

2. Hartree-Fock formalism

2.1 Slater determinants

One speaks of the Hartree-Fock (HF) approximation and of the HF method. The former is also called the self-consistent field approximation, or mean field approximation. Its meaning is that every electron moves due to the action of an electrostatic field created by the presence of all other electrons (plus external field sources). In this sense it is close to what we applied while deriving the Thomas-Fermi formalism. The difference is that we won't deal with the charge density from the very beginning. Instead, we'll try to trace what happens with the wave functions. We'll come back to the concept of density at the end of the route.

The HF approximation, or the mean-field approximation, is an essential part of the apparatus of theory, often used to solve different models. It introduces an approximation that sometimes allows to solve a certain physical problem analytically.

The HF method is more about solving complex many-body problems numerically. In doing so, one essentially applies the self-consistent field approximation. But there are many approaches that pursue this way – start from a trial wavefunction, calculate the potential generated by corresponding charge distribution, etc. Essentially, the starting point is again the stationary Schrödinger equation (1.1). What is specific for the HF method is the Ansatz used to represent a many-body wavefunction. It is, in the HF method the wave function is searched for as a Slater determinant constructed from one-particle wave functions. Lets discuss what this is. If we consider the simplest case of particles which *do not interact*, the probability to find each particle near certain place in space is the same and independent on that of other particles. One would expect the density $\rho(\mathbf{r})$ to be simply N times the one-particle density,

$$\rho(\mathbf{r}) = N\varphi(\mathbf{r}) . \quad (2.1)$$

On the other side, the density is related with many-body wavefunction via Eq.(1.3). A possible consistent *Ansatz* is to construct the many-body wavefunction as a product of (normalized) individual wave functions, then (2.1) will obviously hold:

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \varphi_1(\mathbf{r}_1)\varphi_2(\mathbf{r}_2) \dots \varphi_N(\mathbf{r}_N) . \quad (2.2)$$

This *Ansatz* is known; it leads to the Hartree method, not in use any more, because it neglects an important property of electrons – that they are Fermi particles, and the wavefunction of a system of fermions must be antisymmetric with respect to interchanging any pair of particles:

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_k, \dots, \mathbf{r}_l, \dots, \mathbf{r}_N) = -\Psi(\mathbf{r}_1, \dots, \mathbf{r}_l, \dots, \mathbf{r}_k, \dots, \mathbf{r}_N) . \quad (2.3)$$

We emphasize here that the *position* of an argument in Ψ fixes the number of particular electron, and the argument value – the actual coordinate of that electron. Obviously

enough, the wave function constructed according to (2.2) does not possess this property. Actually, it does not have any particular symmetry property with respect to interchanging particles. But we can easily force the wave function to obey Eq.(2.3); for this, we simply take products like (2.2), interchange there positions of all particles pairwise and construct the combinations which are *a priori* antisymmetric. This is easy to do for two particles:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} [\varphi_1(\mathbf{r}_1)\varphi_2(\mathbf{r}_2) - \varphi_1(\mathbf{r}_2)\varphi_2(\mathbf{r}_1)] . \quad (2.4)$$

The factor $1/\sqrt{2}$ is introduced in order to keep the normalization. If our one-particle wave functions are normalized to 1, i.e., the probability to find one electron somewhere in space

$$\int |\varphi_i(\mathbf{r})|^2 d\mathbf{r} = 1 , \quad (2.5)$$

then the probability to find two particles anywhere in space must be 1, and indeed

$$\begin{aligned} \int |\Psi(\mathbf{r}_1, \mathbf{r}_2)|^2 d\mathbf{r}_1 d\mathbf{r}_2 &= \frac{1}{2} \left\{ \underbrace{\int |\varphi_1(\mathbf{r}_1)|^2 d\mathbf{r}_1}_{=1} \underbrace{\int |\varphi_2(\mathbf{r}_1)|^2 d\mathbf{r}_2}_{=1} - \right. \\ &\quad - \underbrace{\left[\int \varphi_2^*(\mathbf{r}_1)\varphi_1(\mathbf{r}_1)d\mathbf{r}_1 \right]}_{=0} \underbrace{\left[\int \varphi_1^*(\mathbf{r}_2)\varphi_2(\mathbf{r}_1)d\mathbf{r}_2 \right]}_{=0} - \\ &\quad - \underbrace{\left[\int \varphi_1^*(\mathbf{r}_1)\varphi_2(\mathbf{r}_1)d\mathbf{r}_1 \right]}_{=0} \underbrace{\left[\int \varphi_2^*(\mathbf{r}_2)\varphi_1(\mathbf{r}_2)d\mathbf{r}_2 \right]}_{=0} + \\ &\quad \left. + \underbrace{\int |\varphi_2(\mathbf{r}_1)|^2 d\mathbf{r}_1}_{=1} \underbrace{\int |\varphi_1(\mathbf{r}_2)|^2 d\mathbf{r}_2}_{=1} \right\} = 1 . \end{aligned}$$

In doing so, we assumed that individual one-particle wavefunctions are all orthogonal. This is indeed the case if they are solutions of the same Hamilton operator. If they are not – for some reason – but still form the complete basis of solutions to the corresponding one-particle problem, they can be one by one orthogonalized before proceeding further with the construction of the many-body wavefunction.

How do we proceed if there are more than 2 electrons? There are $N!$ possibilities to interchange them. We sum up over all of them, try all possibilities to interchange every two electrons and write down antisymmetric terms like in Eq.(2.4). This results in a fully antisymmetric wave function:

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \sum_P \text{sign}(P) \cdot \varphi_{P1}(\mathbf{r}_1) \varphi_{P2}(\mathbf{r}_2) \dots \varphi_{PN}(\mathbf{r}_N) . \quad (2.6)$$

P runs over all permutations of electrons, $\text{sign}(P)=1$ for even permutations and $\text{sign}(P)=-1$ for odd permutations.

It is common and convenient to write down the wavefunctions as determinants, because (2.6) is similar to how the determinant of a matrix is determined, and that's why the wave

function of this form is called Slater determinant:

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(\mathbf{r}_1) & \cdots & \varphi_1(\mathbf{r}_N) \\ \vdots & & \vdots \\ \varphi_N(\mathbf{r}_1) & \cdots & \varphi_N(\mathbf{r}_N) \end{vmatrix}. \quad (2.7)$$

The determinant form helps to illustrate important properties of a many-particle wavefunction. Each line corresponds to a certain one-electron state, and each column – to a certain position in space, among N positions $\mathbf{r}_1, \dots, \mathbf{r}_N$ of particles we consider. The interchange of either two rows or two columns means that we interchanged two particles; the wave function then changes sign by construction. Moreover, if there happen two identical lines or two identical columns, it means that two particles share the same spatial coordinates; the determinant then equals zero, meaning that such situation is physically impossible.

Actually, the latter is only true if two electrons in question have the same spin direction; otherwise, they can well share the same cell in the same phase space, i.e. have the same one-particle wave function and the same spatial coordinate. In order to allow for that, we introduce a generalized coordinate incorporating position and spin, $x = \{\mathbf{r}, \sigma\}$, and we'll write $\int dx \dots$ for $\sum_{\sigma} \int d\mathbf{r} \dots$ then (2.7) must be written as

$$\Phi(x_1, \dots, x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(x_1) & \cdots & \varphi_1(x_N) \\ \vdots & & \vdots \\ \varphi_N(x_1) & \cdots & \varphi_N(x_N) \end{vmatrix}. \quad (2.8)$$

We shall keep for Slater determinants a special notation Φ , to distinguish them from general-form $\Psi(x_1, \dots, x_N)$.

So far, we concentrated on symmetry properties of a many-body wavefunction, and we did not specify the shape of one-particle wavefunctions which constitute a Slater determinant. They could be taken from the solution of a corresponding one-electron problem (i.e., neglecting the interaction between the electrons), but it will be hardly a good approximation to Ψ with interaction. What we'll do next is to search for the “best” one-electron wavefunctions $\varphi(x)$ which will allow to construct the “best” approximation to the “true” many-body wavefunction, keeping the determinantal form (2.8) for our approximations to Ψ . As a criterion for the “best” functions, we'll rely on the variational principle. As in the course of deriving the Thomas-Fermi equation, we'll search for those individual φ 's which minimize the total energy.

