

# Chapter 1

## Introduction

### 1.1 The Many-Body Hamilton Operator

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

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

Here, the many-body wave function depends on the coordinates of all the atoms,  $\mathbf{R}_I$ , and on the coordinates and spin coordinates of all electrons. In general, this wave function will not separate into  $\mathbf{R}_I$  and  $(\mathbf{r}_k, \sigma_k)$  dependent components. This should be kept in mind when below, and in most parts of this lecture, we will introduce such separation. Of course, we will also discuss the range of its validity. The properties of matter are determined by the electrons and nuclei and in particular by their interaction ( $10^{23}$  particles per  $\text{cm}^3$ ). For many quantum mechanical investigations it is useful to start with an approximation, which is called the “frozen-core approximation”. This is a reasonable approximation although *a priori* it is not clear why it is simplifying the theoretical treatment. Later, however, we will realize that the frozen-core approximation in general provides a higher accuracy and reliability to quantitative calculations. This approximation is often helpful or convenient, but not necessarily required, i.e., the many-body problem can also be solved without introducing this approximation.

We will assume that when condensed matter is formed from free atoms, only the valence electrons contribute (significantly) to the interaction between atoms. The electrons close to the nuclei (core electrons), which are in closed shells, in general will only have a small influence on the properties of solids. Exceptions are 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:

$Z$ : nuclear charge of the atom

$R_c$ : radial extension of the core electrons

$Z_v$ : number of valence electrons of the neutral atom

Then the number of core electrons is  $Z - Z_v$ . The solid is composed of these ions (lattice components) and the valence electrons. As mentioned before, this approximation is not

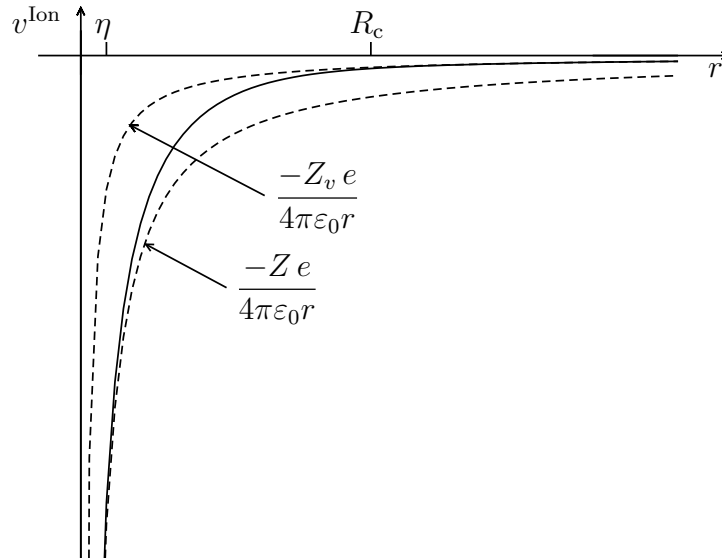


Figure 1.1: Potential of a positive ion (full line), where all electrons, except those in closed shells, have been removed. The dashed curves show the asymptotic behavior for small and large distances.

required in a strict sense. We also did not achieve a lot, because in spite of the frozen-core approximation the quantum mechanical problem still contains  $10^{23}$  particles.

Still the approximation is reasonable and 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)  $\eta$  is a small number roughly of the order of  $R_c/(100 Z)$ . 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. We note that the particular form of  $v^{\text{Ion}}(\mathbf{r})$  and the number of valence electrons  $Z_v$  have no influence on the form of the equations that will be discussed later in this lecture.

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	$r \geq R_c : -8/r$ $\eta \leq r \leq R_c : ?$ $r < \eta : -28/r$

For the construction of the Hamilton operator of the many-body Schrödinger equation of a solid, we first start with the classical Hamilton function and subsequently replace the

momentum  $\mathbf{p}$  by  $(\hbar/i)\nabla$ .

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

- 1) The kinetic energy of the electrons

$$T^e = \sum_{k=1}^N \frac{\mathbf{p}_k^2}{2m} \quad . \quad (1.1)$$

- 2) The kinetic energy of the ions (i.e. of the nuclei plus core electrons)

$$T^{\text{Ion}} = \sum_{I=1}^M \frac{\mathbf{P}_I^2}{2M_I} \quad . \quad (1.2)$$

If the solid contains only one type of atom, then  $N = Z_v M$ .

- 3) The electron-electron interaction

$$V^{e-e}(\{\mathbf{r}_k \sigma_k\}) \approx \frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_{\substack{k,k' \\ k \neq k'}}^{N,N} \frac{e^2}{|\mathbf{r}_k - \mathbf{r}_{k'}|} \quad . \quad (1.3)$$

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 ??.

- 4) The interaction of the ions

$$V^{\text{Ion-Ion}}(\{\mathbf{R}_I\}) \approx \frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_{\substack{I,J \\ I \neq J}}^{M,M} \frac{e^2}{|\mathbf{R}_I - \mathbf{R}_J|} Z_{v_I} Z_{v_J} \quad . \quad (1.4)$$

Also here (even better justified than for the electrons) we did not consider the spin of the particles. Further we have assumed that the ions cannot get too close to each other, i.e., their interaction potentials can be described by  $(Z_v e^2/d) \frac{1}{4\pi\epsilon_0}$ . Thus, we also assumed that the distance of two ions  $d$  is larger than or equal to  $2R_c$ , in order to avoid an overlap of the charge densities of the core electrons. If the condition  $d \geq 2R_c$  is not valid, the frozen-core approximation cannot be applied. Then  $v^{\text{Ion}} \rightarrow v^{\text{Nuc.}} = \frac{1}{4\pi\epsilon_0} \frac{e^2 Z}{r}$  has to be used.

