

Problem Set PS03

ISSUED: 9/12/02 Due: 9/19/02

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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. Calculate $[\hat{x}, \hat{d}]$ where $\hat{x}f = xf$ and $\hat{d}f = \frac{df}{dx}$. Hint: when calculating commutators the trick is to evaluate $[\hat{x}, \hat{d}]f(x)$ where $f(x)$ is any arbitrary function of x , then factor out the $f(x)$ leaving the expression for $[\hat{x}, \hat{d}]$.
2. A set of functions, $\{f_n(x)\}$ is said to be *orthogonal* over the interval $a \leq x \leq b$ if $\int_a^b f_n^*(x)f_m(x)dx = 0$ when $m \neq n$. Show that the set of functions $\{e^{inx}\}$ are orthogonal over the interval $0 \leq x \leq 2\pi$.

Exercises

3. Show that the position and momentum operators do not commute (i.e., $[\hat{x}, \hat{p}_x] \neq 0$).
4. Evaluate $\langle \hat{x}^2 \rangle$ and $\langle \hat{T} \rangle$ for a particle in states ψ_1 , ψ_5 , and ψ_7 of a particle in a box. You can use MATHEMATICA to do the integrals.
5. When talking about the harmonic oscillator one often defines two operators called the lowering and raising operators, \hat{a} and \hat{a}^\dagger respectively. These are defined in terms of the position and momentum operators as

$$\hat{a} \equiv \sqrt{\frac{m\omega}{2\hbar}} \left(\hat{x} + \frac{i\hat{p}}{m\omega} \right) \quad (1)$$

and

$$\hat{a}^\dagger \equiv \sqrt{\frac{m\omega}{2\hbar}} \left(\hat{x} - \frac{i\hat{p}}{m\omega} \right). \quad (2)$$

These operators get their names because when the lowering (raising) operator acts on a wavefunction in state n , the result is to lower (raise) the state to $n - 1$ ($n + 1$).

- (a) By adding or subtracting the above equations, show that the position operator can be written as

$$\hat{x} = \sqrt{\frac{2\hbar}{4m\omega}} (\hat{a} + \hat{a}^\dagger), \quad (3)$$

and the momentum operator can be written as

$$\hat{p} = \frac{\sqrt{2\hbar m\omega}}{2i} (\hat{a} - \hat{a}^\dagger). \quad (4)$$

(b) The Hamiltonian operator for the harmonic oscillator is

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2 \hat{x}^2}{2}. \quad (5)$$

By substituting in Eqs. (3) and (4) into Eq. (5), show that the Hamiltonian can be written in terms of the lowering and raising operators as

$$\hat{H} = \hbar\omega \left(\hat{a}^\dagger \hat{a} + \frac{1}{2} \right). \quad (6)$$

Remember that you are working with operators that do not commute. In fact you will need to use $[\hat{a}, \hat{a}^\dagger] \equiv \hat{a}\hat{a}^\dagger - \hat{a}^\dagger\hat{a} = 1$ in your derivation.

6. In the previous problems we learned about the lowering and raising operators. We said that the lowering operator reduces the quantum number and the raising operator increases the quantum number. To be more explicit,

$$\hat{a}\psi_n = \sqrt{n}\psi_{n-1} \quad (7)$$

and

$$\hat{a}^\dagger\psi_n = \sqrt{n+1}\psi_{n+1}. \quad (8)$$

Evaluate $\langle \hat{x} \rangle$, $\langle \hat{x}^2 \rangle$ and $\langle \hat{p} \rangle$ for the first two states of the harmonic oscillator (ψ_0 and ψ_1) using the raising and lowering operator expressions for \hat{x} and \hat{p} . You will need to use Eqs. (7) and (8). You will also need to exploit the fact that the wavefunctions for the harmonic oscillator form an orthogonal set of functions (see mathematical exercise 2). The harmonic oscillator wavefunctions are also normalized. Note: you should work only with the ψ s and not the explicit functions of the ψ s.

7. Show $[\hat{a}, \hat{a}^\dagger] \equiv \hat{a}\hat{a}^\dagger - \hat{a}^\dagger\hat{a} = 1$ by evaluating $[\hat{a}, \hat{a}^\dagger] \psi_n$.
8. Treat benzene as a particle in a box such that the length of the box is the perimeter of benzene. Draw the energy level diagram filled with the appropriate number of electrons. Experimental benzene absorbs light around 270nm or so. Does your crude treatment of the electrons in benzene jive with experiment?

