

Chapter 3

Electron-Electron Interaction

In the adiabatic approximation the motion of the electrons and the nuclei are decoupled. Still, equations (1.9) and (1.13) describe systems containing 10^{23} particles. In the following, we will discuss methods that enable us to deal with a many-body Schrödinger equation like Eq. (1.9). The wave function $\Phi_\nu(\{\mathbf{r}_i\sigma_i\})$ and its energy E_ν^e are determined by the equations (1.9) and (1.10). We write down Eq. (1.10) once more

$$H^e = \sum_{k=1}^N -\frac{\hbar^2}{2m} \nabla_{\mathbf{r}_k}^2 + \sum_{k=1}^N v(\mathbf{r}_k) + \frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_{\substack{k,k' \\ k \neq k'}}^{N,N} \frac{e^2}{|\mathbf{r}_k - \mathbf{r}_{k'}|} \quad . \quad (3.1)$$

$v(\mathbf{r}_k)$ is the potential of the lattice components (ions or nuclei) of the solid. Often it is called “external potential”.

At this point we briefly recall the meaning of the many-body wave function. It depends on $3N$ spatial coordinates and N spin coordinates. Because the spatial coordinates are all coupled by the operator V^{e-e} , generally they cannot be dealt with separately. In a certain sense this is analogous to the single-particle problem. Here, the wave function $\varphi(x, y, z)$ depends on three spatial coordinates (the spin will be neglected here), and the motion in x -direction is generally not independent of the y -direction. The same is true for x and z , and for y and z . This means, $\varphi(x, y, z)$ does not describe 3 independent one-dimensional particles, but 1 particle with 3 spatial coordinates. In the same way the N -particle Schrödinger equation has to be treated as a many-body equation with $3N$ spatial coordinates. One can say that the total of all the electrons is like a glue, or a mush and not like $3N$ independent particles.

If the electron-electron interaction would be negligible or if it could be described as

$$V^{e-e} \stackrel{?}{=} \sum_{k=1}^N v^{e-e}(\mathbf{r}_k) \quad , \quad (3.2)$$

i.e., the potential at position \mathbf{r}_k does not explicitly depend on the positions of the other electrons, then it would not be a major problem to solve the many-body Schrödinger equation. Unfortunately, such a neglect cannot be justified: The electron-electron interaction is Coulombic; it has an infinite range and for small separations it becomes very strong. Learning about this electron-electron interaction is the most interesting part of solid-state theory. Thus, now we will describe methods, that enable us to take into account the electron-electron interaction in an appropriate manner. There are four methods (or concepts) that can be used:

1. Method of the “effective single-particle theory”: Here we will emphasize in particular the importance of density-functional theory (DFT)¹. Primarily, DFT refers to the

¹1998 Walter Kohn was awarded the Nobel prize in chemistry for the development of density-functional theory.

ground state, E_0^e . In principle it can be used also to calculate excited states. In this chapter we will discuss DFT (and its precursors) with respect to the ground state, and in part II of this lecture we will describe the calculation of excited states and time-dependent DFT (TD-DFT).

2. The Green-function self-energy theory: This method is very general, but not applicable in most cases. One constructs a series expansion in interactions and necessarily many terms have to be neglected, which are believed to be unimportant (cf. e.g. the book by Inkson and the book by Mahan). We will come back to this method in part II of this lecture, because it allows for the calculation of excited states. The first term of such series expansion of Feynman-diagrams is called the *GW*-approximation. Here G is the operator of the Green-function, which e.g. belongs to the *effective* single-particle problem of the Hartree theory or of the density-functional theory, and W is the screened Coulomb interaction of the electrons.
3. Many-body wavefunction approaches (quantum chemistry): Here the basic variable is the many-body wavefunction. There are different methods which seek to obtain increasingly accurate (sophisticated) approximations to the many-body wavefunction. The starting point or lowest level is Hartree-Fock theory, where the wavefunction is described by a single Slater-determinant (as discussed in 3.2, Hartree-Fock theory reduces the to an effective single-particle method). Higher-level methods seek to improve the wavefunction within many-body perturbation theory (here, 2nd and higher-order Møller-Plesset approaches [MPx] are widely used) or non-perturbatively (such as Coupled Cluster [CC] and configuration interaction [CI] approaches). Though these approaches are very successful for molecules, they become computationally too expensive to deal with systems that contain more than ≈ 100 electrons (≈ 1000 if one tries very hard). For solids, these approaches are in general not (yet) feasible.
4. The quantum Monte Carlo method: Here the expectation value of the many-body Hamilton operator H^e is calculated using a very general ansatz of many-body wave functions in the high-dimensional configurational space. Then the wave functions are varied and the minimum of the expectation value $\langle \Phi | H^e | \Phi \rangle / \langle \Phi | \Phi \rangle$ is determined. Due to the availability of fast computers and several methodological developments in recent years this method has gained in importance. It will be discussed in part II of this lecture.

Now we will discuss density-functional theory in detail. This will be done step by step to clarify the physical contents of the theory. Thus, we begin with the Hartree and Hartree-Fock theory and then proceed, via Thomas-Fermi theory, to density-functional theory.

3.1 Hartree Approximation

The ansatz of Hartree shows how a theory evolves or can evolve. Often initially an intuitive feeling is present. Only after that one attempts to derive things in a mathematical way. Hartree (Proc. Camb. Phil. Soc. **24**, 89, 111, 426 (1928)) started from the following idea:

The effect of the electron-electron interaction on a certain electron at position \mathbf{r} should approximately be given by the electrostatic potential, which is generated by all other electrons on average at position \mathbf{r} , i.e., it should approximately be possible to replace the potential $V^{e-e}(\{\mathbf{r}_i\})$ of the many-body Schrödinger equation by

$$V^{e-e}(\{\mathbf{r}_i\}) \approx \sum_{k=1}^N v^{\text{Hartree}}(\mathbf{r}_k) \quad (3.3)$$

with

$$v^{\text{Hartree}}(\mathbf{r}) = \frac{e^2}{4\pi\epsilon_0} \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' \quad . \quad (3.4)$$

Then the many-body Hamilton operator decomposes into N single-particle operators

$$H^e = \sum_{k=1}^N h(\mathbf{r}_k) \quad . \quad (3.5)$$

Each electron would then be described by an effective single-particle Schrödinger equation with a Hamilton operator

$$h = -\frac{\hbar^2}{2m} \nabla^2 + v(\mathbf{r}) + v^{\text{Hartree}}(\mathbf{r}) \quad . \quad (3.6)$$

The validity of Eqs. (3.3) – (3.6) may seem to be reasonable. Often, however, this approach is an (often drastic) approximation. Only a more precise treatment can show how problematic this approximation is, and this shall be done now.

Mathematical Derivation of the Hartree Equations

Starting from the general many-body equation, Eqs. (3.3) – (3.6) shall be derived. In particular the approximation connected with Eq. (3.6) shall be identified. Before we start, we note that H^e does not contain the spin of the electrons explicitly and therefore, also no coupling between the spin and position is included. Thus, for the eigenfunctions of H^e we must have

$$\Phi_\nu(\{\mathbf{r}_i\sigma_i\}) = \Phi_\nu(\{\mathbf{r}_i\}) \chi_\nu(\{\sigma_i\}) \quad . \quad (3.7)$$

To take into account orbital as well as spin quantum numbers, from now on we will label the set k of quantum numbers as follows

$$\nu \equiv o_\nu s_\nu \quad ,$$

with o_ν representing the orbital quantum numbers of set ν and s_ν the spin quantum numbers. In the free electron gas (cf. Chapter 2) o_ν represents all possible values of the 3 numbers: k_x, k_y, k_z . For each state s_ν is \uparrow or \downarrow .

For the spin component we have (because H^e does not contain spin-orbit and spin-spin coupling)

$$\chi_\nu(\{\sigma_i\}) = \chi_{s_1}(\sigma_1) \chi_{s_2}(\sigma_2) \dots \chi_{s_N}(\sigma_N) \quad . \quad (3.8)$$

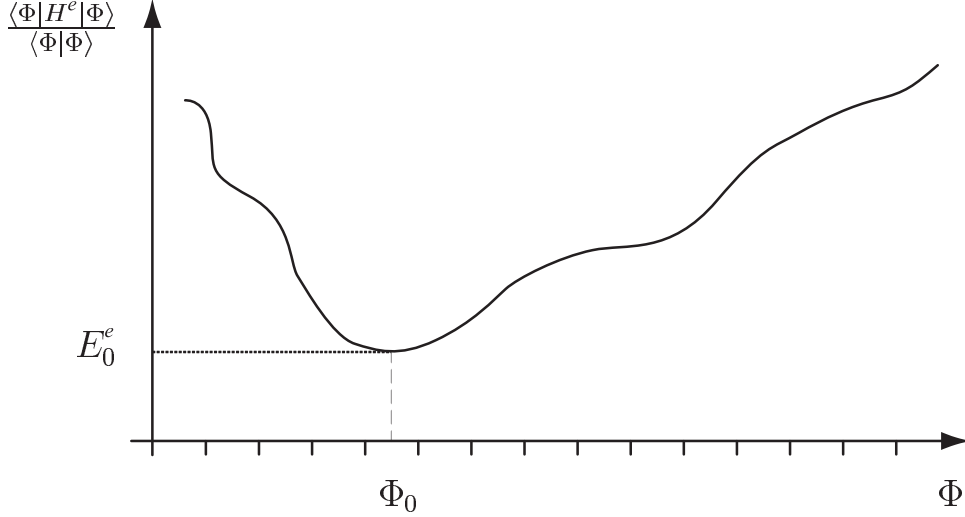


Figure 3.1: Schematic representation of the expectation value of the Hamilton operator as a “function” of the vectors of the Hilbert space. The dashes at the Φ -axis label the wave functions of type Φ^{Hartree} . They cannot reach the function Φ_0 , but can get close to it.

Here, we have $\chi_{\uparrow}(\sigma) = \begin{cases} 1 & \text{for } \sigma = +1/2 \\ 0 & \text{for } \sigma = -1/2 \end{cases}$ and $\chi_{\downarrow}(\sigma) = \begin{cases} 0 & \text{for } \sigma = +1/2 \\ 1 & \text{for } \sigma = -1/2 \end{cases}$, i.e. σ labels two components of the Pauli spinors, $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$, respectively. For the spatial part such a product ansatz is invalid, because H^e due to the electron-electron interaction couples the positions of “different” electrons. For the lowest eigenvalue of the Schrödinger equation the variational principle holds, i.e., for the ground state of H^e we have

$$E_0^e \leq \frac{\langle \Phi | H^e | \Phi \rangle}{\langle \Phi | \Phi \rangle} \quad , \quad (3.9)$$

where the Φ are arbitrary functions of the N -particle Hilbert space, which can be differentiated twice and can be normalized. If we constrain the set of functions Φ and consider the Hilbert space defined by the subset given by the eigenfunctions of H^e , we most probably will not obtain E_0^e exactly. Consequently, the ansatz for independent particles

$$\Phi(\{\mathbf{r}_i\}) \approx \Phi^{\text{Hartree}}(\{\mathbf{r}_i\}) = \varphi_{o_1}(\mathbf{r}_1)\varphi_{o_2}(\mathbf{r}_2) \dots \varphi_{o_N}(\mathbf{r}_N) \quad (3.10)$$

in general is an approximation. Functions that can be written as Eq. (3.10) do not span the full Hilbert space of the functions $\Phi(\{\mathbf{r}_i\})$, which can be differentiated twice and can be normalized. A certain restriction of the set of the allowed functions is acceptable, but we also note that an estimation (determination) of E_0^e using the variational principle is “dangerous”, i.e., it is unknown, how close to E_0^e the result will be. Generally we are not interested in the exact value of E_0^e , but an error of 0.1 eV could be acceptable. Schematically, the variational principle can be described by Fig. 3.1. Because the Hartree ansatz (Eq. (3.10)) for sure is an approximation, we have

$$E_0^e < \frac{\langle \Phi^{\text{Hartree}} | H^e | \Phi^{\text{Hartree}} \rangle}{\langle \Phi^{\text{Hartree}} | \Phi^{\text{Hartree}} \rangle} \quad . \quad (3.11)$$

Due to the normalization condition we have

$$\langle \Phi^{\text{Hartree}} | \Phi^{\text{Hartree}} \rangle = \int \dots \int |\Phi^{\text{Hartree}}(\{\mathbf{r}_i\})|^2 d^3\mathbf{r}_1 \dots d^3\mathbf{r}_N = 1 \quad , \quad (3.12)$$

$$\langle \varphi_{o_i} | \varphi_{o_i} \rangle = \int |\varphi_{o_i}(\mathbf{r})|^2 d^3\mathbf{r} = 1 \quad . \quad (3.13)$$

Orthogonality of the different φ_{o_i} is not required, because we do not want to restrict Φ^{Hartree} any further than we have already done by Eq. (3.10). However, we will obtain that it is – quasi automatically – fulfilled. With the Hartree ansatz (Eq. (3.10)) the expectation value of the energy is

$$\begin{aligned} \langle \Phi^{\text{Hartree}} | H^e | \Phi^{\text{Hartree}} \rangle &= \int \varphi_{o_1}^*(\mathbf{r}_1) \varphi_{o_2}^*(\mathbf{r}_2) \dots \varphi_{o_N}^*(\mathbf{r}_N) \left[\sum_{k=1}^N \frac{-\hbar^2}{2m} \nabla_{\mathbf{r}_k}^2 + v(\mathbf{r}_k) \right] \\ &\quad \varphi_{o_1}(\mathbf{r}_1) \varphi_{o_2}(\mathbf{r}_2) \dots \varphi_{o_N}(\mathbf{r}_N) d^3\mathbf{r}_1 \dots d^3\mathbf{r}_N \\ &+ \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \int \varphi_{o_1}^*(\mathbf{r}_1) \varphi_{o_2}^*(\mathbf{r}_2) \dots \varphi_{o_N}^*(\mathbf{r}_N) \left[\sum_{\substack{k,k'=1 \\ k \neq k'}}^{N,N} \frac{1}{|\mathbf{r}_k - \mathbf{r}_{k'}|} \right] \\ &\quad \varphi_{o_1}(\mathbf{r}_1) \varphi_{o_2}(\mathbf{r}_2) \dots \varphi_{o_N}(\mathbf{r}_N) d^3\mathbf{r}_1 \dots d^3\mathbf{r}_N \quad . \\ &= \sum_{k=1}^N \int \varphi_{o_k}^*(\mathbf{r}_k) \left\{ -\frac{\hbar^2}{2m} \nabla^2 + v(\mathbf{r}_k) \right\} \varphi_{o_k}(\mathbf{r}_k) d^3\mathbf{r}_k \\ &+ \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\substack{k,k'=1 \\ k \neq k'}}^{N,N} \iint \varphi_{o_k}^*(\mathbf{r}_k) \frac{\varphi_{o_{k'}}^*(\mathbf{r}_{k'}) \varphi_{o_{k'}}(\mathbf{r}_{k'}) \varphi_{o_k}(\mathbf{r}_k) d^3\mathbf{r}_k d^3\mathbf{r}_{k'}}{|\mathbf{r}_k - \mathbf{r}_{k'}|} \quad (3.15) \end{aligned}$$

Equation (3.14) can be understood as an energy functional:

$$\langle \Phi^{\text{Hartree}} | H^e | \Phi^{\text{Hartree}} \rangle \stackrel{!}{=} \tilde{E}^{\text{Hartree}} [\varphi_{o_1}, \varphi_{o_2} \dots \varphi_{o_N}, \varphi_{o_1}^*, \varphi_{o_2}^* \dots \varphi_{o_N}^*] \quad (3.16)$$

Here φ and φ^* are considered as two independent functions. Alternatively, the real and the imaginary part of φ could be considered as separate variables.

Ansatz (Eq. (3.10)) represents a significant restriction to the possible functions. Still, we will continue and determine “the best” single-particle functions from this set of functions, i.e., those single-particle functions, which minimize $\tilde{E}^{\text{Hartree}}[\varphi_{o_1} \dots \varphi_{o_N}^*]$. The hope is that the minimum of $\langle \Phi^{\text{Hartree}} | H^e | \Phi^{\text{Hartree}} \rangle$ will be rather close to the true ground state energy E_0^e . Thus, we vary the expression (Eq. (3.14)) with respect to the functions $\varphi_{o_i}^*(\mathbf{r})$ and $\varphi_{o_i}(\mathbf{r})$. The variation is not fully free, because only those functions can be considered, that can be normalized to one. This constraint (Eq. (3.13)) can be taken into account in the variational problem using the method of Lagrange multipliers. Then we obtain an equation to determine the best $\varphi_{o_i}(\mathbf{r})$:

$$\begin{aligned} Q[\varphi_{o_1}, \dots, \varphi_{o_N}, \varphi_{o_1}^*, \dots, \varphi_{o_N}^*] &= \tilde{E}^{\text{Hartree}}[\varphi_{o_1} \dots \varphi_{o_N}, \varphi_{o_1}^* \dots \varphi_{o_N}^*] \\ &\quad - \sum_{k=1}^N \{ \epsilon_{o_k} (1 - \langle \varphi_{o_k} | \varphi_{o_k} \rangle) \} \equiv \text{minimum} \quad , \quad (3.17) \end{aligned}$$

where the ϵ_{o_k} are the Lagrange-multipliers.

Equation (3.16) can be formulated in the following way: We search for the minimum of the functional Q , and for the minimum we have:

$$\begin{aligned} \delta Q = Q [\varphi_{o_1}, \varphi_{o_2}, \dots, \varphi_{o_N}, \varphi_{o_1}^*, \varphi_{o_2}^*, \dots, \varphi_{o_i}^* + \delta\varphi_{o_i}^*, \dots, \varphi_{o_N}^*] \\ - Q [\varphi_{o_1}, \dots, \varphi_{o_N}, \varphi_{o_1}^*, \dots, \varphi_{o_i}^*, \dots, \varphi_{o_N}^*] = 0 \quad , \end{aligned} \quad (3.18)$$

for an arbitrary variation $\delta\varphi_{o_i}^*$, $i = 1 \dots N$, or $\delta\varphi_{o_i}$, $i = 1 \dots N$.

Therefore, if we vary $\varphi_{o_i}^*(\mathbf{r})$, with Eq. (3.16) we obtain

$$\left\langle \delta\varphi_{o_i} \left| -\frac{\hbar^2}{2m} \nabla^2 + v(\mathbf{r}) \right| \varphi_{o_i} \right\rangle + \sum_{\substack{k=1 \\ k \neq i}}^N \frac{e^2}{4\pi\epsilon_0} \left\langle \delta\varphi_{o_i} \varphi_{o_k} \left| \frac{1}{|\mathbf{r}_k - \mathbf{r}_i|} \right| \varphi_{o_k} \varphi_{o_i} \right\rangle = \epsilon_{o_i} \langle \delta\varphi_{o_i} | \varphi_{o_i} \rangle \quad . \quad (3.19)$$

Because the constraint (normalization of the φ_{o_i}) is taken into account by the method of the Lagrange-multipliers, this equation is valid for arbitrary variations $\delta\varphi_{o_i}$. Thus, the equation used to determine the functions $\varphi_{o_i}(\mathbf{r})$ is

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + v(\mathbf{r}) \right] \varphi_{o_i}(\mathbf{r}) + \sum_{\substack{k=1 \\ k \neq i}}^N \frac{e^2}{4\pi\epsilon_0} \left\langle \varphi_{o_k} \left| \frac{1}{|\mathbf{r}_k - \mathbf{r}|} \right| \varphi_{o_k} \right\rangle \varphi_{o_i}(\mathbf{r}) = \epsilon_{o_i} \varphi_{o_i}(\mathbf{r}) \quad . \quad (3.20)$$

We rewrite this equation and obtain

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + v(\mathbf{r}) + v^{\text{Hartree}}(\mathbf{r}) + v_{o_i}^{\text{SIC}}(\mathbf{r}) \right] \varphi_{o_i}(\mathbf{r}) = \epsilon_{o_i} \varphi_{o_i}(\mathbf{r}) \quad , \quad (3.21)$$

where

$$v^{\text{Hartree}}(\mathbf{r}) = \frac{e^2}{4\pi\epsilon_0} \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' \quad (3.22)$$

with

$$n(\mathbf{r}) = \langle \Phi | \sum_{k=1}^N \delta(\mathbf{r} - \mathbf{r}_k) | \Phi \rangle = \sum_{k=1}^N |\varphi_{o_k}(\mathbf{r})|^2 \quad , \quad (3.23)$$

and

$$v_{o_i}^{\text{SIC}}(\mathbf{r}) = -\frac{e^2}{4\pi\epsilon_0} \int \frac{|\varphi_{o_i}(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' \quad . \quad (3.24)$$

$n(\mathbf{r})$ is the particle density of all electrons and $-en(\mathbf{r})$ is the charge density of all electrons. The first equals sign in Eq. (3.22) holds in general, i.e., this is the quantum mechanical definition of the electron density. The second equals sign is valid only for independent particles and for the Hartree approximation.

The term $v^{\text{Hartree}}(\mathbf{r})$, generally called the Hartree potential, can also be expressed in the differential form of electrostatics (Poisson equation):

$$\nabla^2 v^{\text{Hartree}}(\mathbf{r}) = -\frac{e^2}{\epsilon_0} n(\mathbf{r}) \quad (3.25)$$

The potential $v_{\sigma_i}^{\text{SIC}}(\mathbf{r})$ is the self-interaction correction of the Hartree potential. It takes into account that an electron in orbital $\varphi_{o_i}(\mathbf{r})$ shall not interact with itself, but only with the $(N - 1)$ remaining electrons of the system. Equation (3.20) is now “sufficiently simple” to be solved using modern numerical methods. Often the potential $v_{\sigma_i}^{\text{SIC}}(\mathbf{r})$ is then neglected. However, since recent years it became clear that this additional approximation is typically not justified. If the functions $\varphi_{o_i}(\mathbf{r})$ were known, we could calculate the total energy from Eq. (3.14) or the electron distribution using Eq. (3.22). The latter can be compared to measurements (e.g. X-ray diffraction). Additionally, using the charge distribution of the electrons, the nature of the forces, which stabilize the solid, can be understood. One finds that several quantities obtained from the Hartree approximation agree well with experimental data. Further, we find that the negative values of the Lagrange parameters ϵ_{o_i} , introduced due to the normalization, agree approximately with measured ionization energies. An exact discussion of the physical meaning of the Lagrange parameters will be given later (in the context of the Hartree-Fock theory).

Obviously, the Hartree Eq. (3.20) is no ordinary single-particle equation. Formally, it can be written as a single-particle equation,

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + v^{\text{eff}}(\mathbf{r}) \right\} \varphi_{o_i}(\mathbf{r}) = \epsilon_{o_i} \varphi_{o_i}(\mathbf{r}) \quad . \quad (3.26)$$

However, the “effective potential” itself depends on the solutions $\varphi_{o_i}(\mathbf{r})$. Therefore, Eq. (3.25) is an effective (but not a true) single-particle equation. This, for example, implies that the total energy is not equal to the sum of the ϵ_{o_i} , which would be the case for non-interacting particles in the single-particle states $\varphi_{o_i}(\mathbf{r})$.

Nevertheless, using the φ_{o_i} via Eq. (3.14) the total energy can be obtained. How can an equation like Eq. (3.25) be solved, if the potential

$$v^{\text{eff}}(\mathbf{r}) = v(\mathbf{r}) + v^{\text{Hartree}}(\mathbf{r}) + v_{\sigma_i}^{\text{SIC}}(\mathbf{r}) \quad (3.27)$$

initially is unknown, because $n(\mathbf{r})$ is not known? For this purpose the so-called self-consistent field method (SCF) is applied. First, one starts with a reasonable guess, i.e., one estimates $n(\mathbf{r})$. Then the density is improved step by step until the correct result is obtained.

