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## **Micro-thoughts on science**

Sparkly micro-comments on science, with an emphasis on education.

**Tuesday, October 09, 2007**

### **The p orbital paradox**

Quantum mechanics is weird. You often heard this. Well, maybe. It depends on the definition of weird. If weird is not how nature works then quantum mechanics is far from being weird.

Quantum mechanics is often thought in the classroom under an extra fog of mystery. I remember when I took my first course in quantum theory. A friend, who had been taking the course by the past two years<sup>#</sup>, said me the day one: uff tío, ahora was a flipar con la cuántica.

I do not know how translate that exactly, but may be close to Wow brother, you will shock with the quantum now. This and knowing that the course got a fame of being very hard for students did panic me before taking my first lesson.

During course, teacher described lot of paradoxes and weird behaviour. More the weird was more I opened my eyes. Remember perfectly the day that teacher was speaking about 'ghosts'. He said us that ghost-like behaviour was available at quantum level. It was called quantum tunnelling. You could heard a sound ooh in the classroom that day. Everyone was puzzled.

Often you read,  
when a particle tunnels through a potential barrier, it never appears under the barrier... it just disappears from one side and reappears on the other.

Weird enough!

The problem is on that above quote is technically incorrect. I introduce here because represents a too common misconception about quantum mechanics. I will not revise all misconceptions about quantum mechanics here. A revision of fifteen commonly held misconceptions is done in [Styer, 1996].

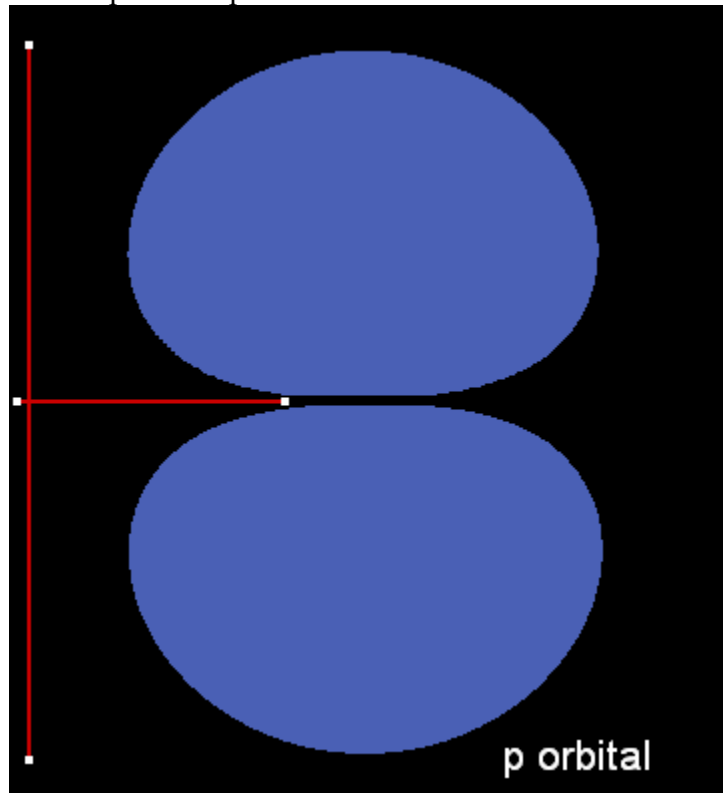
In this microthought I will revise the paradox of p orbitals and will provide a model to understand is going on with the electron.

P orbitals come from solving the non-relativistic time-independent Schrödinger equation

$$\hat{H} | \Psi \rangle = E | \Psi \rangle$$

If you are interested in details of calculation you can find them on standard textbooks like [Levine, 2000].

The shape of the p orbital is

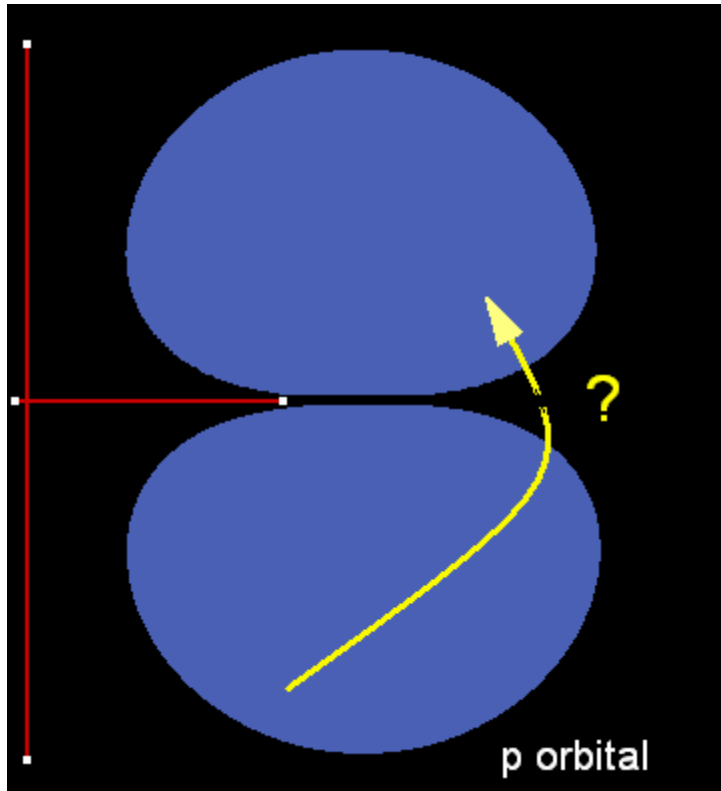


With two lobes separated by a nodal plane.

Many textbooks for physicists and chemists [Tang, 2005; Feng & Jin, 2005; Murray, 1977] show different 'artistic' representations (elongated-shapes, spheres, donuts...) of p orbitals instead the accurate shape of above.

Since the probability to find an electron which occupies a p-orbital in the nodal plane is zero, the paradox is usually stated as follow:  
How does a particle get through a node in its wavefunction?

We can represent the paradox graphically like



See also [Allendoerfer, 1990; Nelson, 1990]. Eric Scerri warns us how this paradox is present on some general chemistry textbooks [Scerri, 1999]. And adds that Dirac's relativistic treatment of orbitals eliminates nodes whatsoever. Scerri does a good discussion of observability of orbitals.

Some authors think that non-zero probabilities eliminate the paradox. Appeals to relativistic probabilities during discussion fail to disclose a misconception about quantum mechanics and would be avoided.

The formulation of the paradox begins by assuming that a single electron finds in some point of a lobe at instant  $t$  and in another point of the other lobe at some posterior instant  $t'$ . Then the paradox arises when trying to unite both points with a trajectory without passing by the nodal plane. It is not possible!

Some physicists would say you that the problem was in the assumption of any trajectory linking initial and final points. Messiah even states we may renunciate to the concept of trajectories in quantum mechanics [Messiah, 1999].

I dislike that kind of reply by two motives. The first reason is methodological. I think one would address the mistake being done during the early assumption, i.e. that a single electron finds in some point of the lobe at instant  $t$ , before we discuss about trajectories. The second reason is technical, if quantum mechanics had no room for a concept of trajectories, then would not agree with classical motion in the limit  $\hbar \rightarrow 0$ , right?

**Note:** If either there still exist difficulties to make strict the limit.

Styer [Styer, 1996] directly addresses the mistake done in the early assumption. And does by correctly pointing that the wavefunction is describing a single electron at a single instant of time.

The wavefunction is not some kind of average over some amount of time. Therefore, you cannot begin by assuming that the electron was in some point of a lobe at instant  $t$  and in another point at some posterior  $t'$ . Of course the idea of uniting both points by a classical trajectory passing by the nodal plane is another mistake, but a posterior one.

Whereas Styer explanation is technically correct, it relies on an understanding of both the time-dependent and the time-independent Schrödinger equations. This dependence may be inadequate for first courses. For instance, elementary textbooks on general chemistry or physics often introduce atomic orbitals without present the Schrödinger equation to readers.

You can get a visual model of the electron in a p-orbital from charge densities

$$\rho = e|\Psi|^2$$

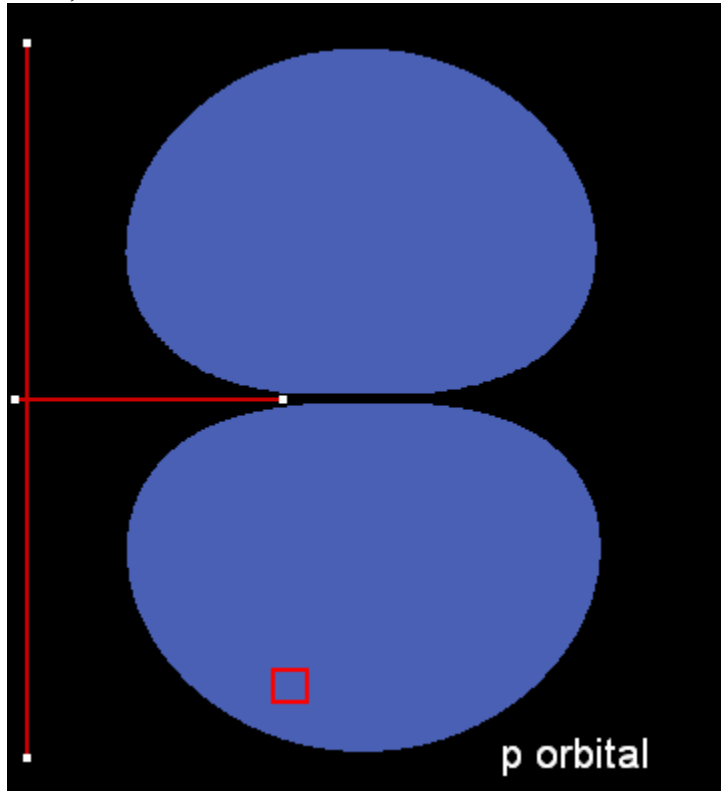
with  $e$  the electron charge and  $\Psi$  the orbital.

**Note:** Of course the picture model can be thought on elementary courses without introducing the equations for the densities. I make here for completeness.

Therefore, we can interpret now the p orbital like a diffuse cloud. An electron is a particle (or a region of space) with charge  $e$ . An electron in a p-orbital would be not considered a little hard charged ball but like a cloud of charge. In this picture each lobe contains a

part of the electron (remember that in a relativistic treatment both lobes are connected).

Now, take a small volume  $\tau$



Computing the total charge  $Q$  inside

$$Q = e \int_{\tau} |\Psi|^2 d\tau < e$$

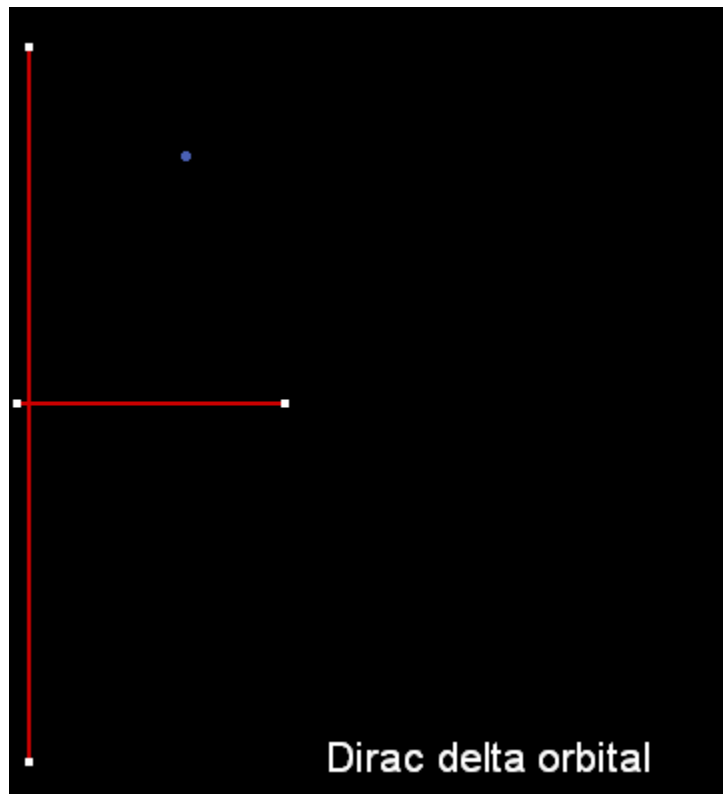
You can see that the volume  $\tau$  has not enough charge to contain a whole electron. And the same conclusion when considering an element of volume in the other lobe.

In this simple way, you can understand that the electron is not contained in a volume  $\tau$  at some time and then moves to another volume at posterior times. Since both premises are not right, the posterior search for a trajectory uniting both volumes has no sense.

This picture helps you to visualize the dynamics too. The electron is not a small hard ball moving inside the orbital in some weird way. Forget that picture. The orbital describes a stationary cloud of charge. No part of that cloud is moving following classical trajectories. It is stationary, because the orbital was obtained by solving the time-independent Schrödinger equation.

I. N. Levine does not like this cloud interpretation [**Levine, 2000**]. He argues that electrons behave like indivisible entities because no fraction of an electron has been detected. Well, that is right. We do not measure half or  $1/5$  electrons. Is then a cloud picture of the lobes wrong?

