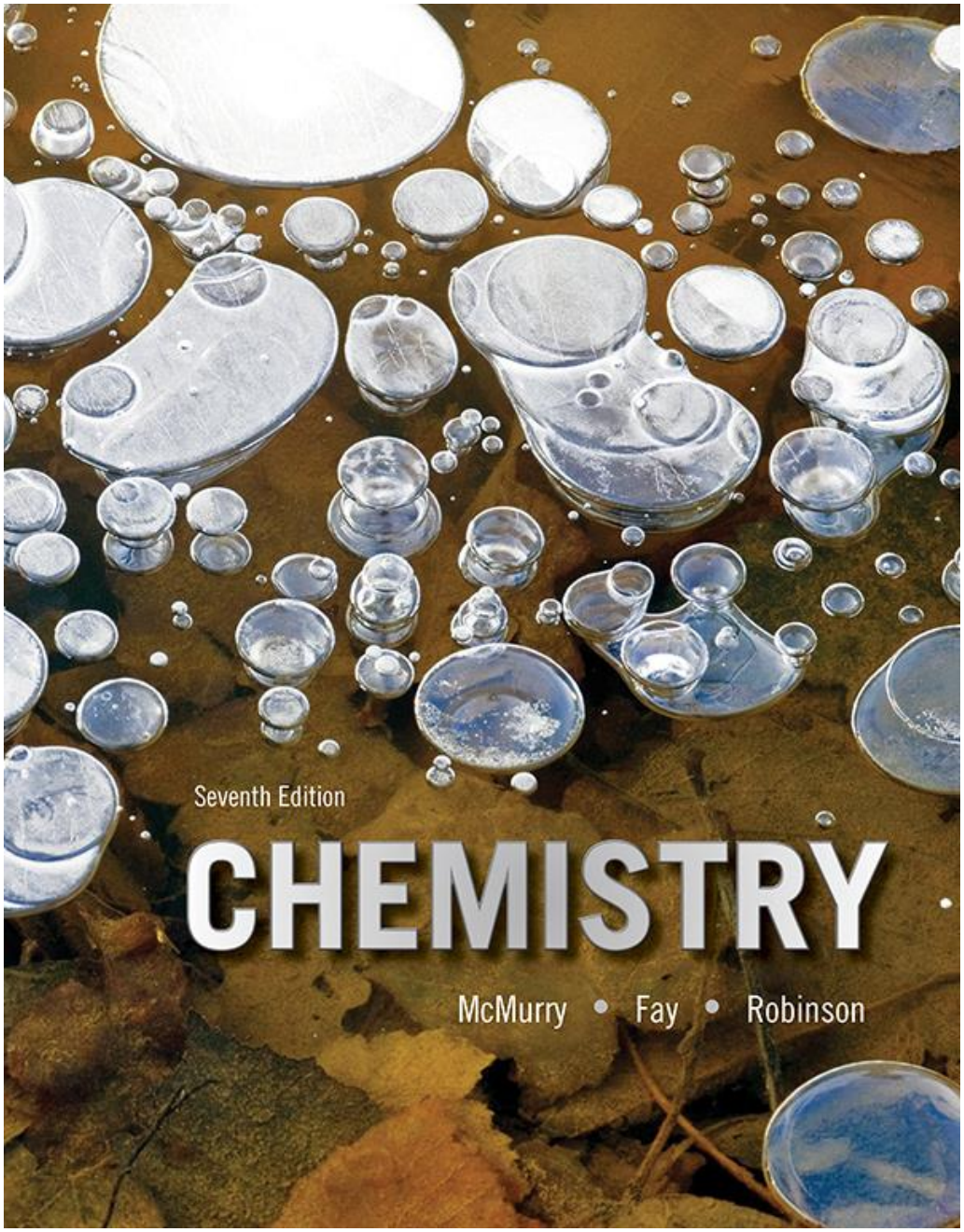


Lecture Presentation

Chapter 8

Covalent Compounds: Bonding Theories and Molecular Structure

John E. McMurry
Robert C. Fay

Instructor's Resource Materials (Download only) for *Chemistry,* 7e
John E. McMurry, Robert C. Fay, Jill Robinson

Molecular Shapes: The VSEPR Model

Step 1

- Write an electron-dot structure for the molecule, and count the number of electron charge clouds surrounding the atom of interest.

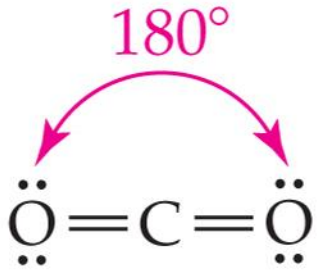
Step 2

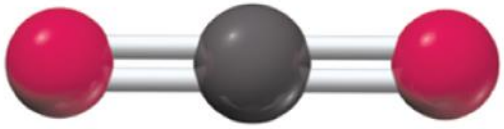
- Predict the geometric arrangement of charge clouds by assuming that the charge clouds are oriented in space as far away from one another as possible.

Molecular Shapes: The VSEPR Model

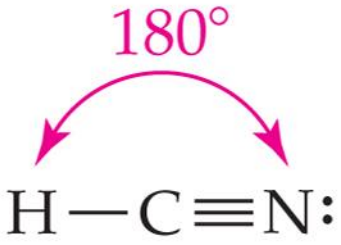
Two Charge Clouds

A CO_2 molecule is linear, with a bond angle of 180°.



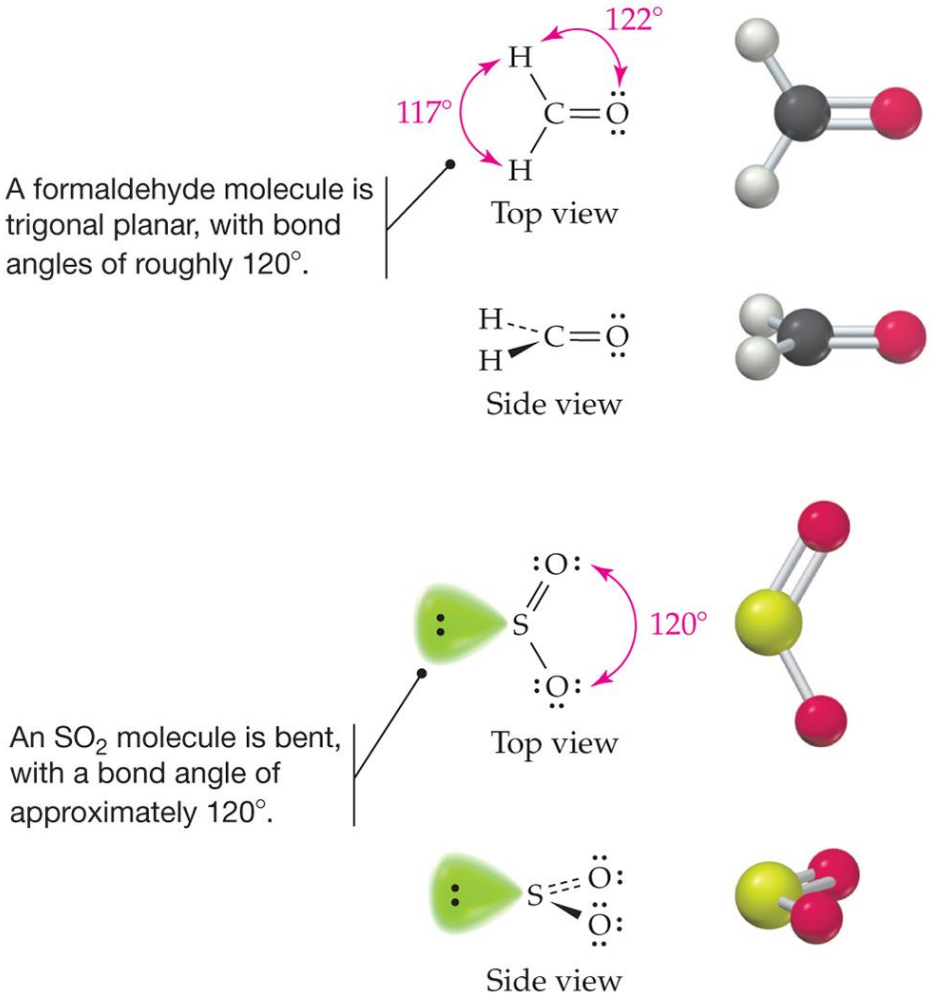


An HCN molecule is linear, with a bond angle of 180°.



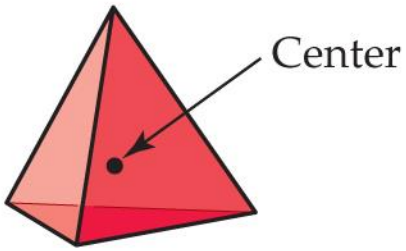
Molecular Shapes: The VSEPR Model

Three Charge Clouds



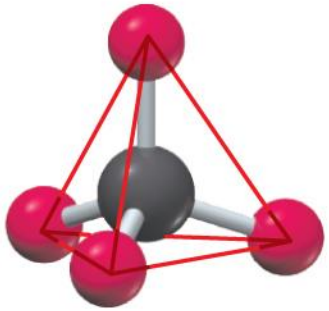
Molecular Shapes: The VSEPR Model

Four Charge Clouds

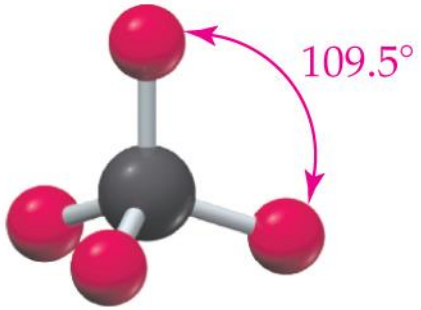


A regular tetrahedron

The atom is located in the **center** of a regular tetrahedron.



The four charge clouds point to the **four corners** of the tetrahedron.



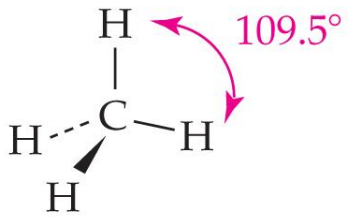
A tetrahedral molecule

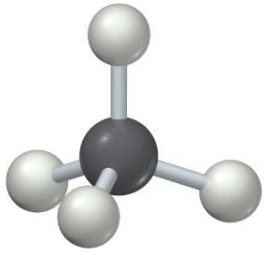
The angle between any two bonds is 109.5°.

Molecular Shapes: The VSEPR Model

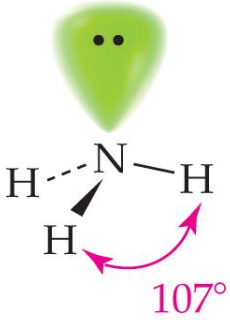
Four Charge Clouds

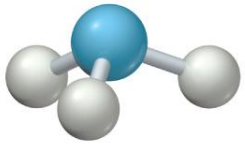
A methane molecule is tetrahedral, with bond angles of 109.5°.



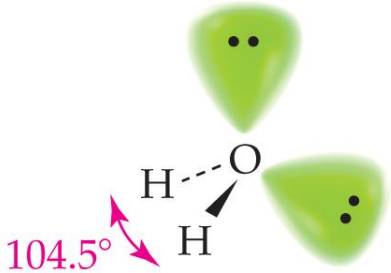


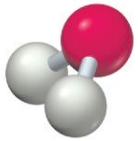
An ammonia molecule is trigonal pyramidal, with bond angles of 107°.





