

# **A Brief Introduction to the Density Functional Theory**

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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. Accordingly, 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.

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  $\Psi^{en}(\mathbf{r},\mathbf{R}) \approx \Psi(\mathbf{r})\cdot\Theta(\mathbf{R})$  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  $1\text{ cm}^3$ . 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  $\psi_\kappa(\mathbf{r})$  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 idea of DFT belongs to this approach.

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

- 3) Use Hartree-like single-electron wavefunctions  $\psi_\kappa^{KS}(\mathbf{r})$  that shall generate the exact density  $n(\mathbf{r}) = |\Psi(\mathbf{r})|^2 = \sum_\kappa |\psi_\kappa^{KS}(\mathbf{r})|^2$ . According to DFT, this density would then generate the exact total energy  $E$ . The Kohn-Sham equation  $\{-\hbar^2\nabla^2/2m_e + V_{eff}(\mathbf{r})\}\psi_\kappa^{KS}(\mathbf{r}) = \epsilon_\kappa^{KS}\psi_\kappa^{KS}(\mathbf{r})$  is utilized to determine  $E$ .

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 equations.

## 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. |

## 2 An electron in a solid

The single-electron Schrödinger equation of an electron in a crystal is described in most introductory courses of solid state physics and in many applied quantum-physics courses. Consider a crystalline material. We assume that our crystal potential has a periodicity

$$\left( -\frac{\hbar^2 \nabla^2}{2m_e} + V_{ext}(\mathbf{r}) \right) \psi_{\kappa}(\mathbf{r}) = \varepsilon_{\kappa} \psi_{\kappa}(\mathbf{r}), \quad \text{where } V_{ext}(\mathbf{r}) = V_{ext}(\mathbf{r} + \mathbf{R}). \quad (2.1)$$

The primitive unit cell of the crystal is spanned by the primitive lattice vectors  $\mathbf{a}_1$ ,  $\mathbf{a}_2$ , and  $\mathbf{a}_3$ . A perfect crystal has the property that the potential of the primitive unit cell has translation symmetry:  $V_{ext}(\mathbf{r}) = V_{ext}(\mathbf{r} + \mathbf{R})$  where  $\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$  with integer numbers for  $n_j = 0, 1, 2, 3, \dots, \infty$ . 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, which we also shall call "the  $\mathbf{k}$ -space").

$$\mathbf{b}_1 = \frac{2\pi \mathbf{a}_2 \times \mathbf{a}_3}{\Omega_{vol}}, \quad \mathbf{b}_2 = \frac{2\pi \mathbf{a}_3 \times \mathbf{a}_1}{\Omega_{vol}}, \quad \text{and} \quad \mathbf{b}_3 = \frac{2\pi \mathbf{a}_1 \times \mathbf{a}_2}{\Omega_{vol}} \quad \text{where } \Omega_{vol} = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3) \quad (2.2)$$

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 integers  $m_j = 0, 1, 2, 3, \dots, \infty$ .

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

$$V_{ext}(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}} \cdot e^{i\mathbf{G}\mathbf{r}}. \quad (2.3)$$

An eigenfunction is not an observable quantity, and does not have to obey crystal periodicity. Instead, we shall choose another boundary condition for the electrons, namely  $\psi_{\mathbf{k}}(\mathbf{r}) = \psi_{\mathbf{k}}(\mathbf{r} + \mathbf{L})$  with  $\mathbf{L} = L_1 \hat{\mathbf{a}}_1 + L_2 \hat{\mathbf{a}}_2 + L_3 \hat{\mathbf{a}}_3 = N_1 \mathbf{a}_1 + N_2 \mathbf{a}_2 + N_3 \mathbf{a}_3$ , where  $N_1$ ,  $N_2$  and  $N_3$  are three sufficiently large integers.

With this condition the eigenfunction has to be in the form of  $\psi_{\mathbf{k}}(\mathbf{r}) \sim A \cdot \exp(i\mathbf{k} \cdot \mathbf{r})$ , where  $k_j = \eta_j 2\pi/L_j$ , 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.  $\eta_j = \pm 0, 1, 2, 3, \dots, \infty$  and thus, only discrete  $\mathbf{k}$ -states are allowed for the electrons in the crystal. The eigenfunctions must consider also the potential of each crystal primitive cells. That part of the eigenfunction is described by the function  $u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r} + \mathbf{R})$ , and the general form of the eigenfunctions is  $\psi_{\mathbf{k}}(\mathbf{r}) = A \cdot \exp(i\mathbf{k} \cdot \mathbf{r}) \cdot u_{\mathbf{k}}(\mathbf{r})$ . This type of eigenfunction is known as Bloch function. Since  $u_{\mathbf{k}}(\mathbf{r})$  shall have periodicity of the crystal primitive cells, it can be written as  $u_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} u_{\mathbf{k}+\mathbf{G}} \cdot \exp(i\mathbf{G} \cdot \mathbf{r})$ .

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 should be periodic with the same periodicity  $n(\mathbf{r}) = n(\mathbf{r} + \mathbf{R})$ . Second, we have the artificial periodicity of the wavefunction  $\psi_{\mathbf{k}}(\mathbf{r}) = \psi_{\mathbf{k}}(\mathbf{r} + \mathbf{L})$ . The relation between  $\mathbf{L}$  and the crystal lattice is important. With that condition the wavefunction  $\psi_{\mathbf{k}}(\mathbf{r}) = A \cdot \exp(i\mathbf{k} \cdot \mathbf{r}) \cdot u_{\mathbf{k}}(\mathbf{r})$  contains both periodicities. The Bloch periodic part obeys both the crystal potential and the artificial periodicity  $u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{\mathbf{k}}(\mathbf{r} + \mathbf{L})$ , whereas the plane waves obey only the artificial periodicity  $\exp(i\mathbf{k} \cdot \mathbf{r}) = \exp(i\mathbf{k} \cdot (\mathbf{r} + \mathbf{L}))$ . 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. And since the density is  $n(\mathbf{r}) = \sum_{\mathbf{k}} |\psi_{\mathbf{k}}(\mathbf{r})|^2$ , it is clear that  $n(\mathbf{r}) = n(\mathbf{r} + \mathbf{R})$ .

