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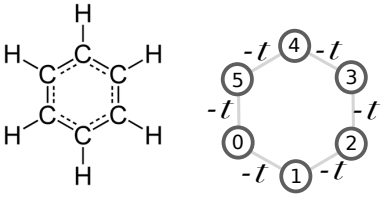
Seminar on problem solving in physics NFPL087, Wed 10:40, F052

Problem Sheet 3

1 **Benzene and a linear tight-binding chain**

A simple model of benzene (C_6H_6, left 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 Electronic and crystalline structure of graphene

Graphene, a carbon allotrope, is a two-dimensional material in which the carbon atoms are arranged in a honeycomb pattern.

(a) Familiarize yourself with the crystalline structure of graphene. Discuss the symmetry properties of graphene: inversion symmetry, reflection planes, *etc.*

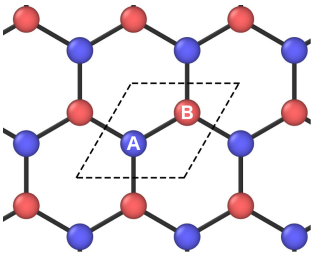
(b) Suggest a unit cell of graphene. What is the minimum number of atoms in a unit cell? Write the direct and reciprocal lattice vectors!

(c) Familiarize yourself with the concept of sp^2 hybridization and π bonds.

(d) Motivated by the intuitive picture of the sp^2 hybridization, we introduce a simple model of the electronic structure of graphene, which contains a single orbital (the p_z orbital) per site and does not involve electron-electron interactions *explicitly*. Thus, the basis functions can be labelled as $|\mathbf{R}, l\rangle$, where $\mathbf{R}$ labels the unit cell (vector from a direct lattice) and $l = A, B$ is the sublattice index; see figure below. Furthermore, we assume a simple tight-binding picture, in which the electron can tunnel to the nearest neighboring site only, and we disregard overlaps of the basis functions, *i.e* $\langle \mathbf{R}, l|\mathbf{R}', l'\rangle = \delta_{\mathbf{R}\mathbf{R}'}\delta_{ll'}$. The Hamiltonian reads

$$\hat{H} = -t \sum_{\langle \mathbf{R},l;\mathbf{R}',l'\rangle} \left[|\mathbf{R}, l\rangle\langle \mathbf{R}', l'| + |\mathbf{R}', l'\rangle\langle \mathbf{R}, l| \right], \tag{4}$$

where the sum runs over pairs of nearest neighbors. Use Bloch's theorem to find the energy eigenvalues, $\varepsilon_b(\mathbf{k})$, where b is a band index and $\mathbf{k}$ runs in the first Brillouin zone!



The picture on the left shows part of a hexagonal lattice, divided into two sublattices, A (blue) and B (red). Notice that every atom has three nearest neighbors from the other sublattice (one in the same unit cell and two in the neighboring cells). Lattices in which every atom binds only to the atoms of the other sublattice are called bipartite. The dashed line in the picture encloses a unit cell.

(e) Analyze the properties of $\varepsilon_b(\mathbf{k})$! Describe the properties of the spectrum (symmetry in the reciprocal space, particle-hole symmetry, Fermi surface). Find a linear approximation to the spectrum near the Fermi energy and comment in its form! What other (quasi-)particles have the same dispersion relation?

Literature: tight-binding approximation: Ashcroft & Mermin,
band-structure: A. H. Castro Neto, *et al.* The electronic properties of graphene, Rev. Mod. Phys. 81(1), 109 (2009),
original work: P. R. Wallace, The band theory of graphite, Phys. Rev. 71 (1947), 622–34