How is all this justified? How do we know that the wave function of the form (2.8) is a reasonable one? So far, we only used Slater determinants as an “Ansatz” in order to achieve the antisymmetry of the many-body wave function, without any reference to its other properties. The importance of Slater determinants lies in the fact that, for a given number of electrons N , the Slater determinants (constructed from all possible one-electron functions) form a complete basis set. In other words, if we have the Hilbert space of one-particle wavefunctions $\mathbf{H}(1)$, then the Hilbert space of many-body wavefunctions is obviously a direct product of one-particle Hilbert spaces:

$$\mathbf{H}(N) = \underbrace{\mathbf{H}(1) \otimes \mathbf{H}(1) \otimes \dots \otimes \mathbf{H}(1)}_N \quad (2.9)$$

It means e.g. that any many-body wavefunction can be expanded into a sum of products of appropriate one-particle functions:

$$\Psi(x_1, \dots, x_N) = \sum_{\nu_1 \nu_2 \dots \nu_N} a_{\nu_1 \nu_2 \dots \nu_N} \varphi_{\nu_1}(x_1) \varphi_{\nu_2}(x_2) \dots \varphi_{\nu_N}(x_N); \quad (2.10)$$

It can be shown that the basis of N -particle Slater determinants (constructed from all possible one-electron wavefunctions in $\mathbf{H}(1)$) is a complete basis in $\mathbf{H}(N)$, i.e. *any* anti-symmetric N -particle wavefunction can be expanded over it:

$$\Psi(x_1 \dots x_N) = \sum_{\mu} C_{\mu} \Phi(x_1 \dots x_N). \quad (2.11)$$

This is the so-called theorem of completeness. It emphasizes the importance of Slater determinants in the treatment of many-electron systems.

Now, the HF approach assumes that from the expansion (2.11) one keeps only one term, but the possible best one. In the search for the “best” Slater determinant, we vary the constituent $\varphi_i(x_i)$ functions.

2.2 Derivation of the HF equations

We start from the Hamiltonian of a many-body system, as in (1.1). We only write it down in a form that emphasizes the difference between one-particle and two-particle operators:

$$\mathcal{H} = \sum_{i=1}^N \left[-\frac{\hbar^2}{2m} \nabla_i^2 + u(x_i) \right] + \frac{1}{2} \sum_{i \neq j}^N v(x_i, x_j). \quad (2.12)$$

∇_i differentiates with respect to coordinates of the i th electron; $u(x_i)$ is one-electron operator that can typically be the field of a nucleus (or nuclei) in an atom (or a molecule), situated at R_{α} :

$$u(x_i) = \sum_{\alpha} \frac{Z_{\alpha} e}{|\mathbf{r}_i - \mathbf{R}_{\alpha}|}$$

independently on spin, but it can be spin-dependent as well (e.g., an external magnetic field). $v(x_i, x_j)$ incorporates all interactions which may depend on the coordinates (and spins) within each particle pair; in the following, it will be everywhere the Coulomb interaction between two electrons:

$$v(x_i, x_j) = \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}.$$

We construct the total energy as the expectation value of this Hamiltonian, $\langle \Phi | \mathcal{H} | \Phi \rangle$, and minimize it in a variational approach – similarly to how we have it done in the Thomas-Fermi part – under considering the normalization condition:

$$\frac{\delta}{\delta \varphi_{\alpha}^*(x)} \left[\langle \Phi | \mathcal{H} | \Phi \rangle - \sum_{i=1}^N \varepsilon_i \int dy \varphi_i(y) \varphi_i^*(y) \right] = 0. \quad (2.13)$$

The Lagrange multipliers ε_i take care of the normalization of each one-particle function $\varphi_i(x)$ separately. Using (2.6), $\langle \Phi | \mathcal{H} | \Phi \rangle$ becomes:

$$\begin{aligned} \langle \Phi | \mathcal{H} | \Phi \rangle &= \frac{1}{N!} \sum_{\nu\mu} \text{sign}(\nu)\text{sign}(\mu) \int dx_1 \dots x_N \varphi_{\nu 1}^*(x_1) \dots \varphi_{\nu N}^*(x_N) \left\{ \sum_{i=1}^N \left[-\frac{\hbar^2}{2m} \nabla_i^2 + u(x_i) \right] \right. \\ &\quad \left. + \frac{1}{2} \sum_{i \neq j}^N v(x_i, x_j) \right\} \varphi_{\nu 1}(x_1) \dots \varphi_{\nu N}(x_N). \end{aligned}$$

Let us discuss the effect of one-particle and two-particle contributions in the Hamiltonian separately. The one-particle operator selects only functions with the argument x_i ; the rest is integrated over variables different from x_i . The integrals $\int dx_k \varphi_{\nu k}^*(x_k) \varphi_{\mu k}(x_k)$ give 1 if permuted indices $\nu k = \mu k$ and zero otherwise; in other words, this condition works as $\delta_{\nu\mu}$ under the double sum over permutations. Since only identical permutations $\nu = \mu$ contribute, $\text{sign}(\nu) \cdot \text{sign}(\mu) = 1$ in all terms, independently on whether the permutation in question is odd or even; one sum over permutations is lifted, and the remaining one contains $N!$ terms, all permuting the index i of the one-particle wave function. Taken together with the summation in i , the sum over permutations gives simply a sum over orbital numbers 1 to N , each number appearing $N!$ times. The result is:

$$\left[\begin{array}{l} \text{one-particle} \\ \text{contribution} \end{array} \text{ to } \langle \Phi | \mathcal{H} | \Phi \rangle \right] = \sum_{i=1}^N \int dx \varphi_i^*(x) \left[-\frac{\hbar^2}{2m} \nabla^2 + u(x) \right] \varphi_i(x). \quad (2.14)$$

Similarly in the two-particle part, the integration over variables *not* appearing in the two-particle interaction term gives 1 whenever the indices of φ^* and φ , each obtained by its corresponding permutation, turn out to be equal. This reduces the sum to:

$$\begin{aligned} \left[\begin{array}{l} \text{two-particle} \\ \text{contribution} \end{array} \text{ to } \langle \Phi | \mathcal{H} | \Phi \rangle \right] &= \frac{1}{N!} \frac{1}{2} \sum_{i \neq j}^N \sum_{\nu\mu} \text{sign}(\nu)\text{sign}(\mu) \times \\ &\quad \times \int dx_i dx_j \varphi_{\nu i}^*(x_i) \varphi_{\nu j}^*(x_j) v(x_i, x_j) \varphi_{\mu i}(x_i) \varphi_{\mu j}(x_j). \end{aligned}$$

Since all functions but two have been already used in non-zero terms, there are only two possibilities how the indices ν_i, μ_j may relate:

- 1) $\nu_i = \mu_i$ and $\nu_j = \mu_j \Rightarrow \nu$ and μ are identical, $\text{sign}(\nu) \cdot \text{sign}(\mu) = 1$;
- 2) $\nu_i = \mu_j$ and $\nu_j = \mu_i \Rightarrow \mu$ is identical to ν , with subsequent interchanging of functions i and j ; $\text{sign}(\nu) \cdot \text{sign}(\mu) = -1$.

