CHEM 352: Examples for chapter 1.

1. The ground state wavefunction for a hydrogen atom is $\psi_0(r) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$.

   (a) What is the probability for finding the electron within radius of a_0 from the nucleus?

   (b) Two excited states of hydrogen atom are given by the following wavefunctions:

   $$\psi_1(r) = A(2 + \lambda r)e^{-\frac{r}{2a_0}} \text{ and } \psi_2(r) = Br\sin(\theta)\cos(\phi)e^{-\frac{r}{2a_0}}$$

   Proceed in the following order: 1) obtain λ from the orthogonality requirement between ψ_0 and ψ_1, 2) use the normalization requirement sepratately for ψ_1 and ψ_2 to get constants A and B, respectively.

Solution:

(a) The probability P for finding the electron within a_0 (a ball with radius a_0; denoted by V below) is:

$$P = \int_V \psi_0^* \psi_0 d\tau = \frac{1}{\pi a_0^3} \int_0^{a_0} e^{-2r/a_0} \underbrace{4\pi r^2 dr}_{=d\tau}$$

$$= \frac{4}{a_0^3} \times \frac{a_0^3 - 5a_0^3 e^{-2}}{4} = 1 - 5e^{-2} \approx 0.323$$

Note that the 4π in the volume element above comes from the fact that the function in the integral does not depend on the angles θ and ϕ and therefore the angular part can be integrated independently to yield 4π (i.e. the original volume element $d\tau = r^2 \sin(\theta) d\theta d\phi dr$ is then effectively just $4\pi r^2 dr$). Above we have used the following result from a tablebook:

$$\int x^2 e^{ax} dx = \frac{a^{ax}}{a}\left(x^2 - \frac{2x}{a} + \frac{2}{a^2}\right)$$

This was applied in the following form:

$$\int_0^{a_0} e^{-2r/a_0} r^2 dr$$
$$= \frac{e^{-2r/a_0}}{-2/a_0}\left(r^2 - \frac{2r}{-2/a_0} + \frac{2}{(-2/a_0)^2}\right) - \frac{1}{-2/a_0} \times \frac{2}{(-2/a_0)^2}$$
$$= -\frac{a_0 e^{-2}}{2}\left(a_0^2 + a_0^2 + \frac{a_0^2}{2}\right) + \frac{a_0^3}{4}$$
$$-\frac{5a_0^3 e^{-2}}{4} + \frac{a_0^3}{4} = \frac{a_0^3 - 5a_0^3 e^{-2}}{4}$$

(b) First recall the wavefunctions:

$$\psi_0(r,\theta,\phi) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$
$$\psi_1(r,\theta,\phi) = A(2+\lambda r)e^{-r/(2a_0)}, \psi_2(r,\theta,\phi) = B\sin(\theta)\cos(\phi) r e^{-r/(2a_0)}$$

First we calculate λ from the orthogonality:

$$\int \psi_1^* \psi_0 d\tau = 4\pi \int_0^\infty \psi_1^*(r)\psi_0(r) r^2 dr = \frac{4\pi A}{\sqrt{\pi a_0^3}} \int_0^\infty (2+\lambda r) e^{-3r/(2a_0)} r^2 dr = 0$$
$$\Rightarrow \int_0^\infty (2+\lambda r) e^{-3r/(2a_0)} r^2 dr = 0$$
$$\Rightarrow 2\int_0^\infty e^{-3r/(2a_0)} r^2 dr + \lambda \int_0^\infty e^{-3r/(2a_0)} r^3 dr = 0$$
$$\Rightarrow 2 \times \frac{16a_0^3}{27} + \frac{96\lambda}{81} a_0^4 = 0$$
$$\Rightarrow a_0^3 + \lambda a_0^4 = 0 \Rightarrow \lambda = -\frac{1}{a_0}$$

Then determine A from the normalization condition:

$$\int_{r=0}^{\infty}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} |\psi_1(r,\theta,\phi)|^2 r^2 \sin(\theta) dr d\theta d\phi$$

$$= 4\pi A^2 \int_{r=0}^{\infty} \left(2 - \frac{r}{a_0}\right)^2 e^{-r/a_0} r^2 dr$$

$$= 4\pi A^2 \left(4 \int_{r=0}^{\infty} r^2 e^{-r/a_0} dr - \frac{4}{a_0} \int_{r=0}^{\infty} r^3 e^{-r/a_0} dr + \frac{1}{a_0^2} \int_{r=0}^{\infty} r^4 e^{-r/a_0} dr\right)$$

$$= 4\pi A^2 \left(4 \frac{2!}{(1/a_0)^3} - \frac{4}{a_0}\frac{3!}{(1/a_0)^4} + \frac{1}{a_0^2}\frac{4!}{(1/a_0)^5}\right)$$

