

C2: Band structure

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1 Introduction

When you buy a diamond for your girl/boy friend, what you pay for is a band gap of ~ 6 eV.

Band structure is one of the most important concepts in solid state physics. Actually, any excitation in a crystalline solid can be characterized by a Bloch vector \mathbf{k} , but usually bandstructure refers to the structure of the electronic energy levels. The electronic structure determines the chemical bonds which keep the atoms together. A material is a conductor or insulator depending on how the Fermi energy is located relative to the band gaps. The electronic structure indirectly also determines the vibrational levels *i.e.* the phonons. Optical and magnetic properties depend crucially on the underlying band structure, but these properties also depend more directly on how the electrons interact with one another.

In its most naive form, band structure theory assumes that each particle moves in an average potential $V(\mathbf{r})$ from all the nuclei and electrons in the system, so-called mean-field theory. In a crystalline material this potential is lattice periodic, and the electron orbitals can be chosen to have Bloch symmetry involving a Bloch label \mathbf{k} and a band index n , $\phi(\mathbf{r}) = \phi_{\mathbf{k}n}(\mathbf{r})$. However, the band structure concept remains valid also when the electrons interact with one another, and the energy bands are experimentally measurable with experiments such as angle-resolved photoemission. In the real band structure, the electron states have a finite lifetime away from the Fermi energy, and the band energies $\epsilon_{\mathbf{k}n}$ may differ from those obtained from simple mean-field approximations.

In order to determine ground-state properties, the mean-field approach can be made formally exact by adding terms to the effective potential which account for the interaction and Pauli principle, so-called density-functional theory (DFT). In this form, band-structure theory has been very successful for predicting ground-state properties such as cohesive energies, crystallographic structure and chemical bond lengths and lattice parameters with e^2 and \hbar as the only input parameters. In the adiabatic approximation, the electrons are considered to remain in the instantaneous (electronic) ground state when the lattice vibrates. Consequently, also adiabatic phonon frequencies can be obtained from DFT.

In order to predict correct excitation energies beyond mean-field theory, the potential must include terms which account for the interaction with all other electrons in a dynamical way. Consequently, excitation energies are more difficult to predict than are the ground-state properties mentioned above. Approximations from so-called many-body perturbation theory have in recent years been remarkably successful for predicting correct excitation energies and band gaps in sp-bonded materials like Si, GaAs, etc. There is a large number of band-structure codes available which solve the band-structure problem within a density-functional framework relevant to ground-state properties. Also codes for excited-state properties are becoming available. Many of these codes are results of open-source efforts in the scientific community and are available free of charge.

In this exercise, we will illustrate the bandstructure concept by doing simulations of model systems in one and two dimensions. We use two Matlab scripts named *band.m* and *lab.m*. In the first program we look at how band structure emerge in one dimension, and how it depends on the strength of the potential and the separation between the ions. Moreover, we will discuss the reduced band scheme and the meaning of the reciprocal lattice vectors. In the second program a two-dimensional model is considered, and we will look at the importance of the potential strength and how bands may overlap in energy.

2 The Bloch theorem

Please read the notes *An introduction to the concept of band structure* which are available at http://www.matfys.lth.se/Andreas.Wacker/Scripts/bandstructure_intro.pdf. Elaborating the five exercises is part of your project report.

3 Construction of eigenstates

Even a simple one-dimensional Schrödinger equation cannot usually be solved in closed form by some formulae, so one needs almost always to use some approximate method (grid methods, basis sets, etc.) For solving electronic eigenstates in solids and molecules, methods using basis sets and the variational theorem are dominating. Thus, the eigenstates are found by minimizing

$$E = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}$$

where the trial wave functions ψ are chosen as linear combinations of some given basis functions $\phi_1, \phi_2, \dots, \phi_n$,

$$\psi(\mathbf{r}) = \sum_{\nu} c_{\nu} \phi_{\nu}(\mathbf{r}).$$

This gives

$$E = \frac{\sum_{kl} c_k^* c_l H_{kl}}{\sum_{kl} c_k^* c_l S_{kl}} \quad (3.1)$$

where

$$H_{kl} = \int \phi_k^*(\mathbf{r}) H \phi_l(\mathbf{r}) d^3r, \quad S_{kl} = \int \phi_k^*(\mathbf{r}) \phi_l(\mathbf{r}) d^3r, \quad (3.2)$$

Question 1: Derive Eqs. (3.1, 3.2).

