

More on Atomic Orbitals

1. Nature of the solutions

We won't be concerned with the details of "solving" the Schrodinger Equation for the H atom in this course, but, it's not too hard to show that one may break it down into 3 separate equations, each depending on only one of the 3 variables r , Θ , and ϕ . Whenever this happens, one finds that the well behaved solutions (the orbitals) are products of 3 functions, each depending on only r , Θ or ϕ and each orbital is characterized by 3 integer quantum numbers, n , l , and m , (3 because space is 3-dimensional).

$$\begin{aligned} \psi_{n\ell m} &= R_{n\ell}(r) \Theta_{\ell m}(\Theta) \Phi_m(\phi) \\ &= \left(L_{n+\ell}^{2\ell+1} \left(\frac{2Zr}{na_0} \right) e^{-\frac{Zr}{na_0}} \right) P_{\ell}^{|\ell m|}(\cos \Theta) e^{im\phi} \\ &= \left(L_{n+\ell}^{2\ell+1} \left(\frac{e}{z} \right) e^{-\frac{e}{z}} \right) \cdot Y_{\ell, m}(\Theta, \phi) \end{aligned}$$

The $P_{\ell}^{|\ell m|}$ are the famous associated Legendre polynomials each has powers of $\cos \Theta$ in it. The product of the two angular parts is the same for every spherical problem, not just for quantum mechanics of atoms. Thus it's given a special name and symbol.

$$Y_{\ell, m}(\Theta, \phi) = \text{SPHERICAL HARMONICS}$$

The $R_{n\ell}(r)$ describes the Radial Motion (in and out). The $L_{n+\ell}^{2\ell+1}$ are the famous associated Laguerre Polynomials. All these equations and solutions were known and solved by mathematicians in the 1800's or earlier. This should

serve to make the distinction between theory and mathematics. The same math appears in many different theories. What Schroedinger did was discover how to map physical reality onto existing mathematics.

We will note at this point only that l , the measure of angular momentum affects the radial function because of the "centrifugal force" as discussed above. (Handout # 6)

2. The Φ Equation

Its fairly easy to show that $\frac{\partial^2 \Phi}{\partial \phi^2} = -a \Phi$

and that $\Phi = N e^{-im\phi}$

$$m = 0, \pm 1, \pm 2, \dots$$

Integer values come from requirement that $\Phi(\phi) = \Phi(\phi + 2\pi)$

The significance is found from noting that

$$L_z = (P_{ang})_z r \sin \theta$$

$$\frac{L_z^2}{2\mu (r \sin \theta)^2} = \frac{(P_{ang})_z^2}{2\mu} \quad \begin{array}{l} \text{Angular} \\ = \text{Kinetic energy} \end{array}$$

due to motion around the z axis, i.e., that in xy plane.

Examine the Schroedinger Equation and note that

$$\mathcal{L}_z^2 = -\hbar^2 \frac{\partial^2}{\partial \phi^2}$$

so

$$\mathcal{L}_z = -i\hbar \frac{\partial}{\partial \phi}$$

Note the parallel to linear momentum.

Thus $\mathcal{L}_z \Phi_m = m\hbar \Phi_m$

and Φ_m are eigenfunctions of \mathcal{L}_z with eigenvalues $m\hbar$.

Clearly $L_z^2 \Phi_m = m^2 \hbar^2$ so that $\frac{m^2 \hbar^2}{2\mu(r \sin\theta)^2}$

gives the total kinetic energy about z axis.

Relation of m and l:

$$l(l+1)\hbar^2 = \text{total square of angular momentum} = L^2$$

where $L^2 = L_x^2 + L_y^2 + L_z^2$

Suppose $l = 1$ (a p orbital)

$$L^2 = 1(1+1)\hbar^2 = 2\hbar^2$$

Now, how large can m be? Recall that $m^2 \hbar^2$ is just the z part of L^2

so $m^2 \hbar^2 \leq l(l+1)\hbar^2$

or $m^2 \hbar^2 \leq (l^2 + l)\hbar^2$

Suppose the $m = 2$; then $L_z^2 = m^2 \cdot \hbar^2 = 4\hbar^2$ This could not be

since we have the ridiculous result that the part is twice as big as the

whole! In fact, since $(l+1)^2 > l(l+1)$, obviously m is

required to range only from $-l$ to $+l$.

