CHEM 352: Homework 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.

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.

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.

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.

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 $[0, L]$.

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)

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. $I_1/I_2 = ?$).

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?

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