Lecture for Bob

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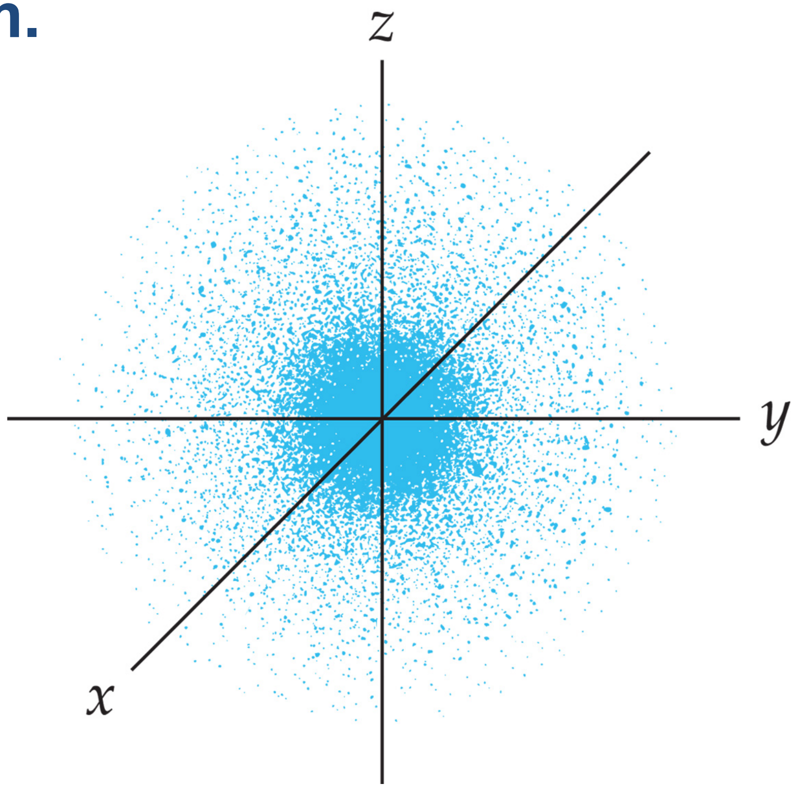
Quantum Mechanics

Plot of Ψ^2 for hydrogen atom.

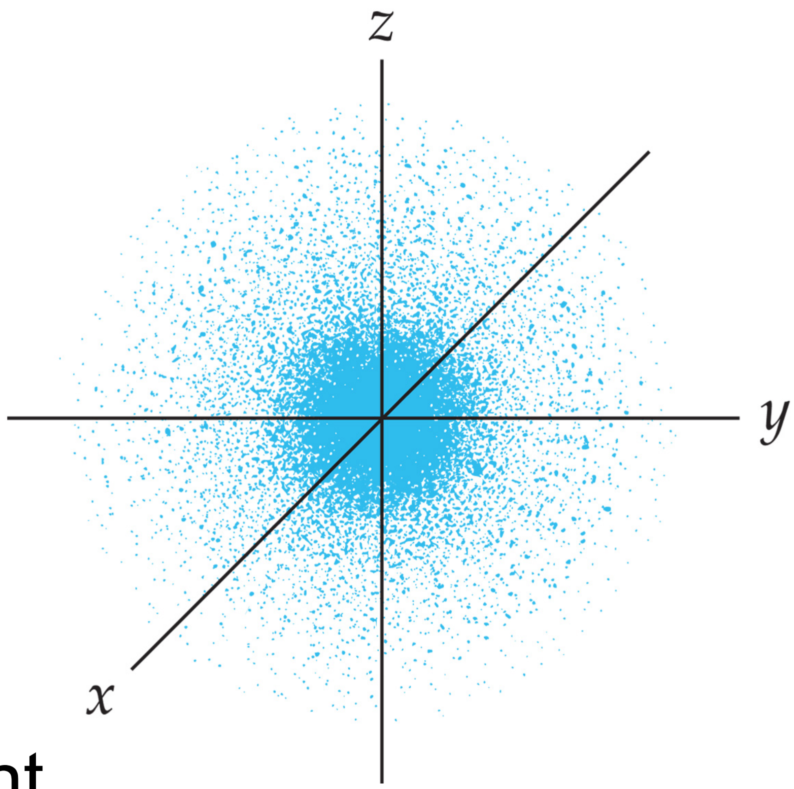
The closest thing we now have to a physical picture of an electron.



90% contour, will find electron in blue stuff 90% of the time.

Quantum Mechanics

- The wave equation is designated with a lower case Greek *psi* (ψ).
- The square of the wave equation, ψ^2, gives a probability density map of where an electron has a certain statistical likelihood of being at any given instant in time.



Quantum Numbers

- Solving the wave equation gives a set of wave functions, or orbitals, and their corresponding energies.
- Each orbital describes a spatial distribution of electron density.
- An orbital is described by a set of three quantum numbers (integers)
- Why three?

Quantum numbers

- 3 dimensions.

- Need three quantum numbers to define a given wavefunction.
- Another name for wavefunction: Orbital (because of Bohr).

Principal Quantum Number, *n*

- The principal quantum number, *n*, describes the **energy level** on which the orbital resides.
- The values of *n* are integers > 0.
- 1, 2, 3,...n.

Azimuthal Quantum Number, *l*

- defines **shape** of the orbital.
- Allowed values of *l* are integers ranging from 0 to $n - 1$.
- We use letter designations to communicate the different values of *l* and, therefore, the shapes and types of orbitals.

Azimuthal Quantum Number, *l*

$l = 0, 1 \ldots, n-1$

Value of *l*	0	1	2	3
Type of orbital	*s*	*p*	*d*	*f*

So each of these letters corresponds to a shape of orbital.

Magnetic Quantum Number, m_l

- Describes the **three-dimensional orientation** of the orbital.
- Values are integers ranging from -*l* to *l*:

$$-l \leq m_l \leq l.$$

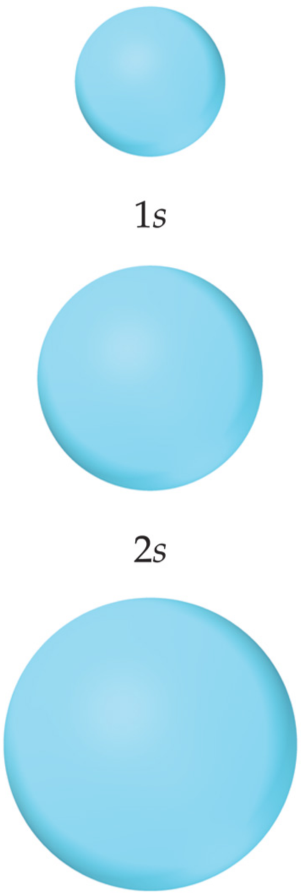
- Therefore, on any given energy level, there can be up to:
- 1 *s (l=0)* orbital (m_l=0),
- 3 *p (l=1)* orbitals, (m_l=-1,0,1)
- 5 *d (l=2)* orbitals, (m_l=-2,-1,0,1,2)
- 7 *f (l=3)* orbitals, (m_l=-3,-2,-1,0,1,2,3)

Magnetic Quantum Number, m_l

- Orbitals with the same value of *n* form a shell.
- Different orbital types within a shell are subshells (s, p, d, f).

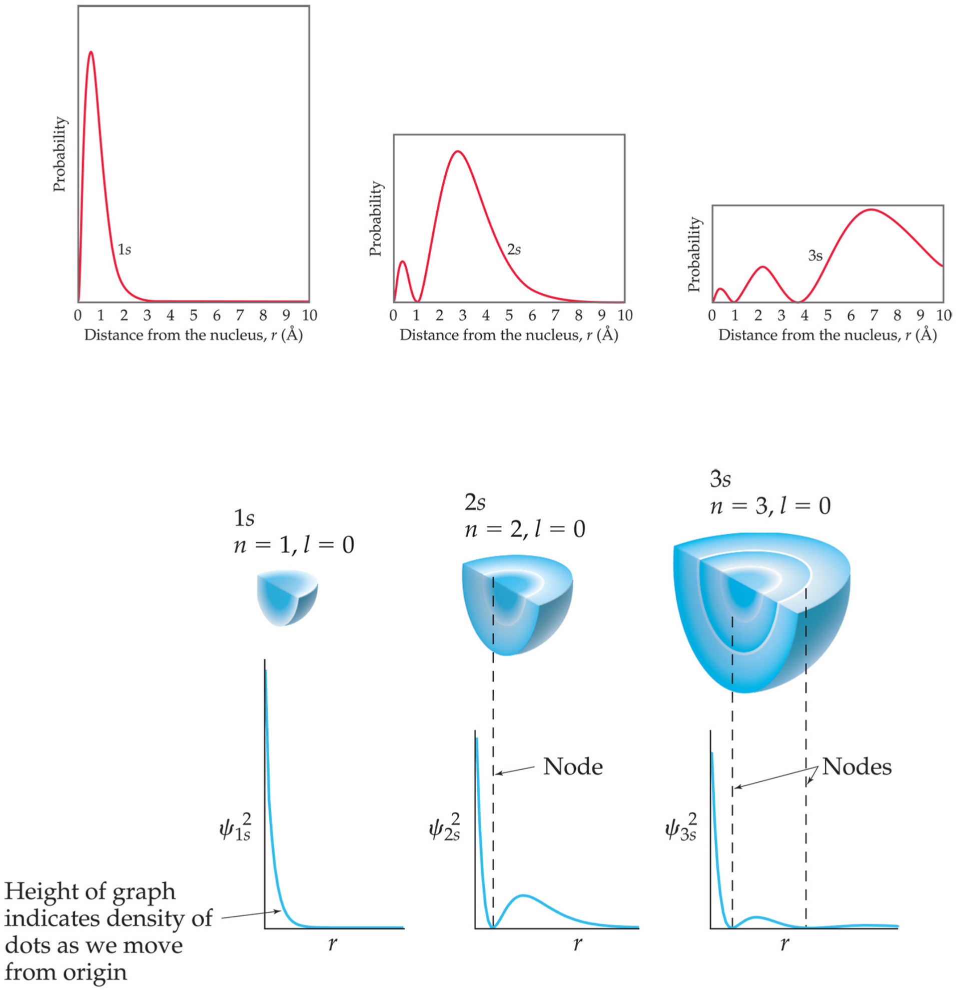
n	Possible Values of *l*	Subshell Designation	Possible Values of m_l	Number of Orbitals in Subshell	Total Number of Orbitals in Shell
1	0	1*s*	0	1	1
2	0	2*s*	0	1	
	1	2*p*	1, 0, −1	3	4
3	0	3*s*	0	1	
	1	3*p*	1, 0, −1	3	
	2	3*d*	2, 1, 0, −1, −2	5	9
4	0	4*s*	0	1	
	1	4*p*	1, 0, −1	3	
	2	4*d*	2, 1, 0, −1, −2	5	
	3	4*f*	3, 2, 1, 0, −1, −2, −3	7	16

s Orbitals



- Value of l = 0.
- Spherical in shape.
- Radius of sphere increases with increasing value of n.

