Chem C1403 Lecture 10. Monday, October 10, 2005

Some movies describing waves, resonance between waves, the uncertainty principle and the quantum hydrogen atom.

Review of the Bohr atom and some computations

Waves and solutions to the Schroedinger equation

Quantum numbers and orbitals

Exercises involving quantum numbers

"Certain ideas at certain times are in the air: if one man does not enunciate them, another will do so soon afterwards."

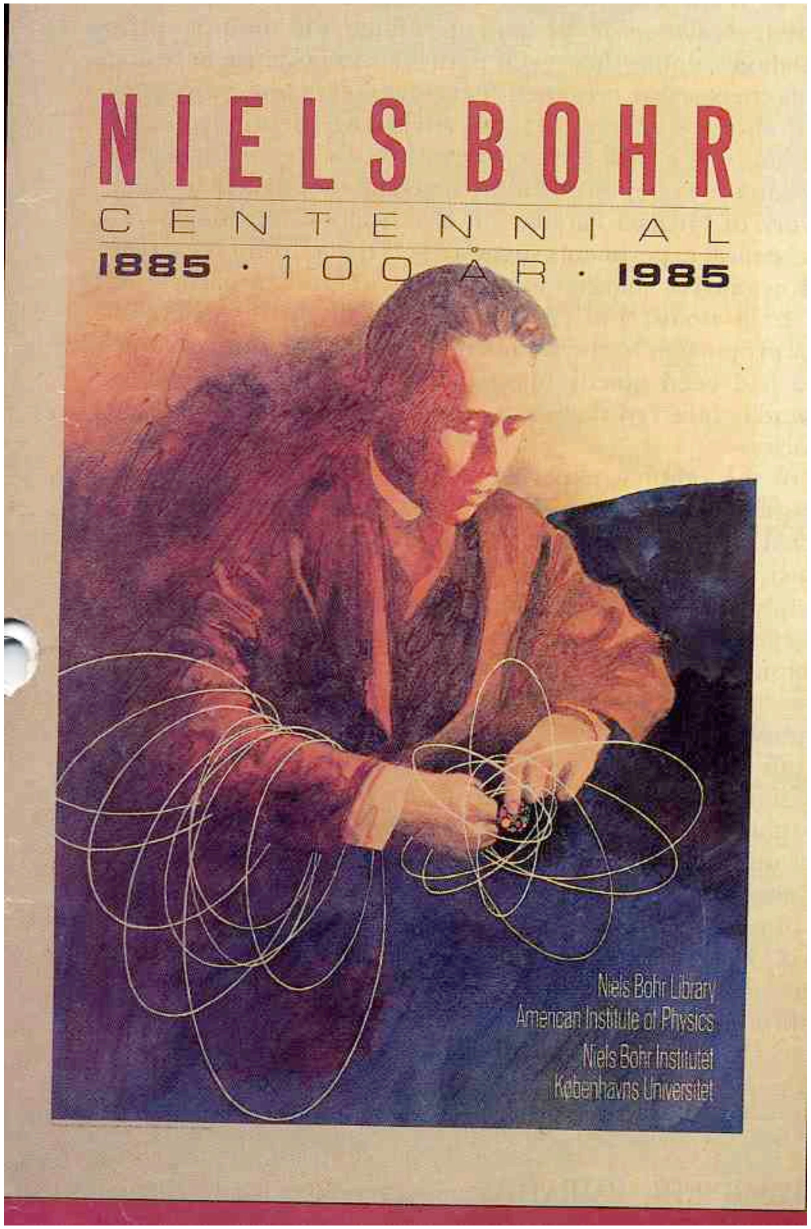
Bohr's new paradigm for the atom:

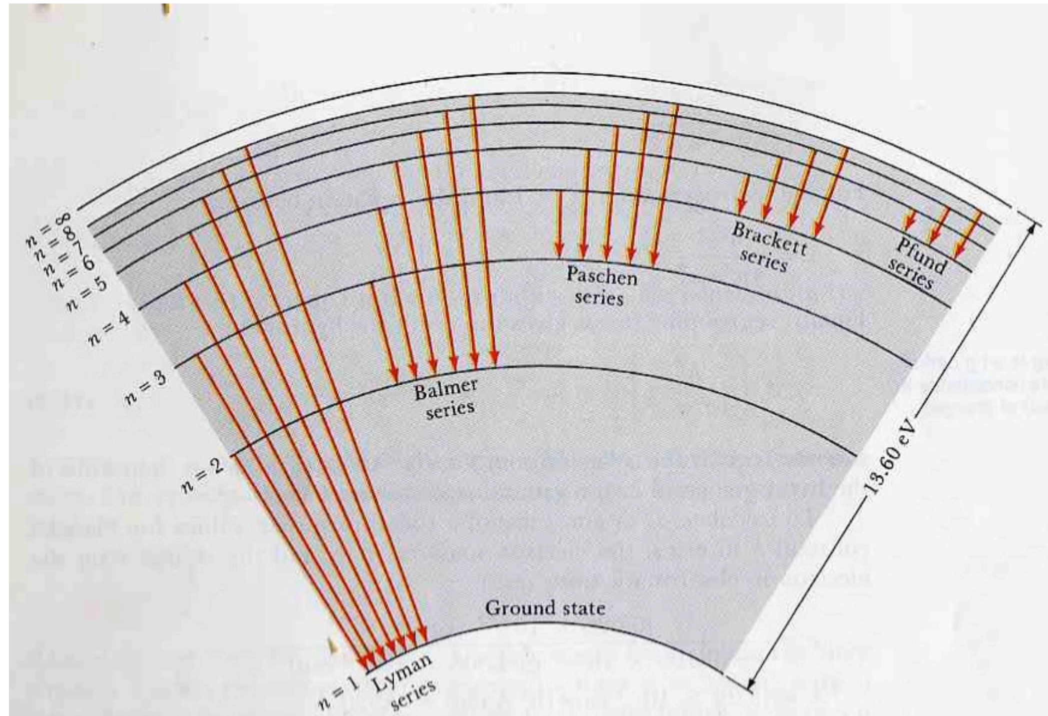
(1) Assumption that only certain allowed orbits, r_n, are allowed for electrons of an atom. These orbits have associated quantum numbers, n, and energies, E_n

(2) Ad hoc postulation of electron stability associated with allowed orbits in violation of classical paradigm

(3) Assumption absorption and emission of light results from transitions between energy levels and $E_i - E_f = \Delta E = h\nu$: resonance!

(4) Assumption that absorption and emission of light is an all or nothing process and occurs suddenly with the absorption or emission of photons.





$$E_n = -Ry(Z^2/n^2)$$

Each photon corresponds to a jump of and electron from an initial orbit of energy E_i to a final orbit of energy E_f.

$$\Delta E = -RyZ^2(1/n_f^2 - 1/n_i^2)$$

Waves and light

$c = \nu\lambda = 3.00 \times 10^{8}$ m-s^{-1} $= 3.00 \times 10^{17}$ nm-s^{-1}

$\nu = c/\lambda, \ \lambda = c/\nu$

c = speed of light
ν = frequency of light
λ = speed of light

What is the frequency of 500 nm light?

Answer: $\nu = c/\lambda$; $\nu = (3.00 \times 10^{17}$ nm-s$^{-1})/500$ nm
$\nu = 6.00 \times 10^{14}\ s^{-1}$

What is the energy (E) of a photon whose wavelength is 500 nm?

$$E = h\nu$$

$$h = 6.63 \times 10^{-34}\ \text{J-s}$$

$$\nu = 6.00 \times 10^{14}\ \text{s}^{-1}\ \text{(from previous answer)}$$

$$E = (6.63 \times 10^{-34}\ \text{J-s})(6.00 \times 10^{14}\ \text{s}^{-1}) = 3.98 \times 10^{-19}\ \text{J}$$

Alternatively: $E = h\nu = hc/\lambda$

$$hc = (6.63 \times 10^{-34}\ \text{J-s})(3.00 \times 10^{17}\ \text{nm-s}^{-1})$$

$$hc = 1.99 \times 10^{-16}\ \text{J-nm}$$

$$E = hc/\lambda = (1.99 \times 10^{-16}\ \text{J-nm})/500\ \text{nm} = 3.98 \times 10^{-19}\ \text{J}$$

What is the energy of a mole of photons whose energy is 500 nm?

$$E(\text{mole}) = N_0 h\nu = (3.98 \times 10^{-19}\ J)N_0$$

N_0 (Avogadro's number) = 6.02×10^{23}

$$E(500\ \text{nm photon}) = 3.98 \times 10^{-19}\ J$$

$$E(\text{mole}) = N_0 h\nu = (3.98 \times 10^{-19}\ J)(6.02 \times 10^{23})$$
$$= 2.40 \times 10^{5}\ J = 240\ \text{kJ-mol}^{-1}$$

Some computations involving electronic transitions for the Bohr (one electron) atom:

The energy of the lowest energy orbit (n=1) of a Bohr atoms is -2.18×10^{-18} J (one Ry). What is the wavelength and frequency of light corresponding to this energy?

$c = \nu\lambda$; $E = h\nu = hc/\lambda$; $\nu = E/h$; $\lambda = hc/E$

You can use the absolute value of the energy in computing wavelength and frequency (always positive numbers):

$$\nu = E/h = [2.18 \times 10^{-18}\ \text{J}/6.63 \times 10^{-34}\ \text{J-s}] = 3.46 \times 10^{15}\ \text{s}^{-1}$$

$$\lambda = hc/E = 1.99 \times 10^{-16}\ \text{J-nm}/2.18\times10^{-18}\ \text{J} = 91\ \text{nm}$$

Computation of the energies of the orbits of one electron ionized atoms: He^{1+}, Li^{2+}, Be^{3+}

$$E_n = -Ry(Z^2/n^2)$$

What is the energy of the n = 1 orbit of He+ (Z = 2)?

