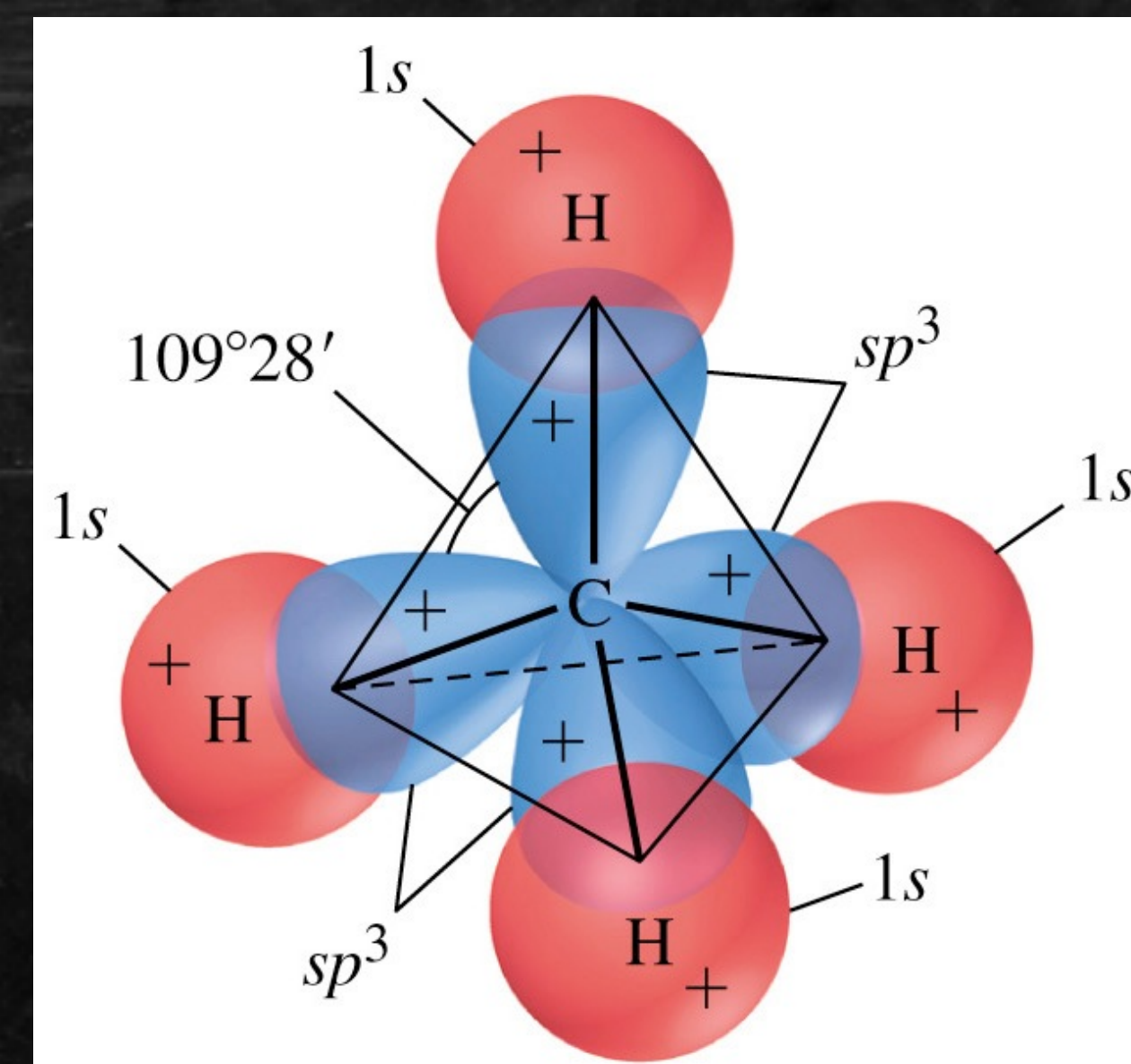


Chemical Bonding



Introduction to Chemical Bonding

Chemical bond → *is a mutual electrical attraction between the nuclei and valence electrons of different atoms that binds the atoms together*

Why are most atoms chemically bonded to each other?

As independent particles, they are at relatively high potential energy

Nature, however, favors arrangements in which potential energy is minimized

This means that most atoms are less stable existing by themselves than when they are combined

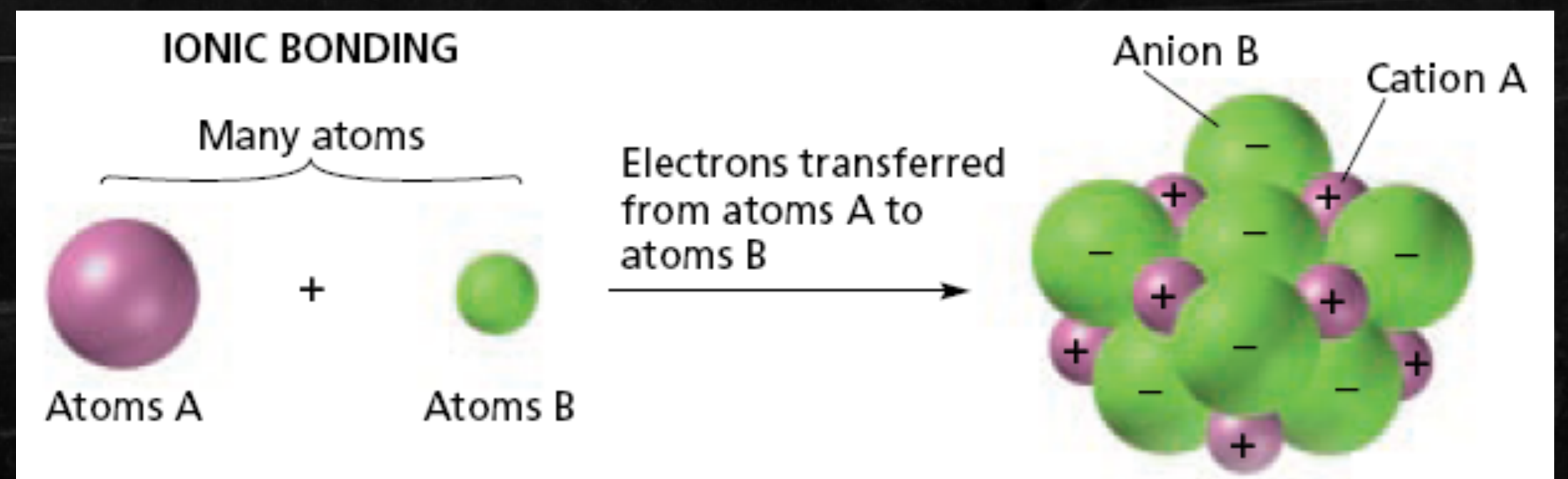
By bonding with each other, atoms decrease in potential energy, thereby creating more stable arrangements of matter

Types of Chemical Bonding

Bond – valence electrons rearranged to make atom more stable

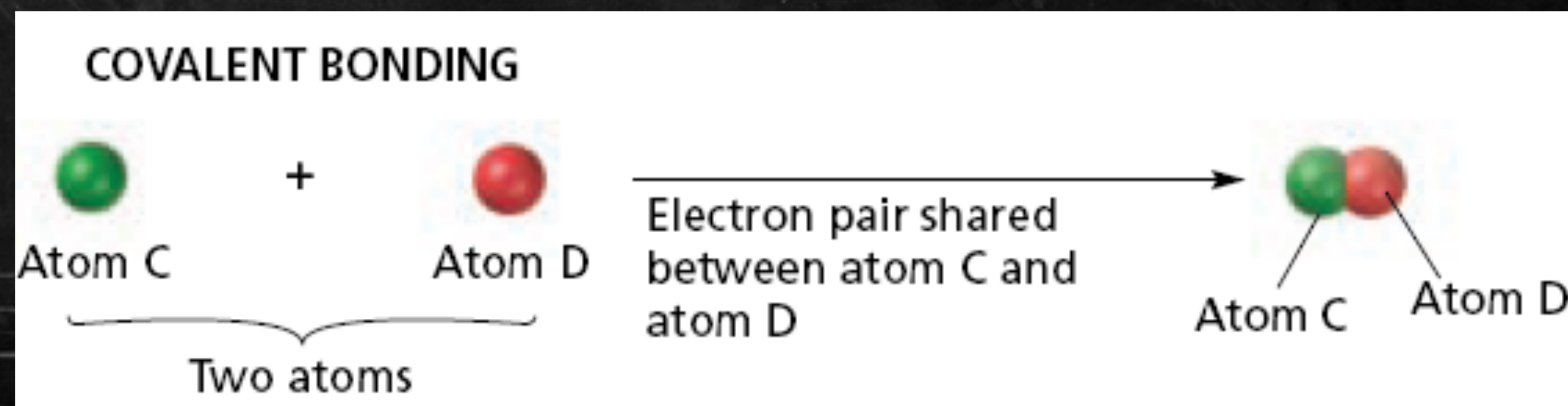
Way they are rearranged depends on type of bond

Ionic bonding → *chemical bonding that results from the electrical attraction between*



Covalent bonding → *results from the sharing of electron pairs between two atoms*

In purely covalent bond, electrons shared *equally* between two atoms



Ionic or Covalent?

Bonding is rarely purely one or the other

Depending on how strongly the atoms attract electrons, falls somewhere between

Electronegativity (EN) → atom's ability to attract electrons

Degree of bonding between atoms of 2 elements being ionic or covalent estimated by calculating difference in elements' ENs

Example

Fluorine's EN = 4.0,
Cesium's EN = 0.7

$$4.0 - 0.7 = 3.3$$

According to table, F-Cs is
ionic

The greater the difference,
the more ionic the bond

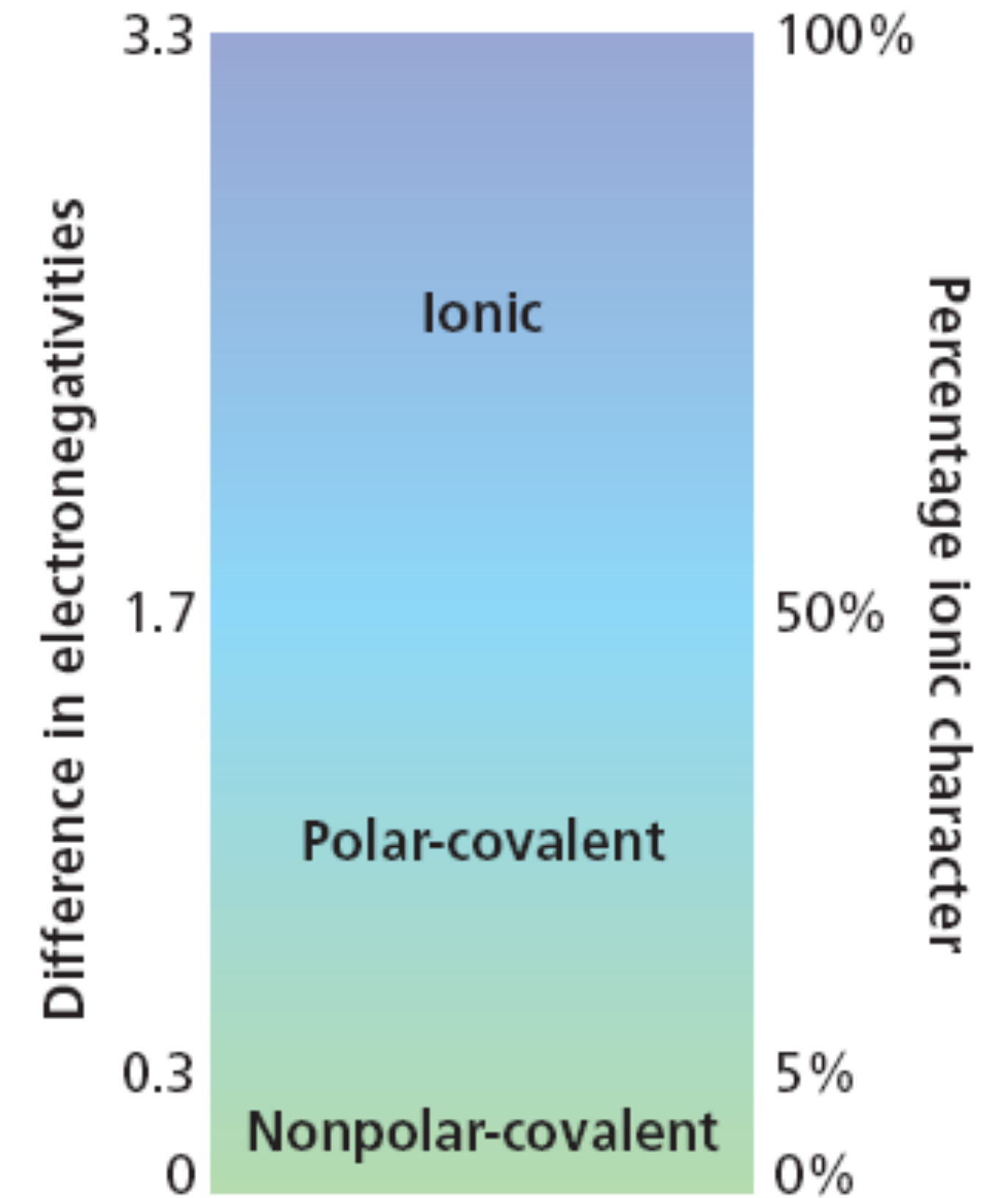
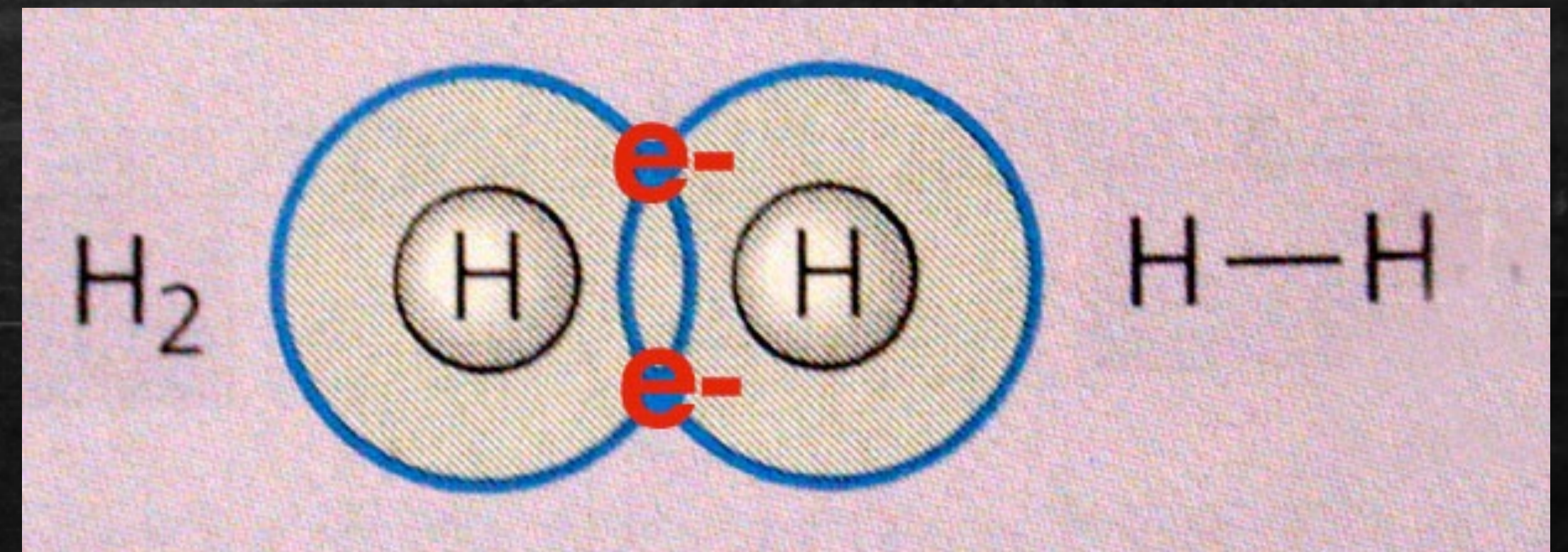


FIGURE 6-2 Differences in electronegativities reflect the character of bonding between elements. The electronegativity of the less-electronegative element is subtracted from that of the more-electronegative element. The greater the electronegativity difference, the more ionic is the bonding.

Bonding between atoms with EN difference of less than or equal to (\leq) 1.7 has ionic character less than or equal to (\leq) 50%

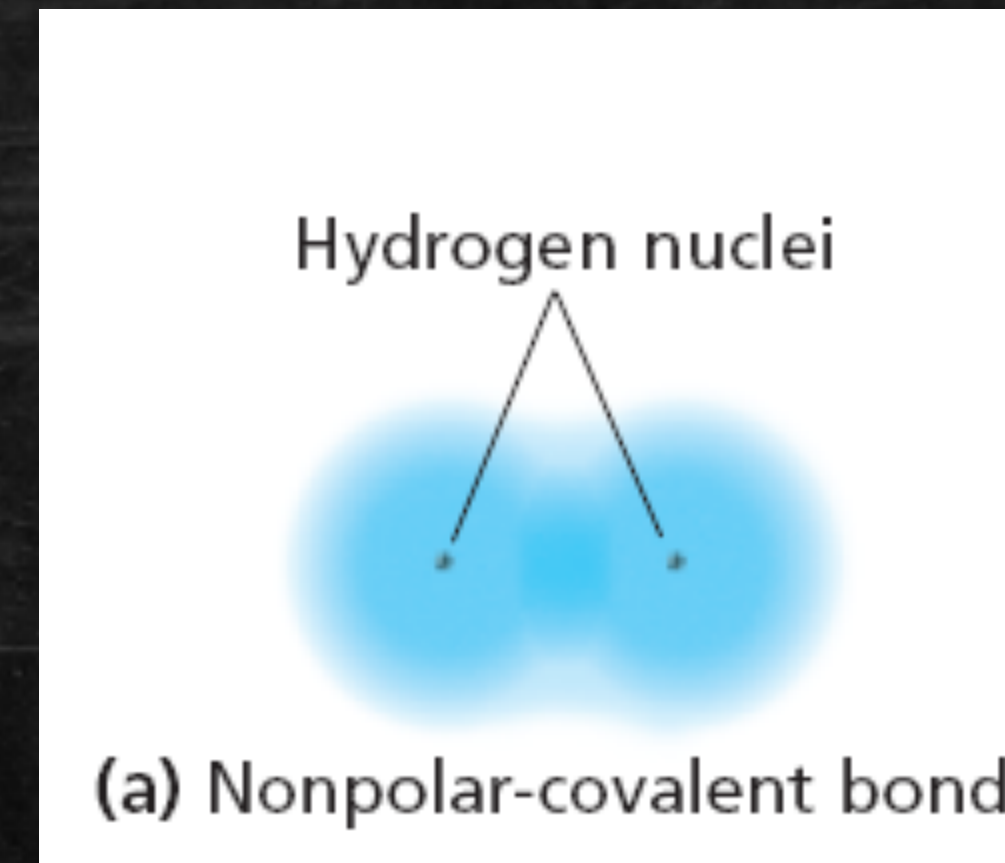
Classified as covalent



Bonding between atoms of same element is completely covalent

Nonpolar-covalent

H-H bond has 0% ionic character



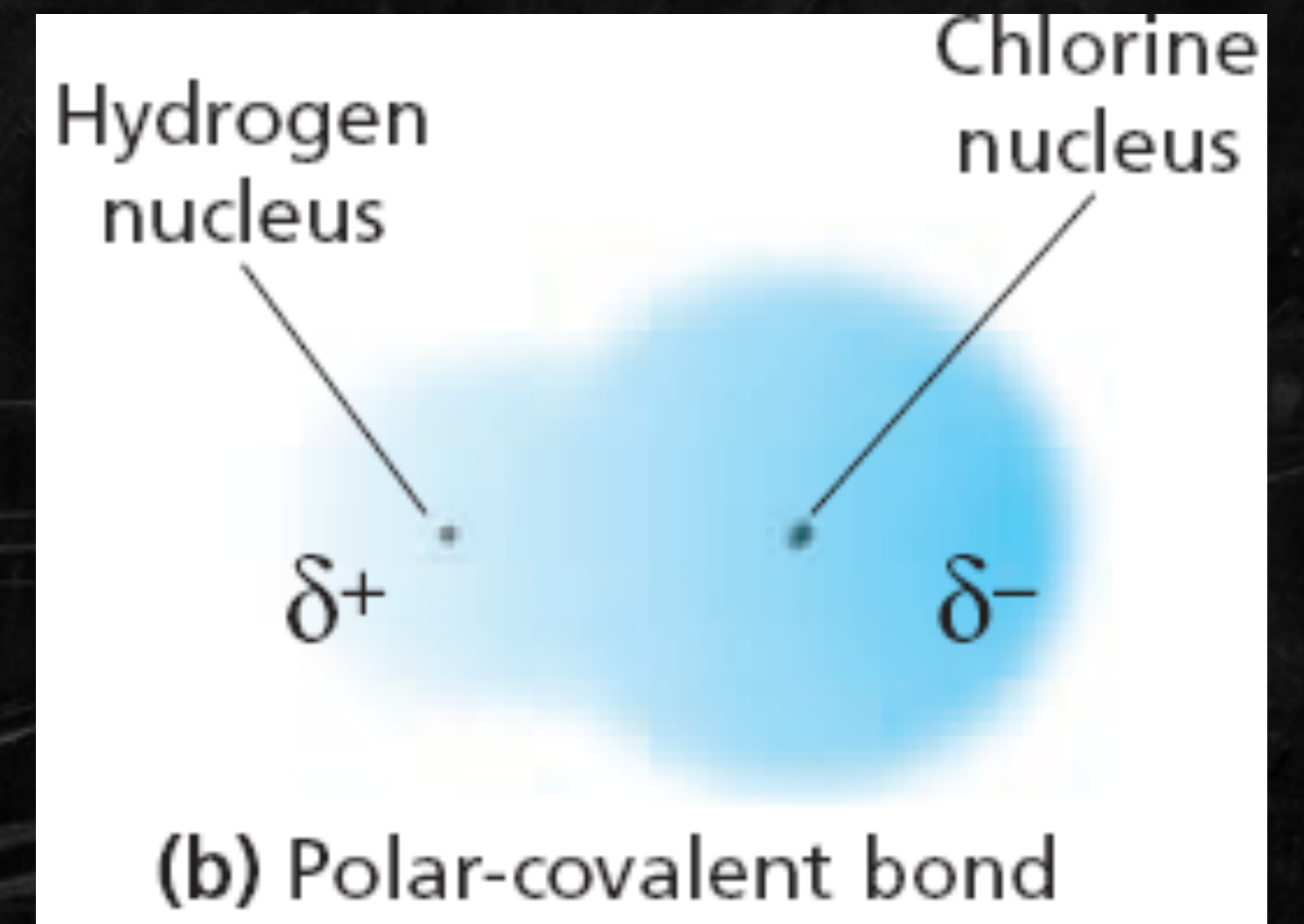
Nonpolar-covalent bond → *a covalent bond in which the bonding electrons are shared equally by the bonded atoms, resulting in a balanced distribution of electrical charge*

0-5% ionic character (0-0.3 EN difference) is nonpolar-covalent bond

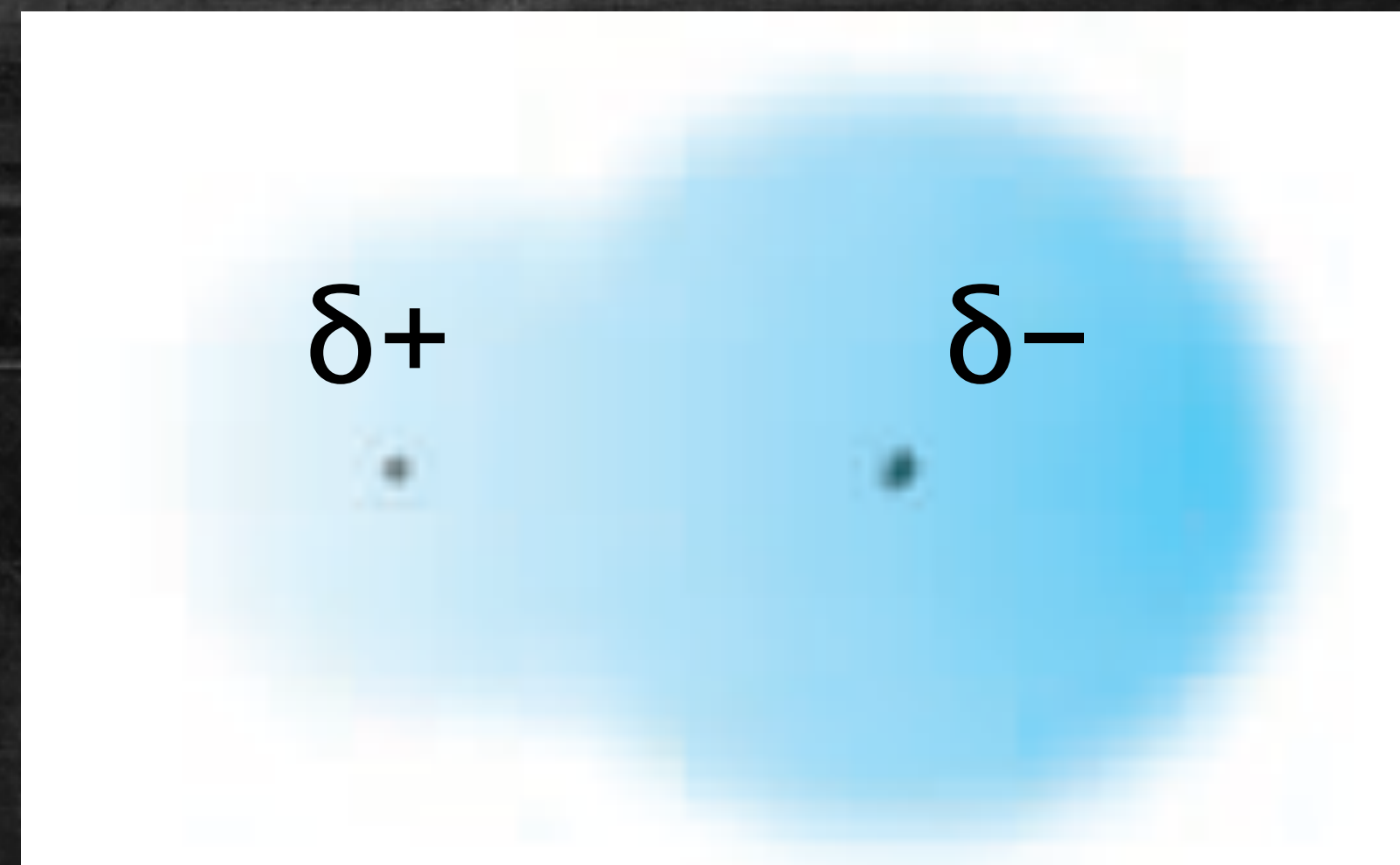
Polar-covalent Bonds

Bonds that have significantly different
ENs, electrons more strongly attracted by
more-EN atom

These bonds are polar → *they have an
uneven distribution of charge*



Covalent bonds with 5-50% ionic character (0.3-1.7 EN difference) are polar



Polar-covalent bond → *covalent bond in which the bonded atoms have an unequal attraction for the shared electrons*

Sample Problem

Use electronegativity differences to classify bonding between sulfur, S, and the following elements: hydrogen, H; cesium, Cs; and chlorine, Cl. In each pair, which atom will be more negative?

