An Introduction to the Concept of Band Structure

Andreas Wacker[1]

Mathematical Physics, Lund University

November 20, 2018

1   Introduction

Band structure is one of the most important concepts in solid state physics. It provides the electronic levels in (ideal) crystal structures, which are characterized by two quantum numbers, the Bloch vector $\mathbf{k}$ and the band index n. Here the Bloch vector is an element of the reciprocal space (in units 1/length) and the energy of the electron $E_n(\mathbf{k})$ is a continuous function of $\mathbf{k}$, so that one obtains a continuous range of energies referred to as the energy band. Many electrical, optical, and even some magnetic properties of crystals can be explained in terms of the bandstructure. Of particular importance is the location of the Fermi energy, until which all levels are occupied at zero temperature. If the Fermi energy is located in a band gap, the material is insulating (or semiconducting) while it is metallic otherwise.

In these notes we consider single electrons in a periodic potential. This potential results both from the interaction of the electron with the ions and the other electrons, which are considered to provide a fixed background (called mean-field). This entirely neglects correlations between the kinetics of the single electron and the others, and thus only serves as an approximation for the complex many-particle physics scenario. However, this is rather good for many purposes, in particular if more complicated potentials are used as justified within density functional theory.

2   A simple one-dimensional example

We consider an electron in the potential

$$V(x) = 2U\cos(gx) = U(\mathrm{e}^{igx} + \mathrm{e}^{-igx}), \quad \text{where} \quad g = \frac{2\pi}{d}. \tag{1}$$

As $V(x + d) = V(x)$ for all x, the potential exhibits the period d and can be thought as the potential resulting from a lattice of ions. Now we solve the stationary Schrödinger equation

$$\hat{H}\Psi(x) = E\Psi(x) \quad \text{with the Hamilton operator} \quad \hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x) \tag{2}$$

In order to normalize the wave functions, we consider a finite crystal with N periods and use periodic boundary conditions $\Psi(x + Nd) = \Psi(x)$. Then the wave function can be expanded in a discrete Fourier series
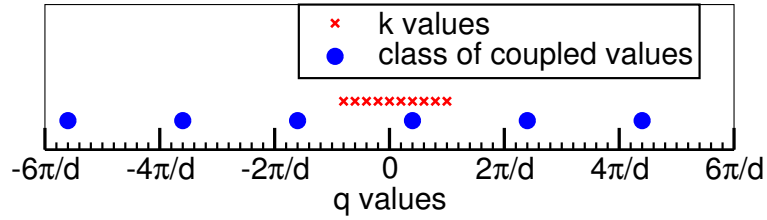
$$\Psi(x) = \sum_q a_q \mathrm{e}^{iqx} \tag{3}$$

Figure 1: Set of q values for a finite crystal consisting of $N = 10$ periods with period d. The blue balls indicate one class of values coupled by Eq. (5), which can be written as $k + l2\pi/d$ with integer l.

where q is an integer multiple of $2\pi/Nd$. At a later stage we allow N to become arbitrarily large, so that the artificial periodicity does not matter and the spacing of q values becomes infinitesimal small. Inserting into the Schrödinger equation (2) provides

$$\sum_{q'} \left(\frac{\hbar^2 q'^2}{2m} e^{iq'x} + U e^{i(q'+g)x} + U e^{i(q'-g)x} \right) a_{q'} = E \sum_{q'} e^{iq'x} a_{q'} \tag{4}$$

Now we multiply both sides with e^{-iqx}/Nd and perform the integral $\int_{-Nd/2}^{Nd/2} dx$ resulting in

$$\frac{\hbar^2 q^2}{2m} a_q + U a_{q-g} + U a_{q+g} = E a_q \tag{5}$$

This shows that Fourier components with different q couple to each other if their difference matches g. This defines a class of q-values which couple to each other, as sketched in Fig. 1. This class can be uniquely described to be all the values q which can be written as $q = k + lg$ with $l \in \mathbb{Z}$, where k is a fixed value in the interval $-\pi/d < k \leq \pi/d$. Setting $a_{k+lg} = a_l^{(k)}$ we find for each k an infinite set of equations

$$\frac{\hbar^2(k+lg)^2}{2m} a_l^{(k)} + U a_{l-1}^{(k)} + U a_{l+1}^{(k)} = E a_l^{(k)} \quad \text{for} \quad l = \dots, -2, -1, 0, 1, 2, \dots \tag{6}$$