In both cases, one can introduce $\delta_{\nu\mu}$ and lift one summation over permutations, and the second summation produces $N!$ identical terms, resulting in:

$$\begin{aligned} \left[\begin{array}{l} \text{two-particle} \\ \text{contribution} \end{array} \text{ to } \langle \Phi | \mathcal{H} | \Phi \rangle \right] &= \frac{1}{2} \sum_{i \neq j}^N \int dx dy \left[\varphi_i^*(x) \varphi_j^*(y) \varphi_i(x) \varphi_j(y) - \right. \\ &\quad \left. \varphi_i^*(x) \varphi_j^*(y) \varphi_i(y) \varphi_j(x) \right] v(x, y). \quad (2.15) \end{aligned}$$

Summarizing, the function to be varied in (2.13) is:

$$\begin{aligned}
& \left[\langle \Phi | \mathcal{H} | \Phi \rangle - \sum_{i=1}^N \varepsilon_i \int dy \varphi_i(y) \varphi_i^*(y) \right] = \sum_{i=1}^N \int dx \varphi_i^*(x) \left[-\frac{\hbar^2}{2m} \nabla^2 + u(x) \right] \varphi_i(x) + \\
& + \frac{1}{2} \sum_{i \neq j}^N \int dx dy \left[\varphi_i^*(x) \varphi_j^*(y) \varphi_i(x) \varphi_j(y) - \varphi_i^*(x) \varphi_j^*(y) \varphi_i(y) \varphi_j(x) \right] v(x, y) - \\
& - \sum_{i=1}^N \varepsilon_i \int \varphi_i^*(x) \varphi_i(x) dx .
\end{aligned} \tag{2.16}$$

Its variation in $\delta\varphi_\alpha^*(x)$ gives:

$$\begin{aligned}
\delta[\dots] &= \int dx \delta\varphi_\alpha^*(x) \left\{ \left[-\frac{\hbar^2}{2m} \nabla^2 + u(x) \right] \varphi_\alpha(x) + \right. \\
& \left. + \sum_{j \neq \alpha} \int dy \left[\varphi_j^*(y) \varphi_\alpha(x) \varphi_j(y) - \varphi_j^*(y) \varphi_\alpha(y) \varphi_j(x) \right] v(x, y) - \varepsilon_\alpha \varphi_\alpha(x) \right\} = 0 .
\end{aligned}$$

The factor $\frac{1}{2}$ in front of the two-particle term disappears because the one-particle function being varied, φ_α^* , may coincide with both φ_i^* and φ_j^* . The condition $\delta[\dots] = 0$ for arbitrary $\delta\varphi_\alpha^*(x)$ leads to the HF equation(s):

$$\begin{aligned}
& \left[-\frac{\hbar^2}{2m} \nabla^2 + u(x) + \sum_{j \neq \alpha} \int dy v(x, y) \varphi_j^*(y) \varphi_j(y) \right] \varphi_\alpha(x) - \\
& - \sum_{j \neq \alpha} \int dy v(x, y) \varphi_j^*(y) \varphi_j(x) \varphi_\alpha(y) = \varepsilon_\alpha \varphi_\alpha(x) .
\end{aligned} \tag{2.17}$$

The term

$$\sum_{j \neq \alpha} \int dy v(x, y) \varphi_j^*(y) \varphi_j(y)$$

has a clear meaning of a *Coulomb* potential which acts on the electron in \mathbf{r} due to the presence of all other electrons. The next sum which can be formally represented as

$$- \sum_{j \neq \alpha} \int dy v(x, y) \frac{\varphi_j^*(y) \varphi_\alpha^*(x) \varphi_\alpha(y) \varphi_j(x)}{\varphi_\alpha^*(x) \varphi_\alpha(x)} \varphi_\alpha(x) \tag{2.18}$$

introduces the *exchange* potential acting effectively on the one-particle function in question, $\varphi_\alpha(x)$; it is a correction to the Coulomb potential and is due to the antisymmetry of the many-particle wave function. This term depends on the unknown function $\varphi_\alpha(x)$ itself.

The HF equations is a system of integro-differential equations, which couple N functions. The solution is typically done by iterations. With all functions $\varphi_\alpha(x)$ found, the one-determinant many-body wavefunction can be constructed.

2.3 Formulation in terms of density and density matrix

Note that the requirement $j \neq \alpha$ can be dropped in (2.17), because for $j = \alpha$ the Coulomb and exchange terms exactly cancel. The summation in j is over occupied orbitals. With the condition $j \neq \alpha$ lifted, the sum in the Coulomb term $\sum_j \varphi_j^*(x) \varphi_j(x)$ gives the particle density defined by Eq. (1.3). Let us show it. In doing so, we'll generalize (1.3) as depending on x , i.e., our density will be \mathbf{r} -dependent and have a certain spin index. Using the determinant form of the many-body wave function,

$$\begin{aligned} & \int \Psi^*(x, x_2, \dots, x_N) \Psi(x, x_2, \dots, x_N) dx_2 \dots dx_N = \\ &= \frac{1}{N!} \sum_{\nu\mu} \text{sign}(\nu) \text{sign}(\mu) \varphi_{\nu 1}^*(x) \varphi_{\mu 1}(x) \left[\int \varphi_{\nu 2}^*(x_2) \varphi_{\mu 2}(x_2) dx_2 \right] \dots \left[\int \varphi_{\nu N}^*(x_N) \varphi_{\mu N}(x_N) dx_N \right]. \end{aligned}$$

The integrals over $x_2 \dots x_N$ are non-zero only if all $\nu i = \mu i$ (and are =1 in this case), due to orthonormality of one-electron functions. This demands in non-zero terms to be $\nu 1 = \mu 1$ as well and hence the permutations ν and μ to be identical, that lifts one sum in permutations. Then

$$\int \Psi^*(x, x_2, \dots, x_N) \Psi(x, x_2, \dots, x_N) dx_2 \dots dx_N = \frac{1}{N!} \sum_{\nu} \varphi_{\nu}^*(x) \varphi_{\nu}(x).$$

The sum over permutations includes $N!$ terms, among them N that permute the first index and, for each of them, $(N-1)!$ possibilities to permute other indices, which are however not anymore explicitly present. Hence

$$\sum_{\nu} \varphi_{\nu 1}^*(x) \varphi_{\nu 1}(x) = \sum_j (N-1)! \varphi_j^*(x) \varphi_j(x).$$

Considering the factor N in the definition of $\rho(\mathbf{r})$, Eq. (1.3), one arrives at

$$\rho(x) = \sum_j \varphi_j^*(x) \varphi_j(x) \quad (2.19)$$

in the HF formalism. So, the Coulomb term in the HF equation (2.17) can be transformed to explicitly include the (spin)-density. The spin component is implicitly present in $x = \{\mathbf{r}, \sigma\}$. If we wish to express the density irrespectively of spin, it will suffice to sum up over spin components in x , i.e.,

$$\rho(\mathbf{r}) = \rho(\mathbf{r}, \uparrow) + \rho(\mathbf{r}, \downarrow).$$

Now, if we do a similar trick with the exchange term, it will be reduced to the form containing the *density matrix* $\gamma(x; y)$. The definition of the latter is

$$\gamma(x; y) = N \int \Psi^*(y, x_2, \dots, x_N) \Psi(x, x_2, \dots, x_N) dx_2 \dots dx_N, \quad (2.20)$$

so that

$$\rho(x) = \gamma(x; x). \quad (2.21)$$

We follow exactly the same arguments as for $\rho(x)$, just keeping y different from x , and arrive at

$$\gamma(x; y) = \sum_j \varphi_j^*(y) \varphi_j(x) . \quad (2.22)$$

The HF equation (2.17) then transforms into:

$$-\frac{\hbar^2}{2m} \nabla^2 + u(x) + \int dy v(x, y) \rho(y) \cdot \varphi_\alpha(x) - \int dy v(x, y) \gamma(x; y) \varphi_\alpha(y) = \varepsilon_\alpha \varphi_\alpha(x) . \quad (2.23)$$

This can be looked at as an (integro-differential) operator acting on each one-particle function $\varphi_\alpha(x)$:

$$\hat{h}_{\text{HF}} \varphi_\alpha(x) = \varepsilon_\alpha \varphi_\alpha(x) ; \quad (2.24)$$

$$\hat{h}_{\text{HF}} = -\frac{\hbar^2}{2m} \nabla^2 + u(x) + \int v(x, y) \rho(y) dy - \int v(x, y) \gamma(x; y) \underbrace{\quad}_{\quad} dy \quad (2.25)$$

is called the Fock operator. It is the same for all orbitals and is hermitian. In order to show that, we construct matrix elements of it between any functions f and g from the same Hilbert space as one-electron functions:

$$\begin{aligned} \langle f | \hat{h}_{\text{HF}} | g \rangle &= -\frac{\hbar^2}{2m} \int dx f^*(x) \nabla^2 g(x) + \int dx f^*(x) u(x) g(x) + \\ &+ \int dx f^*(x) g(x) \int dy v(x, y) \rho(y) - \int dx f^*(x) \int dy v(x, y) \gamma(x; y) g(y) ; \end{aligned}$$

on the other hand, using $\rho^*(x) = \rho(x)$, $\gamma^*(x; y) = \gamma(y; x)$, $v^*(x, y) = v(x, y) = v(y, x)$,

$$\begin{aligned} (\langle g | \hat{h}_{\text{HF}} | f \rangle)^* &= -\frac{\hbar^2}{2m} \int dx g(x) \nabla^2 f^*(x) + \int dx g(x) u(x) f^*(x) + \\ &+ \int dx g(x) f^*(x) \int dy v(x, y) \rho(y) - \int dx g(x) \int dy v(x, y) \gamma(x; y) f^*(y) . \end{aligned}$$

Last terms are identical after renaming integration variables $x \leftrightarrow y$ in one of them, and the first terms (those with ∇^2) become identical via integration by parts for the functions f, g which are zero at infinity. Hence the Fock operator is hermitian and its eigenvalues real.

