

Chapter 8

Electron Configurations

What are the four quantum numbers to describe an electron in an atom?

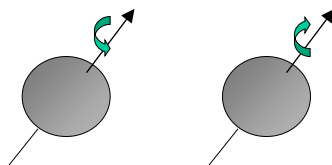
Characteristics of Many-Electron Atoms

Three additional features become important in many-electron atoms:

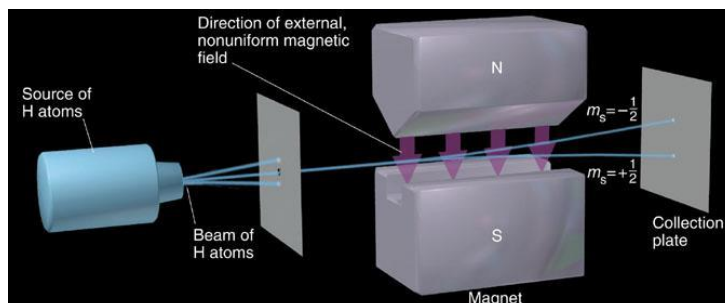
1. A fourth quantum number;
2. The number of electrons allowed in an atomic orbital; and,
3. The splitting of energy levels into sublevels.

The Electron- Spin Quantum Number

An electron can have one of two possible values of spin. As electrons spin they generate tiny magnetic fields. The fields generated by electrons having opposite spin oppose one another.



Experimental evidence for opposite electron spin was shown by Stern and Gerlach (**Figure 8.1**).



When a beam of hydrogen atoms passes through a non-uniform magnet field, the beam splits into two beams that bend away from each other.

Spin is an intrinsic property of the electron, and the **spin quantum number** (m_s) is assigned a value of either $+\frac{1}{2}$ or $-\frac{1}{2}$.

We can write four quantum numbers for any electron – the first three describe the atomic orbital and the fourth describes its spin.

What are the four quantum numbers to describe an electron in an atom?

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Table 8.1 Summary of Quantum Numbers of Electrons in Atoms

Name	Symbol	Permitted Values	Property
Principal	n	Positive integers (1, 2, 3, . . .)	Orbital energy (size)
Angular momentum	l	Integers from 0 to $n - 1$	Orbital shape (the l values 0, 1, 2, and 3 correspond to s , p , d , and f orbitals, respectively)
Magnetic	m_l	Integers from $-l$ to 0 to $+l$	Orbital orientation
Spin	m_s	$+\frac{1}{2}$ or $-\frac{1}{2}$	Direction of e^- spin

How many electrons have the principle quantum number equal to 1?

The Exclusion Principle and Orbital Occupancy

The set of quantum numbers for the lone electron in a hydrogen atom is $n = 1$, $l = 0$, $m_l = 0$ and $m_s = +\frac{1}{2}$.

By convention, we assign $+1/2$ to the first electron in an orbital.

First electron:

Second electron:



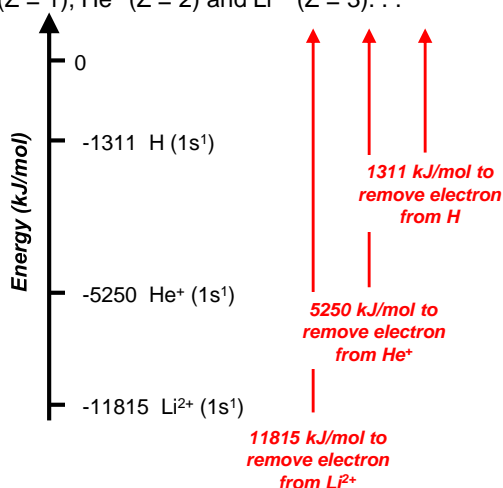
Wolfgang Pauli Received the Nobel Prize in Physics in 1945.

How many electrons have the principle quantum number equal to 1?

Electrostatic Effects and Energy Level Splitting

Effects of Nuclear Charge (Z) on Sublevel Energy. We can see that higher nuclear charge lowers the 1s orbital energy observed in the one electron atomic species: H atom ($Z = 1$), He^+ ($Z = 2$) and Li^{2+} ($Z = 3$). . .

