University of California at San Diego – Department of Physics – TA: Shauna Kravec

Quantum Mechanics A (Physics 212A) Fall 2018
Worksheet 3 – Solutions

Problems

1. **Benzene**

   Benzene is a nearly planar hydrocarbon molecule pictured below:

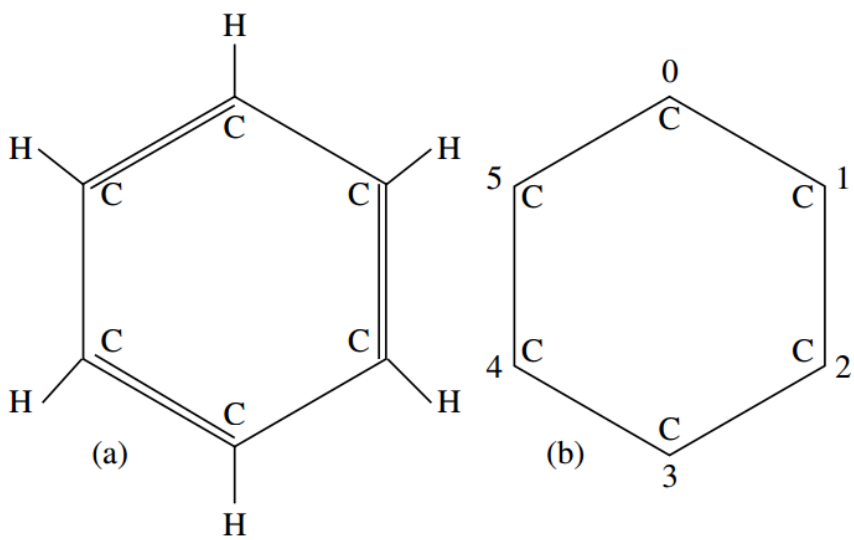


Figure 1: The σ-bond skeleton of Benzene. The average bond length is $\ell = 1.4$ Angstroms

There are 6 π-electrons to participate in bonding. What states can they occupy? This problem will explore this question with two simplified models.

(a) What are the energies and eigenstates for a free particle on a ring? Assume the particle is mass M and the ring is radius R.

$E_m = \frac{\hbar^2 m^2}{2MR^2}$ for $m \in \mathbb{Z}$ and $\psi_m \propto e^{\mathbf{i}m\phi}$ where ϕ is the angular coordinate. This follows from the Hamiltonian being L_z^2

(b) Suppose the π-electrons occupy eigenstates of this form. Using the Pauli exclusion principle, what states do the 6 electrons occupy?

The first two electrons (remember it's two because of the spin) occupy the $m = 0$ level. The next 4 electrons should be paired in $m = \pm 1$.

(c) Given the average bond length ℓ, what would you estimate to be the effective radius of the molecule?

There are 6 bonds. So the circumference is $C = 6 * 1.40\mathbf{A} = 8.4\mathbf{A}$ which is related to the radius by $C = 2\pi R \implies R = 1.34\mathbf{A}$ or .134nm

(d) What is the energy of the electron in the highest occupied state? This is called the HOMO for 'highest occupied molecular orbital'.

From $E_m = \frac{\hbar^2 m^2}{2MR^2}$ I got $E_1 = 2.12\text{eV}$

(e) What is the energy of the lowest unoccupied state? This is called the LUMO for 'lowest unoccupied molecular orbital'.

$E_2 = 8.49\text{eV}$

(f) Suppose a stray photon came by an knocked an electron to the next highest orbital. What wavelength would that photon have to be?

The energy would be $E_{\text{photon}} = E_2 - E_1 = 6.37\text{eV}$

So by $E = \frac{hc}{\lambda}$ we find $\lambda = 194.6\text{nm}$

Benzene actually has an absorption maximum at $\lambda = 256\text{nm}$ so experimentally the HOMO-LUMO gap is at about $\Delta E \approx 4.84\text{eV}$.[1] Can we do better?

Consider a tight-binding model of the π-electrons. There are 6 sites they can occupy so our Hilbert space is $\mathcal{H} = \text{span}\{|n\rangle\}$ for $n = \{0, 1, \cdots, 5\}$

Suppose there's some localization energy E_0 and some delocalization energy β between neighbors.

(a) Write a Hamiltonian for this simplified system.

$H = \sum_n E_0 |n\rangle\langle n| - \beta(|n+1\rangle\langle n| + |n\rangle\langle n+1|)$ where $n = 6 \equiv 0$

(b) Recall the translation operator $T = \sum_n |n+1\rangle\langle n|$. Rewrite the Hamiltonian with this operator and $\mathbb{1}$, replacing all sums.

$H = E_0 \mathbb{1} - \beta(T + T^\dagger)$

(c) Show that $[H, T] = 0$. This is a *symmetry* of our model coming from the symmetry of benzene. This implies we can simultaneously diagonalize T and H. Do so and compute the energies.

From our previous discussion of clock-shift operators the eigenstates of T are $|j\rangle = \sum_n e^{\frac{2\pi \mathbf{i} jn}{N}} |n\rangle$ where $j = \{0, 1, \cdots, N-1\}$ and $N = 6$ for our case

This gives eigenvalues $\lambda_j = e^{\frac{2\pi \mathbf{i} j}{6}}$ thus $E_j = E_0 - 2\beta\cos(\frac{2\pi j}{6})$

(d) Suppose the π-electrons occupy eigenstates of this form. Using the Pauli exclusion principle, what states do the 6 electrons occupy?

Two occupy $j = 0$ which has lowest energy of $E_0 - 2\beta$. The remaining four occupy $j = 1$ and $j = 5$ which are degenerate at $E_1 = E_0 - \beta$

(e) Calculate the HOMO-LUMO gap in terms of β.

