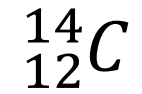


# Atomic Structure & Periodicity

“How are BONDS formed?” – Chapter 6 & 7

# What's inside an atom?

Atomic symbols:



Too many or too few electrons:

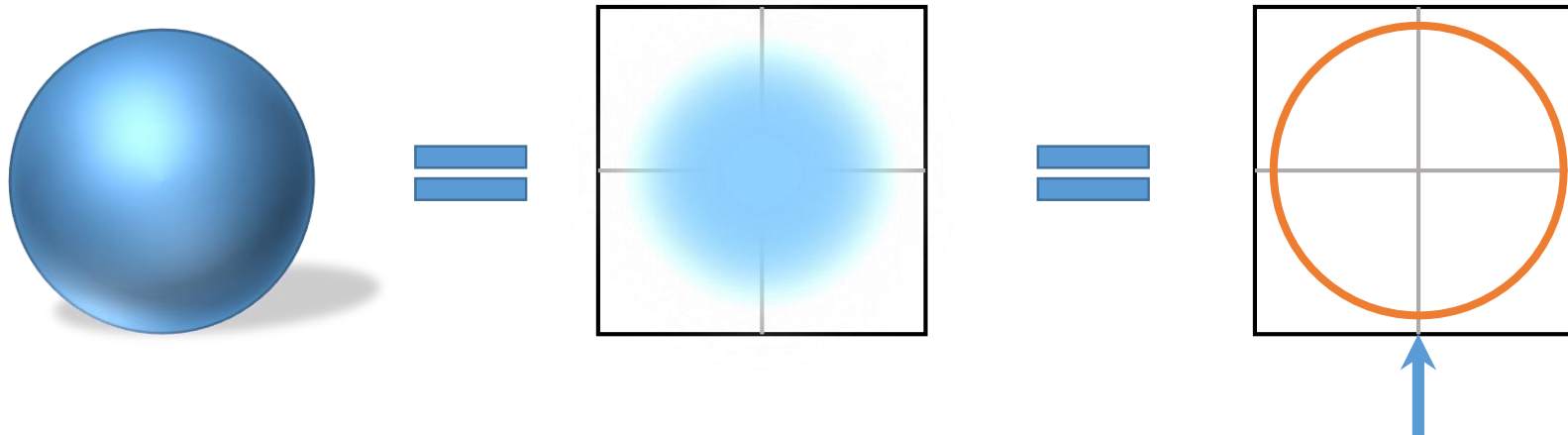
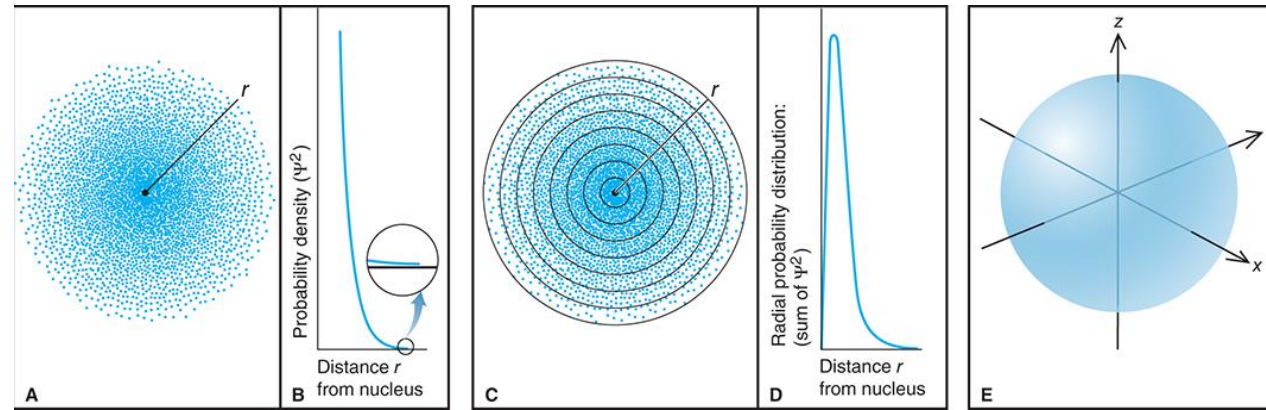


# Electronic Structure

Electrons in an atom are arranged in *shells, subshells, and orbitals*.

- **Orbitals** describe the physical distribution of electrons within an atom. There are several kinds of orbitals, each with a characteristic shape. Each orbital can contain a maximum of 2 electrons.
- **Subshells** are collections of orbitals with a similar shape. These are usually described by letters (*s, p, d, f, ...*) where all orbitals in the *p* subshell have a similar shape.
- **Shells**, or energy levels, are numbered ( $n = 1, 2, 3, \dots$ ) with each shell describing orbitals and subshells with a similar size and energy. Lower-numbered shells are lower energy and smaller.

