Hydrogen-like atoms - Chapter 6

one electron - any nuclear charge

potential energy $V(r) = \dfrac{(-e)(Ze)}{4\pi\epsilon_0 r}$

$4\pi\epsilon_0 = 1.11265 \times 10^{-10}\ C^2 J^{-1} M^{-1}$

$e = 1.602 \times 10^{-19}\ C$

potential describes H, He^+, Li^{+2}, ... F^{+8}, ... U^{+91}

Schrodinger Equation

$$\hat{H}\psi = E\psi$$

$\hat{H} = -\dfrac{\hbar^2}{2m}\nabla^2 + V$; m = electron mass - assumes mass of nucleus $= \infty$.

In spherical polar coordinates

$$-\frac{\hbar^2}{2m}\nabla^2 = \underbrace{-\frac{\hbar^2}{2mr^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)}_{\text{radial kinetic energy operator}} + \underbrace{\frac{\hat{L}^2}{2mr^2}}_{\text{angular kinetic energy operator}}$$

$$\psi_{N\ell M} = R_{N\ell}(r)\, Y_\ell^M(\theta,\phi)$$

$$\hat{H}\psi_{N\ell m} = E_N \psi_{N\ell m}$$

$E_N = -\dfrac{e^2}{(4\pi\epsilon_0)a_0}\left(\dfrac{Z^2}{2N^2}\right)$; a_0 = Bohr radius $= \dfrac{\hbar^2 4\pi\epsilon_0}{me^2} \doteq 0.529177 \times 10^{-10}\ M$

note $\langle \psi_{N\ell M} | \psi_{N'\ell' M'} \rangle = \delta_{NN'}\delta_{\ell\ell'}\delta_{MM'}$

Note constraints on quantum numbers

$N = 1, 2, 3, \ldots$ (principal QN)

$\ell = 0, 1, 2, \ldots N-1$ (angular momentum QN)

$-\ell \leq M \leq +\ell$ (magnetic QN)

Since E_N depends only on N the solutions are degenerate

$N=1$	$1s$	(1)
$N=2$	$2s, 2p_{\pm 1}, 2p_0$	(4) degeneracy
$N=3$	$3s, 3p_{\pm}, 3p_0, 3d_0, 3d_{\pm 1}, 3d_{\pm 2}$	(9)

degeneracy of level N is N^2.

Form of $R_{N\ell}(r)$

$$R_{10}(r) = R_{1s}(r) = 2\left(\frac{Z}{a}\right)^{3/2} e^{-Zr/a}$$

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

$$R_{21}(r) = R_{2p}(r) = \frac{1}{\sqrt{6}\,2}\left(\frac{Z}{a}\right)^{5/2} r\, e^{-Zr/2a}$$

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

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

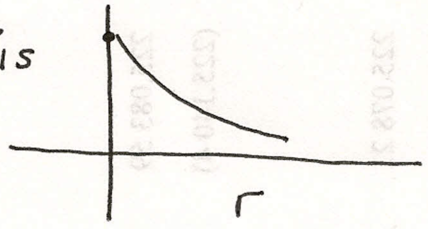
$$R_{32}(r) = R_{3d}(r) = \frac{4}{81\sqrt{30}}\left(\frac{Z}{a}\right)^{7/2} r^2 e^{-Zr/3a}$$

Properties of ground state; $N=1$

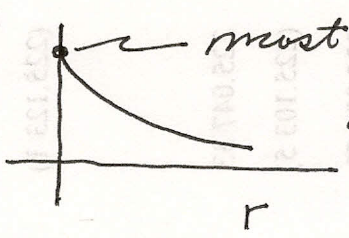
Ionization energy $= 13.598\, Z^2$ (eV)

$\psi = R_{1s} Y_0^0$; ψ is spherically symmetric
no angular dependency

R_{1s}



ψ_{1s}^2



most likely point where one would find election

Radial distribution function (general)

given $\psi_{N\ell m}$ what is probability of finding e inside a sphere (nucleus at center) of radius r_0?

$$P(r_0) = \int_{\substack{\text{Volume of}\\ \text{sphere}}} \psi^*_{N\ell m}\, \psi_{N\ell m}\, dV = \int_0^{r_0} R^2_{N\ell}(r)\, r^2 dr$$

(since $\int_\Omega Y_{\ell m}^* Y_\ell^m\, d\Omega = 1$)

Probability of finding e inside a larger sphere $r_0 + \Delta$

$$P(r_0+\Delta) = \int_0^{r_0+\Delta} R^2_{N\ell}(r)\, r^2 dr$$

In region between two spheres?

