CHAPTER 6
THE HYDROGEN ATOM
OUTLINE

Homework Questions Attached

SECT   **TOPIC**

1.   The Hydrogen Atom Schrödinger Equation

2.   The Radial Equation (Wavefunctions and Energies)

3.   The HydrogenAtom Wavefunctions (Complex and Real)

4.   Use of the Wavefunctions (Calculating Averages)

5.   The Radial Distribution Function

6.   Atomic Units

Chapter 6 Homework

1. The energy levels of hydrogenlike atoms are given by: $E_n = -\dfrac{1}{2}\dfrac{e^2}{4\pi\varepsilon_0 a_0}\dfrac{Z^2}{n^2}$

   (a) Calculate the wavelength, in nm, of the n=6 to n=3 radiative transition in He$^+$.

   (b) Calculate the ionization energy of He$^+$, in eV

   Note: $\dfrac{e^2}{4\pi\varepsilon_0 a_0} = 2625\ kJ\,/\,mol$

2. The 1s and 2s wavefunctions of hydrogenlike atoms are:

   $$\psi_{1s} = A_{1s}e^{-Zr\,/\,a_0} \qquad \psi_{2s} = A_{2s}\left(1 - \frac{Zr}{2a_0}\right)e^{-Zr\,/\,2a_0}$$

   (a) Prove the ψ_{1s} and ψ_{2s} are orthogonal to each other.

   (b) Calculate the normalization constant, A_{1s}.

   (c) Calculate the most probable value of r for an electron in a 1s orbital.

   (d) Calculate <r> for an electron in a 1s orbital (Note: first normalize the radial distribution function).

   (e) Calculate the probability that the electron in a 1s orbitl is between r=0 and r=2a$_0$/Z

   (f) Calculate the probability that r is in the range: $a_0/Z \le r \le 4a_0/Z$

   (g) Calculate the average potential energy of an electron in a =1s orbital.

   (h) Show that the Radial component of ψ_{1s} is an eigenfunction of the radial Schrödinger equation (below) with l = 0

3. The 2p$_x$ wavefunction of hydrogenlike atoms is given by:

   $$\psi_{2px} = Are^{-Zr/2a_0}\sin\theta\cos\phi$$

   (a) Calculate the most probably value of r for an electron in a 2p$_x$ orbital.

   (b) Calculate <r^2> for an electron in a 2p$_x$ orbital (Note: first normalize the radial distribution function).

4. One of the wavefunctions of hydrogenlike atoms is:

   $$\psi = A\cdot R(r)\cdot Y_{lm}(\theta,\varphi) = Ar^2 e^{-Zr/3a_0}\sin^2\theta e^{2i\varphi}$$

   (a) Show that $Y_{lm}(\theta,\phi)$ is an eigenfunction of the L^2 operator (below). What is the eigenvalue?

(b) Show that $Y_{lm}(\theta,\phi)$ is an eigenfunction of the L_z operator (below). What is the eigenvalue?

(c) Set up the product of 3 integrals in spherical polar coordinates required to calculate $<y^2>$. You do NOT have to perform the integrals.

5.   Two of the complex hydrogen atom d (l=2) wavefunctions are:

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

Use the Euler Relations below to show how these can be combined to yield two real forms of the hydrogen atom d wavefunctions.

DATA

$h = 6.63 \times 10^{-34}$ J·s

$\hbar = h/2\pi = 1.05 \times 10^{-34}$ J·s

$c = 3.00 \times 10^8$ m/s $= 3.00 \times 10^{10}$ cm/s

$N_A = 6.02 \times 10^{23}$ mol^{-1}

$k = 1.38 \times 10^{-23}$ J/K

$R = 8.31$ J/mol-K

$R = 8.31$ Pa-m^3/mol-K

$m_e = 9.11 \times 10^{-31}$ kg (electron mass)

