Homework #2 Chem 1410. Due Sept 13.

2.1.a $\frac{d^2y}{dx^2} - 4\frac{dy}{dx} + 3y = 0$

try $y = e^{ax}$

$a^2e^{ax} - 4ae^{ax} + 3e^{ax} = 0 \Rightarrow a^2 - 4a + 3 = 0$

$a = 1, 3$

$y = Ce^{x} + De^{3x}$

2.2.b $\frac{d^2y}{dx^2} - 5\frac{dy}{dx} + 6y = 0$

try $y = e^{ax} \longrightarrow$

$a^2 - 5a + 6 = 0 \Rightarrow a = 2, 3$

$y = Ce^{2x} + De^{3x}$

$\left.\begin{array}{l} y(0) = -1 = C + D \\ y'(0) = 0 = 2C + 3D \end{array}\right\} \longrightarrow C = -3, \ D = 2$

$y = -3e^{2x} + 2e^{3x}$

3.4 Show $(\cos ax)(\cos by)(\cos cz)$ is an eigenfunction of ∇^2.

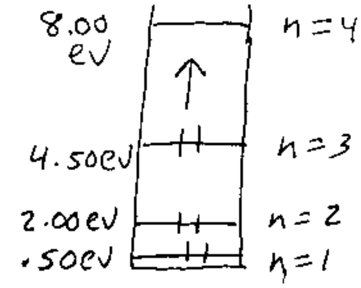
$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)(\cos ax)(\cos by)(\cos cz) =$

$(-a^2 - b^2 - c^2)(\cos ax)(\cos by)(\cos cz)$

Yes, it is an eigenfunction with the eigenvalue $-a^2 - b^2 - c^2$

3-6. Free electron model of hexatriene with

$a = 867$ pm.



$$E_n = \frac{h^2 n^2}{8ma^2}$$

$$\frac{(4^2-3^2)h^2}{8ma^2} = \frac{(6.626\times10^{-34}\,J.s)^2 \cdot 7}{8\,(9.109\times10^{-31}\,Kg)(867\times10^{-12}\,m)^2}$$

$$= 7\times 8.02\times10^{-20}\,J \longrightarrow 3.50\ eV \longrightarrow 2.82\times10^{4}\,cm^{-1}$$

3-16 Show that the particle-in-a-box wavefunctions satisfy $\int_0^a \psi_n^*(x)\,\psi_m(x)\,dx = 0, \quad m \neq n$

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

$$= -\frac{\pi}{2a}\left[\frac{1}{(n-m)}\sin(n-m)\frac{\pi x}{a} - \frac{1}{(n+m)}\sin(n+m)\frac{\pi x}{a}\right]\Bigg|_0^a = 0$$

3-18 Show that the functions $\phi_n(\theta) = \frac{1}{\sqrt{2\pi}}e^{in\theta}$ $\quad 0 \leq \theta \leq 2\pi$

are orthonormal.

$$\frac{1}{2\pi}\int_0^{2\pi} e^{-in\theta}\,e^{im\theta}\,d\theta = \frac{1}{2\pi}\int_0^{2\pi} e^{i(m-n)\theta}\,d\theta$$

$$= \frac{1}{2\pi}\,\frac{e^{i(m-n)\theta}}{i(m-n)}\Bigg|_0^{2\pi} \xrightarrow[m \neq n]{\text{suppose}} \frac{e^{i(m-n)2\pi} - e^{i(m-n)0}}{2\pi i(m-n)}$$

$$= \frac{1-1}{2\pi i(m-n)} = 0 \quad \text{since } m \text{ and } n \text{ are integers}$$

Now consider the case where $m = n$

$$\frac{1}{2\pi} \left. \frac{e^{i(m-n)\theta}}{i(m-n)} \right|_0^{2\pi} = \frac{e^0 - e^0}{2\pi(0)} = \frac{0}{0}$$

So we have to look at this more closely.

$$e^x = 1 + x + \cdots$$

$$e^{i(m-n)2\pi} = 1 + 2\pi(m-n)i + \cdots$$

So we get

$$\frac{1}{2\pi} \frac{1 + 2\pi(m-n)i - 1}{i(m-n)} \rightarrow 1 \quad \text{as } m \rightarrow n$$

3-28 $\quad -\frac{\hbar^2}{2I}\frac{d^2\psi}{d\theta^2} = E\psi, \quad 0 \le \theta \le 2\pi, \quad I = ma^2$

Show that $\psi = Ae^{in\theta}$, $n = \pm\frac{\sqrt{2IE}}{\hbar} = 0, \pm 1, \pm 2, \ldots$

are the solutions, and $A = 1/\sqrt{2\pi}$

$$-\frac{\hbar^2}{2I}\frac{d^2}{d\theta^2} Ae^{in\theta} = -\frac{\hbar^2}{2I} i^2 n \cancel{A} \cancel{e^{in\theta}} = E \cancel{A} \cancel{e^{in\theta}}$$

$$E = \frac{\hbar^2 n^2}{2I} \longrightarrow \frac{E\,2I}{\hbar^2} = n^2 \rightarrow n = \pm\frac{\sqrt{2IE}}{\hbar}$$

Now find A.

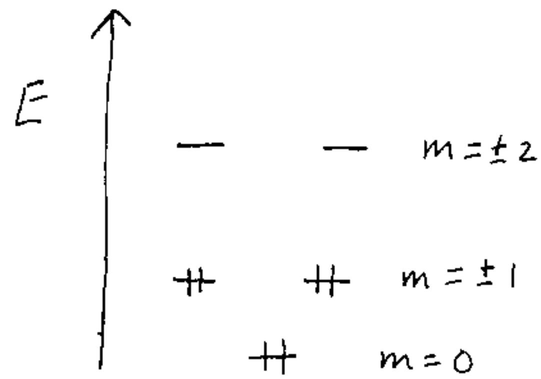
$$\int_0^{2\pi} A^* e^{-in\theta} A e^{in\theta} \, d\theta = 1$$

$$A^*A \int_0^{2\pi} 1 \, d\theta = A^*A\, 2\pi = 1 \Rightarrow A = \frac{1}{\sqrt{2\pi}}$$

How could you apply this model to benzene?

We could choose a to correspond to the distance from the center of the benzene ring to the carbon atom.

Benzene has six π electrons. These fill the $m = 0$, $+1$, and -1 levels in this model.



Note that the particle-on-a-ring problem predicts that the highest occupied orbital and the lowest unoccupied orbitals of benzene are degenerate. This is indeed the case.