

Problem Set PS01
ISSUED: 1/7/02 Due: 1/17/02

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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 $\{\hat{x}, \hat{d}, \hat{d}^2, \hat{i}\}$ which are defined on page 157 of the notes. 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?
2. The following set of operators, defined as 2×2 matrices,

$$\hat{1} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}, \quad \hat{\sigma}_1 = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \quad \hat{\sigma}_2 = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \quad \hat{\sigma}_3 = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix},$$

are called the Pauli spin matrices ($\hat{1}$ is called the unit or identity matrix). These are often used when talking about spin systems such as electrons or protons in ESR and NMR respectively. Verify the following properties of these operators. (It might be helpful to use MATHEMATICA)

(a) $\hat{\sigma}_i^2 = \hat{1}$

(b) $[\hat{\sigma}_i, \hat{\sigma}_j] = 2i\epsilon_{ijk}\hat{\sigma}_k$, ϵ_{ijk} is the Levi-Civita symbol:

$$\epsilon_{ijk} = \begin{cases} +1 & (ijk) = (123), (312), \text{ or } (231) \\ -1 & (ijk) = (132), (213), \text{ or } (321) \\ 0 & \text{else} \end{cases}$$

- (c) The Pauli matrices are Hermitian, $\hat{\sigma}_i = \hat{\sigma}_i^\dagger$. That is, the matrices are equal to the conjugate transpose of themselves. MATHEMATICA are **Conjugate** and **Transpose**.
- (d) $\text{Tr}[\hat{\sigma}_j] = 0$ and $|\hat{\sigma}_j| = -1$. MATHEMATICA are **Det** and **Tr**.

Exercises

3. Redo section 11.1.1 of the notes for a particle in a 2D box.
4. Sketch the energy level diagram for a particle in a rectangle $a < b$. Qualitatively compare the energy level diagrams for $a \ll b$ and for $a \simeq b$.
5. Considering a particle in a 2D box of sides a and b , how should a and b be related in order for $E_{1,3} = E_{2,1}$.

- Evaluate $\langle xyz \rangle$ for the ground state of a particle in a cube.
- Using the fact that the Hamiltonian operator is a linear operator operate on

$$\Psi = \sum_n a_n \psi_n,$$

where the ψ_n satisfy $\hat{H}\psi_n = E_n\psi_n$, with the Hamiltonian.

- 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 $\hat{x}\hat{p}_x - \hat{p}_x\hat{x} = [\hat{x}, \hat{p}_x]$.)
- Using the previous exercise and Eqs. (11.34)–(11.36) verify the basic commutator $[\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x$.

Conceptual Problems

- Sketch the energy level diagram for a particle in a 3D box where $a = b < c$.
- Explain in words, the superposition principle as it applies to quantum mechanics.
- Draw a picture of the following (unnormalized) wavefunctions for a particle in a box: $\psi_+ = \varphi_1 + \varphi_3$ and $\psi_- = \varphi_1 - \varphi_3$, where φ_1 and φ_3 are the eigenfunctions of the particle in a box.

Computer Problems

- Use MATHEMATICA to plot $\psi_{n_x, n_y}(x, y)$ and $|\psi_{n_x, n_y}(x, y)|^2$ for a particle in a square box. Make plots for the nine lowest energy states. What do these plots represent? You can make a superposition (often called a wavepacket) wavefunction that represents a case where the particle is fairly localized in one corner of the box by

$$\Psi = \psi_{12} + \psi_{21} + \psi_{22}.$$

Try to come up with three other wavepackets (using these same three eigenfunctions) that localize the particle in each of the three remaining corners of the box.

- A particle in a box is prepared with the wavefunction $\psi = \sum_n \frac{1}{n^2} \varphi_n$. The φ_n are the eigenfunctions for the particle in a box. Plot ψ and $|\psi|^2$ (sum the first 20 terms or so).
- Download the MATHEMATICA notebook for a particle in a 3D box from the PChem website. This program produces a density plot of $|\psi_{n_x n_y n_z}|^2$ for a particle in a cube. Get a feel for the different wavefunctions. You can use the 3D viewpoint selector the get different views. (Remember the ground state is ψ_{111} not ψ_{000}).

