## 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:

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

Proceed in the following order: 1) obtain  $\lambda$  from the orthogonality requirement between  $\psi_0$  and  $\psi_1$ , 2) use the normalization requirement sepratately for  $\psi_1$  and  $\psi_2$  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  $4\pi$  in the volume element above comes from the fact that the function in the integral does not depend on the angles  $\theta$  and  $\phi$  and therefore the angular part can be integrated independently to yield  $4\pi$  (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:

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

This was applied in the following form:

$$\begin{split} &\int_{0}^{a_{0}} e^{-2r/a_{0}} r^{2} dr \\ &= \frac{e^{-2r/a_{0}}}{-2/a_{0}} \left( r^{2} - \frac{2r}{-2/a_{0}} + \frac{2}{(-2/a_{0})^{2}} \right) - \frac{1}{-2/a_{0}} \times \frac{2}{(-2/a_{0})^{2}} \\ &= -\frac{a_{0}e^{-2}}{2} \left( a_{0}^{2} + a_{0}^{2} + \frac{a_{0}^{2}}{2} \right) + \frac{a_{0}^{3}}{4} \\ &- \frac{5a_{0}^{3}e^{-2}}{4} + \frac{a_{0}^{3}}{4} = \frac{a_{0}^{3} - 5a_{0}^{3}e^{-2}}{4} \end{split}$$

(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  $\lambda$  from the orthogonality:

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

Then determine A from the normalization condition:

$$\begin{split} &\int_{r=0}^{\infty} \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} |\psi_1(r,\theta,\phi)|^2 r^2 \sin(\theta) dr d\theta d\phi \\ &= 4\pi A^2 \int_{r=0}^{\infty} \left(2 - \frac{r}{a_0}\right)^2 e^{-r/a_0} r^2 dr \\ &= 4\pi A^2 \left(4 \int_{r=0}^{\infty} r^2 e^{-r/a_0} dr - \frac{4}{a_0} \int_{r=0}^{\infty} r^3 e^{-r/a_0} dr + \frac{1}{a_0^2} \int_{r=0}^{\infty} r^4 e^{-r/a_0} dr\right) \end{split}$$

$$= 4\pi A^2 \left( 4\frac{2!}{(1/a_0)^3} - \frac{4}{a_0}\frac{3!}{(1/a_0)^4} + \frac{1}{a_0^2}\frac{4!}{(1/a_0)^5} \right)$$
$$= 4\pi A^2 \left( 8a_0^3 - 24a_0^3 + 24a_0^3 \right) = 32\pi A^2 a_0^3 = 1$$
$$\Rightarrow A = \frac{1}{\sqrt{32\pi a_0^3}} = \frac{1}{4\sqrt{2\pi a_0^3}}$$

 ${\cal B}$  can also be determined from normalization:

$$\int_{r=0}^{\infty} \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} |\psi_2(r,\theta,\phi)|^2 r^2 \sin(\theta) dr d\theta d\phi$$
  
=  $B^2 \int_{r=0}^{\infty} r^4 e^{-r/a_0} dr \int_{\theta=0}^{\pi} \sin^3(\theta) d\theta \int_{\phi=0}^{2\pi} \cos^2(\phi) d\phi$   
 $B^2 \left(\frac{24}{(1/a_0)^5}\right) \times \frac{4}{3} \times \pi = 32B^2 \pi a_0^5 = 1 \Rightarrow B = \frac{1}{\sqrt{32\pi a_0^5}}$   
=  $\frac{1}{4\sqrt{2\pi a_0^5}}$ 

Above we have used the following integrals (tablebook):

$$\int_{0}^{\infty} x^{n} e^{-ax} dx = \frac{n!}{a^{n+1}}$$
$$\int \sin^{3}(ax) dx = \frac{\cos(3ax)}{12a} - \frac{3\cos(ax)}{4a}$$
$$\int \cos^{2}(ax) dx = \frac{x}{2} + \frac{\sin(2ax)}{4a}$$

- 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 ( $\Delta$ ) and calculate the corresponding eigenvalue.
  - (c) Calculate the standard deviation  $\Delta r$  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.

- (a)  $\frac{d(e^{ikx})}{dx} = ike^{ikx} =$  "constant × 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×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 × 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 × 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 × 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:

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

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

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

- 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  $\hat{p}_x$ :

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

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:

$$\begin{bmatrix} \hat{x}^2, \hat{I} \end{bmatrix} \psi(x) = \left( \hat{x}^2 \hat{I} - \hat{I} \hat{x}^2 \right) \left( \frac{\pi}{\alpha} \right)^{-1/4} e^{-\alpha x^2/2}$$
$$= x^2 \left( \frac{\pi}{\alpha} \right)^{-1/4} e^{-\alpha (-x)^2/2} - (-x)^2 \left( \frac{\pi}{\alpha} \right)^{-1/4} e^{-\alpha (-x)^2/2}$$
$$= x^2 \left( \frac{\pi}{\alpha} \right)^{-1/4} e^{-\alpha x^2/2} - x^2 \left( \frac{\pi}{\alpha} \right)^{-1/4} e^{-\alpha x^2/2} = 0$$
$$\Rightarrow \hat{x}^2 \text{ and } \hat{I} \text{ commute for the given function.}$$