$$= 4\pi A^2 \left(8a_0^3 - 24a_0^3 + 24a_0^3\right) = 32\pi A^2 a_0^3 = 1$$

$$\Rightarrow A = \frac{1}{\sqrt{32\pi a_0^3}} = \frac{1}{4\sqrt{2\pi a_0^3}}$$

B can also be determined from normalization:

$$\int_{r=0}^{\infty}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} |\psi_2(r,\theta,\phi)|^2 r^2 \sin(\theta) dr d\theta d\phi$$

$$= B^2 \int_{r=0}^{\infty} r^4 e^{-r/a_0} dr \int_{\theta=0}^{\pi} \sin^3(\theta) d\theta \int_{\phi=0}^{2\pi} \cos^2(\phi) d\phi$$

$$B^2 \left(\frac{24}{(1/a_0)^5}\right) \times \frac{4}{3} \times \pi = 32 B^2 \pi a_0^5 = 1 \Rightarrow B = \frac{1}{\sqrt{32\pi a_0^5}}$$

$$= \frac{1}{4\sqrt{2\pi a_0^5}}$$

Above we have used the following integrals (tablebook):

$$\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$$

$$\int \sin^3(ax) dx = \frac{\cos(3ax)}{12a} - \frac{3\cos(ax)}{4a}$$

$$\int \cos^2(ax) dx = \frac{x}{2} + \frac{\sin(2ax)}{4a}$$

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2. (a) Which of the following functions are eigenfunctions of d/dx and d^2/dx^2: $\exp(ikx)$, $\cos(kx)$, k, and $\exp(ax^2)$.

   (b) Show that the function $f(x, y, z) = \cos(ax)\cos(by)\cos(cz)$ is an eigenfunction of the Laplacian operator (Δ) and calculate the corresponding eigenvalue.

   (c) Calculate the standard deviation Δr for the ground state of hydrogen atom $\psi_0(r)$.

   (d) Calculate the expectation value for potential energy ($V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$) in hydrogen atom ground state $\psi_0(r)$. Express the result finally in the units of eV.

   Solution:

   (a)
   - $\frac{d(e^{ikx})}{dx} = ike^{ikx} =$ "constant $\times$ original function". Thus this is an eigenfunction of the given operator.
   - $\frac{d^2(e^{ikx}}{dx^2} = \frac{d}{dx}(ike^{ikx}) = -k^2e^{ikx} =$ "constant$\times$original function". Thus this is an eigenfunction of the given operator.
   - $\frac{d(k)}{dx} = \frac{d^2(k)}{dx^2} = 0$. This could be considered as en eigenfunction with zero eigenvalue.
   - $\frac{d(e^{ax^2})}{dx} = 2axe^{ax^2} \neq$ "constant $\times$ original function", thus not an eigenfunction.
   - $\frac{d^2(e^{ax^2})}{dx^2} = \frac{d(2axe^{ax^2})}{dx} = 2a(2ax^2+1)e^{ax^2} \neq$ "constant $\times$ original function", thus not an eigenfunction.
   - $\frac{d(\cos(kx))}{dx} = -k\sin(kx)$. Not an eigenfunction.

- $\frac{d^2(\cos(kx))}{dx^2} = \frac{d(-k\sin(kx))}{dx} = -k^2\cos(kx)$. This is an eigenfunction (with eigenvalue $-k^2$).

(b) $f(x,y,z) = \cos(ax)\cos(by)\cos(cz)$. The partial derivatives are:

$$\frac{\partial f(x,y,z)}{\partial x} = -a\sin(ax)\cos(by)\cos(cz)$$
$$\frac{\partial f(x,y,z)}{\partial y} = -b\cos(ax)\sin(by)\cos(cz)$$
$$\frac{\partial f(x,y,z)}{\partial z} = -c\cos(ax)\cos(by)\sin(cz)$$

and

$$\frac{\partial^2 f(x,y,z)}{\partial x^2} = -a^2\cos(ax)\cos(by)\cos(cz)$$
$$\frac{\partial^2 f(x,y,z)}{\partial y^2} = -b^2\cos(ax)\cos(by)\cos(cz)$$
$$\frac{\partial^2 f(x,y,z)}{\partial z^2} = -c^2\cos(ax)\cos(by)\cos(cz)$$

Therefore $\Delta f(x,y,z) = -(a^2+b^2+c^2)f(x,y,z) =$ "constant $\times$ original function" and this is an eigenfunction with the corresponding eigenvalue $-(a^2+b^2+c^2)$.