- The higher nuclear charge on the He^+ and Li^{2+} lowers the energy of the 1s atomic orbital compared to that of the H atom
- As a consequence, it takes more energy to remove the electron from He^+ (and even more from Li^{2+}) than required to remove the electron in the H atom

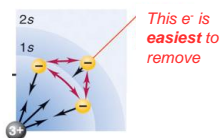


Shielding: The Effect of Electron Repulsions on Sublevel Energy.

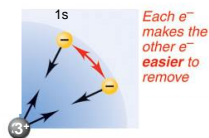
Electrons occupying lower energy levels (i.e., lower values of n) “shield” the outer electrons.

- This shielding reduces the full nuclear charge to the **effective nuclear charge** (Z_{eff}) felt by the outer electrons
- Thus, the outer electrons easier to remove

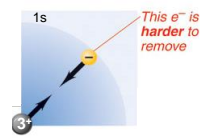
Let's look at the shielding that occurs in a Lithium atom. . .



Li atom
520 kJ/mol to
remove first electron



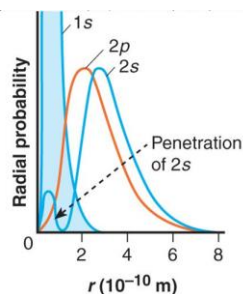
Li⁺ ion
2954 kJ/mol to
remove first electron



Li²⁺ ion
11815 kJ/mol to
remove first electron

Why does the third electron in a lithium atom go into the 2s- and not the 2p-atomic orbital?

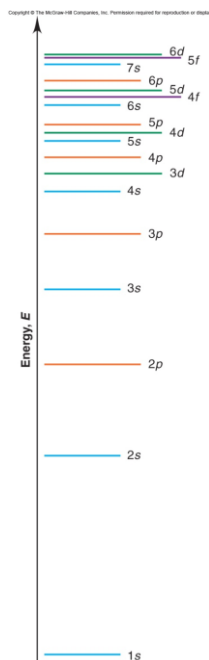
An electron in the 2s- atomic orbital experiences slightly less shielding (and more attraction to the nucleus) making it more difficult to remove compared to an electron occupying the 2p-atomic orbital.



The combination of penetration and shielding cause the splitting of the energy levels into sublevels of differing energy.

For a given value of n , the lower the l value, the lower the energy level

$$s < p < d < f$$



Which element has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^4$?

The Quantum-Mechanical Model and the Periodic Table

MAIN-GROUP ELEMENTS																MAIN-GROUP ELEMENTS														
1A (1)																8A (18)														
1	1															2														
1	H															He														
	1.008															4.003														
2	3 4															5 6 7 8 9 10														
	Li Be															B C N O F Ne														
	6.941 9.012															10.81 12.01 14.01 16.00 19.00 20.18														
3	11 12																13 14 15 16 17 18													
	Na Mg																Al Si P S Cl Ar													
	22.99 24.31																26.98 28.09 30.97 32.07 35.45 39.95													
4	19 20 21 22 23 24 25 26 27 28 29 30																31 32 33 34 35 36													
	K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn																Ga Ge As Se Br Kr													
	39.10 40.08 44.96 47.88 50.94 52.00 54.94 55.85 58.93 58.69 63.55 65.39																69.72 72.61 74.92 78.96 79.90 83.80													
5	37 38 39 40 41 42 43 44 45 46 47 48																49 50 51 52 53 54													
	Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd																In Sn Sb Te I Xe													
	85.47 87.62 88.91 91.22 92.91 95.94 (98) 101.1 102.9 106.4 107.9 112.4 114.8 118.7 121.8 127.6 126.9 131.3																													
6	55 56 57 72 73 74 75 76 77 78 79 80																81 82 83 84 85 86													
	Cs Ba La Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn																													
	132.9 137.3 138.9 178.5 180.9 183.9 186.2 190.2 192.2 195.1 197.0 200.6 204.4 207.2 209.0 (209) (210) (222)																													
7	87 88 89 104 105 106 107 108 109 110 111 112																114													
	Fr Ra Ac Rf Db Sg Bh Hs Mt																													
	(223) (226) (227) (261) (262) (266) (262) (265) (266) (269) (272) (277) (285)																													
TRANSITION ELEMENTS																														
3B (3) 4B (4) 5B (5) 6B (6) 7B (7) 8B (8) 9 (9) 10 (10) 11B (11) 12B (12)																														
INNER TRANSITION ELEMENTS																														
6	Lanthanides																													
	58 Ce 59 Pr 60 Nd 61 Pm 62 Sm 63 Eu 64 Gd 65 Tb 66 Dy 67 Ho 68 Er 69 Tm 70 Yb 71 Lu																													
	140.1 140.9 144.2 (145) 150.4 152.0 157.3 158.9 162.5 164.9 167.3 168.9 173.0 175.0																													
7	Actinides																													
	90 Th 91 Pa 92 U 93 Np 94 Pu 95 Am 96 Cm 97 Bk 98 Cf 99 Es 100 Fm 101 Md 102 No 103 Lr																													
	232.0 (231) 238.0 (237) (242) (243) (247) (247) (251) (252) (257) (258) (259) (260)																													

