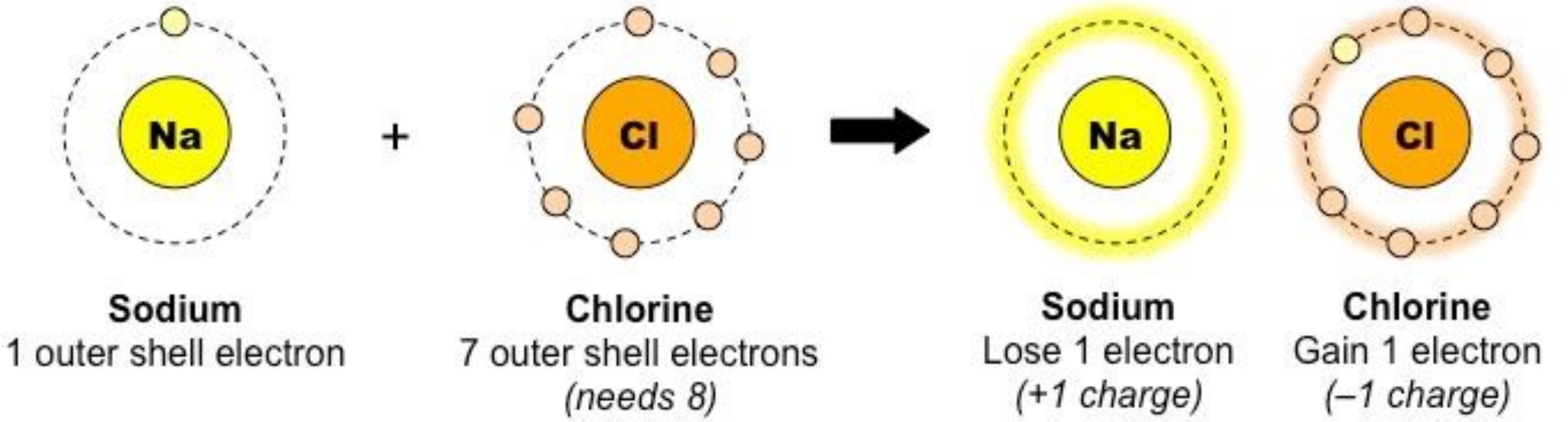
# Unit 2: Molecular & Ionic Compound Structure & Properties

# 2.1 Types of Chemical Bonds
# 2.3 Structure of Ionic Solids
# 2.4 Structure of Metals & Alloys

- Ionic, Covalent and Metallic Bonds
- Determining Bond Type
- Introduction to Unit Cells

# Ionic Bonds

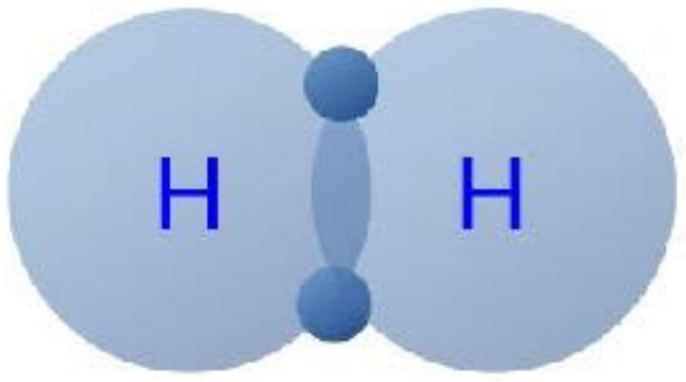
Metals transfer electrons to non-metals and the two form bonds due to *electrostatic attractions* between them.



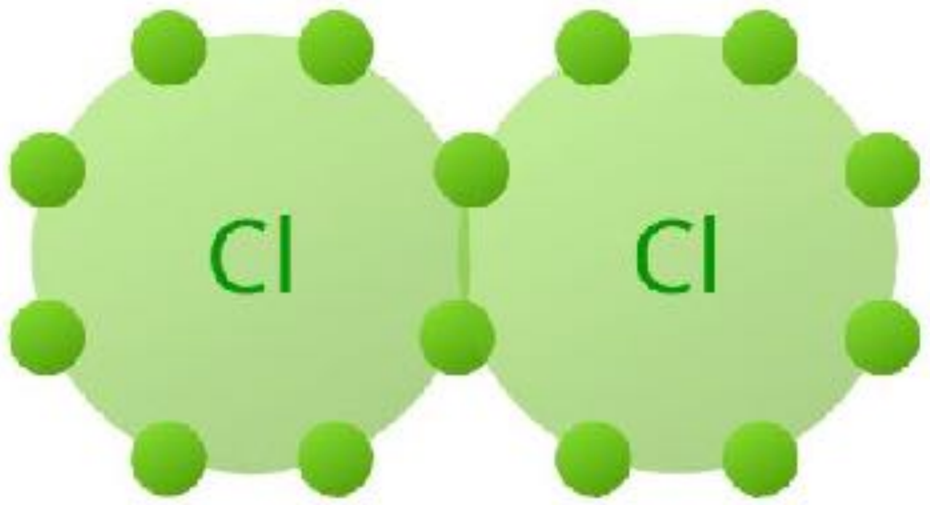

Or… cations (metal ions) and anions (non-metal ions) form electrostatic bonds based on opposite charges. (Cations and anions may be polyatomic)

# Covalent Bonds

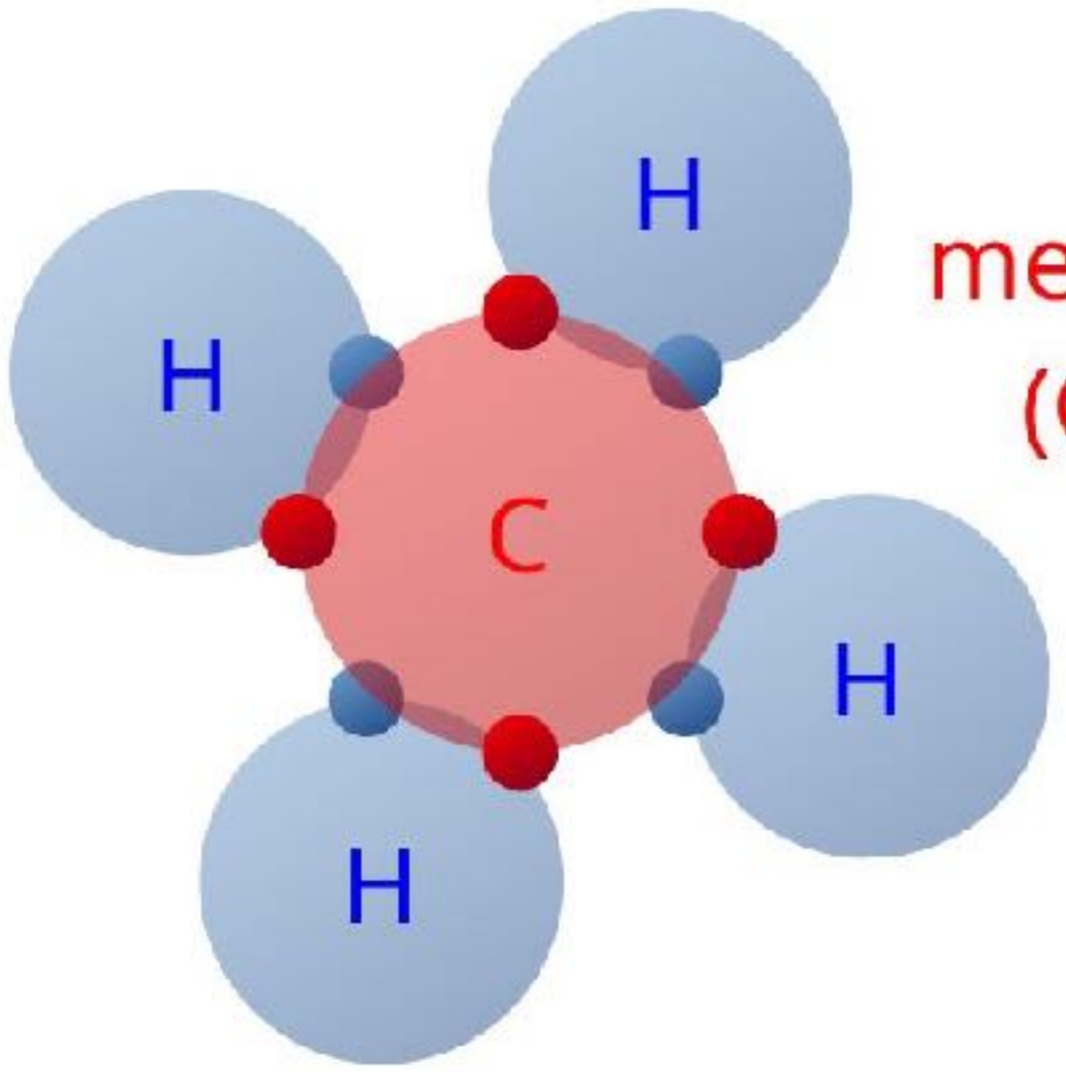
One <u>non-metal</u> atom shares one or more pairs of electrons with another <u>non-metal</u> atom so that both acquire full octets.




elementary hydrogen ($H_2$)

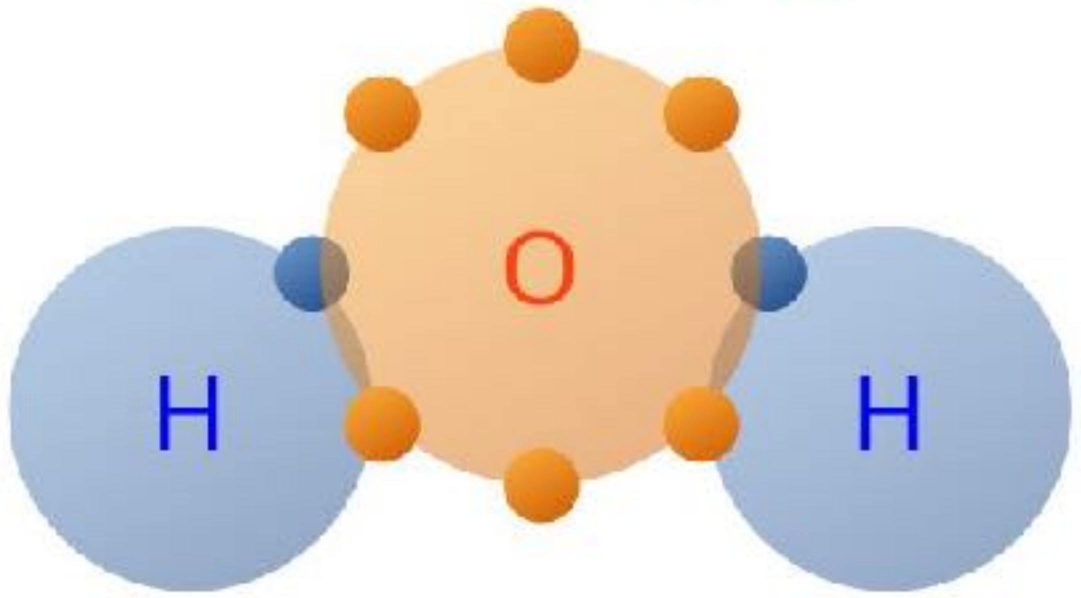



elementary chlorine ($Cl_2$)




methane ($CH_4$)

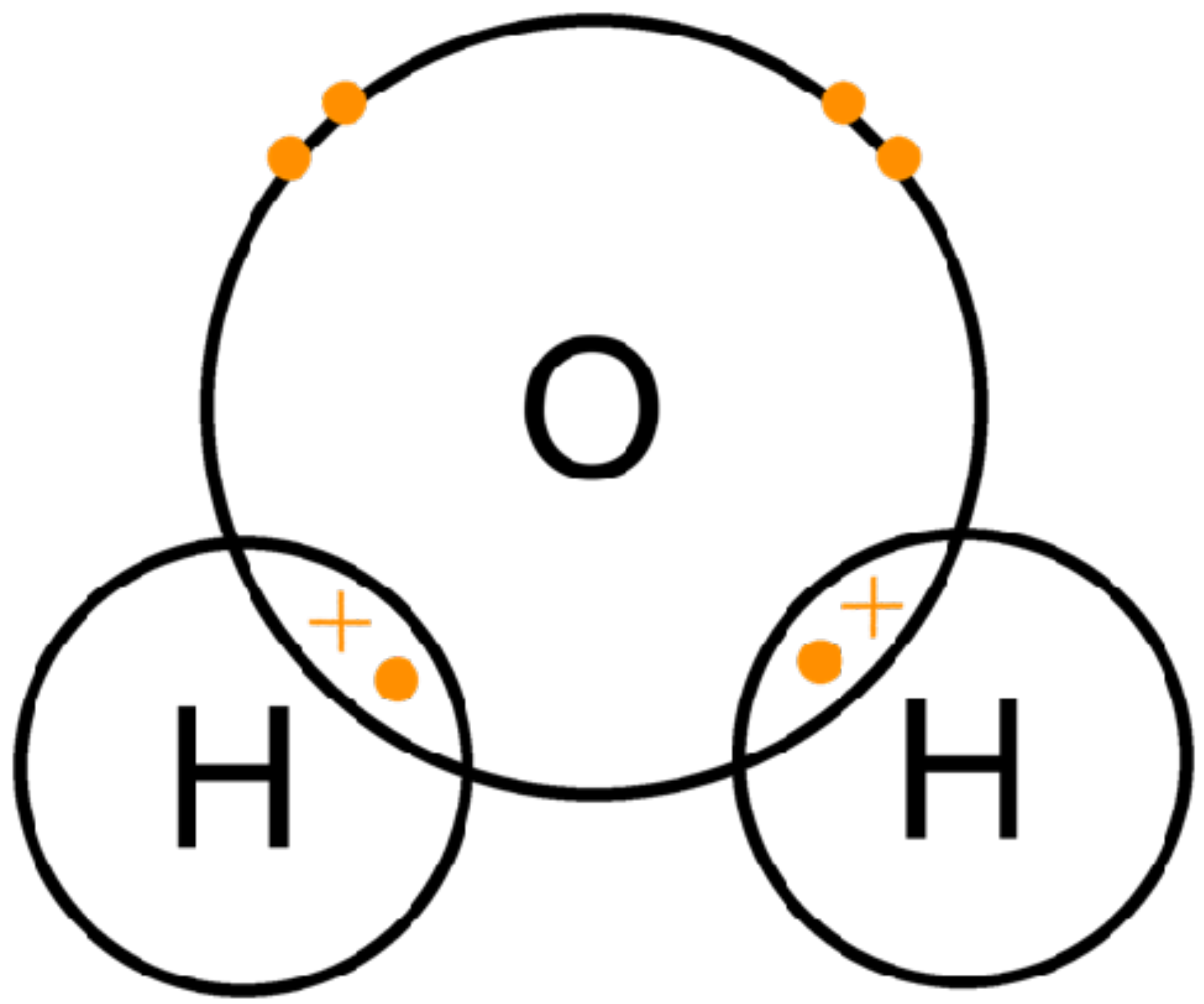
water ($H_2O$)



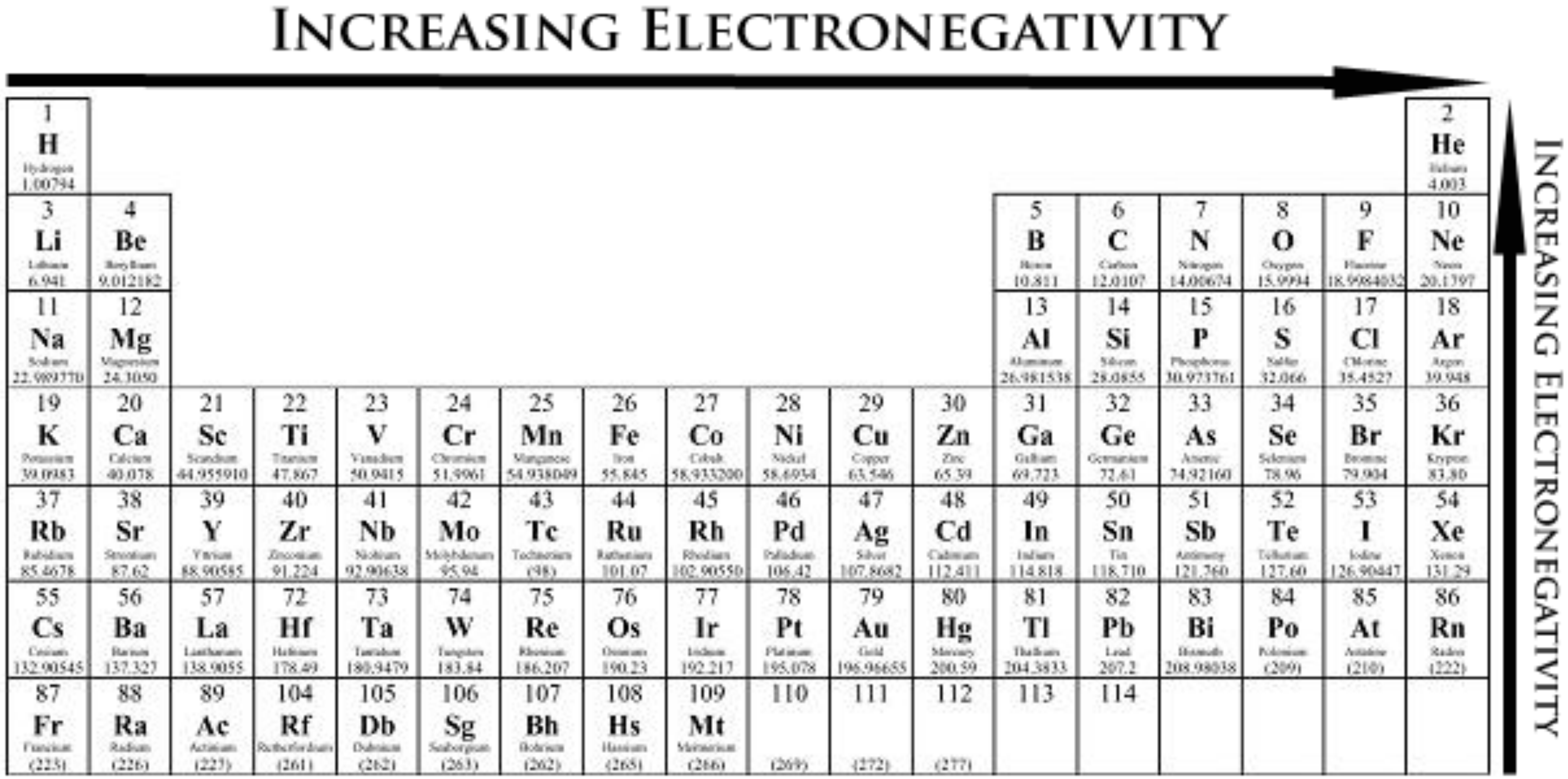
# Molecular Compounds Defined

**Molecules:**

- Two or more non-metals bonded together to form a compound.
- Bonds between atoms are non polar covalent or polar covalent, based on differences in Electronegativity.
  - an elements ability to attract bonding electrons toward itself in a chemical bond.
  - Electronegativity increases as atomic radius decreases.

