Chemistry 3P51 – Fall 2013
Quantum Chemistry

Lecture No. 22
Oct 30th, 2013

Objectives

- To present the wave-function for hydrogenic atoms.
- To introduce the spectroscopic designation of hydrogenic states.
- To introduce the concept of contour surface plots of hydrogenic orbitals.
- To present real-valued orbitals and probability densities for the electron in the hydrogen atom.

Eigenfunctions (orbitals) and probability densities for hydrogenic atoms

A wave function of a one-electron system is called an **orbital**.
For atoms, one-electron wavefunctions are called **atomic orbitals**.

The atomic orbitals of hydrogenic atoms are of the form

$$\psi_{nlm}(r,\theta,\varphi) = R_{nl}(r)Y_l^m(\theta,\varphi)$$

$$\begin{aligned} &n = 1, 2, 3, \dots \\ &l = 0, 1, 2, \dots, n-1 \\ &m = 0, \pm 1, \pm 2, \dots, \pm l \end{aligned}$$

There are three **quantum numbers** (n,l,m) that characterize each state.

These quantum numbers are used as labels for the wave function.

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Some radial wave-functions for hydrogenic atoms

$$R_{10}(r) = 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$$

$$R_{20}(r) = \frac{1}{\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2}\left(1-\frac{Zr}{2a_0}\right)e^{-Zr/2a_0}$$

$$R_{21}(r) = \frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{5/2} re^{-Zr/2a_0}$$

$$R_{30}(r) = \frac{2}{3\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2}\left(1-\frac{2Zr}{3a_0}+\frac{2Z^2r^2}{27a_0^2}\right)e^{-Zr/3a_0}$$

$$R_{31}(r) = \frac{8}{27\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}-\frac{Z^2r^2}{6a_0^2}\right)e^{-Zr/3a_0}$$

$$R_{32}(r) = \frac{4}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2} r^2e^{-Zr/3a_0}$$

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Wave-functions (orbitals) for the hydrogen atom

Let us define $\rho \equiv \dfrac{r}{a_0}$

– distance in units of bohrs

$$\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-\rho}$$

$$\psi_{200} = \frac{1}{\sqrt{32\pi}}\left(\frac{1}{a_0}\right)^{3/2} (2-\rho)e^{-\rho/2}$$

$$\psi_{210} = \frac{1}{\sqrt{32\pi}}\left(\frac{1}{a_0}\right)^{3/2} \rho e^{-\rho/2}\cos\theta$$

$$\psi_{21\pm1} = \frac{1}{\sqrt{64\pi}}\left(\frac{1}{a_0}\right)^{3/2} \rho e^{-\rho/2}\sin\theta\, e^{\pm i\varphi}$$

$$\psi_{300} = \frac{1}{81\sqrt{3\pi}}\left(\frac{1}{a_0}\right)^{3/2} (27-18\rho+2\rho^2)e^{-\rho/3}$$

$$\psi_{310} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} (6\rho-\rho^2)e^{-\rho/3}\cos\theta$$

$$\psi_{31\pm1} = \frac{1}{81\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} (6\rho-\rho^2)e^{-\rho/3}\sin\theta\, e^{\pm i\varphi}$$

$$\psi_{320} = \frac{1}{81\sqrt{6\pi}}\left(\frac{1}{a_0}\right)^{3/2} \rho^2 e^{-\rho/3}(3\cos^2\theta-1)$$

$$\psi_{32\pm1} = \frac{1}{81\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} \rho^2 e^{-\rho/3}\sin\theta\cos\theta\, e^{\pm i\varphi}$$

$$\psi_{32\pm2} = \frac{1}{162\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} \rho^2 e^{-\rho/3}\sin^2\theta\, e^{\pm 2i\varphi}$$

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Spectroscopic designation of hydrogenic states

The hydrogen orbitals depend on three quantum numbers: n, l, m.

It is customary to denote the value of l by a letter according to the following convention:

The value of l	0	1	2	3	4	5
Designation	s	p	d	f	g	h

The quantum number n is shown first, followed by one of the above letters for l, and m is indicated by a subscript.