(c) The standard deviation can be calculated as:

$$\psi_0(r) = \frac{1}{\sqrt{\pi a_0^3}}e^{-r/a_0}$$
$$\langle \hat{r}^2 \rangle = \frac{1}{\pi a_0^3}\int_0^\infty e^{-2r/a_0} r^2 \underbrace{4\pi r^2 dr}_{d\tau} = \frac{4}{a_0^3} \times \frac{3a_0^5}{4} = 3a_0^2$$
$$\langle \hat{r} \rangle = \frac{1}{\pi a_0^3}\int_0^\infty e^{-2r/a_0} r \underbrace{4\pi r^2 dr}_{d\tau} = \frac{3a_0}{2}$$
$$\langle \hat{r} \rangle^2 = \frac{9a_0^2}{4}$$
$$\langle \hat{r}^2 \rangle - \langle \hat{r} \rangle^2 = 3a_0^2 - \frac{9a_0^2}{4} = \frac{3a_0^2}{4}$$
$$\sqrt{\langle \hat{r}^2 \rangle - \langle \hat{r} \rangle^2} = \frac{\sqrt{3}}{2}a_0 \approx 0.87a_0$$

(d) The potential energy expectation can be calculated as:

$$\psi_0(r) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0} \text{ and } V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$$

$$\left\langle \hat{V} \right\rangle = -\frac{e^2}{4\pi^2\epsilon_0 a_0^3} \int\limits_{r=0}^{\infty} e^{-2r/a_0} \frac{1}{r} \underbrace{4\pi r^2 dr}_{d\tau} = -\frac{e^2}{\pi\epsilon_0 a_0^3} \int\limits_{r=0}^{\infty} e^{-2r/a_0} r dr$$

$$= -\frac{e^2}{\pi\epsilon_0 a_0^3} \times \frac{a_0^2}{4} = -\frac{e^2}{4\pi\epsilon_0 a_0} \approx -27.2 \text{ eV}$$

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3. Consider function $\psi(x) = \left(\frac{\pi}{\alpha}\right)^{-\frac{1}{4}} e^{-\alpha x^2/2}$. Using (only) this function, show that:

   (a) Operators $\hat{x}$ and $\hat{p}_x$ do not commute.

   (b) Operators $\hat{x}^2$ and the inversion operator $\hat{I}$ commute ($\hat{I}x = -x$).

   Note that consideration of just one function does not prove a given property in general.

   Solution:

   (a)

$$\psi(x) = \left(\frac{\pi}{\alpha}\right)^{-1/4} e^{-\alpha x^2/2}$$

$$\hat{p}_x = -i\hbar \frac{d}{dx} \text{ and } [\hat{x}, \hat{p}_x]\,\psi(x) = (\hat{x}\hat{p}_x - \hat{p}_x\hat{x})\,\psi(x)$$

   To obtain the commutator, we need to operate with $\hat{x}$ and $\hat{p}_x$:

$$(\hat{x}\hat{p}_x)\,\psi(x) = -i\hbar\left(\frac{\pi}{\alpha}\right)^{-1/4} x\frac{d}{dx}e^{-\alpha x^2/2} = i\hbar\alpha\left(\frac{\pi}{\alpha}\right)^{-1/4} x^2 e^{-\alpha x^2/2}$$

$$(\hat{p}_x\hat{x})\,\psi(x) = -i\hbar\left(\frac{\pi}{\alpha}\right)^{-1/4} \frac{d}{dx}\left(x e^{-\alpha x^2/2}\right)$$

$$= i\hbar\alpha\left(\frac{\pi}{\alpha}\right)^{-1/4} x^2 e^{-\alpha x^2/2} - i\hbar\left(\frac{\pi}{\alpha}\right)^{-1/4} e^{-\alpha x^2/2}$$

   When these are subtracted, we get:

$$(\hat{x}\hat{p}_x)\,\psi(x) - (\hat{p}_x\hat{x})\,\psi(x) = i\hbar\left(\frac{\pi}{\alpha}\right)^{-1/4} e^{-\alpha x^2/2}$$

When the wavefunction $\psi(x)$ is removed, we have:

$$[\hat{x}, \hat{p}_x] = i\hbar$$

Because the commutator between these operators is non-zero, it means that they are complementary.

(b) The commutator for the given function is:

$$\left[\hat{x}^2, \hat{I}\right]\psi(x) = \left(\hat{x}^2\hat{I} - \hat{I}\hat{x}^2\right)\left(\frac{\pi}{\alpha}\right)^{-1/4} e^{-\alpha x^2/2}$$
$$= x^2\left(\frac{\pi}{\alpha}\right)^{-1/4} e^{-\alpha(-x)^2/2} - (-x)^2\left(\frac{\pi}{\alpha}\right)^{-1/4} e^{-\alpha(-x)^2/2}$$
$$= x^2\left(\frac{\pi}{\alpha}\right)^{-1/4} e^{-\alpha x^2/2} - x^2\left(\frac{\pi}{\alpha}\right)^{-1/4} e^{-\alpha x^2/2} = 0$$

$\Rightarrow \hat{x}^2$ and $\hat{I}$ commute for the given function.

