

1 Introduction

1.1 Many-Body Hamilton Operator

The starting point of a quantitative theoretical investigation of the properties of solids is the many-body Schrödinger equation

$$H\Psi = E\Psi, \text{ with } \Psi = \Psi(\{\mathbf{R}_I\}, \{\mathbf{r}_k, \sigma_k\}) \quad . \quad (1.1)$$

Here, the many-body wave function depends on the coordinates of all the atoms, $\{\mathbf{R}_I\}$, and on the space and spin coordinates of all electrons. In general, this wave function will not separate into \mathbf{R}_I - and (\mathbf{r}_k, σ_k) -dependent components. This should be kept in mind when we will introduce such a separation below and use it in most parts of this lecture. Of course, this separation is an approximation, but an extremely useful one and we will discuss its range of validity.

The properties of condensed matter are determined by the electrons and nuclei and, in particular, by their interaction ($\sim 10^{23}$ particles per cm^3). For many quantum-mechanical investigations it is useful to start with an approximation, which is called the “frozen-core approximation”. This approximation is often helpful or convenient, but it is not necessary, i.e., the many-body problem can also be solved without introducing this approximation. While most theoretical work still introduces this approximation, at the FHI we developed a methodology that treats the full problem with the same efficiency (in terms of CPU time and memory) as the “frozen-core approximation”. In terms of qualitatively discussing and understanding numerical results, as the inter-atomic interactions, it is nevertheless useful to focus on the valence electrons.

The frozen-core approximation assumes that, when condensed matter is formed from free atoms, only the valence electrons contribute to the interaction between atoms. Indeed, the electrons close to the nuclei (core electrons), which are in closed shells, will typically only have a small influence on the properties of solids. Exceptions are situations at very high pressure (small inter-atomic distances) and experiments, which more or less directly measure the core electrons or the region close to the nuclei [e.g. X-ray photo emission (XPS), electron spin resonance (ESR)]. Therefore it is reasonable to introduce the following separation already in the atom, before turning to solids: Nucleus and core electrons shall be regarded as a unit, i.e., the neutral atom consists of a positive, spherically symmetric ion of charge $Z_v e$ and of Z_v valence electrons.

This ion acts on each valence electron with a potential that looks like that shown in Fig. 1.1. The symbols have the following meaning:

Ze : nuclear charge of the atom

$Z_v e$: charge of the ion

R_c : radial extension of the core electrons

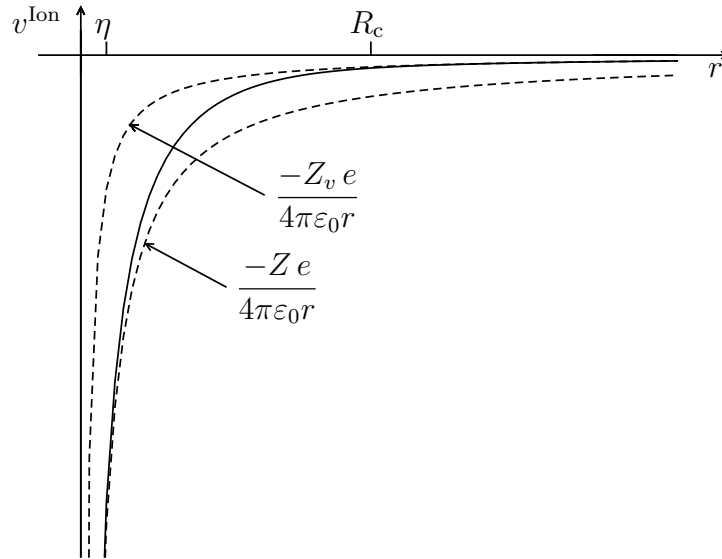


Figure 1.1: Potential of a positive ion (full line), where all valence electrons have been removed, i.e., only the electrons in closed shells are kept. The dashed curves show the asymptotic behavior for small and large distances.

Thus, the number of core electrons is $Z - Z_v$, and the solid is considered being composed of these ions and the valence electrons.

The frozen-core approximation is conceptionally appropriate, because it corresponds to the nature of the interaction. In Table 1.1, I give the electronic configuration and the ionic potentials for four examples. Here (and in Fig. 1.1), η is a small number roughly of the order of $R_c/(100Z)$. The question marks in the range $\eta \leq r \leq R_c$ indicate that in this range no analytic form of the potential can be given.

Though the field frequently uses a language (and often also a theory) in terms of ions and valence electrons, we will continue in this lecture by talking about nuclei and electrons. For the construction of the Hamilton operator of the many-body Schrödinger equation of a solid, we start with the classical Hamilton function and subsequently utilize the correspondence principle by replacing the classical momentum \mathbf{p} with the operator $(\hbar/i)\nabla$.

The many-body Hamilton operator of the solid has the following contributions:

- 1) Kinetic energy of the electrons

$$T^e = \sum_{k=1}^N \frac{\mathbf{p}_k^2}{2m} . \quad (1.2)$$

Table 1.1: Electronic configuration and ionic (frozen-core) potentials for different atoms.

atom	electronic configuration	Z	Z_v	R_c (bohr)	$v^{\text{Ion}}(r)$ (Ry)
H	$1s^1$	1	1	0	$-2/r$
He	$1s^2$	2	2	0	$-4/r$
C	$[1s^2]2s^22p^2$	6	4	0.7	$r \geq R_c$: $-8/r$ $\eta \leq r \leq R_c$: ? $r < \eta$: $-12/r$
Si	$[1s^22s^22p^6]3s^23p^2$	14	4	1.7	$r \geq R_c$: $-8/r$ $\eta \leq r \leq R_c$: ? $r < \eta$: $-28/r$

2) Kinetic energy of the nuclei

$$T^{\text{Nuc}} = \sum_{I=1}^M \frac{\mathbf{P}_I^2}{2M_I} \quad . \quad (1.3)$$

If the solid is neutral and contains only one type of atom, then $N = ZM$, where Z is the nuclear number of the atoms.

3) Electron-electron interaction

$$V^{e-e}(\{\mathbf{r}_k\sigma_k\}) \approx \frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_{\substack{k,k' \\ k \neq k'}}^{N,N} \frac{e^2}{|\mathbf{r}_k - \mathbf{r}_{k'}|} \quad . \quad (1.4)$$

We use $\{\mathbf{r}_k\sigma_k\}$ as a short-hand notation for all position and spin coordinates of the electrons: $\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2, \mathbf{r}_3, \sigma_3, \dots, \mathbf{r}_N, \sigma_N$. Here we have considered only the electrostatic interaction. In general, also the spin of the electrons and the magnetic interaction should and could be taken into account. Spin and magnetism in general require to solve the Dirac equation. Often, however, a scalar-relativistic treatment is sufficient. We will get back to this in Chapter 3 (Electron-Electron Interaction).