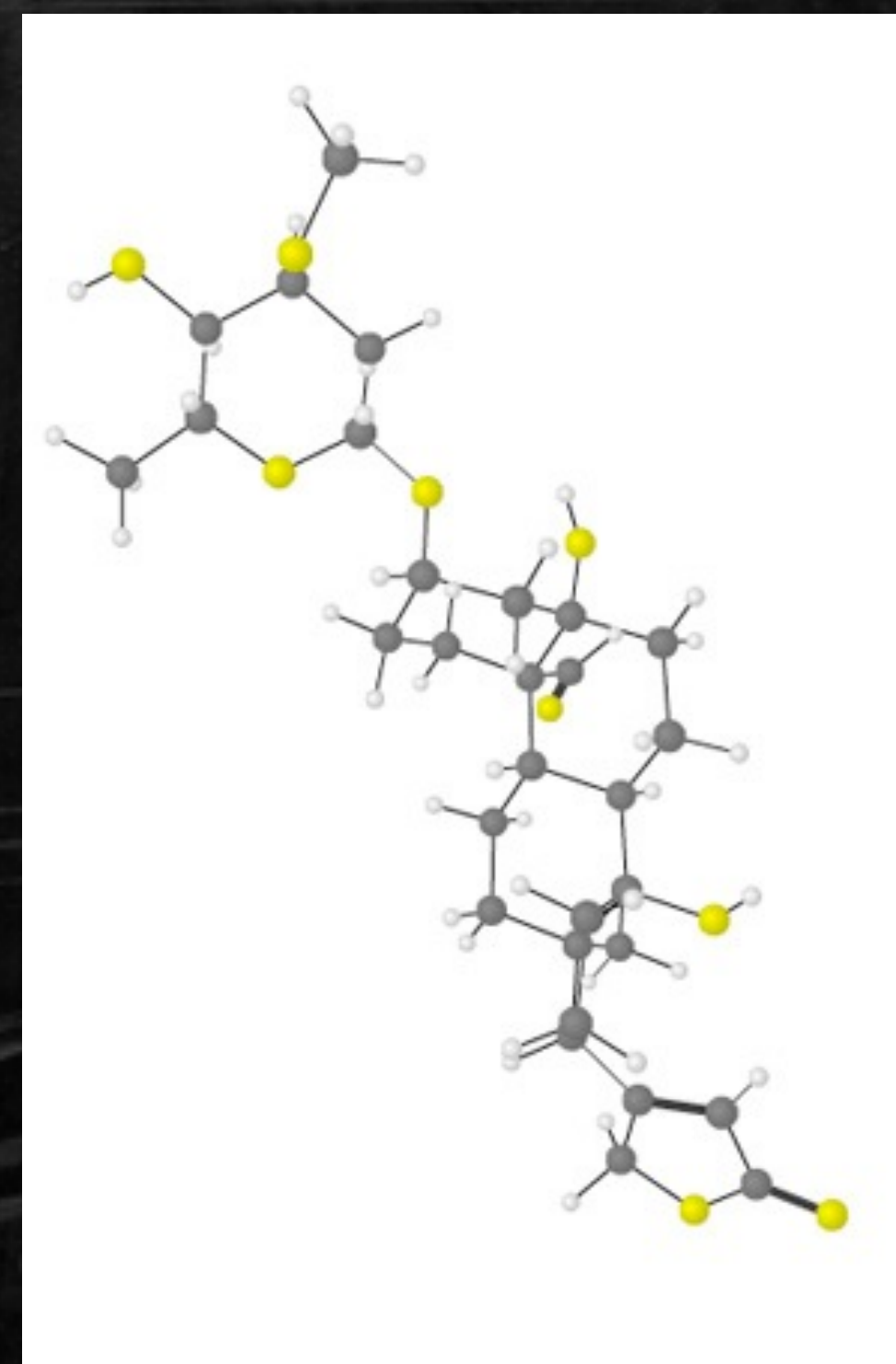
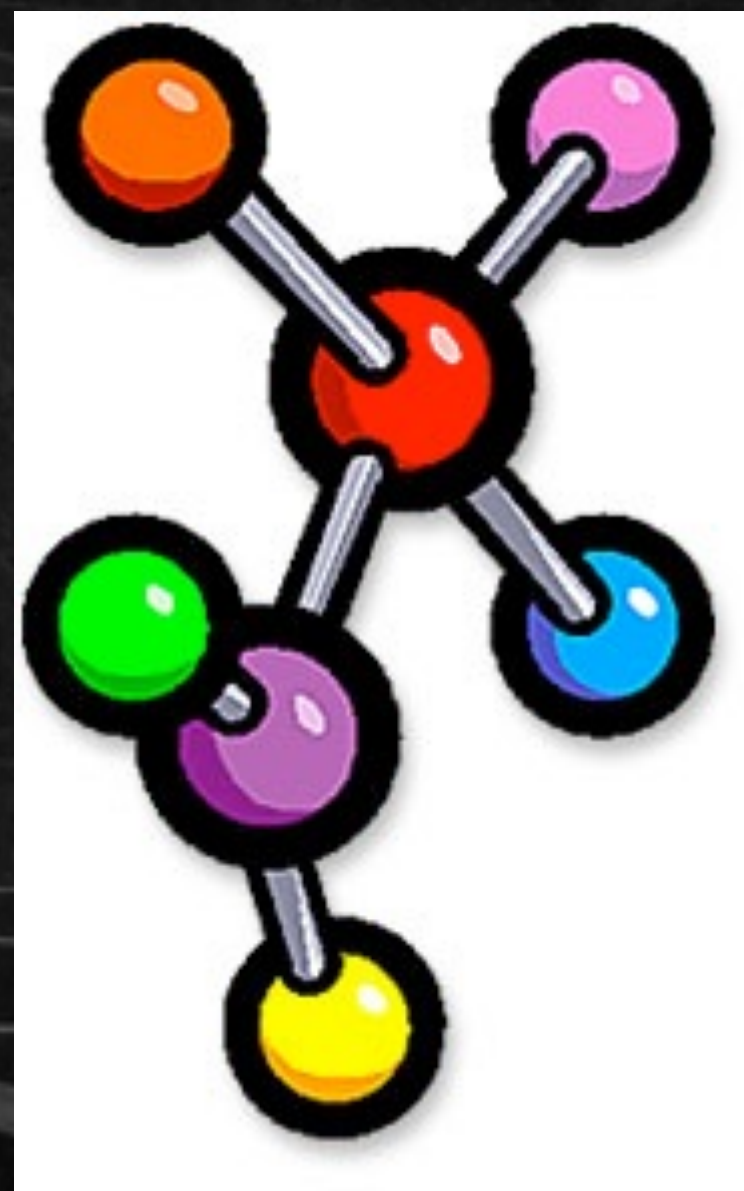
| Bonding between sulfur and | EN difference | Bond type | More-negative atom |
|----------------------------|-------------------|----------------|--------------------|
| Hydrogen | $2.5 - 2.1 = 0.4$ | Polar-covalent | Sulfur |
| Cesium | $2.5 - 0.7 = 1.8$ | Ionic | Sulfur |
| Chlorine | $3.0 - 2.5 = 0.5$ | Polar-covalent | chlorine |

Practice Problem

Use electronegativity differences to classify bonding between chlorine, Cl, and the following elements: calcium, Ca; oxygen, O; and bromine, Br. Indicate the more-negative atom in each pair.

| Bonding between chlorine and | EN difference | Bond type | More-negative atom |
|------------------------------|-------------------|-------------------|--------------------|
| Calcium | $3.0 - 1.0 = 2.0$ | Ionic | Chlorine |
| Oxygen | $3.5 - 3.0 = 0.5$ | Polar-covalent | Oxygen |
| Bromine | $3.0 - 2.8 = 0.2$ | Nonpolar-covalent | Chlorine |

Section 2 – Covalent Bonding and Molecular Compounds



Many chemical compounds are molecules

Molecule → *neutral group of atoms that are held together by covalent bonds*

Single molecule of compound is individual unit

Capable of existing on its own

May consist of 2 or more atoms of same element or two or more different atoms

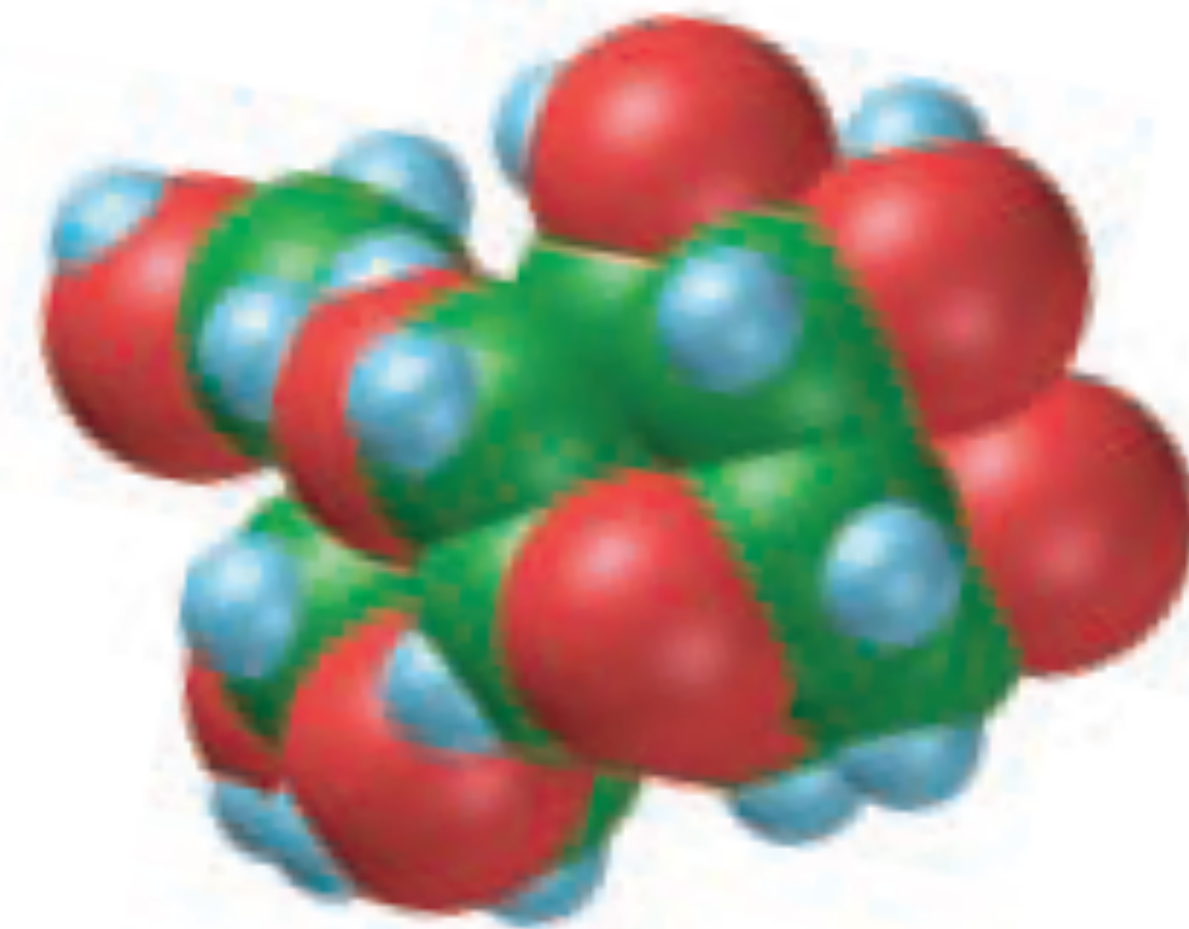
Molecular compound → *chemical compound whose simplest units are molecules*



(a) Water molecule,
 H_2O



(b) Oxygen molecule,
 O_2



(c) Sucrose molecule,
 $\text{C}_{12}\text{H}_{22}\text{O}_{11}$

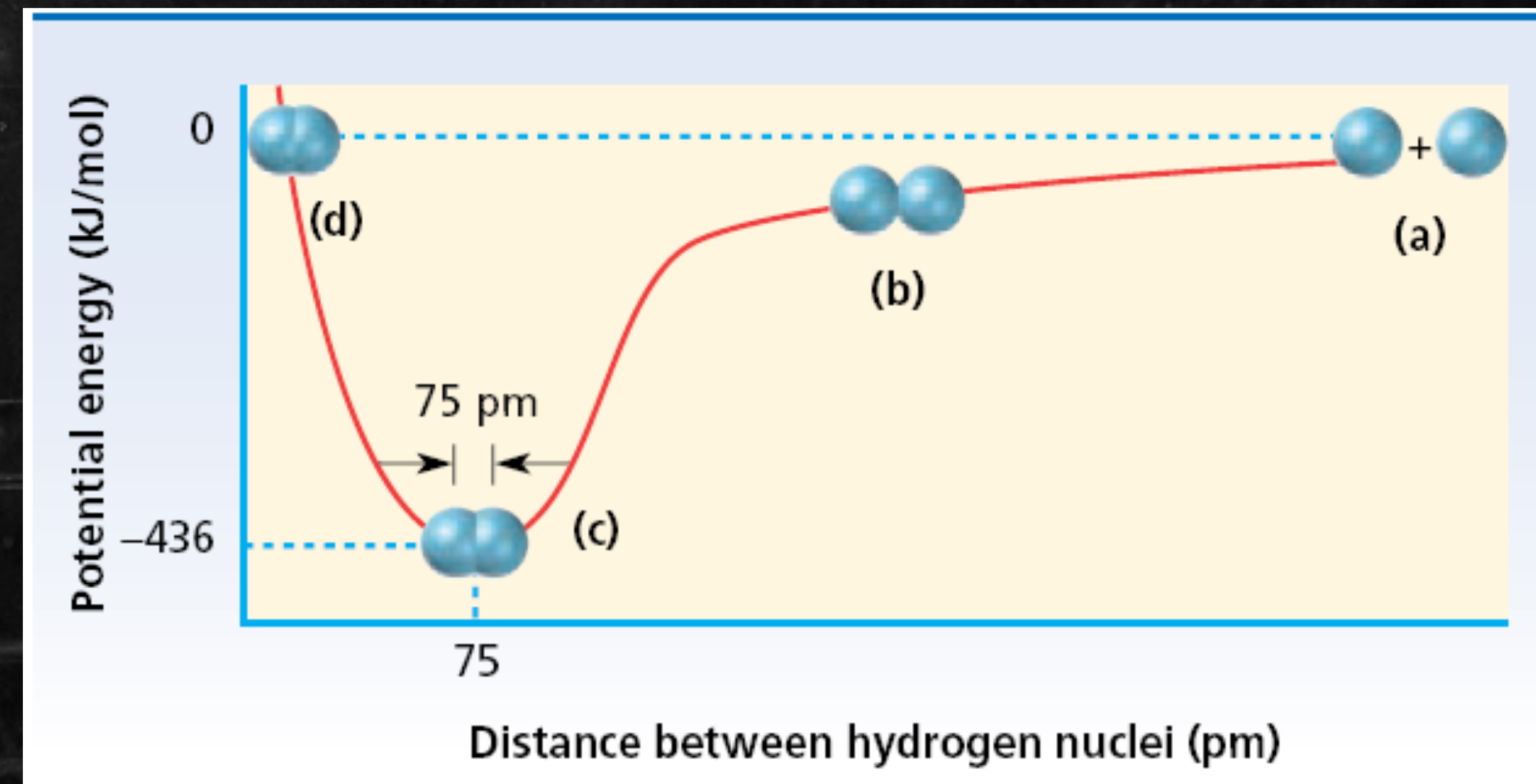
FIGURE 6-4 The models for (a) water, (b) oxygen, and (c) sucrose, or table sugar, represent a few examples of the many molecular compounds in and around us. Atoms within molecules may form one or more covalent bonds.

Formation of Covalent Bond

Bonded atoms have lower potential energy than unbonded atoms

At large distance atoms don't influence each other

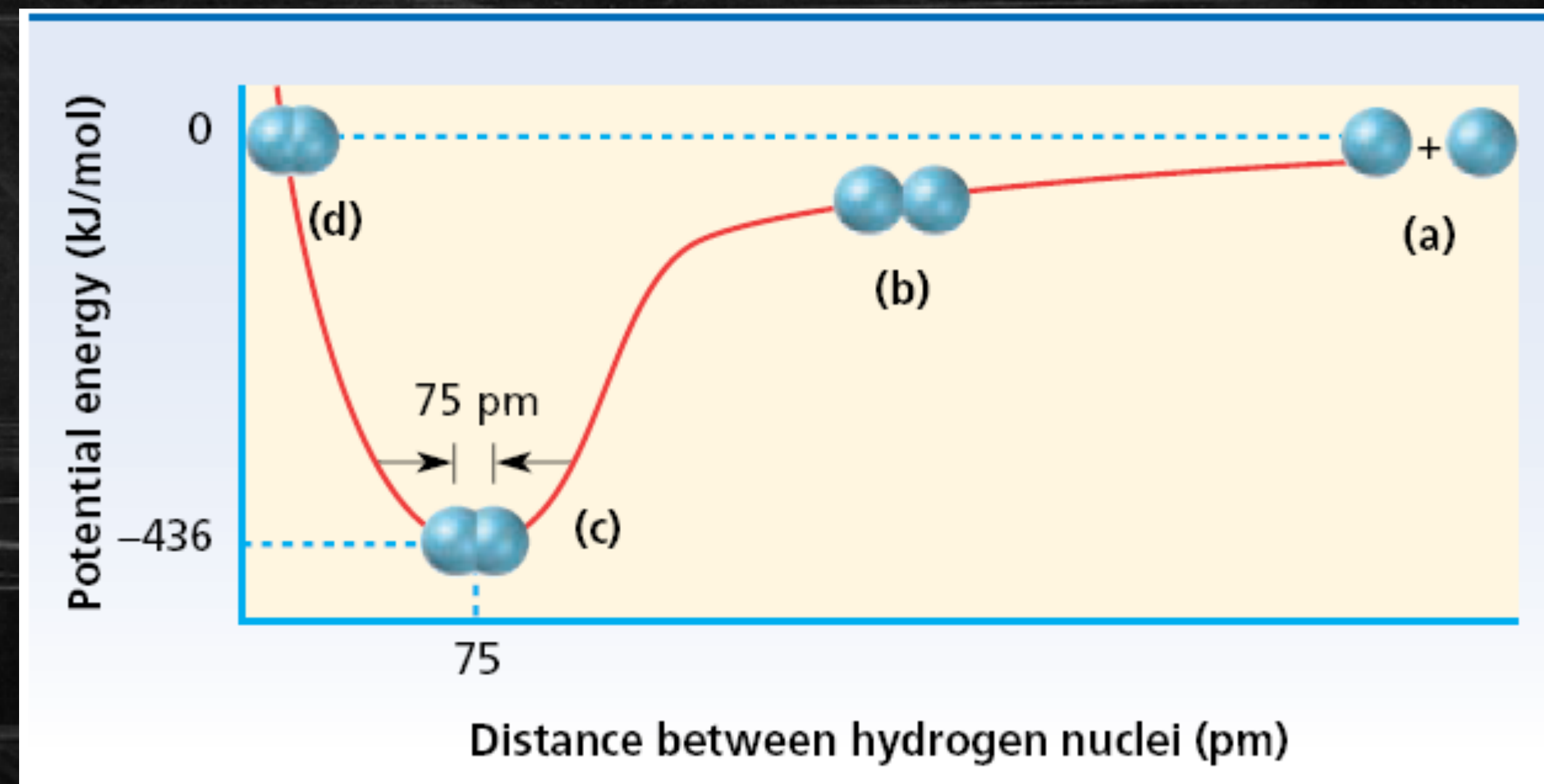
Potential energy set at 0



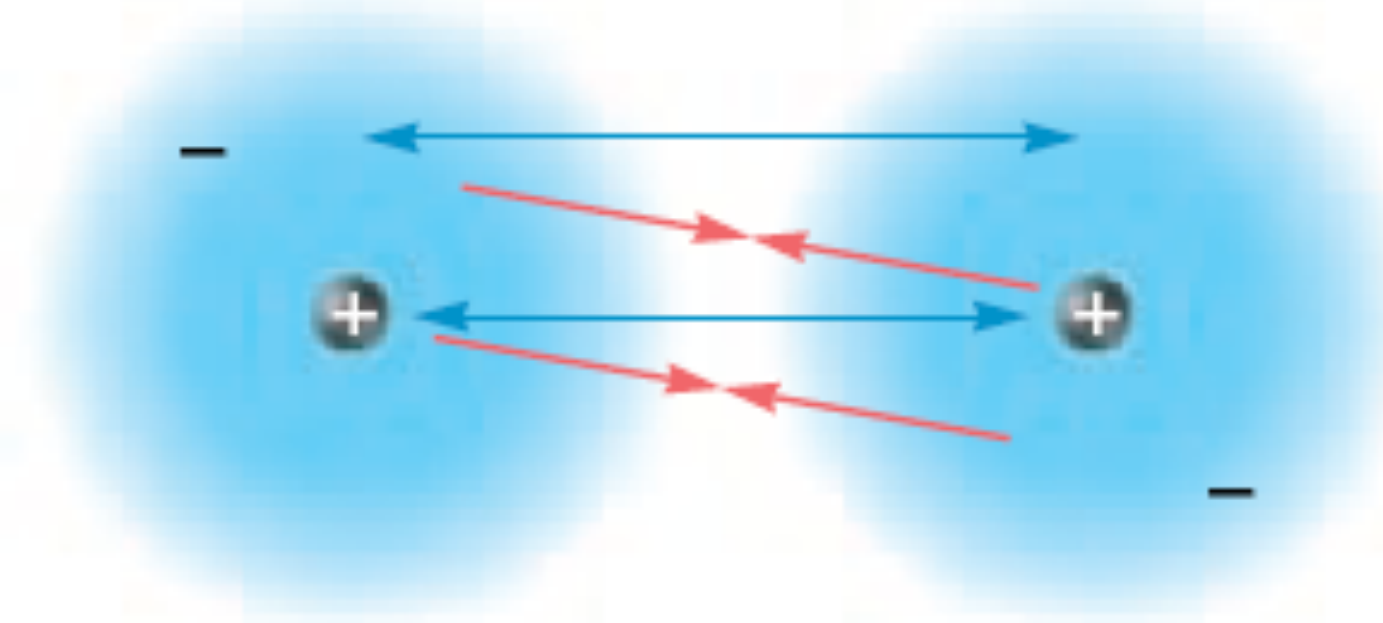
Each H has (+) proton

Nucleus surrounded by (-) electron

As atoms near each other, charged particles start to interact



↔ Both nuclei repel each other, as do both electron clouds.



↔ The nucleus of one atom attracts the electron cloud of the other atom, and vice versa.

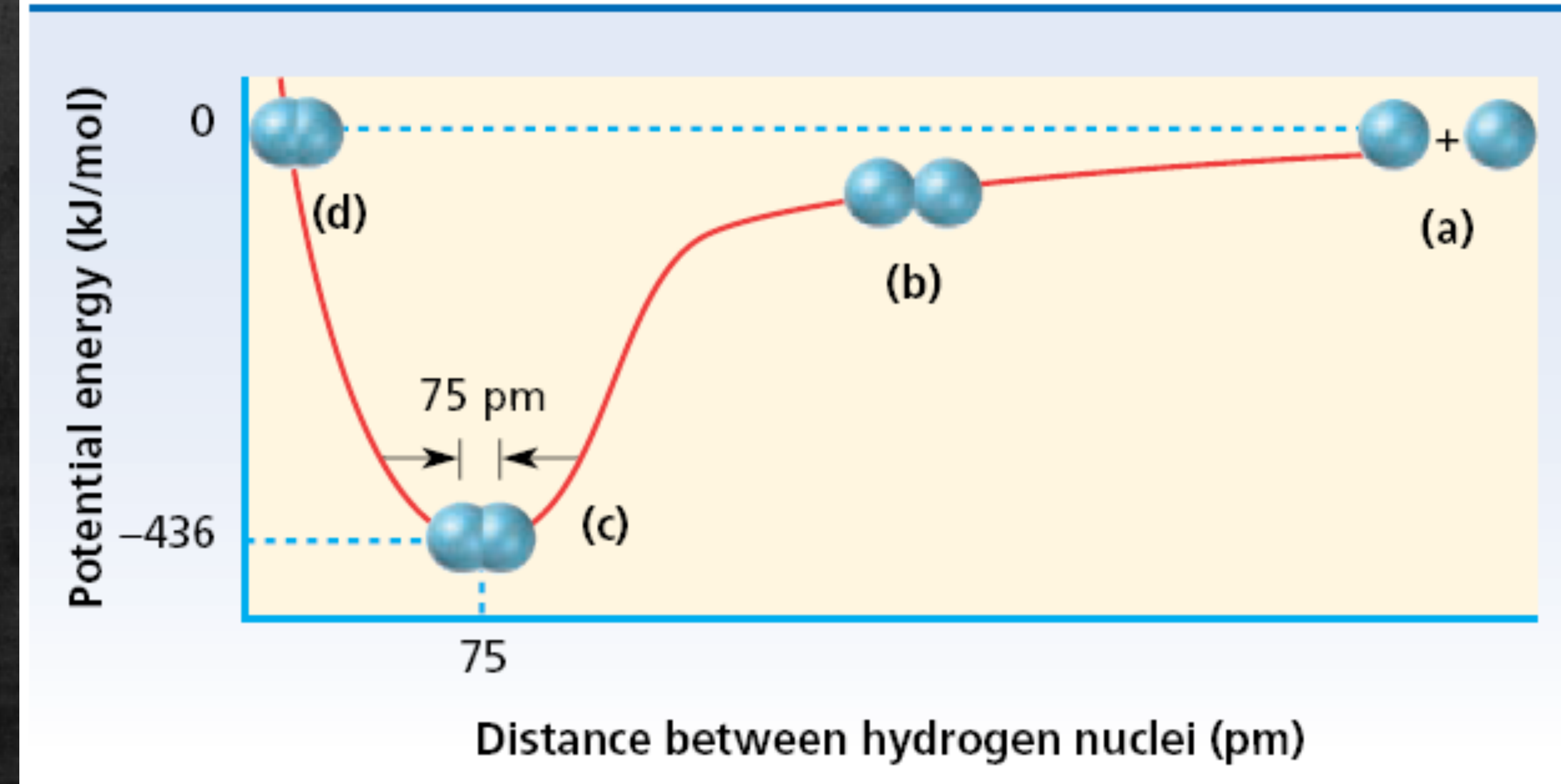
FIGURE 6-6 The arrows indicate the attractive and repulsive forces between the electrons (shown as electron clouds) and nuclei of two hydrogen atoms. Attraction between particles corresponds to a decrease in potential energy of the atoms, while repulsion corresponds to an increase.