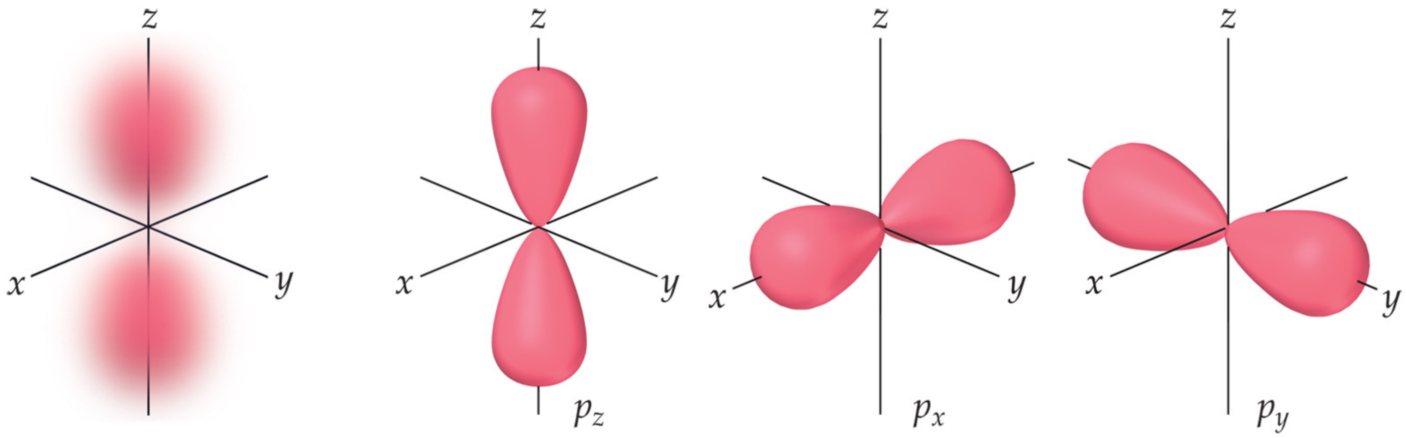
s Orbitals



s orbitals possess *n*−1 nodes, or regions where there is 0 probability of finding an electron.

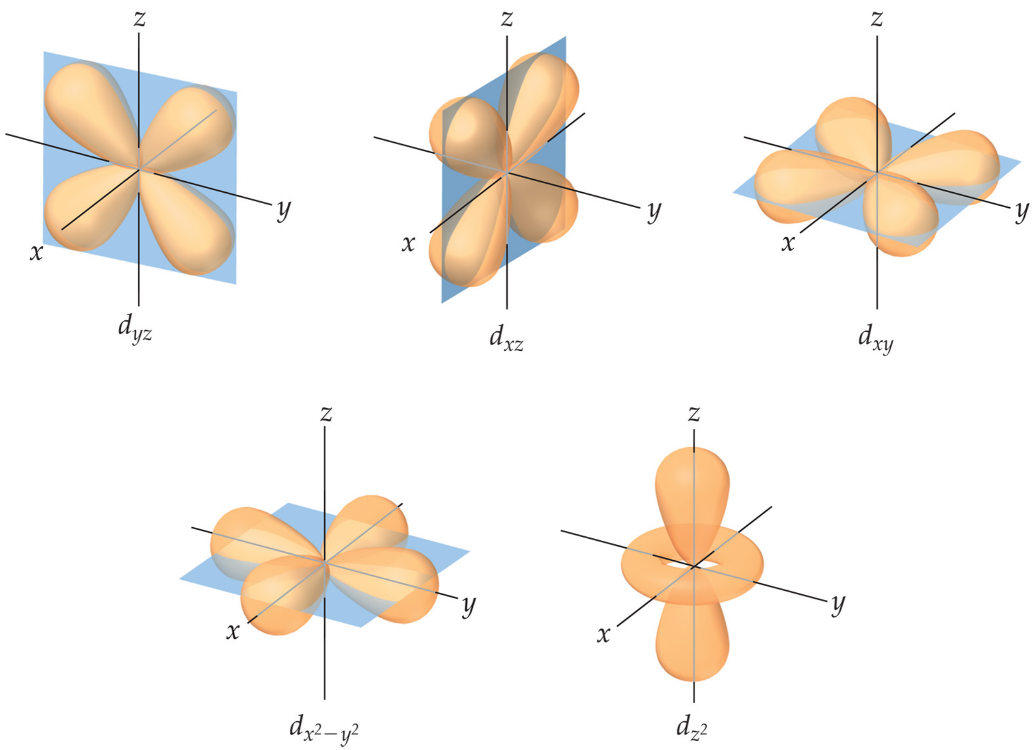
p Orbitals

- Value of *l* = 1.
- Have two lobes with a nodal plane between them.



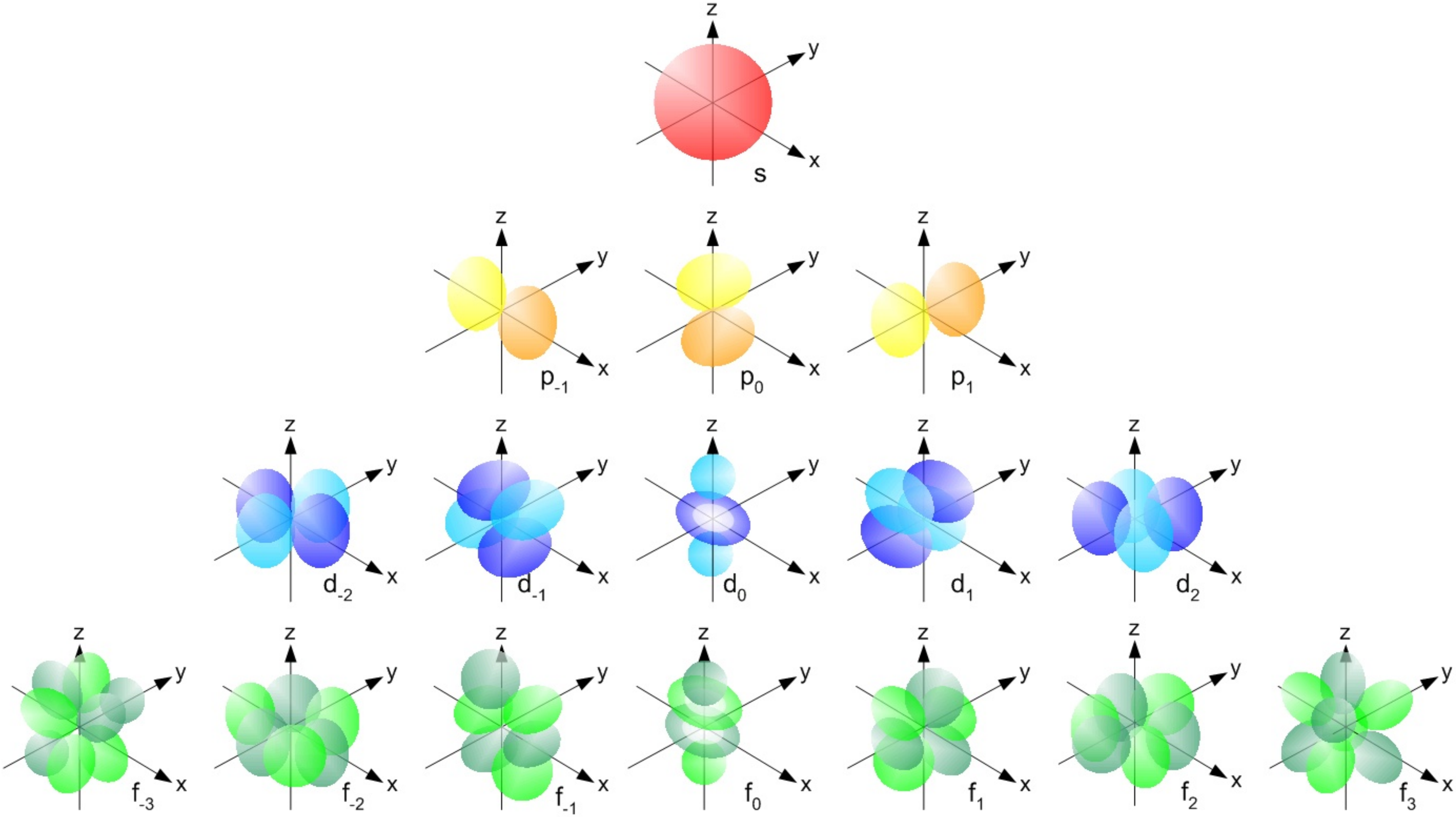
Note: always 3 p orbitals for a given n

d Orbitals



- Value of *l* is 2.
- 2 nodal planes
- Four of the five orbitals have 4 lobes; the other resembles a *p* orbital with a doughnut around the center.

