correlation energy is the Galilean covariance:

$$v_C[n'](\boldsymbol{r}') = v_C[n](\boldsymbol{r}) = v_C[n](\boldsymbol{r}' + \boldsymbol{L}) \tag{7.5.15}$$

Similar conditions can be proved from rotational invariance. For example the torque:

$$\int \boldsymbol{r} \times \boldsymbol{\nabla}v_C[n](\boldsymbol{r})\,n(\boldsymbol{r})d^3r = 0 \tag{7.5.16}$$

G. Holes and the adiabatic connection

i. The exchange and correlation holes

Let us now take a step back and return to wave function theory. We examine the electron-electron interaction energy

$$U = \langle \Psi_{gs} | \hat{U} | \Psi_{gs} \rangle \tag{7.6.1}$$

Which we write using the following operator:

$$\hat{U} = \frac{e^2}{2}\sum_{i\neq j}\frac{1}{r_{ij}} = \frac{e^2}{2}\iint \frac{\hat{n}_2(\boldsymbol{r},\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}d^3rd^3r' \tag{7.6.2}$$

In the first term, we sum over the pairs of r-vectors of each of the N coordiantes (indices i and j). In the second term we use the definition:

$$\hat{n}_2(\boldsymbol{r},\boldsymbol{r}') = \sum_{i\neq j} \delta(\boldsymbol{r}-\hat{\boldsymbol{r}}_i)\delta\left(\boldsymbol{r}-\hat{\boldsymbol{r}}_j\right), \tag{7.6.3}$$

which is the pair density *operator*. Note the relation between the one and two densties:

$$\begin{aligned}\hat{n}_2(\boldsymbol{r},\boldsymbol{r}') &= \sum_{i,j} \delta(\boldsymbol{r}-\hat{\boldsymbol{r}}_i)\delta\left(\boldsymbol{r}'-\hat{\boldsymbol{r}}_j\right) - \sum_{i} \delta(\boldsymbol{r}-\hat{\boldsymbol{r}}_i)\delta(\boldsymbol{r}'-\hat{\boldsymbol{r}}_i) \\ &= \hat{n}(\boldsymbol{r})\hat{n}(\boldsymbol{r}') - \delta(\boldsymbol{r}-\boldsymbol{r}')\hat{n}(\boldsymbol{r}) = \hat{n}(\boldsymbol{r})[\hat{n}(\boldsymbol{r}') - \delta(\boldsymbol{r}-\boldsymbol{r}')].\end{aligned} \tag{7.6.4}$$

With $\hat{n}(\boldsymbol{r}) = \sum_{i=0}^{N} \delta(\boldsymbol{r}-\boldsymbol{r}_i)$. With this definition, we have:

$$\begin{aligned}\int \hat{n}(\boldsymbol{r})d^3r &= N \\ \int \hat{n}_2(\boldsymbol{r},\boldsymbol{r}')d^3r' &= (N-1)\hat{n}(\boldsymbol{r}) \\ \int \hat{n}_2(\boldsymbol{r},\boldsymbol{r}')d^3r'd^3r &= N(N-1)\hat{n}(\boldsymbol{r})\end{aligned} \tag{7.6.5}$$

The expectation value of $\hat{n}(\boldsymbol{r},\boldsymbol{r}')$ is the "two electron density function":

$$\Gamma(\boldsymbol{r},\boldsymbol{r}') = \left\langle \Psi_{gs} \middle| \hat{n}_2(\boldsymbol{r},\boldsymbol{r}') \middle| \Psi_{gs} \right\rangle \tag{7.6.6}$$

With the two-electron density function, the interaction energy is:

$$U = \frac{e^2}{2} \iint \frac{\Gamma(\boldsymbol{r},\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} d^3r d^3r' \tag{7.6.7}$$

This pair density function has the symmetry, positivity and normalization properties given by:

$$\begin{aligned}\Gamma(\boldsymbol{r},\boldsymbol{r}') &= \Gamma(\boldsymbol{r}',\boldsymbol{r}) \\ \Gamma(\boldsymbol{r},\boldsymbol{r}') &\geq 0 \\ \int \Gamma(\boldsymbol{r},\boldsymbol{r}')d^3r' &= (N-1)n(\boldsymbol{r}) \\ \int \Gamma(\boldsymbol{r},\boldsymbol{r}')d^3r &= (N-1)n(\boldsymbol{r}')\end{aligned} \tag{7.6.8}$$

$$\iint \Gamma(\boldsymbol{r},\boldsymbol{r}')d^3rd^3r' = (N-1)N$$

The normalization allows interpretation of $\frac{\Gamma(r.r')}{N(N-1)}$ as the probability density to find an electron at $\boldsymbol{r}$ and *another* electron at $\boldsymbol{r}'$. One property that is intuitively expected of $\Gamma(\boldsymbol{r},\boldsymbol{r}')$ is as the limit $|\boldsymbol{r}-\boldsymbol{r}'|\to\infty$ is approached electrons will gradually uncorrelate and $\Gamma(\boldsymbol{r},\boldsymbol{r}')$ collapse to the density product $n(\boldsymbol{r}_1)n(\boldsymbol{r}_2)$. Indeed, this is insight bears out in most cases:

