

**Chemistry 1B**  
**Fall 2016**  
**sessions-lectures 3-4**

(537-542, \*(543-549), 549-557)

1

*quantization of energy*

---

$$E_{\text{photon}} = h\nu$$

absorption and emission spectra of hydrogen atom

$$E_n = -2.178 \times 10^{-18} \text{ J} \left( \frac{Z^2}{n^2} \right) \quad Z=1 \text{ for H atom, } n=1, 2, 3, \dots$$


$$\frac{1}{\lambda} = \frac{2.178 \times 10^{-18} \text{ J}}{hc} Z^2 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = 1.0967 \times 10^7 \text{ m}^{-1} Z^2 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

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Chemistry 1B Fall 2016  
Sessions 3-4

*wave-particle duality*

---

- diffraction of electrons-  
(Davisson-Germer Experiment; p. 530)
- De Broglie relationship (p. 528) (HW#1 12.32,12.35)
- What is “meaning” of electron wave??  
(<http://phys.educ.ksu.edu/vqm/html/doubleslit/index.html>)  
(<http://www.youtube.com/watch?v=DfPeprQ7oGc>) 
- Wavelengths of “ordinary” objects  
(p. 528, example 12.2) Silberberg [Table 7.1](#) (HW#1 prob S2)
- Compton Experiment
- [Heisenberg uncertainty principle \(p. 539\)](#) *boing!!* (HW#1 12.49)

3

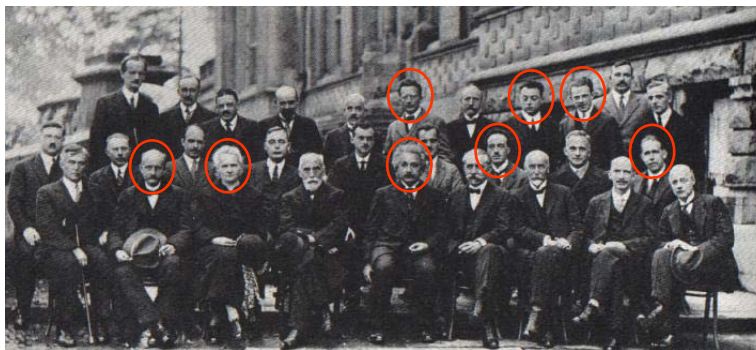
*What to do ??*

*invent quantum mechanics !!!*

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## Chemistry 1B Fall 2016 Sessions 3-4

### Solvay Conference 1927



The mid-1920's saw the development of the quantum theory, which had a profound effect on chemistry. Many theories in science are first presented at international meetings. This photograph of well-known scientists was taken at the international Solvay Conference in 1927. Among those present are many whose names are still known today. Front row, left to right: I. Langmuir, **M. Planck**, **M. Curie**, H. A. Lorentz, **A. Einstein**, P. Langevin, C. E. Guye, C. T. R. Wilson, O. W. Richardson. Second row, left to right: P. Debye, M. Knudsen, W. L. Bragg, H. A. Kramers, P. A. M. Dirac, A. H. Compton, **L. V. de Broglie**, M. Born, **N. Bohr**. Standing, left to right: A. Piccard, E. Henriot, P. Ehrenfest, E. Herzen, T. De Donder, **E. Schroedinger**, E. Verschaffelt, **W. Pauli**, **W. Heisenberg**, R. H. Fowler, L. Brillouin.

5

### 'fuel' for quantum mechanics



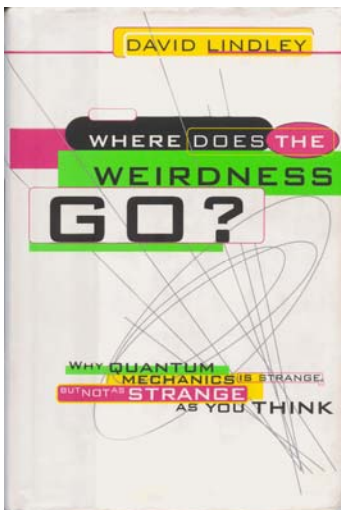
Werner Heisenberg and Niels Bohr dining in Copenhagen in 1934.

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*quantum mechanics: WEIRD*

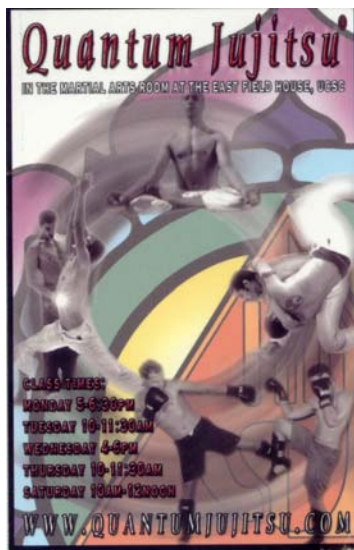
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7

*Quantum Jujitsu ≠ Quantum Mechanics*

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8

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*what quantum mechanics must "include"*

---

- **particles have wave-like properties**
- **some properties, like energy, can only have certain values (energy is quantized)**
- **the emission or absorption of photons result in the system going from one state to another**

9

*goals of lectures 3-4*

---

Hydrogen Atom



**the quantum mechanics of the hydrogen atom  
(nucleus + electron)**

- what is the quantum mechanical equation that determines the properties of electrons in atoms and molecules?
- what are the "allowed" (stationary) states in which the electron in an hydrogen atom can exist ?
- what will be the energy of an electron in a given state ?
- what are the "probability waves" (orbitals) that describe the where an electron in a given state will be "found"?

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*Bohr model vs Quantum*

- Bohr model got the energies of allowed levels correctly
- However Bohr model assumed electrons traveling around nucleus in orbits of fixed radius (different radii for different n's) and with specific  $E_n$
- This is inconsistent with the wave properties of electron and Heisenberg Uncertainty Principle



electron orbits: no, no

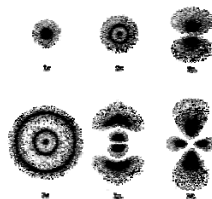


Figure 2.1. Probability density plots for various hydrogen atomic orbitals. The density of the dots represents the probability of finding the electron in that region.  
© 2013 University Science Books, Quantum Chemistry, by Donald A. McQuinn

electron orbitals : si, si  
(probability waves)

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*Schrödinger equation (see pp 540 and 549)*

**SCHRÖDINGER EQUATION**



$$\mathcal{H} \Psi = E \Psi$$

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + V \right] \Psi = E \Psi$$



- **basic equation of quantum mechanics**
- **what does it involve ?? (chem 163A)**
- **what does it tell you ??  $\Psi$   $E$**
- **where can you learn ALL about it in upper division chemistry?**

not responsible for pp. (543-549)\*, Table 12.1

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*hydrogen's electron waves: the three quantum numbers (pp. 550-551)*

---

$$\Psi_{n,\ell,m_\ell} \left( \overbrace{r, \theta, \phi}^{\text{point in space}} \right)$$

$n$  the principal quantum number

$\ell$  the angular momentum quantum number

$m_\ell$  the magnetic quantum number

Table 12.1\*\*\*\*

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Chemistry 1B -AL

the Hydrogen Atom

Allowed Quantum Numbers

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# Chemistry 1B Fall 2016 Sessions 3-4

## study guide II, section III (clicker credit)

Chemistry 1B-AL Fall 2016, Study Guide and Worksheet II

**Learning Objectives and Worksheet II**  
Chemistry 1B-AL Fall 2016

Lectures (3-4) the Quantum Mechanics of the Hydrogen Atom and Atomic Orbitals

Read pp. 537-542 and 549-557 (you will not be responsible for the material on pp-543-548; however the CHEM1B-AL staff would be more than happy to discuss these concepts with you)

I. Regarding the "allowed states" of the Bohr hydrogen atom:

1. What features of the Bohr treatment of the hydrogen are correct?

2. What feature is inconsistent with the wave properties of the electron?

ii. Although you will have to await the charms of CHEM 163A "Quantum Mechanics And Basic Spectroscopy" to fully understand and solve the basic equation that gives the properties of electrons in atoms and molecules, CHEM1B students should have an acquaintance with:

1. What is the name of the famous equation of quantum mechanics that yields the properties of the allowed states of electrons in atoms and molecules?

