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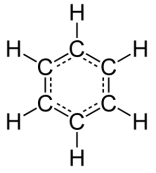
http://ctcm.kfkl.cz/srfp2020

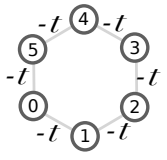
Seminar on problem solving in physics NFPL087, Tue 15:00

Problem Sheet 4

1 **Benzene as a tight-binding ring**

A simple model of benzene (C_6H_6, left scheme in the figure) contains six orbitals $\{|i\rangle, i = 0, \dots 5\}$, among which the electrons can tunnel. In this problem, we first solve the quantum mechanical problem for a single electron. We will include the many-electron aspects at the end. Let us denote the tunneling amplitude to the nearest neighboring orbital by $-t$ and disregard tunneling to more remote orbitals. E_0 denotes the energy of each orbital. Finally, we assume that the electron's spin leads only to a straightforward twofold degeneracy, which we do not consider when writing the Hamiltonian.





Thus motivated, the Hamiltonian describing the electron on a 6 orbital ring reads

$$\hat{H} = -t\Big[|0\rangle\langle 1| + |1\rangle\langle 2| + |2\rangle\langle 3| + |3\rangle\langle 4| + |4\rangle\langle 5| + |5\rangle\langle 0| + \\ + |1\rangle\langle 0| + |2\rangle\langle 1| + |3\rangle\langle 2| + |4\rangle\langle 3| + |5\rangle\langle 4| + |0\rangle\langle 5|\Big] + \\ + E_0\Big[|1\rangle\langle 1| + |2\rangle\langle 2| + |3\rangle\langle 3| + |4\rangle\langle 4| + |5\rangle\langle 5| + |0\rangle\langle 0|\Big]. \quad (1)$$

Notice that the parameters t, E_0 are position-independent due to the symmetry. The figure on the right depicts the ring schematically. In the next steps, explore the properties of the Hamiltonian.

(a) Write down a 6×6 matrix of the Hamiltonian, *i.e.* $H_{ij} = \langle i|\hat{H}|j\rangle$!

(b) Introduce a new basis $|i'\rangle$, given by the prescription

$$|0'\rangle = |1\rangle,\ |1'\rangle = |2\rangle,\ |2'\rangle = |3\rangle,\ |3'\rangle = |4\rangle,\ |4'\rangle = |5\rangle,\ |5'\rangle = |0\rangle. \quad (2)$$

What physical operation does it reflect? Give the Hamiltonian matrix in the new basis, *i.e.* $\langle i'|\hat{H}|j'\rangle$.

(c) In the original basis $\{|i\rangle\}$ we express 6 state vectors

$$\phi_K = \frac{1}{\sqrt{6}}\left(e^{-\mathrm{i}K\frac{2\pi}{6}0},\ e^{-\mathrm{i}K\frac{2\pi}{6}1},\ e^{-\mathrm{i}K\frac{2\pi}{6}2},\ e^{-\mathrm{i}K\frac{2\pi}{6}3},\ e^{-\mathrm{i}K\frac{2\pi}{6}4},\ e^{-\mathrm{i}K\frac{2\pi}{6}5}\right)^{\mathrm{T}}, \quad (3)$$

where the index K has the following values $K = -2, -1, 0, 1, 2, 3$. These vectors are column matrices; T denotes matrix transposition. Show, that they are normalized!

(d) By a direct calculation verify, that all these 6 vectors ϕ_k are eigenvectors of the matrix H_{ij}, with eigenenergies $E_K = E_0 - 2t\cos(\frac{2\pi K}{6})$.

Hint: Perhaps the fastest way is to consider a general integer-valued k. The identity $e^{-\mathrm{i}K\frac{2\pi}{6}6} = 1$ is useful, as it leads to formulae $e^{-\mathrm{i}K\frac{2\pi}{6}5} = e^{+\mathrm{i}K\frac{2\pi}{6}1}$ and similar ones.

(e) Draw the spectrum of the Hamiltonian: let the ordinate denote $(E_K - E_0)/(2t)$ and the coordinate be K. Is the spectrum degenerate?

(f) The eigenvectors of the two non-degenerate levels have a simple form (show!).

