Condensed matter physics 2013
Solutions to exercise 11

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Solution to problem 41

a) If you read the script, you may proceed to the next problem.

b)
- Weakest – van der Waals binding

  Relevant for example for neutral noble gas atoms or carbon nanotubes on a surface, where the interaction between fluctuations in the electron distribution leads to an attractive force (first order: dipole-dipole). The binding energy varies with the distance like r^{-6}.
- Metallic binding

  In a metal, the atoms' valence electrons are delocalised over the whole crystal and the interaction with all positive ion cores contributes significantly to the binding. Further contributions arise from electron-electron and the exchange interaction (Pauli principle). The binding energies are smaller than for the ionic binding and span a broad energy range.
- Ionic bonding

  In this case it is sufficient to consider the interaction between the opposite electrostatic ionic charges in a classical picture. Ionic bonds form between many different binding partners (→ Madelung constant). Binding energies are in the range of 5...10 eV.
- Strongest – Covalent bonding

  Due to the overlap of the atom's orbitals their valence electrons become delocalised between nearest neighbours when a covalent crystal is formed. This makes covalent bonds directional and stronger than ionic bonds. Covalent bonds often are partly ionic.

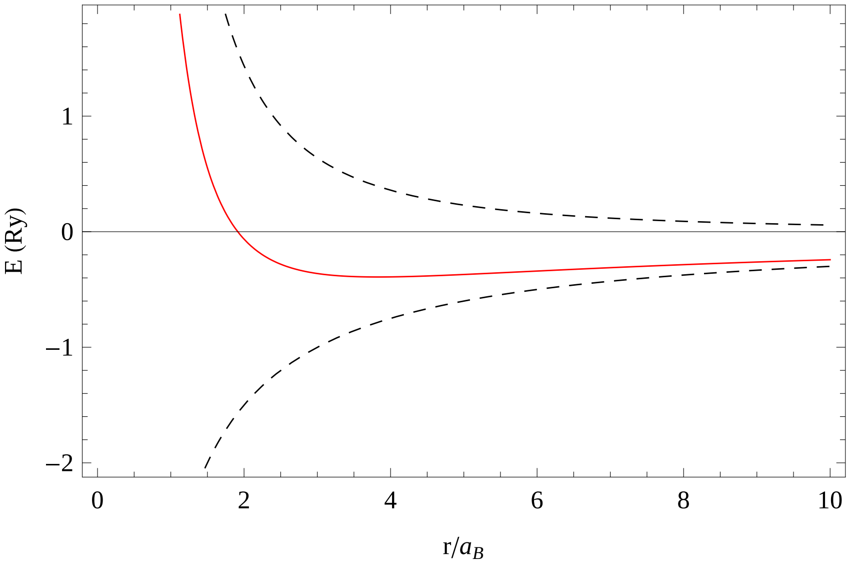


Figure 1: Potential for problem 35.**c)**.*i*)

c) *i*) The potential is plotted in fig. 1.

ii) There's an attractive term from the Coulomb interaction and a repulsive term from the Pauli principle. Setting the derivative of the total energy (equation 5.25 in the script) with respect to r to zero, one obtains the equilibrium radius:

$$\frac{dE}{dr} = 1\text{Ry} \cdot \left[-5.74 \frac{a_\text{B}^2}{r^3} - \frac{a_\text{B}}{r^2} \left(-3 + 5.74 \frac{a_\text{B}}{r} \right) \right] \overset{!}{=} 0 \tag{1}$$

$$\Rightarrow r_{eq} = \frac{2 \cdot 5.74 \cdot a_\text{B}}{3} = 2.03 \text{ Å} \tag{2}$$

Inserted this radius into 5.25 gives the binding energy $E_B = -5.33$ eV.

iii) In our model r_{eq} is equal to the lattice constant a – here we use simply $r_{eq} = n^{-1/3}$. Comparing the calculated binding energy to real values of the solids' cohesion energies per atom as well as their ionisation energies (e.g. script page 5.29 or table below, taken from C. Kittel, Introduction to solid state physics, 7th ed., Wiley 1996) shows that the model is not very accurate. However, it reproduces the ionisation energyfairly well. The difference between our calculation and the measured values are due to the fact that we have neglected electron-electron and exchange interactions.

