Chemistry 331 **Assignment #4** (due Monday, 26 October, in class)

(ver. 2)

1. **a)** Use the particle-in-a-box model to calculate the ground-state energy of a mole of π electrons in an ethylene molecules (length $L = 0.14$ nm).

b) Repeat part **a** for π electrons in 1,2-butadiene ($L = 0.43$ nm).

[3] **c)** Organic chemists tell us that organic molecules with conjugated π-bonds are stabilized by **delocalization**. Use parts **a** and **b** to give a quantum mechanical explanation of delocalization.

2. Short-chain conjugated molecules, such as 1,2-butadiene, are colorless. But long-chain and polycyclic conjugated molecules are colored. Why? [β-carotene, for example, is yellow-orange, the
[1] color of carrots, and phenolphthalein ions are pink in alkaline solutions.]

3. Solving the Schrodinger differential equation with appropriate boundary conditions gives

$$E_n = \frac{n^2h^2}{8mL^2} \qquad n = 1, 2, 3, \ldots$$

for the energy of particle of mass m in a box of width L. *There's an easier way to get this result*!

a) A particle in a box of width L must have de Broglie wavelengths $\lambda = 2L/n$. Why?

[4] **b)** Give the de Broglie momentum of the particle.

c) Give the de Broglie kinetic energy of the particle.

d) Show the energy of the particle calculated from its de Broglie wavelength agrees with the value $n^2h^2/8mL^2$ calculated from the Schrodinger equation.

4. Many scientists believe that all energies are discrete (not continuous) as a consequence of quantum mechanics. *Mmmm...*

[1] A particle confined within a box of width L becomes a free particle in the limit $L \to \infty$. Show the energies of free particles are continuous ($E \geq 0$, not quantized).

5. The wave equation for a particle of mass m in a box extending from $x = 0$ to $x = L$ is

$$\psi(x) = \sqrt{2/L}\,\sin(n\pi x/L)$$

[3] **a)** Show that $\psi(x)$ is normalized.

b) Show $\psi(x)$ is an eigenfunction of the kinetic energy operator with eigenvalue $n^2h^2/8mL^2$.

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6. Because a wave function can be complex, it can be represented as the sum

[1]
$$\psi = R + iI$$

of real (R) and imaginary (iI) components. Prove $\psi^*\psi$ is always real.

7. The eigenvalues a of quantum mechanical operators $\hat{A}$ must be real. Why?

[1]
$$\hat{A}\psi(x) = a\psi(x)$$

8. For quantum mechanical operators show

$$\int \psi^* \hat{A}\psi \,\mathrm{d}x = \int \psi \hat{A}^* \psi^* \,\mathrm{d}x$$

[2] Operators obeying this relation are called **Hermitian**.

Hints: i) Multiply ψ^* by $\hat{A}\psi$ and integrate. ii) Multiply ψ by $\hat{A}^*\psi^*$ and integrate. iii) Compare the two integrals. (Because ψ is normalized, the integral of $\psi^*\psi$ equals 1).

9. Question 7 shows quantum mechanical operators are Hermitian. For Hermitian operators, more generally, it can be shown that

$$\int \psi_m^* \hat{A}\psi_n \,\mathrm{d}x = \int \psi_n \hat{A}^* \psi_m^* \,\mathrm{d}x$$

So what? As an important consequence, prove the eigenfunctions of quantum mechanical operators are **orthogonal**:

$$\int \psi_m^* \hat{A}\psi_n \,\mathrm{d}x = 0 \qquad \text{if } m \neq n$$

[2] *Hints:* i) Multiply ψ_m^* by $\hat{A}\psi_n = a_n\psi_n$ and integrate. ii) Multiply ψ_n by the complex conjugate of $\hat{A}\psi_m = a_m\psi_m$ and integrate. iii) Compare the two integrals. (Note that if $m \neq n$, then ψ_m and ψ_n describe different states of the system for which $a_m \neq a_n$.)

10. Use the trigonometric identity

$$\sin\alpha \sin\beta = \frac{1}{2}\cos(\alpha+\beta) - \frac{1}{2}\cos(\alpha-\beta)$$

[2] to prove the wave functions

$$\psi(x) = \sqrt{2/L}\,\sin(n\pi x/L)$$

for a particle in a box extending from $x = 0$ to $x = L$ are orthogonal.