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

$$\psi_{\mathbf{k}+\mathbf{G}}(\mathbf{r}) = e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}} \sum_{\mathbf{G}'} u_{\mathbf{k}+\mathbf{G}+\mathbf{G}'} e^{i\mathbf{G}'\mathbf{r}} = e^{i\mathbf{k}\mathbf{r}} \sum_{\mathbf{G}'} u_{\mathbf{k}+\mathbf{G}+\mathbf{G}'} e^{i(\mathbf{G}+\mathbf{G}')\mathbf{r}} = e^{i\mathbf{k}\mathbf{r}} \sum_{\mathbf{G}} u_{\mathbf{k}+\mathbf{G}} e^{i\mathbf{G}\mathbf{r}} = \psi_{\mathbf{k}}(\mathbf{r}). \quad (2.4)$$

Here,  $\mathbf{G}$  and  $\mathbf{G}'$  are reciprocal lattice vectors, and we are allowed to re-order the summation by writing  $\mathbf{G} + \mathbf{G}' = \mathbf{G}'' \rightarrow \mathbf{G}$ .

Now, with the property  $\psi_{\mathbf{k}}(\mathbf{r}) = \psi_{\mathbf{k}+\mathbf{G}}(\mathbf{r})$  one can make a very smart representation of the energy states. Instead of using all  $\mathbf{k}$ -states in the infinite  $\mathbf{k}$ -space, we can represent all states within the first Brillouin zone (BZ); see Fig 2.2. If an eigenfunction  $\psi_{\mathbf{k}'}(\mathbf{r}) = \psi_{\mathbf{k}+\mathbf{G}}(\mathbf{r})$  with  $\mathbf{k}' = \mathbf{k} + \mathbf{G}$  is a  $\mathbf{k}$ -state outside the first BZ, one transfer that state into an eigenfunction  $\psi_{\mathbf{k}}(\mathbf{r})$  into the first BZ. To distinguish different eigenfunctions  $\psi_{\mathbf{k}+\mathbf{G}}(\mathbf{r})$  that are transferred, we use the band index  $n$ . This is called band folding.

$$\psi_{n\mathbf{k}+\mathbf{G}}(\mathbf{r}) = \psi_{n'\mathbf{k}}(\mathbf{r}) \neq \psi_{n\mathbf{k}}(\mathbf{r}). \quad (2.5)$$

$$V_{ext}(\mathbf{r}) = V_{ext}(\mathbf{r} + \mathbf{R})$$

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3; \quad n_j = \pm 0, 1, 2, \dots, \infty$$

$$V_{ext}(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}} \cdot e^{i\mathbf{G}\mathbf{r}}$$

$$\mathbf{G} = m_1\mathbf{b}_1 + m_2\mathbf{b}_2 + m_3\mathbf{b}_3; \quad m_j = \pm 0, 1, 2, \dots, \infty$$

$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} \cdot u_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} \sum_{\mathbf{G}} u_{n\mathbf{k}+\mathbf{G}} \cdot e^{i\mathbf{G}\mathbf{r}}$$

$$n = 1, 2, \dots, \infty = \text{band index}$$

$$\mathbf{k} = k_1\hat{\mathbf{b}}_1 + k_2\hat{\mathbf{b}}_2 + k_3\hat{\mathbf{b}}_3$$

$$k_j = \eta_j 2\pi/L_j \quad j = 1, 2, \text{ and } 3$$

$$\eta_j = \pm 0, 1, 2, \dots \quad \text{for } k_j \in \text{1st BZ}$$

$$\psi_{n\mathbf{k}}(\mathbf{r} + \mathbf{L}) = \psi_{n\mathbf{k}}(\mathbf{r})$$

$$\psi_{n\mathbf{k}+\mathbf{G}}(\mathbf{r}) = \psi_{n'\mathbf{k}}(\mathbf{r})$$

The allowed  $\mathbf{k}$ -states for the electrons are specific and discrete set of  $\mathbf{k}$ -points.

- $\mathbf{k}$  is a quantum state, describing a translation symmetry of  $\exp(i\mathbf{k}\cdot\mathbf{r})$ .
- The wave length of  $\exp(i\mathbf{k}\cdot\mathbf{r})$  is obtained from  $\lambda = 2\pi/|\mathbf{k}|$ .
- Band index  $n$  comes from band folding as  $\psi_{\mathbf{k}} = \psi_{\mathbf{k}+\mathbf{G}}$ .
- At most two electrons (spin up- and spin down-like) can simultaneously be in a  $\{n, \mathbf{k}\}$ -state.
- For electrons in a crystal,  $\hbar\mathbf{k}$  is called the crystal momentum.

### 3 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 to determine the ground state.

The idea is to vary the general wavefunction  $\psi(\mathbf{r})$  and minimize the total energy  $\varepsilon$ . The wavefunction with the lowest energy is the ground state  $\psi_0(\mathbf{r})$  with the energy  $\varepsilon_0$  because

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

Thus, we shall find the wavefunction that minimizes the energy. 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,  $\delta\varepsilon/\delta\psi(\mathbf{r}) = 0$ . However, the wavefunction must be normalized. Thus, we shall minimize the energy with the constraint that the wavefunction shall be normalized. The Lagrange multiplier is a method for that.

$$\frac{\delta}{\delta\psi} \{ \varepsilon - \lambda g \} = \frac{\delta}{\delta\psi} \left\{ \int \psi^*(\mathbf{r}) H \psi(\mathbf{r}) d\mathbf{r} - \lambda \left( \int \psi^*(\mathbf{r}) \psi(\mathbf{r}) d\mathbf{r} - 1 \right) \right\} = 0 \quad (3.2)$$

This is the variational method. Notice that we get only the ground state  $\psi_0(\mathbf{r})$  with this method. We will show that the variational method implies that 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.

