

Chapter 17 Many-Electron Atoms and Chemical Bonding

17.1 Many-Electron Atoms and the Periodic Table

17.2 Experimental Measures of Orbital Energies

17.3 Sizes of Atoms and Ions

17.4 Properties of the Chemical Bond

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17.1 Many-Electron Atoms

Many electron atoms and the periodic table

Building up electron configurations

Building up from H to Ar: Pauli and Aufbau principles

Hund's rule: paramagnetism and diamagnetism.

Building from K to Kr: Transition elements and d orbitals

Electron shells, effective nuclear charge

Correlations of periodic properties of families of elements and electron configurations

Multielectron atoms:

Every electron in a multielectron atom is assigned *four quantum numbers* (n , l , m_l and m_s) that uniquely define its chemical and physical properties.

From the use of quantum numbers, we can envision every electron of a multielectron atom in terms of a characteristic energy (E_n), size (r), shape (l), orientation (m_l) and spin (m_s).

The highest energy (valence) electrons are of greatest chemical interest

Electronic structure of atoms of the elements:

Atoms of the various elements differ from each other in their values of Z (atomic number) and electrons.

Electrons in atoms are arranged in **orbitals, shells and subshells**. Orbitals having the same value of n are said to be in the same **shell**. Orbitals having the same values of n and l are said to be in the same **subshell**.

Orbitals of all elements are hydrogen like and are characterized by the quantum numbers n , l and m_l .

Energies of orbitals depend on $(n + l)$, not just n .

For atoms with more than one electron, approximations are required in order to make quantitative quantum mechanical approximations.

The orbital approximation: The electron density of an isolated **many-electron atom** is approximately the **sum** of the electron densities of each of the individual electrons taken separately.

The approximation amounts to treat each electron as if it were moving in a field of charge that is the net result of the nuclear attraction and the **average repulsions** of all the other electrons.

Building up the ground state electron configurations of atoms

An electron configuration is a list of the occupied orbitals and the number of electrons in each.

The electron configuration of lowest energy is termed the **ground state electronic configuration**.

The ground state electron configuration is built by filling the lowest energy orbitals first (Aufbau principle) and obeying the Pauli principle and Hund's rule

Shells, subshells and orbitals: definitions

Shell: a collection of orbitals with the same value of n

Example: the three orbitals 3s, 3p, 3d comprise a **shell** with $n = 3$

Subshell: a collection of orbitals with the same value of n and l .

The orbitals of a **subshell** have the same energy for the same value of l .

Example: for the $n = 3$ shell there are three subshells, the 3s subshell ($l = 0$), the 3p subshell ($l = 1$), and the 3d subshell ($l = 2$),

Orbitals: the individual components of a shell or subshell

Example: the p_x , p_y and p_z orbitals are the components of any p ($l = 1$) subshell and each orbital has the same energy

The Bohr one electron atom as a starting point for the electron configurations of multielectron atoms.

$$E_n = -(Z_{\text{eff}}^2/n^2)Ry = \text{energy of electron in orbit}$$

$$r_n = (n^2/Z_{\text{eff}})a_0 = \text{radius of a Bohr orbit}$$

Replace Z (actual charge) with Z_{eff} (effective charge)

Structure of multielectron atoms:

Quantum numbers of electrons: n, l, m_l, m_s

Electron configurations: $1s^x 2s^x 2p^x 3s^x 3p^x$, etc (x = number of electrons)

Core electrons and valence electrons (Highest value of n)

Some periodic properties of atoms we shall study:

Energy required to remove and add an electron (E_n)

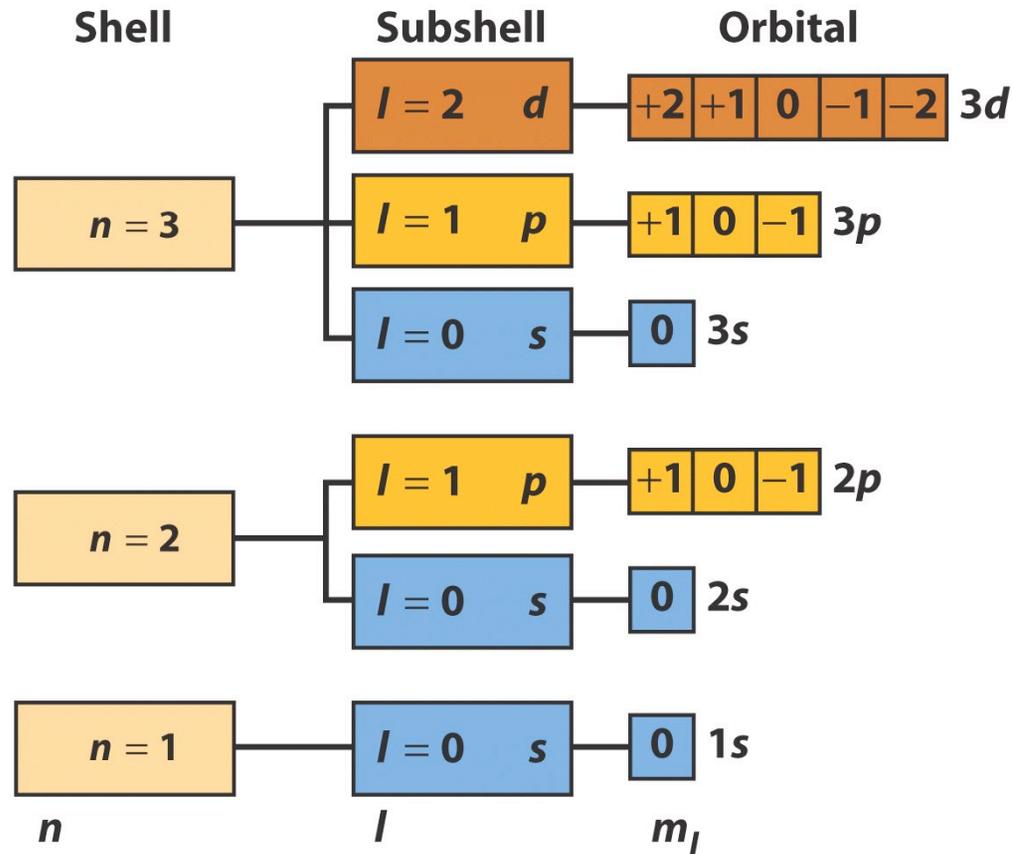
Size of atoms (r_n)

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

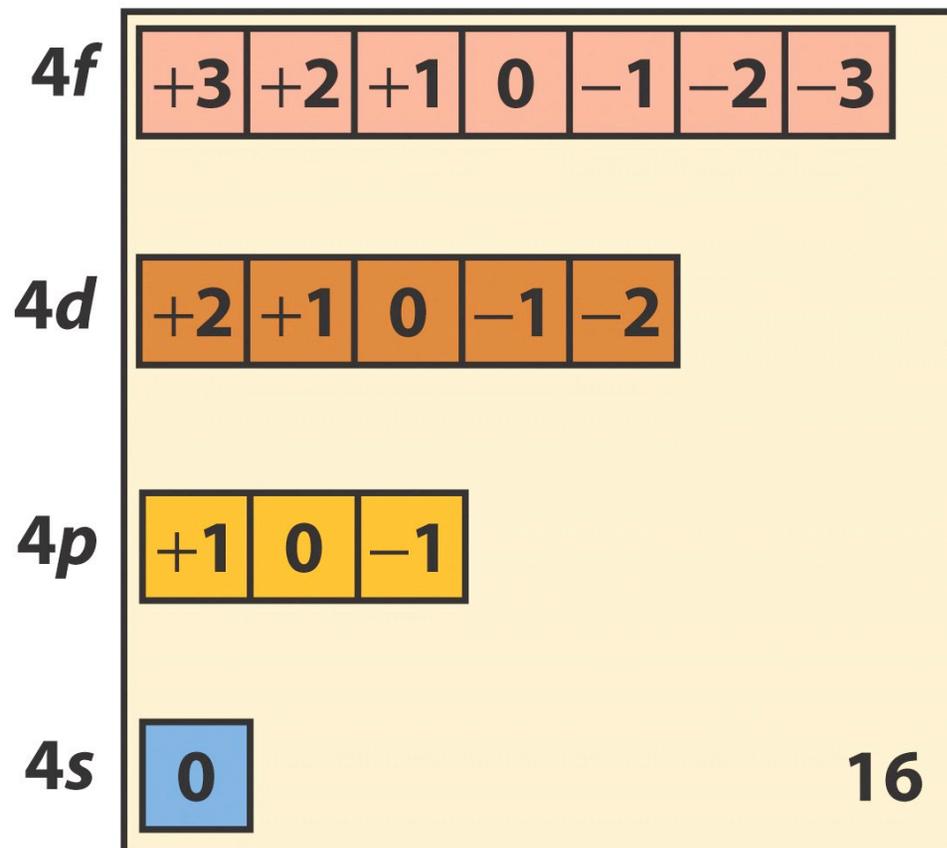
subshell = all orbitals with the same value of n and l

an orbital is fully defined by three quantum numbers, n , l , and m_l



For a multielectron atom, the energy of subshells increase with l for a given value of n