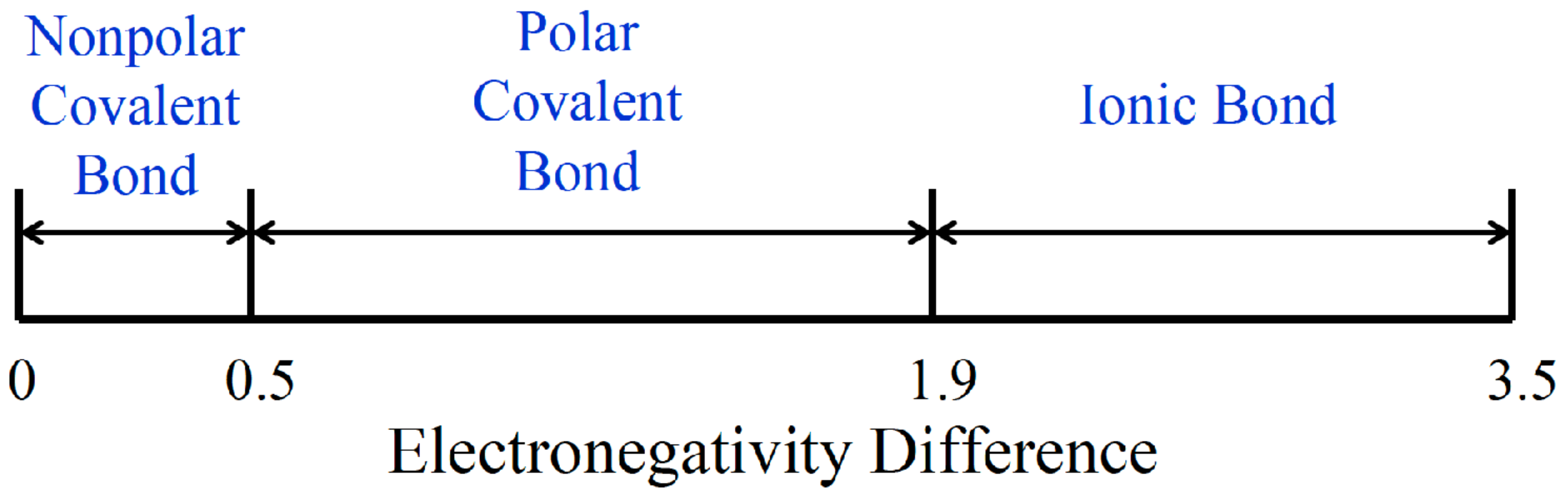


# Electronegativity Trends




More protons are added to the nucleus and the valence electrons are in the same shell. A greater force of attraction is exerted on the electrons in accordance with Coulomb's Law. This pulls electrons closer to the nucleus and decreases the radius.

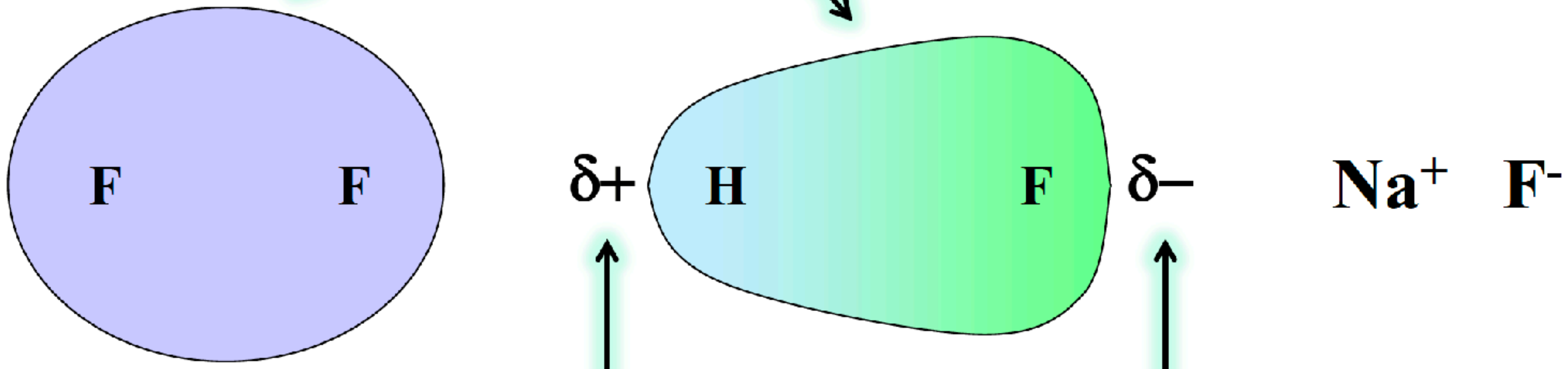
# Electronegativity and Bond Polarity




The difference between these classifications is not distinct - it is a continuum. All polar covalent bond have some ionic character and ionic bonds can have some covalent character.

# Types of Bonds

Electron density distribution




Nonpolar Covalent Bond

Polar Covalent Bond

Ionic

Partial charges are equal in magnitude and opposite in sign.

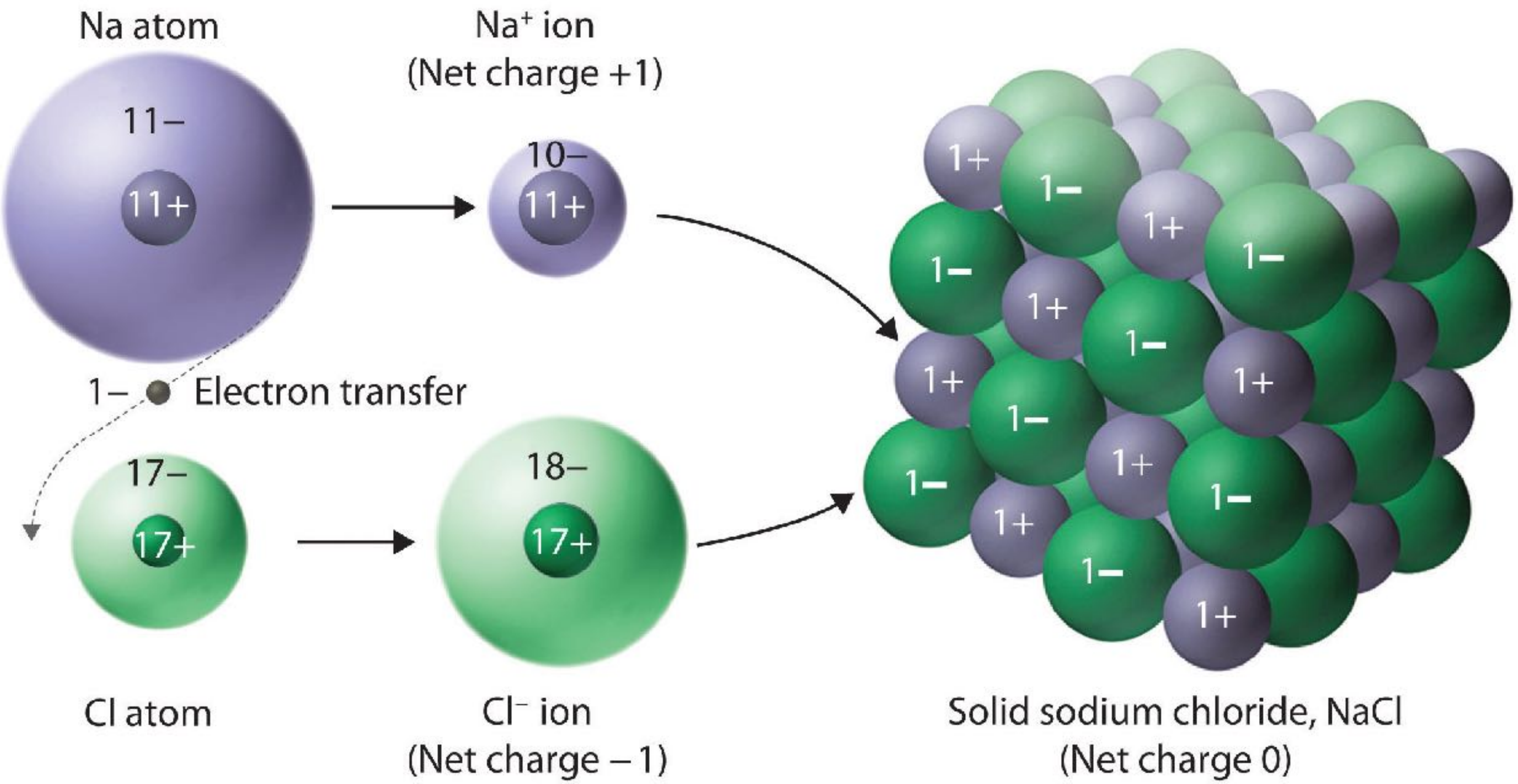
# Determining Bond Type

| Bond | Electronegativity | Type of Bond |
|---|---|---|
| H–H | 0.0 | Nonpolar Covalent |
| H–C | 0.4 | Nonpolar Covalent |
| H–Br | 0.7 | Polar Covalent |
| O–C–O | 1.0 | Polar Covalent |
| LiF | 3.0 | Ionic |

- Electronegativity difference is not the only factor that determines whether a bond is covalent or ionic.
- Metal / nonmetal bonds are ionic and nonmetal / nonmetal bonds are covalent.
- Examining properties is the best way to characterize the bond type.

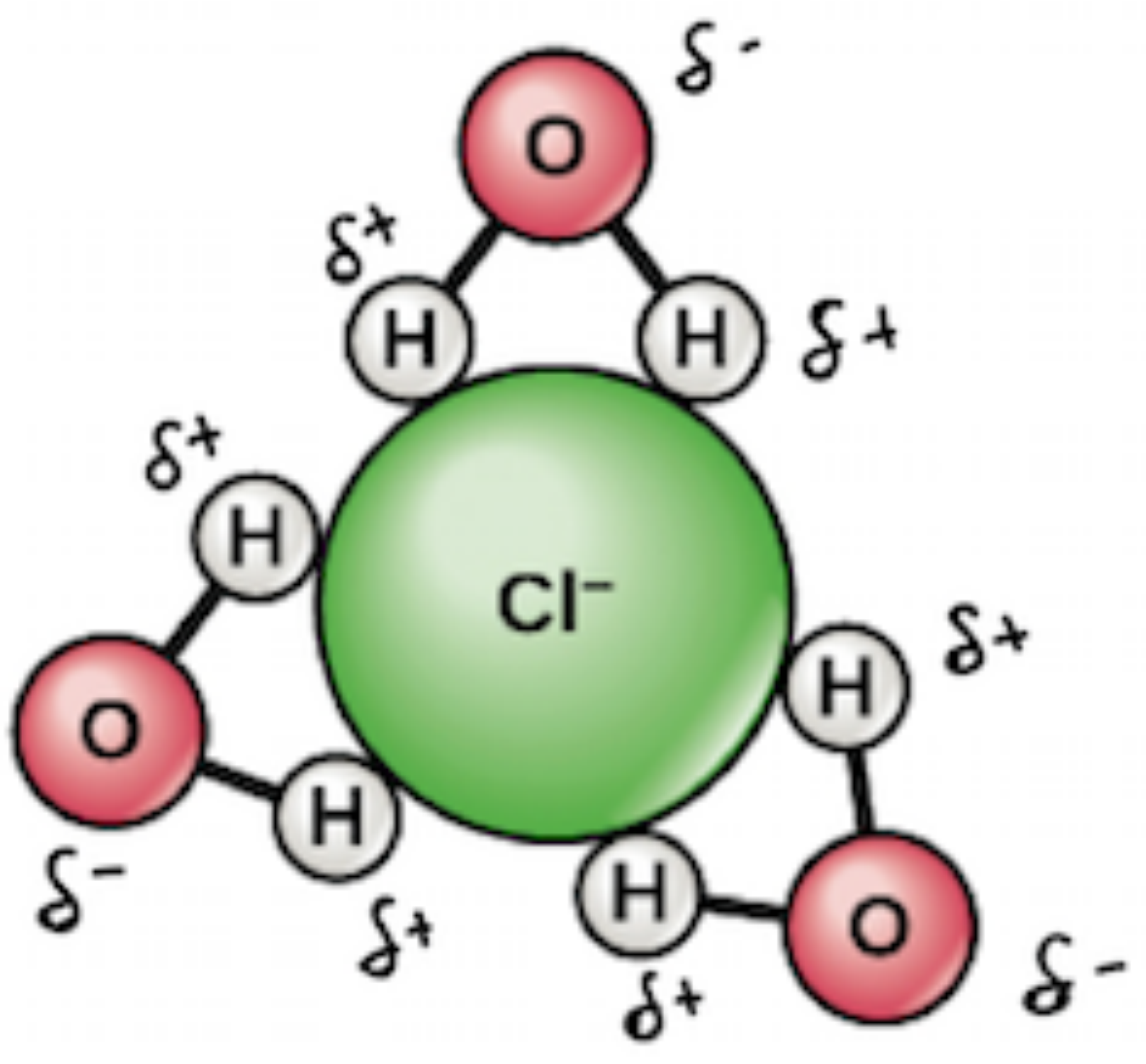
# Properties of Ionic Solids

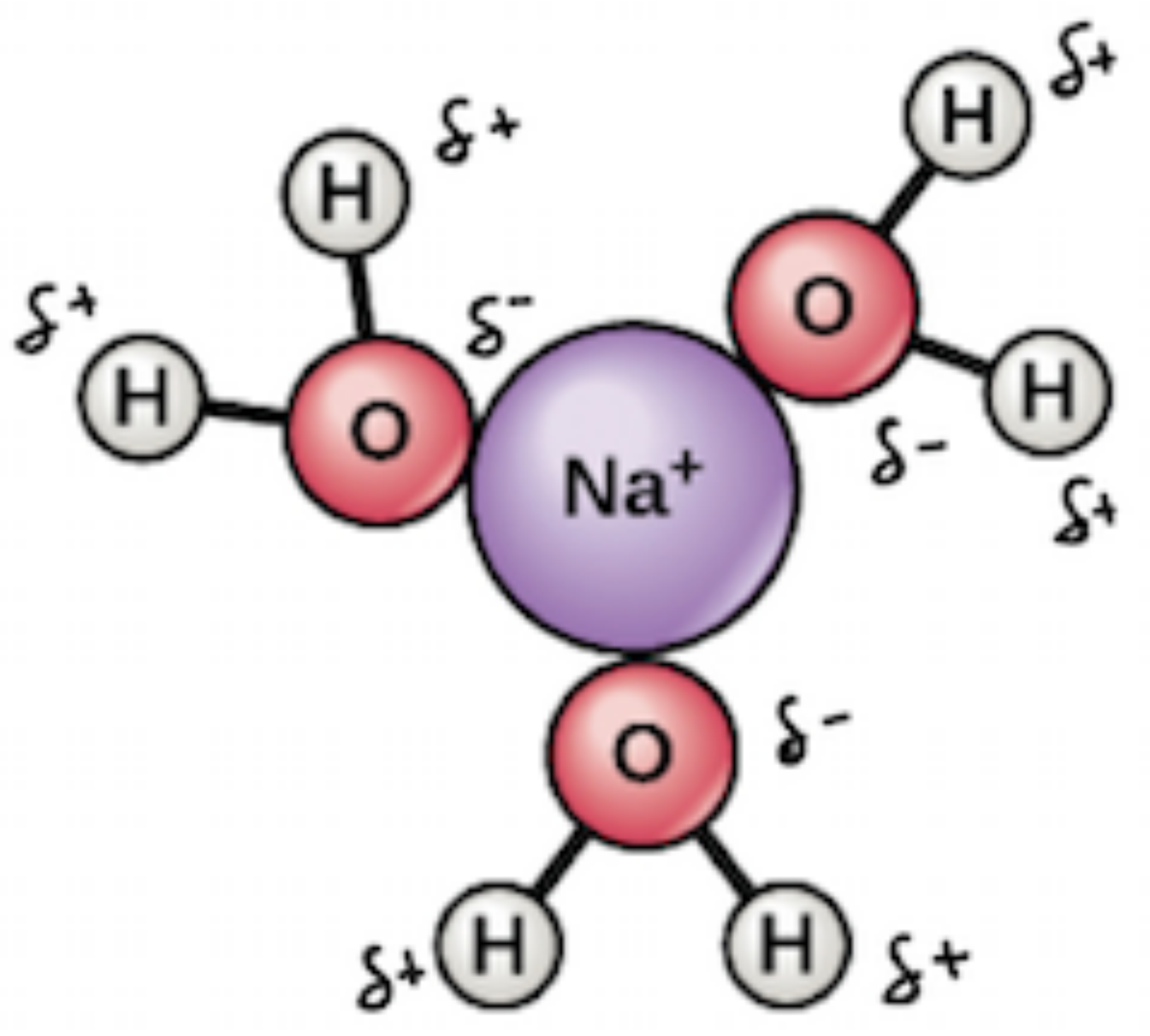
- STRONG BONDS (Coulombic forces of attraction)
  - High melting points
  - Very hard
  - Low volatility
  - Cleave along planes
  - Not malleable or ductile