## 4 The many-particle Schrödinger equation

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  $\mathbf{R}_\alpha$  describes the coordinates of the  $\alpha$ :th nucleus. The superscript “en” only indicates that we describe a wavefunction with both electrons and nuclei. The many-particle Schrödinger equation is

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

where  $E_\kappa^{en}$  is the total energy eigenvalue for the whole system in eigenstate  $\kappa$ . And the many-particle Hamiltonian is

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

where  $m_e$  is electron mass, and  $Z_\alpha$  and  $m_\alpha$  are atom number and mass of the nuclei, respectively.  $\nabla_j$  means the derivative of the  $j$ :th electron coordinate (correspondingly,  $\nabla_\alpha$  for the nuclei).

Here, the five terms describe:

$$\begin{aligned} T_e &= -\sum_{j=1}^{N_e} \frac{\hbar^2 \nabla_j^2}{2m_e} && : \text{kinetic energy of all electrons} \\ T_n &= -\sum_{\alpha=1}^{N_n} \frac{\hbar^2 \nabla_\alpha^2}{2m_\alpha} && : \text{kinetic energy of all nuclei} \\ U_{ee} &= +\sum_{j=1}^{N_e} \sum_{j' < j} \frac{q^2}{|\mathbf{r}_j - \mathbf{r}_{j'}|} && : \text{repulsive electron-electron static Coulomb interactions} \\ U_{nn} &= +\sum_{\alpha=1}^{N_n} \sum_{\alpha' < \alpha} \frac{q^2 Z_\alpha Z_{\alpha'}}{|\mathbf{R}_\alpha - \mathbf{R}_{\alpha'}|} && : \text{repulsive nucleus-nucleus interactions} \\ U_{en} &= -\sum_{j=1}^{N_e} \sum_{\alpha=1}^{N_n} \frac{q^2 Z_\alpha}{|\mathbf{r}_j - \mathbf{R}_\alpha|} && : \text{attractive electron-nucleus interactions.} \end{aligned} \quad (5.3)$$

Notice that  $j' \neq j$  because an electron should not interact with itself ( $\alpha' \neq \alpha$  for the nuclei). The Hamiltonian here includes only the kinetic energy and electrostatic Coulomb interactions. Other types of interactions could have been included, like relativistic terms and interaction with an external electromagnetic field, but we simplify the discussion to include the basic terms.

One of the problems with the many-particle equation is that materials have roughly  $10^{23}$  nuclei and electrons in a crystal with volume  $1 \text{ cm}^3$ . This is of course a huge numerical problem. However, there is a more conceptual issue. While the Hamiltonian  $H^{en}$  above contains single- and two-particle operators that shall be applied to the single-particle wavefunctions, we do not have the prior knowledge how  $\Psi^{en}$  depends on these single-particle wavefunctions. Thus, we do not know how to operate  $H^{en}$  on the many-particle function  $\Psi^{en}$ . One can attack this problem in two different ways:

- Try to describe  $\Psi^{en}$  in terms of the single-particle wavefunctions and use the regular Hamiltonian  $H^{en}$ . The Hartree and Hartree-Fock approximations belong to this approach. In more sophisticated methods, one tries to find a more general form of  $\Psi^{en}$ .
- Try to find an expression for  $H$  that can operate directly on  $\Psi^{en}$ , or alternatively, find a relation between  $\Psi^{en}$  and  $E$ . The original DFT belongs to this approach; we discuss this in Chapter 6.

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, but use the DFT to derive a modified Schrödinger equation. The new equation shall of course generate the exact total energy. This is the Kohn-Sham equation, which will be described in Chapter 7.



## 5 The Born-Oppenheimer approximation

The many-particle eigenfunction  $\Psi_{\kappa}^{en}(\mathbf{r}, \mathbf{R}) = \Psi_{\kappa}^{en}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N_e}, \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{N_n})$  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 ( $m_{\alpha} \approx 2 \times 10^{-27}$  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 describes 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  $\Psi_{\kappa}^{en}(\mathbf{r}, \mathbf{R}) \approx \Psi_{\kappa}(\mathbf{r}; \mathbf{R})\Theta_{\kappa}(\mathbf{R})$ . This is justified by the fact that nuclei are treated as point charges.

Starting from the eigenvalue problem, and using the variable separation:

$$H^{en} \Psi_{\kappa}(\mathbf{r}; \mathbf{R})\Theta_{\kappa}(\mathbf{R}) = E_{\kappa}^{en} \Psi_{\kappa}(\mathbf{r}; \mathbf{R})\Theta_{\kappa}(\mathbf{R}) \quad (6.1)$$

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

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

The right hand side could be simplify because  $\Theta_{\kappa}(\mathbf{R})$  does not depend on  $\mathbf{r}$ , and  $\Psi_{\kappa}$  is normalized.