$$E_n = -Ry(Z^2/n^2) = -Ry(2^2/1^2) = -4 \text{ Ry}$$

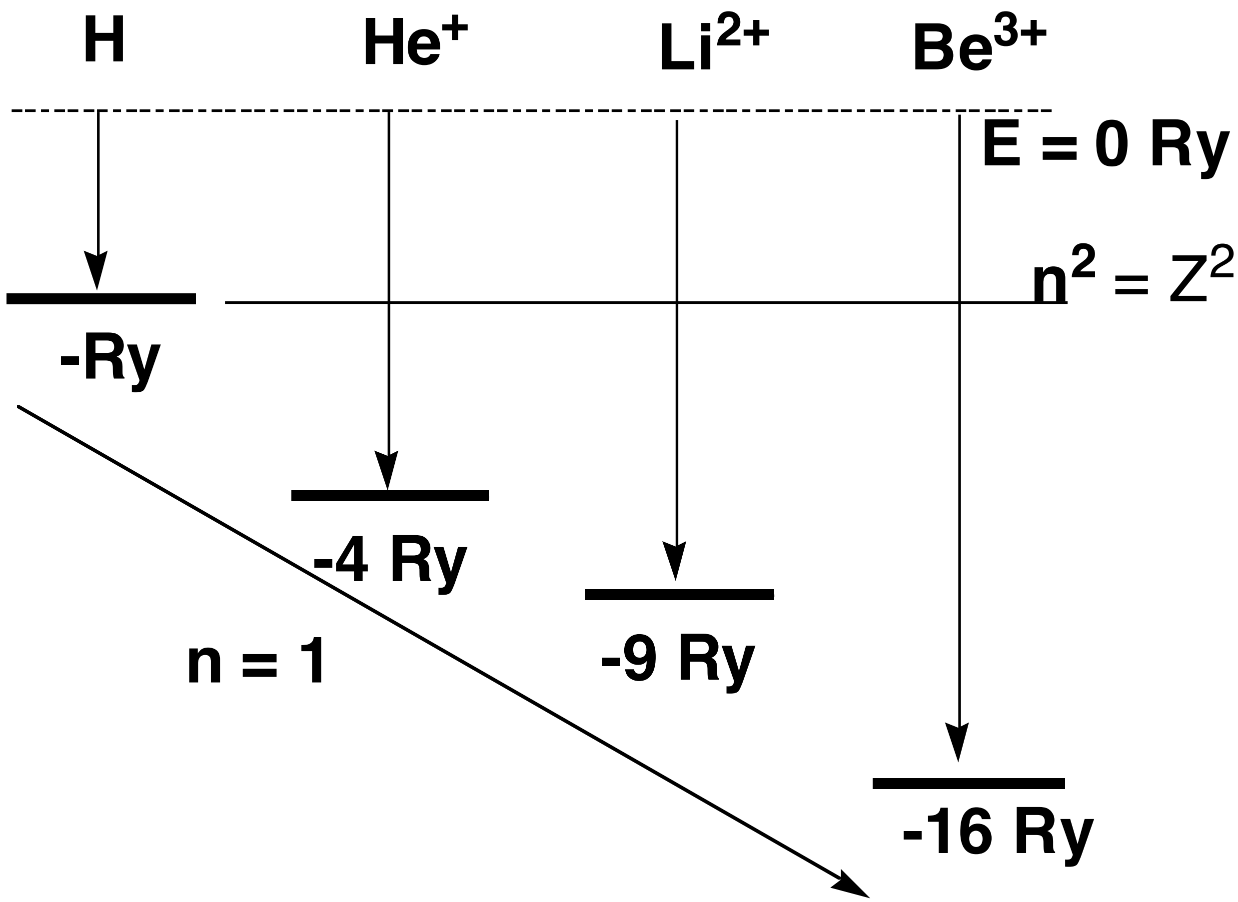
What is the energy of the n = 1 orbit of Li^{2+} (Z = 3)?

$$E_n = -Ry(Z^2/n^2) = -Ry(3^2/1^2) = -9 \text{ Ry}$$

What is the energy of the n = 1 orbit of Be^{3+} (Z = 4)?

$$E_n = -Ry(Z^2/n^2) = -Ry(4^2/1^2) = -16 \text{ Ry}$$

An energy level description of the one electron ions of the first 4 elements:



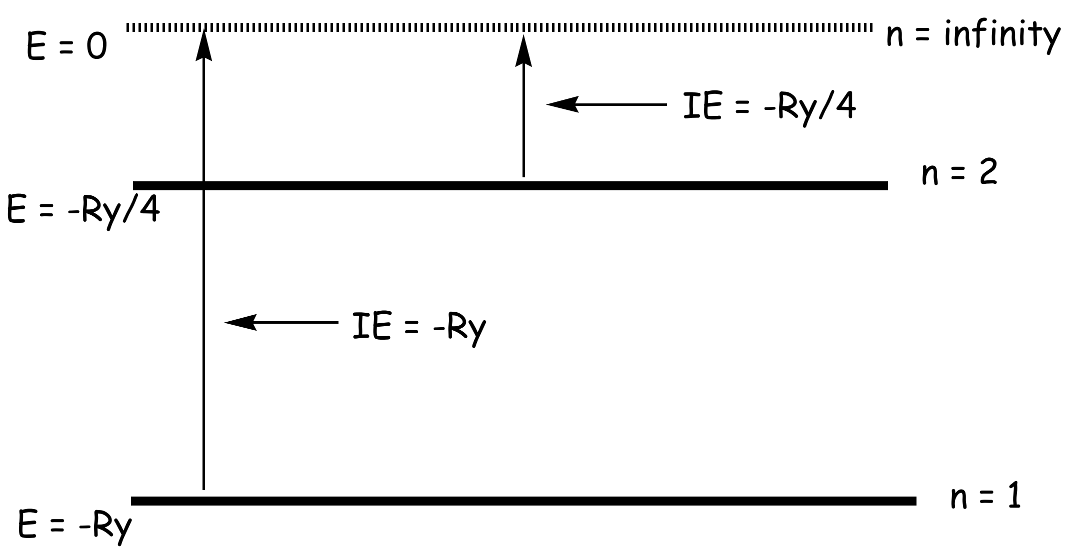
$E_n = -Ry(Z^2/n^2)$

Note: if $n = Z$, $E_n = -Ry$

The ionization energy (IE) of a one electron atom is the energy it takes to remove an electron from an orbit (usually the n = 1 orbit) to infinity. Ionization energies are always positive quantities.

What is the ionization energy in Ry of a hydrogen atom with an electron in the n = 1 orbit? For a hydrogen atom with an electron in the n = 2 orbit?

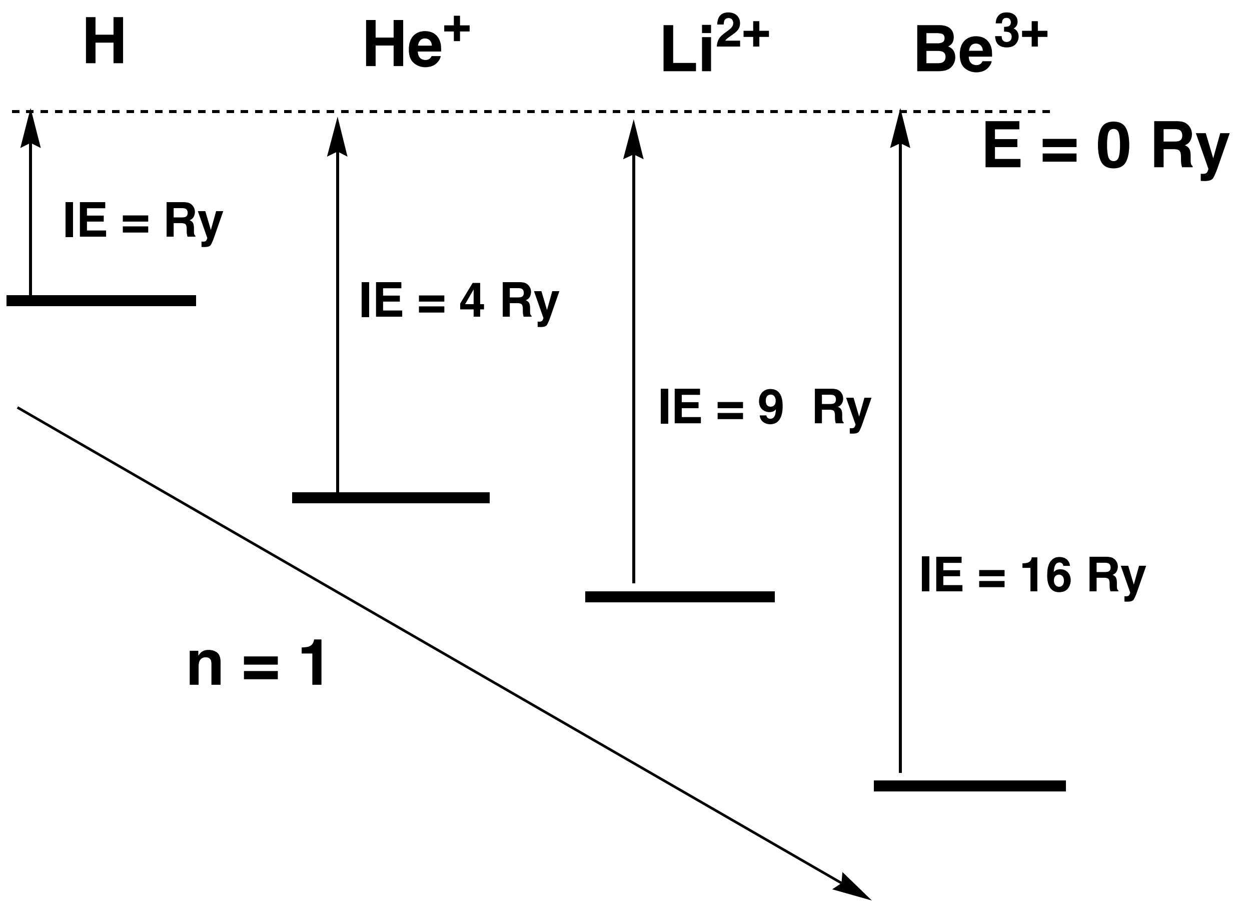
Since the final state has a value of E = 0, the energy required to reach this state is the same as the absolute value of the energy level of the electron.



$$IE = -0Ry - [-Ry/n_i^2]$$

$$IE = Ry/n_i^2 \text{ (positive)}$$

What are the IE values of the one electron atoms of the first 4 elements (H, He^{1+}, Li^{2+}, Be^{3+}?



What is the energy required to ionize one mole of hydrogen atoms (all in their ground state, $n = 1$)?

The energy required to ionize one H atom in $n = 1$ is
$IE(atom) = 2.18 \times 10^{-18}$ J

$$IE(mole) = (2.18 \times 10^{-18}\ J)N_0$$

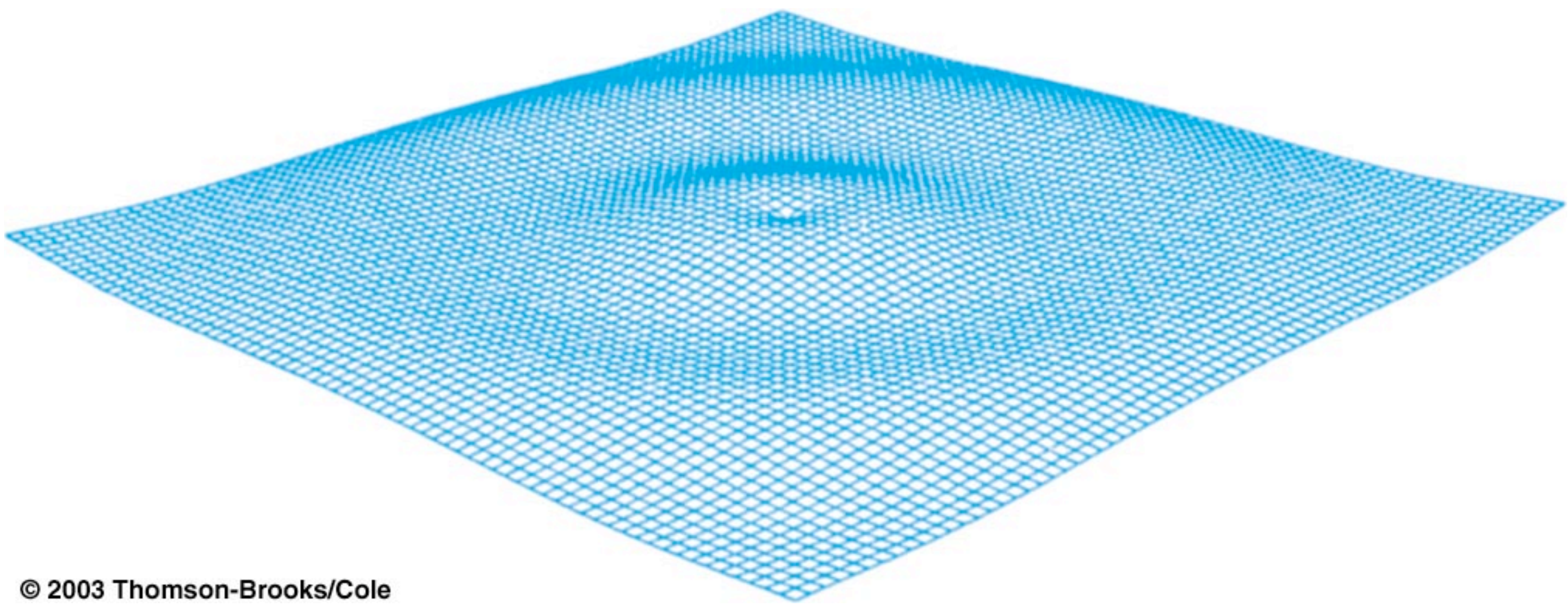
$$IE(mole) = (2.18 \times 10^{-18}\ J)(6.02 \times 10^{23})$$

