Lecture 5

The Hydrogen Atom

Outline

1. The Hydrogen Atom Schrödinger Equation
2. The Radial Equation Solutions (Wavefunctions and Energies)
3. The Hydrogen Atom Wavefunctions (Complex and Real)
4. Use of the Wavefunctions (Calculating Averages)
5. **The Radial Distribution Function**
6. Atomic Units
7. Zeeman effect

1. The Hydrogen Atom Schrödinger Equation

The Potential Energy

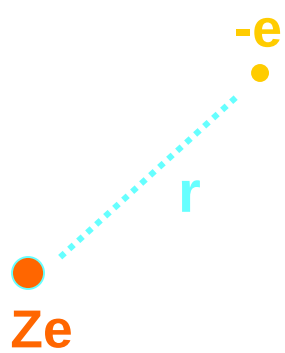
For two charges, q_1 and q_2, separated by a distance, r:

Force: $$f = \frac{q_1 q_2}{4\pi\varepsilon_0 r^2}$$

Potential Energy: $$V(r) = \frac{q_1 q_2}{4\pi\varepsilon_0 r}$$

If the charges are of opposite sign, the potential energy, V(r), is negative; i.e. attractive.

"Hydrogenlike" Atoms (H, He^+, Li^{2+}, etc.)



$$V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r}$$

The Schrödinger Equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi \longrightarrow -\frac{\hbar^2}{2m}\nabla^2\psi - \frac{Ze^2}{4\pi\varepsilon_0 r}\psi = E\psi$$

In this equation, m represents the mass of an electron (9.11×10^{-31} kg). Strictly speaking, one should use the reduced mass, μ, of an electron and proton. However, because the proton is ~1830 times heavier, $\mu = 0.9995m$. Therefore, we just use the electron mass.

Because V = V(r), one can solve the equation exactly if the Laplacian is written in spherical polar coordinates, giving:

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin(\theta)}\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2(\theta)}\frac{\partial^2}{\partial\varphi^2}\right]\psi - \frac{Ze^2}{4\pi\varepsilon_0 r}\psi = E\psi$$

$$\downarrow$$

$$\left[-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{2mr^2}\left(-\hbar^2\right)\left\{\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial\varphi^2}\right\}\right]\psi - \frac{Ze^2}{4\pi\varepsilon_0 r}\psi = E\psi$$

$$\left[-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{2mr^2}\boxed{\left(-\hbar^2\right)\left\{\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial\varphi^2}\right\}}\right]\psi-\frac{Ze^2}{4\pi\varepsilon_0 r}\psi=E\psi$$

$\hat{L}^2$ **Operator**

$$\left[-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{L^2}{2mr^2}\right]\psi-\frac{Ze^2}{4\pi\varepsilon_0 r}\psi=E\psi$$

The sole dependence of this equation on θ or φ is embodied in the $\hat{L}^2$ operator.

We learned in Lecture 4 (The Rigid Rotor) that the Spherical Harmonics, $Y_{l,m}(\theta, \varphi)$, are eigenfunctions of $\hat{L}^2$.

$$\hat{L}^2 Y_{\ell m}(\theta,\varphi)=\ell(\ell+1)\hbar^2 Y_{\ell m}(\theta,\varphi)$$

They are also eigenfunctions of $\hat{L}_z$: $\hat{L}_z Y_{\ell m}(\theta,\varphi)=m\hbar Y_{\ell m}(\theta,\varphi)$

$$\left[-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{L^2}{2mr^2}\right]\psi-\frac{Ze^2}{4\pi\varepsilon_0 r}\psi=E\psi$$

One can remove the dependence of this equation on θ and ϕ, embodied in $\hat{L}^2$, by assuming that:

$$\psi(r,\theta,\varphi)=R(r)\bullet Y_{\ell m}(\theta,\varphi)$$

This gives:

$$\left[-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{L^2}{2mr^2}\right]R(r)Y_{\ell m}(\theta,\varphi)-\frac{Ze^2}{4\pi\varepsilon_0 r}R(r)Y_{\ell m}(\theta,\varphi)=ER(r)Y_{\ell m}(\theta,\varphi)$$

Because $L^2Y_{\ell m}(\theta,\varphi)=\ell(\ell+1)\hbar^2Y_{\ell m}(\theta,\varphi)$

$$\left[-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{\ell(\ell+1)\hbar^2}{2mr^2}\right]R(r)Y_{\ell m}(\theta,\varphi)-\frac{Ze^2}{4\pi\varepsilon_0 r}R(r)Y_{\ell m}(\theta,\varphi)=ER(r)Y_{\ell m}(\theta,\varphi)$$

$$\left[-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{\ell(\ell+1)\hbar^2}{2mr^2}\right]R(r)\cancel{Y_{\ell m}(\theta,\varphi)}-\frac{Ze^2}{4\pi\varepsilon_0 r}R(r)\cancel{Y_{\ell m}(\theta,\varphi)}=ER(r)\cancel{Y_{\ell m}(\theta,\varphi)}$$

We can now remove the dependence on θ and ϕ completely.

$$\left[-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{\ell(\ell+1)\hbar^2}{2mr^2}-\frac{Ze^2}{4\pi\varepsilon_0 r}\right]R(r)=ER(r)$$

We now have the "Radial Equation" for the hydrogen atom.

This equation must be solved subject to the boundary condition:
$R(r) \to 0$ as $r \to \infty$.

The solution to this equation is ***non-trivial*** to say the least.
We will just present the solutions below.

Note: In retrospect, it should not be surprising that the angular solutions of the hydrogen atom are the same as the Rigid Rotor (Lecture 4).

Neither potential energy function (V=0 for the Rig. Rot.) depends on θ or ϕ, and they must satisfy the same angular Boundary Conditions.

2. The Radial Equation Solutions

The Third Quantum Number

$$\left[-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{\ell(\ell+1)\hbar^2}{2mr^2}-\frac{Ze^2}{4\pi\varepsilon_0 r}\right]R(r)=ER(r)$$

When the equation is solved and the boundary condition, $R(r) \to 0$ as $r \to \infty$, is applied, one gets a new quantum number, n, with the restriction that:

$n > \ell$ or, equivalently $\ell < n$

Together with the two quantum numbers that came from solution to the angular equations, one has three quantum numbers with the allowed values:

$$n = 1, 2, 3, 4, \ldots$$

$$\ell = 0, 1, 2, \ldots\ n-1$$

$$m = 0, \pm 1, \pm 2, \ldots\ \pm \ell$$

The Radial Wavefunctions

The functions which are solutions of the Radial Equation are dependent upon both n and l and are of the form:

$$R_{n\ell}(r) = Poly\left(\frac{Zr}{na_0}\right)\cdot e^{\frac{-Zr}{na_0}} \quad \text{where} \quad a_0 = \frac{4\pi\varepsilon_0\hbar^2}{me^2}$$