# Properties of Ionic Solids..continued

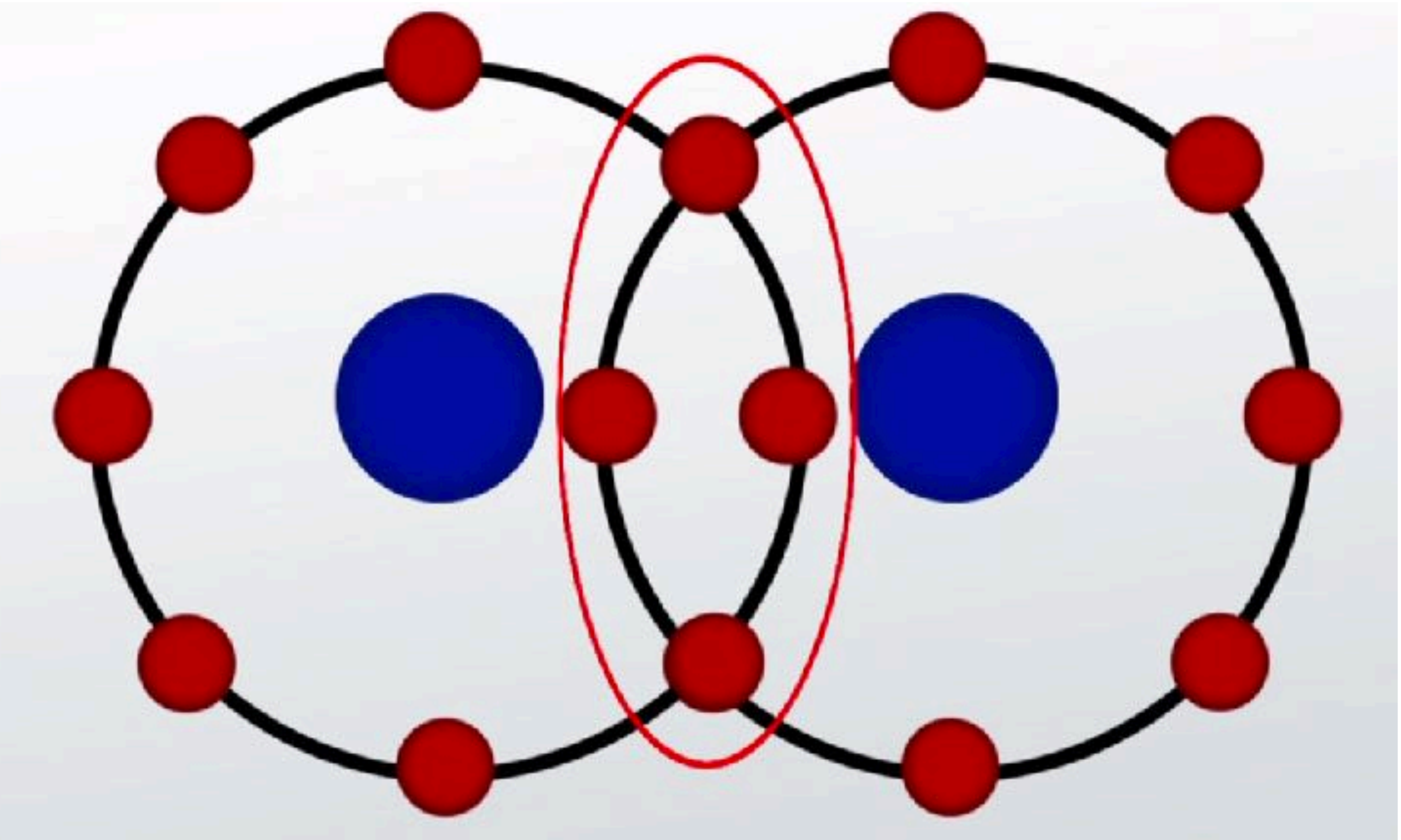
- SOLUBILITY and CONDUCTIVITY
  - Most are soluble in polar solvents ($H_2O$)
  - Conduct electricity only when molten or dissolved in a polar solvent.
    - The higher the concentration of ions in a solution, the higher the electrical conductivity.



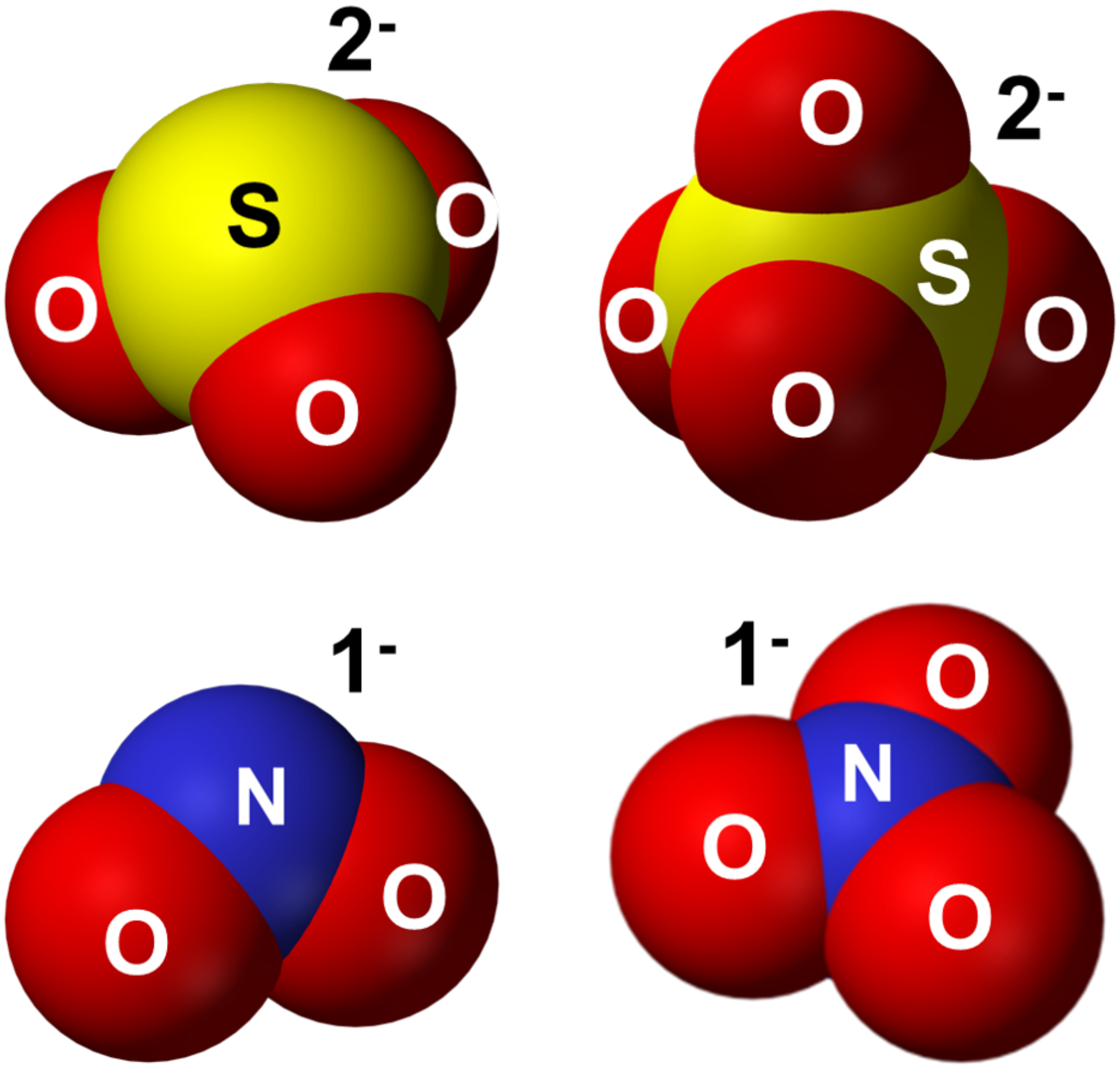
# Properties of Covalent Compounds

- Most covalent compounds have much lower melting and boiling points than ionic compounds.
- Covalent solids are usually soft and flexible.
- Most covalent compounds do not conduct electricity when dissolved in water. (Acids are an exception to this rule.)



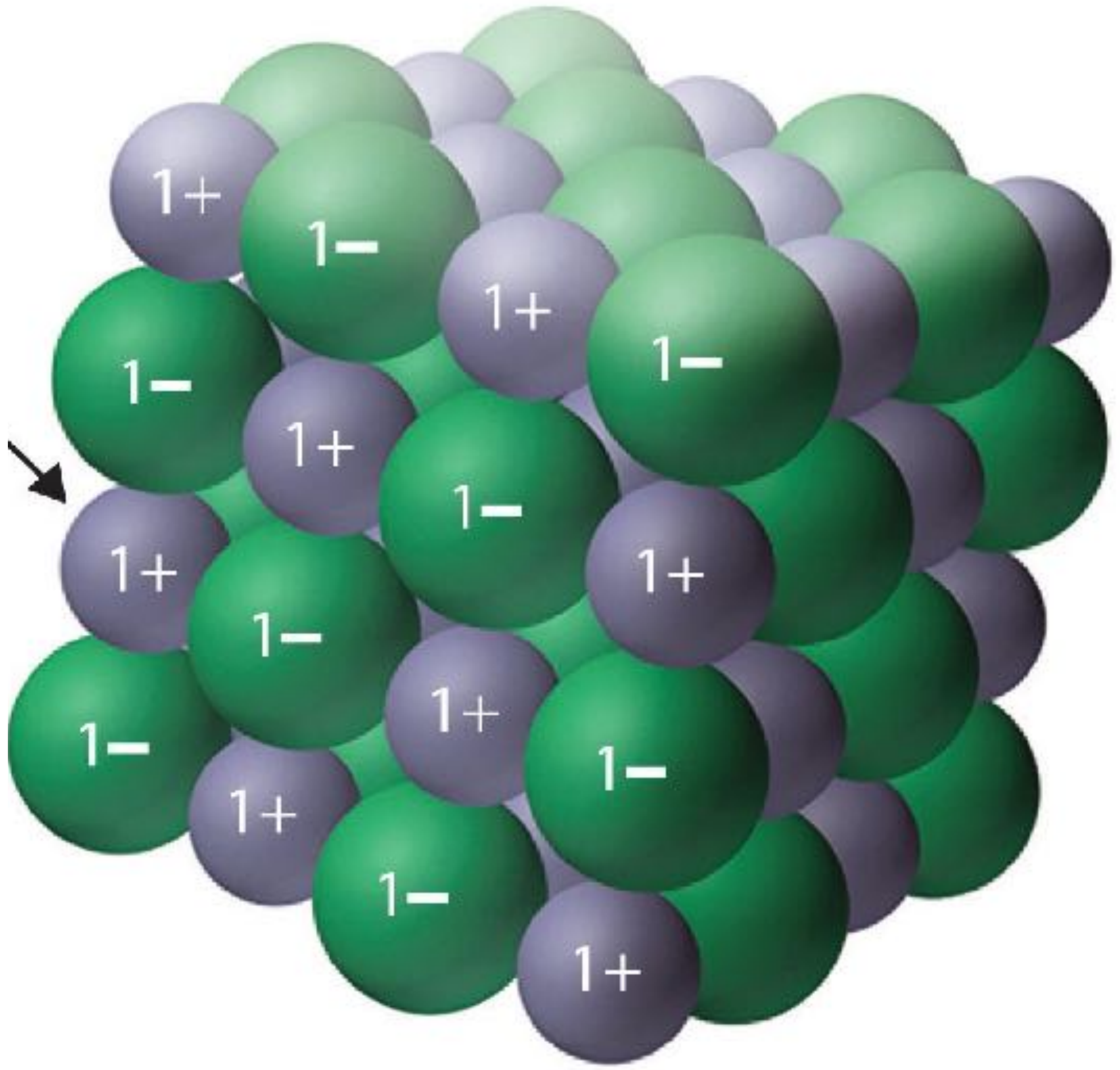
# Polyatomic Ions

- A combination of non-metals or metals and non-metals bonded together to form a polyatomic ion.
- Bonds between atoms are non polar covalent or polar covalent.



# Crystalline Solids

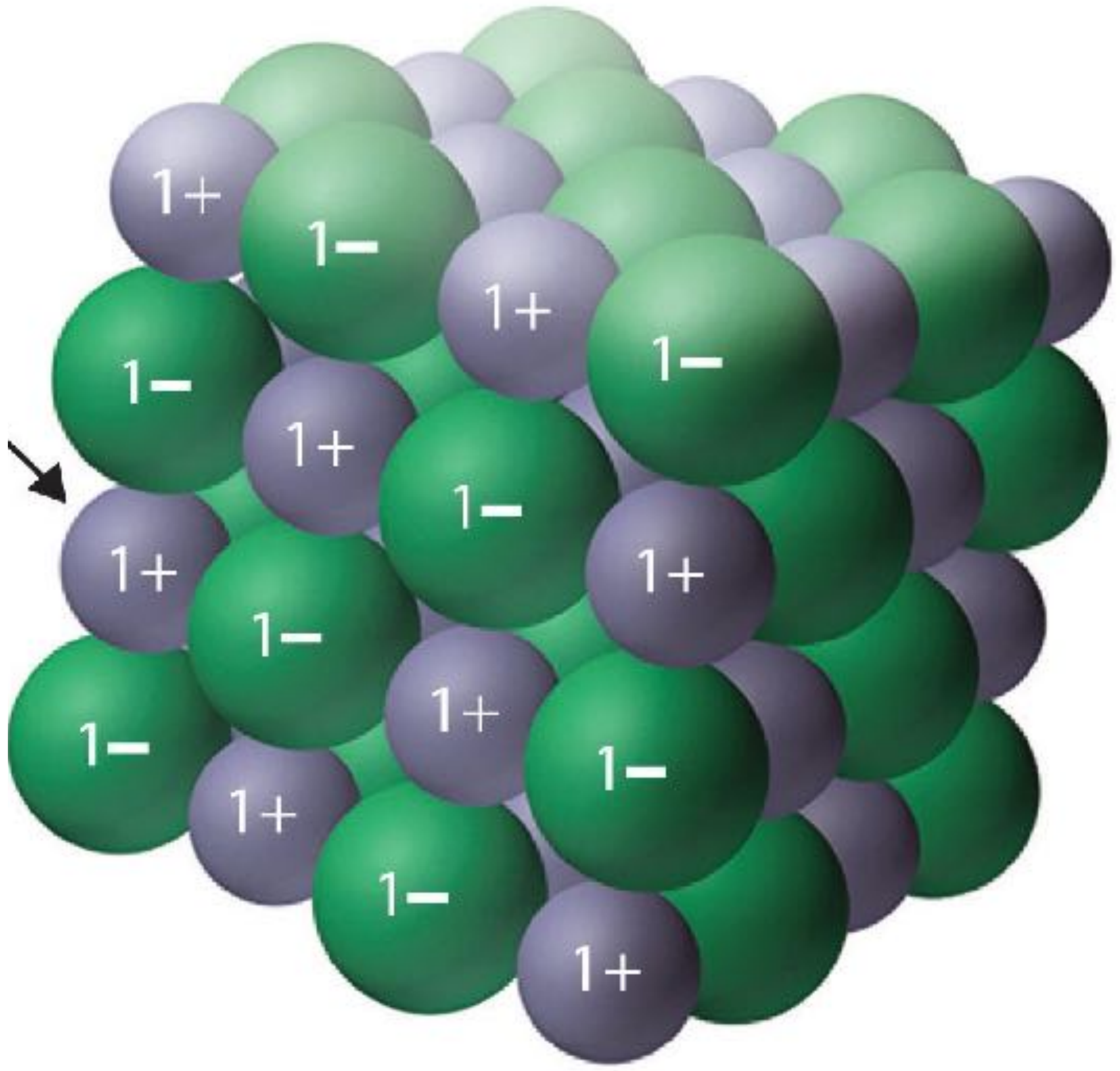
- Ionic compounds do not exist as individual units containing one cation and one anion.
- Ions are instead arranged in an orderly fashion that follows a pattern of repetition in three dimensions. The segments are called *unit cells*.
- Macroscopic structures usually have flat surfaces that make definite angles to one another (remember they break (cleave) along planes)