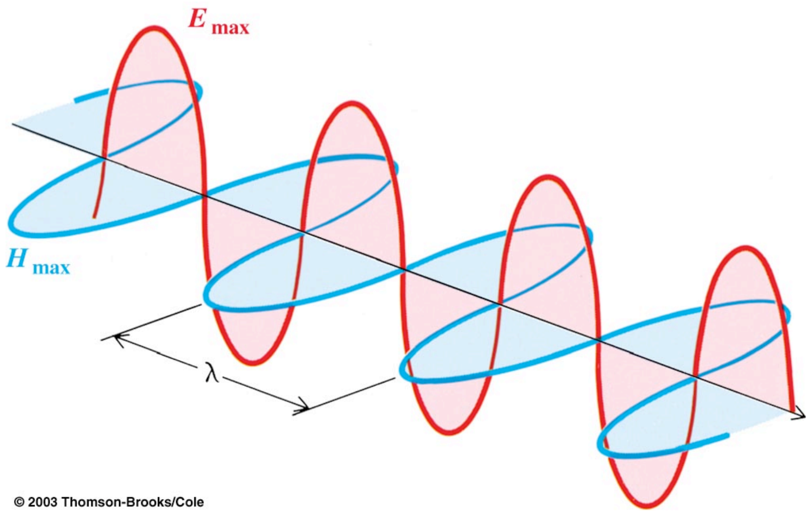
$$IE(mole) = 1.31 \times 10^{6}\ J\text{-}mol^{-1} = 1310\ kJ\text{-}mol^{-1}$$

The energy required to break the H-H bond is about 400 kJ-mol^{-1}

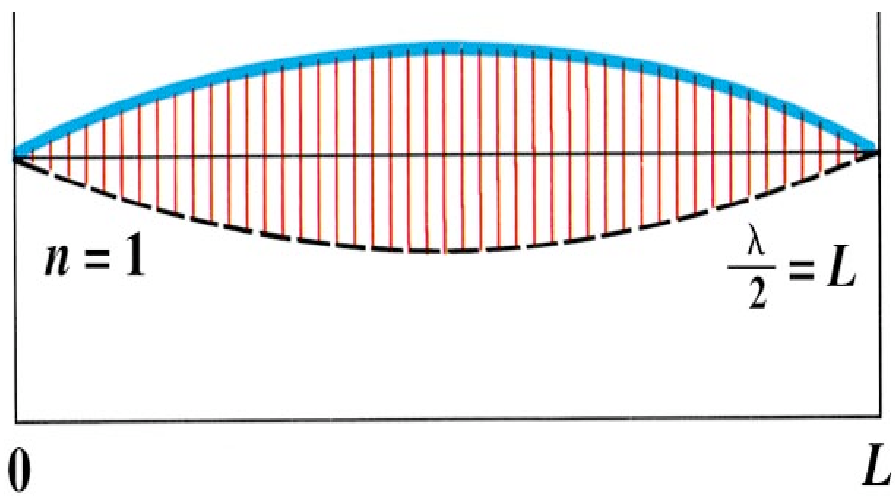
Waves spread and are hard to pin down in space whereas we treat macroscopic particles as having a precise spatial location. Particles of small size (atoms, electrons) are no longer accurately described in terms of "mathematic points" but must be considered as spread out entities in space.

A wave

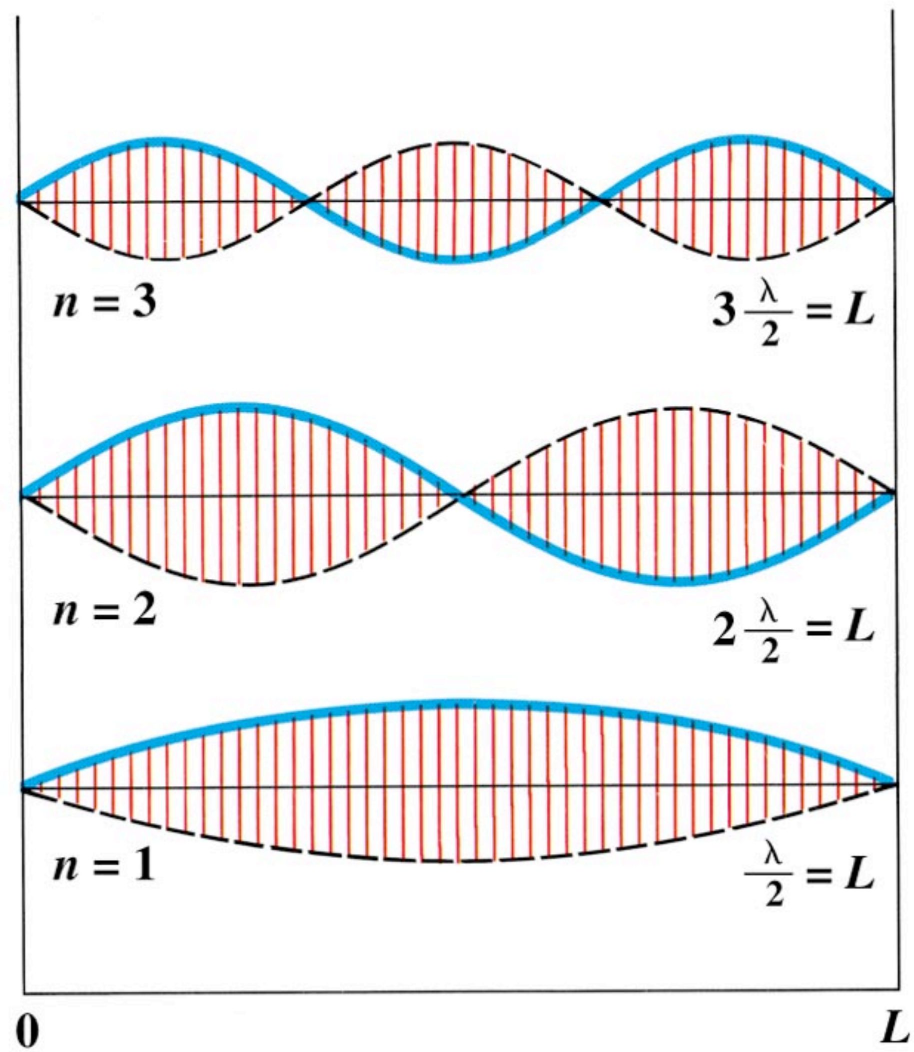




Light: a traveling wave



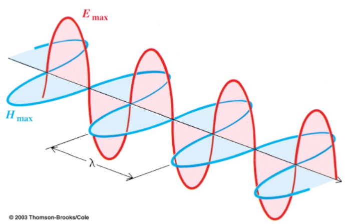
Electron: a standing wave



Excited state: n = 3

For standing waves,the values of the wavelengths (and associated energies) are restricted to discrete values and are said to be "quantized". The values of the possible frequencies are also quantized.

Ground state: n = 1



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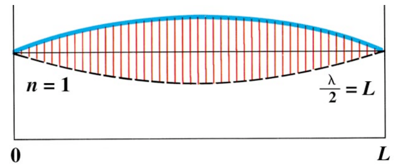
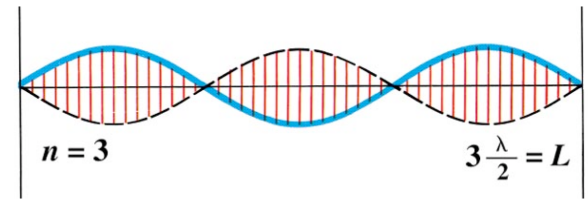


Absorption

Emission



Photon as a traveling wave: Pure energy

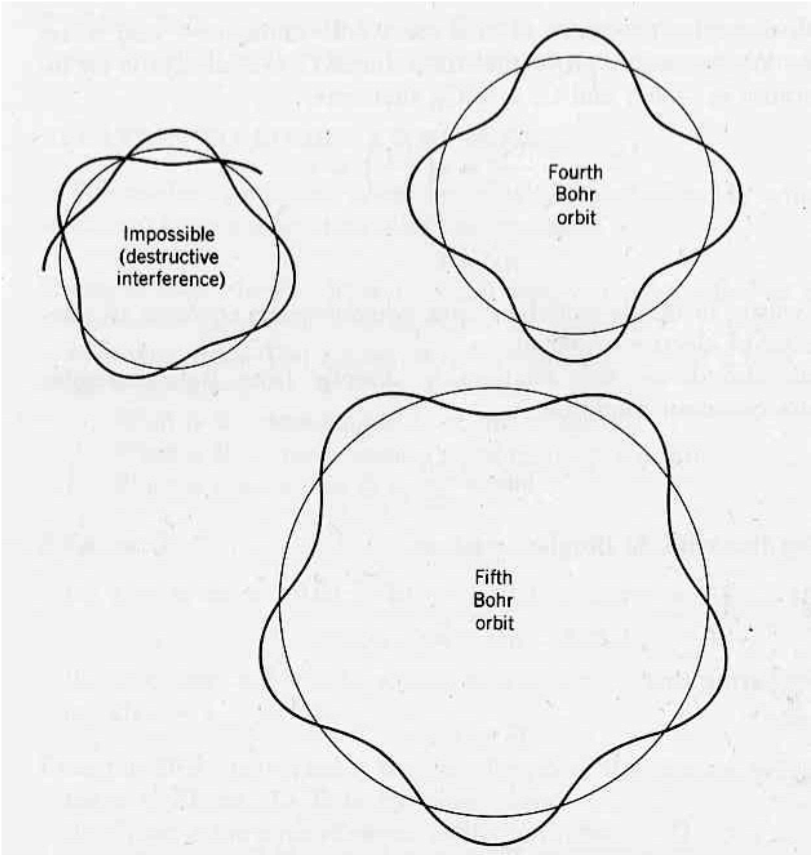
Electron as a standing matter wave

Electron as an excited standing matter wave: photon energy captured

Absorption or emission of a photon requires a “resonance” between a traveling light wave (photon) and a standing wave (electron).