1 J $= 1$ kg·m^2/s^2

1 Å $= 10^{-10}$ m

$k \cdot N_A = R$

1 amu $= 1.66 \times 10^{-27}$ kg

1 atm. $= 1.013 \times 10^5$ Pa

1 eV $= 1.60 \times 10^{-19}$ J

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

$$\int_0^2 x^2 e^{-x} dx = 0.647$$

$$\int_0^4 x^2 e^{-x} dx = 1.524$$

$$\int_0^8 x^2 e^{-x} dx = 1.972$$

Radial Schrödinger Equation: $-\dfrac{\hbar^2}{2m}\left[\dfrac{d^2 R}{dr^2} + \dfrac{2}{r}\dfrac{dR}{dr} - \dfrac{l(l+1)}{r^2} + \dfrac{2Z}{a_0 r}R\right] = ER$

L_z Operator: $\hat{L}_z = \dfrac{\hbar}{i}\dfrac{\partial}{\partial\varphi}$

L^2 Operaor: $L^2 = -\hbar^2\left\{\dfrac{1}{\sin\theta}\dfrac{\partial}{\partial\theta}\left(\sin\theta\dfrac{\partial}{\partial\theta}\right) + \dfrac{1}{\sin^2\theta}\dfrac{\partial^2}{\partial\varphi^2}\right\}$

Euler Relations: $e^{ix} = \cos(x) + i\sin(x)$ and $e^{-ix} = \cos(x) - i\sin(x)$

Chapter 6

The Hydrogen Atom

Outline

- **The Hydrogen Atom Schrödinger Equation**

- The Radial Equation Solutions (Wavefunctions and Energies)

- The Hydrogen Atom Wavefunctions (Complex and Real)

- Use of the Wavefunctions (Calculating Averages)

- The Radial Distribution Function
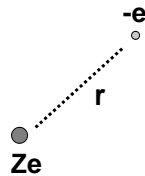
- Atomic Units

The Hydrogen Atom Schrödinger Equation

The Potential Energy

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

Force: $\quad f = \dfrac{q_1 q_2}{4\pi\varepsilon_0 r^2}$ $\qquad$ Potential Energy: $\quad V(r) = \dfrac{q_1 q_2}{4\pi\varepsilon_0 r}$

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

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

-e

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

Ze

The Schrödinger Equation

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

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 $\sim$1830 times heavier, $\mu = 0.9995m$. Therefore, many texts (including ours) 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:

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

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

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

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

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

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

We learned in Chapter 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 $\hat{L}_z$: $\hat{L}_z Y_{\ell m}(\theta,\varphi)=m\hbar Y_{\ell m}(\theta,\varphi)$

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

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:

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

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

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

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

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:
$R(r) \rightarrow 0$ as $r \rightarrow \infty$.

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
(Chapter 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.

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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,
$R(r) \rightarrow 0$ as $r \rightarrow \infty$, is applied, one gets a new quantum number, n, with the restriction that:

$$n > \ell \quad \text{or, equivalently} \quad \ell < n$$

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:

$$R_{n\ell}(r) = Poly\left(\frac{Zr}{na_0}\right)\cdot e^{-\frac{Zr}{na_0}} \quad \text{where} \quad a_0 = \frac{4\pi\varepsilon_0\hbar^2}{me^2} = 0.529 \text{ Å}$$

Bohr Radius

Several of the Radial functions are:

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

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

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

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

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

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

The Energies

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

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

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.

∞ ——— 0
4 ——— -k/16
3 ——— -k/9
2 ——— -k/4

Energy

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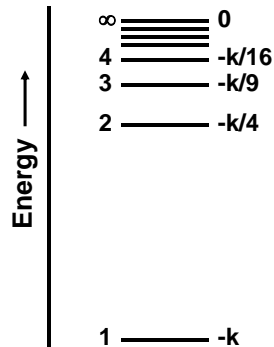
Show that $R_{10}(r)$ is an eigenfunction of the Radial equation and that the eigenvalue is given by E_1 (below).

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

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

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

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

Note: the alternative forms above have been obtained using:

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

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

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

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

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

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

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

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

Therefore:

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

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

$$\downarrow$$

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

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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 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)

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

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

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

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

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

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

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

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

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

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

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

Spherical Polar Coords.

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

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

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

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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.)