2. When this equation is solved for a particular atom or molecule two important aspects of the solutions for the are:

i. the \_\_\_\_\_ of the allowed state

ii. and the \_\_\_\_\_ which is related to the \_\_\_\_\_ of finding the electron at various positions in space

iii. The solutions of the Schrödinger equation for the allowed states of the electron in the hydrogen atom are:

1. characterized by three integer quantum numbers \_\_\_\_\_ and \_\_\_\_\_

Chemistry 1B-AL Fall 2016, Study Guide and Worksheet II

2. the values that these integers can take are:

i.  $n =$  \_\_\_\_\_

ii. for a given  $n$ ,  $l =$  \_\_\_\_\_

iii. for a given  $l$ ,  $m_l =$  \_\_\_\_\_

iv. the "names" for different values of  $l$  are  $l=0$ ,  $l=1$ ,  $l=2$ ,  $l=3$  \_\_\_\_\_

v. thus for  $n=3$  there would be \_\_\_\_\_ different orbitals.

IV. The properties of the allowed states are:

1. In the hydrogen atom, all states with the same \_\_\_\_\_ have the same energy. States with differing quantum numbers, but which have the same energy, are called \_\_\_\_\_ states.

2. Properties of an electron in orbital  $\psi_{n,l,m_l}$  associated related to each of the three quantum numbers are:

i.  $n$ : \_\_\_\_\_

ii.  $l$ : \_\_\_\_\_

iii.  $m_l$ : \_\_\_\_\_

3. Shapes of the orbitals:

i. Be familiar with the shapes of the radial and angular components of the s, p, and d orbitals pictured in the text and in the handouts and the various ways that orbitals and related electron densities are graphically portrayed.

ii. The + and - values associated with a diagram of an orbital give which (cross out incorrect and circle correct choice)?  
the + or - electronic charge in that region of the orbital?  
or  
the relative phase or sign (±) of the probability wave in that region of the orbital

iii. How do the quantities  $\psi^2$  and  $4\pi r^2 \psi^2$  differ in describing electron density in an orbital?

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## Schrödinger equation (see pp 540 and 549)

### SCHRÖDINGER EQUATION



$$\mathcal{H} \Psi = E \Psi$$

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + V \right] \Psi = E \Psi$$



- **basic equation of quantum mechanics**
- **what does it involve ??**
- **what does it tell you ??**
- **where can you learn ALL about it in upper division chemistry?**

not responsible for pp. (543-549)\*, Table 12.1

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Chemistry 1B Fall 2016  
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*hydrogen's electron waves: the three quantum numbers (pp. 550-551)*

---

$$\mathcal{H} \Psi = E \Psi$$

$$\Psi_{n,\ell,m_\ell}$$

wavefunction or orbital that describes  
allowed states of electron

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*hydrogen's electron waves: the three quantum numbers (pp. 550-551)*

---

$$\Psi_{n,\ell,m_\ell} \overbrace{(r, \theta, \phi)}^{\text{point in space}}$$

$n$  the principal quantum number

$\ell$  the angular momentum quantum number

$m_\ell$  the magnetic quantum number

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*rules for allowed quantum numbers*

---

principal quantum number

$n$

$$n = 1, 2, 3, \dots, \infty$$

*positive, non-zero, integers*

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*rules for allowed quantum numbers*

---

angular momentum quantum number

$l$

for given value of  $n$

$$l = 0, 1, 2, \dots (n-1)$$

*zero and positive integers  $< n$*

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Chemistry 1B Fall 2016  
Sessions 3-4

*rules for allowed quantum numbers*

---

angular momentum quantum number  
 $l$

designations of orbitals with various values of  $l$

$l$		<i>'from spectroscopy'</i>
0	→ s orbital	<b>s</b> harp
1	→ p orbital	<b>p</b> rincipal
2	→ d orbital	<b>d</b> iffuse
3	→ f orbital	<b>f</b> undamental
·	·	
·	·	

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The screenshot shows a video player window titled "Windows Media Player" with the video file "Video2\_HydrogenQNos". The slide content includes:

- Text: "for example  $n=3$ "
- Question box: "What values of  $l$  are allowed for orbitals with principal quantum number  $n=3$ ?"
- Handwritten notes in red:
  - $n=3$
  - $l < n$
  - $l = 0, 1, 2$
  - Below these, vertical lines connect  $0$  to  $s$ ,  $1$  to  $p$ , and  $2$  to  $d$ .
  - Below that, the orbitals are listed as  $3s, 3p, 3d$ .
- Two cartoon characters on the right side of the slide, one labeled "HW#1 10, 11, 12" and another labeled "HW#14, 15, 16".
- A small number "9" in the bottom right corner of the slide.

The video player controls at the bottom show a timestamp of 06:57 and various playback buttons.

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Chemistry 1B Fall 2016  
Sessions 3-4

rules for allowed quantum numbers

magnetic quantum number

$$m_l$$

for given value of  $l$

allowed  $m_l$  are positive and negative integers  
from  $-l$  to  $+l$  including 0

$$m_l = -l, -l+1, \dots, -1, 0, +1, +2 \dots +l$$

$$\text{or } m_l = 0, \pm 1, \pm 2, \dots \pm l$$

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Windows Media Player  
Video2\_HydrogenQNos

for example 2p and 3f orbitals

what are the possible 2p orbitals ?

$n=2, l=1$   $m_l = -1, 0, +1$   
components of 2p

the orbitals associated with a given  $n$  and  $l$  are often called the orbital's components. Thus a 2p orbital has "three  $m_l$  components."

does a 3f orbital exist ??

$n=3$   
 $f \Rightarrow l=3$   $l < n$  ~~NO 3f!~~

HW#1 10, 11, 12  
HW#2 14, 15, 16

11

09:59

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# Chemistry 1B Fall 2016 Sessions 3-4

for example how many 3p orbitals ??

---

how many 3p orbitals ?

$$3p$$


$$|$$

$$n=3$$

$$\ell=1$$

$$m_\ell = -1, 0, 1$$

3 different 3p components




HW#1 10, 11, 12

---

how many orbitals with n=3 ?

study guide & learning objectives II

v. thus for n=3 there would be \_\_\_\_\_ different orbitals.