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4. A particle is described by the following wavefunction: $\psi(x) = \cos(\chi)\phi_k(x) + \sin(\chi)\phi_{-k}(x)$ where χ is a parameter (constant) and ϕ_k and ϕ_{-k} are orthonormalized eigenfunctions of the momentum operator with the eigenvalues $+\hbar k$ and $-\hbar k$, respectively.

   (a) What is the probability that a measurement gives $+\hbar k$ as the momentum of the particle?

   (b) What is the probability that a measurement gives $-\hbar k$ as the momentum of the particle?

   (c) What wavefunction would correspond to 0.90 probability for a momentum of $+\hbar k$?

   (d) Consider another system, for which $\psi = 0.9\psi_1 + 0.4\psi_2 + c_3\psi_3$. Calculate c_3 when ψ_1, ψ_2 and ψ_3 are orthonormal. Use the normalization condition for ψ.

   Solution:

(a) The probability for measuring $+\hbar k$ is $\cos^2(\chi)$. We have a superposition of the eigenfunctions of momentum and therefore the squares of the coefficients for each eigenfunction give the corresponding probability.

(b) The probability for measuring $-\hbar k$ is $\sin^2(\chi)$.

(c) Given $\cos^2(\chi) = 0.90$ (hence $\cos(\chi) = \pm 0.95$) we use the normalization condition $\cos^2(\chi) + \sin^2(\chi) = 1$ where we solve for $\sin(\chi) = \pm 0.32$. The overall sign for the wavefunction does not matter and therefore we have two possibilities for our wavefunction: $\psi = 0.95e^{ikx} \pm 0.32e^{-ikx}$.

(d) Normalization condition: $1 = (0.9)^2 + (0.4)^2 + c_3^2$. Thus $c_3 = \pm 0.17$.

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5. Consider a particle in the following one-dimensional infinitely deep box potential:

$$V(x) = \begin{cases} 0, & \text{when } |x| \leq a \\ \infty, & \text{when } |x| > a \end{cases}$$

Note that the position of the potential was chosen differently than in the lectures. The following two wavefunctions are eigenfunctions of the Hamiltonian corresponding to this potential:

$$\psi_1(x) = \frac{1}{\sqrt{a}} \cos\left(\frac{\pi x}{2a}\right) \text{ and } \psi_2(x) = \frac{1}{\sqrt{a}} \sin\left(\frac{\pi x}{a}\right)$$

with the associated eigenvalues are $E_1 = 1$ eV and $E_2 = 4$ eV. Define a superposition state ψ as $\psi = \frac{1}{\sqrt{2}}(\psi_1 + \psi_2)$.

(a) What is the average energy of the above superposition state (e.g. $< \hat{H} >$)?

(b) Plot ψ_1 and ψ_2 and determine the most probable positions for a particle in these states.

(c) What are the most probable positions for the particle given by wavefunction $\psi_3(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{3\pi x}{L}\right)$ where the box potential is now located between $[0, L]$.

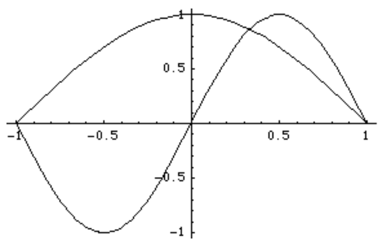
Solution:

(a) We calculate the expectation value ($\hat{H}\psi_1 = E_1\psi_1$ and $\hat{H}\psi_2 = E_2\psi_2$):

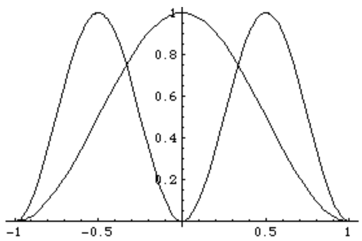
$$\left\langle \hat{H} \right\rangle = \int \psi^*(x)\hat{H}\psi(x)dx$$
$$= \frac{1}{2}\int \left(\psi_1^*(x) + \psi_2^*(x)\right)\hat{H}\left(\psi_1(x) + \psi_2(x)\right)dx$$

$$= \frac{1}{2}\int \left(\psi_1^*(x) + \psi_2^*(x)\right)\left(E_1\psi_1(x) + E_2\psi_2(x)\right)dx = \frac{1}{2}\left(E_1 + E_2\right)$$
$$= 2.5 \text{ eV}$$

(b) For $a = 1$ both $\psi_1(x)$ (one maximum) and $\psi_2(x)$ (maximum and minimum) are shown below:



The most probable values for position can be obtained from the squared wavefunctions:



ψ_1 has the maximum value at $x = 0$ whereas ψ_2 has two maxima at ± 0.5. Note that on average both will give an outcome of $\langle \hat{x} \rangle = 0$.