Note: always 5 d orbitals for a given n.


s
p-1
p0
p1
d-2
d-1
d0
d1
d2
f-3
f-2
f-1
f0
f1
f2
f3
x
y
z

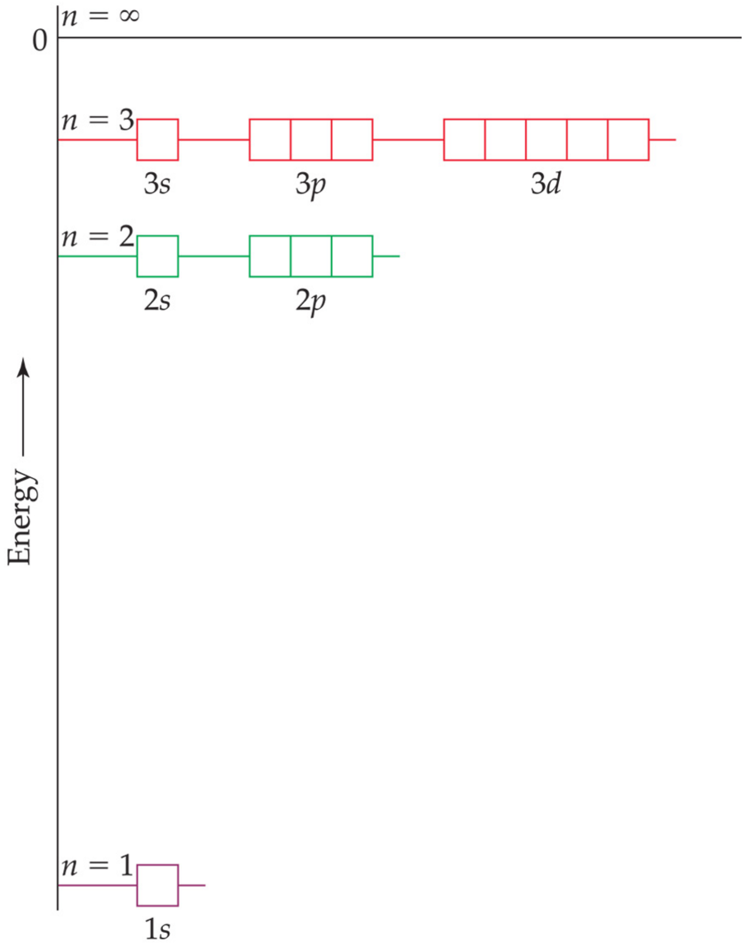
Orbitals and nodes

Orbital	Symmetry	Node geometry	Spherical nodes/shell*	Orbitals/set
s	spherical	spherical	n-1	1
p	cylindrical around x, y, or z axis	1 planar remainder spherical	n - 1	3
d	complex	2 planar surfaces diagonal to Cartesian axis; remainder spherical	n - 2	5
f	complex	complex	n - 3	7

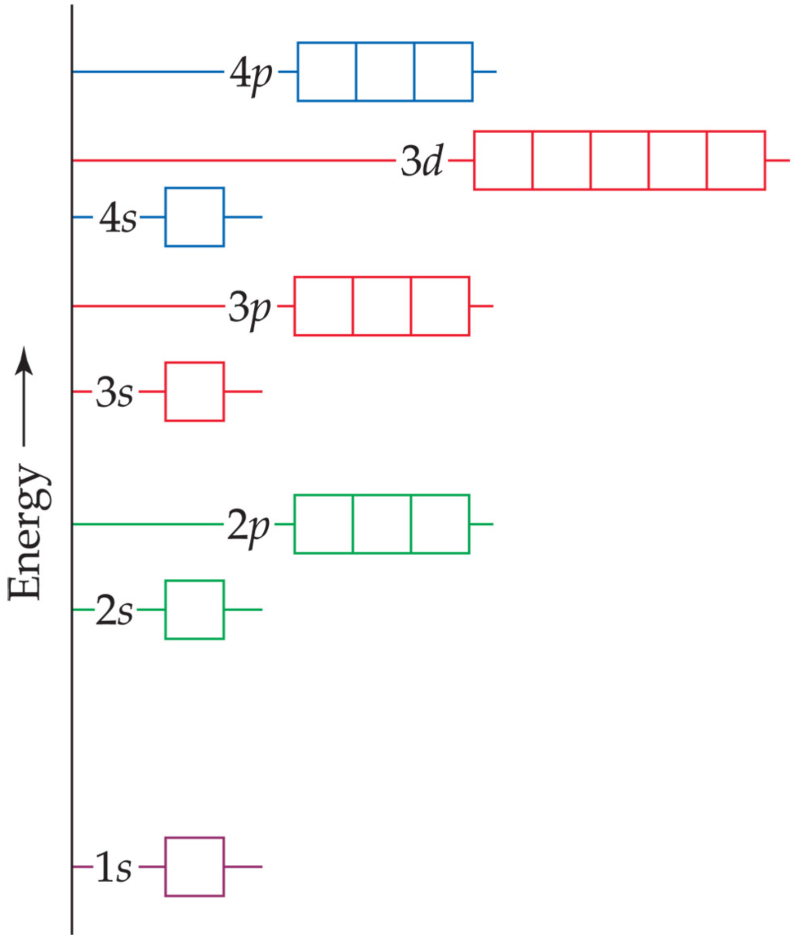
* n = the shell, with n = 1 the ground state or lowest possible energy shell. Thus n may have values from 1 - infinity.

Energies of Orbitals

- For a one-electron hydrogen atom, orbitals on the same energy level have the same energy.
- That is, they are degenerate.

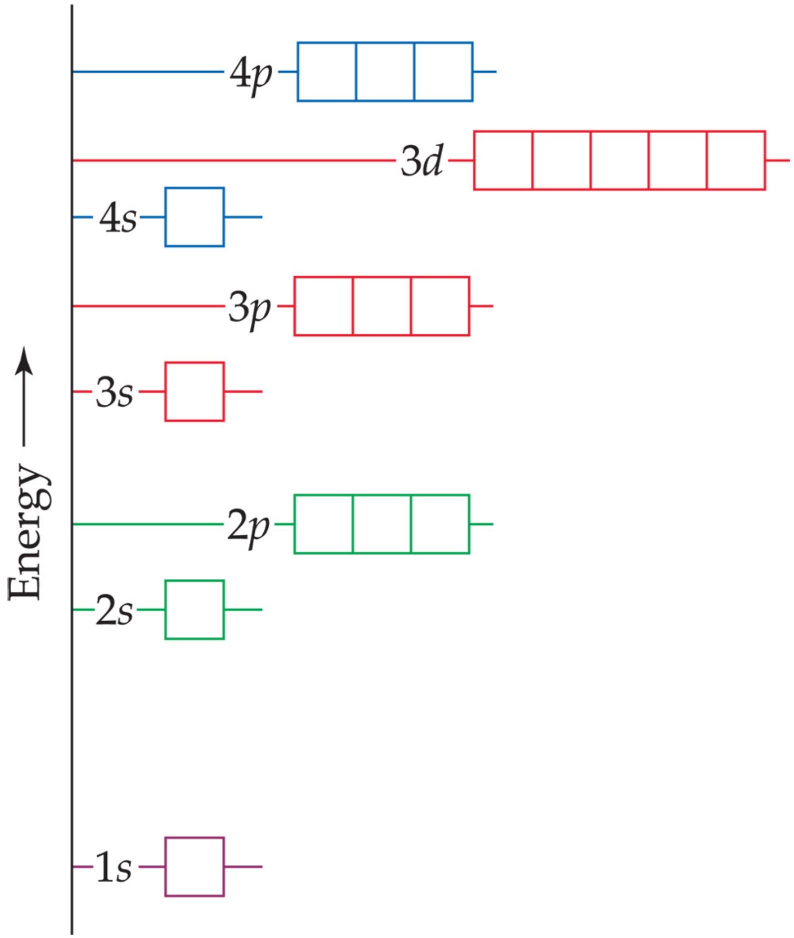


Energies of Orbitals



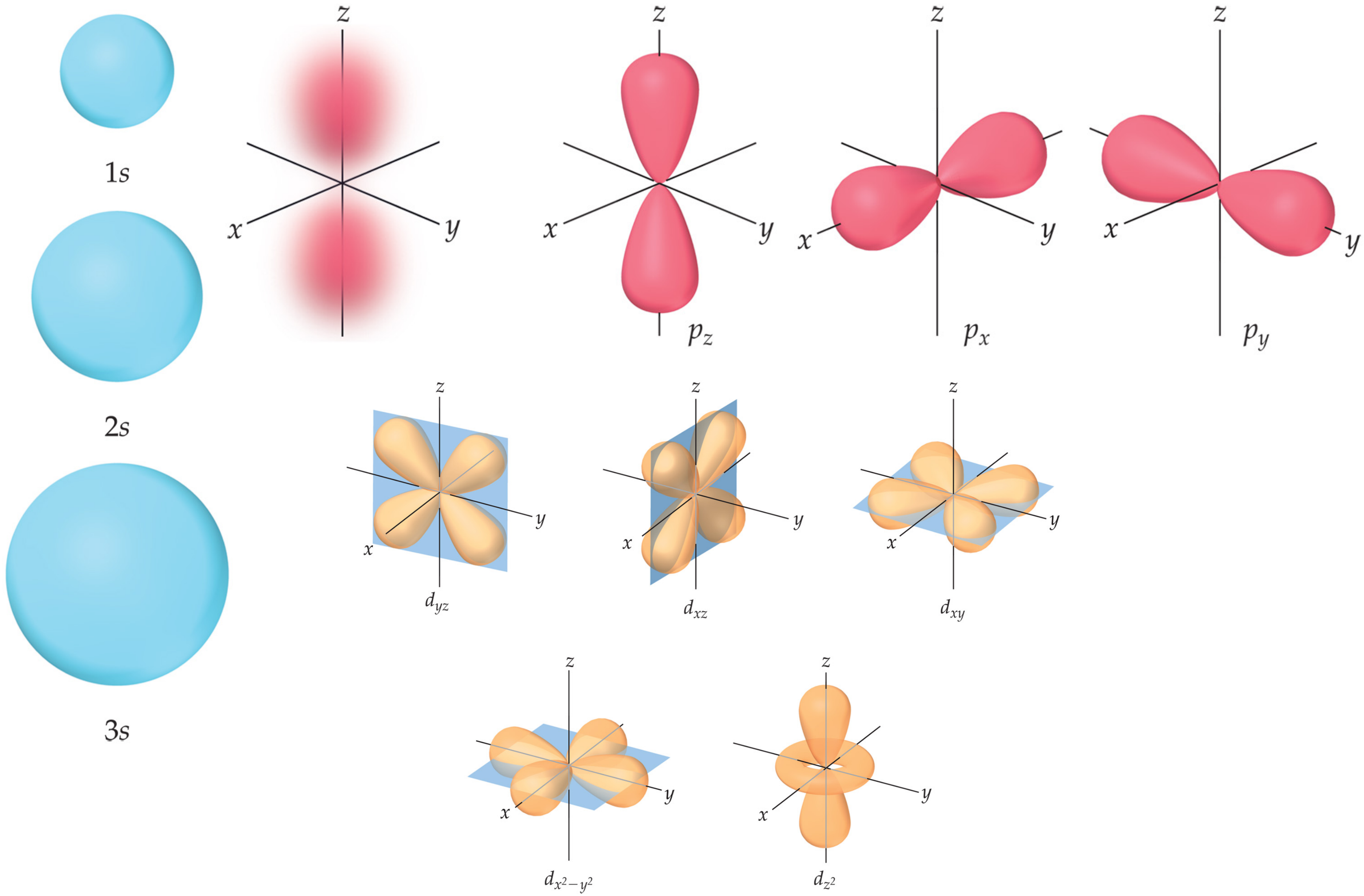
- As the number of electrons increases, though, so does the repulsion between them.
- Therefore, in many-electron atoms, orbitals on the same energy level are no longer degenerate.