Chem 331 Assignment #4

Q1 a) for a π electron in ethylene ($L \approx 0.14$ nm)

ground state, $n = 1$

$$E_1 = \frac{n^2 h^2}{8 m_e L^2} = \frac{(1)^2 (6.626 \times 10^{-34})^2}{8\,(9.110 \times 10^{-31})(0.14 \times 10^{-9})^2}$$

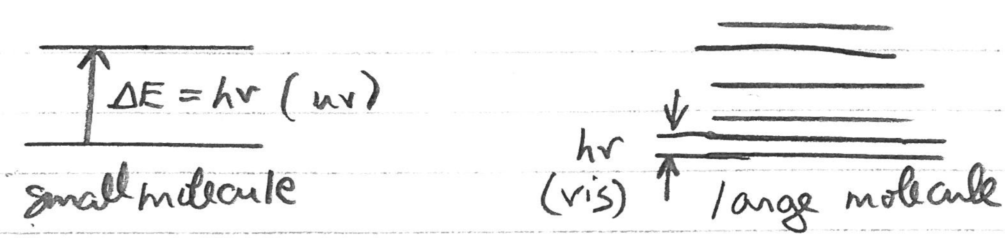
$$= 3.07 \times 10^{-18}\ \mathrm{J} = 19.2\ \mathrm{eV}\ \boxed{(1.85 \times 10^{6}\ \mathrm{J\,mol^{-1}})}$$

b) for a π electron in butadiene ($L \approx 0.43$ nm)

$$E_1 = 3.25 \times 10^{-19}\ \mathrm{J} = 2.03\ \mathrm{eV}\ \boxed{(1.96 \times 10^{5}\ \mathrm{J\,mol^{-1}})}$$

c) delocalization of π electrons is equivalent to placing them in a "larger box," with a larger value of L, reducing the energies of the electrons ($E_n \propto \frac{1}{L^2}$)

Q2 For "small" molecules, such as ethylene, the π electron energies are relatively large, leading to absorption at uv wavelengths. For larger molecules (larger L, smaller E_n) the absorptions shift to visible frequencies.

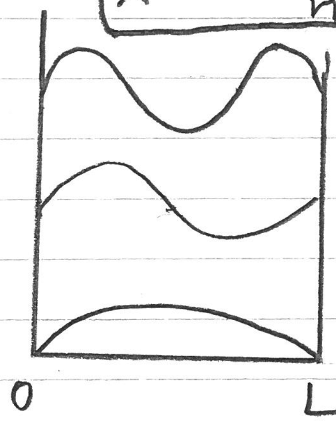


(Q3) a) To satisfy the boundary conditions

$$\psi(x=0) = 0 \qquad \psi(x=L) = 0$$

only waves of lengths $2L,\ L,\ \frac{2}{3}L, \ldots$ are allowed, giving

$$\boxed{\lambda = \frac{2L}{n}} \qquad n = 1, 2, 3, \ldots \qquad \boxed{L = \frac{n\lambda}{2}}$$



$n=3 \qquad \lambda = \frac{2}{3}L \qquad L = \frac{3}{2}\lambda$

$n=2 \qquad \lambda = L \qquad L = \lambda$

$n=1 \qquad \lambda = 2L \qquad L = \frac{1}{2}\lambda$

b) de Broglie relation $\quad \lambda = \dfrac{h}{p_x}$

$$p_x = \frac{h}{\lambda} = \frac{h}{2L/n} = \frac{nh}{2L}$$

c) kinetic energy $\quad T = \frac{1}{2} m v_x^2 = \frac{1}{2m}(m v_x)^2 = \frac{p_x^2}{2m}$

$$T = \frac{\left(\frac{nh}{2L}\right)^2}{2m} = \frac{n^2 h^2}{8mL^2}$$

d) the energy of the particle calculated from its de Broglie wavelength is identical to that obtained by solving the Schrodinger equation

Q4 $E_n = \dfrac{n^2 h^2}{8 m L^2}$

$\Delta E =$ energy level spacing $= E_{n+1} - E_n$

$$= \left[(n+1)^2 - n^2\right] \frac{h^2}{8 m L^2}$$

$$= (2n+1) \frac{h^2}{8mL^2}$$

$$\Delta E \to 0 \text{ as } L \to \infty$$

energy becomes continuous as the box width goes to infinity (free particle)

Q5 a) show $\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$ is normalized $(0 \leq x \leq L)$

$$\int_0^L \psi_n^*(x)\, \psi_n(x)\, dx$$

$$= \int_0^L \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) dx$$

(integral from course notes)

$$= \frac{2}{L} \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx = \frac{2}{L}\left[\frac{1}{2}x - \frac{1}{\frac{4n\pi}{L}} \sin\left(\frac{2n\pi x}{L}\right)\right]\Bigg|_0^L$$

$$= \frac{2}{L}\, \frac{1}{2}(L-0) - \frac{2}{L}\, \frac{L}{4n\pi}\left[\cancelto{0}{\sin(2n\pi)} - \cancelto{0}{\sin(0)}\right] = 1$$