A first crude approximation for $n(\mathbf{r})$ of a solid is obtained by assuming that it can be written as a simple superposition of the electron densities of the individual atoms

$$n^{\text{start}}(\mathbf{r}) = \sum_{I=1}^M n_I^{\text{Atom}}(|\mathbf{r} - \mathbf{R}_I|) \quad . \quad (3.28)$$

This is correct for large interatomic distances, but it is a severe approximation when the electron densities of different atoms overlap. Nevertheless, Eq. (3.27) is a possible and not bad “zeroth approximation”. Once a “zeroth approximation” has been made, one proceeds as shown in Fig. 3.2. At the end of such a calculation the wave functions $\varphi_{o_k}(\mathbf{r})$ and

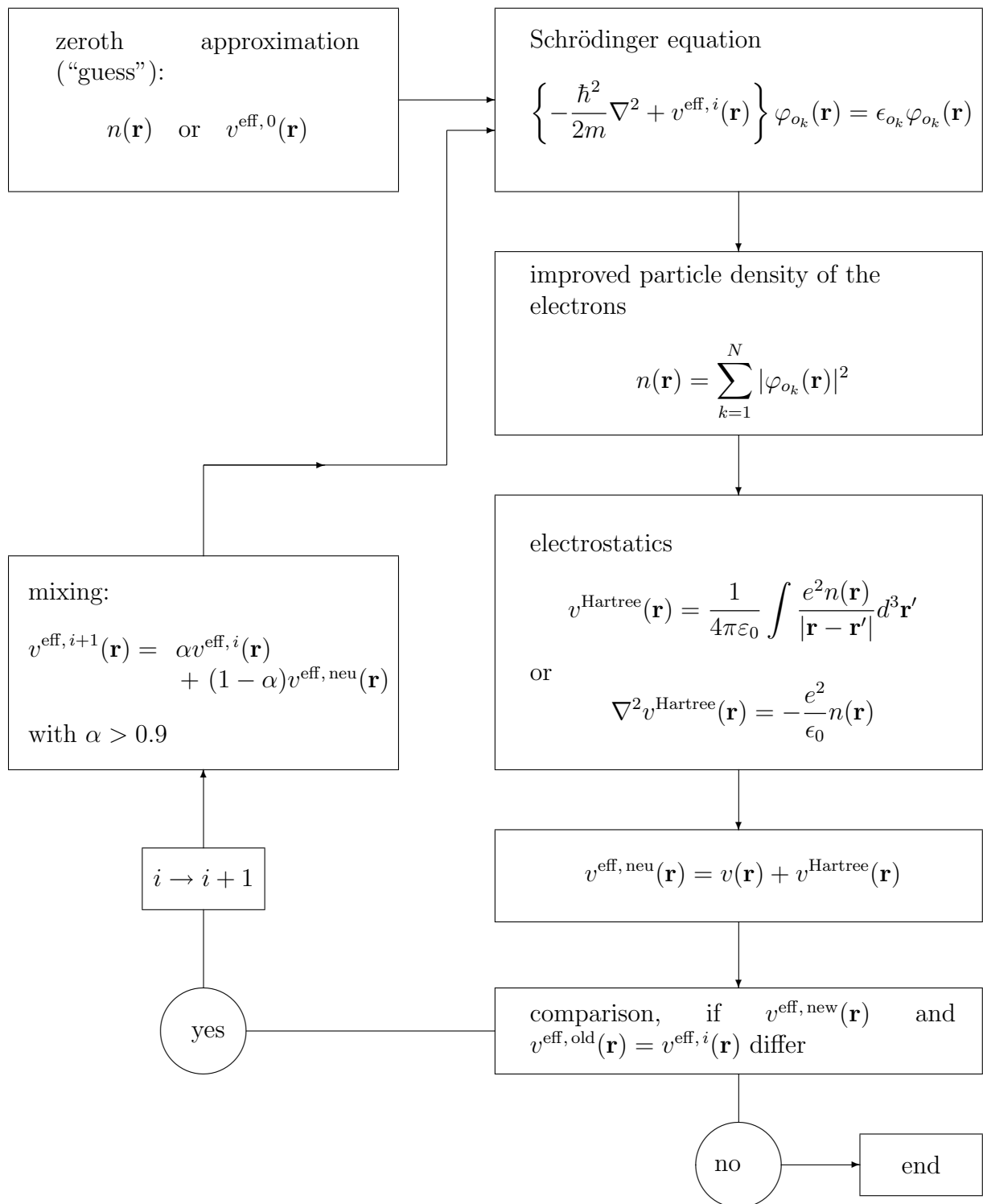


Figure 3.2: Scheme of the self-consistent field method for the solution of the Hartree equation. Here, v^{SIC} has been neglected. Analogous diagrams exist for Hartree-Fock and density-functional theory.

the potential $v^{\text{eff}}(\mathbf{r})$ are *self-consistent*, i.e., their differences in two subsequent iterations are arbitrarily small. Typically, between 5 and 50 iterations are required.

3.2 Hartree-Fock Approximation

The Hartree wave function (Eq. (3.10)) has an important disadvantage: It does not satisfy the Pauli principle. Due to the variational principle, this does not necessarily have a drastic impact on the calculated energy, but for sure it would be better, to remove or reduce this disadvantage. In a many-electron system there is an important interaction between the particles, which in the single-particle picture is formulated in the following way: A single-particle wave function can be occupied by only one electron. More generally, in the many-body picture, the Pauli principle states that the N -particle wave function of fermions has to be antisymmetric with respect to the interchange of all coordinates (spatial and spin) of two particles.

In order to fulfill the Pauli principle, Fock suggested to replace the wave function used in Hartree theory by a suitable linear combination, a so-called Slater determinant²

$$\Phi^{\text{HF}}(\{\mathbf{r}_i\sigma_i\}) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_{o_1s_1}(\mathbf{r}_1\sigma_1) \cdots \varphi_{o_Ns_N}(\mathbf{r}_1\sigma_1) \\ \varphi_{o_1s_1}(\mathbf{r}_2\sigma_2) \cdots \varphi_{o_Ns_N}(\mathbf{r}_2\sigma_2) \\ \cdots \\ \varphi_{o_1s_1}(\mathbf{r}_N\sigma_N) \cdots \varphi_{o_Ns_N}(\mathbf{r}_N\sigma_N) \end{vmatrix} . \quad (3.29)$$

The factor $1/\sqrt{N!}$ ensures the normalization of the many-body wave function. The many-body wave function (Eq. (3.28)) changes sign on interchange of the coordinates (spatial and spin) of two particles. For a determinant this is obvious, because the interchange of two particles corresponds to the interchange of two rows of the determinant.

For two-electron systems (e.g. H^- or He) the wave function reads

$$\Phi^{\text{HF}} = \frac{1}{\sqrt{1 \times 2}} (\varphi_1(\mathbf{r}_1\sigma_1)\varphi_2(\mathbf{r}_2\sigma_2) - \varphi_2(\mathbf{r}_1\sigma_1)\varphi_1(\mathbf{r}_2\sigma_2)) \quad , \quad (3.30)$$

where the one-particle states $i =: (o_i s_i)$ can be, for instance, $1 =: (o_1 \uparrow)$, $2 =: (o_1 \downarrow)$ (two electrons with opposite spin in the same orbital) or $1 =: (o_1 \uparrow)$, $2 =: (o_2 \uparrow)$ (two electrons with the same spin in different orbitals).

²From here on we label the one-particle states by quantum numbers o_i instead of k_i to emphasize that they refer to the position-space component of these states.

And also the normalization is fulfilled:

$$\begin{aligned}
\langle \Phi^{\text{HF}} | \Phi^{\text{HF}} \rangle &= \frac{1}{2!} \sum_{\sigma_1, \sigma_2} \iint \left\{ \varphi_1^*(\mathbf{r}_1 \sigma_1) \varphi_2^*(\mathbf{r}_2 \sigma_2) \varphi_1(\mathbf{r}_1 \sigma_1) \varphi_2(\mathbf{r}_2 \sigma_2) \right. \\
&\quad - \varphi_1^*(\mathbf{r}_1 \sigma_1) \varphi_2^*(\mathbf{r}_2 \sigma_2) \varphi_1(\mathbf{r}_2 \sigma_2) \varphi_2(\mathbf{r}_1 \sigma_1) \\
&\quad - \varphi_1^*(\mathbf{r}_2 \sigma_2) \varphi_2^*(\mathbf{r}_1 \sigma_1) \varphi_1(\mathbf{r}_1 \sigma_1) \varphi_2(\mathbf{r}_2 \sigma_2) \\
&\quad \left. + \varphi_1^*(\mathbf{r}_2 \sigma_2) \varphi_2^*(\mathbf{r}_1 \sigma_1) \varphi_1(\mathbf{r}_2 \sigma_2) \varphi_2(\mathbf{r}_1 \sigma_1) \right\} d^3 \mathbf{r}_1 d^3 \mathbf{r}_2 \\
&= \frac{1}{2} (1 + 0 + 0 + 1) \\
&= 1 \quad .
\end{aligned} \tag{3.31}$$

The single-particle functions shall be normalized and orthogonal,

$$\langle \varphi_{o_i s_i} | \varphi_{o_j s_j} \rangle = \delta_{o_i, o_j} \delta_{s_i, s_j} \quad \text{with} \quad \varphi_{o_i s_i}(\mathbf{r}, \sigma) = \varphi_{o_i s_i}(\mathbf{r}) \chi_{s_i}(\sigma) \quad . \tag{3.32}$$

Note that the spatial functions for spin \uparrow and spin \downarrow states do not have to be the same. In Hartree theory the spatial functions were assumed to be independent of the spin states so that the spin quantum numbers s_i could be omitted. In Hartree-Fock theory this is not the case anymore.³

Now we proceed in the same way as in the Hartree theory, i.e., we will make use of the variational principle $\langle \Phi | H^e | \Phi \rangle = E[\Phi] \geq E_0^e$. It should be noted that ansatz (Eq. (3.28)) still is not general. It allows for an infinite number of possibilities, because the $\varphi_{o_i s_i}(\mathbf{r}, \sigma)$ are arbitrary functions (which can be normalized), but still the set of all vectors in Hilbert space that can be written like Eq. (3.28), do only form a subset of the Hilbert space of the N -particle problem. Many vectors in Hilbert space can only be expressed as a linear combination of Slater determinants. Consequently, again we will not necessarily obtain the ground state energy exactly, but often an approximation will be obtained. However, most probably the approximation will be better than the approximation obtained in Hartree theory, because now the subset of the Hilbert space satisfies the quantum mechanical properties (Pauli principle) of the electrons. Similar to Hartree theory, using Eq.

³Because the (non-relativistic) Hamilton operator of Eq. (3.1) commutes with the operators for the total spin and its z -projection, the exact solutions of the many-electron Schrödinger equation should be eigenfunctions of all of these operators. In principle, this imposes constraints on the form of Φ and the one-particle orbitals. On the other hand, such (spin symmetry) constraints typically lead to higher (i.e. poorer) ground state energies compared to freely varied orbitals. In the context of Hartree-Fock theory, one may make restrict the orbitals $\varphi_{o_i \uparrow} \equiv \varphi_{o_i \downarrow}$ to ensure that Φ^{HF} has the proper spin symmetry (say, for a singlet or triplet He atom). This approach is often referred to as “restricted open-shell Hartree-Fock” (RHF). Or, one may allow the spin-up and -down orbitals to differ. For systems with an unequal number of spin-up and -down electrons, such “unrestricted Hartree-Fock” (UHF) calculations yield indeed lower ground state energies than RHF. The price is that Φ^{UHF} in general does not describe a pure spin state but a mixture of different spin states.

(3.28) we now obtain the expectation value of the energy

$$\begin{aligned}
E^{\text{HF}}[\Phi^{\text{HF}}] &= \langle \Phi^{\text{HF}} | H^e | \Phi^{\text{HF}} \rangle \\
&= \sum_{i=1}^N \sum_{\sigma} \int \varphi_{o_i s_i}^*(\mathbf{r}, \sigma) \left\{ -\frac{\hbar^2}{2m} \nabla^2 + v(\mathbf{r}) \right\} \varphi_{o_i s_i}(\mathbf{r}, \sigma) d^3 \mathbf{r} \\
&\quad + \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\substack{i,j \\ i \neq j}}^{N,N} \sum_{\sigma, \sigma'} \iint \frac{\varphi_{o_i s_i}^*(\mathbf{r}', \sigma') \varphi_{o_j s_j}^*(\mathbf{r}, \sigma) \varphi_{o_i s_i}(\mathbf{r}', \sigma') \varphi_{o_j s_j}(\mathbf{r}, \sigma)}{|\mathbf{r} - \mathbf{r}'|} d^3 \mathbf{r} d^3 \mathbf{r}' \\
&\quad - \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\substack{i,j \\ i \neq j}}^{N,N} \sum_{\sigma, \sigma'} \iint \frac{\varphi_{o_j s_j}^*(\mathbf{r}', \sigma') \varphi_{o_i s_i}^*(\mathbf{r}, \sigma) \varphi_{o_i s_i}(\mathbf{r}', \sigma') \varphi_{o_j s_j}(\mathbf{r}, \sigma)}{|\mathbf{r} - \mathbf{r}'|} d^3 \mathbf{r} d^3 \mathbf{r}' .
\end{aligned} \tag{3.33}$$

The sums over the spins vanish, because $\varphi_{o_i s_i}(\mathbf{r}, \sigma) = \varphi_{o_i s_i}(\mathbf{r}) \chi_{s_i}(\sigma)$ and

$$\sum_{\sigma} \chi_{s_i}^*(\sigma) \chi_{s_j}(\sigma) = \delta_{s_i, s_j} . \tag{3.34}$$

In the first line of Eq. (3.32) we obtain

$$\sum_{\sigma} \chi_{s_i}^*(\sigma) \chi_{s_i}(\sigma) = 1 . \tag{3.35}$$

In the second line we obtain

$$\sum_{\sigma, \sigma'} \chi_{s_i}^*(\sigma') \chi_{s_i}(\sigma') \chi_{s_j}^*(\sigma) \chi_{s_j}(\sigma) = 1 . \tag{3.36}$$

In the third line we obtain

$$\sum_{\sigma, \sigma'} \chi_{s_j}^*(\sigma') \chi_{s_i}^*(\sigma) \chi_{s_i}(\sigma') \chi_{s_j}(\sigma) = \sum_{\sigma} \delta_{s_i, s_j} \chi_{s_i}^*(\sigma) \chi_{s_j}(\sigma) = \delta_{s_i, s_j} . \tag{3.37}$$

This means that in Eq. (3.32) all sums, $\sum_{\sigma, \sigma'}$, can be removed. Only in the last line this sum has to be replaced by a Kronecker symbol. A comparison of Eq. (3.28) with the corresponding equation of Hartree theory (Eq. (3.14)) shows that we now have obtained an additional term

$$\tilde{E}^{\text{x}}[\{\varphi_{o_i s_i}^*, \varphi_{o_i s_i}\}] = -\frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\substack{i,j \\ i \neq j}}^{N,N} \delta_{s_i, s_j} \iint \frac{\varphi_{o_i s_i}^*(\mathbf{r}) \varphi_{o_j s_j}^*(\mathbf{r}') \varphi_{o_i s_i}(\mathbf{r}') \varphi_{o_j s_j}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d^3 \mathbf{r} d^3 \mathbf{r}' . \tag{3.38}$$

This term enters because of the inclusion of the exchange interaction (Pauli principle). Thus the letter x is used as index. It is an abbreviation for the word “exchange”.

This term has a negative sign. Compared to Hartree theory it therefore lowers the energy. Now it is clear that Hartree-Fock theory is a better approximation than Hartree theory. In Eq. (3.28) the condition $i \neq j$ in both sums can be omitted, because for $i = j$ the last two terms cancel each other. By summing over the spins we obtain

$$\begin{aligned}
E^{\text{HF}}[\{\varphi_{o_i s_i}^*, \varphi_{o_i s_i}\}] &= T_s[\{\varphi_{o_i s_i}^*, \varphi_{o_i s_i}\}] + E^{e-\text{Ion}}[\{\varphi_{o_i s_i}^*, \varphi_{o_i s_i}\}] \\
&\quad + E^{\text{Hartree}}[\{\varphi_{o_i s_i}^*, \varphi_{o_i s_i}\}] + E^{\text{x}}[\{\varphi_{o_i s_i}^*, \varphi_{o_i s_i}\}] , \tag{3.39}
\end{aligned}$$

with

$$T_s[\{\varphi_{o_i s_i}^*, \varphi_{o_i s_i}\}] = \sum_{i=1}^N \int \varphi_{o_i s_i}^*(\mathbf{r}) \left\{ -\frac{\hbar^2}{2m} \nabla^2 \right\} \varphi_{o_i s_i}(\mathbf{r}) d^3\mathbf{r} \quad , \quad (3.40)$$

the functional of the kinetic energy of non-interacting electrons in the single-particle states $\varphi_{o_i s_i}(\mathbf{r})$. The other quantities are:

$$E^{e-Ion}[\{\varphi_{o_i s_i}^*, \varphi_{o_i s_i}\}] = \int v(\mathbf{r}) n(\mathbf{r}) d^3\mathbf{r} \quad , \quad (3.41)$$

$$E^{\text{Hartree}}[\{\varphi_{o_i s_i}^*, \varphi_{o_i s_i}\}] = \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r} d^3\mathbf{r}' \quad , \quad (3.42)$$

and

$$E^x[\{\varphi_{o_i s_i}^*, \varphi_{o_i s_i}\}] = -\frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{i,j}^{N,N} \delta_{s_i, s_j} \iint \frac{\varphi_{o_i s_i}^*(\mathbf{r}) \varphi_{o_j s_j}^*(\mathbf{r}') \varphi_{o_i s_i}(\mathbf{r}') \varphi_{o_j s_j}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r} d^3\mathbf{r}' \quad . \quad (3.43)$$

The electron density is

$$n(\mathbf{r}) = \sum_{i=1}^N |\varphi_{o_i s_i}(\mathbf{r})|^2 \quad . \quad (3.44)$$

For the last term in Eq. (3.42) we have written E^x (without tilde): $E^x = \tilde{E}^x - E^{\text{SIC}}$. Here, E^{SIC} is the term $i = j$, which does not appear in Eq. (3.37). Nowadays the quantity E^x is called exchange energy. Consequently, E^{Hartree} now contains the self-interaction of the electrons, while E^x takes into account the correction of this self-interaction, and additionally E^x makes sure the Pauli principle is fulfilled.

The “best” functions $\varphi_{o_i s_i}(\mathbf{r})$, i.e., the functions yielding the lowest energy, are obtained if Eq. (3.42) is varied in the $\varphi_{o_i s_i}^*(\mathbf{r})$ or in the $\varphi_{o_i s_i}(\mathbf{r})$, respectively. This again has to be done taking into account the normalization and the orthogonality of the $\varphi_{o_i s_i}(\mathbf{r})$. Both have been used already in the construction of Eq. (3.32) and (3.38). We have

$$\delta \left\{ E^{\text{HF}}[\{\varphi_{o_i s_i}^*, \varphi_{o_i s_i}\}] + \sum_{i,j}^{N,N} \lambda_{o_i s_i, o_j s_j} [\delta_{o_i s_i, o_j s_j} - \langle \varphi_{o_i} | \varphi_{o_j} \rangle] \right\} = \delta Q = 0 \quad . \quad (3.45)$$

In the derivation of the Hartree theory only the normalization has been considered as a constraint. This is sufficient here as well; but mathematically it is easier to consider both, orthogonality and normalization as constraints (cf. Slater “The Self-consistent Field ...”, Vol. 2, Chapter 17). The functional in the curly brackets in Eq. (3.44) we call $Q[\varphi_{o_1 s_1}^*, \dots, \varphi_{o_N s_N}^*, \varphi_{o_1 s_1}, \dots, \varphi_{o_N s_N}]$. If we form the functional derivative of this functional⁴ Q and take into account that $\varphi_{o_i s_i}^*$ and $\varphi_{o_i s_i}$ have to be treated as independent variables (which are given by their real and imaginary parts, i.e., by two functions), for the variation of $\varphi_{o_i s_i}^*$

$$\frac{\delta}{\delta \varphi_{o_k s_k}^*(\mathbf{r})} Q[\{\varphi_{o_i s_i}^*, \varphi_{o_i s_i}\}] = 0 \quad \text{for} \quad k = 1 \dots N \quad , \quad (3.46)$$

⁴Note: $\frac{\delta}{\delta f(x)} \int f(x') g(x') dx' = g(x)$.

we obtain the set of equations

$$\begin{aligned} & \left\{ -\frac{\hbar^2}{2m} \nabla^2 + v(\mathbf{r}) + v^{\text{Hartree}}(\mathbf{r}) \right\} \varphi_{o_k s_k}(\mathbf{r}) - \frac{e^2}{4\pi\epsilon_0} \sum_{j=1}^N \delta_{s_k, s_j} \int \frac{\varphi_{o_j s_j}^*(\mathbf{r}') \varphi_{o_k s_k}(\mathbf{r}') \varphi_{o_j s_j}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d^3 \mathbf{r}' \\ & = \sum_{j=1}^N \lambda_{o_k s_k, o_j s_j} \varphi_{o_j s_j}(\mathbf{r}) \quad , \end{aligned} \quad (3.47)$$

with

$$v^{\text{Hartree}}(\mathbf{r}) = \frac{e^2}{4\pi\epsilon_0} \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 \mathbf{r}' \quad . \quad (3.48)$$

At a first glance, this equation looks unfamiliar. Due to the exchange term and due to the right side it does not look like a Schrödinger equation. However, it can be easily shown that it can be written in a familiar form. To show this we investigate the matrix $\lambda_{o_j s_j, o_i s_i}$. Multiplying Eq. (3.46) from the left by $\varphi_{o_l s_l}^*(\mathbf{r})$ and integrate over \mathbf{r} , we obtain

$$A_{lk} + B_{lk} = \lambda_{o_l s_l, o_k s_k} \quad , \quad (3.49)$$

where

$$A_{lk} = \int \varphi_{o_l s_l}^*(\mathbf{r}) \left\{ -\frac{\hbar^2}{2m} \nabla^2 + v(\mathbf{r}) + v^{\text{Hartree}}(\mathbf{r}) \right\} \varphi_{o_k s_k}(\mathbf{r}) d^3 \mathbf{r} \quad (3.50)$$

and

$$B_{lk} = -\frac{e^2}{4\pi\epsilon_0} \sum_{j=1}^N \delta_{s_k, s_j} \iint \frac{\varphi_{o_l s_l}^*(\mathbf{r}) \varphi_{o_j s_j}^*(\mathbf{r}') \varphi_{o_k s_k}(\mathbf{r}') \varphi_{o_j s_j}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d^3 \mathbf{r} d^3 \mathbf{r}' \quad . \quad (3.51)$$

The matrix A defined this way is obviously Hermitian, i.e., we have $A_{lk} = A_{kl}^*$. If we take the complex conjugate of B we obtain

$$B_{kl}^* = -\frac{e^2}{4\pi\epsilon_0} \sum_{j=1}^N \delta_{s_j, s_k} \iint \frac{\varphi_{o_k s_k}(\mathbf{r}) \varphi_{o_j s_j}(\mathbf{r}') \varphi_{o_l s_l}^*(\mathbf{r}') \varphi_{o_j s_j}^*(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d^3 \mathbf{r} d^3 \mathbf{r}' = B_{lk} \quad . \quad (3.52)$$

Therefore, also B is Hermitian and thus $\lambda_{o_l s_l, o_k s_k}$ as well. It follows that there must be a unitary transformation

$$\sum_{o_l} U_{o_k, o_l} \varphi_{o_k}(\mathbf{r}) = \tilde{\varphi}_{o_k}(\mathbf{r}) \quad (3.53)$$

and

$$\sum_{o_m, o_n} U_{o_k, o_m}^\dagger \lambda_{o_m s_l, o_n s_k} U_{o_n, o_l} = \epsilon_{o_k s_k} \delta_{o_l s_l, o_k s_k} \quad , \quad (3.54)$$

so that matrix λ is transformed into a real, diagonal matrix. We obtain the equation to determine the $\tilde{\varphi}_{o_k s_k}(\mathbf{r})$

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + v(\mathbf{r}) + v^{\text{Hartree}}(\mathbf{r}) + v_k^x(\mathbf{r}) \right\} \tilde{\varphi}_{o_k s_k}(\mathbf{r}) = \epsilon_{o_k s_k} \tilde{\varphi}_{o_k s_k}(\mathbf{r}) \quad (3.55)$$

with

$$v_k^x(\mathbf{r})\tilde{\varphi}_{o_k s_k}(\mathbf{r}) = -\frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^N \delta_{s_i s_k} \int \frac{\tilde{\varphi}_{o_i s_i}^*(\mathbf{r}')\tilde{\varphi}_{o_k s_k}(\mathbf{r}')\tilde{\varphi}_{o_i s_i}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' \quad . \quad (3.56)$$

Equation (3.54) is called the *Hartree-Fock equation*. Once the single-particle wave functions $\{\tilde{\varphi}_{o_i s_i}\}$ have been obtained using Eq. (3.54), in the next step the total energy can be calculated using Eq. (3.38).