Thus if $l = 0$	$m = 0$	1 type of s orbital
$l = 1$	$m = -1, 0, +1$	3 types of p orbitals
$l = 2$	$m = -2, -1, 0, 1, 2$	5 types of d orbitals
$l = 3$	$m = -3, -2, -1, 0, 1, 2, 3$	7 types of f orbitals

etc.

Consider the p orbitals $m = +1$



Counter clock wise motion

$m = -1$



Clock wise motion

i.e. the + and - mean angular momentum is $m\hbar$ in clockwise or counter clockwise direction about z. But, as you proved in the last homework, this requires complex functions $e^{\pm i\phi}$. What happened to good old P_x and P_y ? In molecules its more convenient to use real orbitals, which are simply linear combinations of these. Thus,

$$P_x \propto \frac{e^{i\phi} + e^{-i\phi}}{2} = \cos \phi$$

$$P_y \propto \frac{e^{i\phi} - e^{-i\phi}}{2i} = \sin \phi$$

In general, for a given l the real Φ_m functions are: $\cos \phi$, $\cos 2\phi$,
1, $\sin \phi$, $\sin 2\phi$,

up to $\cos l\phi$, $\sin l\phi$, i.e. $\cos m\phi$, $\sin m\phi$, $m = 0$ to l

Φ Nodes: show to your satisfaction that the real Φ_m functions have m planar nodes which are \perp to x, y plane (contain the z axis).