$$\Gamma(\boldsymbol{r},\boldsymbol{r}') \to n(\boldsymbol{r})n(\boldsymbol{r}') \quad (|\mathbf{r}-\mathbf{r}'|\to\infty, \text{in most cases}), \tag{7.6.9}$$

but not always. For example, the ground state wavefunction of the Carbon atom $\Psi_{\mathrm{C}}(\boldsymbol{r}_1,\boldsymbol{r}_2,\dots)$ (we are neglecting to write spin indices for sake of notational simplicity) in the large $\boldsymbol{r}_1$ limit: for minimal energy reasons the remaining electrons will lower their energy to a maximal extent thus, the wave function should obey: $\Psi_{\mathrm{C}}(\boldsymbol{r}_1,\boldsymbol{r}_2,\dots)\to\sqrt{\frac{n(r_1)}{N}}\Psi_{\mathrm{C}^+,\mathbf{r}_1}(\boldsymbol{r}_2,\dots)$ where $\Psi_{\mathrm{C}^+,\mathbf{r}_1}(\boldsymbol{r}_2,\dots)$ is the ground state wave function of the cation C^+ and $\sqrt{\frac{n(r_1)}{N}}$ is the root of the propability to find an electron far at $\boldsymbol{r}_1$. Note however that this cation has a 3-fold degeneracy in its groundstate energy and thus for any finite $\boldsymbol{r}_1$, no matter how large, the $\Psi_{\mathrm{C}^+,\mathbf{r}_1}(\boldsymbol{r}_2,\dots)$ wave function is that degenerate wave function distorts in a certain fashion in correlation with the direction $\boldsymbol{r}_1/r_1$ (for more details see Phys. Rev. A **49**, 809 (1994) or J. Chem. Phys. **105**, 2798 (1996)).

We can also look at the *conditional probability density* to find an electron at $\boldsymbol{r}$ *given* that there is one at $\boldsymbol{r}'$ (this latter probability is $n(\boldsymbol{r}')/N_e$), given by

$$P(\boldsymbol{r}|\boldsymbol{r}') = \frac{\Gamma(\boldsymbol{r},\boldsymbol{r}')}{(N_e-1)n(\boldsymbol{r}')} \tag{7.6.10}$$

Obviously, if one integrates on $\boldsymbol{r}$ one gets unity. We can thus view:

$$n_{cond}(\boldsymbol{r}|\boldsymbol{r}') = (N_e - 1)P(\boldsymbol{r}|\boldsymbol{r}') = \frac{\Gamma(\boldsymbol{r},\boldsymbol{r}')}{n(\boldsymbol{r}')} \tag{7.6.11}$$

as a "conditional" density, the density at $\boldsymbol{r}$ of $N_e - 1$ electrons: all "other" electrons except that one electron is known to be at $\boldsymbol{r}'$. Indeed, upon integration over $\boldsymbol{r}$, we get, irrespective of $\boldsymbol{r}'$:

$$\int n_{cond}(\boldsymbol{r}|\boldsymbol{r}')d^3r = (N_e - 1) \tag{7.6.12}$$

Furthermore, we have for $|\boldsymbol{r}-\boldsymbol{r}'| \to \infty$:

$$n_{cond}(\boldsymbol{r}|\boldsymbol{r}') \to n(\boldsymbol{r}) \quad (|\mathbf{r}-\mathbf{r}'| \to \infty, \text{in most cases}), \tag{7.6.13}$$

This shows that the density far from the localized electron is unperturbed. Now, let us subtract from this conditional density the total N_e-electron density $n(\boldsymbol{r})$ and obtain the Fermi-Coulomb hole function:

$$n_{FC}(\boldsymbol{r}|\boldsymbol{r}') \equiv n_{cond}(\boldsymbol{r}|\boldsymbol{r}') - n(\boldsymbol{r}) \tag{7.6.14}$$

Since we localized an electron at $\boldsymbol{r}'$ the rest of the electrons will "rearrange" so as to be repelled from the stationary source. This will give us a "missing density" or "hole density", i.e. the charge density at $\boldsymbol{r}$ expelled by an electron at $\boldsymbol{r}'$. We expect the total charge of the hole is -1. Indeed plugging Eq. (7.6.14) into (7.6.12) we find:

$$\int n_{FC}(\boldsymbol{r}|\boldsymbol{r}')d^3r = -1. \tag{7.6.15}$$

Furthermore far from the hole center we have from Eqs. (7.6.13) and (7.6.14) :

$$\frac{n_{FC}(\boldsymbol{r}|\boldsymbol{r}')}{n(\boldsymbol{r})} \to 0 \quad (|\mathbf{r}-\mathbf{r}'| \to \infty, \text{in most cases}), \tag{7.6.16}$$

This shows that the FC hole decays faster than the density far from the system: for localized systems it is, in most cases, a highly localized overall singly charged distribution.

