*Name*____

Chemistry 344

Exam I
Monday September 24, 2001
2:00 -2:50 PM

NO CALCULATORS PERMITTED

5. A particle of mass m in a potential well (with infinitely high walls) in the x dimension is known to be in either the $n = 2$ or $n = 3$ eigenstates with equal probability. The eigenfunctions of these states are $\psi_2(x) = (2/a)^{1/2} \sin[2\pi x/a]$ and $\psi_3(x) = (2/a)^{1/2} \sin[3\pi x/a]$, respectively.

(a) *Write an appropriate wavefunction* Ψ for the system that reflects our knowledge of the state of the system.

Since according to the conditions of the problem both states are equally probable, we need to have the wavefunction be a superposition (a linear combination) of $\psi_2(x)$ and $\psi_3(x)$ with coefficients whose absolute squares are equal.

$\Psi(x) = c_2\psi_2(x) + c_3\psi_3(x)$ such that $c_2^2 = c_3^2 = \frac{1}{2}$ since $c_2^2 + c_3^2 = 1$ NORMALIZATION

Therefore

$$\Psi(x) = \frac{1}{\sqrt{2}}\left\{\left(\frac{2}{a}\right)^{1/2}\sin\left(\frac{2\pi}{a}x\right) + \left(\frac{2}{a}\right)^{1/2}\sin\left(\frac{3\pi}{a}x\right)\right\}$$

or

$$\Psi(x) = \frac{1}{\sqrt{2}}\left\{\left(\frac{2}{a}\right)^{1/2}\sin\left(\frac{2\pi}{a}x\right) - \left(\frac{2}{a}\right)^{1/2}\sin\left(\frac{3\pi}{a}x\right)\right\}$$

(b) *Prove* that $\psi_2(x) = (2/a)^{1/2} \sin[2\pi x/a]$ is an eigenfunction of the Hamiltonian operator for this particle.

$\mathcal{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$ coming from $K.E. = \frac{p^2}{2m}$ and $V = 0$ and $\hat{p}_x = \frac{\hbar}{i}\frac{d}{dx}$

Show $\psi_2(x)$ satisfies the eigenfunction eigenvalue equation:

$$\mathcal{H}\psi_2(x) = ? = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\left(\frac{2}{a}\right)^{1/2}\sin\left(\frac{2\pi x}{a}\right) = \frac{-\hbar^2}{2m}\left(\frac{2}{a}\right)^{1/2}\left(\frac{2\pi}{a}\right)^2\left(-\sin\left(\frac{2\pi x}{a}\right)\right)$$

from $\frac{d}{dx}\sin\frac{2\pi}{a}x = +\frac{2\pi}{a}\cos\frac{2\pi}{a}x$ and $\frac{d}{dx}\cos\frac{2\pi}{a}x = -\left(\frac{2\pi}{a}\right)\sin\frac{2\pi x}{a}$

$$\mathcal{H}\psi_2(x) = +\frac{\hbar^2}{2m}\left(\frac{2\pi}{a}\right)^2\left(\frac{2}{a}\right)^{1/2}\sin\left(\frac{2\pi x}{a}\right) = \underbrace{\frac{h^2}{2ma^2}}_{\text{a number}}\cdot\underbrace{\left(\frac{2}{a}\right)^{1/2}\sin\left(\frac{2\pi x}{a}\right)}_{\psi_2(x)\text{ itself}}$$

more space on next page

We got $\mathcal{H}\,\psi_2(x) = \frac{h^2}{2ma^2}\,\psi_2(x)$. Therefore $\psi_2(x)$ has been proven to be an eigenfunction of $\mathcal{H}$ with eigenvalue $\frac{h^2}{2ma^2}$ or $2^2\frac{h^2}{8ma^2}$

(c) ***What energies*** might be obtained if the energy of the particle is measured?

The energy eigenvalues $\frac{2^2 h^2}{8ma^2}$ and $\frac{3^2 h^2}{8ma^2}$ only.

(d) ***Determine the expected average*** of a series of measurements of the energy of the particle.