Bohr Radius

Several of the Radial functions are:

$$R_{10}(r) = N_{10}e^{-\frac{Zr}{a_0}}$$

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

$$R_{21}(r) = N_{21}\frac{Zr}{2a_0}e^{-\frac{Zr}{2a_0}}$$

$$R_{30}(r) = N_{30}\left(27-18\frac{Zr}{3a_0}+2\left(\frac{Zr}{3a_0}\right)^2\right)e^{-\frac{Zr}{3a_0}}$$

$$R_{31}(r) = N_{31}\left(6\frac{Zr}{3a_0}-\left(\frac{Zr}{3a_0}\right)^2\right)e^{-\frac{Zr}{3a_0}}$$

$$R_{32}(r) = N_{32}\left(\frac{Zr}{3a_0}\right)^2 e^{-\frac{Zr}{3a_0}}$$

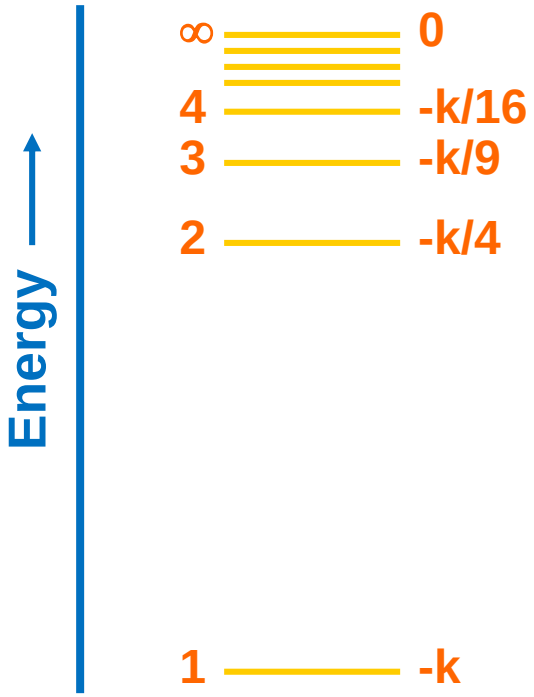
The Energies

The energy eigenvalues are dependent upon n only and are given by:

$$E_n = -\frac{mZ^2e^4}{2(4\pi\varepsilon_0)^2\hbar^2}\cdot\frac{1}{n^2} = -\frac{1}{2}\frac{e^2}{(4\pi\varepsilon_0)a_0}\cdot\frac{Z^2}{n^2} = -\frac{1}{2}2625\frac{Z^2}{n^2}\ \text{kJ/mol}$$

This expression for the energy levels of “hydrogenlike” atoms is identical to the Bohr Theory expression.

However, the picture of electron motion furnished by Quantum Mechanics is completely different from that of the semi-classical Bohr model of the atom.



Examples

Show that $R_{10}(r)$ is an eigenfunction of the Radial equation and that the eigenvalue is given by E_1 (below).

$$R_{10}(r) = N_{10} e^{-\frac{Zr}{a_0}}$$

$$\left[-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) + \frac{\ell(\ell+1)\hbar^2}{2mr^2} - \frac{Ze^2}{4\pi\varepsilon_0 r}\right] R(r) = ER(r)$$

or $$\boxed{\left[-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) + \frac{\ell(\ell+1)\hbar^2}{2mr^2} - \frac{Z\hbar^2}{ma_0 r}\right] R(r) = ER(r)}$$

$$E_1 = -\frac{Z^2 e^2}{2(4\pi\varepsilon_0)a_0}\cdot\frac{1}{1^2}$$ or $$\boxed{E_1 = -\frac{Z^2\hbar^2}{2ma_0^2}\cdot\frac{1}{1^2}}$$

Note: the alternative forms above have been obtained using:

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{me^2}$$

$$R_{10}(r) = N_{10} e^{-\frac{Zr}{a_0}} \qquad \left[-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) + \frac{\ell(\ell+1)\hbar^2}{2mr^2} - \frac{Z\hbar^2}{ma_0 r}\right] R(r) = E R(r) \qquad E_1 = -\frac{Z^2\hbar^2}{2ma_0^2}\cdot\frac{1}{1^2}$$

$$r^2 \frac{\partial R}{dr} = -\frac{Z}{a_0} N_{10} r^2 e^{-\frac{Zr}{a_0}}$$

$$\frac{\partial}{\partial r}\left(r^2 \frac{\partial R}{dr}\right) = -\frac{Z}{a_0} N_{10}\left[r^2\left(-\frac{Z}{a_0} e^{-\frac{Zr}{a_0}}\right) + e^{-\frac{Zr}{a_0}}(2r)\right] = \frac{Z^2}{a_0^2} r^2 N_{10} e^{-\frac{Zr}{a_0}} - \frac{2Z}{a_0} r N_{10} e^{-\frac{Zr}{a_0}}$$

$$= \frac{Z^2}{a_0^2} r^2 R - \frac{2Z}{a_0} r R$$

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial R}{\partial r}\right) = -\frac{\hbar^2}{2mr^2}\left(\frac{Z^2}{a_0^2} r^2 R - \frac{2Z}{a_0} r R\right) = -\frac{Z^2\hbar^2}{2ma_0^2} R + \frac{Z\hbar^2}{ma_0 r} R$$

$$R_{10}(r) = N_{10} e^{-\frac{Zr}{a_0}} \qquad \left[-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) + \frac{\ell(\ell+1)\hbar^2}{2mr^2} - \frac{Z\hbar^2}{ma_0 r} \right] R(r) = E R(r) \qquad E_1 = -\frac{Z^2\hbar^2}{2ma_0^2}\cdot\frac{1}{1^2}$$

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial R}{\partial r}\right) = -\frac{Z^2\hbar^2}{2ma_0^2} R + \frac{Z\hbar^2}{ma_0 r} R$$

Therefore:

$$\left[-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) + \frac{\ell(\ell+1)\hbar^2}{2mr^2} - \frac{Z\hbar^2}{ma_0 r} \right] R(r) = -\frac{Z^2\hbar^2}{2ma_0^2} R + \frac{Z\hbar^2}{ma_0 r} R + 0 - \frac{Z\hbar^2}{ma_0 r} R$$

$$= -\frac{Z^2\hbar^2}{2ma_0^2} R = E_1 R$$

$$\downarrow$$

$$E_1 = -\frac{Z^2\hbar^2}{2ma_0^2}$$

3. The Hydrogen Atom Wavefunctions

The Complete Wavefunction (Complex Form)

$$\psi_{nlm}(r,\theta,\varphi) = R_{nl}(r)\cdot\Phi_m(\varphi)\cdot\Theta_{l|m|}(\theta) = R_{nl}(r)\cdot e^{im\varphi}\cdot P_l^{|m|}(\theta) = R_{nl}(r)\cdot Y_{lm}(\theta,\varphi)$$

Note that these wavefuntions are complex functions because of the term, $e^{im\phi}$.