Let us now assume that $a_l^{(k)} = 0$ for $|l| > l_{\max}$. (This approximation is actually valid if one restricts to energies E which are significantly smaller than $(\hbar l_{\max} g)^2/2m$ and can be easily controlled by comparing solutions with different $l_{\max}$.) This provides an eigenvalue problem in a $(2l_{\max} + 1)$ dimensional space. E.g. for $l_{\max} = 2$ we find

$$\mathcal{M} \begin{pmatrix} a_2^{(k)} \\ a_1^{(k)} \\ a_0^{(k)} \\ a_{-1}^{(k)} \\ a_{-2}^{(k)} \end{pmatrix} = E \begin{pmatrix} a_2^{(k)} \\ a_1^{(k)} \\ a_0^{(k)} \\ a_{-1}^{(k)} \\ a_{-2}^{(k)} \end{pmatrix} \quad \text{with} \quad \mathcal{M} = \begin{pmatrix} \frac{\hbar^2(k+2g)^2}{2m} & U & 0 & 0 & 0 \\ U & \frac{\hbar^2(k+g)^2}{2m} & U & 0 & 0 \\ 0 & U & \frac{\hbar^2 k^2}{2m} & U & 0 \\ 0 & 0 & U & \frac{\hbar^2(k-g)^2}{2m} & U \\ 0 & 0 & 0 & U & \frac{\hbar^2(k-2g)^2}{2m} \end{pmatrix} \tag{7}$$

This is a standard eigenvalue problem and a numerical solution of the polynomial equation $\det\{\mathcal{M} - E\mathcal{I}\} = 0$ provides $(2l_{\max} + 1)$ eigenvalues of the matrix $\mathcal{M}$. These eigenvalues are labeled by the index $n = 1, 2, \dots, (2l_{\max} + 1)$ and denoted as $E_n(k)$. An example is plotted in Fig. 2. We see, that for each n (called *band index*) the energies $E_n(k)$ form a continuous function of k (called *Bloch number*[2]). The set of energies $E_n(k)$ for a given index n and for all possible $k \in (-\pi/d, \pi/d]$ is called an *energy band*. It is interesting to see that there are ranges of energies between the bands, where there are no solutions $E_n(k)$. These energy ranges are called *gaps*.

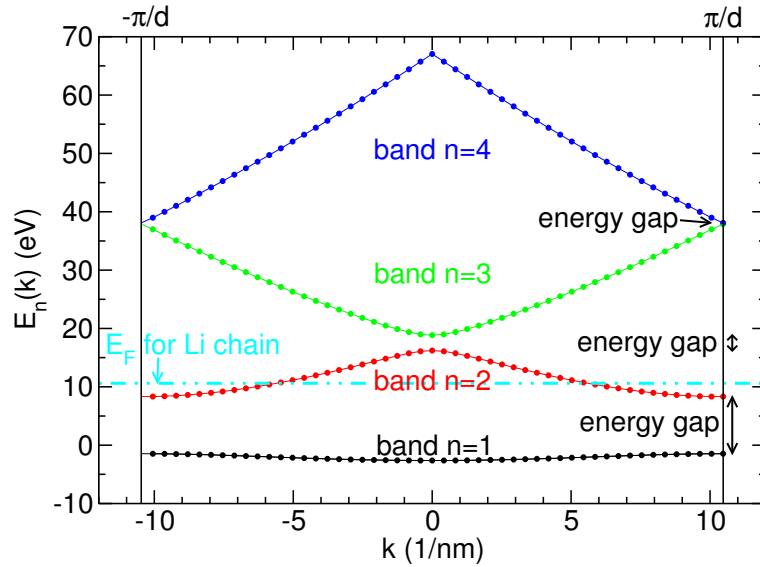[2]More common is the term Bloch vector in higher dimensions.

Figure 2: Energy bands calculated for Eq. (6) using $U = 5$ eV and $d = 0.3$ nm (a typical distance between atoms in solids) for $N = 50$ periods. Here a cut-off $l_{\max} = 5$ is used after checking that larger values do not change the results. The energy gap between bands 3 and 4 is hardly visible. The dash-dotted line is the Fermi energy for a hypothetical chain of equally spaced Li atoms.