Now, because $\Gamma(\boldsymbol{r},\boldsymbol{r}') = n(\boldsymbol{r}')n_{cond}(\boldsymbol{r}|\boldsymbol{r}') = n(\boldsymbol{r}')\big(n(\boldsymbol{r}) + n_{FC}(\boldsymbol{r}|\boldsymbol{r}')\big)$, the Coulomb interaction energy can be written as:

$$U = \frac{e^2}{2}\iint \frac{n(\boldsymbol{r}')\big(n(\boldsymbol{r}) + n_{FC}(\boldsymbol{r}|\boldsymbol{r}')\big)}{|\boldsymbol{r}-\boldsymbol{r}'|} d^3r d^3r' \qquad (7.6.17)$$

And in terms of the FC hole:

$$U = E_H + \frac{e^2}{2}\iint \frac{n(\boldsymbol{r}')n_{FC}(\boldsymbol{r}|\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} d^3r d^3r' \qquad (7.6.18)$$

Thus the part of the interaction energy beyond the Hartree energy is the sum of all interaction energies $\epsilon_{FC}(\boldsymbol{r}') = \frac{e^2}{2}\int \frac{n_{FC}(\boldsymbol{r}|\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} d^3r$ between an electron at $\boldsymbol{r}'$ and its Fermi-Coulomb hole $n_{FC}(\boldsymbol{r}|\boldsymbol{r}')$. We will shortly see that the correlation energy adimits a similar analysis only with slightly modified quantities.

By using non-interacting electrons we can also pull out of the integral the exchange energy and write:

$$U = U_S + \frac{e^2}{2}\iint \frac{n(\boldsymbol{r}')n_C(\boldsymbol{r}|\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} d^3r d^3r' \qquad (7.6.19)$$

This leaves a Coulomb hole which is overall neutral. It too is localized. We discuss this in the section after next.

ii. The Fermi-Coulomb hole for harmonic electrons

Let us calculate these quantities for our 2-harmonic electrons in their ground state triplet (so we have both exchange and correlation). The pair density and density for the wave function in **Error! Reference source not found.** is:

$$\Gamma(x_1, x_2) = \frac{2}{\pi}\sqrt{\Omega_2^3\Omega_1} e^{-\frac{\Omega_1(x_1+x_2)^2+\Omega_2(x_1-x_2)^2}{2}}(x_1 - x_2)^2 \qquad (7.6.20)$$

The density can be obtained by integrating:

$$n(x) = \sqrt{\frac{8}{\pi}\frac{\sqrt{\Omega_2^3\Omega_1}}{(\Omega_1+\Omega_2)^{5/2}}}e^{-2\frac{\Omega_1\Omega_2}{\Omega_1+\Omega_2}x^2}\left(\Omega+\Omega_2+4x^2\Omega^2{}_{-}\right) \tag{7.6.21}$$

The density is plotted for several values of the correlation constant θ, $\cos\theta = \left(\frac{\gamma}{\omega}\right)^2$. This calculation is for $\omega = 1$:

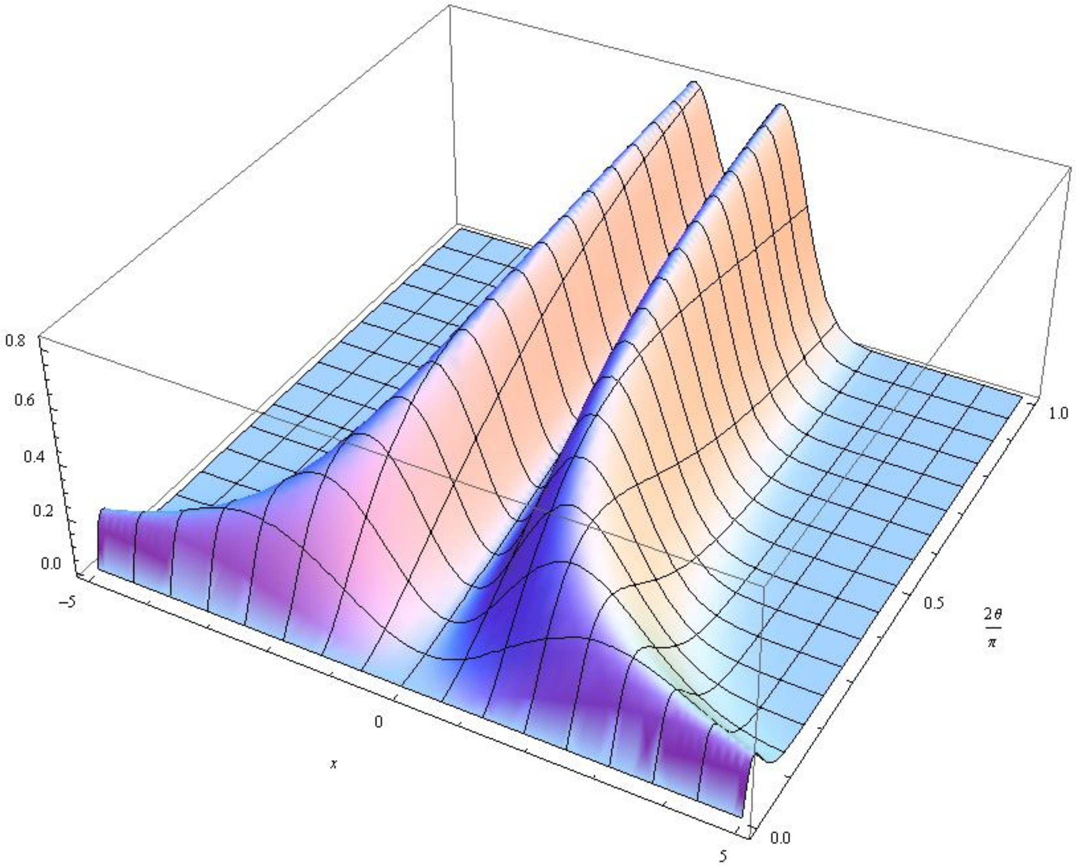


Figure VII-1: The 1-particle density, for a system of two harmonic fermions placed in a harmonic well in their triplet ground state for various interaction strengths. When $\theta = \frac{\pi}{2}$ there is no interaction and the dip in $x = 0$ is due to the "Pauli repulsion". As interaction grows the dip becomes deeper and broader.

We plot the conditional probability $p(x|x_1)$ for this system in Figure VII-2.

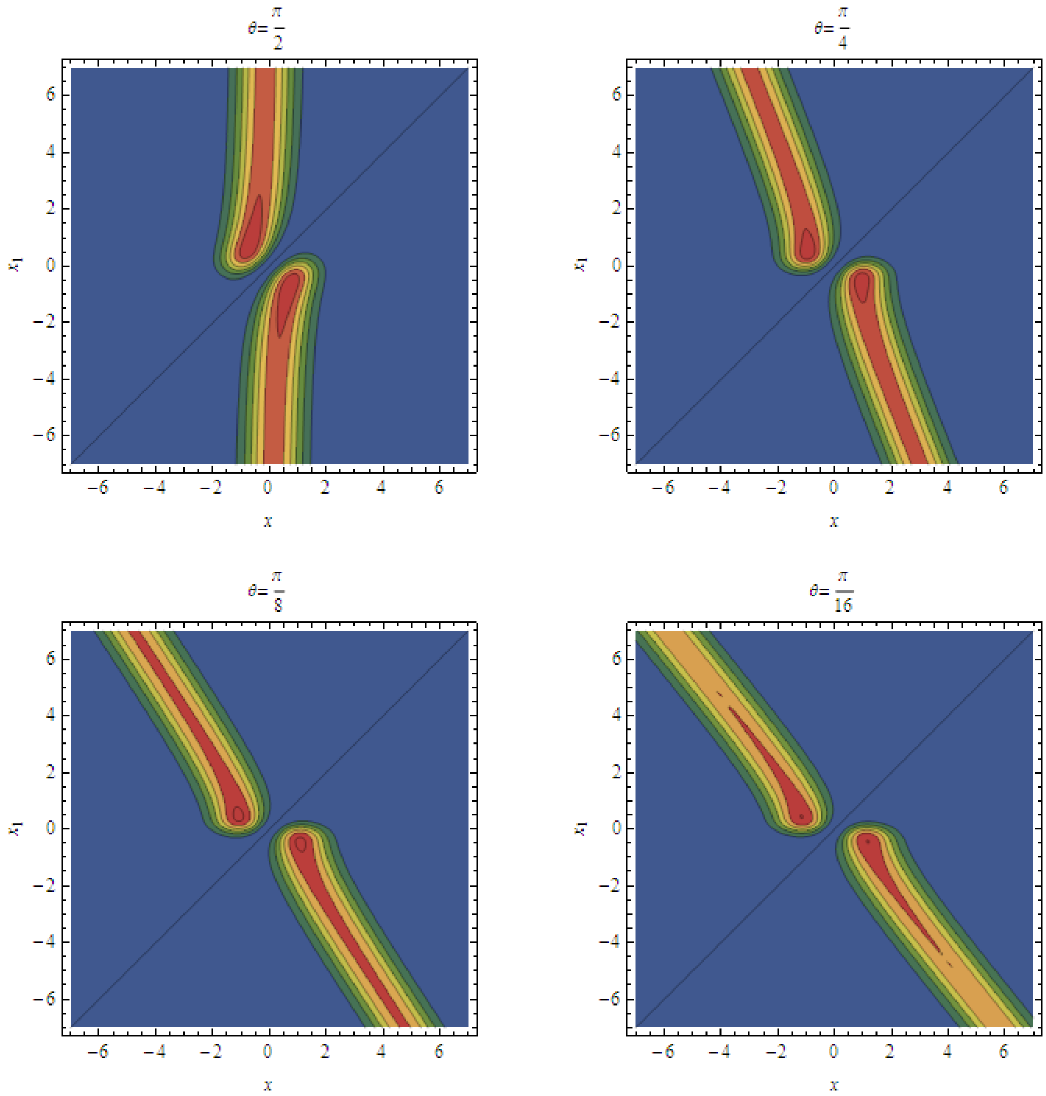


Figure VII-2: Contour plots for the conditional probability distribution $p(x|x_1)$ for a system of two Fermions in their triplet ground state for various interaction strengths. When $\theta = \frac{\pi}{2}$ there is no interaction and the only correlation is due to the Pauli principle. As interaction grows the probability distribution rotates by 45^o.