Example: f orbitals



Determining the ground state electronic configuration of neutral atoms

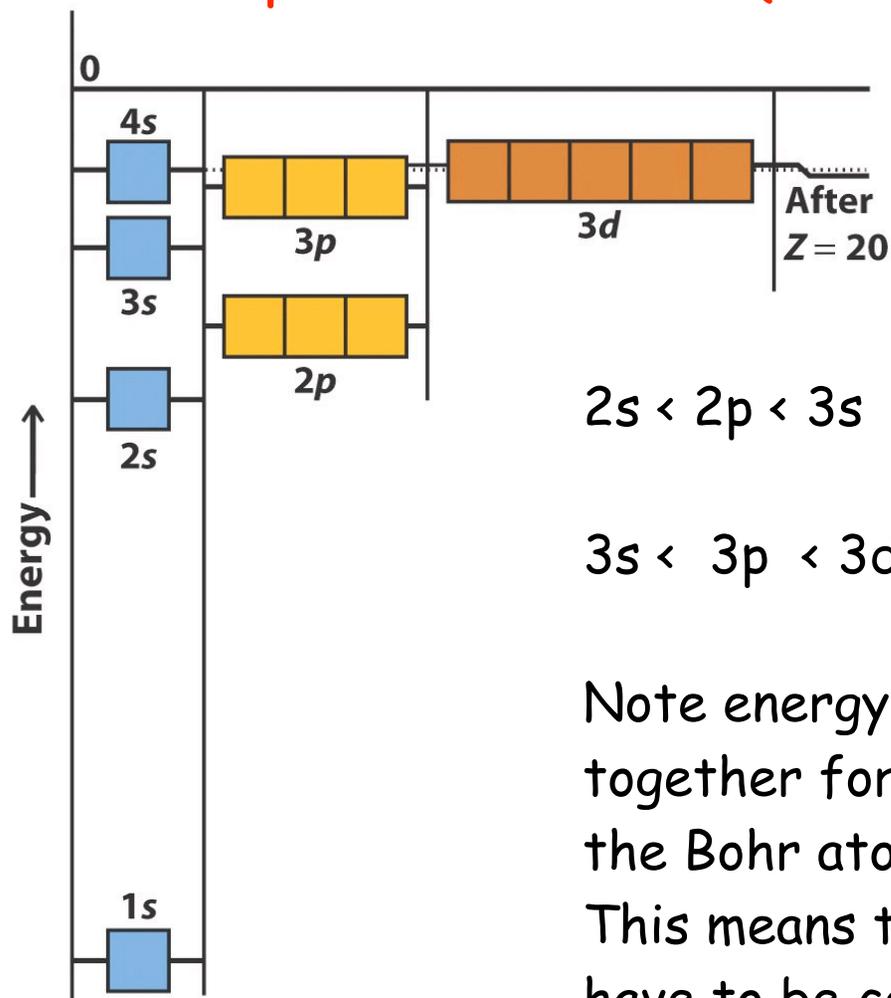
- (1) Use the $(n + l)$ rule to determine the relative energies of the atomic orbitals from $1s$ to $n/$
- (2) Imagine a bare nucleus of charge $+Z$ surrounded by empty atomic orbitals.
- (3) Add Z electrons to the empty orbitals starting with the lowest energy orbital first, obeying the Pauli principle as required.
- (4) Electrons are placed in orbitals of lowest energy according to the Aufbau principle to obtain the ground state electron configuration. Apply other rules as required.

The $(n + l)$ rule: The ordering of the energies of the orbitals in a multielectron atom increases with the value of $n + l$.

Sub-rule: When two orbitals of different n have the same value of $n + l$ the orbital with the lower value of n has the lower energy state.

Orbital	$(n + l)$	Comment
1s	$(1 + 0 = 1)$	
2s	$(2 + 0 = 2)$	
2p	$(2 + 1 = 3)$	
3s	$(3 + 0 = 3)$	Lower n (2p versus 3s) has lower energy
3p	$(3 + 1 = 4)$	
4s	$(4 + 0 = 4)$	Lower n (3p versus 4s) has lower energy
3d	$(3 + 2 = 5)$	
4p	$(4 + 1 = 5)$	Lower n (3d versus 4p) has lower energy
5s	$(5 + 1 = 6)$	

Relative orbital energies for the multielectron atom.
 The energy of an orbital of a multielectron atom depends on n and l (but not m_l)

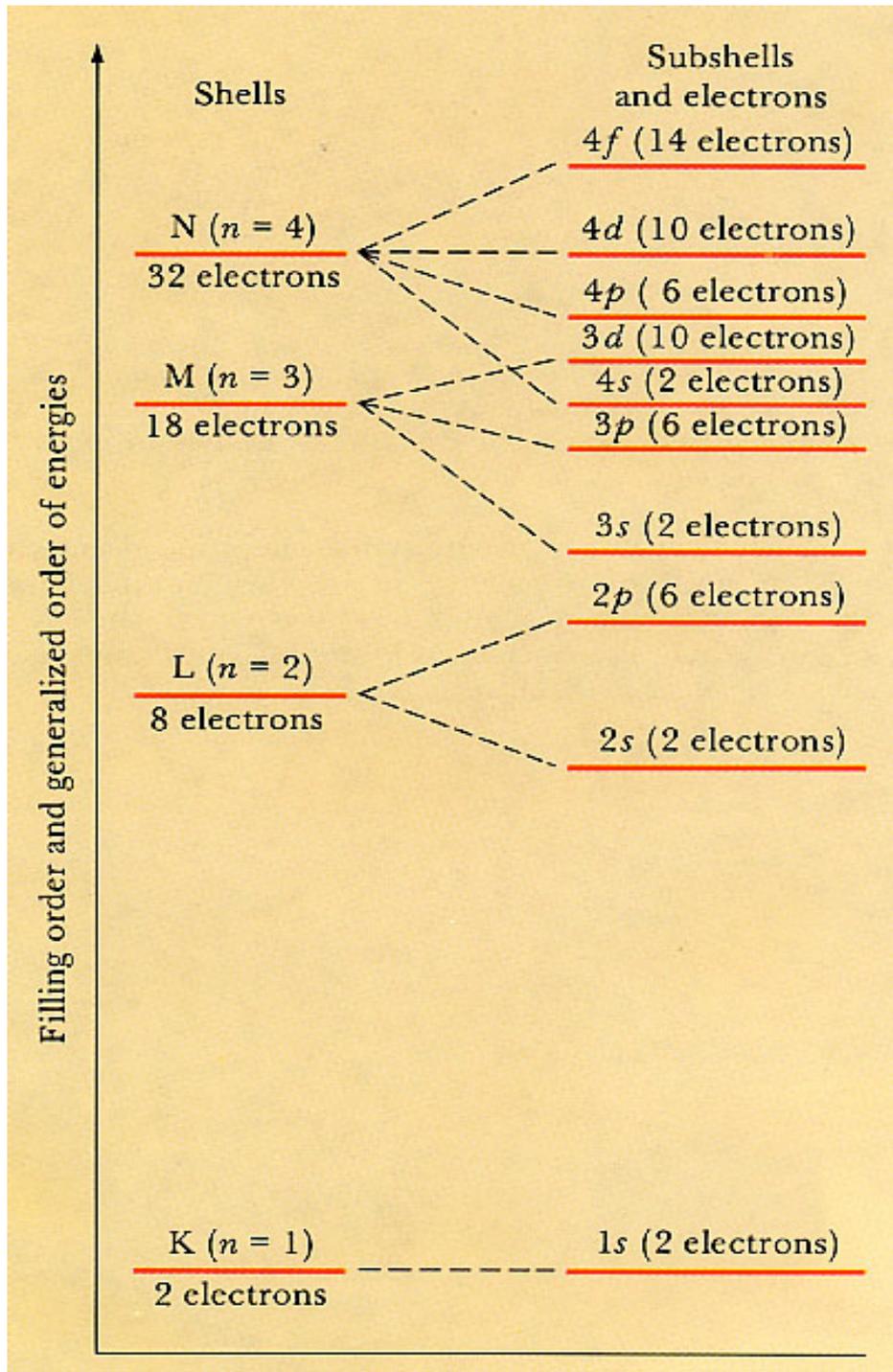


$$2s < 2p < 3s$$

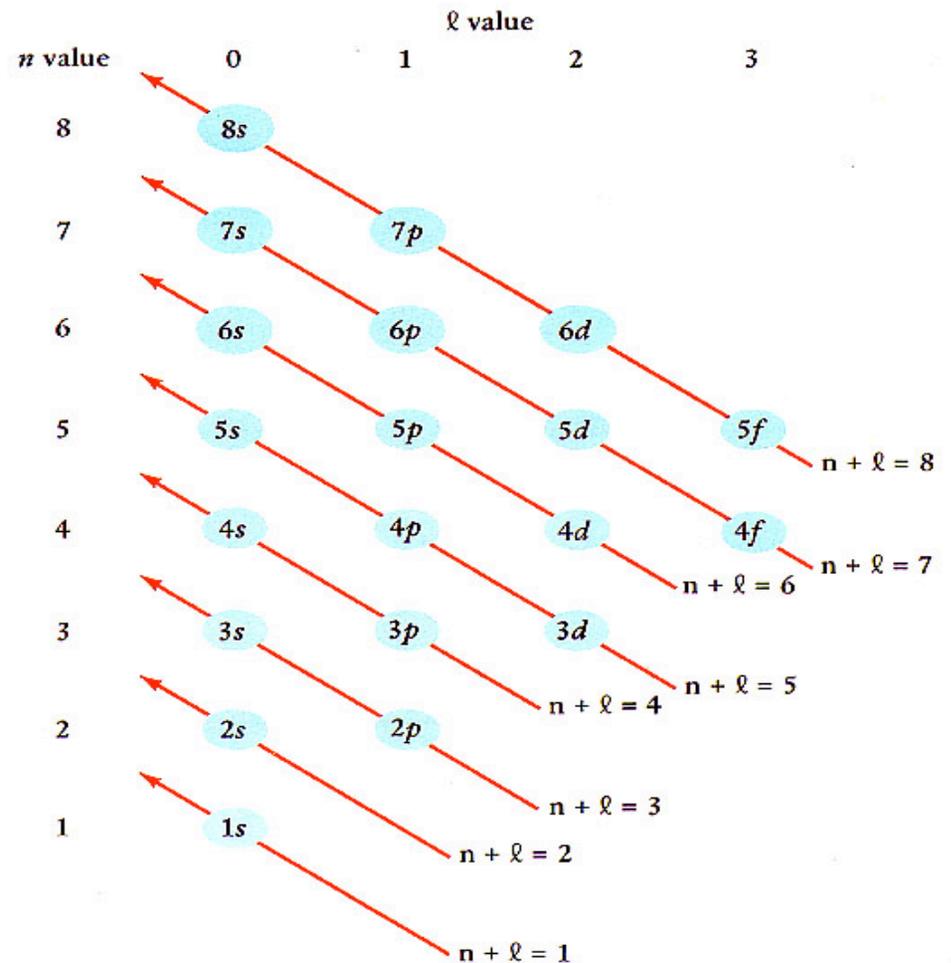
$$3s < 3p < 3d \sim 4s \text{ (may switch with } Z)$$

Note energy levels are getting closer together for $n = 3$ as expected from the Bohr atom.

