

Brief Introduction to the Density Functional Theory

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Lecture Notes to MSc course FYS-MENA4111 - Quantum Mechanical Modeling of Nano-Materials at University of Oslo, 2013.

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1 Introduction

The density functional theory (DFT) in conjunction with the Kohn-Sham (KS) equation and the local density approximation (LDA) has during the last 30–40 years been extremely successful to describe systems with a large number of atoms, like for instance solids, nanostructures, and large molecules. Employing the DFT, theoreticians are supporting experimental studies, analyzing the underlying physics of many-atom systems, as well as exploring new material and molecular structures. The DFT is one of the most popular approaches to explore many-atoms systems. Now, there are more than 15,000 published scientific papers per year, and the number of publications is rapidly increasing (Ref. www.psi-k.org). In 1998, Prof. John A. Pople and Prof. Walter Kohn shared the Nobel Prize in Chemistry for their contributions to develop the DFT and computational methods.

This compendium is based on lecture notes for the MSc course FYS-MENA4111 “Quantum Mechanical Modeling of Nano-Materials” at the University of Oslo. In the course, we learn the basic ideas and theories of the DFT, and how one can employ this theory to calculate physical properties of condensed matter. The compendium has no intention to give the full insight of all aspects of DFT, but instead be an informal guide to the concepts of the theories behind the DFT and the Kohn-Sham equation.

In order to analyze theoretically a material, one first has to solve the quantum-mechanical Schrödinger equation for the material. That is, we shall solve $H^{en}\Psi^{en}(\mathbf{r},\mathbf{R}) = E^{en}\Psi^{en}(\mathbf{r},\mathbf{R})$ where H^{en} is the Hamiltonian of the many-particle equation, E^{en} is the total energy of the whole system, and $\Psi^{en}(\mathbf{r},\mathbf{R})$ is the many-particle wavefunction which describes all the electrons and all the nuclei. Within the Born-Oppenheimer approximation, the variable separation $\Psi^{en}(\mathbf{r},\mathbf{R}) \approx \Psi(\mathbf{r})\Theta(\mathbf{R})$ yields the many-electron Schrödinger equation $H\Psi(\mathbf{r}) = E\Psi(\mathbf{r})$, where E is the total energy of the electronic system and $\Psi(\mathbf{r})$ correspondingly includes all the electrons.

One of the problems with this equation is that we have roughly 10^{22} nuclei and 10^{23} electrons in a solid material with the volume of 1 cm^3 . This is of course a huge numerical problem. However, there is a more conceptual problem: while the Hamiltonian H contains operators that apply to the single electrons, we do not have a prior knowledge how $\Psi(\mathbf{r})$ depends on the single-electron wavefunctions. Thus, we do not know how to operate H on the many-electron function $\Psi(\mathbf{r})$. One can attack this problem in two ways:

- 1) Try to describe or guess $\Psi(\mathbf{r})$ in terms of single-electron wavefunctions $\psi_j(\mathbf{r})$ and use the regular H . The Hartree and Hartree-Fock based methods belong to this approach.
- 2) Try to find an expression for H that can operate directly on $\Psi(\mathbf{r})$, or alternatively, find an explicit relation between $\Psi(\mathbf{r})$ and E . The original DFT belongs to this approach. Two theorems within DFT state that E can be expressed in terms of the electron density $n(\mathbf{r}) = |\Psi(\mathbf{r})|^2$.

Both these approaches have “pros and cons”. There is actually a third approach. One can use a mixture of the two approaches. That is:

- 3) Start from the DFT, but use auxiliary single-electron wavefunctions $\psi_\kappa^{KS}(\mathbf{r})$ to generate the exact density $n(\mathbf{r}) = |\Psi(\mathbf{r})|^2 = \sum_\kappa |\psi_\kappa^{KS}(\mathbf{r})|^2$ and thereby also the exact total energy E . The Kohn-Sham equation $\{-\hbar^2\nabla^2/2m_e + V_{eff}(\mathbf{r})\}\psi_\kappa^{KS}(\mathbf{r}) = \epsilon_\kappa^{KS}\psi_\kappa^{KS}(\mathbf{r})$ does this.

In this compendium, we will derive the Kohn-Sham equation, and we will show that it is (in principle) possible to exactly solve the many-electron problem by using single-electron wavefunctions.

DFT together with the Kohn-Sham equation is a method to map the many-electron problem into many single-electron equations with an effective potential $V_{eff}(\mathbf{r})$. This effective potential includes all electron-electron interactions. The advantage of describing all the electron-electron interactions by an effective potential is immense. Importantly, the method shows that it is possible to generate the exact ground-state density and the exact ground-state total energy if one finds the universal expression of the effective potential that correctly includes the many-electron interactions.

The DFT is in principles an exact method. However, we have to date not the full explicit expression of the universal potential that shall describes the often complex many-electron interactions. One therefore has to rely on approximations of it, and the local density approximation (LDA) is the first method to

model the interactions. Here lies the main approximation within the Kohn-Sham approach. The simple LDA has however been extremely successful to describe the many-electron interactions, although the approximation has deficiencies. Other approximations are available, and the development of improved effective potential is still an ongoing research activity. An essential advantage with the DFT/Kohn-Sham approach is that whenever a new effective potential has been developed, this potential can directly be implemented into the Kohn-Sham equation without changing the underlying DFT theory. Thus, one does not have to re-derive a new single-electron equation for each new improvement of the effective potential. The drawback is, however, that because it is relatively easy to implement new effective potential, there are today hundreds of them, and this undermines the underlying idea that the DFT/Kohn-Sham approach involves a universal expression of the effective potential.

We will derive the Kohn-Sham equation starting from the many-particle Schrödinger equation $H^{\text{em}}\Psi^{\text{en}}(\mathbf{r},\mathbf{R}) = E^{\text{em}}\Psi^{\text{en}}(\mathbf{r},\mathbf{R})$. The procedure involves four main steps. In short:

The Born-Oppenheimer approximation (BOA):

The full wavefunction $\Psi^{\text{en}}(\mathbf{r},\mathbf{R})$ is divided into an electronic part $\Psi(\mathbf{r})$ and a nuclei part $\Theta(\mathbf{R})$. Thereby, the problem is reduced to solving the many-electron Schrödinger equation $H\Psi(\mathbf{r}) = E\Psi(\mathbf{r})$.

Question: What approximations are connected to this variable separation?

The density functional theory (DFT):

The DFT states that the total energy $E[n]$ is a functional of the electron density $n(\mathbf{r})$. We can find the ground-state energy E_0 by the minimizing energy with respect to density. That is, by knowing only the ground-state $n_0(\mathbf{r}) = |\Psi_0(\mathbf{r})|^2$, and no other information of the single electrons, we can obtain the ground-state energy of the system.

Question: Why can we not use the DFT in its original form?

The Kohn-Sham (KS) equation:

The KS approach is a method to solve the DFT using the auxiliary single-electron eigenfunctions $\psi_{\kappa}^{\text{KS}}(\mathbf{r})$. The KS equation $\{-\hbar^2\nabla^2/2m_e + V_{\text{eff}}(\mathbf{r})\}\psi_{\kappa}^{\text{KS}}(\mathbf{r}) = \epsilon_{\kappa}^{\text{KS}}\psi_{\kappa}^{\text{KS}}(\mathbf{r})$ can in principle generate the exact many-electron ground-state density $n_0(\mathbf{r}) = \sum_{\kappa} |\psi_{\kappa}^{\text{KS}}(\mathbf{r})|^2$. Here, the effective potential $V_{\text{eff}}(\mathbf{r})$ includes an exchange-correlation potential $V_{\text{xc}}(\mathbf{r})$ that describes the many-electron interactions. Importantly, this potential is the derivative of a universal energy functional $V_{\text{xc}}(\mathbf{r}) = \partial E_{\text{xc}}[n]/\partial n$. Since $E_{\text{xc}}[n]$ is a functional of the density, also the exact ground-state $V_{\text{xc}}(\mathbf{r})$ is determined from $n_0(\mathbf{r})$. Moreover, according to DFT, the exact ground-state energy E_0 is determined from the exact $n_0(\mathbf{r})$.

Question: What are the approximations in the KS equation?

The local density approximation (LDA):

We have today not the exact universal energy functional $E_{\text{xc}}[n]$, and we can thus not generate the exact exchange-correlation $V_{\text{xc}}(\mathbf{r})$. In the LDA, the $V_{\text{xc}}(\mathbf{r})$ is approximated by an expression obtained from the theory of a homogenous electron gas.

Question: How good is the LDA? How can we improve this approximation?

An overall question to consider: Assume that we use the BOA in conjunction with the DFT/Kohn-Sham-equation and describe the exchange-correlation by the LDA. What can we expect from the calculations of different types of materials? That is, what physical properties can we describe, and to what accuracy? Also, what physical properties can we not describe?

History of the DFT

- 1926 Schrödinger equation.
- 1927 Born-Oppenheimer approximation.
- 1927 Thomas-Fermi model, a rough approximation of atoms involving electron density.
- 1930 Hartree-Fock model for anti-symmetry wavefunction.
- 1964 Hohenberg-Kohn's theorems for exact DFT.
- 1965 Kohn-Sham equation and the LDA.
- 1980s DFT/LDA becomes popular in computational solid-state physics.
- 1998 Nobel Prize in Chemistry awarded to Kohn and Pople for the development of DFT.
- 2012 DFT is used in more than 15,000 scientific articles per year.

2 The single-electron Schrödinger equation

The single-electron Schrödinger equation is described in quantum-physics courses; see for instance D. J. Griffiths *Introduction to Quantum Mechanics*. In this chapter, we will recapitulate the basic concepts.

2.1 Eigenfunctions and energy eigenvalues

We start from the time-dependent Schrödinger equation for one electron

$$i\hbar \frac{\partial}{\partial t} \psi(\mathbf{r}, t) = H\psi(\mathbf{r}, t), \quad \text{with} \quad H = T + U = -\frac{\hbar^2 \nabla^2}{2m_e} + V(\mathbf{r}, t). \quad (2.1)$$

Here, m_e is the electron mass, $\psi(\mathbf{r}, t)$ is the wavefunction of the electron, and the Hamiltonian operator H describes the total energy of the system. The Hamiltonian $H = T + U$ contains the kinetic energy operator $T = -\hbar^2 \nabla^2 / 2m_e$ and the potential energy operator U , where U normally is an external potential $V(\mathbf{r})$.

The wavefunction $\psi(\mathbf{r}, t)$ can have an (almost) arbitrary shape and still being a solution to Eq. (2.1), but there are wavefunctions with special physical properties and these are the wavefunctions of stationary states. If the wavefunction describes a stationary state, the wavefunction is also an eigenfunction to H , with a well-defined energy eigenvalue that does not change over time. We denote the eigenfunction as $\psi_\kappa(\mathbf{r}, t)$ with its corresponding energy eigenvalue $\varepsilon_\kappa = \hbar\omega_\kappa$. The subscript indicates the κ :th eigenstate.

Importantly, if the potential is independent of time [that is, if $V(\mathbf{r}, t) = V(\mathbf{r})$] the eigenfunctions (but not a general wavefunction) can be simplified by a variable separation $\psi_\kappa(\mathbf{r}, t) = \psi_\kappa(\mathbf{r})\rho_\kappa(t)$. In this case, the Schrödinger equation can be split into a time-independent room part and a room-independent time part[†]

$$H\psi_\kappa(\mathbf{r}) = \left(-\frac{\hbar^2 \nabla^2}{2m_e} + V(\mathbf{r}) \right) \psi_\kappa(\mathbf{r}) = \varepsilon_\kappa \psi_\kappa(\mathbf{r}) \quad \text{room part,} \quad (2.2)$$

$$i\hbar \frac{\partial}{\partial t} \rho_\kappa(t) = \varepsilon_\kappa \rho_\kappa(t) \quad \text{time part.} \quad (2.3)$$

These two sub-equations are connected by the constant ε_κ , which is the energy of the eigenfunction [since $H\psi_\kappa(\mathbf{r}) = \varepsilon_\kappa \psi_\kappa(\mathbf{r})$]. Equation (2.2) is thus the time-independent Schrödinger equation which depends explicitly on the potential $V(\mathbf{r})$. Equation (2.3) is the time-dependent part, and the solution is simply $\rho_\kappa(t) = A \cdot \exp(-i \cdot \varepsilon_\kappa \cdot t / \hbar)$, where A can be set to 1 if we normalize the room part $\psi_\kappa(\mathbf{r})$. ε_κ has to be determined in the time-independent equation.

It is important to distinguish if one considers a general wavefunction $\psi(\mathbf{r}, t)$ or an eigenfunction $\psi_\kappa(\mathbf{r}, t)$. In contrast to a general wavefunction, the shape of the eigenfunction has normally high spatial symmetry that depends directly on the symmetry of $V(\mathbf{r})$. Knowing the shape and symmetry of the eigenfunction is very important when analyzing physical properties of materials.

An eigenfunction can thus be written as $\psi_\kappa(\mathbf{r}, t) = \psi_\kappa(\mathbf{r}) \cdot \exp(-i \cdot \varepsilon_\kappa \cdot t / \hbar)$ with $\varepsilon_\kappa = \hbar\omega_\kappa$. The eigenfunctions are orthogonal and normalized

$$\int \psi_\kappa^*(\mathbf{r}, t) \psi_{\kappa'}(\mathbf{r}, t) d\mathbf{r} = \langle \psi_\kappa(\mathbf{r}, t) | \psi_{\kappa'}(\mathbf{r}, t) \rangle = \delta_{\kappa\kappa'}. \quad (2.4)$$

A general wavefunction can be generated by a summation of eigenfunctions $\psi(\mathbf{r}, t) = \sum_\kappa c_\kappa \cdot \psi_\kappa(\mathbf{r}, t) = \sum_\kappa c_\kappa \cdot \psi_\kappa(\mathbf{r}) \cdot \exp(-i \cdot \varepsilon_\kappa \cdot t / \hbar)$, thus a mixture of eigenfunctions. The general wavefunction is a solution to the

[†] Separation in variables is not always possible. One can re-phrase it like this: If $V(\mathbf{r}, t) = V(\mathbf{r})$, there exist solutions in the form $\psi_\kappa(\mathbf{r}, t) \sim f_\kappa(\mathbf{r})g_\kappa(t)$, and these special solutions are called the stationary states. The stationary states $\psi_\kappa(\mathbf{r}, t)$ have well-defined energies ε_κ , and $f_\kappa(\mathbf{r})$ are thus eigenfunctions to the time-independent Schrödinger equation $Hf_\kappa(\mathbf{r}) = \varepsilon_\kappa f_\kappa(\mathbf{r})$.

Eq. (2.1) but not to Eq. (2.2). They are often normalized, but they are seldom orthogonal. In general, they do not describe stationary states, so they do not have well-defined/distinct energies. Instead, the energy is represented statistically by the expectation value $E = \langle \psi(\mathbf{r}, t) | H | \psi(\mathbf{r}, t) \rangle = \sum_{\kappa} |c_{\kappa}|^2 \varepsilon_{\kappa}$; this energy value can be regarded as an average value. When experimentally measuring the energy, the wavefunction collapses (with the probability of $|c_{\kappa}|^2$) into the κ :th eigenstate, and one measures the energy ε_{κ} . For example, the general wavefunction can be a mixture of “a dead cat” and “a living cat” in the famous gedanken experiment “Schrödinger’s cat”. Here, the “dead” and “alive” are two eigenstates. When looking into the box, the general wavefunction of the cat collapses into one of the two eigenstates.

It is much more convenient to solve the Schrödinger equation for the eigenfunctions $\psi_{\kappa}(\mathbf{r})$ instead of solving it for a general wavefunction $\psi(\mathbf{r}, t)$. We will focus on the eigenfunctions, and we can then use the time-independent Schrödinger equation.

$$\left(-\frac{\hbar^2 \nabla^2}{2m_e} + V(\mathbf{r}) \right) \psi_{\kappa}(\mathbf{r}) = \varepsilon_{\kappa} \psi_{\kappa}(\mathbf{r}) \quad \text{room part.} \quad (2.4)$$

Note, the Schrödinger equation is a regular second-order homogeneous linear differential equation

$$f''(\mathbf{r}) + h(\mathbf{r})f(\mathbf{r}) = 0 \quad (\text{with no } f'(\mathbf{r}) \text{ term}), \quad (2.5)$$

with $h(\mathbf{r}) = [\varepsilon_{\kappa} - V(\mathbf{r})] \cdot 2m_e/\hbar^2$. The function $f(\mathbf{r}) = \psi_{\kappa}(\mathbf{r})$ is the solution to be determined. If the potential $V(\mathbf{r})$ is constant, we have $f''(\mathbf{r}) + a \cdot f(\mathbf{r}) = 0$ which is easy to solve from the characteristic equation $z^2 + a \cdot z = 0$ yielding $f(\mathbf{r}) = \exp(-i\sqrt{a} \cdot \mathbf{r})$. For a more general potential, we have to find the solution for each case. In quantum-physics courses one normally derives analytic expressions for specific cases, like the spherical potential $V(\mathbf{r}) = a/|\mathbf{r}|$, the harmonic approximation $V(\mathbf{r}) = a \cdot \mathbf{r}^2$, and the delta-function $V(\mathbf{r}) = a \cdot \delta(|\mathbf{r}|)$. There are in principle no differences in solving the Schrödinger equation for these three potentials, however, in practice one employs different techniques to obtain the analytic expression. (For example, one defines ladder operators for the harmonic approximation.)

Notice that the eigenvalue equation in Eq. (2.4) is an equation for a sole electron (not for two or more electrons as in Chapters 4 and 5). However, when solving the single-electron equation, we obtain several eigenstates (very often infinite number of eigenstates). The electron can be in any of these stationary eigenstates, and it can be even in a non-stationary mixed state. The state with the lowest energy is called the ground state. This is an eigenstate and we will indicate that state by $\kappa = 0$, thus $\psi_0(\mathbf{r})$. The ground state is the most important state to analyze, because it is normally the highest probability to find the electron there.[†]

The shape of the eigenfunctions $\psi_{\kappa}(\mathbf{r})$ depends on $V(\mathbf{r})$ and on the boundary conditions. Knowing the eigenfunctions is very important for analyzing the physical properties of materials. We therefore have to understand how electronic wavefunctions look like in crystalline materials. Does the single electron eigenfunction forms a bond between two neighboring atoms, or is it spread over several bonds of neighboring atoms, or maybe the electron eigenfunction is spread over a much larger spatial region? If the latter case, what is an electronic bond? In the next chapter, we will discuss the shape and symmetry of the eigenfunctions in crystalline materials.

Throughout this compendium we will

- only consider the time-independent Schrödinger equation.
- as much as possible avoid discussing spin. We shall however remember that each eigenstate can simultaneously be occupied by two electrons, distinguished by the quantum numbers spin-up and spin-down. We assume that these two states have equal energy.

[†] In reality, only the ground state is a true stationary state since an electron in a higher state (eigenstate or mixed state) will always decay into the ground state, for instance by emitting a photon.

- assume that the nuclei are point-like charges. This is reasonable since the size of the nucleus ($\sim 2 \times 10^{-15}$ m for the hydrogen atom) is typically 10,000 times smaller than that radius of the electrons orbiting the nuclei (Bohr radius is $a_0 \approx 5 \times 10^{-11}$ m).

2.2 A free electron

Consider an electron that does not feel any potential (Griffiths, Chapt. 2.4). This is a free electron, and the electron has only kinetic energy.

$$\left(-\frac{\hbar^2 \nabla^2}{2m_e} + V(\mathbf{r}) \right) \psi_{\kappa}(\mathbf{r}) = \varepsilon_{\kappa} \psi_{\kappa}(\mathbf{r}), \quad \text{where } V(\mathbf{r}) = 0 \quad (2.6)$$

Since the potential is zero everywhere, there are no boundary conditions for $\psi_{\kappa}(\mathbf{r})$.

It is easy to verify that $\psi_{\kappa}(\mathbf{r}) = A \cdot \exp(i \cdot \mathbf{k}_{\kappa} \cdot \mathbf{r})$ are proper solutions, and that the energies are $\varepsilon_{\kappa} = \hbar^2 \mathbf{k}_{\kappa}^2 / 2m_e$. With the momentum operator $\mathbf{p} = -i\hbar \nabla$, one can also show that $\hbar \mathbf{k}_{\kappa}$ is the momentum eigenvalue. An electron can be in any of the eigenstates \mathbf{k}_{κ} (but electrons can also be in a mixed state).

Instead of numbering the eigenstates by $\kappa = 1, 2, 3, \dots$, we will use the quantum numbers as the index. That is, for free electrons we write the eigenfunctions as $\psi_{\mathbf{k}}(\mathbf{r}) = A \cdot \exp(i \cdot \mathbf{k} \cdot \mathbf{r})$. We have to remember that each \mathbf{k} -state includes two states (spin-up and spin-down). Moreover, the complex-valued function with the shape $A \cdot \exp(i \cdot \mathbf{k} \cdot \mathbf{r})$ is called a plane wave.

There is however a fundamental problem to describe free electrons. Since there are no boundary conditions for $\psi_{\mathbf{k}}(\mathbf{r})$, the eigenstates can have any value of \mathbf{k} and thus also the energy $\varepsilon_{\mathbf{k}}$ can be any real positive number. As a consequence, there are no “quanta” of the energies. This problem is related to the fact that the eigenfunctions cannot be normalized. That is, since the potential looks the same from any point in the whole universe, the probability of finding the electron is the same for all points in the whole universe. This is of course unphysical, and a free electron can therefore never be in a stationary state with an eigenfunction $\psi_{\mathbf{k}}(\mathbf{r})$ and a definite energy.

To overcome this problem for a free electron, one considers normally a general wavefunction that is localized in \mathbf{r} -space. A general wavefunction is created by summation of the eigenfunctions (see above). However, in the case of a free electron we can use an integral over all eigenstates $\psi_{\mathbf{k}}(\mathbf{r})$ since the allowed \mathbf{k} -states is a continuous variable. We thus construct the wavefunction by $\psi(\mathbf{r}) = (1/\sqrt{2\pi}) \cdot \int \zeta(\mathbf{k}) \psi_{\mathbf{k}}(\mathbf{r}, t) d\mathbf{k}$, and one normally call this wavefunction a free electron wave-package. There are no rules how to choose or construct the amplitude function $\zeta(\mathbf{k})$, and the shape of the wave-package is therefore not unique.

... one can always discuss if it is correct to use the time-independent Schrödinger equation for stationary states if there exist no stationary states, and the electron can never decay into the ground state, ... but that is more a philosophical discussion.

2.3 An electron in a box

Consider an electron that is confined in an infinity deep square well (eg. Griffiths Chapt. 2.2):

$$\left(-\frac{\hbar^2 \nabla^2}{2m_e} + V(x) \right) \psi_k(x) = \varepsilon_k \psi_k(x), \quad \text{where } V(x) = \begin{cases} 0 & 0 \leq x \leq L \\ \infty & \text{otherwise} \end{cases} \quad (2.7)$$

In the one-dimensional case, we have the boundary condition $\psi_k(0) = \psi_k(L) = 0$. The solution is $\psi_k(x) = \sqrt{2/L} \cdot \sin(kx)$ with $k = n \cdot \pi / L$ and with the energy $\varepsilon_k = \hbar^2 k^2 / 2m_e$, see Fig. 2.1(a).

