CHEM 4616: Homework #2

Corresponds to the quiz to be given in class on Thursday, January 31st, 2008

Chang, Chapter 14: Problems 25, 26, 28-31

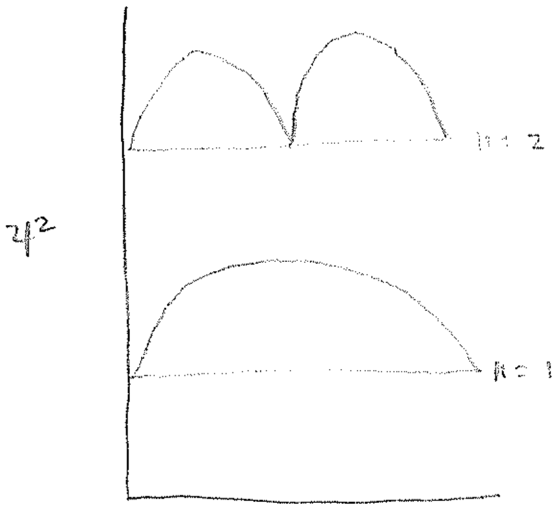
14.29 $\lambda = \dfrac{8 m_e L^2 c}{h(N+1)}$ (N = # carbons in chain = # π electrons)

L = chain length = (1.54 × # single bonds + 1.35 × # double bonds + 2 × 0.77) Å

N	L/Å	λ/nm
6	8.67	354
8	11.56	490
10	14.45	626

→ As the chain gets longer, the transition wavelength moves from the UV to the visible, lending a color to a sample of the polyene.

14.30 The plot of ψ^2 vs x for the n = 1 and n = 2 states are:



∴ The transition from the n = 1 → 2 must take place where both ψ^2 have non-zero values.

14.31 n = 1 ℓ = 2.000 nm

(a) Between 0.500 and 0.502 nm → $dx \doteq \Delta x = 0.002$ nm avg. x = 0.501 nm

$$\psi^2(0.501)\Delta x = \frac{2}{L}\sin^2\left(\frac{\pi(0.501)}{L}\right)\Delta x$$

$$= 1.0 \times 10^{-3}$$

(b) Between 0.999 nm and 1.001 nm → $dx \doteq \Delta x = 0.002$ nm avg. x = 1.000 nm

$$\psi^2(1.000)\Delta x = \frac{2}{L}\sin^2\left(\frac{\pi(1.000)}{(2.000)}\right)\Delta x = 2 \times 10^{-3}$$

14 26

$$\int_{L/4}^{3L/4} \psi^2\,dx = \frac{2}{L}\int_{L/4}^{3L/4} \sin^2\left(\frac{\pi x}{L}\right)dx = \frac{2}{L}\left[\frac{x}{2} - \frac{L}{4\pi}\sin\left(\frac{2\pi x}{L}\right)\right]_{L/4}^{3L/4}$$

(see footnote on p. 585)

$$= \frac{2}{L}\left[\frac{3L}{8} - \frac{L}{8} - \frac{L}{4\pi}\left(\sin\frac{3\pi}{2} - \sin\frac{\pi}{2}\right)\right]$$

$$= \frac{2}{L}\left[\frac{2L}{8} - \frac{L}{4\pi}(-2)\right] = \frac{1}{2} + \frac{1}{\pi} = \boxed{0.82}$$

14 28 $\psi_1 = A\sin\frac{\pi x}{L}$ $\psi_2 = A\sin\frac{2\pi x}{L}$

$$\int_0^L \psi_1\psi_2\,dx = A^2\int_0^L \sin\frac{\pi x}{L}\sin\frac{2\pi x}{L}\,dx$$

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

$$= A^2\int_0^L \left[\frac{1}{2}\cos\frac{\pi x}{L} - \frac{1}{2}\cos\frac{3\pi x}{L}\right]dx$$

$$= \frac{A^2}{2}\left[\int_0^L \cos\frac{\pi x}{L}dx - \int_0^L \cos\frac{3\pi x}{L}dx\right] = \frac{A^2}{2}\left[\frac{L}{\pi}\sin\frac{\pi x}{L}\Big]_0^L - \frac{L}{3\pi}\sin\frac{3\pi x}{L}\Big]_0^L\right]$$

$$= \frac{A^2}{2}\frac{L}{\pi}\left[\sin\pi - \sin 0 - \frac{1}{3}(\sin 3\pi - \sin 0)\right] = 0 \checkmark$$