Problem Set PS01

ISSUED: 1/4/99 **Due: 1/13/00**

Prof. Darin J. Ulness Name __________________________________

Instructions. Complete all questions before class on the due date. You are encouraged to work together. Be sure to struggle with the problem before seeking help. Many of the exercises are very similar to problems in the book. Understanding the solution to these problems will be helpful in completing the assigned exercises.

Mathematical Exercises

1. Consider the following set of operators $\left\{\widehat{\cos}, \widehat{\sin}, \widehat{\arccos}, \widehat{\arcsin}\right\}$ which are defined as $\widehat{\cos} f(x) = \cos f(x)$, $\widehat{\sin} f(x) = \sin f(x)$, $\widehat{\arccos} f(x) = \arccos f(x)$ and $\widehat{\arcsin} f(x) = \arcsin f(x)$ (n.b., arccos is the inverse cosine and arcsin is the inverse sine). Verify the algebra rules for operators holds for this set. Do all of these operators commute with one another? Do any pair of these operators commute? Are any of these operators linear operators?

Exercises

2. Redo section 11.1.1 of the notes for a particle in a 2D box.
3. Sketch the energy level diagram for a particle is a rectangle $a < b$. Qualitatively compare the energy level diagrams for $a \ll b$ and for $a \simeq b$.
4. Considering the above two exercises, how should a and b be related in order for $E_{1,4} = E_{2,1}$
5. Determine $[\hat{x}, \hat{p}_x]$. (Hint: the best way to do this is to evaluate $\hat{x}(\hat{p}_x f(x)) - \hat{p}_x(\hat{x} f(x))$ and since $f(x)$ is any arbitrary function we have $\hat{x}\hat{p}_x - \hat{p}_x\hat{x} = [\hat{x}, \hat{p}_x]$.)
6. Using the previous exercise and Eqs. (11.34)–(11.36) verify the basic commutator $\left[\hat{L}_x, \hat{L}_y\right] = i\hbar\hat{L}_z$.

Conceptual Problems

7. Explain in words, the superposition principle as it applies to quantum mechanics.
8. Draw a picture of the following (unormalized) wavefunctions for a particle in a box: $\psi_+ = \varphi_1 + \varphi_2$ and $\psi_- = \varphi_1 - \varphi_2$, where φ_1 and φ_2 are the eigenfunctions of the particle in a box.
9. Compare and contrast the wavefunctions, quantum numbers, and energy levels for a particle in a box of length $a = 2\pi$ and a particle on a ring.
10. Consider the inversion operator in one dimension: $\hat{\imath} f(x) = f(-x)$. Does $\hat{\imath}$ commute with $\hat{x}$? How about with $\hat{d}$

Computer Problems

11. Use MATHEMATICA to plot $\left|\psi_{n_x,n_y}(x,y)\right|^2$ for a particle in a square box. Make plots for the nine lowest energy states. What do these plots represent?

12. A particle in a box is prepared with the wavefunction $\psi = \sum_n \frac{1}{n}\varphi_n$. Where the φ_n are the eigenfunctions for the particle in a box. Plot ψ and $|\psi|^2$ (sum the first 10 terms or so).

Chem 352 PS01

① Equality let $\hat{\alpha} = \widehat{\cos}$ and $\hat{\beta} = \widehat{\cos}$

Then $\hat{\alpha} f(x) = \widehat{\cos} f(x) = \hat{\beta} f(x)$ ✓

$\quad\quad\quad\quad\quad\quad \parallel$

$\quad\quad\quad\quad\quad \cos f(x)$

Same for others in the set.

Addition

$\widehat{\cos} f(x) + \widehat{\sin} g(x) = \cos f(x) + \sin g(x)$ ✓ Same for ~~other~~ other pairs

Multiplication

$\widehat{\cos}\widehat{\sin} f(x) = \widehat{\cos} \sin f(x) = \cos(\sin f(x)) = \widehat{\cos}(\widehat{\sin} f(x))$ ✓

Same for other pairs

Inverse

let $g(x) = \cos f(x)$

Now $\widehat{\cos} f(x) = \cos f(x) = g(x)$ ✓

$\widehat{\arccos}\, g(x) = \arccos(\cos f(x)) = f(x)$ ✓ } so $\widehat{\arccos} = \widehat{\cos}^{-1}$

Same for $\widehat{\arcsin}$ and $\widehat{\sin}$

The set of operators is not commutative

For example $\widehat{\cos}\,\widehat{\sin} f(x) = \cos(\sin f(x)) \neq \sin(\cos f(x)) = \widehat{\sin}\widehat{\cos} f(x)$

but $\widehat{\cos}\,\widehat{\arccos} f(x) = f(x) = \widehat{\arccos}\,\widehat{\cos} f(x)$

so $[\widehat{\cos}, \widehat{\arccos}] = 0 = [\widehat{\sin}, \widehat{\arcsin}]$

The operators are not linear

$\widehat{\cos}(f(x) + g(x)) \neq \widehat{\cos} f(x) + \widehat{\cos}\, g(x)$

Same for others

The 2D Particle in a Box Problem

The potential is

$$V(x,y) = \begin{cases} 0, & 0 < x < a, 0 < y < b \\ \infty, & \text{else} \end{cases}. \tag{1}$$