When the resonance condition is met, there is a certain probability that there will be a strong interaction and the photon will be absorbed causing the electron to be excited.

Interference in standing waves explains why only certain wavelengths exist for each orbit of a Bohr atom or for each orbital of a Schroedinger atom:
If fractional wavelengths occur, on successive cycles, they interfere with one another and destroy the wave.



deBroglie: for a circular standing wave to be stable, a whole number of wavelengths must fit into the circumference of the circle $2\pi r$

$$2\pi r = n\lambda$$

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

Schroedinger thinking about his equation.

Schroedinger: If electrons are waves, their postion and motion in space must obey a wave equation.

Solutions of wave equations yield wavefunctions, Ψ, which contain the information required to describe ALL of the properties of the wave.

Provides a picture of the electronic distributions of the electrons about an the nucleus of an atom and about the connected nuclei of a molecule.

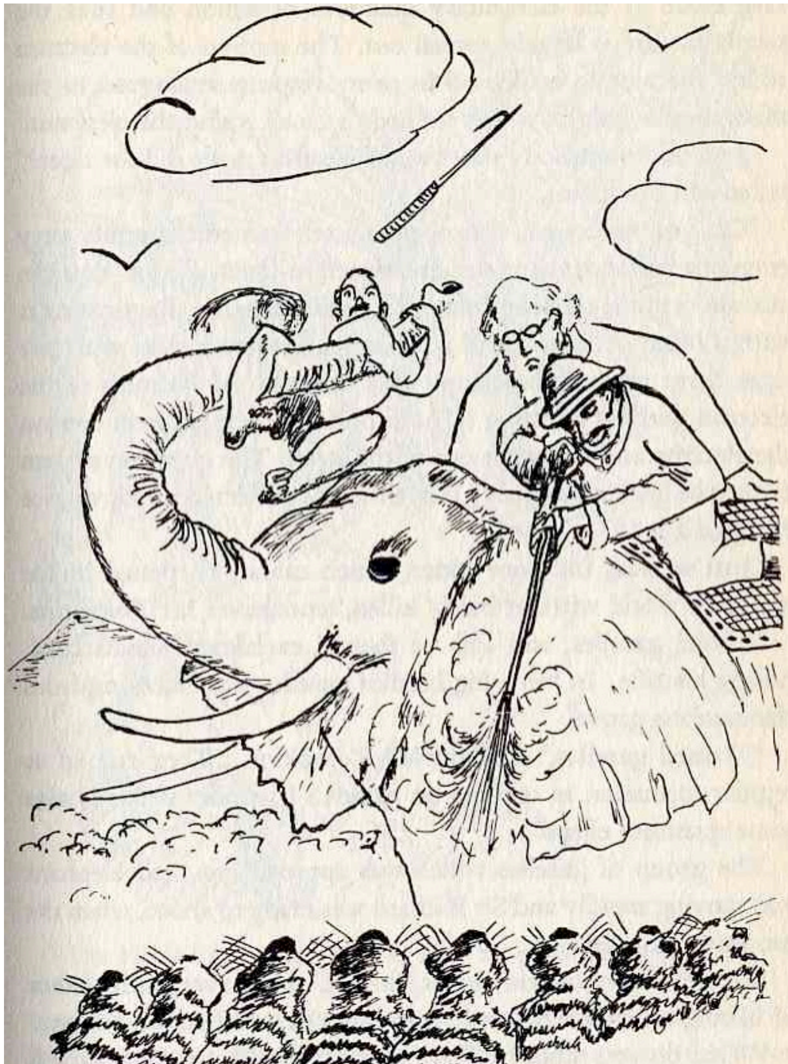
The Schroedinger wave functions, Ψ, for the H atom: set up wave equation and compute solutions, Ψ.

(1) An electron in an atom behaves like a standing wave. Only certain wavefunctions, Ψ, are allowed to describe the electron wave.

(2) Each Ψ is associated with an energy E_n.

(3) Since only certain Ψ are solutions, only certain energies, E, are allowed for the electron as a standing wave. Quantization is an automatic consequence of the wave character of the electron.

The quantum jungle
Wavy tigers are hard to hit!



A large pack of fuzzy-looking tigers was attacking their elephant

is why the quantum laws have not been observed in the ordinary world even for such light bodies as particles of dust, but become quite important for electrons, which are billions of billions of times lighter. Now, in the quantum jungle, the quantum constant is rather large, but still not large enough to produce striking effects in the behaviour of such a heavy animal as an elephant. The uncertainty of the position of a quantum elephant can be noticed only by close inspection of its contours. You may have noticed that the surface of its skin is not quite definite and seems to be slightly fuzzy. In course of time this uncertainty increases very slowly, and I think this is the origin of the native legend that very old elephants from the quantum jungle possess long fur. But I expect that all smaller animals will show very remarkable quantum effects.'

The professor grabbed another rifle and the cannonade of shooting became mixed up with the roar of the quantum tiger. An eternity passed, so it seemed to Mr Tompkins, before all was over. One of the bullets 'hit the spot' and, to his great surprise, the tiger, which became suddenly one, was vigorously hurled away, its dead body describing an arc in the air, and landing somewhere behind the distant palm grove.

Interpretation of the wavefunction Ψ and the square of the wavefunction Ψ^2

Ψ corresponds to the value of the amplitude of the electron-wave at any position in space.

Ψ^2 corresponds to the probability of finding the electron at any point in space.

Solutions to the wave equation for the H atom in 3D:
Yield wavefunctions corresponding to three quantum numbers: n, l and m_l.

Bohr H atom: one quantum number, n

Schroedinger H atom: three quantum numbers, n, l and m_l

Electron shells and magic (quantum) numbers

Quantum Numbers

Principal Quantum Number (n):

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

Angular momentum Quantum Number *(l)*:

$l = 0, 1, 2, 3\ldots.(n-1)$

Rule: $l = (n - 1)$

Magnetic Quantum Number (m_l):

$m_l = \ldots-2, -1, 0, 1, 2, ..$

Rule: $-l\ldots.0\ldots.+l$

A wavefunction (orbital) is completely characterized by the quantum numbers n, l and m_l

Shorthand notation (nicknames) for orbitals:

l = 0, s orbital;

l = 1, p orbital;

l = 2, d orbital;

l = 3, f orbital

Relative energies of the orbitals of a one electron atom:

1s << 2s = 2p < 3s = 3p = 3d, etc.

All orbitals of the same value of n have the same energy.

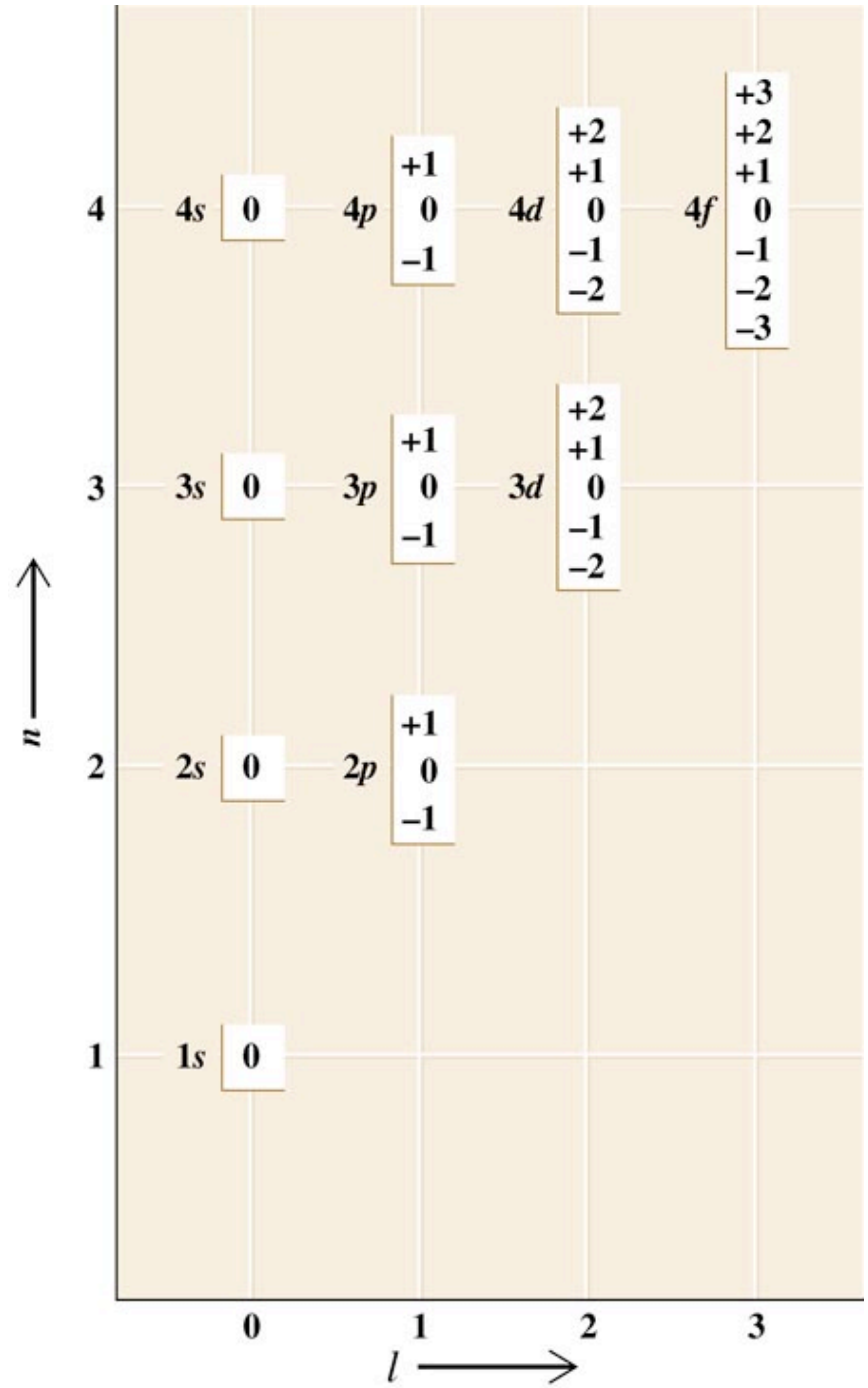
For a one electron atom the energy of an electron in an orbital only depends on n.

Thus,
1s (only orbital)

2s = 2p

3s = 3p = 3d

4s = 4p = 4d = 4f



The relative energies of orbitals of the H atom follow the same pattern as the energies of the orbits of the H atom.

