

## Assignments to Condensed Matter Theory I

### Sheet 5

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 Mon 29.05 (h 10.15)

sheet online: <http://www-MCG.uni-R.de/teaching/>

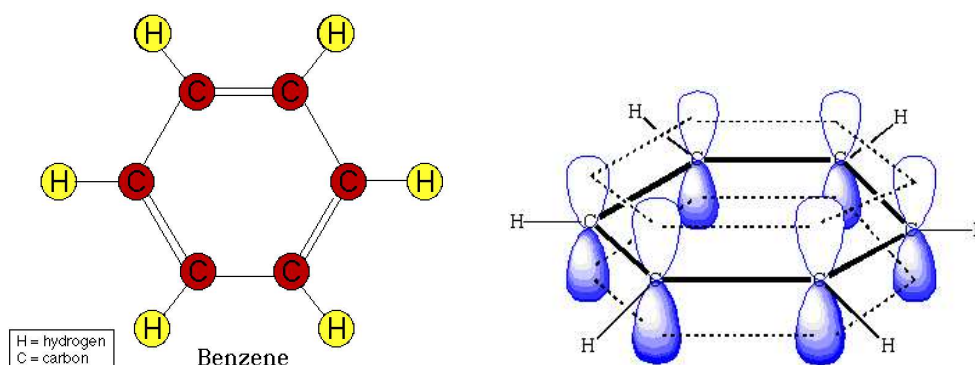
### Problem set: From Molecular Orbitals to Bloch states

#### 5.1. 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  $\mathbf{R}_i$  ( $i = 1, \dots, 6$ ).

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  $i$  ( $i = 1, \dots, 6$ ) so that we can write

$$\langle \mathbf{r} | i \rangle = \phi_i(\mathbf{r}) = \phi(\mathbf{r} - \mathbf{R}_i),$$

where  $\phi(\mathbf{r})$  is the  $2p_z$  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):

$$\Psi = \sum_{i=1}^6 k_i \phi_i.$$

The single particle Hamiltonian in the  $2p_z$  orbital basis can be given in good approximation by the on-site energy  $E_0$  and the nearest neighbor hopping  $t$ . In second quantization, it follows

$$H = \sum_{i=1}^6 [E_0 c_i^\dagger c_i - t(c_i^\dagger c_{i+1} + c_{i+1}^\dagger c_i)] \quad (1)$$

where the operator  $c_i^\dagger$  creates a  $2p_z$  electron on the carbon atom in position  $i$  and we neglect at this level the spin of the electron. The index  $i$  should be considered with periodic boundary conditions:  $i + 6 = i$ , this means that the ring is closed and the electrons can jump from C-atom 1 to C-atom 6 (and vice versa).

- (a) Prove the identity  $[H, L] = 0$ , with  $L = \sum_{\ell=1}^6 \ell \tilde{c}_\ell^\dagger \tilde{c}_\ell$  where

$$\tilde{c}_\ell^\dagger = \frac{1}{\sqrt{6}} \sum_{i=1}^6 e^{-i\frac{2\pi}{6}\ell i} c_i^\dagger$$

- (b) Using the relation just proved in the previous point find the eigenvalue and eigenvectors for the Hamiltonian (1).

**Hint:** Remember that commuting operators share a complete set of common eigenstates.

- (c) Extend the results obtained in point (a) and (b) to the general case of a linear chain of  $N$  atoms with periodic boundary conditions.
- (d) Plot the energy spectrum vs.  $N$  (see figure below) and verify that the density of energy levels can be written as:

$$DOS_\eta^{(N)}(E) = \frac{1}{N} \sum_{l=1}^N \delta_\eta(E - E_0 + 2t \cos(2\pi l/N))$$

where

$$\delta_\eta(E) = \frac{1}{\pi} \frac{\eta}{E^2 + \eta^2} \quad \text{for } \eta \ll \left(\frac{2\pi}{N}\right)^2 t$$

- (e) **[Kür]** Show numerically that in the limit  $N \rightarrow \infty$

$$\lim_{\eta \rightarrow 0^+} \lim_{N \rightarrow \infty} DOS_\eta^{(N)}(E) = \frac{1}{\pi} \frac{1}{\sqrt{(2t)^2 - E^2}}$$

numerically, but –even better– analytically.

- (f) **[Kür]** Can you extend the previous results (a-e) to the case of open boundary conditions? What is similar, what is changing?

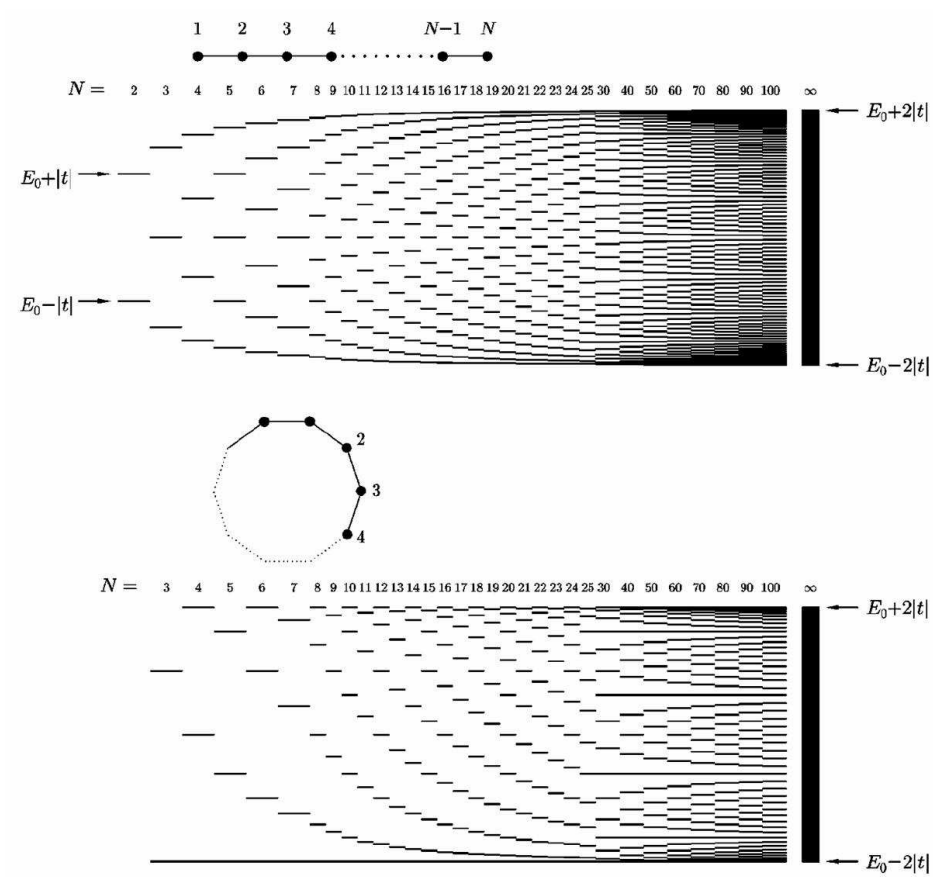


Figure 1: Example of the plot of the energy levels. You should be able to reproduce it from your calculations.