

Physics 520 – Graduate Quantum Mechanics I

Homework VII, due 2:00 p.m. October 24, 2007

This homework has three pages

1. Reading

G&Y Chap. 2.5(d)-(f), Chap 3.1.

2. Ethylene

Consider the molecule CH_2CH_2 . The doubly ionized core appears as in Fig. 1(a). An electron can be situated at either of the carbon sites.

(a) Write down the Hamiltonian for the two electrons, assuming no electron-electron interactions in two cases. Let the on-site, localized energy be characterized by E_0 and the hopping, or delocalization energy be characterized by A . Provide two matrix representations of the Hamiltonian: (i) a site-localized basis; (ii) symmetric and anti-symmetric delocalized eigenstates.

(b) Obtain the position representation formally and sketch spatial representations of the basis wavefunctions for both cases.

(c) What is the parity of the eigenstates of this Hamiltonian? When does one obtain definite parity eigenstates? Be specific.

(d) Calculate the delocalization energy, i.e., the energy relative to the localized case, in terms of A .

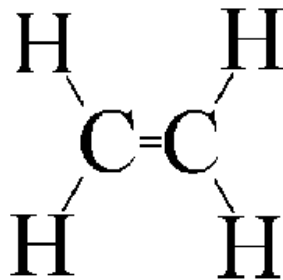
3. Benzene

Consider the molecule benzene, an essential ingredient in many industrial processes, shown in Fig. 1(b). The neutral molecule has 6 electrons distributed in π -orbitals on the six carbon sites. Let us define the Hamiltonian by

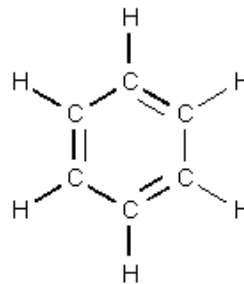
$$\hat{H}|\phi_n\rangle = E_0|\phi_n\rangle - A(|\phi_{n+1}\rangle + |\phi_{n-1}\rangle), \quad (1)$$

so that it couples nearest neighbors. We can further define a unitary “hopping” operator \hat{U}_p which acts on localized states $|\phi_n\rangle$ as

$$\begin{aligned} \hat{U}_p|\phi_n\rangle &= |\phi_{n+1}\rangle, \\ \hat{U}_p^\dagger|\phi_n\rangle &= |\phi_{n-1}\rangle. \end{aligned} \quad (2)$$



(a)



(b)

Figure 1: Chemical formulae of (a) ethylene and (b) benzene.

The operator \hat{U}_p can also be thought of as a discrete translation operator under periodic boundary conditions.

- (a) What is the dimensionality of the Hilbert space for this problem?
- (b) Show that the Hamiltonian commutes with \hat{U}_p .
- (c) Find the eigenvalues of \hat{U}_p in terms of an integer s . *Hint: How many times do you have to apply the unitary transformation to obtain the identity?*
- (d) Find the the eigenkets $|\chi_s\rangle$ of \hat{U}_p in the $\{|\phi_n\rangle\}$ basis. Why is $\{|\chi_s\rangle\}$ a simultaneous basis of \hat{H} ? Remark: In the limit in which the number of sites tends to infinity, the localized states $|\phi_n\rangle$ are called *Wannier states* and the delocalized states $|\chi_s\rangle$ are called *Bloch waves*.
- (e) Using the information you obtained about the eigenstates and eigenvalues of the discrete translation operator \hat{U}_p , find the eigenstates and eigenvalues of the Hamiltonian.
- (f) Determine the total energy of the six non-interacting electrons distributed on benzene. Recall that two electrons can occupy each energy level, since they are spin-1/2.
- (g) Finally, sketch the position representation of the energy eigenstates. Comment on delocalization or lack thereof, and compare to ethylene.

4. Sliced Benzene

Imagine we took the benzene molecule and cut the connection between two sites, say 1 and 6. Let's explore how the properties of the electron wavefunctions would change. The Hamiltonian for the N -site generalization of this idea is

$$\begin{aligned}\hat{H}|\phi_n\rangle &= E_0|\phi_n\rangle - A(|\phi_{n-1}\rangle + |\phi_{n+1}\rangle) \text{ for all } n \neq 1, N, \\ \hat{H}|\phi_1\rangle &= E_0|\phi_1\rangle - A|\phi_2\rangle, \\ \hat{H}|\phi_N\rangle &= E_0|\phi_N\rangle - A|\phi_{N-1}\rangle,\end{aligned}\tag{3}$$

where A is the positive real hopping energy.

- (a) Find the matrix representation of \hat{H} in the $\{|\phi_n\rangle\}$ basis.
- (b) The most general case for an electron in this system is

$$|\chi\rangle = \sum_{n=1}^N c_n |\phi_n\rangle.\tag{4}$$

To adapt the method used in the case of benzene, we define two fictitious states $|\phi_0\rangle$ and $|\phi_{N+1}\rangle$ and two components $c_0 = c_{N+1} = 0$, which allows one to rewrite $|\chi\rangle$ as

$$|\chi\rangle = \sum_{n=0}^{N+1} c_n |\phi_n\rangle.\tag{5}$$

Prove that

$$\hat{H}|\chi\rangle = E_0|\chi\rangle - A \sum_{n=1}^N (c_{n-1} + c_{n+1})|\phi_n\rangle.\tag{6}$$

- (c) Inspired by the method used in benzene, one seeks c_n of form

$$c_n = \frac{c}{2i} (e^{in\delta} - e^{-in\delta})\tag{7}$$

which satisfies $c_0 = 0$. Show that one must choose

$$\delta = \frac{\pi s}{N + 1}, \quad (8)$$

where $s \in \{1, \dots, N\}$ in order to also have $c_{N+1} = 0$.

(d) Show that the eigenvalues of \hat{H} are given by

$$E_s = E_0 - 2A \cos \delta. \quad (9)$$

and find the corresponding eigenvectors $|\chi_s\rangle$. Show that the normalization constant is $\sqrt{2/(N + 1)}$.

(e) Obtain the position representation formally and sketch spatial representations of $|\chi_s\rangle$ for $N = 6$. Compare and contrast with benzene. Explain how and why the wavefunctions are modified by “slicing” the molecule.

5. Current Research: Nanoengineering with Benzene

Read the article D. M. Cardamone, C. A. Stafford, and S. Mazumdar, “Controlling Quantum Transport through a Single Molecule,” *Nano Letters* **6** 2422 (2006). You can download this article from <http://www.physics.arizona.edu/~stafford/nano2.html>, as well as popular science descriptions of this result.

(a) Explain the basic principle behind this device.

(b) What calculational techniques and/or basic quantum mechanical features do you recognize from the article? What techniques and aspects are unfamiliar?

(c) Can you suggest ways of improving on this calculation? What features of this problem have the authors not considered, if any?

Remark: by the end of the year-long course you will have developed a sufficient knowledge of quantum mechanics to follow this article in nearly every detail.

Note: All responses to this question must be typed in single-spaced, 12 point, standard fonts (Times New Roman, Arial, or Courier are ok). No credit will be given for responses not provided in this standard format.