Table 1: Binding energies for several metals calculated from the model. E_coh is the cohesive energy of a solid, E_ion its ionisation energy.

Material	crystal	a	R	E_B	E_coh	E_ion
Fe	bcc	2.87 Å	2.28 Å	-5.3 eV	-4.28 eV	7.9 eV
K	bcc	5.22 Å	4.14 Å	-3.9 eV	-0.93 eV	4.34 eV
Au	fcc	4.08 Å	2.57 Å	-5.1 eV	-3.81 eV	9.22 eV
Cu	fcc	3.61 Å	2.27 Å	-5.3 eV	-3.49 eV	7.72 eV
Zn	hcp	2.66 Å	2.11 Å	-5.3 eV	-1.35 eV	9.39 eV

d) The Madelung constant is characteristic for ionic crystal structures (script page 5.33) and can be found by adding all Coulomb terms in electrically neutral cells (script page 5.36) – which is not mathematically required, but leads to better convergence in the calculations. For the two-dimensional NaCl crystal this is shown in the figure below, where one species, e.g. the positively charged, is shown as white circles, the other as gray circles. The total Coulomb energy of a given atom (here shown as red circle) is the sum over all other atoms: $E_\text{C} = \sum \text{sign}(i,j) \frac{e^2}{4\pi\epsilon_0 r}$ with $r_{i,j}$ the distance to the other atom. r can be expressed in lattice constants, $r_{i,j} = d_{i,j} \cdot R$ and one finds $E_\text{C} = \frac{e^2}{4\pi\epsilon_0 R} \cdot M$ with the Madelung constant $M = \sum \text{sign}(i,j)/d_{i,j}$.

Solution to the problem:

For the first cell, shown in Fig. (a) one finds:

$$M_1 = -4 \cdot \frac{1}{2} \cdot \frac{1}{1} + 4 \cdot \frac{1}{4} \cdot \frac{1}{\sqrt{2}} = -2 + \frac{1}{\sqrt{2}} \approx -1.29 \Rightarrow \alpha = 1.29$$

Similarly, we find

$$M_2 = -4 \cdot \frac{1}{1} \cdot \frac{1}{1} + 4 \cdot \frac{1}{1} \cdot \frac{1}{\sqrt{2}} - 8 \cdot \frac{1}{2} \cdot \frac{1}{\sqrt{5}} + 4 \cdot \frac{1}{2} \cdot \frac{1}{2} + 4 \cdot \frac{1}{4} \cdot \frac{1}{\sqrt{8}} \approx -1.61$$

After two steps, you obtain the Madelung constant $\alpha = 1.61$.

