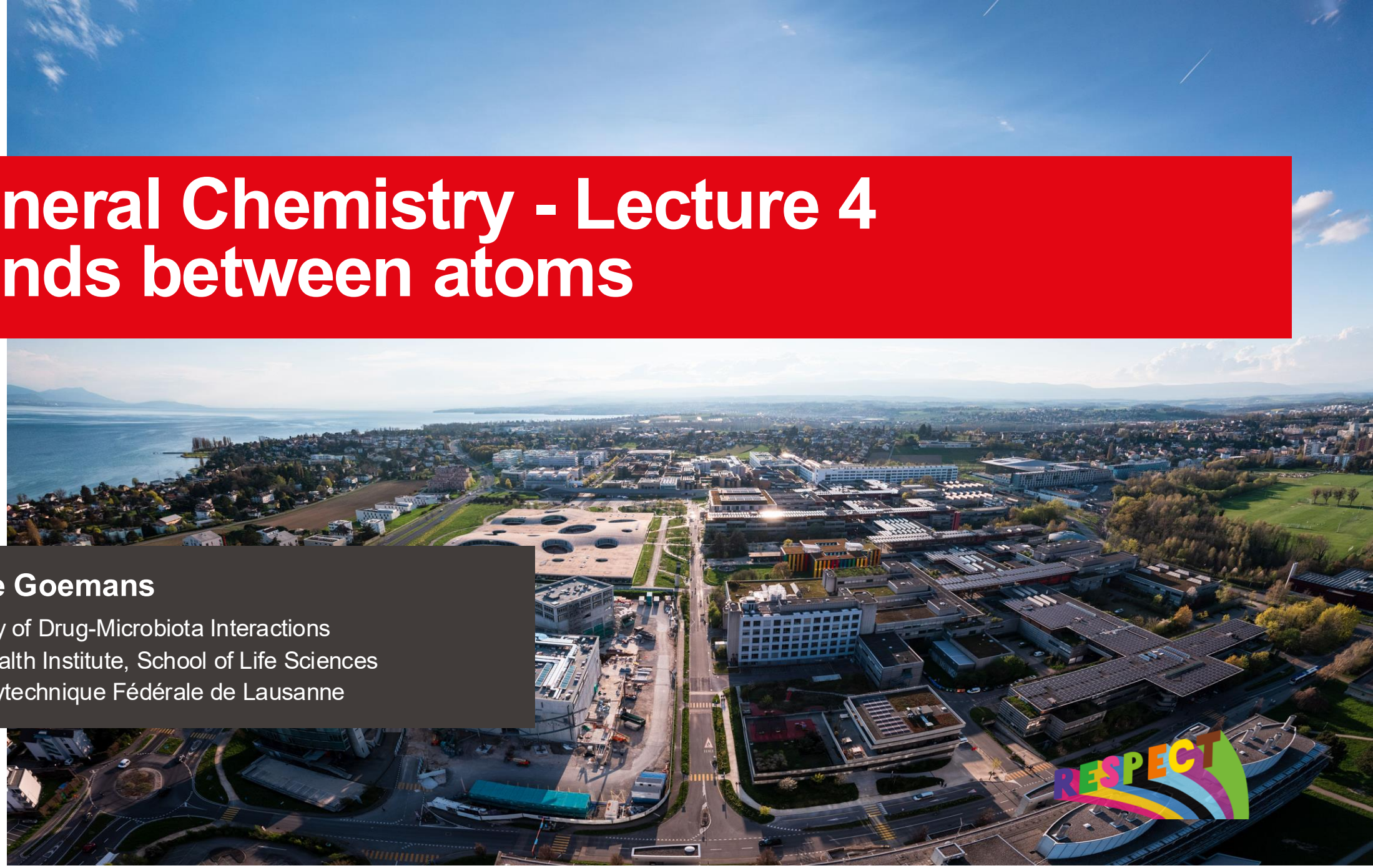
General Chemistry - Lecture 4
Bonds between atoms



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Questions from last week

- **What defines how a wave behaves after passing through a slit (double slit experiment)**
  - **Diffraction** is the bending and spreading of waves when they encounter an obstacle or pass through a narrow opening.
  - Occurs with all types of waves – sound, water, light, and even matter waves (like electrons).
  - More noticeable when the obstacle or opening is comparable in size to the wavelength of the wave.
  - **Results in wave spreading** instead of continuing in a straight line.

Questions from last week

- **Are electrons particles that move on waves?**
  - Electrons are not particles *on* waves — they are **quantum objects** that can be described as both a localized particle *and* a spread-out wave of probability.
  - Electrons do **not** literally wiggle or travel like a water wave. Instead:
    - The **wave** in quantum mechanics is the **wavefunction** (Ψ).
    - This wavefunction is not a physical wave of matter, but a **mathematical description** of where the electron is likely to be.
    - The square of the wavefunction's amplitude $|\Psi|^2$ gives the **probability density** — i.e. the chance of finding the electron at a certain position if you measure it.

Questions from last week

- **Can you clarify the uncertainty principle?**
  - You **cannot know everything about a particle at once with perfect accuracy.**

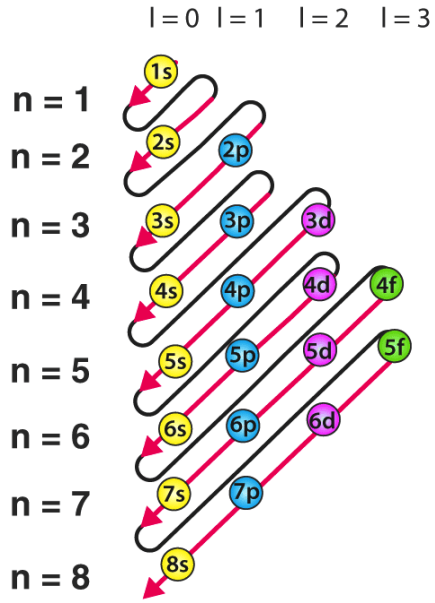
    Specifically, you can't know both:
    - **where it is** (position), and
    - **how fast it's moving / in what direction** (momentum).
    - The more precisely you measure one, the fuzzier the other becomes.
  - Imagine trying to take a photo of a racing car at night:
    - If you use a very **short exposure**, you get a sharp picture of *where* the car is — but it looks frozen, so you can't tell how fast it was going.
    - If you use a **long exposure**, you see the streak (showing speed/direction) — but now you've lost the precise position.
    - That's basically the uncertainty principle!

Information on Exam

- It will last **?h**
- You can bring a **pen, eraser** and **simple calculator**
- You will have **12 multiple choice questions** (each 2.5 points, no negative points) and **3 open questions** (each 10 points) --> total of **60** points
- In the last weeks of the semester, we will provide a **mock exam** for you to test yourselves but in general, the best preparation is to be able to do the **exercise series**!

Orbitals – filling and ion formation

- When we fill orbitals, we follow the energy level – this tells us how many electrons are in each orbital.
  - When we write the electron configuration, we can either follow the energy level (Br- : [Ar] $4s^2\ 3d^{10}\ 4p^6$) or the principal quantum number (Br- : [Ar] $3d^{10}\ 4s^2 4p^6$) – both are **correct**



Orbitals – filling and ion formation

- When we add or remove electrons to form ions:
  - For main-group elements (s- and p-block):
    - When forming **cations**, electrons are removed from the orbital with the **highest principal quantum number (n)** first (the outermost shell).
    - When forming **anions**, electrons are **added** to the orbital with the **lowest available energy** (usually the lowest empty p orbital in that shell).
  - For transition metals (d-block):
    - This is the tricky part: although the 3d orbitals fill after 4s, when forming cations we remove electrons from the **4s (n=4) orbital before 3d (n=3)**, because 4s is higher in energy once the d orbitals have electrons.

Example:
Fe ([Ar] $4s^2$ $3d^6$) → Fe^{2+} = [Ar] $3d^6$ (remove 4s first).

Orbitals – filling and ion formation

So the general rule:

👉 Electrons are removed first from the orbital with the highest principal quantum number (n).

👉 If two orbitals have the same n, the one with the higher azimuthal quantum number (l) is removed first (so p before s, d before p, etc.).

Plan

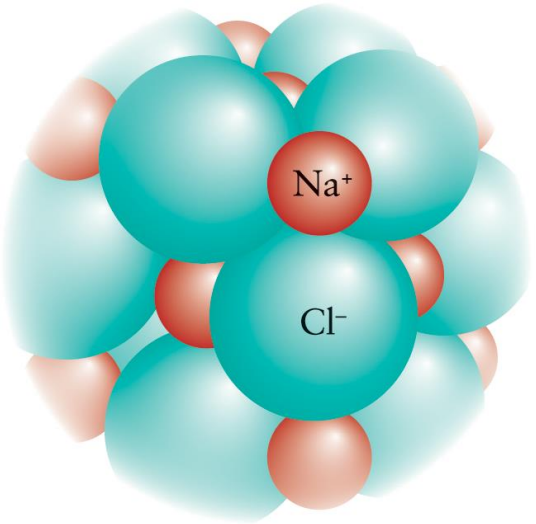
- **Introduction**
  - What is a chemical bond
  - What are the different types of bonds
- Lewis representation
  - Octet rule
  - Examples
  - Limitations
- Geometric representation (VSEPR)
- Quantum approach

Bonds between atoms

- Each atom is unique due to their differing sizes, electron affinities, and ionization energies
- Atoms minimize these imbalances by forming bonds
- Atoms strive to fill their outer shell with electrons just like a noble gas does
- In a generalized way, atoms can achieve satisfaction by forming three types of bonds
    - **Ionic bonds** are formed by *gaining & losing* electrons.
    - **Covalent bonds** are formed by *sharing* electrons.
    - **Metallic bonds**

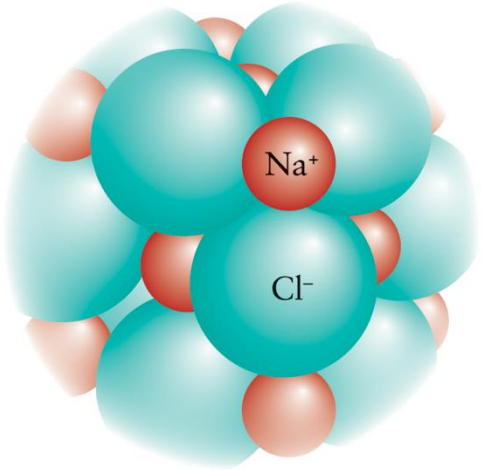
Ionic bonding

- **Ionic bonds** form when one element loses electrons and the other atom gains electrons, until both atoms reach a *noble-gas configuration*
- This typically happens in metal-nonmetal bond where the electrons of the metal go to the nonmetal
- Ionic bond is a bond between ions of opposite charge (+ and -)
- The entire compound is held together by electrostatic attractions between all the ions.
- This happens when there is a large electronegativity difference between the atoms (>1.7)
- The new ionic partnership is lower in energy than the separate atoms.