The exchange term $v_k^x(\mathbf{r})$ does not look like a normal potential, because it is an integral operator. In 1951 Slater pointed out that it can be written in a familiar form. For this purpose (Eq. (3.55)) is multiplied by

$$\frac{\tilde{\varphi}_{o_k s_k}(\mathbf{r})}{\tilde{\varphi}_{o_k s_k}(\mathbf{r})} = 1 \quad . \quad (3.57)$$

Using the definition

$$n_k^{\text{HF}}(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^N \delta_{s_i, s_k} \frac{\tilde{\varphi}_{o_i s_i}^*(\mathbf{r}')\tilde{\varphi}_{o_k s_k}(\mathbf{r}')\tilde{\varphi}_{o_i s_i}(\mathbf{r})}{\tilde{\varphi}_{o_k s_k}(\mathbf{r})} \quad (3.58)$$

for the exchange particle density the exchange potential adopts the following form

$$v_k^x(\mathbf{r}) = -\frac{e^2}{4\pi\epsilon_0} \int \frac{n_k^{\text{HF}}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' \quad . \quad (3.59)$$

Now, the potential v_k^x is almost a “normal” multiplicative operator, but it is different for each particle. $v^{\text{Hartree}} + v_k^x$ describes the interaction of electron k with the other electrons. This interaction, v_k^x , is present only for those electrons, which have the same spin, i.e., $s_i = s_k$. In principle, the expression (Eq. (3.57)) is not defined at the points where $\tilde{\varphi}_{o_k s_k}(\mathbf{r})$ are zero, but this is not a problem, because $n_k^{\text{HF}}(\mathbf{r}, \mathbf{r}')$ can be extended continuously. From now on, when talking about the Hartree-Fock equation, we mean Eq. (3.54), and we will now leave away the tilde on the $\varphi_{o_k s_k}(\mathbf{r})$.

3.3 The Exchange Interaction

Here, the physical meaning of the Hartree and the Hartree-Fock equations will be investigated in more detail. In particular the exchange energy will be made plausible, and the problems of Hartree-Fock theory will be discussed, i.e., which physical many-body effects are missing in this theory. The effective single-particle Hamilton operator of the Hartree and of the Hartree-Fock equations is:

$$h = -\frac{\hbar^2}{2m}\nabla^2 + v(\mathbf{r}) + v^{\text{Hartree}}(\mathbf{r}) + \begin{cases} -\frac{e^2}{4\pi\epsilon_0} \int \frac{n_k^{\text{H}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' = v_k^{\text{SIC}}(\mathbf{r}) & \text{Hartree,} \\ -\frac{e^2}{4\pi\epsilon_0} \int \frac{n_k^{\text{HF}}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' = v_k^x(\mathbf{r}) & \text{Hartree-Fock,} \end{cases} \quad (3.60)$$

with

$$n_k^{\text{H}}(\mathbf{r}') = |\varphi_{o_k}(\mathbf{r}')|^2 \quad (3.61)$$

and $n_k^{\text{HF}}(\mathbf{r}, \mathbf{r}')$ from Eq. (3.57). Nowadays, v_k^{SIC} is often neglected, and the ansatz $v^{\text{eff}} = v + v^{\text{Hartree}}$ is termed Hartree approximation. We will not introduce this additional approximation here.

We have

$$\int n_k^{\text{H}}(\mathbf{r}') d^3\mathbf{r}' = 1 \quad (3.62)$$

$$\int n_k^{\text{HF}}(\mathbf{r}, \mathbf{r}') d^3\mathbf{r}' = 1 \quad . \quad (3.63)$$

Both densities $n_k^{\text{H}}(\mathbf{r}')$ and $n_k^{\text{HF}}(\mathbf{r}, \mathbf{r}')$ represent one electron, i.e., in both cases the self-interaction included in v^{Hartree} is removed. Equation (3.62) is an important sum rule, which also holds for the exact theory. However, $n_k^{\text{HF}}(\mathbf{r}, \mathbf{r}')$ contains more than just the correction of the self-interaction. We will investigate this for a simple system now. Because now we are dealing with the electron-electron interaction (and not with the electron-ion interaction), we investigate a system, in which the potential of the lattice components (i.e., of the ions) varies only weakly. Thus we set $v(\mathbf{r}) = v \equiv \text{constant}$. We want to use this to demonstrate the meaning of the exchange interaction. For such a jellium system the Hartree-Fock equations are solved by plane waves. This will be the result of our discussion (but we note in passing that there are also more complex solutions: “spin density waves”). Therefore, the single-particle wave functions are

$$\varphi_{o_i s_i}(\mathbf{r}) = \frac{1}{\sqrt{V_g}} e^{i\mathbf{k}_i \mathbf{r}} \quad . \quad (3.64)$$

With these wave functions we obtain:

$$n_k^{\text{H}}(\mathbf{r}') = \frac{1}{V_g} = \text{constant} \quad , \quad (3.65)$$

i.e., the density n_k^{H} and the electron k , respectively, is smeared out uniformly over the whole volume. The particle density interacting with the Hartree particle k is

$$n(\mathbf{r}') - n_k^{\text{H}}(\mathbf{r}') = \frac{N}{V_g} - \frac{1}{V_g} \quad . \quad (3.66)$$

If particle k is located at $\mathbf{r} = 0$, the distribution of the other electrons is as shown in Fig. 3.3. Strictly speaking the line in Fig. 3.3 is at $(1 - \frac{1}{N})$. But because N is arbitrarily large, this cannot be distinguished from 1.

Therefore, for extended wave functions, $v_k^{\text{SIC}}(\mathbf{r})$ is negligible.

The corresponding particle density interacting with an electron in single-particle state $\varphi_{o_k s_k}$ in the Hartree-Fock theory is

$$n(\mathbf{r}') - n_k^{\text{HF}}(\mathbf{r}, \mathbf{r}') \quad . \quad (3.67)$$

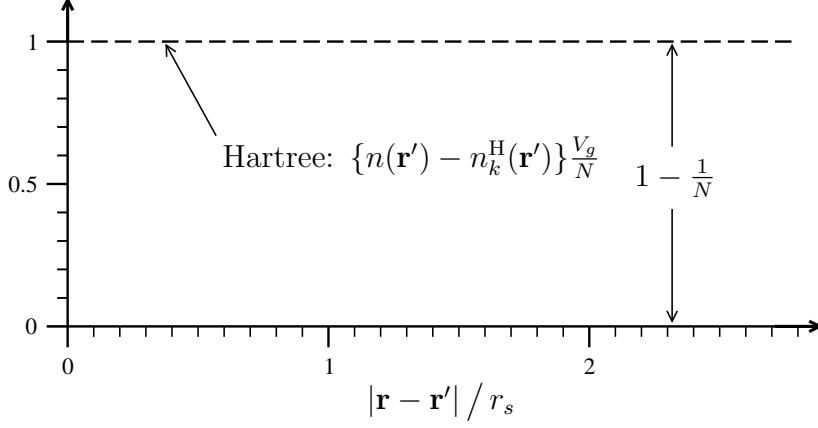


Figure 3.3: Distribution of the $(N - 1)$ electrons seen by particle $\varphi_k(\mathbf{r})$, which is located at $\mathbf{r} = 0$ (in the Hartree approximation and for jellium).

If particle k is at position \mathbf{r} , then the $(N - 1)$ other particles have a distribution, which is given by Eq. (3.66). Like in the Hartree approximation (Eq. (3.66)) also contains exactly $N - 1$ particles. What does this density look like?

$$n_k^{\text{HF}}(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^N \delta_{s_i, s_k} \frac{\varphi_{o_i s_i}^*(\mathbf{r}') \varphi_{o_k s_k}(\mathbf{r}') \varphi_{o_i s_i}(\mathbf{r})}{\varphi_{o_k s_k}(\mathbf{r})} \quad (3.68)$$

$$= \frac{1}{V_g} \sum_{\mathbf{k}_i}^{\frac{N}{2}} e^{-i\mathbf{k}_i \mathbf{r}'} e^{i\mathbf{k}_k \mathbf{r}'} e^{i\mathbf{k}_i \mathbf{r}} e^{-i\mathbf{k}_k \mathbf{r}} \quad (3.69)$$

$$= \frac{1}{V_g} \sum_{\mathbf{k}_i}^{\frac{N}{2}} e^{i(\mathbf{k}_i - \mathbf{k}_k)(\mathbf{r} - \mathbf{r}')} \quad (3.70)$$

In order to simplify the representation, here we have assumed that the system is nonmagnetic and therefore each spatial state $\varphi_{o_i}(\mathbf{r})$ is occupied by two electrons. Because n_k^{HF} is different for each state, one obtains a better impression of the meaning of Eq. (3.69), if one averages over all electrons:

$$\bar{n}^{\text{HF}}(\mathbf{r}, \mathbf{r}') \stackrel{!}{=} \sum_{k=1}^N \frac{\varphi_{o_k}^*(\mathbf{r}) n_k^{\text{HF}}(\mathbf{r}, \mathbf{r}') \varphi_{o_k}(\mathbf{r})}{n(\mathbf{r})} \quad (3.71)$$

$$= \frac{V_g}{N} \frac{1}{V_g} \frac{1}{V_g} 2 \sum_{\mathbf{k}_k}^{\frac{N}{2}} e^{-i\mathbf{k}_k(\mathbf{r} - \mathbf{r}')} \sum_{\mathbf{k}_i}^{\frac{N}{2}} e^{i\mathbf{k}_i(\mathbf{r} - \mathbf{r}')} \quad (3.72)$$

The sum over the vectors \mathbf{k}_i and \mathbf{k}_k can be evaluated easily, if one changes from a discrete to a continuous representation (cf. the discussion following Eq. (2.18)):

$$\sum_{\mathbf{k}_i}^{\frac{N}{2}} \rightarrow \int_0^{k_{\text{F}}} \frac{V_g}{(2\pi)^3} d^3 \mathbf{k} \quad (3.73)$$

We obtain

$$\frac{V_g}{(2\pi)^3} \int_0^{k_{\text{F}}} e^{i\mathbf{k}(\mathbf{r} - \mathbf{r}')} d^3 \mathbf{k} = \frac{3}{2} N \frac{(k_{\text{F}} \hat{r}) \cos(k_{\text{F}} \hat{r}) - \sin(k_{\text{F}} \hat{r})}{(k_{\text{F}} \hat{r})^3} \quad (3.74)$$

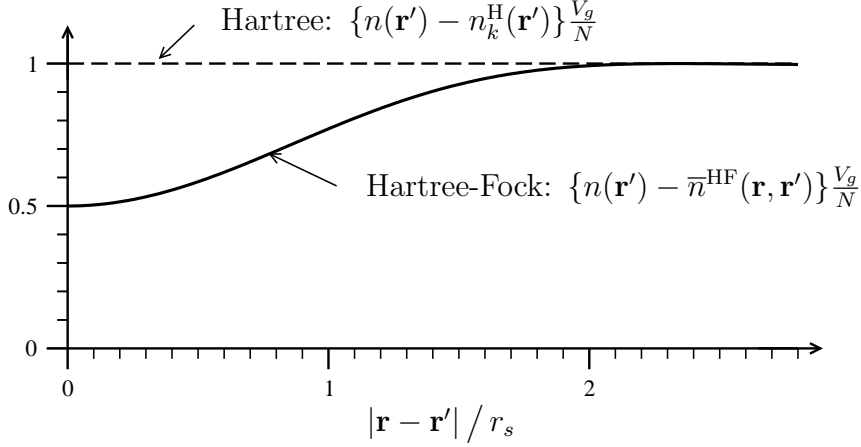


Figure 3.4: Distribution (averaged) of the $(N - 1)$ other electrons with respect to a particle that is located at position $\mathbf{r} = 0$ (in the Hartree-Fock approximation and for jellium).

with $\hat{r} = |\mathbf{r} - \mathbf{r}'|$.

It follows:

$$\bar{n}^{\text{HF}}(\hat{r}) = \frac{9}{2} \frac{N}{V_g} \left(\frac{(k_F \hat{r}) \cos(k_F \hat{r}) - \sin(k_F \hat{r})}{(k_F \hat{r})^3} \right)^2, \quad (3.75)$$

\bar{n}^{HF} therefore is spherically symmetric. The particle density of the other electrons felt by a (averaged) Hartree-Fock particle, looks like that shown in Fig. 3.4. The concentration of the electrons of like spin is lowered in the neighborhood of the investigated electron. This is formulated in the following way: An electron is surrounded by its exchange hole. The quantity $n_k^{\text{HF}}(\mathbf{r}, \mathbf{r}')$ is called particle density (with respect to \mathbf{r}') of the exchange hole of an electron at position \mathbf{r} .

The difference between the Hartree and the Hartree-Fock approximation (cf. Fig. 3.4, or the equations (3.64) and (3.74)) is that $n_k^{\text{H}}(\mathbf{r}')$ only depends on \mathbf{r}' , i.e., it is the same for each position \mathbf{r} of the observed particle. But $n_k^{\text{HF}}(\mathbf{r}, \mathbf{r}')$ and $\bar{n}^{\text{HF}}(\mathbf{r}, \mathbf{r}')$ depends on the position of the particle, i.e., on the position of the particle for which we are actually solving the Hartree-Fock equation using n_k^{HF} . n_k^{HF} fulfills the Pauli principle: If the investigated electron k is at position \mathbf{r} , then all other electrons of like spin are displaced from position \mathbf{r} . Due to the Pauli principle the electrons of like spin do not move independently of each other, but their motion is correlated, because in its neighborhood an electron displaces the other electrons. Although we have solved the time-independent Schrödinger equation, this dynamic Pauli correlation is taken into account. This is because the Pauli interaction is not explicitly included in the Hamilton operator, but is taken into account via the constraint of an “antisymmetric wave function”. Another correlation should appear (in an exact theory) due to the Coulomb repulsion for all electrons, i.e., also for electrons of unlike spins there must be a displacement of electrons. But this Coulomb repulsion is included only in an averaged way in Hartree as well as in Hartree-Fock theory, so that the correlation resulting from the Coulomb repulsion is missing in both theories. Hartree-Fock therefore contains a part of the correlation, the so-called Pauli correlation. Nevertheless, it is commonly agreed that the term correlation is used for all that is missing in Hartree-

Fock. This usage is not very fortunate, but it has become generally accepted⁵.

For the exchange potential (cf. Eq. (3.58)) of a jellium system we obtain (with plane waves as eigenfunctions) for the dependence of v^x on state \mathbf{k}_m the result shown in Fig. 3.5. In Chapter 2.3 we have set the potential as spatially constant and the same (state-independent) for *all* (free) electrons. Here we will see how far this can be justified for interacting (real) electrons.

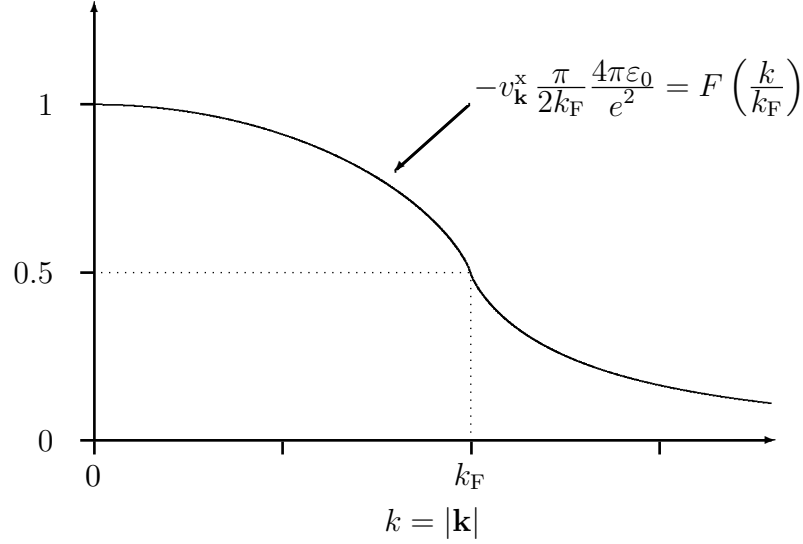


Figure 3.5: The exchange potential as a function of state \mathbf{k} for a jellium system.

The calculation goes as follows:

$$\begin{aligned} v_{\mathbf{k}}^x(\mathbf{r}) &= -\frac{e^2}{4\pi\epsilon_0} \int \frac{n_{\mathbf{k}}^{\text{HF}}(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' \quad , \\ &= -\frac{e^2}{4\pi\epsilon_0} \frac{1}{(2\pi)^3} \int_0^{k_F} \int \frac{e^{i(\mathbf{k}' - \mathbf{k})\hat{\mathbf{r}}}}{|\hat{\mathbf{r}}|} d^3\hat{\mathbf{r}} d^3\mathbf{k}' \quad , \end{aligned} \quad (3.76)$$

where $\hat{\mathbf{r}} = \mathbf{r} - \mathbf{r}'$. We have

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = 4\pi \frac{1}{(2\pi)^3} \int \frac{e^{i\mathbf{q}(\mathbf{r} - \mathbf{r}')}}{q^2} d^3\mathbf{q} \quad . \quad (3.77)$$

Thus, we obtain

$$v_{\mathbf{k}}^x = -\frac{e^2}{4\pi\epsilon_0} \frac{4\pi}{(2\pi)^3} \int_0^{k_F} \frac{1}{|\mathbf{k} - \mathbf{k}'|^2} d^3\mathbf{k}' \quad . \quad (3.78)$$

We have used

$$\int e^{i(\mathbf{q} - \mathbf{k} + \mathbf{k}')\hat{\mathbf{r}}} d^3\hat{\mathbf{r}} = (2\pi)^3 \delta(\mathbf{q} + \mathbf{k}' - \mathbf{k}) \quad . \quad (3.79)$$

⁵In the field of density-functional theory the definition is modified.

If the integration is done, one obtains

$$v_{\mathbf{k}}^x = -\frac{e^2}{4\pi\epsilon_0} \frac{2k_F}{\pi} F\left(\frac{k}{k_F}\right) \quad , \quad (3.80)$$

where

$$F(x) = \frac{1}{2} + \frac{1-x^2}{4x} \ln \left| \frac{1+x}{1-x} \right| \quad . \quad (3.81)$$

The function $F\left(\frac{k}{k_F}\right)$ is shown in Fig. 3.5.

For the further discussion of Hartree-Fock theory we have a look at the eigenvalues of the Hartree-Fock equation. In the jellium approximation it follows:

$$\langle \varphi_{\mathbf{k}} | h | \varphi_{\mathbf{k}} \rangle = \epsilon(\mathbf{k}) = \frac{\hbar^2 \mathbf{k}^2}{2m} + \langle \varphi_{\mathbf{k}} | v_{\mathbf{k}}^x | \varphi_{\mathbf{k}} \rangle \quad . \quad (3.82)$$

Here, the zero point of the energy was set to the average electrostatic potential:

$$v(\mathbf{r}) + \frac{e^2}{4\pi\epsilon_0} \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' = 0 \quad . \quad (3.83)$$

The expectation value of the exchange potential is given by Eq. (3.77):

$$\langle \varphi_{\mathbf{k}} | v_{\mathbf{k}}^x | \varphi_{\mathbf{k}} \rangle = v_{\mathbf{k}}^x \langle \varphi_{\mathbf{k}} | \varphi_{\mathbf{k}} \rangle = -\frac{e^2}{4\pi\epsilon_0} \frac{2k_F}{\pi} F\left(\frac{k}{k_F}\right) \quad , \quad (3.84)$$

and for Eq. (3.81) we obtain:

$$\epsilon(\mathbf{k}) = \frac{\hbar^2 \mathbf{k}^2}{2m} - \frac{e^2}{4\pi\epsilon_0} \frac{2k_F}{\pi} F\left(\frac{k}{k_F}\right) \quad (3.85)$$

with $F(x)$ from Eq. (3.80).

This derivation shows that plane waves are in fact eigenfunctions of the Hartree-Fock Hamilton operator, i.e., they diagonalize the Hartree-Fock operator. However, we do not have the dispersion relation of free electrons anymore, but there is an additional term, which depends on k and which gives rise to a lowering of the single-particle energies. If we now compare the relation (Eq. (3.83)) of Hartree-Fock theory with the one of free electrons ($v^{\text{eff}}(\mathbf{r}) = \text{constant}$) or with Hartree theory, we obtain Fig. 3.6.

In Fig. 3.6 it can be seen:

1. For very small \mathbf{k} the dispersion of Hartree-Fock particles is parabolic. The curvature of this parabola is different from the one of free electrons. If \mathbf{k} is very small we obtain

$$\epsilon(\mathbf{k}) = \frac{\hbar^2 \mathbf{k}^2}{2m^*} + C \quad \text{for} \quad |\mathbf{k}| \rightarrow 0 \quad . \quad (3.86)$$

For the effective mass of the Hartree-Fock particles we have:

$$\frac{m^*}{m} = \frac{1}{1 + 0.22 (r_s/a_B)} \quad \text{for} \quad |\mathbf{k}| \rightarrow 0 \quad , \quad (3.87)$$

for $k \rightarrow 0$, m^* is smaller than m (r_s is typically between 2 and 3 bohr).

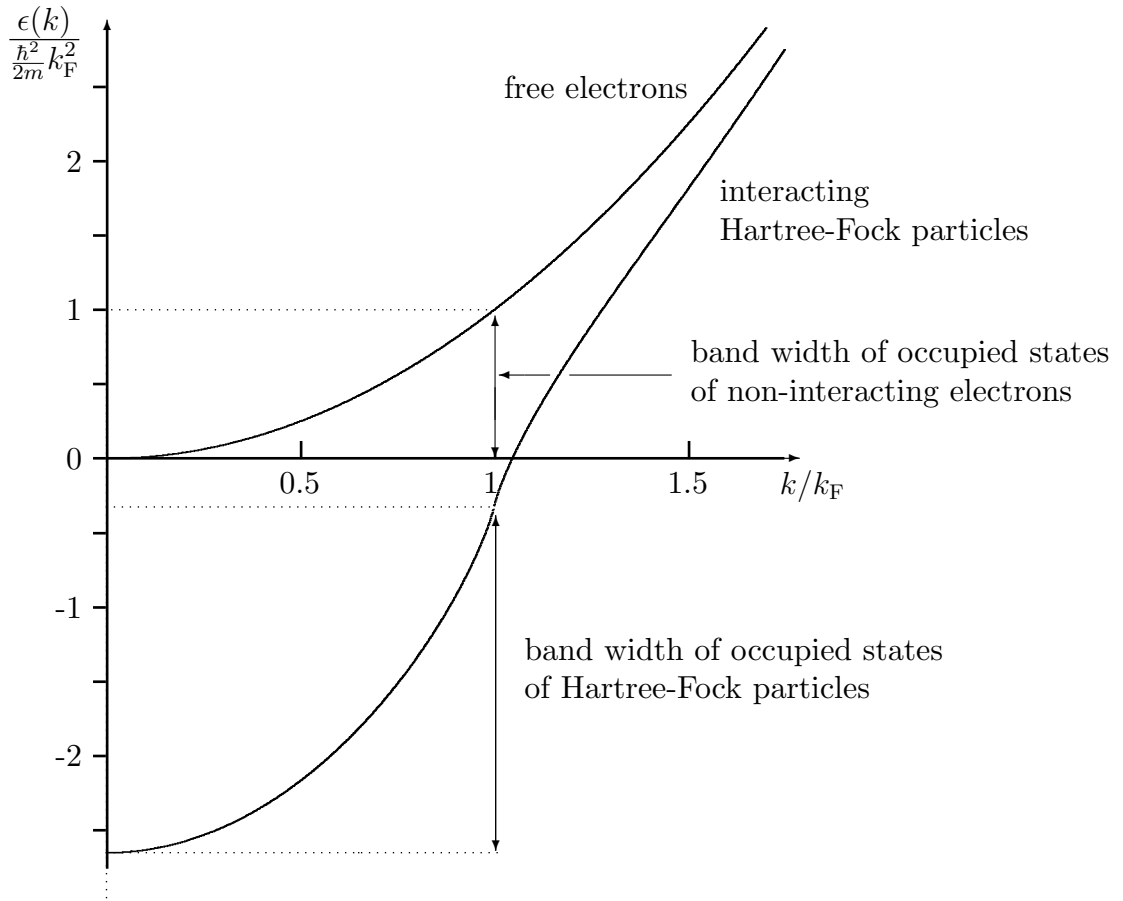


Figure 3.6: Dispersion of the single-particle energies in jellium for free electrons (or Hartree particles) and for Hartree-Fock particles (Eq. (3.83)), shown here for the density parameter ($r_s = 4$ bohr).