This does not create a problem because the probability of finding the electron in the volume element, $dV = r^2\sin(\theta)drd\theta d\phi$ is given by:

$$P(r,\theta,\varphi)dV = \psi^*(r,\theta,\varphi)\psi(r,\theta,\varphi)r^2\sin(\theta)drd\theta\varphi$$

$$= \left[R_{nl}(r)\cdot e^{im\varphi}\cdot P_l^{|m|}(\theta)\right]^* \bullet \left[R_{nl}(r)\cdot e^{im\varphi}\cdot P_l^{|m|}(\theta)\right] r^2\sin(\theta)drd\theta\varphi$$

$$= \left[R_{nl}(r)\right]^2 \bullet \left[P_l^{|m|}(\theta)\right]^2 r^2\sin(\theta)drd\theta\varphi$$

Real Hydrogen Like wavefunction

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

$$2s = \frac{1}{4(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{3/2}\left(2 - \frac{Zr}{a}\right)e^{-Zr/2a}$$

$$2p_z = \frac{1}{4(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{5/2} re^{-Zr/2a}\cos\theta$$

$$2p_x = \frac{1}{4(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{5/2} re^{-Zr/2a}\sin\theta\cos\phi$$

$$2p_y = \frac{1}{4(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{5/2} re^{-Zr/2a}\sin\theta\sin\phi$$

$$3s = \frac{1}{81(3\pi)^{1/2}}\left(\frac{Z}{a}\right)^{3/2}\left(27 - 18\frac{Zr}{a} + 2\frac{Z^2r^2}{a^2}\right)e^{-Zr/3a}$$

$$3p_z = \frac{2^{1/2}}{81\pi^{1/2}}\left(\frac{Z}{a}\right)^{5/2}\left(6 - \frac{Zr}{a}\right)re^{-Zr/3a}\cos\theta$$

$$3p_x = \frac{2^{1/2}}{81\pi^{1/2}}\left(\frac{Z}{a}\right)^{5/2}\left(6 - \frac{Zr}{a}\right)re^{-Zr/3a}\sin\theta\cos\phi$$

$$3p_y = \frac{2^{1/2}}{81\pi^{1/2}}\left(\frac{Z}{a}\right)^{5/2}\left(6 - \frac{Zr}{a}\right)re^{-Zr/3a}\sin\theta\sin\phi$$

$$3d_{z^2} = \frac{1}{81(6\pi)^{1/2}}\left(\frac{Z}{a}\right)^{7/2} r^2e^{-Zr/3a}(3\cos^2\theta - 1)$$

$$3d_{xz} = \frac{2^{1/2}}{81\pi^{1/2}}\left(\frac{Z}{a}\right)^{7/2} r^2e^{-Zr/3a}\sin\theta\cos\theta\cos\phi$$

$$3d_{yz} = \frac{2^{1/2}}{81\pi^{1/2}}\left(\frac{Z}{a}\right)^{7/2} r^2e^{-Zr/3a}\sin\theta\cos\theta\sin\phi$$

$$3d_{x^2-y^2} = \frac{1}{81(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{7/2} r^2e^{-Zr/3a}\sin^2\theta\cos 2\phi$$

$$3d_{xy} = \frac{1}{81(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{7/2} r^2e^{-Zr/3a}\sin^2\theta\sin 2\phi$$

Real Form of the Wavefunctions

It is common to take the appropriate linear combinations of the complex wavefunctions to obtain real wavefunctions.

This is legal because the energy eigenvalues depend only on n and are independent of l and m; i.e. wavefunctions with different values of l and m are degenerate.

Therefore, any linear combination of wavefunctions with the same value of n is also an eigenfunction of the Schrödinger Equation.

p wavefunctions (l = 1)

$$\psi_{n11}(r,\theta,\varphi) = R_{n1}(r)\cdot P_1^1(\theta)\cdot e^{i\varphi} = R_{n1}(r)\cdot \sin(\theta)\cdot e^{i\varphi}$$

$$\psi_{n10}(r,\theta,\varphi) = R_{n1}(r)\cdot P_1^0(\theta)\cdot e^{0i\varphi} = R_{n1}(r)\cdot \cos(\theta)$$

Already real

$$\psi_{n1-1}(r,\theta,\varphi) = R_{n1}(r)\cdot P_1^1(\theta)\cdot e^{-i\varphi} = R_{n1}(r)\cdot \sin(\theta)\cdot e^{-i\varphi}$$

p wavefunctions (l = 1) (Cont'd)

$$\psi_{np_x} = \frac{1}{\sqrt{2}}\left(\psi_{n11} + \psi_{n1-1}\right) = \frac{1}{\sqrt{2}}\left[R_{n1}(r)\cdot\sin(\theta)\cdot e^{i\varphi} + R_{n1}(r)\cdot\sin(\theta)\cdot e^{-i\varphi}\right]$$

$$\psi_{np_x} = \frac{1}{\sqrt{2}}R_{n1}(r)\cdot\sin(\theta)\left[\left(\cos(\varphi) + i\sin(\varphi)\right) + \left(\cos(\varphi) - i\sin(\varphi)\right)\right]$$

$$\psi_{np_x} = \sqrt{2}R_{n1}(r)\cdot\sin(\theta)\cos(\varphi)$$ Real

$$\psi_{np_y} = \frac{1}{\sqrt{2}i}\left(\psi_{n11} - \psi_{n1-1}\right) = \frac{1}{\sqrt{2}i}\left[R_{n1}(r)\cdot\sin(\theta)\cdot e^{i\varphi} - R_{n1}(r)\cdot\sin(\theta)\cdot e^{-i\varphi}\right]$$

$$\psi_{np_y} = \frac{1}{\sqrt{2}i}R_{n1}(r)\cdot\sin(\theta)\left[\left(\cos(\varphi) + i\sin(\varphi)\right) - \left(\cos(\varphi) - i\sin(\varphi)\right)\right]$$

$$\psi_{np_y} = \sqrt{2}R_{n1}(r)\cdot\sin(\theta)\sin(\varphi)$$ Real

p wavefunctions (l = 1) (Cont'd)

Spherical Polar Coords.

$$\psi_{np_x} = \sqrt{2}R_{n1}(r)\cdot\sin(\theta)\cos(\varphi)$$

$x = r\sin(\theta)\cos(\phi)$

$$\psi_{np_y} = \sqrt{2}R_{n1}(r)\cdot\sin(\theta)\sin(\varphi)$$

$y = r\sin(\theta)\sin(\phi)$

$$\psi_{np_z} = R_{n1}(r)\cdot\cos(\theta)$$

$z = r\cos(\theta)$

d wavefunctions (l = 2)

$$\psi_{n22}(r,\theta,\varphi) = R_{n2}(r)\cdot P_2^2(\theta)\cdot e^{2i\varphi} = R_{n2}(r)\cdot \sin^2(\theta)\cdot e^{2i\varphi}$$

$$\psi_{n21}(r,\theta,\varphi) = R_{n2}(r)\cdot P_2^1(\theta)\cdot e^{i\varphi} = R_{n2}(r)\cdot \sin(\theta)\cos(\theta)\cdot e^{i\varphi}\theta$$

$$\psi_{n20}(r,\theta,\varphi) = R_{n2}(r)\cdot P_2^0(\theta)\cdot e^{0i\varphi} = R_{n2}(r)\cdot\left(3\cos^2(\theta)-1\right)$$

Already real

$$\psi_{n2-1}(r,\theta,\varphi) = R_{n2}(r)\cdot P_2^1(\theta)\cdot e^{-i\varphi} = R_{n2}(r)\cdot \sin(\theta)\cos(\theta)\cdot e^{-i\varphi}$$

$$\psi_{n2-2}(r,\theta,\varphi) = R_{n2}(r)\cdot P_2^{-2}(\theta)\cdot e^{-2i\varphi} = R_{n2}(r)\cdot \sin^2(\theta)\cdot e^{-2i\varphi}$$

d wavefunctions (l = 2) (Cont'd.)