Approaching nuclei and electrons are *attracted* to each other

Decrease in total potential energy

At the same time, two nuclei and two electrons *repel* each other

Increase in potential energy



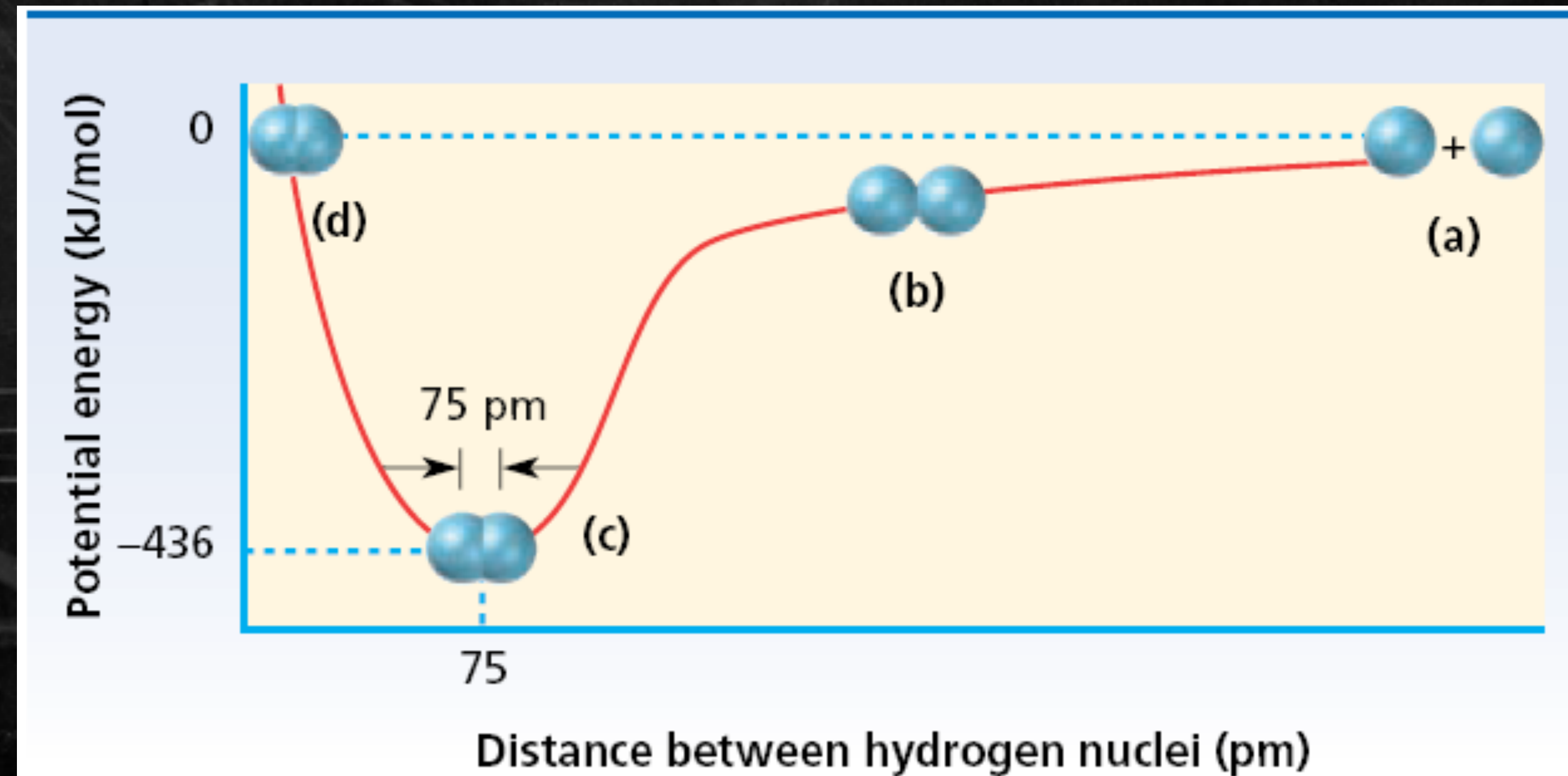
The amount of attraction/repulsion depends on how close the atoms are to each other

When atoms first “see” each other, electron-proton attraction stronger than e-e or p-p repulsions

So atoms drawn to each other and potential energy lowered

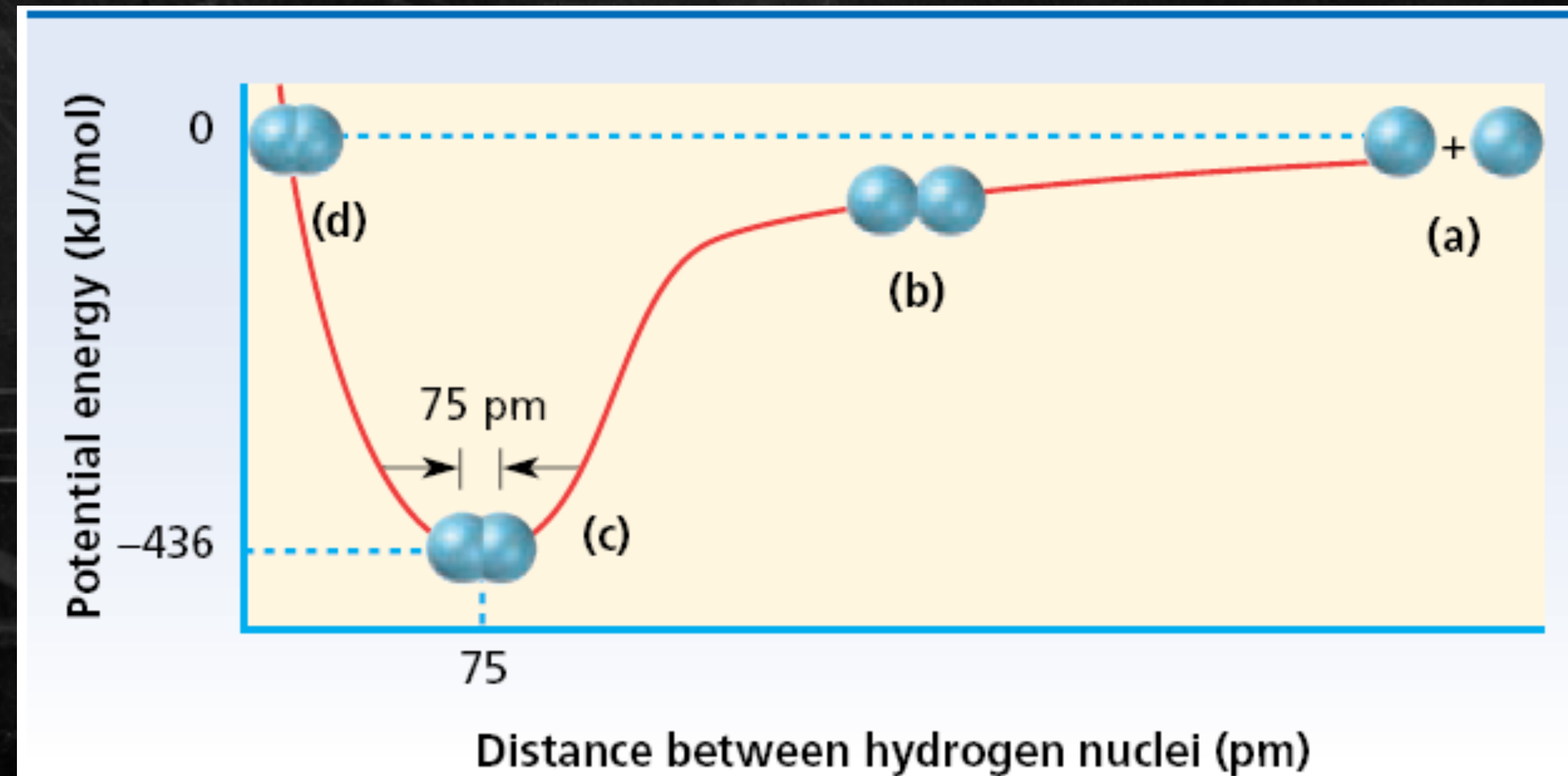
Attractive force dominates until a distance is reached where repulsion equals attraction

Valley of the curve



Closer the atoms get, potential energy rises sharply

Repulsion becomes greater than attraction

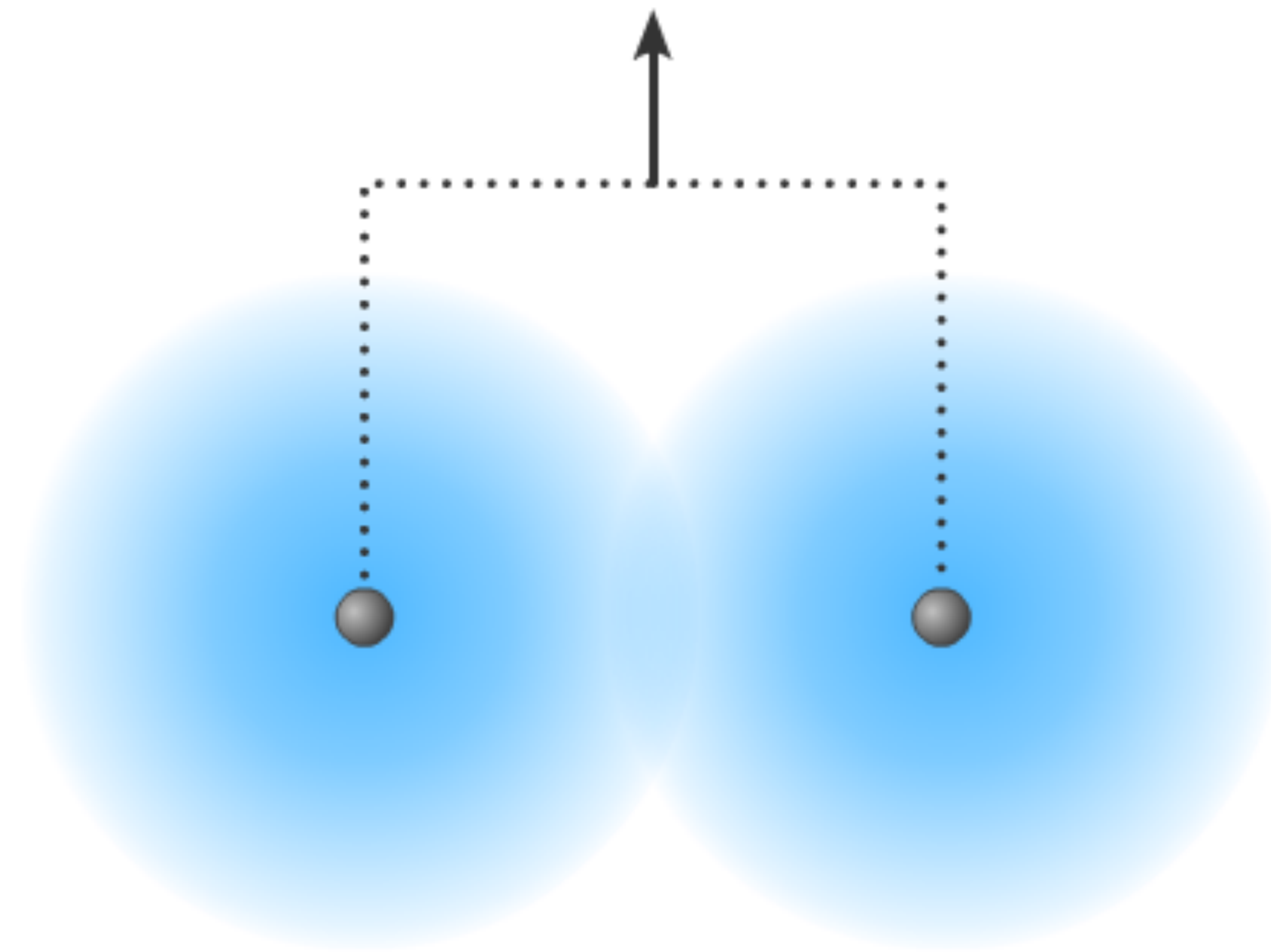


Bonded atoms vibrate a bit

As long as energy stays close to minimum they stay covalently bonded

Bond length → *the distance between two bonded atoms at their minimum potential energy (average distance between two bonded atoms)*

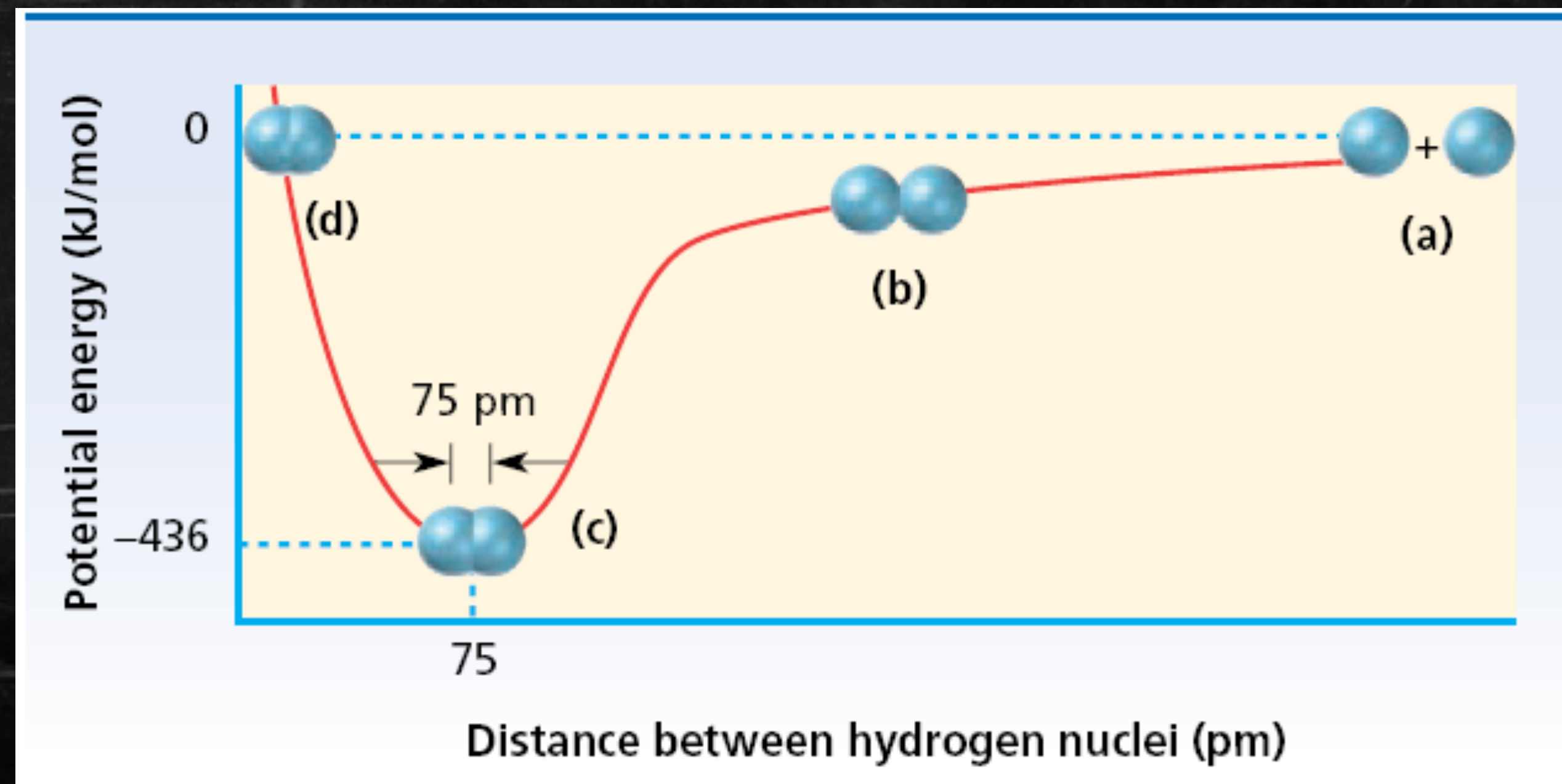
Bond length: 75 pm



Hydrogen atoms

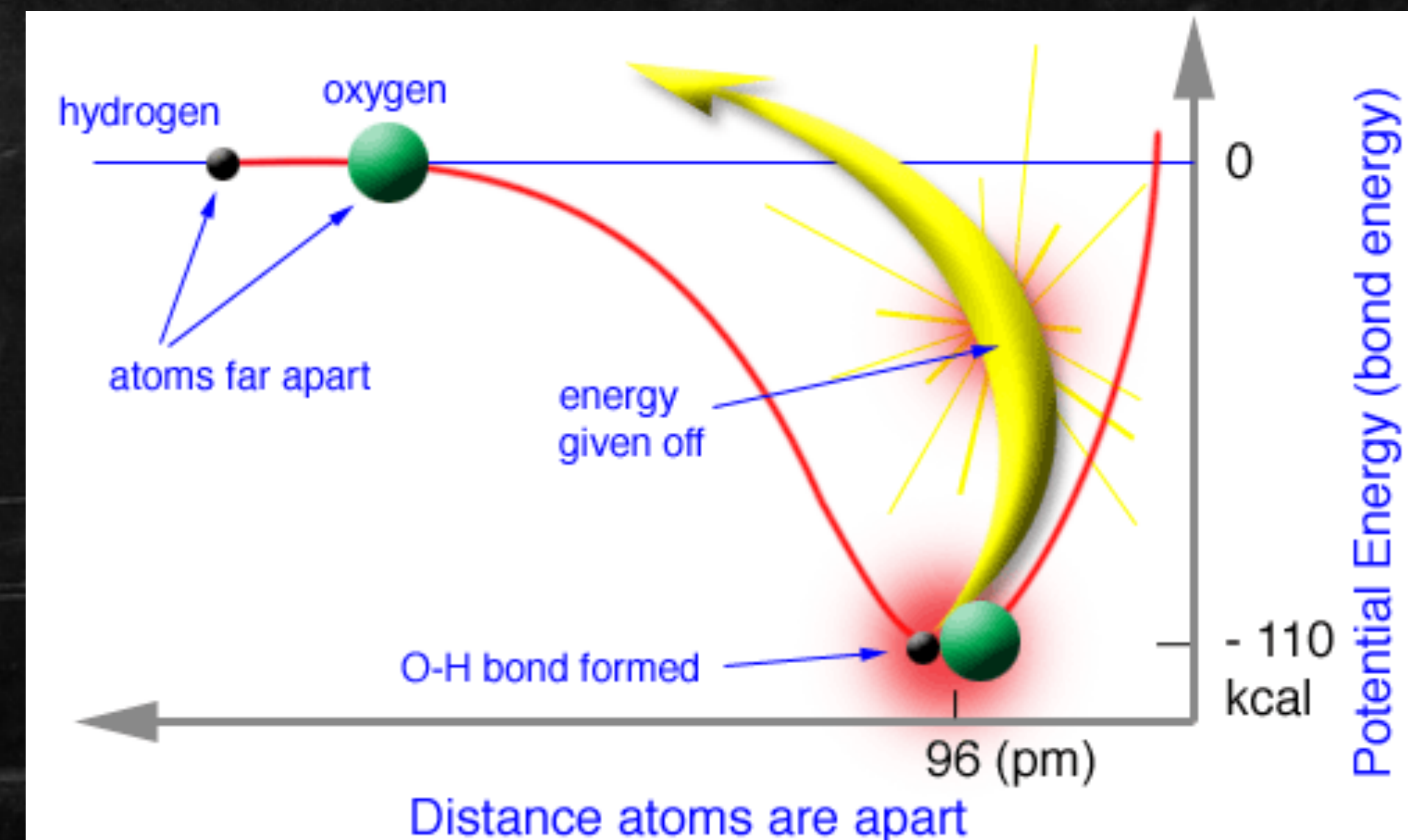
To form covalent bond, hydrogen atoms need to release energy

Amount of energy equals difference between potential energy at zero level (separated atoms) and at bottom of valley (bonded atoms)



Same amount of energy must be added to separate bonded atoms

Bond energy → *energy required to break a chemical bond and form neutral isolated atoms*



Units of bond energy usually kJ/mol

Indicates energy required to break one mole of bonds in isolated molecules

Ex. 436 kJ/mol is energy needed to break H-H bonds in 1 mol hydrogen molecules and form 2 mol of separated H atoms

Bond lengths and bond energies vary with the types of atoms that have combined

TABLE 6-1 Bond Lengths and Bond Energies for Selected Covalent Bonds

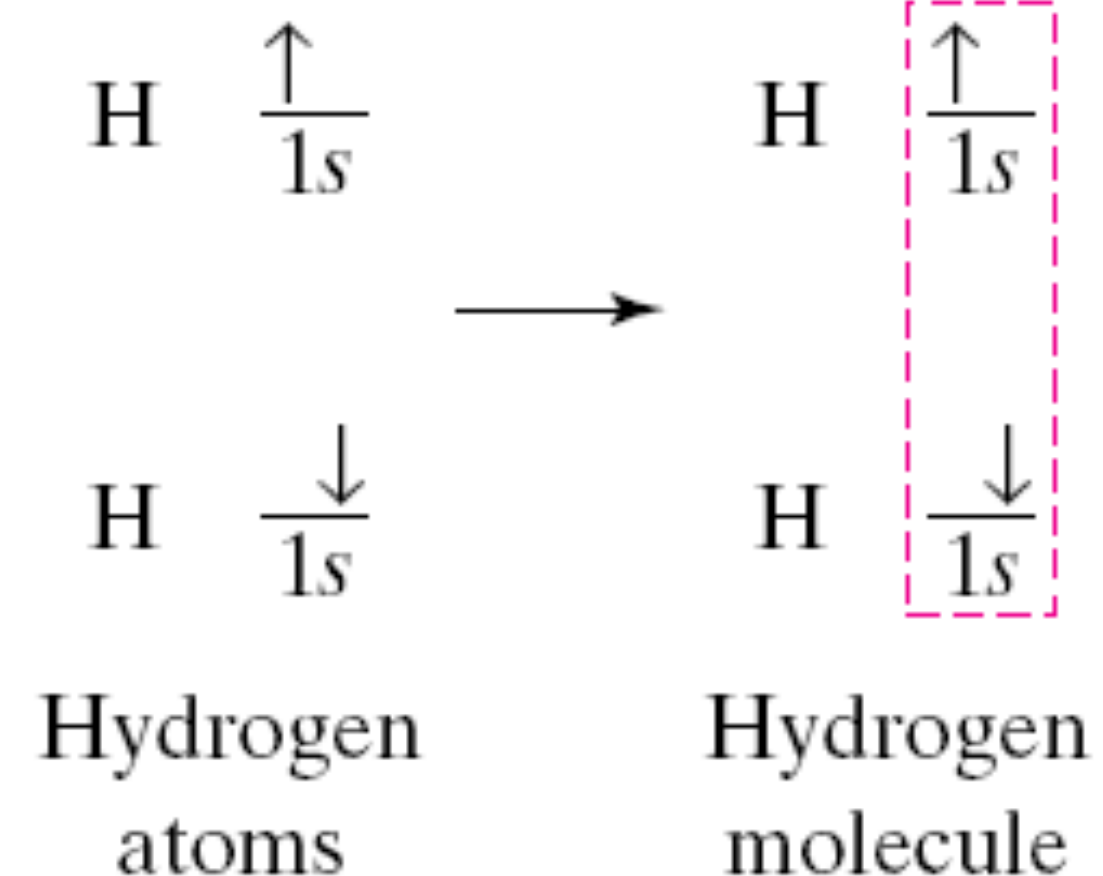
| Bond | Bond length (pm) | Bond energy (kJ/mol) | Bond | Bond length (pm) | Bond energy (kJ/mol) |
|-------|------------------|----------------------|------|------------------|----------------------|
| H–H | 74 | 436 | C–C | 154 | 346 |
| F–F | 141 | 159 | C–N | 147 | 305 |
| Cl–Cl | 199 | 243 | C–O | 143 | 358 |
| Br–Br | 228 | 193 | C–H | 109 | 418 |
| I–I | 267 | 151 | C–Cl | 177 | 327 |
| H–F | 92 | 569 | C–Br | 194 | 285 |
| H–Cl | 127 | 432 | N–N | 145 | 163 |
| H–Br | 141 | 366 | N–H | 101 | 386 |
| H–I | 161 | 299 | O–H | 96 | 459 |

All individual H atoms contain single,
unpaired e⁻ in 1s orbital

Sharing allows electrons to experience
effect of stable electron configuration of
helium, 1s²

FIGURE 6-8 By sharing electrons in overlapping orbitals, each hydrogen atom in a hydrogen molecule experiences the effect of a stable 1s² configuration.