Then we divide the total Hamiltonian  $H^{en}$  into an electronic part  $H^e \equiv H$  and a nuclear part  $H^n$

$$H^{en} = H + H^n, \text{ where} \quad (6.3)$$

$$H = T_e + U_{ee} + U_{en} = -\sum_{j=1}^{N_e} \frac{\hbar^2 \nabla_j^2}{2m_e} + \sum_{j=1}^{N_e} \sum_{j' < j} \frac{q^2}{|\mathbf{r}_j - \mathbf{r}_{j'}|} - \sum_{j=1}^{N_e} \sum_{\alpha=1}^{N_n} \frac{q^2 Z_{\alpha}}{|\mathbf{r}_j - \mathbf{R}_{\alpha}|}$$

$$H^n = T_n + U_{nn} = -\sum_{\alpha=1}^{N_n} \frac{\hbar^2 \nabla_{\alpha}^2}{2m_{\alpha}} + \sum_{\alpha=1}^{N_n} \sum_{\alpha' < \alpha} \frac{q^2 Z_{\alpha} Z_{\alpha'}}{|\mathbf{R}_{\alpha} - \mathbf{R}_{\alpha'}|}.$$

Moreover, we define the electronic Schrödinger equation as

$$H \Psi_{\kappa}(\mathbf{r}; \mathbf{R}) = E_{\kappa}(\mathbf{R}) \Psi_{\kappa}(\mathbf{r}; \mathbf{R}), \quad (6.4)$$

where  $E_{\kappa}$  shall describe the total energy of the electrons in the state  $\kappa$ . Since the electrons, i.e.  $\Psi_{\kappa}(\mathbf{r}; \mathbf{R})$ , depend on the nucleus positions  $\mathbf{R}$ , so does the energy. We indicate that by  $E_{\kappa} = E_{\kappa}(\mathbf{R})$ .

With the divided Hamiltonian, Eq. 6.2 becomes

$$\int \Psi_{\kappa}^*(\mathbf{r}; \mathbf{R}) H \Psi_{\kappa}(\mathbf{r}; \mathbf{R})\Theta_{\kappa}(\mathbf{R}) d\mathbf{r} + \int \Psi_{\kappa}^*(\mathbf{r}; \mathbf{R}) H^n \Psi_{\kappa}(\mathbf{r}; \mathbf{R})\Theta_{\kappa}(\mathbf{R}) d\mathbf{r} = E_{\kappa}^{en} \Theta_{\kappa}(\mathbf{R})$$

Since  $\Theta_{\kappa}(\mathbf{R})$  does not depend on  $\mathbf{r}$ , and the electronic Hamiltonian  $H$  operates only on  $\Psi_{\kappa}$ , the left can be simplified so the expression becomes

$$E_{\kappa}(\mathbf{R}) \Theta_{\kappa}(\mathbf{R}) + \int \Psi_{\kappa}^*(\mathbf{r}; \mathbf{R}) \left\{ \sum_{\alpha=1}^{N_n} \frac{-\hbar^2}{2m_{\alpha}} \nabla_{\alpha}^2 + U_{nn} \right\} \Psi_{\kappa}(\mathbf{r}; \mathbf{R})\Theta_{\kappa}(\mathbf{R}) d\mathbf{r} = E_{\kappa}^{en} \Theta_{\kappa}(\mathbf{R}) \quad (6.5)$$

The integrand involves the nuclear Hamiltonian  $H^n$ . The term containing  $\nabla_\alpha^2 \Psi_\kappa \Theta_\kappa$  is expanded by the product rule:

$$\Psi_\kappa^* \left\{ \nabla_\alpha^2 \Psi_\kappa \Theta_\kappa \right\} = \Psi_\kappa^* \left\{ \Psi_\kappa \nabla_\alpha^2 + 2(\nabla_\alpha \Psi_\kappa) \nabla_\alpha + (\nabla_\alpha^2 \Psi_\kappa) \right\} \Theta_\kappa.$$

Then, by defining

$$\begin{aligned} T_n &= - \sum_{\alpha=1}^{N_n} \frac{\hbar^2}{2m_\alpha} \int \Psi_\kappa^* \Psi_\kappa \mathbf{d}\mathbf{r} \nabla_\alpha^2 = - \sum_{\alpha=1}^{N_n} \frac{\hbar^2}{2m_\alpha} \nabla_\alpha^2 \\ T_n' &= - \sum_{\alpha=1}^{N_n} \frac{\hbar^2}{2m_\alpha} 2 \int \Psi_\kappa^* \nabla_\alpha \Psi_\kappa \mathbf{d}\mathbf{r} \nabla_\alpha \\ T_n'' &= - \sum_{\alpha=1}^{N_n} \frac{\hbar^2}{2m_\alpha} \int \Psi_\kappa^* \nabla_\alpha^2 \Psi_\kappa \mathbf{d}\mathbf{r}, \end{aligned}$$

the kinetic energy of the nuclei in Eq. 6.5 can be written as  $\{T_n + T_n' + T_n''\} \Theta_\kappa(\mathbf{R})$ .

Moreover, the nucleus-nucleus interactions in Eq. 6.5 is simplified to  $U_{nn} \Theta_\kappa(\mathbf{R})$ , because only  $\Psi_\kappa^* \Psi_\kappa$  is affected by the integration and  $\int \Psi_\kappa^* \Psi_\kappa \mathbf{d}\mathbf{r} = 1$ . Thereby, Eq. 6.5 can be written as:

$$E_\kappa(\mathbf{R}) \Theta_\kappa(\mathbf{R}) + \{T_n + T_n' + T_n'' + U_{nn}\} \Theta_\kappa(\mathbf{R}) = E_\kappa^{en} \Theta_\kappa(\mathbf{R}) \quad (6.6)$$

Further, if we neglect  $T_n'$  and  $T_n''$  in Eq. 6.6, and use the definition in Eq. 6.4, we obtain

$$\{T_e + U_{ee} + U_{en}\} \Psi_\kappa(\mathbf{r}, \mathbf{R}) = E_\kappa(\mathbf{R}) \Psi_\kappa(\mathbf{r}, \mathbf{R}) \quad \text{electronic Schrödinger eq.} \quad (6.7a)$$

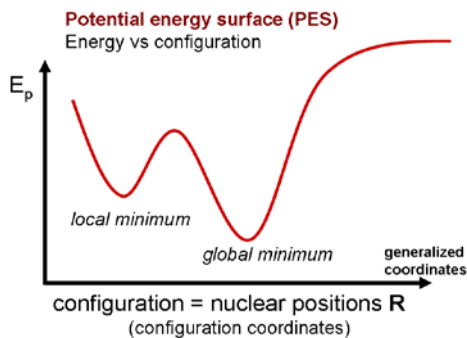
$$\{T_n + U_{nn} + E_\kappa(\mathbf{R})\} \Theta_\kappa(\mathbf{R}) = E_\kappa^{en} \Theta_\kappa(\mathbf{R}) \quad \text{nuclear Schrödinger eq.} \quad (6.7b)$$

This is the common Born-Oppenheimer approximation (BOA). These two equations are coupled via the total electronic energy  $E_\kappa(\mathbf{R})$  for the  $\kappa$ :th eigenstate. That is, the total energy in the electronic equation contributes to the potential in the nuclear equation.