Properties of ionic compounds

- Cations and anions stack into alternating, oppositely charged ions that line up in three dimensions, to form an ionic crystalline solid
- Bonding energy is high and fusion points are also high
- Soluble in water but not in organic solvants
- Conduct electricity in water solution



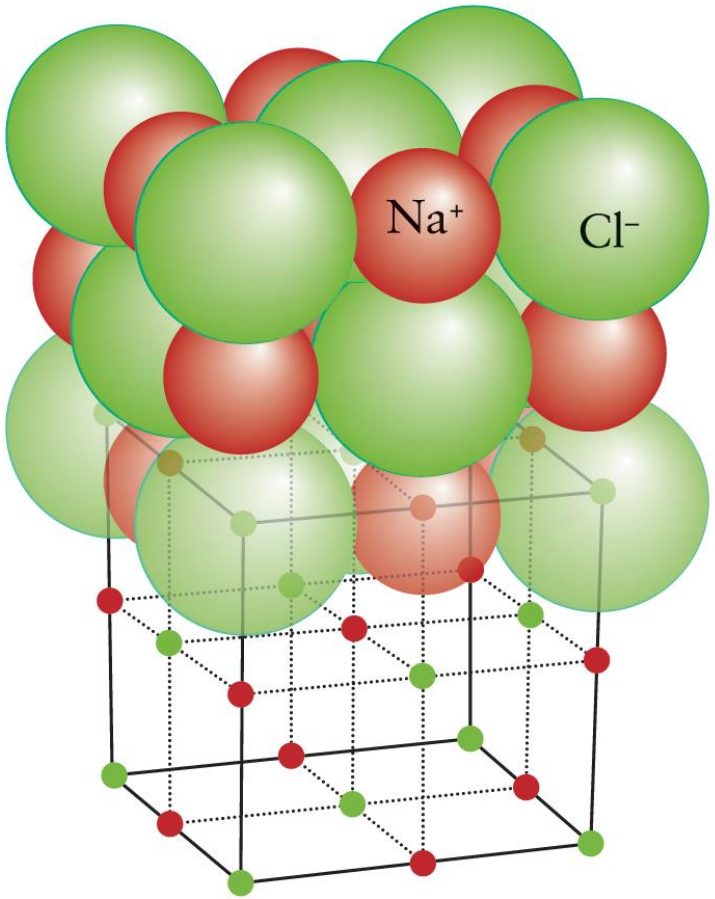
(d)

(e)

Parts (d) and (e) Paul Silverman/Fundamental Photographs.

Ion crystal formation

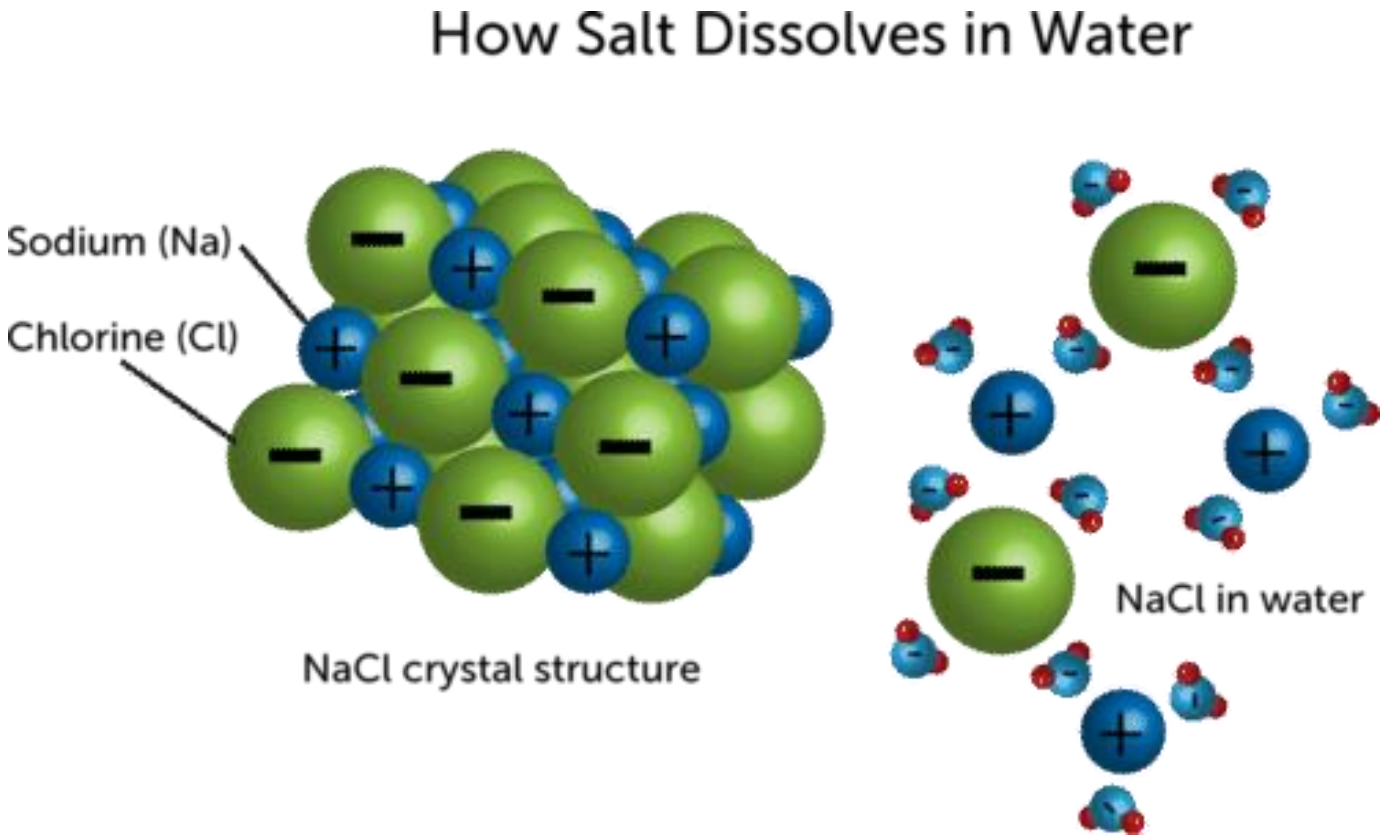
Large numbers of oppositely charged ions combine, releasing large amounts of energy.



(a)

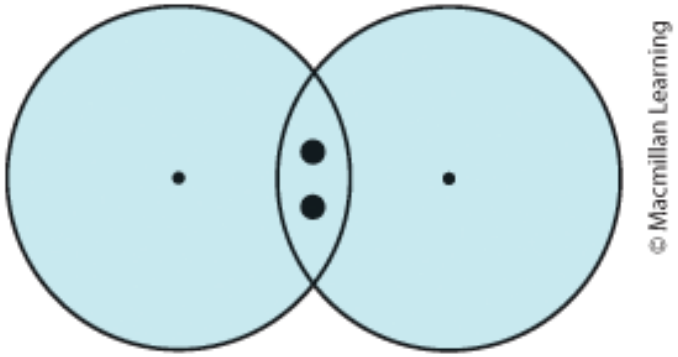
NaCl in water (remember electrolytes)

- Solid NaCl does not conduct electricity as charges are not motile
- In water, Cl^- and Na^+ become motile and conduct electricity

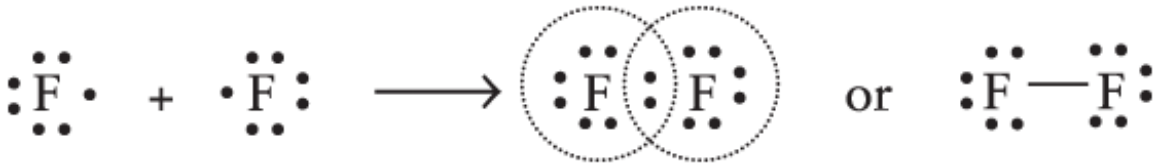


Covalent bonding

- Bonds between nonmetals
- **Covalent bonds** form by atoms sharing electrons until they reach a *noble-gas configuration*.
- Lewis called this principle the **octet rule.**

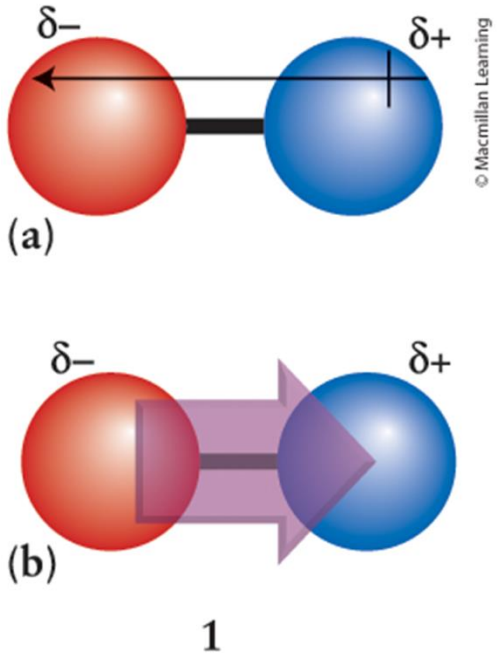


1 Shared electron pair



Are the electrons shared equally? Electronegativity

Electronegativity = electron-pulling ability of an atom in a molecule



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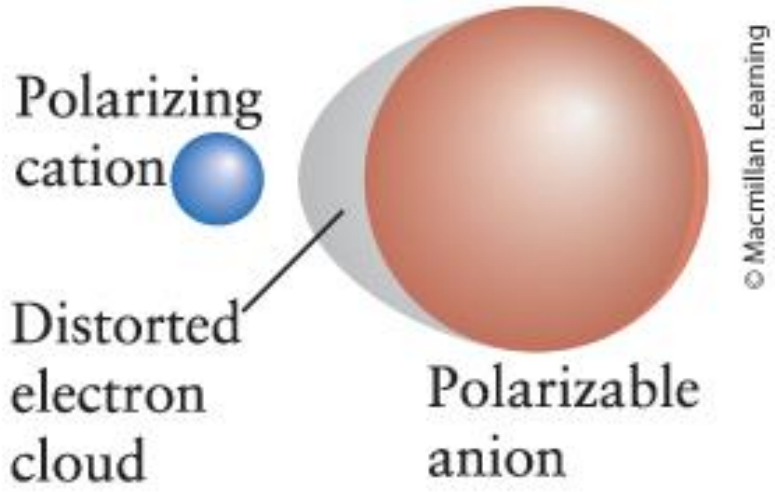
- The **partial charges** (+δ, −δ)—not true charges.
- (a) is an older convention whereas (b) is the newer convention. Style (b) is the currently adopted method.

Differences in electronegativity create polarity

- The atom with the **highest electronegativity** has the tendency to drag electrons towards itself.
- The electron density is then not in the middle but closer to the most electronegative atom.