Bonding electron pair in overlapping orbitals



The Octet Rule

Noble-gas atoms have minimum energy existing on their own b/c of electron configurations

Outer orbitals completely full

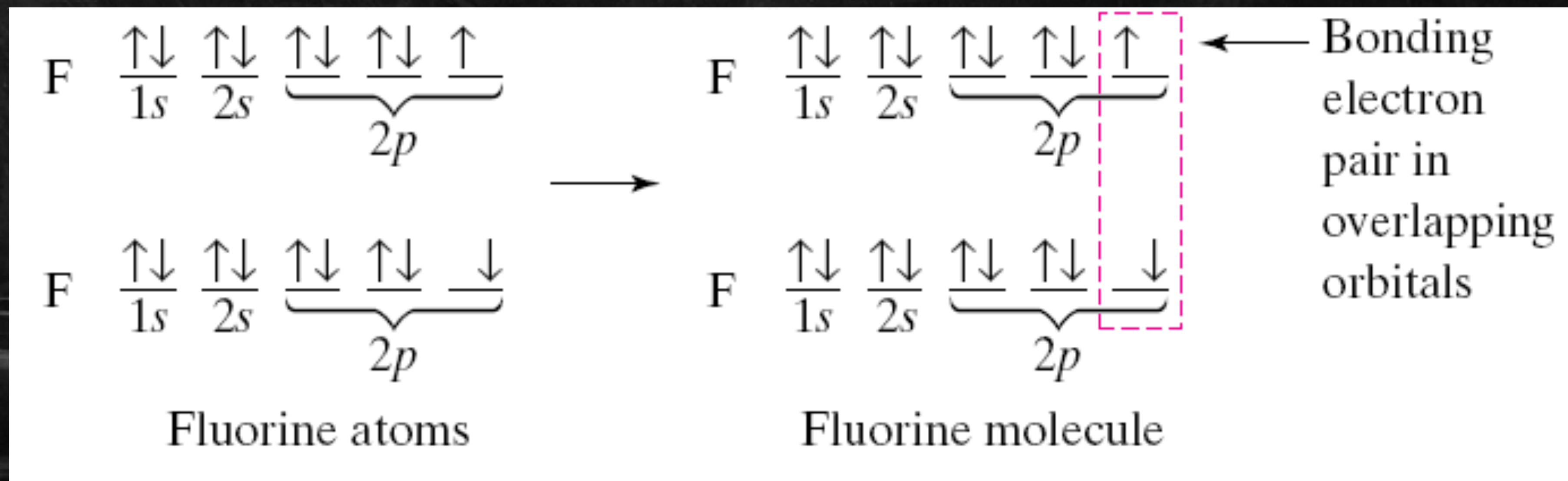
Other atoms fill orbitals by sharing electrons

Bond formation follows **octet rule** → *chemical compounds tend to form so that each atom, by gaining, losing, or sharing electrons, has an octet of electrons in its highest occupied energy level*

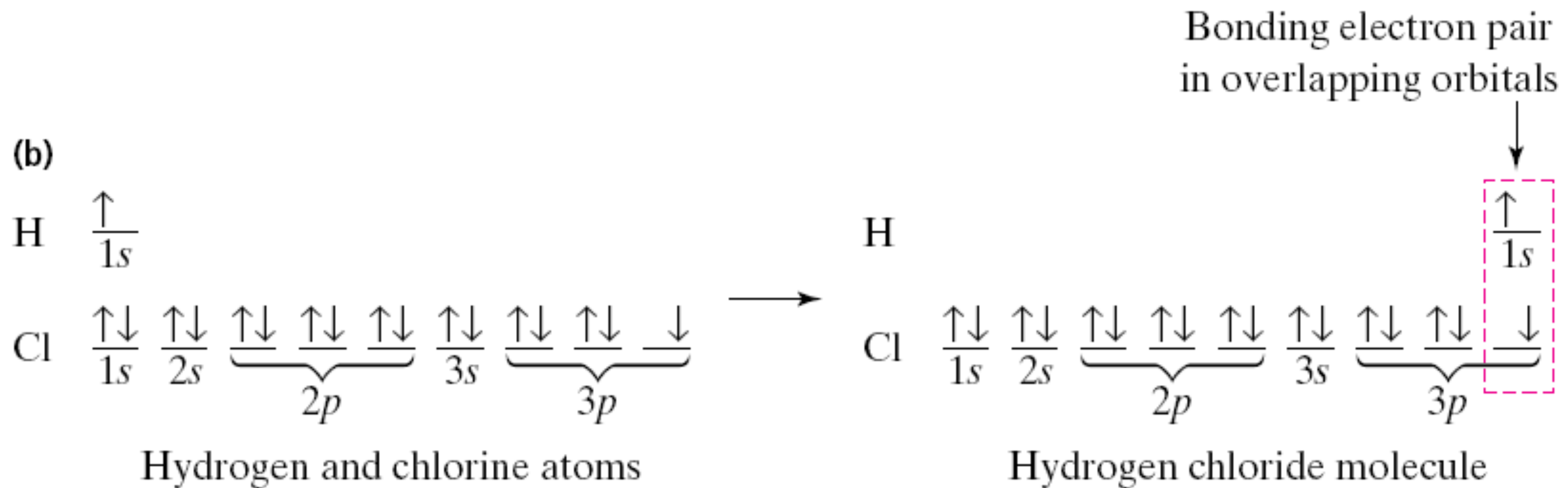
Example: Bonding of Fluorine

2 F atoms bond to form F_2

7 e^- in highest energy level



Example: HCl



Exceptions to Octet Rule

Most main-group elements form covalent bonds according to octet rule

Ex. H-H only 2 electrons

Boron, B, has 3 valence electrons ($[\text{He}]2s^22p^1$)

Boron tends to form bonds where it is surrounded by 6 e⁻ (e⁻ pairs)

Others can be surrounded by *more* than 8 when bonding to highly electronegative elements

Electron Dot Notation

To keep track of valence electrons, it is helpful to use **electron dot notation** → *electron-configuration notation in which only the valence electrons of an atom of a particular element are shown, indicated by dots placed around the element's symbol*

Inner-shell electrons NOT shown



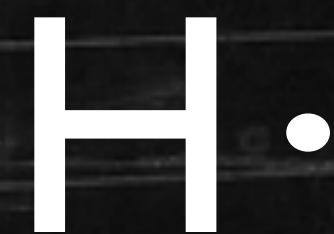
| Number of valence electrons | Electron-dot notation | Example |
|-----------------------------|-----------------------|------------|
| 1 | X· | Na· |
| 2 | ·X· | ·Mg· |
| 3 | ·Ẋ· | ·Ḃ· |
| 4 | ·Ẋ̇· | ·Ċ̇· |
| 5 | ·Ẋ̇̇: | ·Ṅ̇̇: |
| 6 | :Ẋ̇̇̇: | :Ȯ̇̇̇: |
| 7 | :Ẋ̇̇̇̇: | :Ḟ̇̇̇̇: |
| 8 | :Ẋ̇̇̇̇̇: | :Nė̇̇̇̇̇: |

FIGURE 6-10 To write an element's electron-dot notation, determine the element's number of valence electrons. Then place a corresponding number of dots around the element's symbol, as shown.

Sample Problem 1

Write the electron-dot notation for hydrogen.

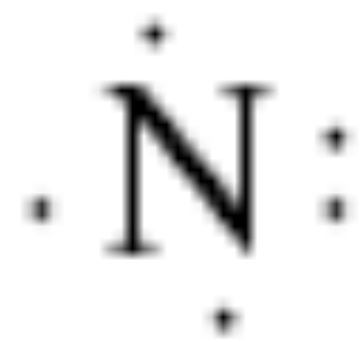
A hydrogen atom has only one occupied energy level, the $n=1$ level, which contains a single electron. So, e-dot notation is written as



Sample Problem 2

Write the e-dot notation for nitrogen.

Group notation for nitrogen's family is ns^2np^3 which means nitrogen has 5 valence electrons. E-dot notation is written as



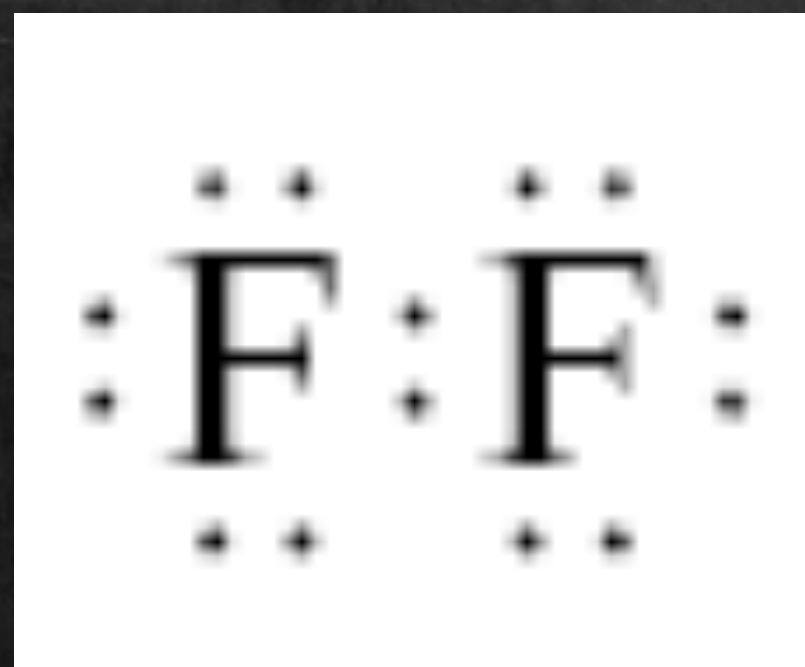
Lewis Structures

E-dot notation can also be used to represent molecules

Ex. H_2 represented by combining notations of 2 individual H atoms



Pair of dots represents e^- being shared

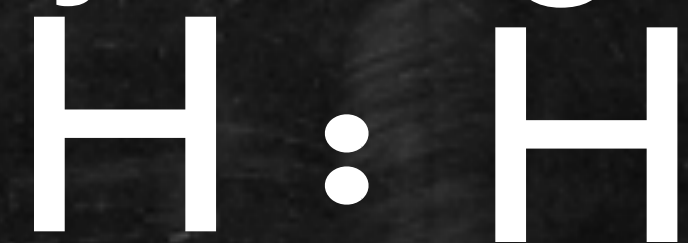
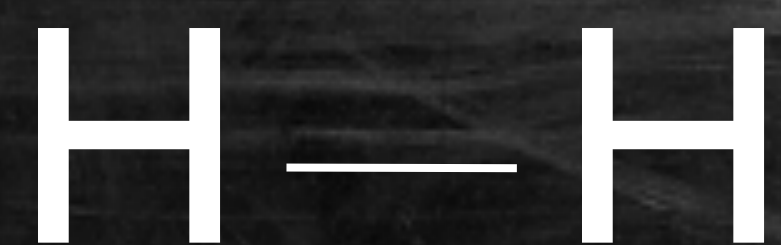


Each F atom surrounded by 3 pairs e- that are not shared in bonds

Unshared (lone) pair → *pair of e- that is not involved in bonding and that belongs completely to one atom*

Lewis Structures

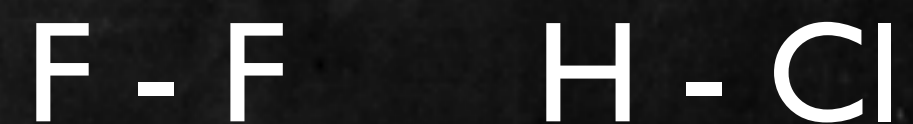
Pair of dots representing shared pair in covalent bond often replaced by long dash



Lewis structures \rightarrow *formulas in which atomic symbols represent nuclei and inner-shell electrons, dot-pairs or dashes between two atomic symbols represent electron pairs in covalent bonds, and dots next to only one atomic symbol represent unshared electrons*

Common to write Lewis structures that show only shared e⁻ using dashes

Structural formula → *indicates the kind, number, arrangement, and bonds but not the unshared pairs of ato in a molecule*



Lewis structures and structural formulas for many molecules can be drawn if you know the composition of the molecule and which atoms are bonded to each other

Single bond \rightarrow *covalent bond made by sharing of one pair of e^- between 2 atoms*

Sample Problem

Draw the Lewis structure of iodomethane,
 CH_3I .

1. Determine type and number of atoms in molecule.

1 C, 1 I, 3 H

2. Determine the total number of valence e⁻ in the atoms to be combined.

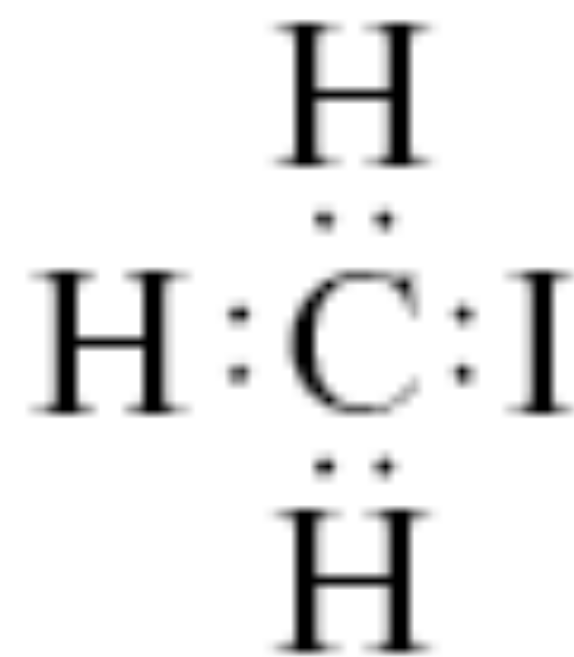


3. Arrange the atoms to form a skeleton structure for the molecule

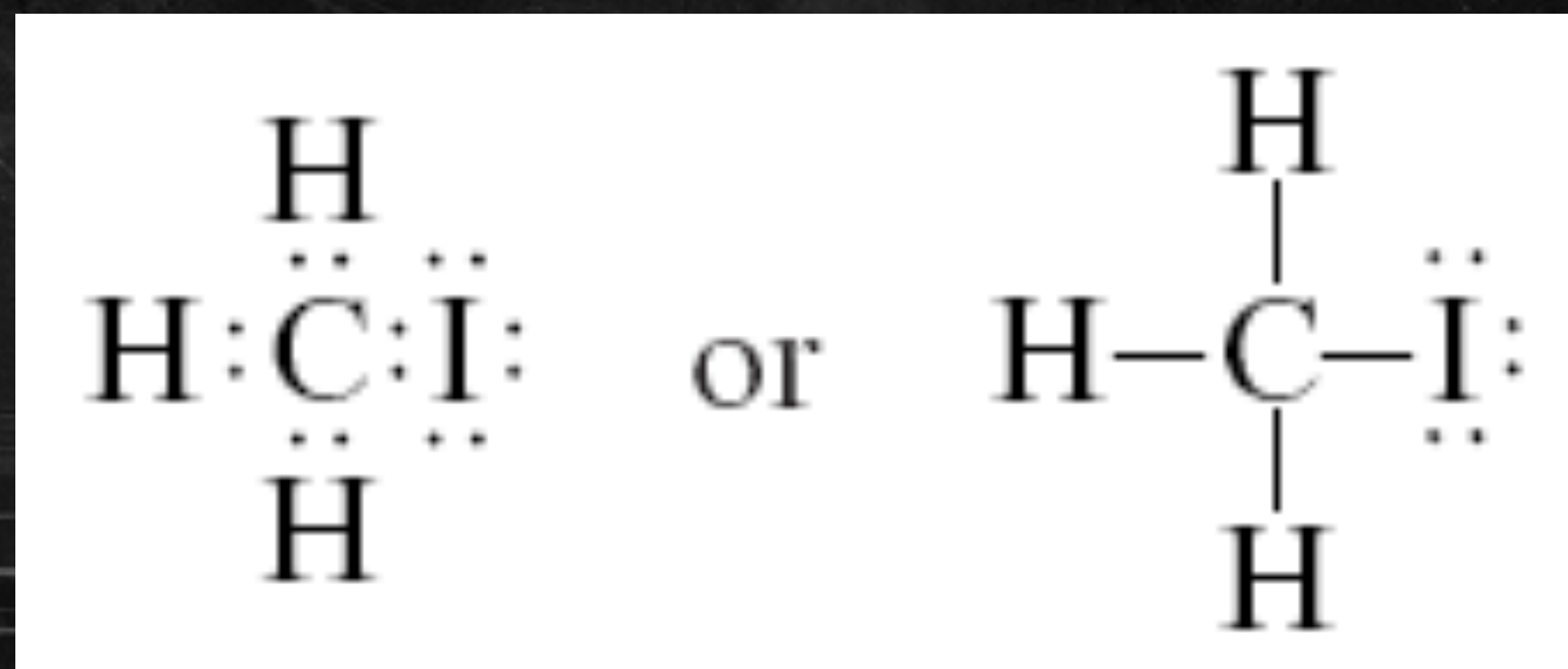
If carbon is present, it is the central atom

Otherwise, the least-electronegative atom is central (except for hydrogen which is NEVER central)

Then connect the atoms by electron-pair bonds.



4. Add unshared pairs of electrons so that each hydrogen atom shares a pair of electrons and each other nonmetal is surrounded by 8 electrons.



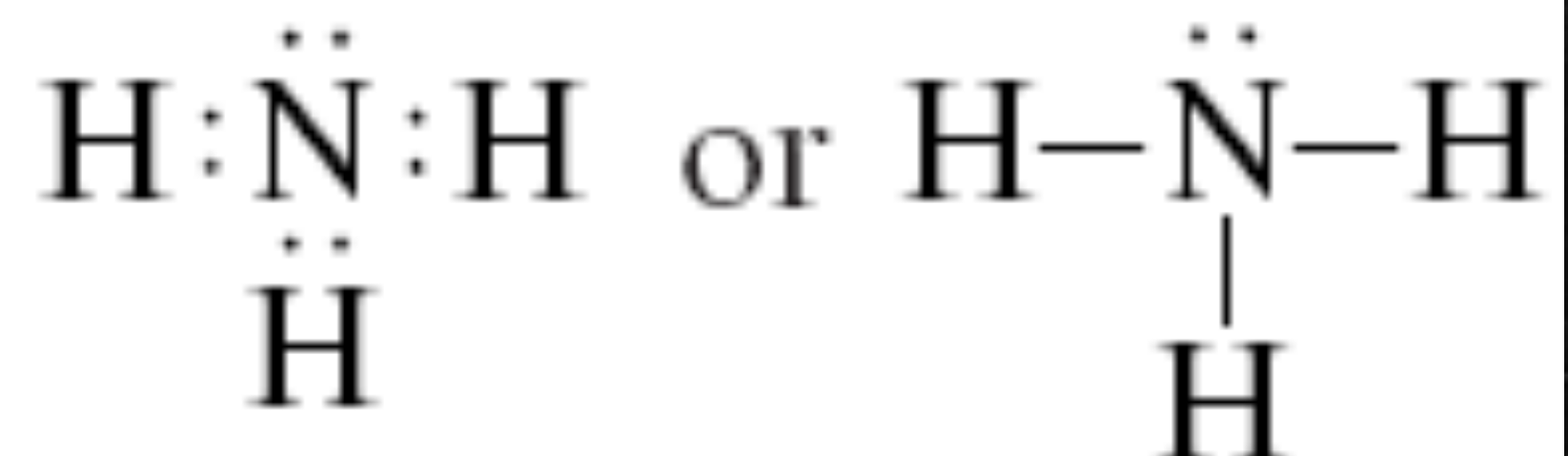
5. Count the electrons in the structure to be sure that the number of valence e- used equals the number available. Be sure the central atom and other atoms besides H have an octet.

There are eight e- in the four covalent bonds and six e- in the three unshared pairs, giving the correct total of 14 valence electrons

Practice Problem

Draw the Lewis structure of ammonia,
 NH_3 .

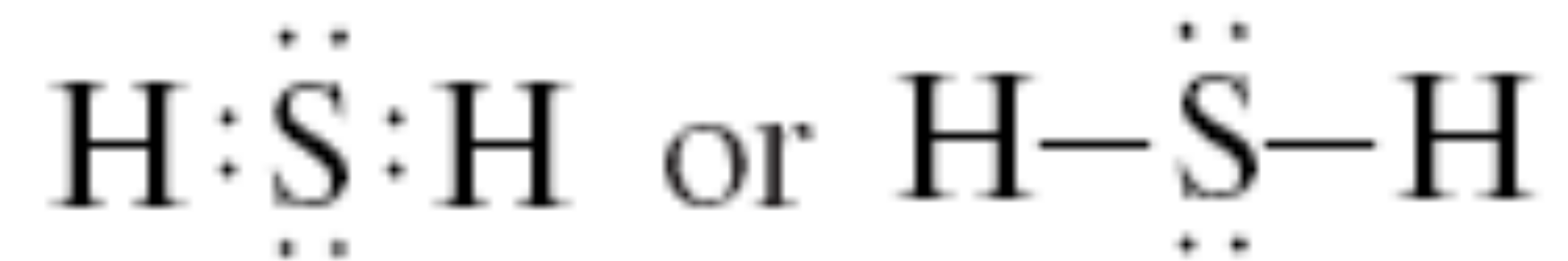
Answer



Practice Problem

Draw the Lewis structure for hydrogen sulfide, H₂S.

Answer



Multiple bonds → *double and triple bonds*

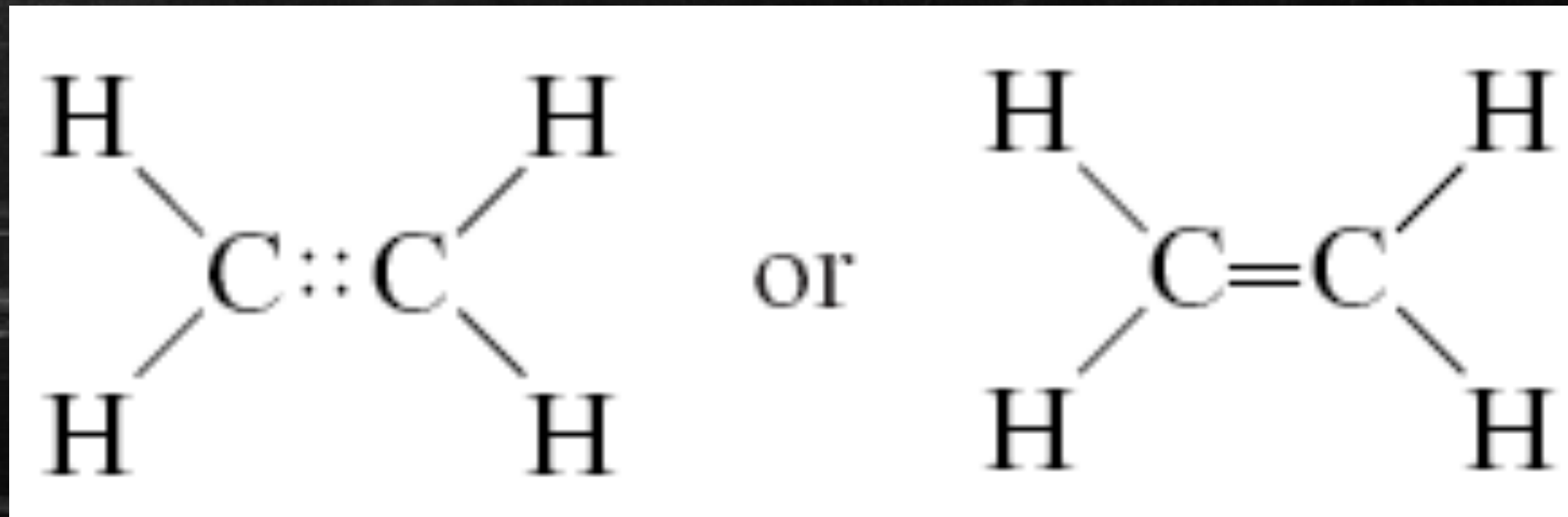
Double bonds have higher bond energies and are shorter than single bonds

Triple bonds have higher bond energies and are shorter than double bonds

Multiple Covalent Bonds

Atoms of same elements (especially C, N and O) can share more than one e- pair

Double bond → *covalent bond made by the sharing of two pairs of e- between two atoms*



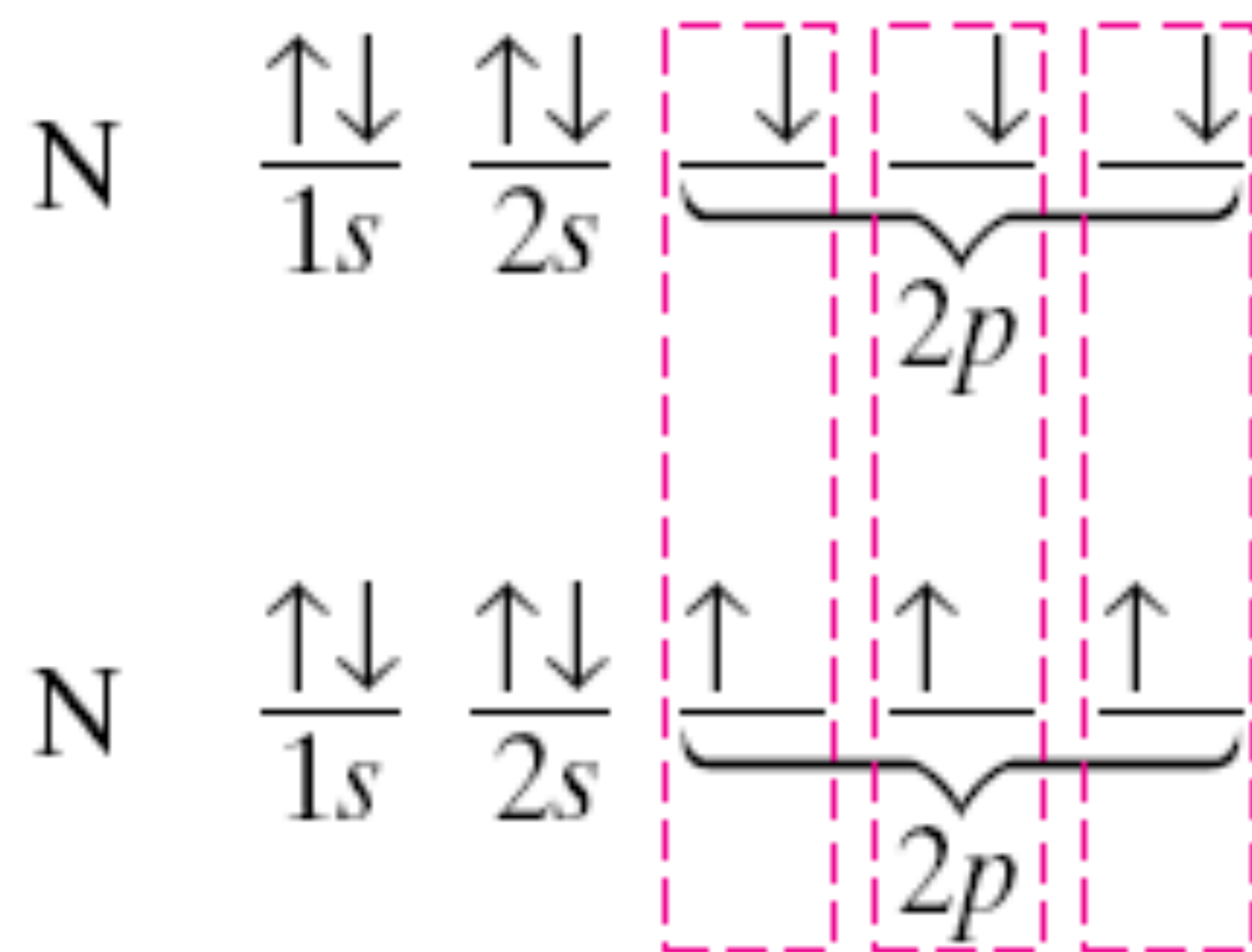
Triple bond → *covalent bond made by sharing of 3 pairs of e- between 2 atoms*

Ex. N₂

Each N has 5 valence

Each N shares 3 e- with other





Nitrogen molecule

FIGURE 6-11 In a molecule of nitrogen, N_2 , each nitrogen atom is surrounded by six shared electrons plus one unshared pair of electrons. Thus, each nitrogen atom follows the octet rule in forming a triple covalent bond.

