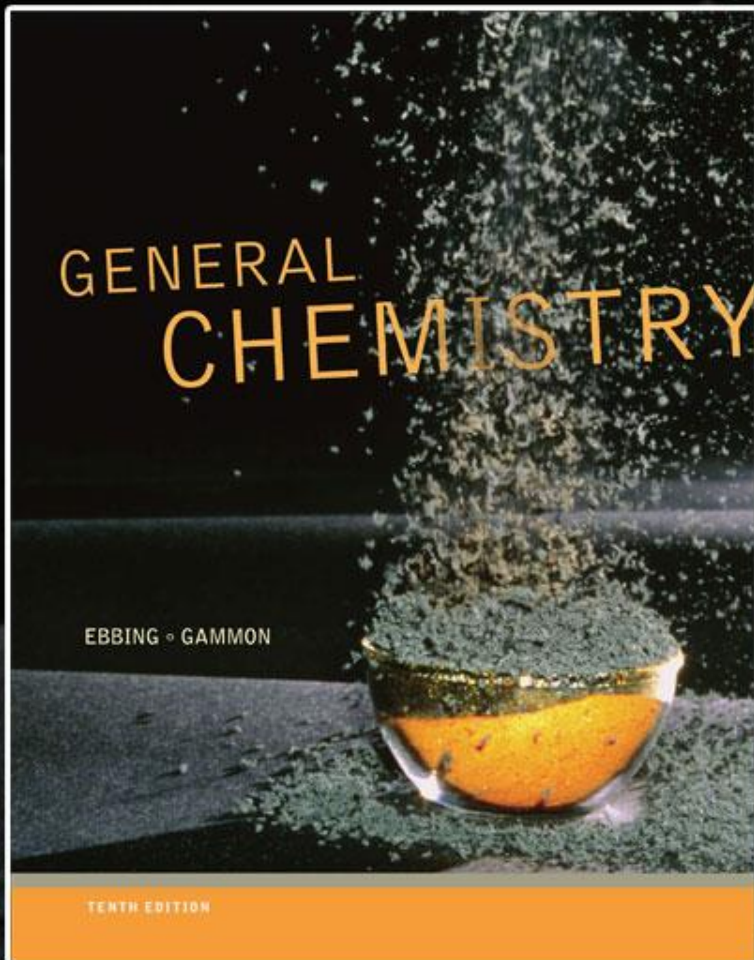
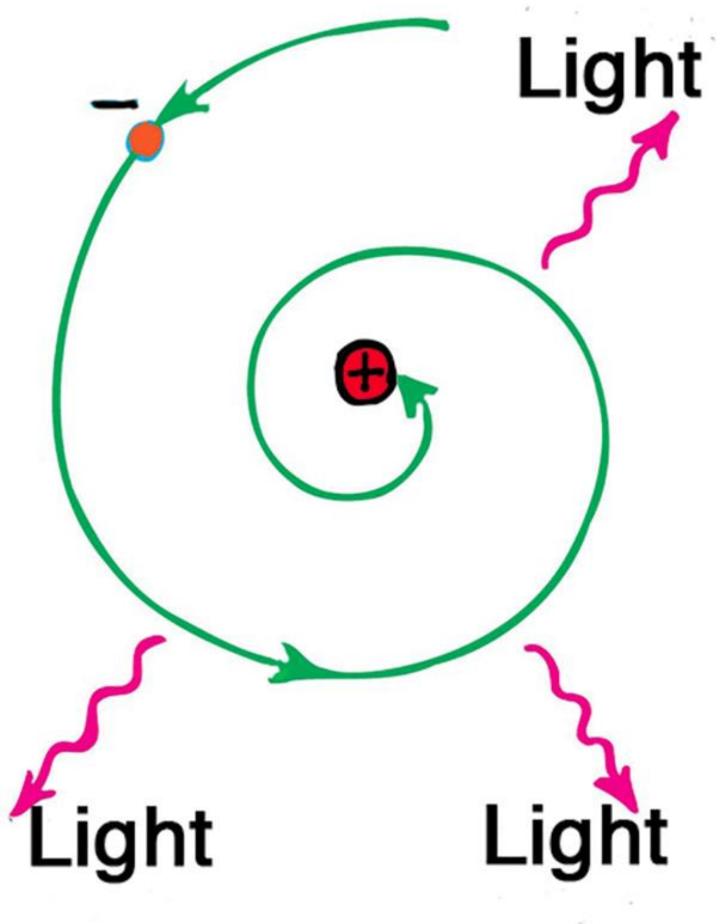


Lecture 03 Quantum Mechanical Model of Atom and Electron Configuration

Classical model of atom: problem?



Atom cannot exist!

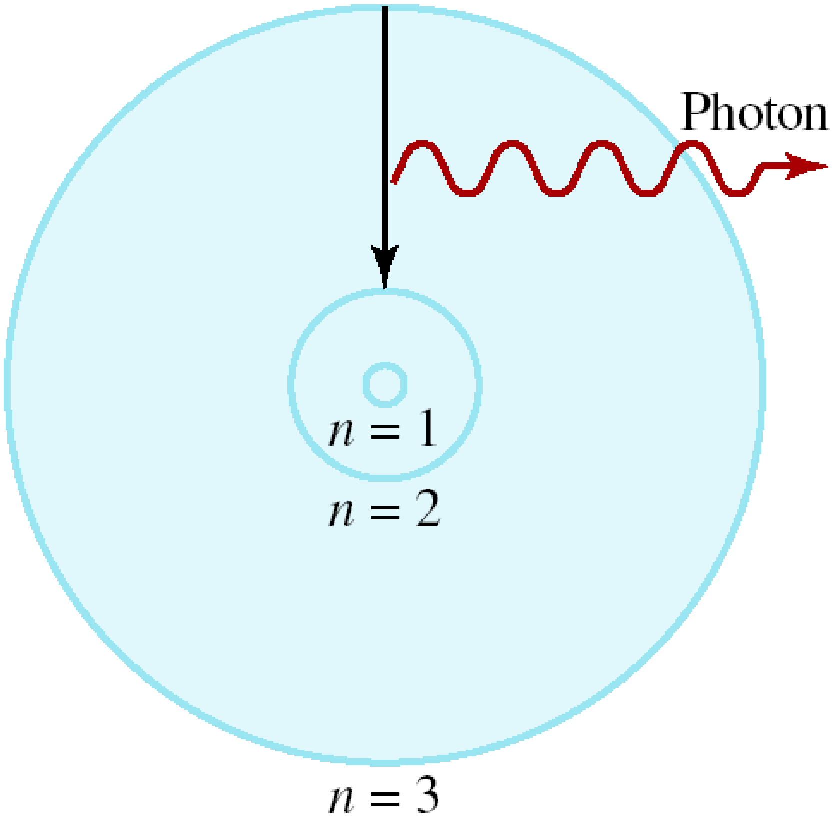
Rutherford's model of the atom was unstable. Maxwell's classical electromagnetic theory: if a charged particle accelerates, it radiates energy.

The energy is emitted in the form of electromagnetic waves. Thus, an electron revolving around the nucleus will lose the energy and its radius will keep shrinking until it collapses into its nucleus.

Bohr's Model of the Atom (1913)

1. e^- can only have specific (quantized) energy values
2. light is emitted as e^- moves from one energy level to a lower energy level

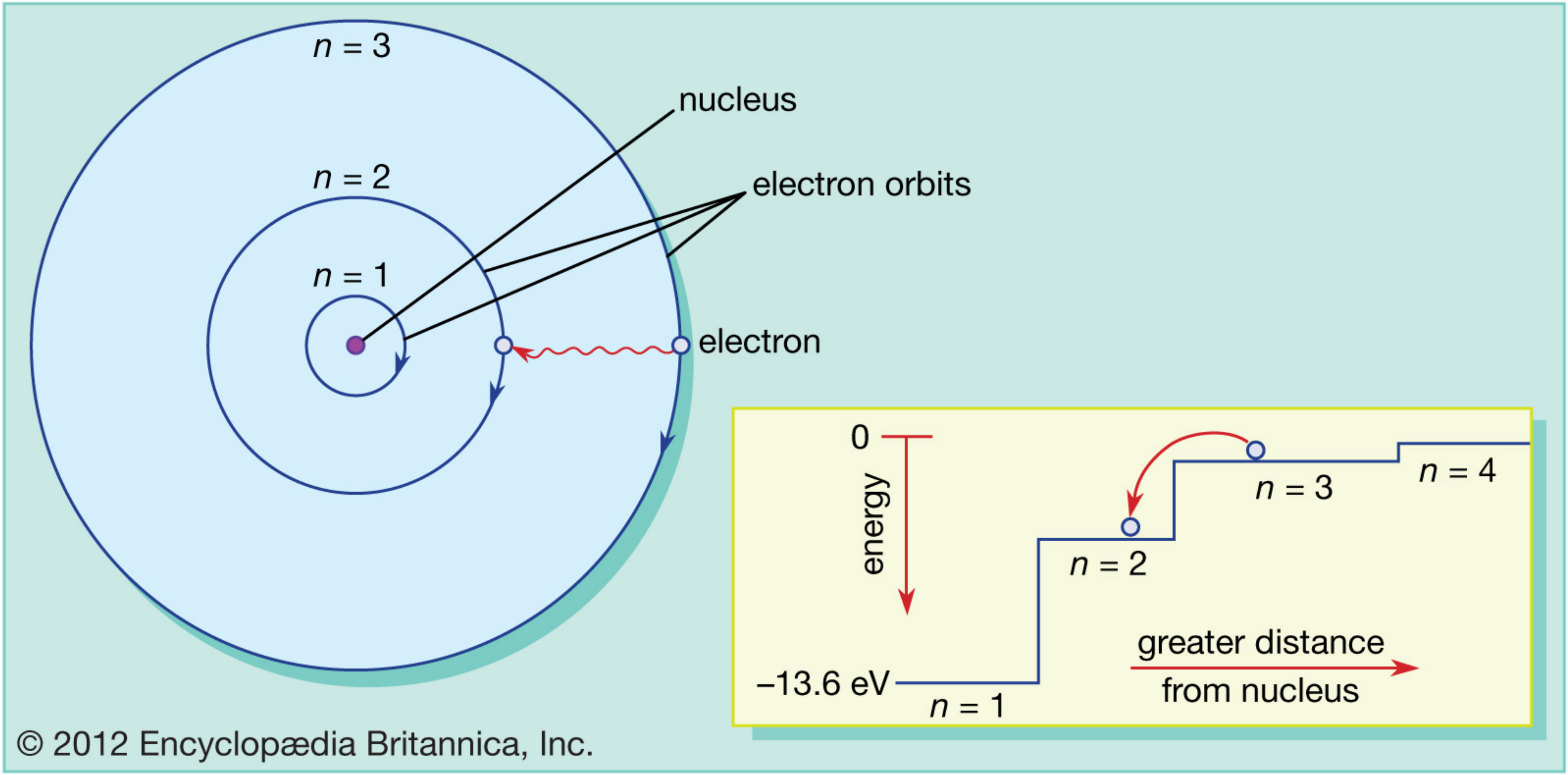
$$E_n = -R_H \left(\frac{1}{n^2} \right)$$