2.4 Meaning of HF eigenvalues; Koopmans theorem

We discuss now the meaning of ε_α , which have been initially introduced as Lagrange multipliers taking care of the normalization condition in the variational approach. We construct the expectation value of the total energy of the system with all N electrons and with an electron in the state α removed. $E_{\text{HF}}(N) = \langle \Phi | \mathcal{H} | \Phi \rangle$, that is (2.16) without the last term.

$$E_{\text{HF}}(N - 1_\alpha) = \sum_{i \neq \alpha}^N \int \varphi_i^*(x) \left[-\frac{\hbar^2}{2m} \nabla^2 + u(x) \right] \varphi_i(x) dx +$$

$$\begin{aligned}
& + \frac{1}{2} \sum_{\substack{i \neq \alpha \\ j \neq \alpha}}^N \int [\varphi_i^*(x) \varphi_j^*(y) \varphi_i(x) \varphi_j(y) - \varphi_i^*(x) \varphi_j^*(y) \varphi_i(y) \varphi_j(x)] v(x, y) dx dy = \\
& = E_{\text{HF}}(N) - \int \varphi_\alpha^*(x) \left[-\frac{\hbar^2}{2m} \nabla^2 + u(x) \right] \varphi_\alpha(x) dx - \\
& - \frac{1}{2} \sum_{j \neq \alpha}^N \int [\varphi_\alpha^*(x) \varphi_j^*(y) \varphi_\alpha(x) \varphi_j(y) - \varphi_\alpha^*(x) \varphi_j^*(y) \varphi_\alpha(y) \varphi_j(x)] v(x, y) dx dy - \\
& - \frac{1}{2} \sum_{i \neq \alpha}^N \int [\varphi_i^*(x) \varphi_\alpha^*(y) \varphi_i(x) \varphi_\alpha(y) - \varphi_i^*(x) \varphi_\alpha^*(y) \varphi_i(y) \varphi_\alpha(x)] v(x, y) dx dy .
\end{aligned}$$

With $i \leftrightarrow j$ and $x \leftrightarrow y$ two last sums become identical, hence

$$\begin{aligned}
E_{\text{HF}}(N - 1_\alpha) & = E_{\text{HF}}(N) - \\
& - \int dx \varphi_\alpha^*(x) \left[-\frac{\hbar^2}{2m} \nabla^2 + u(x) + \underbrace{\sum_{j \neq \alpha}^N \int dy v(x, y) \varphi_j^*(y) \varphi_j(y)} \right] \varphi_\alpha(x) - \\
& - \underbrace{\int dx \varphi_\alpha^*(x) \sum_{j \neq \alpha}^N \int dy v(x, y) \varphi_j^*(y) \varphi_\alpha(y) \varphi_j(x)}
\end{aligned}$$

Comparing this with (2.17) we see that the underlined terms together give exactly $\varepsilon_\alpha \varphi_\alpha(x)$, then

$$\begin{aligned}
E_{\text{HF}}(N - 1_\alpha) & = E_{\text{HF}}(N) - \int \varphi_\alpha^*(x) \varepsilon_\alpha \varphi_\alpha(x) dx ; \\
\varepsilon_\alpha & = E_{\text{HF}}(N) - E_{\text{HF}}(N - 1_\alpha) .
\end{aligned} \tag{2.26}$$

This is the theorem of Koopmans. It is important to mention that in the course of deriving it, we assumed that one-electron wavefunctions remained unchanged, as one electron was removed. In reality this would not be the case. In a practical calculation, one would estimate the excitation energy $E_{\text{HF}}(N) - E_{\text{HF}}(N - 1)$ (e.g., in photoemission) as difference of total energies in initial and final states with relaxation of one-electron wavefunctions taken into account, i.e. from two self-consistent calculations corresponding to different electron configurations of the system.

The Hamiltonian operator of a non-relativistic atom commutes with \hat{L}^2 , \hat{L}_z , \hat{S}^2 , \hat{S}_z ; the exact solutions of many-body Schrödinger equation are supposed to do the same. The Fock operator by its construction does not have any special reason to commute with any of these operators; hence the most general form of the HF solutions does not have any particular symmetry properties. A HF orbital of general form looks like

$$\varphi_\alpha(x) \equiv \varphi_\alpha^{(+)}(\mathbf{r}) \chi_+(\sigma) + \varphi_\alpha^{(-)}(\mathbf{r}) \chi_-(\sigma) \tag{2.27}$$

where $\chi(\sigma)$ are Pauli spinors

$$\chi_+(\sigma) = \begin{cases} 1 & \text{for } \sigma = 1/2 \\ 0 & \text{for } \sigma = -1/2 \end{cases} ; \quad \chi_-(\sigma) = \begin{cases} 0 & \text{for } \sigma = 1/2 \\ 1 & \text{for } \sigma = -1/2 \end{cases} . \tag{2.28}$$

The general form of the solution (2.27) allows to treat systems with non-collinear magnetic density.

From the general form (2.27) one can demand that the solution commutes with \hat{S}_z , i.e. the spin direction will be fixed for each orbital, and no mixing of $\sigma = 1/2$ and $\sigma = -1/2$ is possible. This is known as *unrestricted Hartree-Fock* (UHF), although this is actually a restriction within a more general formalism. The one-particle wavefunctions in UHF may be numbered as

$$\begin{aligned}\varphi_\alpha^{\text{UHF}}(x) &= \varphi_\alpha^{(+)}(\mathbf{r}) \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{for } \alpha = 1, \dots, N^{(+)}, \\ \varphi_\alpha^{\text{UHF}}(x) &= \varphi_\alpha^{(-)}(\mathbf{r}) \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad \text{for } \alpha = N^{(+)}+1, \dots, N,\end{aligned}$$

if α runs through *all orbitals*. In principle, one could number orbitals corresponding to both spin directions separately, because they are now completely decoupled. Only the total number of particles must be conserved:

$$\begin{aligned}\varphi_\alpha^{\text{UHF}}(x) &= \varphi_\alpha^{(+)}(\mathbf{r}) \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{for } \alpha = 1, \dots, N^{(+)}, \\ \varphi_\beta^{\text{UHF}}(x) &= \varphi_\beta^{(-)}(\mathbf{r}) \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad \text{for } \beta = 1, \dots, N^{(-)}, \\ N^{(+)} + N^{(-)} &= N.\end{aligned}\tag{2.29}$$

These functions are now eigenfunctions of the spin projection operator,

$$\hat{S}_z \varphi_\alpha^{\text{UHF}}(x) = \begin{cases} +\frac{\hbar}{2} \varphi_\alpha^{\text{UHF}}(x) & \text{for } \alpha \in \{1, \dots, N^{(+)}\}, \\ -\frac{\hbar}{2} \varphi_\alpha^{\text{UHF}}(x) & \text{for } \alpha \in \{1, \dots, N^{(-)}\}, \end{cases}$$

and the action of \hat{S}_z on the Slater determinant gives:

$$\hat{S}_z \Phi^{\text{UHF}}(x_1, \dots, x_N) = \frac{\hbar}{2} [N^{(+)} - N^{(-)}] \Phi^{\text{UHF}}(x_1, \dots, x_N).$$