Well, one would remember that a p-orbital is. A p-orbital is a stationary solution for a single electron in an atom. When a measurement is done over an electron in a p-orbital, the measurement apparatus collapses the initial p-orbital into a Dirac delta function. This is illustrated in next figure



This illustrates why measured electrons behave like small hard balls. There exists not contradiction with a cloud picture before the measurement.

### Summarizing

The  $p$  paradox arises from trying to consider the electron like a small hard ball moving according to the trajectories of classical mechanics.

In a cloud interpretation each lobe contains a part of the stationary electron. The electron is not here or there, but spread over the whole stationary distribution of charge  $e$ . There is not paradox.

After a measurement of position, the cloud collapses into a Dirac delta like distribution doing the electron behaves like a pointlike

particle. The cloud interpretation does not contradict the pointlike character of electrons.

Relativistic corrections to orbitals are not needed for discussing the 'paradox'.

# This was usual since the course rank between the more difficult courses of the University.

### **Acknowledgement**

Tom pointed to me a number of additional references on the topic of teaching quantum mechanics to students. One article I have not read at the time of writing this but seems interesting is,

Teaching quantum mechanics on an introductory level. Am. J. of Phys. 2002, 70(3), 200–209. Müller, Rainer; Wiesner, Hartmut.

Additional resources are

<http://www.physik.uni-mainz.de/lehramt/epec/koopman> (pdf)

<http://www.physicstoday.org/vol-59/iss-8/p43.html>

Carl Brannen and Peter did useful remarks about quantum mechanics and the limitations of p-orbital models.

I also greet comments by Rich L. and PD.

### **References:**

#### **[Allendoerfer, 1990]**

Teaching the shapes of the hydrogenlike and hybrid atomic orbitals. Journal of Chemical Education 1990, 67, 37–39. Allendoerfer, R. D.

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**[Murray, 1977]**

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How do electrons get across nodes? Journal of Chemical Education 1990, 67, 643–647. Nelson, P. G.

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A critique of atkins' periodic kingdom and some writings on electronic structure. Foundations of Chemistry 1999, 1, 297–305. Scerri, Eric R.

**[Styer, 1996]**

Common Misconceptions Regarding Quantum Mechanics. Am. J. of Phys. 1996, 64, 31–34. Styer, Daniel F.

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Fundamentals of Quantum Mechanics: For Solid State Electronics and Optics. Cambridge University Press; 2005. Pages 99-100. Tang, C. L.

Labels: [chemistry](#), [p orbital](#), [paradox](#), [quantum mechanics](#)

**The scientist**

Juan R. González-Álvarez

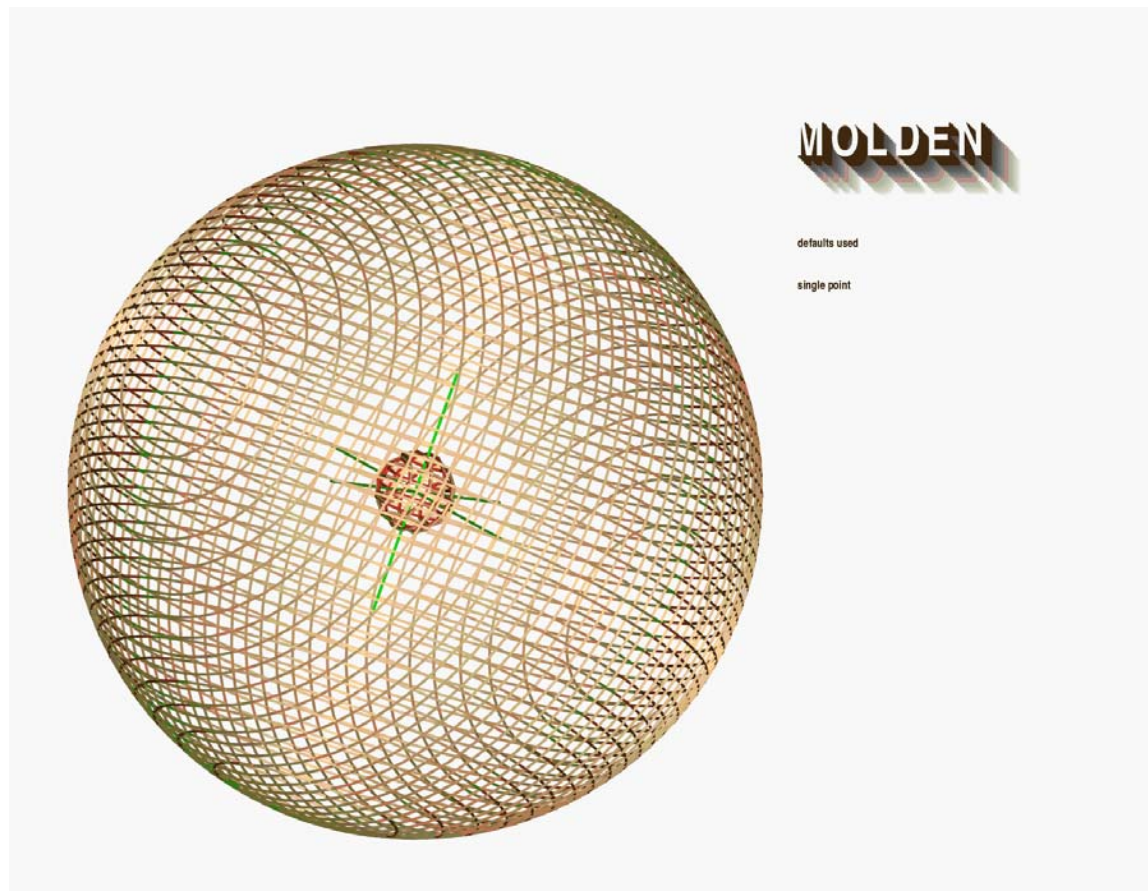
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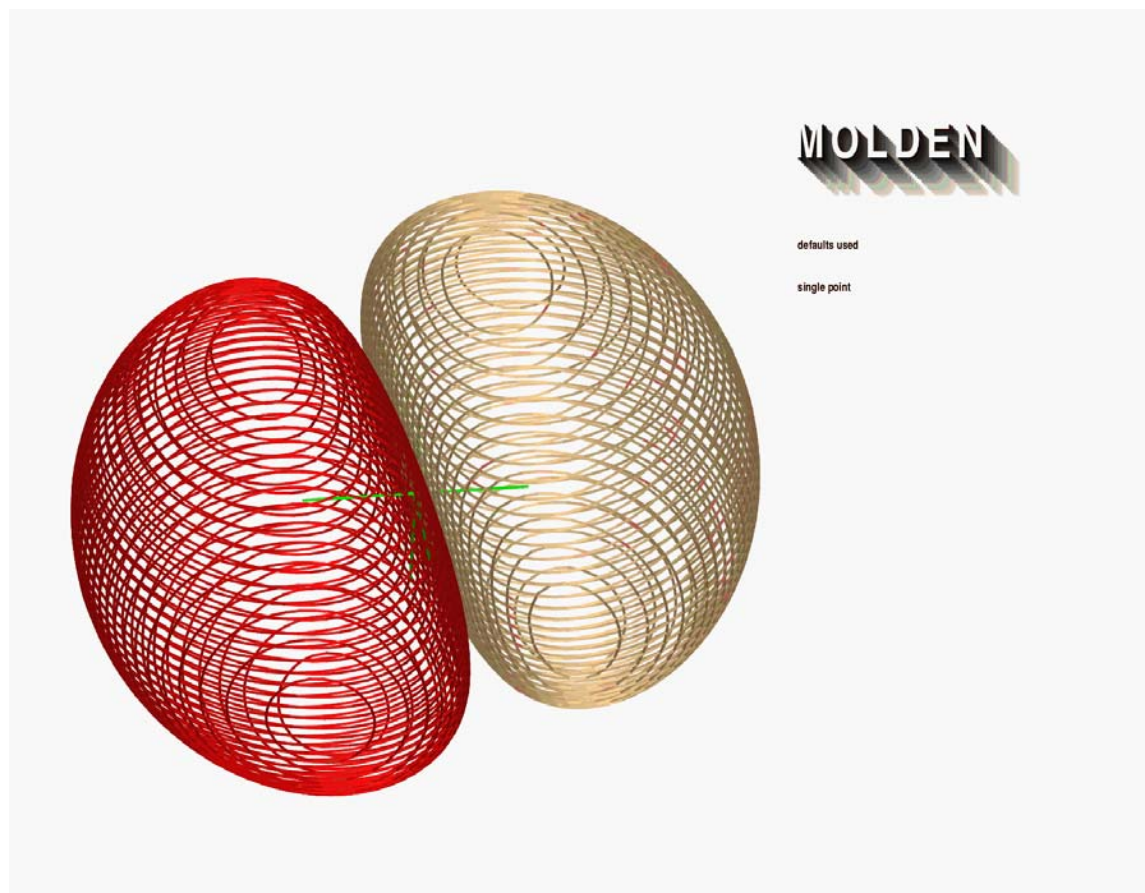
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### **Dr. Gutow's Nice Atomic Orbital Pictures**

Below are some images created using the [GAMESS](#) *ab initio* quantum mechanics package and Molden-4.4. [Molden](#) is visualization software designed for viewing the output of quantum calculations. The orbitals were generated from the GAMESS .log file from a single point energy calculation on Cl at the 6-311G++(2d,p) level of theory. The major goal of these images is to help you visualize how the radial nodes show up in the orbitals as we go to higher and higher levels. The images below start with the lower energy orbitals and go on up. Each time the mesh surface changes color a node has been crossed. A node is a region of space in which the electron occupying the orbital cannot be found. Just a representative selection of orbitals is shown.



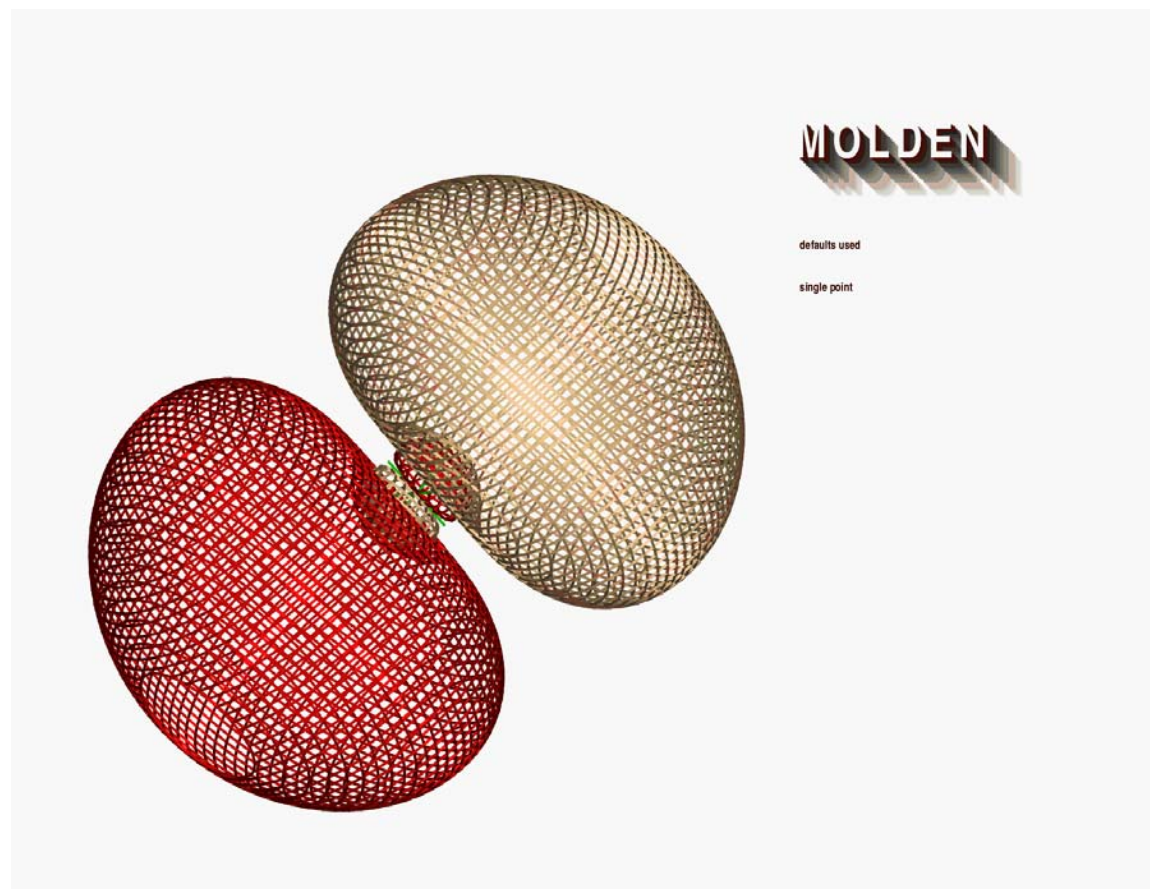
**2s orbital.** Notice there is 1 radial nodes. The 1s, which is lower in energy, has no nodes.