This means that factors ignored may have to be considered



Atomic Energy Levels according to the ($n + \ell$) rule



Ground state electron configuration of a many electron atom: Governs reactivity of atoms under normal condition

- (1) Imagine a bare nucleus of charge $+Z$
Imagine empty orbitals surrounding the nucleus
- (2) Fill the orbitals with Z electrons for the neutral atom following two principles:
- (3) **Aufbau principle:** fill lowest energy orbitals first
- (4) **Pauli exclusion principle:** each electron must have four different quantum numbers (maximum of 2 electrons in an orbital).

The Aufbau principle.

Systems in nature tend to minimize their energy.

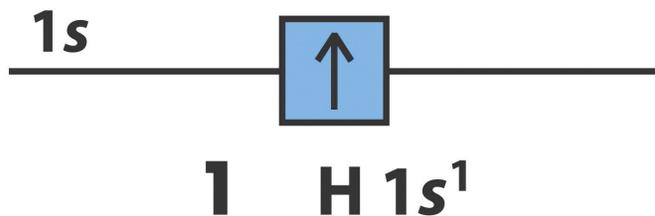
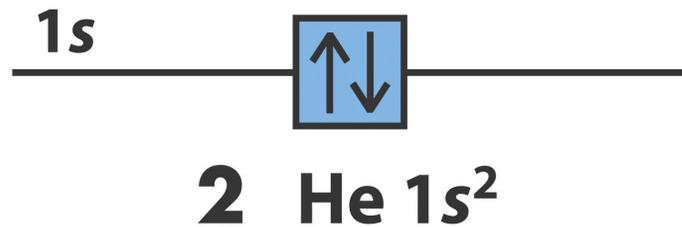
The ground state of an atom is the one with the lowest energy.

All other allowed states are excited states of the atom.

The Aufbau principle for atoms: *The systematic adding electrons to orbitals of an atom (${}^Z A$) with atomic number Z , beginning with the orbital of lowest energy and continuing to add electrons, in accordance with the Pauli principle, until Z electrons are added to the atom.*

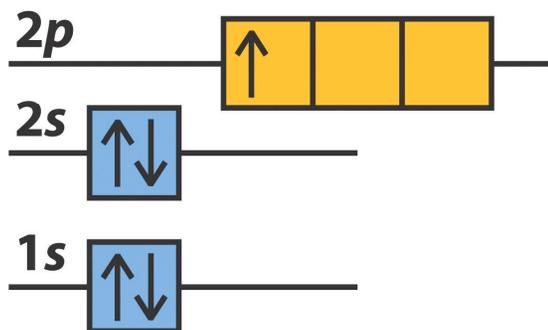
Constructing the periodic table by filling orbitals with electrons (electron configurations) in accordance with the Pauli and Aufbau principles.

Construction of the first row of the periodic table.
Electron configurations: ${}^1\text{H}$ and ${}^2\text{He}$.



Aufbau: Fill 1s orbital first
Pauli: no more than two electrons in the 1s orbital
The basis of the duet rule:
filling a shell 1s subshell filled with ${}^2\text{He}$ = stable electron core given symbol [He].

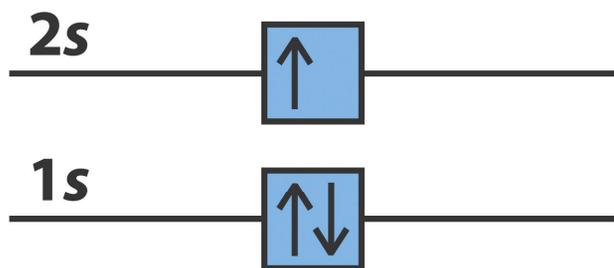
Filling the orbitals of ${}^3\text{Li}$, ${}^4\text{Be}$ and ${}^5\text{B}$



5 B $1s^2 2s^2 2p^1$, $[\text{He}]2s^2 2p^1$

Aufbau: Fill 1s orbital first, then 2s, then 2p.
Pauli: no more than two electrons in the 1s orbital.

2s subshell filled with ${}^4\text{Be}$.

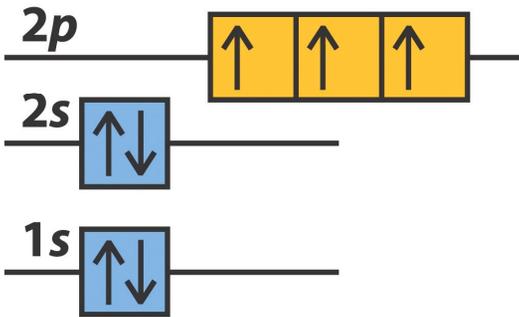


3 Li $1s^2 2s^1$, $[\text{He}]2s^1$



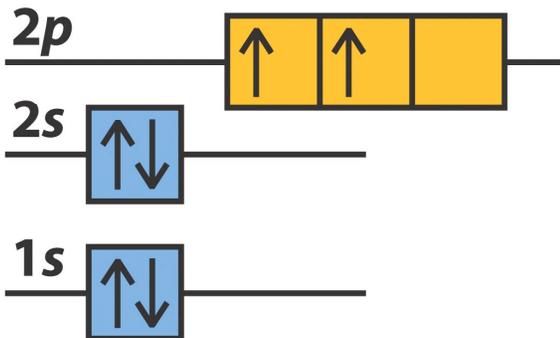
4 Be $1s^2 2s^2$, $[\text{He}]2s^2$

Filling the orbitals of ${}^6\text{C}$ and ${}^7\text{N}$. The need for a third rule (Hund's rule):



7 N $1s^2 2s^2 2p^3$, $[\text{He}]2s^2 2p^3$

For nitrogen, how do the **three 2 p electrons** distribute themselves in the three 2p orbitals?



6 C $1s^2 2s^2 2p^2$, $[\text{He}]2s^2 2p^2$

For carbon, how do the **two 2p electrons** distribute themselves in the three 2p orbitals?

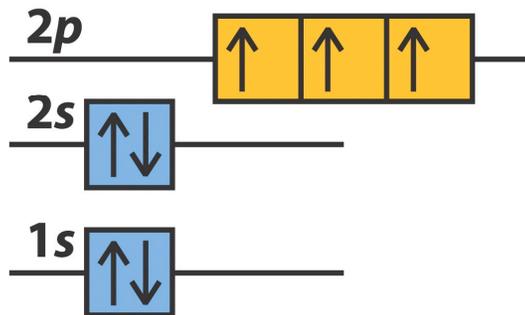
Hund's rule: Applies when filling the orbitals of a subshell with electrons (np or nd or nf subshells). Or more generally when filling orbitals of identical energy

When adding electrons to a subshell, the ground state electronic configuration is formed by maximizing the number of electrons with parallel spins (\uparrow)(\uparrow) before pairing two electrons in one orbital ($\uparrow\downarrow$)($$).

Example: ${}^6\text{C} = [\text{He}]2s^2 2p_x(\uparrow) 2p_y(\uparrow) 2p_z() = \text{ground state}$

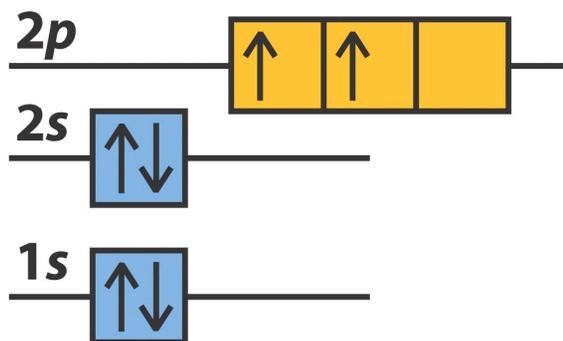
Example: ${}^6\text{C} = [\text{He}]2s^2 2p_x(\uparrow\downarrow) 2p_y() 2p_z() = \text{excited state}$

Filling the orbitals of ${}^6\text{C}$ and ${}^7\text{N}$. The need for a third rule
(Hund's rule):



7 N $1s^2 2s^2 2p^3$, $[\text{He}]2s^2 2p^3$

Hund's Rule: When electrons occupy orbitals of the same energy, the lowest energy state corresponds to the configuration with the *greatest number of orbitally and spin unpaired electrons*.



6 C $1s^2 2s^2 2p^2$, $[\text{He}]2s^2 2p^2$

When the configuration is written as $1s^2 2s^2 2p^2$ it is understood that two different p orbitals (p_x , p_y) are occupied.

Paramagnetic and diamagnetic substances

The presence of two orbitally and spin unpaired electrons in the ground state of carbon makes the atom *paramagnetic*.

A *paramagnetic* substance is attracted to a magnetic field. A *diamagnetic* substance is repelled from a magnetic field.

All substances which possess one or more orbitally unpaired electrons are *paramagnetic*.

All substances which possess only spin paired electrons are *diamagnetic*.

Examples of diamagnetic and paramagnetic atoms

Which of the following atoms are paramagnetic?

${}^1\text{H}$, ${}^2\text{He}$, ${}^3\text{Li}$, ${}^4\text{Be}$, ${}^5\text{B}$, ${}^6\text{C}$, ${}^7\text{N}$, ${}^8\text{O}$, ${}^9\text{F}$, ${}^{10}\text{Ne}$

${}^1\text{H}$, ${}^3\text{L}$, ${}^5\text{B}$, ${}^7\text{N}$, ${}^9\text{F}$ must be paramagnetic since they possess an odd number of electrons.

${}^2\text{He}$ and ${}^{10}\text{Ne}$ are diamagnetic (filled shells).

${}^4\text{Be}$, ${}^6\text{C}$ and ${}^8\text{O}$ paramagnetic or diamagnetic?