Solid sodium chloride, NaCl
(Net charge 0)

# Arrangement of Ions

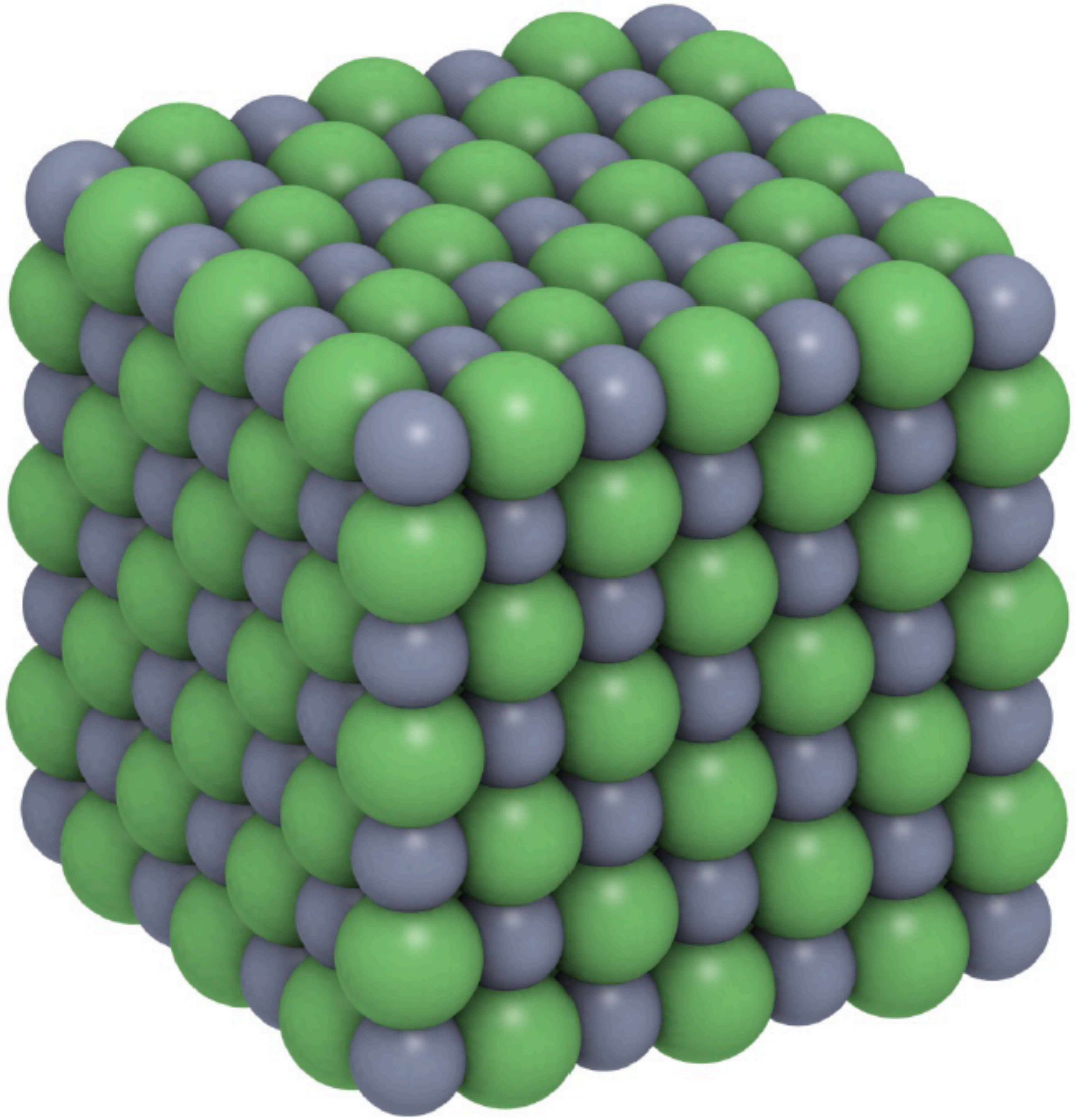
- Ions in an ionic solid are arranged in order to maximize Coulombic forces of attraction between cations and anions and to minimize repulsive forces between ions with like charges.
- The way in which ions are arranged depends on:
  - relative size of the cations and anions
  - the ratio of cations to anions.



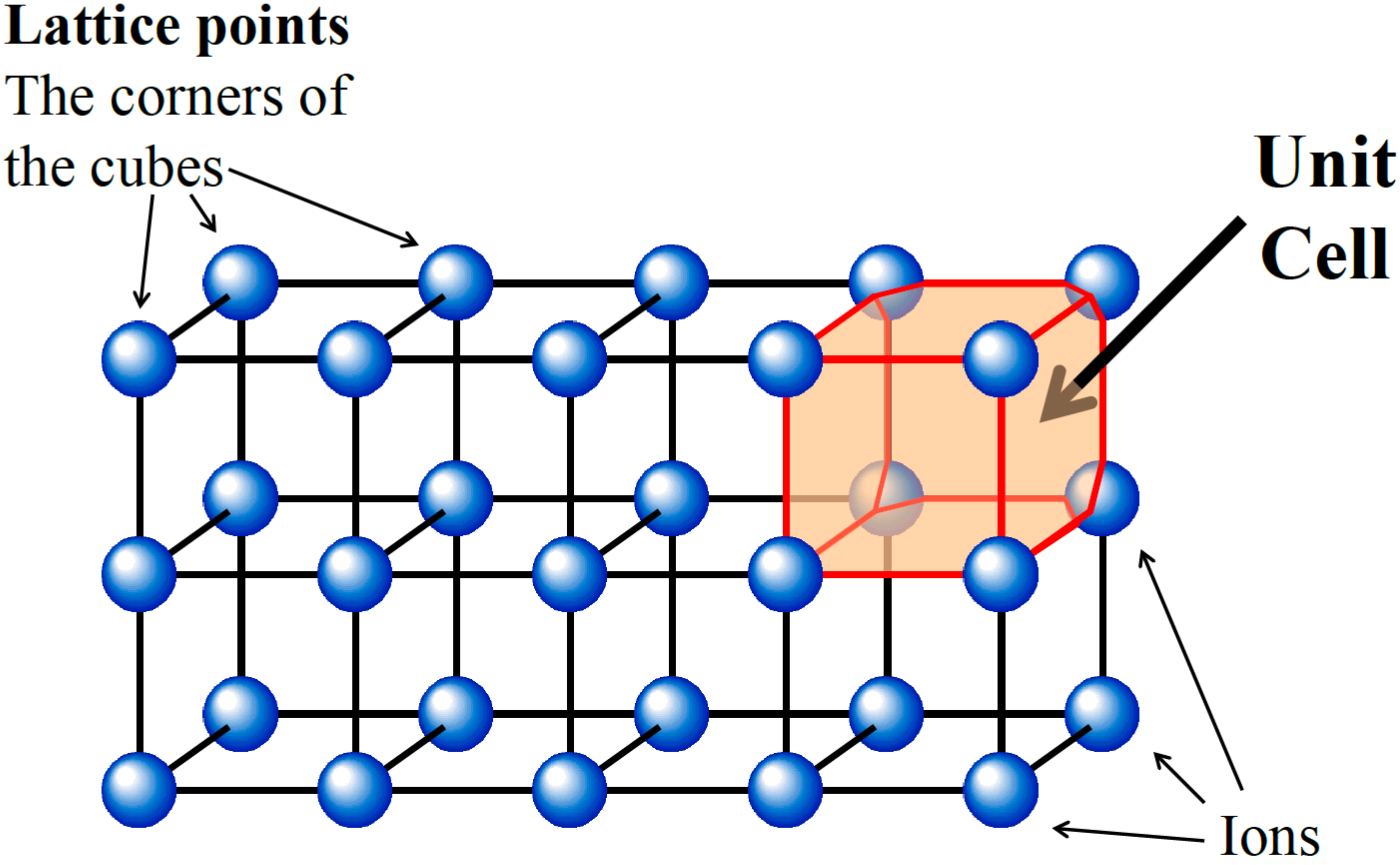

Solid sodium chloride, NaCl
(Net charge 0)

# The Structure of NaCl

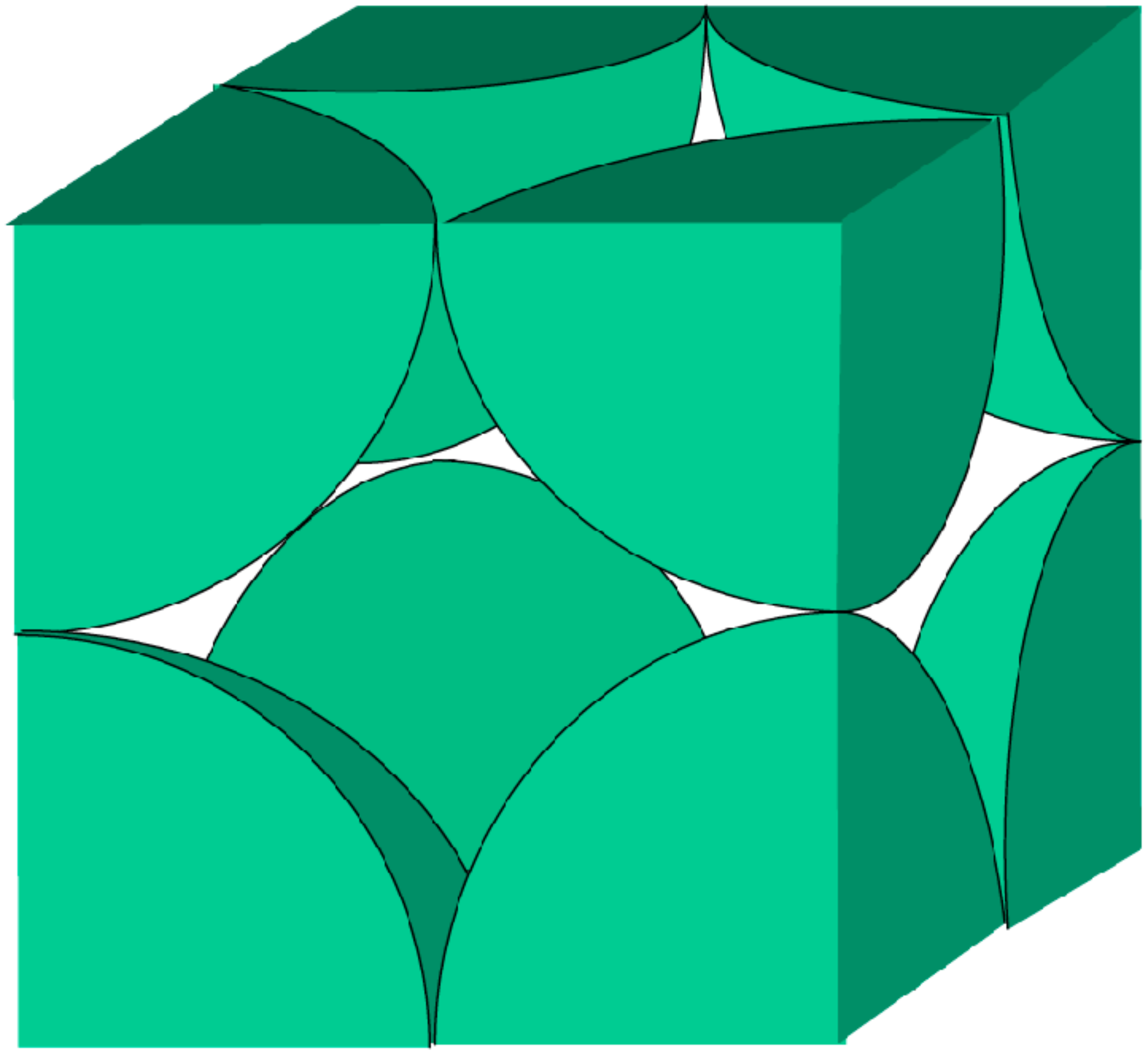
- Each sodium cation is surrounded by six chlorine anions.
- Each chlorine anion is surrounded by 6 sodium cations.