5) The electron-ion-interaction (without nuclear spin)

$$V^{e-\text{Ion}}(\{\mathbf{r}_k\sigma_k\}; \{\mathbf{R}_I\}) = \sum_{I=1}^M \sum_{k=1}^N v^{\text{Ion}}(|\mathbf{R}_I - \mathbf{r}_k|) \quad , \quad (1.5)$$

which is often summarized as:

$$\sum_{I=1}^M v^{\text{Ion}}(|\mathbf{R}_I - \mathbf{r}_k|) = v(\mathbf{r}_k) \quad . \quad (1.6)$$

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

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

$$H = T^e + T^{\text{Ion}} + V^{e-e} + V^{e-\text{Ion}} + V^{\text{Ion-Ion}} \quad . \quad (1.7)$$

## 1.2 Separation of the Dynamics of Electrons and Ions

### 1.2.1 Adiabatic Approximation or Born-Oppenheimer Approximation

The dynamics is described by the time-dependent Schrödinger equation

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

where  $H$  is defined in Section 1.1 above (Eq. 1.7). Thus

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

Obviously this is the equation we like to solve, but in order to do so, 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 make the idea plausible: The electrons can react to an external perturbation much faster than the nuclei. This is reflected in the ratio of the (inert) masses of the nuclei and the electrons. Some examples are:

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

Thus it seems to be reasonable to assume that the electrons adjust without noticeable delay to the current lattice geometry  $\{\mathbf{R}_I\}$ . Then for each lattice geometry, the electrons move independently of the motion of the nuclei (adiabatic principle). Formulated more precisely it can be said that electrons in general 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). We assume that from the electrons point of view the ions do not move (or move sufficiently slow).

To 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:

$$H^e(\{\mathbf{R}_I\})\Phi_\nu(\{\mathbf{R}_I\}, \{\mathbf{r}_k\sigma_k\}) = E_\nu^e\Phi_\nu \quad , \quad (1.8)$$

with

$$H^e = T^e + V^{e-\text{Ion}} + V^{e-e} \quad . \quad (1.9)$$

If the kinetic energy of the lattice components 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  $\Phi_\nu$  defined by Eq. (1.8) is only that of basis functions. The arguments  $\{\mathbf{R}_I\}$  in the electronic wave function cannot be interpreted as a common variable of the wave function, but as parameters which classify the Hamilton operator  $H^e$  (similar to the nuclear charge  $Z$ ).

The following statement is exact: The solutions of  $H$  (defined by Eq. (1.1) - (1.5)) can be expanded in terms of the functions  $\Phi_\nu$  (the eigenfunctions of Eq. (1.8))

$$\Psi = \sum_{\nu} \Lambda_\nu(\{\mathbf{R}_I\})\Phi_\nu(\{\mathbf{R}_I\}, \{\mathbf{r}_k\sigma_k\}) \quad . \quad (1.10)$$

The meaning of Eq. (1.8) and (1.10) 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 1.2.2. Now, we investigate the equation  $H\Psi = E\Psi$ , representing  $\Psi$  by Eq. (1.10).

Obviously, for the operator  $H^e$  we have

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

Also  $V^{\text{Ion}-\text{Ion}}$  can be interchanged with  $\Lambda_\nu$ , but not  $T^{\text{Ion}}$ . Applying the chain rule we obtain

$$\nabla_{\mathbf{R}_I}^2(\Lambda_\nu\Phi_\nu) = \Lambda_\nu(\nabla_{\mathbf{R}_I}^2\Phi_\nu) + 2(\nabla_{\mathbf{R}_I}\Lambda_\nu)(\nabla_{\mathbf{R}_I}\Phi_\nu) + (\nabla_{\mathbf{R}_I}^2\Lambda_\nu)\Phi_\nu \quad . \quad (1.11)$$

Now Eq. (1.7) for the state  $(E, \Psi)$  is multiplied from the left by  $\Phi_\mu^*$  and integrated over the electronic coordinates. Using Eq. (1.8), the equation used to determine the “wave function of the electrons”, i.e.,  $\Phi_\mu$ , we obtain

$$\langle \Phi_\mu | H | \Psi \rangle = E \Lambda_\mu = (E_\mu^e + T^{\text{Ion}} + V^{\text{Ion-Ion}}) \Lambda_\mu + \sum_\nu \sum_{I=1}^M -\frac{\hbar^2}{2M_I} \{ \langle \Phi_\mu | \nabla_{\mathbf{R}_I}^2 | \Phi_\nu \rangle \Lambda_\nu + 2 \langle \Phi_\mu | \nabla_{\mathbf{R}_I} | \Phi_\nu \rangle \nabla_{\mathbf{R}_I} \Lambda_\nu \} . \quad (1.12)$$

For each electronic state  $(E_\mu^e, \Phi_\mu)$  there is one such equation. The difficult part in solving Eq. (1.12) are the terms coupling  $\Phi_\mu$  and  $\Phi_\nu$ .

This coupling of different electronic states is caused by the dynamics of the lattice atoms. It is called electron-phonon coupling.