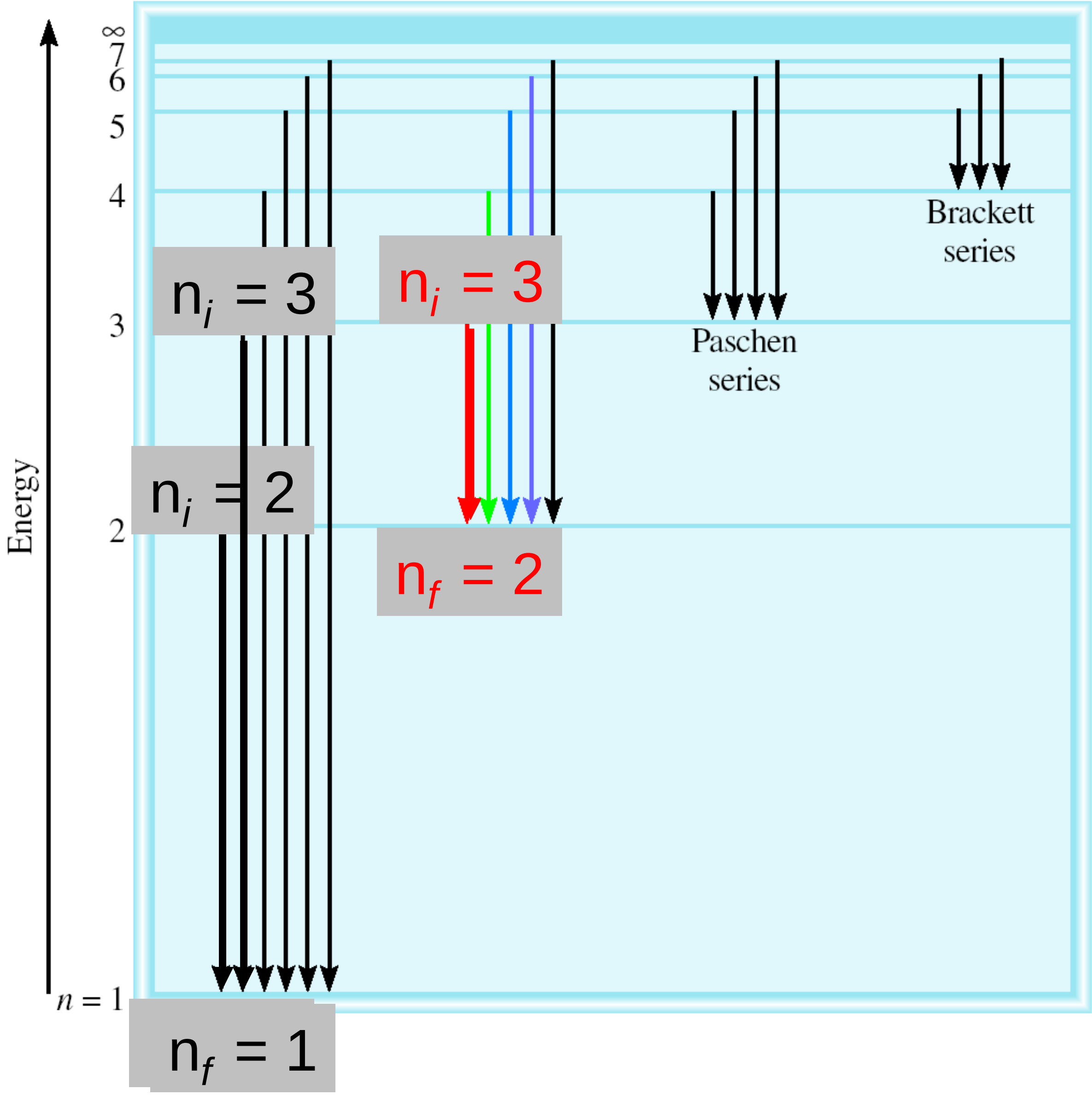
n (principal quantum number) = 1,2,3,…

R_H (Rydberg constant) = 2.18×10^{-18}J

Niels Bohr’s model



Niels Bohr's model



$$E_{\text{photon}} = \Delta E = E_{\text{f}} - E_{\text{i}}$$

$$E_f = -R_{\text{H}} \left(\frac{1}{n_f^2} \right)$$

$$E_i = -R_{\text{H}} \left(\frac{1}{n_i^2} \right)$$

$$\Delta E = R_{\text{H}} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

Niels Bohr's model

TABLE 7.1 The Various Series in Atomic Hydrogen Emission Spectrum

Series	n_f	n_i	Spectrum Region
Lyman	1	2, 3, 4, . . .	Ultraviolet
Balmer	2	3, 4, 5, . . .	Visible and ultraviolet
Paschen	3	4, 5, 6, . . .	Infrared
Brackett	4	5, 6, 7, . . .	Infrared

Niels Bohr's model

Calculate the wavelength (in nm) of a photon emitted by a hydrogen atom when its electron drops from the n = 5 state to the n = 3 state.

$$E_{\text{photon}} = \Delta E = R_{\text{H}}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

$$E_{\text{photon}} = 2.18 \times 10^{-18} \text{ J} \times (1/25 - 1/9)$$

$$E_{\text{photon}} = \Delta E = -1.55 \times 10^{-19} \text{ J}$$

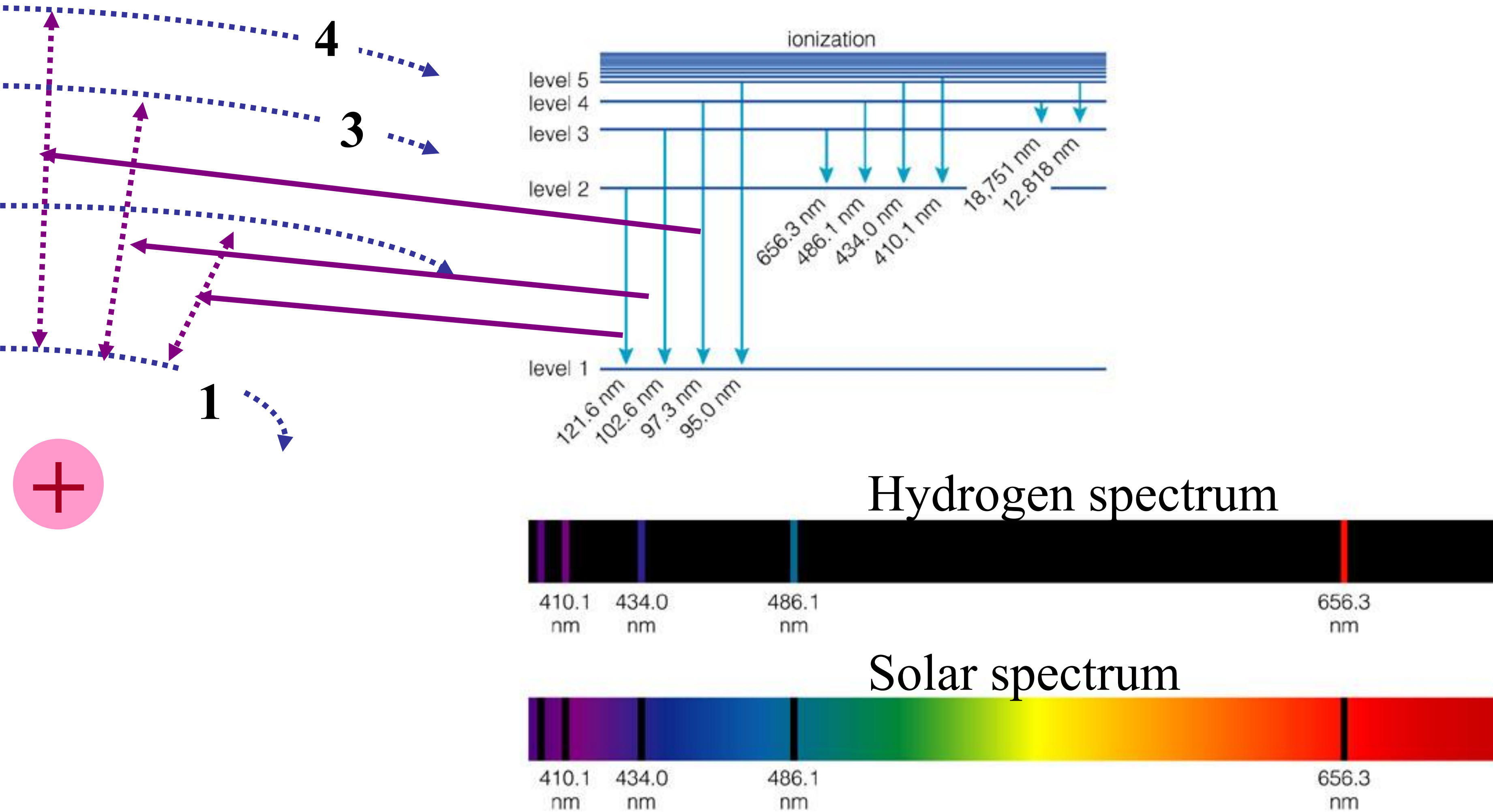
$$E_{\text{photon}} = h \times c / \lambda$$

$$\lambda = h \times c / E_{\text{photon}}$$

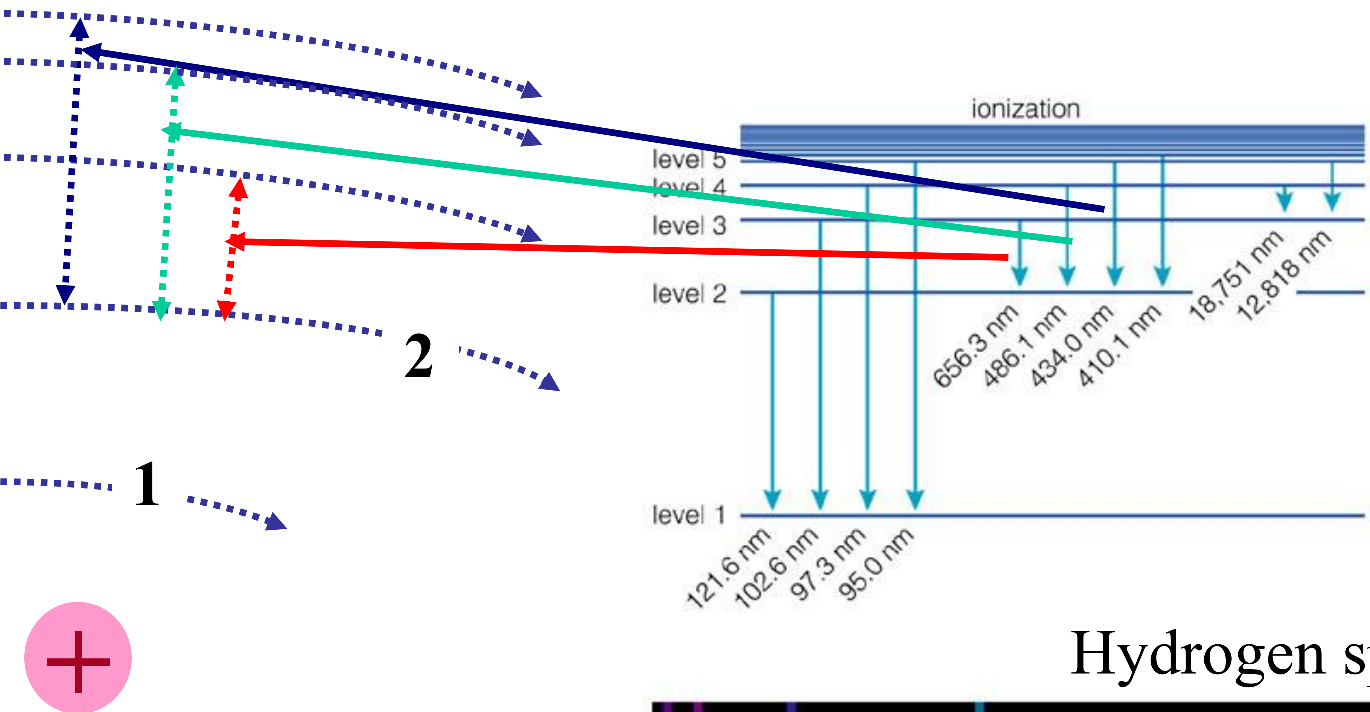
$$\lambda = 6.63 \times 10^{-34} (\cancel{\text{J}}\bullet\cancel{\text{s}}) \times 3.00 \times 10^{8} (\text{m}/\cancel{\text{s}})/1.55 \times 10^{-19} \cancel{\text{J}}$$

$$\lambda = 1280 \text{ nm}$$

Niels Bohr's model

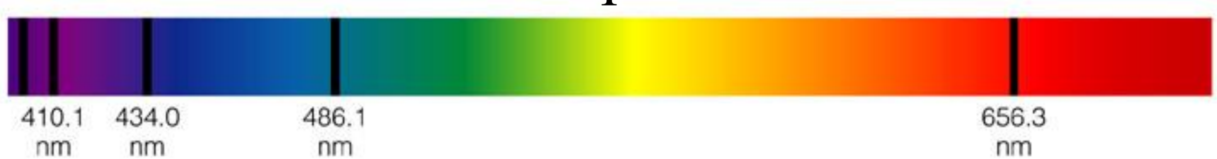


Niels Bohr’s model



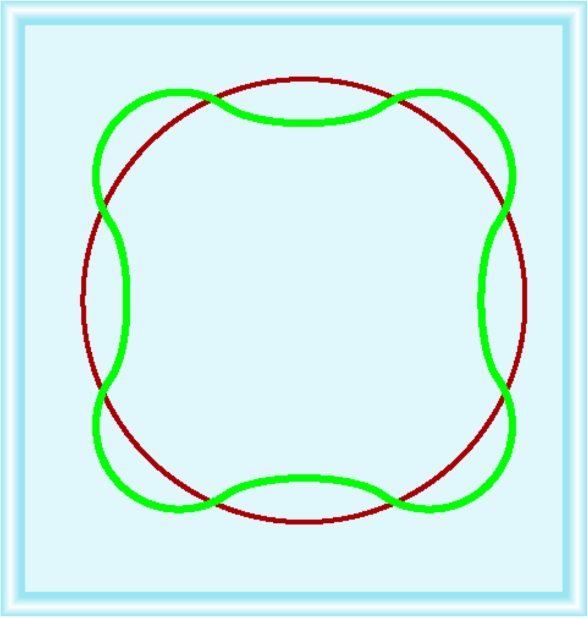
Hydrogen spectrum

Solar spectrum



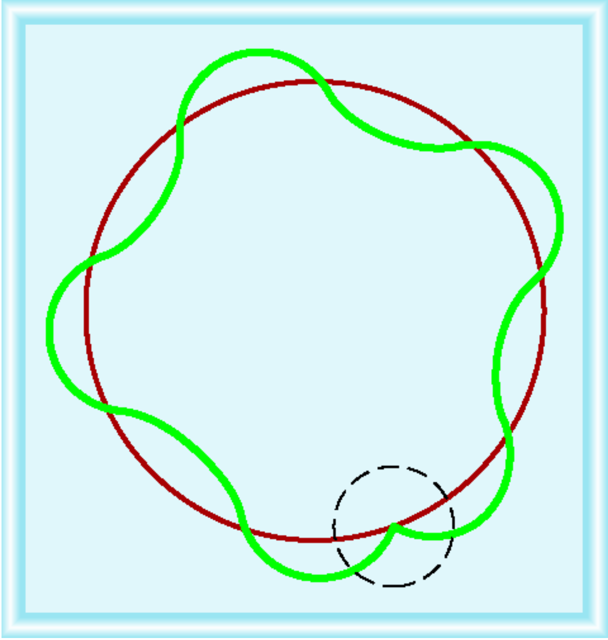
Louis-Victor de Broglie:

Wave-particle duality



Why is e^- energy quantized?