4) Interaction between the nuclei

$$V^{\text{Nuc-Nuc}}(\{\mathbf{R}_I\}) \approx \frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_{\substack{I,J \\ I \neq J}}^{M,M} \frac{e^2}{|\mathbf{R}_I - \mathbf{R}_J|} Z_I Z_J \quad . \quad (1.5)$$

Also here (even better justified than for the electrons) we did not consider the spin of the particles.

5) Electron-nucleus interaction (without nuclear spin)

$$V^{e-\text{Nuc}}(\{\mathbf{r}_k\sigma_k\}; \{\mathbf{R}_I\}) \approx - \sum_{I=1}^M \sum_{k=1}^N \frac{e^2}{|\mathbf{R}_I - \mathbf{r}_k|} Z_I \quad , \quad (1.6)$$

which is often summed up as:

$$-\sum_{I=1}^M \frac{e^2}{|\mathbf{R}_I - \mathbf{r}_k|} Z_I = v(\mathbf{r}_k) \quad . \quad (1.7)$$

Here, $v(\mathbf{r}_k)$ is the potential due to all the nuclei.

Consequently, the many-body Hamilton operator of the solid reads

$$H = T^e + T^{\text{Nuc}} + V^{e-e} + V^{e-\text{Nuc}} + V^{\text{Nuc}-\text{Nuc}} \quad . \quad (1.8)$$

1.2 Separation of Dynamics of Electrons and Nuclei

1.2.1 Adiabatic Approximation or Born-Oppenheimer Approximation

The dynamics of the electrons and nuclei is described by the time-dependent Schrödinger equation

$$i\hbar \frac{\partial \Psi(t)}{\partial t} = H \Psi(t) \quad , \quad (1.9)$$

where H is defined in Eq. (1.8). Thus

$$\Psi(t) = e^{-iH \cdot (t-t_0)/\hbar} \Psi(t_0) \quad . \quad (1.10)$$

In order to solve this equation, we have to bring it into a more tractable form. How can we split things up? How can we divide the problem into smaller and tractable pieces in order to conquer the whole?

Before we start the mathematical discussion, let me give an initial remark to motivate the goal: Considering the (inert) masses of nuclei and electrons, it seems to be plausible that electrons react to an external perturbation much faster than nuclei. This is reflected in the ratio of the masses, e.g.:

$$\begin{aligned} M_{\text{H}}/m &= 1,840 \quad , \\ M_{\text{Si}}/m &= 25,760 \quad , \\ M_{\text{Ag}}/m &= 86,480 \quad . \end{aligned}$$

Thus, it seems to be reasonable to assume that electrons adjust without noticeable delay to the current positions of the atoms $\{\mathbf{R}_I\}$. Formulated more precisely, it can be said that electrons in general¹ react to a perturbation on a time scale of femtoseconds (10^{-15} s), while nuclei require times of the order of picoseconds (10^{-12} s). Thus, we may assume that from the electrons point of view the nuclei do not move (or move sufficiently slowly).

¹The term “in general” implies that exceptions are possible. We will get back to such situations later in this lecture.

To check (and justify) this decoupling of the motion of the electrons and the nuclei we now give an (initially) exact discussion.

We define an operator H^e , in order to use its eigenfunctions as basis set:

$$H^e(\{\mathbf{R}_I\})\Phi_\nu(\{\mathbf{R}_I\}, \{\mathbf{r}_k\sigma_k\}) = E_\nu^e\Phi_\nu \quad , \quad (1.11)$$

with terms defined in Eqs. (1.2), (1.4), (1.6)

$$H^e = T^e + V^{e-\text{Nuc}} + V^{e-e} \quad . \quad (1.12)$$

If the kinetic energy of the nuclei would be zero (or $M_I/m \rightarrow \infty$), the electrons could be described by this equation. But strictly speaking, the meaning of the functions Φ_ν defined by Eq. (1.11) is only that of basis functions. The arguments $\{\mathbf{R}_I\}$ in the electronic wave functions should not be interpreted as a variable of the wave function, but as parameters which classify the Hamilton operator H^e (similar to the nuclear numbers Z_I).

The following statement is exact: The solutions of Eq. (1.1) with the Hamiltonian defined by Eq. (1.8) can be expanded in terms of the functions Φ_ν [the eigenfunctions of Eq. (1.11)]

$$\Psi = \sum_{\nu} \Lambda_\nu(\{\mathbf{R}_I\})\Phi_\nu(\{\mathbf{R}_I\}, \{\mathbf{r}_k\sigma_k\}) \quad . \quad (1.13)$$

The meaning of Eq. (1.11) and (1.13) can also be expressed as: The eigenfunctions of H^e for each atomic configuration $\{\mathbf{R}_I\}$ form a complete set of functions. Strictly speaking, the eigenfunctions of *one* atomic configuration $\{\mathbf{R}_I\}$ are complete (with respect to the electronic coordinates), i.e., the Hilbert spaces of different atomic configurations $\{\mathbf{R}_I\}$ are the same. Still it is reasonable (here) to consider the functions $\Phi_\nu(\{\mathbf{R}_I\}, \{\mathbf{r}_k\sigma_k\})$ as being dependent of \mathbf{R}_I . Mathematically it would also be correct to take the $H^e(\mathbf{R}_I)$ and the $\Phi_\nu(\{\mathbf{R}_I\}, \{\mathbf{r}_k\sigma_k\})$ of a certain configuration \mathbf{R}_I^0 and to consider the dependence on \mathbf{R}_I only by the coefficients $\Lambda_\nu(\{\mathbf{R}_I\})$. This will be discussed in Section 1.2.2. Now, we investigate the equation $H\Psi = E\Psi$, representing Ψ by Eq. (1.13) and

$$H = H^e + T^{\text{Nuc}} + V^{\text{Nuc}} + V^{\text{Nuc}-\text{Nuc}} \quad . \quad (1.14)$$

Obviously, for the operator H^e we have

$$H^e\Lambda_\nu\Phi_\nu = \Lambda_\nu H^e\Phi_\nu = \Lambda_\nu E_\nu^e\Phi_\nu \quad . \quad (1.15)$$

Considering the full Schrödinger equation (1.1) together with Eqs. (1.8) and (1.13), $V^{\text{Nuc}-\text{Nuc}}$ can be interchanged with Λ_ν , but not T^{Nuc} . Applying the chain rule we obtain

$$\nabla_{\mathbf{R}_I}^2(\Lambda_\nu\Phi_\nu) = \Lambda_\nu(\nabla_{\mathbf{R}_I}^2\Phi_\nu) + 2(\nabla_{\mathbf{R}_I}\Lambda_\nu)(\nabla_{\mathbf{R}_I}\Phi_\nu) + (\nabla_{\mathbf{R}_I}^2\Lambda_\nu)\Phi_\nu \quad . \quad (1.16)$$