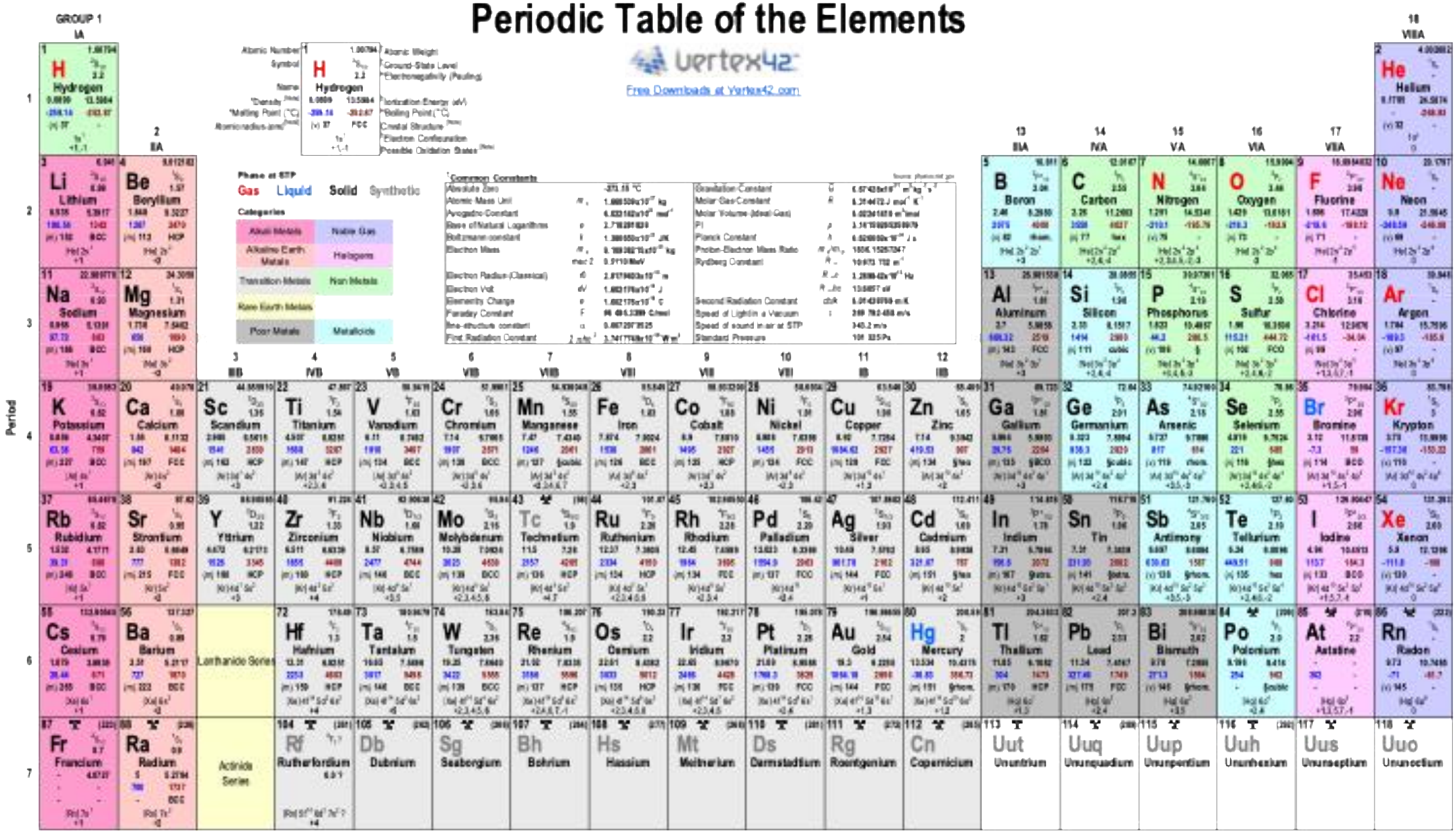


Electronegativity difference

- There is no specific dividing line between ionic and covalent bonding.
- Electronegativity difference > 1.7 means likely ionic
- Electronegativity difference < 1.7 means likely covalent

Ionic and covalent bonding are two extreme bonding models. Most bonds lie somewhere between purely ionic and purely covalent.

Periodic Table of the Elements

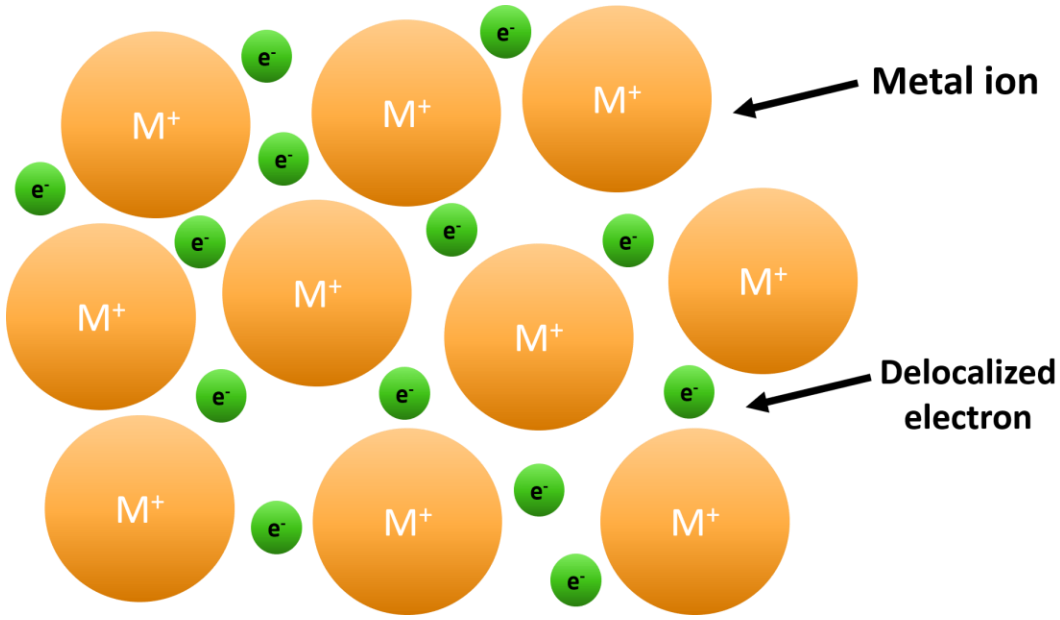


Notes:

- Density units are g/cm³ for solids and g/L or kg/cm³ at 0° Celsius for gases
- Atomic Weight based on ¹²C

Metallic binding

- Valence electrons are shared between all atoms in the metal which ensures the electric conductivity

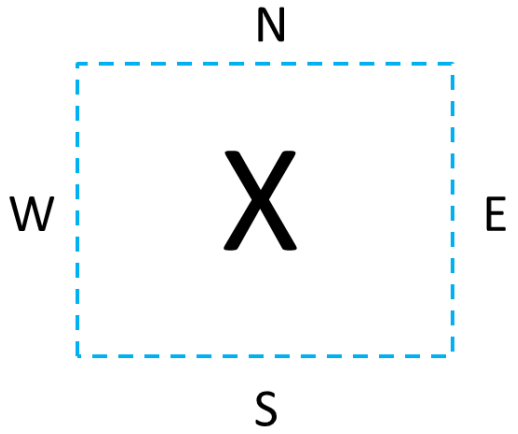


Plan

- Introduction
  - What is a chemical bond
  - What are the different types of bonds
- **Lewis representation**
  - Octet rule
  - Examples
  - Limitations
- Geometric representation (VSEPR)
- Quantum approach

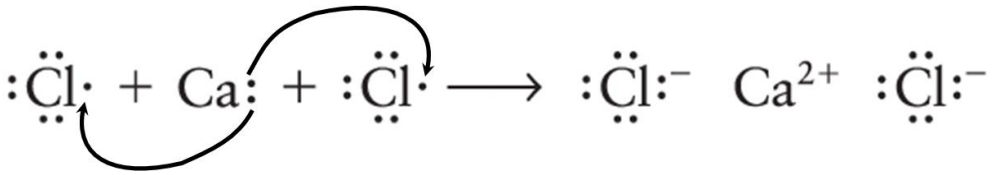
How can we represent these bonds? Lewis representation

- A single dot represents a valence electron (=*electron in the last shell)* in the atom
- A pair of dots represents two paired electrons sharing an orbital
- Each symbol is thought of as having four sides, a north, south, east, and west position, where valance electrons are shown as dots



Lewis structures

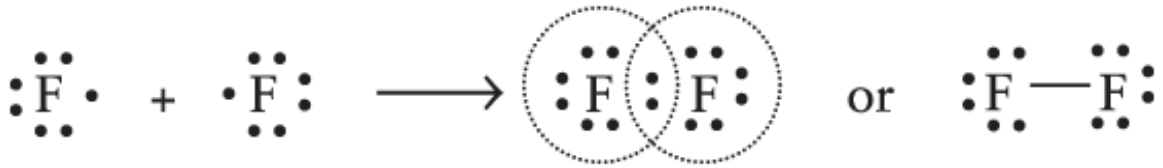
For **ionic bonds,** we start by removing valance electrons from the metal and transferring them to the nonmetal atom to complete its valence shell.



- The calcium atom loses its two valence electrons while each chlorine atom has one vacancy electron therefore it forms one bond
- Two chloride ions (Cl^-) *balance the charge* for each calcium ion (Ca^{2+}) resulting in the formula $CaCl_2$; the overall charge is zero
- There are no $CaCl_2$ molecules, only crystals of three-dimensional arrays of $CaCl_2$ ions held by the vast array of opposite charges spread throughout the crystal

Covalent bonds: the octet rule

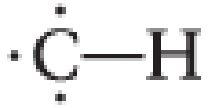
- Atoms in a molecule each need to have eight electrons in their valence shells, with the exceptions of H which needs two electrons (and other exceptions like Be, and B)
- For example, a fluorine atom can achieve an octet by accepting a share in an electron from another fluorine atom.
- The *octet* (or duplet) shows *lines* (covalent bonding pairs) and *dots* (lone pairs).

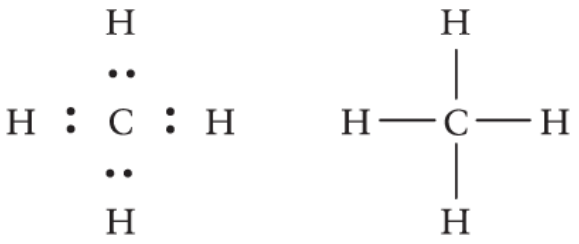


Example: Write the Lewis Structure of H_2O, CO_2 and N_2

Lewis structures for molecules with covalent bonds

Example: Lewis structure for methane, CH_4

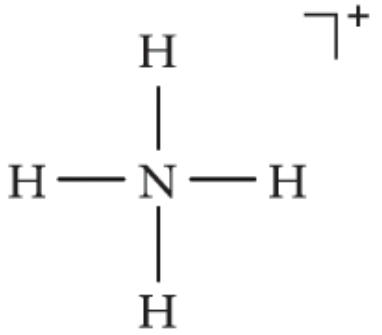




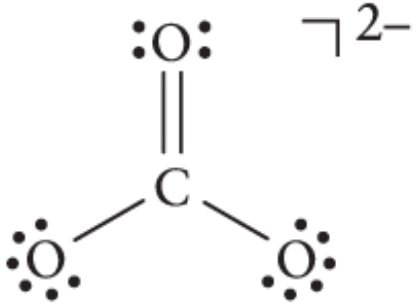
2 Methane, CH_4

- The first element in the formula is typically the central atom
- Arrange the dots representing electrons so that C has an octet and each H atom has a duplet
- Because the carbon atom is linked by four bonds, the carbon is *tetravalent*: It has a valence of 4.