# Unit Cell

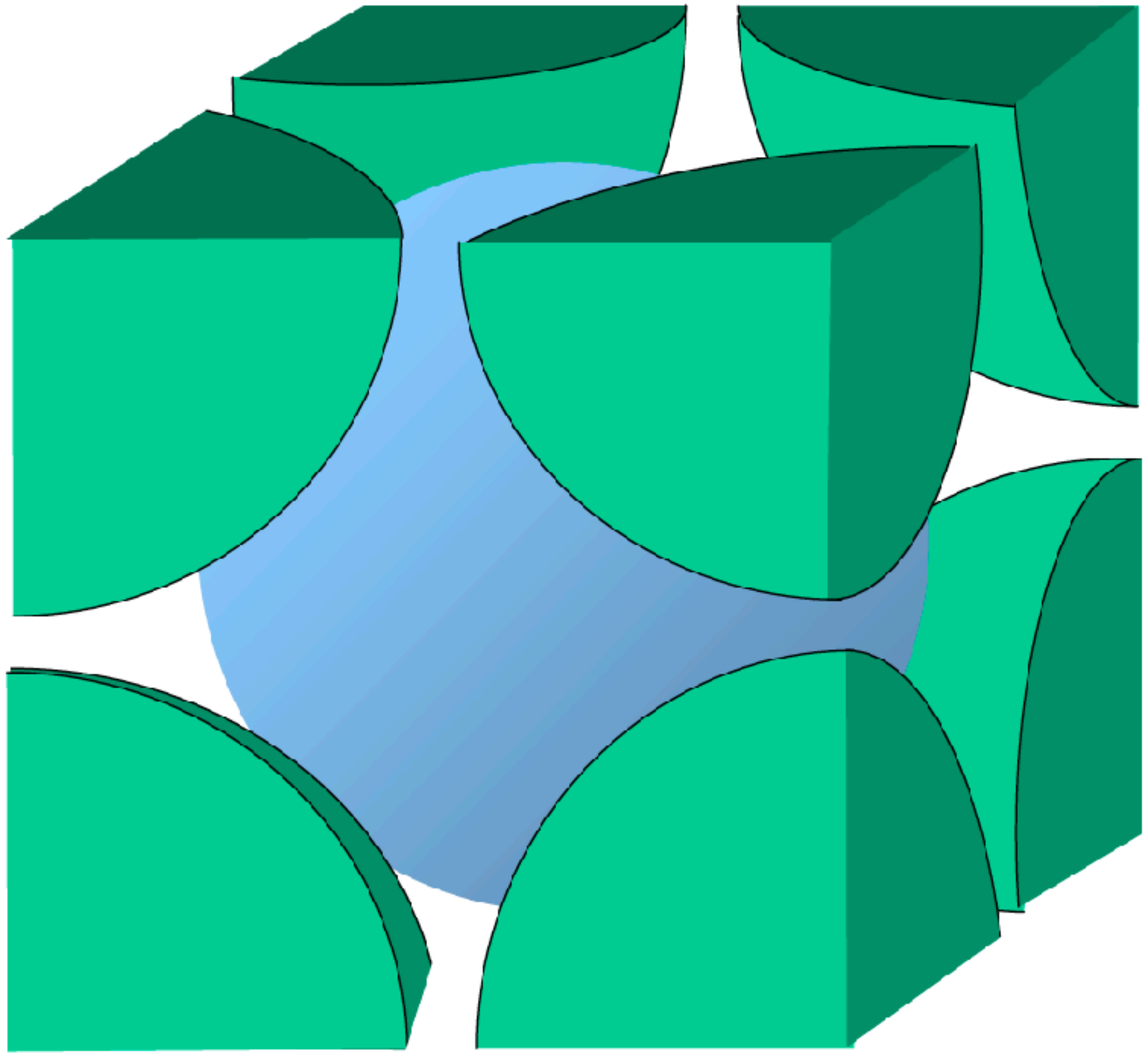


# Possible Arrangements of Ions



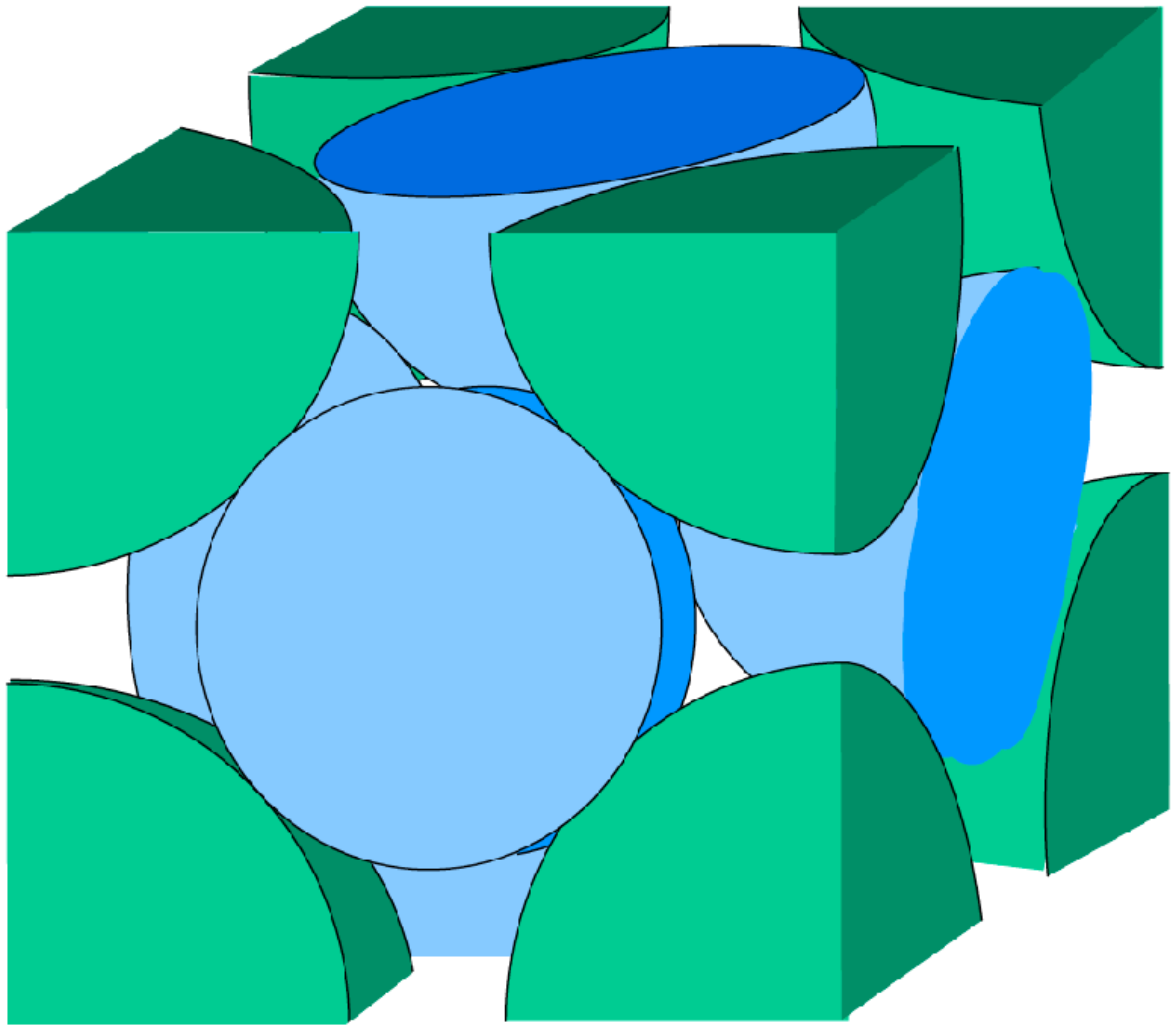
This unit cell contains **8 corners x 1/8 of an ion = 1 ion/unit cell**.

# Possible Arrangements of Ions



This unit cell contains **8 corners x 1/8 of an ion + 1 central ion = 2 ions/unit cell**.

# Possible Arrangements of Ions



This unit cell contains **8 corners x 1/8 of an ion + 6 faces x 1/2 of an ion = 4 ions/unit cell**.

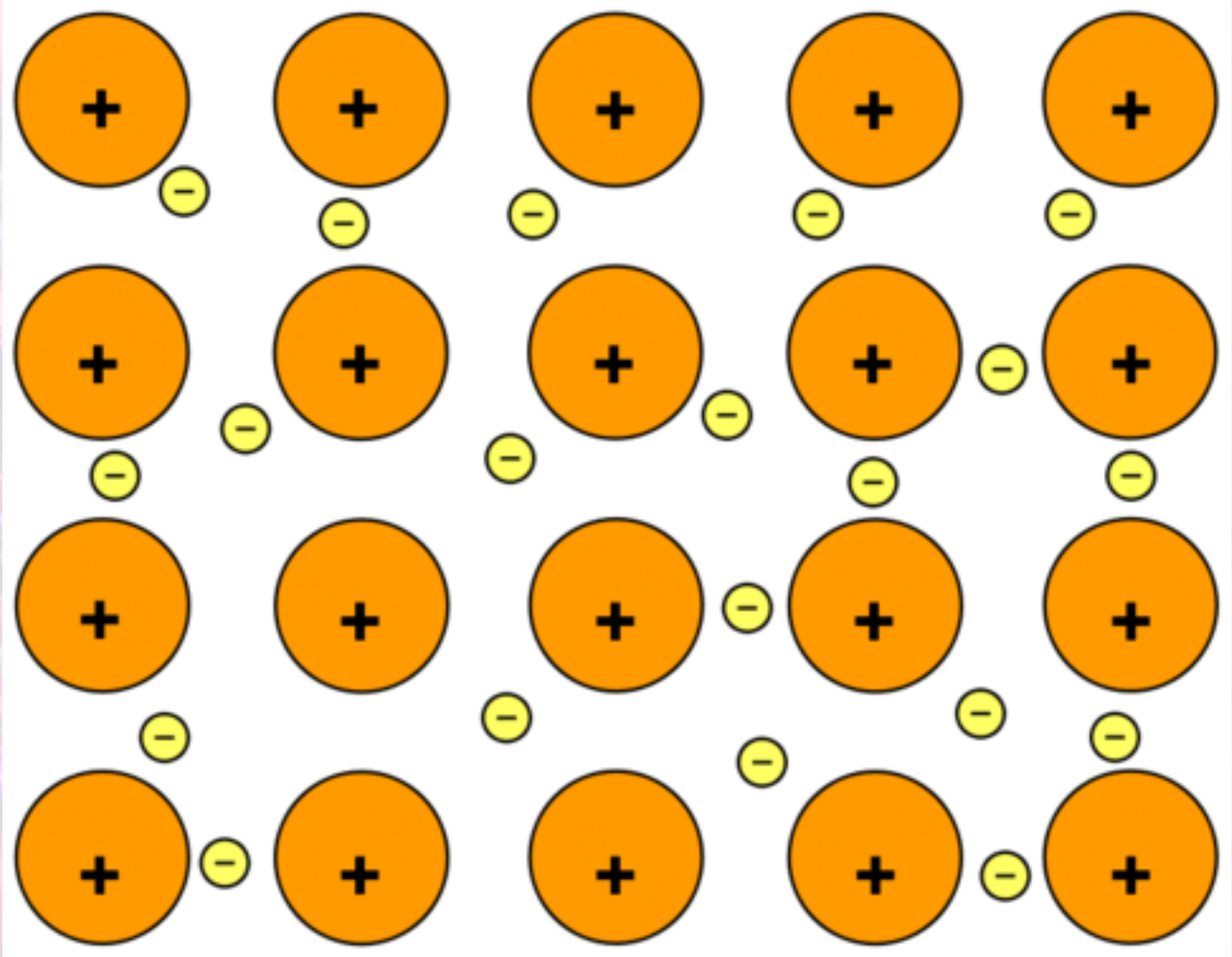
# Metallic Solids

- Bonding is NOT covalent (not enough electrons to fill octets)
- Bonding results from attractions between nuclei and delocalized valence electrons (sea of electrons).
- Bond strength increases as the number of bonding electrons increases.

- Na ($1e^-$): melting point = 97.5°C
- Fe ($8e^-$): melting point = 1538°C

# Metallic Bonding

- Nuclei and inner core electrons are localized, while valence electrons are free to move throughout the solid.
    - conduct electricity & heat
    - malleable and ductile (lack directional bonds like ionic solids)



# Terminology

**Solution**

- A homogeneous mixture of two or more substances.

**Solvent**

- The substance that is more plentiful in a solution.

**Solute**

- The substance that is less plentiful in a solution.

**Alloy**

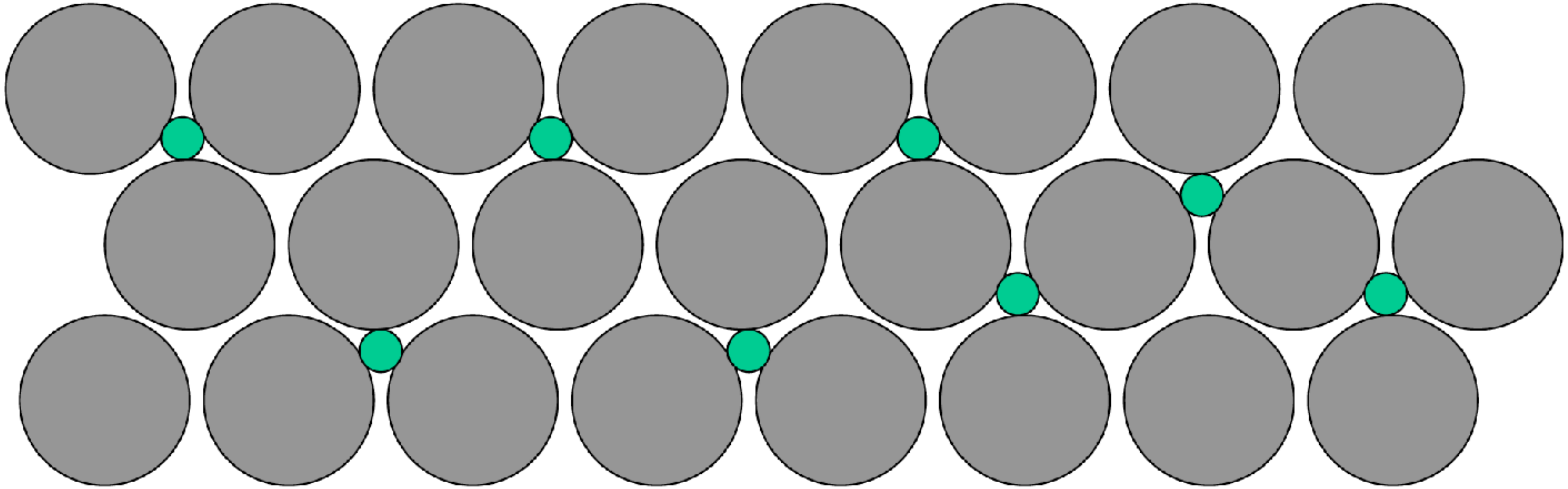
- A solid solution composed of two or more metals, or one or more metals and one or more non-metals.

# Interstitial Alloys

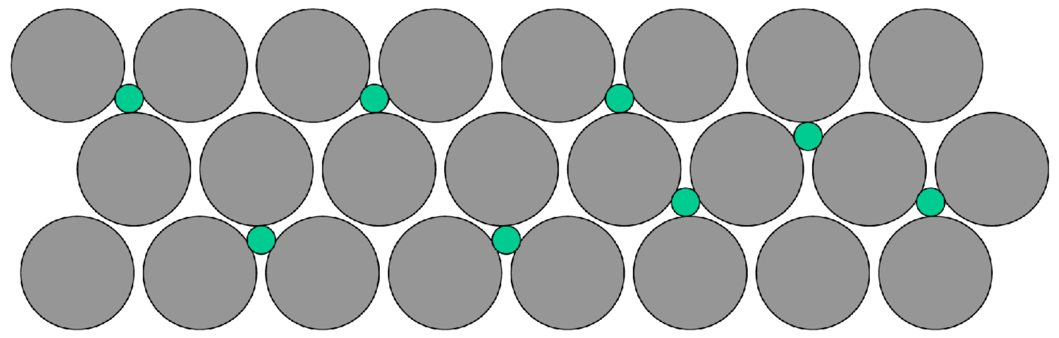
- Atoms with a small radius occupies the spaces between atoms with a larger radius.

**Steel - An interstitial alloy**

- Carbon fills some spaces between iron atoms.



# Properties of Steel



- Pure iron lacked directional bonds
- Steel is more rigid, less malleable and less ductile that pure iron, resulting in strong directional bonds between carbon and iron atoms.
- Density of steel is greater than that of pure iron, as interstitial atoms do not expand the lattices much.

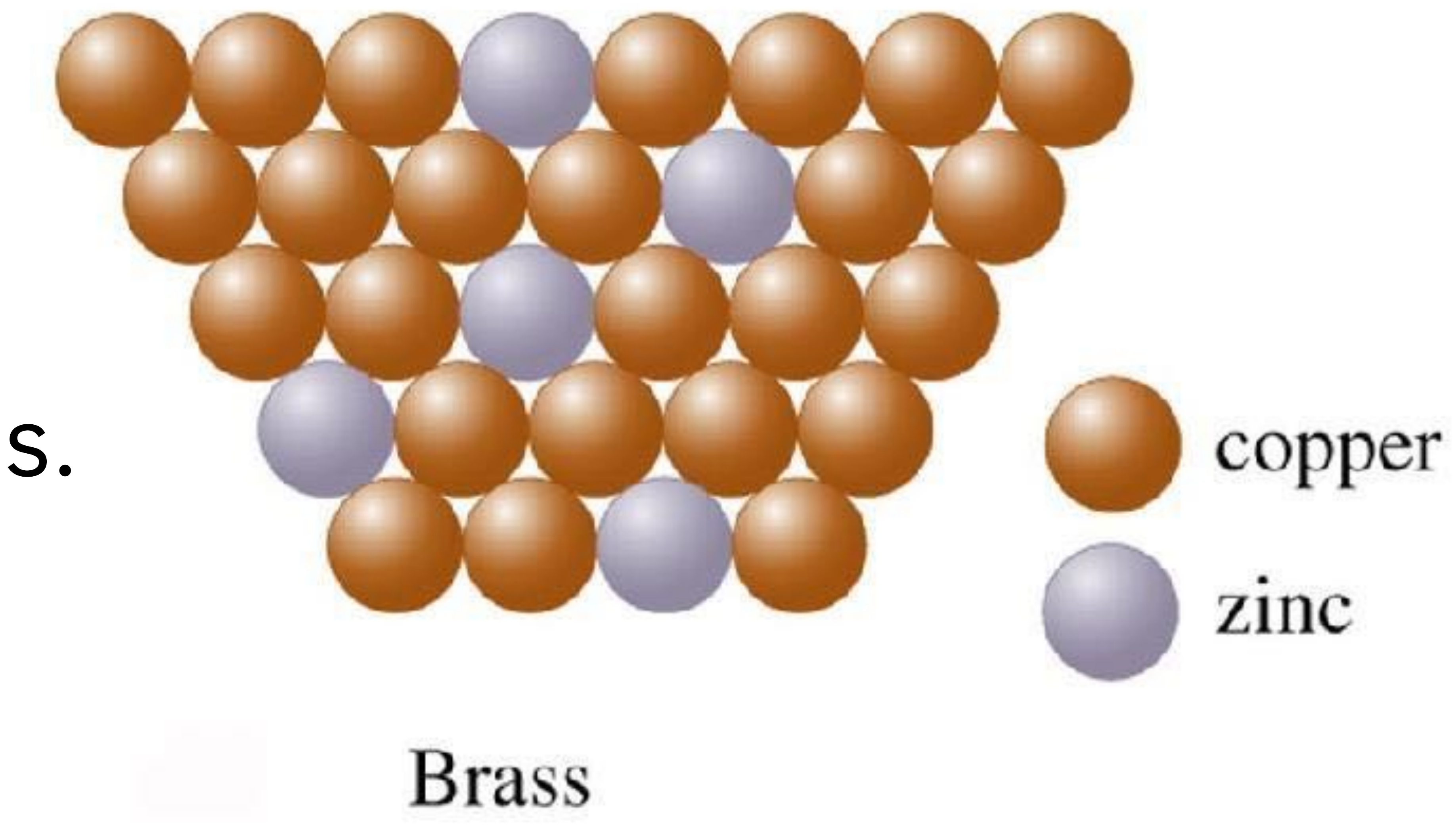
$$Density = \frac{Mass}{Volume}$$

# Substitutional Alloys

- The radii of the solute and solvent atoms are similar.

**Brass - A substitutional alloy**

- Zinc atoms are substituted for some copper atoms.
- Alloys remain malleable and ductile.
- Density lies BETWEEN those of the component metals.