Postulate 3 expected average is

$$\langle E \rangle = \int_0^a \Psi^*(x)\,\mathcal{H}\,\Psi(x)\,dx$$

since we have already normalized $\Psi(x)$

$$= \int_0^a \left(\tfrac{1}{\sqrt{2}}\psi_2(x) \pm \tfrac{1}{\sqrt{2}}\psi_3(x)\right)^* \mathcal{H}\left(\tfrac{1}{\sqrt{2}}\psi_2(x) \pm \tfrac{1}{\sqrt{2}}\psi_3(x)\right)dx$$

$$= \left(\tfrac{1}{\sqrt{2}}\right)^2 \int_0^a \psi_2^*(x)\,\underbrace{\mathcal{H}\,\psi_2(x)}_{\text{gives back } E_2\psi_2(x)}\,dx + \left(\tfrac{1}{\sqrt{2}}\right)^2 \int_0^a \psi_3^*(x)\,\underbrace{\mathcal{H}\,\psi_3(x)}_{\text{gives } E_3\psi_3(x)}\,dx$$

$$+ \left(\tfrac{1}{\sqrt{2}}\right)^2 \Big[\int_0^a \psi_2^*(x)\,\underbrace{\mathcal{H}\psi_3(x)}_{\text{gives back } \psi_3(x)}\,dx \pm \int_0^a \psi_3^*(x)\,\underbrace{\mathcal{H}\,\psi_2(x)}_{\text{gives } E_2\psi_2(x)}\,dx\Big]$$

$$\tfrac{1}{2}E_3\int_0^a \psi_2^*(x)\psi_3(x)\,dx = 0 \qquad \text{so integral is } E_2\int \psi_3^*(x)\,\psi_2(x)\,dx = 0$$

since eigenfunctions corresponding to different eigenvalues are ORTHOGONAL

$$= \frac{1}{2}\int_0^a \psi_2^*(x)\,E_2\,\psi_2(x)\,dx + \frac{1}{2}\int_0^a \psi_3^*(x)\,E_3\,\psi_3(x)\,dx$$

$$\langle E \rangle = \tfrac{1}{2}E_2 + \tfrac{1}{2}E_3 = \tfrac{1}{2}(2^2+3^2)\,h^2/8ma^2$$

(e) ***Which postulate*** predicts the standard deviation of such a series of measurements? State it.

Postulate 3. The expected average of a series of measurements of an observable whose operator is O_p is given by $\langle\ \rangle = \int \Psi^*\,O_p\,\Psi\,d\tau$

Write the equation that shows how the <u>expected</u> <u>mean square deviation</u> of any series of measurements of the energy of the particle can be calculated.

Operator for square of the deviation in measurements of energy is $\mathcal{O} = (\mathcal{H} - \langle E \rangle)^2$

$$\text{mean square deviation} = \int_0^a \Psi^*(x)\,(\mathcal{H} - \langle E \rangle)^2\,\Psi(x)\,dx$$

(f) *Carry out the solution* of (e), and then from the final result, determine the expected standard deviation of the series of measurements.

standard deviation $= \sqrt{\text{mean square deviation}}$

$$\text{mean square deviation} = \int_0^a \left(\tfrac{1}{\sqrt{2}}\psi_2(x) + \tfrac{1}{\sqrt{2}}\psi_3(x)\right)^* \underbrace{(\mathcal{H} - \langle E \rangle)^2}_{\text{multiply it out}} \left(\tfrac{1}{\sqrt{2}}\psi_2(x) + \tfrac{1}{\sqrt{2}}\psi_3(x)\right)dx$$

$$\mathcal{H}^2 - 2\langle E \rangle \mathcal{H} + \langle E \rangle^2$$

Note that $\mathcal{H}\psi_2(x) = E_2\psi_2(x)$

$$\mathcal{H}^2\psi_2(x) = E_2\mathcal{H}\psi_2(x) = E_2^2\psi_2(x)$$

$$-2\langle E \rangle \mathcal{H}\psi_2(x) = -2\langle E \rangle E_2\psi_2(x)$$

↑ a number

$$\langle E \rangle^2\psi_2(x) = \langle E \rangle^2\psi_2(x)$$

Then use orthogonality of $\psi_2(x)$ and $\psi_3(x)$ and normalization of each in integrating below