De Broglie (1924) reasoned that e^- is both particle and wave.



$$2\pi r = n\lambda \qquad \lambda = \frac{h}{mu}$$

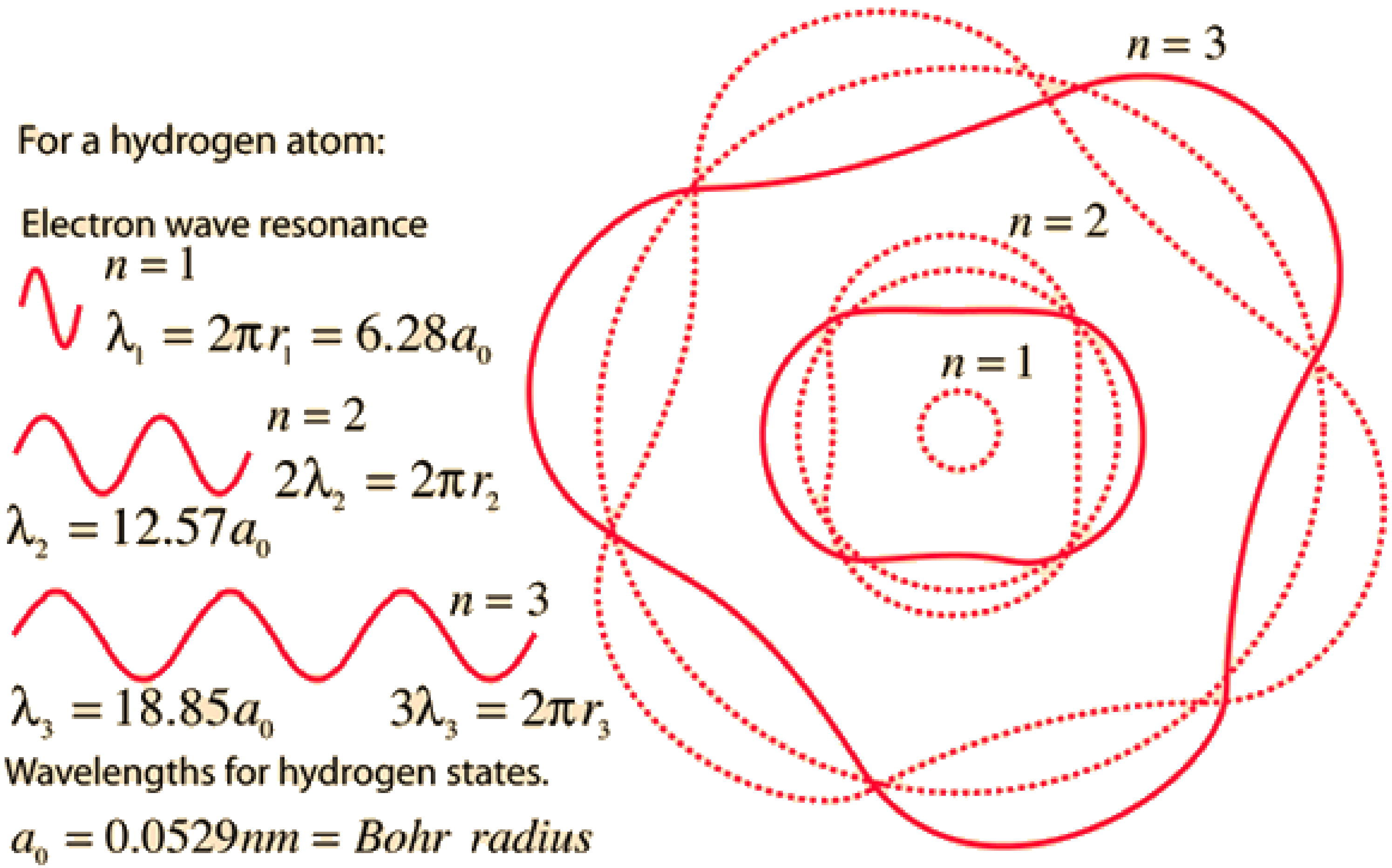
u = velocity of e-

m = mass of e-

Only certain orbits allow the electron to satisfy both its particle and wave properties at the same time.

Louis-Victor de Broglie:

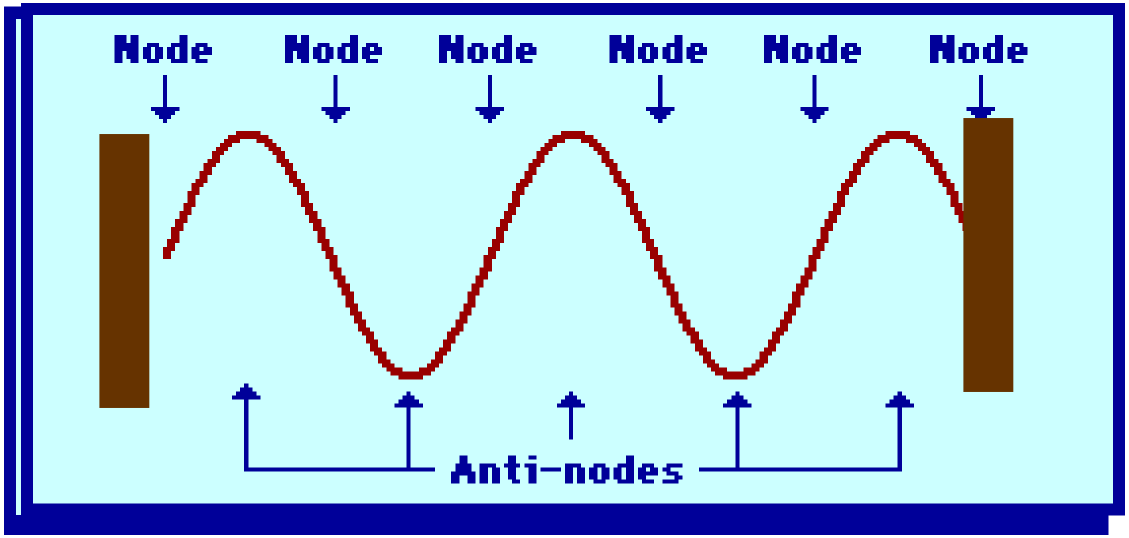
Wave-particle duality



Electrons in atoms are confined matter waves

Recall what happens when we force waves into confined spaces:

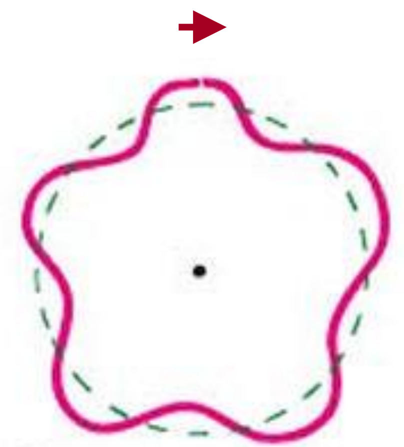
Electrons in atoms are confined matter waves



Only waves with wavelengths that **just fit in** survive (all others cancel themselves out)

Electrons in atoms are confined matter waves

However, if the circumference is exactly an integer number of wavelengths, successive turns will interfere constructively



a

Bohr's allowed energy states correspond to those with orbits that are integer numbers of wavelengths

Niels Bohr’s model: Failures

Bohr’s Atomic Model failed for many-electron species. Any atom with more than one electron couldn’t fit into the theory.

Bohr’s Model violates the Heisenberg’s Uncertainty Principle, which states that we cannot determine the exact position and velocity of a moving particle simultaneously and accurately.

…

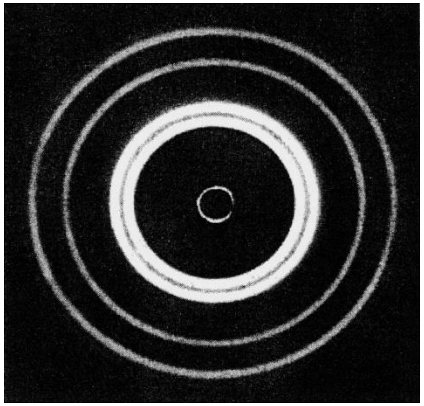
Quantum Mechanical Model of Atom

In 1926 Schrodinger wrote an equation that described both the particle and wave nature of the e^-

Wave function (ψ) describes:

1. energy of e^- with a given ψ
2. probability of finding e^- in a volume of space

Schrodinger's equation can only be solved exactly for the hydrogen atom. Must approximate its solution for multi-electron systems.



Quantum Mechanical Model of Atom

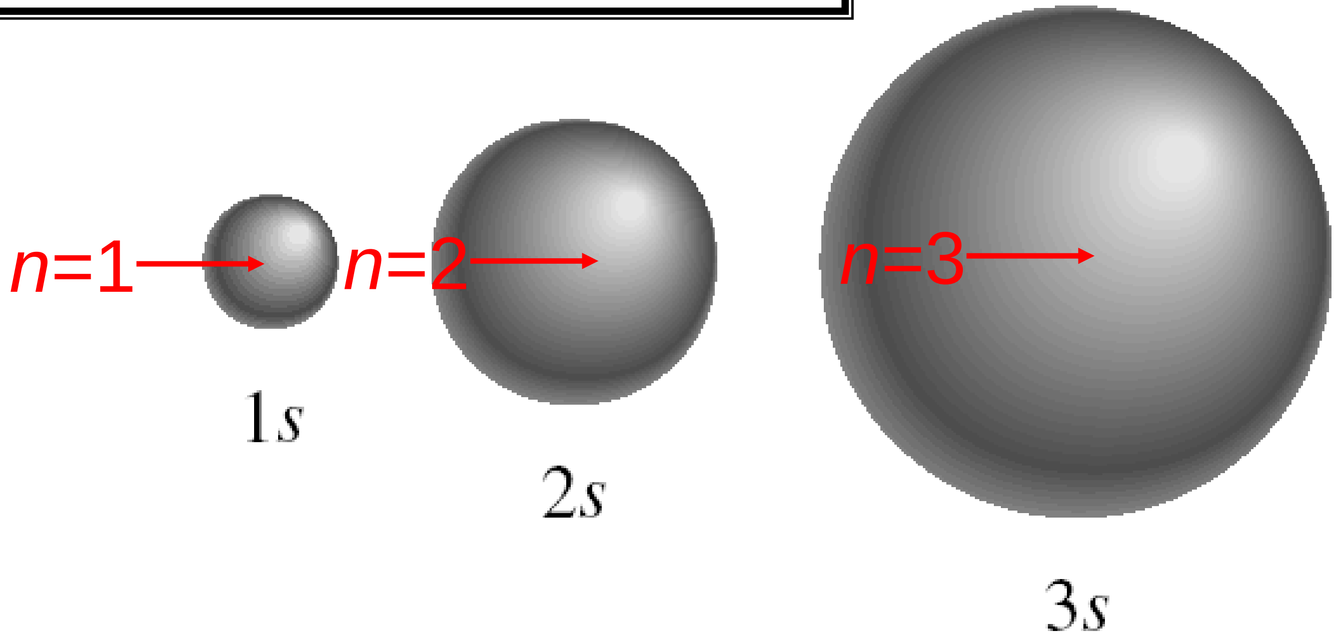
ψ is a function of four numbers called

quantum numbers (n, l, m_l, m_s)

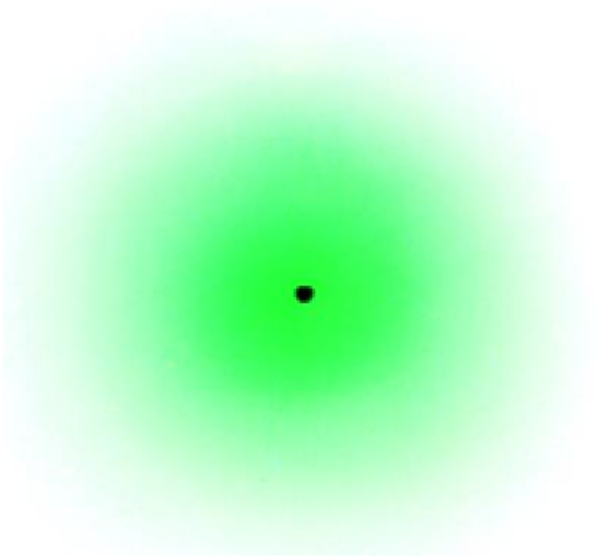
principal quantum number n

n = 1, 2, 3, 4, ….