So, the essence of UHF is that it allows to treat magnetic systems. Not only the orbitals, but the density matrices are now labeled by spin index:

$$\gamma^{(\pm)}(\mathbf{r}; \mathbf{r}') = \sum_{\alpha}^{N^{(\pm)}} \varphi_{\alpha}^{(\pm)*}(\mathbf{r}') \varphi_{\alpha}^{(\pm)}(\mathbf{r});\tag{2.30}$$

$$\rho^{(\pm)}(\mathbf{r}) = \gamma^{(\pm)}(\mathbf{r}; \mathbf{r}),\tag{2.31}$$

and the HF system splits into two parts, labeled by spin:

$$\begin{aligned}\left[-\frac{\hbar^2}{2m} \nabla^2 + u(\mathbf{r}) + \int d\mathbf{r}' \rho(\mathbf{r}') v(\mathbf{r}, \mathbf{r}') \right] \varphi_{\alpha}^{(+)}(\mathbf{r}) - \int d\mathbf{r}' \gamma^{(+)}(\mathbf{r}; \mathbf{r}') v(\mathbf{r}, \mathbf{r}') \varphi_{\alpha}^{(+)}(\mathbf{r}') &= \\ &= \varepsilon_{\alpha}^{(+)} \varphi_{\alpha}^{(+)}(\mathbf{r}); \\ \left[-\frac{\hbar^2}{2m} \nabla^2 + u(\mathbf{r}) + \int d\mathbf{r}' \rho(\mathbf{r}') v(\mathbf{r}, \mathbf{r}') \right] \varphi_{\alpha}^{(-)}(\mathbf{r}) - \int d\mathbf{r}' \gamma^{(-)}(\mathbf{r}; \mathbf{r}') v(\mathbf{r}, \mathbf{r}') \varphi_{\alpha}^{(-)}(\mathbf{r}') &= \\ &= \varepsilon_{\alpha}^{(-)} \varphi_{\alpha}^{(-)}(\mathbf{r}),\end{aligned}\tag{2.32}$$

where the external field $u(\mathbf{r})$ may be also spin-dependent (e.g., in the presence of a magnetic field). The coupling between two parts is achieved by the fact that the total density

$$\rho(\mathbf{r}) = \rho^{(+)}(\mathbf{r}) + \rho^{(-)}(\mathbf{r})$$

enters both equations; moreover, the total number of particles is constant, $N = N^{(+)} + N^{(-)}$. The numbers $N^{(+)}$ and $N^{(-)}$ however are not fixed and may vary (from iteration to iteration). In a practical calculation, one would expand the orbitals over a basis set which is larger than N , and as in the course of solution on each iteration one gets eigenvalues, separately for (+) and (-), the N lowest in energy among them all will be occupied, that determines $N^{(+)}$ and $N^{(-)}$, $\rho^{(+)}$, $\rho^{(-)}$ etc. for this iteration.⁶

It is noteworthy that the density matrices $\gamma^{(\pm)}(\mathbf{r}; \mathbf{r}')$ are labeled by spin. This is so because the exchange interaction only involves the one-electron states with the same spin state. The effect of exchange can be looked at as the Coulomb interaction of an orbital searched for, say, $\varphi_{\alpha}^{(+)}(\mathbf{r})$ with a corresponding “exchange density” $\rho_{\mathbf{r}\alpha}^{(+)}(\mathbf{r}')$:

$$\int d\mathbf{r}' \gamma^{(+)}(\mathbf{r}; \mathbf{r}') v(\mathbf{r}, \mathbf{r}') \varphi_{\alpha}^{(+)}(\mathbf{r}') \Rightarrow \left[\int d\mathbf{r}' \frac{\gamma^{(+)}(\mathbf{r}; \mathbf{r}') v(\mathbf{r}, \mathbf{r}') \varphi_{\alpha}^{(+)}(\mathbf{r}')}{\varphi_{\alpha}^{(+)}(\mathbf{r})} \right] \varphi_{\alpha}^{(+)}(\mathbf{r});$$

$$\rho_{\mathbf{r}\alpha}^{(+)}(\mathbf{r}') = \frac{\gamma^{(+)}(\mathbf{r}; \mathbf{r}') \varphi_{\alpha}^{(+)}(\mathbf{r}')}{\varphi_{\alpha}^{(+)}(\mathbf{r})}. \quad (2.33)$$

The exchange density is *non-local* (it depends on both \mathbf{r} and \mathbf{r}'), and for every orbital index α it integrates over \mathbf{r}' exactly to 1:

$$\int d\mathbf{r}' \rho_{\mathbf{r}\alpha}^{(+)}(\mathbf{r}') = \sum_{i=1}^{N^{(+)}} \underbrace{\int d\mathbf{r}' \varphi_i^{(+)*}(\mathbf{r}') \varphi_{\alpha}^{(+)}(\mathbf{r}')}_{\delta_{i\alpha}} \frac{\varphi_i^{(+)}(\mathbf{r})}{\varphi_{\alpha}^{(+)}(\mathbf{r})} = \sum_{i=1}^{N^{(+)}} \delta_{i\alpha} = 1,$$

that means that each electron is surrounded by its corresponding “exchange hole”, from where the charge density is exactly one electron of the same spin is excluded.

We proceed discussing symmetry aspects. If one demands that individual orbitals do possess a good angular momentum value, for instance can be casted as

$$\varphi_{\nu}(x) = R_{n\nu}(r) Y_{l\nu m\nu}(\theta, \phi) \chi_{\sigma}(\sigma)$$

(in an atom), then one arrives at the so-called *restricted Hartree-Fock* (RHF) formalism. For a multiatomic system, one can generalize this demand by taking into account appropriate (by symmetry) combinations of atom-centered functions with the same angular momentum value. Then for each orbital

$$\hat{l}_z \varphi_{\nu}(x) = \hbar m_{\nu} \varphi_{\nu}(x),$$

and for the Slater determinant

$$\hat{L}_z \Phi(x_1, \dots, x_N) = \hbar \left(\sum_{\nu} m_{\nu} \right) \Phi^{\text{RHF}}(x_1, \dots, x_N).$$

⁶this scheme is referred to as the *aufbau principle*.

The more severe the symmetry constraint is, the more restricted the variational space for one-electron wavefunctions and the higher the calculated ground-state energies. The ultimately best energies (the HF limit) can be obtained only with freely variable orbitals which do not possess any particular symmetry properties. This situation is known as the “symmetry dilemma” in the HF formalism.

The exchange density $\rho_{\mathbf{r},\alpha}^{(+)}(\mathbf{r}')$ introduced in Eq.(2.33) is non local, as it should be from physical considerations, but the fact that it depends on the orbital index is not physically motivated. Slater (1951) proposed⁷ to weight it over occupied orbitals, according to their corresponding partial densities:

$$\overline{\rho_{\mathbf{r}}^{(+)}(\mathbf{r}')} = \rho_{\mathbf{X}}^{(+)}(\mathbf{r}, \mathbf{r}') = \frac{\sum_i \rho_{\mathbf{r}i}^{(+)}(\mathbf{r}') \varphi_i^*(\mathbf{r}) \varphi_i(\mathbf{r})}{\sum_j \varphi_j^*(\mathbf{r}) \varphi_j(\mathbf{r})} = \frac{\sum_{ij} \varphi_j^*(\mathbf{r}') \varphi_j(\mathbf{r}) \varphi_i^*(\mathbf{r}) \varphi_i(\mathbf{r}')}{\sum_j \varphi_j^*(\mathbf{r}) \varphi_j(\mathbf{r})}. \quad (2.34)$$

After summation, the eXchange density $\rho_{\mathbf{X}}^{(+)}(\mathbf{r}, \mathbf{r}')$ does not depend on the orbital index anymore.