Exercise 1: Calculate the energy bands using only the components $l = 0$ and $l = -1$ analytically. Sketch the first two bands for $k > 0$ both for $U = 0$ and finite U. How large is the energy gap between the first and the second band?

For a given band index n and Bloch number k, the coefficients of the eigenvector corresponding to the eigenvalue $E_n(k)$ in Eq. (7) are denoted by $a_l^{(nk)}$. Than the corresponding wave function is given by Eq. (3)

$$\Psi_{nk}(x) = e^{ikx} u_{nk}(x), \quad \text{with} \quad u_{nk}(x) = \sum_l a_l^{(nk)} e^{ilgx}.$$

As the functions $u_{nk}(x)$ only contain Fourier components with integer multiples of g, we find $u_{nk}(x + d) = u_{nk}(x)$ and the function $u_{nk}(x)$ has the same periodicity as the lattice. Thus the wave function (called *Bloch function*) contains two parts: a wave e^{ikx} determined by the Bloch number and a lattice periodic part $u_{nk}(x)$. Note, that the Bloch function itself has NOT the periodicity of the lattice if $k \neq 0$.

The band structure obtained numerically can be understood for weak potentials $U \ll \hbar^2 g^2/2m$ within a simple free particle model. For vanishing potential $V(x)$ the eigenstates of Eq. (2) are given by plane waves e^{iqx} with energy $E(q) = \hbar^2 q^2/2m$. Decomposing $q = k + lg$, where $-\pi/d < k \leq \pi/d$ and $l \in \mathbb{Z}$ we obtain bands $E_l(k) = \hbar^2(k + lg)^2/2m$ and corresponding Bloch functions $\Psi_{lk}(x) = e^{ikx} u_{lk}(x)$ with $u_{lk}(x) = e^{ilgx}$. This operation corresponds to moving the branches of the parabola $\hbar^2 q^2/2m$ into the region of Bloch numbers, see Fig. 3. The resulting band structure[3] resembles the numerical result for small U, where the main difference is the appearance of band gaps at points where the different branches of the free-electron solution cross. (This splitting of degenerate levels is a general consequence of perturbation theory.)

---

[3]Note that the conventional numbering of bands is obtained by $l = 0 \to n = 1$, $l = \pm 1 \to n = 2$, $l = \mp 1 \to n = 3$ for $k > / < 0$, respectively.
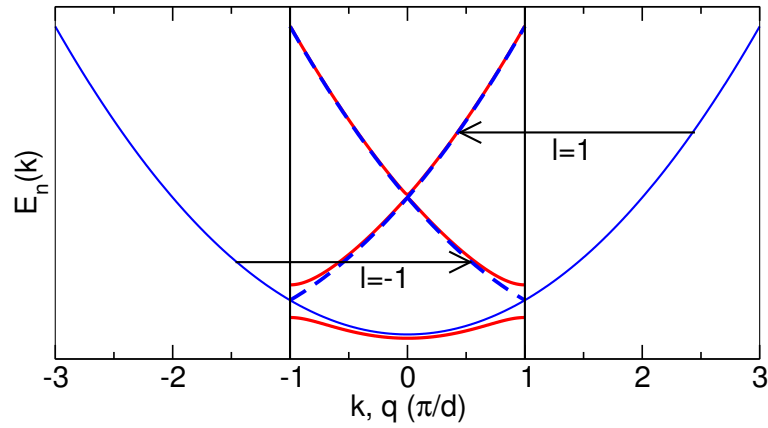
Figure 3: Free electron dispersion $E(k) = \hbar^2 k^2/2m$ (blue full line) and corresponding band structure (blue dashed lines) for a $d = 0.3$ nm lattice obtained by shifting branches by multiples of g. The red lines provides the band structure calculated from Eq. (6) for $U = 2$ eV.

Here we considered a special potential of cosine shape, which made the calculations particularly simple. The same result holds for a general potential with period d. Such a potential can be written as $V(x) = \sum_{j=-\infty}^{\infty} U_j e^{ijgx}$ and one obtains an eigenvalue problem similar to Eq. (6) where couplings between a_n and arbitrary a_{n+j} appear.