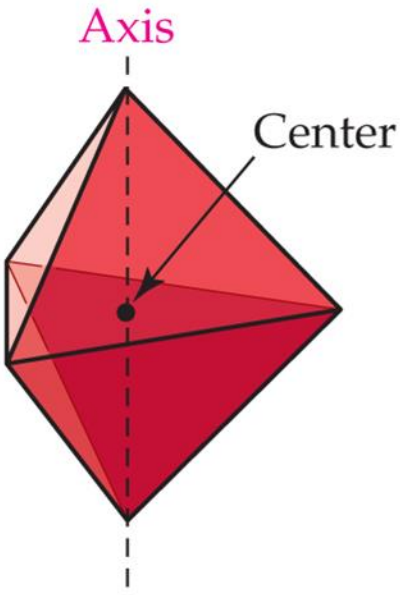
A water molecule is bent, with a bond angle of 104.5°.



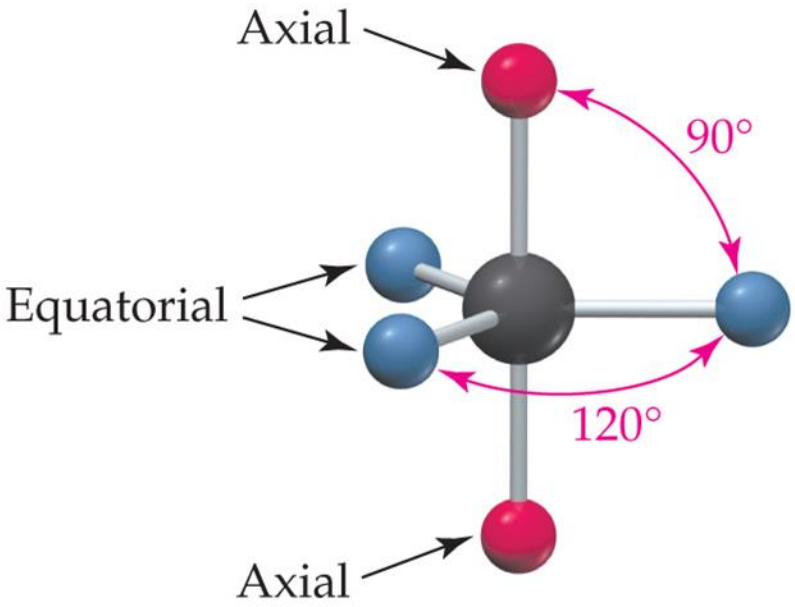


Molecular Shapes: The VSEPR Model

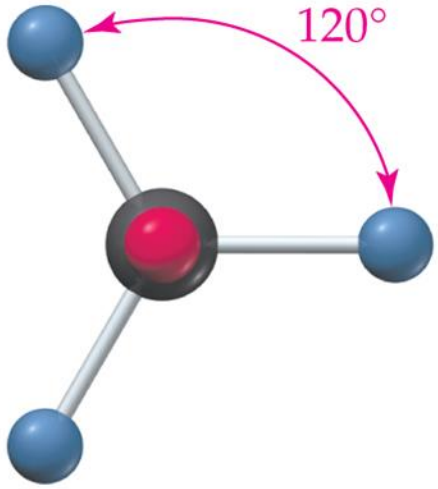
Five Charge Clouds



A trigonal bipyramid



Side view

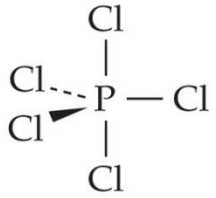


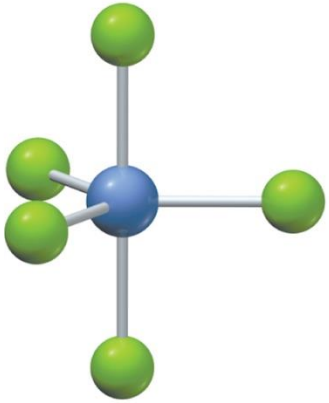
Top view

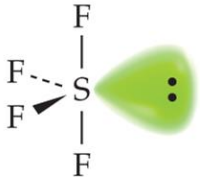
Molecular Shapes: The VSEPR Model

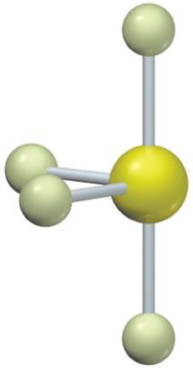
Five Charge Clouds

A PCl_5 molecule is trigonal bipyramidal.









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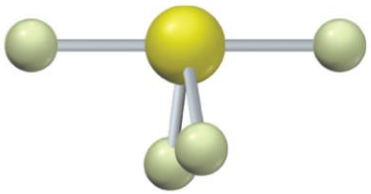
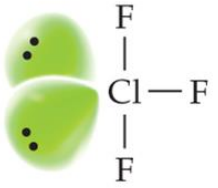


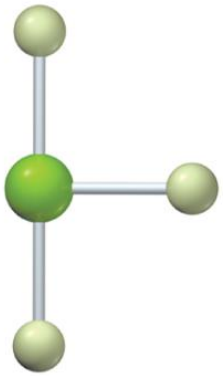
In this orientation, an SF_4 molecule takes on a shape like a seesaw.

Molecular Shapes: The VSEPR Model

Five Charge Clouds

A ClF_3 molecule is T-shaped.





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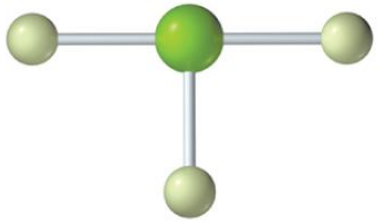
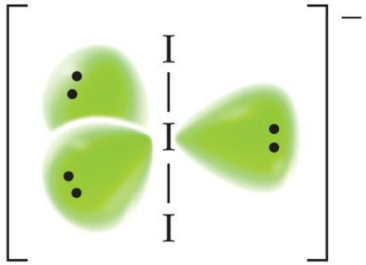
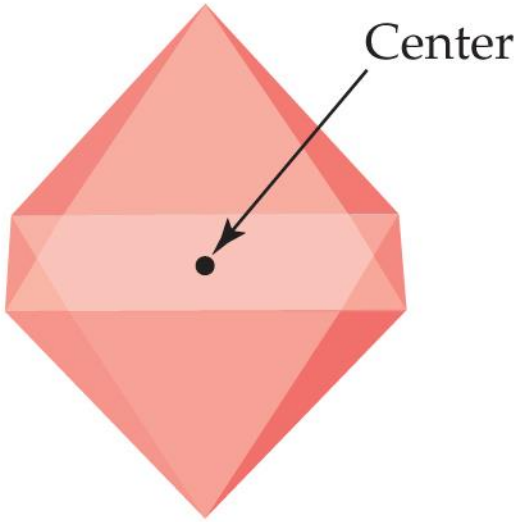


An I_3^- ion is linear.

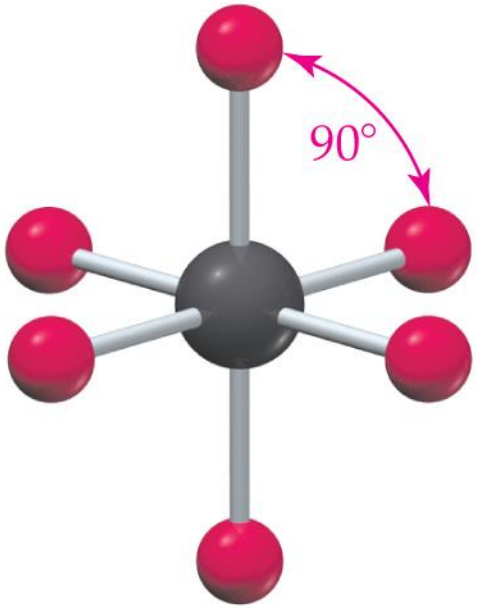


Molecular Shapes: The VSEPR Model

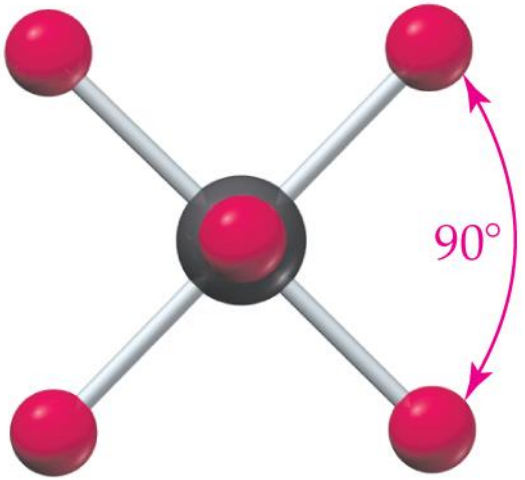
Six Charge Clouds



A regular octahedron



Side view

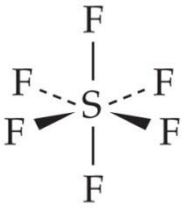


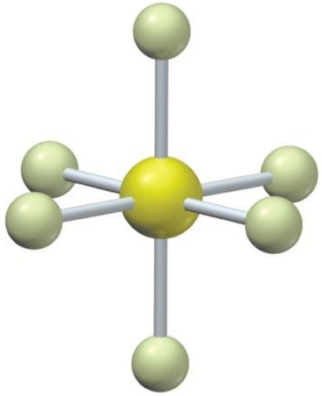
Top view

Molecular Shapes: The VSEPR Model

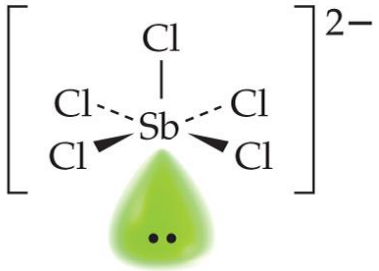
Six Charge Clouds

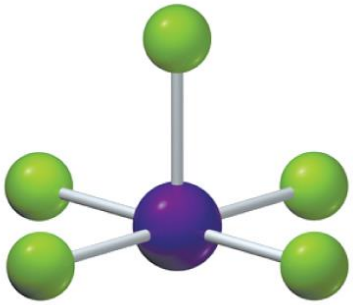
An SF_6 molecule is octahedral.





An $SbCl_5^{2-}$ ion has a square pyramidal shape.

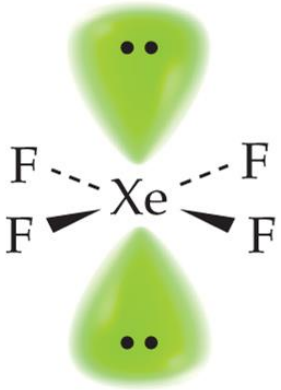




Molecular Shapes: The VSEPR Model

Six Charge Clouds

An XeF_4 molecule has a square planar shape.