**2p orbital.** Notice that this orbital has no radial nodes, just one angular nodal plane

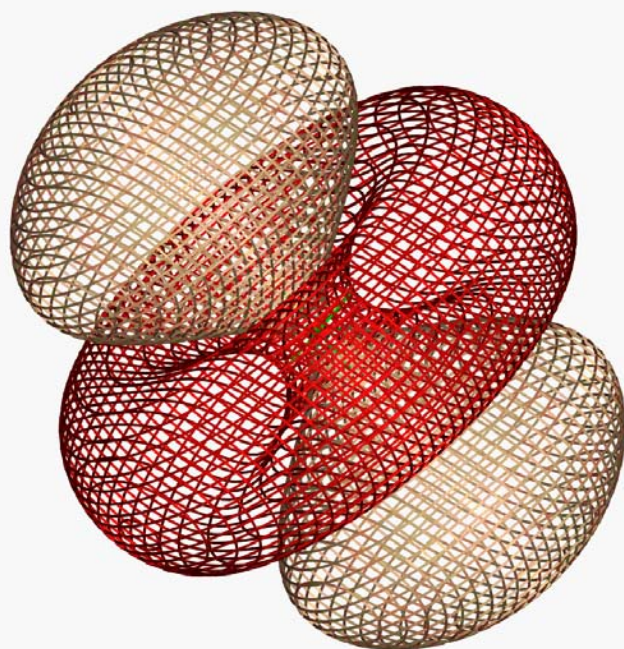


**3s orbital.** Notice that this orbital has 2 radial nodes



**3p orbital.** Notice that this orbital has 1 radial node in addition to the angular nodal plane of a p orbital



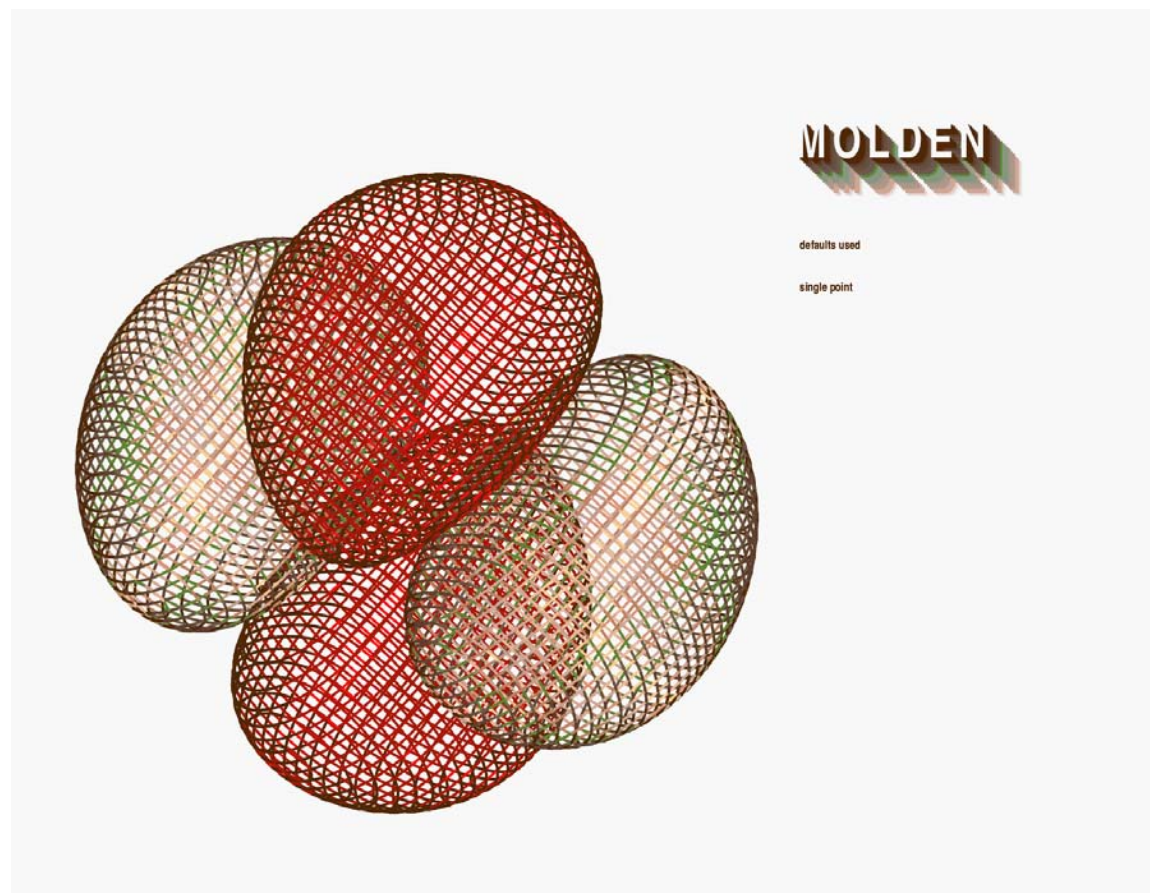


**MOLDEN**

defaults used

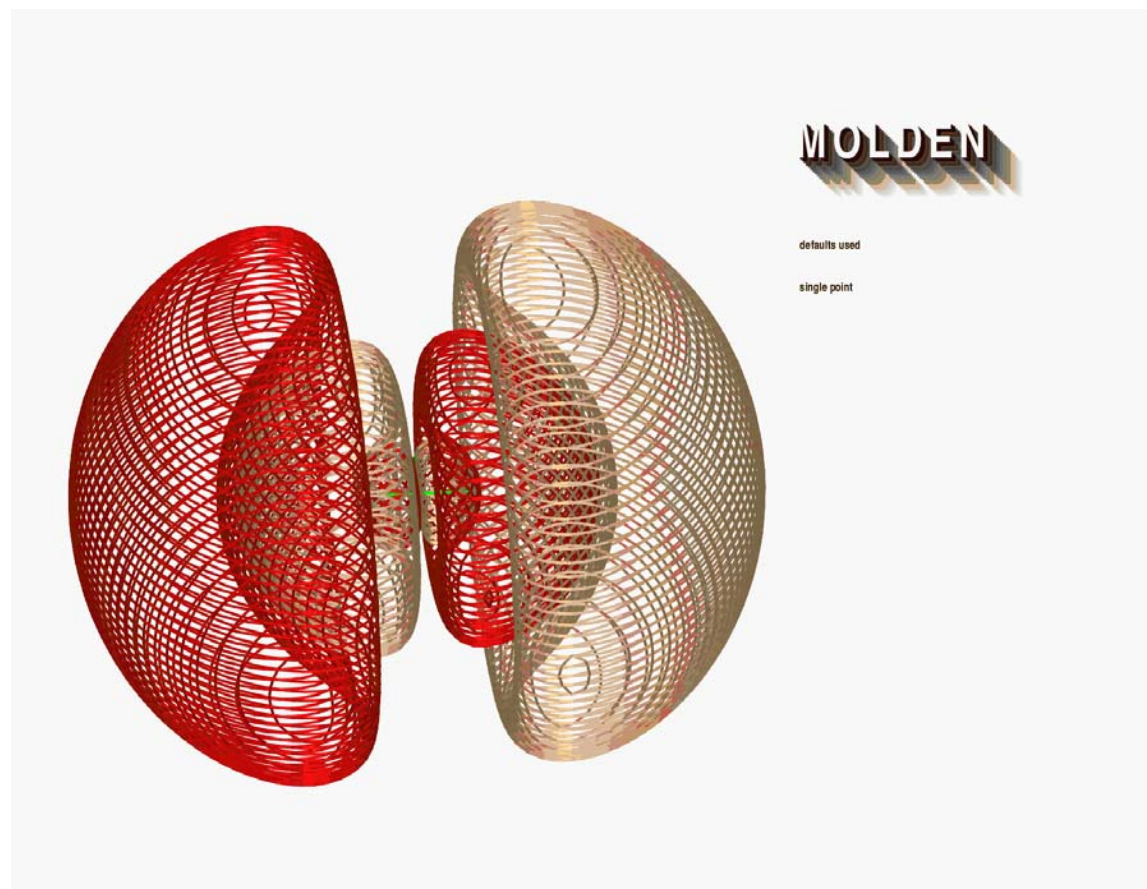
single point

**$3d_z^2$  orbital.** Notice that this orbital has only angular nodes



**$3d_{xy}$  orbital.** Again notice the orbital has only angular nodes





**4p orbital.** Notice this orbital has 2 radial nodes in addition to the angular nodal plane of a p orbital.

Polar graphs of p orbitals

<http://www.math.ubc.ca/~cass/courses/m308-02b/projects/alo/p-Orbitals.html>

p-Orbitals are governed by their radial functions and two angular elements. Many of the principles of radial orbitals for the p-Orbitals are same as in the s-Orbitals. As such, their angular elements are discussed here. The three equations for the 2p orbitals are given by:

$$\begin{aligned}Y_+ &= (3/4\pi)^{1/2} \sin \Theta \cos \Phi \\Y_- &= (3/4\pi)^{1/2} \sin \Theta \sin \Phi \\Y_0 &= (3/4\pi)^{1/2} \cos \Theta\end{aligned}$$

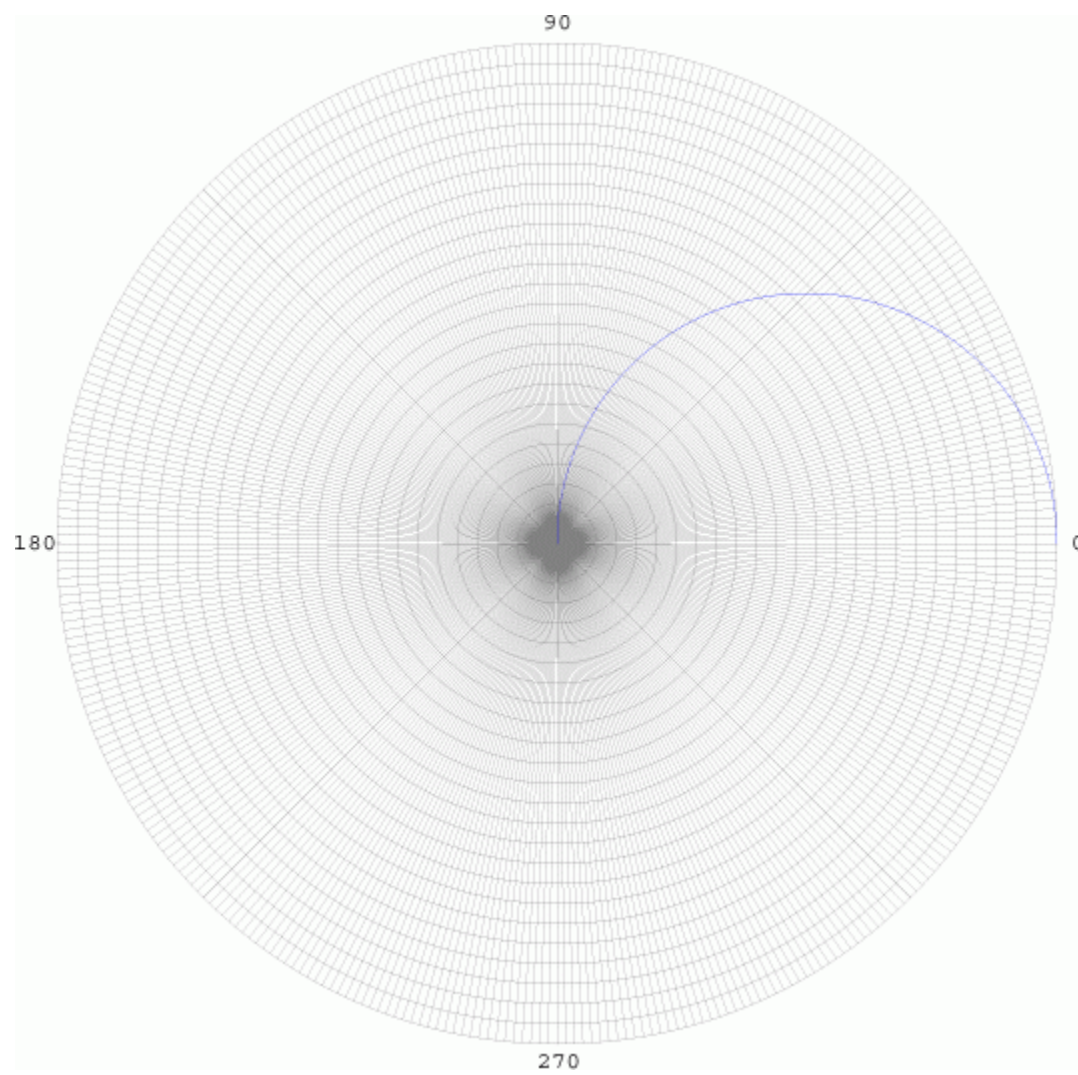
Each of the three orbitals has the different radial elements, since two of the functions depend on  $\Phi$  and  $\Theta$ . It will turn out that the three orbitals are each aligned along a different axis in the Cartesian plane. Using the Cartesian-Spherical conversion, we use the following conversion formulas:

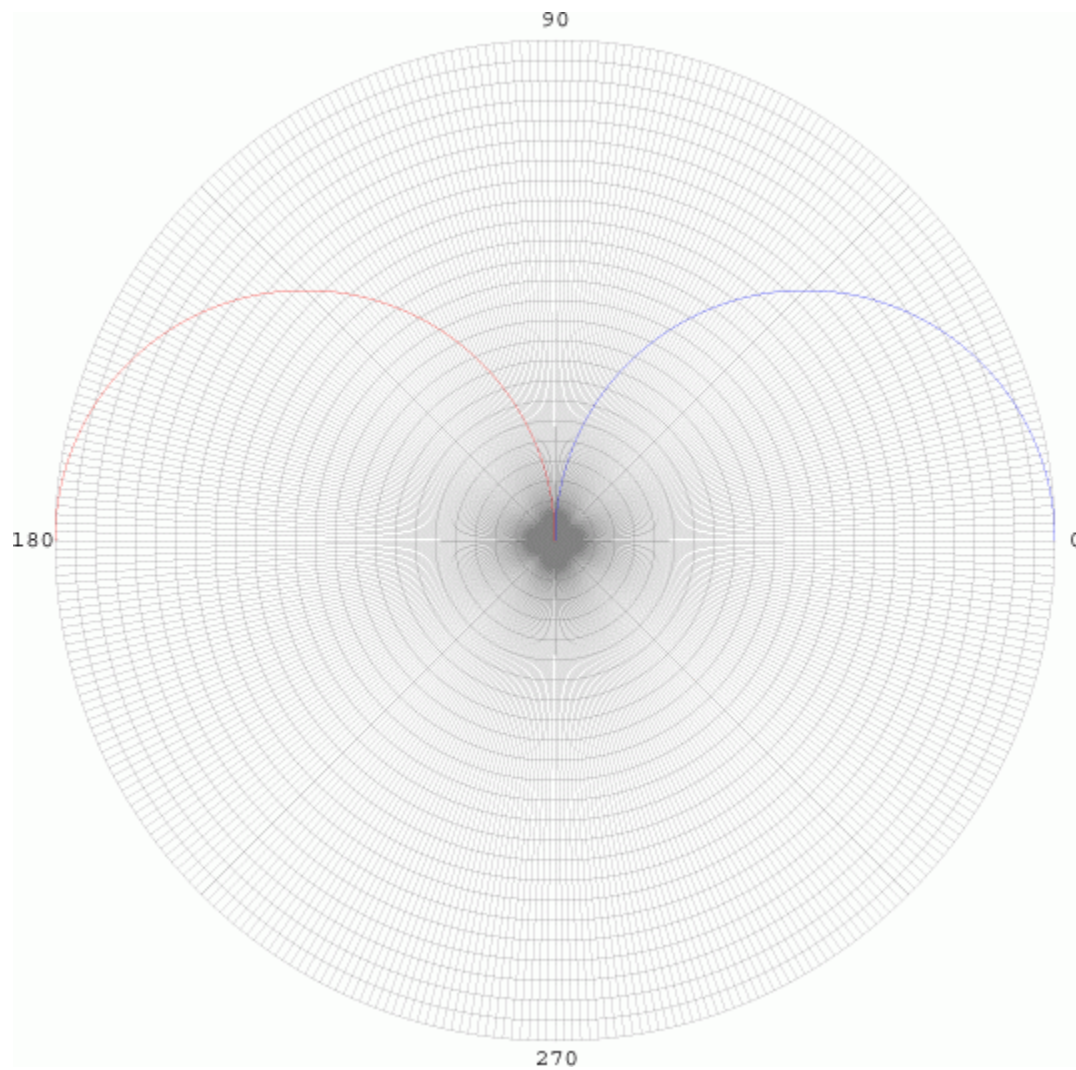
$$\begin{aligned}x &= \sin \Theta \cos \Phi \\y &= \sin \Theta \sin \Phi \\z &= \cos \Theta\end{aligned}$$

we obtain:

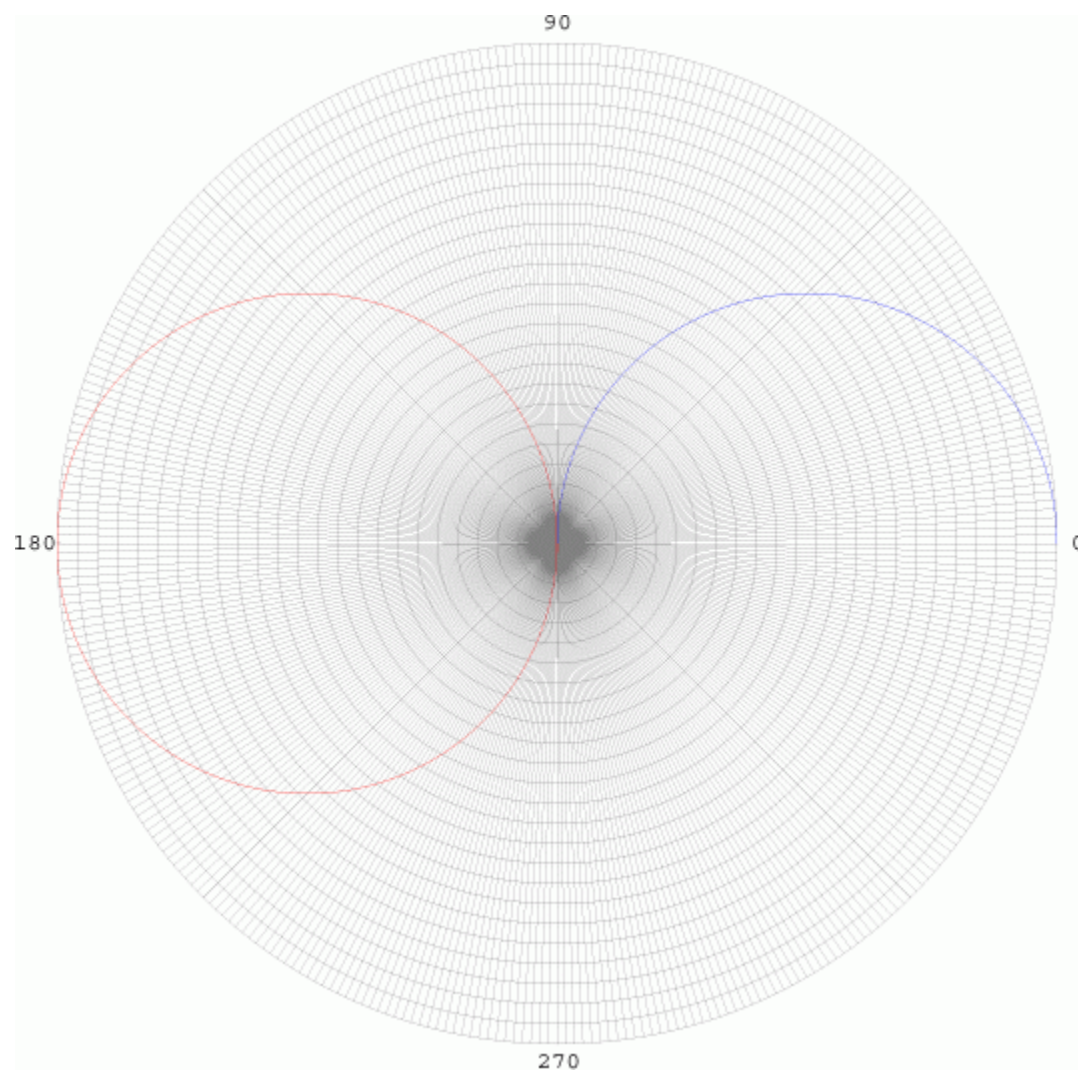
$$\begin{aligned}Y_{p_x} &= (3/4\pi)^{1/2} \sin \Theta \cos \Phi = (3/4\pi)^{1/2} x/r \\Y_{p_y} &= Y_- = (3/4\pi)^{1/2} \sin \Theta \sin \Phi = (3/4\pi)^{1/2} y/r \\Y_{p_z} &= Y_0 = (3/4\pi)^{1/2} \cos \Theta = (3/4\pi)^{1/2} z/r\end{aligned}$$

This means that we can graph one function with respect to an axis ( $x$ ,  $y$ , or  $z$ ), and then rotate  $90^\circ$  to the other two axes, and we have a full set of p orbitals. The angular element is given by  $\cos \Theta$ . We graph in polar co-ordinates on a polar grid:

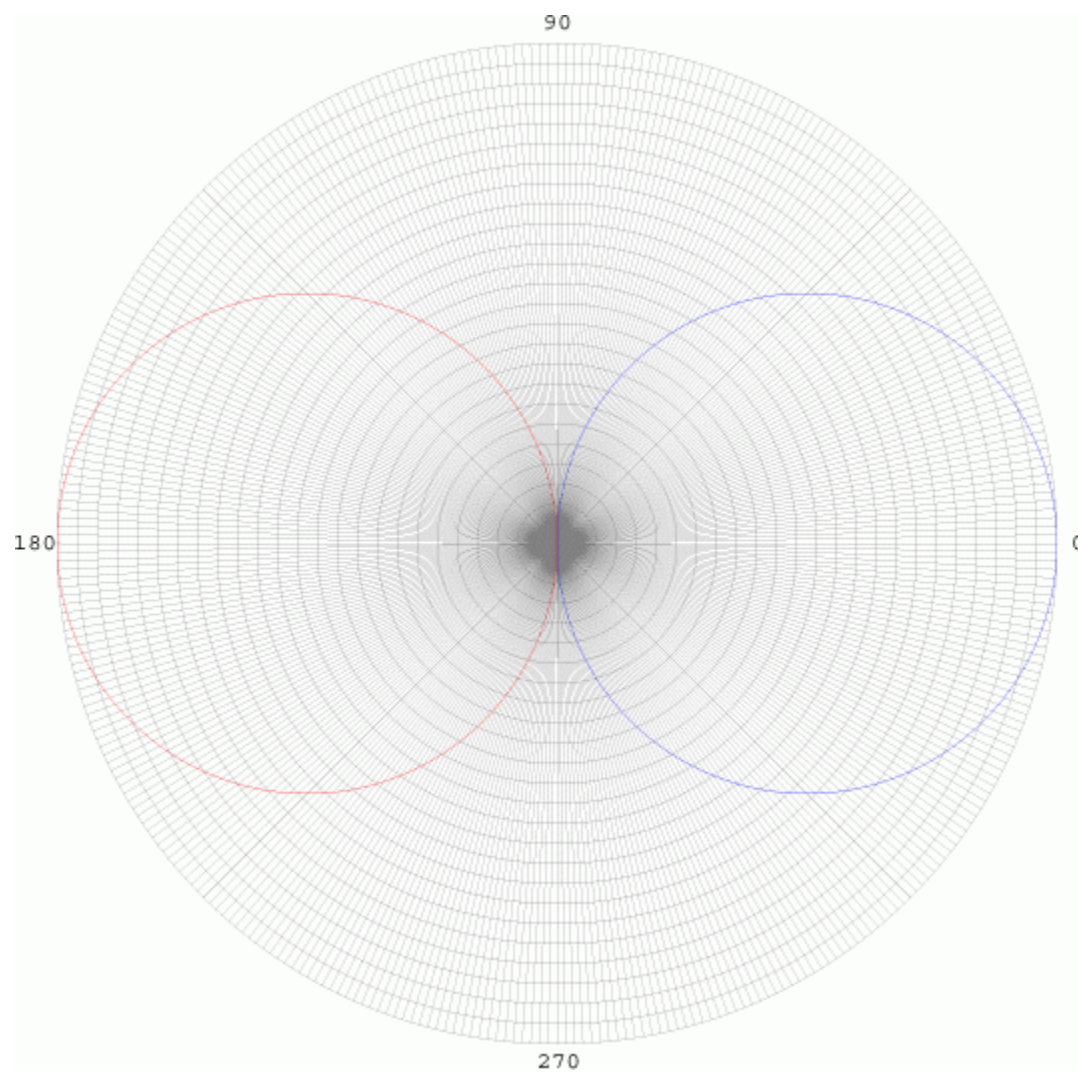


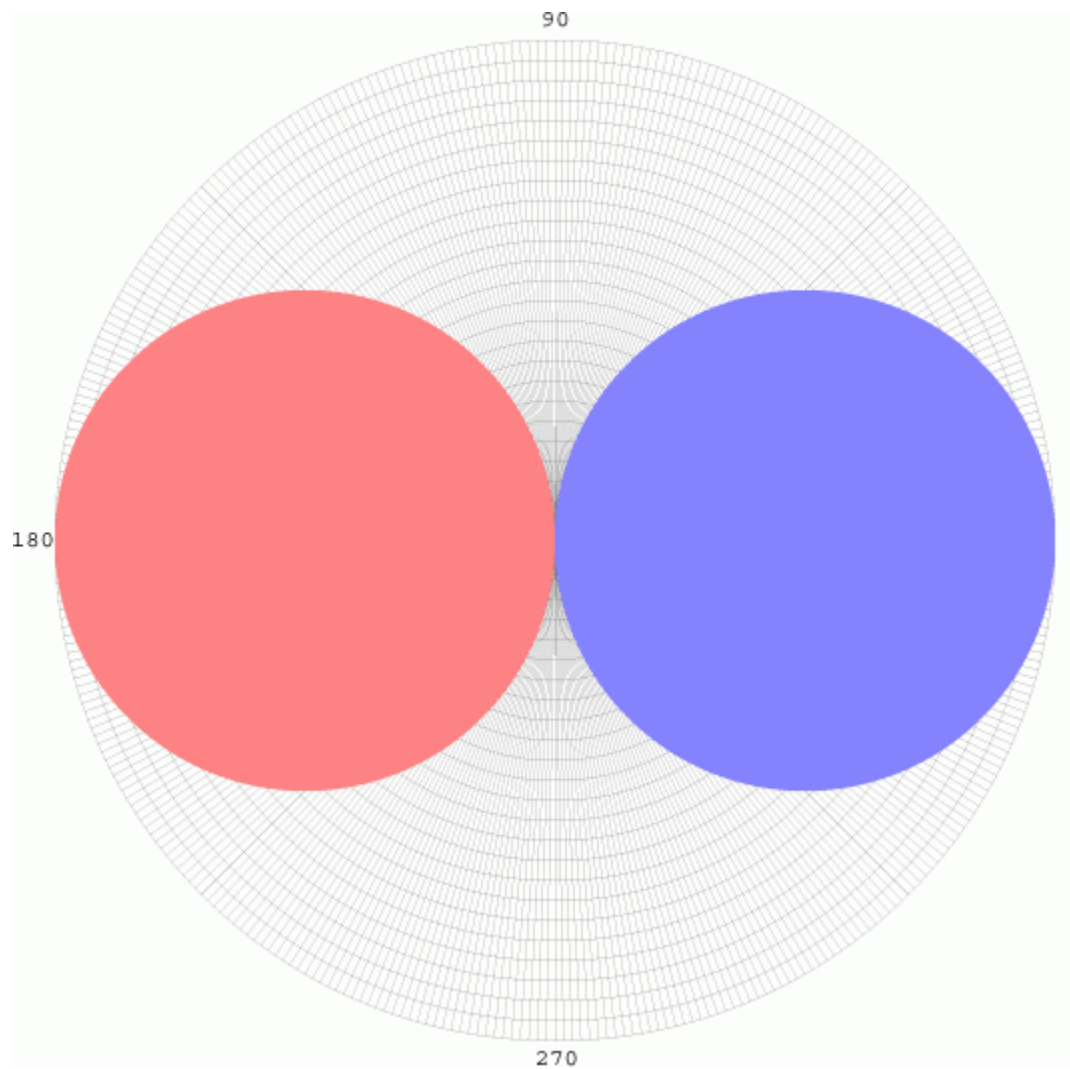


From 0 to 90 degrees, the radius is positive, so the curve is drawn as blue (Top Left). As the curve goes between 90 and 180 degrees, the radius becomes negative, and is graphed in red. While this has no significant realistic interpretations, it does have









Since there is no dependency on  $\Phi$ , the graph is sketched as a pair of tangential spheres. However, when we evaluate probabilities, we often are square integrating the function, so we have to take the square of function (in the case, the square of the radius)

[csi.chemie.tu-darmstadt.de/.../atomic.html](http://csi.chemie.tu-darmstadt.de/.../atomic.html)

## Atomic Orbitals

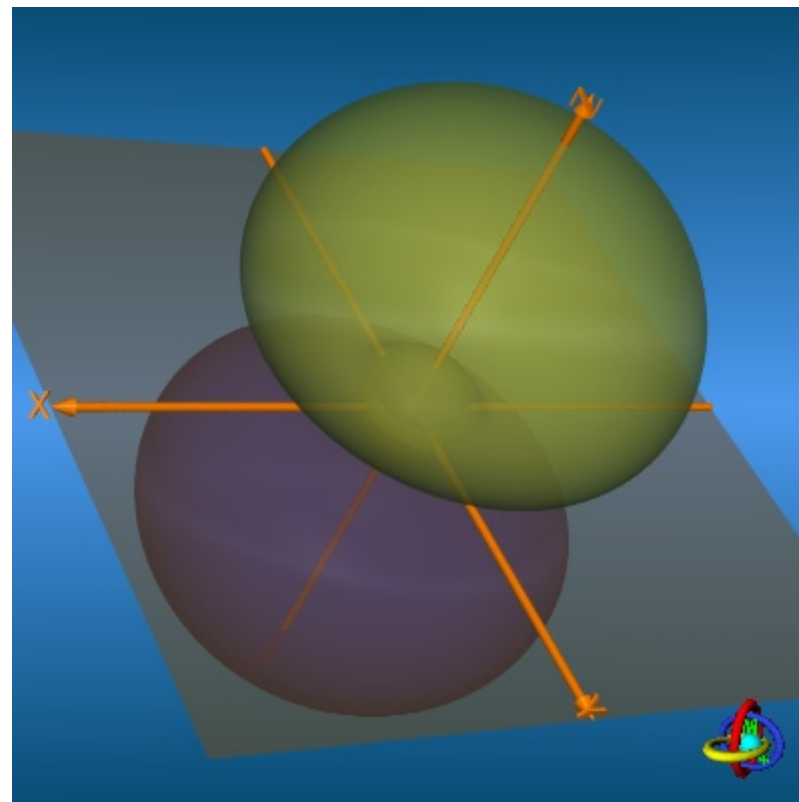
Although the Schrödinger equation may not be explicitly solved for many electron systems, *DFT* and *ab initio* calculations can be used to numerically and iteratively solve the problem. Using this methodology, atomic and molecular orbitals can be computed, and the values of the wave functions or electron densities can be generated on three dimensional grids around atoms or molecules. This page gives an overview on some atomic orbitals calculated for "real" atoms. Orbitals were generated for the corresponding noble gases ( $n = 1$ : He,  $n = 1$ : Ne,  $n = 3$ : Ar,  $n = 4$ : Kr), with exception of the f-orbitals that were generated for the Luthetium (Lu). For more information on the Quantum numbers, and other orbitals of higher states (from the 1s up to the 6d level), see the [hydrogenic orbitals](#) generated for single electron systems (H,  $\text{He}^+$ ,  $\text{Li}^{2+}$ , ...).

- [Calculations](#)
- [Visualizations](#)

The following table provides an overview on the different types and shapes of orbitals from the 1s up to the 4f level. The orbitals are usually visualized as iso-contour surfaces on the electron density, thus a 90% probability surface displays the three-dimensional volume in which an electron is to be found with a 90% chance. Yellow and blue colors indicate regions of opposite sign of the wave function  $\psi$  (the electron density is proportional to  $\psi^2$ ); and the "nodal" planes indicate spatial areas (actually planes, spheres, and cones) where the wave function passes through zero and changes sign.

### ▲ Atomic Orbitals - Calculations

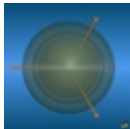
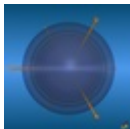
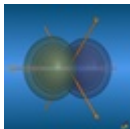
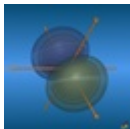
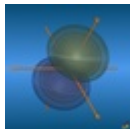
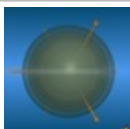
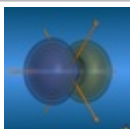
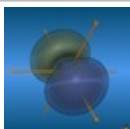
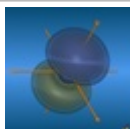
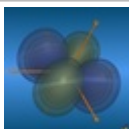

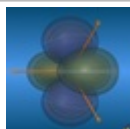



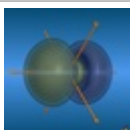



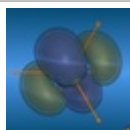
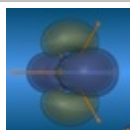


In contrast to the [hydrogenic orbitals](#) generated from pure Cartesian wave functions, these images are for the "real" atoms, and all graphics were generated at a constant scale factor. Therefore, the size of the orbitals may be compared to each other for the different atoms (He, Ne, Ar, Kr, and Lu). Click on the individual images to obtain enlarged visualizations of the orbitals, respectively.

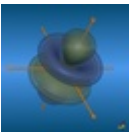
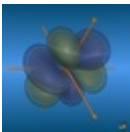
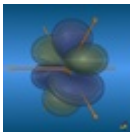
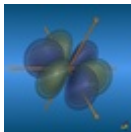
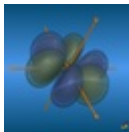
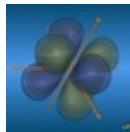
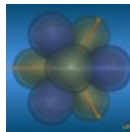
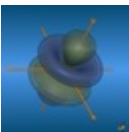
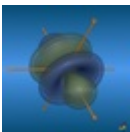
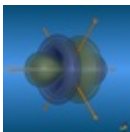
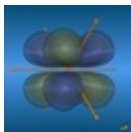


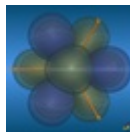


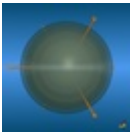
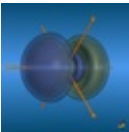
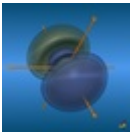
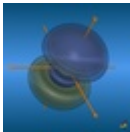
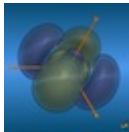
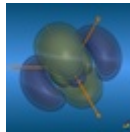
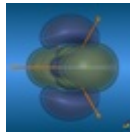
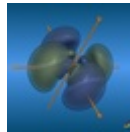
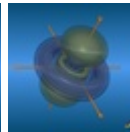
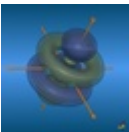
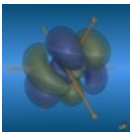
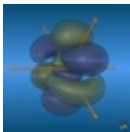
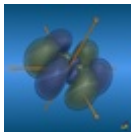
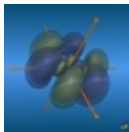
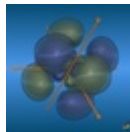
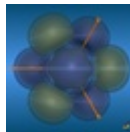

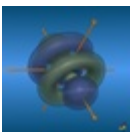
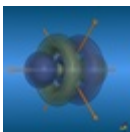
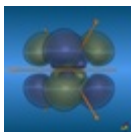
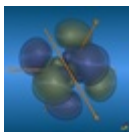
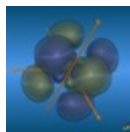
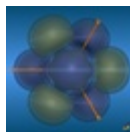

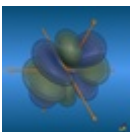
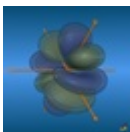
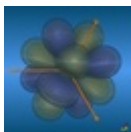

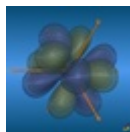

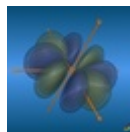
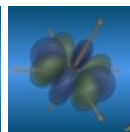
▲ Lobes and Nodes of a 3p-Orbital

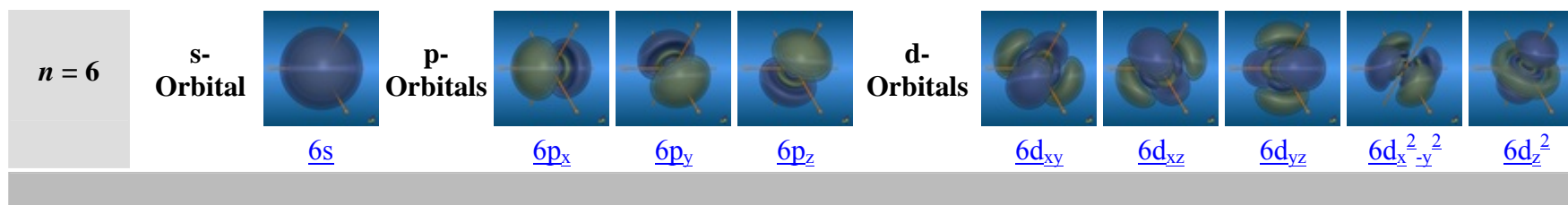


For more information on other research topics, please refer to the complete [list of publications](#) and to the [gallery of graphics and animations](#).