${}^4\text{Be}$: $1s^2 2s^2$ Two filled shells: diamagnetic

${}^6\text{C}$: $1s^2 2s^2 p^2$ Hund's rule: $p_x(\uparrow)p_y(\uparrow)$

${}^8\text{O}$: $1s^2 2s^2 p^4$ Let's see

The Pauli exclusion principle does not forbid the existence of any of the Pauli allowed configurations.

If there are more than one electron configuration one allowed Pauli configuration, the lowest energy one (ground state) will be predicted by Hund's rule and the others will be excited states.

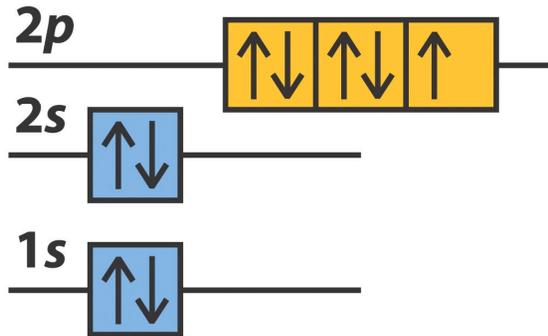
Are the following two configurations allowed for ${}^7\text{N}$ by the Pauli principle?



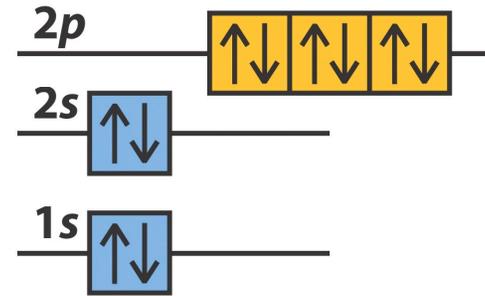
Ans: Yes. Which is more stable?

$1s^2 2s^2 2p_x(\uparrow) 2p_y(\uparrow) 2p_z(\uparrow)$ is more stable than $1s^2 2s^2 2p_x(\uparrow\downarrow) 2p_y(\uparrow) 2p_z()$ by Hund's rule

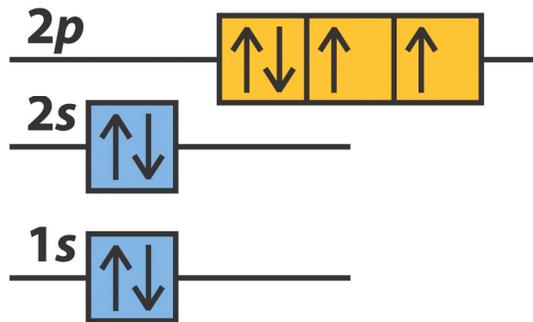
Filling the orbitals of ${}^8\text{O}$, ${}^9\text{F}$ and ${}^{10}\text{Ne}$



9 F $1s^2 2s^2 2p^5$, $[\text{He}]2s^2 2p^5$



10 Ne $1s^2 2s^2 2p^6$, $[\text{He}]2s^2 2p^6$



8 O $1s^2 2s^2 2p^4$, $[\text{He}]2s^2 2p^4$

Filling the 2p subshell produces another stable configuration of electrons which serves as the core shell of the third row: symbol $[\text{Ne}]$

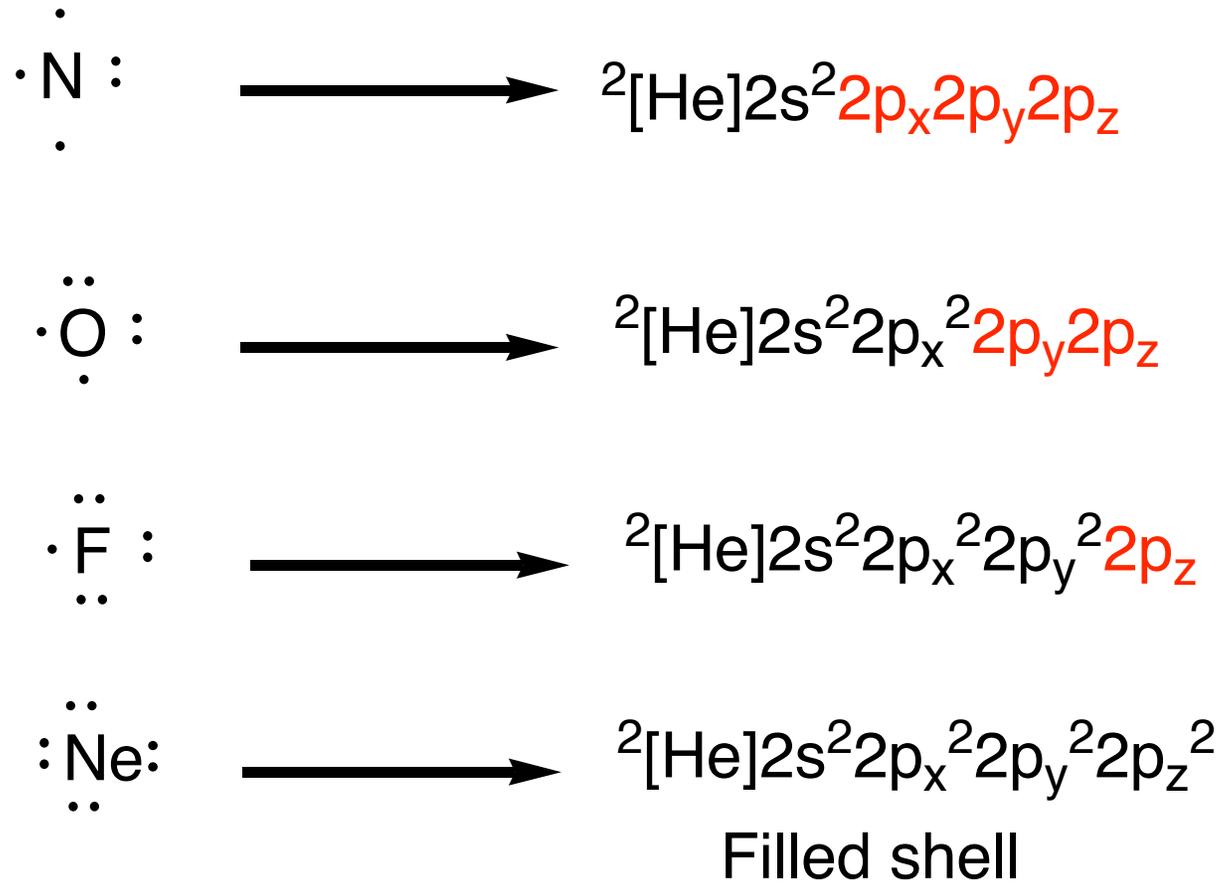
Building up the Periodic Table

From ${}^3\text{Li}$ to ${}^{10}\text{Ne}$: Paramagnetism and Diamagnetism

Atom	Configuration Core/Valence electrons	Magnetic Properties
${}^3\text{Li}$	$[\text{Ne}]2s \ (\uparrow)$	Paramagnetic
${}^4\text{Be}$	$[\text{Ne}] 2s^2 \ (\uparrow\downarrow)$	Diamagnetic (Closed shell)
${}^5\text{B}$	$[\text{Ne}] 2s^2 2p^1 \ (\uparrow)$	Paramagnetic
${}^6\text{C}$	$[\text{Ne}] 2s^2 2p^2 \ (\uparrow\uparrow)$	Paramagnetic
${}^7\text{N}$	$[\text{Ne}] 2s^2 2p^3 \ (\uparrow\uparrow\uparrow)$	Paramagnetic
${}^8\text{O}$	$[\text{Ne}] 2s^2 2p^4 \ (\uparrow\downarrow\uparrow\uparrow)$	Paramagnetic
${}^9\text{F}$	$[\text{Ne}] 2s^2 2p^5 \ (\uparrow\downarrow\uparrow\downarrow\uparrow)$	Paramagnetic
${}^{10}\text{Ne}$	$[\text{Ne}] 2s^2 2p^6 \ (\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow)$	Diamagnetic (Closed shell)

How do electronic configurations connect with valence electrons and Lewis structures?

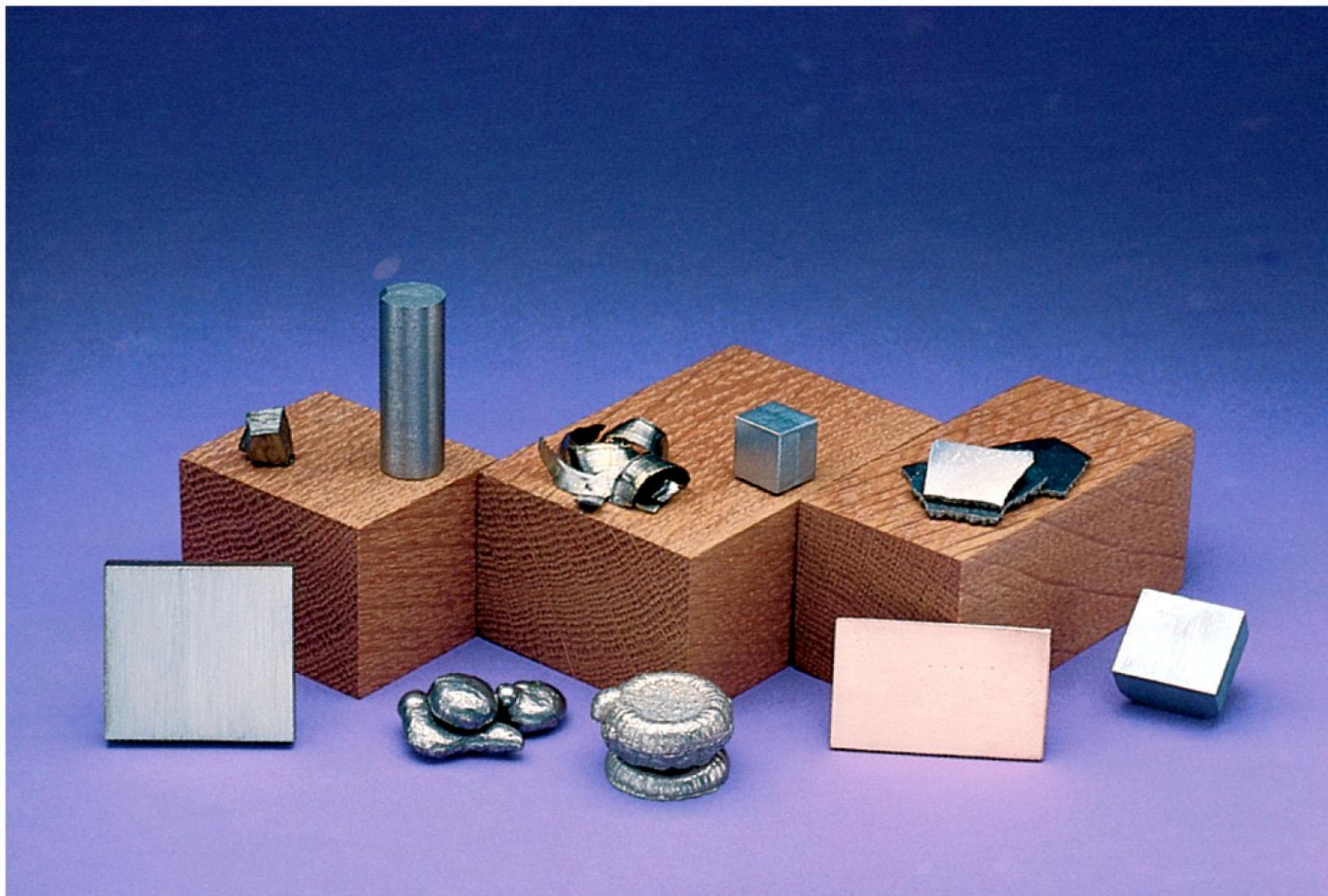
Correlation of valence electron and Lewis structures: **2p** indicates an unpaired electron in a 2p orbital