By the same procedures used above for the p wavefunctions, one finds:

$$\psi_{nd_{z^2}} = \psi_{n20} = R_{n2}(r)\cdot\left(3\cos^2(\theta)-1\right)$$

$$\psi_{nd_{xz}} = \frac{1}{\sqrt{2}}\left(\psi_{n21}+\psi_{n2-1}\right) = \sqrt{2}R_{n2}(r)\cdot\sin(\theta)\cos(\theta)\cos(\varphi)$$

$$\psi_{nd_{yz}} = \frac{1}{\sqrt{2}i}\left(\psi_{n21}-\psi_{n2-1}\right) = \sqrt{2}R_{n2}(r)\cdot\sin(\theta)\cos(\theta)\sin(\varphi)$$

$$\psi_{nd_{x^2-y^2}} = \frac{1}{\sqrt{2}}\left(\psi_{n22}+\psi_{n2-2}\right) = \sqrt{2}R_{n2}(r)\cdot\sin^2(\theta)\cos(2\varphi)$$

$$\psi_{nd_{xy}} = \frac{1}{\sqrt{2}i}\left(\psi_{n22}-\psi_{n2-2}\right) = \sqrt{2}R_{n2}(r)\cdot\sin^2(\theta)\sin(2\varphi)$$

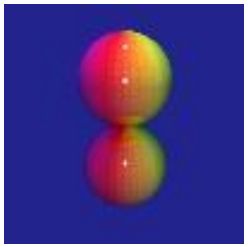
Plotting the Angular Functions

Below are the familiar polar plots of the angular parts of the hydrogen atom wavefunctions.

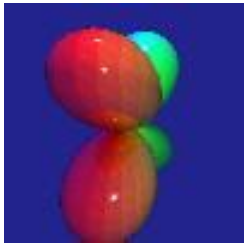
ns

np_x

np_y

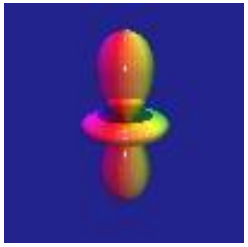


np_z

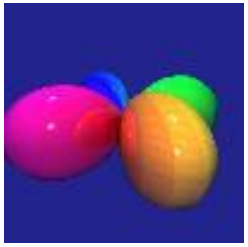


nd_{xz}

nd_{yz}



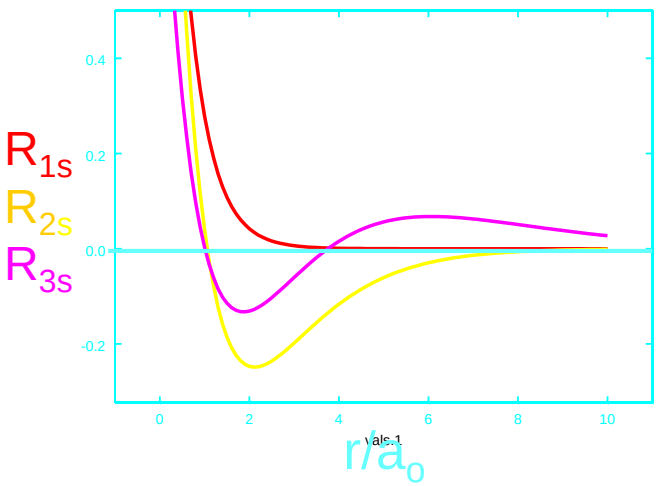
nd_{z^2}



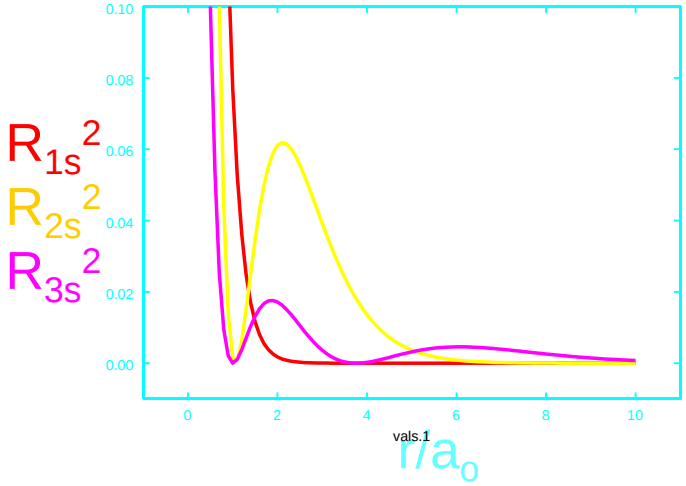
nd_{xy}

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

Plotting the Radial Functions

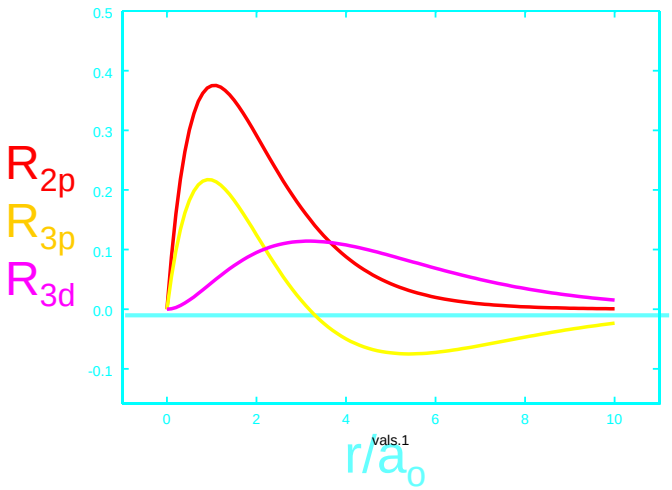


(r R1S R2S R3S)

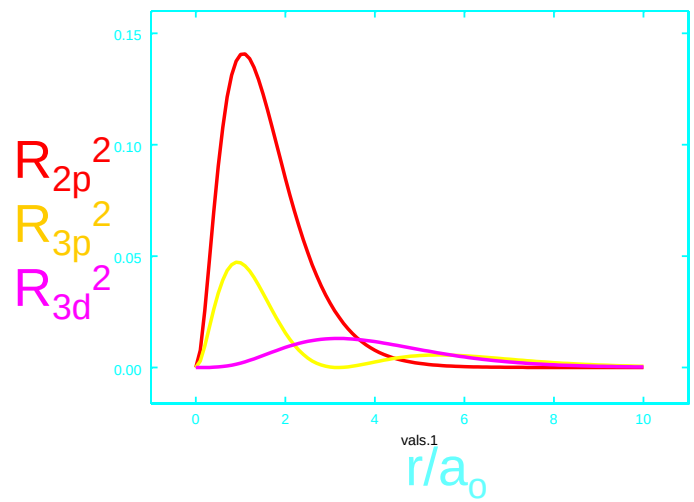


(r R1S2 R2S2 R3S2)

R_{1s} has no nodes
R_{2s} has 1 node
R_{3s} has 2 nodes



(r R2P R3P R3D)



(r R2P2 R3P2 R3D2)

R_{2p} has no nodes
R_{3p} has 1 node
R_{3d} has no nodes

In General: (a) A wavefunction has a total of n-1 nodes

(b) There are l angular nodes (e.g. s-0, p-1, d-2)c

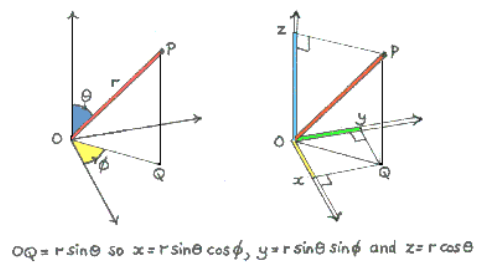
(c) The remainder (n-1-l) are radial nodes.