The stationary solutions obey $\partial E/\partial c_k^* = 0$ which gives

$$H_{k1}c_1 + H_{k2}c_2 + \cdots + H_{kn}c_n = E(S_{k1}c_1 + S_{k2}c_2 + \cdots + S_{kn}c_n), \quad k = 1, 2, \dots, n$$

(The condition $\partial E/\partial c_k = 0$ gives just the Hermitian conjugate of the above equation and thus not anything new.) The problem of finding eigenstates has thus been reduced to a much simpler problem of finding (generalized) eigenvalues to a Hamiltonian matrix $\mathcal{H} = (H_{kl})$,

$$\mathcal{H} = E\mathcal{S},$$

and the eigenvalues are obtained from

$$\det(\mathcal{H} - E\mathcal{S}) = 0.$$

By increasing the number of basis functions can in principle obtain solutions of arbitrarily high accuracy. When the basis functions ϕ_k are chosen orthonormal, the ‘overlap matrix’ \mathcal{S} becomes the unit matrix, $S_{kl} = \delta_{kl}$.

In the context of bandstructure calculations there are primarily two kinds of basis functions in common use. One involves basis functions localized on each atom, and the other consists of completely delocalized plane waves. In the exercise we are using localized Gaussian basis functions in the one-dimensional case, and plane waves in the model two-dimensional bandstructure.

3.1 Local basis functions in 1D

The smallest basis we can ever have consists of just one orbital $\phi(x - na)$ localized on each atom. We know that the eigenstates can be chosen to have Bloch symmetry. There is then one single independent combination of basis function for each Bloch vector k ,

$$\psi_k = \frac{1}{\sqrt{N}} \sum_{n=0}^{N-1} e^{ikna} \phi(x - na) \quad (3.3)$$

(\sqrt{N} is introduced merely for size consistency). Because of the lattice symmetry,

$$H_{nm} = \int \phi^*(x - na) H \phi(x - ma) dx \equiv H_{n-m}$$

is a function only of $n - m$. With only one orbital per atom, there is no variational degree of freedom left in the Bloch sum in Eq. (3.3), and the energy is just given by

$$\epsilon_k = \frac{\langle \psi_k | H | \psi_k \rangle}{\langle \psi_k | \psi_k \rangle} = \frac{H_k}{S_k} \quad (3.4)$$

where

$$H_k = \frac{1}{N} \sum_{nm} e^{-iak(n-m)} H_{n-m} = \sum_n e^{-iakn} H_{n-0}, \quad (3.5)$$

$$S_k = \frac{1}{N} \sum_{nm} e^{-iak(n-m)} S_{n-m} = \sum_n e^{-iakn} S_{n-0}. \quad (3.6)$$

Question 2: derive Eqs(3.4 - 3.6).

In order to increase the variational freedom and thus the accuracy, we may use several local orbitals per atom, $\phi_1(x), \phi_2(x), \dots, \phi_r(x)$, and form the Bloch sums

$$\psi_k(x) = \frac{1}{\sqrt{N}} \sum_{n=0}^{N-1} \sum_{\nu=1}^r c_{k\nu} e^{ikna} \phi_\nu(x - na).$$

In this case, there are n free parameters $c_{k,1}, c_{k,2}, \dots, c_{k,n}$ to optimize for each k . The variational calculation leads in this case to a $n \times n$ matrix eigenvalue problem to solve for each k . This is how the matlab script in the exercise obtains the one-dimensional band states. The potential is modeled by an attractive Gaussian potential well, and the basis functions of the form $x^\nu \exp(-\alpha x^2)$. By increasing the size of the basis, we obtain gradually a more and more accurate solution to the lattice Schrödinger equation.