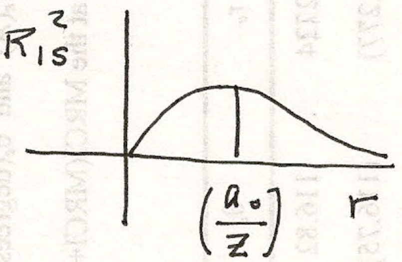
$$P(r_0+\Delta) - P(r_0) = \int_{r_0}^{r_0+\Delta} R^2_{N\ell}(r)\, r^2 dr$$

let Δ be very small, then

$$P(r_0+\Delta) - P(r_0) \cong \Delta\, R_{N\ell}^2(r_0)\, r_0^2$$

& ~~as~~ $$\lim_{\Delta \to 0} \frac{P(r_0+\Delta) - P(r_0)}{\Delta} = r_0^2 R_{N\ell}^2(r_0)$$

~~Eo~~ $r^2 R_{N\ell}^2(r)$ is called the radial distribution function & measures the probability of finding the electron on the surface of a sphere of radius r.



electron in 1s state is most likely to be found on a sphere of radius a_0/Z.

Another measure of the electrons location is $\langle r \rangle$

$$\langle r \rangle = \int \psi_{1s}^2(r)\, r\, dv = \int_0^\infty r^3 R_{1s}^2(r)\, dr$$

$$= \frac{3}{2}\left(a/Z\right)$$

& yet a third is found by asking for the size of a sphere containing the electron 90% of the time. The equation that must be satisfied is

$$\int_0^{r_0} r^2 dr \int_\Omega d\Omega\, \psi_{1s}^2(r) = 0.9 = \int_0^{r_0} R_{1s}^2(r)\, r^2 dr$$

with the substitution $x = 2Zr/a$ the equation becomes

$$\frac{1}{2}\int_0^{x_0} x^2 e^{-x}\,dx = 0.9 = \frac{1}{2}\left(2 - e^{-x_0}(x_0^2 + 2x_0 + 2)\right)$$

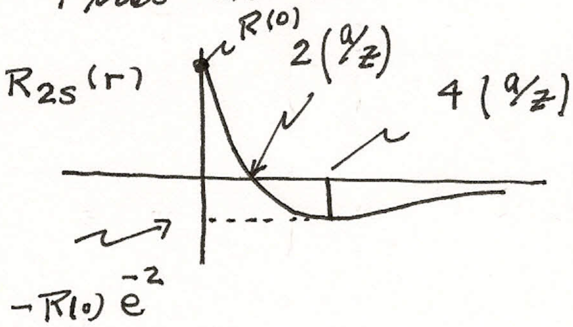
with $x_0 = \frac{2Zr_0}{a}$. solving this numerically results

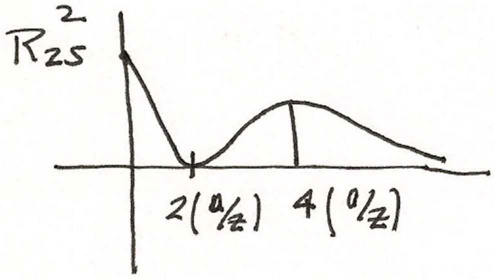
in $r_0 = 2.66\left(\frac{a}{Z}\right)$

Consider now the $N = 2$ solutions

$$N = 2;\quad \ell = 0,\ 1$$
$$\downarrow\ \ \downarrow$$
$$2s\ \ 2P_M$$

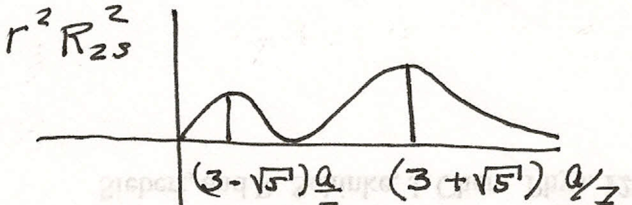
First the 2s





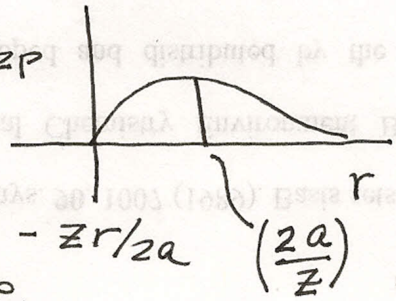
Then radial distribution function.

$$r^2 R_{2s}^2 = \frac{1}{2}\left(\frac{Z}{a}\right)^3\left(1 - \frac{Zr}{2a}\right)^2 e^{-Zr/a}\, r^2$$