2. The band width of the occupied states is significantly larger for Hartree-Fock particles than for Hartree particles, a factor 2.33 in Fig. 3.6.
3. For $k = k_F$ there is an obviously unphysical result:

The derivation

$$\frac{\partial \epsilon(\mathbf{k})}{\partial k} \rightarrow \infty \quad \text{for} \quad k \rightarrow k_F \quad (3.88)$$

becomes logarithmically infinite. This has consequences for metallic properties and for the heat capacity. Both are described mainly by the electrons close to the Fermi energy. The reason for the singularity is in the $\frac{1}{|\mathbf{r}-\mathbf{r}'|}$ behavior of the electron-electron interaction. If the interaction was screened, e.g.

$$\frac{e^{-\lambda(|\mathbf{r}-\mathbf{r}'|)}}{|\mathbf{r}-\mathbf{r}'|}, \quad (3.89)$$

the singularity would not exist (cf. Ashcroft-Mermin, p. 337).

4. The potential v_k^x is typically in the range of 5-15 eV. Because many phenomena in solid-state physics are determined by energy differences in the order of 0.1-0.5 eV, an exact treatment of the exchange interaction is crucial.

3.4 Koopmans' Theorem⁶

In the discussion of the Hartree equation we pointed out that the Lagrange parameters ϵ_{o_i} seem to correspond (at least approximately) to ionization energies. This statement will be investigated in more detail now for the Hartree-Fock equation.

The energy, which is required to remove an electron from state k in an N electron system is

$$I_k = E_k^{N-1} - E^N = \langle \Phi_k^{N-1} | H^{e,N-1} | \Phi_k^{N-1} \rangle - \langle \Phi^N | H^{e,N} | \Phi^N \rangle \quad (3.90)$$

Here we assume that the removed electron is excited to the zero point of the energy (the vacuum level), and there is a free particle of zero kinetic energy. Φ^N is the ground state wave function of the N electron system and Φ_k^{N-1} the wave function of the $N-1$ electron system, the state k being unoccupied. If state k is the highest occupied state of the N electron system (i.e., state N), then I_k is the ionization energy. In order to investigate Eq. (3.90) we make the following assumptions:

- 1) Removing an electron has no influence on lattice geometry, or more precisely, we assume that the electron removal happens very fast (e.g. by optical excitation), so that the lattice components do move only after the ionization (Franck-Condon principle).
- 2) The many-body wave functions shall be single Slater determinants (i.e., the discussion refers to the Hartree-Fock approximation).
- 3) Removing the k -th electron does not affect the single-particle wave functions of the other electrons. This assumption is reasonable, as long as the number of electrons is large and the density $|\varphi_{o_k}(\mathbf{r})|^2$ of the electron being removed is rather extended. Then $v^{\text{Hartree}}(\mathbf{r})$ and $n_j^{\text{HF}}(\mathbf{r}, \mathbf{r}')$ remain basically unchanged, and, consequently also all φ_{o_i, s_i} remain essentially unchanged.

In particular assumptions 2) and 3) are rather drastic. These two assumptions mean that the wave function Φ^{N-1} is derived from the wave function Φ^N by deleting line k and column k in the Slater determinant Φ^N . Then we obtain, using Eq. (3.89), (3.32), and (3.54)

$$\begin{aligned} I_k = & \langle \Phi_k^{N-1} | \sum_{\substack{i=1 \\ i \neq k}}^N -\frac{\hbar^2}{2m} \nabla_{\mathbf{r}_i}^2 + v(\mathbf{r}_i) | \Phi_k^{N-1} \rangle + \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \langle \Phi_k^{N-1} | \sum_{\substack{i,j=1 \\ i \neq j \\ i,j \neq k}}^{N,N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} | \Phi_k^{N-1} \rangle \\ & - \langle \Phi^N | \sum_{i=1}^N -\frac{\hbar^2}{2m} \nabla_{\mathbf{r}_i}^2 + v(\mathbf{r}_i) | \Phi^N \rangle - \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \langle \Phi^N | \sum_{\substack{i,j=1 \\ i \neq j}}^{N,N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} | \Phi^N \rangle \end{aligned}$$

$$\begin{aligned}
&\approx -\langle \varphi_{o_k s_k} | -\frac{\hbar^2}{2m} \nabla^2 + v(\mathbf{r}) | \varphi_{o_k s_k} \rangle \\
&\quad - \frac{e^2}{4\pi\epsilon_0} \sum_{\substack{i=1 \\ i \neq k}}^N \iint \frac{\varphi_{o_k s_k}^*(\mathbf{r}') \varphi_{o_i s_i}^*(\mathbf{r}) \varphi_{o_i s_i}(\mathbf{r}) \varphi_{o_k s_k}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r} d^3\mathbf{r}' \\
&\quad + \frac{e^2}{4\pi\epsilon_0} \sum_{\substack{i=1 \\ i \neq k}}^N \delta_{s_k, s_i} \iint \frac{\varphi_{o_k s_k}^*(\mathbf{r}) \varphi_{o_i s_i}^*(\mathbf{r}') \varphi_{o_i s_i}(\mathbf{r}) \varphi_{o_k s_k}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r} d^3\mathbf{r}' \\
&= -\langle \varphi_{o_k s_k} | h^{\text{HF}} | \varphi_{o_k s_k} \rangle \\
&= -\epsilon_{o_k s_k} \quad .
\end{aligned} \tag{3.91}$$

Thus what we had assumed before is valid approximately, indeed: The meaning of the quantities introduced as Lagrange parameters ϵ_{o_k} or $\epsilon_{o_k s_k}$ is (approximately) the negative value of the energy that is required to remove an electron from orbital k . It follows that also excitation energies, i.e., a transition from an occupied state i to an unoccupied state j is (approximately) determined by the ϵ_{o_k} :

$$\Delta E_{i \rightarrow j} \approx \epsilon_j - \epsilon_i \tag{3.92}$$

These statements (Eq. (3.91)) and (Eq. (3.92)) are called Koopmans' theorem. They are valid approximately for the valence electrons of atoms and for extended states of solids. However, when one excites an electron from a localized state, one does not only obtain a single discrete line. Due to many-body effects (electronic relaxation and excitations) one obtains several "peaks". Then Koopmans' theorem (approximately) gives the center of mass of the function $I_k(\epsilon)$.

3.5 The X_α Method

(Hartree-Fock-Slater Method)

Initially, the Hartree-Fock method was applied to atoms without major difficulties. For solids, however, it was realized that it is very complicated⁷. This is only due to the exchange term. Because of these difficulties in 1951 Slater suggested (Phys. Rev. **81**, 385 (1951); **82**, 5381 (1951)), to simplify this term. This simplification, although introduced ad hoc, was very successful. Later, i.e., by density-functional theory, it was realized that the treatment introduced by Slater as a simplification in fact corresponds to an important physical theorem and is not an approximation but even an improvement of Hartree-Fock theory.

The difficulty in Hartree-Fock theory is that the exchange potential is state-dependent. For jellium the expectation value of the exchange potential $v_{\mathbf{k}}^x$ is given by Eq. (3.79) and it reads

⁷In recent years there have been several better Hartree-Fock calculations for solids: Stollhoff (1987), Gigy-Baldereschi (1987), Louie (1988). In particular Dovesi *et al.* have developed a Hartree-Fock program ("CRYSTAL") for solids. The next step is to take into account "exact exchange" in the context of density-functional theory.

$$v_{\mathbf{k}}^x = -\frac{e^2}{4\pi\epsilon_0} \frac{2k_F}{\pi} k_F F \left(\frac{k}{k_F} \right) \quad \text{with} \quad k_F = \sqrt[3]{3\pi^2 n} \quad . \quad (3.93)$$

The complicated aspect of the exchange potential is that it is different for different states \mathbf{k} . Slater therefore introduced the idea to average over all \mathbf{k} to obtain a (state-independent) “average potential”. However, how should such “average” be performed? If one averages over all occupied states the function $F(k/k_F)$ becomes the number 0.75. But one could also claim that only the states at k_F are important: Electrons can react to external perturbations only by transitions to excited states, and the energetically lowest excitations happen at ϵ_F (or k_F). At k_F F has the value 0.5. Exactly this value ($F = 0.5$) is also obtained, if one averages over all states in the expression for the total energy (Eq. (3.42)), *before* the functional derivative $\delta E^{\text{HF}}/\delta\varphi$ is calculated. This is because a variation after averaging mainly refers to the Fermi edge. One obtains:

$$v_{F=\frac{3}{4}}^x(\mathbf{r}) = -\frac{3}{2\pi} \frac{e^2}{4\pi\epsilon_0} \sqrt[3]{3\pi^2 n(\mathbf{r})} \quad \begin{array}{l} \text{averaging over all occupied} \\ \text{states of the Hartree-Fock} \\ \text{equation } (F = 0.75). \end{array} \quad (3.94)$$

$$v_{F=\frac{1}{2}}^x(\mathbf{r}) = -\frac{1}{\pi} \frac{e^2}{4\pi\epsilon_0} \sqrt[3]{3\pi^2 n(\mathbf{r})} \quad \begin{array}{l} \text{Averaging in the expression of} \\ \text{the total energy or by taking} \\ \text{into account only the states at } k_F \\ \text{of the Hartree-Fock equation} \\ (F = 0.5). \end{array} \quad (3.95)$$

Now in $n(\mathbf{r})$ we have again noted the \mathbf{r} dependence, to indicate that the discussion is also valid for slowly varying densities. Because Hartree-Fock theory is not exact anyway (Coulomb correlation is missing), Slater suggested to introduce the following quantity for the impractical exchange potential

$$v^{x\alpha}(\mathbf{r}) = -\alpha \frac{3}{2\pi} \frac{e^2}{4\pi\epsilon_0} \sqrt[3]{3\pi^2 n(\mathbf{r})} \quad , \quad (3.96)$$

where α is a parameter of value

$$\frac{2}{3} < \alpha < 1 \quad . \quad (3.97)$$

The higher value (i.e., $\alpha = 1$) corresponds to the exchange potential originally derived by Slater ($F = 0.75$). Today, from the point of view of density-functional theory, the potential for $\alpha = 2/3$ (for $F = 0.5$) would be called exchange potential. In the seventies α was determined for atomic calculations and then transferred to solids and molecules (K. Schwarz, Vienna). If α is chosen to obtain a good agreement with experimental total energies one finds that α should obtain a value of $\approx \frac{2}{3}$. Slater believed that the obtained $\alpha \approx \frac{2}{3}$ -exchange potential represents an improvement, because the Coulomb correlation is taken into account semi-empirically. Today this is interpreted differently [cf. Kohn, Sham, Phys. Rev. **140**, A 1193 (1965), Gaspar, Acta Phys. Acad. Sci. Hung. **3**, 263 (1954)].

From a puristic theoretician’s point of view Slater’s empirical treatment was not satisfying, because the derivation was not really justified. Still this treatment had impressive

success. The X_α -potential is illustrated in Fig. 3.7. It gives an impression of the dependence on the density and of the strength of the exchange interaction. Most metals have a density of $r_s = 2$ bohr, or $n = 0.03$ bohr $^{-3}$. Here, the exchange potential has a value of about 7 eV, and consequently one recognizes that for an accurate theoretical treatment in general it will be very important to take into account the exchange potential precisely.

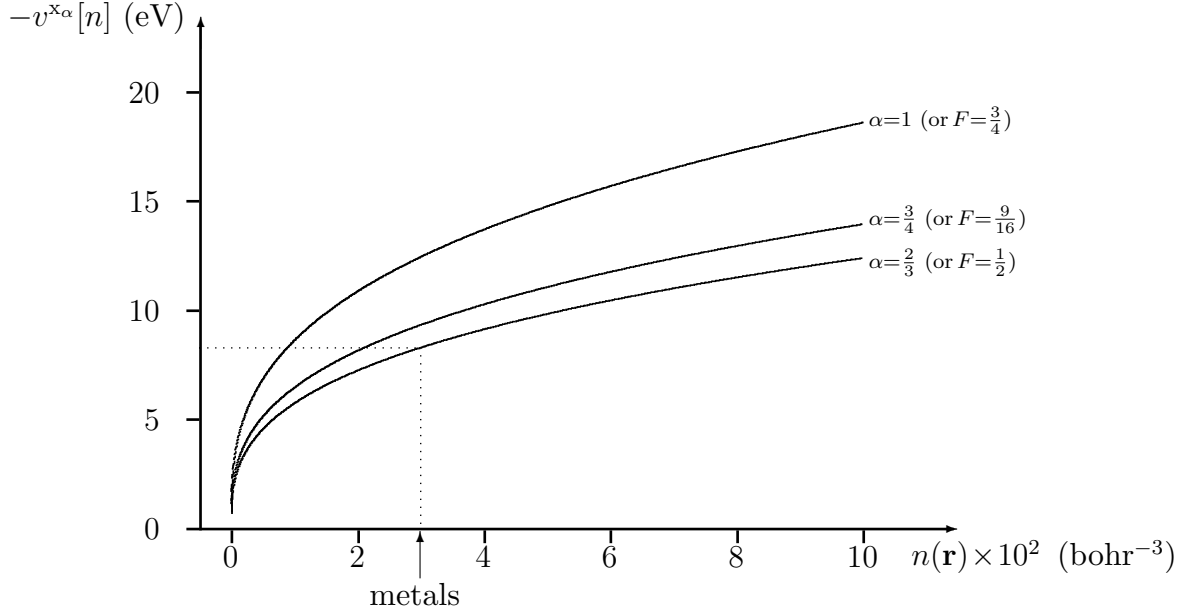


Figure 3.7: The X_α -potential as a function of the density n (atomic units). the density, as usual, depends on the position, the value n is different for each \mathbf{r} . And for this value of n , the figure gives $v^{x_\alpha}(\mathbf{r})$.

3.6 Thomas-Fermi Theory and the Concept of Screening

The basic concept behind this approach is very useful. The main reason for solving the Hamilton operator of the solid is to learn something about the distribution of the electrons of the solid in the many-body ground state Φ , i.e., about the electron density:

$$n(\mathbf{r}) = \left\langle \Phi \left| \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \right| \Phi \right\rangle . \quad (3.98)$$

The question arises if it is really necessary to calculate the many-body wave function Φ . When thinking of the approaches of Hartree, Hartree-Fock, and Hartree-Fock-Slater, one could ask, if one really has to calculate $\sim 10^{23}$ single-particle wave functions $\varphi_{o_i}(\mathbf{r})$, in order to calculate

$$n(\mathbf{r}) = \sum_{i=1}^N |\varphi_{o_i}(\mathbf{r})|^2 , \quad (3.99)$$

or if $n(\mathbf{r})$ can be calculated directly. We start from the effective single-particle equation

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + v^{\text{eff}}(\mathbf{r}) \right\} \varphi_i(\mathbf{r}) = \epsilon_i \varphi_i(\mathbf{r}) \quad , \quad (3.100)$$

where the effective potential is taken e.g. from the Hartree or Hartree-Fock-Slater theory. We ask ourselves if it is possible to calculate the density directly from the potential $v(\mathbf{r})$, without calculating the wave function and without solving the Schrödinger equation. In this context we note that $n(\mathbf{r})$ is a functional of the external potential $v(\mathbf{r})$: $v(\mathbf{r})$ defines the many-body Hamilton operator and the latter determines everything, also $n(\mathbf{r})$. It is unclear, however, if the particle density $n(\mathbf{r})$ can be expressed explicitly as a functional of the potential of the ions (lattice components). To continue, we start with the jellium model: Then the single-particle wave functions are plane waves, and the expectation value of the single-particle Hamiltonian is:

$$\epsilon_i = \frac{\hbar^2}{2m} k_i^2 + v^{\text{eff}} \quad . \quad (3.101)$$

For the highest occupied state, i.e., for the weakest bound electron, we have:

$$\frac{\hbar^2}{2m} k_F^2 + v^{\text{eff}} = \epsilon_N = \mu \quad . \quad (3.102)$$

The fact that $\epsilon_N = \mu$ will be shown below. For a non-jellium system, as long as the potential $v^{\text{eff}}(\mathbf{r})$ varies slowly in \mathbf{r} , Eq. (3.101) is still valid, but only approximately. Actually, one should replace $v^{\text{eff}}(\mathbf{r})$ by $\langle \varphi_{o_N} | v^{\text{eff}} | \varphi_{o_N} \rangle$. Because this is not done here, the following derivation should be considered as a semi-classical approximation.

For the jellium system (and for slowly varying densities) we can define a (position dependent) Fermi- \mathbf{k} -vector (cf. Eq. (2.30)),

$$k_F(\mathbf{r}) = \sqrt[3]{3\pi^2 n(\mathbf{r})} \quad (3.103)$$

and obtain the following equation for the electron of the highest energy:

$$\frac{\hbar^2}{2m} (3\pi^2 n(\mathbf{r}))^{2/3} + v^{\text{eff}}(\mathbf{r}) = \mu \quad . \quad (3.104)$$

Since μ is the energy of the weakest bound electron, it has to be spatially constant. The first term of the left side of Eq. (3.103) is the kinetic, the second the potential energy. This equation enables us for a given μ to calculate the density $n(\mathbf{r})$ from $v(\mathbf{r})$ without solving a Schrödinger equation. The $\sim 10^{23}$ particles do not appear explicitly as individual particles. Equation (3.104) tells that there is a discrete relation between $v^{\text{eff}}(\mathbf{r})$ and $n(\mathbf{r})$, at least for jellium, or close to jellium systems

Equation (3.103) is called the *Thomas-Fermi equation*. For $v^{\text{eff}} = v + v^{\text{Hartree}}$ it is equivalent to the Hartree equation, and for $v^{\text{eff}} = v + v^{\text{Hartree}} + v^{\text{x}\alpha}$ it is equivalent to the Hartree-Fock-Slater Equation.

The Thomas-Fermi equation (3.102) can also be derived from a variational principle. This shall be done here for the Hartree theory. We have:

$$\begin{aligned}
E^e &= \langle \Phi | H^e | \Phi \rangle \\
&= \sum_{i=1}^N \left\langle \varphi_{o_i} \left| -\frac{\hbar^2}{2m} \nabla^2 \right| \varphi_{o_i} \right\rangle + \int v(\mathbf{r}) n(\mathbf{r}) d^3\mathbf{r} + \frac{e^2}{4\pi\epsilon_0} \frac{1}{2} \iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r} d^3\mathbf{r}' \quad ,
\end{aligned} \tag{3.105}$$

and for jellium we have:

$$\begin{aligned}
\sum_{i=1}^N \left\langle \varphi_{o_i} \left| -\frac{\hbar^2}{2m} \nabla^2 \right| \varphi_{o_i} \right\rangle &= \frac{V_g}{V_g(2\pi)^3} 2 \int_0^{k_F} \frac{\hbar^2}{2m} k^2 d^3\mathbf{k} \\
&= 4\pi \frac{2}{(2\pi)^3} \frac{\hbar^2}{2m} \int_0^{k_F} k^4 dk = \frac{1}{5\pi^2} \frac{\hbar^2}{2m} k_F^5 \\
&= \frac{1}{5\pi^2} \frac{\hbar^2}{2m} (3\pi^2 n)^{5/3} = T_s^{\text{Jellium}}[n] \quad .
\end{aligned} \tag{3.106}$$

Thus, we have found that for jellium and probably also for slowly and weakly varying densities $n(\mathbf{r})$, the expectation value $\langle \Phi | H^e | \Phi \rangle$ can be written as a functional of the density (at least in the Hartree approximation). Then for jellium we obtain

$$\frac{\delta T_s^{\text{Jellium}}[n]}{\delta n(\mathbf{r})} = \frac{\hbar^2}{2m} (3\pi^2 n(\mathbf{r}))^{2/3} \quad . \tag{3.107}$$

Because the total energy of the ground state is $E_0^e = \text{Min}_{\Phi^N} \langle \Phi^N | H^e | \Phi^N \rangle$, we write

$$E_0^e = \text{Min}_{n(\mathbf{r})} E^e[n] \quad . \tag{3.108}$$

With the assumption that the total number of particles remains constant, the minimization is written as

$$\frac{\delta \{ E^e[n] - \mu (\int n(\mathbf{r}) d^3\mathbf{r} - N) \}}{\delta n(\mathbf{r})} = 0 \quad . \tag{3.109}$$

Here μ is the Lagrange parameter taking care of the constraint that the total number of electrons is N . Equation (3.108) apparently is equal to the Thomas-Fermi equation

$$\mu = \frac{\hbar^2}{2m} (3\pi^2 n(\mathbf{r}))^{2/3} + v^{\text{eff}}(\mathbf{r}) \quad , \tag{3.110}$$

with

$$v^{\text{eff}}(\mathbf{r}) = v(\mathbf{r}) + \frac{e^2}{4\pi\epsilon_0} \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' \quad . \tag{3.111}$$

We did not prove that the variational principle is really valid (Eq. (3.108)), but we have “simply” assumed its validity. Further, it should be mentioned that in addition to the condition of the conservation of the particle number actually other constraints would be important as well, namely that only densities $n(\mathbf{r})$ must be considered that are physically meaningful, e.g.: $n(\mathbf{r})$ must be real and always positive.

We had already see that μ is the energy of the weakest bound electron. Let is look again at the meaning in terms of the variational principle. Equation (3.109) gives

$$\frac{\delta E^e[n]}{\delta n(\mathbf{r})} = \mu \quad ,$$

and if we specify this variation to a change in electron number, we obtain as a special case

$$\frac{d E^e}{d N} = \mu$$

which is, in fact, the definition of the chemical potential. Consequently, μ is the chemical potential, i.e., the energy required to change the particle number.

