Lecture #5

Reading:
1.9-Atomic Orbitals

Topics: Hydrogen Atom Wavefunctions
I. Wavefunctions (orbitals) for the hydrogen atom ($H\underline{\Psi} = E\underline{\Psi}$)
II. Shapes of H-atom wavefunctions: s orbitals
III. Radial probability distributions

ENERGY LEVELS (continued from Lecture #5)

The Rydberg formula can be used to calculate the frequency (and also the E or λ, using $E = h\nu$ or $\lambda = c/\nu$) of light emitted or absorbed by any 1-electron atom or ion.

$$\nu = \frac{Z^2 R_H}{h}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \qquad\qquad \nu = \frac{Z^2 R_H}{h}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

$$\text{for } n_i > n_f \qquad\qquad\qquad\qquad \text{for } n_f > n_i$$

$n_f > n_i$ in _____. Electrons absorb energy causing them to go from a lower to a higher E level.

$n_i > n_f$ in _____. Electrons emit energy causing them to go from a higher to a lower E level.

I. WAVEFUNCTIONS (ORBITALS) FOR THE HYDROGEN ATOM

When solving $H\Psi = E\Psi$, the solutions are E_n and $\Psi(r,\theta,\phi)$.

$\Psi(r,\theta,\phi) \equiv$ stationary state wavefunction: time-independent
In solutions for $\Psi(r,\theta,\phi)$, two new quantum numbers appear! A total of 3 quantum numbers are needed to describe a wavefunction in 3D.

1. $n \equiv$ principal quantum number
      $n = 1, 2, 3 \ldots \ldots \infty$
         determines binding energy

2. $l \equiv$ angular momentum quantum number

      $l = \dfrac{0, 1, 2, 3, \ldots , n\text{-}1}{}$
      l is related to n
      largest value of $l = n - 1$
      determines angular momentum

3.   m ≡ magnetic quantum number

m = __-l, ... 0 ..., l__

       m is related to l
       largest value is $+l$, smallest is $-l$
       determines behavior of atom in magnetic field

To completely describe an orbital, we need to use all three quantum numbers:

$$\Psi_{nlm}(r,\theta,\phi)$$

The wavefunction describing the ground state is __$_{100}$ (, ,)__.
Using the terminology of chemists, the Ψ_{100} orbital is instead called the "_1s_" orbital.

An orbital is (the spatial part) of a wavefunction; n(shell) l(subshell) m(orbital)

$l = 0 \Rightarrow$ _s_ orbital $l = 1 \Rightarrow$ _p_ orbital $l = 2 \Rightarrow$ _d_ orbital $l = 3 \Rightarrow$ _f_ orbital

for $l = 1$:   m = 0 _p_z_ orbital,   m = ±1 states combine to give _p_x_ and _p_y_ orbitals

	State label	wavefunction	orbital	E_n	$E_n[J]$
n = 1 $l = 0$ m = 0	100	Ψ_{100}	1s	$-R_H/1^2$	-2.18×10^{-18} J
n = 2 $l = 0$ m = 0	200	200	2s	$-R\_H/2^{\wedge}2$	-5.45×10^{-19} J
n = 2 $l = 1$ m = +1	211	211	2P_z	$-R\_H/2^{\wedge}2$	-5.45×10^{-19} J
n = 2 $l = 1$ m = 0	210	Ψ_{210}	2P_x	$-R_H/2^2$	-5.45×10^{-19} J
n = 2 $l = 1$ m = -1	21-1	Ψ_{21-1}	2P_y	$-R_H/2^2$	-5.45×10^{-19} J

For a __H-atom( )__ orbitals with the same n value have the same energy: $E = -R_H/n^2$.

- Degenerate ≡ having the same energy
- For any principle quantum number, n, there are __n^2__ degenerate orbitals in hydrogen (or any other 1 electron atom).

Energy Level Diagram

9 degenerate states at second excited energy level

E [J]

	3s	3p_x	3p_z	3p_y	3d_xy	3d_yz	3d_z^2	3d_xz	3d_x^2-y^2
-0.242×10^{-18}	$n = 3$ $\ell = 0$ $m = 0$	3 $\ell = 1$ $m = \pm 1$	3 $\ell = 1$ $m = 0$	3 $\ell = 1$ $m = \pm 1$	3 $\ell = 2$ $\pm 1, \pm 2$	3 $\ell = 2$ $\pm 1, \pm 2$	3 $\ell = 2$ $m = 0$	3 $\ell = 2$ $\pm 1, \pm 2$	3 $\ell = 2$ $\pm 1, \pm 2$