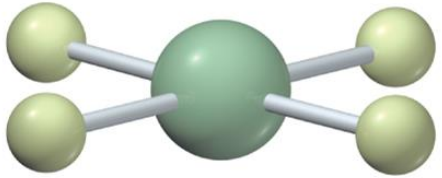
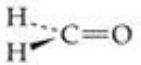
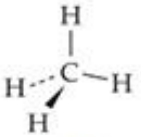
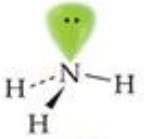
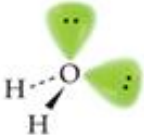
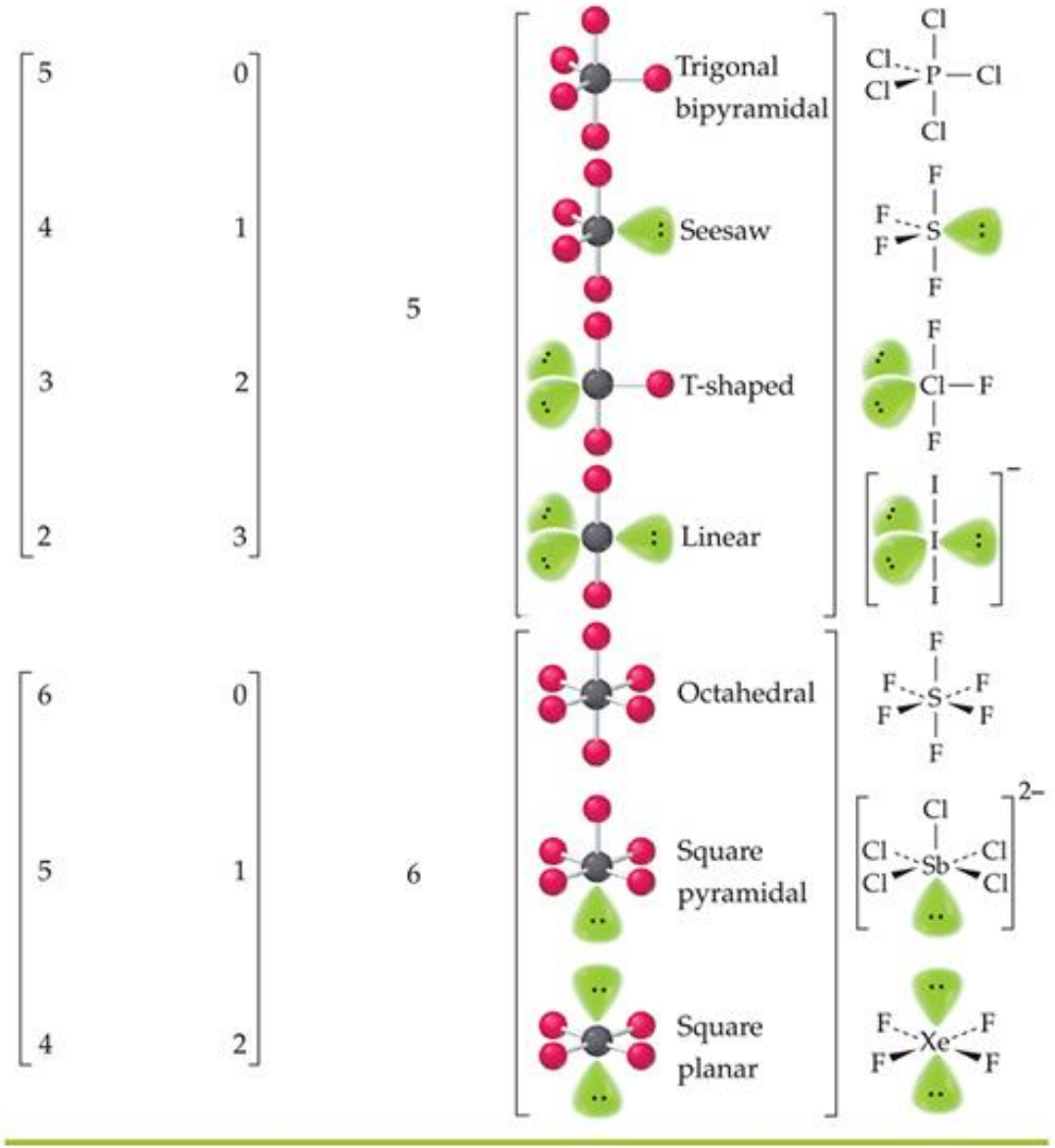


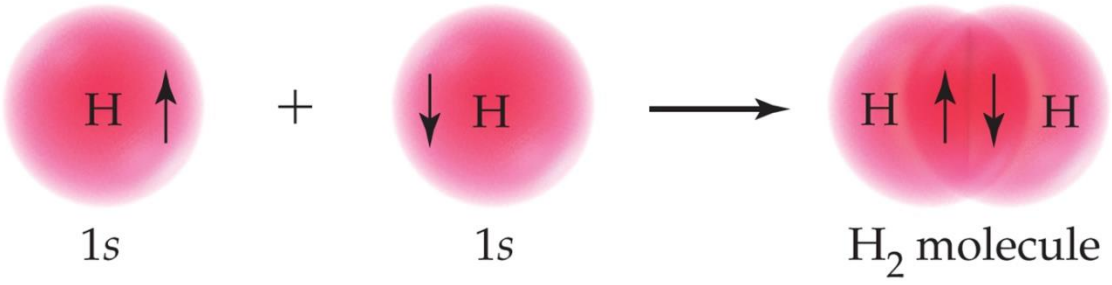
TABLE 8.1 Geometry Around Atoms with 2, 3, 4, 5, and 6 Charge Clouds

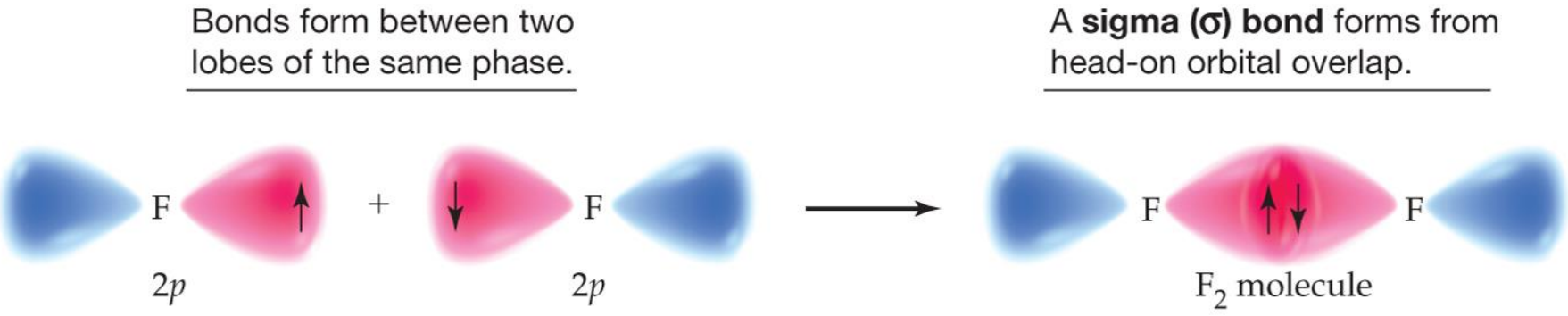
Number of Bonds	Number of Lone Pairs	Number of Charge Clouds	Geometry and Shape	Example
2	0	2	 Linear	
3	0	3	 Trigonal planar	
2	1		 Bent	
4	0	4	 Tetrahedral	
3	1		 Trigonal pyramidal	
2	2		 Bent	



Valence Bond Theory

Valence Bond Theory: A quantum mechanical model that shows how electron pairs are shared in a covalent bond





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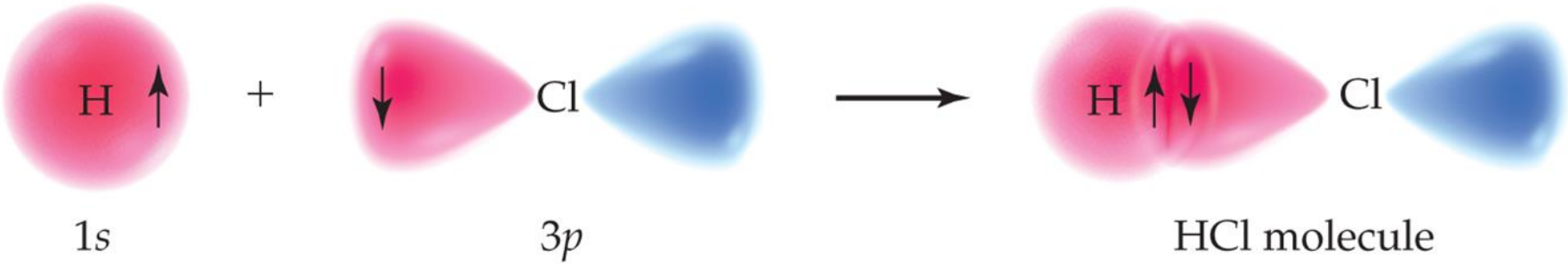


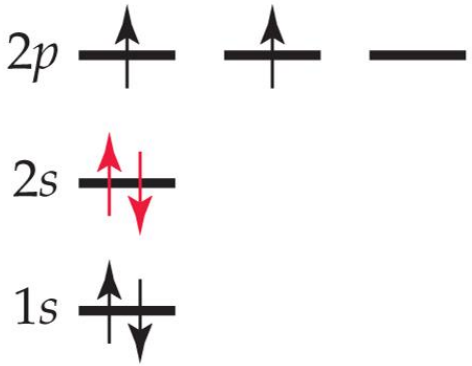
Valence Bond Theory

- Covalent bonds are formed by overlap of atomic orbitals, each of which contains one electron of opposite spin.
- Each of the bonded atoms maintains its own atomic orbitals, but the electron pair in the overlapping orbitals is shared by both atoms.
- The greater the amount of overlap, the stronger the bond.

Hybridization and sp^3 Hybrid Orbitals

How can the bonding in CH_4 be explained?

4 valence electrons
2 unpaired electrons

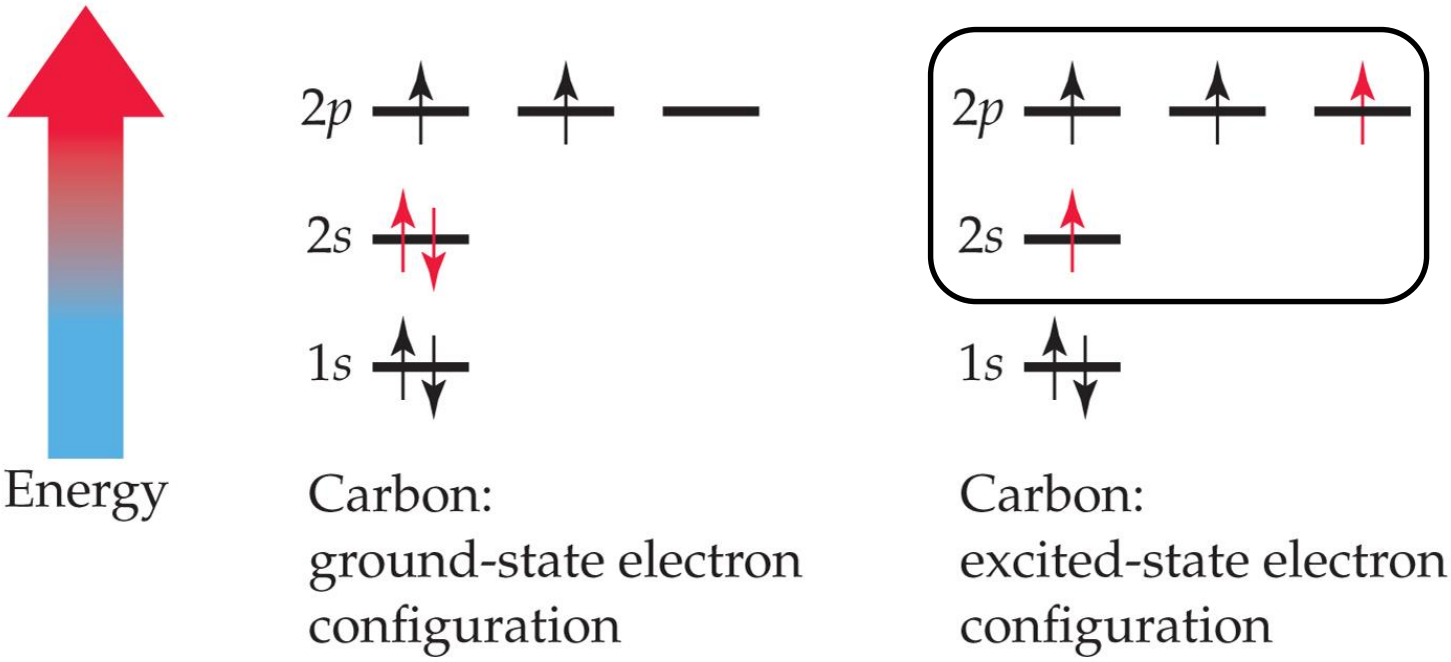


Carbon:
ground-state electron
configuration

Hybridization and sp^3 Hybrid Orbitals

How can the bonding in CH_4 be explained?