Now Eq. (1.1) for the ground state E_0 , Ψ_0 is multiplied from the left by Φ_μ^* and integrated over the electronic coordinates. Using Eq. (1.11), the equation used to determine the “wave function of the electrons” Φ_ν , we obtain

$$\langle \Phi_\mu | H | \Psi_0 \rangle = E_0 \Lambda_\mu = (E_\mu^e + T^{\text{Nuc}} + V^{\text{Nuc-Nuc}}) \Lambda_\mu + \sum_\nu \sum_{I=1}^M -\frac{\hbar^2}{2M_I} [\langle \Phi_\mu | \nabla_{\mathbf{R}_I}^2 | \Phi_\nu \rangle \Lambda_\nu + 2 \langle \Phi_\mu | \nabla_{\mathbf{R}_I} | \Phi_\nu \rangle (\nabla_{\mathbf{R}_I} \Lambda_\nu)] \quad . \quad (1.17)$$

For each electronic state Φ_μ , E_μ^e there is one such equation. The difficult part in solving Eq.(1.17) are the terms coupling Φ_μ and Φ_ν . They describe that the dynamics of the lattice atoms the $(\nabla_{\mathbf{R}_I}$ and $\nabla_{\mathbf{R}_I}^2$ operators) couples different electronic states. These terms are called electron-phonon (or electron-vibrational) coupling.²

The electron-phonon coupling can be calculated. Then one often finds that for many properties of solids it is not very important and can be neglected. However, for the “standard superconductivity” (BCS-theory) it is essential. Initially, for the new superconductors it was believed that the electron-phonon interaction is not the main origin of superconductivity. Nowadays, this is not generally accepted anymore, and it is still debated what the actuating mechanism is. For some solids electron-phonon coupling has measurable influence on the spectrum of the lattice vibrations, and for some situations the electron-phonon coupling is responsible for structural instabilities. Keywords are, for example, Kohn-anomaly, Jahn-Teller-effect, and Peierls instability. These mechanisms become important because of certain aspects of the electronic structure. They will be discussed later, when we discuss defects and surfaces. Electron-phonon coupling is also relevant for and noticeable in electron spectroscopy of solids, e.g., when measuring the band gaps of semiconductors. The corresponding theory and actual calculations represent the current state-of-the-art in this field.

Up to this point our derivation is exact. More general statements concerning the importance of the electron-phonon coupling are usually not possible. Now we will introduce two approximations:

- 1) We assume that at each time, i.e., for each lattice geometry $\{\mathbf{R}_I\}$, the electrons are in an eigenstate of H^e . Thus, we assume that the motion of the lattice does not induce transitions from Φ_μ to Φ_ν . The reasoning behind this assumption is that the electrons (typically) react fast and therefore follow the nuclear motion instantaneously. One may also say that the electrons do not feel the nuclear motion and are always in the electronic ground state. In this case, the matrix elements $\langle \Phi_\mu | \nabla_{\mathbf{R}_I}^2 | \Phi_\nu \rangle$ and $\langle \Phi_\mu | \nabla_{\mathbf{R}_I} | \Phi_\nu \rangle$ in Eq. (1.17) are zero for $\mu \neq \nu$.

This is called the adiabatic principle or Born-Oppenheimer approximation. In general, its quantitative validity, i.e., the importance of the off-diagonal elements, is hard to evaluate.

²Later in this lecture there will be a full Chapter on lattice vibrations (phonons).

2) The magnitude of the diagonal elements of the electron-phonon interaction can be estimated:

- a) The term $\langle \Phi_\mu | \nabla_{\mathbf{R}_I} | \Phi_\mu \rangle = \frac{1}{2} \nabla_{\mathbf{R}_I} \langle \Phi_\mu | \Phi_\mu \rangle$ vanishes exactly, because $\langle \Phi_\mu | \Phi_\mu \rangle = 1$, i.e., it is constant. The derivative of a constant is zero.
- b) For the term

$$-\frac{\hbar^2}{2M_I} \langle \Phi_\mu | \nabla_{\mathbf{R}_I}^2 | \Phi_\mu \rangle \quad (1.18)$$

the strongest imaginable dependence would exist, if the electrons would follow the atoms without any delay and distortion. This means

$$|\langle \Phi_\mu | \nabla_{\mathbf{R}_I}^2 | \Phi_\mu \rangle| \lesssim |\langle \Phi_\mu | \nabla_{\mathbf{r}_k}^2 | \Phi_\mu \rangle| \quad (1.19)$$

and further

$$\begin{aligned} \left| -\frac{\hbar^2}{2M_I} \langle \Phi_\mu | \nabla_{\mathbf{R}_I}^2 | \Phi_\mu \rangle \right| &\lesssim \frac{m}{M_I} \left| -\frac{\hbar^2}{2m} \langle \Phi_\mu | \nabla_{\mathbf{r}_k}^2 | \Phi_\mu \rangle \right| \\ &\approx 10^{-4} \times \text{kinetic energy of an electron.} \end{aligned} \quad (1.20)$$

Thus, for the diagonal elements $\mu = \nu$, but unfortunately only for these, a rough estimation is possible.

With Eq. (1.20) and the adiabatic approximation we obtain the Schrödinger equation for “the wave functions of the nuclei”:

$$(T^{\text{Nuc}} + V^{\text{Nuc-Nuc}} + E_\mu^e) \Lambda_\mu = E_0 \Lambda_\mu \quad . \quad (1.21)$$

For the energetically lowest electronic state we will often write

$$V^{\text{Nuc-Nuc}} + E_{\mu=0}^e = V^{\text{BO}} \quad , \quad (1.22)$$

and V^{BO} is called “potential-energy surface” (PES) or “Born-Oppenheimer energy surface”. The PES is the energy surface the nuclei are moving on according to Eq.(1.21).

When neglecting the coupling terms $\langle \Phi_\mu | \dots | \Phi_\nu \rangle$ in Eq. (1.17), the eigenfunction of the ground state of H has the form:

$$\Psi \rightarrow \Psi^{\text{BO}} = \Lambda_0(\{\mathbf{R}_I\}) \Phi_0(\{\mathbf{R}_I\}, \{\mathbf{r}_k, \sigma_k\}) \quad , \quad (1.23)$$

where Φ_0 is determined by Eq.(1.11) and Λ_0 by Eq. (1.21). Equation (1.11) and Eq. (1.21) can be calculated reliably using modern methods.

Strictly, the motion of the nuclei on the Born-Oppenheimer surface would have to be described quantum mechanically. When the respective equations are solved, one finds that they can be almost always replaced by the classical (Newton) equations of motion. Quantum-mechanical effects like zero-point vibrations and tunneling only rarely play an

important role. Hydrogen, as the lightest element, is an exception, but already for the deuteron a classical treatment is sufficient in most cases.