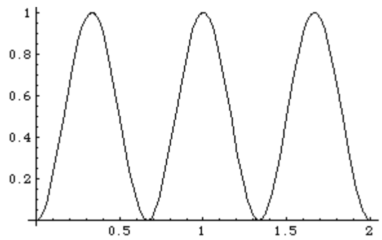
(c) The most probable positions are given by the square of the wavefunction $\psi_0(x) = (2/L)^{1/2}\sin(3\pi x/L)$. The probability function is then $|\psi_0(x)|^2 \propto \sin^2(3\pi x/L)$. The extremum points for this function can be obtained by:

$$\frac{d}{dx}\left(\sin^2(3\pi x/L)\right) = 0 \Rightarrow \sin(3\pi x/L)\cos(3\pi x/L) = 0$$
$$\Rightarrow \frac{3\pi x}{L} = n\pi \text{ or } \frac{3\pi x}{L} = \left(n + \frac{1}{2}\right)\pi$$
$$\Rightarrow x = \frac{n}{3}L \text{ or } x = \frac{n + 1/2}{3}L$$

Second derivatives can be used to identify the extrema:

$$\frac{d^2}{dx^2}\left(\sin^2(3\pi x/L)\right) \propto \cos^2\left(\frac{3\pi x}{L}\right) - \sin^2\left(\frac{3\pi x}{L}\right)$$

At $x = \frac{n}{3}L$ the values are positive which means that these correspond to (local) minima. For $x = \frac{n+1/2}{3}L$ the values are negative and these points correspond to (local) maxima. For example, when $L = 2$ the probability function looks like:



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6. Calculate the uncertainty product $\Delta p \Delta x$ for the following wavefunctions:

   (a) $\psi_n(x) = \left(\frac{2}{a}\right)^{1/2} \sin\left(\frac{n\pi x}{a}\right)$ with $0 \leq x \leq L$ (particle in a box)

   (b) $\psi_n(x) = N_v H_v\left(\sqrt{\alpha}x\right)\exp\left(-\frac{\alpha x^2}{2}\right)$ (harmonic oscillator)

   Solution:

(a) For momentum:

$$\psi_n(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right), \text{ where } 0 \le x \le L$$

$$\langle \hat{p}_x \rangle = \int_0^L \underbrace{\left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right)}_{\psi_n^*(x)} \underbrace{\left(-i\hbar \frac{d}{dx}\right)}_{\hat{p}_x} \underbrace{\left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right)}_{\psi_n(x)} dx$$

$$= -\frac{2i\hbar}{L} \int_0^L \sin\left(\frac{n\pi x}{L}\right) \frac{d}{dx}\left(\sin\left(\frac{n\pi x}{L}\right)\right) dx$$

$$= -\frac{2\pi n i\hbar}{L^2} \underbrace{\int_0^L \sin\left(\frac{n\pi x}{L}\right) \cos\left(\frac{n\pi x}{L}\right) dx}_{=0} = 0$$

$$\langle \hat{p}_x^2 \rangle = \int_0^L \underbrace{\left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right)}_{\psi_n^*} \underbrace{\left(-i\hbar \frac{d}{dx}\right)^2}_{\hat{p}_x^2} \underbrace{\left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right)}_{\psi_n} dx$$

$$= -\frac{2\hbar^2}{L} \int_0^L \sin\left(\frac{n\pi x}{L}\right) \frac{d^2}{dx^2} \sin\left(\frac{n\pi x}{L}\right) dx$$

$$= \frac{2n^2\pi^2\hbar^2}{L^3} \underbrace{\int_0^L \sin\left(\frac{n\pi x}{L}\right) \sin\left(\frac{n\pi x}{L}\right) dx}_{=\frac{L}{2}} = \frac{n^2\pi^2\hbar^2}{L^2}$$

Now we can calculate $\Delta p = \sqrt{\langle \hat{p}_x^2 \rangle - \langle \hat{p}_x \rangle^2} = \frac{n\pi\hbar}{L}$. For position we have:

$$\langle\hat{x}\rangle = \int_0^L \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right) x \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right) dx$$

$$= \frac{2}{L}\int_0^L x\sin^2\left(\frac{n\pi x}{L}\right) dx = L/2$$

$$\langle\hat{x}^2\rangle = \int_0^L \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right) x^2 \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right) dx$$

$$= \frac{2}{L}\underbrace{\int_0^L x^2\sin^2\left(\frac{n\pi x}{L}\right) dx}_{=\frac{L^3(4n^2\pi^2-6)}{24\pi^2n^2}} = \frac{L^2(2\pi^2n^2-3)}{6\pi^2n^2} = \frac{L^2}{3}\left(1-\frac{3}{2\pi^2n^2}\right)$$