# 2.2 Intramolecular Force & Potential Energy

- Strength of Ionic Bonds
- Potential Energy and Bonds
- Bond Energy and Bond Length

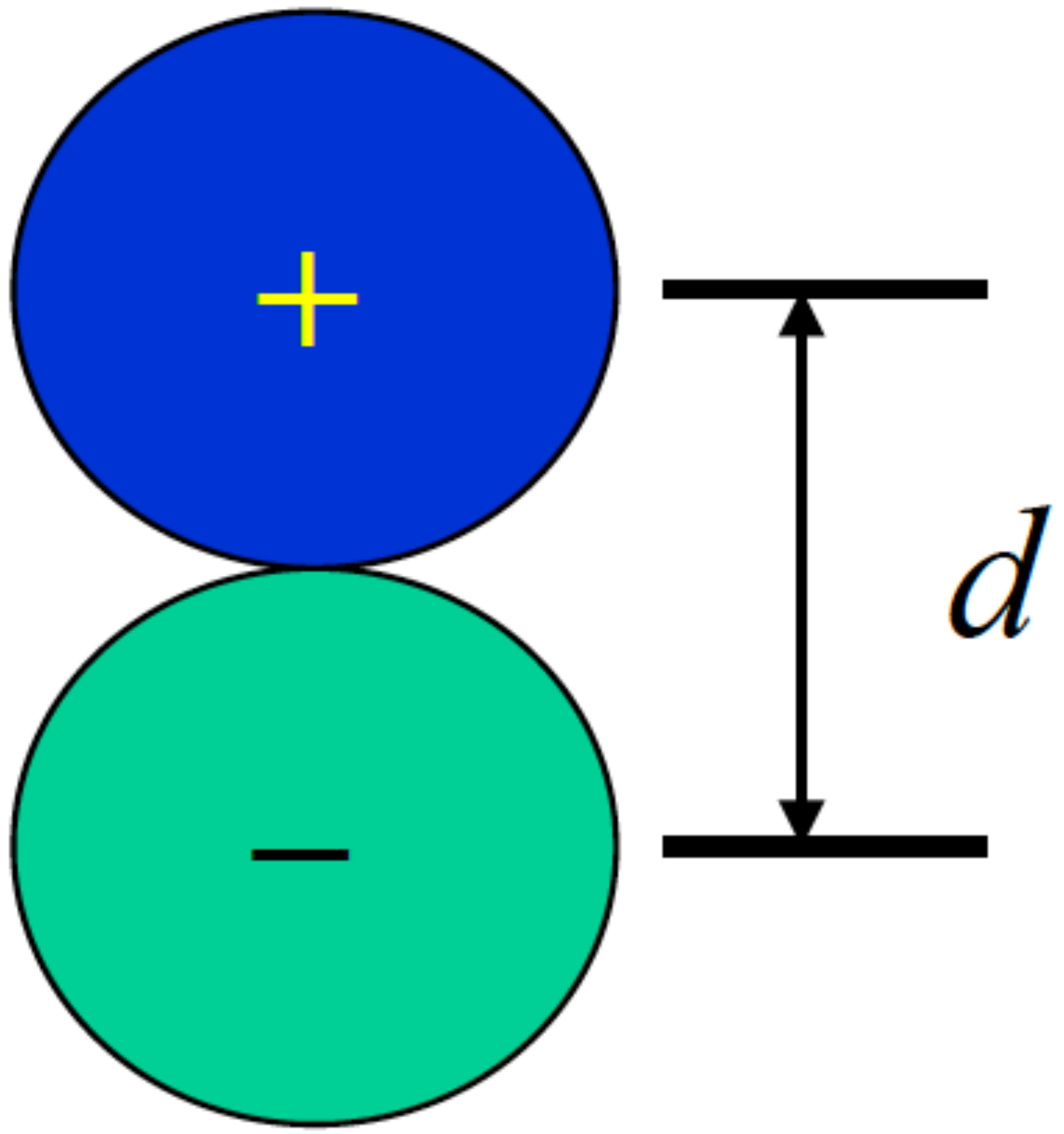
# Strength of Ionic Bonds

- Ionic bonds are very strong, so it requires a lot of energy to melt or vaporize these solids (VERY Endothermic)

$$NaCl_{(s)} \rightarrow Na^+_{(g)} + Cl^-_{(g)} \qquad \Delta H_{\text{lattice}} = +788 \text{ kJ/mol}$$

# Factors Affecting Melting Points of Ionic Solids

- Coulomb's Law




$$F = k\frac{Q_1 Q_2}{d^2}$$

$k = 8.99 \times 10^9\ Nm^2/C^2$

$d$ = distance between ionic centers

$Q$ = the charge of a single ion

*Charge / size relationship*

# Example: MP of Ionic Solids

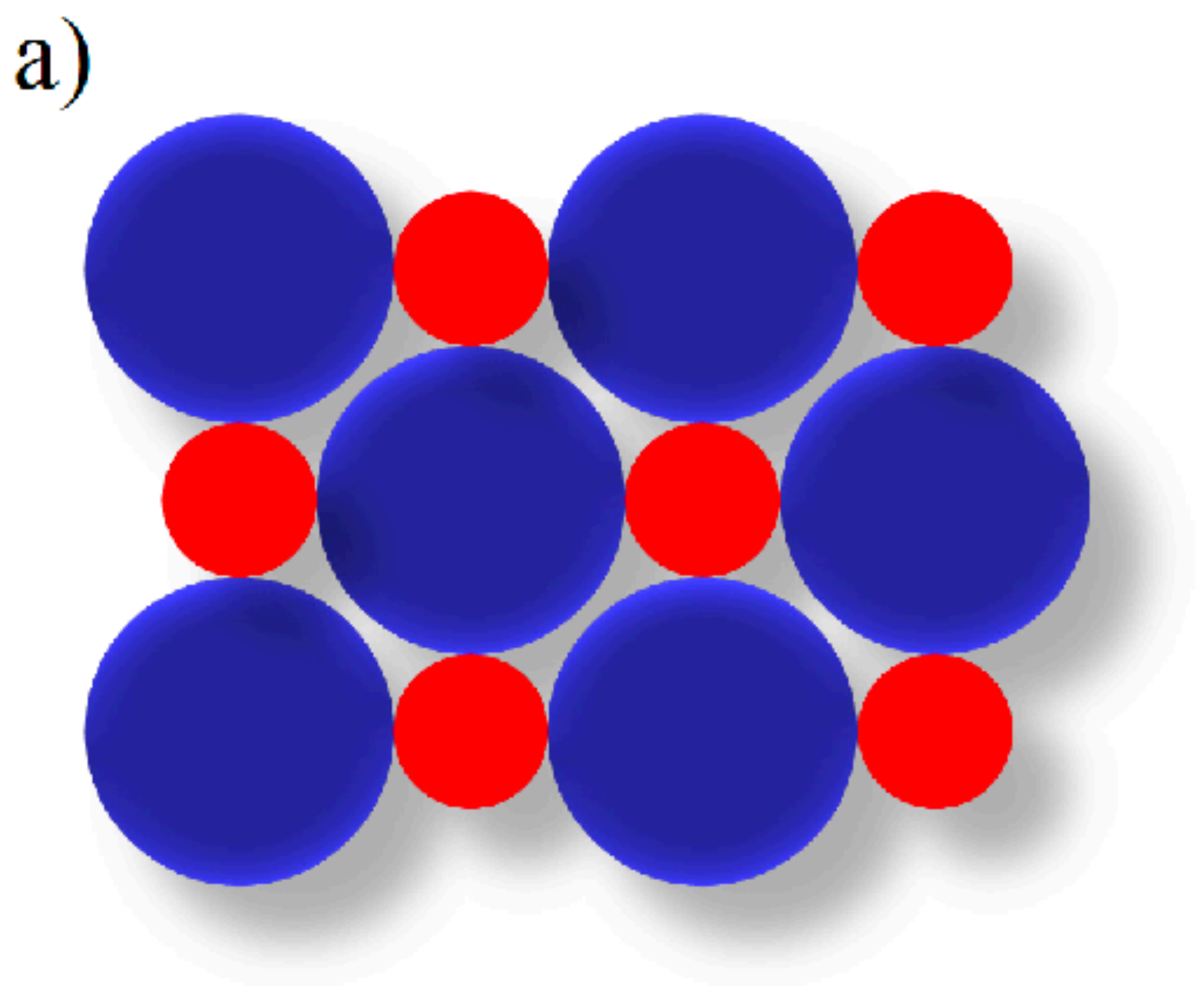
Which compound from each set has the greatest melting point? Why?

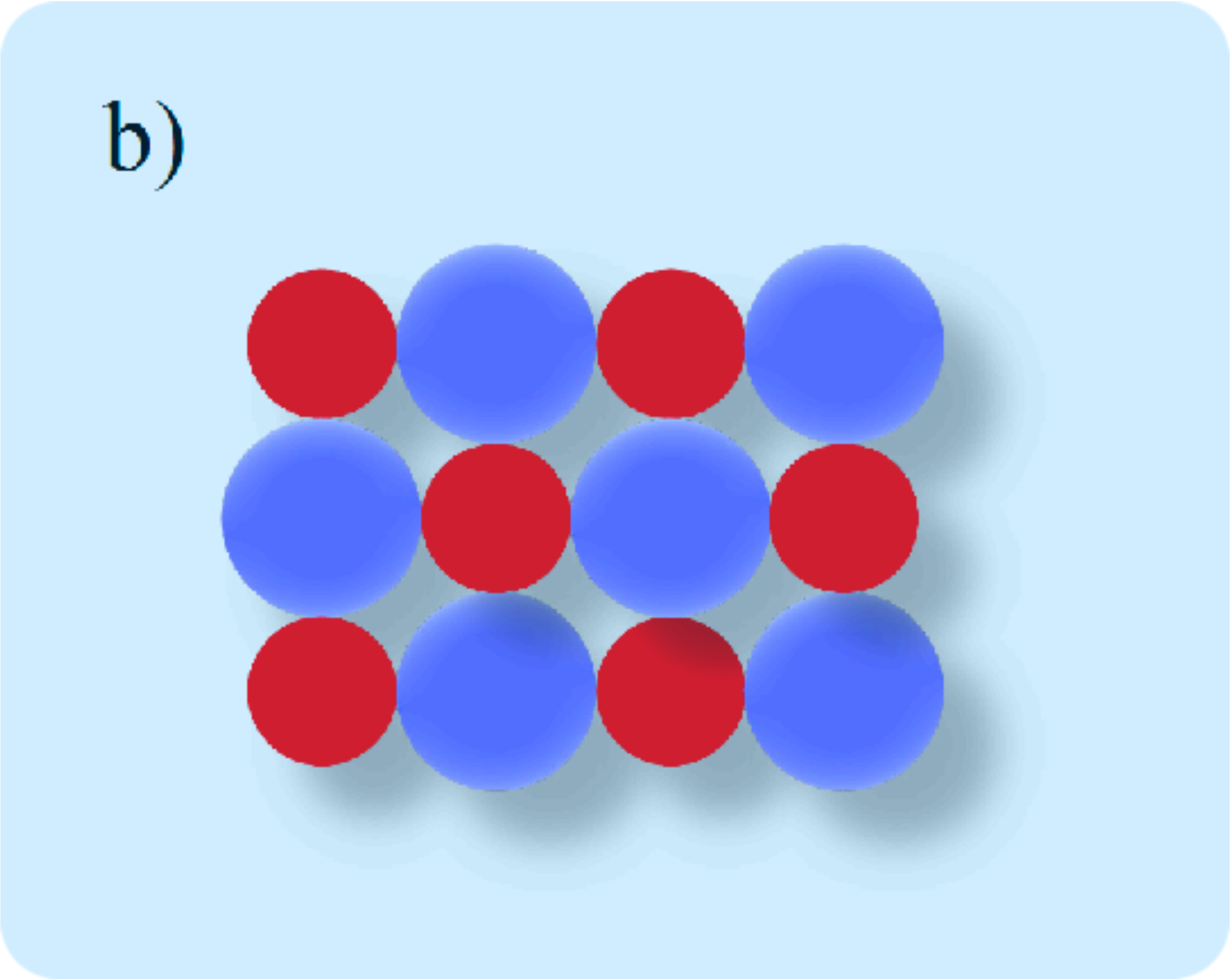
| Compound 1 | Compound 2 | Reason |
|---|---|---|
| LiF | LiI | $F^-$ is smaller than $I^-$ |
| $MgCl_2$ | MgO | $MgCl_2$ (+2)(-1), MgO (+2)(-2) |
| NaF | $MgI_2$ | Greater chargers are always more significant than smaller distance. |

$$F = k\frac{Q_1Q_2}{d^2}$$

# Example: MP of Ionic Solids

Which of the following metal fluorides would have the highest melting point? Why?



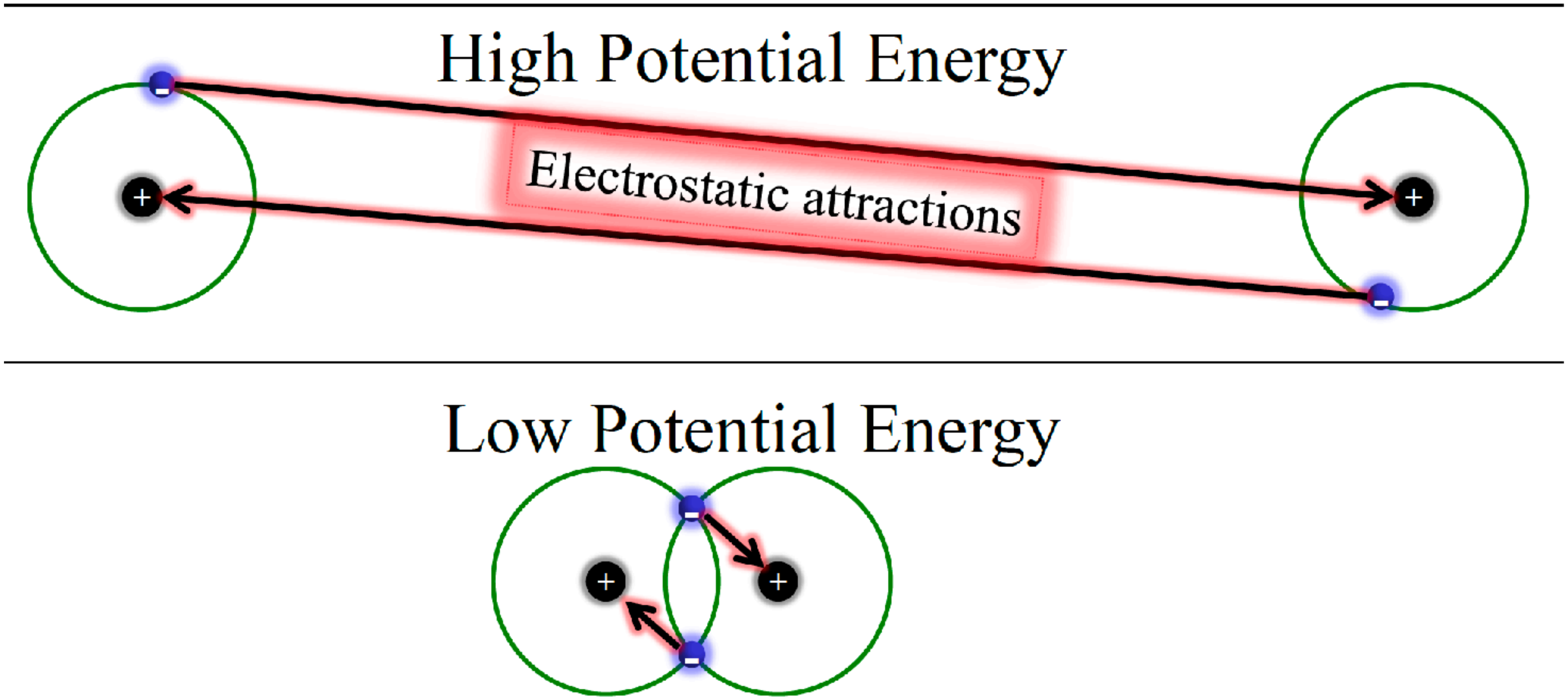




The ionic charges are +1 and -1 for both compounds, but the metal cation in (b) has a smaller radius.

$$F = k\frac{Q_1Q_2}{d^2}$$

# Bond Energy

- The potential energy of valence electrons decreases as they approach the nucleus of another atom.



# Bond Energy

- Bond Formation: Energy is RELEASED. (Exothermic)
  - Potential energy decreases as the atoms move closer together.
- Bond Breakage: Energy is ABSORBED. (Endothermic)
  - The same amount of energy must be added in order to break that specific bond. (**Conservation of Energy**)
  - Potential energy increases as the atoms move away from one another.