HW#1 14, 15, 16

12

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## Zumdahl Tables 12.2 and 12.3

**TABLE 12.2** The Angular Momentum Quantum Numbers and Corresponding Letter Symbols

Value	Letter Used
0	s
1	p
2	d
3	f
4	g

**TABLE 12.3** Quantum Numbers for the First Four Levels of Orbitals in the Hydrogen Atom

$n$	$\ell$	Orbital Designation	$m_\ell$	Number of Orbitals
1	0	1s	0	1
2	0	2s	0	1
3	1	2p	-1, 0, +1	3
	0	3s	0	1
	1	3p	-1, 0, 1	3
4	2	3d	-2, -1, 0, 1, 2	5
	0	4s	0	1
	1	4p	-1, 0, 1	3
	2	4d	-2, -1, 0, 1, 2	5
	3	4f	-3, -2, -1, 0, 1, 2, 3	7

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# Chemistry 1B Fall 2016 Sessions 3-4

## learning objectives II (and clickey-click)

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III. The solutions of the Schrödinger equation for the allowed states of the electron in the hydrogen atom are:

1. characterized by three integer quantum numbers \_\_\_\_\_, \_\_\_\_\_, and \_\_\_\_\_



Chemistry 1B-AL Fall 2016, Study Guide and Worksheet II

2. the values that these integers can take are:

i.  $n =$  \_\_\_\_\_

ii. for a given  $n$   $\ell =$  \_\_\_\_\_

iii. for a given  $\ell$   $m_\ell =$  \_\_\_\_\_

iv. the "names" for different values of  $\ell$  are  $\ell=0$  \_\_\_\_\_,  $\ell=1$  \_\_\_\_\_,  $\ell=2$  \_\_\_\_\_,  $\ell=3$  \_\_\_\_\_

v. thus for  $n=3$  there would be \_\_\_\_\_ different orbitals.



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## quantum mechanics of the hydrogen atom (the electron waves in H atom and their physical meaning)

---

- quantum numbers of "allowed" orbitals  
[table 12.2 and 12.3](#) →
- energies and 'sizes' of orbitals
- orbitals and the electron density diagram
  - orbital (wavefunction,  $\Psi$ ) [ $\Psi$  can have relative sign,  $\pm$  values]
  - electron density (probability,  $\Psi^2$ ) [ $\Psi^2 \geq 0$ ]
  - radial probability distribution ( $4\pi r^2 \Psi^2$ )  
→  
[Fig 12-16 & 12-17](#) [handout figures](#)

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**CHEM 1B-AL video 2**  
**is**  
**Finis**

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Wednesday, 4 October !!!



iClicker-Check-Up exercise 2  
Study Guide 2 I-III



How's your  
CHEM1B-AL  
health?

Chemistry 1B Fall 2016  
Sessions 3-4

*quantum mechanics of the hydrogen atom  
(the electron waves in H atom and their physical meaning)*

---

- quantum numbers of “allowed” orbitals

[table 12.2 and 12.3](#) →

- orbitals and the electron density diagram

- orbital (wavefunction,  $\Psi$ ) [ $\Psi$  can have relative sign,  $\pm$  values]

- electron density (probability,  $\Psi^2$ ) [ $\Psi^2 \geq 0$ ]

- radial probability distribution ( $4\pi r^2 \Psi^2$ )

[Fig 12-16 & 12-17](#) [handout figures](#)



- orbital identification [team activity](#) Friday, 7 October

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*energies of hydrogen orbitals*

---

- $$E_n = -\frac{me^4}{8\epsilon_0^2 h^2} \frac{Z^2}{n^2} = -\left(\frac{2.178 \times 10^{-18} \text{ J}}{n^2}\right) \frac{Z^2}{n^2}$$

for H atom,  $Z=1$

- in hydrogen atom, energy only depends on n quantum number

[Fig. 12.23](#) →

- the ‘size’ of the orbital is approximated by

$$r_{\text{avg}} \equiv \bar{r} \approx a_0 \frac{n^2}{Z} = (5.29 \times 10^{-11} \text{ m}) \frac{n^2}{Z}$$

(where  $a_0$  is a constant, the Bohr radius)

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Sessions 3-4

*segue/review*

---

1.  $\Psi_{n,\ell,m_\ell}$  possible allowed states  $\leftrightarrow$  waves for an electron in H atom
2. Allowed values of  $n$ ,  $\ell$ ,  $m_\ell$
3.  $E_n = -\left(2.178 \times 10^{-18} \text{ J}\right) \frac{Z^2}{n^2}$   $Z=1$  for H atom  
states of given  $n$  but various  $\ell$ ,  $m_\ell$  have same energy (are degenerate)
4. Shapes of orbitals,  $\Psi$ ,  $\Psi^2$ ,  $4\pi r^2 \Psi^2$   
 $n - \ell - 1$  radial (spherical) nodes  $\ell$  angular (planar) nodes
5. use  $r_{\text{BOHR}} \approx r_{\text{avg}} \equiv \bar{r} \approx \frac{n^2}{Z} a_0 = (5.29 \times 10^{-11} \text{ m}) \frac{n^2}{Z}$

$$r_{\text{most probable}} = a_0$$

$$[\text{actually: } \bar{r} = \frac{n^2}{Z} a_0 \left\{ 1 + \frac{1}{2} \left( 1 - \frac{\ell(\ell+1)}{n^2} \right) \right\}]$$

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*shapes of orbitals nodal surfaces (identifying orbitals)*

---

**radial and angular “nodes” of atomic orbitals**

**radial node:** a spherical shell (of radius  $r$ ) where  $\Psi=0$  (and  $\Psi^2=0$ );  
 $\Psi$  has different sign on opposite sides of radial node

**angular node:** a surface (plane) where  $\Psi=0$  (and  $\Psi^2=0$ );  
 $\Psi$  has different sign on opposite sides of angular node

**d' rules !!**

an orbital with quantum numbers  $n$ ,  $\ell$ ,  $m_\ell$  **will have**

**$n - \ell - 1$**  radial nodes

**$\ell$**  angular nodes

**$n - 1$**  total nodes

and  **$2\ell + 1$**  components in different orientations

(from the different possible  $m_\ell$  values)

“hold your horses”



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Sessions 3-4

*shapes of orbitals*

---

- radial and angular “nodes”
- s-orbitals [Fig. 12.18](#) →
- p-orbitals [Fig. 12.19 & 12.20](#) →
- d-orbitals [Fig. 12.21](#) →
- orbital pics in [handouts](#) →

[WWW orbital viewers](#) →

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*properties associated with  $n$ ,  $\ell$ ,  $m_\ell$  (HW#2 Prob x)*

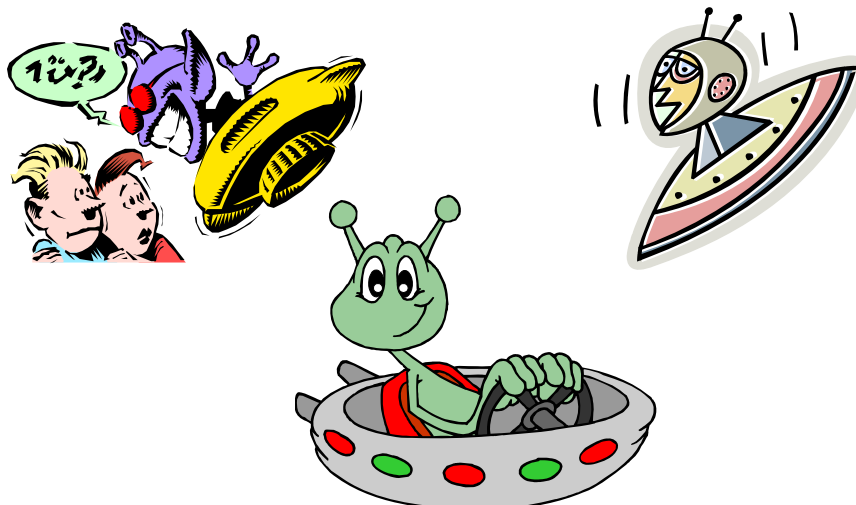
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- **$n$** 
  - energy
  - radial and total nodes
  - average distance from the nucleus
- **$\ell$** 
  - angular velocity (angular momentum)
  - shape (angular nodal planes )
- **$m_\ell$** 
  - orientation of orbital

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Sessions 3-4

*a sighting !!!!!*



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*no not aliens !!! just d-orbital electrons*

**news and views**

## Electrons seen in orbit

Colin J. Humphreys

The classic textbook shape of electron orbitals has now been directly observed. As well as confirming the established theory, this work may be a first step to understanding high-temperature superconductivity.