Exercise 2: Determine the equivalent to Eq. (6) for the periodic potential $V(x) = a + b\cos(2gx) + c\cos(3gx)$

Finally, we want to count the number of energy eigenvalues in a given band. As there is one value for each value of k, this is just the number of possible k values with $-\pi/d < k \leq \pi/d$. Considering a finite system of length Nd (see above) we found that the q-values in Eq. (3) have a spacing of $2\pi/(Nd)$ and the same holds for the Bloch numbers k. Thus we conclude, that there are precisely N different values of k in the interval $-\pi/d < k \leq \pi/d$. Thus the number of states in a given band is equal to the number of periods in the finite system.

3 Bloch Theorem

The findings from section 2 for a one-dimensional system can be easily generalized to D dimensions. Here the period d is replaced by the primitive vectors $\mathbf{a}_1, \ldots \mathbf{a}_D$, spanning the primitive unit cell (i.e. the unit cell with the minimal possible volume) and forming the Bravais lattice $\mathbf{R} = \sum_{i=1}^{D} n_i \mathbf{a}_i$ with integer coefficients n_i. Similarly g is replaced by the reciprocal lattice vectors $\mathbf{b}_1, \ldots \mathbf{b}_D$ satisfying $\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{i,j}$ and spanning the reciprocal lattice $\mathbf{G} = \sum_{i=1}^{D} l_i \mathbf{b}_i$ with integer coefficients l_i. Finally, the region $-\pi/d < k \leq \pi/d$ becomes the first Brillouin zone, which is the set of vectors $\mathbf{k}$ being closer to the origin then to any other vector $\mathbf{G}$ of the reciprocal lattice. In analogy to the one-dimensional case one finds

---

Bloch Theorem: For ideal crystals with a lattice-periodic Hamiltonian satisfying $\hat{H}(\mathbf{r} + \mathbf{R}) = \hat{H}(\mathbf{r})$ for all vectors $\mathbf{R}$ of the Bravais lattice, a complete set of eigenstates can be written in the form $\Psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r})$ where $u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r})$ is a lattice-periodic function. The corresponding energies $E_n(\mathbf{k})$ are continuous functions in the *Bloch vector* $\mathbf{k}$ for each *band index n* and constitute the *energy bands*. The Bloch vectors are restricted to the first Brillouin zone and for finite crystals there are as many different Bloch vectors $\mathbf{k}$ in each band as there are primitive unit cells in the crystal.

The corresponding proof can be found in many textbooks, such as section 6.3 of [1].

The existence of a band structure is a general consequence of the spatial periodicity of a lattice, see [2] for details. Thus these features are much more general than the eigenstates of a stationary single-particle Schrödinger equation addressed here. In general any excitation in a crystalline solid can be characterized by such a Bloch vector $\mathbf{k}$, which is directly accessible in scattering experiments. Consequently, the term bandstructure is sometimes applied to non-electronic excitations such as phonons, as well. [4]

The nature of energy eigenstates is generally connected to the symmetry of the problem. We know this from atomic physics, where the spherical symmetry of the potential results in orbital quantum numbers l, m, which represent the angle-dependence $Y_{lm}(\theta, \varphi)$ of the wave function. In addition, there is the principle quantum number n, related to the spherically symmetric part $R_{nl}(r)$, so that the energies are E_{nl}. In crystals, the lattice-periodicity implies the quantum number $\mathbf{k}$, associated with a plane wave behavior $e^{i\mathbf{k}\cdot\mathbf{r}}$. The band index n relates to the lattice-periodic part $u_{n\mathbf{k}}(\mathbf{r})$ and the bandstructure $E_n(\mathbf{k})$. Note, that the eigen-functions do *not* have the same symmetry as the potentials: Neither are atomic orbitals rotational symmetric (except for $l = 0$), nor are Bloch functions lattice-periodic (except for $\mathbf{k} = 0$).

As an example, Fig. 4 shows the band structure of silicon. Silicon crystallizes in a fcc lattice with two atoms per primitive unit cell (diamond structure) and the corresponding Brillouin zone is depicted on the left hand side. The energy bands are functions of the three-dimensional Bloch-vector $\mathbf{k}$, which takes all values within the Brillouin zone. In order to visualize the corresponding energies $E_n(\mathbf{k})$ one typically considers certain lines through the Brillouin zone, which connect points of high symmetry. In particular, the Γ point denotes $\mathbf{k} = 0$. In the right panel the energies are plotted along these lines for a certain number of bands.