The Concept of Screening

Equation (3.103) shows that $n(\mathbf{r})$ is a functional of $v^{\text{eff}}(\mathbf{r})$:

$$n(\mathbf{r}) = F_1[v^{\text{eff}}(\mathbf{r}); \mu] \quad (3.112)$$

$$= \frac{1}{3\pi^2} \left[\frac{2m}{\hbar^2} (\mu - v^{\text{eff}}(\mathbf{r})) \right]^{3/2} . \quad (3.113)$$

Now we introduce a small perturbation

$$v^{\text{eff}}(\mathbf{r}) \longrightarrow v^{\text{eff}}(\mathbf{r}) + \Delta v^{\text{eff}}(\mathbf{r}) \quad . \quad (3.114)$$

Here μ shall remain unchanged, i.e., the energy, that is required to remove the weakest bound electron shall stay the same as it was without perturbation, because the perturbation is small. This will hold, e.g. when Δv^{eff} is a spatially localized perturbation of the potential in a macroscopic system, e.g. a defect atom in a semiconductor. Now we ask, how the particle density will change

$$n(\mathbf{r}) \longrightarrow \tilde{n}(\mathbf{r}) = n(\mathbf{r}) + \Delta n(\mathbf{r}) \quad . \quad (3.115)$$

For the perturbed system we have the Thomas-Fermi equation for \tilde{n} :

$$\mu = \frac{\hbar^2}{2m} [3\pi^2 \tilde{n}(\mathbf{r})]^{2/3} + v^{\text{eff}}(\mathbf{r}) + \Delta v^{\text{eff}}(\mathbf{r}) \quad , \quad (3.116)$$

and the comparison with Eq. (3.113) yields

$$\tilde{n}(\mathbf{r}) = F_1[v^{\text{eff}} + \Delta v^{\text{eff}}; \mu] = F_1[v^{\text{eff}}(\mathbf{r}); \mu - \Delta v^{\text{eff}}(\mathbf{r})] \quad . \quad (3.117)$$

Now we call $\mu - v^{\text{eff}} = \alpha$ and expand (3.117) in a Taylor series around the point $\alpha = \mu$. This yields

$$\tilde{n}(\mathbf{r}) = F_1[v^{\text{eff}}(\mathbf{r}); \alpha] \Big|_{\alpha=\mu} - \frac{\partial F_1[v^{\text{eff}}(\mathbf{r}); \alpha]}{\partial \alpha} \Big|_{\alpha=\mu} \cdot \Delta v^{\text{eff}}(\mathbf{r}) + O([\Delta v^{\text{eff}}]^2) \quad . \quad (3.118)$$

It follows

$$\begin{aligned} \Delta n(\mathbf{r}) &= \tilde{n}(\mathbf{r}) - n(\mathbf{r}) \\ &= - \frac{\partial F_1[v^{\text{eff}}(\mathbf{r}); \alpha]}{\partial \alpha} \Big|_{\alpha=\mu} \cdot \Delta v^{\text{eff}}(\mathbf{r}) + O([\Delta v^{\text{eff}}]^2) \quad . \end{aligned} \quad (3.119)$$

Actually we are interested in the relation between $v(\mathbf{r})$ and $n(\mathbf{r})$, or between $\Delta v(\mathbf{r})$ and $\Delta n(\mathbf{r})$. To obtain this relation, we consider here the Hartree approximation. Then we have:

$$\Delta v^{\text{eff}}(\mathbf{r}) = \Delta v(\mathbf{r}) + \frac{e^2}{4\pi\epsilon_0} \int \frac{\Delta n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' \quad (3.120)$$

or with the Poisson equation,

$$\nabla^2(\Delta v^{\text{eff}}(\mathbf{r})) = \nabla^2(\Delta v(\mathbf{r})) - \frac{e^2}{\epsilon_0} \Delta n(\mathbf{r}) \quad . \quad (3.121)$$

In the Fourier representation we have:

$$\Delta n(\mathbf{k}) = \frac{\epsilon_0}{e^2} k^2 [\Delta v^{\text{eff}}(\mathbf{k}) - \Delta v(\mathbf{k})] = - \left. \frac{\partial F_1[v^{\text{eff}}(\mathbf{r}); \alpha]}{\partial \alpha} \right|_{\alpha=\mu} \cdot \Delta v^{\text{eff}}(\mathbf{k}) \quad . \quad (3.122)$$

If we set $\left. \frac{\partial F_1}{\partial \alpha} \right|_{\alpha=\mu} = \frac{\epsilon_0}{e^2} k_0^2$, we obtain

$$\frac{k^2 + k_0^2}{k^2} \Delta v^{\text{eff}}(\mathbf{k}) = \Delta v(\mathbf{k}) \quad . \quad (3.123)$$

The quantity k_0 is called the Thomas-Fermi wave vector. We have now derived an equation, which (in the Hartree approximation and for a jellium-type system) describes the relation between the origin of the perturbation (change of the potential of the ions) and the potential (effective potential) acting on the single-particle wave functions. This equation corresponds closely to a description, which is known from electrodynamics: The relation between the strength of an electric field \mathbf{E} and the dielectric displacement \mathbf{D} is

$$\mathbf{D} = \epsilon \mathbf{E} \quad , \quad (3.124)$$

where ϵ is the dielectric constant (generally a tensor). Therefore, we can and want to continue our investigation by starting from the relation $\Delta v(\mathbf{r}) \rightleftharpoons \Delta v^{\text{eff}}(\mathbf{r})$, and considering in terms of a microscopic materials equation of electrodynamics. In the context of Thomas-Fermi theory in \mathbf{k} -space we write (cf. Eq. (3.123)):

$$\Delta v(\mathbf{k}) = \epsilon(\mathbf{k}) \Delta v^{\text{eff}}(\mathbf{k}) \quad (3.125)$$

with the Thomas-Fermi dielectric constant

$$\epsilon(\mathbf{k}) = \frac{\mathbf{k}^2 + k_0^2}{\mathbf{k}^2} \quad . \quad (3.126)$$

For small values of \mathbf{k}^2 , i.e., large wave lengths, the jellium approximation is well justified and then equations (3.125) and (3.126) are equivalent to the Hartree theory. Still k_0 is unknown, but it will be determined below (Eq. (3.137)). In real space we obtain

$$\Delta v(\mathbf{r}) = \int \epsilon(\mathbf{r}, \mathbf{r}') \Delta v^{\text{eff}}(\mathbf{r}') d^3\mathbf{r}' \quad . \quad (3.127)$$

All the many-body quantum mechanics is now hidden in the dielectric constant. In case we were dealing with a spatially isotropic, uniform and homogenous system, we would have:

$$\epsilon(\mathbf{r}, \mathbf{r}') = \epsilon(|\mathbf{r} - \mathbf{r}'|) \quad . \quad (3.128)$$

To demonstrate the scientific content of the Thomas-Fermi theory we will now discuss the screening in the neighborhood of a point charge in a solid (e.g. a defect in a crystal). We start from:

$$\Delta v(\mathbf{r}) = \frac{-e^2 Z}{4\pi\epsilon_0 r} \quad . \quad (3.129)$$

In \mathbf{k} -space we obtain

$$\Delta v(\mathbf{k}) = \frac{-e^2 Z}{4\pi\epsilon_0 k^2} \quad , \quad (3.130)$$

and for the effective potential we obtain:

$$\Delta v^{\text{eff}}(\mathbf{k}) = \frac{k^2}{k^2 + k_0^2} \Delta v(\mathbf{k}) = \frac{-e^2 Z}{4\pi\epsilon_0} \frac{Z}{k^2 + k_0^2} \quad . \quad (3.131)$$

When we go back into real space, we have

$$\Delta v^{\text{eff}}(\mathbf{r}) = \frac{-e^2 Z}{4\pi\epsilon_0} \frac{Z}{r} e^{-k_0 r} \quad . \quad (3.132)$$

Now it is clear that not an “external” perturbation charge $Z \cdot e$, with a potential $\frac{-e^2 Z}{4\pi\epsilon_0 r}$ is acting on the electron, but a *screened* Coulomb potential (Eq. (3.132)). This potential is also called Yukawa potential (the name originates from the theory of mesons, where this potential also plays a role). The Thomas-Fermi wave vector k_0 determines the strength of the screening. When $1/k_0$ becomes infinite, then there is no screening. The effective potential of Eq. (3.132) is shown in Fig. 3.8.

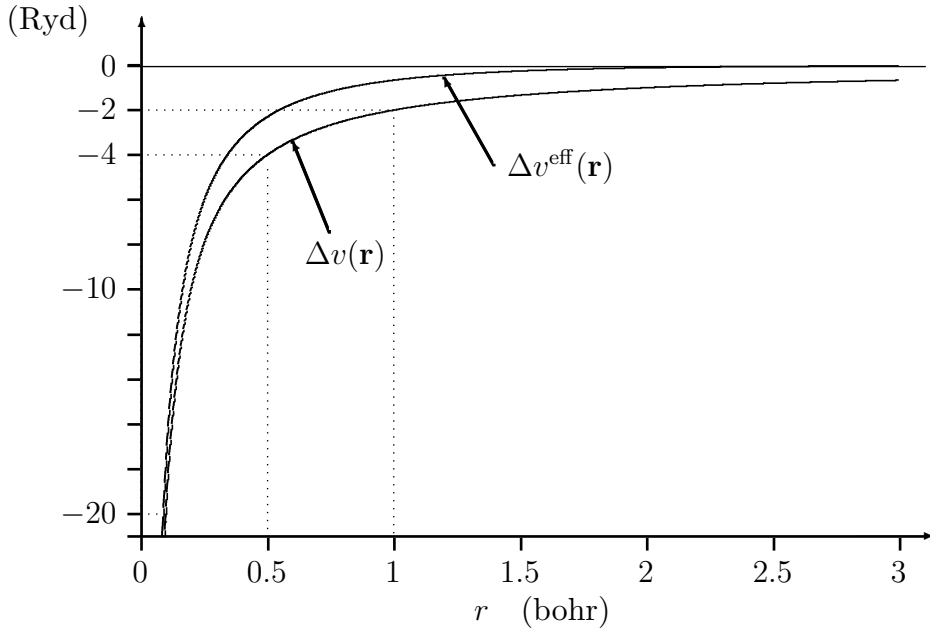


Figure 3.8: Change of the effective potential induced by a point charge at $\mathbf{r} = 0$ with $Z = 1$. In the Thomas-Fermi approximation with $k_0 = 1.1 \text{ bohr}^{-1}$, i.e. for $r_s \simeq 2 \text{ bohr}$.

This polarization charge density, $\Delta n(\mathbf{r})$, i.e., the change of the electron density induced by the perturbation, according to Eq. (3.124) with (3.133) is:

$$\Delta n(\mathbf{k}) = -\frac{\varepsilon_0}{e^2} k_0^2 \Delta v^{\text{eff}}(\mathbf{k}) = Z \frac{k_0^2}{k^2 + k_0^2} \cdot \frac{1}{4\pi} \quad . \quad (3.133)$$

In real space we obtain the result,

$$\Delta n(\mathbf{r}) = Z \frac{k_0^2}{4\pi} \frac{e^{-k_0 r}}{r} \quad , \quad (3.134)$$

which is shown in Fig. 3.9. Physically this result means that a positive perturbation charge at $\mathbf{r} = 0$ induces an attraction of the valence electrons of the solid to the perturbation charge. This increases the negative charge density in the neighborhood of $\mathbf{r} = 0$, and the perturbation is screened. One says that the “valence charge density is polarized”.

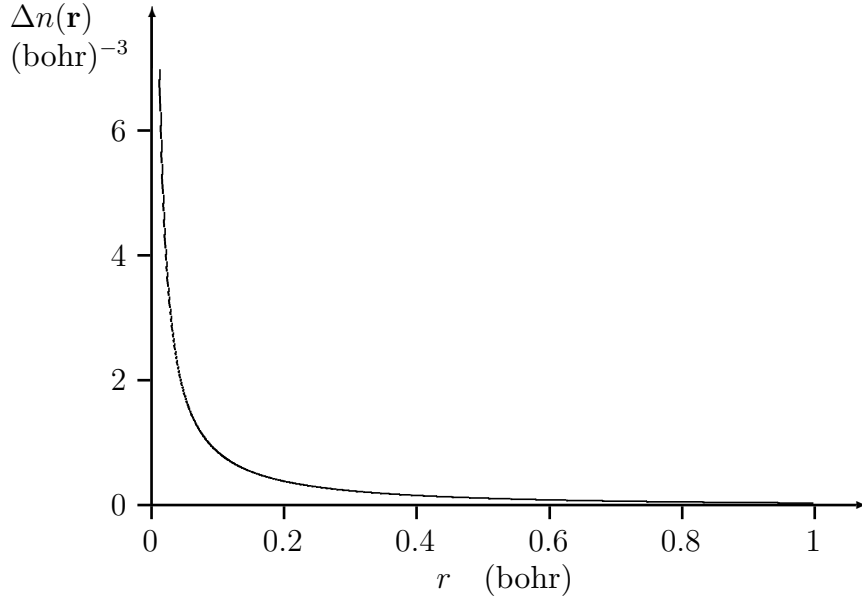


Figure 3.9: Change of the electron density induced by a positive point charge at $\mathbf{r} = 0$ with $Z = 1$. In the Thomas-Fermi approximation with $k_0 = 1.1 \text{ bohr}^{-1}$ and $r_s \simeq 2 \text{ bohr}$.

The area under the curve is equal to $Z = \int \Delta n(\mathbf{r}) d^3\mathbf{r}$, i.e., the charge belonging to $\Delta n(\mathbf{r})$, is exactly equal to the perturbation charge, but with an opposite sign. How important, or how efficient is this screening; i.e., how large is k_0 for realistic systems?

$$\begin{aligned} \frac{\varepsilon_0}{e^2} k_0^2 &= \left. \frac{\partial F_1[v^{\text{eff}}(\mathbf{r}); \alpha]}{\partial \alpha} \right|_{\alpha=\mu} = \left. \frac{\partial}{\partial \alpha} \frac{1}{3\pi^2} \left\{ \frac{2m}{\hbar^2} (\alpha - v^{\text{eff}}) \right\}^{3/2} \right|_{\alpha=\mu} \\ &= \left. \frac{3}{2} \frac{2m}{\hbar^2 3\pi^2} \left\{ \frac{2m}{\hbar^2} (\alpha - v^{\text{eff}}) \right\}^{1/2} \right|_{\alpha=\mu} = \frac{m}{\hbar^2 \pi^2} k_F \quad . \quad (3.135) \end{aligned}$$

We have:

$$k_0^2 = \frac{e^2}{\varepsilon_0} \frac{m}{\hbar^2 \pi^2} k_F = \frac{e^2}{\varepsilon_0} \frac{m}{\hbar^2 \pi^2} [3\pi^2 n]^{1/3} \quad (3.136)$$

If we express the density by the density parameter r_s , we have

$$k_0 = \frac{2.95}{\sqrt{r_s/a_B}} \text{\AA}^{-1} . \quad (3.137)$$

Because r_s is generally in the range $1 \dots 6$ bohr, the screening happens very fast, i.e., on a length scale of $1/k_0 \approx 0.5 \text{\AA}$. This length is comparable to, or even shorter than, the distance between the atoms in a crystal (typically $2\text{--}3 \text{\AA}$). A more accurate calculation yields *qualitatively* the same result. But there are also significant differences. A more accurate calculation (which is significantly more complicated) is shown in Fig. 3.10. The reasons for the differences to Fig. 3.9 are that now not $T^{\text{Jellium}}[n]$, but the correct kinetic energy has been used. Further, no semiclassical approximation for v^{eff} has been assumed, and no Taylor-series expansion and approximation for $F_1[v^{\text{eff}}; \alpha]$ has been used, and the exchange interaction has been taken into account. The correct kinetic energy, T , yields oscillations (Friedel oscillations).

The basic idea of Thomas-Fermi theory to calculate $n(\mathbf{r})$ directly from $v(\mathbf{r})$ is for sure interesting. However, generally the mentioned approximations are too drastic. Improvements of the kinetic energy term (cf. Eq. (3.106)) have been suggested by C.F. Weizsäcker. The correction term is proportional to $|\nabla n(\mathbf{r})|^2/n(\mathbf{r})$.

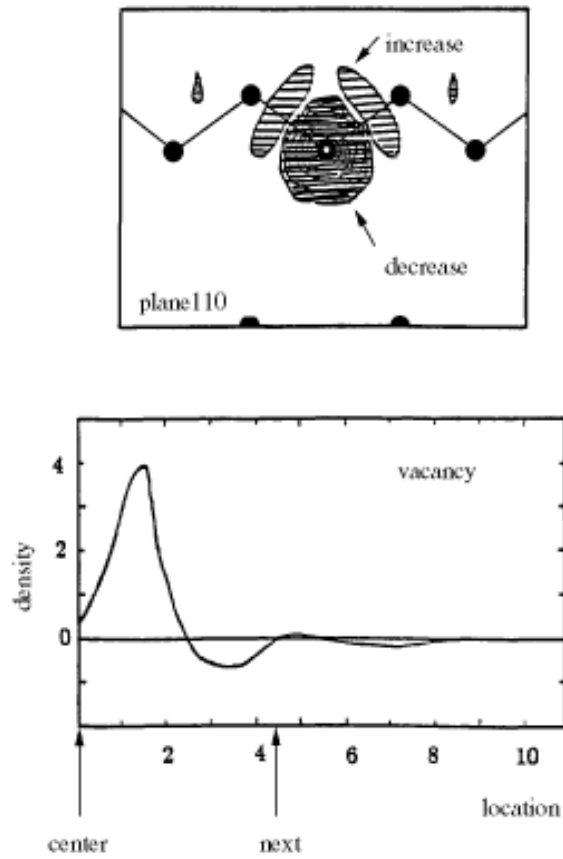


Figure 3.10: Change in the charge density induced by a defect atom (arsenic) in a silicon crystal. The top figure shows a contour plot in the (110) plane, and the bottom shows the density change along the [111] direction.

3.7 Density-Functional Theory⁸

We are still interested in the properties of a solid, which is described by the many-body Hamilton operator

$$H^e = \sum_{i=1}^N -\frac{\hbar^2}{2m} \nabla_{\mathbf{r}_i}^2 + v(\mathbf{r}_i) + \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\substack{i,j \\ i \neq j}}^{N,N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad . \quad (3.138)$$

We will assume that the ground state of

$$H^e \Phi = E^e \Phi \quad (3.139)$$

is non-degenerate. Further we will assume that the system is non-magnetic, i.e., the particle density of the spin-up and spin-down electrons shall be the same:

$$n_{\uparrow}(\mathbf{r}) = n_{\downarrow}(\mathbf{r}) \quad , \quad (3.140)$$

where for the total particle density as usual we have:

$$n(\mathbf{r}) = n_{\uparrow}(\mathbf{r}) + n_{\downarrow}(\mathbf{r}) \quad (3.141)$$

$$= \left\langle \Phi \left| \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \right| \Phi \right\rangle \quad . \quad (3.142)$$

From (3.140) and (3.141) we then obtain

$$n_{\uparrow}(\mathbf{r}) = n_{\downarrow}(\mathbf{r}) = \frac{n(\mathbf{r})}{2} \quad (3.143)$$

The assumptions of a “non-degenerate ground state” and Eqs. (3.141) and (3.143) can also be omitted, but the following discussion is simpler when they are made. First, we give the theorem of Hohenberg und Kohn, and subsequently we will prove its validity:

The expectation value of H^e is a functional of the particle density $n(\mathbf{r})$:

$$\langle \Phi | H^e | \Phi \rangle = E_v[n] = \int v(\mathbf{r}) n(\mathbf{r}) d^3\mathbf{r} + F[n] \quad . \quad (3.144)$$

Here the functional $F[n]$ does not depend explicitly on $v(\mathbf{r})$.

Proof of this statement: It is immediately clear that $F = \langle \Phi | T^e + V^{e-e} | \Phi \rangle$ is a functional of Φ , but initially it is surprising that it is supposed to be a functional of $n(\mathbf{r})$. Now we will show that Φ is a functional of $n(\mathbf{r})$, as long as we constrain ourselves to functions, which are defined according to Eq. (3.144) and Φ is the ground state wave function of an *arbitrary* N -particle problem. Because of the word “arbitrary”, i.e., $v(\mathbf{r})$ is arbitrary,

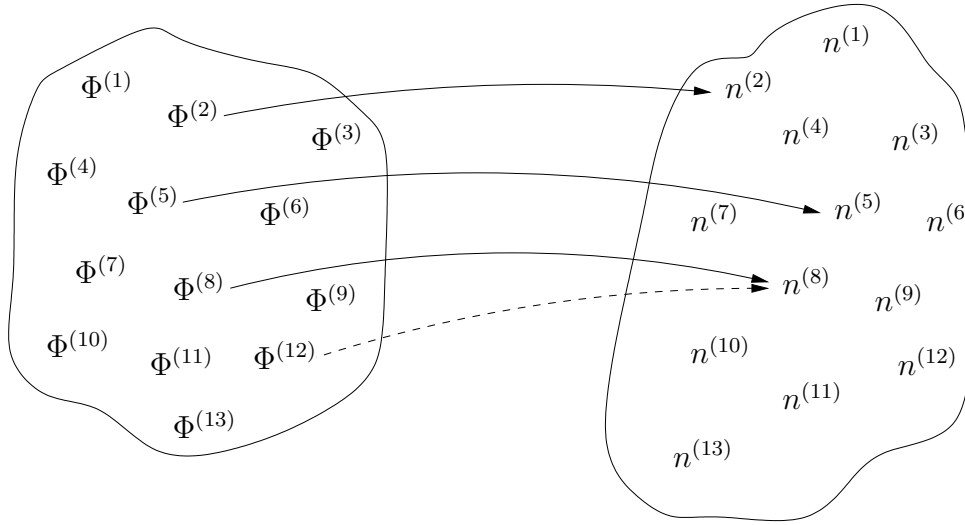
⁸References: P. Hohenberg, W. Kohn, Phys. Rev. **136**, B 864 (1964); W. Kohn, L. Sham, Phys. Rev. A **140**, 1133 (1965); M. Levy, Proc. Natl. Acad. Sci. USA **76**, 6062 (1979); R.M. Dreizler, E.K.U. Gross, Density Functional Theory (Springer, 1990); R.G. Parr, W. Yang, Density-Functional Theory of Atoms and Molecules (Oxford University Press 1994); R.O. Jones and O. Gunnarsson, Rev. Mod. Phys. **61**, 689 (1989)

this is not a constraint of physical relevance. Mathematically, however, this is a noticeable restriction.

The opposite of our goal is known: $n(\mathbf{r})$ is a functional of Φ :

$$n(\mathbf{r}) = \left\langle \Phi \left| \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \right| \Phi \right\rangle . \quad (3.145)$$

The question to be answered is: Is the mapping of Eq. (3.144) reversibly unique (cf. Fig. 3.11)?



The set of non-degenerate ground state wave functions Φ of arbitrary N -particle Hamilton operators of type of Eq. (3.1) or Eq. (3.142).

The set of the particle densities $n(\mathbf{r})$, which belong to non-degenerate ground states of the N -particle problem.

Figure 3.11: Relation between wave functions and particle densities. The Hohenberg-Kohn theorem states that the dashed case does not exist, i.e., two different many-body wave functions have to yield different densities.

The proof of the theorem of Hohenberg and Kohn and of the statement $\Phi = \Phi[n]$ is done following the principle “reductio ad absurdum”:

Starting point: $v(\mathbf{r})$ and $\tilde{v}(\mathbf{r})$ shall be two physically different potentials, i.e., we have

$$v(\mathbf{r}) - \tilde{v}(\mathbf{r}) \neq \text{constant} . \quad (3.146)$$

These two potentials define two Hamilton operators H^e and \tilde{H}^e (for simplicity we constrain ourselves to operators, that have a non-degenerate ground state (for a more general discussion we refer to the work of Levy).

Assumption 1: Both Hamilton operators have the same ground state wave function. It follows

$$(\tilde{H}^e - H^e)\Phi_0 = \sum_{i=1}^N \{\tilde{v}(\mathbf{r}_i) - v(\mathbf{r}_i)\} \Phi_0 = (\tilde{E}_0^e - E_0^e)\Phi_0 \quad , \quad (3.147)$$

and from this one obtains (with the exception of a discrete number of points, for which Φ_0 is zero)

$$\sum_{i=1}^N \{\tilde{v}(\mathbf{r}_i) - v(\mathbf{r}_i)\} = \tilde{E}_0^e - E_0^e \quad . \quad (3.148)$$

This means that $\tilde{v}(\mathbf{r}) - v(\mathbf{r})$ is constant which is in contradiction to the starting point. It follows: Our assumption 1 that H^e and \tilde{H}^e have the same eigenfunction, is wrong. Therefore, we have that Φ_0 and $\tilde{\Phi}_0$ are different.

Assumption 2: We assume that Φ_0 and $\tilde{\Phi}_0$ (even though $\Phi_0 \neq \tilde{\Phi}_0$) both can give rise to the same particle density $n(\mathbf{r})$. This corresponds to the dashed arrows in Fig. 3.11. We then get

$$E_0^e = \langle \Phi_0 | H^e | \Phi_0 \rangle < \langle \tilde{\Phi}_0 | H^e | \tilde{\Phi}_0 \rangle = \left\langle \tilde{\Phi}_0 \left| \tilde{H}^e - \sum_{i=1}^N \tilde{v}(\mathbf{r}_i) + \sum_{i=1}^N v(\mathbf{r}_i) \right| \tilde{\Phi}_0 \right\rangle \quad , \quad (3.149)$$

therefore,

$$E_0^e < \tilde{E}_0^e + \left\langle \tilde{\Phi}_0 \left| \sum_{i=1}^N \{v(\mathbf{r}_i) - \tilde{v}(\mathbf{r}_i)\} \right| \tilde{\Phi}_0 \right\rangle \quad (3.150)$$

and

$$E_0^e < \tilde{E}_0^e + \int \{v(\mathbf{r}) - \tilde{v}(\mathbf{r})\} n(\mathbf{r}) d^3\mathbf{r} \quad . \quad (3.151)$$

Similarly, we obtain for $\tilde{E}_0^e = \langle \tilde{\Phi}_0 | \tilde{H}^e | \tilde{\Phi}_0 \rangle$:

$$\tilde{E}_0^e < E_0^e - \int \{v(\mathbf{r}) - \tilde{v}(\mathbf{r})\} n(\mathbf{r}) d^3\mathbf{r} \quad (3.152)$$

If we add equations (3.151) and (3.152), we obtain

$$E_0^e + \tilde{E}_0^e < E_0^e + \tilde{E}_0^e \quad , \quad (3.153)$$

a contradiction. This means that assumption 2 is wrong. Thus we have proven:

Two different ground states Φ_0 and $\tilde{\Phi}_0$ must yield two different particle densities $n(\mathbf{r})$ and $\tilde{n}(\mathbf{r})$. This has the following consequences:

- a) $E_v[n] \stackrel{!}{=} \langle \Phi | H^e | \Phi \rangle$ is a functional of $n(\mathbf{r})$. In fact, what we had shown was even more general, namely: $\Phi = \Phi[n]$. Here, the functionals are only defined for the set of particle densities, that can be constructed from a ground state wave function of an arbitrary N -particle Hamilton operator H^e , where $v(\mathbf{r})$ is an arbitrary function (cf. Fig. 3.11).

b) In the expression

$$E_v[n] = \int n(\mathbf{r})v(\mathbf{r}) d^3\mathbf{r} + F[n] \quad (3.154)$$

$F[n]$ is a universal functional of $n(\mathbf{r})$. This means that the functional F is independent of the “external” potential $v(\mathbf{r})$.

c) $E_v[n]$ obtains under the constraint

$$\int n(\mathbf{r})d^3\mathbf{r} = N \quad (3.155)$$

a minimum for the correct particle density. This minimum defines the ground state energy and the ground state electron density n_0 :

$$E_0^e = \text{Min}_{n(\mathbf{r})} E_v[n] = E_v[n_0] \quad . \quad (3.156)$$

Thus, the variational principle for $\langle \Phi | H^e | \Phi \rangle$ can exactly be reformulated in terms of a variational principle for $E_v[n]$. The new variational principle is:

$$\delta \left\{ E_v[n] - \mu \left(\int n(\mathbf{r})d^3\mathbf{r} - N \right) \right\} = 0 \quad , \quad (3.157)$$

or

$$\left. \frac{\delta E_v[n]}{\delta n(\mathbf{r})} \right|_{n_0} = \mu \quad . \quad (3.158)$$

Here the constraint of a constant total number of particles being equal to N is taken into account by the method of Lagrange multipliers, i.e., we have included the condition

$$\int n(\mathbf{r})d^3\mathbf{r} = N \quad . \quad (3.159)$$

Still some physically important conditions are missing, e.g. that $n(\mathbf{r}) \geq 0$ and that $n(\mathbf{r})$ has to be continuous. These are necessary conditions, which have to be fulfilled by the functions of the range of $E_v[n]$, and which we will have to take into account when doing the variation in an actual calculation. Compared to Hartree and Hartree-Fock theory we achieved a significant advantage: Earlier we had to insert a wave function depending on 10^{23} coordinates in the functional to be minimized. This treatment led to obvious difficulties and approximations, which were introduced *before* the actual variation was performed. Now we have to insert functions depending on three coordinates only into the functional, and, up to now, i.e., up to Eq. (3.158), we have introduced *no* approximation.