We perform now this summation analitically for the easiest case of free particles, with one-electron eigenvalues

$$\varphi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\mathbf{r}},$$

where V is the volume of the “box” including the N electrons, and periodical boundary conditions are assumed. The summation will be substituted by the integration in the momentum space up to $k_{\text{F}} = p_{\text{F}}/\hbar$, so that the lowest states with energies up to $E_{\text{F}} = \hbar^2 k_{\text{F}}^2/2m$ are occupied. k_{F} is related to density as defined by Eq. (1.7), $k_{\text{F}} = (3\pi^2 \rho)^{1/3}$, and

$$\sum_i \rightarrow \int_0^{k_{\text{F}}} dN; \quad dN = \frac{2V}{(2\pi)^3} d^3k = \frac{V}{4\pi^3} k^2 dk \sin \theta_k d\theta_k d\phi_k.$$

When the electron gas is not spin polarized, $N^{(+)} = N^{(-)} = N/2$, the summation over orbitals of each spin component runs over

$$dN^{(\pm)} = \frac{V}{8\pi^3} k^2 dk \sin \theta_k d\theta_k d\phi_k.$$

The denominator of Eq.(2.34) gives:

$$\sum_j \varphi_j^*(\mathbf{r}) \varphi_j(\mathbf{r}) \rightarrow \frac{V}{8\pi^3} \frac{1}{V} \frac{4\pi}{3} k_{\text{F}}^3 = \frac{k_{\text{F}}^3}{6\pi^2} = \frac{\rho}{2}. \quad (2.35)$$

The numerator of Eq.(2.34)

$$\begin{aligned} \sum_{ij} \varphi_j^*(\mathbf{r}') \varphi_j(\mathbf{r}) \varphi_i^*(\mathbf{r}) \varphi_i(\mathbf{r}') \rightarrow & \underbrace{\left(\frac{V}{8\pi^3}\right)^2 \int_0^{k_{\text{F}}} k'^2 dk' \sin \theta_{k'} d\theta_{k'} d\phi_{k'} \frac{1}{V} e^{i\mathbf{k}(\mathbf{r}'-\mathbf{r})}}_{\sum_i} \times \\ & \times \underbrace{\int_0^{k_{\text{F}}} k^2 dk \sin \theta_k d\theta_k d\phi_k \frac{1}{V} e^{i\mathbf{k}(\mathbf{r}-\mathbf{r}')}}_{\sum_j}. \end{aligned}$$

⁷Phys. Rev. **81**, 385 (1951)

Each of the integrals in k yields:

$$\begin{aligned} \int_0^{k_F} k^2 dk \sin \theta_k d\theta_k d\phi_k e^{i\mathbf{k}\mathbf{R}} &= 2\pi \int_0^{k_F} k^2 dk \int_0^\pi \sin \theta_k d\theta_k e^{ikR \cos \theta_k} = \\ &= \frac{4\pi}{R} \int_0^{k_F} k dk \sin(kR) = \frac{4\pi}{R^3} [\sin(k_F R) - k_F R \cos(k_F R)] . \end{aligned}$$

Finally

$$\begin{aligned} \sum_{ij} \varphi_j^*(\mathbf{r}') \varphi_j(\mathbf{r}) \varphi_i^*(\mathbf{r}) \varphi_i(\mathbf{r}') \rightarrow \\ \rightarrow \frac{1}{(8\pi^3)^2} (4\pi k_F^3)^2 \left[\frac{\sin(k_F |\mathbf{r} - \mathbf{r}'|) - k_F |\mathbf{r} - \mathbf{r}'| \cos(k_F |\mathbf{r} - \mathbf{r}'|)}{(k_F |\mathbf{r} - \mathbf{r}'|)^3} \right]^2 . \end{aligned} \quad (2.36)$$

Substituting (2.35) and (2.36) into (2.34), we get

$$\begin{aligned} \rho_X^{(+)}(\mathbf{r}, \mathbf{r}') &= \frac{3k_F^3}{2\pi^2} \left[\frac{\sin(k_F |\mathbf{r} - \mathbf{r}'|) - k_F |\mathbf{r} - \mathbf{r}'| \cos(k_F |\mathbf{r} - \mathbf{r}'|)}{(k_F |\mathbf{r} - \mathbf{r}'|)^3} \right]^2 \\ &= \frac{9}{2} \rho \left[\frac{j_1(k_F |\mathbf{r} - \mathbf{r}'|)}{k_F |\mathbf{r} - \mathbf{r}'|} \right]^2 . \end{aligned} \quad (2.37)$$

The plot of the function involved is shown in Fig. 2.1.

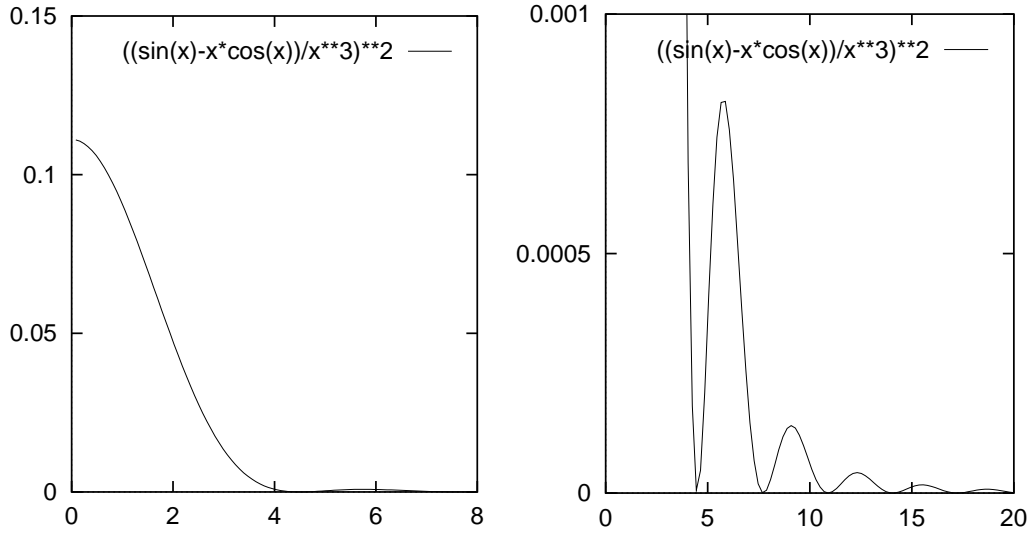


Figure 2.1: Plot of $\left(\frac{j_1(x)}{x}\right)^2$

We now come back to the HF equations (2.32) where the exchange term was transformed according to Eq.(2.33)

$$- \int d\mathbf{r}' \gamma^{(+)}(\mathbf{r}; \mathbf{r}') v(\mathbf{r}, \mathbf{r}') \varphi_\alpha^{(+)}(\mathbf{r}') \rightarrow - \int d\mathbf{r}' \rho_{\mathbf{r}\alpha}^{(+)}(\mathbf{r}') v(\mathbf{r}, \mathbf{r}') \varphi_\alpha^{(+)}(\mathbf{r})$$

so it took a form of a potential acting on the orbital we search for,

$$\rightarrow v_X^{(+)}(\mathbf{r}) \varphi_\alpha^{(+)}(\mathbf{r}) ,$$

and now that after statistical averaging $\rho_{\mathbf{r}\alpha}^{(+)}$ does not depend on the orbital index α anymore, the exchange potential is the same for all orbitals. Using the result (2.37) for the exchange density,

$$\begin{aligned}
v_{\mathbf{X}}^{(+)}(\mathbf{r}) &= -e \int \frac{\rho_{\mathbf{X}}^{(+)}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' = \\
&\quad \text{(centering the coordinate system at } \mathbf{r} \text{)} \\
&= -4\pi e \int_0^\infty r'^2 dr' \frac{1}{r'} \frac{3k_{\text{F}}^3}{2\pi^2} \left[\frac{\sin(k_{\text{F}}r') - (k_{\text{F}}r') \cos(k_{\text{F}}r')}{(k_{\text{F}}r')^3} \right]^2 \\
&= -6e \left(\frac{3}{\pi} \right)^{1/3} \rho^{1/3} \underbrace{\int_0^\infty x dx \left(\frac{\sin x - x \cos x}{x^3} \right)^2}_{1/4} = -e \frac{3}{2} \left(\frac{3}{\pi} \right)^{1/3} \rho^{1/3}. \quad (2.38)
\end{aligned}$$