Energies of Orbitals



- For a given energy level (n):
- Energy:
- s<p<d<f
- s lowest energy, where electrons go first
- Next p
- Then d

Why?



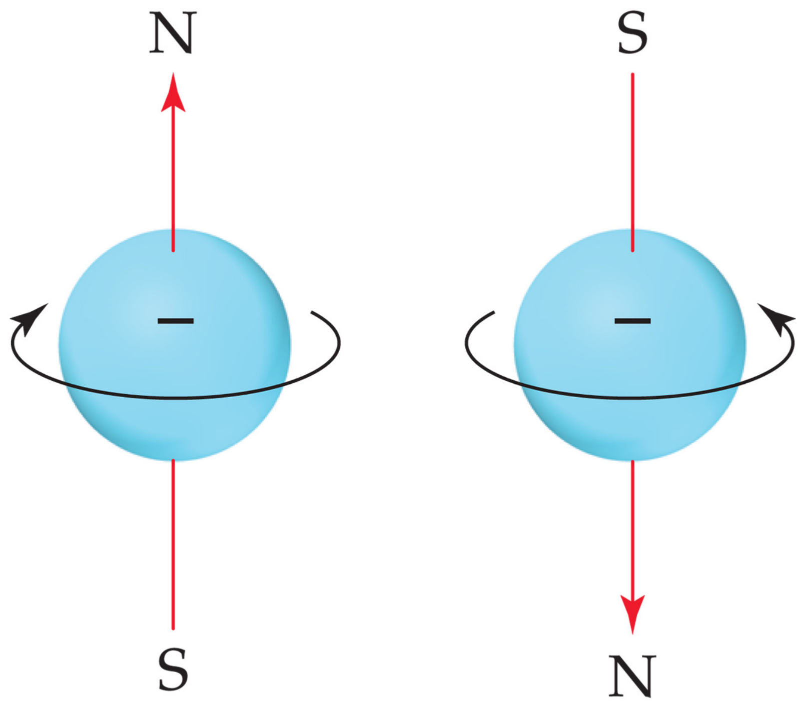
The closer to the nucleus, the lower the energy

The problem with quantum mechanics

- It's not hard to solve equations for the various wavefunctions if they are all alone (like H)
- The problem is what happens in the presence of other electrons
- The electron interaction problem
- Many body problem
- Electron probabilities overlap a lot, must interact a lot, repulsion keeps them from ever "touching"

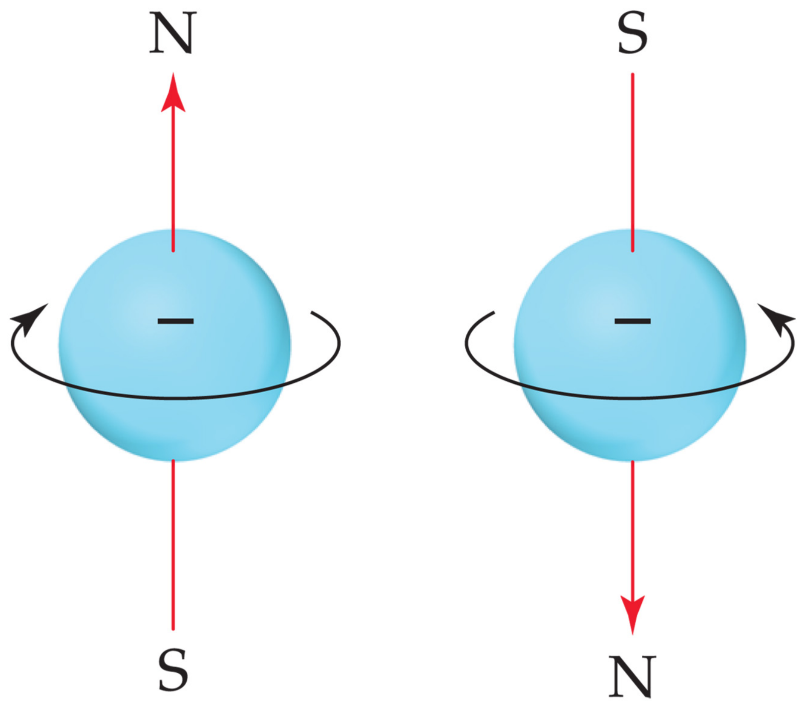
Spin Quantum Number, m_s

- A fourth dimension required. Why?



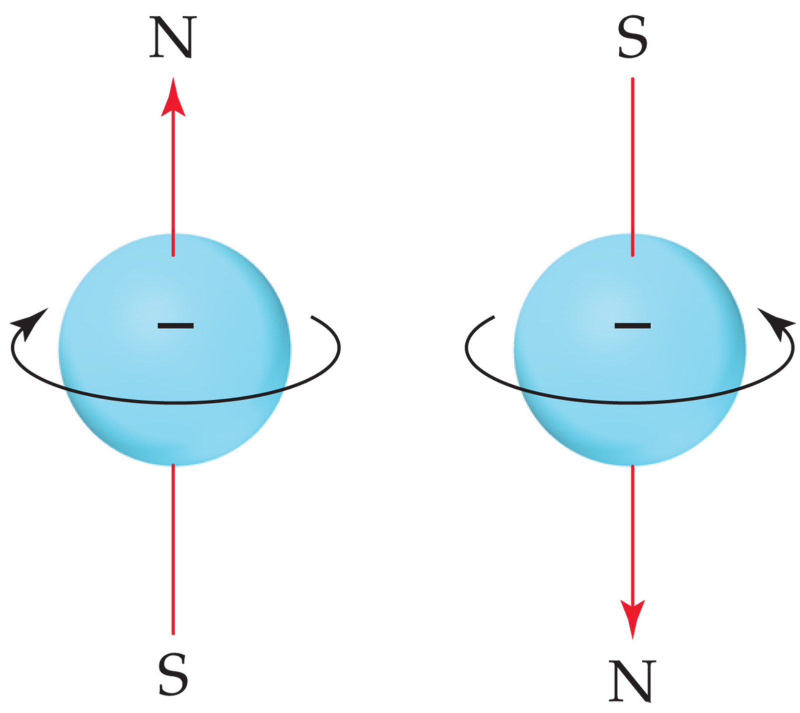
Spin Quantum Number, m_s

- A fourth dimension required. Why?
- Time. Adding time changes E
- Another integer (quantum number) needed.
- Time *dependent Schroedinger equation.*

