Solid State Theory

Exercise sheet 5

This exercise sheet will be discussed on Friday, December 21st 2018.
You should hand in your solution of the exercise marked with (★)
in the mail box or email by 16:00 on Thursday December 20th 2018.

Exercise sheets online at www.thp.uni-koeln.de/trebst/Lectures/2018-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

$$\langle m|n\rangle = \delta_{m,n}\,. \tag{1}$$

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

$$H = K + \sum_n V_n\,, \tag{2}$$

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:

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

$$= \epsilon_n|n\rangle + \sum_{m \neq n} V_m|n\rangle\,. \tag{4}$$

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

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

   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

$$|\psi\rangle = \sum_n \phi_n|n\rangle\,. \tag{6}$$

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

$$\sum_n H_{m,n}\phi_n = E\phi_m. \tag{7}$$

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.

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

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

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

2. Use the same *Ansatz* as in the previous exercise for each of the atom types. This will lead you to an eigenvalue problem that results in the dispersion relation for the diatomic tight binding chain

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

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?

3 Peierl's instability

We now consider a chain of atoms that are all of equal type but with alternating short and long bonds between atoms. This results in a modified hopping element that we write as $(1-\delta)\,t$ and $(1+\delta)\,t$, respectively. Because all atoms are of the same type, we can safely set their on-site energies to 0, simplifying the calculations a little. The unit cell continues to contain two atoms due to the unequal hopping strengths.

1. Proceed as in the previous exercise to find the dispersion relation

$$E_\pm(k) = \pm|2t|\sqrt{\delta^2 + (1-\delta^2)\cos^2{(ka/2)}}\,. \tag{11}$$

2. We now assume that the lowest band is completely filled. We now study how the energy of the system depends on δ. In the limit of a very long chain, the energy is given as

$$E_{\text{lower}} = 2L \int \frac{\mathrm{d}k}{2\pi} E(k)\,. \tag{12}$$

   This is an elliptic integral and is as such not easily solved analytically. One approach is to use a numerical solver and calculate the integral for all desired values of δ. Another option is to seek an approximate solution:

   Right at the boundary of the Brillouin zone, the cosine does not contribute and the energy of the lower band is lowered by $-|2t\delta|$. Moving away, once $\pi - ka$ is of the order of δ, the cosine begins to dominate. To estimate the effect of a finite δ, approximate the cosine to first order and calculate ΔE, the difference in energy between the undistorted, i.e. $\delta = 0$, and the distorted chain. Integrate ΔE from $k = -(\pi/2 - \delta)$ to some cutoff c, which we will leave unspecified. Show that the result scales as $\Delta E \propto \delta^2 \log \delta$.

3. Finally, we know from Hooke's law that the energy needed to compress or stretch a spring slightly is proportional to δ^2. What does that imply happens for small values of δ in a system with a fully filled lower band?

This effect is known as Peierl's instability or Peierl's distortion and has been observed in many compounds. One example are materials made up of weakly coupled molecular chains, where the quasi one-dimensional nature allows this distortion to happen. If you are interested, a very accessible article by Robert Thorne that appeared in Physics Today shows some of the actual lattice structures underlying materials where this effect has been observed.