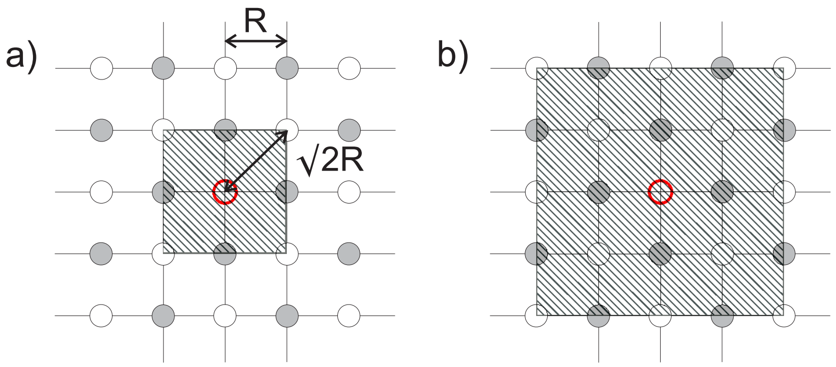


Figure 2: Calculation of the Madelung constant

Solution to problem 42

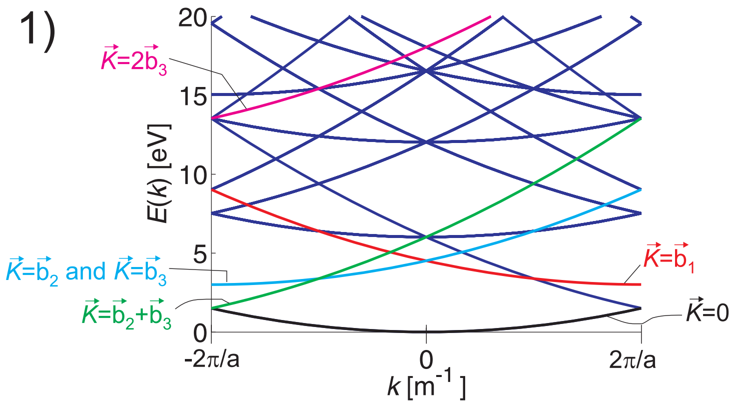
The solution can be found on the left hand side of figure 1.27 in the script on page 1.29. This figure also contains a schematic of the first Brillouin zone (BZ) for orientation.
To calculate the band diagram in the free electron model, we assume a parabolic dispersion relation given by the free electron mass m, and a lattice parameter $a = 1\,\mathrm{nm}$. Each band is obtained by the formula given in the script on page 6.18:

$$E(\boldsymbol{k}) = \frac{\hbar^2}{2m}(\boldsymbol{k} + \boldsymbol{K})^2, \tag{3}$$

where $\boldsymbol{k} \in 1$. BZ. The reciprocal lattice of fcc with the edge length a is bcc with edge length $\frac{4\pi}{a}$. This results in a series of parabolas centered at lattice vectors $\boldsymbol{K} \in G^*$, given by multiples of the primitive basis vectors, $\boldsymbol{K} = m_1\boldsymbol{b}_1 + m_2\boldsymbol{b}_2 + m_3\boldsymbol{b}_3$ $(m_i \in \mathbb{Z})$, for example with the basis vectors

$$\boldsymbol{b}_1 = \frac{1}{2}\frac{4\pi}{a}\begin{pmatrix} -1 \\ 1 \\ 1 \end{pmatrix}, \quad \boldsymbol{b}_2 = \frac{2\pi}{a}\begin{pmatrix} 1 \\ -1 \\ 1 \end{pmatrix} \quad \boldsymbol{b}_3 = \frac{2\pi}{a}\begin{pmatrix} 1 \\ 1 \\ -1 \end{pmatrix} \tag{4}$$

(Ashcroft and Mermin, page 88, or by construction like in script page 1.27). The figure below shows a series of such parabolas, restricted to the first BZ in the Γ-X direction, i.e. $\boldsymbol{k} = (k, 0, 0)$ and $k \in [-2\pi/a, 2\pi/a]$. Every curve is n-fold degenerate, i.e. n different $\boldsymbol{K}$ lead to the same curve with the energy $E = \frac{\hbar^2}{2m}(K_x + k)^2 + (K_y^2 + K_z^2)$. Therefore, K-vectors with the same K_x and the same $K_y^2 + K_z^2$ lead to the same curve in this direction. Several special cases are plotted in different colors, e.g. the lowest band for $\boldsymbol{K} = 0$ (degeneracy 1) in black. The degeneracy of the red curve is 4, given by $\vec{K} \in \{\vec{b}_1, -\vec{b}_2, -\vec{b}_3, -\vec{b}_1 - \vec{b}_2 - \vec{b}_3\}$. The degeneracies of the cyan and magenta curves is 4 as well, the one of the green curve is 1. The other curves shown are eight-fold degenerate.