- 4. A particle is described by the following wavefunction:  $\psi(x) = \cos(\chi)\phi_k(x)$ +  $\sin(\chi)\phi_{-k}(x)$  where  $\chi$  is a parameter (constant) and  $\phi_k$  and  $\phi_{-k}$  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  $\psi_1$ ,  $\psi_2$  and  $\psi_3$  are orthonormal. Use the normalization condition for  $\psi$ .

- (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  $c_3 = \pm 0.17$ .
- 5. Consider a particle in the following one-dimensional infinitely deep box potential:

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

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:

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

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

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

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



 $\psi_1$  has the maximum value at x = 0 whereas  $\psi_2$  has two maxima at  $\pm 0.5$ . 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:



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  $0 \le x \le L$  (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)

(a) For momentum:

$$\psi_n(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right), \text{ where } 0 \le x \le L$$
$$\langle \hat{p}_x \rangle = \int_0^L \underbrace{\left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right)}_{\psi_n^*(x)} \underbrace{\left(-i\hbar \frac{d}{dx}\right)}_{\hat{p}_x} \underbrace{\left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right)}_{\psi_n(x)} dx$$
$$= -\frac{2i\hbar}{L} \int_0^L \sin\left(\frac{n\pi x}{L}\right) \frac{d}{dx} \left(\sin\left(\frac{n\pi x}{L}\right)\right) dx$$

$$= -\frac{2\pi ni\hbar}{L^2} \int_{0}^{L} \sin\left(\frac{n\pi x}{L}\right) \cos\left(\frac{n\pi x}{L}\right) dx = 0$$

$$= 0$$

$$\langle \hat{p}_x^2 \rangle = \int_{0}^{L} \underbrace{\left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right)}_{\psi_n^*} \underbrace{\left(-i\hbar \frac{d}{dx}\right)^2}_{\hat{p}_x^2} \underbrace{\left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right)}_{\psi_n} dx$$

$$= -\frac{2\hbar^2}{L} \int_{0}^{L} \sin\left(\frac{n\pi x}{L}\right) \frac{d^2}{dx^2} \sin\left(\frac{n\pi x}{L}\right) dx$$

$$= \frac{2n^2 \pi^2 \hbar^2}{L^3} \int_{0}^{L} \sin\left(\frac{n\pi x}{L}\right) \sin\left(\frac{n\pi x}{L}\right) dx = \frac{n^2 \pi^2 \hbar^2}{L^2}$$

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:

$$\begin{aligned} \langle \hat{x} \rangle &= \int_{0}^{L} \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right) x \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right) dx \\ &= \frac{2}{L} \int_{0}^{L} x \sin^{2}\left(\frac{n\pi x}{L}\right) dx = L/2 \\ \langle \hat{x}^{2} \rangle &= \int_{0}^{L} \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right) x^{2} \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right) dx \\ &= \frac{2}{L} \int_{0}^{L} x^{2} \sin^{2}\left(\frac{n\pi x}{L}\right) dx = \frac{L^{2}(2\pi^{2}n^{2}-3)}{6\pi^{2}n^{2}} = \frac{L^{2}}{3} \left(1 - \frac{3}{2\pi^{2}n^{2}}\right) \\ &= \frac{L^{3}(4n^{2}\pi^{2}-6)}{24\pi^{2}n^{2}} \end{aligned}$$

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

$$\psi_n(x) = N_v H_v \left(\sqrt{\alpha}x\right) e^{-\alpha x^2/2}$$
, 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:

$$\begin{aligned} \langle \hat{x} \rangle &= N_v^2 \int_{-\infty}^{\infty} H_v \left( \sqrt{\alpha} x \right) e^{-\alpha x^2/2} x H_v \left( \sqrt{\alpha} x \right) e^{-\alpha x^2/2} dx \\ &= \frac{N_v^2}{\alpha} \int_{-\infty}^{\infty} H_v(y) e^{-y^2/2} y H_v(y) e^{-y^2/2} dy \\ &= \frac{N_v^2}{\alpha} \int_{-\infty}^{\infty} \underbrace{H_v(y) y}_{=\frac{1}{2} H_{v+1}(y) + v H_{v-1}(y)} H_v(y) e^{-y^2} dy = 0 \end{aligned}$$