Now $\Delta x = \sqrt{\langle\hat{x}^2\rangle - \langle\hat{x}\rangle^2} = \sqrt{\frac{L^2}{3}\left(1-\frac{3}{2\pi^2n^2}\right) - \frac{L^2}{4}} = L\sqrt{\frac{1}{12}-\frac{1}{2\pi^2n^2}}$. Since we have both Δx and Δp, we can evaluate the uncertainty product:

$$\Delta p\Delta x = \hbar\sqrt{\frac{n^2\pi^2}{12}-\frac{6}{12}}$$

The smallest value is obtained with $n = 1$: $\Delta p\Delta x \approx 0.568\times\hbar > \frac{\hbar}{2}$.

(b) First recall that:

$$\psi_n(x) = N_v H_v\left(\sqrt{\alpha}x\right) e^{-\alpha x^2/2}, \text{ where } N_v = \frac{1}{\sqrt{2^v v!}}\left(\frac{\alpha}{\pi}\right)^{1/4}$$

Also the following relations for Hermite polynomials are used (lecture notes & tablebook):

$$H_{v+1} = 2yH_v - 2vH_{v-1}$$

$$\int_{-\infty}^{\infty} H_{v'}(y)H_v(y)e^{-y^2}dy = \begin{cases} 0, & \text{if } v \neq v' \\ \sqrt{\pi}2^v v!, & \text{if } v = v' \end{cases}$$

Denote $y = \sqrt{\alpha}x$ and hence $dy = \sqrt{\alpha}dx$. Now $\langle \hat{x} \rangle$ is given by:

$$\langle \hat{x} \rangle = N_v^2 \int_{-\infty}^{\infty} H_v\left(\sqrt{\alpha}x\right) e^{-\alpha x^2/2} x H_v\left(\sqrt{\alpha}x\right) e^{-\alpha x^2/2} dx$$

$$= \frac{N_v^2}{\alpha} \int_{-\infty}^{\infty} H_v(y) e^{-y^2/2} y H_v(y) e^{-y^2/2} dy$$

$$= \frac{N_v^2}{\alpha} \int_{-\infty}^{\infty} \underbrace{H_v(y) y}_{=\frac{1}{2}H_{v+1}(y) + vH_{v-1}(y)} H_v(y) e^{-y^2} dy = 0$$

The last two steps involved using the recursion relation for Hermite polynomials as well as their orthogonality property. Next we calculate $\langle \hat{x}^2 \rangle$:

$$\left\langle \hat{x}^2 \right\rangle = \frac{N_v^2}{\alpha^{3/2}} \int_{-\infty}^{\infty} \left(y H_v(y)\right)^2 e^{-y^2} dy$$

$$= \frac{N_v^2}{\alpha^{3/2}} \int_{-\infty}^{\infty} \left(\frac{1}{2} H_{v+1}(y) + v H_{v-1}(y)\right)^2 e^{-y^2} dy$$

$$= \sqrt{\pi} \frac{N_v^2}{\alpha^{3/2}} \left(\frac{2^{v+1}(v+1)!}{4} + v^2 2^{v-1}(v-1)!\right)$$

$$= \frac{1}{2\alpha}\left((v+1) + v\right) = \frac{1}{\alpha}\left(v + \frac{1}{2}\right) = \frac{\hbar}{\sqrt{\mu k}}\left(v + \frac{1}{2}\right)$$

Combining the above calculations gives $\Delta x = \sqrt{\left(v + \frac{1}{2}\right) \frac{\hbar}{\sqrt{\mu k}}}$. Next we calculate Δp:

$$\hat{p} = -i\hbar \frac{d}{dx} \text{ and } dy = \sqrt{\alpha} dx.$$

$$\langle \hat{p} \rangle = \int_{-\infty}^{\infty} N_v H_v(y) e^{-y^2/2} \hat{p} \left(N_v H_v(y) e^{-y^2/2}\right) dy$$

$$= -i\hbar N_v^2 \int_{-\infty}^{\infty} H_v(y) e^{-y^2/2} \frac{d}{dx} \left(H_v(y) e^{-y^2/2}\right) dy$$

Above differentiation of the eigenfunction changes parity and therefore the overall parity of the integrand is odd. Integral of odd function is zero and thus $\langle \hat{p} \rangle = 0$. For $\langle \hat{p}^2 \rangle$ we have:

$$\left\langle \hat{p}^2 \right\rangle = \int_{-\infty}^{\infty} N_v H_v(y) e^{-y^2/2} \hat{p}^2 N_v H_v(y) e^{-y^2/2} \frac{dy}{\sqrt{\alpha}}$$

