
Solid State Theory

Exercise sheet 5

This exercise sheet will be discussed on Friday, January 20th 2023.
You should hand in your solution of the exercise marked with (★) via mail
(gresista@thp.uni-koeln.de) by 10:00 on Thursday January 19th 2023.

Exercise sheets online at www.thp.uni-koeln.de/trebst/Lectures/2022-SolidState.shtml

1 Tight binding chain (★)

In this exercise, we are revisiting the results we obtained studying the chemical bonds on the 2nd problem sheet to gain insight into electron waves in solids. We considered a system of two nuclei, each with one orbital, and a wavefunction that is a superposition of the two orbitals whose coefficients were found by a variational approach. For this exercise, we are going to consider a chain of N nuclei with periodic boundary conditions. On each nucleus n there is an orbital $|n\rangle$ that we consider to be mutually orthogonal to each other

$$\langle m|n\rangle = \delta_{m,n} . \quad (1)$$

The Hamiltonian for one electron interacting with the nuclei via an interaction V_n looks as follows:

$$H = K + \sum_n V_n , \quad (2)$$

where the V_n are the interaction terms of the electron with the n -th nucleus. Thus, each orbital $|n\rangle$ is an eigenvector of the operator $K + V_n$. We continue by splitting the Hamiltonian operator into a part that is diagonal and one that is off-diagonal:

$$H |n\rangle = (K + V_n) |n\rangle + \sum_{m \neq n} V_m |n\rangle \quad (3)$$

$$= \epsilon_n |n\rangle + \sum_{m \neq n} V_m |n\rangle . \quad (4)$$

1. By multiplying a $\langle m|$ from the left, use the expression above to write down the entry $H_{m,n} = \langle m|H|n\rangle$ of the Hamiltonian matrix.
2. Give an interpretation of the three different terms that appear in the summation $\sum_j \langle n|V_j|m\rangle$.
3. Combine the diagonal elements into one term with prefactor $\epsilon_{0,n}$ and argue why we can approximate the above expression in the form

$$H_{m,n} = \epsilon_{0,n} \delta_{m,n} - t (\delta_{n+1,m} + \delta_{n-1,m}) \quad (5)$$

Which part of this equation encodes the geometry of the chain?

The trial wavefunction we are going to use is a superposition of all orbitals

$$|\psi\rangle = \sum_n \phi_n |n\rangle . \quad (6)$$

Remember from our previous study on chemical bonding that the Schrödinger equation is then given as

$$\sum_n H_{m,n} \phi_n = E \phi_m. \quad (7)$$

To simplify the following calculation, we choose all ϵ_n and V_n to be equal, thus $\epsilon_{0,n} = \epsilon \forall n$.

4. Use the *Ansatz* $\phi_n = N^{-\frac{1}{2}} e^{-inka}$ on both sides of the equation to derive the dispersion relation of the chain, where a is the distance between two nuclei.
5. Compare your result to the dispersion of free electrons. How many distinct eigenstates are there? Why are these energy levels also referred as an energy band?

2 Diatomic tight binding chain

We now exchange every second atom for another species so that the chain is made up of atoms of types A and B whose on-site energies are ϵ_A and ϵ_B . To keep the notation clean, we will also double the length of our chain such that there is a total number of N *unit cells*, i.e. N atoms of type A and N atoms of type B . Accordingly, the coefficients of the trial wavefunction acquire an index n for the unit cell and a second index A or B for the type of atom.

1. Show that the Schrödinger equation now becomes the set of coupled equations

$$E \phi_n^A = \epsilon_A \phi_n^A - t (\phi_n^B + \phi_{n-1}^B) \quad (8)$$

$$E \phi_n^B = \epsilon_B \phi_n^B - t (\phi_n^A + \phi_{n+1}^A). \quad (9)$$

2. Use the same *Ansatz* as in the previous exercise for each of the atom types, but with different amplitudes (i.e. $\phi_n^A = N^{-1/2} A e^{inka}$, $\phi_n^B = N^{-1/2} B e^{inka}$). This will lead you to an eigenvalue problem that results in the dispersion relation for the diatomic tight binding chain

$$E_{\pm}(k) = \frac{1}{2} \left(\epsilon_A + \epsilon_B \pm \sqrt{(\epsilon_A - \epsilon_B)^2 + 4t^2(2 + 2\cos(ka))} \right) \quad (10)$$

3. Show that in the limit $\epsilon_A = \epsilon_B$ the dispersion from the first exercise is recovered. What happens to the band structure once the on-site energies differ by an infinitesimal δ ?
Hint: Use $\sqrt{2 + \cos x} = 2 \cos(x/2)$ for $x \in [-\pi, \pi]$

3 Tight binding in second quantisation

Solving a tight binding model becomes particularly easy if the formulation of second quantisation is used. We will do this for a variety of lattices in this exercise. Setting up the Hamiltonian matrix becomes rather tedious when the lattice has a large number of atoms in the unit cell, if you are interested we provide an IPython notebook that contains routines to solve the tight binding problem for arbitrary lattices. **However there is no need to use this IPython notebook for this particular exercise.**

We start by recapitulating the essentials of the tight binding technique and solve a few simple models using second quantisation.