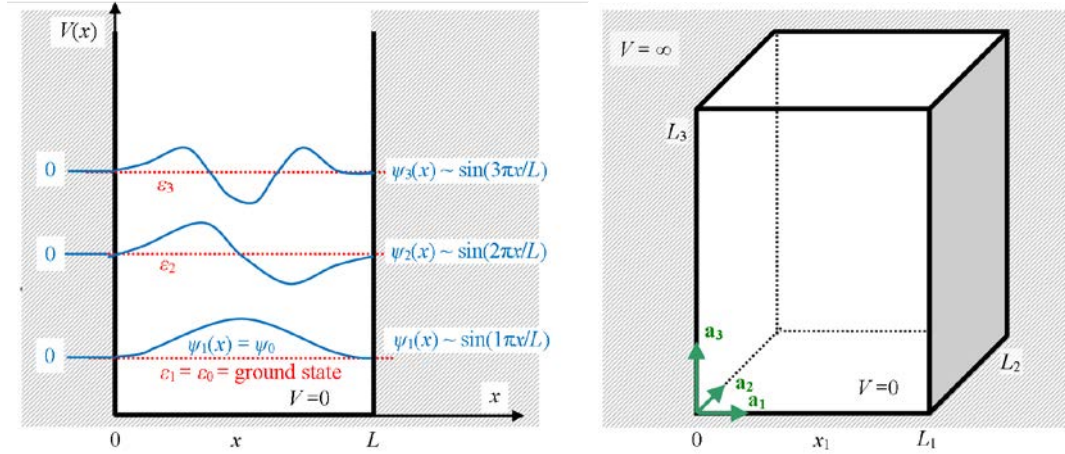


Fig. 2.1: (a) Electron in a box in one dimension. (b) Corresponding potential in three dimensions.

We will however use the following generalization. Assume a potential box in a shape of a parallelepiped. That is, a 3D-box spanned by the vectors \mathbf{a}_1 , \mathbf{a}_2 and \mathbf{a}_3 [Fig. 2.1(b)]. We will allow non-cubic cases, that is, the angles between these vectors are in general not 90° . The reason for this generalization is that we need that when we describe electrons in a crystal.

A position in the \mathbf{r} -space is now $\mathbf{r} = x_1\mathbf{a}_1 + x_2\mathbf{a}_2 + x_3\mathbf{a}_3$. For the infinity deep square well, the potential is zero inside the box and infinitely large outside the box. Thus, $V(\mathbf{r}) = V(x_1, x_2, x_3) = 0$ if $0 \leq x_j \leq L_j$ for $j = 1, 2$, and 3 . Here, $L_j = N_j\mathbf{a}_j$.

$$\left(-\frac{\hbar^2 \nabla^2}{2m_e} + V(\mathbf{r}) \right) \psi_{\mathbf{k}}(\mathbf{r}) = \epsilon_{\mathbf{k}} \psi_{\mathbf{k}}(\mathbf{r}), \quad \text{where } V(\mathbf{r}) = \begin{cases} 0 & 0 \leq \{x_1, x_2, x_3\} \leq \{L_1, L_2, L_3\} \\ \infty & \text{otherwise} \end{cases} \quad (2.8)$$

Moreover, we will assume periodic boundary condition $\psi_{\mathbf{k}}(\mathbf{r} + \mathbf{L}) = \psi_{\mathbf{k}}(\mathbf{r})$ with $\mathbf{L} = N_1\mathbf{a}_1 + N_2\mathbf{a}_2 + N_3\mathbf{a}_3$. The solution is very similar to the 1D case, but now with three quantum numbers, namely k_1 , k_2 , and k_3 .

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i\mathbf{k}\mathbf{r}} \quad \text{where } \Omega = L_1 L_2 L_3 \text{ is the normalization factor, and} \quad (2.9)$$

$$\epsilon_{\mathbf{k}} = \frac{\hbar^2 \mathbf{k}^2}{2m_e} \quad \text{where } \mathbf{k}^2 = k_1^2 + k_2^2 + k_3^2 \text{ and } k_j = \frac{2\pi m_j}{L_j} \text{ with } m_j \text{ is an integer.}$$

The boundary condition $\psi_{\mathbf{k}}(\mathbf{r} + \mathbf{L}) = \psi_{\mathbf{k}}(\mathbf{r})$ is fulfilled because $\exp(i\mathbf{k}(\mathbf{r} + \mathbf{L})) = \exp(i\mathbf{k}\mathbf{r}) \cdot \exp(i\mathbf{k}\mathbf{L})$ and $\mathbf{k}\mathbf{L} = 2\pi \times \text{integer}$. Thus, $\exp(i\mathbf{k}\mathbf{L}) = 1$ and $\exp(i\mathbf{k}(\mathbf{r} + \mathbf{L})) = \exp(i\mathbf{k}\mathbf{r})$.

One can compare the solution for an electron in the box with the corresponding results for a free electron. The main difference is that we now have discrete \mathbf{k} -states. With this constraint on the eigenfunction, only certain solutions are allowed. That is, the boundary condition allows only certain \mathbf{k} -states. Moreover, since the electron is confined inside the box, we can normalize the eigenfunctions. \mathbf{k} describes the wave length $\lambda = 2\pi/|\mathbf{k}|$, of the plane wave, and only certain wave lengths fit into the 3D box.

2.4 An electron at an atom

Consider an electron that feels the potential from a hydrogen atom (Griffiths Chapter 4.2):

$$\left(-\frac{\hbar^2 \nabla^2}{2m_e} + V(\mathbf{r}) \right) \psi_{\kappa}(\mathbf{r}) = \varepsilon_{\kappa} \psi_{\kappa}(\mathbf{r}), \quad \text{where } V(\mathbf{r}) = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r} = -\frac{q^2}{r}. \quad (2.10)$$

Here, the potential has spherical symmetry $V(\mathbf{r}) = V(|\mathbf{r}|)$, and we make the substitute $q = e/\sqrt{4\pi\epsilon_0}$, where e is the elementary charge. The boundary condition for the bound states (with $\varepsilon_{\kappa} < 0$) is that $\psi_{\kappa}(\mathbf{r}) \rightarrow 0$ when $\mathbf{r} \rightarrow \infty$.

The first thing is to choose which coordinate system one shall use. Since we have spherical symmetry of the potential, it is convenient to use spherical coordinates: $V(\mathbf{r}) = V(r, \theta, \varphi)$ and $\psi_{\kappa}(\mathbf{r}) = \psi_{\kappa}(r, \theta, \varphi)$. Moreover, the potential does not depend on the angles θ and φ . Thereby, we can use variable separation for the eigenfunctions $\psi_{\kappa}(\mathbf{r}) = \psi_{nlm}(r, \theta, \varphi) = R_{nl}(r)Y_{lm}(\theta, \varphi)$ where $Y_{lm}(\theta, \varphi)$ is a spherical harmonic. This variable separation significantly simplifies the analysis of the eigenfunctions.[†]

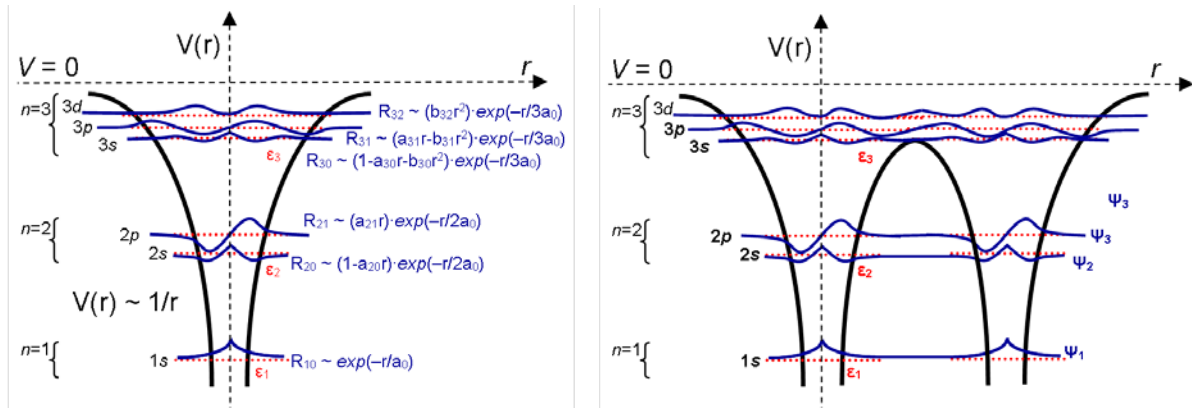


Fig. 2.2: (a) Radial function of an electron at an atom. (b) The eigenfunction of one electron in a two-atom system.

In spherical coordinates, the Schrödinger equation reads

$$\left(-\frac{\hbar^2}{2m_e} \left\{ \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right\} + V(\mathbf{r}) \right) \psi_{nlm}(\mathbf{r}) = \varepsilon_{nl} \psi_{nlm}(\mathbf{r}). \quad (2.11)$$

The boundary conditions are now $R_{nl}(r) \rightarrow 0$ when $r \rightarrow \infty$. The potential together with the boundary condition yields the main quantum number n which describe the energy of the n :th state. Moreover, the angular part of the eigenfunctions has the boundary conditions $Y_{lm}(\theta + \pi, \varphi) = Y_{lm}(\theta, \varphi)$ and $Y_{lm}(\theta, \varphi) = Y_{lm}(\theta, \varphi + 2\pi)$. These boundary conditions results in the quantum number $l = 1, 2, \dots, n$ and $m = -l, l+1, \dots, 0, \dots, l-1, l$.

The solution for a hydrogen atom is

$$\psi_{\kappa}(\mathbf{r}) = \psi_{nlm}(r, \theta, \varphi) = R_{nl}(r)Y_{lm}(\theta, \varphi), \quad \text{where } Y_{lm}(\theta, \varphi) \text{ are spherical harmonics, and} \quad (2.12)$$

$$\varepsilon_{\kappa} = \varepsilon_{nl} = -\frac{1}{n^2} \frac{m_e q^4}{2\hbar^2} = -\frac{1}{n^2} \frac{m_e e^4}{32\pi^2 \hbar^2 \epsilon_0^2}, \quad a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2} \text{ is the Bohr radius.}$$

The angular part of the eigenfunction $Y_{lm}(\theta, \varphi)$ does not depend on the shape of the potential (as long as it is spherical symmetry). The radial part of the solution is depicted in Fig. 2.2(a). The energy for the ground state $\psi_{100}(r, \theta, \varphi)$ of a hydrogen atom is $\varepsilon_{10} = -13.6$ eV. This is a good number to remember.

One can notice from Fig. 2.2(a) that the eigenstates with low energies (1s, 2s, and 2p) are more spatial localized near the nuclei, whereas the higher eigenstates are more spread out in space. States with $n \rightarrow \infty$ have spatially much more delocalized eigenfunctions.

[†] $Y_{lm}(\theta, \varphi) = \Theta_l(\theta)\Phi_m(\varphi)$ is a further possible variable separation.

Assume now that we have two equivalent nuclei, but only one electron. If the two nuclei are sufficiently well separated in space, then the problem can be regarded as two separate single-nucleus problems. The single-electron eigenfunction will then be localized at one of the nuclei. However, when the two nuclei come closer together, their potentials start to overlap Fig. 2.2(b). Now, there are important quantum-mechanical properties. First, the electron will have same probability to be at atom #1 and atom #2, thus the single-electron eigenfunction is localized around both nuclei. That is, the eigenfunction has to describe an electron that is located at both atoms. Second, we can not any longer describe the eigenstates with $1s$, $2s$, $2p$, *etc*, since the spherical symmetry is lost. However, for the energetically localized states the eigenfunction is atomic-like near atom #1 and atom #2. We therefore say that these states are $1s$ -like, $2s$ -like, $2p$ -like for these localized states. Third, for the energetically higher states ($3s$, $3p$, $3d$ - like, *etc*), the potential is small in the region between the two nuclei. Thereby, these states will be much more delocalized in states.

Hence, when two (or more atoms) are close together we will have an eigenfunction that is still atomic-like, but that can be located at both (or all) atoms. It may seem a little strange that the electron is atomic-like but at the same time localized at all atoms, but this is the nature of quantum physics (eg. the particle-wave dualism). We cannot distinguish if the electron is located at one atom or the other. Moreover, the electron will be more atomic-like if the electron is energetically very localized (for small n), whereas the electron will be spatially delocalized and spread out in space if its energy is high (high n). It is a challenge to describe both localized and delocalized states with the same physical model. That becomes very apparent for an electron in a solid.

2.5 An electron in a solid

Consider a crystalline material. We assume that our crystal potential has a periodicity

$$\left(-\frac{\hbar^2 \nabla^2}{2m_e} + V(\mathbf{r}) \right) \psi_{\kappa}(\mathbf{r}) = \varepsilon_{\kappa} \psi_{\kappa}(\mathbf{r}), \quad \text{where } V(\mathbf{r}) = V(\mathbf{r} + \mathbf{R}). \quad (2.13)$$

The primitive unit cell of the crystal is spanned by the primitive lattice vectors \mathbf{a}_1 , \mathbf{a}_2 , and \mathbf{a}_3 ; see Figs. 2.1(b) and 2.3. A perfect crystal has the property that the potential of the primitive unit cell has translation symmetry. That is, $V(\mathbf{r}) = V(\mathbf{r} + \mathbf{R})$ where $\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$ with integer numbers for n_j . From the primitive lattice vectors \mathbf{a}_1 , \mathbf{a}_2 , and \mathbf{a}_3 (that span the real space) one can directly generate the primitive reciprocal lattice vectors \mathbf{b}_1 , \mathbf{b}_2 , and \mathbf{b}_3 (that span the reciprocal space; the \mathbf{k} -space).

$$\mathbf{b}_1 = \frac{2\pi \mathbf{a}_2 \times \mathbf{a}_3}{\Omega_{vol}}, \quad \mathbf{b}_2 = \frac{2\pi \mathbf{a}_3 \times \mathbf{a}_1}{\Omega_{vol}}, \quad \text{and} \quad \mathbf{b}_3 = \frac{2\pi \mathbf{a}_1 \times \mathbf{a}_2}{\Omega_{vol}} \quad \text{where } \Omega_{vol} = \mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3 \quad (2.14)$$

Any vector in the continuous real space can be described by $\mathbf{r} = u_1 \mathbf{a}_1 + u_2 \mathbf{a}_2 + u_3 \mathbf{a}_3$, and any vector in the continuous \mathbf{k} -space can be described by $\mathbf{g} = v_1 \mathbf{b}_1 + v_2 \mathbf{b}_2 + v_3 \mathbf{b}_3$.

We define the reciprocal lattice vectors as $\mathbf{G} = m_1 \mathbf{b}_1 + m_2 \mathbf{b}_2 + m_3 \mathbf{b}_3$ with integer numbers for m_j .

Since the potential is periodic $V(\mathbf{r}) = V(\mathbf{r} + \mathbf{R})$, we can use the Fourier analysis to describe it:

$$\begin{aligned} V(\mathbf{r}) &= \sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}} \\ V(\mathbf{r} + \mathbf{R}) &= \sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G} \cdot (\mathbf{r} + \mathbf{R})} = \sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}} e^{i\mathbf{G} \cdot \mathbf{R}} = \sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}} = V(\mathbf{r}) \end{aligned} \quad (2.15)$$

The latter relation is fulfilled because

$$e^{i\mathbf{G} \cdot \mathbf{R}} = e^{i(m_1 \mathbf{b}_1 + m_2 \mathbf{b}_2 + m_3 \mathbf{b}_3) \cdot (n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3)} = 1 \quad \text{from} \quad \mathbf{b}_j \cdot \mathbf{a}_{j'} = 2\pi \delta_{jj'}. \quad (2.16)$$

Thus, the reciprocal lattice vectors \mathbf{G} are the proper vectors to describe a crystal periodic function $V(\mathbf{r}) = V(\mathbf{r} + \mathbf{R})$. That is actually not so surprising because \mathbf{G} is constructed by integer numbers of \mathbf{b}_j , which in turn are related to the crystal symmetry via the lattice vectors \mathbf{a}_j .

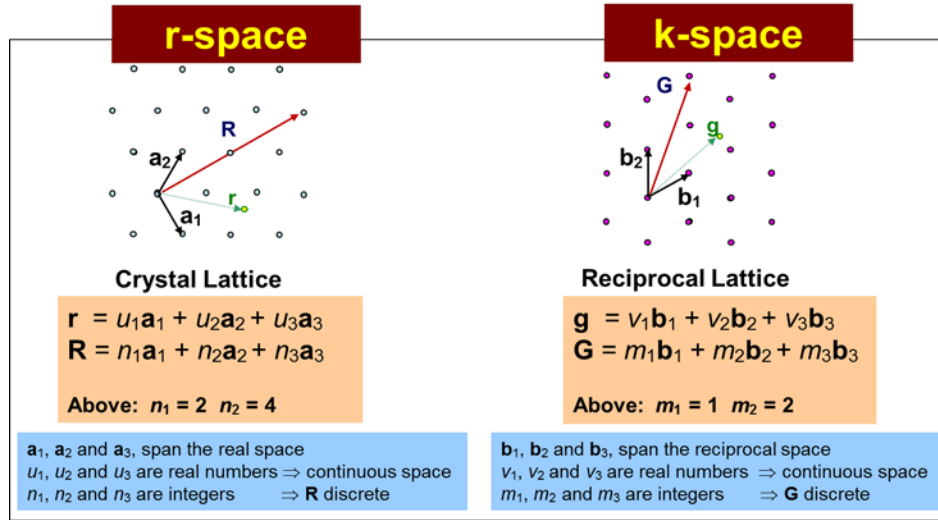


Fig. 2.3: The reciprocal space (**k**-space) is a continuous space spanned by the vectors $\mathbf{b}_1, \mathbf{b}_2$, and \mathbf{b}_3 , analogously to the crystal volume (real space) spanned by the vectors $\mathbf{a}_1, \mathbf{a}_2$, and \mathbf{a}_3 .

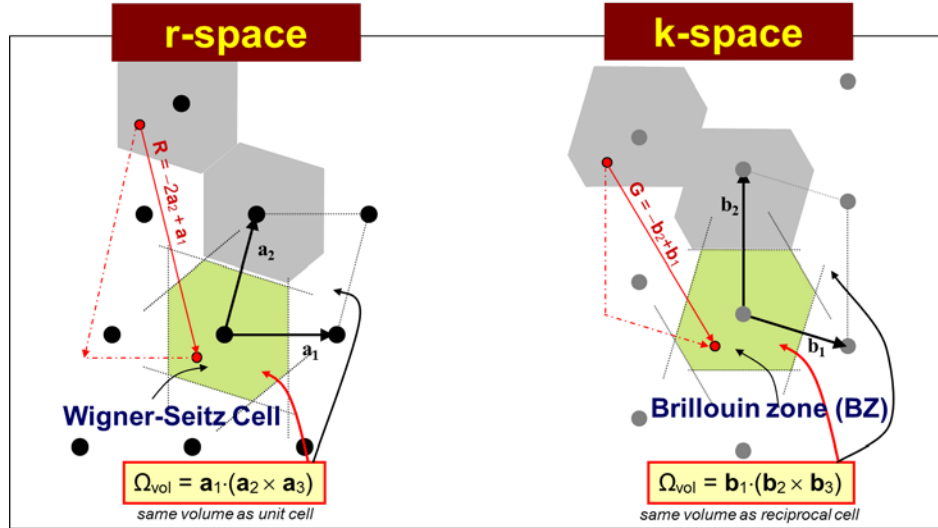


Fig. 2.4: The whole **r**-space can be built by the Wigner-Seitz cell plus lattice vectors \mathbf{R} , and the whole **k**-space can be built up by the first Brillouin zone plus the reciprocal lattice vectors \mathbf{G} .

So far we have only discussed the symmetry of the crystal. From the primitive unit cell of the crystal, we have defined the **k**-space and the reciprocal lattice vectors \mathbf{G} . We know that any function with the periodicity $f(\mathbf{r}) = f(\mathbf{r} + \mathbf{R})$ can be described as $f(\mathbf{r}) = \sum_{\mathbf{G}} f_{\mathbf{G}} \exp(i \cdot \mathbf{G} \cdot \mathbf{r})$.

Now, assume that we want to analyze the electrons in a solid crystal. First, we know from Fig 2.2 that the atomic like states become delocalized when atoms form molecules and crystals. How shall we describe that for a crystal? A very simple approximation would be to form a linear combination of atomic orbitals centered at the atom positions $\sum_{alm} \{A_{alm} R_{nl}(r-r_a) Y_{lm}(\theta, \varphi)\}$, where a represents all atoms. This could be a reasonable approximation for very localized states (i.e., $1s$ states), but not for the energetically high states. These states are almost like free electrons, located inside the crystal, that is, almost like electrons in a box. We know that such states have eigenfunctions $\exp(i \cdot \mathbf{k} \cdot \mathbf{r})$ and discrete set of allowed **k**-states. One could combine these two pictures and create wavefunctions in the form $\exp(i \cdot \mathbf{k} \cdot \mathbf{r}) \times \sum_{alm} \{A_{alm} R_{nl}(r-r_a) Y_{lm}(\theta, \varphi)\}$. However, we shall be more general and not use atomic-like orbitals, and instead we write the electron wavefunction as $\psi_{nk}(\mathbf{r}) = \exp(i \cdot \mathbf{k} \cdot \mathbf{r}) u_{nk}(\mathbf{r})$. Here, $u_{nk}(\mathbf{r})$ is called the Bloch-periodic part,

and it needs to have the periodicity $u_{nk}(\mathbf{r}) = u_{nk}(\mathbf{r}+\mathbf{R})$. The subscript n is related to the atomic main quantum number, but it is not exactly the same. n is an index of energy bands (see below).

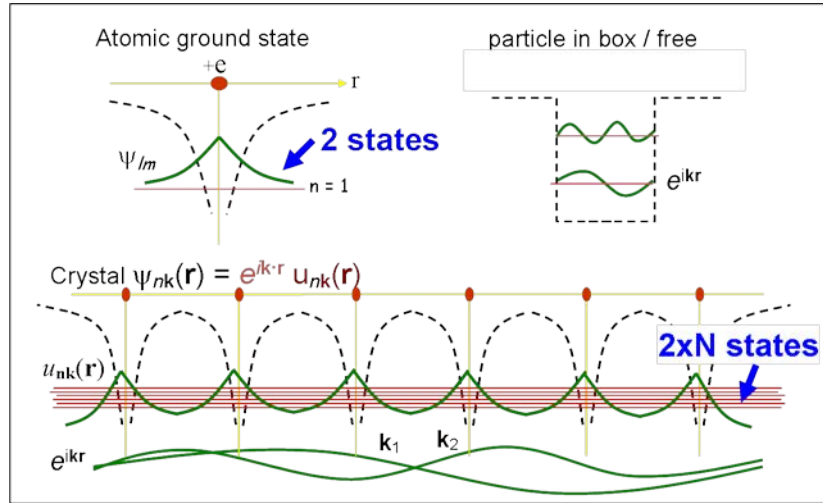


Fig. 2.5: The atoms has two 1s states (spin up and down). In a crystal with N atoms, these $2 \times N$ states form a 1s-band, and the eigenfunctions are spread out in the whole crystal with the help of the plane wave part $\exp(i\mathbf{k}\mathbf{r})$.

As for any physical problem, we must decide three things before calculating a physical property: (1) what model shall we use. In our case, this is of course the quantum mechanics. (2) Boundary condition: this was an easy task for the electron in a box, but we had problem with the boundary condition for a free electron. (3) Coordinate system: we could of course use the Cartesian coordinates for every physical system, however, using spherical coordinates for an electron at an atom simplifies the calculation significantly. More importantly, it helps us analyze the symmetry of the atomic eigenfunctions.

For the electrons in a condensed matter, we thus have to choose boundary conditions and coordinate system. We could use $\psi_k(\mathbf{r}) \rightarrow 0$ when $\mathbf{r} \rightarrow \infty$, because a crystal is not infinite large and we assume that the electrons are localized inside the material. However, that type of boundary condition includes no information about the translation symmetry inside the crystal. The translation symmetry lies in the crystal periodic property $V(\mathbf{r}) = V(\mathbf{r}+\mathbf{R})$. Since the potential is periodic, also the Hamiltonian $H = T + V$ is periodic. Therefore, all observable properties must have this crystal symmetry, for instance the density $n(\mathbf{r}) = n(\mathbf{r}+\mathbf{R})$. However, an eigenfunctions is not an observable quantity, and we cannot be sure that the eigenfunction obeys the crystal periodicity. Instead, we shall choose another boundary condition for these electrons, namely $\psi_k(\mathbf{r}) = \psi_k(\mathbf{r}+\mathbf{L})$ where $\mathbf{L} = L_1\mathbf{a}_1 + L_2\mathbf{a}_2 + L_3\mathbf{a}_3 = N_1n_1\mathbf{a}_1 + N_2n_2\mathbf{a}_2 + N_3n_3\mathbf{a}_3$, where N_j are very large integer numbers. That is, we assume that the eigenfunctions are periodic in a large box. This is a choice we do, but it is actually a very smart choice. (... *but can we improve it?*).