In general, the functions Λ_0 are narrowly peaked and centered at the atomic sites $\{\mathbf{R}_I\}$. Consequently, for the ground state of Eq. (1.21) we have:

$$E_0 = E_0^e(\{\mathbf{R}_I^0\}) + \frac{1}{4\pi\epsilon_0} \frac{1}{2} \sum_{\substack{I,J \\ I \neq J}}^{M,M} \frac{e^2}{|\mathbf{R}_I^0 - \mathbf{R}_J^0|} Z_I Z_J + \langle \Lambda_0 | T^{\text{Nuc}} + V^{\text{BO}}(\{\mathbf{R}_I^0 - \mathbf{R}_I\}) | \Lambda_0 \rangle \quad (1.24)$$

The last term describes the zero-point vibrations. Equation (1.24) forms the basis of the *ab initio* calculation of the electronic, structural, elastic, and vibrational properties of solids. E_0 is often called total energy (or structural energy). It is based on just one approximation, the Born-Oppenheimer (or adiabatic) approximation.

The Born-Oppenheimer potential, $V^{\text{BO}}(\{\mathbf{R}_I\})$ refers to the *actual* position of the nuclei (which typically changes with time), and it assumes that the functions $\Phi_\mu(\{\mathbf{R}_I\}, \{\mathbf{r}_k, \sigma_k\})$ refer to exactly these positions. A hard proof of the validity of the Born-Oppenheimer approximation is not possible and, in fact, the quality of this approximation depends on the actual problem, because there might be situations, in which the electrons react slower than assumed above, and then they will not be able to follow the motion of the nuclei instantaneously, but only with some delay and distortion. The latter means that there are electronic transitions between the electronic ground state and excited states. Systematic studies of electron-vibrational coupling are a timely and increasingly important research topic.

The derivation in this section was reasonable in order to show the form of the matrix elements of the electron-phonon interaction. Further, we wanted to estimate the order of magnitude of the matrix elements. In principle, for each calculation the validity of the Born-Oppenheimer-approximation should be checked by an explicit calculation of the matrix elements in Eq. (1.17) or at least by an estimation.

1.2.2 Static Approximation

We now briefly give an alternative derivation, which is often called the “static approximation”. The nuclei are always in motion, but in many cases they will just vibrate around a position that represents a minimum of the Born-Oppenheimer potential energy, $\{\mathbf{R}_I^0\}$. We now investigate the Hamilton operator $H^e(\{\mathbf{R}_I^0\})$, which yields the wave functions of the electrons $\Phi_\nu(\{\mathbf{R}_I^0\}, \{\mathbf{r}_k, \sigma_k\})$ at these equilibrium positions $\{\mathbf{R}_I^0\}$ (cf. Eqs. (1.11), (1.12)). Again, these Hamiltonian $H^e(\{\mathbf{R}_I^0\})$ defines (by its eigenvectors) a complete set of functions, which we can use as a basis set for the general problem. Though this basis now refers to a fixed (static) geometry the treatment is as general as that of Sec. 1.2.1 above. Although the final equations look different, they describe the same physics.

In the present treatment the wave function of the solid is

$$\Psi(\{\mathbf{R}_I\}, \{\mathbf{r}_k\sigma_k\}) = \sum_{\nu} \hat{\Lambda}_{\nu}(\{\mathbf{R}_I\}) \Phi_{\nu}(\{\mathbf{R}_I^0\}, \{\mathbf{r}_k\sigma_k\}) \quad . \quad (1.25)$$

This equation is (so far) exact, too. But the expansion coefficients are different; therefore we added a “hat” to the Λ . Using $\Delta\mathbf{R}_I = \mathbf{R}_I - \mathbf{R}_I^0$, the components of the Hamilton operator containing the nucleus-nucleus and the electron-nucleus interaction [cf. Eqs. (1.5) and (1.6)] can be formally rewritten as:

$$V^{\text{Nuc-Nuc}}(\{\mathbf{R}_I\}) = V^{\text{Nuc-Nuc}}(\{\mathbf{R}_I^0\}) + V^{\text{ph}}(\{\Delta\mathbf{R}_I\}) \quad , \quad (1.26)$$

$$V^{e-\text{Nuc}}(\{\mathbf{R}_I\}, \{\mathbf{r}_k\sigma_k\}) = V^{e-\text{Nuc}}(\{\mathbf{R}_I^0\}, \{\mathbf{r}_k\sigma_k\}) + V^{e-\text{ph}}(\{\Delta\mathbf{R}_I\}, \{\mathbf{r}_k\sigma_k\}) \quad . \quad (1.27)$$

This defines two terms: The phonon potential energy $V^{\text{ph}}(\{\Delta\mathbf{R}_I\})$ and the electron-phonon coupling $V^{e-\text{ph}}(\{\Delta\mathbf{R}_I\}, \{\mathbf{r}_k\sigma_k\})$. From this we obtain the equation that determines the coefficients of the expansion and the energy eigenvalues of the solid

$$E_{\mu}^e \hat{\Lambda}_{\mu} + T^{\text{Nuc}} \hat{\Lambda}_{\mu} + V^{\text{Nuc-Nuc}}(\{\mathbf{R}_I^0\}) \hat{\Lambda}_{\mu} + \sum_{\nu} \langle \Phi_{\mu}(\{\mathbf{R}_I^0\}, \{\mathbf{r}_k\sigma_k\}) | V^{e-\text{ph}} + V^{\text{ph}} | \Phi_{\nu}(\{\mathbf{R}_I^0\}, \{\mathbf{r}_k\sigma_k\}) \rangle \hat{\Lambda}_{\nu} = E_0 \hat{\Lambda}_{\mu} \quad . \quad (1.28)$$

The difference of this equation to Eq. (1.17) is that in the second line now there is no differential operator. Also, E_{μ}^e is no longer a function of $\{\mathbf{R}_I\}$, but it is evaluated at the fixed geometry $\{\mathbf{R}_I^0\}$.

If we neglect the coupling terms $\langle \Phi_{\mu} | \dots | \Phi_{\nu} \rangle$ in Eq. (1.28), we obtain for the general wave function of the ground state

$$\Psi \rightarrow \Psi^{\text{static}} = \hat{\Lambda}_0 \Phi_0 \quad .$$

Here Φ_0 is the solution of $H^e(\{\mathbf{R}_I^0\})$ and $\hat{\Lambda}_0$ is the solution of $[T^{\text{Nuc}} + E_0^e(\{\mathbf{R}_I^0\}) + V^{\text{Nuc-Nuc}}(\{\mathbf{R}_I^0\})] \hat{\Lambda}_0 = E_0 \hat{\Lambda}_0$. The error which is introduced by this ansatz and by neglecting the coupling of Φ_{μ} and Φ_{ν} in Eq. (1.28) is typically small and actually approaches zero in a first order perturbational approach.

1.2.3 Examples

What can we learn from the Born-Oppenheimer PES or, slightly more general, from

$$E_0 = V^{\text{BO}} + \text{quantum mechanical corrections for lattice vibrations} \quad ? \quad (1.29)$$

The difficulty, i.e., getting to know E_0^e (solving the Schrödinger equation of the electrons), will be ignored for the moment. It will be addressed later (in Chapter 3). Here we simply assume that $E_0^e(\{\mathbf{R}_I\})$ and $V^{\text{BO}}(\{\mathbf{R}_I\})$ are known.