Solution to problem 43

A short introduction to perturbation theory

This part gives a short introduction to time-independent perturbation theory in order to derive the terms necessary to solve this problem (see below). This part can be skipped by the more experienced students. The introduction largely follows the book ”Physics of atoms and molecules” by B. H. Bransden and C. J. Joachain (Prentice Hall, Harlow/UK, 2nd edition, 2003), chapter 2.8.

Time-independent perturbation theory can be used when a small perturbation induces H' is added to the system described by the Hamiltonian H_0 with known eigenstates:

$$H = H_0 + \lambda H'.$$

What ”small” means should be critically assessed later. λ is used to turn on the perturbation. The unperturbed system H_0 has known eigenvalues $E_k^{(0)}$ and eigenstates $\psi_k^{(0)}$ with the orthonormal relations

$$\int \psi_i^{*(0)} \psi_j^{(0)} dx = \delta_{ij}$$

The goal is to solve the eigenvalue problem of the perturbed system,

$$H\psi_k = E_k \psi_k, \tag{5}$$

with the perturbed eigenvalues E_k. Let $\psi_k^{(0)}$ be non-degenerate. We require that the weak perturbation modifies the energy level only to that extent that the perturbed level, E_k, is still much closer to $E_k^{(0)}$ than to other E values. E_k and ψ_k may then be expanded in powers of λ:

$$\psi_k = \sum_{i=0}^{\infty} \lambda^i \psi_k^{(i)}, \quad \text{and} \quad E_k = \sum_{i=0}^{\infty} \lambda^i E_k^{(i)} \tag{6}$$

i is the order of the perturbation. Now the expansions are substituted in the eigenvalue problem eqn. (5), which yields:

$$\begin{aligned}(H_0 + \lambda H') &\left(\psi_k^{(0)} + \lambda \psi_k^{(1)} + \lambda^2 \psi_k^{(0)} + \dots\right) \\ &\left(E_k^{(0)} + \lambda E_k^{(1)} + \lambda^2 E_k^{(2)} + \dots\right)\left(\psi_k^{(0)} + \lambda \psi_k^{(1)} + \lambda^2 \psi_k^{(0)} + \dots\right)\end{aligned}$$

Equating equal powers of λ yields

$$\begin{aligned} H_0 \psi_k^{(0)} &= E_k^{(0)} \psi_k^{(0)} \\ H_0 \psi_k^{(1)} + H' \psi_k^{(0)} &= E_k^{(0)} \psi_k^{(1)} + E_k^{(1)} \psi_k^{(0)} \end{aligned} \tag{7}$$

etc. The first-order energy correction is obtained by premultiplying eqn. (7) with $\psi_k^{*(0)}$ and integrating over space which then yields

$$\int \psi_k^{*(0)} (H_0 - E_k^{(0)}) \psi_k^{(1)} dx + \int \psi_k^{*(0)} (H' - E_k^{(1)}) \psi_k^{(0)} dx = 0$$

With the unperturbed eigenvalue problem and the fact that H_0 is hermitian, the first term vanishes. The second term reduces to

$$\boxed{E_k^{(1)} = \int \psi_k^{*(0)} H' \psi_k^{(0)} dx =: H'_{kk}\,,} \tag{8}$$

a matrix element which is the expectation value of H' with respect to the unperturbed states of the system, i. e., the first-order energy correction of the perturbed energy levels in the *non-degenerate case.* We're presently not interested in higher orders, so let's stop here. Higher-order corrections are obtained in a similar way, i. e. comparing the equal powers of λ.