Building up the third row of the periodic table: From Na to Ar: Paramagnetism and Diamagnetism

Atom	Configuration	Magnetic properties
	Core/Valence electrons	
^{11}Na	$[\text{Ne}] 3s \quad (\uparrow)$	Paramagnetic
^{12}Mg	$[\text{Ne}] 3s^2 \quad (\uparrow\downarrow)$	Diamagnetic (Closed shell)
^{13}Al	$[\text{Ne}] 3s^2 3p^1 \quad (\uparrow)$	Paramagnetic
^{14}Si	$[\text{Ne}] 3s^2 3p^2 \quad (\uparrow\uparrow)$	Paramagnetic
^{15}P	$[\text{Ne}] 3s^2 3p^3 \quad (\uparrow\uparrow\uparrow)$	Paramagnetic
^{16}S	$[\text{Ne}] 3s^2 3p^4 \quad (\uparrow\downarrow\uparrow\uparrow)$	Paramagnetic
^{17}Cl	$[\text{Ne}] 3s^2 3p^5 \quad (\uparrow\downarrow\uparrow\downarrow\uparrow)$	Paramagnetic
^{18}Ar	$[\text{Ne}] 3s^2 3p^6 \quad (\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow)$	Diamagnetic (Closed shell)

So far, so good, but now for something totally different:
The transition metals: Sc through Zn. Filling the d orbitals



Electron configuration of the transition elements:

^{21}Sc through ^{30}Zn

d orbitals raise their ugly lobes!

The d block elements:

^{21}Sc , ^{22}Ti , ^{23}V , ^{24}Cr , ^{25}Mn , ^{26}Fe , ^{27}Co , ^{28}Ni , ^{29}Cu , ^{30}Zn

The fourth row of the periodic table: From ^{19}K to ^{36}Kr
 From the results of the second and third row we expect for the
 representative elements of Groups I-VIII:

Atom	Configuration
^{19}K (Group I)	$^{18}[\text{Ar}]4s$
^{20}Ca (Group II)	$^{18}[\text{Ar}]4s^2$
<hr/>	
^{31}Ga (Group III)	$^{18}[\text{Ar}] 4s^2 3d^{10} 4p^1$
^{32}Ge (Group IV)	$^{18}[\text{Ar}] 4s^2 3d^{10} 4p^2$
^{33}As (Group V)	$^{18}[\text{Ar}] 4s^2 3d^{10} 4p^3$
^{34}Se (Group VI)	$^{18}[\text{Ar}] 4s^2 3d^{10} 4p^4$
^{35}Cl (Group VII)	$^{18}[\text{Ar}] 4s^2 3d^{10} 4p^5$
^{36}Kr (Group VIII)	$^{18}[\text{Ar}] 4s^2 3d^{10} 4p^6$

d orbitals fill up

How do the d orbital fill up for ^{21}Sc through ^{30}Zn ?

Building the third full row of the periodic table:

^{19}K - ^{36}Kr

The 4s and 3d orbitals are close in energy in the one electron atom.

Difficult to predict stability for multielectron atom.

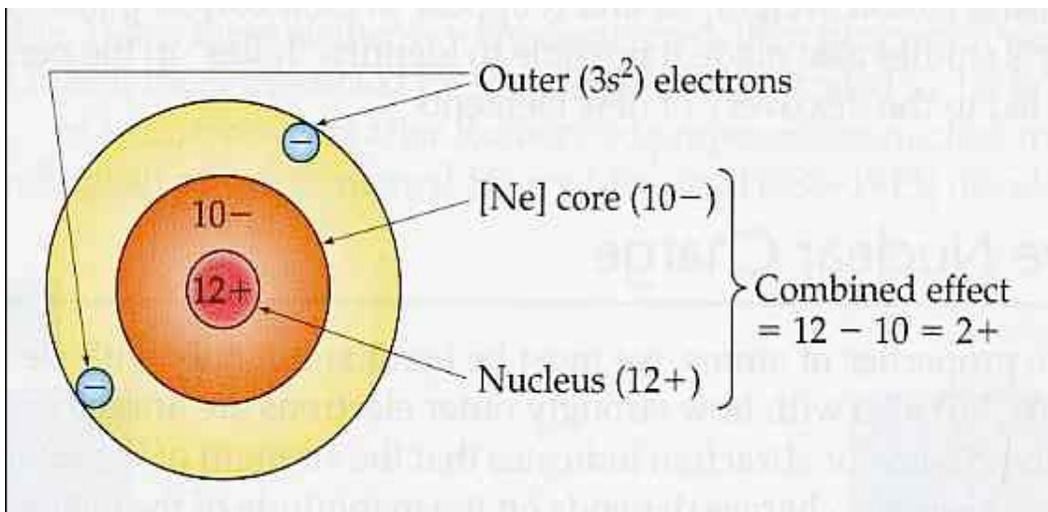
The 4s orbital is slightly more stable than the 3d orbital at the beginning of the third full period of the periodic table:



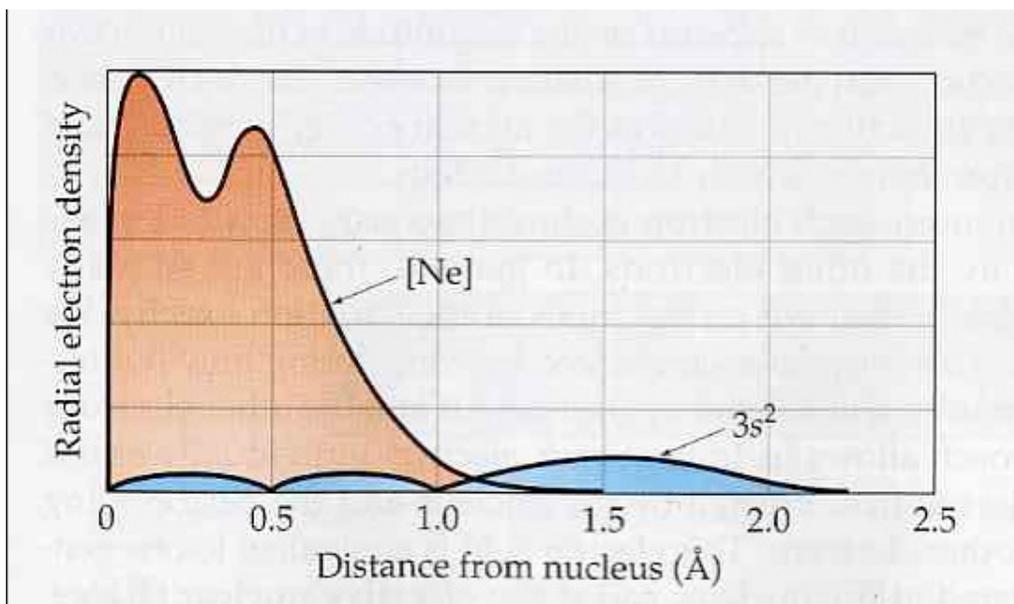
The reason is that the 4s orbital has a higher probability of being closer to the nucleus and see a greater effective Z_{eff} than a 3d orbital.

Let's take a look at how the core electrons screen Z .