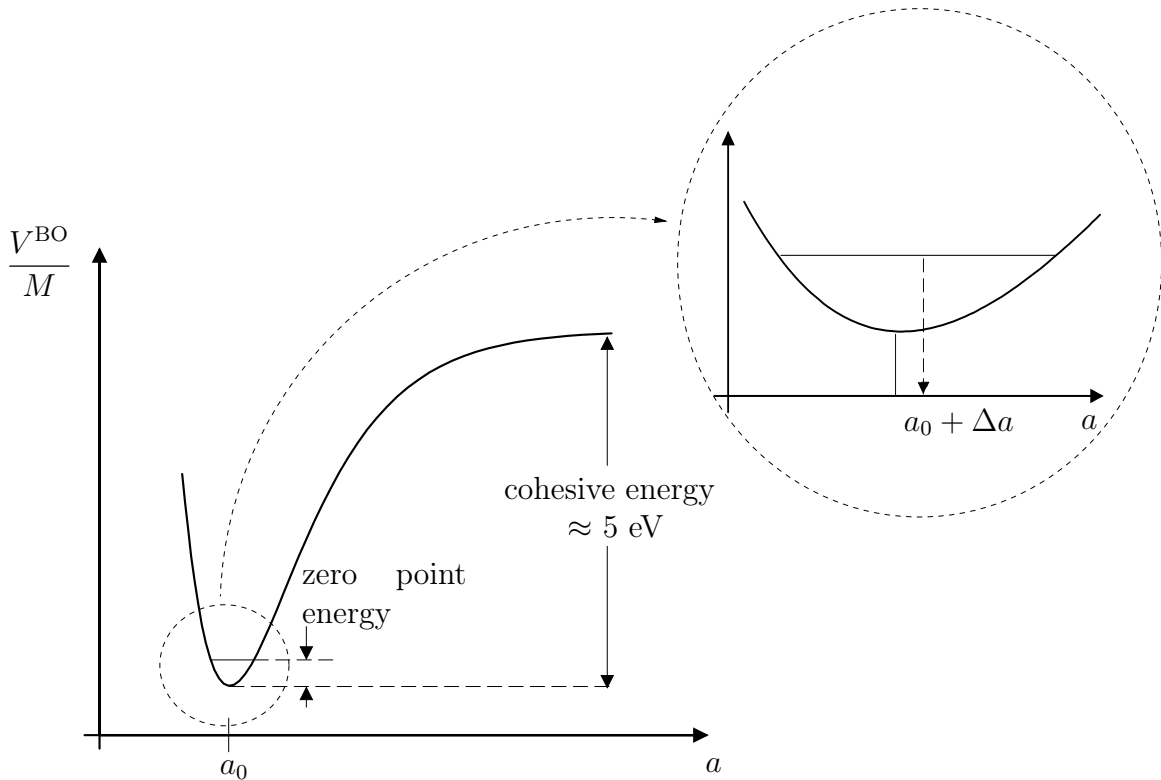


Figure 1.2: The total energy per atom (without zero-point vibrations) as a function of the inter-atomic distance. The minimum of the curve determines the stable equilibrium geometry. The lattice constant, as measured, does not correspond to the minimum of the curve, but to the average over the zero point vibrations: $a_0 + \Delta a$.

1.2.3.1 Structure, Lattice Constant, and Elastic Properties of Perfect Crystals

For a cubic crystal, due to the periodicity, the dependence of the total energy E_0 in Eq. (1.29) on the $\{\mathbf{R}_I\}$ is reduced to a single variable a , which determines the inter-atomic distances in a crystal. In Fig. 1.2 the total energy per atom is shown schematically: The cohesive energy is the energy, which is gained by the formation of the crystal from the individual atoms.

The minimum of the total energy determines the equilibrium position and therefore the lattice constant a_0 of the crystal. The “bulk modulus” B_0 , which describes the dependence of the equilibrium geometry on the external pressure, can be determined from the energy curve $E(a)$. It is defined as the product of the second derivative (curvature) of the energy times the volume V (at the equilibrium distance a_0):

$$B_0 = \frac{1}{K} = V \left. \frac{\partial^2 V^{\text{BO}}(V)}{\partial V^2} \right|_{a=a_0}, \quad (1.30)$$

where V is the volume per atom (for a cubic crystal $V = a^3$) and K is the compressibility.

Figure 1.2 shows the typical behavior of the binding energy of polyatomic systems as a function of the inter-atomic distance, and this form is often called “equation of state”.

Typically V^{BO} is calculated for about 10 geometries and then the curve is represented by an analytical fit.

The minimum of the “equation of state” is close to, but not exactly at, the lattice constant of the solid, because the “equation of state” shows a clear asymmetry.

The order of magnitude of the zero point vibrations can be estimated from the uncertainty relation:

$$\Delta P \Delta X \geq \hbar/2 \quad .$$

If $\Delta X = 0.1$ bohr (a typical inter-atomic distance is 5 bohr ≈ 2.5 Å), it follows

$$\frac{P^2}{2M} \approx 0.02 \text{eV/atom} \quad .$$

In comparison to the binding energy of the solid (cohesive energy) this is a small number ($\approx \frac{1}{200} E^{\text{coh}}$), but still, the zero point vibrations do have a measurable effect: $\approx 0.1\%$ increase of the lattice constant compared to a neglect of $\langle \Lambda_0 | T^{\text{Nuc}} + V^{\text{BO}}(\{\Delta \mathbf{R}_I\}) | \Lambda_0 \rangle$.

In Chapter 6 (cohesion) we will return to the “equation of state” and there we will compare crystal structures.

Obviously, when higher-energy vibrations are excited (by higher temperatures) the lattice constant increases³. This is due to the non-harmonic behavior of V^{BO} around its minimum (cf. Fig. 1.2): For a value smaller than a_0 the potential energy increases steeply due to Pauli repulsion. All solids with one atom per unit cell show such thermal expansion.

1.2.3.2 Lattice Waves (Phonons)

When intending to calculate the energy of lattice waves (phonons), E_0 has to be investigated as a function of the wavelength λ and the direction of the lattice wave. Figure 1.3 shows the example of a “frozen phonon”.⁴ The magnitude of η “tells”, how many phonons of wave length λ are excited. The energy of this lattice wave follows from the energy difference $E_0(\{\mathbf{R}_I\}) - E_0(\{\mathbf{R}_I^0\})$, where $\{\mathbf{R}_I^0\}$ is the geometry of the minimum of the PES (cf. Fig. 1.2), and $\{\mathbf{R}_I\}$ is the periodically distorted geometry sketched in Fig. 1.3.