If the level $E_k^{(0)}$ is α-fold degenerate, several unperturbed wavefunctions $\psi_{kr}^{(0)}$ with $r = 1 \dots \alpha$ correspond to $E_k^{(0)}$. If the functions $\psi_{kr}^{(0)}$ are not orthogonal initially, it is possible to construct an orthogonal set from them – let's assume without loss of generality that this has already been done, i.e.

$$\int \psi_{kr}^{*(0)} \psi_{ks}^{(0)} dx = \delta_{rs}.$$

Now we again expand the wavefunctions and energies in equal powers of λ, similar to eqn. (6). To take the degeneracy into account, we now have to replace the first term of the expansion with the new zero-order wave functions $\chi_{kr}^{(0)}$ which are linear combinations of the α unperturbed wave functions[1] $\psi_{kr}^{(0)}$:

$$\chi_{kr}^{(0)} := \sum_{s=1}^{\alpha} c_{rs} \psi_{ks}^{(0)}, \quad r = 1 \dots \alpha.$$

The determination of the coefficients c_{rs} ultimately[2] leads – for each r – to the equation

$$\boxed{\det \left| \underbrace{\int \psi_{ku}^{*(0)} H' \psi_{ks}^{(0)} dx}_{=:H'_{us}} - E_{kr}^{(1)} \delta_{us} \right| = 0, \quad s, u = 1, \dots \alpha} \tag{9}$$

with the integral matrix element H'_{us}. This equation[3] (that is, the determinant of the matrix) has α roots, $E_{k1}^{(1)}, E_{k2}^{(1)}, \dots, E_{k\alpha}^{(1)}$, which denote the first-order energy correction of the perturbed energy levels in the *degenerate case.* If they are distinct, the degeneracy is said to be removed to first order in the perturbation. Otherwise it is partially or not removed to first order, but higher orders of perturbation theory may still lift the degeneracy.

Solution to the problem

Important: note that the focus of this problem is not on the calculations, but rather on the results: energy gaps open in the dispersion relation of free electrons subject to a weak periodic potential.

a) The system is very large and has a length of L. The unperturbed eigenfunctions $\psi_{\pm k}(x) = Ce^{\pm ikx}$ where $C = L^{-1/2}$ have the same energy for those k values satisfying

$$k_n = \frac{n\pi}{a}, \quad n \in \mathbb{Z},$$

which are the Brillouin zone boundaries. These solutions are degenerate, since the differing wavefunctions ψ_k and ψ_{-k} have the same energy $E_k = E_{-k}$ at these boundaries, as seen in fig. 3. This accounts for a two-fold degeneracy and we have to find the roots of the 2×2 determinant given by eqn. (9).

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[1] In the problem below, we're dealing with α = 2-fold degenerate wavefunctions which also already fulfill the orthogonality requirement

[2] Equating equal powers of λ and integrating over space have been skipped here

[3] …is the eigenvalue problem of the $\alpha \times \alpha$ perturbation matrix in the degenerate case. In eqn. (8), the non-degenerate matrix elements were derived – note that in this case the off-diagonal matrix elements vanish.