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. Actually, it is not clear which is the determining mechanism. For some solids the influence of the electron-phonon coupling on the spectrum of the lattice vibrations can be measured, and for some low-dimensional systems the electron-phonon coupling is even responsible for structural instabilities. The keywords are “Kohn-anomaly”, “Jahn-Teller-effect” and “Peierls instability”. These mechanisms are activated by some properties of the electronic structure. They will be discussed later, when we discuss defects and surfaces.

Up to this point our derivation is exact and general statements concerning the importance of the electron-phonon coupling are usually NOT possible. Still, we now introduce two approximations:

- 1) We assume that the electrons at each time, i.e., for each lattice geometry  $\{\mathbf{R}_I\}$ , are in an eigenstate of  $H^e$  (the motion of the lattice shall not induce transitions from  $\Phi_\mu$  to  $\Phi_\nu$ ). The reason is that the electrons react fast and in fact follow instantaneously the nuclear motion. Therefore, the electrons do not feel the nuclear motion and are always in the electronic ground state. 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 (1.12) then are zero for  $\mu \neq \nu$ .

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

- 2) Further we want to estimate the diagonal elements of the electron-phonon interaction:

- 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

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

we find that the electronic wave functions  $\Phi_\mu$  do not depend directly on the nuclear positions  $\mathbf{R}_I$ . The strongest imaginable dependence would exist, if the electrons would follow the atoms without any delay and distortion. If we, for example, had a system containing only one valence electron per atom and each electron follows “its” atom without delay (i.e., the valence electrons instantaneously follow the nucleus. This means

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

and further

$$\begin{aligned} \left| \frac{\hbar^2}{2M_I} \langle \Phi_\mu | \nabla_{\mathbf{R}_I}^2 | \Phi_\mu \rangle \right| &\lesssim \left| \frac{m}{M_I} \left\langle \Phi_\mu \left| -\frac{\hbar^2}{2m} \nabla_{\mathbf{r}_k}^2 \right| \Phi_\mu \right\rangle \right| \\ &\approx 10^{-4} \times \text{kinetic energy of an electron.} \end{aligned} \quad (1.13)$$

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

From Eq. (1.13) and the adiabatic approximation we obtain the Schrödinger equation for the wave functions of the ions:

$$(T^{\text{Ion}} + V^{\text{Ion-Ion}} + E_\mu^e) \Lambda_\mu = E \Lambda_\mu \quad . \quad (1.14)$$

For the energetically lowest state we will often write

$$V^{\text{Ion-Ion}} + E_{\mu=0}^e = V^{\text{BO}} \quad , \quad (1.15)$$

and  $V^{\text{BO}}$  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. (1.14).

When neglecting the coupling terms  $\langle \Phi_\mu | \dots | \Phi_\nu \rangle$  in Eq. (1.13), the eigenfunction of the ground state of  $H$  has the form:

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

where  $\Phi_0$  is determined by Eq. (1.8) and  $\Lambda_0$  by Eq. (1.14). Equation (1.8) and Eq. (1.14) can be calculated reliably using modern computational methods.

Strictly, the motion of the ions would have to be described quantum mechanically. When Eq. (1.14) is solved, one finds that almost always it can be 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 deuterium a classical treatment is sufficient in most cases.

In general, at stable geometries the functions  $\Lambda_0$  are narrowly peaked and centered at the atomic sites  $\{\mathbf{R}_I\}$ . Consequently, for the ground state of Eq. (1.15) we have:

$$E_0 = E_0^e(\{\mathbf{R}_I^0\}) + \frac{1}{4\pi\epsilon_0} \frac{1}{2} \sum_{\substack{I,J \\ I \neq J}}^{M,M} \frac{e^2}{|\mathbf{R}_I^0 - \mathbf{R}_J^0|} Z_{v_I} Z_{v_J} + \langle \Lambda_0 | T^{\text{Ion}} + V^{\text{BO}}(\{\mathbf{R}_I^0 - \mathbf{R}_I\}) | \Lambda_0 \rangle \quad (1.16)$$

The last term describes the quantum mechanical corrections, i.e. zero-point vibrations. Equation (1.17) 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). We have recommended (but it is not necessary) to use the frozen-core approximation for  $V^{e-\text{Ion}}$  and we have applied the adiabatic approximation.

The Born-Oppenheimer potential,  $V^{\text{BO}}(\{\mathbf{R}_I\})$  refers to the *actual* position of the ions (which typically change 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 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 exactly, but with some delay and distortion.

The derivation in this paragraph 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 a explicit calculation of the matrix elements in Eq. (1.13) 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 will just vibrate around a position that represents a minimum of the Born-Oppenheimer potential energy,  $\{\mathbf{R}_I^0\}$ , and we now investigate the Hamilton operator  $H^e(\{\mathbf{R}_I^0\})$ , which yields the wave functions of the electrons  $\Phi_\nu(\{\mathbf{R}_I^0\}, \{\mathbf{r}_k, \sigma_k\})$  (cf. Eq. (1.8)). Also the 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 Section 1.2.2. However, the equation will look different. Nevertheless, they describe the same physics.