From the energy of the lattice wave we can for example obtain the specific heat of the lattice (cf. Ashcroft and Mermin, p. 452-454) and the thermal expansion.

³Some materials exhibit a “negative thermal expansion”, i.e., they shrink with increasing temperature. This is actuated by entropy effects or by a change in magnetism. We will get back to such cases later during the lecture.

⁴The detailed introduction and discussion of phonons will be described later in a full chapter.

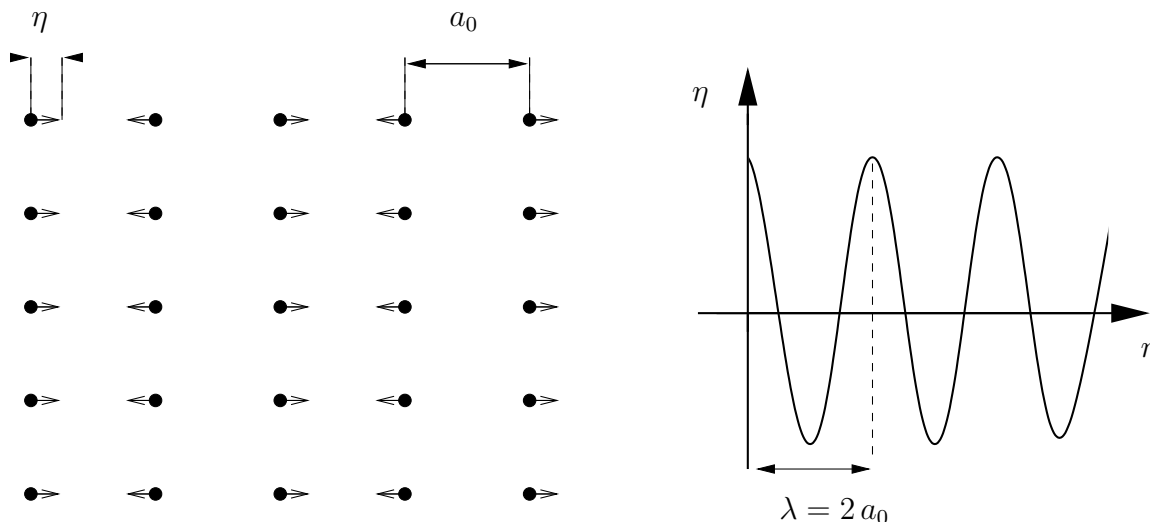


Figure 1.3: Schematic picture of a snapshot of a lattice wave (frozen phonon). The arrows give the direction of the distortion of the atoms. The wave length is $\lambda = 2a_0$, and a_0 is the equilibrium distance of the atoms. The amplitude of the distortion is η .

1.3 The Ewald Method

(References: J.C. Slater, Insulators, Semiconductors and Metals, Quantum Theory of Molecules and Solids, Vol. 3, McGraw Hill, 1967, S. 215-220)

The sum appearing in Eq. (1.24), now evaluated per atom,

$$\frac{E^{\text{Nuc-Nuc}}}{M} = \frac{1}{M} \frac{1}{4\pi\epsilon_0} \frac{1}{2} \sum_{\substack{I,J \\ I \neq J}}^{M,M} \frac{e^2}{|\mathbf{R}_I - \mathbf{R}_J|} Z_I Z_J \quad , \quad (1.31)$$

exhibits an interesting (and often important) aspect. It cannot be calculated directly, because it converges very slowly or not at all. Even for a very large number of atoms M the result depends on the order of summation, or on the shape of the surface that includes the already summed up terms.

In general, the sum in Eq. (1.31) is an important contribution to the total energy. And for ionic crystals (e.g. if one considers NaCl as being composed of Na^+ and Cl^- nuclei) it is even the dominating part of the total energy. The poor convergence of the sum in Eq. (1.31) is therefore somewhat unexpected. The reason is the long range of the Coulomb interaction. The methodical treatment for evaluating Eq. (1.31) is important for actual calculations, but it is also interesting, because it clarifies a methodical approach that in analogous ways is also helpful for other problems. In general the procedure can be described as follows: If there is an apparently unsolvable problem, first a similar (and possibly uninteresting) problem is solved and then the *difference* of the two systems is investigated.

The problem in the calculation of the sum in Eq. (1.31), i.e., the poor convergence, originates from the fact that the number of atoms that are at the same distance from a chosen center is growing with this distance. We discuss the example of a periodic solid

with only one atom per unit cell⁵ (and therefore only one atom type) located at \mathbf{R}_1 . It follows

$$\frac{E^{\text{Nuc-Nuc}}}{M} = \frac{1}{4\pi\epsilon_0} \frac{1}{2} \sum_{I=2}^M \frac{Z^2 e^2}{|\mathbf{R}_I - \mathbf{R}_1|} = \frac{1}{2} Z e \phi(\mathbf{R}_1) \quad . \quad (1.32)$$

Here, $\phi(\mathbf{R}_1)$ is the electrostatic potential generated at the position \mathbf{R}_1 of the $I = 1$ ion by all other ions $I = 2, 3, \dots, M$, i.e., the periodic images of $I = 1$. Because of this periodicity we have $\phi(\mathbf{R}_1) = \phi(\mathbf{R}_2) = \phi(\mathbf{R}_3)$, etc.. The electrostatic potential can be calculated from the Poisson equation. If $e n^+(\mathbf{r})$ is the charge density of the nuclei, we have

$$\nabla^2 \tilde{\phi}(\mathbf{r}) = -\frac{e}{\epsilon_0} n^+(\mathbf{r}) \quad . \quad (1.33)$$

Initially, we take into account *all* atoms in this equation, including $I = 1$. Later we will remove the contribution of $I = 1$, as it should not appear in Eq. (1.32). We have:

$$\phi(\mathbf{R}_1) = \tilde{\phi}(\mathbf{R}_1) - \text{contribution of the charge density of the nucleus \#1} \quad . \quad (1.34)$$

First, the reason for the difficulties in evaluating Eq. (1.33) will be pointed out. Because in a periodic crystal $n^+(\mathbf{r})$ is periodic, we have

$$n^+(\mathbf{r}) = \sum_{\mathbf{G}_n} n^+(\mathbf{G}_n) e^{i\mathbf{G}_n \mathbf{r}} \quad (1.35)$$

with

$$n^+(\mathbf{G}_n) = \frac{1}{\Omega} \int_{\Omega} n^+(\mathbf{r}) e^{-i\mathbf{G}_n \mathbf{r}} d^3\mathbf{r} \quad (1.36)$$

and $\mathbf{R}_n \mathbf{G}_n = 2\pi\Gamma$, where Γ is an integer number. Ω is the volume of the unit cell⁵ (cf. Chapter 4). We have

$$n^+(\mathbf{G}_n = 0) = \frac{1}{\Omega} Z \quad ; \quad (1.37)$$

and because of the Poisson-equation (1.33) it follows for the electrostatic potential $\tilde{\phi}$

$$\nabla^2 \tilde{\phi}(\mathbf{r}) = -\frac{e}{\epsilon_0} \sum_{\mathbf{G}_n} n^+(\mathbf{G}_n) e^{i\mathbf{G}_n \mathbf{r}} \quad (1.38)$$

and therefore

$$\tilde{\phi}(\mathbf{r}) = \frac{e}{\epsilon_0} \sum_{\mathbf{G}_n} \frac{n^+(\mathbf{G}_n) e^{i\mathbf{G}_n \mathbf{r}}}{|\mathbf{G}_n|^2} + C \quad , \quad (1.39)$$

which is easily verified by evaluating $\nabla^2 \tilde{\phi}(\mathbf{r})$. We point out that the singularity of Eq. (1.39) for $\mathbf{G}_n = 0$ does not play a role. It is cancelled by a corresponding singularity in the other contributions to the total energy, which appear in V^{e-e} and $V^{e-\text{Nuc}}$. This is reasonable,