4 Pauli principle and Fermi energy

A real crystal contains not only a single electron as considered above, but typically several electrons per unite cell. Many-particle quantum physics tells us, that valid many-particle states can only be constructed, if one does not allow two electrons to occupy the same single particle level. Thus (an approximation for) the ground state of the many-electron system is obtained by subsequently filling the lowest energy levels with electrons. The energy of the level filled with the last electron is called the *Fermi energy E_F*. In order to determine E_F, we need to count the number of k-values, which is easy for a finite crystal. As mentioned above, the first Brillouin zone contains as many $\mathbf{k}$ points as there are unit cells in a finite crystal. In this context the spin degree of freedom has to be taken into account. In most cases the energy bands are (almost) identical for both spin directions[5]. Thus each state with a given Bloch vector and band index can accommodate two electrons and consequently each band can take two electron per primitive unit cell (assuming spin degeneracy). Extended crystals do not allow

---

[4]The analogy for time periodic systems is referred to as Floquet states.

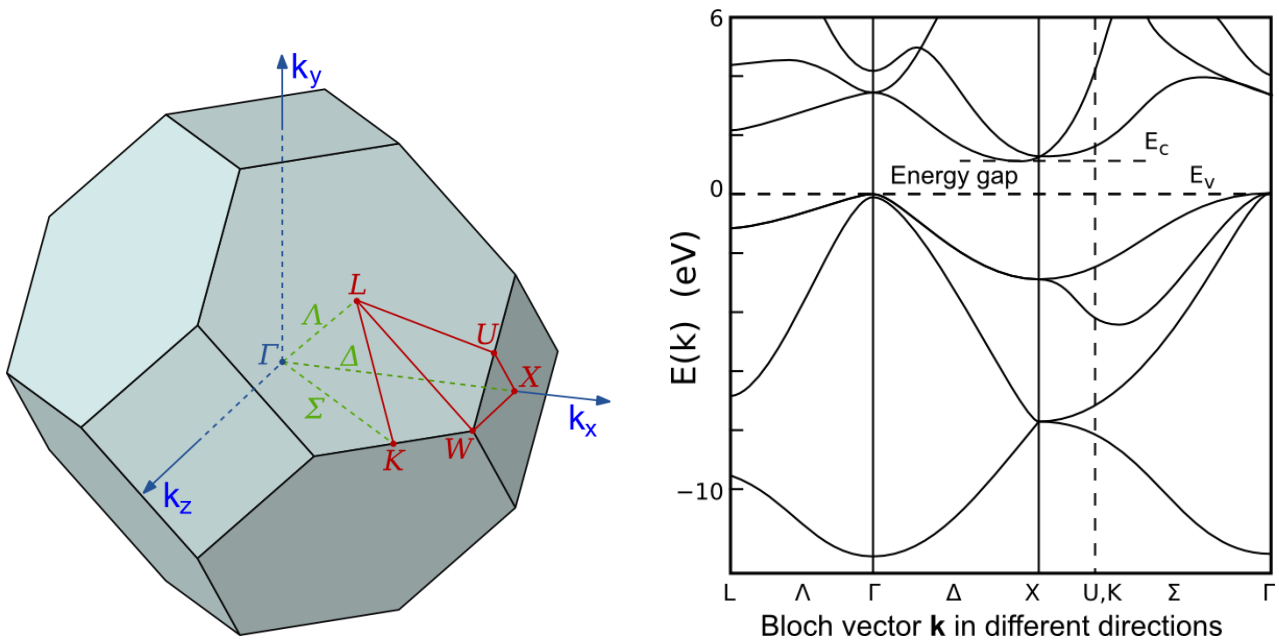[5]Of course this is not true for magnetic systems.

Figure 4: Left: Brillouin zone for the fcc lattice. Right: Sketch of band structure for silicon [after J.R. Chelikowsky and M.L. Cohen, Phys. Rev B **10**, 5095 (1974)]. The figures are based on files from Wikimedia Commons [Original files: `Brillouin_Zone_(1st,_FCC)`, public domain; `Band structure Si schematic`, CC-BY-SA Cepheiden.]

for a macroscopic net charge due to the Coulomb repulsion. Thus the total number of electrons must match the charges of the nuclei. This rule provides the Fermi energy for a given crystal.