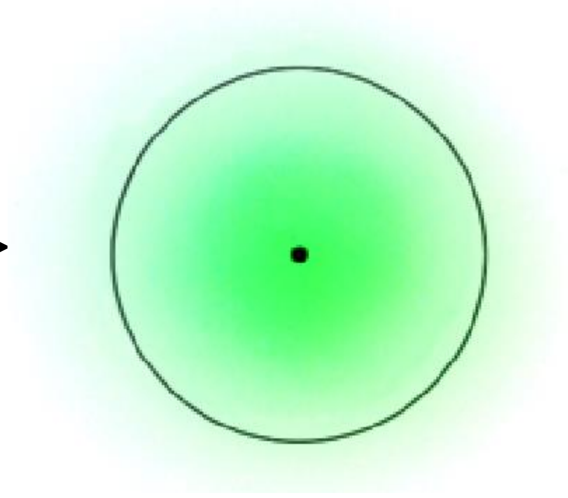
distance of e^- from the nucleus

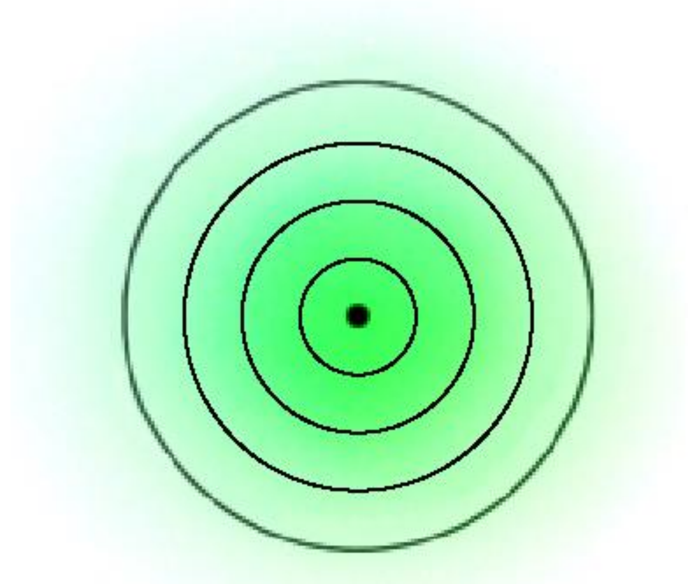


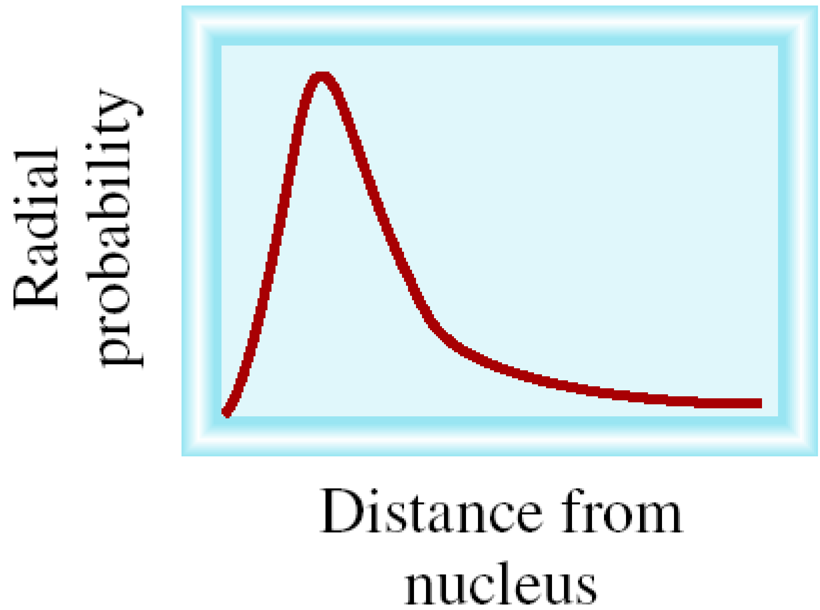
Quantum Mechanical Model of Atom



Where 90% of the e^- density is found for the 1s orbital







Schrodinger Wave Equation

quantum numbers: (n, l, m_l, m_s)

angular momentum quantum number l

for a given value of n, $l = 0, 1, 2, 3, \ldots n-1$

$n = 1$, $l = 0$
$n = 2$, $l = 0$ **or** 1
$n = 3$, $l = 0, 1,$ **or** 2

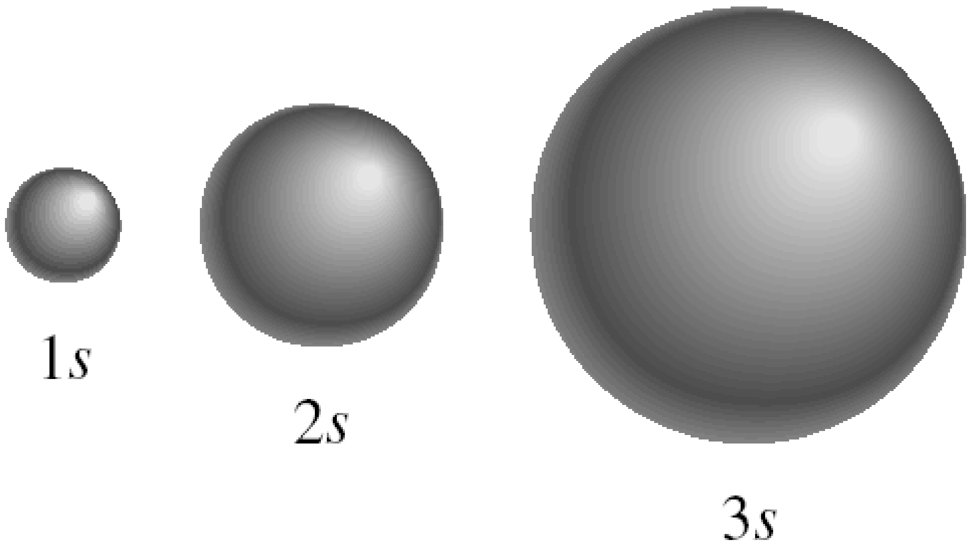
$l = 0$ *s* orbital
$l = 1$ *p* orbital
$l = 2$ *d* orbital
$l = 3$ *f* orbital

Shape of the "volume" of space that the e^- occupies

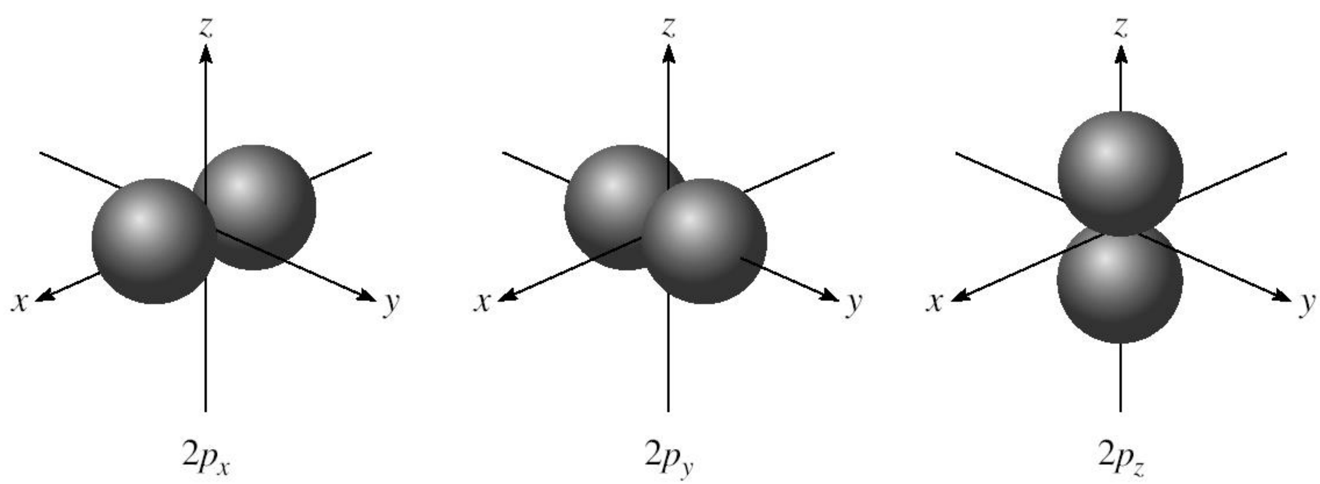
Table 7.1 Permissible Values of Quantum Numbers for Atomic Orbitals

n	l	m_l*	Subshell Notation	Number of Orbitals in the Subshell
1	0	0	1*s*	1
2	0	0	2*s*	1
2	1	$-1, 0, +1$	2*p*	3
3	0	0	3*s*	1
3	1	$-1, 0, +1$	3*p*	3
3	2	$-2, -1, 0, +1, +2$	3*d*	5
4	0	0	4*s*	1
4	1	$-1, 0, +1$	4*p*	3
4	2	$-2, -1, 0, +1, +2$	4*d*	5
4	3	$-3, -2, -1, 0, +1, +2, +3$	4*f*	7

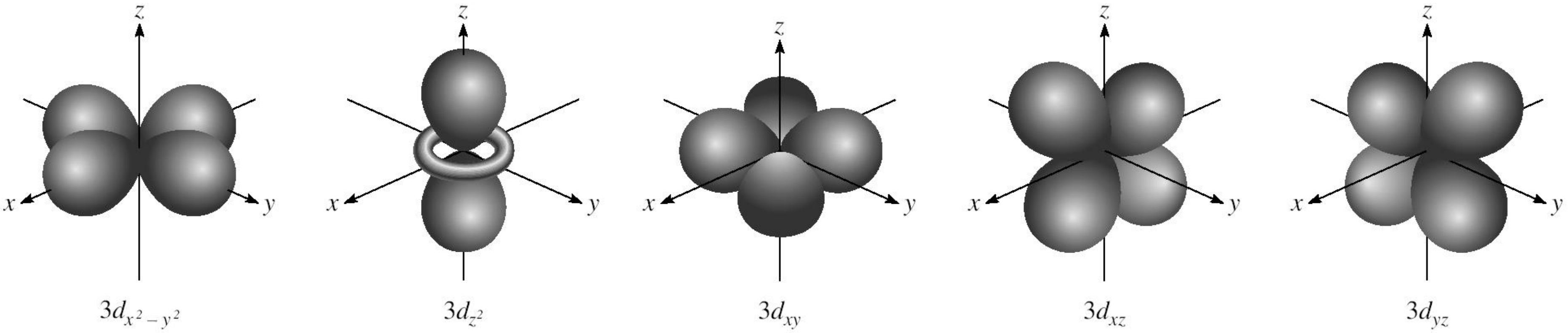
l = 0 (*s* orbitals)



l = 1 (*p* orbitals)



l = 2 (d orbitals)