In the present treatment the wave function of the solid is

$$\Psi(\{\mathbf{R}_I\}, \{\mathbf{r}_k, \sigma_k\}) = \sum_{\nu} \hat{\Lambda}_{\nu}(\{\mathbf{R}_I\}) \Phi_{\nu}(\{\mathbf{R}_I^0\}, \{\mathbf{r}_k, \sigma_k\}) \quad . \quad (1.17)$$

This equation is (so far) exact, too. But the expansion coefficients are different; therefore the “hat” above the  $\Lambda$ . The components of the Hamilton operator containing the ion-ion



and the electron-ion interaction (cf. Eq. (1.4) and (1.5)), (using  $\Delta\mathbf{R}_I = \mathbf{R}_I - \mathbf{R}_I^0$ ) we write as :

$$V^{\text{Ion-Ion}}(\{\mathbf{R}_I\}) = V^{\text{Ion-Ion}}(\{\mathbf{R}_I^0\}) + V^{\text{ph}}(\{\Delta\mathbf{R}_I\}) \quad , \quad (1.18)$$

$$V^{e\text{-Ion}}(\{\mathbf{R}_I\}, \{\mathbf{r}_k\sigma_k\}) = V^{e\text{-Ion}}(\{\mathbf{R}_I^0\}, \{\mathbf{r}_k\sigma_k\}) + V^{e\text{-ph}}(\{\Delta\mathbf{R}_I\}) \quad . \quad (1.19)$$

From this we obtain the equation for the determination of the coefficients of the expansion and the energy eigenvalues of the solid

$$E_\mu^e \hat{\Lambda}_\mu + T^{\text{Ion}} \hat{\Lambda}_\mu + V^{\text{Ion-Ion}}(\{\mathbf{R}_I^0\}) \hat{\Lambda}_\mu + \sum_\nu \langle \Phi_\mu(\{\mathbf{R}_I^0\}, \{\mathbf{r}_k\sigma_k\}) | V^{e\text{-ph}} + V^{\text{ph}} | \Phi_\nu(\{\mathbf{R}_I^0\}, \{\mathbf{r}_k\sigma_k\}) \rangle \hat{\Lambda}_\nu = E_\mu \hat{\Lambda}_\mu \quad . \quad (1.20)$$

The difference to Eq. (1.12) is that in the second line now there is no differential operator, and  $E_\mu^e$  is no more a function of  $\{\mathbf{R}_I\}$ , but is evaluated at point  $\{\mathbf{R}_I^0\}$ .

Typically the Born-Oppenheimer potential-energy surface has many minima. These correspond to stable or metastable geometries.  $V^{\text{BO}}$  now is only one point of the Born-Oppenheimer-surface, a minimum. At low temperature this minimum defines the equilibrium geometry.

If we neglect the coupling terms  $\langle \Phi_\mu | \dots | \Phi_\nu \rangle$  in Eq. (1.20), for the general wave function of the ground state we have

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

Here  $\Phi_0$  is the solution of  $H^e(\{\mathbf{R}_I^0\})$  and  $\hat{\Lambda}_0$  is the solution of  $[T^{\text{Ion}} + E_0^e(\{\mathbf{R}_I^0\}) + V^{\text{Ion-Ion}}(\{\mathbf{R}_I^0\})] \hat{\Lambda}_0 = E_0 \hat{\Lambda}_0$ . The error which is introduced by this ansatz and by the neglect of the coupling constants of  $\Phi_\mu$  and  $\Phi_\nu$  in Eq. (1.20), respectively, will be discussed in the exercises by a perturbation approach (the result is that in first order the error is zero).

### 1.2.3 Examples

What can we learn from  $V^{\text{BO}}$  and the equation

$$E_0 = E_0^e(\{\mathbf{R}_I^0\}) + \frac{1}{4\pi\epsilon_0} \frac{1}{2} \sum_{\substack{I,J \\ I \neq J}}^{M,M} \frac{e^2}{|\mathbf{R}_I^0 - \mathbf{R}_J^0|} Z_{v_I} Z_{v_J} + \text{quantum mechanical corrections for lattice vibrations} \quad ? \quad (1.21)$$

The difficulty in the evaluation of Eq. (1.23) or Eq. (1.8) is the calculation of  $E_0^e$ , i.e., the solution of the Schrödinger equation of the electrons. This will be done later (in part 3), and there it will be discussed in greater detail. Now we assume that  $E_0^e(\{\mathbf{R}_I\})$  is known, in order to show for two examples, what we can learn using Eq. (1.23).