Conceptual Problems

9. A certain particle in a box system scales such that mass is inversely proportional to the length of the box squared (e.g., if the length quadruples the mass halves). How does the energy level spacing scale for this system? Note: length and mass have this relation only for the special system in this problem; in general length and mass are independent parameters for the particle in a box.
10. A harmonic oscillator system scales such that mass is proportional to the force constant squared of the oscillator (e.g., if the mass doubles the force constant quadruples) How does the energy level spacing scale for this system? Note: force constant and mass have this relation only for the special system in this problem; in general force constant and mass are independent parameters for the harmonic oscillator.

- Order of the following molecules with respect to what you would predict for their UV-visible absorbance spectrum from ‘reddest’ to ‘bluest’: glutamate, vitamin A, anthracene and β -carotene. Explain.
- Order of the following molecules with respect to what you would predict for their IR absorbance spectrum for the stretch indicated by the explicitly drawn bond from ‘reddest’ to ‘bluest’: $\text{HC}\equiv\text{N}$, $\text{OC}=\text{O}$, $\text{SC}=\text{S}$, $\text{H}_3\text{C}-\text{H}$, $\text{H}_3\text{C}-\text{I}$. Explain.
- How do the spectra of a particle in a box and a harmonic oscillator compare?
- Is the zero point energy an artifact of our choice of $E = 0$. That is, can we simply define our zero of energy such that the zero point energy vanishes? Explain.
- The half-harmonic oscillator is described by the potential,

$$V(x) = \begin{cases} \infty & x < 0 \\ kx^2 & x \geq 0 \end{cases} ,$$

so for negative x it looks like a particle in a box and for positive x it looks like a harmonic oscillator. It turns out that when you solve the Schrödinger equation for this system you get a subset of the full set of wavefunctions for the regular harmonic oscillator. This is the half-harmonic oscillator has some of the exact same wavefunctions. What do you think are the wavefunctions for the half-harmonic oscillator.

Computer Problems

- Use MATHEMATICA to convince yourself through a number of examples that the Hermite polynomials are orthogonal over the interval $x = -\infty$ to $x = \infty$ with respect to weight function e^{-x^2} . That is, test

$$\int_{-\infty}^{\infty} H_n(x)H_m(x)e^{-x^2} dx = 0$$

for $m \neq n$ on few examples.

Reflective Exercises

- Is all the work required to become a chemistry major worth it for you?
- Up to this point in your career, what area of chemistry do you find the most interesting. Do you think that you might enjoy a career in that area of chemistry. (If you can’t come up with an answer to this question, is your answer to the previous question “no”?)
- During this past summer there were a number of cases where children were stolen and ultimately killed. Presumably any “reasonable” person would have a difficult time imagining a more evil act. Reports of these acts remind us that there are social ills that will require much more than good science to solve. Nonetheless skillful scientists can apply their talents towards these social problems. Can you think of several ways that science could be applied as one part of the puzzle in solving the social problem mentioned above?

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

2) $\int_0^{2\pi} e^{-imx} e^{inx} dx = \int_0^{2\pi} e^{i(n-m)x} dx = \frac{1}{i(n-m)} e^{i(n-m)x} \Big|_0^{2\pi}$
 $= \frac{1}{i(n-m)} [e^{i(n-m)2\pi} - 1] = 0$ if $n-m$ an integer
 so orthogonal

3) Just like problem 1
 $[\hat{x}, \hat{p}]^2 \psi = \hat{x}\hat{p}\hat{p}\psi - \hat{p}\hat{x}\hat{p}\psi = -i\hbar x \frac{d^2\psi}{dx^2} + i\hbar x \frac{d^2\psi}{dx^2} + \hbar^2 \psi$
 so $[\hat{x}, \hat{p}]^2 = i\hbar$