We have shown: The ground state electron density determines the many-body Hamiltonian, uniquely. As the many-body Hamiltonian determines everything, we can also tell – in principle – the ground state electron density determines everything: the ground state, all excited states, all physical properties.

So far, we have shown that the functional $E_v[n]$ does exist. However, we have not shown how it looks like. In fact, we also have not shown that it can be written as a closed mathematical expression.

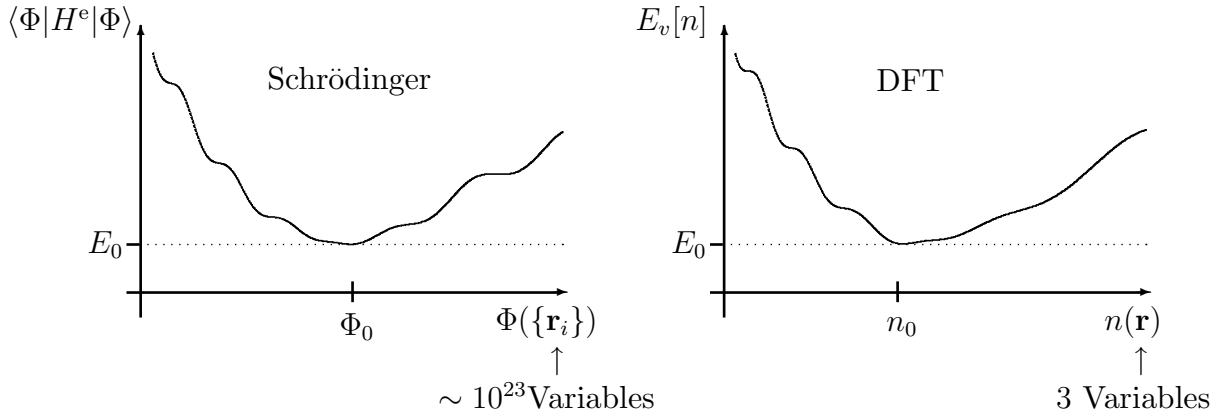


Figure 3.12: Schematic figure for the variational principle of $\langle \Phi | H^e | \Phi \rangle$ and $E_v[n]$.

For the actual variation Kohn and Sham suggested the following procedure. We write:

$$E_v[n] = T_s[n] + \int v(\mathbf{r})n(\mathbf{r})d^3\mathbf{r} + E^{\text{Hartree}}[n] + E^{\text{xc}}[n] \quad (3.160)$$

with

$$E^{\text{Hartree}}[n] = \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}d^3\mathbf{r}' \quad . \quad (3.161)$$

$T_s[n]$ is the kinetic energy functional of non-interacting electrons. Although generally it is not explicitly known as a function of $n(\mathbf{r})$, it will be introduced here. In fact, $T_s[n]$ cannot be written down in a closed mathematical form as a functional of the density. However, we know a series expansion:

$$T_s[n] = \frac{1}{5\pi^2} \frac{\hbar^2}{2m} (3\pi^2 n(\mathbf{r}))^{5/3} + \mathcal{O}(\nabla n(\mathbf{r})) \quad , \quad (3.162)$$

where the first term is the result for jellium, i.e. when $\nabla n(\mathbf{r}) = 0$.

$$\frac{\delta T_s}{\delta n(\mathbf{r})} = \frac{\hbar^2}{2m} (3\pi^2 n(\mathbf{r}))^{2/3} \quad (3.163)$$

was used in the Thomas-Fermi theory, i.e. for jellium.

Introducing here $T_s[n]$ – the exact one, not Thomas-Fermi – is still an approximation in mathematical terms. There may be physically reasonable densities that ly outside the range of definition of $T_s[n]$. However, from a physicist's point of view it appears to be plausible that all physically meaningful densities can be constructed from

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + \tilde{v}(\mathbf{r}) \right) \varphi_{o_i}(\mathbf{r}) = \epsilon_{o_i} \varphi_{o_i}(\mathbf{r}) \quad , \quad (3.164)$$

$$\text{with } n(\mathbf{r}) = \sum_{i=1}^N |\varphi_{o_i}(\mathbf{r})|^2 \quad (3.165)$$

and arbitrary $\tilde{v}(\mathbf{r})$. For such densities the kinetic energy is

$$T_s[n] = \sum_{i=1}^N \langle \varphi_{o_i} | -\frac{\hbar^2}{2m} \nabla^2 | \varphi_{o_i} \rangle \quad . \quad (3.166)$$

We note that Eq. (3.164) formally describes the ground state of a system of non-interacting electrons moving in the potential $\tilde{v}(\mathbf{r})$.⁹

For the exchange-correlation functional we obtain

$$\begin{aligned} E^{\text{xc}}[n] &= \langle \Phi | H^e | \Phi \rangle - \int v(\mathbf{r})n(\mathbf{r})d^3\mathbf{r} - T_s[n] - E^{\text{Hartree}}[n] \\ &= F[n] - T_s[n] - E^{\text{Hartree}}[n] \quad . \end{aligned} \quad (3.167)$$

The variational principle Eq. (3.158) applied to the energy functional Eq. (3.160) yields

$$\left. \frac{\delta T_s[n]}{\delta n(\mathbf{r})} \right|_{n_0} + v^{\text{eff}}([n_0], \mathbf{r}) = \mu \quad (3.168)$$

with

$$\begin{aligned} v^{\text{eff}}([n], \mathbf{r}) &= \frac{\delta \left\{ \int v(\mathbf{r})n(\mathbf{r})d^3\mathbf{r} + E^{\text{Hartree}}[n] + E^{\text{xc}}[n] \right\}}{\delta n(\mathbf{r})} \\ &= v(\mathbf{r}) + \frac{e^2}{4\pi\epsilon_0} \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' + \frac{\delta E^{\text{xc}}[n]}{\delta n(\mathbf{r})} \quad . \end{aligned} \quad (3.169)$$

We note that Eq. (3.168) determines the ground state density of *interacting* electrons. Formally, it is an equation for *non-interacting* electrons moving in the potential $v^{\text{eff}}([n], \mathbf{r})$, because per definition $T_s[n]$ is the kinetic energy of non-interacting electrons of density $n(\mathbf{r})$ (see Eqs. (3.164) – (3.166)). It seems plausible that the set of densities defined this way covers all physically reasonable densities or at least come arbitrarily close. As long as $T_s[n]$ is a well behaved functional, the assumption (of “being arbitrarily close”) should be sufficient. But this point still has not been discussed conclusively in the literature.

From Eq. (3.168) we obtain the equivalent single-particle Schrödinger equation

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + v^{\text{eff}}([n], \mathbf{r}) \right\} \varphi_{o_i}(\mathbf{r}) = \epsilon_{o_i} \varphi_{o_i}(\mathbf{r}) \quad . \quad (3.170)$$

Obviously, this is an *effective* single-particle equation, because v^{eff} depends on the solutions that we are seeking.

Equation (3.170) together with Eq. (3.165) and (3.169) is called the *Kohn-Sham equation*. It is solved using an SCF procedure. Although the functional $T_s[n]$ is not explicitly known as a functional in n , we can, by replacing Eq. (3.168) by the equivalent Eq. (3.170), still

⁹For non-interacting electrons the Hamiltonian is $H' = \sum_{i=1}^N \left(-\frac{\hbar^2}{2m} \nabla_{\mathbf{r}_i}^2 + \tilde{v}(\mathbf{r}_i) \right)$ and the many-body wavefunction $\Phi(\{\mathbf{r}_i\})$ is a Slater-determinant. The ground state for N such particles is determined by minimization with respect to the single-particle orbitals, $\frac{\delta}{\delta \varphi_{o_i}(\mathbf{r})} \left\{ \langle \Phi | H | \Phi \rangle - \epsilon_{o_i} \left(\int n(\mathbf{r})d^3\mathbf{r} - N \right) \right\} = \left\{ -\frac{\hbar^2}{2m} \nabla^2 + \tilde{v}(\mathbf{r}) - \epsilon_{o_i} \right\} \varphi_{o_i}(\mathbf{r}) \equiv 0$ (and *c.c.*), i.e. Eq. (3.164). According to the Hohenberg-Kohn theorem, we can also obtain the ground state from the density functional $E'_v[n] = \int n(\mathbf{r})\tilde{v}(\mathbf{r})d^3\mathbf{r} + T_s[n]$, i.e. $T_s[n]$ defines the functional $F[n]$ of Eq. (3.154) for non-interacting electrons. The variational principle, Eq. (3.158), then yields $\left. \frac{\delta E'_v[n]}{\delta n(\mathbf{r})} \right|_{n_0} = \left. \frac{\delta T_s[n]}{\delta n(\mathbf{r})} \right|_{n_0} + \tilde{v}(\mathbf{r}) = \mu$.

treat it exactly. This has the technical disadvantage that we end up with the N single-particle functions, which we wanted to avoid. For the evaluation of the total energy $E_v[n]$ we need $T_s[n]$. The calculation of $T_s[n]$ is done using one of the two following equations. Generally, for non-interacting particles we have:

$$T_s[n] = \sum_{i=1}^N \langle \varphi_{o_i} \left| -\frac{\hbar^2}{2m} \nabla^2 \right| \varphi_{o_i} \rangle \quad , \quad (3.171)$$

$$= \sum_{i=1}^N \epsilon_{o_i} - \int v^{\text{eff}}[n^{\text{in}}](\mathbf{r}) n(\mathbf{r}) d^3\mathbf{r} \quad . \quad (3.172)$$

Here $v^{\text{eff}}(\mathbf{r})$ is determined from Eq. (3.169), and ϵ_{o_i} is obtained from Eq. (3.170). Thus, we have proven that T_s is a functional of n . Here v^{eff} has to be calculated from a density $n^{\text{in}}(\mathbf{r})$, because if we interpret $T_s[n]$ as a *functional*, v^{eff} has to be exactly the potential, which generates the ϵ_{o_i} and the $\varphi_{o_i}(\mathbf{r})$ and $n(\mathbf{r})$. Generally, $n^{\text{in}}(\mathbf{r})$, which is used for the calculation of $v^{\text{eff}}(\mathbf{r})$ will differ from $n(\mathbf{r})$. Only at the end of the SCF cycle both densities are the same.

As a side remark we note that the self-consistent solution of the variational principle would not be changed if $T_s[n]$ was not be used, but e.g.

$$\tilde{T}[n] = \sum_{i=1}^N \epsilon_{o_i} - \int v^{\text{eff}}([n], \mathbf{r}) n(\mathbf{r}) d^3\mathbf{r} \quad , \quad (3.173)$$

or different equations, which differ only by $O(n^{\text{in}} - n)$ from $T_s[n]$. But here we continue using $T_s[n]$.

Up to now no approximation has been introduced (apart from the reasonable assumption described by Eq. (3.165)). Therefore we have – in contrast to Hartree and Hartree-Fock – first made use of the variational principle of the ground state, and now we will start to think about approximations.

In Hartree and Hartree-Fock theory *first* an approximation (ansatz of the wave function) was introduced and then the expectation value of H^e was investigated. Experience shows that it is particularly important to treat $T_s[n]$ as accurately as possible, in order to obtain e.g. the shell structure of the electrons in atoms (*s*-, *p*-, *d*-electrons), which cannot be described with Thomas-Fermi theory. The Kohn-Sham ansatz permits one to treat $T_s[n]$ exactly.

Using Eq. (3.171) or (3.172) we can evaluate $T_s[n]$ without knowing the functional explicitly. Just one thing remains unknown: $E^{\text{xc}}[n]$ and $v^{\text{xc}}(\mathbf{r}) = \frac{\delta E^{\text{xc}}[n]}{\delta n(\mathbf{r})}$. We know that $E^{\text{xc}}[n]$ is a universal functional¹⁰, i.e., the functional does not depend on the system: The hydrogen atom, the diamond crystal etc. are described by the same functional. Unfortunately, we do not know the exact form of $E^{\text{xc}}[n]$. It is also not clear, if the functional can be given in a simple, closed form at all, or if E^{xc} is similar to T_s . Analogous to the

¹⁰Strictly, $F[n]$ is a universal functional in n . Because $F[n] = T_s[n] + E^{\text{Hartree}}[n] + E^{\text{xc}}[n]$, cf. Eq. (3.165), this is also valid for $E^{\text{xc}}[n]$.

Thomas-Fermi-Weizsäcker ansatz for $T_s[n]$, we consider a series expansion starting from jellium (the homogeneous, interacting electron gas, where we have $v(\mathbf{r}) = \text{constant}$ and $n(\mathbf{r}) = \text{constant}$),

$$E^{\text{xc}}[n] = E^{\text{xc-jellium}}[n] + O(\nabla n) \quad . \quad (3.174)$$

We rewrite the exchange-correlation energy as follows

$$E^{\text{xc}}[n] = \int \epsilon^{\text{xc}}[n] n(\mathbf{r}) d^3\mathbf{r} \quad , \quad (3.175)$$

and

$$E^{\text{xc-jellium}}[n] = \int \epsilon^{\text{xc-jellium}}[n] n(\mathbf{r}) d^3\mathbf{r} \quad . \quad (3.176)$$

Here $\epsilon^{\text{xc-jellium}}[n]$ is the exchange-correlation energy per particle in a jellium system of constant density n . Because $n(\mathbf{r})$ is constant, i.e., n is just a number, $\epsilon^{\text{xc-jellium}}$ then is a *function* of the density: $\epsilon^{\text{xc-jellium}}(n)$. We generalize this expression to the following statement: For systems with a slowly varying density, $E^{\text{xc}}[n]$ can be replaced by

$$E^{\text{xc-LDA}}[n] = \int n(\mathbf{r}) \epsilon^{\text{xc-jellium}}(n(\mathbf{r})) d^3\mathbf{r} \quad . \quad (3.177)$$

Here n is the local density, i.e., the density at position \mathbf{r} .

“Slowly varying” means that the system can be regarded as a collection of jellium systems, where neighboring systems have only slightly different densities. Therefore, in a strict sense, $n(\mathbf{r})$ at a scale of $\frac{2\pi}{k_F}$ must change only marginally. $\frac{2\pi}{k_F}$ is the shortest wave length, appearing in the occupied states of a jellium system. Generally, for real systems this “mathematical requirement” for $n(\mathbf{r})$ is not fulfilled, i.e., $\frac{2\pi}{k_F} \approx 5\text{\AA}$ is of the same order as the interatomic distances. Still, experience shows that the ansatz Eq. (3.177)

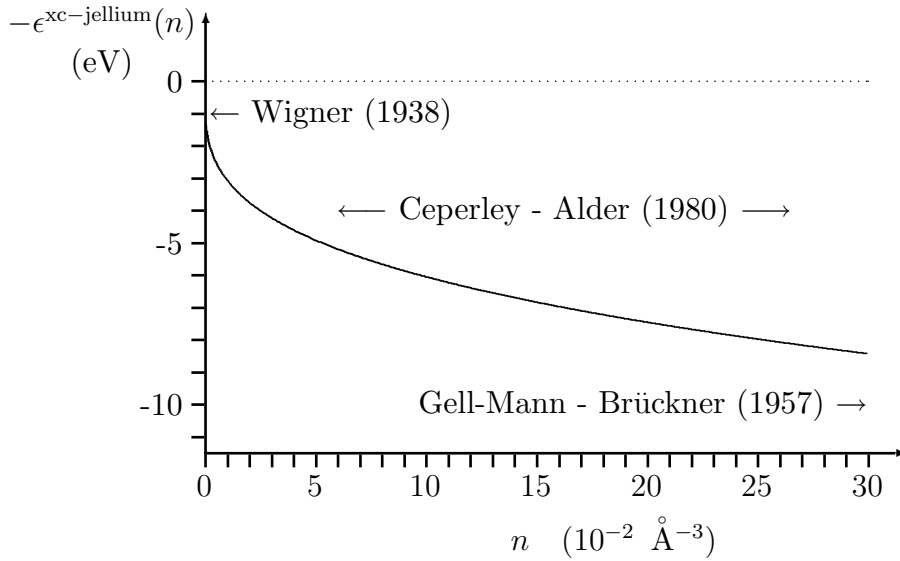


Figure 3.13: The exchange-correlation energy per particle for jellium systems of density n .

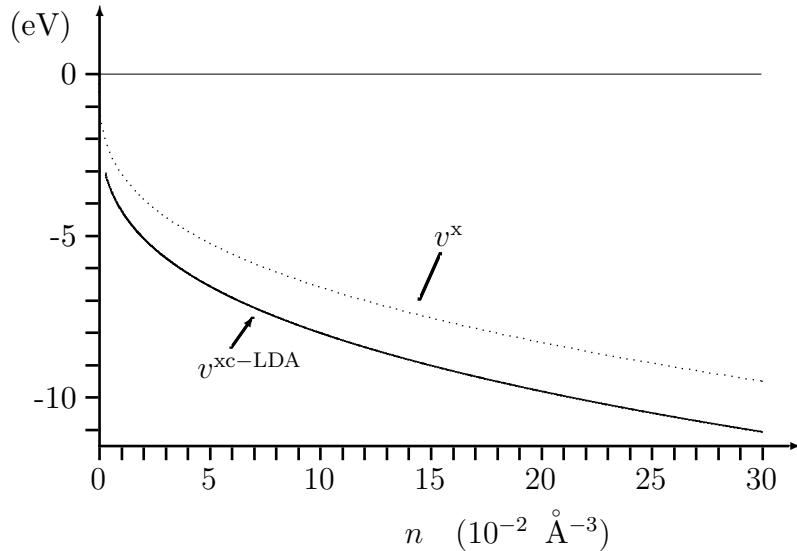


Figure 3.14: Exchange potential ($F = 0.5$ or $\alpha = 2/3$, cf. Eq. (3.85)) and the exchange-correlation potential as a function of the electron-density. The difference of both is the correlation potential.

works surprisingly well. This will be explained later. As a side remark we note that for $T_s[n]$ a local-density approximation is very poor, but for $E^{\text{xc}}[n]$ such an approximation is apparently acceptable.

The approximation (3.177) is called the *local-density approximation* (LDA). In this approximation each point in space (only for $E^{\text{xc}}[n]$) is treated like a jellium system. For the density at this point $n(\mathbf{r})$ then $E^{\text{xc}}[n]$ for jellium of density n is inserted. For this the function $\epsilon^{\text{xc-jellium}}(n)$ is required. What does $\epsilon^{\text{xc-jellium}}(n)$ look like? Already in 1938 Wigner determined ϵ^{xc} for jellium in the limit of small densities (Trans. Faraday Soc. **34**, 678 (1938)). In 1957 Gell-Mann and Brückner discussed the limit of high densities using many-body theories (Phys. Rev. **106**, 364 (1957)). In 1980 it became possible using computer calculations to address also the range in between (Ceperley, Alder, Phys. Rev. Lett. **45**, 566 (1980)). Today, the function $\epsilon^{\text{xc-jellium}}(n)$, or $\epsilon^{\text{xc-jellium}}(r_s)$ ($r_s = \sqrt[3]{\frac{3}{4\pi n}}$), is numerically well known. It is shown in Fig. 3.13. Table 3.1 gives the average electron density and the corresponding r_s parameter for some metals.

If we know $\epsilon^{\text{xc}}[n]$, the exchange-correlation potential of the Kohn-Sham equation can be calculated:

$$\begin{aligned}
 v^{\text{xc-LDA}}(\mathbf{r}) &= \frac{\delta E^{\text{xc-LDA}}[n]}{\delta n(\mathbf{r})} = \frac{\partial}{\partial n} \left(n \epsilon^{\text{xc-jellium}}(n) \right) \Bigg|_{n=n(\mathbf{r})} \\
 &= \epsilon^{\text{xc-jellium}}(n) + n \frac{\partial \epsilon^{\text{xc-jellium}}(n)}{\partial n} \Bigg|_{n=n(\mathbf{r})} . \quad (3.178)
 \end{aligned}$$

Figure 3.14 shows the correct v^{xc} potential for jellium in comparison to the previous Hartree-Fock-Slater result.

atom	number of valence electrons in the atom	number of atoms per primitive unit cell	lattice constant (Å)	average density (10^{22} cm^{-3})	r_s (bohr)
Li	1	1	3.49	4.70	3.25
Na	1	1	4.23	2.65	3.93
K	1	1	5.23	1.40	4.86
Cs	1	1	6.05	0.91	5.62
Cu	1	1	3.61	8.47	2.67
Ag	1	1	4.09	5.86	3.02
Al	3	1	4.05	18.1	2.07
Ga	3	1	4.51	15.4	2.19

Table 3.1: Average electron density of metals. For Cu and Ag the electrons of the $3d$ - and $4d$ -shells have not been counted as valence electrons. For several problems this approximation is too crude.

In order to interpret the exchange-correlation potential of DFT-LDA theory, we proceed like for Hartree and Hartree-Fock (cf. the discussion of Fig. 3.4). We write:

$$E^{\text{Hartree}}[n] + E^{\text{xc}}[n] = \frac{e^2}{8\pi\epsilon_0} \int n(\mathbf{r}) \int \frac{n(\mathbf{r}') - n^{\text{xc}}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r} d^3\mathbf{r}' \quad . \quad (3.179)$$

The density $n - n^{\text{xc}}$ is shown in Fig. 3.15. The interpretation is to view the exchange-correlation energy as a correction of the Coulomb interaction of the Hartree term, i.e., a particle at position \mathbf{r} does not interact with particles being distributed like $n(\mathbf{r}')$, but it feels a particle distribution $n(\mathbf{r}') - n^{\text{xc}}(\mathbf{r}, \mathbf{r}')$.¹¹ For the corresponding terms in the effective potential we have:

$$\begin{aligned} v^{\text{Hartree}}(\mathbf{r}) + v^{\text{xc}}(\mathbf{r}) &= \frac{\delta}{\delta n(\mathbf{r})} (E^{\text{Hartree}}[n] + E^{\text{xc}}[n]) \\ &= \frac{e^2}{4\pi\epsilon_0} \int \frac{n(\mathbf{r}') - n^{\text{xc}}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' - \frac{e^2}{8\pi\epsilon_0} \iint \frac{n(\mathbf{r}') \left(\frac{\delta}{\delta n(\mathbf{r})} \frac{n^{\text{xc}}(\mathbf{r}, \mathbf{r}'')}{n(\mathbf{r}'')} \right) n(\mathbf{r}'')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' d^3\mathbf{r}'' \quad , \end{aligned} \quad (3.180)$$

where the first term again shows that a particle at position \mathbf{r} interacts with a particle distribution $n(\mathbf{r}') - n^{\text{xc}}(\mathbf{r}, \mathbf{r}')$. The second term includes in addition changes of the particle distribution n^{xc} when the density is varied.

¹¹Here we have expressed the exchange-correlation energy as $-\frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \iint \frac{n(\mathbf{r})n^{\text{xc}}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r} d^3\mathbf{r}'$. In the literature, exchange-correlation is often discussed in terms of the so-called exchange-correlation hole $h^{\text{xc}}(\mathbf{r}, \mathbf{r}') \equiv -n^{\text{xc}}(\mathbf{r}, \mathbf{r}')$. The function $n(\mathbf{r})n(\mathbf{r}') - n^{\text{xc}}(\mathbf{r}, \mathbf{r}')$ is identical to the (coupling constant averaged) pair-correlation function, i.e. the probability of finding an electron at position \mathbf{r}' if there is already one at \mathbf{r} .