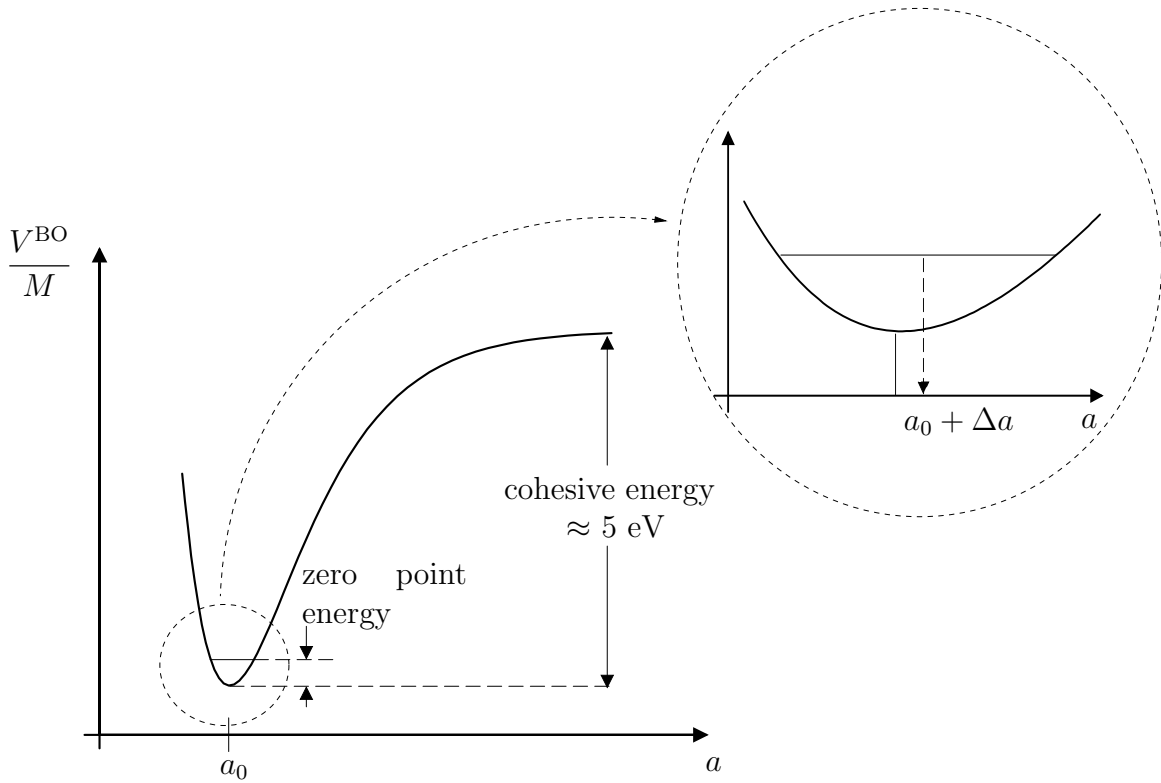


Figure 1.2: The total energy per atom (without zero point vibrations) as a function of the interatomic distance. The minimum of the curve determines the stable equilibrium geometry. The lattice constant, as measured, is not exactly at the minimum of the curve, but it is the average over the zero point vibrations:  $a_0 + \Delta a$ .

### 1.2.3a 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. (1.23) on the  $\{\mathbf{R}_I\}$  is reduced to a single variable  $a$ , which determines the interatomic distance 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  $a_0$ ):

$$B_0 = \frac{1}{K} = V \left. \frac{\partial^2 E(V)}{\partial V^2} \right|_{a=a_0}, \quad (1.22)$$

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 course of the binding energy of polyatomic systems as a function of the interatomic distance, and this form is often called “equation of state”. Typically

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

The minimum of the “equation of state” is close to, but not exactly 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 interatomic distance is 5 bohr  $\approx 2.5$  Å), for silicon 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 measureable effect (e.g.  $\approx 0.1 - 0.5\%$  increase of the lattice constant compared to a neglect of  $\langle \Lambda_0 | T^{\text{ion}} + V^{\text{BO}}(\{\Delta \mathbf{R}_I\}) | \Lambda_0 \rangle$ ).

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

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

### 1.2.3b Lattice Waves (Phonons)

When intending to calculate the energy of lattice waves (phonons),  $E_0$  has to be investigated as function of the wave length  $\lambda$  and the direction of the lattice wave. Figure 1.3 shows the example of a “frozen phonon”. The magnitude of  $\eta$  “tells”, how many phonons of wave length  $\lambda$  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  $\{\mathbf{R}_I^0\}$  gives the equilibrium geometry of the lattice and  $\{\mathbf{R}_I\}$  the periodically distorted geometry.

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

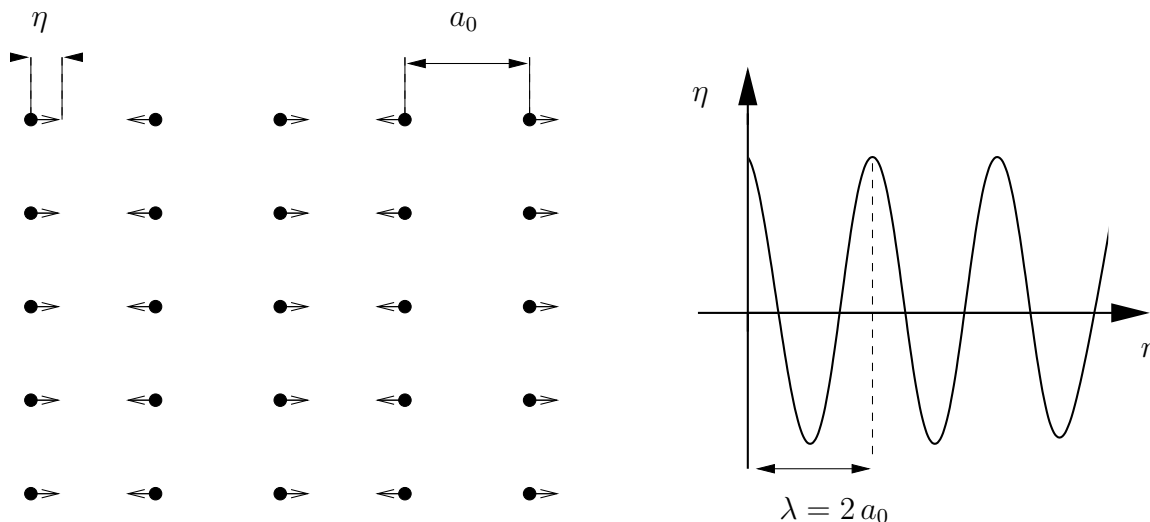


Figure 1.3: Schematic picture of a snapshot of a lattice wave (frozen phonon). The arrows give the direction of the distortion of the atoms. The wave length is  $\lambda = 2a_0$ , and  $a_0$  is the equilibrium distance of the atoms. The amplitude of the distortion is  $\eta$ .

