Quantum Mechanics A (Physics 212A) Fall 2016
Worksheet 2 – Solutions

Announcements

- The 212A web site is:

  http://keni.ucsd.edu/f16/ .

  Please check it regularly! It contains relevant course information!

Problems

1. **Interferometry**

   We can consider the path taken of a photon as (approximately) a two-state quantum system spanned by $|u\rangle$, $|d\rangle$ for whether it went up or down respectively.

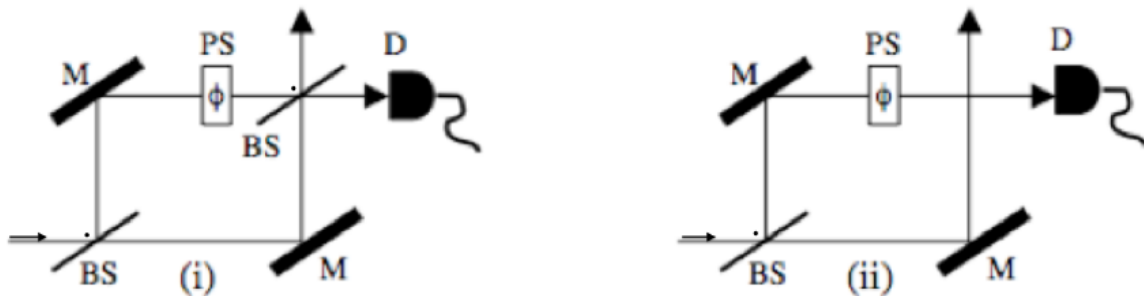   Consider the following two interferometers:

   Figure 1: A balanced Mach-Zender interferometer (i) and another with the final beam splitter removed (ii)

   The elements BS are beam splitters which implement the Hadamard gate on the incoming beam: $H = \frac{1}{\sqrt{2}}[(|u\rangle + |d\rangle)\langle u| + (|u\rangle - |d\rangle)\langle d|]$

   The elements M are mirrors which transform $|\text{In}\rangle \to |\text{Out}\rangle = -|\text{In}\rangle$

   The element PS is a phase shifter which transform $|\text{In}\rangle \to |\text{Out}\rangle = e^{i\phi}|\text{In}\rangle$

   The element D is a detector which measures photons going in.

   For each device, determine the probability for detecting a photon as a function of ϕ.

   Let's do setup (ii) first.

After the first beam splitter the state is $|1\rangle = \frac{1}{\sqrt{2}}(|u\rangle + |d\rangle)$

The pair of mirrors introduces an overall minus sign $|2\rangle = -|1\rangle$ which is irrelevant

The phase shifter then acts on the up travelling beam $|3\rangle = \frac{1}{\sqrt{2}}(e^{i\phi}|u\rangle + |d\rangle)$

But then the only part of the beam entering the detector D is the up component. Therefore $P(\phi) = |\langle u|3\rangle|^2 = \frac{1}{2}$. Pretty boring.

For the true MZ interferometer (i) we apply the Hadamard:

$|4\rangle = H|3\rangle = \frac{1}{2}(e^{i\phi} + 1)|u\rangle + \frac{1}{2}(e^{i\phi} - 1)|d\rangle$

Then again it's measuring 'up' component so $P(\phi) = |\langle u|4\rangle|^2 = \frac{1}{4}|e^{i\phi}+1|^2 = \frac{1}{2}(1+\cos\phi)$

2. **Benzene**

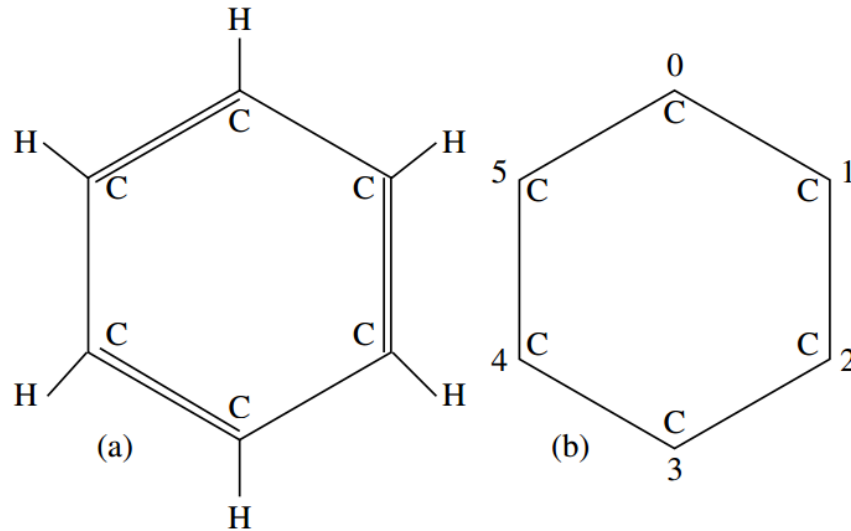   Benzene is a nearly planar hydrocarbon molecule pictured below:

Figure 2: 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 $\psi_m \propto e^{im\phi}$ 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 $E_1 = 2.12$eV

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

$E_2 = 8.49$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 $E_{\text{photon}} = E_2 - E_1 = 6.37$eV

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

Benzene actually has an absorption maximum at $\lambda = 256$nm so experimentally the HOMO-LUMO gap is at about $\Delta E \approx 4.84$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 $|j\rangle = \sum_n e^{\frac{2\pi i j n}{N}}$ where $j = \{0, 1, \cdots, N-1\}$ and $N = 6$ for our case

This gives eigenvalues $\lambda_j = e^{\frac{2\pi i j}{6}}$ 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 $E_1 = E_0 - \beta$

[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

(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 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.

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