Compare with the electron-in-a-box problem, Section 2.3. With the condition $\psi_{nk}(\mathbf{r}) = \psi_{nk}(\mathbf{r}+\mathbf{L})$ the eigenfunction has to be in the form of $\psi_k(\mathbf{r}) = A \cdot \exp(i\mathbf{k} \cdot \mathbf{r})$, where $k_j = \pm 2\pi/L_j, \pm 4\pi/L_j, \pm 6\pi/L_j, \dots$, where $j = 1, 2$, and 3 indicates the three directions $\mathbf{b}_1, \mathbf{b}_2$, and \mathbf{b}_3 in the \mathbf{k} -space. Thus, only discrete \mathbf{k} -states are allowed for the electrons in the crystal. However, we also need the Bloch-periodic function, and thus the crystal electron wavefunction is described as $\psi_k(\mathbf{r}) = A \cdot \exp(i\mathbf{k} \cdot \mathbf{r}) \cdot u_k(\mathbf{r})$.

Notice that there are two periodicities to consider. First, we have the natural periodicity of the crystal potential $V(\mathbf{r}) = V(\mathbf{r}+\mathbf{R})$. This implies that the density has to be periodic with the same periodicity $n(\mathbf{r}) = n(\mathbf{r}+\mathbf{R})$. Second, we have the artificial periodicity of the wavefunction $\psi_k(\mathbf{r}) = \psi_k(\mathbf{r}+\mathbf{L})$. The relation between \mathbf{L} and the crystal lattice is very important, that is $\mathbf{L} = L_1\mathbf{a}_1 + L_2\mathbf{a}_2 + L_3\mathbf{a}_3 = N_1n_1\mathbf{a}_1 + N_2n_2\mathbf{a}_2 + N_3n_3\mathbf{a}_3$. With that condition the wavefunction $\psi_k(\mathbf{r}) = A \cdot \exp(i\mathbf{k} \cdot \mathbf{r}) \cdot u_k(\mathbf{r})$ contains both periodicities. The Bloch periodic part obeys both the crystal potential and the artificial periodicity $u_k(\mathbf{r}) = u_k(\mathbf{r}+\mathbf{R}) = u_k(\mathbf{r}+\mathbf{L})$, whereas the plane wave obeys only the artificial periodicity $\exp(i\mathbf{k} \cdot \mathbf{r}) = \exp(i\mathbf{k} \cdot (\mathbf{r}+\mathbf{L}))$ per

definition. It is easy to verify that the observable probability function $|\psi_{\mathbf{k}}(\mathbf{r})|^2 = |u_{\mathbf{k}}(\mathbf{r})|^2 = |u_{\mathbf{k}}(\mathbf{r}+\mathbf{R})|^2$ has the correct periodicity.

Another very important property of the eigenfunctions are $\psi_{\mathbf{k}}(\mathbf{r}) = \psi_{\mathbf{k}+\mathbf{G}}(\mathbf{r})$. That can be proven by

$$\psi_{\mathbf{k}+\mathbf{G}}(\mathbf{r}) = e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \sum_{\mathbf{G}'} u_{\mathbf{k}+\mathbf{G}+\mathbf{G}'} e^{i\mathbf{G}'\cdot\mathbf{r}} = e^{i\mathbf{k}\cdot\mathbf{r}} \sum_{\mathbf{G}'} u_{\mathbf{k}+\mathbf{G}+\mathbf{G}'} e^{i(\mathbf{G}+\mathbf{G}')\cdot\mathbf{r}} = e^{i\mathbf{k}\cdot\mathbf{r}} \sum_{\mathbf{G}} u_{\mathbf{k}+\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} = \psi_{\mathbf{k}}(\mathbf{r}). \quad (2.17)$$

Here, \mathbf{G} and \mathbf{G}' are reciprocal lattice vectors, and therefore $\mathbf{G} + \mathbf{G}' = \mathbf{G}''$ is another reciprocal lattice vector. Since we shall sum over all reciprocal lattice vectors, we are allowed to re-order the summation by writing $\mathbf{G} + \mathbf{G}' = \mathbf{G}'' \rightarrow \mathbf{G}$. Notice that $\psi_{\mathbf{k}}(\mathbf{r}) = \psi_{\mathbf{k}+\mathbf{G}}(\mathbf{r})$ is valid for crystal electrons with $\psi_{\mathbf{k}}(\mathbf{r}) = A \cdot \exp(i\mathbf{k}\cdot\mathbf{r}) \cdot u_{n\mathbf{k}}(\mathbf{r})$, but it is not valid for free electrons which do not have crystal periodicity because $\exp(i\mathbf{k}\cdot\mathbf{r}) \neq \exp(i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r})$.

With a similar procedure, one can show that also the momentum of the electron obeys this property, that is $\langle p_{\mathbf{k}} \rangle = \langle p_{\mathbf{k}+\mathbf{G}} \rangle$. That is, instead of using all \mathbf{k} -states in the infinite \mathbf{k} -space, we can represent all states within the first Brillouin zone; see Fig 2.4. If one has an eigenfunction $\psi_{\mathbf{k}+\mathbf{G}}(\mathbf{r})$ in a \mathbf{k} -state outside the first Brillouin zone $\psi_{n\mathbf{k}+\mathbf{G}}(\mathbf{r})$, one can transfer that state into the eigenfunction $\psi_{n\mathbf{k}}(\mathbf{r})$ in the Brillouin zone. To distinguish different eigenfunctions $\psi_{\mathbf{k}+\mathbf{G}}(\mathbf{r})$ that are transferred to the first Brillouin zone, we use the band index n . This is called band folding.

$$\psi_{n\mathbf{k}+\mathbf{G}}(\mathbf{r}) = \psi_{n'\mathbf{k}}(\mathbf{r}) \neq \psi_{n\mathbf{k}}(\mathbf{r}). \quad (2.18)$$

This is not only a matter of indices. The states are orthogonal

$$\int \psi_{n'\mathbf{k}'}^*(\mathbf{r}) \psi_{n\mathbf{k}}(\mathbf{r}) d\mathbf{r} = \delta_{n'n} \delta_{\mathbf{k}'\mathbf{k}} \quad (2.19)$$

One can show that the number of \mathbf{k} -states in the first Brillouin zone is the same as the number of primitive unit cells in the volume spanned by L_1 , L_2 , and L_3 . Thus, increasing L_j by a factor of (for example) 2 will increase the number of electrons by 2^3 inside the volume $L_1 L_2 L_3 \cdot (\mathbf{a}_1 \times \mathbf{a}_2 \times \mathbf{a}_3)$. However, also the number of primitive cells increases also by 2^3 , and so also the number of \mathbf{k} -states. Thus, the larger L_j , the denser \mathbf{k} -mesh; this can also understood from $\Delta k_1 = 2\pi/L_1$. Therefore, the population of the energy bands in the Brillouin zone will qualitatively be the same. That is, the highest populated state is not affect how large one choses L_j , as long as L_j are large enough.

Since we use periodic coordinates to describe the potential $V(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}$ and the Bloch periodic part of the eigenfunction $u_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} u_{n\mathbf{k}+\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}$, we shall also transform the Schrödinger equation into the periodic coordinates, that is, into the reciprocal space. That is relatively easy to do. We start with

$$\left(-\frac{\hbar^2 \nabla^2}{2m_e} + V(\mathbf{r}) \right) \psi_{n\mathbf{k}}(\mathbf{r}) = \varepsilon_{n\mathbf{k}} \psi_{n\mathbf{k}}(\mathbf{r}), \text{ where } V(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}; \psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \sum_{\mathbf{G}} u_{n\mathbf{k}+\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} \quad (2.20)$$

$$\left(-\frac{\hbar^2 \nabla^2}{2m_e} + \sum_{\mathbf{G}'} V_{\mathbf{G}'} e^{i\mathbf{G}'\cdot\mathbf{r}} \right) \sum_{\mathbf{G}} u_{n\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} = \varepsilon_{n\mathbf{k}} \sum_{\mathbf{G}} u_{n\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}.$$

For the kinetic energy, we derivate twice, and for the potential energy we perform the summation

$$\left(\frac{\hbar^2}{2m_e} (\mathbf{k} + \mathbf{G})^2 \sum_{\mathbf{G}} u_{n\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} + \sum_{\mathbf{G}\mathbf{G}'} V_{\mathbf{G}'} u_{n\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G}+\mathbf{G}')\cdot\mathbf{r}} \right) = \varepsilon_{n\mathbf{k}} \sum_{\mathbf{G}} u_{n\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}. \quad (2.21)$$

As discussed above, $\mathbf{G} + \mathbf{G}' = \mathbf{G}''$ is a reciprocal lattice vector. For the terms involving the potential, we re-order the summation over all reciprocal lattice vectors by writing $\mathbf{G} + \mathbf{G}' = \mathbf{G}'' \rightarrow \mathbf{G}$, yielding

$$\left(\frac{\hbar^2}{2m_e} (\mathbf{k} + \mathbf{G})^2 \sum_{\mathbf{G}} u_{n\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} + \sum_{\mathbf{G}\mathbf{G}'} V_{\mathbf{G}'} u_{n\mathbf{k}+\mathbf{G}-\mathbf{G}'} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \right) = \varepsilon_{n\mathbf{k}} \sum_{\mathbf{G}} u_{n\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}. \quad (2.22)$$

$$\sum_{\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}} \left(\frac{\hbar^2}{2m_e} (\mathbf{k}+\mathbf{G})^2 u_{n\mathbf{k}+\mathbf{G}} + \sum_{\mathbf{G}'} V_{\mathbf{G}'} u_{n\mathbf{k}+\mathbf{G}-\mathbf{G}'} \right) = \sum_{\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}} (\varepsilon_{n\mathbf{k}} u_{n\mathbf{k}+\mathbf{G}})$$

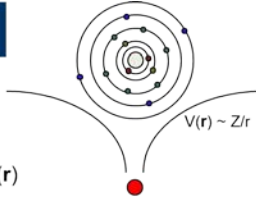
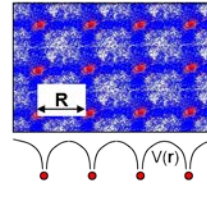
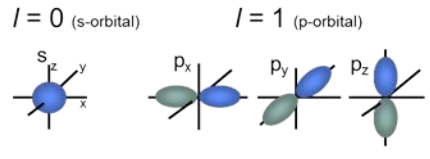
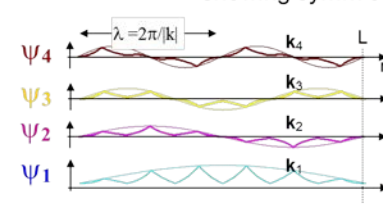
This equation has to be true for any \mathbf{r} , and therefore we can eliminate $\exp(i(\mathbf{k}+\mathbf{G})\mathbf{r})$. That results in

$$\left(\frac{\hbar^2}{2m_e} (\mathbf{k}+\mathbf{G})^2 u_{n\mathbf{k}+\mathbf{G}} + \sum_{\mathbf{G}'} V_{\mathbf{G}'} u_{n\mathbf{k}+\mathbf{G}-\mathbf{G}'} \right) = \varepsilon_{n\mathbf{k}} u_{n\mathbf{k}+\mathbf{G}} \quad (2.23)$$

Again, changing the order of the summation $\mathbf{G} - \mathbf{G}' = \mathbf{G}'' \rightarrow \mathbf{G}'$

$$\sum_{\mathbf{G}'} \left(\frac{\hbar^2 (\mathbf{k}+\mathbf{G}')^2}{2m_e} \delta_{\mathbf{G}\mathbf{G}'} + V_{\mathbf{G}-\mathbf{G}'} \right) u_{n\mathbf{k}+\mathbf{G}'} = \varepsilon_{n\mathbf{k}} u_{n\mathbf{k}+\mathbf{G}}. \quad (2.24)$$

This is the Schrödinger equation in the reciprocal space. This eigenvalue problem for a Hamiltonian matrix with indices \mathbf{G} and \mathbf{G}' is solved by traditional diagonalization routines. The result yields the eigenvalues $\varepsilon_{n\mathbf{k}}$ and the coefficients $u_{n\mathbf{k}+\mathbf{G}}$ from which we can generate the eigenfunctions.

Atom	Crystal
 <p>$\{T+V\}\psi(\mathbf{r}) = \varepsilon \psi(\mathbf{r})$</p> <p>$V(\mathbf{r}) \sim 1/r$ spheric symmetry $\psi(\mathbf{r}) = 0$ for $r \rightarrow 0$ far away from atom</p>	 <p>$\{T+V\}\psi(\mathbf{r}) = \varepsilon \psi(\mathbf{r})$</p> <p>$V(\mathbf{r}+\mathbf{R}) = V(\mathbf{r})$ crystal periodicity $\psi(\mathbf{r}+\mathbf{L}) = \psi(\mathbf{r})$ periodic; $\mathbf{L} = N^* \mathbf{a} \gg \mathbf{a}$</p>
<p>Use spherical coordinates: (r, θ, ϕ)</p> $\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2\mu}{\hbar^2} (E - V) \psi = 0$ <p>$\psi(\mathbf{r}) \sim Y_{lm}(\theta, \phi)$ spherical harmonics. $\{l, m\}$ are quantum no showing symm of $\psi(\mathbf{r})$</p>	<p>Use periodic coord: Fourier-, reciprocal-, \mathbf{k}-space.</p> $\sum_{\mathbf{G}} \left\{ \frac{\hbar^2 (\mathbf{k}+\mathbf{G})^2}{2m} \delta_{\mathbf{G}\mathbf{G}'} + V_{\mathbf{G}-\mathbf{G}'} \right\} c_{\mathbf{k}+\mathbf{G}'} = \varepsilon_{\mathbf{k}} c_{\mathbf{k}+\mathbf{G}}$ <p>$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u(\mathbf{r})$ plane wave. \mathbf{k} is quantum no showing symm of $\psi(\mathbf{r})$</p>
<p>$l = 0$ (s-orbital) $l = 1$ (p-orbital)</p> 	

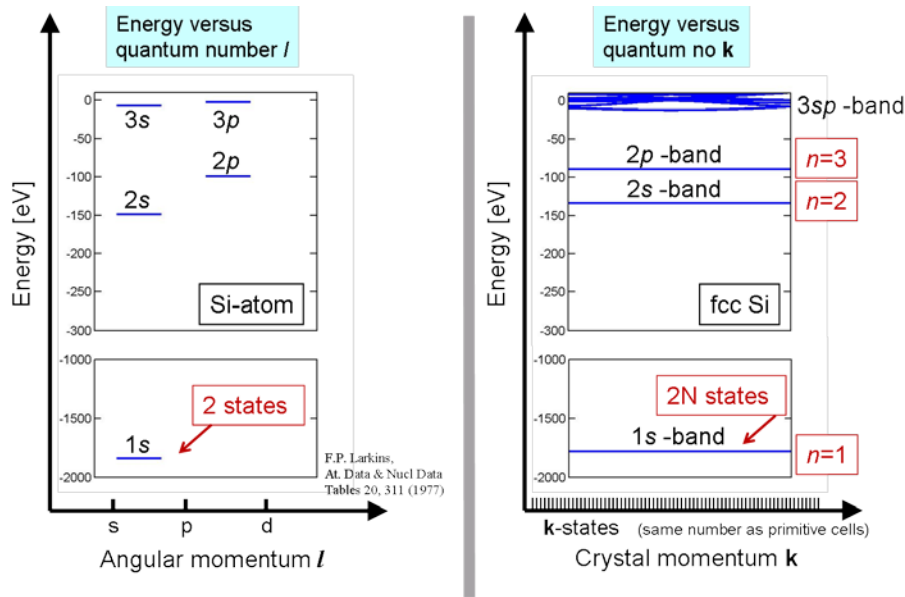


Fig. 2.6: Angular momentum $\{l, m\}$ represents symmetry of eigenfunctions in atoms, and the crystal momentum \mathbf{k} represents symmetry of eigenfunctions in crystals. Atoms have distinct energy levels, whereas energy states in crystals form energy bands.

2.6 What is a \mathbf{k} -state?

The reciprocal space (or the \mathbf{k} -space) is a continuous space, spanned by the vectors \mathbf{b}_1 , \mathbf{b}_2 , and \mathbf{b}_3 . The electronic eigenstates in the crystal have specific and discrete set of \mathbf{k} -points in this continuous \mathbf{k} -space. The set of allowed \mathbf{k} -points for the eigenfunctions is called the \mathbf{k} -states of the crystal electrons.

- n and \mathbf{k} are quantum numbers. According to the Pauli exclusion principle, at most two electrons (spin up and down) can simultaneously be in a $\{n, \mathbf{k}\}$ -state.
- \mathbf{k} is a quantum number, just like l and m in $Y_{lm}(\theta, \varphi)$ for a central-symmetric problem.
- \mathbf{k} describes the symmetry of $\psi_{n\mathbf{k}}(\mathbf{r}) = A \cdot \exp(i \cdot \mathbf{k} \cdot \mathbf{r})$, just like l and m describe symmetry of $Y_{lm}(\theta, \varphi)$.
- The wave length of $A \cdot \exp(i \cdot \mathbf{k} \cdot \mathbf{r})$ is obtained from $\lambda = 2\pi/|\mathbf{k}|$, and \mathbf{k} is thus the wave number.
- Subscript $\{n, \mathbf{k}\}$ in $\psi_{n\mathbf{k}}(\mathbf{r})$ acts also as numbering of the eigenfunctions (instead of $j = 1, 2, \dots, N_e$).
- $\hbar\mathbf{k}$ is the momentum of free electron with $\psi_{n\mathbf{k}}(\mathbf{r}) = A \cdot \exp(i \cdot \mathbf{k} \cdot \mathbf{r})$. For electrons in a crystal with $\psi_{n\mathbf{k}}(\mathbf{r}) = \exp(i \cdot \mathbf{k} \cdot \mathbf{r}) u_{n\mathbf{k}}(\mathbf{r})$, the $\hbar\mathbf{k}$ is called the crystal momentum. Crystal momentum describes the electron momentum coupled to the crystal.
- Notice that $\mathbf{k}\mathbf{r} \equiv \mathbf{k} \cdot \mathbf{r}$ is a scalar parameter. That is, \mathbf{k} is a row vector and \mathbf{r} is a column vector, and in Cartesian coordinates the product is $\mathbf{k}\mathbf{r} = k_x \cdot x + k_y \cdot y + k_z \cdot z$.

One shall remember that choosing the boundary condition as $\psi_{n\mathbf{k}}(\mathbf{r}) = \psi_{n\mathbf{k}}(\mathbf{r} + \mathbf{L})$ where $\mathbf{L} = N_1 n_1 \mathbf{a}_1 + N_2 n_2 \mathbf{a}_2 + N_3 n_3 \mathbf{a}_3$ is an artificial choice that we do, but it is actually a smart choice. The advantage is that we can (1) describe both localized and delocalized electrons, (2) represent the electron states by \mathbf{k} -states in the first Brillouin zone, and (3) in a natural way include crystal periodicity in the eigenfunctions, and thereby understand physical processes in the material. The main disadvantage is however that we assume periodic symmetry in infinity, and we thus do not have a natural basis set to describe local structures in the crystal like defects and surface structures. For these non-periodic structures one can still use Bloch functions and periodic functions if one construct supercells (this technique will be discussed in the course).

3 Some basic concepts

3.1 Variational principle

When solving the eigenvalue problem $H\psi_\kappa(\mathbf{r}) = \varepsilon_\kappa\psi_\kappa(\mathbf{r})$ for a single-electron problem one normally tries with an ansatz, that is, a clever guess for $\psi_\kappa(\mathbf{r})$. This is a good tactic for simple problems, but it is much more difficult for a more complex many-electron system. There is however an alternative way to solve the eigenvalue problem: one can employ the variational principle.

The idea is to vary the general wavefunction $\psi(\mathbf{r})$ and minimize the total energy ε . The wavefunction with the lowest energy is the ground state $\psi_0(\mathbf{r})$ with the energy ε_0 because

$$\varepsilon_0 = \int \psi_0^*(\mathbf{r}) H \psi_0(\mathbf{r}) d\mathbf{r} = \langle \psi_0 | H | \psi_0 \rangle < \langle \psi | H | \psi \rangle = \int \psi^*(\mathbf{r}) H \psi(\mathbf{r}) d\mathbf{r} = \varepsilon \quad \text{if } \psi(\mathbf{r}) \neq \psi_0(\mathbf{r}). \quad (3.1)$$

Thus, we shall find the wavefunction that minimizes the energy

$$\varepsilon_0 = \min_{\psi \rightarrow \psi_0} \varepsilon = \min_{\psi \rightarrow \psi_0} \int \psi^*(\mathbf{r}) H \psi(\mathbf{r}) d\mathbf{r}. \quad (3.2)$$

Mathematically, this can be expressed that the change in energy $\delta\varepsilon$ for a small variation in wavefunction $\delta\psi(\mathbf{r})$ shall be zero, that is, $\delta\varepsilon/\delta\psi(\mathbf{r}) = 0$. In the minimization process we vary the wavefunction $\psi(\mathbf{r}) \rightarrow \psi(\mathbf{r}) + \delta\psi(\mathbf{r})$. The wavefunction $\psi(\mathbf{r}) + \delta\psi(\mathbf{r})$ must be allowed to be a general wavefunction and it is generally not normalized. It is therefore a risk that also the final solution will be for wavefunction that is not normalized or even orthogonal. Thus, we shall minimize the energy with the constraint that $\int \psi(\mathbf{r})^* \psi(\mathbf{r}) d\mathbf{r} = 1$ for the final solution $\psi(\mathbf{r}) = \psi_0(\mathbf{r})$. The Lagrange multiplier is a method for that (see Appendices in Section 9.2).

$$\frac{\delta}{\delta\psi(\mathbf{r})} \{\varepsilon - \lambda g\} = \frac{\delta}{\delta\psi(\mathbf{r})} \left\{ \int \psi^*(\mathbf{r}) H \psi(\mathbf{r}) d\mathbf{r} - \lambda \left(\int \psi^*(\mathbf{r}) \psi(\mathbf{r}) d\mathbf{r} - 1 \right) \right\} = 0. \quad (3.3)$$

This is the variational method, and we will use it for solving the many-electron problem both in the Hartree approximation and in the DFT. Notice that we get only the ground state $\psi_0(\mathbf{r})$ with this method, and thus not the energetically higher eigenstates $\psi_\kappa(\mathbf{r})$. We will show that the variational method implies two important things:

- it solves the eigenvalue problem for the ground state, and
- it transforms the many-electron problem into single-electron equations that are much easier to solve.

In Eq. (3.2), the energy ε depends on the wavefunction $\psi(\mathbf{r})$. That is, ε is a function of functions, and this is the definition of a functional. We denote that by $\varepsilon[\psi]$. In order to solve the derivative $\delta\{\varepsilon - \lambda g\}/\delta\psi(\mathbf{r})$, we have to understand the basic properties of functionals and their derivatives.

3.2 Functionals

A function $f(x)$ is a mathematical tool to maps a number to another number, for example

$$f(x) = e^{-x^2} \quad \Rightarrow \quad f(2) = e^{-2^2} = 0.018. \quad (3.4)$$

An operator \hat{F} maps a function onto another function, for example

$$\hat{F} = \nabla \quad \Rightarrow \quad \hat{F}f(x) = -2xe^{-x^2} = g(x). \quad (3.5)$$

A functional $F[f]$ takes a function as input and outputs a number. For example, consider the functional to integrate a function of x from $-\infty$ to ∞

$$\begin{aligned}
 F[f] = \int_{-\infty}^{\infty} f(x) dx = y & \quad \Rightarrow \quad F[f] = 1.77 \quad \text{if } f(x) = e^{-x^2} \\
 \text{and } F[g] = 0 & \quad \text{if } g(x) = -2xe^{-x^2}.
 \end{aligned} \tag{3.6}$$

A functional derivative $\delta F[f]/\delta f$ represents how the functional is changed when the input function is changed from $f(x)$ to $f(x) + \delta f(x)$. Thus, it is the whole function $f(x)$ over x -space that is varied by $\delta f(x)$. Similar to the derivative of a function, the derivative of a functional $\delta F/\delta f$ can be determined from $\delta F[f] = F[f + \delta f] - F[f]$. A mathematical derivation of functional derivatives is found in Chapt. 9.3. Here, we present an alternative way using the substitution $\delta f(x) \rightarrow \varepsilon \delta(x - x')$. That is, to specify the variation by a Dirac-delta function. Then, one can show that which in the limit of $\varepsilon \rightarrow 0$ is equivalent to

$$\frac{\delta F[f]}{\delta f(x)} = \lim_{\varepsilon \rightarrow 0} \frac{F[f + \varepsilon \delta(x - x')] - F[f]}{\varepsilon}. \tag{3.7}$$

This looks like the derivative of a regular function. However, one has to be more careful to ensure that the limit $\varepsilon \rightarrow 0$ is leading vanishing factor. This simplified way of using the Dirac-delta function is mathematically less rigorous compared to Eq. (9.10).