The XC hole is plotted next in Figure VII-3.

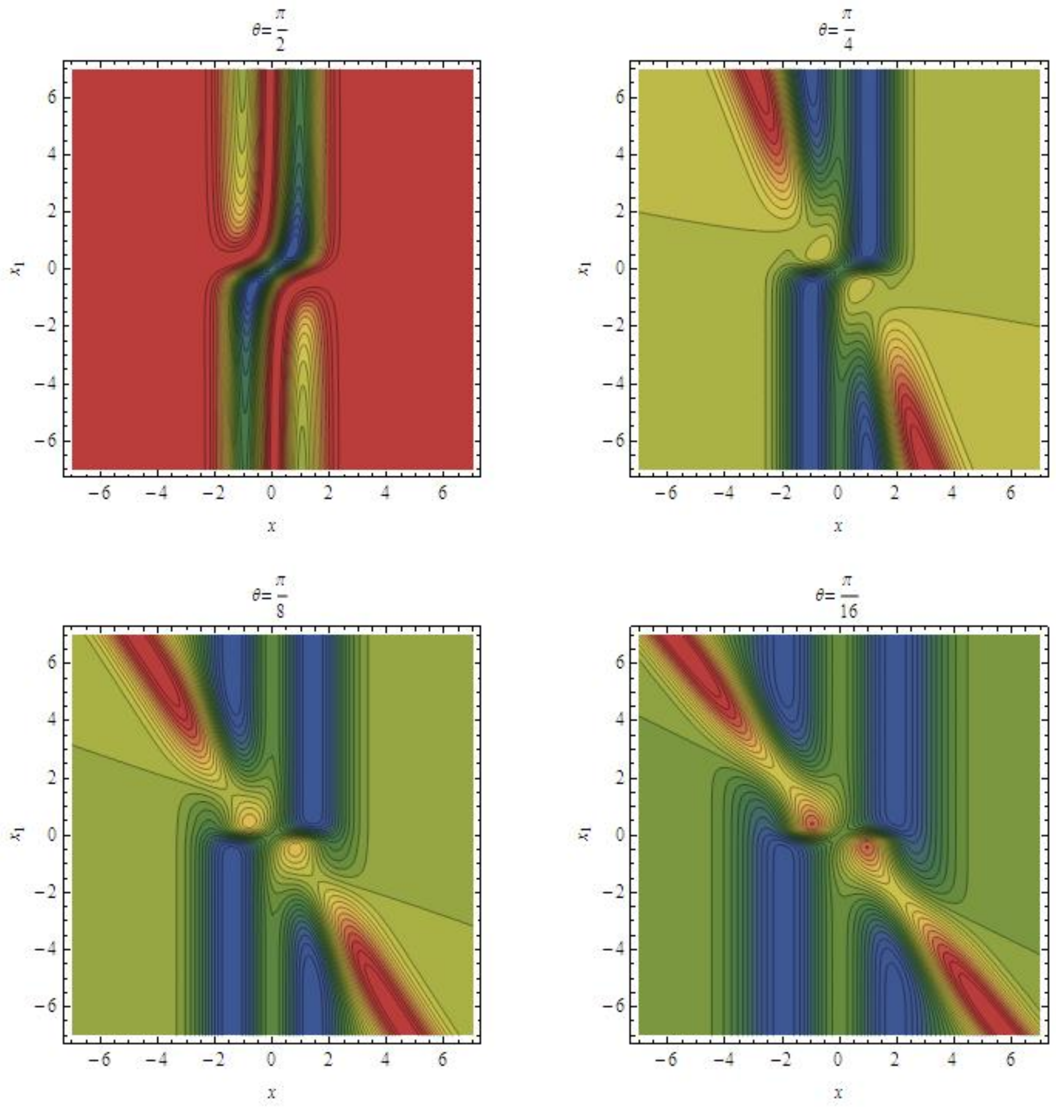


Figure VII-3: Contour plots for the FC hole $n_{XC}(x,x_1)$ for a system of two Fermions in their triplet ground state for various interaction strengths. When $\theta=\frac{\pi}{2}$ there is no interaction and the only correlation is due to the Pauli principle.

iii. The Fermi hole in the non-interacting system

Let us consider now the FC hole in the non-interacting system. Since there is no correlation in absence of interactions, we attribute the hole only to the exchange (Fermi) effects. A non-interacting system having the density $n(\boldsymbol{r})$ that has a closed shell Kohn-Sham determinant, composed of orthonormal orbitals $\phi_a(\boldsymbol{r})$, where 1 indicates spin up and -1 spin down.