Schrodinger Wave Equation

quantum numbers: (n, l, m_l, m_s)

magnetic quantum number m_l

for a given value of l

$m_l = -l, \ldots., 0, \ldots. +l$

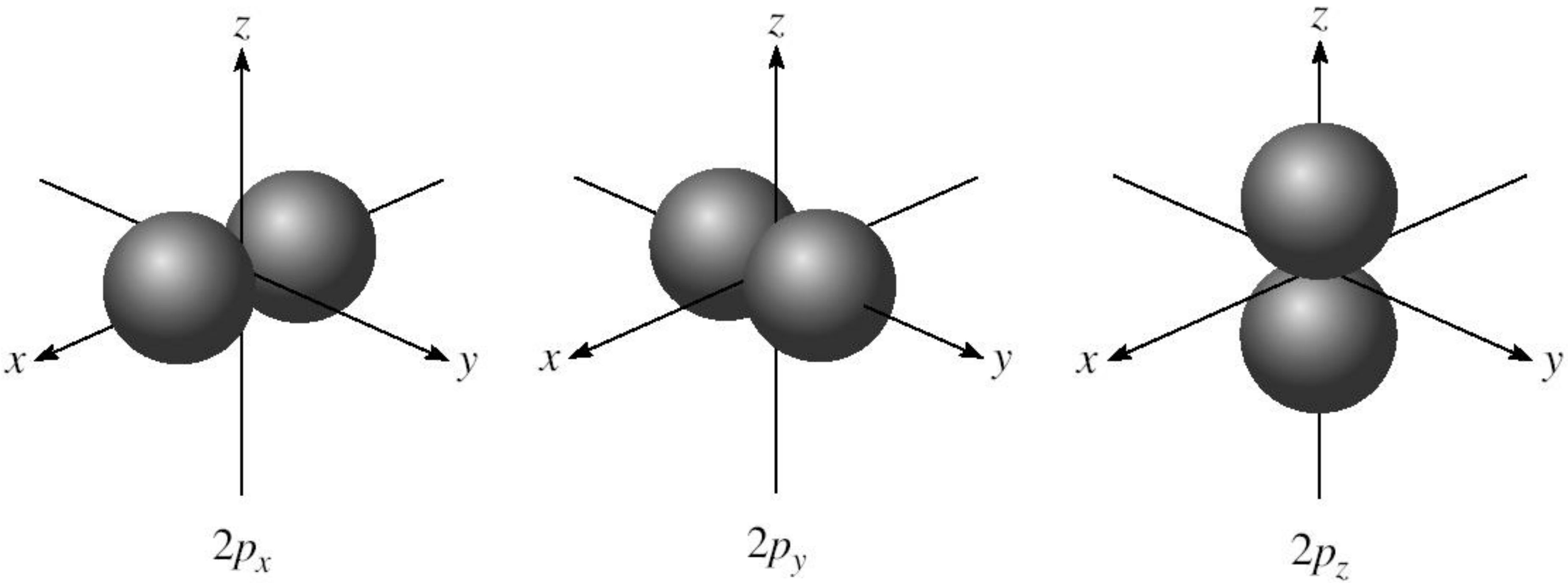
if $l = 1$ (p orbital), $m_l = -1, 0,$ **or** 1

if $l = 2$ (d orbital), $m_l = -2, -1, 0, 1,$ **or** 2

$\boxed{\text{orientation of the orbital in space}}$

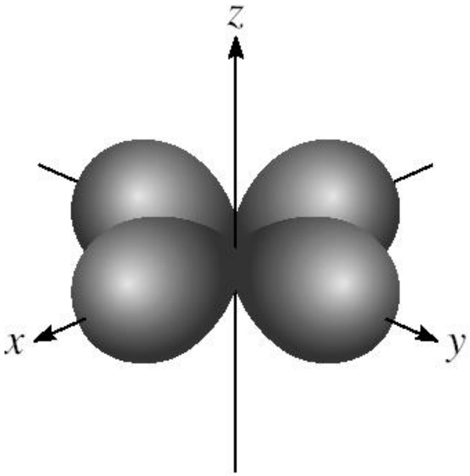
m_l = -1, 0, **or** 1

3 orientations is space

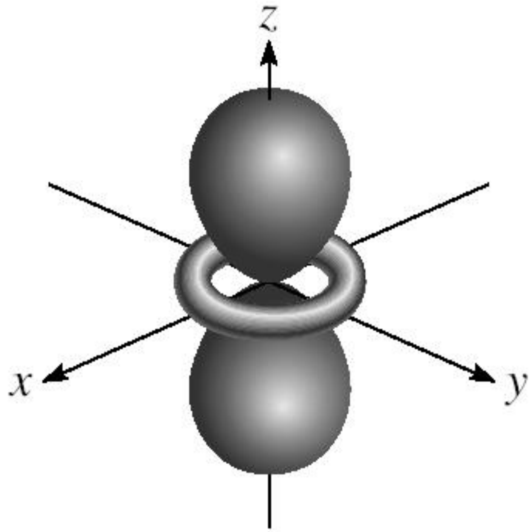


m_l = -2, -1, 0, 1, **or** 2

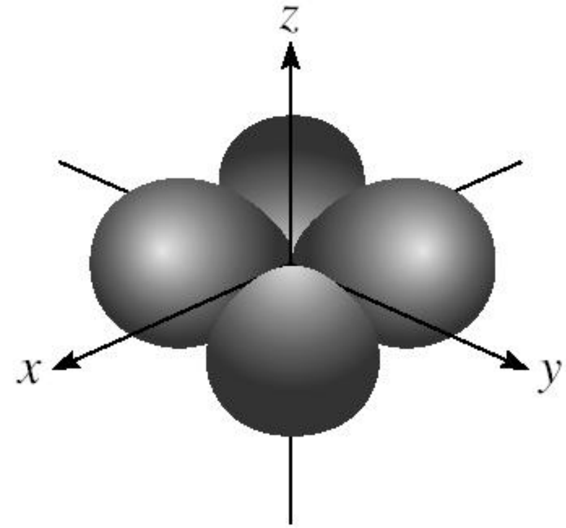
5 orientations is space



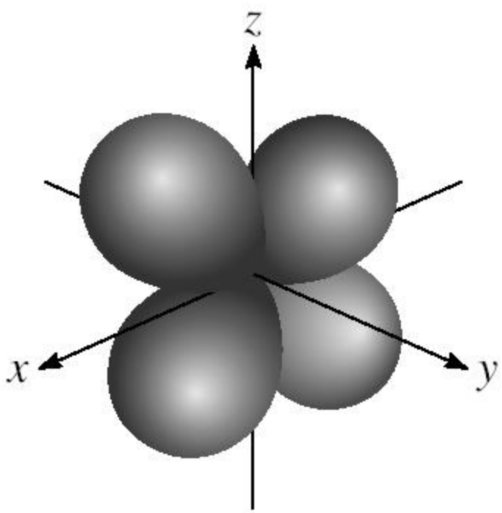
$3d_{x^2-y^2}$



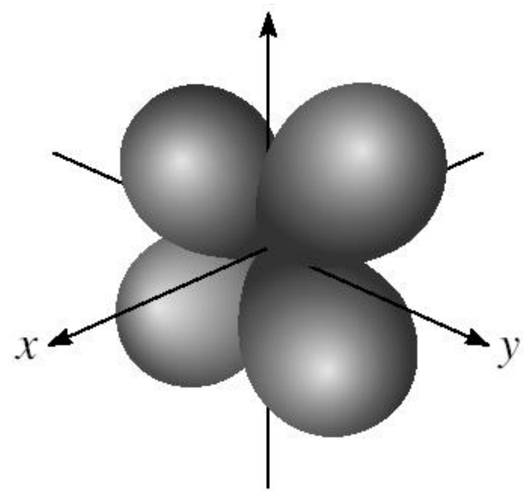
$3d_{z^2}$



$3d_{xy}$



$3d_{xz}$



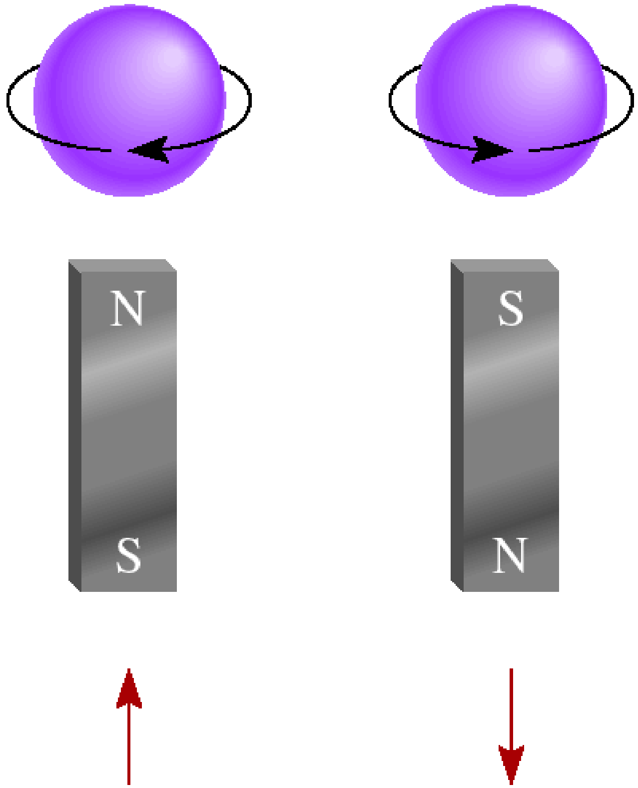
$3d_{yz}$

Schrodinger Wave Equation

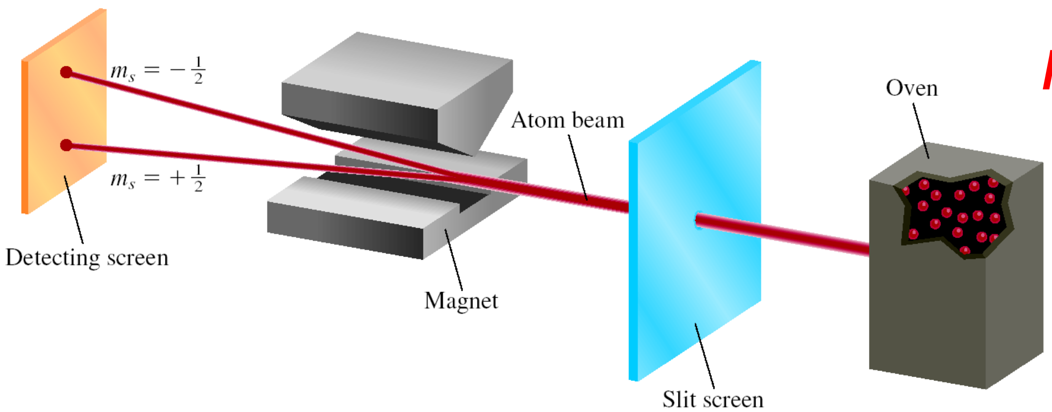
(n, l, m_l, m_s)

spin quantum number m_s

m_s = +½ **or** -½



m_s = +½ m_s = -½



Schrodinger Wave Equation

quantum numbers: (n, l, m_l, m_s)

Shell – electrons with the same value of n

Subshell – electrons with the same values of n **and** l

Orbital – electrons with the same values of $n, l,$ **and** m_l

How many electrons can an orbital hold?

If $n, l,$ and m_l are fixed, then $m_s = ½$ or $- ½$

$$\psi = (n, l, m_l, ½) \text{ or } \psi = (n, l, m_l, -½)$$

An orbital can hold 2 electrons

How many 2*p* orbitals are there in an atom?

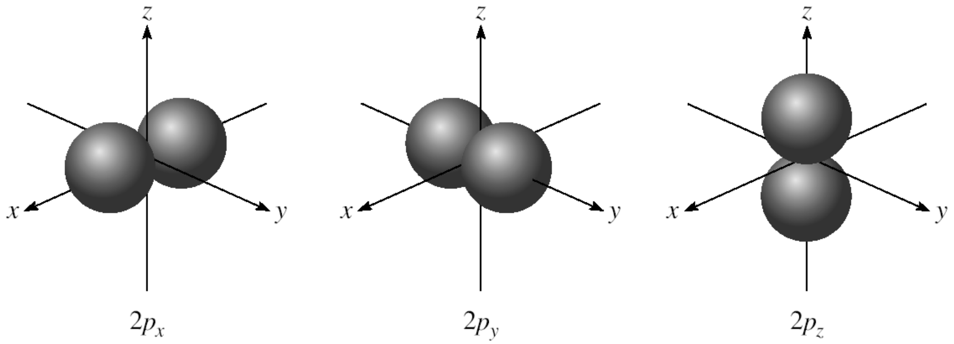
n=2

2*p*

l = 1

If l = 1, then m_l = -1, 0, or +1

3 orbitals



How many electrons can be placed in the 3*d* subshell?