Condensed Electron Configurations

Mn

Cd

Sn

Which element has the electron configuration
 $1s^2 2s^2 2p^6 3s^2 3p^4$?

Note, two very important exceptions to Hund's rules for filling atomic orbitals are observed for Cr ($Z = 24$) and Cu ($Z = 29$).

Cr ($Z = 24$) [Ar] $4s^2 3d^4$ Experimental Electron Configuration: [Ar] $4s^1 3d^5$

Hund's Rules predict

Not

$\begin{array}{ccccccc} \uparrow\downarrow & \uparrow & \uparrow & \uparrow & \uparrow & & \\ 4s & & & 3d & & & \end{array} \leftarrow \text{experimentally observed!}$

$\begin{array}{ccccccc} \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \\ 4s & & & 3d & & & \end{array}$

Cu ($Z = 29$) [Ar] $4s^2 3d^9$ Experimental Electron Configuration: [Ar] $4s^1 3d^{10}$

Hund's Rules predict

Not

$\begin{array}{ccccccc} \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow & \\ 4s & & & 3d & & & \end{array} \leftarrow \text{experimentally observed!}$

$\begin{array}{ccccccc} \uparrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \\ 4s & & & 3d & & & \end{array}$

Both of these observations lead us to conclude that **half-filled** and **filled** atomic orbitals are unexpectedly stable – that is, lower in energy!

How many valence electrons does Fe have?

Categories of Electrons

1. **Inner (core) electrons** – occupy completely filled atomic orbitals of previous noble gas plus any completed d- or f- atomic orbitals
2. **Outer electrons** – occupy highest n value atomic orbitals
3. **Valence electrons** – involved in forming compounds

Examples:

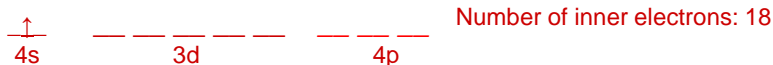
Main Group Elements: occupy highest n value atomic orbitals

Transition Elements: occupy highest n value atomic orbitals plus $(n - 1)d$ atomic orbitals

Sample Problems 8.2 – Using the periodic table give the condensed electron configurations, partial orbital diagrams showing valence electrons and number of inner electrons.

(a) Potassium ($Z = 19$) $\Rightarrow [\text{Ar}]4s^1$

Potassium is a Main Group Element; therefore, the partial orbital diagram for the valence electrons includes the 4s atomic orbital.



(b) Technetium ($Z=43$) $\Rightarrow [\text{Kr}]5s^24d^5$

Technetium is a Transition Element; therefore, the partial orbital diagram for the valence electrons includes the 5s and 4d atomic orbitals.



(c) Lead ($Z = 82$) $\Rightarrow [\text{Xe}]6s^24f^{14}5d^{10}6p^2$

Lead is a Main Group Element; therefore, the partial orbital diagram for the valence electrons includes the 6s and 6p atomic orbitals.



How many valence electrons does Fe have?

Using only the periodic table rank each set of Main-Group elements in order of **decreasing** atomic size.

Ca, Mg, Sr

Trends in Atomic Properties

All physical and chemical behavior of the elements is based on the electron configurations of their atoms.

We will focus on trends observed for

- Atomic size
- Ionization energy
- Metallic character
- Electron affinity

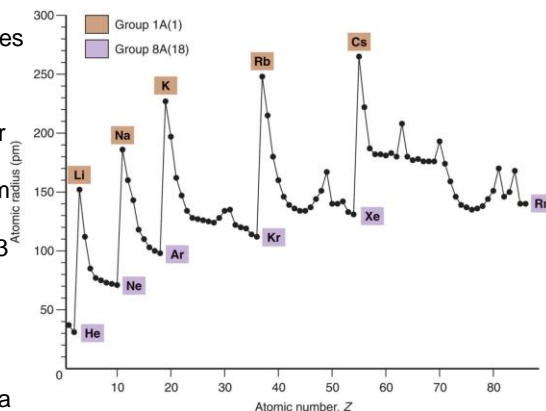
Trends in Atomic Size

- Atomic radius increases going down a group

• **WHY?** You fill a higher energy levels with electrons as you go from period 1 to period 2 and from period 2 to period 3 and so on. . .