Now the Schrödinger equation is

$$\hat{H}\psi = E\psi \;\Rightarrow\; \frac{-\hbar^2}{2m}\nabla^2\psi = E\psi$$
$$\Rightarrow\; \frac{-\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2}\right) = E\psi. \tag{2}$$

It is generally true that when the Hamiltonian is a sum of independent terms, we can write the wavefunction as a product of wavefunctions

$$\psi(x,y) = \psi_x(x)\psi_y(y). \tag{3}$$

Subbing the product wavefunction into the Schrödinger equation we get

$$\frac{-\hbar^2}{2m}\left(\frac{\partial^2\psi_x\psi_y}{\partial x^2} + \frac{\partial^2\psi_x\psi_y}{\partial y^2}\right) = E\psi_x\psi_y \tag{4}$$
$$\frac{-\hbar^2}{2m}\left(\frac{\psi_y\partial^2\psi_x}{\partial x^2} + \frac{\psi_x\partial^2\psi_y}{\partial y^2} +\right) = E\psi_x\psi_y.$$

We now divide both sides by $\psi_x\psi_y$ to get

$$\frac{-\hbar^2}{2m}\left(\frac{1}{\psi_x}\frac{\partial^2\psi_x}{\partial x^2} + \frac{1}{\psi_y}\frac{\partial^2\psi_y}{\partial y^2}\right) = E. \tag{5}$$

This equation is now of the form

$$f(x) + g(y) = C, \tag{6}$$

where C is a constant.

If we take the derivative with respect to x we get

$$\frac{d}{dx}f(x) + g(y) + h(z) = C,$$
$$\frac{df(x)}{dx} + \cancelto{0}{\frac{dg(y)}{dx}} = \cancelto{0}{\frac{dC}{dx}},$$
$$\frac{df(x)}{dx} = 0, \tag{7}$$

So, $f(x)$ is a constant. Similarly for $g(y)$.

Applying this to our Schrödinger equation means that we have converted our partial differential equation into two independent ordinary differential equations,

$$\frac{-\hbar^2}{2m}\frac{1}{\psi_x}\frac{d^2\psi_x}{dx^2} = E_x \Longrightarrow \frac{-\hbar^2}{2m}\frac{d^2\psi_x}{dx^2} = E_x\psi_x \tag{8}$$
$$\frac{-\hbar^2}{2m}\frac{1}{\psi_y}\frac{d^2\psi_y}{dy^2} = E_y \Longrightarrow \frac{-\hbar^2}{2m}\frac{d^2\psi_y}{dy^2} = E_y\psi_y$$

which we recognize as the 1D particle in a box equations.

Hence we immediately have

$$\psi_x = \sqrt{\frac{2}{a}}\sin\frac{n_x\pi x}{a}, \tag{9}$$
$$\psi_y = \sqrt{\frac{2}{b}}\sin\frac{n_y\pi y}{b},$$

and

$$E_{x,n_x} = \frac{n_x^2h^2}{8ma^2}, \tag{10}$$
$$E_{y,n_y} = \frac{n_y^2h^2}{8mb^2}.$$

The total wavefunction is

$$\psi = \frac{2}{\sqrt{ab}}\sin\frac{n_x\pi x}{a}\sin\frac{n_y\pi y}{b} \tag{11}$$

and the total energy is

$$E = E_{x,n_x} + E_{y,n_y}. \tag{12}$$

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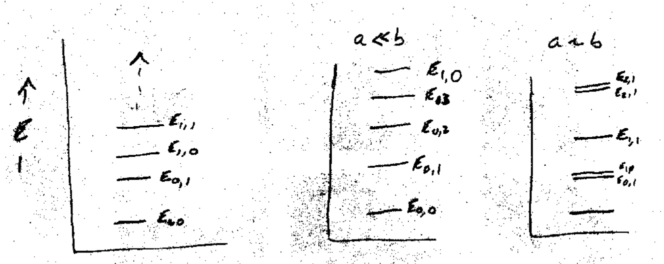
③ $E_{n_a,n_b} = \frac{n_a^2 h^2}{8ma^2} + \frac{n_b^2 h^2}{8mb^2} \quad a < b$



④ $E_{2,1} = \frac{2^2 h^2}{8ma^2} + \frac{1^2 h^2}{8mb^2} = \frac{1^2 h^2}{8ma^2} + \frac{4^2 h^2}{8mb^2} = E_{1,4}$

$\frac{4}{a^2} + \frac{1}{b^2} = \frac{1}{a^2} + \frac{16}{b^2}$

$4b^2 + a^2 = b^2 + 16a^2$

$3b^2 = 15a^2$

$b^2 = 5a^2 \Rightarrow b = \sqrt{5}\, a$

⑤ $[\hat{X}, \hat{P}_x] = \hat{x}\hat{P}_x - \hat{P}_x\hat{x}$

$\hat{x}\hat{P}_x f(x) = x(-i\hbar)\frac{d}{dx} f(x) = -i\hbar\, x f'(x)$ $f'(x) \equiv \frac{d f(x)}{dx}$