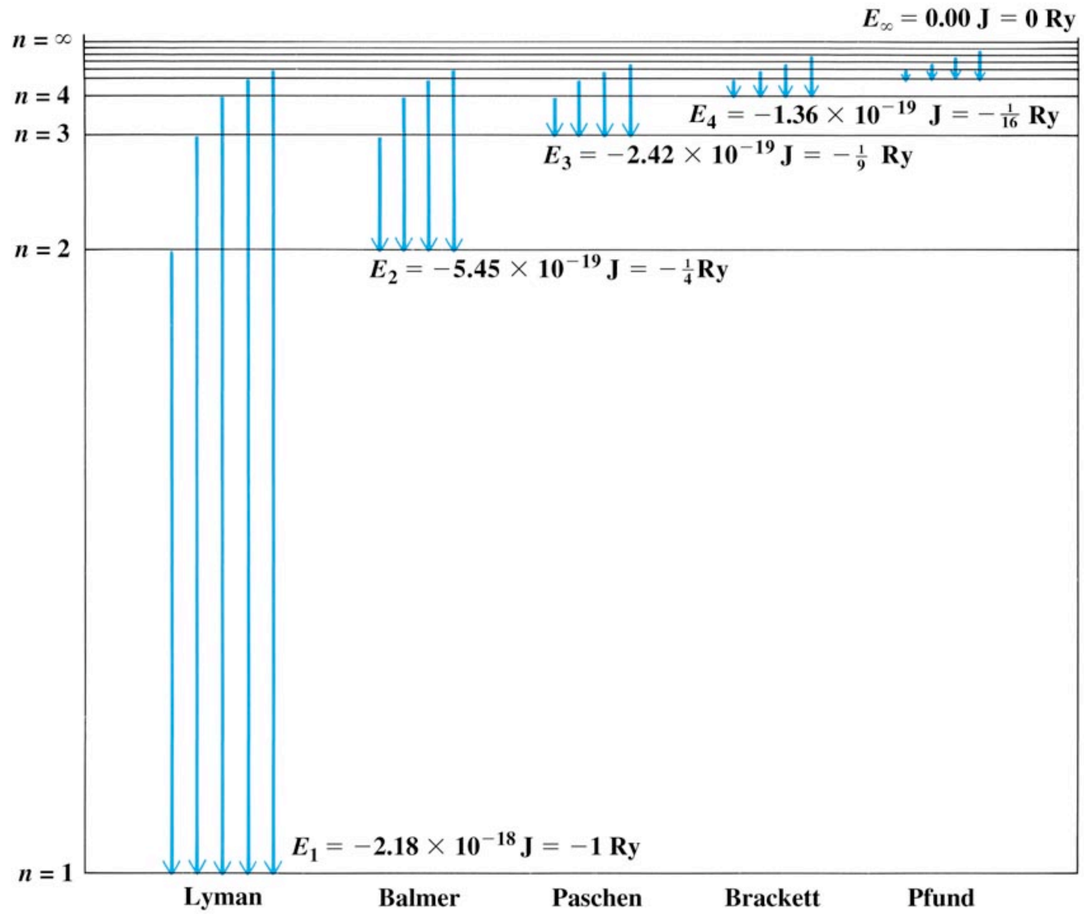
Schroedinger
H atom

4s, 4p, 4d, 4f
3s, 3p, 3d

2s, 2p

1s

Bohr
H atom



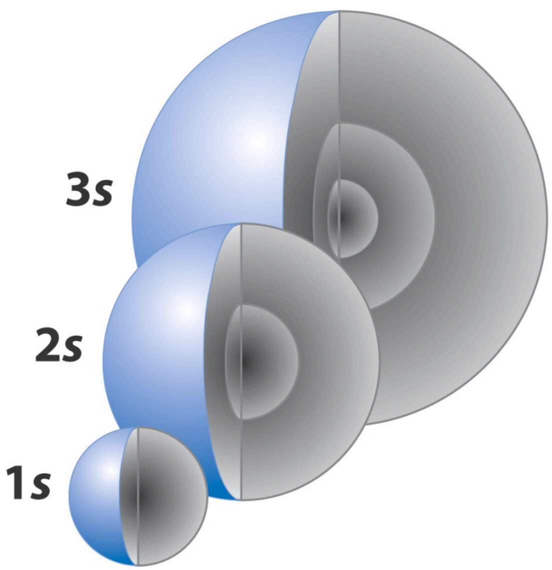
Wavefunctions and orbitals

Obital: A wavefunction defined by the quantum numbers n, l and m_l (which are solutions of the wave equation)

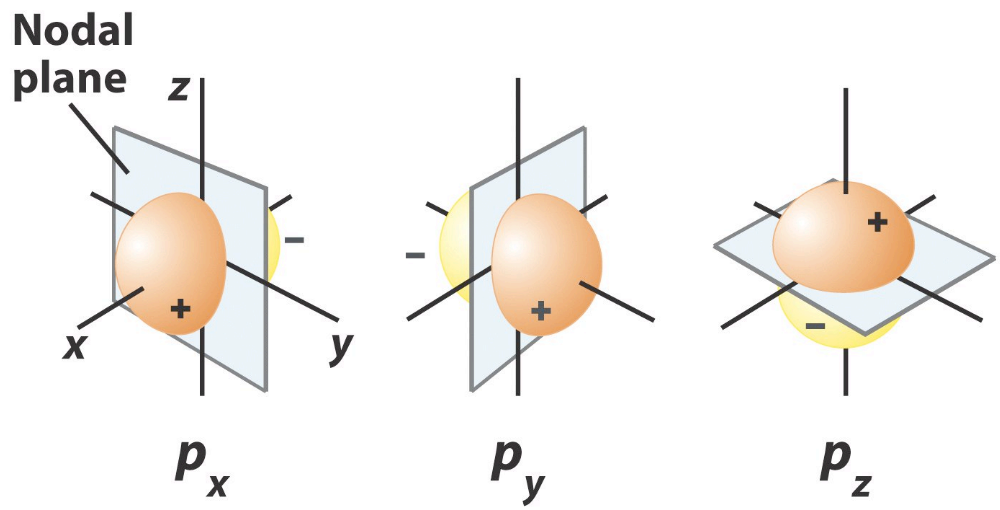
Orbital is a region of space occupied by an electron

Orbitals has energies, shapes and orientation in space

s orbitals



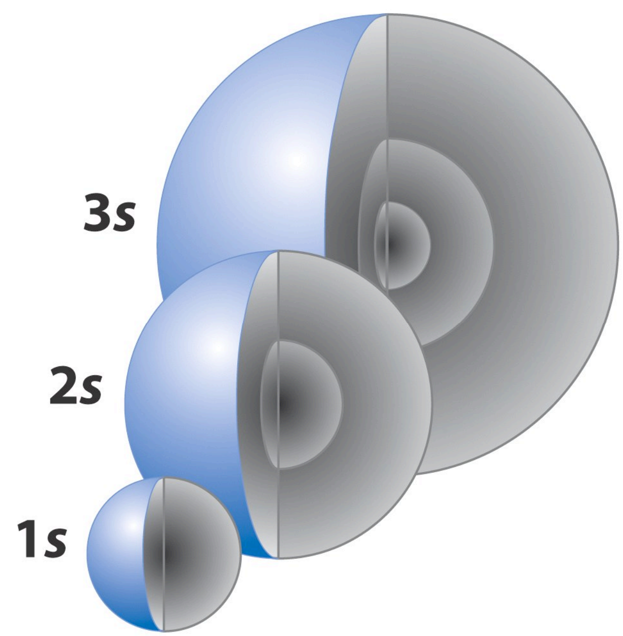
p orbitals



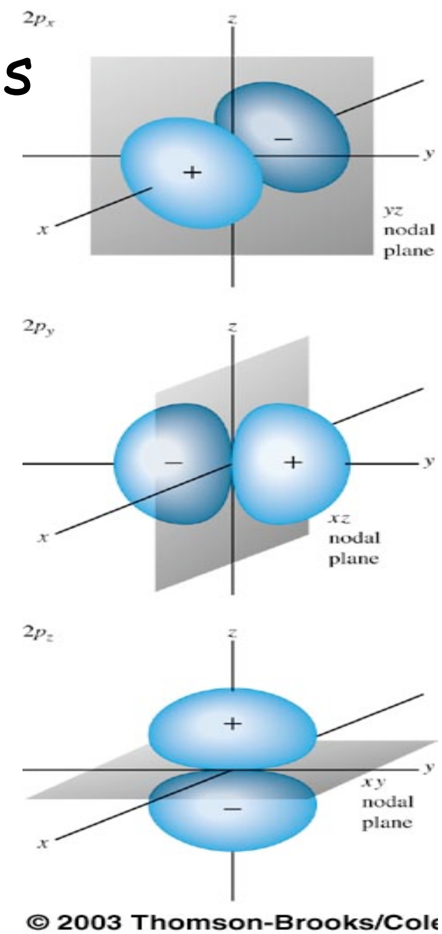
Sizes, Shapes, and orientations of orbitals

n determines size; l determines shape; m_l determines orientation

ns orbitals



np orbitals



The hydrogen s orbitals (solutions to the Schroedinger equation)

Radius of 90%
Boundary sphere:
r_{1s} = 1.4 Å
r_{2s} = 3.3 Å
r_{3s} = 10 Å

Value of Ψ as a function of the distance r from the nucleus

Probability of finding an electron in a spherical shell or radius r from the nucleus ($\Psi^2 4\pi r^2$). r^2 captures volume.