### 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. (1.16)

$$\frac{\langle \Lambda_0 | V^{\text{Ion-Ion}} | \Lambda_0 \rangle}{M} = \frac{E^{\text{Ion-Ion}}}{M} = \frac{1}{M} \frac{1}{4\pi\epsilon_0} \frac{1}{2} \sum_{\substack{I,J \\ I \neq J}}^{M,M} \frac{e^2}{|\mathbf{R}_I^0 - \mathbf{R}_J^0|} Z_{v_I} Z_{v_J} \quad , \quad (1.23)$$

gives the electrostatic interaction energy of the ions and is an important contribution to the total energy. For ionic crystals (e.g. if one considers NaCl as being composed of  $\text{Na}^+$  and  $\text{Cl}^-$  ions) it is even the dominating part of the total energy. Strictly speaking, only the combined electrostatic energy of the ions and the electrons (see Chapter 3), i.e. of the charge neutral solid, is a mathematically well-defined quantity. While the physical meaning of the sum of Eq. (1.23) is clear, summing up the interactions of the point-like charges of the ions is a non-trivial problem. This is because the sum *converges very slowly or not at all*, i.e., even for a very large number of atoms  $M$  the result depends on the order of summation, or on the shape of the surface which includes the part already summed up. The reason is the long range of the Coulomb interaction.

In the following we discuss a simple reformulation of the problem which provides a well-behaved expression for the ionic interaction energy. The main idea is to rewrite the interaction energy by (i) adding charge clouds that compensate (or screen) the point-like ions and thereby result in a rapidly convergent sum over charge neutral units, and (ii) subtracting the electrostatic interaction energy of these fictitious charge clouds which is readily obtained from the Poisson equation in Fourier (or reciprocal) space.

The methodical treatment of Eq. (1.23) is important for actual calculations, but it is also interesting, because it clarifies a methodical approach that in a similar way 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. (1.23), i.e., the poor convergence, originates from the fact that the number of atoms of the same distance is growing with separation. We discuss the example of a periodic solid with only one atom per unit cell<sup>1</sup> (and therefore only one atom type). It follows

$$\frac{E^{\text{Ion-Ion}}}{M} = \frac{1}{4\pi\epsilon_0} \frac{1}{2} \sum_{I=2}^M \frac{Z_v^2 e^2}{|\mathbf{R}_I - \mathbf{R}_1|} = \frac{1}{2} Z_v e \phi(\mathbf{R}_1) \quad . \quad (1.24)$$

$\phi(\mathbf{R}_1)$  is the electrostatic potential generated by the ions  $I = 2, 3, \dots, M$  at position  $\mathbf{R}_1$ , and because of the 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 and the core electrons, then we have (Poisson-equation)

$$\nabla^2 \tilde{\phi}(\mathbf{r}) = -\frac{e}{\epsilon_0} n^+(\mathbf{r}) \quad . \quad (1.25)$$

In these equations initially we take into account *all* atoms including ( $I = 1$ ). Later we will remove the contribution of ( $I = 1$ ), which does not appear in Eq. (1.24). We have:

$$\phi(\mathbf{R}_1) = \tilde{\phi}(\mathbf{R}_1) - \text{contribution of the charge density of the ion \#1} \quad . \quad (1.26)$$

First, the reason for the difficulties in evaluating Eq. (1.26) will be pointed out. Because in a periodic crystal  $n^+(\mathbf{r})$  is periodic, we have

$$n^+(\mathbf{r}) = \sum_{\mathbf{G}_n} n^+(\mathbf{G}_n) e^{i\mathbf{G}_n \mathbf{r}} \quad (1.27)$$

with

$$n^+(\mathbf{G}_n) = \frac{1}{\Omega} \int_{\Omega} n^+(\mathbf{r}) e^{-i\mathbf{G}_n \mathbf{r}} d^3\mathbf{r} \quad (1.28)$$

and  $\mathbf{R}_n \mathbf{G}_n = 2\pi\Gamma$ , where  $\Gamma$  is an integer number.  $\Omega$  is the volume of the unit cell<sup>1</sup> (cf. Chapter 4). We have

$$n^+(\mathbf{G}_n = 0) = \frac{1}{\Omega} Z_v \quad ; \quad (1.29)$$

and because of the Poisson-equation (1.28) it follows for the electrostatic potential  $\tilde{\phi}$

$$\nabla^2 \tilde{\phi}(\mathbf{r}) = -\frac{e}{\epsilon_0} \sum_{\mathbf{G}_n} n^+(\mathbf{G}_n) e^{i\mathbf{G}_n \mathbf{r}} \quad (1.30)$$

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<sup>1</sup>The unit cell is the smallest unit which can be used to construct a periodic solid.

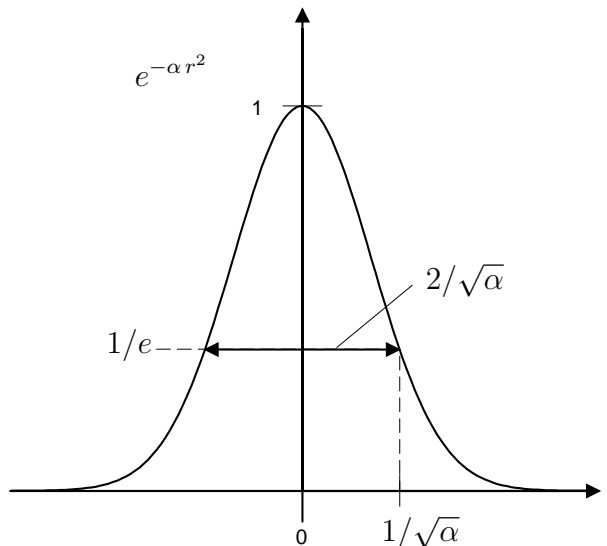


Figure 1.4: Gaussian function  $e^{-\alpha r^2}$ . The width (at value  $e^{-\alpha r^2} = 1/e = 0.368$ ) is  $2/\sqrt{\alpha}$ .