Effective nuclear charge (E_{eff}) is the nuclear charge experienced by an outer (valence) electron after the shielding due to the shielding of the inner (core) electrons are taken into account



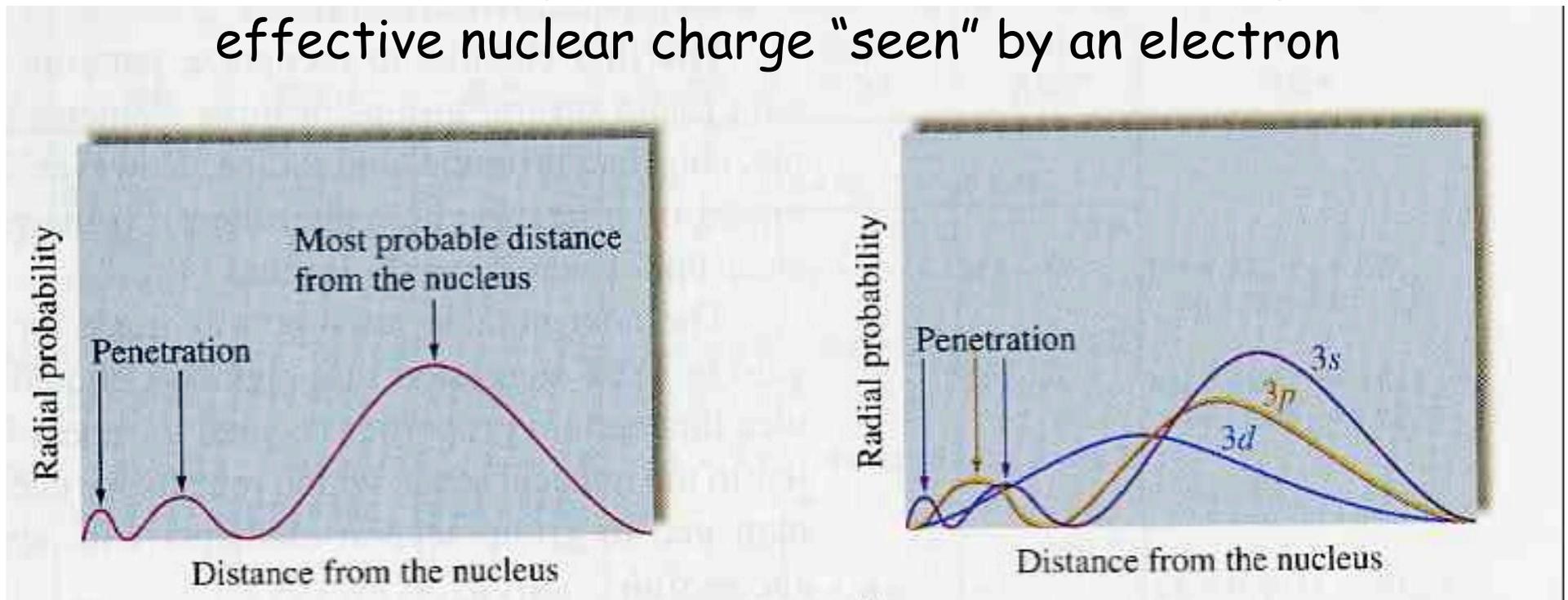
Effective nuclear charge (E_{eff}) for ^{12}Mg is $Z(\text{Mg}) - [\text{Ne}]$ core electrons = $12 - 10 = 2+$



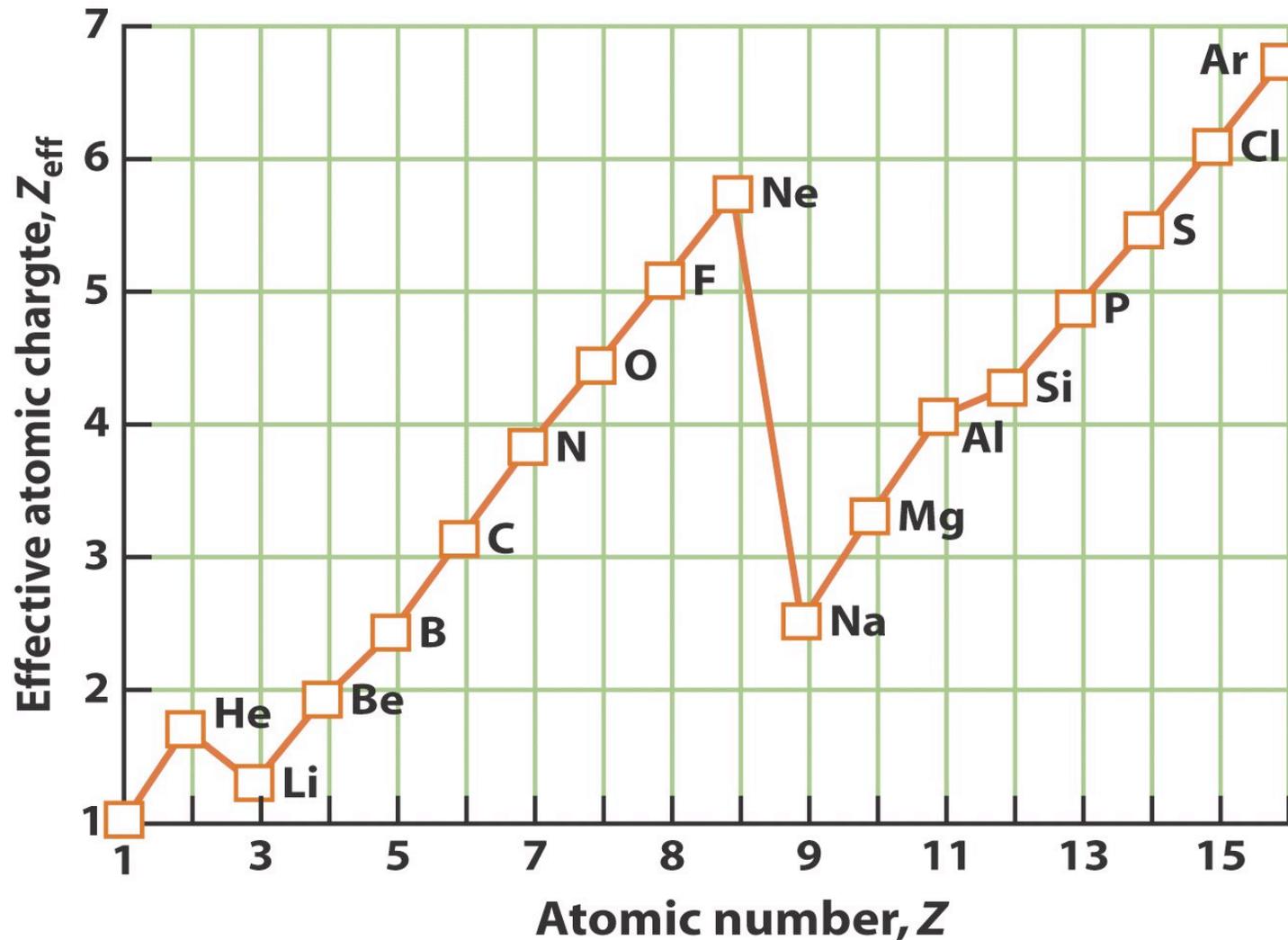
Electron shielding (screening) of the nuclear charge by other electrons

Why is the energy of a 3s orbital lower than that of a 3p orbital? Why is the energy of a 3p orbital lower than the energy of a 3d orbital?

A qualitative explanation is found in the concept of effective nuclear charge "seen" by an electron



Effective charge, Z_{eff} , seen by valence electrons*



*Note x-axis is incorrect. What should it be?

Two new features for the transition elements: the energy "switch" of the 4s and 3d orbitals and the Cr and Cu anomalies.

The 4s and 3d orbitals are very close in energy in the one electron atom.

Depending on the screening (E_{eff}) $4s < 3d$ or $3d < 4s$.

From detailed computation and from experiment:

$4s < 3d$ in the neutral atoms at the beginning of the 4th period



Note in the cations of transition metals, 3d is lower than 4s:



Some rules about filling shell and subshells for $n = 3$ or greater:

There is a special stability of a filled **subshell** and a **half-filled subshell**.

This special stability of filled and half-filled subshells causes the Cr and Cu electron ground state configurations to be different from that predicted from the Aufbau principle alone

Cr: $[\text{Ar}]4s^23d^4$ is expected to be the ground state from Aufbau but $[\text{Ar}]4s^13d^5$ (two half filled subshells) is the ground state

Cu: $[\text{Ar}]4s^23d^9$ is expected to be the ground state from Aufbau but $[\text{Ar}]4s^13d^{10}$ (a half filled subshell and a filled subshell) is the ground state

Following the (n + l) rule, the electron configurations of the transition elements of the fourth row

	"Expected"	Found
^{21}Sc	$^{18}[\text{Ar}]4s^23d$	
^{22}Ti	$^{18}[\text{Ar}]4s^23d^2$	
^{23}V	$^{18}[\text{Ar}]4s^23d^3$	
^{24}Cr	$^{18}[\text{Ar}]4s^23d^4$	$^{18}[\text{Ar}]4s^1(\uparrow)3d^5 (\uparrow\uparrow\uparrow\uparrow\uparrow)$ half filled half filled
^{25}Mn	$^{18}[\text{Ar}]4s^23d^5$	
^{26}Fe	$^{18}[\text{Ar}]4s^23d^6$	
^{27}Co	$^{18}[\text{Ar}]4s^23d^7$	
^{28}Ni	$^{18}[\text{Ar}]4s^23d^8$	
^{29}Cu	$^{18}[\text{Ar}]4s^23d^9$	$^{18}[\text{Ar}]4s^1(\uparrow)3d^{10} (\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow)$ half filled filled
^{30}Zn	$^{18}[\text{Ar}]4s^23d^{10}$	

The "surprises" for electron configurations at ^{24}Cr and ^{29}Cu are due to the special stability of half filled subshells and filled subshells.