Bonds in Lewis structures



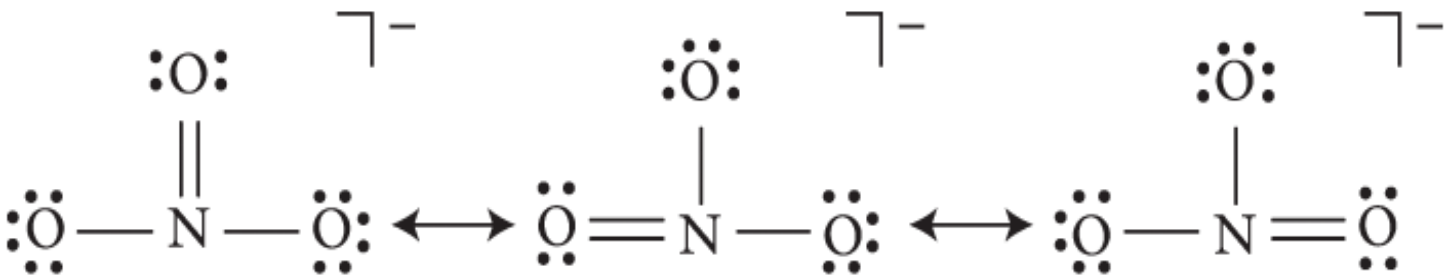
- A **single bond** represents two electrons and is shown with a single line
- A **double bond** represents four electrons and is shown with two lines
- A **triple bond** represents six electrons and is shown with three lines.



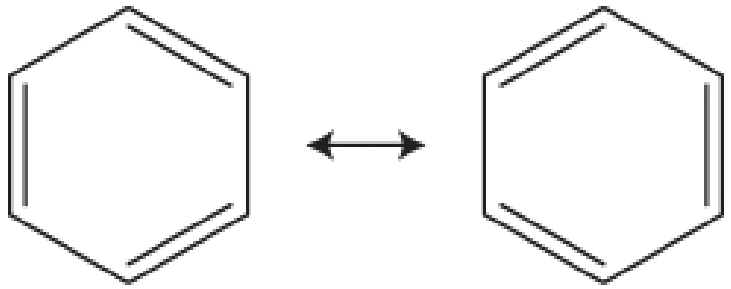
10 Carbonate ion, CO_3^{2-}

Resonance structures

Delocalized electrons move from one atom to another



6 Nitrate ion, NO_3^-

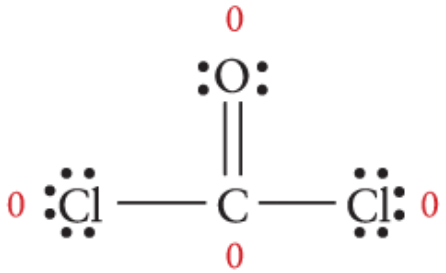


11 Benzene resonance

12 Benzene, C_6H_6

Formal charge (FC)

$$Formal\ Charge = V - \left(L + \frac{1}{2}B\right)$$



16 Phosgene, $COCl_2$

O $6 - (4 + ½ \times 4) = 0$

Cl $7 - (6 + ½ \times 2) = 0$

C $4 - (0 + ½ \times 8) = 0$

- FC= [number of valence e- in the free atom]-[number of electrons in free pairs]-1/2[number of binding electrons]
- The sum of formal charges is equal to the overall charge of the molecule or ion; electrically neutral molecules have a formal charge of zero.

Formal charge (FC)

- Formal charges can predict the most *favorable* Lewis structure
- The structure with the lowest formal charges on each atom is the most plausible (lowest energy) structure.

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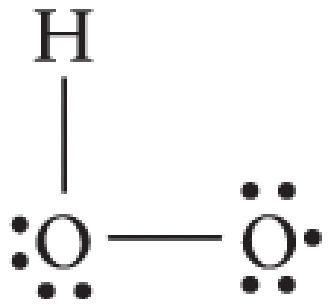
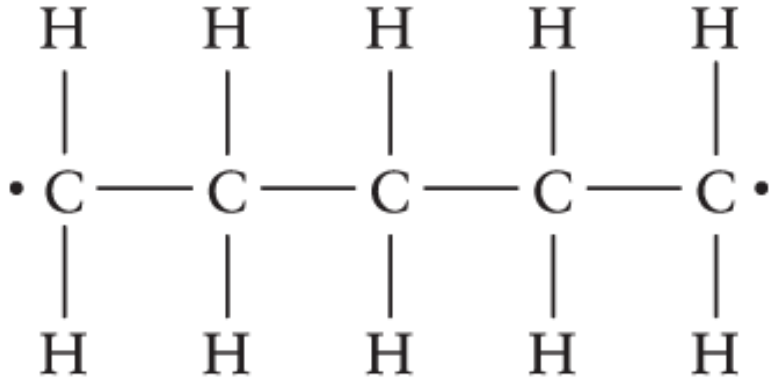
Exceptions to the octet rule

- **Radicals** are something you cannot isolate, are unstable, and are highly reactive. Their formation ”violates” the octet rule
- **Antioxidants** (Vitamins A, C, and E) react with radicals before they are able to do damage



4 Hydrogenperoxyl, $HO_2\cdot$



3 A biradical

Exceptions to the octet rule

- Carbon, nitrogen, oxygen, and fluorine obey the octet rule rigorously (only a few atoms but make the majority of molecules on earth).

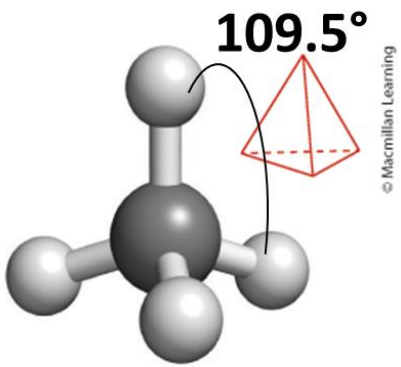
- Period 3 and subsequent periods can accommodate *more than 8 electrons* in its valence shell, up to 12 electrons.

Plan

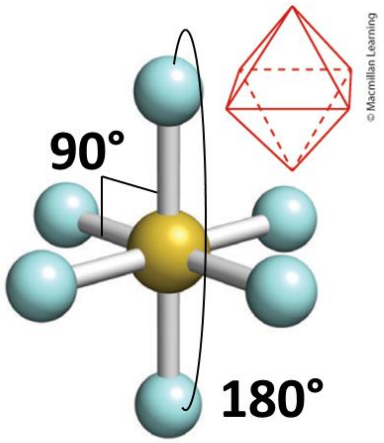
- Introduction
  - What is a chemical bond
  - What are the different types of bonds
- Lewis representation
  - Octet rule
  - Examples
  - Limitations
- **Geometric representation (VSEPR) – applies only to covalent bonds!**
- Quantum approach

Geometric representation: the basic VSEPR model

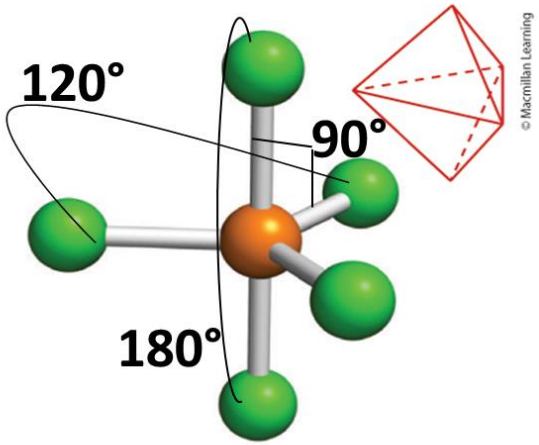
- VSEPR = valence shell electron pair repulsion theory
- Molecules consist of one central atom attached to other atoms, in which electron pairs tend to minimize repulsion energy.
- This creates distinct geometrical shapes, with fixed bond angles.



4 Methane, CH_4



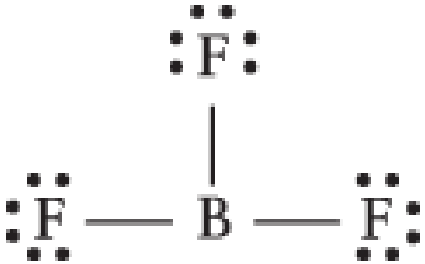
8 Sulfur hexafluoride, SF_6

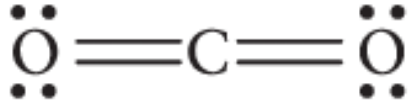


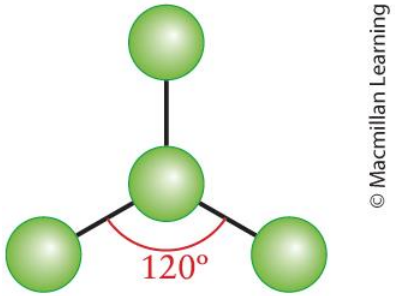
6 Phosphorus pentachloride, PCl_5

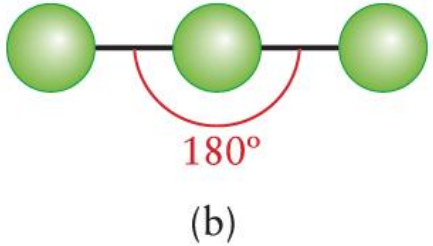
The basic VSEPR model

- Lewis structures are two-dimensional representations of linked atoms
- The **valence-shell electron pair repulsion model (VSEPR model)** extends Lewis's theory to account for molecular shapes by adding rules for bond angles