The world-famous bongo drums player, Richard Feynman, who also won the Nobel Prize for Physics, once asked the following question: if you had only one sentence in which to pass on to the next generation the most important scientific knowledge we possess, what would that sentence be? Feynman's own answer was "everything is made of atoms". "But what is their size and shape," the next generation might reply, "and how do they stick together?"

orange. But in reality, many atoms are not spherical and the shape of atoms critically affects how they bond together."

On page 49 of this issue, Zuo *et al.*<sup>3</sup> use a combination of electron and X-ray diffraction to study the shape and bonding of oranges — in this case, copper atoms in copper oxide. For the first time the striking shape of some of the electron orbitals is revealed experimentally. These methods could be used to determine bonding in high-tempera-

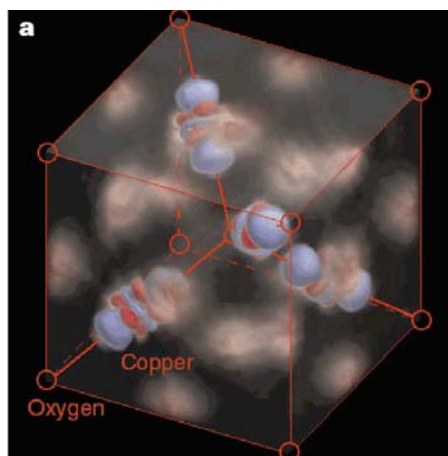
single electron at a distance  $r$  from the nucleus is attracted to the nuclear charge  $e^+$  by a potential  $V = -e^2/r$ . Solving the quantum-mechanical Schrödinger equation for this potential tells us which electron states are allowed. Because  $V$  has spherical symmetry about the nucleus, the simplest solutions also have spherical symmetry. The lowest energy state, or ground state, is called the  $1s$  orbital. So, the hydrogen atom in its ground state may be visualized as being a spherical charge dis-

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Zuo, Kim, O'Keeffe and Spence, *Nature*, 1999.

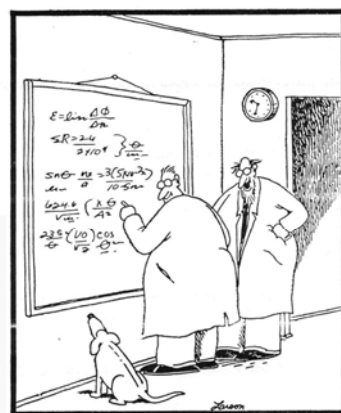
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Larsen

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DECEMBER  
**12**  
TUESDAY

"Ohhhhhh ... Look at that, Schuster  
... Dogs are so cute when  
they try to comprehend quantum mechanics."

40

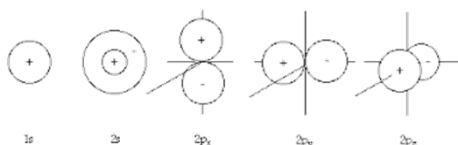
Chemistry 1B Fall 2016  
Sessions 3-4

WHEW !!!

end of lectures 3-4

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*the sign  $\pm$  of  $\Psi$*



[http://www.ch.ic.ac.uk/vchemlib/course/mo\\_theory/](http://www.ch.ic.ac.uk/vchemlib/course/mo_theory/)

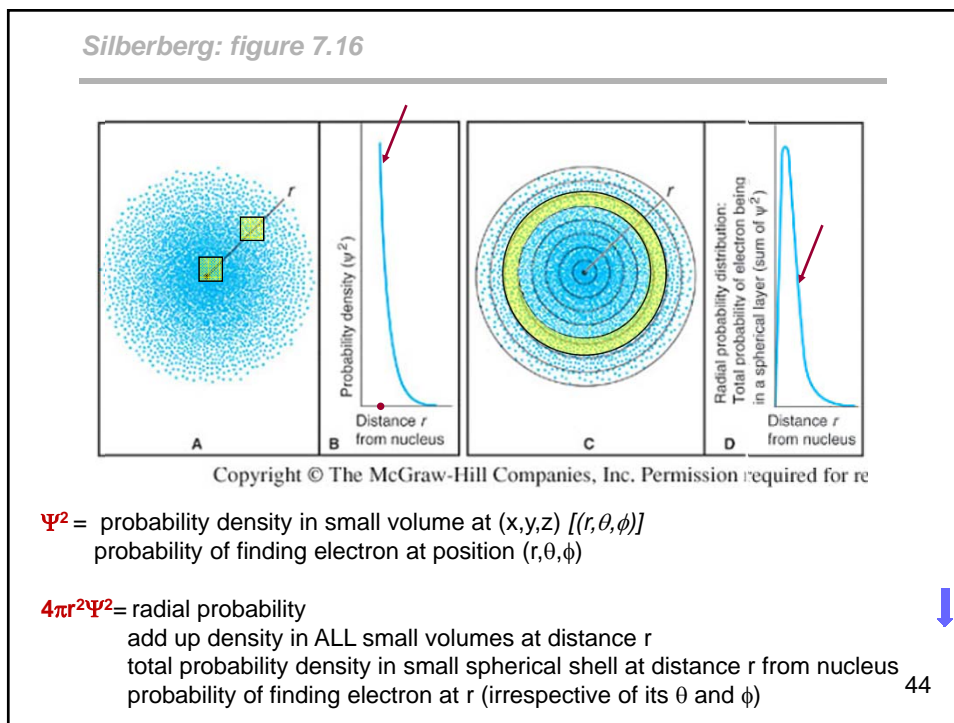
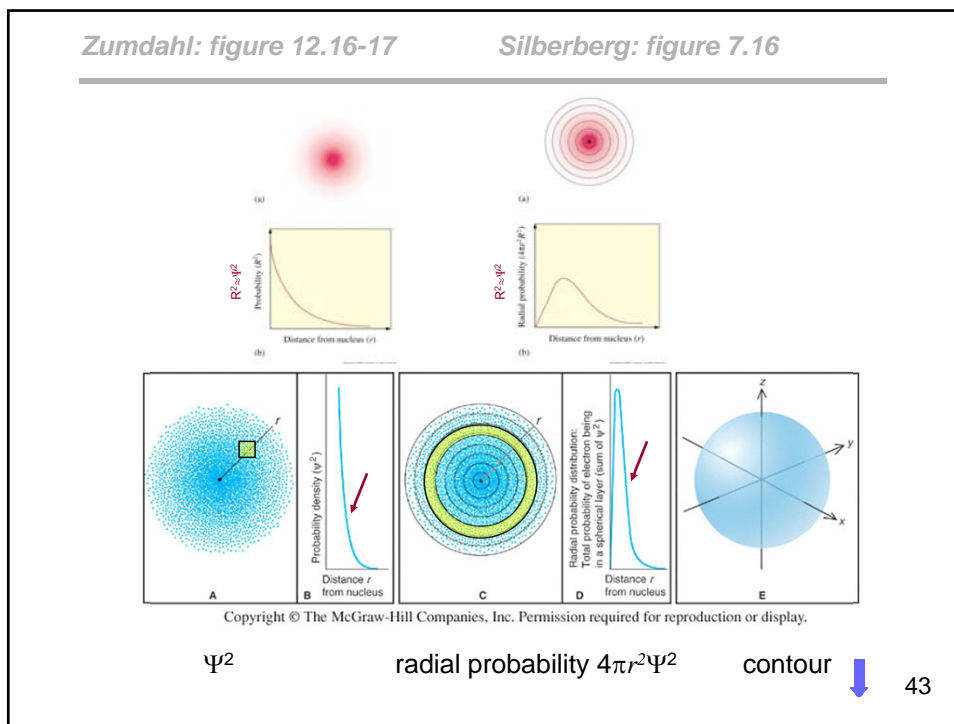
- $\Psi$ , the orbital or wave function, can have differing signs  $\pm$  in differing spatial regions; but  $\Psi^2$ , the probability of finding an electron at a position, is always **positive**
- In going between + and - regions there will be a place where  $\Psi=0$ . This is a **node** of the orbital.
- Does the  $\pm$  of  $\Psi$  indicate regions of + charge and - charge?  
**NO !!! Repeat after me:**