⁵The unit cell is the smallest unit which can be used to construct a periodic solid.

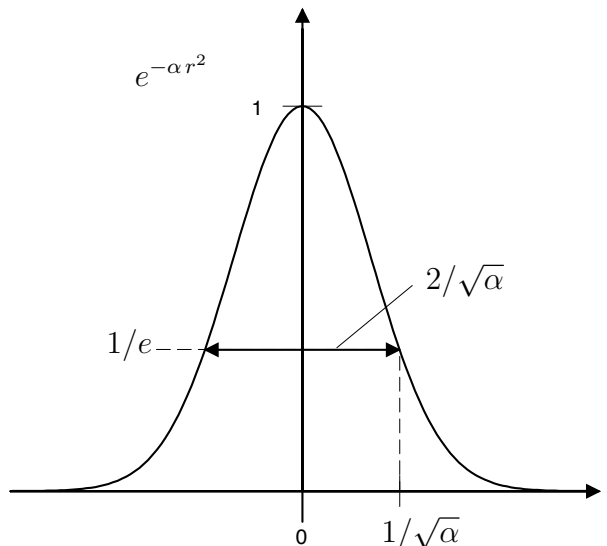


Figure 1.4: Gaussian function $e^{-\alpha r^2}$. The width (at value $e^{-\alpha r^2} = 1/e = 0.368$) is $2/\sqrt{\alpha}$.

because for a neutral system the term $\mathbf{G}_n = 0$ has to disappear after all. The singularity for $\mathbf{G}_n = 0$ in Eq. (1.39) will therefore be ignored.

If $e n^+(\mathbf{r})$ would only contain the nuclear charges, i.e., δ -functions, then for all terms we have $n^+(\mathbf{G}_n) = \frac{Zv}{\Omega}$. We note for Eq. (1.32) and (1.39) that *the potential of δ -shaped charge densities converges poorly in real space and in Fourier space.*

On the other hand in Eq. (1.39) one recognizes that the convergence of the series would be better if we had a charge density $n^+(\mathbf{r})$, for which $n^+(\mathbf{G}_n)$ decreases with increasing $|\mathbf{G}_n|^2$. An exponential decay would be best. It follows that a sum of Gaussian functions has to converge nicely. Thus we first investigate such Gaussian-shaped charge densities, although this does not directly correspond to what we are interested in:

$$n_{\text{Gauss}}^+(\mathbf{r}) = Z \sum_{I=1}^M \left(\frac{\alpha}{\pi}\right)^{3/2} e^{-\alpha|\mathbf{r}-\mathbf{R}_I|^2} \quad . \quad (1.40)$$

We have normalized the individual Gaussian functions, i.e., we have

$$\int \left(\frac{\alpha}{\pi}\right)^{3/2} e^{-\alpha|\mathbf{r}-\mathbf{R}_I|^2} d\mathbf{r} = 1 \quad , \quad (1.41)$$

and $2/\sqrt{\alpha}$ is the width of the individual Gaussians (cf. Fig. 1.4). The Fourier representation of $n_{\text{Gauss}}^+(\mathbf{r})$ has the form:

$$n_{\text{Gauss}}^+(\mathbf{G}_n) = \frac{Z}{\Omega} \sum_{I=1}^M \int_{\Omega} \left(\frac{\alpha}{\pi}\right)^{3/2} e^{-\alpha|\mathbf{r}-\mathbf{R}_I|^2} e^{-i\mathbf{G}_n \mathbf{r}} d^3\mathbf{r} = \frac{Z}{\Omega} e^{-\left(\frac{\mathbf{G}_n^2}{4\alpha}\right)} \quad , \quad (1.42)$$

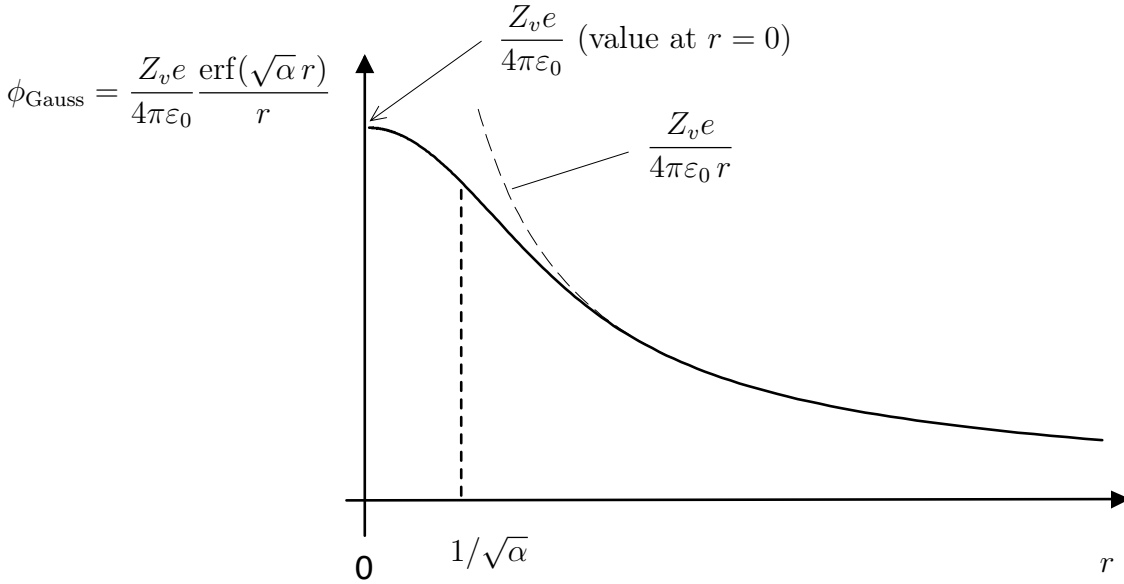


Figure 1.5: The electrostatic potential of a Gaussian shaped charge density of charge $e Z_v$. For large ($r > 1/\sqrt{\alpha}$) the function become identical to $\frac{Z_v e}{4\pi\epsilon_0 r}$.