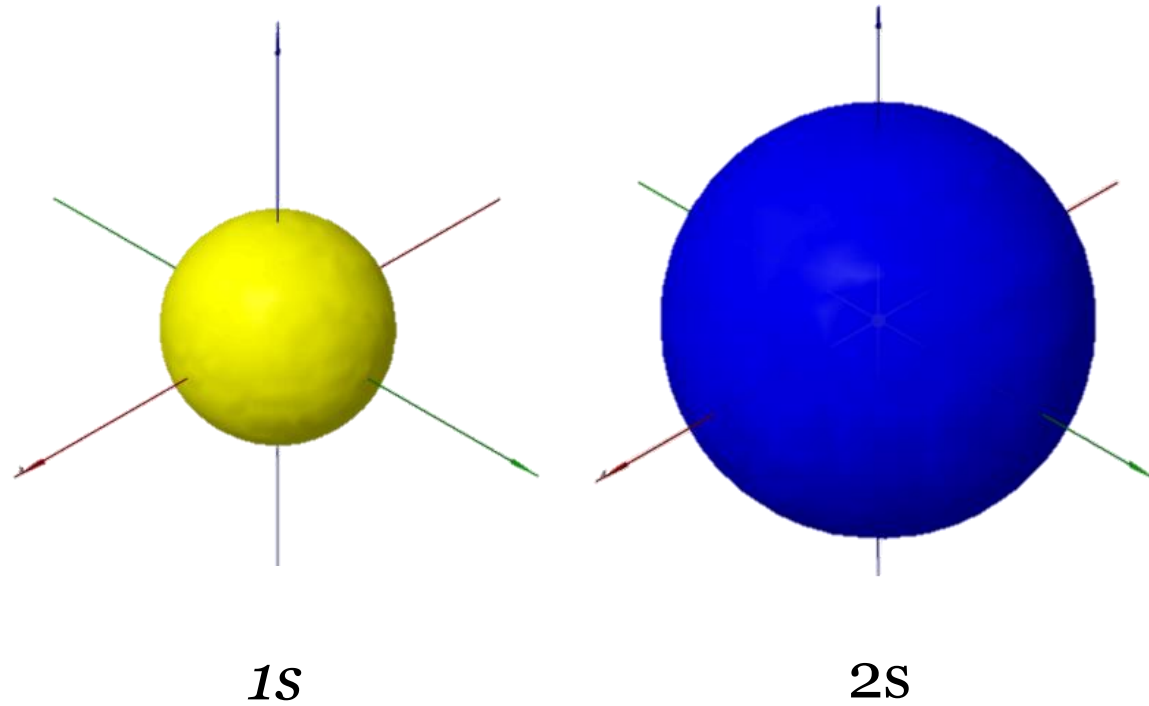
# Representations of Orbitals



90% probability of finding the electron within this circle

✓ Recognize atomic orbital shapes ( $s$ ,  $p$  and  $d$ ) and predict their relative energies.

# s orbitals

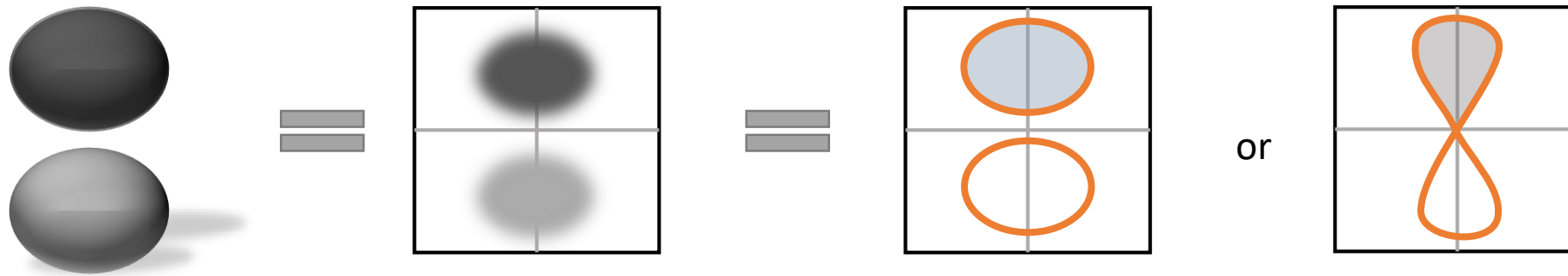


s orbitals are spherical.

There is only one s orbital per subshell.

The s subshell is the lowest-energy subshell in any energy level.

# $p$ orbitals

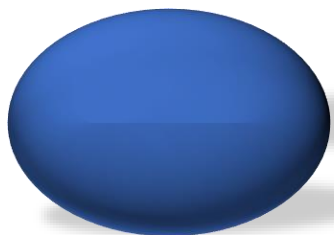
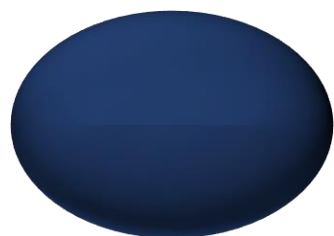
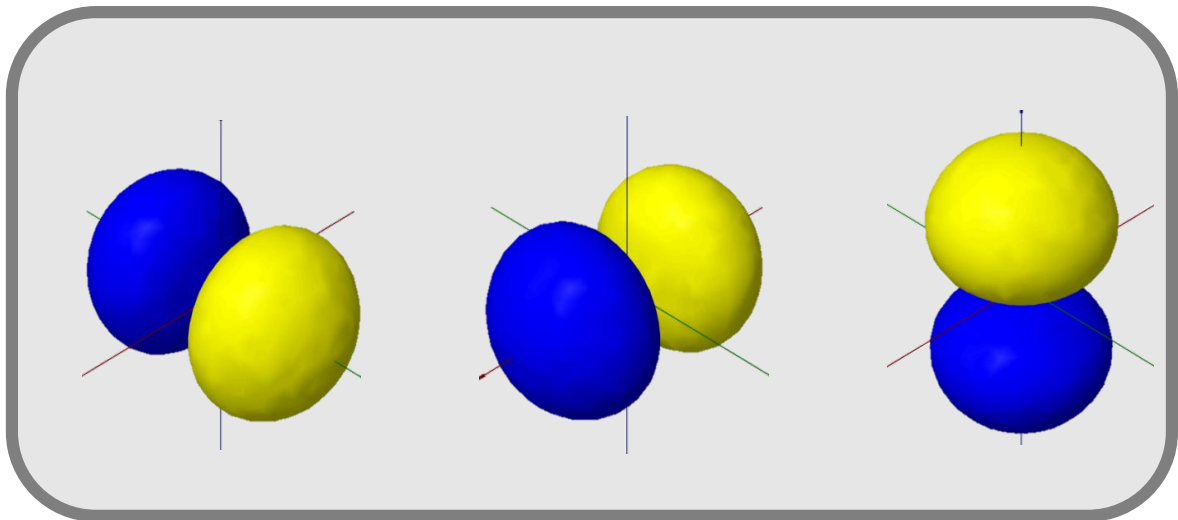


$p$  orbitals have one *angular node* – one region where there is zero electron density.

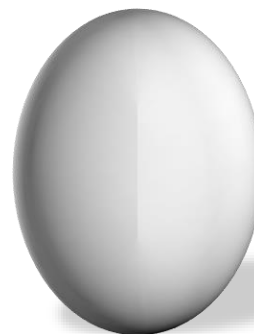
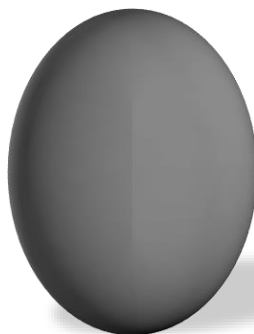
There are three possible orientations for  $p$  orbitals ( $x$ ,  $y$ ,  $z$ ) – and so three  $p$  orbitals per subshell.

The  $p$  subshell is higher energy than the  $s$  subshell in the same energy level.