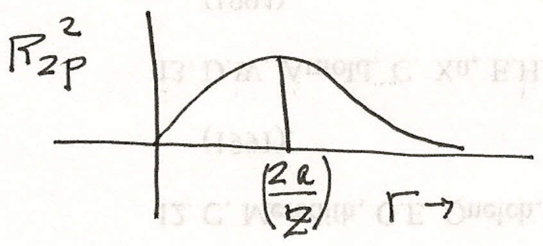


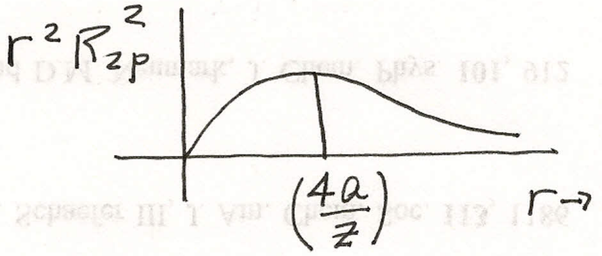
Now for 2p

First radial R_{2p}



$$R_{2p} = \frac{1}{2\sqrt{6}}\left(\frac{Z}{a}\right)^{5/2} r\, e^{-Zr/2a}$$



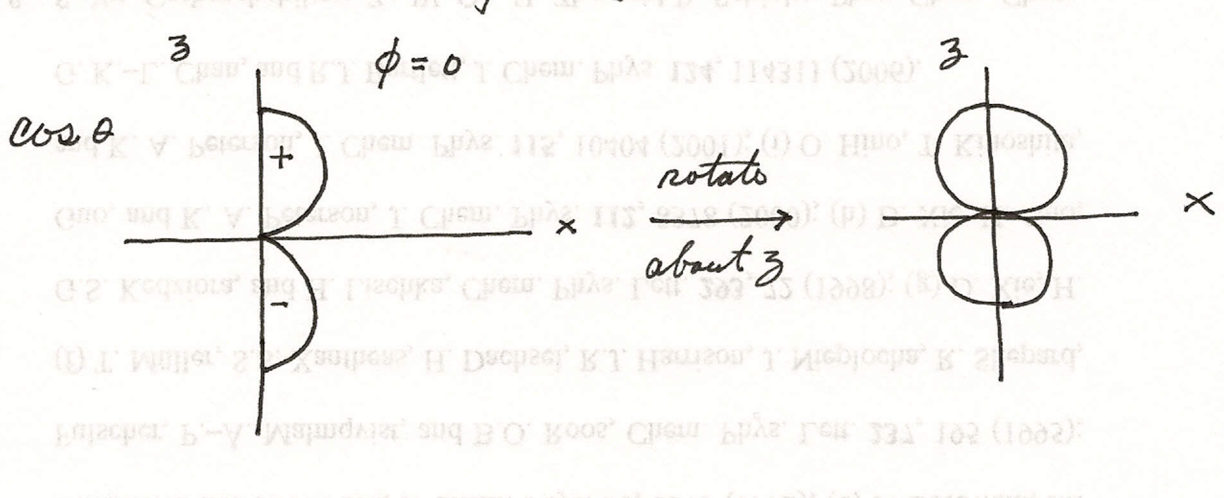


Now angular terms: There are 3.

$$Y_1^{\pm 1} = \sqrt{\frac{3}{8\pi}}\, \sin\theta\, e^{\pm i\phi} \quad \& \quad Y_1^0 = \sqrt{\frac{3}{4\pi}}\, \cos\theta$$

first consider Y_1^0 since it is a real function

we will construct a polar plot in the x z plane



because ψ_{211} & ψ_{21-1} have the same energy any linear combination is also an eigenfunction of $\hat{H}$

$$\hat{H}\left(c_1\psi_{211}+c_2\psi_{21-1}\right) = E_2\left(c_1\psi_{211}+c_2\psi_{21-1}\right)$$

where c_1 & c_2 are arbitrary

also $\hat{L}^2\left(c_1\psi_{211}+c_2\psi_{21-1}\right) = 2(2+1)\hbar^2\left(c_1\psi_{211}+c_2\psi_{21-1}\right)$

we will choose c_1 & c_2 so that the two real functions are orthogonal. Note that since ψ_{211} & ψ_{21-1} have the same radial functions we need only consider the angular parts. Note

$$Y_1^{+1} \pm Y_1^{-1} = \mp\sqrt{\frac{3}{8\pi}}\sin\theta\left(e^{i\phi} \pm e^{-i\phi}\right)$$