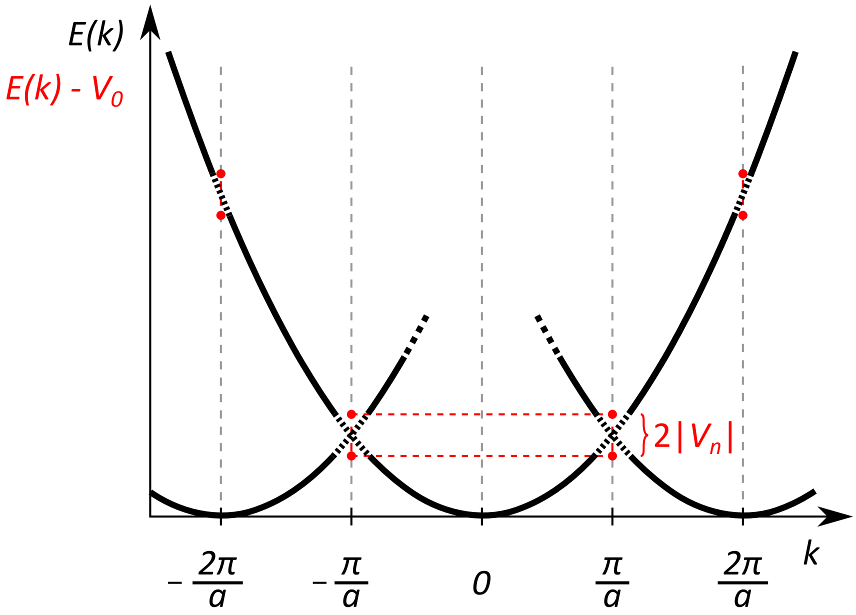


Figure 3: Parabola $E(k)$ for free electrons with the Brillouin zone boundaries $n\pi/a$ as requested in problem **a)**. The red dots derived in **d)** denote the corrections from the first order of perturbation theory and show the size of the gap. For clearness' sake, the middle parabolae were not fully drawn. V_n is the nth Fourier component of the potential (see below); e. g. for $k = 2\pi/a$, the splitting would be $2\,|V_2|$.

b) The periodic potential $V(x)$ can be written as a Fourier series using the above expression for k_n:

$$V(x) = \sum_{-\infty}^{\infty} V_n e^{ik_n x}$$

with the properties $V(x) = V(-x)$ and $V_n = V_{-n}$. The diagonal matrix elements H'_{11} and H'_{22} of the perturbation matrix are

$$H'_{11} = \int_0^L \psi^*_{\pm k} V(x) \psi_{\pm k} dx =: V_{\pm k, \pm k}$$

The off-diagonal matrix elements are

$$V_{\pm k, \mp k} = \int_0^L \psi^*_{\pm k}\, V(x) \psi_{\mp k} dx$$

We have to find the roots $E_{k1,2}$ of

$$\begin{vmatrix} V_{k,k} - E^{(1)}_{k1,2} & V_{k,-k} \\ V_{-k,k} & V_{-k,-k} - E^{(1)}_{k1,2} \end{vmatrix} = 0. \qquad (10)$$

The unperturbed wave functions $\psi^{(0)}_{\pm k}$ are of the form of plane waves.

c) For the case $\boldsymbol{k \neq n\pi/a}$, the off-diagonal matrix elements are identical to 0, i. e. $V_{k,-k} \equiv 0$.

Calculation of $V_{\pm k,\pm k}$:

$$
\begin{aligned}
V_{k,k} &= \frac{1}{L}\int_{-L/2}^{L/2} e^{-ikx}\cdot\left(\sum_{n=-\infty}^{\infty} V_n\cdot e^{ik_nx}\right)e^{ikx}dx \\
&= \sum_n \frac{V_n}{L}\int_{-L/2}^{L/2} e^{ik_nx}dx = \sum_n V_n\frac{\sin(k_nL/2)}{k_nL/2}.
\end{aligned}
\tag{11}
$$

For a very large system, we may use

$$
\lim_{L\to\infty}\frac{\sin(k_nL/2)}{k_nL/2} = \delta(k_n),
$$

hence

$$
V_{k,k} = \sum_n V_n\delta(k_n) = V_0,
$$

since this sum only contributes for $n = 0$. $V_{-k,-k}$ yields the same offset V_0. The off-diagonal elements of the perturbation matrix vanish and the unperturbed wavefunctions are already good basis functions, so that eqn. (8) may be used for the calculations. The energy values off the full, perturbed system are:

$$
E_k = E_k^{(0)} + V_0 = \frac{\hbar^2}{2m}k^2 + V_0,
$$

since $E_k^{(0)}$ is the energy of the free electron.

d) For $\boldsymbol{k = n\pi/a}$, the periodic potential yields additional contributions and the full perturbation matrix eqn. (10) comes into play. We see this when we calculate $V_{\pm k,\mp k}$:

$$
\begin{aligned}
V_{k,-k} &= \frac{1}{L}\int_{-L/2}^{L/2} e^{-ikx}\cdot\left(\sum_{n=-\infty}^{\infty} V_n\cdot e^{ik_nx}\right)e^{-ikx}dx \\
&= \sum_n \frac{V_n}{L}\int_{-L/2}^{L/2} e^{i(k_n-2k)}dx \overset{\lim_{L\to\infty}}{=} \sum_n V_n\delta(k_n-2k).
\end{aligned}
\tag{12}
$$