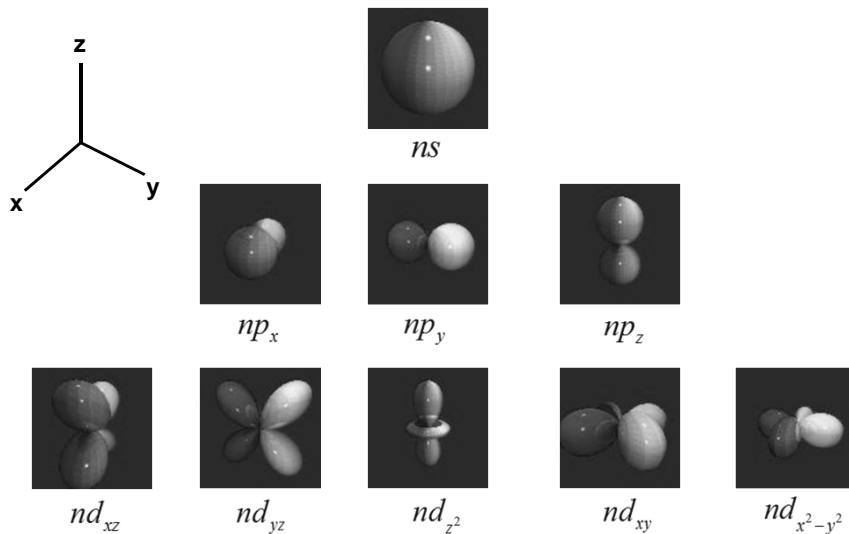By the same procedures used above for the p wavefunctions, one finds:

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

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

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

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

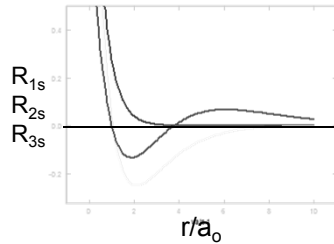$$\psi_{nd_{xy}} = \frac{1}{\sqrt{2}i}\left(\psi_{n22} - \psi_{n2-2}\right) = \sqrt{2}R_{n2}(r) \cdot \sin^2(\theta)\sin(2\varphi)$$

Plotting the Angular Functions

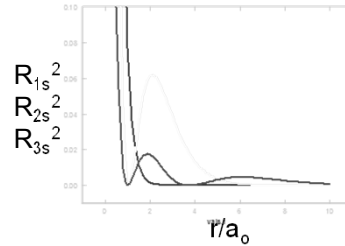Below are the familiar polar plots of the angular parts of the hydrogen atom wavefunctions.

ns

np_x np_y np_z
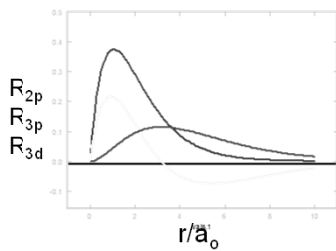
nd_{xz} nd_{yz} nd_{z^2} nd_{xy} $nd_{x^2-y^2}$

Plotting the Radial Functions

R_{1s}
R_{2s}
R_{3s}

(r R1S R2S R3S)

R_{1s}^2
R_{2s}^2
R_{3s}^2

(r R1S2 R2S2 R3S2)

r/a_o

r/a_o

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

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R_{2p}
R_{3p}
R_{3d}

(r R2P R3P R3D)

R_{2p}^2
R_{3p}^2
R_{3d}^2

(r R2P2 R3P2 R3D2)

r/a_o

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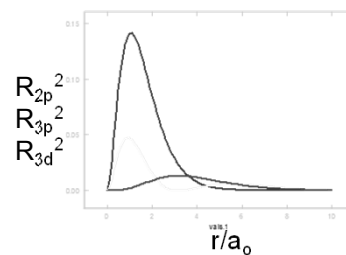
R_{2p} has no nodes
R_{3p} has 1 node
R_{3d} has no nodes

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.