The operator must also be transformed from x to y: $\hat{p}^2 = (-i\hbar d/dx)^2$ $= (-i\hbar\sqrt{\alpha} d/dx)^2)$. The above becomes now:

$$\int_{-\infty}^{\infty} N_v H_v(y) e^{-y^2/2} \left(-\hbar^2 \alpha \frac{d^2}{dy^2} \right) \left(N_v H_v(y) e^{-y^2/2} \right) \frac{dy}{\sqrt{\alpha}}$$

$$= -\hbar^2 \sqrt{\alpha} N_v^2 \int_{-\infty}^{\infty} H_v(y) e^{-y^2/2} \frac{d^2}{dy^2} \left(H_v(y) e^{-y^2/2} \right) dy$$

$$= -\hbar^2 \sqrt{\alpha} N_v^2 \int_{-\infty}^{\infty} H_v(y) \left[(y^2 - 1) H_v(y) \underbrace{-2y H_v'(y) + H_v''(y)}_{=-2vH_v(y)} \right] e^{-y^2} dy$$

$$= -\hbar^2 \sqrt{\alpha} N_v^2 \int_{-\infty}^{\infty} H_v(y) \left[(y^2 - 1) H_v(y) - 2v H_v(y) \right] e^{-y^2} dy$$

$$= -\hbar^2 \sqrt{\alpha} N_v^2 \left[(-2v - 1) \underbrace{\int_{-\infty}^{\infty} H_v^2(y) e^{-y^2} dy}_{=\sqrt{\pi} 2^v v!} + \int_{-\infty}^{\infty} \underbrace{y^2 H_v^2(y)}_{=\left(\frac{1}{2} H_{v+1}(y) + v H_{v-1}(y)\right)^2} e^{-y^2} dy \right]$$

$$= -\hbar^2 \sqrt{\alpha} N_v^2 \left[(-2v - 1) \sqrt{\pi} 2^v v! + \frac{1}{4} \sqrt{\pi} 2^{v+1} (v+1)! + v^2 \sqrt{\pi} 2^{v-1} (v-1)! \right]$$

$$= \hbar^2 \sqrt{\alpha} N_v^2 \sqrt{\pi} 2^v v! \left[2v + 1 - \frac{v+1}{2} - \frac{v}{2} \right] = \hbar^2 \alpha \left[v + \frac{1}{2} \right]$$

$$= \hbar \sqrt{mk} \left[v + \frac{1}{2} \right]$$

Therefore we have $\Delta p = \sqrt{\hbar\sqrt{mk}\left[v+\frac{1}{2}\right]}$. Overall we then have $\Delta x \Delta p = \sqrt{\left(v+\frac{1}{2}\right)\frac{\hbar}{\sqrt{mk}}}\sqrt{\hbar\sqrt{mk}\left[v+\frac{1}{2}\right]} = \hbar(v+\frac{1}{2}) \geq \frac{\hbar}{2}$.

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7. Scanning tunneling microscopy (STM) is a technique for visualizing samples at atomic resolution. It is based on tunneling of electron through the vacuum space between the STM tip and the sample. The tunneling current ($I \propto |\psi|^2$ where ψ is the electron wavefunction) is very sensitive to the distance between the tip and the sample. Assume that the wavefunction for electron tunneling through the vacuum is given by $\psi(x) = B\exp^{-Kx}$ with $K = \sqrt{2m_e(V-E)/\hbar^2}$ and $V - E =$ 2.0 eV. What would be the relative change in the tunneling current I when the STM tip is moved from $x_1 = 0.50$ nm to $x_2 = 0.60$ nm from the sample (e.g. $I_1/I_2 = ?$).

   Solution:

   The current is proportional to the square the wavefunction ($|\psi(x)|^2$):

$$
\begin{aligned}
& I \propto |\psi(x)|^2 = B^2 e^{-2Kx} \\
& \frac{I_1}{I_2} = e^{-2K(x_1-x_2)} \\
& K = \left(2m_e \underbrace{(V-E)}_{=2\text{ eV}}/\hbar^2\right)^{1/2} \\
& = \left(\frac{2(9.11\times10^{-31}\text{ kg})(2.0\text{ eV})(1.602\times10^{-19}\text{J/eV})}{(1.0546\times10^{-34}\text{ Js})^2}\right)^{1/2} \\
& -2K(x_1-x_2) = -2K\times(0.10\times10^{-9}\text{ m}) \approx 1.45 \\
& \Rightarrow \frac{I_1}{I_2} \approx 4.3
\end{aligned}
$$

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8. Show that the sperhical harmonic functions a) $Y_{0,0}$, b) $Y_{2,-1}$ and c) $Y_{3,3}$ are eigenfunctions of the (three-dimensional) rigid rotor Hamiltonian. What are the rotation energies and angular momenta in each case?