	2s	2p_x	2p_z	2p_y	
-0.545×10^{-18}	$n = 2$ $\ell = 0$ $m = 0$	2 $\ell = 1$ $m = \pm 1$ $+1$	2 $\ell = 1$ $m = 0$	2 $\ell = 1$ $m = \pm 1$ -1	4 degenerate states at first excited energy level

	1s	
-2.18×10^{-18}	$n = 1$ $\ell = 0$ $m = 0$	1 state at ground energy level 1s state described by ψ_{100} or 1s

II. SHAPES OF H-ATOM WAVEFUNCTIONS: S ORBITALS

THE PHYSICAL INTERPRETATION OF A WAVEFUNCTION

Max Born (German physicist, 1882-1970). The probability of finding a particle (the electron!) in a defined region is proportional to the square of the wavefunction.

$$[\Psi_{n\ell m}(r,\theta,\phi)]^2 = \text{PROBABLITY DENSITY}$$
probability of finding an electron per unit volume at r, θ, φ

To consider the shapes of orbitals, let's first rewrite the wavefunction as the product of a radial wavefunction, $R_{n\ell}(r)$, and an angular wavefunction $Y_{\ell m}(\theta,\phi)$

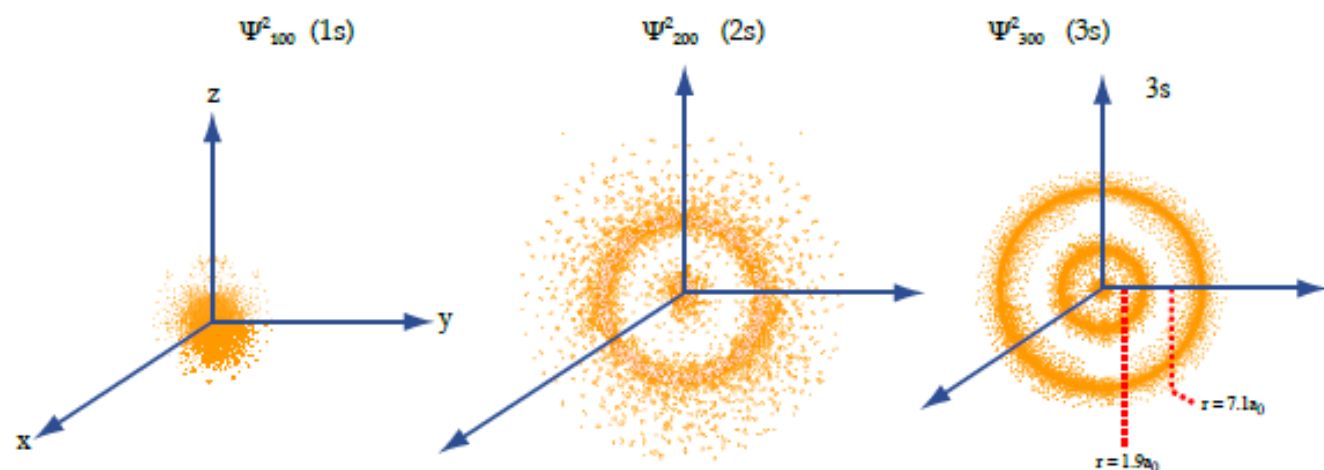$$\Psi_{n\ell m}(r,\theta,\phi)] = \underline{\quad R\_nl(r) \quad} \times \underline{\quad Y\_lm(\ ,\ ) \quad}$$

for a ground state H-atom:

$$\Psi_{100}(r,\theta,\phi) = \underbrace{\frac{2e^{-r/a_o}}{a_o^{3/2}}}_{R(r)} \times \underbrace{\left[\frac{1}{4\pi}\right]^{1/2}}_{Y(\theta,\phi)} = \frac{e^{-r/a_o}}{(\pi a_o^3)^{1/2}}$$
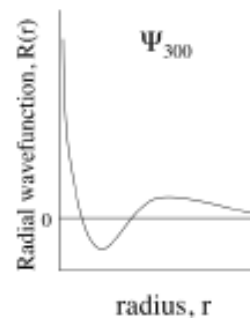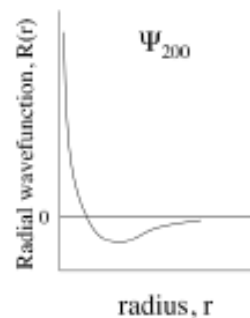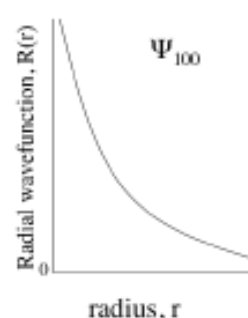
where $a_0 = \underline{\quad \text{Bohr radius} \quad}$ (a constant) $= 52.9$ pm $(\quad\quad)$

- For all s orbitals (1s, 2s, 3s, etc.), the angular wavefunction, Y, is a __constant__.
- s-orbitals are spherically symmetrical – independent of _____ and _____.