Especially, one can show that

$$\text{if } F[f] = \int h(f(x)) dx \quad \text{then } \frac{\delta F[f]}{\delta f(x)} = \frac{\partial h(f(x))}{\partial f} \tag{3.8}$$

$$\text{Example: } F[f] = \int f(x)^n dx \quad \Rightarrow \quad \frac{\delta F[f]}{\delta f(x)} = n \cdot f(x)^{n-1}$$

$$\text{Example: } F[f] = \iint \frac{f(x)f(x')}{|x - x'|} dx dx' \quad \Rightarrow \quad \frac{\delta F[f]}{\delta f(x)} = 2 \int \frac{f(x')}{|x - x'|} dx'$$

and

$$\text{if } F[f] = \int h(f(x), f'(x), f''(x), \dots) dx \quad \text{then } \frac{\delta F[f]}{\delta f(x)} = \frac{\partial h}{\partial f} - \frac{d}{dx} \frac{\partial h}{\partial f'} + \frac{d^2}{dx^2} \frac{\partial h}{\partial f''} \dots \tag{3.9}$$

$$\text{Example: } F[f] = \int f(x) f''(x) dx \quad \Rightarrow \quad \frac{\delta F[f]}{\delta f(x)} = f''(x) + \frac{d^2}{dx^2} f(x) = 2f''(x).$$

These functional derivatives are very useful when analyzing the variational principles in quantum mechanics.

3.3 Dirac equation and scalar-relativistic approximation

The Schrödinger equation in Chapter 2 is actually valid only for spin-less particles, thus not for electrons with spin 1/2. Moreover, it is a non-relativistic equation. For electrons, one shall instead use the relativistic Dirac equation $(c\boldsymbol{\alpha}\mathbf{p} + \boldsymbol{\beta}m_e c^2 + V(\mathbf{r}))\bar{\psi}_\kappa(\mathbf{r}) = \varepsilon_\kappa \bar{\psi}_\kappa(\mathbf{r})$. However, $\bar{\psi}_\kappa(\mathbf{r})$ is a 4-component eigenfunction and the equation is rather cumbersome to model in the solid state computer codes. One therefore employs the scalar-relativistic approximation (see Appendices, Chapt 9.1). One type of scalar-relativistic approximation is the Pauli equation

$$\left(-\frac{\hbar^2 \nabla^2}{2m_e} + V(\mathbf{r}) - \frac{\hbar^4 \nabla^4}{8m_e^3 c^2} - \frac{\hbar^2 (\nabla V(\mathbf{r})) \cdot \nabla}{4m_e^2 c^2} \right) \psi_\kappa(\mathbf{r}) = \varepsilon_\kappa \psi_\kappa(\mathbf{r}). \quad (3.10)$$

To simplify reading however, we write the Schrödinger eigenvalue equation as

$$\left(-\frac{\hbar^2 \nabla^2}{2m_e} + V(\mathbf{r}) \right) \psi_\kappa(\mathbf{r}) = \varepsilon_\kappa \psi_\kappa(\mathbf{r}), \quad (3.11)$$

where $\psi_\kappa(\mathbf{r})$ is the eigenfunction of the κ :th state, having the energy ε_κ .

4 The two-electron Schrödinger equation

4.1 Hamiltonian and eigenfunction

Assume that we have two electrons: $N_e = 2$. The two-electron wavefunction $\Psi(\mathbf{r}) \equiv \Psi(\mathbf{r}_1, \mathbf{r}_2)$ shall include the two single-electron wavefunctions $\psi_1(\mathbf{r}_1)$ and $\psi_2(\mathbf{r}_2)$ to describe the two electrons. The question is however what is the form of $\Psi(\mathbf{r}_1, \mathbf{r}_2) = f(\psi_1, \psi_2)$.

The eigenvalue problem in Eq. (2.2) is expanded into a two-particle Schrödinger equation

$$\left(-\frac{\hbar^2 \nabla_1^2}{2m_e} - \frac{\hbar^2 \nabla_2^2}{2m_e} + \frac{q^2}{|\mathbf{r}_1 - \mathbf{r}_2|} + V(\mathbf{r}) \right) \Psi_\kappa(\mathbf{r}_1, \mathbf{r}_2) = E_\kappa \Psi_\kappa(\mathbf{r}_1, \mathbf{r}_2). \quad (4.1)$$

The first and second terms determine the kinetic energy of the first $\psi_1(\mathbf{r}_1)$ and the second $\psi_2(\mathbf{r}_2)$ single-electron state, respectively. The subscript on ∇ indicates that the derivative is with respect to the 1 and 2 electron coordinates, respectively. The third term is a potential energy that describes the repulsive Coulomb interaction between the two electrons. The fourth term is an external potential $V(\mathbf{r})$, just as in the case for the single-electron problem.

Similar to the single-electron eigenfunctions, the two-electron eigenfunctions are orthonormal

$$\int \int \Psi_\kappa^*(\mathbf{r}_1, \mathbf{r}_2) \Psi_{\kappa'}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 = \langle \Psi_\kappa(\mathbf{r}_1, \mathbf{r}_2) | \Psi_{\kappa'}(\mathbf{r}_1, \mathbf{r}_2) \rangle = \delta_{\kappa\kappa'}. \quad (4.2)$$

The density is determined by

$$n_\kappa(\mathbf{r}) = n_\kappa(\mathbf{r}_1) = N_e \int |\Psi_\kappa(\mathbf{r}_1, \mathbf{r}_2)|^2 d\mathbf{r}_2. \quad (4.3)$$

This may look a little strange. Why is $n_\kappa(\mathbf{r}) = n_\kappa(\mathbf{r}_1)$, and why do we integrate over only \mathbf{r}_2 ? The reason is related to the properties of indistinguishable particles. This property implies that $n_\kappa(\mathbf{r}_1)$ is equal to $n_\kappa(\mathbf{r}_2)$.

Integration of the density over the whole \mathbf{r} -space yields the number of electron

$$\int n_\kappa(\mathbf{r}) d\mathbf{r} = \int n_\kappa(\mathbf{r}_1) d\mathbf{r}_1 = N_e \int \int |\Psi_\kappa(\mathbf{r}_1, \mathbf{r}_2)|^2 d\mathbf{r}_1 d\mathbf{r}_2 = N_e. \quad (4.4)$$

Notice, the two-electron Hamiltonian in Eq. (4.1) contains single-electron operators. For instance, the kinetic energy operator is applied to each single-electron functions. However, we do not have the explicit form of $\Psi_\kappa(\mathbf{r}_1, \mathbf{r}_2) = f(\psi_1, \psi_2)$, that is, as a functions of $\psi_1(\mathbf{r}_1)$ and $\psi_2(\mathbf{r}_2)$. This means that either we have to find a rule how to generate $f(\psi_1, \psi_2)$, or we have to guess $f(\psi_1, \psi_2)$.

It is actually difficult to find $\Psi_\kappa(\mathbf{r}_1, \mathbf{r}_2) = f(\psi_1, \psi_2)$. For instance, assume we have two electrons but that there are no Coulomb interactions between them, and that $V(\mathbf{r}) = 0$ everywhere. Both electrons are thus free and independent of each other. If the two electrons are located in two different universes, we could use two separate solutions to the single-electron Schrödinger equation (Eq. 2.4). Then, $\Psi_j(\mathbf{r}_{\text{univ}1}, \mathbf{r}_{\text{univ}2}) = \psi_{\mathbf{k}}(\mathbf{r}_{\text{univ}1}) + \psi_{\mathbf{k}'}(\mathbf{r}_{\text{univ}2})$ where $\psi_{\mathbf{k}}(\mathbf{r}) = A \cdot \exp(i \cdot \mathbf{k} \cdot \mathbf{r})$. However, if the electrons are located in the same space, one can easily verify that this is not a solution to the two-electron Schrödinger equation, thus $\Psi_\kappa(\mathbf{r}_1, \mathbf{r}_2)$ can not be equal to $\psi_1(\mathbf{r}_1) + \psi_2(\mathbf{r}_2)$; see exercises.

Instead, if one assumes that the two electrons are independent of each other, a guess would maybe to do similar to the variable separation in Eqs. 2.2-2.3 and 2.12, wherein we had independent variables. Thus, to try with the ansatz $\Psi_\kappa(\mathbf{r}_1, \mathbf{r}_2) = A \cdot \psi_1(\mathbf{r}_1) \psi_2(\mathbf{r}_2)$. This is the Hartree approach. However, in the next section we will see that this form is not flexible enough to describe the two-electron wavefunction.

4.2 Hartree and Hartree-Fock approximations

The first clever guess of a two-electron function is to assume that $\psi_1(\mathbf{r}_1)$ and $\psi_2(\mathbf{r}_2)$ are independent, although interacting via the two-electron interaction [third term in Eq. (4.1)]. Then one can regard the full eigenfunction as a variable separation of the single-particle wavefunctions

$$\Psi_{\kappa}(\mathbf{r}_1, \mathbf{r}_2) = f(\psi_1, \psi_2) = \Psi_{\kappa\pm}(\mathbf{r}_1, \mathbf{r}_2) = \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2). \quad (4.5)$$

This is the Hartree approximation. With a well-defined form of $\Psi_{\kappa}(\mathbf{r}_1, \mathbf{r}_2) = f(\psi_1, \psi_2)$ one can apply the single-particle operators of the Schrödinger equation in Eq. (4.1).

The disadvantage is however that the Hartree wavefunction is not anti-symmetric with respect to the particle coordinates. That is, the particles are distinguishable, and do not obey the Pauli exclusion principle for fermions. To overcome this, one can generate an anti-symmetric wavefunction which makes the electrons indistinguishable

$$\Psi_{\kappa}(\mathbf{r}_1, \mathbf{r}_2) = f(\psi_1, \psi_2) = \Psi_{\kappa\pm}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \{ \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \pm \psi_1(\mathbf{r}_2)\psi_2(\mathbf{r}_1) \} \chi_{\mp}(s_1, s_2). \quad (4.6)$$

This is the Hartree-Fock approximation of the wavefunction. The spin function $\chi_{\mp}(s_1, s_2)$ is symmetric if room-part is anti-symmetric and vice versa, so that $\Psi(\mathbf{r}_1, \mathbf{r}_2) = -\Psi(\mathbf{r}_2, \mathbf{r}_1)$.

Notice that we have not changed the Hamiltonian in Eq. (4.1), and thus we have not changed the interaction terms. We have only expanded the form the two-electron function. However, thereby the solution of the Schrödinger equation will change, and it will generate a different energy of the system. This correction of the energy due to the change in the wavefunction (to obey the Pauli exclusion principle) is called the exchange energy.[†]

It is important to understand that both the Hartree and the Hartree-Fock wavefunctions are not sufficient to fully describe the complex two-electron interaction problem, even for the simple interaction described by Eq. (4.1). The wavefunctions are not flexible enough. The Hartree-Fock wavefunction can describe the exchange interaction (from the Pauli exclusion principle) but it does not incorporate the correlation energy between the electrons.

4.3 Hartree single-electron equation

We will here derive the Hartree single-particle equation in order to illustrate how one transforms a two-particle equation into two single-particle equations. The same technique can be used for the Hartree-Fock approximation. The same technique is also utilized for system with more than two electrons, *i.e.*, for a many-electron wavefunction. Moreover, the derivation will be used in the DFT/Kohn-Sham equation in Section 8.1.

We will use the variational method (see Section 3.1) to simplify the Hartree two-electron problem. We thus assume the Hartree form of the two-particle function: $\Psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)$. The variational method generates the ground-state eigenfunction, but we will see that the derivation also transforms the two-particle equation into two single-electron equations for $\psi_1(\mathbf{r}_1)$ and $\psi_2(\mathbf{r}_2)$, respectively. First, we use the minimization procedure with the Lagrange multiplier [see Eq. (3.3)].

We start from the general formula for energy $E = \langle \psi_1\psi_2 | H | \psi_1\psi_2 \rangle$ and we shall minimize the total energy E with respect to the two single-electron wavefunctions. By minimizing the expectation value energy E we obtain the ground-state energy; see Eq. (3.2).

[†] One might expect that the exchange energy is a small correction to the Coulomb interaction. That is certainly not true. The spin and the Pauli exclusion principle are responsible for the covalent bonds between atoms; for instance the bonds in a hydrogen molecule H₂. Most of the materials have very strong covalent character. Thus, without spin and/or without the Pauli exclusion principle our world would have looked very different.

In this minimization process, we shall ensure that both electrons are fully represented. That is, our constraint is that the two single-electron wavefunctions are normalized $\langle \psi_1 | \psi_1 \rangle = \langle \psi_2 | \psi_2 \rangle = 1$. This is a very reasonable constraint because we believe that $\psi_1(\mathbf{r}_1)$ in some sense represents a true electron, and the probability of finding the electron somewhere in the room shall be 1. However, we also demand that $\psi_1(\mathbf{r}_1)$ and $\psi_2(\mathbf{r}_2)$ shall be orthogonal; this is not a necessary condition, but it simplifies the derivation.

The energy $E[\psi_1, \psi_2]$ is a functional of the two single-electron wavefunction.

$$E[\psi_1, \psi_2] = \iint \psi_1^*(\mathbf{r}_1) \psi_2^*(\mathbf{r}_2) \left(-\frac{\hbar^2 \nabla_1^2}{2m_e} - \frac{\hbar^2 \nabla_2^2}{2m_e} + \frac{q^2}{|\mathbf{r}_1 - \mathbf{r}_2|} + V(\mathbf{r}) \right) \psi_1(\mathbf{r}_1) \psi_2(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2. \quad (4.7)$$

From Eq. (3.3) we set up the variational equation as

$$\frac{\delta}{\delta \psi_1^*(\mathbf{r})} \left\{ E[\psi_1, \psi_2] - \sum_{i,i'=1,2} \lambda_{ii'} \left(\int \psi_i^*(\mathbf{r}) \psi_{i'}(\mathbf{r}) d\mathbf{r} - 1 \right) \right\} = 0. \quad (4.8)$$

Here, we present the minimization with respect to $\psi_1^*(\mathbf{r})$, but we shall remember that we also shall minimize the expression with respect to $\psi_2^*(\mathbf{r})$, $\psi_1(\mathbf{r})$, and $\psi_2(\mathbf{r})$. We are allowed to minimize $\psi_1^*(\mathbf{r})$ and $\psi_1(\mathbf{r})$ separately as they were two independent functions, because the constraint of orthogonal wavefunctions implies that $\psi_1^*(\mathbf{r})$ will be the complex conjugate of $\psi_1(\mathbf{r})$ in the final solution. For aesthetical reasons, we minimize with respect to complex conjugate $\psi_1^*(\mathbf{r})$ and not with respect to $\psi_1(\mathbf{r})$, because that will generate an equation for $\psi_1(\mathbf{r})$ and not for $\psi_1^*(\mathbf{r})$.

First, the second term in Eq. (4.8) is easy to determine from the derivative of functionals. The derivative of the constraint yields $\lambda_{i1} \psi_1(\mathbf{r})$, and the equation becomes

$$\frac{\delta}{\delta \psi_1^*(\mathbf{r})} E[\psi_1, \psi_2] = \lambda_{i1} \psi_1(\mathbf{r}). \quad (4.8)$$

Second, we divide the total energy in terms of the kinetic, electron-electron, and electron-nucleus interactions

$$E[\psi_1, \psi_2] = \iint \psi_1^*(\mathbf{r}_1) \psi_2^*(\mathbf{r}_2) H \psi_1(\mathbf{r}_1) \psi_2(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (4.9)$$

$$E[\psi_1, \psi_2] = T[\psi_1, \psi_2] + U_{ee}[\psi_1, \psi_2] + U_{en}[\psi_1, \psi_2], \quad (4.10)$$

where

$$\begin{aligned} T[\psi_1, \psi_2] &= \iint \psi_1^*(\mathbf{r}_1) \psi_2^*(\mathbf{r}_2) \left\{ - \sum_{j=1,2} \frac{\hbar^2 \nabla_j^2}{2m_e} \right\} \psi_1(\mathbf{r}_1) \psi_2(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 && \text{kinetic energy} \\ &= \sum_{j=1,2} \int \psi_j^*(\mathbf{r}) \frac{-\hbar^2 \nabla_j^2}{2m_e} \psi_j(\mathbf{r}) d\mathbf{r} \\ U_{ee}[\psi_1, \psi_2] &= \iint \psi_1^*(\mathbf{r}_1) \psi_2^*(\mathbf{r}_2) \left\{ \frac{q^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \right\} \psi_1(\mathbf{r}_1) \psi_2(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 && \text{electron-electron interaction} \\ &= \frac{1}{2} \iint q^2 \left\{ \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \sum_{j=1,2} \frac{n_j(\mathbf{r})n_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right\} d\mathbf{r} d\mathbf{r}' \\ U_{en}[\psi_1, \psi_2] &= \iint \psi_1^*(\mathbf{r}_1) \psi_2^*(\mathbf{r}_2) \{ V_{en}(\mathbf{r}) \} \psi_1(\mathbf{r}_1) \psi_2(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2. && \text{electron-nucleus interaction} \\ &= \int n(\mathbf{r}) V_{en}(\mathbf{r}) d\mathbf{r} \end{aligned} \quad (4.11)$$

These three interaction terms are of course functional of the two single-electron wavefunction. We have used $|\psi_j(\mathbf{r})|^2 = n_j(\mathbf{r})$, $\sum_j n_j(\mathbf{r}) = n(\mathbf{r})$, and change the dummy variables $\mathbf{r}_1 \rightarrow \mathbf{r}$ and $\mathbf{r}_2 \rightarrow \mathbf{r}'$.

The derivative of the kinetic energy is

$$\begin{aligned} \frac{\delta}{\psi_1^*(\mathbf{r})} T[\psi_1, \psi_2] &= \frac{\delta}{\psi_1^*(\mathbf{r})} \int \int \psi_1^*(\mathbf{r}_1) \psi_2^*(\mathbf{r}_2) \left\{ - \sum_{j=1,2} \frac{\hbar^2 \nabla_j^2}{2m_e} \right\} \psi_1(\mathbf{r}_1) \psi_2(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \frac{\delta}{\delta \psi_1^*(\mathbf{r})} \left\{ - \frac{\hbar^2}{2m_e} \int \psi_1^*(\mathbf{r}_1) \nabla_1^2 \psi_1(\mathbf{r}_1) d\mathbf{r}_1 - \frac{\hbar^2}{2m_e} \int \psi_2^*(\mathbf{r}_2) \nabla_2^2 \psi_2(\mathbf{r}_2) d\mathbf{r}_2 \right\} = - \frac{\hbar^2}{2m_e} \nabla_1^2 \psi_1(\mathbf{r}). \end{aligned} \quad (4.12)$$

Here, we utilized Eq. (3.9), that ∇_j operates only on j :the electron, and that $\psi_1^*(\mathbf{r}_1) \neq \psi_1(\mathbf{r}_1)$.

The derivative of the electron-electron interaction energy is, using Eq. (3.8)

$$\begin{aligned} \frac{\delta}{\delta \psi_1^*} U_{ee}[\psi_1, \psi_2] &= \frac{\delta}{\delta \psi_1^*} \int \int \psi_1^*(\mathbf{r}_1) \psi_2^*(\mathbf{r}_2) \left\{ \frac{q^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \right\} \psi_1(\mathbf{r}_1) \psi_2(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \left\{ \int \psi_2^*(\mathbf{r}_2) \left\{ \frac{q^2}{|\mathbf{r} - \mathbf{r}_2|} \right\} \psi_2(\mathbf{r}_2) d\mathbf{r}_2 \right\} \psi_1(\mathbf{r}) = \quad / \text{change dummy } \mathbf{r}_2 \rightarrow \mathbf{r}' = \\ &= \left\{ \int \psi_2^*(\mathbf{r}') \left\{ \frac{q^2}{|\mathbf{r} - \mathbf{r}'|} \right\} \psi_2(\mathbf{r}') d\mathbf{r}' \right\} \psi_1(\mathbf{r}). \end{aligned} \quad (4.13)$$

Finally, the derivative of the electron-nucleus interaction energy is

$$\begin{aligned} \frac{\delta}{\delta \psi_j^*(\mathbf{r})} U_{en}[\psi_1, \psi_2] &= \frac{\delta}{\delta \psi_j^*(\mathbf{r})} \int \int \psi_1^*(\mathbf{r}_1) \psi_2^*(\mathbf{r}_2) \{ V_{en}(\mathbf{r}) \} \psi_1(\mathbf{r}_1) \psi_2(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \\ &= V_{en}(\mathbf{r}) \psi_1(\mathbf{r}), \end{aligned} \quad (4.14)$$

utilizing $\int \psi_2^*(\mathbf{r}_2) \psi_2(\mathbf{r}_2) d\mathbf{r}_2 = 1$.

Hence, Eq. (4.8) turns into

$$\left\{ - \frac{\hbar^2}{2m_e} \nabla_1^2 + \int \psi_2^*(\mathbf{r}') \left\{ \frac{q^2}{|\mathbf{r} - \mathbf{r}'|} \right\} \psi_2(\mathbf{r}') d\mathbf{r}' + V_{en}(\mathbf{r}) \right\} \psi_1(\mathbf{r}) = \lambda_1 \psi_1(\mathbf{r}) \quad (4.14)$$

Now, we can identify $\lambda_1 = \varepsilon_1$ to be the eigenvalue for this single-electron Hartree equation. Moreover, if we do the variation with respect to $\psi_2^*(\mathbf{r})$ we obtain the second single-electron Hartree equation. Thus,

$$\begin{aligned} \left\{ - \frac{\hbar^2}{2m_e} \nabla^2 + \int \psi_2^*(\mathbf{r}') \left\{ \frac{q^2}{|\mathbf{r} - \mathbf{r}'|} \right\} \psi_2(\mathbf{r}') d\mathbf{r}' + V_{en}(\mathbf{r}) \right\} \psi_1(\mathbf{r}) &= \varepsilon_1 \psi_1(\mathbf{r}) \\ \left\{ - \frac{\hbar^2}{2m_e} \nabla^2 + \int \psi_1^*(\mathbf{r}') \left\{ \frac{q^2}{|\mathbf{r} - \mathbf{r}'|} \right\} \psi_1(\mathbf{r}') d\mathbf{r}' + V_{en}(\mathbf{r}) \right\} \psi_2(\mathbf{r}) &= \varepsilon_2 \psi_2(\mathbf{r}) \end{aligned} \quad (4.15)$$

Since $\psi_j^*(\mathbf{r}) \psi_j(\mathbf{r}) = |\psi_j(\mathbf{r})|^2 = n_j(\mathbf{r})$ and $\sum_j |\psi_j(\mathbf{r})|^2 = n(\mathbf{r})$, we can write the two equations as

$$\left\{ - \frac{\hbar^2}{2m_e} \nabla^2 + \int q^2 \frac{n(\mathbf{r}') - n_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{en}(\mathbf{r}) \right\} \psi_j(\mathbf{r}) = \varepsilon_j \psi_j(\mathbf{r}) \quad j = 1 \text{ and } 2. \quad (4.16)$$

This is now the two Hartree single-electron equations for the two-electron system.