Isotropic chain

Consider a one-dimensional chain described by a Hamiltonian

$$H = -t \sum_{i=1}^N \left(c_{i-1}^\dagger c_i + c_i^\dagger c_{i-1} \right). \quad (11)$$

with periodic boundary conditions ($c_0^\dagger = c_N^\dagger$, $c_0 = c_N$)

- a) Fourier transforming the creation/annihilation operators to show that each term of the form $c_i^\dagger c_j$ contributes $c_k^\dagger c_k e^{ik(r_i - r_j)}$.
- b) Use this to solve for the energy spectrum $\xi(k)$ of the tight binding chain by rewriting the Hamiltonian in the form $H = \sum_k \xi(k) c_k^\dagger c_k$.

Hint: Use the definitions for Fourier-transformation given on the first exercise sheet (you can set the lattice constant to $a = 1$.)

Square lattice

Tight binding is applicable regardless of the dimensionality of the problem. Only the phase factor $c_k^\dagger c_k e^{ik(r_i - r_j)}$ changes such that each term is now determined by a scalar product $c_k^\dagger c_k e^{i\mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j)}$. Our first example is easily extended to two dimensions:

$$H = -t \sum_{\langle i,j \rangle} \left(c_i^\dagger c_j + c_j^\dagger c_i \right) \quad (12)$$

where the sum runs over all nearest neighbors i, j .

- c) Proceed as previously to determine the energy spectrum of the square lattice.

Diatomic chain

The number of bands that we find for a given Hamiltonian depends on the number of atoms per unit cell. If we change the hopping parameters to be alternating

$$H = -t \sum_{i=1}^{N/2} c_{2i-1}^\dagger c_{2i} - t' \sum_{i=1}^{N/2} c_{2i}^\dagger c_{2i+1} + \text{h.c.}, \quad (13)$$

we are dealing with two atoms A and B , per unit cell which will be described by two types of annihilation and creation operators that we may call a, a^\dagger and b, b^\dagger , respectively.

- d) Rewrite the Hamiltonian using these new operators.

- e) Continue by transforming the Hamiltonian into Fourier space and rewrite the result in the form of a vector-matrix-vector product.
- f) Solve for the energy spectrum by diagonalizing this matrix.

Bonus: Honeycomb lattice

As our final example we take the honeycomb lattice. This is the lattice upon which carbon atoms are placed to form graphene. The basis vectors are given by

$$\mathbf{a}_1 = \frac{1}{2} \begin{pmatrix} 3 \\ \sqrt{3} \end{pmatrix}, \quad \mathbf{a}_2 = \frac{1}{2} \begin{pmatrix} -3 \\ \sqrt{3} \end{pmatrix} \quad (14)$$

The two atoms A and B in same the unit cell are connected by a vector

$$\delta_1 = (1, 0) . \quad (15)$$

Connecting one atom of species A to its remaining two neighbors in surrounding unit cells is achieved by the

$$\delta_2 = \frac{1}{2} \begin{pmatrix} 1 \\ \sqrt{3} \end{pmatrix}, \quad \delta_3 = \frac{1}{2} \begin{pmatrix} 1 \\ -\sqrt{3} \end{pmatrix} \quad (16)$$

- g) Draw a quick sketch of one unit cell as defined above and its neighboring unit cells. Label the connecting vectors between atoms in the unit cell and its neighbors with $\delta_1, \delta_2,$ and δ_3 .
- h) Set up the Hamiltonian matrix and solve for the dispersion relation as a function of k .
- i) Now switch to the notebook or another computer programme (e.g. Mathematica) and compute the spectrum along the following path in the Brillouin zone:

$$\Gamma = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \rightarrow \mathbf{K}_1 = \frac{2\pi}{3} \begin{pmatrix} 1 \\ 1/\sqrt{3} \end{pmatrix} \rightarrow \mathbf{K}_2 = \frac{2\pi}{3} \begin{pmatrix} 1 \\ -1/\sqrt{3} \end{pmatrix} \rightarrow \Gamma \quad (17)$$

Do you observe any special features along this path?