n=3

3*d*

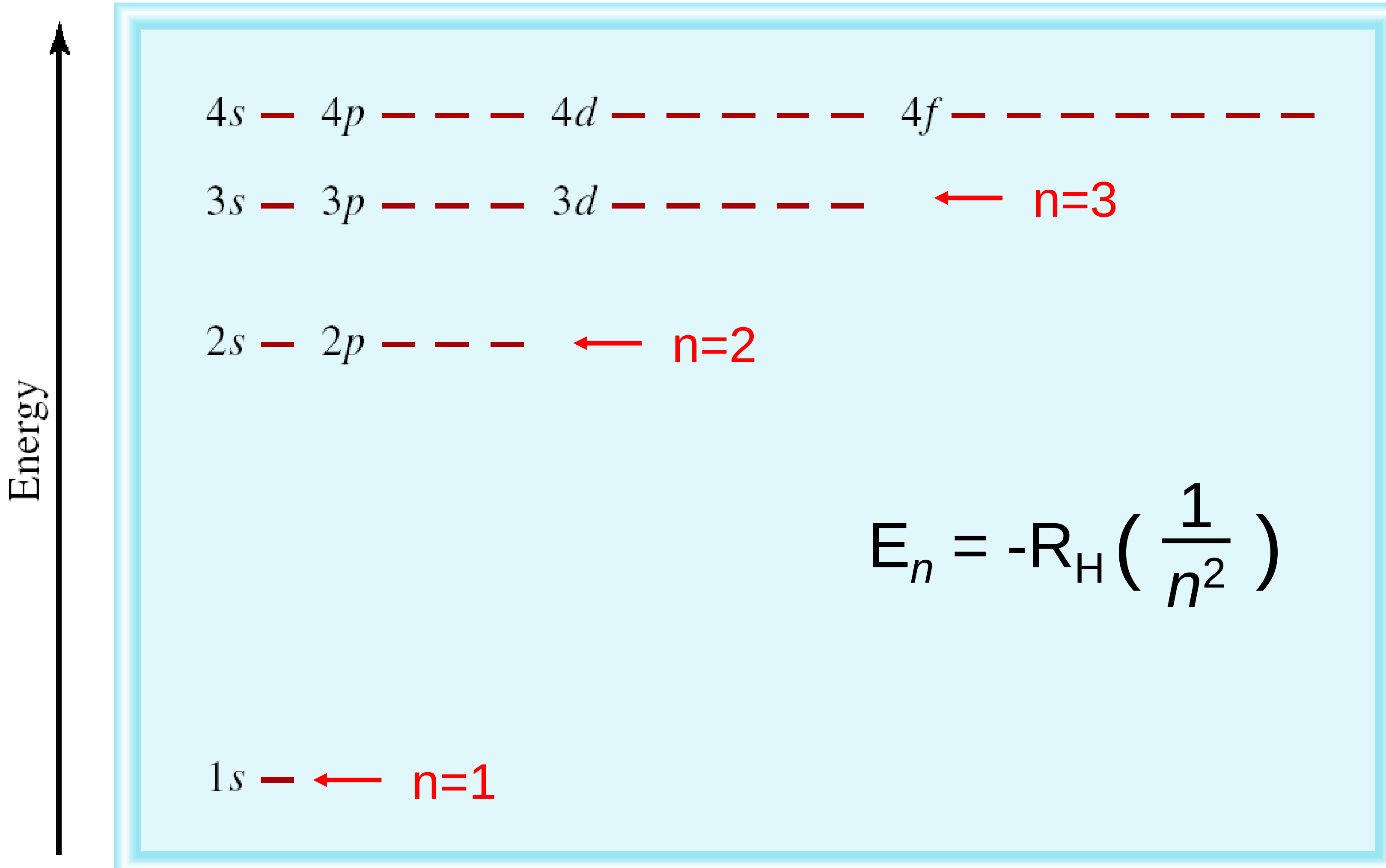
l = 2

If l = 2, then m_l = -2, -1, 0, +1, or +2

5 orbitals which can hold a total of 10 e^-

Energy of orbitals in a ***single*** electron atom

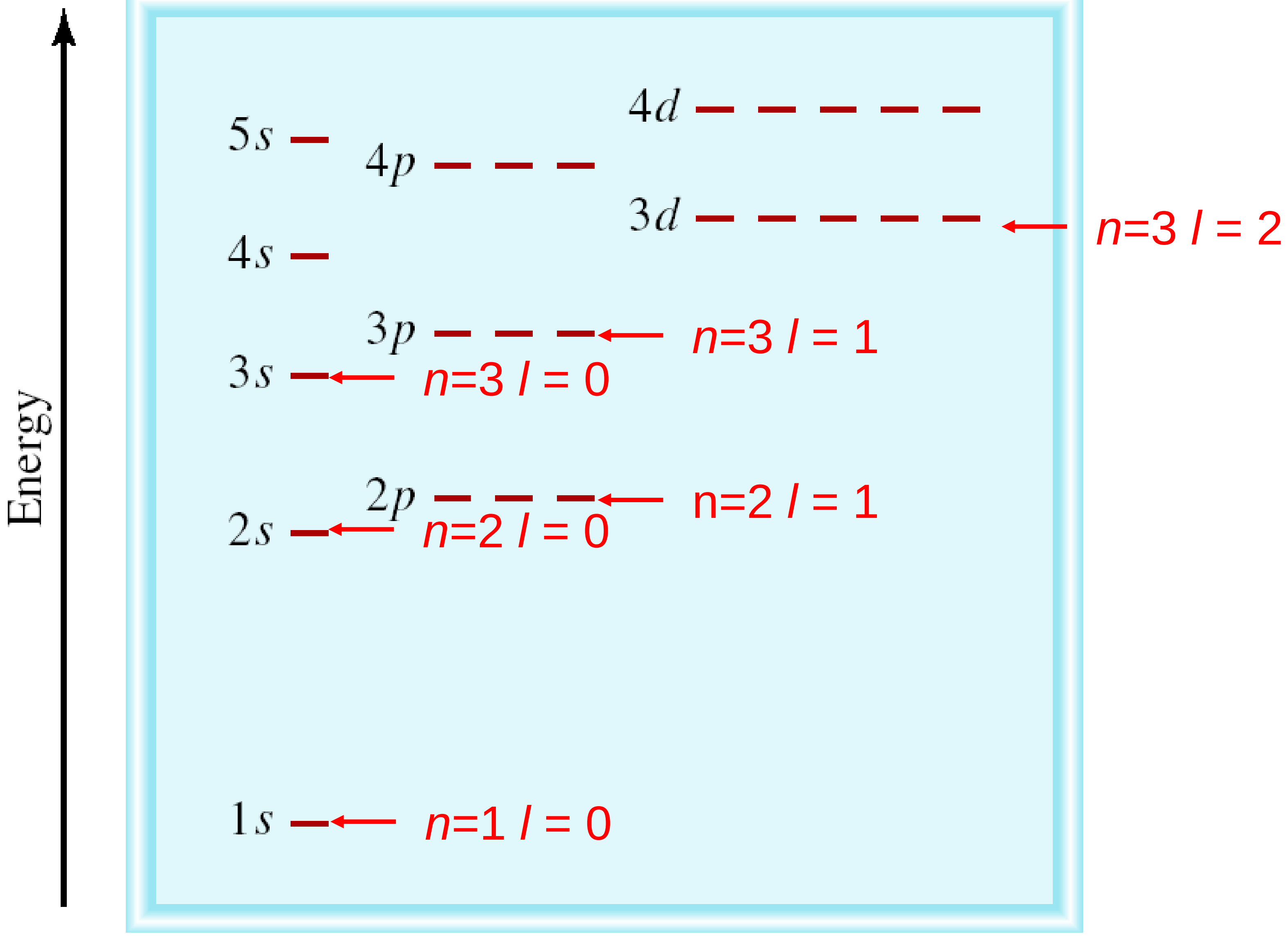
Energy only depends on principal quantum number ***n***



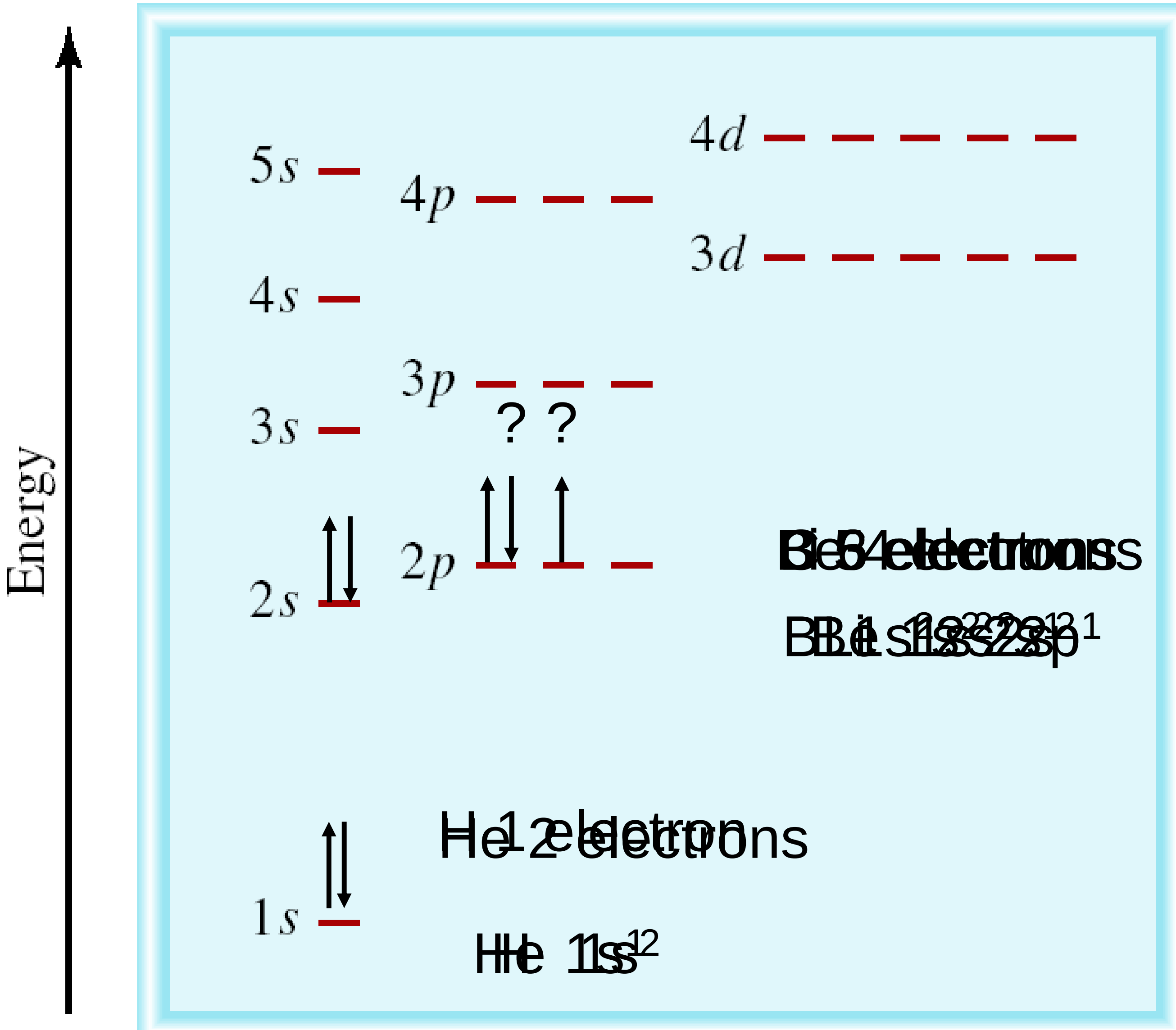
$$E_n = -R_H\left(\frac{1}{n^2}\right)$$