The total energy $E = T + U_{ee} + U_{en}$ in Eqs. 4.7 and 4.10 is an utmost important property to be calculated. We shall derive an expression that depends on the density $n(\mathbf{r})$ that is independent of the eigenfunctions $\psi_j(\mathbf{r})$. We shall therefore replace T in Eq. (4.10). Start from Eq. 4.16, multiply by $\sum_{j=1,2} \psi_j^*(\mathbf{r})$ on the left and integrate:

$$\int \sum_{j=1,2} \psi_j^*(\mathbf{r}) \left\{ -\frac{\hbar^2}{2m_e} \nabla^2 + \int q^2 \frac{n(\mathbf{r}') - n_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{en}(\mathbf{r}) \right\} \psi_j(\mathbf{r}) d\mathbf{r} = \int \sum_{j=1,2} \varepsilon_j \psi_j^*(\mathbf{r}) \psi_j(\mathbf{r}) d\mathbf{r}, \quad (4.17)$$

which is equal to

$$T + \iint \left\{ q^2 \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \sum_{j=1,2} \frac{n_j(\mathbf{r})n_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right\} d\mathbf{r}' d\mathbf{r} + \int n(\mathbf{r}) V_{en}(\mathbf{r}) d\mathbf{r} = \sum_{j=1,2} \varepsilon_j. \quad (4.18)$$

By combining 4.18 and Eq. 4.10, one obtains

$$E = \left\{ \sum_{j=1,2} \varepsilon_j - \iint \left\{ q^2 \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \sum_{j=1,2} \frac{n_j(\mathbf{r})n_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right\} d\mathbf{r}' d\mathbf{r} - \int n(\mathbf{r}) V_{en}(\mathbf{r}) d\mathbf{r} \right\} + U_{ee} + U_{ne}, \quad (4.19)$$

which in turn is simplified by using Eq. 4.11 to

$$E = \sum_{j=1,2} \varepsilon_j - \frac{1}{2} \iint q^2 \left\{ \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \sum_{j=1,2} \frac{n_j(\mathbf{r})n_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right\} d\mathbf{r}' d\mathbf{r}. \quad (4.20)$$

The total energy is thus a summation of the energy eigenvalues plus an electronic interaction term.

Notice that

- We used the variational method to take the two-electron problem into two single-electron problems. This essentially simplifies the calculations.
- Since we used the variational method, the equations are valid only for the ground state.
- The total energy is not only the summation of the single-electron eigenfunctions.
- The electron in Eq. (4.16) interacts with the other electrons via the density of the other electrons. The electron does not feel its own density [therefore the term $-n_j(\mathbf{r}')$]. This is correct, because an electron does not interact with itself.
- Very often in many-electron problems one neglects the $-n_j(\mathbf{r}')$ term, and thereby one allows the electrons to interact with itself (a self-interaction error). Then,

$$\left\{ -\frac{\hbar^2}{2m_e} \nabla^2 + \int q^2 \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{en}(\mathbf{r}) \right\} \psi_j(\mathbf{r}) = \varepsilon_j \psi_j(\mathbf{r}) \quad j = 1 \text{ and } 2 \quad (4.21)$$

$$E = \sum_j \varepsilon_j - \frac{1}{2} \iint q^2 \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' d\mathbf{r} \quad (4.22)$$

This Hartree equation is simpler because the second term in Eq. (4.21) is now equal for all electrons (for $j = 1, 2, \dots, N_e$). The second term in Eq. (4.17) is called the Hartree potential $V_H(\mathbf{r})$. The Hartree potential describes the electron-electron interaction that the single-electron wavefunction feels.

- The Hartree equation is important also in the Kohn-Sham equation (Chapt 8).

It is relatively easy to verify that Eqs. 4.21 and 4.22 are valid also for the generalization to the many-electron system assuming the Hartree wavefunction $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N_e}) = \psi_1(\mathbf{r}_1) \psi_2(\mathbf{r}_2) \psi_3(\mathbf{r}_3) \dots \psi_{N_e}(\mathbf{r}_{N_e})$ and $j = 1, 2, \dots, N_e$. In this case, the variational method takes the N_e -electron problem into N_e number of single-electron problems. This leads us in to the next Chapter.

5 The many-particle Schrödinger equation

The many-particle problem can be regarded as an extension to the two-particle problem. We will consider a realistic system, namely materials that contain atoms. Thus, we have electrons and nuclei. We will assume no additional external potential. One of the challenges is to accurately calculate the interactions between all electrons and all nuclei. In one cube-centimeter of a condensed matter, there are roughly 10^{23} electrons. Actually, this number is roughly the estimated number of stars in our universe. There is a famous expression by Carl Sagan: "*The total number of stars in the Universe is larger than all the grains of sand on all the beaches of the planet Earth.*" (TV series Cosmos: A Personal Voyage, episode 8 Nov 1980). This statement is true. Moreover, one can estimate that the number of grain of sand on all beaches on the earth is roughly the same as the number of stars.

Thus, the number of atoms in 1 cm^3 of a solid material is roughly the same as the number of stars in universe, and roughly the same as the number of grain of sand on all beaches.

5.1 Ground state energy

Assume that we have N_e electrons and N_n nuclei. The many-particle wavefunction shall then be described as $\Psi^{en}(\mathbf{r}, \mathbf{R}) \equiv \Psi^{en}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N_e}, \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{N_n})$ where \mathbf{r}_j describe the coordinates of the j :th electron and \mathbf{R}_α describes the coordinates of the α :th nucleus. The superscript "en" only indicates that we describe a wavefunction with both electrons and nuclei.

We write the many-particle Schrödinger eigenvalue equation as

$$H_\kappa^{en} \Psi_\kappa^{en}(\mathbf{r}, \mathbf{R}) = E_\kappa^{en} \Psi_\kappa^{en}(\mathbf{r}, \mathbf{R}). \quad (5.1)$$

Starting from the time-independent Hamiltonian (Eq. 2.2) and expand it into a many-particle Hamiltonian, we obtain

$$H^{en} = - \sum_{j=1}^{N_e} \frac{\hbar^2 \nabla_j^2}{2m_e} - \sum_{\alpha=1}^{N_n} \frac{\hbar^2 \nabla_\alpha^2}{2m_\alpha} + \sum_{j < j'}^{N_e} \frac{q^2}{|\mathbf{r}_j - \mathbf{r}_{j'}|} + \sum_{\alpha < \alpha'}^{N_n} \frac{q^2 Z_\alpha Z_{\alpha'}}{|\mathbf{R}_\alpha - \mathbf{R}_{\alpha'}|} - \sum_{j=1}^{N_e} \sum_{\alpha=1}^{N_n} \frac{q^2 Z_\alpha}{|\mathbf{r}_j - \mathbf{R}_\alpha|}, \quad (5.2)$$

where Z_α and m_α are the atom number and mass of the nuclei, respectively.

The five terms in the Hamiltonian are

$$\begin{aligned} T_j &= - \sum_{j=1}^{N_e} \frac{\hbar^2 \nabla_j^2}{2m_e} && : \text{kinetic energy of all electrons, with mass } m_e \\ T_\alpha &= - \sum_{\alpha=1}^{N_n} \frac{\hbar^2 \nabla_\alpha^2}{2m_\alpha} && : \text{kinetic energy of all nuclei, with masses } m_\alpha \\ U_{jj} &= + \sum_{j < j'}^{N_e} \frac{q^2}{|\mathbf{r}_j - \mathbf{r}_{j'}|} && : \text{repulsive electron-electron interactions} \\ U_{\alpha\alpha} &= + \sum_{\alpha < \alpha'}^{N_n} \frac{q^2 Z_\alpha Z_{\alpha'}}{|\mathbf{R}_\alpha - \mathbf{R}_{\alpha'}|} && : \text{repulsive nuclei-nuclei interactions} \\ U_{j\alpha} &= - \sum_{j=1}^{N_e} \sum_{\alpha=1}^{N_n} \frac{q^2 Z_\alpha}{|\mathbf{r}_j - \mathbf{R}_\alpha|} && : \text{attractive electron-nuclei interactions.} \end{aligned} \quad (5.3)$$

Notice that

- ∇_j means the derivative of the j :th electron coordinate.
- We do not count the two-electron interactions twice, therefore $j < j'$ where $j = 1, 2 \dots N_e$.
- $j \neq j'$ because an electron cannot interact with itself. Actually, this term is important to remember because it is often included (see discussion in Eq. 4.21).

- We have constructed the many-particle Hamiltonian from the two-particle Hamiltonian. Therefore, the many-particle equation contains only single-particle and two-particle operators. Thus, in the equation above, we have neglected operators that explicitly involve three and more particles.
- We assume that there are single-electron wavefunctions $\psi_f(\mathbf{r}_j)$ in $\Psi^{en}(\mathbf{r}, \mathbf{R})$, and that H can operate on these electron wavefunctions.

5.2 Why difficult to solve the many-particle equation?

One of the problems with the many-particle equation is that we have roughly 10^{22} nuclei and 10^{23} electrons in a crystal with volume 1 cm^3 . That implies that the two-particle operators in Eq. (5.2) involve a summation of roughly 10^{40} terms. Even for small a nanoparticle with the size $10 \times 10 \times 10 \text{ nm}^3$ one has about one million particles, and such system will imply $\sim 10^{12}$ interaction terms. This is of course a huge numerical problem.

However, there is a more conceptual issue. While the Hamiltonian H above contains single- and two-particle operators that shall be applied to the single-particle wavefunctions, we do not have the prior knowledge how $\Psi^{en}(\mathbf{r}, \mathbf{R})$ depends on these single-particle wavefunctions. Thus, we do not know how to operate H on the many-particle function $\Psi^{en}(\mathbf{r}, \mathbf{R})$. One can attack this problem in two ways

- Try to describe $\Psi^{en}(\mathbf{r}, \mathbf{R})$ in terms of the single-particle wavefunctions and use the regular Hamiltonian H . The Hartree and Hartree-Fock approximations belong to this approach. In more sophisticated methods, one tries to find a more general form of $\Psi^{en}(\mathbf{r}, \mathbf{R}) = f(\psi_1, \psi_2, \psi_3, \dots)$. eigenfunctions.[†]
- Try to find an expression for H that can operate directly on $\Psi^{en}(\mathbf{r}, \mathbf{R})$, or alternatively, find a relation between $\Psi^{en}(\mathbf{r}, \mathbf{R})$ and E . The original DFT belongs to this approach, where E is expressed in terms of the electron density $n(\mathbf{r}) = |\Psi(\mathbf{r})|^2$. We discuss this approach in Chapter 7.

There is also a third method.

- One can combine the two approaches above. That is, to use an approximate form of the wavefunction, for instance the Hartree wavefunction $\Psi^{en}(\mathbf{r}, \mathbf{R}) = \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\psi_3(\mathbf{r}_3) \dots \psi_{N_e}(\mathbf{r}_{N_e})$, but use the DFT to derive an modified Schrödinger equation. The new equation shall of course generate the exact total energy for the approximated of the wavefunction. This is the Kohn-Sham equation which is described in Chapter 8.

Before discussing the DFT and Kohn-Sham equation, we shall simplify the many-particle equation, so that the full wavefunction $\Psi^{en}(\mathbf{r}, \mathbf{R})$ is divided into an electronic part $\Psi(\mathbf{r})$ and a nuclei part $\Theta(\mathbf{R})$. Thereby, we have reduced the problem to involve only an electronic Schrödinger equation $H\Psi(\mathbf{r}) = E\Psi(\mathbf{r})$. This is the Born-Oppenheimer approximation.

[†] The determinant wavefunction in the Hartree-Fock approximation can be generalized to a linear combination of several determinant wavefunctions. For instance, the configuration interaction and the multi-configurational self-consistent field are two Hartree-Fock based methods. The advantage with this approach is that the wavefunction is anti-symmetric and obeys the Pauli exclusion principles. The disadvantage is that one needs numerous determinants to describe a complex many-particle system.

6 The Born-Oppenheimer approximation (BOA)

6.1 Electronic and nuclear Schrödinger equations

The many-particle eigenfunction $\Psi_{\kappa}^{en}(\mathbf{r}, \mathbf{R}) = \Psi_{\kappa}^{en}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N_e}, \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{N_n})$ in Eq 5.1 contains the wavefunctions of all N_e electrons and the wavefunctions of all N_n nuclei. In order to simplify the solution of the Schrödinger equation, we want to find a way to solve the electronic part and the nuclear part separately. This would be a reasonable approximation because: First, one can assume that the nuclei are point-like charges, so that nuclear wavefunction is trivial. Second, the nuclei are moving slowly compared with the electrons because the mass of the nuclei ($m_a \approx 2 \times 10^{-27}$ kg for one proton) is much larger than the electron mass ($m_e \approx 9 \times 10^{-31}$ kg). Thus, if the nuclei are suddenly moved, we can assume that all electrons respond instantaneously on the nuclei motion. We will therefore assume that the nuclei are point-like charges with fixed positions, while the electrons are moving around them.

Now, we believe that the full eigenfunction $\Psi_{\kappa}^{en}(\mathbf{r}, \mathbf{R})$ can be divided into one eigenfunction $\Psi_{\kappa}(\mathbf{r}) = \Psi_{\kappa}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N_e})$ that describes only the electrons and one eigenfunction $\Theta_{\kappa}(\mathbf{R}) = \Theta_{\kappa}(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{N_n})$ that describe only the nuclei. The electronic eigenfunction depends indirectly on the positions of the nuclei, and we therefore indicate that by writing $\Psi_{\kappa}(\mathbf{r}) = \Psi_{\kappa}(\mathbf{r}, \mathbf{R})$.

In the simplest approximation, we will assume the variable separation $\Psi_{\kappa}^{en}(\mathbf{r}, \mathbf{R}) \approx \Psi_{\kappa}(\mathbf{r}, \mathbf{R})\Theta_{\kappa}(\mathbf{R})$ which is justified by the fact that nuclei are treated as point charges. That is, its wavefunction does only depend on positions of the nuclei. The electrons feel the potential from the nuclei, and thus the electronic wavefunction depends on the nucleus positions.[†]

Starting from the eigenvalue problem, and use the variable separation

$$\begin{aligned} H^{en}\Psi_{\kappa}^{en}(\mathbf{r}, \mathbf{R}) &= E_{\kappa}^{en}\Psi_{\kappa}^{en}(\mathbf{r}, \mathbf{R}) \\ H^{en}\Psi_{\kappa}(\mathbf{r}, \mathbf{R})\Theta_{\kappa}(\mathbf{R}) &= E_{\kappa}^{en}\Psi_{\kappa}(\mathbf{r}, \mathbf{R})\Theta_{\kappa}(\mathbf{R}) \end{aligned} \quad (6.1)$$

Next, multiply $\Psi_{\kappa}^*(\mathbf{r}, \mathbf{R})$ to the left on both sides and integrate with respect to electronic \mathbf{r} -space:

$$\int \Psi_{\kappa}^*(\mathbf{r}, \mathbf{R}) H^{en} \Psi_{\kappa}(\mathbf{r}, \mathbf{R}) \Theta_{\kappa}(\mathbf{R}) d\mathbf{r} = E_{\kappa}^{en} \int \Psi_{\kappa}^*(\mathbf{r}, \mathbf{R}) \Psi_{\kappa}(\mathbf{r}, \mathbf{R}) \Theta_{\kappa}(\mathbf{R}) d\mathbf{r} \quad (6.2)$$

Right hand side is easy to simplify because $\Theta_{\kappa}(\mathbf{R})$ does not depend on \mathbf{r} , and moreover, $\Psi_{\kappa}(\mathbf{r}, \mathbf{R})$ is orthonormalized: $\int \Psi_{\kappa}^*(\mathbf{r}, \mathbf{R}) \Psi_{\kappa}(\mathbf{r}, \mathbf{R}) d\mathbf{r} = 1$. On the left hand side, we divide the total Hamiltonian H^{en} into the electronic and nuclear Hamiltonians:

$$\begin{aligned} H^{en} &= H + H^n, \text{ where} \\ H &= T_j + U_{jj} + U_{ja} = -\sum_{j=1}^{N_e} \frac{\hbar^2 \nabla_j^2}{2m_e} + \sum_{j < j'}^{N_e} \frac{q^2}{|\mathbf{r}_j - \mathbf{r}_{j'}|} - \sum_{j=1}^{N_e} \sum_{\alpha=1}^{N_n} \frac{q^2 Z_{\alpha}}{|\mathbf{r}_j - \mathbf{R}_{\alpha}|} \quad \text{electronic Hamiltonian} \\ H^n &= T_{\alpha} + U_{\alpha\alpha} = -\sum_{\alpha=1}^{N_n} \frac{\hbar^2 \nabla_{\alpha}^2}{2m_{\alpha}} + \sum_{\alpha < \alpha'}^{N_n} \frac{q^2 Z_{\alpha} Z_{\alpha'}}{|\mathbf{R}_{\alpha} - \mathbf{R}_{\alpha'}|} \quad \text{nuclear Hamiltonian.} \end{aligned} \quad (6.3)$$

Equation (6.2) becomes

$$\begin{aligned} \int \Psi_{\kappa}^*(\mathbf{r}, \mathbf{R}) \{H + H^n\} \Psi_{\kappa}(\mathbf{r}, \mathbf{R}) \Theta_{\kappa}(\mathbf{R}) d\mathbf{r} &= E_{\kappa}^{en} \Theta_{\kappa}(\mathbf{R}) \\ \int \Psi_{\kappa}^*(\mathbf{r}, \mathbf{R}) H \Psi_{\kappa}(\mathbf{r}, \mathbf{R}) \Theta_{\kappa}(\mathbf{R}) d\mathbf{r} + \int \Psi_{\kappa}^*(\mathbf{r}, \mathbf{R}) H^n \Psi_{\kappa}(\mathbf{r}, \mathbf{R}) \Theta_{\kappa}(\mathbf{R}) d\mathbf{r} &= E_{\kappa}^{en} \Theta_{\kappa}(\mathbf{R}) \\ E_{\kappa}(\mathbf{R}) \Theta_{\kappa}(\mathbf{R}) + \int \Psi_{\kappa}^*(\mathbf{r}, \mathbf{R}) H^n \Psi_{\kappa}(\mathbf{r}, \mathbf{R}) \Theta_{\kappa}(\mathbf{R}) d\mathbf{r} &= E^{en} \Theta_{\kappa}(\mathbf{R}) \end{aligned} \quad (6.4)$$

In the last step, we have again utilized that $\Theta_{\kappa}(\mathbf{R})$ does not depend on \mathbf{r} , and the electronic Hamiltonian H only operates on $\Psi_{\kappa}(\mathbf{r}, \mathbf{R})$ resulting in $H\Psi_{\kappa}(\mathbf{r}, \mathbf{R}) = E\Psi_{\kappa}(\mathbf{r}, \mathbf{R})$ where E is the total energy of the electronic

[†] A general wavefunction can be expanded in $\Psi^{en}(\mathbf{r}, \mathbf{R}) = \sum_k \Psi_k(\mathbf{r}, \mathbf{R})\Theta_k(\mathbf{R})$. This yields a more correct solution, but with standard approximations the final BOA expression is the same as derived here.

wave function. Since $\Psi_\kappa(\mathbf{r}, \mathbf{R})$ depends indirectly on positions of nuclei, also the electronic energy depends indirectly on positions, and we indicate this by writing $E_\kappa = E_\kappa(\mathbf{R})$. The second term can be simplified by taking the derivative of the product

$$\begin{aligned} \Psi_\kappa^*(\mathbf{r}, \mathbf{R}) \nabla_\alpha^2 \Psi_\kappa(\mathbf{r}, \mathbf{R}) \Theta_\kappa(\mathbf{R}) \\ = \Psi_\kappa^*(\mathbf{r}, \mathbf{R}) \left\{ \Psi_\kappa(\mathbf{r}, \mathbf{R}) \nabla_\alpha^2 + 2 \nabla_\alpha \Psi_\kappa(\mathbf{r}, \mathbf{R}) \nabla_\alpha + \left(\nabla_\alpha^2 \Psi_\kappa(\mathbf{r}, \mathbf{R}) \right) \right\} \Theta_\kappa(\mathbf{R}), \end{aligned} \quad (6.5)$$

which results in

$$\begin{aligned} E(\mathbf{R}) \Theta_\kappa(\mathbf{R}) + \{ T + T' + T'' + U_{\alpha\alpha} \} \Theta_\kappa(\mathbf{R}) &= E_\kappa^{en} \Theta_\kappa(\mathbf{R}) \\ \Rightarrow \{ T + T' + T'' + U_{\alpha\alpha} + E(\mathbf{R}) \} \Theta_\kappa(\mathbf{R}) &= E_\kappa^{en} \Theta_\kappa(\mathbf{R}) \end{aligned} \quad (6.6)$$

where

$$\begin{aligned} T_\alpha &= - \sum_{\alpha=1}^{N_n} \frac{\hbar^2}{2m_\alpha} \nabla_\alpha^2 \\ T'_\alpha &= - \sum_{\alpha=1}^{N_n} \frac{\hbar^2}{2m_\alpha} 2 \int \Psi_\kappa^*(\mathbf{r}, \mathbf{R}) \nabla_\alpha \Psi_\kappa(\mathbf{r}, \mathbf{R}) d\mathbf{r} \nabla_\alpha \\ T''_\alpha &= - \sum_{\alpha=1}^{N_n} \frac{\hbar^2}{2m_\alpha} \int \Psi_\kappa^*(\mathbf{r}, \mathbf{R}) \nabla_\alpha^2 \Psi_\kappa(\mathbf{r}, \mathbf{R}) d\mathbf{r} \\ U_{\alpha\alpha} &= \sum_{\alpha \neq \alpha'}^{N_n} \frac{q^2 Z_\alpha Z_{\alpha'}}{|\mathbf{R}_\alpha - \mathbf{R}_{\alpha'}|} \end{aligned} \quad (6.6)$$

If we neglect T' and T'' , we obtain the common Born-Oppenheimer approximation (BOA)

$$\{ T_j + U_{jj} + U_{j\alpha} \} \Psi_\kappa(\mathbf{r}, \mathbf{R}) = E_\kappa(\mathbf{R}) \Psi_\kappa(\mathbf{r}, \mathbf{R}) \quad = \text{electronic Schrödinger eq.} \quad (6.7)$$

$$\{ T_\alpha + U_{\alpha\alpha} + E_\kappa(\mathbf{R}) \} \Theta_\kappa(\mathbf{R}) = E_\kappa^{en} \Theta_\kappa(\mathbf{R}) \quad = \text{nuclear Schrödinger eq.} \quad (6.8)$$

These two equations are coupled via the total electronic energy $E_\kappa(\mathbf{R})$ for the κ :th eigenstate. That is, the total energy in the electronic Schrödinger equation is a potential in the nuclear Schrödinger equation.

Notice, the nucleus-nucleus interaction $U_{\alpha\alpha}$ depends only on nuclear the positions $U_{\alpha\alpha} = U_{\alpha\alpha}(\mathbf{R})$. This interaction can be calculated relatively easily since we assume point-like charges. This interaction is actually sometimes included in the electronic Schrödinger equation. The main reason is that one normally is not interested in the kinetic energy of the nuclei, and therefore by incorporating $U_{\alpha\alpha}$ in Eq. (6.7) one can determine the total energy without solving the nuclear equation.

6.2 Potential energy surface (PES)

$E_\kappa(\mathbf{R})$ depends indirectly on the configuration of the nuclei. By nuclear configuration, we mean the positions $\mathbf{R} = \{\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{N_n}\}$ of all the N_n nuclei. As discussed above, $E_\kappa(\mathbf{R})$ is the total electronic energy [Eq. (6.7)], but it also acts as a potential energy operator in the nuclear equation [Eq. (6.8)].

The total potential energy operator in Eq. (6.8) is $U_{\alpha\alpha}(\mathbf{R}) + E_\kappa(\mathbf{R})$. We therefore define the potential energy surface (PES) as $E_P(\mathbf{R}) = U_{\alpha\alpha}(\mathbf{R}) + E_\kappa(\mathbf{R})$. This potential energy surface is very important when we want to relax the atom positions of a crystalline structure or analyze crystal phase stability. Since the kinetic energy of the nuclei is zero in our model, the most stable crystal structure is found for the nuclear configuration with the lowest potential energy $E_P(\mathbf{R})$.