4. Use of Hydrogen-like Atom Wavefunctions

To illustrate how the hydrogen-like atom wavefunctions may be used to compute electronic properties, we will use the $2p_z$ ($=2p_0$) wavefunction.

$$\psi_{2pz} = \psi_{210} = AR(r)\Theta(\theta)\Phi(\varphi) = A\left(\frac{Zr}{a_0}\right)e^{-\frac{Zr}{2a_0}}\cos(\theta)$$

Review: Spherical Polar Coordinates



r	$0 \le r < \infty$	Distance of point from origin (OP)
θ	$0 \le \theta \le \pi$	Angle of vector (OP) from z-axis
ϕ	$0 \le \phi \le 2\pi$	Angle of x-y projection (OQ) from x-axis

$$dV = r^2 \sin(\theta)\, dr\, d\theta\, d\varphi$$

$$\psi = Are^{-\frac{Zr}{2a_0}}\cos(\theta)$$

Wavefunction Normalization

$$\int\int\int \psi^* \psi \, dV = 1 \quad = \int\int\int \left[Are^{-\frac{Zr}{2a_0}}\cos(\theta) \right]^2 r^2 \sin(\theta) dr d\theta d\varphi$$

$$1 = A^2 \int_0^\infty r^4 e^{-\frac{Zr}{a_0}} dr \cdot \int_0^\pi \cos^2(\theta)\sin(\theta) d\theta \cdot \int_0^{2\pi} d\varphi$$

$$1 = A^2 \cdot I_R \cdot I_\Theta \cdot I_\Phi$$

$$1 = A^2 \int_0^\infty r^4 e^{-\frac{Zr}{a_0}} dr \cdot \int_0^\pi \cos^2(\theta)\sin(\theta) d\theta \cdot \int_0^{2\pi} d\varphi \quad = A^2 \cdot I_R \cdot I_\Theta \cdot I_\Phi$$

$$I_R = \int_0^\infty r^4 e^{-\frac{Zr}{a_0}} dr \; = \frac{4!}{\left(\frac{Z}{a_0}\right)^5} = 24\left(\frac{a_0}{Z}\right)^5$$

$$\int_0^\infty x^n e^{-\alpha x} dx = \frac{n!}{\alpha^{n+1}}$$

$$I_\Theta = \int_0^\pi \cos^2(\theta)\sin(\theta) d\theta$$

$$\int \cos^2(x)\sin(x) dx = -\frac{1}{3}\cos^3(x)$$

$$I_\Theta = \left[\left(-\frac{1}{3}\cos^3(\pi)\right) - \left(-\frac{1}{3}\cos^3(0)\right)\right] = \frac{2}{3}$$

$$I_\Phi = \int_0^{2\pi} d\varphi = [2\pi - 0] = 2\pi$$

$$I_R = 24\left(\frac{a_0}{Z}\right)^5 \qquad I_\Theta = \frac{2}{3} \qquad I_\Phi = 2\pi$$

$$1 = A^2\int_0^\infty r^4 e^{-\frac{Zr}{a_0}}dr \cdot \int_0^\pi \cos^2(\theta)\sin(\theta)d\theta \cdot \int_0^{2\pi} d\varphi = A^2 \cdot I_R \cdot I_\Theta \cdot I_\Phi$$

$$1 = A^2 \cdot 24\left(\frac{a_0}{Z}\right)^5 \cdot \frac{2}{3} \cdot 2\pi = A^2 \cdot \left(\frac{a_0}{Z}\right)^5 \cdot 32\pi$$

$$A^2 = \frac{1}{32\pi}\left(\frac{Z}{a_0}\right)^5 \longrightarrow \boxed{A = \frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{5/2}}$$

$$\psi = Are^{-\frac{Zr}{2a_0}}\cos(\theta) = \frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{5/2} \cdot r \cdot e^{-\frac{Zr}{2a_0}}\cos(\theta)$$

$$\psi = Are^{-\frac{Zr}{2a_0}}\cos(\theta) \qquad A = \frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{5/2}$$

Calculation of <r>

$$\langle r \rangle = \iiint \psi^* r \psi \, dV = \iiint r\left[Are^{-\frac{Zr}{2a_0}}\cos(\theta)\right]^2 r^2 \sin(\theta) dr d\theta d\varphi$$

$$\langle r \rangle = A^2 \int_0^\infty r^5 e^{-\frac{Zr}{a_0}} dr \cdot \int_0^\pi \cos^2(\theta)\sin(\theta) d\theta \cdot \int_0^{2\pi} d\varphi = A^2 \cdot I_R \cdot I_\Theta \cdot I_\Phi$$

$$I_\Theta = \frac{2}{3}$$ and $$I_\Phi = 2\pi$$ Same as before

$$I_R = \int_0^\infty r^5 e^{-\frac{Zr}{a_0}} dr = \frac{5!}{\left(\frac{Z}{a_0}\right)^6} = 120\left(\frac{a_0}{Z}\right)^6$$

$$\int_0^\infty x^n e^{-\alpha x} dx = \frac{n!}{\alpha^{n+1}}$$

$$I_R = 120\left(\frac{a_0}{Z}\right)^6 \qquad I_\Theta = \frac{2}{3} \qquad I_\Phi = 2\pi \qquad A = \frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{3/2}$$

$$\langle r \rangle = A^2 \cdot I_R \cdot I_\Theta \cdot I_\Phi = \frac{1}{32\pi}\left(\frac{Z}{a_0}\right)^5 \cdot 120\left(\frac{a_0}{Z}\right)^6 \cdot \frac{2}{3} \cdot 2\pi$$

$$\langle r \rangle = \frac{480\pi}{96\pi} \cdot \frac{a_0}{Z} = 5\frac{a_0}{Z}$$

Calculation of other Averages

We use the same procedures. For example, I'll set up the calculation for the calculation of $\langle y^2 \rangle$, where $y = r\sin(\theta)\sin(\phi)$

$$\left\langle y^2 \right\rangle = \int\int\int \psi^* y^2 \psi \, dV = \int\int\int \left[r\sin(\theta)\sin(\varphi) \right]^2 \left[A\left(\frac{Zr}{a_0}\right) e^{-\frac{Zr}{2a_0}} \cos(\theta) \right]^2 r^2 \sin(\theta) dr d\theta d\varphi$$

$$\left\langle y^2 \right\rangle = A^2 \int_0^\infty r^6 e^{-\frac{Zr}{a_0}} dr \cdot \int_0^\pi \sin^3(\theta)\cos^2(\theta) d\theta \cdot \int_0^{2\pi} \sin^2(\varphi) d\varphi$$