We compare this result with (1.26) from the Thomas-Fermi section and see that the exchange potential is indeed proportional to $\rho^{1/3}$, as was argued there based on dimensionality considerations. The prefactor must be dependent on the spatial distribution of density; it is constant in this case because we assumed homogeneous density distribution in the derivation. Otherwise, $v_{\mathbf{X}}^{(+)}(\mathbf{r})$ would have got an explicit dependence on \mathbf{r} . We note that, although the exchange density $\rho_{\mathbf{X}}^{(+)}(\mathbf{r}, \mathbf{r}')$ integrates over \mathbf{r}' *exactly* to 1 for every \mathbf{r} , the value of the integral $\int d\mathbf{r}' \rho_{\mathbf{X}}^{(+)}(\mathbf{r}, \mathbf{r}')/|\mathbf{r} - \mathbf{r}'|$ would of course depend on the shape of $\rho_{\mathbf{X}}^{(+)}(\mathbf{r}, \mathbf{r}')$. However, since the Coulomb interaction $1/|\mathbf{r} - \mathbf{r}'|$ has spherical symmetry, only spherically averaged part of $\rho_{\mathbf{X}}^{(+)}(\mathbf{r}, \mathbf{r}')$, i.e. dependent only on $|\mathbf{r} - \mathbf{r}'|$, will contribute to the value of the exchange potential at any given position \mathbf{r} .

Finally, we note that one can cast the exchange energy in the HF scheme, after a statistical averaging, in the form of a spatial integral over exchange energy density,

$$E_{\text{X}} = \int d\mathbf{r} \epsilon_{\text{X}}(\mathbf{r});$$

obviously $\epsilon_{\text{X}} \sim \rho^{4/3}$ for the homogeneous electron gas. This result will be later on used and generalized for the case of a slowly varying density.

2.5 Pair correlation function

The exchange density $\rho_{\mathbf{X}}(\mathbf{r})$ has the meaning of the particle density expelled from the vicinity of each electron as a consequence of the Pauli principle. The same effect can be characterized by a dimensionless property, a *pair correlation function*, which shows how any two particles tend to avoid each other. We start from some general definitions. In addition to the 1st order density matrix previously defined in Eq. (2.20), we introduce now the *two-particle density matrix*,

$$\gamma_2(x_1, x_2; y_1, y_2) = \frac{N(N-1)}{2!} \int \Psi^*(y_1, y_2, x_3, \dots, x_N) \Psi(x_1, x_2, x_3, \dots, x_N) dx_3 \dots dx_N. \quad (2.39)$$

2! in the denominator stands for generality, showing how to introduce higher-order density matrices. Obviously γ_2 is related to the 1st order matrix γ by

$$\gamma(x; y) = \frac{2}{N-1} \int \gamma_2(x, x_2; y, x_2) dx_2. \quad (2.40)$$

Taking a diagonal of γ_2 we obtain *another* property depending on the coordinates of two particles, that is the pair density ρ_2 :

$$\rho_2(x, y) = 2\gamma_2(x, y; x, y). \quad (2.41)$$

From this, two different pair correlation functions are derived:

$$g(x, y) = \frac{\rho_2(x, y)}{\rho(x)\rho(y)}; \quad (2.42)$$

$$h(x, y) = \rho_2(x, y) - \rho(x)\rho(y). \quad (2.43)$$

For large spatial distances between particles, $g \rightarrow 1$ and $h \rightarrow 0$.

These definitions are quite general. In order to conclude the HF part, we calculate pair density in the HF approximation for the same model case, a homogeneous electron gas. First we construct the two-particle density matrix for Slater determinants. Similarly to how we proceeded for the one-particle density resulting in Eq. (2.19),

$$\begin{aligned} \gamma_2(x_1, x_2; y_1, y_2) &= \frac{N(N-1)}{2N!} \sum_{\nu\mu} \text{sign}(\nu) \text{sign}(\mu) \times \\ &\times \varphi_{\nu 1}^*(y_1) \varphi_{\nu 2}^*(y_2) \varphi_{\mu 1}(x_1) \varphi_{\mu 2}(x_2) \prod_{i=3}^N \left[\int dx_i \varphi_{\nu i}^*(x_i) \varphi_{\mu i}(x_i) \right]. \end{aligned}$$

In analogy with considering two-particle contributions to $\langle \Psi | \mathcal{H} | \Psi \rangle$, Eq. (2.15), we conclude that $\nu i = \mu i$ for $i \geq 3$, that leaves the combinations

$$\begin{aligned} \nu 1 = \mu 1, \nu 2 = \mu 2; \quad \text{sign}(\nu) \text{sign}(\mu) &= 1; \\ \nu 1 = \mu 2, \nu 2 = \mu 1; \quad \text{sign}(\nu) \text{sign}(\mu) &= -1 \end{aligned}$$

and $(N-2)!$ possibilities to permute other indices. Finally

$$\begin{aligned} \gamma_2(x_1, x_2; y_1, y_2) &= \frac{1}{2} \sum_{i,j}^N \left[\varphi_i(x_1) \varphi_j(x_2) \varphi_i^*(y_1) \varphi_j^*(y_2) - \right. \\ &\quad \left. - \varphi_i(x_1) \varphi_j(x_2) \varphi_j^*(y_1) \varphi_i^*(y_2) \right]. \end{aligned} \quad (2.44)$$

This can be further on written down as

$$\begin{aligned} \gamma_2(x_1, x_2; y_1, y_2) &= \frac{1}{2} \left\{ \left[\sum_i^N \varphi_i^*(y_1) \varphi_i(x_1) \right] \left[\sum_j^N \varphi_j^*(y_2) \varphi_j(x_2) \right] - \right. \\ &\quad \left. - \left[\sum_i^N \varphi_i^*(y_2) \varphi_i(x_1) \right] \left[\sum_j^N \varphi_j^*(y_1) \varphi_j(x_2) \right] \right\} \\ &= \frac{1}{2} \begin{vmatrix} \gamma(x_1; y_1) & \gamma(x_1; y_2) \\ \gamma(x_2; y_1) & \gamma(x_2; y_2) \end{vmatrix}. \end{aligned} \quad (2.45)$$

Note that this does not hold not in the general case anymore, but only for Slater determinants. Using (2.41), we obtain for $\rho_2(x, y)$:

$$\rho_2(x, y) = 2 \cdot \frac{1}{2} \begin{vmatrix} \gamma(x; x) & \gamma(x; y) \\ \gamma(y; x) & \gamma(y; y) \end{vmatrix} = \rho(x) \rho(y) - |\gamma(x; y)|^2 . \quad (2.46)$$

Now, in order to specify spatial dependencies in the density matrices and two-particle density, we must decide how are occupied one-particle states distributed over two spin components. Assuming paramagnetic electron gas, $N^{(+)} = N^{(-)} = N/2$,

$$\begin{aligned} \gamma(\mathbf{r}, \mathbf{r}') &= \sum_{\sigma\sigma'} \gamma(\mathbf{r}\sigma; \mathbf{r}'\sigma') = \sum_{i=1}^{N/2} \left[\varphi_i^{(+)*}(\mathbf{r}') \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \varphi_i^{(+)}(\mathbf{r}) + \right. \\ &\quad \left. + \underbrace{\varphi_i^{(-)*}(\mathbf{r}') \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}}_{=0} \varphi_i^{(+)}(\mathbf{r}) + \varphi_i^{(+)*}(\mathbf{r}') \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \varphi_i^{(-)}(\mathbf{r}) + \right. \\ &\quad \left. + \varphi_i^{(-)*}(\mathbf{r}') \begin{pmatrix} 0 & 1 \\ 0 & 1 \end{pmatrix} \varphi_i^{(-)}(\mathbf{r}) \right] = \\ &= \sum_{i=1}^{N/2} \left[\varphi_i^{(+)*}(\mathbf{r}') \varphi_i^{(+)}(\mathbf{r}) + \varphi_i^{(-)*}(\mathbf{r}') \varphi_i^{(-)}(\mathbf{r}) \right] = \\ &= \gamma^{(+)}(\mathbf{r}; \mathbf{r}') + \gamma^{(-)}(\mathbf{r}; \mathbf{r}') . \end{aligned} \quad (2.47)$$

From this it follows

$$\rho(\mathbf{r}) = \rho^{(+)}(\mathbf{r}) + \rho^{(-)}(\mathbf{r}) ,$$

as it should be.