Examples:

$1s$ ψ_{100}, an orbital with $n = 1$, $l = 0$, and $m = 0$; (the subscript 0 is omitted because it is the only possibility)

$2p_{-1}$ ψ_{21-1}, an orbital with $n = 2$, $l = 1$, and $m = -1$

$4d_2$ ψ_{422}, an orbital with $n = 4$, $l = 2$, and $m = +2$

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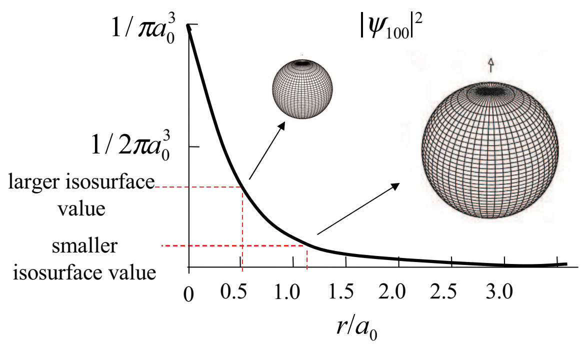
Contour surface plots of hydrogenic orbitals

An orbital may be represented by a **probability density isosurface**, that is, a contour surface of some chosen fixed value of $|\psi_{nlm}|^2$. If $|\psi_{nlm}|^2$ is constant on a given surface, then $|\psi_{nlm}|$ is also constant on that surface.



Isosurface plots of the 1s orbital for two different constant values of $|\psi_{100}|^2$

Usually, the constant is chosen so that the surface encloses the region of space within which the probability of finding the electron is, say, 95% (or some other value).

The real-valued 2p-orbitals

The p_x and p_y orbitals are **real-valued functions** constructed as linear combinations of the actual (complex) hydrogenic orbitals:

$$\boxed{\psi_{21\pm1} = \frac{1}{\sqrt{64\pi}}\left(\frac{1}{a_0}\right)^{5/2} re^{-r/2a_0}\sin\theta\, e^{\pm i\varphi}}$$

$$\psi_{2p_x} = \frac{1}{\sqrt{2}}(\psi_{211}+\psi_{21-1}) = \frac{1}{\sqrt{32\pi}}\left(\frac{1}{a_0}\right)^{5/2} re^{-r/2a_0}\sin\theta\cos\varphi$$

$$= \frac{1}{\sqrt{32\pi}}\left(\frac{1}{a_0}\right)^{5/2} xe^{-r/2a_0}$$

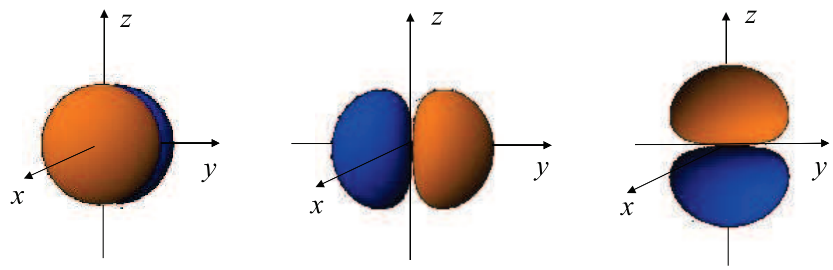
$$\psi_{2p_y} = \frac{1}{i\sqrt{2}}(\psi_{211}-\psi_{21-1}) = \frac{1}{\sqrt{32\pi}}\left(\frac{1}{a_0}\right)^{5/2} re^{-r/2a_0}\sin\theta\sin\varphi$$

$$= \frac{1}{\sqrt{32\pi}}\left(\frac{1}{a_0}\right)^{5/2} ye^{-r/2a_0}$$

The p_z orbital is already real-valued:

$$\psi_{2p_z} = \psi_{210} = \psi_{2p_0} = \frac{1}{\sqrt{32\pi}}\left(\frac{1}{a_0}\right)^{5/2} re^{-r/2a_0}\cos\theta = \frac{1}{\sqrt{32\pi}}\left(\frac{1}{a_0}\right)^{5/2} ze^{-r/2a_0}$$

Contour surface plot of the three $2p$ orbitals are shown below.



$2p_x$ $2p_y$ $2p_0 = 2p_z$

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Real orbitals which are linear combinations of eigenfunctions of different eigenvalues m are **not** eigenfunctions of the operator L_z.