# Bond Energy

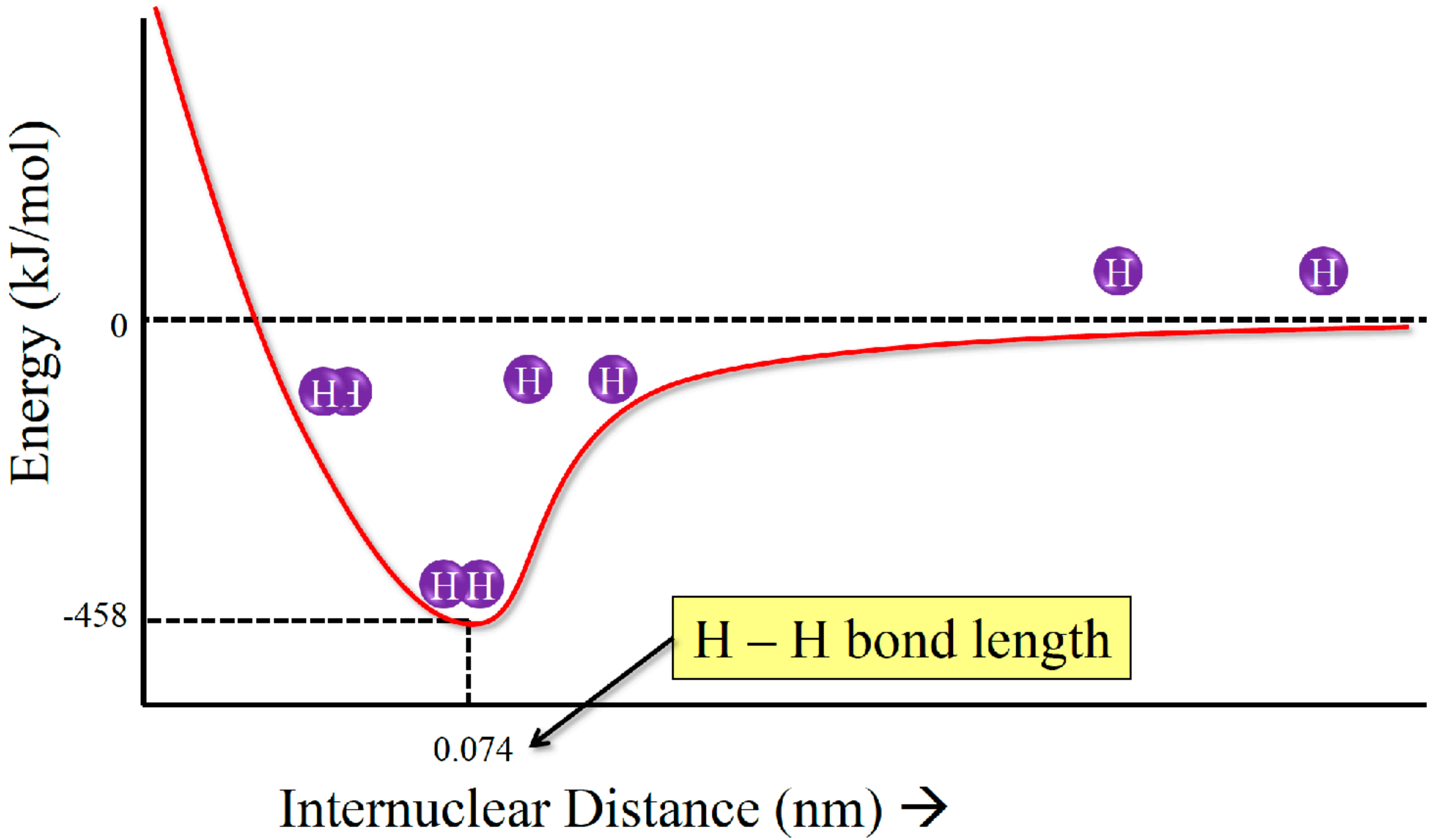
$$H{:}\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}{:} \rightarrow H^{\bullet} + \cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}{:} \qquad \Delta H_{298} = +432\ \text{kJ}$$

- It requires 432 kJ mol$^{-1}$ of energy to break the bonds between chlorine and hydrogen.

$$H^{\bullet} + \cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}{:} \rightarrow H{:}\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}{:} \qquad \Delta H_{298} = -432\ \text{kJ}$$

- 432 kJ mol$^{-1}$ of energy is released when bonds between chlorine and hydrogen are formed.

# Bond Energy vs. Bond Length



# Bond Energy vs. Bond Length

- As the atomic radii of bonding atoms increase, the bond length increases, *PE* increases and the bond energy decreases

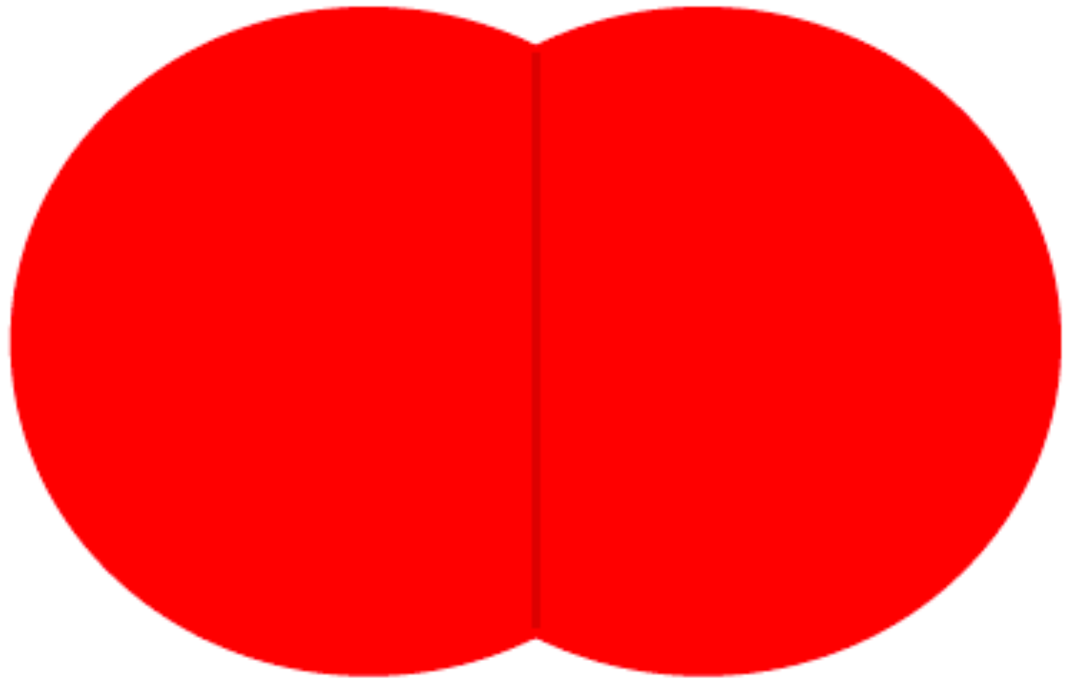
| Bond | Bond Type | Bond Energy (kJ/mol) | Bond Length (nm) |
|---|---|---|---|
| C – Cl | Single | 339 | 0.177 |
| C – Br | Single | 276 | 0.194 |
| C – I | Single | 216 | 0.213 |

# Ex. Bond Energy vs. Bond Length

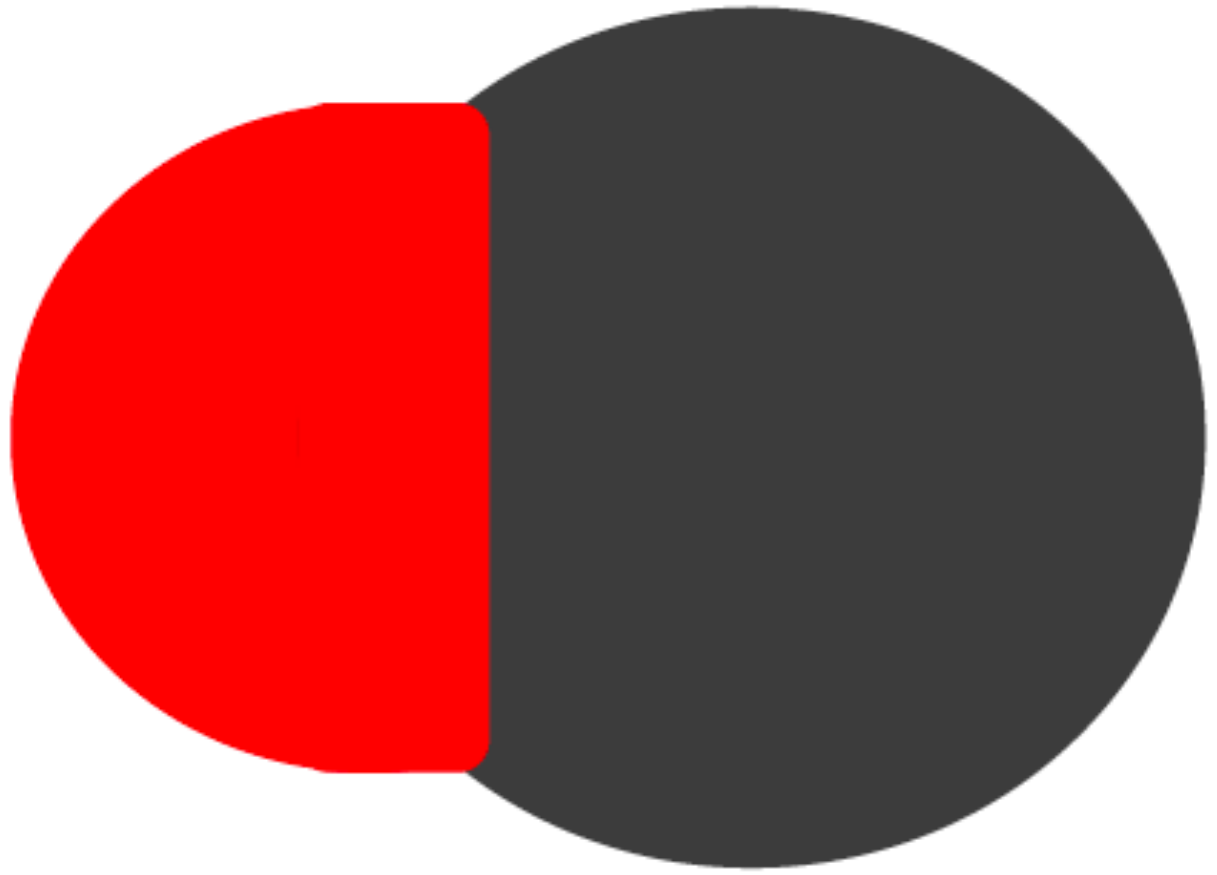
- Consider the space-filling models below. Which molecule has the least amount of *PE* associated with its bond?

- Which bond has the lowest bond energy?

I.



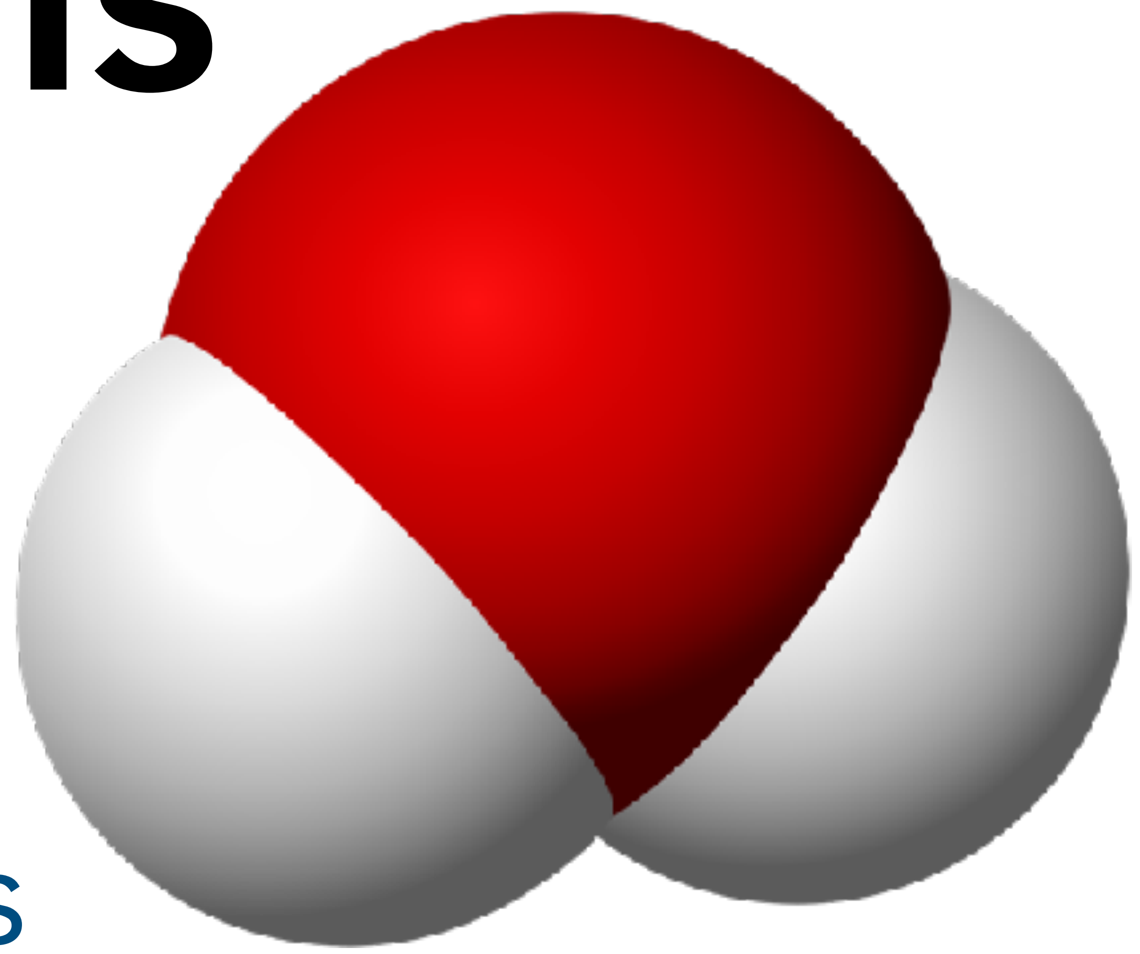
II.



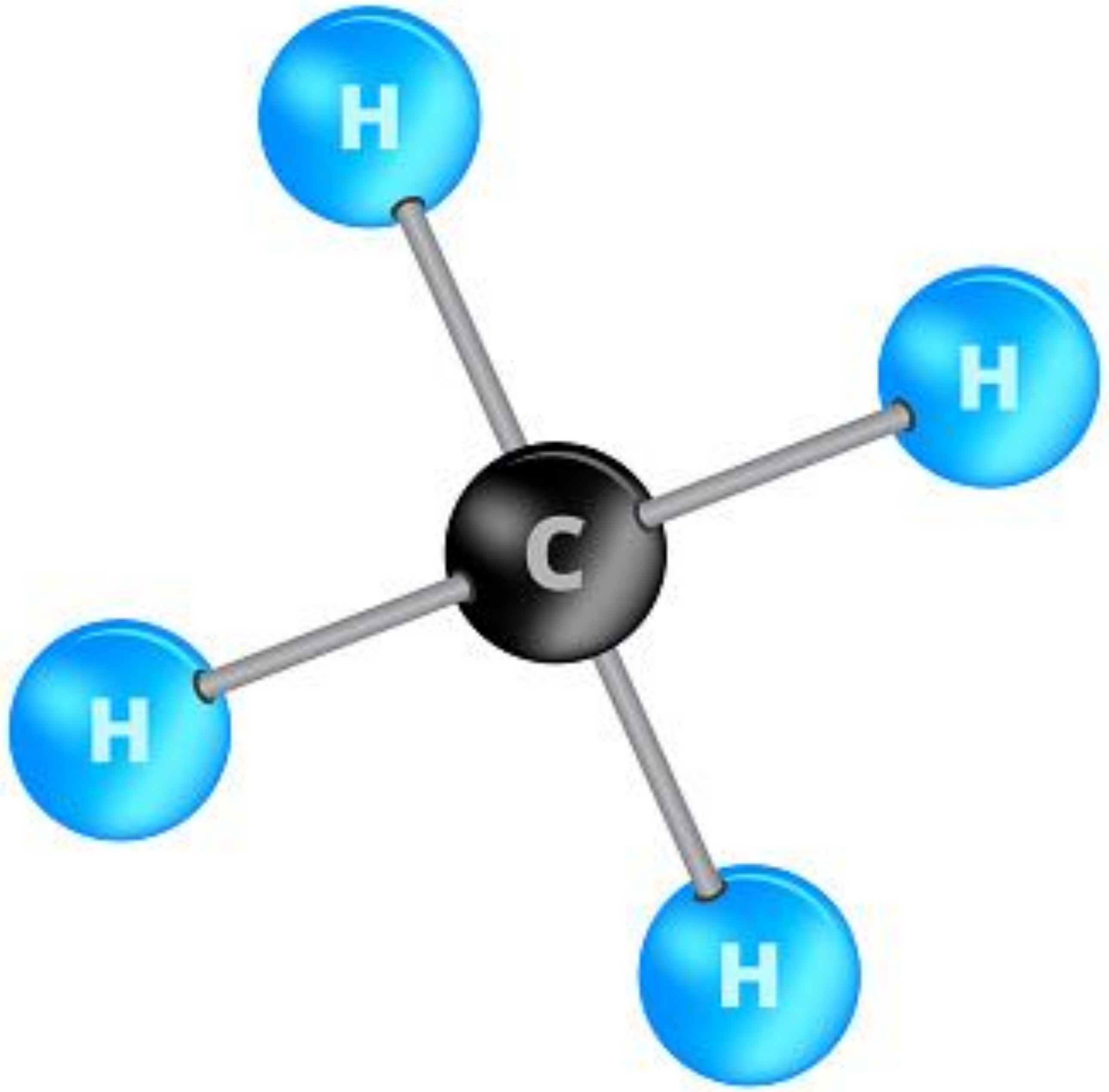
Lowest *PE* as it has the shortest bond length.

Lowest *bond energy* as it has the longest bond length.