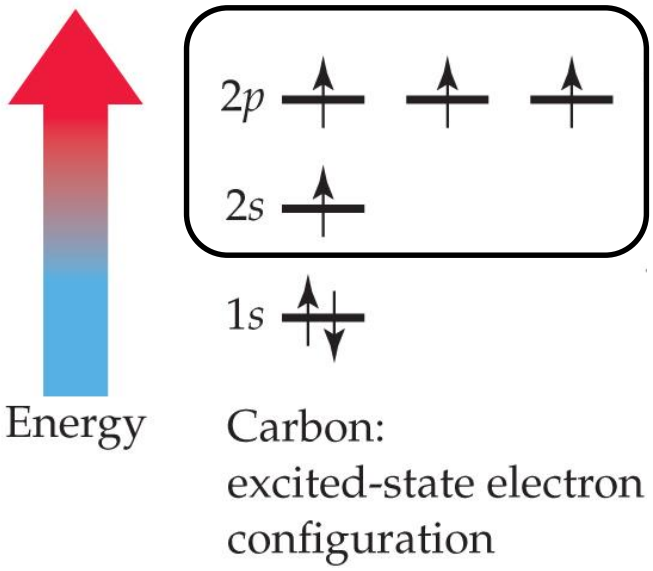
4 valence electrons
2 unpaired electrons



Hybridization and sp^3 Hybrid Orbitals

How can the bonding in CH_4 be explained?

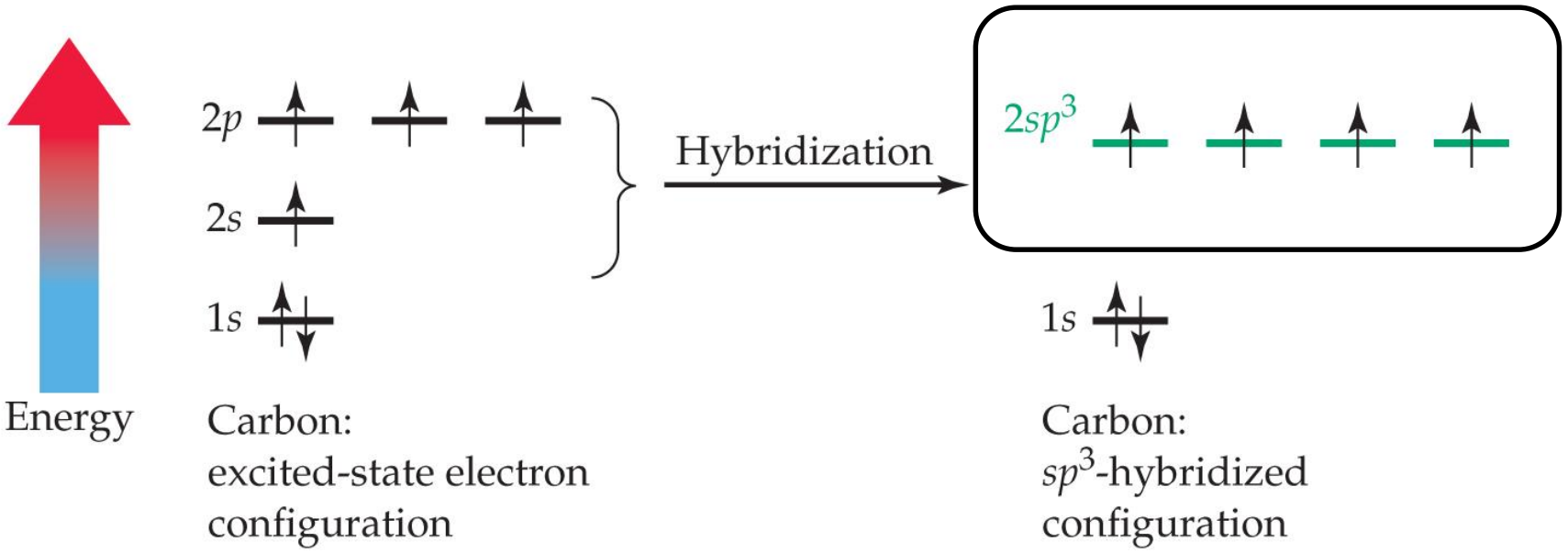
4 **nonequivalent** orbitals



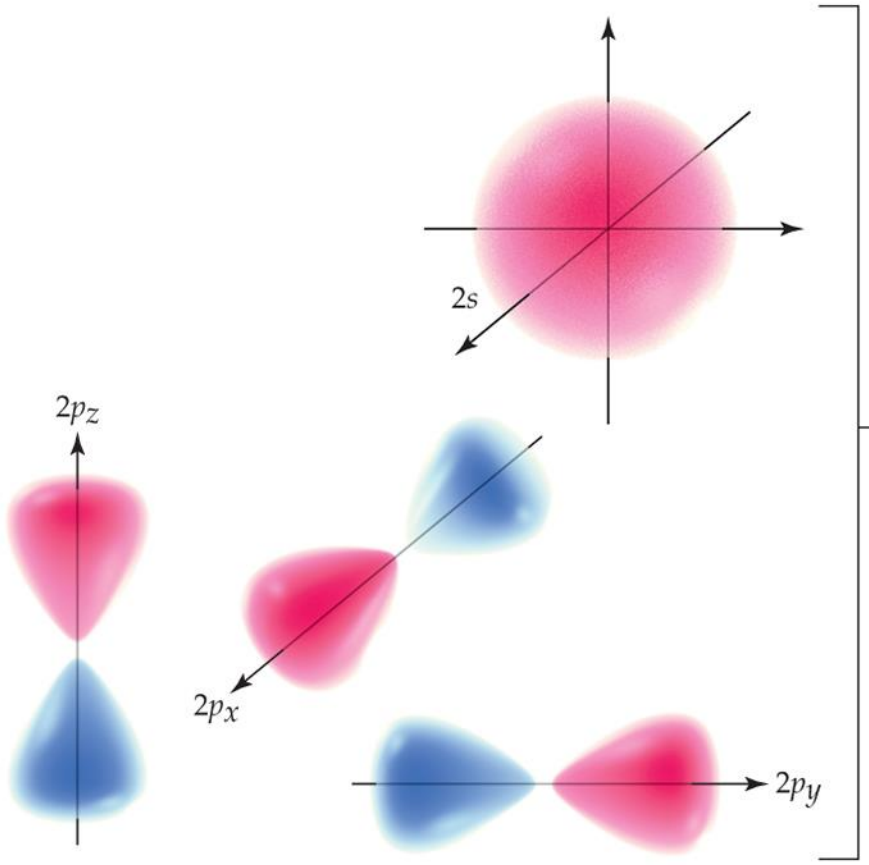
Hybridization and sp^3 Hybrid Orbitals

How can the bonding in CH_4 be explained?

4 **equivalent** orbitals



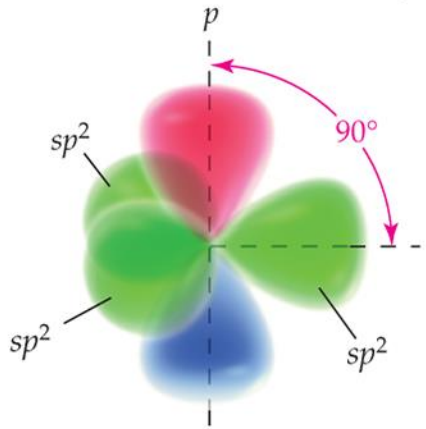
Hybridization and sp^3 Hybrid Orbitals



Hybridization

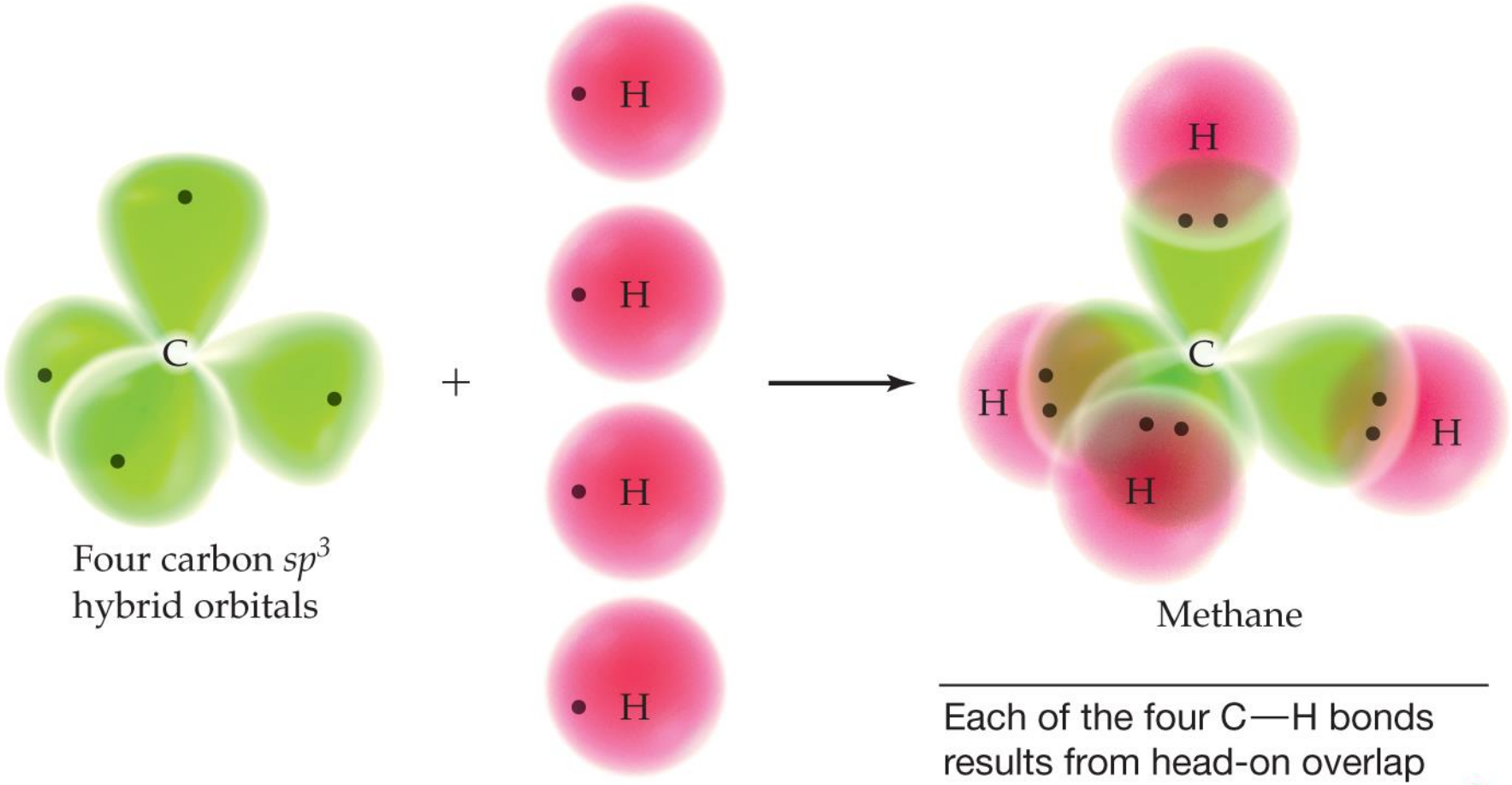
An sp^2 hybrid orbital has two lobes of different phase, one of which is larger than the other.