For a very large system, we may use

$$
\lim_{L\to\infty}\frac{1}{L}\int_0^L e^{i(k_n-2k)}dx = \delta(k_n-2k).
$$

Since we only look at $k = n\pi/a$, the integral remains finite and $V_{k,-k}$ evaluates to delta spikes (i. e., at the dashed gray lines in fig. 3). At these points (and only there), the potential gives the additional contribution mentioned above:

$$
V_{k,-k} = \sum_n V_n\delta(k_n-2k) = V_n.
$$

The matrix element $V_{-k,k}$ evaluates to the same result. The perturbation matrix for the k_n points now looks like this:

$$
\begin{vmatrix}
V_0 - E_{k1,2}^{(1)} & V_n \\
V_n & V_0 - E_{k1,2}^{(1)}
\end{vmatrix} = 0.
$$

The eigenvalues of this matrix denote the energetic first-order perturbation term, $E^{(1)}_{k1,2} = E_k - E^{(0)}_k$ and the equation is

$$(V_0 - E^{(1)}_{k1,2})^2 - V_n^2 = 0$$

Its solutions $E^{(1)}_{k1,2} = V_0 \pm V_n$ yield the perturbed energy values

$$E_k = \frac{\hbar^2}{2m}k^2 + V_0 \pm V_n$$

This result means that at these points in k space the degeneracy is lifted because the free electron parabolas are split at the zone boundaries (red dots in fig. 3). This energy splitting (or, gap) has a magnitude of $2V_n$. In other words, a weak periodic potential acting on free electrons generally introduces an energy gap which is caused by lifting the degeneracy of the wave functions at the Brillouin zone boundaries.

e) We remain at the k_n points. The perturbed wavefunctions are linear combinations of the unperturbed ones, i. e.

$$\psi^{(1)}_k = c_1\psi^{(0)}_k + c_2\psi^{(0)}_{-k} = \frac{1}{\sqrt{L}}\left(c_1 e^{ikx} + c_2 e^{-ikx}\right)$$

The coefficients must satisfy the equations

$$\begin{aligned} c_1(V_0 - E^{(1)}_{k1,2}) + c_2 V_n &= 0 \\ c_1 V_n + c_2(V_0 - E^{(1)}_{k1,2}) &= 0. \end{aligned}$$

With $E^{(1)}_{k1,2} = V_0 \pm V_n$, this yields

$$\begin{aligned} V_n(\mp c_1 + c_2) &= 0 \\ V_n(c_1 \mp c_2) &= 0 \end{aligned}$$

The solutions are

$$\begin{aligned} c_1 = c_2 &\quad \text{for} \quad E^{(1)}_{k1,2} = V_0 + V_n \\ c_1 = -c_2 &\quad \text{for} \quad E^{(1)}_{k1,2} = V_0 - V_n \end{aligned}$$

Hence, the new wavefunctions at the points $k = k_n$ can be written as

$$\psi_{\pm k_n} = \frac{1}{\sqrt{L}}\left(e^{ik_nx} \pm e^{-ik_nx}\right)$$

This superposition yields standing waves of cosine and sine type and arise from the electrons being Bragg reflected. These waves, in turn, describe the probability density of the electrons' positions: For the lower energy values, the probability to find the electrons near the core, is high. For the high energy values, finding the electrons near the core, is low, but finding the between the cores is high (see e. g. C. Kittel, "Introduction to Solid State Physics", chapter "Energy bands"). Consequently, these different groups of electrons see different potentials: The electrons near the core feel the attractive Coulomb interaction. Electrons away from the core have higher energy and to be able to reach these states, they have to overcome the Coulomb forces. n also denotes the scattering order.