Ground State Electron Configurations: d block elements

Paramagnetism and Hund's Rule

		$3d$					$4s$	
		$m_l = +2$	$+1$	0	-1	-2	0	
Ca	[Ar] $4s^2$						↑↓	Diamagnetic
Sc	[Ar] $3d^1 4s^2$	↑					↑↓	<div style="text-align: center;"> <hr style="width: 50%; margin: 0 auto;"/> ↑ ↓ <hr style="width: 50%; margin: 0 auto;"/> </div>
Ti	[Ar] $3d^2 4s^2$	↑	↑				↑↓	
V	[Ar] $3d^3 4s^2$	↑	↑	↑			↑↓	
Cr*	[Ar] $3d^5 4s^1$	↑	↑	↑	↑	↑	↑	
Mn	[Ar] $3d^5 4s^2$	↑	↑	↑	↑	↑	↑↓	
Fe	[Ar] $3d^6 4s^2$	↑↓	↑	↑	↑	↑	↑↓	
Co	[Ar] $3d^7 4s^2$	↑↓	↑↓	↑	↑	↑	↑↓	
Ni	[Ar] $3d^8 4s^2$	↑↓	↑↓	↑↓	↑	↑	↑↓	
Cu*	[Ar] $3d^{10} 4s^1$	↑↓	↑↓	↑↓	↑↓	↑↓	↑	
Zn	[Ar] $3d^{10} 4s^2$	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	

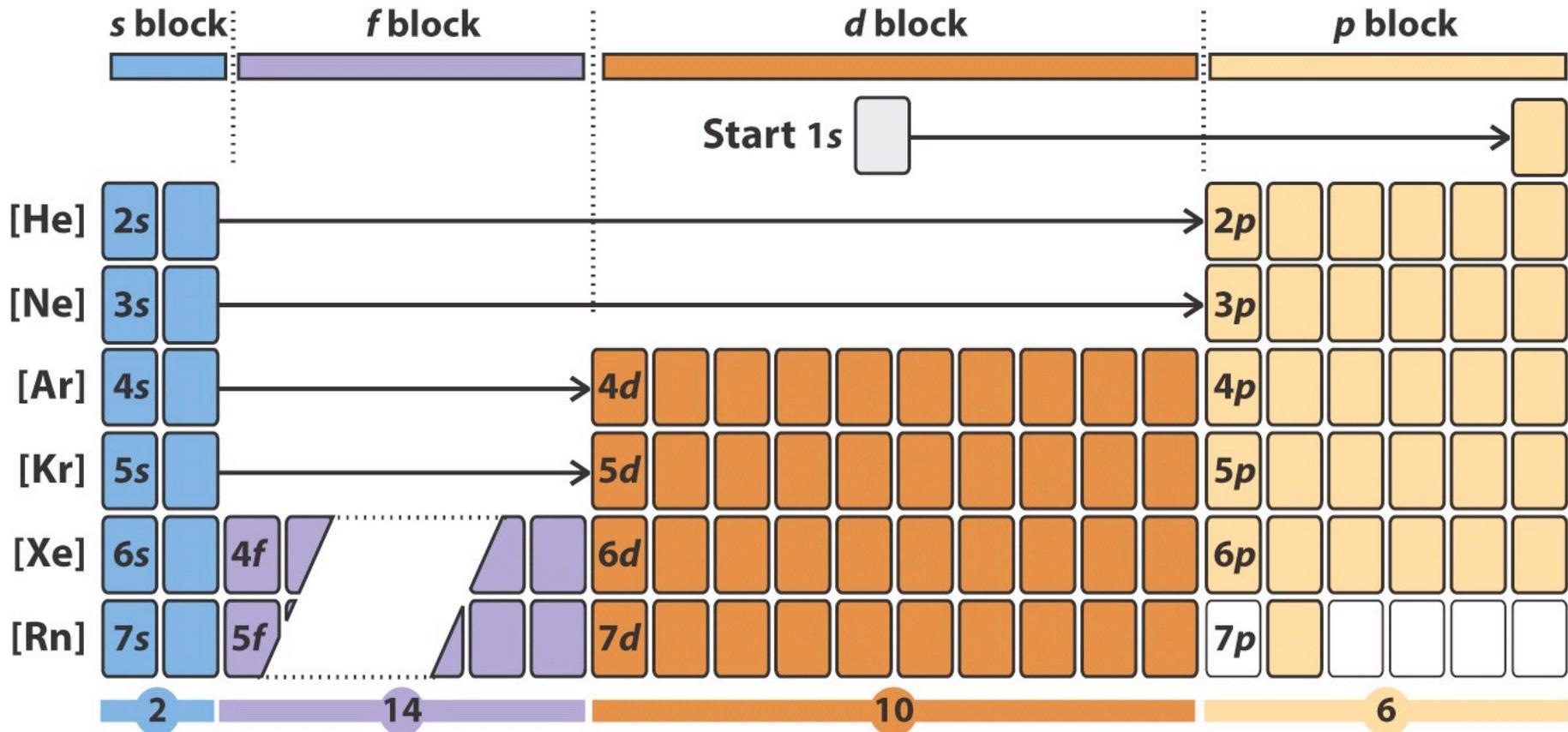
The closed shell electron configurations of multielectron atoms

Row	Configuration	Shorthand
First:	$1s^2$	$^2[\text{He}]$
Second:	$2s^2 2p^6$	$^{10}[\text{Ne}]$
Third:	$3s^2 3p^6$	$^{18}[\text{Ar}]$
Fourth:	$4s^2 3d^{10} 4p^6$	$^{36}[\text{Kr}]$
Fifth:	$5s^2 4d^{10} 5p^6$	$^{54}[\text{Xe}]$

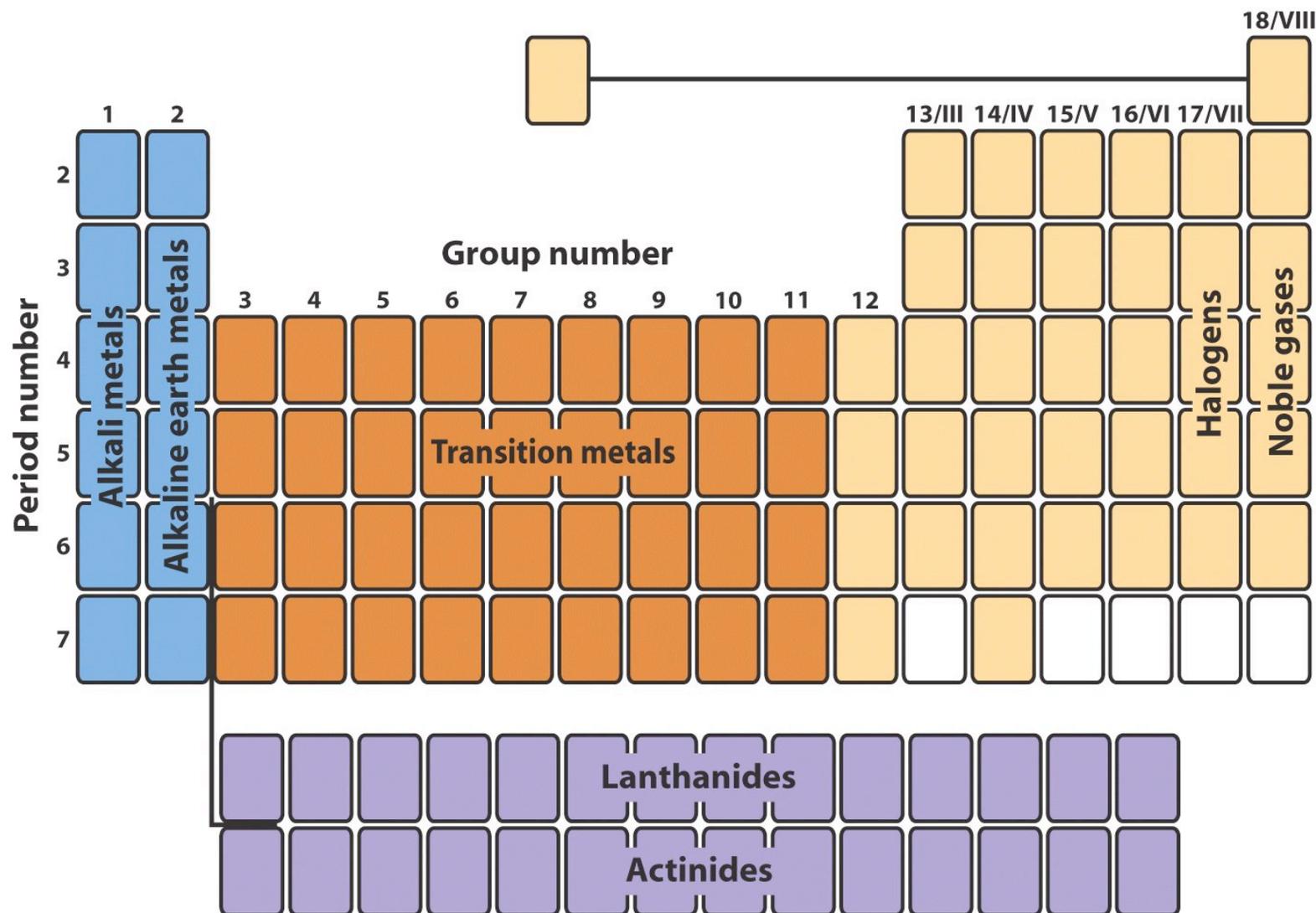
The electron configurations of the valence shell of the main group elements

Group I:	ns^1np^0	The alkali metals: (H) Li, Na, K, Rb, Cs
Group II:	ns^2np^0	The alkali earth metals: Be, Mg, Ca, Sr, Ba
Group III:	ns^2np^1	The boron family: B, Al, Ga, In, Tl
Group IV:	ns^2np^2	The carbon family: C, Si, Ge, Sn, Pb
Group V:	ns^2np^3	The nitrogen family: N, P, As, Sb, Bi
Group VI:	ns^2np^4	The chalcogens: O, S, Se, Te, Po
Group VII:	ns^2np^5	The halogens: F, Cl, Br, I
Group VIII:	ns^2np^6	The noble gases: (He) Ne, Ar, Kr, Xe,

The periodic table by orbital filling



The atomic electron configurations of first five rows of the periodic table give the elements their signature characteristics of metals and non-metals



Electronic structure and the periodic table

Electrons in the outermost shell of an atom are the most important in determining chemical properties. Chemical reactions involve only the outer (valence) electrons. The inner (core) electrons are not involved in chemical reactions.

Elements in a given vertical column (families) of the periodic table have similar outer-shell electron configurations and similar properties. They are isoelectronic with respect to the number of valence electrons.

Elements in a row show regular trends in their properties due to the continuing increase in the number of valence electrons until a shell is filled.