An sp^2 orbital



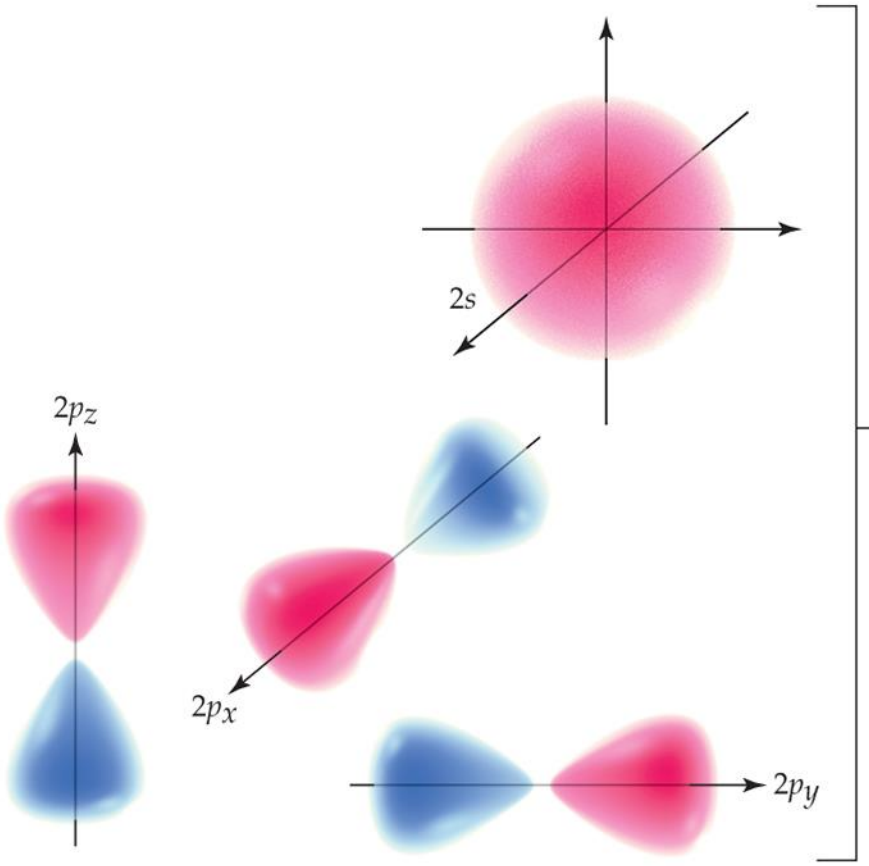
The hybrid orbitals lie in a plane at angles of 120° to one another, and one unhybridized *p* orbital remains, oriented at a 90° angle to the sp^2 hybrids. The large lobes of the hybrid orbitals are shown in green, and the small lobes are not shown.

Hybridization and sp^3 Hybrid Orbitals



Each of the four C—H bonds results from head-on overlap of a singly occupied **carbon sp^3 hybrid orbital** with a singly occupied **hydrogen 1s orbital**.

Other Kinds of Hybrid Orbitals



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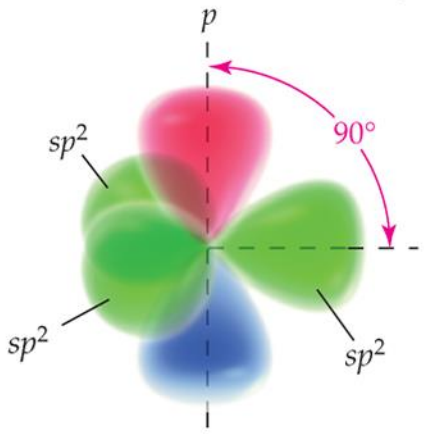
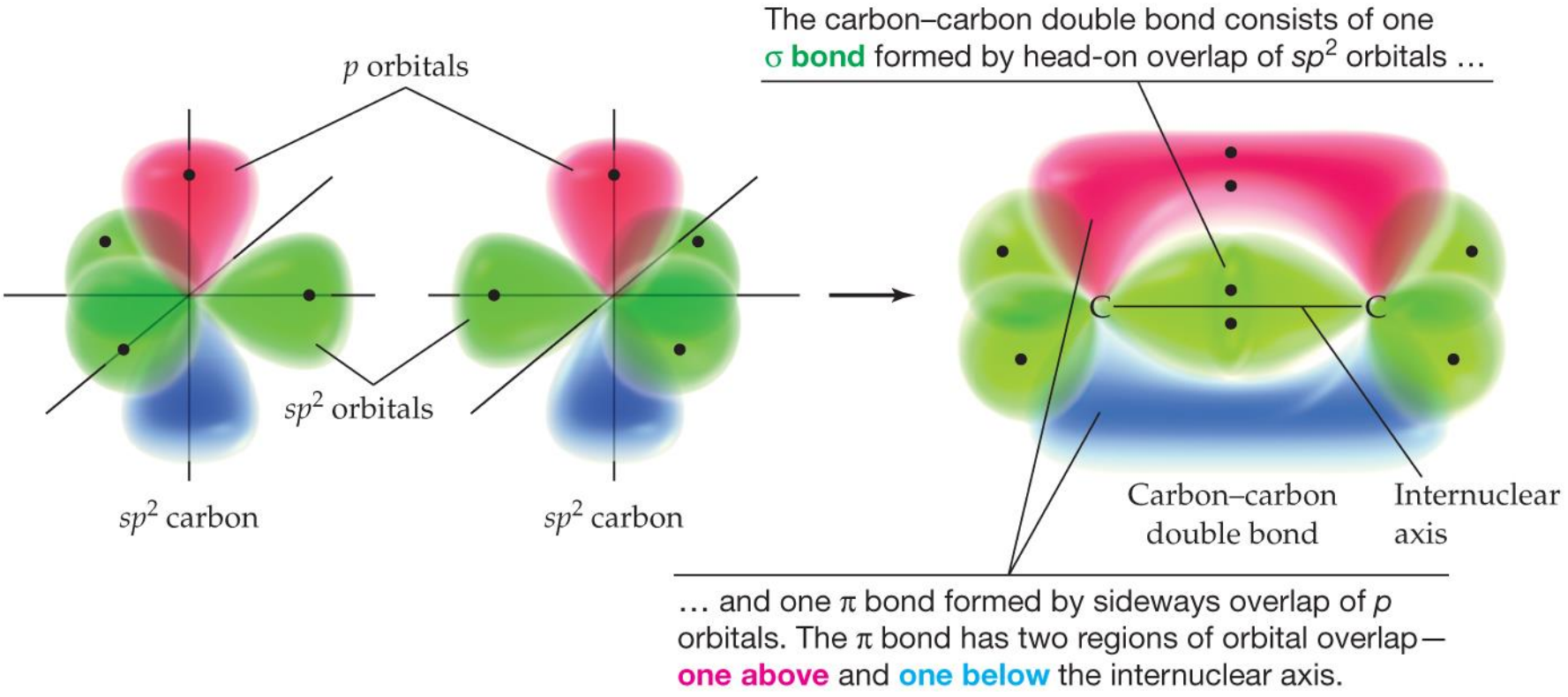
An sp^2 orbital



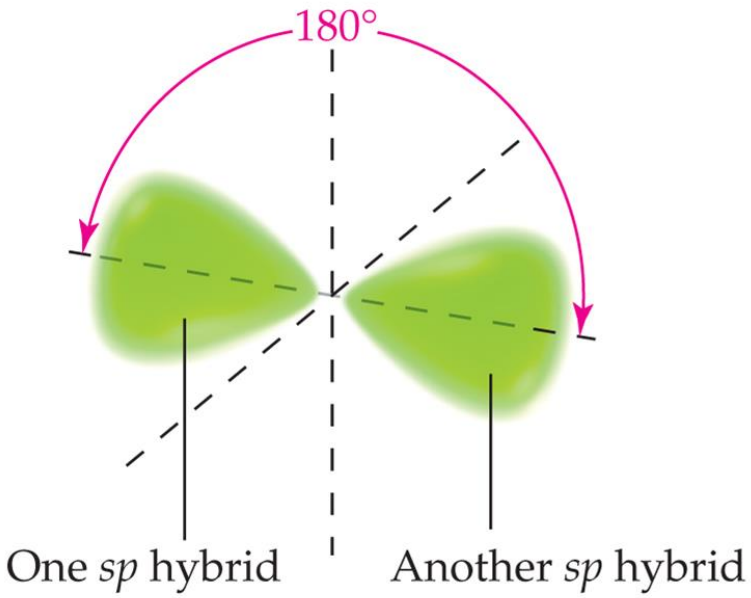
The hybrid orbitals lie in a plane at angles of 120° to one another, and one unhybridized *p* orbital remains, oriented at a 90° angle to the sp^2 hybrids. The large lobes of the hybrid orbitals are shown in green, and the small lobes are not shown.