Notice that the nucleus-nucleus interaction  $U_{nn}$  depends only on the nuclear positions. This interaction can be calculated relatively easily if we assume point-like nucleus charge distribution. The interaction is actually often included in the electronic Schrödinger equation.

## 5.1 Potential energy surface (PES) and forces

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. The total potential energy operator acting on the nuclei is  $U_{nn}(\mathbf{R}) + E_\kappa(\mathbf{R})$ . We therefore define  $E_P(\mathbf{R}) = U_{nn}(\mathbf{R}) + E_\kappa(\mathbf{R})$  as the potential energy surface (PES).



**Fig. 6.1:** Schematic figure of the potential energy surface for different positions of the nuclei.

From the PES we can directly calculate the forces on the atoms (or on the nuclei). Classically, and in this course, the force  $\mathbf{F}_\alpha$  on  $\alpha$ :th nuclei is defined by Newton's second law, but also from the work  $W$  done by the force  $W_\alpha = -\Delta V_\alpha = \int \mathbf{F}_\alpha d\mathbf{R}_\alpha$ , and thereby

$$\mathbf{F}_\alpha = -\nabla_\alpha E_P(\mathbf{R}_\alpha). \quad (6.8)$$

The forces on atoms are used to find the geometry of the crystals. When  $\mathbf{F}_\alpha = 0$  for all atoms, then the configuration is in an equilibrium; either in the most stable phase (i.e., in the global minimum), or at least in a metastable phase (i.e., in a local minimum). PES and forces are important also when analyzing, for instance, chemical interaction, adsorption, or vibrations of atoms. This will be discussed later in the course.

### 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 an external potential significantly simplifies also the derivation of the Kohn-sham equation.

#### The disadvantage with the BOA is that

- Neglected  $T_n'$  and  $T_n''$  is an approximation. These terms can be included by Eq. 6.6, but that requires extra consideration and extra computational efforts.
- $\Psi_{\kappa}^{en}(\mathbf{r}, \mathbf{R}) \approx \Psi_{\kappa}(\mathbf{r}, \mathbf{R})\Theta_{\kappa}(\mathbf{R})$  is an approximation.
- 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 nuclear vibrations.

## 6 The density functional theory

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. How can we overcome that problem? Is there any method that determines the material properties only by knowing the full many-electron eigenfunction  $\Psi_\kappa(\mathbf{r})$ , and not  $\psi_f(\mathbf{r})$ ? If so, such method must probably be very advanced, because it shall be capable to describe very complex many-electron eigenfunctions. The density functional theory (DFT) is actually an approach for this.

The DFT 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.

That means we can work with  $n(\mathbf{r})$  instead of  $\Psi_\kappa(\mathbf{r})$ . One huge 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  $z$ ).

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

**The 1st 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  $V_{ext}(\mathbf{r})$  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  $V_{ext}(\mathbf{r})$  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  $n_0(\mathbf{r})$ .

Here,  $V_{ext}(\mathbf{r}) = V_{en}(\mathbf{r})$  is the potential which the electrons feel due to the presence of the nuclei.

**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 ground-state energies  $[E_0(\mathbf{r}) \text{ and } E_0' ]$ .

Since they are ground states to respective wavefunction, we know that

$$E_0 = \langle \Psi_0 | H | \Psi_0 \rangle < \langle \Psi_0' | H | \Psi_0' \rangle \quad (7.1a)$$

$$E_0' = \langle \Psi_0' | H' | \Psi_0' \rangle < \langle \Psi_0 | H' | \Psi_0 \rangle. \quad (7.1b)$$

Then, from Eq. 7.1a

$$\begin{aligned} E_0 &= \langle \Psi_0 | H | \Psi_0 \rangle = \langle \Psi_0 | T + U_{ee} + U_{en} | \Psi_0 \rangle = \langle \Psi_0 | T + U_{ee} | \Psi_0 \rangle + \int V_{en}(\mathbf{r}) n_0(\mathbf{r}) d\mathbf{r} \\ &< \langle \Psi_0' | H | \Psi_0' \rangle = \langle \Psi_0' | T + U_{ee} + U_{en} | \Psi_0' \rangle = \langle \Psi_0' | T + U_{ee} + U_{en}' + (U_{en} - U_{en}') | \Psi_0' \rangle \\ &= \langle \Psi_0' | T + U_{ee} + U_{en}' | \Psi_0' \rangle + \int (V_{en}(\mathbf{r}) - V_{en}'(\mathbf{r})) n_0(\mathbf{r}) d\mathbf{r} \\ &= \langle \Psi_0' | H' | \Psi_0' \rangle + \int (V_{en}(\mathbf{r}) - V_{en}'(\mathbf{r})) n_0(\mathbf{r}) d\mathbf{r} \end{aligned} \quad (7.2)$$

Hence,

$$E_0 < E_0' + \int (V_{en}(\mathbf{r}) - V_{en}'(\mathbf{r})) n_0(\mathbf{r}) d\mathbf{r}. \quad (7.3a)$$

Correspondingly from Eq. 7.1b, we can derive

$$E_0' < E_0 + \int (V_{en}'(\mathbf{r}) - V_{en}(\mathbf{r})) n_0(\mathbf{r}) d\mathbf{r}. \quad (7.3b)$$

Adding the right hand sides and adding the left hand sides of Eqs. 7.3a and 7.3b, yields the contradicting result  $E_0 + E_0' < E_0 + E_0'$ . Thus, two external potentials cannot have the same ground-state density, and  $V_{en}(\mathbf{r})$  is determined uniquely (except for a constant) by  $n_0(\mathbf{r})$ .