E_1 is the HOMO energy and $E_2 = E_0 + \beta$ is the LUMO energy giving $\Delta E = 2\beta$

(f) A first principles formula[2] for β in hydrocarbons is $\beta = .63\frac{\hbar^2}{m_e \ell^2}$ where m_e is the electron mass and ℓ is the bond length. Calculate β, ΔE, and the predicted absorption peak.

[1] Chemistry point, for benzene this actually is the $\pi - \pi^*$ gap but not in all planar organics. Polyenes and some heterocyclic organic compounds are counter examples

[2] This is really just dimensional analysis aside from the order 1 proportionality constant.

$\beta = 2.45\text{eV},\ \Delta E = 4.9\text{eV},\ \lambda = 253\text{nm}$

2. **Linear Polyenes**

   Now that we've built the basic machinery, let's study a different molecular geometry.

   Polyenes are molecules with chains of alternating single/double carbon bonds. For example, this cyanine dyes:

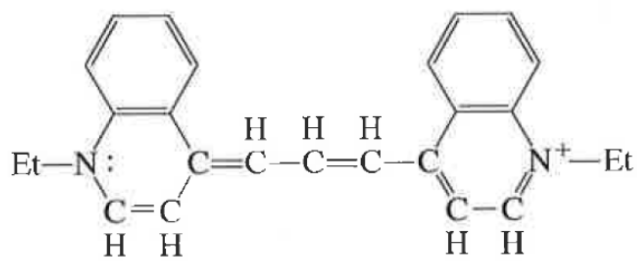
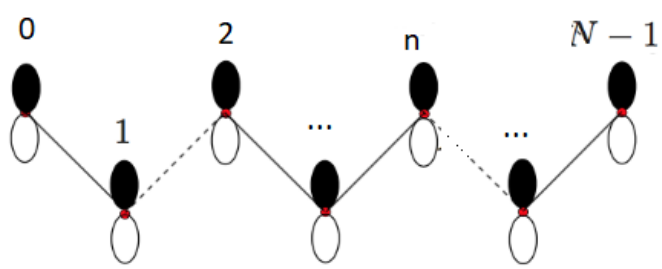


Figure 2: The σ-bond skeleton of cryptocyanine. The average bond length is still $\ell = 1.4$ Angstroms but with more variation between bonds. The relevant hopping parameter is $\beta = .8\frac{\hbar^2}{m_e \ell^2} \approx 3.1\text{eV}$

   Like before, we'll focus exclusively on the π-electrons that compose the carbon bonds. We can then model this as a finite length chain composed of N sites.



   The difference between this and the cyclic chain is that we no longer have translation symmetry; the chain simply ends.

   A trick for dealing with this is to introduce a fictious site, which connects the two ends, and then impose the boundary condition that the wavefunction must vanish there.

   (a) Write the hopping Hamiltonian, as before, but including this fictional site. Use the form of the translation generators T.
   $H = \sum_{n=0}^{N} E_0 |n\rangle\langle n| - \beta(|n+1\rangle\langle n| + |n\rangle\langle n+1|)$
   Where $|N\rangle$ is the wavefunction at the fictional site and $|N+1\rangle \equiv |0\rangle$
   Using $T = \sum_n |n+1\rangle\langle n|$ and $\mathbb{1} = \sum_n |n\rangle\langle n|$ we have
   $H = E_0 \mathbb{1} - \beta(T + T^\dagger)$

(b) Write the eigenvectors, and eigenvalues, of the operator $T + T^\dagger$ which satisfy the boundary condition.

We'd like to write down the analog of $|j\rangle$. We know that because $T|n\rangle = |n+1\rangle$ we must take a superposition over all $|n\rangle$ to have a chance at making an eigenvector.

Let's write $|j\rangle = \sum_n f(j,n)|n\rangle$ for some function $f(j,n)$; up to a normalization factor.

The vanishing boundary condition implies $f(j,N) = 0 = f(j,-1)$

We're diagonalizing $T + T^\dagger$ and the original/naive $f(j,n)$ was an exponential, it makes sense to guess a trig function.

The function $f(j,n) = \sin(\frac{j\pi}{N+1}(n+1))$ satisfies the boundary condition above where $j \in (1, \cdots, N)$

It remains to be shown that $|j\rangle$ with the above function is an eigenvector of $T+T^\dagger$. Since the action of T is to shift the n label, the eigenvalue equation reduces to checking that ratio is a function independent of n

Consider: $\frac{f(j,n+1)}{f(j,n)} + \frac{f(j,n-1)}{f(j,n)} = 2\cos(\frac{j\pi}{N+1})$ which is independent of n as required

(c) Write down the spectrum of the Hamiltonian as before. Is there any degeneracy like for benzene?

From the above we have: $E_j = E_0 - 2\beta\cos(\frac{j\pi}{N+1})$

Unlike benzene there is no doubly degenerate spectrum

(d) Assume that for N-carbons there are N many π-electrons. What is the HOMO-LUMO gap as function of the system size?

Since the electron has 2 spin states, the highest occupied state has $j = \frac{N}{2}$. The lowest unoccupied state then has to have $j' = j + 1$ as the spectrum is monotonically increasing with j.

Therefore $\Delta E = E_{j=\frac{N}{2}+1} - E_{j=\frac{N}{2}} = 4\beta\sin(\frac{\pi}{2(N+1)})$

(e) The absorption peak for cryptocynanine is $\lambda = 648$nm. How does this compare to the model with $N = 9$ carbons?

For $N = 9$ we have $\lambda_{predicted} = 639$nm