Quantum Numbers		angular QN ( $l$ )	$l = 0$	$l = 1$	$l = 2$								
principal QN ( $n$ )		magnetic QN ( $m_l$ )	$m_l = 0$	$m_l = -1, 0, +1$	$m_l = -2, -1, 0, +1, +2$								
$n = 1$	s-Orbital		<a href="#">1s</a>										
$n = 2$	s-Orbital		<a href="#">2s</a>	p-Orbitals	 <a href="#">2p_x</a>	 <a href="#">2p_y</a>	 <a href="#">2p_z</a>						
$n = 3$	s-Orbital		<a href="#">3s</a>	p-Orbitals	 <a href="#">3p_x</a>	 <a href="#">3p_y</a>	 <a href="#">3p_z</a>	d-Orbitals	 <a href="#">3d_xy</a>	 <a href="#">3d_xz</a>	 <a href="#">3d_yz</a>	 <a href="#">3d_x^2-y^2</a>	 <a href="#">3d_z^2</a>
$n = 4$	s-Orbital		<a href="#">4s</a>	p-Orbitals	 <a href="#">4p_x</a>	 <a href="#">4p_y</a>	 <a href="#">4p_z</a>	d-Orbitals	 <a href="#">4d_xy</a>	 <a href="#">4d_xz</a>	 <a href="#">4d_yz</a>	 <a href="#">4d_x^2-y^2</a>	 <a href="#">4d_z^2</a>

$l = 3$ $m_l = -3, \dots +3$ (general set)	f-Orbitals	 $4f_z^3$	 $4f_{xz}^2$	 $4f_{yz}^2$	 $4f_{y(3x^2-y^2)}$	 $4f_{x(x^2-3y^2)}$	 $4f_{z(x^2-y^2)}$	 $4f_{xyz}$
$l = 3$ $m_l = -3, \dots +3$ (cubic set)	f-Orbitals	 $4f_z^3$	 $4f_y^3$	 $4f_x^3$	 $4f_{x(z^2-y^2)}$	 $4f_{y(z^2-x^2)}$	 $4f_{z(x^2-y^2)}$	 $4f_{xyz}$

$n = 5$	s-Orbital	 $5s$	p-Orbitals	 $5p_x$	 $5p_y$	 $5p_z$	d-Orbitals	 $5d_{xy}$	 $5d_{xz}$	 $5d_{yz}$	 $5d_{x^2-y^2}$	 $5d_{z^2}$
	$l = 3$ $m_l = -3, \dots +3$ (general set)	f-Orbitals	 $5f_z^3$	 $5f_{xz}^2$	 $5f_{yz}^2$	 $5f_{y(3x^2-y^2)}$	 $5f_{x(x^2-3y^2)}$	 $5f_{z(x^2-y^2)}$	 $5f_{xyz}$			
	$l = 3$ $m_l = -3, \dots +3$ (cubic set)	f-Orbitals	 $5f_z^3$	 $5f_y^3$	 $5f_x^3$	 $5f_{x(z^2-y^2)}$	 $5f_{y(z^2-x^2)}$	 $5f_{z(x^2-y^2)}$	 $5f_{xyz}$			
	$l = 4$ $m_l = -4, \dots +4$	g-Orbitals	 $5g_z^4$	 $5g_z^3_x$	 $5g_z^3_y$	 $5g_z^2_{xy}$	 $5g_z^2_{(x^2-y^2)}$	 $5g_{zx}^3$	 $5g_{zy}^3$	 $5g_{xy(x^2-y^2)}$	 $5g_{x^4+y^4}$	



Note: The f-orbitals are special in as much as two different sets of functions are commonly in use, the general and the cubic set. The latter cubic set may be appropriate for describing atoms in an environment of cubic symmetry. Both sets have three orbitals in common ( $nf_z^3$ ,  $nf_{xyz}$ , and  $nf_{z(x^2-y^2)}$ ) with  $n = 4$  (4f), 5 (5f), ...).

[www.chemistry.mcmaster.ca/.../section\\_2.html](http://www.chemistry.mcmaster.ca/.../section_2.html)

## The Probability Distributions for the Hydrogen Atom

To what extent will quantum mechanics permit us to pinpoint the position of an electron when it is bound to an atom? We can obtain an order of magnitude answer to this question by applying the uncertainty principle

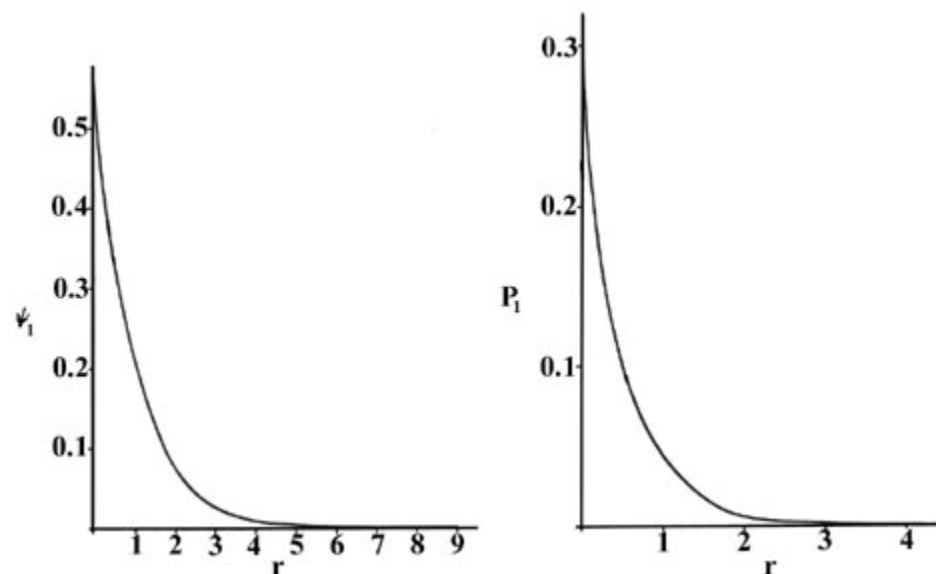
$$\Delta x \Delta p = h$$

to estimate  $\Delta x$ . The value of  $\Delta x$  will represent the minimum uncertainty in our knowledge of the position of the electron. The momentum of an electron in an atom is of the order of magnitude of  $9 \times 10^{-19}$  g cm/sec. The **uncertainty** in the momentum  $\Delta p$  must necessarily be of the same order of magnitude. Thus

$$\Delta x = \frac{7 \times 10^{-27}}{9 \times 10^{-19}} \sim 10^{-8} \text{ cm}$$

The uncertainty in the position of the electron is of the same order of magnitude as the diameter of the atom itself. As long as the electron is bound to the atom, we will not be able to say much more about its position than that it is in the atom. Certainly all models of the atom which describe the electron as a particle following a definite trajectory or orbit must be discarded.

We can obtain an energy and one or more wave functions for every value of  $n$ , the principal quantum number, by solving Schrödinger's equation for the hydrogen atom. A knowledge of the wave functions, or probability amplitudes  $\psi_n$ , allows us to calculate the probability distributions for the electron in any given quantum level. When  $n = 1$ , the wave function and the derived probability function are independent of direction and depend only on the distance  $r$  between the electron and the nucleus. In [Fig. 3-4](#), we plot both  $\psi_1$  and  $P_1$  versus  $r$ , showing the variation in these functions as the electron is moved further and further from the nucleus in any one direction. (These and all succeeding graphs are plotted in terms of the atomic unit of length,  $a_0 = 0.529 \times 10^{-8}$  cm.)



**Fig. 3-4.** The wave function and probability distribution as functions of  $r$  for the  $n = 1$  level of the H atom. The functions and the radius  $r$  are in atomic units in this and succeeding figures.

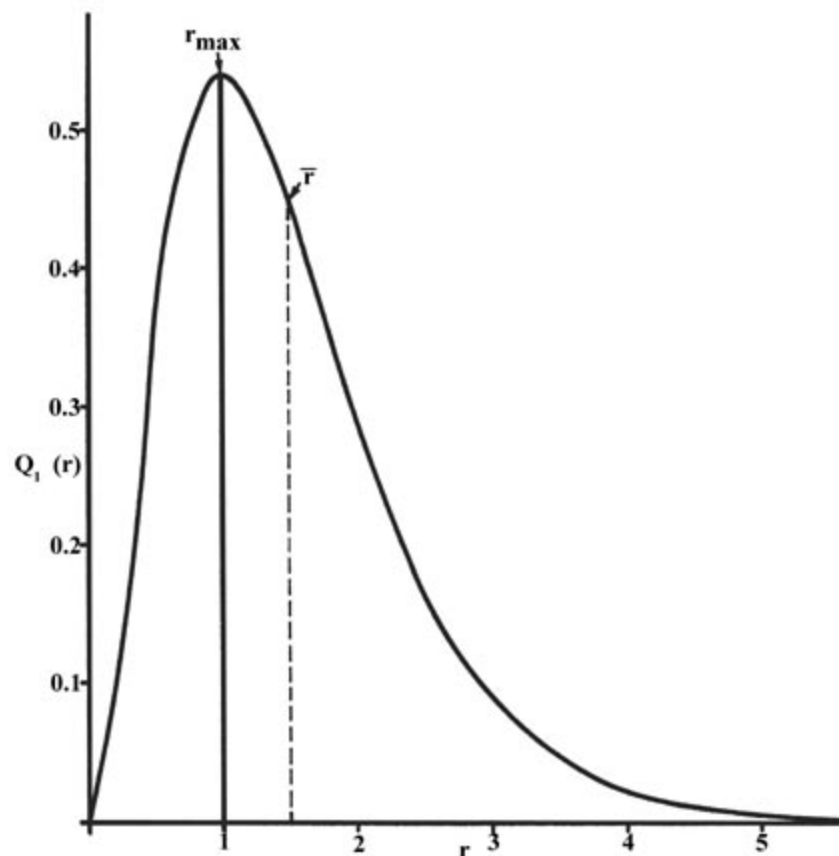
Two interpretations can again be given to the  $P_1$  curve. An experiment designed to detect the position of the electron with an uncertainty much less than the diameter of the atom itself (using light of short wavelength) will, if repeated a large number of times, result in Fig. 3-4 for  $P_1$ . That is, the electron will be detected close to the nucleus most frequently and the probability of observing it at some distance from the nucleus will decrease rapidly with increasing  $r$ . The atom will be ionized in making each of these observations because the energy of the photons with a wavelength much less than  $10^{-8}$  cm will be greater than  $K$ , the amount of energy required to ionize the hydrogen atom. If light with a wavelength comparable to the diameter of the atom is employed in the experiment, then the electron will not be excited but our knowledge of its position will be correspondingly less precise. In these experiments, in which the electron's energy is not changed, the electron will appear to be "smeared out" and we may interpret  $P_1$  as giving the fraction of the total electronic charge to be found in every small volume element of space. (Recall that the addition of the value of  $P_n$  for every small volume element over all space adds up to unity, i.e., one electron and one electronic charge.)

When the electron is in a definite energy level we shall refer to the  $P_n$  distributions as **electron density distributions**, since they describe the manner in which the total electronic charge is distributed in space. The electron density is expressed in terms of the number of electronic charges per unit volume of space,  $e^-/V$ . The volume  $V$  is usually expressed in atomic units of length cubed, and one atomic unit of electron density is then  $e^-/a_0^3$ . To give an idea of the order of magnitude of an atomic density unit, 1 au of charge

density  $e^-/a_0^3 = 6.7$  electronic charges per cubic Ångstrom. That is, a cube with a length of  $0.52917 \times 10^{-8}$  cm, if uniformly filled with an electronic charge density of 1 au, would contain 6.7 electronic charges.

$P_r$  may be represented in another manner. Rather than considering the amount of electronic charge in one particular small element of space, we may determine the total amount of charge lying within a thin spherical shell of space. Since the distribution is independent of direction, consider adding up all the charge density which lies within a volume of space bounded by an inner sphere of radius  $r$  and an outer concentric sphere with a radius only infinitesimally greater, say  $r + \Delta r$ . The area of the inner sphere is  $4\pi r^2$  and the thickness of the shell is  $\Delta r$ . Thus the volume of the shell is  $4\pi r^2 \Delta r$  ([Click here for note.](#)) and the product of this volume and the charge density  $P_r(r)$ , which is the charge or number of electrons per unit volume, is therefore the total amount of electronic charge lying between the spheres of radius  $r$  and  $r + \Delta r$ . The product  $4\pi r^2 P_r$  is given a special name, the radial distribution function, which we shall label  $Q_r(r)$ .

The radial distribution function is plotted in [Fig. 3-5](#) for the ground state of the hydrogen atom.

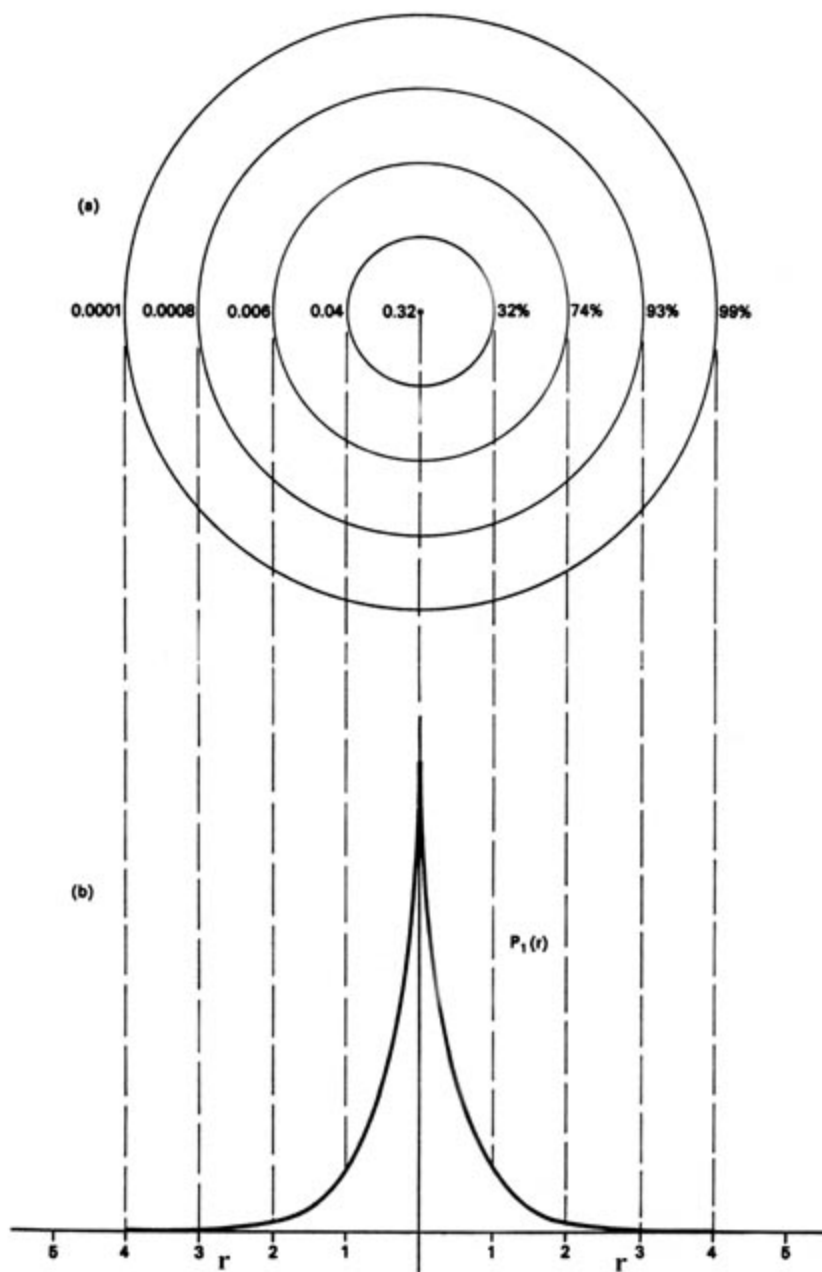


**Fig. 3-5.** The radial distribution function  $Q_1(r)$  for an H atom. The value of this function at some value of  $r$  when multiplied by  $\Delta r$  gives the number of electronic charges within the thin shell of space lying between spheres of radius  $r$  and  $r + \Delta r$ .