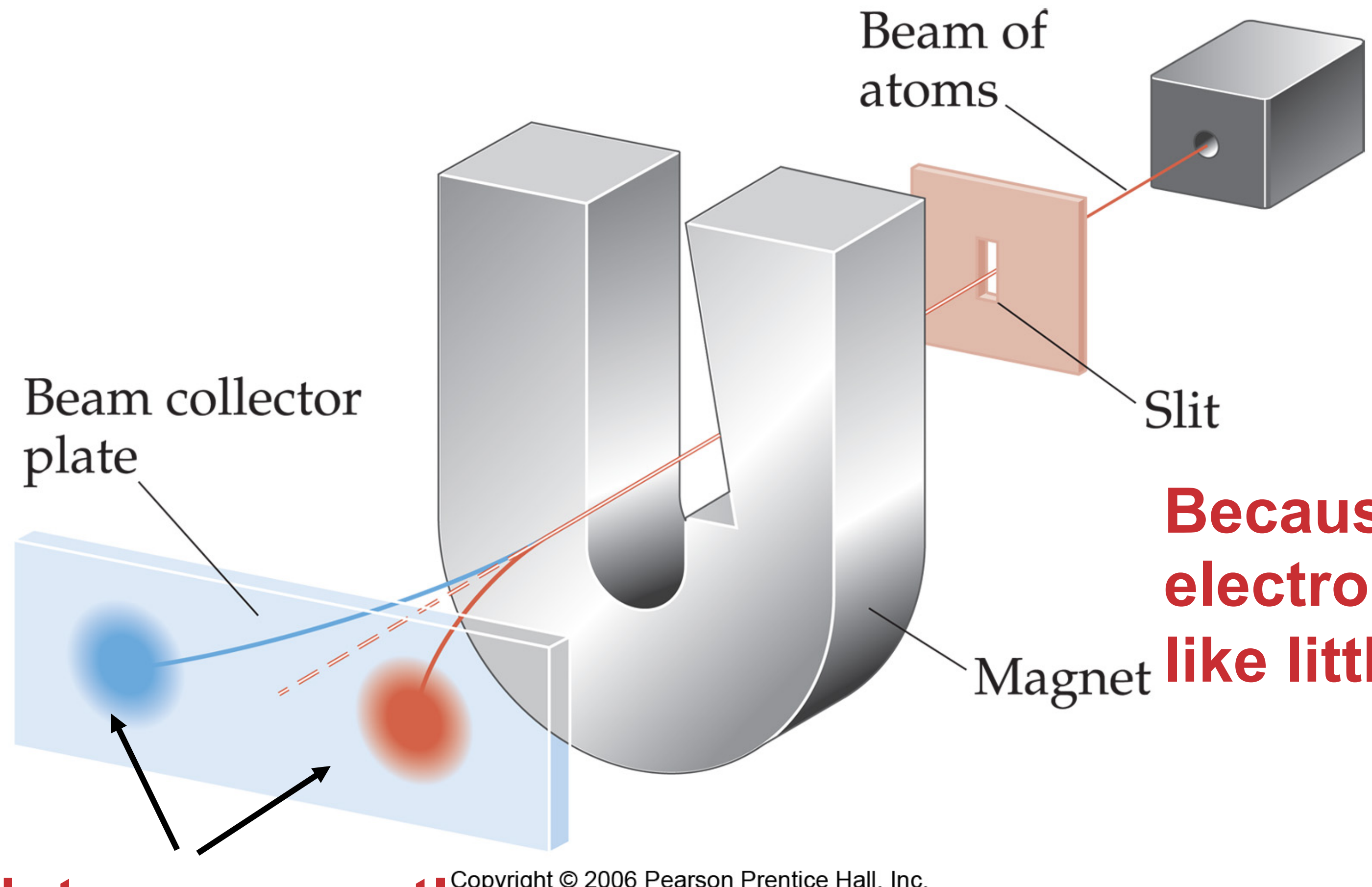


Spin Quantum Number, m_s

- This leads to a fourth quantum number, the spin quantum number m_s.
- The spin quantum number has only 2 values **+1/2 and -1/2**
- **Describes magnetic field vector of electron**



Why do we call it "spin"

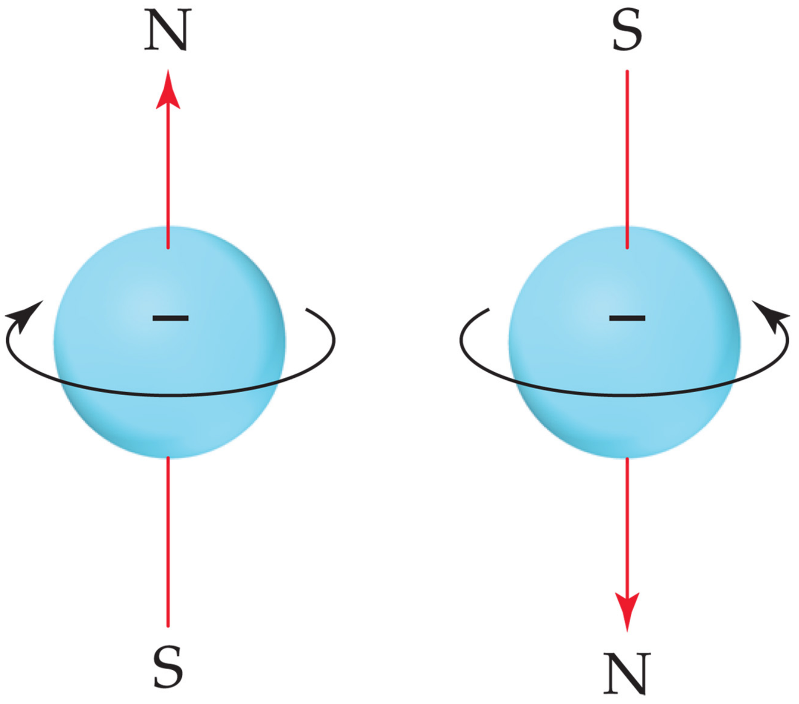


Because electrons behave like little magnets

Note: apparently only two values for the magnetic field

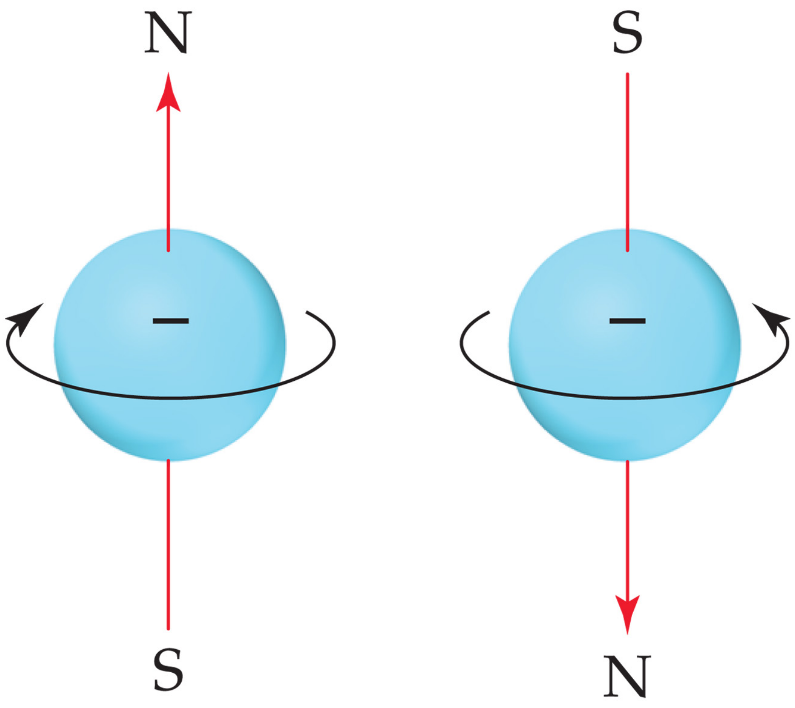
Why do we call it "spin"

- And charges that spin produce magnetic fields



Pauli Exclusion Principle

- No two electrons in the same atom can have exactly the same energy.
- For example, no two electrons in the same atom can have identical sets of quantum numbers.



Electron Configurations Every electron has a name

- Name of each electron unique
- Name consists of four numbers:
- n, l, m_l, m_s
- We must learn to name our electrons
- There is a lot in the "name" of an electron.

$4p^5$

Electron Configurations

$4p^5$

- Distribution of all electrons in an atom
- Consist of
  - Number denoting the energy level

Electron Configurations

$4p^5$

- Distribution of all electrons in an atom
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  - Letter denoting the type of orbital

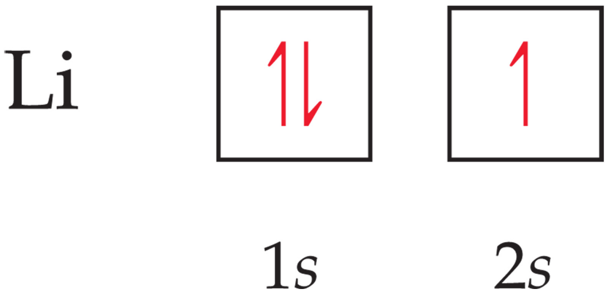
Electron Configurations

$4p^5$

- Distribution of all electrons in an atom.
- Consist of
  - Number denoting the energy level.
  - Letter denoting the type of orbital.
  - Superscript denoting the number of electrons in those orbitals.

Orbital Diagrams

- Each box represents one orbital.
- Half-arrows represent the electrons.
- The direction of the arrow represents the spin of the electron.



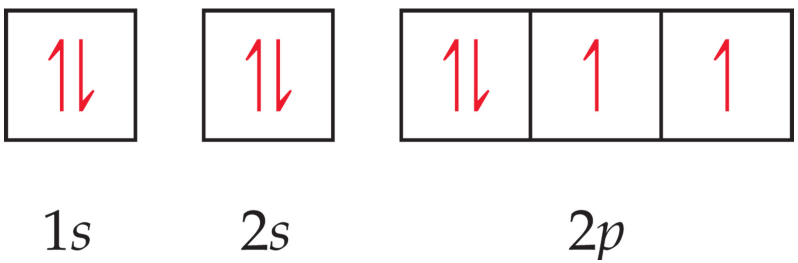
$1s^2 2s^1$

Rules and principles

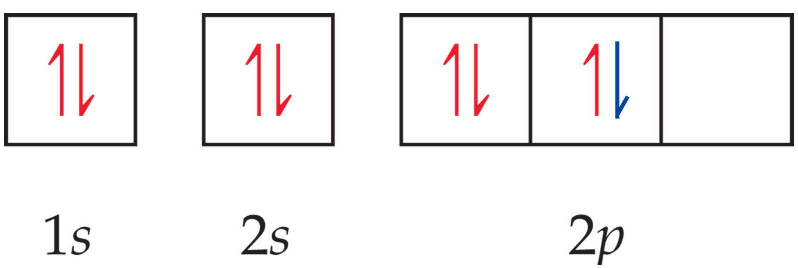
- We've seen the Pauli exclusion principle
- Aufbau principle: Lower energy orbitals are filled before higher energy orbitals
- Hund's rule
- Madelung rule

Hund's Rule

(of maximum multiplicity)

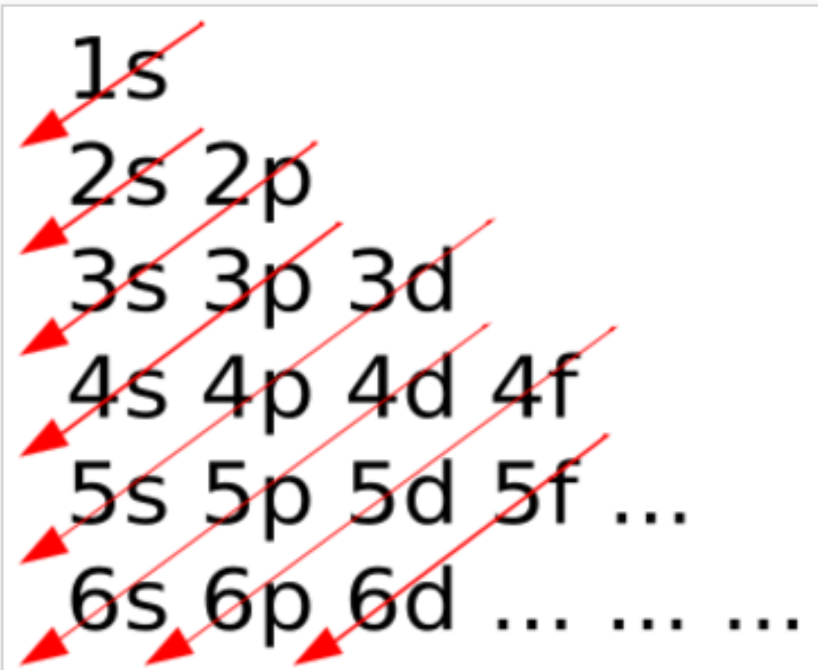


NOT:



"For degenerate orbitals, the lowest energy is attained when the number of electrons with the same spin is maximized."