3.2 Plane wave basis

We expand the periodic potential in a Fourier series

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

where \mathbf{G} are reciprocal lattice vectors. As basis functions we take plane waves,

$$\phi_{\mathbf{k}+\mathbf{K}} = \frac{1}{\sqrt{V_c}} e^{i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}} \quad (3.7)$$

and the the variational *Ansatz* takes of the form

$$\psi(\mathbf{r}) = \frac{1}{\sqrt{V_c}} \sum_{\mathbf{K}} c_{\mathbf{k}+\mathbf{K}} e^{i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}},$$

where \mathbf{k} is the Bloch vector and \mathbf{K} reciprocal lattice vectors. In the plane wave basis the Hamiltonian matrix becomes

$$H_{\mathbf{k}+\mathbf{K}, \mathbf{k}+\mathbf{K}'} = \frac{\hbar^2(\mathbf{k} + \mathbf{K})^2}{2m} + V_{\mathbf{K}-\mathbf{K}'}$$

and the overlap matrix is unity. The secular problem becomes

$$\left(\frac{\hbar^2(\mathbf{k} + \mathbf{K})^2}{2m} - \epsilon \right) c_{\mathbf{k}+\mathbf{K}} + \sum_{\mathbf{G}} c_{\mathbf{k}+\mathbf{K}-\mathbf{G}} V_{\mathbf{G}} = 0$$

where \mathbf{k} vectors up to a given maximum value are included, $|\mathbf{k} + \mathbf{K}| \leq K_{max}$.

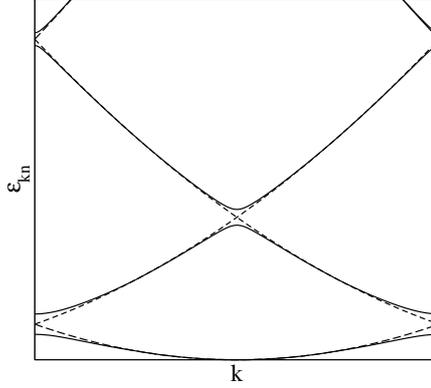


Figure 1: Band structure in 1D with (solid line) and without (dashed line) a weak lattice potential

3.3 Weak potentials (nearly free electrons)

If there is no lattice potential at all, the plane wave basis functions in Eq. (3.7) solve the Schrödinger equation, and the band energies equal the unperturbed energies

$$\epsilon_{\mathbf{k},\mathbf{K}}^0 = \frac{\hbar^2(\mathbf{k} + \mathbf{K})^2}{2m}. \quad (3.8)$$

In 1D, this gives the band structure in Fig. 1. Let us estimate the leading corrections from a lattice potential in perturbation theory. The first-order correction

$$\epsilon_{\mathbf{k},\mathbf{K}}^{(1)} = \langle \phi_{\mathbf{k}+\mathbf{K}} | V | \phi_{\mathbf{k}+\mathbf{K}} \rangle = \frac{1}{V_c} \int_{V_c} V(\mathbf{r}) d^3r = V_0$$

gives just a constant shift of all levels and can be incorporated by shifting the zero level of energies. In second order, the contribution from a particular Fourier component $V_{\mathbf{G}}$ gives

$$\epsilon_{\mathbf{k},\mathbf{K}}^{(2)} = \frac{|\langle \phi_{\mathbf{k}+\mathbf{K}+\mathbf{G}} | V | \phi_{\mathbf{k}+\mathbf{K}} \rangle|^2}{\epsilon_{\mathbf{k}+\mathbf{K}+\mathbf{G}}^0 - \epsilon_{\mathbf{k}+\mathbf{K}}^0} = \frac{|V_{\mathbf{G}}|^2}{\epsilon_{\mathbf{k}+\mathbf{K}+\mathbf{G}}^0 - \epsilon_{\mathbf{k}+\mathbf{K}}^0}$$

