CHEM 450 HW2 Hand-in Solutions

P2.31

$\Phi_n \theta = e^{in\theta}$, test over $0 \le \theta \le 2\pi$ to see if orthogonal

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

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

$$= \frac{1}{i(m-n)} e^{2\pi(m-n)i} - \frac{1}{i(m-n)} e^{0} \longrightarrow = \frac{1}{i(m-n)}$$

this difference is always zero. To see this clearly, use $e^{ix} = \cos x + i\sin x$

Below, $p = m-n$, since this is always a non-zero integer.

$$\frac{1}{i(m-n)}\Big[\underbrace{\cos 2\pi p}_{\text{always } 1} + \underbrace{i \sin 2\pi p}_{\text{always } 0}\Big] = \frac{1}{i(m-n)}$$

Thus,

$$\int_0^{2\pi} e^{i\theta(m-n)}\, d\theta = \frac{1}{i(m-n)} - \frac{1}{i(m-n)} \boxed{=0}$$

QED

P4.20

a) The two-dimensional analogue of Eq. 4.19 only has x, y:

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)\psi(x,y) = E\psi(x,y)$$

Since we already have ψ, we can get E by substitution (with N)

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) N \sin\frac{n_x \pi x}{a} \sin\frac{n_y \pi y}{b}$$

The x derivative: $$\frac{\partial^2}{\partial x^2} \sin\frac{n_x \pi x}{a} \sin\frac{n_y \pi y}{b} = -\frac{n_x^2 \pi^2}{a^2} \overbrace{\sin\frac{n_x \pi x}{a} \sin\frac{n_y \pi y}{b}}^{\psi \text{ (with N)}}$$

$$\frac{\partial^2}{\partial y^2} \sin\frac{n_x \pi x}{a} \sin\frac{n_y \pi y}{b} = -\frac{n_y^2 \pi^2}{b^2} \underbrace{\left(\sin\frac{n_x \pi x}{a} \sin\frac{n_y \pi y}{b}\right)}_{\psi \text{ (with N)}}$$

Thus,

$$E_{n_x, n_y} = \frac{\hbar^2}{2m}\left(\frac{n_x^2 \pi^2}{a^2} + \frac{n_y^2 \pi^2}{b^2}\right) \qquad \hbar^2 = \frac{h^2}{4\pi^2}$$

$$\boxed{= \frac{h^2}{8m}\left(\frac{n_x^2}{a} + \frac{n_y^2}{b}\right)}$$

b) use the number of nodes in each direction. There are n−1 nodes (don't count the edges of the box!)

a) no nodes in x or y, so $n_x = 1$, $n_y = 1$

b) one node in x, 2 nodes in y, so $n_x = 2$, $n_y = 3$

c) two nodes in x, none in y ; $n_x = 3$, $n_y = 1$

d) one each, $n_x = 2$, $n_y = 2$

e) no x nodes, 4 in y, so $n_x = 1$, $n_y = 5$

f) one x, no y, so $n_x = 2$, $n_y = 1$

P4.30

Normalized means $\int_{-\infty}^{\infty} \Psi^*(x)\,\Psi(x)\,dx = 1$

We note that $\{\phi_1(x),\ \phi_2(x),\ \phi_3(x)\}$ is an orthonormal set, meaning that any terms that look like

$$\int_{-\infty}^{\infty} \phi_n^* \phi_n\,dx = 1 \quad \underline{\text{and}} \quad \int_{-\infty}^{\infty} \phi_n^* \phi_m\,dx = 0$$

so...

$$\int_{-\infty}^{\infty} \Psi^*(x)\,\Psi(x)\,dx = \int_{-\infty}^{\infty} \left[\left(\frac{\sqrt{3}}{4}\phi_1^*(x) + \frac{\sqrt{3}}{2\sqrt{2}}\phi_2^*(x) + \frac{2-i\sqrt{3}}{4}\phi_3^*(x)\right) \times \left(\frac{\sqrt{3}}{4}\phi_1(x) + \frac{\sqrt{3}}{2\sqrt{2}}\phi_2(x) + \frac{2+i\sqrt{3}}{4}\phi_3(x)\right)\right] dx$$

This looks bad at first, but most terms are like, for example,

$$\int_{-\infty}^{\infty} \left(\frac{\sqrt{3}}{2\sqrt{2}}\right)\left(\frac{\sqrt{3}}{4}\right)\phi_2^*(x)\phi_1(x)\,dx = 0 \quad \text{(orthogonal)}$$

The rest do contribute, but are easy:

$$\int_{-\infty}^{\infty} \left(\frac{\sqrt{3}}{4}\right)\left(\frac{\sqrt{3}}{4}\right)\phi_1^*(x)\phi_1(x)\,dx + \int_{-\infty}^{\infty} \left(\frac{\sqrt{3}}{2\sqrt{2}}\right)\left(\frac{\sqrt{3}}{2\sqrt{2}}\right)\phi_2^*(x)\phi_2(x)\,dx + \int_{-\infty}^{\infty} \left|\frac{2+i\sqrt{3}}{4}\right|^2 \phi_3^*\phi_3(x)\,dx$$

$$= \frac{3}{16} + \frac{3}{8} + \frac{4+3}{16} = \underline{\underline{1}}$$

Note: The big message for an orthonormal basis, the coefficients squared tells how much of each basis vector is present.

b) The only possible energies that can ever be measured are the eigenvalues, E_1, $2E_1$, and $4E_1$.

c) As in a, the probabilities of each are the squares of the coefficients:

E_1 : $3/16$
$2E_1$: $3/8$
$4E_1$: $7/16$

d) The expectation value $\langle E\rangle$ gives the average energy that would be measured. Although it is defined as

$$\langle E\rangle = \frac{\int_{-\infty}^{\infty} \Psi^*(\tau)\,\hat{H}\,\Psi(\tau)\,d\tau}{\int_{-\infty}^{\infty} \Psi^*(\tau)\,\Psi(\tau)\,d\tau},$$

we know the values of each "matrix element": $\left(\int_{-\infty}^{\infty} \phi_n^* \hat{H}\,\phi_m\right)$

Since $\hat{H}\phi = E\phi$, $\quad \hat{H}\phi_1 = E_1\phi_1$, $\hat{H}\phi_2 = 2E_1\phi_2$, $\hat{H}\phi_3 = 4E_1\phi_3$.

This means that, for $m \neq n$, $\int_{-\infty}^{\infty} \phi_m^*(\tau)\,\hat{H}\,\phi_n(\tau)\,d\tau = 0$, so only the "diagonal" terms count; and we know their values. (from B)

$$\langle E\rangle = \left(\frac{\sqrt{3}}{4}\right)^2 E_1 + \left(\frac{\sqrt{3}}{2\sqrt{2}}\right)^2 E_2 + \frac{|2+i\sqrt{3}|^2}{4^2} E_3$$

$$= \frac{3}{16}E_1 + \frac{3}{4}E_1 + \frac{7}{4}E_1 = \boxed{2.6875\ E_1}$$