Transitivity obviously holds
 $\hat{x}\hat{p} = (\hat{x}\hat{p})$ and so on so associativity holds
 there is no identity
 $\hat{x}^{-1} = \frac{1}{x}$, $\hat{p}^{-1} = \int \hat{a}^{-1} = \iint \hat{i}^{-1} = \hat{i}$
 all \hat{a}^2 count
 they are linear operators.

The 2D Particle in a Box Problem

The potential is

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

Now the Schrödinger equation is

$$\hat{H}\psi = E\psi \Rightarrow \frac{-\hbar^2}{2m}\nabla^2\psi = E\psi$$

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

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

$$\psi(x, y) = \psi_x(x)\psi_y(y). \quad (3)$$

Subbing the product wavefunction into the Schrödinger equation we get

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

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

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

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

This equation is now of the form

$$f(x) + g(y) = C, \quad (6)$$

where C is a constant.

If we take the derivative with respect to x we get

$$\frac{d}{dx} f(x) + g(y) + h(x) = C,$$

$$\frac{df(x)}{dx} + \frac{dg(y)}{dx} = \frac{dC}{dx},$$

$$\frac{df(x)}{dx} = 0, \quad (7)$$

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In[8]:= sig1 = {{0, 1}, {1, 0}};
In[9]:= sig2 = {{0, -1}, {1, 0}};
In[10]:= sig3 = {{1, 0}, {0, -1}};
In[12]:= MatrixForm[sig1.sig1]
Out[12]//MatrixForm=
  ( 1 0
  0 1 )
In[13]:= MatrixForm[sig2.sig2]
Out[13]//MatrixForm=
  ( 1 0
  0 1 )
In[14]:= MatrixForm[sig3.sig3]
Out[14]//MatrixForm=
  ( 1 0
  0 1 )
In[20]:= MatrixForm[sig1.sig2 - sig2.sig1]
Out[20]//MatrixForm=
  ( 2i 0
  0 -2i )
In[17]:= MatrixForm[sig1.sig3 - sig3.sig1]
Out[17]//MatrixForm=
  ( 0 -2
  2 0 )
In[18]:= MatrixForm[sig2.sig3 - sig3.sig2]
Out[18]//MatrixForm=
  ( 0 2i
  2i 0 )

In[24]:= MatrixForm[Conjugate[Transpose[sig1]]]
Out[24]//MatrixForm=
  ( 0 1
  1 0 )
In[25]:= MatrixForm[Conjugate[Transpose[sig2]]]
Out[25]//MatrixForm=
  ( 0 -1
  1 0 )
In[27]:= MatrixForm[Conjugate[Transpose[sig3]]]
Out[27]//MatrixForm=
  ( 1 0
  0 -1 )

In[30]:= Det[sig1]
Out[30]= -1
In[32]:= Det[sig2]
Out[32]= -1
In[31]:= Det[sig3]
Out[31]= -1
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3 cu

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,

$$\frac{-\hbar^2}{2m}\frac{1}{\psi_x}\frac{d^2\psi_x}{dx^2} = E_x \Rightarrow \frac{-\hbar^2}{2m}\frac{d^2\psi_x}{dx^2} = E_x\psi_x \quad (8)$$

$$\frac{-\hbar^2}{2m}\frac{1}{\psi_y}\frac{d^2\psi_y}{dy^2} = E_y \Rightarrow \frac{-\hbar^2}{2m}\frac{d^2\psi_y}{dy^2} = E_y\psi_y$$

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

$$\psi_x = \sqrt{\frac{2}{a}}\sin\frac{n_x\pi x}{a}, \quad (9)$$

$$\psi_y = \sqrt{\frac{2}{b}}\sin\frac{n_y\pi y}{b},$$

and

$$E_{x,n_x} = \frac{n_x^2\hbar^2}{8ma^2}, \quad (10)$$

$$E_{y,n_y} = \frac{n_y^2\hbar^2}{8mb^2}.$$

The total wavefunction is

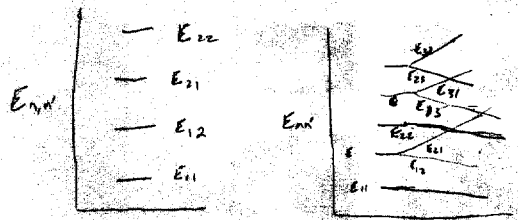
$$\psi = \frac{2}{\sqrt{ab}}\sin\frac{n_x\pi x}{a}\sin\frac{n_y\pi y}{b} \quad (11)$$