Generally, the second-order contribution is small, but near a zone boundary where $|\mathbf{k} + \mathbf{K} + \mathbf{G}| = |\mathbf{k} + \mathbf{K}|$ the basis functions $\phi_{\mathbf{k}+\mathbf{K}+\mathbf{G}}$ and $\phi_{\mathbf{k}+\mathbf{K}}$ become degenerate and non-degenerate perturbation theory breaks down. To describe the band structure near the degeneracy point we make a simple variational calculation with the two nearly degenerate states above as basis functions. This gives a Hamiltonian matrix

$$\begin{pmatrix} \epsilon_{\mathbf{k}+\mathbf{K}}^0 & V_{-\mathbf{G}} \\ V_{\mathbf{G}} & \epsilon_{\mathbf{k}+\mathbf{K}+\mathbf{G}}^0 \end{pmatrix}$$

with energy eigenvalues

$$\epsilon = \frac{\epsilon_{\mathbf{k}+\mathbf{K}}^0 + \epsilon_{\mathbf{k}+\mathbf{K}+\mathbf{G}}^0}{2} \pm \left(\frac{(\epsilon_{\mathbf{k}+\mathbf{K}}^0 - \epsilon_{\mathbf{k}+\mathbf{K}+\mathbf{G}}^0)^2}{4} + |V_{\mathbf{G}}|^2 \right)^{1/2}$$

We see that a band gap of $2|V_{\mathbf{G}}|$ opens up, and this occurs in general for each \mathbf{G} , *i.e.* at every zone boundary.

Question 3: How many electron states (including spin) are there in each band if the lattice consists of N sites?

Question 4: Consider a hypothetical 1D solid with two electrons per atom. Is the material metallic or is it an insulator?

4 Simulations

4.1 Simulations in 1D

In this part you will use the program *band.m*. The use of the program is quite easy. Try for yourself to figure out how it works and then answer the following question.

First we consider the potential plot.

Question 5: What is the blue line? The red lines? And the yellow line?

Question 6: What happens when you enlarge the lattice constant? And when it is diminished?

Look at the form of the single ion potential. It is chosen to be Gaussian.

Question 7: Do you know other kinds of single ion potentials?

Now we are ready to look at the *Energy Band Structure*-plot. Press *Reset* and then look at the band structure and the potential when you decrease the lattice constant.

Question 8: What happens with the band structure? Does it look like something you know?

Reset the program again, and then lower the potential to its minimum value. The potential is almost flat and we see a band scheme as for a free electron. Now increase the potential strength and try to describe what happens to the bands.

Question 9: What is the difference between the lowest band and the higher ones? *Hint: Look at the energy of the bands and compare it to the potential. Try also to plot more bands.*

Question 10: Reset the program once more, and then increase the lattice constant. What do you see? Plot more bands and see what happens.

Finally we look at *Band structure for different lattice constants* for a fixed potential. Change the lattice constant and describe what you see. After having done that for a few different lattice constants, press *All lattice constants*. Do the same for different potentials. This will summarize what you have already done.