- Atomic radius decreases as you move from left to right across a period

WHY? The effective nuclear charge increases as the atomic number increases across a period. The higher Z_{eff} pulls the electrons closer to the nucleus!



Using only the periodic table rank each set of Main-Group elements in order of **decreasing** atomic size.

Ca, Mg, Sr

All in Group 2A!

Sr > Ca > Mg

Which of the following atoms has the largest first ionization energy?

Si, Na, S, Te, Ba

Trends in Ionization Energy

The **ionization energy** (IE) is the energy (in kJ) required to completely remove 1 mol electrons from 1 mol gaseous atoms or ions.

Because you are putting energy into the atom, the IE is always positive.

- The first ionization energy (IE_1) removes the outermost electron from the gaseous atom:



- The second ionization energy (IE_2) removes the next electron from the gaseous ion so that IE_2 is always greater than IE_1 :



Note: Elements with low IE_1 always form cations and elements with high IE_1 always form anions.

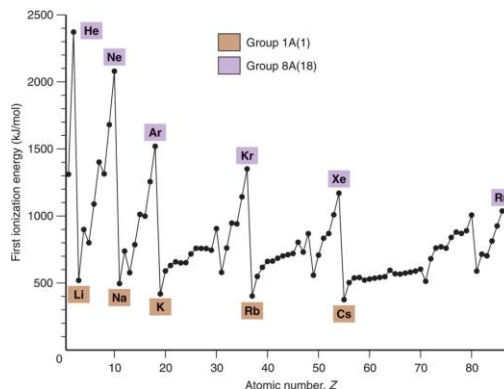
Trends in Ionization Energy

- IE decreases going down a group

• **WHY?** The outer electrons get farther and farther away from the nucleus as you go from period 1 to period 2 and from period 2 to period 3 and so on. . .

- IE increases as you move from left to right across a period

WHY? The Z_{eff} increases as the atomic number increases and pulls the electrons closer to the nucleus making it harder to remove one!



Variations in Successive Ionization Energies

Table 8.5 Successive Ionization Energies of the Elements Lithium Through Sodium

		Number of Valence Electrons	Ionization Energy (MJ/mol)*											
Z	Element		IE ₁	IE ₂	IE ₃	IE ₄	IE ₅	IE ₆	IE ₇	IE ₈	IE ₉	IE ₁₀		
3	Li	1	0.52	7.30	11.81	CORE ELECTRONS								
4	Be	2	0.90	1.76	14.85								21.01	
5	B	3	0.80	2.43	3.66								25.02	32.82
6	C	4	1.09	2.35	4.62								6.22	37.83
7	N	5	1.40	2.86	4.58	7.48	9.44	53.27	64.36	CORE ELECTRONS				
8	O	6	1.31	3.39	5.30	7.47	10.98	13.33	71.33					
9	F	7	1.68	3.37	6.05	8.41	11.02	15.16	17.87				92.04	
10	Ne	8	2.08	3.95	6.12	9.37	12.18	15.24	20.00				23.07	
11	Na	1	0.50	4.56	6.91	9.54	13.35	16.61	20.11	25.49	28.93	141.37		

*MJ/mol, or megajoules per mole = 10^3 kJ/mol.

Valence electrons are easier to remove than core electrons.

Example:

Which element Lithium (Li, Z=3) or Beryllium (Be, Z=4) will have the greater $IE_2:IE_1$ ratio?

Li: $1s^2 2s^1$ 1 valence e⁻; 2 core e⁻

Be: $1s^2 2s^2$ 2 valence e⁻; 2 core e⁻

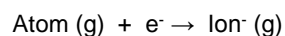
Lithium will have a greater $IE_2:IE_1$ ratio compared to beryllium because the second electron removed from lithium is a core electron.

Which of the following atoms has the largest first ionization energy?

