

# Workshop: One-electron-atom orbitals

## Quantum aspects of physical chemistry

<http://quantum.bu.edu/PLTL/7.pdf>

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Three-dimensional wave functions of an electron in a one-electron atom are known as one-electron-atom *orbitals*. Electrons in many-electron atoms can be approximately represented in terms of these orbitals. The spatial properties of these orbitals are essential components in understanding the periodic properties of many-electron atoms, the bonding of diatomic molecules, and the shapes of polyatomic molecules. For these reasons it is important to be familiar with the three-dimensional structure of one-electron-atom orbitals. In this workshop you will explore the properties of these orbitals.

You will derive the greatest benefit from this workshop if you carry it out "by hand" and, in particular, please do *not* use graphing calculators or computer graphing tools.

### ■ Summary of one-electron atom properties

A one-electron-atom orbital can be expressed as

$$\psi_{j\ell m}(r, \theta, \phi) = R_{jZ\ell}(r) Y_{\ell m}(\theta, \phi) = \frac{1}{r} P_{jZ\ell}(r) Y_{\ell m}(\theta, \phi),$$

where the radial variation of the wave function is given by radial wave functions,  $R_{jZ\ell}$ , or alternatively by the shell amplitude  $P_{jZ\ell}$ , and the angular variation of the orbital is given by the spherical harmonics,  $Y_{\ell m}$ . The shell amplitudes satisfy the Schrödinger equation

$$\left( -\frac{d^2}{dr^2} + v_{\text{eff},Z\ell}(r) \right) P_{jZ\ell}(r) = \epsilon_{jZ\ell} P_{jZ\ell}(r),$$

Energy is in units of rydberg,  $E_r$ , length is in units of bohr,  $a_0$ , and the effective potential energy and eigenvalues are

$$v_{\text{eff},Z\ell}(r) = \frac{\ell(\ell+1)}{r^2} - \frac{2Z}{r},$$
$$\epsilon_{jZ\ell} = -\frac{Z^2}{(j+\ell)^2} = \epsilon_{nZ} = -\frac{Z^2}{n^2}.$$

Here  $j = 1, 2, \dots$ , is the number of loops in the shell amplitude  $P_{jZ\ell}$  and  $\ell = 0, 1, \dots$ , is the orbital momentum quantum number. For historical reasons, the first four values of  $\ell$  are usually expressed as a letter, as follows: s ( $\ell = 0$ ), p ( $\ell = 1$ ), d ( $\ell = 2$ ), and f ( $\ell = 3$ ). Also for historical reasons,  $j + \ell$  is taken to define a new quantum number  $n$ , called the principal quantum number. Because of the relation  $n = j + \ell$ , the shell amplitude  $P_{jZ\ell}$  and radial wave function  $R_{jZ\ell}$  are usually written instead in terms of the principal quantum number, as  $P_{n\ell}$  and  $R_{n\ell}$ , with the additional understanding that the atomic number  $Z$  is not written explicitly. We will use this notation here.

The fraction of the electron within a small volume  $r^2 dr \sin(\theta) d\theta d\phi$  of the point  $r, \theta, \phi$  is

$$|\psi_{n\ell m}(r, \theta, \phi)|^2 r^2 dr \sin(\theta) d\theta d\phi = |P_{n\ell}(r) Y_{\ell m}(\theta, \phi)|^2 dr \sin(\theta) d\theta d\phi$$

The fraction of the electron anywhere within  $dr$  of the surface of a sphere of radius  $r$  is

$$\int_0^\pi \int_0^{2\pi} \left| \psi_{n\ell m}(r, \theta, \phi) \right|^2 r^2 dr \sin(\theta) d\theta d\phi = |P_{n\ell}(r)|^2 dr$$

This is the reason  $|P_{n\ell}(r)|^2$  is called the *shell density* of the electron, and so that we call  $P_{n\ell}$  the shell amplitude. The fraction of the electron anywhere at all is

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} \left| \psi_{n\ell m}(r, \theta, \phi) \right|^2 r^2 dr \sin(\theta) d\theta d\phi = \int_0^\infty |P_{n\ell}(r)|^2 dr = 1$$

That is, the total probability of finding the electron somewhere is unity.

## ■ Classical turning points

Classical turning points are when the kinetic energy equals zero.

1. Show that the inner and outer classical turning points are given by the following expressions.

$$r_{\text{in}} = n \left( n - \sqrt{n^2 - \ell(\ell + 1)} \right) / Z,$$

$$r_{\text{out}} = n \left( n + \sqrt{n^2 - \ell(\ell + 1)} \right) / Z,$$

2. What are the values of the turning points for a 4s electron in hydrogen ( $Z = 1$ )?
3. What are the values of the turning points for a 4p electron in hydrogen?
4. What are the values of the turning points for a 4d electron in hydrogen?
5. Summarize your results in the following table.