Madelung energy ordering rule



Order in which orbitals are arranged by increasing energy according to the Madelung rule. Each diagonal red arrow corresponds to a different value of $n + \ell$.

- AKA Janet rule
- AKA Klechovsky rule
- Orbitals with a lower n + l value are filled before those with a higher n + l value

Electron configurations

TABLE 6.3 Electron Configurations of Several Lighter Elements

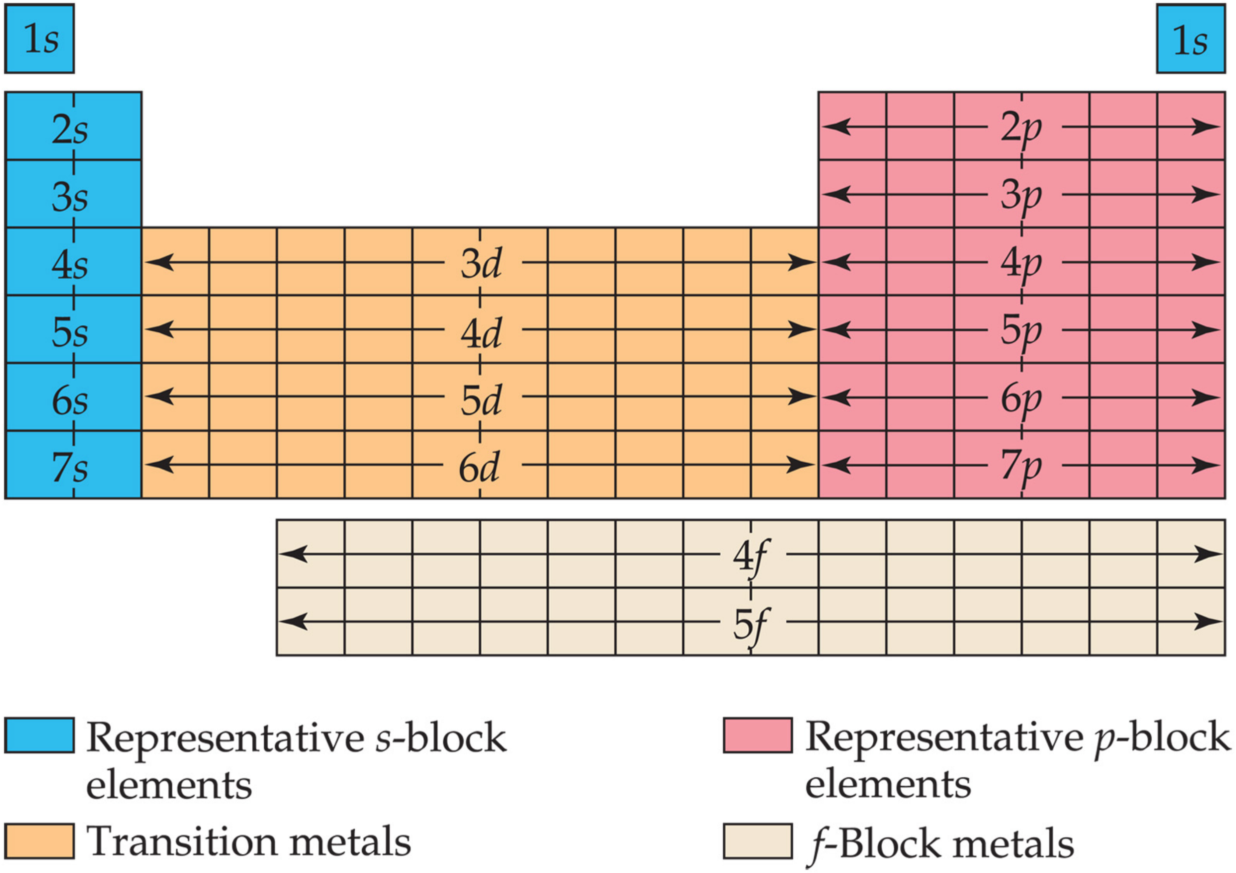
Element	Total Electrons	Orbital Diagram 1s	2s	2p			3s	Electron Configuration
Li	3	↑↓	↑					$1s^2 2s^1$
Be	4	↑↓	↑↓					$1s^2 2s^2$
B	5	↑↓	↑↓	↑				$1s^2 2s^2 2p^1$
C	6	↑↓	↑↓	↑	↑			$1s^2 2s^2 2p^2$
N	7	↑↓	↑↓	↑	↑	↑		$1s^2 2s^2 2p^3$
Ne	10	↑↓	↑↓	↑↓	↑↓	↑↓		$1s^2 2s^2 2p^6$
Na	11	↑↓	↑↓	↑↓	↑↓	↑↓	↑	$1s^2 2s^2 2p^6 3s^1$

Why do we accept this stuff?

- It must explain all the data
- It should predict things

- Q.M. is consistent with all our data (photoelectric effect, emission spectra of elements, dual wave/ particle weirdness, etc.
- One prediction: elements with similar electron configuration should have similar chemical properties

It predicts the periodicity of the periodic table!!