The potential energy surface is important when analyzing for instance chemical interaction, adsorption, or vibrations of atoms. For these dynamic properties, it may sound as we include a time-aspect in the calculations. However, we will not allow the atoms to move over time. Instead, we calculate $E_P(\mathbf{R})$ for

different set of static nuclear configurations and draw conclusions from that. For example, the vibration frequency of a carbon-oxygen molecule can be determined from $\partial^2 E_p(\mathbf{R})/\partial \mathbf{r}_{\text{CO}}^2$ in the harmonic approximation where \mathbf{r}_{CO} is the distance between the C and O atoms (see Chapt. 5 in the DFT-book).

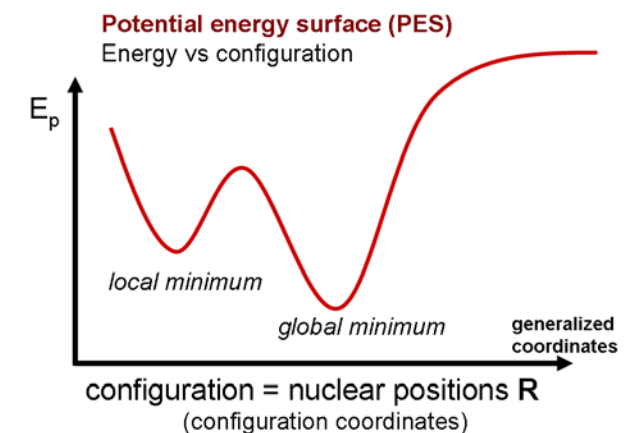


Fig. 6.1: Schematic figure of the potential energy surface, describing the total energy for different positions of the nuclei. The energy is obtained from the nuclear Schrödinger equation Eq. (6.8), where $E_\kappa(\mathbf{R})$ is the electronic energy from Eq. (6.7).

6.3 Forces on the atoms

From the potential energy surface $E_P(\mathbf{R})$ we can directly calculate the forces on the atoms (or on the nuclei). Classically, the force \mathbf{F}_α on α :th nuclei is defined by Newton's second law $\mathbf{F}_\alpha = \mathbf{a}_\alpha m_\alpha = \partial^2 \mathbf{R}_\alpha / \partial t^2$, but also from the work W done by the force $W = -\Delta V = \int \mathbf{F}_\alpha d\mathbf{R}_\alpha$. Since $\Delta V = \Delta E_P(\mathbf{R})$ is the change in the potential, we can determine the force from

$$\mathbf{F}_\alpha = -\nabla_\alpha E_P(\mathbf{R}). \quad (6.9)$$

6.4 Pros and cons of the BOA

The main advantage with the BOA is

- We do not have to solve the Schrödinger equation for electrons and nuclei simultaneously.
- Describing the nuclei as fixed point-charges, and thereby including the electron-nucleus interactions as a time-independent external potential significantly simplifies also the derivation of the Kohn-sham equation.

The disadvantage with the BOA is that

- We have decoupled the electronic and the nuclei parts of the Schrödinger equations. It means that it is difficult to calculate how the electronic wavefunction is affected when the nuclei moves. For instance, we cannot directly describe the electron-phonon coupling wherein the electrons interact with the nuclei vibrations.
- We have neglected the T' and T'' terms in the equation.

7 The density functional theory (DFT)

As we discussed in Section 4, one fundamental problem when trying to solve the many-electron Schrödinger equation is that we do not know how the full wavefunction depends on the single-electron functions $\Psi_\kappa(\mathbf{r}) \equiv \Psi_\kappa(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N_e}) = f(\psi_1, \psi_2, \psi_3, \dots, \psi_{N_e})$. How can we overcome this problem? Is there any method that determines the material properties only by knowing the full many-electron eigenfunction $\Psi_\kappa(\mathbf{r})$, and not $\psi_j(\mathbf{r})$? For instance, is there any Hamiltonian that can operate directly on the many-electron eigenfunction, that is $H\Psi_\kappa = E_\kappa\Psi_\kappa$? If so, such Hamiltonian must probably be very complex, because it shall be capable to describe $\Psi_\kappa(\mathbf{r})$ for various types of systems with very different electron distributions, for instance solids, surface structure, nanostructures, liquids, gases, molecules, *etc.* The Hamiltonian operating on $\Psi_\kappa(\mathbf{r})$ must to be able to determine the total energy E_κ for all these different types of systems.

The density functional theory (DFT) is actually an approach for this. The theory states that all physical ground-state properties of the many-electron system are unique functionals of the density. That is, by knowing the ground-state density $n_0(\mathbf{r}) = |\Psi_0(\mathbf{r})|^2$, it shall be possible to determine the total energy, magnetic moment, heat capacity, *etc.*, of the material.

In other words, all material ground-state properties are completely determined from the ground-state density, and thus, we can work with $n(\mathbf{r})$ instead of $\Psi_\kappa(\mathbf{r})$. One major advantage is that many-electron eigenfunction $\Psi_\kappa(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N_e})$ of an N_e -electron system includes $3N_e$ variables, whereas the density $n(\mathbf{r})$, no matter how large the system is, has only 3 variables (x , y , and z). Therefore, utilizing the functional of the density will significantly reduce the computational efforts.

However, even if the DFT states that it is possible to work with $n(\mathbf{r})$, we have not to date a derived expression that solves the many-particle equation within the original DFT. Nevertheless, we will discuss the DFT since it is the foundation for the very well-used Kohn-Sham equation (Chapter 8)

7.1 Hohenberg-Kohn's theorems

The DFT is based on two main theorems, called the Hohenberg-Kohn theorems.

The first theorem: the density of the system determines all *ground-state* properties of that system. For instance, the total ground-state energy $E_0 = E[n_0]$ where $n_0(\mathbf{r}) = |\Psi_0(\mathbf{r})|^2$ is the ground-state density. All ground-state properties of the many-body system are determined by the ground state density $n_0(\mathbf{r})$. Each property is thus a functional $f[n]$ and the ground-state property is obtained from $f[n_0]$.

The theorem states that the external potential $V_{en}(\mathbf{r})$ for any system of electrons is determined uniquely (except for a constant) by the ground-state density $n_0(\mathbf{r})$. This implies that if the ground-state density $n_0(\mathbf{r})$ is known, the external potential $V_{en}(\mathbf{r})$ is known, and therefore also H is known. In turn, also eigenfunction $\Psi_0(\mathbf{r})$ is known. Hence, all ground-state properties are determined from $n_0(\mathbf{r})$.

Proof: Assume that two external potentials $[V_{en}(\mathbf{r}) \text{ and } V_{en}'(\mathbf{r}) \neq V_{en}(\mathbf{r}) + \text{constant}]$ have the same ground-state density $n_0(\mathbf{r})$. The two potentials leads to two different Hamiltonian (H and H') having different ground-state eigenfunctions $[\Psi_0(\mathbf{r}) \text{ and } \Psi_0'(\mathbf{r})]$ with different eigenvalues $[E_0(\mathbf{r}) \text{ and } E_0']$. Since they are ground states, we know that

$$\begin{aligned} E_0 &= \langle \Psi_0 | H | \Psi_0 \rangle < \langle \Psi_0' | H | \Psi_0' \rangle \\ E_0' &= \langle \Psi_0' | H' | \Psi_0' \rangle < \langle \Psi_0 | H' | \Psi_0 \rangle. \end{aligned} \quad (7.1)$$

Then,

$$\begin{aligned}
E_0 &= \langle \Psi_0 | H | \Psi_0 \rangle = \langle \Psi_0 | T + U_{ee} + U_{en} | \Psi_0 \rangle \\
&= \langle \Psi_0 | T + U_{ee} | \Psi_0 \rangle + \int \Psi_0^*(\mathbf{r}) V_{en}(\mathbf{r}) \Psi_0(\mathbf{r}) d\mathbf{r} \\
&= \langle \Psi_0 | T + U_{ee} | \Psi_0 \rangle + \int V_{en}(\mathbf{r}) n_0(\mathbf{r}) d\mathbf{r} \\
&< \langle \Psi'_0 | H | \Psi'_0 \rangle = \langle \Psi'_0 | T + U_{ee} + U_{en} | \Psi'_0 \rangle \\
&= \langle \Psi'_0 | T + U_{ee} + U'_{en} + (U_{en} - U'_{en}) | \Psi'_0 \rangle \\
&= \langle \Psi'_0 | T + U_{ee} + U'_{en} | \Psi'_0 \rangle + \int (V_{en}(\mathbf{r}) - V'_{en}(\mathbf{r})) n_0(\mathbf{r}) d\mathbf{r} \\
&= \langle \Psi'_0 | H' | \Psi'_0 \rangle + \int (V_{en}(\mathbf{r}) - V'_{en}(\mathbf{r})) n_0(\mathbf{r}) d\mathbf{r} \\
&= E'_0 + \int (V_{en}(\mathbf{r}) - V'_{en}(\mathbf{r})) n_0(\mathbf{r}) d\mathbf{r}.
\end{aligned} \tag{7.2}$$

Thus,

$$E_0 < E'_0 + \int (V_{en}(\mathbf{r}) - V'_{en}(\mathbf{r})) n_0(\mathbf{r}) d\mathbf{r} \tag{7.3}$$

and similarly, using the second equation in Eq. (7.1) we can also derive

$$E'_0 < E_0 + \int (V'_{en}(\mathbf{r}) - V_{en}(\mathbf{r})) n_0(\mathbf{r}) d\mathbf{r}. \tag{7.4}$$

By adding right hand side and adding left hand side, one obtains $E_0 + E'_0 < E_0 + E'_0$ and that is a contradiction. Thus, two external potentials cannot have the same ground-state density, and $V_{en}(\mathbf{r})$ is determined uniquely (except for a constant) by $n_0(\mathbf{r})$.

Notice that $V_{en}(\mathbf{r})$ is the potential which the electrons feel due to the presence of nuclei. This potential is here regarded as an external potential, i.e., $V_{en}(\mathbf{r}) = V_{ext}(\mathbf{r})$. However, in a more general case, the external potential can include also a contribution from an external source.

The second theorem: there exists a variational principle for the energy density functional such that, if n is not the ground-state density, then $E[n_0] < E[n]$.

That is, there exists a universal function for the energy $E[n]$ of the density $n(\mathbf{r})$ for any $V_{en}(\mathbf{r}) = V_{ext}(\mathbf{r})$, i.e., all electron systems. For a given $V_{en}(\mathbf{r})$, the exact ground-state energy E_0 is the global minimum, and the density $n(\mathbf{r})$ that minimizes this energy functional is the exact ground-state density $n_0(\mathbf{r})$.

Proof: According to the first theorem, all ground-state properties are uniquely determined from $n(\mathbf{r})$, and therefore each such property can be viewed as a functional. For instance, the kinetic energy and the potential energies are functionals of the density. We can thereby divide the energy functional into

$$E[n] = T[n] + U_{ee}[n] + U_{en}[n], \tag{7.5}$$

where $T[n]$, $U_{ee}[n]$, and $U_{en}[n]$ are the energy functionals from the kinetic energy, electron-electron interactions, and the external nuclei-electron interactions. Since

$$U_{en}[n] = \int \Psi^*(\mathbf{r}) V_{en}(\mathbf{r}) \Psi(\mathbf{r}) d\mathbf{r} = \int V_{en}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}, \tag{7.6}$$

we can write

$$E[n] = T[n] + U_{ee}[n] + \int V_{en}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}. \tag{7.7}$$

The two first terms together are called the Hohenberg-Kohn functional $F[n]$.

$$E[n] = F[n] + \int V_{en}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \quad \text{with } F[n] = T[n] + U_{ee}[n]. \tag{7.8}$$

Since $F[n]$ does not depend on the external potential $V_{en}(\mathbf{r})$, it has to be universal according to the first theorem. That is, $F[n]$ has the same form/expression for all systems of electrons.

Now, consider the ground-state density $n_0(\mathbf{r})$ that corresponds to $V_{en}(\mathbf{r})$. Knowing $V_{en}(\mathbf{r})$, we know H , and thus the corresponding ground-state eigenfunction $\Psi_0(\mathbf{r})$ is determined. Assume also a different density $n(\mathbf{r})$ that corresponds to the wavefunction $\Psi(\mathbf{r})$ which is not the ground state. Then

$$E_0 = E[n_0] = \langle \Psi_0 | H | \Psi_0 \rangle < \langle \Psi | H | \Psi \rangle = E[n]. \quad (7.9)$$

The total energy of the ground-state density $n_0(\mathbf{r})$ is lower than for any other densities $n(\mathbf{r})$. We can therefore find the correct ground-state density by minimizing the energy with respect to the density, for instance by utilizing the variational method

$$\frac{\delta}{\delta n(\mathbf{r})} \{E[n] - \lambda g\} = \frac{\delta}{\delta n(\mathbf{r})} \{E[n] - \lambda \left(\int n(\mathbf{r}) d\mathbf{r} - N_e \right)\} = 0 \quad \Rightarrow \quad \frac{\delta}{\delta n(\mathbf{r})} E[n] = \lambda \quad (7.10)$$

with the constraint that the density shall include the correct number of electrons.

Alternatively, one can obtain the ground-state energy from

$$E_0 = \min_{n(\mathbf{r}) \rightarrow n_0(\mathbf{r})} \langle \Psi | H | \Psi \rangle, \quad (7.11)$$

with normalized wavefunctions. In this approach, the Levy-Lieb theory allows also a search for the energy utilizing the many-electron wavefunction

$$E_0 = \min_{\Psi(\mathbf{r}) \rightarrow \Psi_0(\mathbf{r})} \langle \Psi | H | \Psi \rangle. \quad (7.12)$$

The two DFT theorems are rather simple, but very powerful. Without saying anything about the electronic system, the first theorem states that it is possible to obtain the total energy from the density. The second theorem provides a method to find the correct density via a minimization procedure.

To conclude, there exists a universal function for the energy $E[n]$ of the density $n(\mathbf{r})$ for all electron systems. The exact ground-state energy is the global minimum for a given $V_{en}(\mathbf{r})$, and the density which minimize this functional is the exact ground-state density $n_0(\mathbf{r})$.[†]

However, the Hohenberg-Kohn theorems do not tell us the form of $E[n]$. That is, the expression of the functional $E[n]$ is unknown. It exist a unique expression for $E[n]$, but we do not have it today. Since the Hohenberg-Kohn functional $F[n]$ in Eq. 7.8 does not depend on external potential, there is a unique expression that depends only on the electron density. That is, if we find the correct expression for $F[n]$, then we can calculated the many-particle problem for any system. Most likely, the expression of $F[n]$ must be very complicated since it shall be able to describe different types of systems (solids, liquids, molecules, etc).

7.2 Pros and cons of the DFT

The advantages of the DFT are

- It is an exact theory of many-electron systems.
- It describes any electronic system, thus electrons is metals, insulators, molecules, liquids, *etc, etc*. It has been proven that the functional $F[n]$ is a unique functional of the electron density $n(\mathbf{r})$, and thus there exists a unique expression that can be employed for any electronic system.
- The theory states that it is possible to obtain the ground-state properties from the density alone, without knowing anything about the single-electron wavefunctions.

[†] (i) The first theorem was originally derived by assuming non-degenerate ground states, but a different way of formulating the DFT allows also degenerate states. (ii) The original proof was made for *some* external potential, which restricts the space of possible ground-state densities. It is not proven that the minimization procedure [involving variation of $n(\mathbf{r})$] will generate the ground-state density of the external potential (called V-representable). (iii) One has also questioned if the density is arising from an anti-symmetric wavefunction (N-representability) but that has be proven to not be a problem.

DFT has problematic disadvantages

- The main issue is of course that we do not know (to date) the explicit expression of $F[n]$.
- DFT does not generate the single-electron eigenfunctions and their energies.

Thus, the main problem in the DFT is that we do not have the explicit expression for the energy function $E[n_0]$ in terms of the ground-state density $n_0(\mathbf{r})$. So, did we gain anything by deriving the DFT? Well, we actually gained much information. We now know that if we find the correct ground-state density, then we also have a possibility to get the exact ground-state energy. This knowledge is used in the Kohn-Sham equation that is described in the next Chapter.

8 The Kohn-Sham equation (KS-eq)

The DFT states that the total ground-state energy $E[n_0]$ can, in principle, be determined exactly once we have found the exact density $n_0(\mathbf{r})$. The problem is that we do not know how to express the energy in terms of the density. However, if it is possible to generate the exact ground-state density with some other method, then the DFT guarantees that the corresponding total energy is the exact ground-state energy. This is the underlying idea of the Kohn-Sham (KS) equation.

8.1 Ansatz and derivation

Start with an arbitrary many-electron system. Assume that we can generate the exact ground-state density $n_0(\mathbf{r})$ by using a Hartree-like total wavefunction $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{Ne}) = \psi_1^{KS}(\mathbf{r}_1) \psi_2^{KS}(\mathbf{r}_2) \psi_3^{KS}(\mathbf{r}_3) \dots \psi_{Ne}^{KS}(\mathbf{r}_{Ne})$ where $\psi_j^{KS}(\mathbf{r}_j)$ are some auxiliary independent single-particle wavefunctions.[†]

With these simple auxiliary wavefunctions, the density is given by

$$n(\mathbf{r}) = \sum_j |\psi_j^{KS}(\mathbf{r})|^2 \quad (8.1)$$

By our ansatz, the density is exact even though the KS wavefunctions are not the true/correct single-particle wavefunctions

Since the density is exact, DFT ensures that the total energy can be described exactly as

$$E[n] = F[n] + \int V_{en}(\mathbf{r})n(\mathbf{r})d\mathbf{r} = T[n] + U_{ee}[n] + U_{en}[n]. \quad (8.2)$$

$T[n]$ is the kinetic energy of the many-electron system, and $U_{ee}[n]$ is the many-electron interaction energy. These functionals are unique, but unknown to date. Thus, even if we have the exact density we are not capable to calculate the exact energy.

Now, the trick in the KS theory is that we rewrite the expression as

$$E[n] = T_s[n] + U_s[n] + U_{en}[n] + \{(T[n] - T_s[n]) + (U_{ee}[n] - U_s[n])\}. \quad (8.3)$$

Here, $T_s[n]$ and $U_s[n]$ are the kinetic and interaction energy of the auxiliary wavefunction $\Psi(\mathbf{r}) = \psi_1^{KS}(\mathbf{r}_1) \psi_2^{KS}(\mathbf{r}_2) \psi_3^{KS}(\mathbf{r}_3) \dots \psi_{Ne}^{KS}(\mathbf{r}_{Ne})$. $U_{en}[n]$ is the electron-nucleus interaction. These three terms (*i.e.*, $T_s[n]$, $U_s[n]$, and $U_{en}[n]$) are something that we relatively easily can calculate exactly. The remaining part will be defined as the exchange-correlation energy

$$E_{xc}[n] = \Delta T + \Delta U = (T[n] - T_s[n]) + (U_{ee}[n] - U_s[n]). \quad (8.4)$$

This exchange-correlation energy contains the complex many-electron interaction, but it also contains a kinetic energy part (this fact is often forgotten when discussing the corrections). We have transformed the many-electron problem in Eq. (8.2) into an unknown exchange-correlation energy $E_{xc}[n]$. $E_{xc}[n]$ is zero for a non-interacting system, but for a general system the energy has most likely very complicated expression. Our aim is to find a good approximation to this term.

The total energy is

$$E[n] = T_s[n] + U_s[n] + U_{en}[n] + E_{xc}[n]. \quad (8.5)$$

where

$$T_s[n] = \sum_j \int \psi_j^{KS*} \frac{-\hbar^2 \nabla^2}{2m} \psi_j^{KS} d\mathbf{r} \quad : \text{kinetic energy in the Hartree approx.} \quad (8.6)$$

[†] We could also have started from a Hartree-Fock like wavefunction. Then, we would have found a corresponding Kohn-Sham equation where exchange interaction is included in a potential $V_{HF}(\mathbf{r})$, and the remaining correlation energy is unknown.

$$\begin{aligned}
U_s[n] &= \frac{1}{2} \int \int q^2 \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' && : \text{electron interaction energy in Hartree approx} \\
U_{en}[n] &= \int V_{en}(\mathbf{r})n(\mathbf{r})d\mathbf{r} && : \text{electron-nucleus interaction energy} \\
E_{xc}[n] &= (T[n] - T_s[n]) + (U_{ee}[n] - U_s[n]). && : \text{exchange-correlation energy (unknown)}
\end{aligned}$$

We have actually done nothing here, apart from rewriting the DFT expression for the total energy. Thus, the expression is exact if $E_{xc}[n]$ is exact. Notice that we have used the Hartree energy where the self-interaction correction the (the $-n_j(\mathbf{r}')$ term in Eqs. 4.11 and 4.21) is neglected, and this correction shall thus be included in the exchange correlation term. The exchange-correlation energy can be regarded as the “left-over energy” that includes everything that we do not describe with T_s , U_s , and U_{en} .

Just like for the Hartree approximation (see Chapt. 4.3), the next step is to use the variational method to find the ground-state energy, and to transform the many-electron system into many single-particle equations. Since we will calculate density and kinetic energy from the single-electron wavefunctions, we minimize the total energy with respect to $\psi_j^{KS}(\mathbf{r}_j)$, just like for the Hartree approximation. The constraint is that the wavefunctions shall be orthonormalized

$$\frac{\delta}{\delta \psi_j^{KS*}(\mathbf{r})} \left\{ E[n] - \sum_{i,i'} \lambda_{ii'} \left(\int \psi_i^{KS*}(\mathbf{r}_i) \psi_{i'}^{KS}(\mathbf{r}_{i'}) d\mathbf{r}_i d\mathbf{r}_{i'} - \delta_{ii'} \right) \right\} = 0. \quad (8.7)$$

We express the total energy functional in the kinetic, electron-electron and electron-nuclei parts

$$\frac{\delta}{\delta \psi_j^{KS*}(\mathbf{r})} \{ T_s[n] + U_s[n] + V_{en}[n] + E_{xc}[n] \} = \lambda_j \psi_j^{KS}(\mathbf{r}_j). \quad (8.8)$$

It is convenient to derivate the kinetic energy with respect to the wavefunction, whereas the two remaining functionals are easiest to derivate with respect to the density, utilizing the chain rules for functional derivatives

$$\begin{aligned}
\frac{\delta}{\delta \psi_j^{KS*}(\mathbf{r})} T[n] + \frac{\delta}{\delta n(\mathbf{r})} \{ U_{ee}[n] + V_{en}[n] + E_{xc}[n] \} \frac{\delta n(\mathbf{r})}{\delta \psi_j^{KS*}(\mathbf{r})} &= \lambda_j \psi_j^{KS}(\mathbf{r}), \text{ where} \\
\frac{\delta n(\mathbf{r})}{\delta \psi_j^{KS*}(\mathbf{r})} &= \frac{\delta}{\delta \psi_j^{KS*}(\mathbf{r})} \sum_j \psi_j^{KS*}(\mathbf{r}) \psi_j^{KS}(\mathbf{r}) = \psi_j^{KS}(\mathbf{r}).
\end{aligned} \quad (8.9)$$

Thus, we shall minimize

$$\frac{\delta}{\delta \psi_j^{KS*}(\mathbf{r})} T[n] + \frac{\delta}{\delta n(\mathbf{r})} \{ U_{ee}[n] + V_{en}[n] + E_{xc}[n] \} \psi_j^{KS}(\mathbf{r}) = \lambda_j \psi_j^{KS}(\mathbf{r}). \quad (8.10)$$

The variation is very similar as for the Hartree equation (Chapt. 4.3) apart from that the variation of the exchange-correlation energy. Therefore, we can directly write down the results as

$$\left\{ -\frac{\hbar^2}{2m_e} \nabla_j^2 + \int \sum_{j' \neq j} \psi_{j'}^{KS*}(\mathbf{r}') \left\{ \frac{q^2}{|\mathbf{r}-\mathbf{r}'|} \right\} \psi_{j'}^{KS}(\mathbf{r}') d\mathbf{r}' + V_{en}(\mathbf{r}) + \frac{\delta E_{xc}[n]}{\delta n} \right\} \psi_j^{KS}(\mathbf{r}) = \varepsilon_j^{KS} \psi_j^{KS}(\mathbf{r}) \quad (8.11)$$

Now we define the exchange-correlation potential as $V_{xc}(\mathbf{r}) = \delta E_{xc}[n] / \delta n$

$$\left\{ -\frac{\hbar^2}{2m_e} \nabla_j^2 + \int \sum_{j' \neq j} \psi_{j'}^{KS*}(\mathbf{r}') \left\{ \frac{q^2}{|\mathbf{r}-\mathbf{r}'|} \right\} \psi_{j'}^{KS}(\mathbf{r}') d\mathbf{r}' + V_{en}(\mathbf{r}) + V_{xc}(\mathbf{r}) \right\} \psi_j^{KS}(\mathbf{r}) = \varepsilon_j^{KS} \psi_j^{KS}(\mathbf{r}) \quad (8.12)$$

This is the Kohn-Sham single-electron equation. In practice, for condensed matter one solves this equation in the reciprocal space (see Chapt. 2.5). Notice that we have derived this equation directly from

the DFT, and thus the total energy is exact if the exchange-correlation term $E_{xc}[n]$ is exact. This is somewhat amazing since we have used independent auxiliary wavefunctions $\psi_j^{KS}(\mathbf{r})$. The complex many-electron interaction is included in $V_{xc}(\mathbf{r})$.