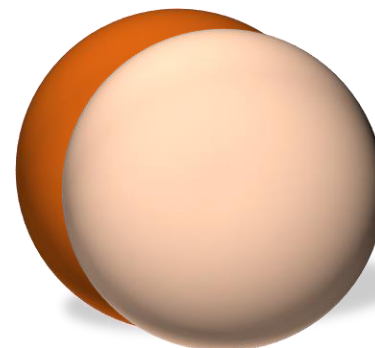
$p_y$



nucleus

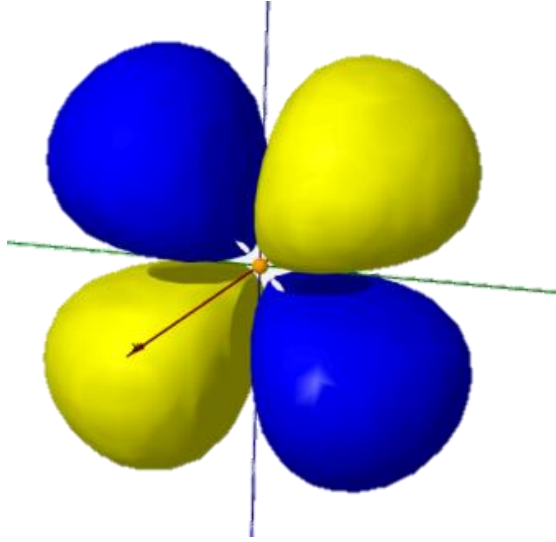


$p_x$



$p_z$

# $d$ orbitals



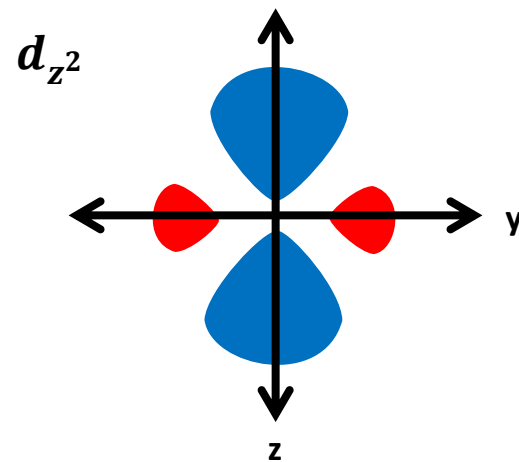
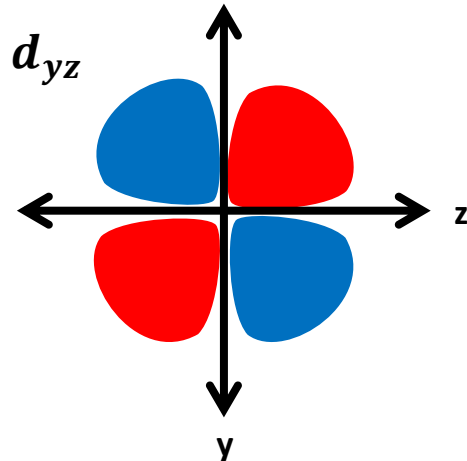
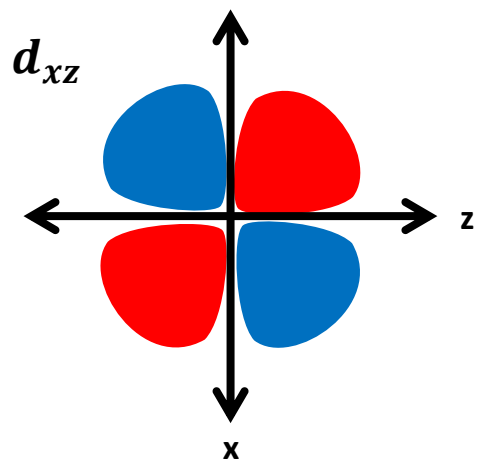
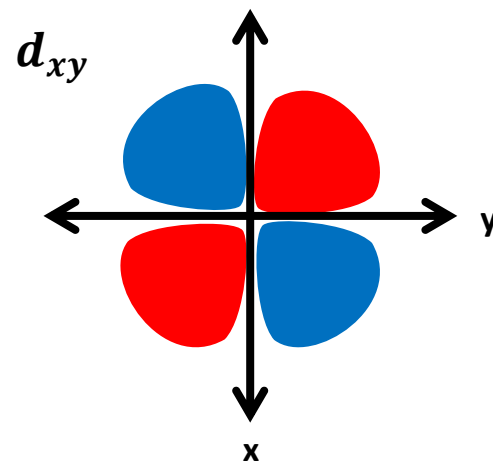
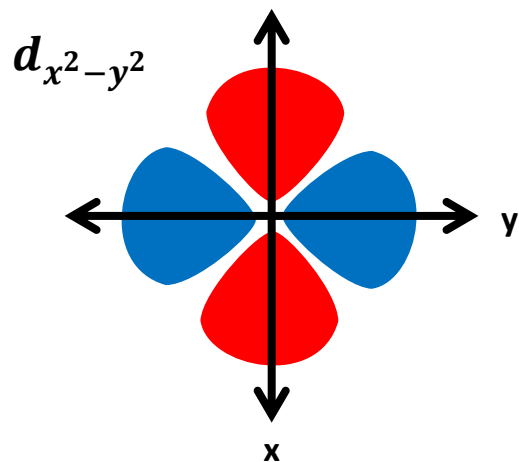
$d$  orbitals have two *angular nodes*.

There are five possible orientations and so five  $d$  orbitals per subshell.

The  $d$  subshell is higher energy than the  $s$  and  $p$  subshells in the same energy level.

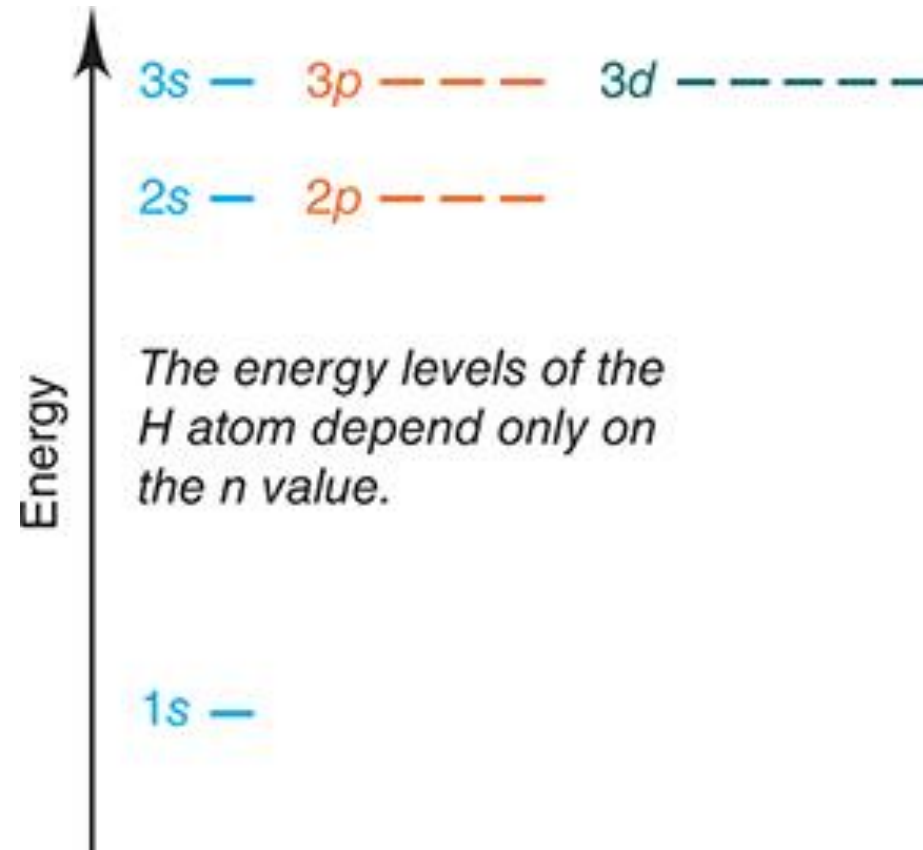
✓ Recognize atomic orbital shapes ( $s$ ,  $p$  and  $d$ ) and predict their relative energies.