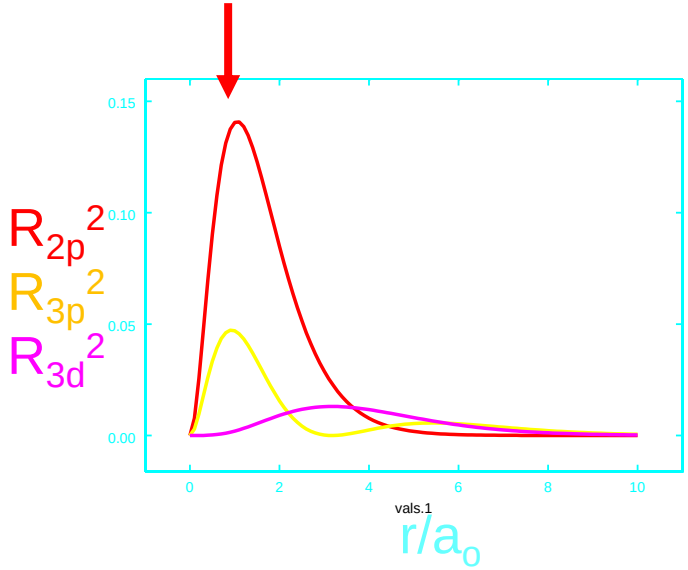
$$= A^2 \cdot I_R \cdot I_\Theta \cdot I_\Phi$$ and evaluate.

5. The Radial Distribution Function

Often, one is interested primarily in properties involving only r, the distance of the electron from the nucleus.

In these cases, it is simpler to integrate over the angles, θ and ϕ.

One can then work with a one dimensional function (of r only), called the Radial Distribution Function, which represents the probability of finding the electron between r and r+dr.



(r R2P2 R3P2 R3D2)

Is the most probable value of r for an electron in a hydrogen 2p orbital the maximum in R_{2p}^2 ?

No!! Relative values of R_{2p}^2 represent the relative probability of finding an electron at this value of r for a specific pair of values of θ and ϕ.

To obtain the relative probability of finding an electron at a given value of r and ***any*** angle, one must integrate $\psi^*\psi$ over all values of θ and ϕ.

One can write the wavefunction as: $\psi(r,\theta,\varphi) = A \cdot R(r) \cdot P(\theta) \cdot F(\varphi)$

The probability of finding an electron at a radius r, independent of θ and ϕ is:

$$P(r)dr = \int_\theta \int_\varphi \psi^* \psi \; r^2 \sin(\theta) dr d\theta d\varphi = \int_\theta \int_\varphi (A \cdot R \cdot P \cdot F)^* A \cdot R \cdot P \cdot F \; r^2 \sin(\theta) dr d\theta d\varphi$$

$$P(r)dr = A^2 R(r)^* R(r) r^2 dr \cdot \int_0^\pi P^* P \sin(\theta) d\theta \cdot \int_0^{2\pi} F^* F d\varphi$$

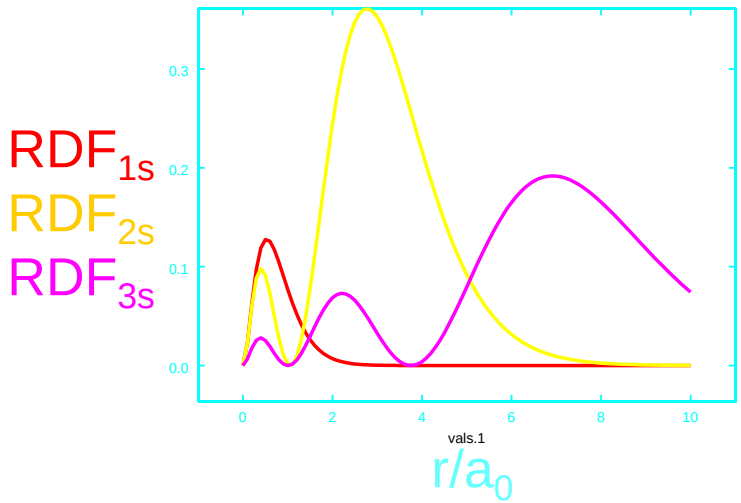
or $$\boxed{P(r)dr = Br^2 \left|R(r)\right|^2 dr}$$

where $B = A^2 \bullet \int_0^\pi P^* P \sin(\theta) d\theta \bullet \int_0^{2\pi} F^* F d\varphi$

i.e. we've incorporated the integrals over θ and ϕ into B

$$\boxed{P(r) = Br^2 \left|R(r)\right|^2}$$ is called the Radial Distribution Function (or Radial Probability Density in this text)

We'll use RDF(r) ≡ P(r)



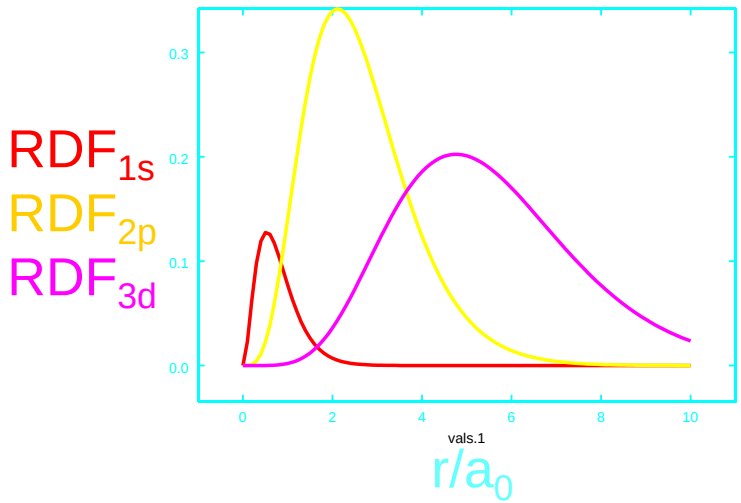
(r RD1S2 RD2S2 RD3S2)

This is because:

RDF_{1s} has 1 maximum
RDF_{2s} has 2 maxima
RDF_{3s} has 3 maxima

R_{1s} has no nodes
R_{2s} has 1 node
R_{3s} has 2 nodes

We'll use RDF(r) ≡ P(r



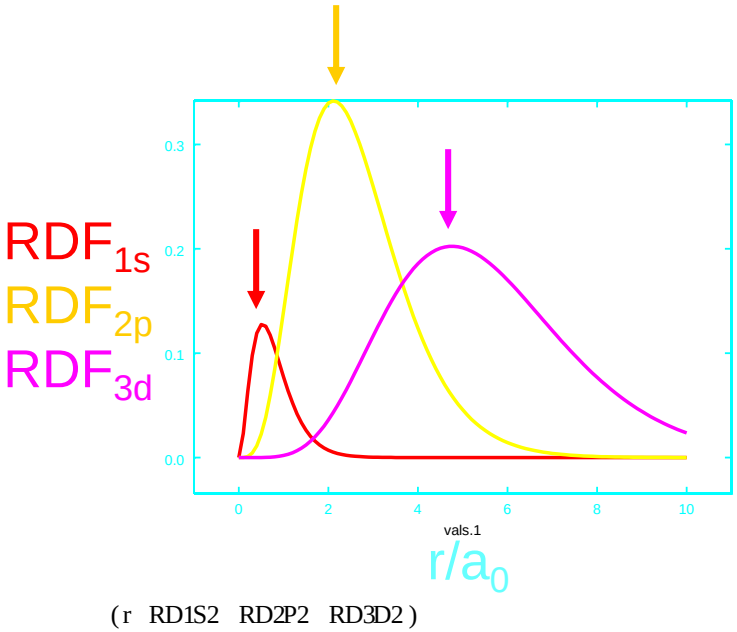
(r RD1S2 RD2P2 RD3D2)