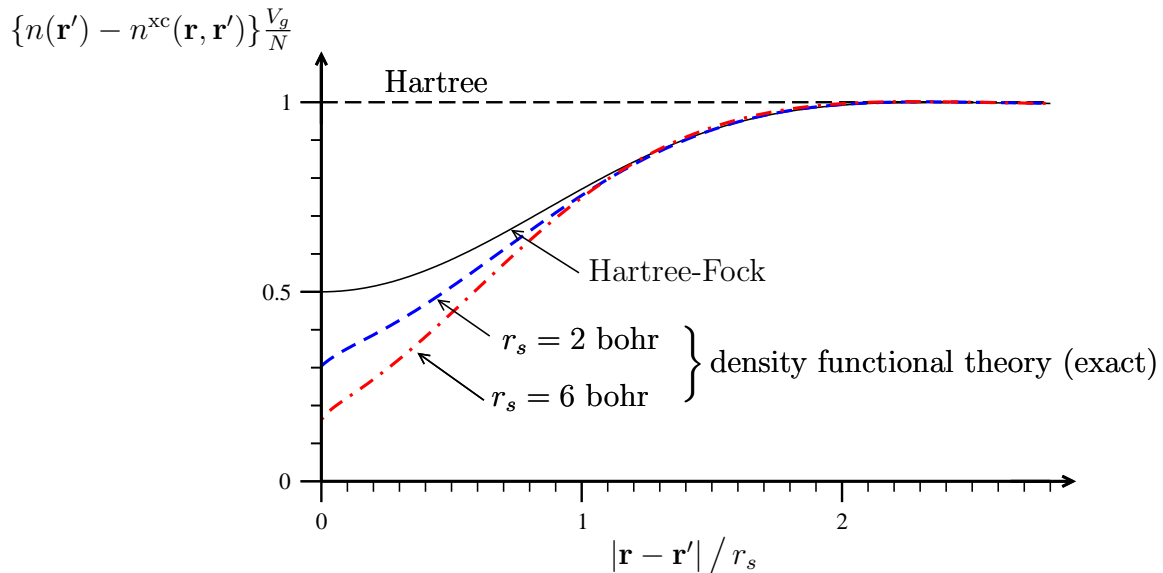


Figure 3.15: Distribution of the $N - 1$ other electrons with respect to a particle that is located at position $\mathbf{r} = 0$, i.e. the pair-correlation function (for jellium).

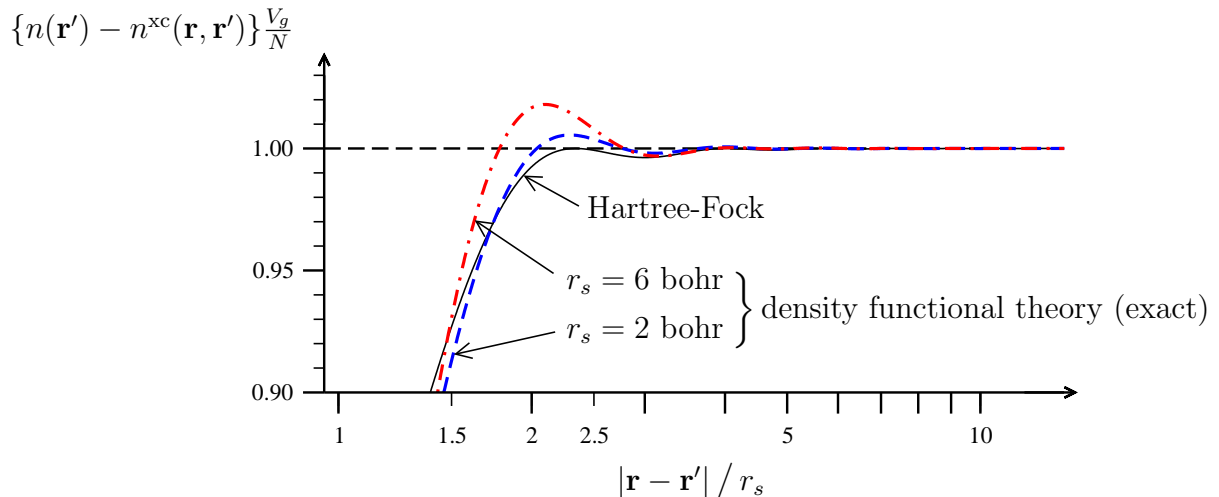


Figure 3.16: Like Fig. 3.15, but for larger electron-electron separations.

In the neighborhood of a particle the density is reduced. The origins of this reduction are the Pauli principle and the Coulomb repulsion. Strictly, this reduction has to be explained by a dynamical treatment. This is the origin of the term correlation (of the motion). But in a time-independent theory dynamic correlation can also be described as mentioned above. We summarize: Hartree theory does not include correlation, i.e., a Hartree particle sees a distribution of the other particles, which is independent of its position. Hartree-Fock theory includes the correlation of electrons of like spin originating from the Pauli principle. This “Pauli correlation” is called exchange interaction. In principle density-functional theory is exact (and for jellium it can be carried out numerically exact). It contains exchange as well as the correlation caused by the Coulomb repulsion. But since the functional $E^{\text{xc}}[n]$ in its general form is unknown, DFT combined with the LDA is accurate only for interacting electronic systems of slowly varying densities. For inhomogeneous systems the LDA is an approximation, but a surprisingly good one! For no

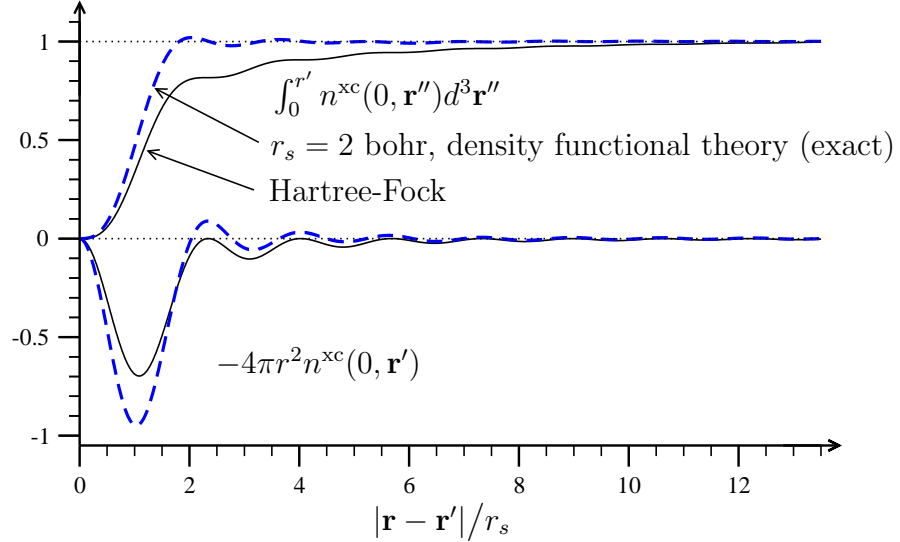


Figure 3.17: Exchange-correlation hole $-n^{\text{xc}}(0, \mathbf{r}')$ of an electron at position $\mathbf{r} = 0$ (for jellium). The lower part of the plot shows how many electrons are removed from, or shifted into, a spherical shell $r' \pm \delta r'$ due to exchange and correlation, respectively. The top part shows how $n^{\text{xc}}(0, \mathbf{r}')$ integrates up to satisfy the sum rule Eq. (3.181).

interacting many-body problem Hartree is exact and the Hartree-Fock approximation is exactly right only for those systems, for which the ground state is one Slater determinant.

Surprisingly, it turned out that DFT-LDA yields rather reliable results also for systems of strongly varying densities. This can be made plausible: The LDA can be understood as an approximation for the *shape* of the exchange-correlation hole, and because in E^{xc} and in v^{xc} only the integral over n^{xc} enters, the errors in the shape of the exchange-correlation hole cancel to some extent¹².

The exchange-correlation hole $-n^{\text{xc}}(\mathbf{r}, \mathbf{r}')$, i.e. the reduction of electron density $n(\mathbf{r}') - n^{\text{xc}}(\mathbf{r}, \mathbf{r}')$ around the position of an electron at \mathbf{r} , is a plausible consequence of the Pauli exclusion principle and Coulomb repulsions. Figure 3.15 illustrates their effect for jellium. In Hartree theory the electrons are essentially treated as if they moved independently from one another (like in an ideal gas of non-interacting fermions), i.e. their exchange-correlation hole is zero. The effect of the Pauli exclusion principle is to reduce the probability of finding electrons with the spin σ around an electron at position \mathbf{r} with the same spin σ ; therefore the probability of finding two electrons at the same position is 0.5 (for jellium with $n_{\uparrow} = n_{\downarrow}$). Coulomb repulsion pushes the electrons further apart and thus reduces the pair-correlation function (deepen the exchange-correlation hole) at short electron-electron separations and increases it at larger separations (see Fig.). At $\mathbf{r} = \mathbf{r}'$ the pair-correlation function displays a “cusp”, i.e. a finite slope, which is a consequence of the the $1/r$ singularity of the Coulomb interaction. Here, in Fig. 3.15, we also see the quantum mechanical nature of the electron. For a classical particle the density of the exchange-correlation hole must go to zero at $\mathbf{r} = \mathbf{r}'$, because when a particle is at position

¹²For a detailed discussion cf. Barth, Williams, in “The inhomogeneous electron gas”, also R.O. Jones and O. Gunnarsson, Rev. Mod. Phys. **61**, 689 (1989).

\mathbf{r} not other particle can be at the same position. In quantum mechanics the uncertainty principle weakens the meaning of “particle at position \mathbf{r} ” and therefore $n(\mathbf{r}') - n^{\text{xc}}(\mathbf{r}, \mathbf{r}')$ is non-zero at $\mathbf{r} = \mathbf{r}'$.

Without proof, we also state another strict property of $n^{\text{xc}}(\mathbf{r}, \mathbf{r}')$: As each electron of the N -electron problem interacts with the $(N - 1)$ other electrons, and because

$$\int n(\mathbf{r}') d^3\mathbf{r}' = N \quad ,$$

it follows that

$$\int n^{\text{xc}}(\mathbf{r}, \mathbf{r}') d^3\mathbf{r}' = 1 \quad . \quad (3.181)$$

This sum rule is illustrated in Fig. 3.17 for jellium. Any reasonable approximation to $E^{\text{xc}}[n]$ must fulfil this condition, for instance it is fulfilled by the LDA.

3.7.1 Meaning of the Kohn-Sham Single-Particle Energies ϵ_{o_k} – The DFT Analog of Koopmans’ Theorem –

Density-functional theory was derived with the goal that $n(\mathbf{r})$ and $E_0^e = \text{Min}_{n(\mathbf{r})} E_v[n]$ are physical quantities. There was no meaning assigned to $\varphi_{o_k}(\mathbf{r})$ or ϵ_{o_k} . These appeared in the theory as technical quantities, somewhat similar to the single-particle energies which appeared in Hartree-Fock theory. Only via Koopmans’ theorem we found out that the Hartree-Fock single-particle energies are approximate ionization energies.

Often one reads that in DFT Koopmans’ theorem is not valid and that the single-particle energies of the Kohn-Sham equation have no physical meaning. In narrow terms this statement is right. However, we like to emphasize that there is a theorem in DFT that is practically equivalent to Koopmans’ theorem. As mentioned above, i.e. considering the derivation of the Kohn-Sham equation, the Kohn-Sham single-particle energies do not seem to have a *direct* physical meaning. However, we found that the ϵ_{o_k} are nevertheless required, i.e. in the expression of the kinetic energy when the total energy has to be calculated (cf. Eq. (3.172)). Only the highest occupied Kohn-Sham level has a direct physical meaning: The highest occupied level (of the exact DFT) is the ionization energy (Almbladh, v. Barth, Phys. Rev. B **31**, 3231 (1985)).

In order to clarify the physical meaning of the Kohn-Sham single-particle energies we introduce occupation numbers:

$$n(\mathbf{r}) = \sum_{k=1}^N |\varphi_{o_k}(\mathbf{r})|^2 \quad (3.182)$$

$$= \sum_{k=1}^{\infty} f_{o_k} |\varphi_{o_k}(\mathbf{r})|^2 \quad . \quad (3.183)$$

At zero temperature we have

$$f_{o_k} = \begin{cases} 1 & \text{for } k = 1 \dots N \\ 0 & \text{otherwise} \quad , \end{cases} \quad (3.184)$$

and

$$T_s[n] = \sum_{k=1}^{\infty} f_{o_k} \epsilon_{o_k} - \int v^{\text{eff}}(\mathbf{r}) n(\mathbf{r}) d^3\mathbf{r} \quad . \quad (3.185)$$

Strictly, $E_v[n]$ is defined only for $f_{o_k} = 0$ or 1. Now we will assume that the range of the f_{o_k} can be extended to non-integer occupations. For example, for a finite temperature description the occupation numbers would be given by the Fermi function. This extension of the f_{o_k} is obviously not a problem for all parts of the energy functional, except for E^{xc} , as we do not know it exactly. However, for all known approximations of E^{xc} this extension of the range of possible f_{o_k} is unproblematic. We then get

$$\frac{\partial E_v[n]}{\partial f_{o_k}} = \int \frac{\delta E_v[n]}{\delta n(\mathbf{r})} \frac{\partial n(\mathbf{r})}{\partial f_{o_k}} d^3\mathbf{r} \quad , \quad (3.186)$$

where

$$\frac{\partial n(\mathbf{r})}{\partial f_{o_k}} = |\varphi_{o_k}(\mathbf{r})|^2 \quad , \quad (3.187)$$

because the φ_{o_k} (for a given v^{eff}) do not depend explicitly on the occupation numbers. We do not want to assume here that the variational principle $\frac{\delta E_v[n]}{\delta n(\mathbf{r})} = \mu$ is fulfilled, and therefore calculate $\frac{\delta E_v[n]}{\delta n(\mathbf{r})}$:

$$\frac{\delta E_v[n]}{\delta n(\mathbf{r})} = \frac{\delta T_s[n]}{\delta n(\mathbf{r})} + v^{\text{Hartree}}(\mathbf{r}) + v^{\text{xc}}(\mathbf{r}) + v(\mathbf{r}) \quad (3.188)$$

$$= \frac{\delta T_s[n]}{\delta n(\mathbf{r})} + v^{\text{eff}}(\mathbf{r}) \quad . \quad (3.189)$$

It follows that

$$\begin{aligned} \frac{\partial E_v[n]}{\partial f_{o_k}} &= \int \frac{\delta E_v[n]}{\delta n(\mathbf{r})} \frac{\partial n(\mathbf{r})}{\partial f_{o_k}} d^3\mathbf{r} \\ &= \int \frac{\delta T_s[n]}{\delta n(\mathbf{r})} |\varphi_{o_k}(\mathbf{r})|^2 d^3\mathbf{r} + \int v^{\text{eff}}(\mathbf{r}) |\varphi_{o_k}(\mathbf{r})|^2 d^3\mathbf{r} \quad . \end{aligned} \quad (3.190)$$

Because

$$\int \frac{\delta T_s[n]}{\delta n(\mathbf{r})} |\varphi_{o_k}(\mathbf{r})|^2 d^3\mathbf{r} = \frac{\partial T_s[n]}{\partial f_{o_k}} \quad , \quad (3.191)$$

and with

$$\frac{\partial T_s}{\partial f_{o_k}} = \epsilon_{o_k} - \int v^{\text{eff}}(\mathbf{r}) |\varphi_{o_k}(\mathbf{r})|^2 d^3\mathbf{r} \quad , \quad (3.192)$$

we obtain the result

$$\frac{\partial E_v[n]}{\partial f_{o_k}} = \epsilon_{o_k} \quad . \quad (3.193)$$

This equation also holds for the highest occupied state, $k = N$, which, at least in metals, is called the Fermi energy:

$$\frac{\partial E_v[n]}{\partial f_{o_N}} = \epsilon_{o_N} = \epsilon_{\text{F}} \quad , \quad (3.194)$$

and because $\frac{\delta E_v[n]}{\delta n(\mathbf{r})} = \mu$ it follows that $\mu = \epsilon_{\text{F}}$. Figure 3.18 shows an example for ϵ_{o_k} as function of the occupation number. However, here the local spin-density approximation

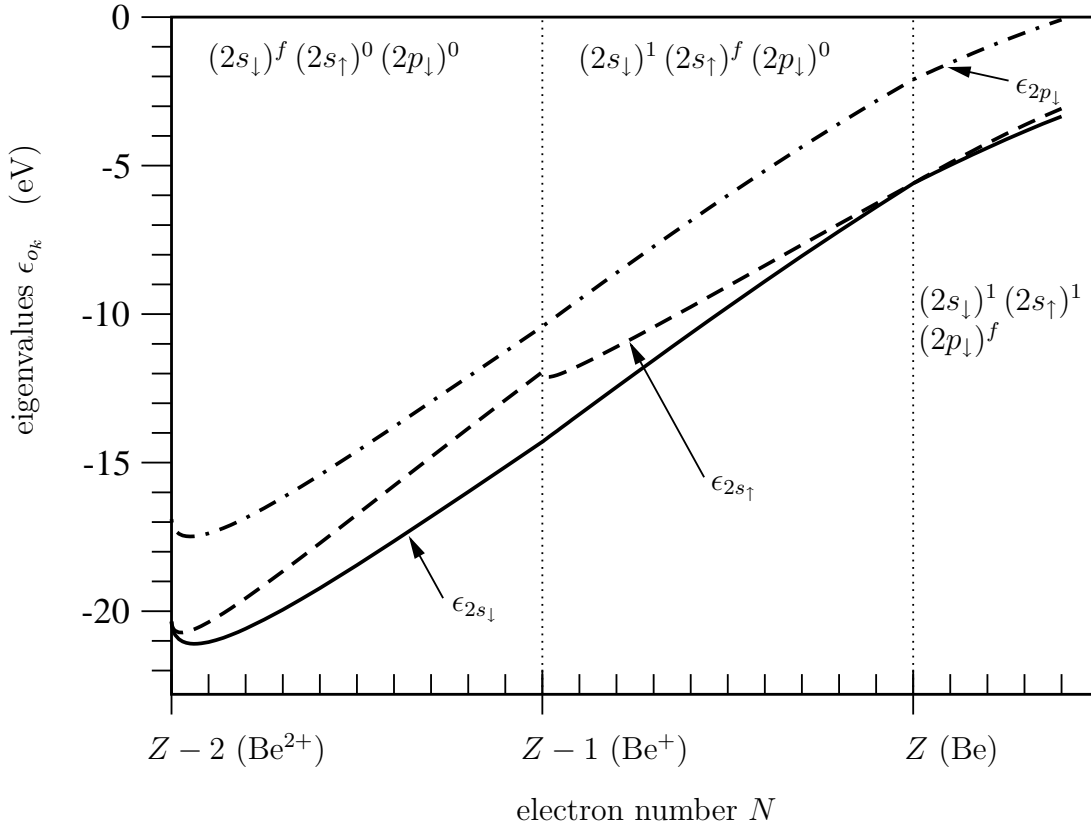


Figure 3.18: The function $\epsilon_{o_k}(N)$ for the $2s$ and $2p$ states of the Be atom ($Z = 4$) as a function of the electron number (from $N = 2$ to $N = 4.4$). The neutral Be atom has the configuration $1s^2 2s^2$. At first the occupation of the $2s_{\downarrow}$ level is changed from zero to one (from left to right). Then the occupation of the $2s_{\uparrow}$ level is changed and then that of the $2p_{\downarrow}$ level. The local spin-density approximation is employed.

for E^{xc} has been used. This represents an improvement over the ansatz $n_{\uparrow} = n_{\downarrow}$, and it will be discussed in Section 3.7.3 below. Due to the kinetic energy, the functions $\epsilon_{o_k}(f)$ are not differentiable at some points. These points are found at integer values of N where a new spin channel or a new shell is added.

Now we look at an ionization event, i.e., the transition from the ground state Φ^N to the state Φ_k^{N-1} plus a free electron of zero energy. The index k of the wave function marks that the level k is no more occupied. In the exact meaning of the word, ionization refers to the highest level, i.e. $o_k = o_N$. However, in general (e.g. by photoemission) one can also remove more strongly bound electrons.

The ionization energy is

$$I_k = E_k^{N-1} - E^N \quad (3.195)$$

$$= - \int_0^1 \frac{\partial E_v[n]}{\partial f_{o_k}} df_{o_k} \quad (3.196)$$

$$= - \int_0^1 \epsilon_{o_k}(f_{o_k}) df_{o_k} \quad (3.197)$$

Here we assume that the geometry of the lattice is not changed by the ionization. For the ionization from extended levels of a solid this assumption is justified. And in general it represents the Franck-Condon principle which states that the displacement of the nuclei follows the electronic excitation (or the ionization) with some delay. Using the mean value theorem of calculus we obtain:

$$I_k = -\epsilon_{o_k}(0.5) \quad . \quad (3.198)$$

This expression is called Slater-Janak-“transition-state”. When a calculation is carried out and the level k is occupied by only half an electron, the energy ϵ_{o_k} approximately equals the ionization energy. If the functions $\varphi_k(\mathbf{r})$ are extended, $n(\mathbf{r})$ and therefore also $v^{\text{eff}}(\mathbf{r})$ and thus also the values of ϵ_{o_k} practically will not change, if the occupation of a level, f_{o_k} , is changed. Then we have $\epsilon_{o_k}(f_{o_k} = 1) \approx \epsilon_{o_k}(f_{o_k} = 0.5)$ and the single-particle levels correspond to the ionization energies: $I_k = -\epsilon_{o_k}$. Thus, we get the same result as obtained by Koopmans’ theorem of Hartree-Fock theory, and the proof is even more plausible here in DFT than it was before in Hartree-Fock theory.

We mention here only in passing another shortcoming of the LDA, besides the mentioned poor correction of the electron self-interaction. It can be shown that the true $E^{\text{xc}}[n]$ functional has kinks at integer values of N when plotted as a continuous function of the number of electrons. This is somewhat analogous to $T_s[n]$ which also has kinks due to the level structure of the Kohn-Sham eigenvalues (e.g. the shell structure of atomic orbitals). These kinks in $E^{\text{xc}}[n]$ give rise to discontinuities in $\frac{\delta E^{\text{xc}}}{\delta n} = v^{\text{xc}}$ when studied as a function of particle number. We may get back to this point and the current theories for excited states at the end of the semester. The LDA does not have such kinks in E^{xc} or discontinuities in v^{xc} .

Experience shows that although $E_0^e = \min_{n(\mathbf{r})} E_v[n]$ is affected by the approximation to the xc-functional, I (as an energy difference) is often rather accurate; the errors of the LDA cancel to some extent in the calculation of the difference. This is reasonable but not proven. It shall be illustrated now for the (extreme) example of the hydrogen atom. There is hardly any similarity between the hydrogen atom and the many-body problem of an extended solid. But it points to the problems of the LDA and the error compensation. In density-functional theory we have:

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r} + \frac{e^2}{4\pi\epsilon_0} \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' + v^{\text{xc}}(\mathbf{r}) \right\} \varphi(\mathbf{r}) = \epsilon \varphi(\mathbf{r}) \quad (3.199)$$

In an exact calculation for the ground state of a hydrogen atom we have:

$$\frac{e^2}{4\pi\epsilon_0} \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' + v^{\text{xc}}(\mathbf{r}) = 0 \quad , \quad (3.200)$$

because in a one-electron system there is no electron-electron interaction. The corresponding (exact) lowest energy value then is $\epsilon_{1s} = -13.6$ eV. In the LDA, however, the two terms in Eq. 3.200 do not cancel. The eigenvalue obtained from the LDA therefore is significantly above the exact eigenvalue: $\epsilon_{1s}^{\text{LDA}} = -6.4$ eV. Thus, for the hydrogen atom the jellium approximation for v^{xc} is very bad. Quite obviously, the orbital of a hydrogen atom is not extended but very localized. Nevertheless, even here we see that differences of total energies are rather good: $I \approx -\epsilon_{1s}^{\text{LDA}} \left(\frac{1}{2}\right) = +12.4$ eV. Generally we have: Due to

the poorly corrected self-interaction in the LDA the eigenvalues ϵ_k^{LDA} are too high, i.e., they correspond to too small ionization energies. This is the more true, the more a state is localized¹³. Consequently, for localized states the ϵ_{o_k} are no good approximation for ionization energies, but in general $\epsilon_{o_k}(0.5)$ is a rather good approximation.