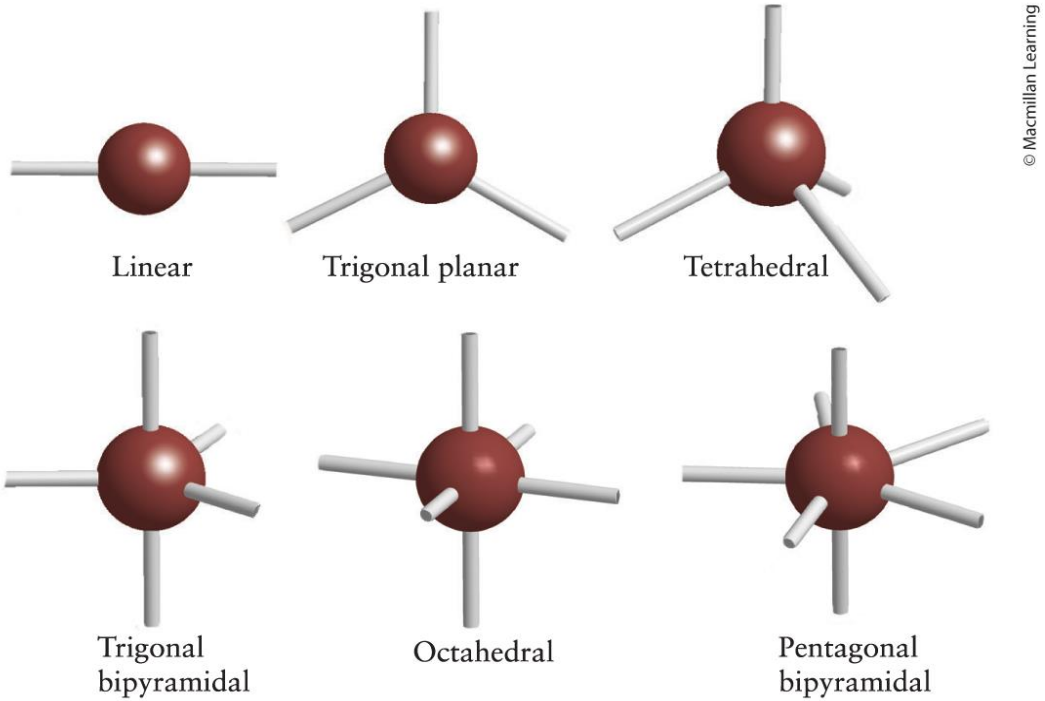




The basic VSEPR model

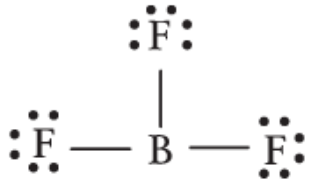
VSEPR theory states that shapes of molecules correspond to how (1) *electrons pairs* repel one another, and (2) that *electrons pairs* as far apart as possible

Rule 1. Regions of high electron density are either **bonding or lone pairs** which repel one another to minimize electron–electron repulsions.



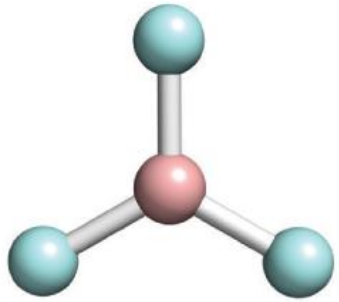
Example: arrangement of electron regions of BF_3

Lewis structure



2 Boron trifluoride, BF_3

BF_3 has *three electron regions*, therefore it has a trigonal planar shape of electron regions.



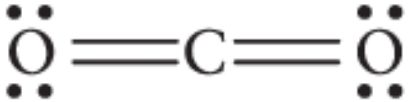
3 Boron trifluoride, BF_3

VSEPR 3D shape

VSEPR treats single and multiple bonds the same

Rule 2. Electron pairs in multiple bonds are treated the *same* as single bonds.

Lewis Structure



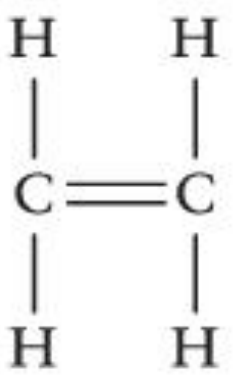
VSEPR 3D shape

9 Carbon dioxide, CO_2

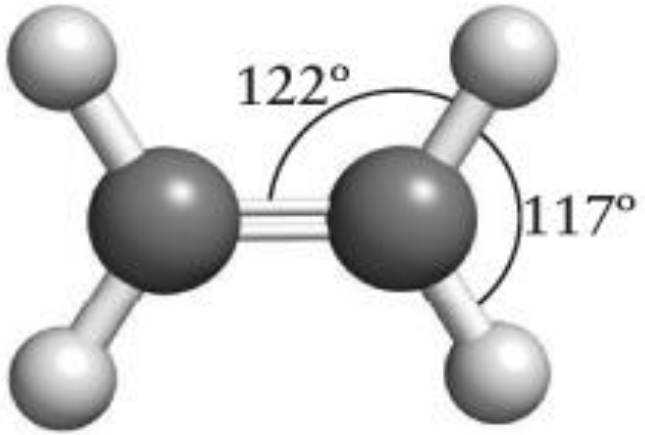
CO_2 has two electron regions, therefore it has a linear shape of electron regions.

VSEPR for molecules with multiple central atoms

When there is more than one central atom, we consider the bonding about each atom independently.



13 Ethene, C_2H_4

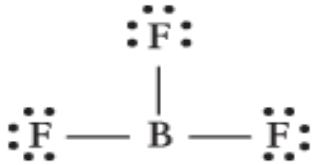


14 Ethene, C_2H_4

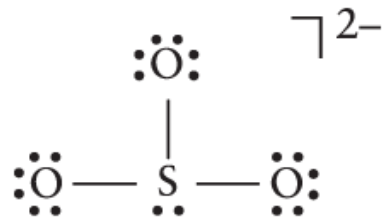
trigonal planar around each carbon atom

VSEPR for molecules with central atom lone pairs

- The generic VSEPR formula "AX_nE_m" helps identify bonding pair, and lone pairs attachments to the central atom
- "A" represent a central atom, "X" an attached atom, and "E" a lone pair.



AX_3



15 Sulfite ion, SO_3^{2-}

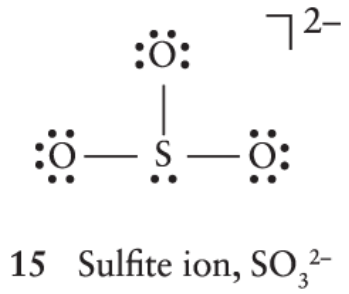
AX_3E

! Lone pairs also count for the geometry of the molecule

Electron Arrangement vs. Molecular Shape

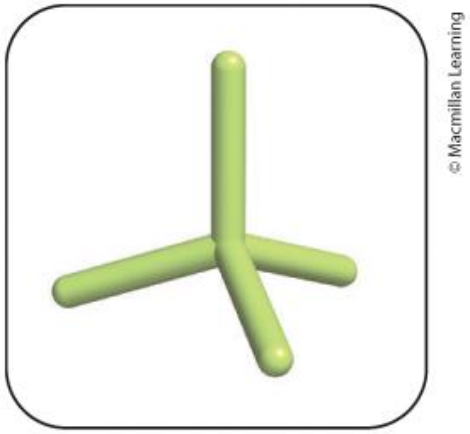
If lone pairs are present, the *molecular shape name* differs from the *electron arrangement name*.

Rule 3. The **molecular arrangement** only considers positions of **atoms** (not lone pairs) when reporting the *shape of a molecule*.

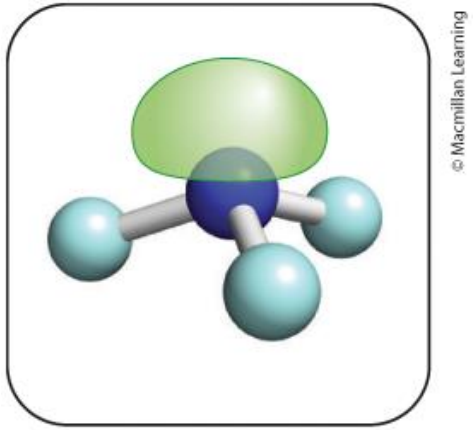


15 Sulfite ion, SO_3^{2-}

Lewis structure



Electron group
Tetrahedral



Molecular arrangement
Trigonal pyramidal

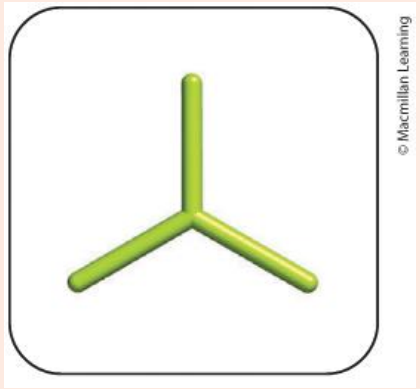
Lewis structure, VSEPR Electron Arrangement and molecular shape of O_3

Lewis structure, VSEPR Electron Arrangement and molecular shape of O_3

Draw the Lewis structure.

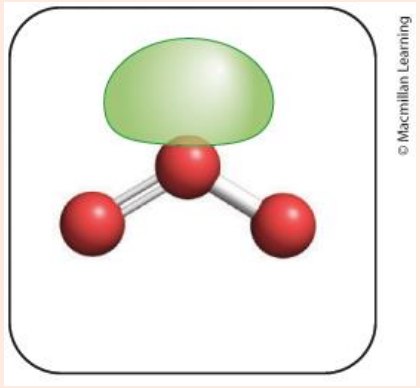
O_3

Count the bonds and lone pairs on the central atom. Draw the 3D shape. Assign the electron arrangement.



Trigonal planar

Identify the shape considering only atoms.



Angular or bent

Some consequences of molecular shapes

Is H_2O really polar? And CO_2?

Plan

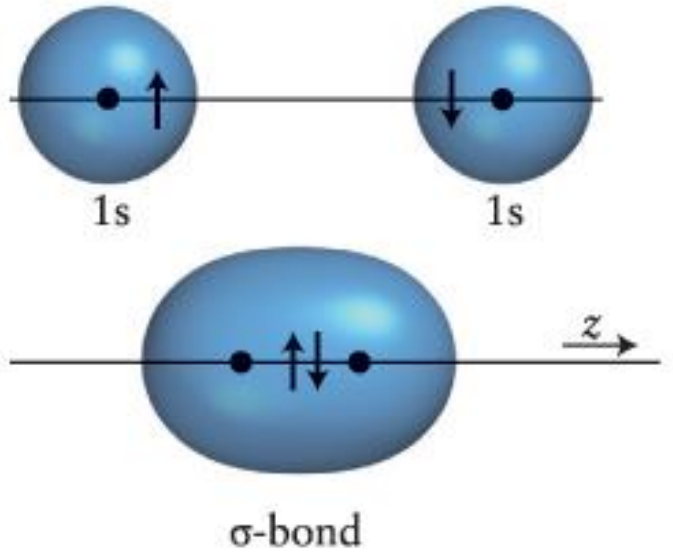
- Introduction
  - What is a chemical bond
  - What are the different types of bonds
- Lewis representation
  - Octet rule
  - Examples
  - Limitations
- Geometric representation (VSEPR)
- **Quantum approach**

Valence bond theory

- The lewis structures and VSEPR model are very useful qualitative models
- They cannot be used for calculations because they consider electrons as dot-like particles only
- **Valence bond theory** is a description of covalent bonding in terms of atomic orbitals, so taking their wave nature into account
- The idea is that molecular orbitals are hybrids of atomic orbitals
- This theory does not rely on experimental proof, but it explains chemistry well