Thus, for example, the $2p_z$ orbital

$$\psi_{210} \equiv \psi_{2p_z} = \psi_{2p_0} = \frac{1}{\sqrt{32\pi}}\left(\frac{1}{a_0}\right)^{5/2} re^{-r/2a_0}\cos\theta$$

has a definite value of the magnetic quantum number m, while the $2p_x$ and $2p_y$ orbitals,

$$\psi_{2p_x} \equiv \frac{1}{\sqrt{2}}(\psi_{211} + \psi_{21-1}) = \frac{1}{\sqrt{32\pi}}\left(\frac{1}{a_0}\right)^{5/2} re^{-r/2a_0}\sin\theta\cos\varphi$$

$$\psi_{2p_y} \equiv \frac{1}{i\sqrt{2}}(\psi_{211} - \psi_{21-1}) = \frac{1}{\sqrt{32\pi}}\left(\frac{1}{a_0}\right)^{5/2} re^{-r/2a_0}\sin\theta\sin\varphi$$

do not have a definite value of the quantum number m.

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The real-valued 3d-orbitals

$$\psi_{3d_{z^2}} = \psi_{320} = \frac{1}{81\sqrt{6\pi}}\left(\frac{1}{a_0}\right)^{7/2} r^2 e^{-r/3a_0}(3\cos^2\theta - 1)$$

$$\psi_{3d_{xz}} = \frac{1}{\sqrt{2}}(\psi_{321} + \psi_{32-1}) = \frac{2}{81\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{7/2} r^2 e^{-r/3a_0} \sin\theta\cos\theta\cos\varphi$$

$$\psi_{3d_{yz}} = \frac{1}{i\sqrt{2}}(\psi_{321} - \psi_{32-1}) = \frac{2}{81\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{7/2} r^2 e^{-r/3a_0} \sin\theta\cos\theta\sin\varphi$$

$$\psi_{3d_{x^2-y^2}} = \frac{1}{\sqrt{2}}(\psi_{322} + \psi_{32-2}) = \frac{1}{81\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{7/2} r^2 e^{-r/3a_0} \sin^2\theta\cos 2\varphi$$

$$\psi_{3d_{xy}} = \frac{1}{i\sqrt{2}}(\psi_{322} - \psi_{32-2}) = \frac{1}{81\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{7/2} r^2 e^{-r/3a_0} \sin^2\theta\sin 2\varphi$$

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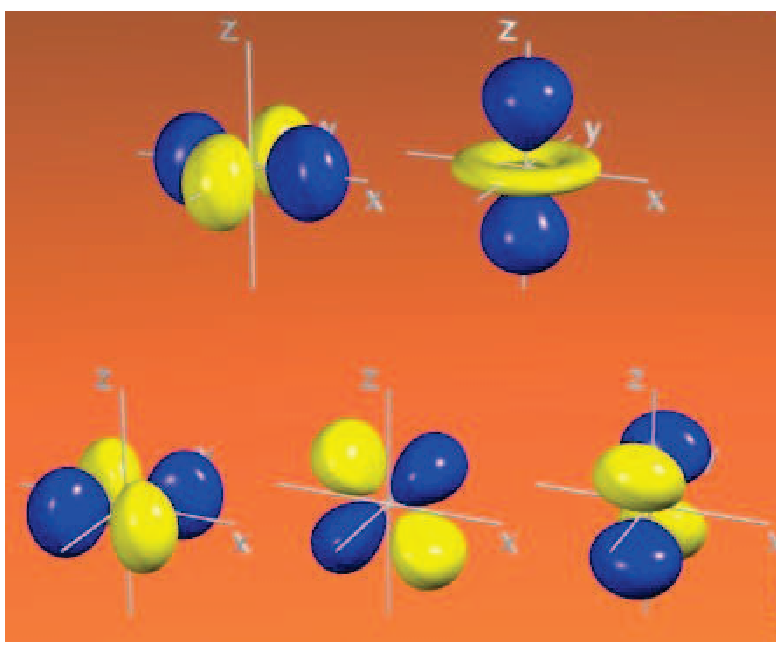
Contour surface plots of the five real 3*d*-orbitals