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4) In[2]:= psi[n_, x_] := Sqrt[2/a] Sin[n Pi x / a]
In[5]:= Simplify[Integrate[psi[1, x] x^2 psi[1, x], {x, 0, a}]]
Out[5]= a^2 (-3 + 2 Pi^2) / (6 Pi^2)
In[8]:= Simplify[Integrate[psi[5, x] x^2 psi[5, x], {x, 0, a}]]
Out[8]= 1/150 a^2 (50 - 3 Pi^2)
In[9]:= Simplify[Integrate[psi[7, x] x^2 psi[7, x], {x, 0, a}]]
Out[9]= 1/294 a^2 (98 - 3 Pi^2)
In[10]:= Simplify[-h^2 / (2m) Integrate[psi[1, x] D[psi[1, x], {x, 2}], {x, 0, a}]]
Out[10]= h^2 Pi^2 / (2 a^2 m)
In[13]:= Simplify[-h^2 / (2m) Integrate[psi[5, x] D[psi[5, x], {x, 2}], {x, 0, a}]]
Out[13]= 25 h^2 Pi^2 / (2 a^2 m)
In[12]:= Simplify[-h^2 / (2m) Integrate[psi[7, x] D[psi[7, x], {x, 2}], {x, 0, a}]]
Out[12]= 49 h^2 Pi^2 / (2 a^2 m)
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$\langle P \rangle_0 = \frac{\sqrt{2\pi\hbar m \omega}}{2i} \int \psi_0 (a-a^\dagger) \psi_0 = \frac{\sqrt{2\pi\hbar m \omega}}{2i} (\int \psi_0 a^\dagger \psi_0 - \int \psi_0 a \psi_0)$
 $= \frac{\sqrt{2\pi\hbar m \omega}}{2i} (-\sqrt{i} \int \psi_0 \psi_1) = 0$


$\langle P \rangle_1 = \frac{\sqrt{2\pi\hbar m \omega}}{2i} \int \psi_1 (a-a^\dagger) \psi_1 = \frac{\sqrt{2\pi\hbar m \omega}}{2i} (\int \psi_1 a^\dagger \psi_1 - \int \psi_1 a \psi_1)$
 $= \frac{\sqrt{2\pi\hbar m \omega}}{2i} (\sqrt{i} \int \psi_1 \psi_0 + \sqrt{-i} \int \psi_1 \psi_2) = 0$

7) $[\hat{a}, \hat{a}^\dagger] \psi_n = (\hat{a}\hat{a}^\dagger - \hat{a}^\dagger\hat{a}) \psi_n = \sqrt{n+1}\sqrt{n+1} \psi_n - \sqrt{n}\sqrt{n} \psi_n$
 $= (n+1 - n) \psi_n = \psi_n$

so $[\hat{a}, \hat{a}^\dagger] = 1$

9) $E_n = \frac{n\hbar^2}{8ma^2}$ $E \downarrow$ as $a \uparrow$

10) $E_n = \hbar\omega(n + \frac{1}{2})$ $E \uparrow$ as $k \uparrow$
 $\omega = \sqrt{\frac{k}{m}}$

8)  perimeter = 1.3 Å * 4 = 5.2 Å
 6π electrons so $N=3$
 $\Delta E = \frac{(2n+1)\hbar^2}{8ma^2} = \frac{2(3+1)\hbar^2}{8(9 \times 10^{-20} \text{ kg})(5.2 \times 10^{-10} \text{ m})^2} = 6.9 \times 10^{-19} \text{ J}$
 $\lambda = \frac{hc}{\Delta E} = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3.0 \times 10^8 \text{ m/s})}{6.9 \times 10^{-19} \text{ J}} = 2.88 \times 10^{-7} \text{ m}$
 $= 288 \text{ nm}$

5) $\hat{a} + \hat{a}^\dagger = 2\sqrt{\frac{m\omega}{\hbar}} \hat{x}$ solve for \hat{x}
 $\hat{x} = \frac{\sqrt{\hbar}}{\sqrt{4m\omega}} (\hat{a} + \hat{a}^\dagger)$ ✓

$\hat{a} - \hat{a}^\dagger = 2\sqrt{\frac{m\omega}{\hbar}} \frac{i\hat{p}}{m\omega} = \frac{2i}{\sqrt{2\pi\hbar m \omega}} \hat{p}$ solve for \hat{p}
 $\hat{p} = \frac{\sqrt{2\pi\hbar m \omega}}{2i} (\hat{a} - \hat{a}^\dagger)$

6) $\hat{H} = \frac{\hat{p}^2}{2m} + m\omega^2 \frac{\hat{x}^2}{2} = \frac{1}{2m} \left(\frac{2\pi\hbar m \omega}{-i} \right) (\hat{a} - \hat{a}^\dagger)(\hat{a} - \hat{a}^\dagger) + \frac{m\omega^2}{2} \frac{\hbar}{4m\omega} (\hat{a} + \hat{a}^\dagger)(\hat{a} + \hat{a}^\dagger)$