$\hat{P}_x\hat{x} f(x) = -i\hbar \frac{d x f(x)}{dx} = -i\hbar(x f'(x) + f(x))$

so

$(\hat{x}\hat{P}_x - \hat{P}_x\hat{x}) f(x) = \cancel{-i\hbar x f'(x)} + \cancel{i\hbar x f'(x)} + i\hbar f(x)$

so $[\hat{X}, \hat{P}_x] = i\hbar$

⑥ $[\hat{L}_x, \hat{L}_y] = \hat{L}_x\hat{L}_y - \hat{L}_y\hat{L}_x = (\hat{y}\hat{P}_z - \hat{z}\hat{P}_y)(\hat{z}\hat{P}_x - \hat{x}P_z) - (\hat{z}\hat{P}_x - \hat{x}\hat{P}_z)(\hat{y}\hat{P}_z - \hat{z}\hat{P}$

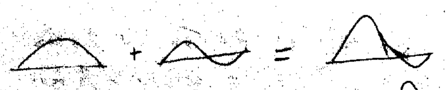
$= \hat{y}\hat{P}_z\hat{z}\hat{P}_x - \cancel{\hat{z}\hat{P}_y\hat{z}\hat{P}_x} - \cancel{\hat{y}\hat{P}_z\hat{x}\hat{P}_z} + \hat{z}\hat{P}_y\hat{x}\hat{P}_z$ be careful of the order

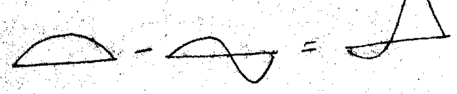
$- \hat{z}\hat{P}_x\hat{y}P_z + \cancel{\hat{z}\hat{P}_x\hat{z}P_y} + \cancel{\hat{x}\hat{P}_z\hat{y}P_z} - \hat{x}\hat{P}_z\hat{z}\hat{P}_y$

$= \underbrace{\hat{y}\hat{P}_x\hat{P}_z\hat{z} - \hat{y}\hat{P}_x\hat{z}P_z}_{\hat{y}\hat{P}_x\underbrace{[P_z, z]}_{-i\hbar}} + \underbrace{\hat{x}\hat{P}_y\hat{z}\hat{P}_z - \hat{x}\hat{P}_y\hat{P}_z\hat{z}}_{\hat{x}\hat{P}_y\underbrace{[z, P_z]}_{i\hbar}}$

$= i\hbar\underbrace{(\hat{x}\hat{P}_y - \hat{y}\hat{P}_x)}_{L_z} = i\hbar L_z$ ✓

⑦ your own words

⑧ $\psi_+ =$ 

$\psi_- =$ 

⑨

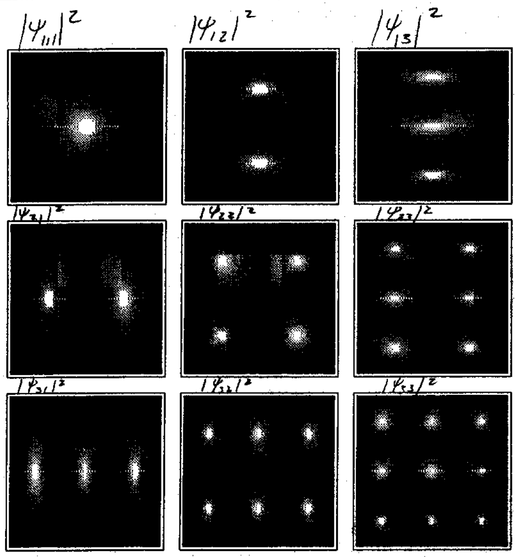
	P in box a=2π	P on Ring
QN	$n = 1, 2, 3 \cdots$	QN $m = 0, \pm1\ \pm2 \cdots$
EL	$E_n = \frac{n^2 h^2}{16\pi^2 m}$	$E_m = \frac{m^2 h^2}{8\pi^2 I}$
ψ	$\psi_n = \frac{1}{\sqrt{\cancel{\pi}}}\sin\frac{n}{2}x$	$\psi_m = \frac{1}{\sqrt{2\pi}}e^{im\phi}$

⑩ $[\hat{i}, \hat{x}] = \hat{i}\hat{x} - \hat{x}\hat{i}$

$\left.\begin{array}{l}\hat{i}\hat{x} f(x) = \hat{i}\, x f(x) = -x f(-x) \\ \hat{x}\hat{i} f(x) = x\,\hat{i} f(x) = x f(-x)\end{array}\right\} \Rightarrow$ does not commute

$[\hat{i}, \hat{d}] = \hat{i}\hat{d} - \hat{d}\hat{i}$

$\left.\begin{array}{l}\hat{i}\hat{d} f(x) = \hat{i}\frac{d f(x)}{dx} = \frac{d f(-x)}{d(-x)} \\ \hat{d}\hat{i} f(x) = \hat{d} f(-x) = \frac{d f(-x)}{dx}\end{array}\right\}$ not the same in general so does not commute



white: Areas where the particle is most likely to be found
dark: Areas where the particle is least likely to be found.