This is because:

RDF_{1s} has 1 maximum
RDF_{2p} has 1 maximum
RDF_{3d} has 1 maximum

R_{1s} has no nodes
R_{2p} has no nodes
R_{3d} has no nodes

Most Probable Value of r



The most probable value of the distance from the nucleus, r, is given by the maximum in the Radial Distribution Function, P(r) ≡ RDF(r)

It can be computed easily by: $$\frac{dP(r)}{dr} = \frac{d\left(Br^2 \left|R(r)\right|^2\right)}{dr} = 0$$

The wavefunction for an electron in a $2p_z$ orbital of a hydrogenlike atom is: $\psi_{2p_z} = Are^{-\frac{Zr}{2a_0}}\cos(\theta)$

We will determine the most probable distance of the electron from the nucleus, r_{mp}.

$$P(r) = Br^2|R|^2 = Br^2\left(re^{-\frac{Zr}{2a_0}}\right)^2 = Br^4e^{-\frac{Zr}{a_0}}$$

$$\frac{d}{dr}\left(Br^4e^{-\frac{Zr}{a_0}}\right) = 0 \quad when\ r = r_{mp}$$

$$0 = B\left[r^4\frac{d}{dr}\left(e^{-\frac{Zr}{a_0}}\right) + e^{-\frac{Zr}{a_0}}\frac{dr^4}{dr}\right] = B\left[r^4\left(-\frac{Z}{a_0}\right)e^{-\frac{Zr}{a_0}} + e^{-\frac{Zr}{a_0}}\left(4r^3\right)\right]$$

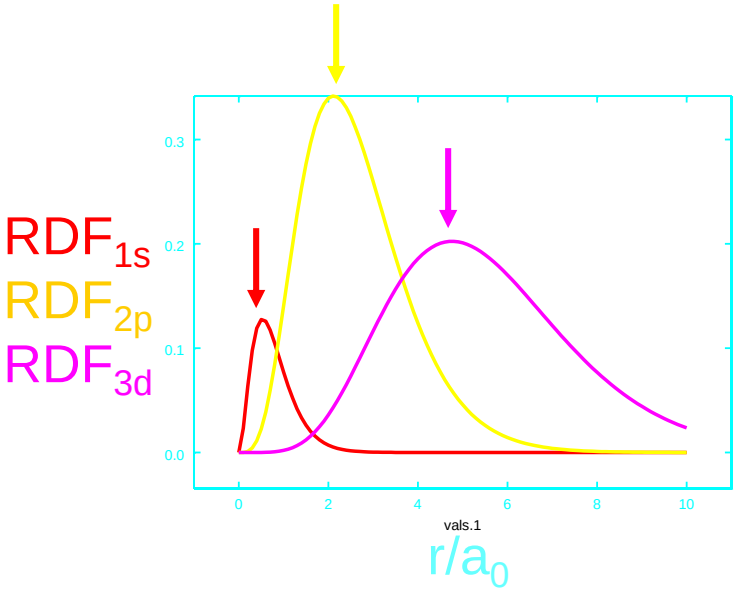
$$0 = B\left[r^4 \left(-\frac{Z}{a_0} \right) e^{-\frac{Zr}{a_0}} + e^{-\frac{Zr}{a_0}} \left(4r^3 \right) \right] = Br^3 e^{-\frac{Zr}{a_0}} \left[-\frac{Zr}{a_0} + 4 \right]$$

Therefore: $$-\frac{Zr_{mp}}{a_0} + 4 = 0$$

$$\downarrow$$

$$r_{mp} = \frac{4a_0}{Z}$$

One gets the same result for any 2p orbital because the Radial portion of the wavefunction does not depend on m.



(r RD1S2 RD2P2 RD3D2)

By the same method, one may calculate r_{mp} for 1s and 3d electrons:

$$r_{mp}(1s) = \frac{a_0}{Z}$$

$$r_{mp}(2p) = \frac{4a_0}{Z}$$

$$r_{mp}(3d) = \frac{9a_0}{Z}$$

These most probable distances correspond to predicted radii for the Bohr orbits:

$$r_n = n^2 \frac{a_0}{Z}$$

Probability of r in a certain range

We will again consider an electron in a 2p orbital, for which: $P(r) = Br^4 e^{-\frac{Zr}{a_0}}$

What is the probability that $0 \le r \le 5a_0/Z$

We will first normalize the RDF

$$1 = \int_0^\infty P(r)dr = B\int_0^\infty r^4 e^{-\frac{Zr}{a_0}} dr = B\frac{4!}{\left(\frac{Z}{a_0}\right)^5} = B \cdot 24\left(\frac{a_0}{Z}\right)^5$$

$$B = \frac{1}{24}\left(\frac{Z}{a_0}\right)^5$$

Some Numerical Integrals

$$\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$$

$$\int_0^3 x^4 e^{-x} dx = 4.43$$

$$\int_0^5 x^4 e^{-x} dx = 13.43$$

$$P(r) = Br^4 e^{-\frac{Zr}{a_0}} \qquad B = \frac{1}{24}\left(\frac{Z}{a_0}\right)^5$$

Some Numerical Integrals

$$\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$$

$$\int_0^3 x^4 e^{-x} dx = 4.43$$

$$\int_0^5 x^4 e^{-x} dx = 13.43$$

What is the probability that $0 \le r \le 5a_0/Z$

$$P(0 \le r \le 5a_0/Z) = \int_0^{5a_0/Z} P(r)dr = B\int_0^{5a_0/Z} r^4 e^{-\frac{Zr}{a_0}} dr$$

Define: $x \equiv \frac{Zr}{a_0}$ Then: $r = \frac{a_0}{Z}x$

$$dr = \frac{a_0}{Z}dx \qquad r = 5\frac{a_0}{Z} \rightarrow x = \frac{Z}{a_0}r = 5$$

$$P(0 \le r \le 5a_0/Z) = B\int_0^5 \left(\frac{a_0}{Z}x\right)^4 e^{-x} \cdot \left(\frac{a_0}{Z}dx\right) = B \cdot \left(\frac{a_0}{Z}\right)^5 \int_0^5 x^4 e^{-x} dx$$

$$= \frac{1}{24}\left(\frac{Z}{a_0}\right)^5 \cdot \left(\frac{a_0}{Z}\right)^5 \cdot 13.43 = \frac{13.43}{24} = 0.56$$

$$P(r) = Br^4 e^{-\frac{Zr}{a_0}} \qquad B = \frac{1}{24}\left(\frac{Z}{a_0}\right)^5$$