**The 2nd 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  $n(\mathbf{r})$ . We divide the energy functional

$$E[n] = T[n] + U_{ee}[n] + U_{en}[n], \quad = T[n] + U_{ee}[n] + \int V_{en}(\mathbf{r})n(\mathbf{r})d\mathbf{r} \quad (7.4)$$

into energy functionals from the kinetic energy  $T[n]$ , electron-electron interactions  $U_{ee}[n]$ , and the electron-nuclei interactions  $U_{en}[n]$ . The two first terms combined are the Hohenberg-Kohn functional  $F[n]$ .

$$E[n] = F[n] + \int V_{en}(\mathbf{r})n(\mathbf{r})d\mathbf{r} \quad \text{with } F[n] = T[n] + U_{ee}[n]. \quad (7.5)$$

Since  $F[n]$  does not depend on the external potential, it has to be universal according to the first theorem.

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

$$E_0 = E[n_0] = \langle \Psi_0 | H | \Psi_0 \rangle < \langle \Psi | H | \Psi \rangle = E[n]. \quad (7.6)$$

The total energy of the ground-state density  $n_0(\mathbf{r})$  is lower than for any other densities  $n(\mathbf{r})$ .

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.

That is, 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  $E[n]$ . The expression of  $E[n]$  is unknown. Since the Hohenberg-Kohn functional  $F[n]$  does not depend on the external potential, there is a unique expression that depends only on the electron density. If we find the correct expression of  $F[n]$ , then we can calculate the many-particle problem for any system. The expression of  $F[n]$  must be very complicated since it shall be able to describe different types of systems (solids, liquids, molecules, etc).

### 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 in metals, insulators, molecules, liquids, *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.
- We know that if we have found the exact ground-state density, then we have the exact ground-state total energy. We can find this via variational method. That it utilized for the Kohn-Sham equation.

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.

## 7 The Kohn-Sham eq.

The DFT tells us 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.

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 generated by

$$n(\mathbf{r}) = \sum_{j=1}^{N_e} |\psi_j^{KS}(\mathbf{r})|^2 \quad (8.1)$$

From our ansatz, the density shall be exact. That actually implies that the KS wavefunctions cannot be 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. The two first functionals are unique, but unknown to date. The third functional,  $U_{en}[n]$ , is easy to handle.

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

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

where  $T_s[n]$  and  $U_s[n]$  are the kinetic and interaction energy of the auxiliary wavefunction.  $U_{en}[n]$  is the electron-nucleus interaction. The remaining part will be defined as the exchange-correlation energy

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

This exchange-correlation energy contains the complex many-electron interaction, but it also contains a kinetic energy part. The exchange-correlation energy can be regarded as the “leftover energy” that includes everything that we do not describe by  $T_s$ ,  $U_s$ , and  $U_{en}$ .

We have transformed the many-electron problem in Eq. (8.2) into an unknown exchange-correlation energy  $E_{xc}[n]$ . Here,  $E_{xc}[n]$  is zero for a non-interacting system with independent electrons, but for a general system the energy functional has to be very complicated expression. Our aim is to find a good approximation to this term.

The total energy terms are

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

$$U_s[n] = \frac{1}{2} \int \int q^2 \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \quad : \text{electron interaction energy in Hartree approx} \quad (8.6b)$$

$$U_{en}[n] = \int V_{en}(\mathbf{r})n(\mathbf{r})d\mathbf{r} \quad : \text{electron-nucleus interaction energy} \quad (8.6c)$$

$$E_{xc}[n] = (T[n] - T_s[\psi]) + (U_{ee}[n] - U_s[n]) \quad : \text{exchange-correlation energy} \quad (8.6d)$$

Notice, we have actually done nothing here, apart from rewriting the DFT expression of the total energy. The expression is exact if  $E_{xc}[n]$  is exact. We have used the Hartree energy where the self-interaction correction is neglected; this correction shall thus be included in the exchange correlation term. Furthermore,  $T_s[\psi]$  is a functional of the single-electron wave functions and not of the density  $n$ , because we have no simple expression for kinetic energy w.r.t density.

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 the density  $n(\mathbf{r})$  and the kinetic energy  $T_s[\psi]$  from the single-electron wavefunctions, we minimize the total energy with respect to  $\psi_j^{KS}$ .

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

The mathematics of the functional derivatives is for another course; here, we present the results.

It is convenient to derivate the kinetic energy with respect to the wavefunction, whereas the three remaining functionals are easiest to derivate with respect to the density using the chain rule:

$$\frac{\delta}{\delta \psi_j^{KS*}} U[n] = \frac{\delta}{\delta n} \left( \frac{dn}{d\psi_j^{KS*}} \right) U[n] = \left( \frac{\delta}{\delta n} U[n] \right) \psi_j^{KS}(\mathbf{r}), \quad (8.8)$$