**The + or - regions of  $\Psi$  DO NOT correspond to regions of positive and negative charge, but just to the relative sign of the wavefunction !!**

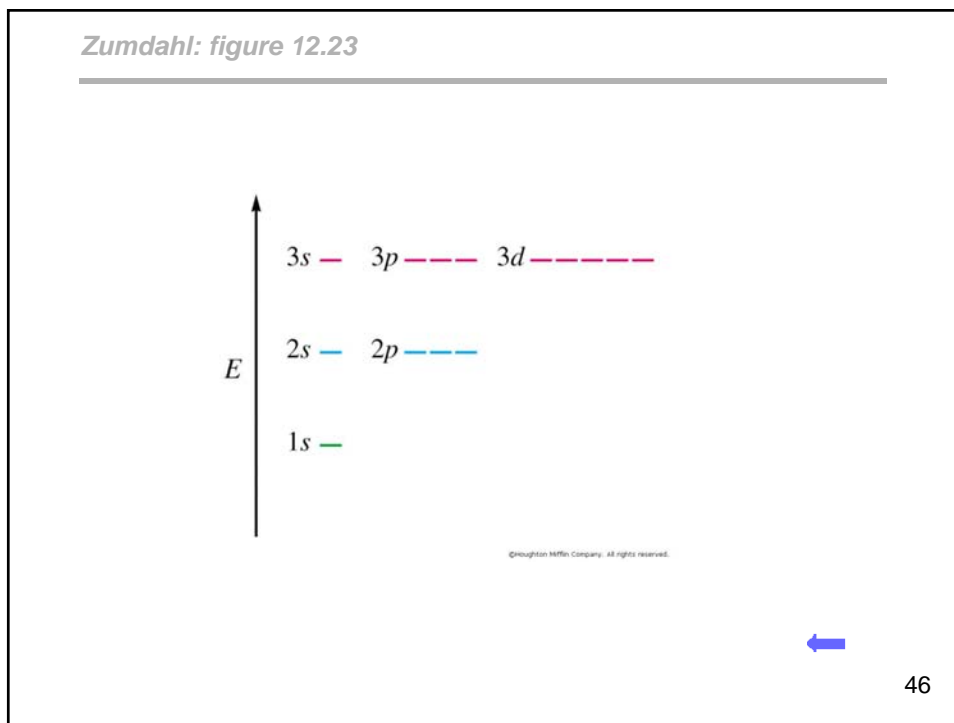
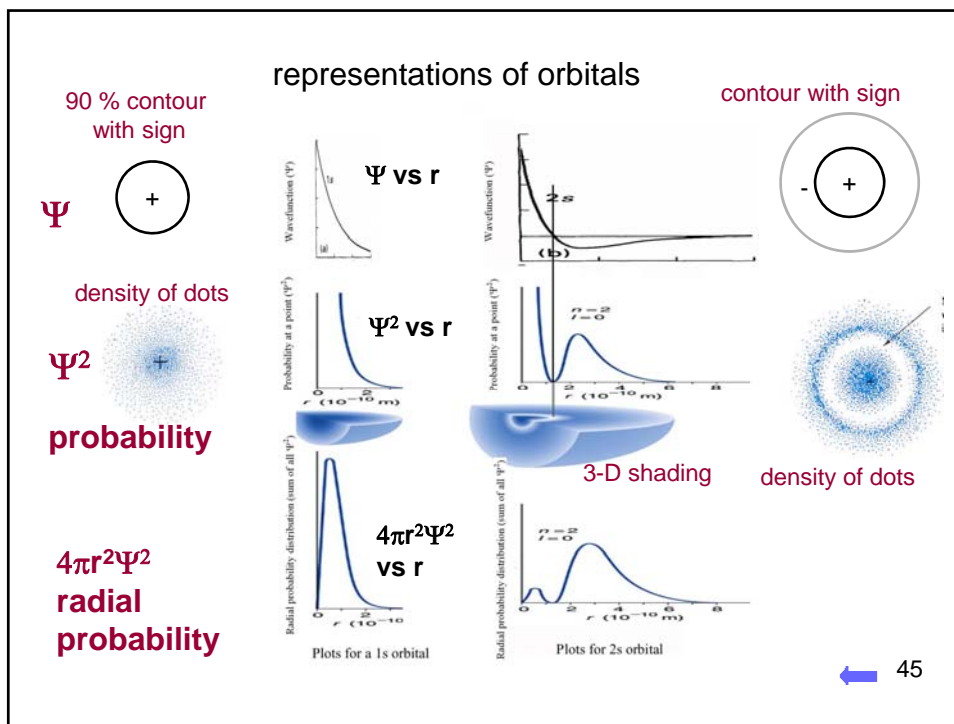


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Sessions 3-4



Chemistry 1B Fall 2016  
Sessions 3-4



# Chemistry 1B Fall 2016 Sessions 3-4

## Zumdahl Tables 12.2 and 12.3

**TABLE 12.2** The Angular Momentum Quantum Numbers and Corresponding Letter Symbols

Value	Letter Used
0	s
1	p
2	d
3	f
4	g

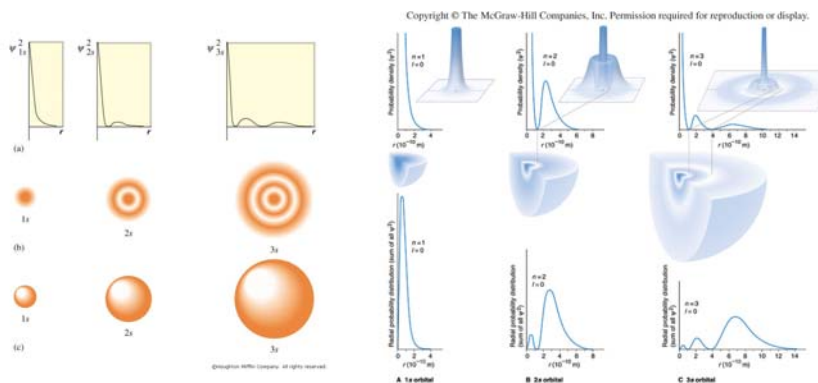
**TABLE 12.3** Quantum Numbers for the First Four Levels of Orbitals in the Hydrogen Atom