	$r_{\text{in}}$	$r_{\text{out}}$
4s		
4p		
4d		

6. Explain how the relative values of the turning points could have been anticipated. *Hint:* Sketch the potential curves, indicating by a horizontal line the total energy.

## ■ Sketching shell amplitudes

A general property of the shell amplitude  $P_{n\ell}(r)$  is that for  $\rho \ll 1$  it is proportional to  $r^{\ell+1}$  (and so the radial wave function,  $R_{n\ell} = P_{n\ell}/r$ , is proportional to  $r^\ell$ ). Using this behavior, the relation between  $n$ ,  $\ell$ , and the number of loops,  $j$ , and the values of the turning points, it is not too hard to make accurate sketches of shell amplitudes.

7. Sketch the shell amplitude  $P_{4s}$ . Mark the classical turning points.
8. Sketch, on the same axes, the shell amplitude  $P_{4p}$ . Mark the classical turning points.
9. Sketch, on the same axes, the shell amplitude  $P_{4d}$ . Mark the classical turning points.
10. Based on your three sketches, which electron do you expect to have the smallest average radius,  $\langle\rho\rangle$ ?
11. Based on your three sketches, which electron do you expect to have the largest average radius,  $\langle\rho\rangle$ ?
12. The exact expression for the average radius is  $\langle\rho\rangle_{n\ell} = n^2(1 + \frac{1}{2}(1 - \frac{\ell(\ell+1)}{n^2}))/Z$ . Do your predictions jibe with the values obtained by the exact expression?
13. Do your predictions make sense in terms of the periodic table?

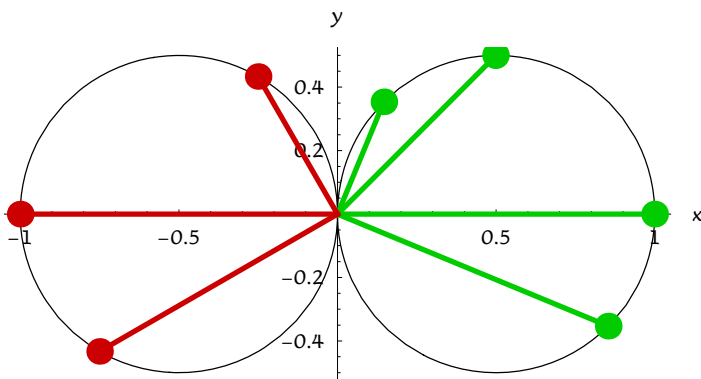
## ■ Sketching spherical harmonics

Spherical harmonics are functions of the two polar angles,  $\theta$  and  $\phi$ . A way to visualize these functions is to construct a *polar plot*. A polar plot represents the *magnitude* (absolute value) of the function as the length of a line centered at the origin, and it represents the values of the angles  $\theta$  and  $\phi$  by the direction of the line. The result will be a three-dimensional surface centered at the origin.

A polar plot in two dimensions results if the value of one of the angles is held constant. For example, setting  $\theta = \pi/2$  we can construct a polar plot of the magnitude of a function in the  $xy$  plane; setting  $\phi = 0$  would give a polar plot in the positive half of the  $zx$  plane; and setting  $\theta = \pi/4$  would give a polar plot parallel to the  $xy$  plane of the magnitude of the function at  $45^\circ$  from the  $z$  axis.

Because spherical harmonics can have both negative and positive values, while polar plots represent only the magnitude of functions, we need a way to distinguish when function values are positive and when they are negative. In chemistry this is usually done by marking those parts of the surface (or curve if one angle is fixed) that correspond to positive function values with a positive sign, +, and by marking those parts of the surface that correspond to negative function values with a negative sign, -.

Here is an example polar plot of the angular dependence of the  $p_x$  spherical harmonic,  $\sin(\theta)\cos(\phi)$ , in the  $xy$  plane, that is, for  $\theta = \pi/2$ .



Polar plot of the  $p_x$  spherical harmonic angular dependence,  $\sin(\theta)\cos(\phi)$ , for  $\theta = \pi/2$ . The right lobe corresponds to positive values and the left lobe corresponds to negative values. The length of each line terminating in a point is the value of  $\cos(\phi)$  for the corresponding value of  $\phi$ .

The right lobe corresponds to positive values and the left lobe corresponds to negative values. The length of each line terminating in a point is the value of  $\cos(\phi)$  for the corresponding value of  $\phi$ .

14. Explain whether the figure represents an electron orbital.

### Real spherical harmonic $p_y$

The  $p_y$  spherical harmonic is  $\sqrt{3/4\pi} \sin(\theta) \sin(\phi)$ .