# $d$ orbitals



# Relative Energies of Orbitals

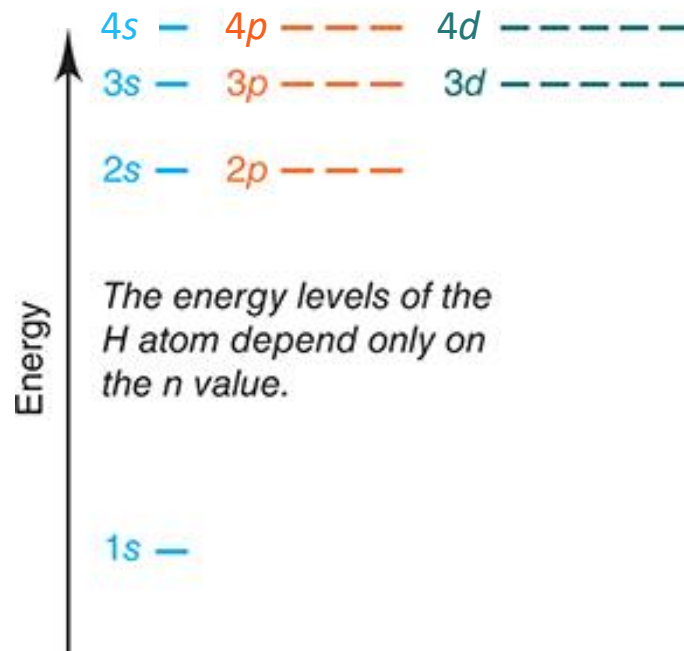
In hydrogen, where there is only one electron, the orbital energy depends only on  $n$ :



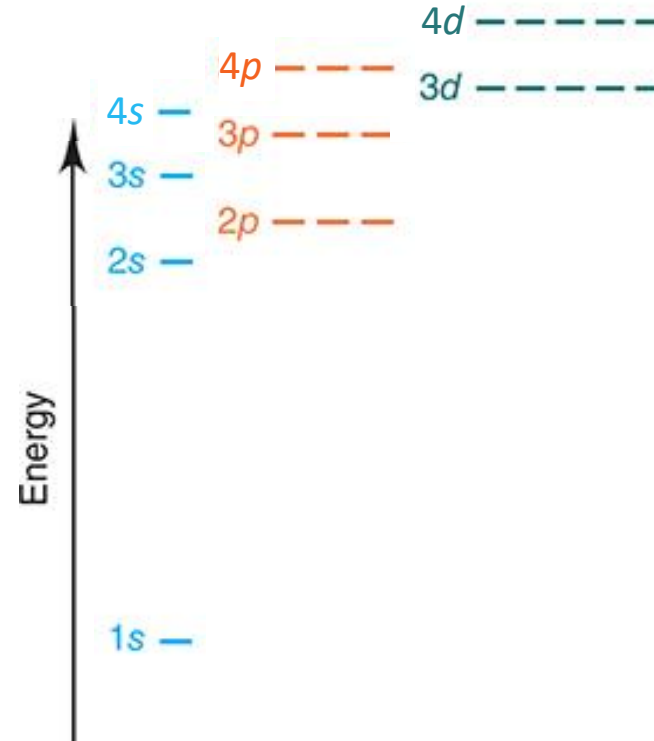
# Energy levels in multielectron atoms

Electrons are *like charges* and repel each other slightly (even when they're paired up). The combined effect of nuclear attraction, electron repulsion, and orbital shape lead to the splitting of the shells into subshell-based energy levels:

Hydrogen (single electron)



Everything else (multielectron)



# Electron Configurations of Atoms

Expressing the organization of electrons into their various shells/subshells/orbitals is the *electron configuration* for an atom.

To build a **ground state** electron configuration, we follow 3 rules:

1. **Aufbau Principle**

2. **Pauli Exclusion Principle**

3. **Hund's Rule**



What is the electron configuration of N?

What is the electron configuration of Mg?

# Core and Valence electrons

**Valence** electrons are the highest energy electrons of an atom, found in the outermost shell. (i.e. the electrons with the highest value of  $n$ ). These are the electrons that are usually involved in reactivity and bonding for an atom.

Electrons in the inner shells are **core** electrons.

How many valence electrons are in oxygen?

{numerical answer}





# “Noble Gas” Shorthand Notation

We can use the next-smallest noble gas as a shorthand for the core electrons of an atom:

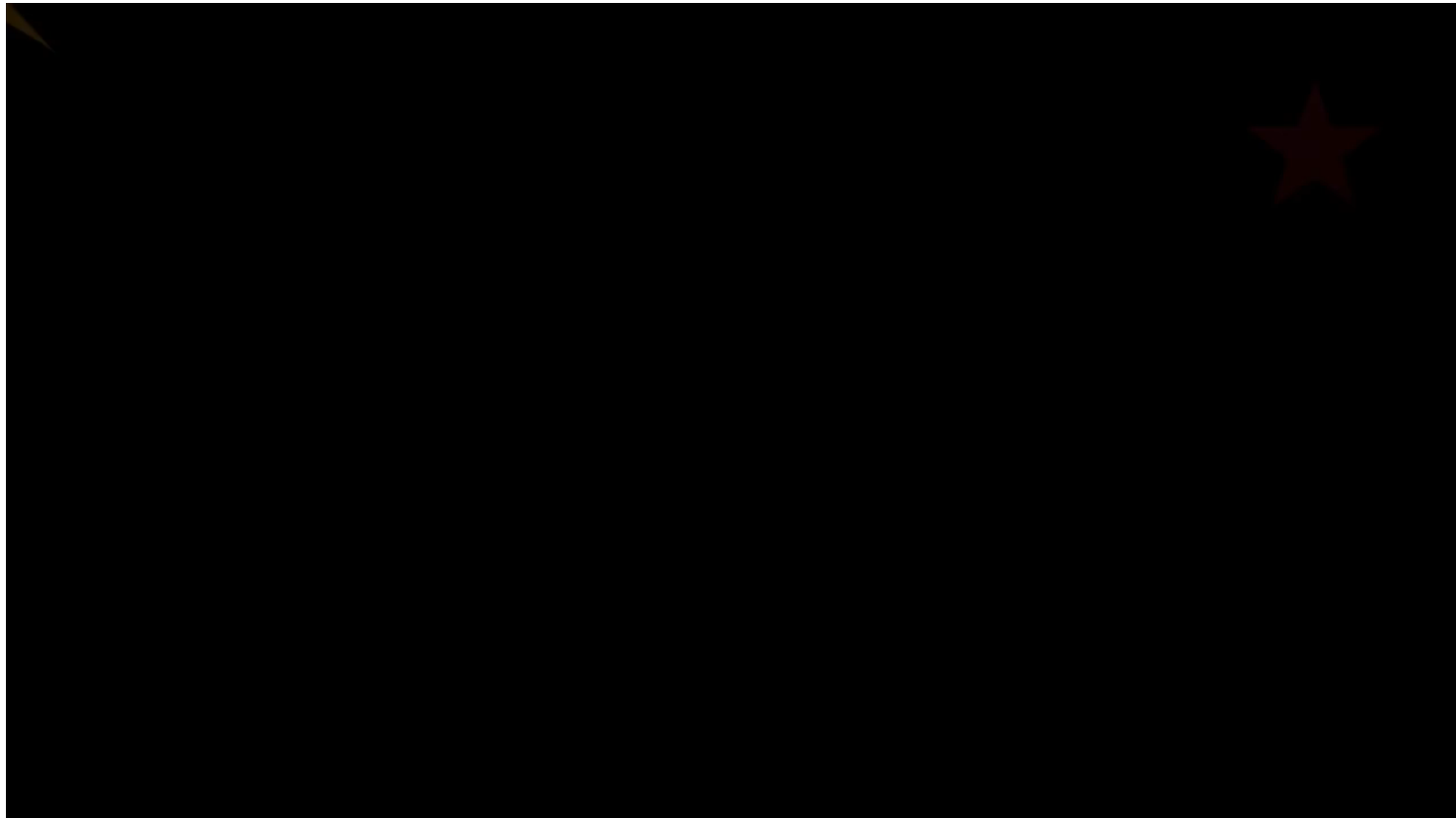
Electron config of Mg:



		Main-Group Elements (s block)												Main-Group Elements (p block)							
		1																		18	
		$ns^1$																		$ns^2np^6$	
Period number: highest occupied energy level	1	1 <b>H</b> $1s^1$	2 $ns^2$													13 $ns^2np^1$	14 $ns^2np^2$	15 $ns^2np^3$	16 $ns^2np^4$	17 $ns^2np^5$	2 <b>He</b> $1s^2$
	2	3 <b>Li</b> $2s^1$	4 <b>Be</b> $2s^2$	Transition Elements (d block)												5 <b>B</b> $2s^22p^1$	6 <b>C</b> $2s^22p^2$	7 <b>N</b> $2s^22p^3$	8 <b>O</b> $2s^22p^4$	9 <b>F</b> $2s^22p^5$	10 <b>Ne</b> $2s^22p^6$
	3	11 <b>Na</b> $3s^1$	12 <b>Mg</b> $3s^2$	3	4	5	6	7	8	9	10	11	12	13 <b>Al</b> $3s^23p^1$	14 <b>Si</b> $3s^23p^2$	15 <b>P</b> $3s^23p^3$	16 <b>S</b> $3s^23p^4$	17 <b>Cl</b> $3s^23p^5$	18 <b>Ar</b> $3s^23p^6$		
	4	19 <b>K</b> $4s^1$	20 <b>Ca</b> $4s^2$	21 <b>Sc</b> $4s^23d^1$	22 <b>Ti</b> $4s^23d^2$	23 <b>V</b> $4s^23d^3$	24 <b>Cr</b> $4s^13d^5$	25 <b>Mn</b> $4s^23d^5$	26 <b>Fe</b> $4s^23d^6$	27 <b>Co</b> $4s^23d^7$	28 <b>Ni</b> $4s^23d^8$	29 <b>Cu</b> $4s^13d^{10}$	30 <b>Zn</b> $4s^23d^{10}$	31 <b>Ga</b> $4s^24p^1$	32 <b>Ge</b> $4s^24p^2$	33 <b>As</b> $4s^24p^3$	34 <b>Se</b> $4s^24p^4$	35 <b>Br</b> $4s^24p^5$	36 <b>Kr</b> $4s^24p^6$		
	5	37 <b>Rb</b> $5s^1$	38 <b>Sr</b> $5s^2$	39 <b>Y</b> $5s^24d^1$	40 <b>Zr</b> $5s^14d^2$	41 <b>Nb</b> $5s^14d^4$	42 <b>Mo</b> $5s^14d^5$	43 <b>Tc</b> $5s^24d^5$	44 <b>Ru</b> $5s^14d^7$	45 <b>Rh</b> $5s^14d^8$	46 <b>Pd</b> $4d^{10}$	47 <b>Ag</b> $5s^14d^{10}$	48 <b>Cd</b> $5s^24d^{10}$	49 <b>In</b> $5s^25p^1$	50 <b>Sn</b> $5s^25p^2$	51 <b>Sb</b> $5s^25p^3$	52 <b>Te</b> $5s^25p^4$	53 <b>I</b> $5s^25p^5$	54 <b>Xe</b> $5s^25p^6$		
	6	55 <b>Cs</b> $6s^1$	56 <b>Ba</b> $6s^2$		72 <b>Hf</b> $6s^25d^2$	73 <b>Ta</b> $6s^25d^3$	74 <b>W</b> $6s^25d^4$	75 <b>Re</b> $6s^25d^5$	76 <b>Os</b> $6s^25d^6$	77 <b>Ir</b> $6s^25d^7$	78 <b>Pt</b> $6s^15d^9$	79 <b>Au</b> $6s^15d^{10}$	80 <b>Hg</b> $6s^25d^{10}$	81 <b>Tl</b> $6s^26p^1$	82 <b>Pb</b> $6s^26p^2$	83 <b>Bi</b> $6s^26p^3$	84 <b>Po</b> $6s^26p^4$	85 <b>At</b> $6s^26p^5$	86 <b>Rn</b> $6s^26p^6$		
	7	87 <b>Fr</b> $7s^1$	88 <b>Ra</b> $7s^2$		104 <b>Rf</b> $7s^26d^2$	105 <b>Db</b> $7s^26d^3$	106 <b>Sg</b> $7s^26d^4$	107 <b>Bh</b> $7s^26d^5$	108 <b>Hs</b> $7s^26d^6$	109 <b>Mt</b> $7s^26d^7$	110 <b>Ds</b> $7s^26d^8$	111 <b>Rg</b> $7s^26d^9$	112 <b>Cn</b> $7s^26d^{10}$	113 $7s^27p^1$	114 $7s^27p^2$	115 $7s^27p^3$	116 $7s^27p^4$		118 $7s^27p^6$		
		Inner Transition Elements (f block)																			
6	*Lanthanides	57 <b>La*</b> $6s^25d^1$	58 <b>Ce</b> $6s^24f^15d^1$	59 <b>Pr</b> $6s^24f^3$	60 <b>Nd</b> $6s^24f^4$	61 <b>Pm</b> $6s^24f^5$	62 <b>Sm</b> $6s^24f^6$	63 <b>Eu</b> $6s^24f^7$	64 <b>Gd</b> $6s^24f^75d^1$	65 <b>Tb</b> $6s^24f^9$	66 <b>Dy</b> $6s^24f^{10}$	67 <b>Ho</b> $6s^24f^{11}$	68 <b>Er</b> $6s^24f^{12}$	69 <b>Tm</b> $6s^24f^{13}$	70 <b>Yb</b> $6s^24f^{14}$	71 <b>Lu</b> $6s^24f^{14}5d^1$					
7	**Actinides	89 <b>Ac**</b> $7s^26d^1$	90 <b>Th</b> $7s^26d^2$	91 <b>Pa</b> $7s^25f^26d^1$	92 <b>U</b> $7s^25f^36d^1$	93 <b>Np</b> $7s^25f^46d^1$	94 <b>Pu</b> $7s^25f^6$	95 <b>Am</b> $7s^25f^7$	96 <b>Cm</b> $7s^25f^76d^1$	97 <b>Bk</b> $7s^25f^9$	98 <b>Cf</b> $7s^25f^{10}$	99 <b>Es</b> $7s^25f^{11}$	100 <b>Fm</b> $7s^25f^{12}$	101 <b>Md</b> $7s^25f^{13}$	102 <b>No</b> $7s^25f^{14}$	103 <b>Lr</b> $7s^25f^{14}6d^1$					