Some Numerical Integrals

$$\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$$

$$\int_0^3 x^4 e^{-x} dx = 4.43$$

$$\int_0^5 x^4 e^{-x} dx = 13.43$$

What is the probability that $3a_0/Z \le r < \infty$

$$P(3a_0/Z \le r < \infty) = 1 - P(0 \le r \le 3a_0/Z)$$

One can use the identical method used above to determine that:

$$P(0 \le r \le 3a_0/Z) = \frac{4.43}{24} = 0.18$$

$$P(3a_0/Z \le r < \infty) = 1 - P(0 \le r \le 3a_0/Z) = 1 - 0.18 = 0.82$$

$$P(r) = Br^4 e^{-\frac{Zr}{a_0}} \qquad B = \frac{1}{24}\left(\frac{Z}{a_0}\right)^5 \qquad \int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$$

Calculate <r> for an electron in a $2p_z$ orbital

(same as worked earlier using the complete wavefunction)

$$\langle r \rangle = \int_0^\infty rP(r)dr = \int_0^\infty r \cdot Br^4 e^{-\frac{Zr}{a_0}} dr = B\int_0^\infty r^5 e^{-\frac{Zr}{a_0}} dr$$

$$\langle r \rangle = \frac{1}{24}\left(\frac{Z}{a_0}\right)^5 \cdot \frac{5!}{\left(\frac{Z}{a_0}\right)^6} = \frac{1}{24} \cdot \frac{120}{\left(\frac{Z}{a_0}\right)^1} = 5\frac{a_0}{Z}$$

Same result as before.

$$P(r) = Br^4 e^{-\frac{Zr}{a_0}} \qquad B = \frac{1}{24}\left(\frac{Z}{a_0}\right)^5 \qquad \int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$$

Calculate the average potential energy for an electron in a $2p_z$ orbital.

$$V(r) = -\frac{Ze \cdot e}{4\pi\varepsilon_0}\frac{1}{r} \longrightarrow \langle V \rangle = \left\langle -\frac{Ze \cdot e}{4\pi\varepsilon_0}\frac{1}{r} \right\rangle = -\frac{Ze^2}{4\pi\varepsilon_0}\left\langle \frac{1}{r} \right\rangle$$

$$\left\langle \frac{1}{r} \right\rangle = \int_0^\infty \frac{1}{r} P(r) dr = \int_0^\infty \frac{1}{r} \cdot Br^4 e^{-\frac{Zr}{a_0}} dr = B\int_0^\infty r^3 e^{-\frac{Zr}{a_0}} dr$$

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{24}\left(\frac{Z}{a_0}\right)^5 \cdot \frac{3!}{\left(\frac{Z}{a_0}\right)^4} = \frac{1}{24} \cdot \left(\frac{Z}{a_0}\right) \cdot 6 = \frac{1}{4} \cdot \left(\frac{Z}{a_0}\right)$$

$$\langle V \rangle = -\frac{Ze^2}{4\pi\varepsilon_0}\left\langle \frac{1}{r} \right\rangle = -\frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{4}\left(\frac{Z}{a_0}\right) = -\frac{Z^2 e^2}{16\pi\varepsilon_0 a_0}$$

$$\langle V \rangle = -\frac{Z^2 e^2}{16\pi\varepsilon_0 a_0}$$ for an electron in a 2p orbital

Total Energy: $E_n = -\frac{Z^2 e^2}{2(4\pi\varepsilon_0)a_0} \cdot \frac{1}{n^2} \longrightarrow E_2 = -\frac{Z^2 e^2}{32\pi\varepsilon_0 a_0}$

Note that <V> = 2•E

Calculation of average kinetic energy, <T>

$$\langle T \rangle + \langle V \rangle = E$$

$$\langle T \rangle + 2E = E$$

$$\langle T \rangle = -E$$

Signs

<V> negative
<T> positive
<E> negative

Also: $\langle V \rangle = 2E = -2\langle T \rangle$

6. Atomic Units

Let's redefine
some basic units:

$m_e = 1$ (mass of electron)

$e = 1$ (charge of electron)

$\hbar = 1$ (angular momentum)

$4\pi\varepsilon_o = 1$ (dielectric permittivity)

Derived Units

Conversions

Length: $$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2} = 1 \text{ au} = 1 \text{ bohr}$$

1 bohr = 0.529 Å

Energy: $$-2E_{1s}(H) = \frac{e^2}{4\pi\varepsilon_0 a_0} = 1 \text{ hartree (h)}$$

1 h = 2625 kJ/mol

1 h = 27.21 eV

Hydrogen Atom Schrödinger Equation

SI Units

$$-\frac{\hbar^2}{2m_e}\nabla^2\psi - \frac{Ze^2}{4\pi\varepsilon_0 r}\psi = E\psi$$

$$E_n = -\frac{m_e Z^2 e^4}{2(4\pi\varepsilon_0)^2\hbar^2}\cdot\frac{1}{n^2}$$

$$E_1 = -\frac{m_e Z^2 e^4}{2(4\pi\varepsilon_0)^2\hbar^2}$$

Atomic Units

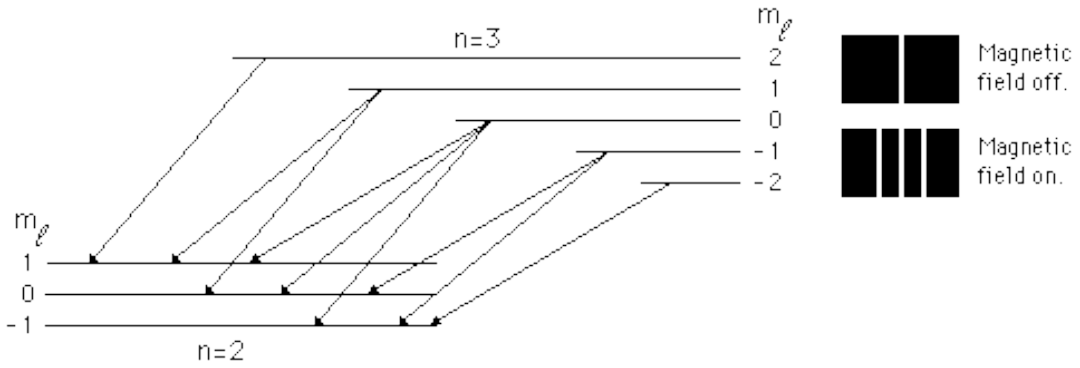
$$-\frac{1}{2}\nabla^2\psi - \frac{Z}{r}\psi = E\psi$$

$$E_n = -\frac{Z^2}{2}\cdot\frac{1}{n^2}$$

$$E_1 = -\frac{Z^2}{2}$$

Zeeman Effect in Hydrogen

When an external magnetic field is applied, sharp spectral lines like the n= 3→ 2 transition of hydrogen ***split into multiple closely spaced lines***. this splitting is attributed to the interaction between the magnetic field and the magnetic dipole moment associated with the orbital angular momentum. In the absence of the magnetic field, the hydrogen energies depend only upon the principal quantum number n, and the emissions occur at a single wavelength.



***the transitions shown follow the selection rule which does not allow a change of more than one unit in the quantum number ml*.**