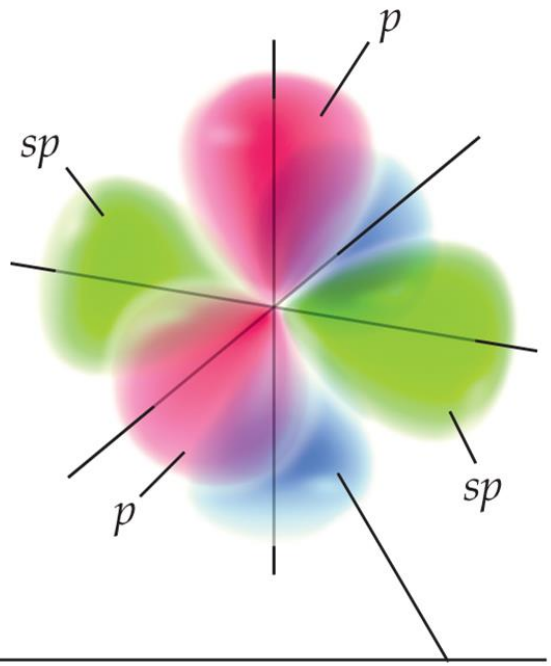
Other Kinds of Hybrid Orbitals



Other Kinds of Hybrid Orbitals

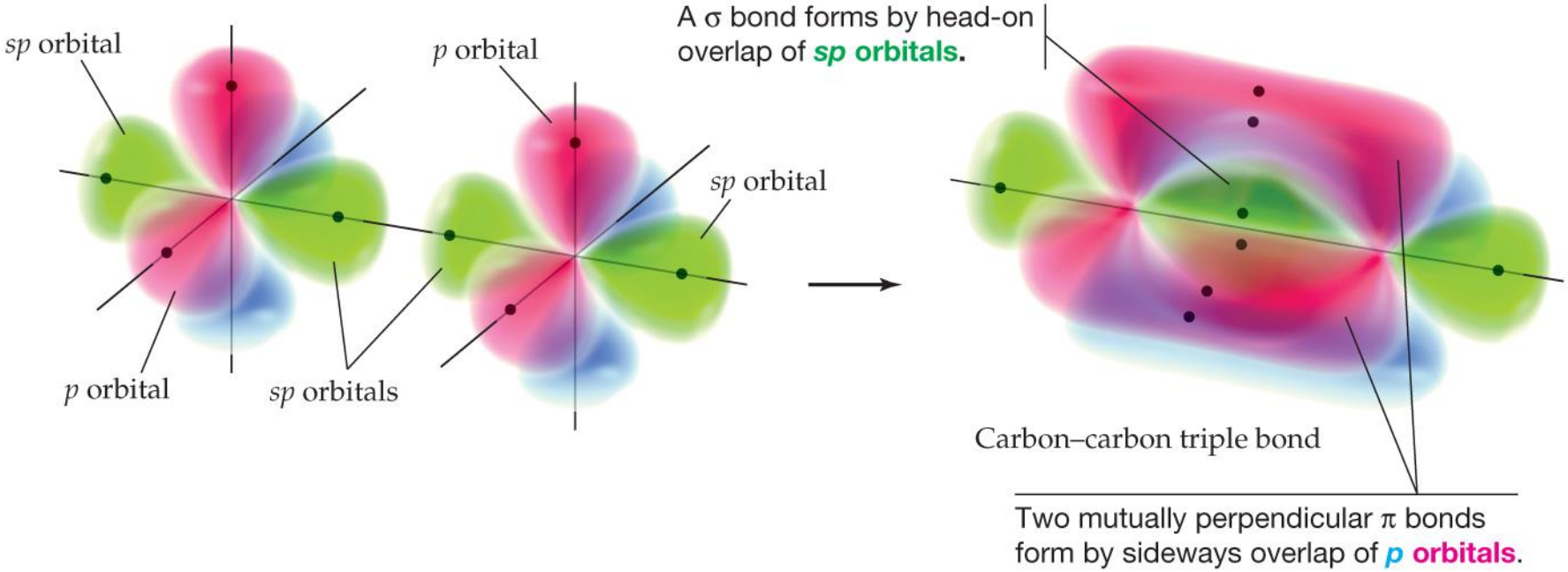
The combination of one *s* and one *p* orbital gives **two *sp* hybrid orbitals** oriented 180° apart.





In addition, two unhybridized ***p* orbitals** remain, oriented at 90° angles to the *sp* hybrids.

Other Kinds of Hybrid Orbitals

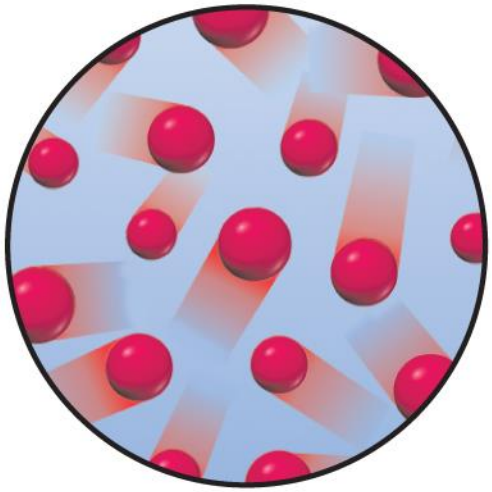


Other Kinds of Hybrid Orbitals

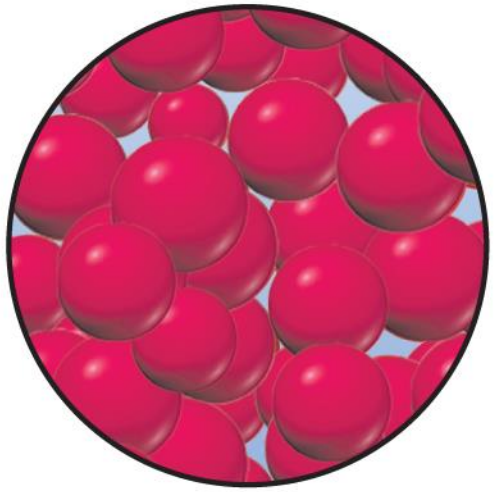
TABLE 8.2 Hybrid Orbitals and Their Geometry

Number of Charge Clouds	Arrangement of Charge Clouds	Hybridization
2	Linear	sp
3	Trigonal planar	sp^2
4	Tetrahedral	sp^3

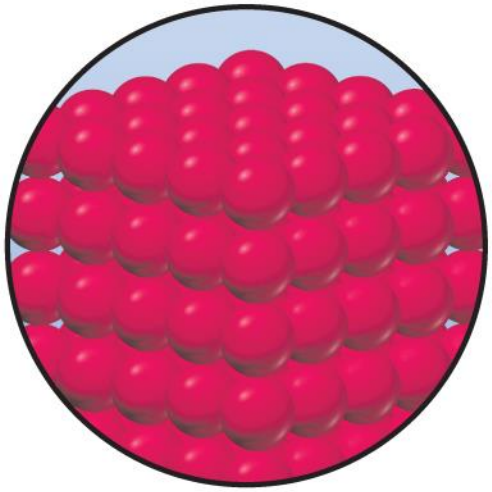
Polar Covalent Bonds and Dipole Moments



In **gases**, the particles feel little attraction for one another and are free to move about randomly.

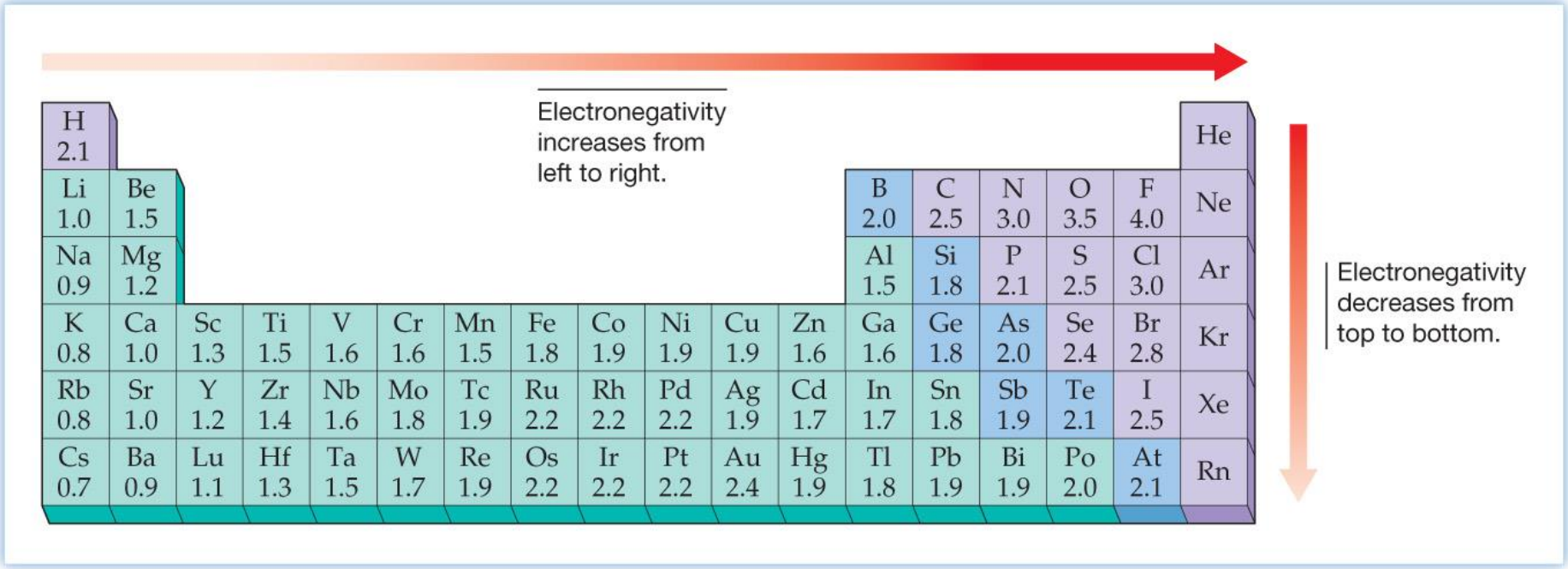


In **liquids**, the particles are held close together by attractive forces but are free to move around one another.

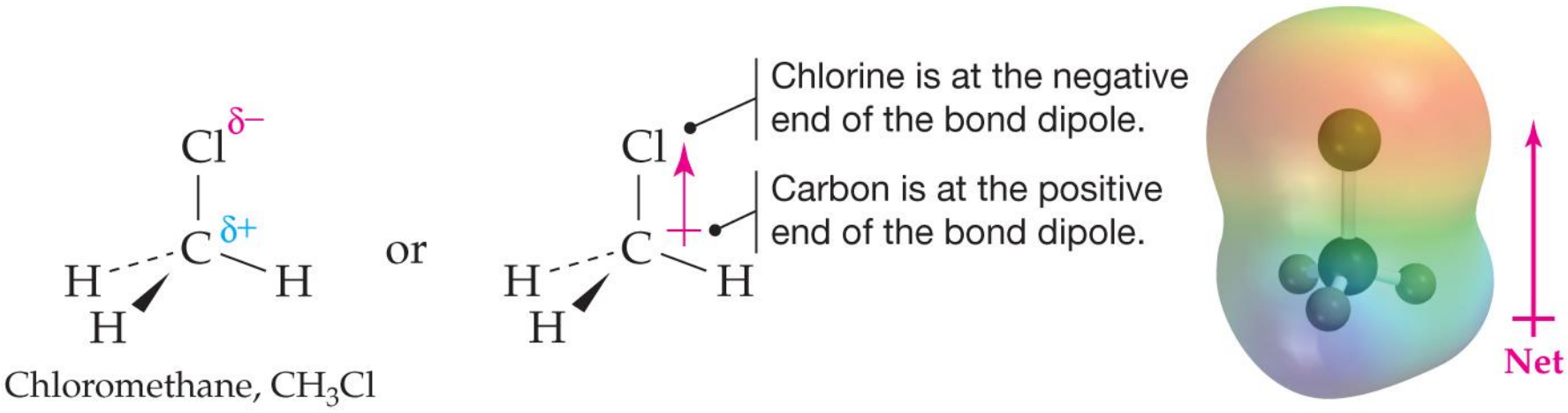


In **solids**, the particles are held in an ordered arrangement.