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Outline

• The Hydrogen Atom Schrödinger Equation

• The Radial Equation Solutions (Wavefunctions and Energies)

• The Hydrogen Atom Wavefunctions (Complex and Real)

• **Use of the Wavefunctions (Calculating Averages)**

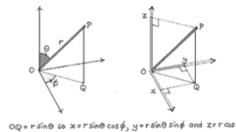• The Radial Distribution Function

• Atomic Units

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

$OQ = r\sin\theta$ so $x = r\sin\theta\cos\phi$, $y = r\sin\theta\sin\phi$ and $z = r\cos\theta$

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

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

$$\psi = A\left(\frac{Zr}{a_0}\right)e^{-\frac{Zr}{2a_0}}\cos(\theta)$$

Wavefunction Normalization

$$\iiint \psi * \psi dV = 1 = \iiint \left[A\left(\frac{Zr}{a_0}\right)e^{-\frac{Zr}{2a_0}}\cos(\theta) \right]^2 r^2 \sin(\theta)drd\theta d\varphi$$

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

$$1 = A^2\left(\frac{Z}{a_0}\right)^2 \cdot I_R \cdot I_\Theta \cdot I_\Phi$$

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

$$I_R = \int_0^\infty r^4 e^{-\frac{Zr}{a_0}}dr = \frac{4!}{\left(\frac{Z}{a_0}\right)^5} = 24\left(\frac{a_0}{Z}\right)^5 \qquad \int_0^\infty x^n e^{-\alpha x}dx = \frac{n!}{\alpha^{n+1}}$$

$$I_\Theta = \int_0^\pi \cos^2(\theta)\sin(\theta)d\theta \qquad\qquad \int \cos^2(x)\sin(x)dx = -\frac{1}{3}\cos^3(x)$$

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

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

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

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

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

$$A^2 = \frac{1}{32\pi}\left(\frac{Z}{a_0}\right)^3 \longrightarrow \boxed{A = \frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{3/2}}$$

$$\psi = A\left(\frac{Zr}{a_0}\right)e^{-\frac{Zr}{2a_0}}\cos(\theta) = \frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \cdot \left(\frac{Zr}{a_0}\right)e^{-\frac{Zr}{2a_0}}\cos(\theta)$$

We could have combined the extra Z/a_0 into the normalization constant

---

$$\psi = A\left(\frac{Zr}{a_0}\right)e^{-\frac{Zr}{2a_0}}\cos(\theta) \qquad A = \frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{3/2}$$

Calculation of <r>

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

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

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

$$I_R = \int_0^\infty r^5 e^{-\frac{Zr}{a_0}} dr = \frac{5!}{\left(\frac{Z}{a_0}\right)^6} = 120\left(\frac{a_0}{Z}\right)^6 \qquad \int_0^\infty x^n e^{-\alpha x} dx = \frac{n!}{\alpha^{n+1}}$$

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

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

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

Calculation of other Averages

We use the same procedures. For example, I'll set up the calculation for the calculation of <y^2>, where y = rsin(θ)sin(ϕ)

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

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

$$= A^2 \left(\frac{Z}{a_0}\right)^2 \cdot I_R \cdot I_\Theta \cdot I_\Phi \qquad \text{and evaluate.}$$

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Outline

- The Hydrogen Atom Schrödinger Equation

- The Radial Equation Solutions (Wavefunctions and Energies)

- The Hydrogen Atom Wavefunctions (Complex and Real)

- Use of the Wavefunctions (Calculating Averages)

- **The Radial Distribution Function**

- Atomic Units

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.

The Radial Distribution Function

R_{2p}^2
R_{3p}^2
R_{3d}^2

r/a_o
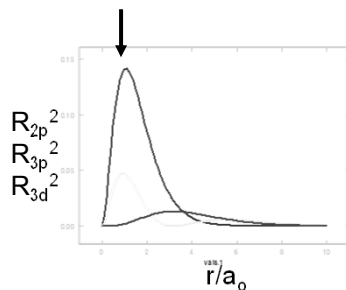
(r R2P2 R3P2 R3D2)

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.