and therefore

$$\tilde{\phi}(\mathbf{r}) = \frac{e}{\varepsilon_0} \sum_{\mathbf{G}_n} \frac{n^+(\mathbf{G}_n) e^{i\mathbf{G}_n \mathbf{r}}}{|\mathbf{G}_n|^2} + C \quad , \quad (1.31)$$

which is easily verified by evaluating  $\nabla^2 \tilde{\phi}(\mathbf{r})$ . We point out that the singularity of Eq. (1.33) 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  $V^{e-\text{Ion}}$ . This is reasonable, 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. (1.33) will therefore be ignored.

If  $e n^+(\mathbf{r})$  would only contain the nuclear charges, i.e.,  $\delta$ -functions, then for all terms we have  $n^+(\mathbf{G}_n) = \frac{Z_v}{\Omega}$ . We note for Eq. (1.24) and (1.31) that *the potential of  $\delta$ -shaped charge densities converges poorly in real space and in Fourier space.*

On the other hand in Eq. (1.33) 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:

$$n_{\text{Gauss}}^+(\mathbf{r}) = Z_v \sum_{I=1}^M \left(\frac{\alpha}{\pi}\right)^{3/2} e^{-\alpha|\mathbf{r}-\mathbf{R}_I|^2} \quad . \quad (1.32)$$

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

$$\int \left(\frac{\alpha}{\pi}\right)^{3/2} e^{-\alpha|\mathbf{r}-\mathbf{R}_I|^2} d\mathbf{r} = 1 \quad , \quad (1.33)$$

and  $2/\sqrt{\alpha}$  is the width of the individual Gaussians (cf. Fig. 1.4). The Fourier representa-

tion of  $n_{\text{Gauss}}^+(\mathbf{r})$  has the form:

$$n_{\text{Gauss}}^+(\mathbf{G}_n) = \frac{Z_v}{\Omega} \sum_{I=1}^M \int_{\Omega} \left(\frac{\alpha}{\pi}\right)^{3/2} e^{-\alpha|\mathbf{r}-\mathbf{R}_I|^2} e^{-i\mathbf{G}_n\mathbf{r}} d^3\mathbf{r} = \frac{Z_v}{\Omega} e^{-\left(\frac{\mathbf{G}_n^2}{4\alpha}\right)} \quad , \quad (1.34)$$

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

$$\tilde{\phi}_{\text{Gauss}}(\mathbf{r}) = \frac{Z_v}{\Omega} \frac{e}{\varepsilon_0} \sum_{\mathbf{G}_n} \frac{e^{-\left(\frac{\mathbf{G}_n^2}{4\alpha}\right)} e^{i\mathbf{G}_n\mathbf{r}}}{|\mathbf{G}_n|^2} + C \quad (1.35)$$

$$= \frac{Z_v e}{4\pi\varepsilon_0} \sum_{I=1}^M \frac{\text{erf}(\sqrt{\alpha}|\mathbf{r}-\mathbf{R}_I|)}{|\mathbf{r}-\mathbf{R}_I|} + C \quad . \quad (1.36)$$

Here erf is the error function

$$\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-x'^2} dx' \quad . \quad (1.37)$$

This means,

$$\frac{Z_v e}{4\pi\varepsilon_0} \times \frac{\text{erf}(\sqrt{\alpha}|\mathbf{r}-\mathbf{R}_I|)}{|\mathbf{r}-\mathbf{R}_I|} \quad (1.38)$$

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 (1.31) this sum (Eq. (1.34) and (1.36)) converges excellently. This is because of the factor  $\exp(-\mathbf{G}_n^2/4\alpha)$ . The smaller  $\alpha$ , 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

$$n^+(\mathbf{r}) = \{n^+(\mathbf{r}) - n_{\text{Gauss}}^+(\mathbf{r})\} + n_{\text{Gauss}}^+(\mathbf{r}) \quad . \quad (1.39)$$

Together, the first two components describe a neutral charge, i.e.,  $\delta$ -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. (1.39) 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:

$$\phi_{1,2}(\mathbf{r}) = \frac{Z_v e}{4\pi\varepsilon_0} \sum_{I=1}^M \left\{ \frac{1 - \text{erf}(\sqrt{\alpha}|\mathbf{r}-\mathbf{R}_I|)}{|\mathbf{r}-\mathbf{R}_I|} \right\} + C \quad . \quad (1.40)$$

The term in the curly brackets of Eq. (1.41) vanishes with increasing distance to the nucleus at position  $\mathbf{R}_I$ . Consequently, the sum converges rapidly. Only a few atomic