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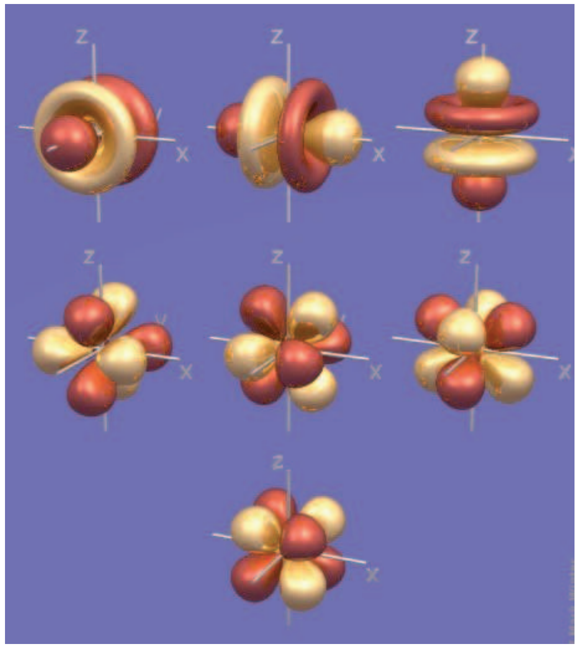
Contour surface plots of the seven real 4*f*-orbitals



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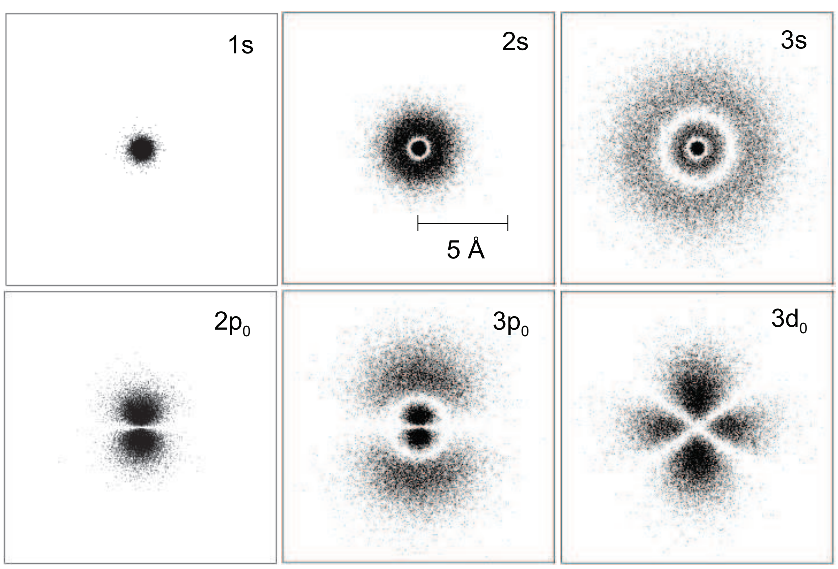
Probability densities of the electron in the H atom



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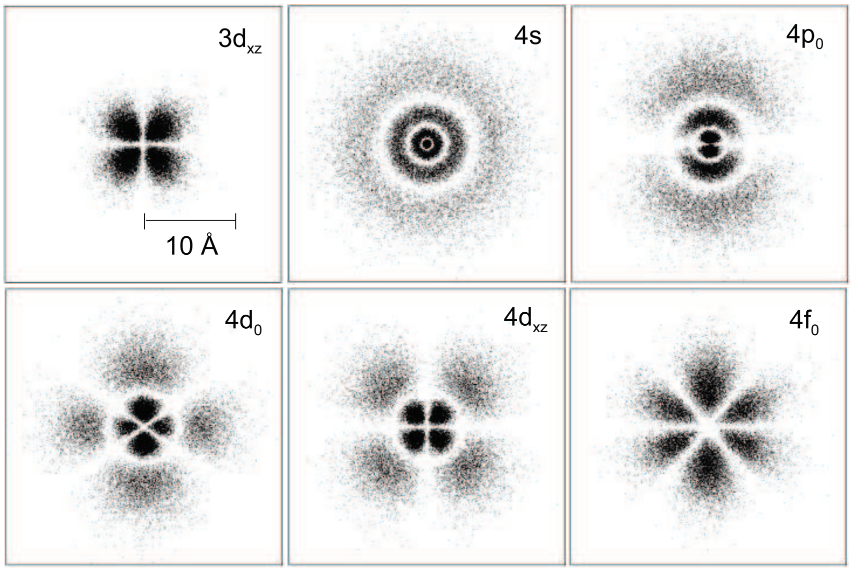
Probability densities of the electron in the H atom



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