Si, Na, S, Te, Ba

Trends in Electron Affinities

The **electron affinity** (EA) is the energy change (in kJ) accompanying the addition of 1 mol electrons to 1 mol gaseous atoms or ions.



$$\Delta E = EA_1$$

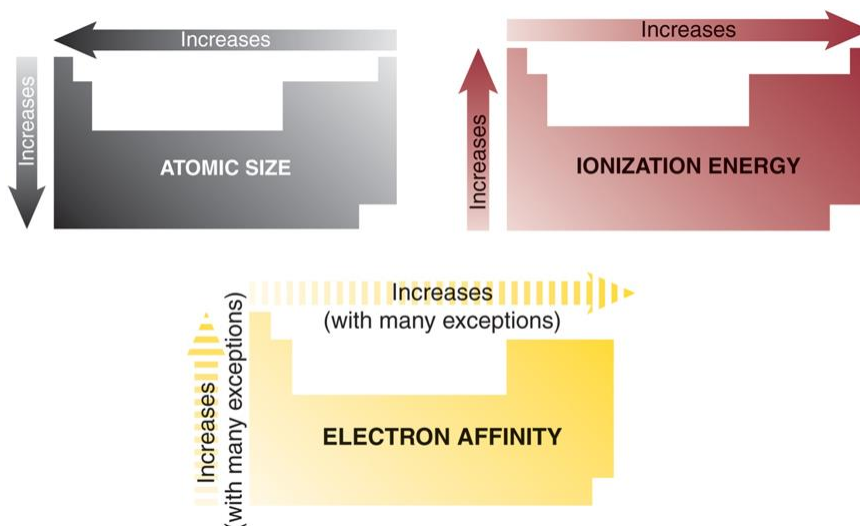
Energy is usually released when the first electron is added; EA_1 is usually negative.

1A (1)								8A (18)	
H -72.8		2A (2)		3A (13)	4A (14)	5A (15)	6A (16)	7A (17)	He (0.0)
Li -59.6	Be ≤0		B -26.7	C -122	N +7	O -141	F -328	Ne (+29)	
Na -52.9	Mg ≤0		Al -42.5	Si -134	P -72.0	S -200	Cl -349	Ar (+35)	
K -48.4	Ca -2.37		Ga -28.9	Ge -119	As -78.2	Se -195	Br -325	Kr (+39)	
Rb -46.9	Sr -5.03		In -28.9	Sn -107	Sb -103	Te -190	I -295	Xe (+41)	
Cs -45.5	Ba -13.95		Tl -19.3	Pb -35.1	Bi -91.3	Po -183	At -270	Rn (+41)	

Trends are not regular for electron affinities. In general we can make three comments:

1. Elements in Groups 1A and 2A have low ionization energies and slightly negative electron affinities. These elements form cations.
2. Elements in Groups 6A and 7A (halogens) have high ionization energies and very large negative electron affinities. These elements form anions.
3. Elements in Group 8A (noble gases) have very high ionization energies and slightly positive electron affinities. These elements are not reactive.

Periodic Trends

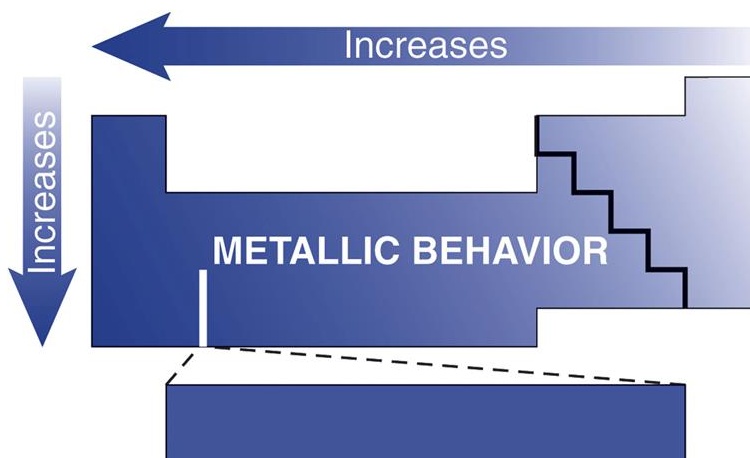


Atomic Properties and Chemical Reactivity

Trends in Metallic Behavior

- Metals are typically shiny solids with moderate to high melting points.
- Metals are good conductors of heat and electricity, and can easily be shaped.
- Metals tend to lose electrons and form cations, i.e., they are easily **oxidized**.
- Metals are generally **strong reducing agents**.
- Most metals form ionic oxides, which are **basic** in aqueous solution.