To simplify this expression, we will include the self interaction. This is of course an approximation, but it simplifies the calculations considerably

$$\left\{ -\frac{\hbar^2}{2m_e} \nabla_j^2 + \int \sum_j \psi_j^{KS*}(\mathbf{r}') \left\{ \frac{q^2}{|\mathbf{r} - \mathbf{r}'|} \right\} \psi_j^{KS}(\mathbf{r}') d\mathbf{r}' + V_{en}(\mathbf{r}) + V_{xc}(\mathbf{r}) \right\} \psi_j^{KS}(\mathbf{r}) = \varepsilon_j^{KS} \psi_j^{KS}(\mathbf{r}) \quad (8.13)$$

$$\Rightarrow \left\{ -\frac{\hbar^2}{2m_e} \nabla_j^2 + \int q^2 \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{en}(\mathbf{r}) + V_{xc}(\mathbf{r}) \right\} \psi_j^{KS}(\mathbf{r}) = \varepsilon_j^{KS} \psi_j^{KS}(\mathbf{r}) \quad (8.14)$$

$$\Rightarrow \left\{ -\frac{\hbar^2}{2m_e} \nabla_j^2 + V_H(\mathbf{r}) + V_{en}(\mathbf{r}) + V_{xc}(\mathbf{r}) \right\} \psi_j^{KS}(\mathbf{r}) = \varepsilon_j^{KS} \psi_j^{KS}(\mathbf{r})$$

$$\Rightarrow \left\{ -\frac{\hbar^2}{2m_e} \nabla_j^2 + V_{eff}(\mathbf{r}) \right\} \psi_j^{KS}(\mathbf{r}) = \varepsilon_j^{KS} \psi_j^{KS}(\mathbf{r}),$$

with $V_{eff}(\mathbf{r}) = V_H(\mathbf{r}) + V_{en}(\mathbf{r}) + V_{xc}(\mathbf{r})$. This is the KS equation (with self-interaction error).

Eq. (8.13) does not give us the total energy. We need an additional expression for that. Just like for the Hartree equation, we derive an expression for the total energy that does not contain wavefunctions. Thus, we shall eliminate the kinetic energy. This is done by combining

$$\begin{aligned} E[n] &= T_s[n] + U_s[n] + U_{en}[n] + E_{xc}[n] \\ &= \int \sum_j \psi_j^{KS*}(\mathbf{r}) \left\{ -\frac{\hbar^2}{2m_e} \nabla^2 \right\} \psi_j^{KS}(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \iint q^2 \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + \int V_{en}(\mathbf{r})n(\mathbf{r})d\mathbf{r} + E_{xc}[n] \end{aligned} \quad (8.15)$$

with the single-electron equations, multiply by $\sum_j \psi_j^*(\mathbf{r})$ on the left

$$\begin{aligned} \sum_j \int \psi_j^{KS*} \left\{ -\frac{\hbar^2}{2m_e} \nabla^2 + V_{ne}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}) \right\} \psi_j^{KS} d\mathbf{r} &= \sum_j \int \psi_j^{KS*} \varepsilon_j^{KS} \psi_j^{KS} d\mathbf{r} \\ \int \sum_j \psi_j^{KS*}(\mathbf{r}) \left\{ -\frac{\hbar^2}{2m_e} \nabla^2 + \int q^2 \frac{n(\mathbf{r}') - n_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{en}(\mathbf{r}) + V_{xc}(\mathbf{r}) \right\} \psi_j^{KS}(\mathbf{r}) d\mathbf{r} &= \sum_j \varepsilon_j^{KS}. \end{aligned} \quad (8.16)$$

The kinetic part is eliminated by subtracting Eq. (8.13) and (8.12), and one obtains

$$E[n] = \sum_j \varepsilon_j^{KS} - \frac{1}{2} \iint q^2 \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{xc}[n] - \int V_{xc}(\mathbf{r})n(\mathbf{r})d\mathbf{r} \quad (8.17)$$

We have thus proven that it is possible to generate the exact total energy (if $E_{xc}[n]$ is exact), using Hartree-like single-electron equations. Notice that this expression for the total energy is equal to the Hartree total energy if $E_{xc}[n] = 0$. It may look like the total energy in Eq. (8.17) depends only on the density (and not on the wavefunction $\psi_j^{KS}(\mathbf{r})$), and that therefore should have derived a pure DFT expression. However, the single-electron energies ε_j^{KS} cannot be determined from the density alone, and we indirectly need the wavefunctions $\psi_j^{KS}(\mathbf{r})$. Thus, even though the Kohn-Sham equation is based on the DFT, the approach is not a full DFT method; it is a combination of the DFT and the Hartree approach.

Notice that this equation is very similar to the Hartree approximation. Above, we have used Hartree-like wavefunction to describe the single-particle wavefunctions $\Psi(\mathbf{r}) = \psi_1^{KS}(\mathbf{r}_1)\psi_2^{KS}(\mathbf{r}_2)\psi_3^{KS}(\mathbf{r}_3)\dots\psi_{Ne}^{KS}(\mathbf{r}_{Ne})$. We know from the Chapter 4 that the Hartree approximation with true single-particle wavefunctions cannot generate the exact result. Therefore, the present auxiliary single-particle wavefunctions cannot be the true single-particle wavefunctions. Instead, we shall regard the auxiliary wavefunctions as functions

that help us generating the exact ground-state density and the exact total energy. There is an important difference between the Hartree approximation and the KS equation: the KS equation includes the correct exchange and correlation energies $E_{xc}[n]$. The Hartree can never become exact (since it using incorrect wavefunction, though correct Hamiltonian), whereas the KS equation is exact if the exchange-correlation energy is exact (although incorrect wavefunction).

Therefore, the “only” thing we have to do now is to find exact $E_{xc}[n]$ as functional of the density $n(\mathbf{r})$. With such expression, we can derive with respect to density to generate $V_{xc}(\mathbf{r}) = \partial E_{xc}[n]/\partial n$. Since we have not the exact expression of $E_{xc}[n]$, we need an approximation to it

8.2 Local density approximation

The Kohn-Sham equation generates the exact total energy if $E_{xc}[n]$ is exact. This exchange-correlation functional has to be very complex in order to exactly describe various types of many-electron systems, and $E_{xc}[n]$ is not (to date) derived. In the local density approximation (LDA), one approximates the exact $E_{xc}[n]$ with the exchange-correlation of a homogeneous electron gas (free electron gas or "jellium"). The LDA is thus based on the free electron gas.

The free electron gas has a constant electron density $n(\mathbf{r}) = n = N_e/\text{volume}$. The exact exchange-correlation energy is expressed energy per electron

$$\varepsilon_{xc}^{gas}(n) = \frac{-3}{4} \left(\frac{3}{\pi} \right)^{1/3} \cdot n^{1/3} + \begin{cases} A \ln r_s + B + C r_s \ln r_s + D r_s & r_s \leq 1 \\ \gamma / (1 + \beta_1 \sqrt{r_s} + \beta_2 r_s) & r_s > 1 \end{cases}; \quad \text{where} \quad r_s = \left(\frac{3}{4\pi n} \right)^{1/3} \quad (8.18)$$

and the total exchange-correlation energy of the homogeneous electron gas is $E_{xc}^{gas} = \varepsilon_{xc}^{gas}(n) \cdot N_e$.

In the LDA, we assume that locally (in the vicinity of all \mathbf{r} -points) the exchange-correlation energy of one electron in our many-particle system is approximately the same as the exchange-correlation energy of the an electron in the free electron gas (independent of surrounding) with $\varepsilon_{xc}^{gas}(n) \rightarrow \varepsilon_{xc}^{gas}(n(\mathbf{r})) = \varepsilon_{xc}^{gas}(\mathbf{r})$ and

$$E_{xc}^{LDA}[n] = \int \varepsilon_{xc}^{gas}(\mathbf{r}) \cdot n(\mathbf{r}) d\mathbf{r} \quad (8.19)$$

One normally divides the exchange-correlation energy into $E_{xc}[n] = E_x[n] + E_c[n]$. The LDA exchange term is

$$E_x^{LDA}[n] = \int \frac{-3e^2}{4} \left(\frac{3}{\pi} \right)^{1/3} n(\mathbf{r})^{1/3} n(\mathbf{r}) d\mathbf{r} = - \int \frac{3e^2}{4} \left(\frac{3}{\pi} \right)^{1/3} n(\mathbf{r})^{4/3} d\mathbf{r}. \quad (8.20)$$

The corresponding exchange potential is obtained by derivative

$$V_x^{LDA}(\mathbf{r}) = \frac{\partial E_x^{LDA}[n]}{\partial n} = -q^2 \left(\frac{3}{\pi} \right)^{1/3} n(\mathbf{r})^{1/3} \quad (8.21)$$

The LDA is the original approximation for the exchange-correlation potential, however, there exist today hundreds of potentials. There are ongoing developments to derive improved potentials. The advantage with the Kohn-Sham equation is that once a new potential is derived, it can relatively easily be implemented in the equation without changing the underlying theories. This is an advantage, but it also implies that there are today numerous exchange-correlation potentials.

8.3 Self-consistent field calculation

The effective potential $V_{\text{eff}}(\mathbf{r})$ depends on the density $n(\mathbf{r})$. However, the density $n(\mathbf{r}) = \sum_j |\psi_j^{KS}(\mathbf{r})|^2$ depends on the eigenfunctions that directly depends on $V_{\text{eff}}(\mathbf{r})$. This mutual dependence of the potential and the density implies that one cannot calculate the density directly by only knowing the external potential $V_{\text{en}}(\mathbf{r})$. Instead, we have to find the density by an iterative method. That is, first we guess an initial density. Thereafter, we solve the Kohn-Sham equation with gives eigenfunctions $\psi_j^{KS}(\mathbf{r})$ and total energy. From the eigenfunctions, we determine the new density from $n(\mathbf{r}) = \sum_j |\psi_j^{KS}(\mathbf{r})|^2$. From the new density, we determined the new effective potential and solve the Kohn-Sham equation again. We do this procedure until the density $n(\mathbf{r})$ is converged, and that the total energy is as low as possible. Then, we have generated the ground-state density. This approach is thus a self-consistent calculation method.

Since LDA produces an approximated density $n(\mathbf{r})$ to the external potential $V_{\text{xc}}(\mathbf{r})$, the DFT is not exactly valid for LDA. That is, the LDA can produce a density and total energy which is lower that the true ground-state energy. However, by experience we know that LDA [and other approximations to $V_{\text{xc}}(\mathbf{r})$] generate very good densities and total energies.

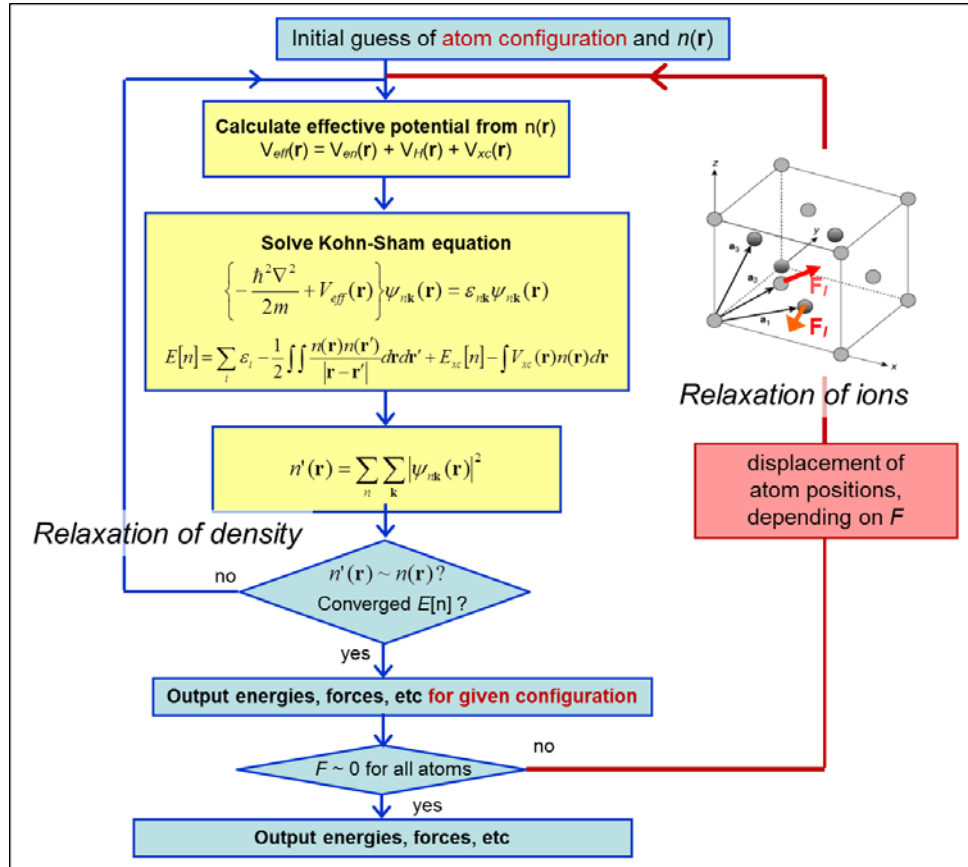


Fig. 8.1: Self-consistent field calculations and relaxation in the DFT/KS approach. In practice, the Kohn-Sham equation is solved in the reciprocal coordinates as discussed in Chapt. 2.5.

8.4 Pros and cons of the KS equation

The KS equation with exact exchange-correlation potential $V_{\text{xc}}(\mathbf{r})$ yields exact total energy, forces, and density. However, even with the exact $V_{\text{xc}}(\mathbf{r})$ the KS eigenstates are not the true electron states. Only the highest occupied state has a physical meaning. Still, it is believed that KS eigenstates are close to the true eigenstates.

DFT/KS in conjunction with LDA has been used in most calculations the last 30 years. The next level in the approximation of $V_{xc}(\mathbf{r})$ is the so called generalized gradient approximation (GGA) wherein also the gradient of the density $V_{xc}(\mathbf{r}) = \nabla n(\mathbf{r})$ is used.

Theories beyond LDA and GGA have normally problem because those calculations are time-costly, memory-costly, and/or numerically less stable. LDA (and GGA) is a very crude approximation, but it has been extremely successful in describing various material properties of metals, semiconductors, nanostructures, big molecules. There are problems with LDA, for instance band-gap energy of semiconductors are normally underestimated by ~50%, and LDA predicts (incorrectly) that ground state of FeAl is magnetic.

DFT (in its original form) is an exact theory for ground states only. Thus, the theory is valid for $T = 0$ K and it cannot describe excitations. However, DFT has been extended for $T > 0$ K (Mermin, Phys. Rev. 137, 1441 (1965)), there exists a fully relativistic DFT (Rajagopal, Phys. Rev. B 7, 1912 (1973)), and DFT has been extended for superconductivity (Oliveira, PRL 60, 2430 (1988)). An extension to a time-dependent density functional theory (TD-DFT) allows us to study time-dependent potentials, such as excitation effect, transport properties, and time-dependent electromagnetic fields (Runge and Gross, PRL 52, 997 (1984)).

The advantages of the KS equation are

- It is an exact theory of the total energy, if/when the exact $V_{xc}(\mathbf{r}) = \partial E_{xc}[n]/\partial n$ is found.
- One can easily implement new approximations to $V_{xc}(\mathbf{r})$ without fundamental changes in the underlying theory.
- It can describe any electronic system, thus electrons in metals, insulators, molecules, liquids, *etc.*

The KS equation has however problematic disadvantages

- The main issue is of course that we do not know (to date) the explicit expression of $E_{xc}[n]$.
- Since we do not have the exact $E_{xc}[n]$, we do not know if the variational method is accurate.
- The KS eigenfunctions are in general not the true single-electron eigenfunctions. However, it is believed that the KS eigenfunctions fairly accurately describes the true eigenfunctions.
- The method uses the single-electron wavefunctions to generate the ground-state properties. Thus, it is in that sense not a full DFT method.

9 Appendices

9.1 The Dirac equation

The Schrödinger equation above is actually valid only for spin-less particles, thus it is not valid for electrons (*i.e.*, spin-1/2 fermion). Moreover, it is a non-relativistic equation. You can see that by the fact there is no speed of light c in the equation.

For electrons, one shall instead use the relativistic Dirac equation

$$i\hbar \frac{\partial}{\partial t} \bar{\psi}(\mathbf{r}, t) = (c\boldsymbol{\alpha}\mathbf{p} + \boldsymbol{\beta}m_e c^2 + V(\mathbf{r}, t)) \bar{\psi}(\mathbf{r}, t). \quad ()$$

\mathbf{p} is the momentum operator, and the equation looks simpler as the traditional Schrödinger equation. However, $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ are vector operators of 4×4 matrices related to the Pauli spin matrices $\boldsymbol{\sigma}$. Moreover, the wavefunction in the Dirac equation has four components $\bar{\psi}(\mathbf{r}, t) = \{\psi_L^\uparrow(\mathbf{r}, t), \psi_L^\downarrow(\mathbf{r}, t), \psi_S^\uparrow(\mathbf{r}, t), \psi_S^\downarrow(\mathbf{r}, t)\}$, therefore called a 4-vector or bi-spinor. The symbols “ \uparrow ” and “ \downarrow ” represent the spin-up and spin-down states, respectively. “ L ” and “ S ” stand for large and small components where the small component is important for velocities near speed of light.

Most computer programs for modeling condensed matter do not employ this Dirac equation, but instead use an approximation called the relativistic Schrödinger equation for electrons. There are a few different ways to make the approximation, and one approach yields the Pauli Hamiltonian

$$i\hbar \frac{\partial}{\partial t} \bar{\psi}(\mathbf{r}, t) = \left(-\frac{\hbar^2 \nabla^2}{2m_e} + V(\mathbf{r}, t) - \frac{\hbar^4 \nabla^4}{8m_e^3 c^2} - \frac{\hbar^2 (\nabla V(\mathbf{r}, t)) \cdot \nabla}{4m_e^2 c^2} - \frac{i\hbar^2 \boldsymbol{\sigma} [\nabla V(\mathbf{r}, t) \times \nabla]}{4m_e^2 c^2} \right) \bar{\psi}(\mathbf{r}, t) \quad ()$$

$$\bar{\psi}(\mathbf{r}, t) = \begin{pmatrix} \psi_L^\uparrow \\ \psi_L^\downarrow \end{pmatrix} \psi(\mathbf{r}, t) = \psi_L^\uparrow = \psi_L^\downarrow.$$

This equation can be derived from the Dirac equation. The two first terms on the right hand side is the standard non-relativistic Schrödinger equation. Third term is the mass-velocity correction. Fourth term is called the Darwin term. The last term describes the spin-orbit coupling. We notice that this relativistic equation turns into the standard Schrödinger equation in the (unphysical) limit of $c \rightarrow \infty$.

In the relativistic Schrödinger equation, the wavefunction $\bar{\psi}(\mathbf{r}, t) = \{\psi^\uparrow(\mathbf{r}, t), \psi^\downarrow(\mathbf{r}, t)\}$ has only two components: the spin-up and spin-down parts (the small component has been neglected). This can be reduced further to contain only a one-component wavefunction if the spin-orbit coupling (fifth term) is neglected, yielding

$$i\hbar \frac{\partial}{\partial t} \psi(\mathbf{r}, t) = \left(-\frac{\hbar^2 \nabla^2}{2m_e} + V(\mathbf{r}, t) - \frac{\hbar^4 \nabla^4}{8m_e^3 c^2} - \frac{\hbar^2 (\nabla V(\mathbf{r}, t)) \cdot \nabla}{4m_e^2 c^2} \right) \psi(\mathbf{r}, t) \quad ()$$

$$\psi(\mathbf{r}, t) = \psi^\uparrow(\mathbf{r}, t) = \psi^\downarrow(\mathbf{r}, t).$$

This approximation is called the scalar-relativistic approximation. Most codes within materials science use today some kind of relativistic Hamiltonian, normally the scalar-relativistic approximation where the spin-orbit coupling can be included in a perturbative way (that is, adding that contribution afterwards).[†]

[†] Spin is actually not a proper quantum number for electrons in materials with periodic boundary condition. There are thus no pure spin-up and spin-down states. Instead the eigenfunctions are in general a mixture of the two spin components. In the scalar-relativistic approximation, however, one assumes pure spin states.

9.2 Lagrange multipliers

Assume we want to minimize (or maximize) the following differentiable function

$$f(x_1, x_2) = 2x_1^2 + 4x_2^2 + 2x_1x_2 \quad \text{with } 0 \leq \{x_1, x_2\} \leq 1.5. \quad (9.1)$$

The minimum of $f(x_1, x_2)$ is determined from the partial derivatives $\partial f(x_1, x_2)/\partial x_1 = 0$ and $\partial f(x_1, x_2)/\partial x_2 = 0$. Since $\partial f/\partial x_1 = 4x_1 + 2x_2$ and $\partial f/\partial x_2 = 8x_2 + 2x_1$ it is easy to see that the minimum is $f(x_1, x_2) = 0$ for the position $\{x_1, x_2\} = \{0, 0\}$; see Fig 9.1(a).

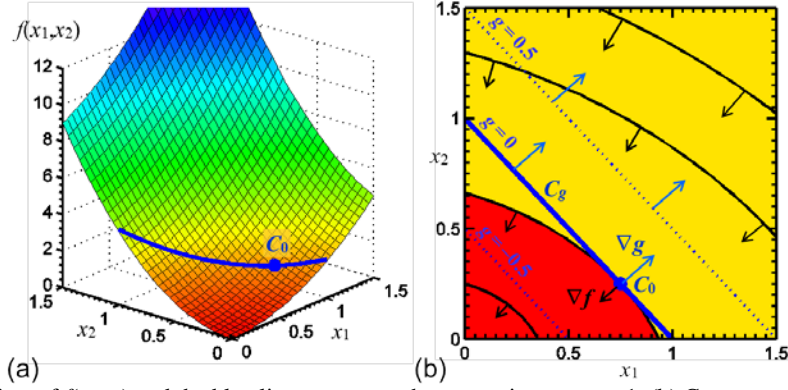


FIG. 9.1: (a) Surface of $f(x_1, x_2)$ and the blue line represents the constraint $x_1 + x_2 = 1$. (b) Corresponding contour plot.