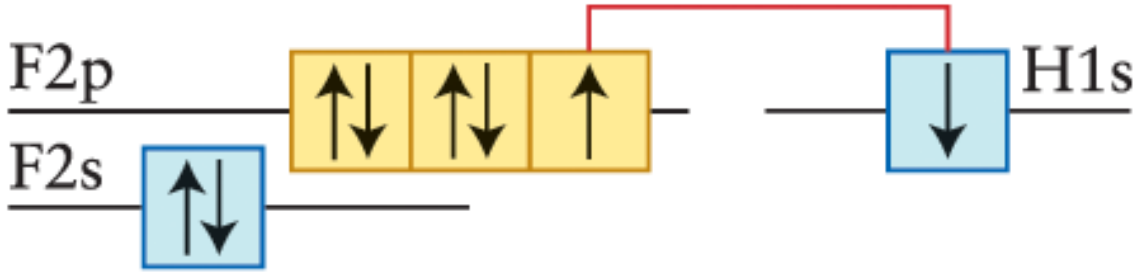
Sigma bonds

- The simplest molecule of all is H_2
- A “ground-state” hydrogen atom has one electron in a 1s-orbital
- As two H atoms come together, their 1s-electrons pair (denoted ↑↓) begin to overlap
- The resulting sausage-shaped distribution of electrons density is between the nuclei and called a **σ-bond** (a sigma bond).
- a σ-bond is **symmetrical and has no nodal plane**
- **= all single bonds**

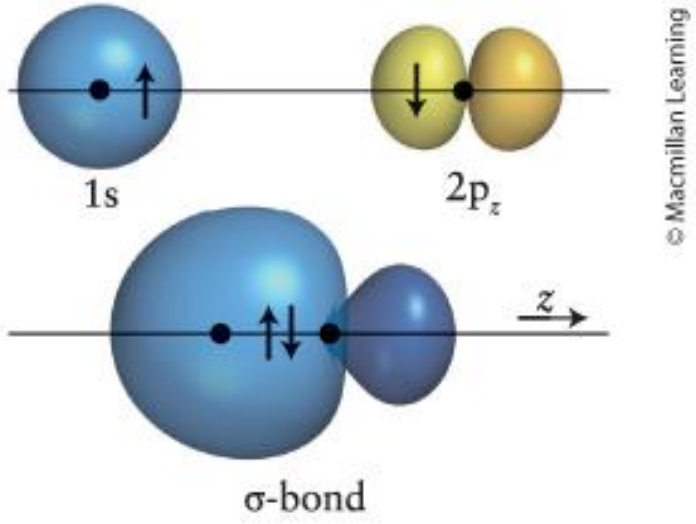


Sigma bonds

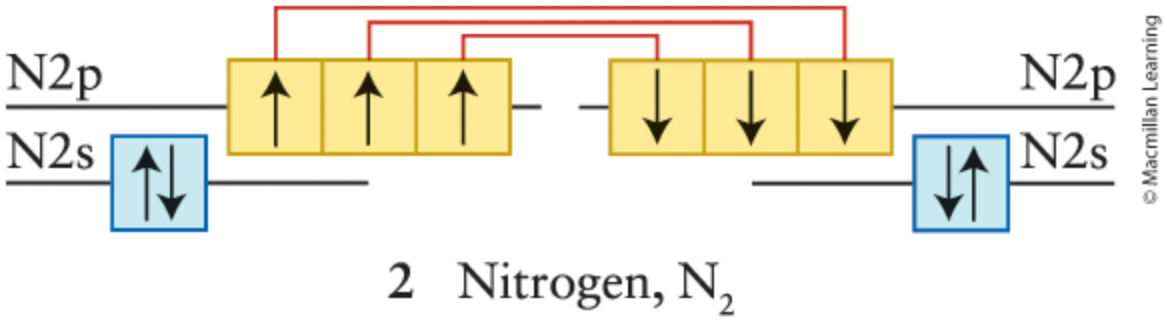
- F has an unpaired electron atom in the $2p_z$-orbital. Hydrogen has an unpaired electron in the 1s-orbital.
- The orbitals **overlap** and merge into a cloud that spreads over both atoms.

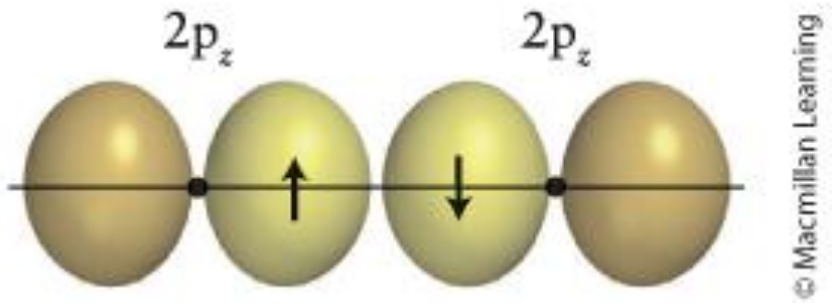


1 Hydrogen fluoride, HF

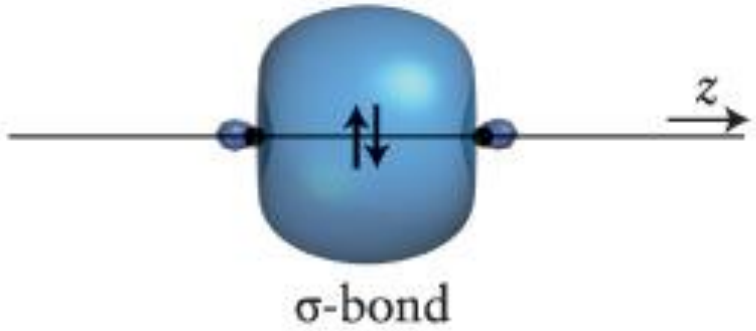


Sigma bonds

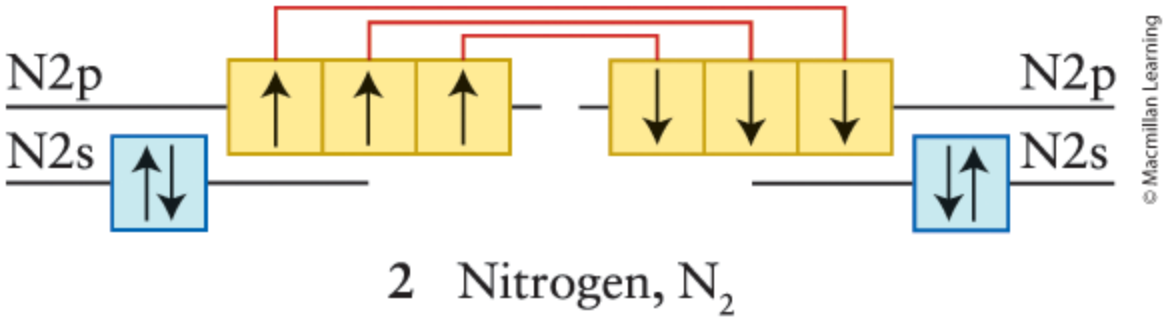




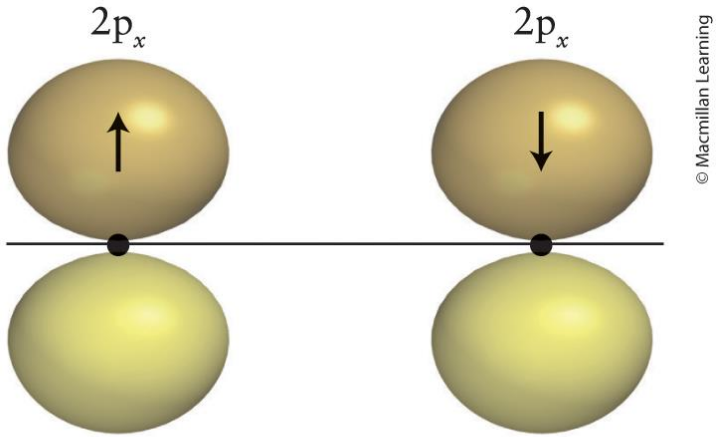
- There is a single electron in each three 2p-orbital
- However, due to bond angles, only one of the three orbitals overlaps end-to-end to form a σ-bond.



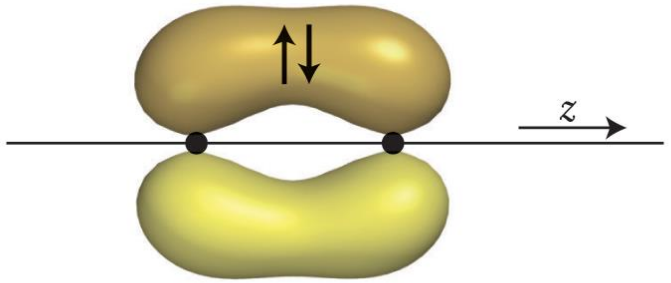
Pi bonds



2 Nitrogen, N_2

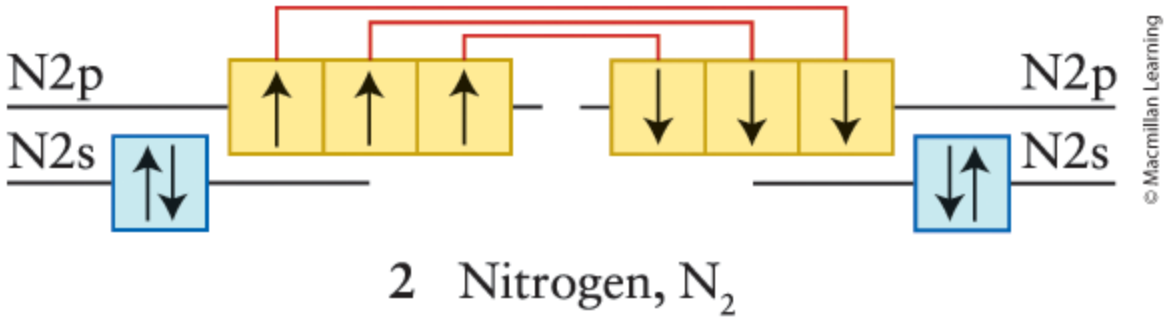


- The other two 2p-orbitals ($2p_x$ and $2p_y$) are perpendicular t internuclear axis.
- These p-orbitals can overlap only in a side-by-side arrangement.
- This overlap results in a **π-bond**.
- A π-bond has **a single nodal plane containing the internuclear axis**