# Magnetism

- Atoms with *unpaired* electrons in their e- config will be attracted to a magnetic field and are **paramagnetic**.
- Atoms where all electrons are paired are weakly repelled by magnetic fields and are **diamagnetic**.
  - Since most atoms in molecules have all paired electrons (we'll see why) most molecular materials are diamagnetic.



Which element(s) below are **diamagnetic** in their ground state?



- a. C
- b. P
- c. Be
- d. O
- e. Ar
- f. Ca

# Electron config. of main-group ions

When an atom ionizes, it loses its highest energy electrons first (i.e. the valence electrons)

Typically it will lose (or gain) enough electrons to achieve a **closed shell configuration** – where all orbitals in a shell are either full or empty. (source of the *octet rule*!)

What is the electron configuration for  $\text{Al}^{3+}$ ?

Based on its' electron configuration, what charge would you expect selenium to take when it ionizes?



- a. +3
- b. +2
- c. +1
- d. 0
- e. -1
- f. -2
- g. -3

# Periodic Trends

The arrangement of atoms in the periodic table was originally based off of trends in chemical properties (which just happens to be dependent on atomic structure!)

Most trends can be rationalized by relating them to:

- Size of the atom
- *Effective nuclear charge* felt by the valence electrons



# Shielding and $Z_{\text{eff}}$

Electrons in the core shells **shield** the valence electrons from some of the nuclear charge. Thus, the valence electrons feel less of the electrostatic attraction to the nucleus than core electrons.