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Probability density plot of s orbitals: density of dots represent probability density

Ψ^2_{100} (1s) Ψ^2_{200} (2s) Ψ^2_{300} (3s)

Figures by MIT OpenCourseWare.

$r = 7.1a_0$

$r = 1.9a_0$

Ψ_{100} Ψ_{200} Ψ_{300}

Radial wavefunction, R(r) — radius, r

NODE: A value for r, θ, or φ for which Ψ (and Ψ^2) = ___0___. In general, an orbital has n -1 nodes.

RADIAL NODE: A value for ___r___ for which Ψ (and Ψ^2) = 0. In other words, a radial node is a distance from the radius for which there is no probability of finding an electron.

In general, an orbital has   n - 1 − l radial nodes.

1s: 1− 1− 0 = 0 radial nodes

2s: $\frac{2}{}$ − $\frac{1}{}$ − $\frac{0}{}$ = $\frac{1}{}$ radial nodes

3s: $\frac{2}{}$ − $\frac{1}{}$ − $\frac{0}{}$ = $\frac{2}{}$ radial nodes

III. RADIAL PROBABILITY DISTRIBUTION

Probability of finding an electron in a spherical shell of thickness dr at a distance r from origin.

Radial Probability Distribution (for s orbitals ONLY) = $4\pi r^2 \Psi^2 \, dr$

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We can plot the radial probability distribution as a function of radius.
Radial probability distribution for a hydrogen 1s orbital:

Bohr radius $= a_0$

RPD

Ψ_{100} (1s)
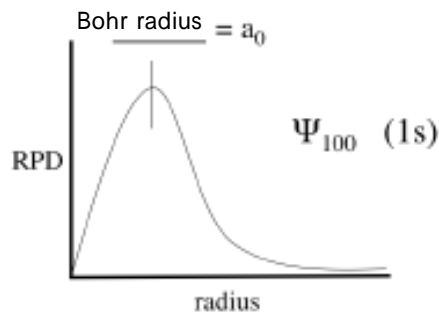
radius

Maximum probability or most probable value of r is denoted r_{mp}.

r_{mp} for a 1s H atom $= a_0 = 0.529 \times 10^{-10} m = 0.529 Å$ $a_0 \equiv$ BOHR radius

1913 Niels Bohr (Danish scientist) predicted quantized levels for H atom prior to

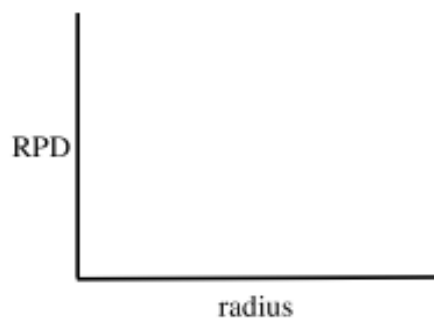$r = a_0$

RP

Bohr's model

radius
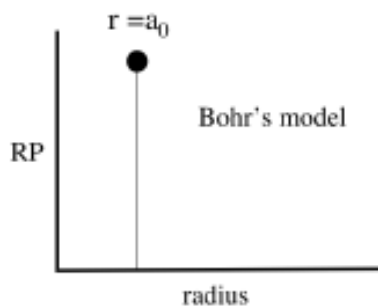
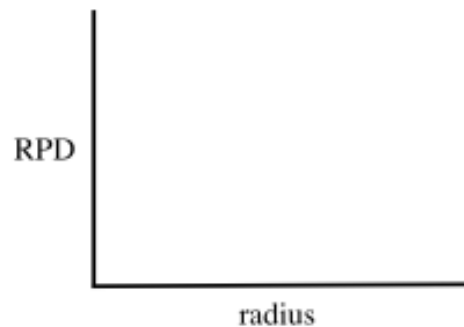QM development, with the electron in well-defined circular orbits.

This was still a purely particle picture of the e^-.

But, an electron does not have well-defined orbits! The best we can do is to find the probability of finding e^- at some position r.

Knowing only probability is one of main consequences of Quantum Mechanics. Unlike CM, QM is non-deterministic. The uncertainty principle forbids us from knowing r exactly.

RPD

radius

Ψ_{200} (2s)

RPD

radius

Ψ_{300} (3s)

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