15. The spherical harmonic  $p_y$  is proportional to  $\sin(\theta) \sin(\phi)$ . Make a polar plot of this angular dependence in the  $xy$  plane.
16. The value of  $\sin(\theta) \sin(\phi)$  can be negative. Indicate on your polar plot of  $p_y$  where the value is negative by placing a negative sign,  $-$ , in all regions enclosed by the curve for which the value is negative. In a similar way, mark where the value is positive by placing a positive sign,  $+$ , in all regions enclosed by the curve for which the value is positive.
17. What, if anything, do these signs have to do with the charge on the electron and the charge on the nucleus?
18. On a new set of axes tilted  $\pi/4$  from the  $xy$  plane, but one the same scale as the previous plot, make a polar plot of the angular dependence of  $p_y$  for  $\theta = \pi/4$ . Mark regions with  $+$  and  $-$  as appropriate.
19. On a new set of axes tilted  $-\pi/4$  from the  $xy$  plane, but one the same scale as the previous two plots, make a polar plot of the angular dependence of  $p_y$  for  $\theta = 3\pi/4$ . Mark regions with  $+$  and  $-$  as appropriate.
20. Your polar plots of the angular dependence of  $p_y$  can be viewed as slices a three dimensional polar plot. Use your polar plots to sketch what the angular dependence of  $p_y$  looks like in three dimensions.
21. Explain whether the three dimensional figure represents an electron orbital.

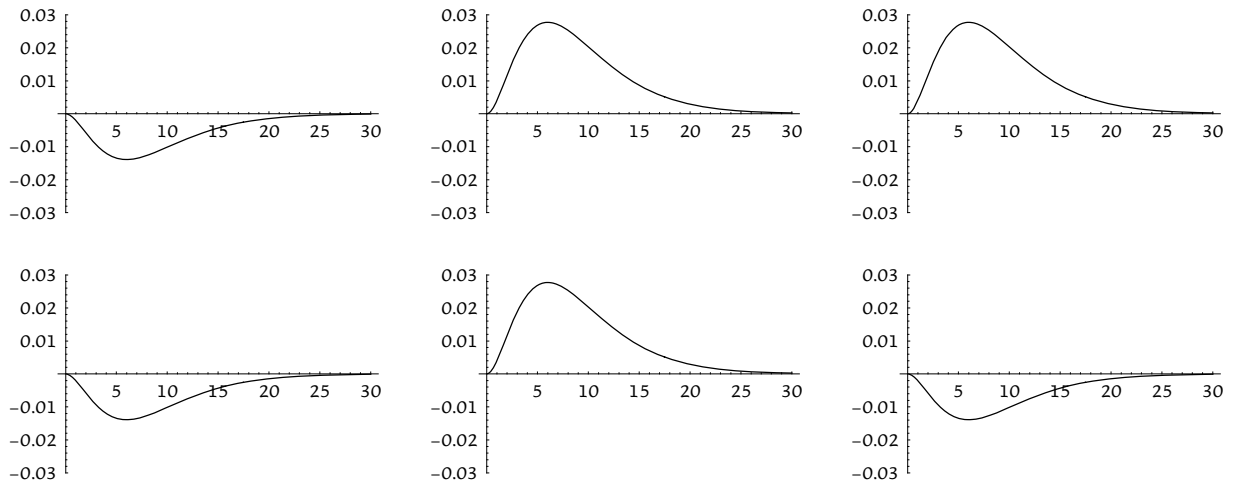
### ■ Sketching orbitals

The  $4p_y$  orbital is  $\psi_{4p_y}(r, \theta, \phi) = r^{-1} P_{4p}(r) p_y(\theta, \phi)$ .

22. Sketch the  $4p_y$  orbital along the  $y$  axis, that is, along the direction  $\theta = \pi/2$ ,  $\phi = \pi/2$ .
23. Sketch the  $4p_y$  orbital along the direction  $\theta = \pi/4$ ,  $\phi = \pi/2$ .
24. Sketch the  $4p_y$  orbital along the direction  $\theta = \pi/8$ ,  $\phi = \pi/2$ .
25. Along which directions,  $\{\theta, \phi\}$  will the  $4p_y$  electron density be greatest?
26. Estimate where in three dimension, that is, at which point or points  $\{r, \theta, \phi\}$ , is the probability density of the hydrogen  $4p_y$  orbital greatest?
27. Characterize the nodal surfaces, if any, of the  $4p_y$  orbital.

## ■ Mystery orbital

Here are plots of the radial variation of an hydrogen orbital along different directions, that is, for different values of  $\theta$  and  $\phi$ .



Radial variation of an unknown hydrogen one-electron orbital for different values of  $\theta$  and  $\phi$ . Clockwise from the upper left the values  $\{\theta, \phi\}$  are  $\{\pi/2, \pi\}$ ,  $\{0, \pi\}$ ,  $\{0, \pi/2\}$ ,  $\{\pi/2, \pi/2\}$ ,  $\{\pi, -\pi/2\}$ , and  $\{\pi/2, -\pi/2\}$ .

28. Which orbital is this?