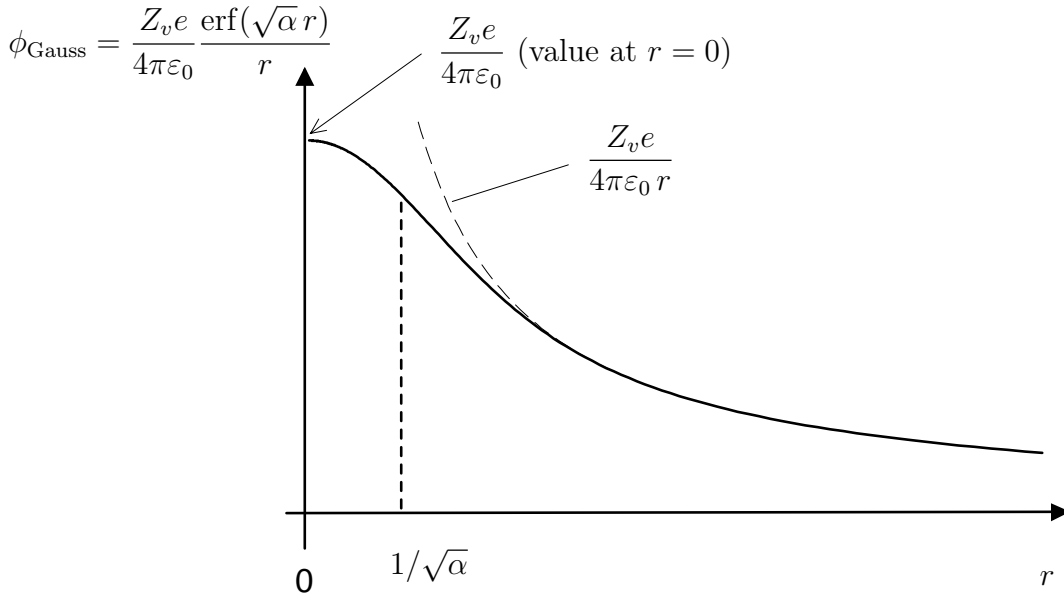


Figure 1.5: The electrostatic potential of a Gaussian shaped charge density of charge  $e Z_v$ . For large ( $r > 1/\sqrt{\alpha}$ ) the function become identical to  $\frac{Z_v e}{4\pi\epsilon_0 r}$ .

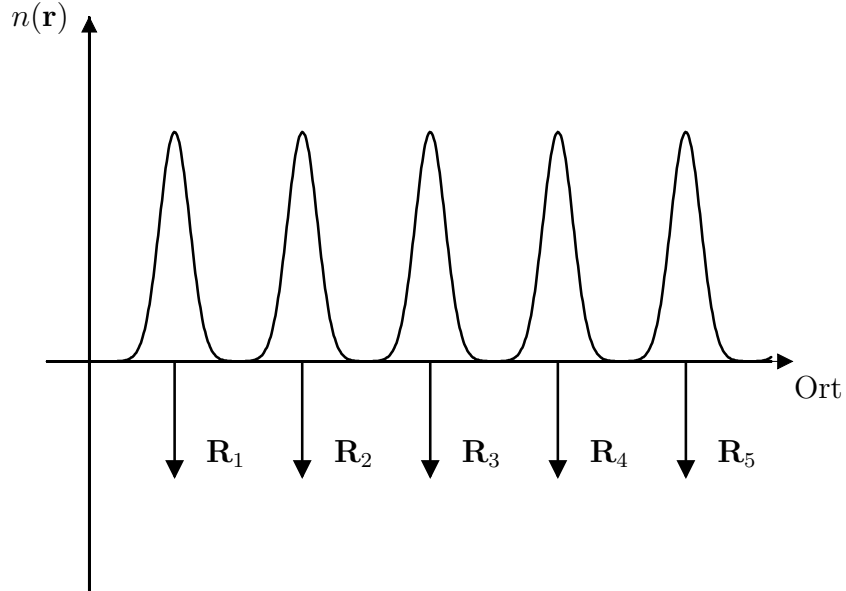


Figure 1.6: Charge distribution of point charges and surrounding Gaussian charge densities. Delta-functions are represented by arrows.

positions in the neighborhood of  $\mathbf{r}$  have to be taken into account. The third contribution in Eq. (1.40) of  $n^+(\mathbf{r})$ , the Gaussian clouds, we describe in the representation (Eq. (1.31)). For the potential that we want to calculate, we obtain

$$\begin{aligned}
 \phi(\mathbf{r}) = & + \frac{Z_v e}{4\pi\epsilon_0} \sum_{I=1}^M \frac{1 - \text{erf}(\sqrt{\alpha}|\mathbf{r} - \mathbf{R}_I|)}{|\mathbf{r} - \mathbf{R}_I|} \\
 & + \frac{Z_v e}{\Omega \epsilon_0} \sum_{\mathbf{G}_n} \frac{e^{-\frac{\mathbf{G}_n^2}{4\alpha}} e^{i\mathbf{G}_n \mathbf{r}}}{|\mathbf{G}_n|^2} - \frac{Z_v e}{4\pi\epsilon_0} \frac{1}{|\mathbf{r} - \mathbf{R}_1|} + C \quad . \quad (1.41)
 \end{aligned}$$



Here we have now removed also the  $\mathbf{R}_I = \mathbf{R}_1$  contribution (cf. Eq. (1.26)).

Finally, I will briefly discuss the integration constant  $C$ . The electrostatic potential  $\phi(\mathbf{r})$ , as written down in Eq. (1.42), depends on  $\alpha$ . 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  $\phi$  should not depend on  $\alpha$  we obtain the integration constant  $C$ . It has to be fulfilled:

$$\frac{d\phi(\mathbf{r})}{d\alpha} = 0 \quad . \quad (1.42)$$

The calculation yields:

$$C = -\frac{\pi Z_v e}{\Omega \alpha} \times \frac{1}{4\pi \epsilon_0} \quad . \quad (1.43)$$