and the total energy is

$$E = E_{x,n_x} + E_{y,n_y}. \quad (12)$$

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$$E_{n_x, n_y} = \frac{\hbar^2 n_x^2}{8ma^2} + \frac{\hbar^2 n_y^2}{8mb^2}$$



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$$E_{n_x, n_y} = \frac{\hbar^2 n_x^2}{8ma^2} + \frac{\hbar^2 n_y^2}{8mb^2}$$

$$E_{13} = E_{21} \Rightarrow \frac{\hbar^2 (1)^2}{8ma^2} + \frac{\hbar^2 (3)^2}{8mb^2} = \frac{\hbar^2 (2)^2}{8ma^2} + \frac{\hbar^2 (1)^2}{8mb^2}$$

$$\frac{\hbar^2}{8mb^2}(1-1) = \frac{\hbar^2}{8ma^2}(4-1)$$

$$\frac{1}{b^2} = \frac{3}{a^2}$$

$$b = \sqrt{\frac{8}{3}}a$$

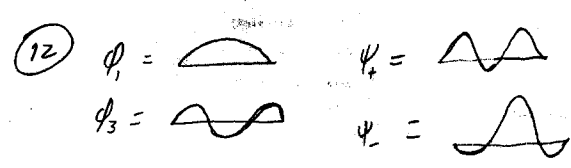
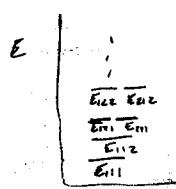
6) $\psi_{xyz} = \frac{2\sqrt{2}}{a^3} \sin \frac{n\pi x}{a} \sin \frac{m\pi y}{a} \sin \frac{l\pi z}{a}$
 ground state
 $\psi_{111} = \frac{2\sqrt{2}}{a^3} \sin \frac{\pi x}{a} \sin \frac{\pi y}{a} \sin \frac{\pi z}{a}$
 $\langle xyz \rangle_{111} = \int_0^a \int_0^a \int_0^a \psi_{111}^* xyz \psi_{111} dx dy dz$
 $= \frac{8}{a^3} \int_0^a \int_0^a \int_0^a xyz (\sin \frac{\pi x}{a})^2 (\sin \frac{\pi y}{a})^2 (\sin \frac{\pi z}{a})^2 dx dy dz$

9) $[\hat{L}_y, \hat{L}_z] = [(\hat{x}\hat{p}_x - \hat{p}_x\hat{x}), (\hat{p}_x\hat{y} - \hat{y}\hat{p}_x)]$
 $\hat{z}\hat{p}_x\hat{p}_y - \hat{x}\hat{p}_z\hat{p}_y - \hat{z}\hat{p}_x\hat{p}_x + \hat{x}\hat{p}_z\hat{p}_x$
 $- \hat{x}\hat{p}_y\hat{z}\hat{p}_x + \hat{x}\hat{p}_y\hat{x}\hat{p}_z + \hat{y}\hat{p}_x\hat{z}\hat{p}_x - \hat{y}\hat{p}_x\hat{x}\hat{p}_z$
 $= \hat{z}\hat{p}_x\hat{p}_y + \hat{x}\hat{p}_z\hat{p}_x - \hat{x}\hat{p}_y\hat{z}\hat{p}_x - \hat{y}\hat{p}_x\hat{x}\hat{p}_z$
 $\hat{z}\hat{p}_x[\hat{p}_y, \hat{x}] + \hat{x}\hat{p}_z[\hat{p}_x, \hat{x}] - \hat{y}\hat{p}_x[\hat{z}\hat{p}_x, \hat{x}] - \hat{y}\hat{p}_x[\hat{x}\hat{p}_z, \hat{x}]$
 $[\hat{x}, \hat{p}_x] = -i\hbar$
 $= i\hbar \hat{y}\hat{p}_z - \hat{z}\hat{p}_y = i\hbar \hat{L}_x$