The curve passes through zero at  $r = 0$  since the surface area of a sphere of zero radius is zero. As the radius of the sphere is increased, the volume of space defined by  $4\pi r^2 \Delta r$  increases. However, as shown in [Fig 3-4](#), the absolute value of the electron density at a given point decreases with  $r$  and the resulting curve must pass through a maximum. This maximum occurs at  $r_{max} = a_0$ . Thus more of the electronic charge is present at a distance  $a_0$ , out from the nucleus than at any other value of  $r$ . Since the curve is unsymmetrical, the average value of  $r$ , denoted by  $\bar{r}$ , is not equal to  $r_{max}$ . The average value of  $r$  is indicated on the figure by a dashed line. A "picture" of the electron density distribution for the electron in the  $n = 1$  level of the hydrogen atom would be a spherical ball of charge, dense around the nucleus and becoming increasingly diffuse as the value of  $r$  is increased.

We could also represent the distribution of negative charge in the hydrogen atom in the manner used previously for the electron confined to move on a plane, [Fig. 2-4](#), by displaying the charge density in a plane by means of a contour map. Imagine a plane through the atom including the nucleus. The density is calculated at every point in this plane. All points having the same value for the electron density in this plane are joined by a contour line ([Fig. 3-6](#)). Since the electron density depends only on  $r$ , the distance from the nucleus, and not on the direction in space, the contours will be circular. A contour map is useful as it indicates the "shape" of the density distribution.





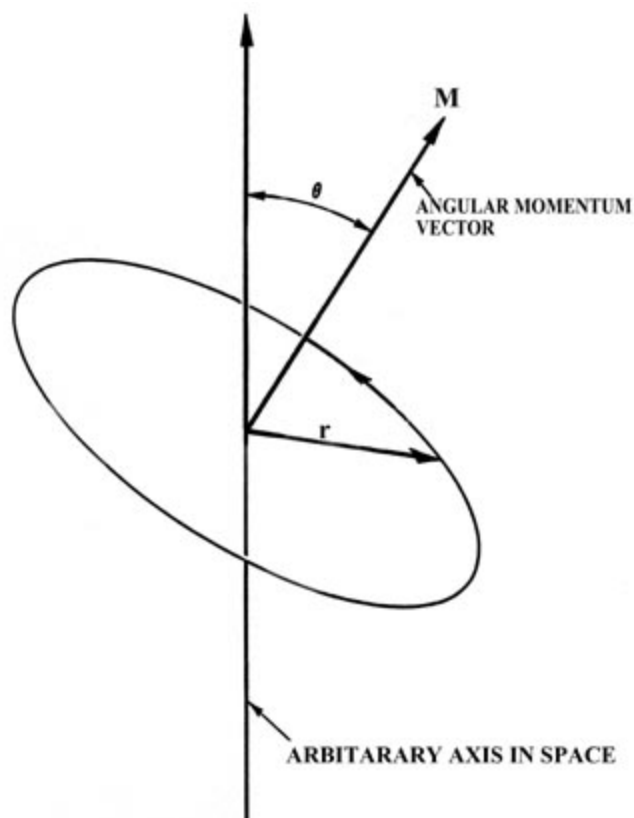
**Fig. 3-6.** (a) A contour map of the electron density distribution in a plane containing the nucleus for the  $n = 1$  level of the H atom. The distance between adjacent contours is 1 au. The numbers on the left-hand side on each contour give the electron density in au. The numbers on the right-hand side give the fraction of the total electronic charge which lies within a sphere of that radius. Thus 99% of the single electronic charge of the H atom lies within a sphere of radius 4 au (or diameter =  $4.2 \times 10^{-8}$  cm).

(b) This is a profile of the contour map along a line through the nucleus. It is, of course, the same as that given previously in [Fig. 3-4](#) for  $P_1$ , but now plotted from the nucleus in both directions.

This completes the description of the most stable state of the hydrogen atom, the state for which  $n = 1$ . Before proceeding with a discussion of the excited states of the hydrogen atom we must introduce a new term. When the energy of the electron is increased to another of the allowed values, corresponding to a new value for  $n$ ,  $\psi_n$  and  $P_n$  change as well. The wave functions  $\psi_n$  for the hydrogen atom are given a special name, **atomic orbitals**, because they play such an important role in all of our future discussions of the electronic structure of atoms. In general the word orbital is the name given to a wave function which determines the motion of a single electron. If the one-electron wave function is for an atomic system, it is called an atomic orbital. ([Click here for note.](#))

For every value of the energy  $E_n$ , for the hydrogen atom, there is a degeneracy equal to  $n^2$ . Therefore, for  $n = 1$ , there is but one atomic orbital and one electron density distribution. However, for  $n = 2$ , there are four different atomic orbitals and four different electron density distributions, all of which possess the same value for the energy,  $E_2$ . Thus for all values of the principal quantum number  $n$  there are  $n^2$  different ways in which the electronic charge may be distributed in three-dimensional space and still possess the same value for the energy. For every value of the principal quantum number, **one** of the possible atomic orbitals is independent of direction and gives a spherical electron density distribution which can be represented by circular contours as has been exemplified above for the case of  $n = 1$ . The other atomic orbitals for a given value of  $n$  exhibit a directional dependence and predict density distributions which are not spherical but are concentrated in planes or along certain axes. The angular dependence of the atomic orbitals for the hydrogen atom and the shapes of the contours of the corresponding electron density distributions are intimately connected with the angular momentum possessed by the electron.

The physical quantity known as angular momentum plays a dominant role in the understanding of the electronic structure of atoms. To gain a physical picture and feeling for the angular momentum it is necessary to consider a model system from the classical point of view. The simplest classical model of the hydrogen atom is one in which the electron moves in a circular orbit with a constant speed or angular velocity ([Fig. 3-7](#)). Just as the ordinary momentum  $m\mathbf{v}$  plays a dominant role in the analysis of straight line or linear motion, so angular momentum plays the central role in the analysis of a system with circular motion as found in the model of the hydrogen atom.



**Fig. 3-7.** The angular momentum vector for a classical model of the atom.

In [Fig. 3-7](#),  $m$  is the mass of the electron,  $\mathbf{v}$  is the linear velocity (the velocity the electron would possess if it continued moving at a tangent to the orbit as indicated in the figure) and  $r$  is the radius of the orbit. The linear velocity  $\mathbf{v}$  is a vector since it possesses at any instant both a magnitude and a direction in space. Obviously, as the electron rotates in the orbit the direction of  $\mathbf{v}$  is constantly changing, and thus the linear momentum  $m\mathbf{v}$  is **not** constant for the circular motion. This is so even though the speed of the electron (the magnitude of  $\mathbf{v}$  which is denoted by  $v$ ) remains unchanged. According to Newton's second law, a force must be acting on the electron if its momentum changes with time. This is the force which prevents the electron from flying on tangent to its orbit. In an atom the attractive force which contains the electron is the electrostatic force of attraction between the nucleus and the electron, directed along the radius  $r$  at right angles to the direction of the electron's motion.

The angular momentum, like the linear momentum, is a vector and is defined as follows:

$$\text{magnitude of angular momentum} = M = mvr$$

The angular momentum vector  $\mathbf{M}$  is directed along the axis of rotation. From the definition it is evident that the angular momentum vector will remain constant as long as the speed of the electron in the orbit is constant ( $v$  remains unchanged) and the plane and radius of the orbit remain unchanged. Thus for a given orbit, the angular momentum is constant as long as the angular velocity of the particle in the orbit is constant. In an atom the only force on the electron in the orbit is directed along  $r$ ; it has no component in the direction of the motion. The force acts in such a way as to change only the linear momentum. Therefore, while the linear momentum is not constant during the circular motion, the angular momentum is. A force exerted on the particle in the direction of the vector  $\mathbf{v}$  would change the angular velocity and the angular momentum. When a force is applied which does change  $\mathbf{M}$ , a *torque* is said to be acting on the system. Thus angular momentum and torque are related in the same way as are linear momentum and force.

The important point of the above discussion is that both the angular momentum and the energy of an atom remain constant if the atom is left undisturbed. ***Any physical quantity which is constant in a classical system is both conserved and quantized in a quantum mechanical system.*** Thus both the energy and the angular momentum are quantized for an atom.

There is a quantum number, denoted by  $l$ , which governs the magnitude of the angular momentum, just as the quantum number  $n$  determines the energy. The ***magnitude*** of the angular momentum may assume only those values given by:

$$(4) \quad M = \sqrt{l(l+1)} \left( \frac{h}{2\pi} \right) \quad l = 0, 1, 2, 3, \dots, n-1$$

Furthermore, the value of  $n$  limits the maximum value of the angular momentum as the value of  $l$  cannot be greater than  $n - 1$ . For the state  $n = 1$  discussed above,  $l$  may have the value of zero only. When  $n = 2$ ,  $l$  may equal 0 or 1, and for  $n = 3$ ,  $l = 0$  or 1 or 2, etc. When  $l = 0$ , it is evident from equation (4) that the angular momentum of the electron is zero. The atomic orbitals which describe these states of zero angular momentum are called  $s$  orbitals. The  $s$  orbitals are distinguished from one another by stating the value of  $n$ , the principal quantum number. They are referred to as the  $1s$ ,  $2s$ ,  $3s$ , etc., atomic orbitals.

The preceding discussion referred to the  $1s$  orbital since for the ground state of the hydrogen atom  $n = 1$  and  $l = 0$ . This orbital, and all  $s$  orbitals in general, predict spherical density distributions for the electron as exemplified by [Fig. 3-5](#) for the  $1s$  density. [Figure 3-8](#)

shows the radial distribution functions  $Q(r)$  which apply when the electron is in a  $2s$  or  $3s$  orbital to illustrate how the character of the density distributions change as the value of  $n$  is increased. ([Click here for note.](#))