However, assume that we want to minimize the same function with a certain constraint of x_1 and x_2 . Then we can use the so called Lagrange multiplier. For instance, assume that we shall find the minimum of $f(x_1, x_2)$ with the condition that the solution shall be on the line $x_1 + x_2 = 1$. Thus, we shall find minimum of $f(x_1, x_2)$ on the blue line in Fig 9.1(a). Now, we first construct a function $g(x_1, x_2)$ that shall be zero for the specific constraint. In our case $g(x_1, x_2) = x_1 + x_2 - 1 = 0$ is a proper choice (but we could have chosen also for instance $g = [x_1 + x_2]^2 - 1 = 0$). This constraint is represented by the blue line in the figure. If $\{x_1, x_2\}$ is not on the line, then $g(x_1, x_2)$ is not zero. Thereafter, we define the Lagrangian $\Lambda(x_1, x_2, \lambda) = f(x_1, x_2) - \lambda g(x_1, x_2)$ and we minimize that function

$$\frac{\partial}{\partial p} \Lambda(x_1, x_2, \lambda) = \frac{\partial}{\partial p} \{f(x_1, x_2) - \lambda g(x_1, x_2)\} = 0, \quad p = x_1, x_2, \text{ and } \lambda. \quad (9.2)$$

That is,

$$\begin{aligned} \frac{\partial}{\partial x_1} \Lambda(x_1, x_2, \lambda) &= 4x_1 + 2x_2 - \lambda = 0, \\ \frac{\partial}{\partial x_2} \Lambda(x_1, x_2, \lambda) &= 8x_2 + 2x_1 - \lambda = 0, \\ \frac{\partial}{\partial \lambda} \Lambda(x_1, x_2, \lambda) &= -(x_1 + x_2 - 1) = -g(x_1, x_2) = 0. \end{aligned} \quad (9.3)$$

There are three equations and three unknown variables. The solution is $\{x_1, x_2, \lambda\} = \{3/4, 1/4, 7/2\}$ yielding $f(3/4, 1/4) = 7/4$. Notice that $x_1 + x_2 = 1$ is fulfilled as required.

One can verify that this is a local minimum of $f(x_1, x_2)$ by the substitution $x_2 = 1 - x_1$ in Eq. (9.1). The function then becomes $f(x_1, 1-x_1) = 4 - 6x_1 + 4x_1^2$, and the derivative $\partial f(x_1, 1-x_1)/\partial x_1 = -6 + 8x_1$ is zero for $x_1 = 3/4$. Second derivative is a positive number. Thus, $f(x_1, 1-x_1)$ has a minimum at $x_1 = 3/4$.

The Lagrange method can be generalized to include several constraints

$$\frac{\partial}{\partial p} \Lambda(x_1, x_2, \lambda) = \frac{\partial}{\partial p} \left\{ f(x_1, x_2) - \sum_i \lambda_i g_i(x_1, x_2) \right\}, \quad p = x_1, x_2, \text{ and } \lambda. \quad (9.4)$$

Here, λ_i are the Lagrange multipliers, and each $g_i(x_1, x_2) = 0$ represents one constraint. It is also straight forward to generalize the method to involved more variables $p = x_1, x_2, x_3, \dots, x_N$.

Why does it work, and why does $\nabla \Lambda = \nabla f - \lambda \nabla g = 0$ determine the minimum of f for $g = 0$? Figure 9.1(b) illustrates the proof. The black lines in the figure display the contour plot of function f . The gradient ∇f is normal to the contour lines (black arrows).

The blue solid line C_g in the figure describes the constraint $g = x_1 + x_2 - 1 = 0$, and the blue dotted lines show contour lines for unconstrained function $g = x_1 + x_2 - 1$. Thus, the blue lines represent the contour plot of the function g , and the gradient ∇g is normal to the contour lines (blue arrows).

We must assume that f has a local minimum along the line C_g otherwise, the problem is not properly designed. We denote that minimum by C_0 . The value at the minimum is $f(C_0)$. There exists one contour line for f that contains C_0 . From the contour plot we can see that the yellow area represents values of f that are larger than $f(C_0)$ and red area represents values that are smaller than $f(C_0)$. The blue solid line C_g is always in the yellow area except for the point where it touches C_0 . Since the contour lines of f and g touch at C_0 , the corresponding gradients ∇f and ∇g have to be parallel there. Thus, $\nabla f - \lambda \nabla g = 0$ at the minimum $f(C_0)$ for some constant value of λ .

9.3 Functionals and their derivatives

Derivative of a traditional function: A function $f(x)$ is a mathematical tool to maps a number to another number. At the point x^0 the function is $f(x^0)$. The derivative of a function near the point x^0 is

$$\left. \frac{\partial f(x)}{\partial x} \right|_{x^0} = \lim_{\delta x \rightarrow 0} \frac{f(x^0 + \delta x) - f(x^0)}{\delta x} \quad \text{or equivalently} \quad \delta f = f(x^0 + \delta x) - f(x^0) = \left. \frac{\partial f(x)}{\partial x} \right|_{x^0} \delta x. \quad (9.5)$$

The latter expression describes how much the function changes δf when x shifts from x^0 to $x^0 + \delta x$.

For a function with several variables $f(x_1, x_2, \dots, x_N)$, the function value at the point $x^0 = \{x_1^0, x_2^0, \dots, x_N^0\}$ is $f(x_1^0, x_2^0, \dots, x_N^0)$. A small shift away from x^0 results in a change in the function by

$$\delta f = \left. \frac{\partial f(x_1)}{\partial x_1} \right|_{x_1^0} \delta x_1 + \left. \frac{\partial f(x_2)}{\partial x_2} \right|_{x_2^0} \delta x_2 + \dots + \left. \frac{\partial f(x_N)}{\partial x_N} \right|_{x_N^0} \delta x_N = \sum_{n=1}^N \left. \frac{\partial f(x_n)}{\partial x_n} \right|_{x_n^0} \delta x_n. \quad (9.6)$$

This generalizes Eq. (9.5), and it describes the partial derivative of the function. For example, with the function $f(\mathbf{r}) = f(r, \theta, \varphi)$ the small change in the function is determined from

$$\delta f = \nabla f(\mathbf{r}) \cdot \delta \mathbf{r} = \frac{\partial f}{\partial r} \delta r + \frac{\partial f}{\partial \theta} \delta \theta + \frac{\partial f}{\partial \varphi} \delta \varphi. \quad (9.7)$$

Defining a functional: A functional $F[g]$ has a function as an input and outputs a number. Here, we will generate $F[g]$ from a function of several variables in order to later on also define the functional derivative $\partial F[g]/\partial g$. First, we will allow the variables x_n in Eq. (9.6) to vary. Define $x_n = g(y_n)$ as a one-to-one map of numbers. The function of several variables is then $f(g(y_1), g(y_2), \dots, g(y_N))$. The map from y_n to x_n depends on how g is defined. Obviously, $g(y_n)$ has N finite number of variables, and $g(y_n)$ is therefore not a proper function of y_n . However, we shall allow $N \rightarrow \infty$ in order to have an infinite number of variables.

Now, y_n spans an interval $[y_0, y_N]$. With the definition $y_{n+1} > y_n$ there is a definite value of $y_{n+1} - y_n = \Delta y_n = \varepsilon_n$. Especially, $y_N - y_0 = \sum_n \Delta y_n \equiv N\varepsilon$. With a well-defined interval, $\varepsilon \rightarrow 0$ and $\Delta y_n \rightarrow 0$ when $N \rightarrow \infty$. In this limit, $g(y_n) = g(y)$ allows any real value of y , and $g(y)$ can be regarded as a function of y .

Then, let us define $F[g] = f(g(y_1), g(y_2), \dots, g(y_N)) = f(g(y))$ in the limit of $N \rightarrow \infty$. $g(y)$ describes the map for any y to x . $g(y)$ can be any function. Since g can be any function, $F[g]$ becomes a function of functions. We say that that $F[g]$ is a functional of g . $F[g] = f(g(y))$ takes thus a function as an input and outputs a number.

Defining functional derivatives: The derivative of functionals can be derived from the derivative of functions in Eq. (9.6). We make the substitution $x_n \rightarrow g(y_n)$ and $f(x_n) = f(g(y_n)) = F[g]$. Then, Eq. (9.6) becomes

$$\delta F[g] = \sum_{n=1}^N \left. \frac{\partial f(x_n)}{\partial x_n} \right|_{x_n^0} \delta x_n = \sum_{n=1}^N \left. \frac{\partial F[g]}{\partial g(y_n)} \right|_{g^0(y_n)} \delta g(y_n). \quad (9.8)$$

With the definition of an integral in terms of a summation:

$$\int_{x_0}^{x_N} f(x) dx = \lim_{N \rightarrow \infty} \sum_{n=1}^N \varepsilon_n f(x_n), \quad (9.9)$$

and by direct identification, one finds that

$$\delta F[g] = \int_{y_0}^{y_N} \left. \frac{\partial F[g]}{\partial g(y)} \right|_{g^0} \delta g(y) dy \quad \text{where the change also is } \delta F[g] = F[g^0 + \delta g] - F[g]. \quad (9.10)$$

Here, $1/\varepsilon_n$ has been included in the denominator. Moreover, $g^0 = g^0(y)$ is the function around which we make the shift δg . Thus, we can describe the variation as

$$\delta F[g] = F[g + \delta g] - F[g] = \int \frac{\partial F[g]}{\partial g(y)} \delta g(y) dy. \quad (9.11)$$

This expression describes how much the functional changes δF when the function is shifted from g to $g + \delta g$. the functional derivative $\partial F[g]/\partial g(y)$ is inside the integral. This is of course a somewhat complicated expression, but we can use Eq. (9.11) to derive basic functional derivatives.

Functional derivatives have important chain rules. If the functional $F[g] = G[g] \cdot H[g]$ is a product of two functional $G[g]$ and $H[g]$, then the derivative can be described by

$$\frac{\partial F[g]}{\partial g(y)} = \frac{\partial G[g]}{\partial g(y)} H[g] + G[g] \frac{\partial H[g]}{\partial g(y)}. \quad (9.12)$$

Moreover, assume that the functional $F[g]$ depends on the function $g(y)$, but that we want to take the derivative with respect to the function $s(y)$, then

$$\frac{\partial F[g]}{\partial s(y)} = \frac{\partial F[g]}{\partial g(y)} \frac{\partial g(y)}{\partial s(y)}, \quad \text{and especially} \quad \frac{\partial F[g]}{\partial g(y')} = \frac{\partial F[g]}{\partial g(y)} \frac{\partial g(y)}{\partial g(y')} = \frac{\partial F[g]}{\partial g(y)} \delta(y - y'). \quad (9.13)$$

Some examples: Derivation of traditional functions follows specific rules. One has similar rules for the functionals. The technique often uses the Taylor expansion of $F[g + \delta g] - F[g]$ and collect terms with first order of δg , and then identify the functional derivative from Eq. (9.10). For example

$$\text{if } F[g] = \int h(g(y)) dy \quad \text{then,} \quad (9.14)$$

$$\begin{aligned} \delta F[g] &\equiv F[g + \delta g] - F[g] = \int h(g(y) + \delta g(y)) dy - \int h(g(y)) dy = \quad / \text{Taylor expansion} / = \\ &= \int \left[h(g(y)) + \frac{\partial h(g(y))}{\partial g} \delta g(y) + O(\delta g(y)^2) \right] - h(g(y)) dy = / \text{sufficiently small } \delta g / = \\ &= \int \left\{ \frac{\partial h(g(y))}{\partial g} \right\} \delta g(y) dy \Rightarrow / \text{compare with Eq. (9.11)} / \Rightarrow \quad \frac{\partial F[g]}{\partial g(y)} = \frac{\partial h(g(y))}{\partial g}. \end{aligned}$$

Especially,

$$\text{if } F[g] = \int g(y)^n dy \quad \text{then} \quad (9.15)$$

$$\begin{aligned}\delta F[g] &\equiv F[g + \delta g] - F[g] = \int (g + \delta g)^n - g^n dy = & / \text{polynomial expansion} / = \\ &= \int (g^n + n g^{n-1} \delta g + O(\delta g^2)) - g^n dy = \int \{n \cdot g^{n-1}\} \delta g dy & \text{since } \delta g \text{ is small.}\end{aligned}$$

$$\text{Thus, } \frac{\partial F[g]}{\partial g(y)} = n \cdot g(y)^{n-1} \quad \text{which is the same as } \frac{\partial g(y)^n}{\partial g} = n \cdot g(y)^{n-1} \quad \text{by utilizing Eq. (9.13).}$$

Moreover,

$$\text{if } F[g] = \int h(g, g') dy = \int h\left(g(y), \frac{\partial g(y)}{\partial y}\right) dy \quad \text{then} \quad (9.16)$$

$$\begin{aligned}\delta F[g] &\equiv F[g + \delta g] - F[g] = \int h(g + \delta g, g' + \delta g') - h(g, g') dy = / \text{Taylor, several variables} / = \\ &= \int \left(h(g, g') + \frac{\partial h(g, g')}{\partial g} \delta g + \frac{\partial h(g, g')}{\partial g'} \delta g' + O(\delta g \delta g') \right) - h(g, g') dy = / \text{small } \delta g / = \\ &= \int \frac{\partial h(g, g')}{\partial g} \delta g + \frac{\partial h(g, g')}{\partial g'} \delta g' dy = & / \text{use } (h \cdot \delta g)' = h' \cdot \delta g + h \cdot \delta g' / = \\ &= \int \frac{\partial h(g, g')}{\partial g} \delta g + \frac{\partial}{\partial y} \left(\frac{\partial h(g, g')}{\partial g'} \delta g \right) - \frac{\partial}{\partial y} \frac{\partial h(g, g')}{\partial g'} \delta g dy = \\ &= \int \left\{ \frac{\partial h(g, g')}{\partial g} - \frac{\partial}{\partial y} \frac{\partial h(g, g')}{\partial g'} \right\} \delta g dy + \left[\frac{\partial h(g, g')}{\partial g'} \delta g \right]_{y_0}^{y_N} & / \text{last term is zero} /.\end{aligned}$$

$$\text{Hence, in this case } \frac{\partial F[g]}{\partial g(y)} = \frac{\partial h(g, g')}{\partial g} - \frac{\partial}{\partial y} \frac{\partial h(g, g')}{\partial g'}.$$

Last term in second last line is zero because it is assumed that $\delta g(y) \rightarrow 0$ at the integration boundaries.

An alternative (simplified) way to analyze the functional derivative is to use the substitution $\delta g(y) \rightarrow \varepsilon \delta(x-y)$. That is, to specify the variation by a Dirac-delta function. Then, one can show that

$$\delta F[g] = F[g + \varepsilon \delta(x-y)] - F[g] = \int \frac{\partial F[g]}{\partial g(y)} \varepsilon \delta(x-y) dy = \frac{\partial F[g]}{\partial g(x)} \varepsilon, \quad (9.17)$$

which in the limit of $\varepsilon \rightarrow 0$ is equivalent to

$$\frac{\partial F[g]}{\partial g(x)} = \lim_{\varepsilon \rightarrow 0} \frac{F[g(y) + \varepsilon \delta(x-y)] - F[g(y)]}{\varepsilon}. \quad (9.18)$$

This looks like the derivative of a regular function. However, one has to be more careful to ensure that the limit $\varepsilon \rightarrow 0$ is the leading vanishing factor. Using a specific variation (*i.e.*, the Dirac-delta function) is however a less rigorous mathematically compared to Eq. (9.11).

10 Further reading

1. D. J. Griffiths, *Introduction to Quantum Mechanics*, 2nd ed. (Pearson Edu., Upper Saddle River NJ, 2005).
2. C. Kittel, *Introduction to Solid State Physics*, 6th ed. (John Wiley & Sons, New York, 1986).
3. U. von Barth, *Basic Density-Functional Theory - an Overview*, Physica Scripta. T109, 9 (2004).
4. J. Hafner, J. Comput. Chem. 29: 2044 (2008).
5. M. Dreizler and E.K.U. Gross, *Density Functional Theory – An Approach to the Quantum Many-Body Problem* (Springer, Berlin, 1990)..
6. *Density Functional Theory I – Functionals and Effective Potentials*, editor R. F. Najawajski (Springer, Berlin, 1996); *ibid*, *Density Functional Theory II – Relativistic and Time Dependent Extensions*.
7. R.G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford Press, New York, 1989).
8. J. Kohanoff and N.I. Gidopoulos, *Density Functional Theory: Basics, New Trends and Applications*, Vol 2, Chapt 26, pp 532–568 in *Handbook of Molecular Physics and Quantum* Editor S. Wilson (John Wiley & Sons, Chichester, 2003)
9. *A Primer in Density Functional Theory*, editors C. Fiolhais, F. Nogueira, M. Marques, Lecture Notes in Physics, vol. 620, p.1-55 (Springer, Berlin, 2003).
10. K. Capelle, *A Bird's-Eye View of Density-Functional Theory*; <http://arxiv.org/abs/cond-mat/0211443v5>
11. K. Burke, *The ABC of DFT*; <http://chem.ps.uci.edu/~kieron/dft/book/>

11 Information about FYS-MENA4111 autumn 2018

In the course, we learn the basic ideas and theories of the density functional theory (DFT), and how one can employ this method to calculate various physical properties of condensed matter. The course includes theoretical and practical exercises as well as a chosen computational assignment.

Course literature:

1. Lecture Notes: "Brief Introduction to the Density Functional Theory", by Clas Persson (UiO, Oslo, 2013).
2. "Density Functional Theory - A Practical Introduction" by David S. Sholl and Janice A. Steckel (John Wiley & Sons, Hoboken NJ, 2009); 238 pages; ISBN 978-0-470-37317-0 (cloth).

Teachers:

Lecturer:	Clas Persson	Clas.Persson@fys.uio.no
Computational exercises:	Ole Martin Løvvik	o.m.lovvik@fys.uio.no

11.1 Course goals and exam

Knowledge: The student will:

- know how the electron structure of atoms of the periodic system is built up,
- explain how the electron structure changes when atoms form molecules and crystals,
- understand the importance of periodic boundary conditions and how this is reflected in the reciprocal rooms
- the importance of Bloch functions and how these are used to describe the band structure,
- explain concepts like density-of-state, energy gap, and effective mass,
- explain how the band structure and material properties change with the spatial dimensionality.
- explain the variation principle, the adiabatic approximation, different approximation methods and the density functional theory (DFT), as well as
- solve simple problems analytically or numerically.

Skills: Students will master:

- practical use of DFT-based software for the calculation of crystal structure and properties of nanomaterials, and
- planning, implementation, and interpretation of DFT calculations in a chosen project.

Specifically:

- Basic theory: be able to explain and discuss the Born-Oppenheimer approximation, the density functional theory, the Kohn-Sham equation, and the concept of reciprocal space and \mathbf{k} -states.
- Physical models: be able to describe models and calculation approaches to analyze bulk materials, surface structures, vibrations and transition states.
- Computational physics: be able to perform atomistic calculations of small system using the VASP package.

Recommended prerequisites

MENA3000 Funksjonelle materialer, MENA3100 Materialkarakterisering, or FYS3410 Kondenserte fasers fysikk

Evaluation and exam

Final oral exam. The project assignment counts 1/3 for the grading. The final grade is determined on the basis of an overall assessment of the individual components included in the assessment.

All exercises (theory and lab reports) shall be completed before taking the examination

Examination:

1. Presentation of your computational project: Monday Dec. 3, Agora in FP
2. Oral examination: Monday Dec. 10, Agora in FP

11.2 Syllabus

Time and place

Lectures in class room Agora at Forskningsparken, Mondays 10:15-12:00

Computer exercises in Datalaboratorium V329 Dept of Physics UiO, Tuesdays 12:15-16:00

Deadline for assignments

Hand in the theoretical exercises no later than Monday 10:00 the following week.

week		Tuesday	Lectures Room: Agora at FP	Assignments
Aug				
34	20/08	10:15-12:00	Chapter 1 in Lecture notes: Introduction to DFT	Exercise #1
35	27/08	10:15-12:00	Chapter 2 in Lecture notes: k-states and plane waves	Exercise #2
Sept				
36	03/09	10:15-12:00	Chapter 4 in Lecture notes: Single-particle Schrödinger eq., Hartree and Hartree-Fock	Exercise #3
37	10/09	10:15-12:00	Chapters 5 and 6 in Lecture notes: Many-particle eq. Born-Oppenheimer approximation	Exercise #4
38	17/09	10:15-12:00	Chapters 7 and 8 in Lecture notes: DFT and derivation of Kohn-Sham equation	Exercise #5
39	24/09	10:15-12:00	Chapter 8 in Lecture notes: Kohn-Sham eq. and exchange-correlation functionals	Exercise #6
Oct				
40	01/10	----	----	
40	08/10	10:15-12:00	Chapter 2 in DFT book: Basic DFT calculations for solids	Exercise #7
42	15/10	10:15-12:00	Chapter 3 in DFT book: Basic DFT calculations for solids	Exercise #8
43	22/10	10:15-12:00	Chapter 4 in DFT book: Surfaces	Exercise #9
44	29/10	10:15-12:00	Chapter 5 in DFT book: Vibrations	Exercise #10
Nov				
45	05/11	----	----	
46	12/11	10:15-12:00	Chapter 6 in DFT book: Chemical processes	Exercise #11
47	19/11	10:15-12:00	Chapter 7 in DFT book: Thermodynamics	Exercise #12
48	26/11	10:15-12:00	Chapters 8 and 10 in DFT book: Electronic structure DFT issues	
Dec				
49	03/12		Project presentation	
50	10/12		Oral exam	

11.3 Checklist

Many-particle Schrödinger equation

- Write down and discuss the many-particle Schrödinger equation.
- Explain the difficulties to solve the many-particle Schrödinger equation.
- Explain the variational principle, and its two functionalities.
- Explain how one uses variational method to derive the Hartree and Kohn-Sham equations

Born-Oppenheimer approximation (BOA)

- Explain the purpose/idea of the BOA.
- Derive the BOA using the approximated variable separation.
- Discuss the potential energy surface.
- Derive force on the atoms.
- Discuss the good aspects (usefulness) and the bad aspects (problems) of the BOA.

Density functional theory (DFT)

- Derive the two Hohenberg-Kohn theorems.
- Explain in what way DFT differs from the Hartree- and Hartree-Fock-based methods.
- What properties can/cannot be exactly described by the DFT?
- Discuss the good aspects (usefulness) and the bad aspects (problems) of the DFT.

Kohn-Sham equation (KS-eq) and local density approximation (LDA)

- Derive the KS-eq, and define the exchange-correlation potential.
- Explain how the KS-eq is related to the DFT and to the Hartree/Hartree-Fock.
- What properties can/cannot be exactly described by the KS-eq?
- Discuss the good aspects (usefulness) and the bad aspects (problems) of the KS-eq.
- Explain the basic principles of the LDA.

k-space

- Discuss crystal lattice vectors and the reciprocal lattice vectors.
- Discuss Bloch's function. Derive the momentum of the wavefunction.
- Describe the periodicity of the potential, of the electron density, and of the wavefunction.
- Describe the shape of the electron wavefunction in a crystal.
- Explain why \mathbf{k} -space is useful for describing wavefunction, and for solving the KS-eq.
- Discuss \mathbf{k} -points, Brillouin zone, band folding, and band structure.
- Discuss number of \mathbf{k} -states in 1st Brillouin zone, band filling, energy bands, and density-of-states.
- Discuss the good aspects (usefulness) and the bad aspects (problems) of wavefunction with \mathbf{k} -state.

Calculation of crystal structures

- Discuss how one relaxes the lattice constant (volume) and the atom positions.
- Discuss prediction of crystalline structure and crystal phase transformation.
- Discuss convergence parameters for achieving an accurate calculation.

Calculation of surfaces

- Explain how the unit cell is created for surfaces, and the choice of corresponding \mathbf{k} -mesh.
- Discuss the problems with this type of unit cell.
- Explain Miller indices.
- Define surface energy, and describe how surface structure and reconstruction are calculated.
- Define adsorption energy, and describe how adsorption and surface coverage are calculated.

Calculation of vibrations

- Derive the equation to calculate vibration energies.
- Discuss the problem to calculate vibration due to unit cell, displacement, and temperature.
- Explain the underlying physics of the zero-point energy.
- Explain the six vibration modes for a two-atom molecule.
- Discuss the difference between calculating vibrations in vacuum, on surface, and in bulk.

Calculation of transition states

- Explain potential energy surface.
- Explain local configuration minima, transition states, and activation energy.
- Discuss the problems when calculating the transition state and minimum energy path.
- Explain the nudged elastic band method.
- Discuss the problem to find the right transition states.
- Briefly discuss quantum tunneling.

Calculation of thermodynamic properties

- Explain the expression of the grand potential.
- Briefly discuss how equilibrium phase transition is modeled.