(Q5 cont.) $\left(\frac{d}{dx}\sin ax = a\cos ax \qquad \frac{d}{dx}\cos ax = -a\sin ax\right)$

b) kinetic energy operator $\hat{T}_x = \frac{\hat{P}_x^2}{2m} = -\frac{h^2}{8\pi^2 m}\frac{\partial^2}{\partial x^2}$

$$\hat{T}_x \psi_n(x) = -\frac{h^2}{8\pi^2 m}\frac{\partial^2}{\partial x^2}\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$$

$$= -\frac{h^2}{8\pi^2 m}\frac{n\pi}{L}\sqrt{\frac{2}{L}}\frac{\partial}{\partial x}\cos\left(\frac{n\pi x}{L}\right)$$

$$= -\frac{h^2}{8\cancel{\pi^2} m}\frac{n\cancel{\pi}}{L}\left(\frac{-n\cancel{\pi}}{L}\right)\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$$

$$= \frac{n^2 h^2}{8mL^2}\psi_n(x)$$

Q6 $\psi^*\psi = (R + iI)^*(R + iI)$

$$= (R - iI)(R + iI)$$

$$= R^2 + \cancel{RiI} - \cancel{iIR} - i^2 I^2$$

$$= R^2 - (-1)I^2$$

$$= R^2 + I^2 \quad (\text{always real})$$

Q7 The eigenvalues of quantum mechanical operators correspond to physical properties such as position, momentum, energy, ... which are real

$\hat{A}\psi = a\psi$ eigenvalue a is real $\boxed{a^* = a}$

Q8 multiply ψ^* by $\hat{A}\psi$ and integrate:

$$\text{(I)} \quad \int \psi^* \hat{A} \psi \, dx = \int \psi^* a \psi \, dx = a \underbrace{\int \psi^* \psi \, dx}_{\text{(normalized)}} = a$$

multiply ψ by $\hat{A}^* \psi^*$ and integrate:

$$\text{(II)} \quad \int \psi \hat{A}^* \psi^* dx = \int \psi (\hat{A}\psi)^* dx$$

$$= \int \psi (a\psi)^* dx$$

$$= a^* \int \psi^* \psi \, dx = a^* = a$$

eigenvalue a is real ($a^* = a$)

from (I) and (II):

$$\int \psi^* \hat{A} \psi \, dx = \int \psi \hat{A}^* \psi^* dx$$

(can show more generally that $\int \psi_m^* \hat{A} \psi_n dx = \int \psi_n \hat{A}^* \psi_m^* dx$)

Q9 multiply ψ_m^* by $\hat{A}\psi_n$ and integrate:

$$\int \psi_m^* \hat{A}_n \psi \, dx = \int \psi_m^* a_n \psi_n \, dx = a_n \int \psi_m^* \psi_n \, dx$$

multiply ψ_n by $(\hat{A}\psi_m)^*$ and integrate:

$$\int \psi_n (\hat{A}\psi_m)^* dx = \int \psi_n (a_m \psi_m)^* dx$$

$$= \int \psi_n a_m^* \psi_m^* dx = \int \psi_n a_m \psi_m^* dx = a_m \int \psi_m^* \psi_n dx$$

notice:

equal

$$\int \psi_m^* \hat{A} \psi_n dx = a_n \int \psi_m^* \psi_n dx \quad \text{(I)}$$

$$\int \psi_n \hat{A}^* \psi_m^* dx = a_m \int \psi_m^* \psi_n dx \quad \text{(II)}$$

(Q9 cont.)

(I) − (II) : $0 = \underbrace{(a_n - a_m)}_{\neq 0} \int \psi_m^* \psi_n \, dx$

divide by $a_n - a_m$:
(not zero, so this is "legal")

$$0 = \int \psi_m^* \psi_n \, dx \qquad (m \neq n)$$

ψ_m and ψ_n are orthogonal

Q10 for a particle in a box

$$\left(\psi_j = \sqrt{\frac{2}{L}} \sin\left(\frac{j\pi x}{L}\right) \quad j = 1, 2, 3, \ldots \quad \psi_j \text{ is real, so } \psi_j^* = \psi_j \right)$$

$$\int_0^L \psi_m^* \psi_n \, dx = \int_0^L \psi_m \psi_n \, dx$$

$$= \int_0^L \sqrt{\frac{2}{L}} \sin\left(\frac{m\pi x}{L}\right) \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) dx$$

$$= \frac{2}{L} \int_0^L \sin\left(\frac{m\pi x}{L}\right) \sin\left(\frac{n\pi x}{L}\right) dx$$

$$= \frac{2}{L} \int_0^L \left[\frac{1}{2} \cos\left[\frac{(m+n)\pi x}{L}\right] - \frac{1}{2} \cos\frac{(m-n)\pi x}{L} \right] dx$$

$$= \frac{1}{L} \int_0^L \left[\cos\left[\frac{(m+n)\pi x}{L}\right] \right] dx - \frac{1}{L} \int_0^L \cos\left[\frac{(m-n)\pi x}{L}\right] dx$$

$$= \frac{1}{L} \left(\sin\left[\frac{(m+n)\pi x}{L}\right] - \sin\left[\frac{(m-n)\pi x}{L}\right] \right) \Bigg|_0^L = 0$$

why zero?
$\sin[(m+n)\pi] = 0$
$\sin[(m-n)\pi] = 0$
$\sin(0) = 0$