$$\begin{aligned}\Gamma_S(\boldsymbol{r},\boldsymbol{r}') &= \langle \Phi[n]_{gs}|\hat{n}(\boldsymbol{r},\boldsymbol{r}')|\Phi[n]_{gs}\rangle \\ &= \sum_{a\neq b}[\phi_a(\boldsymbol{r})^2\phi_b(\boldsymbol{r}')^2 - \phi_a(\boldsymbol{r})\phi_b(\boldsymbol{r})\phi_b(\boldsymbol{r}')\phi_a(\boldsymbol{r}')] \\ &= \sum_{a,b}[\phi_a(\boldsymbol{r})^2\phi_b(\boldsymbol{r}')^2 - \phi_a(\boldsymbol{r})\phi_b(\boldsymbol{r})\phi_b(\boldsymbol{r}')\phi_a(\boldsymbol{r}')] \\ &= n(\boldsymbol{r})n(\boldsymbol{r}') - P(\boldsymbol{r},\boldsymbol{r}')^2\end{aligned} \tag{7.6.22}$$

Where the sum is over the orbitals in Φ_{gs}(the occupied KS orbitals) and we defined the density non-interacting matrix $P(\boldsymbol{r},\boldsymbol{r}') = \sum_a \phi_a(\boldsymbol{r})\phi_a(\boldsymbol{r}')$.

Exercise: Prove that

$$\int P(\boldsymbol{r},\boldsymbol{r}')^2 d^3r = n(\boldsymbol{r}') \tag{7.6.23}$$

Exercise: As a check, integrate $\Gamma_S(\boldsymbol{r},\boldsymbol{r}')$ over $\boldsymbol{r}$ and find:

$$\int \Gamma_S(\boldsymbol{r},\boldsymbol{r}')d^3r = n(\boldsymbol{r}')[N_e - 1] \tag{7.6.24}$$

The Fermi-conditional density is:

$$n(\boldsymbol{r}|\boldsymbol{r}') = n(\boldsymbol{r}) - \frac{P(\boldsymbol{r},\boldsymbol{r}')^2}{n(\boldsymbol{r}')} \tag{7.6.25}$$

And the Fermi-hole is:

$$n_F(\boldsymbol{r}|\boldsymbol{r}') = -\frac{P(\boldsymbol{r},\boldsymbol{r}')^2}{n(\boldsymbol{r}')} \tag{7.6.26}$$

It can be shown[7] that in most cases the density matrix $P(\boldsymbol{r},\boldsymbol{r}')$ decays exponentially as $|\boldsymbol{r}-\boldsymbol{r}'| \to \infty$, although this could be much slower than $n(\boldsymbol{r})$. Thus we may say**:**

$$n_F(\boldsymbol{r}|\boldsymbol{r}') \to 0 \quad (|\mathbf{r}-\mathbf{r}'| \to \infty, \text{in most cases}), \tag{7.6.27}$$

This is weaker than Eq. (7.6.16) for the total FC hole. This shows that $n_C = n_{FC} - n_F$ decays to zero in a similar but opposite way than $n_F(\boldsymbol{r}|\boldsymbol{r}')$:

$$n_F(\boldsymbol{r}|\boldsymbol{r}') \to -n_C(\boldsymbol{r}|\boldsymbol{r}') \quad (|\mathbf{r}-\mathbf{r}'| \to \infty, \text{in most cases}), \tag{7.6.28}$$

Based on Eq. (7.6.23) the Fermi hole carries all the charge of the FC hole:

$$\int n_F(\boldsymbol{r}|\boldsymbol{r}')d^3r = -1 \tag{7.6.29}$$

This allows one to say that it is the Fermi or "exchange"-hole in the non-interacting system that "carries the charge" of the exchange correlation-hole in the interacting system. Once the interacting system has been mapped onto the non-interacting system the Fermi-hole is easily calculated. This can be used to define the Coulomb hole by:

$$n_C(\boldsymbol{r}|\boldsymbol{r}') = n_{FC}(\boldsymbol{r}|\boldsymbol{r}') - n_F(\boldsymbol{r}|\boldsymbol{r}') \tag{7.6.30}$$

It has no total charge:

$$\int n_C(\boldsymbol{r}|\boldsymbol{r}')d^3r = 0 \tag{7.6.31}$$

The interaction energy can be written now as:

$$U = U_S + \frac{1}{2}\iint \frac{n(\boldsymbol{r}')n_C(\boldsymbol{r}|\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} d^3rd^3r' \tag{7.6.32}$$