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

$$\begin{split} \left\langle \hat{x}^2 \right\rangle &= \frac{N_v^2}{\alpha^{3/2}} \int\limits_{-\infty}^{\infty} \left( y H_v(y) \right)^2 e^{-y^2} dy \\ &= \frac{N_v^2}{\alpha^{3/2}} \int\limits_{-\infty}^{\infty} \left( \frac{1}{2} H_{v+1}(y) + v H_{v-1}(y) \right)^2 e^{-y^2} dy \\ &= \sqrt{\pi} \frac{N_v^2}{\alpha^{3/2}} \left( \frac{2^{v+1}(v+1)!}{4} + v^2 2^{v-1}(v-1)! \right) \\ &= \frac{1}{2\alpha} \left( (v+1) + v \right) = \frac{1}{\alpha} \left( v + \frac{1}{2} \right) = \frac{\hbar}{\sqrt{\mu k}} \left( v + \frac{1}{2} \right) \end{split}$$

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

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

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

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

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:

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

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:

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

$$\begin{split} &= -\hbar^2 \sqrt{\alpha} N_v^2 \int_{-\infty}^{\infty} H_v(y) e^{-y^2/2} \frac{d^2}{dy^2} \left( H_v(y) e^{-y^2/2} \right) dy \\ &= -\hbar^2 \sqrt{\alpha} N_v^2 \int_{-\infty}^{\infty} H_v(y) \left[ (y^2 - 1) H_v(y) \underbrace{-2y H_v'(y) + H_v''(y)}_{=-2v H_v(y)} \right] e^{-y^2} dy \\ &= -\hbar^2 \sqrt{\alpha} N_v^2 \int_{-\infty}^{\infty} H_v(y) \left[ (y^2 - 1) H_v(y) - 2v H_v(y) \right] e^{-y^2} dy \\ &= -\hbar^2 \sqrt{\alpha} N_v^2 \left[ (-2v - 1) \int_{\underbrace{-\infty}}^{\infty} H_v^2(y) e^{-y^2} dy + \int_{-\infty}^{\infty} \underbrace{y^2 H_v^2(y)}_{=\left(\frac{1}{2} H_{v+1}(y) + v H_{v-1}(y)\right)^2} e^{-y^2} dy \\ &= -\hbar^2 \sqrt{\alpha} N_v^2 \left[ (-2v - 1) \sqrt{\pi} 2^v v! + \frac{1}{4} \sqrt{\pi} 2^{v+1} (v+1)! + v^2 \sqrt{\pi} 2^{v-1} (v-1)! \right] \\ &= \hbar^2 \sqrt{\alpha} N_v^2 \sqrt{\pi} 2^v v! \left[ 2v + 1 - \frac{v+1}{2} - \frac{v}{2} \right] = \hbar^2 \alpha \left[ v + \frac{1}{2} \right] \\ &= \hbar \sqrt{mk} \left[ v + \frac{1}{2} \right] \end{split}$$

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

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  $\psi$  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  $(|\psi(x)|^2)$ :

$$I \propto |\psi(x)|^{2} = B^{2}e^{-2Kx}$$

$$\frac{I_{1}}{I_{2}} = e^{-2K(x_{1}-x_{2})}$$

$$K = \left(2m_{e}\underbrace{(V-E)}_{=2 \text{ eV}}/\hbar^{2}\right)^{1/2}$$

$$= \left(\frac{2(9.11 \times 10^{-31} \text{ kg})(2.0 \text{ eV})(1.602 \times 10^{-19} \text{ J/eV})}{(1.0546 \times 10^{-34} \text{ Js})^{2}}\right)^{1/2}$$

$$-2K(x_{1}-x_{2}) = -2K \times (0.10 \times 10^{-9} \text{ m}) \approx 1.45$$

$$\Rightarrow \frac{I_{1}}{I_{2}} \approx 4.3$$

8. Show that the sperical 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  $\Lambda^2$ . We operate on the given spherical harmonics by  $\Lambda^2$ .

- (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)  $\Lambda^2 Y_2^{-1}(\theta, \phi) = \dots$  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:  $\Lambda^2 Y_3^3(\theta, \phi) = \dots$  differentiation...  $= -12Y_3^3(\theta, \phi)$ . From this we can get the rotational energy as  $E = \frac{6\hbar^2}{I}$ . Also  $L^2 = 12 \times \hbar^2 \Rightarrow L = \sqrt{12}\hbar$ .
- 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 ( $\phi$  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)  $\psi = \cos(\chi)e^{i\phi} + \sin(\chi)e^{-i\phi}$

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  $\phi$  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  $\hat{L}_z$ :  $\hat{L}_z \cos(\phi) = -i\hbar (-\sin(\phi))$  (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  $\hat{H}$ :  $\hat{H}(\cos(\chi)e^{i\phi} + \sin(\chi)e^{-i\phi}) = -\frac{\hbar^2}{2I}\left((i)^2\cos(\chi)e^{i\phi} + (-i)^2\sin(\chi)e^{-i\phi}\right) = \frac{\hbar^2}{2I}\left(\cos(\chi)e^{i\phi} + \sin(\chi)e^{-i\phi}\right).$