The functional derivatives for each term are:

$$\frac{\delta}{\delta \psi_j^{KS*}} T_s[\psi] = \frac{\delta}{\delta \psi_j^{KS*}} \sum_{j'} \int \psi_{j'}^{KS*} \frac{-\hbar^2 \nabla^2}{2m} \psi_{j'}^{KS} d\mathbf{r} = -\frac{\hbar^2}{2m_e} \nabla_j^2 \psi_j^{KS}(\mathbf{r}) \quad (8.9a)$$

$$\frac{\delta}{\delta n} U_s[n] = \frac{\delta}{\delta n} \frac{1}{2} \int \int q^2 \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' = \int q^2 \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} = V_H(\mathbf{r}) \quad (8.9b)$$

$$\frac{\delta}{\delta n} U_{en}[n] = \frac{\delta}{\delta n} \int V_{en}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} = V_{en}(\mathbf{r}) \quad (8.9c)$$

$$\frac{\delta}{\delta n} E_{xc}[n] \quad \text{is defined to be} \quad = V_{xc}(\mathbf{r}) \quad (8.9d)$$

$$\frac{\delta}{\delta \psi_j^{KS*}} \sum_{i,i'} \lambda_{ii'} \left( \int \psi_i^{KS*} \psi_{i'}^{KS} d\mathbf{r} - \delta_{ii'} \right) = \lambda_{jj} \psi_j^{KS}(\mathbf{r}) \quad (8.9e)$$

Now, identifying/defining that  $\lambda_{jj}$  to be the Kohn-Sham eigenvalue  $\varepsilon_j^{KS}$  of the  $j$ :the electron, the, Kohn-Sham equation (KS-eq) yields.

$$\left\{ -\frac{\hbar^2 \nabla^2}{2m_e} + V_H(\mathbf{r}) + V_{en}(\mathbf{r}) + V_{xc}(\mathbf{r}) \right\} \psi_j^{KS}(\mathbf{r}) = \varepsilon_j^{KS} \psi_j^{KS}(\mathbf{r}) \quad (8.10)$$

By solving this single-electron KS-eq for all ground-state electrons, one can generate the full electron density  $n(\mathbf{r})$ . To obtain the kinetic energy there is a trick to avoid calculating this term, and still be able to obtain the total energy. First, one start with the KS-eq and multiply by  $\sum_j \psi_j^{KS*}(\mathbf{r})$  on the left (on both sides of the equals sign) and integrate over  $\mathbf{r}$ .

$$\int \sum_j \psi_j^{KS*}(\mathbf{r}) \left\{ -\frac{\hbar^2 \nabla^2}{2m_e} + V_H(\mathbf{r}) + V_{en}(\mathbf{r}) + V_{xc}(\mathbf{r}) \right\} \psi_j^{KS}(\mathbf{r}) d\mathbf{r} = \int \sum_j \psi_j^{KS*}(\mathbf{r}) \varepsilon_j^{KS} \psi_j^{KS}(\mathbf{r}) d\mathbf{r} = \sum_j \varepsilon_j^{KS}$$

The first term in the bracket is  $T_s[\psi]$ , and by replacing this with  $T_s[n]$  in Eq. 8.5 we obtain

$$E[n] = \sum_j \varepsilon_j^{KS} - \frac{1}{2} \int V_H(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + E_{xc}[n] - \int V_{xc}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \quad (8.11)$$

Thus, we have proven that it is actually possible to obtain the exact total energy, if  $E_{xc}[n]$  is exact, ... by starting from the DFT and using rather simple Hartree-like single-electron equations. This is somewhat amazing since we have used rather simple for of the many-electron wavefunction  $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{Ne})$ , with independent auxiliary wavefunctions  $\psi_j^{KS}(\mathbf{r})$ . The complex many-electron interaction is instead included in  $E_{xc}[n]$ . Further, since the Hartree potential does include self-interaction, also that correction should be included in  $E_{xc}[n]$ . We know from the DFT that there should exist one unique expression of  $E_{xc}[n]$  with respect to the density  $n(\mathbf{r})$ , and with that expression we should be able to calculate the total energies of any materials, i.e., metals, semiconductors, liquids, gasses, molecules, etc. Therefore, the expression of  $E_{xc}[n]$  is probably very complicated, and perhaps not surprising that the exact expression is yet unknown.

It is important to remember that we have used auxiliary wavefunctions  $\psi_j^{KS}(\mathbf{r})$  for the single electrons. Even if the total density is exact (if using exact  $E_{xc}$ ), these auxiliary KS wavefunctions are not the true single electrons. That also imply that the KS single-electron eigenvalues  $\varepsilon_j^{KS}$  are not the exact single-electron eigenvalues. Instead, we shall regard these 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 Hartree can never become exact (since it using incorrect wavefunction, although a correct Hamiltonian), whereas the KS equation is exact if the exchange-correlation energy is exact (although incorrect wavefunctions).

Now, the “only” thing we have to do is to find the exact  $E_{xc}[n]$  as functional of the density  $n(\mathbf{r})$ . The simplest approach is the local density approximation.

### Local density approximation

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 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

$$\varepsilon_{xc}^{gas}(n) = \frac{-3}{4} \left( \frac{3}{\pi} \right)^{1/3} \cdot n^{1/3} + \begin{cases} A \ln r_s + B + C r_s \ln r_s + D r_s & r_s \leq 1 \\ \gamma / (1 + \beta_1 \sqrt{r_s} + \beta_2 r_s) & r_s > 1 \end{cases}; \quad \text{where } r_s = \left( \frac{3}{4\pi n} \right)^{1/3} \quad (8.12)$$

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

$$E_{xc}^{LDA}[n] = \int \varepsilon_{xc}^{gas}(\mathbf{r}) \cdot n(\mathbf{r}) d\mathbf{r} \quad (8.13)$$

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

$$E_x^{LDA}[n] = - \int \frac{3e^2}{4} \left( \frac{3}{\pi} \right)^{1/3} n(\mathbf{r})^{4/3} d\mathbf{r}. \quad (8.14)$$

The corresponding exchange potential is obtained by the derivative



$$V_x^{LDA}(\mathbf{r}) = \frac{\partial E_x^{LDA}[n]}{\partial n} = -q^2 \left( \frac{3}{\pi} \right)^{1/3} n(\mathbf{r})^{1/3} \quad (8.15)$$

There is no exact formula for the correlation term  $E_c[n]$ , and there are many approximations to it. Most of them have quite complicated expressions, so we do not present them here.