Trends in Metallic Behavior



Acid-base behavior of some element oxides.

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					5A (15)		
					N ₂ O ₅		
3	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₄ O ₁₀	SO ₃	Cl ₂ O ₇
					As ₂ O ₅		
					Sb ₂ O ₅		
					Bi ₂ O ₃		

Oxides become more basic down a group and more acidic across a period.

Predict the ion(s) formed from Indium ($Z = 49$) that has the electron configuration $[\text{Kr}] 5s^2 4d^{10} 5p^1$?

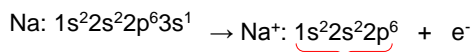
Properties of Monatomic Ions

Recall, our discussion on the Main-group elements earlier in the semester: The atoms of these elements either lose or gain electrons to attain the same number of electrons as the nearest noble gas.

We say that the ions formed are *isoelectronic* with the noble gas.

Let's see what happens when sodium loses one electron to form Na⁺ cation. . .

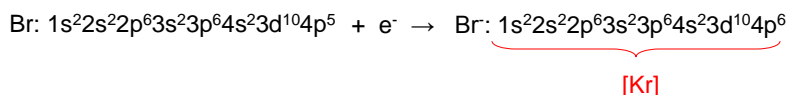
Na (Z = 11)



[Ne]

How about when bromine gain one electron to form the Br⁻ anion. . .

Br (Z = 35)

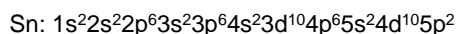


[Kr]

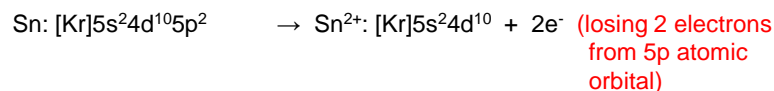
The larger members of Group 3A, 4A and 5A are observed to form more one cation.

These elements tend to empty the outer *np* orbital or empty both the outer *ns* and *np* orbitals.

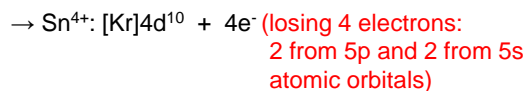
Look at the two cations formed by tin, Sn (Z = 50). . .



[Kr]



OR



Predict the ion(s) formed from Indium ($Z = 49$) that has the electron configuration $[\text{Kr}] 5s^2 4d^{10} 5p^1$?

Electron Configurations of Transition Metal Ions

The typical behavior of a transition element is to form more than one cation by first losing all its ns electrons (generating a $2+$ cation) and one or more $(n - 1)d$ electrons (generating $\geq 3+$ cation).

Go back and look at **Table 2.4**. . .

Iron ($Z=26$): $[\text{Ar}]4s^2 3d^6$ forms Fe^{2+} and Fe^{3+}

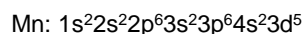
Copper ($Z=29$): $[\text{Ar}]4s^1 3d^{10}$ forms Cu^+ and Cu^{2+}

Species with unpaired electrons are called **paramagnetic**.

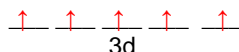
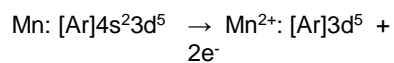
Species having all paired electrons are called **diamagnetic** and are unaffected by an external magnetic field.

Sample Problem 8.7 – Write the electron configurations and predict magnetic behavior of the ions below:

(a) Mn^{2+} ($Z = 25$)



[Ar]



5 unpaired electrons – Paramagnetic!

Rank each set on ions in order of **decreasing** size, and explain your ranking:

Ca^{2+} , Sr^{2+} , Mg^{2+}

MAIN-GROUP ELEMENTS																		MAIN-GROUP ELEMENTS									
Period	1A (1)																		3A (13)		4A (14)	5A (15)	6A (16)	7A (17)	8A (18)		
	1	H 1.008																	2	He 4.003							
	2	3 Li 6.941	4 Be 9.012															5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18				
	3	11 Na 22.99	12 Mg 24.31	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95																		
	4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80								
	5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3								
	6	55 Cs 132.9	56 Ba 137.3	57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0									
	7	87 Fr (223)	88 Ra (226)	89 Ac (227)	90 Th (232)	91 Pa (231)	92 U (238)	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)									
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