Practice Problem

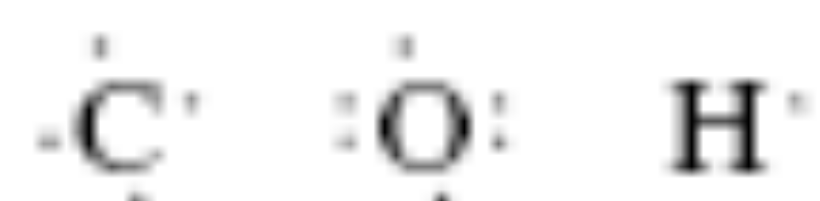
Draw the Lewis structure for methanal, CH_2O , which is also known as formaldehyde.

1. *Determine the number of atoms of each element present in the molecule.*

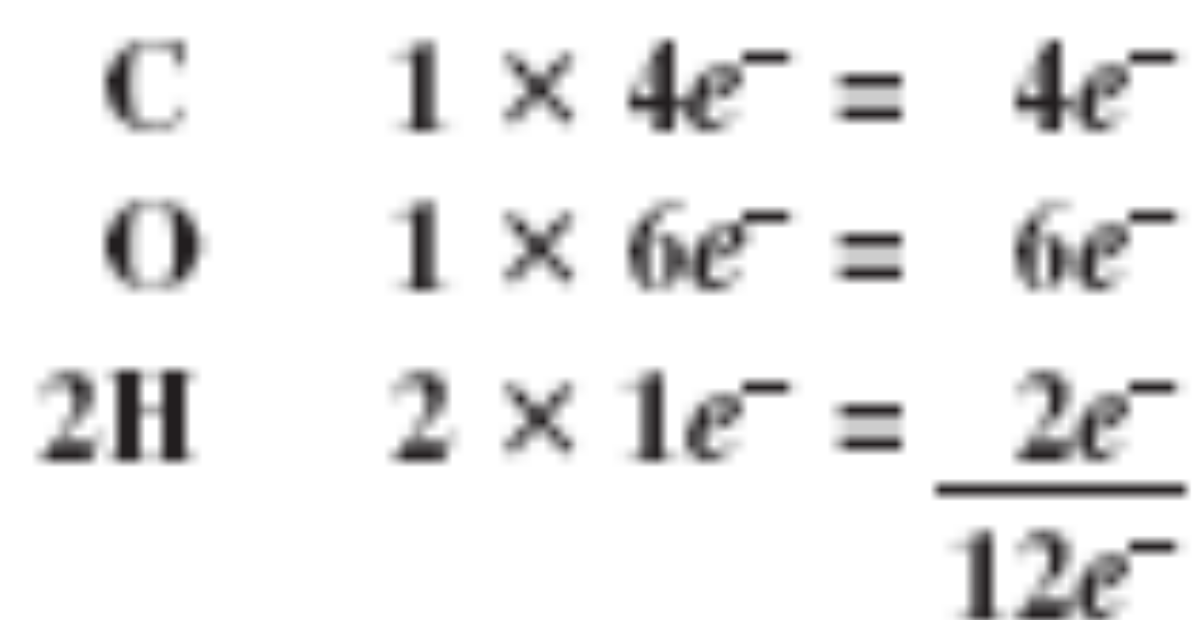
The formula shows one carbon atom, two hydrogen atoms, and one oxygen atom.

2. *Write the electron-dot notation for each type of atom.*

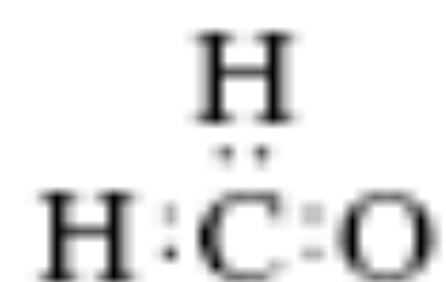
Carbon from Group 14 has four valence electrons. Oxygen, which is in Group 16, has six valence electrons. Hydrogen has only one electron.



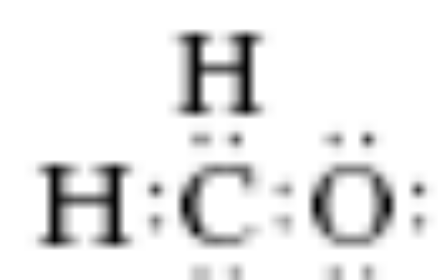
3. *Determine the total number of valence electrons in the atoms to be combined.*



4. *Arrange the atoms to form a skeleton structure for the molecule, and connect the atoms by electron-pair bonds.*



5. Add unshared pairs of electrons so that each hydrogen atom shares a pair of electrons and each other nonmetal is surrounded by eight electrons.

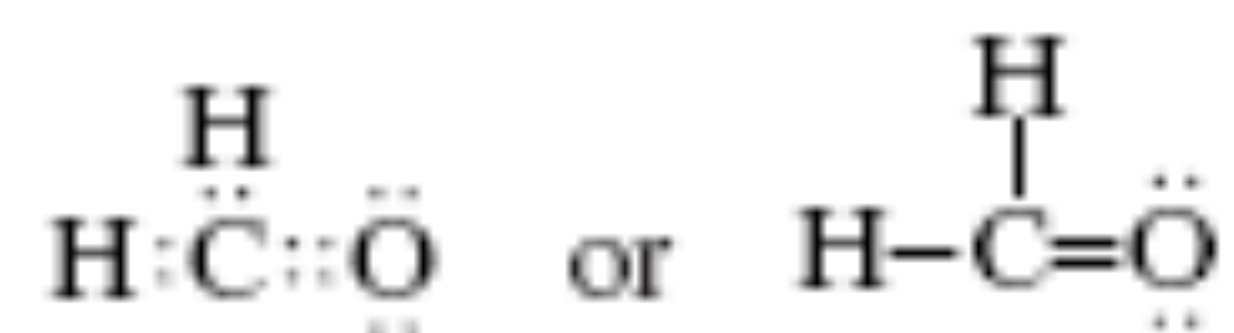


- 6a. Count the electrons in the Lewis structure to be sure that the number of valence electrons used equals the number available.

The structure above has six electrons in covalent bonds and eight electrons in four lone pairs, for a total of 14 electrons. The structure has two valence electrons too many.

- 6b. If too many electrons have been used, subtract one or more lone pairs until the total number of valence electrons is correct. Then move one or more lone electron pairs to existing bonds between non-hydrogen atoms until the outer shells of all atoms are completely filled.

Subtract the lone pair of electrons from the carbon atom. Then move one lone pair of electrons from the oxygen to the bond between carbon and oxygen to form a double bond.

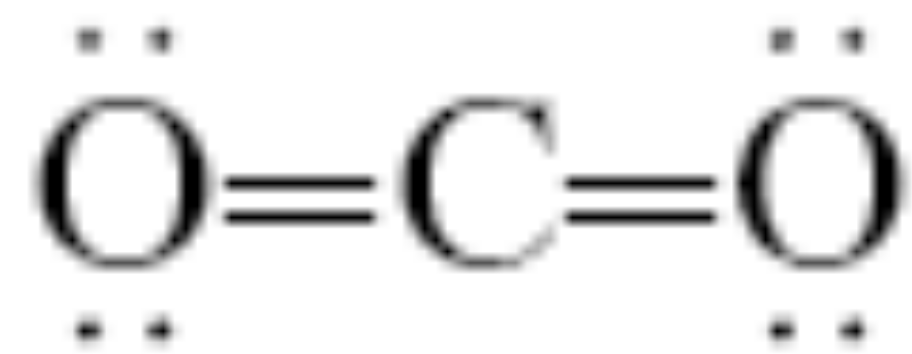


There are eight electrons in covalent bonds and four electrons in lone pairs, for a total of 12 valence electrons.

Practice Problem

Draw the Lewis structure for carbon dioxide.

Answer



Practice Problem

Draw the Lewis structure for hydrogen cyanide, which contains one hydrogen atom, one carbon atom, and one nitrogen atom.

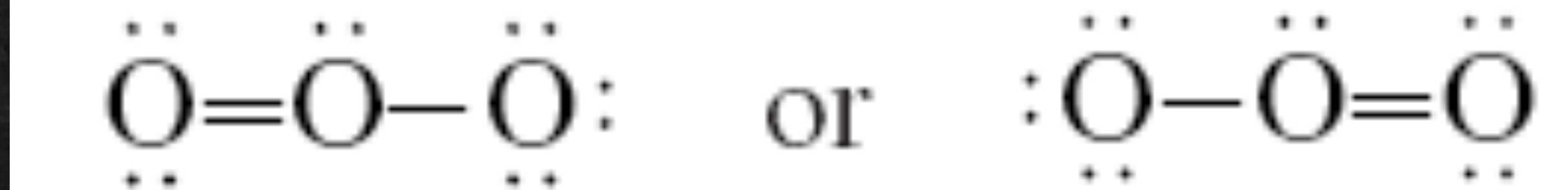
Answer



Resonance Structures

Some molecules/ions cannot be represented correctly by single Lewis structure

Ex. Ozone (O_3)



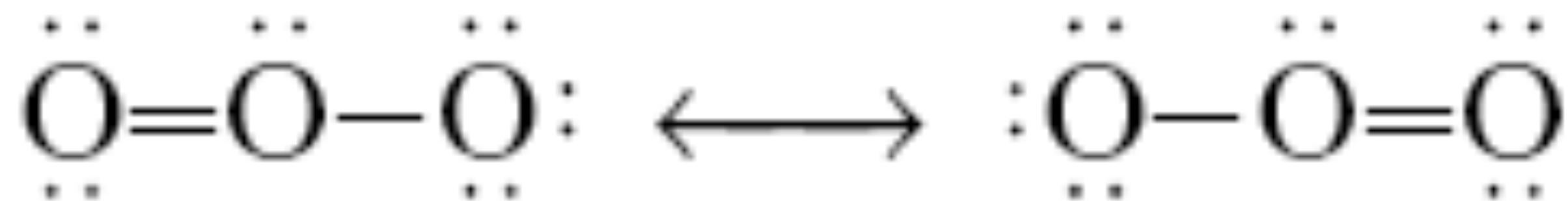
Each structure has one single and one double bond

Chemists used to think ozone spends time alternating or “resonating” between two structures

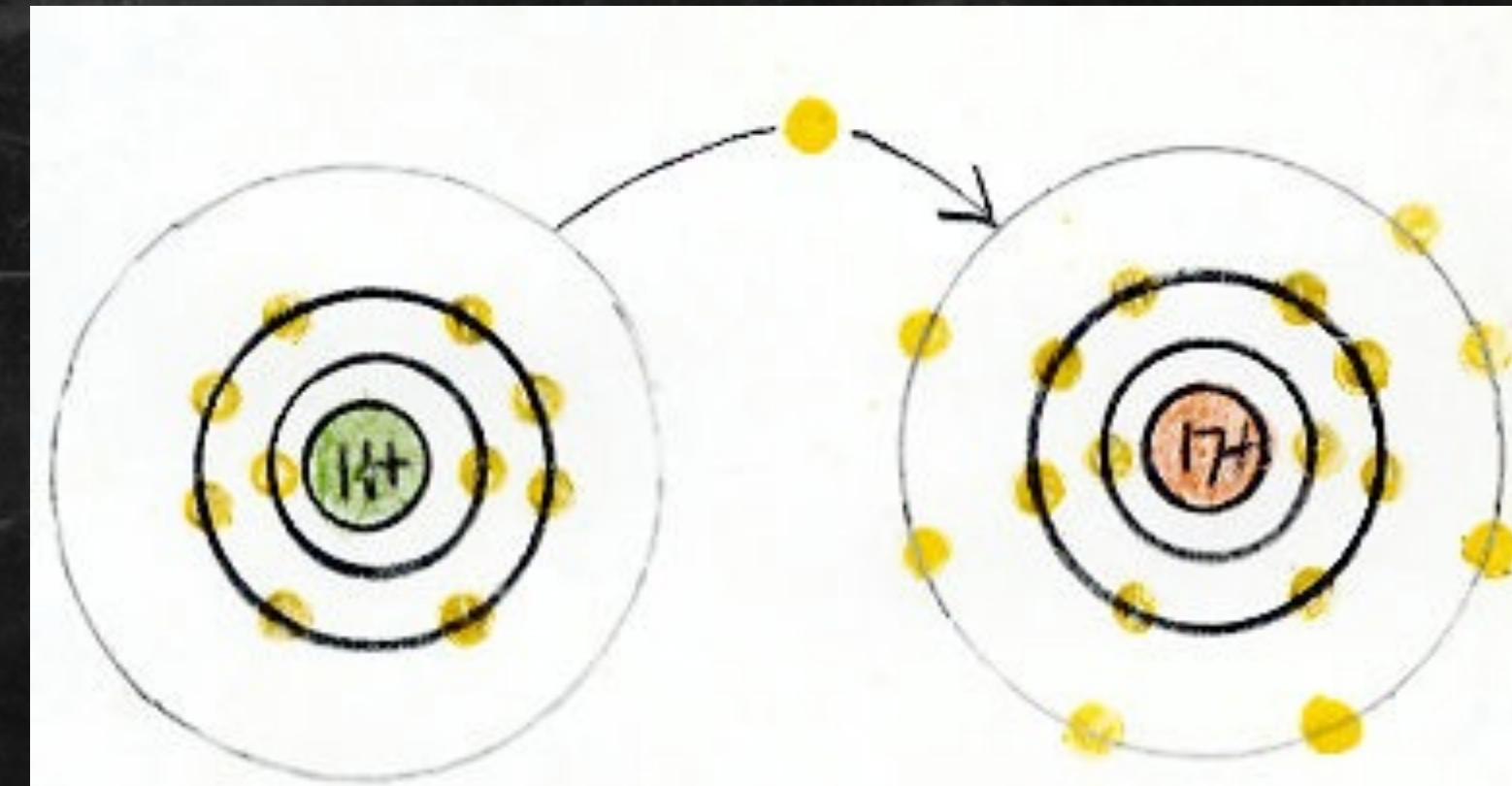
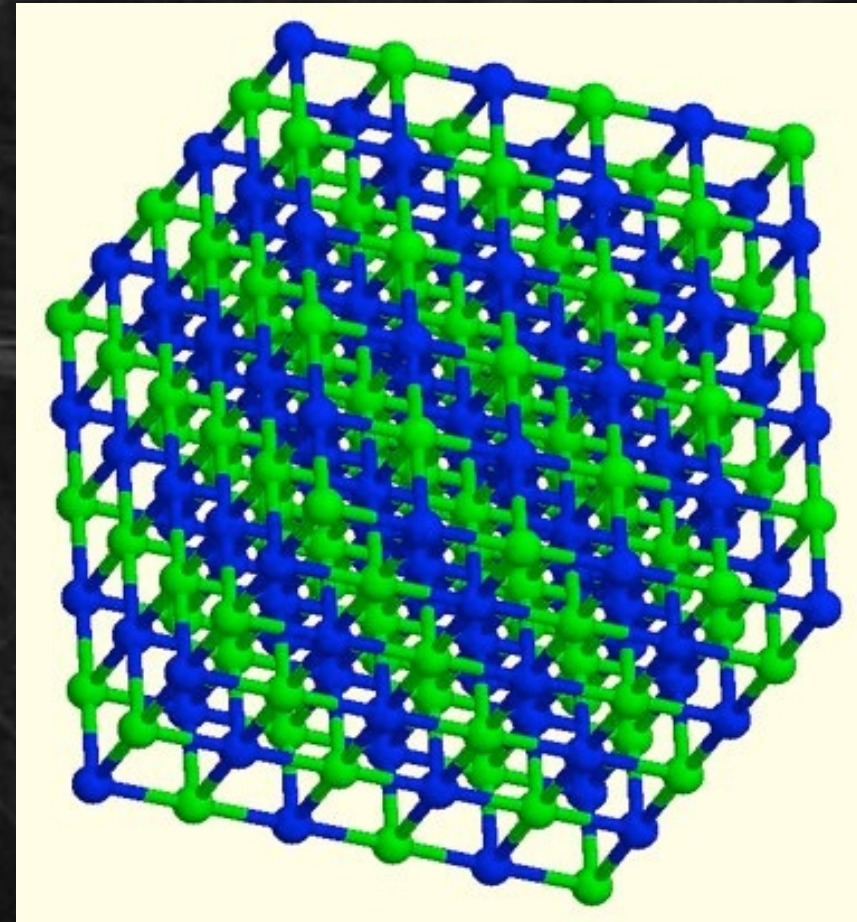
Now know that actual structure is something like an average between the two

Resonance → *bonding in molecules or ions that cannot be correctly represented by a single Lewis structure*

To indicate resonance, double-headed arrow placed between resonance structures

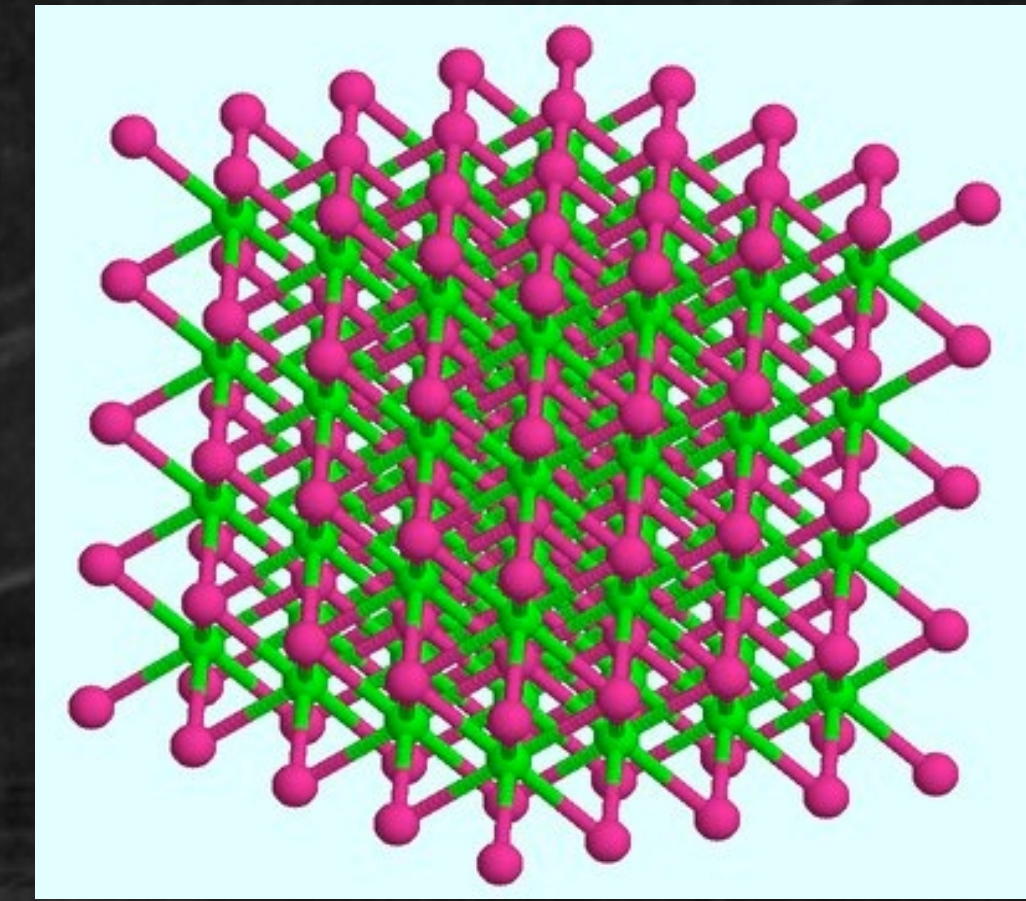


Section 3



Ionic Bonding and Ionic Compounds

Ionic Bonding



Ionic compound → *composed of positive and negative ions that are combined so that the numbers of positive and negative charges are equal*

Most exist as crystalline solids, a 3-D network of (+) and (-) ions mutually attracted to one another

Different from molecular compound b/c ionic compound not made of independent, neutral units

Chemical formula represents simplest ratio of compound's combined ions that give electrical neutrality

Chemical formula of ionic compound shows ratio of ions present in ANY sample of ANY size

Formula unit → *simplest collection of atoms from which an ionic compound's formula can be recognized*

Ex. NaCl is formula unit for sodium chloride
One sodium cation and one chlorine anion

Ratio of ions in formula depends on charges of ions combined

Ex. Calcium and fluorine

Ca^{2+} F^{1-} = total +1

So need 2 F^{1-} to equal $+2+(-2) = 0$

Formula unit is CaF_2

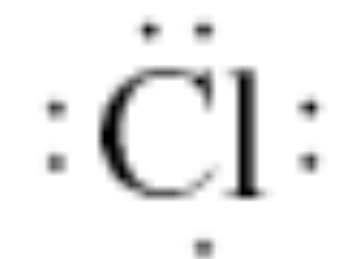
Formation of Ionic Compounds

E-dot notation can be used to demonstrate changes that take place in ionic bonding

Do not usually form by combination of isolated ions

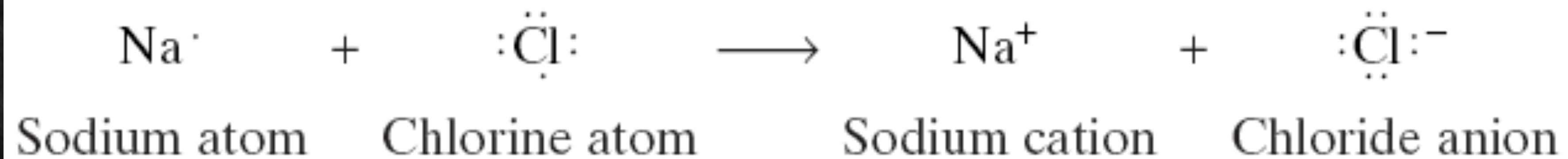


Sodium atom



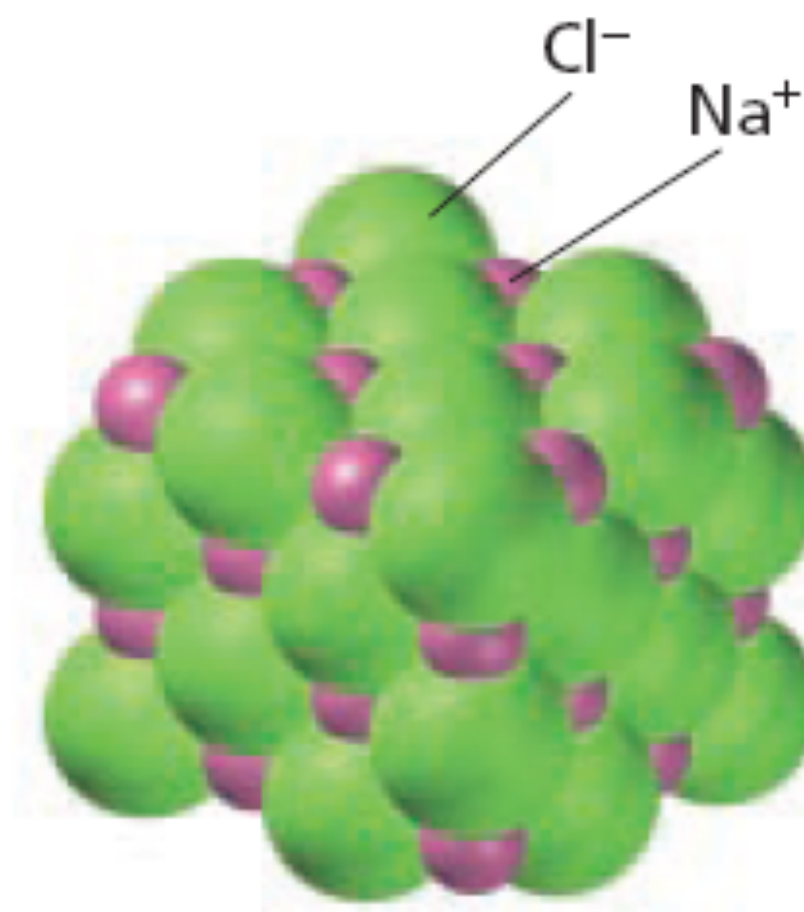
Chlorine atom

Sodium readily gives up 1 e-
Chlorine readily accepts 1 e-

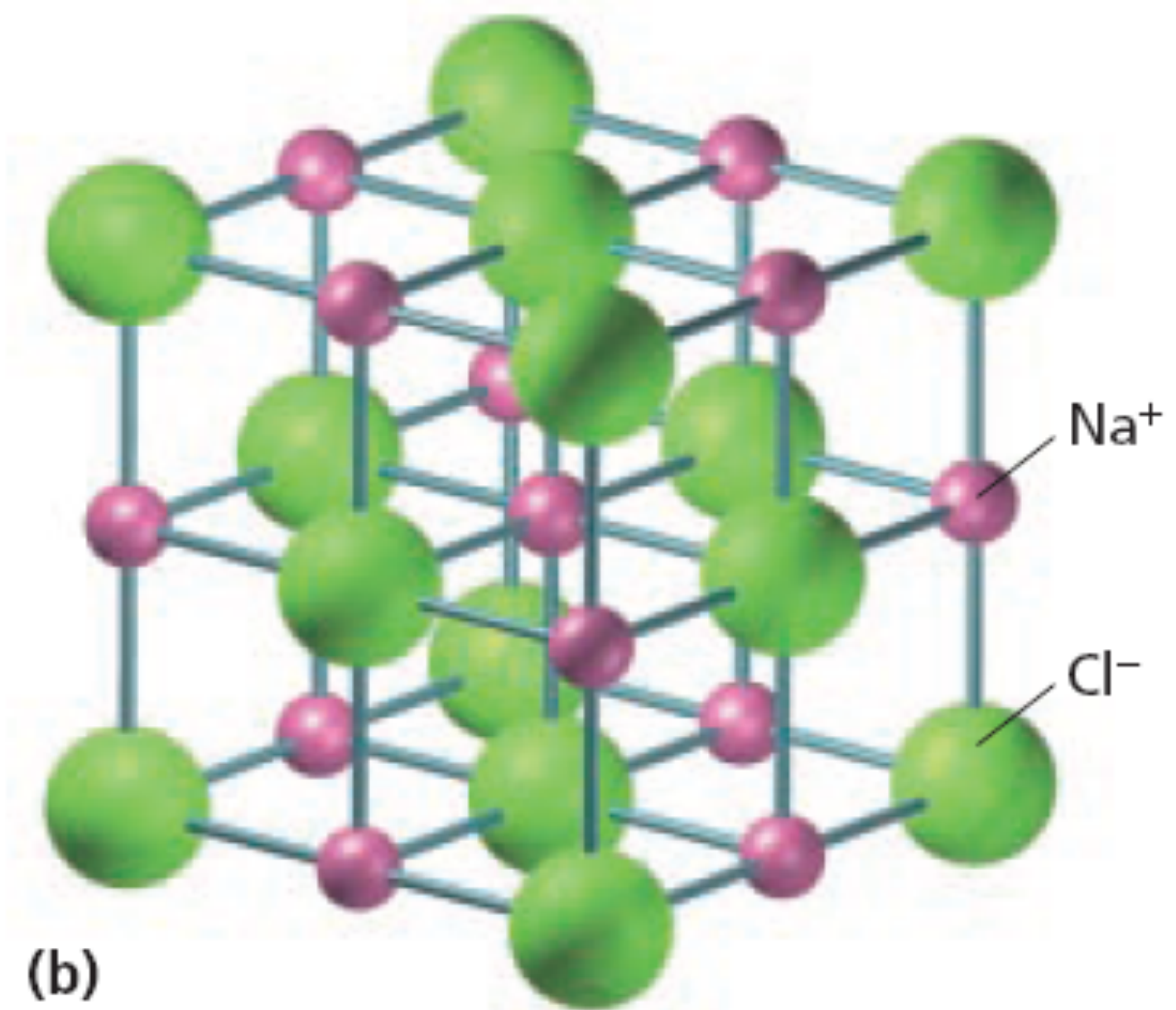


Characteristics of Ionic

In ionic crystals, ions minimize potential energy by combining in *orderly* arrangement called a *crystal lattice*