$$\text{mean square deviation} = \int_0^a \left(\tfrac{1}{\sqrt{2}}\psi_2(x) + \tfrac{1}{\sqrt{2}}\psi_3(x)\right)\Big\{\big[E_2^2\psi_2(x) - 2\langle E \rangle E_2\psi_2(x) + \langle E \rangle^2\psi_2(x)\big] + \big[E_3^2\psi_3(x) - 2\langle E \rangle E_3\psi_3(x) + \langle E \rangle^2\psi_3(x)\big]\Big\}\frac{1}{\sqrt{2}}$$

$$= \tfrac{1}{2}\left[E_2^2 - 2\langle E \rangle E_2 + \langle E \rangle^2 + \left(E_3^2 - 2\langle E \rangle E_3 + \langle E \rangle^2\right)\right]$$

$$= \tfrac{1}{2}\left(E_2^2 + E_3^2\right) - 2\langle E \rangle \underbrace{\left(\frac{E_2 + E_3}{2}\right)} + \langle E \rangle^2$$

$$\text{mean square deviation} = \boxed{\tfrac{1}{2}\left(E_2^2 + E_3^2\right) - \langle E \rangle^2} = \frac{25}{4}\left(\frac{h^2}{8ma^2}\right)^2$$

$\langle E \rangle^2$

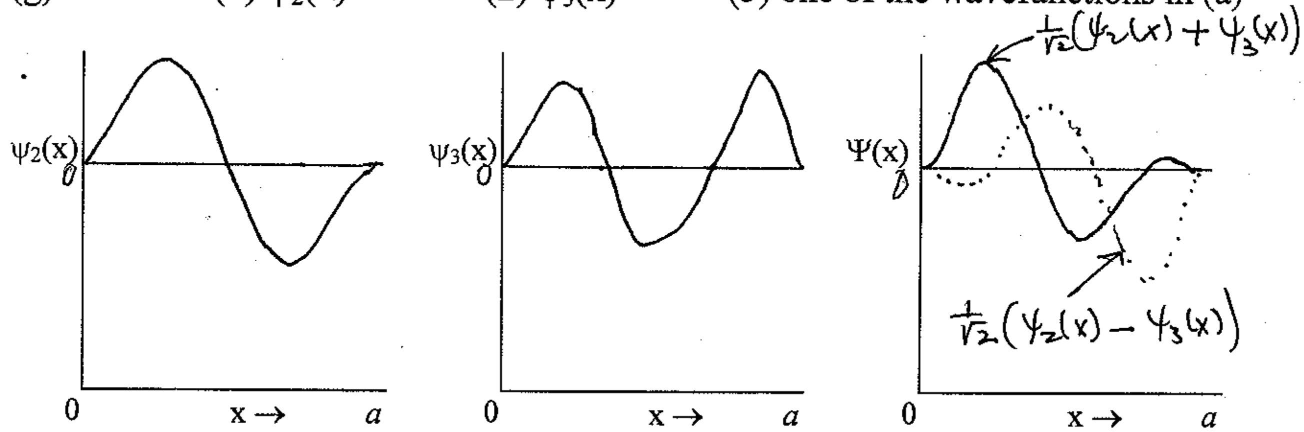
Standard deviation — take square root of this

$$= \frac{5}{2}\frac{h^2}{8ma^2}$$

(e) Illustrate a typical table of results from 10 such measurements. *Fill in* the column "Results" . What is the probability of each outcome?