$n$	$\ell$	Orbital Designation	$m_\ell$	Number of Orbitals
1	0	1s	0	1
2	0	2s	0	1
3	1	2p	-1, 0, +1	3
	0	3s	0	1
4	1	3p	-1, 0, 1	3
	2	3d	-2, -1, 0, 1, 2	5
4	0	4s	0	1
	1	4p	-1, 0, 1	3
	2	4d	-2, -1, 0, 1, 2	5
	3	4f	-3, -2, -1, 0, 1, 2, 3	7

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← 47

## Zumdahl: figure 12.18 and Silberberg: figure 7.17

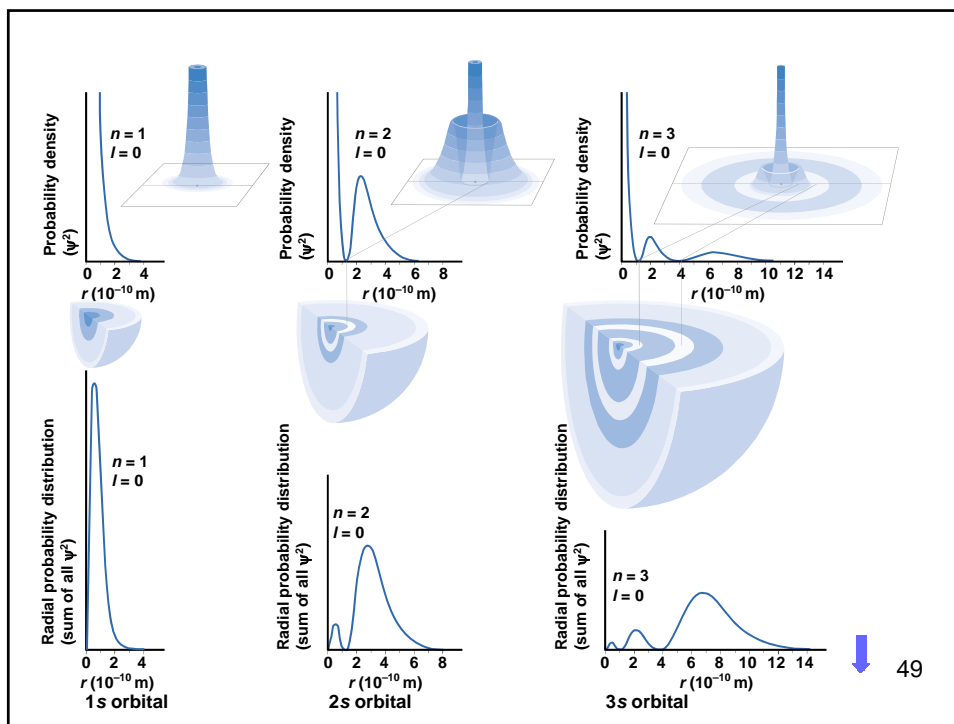


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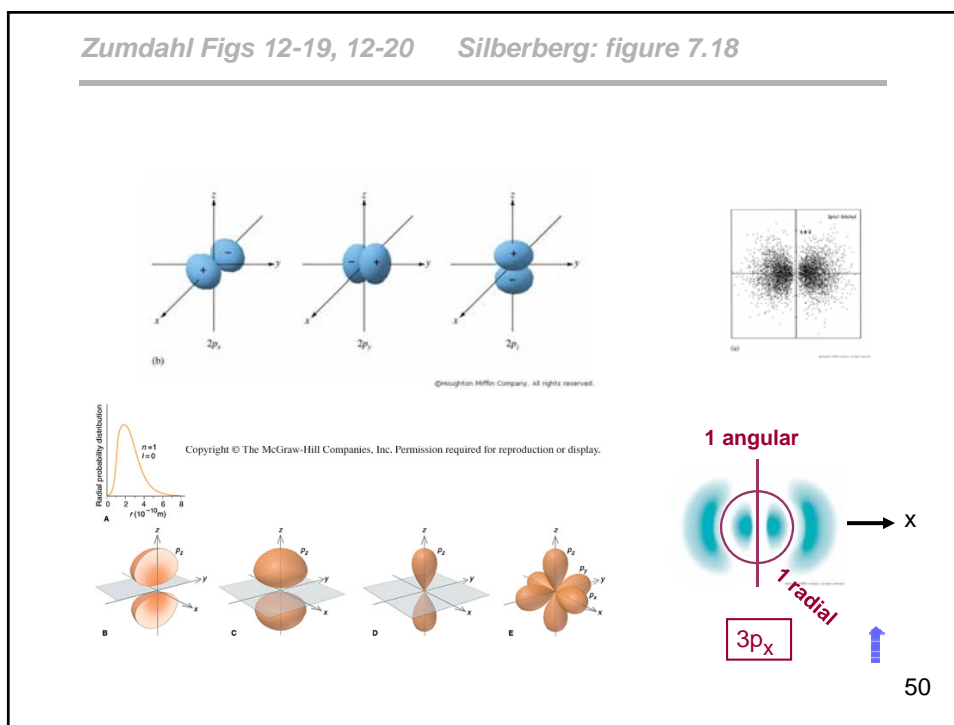
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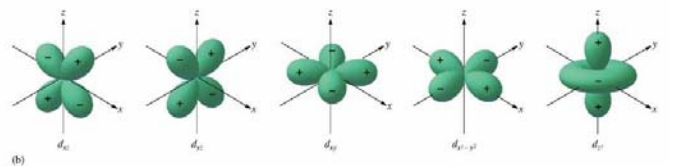


Zumdahl Figs 12-19, 12-20    Silberberg: figure 7.18

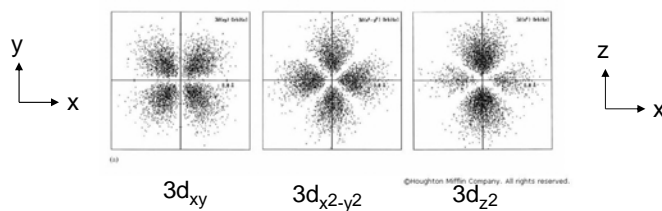


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Zumdahl figure 12.21



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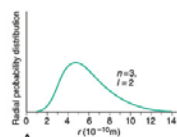
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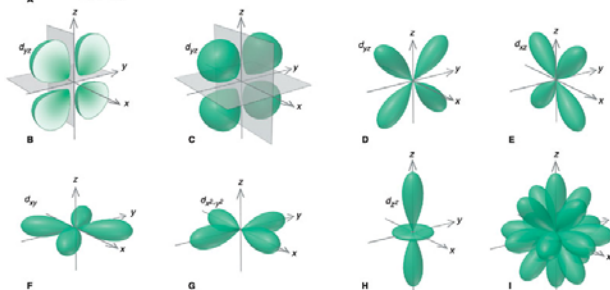
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Silberberg: figure 7.19

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$$n - l - 1 = 3 - 2 - 1 = 0 \text{ radial nodes}$$



