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

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

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:

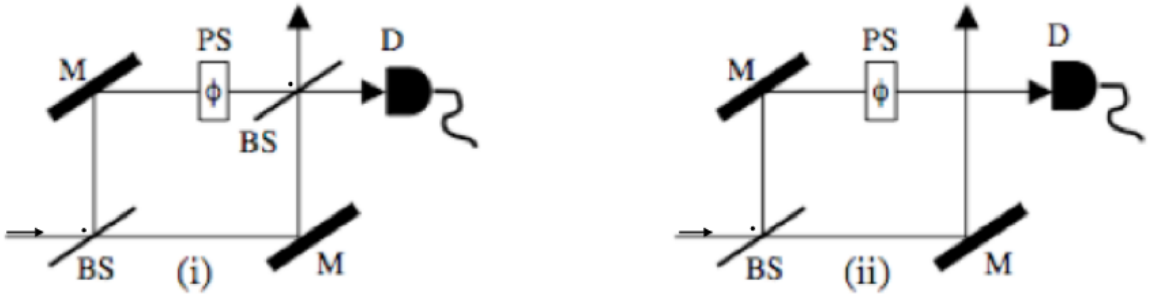

Figure 1: A balanced Mach-Zender interferometer (i) and another with the final beam splitter removed (ii)

   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 $|\text{In}\rangle \to |\text{Out}\rangle = e^{\mathbf{i}\phi}|\text{In}\rangle$

   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.

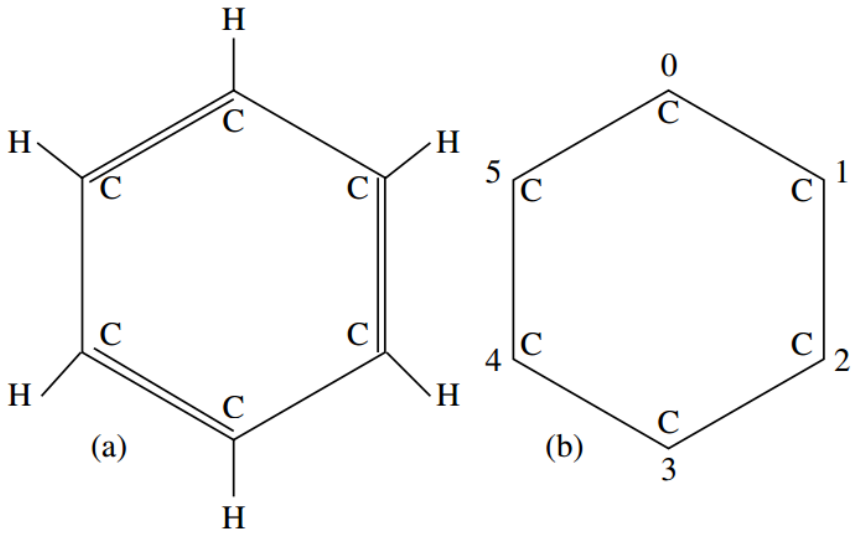

Figure 2: The σ-bond skeleton of Benzene. The average bond length is $\ell = 1.4$ Angstroms

2. **Benzene**

Benzene is a nearly planar hydrocarbon molecule pictured below:

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.

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

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

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

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

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

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 $n = \{0, 1, \cdots, 5\}$

[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

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

(a) Write a Hamiltonian for this simplified system.

(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.

(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.

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

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

(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.