

Experiment 2: Exploring Atomic Orbitals

Report due Friday, March 14 (by 4:00 p.m.)

A friend of mine from Harvey Mudd College and UCLA, Dr. Dean Dauger, is a leader in using Macs for scientific computing. You will be using one of his programs, *Atom in a Box*, to visualize and analyze the orbitals of the hydrogen atom. My hope is that Dean's modeling software will let you interact and think about orbitals in a way that reading your textbook or listening to my lectures cannot provide.

Logistical Basics

- *Atom in a Box* has been installed on each of the Macs in the Chemistry Department Computer Lab. It is not available on a campus-wide server. So you will have to schlep over to Olin-Rice to do the computer modeling work. Remember that the computer lab is open during business hours Monday through Friday, Mondays through Thursdays from 7:00 to 10:00 p.m., and Sunday from 1:00 to 10:00 p.m. (I think tutors have keys to the lab as well.)
- As you will see, the experiment integrates textbook kinds of calculations, use of *Atom in a Box*, and even some Excel work. You do not need to do things in the same order that I present here, but the work you turn in must be in the same order.
- Think of the "lab report" for this experiment as a problem set. That is, no abstract, introduction, procedures, etc., are necessary—just answer the questions below. It is fine for it to be handwritten, but it should be legible!
- As always, each lab team will turn in one report, and all members of the team will share the same grade. How you divide up the work is at your discretion. However, I encourage you to duplicate at least some of the work (*e.g.* the textbook kinds of calculations), so you can check one another.

Running and Using *Atom in a Box*

- Path to the program: Macintosh HD → Applications → Atom in a Box → Atom in a Box with the grey/white orbital icon
- At the top right of the Orbital Window you will see $|\psi\rangle = |n, l, m\rangle$. Here Dean is making use of Dirac notation to represent the wavefunction. (Dirac's paradigm was that the quantum numbers by themselves constitute the most fundamental description of a system.) Note that Dean has left off the "l" subscript from the m quantum number. You can press + and - buttons to change quantum numbers, or select them from the $|n, l, m\rangle$ menu.
- The left panel shows the amplitude of a hydrogen atom wavefunction $\psi(r, \theta, \phi)$ rotating about randomly (which is what actually happens when you have a hydrogen atom in the gas phase). At the upper right corner of the Orbital Window, you can click on Standard 3-D → Phase as Color (just to make the orbitals look prettier!). The variation in color is meant to represent the oscillation in the amplitude of the wavefunction over time. (This assumes that Show Time Evolution is checked under the Display menu.)

- On the right side of the Orbital Window, you will also see the algebraic expression of the wavefunction being displayed. (The notation $\langle r, \theta, \phi | \psi \rangle$ is simply Dirac's way of saying $\psi(r, \theta, \phi)$.) Unfortunately, the font size is too small to read the characters reliably. You will therefore have to consult Atkins and de Paula for the wavefunctions.
- The lower right panel shows the radial distribution function (RDF) $P(r)$, with the location of the global maximum labeled in units of Bohr radius (a_0) and assuming $Z = 1$ (hydrogen atom). Note that the locations of the other local maxima are not shown.

So, what will I be grading you on? Your answers to the following questions:

1. I showed you the 2s orbital in class. Using the information in Atkins and de Paula Table 10.1, calculate the locations of the node and the antinode of the 2s orbital.
2. Sketch the 2s orbital's RDF, as shown by *Atom in a Box*. Use calculus to confirm the location of the global maximum labeled by *Atom in a Box*, and find the location of the other local maximum.
3. Go to the 3s orbital. Under the Display menu, go to Brightness Multiplier and choose 1.5. Also under the Display menu, turn off Show Time Evolution. Then click on the Slice button on the bottom right of the Orbital Window. Now the left panel of the Orbital Window shows both the wavefunction and a pair of white triangles indicating the location of a plane slicing through the wavefunction. That "slice," which is displayed in the right panel, is a two-dimensional cross section through the probability density. (By default, the slice is vertical and goes through the nucleus.) Even though $\psi^*\psi$ is necessarily non-negative, the convention is to label segments of the 2D cross section with the signs they possessed before the wavefunction was squared. To the best of your ability, sketch the slice on the right, using + and - instead of colors to represent the relative signs of the wavefunction amplitude. Note: (1) It is completely arbitrary what color is + and what color is -. (2) There are only two colors. That different parts of the cross section may appear to be different shades of a color is simple Dean's attempt to render the "tightness" or "diffuseness" of different parts of the probability density.
4. Click off the Slice button. This will return you to the original display mode. Write down the location of the global maximum in the RDF for s orbitals from $n = 1$ to $n = 6$. In Excel, fit a polynomial to global maximum location vs. "principal" quantum number n . Include a printout of your spreadsheet and graph in your report.
5. Is your Excel analysis in Question 4 consistent with the Bohr model picture that the location of an electron, r , is proportional to the square of the (principal) quantum number? Briefly explain.
6. Look up the radial part of the $|2,1,0\rangle$ orbital in Atkins and de Paula. Find the value of r at which the amplitude is at a maximum. Explain qualitatively why this location is not at $r = 0$, which is the case for the $|2,0,0\rangle$ orbital.
7. Use *Atom in a Box* to display the $|2,1,0\rangle$ orbital (aka $2p_z$). The orbital will probably be rotating. Click on the orbital and rotate it until the z axis (in the Cartesian axis viewer in the middle of the Orbital Window) is vertical. Click on the Slice button. Sketch the 2D cross section through the boundary surface shown on the right. As before, use + and - to

indicate the relative signs of the amplitude. (As we showed in class a couple of weeks ago, this orbital contains an angular node at $\theta = \pi/2$, that is, the xy plane. Note this cool trick: Setting the subscript, z, equal to zero gives the equation of the angular node!)

8. Explain the “gap” in the two lobes of the orbital that you drew in Question 7. That is, the amplitude of the $2p_z$ orbital is only zero right at $\theta = \pi/2$, so why don't the two parts of the wavefunction touch each other?
9. Note that what you have drawn in Question 7 is a cross section of the probability density of the entire orbital: $R_{21}^*(r)R_{21}(r)Y_{10}^*(\theta, \phi)Y_{10}(\theta, \phi)$. Now, consulting Atkins and de Paula Figure 9.37, sketch a 2D cross section through $Y_{10}^*(\theta, \phi)Y_{10}(\theta, \phi)$ by itself. Note that an accurate representation of a 2p orbital is “fat” like your sketch in Question 7, not “skinny” like your sketch for this question. Skinny p orbitals bug the heck out of me!
10. Sketch the RDF for $2p_z$, label the location of the global maximum, and briefly compare it to the 2s RDF.
11. The RDF shown for $2p_z$ is an average over all possible values of θ . Plot qualitatively what the RDF will look like along the (a) z axis and the (b) x-axis. Note that this is kind of a trick question!
12. Display and draw the 2D slice along the z-axis for the $4p_z$ orbital. As always, use + and – to indicate the relative phase (wavefunction sign) of each segment of the orbital. Note that the wavefunction has to change sign each time you cross a node. Briefly rationalize the details of your sketch.
13. Display the $|3,2,0\rangle$ orbital. Orient it so that the z-axis is vertical. Press the Slice button and draw the vertical slice.
14. Still looking at the $|3,2,0\rangle$ orbital, drag the pair of white arrows until you are slicing the orbital horizontally. Draw a slice (a) below the xy plane, (b) in the xy plane, and (c) above the xy plane.
15. Display the 4f and 5f orbitals whose z-components of orbital angular momentum are zero. Nothing to write down or draw here—I just want you to be able to say you know what the valence orbitals of the lanthanide and actinide elements look like!
16. Finally, display $|2,1,1\rangle$. You can see that, as suggested in Atkins Figure 9.37, the $|2,1,1\rangle$ orbital isn't either $2p_x$ or $2p_y$. (Actually, the orbital is not worth sketching, since the rainbow of colors used in the rendering is meant to indicate that there are imaginary parts to this wavefunction.) Do, however, sketch the RDF for the $|2,1,1\rangle$ orbital. Compare it to the RDF for the $|2,1,0\rangle$ orbital. Briefly explain what you find.