(a)



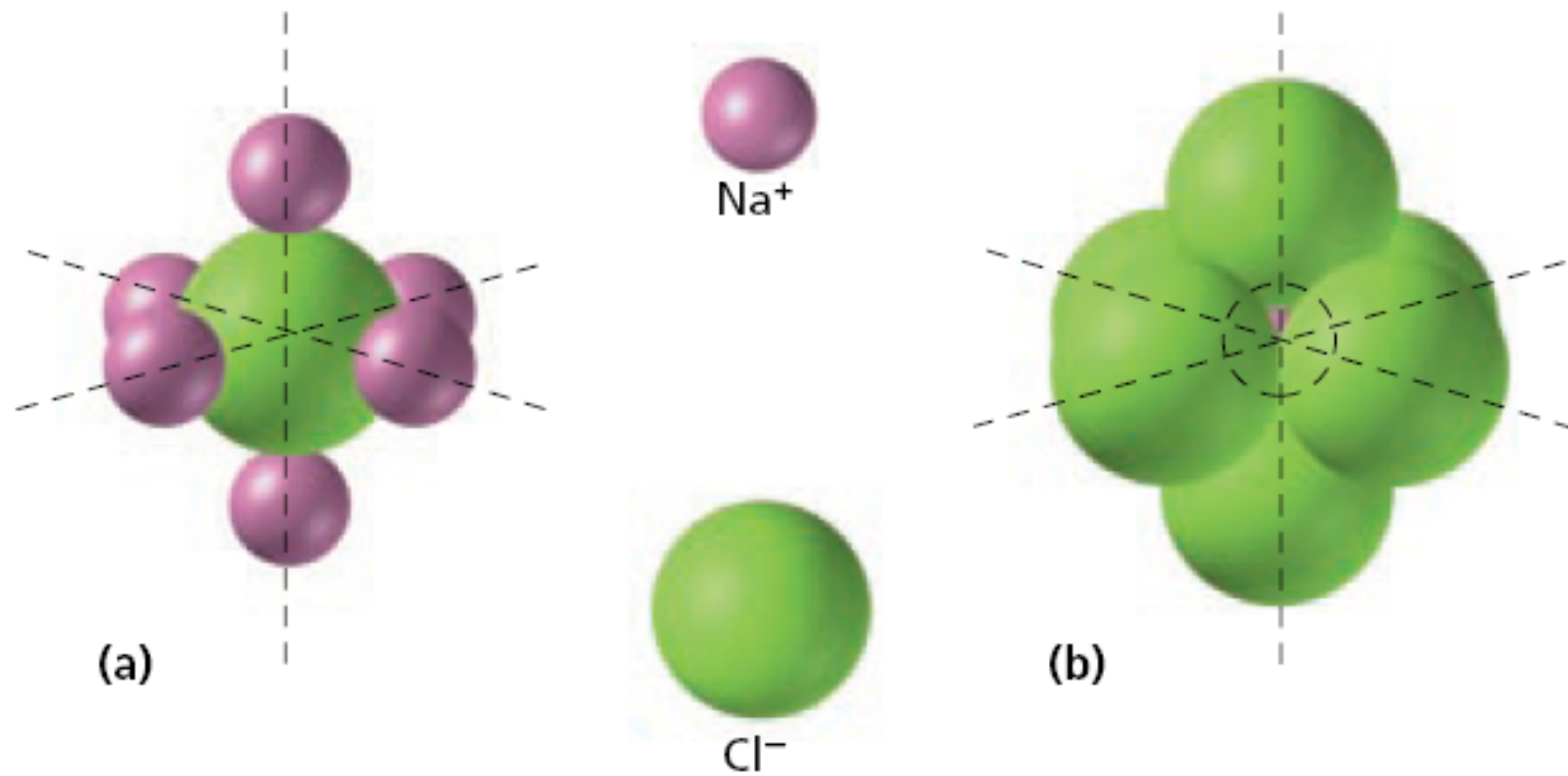
(b)

Attractive forces: between oppositely charged ions (cations and anions) and between nuclei and electrons

Repulsive forces: between like-charged ions and between electrons

Crystal lattice structure represents balance between these two forces

FIGURE 6-15 The figure shows the ions that most closely surround a chloride anion and a sodium cation within the crystal structure of NaCl. The structure is composed such that (a) six Na^+ ions surround each Cl^- ion. At the same time, (b) six Cl^- ions surround each Na^+ ion (which cannot be seen but whose location is indicated by the dashed outline).



Within arrangement, each Na^+ is surrounded by 6 Cl^-

At the same time, each Cl^- is surrounded by 6 Na^+

3-D arrangements of ions and strengths of attraction are different with sizes and charges of ions and number of ions of different charges

Ex. CaF_2 , there are 2 anions for each cation

Each Ca^{2+} is surrounded by 8 F^-

Each F^- is surrounded by 4 Ca^{2+}

Lattice Energy

To compare bond strengths in ionic compounds, chemists compare amounts of energy released when separated ions in gas form crystalline solid

Lattice energy → *energy released when one mole of an ionic compound is formed from gaseous ions*

Comparison of Ionic and Molecular Compounds

Force that holds ions together in ionic compounds is very strong overall between opposite charges

Molecular compound – bonds making up each molecule also strong, but forces *between* molecules not strong

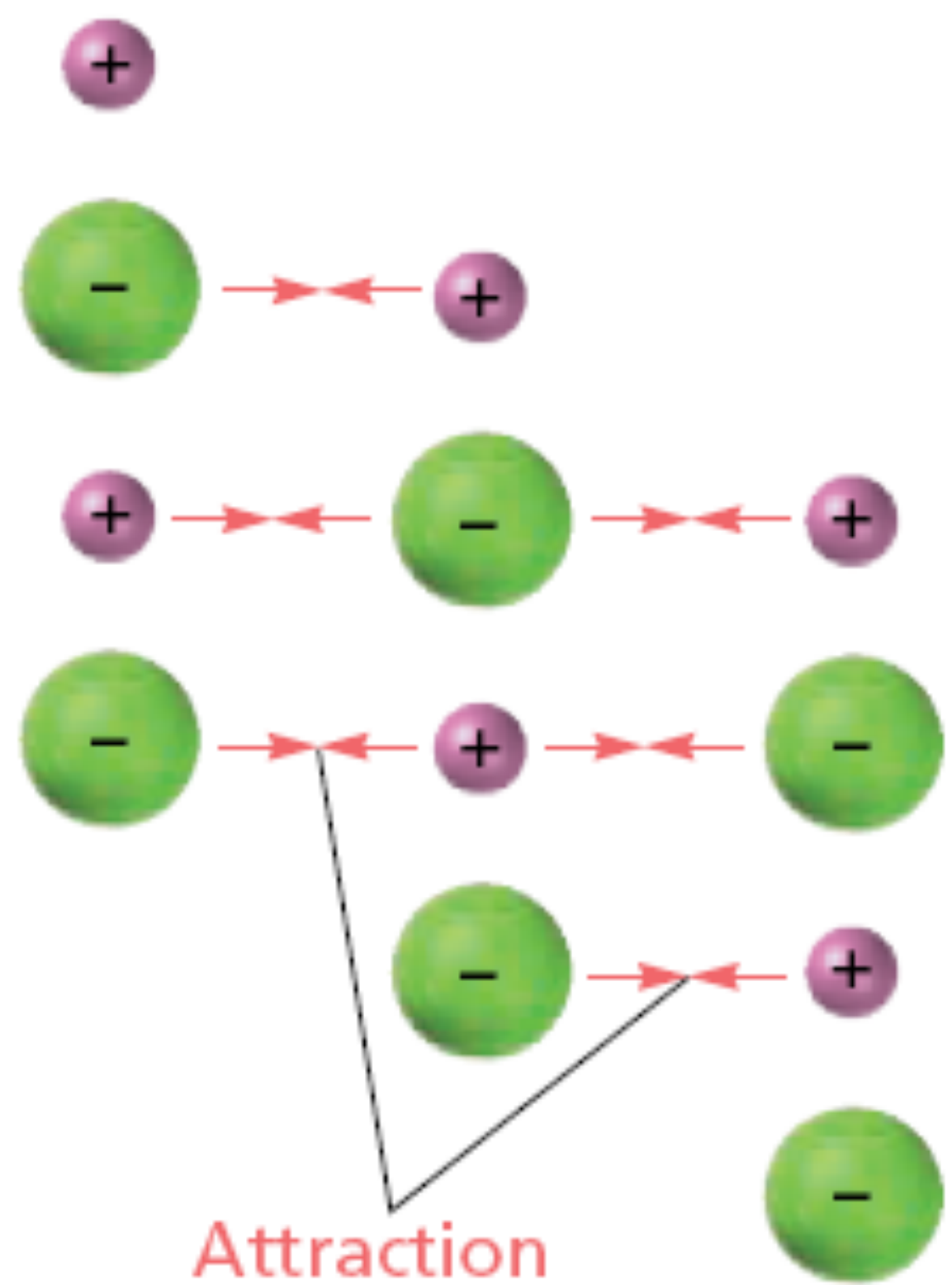
Because of bond strength difference, molecular compounds melt at lower temperatures

Ionic compounds have higher melting and boiling points

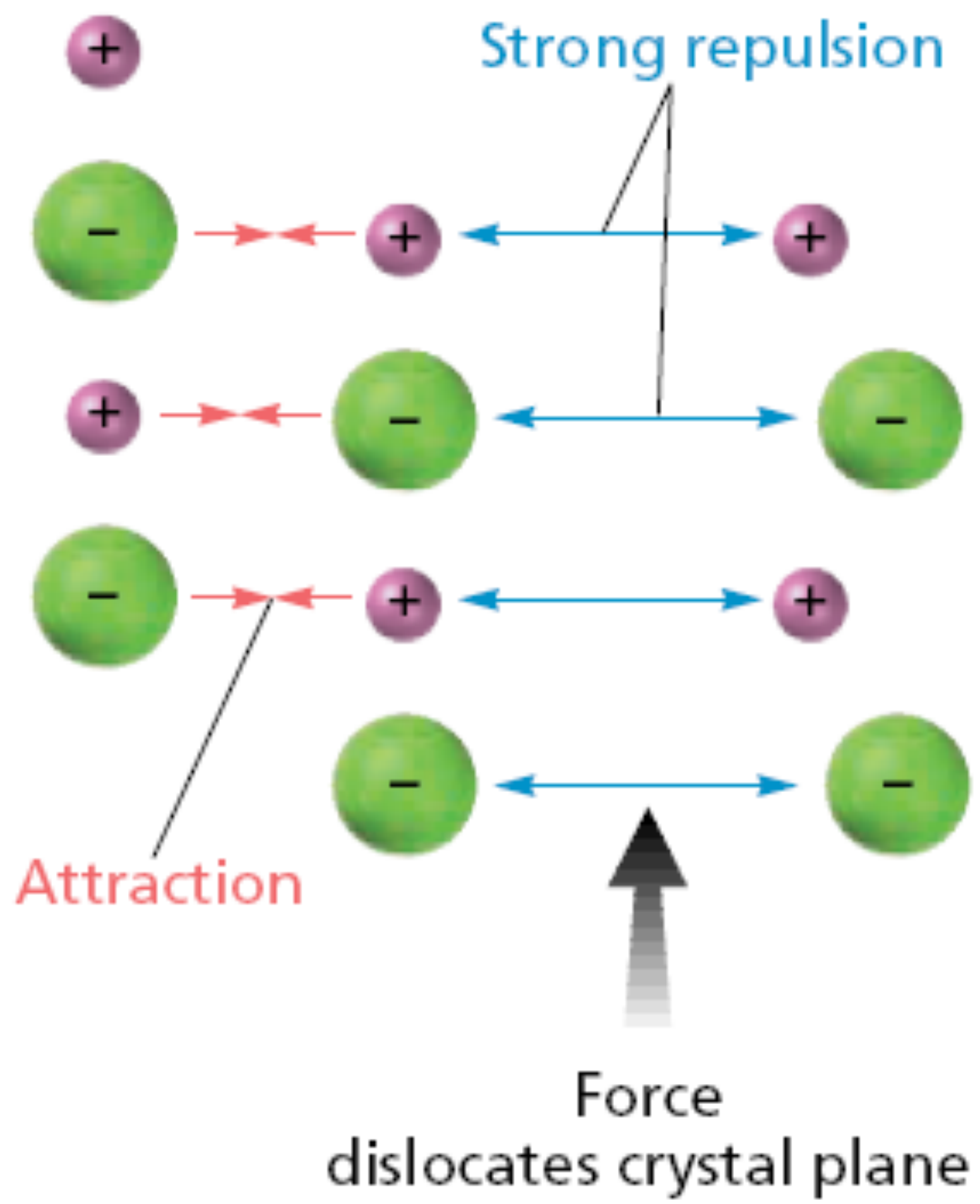
Ionic compounds are hard but brittle

Slight shift of one row of ions causes large buildup of repulsive forces

Repulsive forces make layers split completely



(a)



(b)

FIGURE 6-17 (a) The attraction between positive and negative ions in a crystalline ionic compound causes layers of ions to resist motion. (b) When struck with sufficient force, the layers shift so that ions of the same charge approach each other, causing repulsion. As a result, the crystal shatters along the planes.

In solid state ions cannot move – compounds are not electrical conductors

Molten state – ions can move freely and can carry electric current

Many ionic compounds dissolve in water

Attraction to water molecules overcomes attraction to each other

Polyatomic Ions

Certain atoms bond covalently to each other to form group of atoms that has molecular AND ionic characteristics

Polyatomic ion → *a charged group of covalently bonded atoms*

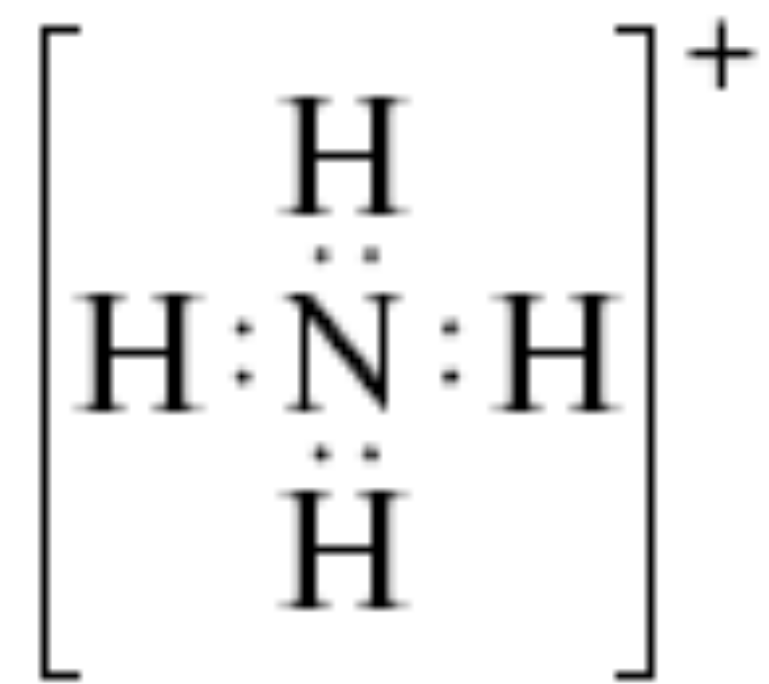
Lewis Structures of Polyatomic Ions

Polyatomic ions combine with ions of opposite charge to form ionic compounds

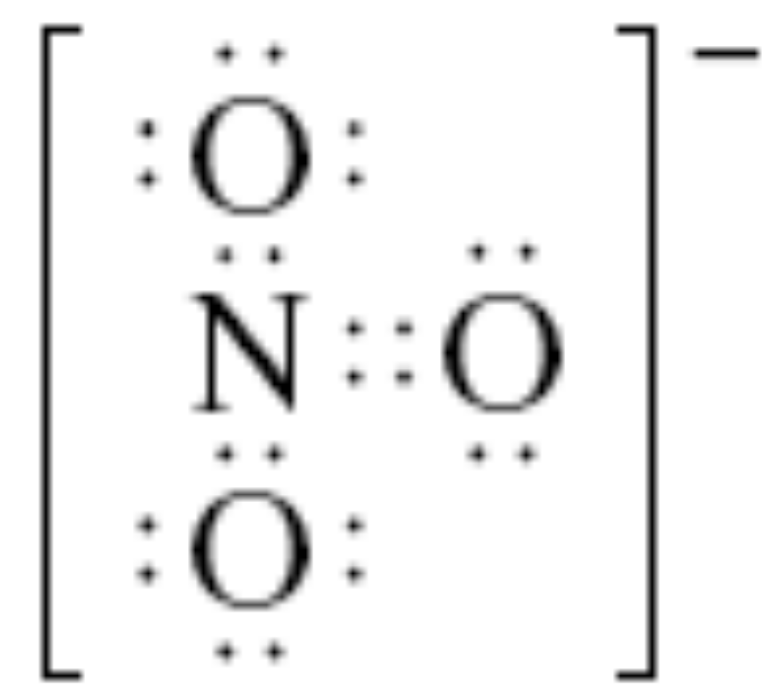
To find Lewis structure, follow previous instructions *except*

If ion is negative, add to the total number of valence electrons a number of e^- same as the ions negative charge

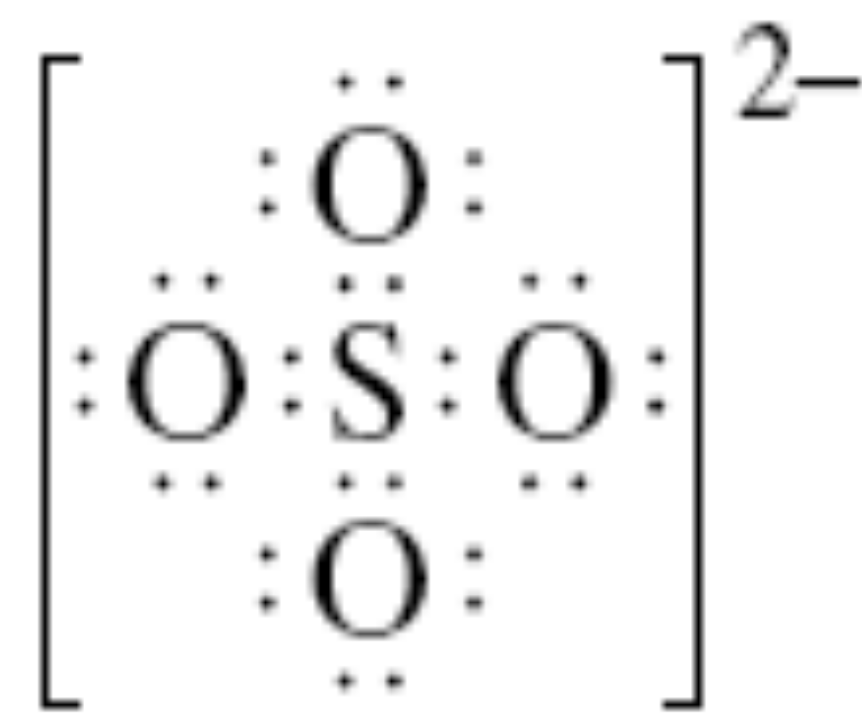
If ion positive, subtract same number of e^- as the positive charge



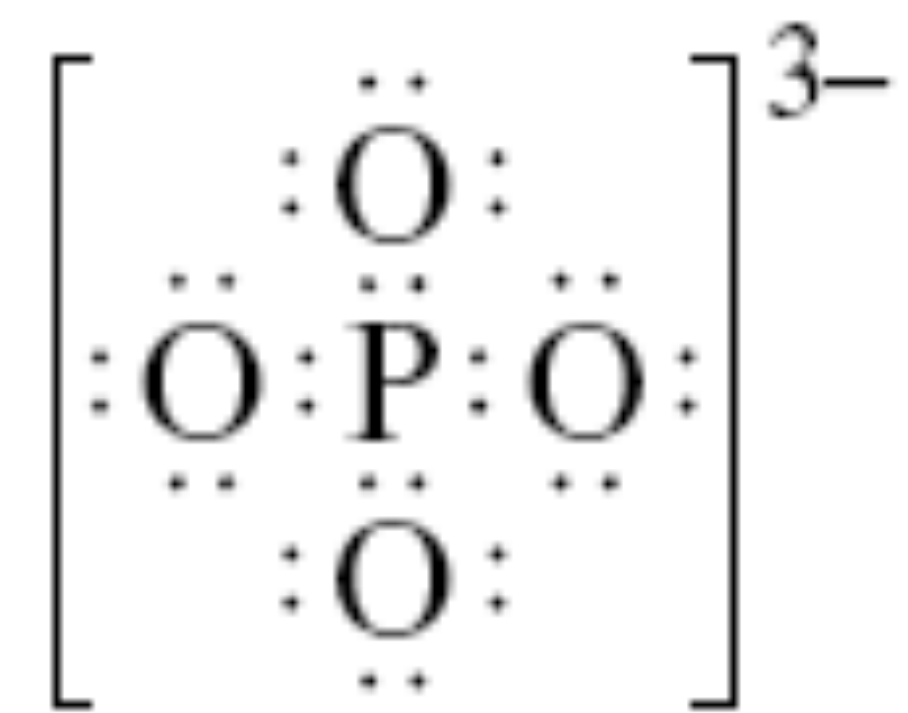
Ammonium ion



Nitrate ion



Sulfate ion



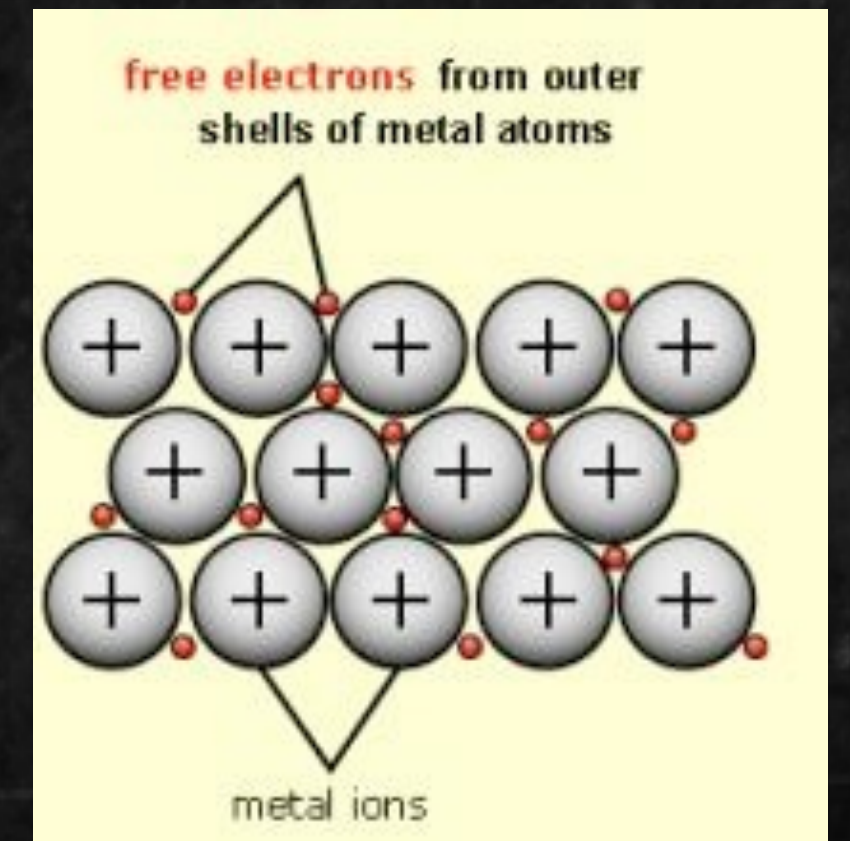
Phosphate ion

Section 4

Metallic Bonding

Metallic Bonding is Different

Metals have unique property of highly movable electrons (why they conduct electricity so well)



In molecular compounds e^- cannot move, held in shared bond

In ionic compounds, e^- cannot move, held to individual ions

Metallic-Bond Model

Highest energy levels of most metal atoms only occupied by few e^-

Ex. s-block metals have one or two valence e^- where all 3 p orbitals are empty

d-block metals have many empty d orbitals just below highest energy level

Overlapping Orbitals

Within metal, empty orbitals in outer energy levels overlap

Allows outer e^- to move freely

e^- are *delocalized* \rightarrow do not belong to any one atom

Metallic bonding \rightarrow *chemical bonding that results from attraction between metal atoms and surrounding sea of electrons*

Metallic Properties

Freedom of e^- to move around causes high electrical and thermal conductivity

b/c many orbitals separated by very small energy differences, metals can absorb wide range of light frequencies

Absorption of light excites e^- to higher energy levels

e^- immediately fall back down to lower levels, giving off light (why metals are shiny)

Malleability → *ability of a substance to be hammered or beaten into thin sheets*

Ductility → *ability of a substance to be pulled into wires*

Both possible because of structure, one line of metal atoms can slide without breaking bonds

Not possible with ionic crystal structures

Metallic Bond Strength

Bond strength varies with nuclear charge of metal atoms and number of e⁻ in metal's e⁻ sea

Both factors reflected as *heat of vaporization*

When metal vaporized, bonded atoms in solid state converted to individual atoms in gas state

Higher heat of vaporization, higher bond strength

Section 5

Molecular Geometry



Molecular Geometry

Properties of molecules depend on bonding of atoms and the 3-Dimensional arrangement of molecule's atoms in space

Polarity of each bond, along with geometry of molecule, determines **molecular polarity**

→ *uneven distribution of molecular charge*

Strongly influences forces that act **BETWEEN** molecules

VSEPR Theory

Diatomic molecules must be linear (only two atoms)

To predict geometries of more complex molecules, consider locations of all e- pairs surrounding bonded atoms

This is basis of VSEPR

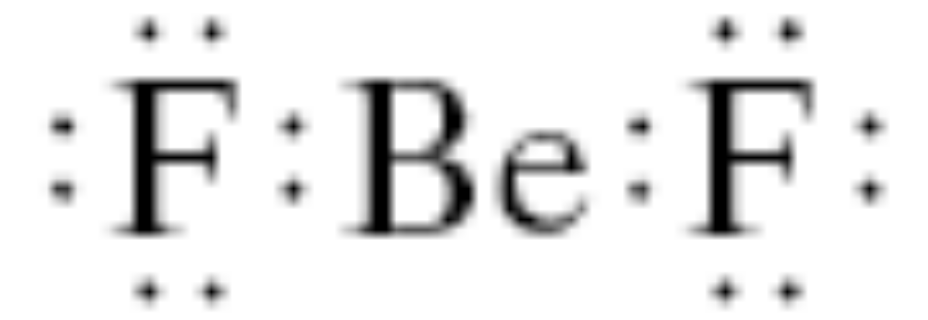
“Valence-shell, electron-pair repulsion”

VSEPR theory → *repulsion between the sets of valence-level e- surrounding an atom causes these set to be oriented as far apart as possible*

How does this account for molecular shape?