Energy of orbitals in a ***multi***-electron atom

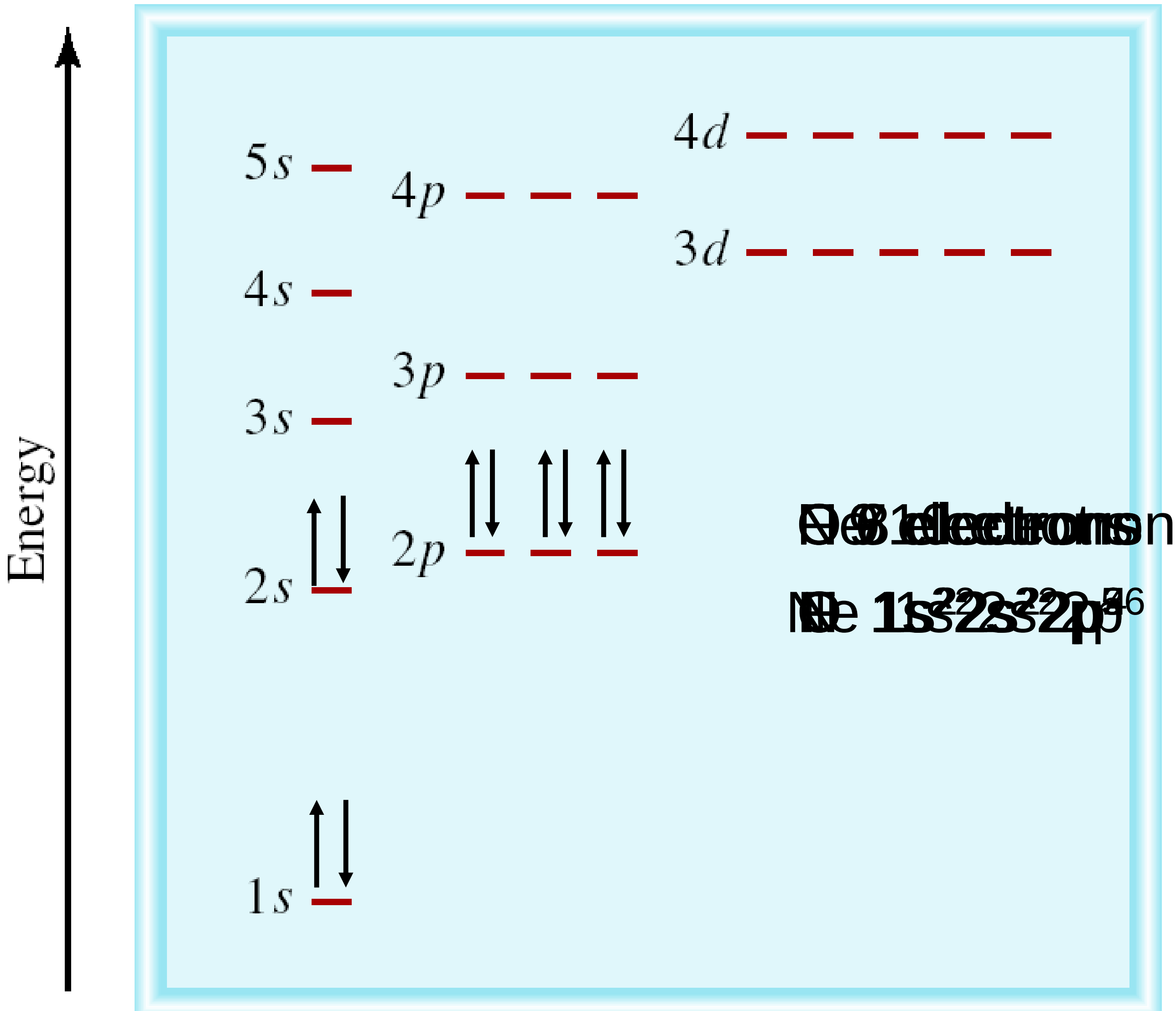
Energy depends on ***n*** and ***l***



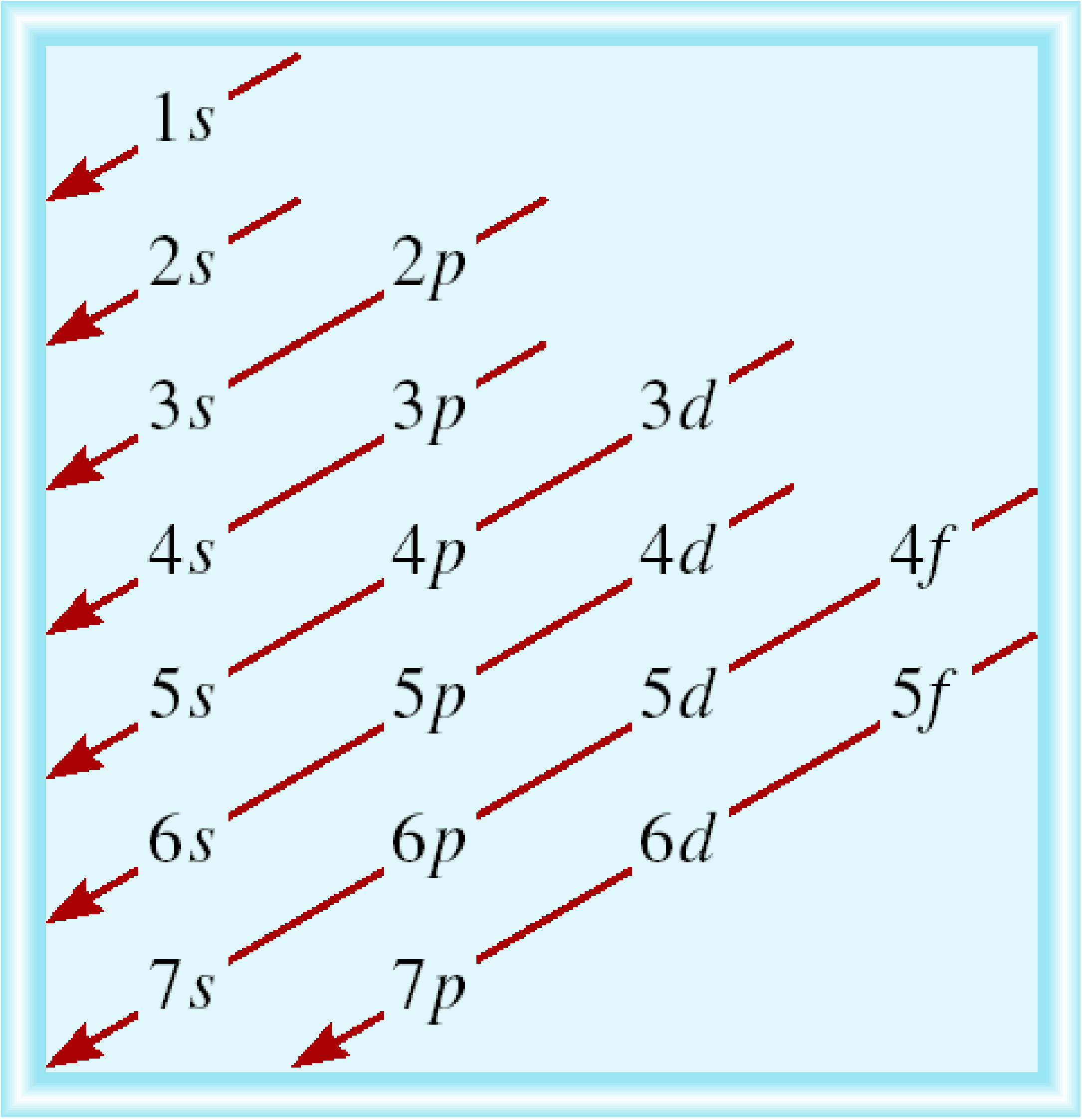
“Fill up” electrons in lowest energy orbitals (***Aufbau principle***)



The most stable arrangement of electrons in subshells is the one with the greatest number of parallel spins (***Hund's rule***).



Order of orbitals (filling) in multi-electron atom



1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s

Electron configuration is how the electrons are distributed among the various atomic orbitals in an atom.

number of electrons in the orbital or subshell

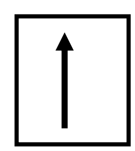
$1s^1$

principal quantum number ***n***

angular momentum quantum number ***l***

Orbital diagram

H



$1s^1$

What is the electron configuration of Mg?

Mg 12 electrons

1s < 2s < 2p < 3s < 3p < 4s

$1s^2 2s^2 2p^6 3s^2$ $2 + 2 + 6 + 2 = 12$ electrons

Abbreviated as $[Ne]3s^2$ $[Ne]\ 1s^2 2s^2 2p^6$

What are the possible quantum numbers for the last (outermost) electron in Cl?

Cl 17 electrons 1s < 2s < 2p < 3s < 3p < 4s

$1s^2 2s^2 2p^6 3s^2 3p^5$ $2 + 2 + 6 + 2 + 5 = 17$ electrons

Last electron added to 3p orbital

$n = 3$ $l = 1$ $m_l = -1, 0, \text{or} +1$ $m_s = \frac{1}{2}$ or $-\frac{1}{2}$

Outermost subshell being filled with electrons

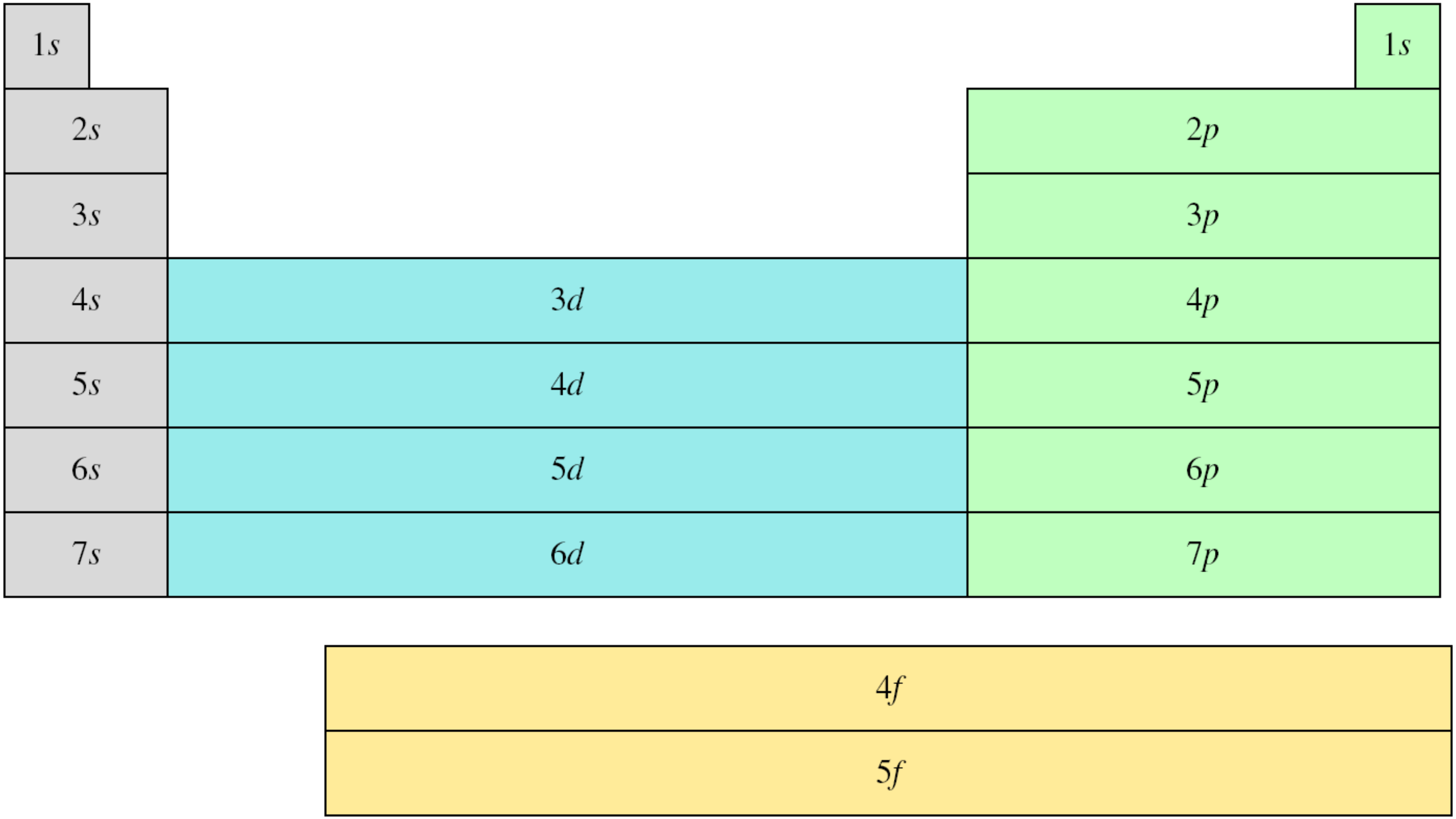


TABLE 7.3	The Ground-State Electron Configurations of the Elements*							
Atomic Number	**Symbol**	**Electron Configuration**	**Atomic Number**	**Symbol**	**Electron Configuration**	**Atomic Number**	**Symbol**	**Electron Configuration**
1	H	$1s^1$	38	Sr	$[Kr]5s^2$	75	Re	$[Xe]6s^2 4f^{14} 5d^5$
2	He	$1s^2$	39	Y	$[Kr]5s^2 4d^1$	76	Os	$[Xe]6s^2 4f^{14} 5d^6$
3	Li	$[He]2s^1$	40	Zr	$[Kr]5s^2 4d^2$	77	Ir	$[Xe]6s^2 4f^{14} 5d^7$
4	Be	$[He]2s^2$	41	Nb	$[Kr]5s^1 4d^4$	78	Pt	$[Xe]6s^1 4f^{14} 5d^9$
5	B	$[He]2s^2 2p^1$	42	Mo	$[Kr]5s^1 4d^5$	79	Au	$[Xe]6s^1 4f^{14} 5d^{10}$
6	C	$[He]2s^2 2p^2$	43	Tc	$[Kr]5s^2 4d^5$	80	Hg	$[Xe]6s^2 4f^{14} 5d^{10}$
7	N	$[He]2s^2 2p^3$	44	Ru	$[Kr]5s^1 4d^7$	81	Tl	$[Xe]6s^2 4f^{14} 5d^{10} 6p^1$
8	O	$[He]2s^2 2p^4$	45	Rh	$[Kr]5s^1 4d^8$	82	Pb	$[Xe]6s^2 4f^{14} 5d^{10} 6p^2$
9	F	$[He]2s^2 2p^5$	46	Pd	$[Kr]4d^{10}$	83	Bi	$[Xe]6s^2 4f^{14} 5d^{10} 6p^3$
10	Ne	$[He]2s^2 2p^6$	47	Ag	$[Kr]5s^1 4d^{10}$	84	Po	$[Xe]6s^2 4f^{14} 5d^{10} 6p^4$
11	Na	$[Ne]3s^1$	48	Cd	$[Kr]5s^2 4d^{10}$	85	At	$[Xe]6s^2 4f^{14} 5d^{10} 6p^5$
12	Mg	$[Ne]3s^2$	49	In	$[Kr]5s^2 4d^{10} 5p^1$	86	Rn	$[Xe]6s^2 4f^{14} 5d^{10} 6p^6$
13	Al	$[Ne]3s^2 3p^1$	50	Sn	$[Kr]5s^2 4d^{10} 5p^2$	87	Fr	$[Rn]7s^1$
14	Si	$[Ne]3s^2 3p^2$	51	Sb	$[Kr]5s^2 4d^{10} 5p^3$	88	Ra	$[Rn]7s^2$
15	P	$[Ne]3s^2 3p^3$	52	Te	$[Kr]5s^2 4d^{10} 5p^4$	89	Ac	$[Rn]7s^2 6d^1$
16	S	$[Ne]3s^2 3p^4$	53	I	$[Kr]5s^2 4d^{10} 5p^5$	90	Th	$[Rn]7s^2 6d^2$
17	Cl	$[Ne]3s^2 3p^5$	54	Xe	$[Kr]5s^2 4d^{10} 5p^6$	91	Pa	$[Rn]7s^2 5f^2 6d^1$
18	Ar	$[Ne]3s^2 3p^6$	55	Cs	$[Xe]6s^1$	92	U	$[Rn]7s^2 5f^3 6d^1$
19	K	$[Ar]4s^1$	56	Ba	$[Xe]6s^2$	93	Np	$[Rn]7s^2 5f^4 6d^1$

There are a few exceptions to the building-up order prediction for the ground state.