Reading : Subject
Orthogonality

Source
Lowe, p 89

Nodes

Streitwieser - Owens Chap 1

Overlap

" " Chap 2
Murrell, et al. p 45

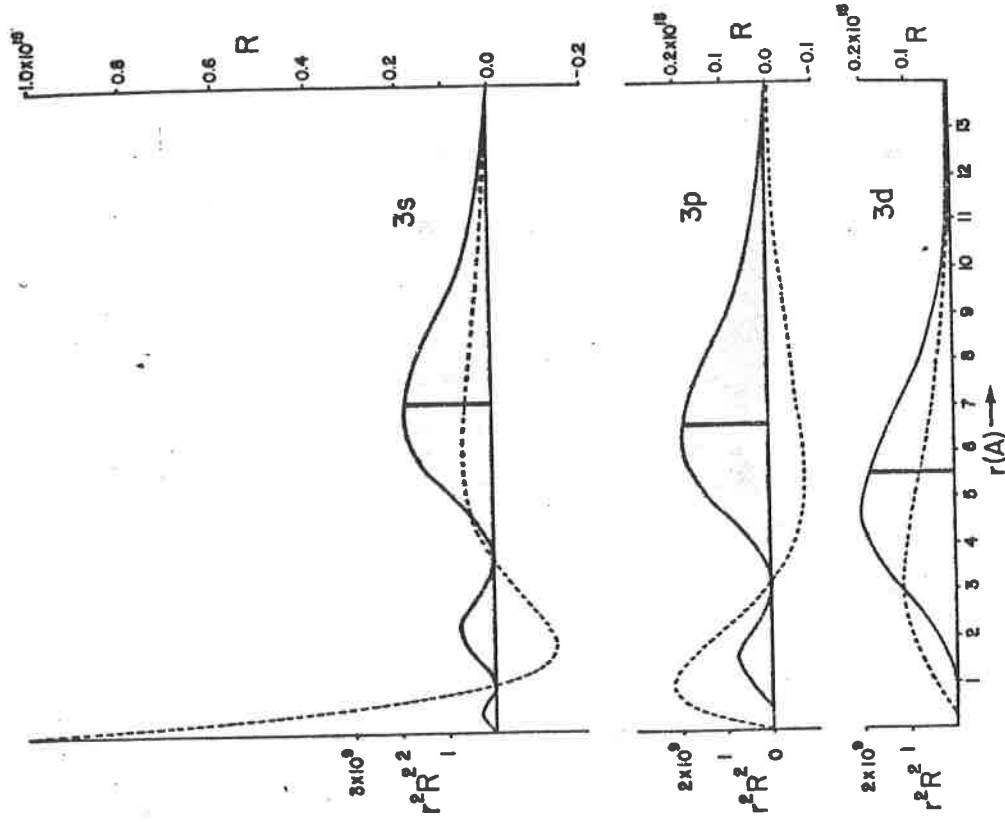
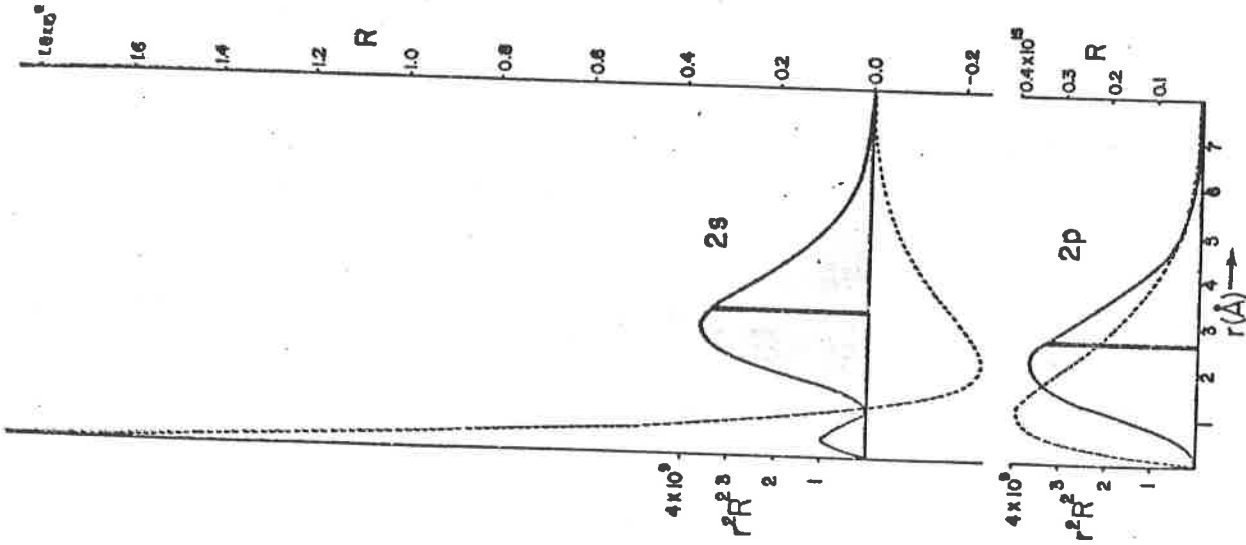
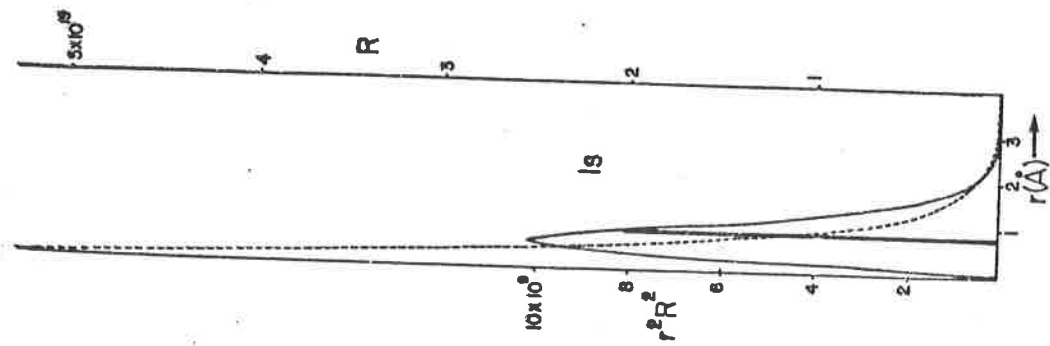


Fig. 4-2. Graphs of radial wave functions, $R_{nl}(r)$ (dashed lines), and distribution functions, $r^2 R_{nl}^2(r)$ (solid lines), for the hydrogen atom. Units of R are $m^{-3/2}$ and units of $r^2 R^2$ are m^{-1} . Vertical lines mark the average value of r for an electron in each orbital.