Let's consider only molecules with no unshared valence e- on central atom

Ex. BeF_2



Be doesn't follow octet rule

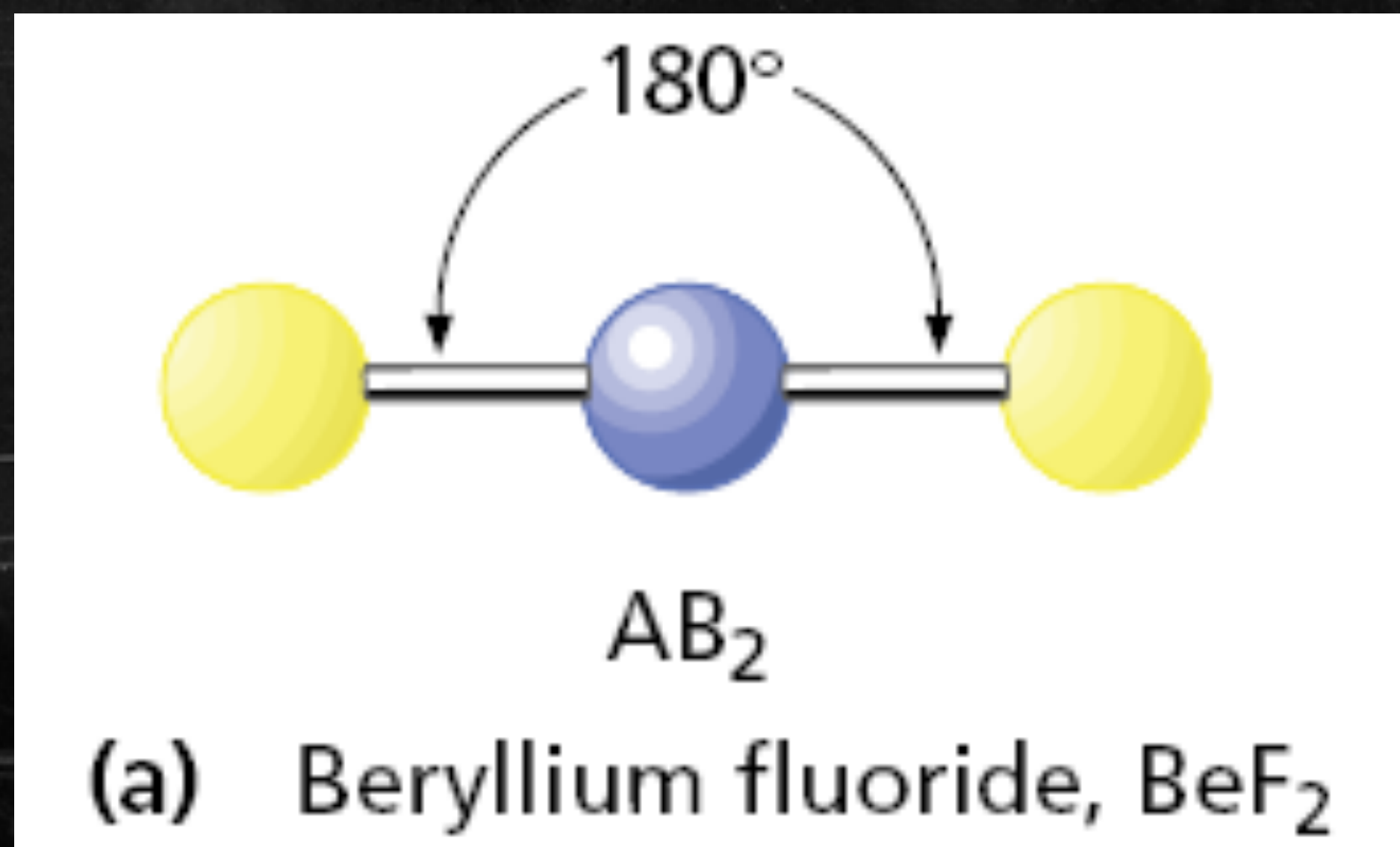
Be forms covalent bond with each F atom

Surrounded by only two electron pairs it shares with F atoms

According to VSEPR, shared pairs oriented as far away from each other as possible

Distance between e- pairs maximized if bonds to F are on opposite sides of Be, 180° apart

So, all 3 atoms lie in straight line – molecule is linear

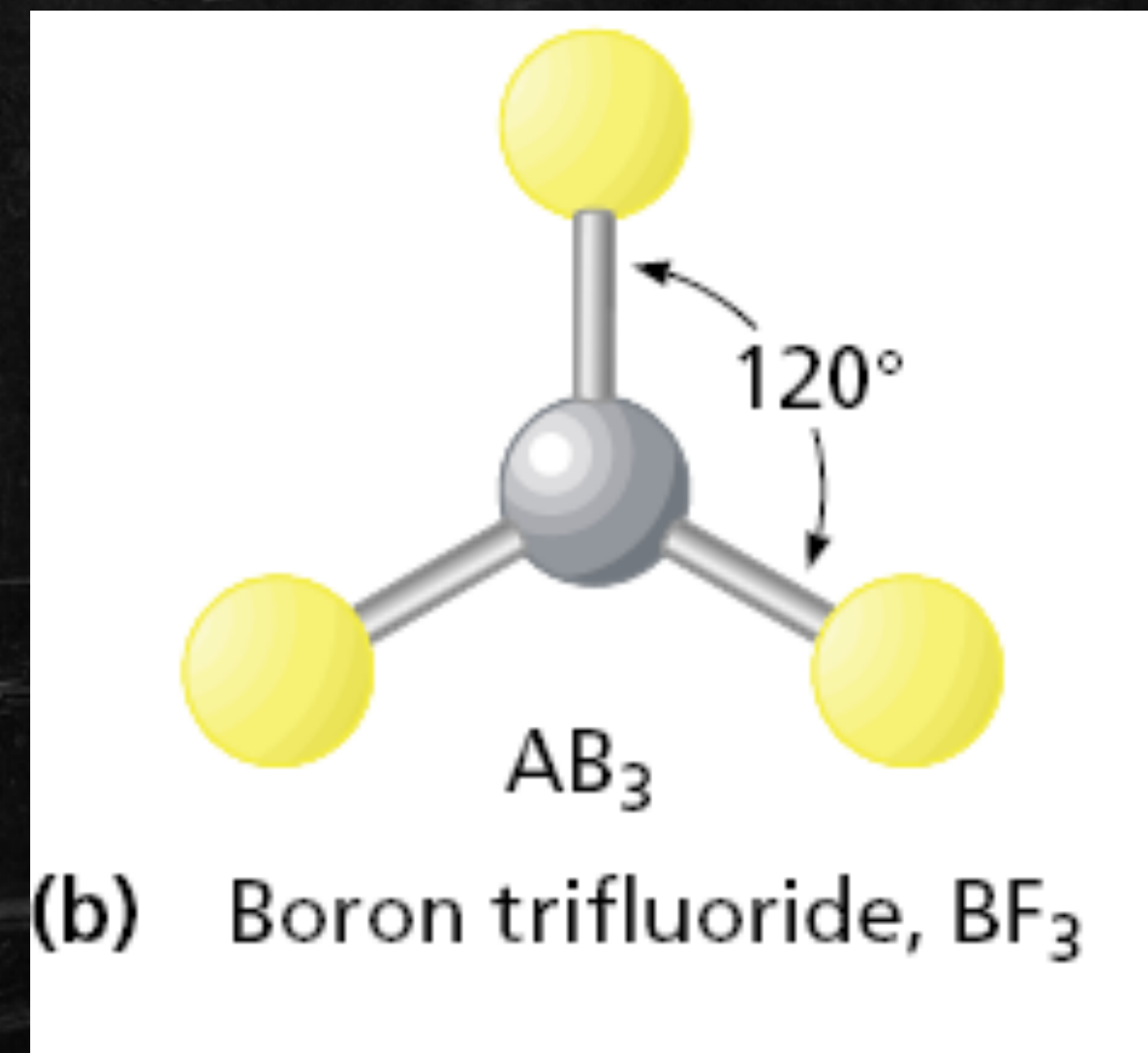


If we represent central atom in molecule by “A”
and atoms bonded to “A” are represented by “B”
then BeF_2 is an example of an AB_2 molecule

AB_2 is linear

What would AB_3 look like?

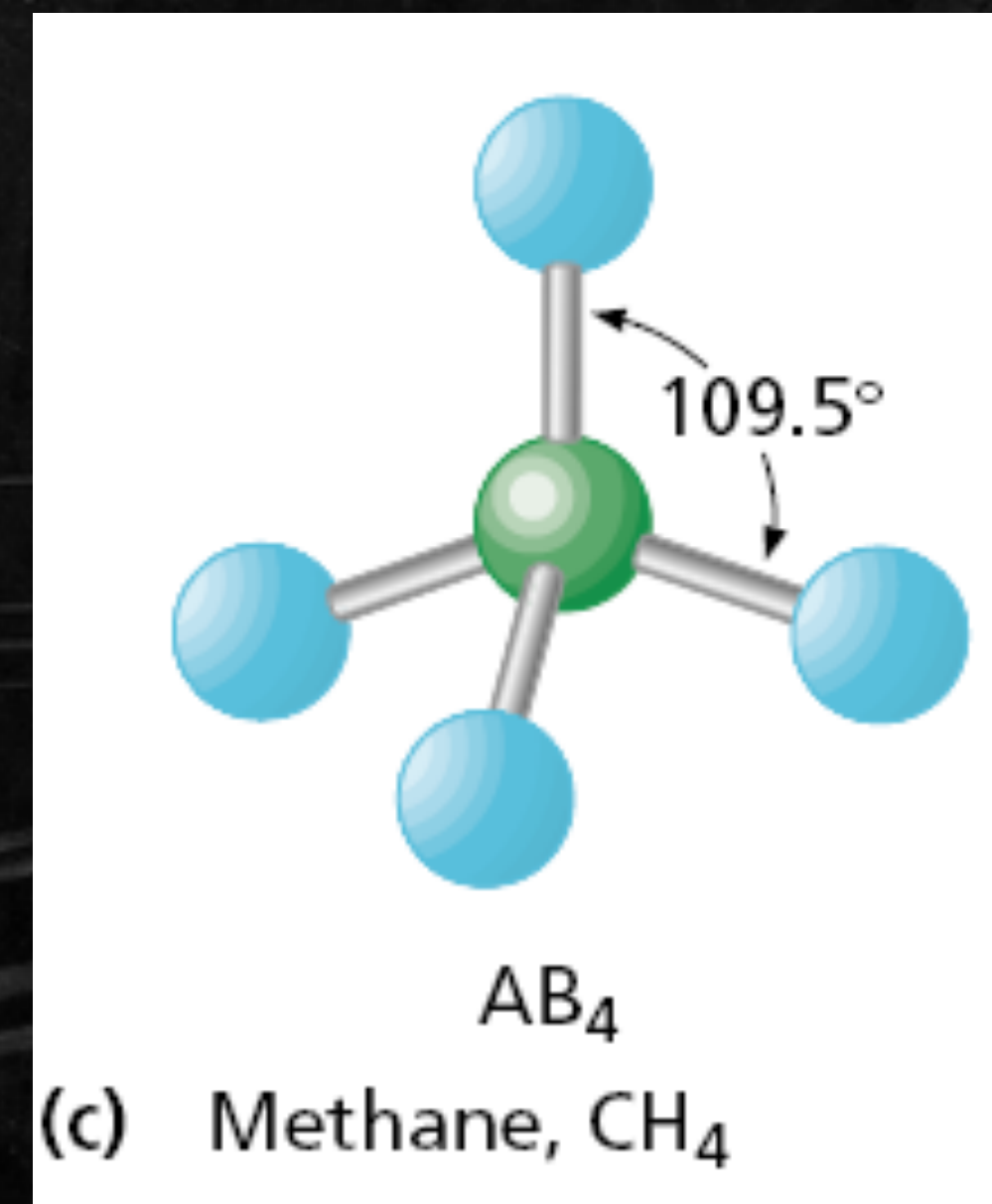
The 3 A-B bonds stay farthest apart by pointing to corners of equilateral triangle, giving 120° between bonds
= **trigonal-planar geometry**



AB_4 molecules following octet rule by sharing 4 e- pairs with B atoms

Distance between e- pairs maximized if each A-B bond points to one of 4 corners of tetrahedron (**tetrahedral geometry**)

Angle is 109.5°



Sample Problem

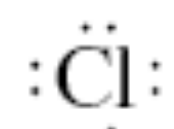
Use VSEPR theory to predict the molecular geometry of aluminum chloride, AlCl_3 .

SOLUTION

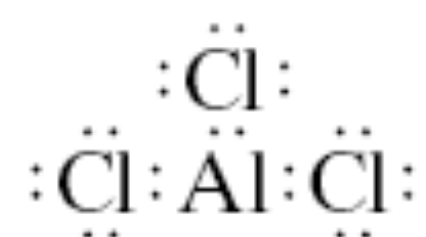
First write the Lewis structure for AlCl_3 . Aluminum is in Group 13 and has three valence electrons.



Chlorine is in Group 17 and has seven valence electrons.



The total number of available valence electrons is therefore $24e^-$ ($3e^-$ from aluminum and $21e^-$ from chlorine). The following Lewis structure uses all $24e^-$.



This molecule is an exception to the octet rule because in this case Al forms only three bonds. Aluminum trichloride is an AB_3 type of molecule. Therefore, according to VSEPR theory, it should have trigonal-planar geometry.

This molecule is an exception to the octet rule because in this case Al forms only three bonds

Aluminum trichloride is an AB_3 type of molecule

Therefore, according to VSEPR theory, it should have trigonal-planar geometry

Practice Problem

Use VSEPR theory to predict the molecular geometry of the following molecules:

a. HI

linear

b. CBr₄

tetrahedral

c. AlBr₃

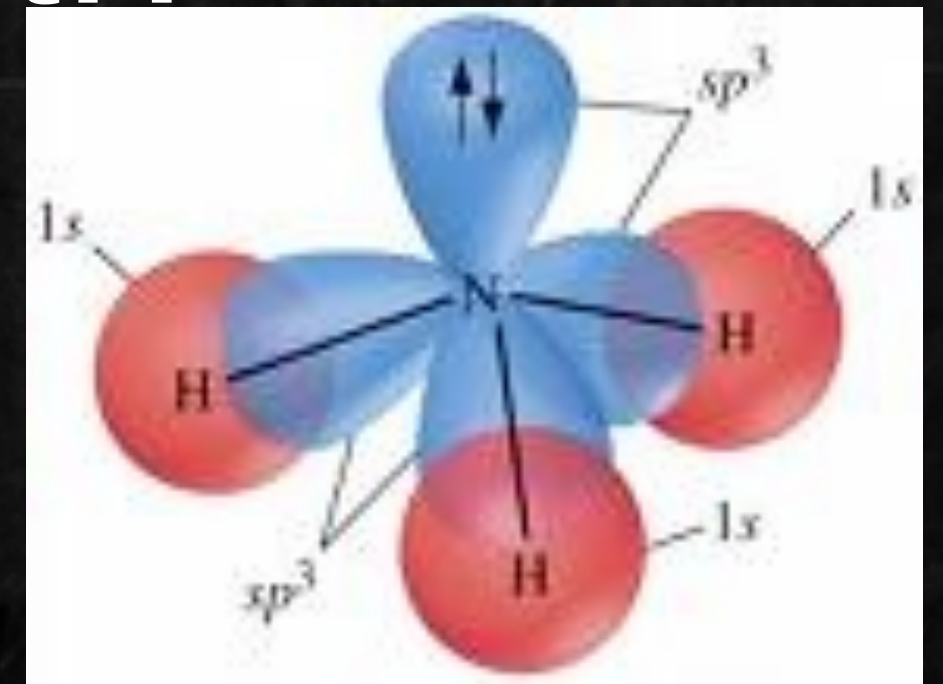
Trigonal-planar

d. CH₂Cl₂

tetrahedral

VSEPR and Unshared e- Pairs

Ammonia, NH_3 , and water, H_2O , are examples of molecules where central atom has both shared and unshared e- pairs



How does VSEPR account for the geometries?

Lewis structure of ammonia shows in addition to 3 e- pairs it shares with 3 H atoms, the central N has one unshared pair of e-

VSEPR theory says that lone pair occupies space around N atom just as bonding pairs do

So, as an AB₄ molecule, e- pairs maximize separation by assuming 4 corners of tetrahedron

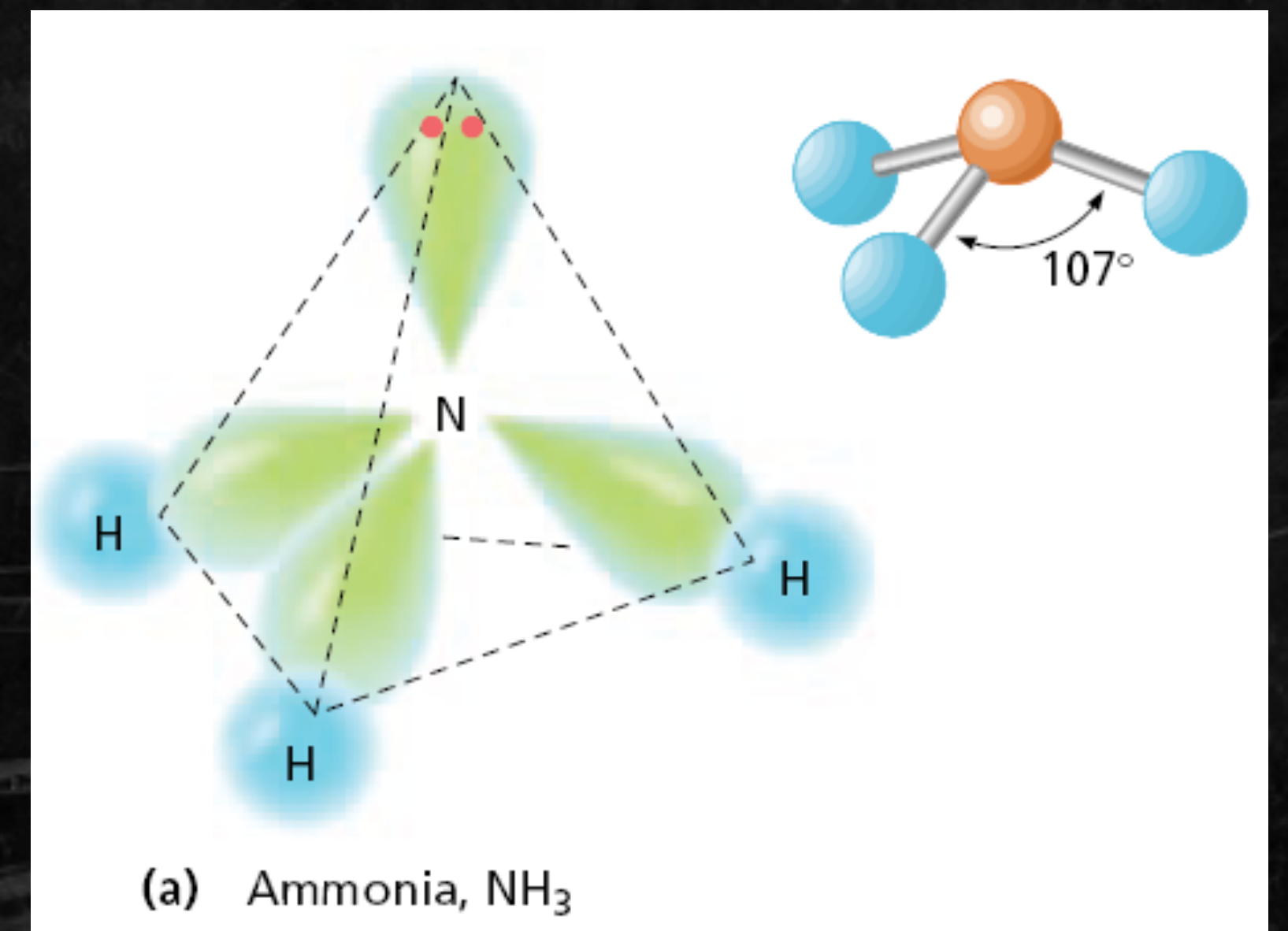


Lone pairs occupy space but description of shape of molecule refers to *positions of atoms only*

So, molecular geometry of ammonia molecule is pyramid with triangular base

General formula is AB_3E

E is unshared e- pair



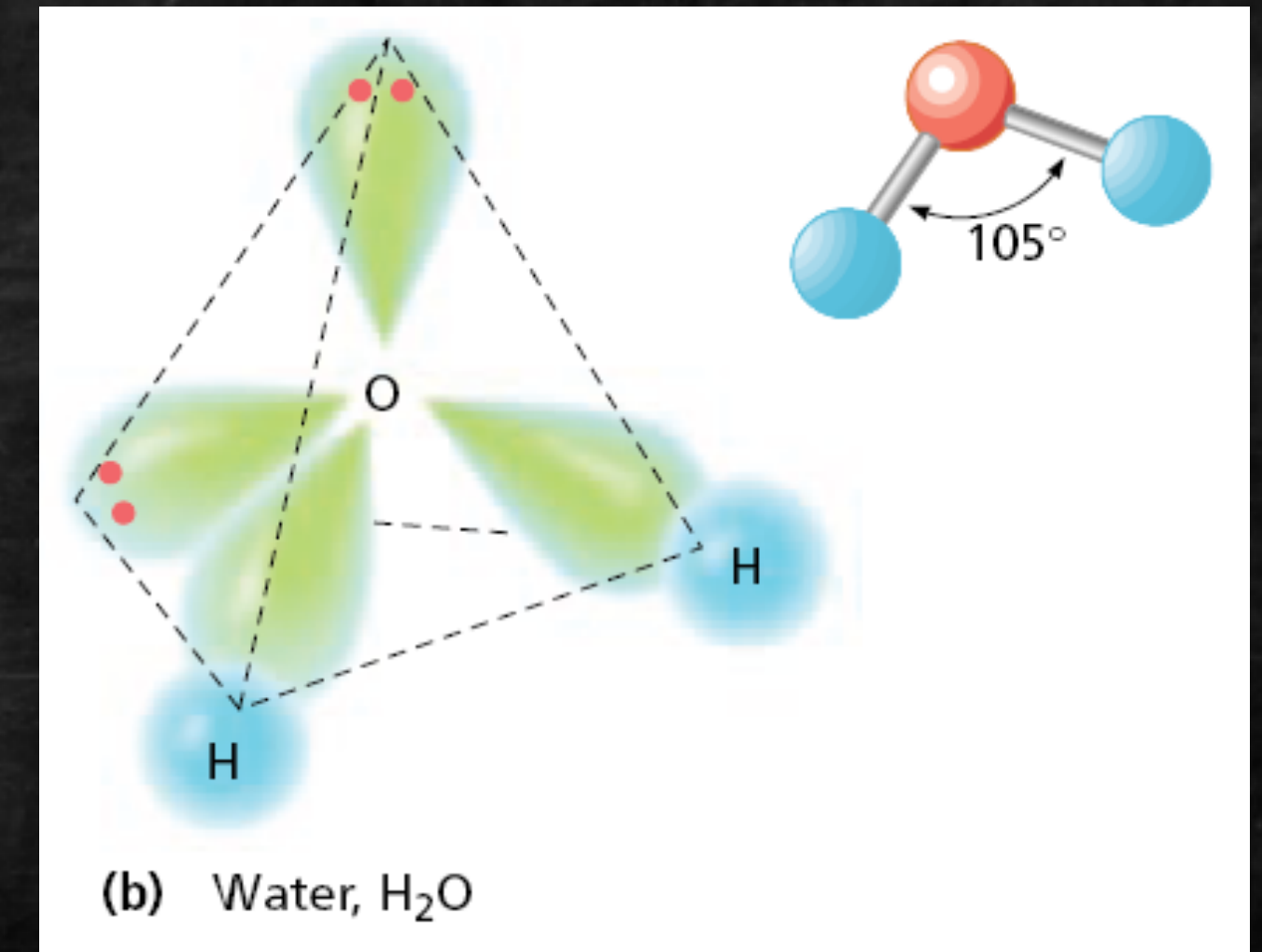
Water molecule has 2 unshared e- pairs




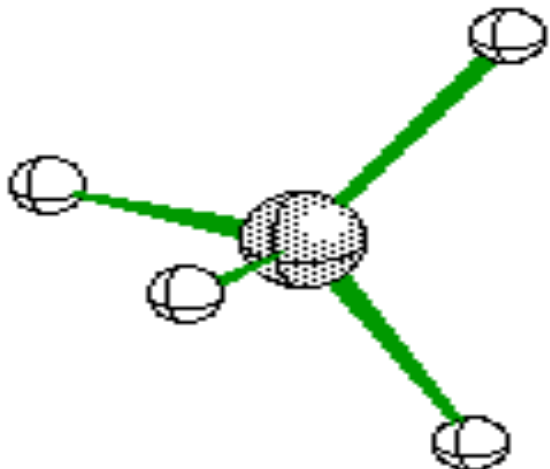
It is AB_2E_2 molecule

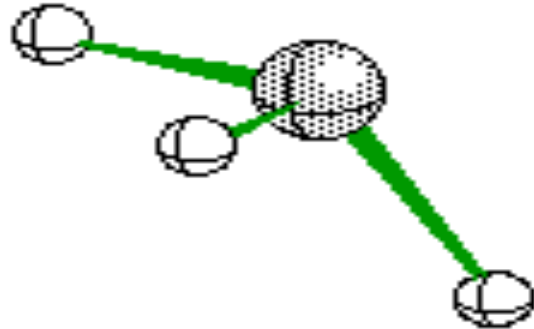
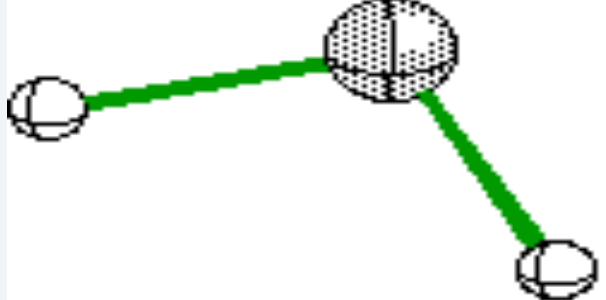
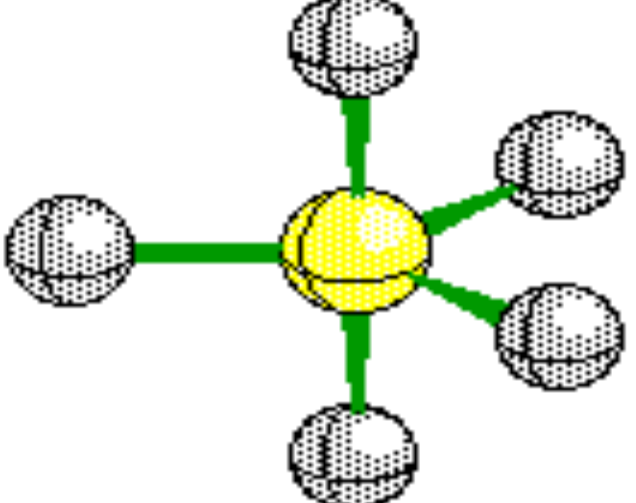
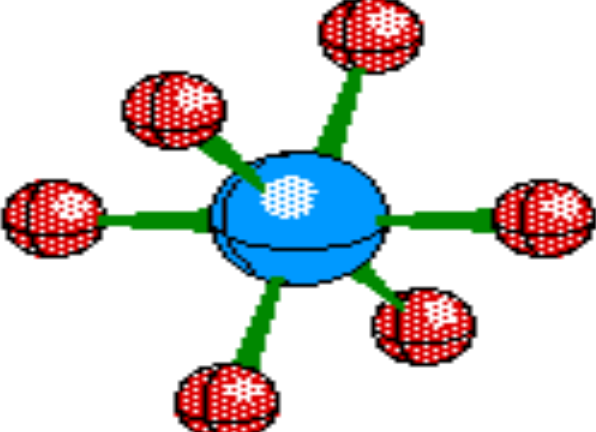
A (O) is at center of tetrahedron

