Problem set: From Molecular Orbitals to Bloch states

4.1. The electron-problem for the benzene molecule (tight binding model)

A benzene molecule consists of a ring of six carbon atoms each accompanied by one hydrogen atom, whereas all atoms are arranged in one plane (as depicted in the left figure below). We consider here only the electronic problem which is separated from the motion of the nuclei. Therefore we assume all the atoms to be in equilibrium position. The carbon atoms are in the corners of a regular hexagon, given by the coordinates $R_i$ ($i = 1, ..., 6$).

Each C-atom is bonded to its two neighboring C-atoms via $\sigma$-bonds, which are built of hybridized $2s$, $2p_x$ and $2p_y$ orbitals from the two C-atoms. Furthermore each C-atom is bonded to an H-atom by the overlap of another hybridized C-orbital and an 1s orbital of the H-atom.

This means that per C-atom remains one $2p_z$ orbital, occupied with one electron. These orbitals are oriented perpendicular to the plane determined by the atoms (see the figure on the right).

The wave functions $\phi_i$ of these orbitals are localized at the positions of the carbon atom $i$ ($i = 1, ..., 6$) so that we can write

$$\phi_i(r) = \phi(r - R_i),$$

where $\phi(r)$ is the $\pi$ orbital wavefunction.

Assume that the wave function for the benzene molecular orbitals is given by a linear combination of these $2p_z$-wave functions (this principle is called LCAO, Linear Combination of Atomic Orbitals):

$$\Psi = \sum_{i=1}^{6} c_i \phi_i.$$
The single particle Hamiltonian in the $\pi$ orbital base is determined by the on-site energy $\varepsilon$ and the nearest neighbor interaction $t$, so that the Hamiltonian can be written as follows

$$H_{i,j} = \varepsilon \delta_{i,j} - t \delta_{i,j+1} - t \delta_{i,j-1}.$$ 

The Kronecker $\delta$'s should be taken within the periodic boundary conditions: $\delta_{6,0} = \delta_{7,1} = 1$, this means that the ring is closed and the electrons can jump from C-atom 1 to C-atom 6 (and vice versa).

(a) Find the coefficients $c_i$ in $\Psi$ using the rotational symmetry of the molecule. First show that the Hamiltonian commutes with an operator $C$ describing a rotation about $\frac{\pi}{3}$ and use the fact that the wave functions $\Psi$ are also eigenfunctions of the rotation operator $C$.

(b) Solve the eigenvalue/eigenvector problem using the $c_i$ from above and discuss the wave functions with respect to symmetry and nodes.

**Hint:** Write the Hamiltonian as a matrix and rewrite the Schrödinger equation in matrix representation.

**Note:** You can also view the problem as a tight binding linear chain of $N = 6$ atoms with periodic boundary conditions. Use Bloch theorem to diagonalize $H$ analytically.

(c) Using a plotting program draw the molecular orbitals for the different eigenenergies knowing the formal expression of the $\pi$ orbital (in polar coordinates):

$$\phi(r) = \phi(r, \theta, \varphi) \propto r \cdot \exp(-\zeta r) \cos \theta,$$

where $\zeta = 16.18$ nm$^{-1}$.

Note that the eigenvalues $\varepsilon \pm t$ are degenerate, how will you choose the eigenfunctions in that case?

You should finally be able to reproduce the plot in the figure below on the right.
4.2. The Kronig-Penney model

The Kronig-Penney model (the Dirac comb) is a simple one-dimensional model to understand the electronic band structure of a crystalline solid. A periodic 1d crystal potential (with the lattice constant $a$) is approximated by a series of $\delta$-functions:

$$V(x) = V_0 \sum_{n=-\infty}^{+\infty} \delta(x - na), \quad V_0 > 0.$$  \hspace{1cm} (1)

As the Hamiltonian $H = p^2/(2m) + V(x)$ is periodic (i.e. $H$ is invariant under translations of multiples of $a$) all physical properties have to be invariant under these translations, too. This is especially relevant for the electron density:

$$|\Psi(x + a)|^2 = |\Psi(x)|^2.$$

As a consequence,

$$\Psi(x + a) = \exp(ia) \cdot \Psi(x).$$

The free parameter $q$ denotes the possible eigenstates (Bloch theorem):

$$\Psi_q(x + a) = \exp(ia) \cdot \Psi_q(x).$$

(a) Show that the solutions of the Schrödinger equation satisfy the Kronig-Penney equation

$$\cos(qa) = \cos(\alpha_q) + P \frac{\sin(\alpha_q)}{\alpha_q}$$

with $P = \frac{V_0 ma}{\hbar}$ and $\alpha_q^2 = \frac{2mE_q}{\hbar^2} a^2$.

Hint: Solve the Schrödinger equation in regions with $V(x) = 0$ using the ansatz

$$\Psi_q(x) = A \exp(ikx) + B \exp(-ikx) \quad \text{with} \quad k^2 = \frac{2mE_q}{\hbar^2}.$$

Use the Bloch theorem, the continuity of $\Psi_q(x)$ and the discontinuity of $\partial_x \Psi_q(x)$ at $x = na$ to determine the coefficients $A$ and $B$.

(b) Plot $f(\alpha_q) = \cos(\alpha_q) + P \frac{\sin(\alpha_q)}{\alpha_q}$ as a function of $\alpha_q$. Show that for $V_0 \neq 0$, the Kronig-Penney equation $\cos(qa) = f(\alpha_q)$ leads to forbidden energy regions (energy gaps).

(c) The original version of the Kronig-Penney model was formulated for a periodic potential of rectangular scatterers. Repeat the previous calculations by replacing the delta distributions in (1) with the following step function
\[
\begin{align*}
  s(x; b) &= \begin{cases} 
    \frac{1}{b} & \text{if } |x| < \frac{b}{2} \\
    0 & \text{elsewhere}
  \end{cases} \\
  \text{so that the potential } V(x) \text{ now reads} \\
  V(x) &= V_0 \sum_{n=-\infty}^{+\infty} s(x - na; b), \quad \lambda > 0, \ b < a.
\end{align*}
\]