Solution to problem 44

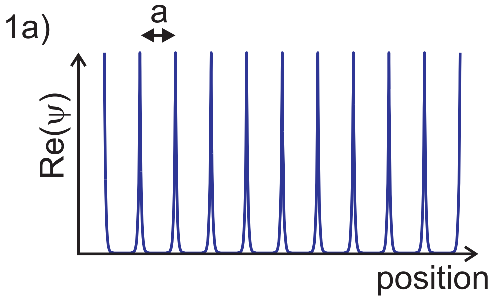
a) Solution by directly inserting $\boldsymbol{R}$ into the equation for $\Psi(\boldsymbol{r})$ on the problem sheet:

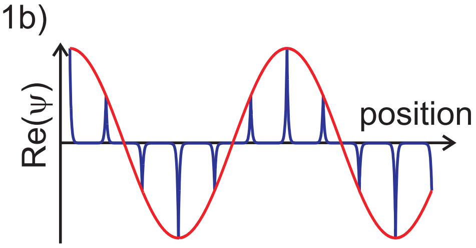
$$\begin{aligned}\Psi(\boldsymbol{r}+\boldsymbol{R}) &= \sum_j e^{i\boldsymbol{k}\boldsymbol{R}_j}\psi([\boldsymbol{r}+\overbrace{\boldsymbol{R}] - \boldsymbol{R}_j}^{=:-\boldsymbol{R}_p}) = \sum_j e^{i\boldsymbol{k}(\boldsymbol{R}_p+\boldsymbol{R})}\psi(\boldsymbol{r}-\boldsymbol{R}_p)\\ &= e^{i\boldsymbol{k}\boldsymbol{R}}\sum_j e^{i\boldsymbol{k}\boldsymbol{R}_p}\psi(\boldsymbol{r}-\boldsymbol{R}_p) = e^{i\boldsymbol{k}\boldsymbol{R}}\sum_p e^{i\boldsymbol{k}\boldsymbol{R}_p}\psi(\boldsymbol{r}-\boldsymbol{R}_p)\\ &= e^{i\boldsymbol{k}\boldsymbol{R}}\Psi(\boldsymbol{r})\end{aligned}$$

In the last step, equation (1) of the problem sheet is used again, and in the step before we use the fact that a summation over *all* lattice sites is independent of the sequence of the summation, i.e. adding $\boldsymbol{R}$ to all arguments does not change the sum and we can change the summation index to p.

b) The 1s wave function has a radial part of the form $\propto e^{(r-r_\mathrm{a})/r_0}$ with the atom positions r_a, spaced by the lattice constant a, and the characteristic radius r_0, e.g. the Bohr radius. For $k = 0$ the phase factor is 1 and Ψ is simply the sum of the atomic wave functions displaced by a lattice vector. The result is shown in figure 1a).

For $k = \frac{\pi}{3a}$, the wave function is multiplied by a phase factor, which leads to the envelope function shown in figure 1b), multiplied with the wave function found in **a)**.





Comment: Sometimes, the wavefunction is multiplied with the electron position r[4]. The absolute square of this new function is the probability of finding the electron at a distance r from the atom. Consequently, each of the blue $1s$ functions in the figure drops to 0 at the atomic positions $\boldsymbol{R}_j$.

MATLAB tutorial: the following code was used to plot the curves in figure 1b) (note: the units are arbitrary):

```
x=0:3000; y=zeros(1,length(x));
for p=0:20
y=y+exp(-abs(x-p*300)/10).*exp(i*p*pi/3);
end;
plot(x,real(y)); hold on; plot(x,real(exp(i*x/300*pi/3))); axis off
```

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[4] See e. g. the poorly labeled graph in fig. 10.7, p. 185 in the book "Solid state physics" by Ashcroft and Mermin, 1976