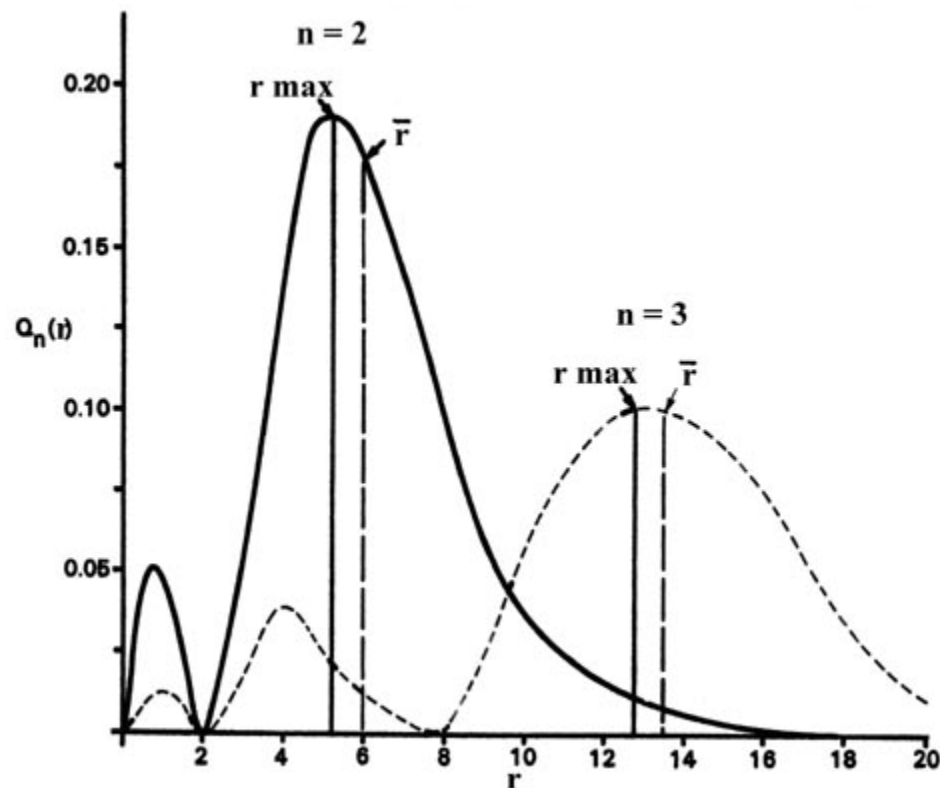
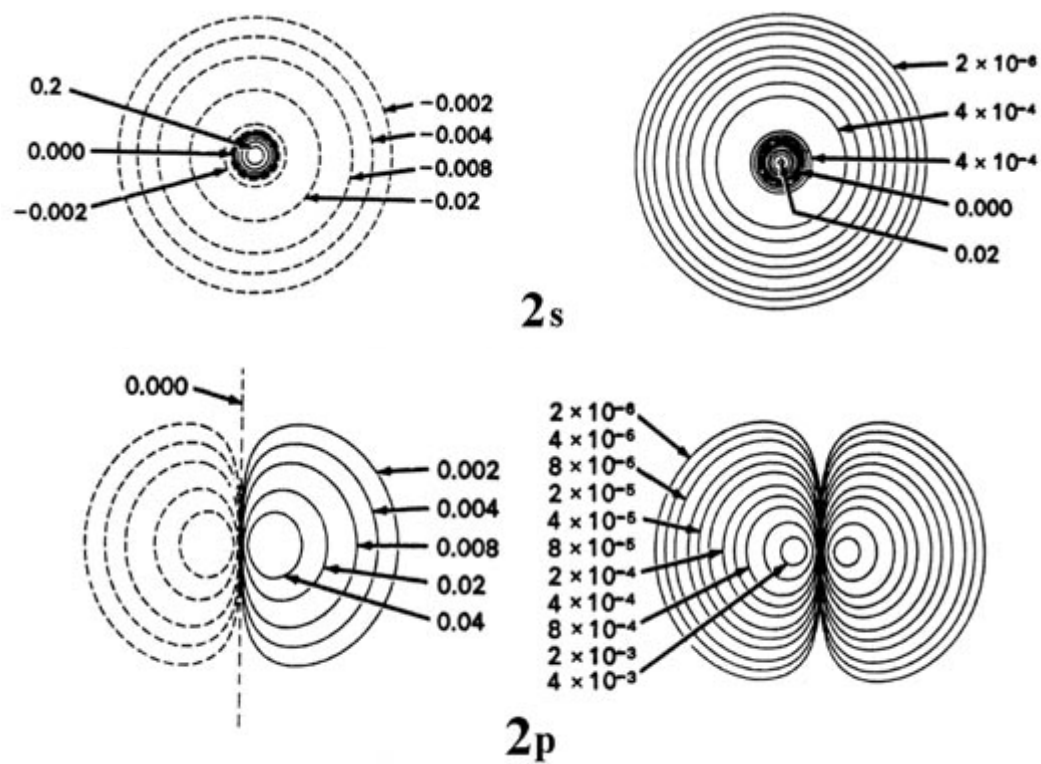
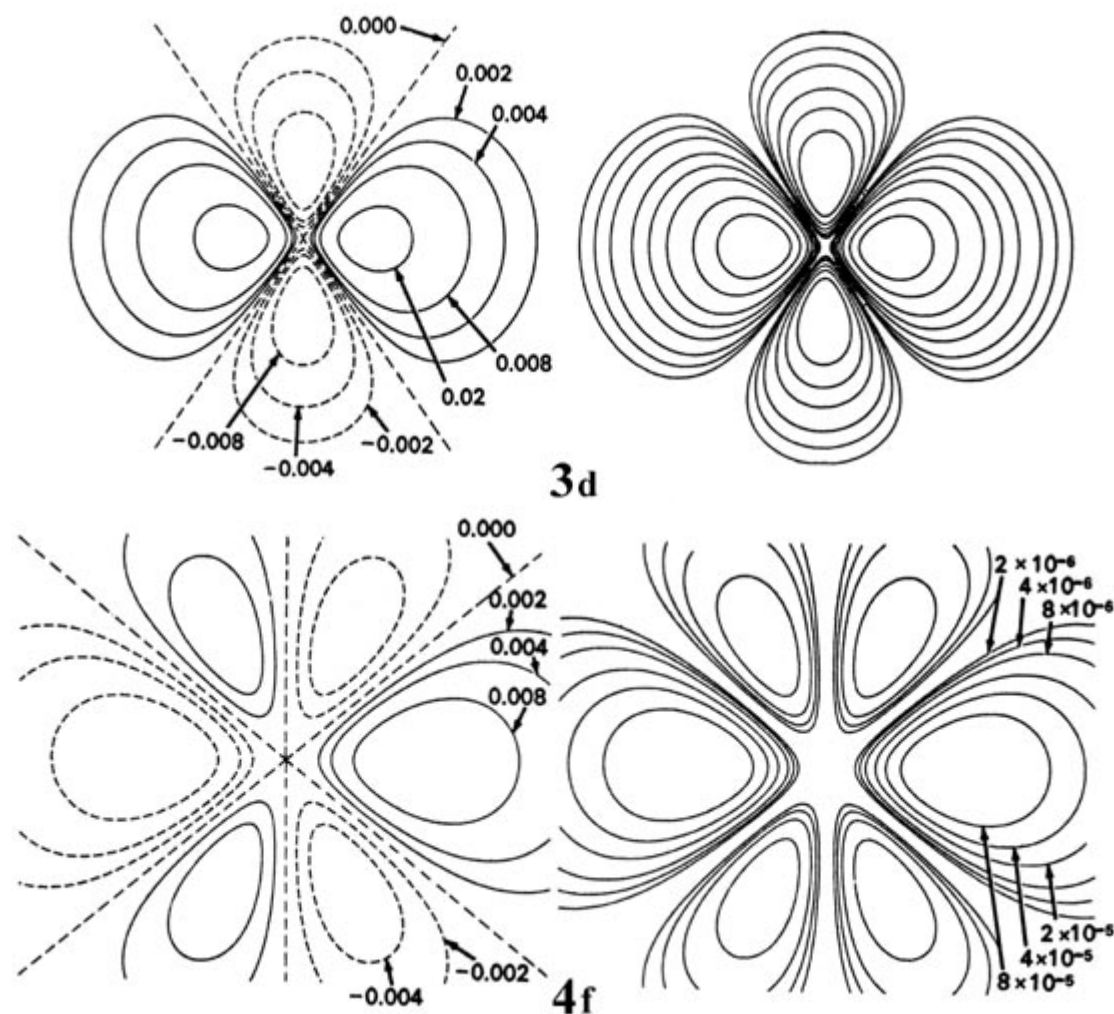


Fig. 3-8. Radial distribution functions for the  $2s$  and  $3s$  density distributions.

Comparing these results with those for the  $1s$  orbital in [Fig. 3-5](#) we see that as  $n$  increases the average value of  $r$  increases. This agrees with the fact that the energy of the electron also increases as  $n$  increases. The increased energy results in the electron being on the average pulled further away from the attractive force of the nucleus. As in the simple example of an electron moving on a line, nodes (values of  $r$  for which the electron density is zero) appear in the probability distributions. The number of nodes increases with increasing energy and equals  $n - 1$ .

When the electron possesses angular momentum the density distributions are no longer spherical. In fact for each value of  $l$ , the electron density distribution assumes a characteristic shape ([Fig. 3-9](#)).

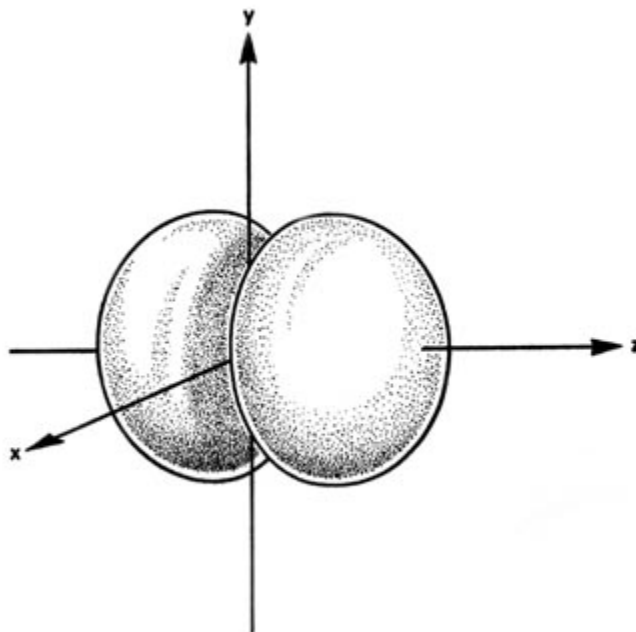




**Fig. 3-9.** Contour maps of the  $2s$ ,  $2p$ ,  $3d$  and  $4f$  atomic orbitals and their charge density distributions for the H atom. The zero contours shown in the maps for the orbitals define the positions of the nodes. Negative values for the contours of the orbitals are indicated by dashed lines, positive values by solid lines.

When  $l = 1$ , the orbitals are called  $p$  orbitals. In this case the orbital and its electron density are concentrated along a line (axis) in space. The  $2p$  orbital or wave function is positive in value on one side and negative in value on the other side of a plane which is

perpendicular to the axis of the orbital and passes through the nucleus. The orbital has a node in this plane, and consequently an electron in a  $2p$  orbital does not place any electronic charge density at the nucleus. The electron density of a  $1s$  orbital, on the other hand, is a maximum at the nucleus. The same diagram for the  $2p$  density distribution is obtained for any plane which contains this axis. Thus in three dimensions the electron density would appear to be concentrated in two lobes, one on each side of the nucleus, each lobe being circular in cross section ([Fig. 3-10](#)).



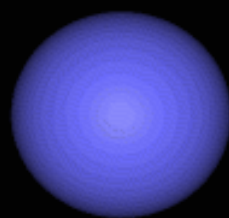
**Fig. 3-10.** The appearance of the  $2p$  electron density distribution in three-dimensional space.

When  $l = 2$ , the orbitals are called  $d$  orbitals and [Fig. 3-9](#) shows the contours in a plane for a  $3d$  orbital and its density distribution. Notice that the density is again zero at the nucleus and that there are now two nodes in the orbital and in its density distribution. As a final example, [Fig. 3-9](#) shows the contours of the orbital and electron density distribution obtained for a  $4f$  atomic orbital which occurs when  $n = 4$  and  $l = 3$ . ([Click here for note.](#)) The point to notice is that as the angular momentum of the electron increases, the density distribution becomes increasingly concentrated along an axis or in a plane in space. Only electrons in  $s$  orbitals with zero angular momentum give spherical density distributions and in addition place charge density at the position of the nucleus.

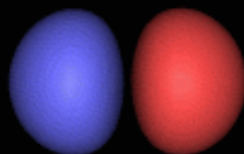


We have not as yet accounted for the full degeneracy of the hydrogen atom orbitals which we stated earlier to be  $n^2$  for every value of  $n$ . For example, when  $n = 2$ , there are four distinct atomic orbitals. The remaining degeneracy is again determined by the angular momentum of the system. Since angular momentum like linear momentum is a vector quantity, we may refer to the component of the angular momentum vector which lies along some chosen axis. For reasons we shall investigate, the number of values a particular component can assume for a given value of  $l$  is  $(2l + 1)$ . Thus when  $l = 0$ , there is no angular momentum and there is but a single orbital, an  $s$  orbital. When  $l = 1$ , there are three possible values for the component ( $2 \times 1 + 1$ ) of the total angular momentum which are physically distinguishable from one another. There are, therefore, three  $p$  orbitals. Similarly there are five  $d$  orbitals, ( $2 \times 2 + 1$ ), seven  $f$  orbitals, ( $2 \times 3 + 1$ ), etc. All of the orbitals with the same value of  $n$  and  $l$ , the three  $2p$  orbitals for example, are similar but differ in their spatial orientations.

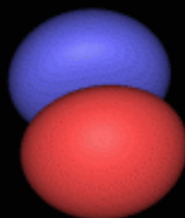
To gain a better understanding of this final element of degeneracy, we must consider in more detail what quantum mechanics predicts concerning the angular momentum of an electron in an atom.



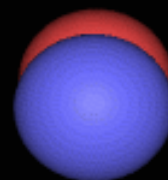
s



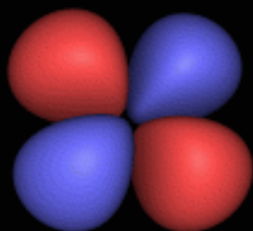
$p_x$



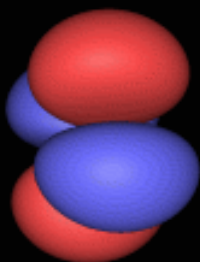
$p_y$



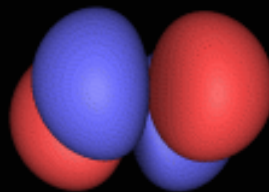
$p_z$



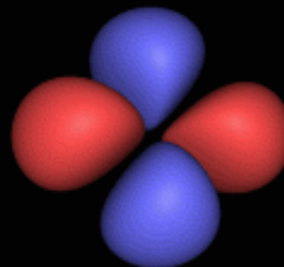
$d_{xy}$



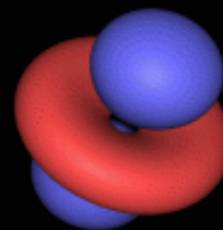
$d_{xz}$



$d_{yz}$



$d_{x^2-y^2}$



$d_{z^2}$