Summary: The Periodic Table built up by electron configurations: the ground state electron configurations of the valence electrons of the elements

1A																8A	
1 H $1s^1$																2 He $1s^2$	
	2A											3A	4A	5A	6A	7A	
3 Li $2s^1$	4 Be $2s^2$											5 B $2s^2 2p^1$	6 C $2s^2 2p^2$	7 N $2s^2 2p^3$	8 O $2s^2 2p^4$	9 F $2s^2 2p^5$	10 Ne $2s^2 2p^6$
11 Na $3s^1$	12 Mg $3s^2$	3B	4B	5B	6B	7B	8B		1B	2B	13 Al $3s^2 3p^1$	14 Si $3s^2 3p^2$	15 P $3s^2 3p^3$	16 S $3s^2 3p^4$	17 Cl $3s^2 3p^5$	18 Ar $3s^2 3p^6$	
19 K $4s^1$	20 Ca $4s^2$	21 Sc $3d^1 4s^2$	22 Ti $3d^2 4s^2$	23 V $3d^3 4s^2$	24 Cr $3d^5 4s^1$	25 Mn $3d^5 4s^2$	26 Fe $3d^6 4s^2$	27 Co $3d^7 4s^2$	28 Ni $3d^8 4s^2$	29 Cu $3d^{10} 4s^1$	30 Zn $3d^{10} 4s^2$	31 Ga $4s^2 4p^1$	32 Ge $4s^2 4p^2$	33 As $4s^2 4p^3$	34 Se $4s^2 4p^4$	35 Br $4s^2 4p^5$	36 Kr $4s^2 4p^6$
37 Rb $5s^1$	38 Sr $5s^2$	39 Y $4d^1 5s^2$	40 Zr $4d^2 5s^2$	41 Nb $4d^4 5s^1$	42 Mo $4d^5 5s^1$	43 Tc $4d^5 5s^2$	44 Ru $4d^7 5s^1$	45 Rh $4d^8 5s^1$	46 Pd $4d^{10}$	47 Ag $4d^{10} 5s^1$	48 Cd $4d^{10} 5s^2$	49 In $5s^2 5p^1$	50 Sn $5s^2 5p^2$	51 Sb $5s^2 5p^3$	52 Te $5s^2 5p^4$	53 I $5s^2 5p^5$	54 Xe $5s^2 5p^6$
55 Cs $6s^1$	56 Ba $6s^2$	57 *La $5d^1 6s^2$	72 Hf $5d^2 6s^2$	73 Ta $5d^3 6s^2$	74 W $5d^4 6s^2$	75 Re $5d^5 6s^2$	76 Os $5d^6 6s^2$	77 Ir $5d^7 6s^2$	78 Pt $5d^9 6s^1$	79 Au $5d^{10} 6s^1$	80 Hg $5d^{10} 6s^2$	81 Tl $6s^2 6p^1$	82 Pb $6s^2 6p^2$	83 Bi $6s^2 6p^3$	84 Po $6s^2 6p^4$	85 At $6s^2 6p^5$	86 Rn $6s^2 6p^6$
87 Fr $7s^1$	88 Ra $7s^2$	89 †Ac $6d^1 7s^2$	104 Rf $6d^2 7s^2$	105 Db $6d^3 7s^2$	106 Sg $6d^4 7s^2$	107 Bh	108 Hs	109 Mt	110	111	112	Unknown	114	Unknown	††116	Unknown	††118

	58 Ce $4f^2 6s^2$	59 Pr $4f^3 6s^2$	60 Nd $4f^4 6s^2$	61 Pm $4f^5 6s^2$	62 Sm $4f^6 6s^2$	63 Eu $4f^7 6s^2$	64 Gd $4f^7 5d^1 6s^2$	65 Tb $4f^9 6s^2$	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 $4f^{14} 6s^2$	71 Lu $4f^{14} 5d^1 6s^2$
†	90 Th $6d^2 7s^2$	91 Pa $5f^2 6d^1 7s^2$	92 U $5f^3 6d^1 7s^2$	93 Np $5f^4 6d^1 7s^2$	94 Pu $5f^6 7s^2$	95 Am $5f^7 7s^2$	96 Cm $5f^7 6d^1 7s^2$	97 Bk $5f^9 7s^2$	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 $5f^{14} 7s^2$	103 Lr $5f^{14} 6d^1 7s^2$

Effective nuclear charge (Z_{eff}) on the outer electrons

Maintain hydrogen atom like orbitals as an approximation, but subshell energies are not equal: $E_{ns} < E_{np} < E_{nd} < E_{nf}$

A **s electron** penetrates to the nucleus more than a **p electron**: a **p electron** penetrates to the nucleus more than a **d electron**: more penetration, more stable, lower energy.

$$\text{Subshell energies: } E_{3s} < E_{3p} < E_{3d}$$

Classification of orbitals of a many electron atom according to their energies.

Orbitals with same value of n and different value of l comprise a **shell**.

Example: $2s$ and $2p$ comprise a shell.

A group of orbitals with **exactly** equal energies comprise a **subshell**.

Example: $2p_x$, $2p_y$ and $2p_z$

The orbital approximation ignores electron-electron repulsion, but takes into account Hund's rule: electrons with parallel spins ($\uparrow\uparrow$) tend to stay apart compared to electrons with antiparallel spins ($\uparrow\downarrow$).

More about orbitals, shells and subshells

Each shell of principal quantum number n contains n subshells

$n = 1$, only one subshell (s)

$n = 2$, two subshells (s, p)

$n = 3$, three subshells (s, p, d)

Each subshell of quantum number l contains $(2l + 1)$ orbitals

$l = 0$, $(2 \times 0 + 1) = 1$ orbital (s)

$l = 1$, $(2 \times 1 + 1) = 3$ orbitals (p_x , p_y , p_z)

$l = 2$, $(2 \times 2 + 1) = 5$ orbitals (d_{xy} , d_{yz} , d_{xz} , $d_{x^2 - y^2}$, d_{z^2})

The number of orbitals for a given n is n^2 (solutions to wave equation)

For $n = 1$, one orbital; for $n = 2$, four orbitals, for $n = 3$, nine orbitals

The number of electrons that can fill a given shell = $2n^2$

For each orbital, there can be a maximum of 2 occupying electrons

The Pauli principle imposes structure on the many electron atom.

Without it, all the electrons might be expected to crowd into the low energy orbitals. With it the electrons are organized, filled orbitals with no more than two electrons.

The ground state of an atom possesses the lowest energy organization of electrons around the nucleus. All electron organizations are described by **electron configurations**.

The ground state of an atom corresponds to the **lowest energy electron configuration**.

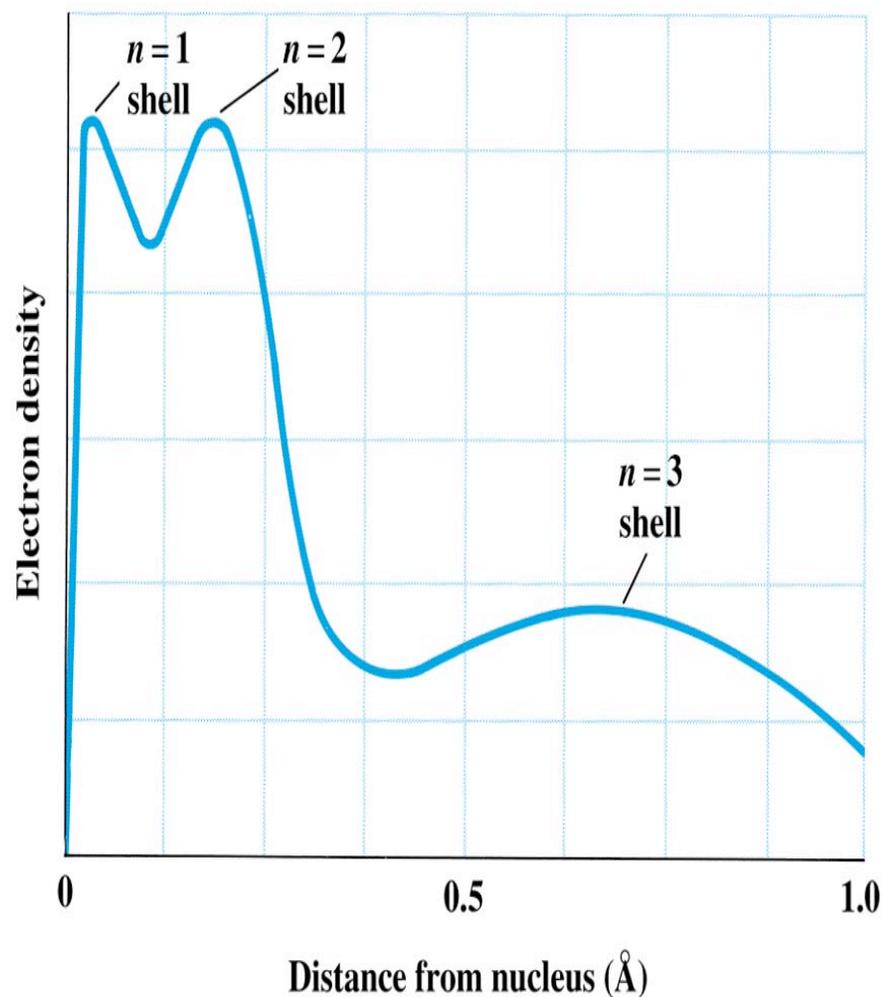
Orbital shells and the building up of the periodic table

A shell is a set of orbitals with the same value of n

The ^{18}Ar atom

($1s^2 2s^2 2p^6 3s^2 3p^6$) has shells as shown (left) in the profile of electron density as a function of distance from the nucleus

The last shell ($3s^2 3p^6$) contains the 8 valence electrons of our Lewis structures!



Building up electronic configurations of atoms:

In Place: the ordering of the energy levels ($n + l$) rule.

Two principles now needed to be applied: The Pauli exclusion principle and the Aufbau principle

The Pauli exclusion principle (A principle not derived from quantum mechanics, but required to explain observations).

Two equivalent statements of the Pauli exclusion principle:

- (1) No two electrons may have the same set of four quantum numbers;
- (2) No more than two electrons may occupy the same orbital.

Because of the Pauli exclusion principle, outer electrons do not "fall" into the inner shell. Thus, the atom is stable.

Furthermore, the principle together with the Aufbau principle leads to "magic" number of electrons in shells