	Result	Deviation		Probability
1	$2^2 h^2/8ma^2$	$-2.5h^2/8ma^2$		$1/2$
2	$2^2 h^2/8ma^2$			
3	$3^2 h^2/8ma^2$	$+2.5h^2/8ma^2$		$1/2$
4	$2^2 h^2/8ma^2$			
5	$3^2 h^2/8ma^2$			
6	$3^2 h^2/8ma^2$			
7	$3^2 h^2/8ma^2$			
8	$2^2 h^2/8ma^2$			
9	$3^2 h^2/8ma^2$			
10	$2^2 h^2/8ma^2$			
Ave	$6.5\, h^2/8ma^2$			

(g) *Sketch* (1) $\psi_2(x)$ (2) $\psi_3(x)$ (3) one of the wavefunctions in (a)



(h) Suppose an electron is contained in a two-dimensional potential well (with infinitely high walls) whose shape is that of a rectangular sheet with dimensions $a \times b$. *Write the Schrodinger equation* that needs to be solved for this system.

$$\mathcal{H}\Psi(x,y) = -\frac{\hbar^2}{2m_e}\left(\frac{d^2}{dx^2}+\frac{d^2}{dy^2}\right)\Psi(x,y) = E\,\Psi(x,y)$$

(i) *Show* that the method of separation of variables may be used to solve this problem, i.e., to find the eigenfunctions and eigenvalues.

Let $\Psi(x, y) = F(x) \cdot G(y)$

$$\frac{-\hbar^2}{2m_e}\left[\frac{d^2}{dx^2} F(x) \cdot G(y) + \frac{d^2}{dy^2} F(x) \cdot G(y)\right] = E\, F(x) \cdot G(y)$$

Dividing both sides by $F(x) \cdot G(y)$ after equating

$$\frac{\frac{-\hbar^2}{2m_e}\left[G(y) \cdot \frac{d^2 F(x)}{dx^2} + F(x) \frac{d^2 G(y)}{dy^2}\right]}{F(x) \cdot G(y)} = \frac{E\, F(x) \cdot G(y)}{F(x) \cdot G(y)} = E$$

$$\frac{-\hbar^2}{2m_e}\left[\underbrace{\frac{d^2 F(x)}{dx^2} \cdot \frac{1}{F(x)}} + \underbrace{\frac{1}{G(y)} \frac{d^2 G(y)}{dy^2}}\right] = E$$

Since each of these can independently take any x values unrelated to y values, ~~and~~ yet the sum has always to be the same constant value E then each term in the sum must itself be a constant, independent of the value of x or y.

$$\underbrace{\frac{-\hbar^2}{2m_e} \frac{d^2 F(x)}{F(x)\, dx^2} = A}_{\text{can solve this}} \quad \underbrace{\frac{-\hbar^2}{2m_e} \frac{1}{G(y)} \frac{d^2 G(y)}{dy}}_{\text{can solve this}} = B, \text{ such that } A + B = E$$

(j) Given the results of your proof above, *write down* the possible energy *eigenfunctions* for an electron confined to a sheet with dimensions $a \times b$. Given the results of your proof above, *write down* the corresponding *energy eigenvalues* opposite the eigenfunction

Solving $\frac{-\hbar^2}{2m_e} \frac{d^2 F(x)}{F(x)\, dx^2} = A$ or $\frac{-\hbar^2}{2m_e} \frac{d^2 F(x)}{dx^2} = A\, F(x)$

eigenvalues are already known, as seen in part (b) of this exam: $A = n_x^2 h^2 / 8ma^2$ $B = \frac{n_y^2 h^2}{8mb^2}$

Both equations have the same form, therefore the solutions are the same form.

$$E = A + B = \frac{n_x^2 h^2}{8 m_e a^2} + \frac{n_y^2 h^2}{8 m_e b^2} \quad \text{where } n_x = 1, 2, 3, \cdots \quad n_y = 1, 2, 3, \cdots$$

Functions are therefore $F(x) \cdot G(y)$ or

$$\Psi(x, y) = \sqrt{\frac{2}{a}} \sin\left(\frac{n_x \pi}{a} x\right) \cdot \sqrt{\frac{2}{b}} \sin\left(\frac{n_y \pi}{b} y\right)$$