# Molecular Models



- Space-Filling Model
  - differences in atomic radii
  - relative bond length
  - does NOT show number of bonds between atoms




- Ball and Stick Model
  - 3D positions of atoms
  - single, double and triple bonds
  - bond length exaggerated

# Bond Energy vs. Bond Length

- As the electron density between the positive nuclei increases, the attractive forces between the protons and the bonding electrons increase.

| Molecue | Bond Type | Bond Energy (kJ/mol) | Bond Length (nm) |
|---|---|---|---|
| $F_2$ | single | 155 | 0.144 |
| $O_2$ | double | 495 | 0.121 |
| $N_2$ | triple | 941 | 0.110 |

# Bond Order

- Bond order is the number of bonds between two atoms.
- When the bond order increases
  - bond length decreases
  - the *PE* associated with the bond decreases
  - the bond energy increases

| Bond Type | Bond Order |
|---|---|
| Single | 1 |
| Double | 2 |
| Triple | 3 |

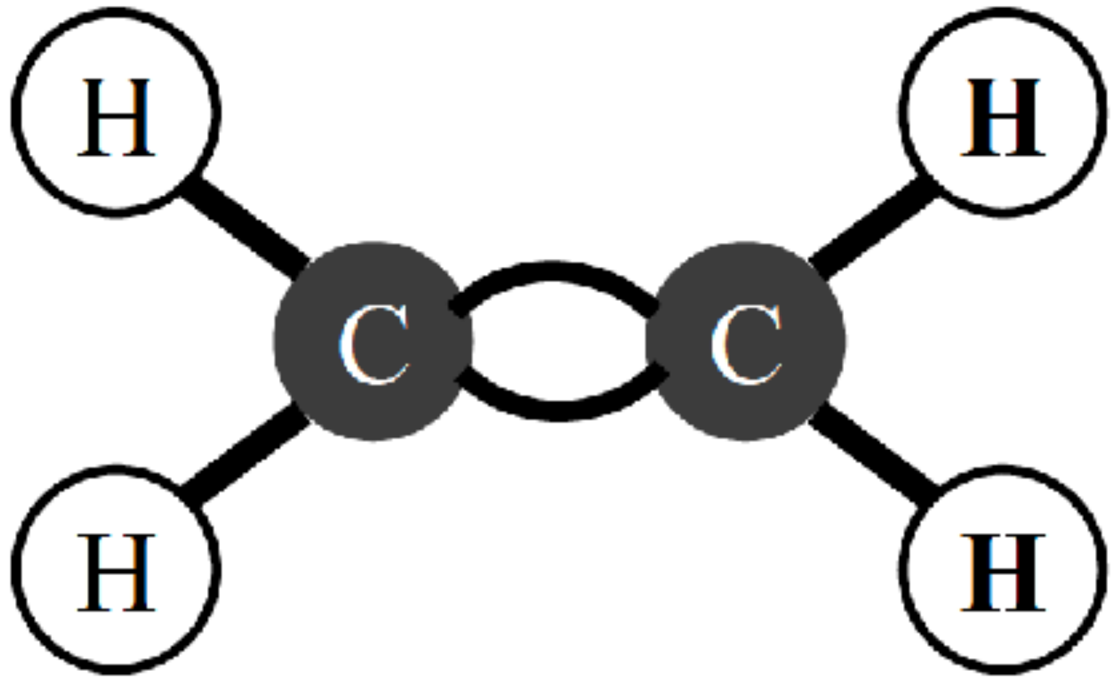
# Ex. Bond Energy / Bond Length

- Consider the ball and stick models below. The carbon-carbon bond in which molecule has the lowest *PE*?

- The carbon-carbon bond in which molecule has the lowest bond energy?

I.


II.




Lowest *PE* as it has the shortest bond length.

Lowest *bond energy* as it has the longest bond length.

# 2.5 Lewis Diagrams

- Lewis Structures
  - help predict shape
- Exceptions to the Octet Rule

# Example: Lewis Structures

<u>Step 1</u>

- Count the total number of valence electrons in the molecule ($PCl_3$).

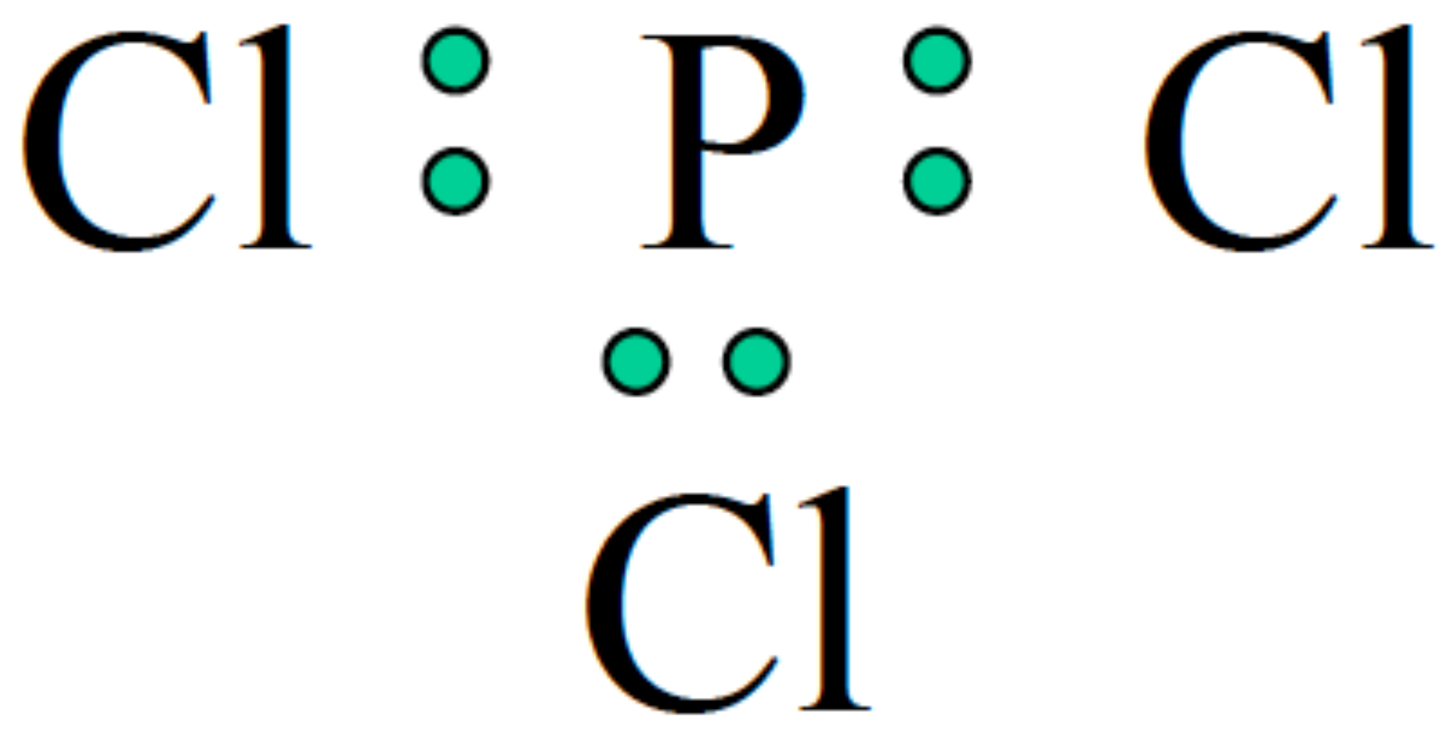
$$PCl_3$$

$$5 + (7 \times 3) = 26$$

# Example:  Lewis Structures

<u>Step 2</u>

- Put the **<u>least</u>** electronegative atom in the center and connect the terminal atoms to it with single bonds.

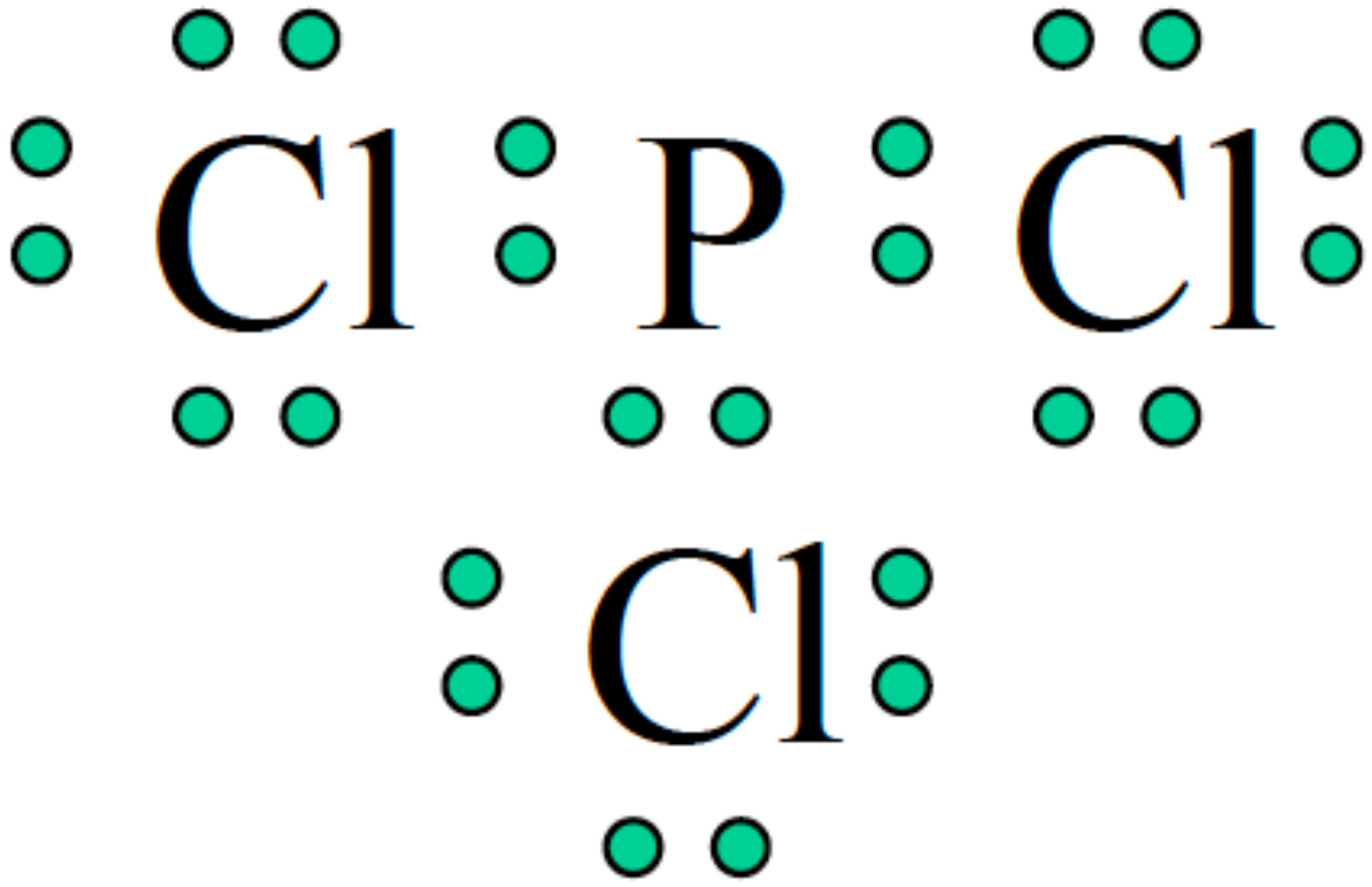



<u>Exception to rule</u>: Hydrogen is ALWAYS a terminal atom as it only needs to share 2 electrons to fill its octet.

# Example:  Lewis Structures

Step 3

- Complete the octets for all terminal atoms except Hydrogen atoms

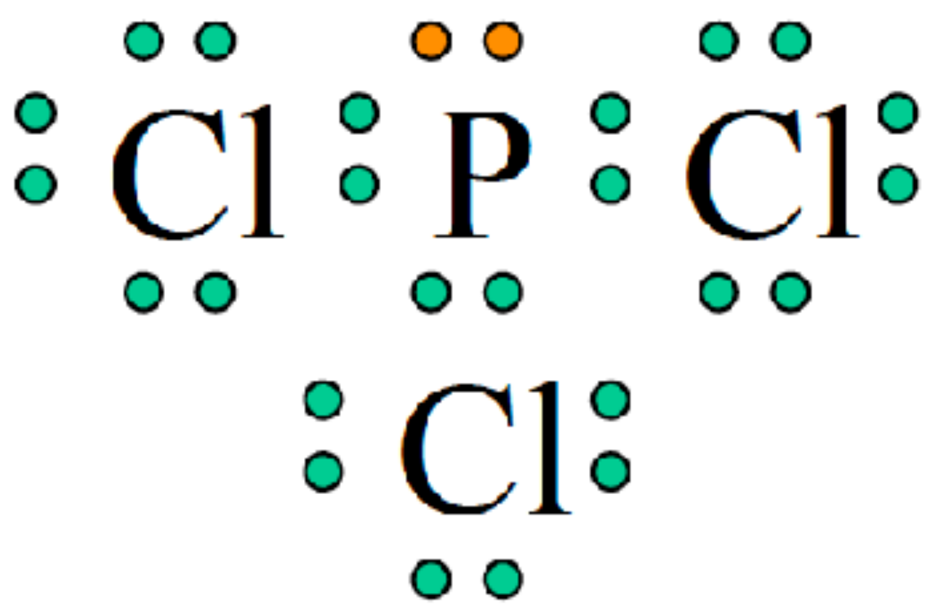


# Example:  Lewis Structures

Step 4

- Add up the electrons you have used and subtract them from the total number of valence electrons (Step 1). Attach leftover electrons to the central atom as **lone pairs**.

$26 - (3 \times 8) = 2$



# Example: Lewis Structures

$CO_2$

- Step 5 - multiple bonds?

# Example: Lewis Structures

In some cases you may need to make triple bonds to complete the octet around the central atom (HCN).

# Example: Lewis Structures

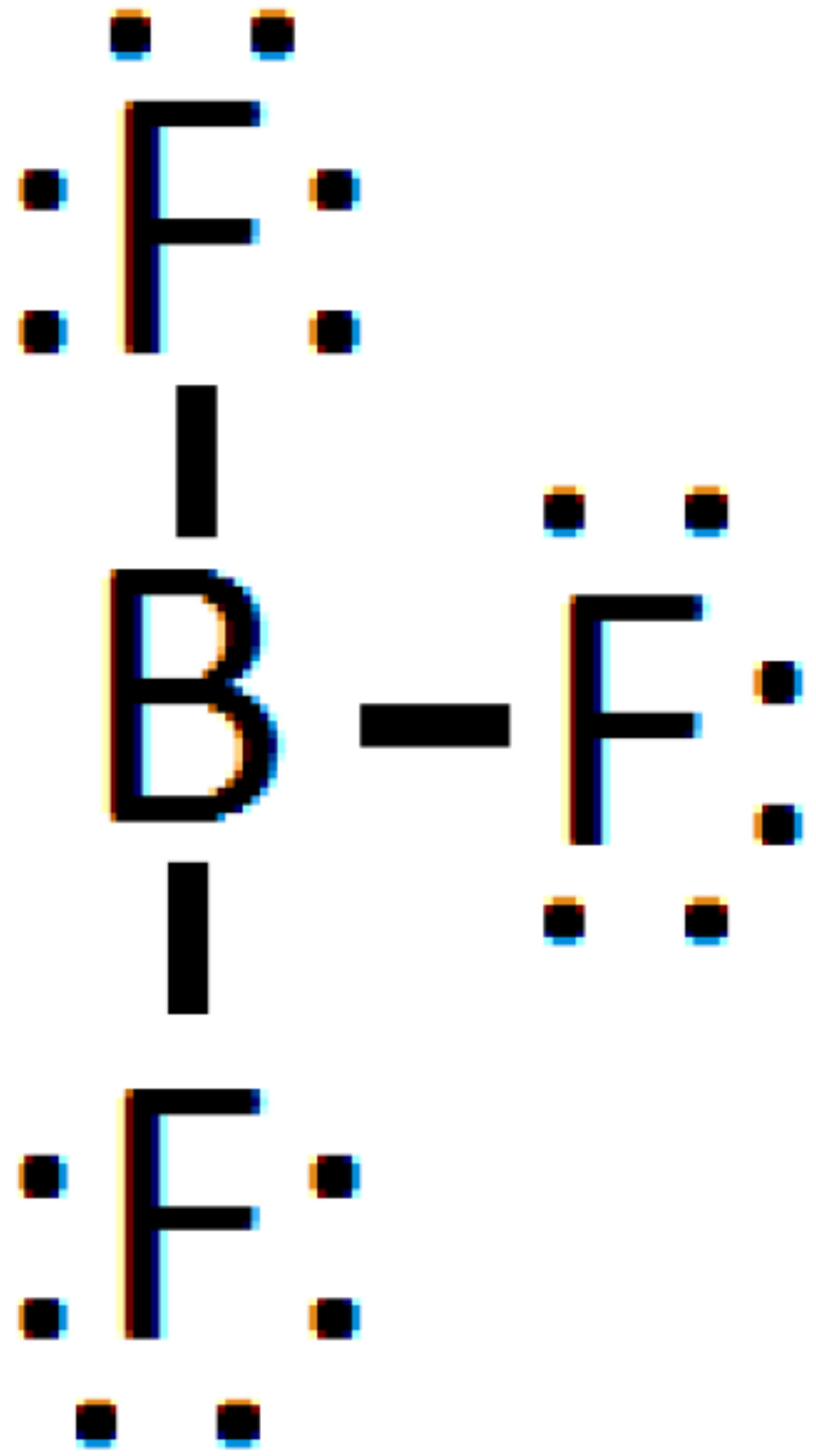
If you are making a Lewis structure for a polyatomic ion, you must take the overall charge of the ion into consideration.

Iodate $IO_3^-$

# Exceptions to the Octet Rule

Incomplete Octets

Boron has less ability to attract electrons to fill its octet as it has only 5 protons.



# Exceptions to the Octet Rule

Expanded Octets

Atoms in periods 3 through 7 can bond with other atoms in such a way they end up with more than eight electrons in their octets.

What????