$\hat{H} = \frac{\hbar\omega}{-4} (\hat{a}\hat{a} - \hat{a}^\dagger\hat{a} - \hat{a}\hat{a}^\dagger + \hat{a}^\dagger\hat{a}) + \frac{\hbar\omega}{4} (\hat{a}\hat{a} + \hat{a}^\dagger\hat{a} + \hat{a}\hat{a}^\dagger + \hat{a}^\dagger\hat{a})$
 $\hat{H} = \frac{2\hbar\omega}{4} [\hat{a}^\dagger\hat{a} + \hat{a}\hat{a}^\dagger]$

use $\hat{a}\hat{a}^\dagger - \hat{a}^\dagger\hat{a} = 1 \rightarrow \hat{a}\hat{a}^\dagger = 1 + \hat{a}^\dagger\hat{a}$

$\hat{H} = \frac{2\hbar\omega}{4} [\hat{a}^\dagger\hat{a} + 1 + \hat{a}^\dagger\hat{a}] = \hbar\omega(\hat{a}^\dagger\hat{a} + \frac{1}{2})$ ✓

6) $\langle \hat{x} \rangle_0 = \int \psi_0^* \frac{\sqrt{\hbar}}{\sqrt{4m\omega}} (\hat{a} + \hat{a}^\dagger) \psi_0 = \frac{\sqrt{\hbar}}{\sqrt{4m\omega}} (\int \psi_0^* \hat{a} \psi_0 + \int \psi_0^* \hat{a}^\dagger \psi_0)$
 $= \frac{\sqrt{\hbar}}{\sqrt{4m\omega}} \sqrt{D+1} \int \psi_0 \psi_1 = 0$ ✓

$\langle x \rangle = \int \psi_1^* \frac{\sqrt{\hbar}}{\sqrt{4m\omega}} (\hat{a} + \hat{a}^\dagger) \psi_1 = \frac{\sqrt{\hbar}}{\sqrt{4m\omega}} (\int \psi_1^* \hat{a} \psi_1 + \int \psi_1^* \hat{a}^\dagger \psi_1)$
 $= \frac{\sqrt{\hbar}}{\sqrt{4m\omega}} (\sqrt{i} \int \psi_1 \psi_0 + \sqrt{-i} \int \psi_1 \psi_2) = 0$

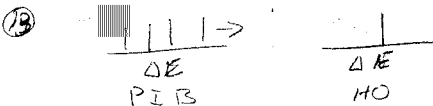
$\langle \hat{x}^2 \rangle_0 = \frac{\hbar^2}{4m\omega} \int \psi_0 (a + a^\dagger)(a + a^\dagger) \psi_0 = \frac{\hbar^2}{4m\omega} (\int \psi_0 a a \psi_0 + \int \psi_0 a a^\dagger \psi_0 + \int \psi_0 a^\dagger a \psi_0 + \int \psi_0 a^\dagger a^\dagger \psi_0)$
 $= \frac{\hbar^2}{4m\omega} (\sqrt{i}\sqrt{i} \int \psi_0 \psi_1^2) = \frac{\hbar^2}{2m\omega}$

$\langle \hat{x}^2 \rangle_1 = \frac{\hbar^2}{4m\omega} (\int \psi_1 a a \psi_1 + \int \psi_1 a a^\dagger \psi_1 + \int \psi_1 a^\dagger a \psi_1 + \int \psi_1 a^\dagger a^\dagger \psi_1)$
 $= \frac{\hbar^2}{4m\omega} (\sqrt{-i}\sqrt{-i} \int \psi_1 \psi_0^2 + \sqrt{i}\sqrt{i} \int \psi_1 \psi_2^2 + \sqrt{-i}\sqrt{i} \int \psi_1 \psi_0 \psi_2) = \frac{3\hbar^2}{2m\omega}$

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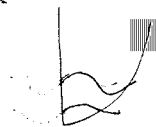
11) β -Carotene, Vitamin C, Anthracene, glutamate

12) $\text{H}_3\text{C}-\text{I}$, $\text{SC}=\text{S}$, $\text{O}=\text{C}=\text{O}$, $\text{HC}=\text{N}$ $\text{H}_3\text{C}-\text{H}$



14) No, zero point energy is fundamental it is measured relative to the bottom of potential well

15) The wavefunctions are the odd ones from the set of HO wavefunctions
 $\{\psi_1, \psi_3, \psi_5\}$



16) see last year's key

17-19) your words