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. One 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; this is deviating from the fundamental idea of DFT that there shall be one expression of  $E_{xc}[n]$  that shall describe any material.

### Self-consistent field calculation

The effective potential  $V_{eff}(\mathbf{r})$  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  $V_{eff}(\mathbf{r})$ . This mutual dependence of the potential and the density implies that 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.

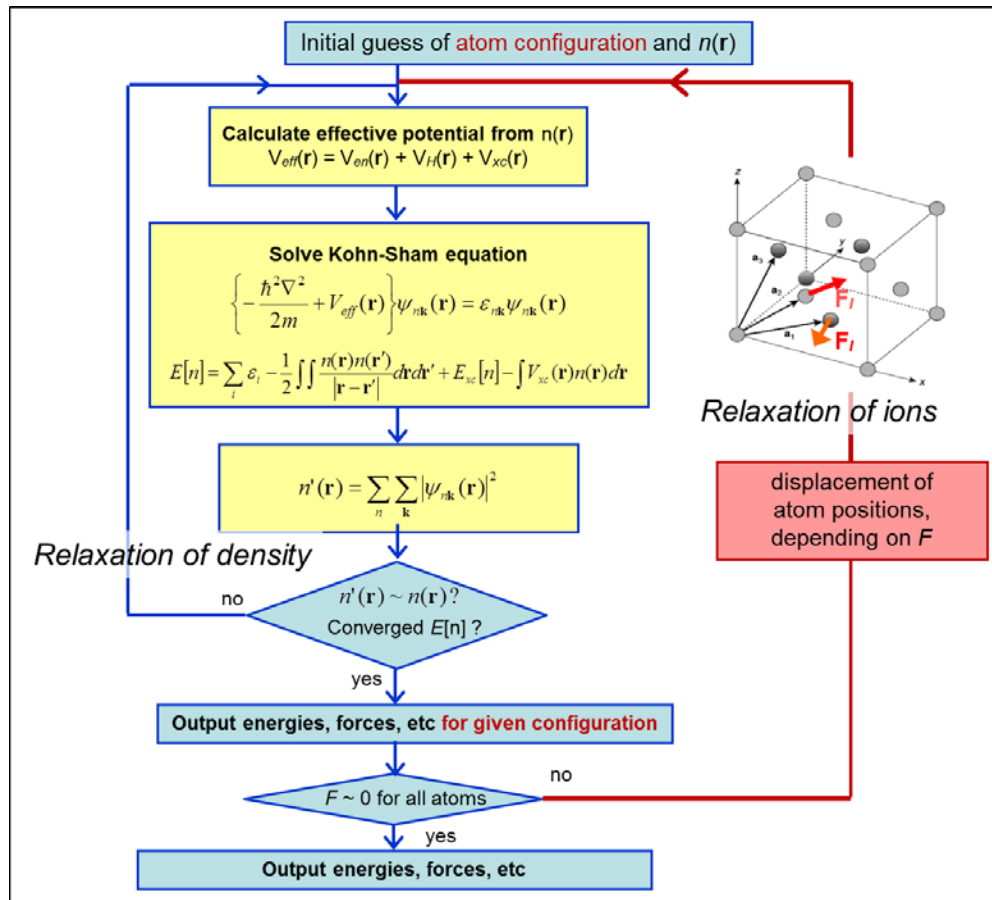


Fig. 8.1: Self-consistent field calculations and relaxation in the DFT/KS approach.

## Pros and cons of the KS equation

The KS equation with exact exchange-correlation potential  $V_{xc}(\mathbf{r})$  yields exact total energy, forces, and density. However, even with the exact  $V_{xc}(\mathbf{r})$  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 40 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  $\nabla n(\mathbf{r})$  is used. Since LDA or GGA produce approximated density  $n(\mathbf{r})$  to the external potential  $V_{xc}(\mathbf{r})$ , the DFT is not exactly valid. That is, the LDA and GGA can produce a density and total energy which is lower than the true ground-state energy. However, by experience we know that LDA, GGA, and other similar approximations to  $V_{xc}(\mathbf{r})$ , generate fairly good densities and total energies.

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, the band-gap energy of semiconductors are normally underestimated by some 50%.

In its original form, DFT is an exact theory for ground states only, and the theory is valid for  $T = 0$  K with no excitations. However, DFT has been extended for  $T > 0$  K, and there exists a fully relativistic DFT. An extension to a time-dependent DFT allows us to study time-dependent potentials, such as excitation effect, transport properties, and time-dependent electromagnetic fields.

### The advantages of the KS equation are

- It is an exact theory of the total energy, if/when the exact  $E_{xc}[n]$  is found.
- LDA, GGA, and approaches beyond are often very sufficient approximations to  $E_{xc}[n]$ .
- One can easily implement new approximations to  $E_{xc}[n]$ , without any fundamental changes in the underlying theory, and with rather small efforts in programming.
- 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 not the true single-electron eigenfunctions. Therefore  $\varepsilon_{nk}$  are not expected to be exact; e.g., the band-gap energy  $E_g$  obtained from KS eigenvalues may not be exact even if one would have the exact  $E_{xc}[n]$ . Nevertheless, it is believed that the KS eigenfunctions fairly accurately represent 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, i.e., as the original idea of DFT.

## 8 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 Hartree and Hartree-Fock approaches.
- Explain the variational principle, and its functionality.
- Explain how variational method is utilized to derive Kohn-Sham eqs.

### 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 pros and cons with 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 pros and cons with 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 pros and cons with the KS-eq.
- Explain the basic principles of the LDA.

### k-space

- Discuss crystal lattice vectors and the reciprocal lattice vectors.
- Discuss **k**-points, Brillouin zone, and band folding.
- Discuss band structure, density-of-states, and band filling.

### 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 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 frequencies.
- 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.
- Discuss how equilibrium phase transition is modeled.
- Describe how defect concentration is calculated.