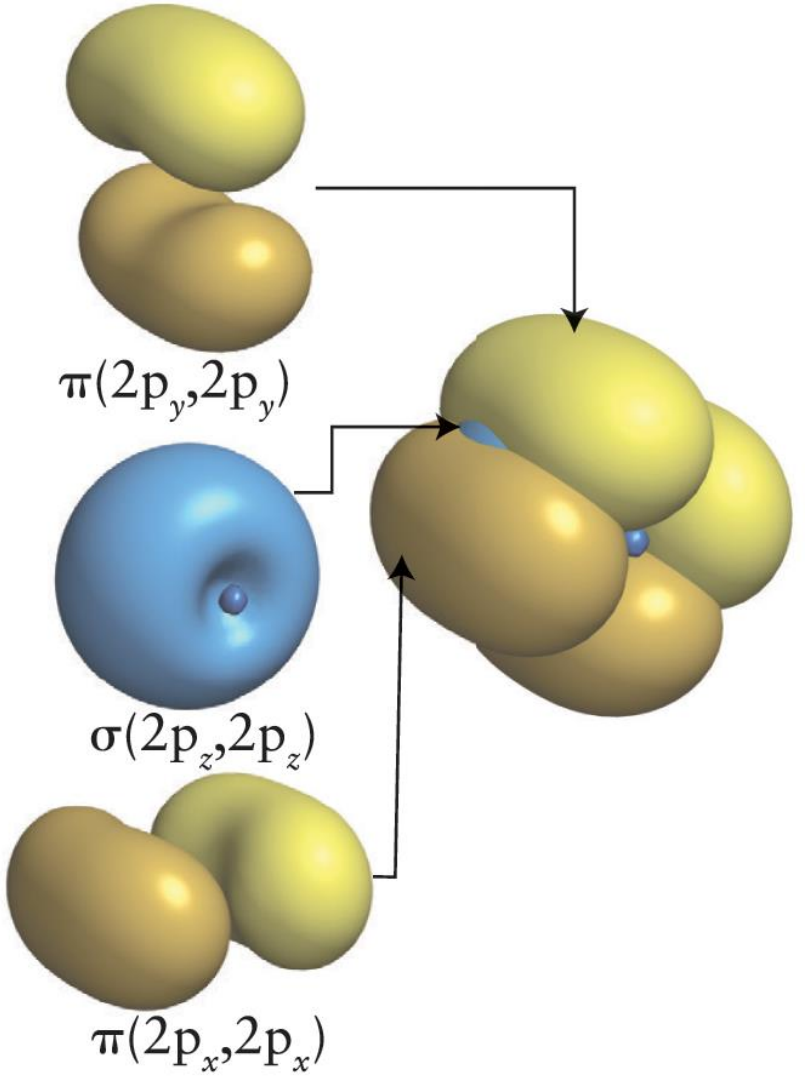


π-bond

Pi bonds

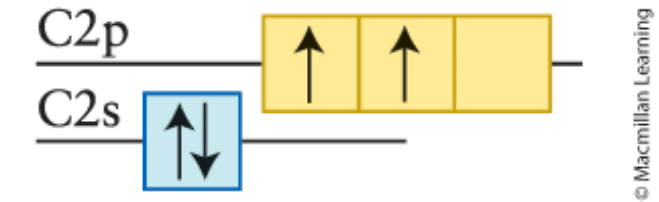


Two π-bonds merge forming a long doughnut-shaped cloud surrounding the σ-bond cloud, resembling a cylindrical hot dog.

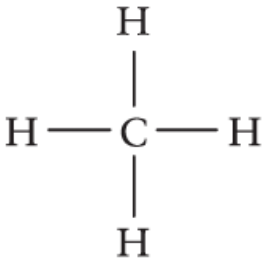


Exceptions in VB theory – orbitals hybridization (for some atoms, not all of them!)

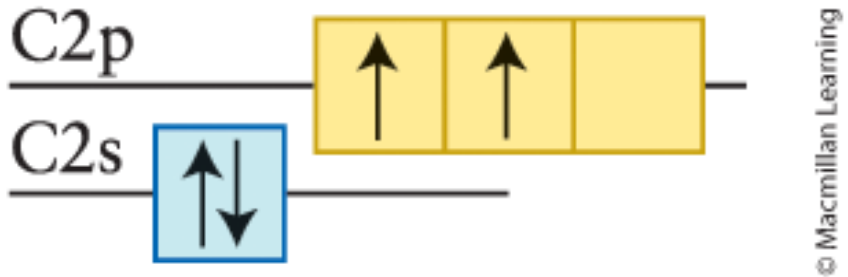
- Orbital hybridization is important for **C, N, O, B, Be, P, S, and transition metals** when they form covalent bonds. It is **not universal** but is most useful for **atoms that need specific molecular geometries**.
- A carbon atom has an electron configuration $[He]2s^2 2p_x^1 2p_y^1$ with four valence electrons.
- It looks as though a carbon atom should have a valence of 2 and form only two perpendicular bonds.
- However, it always has a valence of 4 (it is commonly "tetravalent").



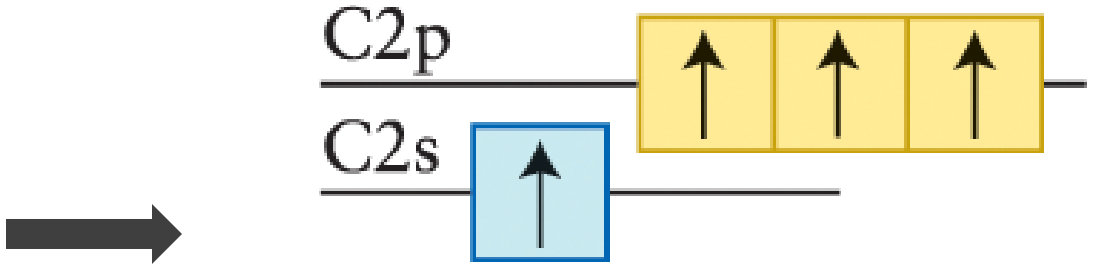
3 Carbon, $[He]2s^2 2p_x^1 2p_y^1$



Electron promotions

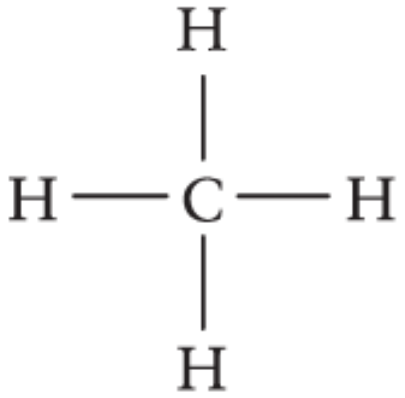


3 Carbon, $[He]2s^2 2p_x^1 2p_y^1$



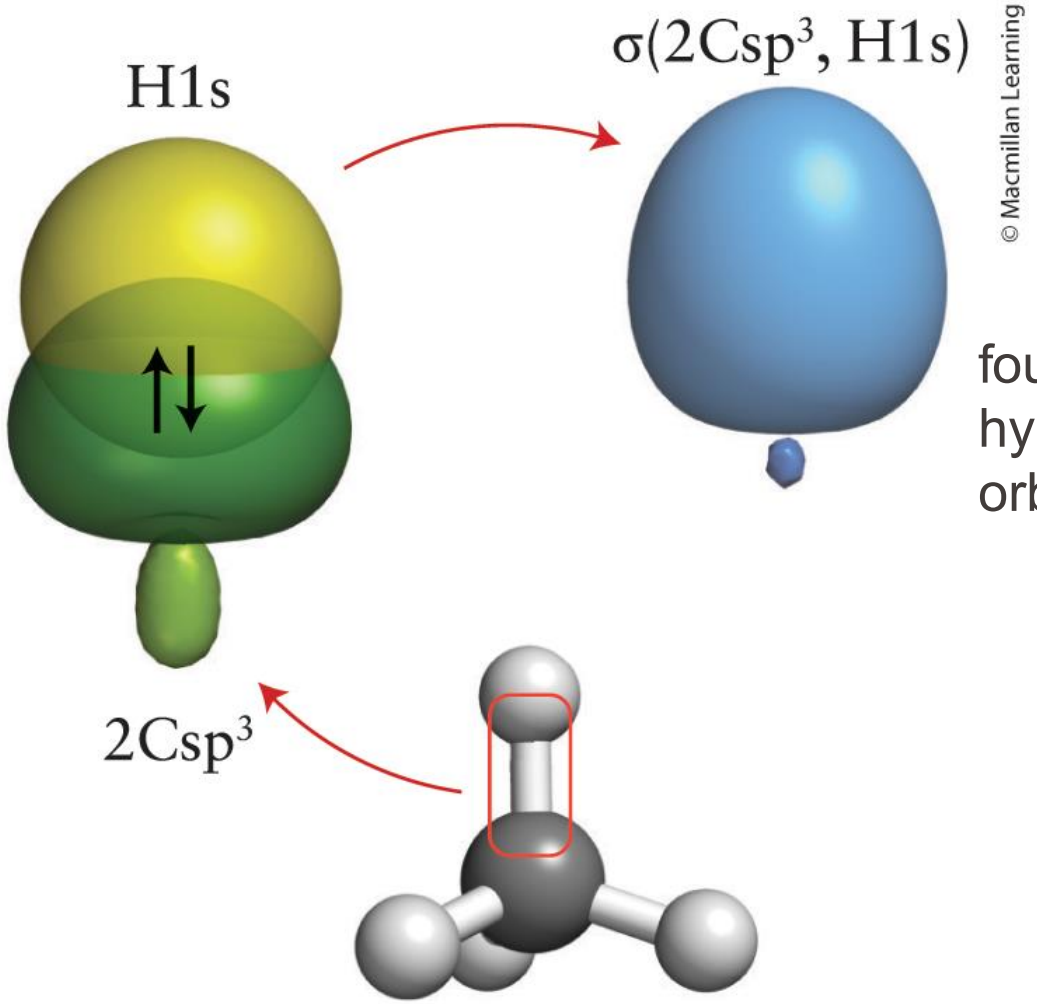
4 Carbon, $[He]2s^1 2p_x^1 2p_y^1 2p_z^1$

To overcome this, we match theory with our observation that carbon is tetravalent by promoting a 2s-electron into an empty 2p-orbital and we get $[He]2s^1 2p_x^1 2p_y^1 2p_z^1$.