& since $e^{\pm i\phi} = \cos\phi \pm i\sin\phi$

$$Y_1^{+1} + Y_1^{-1} = 2\sqrt{\frac{3}{8\pi}}\sin\theta\cos\phi$$

& after normalization the new angular function is

$$\frac{Y_1^{+1}+Y_1^{-1}}{\sqrt{2}} = \sqrt{\frac{6}{8\pi}}\sin\theta\cos\phi \equiv p_x$$

Likewise $Y_1^{+1} - Y_1^{-1} = 2i\sqrt{\frac{3}{8\pi}}\sin\theta\sin\phi$

& so $\dfrac{Y_1^{+1}-Y_1^{-1}}{i\sqrt{2}} = \sqrt{\frac{6}{8\pi}}\sin\theta\sin\phi \equiv p_y$

Polar plots of these two new angular functions are shown below.

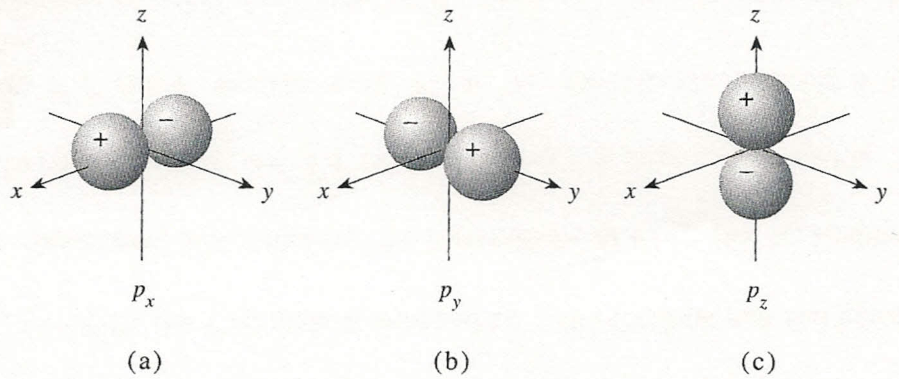


FIGURE 6.4
Three-dimensional polar plots of the angular part of the real representation of the hydrogen atomic wave functions for $l = 1$ (see Equations 6.62 for real representations of p_x and p_y.)

Having done the radial & angular parts of ψ separately we now want to do the entire function. By "do" I mean obtain a sense of its spatial variation.

Contour maps.

A convenient visualization technique is to construct a contour map of the function. Consider the $2p_z$ orbital

$$\psi_{2p_z} = R_{2p}(r)\, p_z(\theta,\phi)$$

$$= \frac{1}{2\sqrt{6}}\left(\frac{Z}{a}\right)^{5/2} r\, e^{-Zr/2a} \sqrt{\frac{3}{4\pi}} \cos\theta$$

$$= C\, z\, e^{-Zr/2a} \quad ; \quad C = \frac{1}{2\sqrt{6}}\sqrt{\frac{3}{4\pi}}\left(\frac{Z}{a}\right)^{5/2}$$

$$\& \quad z = r\cos\theta$$

Lets consider the form of the function in the z, x plane and connect all points in this plane for which the function has the value ψ_0 (a number)

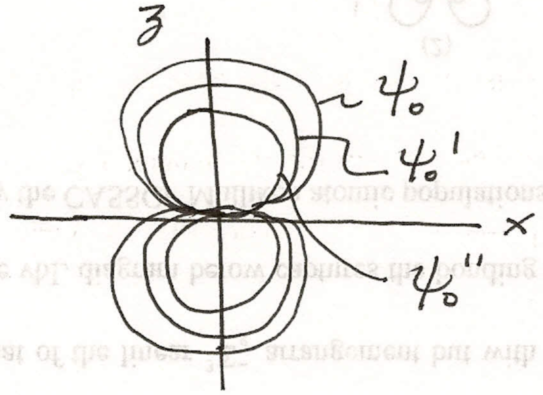
$$\psi_0 = c z e^{-Zr/2a} \; ; \quad r = \sqrt{x^2 + z^2} \quad (y = 0)$$

$$e^{Zr/2a} = \frac{cz}{\psi_0} \quad \text{\& so} \quad \frac{Zr}{2a} = \ln\left(\frac{cz}{\psi_0}\right)$$

so $$r^2 = x^2 + z^2 = \left(\frac{2a}{Z} \ln \frac{cz}{\psi_0}\right)^2$$

$$\text{\&} \therefore \quad x = \pm \sqrt{\left(\frac{2a}{Z} \ln \frac{cz}{\psi_0}\right)^2 - z^2}$$

from which we see



Study figure 6.6 in text.