

HOMEWORK 1
Review of the Fundamentals of Quantum Mechanics
Due Monday, February 2, 4:30 pm

Problem 1: Radial parts of the Hydrogen atomic orbitals

The Schrödinger equation for the hydrogen atom is:

$$-\frac{\hbar^2 \nabla^2 \Psi}{8\pi^2 m} - \frac{e^2}{4\pi\epsilon_0 r} \Psi = E\Psi$$

The solution is obtained by using the spherical symmetry of the atom and expressing the solution in a separated form. The solutions are:

$$\Psi_{nlm}(r, \theta, \phi) = N_{nl} F_{nl}\left(\frac{2r}{na_B}\right) Y_{lm}(\theta, \phi)$$

where N_{nl} is the normalization constant to ensure that the integral of $|\Psi_{nlm}(r, \theta, \phi)|^2$ overall space is unity:

$$N_{nl} = \frac{2}{n^2} \left(\frac{(n-l-1)!}{[a_B(n+l)!]^3} \right)^{1/2}$$

and a_B is the Bohr radius $a_B = \frac{4\pi\epsilon_0 \hbar^2}{me^2}$. $Y_{lm}(\theta, \phi)$ is a spherical harmonic and is a function of

only the angular variables θ and ϕ . The radial part of the solution is $g_{nl}(r) = N_{nl} F_{nl}\left(\frac{2r}{na_B}\right)$ and is normalized so as to satisfy

$$\int_0^\infty r^2 (g_{nl}(r))^2 dr = 1$$

The functions $F_{nl}(\rho)$ are given by:

$$F_{nl}(\rho) = e^{-\rho/2} \rho^l L_{n+1}^{2l+1}(\rho)$$

where $\rho = 2r/a_B$

and $L_{n+1}^{2l+1}(\rho)$ are associated Laguerre polynomials given by

$$L_{n+1}^{2l+1}(\rho) = \sum_{k=0}^{n-l-1} (-1)^{k+2l} \frac{[(n+l)!]^2 \rho^k}{(n-l-1-k)!(2l+1+k)!k!}$$

- a) Using these formulas, obtain the 1s, 2s, 3s, 3p, and 3d radial solutions and sketch them. Comment on the number of nodes.

- b) With the wavefunctions from part (a), find the mean radial positions and mean square radial position of an electron:

$$\langle r \rangle = \int_{\text{all space}} r |\Psi_{nlm}(r, \theta, \phi)|^2 dr = \frac{a_B}{2} (3n^2 - l(l+1))$$

$$\langle r^2 \rangle = \int_{\text{all space}} r^2 |\Psi_{nlm}(r, \theta, \phi)|^2 dr = a_B^2 \frac{n^2}{2} (5n^2 + 1 - 3l(l+1))$$

Notice that for a given n the means decrease as the angular momentum increases. Does this accord with your sketches?

- c) Compare the value for the mean radial position for 3d, 4s, and 4p orbitals.
- d) Returning to the Schrödinger equation, we can understand why in a given shell (i.e. a given n) the orbitals are more contracted the higher the angular momentum by the following argument. The functions F_{nl} are solutions of the radial part of the Schrödinger equation.

$$-\frac{\hbar^2}{8\pi^2 m} \frac{1}{r} \frac{d^2}{dr^2} (rF_l) + \left(\frac{\hbar^2 l(l+1)}{8\pi^2 m r^2} - \frac{e^2}{4\pi\epsilon_0 r} \right) F_l = E F_l.$$

The total energy of the electron E consists of its kinetic energy $mv^2/2$ and its potential energy $V(r)$. The total energy is conserved. The kinetic energy can be resolved into two components. The first component arises from radial oscillations of the electron through the nucleus and equals $mv_r^2/2$, where v_r is the radial velocity. The second component arises from the circulating motion of the electron around the nucleus with angular momentum L . The kinetic energy associated with this is $L^2/2mr^2$. The total energy and the angular momentum are conserved

$$E = mv_r^2/2 + V(r) + L^2/2mr^2.$$

This equation is true both for a classical particle and a quantum particle. By expressing L^2 as $\hbar^2 l(l+1)/4\pi^2$ and

$mv_r^2/2$ as the radial part of $-\frac{\hbar^2 \nabla^2}{8\pi^2 m}$ obtain the above radial Schrödinger equation.