(g) This calculation can actually capture many properties of benzene (see *The Feynman Lectures on Physics (Quantum Mechanics)*). It is now important to realize that the molecule has many electrons. It can be shown (see below) that only six electrons need to be taken into our model, the remaining electrons occupy deeper energy levels. Disregarding electron-electron interaction, use Pauly principle (*Aufbau* principle, or Fermi-Dirac statistics at zero temperature) and show, which of the 6 levels of the ring will be occupied (include spin degeneracy!).

(h) Explain the concept of carbon sp^2 hybridization (important for benzene, but also graphene and graphite) and justify the simple ring model with a single orbital per site of this problem.

2 Particle on a ring: onset of a band structure

The results of the previous problem can be generalized easily to a ring with arbitrary N sites.

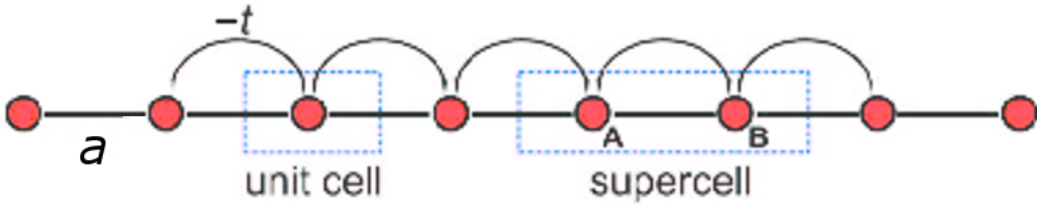
(a) Write down a formula for eigen-energies E_K, valid for any N. Which quantum numbers K are valid?

(b) We proceed to the limit of an extended system (a "thermodynamic limit", $N \to \infty$). It is advantageous to introduce a wavenumber $k = K2\pi/N$. What are the allowed values of k in the thermodynamic limit?

(c) Express the spectrum $E(k)$ and plot a graph of $E(k)$.

(d) How is Bloch's theorem expressed in this simple problem?

3 Linear chain using Bloch formalism



We consider a linear chain of atoms represented by single orbitals, as shown in the figure. The distance between atoms is a, the tunneling amplitude between nearest neighbors is $-t$ and we disregard the overlap between neighboring orbitals. It is well known that the electronic states form a cosine band (*Ashcroft & Mermin, Chap. 10*, see also Problem 2). In this problem you will rederive this simple result.

The Hamiltonian reads

$$\hat{H} = -t \sum_{n=1}^{N} \Big[|n\rangle\langle n+1| \; + \; |n+1\rangle\langle n| \Big]. \tag{4}$$

In this problem, we will calculate the band using the Bloch theorem. The smallest unit cell has a single orbital (atom). We will adopt periodic boundary conditions, namely, that the chain has total N sites; the site $N+1$ is identical to the site 1, *i.e.* the chain is a ring. Rederive the familiar cosine band in the following steps.

(a) Introduce the Bloch states $|k\rangle$ via the relation

$$|n\rangle = \frac{1}{\sqrt{N}} \sum_k e^{-\mathrm{i}kna} |k\rangle, \quad \text{where } k \in \left\langle -\frac{\pi}{a}, \frac{\pi}{a} \right\rangle . \tag{5}$$

The periodic boundary condition $|1\rangle = |N+1\rangle$ imposes a constraint on the allowed values of k inside the interval $\langle -\frac{\pi}{a}, \frac{\pi}{a} \rangle$. You can obtain the constraint in the following way: Use Eq. (5) on the left and right hand sides of the condition $|1\rangle = |N+1\rangle$. Because $|k\rangle$ are linearly independent, it holds that $e^{-\mathrm{i}kNa} = 1$. Write the allowed values of k! *Optionally,* you can convince yourself that the number of Bloch states is the same as the number of sites N in the ring.[1]

(b) Derive the formula $\frac{1}{N} \sum_n e^{-\mathrm{i}na(k-k')} = \delta_{kk'}$. Hint: geometric series.

(c) Insert the Eq. (5) in the Hamiltonian and simplify the result using the formula $\frac{1}{N} \sum_n e^{-\mathrm{i}na(k-k')} = \delta_{kk'}$, where on the right side there is the Kronecker delta.

(d) Convince yourself, that the Hamiltonian is diagonal in $|k\rangle$, namely, $\hat{H} = \sum_k \varepsilon(k) |k\rangle\langle k|$.

[1] In fact, Eq. (5) is just a discrete Fourier transform.