and for the corresponding electrostatic potential we obtain from the Poisson equation

$$\tilde{\phi}_{\text{Gauss}}(\mathbf{r}) = \frac{Z e}{\Omega \epsilon_0} \sum_{\mathbf{G}_n} \frac{e^{-\left(\frac{\mathbf{G}_n^2}{4\alpha}\right)} e^{i\mathbf{G}_n \mathbf{r}}}{|\mathbf{G}_n|^2} + C \quad (1.43)$$

$$= \frac{Z e}{4\pi\epsilon_0} \sum_{I=1}^M \frac{\text{erf}(\sqrt{\alpha}|\mathbf{r} - \mathbf{R}_I|)}{|\mathbf{r} - \mathbf{R}_I|} + C \quad . \quad (1.44)$$

Here $\text{erf}(x)$ is the error function

$$\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-x'^2} dx' \quad . \quad (1.45)$$

This means,

$$\frac{Z e}{4\pi\epsilon_0} \times \frac{\text{erf}(\sqrt{\alpha}|\mathbf{r} - \mathbf{R}_I|)}{|\mathbf{r} - \mathbf{R}_I|} \quad (1.46)$$

is the electrostatic potential, which is created by a Gaussian charge density cloud being centered at position \mathbf{R}_I (cf. Fig. 1.5).

In contrast to $\tilde{\phi}(\mathbf{r})$ in Eq. (1.39), this sum [cf. Eq. (1.42) and (1.44)] converges excellently. This is because of the factor $\exp(-\mathbf{G}_n^2/4\alpha)$. The smaller α , the wider are the Gaussians and the smoother is $\phi_{\text{Gauss}}(\mathbf{r})$ and the better is the convergence with respect to \mathbf{G}_n .

Because we are not interested in Gaussian clouds, we write for the density of interest

$$n^+(\mathbf{r}) = \{n^+(\mathbf{r}) - n_{\text{Gauss}}^+(\mathbf{r})\} + n_{\text{Gauss}}^+(\mathbf{r}) \quad . \quad (1.47)$$

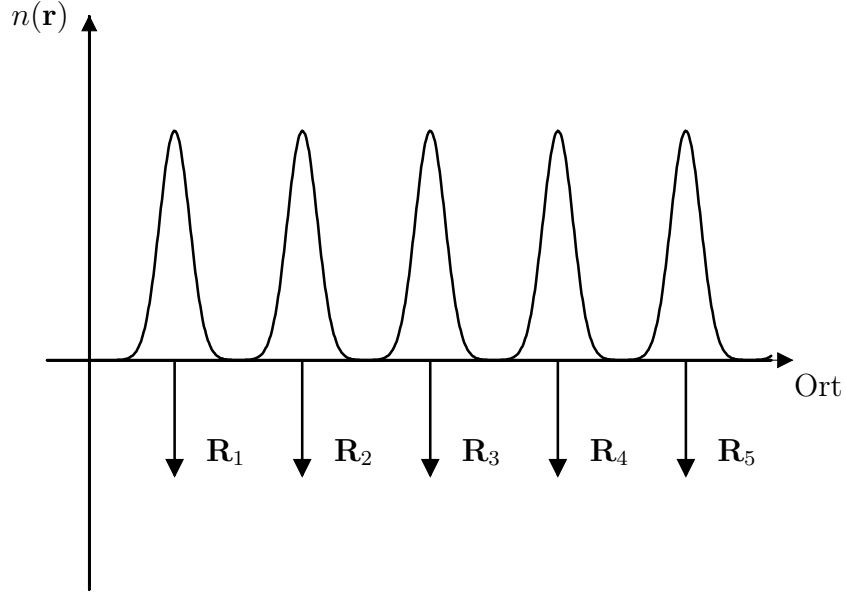


Figure 1.6: Charge distribution of point charges and surrounding Gaussian charge densities. Delta-functions are represented by arrows.

Together, the first two components describe a neutral charge, i.e., δ -shaped point charges, which are surrounded by oppositely charged Gaussian clouds and therefore are screened. It is therefore obvious that the sum over such neutral objects converges rapidly in real space. The charge distribution is shown in Fig. 1.6. The last term in Eq. (1.47) converges, as discussed above, very nicely in Fourier space.

We recognize that the contributions being centered at different positions now do not interact (or interact only weakly). The electrostatic field of these two components is:

$$\phi_{1,2}(\mathbf{r}) = \frac{Ze}{4\pi\epsilon_0} \sum_{I=1}^M \left\{ \frac{1 - \operatorname{erf}(\sqrt{\alpha}|\mathbf{r} - \mathbf{R}_I|)}{|\mathbf{r} - \mathbf{R}_I|} \right\} + C \quad . \quad (1.48)$$

The term in the curly brackets of Eq. (1.48) vanishes with increasing distance to the nucleus at position \mathbf{R}_I . Consequently, the sum converges rapidly. Only a few atomic positions in the neighborhood of \mathbf{r} have to be taken into account. The third contribution in Eq. (1.48) of $n^+(\mathbf{r})$, the Gaussian clouds, we describe in the representation of Eq. (1.44). For the potential that we want to calculate, we thus obtain

$$\begin{aligned} \phi(\mathbf{r}) = & + \frac{Ze}{4\pi\epsilon_0} \sum_{I=1}^M \frac{1 - \operatorname{erf}(\sqrt{\alpha}|\mathbf{r} - \mathbf{R}_I|)}{|\mathbf{r} - \mathbf{R}_I|} \\ & + \frac{Ze}{\Omega\epsilon_0} \sum_{\mathbf{G}_n} \frac{e^{-\frac{\alpha_n^2}{4\alpha}} e^{i\mathbf{G}_n\mathbf{r}}}{|\mathbf{G}_n|^2} - \frac{Ze}{4\pi\epsilon_0} \frac{1}{|\mathbf{r} - \mathbf{R}_1|} + C \quad . \end{aligned} \quad (1.49)$$

Here we have now removed also the $\mathbf{R}_I = \mathbf{R}_1$ contribution (cf. Eq. (1.32)).

Finally, I will briefly discuss the integration constant C . The electrostatic potential $\phi(\mathbf{r})$, as written down in Eq. 1.49), depends on α . Of course this is unphysical and unwanted.

The reason for this dependence is that we have not yet determined the integration constant C , which appeared in the solution of the Poisson-equation for $\phi_{\text{Gauss}}(\mathbf{r})$.

From the condition that ϕ should not depend on α we obtain the integration constant C . It has to be fulfilled:

$$\frac{d\phi(\mathbf{r})}{d\alpha} = 0 \quad . \quad (1.50)$$

The calculation yields:

$$C = -\frac{\pi Z_v e}{\Omega \alpha} \times \frac{1}{4\pi \epsilon_0} \quad . \quad (1.51)$$