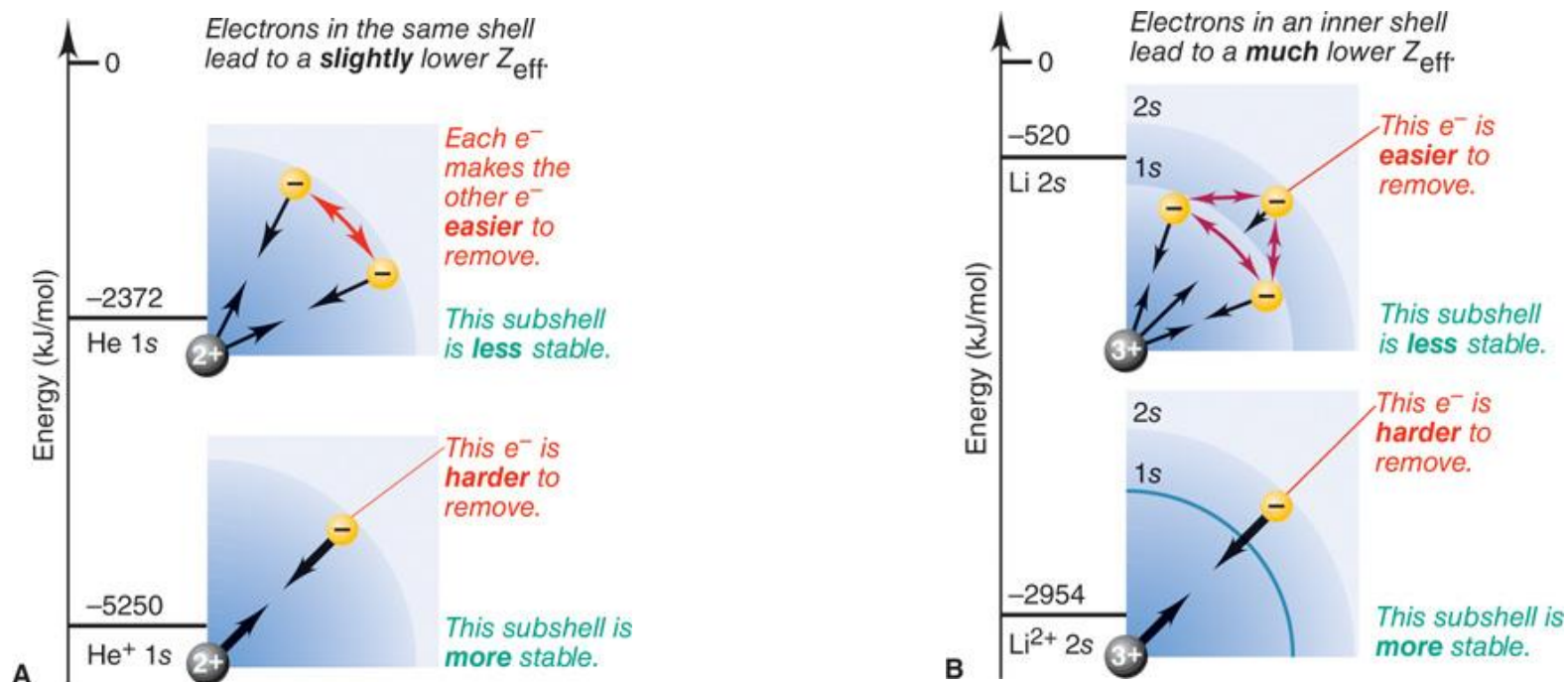
















Figure 7.3

For main-group elements, we can *approximate*  $Z_{\text{eff}}$  as:

$$Z_{\text{eff}} = Z - n_{\text{core}}$$

# Trends in Atomic Size

	1					18
1	H 37 	2				He 31 
2	Li 152 	Be 112 				
3	Na 186 	Mg 160 				
4	K 227 	Ca 197 				
5	Rb 248 	Sr 215 				
6	Cs 265 	Ba 222 				
7	Fr 270 	Ra 220 				































13	14	15	16	17	
B 85 	C 77 	N 75 	O 73 	F 72 	Ne 71 
Al 143 	Si 118 	P 110 	S 103 	Cl 100 	Ar 98 
Ga 135 	Ge 122 	As 120 	Se 119 	Br 114 	Kr 112 
In 167 	Sn 140 	Sb 140 	Te 142 	I 133 	Xe 131 
Tl 170 	Pb 146 	Bi 150 	Po 168 	At 140 	Rn 140 

Fig 7.13

# Trends in Ionic Size

- Cations are **smaller** than their parent atoms, while anions are **larger**.
- Doubly-charged (or more!) ions will have a larger effect.
- For ions with the same charge, the relative size follows the same trends as the parent atoms.
- We often compare atoms that are in an *isoelectronic series*

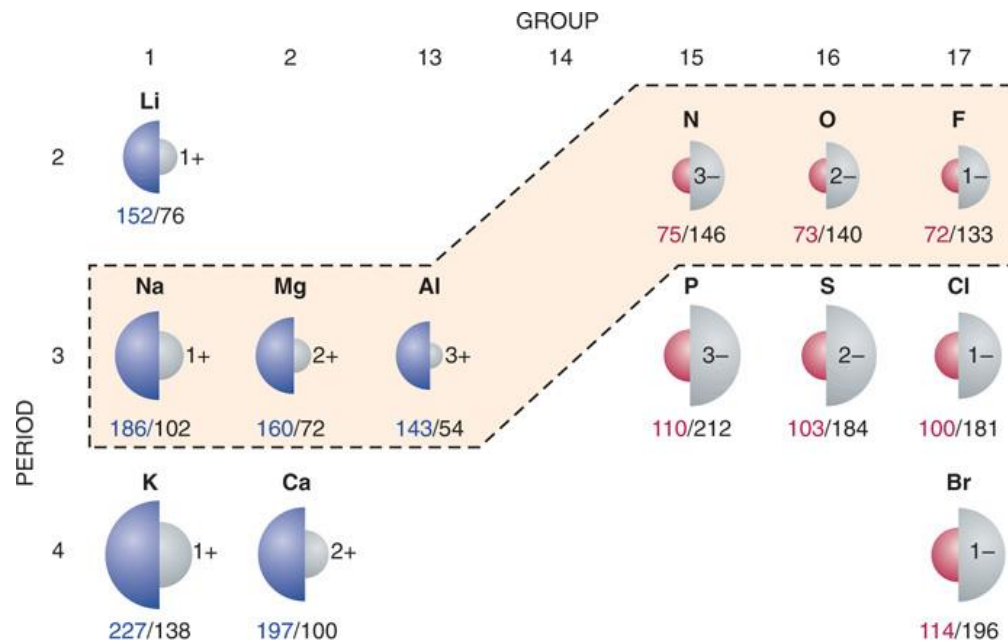


Fig. 7.26



Rank the following species in order from SMALLEST to LARGEST:

- $\text{Br}^-$
- $\text{Sr}^{2+}$
- $\text{Rb}$
- $\text{Rb}^+$

# Ionization Energy

- **Ionization energy** is the energy required to completely remove an electron from an atom.
- This is an endothermic process – we must put energy in to ionize the atom.
- The *first ionization energy* describes the removal of an electron from the neutral atom. The *second ionization energy* describes the removal of an electron from the 1+ cation, the *third IE* from the 2+ cation, and so on.
- Ionization energy generally increases:
  - UP a group in the periodic table
  - From left to right across a period

# 1<sup>st</sup> → 2<sup>nd</sup> → 3<sup>rd</sup> IE trends

- As more electrons are removed from an atom, further ionization becomes more difficult.
- Removing electrons from an atom's core shells is MUCH more difficult than removing valence electrons.

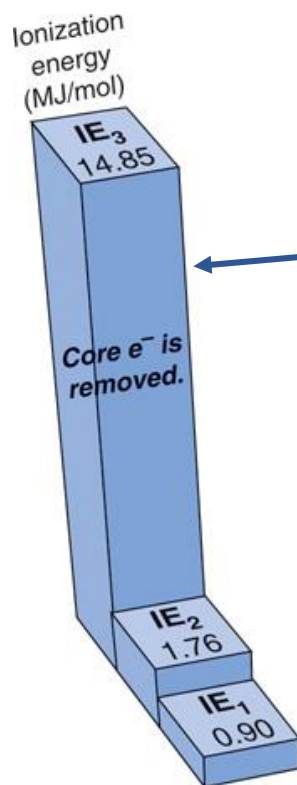


TABLE 7.4		Successive Ionization Energies of the Elements Lithium Through Sodium												
Z	Element	Number of Valence Electrons	Ionization Energy (MJ/mol)*											
			IE <sub>1</sub>	IE <sub>2</sub>	IE <sub>3</sub>	IE <sub>4</sub>	IE <sub>5</sub>	IE <sub>6</sub>	IE <sub>7</sub>	IE <sub>8</sub>	IE <sub>9</sub>	IE <sub>10</sub>		
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					
8	O	6	1.31	3.39	5.30	7.47	10.98	13.33	71.33				84.08	
9	F	7	1.68	3.37	6.05	8.41	11.02	15.16	17.87	92.04	106.43			
10	Ne	8	2.08	3.95	6.12	9.37	12.18	15.24	20.00	23.07	115.38		131.43	
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<sup>3</sup> kJ/mol

# Exceptions to the IE Trend

Ionization energy is also affected by the electron configuration – some electrons are easier to remove than others.