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### Silberberg Table 7.1

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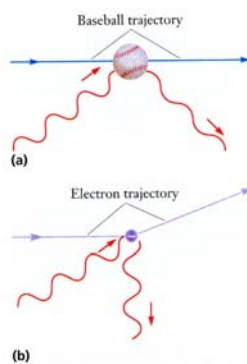
**note mass in g, need to use kg for  $mv\lambda=h$**   
**( $\lambda$  correct in table)**

**Table 7.1** The de Broglie Wavelengths of Several Objects

Substance	Mass (g)	Speed (m/s)	$\lambda$ (m)
Slow electron	$9 \times 10^{-28}$	1.0	$7 \times 10^{-4}$
Fast electron	$9 \times 10^{-28}$	$5.9 \times 10^6$	$1 \times 10^{-10}$
Alpha particle	$6.6 \times 10^{-24}$	$1.5 \times 10^7$	$7 \times 10^{-15}$
One-gram mass	1.0	0.01	$7 \times 10^{-29}$
Baseball	142	25.0	$2 \times 10^{-34}$
Earth	$6.0 \times 10^{27}$	$3.0 \times 10^4$	$4 \times 10^{-63}$

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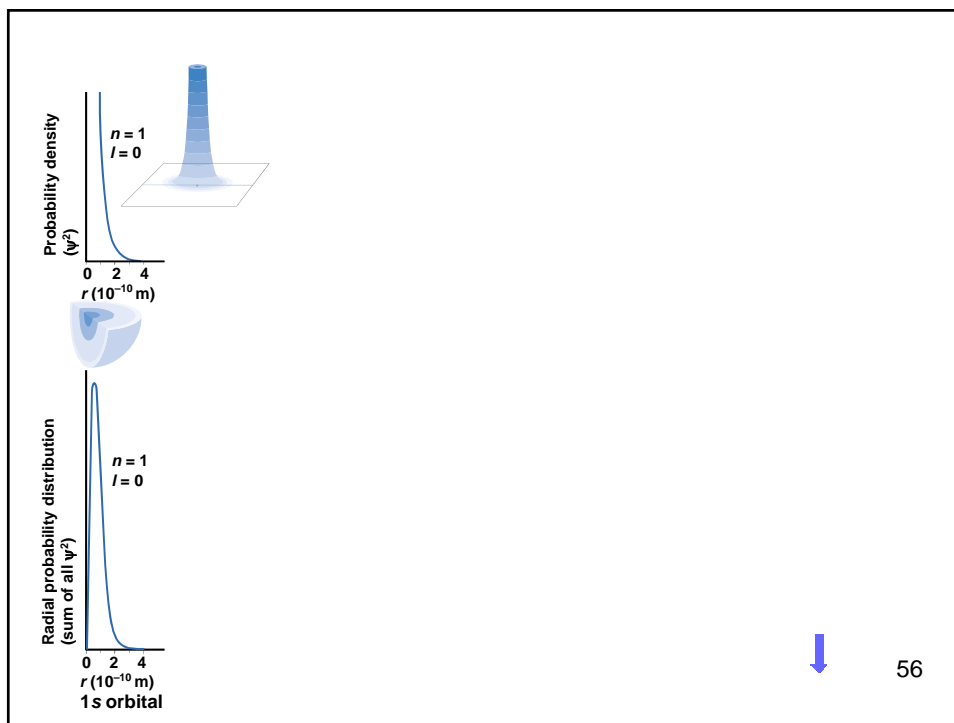
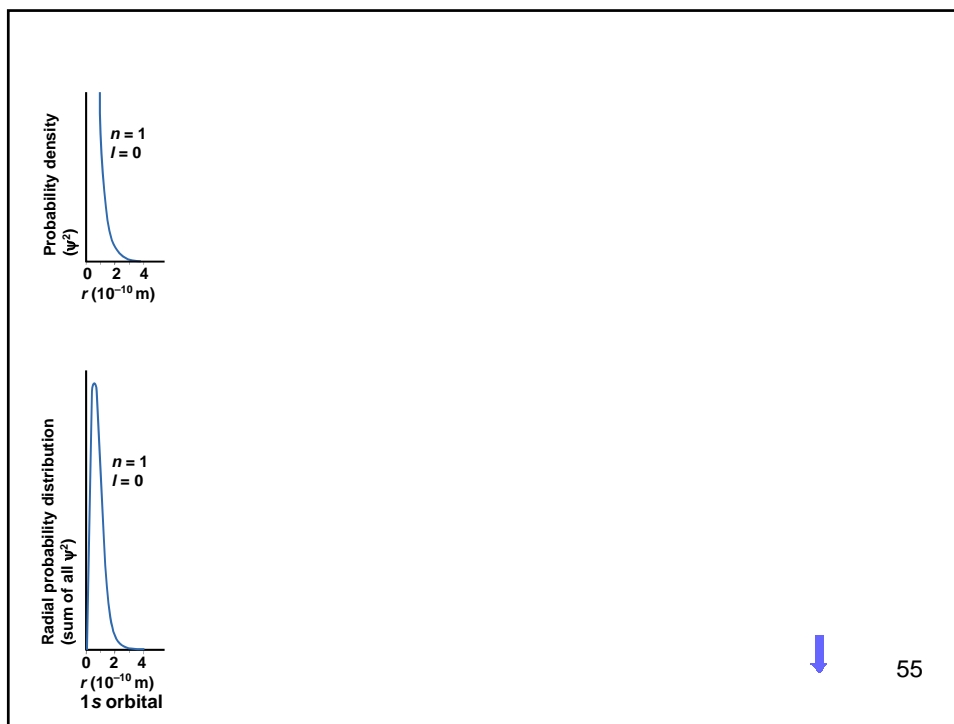
### Uncertainty and measurement