4.2 Simulations in 2D

These simulations intend to illustrate among other things then different bands may overlap in energy as soon as the dimension is higher then one. The simulations are making use of plane waves as basis functions for solving the Schrödinger equation. We consider a square lattice in 2D with lattice parameter a . In Fig. 2 we show the 2D Brillouin zone and the lowest free-electron bands. The free-electron bands are obtained by folding in the free-electron parabola in the first Brillouin. The lowest ones are

$$\begin{aligned}\epsilon_0^0(\mathbf{k}) &= \frac{\hbar^2 k^2}{2m}, \\ \epsilon_{1,2}^0(\mathbf{k}) &= \frac{\hbar^2(k_x \pm G_1)^2}{2m} + \frac{\hbar^2 k_y^2}{2m}, \quad \epsilon_{3,4}^0(\mathbf{k}) = \frac{\hbar^2 k_x^2}{2m} + \frac{\hbar^2(k_y \pm G_1)^2}{2m}, \\ \epsilon_{5,6,7,8}^0(\mathbf{k}) &= \frac{\hbar^2(k_x \pm G_1)^2}{2m} + \frac{\hbar^2(k_y \pm G_1)^2}{2m},\end{aligned}$$

where $G_1 = 2\pi/a$.

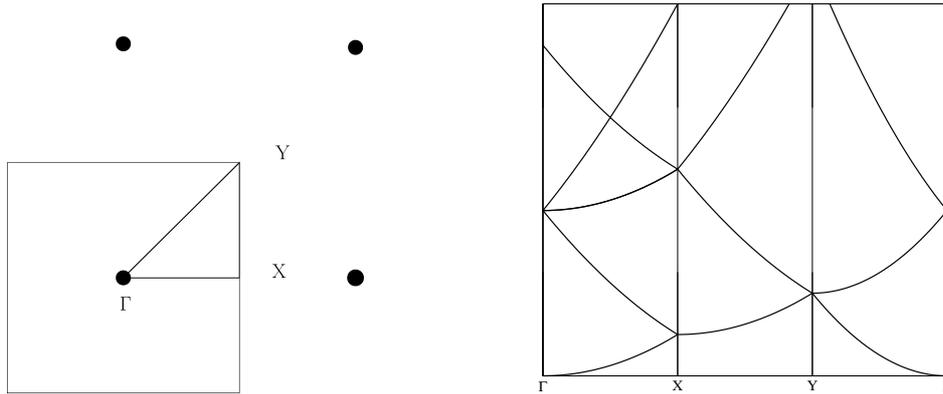


Figure 2: Left: Brillouin zone of a square lattice with special points $\Gamma = (0, 0)$, $X = (\pi/a)(1, 0)$ and $Y = (\pi/a)(1, 1)$. Right: Free-electron bands along the path $\Gamma \rightarrow X \rightarrow Y \rightarrow \Gamma$.

To compute the 2D bandstructure when a lattice potential is added, we use the Matlab script *lab.m*. The script has to be called with two arguments

$$\text{lab}(U, \mu)$$

where U is the strength of the potential and μ is the Fermi level.

Question 11: Try to call it with $(U, \mu) = (0, 0)$. What do you see?

Now increase U and see what happens (try to rotate the figure). Increase the Fermi level afterwards.

Question 12: What do you see on the figure and what does it represent?

Question 13: From the output, sketch how a weak lattice potential modifies the free-electron bandstructure in Fig. 2

Question 14: Can a divalent ‘solid’ in 2D be metallic? What about divalent solids’ in 1D?

For a fixed potential vary the Fermi level.

Question 15: What happens?

Question 16: In the metallic case, sketch the shape of the Fermi surface of the lowest band when it start to touch the zone boundaries. Is the effective mass positive (electron-like) or negative (hole-like)?

Question 17: When the second band starts to fill: Sketch the shape of the Fermi surface of the second band. Is the effective mass electron-like (> 0) or hole-like?

5 Final remarks

As stated in the beginning a diamond has a band gap of ~ 6 eV. Do you understand why this makes it expensive? *Hint: Try to find the energy of a photon in the visible range.*

Another question: Are you aware of why a solid with a band gap cannot conduct current? See Ibach and Lüth.

6 References

Ibach, H. and Lüth, H., *Solid State Physics*, Springer 2003.

Ashcroft, N.W. and Mermin, N.D., *Solid State Physics*, Saunders College Publishing 1976.