7) $\hat{H}\Psi = \hat{H} \sum_n a_n \psi_n = \sum_n a_n \hat{H}\psi_n = \sum_n a_n E_n \psi_n$
 Ψ is not an eigenstate of \hat{H}

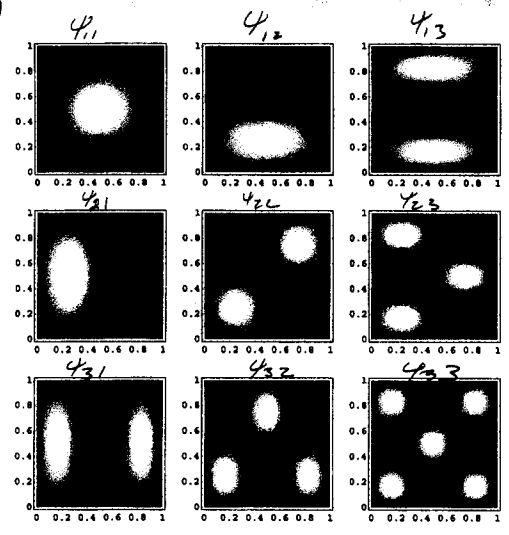
8) $(\hat{x}\hat{p}_x - \hat{p}_x\hat{x}) f(x) = \hat{x}\hat{p}_x f(x) - \hat{p}_x\hat{x} f(x)$
 $= -i\hbar x \frac{d}{dx} f(x) + i\hbar \frac{d}{dx} (x f(x)) = -i\hbar x \frac{df}{dx} + i\hbar (x \frac{df}{dx} + f(x))$
 $= i\hbar f(x)$ so $[\hat{x}, \hat{p}_x] = i\hbar$

11) your words



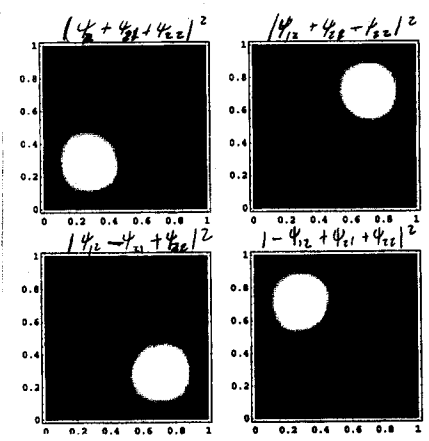
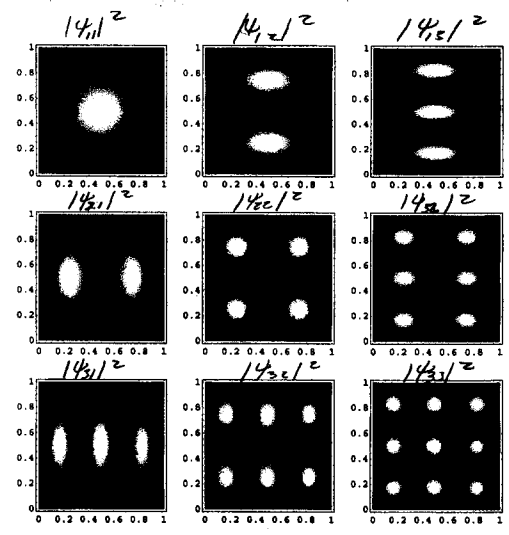
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13



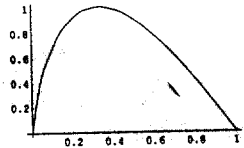
13 cont

ps01-13.nb



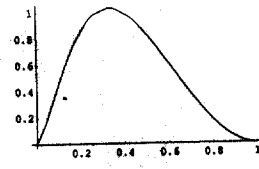
14

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In[64]:= Plot[Evaluate[Sum[1/(n^2) Sin[n Pi x], {n, 1, 20}], {x, 0, 1}]]
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Out[64]= - Graphics -

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In[65]:= Plot[Evaluate[Sum[1/(n^2) Sin[n Pi x], {n, 1, 20}]]^2, {x, 0, 1}]
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Out[65]= - Graphics -

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