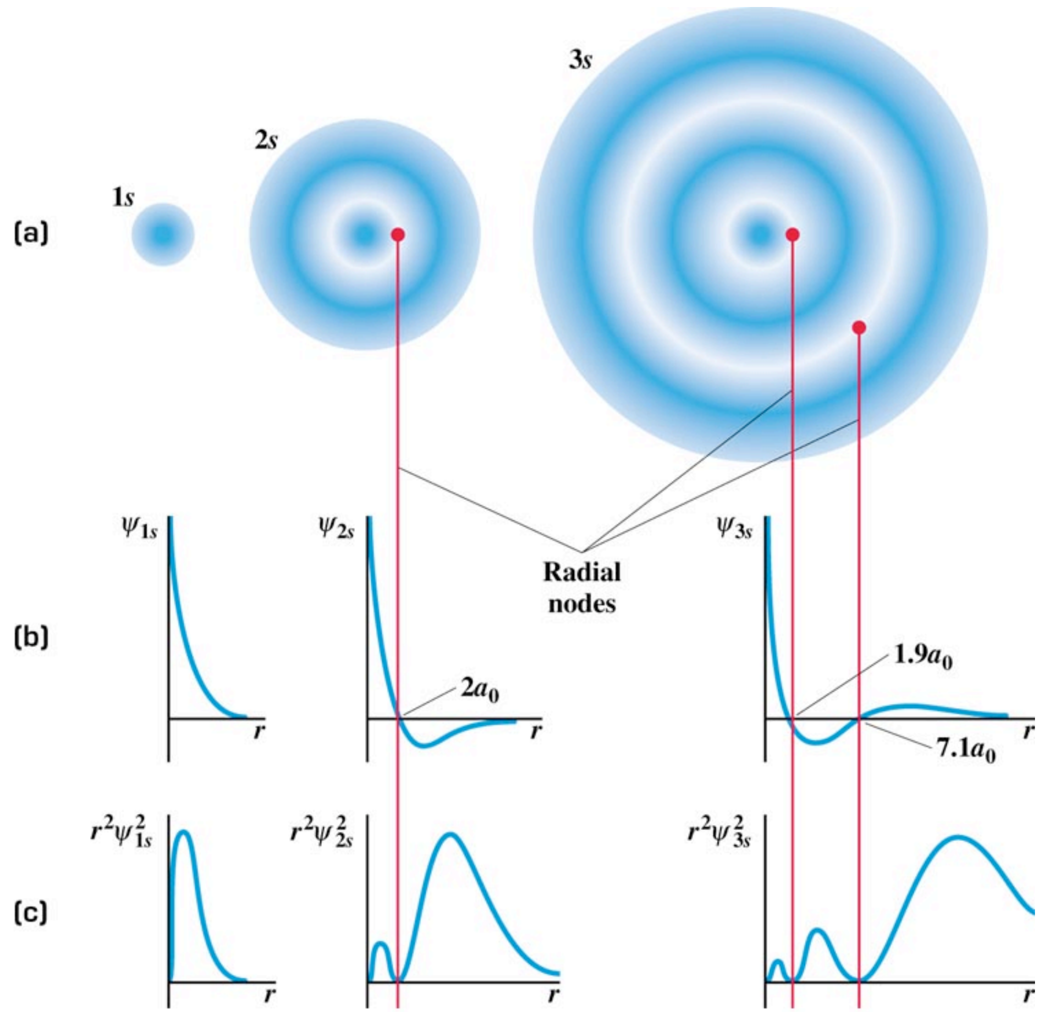
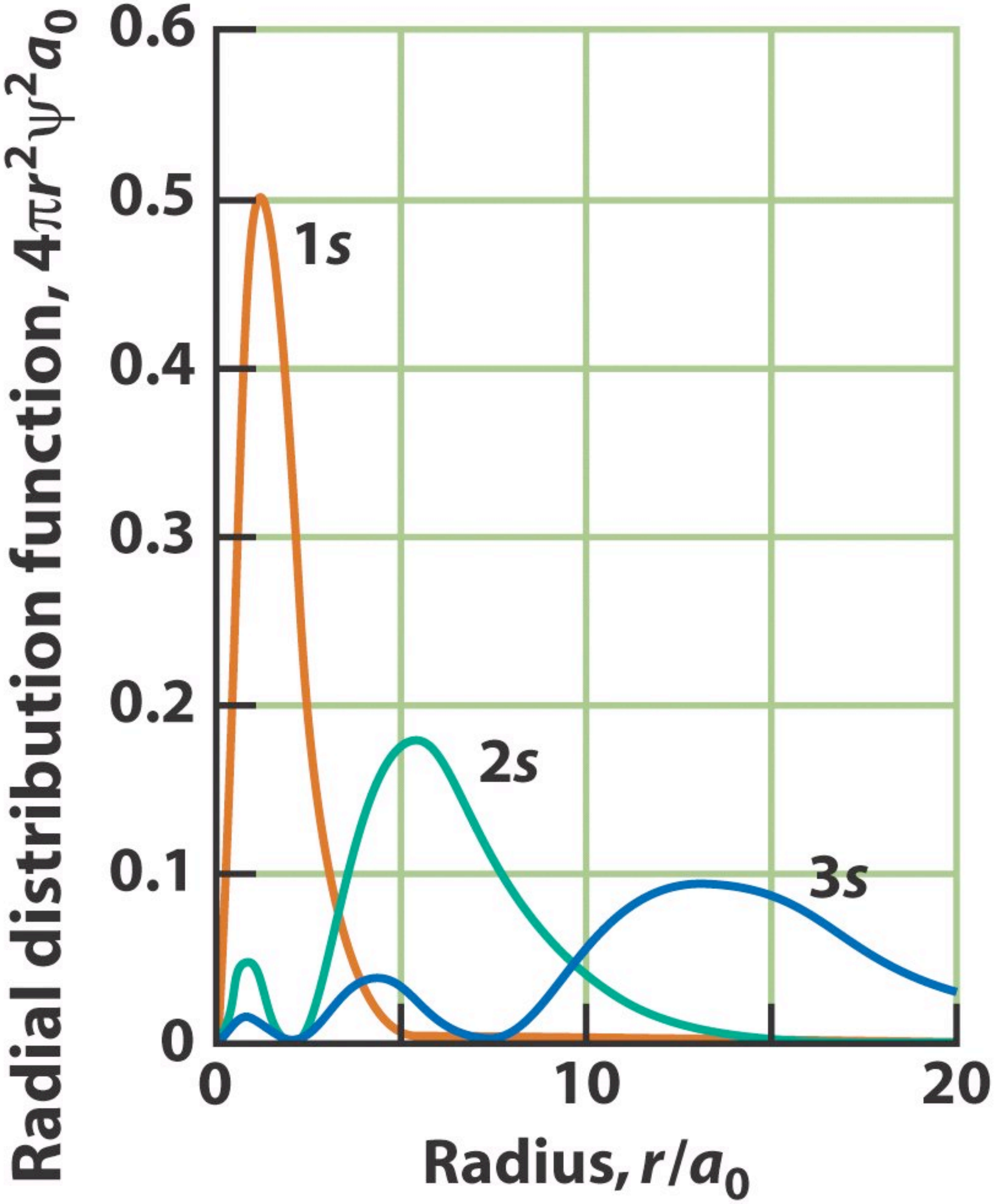


Fig 16-19



Electron probability x space occupied as a function of distance from the nucleus

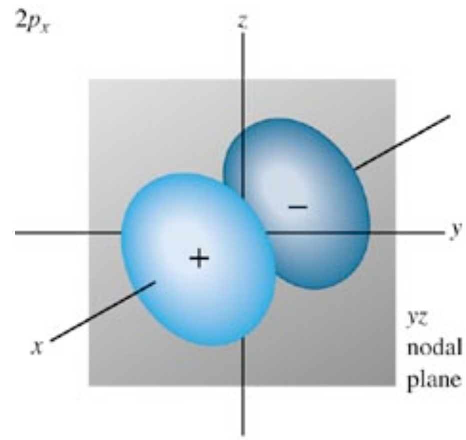
The larger the number of nodes in an orbital, the higher the energy of the orbital

Nodes in orbitals: 2p orbitals: angular node that passes through the nucleus

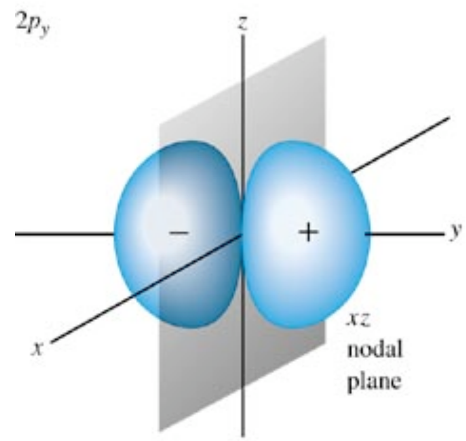
Orbital is "dumb bell" shaped

Important: the + and - that is shown for a p orbital refers to the mathematical sign of the wavefunction, not electric charge!

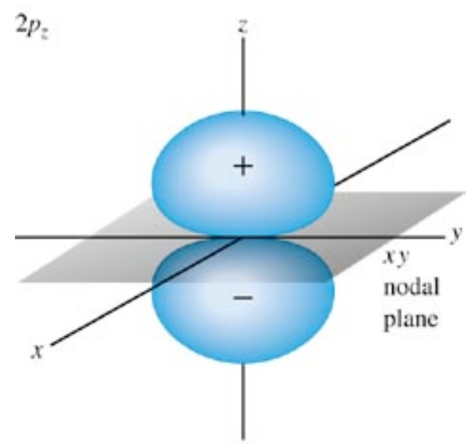
Important: The picture of an orbital refers to the space occupied by a SINGLE electron.



p_x



p_y

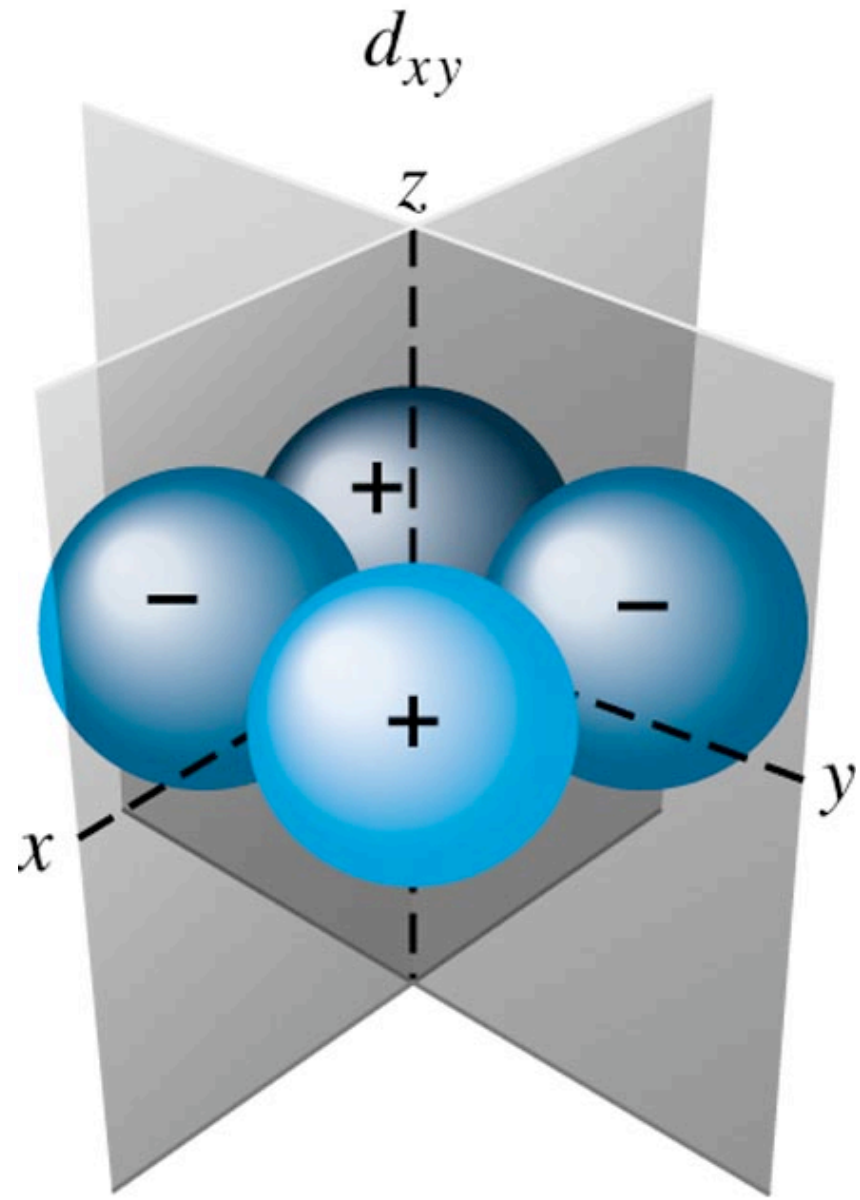


p_z

Nodes in
3d orbitals:
two angular nodes that passes through the nucleus

Orbital is “four leaf clover” shaped

d orbitals are important for metals



(a)