Using the conservation of the total energy and the independence of the total energy on l give a qualitative argument for why the orbitals contract as l increases.

Problem 2: Angular Solutions of the Hydrogen atomic orbitals

In introductory classes to chemistry and quantum mechanics you probably saw the shapes of a few atomic orbitals. The shape of these orbitals depends on the radial term which depends on the spherically symmetric potential. However, a good idea about the shapes of orbitals can be found

by looking at the angular parts which are a linear combination of spherical harmonic functions. The eigenfunctions of the angular dependent part of the Schrödinger equation for the hydrogen atom are the spherical harmonics $Y_{lm}(\vartheta, \phi)$. To do this problem, it may be helpful to refer to the Hydrogen orbital shapes in the course lecture slides or your Quantum Mechanics textbook. Also, Chapter 1 of Sutton's "[Electronic Structure of Materials](#)" will be useful.

- Using Mathematica (or any similar software), plot all the relevant spherical harmonic functions for $l=1$. Create 3D plots of the absolute squares of all three functions. Which of these harmonic functions represents the p_z orbital? If using Mathematica, the SphericalPlot3D and SphericalHarmonicY functions will be useful.
- Guess the functional form of p_x and p_y based on a symmetry argument, starting from what you know about the form of p_z from part (a) above. Then, express each function as a linear combination of the spherical harmonics. **Hint:** What is Y_{10} proportional to in cylindrical coordinates? What should the p_x and p_y orbitals be proportional to? How does this relate to the functional forms of the spherical harmonics from part (a)?
- Plot the rest of the harmonics from $l=0$ to $l=2$. Show that by taking linear combinations of these, the d_{xy} and $d_{3z^2-r^2}$ orbitals can be obtained. Plot these orbitals.

Problem 3: Fermi Holes and Fermi Heaps

When the angular quantum number is greater than zero, more than two electrons can be accommodated in a subshell. What is known as a Fermi heap occurs when the electrons have a high probability of being found near each other; a Fermi hole occurs when the electrons have a low probability of being found near each other. For an atom of Carbon with electron configuration $1s^2 2s^2 2p^2$ consider the two cases of relative electron orientation in the 2p shell: both electrons have the same spin, and the two electrons have opposite spin. Assume one electron in $2p_x$ and the other in $2p_y$ (they will not be in the same due to the electrical repulsion) with these given functional forms in spherical coordinates:

$$2p_x : \frac{e^{-\rho/2} \rho^2 \sin \vartheta \cos \varphi}{4\sqrt{2\pi}}$$

$$2p_y : \frac{e^{-\rho/2} \rho^2 \sin \vartheta \sin \varphi}{4\sqrt{2\pi}}$$

Remember that electron wave-functions must be antisymmetric. Using the above functions, build the wavefunctions corresponding to the two possible configurations. While keeping one electron fixed at a distance of $4a_B$ (a_B being the Bohr radius) from the origin on the xy plane, plot the probability of finding the other electron in the 2p subshell. Based on these visualizations, which configuration is more stable? Which corresponds to a Fermi heap, and which to a Fermi hole? It is important to note that Fermi heaps and Fermi holes are consequences of the Pauli principle, and their stabilities are due to electrical repulsion. **Hint:** Refer to the review titled "Many-electron atoms: Fermi holes and Fermi heaps" by Dan Dill from Boston University found at <http://quantum.bu.edu/notes/QuantumMechanics/FermiHolesAndHeaps.pdf>. The end of the review has visualizations for Carbon to compare your results to. Mathematica will be useful for visualizing and plotting. Remember to consider what coordinate system you are using (either spherical or Cartesian).