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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:

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

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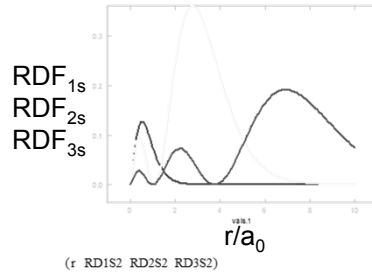
or $\boxed{P(r)dr = Br^2 |R(r)|^2 dr}$

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

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

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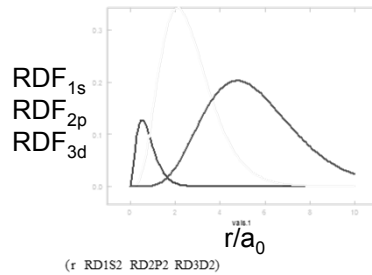
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We'll use RDF(r) $\equiv$ P(r)

RDF_{1s}
RDF_{2s}
RDF_{3s}

r/a_0

(r RD1S2 RD2S2 RD3S2)

This is because:

RDF$_{1s}$ has 1 maximum   R$_{1s}$ has no nodes
RDF$_{2s}$ has 2 maxima   R$_{2s}$ has 1 node
RDF$_{3s}$ has 3 maxima   R$_{3s}$ has 2 nodes

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We'll use RDF(r) $\equiv$ P(r)

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

r/a_0

(r RD1S2 RD2P2 RD3D2)

This is because:

RDF$_{1s}$ has 1 maximum   R$_{1s}$ has no nodes
RDF$_{2p}$ has 1 maximum   R$_{2p}$ has no nodes
RDF$_{3d}$ has 1 maximum   R$_{3d}$ has no nodes

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Most Probable Value of r

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

r/a_0

(r RD1S2 RD2P2 RD3D2)
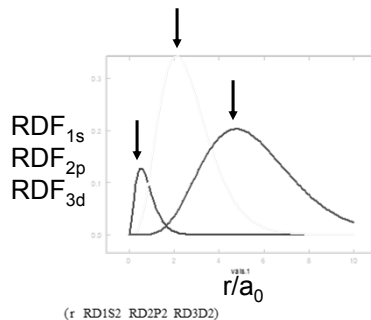
The most probable value of the distance from the nucleus, r, is given by the maximum in the Radial Distribution Function, $P(r) \equiv RDF(r)$

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

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}.

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

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

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

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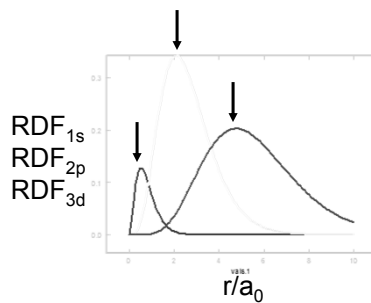
Therefore: $-\dfrac{Zr_{mp}}{a_0} + 4 = 0$

$\downarrow$

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

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

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

r/a_0

(r RD1S2 RD2P2 RD3D2)

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

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

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

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

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 $0 \leq r \leq 5a_0/Z$

We will first normalize the RDF

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

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

Some Numerical Integrals

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

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

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

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

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

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

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

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

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

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

Some Numerical Integrals

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

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

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

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

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

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

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

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

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

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)

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

$$\langle r \rangle = \frac{1}{24}\left(\frac{Z}{a_0}\right)^5 \cdot \frac{5!}{\left(\frac{Z}{a_0}\right)^6} = \frac{1}{24} \cdot \frac{120}{\left(\frac{Z}{a_0}\right)^1} = 5\frac{a_0}{Z} \qquad \text{Same result as before.}$$

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

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

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

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

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

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

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

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

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

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- **Atomic Units**

Atomic Units

All of these funny symbols flying around are giving me a headache. Let's get rid of some of them.

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: $\quad a_0 = \dfrac{4\pi\varepsilon_0 \hbar^2}{m_e e^2} = 1 \ \text{au} = 1 \ \text{bohr}$ $\qquad$ 1 bohr = 0.529 Å

Energy: $\quad -2E_{1s}(H) = \dfrac{e^2}{4\pi\varepsilon_0 a_0} = 1 \ \text{hartree (h)}$ $\qquad$ 1 h = 2625 kJ/mol

1 h = 27.21 eV

Hydrogen Atom Schrödinger Equation

SI Units

Atomic Units

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

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

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

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

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

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