3.7.2 Hellmann-Feynman Theorem

Already in 1933 the theory was very close to an invention of DFT. Back then, i.e. 31 years before the Hohenberg-Kohn paper, it was shown that forces acting on nuclei are only due to electrostatic interactions between the nuclear charges and the electron *density*. When \mathbf{F}_K is the force acting on atom (or nucleus) K , i.e.

$$\mathbf{F}_K = -\frac{\partial E_v[n]}{\partial \mathbf{R}_K} \quad (3.201)$$

in the language of DFT, Hellmann (1933, 1937) and Feynman (1939) showed within an exact derivation, starting from the many-body Schrödinger equation that

$$-\frac{\partial E_v[n]}{\partial \mathbf{R}_K} = \mathbf{F}_K = -\int \frac{\partial v(\mathbf{r}, \{\mathbf{R}_I\})}{\partial \mathbf{R}_K} n(\mathbf{r}) d^3\mathbf{r} \quad . \quad (3.202)$$

Starting from DFT, the proof is simple and will be done in the exercises (see also Scheffler, Vigneron, Bachelet, Phys. Rev. B **31**, 6541 (1985)).

¹³Taking into account the spin in the LSDA improves the value for the ionization energies of the hydrogen atom at the “transition-state” for half-occupation slightly: $I \approx -\epsilon_1^{\text{LSDA}}(\frac{1}{2}) = 13.35$ eV, $\epsilon_1(1) = -7.32$ eV and $\Delta E^e = 13.1$ eV, for the H-atom.

3.7.3 Spin Polarization

References:

Kohn and Sham (1965), Barth, Hedin (1972), Rajagopal, Callaway (1973), Levy.

Strictly, the ground state density alone defines the full problem: The ground state density determines the many-body Hamilton operator, which determines everything. However, the dependence of the total energy on the density is very complicated, and possibly cannot be represented in a closed mathematical form. Therefore, it is reasonable to soften the puristic approach and to start, e.g. for magnetic systems, with densities for spin up and spin down electrons as independent variables. This establishes the spin-density-functional theory (SDFT) and is an important and simple improvement of DFT. In this way, also magnetic effects can be described. For non-magnetic systems SDFT and DFT are identical. In the spin-density-functional theory the *density matrix* is used as the basic variable:

$$n_{s,s'}(\mathbf{r}) = \langle \Phi | \Psi_s^+(\mathbf{r}) \Psi_{s'}(\mathbf{r}) | \Phi \rangle \quad (3.203)$$

here s and s' represent the spin orientations of individual particles: \uparrow or \downarrow . $\Psi_s^+(\mathbf{r})$ and $\Psi_{s'}(\mathbf{r})$ are field operators, i.e., creation of a particle at position \mathbf{r} with spin s and annihilation of a particle at position \mathbf{r} with spin s' . Φ is the ground state wave function of the N electron system. The particle density (the basic variable in DFT) is

$$n(\mathbf{r}) = n_{\uparrow}(\mathbf{r}) + n_{\downarrow}(\mathbf{r}) \quad , \quad (3.204)$$

and the magnetization density is

$$m(\mathbf{r}) = \mu_B \{n_{\uparrow}(\mathbf{r}) - n_{\downarrow}(\mathbf{r})\} \quad . \quad (3.205)$$

Here, instead of $n_{\uparrow\downarrow}$ I have used only n_{\uparrow} and instead of $n_{\downarrow\downarrow}$ only n_{\downarrow} . Thus, we only need the diagonal elements. The Bohr magneton μ_B is defined as

$$\mu_B = \frac{e\hbar}{2mc} \quad . \quad (3.206)$$

Now we want to use

$$n_{\uparrow}(\mathbf{r}) = \langle \Phi | \sum_{k=1}^N \delta_{s_k, \uparrow} \delta(\mathbf{r} - \mathbf{r}_k) | \Phi \rangle \quad (3.207)$$

and

$$n_{\downarrow}(\mathbf{r}) = \langle \Phi | \sum_{k=1}^N \delta_{s_k, \downarrow} \delta(\mathbf{r} - \mathbf{r}_k) | \Phi \rangle \quad (3.208)$$

as the basic variables. Exactly analogous to standard DFT we obtain a single-particle equation:

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + v_{s_k}^{\text{eff}}(\mathbf{r}) \right\} \varphi_{o_k s_k}(\mathbf{r}) = \epsilon_{o_k s_k} \varphi_{o_k s_k}(\mathbf{r}) \quad . \quad (3.209)$$

The wave functions $\varphi_{o_k \uparrow}$ and $\varphi_{o_k \downarrow}$ are now determined from two different equations, but these equations are coupled, because the effective potential depends on n_{\uparrow} and n_{\downarrow} :

$$v_{s_k}^{\text{eff}}(\mathbf{r}) = v(\mathbf{r}) + \frac{e^2}{4\pi\epsilon_0} \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' + v_{s_k}^{\text{xc}}(\mathbf{r}) \quad , \quad (3.210)$$

with

$$v_{s_k}^{\text{xc}}(\mathbf{r}) = \frac{\delta E^{\text{xc}}[n_{\uparrow}, n_{\downarrow}]}{\delta n_{s_k}(\mathbf{r})} \quad , \quad (3.211)$$

and

$$n_{s_k}(\mathbf{r}) = \sum_{i=1}^N \delta_{s_k, s_i} |\varphi_{o_i s_i}(\mathbf{r})|^2 \quad . \quad (3.212)$$

The exchange-correlation potential now depends on the spin orientation. For practical calculations the local spin-density approximation is introduced:

$$E^{\text{xc-LSDA}} = \int n(\mathbf{r}) \epsilon^{\text{xc-jellium}}(n(\mathbf{r}), m(\mathbf{r})) d^3\mathbf{r} \quad . \quad (3.213)$$

Here, $\epsilon^{\text{xc-jellium}}(n, m)$ is the exchange-correlation energy per particle of a homogeneous electron gas of constant particle density n and constant magnetization density m . The exchange-correlation potential of the LSDA depends on the local electron density in a similar way as in LDA. However, the exchange and the correlation contribution of $v_{s_k}^{\text{xc-LSDA}}(\mathbf{r})$ or $\epsilon^{\text{xc-LSDA}}$ additionally depend on the spin-orientation.

Apart from spin-density theory also other generalizations have been investigated: Velocity-dependent forces, spin-orbit-coupling, relativistic formulation (\rightarrow Dirac equation). These will not be discussed here (cf. Rajagopal, Calloway, Phys. Rev. B **87**, 1912 (1973); MacDonald, Vosko: J. Phys. C **11**, L943 (1978); Rajagopal, J. Phys. C **11**, L943 (1978)).

3.7.4 Two Examples

Finally, we will demonstrate for two *examples*, which type of information can be obtained using DFT-LDA and SDFT-LSDA calculations. Later, at the detailed discussion and explanation of the nature of cohesion of solids we will use such calculations again.

Before 1980 systematic high-quality DFT calculation were not possible, partly due to the lack of efficient and reliable algorithms, partly due to the lack of computational power. Therefore, it was often not understood how the electron density is distributed in the crystal and how the solid is stabilized. It was, for example, not clear, why silicon does exist in the diamond structure or why silver has a fcc structure. Using parameter-free, self-consistent DFT calculations an initial understanding was obtained. However, we are still at the beginning, but with good perspectives: Efficient algorithms and powerful hardware are available, and compared to 1980 the efficiency of state-of-the-art algorithms is very much higher. The main advantage of such parameter-free, self-consistent DFT calculations is that the results can be analyzed in detail, i.e., which parts are essential for the stabilization of the solid and which are not. Such theoretical investigations of static and low-frequency dynamical properties usually are performed via the self-consistent calculation of the Kohn-Sham equation. The self-consistent field procedure is almost identical to the Hartree approximation discussed before (cf. Fig. 3.2), but now the effective potential additionally contains exchange and correlation. The only external parameters given (by the scientist) are the nuclear charge (i.e., the decision of the material, e.g. Si or Ag). In general, the lattice geometry will be varied in order to find the most stable geometry, i.e., the lowest

energy structure, and to analyze $n(\mathbf{r})$ for this structure. For these calculations there are still several serious practical problems that are not visible in Fig. 3.2. These problems are:

1. The solution of the effective Schrödinger equation. For this purpose suitable methods have to be developed (cf. Chapter 5). Such an equation cannot be solved analytically (except for the hydrogen atom and the linear harmonic oscillator).
2. The calculation of $n(\mathbf{r})$ as an integral or the summation of the $|\varphi_{o_i}(\mathbf{r})|^2$, respectively.
3. The calculation of the Poisson Eq. (3.104) for arbitrary charge densities $-en(\mathbf{r})$.
4. Approximations for the exchange-correlation functional $E^{\text{xc}}[n]$.

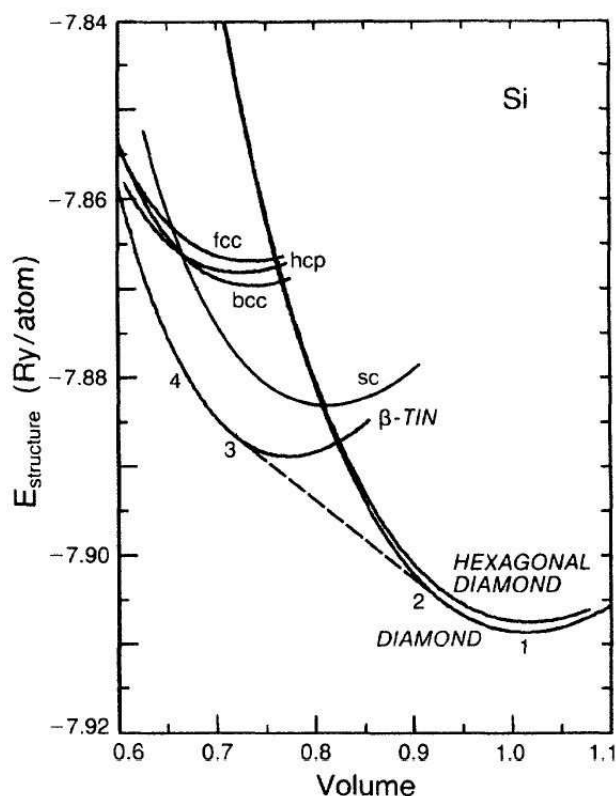


Figure 3.19: Density-functional theory calculations (using the local-density approximation for the exchange-correlation energy) of the total energy for various crystal structures of silicon as function of the volume per atom. The volume-axis is normalized such that the value 1.0 corresponds to the experimental result known for the diamond structure of Si. (M.T. Yin and M.L. Cohen, "Theory of static structural properties, crystal stability, and phase transformations: Application to Si and Ge", Phys. Rev. B **26**, 5668-5687 (1982)).

Figure 3.19 shows a "historic figure", namely what I consider to be the first convincing example demonstrating what type of problems can be tackled by density-functional theory calculations¹⁴. These are calculations performed in the group of Marvin Cohen

¹⁴Another early, impressive example of the power of density-functional theory calculation is the book by V.L. Moruzzi, J.F. Janak, and A. R. Williams, "Calculated Electronic Properties of Metals", Pergamon Press (1978).

in Berkeley. The figure shows the total energy for silicon as function of the volume per atom, where the volume was normalized such that 1.0 is that of the experimentally known result for Si in the diamond structure. The results show clearly that the lowest energy of all considered structures is indeed found for the diamond structure, and the minimum of the theoretical curve is very close to the experimental result. If the volume is reduced the figure also reveals that there is a phase transition that eventually brings the system into the beta-tin structure. The slope of the common tangent of two curves for the beta-tin and the diamond structures gives the pressure at which the phase transition sets in. This common tangent is called the Gibbs construction. Such calculations can predict and explain why solids behave as they do, and new materials of hitherto unknown structure or composition can be investigated as well.

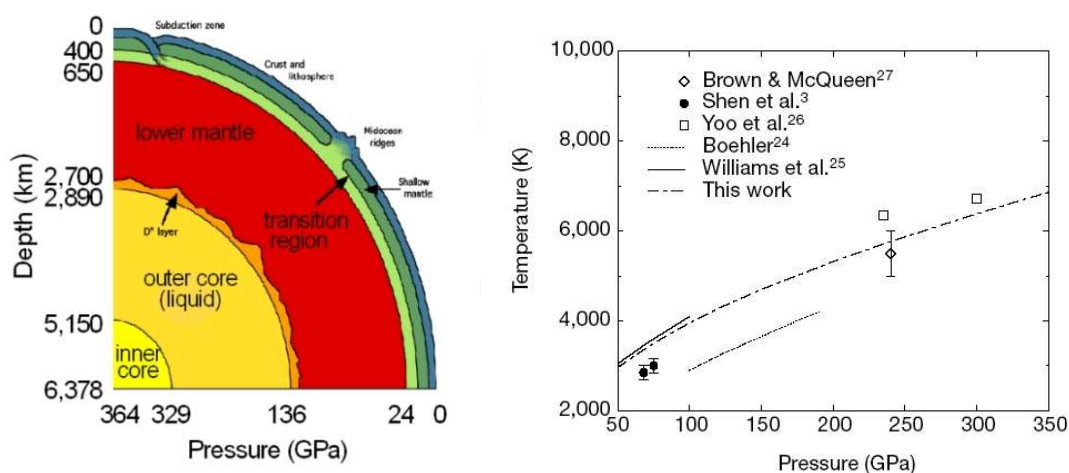


Figure 3.20: A cut through the earth showing the various shells (left) and the calculated melting curve for iron. (D. Alfè, G.D. Price, and M.J. Gillan, “Melting curve of Iron at Earth’s core pressures from ab-initio calculations”, *Nature* **401**, 462-464 (1999).)

In Fig. 3.20 I show a more recent example and this demonstrates how density-functional theory calculations can tell us things about geology that we cannot learn otherwise. Save knowledge about the earth only exists about the crust and the upper mantle. However, it is interesting and indeed important to know more about the central region of our planet, as this, for example contains information about the origin, the development, and the future of the earth. One aspect here also is the question what determines the earth magnetic field and its fluctuations and changes. The structure of the earth (left side in Figure 3.18) is known from measurements of the propagation, time delays, phase differences of earth quake waves, as these are reflected when the composition or the aggregate state in the earth change. The inner core of the earth is most likely solid and then we have the outer core which is liquid. We know the depth and we also quite accurately can estimate the pressure that is present at the phase boundary between the solid and the liquid core. The material down there is mostly iron probably with some fraction of O, S, Se and C. Unclear, however, is the temperature at this place.

In fact, we don’t know at what temperature does iron melt when it is put under such a high pressure of 330 GPa, and we have no idea how such melt may behave. What is

the local structure and what is the viscosity of the melt at such extreme conditions? The problem is that such pressure can hardly be reached in the laboratory. With a diamond anvil cell one gets somewhat close, i.e., to 200 GPa, but not to 330 GPa.

Density-functional theory calculations by Alfè et al. (see also <http://chianti.geol.ucl.ac.uk/~dario/> and <http://chianti.geol.ucl.ac.uk/~dario/resint.htm>) have shown that the melting temperature of iron at 330 GPa is 6.670 K (cf. Fig. 3.18, right). Thus, this must be the temperature at the interface between the inner and the outer core. In simple words one could say, that DFT was used as a thermometer to determine the temperature at an inaccessible place.

Furthermore, the authors studied the viscosity. The previously existing experimental estimates differed by many orders of magnitude. The DFT work showed that liquid iron in the outer core should have a local coordination similar to that of the hcp structure, and the viscosity is only by a factor of 10 higher than that of liquid iron at standard pressure. This is actually on the lowest side of the previous experimental estimates. Of course there are also some uncertainties in the theoretical result. These arise, because a somewhat small supercell was used, the exchange-correlation functional was, of course, treated approximately, and the authors studies pure iron, i.e., without the O, S, etc. fractions that must be there as well. All together the uncertainty of the calculated viscosity may be a factor of 3. This is still a much lower uncertainty than that of experimental studies.

It is now clear that in the outer core local circulations and turbulent convection will occur. At most of the previous, experimentally estimated values for the viscosity this would not be possible.

3.8 Summary (Electron-Electron Interaction)

Chapter 3 was “only” concerned about the properties of the electronic ground state, e.g. the basic equations that one has to solve to learn about the total energy (internal energy), density of the electrons, screening, lattice structure, lattice constant, elastic properties, lattice vibrations, and approximate electronic excitations. In the following summary of the most important equations we assume for clarity that spin polarization is absent, i.e.,

$$n_{\uparrow}(\mathbf{r}) = n_{\downarrow}(\mathbf{r}) = \frac{n(\mathbf{r})}{2} \quad . \quad (3.214)$$

The Hamilton operator of the electrons is

$$H^e = T^e + V^{e-Ion} + V^{e-e} \quad (3.215)$$

$$= \sum_{i=1}^N -\frac{\hbar^2}{2m} \nabla_{\mathbf{r}_i}^2 + \sum_{i=1}^N v(\mathbf{r}_i) + \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\substack{i,j=1 \\ i \neq j}}^{N,N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad . \quad (3.216)$$

The total energy is

$$E_0 = E_0^e + E^{\text{Ion-Ion}} \quad \text{with} \quad E_0^e = \text{Min}_{\Phi} \langle \Phi | H^e | \Phi \rangle \quad . \quad (3.217)$$

The density-functional theory of Hohenberg and Kohn means that the many-body Schrödinger equation with the Hamilton operator (Eq. (3.215)) can be transformed into a self-consistent field theory. Hohenberg and Kohn have shown that

$$\langle \Phi | H^e | \Phi \rangle = \int v(\mathbf{r})n(\mathbf{r})d^3\mathbf{r} + F[n] = E_v[n] \quad (3.218)$$

with the particle density of the electrons

$$n(\mathbf{r}) = \sum_{i=1}^N \langle \Phi | \delta(\mathbf{r} - \mathbf{r}_i) | \Phi \rangle \quad (3.219)$$

and

$$F[n] = \langle \Phi | T^e + V^{e-e} | \Phi \rangle \quad (3.220)$$

For a given external potential $v(\mathbf{r})$ and taking into account the conservation of the number of particles ($\int n(\mathbf{r})d^3\mathbf{r} = N$), $E_v[n]$ assumes a minimum at the correct particle density $n_0(\mathbf{r})$, and at the value E_0^e for the energy of the electronic ground state. We have:

$$\left. \frac{\delta T_s[n]}{\delta n(\mathbf{r})} \right|_{n_0} + v^{\text{eff}}(\mathbf{r}) = \mu \quad (3.221)$$

Here $T_s[n]$ is the kinetic energy functional of independent (non-interacting) particles. It must not be confused with $T^e = \langle \Phi | T^e | \Phi \rangle$, which is defined for interacting systems. We have:

$$\frac{\delta T_s[n]}{\delta n(\mathbf{r})} = \frac{\hbar^2}{2m} (3\pi^2 n(\mathbf{r}))^{2/3} + O(\nabla n(\mathbf{r})) \quad (3.222)$$

It should be noted, however, that this series expansion converges slowly and is therefore probably not useful; using only the Thomas-Fermi approximation to the kinetic energy is very inaccurate.

For $v^{\text{eff}}(\mathbf{r})$ we have:

$$v^{\text{eff}}(\mathbf{r}) = v(\mathbf{r}) + \frac{e^2}{4\pi\epsilon_0} \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' + \frac{\delta E^{\text{xc}}[n]}{\delta n(\mathbf{r})} \quad (3.223)$$

where $E^{\text{xc}}[n]$ is the exchange-correlation functional. We have:

$$E^{\text{xc}}[n] = \langle \Phi | H^e | \Phi \rangle - \int v(\mathbf{r})n(\mathbf{r})d^3\mathbf{r} - T_s[n] - \frac{1}{2} \frac{1}{4\pi\epsilon_0} \iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}d^3\mathbf{r}' \quad (3.224)$$

The quantity μ introduced as a Lagrange parameter in Eq. (3.221) is the chemical potential of the electrons.

The particle density of Eq. (3.219) can also be determined using the Kohn-Sham equation:

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + v^{\text{eff}}(\mathbf{r}) \right\} \varphi_{o_k}(\mathbf{r}) = \epsilon_{o_k} \varphi_{o_k}(\mathbf{r}) \quad (3.225)$$

with

$$n(\mathbf{r}) = \sum_{k=1}^N |\varphi_{o_k}(\mathbf{r})|^2 \quad (3.226)$$

Equation (3.221) means: In principle it is possible to determine $n(\mathbf{r})$ directly from $v(\mathbf{r})$, i.e., the many-body wave function $\Phi(\mathbf{r}_1\sigma_1, \dots, \mathbf{r}_N\sigma_N)$ is not required explicitly.

The problem with the calculation is that the functional $T_s[n]$ is not explicitly known, or that the known approximations are inaccurate or very complicated. Although the functional $T_s[n]$ cannot be given in a closed mathematical form, its value is calculated exactly when the Kohn-Sham equation is used. Experience shows that the exact calculation of $T_s[n]$ is very important.

$E^{\text{xc}}[n]$ is also not known exactly. A known approximation for $E^{\text{xc}}[n]$ and for $v^{\text{xc}}(\mathbf{r}) = \frac{\delta E^{\text{xc}}[n]}{\delta n(\mathbf{r})}$ is the “local-density approximation” (LDA).

Equation (3.225) means that the many-body problem of the Hamilton operator of Eq. (3.215) can be brought into the form of a single-particle equation to be solved self-consistently. The potential, in which the N independent quasi particles $\varphi_{o_k}(\mathbf{r})$ move, $v^{\text{eff}}(\mathbf{r})$, is local (i.e., it is multiplicative) and is identical for all particles. In practical calculations the only approximation introduced concerns $E^{\text{xc}}[n]$.

Approximations:

1. Local-density approximation (LDA):

$$E^{\text{xc}}[n] = \int n(\mathbf{r}) \epsilon^{\text{xc}}[n](\mathbf{r}) d^3\mathbf{r} \quad \rightarrow \quad E^{\text{xc-LDA}}[n] = \int n(\mathbf{r}) \epsilon^{\text{xc-jellium}}(n(\mathbf{r})) d^3\mathbf{r} \quad (3.227)$$

$\epsilon^{\text{xc-jellium}}(n)$ is the exchange-correlation energy per particle of the homogeneous electron gas (jellium) of density n . Strictly, Eq. (3.227) is valid only for slowly varying densities. Experience with this approximation for calculations of atoms, molecules and solids shows that Eq. (3.227) in general can also be applied to these systems.

2. The Hartree-Fock approximation is obtained from Eq. (3.223) and (3.225), when

$$\frac{\delta E^{\text{xc}}[n]}{\delta n(\mathbf{r})} = v^{\text{xc}}(\mathbf{r}) \quad (3.228)$$

is replaced by

$$v_k^{\text{x}}(\mathbf{r}) = -\frac{e^2}{4\pi\epsilon_0} \int \frac{n_k^{\text{HF}}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' \quad (3.229)$$

$$n_k^{\text{HF}}(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^N \delta_{s_i, s_k} \frac{\varphi_{o_i s_i}^*(\mathbf{r}') \varphi_{o_k s_k}(\mathbf{r}') \varphi_{o_i s_i}(\mathbf{r})}{\varphi_{o_k s_k}(\mathbf{r})} \quad (3.230)$$

is called *exchange particle density*. This approximation is obtained, if the many-body wave function is constructed from *one* Slater determinant.

Problems:

- a) $v_k^{\text{x}}(\mathbf{r})$ depends on the index (quantum number) of the wave function to be calculated.

- b) $v_k^x(\mathbf{r})$ contains only exchange, i.e., the correlation of the electrons due to the Pauli principle. The correlation arising from the Coulomb repulsion between electrons is missing.
3. The Hartree approximation is obtained when $E^{xc}[n]$ and $v^{xc}(\mathbf{r})$ are neglected. Strictly, $v^{xc}(\mathbf{r})$ should be replaced by

$$v_k^{\text{SIC}}(\mathbf{r}) = -\frac{e^2}{4\pi\epsilon_0} \int \frac{|\varphi_{o_k}|^2}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' \quad , \quad (3.231)$$

which is, however, typically ignored. This approximation is obtained, if the many-body wave function is constructed as a simple product of single-particle functions.

4. The Thomas-Fermi approximation is obtained from Eq. (3.221), (3.222) and (3.224), if the following approximation is introduced:
- a) in $T_s[n]$ $O(\nabla n)$ is neglected
 - b) in $E^{xc}[n]$ $O(\nabla n)$ is neglected

Problems: The approximation for $T_s[n]$ generally yields an error of 10% in the total energy. The shell structure of the atoms is not described.