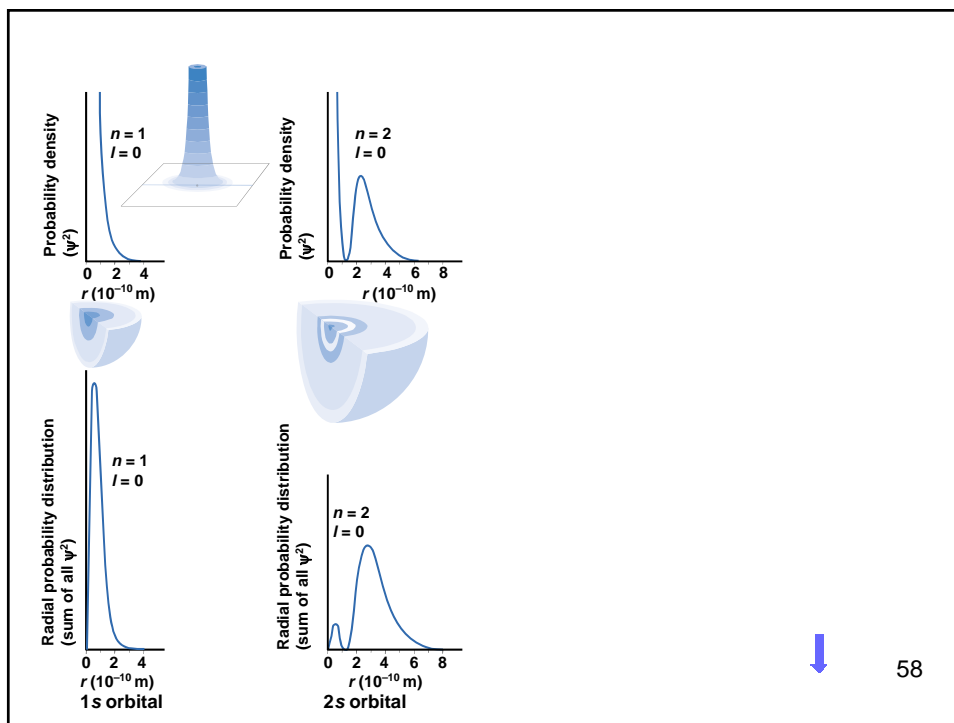
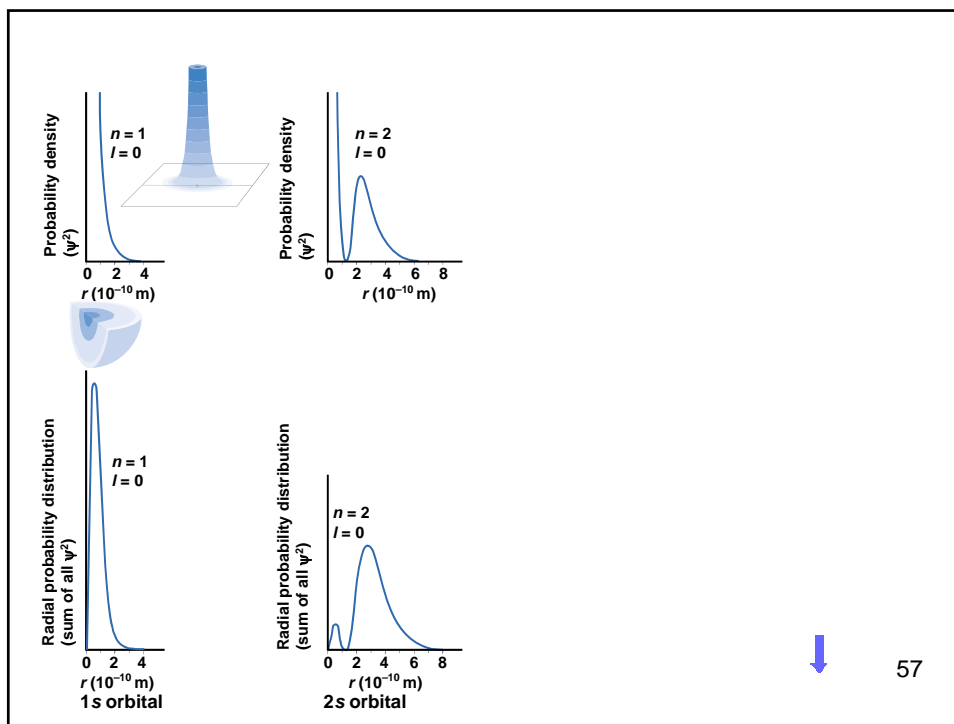
**FIGURE 15.24** A photon, which has a negligible effect on the trajectory of a baseball (a), significantly perturbs the trajectory of the far less massive electron (b).

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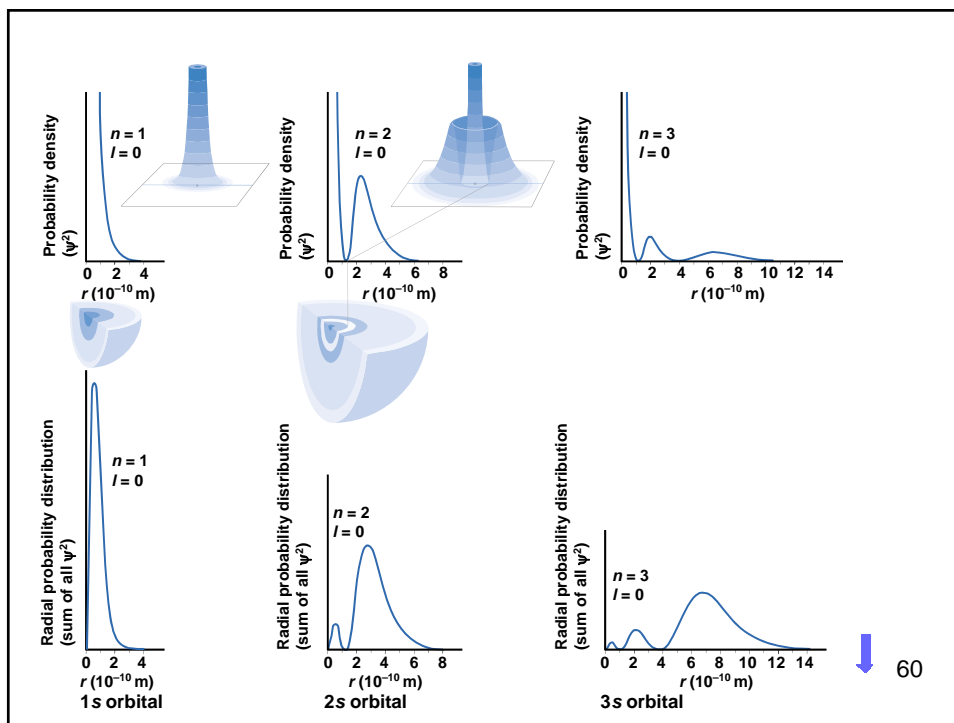
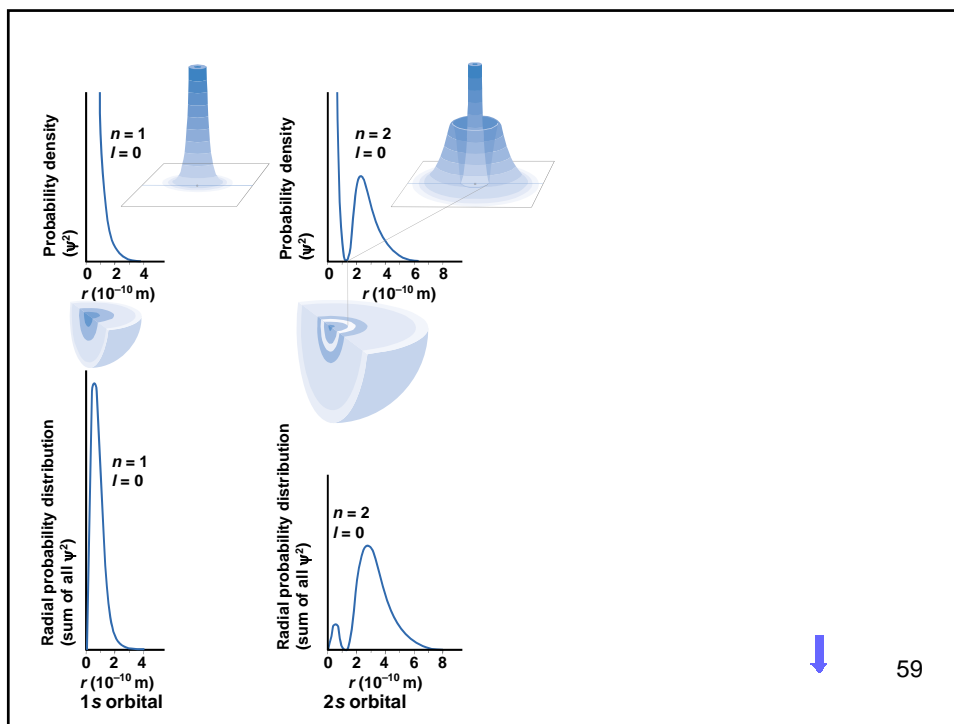
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