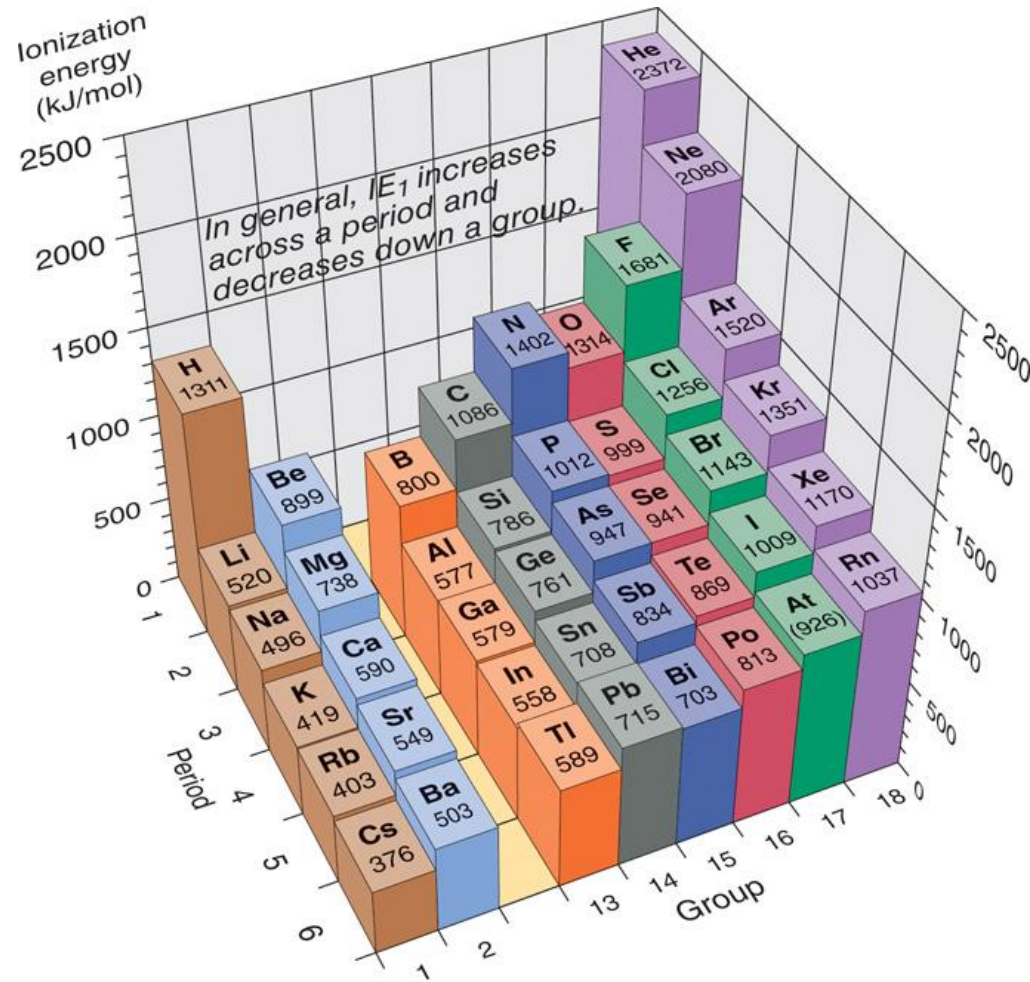


Fig 7.16

Element *J* is a 3<sup>rd</sup>-period element with the approximate ionization energies listed below. What element is it?



(submit the atomic symbol)

$$IE_1 = 700 \text{ kJ/mol}$$

$$IE_2 = 1800 \text{ kJ/mol}$$

$$IE_3 = 3000 \text{ kJ/mol}$$

$$IE_4 = 11600 \text{ kJ/mol}$$

1

1A

2

2A

3

3A

4

4A

5

5A

6

6A

7

7A

8

8A

1

H

1.008

2

He

4.003

3

Li

6.941

4

Be

9.012

11

Na

22.99

12

Mg

24.31

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

65.38

31

Ga

69.72

32

Ge

72.59

33

As

74.92

34

Se

78.96

35

Br

79.90

36

Kr

83.80

13

B

10.81

14

C

12.01

15

N

14.01

16

O

16.00

17

F

19.00

18

Ar

39.95

13

Al

26.98

14

Si

28.09

15

P

30.97

16

S

32.07

17

Cl

35.45

18

Ar

39.95

3

4

5

6

7

8

9

10

11

12

1

H

1.008

← Atomic number (Z)

← Atomic symbol

← Atomic mass (amu)



# Electron Affinity

**Electron affinity** is the energy associated with the addition of an electron to an atom (or ion).

Like I.E., we can refer to the 1<sup>st</sup> EA, 2<sup>nd</sup> EA, etc.

Most electron affinities are negative (exothermic). EA has more irregularities than IE, but some trends generally apply:

Electron affinities for selected elements  
(kJ/mol)

1						18
<b>H</b> -72.8	2					<b>He</b> (0.0)
<b>Li</b> -59.6	<b>Be</b> ≤0	13	14	15	16	17
		<b>B</b> -26.7	<b>C</b> -122	<b>N</b> +7	<b>O</b> -141	<b>F</b> -328
						<b>Ne</b> (+29)
<b>Na</b> -52.9	<b>Mg</b> ≤0	<b>Al</b> -42.5	<b>Si</b> -134	<b>P</b> -72.0	<b>S</b> -200	<b>Cl</b> -349
						<b>Ar</b> (+35)



The first two electron affinity values for oxygen are provided below. Which option best accounts for the difference in the energies?

$\text{O}(\text{g}) + \text{e}^- \rightarrow \text{O}^-(\text{g})$	$\text{EA}_1 = -141 \text{ kJ/mol}$
$\text{O}^-(\text{g}) + \text{e}^- \rightarrow \text{O}^{2-}(\text{g})$	$\text{EA}_2 = +744 \text{ kJ/mol}$

- a. Oxygen tends to form  $1^-$  anions rather than  $2^-$  anions
- b. The second electron is being placed into a full subshell, which is unfavorable
- c. With more electrons, there are more electrostatic repulsions to overcome
- d. As electrons are added, the  $Z_{\text{eff}}$  decreases, making it easier to add further electrons