The five d orbitals of a one electron atom

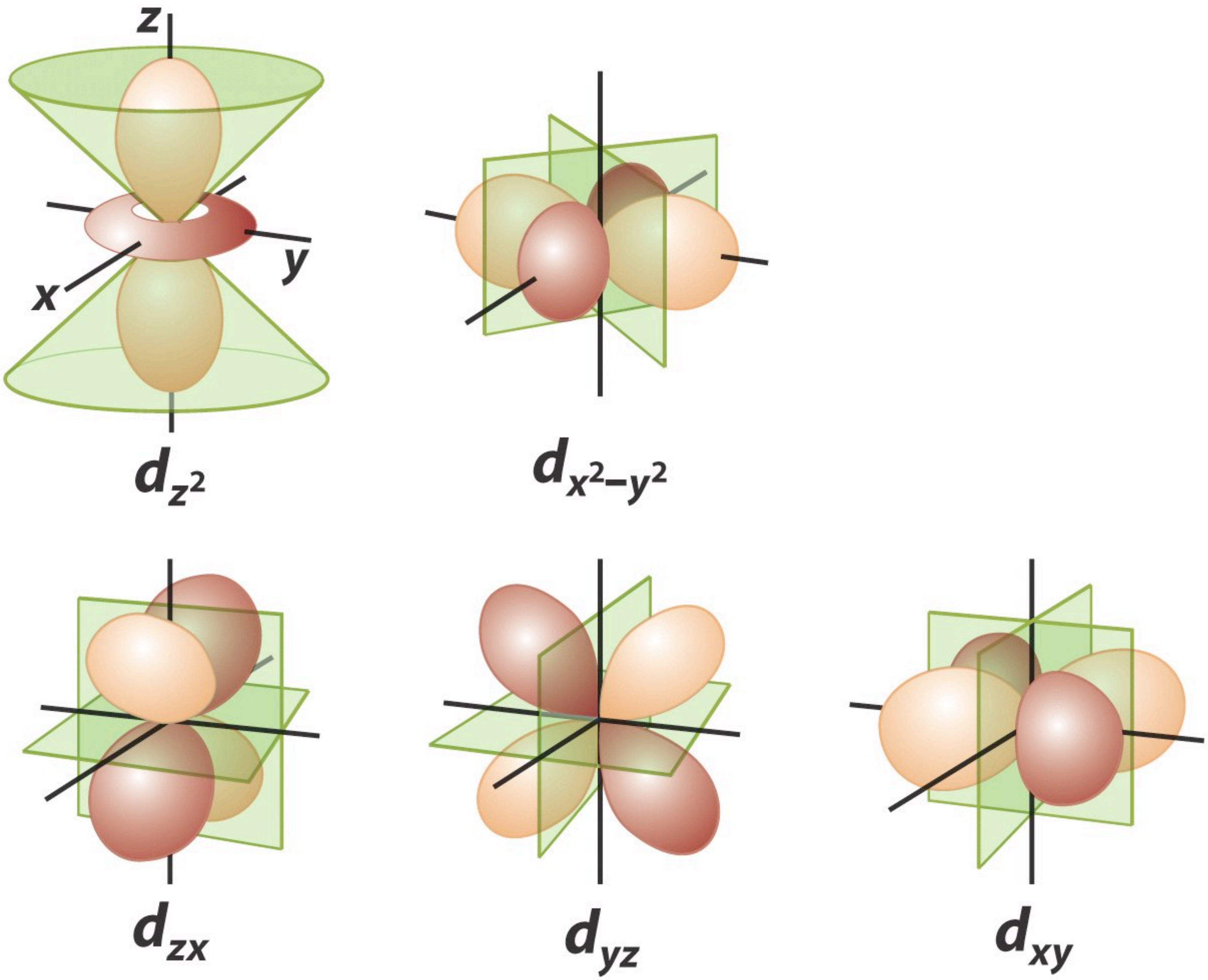
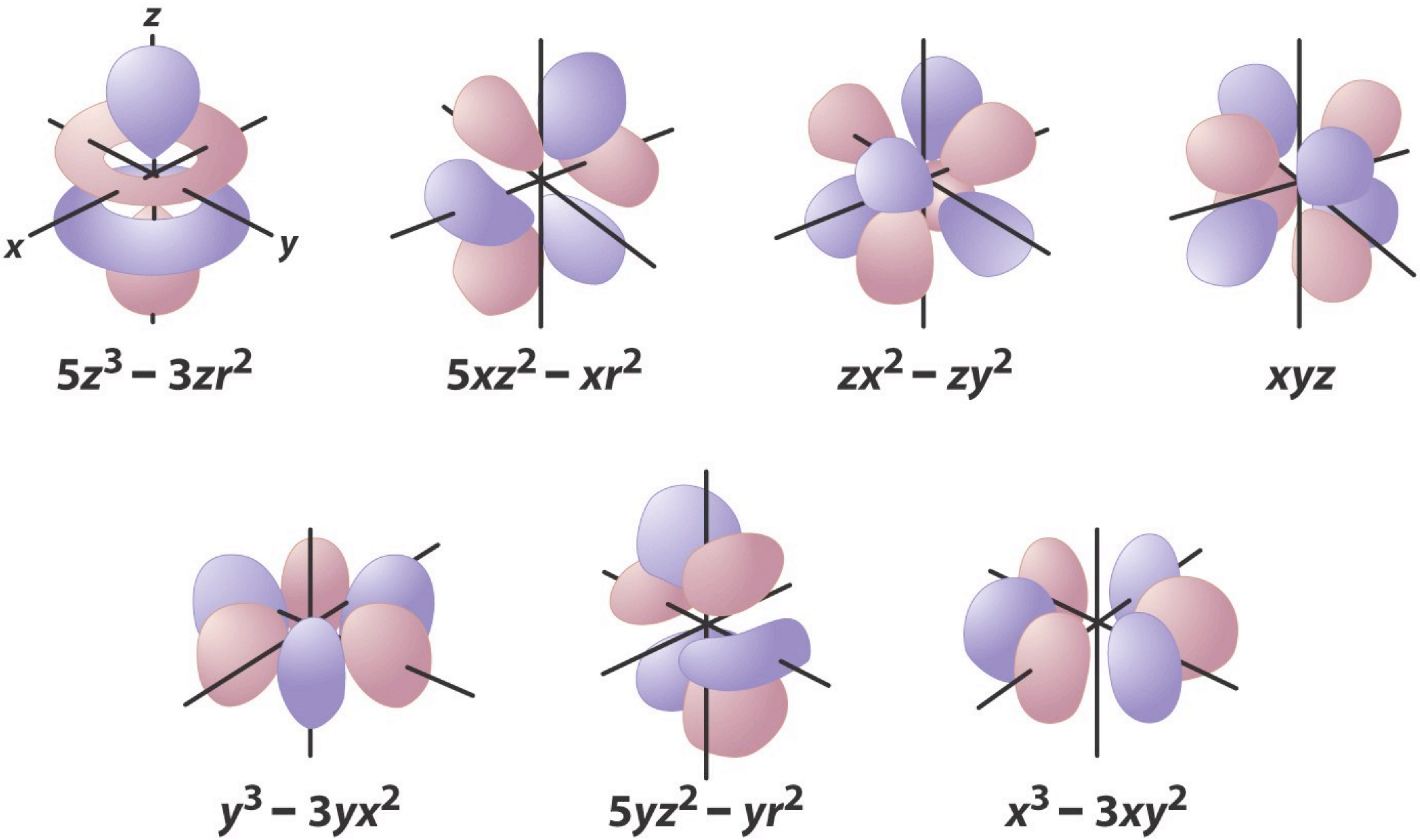
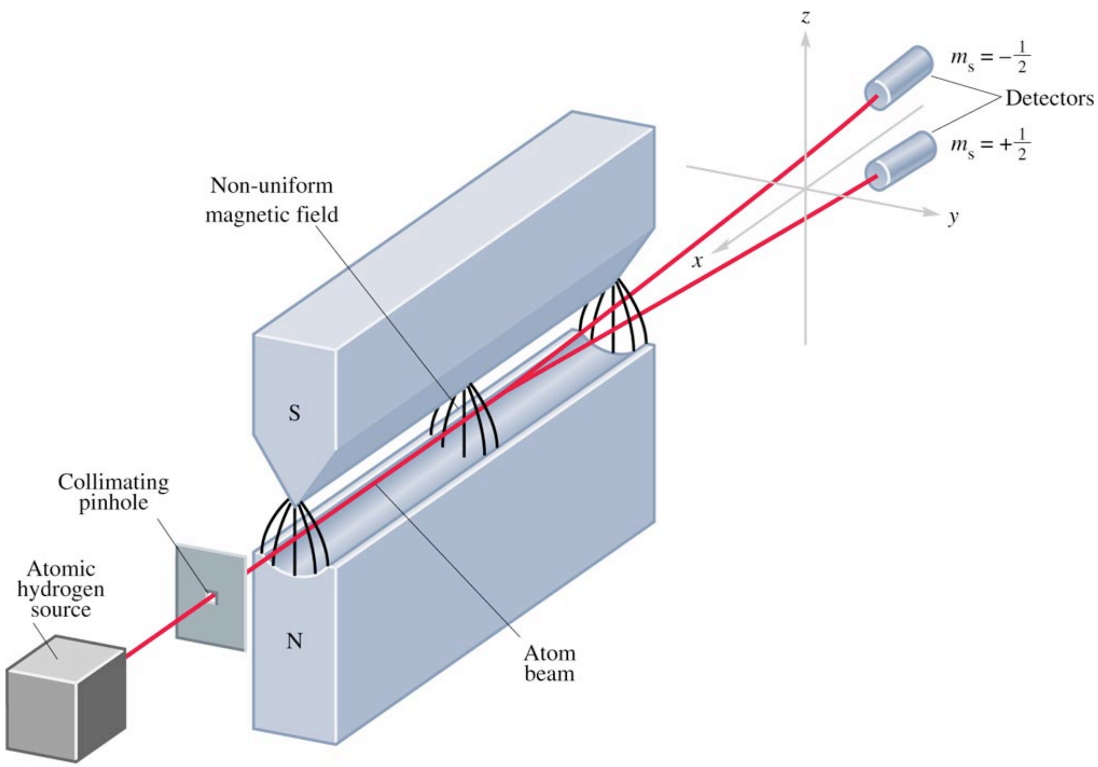