Solution:

$$\hat{H}\psi(r,\theta,\phi) = E\psi(r,\theta,\phi) \text{ where } \hat{H} = -\frac{\hbar^2}{2I}\Lambda^2$$
$$\Lambda^2 = \frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\sin(\theta)\frac{\partial}{\partial\theta}$$

Since $-\frac{\hbar^2}{2I}$ is constant, it is sufficient to show that spherical harmonics are eigenfunctions of Λ^2. We operate on the given spherical harmonics by Λ^2.

(a) $\Lambda^2 Y_0^0(\theta,\phi) = \Lambda^2\frac{1}{2\sqrt{\pi}} = 0$ (no angular dependency). The rotation energy is $E = -\frac{\hbar^2}{2I}\times 0 = 0$. Also $L^2 = 0\times\hbar^2 \Rightarrow L = 0$ (since $\hat{L}^2 = -\hbar^2\Lambda^2$).

(b) $\Lambda^2 Y_2^{-1}(\theta,\phi) =$ ...differentiation... $= -6Y_2^{-1}(\theta,\phi)$. The rotation energy is $E = -\frac{\hbar^2}{2I}\times(-6) = \frac{3\hbar^2}{I}$. Also $L^2 = 6\times\hbar^2 \Rightarrow L = \sqrt{6}\hbar$.

(c) Expression for Y_3^3 was not given in the lecture notes. We use Maxima to obtain the expression: $Y_3^3(\theta,\phi) = \frac{5\sqrt{7}e^{3\phi i}\sin^3(\theta)}{8\sqrt{5\pi}}$. Then we need to evaluate: $\Lambda^2 Y_3^3(\theta,\phi) =$ ...differentiation... $= -12Y_3^3(\theta,\phi)$. From this we can get the rotational energy as $E = \frac{6\hbar^2}{I}$. Also $L^2 = 12\times\hbar^2 \Rightarrow L = \sqrt{12}\hbar$.

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9. Calculate the z-component of angular momentum and the rotational kinetic energy in planar (e.g. 2-dimensional; rotation in xy-plane) rotation for the following wavefunctions (ϕ is the rotation angle with values between $[0, 2\pi[$):

(a) $\psi = e^{i\phi}$

(b) $\psi = e^{-2i\phi}$

(c) $\psi = \cos(\phi)$

(d) $\psi = \cos(\chi)e^{i\phi} + \sin(\chi)e^{-i\phi}$

Solution:

The Hamiltonian for 2-D rotation is $\hat{H} = \frac{\hat{L}_z^2}{2I} = -\frac{\hbar^2}{2I}\frac{d^2}{d\phi^2}$ where the rotation axis is denoted by z and ϕ is the angle of rotation.

(a) Operate first by $\hat{L}_z$ on $e^{i\phi}$: $\hat{L}_z e^{i\phi} = -i\hbar\frac{d}{d\phi}e^{i\phi} = \hbar e^{i\phi}$. Thus $\hat{H}e^{i\phi} = \frac{\hbar^2}{2I}e^{i\phi}$.

(b) The same reasoning gives: $\hat{L}_z e^{-2i\phi} = -i\hbar\frac{d}{d\phi}e^{-2i\phi} = -2\hbar e^{-2i\phi}$ and $\hat{H}e^{-2i\phi} = \frac{4\hbar^2}{2I}e^{-2i\phi}$.

(c) The given wavefunction is not an eigenfunction of $\hat{L}_z$: $\hat{L}_z \cos(\phi) = -i\hbar\left(-\sin(\phi)\right)$ (expectation value is zero). However, it is an eigenfunction of $\hat{H}$: $\hat{H}\cos(\phi) = -\frac{\hbar^2}{2I}\frac{d^2}{d\phi^2}\cos(\phi) = \frac{\hbar^2}{2I}\cos(\phi)$.

(d) Operation by $\hat{L}_z$ would change the plus sign in the middle of the wavefunction into a minus, hence this is not an eigenfunction of $\hat{L}_z$. It is an eigenfunction of $\hat{H}$: $\hat{H}(\cos(\chi)e^{i\phi} + \sin(\chi)e^{-i\phi}) = -\frac{\hbar^2}{2I}\left((i)^2\cos(\chi)e^{i\phi} + (-i)^2\sin(\chi)e^{-i\phi}\right) = \frac{\hbar^2}{2I}\left(\cos(\chi)e^{i\phi} + \sin(\chi)e^{-i\phi}\right)$.