Exercise: Compute the Fermi-hole function of the homogeneous electron gas

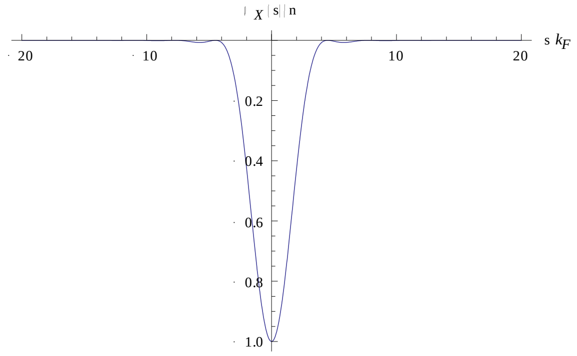
Solution: We already determined the density matrix (see Eq. **Error! Reference source not found.**)

$$P(s) = 3n\frac{j_1(sk_F)}{sk_F} \tag{7.6.33}$$

where $s = |\boldsymbol{r}-\boldsymbol{r}'|$ and $j_1(x) = \frac{\sin x - x\cos x}{x^2}$. The x-hole is of course independent of $\boldsymbol{r}$:

$$n_F^{HEG}(\boldsymbol{r};\boldsymbol{r}+\boldsymbol{s}) = -\frac{P(s)^2}{n} = -9n\frac{j_1(sk_F)^2}{(sk_F)^2} \tag{7.6.34}$$

Plotting shows the form of the HEG x-hole function:



Here $k_F^3 = 3\pi^2 n$ (unpolarized gas). Since $4\pi \int_0^\infty \frac{j_1(x)^2}{x} dx = \pi$, we find HEG exchange energy is, :

$$\begin{aligned}\frac{U_F}{N} &= \frac{1}{N}\frac{1}{2}\iint \frac{n(\boldsymbol{r})n_F^{HEG}(\boldsymbol{r};\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} d^3r d^3r' = \frac{1}{2}4\pi \int_0^\infty \frac{n_F^{HEG}(s)}{s} s^2 ds \\ &= -\frac{9n}{2k_F^2}4\pi \int_0^\infty \frac{j_1(x)^2}{x} dx = -\frac{3}{2\pi}k_F = -3\left(\frac{3}{8\pi}n\right)^{1/3}\end{aligned} \qquad (7.6.35)$$

This is indeed the LDA exchange energy per particle.

iv. The Adiabatic Connection

Having written down the relation between the interaction energy U and the XC hole, we still have no such relation for the correlation energy E_C. We now derive such a relation. Remember the correlation energy is defined as:

$$E_C[n] = T[n] - T_S[n] + (U[n] - U_S[n]) = T_C[n] + U_C[n] \qquad (7.6.36)$$

Given a ground-state electron density $n(\boldsymbol{r})$, consider a family of N_e-"electron" systems, with parameter $0 \le \lambda \le 1$, where:

$$\hat{H}_\lambda = \hat{T} + \int v_\lambda(\boldsymbol{r})\hat{n}(\boldsymbol{r})d^3r + \lambda\hat{U} \qquad (7.6.37)$$

The ground-state is denoted Ψ_λ. The potential $v_\lambda(\boldsymbol{r})$ is chosen in such a manner that the density at the ground-state wave function is $n(\boldsymbol{r})$, i.e.:

$$\langle \Psi_\lambda | \hat{n}(\boldsymbol{r}) | \Psi_\lambda \rangle = n(\boldsymbol{r}) \tag{7.6.38}$$

This is a generalization of the idea by Kohn and Sham, that the interacting electron system is mapped onto a non-interacting electron system with the same density. Except that now we map our system to a system of electrons with interaction $\lambda\hat{U}$. When $\lambda = 0$ we have the non-interacting system and $v_{\lambda=0}(\boldsymbol{r})$ is the Kohn-Sham potential $v_s(\boldsymbol{r})$ and we have:

$$E_0[n] = T_S[n] + \int v_0(\boldsymbol{r}) n(\boldsymbol{r}) d^3r \tag{7.6.39}$$

where $T_S[n]$ is the kinetic energy of non-interacting electrons. When $\lambda = 1$ we have the fully interacting system and $v_{\lambda=1}(\boldsymbol{r}) = v(\boldsymbol{r})$ is the actual external potential on the electron system and the energy is:

$$E_1[n] = E_v[n] = T[n] + \int v_1(\boldsymbol{r}) n(\boldsymbol{r}) d^3r + U[n] \tag{7.6.40}$$

We can also define the obvious quantities:

$$E_\lambda[n] = T_\lambda[n] + \int v_\lambda(\boldsymbol{r}) n(\boldsymbol{r}) d^3r + U_\lambda[n] \tag{7.6.41}$$

From Eq. (7.6.36):

$$\begin{aligned} E_1 - E_0 &= \int [v_1(\boldsymbol{r}) - v_0(\boldsymbol{r})] n(\boldsymbol{r}) d^3r + U_S[n] + E_C[n] \\ E_\lambda - E_0 &= \int [v_\lambda(\boldsymbol{r}) - v_0(\boldsymbol{r})] n(\boldsymbol{r}) d^3r + \lambda U_S[n] + E_{C,\lambda}[n] \end{aligned} \tag{7.6.42}$$