2 corners occupied by B (H)

Other 2 corners occupied by E (unshared e-)



| | Molecular Shape | Atoms bonded to central atom | Lone pairs of electrons | Bond angle |
|-----------------|--|------------------------------|-------------------------|----------------|
| Linear |  | 2 | 0 | 180° |
| Bent or Angular |  | 2 | 1 | Less than 120° |
| Trigonal-planar |  | 3 | 0 | 120° |
| Tetrahedral |  | 4 | 0 | 109.5° |

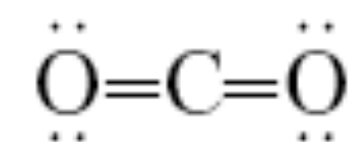
| | Molecular Shape | Atoms bonded to central atom | Lone pairs of electrons | Bond angle |
|----------------------|--|------------------------------|-------------------------|------------------|
| Trigonal-pyramidal |  | 3 | 1 | Less than 109.5° |
| Bent or Angular |  | 2 | 2 | Less than 109.5° |
| Trigonal-bipyramidal |  | 5 | 0 | 90, 120, and 80° |
| Octahedral |  | 6 | 0 | 90 and 180° |

Sample Problem

Use VSEPR theory to predict the shape of a molecule of carbon dioxide, CO_2 .

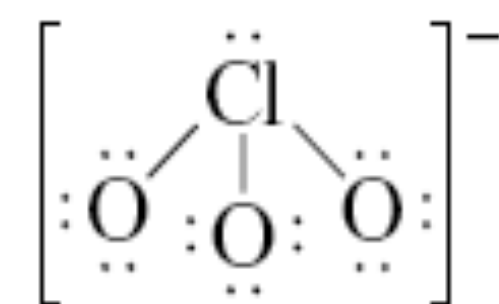
SOLUTION

- a. The Lewis structure of carbon dioxide shows two carbon-oxygen double bonds and no unshared electron pairs on the carbon atom. To simplify the molecule's Lewis structure, we represent the covalent bonds with lines instead of dots.



This is an AB_2 molecule, which is linear.

- b. The Lewis structure of a chlorate ion shows three oxygen atoms and an unshared pair of electrons surrounding a central chlorine atom. Again, lines are used to represent the covalent bonds.



The chlorate ion is an AB_3E type. It has trigonal-pyramidal geometry, with the three oxygen atoms at the base of the pyramid and the chlorine atom at the top.

Hybridization

VSEPR theory useful for explaining shapes of molecules

Doesn't tell the relationship between geometry and orbitals of bonding electrons

Model used to explain this is **hybridization**

Mixing of two or more atomic orbitals of similar energies on the same atom to make new orbitals of equal energies.

Methane (CH_4) provides good example

Orbital notation of C shows it has 4
valence e-

2 in 2s and 2 in 2p

We know from experiments that methane
has tetrahedral geometry

How does C form 4 equal covalent bonds?

2s and 2p orbitals have different shapes

These orbitals *hybridize* to form four new, identical orbitals called sp^3 orbitals

Superscript 3 shows that 3 p orbitals were included in hybridization

Sp^3 all have same energy

More than 2s

Less than 2p

Hybrid orbitals \rightarrow *orbitals of equal energy made by the combination of two or more orbitals on the same atom*

Intermolecular Forces

Intermolecular forces → *forces of attraction between molecules*

Vary in strength

Generally weaker than bonds that hold molecules together (covalent, ionic)

Molecular Polarity and Dipole-Dipole Forces

Strongest intermolecular forces exist between polar molecules

Polar molecules act as tiny dipoles b/c of uneven charge distribution

Dipole → *created by equal but opposite charges that are separated by a short distance*

Direction of dipole is from dipole's positive pole to its negative pole

Represented by arrow with head pointing toward negative pole and crossed tail pointing toward positive pole



Cl more electronegative, and so is negative end

Negative area in one polar molecule attracts the positive area in nearby molecules

Dipole-dipole forces → *forces of attraction between polar molecules*

Dipole-dipole forces are short-range

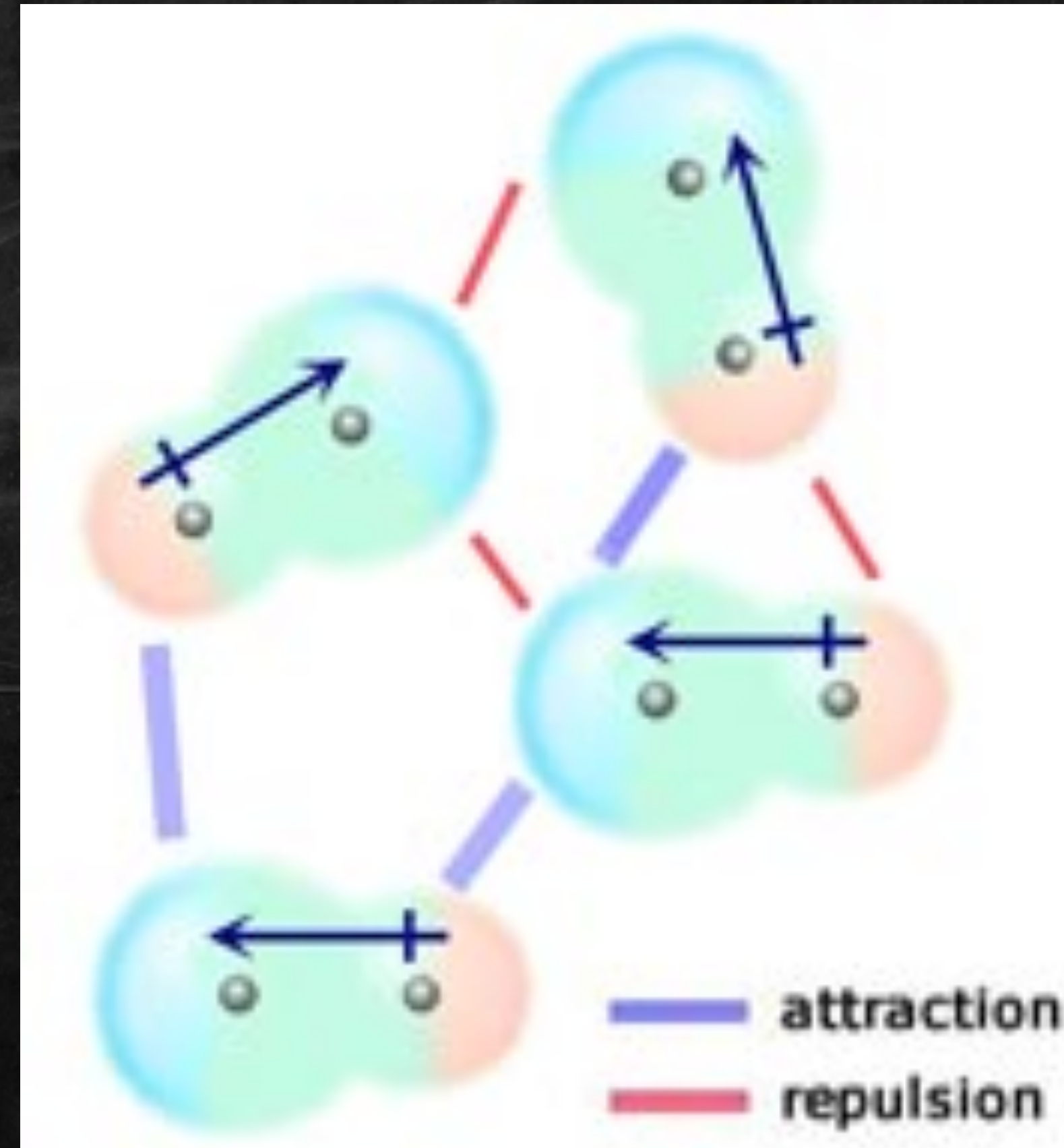
Only act on nearby molecules

Effect reflected by difference between boiling points of Br-F and F-F

Boiling point of polar Br-F is -20°C

Boiling point of F-F is -180°C

Dipole-dipole forces of Br-F are responsible for high boiling point



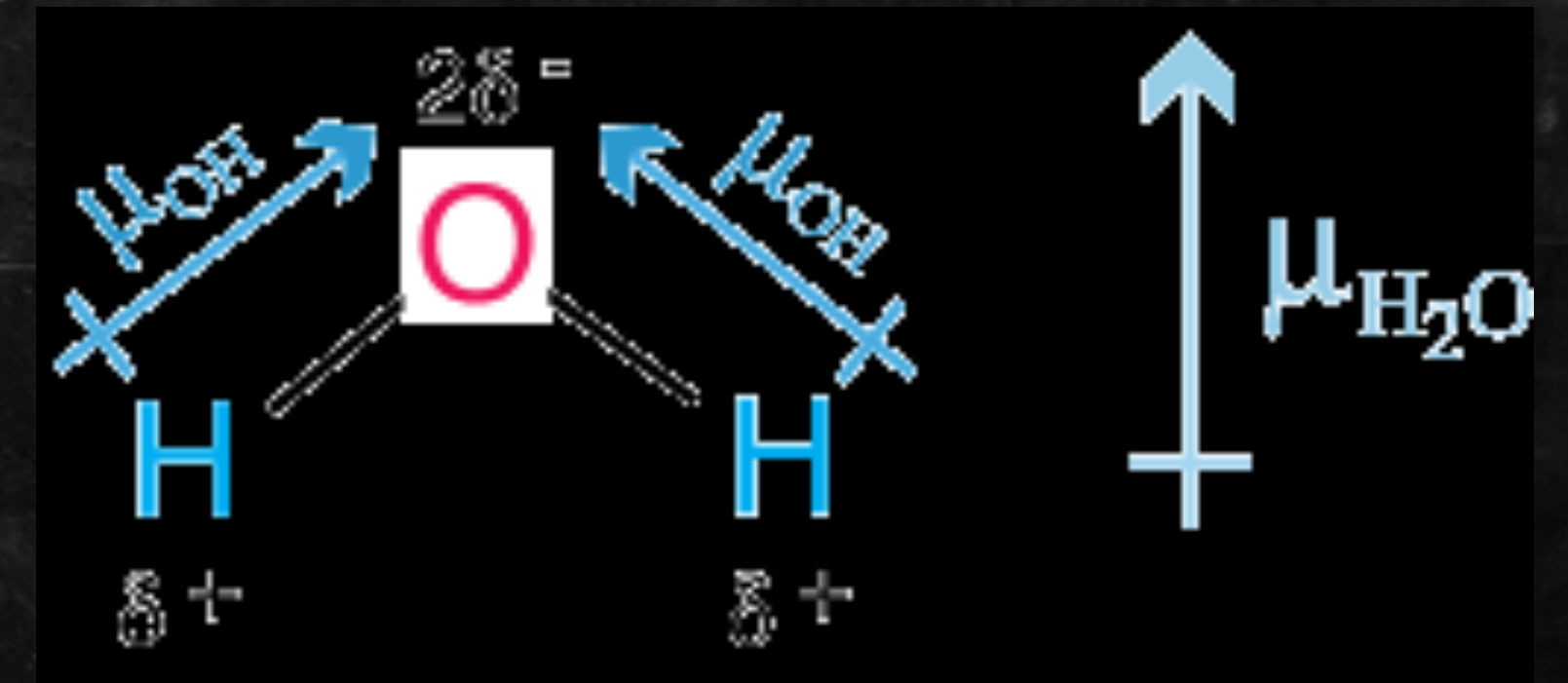
Polarity of diatomic molecules determined by one bond

For molecules with more than 2 atoms, molecular polarity depends on both polarity AND orientation of each bond

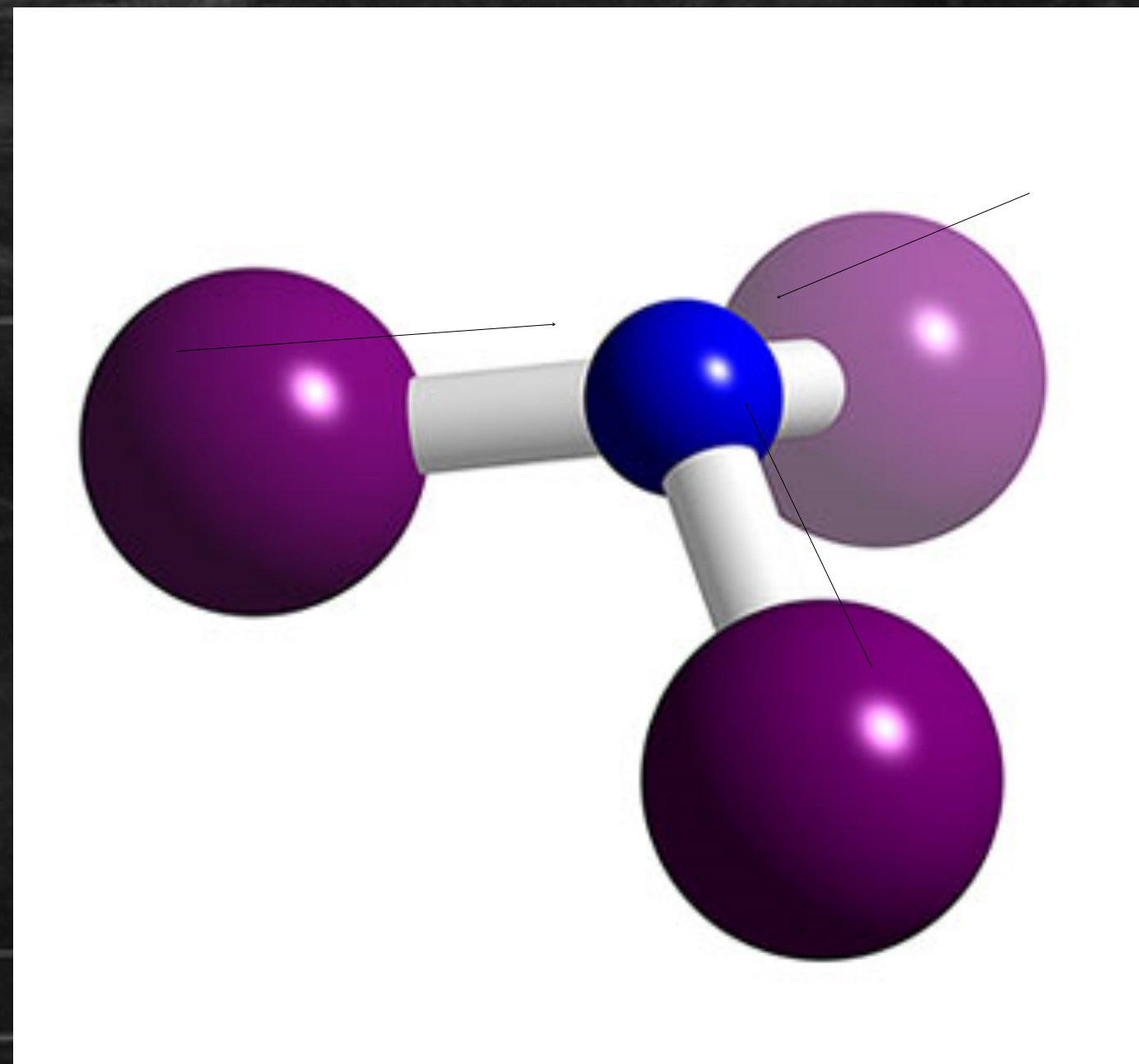
Ex. Water

2 H-O bonds where the more-EN oxygen atom is the negative pole of each bond

Because the molecule is bent, polarities of two bonds combine to make molecule highly polar



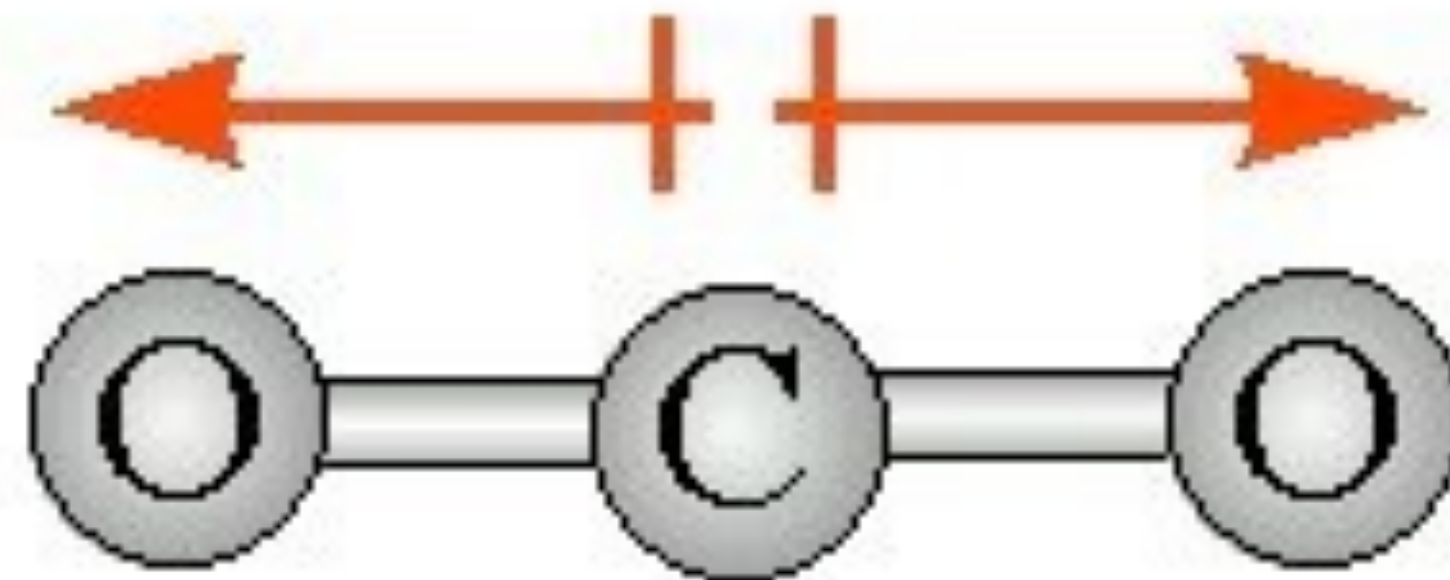
Ammonia is also highly polar because the dipoles of the 3 N-H bonds combine to create a net molecular dipole



Some individual bond dipoles cancel each other

Resulting molecular polarity is zero

Dipoles



Overall
Dipole:

(none)

A polar molecule can cause a dipole in a nonpolar molecule by temporarily attracting its e-

Result is short-range intermolecular force weaker than dipole-dipole force

Accounts for solubility of nonpolar oxygen in water

Positive pole of water molecule attracts outer electrons of oxygen molecule

Oxygen has induced negative pole on side toward water and induced positive pole on opposite side

Result is attraction to water molecule

Hydrogen Bonding

Some H-containing compounds have unusually high boiling points

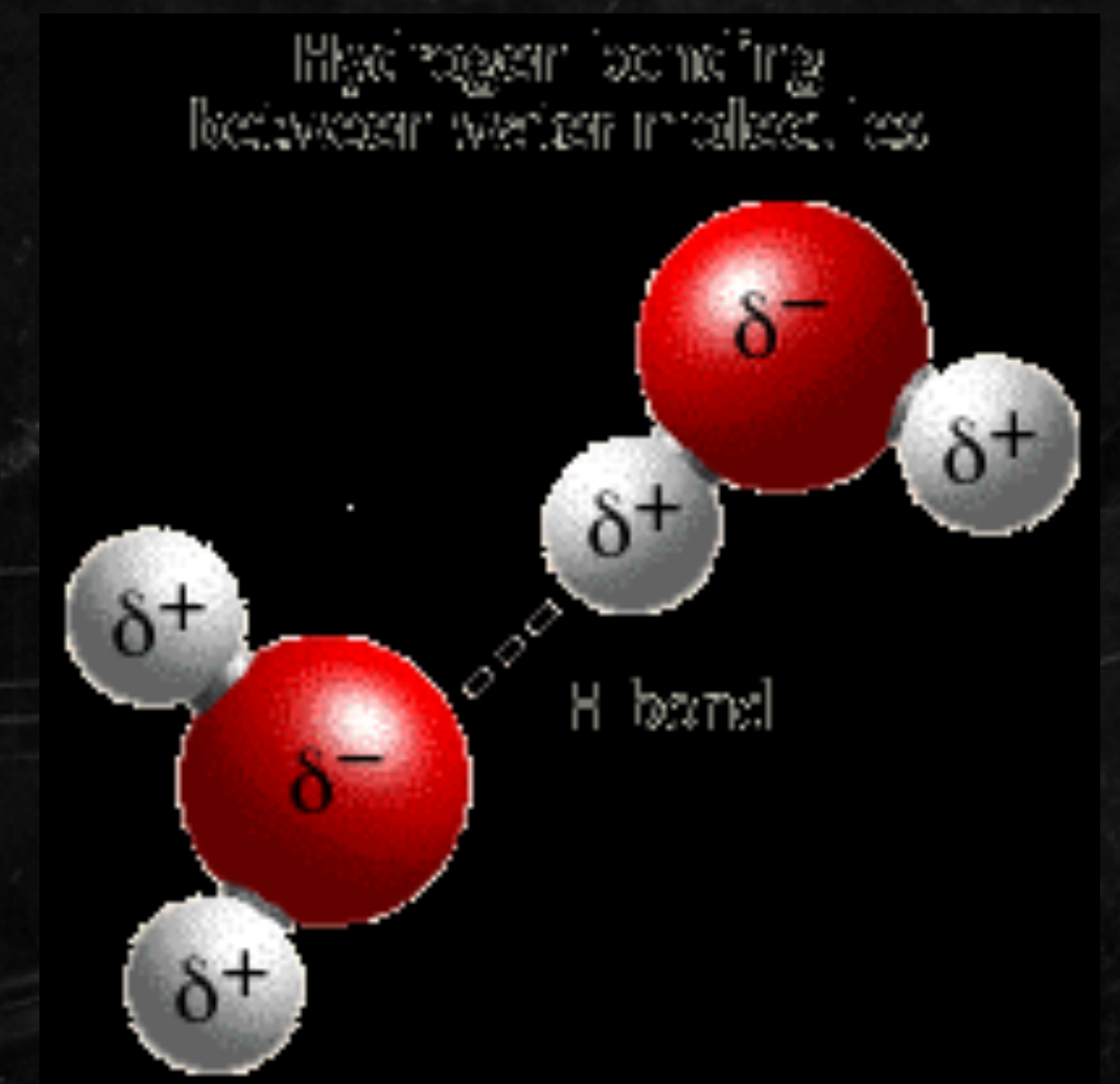
Explained by presence of strong type of dipole-dipole force

In compounds with H-F, H-O, or H-N bonds, large EN differences make the bonds highly polar

This gives H positive charge almost $\frac{1}{2}$ the size of a proton

Hydrogen bonding → *intermolecular force in which a hydrogen atom that is bonded to a highly electronegative atom is attracted to an unshared pair of electrons of an electronegative atom in a nearby molecule*

Usually represented by dotted lines connecting H to unshared e- pair



London Dispersion Forces

Even noble-gas atoms and molecules that are nonpolar have weak intermolecular attraction

e⁻ in all atoms are in continuous motion

As a result, at any moment e⁻ distribution is uneven

Uneven charge creates positive and negative poles

London dispersion forces → *intermolecular attractions resulting from the constant motion of electrons and the creation of instantaneous dipoles*

London forces are the *only* intermolecular forces acting in noble-gas atoms and nonpolar molecules

Reflected in low boiling points of noble gases and nonpolar compounds

Because they are dependent on motion of e^- , the strength increases with number of e^- in interacting atoms or molecules

(increase with increase atomic/molar mass)