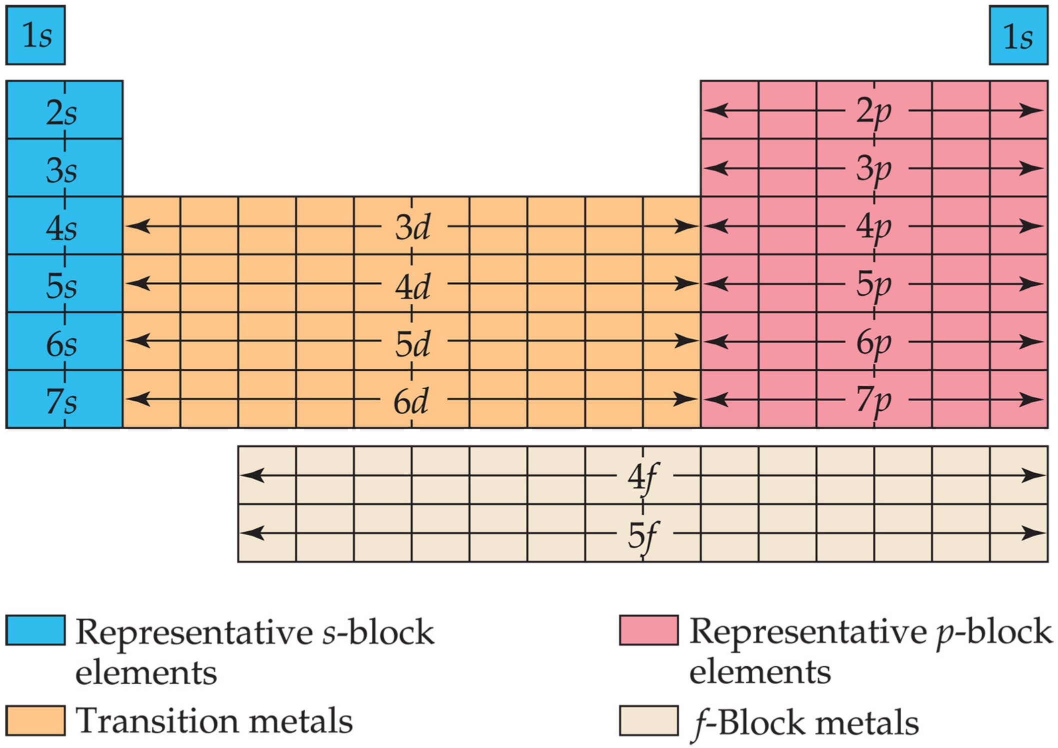


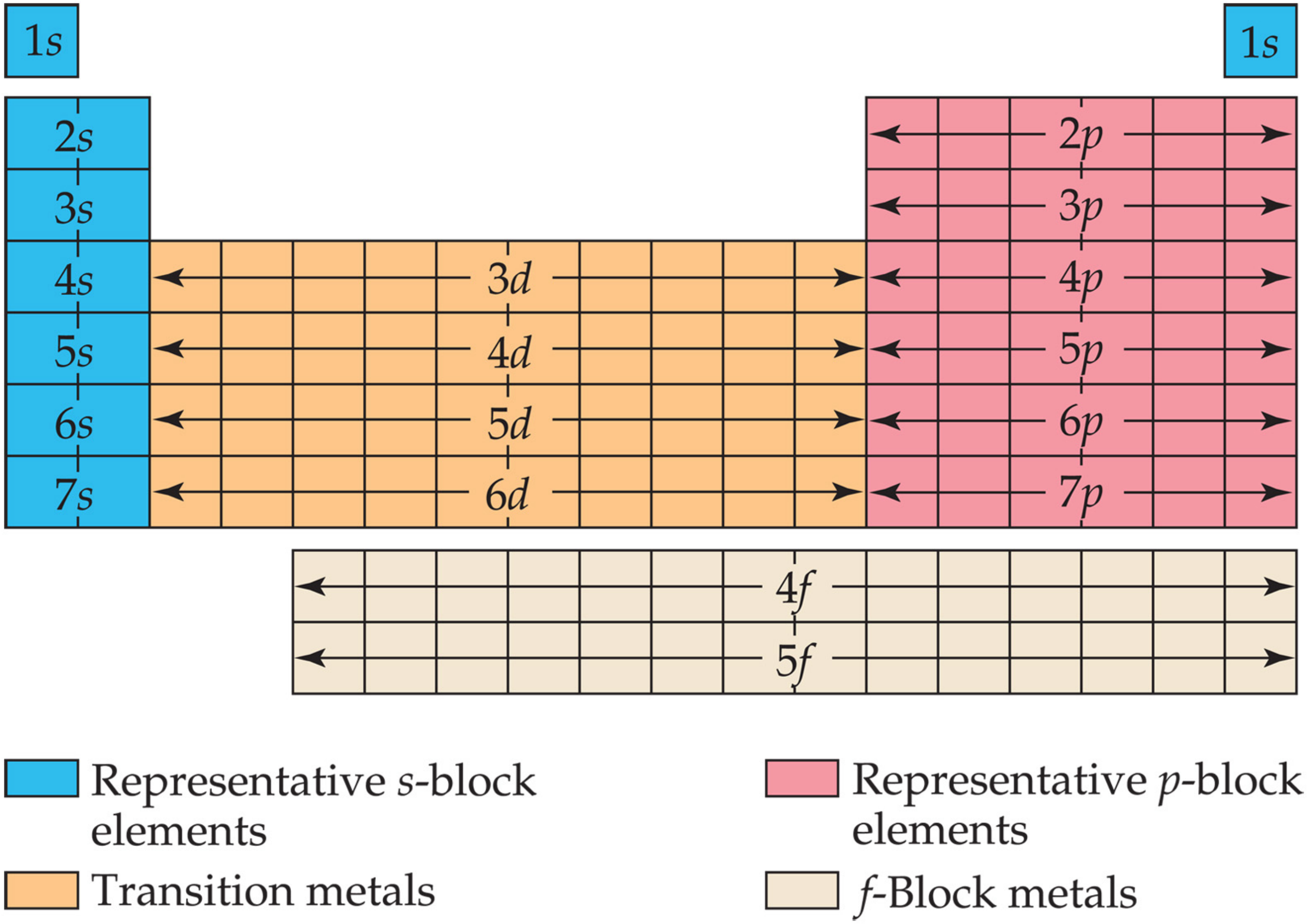
- **We fill orbitals in increasing order of energy.**
- **Different blocks on the periodic table, then correspond to different types of orbitals.**

It predicts the periodicity of the periodic table!!

- **Remember: The periodic table was arranged the way it was based on chemical properties.**

- **Originally totally empirical; Based only on observation.**





- **Periodic table tells you about the last electron that went in**
- **Periodic table also makes it easy to do electron configurations.**

Short cut for writing electron configurations

TABLE 6.4 Electron Configurations of the Group 2A and 3A Elements

Group 2A	
Be	[He]$2s^2$
Mg	[Ne]$3s^2$
Ca	[Ar]$4s^2$
Sr	[Kr]$5s^2$
Ba	[Xe]$6s^2$
Ra	[Rn]$7s^2$
Group 3A	
B	[He]$2s^2 2p^1$
Al	[Ne]$3s^2 3p^1$
Ga	[Ar]$3d^{10} 4s^2 4p^1$
In	[Kr]$4d^{10} 5s^2 5p^1$
Tl	[Xe]$4f^{14} 5d^{10} 6s^2 6p^1$

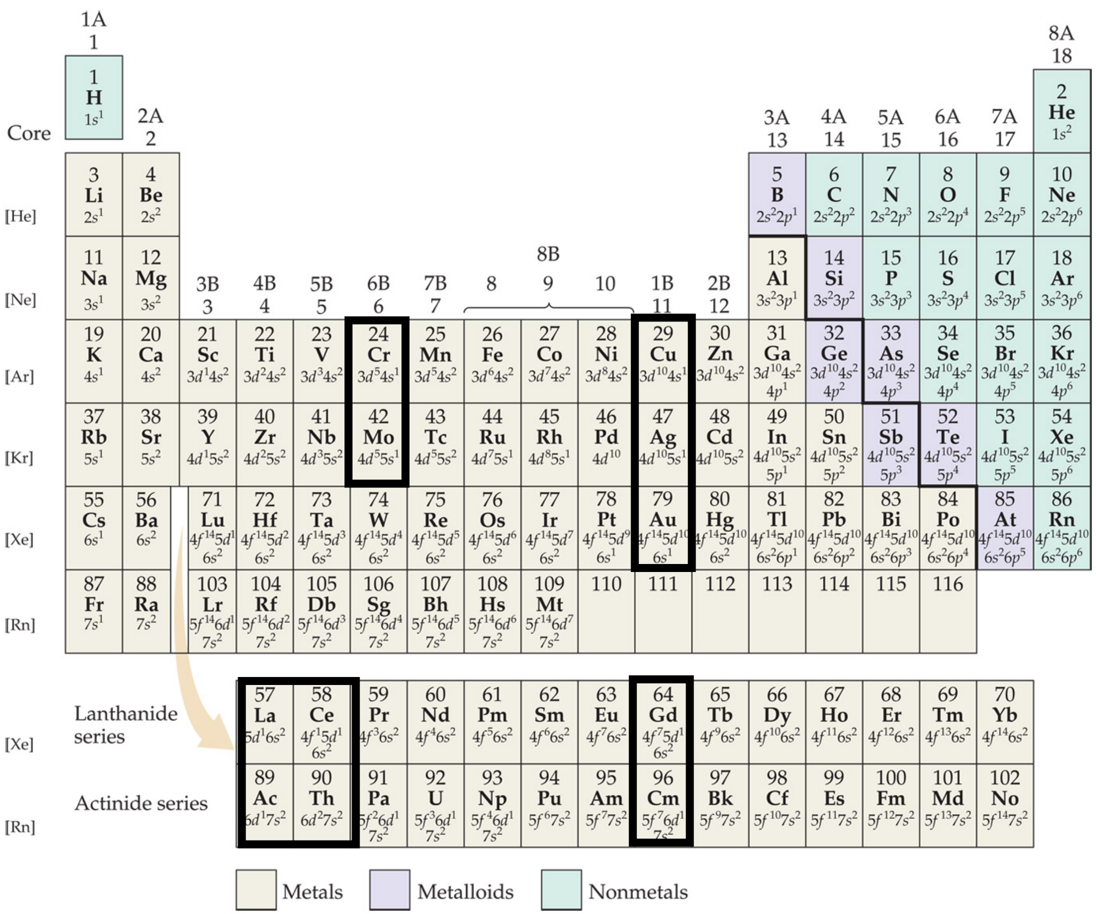
Electron configurations of the elements

Core	1A 1	2A 2	3B 3	4B 4	5B 5	6B 6	7B 7	8B 8	8B 9	8B 10	1B 11	2B 12	3A 13	4A 14	5A 15	6A 16	7A 17	8A 18
Core	1 **H** $1s^1$																	2 **He** $1s^2$
[He]	3 **Li** $2s^1$	4 **Be** $2s^2$											5 **B** $2s^22p^1$	6 **C** $2s^22p^2$	7 **N** $2s^22p^3$	8 **O** $2s^22p^4$	9 **F** $2s^22p^5$	10 **Ne** $2s^22p^6$
[Ne]	11 **Na** $3s^1$	12 **Mg** $3s^2$											13 **Al** $3s^23p^1$	14 **Si** $3s^23p^2$	15 **P** $3s^23p^3$	16 **S** $3s^23p^4$	17 **Cl** $3s^23p^5$	18 **Ar** $3s^23p^6$
[Ar]	19 **K** $4s^1$	20 **Ca** $4s^2$	21 **Sc** $3d^14s^2$	22 **Ti** $3d^24s^2$	23 **V** $3d^34s^2$	24 **Cr** $3d^54s^1$	25 **Mn** $3d^54s^2$	26 **Fe** $3d^64s^2$	27 **Co** $3d^74s^2$	28 **Ni** $3d^84s^2$	29 **Cu** $3d^{10}4s^1$	30 **Zn** $3d^{10}4s^2$	31 **Ga** $3d^{10}4s^2 4p^1$	32 **Ge** $3d^{10}4s^2 4p^2$	33 **As** $3d^{10}4s^2 4p^3$	34 **Se** $3d^{10}4s^2 4p^4$	35 **Br** $3d^{10}4s^2 4p^5$	36 **Kr** $3d^{10}4s^2 4p^6$
[Kr]	37 **Rb** $5s^1$	38 **Sr** $5s^2$	39 **Y** $4d^15s^2$	40 **Zr** $4d^25s^2$	41 **Nb** $4d^35s^2$	42 **Mo** $4d^55s^1$	43 **Tc** $4d^55s^2$	44 **Ru** $4d^75s^1$	45 **Rh** $4d^85s^1$	46 **Pd** $4d^{10}$	47 **Ag** $4d^{10}5s^1$	48 **Cd** $4d^{10}5s^2$	49 **In** $4d^{10}5s^2 5p^1$	50 **Sn** $4d^{10}5s^2 5p^2$	51 **Sb** $4d^{10}5s^2 5p^3$	52 **Te** $4d^{10}5s^2 5p^4$	53 **I** $4d^{10}5s^2 5p^5$	54 **Xe** $4d^{10}5s^2 5p^6$
[Xe]	55 **Cs** $6s^1$	56 **Ba** $6s^2$	71 **Lu** $4f^{14}5d^1 6s^2$	72 **Hf** $4f^{14}5d^2 6s^2$	73 **Ta** $4f^{14}5d^3 6s^2$	74 **W** $4f^{14}5d^4 6s^2$	75 **Re** $4f^{14}5d^5 6s^2$	76 **Os** $4f^{14}5d^6 6s^2$	77 **Ir** $4f^{14}5d^7 6s^2$	78 **Pt** $4f^{14}5d^9 6s^1$	79 **Au** $4f^{14}5d^{10} 6s^1$	80 **Hg** $4f^{14}5d^{10} 6s^2$	81 **Tl** $4f^{14}5d^{10} 6s^26p^1$	82 **Pb** $4f^{14}5d^{10} 6s^26p^2$	83 **Bi** $4f^{14}5d^{10} 6s^26p^3$	84 **Po** $4f^{14}5d^{10} 6s^26p^4$	85 **At** $4f^{14}5d^{10} 6s^26p^5$	86 **Rn** $4f^{14}5d^{10} 6s^26p^6$
[Rn]	87 **Fr** $7s^1$	88 **Ra** $7s^2$	103 **Lr** $5f^{14}6d^1 7s^2$	104 **Rf** $5f^{14}6d^2 7s^2$	105 **Db** $5f^{14}6d^3 7s^2$	106 **Sg** $5f^{14}6d^4 7s^2$	107 **Bh** $5f^{14}6d^5 7s^2$	108 **Hs** $5f^{14}6d^6 7s^2$	109 **Mt** $5f^{14}6d^7 7s^2$	110	111	112	113	114	115	116		