Polar Covalent Bonds and Dipole Moments

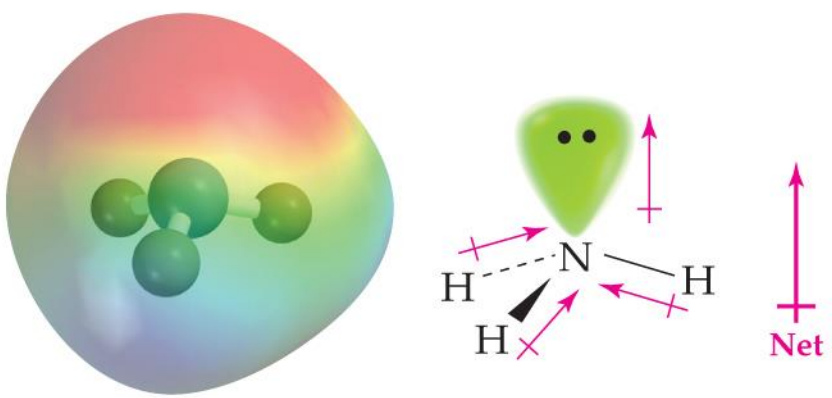


Polar Covalent Bonds and Dipole Moments

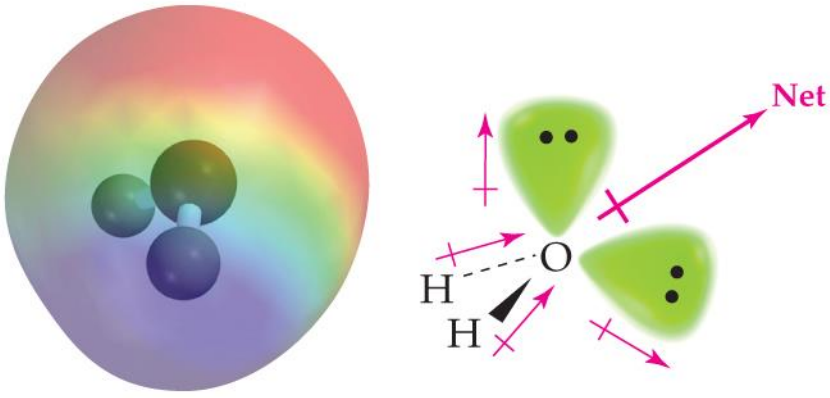


C—Cl bond has a **bond dipole** because of a difference in electronegativities.

Polar Covalent Bonds and Dipole Moments



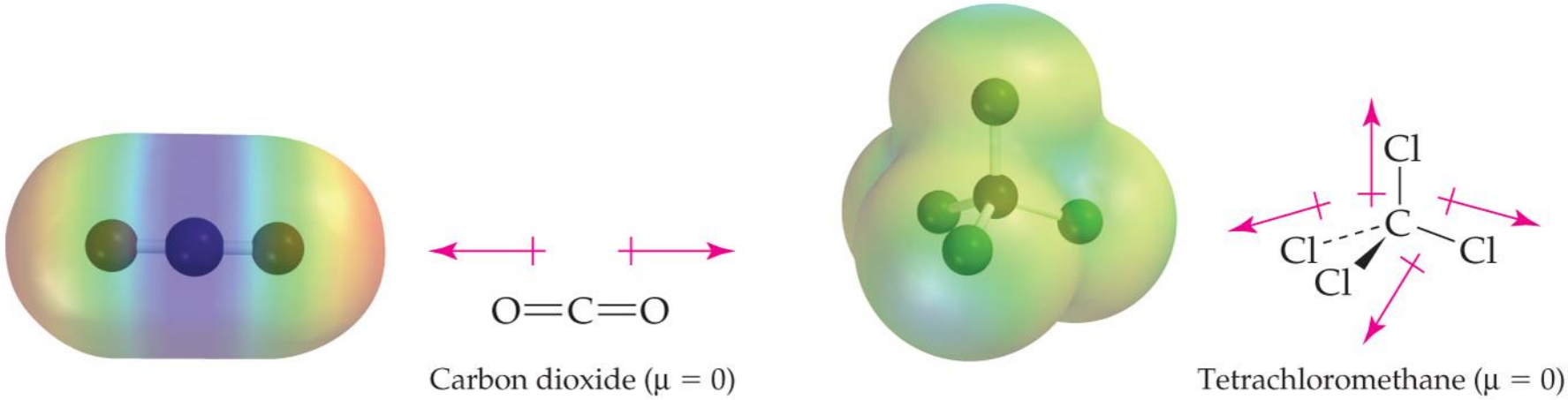
Ammonia (μ = 1.47 D)



Water (μ = 1.85 D)

The individual bond polarities **do not** cancel. Therefore, the molecule has a dipole moment. In other words, the molecule is **polar**.

Polar Covalent Bonds and Dipole Moments



The individual bond polarities cancel. Therefore, the molecule does not have a dipole moment. In other words, the molecule is **nonpolar**.

Intermolecular Forces

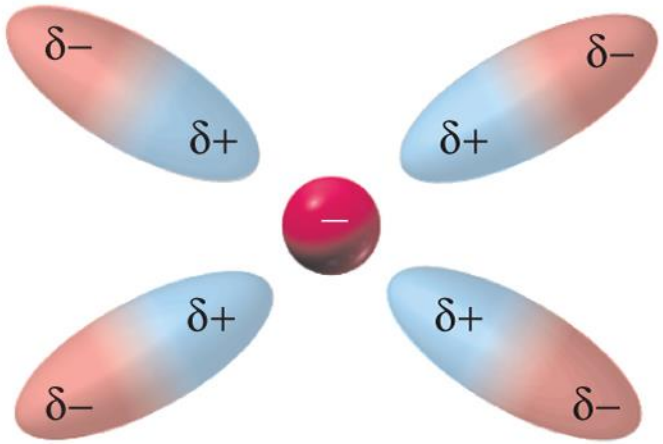
Intermolecular Forces: Attractions between "molecules" that hold them together. These forces are electrical in origin and result from the mutual attraction of unlike charges or the mutual repulsion of like charges.

Types of Intermolecular Forces

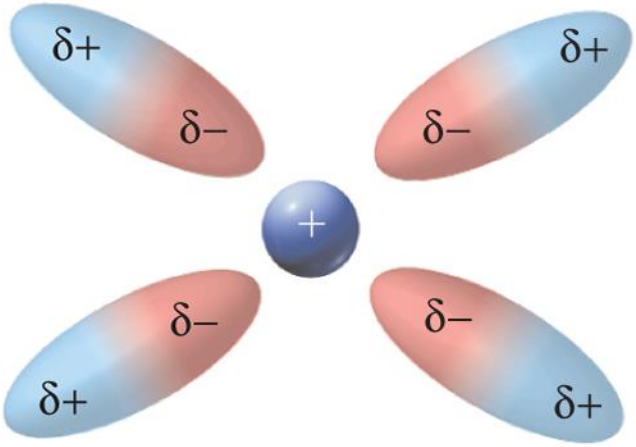
- Ion–dipole forces
- Van der Waals forces
  - Dipole–dipole forces
  - London dispersion forces
  - Hydrogen bonds

Intermolecular Forces

Ion–Dipole Forces: The result of electrical interactions between an ion and the partial charges on a polar molecule



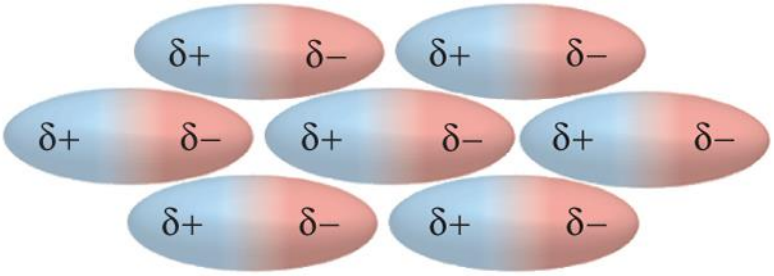
Polar molecules orient toward ions so that the **positive end** of the dipole is near an **anion** and …



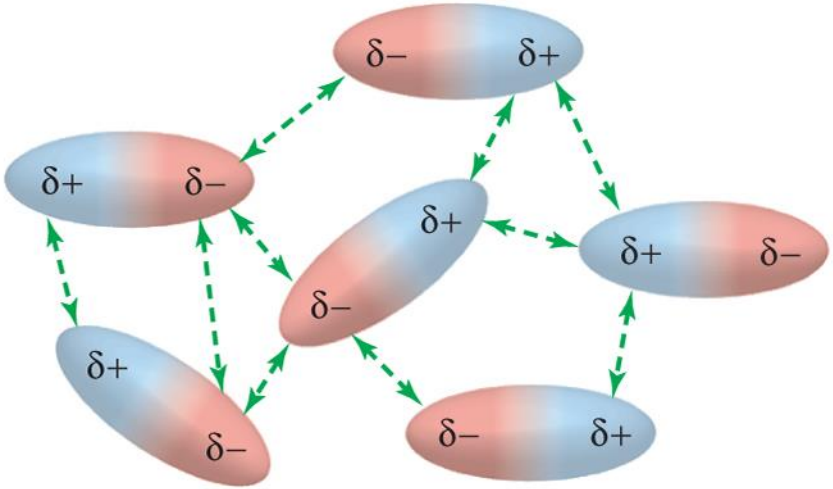
… the **negative end** of the dipole is near a **cation**.

Intermolecular Forces

Dipole–Dipole Forces: The result of electrical interactions among dipoles on neighboring molecules



Polar molecules **attract** one another when they orient with unlike charges close together, but …



… they **repel** one another when they orient with like charges together.

Intermolecular Forces

Dipole–Dipole Forces

TABLE 8.4 Comparison of Molecular Weights, Dipole Moments, and Boiling Points

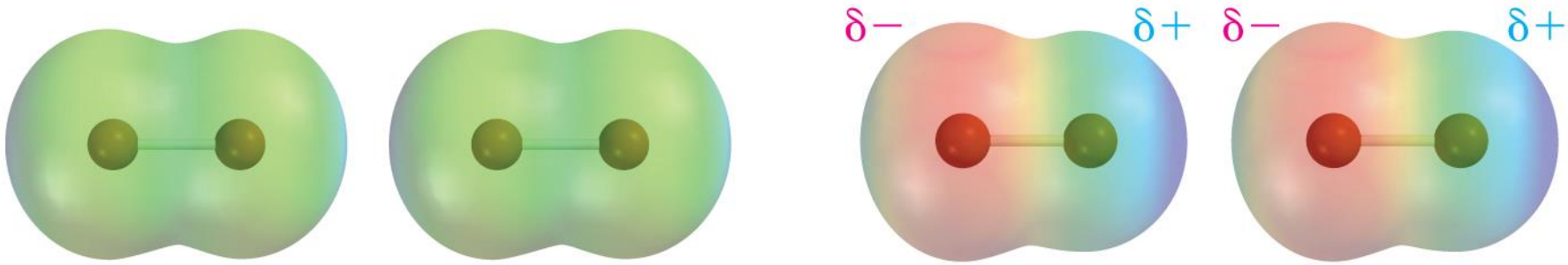
Substance	Mol. Wt.	Dipole Moment (D)	bp (K)
$CH_3CH_2CH_3$	44.10	0.08	231
CH_3OCH_3	46.07	1.30	248
CH_3CN	41.05	3.93	355

As the *dipole moment increases*, the *intermolecular forces increase*.

As the *intermolecular forces increase*, the *boiling point increases*.

Intermolecular Forces

London Dispersion Forces: The result of the motion of electrons that gives the molecule a short-lived dipole moment. This induces temporary dipoles in neighboring molecules.



Averaged over time, the electron distribution in a Br_2 molecule is **symmetrical**.

At any given instant, the electron distribution in a molecule may be **unsymmetrical**, resulting in a temporary dipole and inducing a complementary attractive dipole in neighboring molecules.