Example: We consider a (hypothetical) one-dimensional chain of Lithium atoms regularly spaced by a. Each Li-nucleus has a positive charge $3e$ and thus three electrons per period are required for charge neutrality. Thus the band $n = 1$ is entirely filled and band $n = 2$ is half filled. The corresponding Fermi energy is indicated in Fig. (2).

Exercise 3: Consider a chain of Lithium atoms, where each second atom is moved by a small amount Δ to the right, so that the spacings are in turns given by $a + \Delta$ and $a - \Delta$. Determine the period and the range of k values in terms of a. Sketch the band structure qualitatively and indicate the location of the Fermi energy.

The location of the Fermi energy with respect to the band structure is crucial for the optical and electrical properties of the crystal. If the Fermi energy is located within one band (or several overlapping bands), the solid is a metal. If on the other hand the Fermi energy is located in a band gap between the uppermost entirely filled band (the valence band) and the next entirely empty band (the conduction band), the material is either a semiconductor or an insulator (for larger band gaps), where the differentiation is however not sharp.

Note that the presence of extra charges, such as replacing some atoms by others with a different nuclear charge (doping) or electric potentials at interfaces (e.g. field effect transistors) allow for a (slight) manipulation of the total number of electrons. While the corresponding change in Fermi energy is negligible for metals, in semiconductors any extra electron occupies the conduction band, while any missing electron provides an empty state (called hole) in the valence band. Thus the conductivity of semiconductors can be easily modified, which is the basis for most electronic applications of these materials.

5 Eigenstates by linear combination of atomic orbitals (LCAO)

In Section 2 the Bloch states were determined by an expansion in plane waves e^{iqx}. While such an expansion is always possible in theory, in practice it requires very many ng-components, if the wave functions are localized around the nucleus. Thus an alternate approach is taken here, which is based on localized wavefunctions, such as atomic orbitals. For simplicity a superlattice (SL) is considered here as a one-dimensional example. Superlattices are artificial periodic structures, where different semiconductor materials are grown alternatingly on top of each other. Nevertheless, the results can be easily extended to more dimensions.

The superlattice potential, as depicted in Fig. 5(b) can be described as the sum of infinite many quantum well potentials shifted by the period d:

$$V_{\mathrm{SL}}(x) = \sum_{j=-\infty}^{\infty} V_{\mathrm{well}}(x - jd)$$

The eigenstates of a single quantum well $\phi_\nu(x)$ with energy E_ν, see Fig. 5(a), can be easily determined from the stationary Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V_{\mathrm{well}}(x) \right] \phi_\nu(x) = E_\nu \phi_\nu(x) \tag{8}$$

a problem typically solved in introductory quantum mechanics courses. Now we want to search for solutions of Schrödinger's equation for the superlattice, where we use the wave functions $\phi_\nu(x-jd)$ as a basis. Bloch's theorem tells us that we can chose the solutions as Bloch functions. The most general form of a Bloch function with Bloch number k, which is a linear combination of the wave functions $\phi_\nu(x - jd)$ is:

$$\Psi_{nk}(x) = \sum_{j\nu} a_\nu^{(nk)} e^{ikjd} \phi_\nu(x - jd)$$

Exercise 4: Show that this function has the form of a Bloch function $\Psi_{nk}(x) = e^{ikx} u_{nk}(x)$!

Inserting into Schrödingers equation for $\Psi_{nk}(x)$ with the superlattice potential provides

$$\sum_{j\nu} a_\nu^{(nk)} e^{ikjd} \left(E_\nu + \sum_{j'\neq j} V_{\mathrm{well}}(x - j'd) \right) \phi_\nu(x - jd) = E_{nk} \sum_{j\nu} a_\nu^{(nk)} e^{ikjd} \phi_\nu(x - jd)$$

where Eq. (8) was used. Multiplying by $\phi_\mu^*(x)$ and integrating over x provides

$$\sum_\nu (S_{\mu\nu} E_\nu + V_{\mu\nu}) a_\nu^{(nk)} = E_{nk} \sum_\nu S_{\mu\nu} a_\nu^{(nk)}$$

$$\text{with} \quad S_{\mu\nu} = \sum_j e^{ikjd} \int dx\, \phi_\mu^*(x) \phi_\nu(x - rd) \tag{9}$$

$$\text{and} \quad V_{\mu\nu} = \sum_j e^{ikjd} \int dx\, \phi_\mu^*(x) \left(\sum_{j'\neq j} V_{\mathrm{well}}(x - j'd) \phi_\nu(x - jd) \right)$$