Core	Series														
[Xe]	Lanthanide series	57 **La** $5d^16s^2$	58 **Ce** $4f^15d^1 6s^2$	59 **Pr** $4f^36s^2$	60 **Nd** $4f^46s^2$	61 **Pm** $4f^56s^2$	62 **Sm** $4f^66s^2$	63 **Eu** $4f^76s^2$	64 **Gd** $4f^75d^1 6s^2$	65 **Tb** $4f^96s^2$	66 **Dy** $4f^{10}6s^2$	67 **Ho** $4f^{11}6s^2$	68 **Er** $4f^{12}6s^2$	69 **Tm** $4f^{13}6s^2$	70 **Yb** $4f^{14}6s^2$
[Rn]	Actinide series	89 **Ac** $6d^17s^2$	90 **Th** $6d^27s^2$	91 **Pa** $5f^26d^1 7s^2$	92 **U** $5f^36d^1 7s^2$	93 **Np** $5f^46d^1 7s^2$	94 **Pu** $5f^67s^2$	95 **Am** $5f^77s^2$	96 **Cm** $5f^76d^1 7s^2$	97 **Bk** $5f^97s^2$	98 **Cf** $5f^{10}7s^2$	99 **Es** $5f^{11}7s^2$	100 **Fm** $5f^{12}7s^2$	101 **Md** $5f^{13}7s^2$	102 **No** $5f^{14}7s^2$

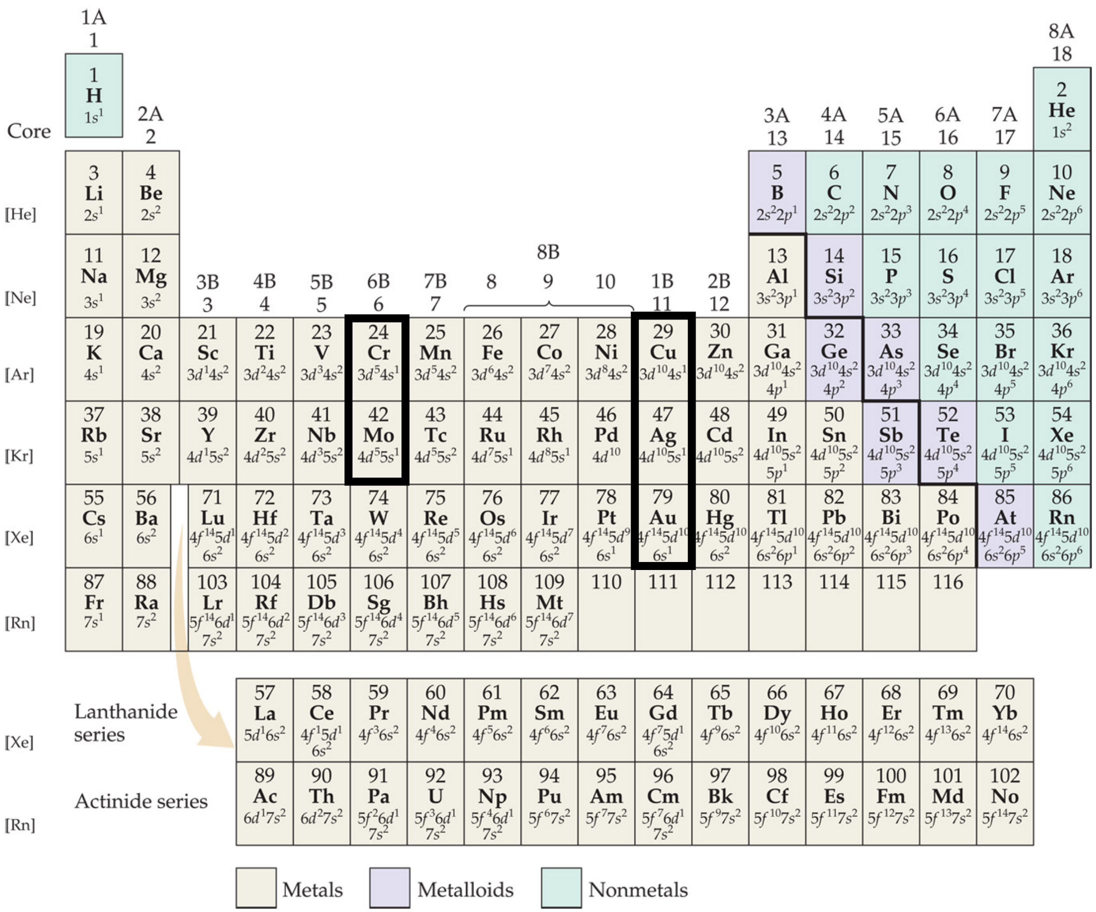
Metals　Metalloids　Nonmetals

Some Anomalies



Some irregularities occur when there are enough electrons to half-fill *s* and *d* orbitals on a given row.

Some Anomalies



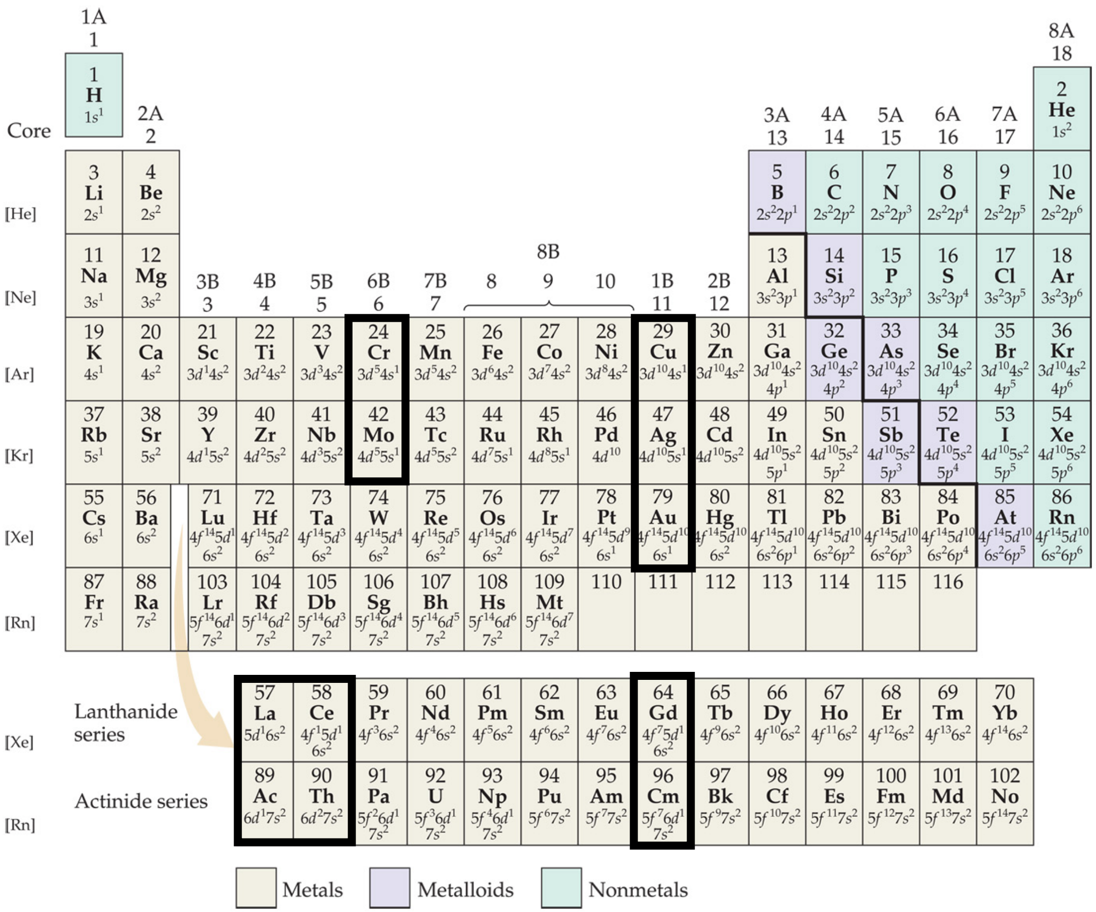
For instance, the electron configuration for Chromium, is

[Ar] $4s^1\ 3d^5$

rather than the expected

[Ar] $4s^2\ 3d^4$.

Some Anomalies



- This occurs because the 4*s* and 3*d* orbitals are very close in energy.
- These anomalies occur in *f*-block atoms, as well.