Chromium (Z=24) and copper (Z=29) have been found by experiment to have the following ground-state electron configurations:

Cr: $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,\boxed{3d^5\,4s^1}$

Cu: $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,\boxed{3d^{10}\,4s^1}$

In each case, the difference is in the 3*d* and 4*s* subshells.

There are several terms describing electron configurations that are important.

The **complete** electron configuration shows every subshell explicitly.

Br: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^5$

The **noble-gas configuration** substitutes the preceding noble gas for the core configuration and explicitly shows subshells beyond that.

Br: $[Ar]3d^{10}4s^{2}4p^{5}$

The **valence configuration** consists of the electrons outside the noble-gas or pseudo-noble-gas core.

Br: $4s^2 4p^5$

?

Write the complete electron configuration of the arsenic atom, As, using the building-up principle.

For arsenic, As, Z = 33.

$\boxed{1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2 4p^3}$

? What are the electron configurations for the valence electrons of arsenic and zinc?

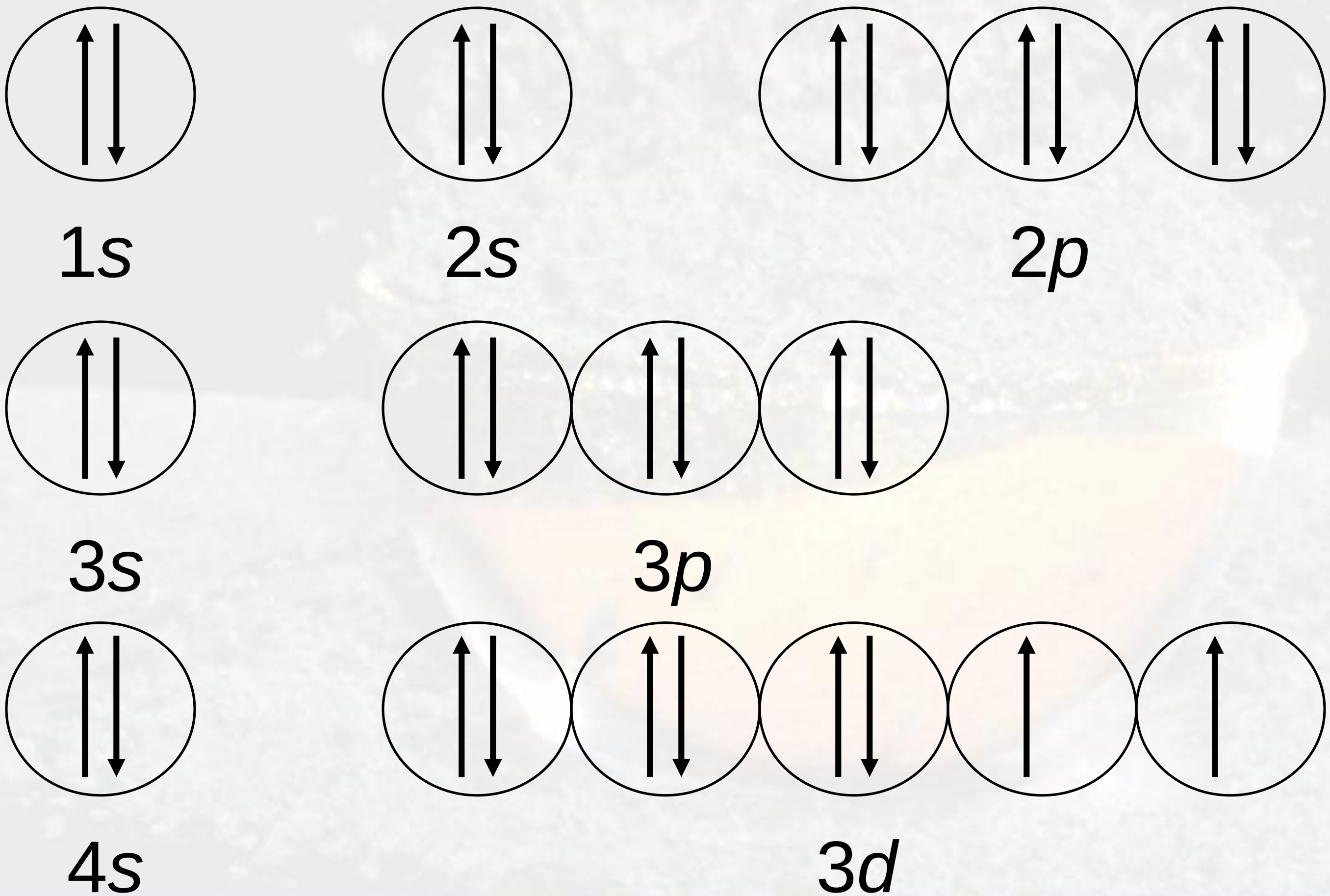
Arsenic is in period 4, Group VA.
Its valence configuration is $\boxed{4s^2 4p^3.}$

Zinc, Z = 30, is a transition metal in the first transition series.
Its noble-gas core is Ar, Z = 18.
Its valence configuration is $\boxed{4s^2 3d^{10}.}$

For nitrogen, the orbital diagram would be

Write an orbital diagram for the ground state of the nickel atom.

For nickel, $Z = 28$.



The lowest-energy configuration of an atom is called its **ground state.**

Any other allowed configuration represents an **excited state.**

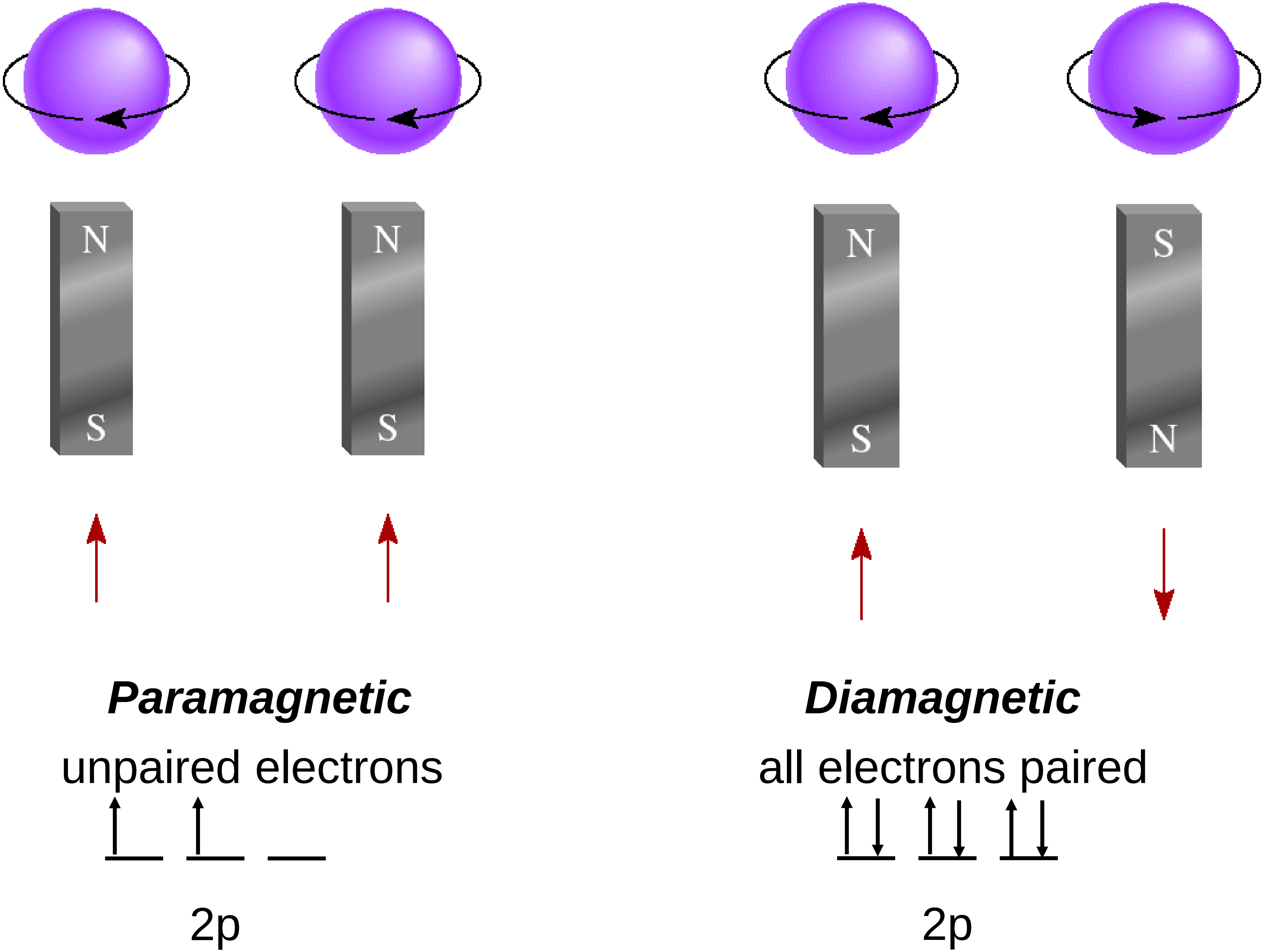
?

Which of the following electron configurations or orbital diagrams are allowed and which are not allowed by the Pauli exclusion principle? If they are not allowed, explain why?

a. $1s^2 2s^1 2p^3$
b. $1s^2 2s^1 2p^8$
c. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8$
d. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{11}$
e. 

$1s$ $2s$

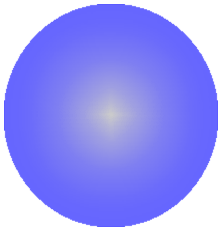
a. Allowed; excited.
b. p^8 is not allowed.
c. Allowed; excited.
d. d^{11} is not allowed.
e. Not allowed; electrons in one orbital must have opposite spins.



N
S
N
S
N
S
S
N
Paramagnetic
unpaired electrons
2p
Diamagnetic
all electrons paired
2p

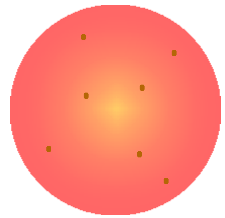
Quantum Mechanical Model of Atom

1803



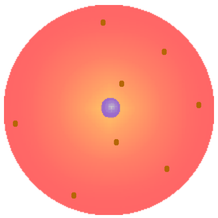
Dalton proposes the indivisible unit of an element is the atom.

1904



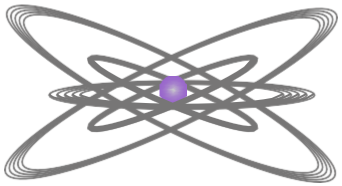
Thomson discovers electrons, believed to reside within a sphere of uniform positive charge (the "plum pudding" model).

1911



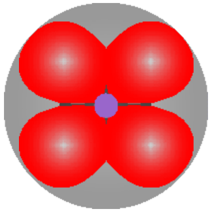
Rutherford demonstrates the existence of a positively charged nucleus that contains nearly all the mass of an atom.

1913



Bohr proposes fixed circular orbits around the nucleus for electrons.

1926



In the current model of the atom, electrons occupy regions of space (orbitals) around the nucleus determined by their energies.