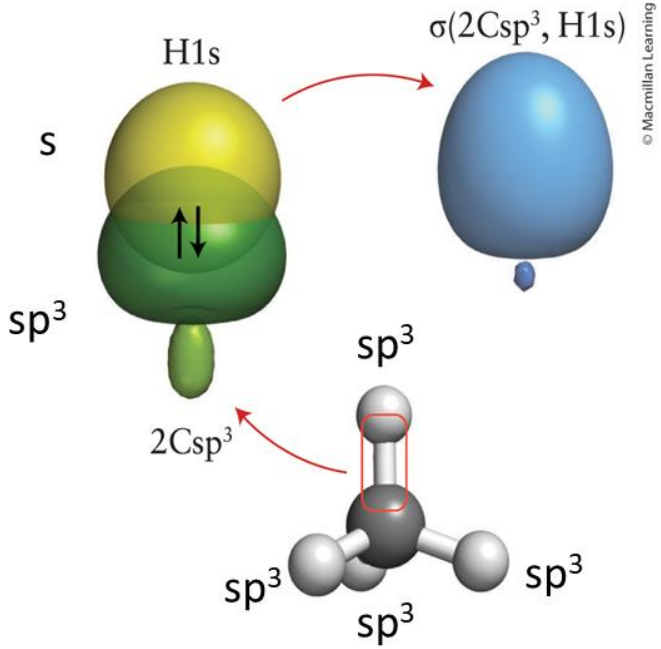
Hybrid orbitals

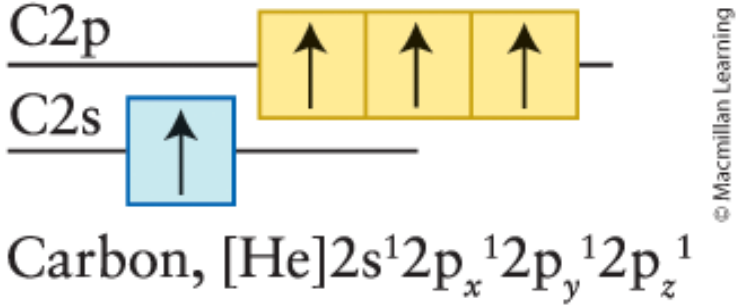
- To explain that the structure of methane is tetrahedral, we have to think of orbitals as waves of electron densities that can interfere with each other
- The wavefunctions overlap (with either positive or negative amplitudes) and constructively reinforce each other = **hybridization**



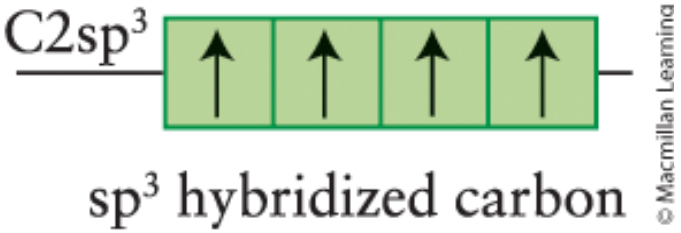
Hybrid orbitals names

Each of the four **hybrid orbitals** is formed from a **linear combination** of the four original **atomic** orbitals:





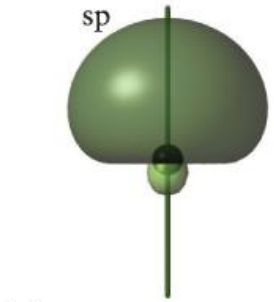
Atomic orbitals



Hybrid orbitals

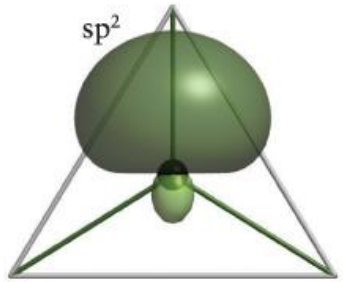
An **sp³ hybrid orbital** is a type of **hybrid atomic orbital** formed when **one s orbital** and **three p orbitals** from the same atom mix together to create **four equivalent orbitals**.

Linear, Trigonal Planar, and Tetrahedral Hybrid σ-Bonds



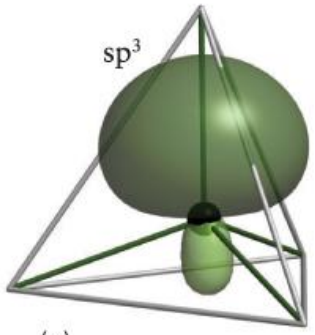
(a)

(a) An s-orbital and p-orbital hybridize into 2 sp hybrid orbitals that point in opposite directions, forming a linear molecular shape.



(b)

(b) An s-orbital and two p-orbitals come together to give 3 sp^2 hybrid orbitals.



(c)

(c) An s-orbital and three p-orbitals come together to give 4 sp^3 hybrid orbitals.

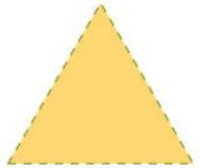
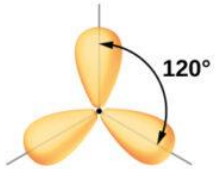
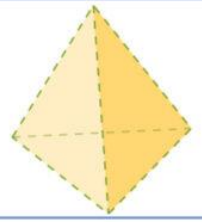
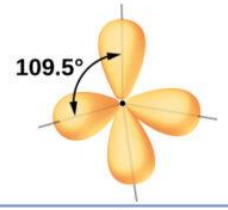
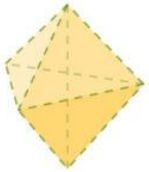
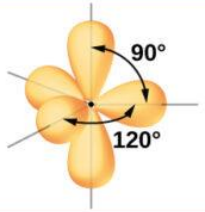
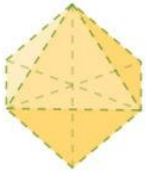
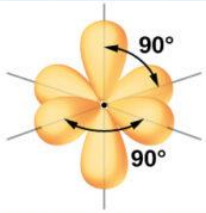
Link with VSEPR: AX_nE_m

If n+m=4 (AX_4, AX_3E_1, AX_2E_2): hybridization sp^3

If n+m=3 (AX_3, AX_2E_1, AX_1E_2): hybridization sp^2

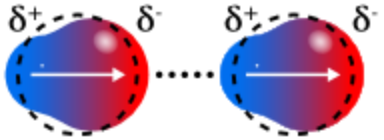
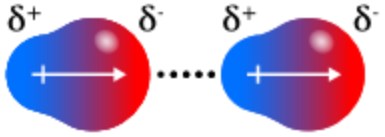
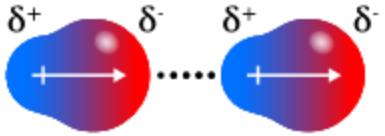
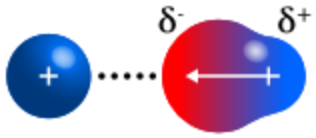
Examples of methane, ethene and ethyne

Recap

Regions of Electron Density	Arrangement		Hybridization	
2		linear	*sp*	
3		trigonal planar	sp^2	
4		tetrahedral	sp^3	
5		trigonal bipyramidal	sp^3d	
6		octahedral	sp^3d^2	

https://chem-textbook.ucalgary.ca/version2/chapter-8-main/hybrid-atomic-orbitals/assignment-of-hybrid-orbitals-to-central-atoms/

Recap

Types of Intermolecular Forces	Present In	Molecular Perspective	Strength
Dispersion*	All molecules and atoms		0.05-40 kJ/mol
Dipole-Dipole	Polar molecules		5-25 kJ/mol
Hydrogen Bonding	Molecules containing H bonded to F, O, or N		10-40 kJ/mol
Ion Dipole	Mixtures of ionic compounds and polar compounds		40-600 kJ/mol

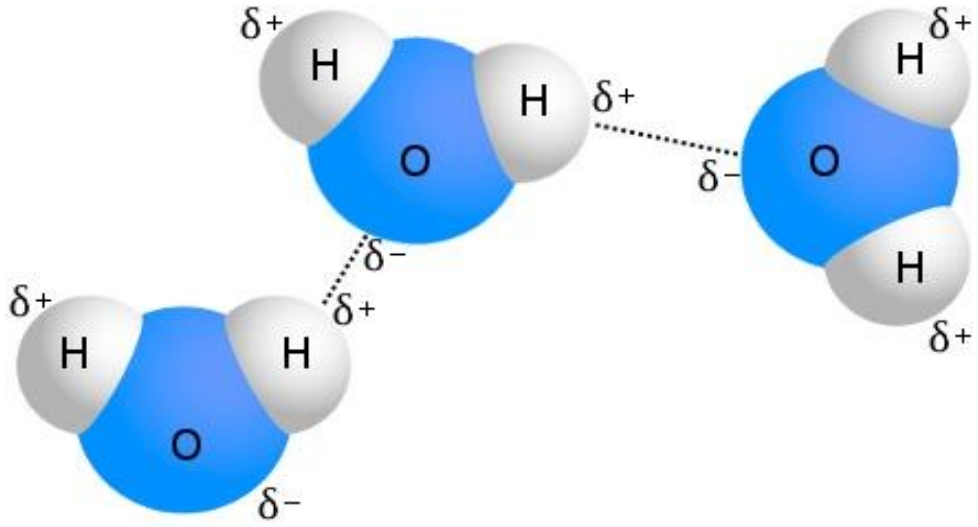
*Dispersion forces can become very strong (as strong and even stronger than the others) for molecules of high molar mass.

https://pressbooks.online.ucf.edu/chemistryfundamentals/chapter/intermolecular-forces/

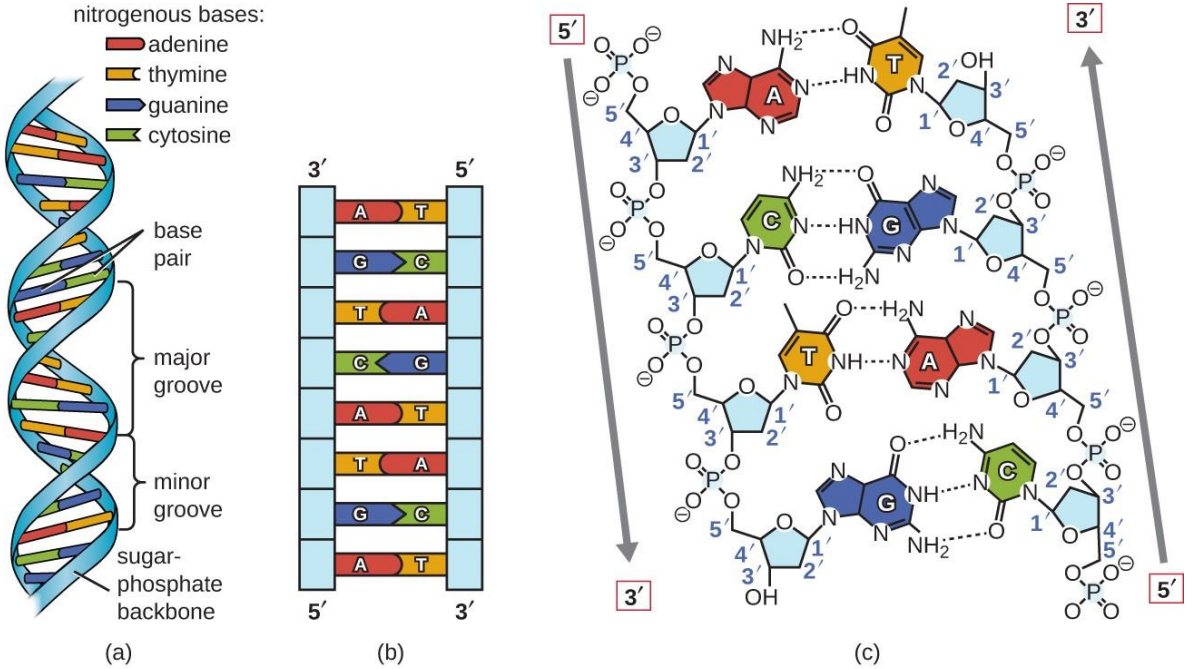
Hydrogen bonds

- Happens when a hydrogen atom is placed between 2 very electronegative atoms
- Only F, O and N are small and electronegative enough for such bonds

In water



In DNA



Have a beautiful day, see you at the exam ☺ + Lecture next Tuesday!