With:

$$E_{C,\lambda}[n] = \langle \Psi_\lambda | \hat{T} + \lambda\hat{U} | \Psi_\lambda \rangle - \langle \Psi_0 | \hat{T} + \lambda\hat{U} | \Psi_0 \rangle$$

Now, the ground-state energy of the intermediately interacting electrons obeys, by Hellmann-Feynman's theorem:

$$\frac{d}{d\lambda}E_\lambda = \left\langle \Psi_\lambda \left| \frac{d}{d\lambda}\hat{H}_\lambda \right| \Psi_\lambda \right\rangle = \int \left[\frac{d}{d\lambda} v_\lambda(\boldsymbol{r})\right] n(\boldsymbol{r}) d^3r + \langle \Psi_\lambda | \hat{U} | \Psi_\lambda \rangle \qquad (7.6.43)$$

From the second equation then:

$$\frac{d}{d\lambda}E_{C,\lambda}[n] = \langle \Psi_\lambda | \hat{U} | \Psi_\lambda \rangle - U_S[n] = U_{C,\lambda}[n] \qquad (7.6.44)$$

This expression is the differential form of the adiabatic connection. If we integrate it with respect to λ from 0 to 1, we find:

$$E_C[n] = \int_0^1 \langle \Psi_{\lambda'} | \hat{U} | \Psi_{\lambda'} \rangle d\lambda' - U_S[n]. \qquad (7.6.45)$$

This formula is called the "adiabatic connection" formula for the XC energy [8]. We may write: $E_{C,\lambda} = T_{C,\lambda} + \lambda U_{C,\lambda}$. Then $\frac{d}{d\lambda}E_{C,\lambda}[n] = \frac{d}{d\lambda}T_{C,\lambda} + U_{C,\lambda} + \lambda \frac{d}{d\lambda}U_{C,\lambda}$ and so

$$\frac{dT_{C,\lambda}[n]}{d\lambda} + \lambda \frac{dU_{C,\lambda}[n]}{d\lambda} = 0. \qquad (7.6.46)$$

We can rewrite $U_{C,\lambda}$ in terms of the correlation hole. Indeed, if $n_C^\lambda(\boldsymbol{r}|\boldsymbol{r}')$, is the correlation hole for the λ system then using (7.6.32):

$$U_{C,\lambda}[n] = \frac{1}{2}\iint \frac{n(\boldsymbol{r}') n_C^\lambda(\boldsymbol{r}|\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} d^3r d^3r' \qquad (7.6.47)$$

From which:

$$E_C[n] = \frac{1}{2}\iint \frac{n(\boldsymbol{r}') \bar{n}_C(\boldsymbol{r}|\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} d^3r' d^3r \qquad (7.6.48)$$

And we see that the correlation energy can be obtained from the the λ-averaged Coulomb hole, called the correlation hole (since it is associated with the correlation energy):

$$\bar{n}_C(\boldsymbol{r}|\boldsymbol{r}') = \int_0^1 n_C^\lambda(\boldsymbol{r}|\boldsymbol{r}')d\lambda \tag{7.6.49}$$

Note that because $\int n_C^\lambda(\boldsymbol{r},\boldsymbol{r}')d^3r = 0$, we have also:

$$\int \bar{n}_C(\boldsymbol{r}|\boldsymbol{r}')d^3r = 0 \tag{7.6.50}$$

It is interesting that the correlation energy, like to Coulomb energy, can be represented as a Coulomb interaction of the density and a hole as in Eq. (7.6.48). Note however that the relevant hole as a coupling-constant (λ) averaged correlation hole and not the Coulomb hole itself.

Let us discuss one of the important consequences of Eq. (7.6.50) i.e. that the total charge of the correlation hole is zero for localized charge systems. If we rewrite the correlation energy as:

$$E_C[n] = \frac{1}{2}\iint \frac{n(\boldsymbol{r}')\,\bar{n}_C(\boldsymbol{r}|\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}d^3r'd^3r \tag{7.6.51}$$

We see that the correlation energy can be written as

$$E_C[n] = \int \epsilon_C(\boldsymbol{r}')n(\boldsymbol{r}')d^3r' \tag{7.6.52}$$

where:

$$\epsilon_C(\boldsymbol{r}') = \frac{e^2}{2}\int \frac{\bar{n}_C(\boldsymbol{r}|\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}d^3r \tag{7.6.53}$$

(Note that this is just a suggestion since adding to $\epsilon_C(\boldsymbol{r}')$ any function $\Delta\epsilon_C(\boldsymbol{r}')$ for which $\int \Delta\epsilon_C(\boldsymbol{r}')n(\boldsymbol{r}')d^3r' = 0$ will give the same correlation energy). Because for a fix $\boldsymbol{r}'$ $\bar{n}_C(\boldsymbol{r}|\boldsymbol{r}')$ is an oveall neutral charge density in $\boldsymbol{r}$ space its "Coulombic potential" $\frac{\epsilon_C(r')}{e}$ is expected to decay relatively fast for r′(faster than $1/r'$).

H. Derivative Discontinuity in the exchange correlation potential functional