This is a generalized eigenvalue problem, providing N_ν eigenvalues E_{nk} for each Bloch number k, where N_ν is the number of states per well used (the dimension of the matrix).
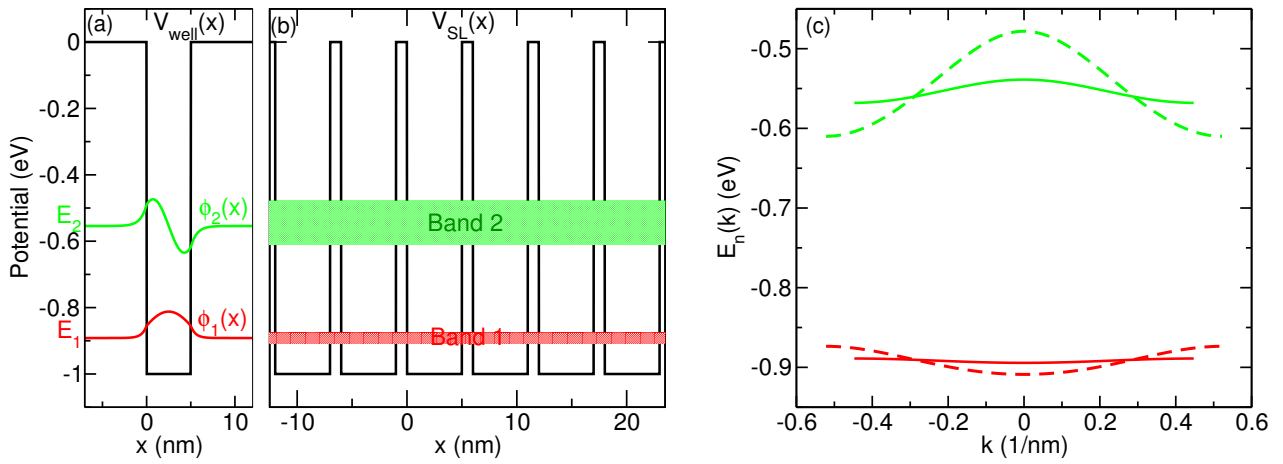
Figure 5: (a) A single GaAs quantum well with a width of 5 nm embedded in AlAs barrier material. The wavefunctions of the two lowest energy levels have been plotted as well. (b) A superlattice structure as a periodic repetition of quantum wells together with the energy regions of the two lowest bands. (c) Bandstructure for superlattices with a barrier width of 2nm [full lines] and 1 nm [dashed lines, structure as in (b)]

For a small spatial overlap of the wave functions $\phi_\nu(x - d)$ and $\phi_\mu(x)$ (and vanishing overlap for larger separations) we find

$$S_{\mu\nu} = \delta_{\mu\nu} + \mathcal{O}(\text{overlap}) \quad V_{\mu\nu} = \mathcal{O}(\text{overlap})$$

and thus the eigenvalues are $E_{nk} = E_\nu + \mathcal{O}(\text{overlap})$. Thus, for vanishing overlap, the bands are degenerate in k (i.e. flat) at the energies of the quantum well levels, while the width is continuously increasing with the overlap of the wave functions (or decreasing barrier width between the wells). This is illustrated in Fig. 5(c).

These features hold also in higher dimensions, and are very useful to understand the band structure in many materials. E.g., lower lying core levels in atoms, which are strongly localized around the nucleus, result in very flat bands in the crystal, which are well below the Fermi energy. Furthermore the valence and conduction band structure of many semiconductors can be fairly well described as a result of the atomic s and p levels in the outer shell, see, e.g. [3]. E.g., the bands depicted in Fig. 4 arise from the atomic 3s and 3p levels. As there are two atoms per unit cell, we have eight such atomic orbitals per unit cell resulting in eight bands. (The uppermost are not entirely displayed.)

Exercise 5: Argue, why the Fermi level for silicon is within the band gap - the last occupied state occurs at $E = 0$ in Fig. 4!

References

[1] P. Hofmann, *Solid State Physics* (Wiley-VCH, Weinheim, 2008).

[2] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Saunders College, Philadelphia, 1976).

[3] P. Y. Yu and M. Cardona, *Fundamentals of Semiconductors* (Springer, Berlin, 1999).