Fig 16-2

The f orbitals of a one electron atom



A need for a fourths quantum number: electron spin

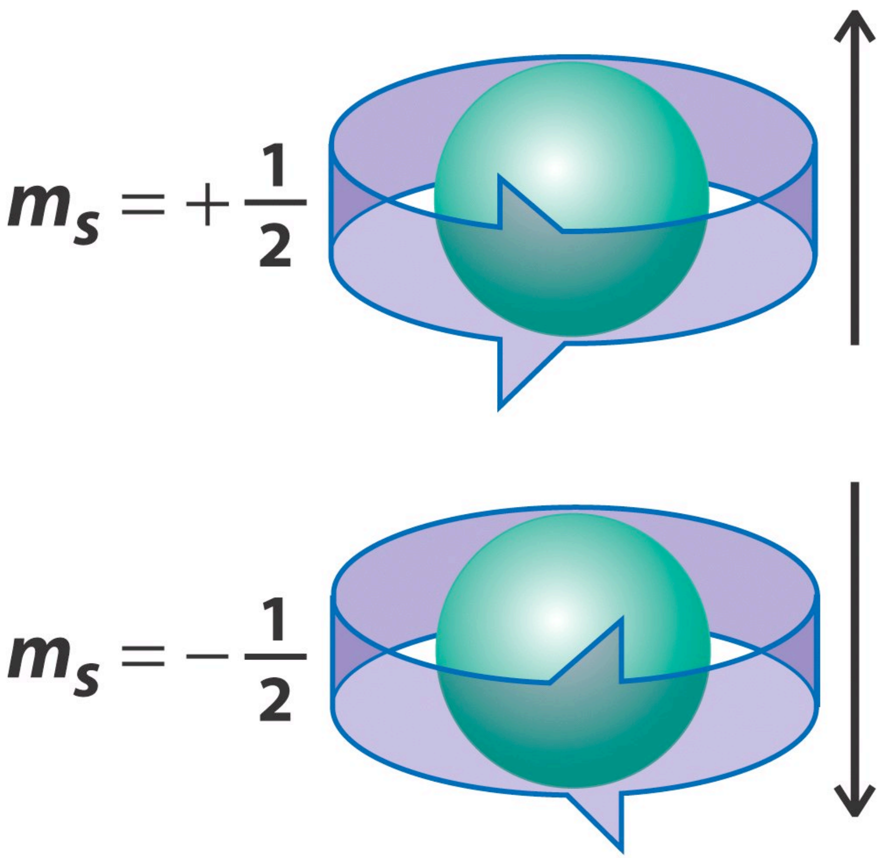


A beam of H atoms in the 1s state is split into two beams when passed through a magnetic field. There must be two states of H which have a different energy in a magnetic field.

The fourth quantum number: Electron Spin

m_s = +1/2 (spin up) or -1/2 (spin down)

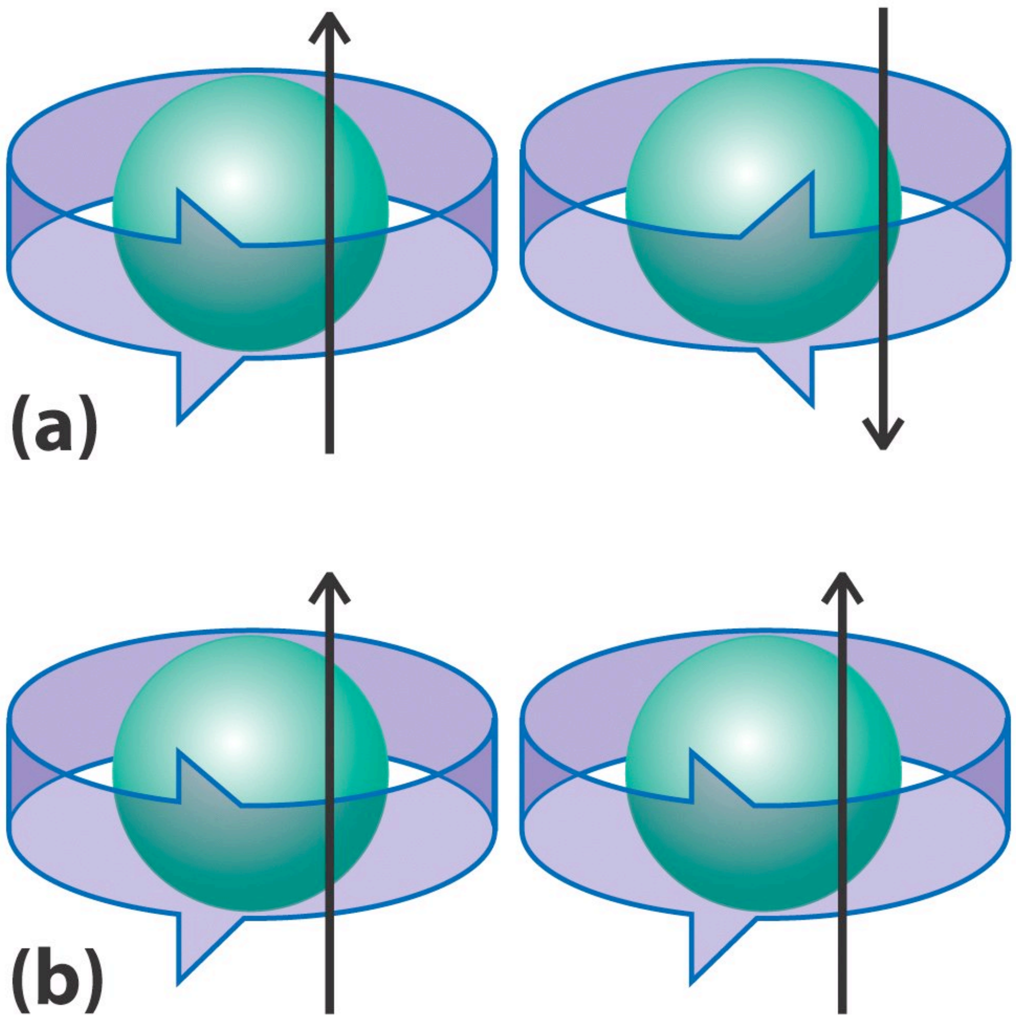
Spin is a fundamental property of electrons, like its charge and mass.



(spin up)

(spin down)

Two electron spins can "couple" with one another to produce singlet states and triplet states.



A singlet state: one spin up, one spin down

A triplet state: both spins up or both spins down

Electrons in an orbital must have different values of m_s

This statement demands that if there are two electrons in an orbital one must have m_s = +1/2 (spin up) and the other must have m_s = -1/2 (spin down)
This is the Pauli Exclusion Principle

An empty orbital is fully described by the three quantum numbers: n, *l* and m_l

An electron in an orbital is fully described by the four quantum numbers: n, *l*, m_l and m_s

Exercises using quantum numbers:

Are the following orbitals possible or impossible?

(1) A 2d orbital

(2) A 5s orbital

(1) Is a 2d orbital possible?

The possible values of *l* can be range from n - 1 to 0.

If n = 2, the possible values of *l* are 1 (= n -1) and 0.

This means that 2s (*l* = 0) and 2p (*l* = 1) orbitals are possible, but 2d (*l* = 2) is impossible.

The first d orbitals are possible for n = 3.

(2) Is a 5s orbital possible?

For n = 5, the possible values of *l* are 4 (g), 3 (f), 2 (d), 1 (p) and 0 (s).

So 5s, 5p, 5d, 5f and 5g orbitals are possible.

Is the electron configuration $1s^2 2s^3$ possible?

The Pauli exclusion principle forbids any orbital from having more than two electrons under any circumstances.

Since any s orbital can have a maximum of two electrons, a $1s^2 2s^3$ electronic configuration is impossible, since $2s^3$ means that there are THREE electrons in the 2s orbital.

Summary of quantum numbers and their interpretation

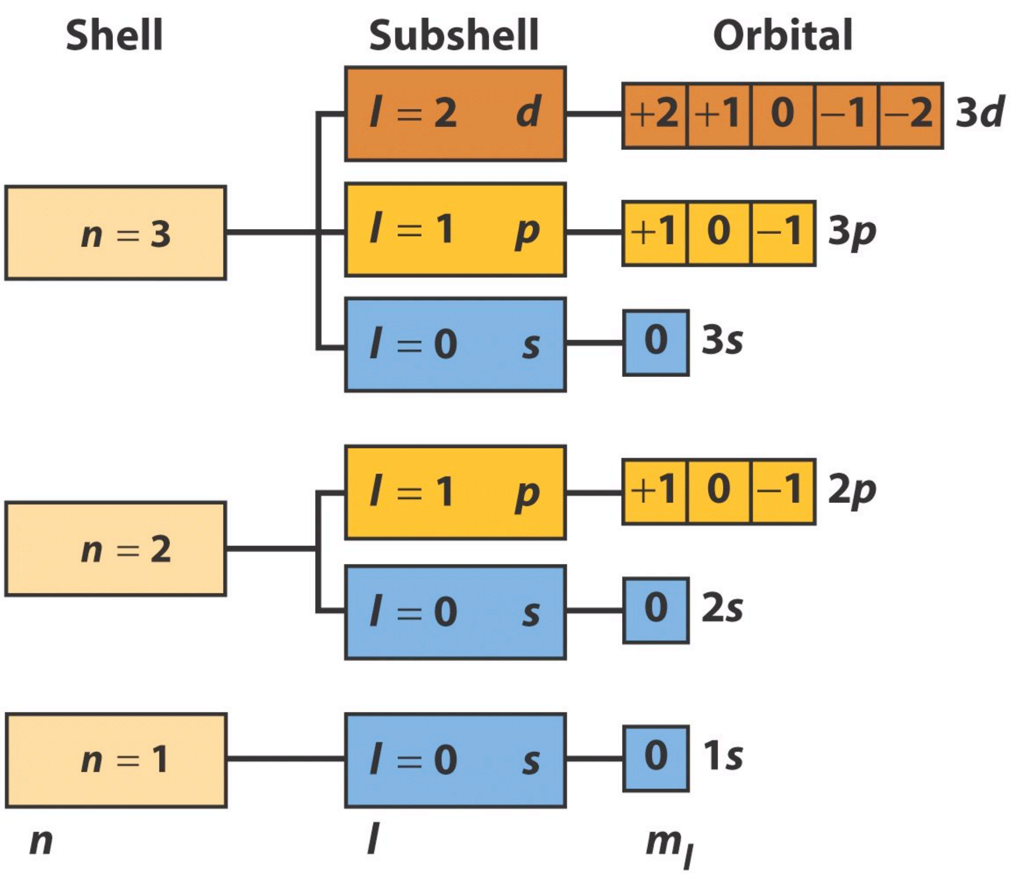
TABLE 1.3 Quantum Numbers for Electrons in Atoms

Name	Symbol	Values	Specifies	Indicates
principal	n	1, 2, . . .	shell	size
orbital angular momentum*	l	$0, 1, \ldots, n-1$	subshell: $l = 0, 1, 2, 3, 4, \ldots$ $s, p, d, f, g, \ldots$	shape
magnetic	m_l	$l, l-1, \ldots, -l$	orbitals of subshell	orientation
spin magnetic	m_s	$+\frac{1}{2}, -\frac{1}{2}$	spin state	spin direction

*Also called the *azimuthal quantum number.*

The energy of an orbital of a hydrogen atom or any one electron atom only depends on the value of n

shell = all orbitals with the same value of n
subshell = all orbitals with the same value of n and *l*
an orbital is fully defined by three quantum numbers, n, *l*, and m_l



Each shell of QN = n contains n subshells

n = 1, one subshell
n= 2, two subshells, etc

Each subshell of QN = *l*, contains 2*l* + 1 orbitals

l = 0, 2(0) + 1 = 1
l = 1, 2(1) + 1 = 3

Aspects of a good scientific theory.

Correlates many seemingly unconnected facts in a single logical, self-consistent connected structure capable of not only correlation but also unanticipated organization.

Suggests new relationships.

Predicts new phenomena that can be checked by experiment.

Simplicity: only a few clearly understandable postulates or assumptions.

Quantification: allows precise correlation between theory and experiment.