For $\gamma_2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2)$ we have to consider $2^4=16$ terms with different spin attribution. We keep only those which do not contain $\varphi_i^{(+)}(\dots)\varphi_i^{(-)}(\dots)$ or $\varphi_j^{(+)}(\dots)\varphi_j^{(-)}(\dots)$ and hence are not orthogonal in spin space. What is explicitly left in the paramagnetic (PM) case:

$$\begin{aligned} \gamma_2^{\text{PM}}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2) &= \sum_{\substack{\sigma_1 \sigma_2 \\ \sigma'_1 \sigma'_2}} \gamma_2(\mathbf{r}_1 \sigma_1, \mathbf{r}_2 \sigma_2; \mathbf{r}'_1 \sigma'_1, \mathbf{r}'_2 \sigma'_2) = \\ &= \frac{1}{2} \sum_{i,j=1}^{N/2} \left[\varphi_i^{(+)*}(\mathbf{r}'_1) \varphi_j^{(+)*}(\mathbf{r}'_2) \varphi_i^{(+)}(\mathbf{r}_1) \varphi_j^{(+)}(\mathbf{r}_2) + \right. \\ &\quad + \varphi_i^{(+)*}(\mathbf{r}'_1) \varphi_j^{(-)*}(\mathbf{r}'_2) \varphi_i^{(+)}(\mathbf{r}_1) \varphi_j^{(-)}(\mathbf{r}_2) + \\ &\quad + \varphi_i^{(-)*}(\mathbf{r}'_1) \varphi_j^{(+)*}(\mathbf{r}'_2) \varphi_i^{(-)}(\mathbf{r}_1) \varphi_j^{(+)}(\mathbf{r}_2) + \\ &\quad + \varphi_i^{(-)*}(\mathbf{r}'_1) \varphi_j^{(-)*}(\mathbf{r}'_2) \varphi_i^{(-)}(\mathbf{r}_1) \varphi_j^{(-)}(\mathbf{r}_2) - \\ &\quad - \varphi_i^{(+)*}(\mathbf{r}'_1) \varphi_j^{(+)*}(\mathbf{r}'_2) \varphi_j^{(+)}(\mathbf{r}_1) \varphi_i^{(+)}(\mathbf{r}_2) - \\ &\quad \left. - \varphi_i^{(-)*}(\mathbf{r}'_1) \varphi_j^{(-)*}(\mathbf{r}'_2) \varphi_j^{(-)}(\mathbf{r}_1) \varphi_i^{(-)}(\mathbf{r}_2) \right] = \\ &= \frac{1}{2} \sum_{i,j=1}^{N/2} \left[4 \varphi_i(\mathbf{r}_1) \varphi_j(\mathbf{r}_2) \varphi_i^*(\mathbf{r}'_1) \varphi_j^*(\mathbf{r}'_2) - \right. \\ &\quad \left. - 2 \varphi_i(\mathbf{r}_1) \varphi_j(\mathbf{r}_2) \varphi_i^*(\mathbf{r}'_2) \varphi_j^*(\mathbf{r}'_1) \right] . \end{aligned} \quad (2.48)$$

From this,

$$\begin{aligned}
\rho_2^{\text{PM}}(\mathbf{r}_1, \mathbf{r}_2) &= \sum_{i,j=1}^{N/2} \left[4 \varphi_i(\mathbf{r}_1) \varphi_j(\mathbf{r}_2) \varphi_i^*(\mathbf{r}'_1) \varphi_j^*(\mathbf{r}'_2) - 2 \varphi_i(\mathbf{r}_1) \varphi_j(\mathbf{r}_2) \varphi_i^*(\mathbf{r}'_2) \varphi_j^*(\mathbf{r}'_1) \right] = \\
&= 4 \left[\sum_i^{N/2} |\varphi_i(\mathbf{r}_1)|^2 \right] \left[\sum_j^{N/2} |\varphi_j(\mathbf{r}_2)|^2 \right] - 2 \left[\sum_i^{N/2} \varphi_i(\mathbf{r}_1) \varphi_i^*(\mathbf{r}_2) \right] \left[\sum_j^{N/2} \varphi_j(\mathbf{r}_2) \varphi_j^*(\mathbf{r}_1) \right] = \\
&= \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) - \frac{1}{2} |\gamma(\mathbf{r}_1; \mathbf{r}_2)|^2 .
\end{aligned} \tag{2.49}$$

The pair correlation function $g(\mathbf{r}_1, \mathbf{r}_2)$ is then

$$g^{\text{PM}}(\mathbf{r}_1, \mathbf{r}_2) = \frac{\rho_2(\mathbf{r}_1, \mathbf{r}_2)}{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)} = 1 - \frac{1}{2} \frac{|\gamma(\mathbf{r}_1; \mathbf{r}_2)|^2}{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)} . \tag{2.50}$$

For the gas of non-interacting electrons with constant density,

$$\gamma(\mathbf{r}_1; \mathbf{r}_2) = 2 \sum_i^{N/2} \varphi_i^*(\mathbf{r}_2) \varphi_i(\mathbf{r}_1) \Rightarrow \frac{V}{4\pi^3} \int k^2 dk \sin \theta_k d\theta_k d\phi_k \frac{e^{i\mathbf{k}(\mathbf{r}_1 - \mathbf{r}_2)}}{V}$$

and calculated as has been already done above, leading to Eq.(2.36). Finally

$$g(r \equiv |\mathbf{r} - \mathbf{r}'|) = 1 - \frac{9}{2} \left[\frac{\sin(k_F r) - (k_F r) \cos(k_F r)}{(k_F r)^3} \right]^2 . \tag{2.51}$$

For fully spin-polarized (“ferromagnetic”) electron gas, one would assume

$$N^{(+)} = N; \quad N^{(-)} = 0; \quad \rho(\mathbf{r}) = \rho^{(+)}(\mathbf{r});$$

$$\gamma^{\text{FM}}(\mathbf{r}; \mathbf{r}') = \sum_{\sigma\sigma'} \gamma(\mathbf{r}\sigma; \mathbf{r}'\sigma') = \sum_{i=1}^{N/2} \left[\varphi_i^{(+)*}(\mathbf{r}') (1 \ 0) \begin{pmatrix} 1 \\ 0 \end{pmatrix} \varphi_i^{(+)}(\mathbf{r}) \right] = \gamma^{(+)}(\mathbf{r}, \mathbf{r}');$$

$$\begin{aligned}
\gamma_2^{\text{FM}}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2) &= \frac{1}{2} \sum_{i,j=1}^{N/2} \left[\varphi_i^{(+)*}(\mathbf{r}'_1) \varphi_j^{(+)*}(\mathbf{r}'_2) \varphi_i^{(+)}(\mathbf{r}_1) \varphi_j^{(+)}(\mathbf{r}_2) - \right. \\
&\quad \left. - \varphi_j^{(+)*}(\mathbf{r}'_1) \varphi_i^{(+)*}(\mathbf{r}'_2) \varphi_i^{(+)}(\mathbf{r}_1) \varphi_j^{(+)}(\mathbf{r}_2) \right];
\end{aligned}$$

$$\rho_2^{\text{FM}}(\mathbf{r}_1, \mathbf{r}_2) = \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) - |\gamma(\mathbf{r}_1; \mathbf{r}_2)|^2 ; \tag{2.52}$$

$$g^{\text{FM}}(\mathbf{r}_1, \mathbf{r}_2) = \frac{\rho_2^{\text{FM}}(\mathbf{r}_1, \mathbf{r}_2)}{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)} = 1 - \frac{|\gamma(\mathbf{r}_1; \mathbf{r}_2)|^2}{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)} . \tag{2.53}$$

Comparing with (2.50), one can see that the correlation function is zero at the origin, since all electrons have the same spin now. k becomes larger and hence the fluctuations in the correlation function have smaller period than in the case of non-magnetic electron gas of the same density.