THEORY

$a_0)^{3/2}$. The orbital energies written

$$\left(\frac{e^2}{a_0}\right) \quad (3.21)$$

mechanical calculations to work in a the fundamental physical quantities. not be changed if say the electronic were at some time in the future given units and are defined by the following

hr. The mass of the electron m is the electron is the unit of charge. $h/2\pi$ is the that the atomic unit of time is not the per equation (1.13) for an electron put in the following simple form

$$\Psi = E\Psi. \quad (3.22)$$

, and the orbital energies are, in

$$\frac{Z^2}{2n^2} \quad (3.23)$$

magnetic radiation an electron jumps tum number n_1 to one with n_2 , then tion or emission of light in order that

$$\left[\frac{1}{n_2^2} - \frac{1}{n_1^2}\right] = h\nu = \frac{hc}{\lambda} \quad (3.24)$$

formula (1.4), and the value of the en by the Bohr theory (1.5). one-electron atoms are given in table

e functions of the electron in a one- s was a two-dimensional figure. If we nding two-dimensional potential then f surfaces in three-dimensional space. ons of three variables and one would al space to illustrate the complete

behaviour of the wave function in one figure. As it is beyond our ability to show such a thing on our two dimensional page we restrict ourselves to showing figures which represent the variation of the wave function with either the radial coordinate, keeping ϑ and φ fixed, or with ϑ and φ keeping r fixed.

TABLE 3.3. Normalized atomic-orbital wave functions for one-electron atoms, ($\rho = 2Zr/na_0$) all to be multiplied by $(Z/a_0)^{3/2}(\pi^{-1/2})$

n	l	$ m $	Wave function
1	0	0	$1s = e^{-\rho/2}$
2	0	0	$2s = (32)^{-1/2}(2 - \rho) e^{-\rho/2}$
2	1	0	$(32)^{-1/2}\rho e^{-\rho/2} \begin{cases} 2p_x = \cos \vartheta \\ 2p_y = \sin \vartheta \cos \varphi \\ 2p_z = \sin \vartheta \sin \varphi \end{cases}$
2	1	1	
2	1	1	
3	0	0	$3s = (972)^{-1/2}(6 - 6\rho + \rho^2) e^{-\rho/2}$
3	1	0	$(648)^{-1/2}(4\rho - \rho^2) e^{-\rho/2} \begin{cases} 3p_x = \cos \vartheta \\ 3p_y = \sin \vartheta \cos \varphi \\ 3p_z = \sin \vartheta \sin \varphi \end{cases}$
3	1	1	
3	1	1	
3	2	0	$(2592)^{-1/2}\rho^2 e^{-\rho/2} \begin{cases} 3d_{z^2} = \sqrt{\frac{1}{3}}(3 \cos^2 \vartheta - 1) \\ 3d_{xz} = \sin 2\vartheta \cos \varphi \\ 3d_{yz} = \sin 2\vartheta \sin \varphi \\ 3d_{x^2-y^2} = \sin^2 \vartheta \cos 2\varphi \\ 3d_{xy} = \sin^2 \vartheta \sin 2\varphi \end{cases}$
3	2	1	
3	2	2	

We start first with the $1s$ orbital. This is spherically symmetric and decreases exponentially with distance from the nucleus. A graph of Ψ_{1s} as a function of r is shown in figure 3.2. The probability density for an electron in this orbital is Ψ_{1s}^2 . The probability of finding an electron at a distance r from the nucleus is obtained by multiplying the probability density by the area of the spherical shell of radius r ; this function, $4\pi r^2 \Psi_{1s}^2$, and Ψ_{1s}^2 are also shown in figure 3.2.

The $1s$ orbital has no variation with the polar angles. We could therefore represent it by contour surfaces, which would be concentric spheres, or by contours on a plane passing through the nucleus which will be concentric circles as in figure 3.3a. We can also draw a spherical boundary surface such that nearly all the electron density (say 90%) is found inside the surface: in a plane this is figure 3.3b.

Effective Potential Energy \rightarrow a.u.

$$\frac{l(l+1)\hbar^2}{2\mu r^2} \quad \text{a.u.}$$

$$-\frac{e^2}{r} + \frac{l(l+1)\hbar^2}{2\mu r^2} \quad \text{a.u.}$$

Centrifugal Potential

Coulomb Potential