Intermolecular Forces

London Dispersion Forces

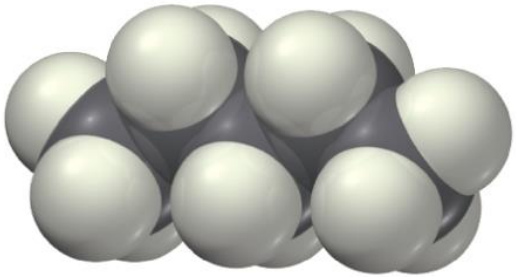
TABLE 8.5 Melting Points and Boiling Points of the Halogens

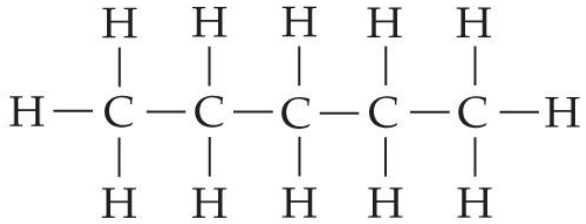
Halogen	mp (K)	bp (K)
F_2	53.5	85.0
Cl_2	171.6	239.1
Br_2	265.9	331.9
I_2	386.8	457.5

As the *dispersion forces* increase, the *intermolecular forces* increase.
As the *intermolecular forces* increase, the *boiling point* increases.

Intermolecular Forces

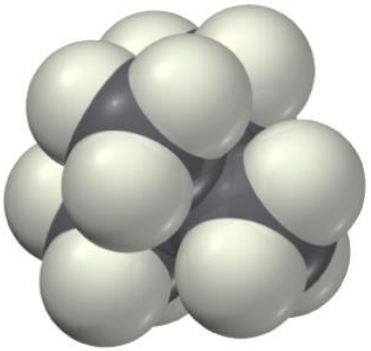
London Dispersion Forces

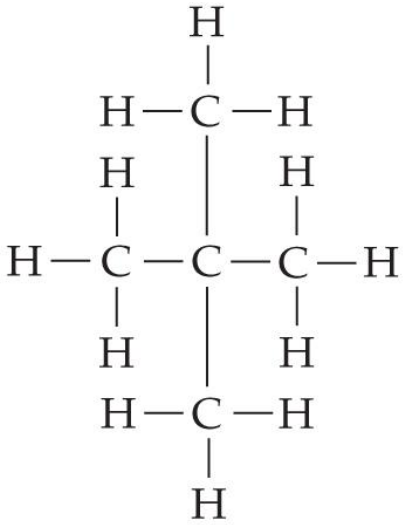




Pentane (bp = 309.2 K)

Longer, **less compact molecules** like pentane feel stronger dispersion forces and consequently have higher boiling points.



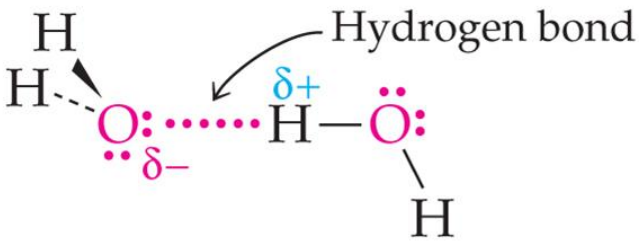


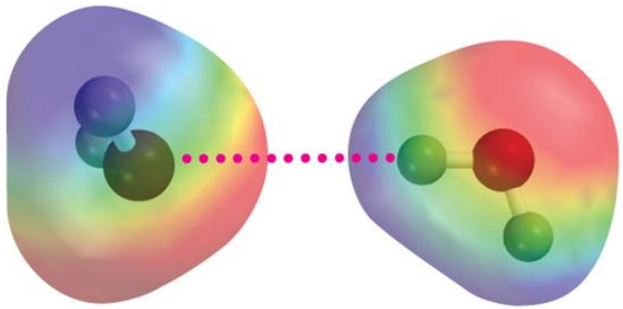
2,2-Dimethylpropane (bp = 282.6 K)

More compact molecules like 2,2-dimethylpropane feel weaker dispersion forces and have lower boiling points.

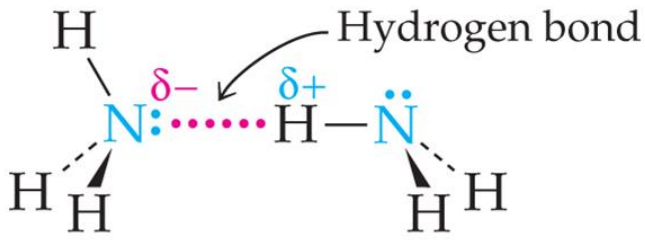
Intermolecular Forces

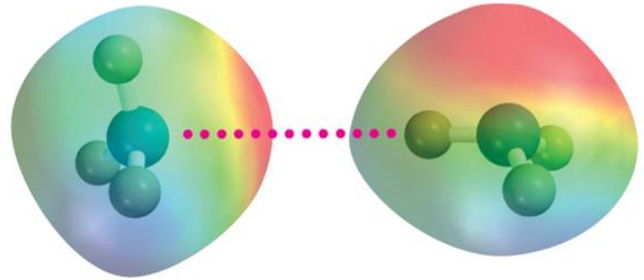
Hydrogen Bond: An attractive force between a hydrogen atom bonded to a very electronegative atom (O, N, or F) and an unshared electron pair on another electronegative atom





Water



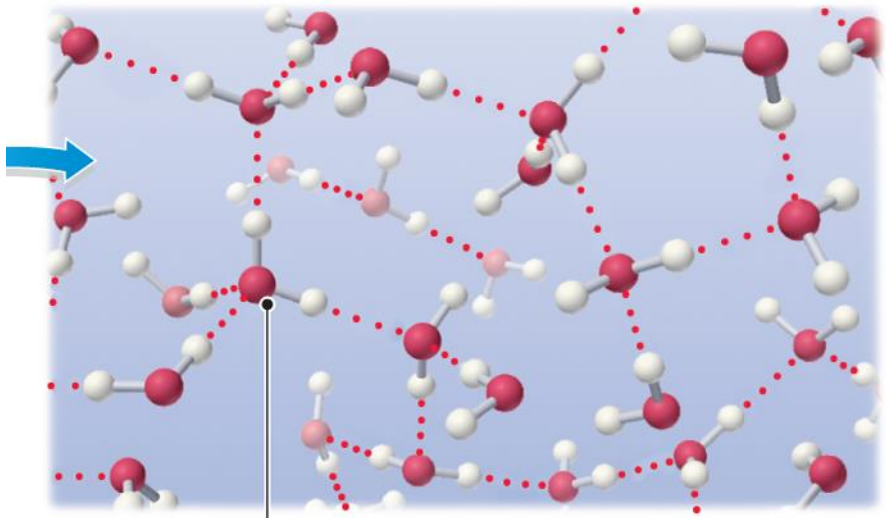


Ammonia

Intermolecular Forces

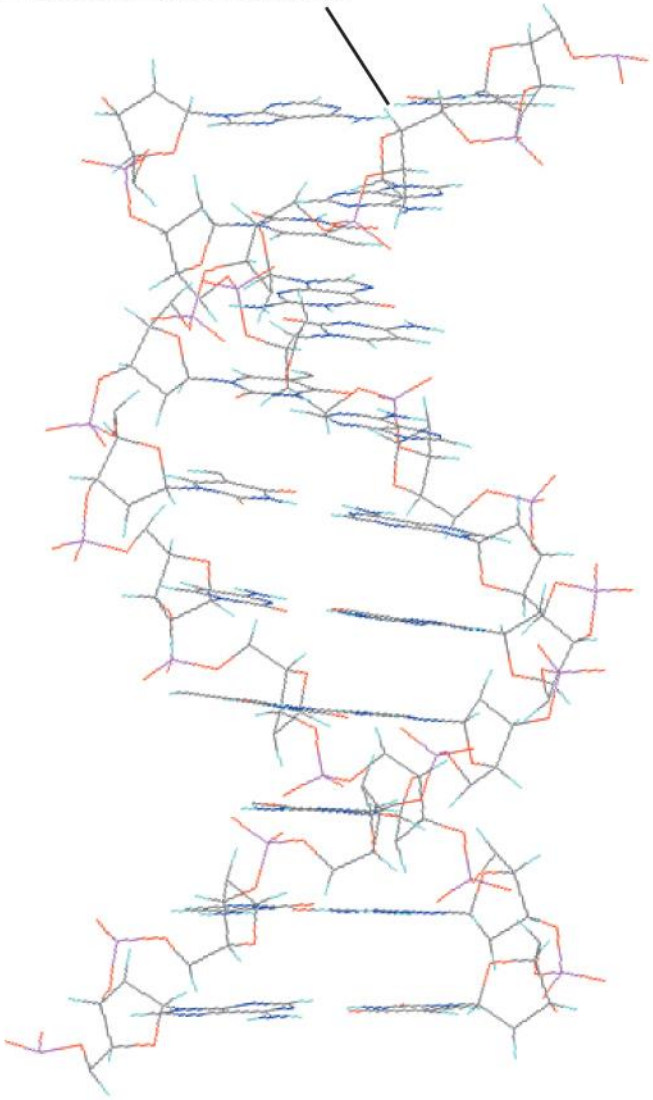
Hydrogen Bond

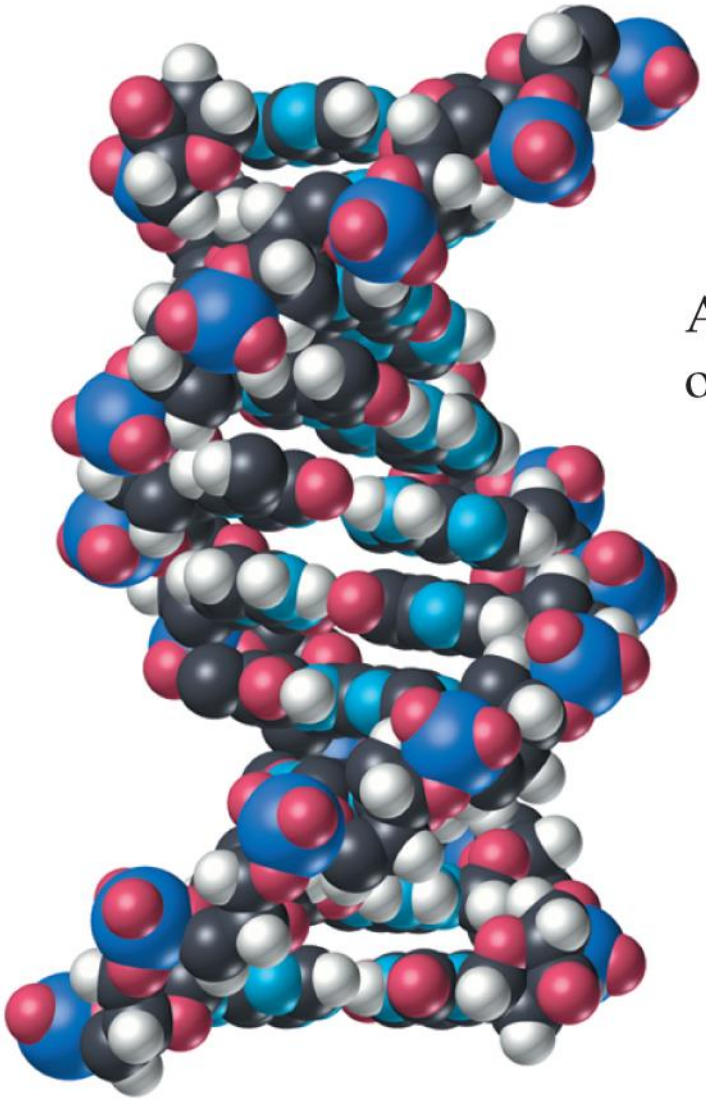
Liquid water contains a vast three-dimensional network of hydrogen bonds resulting from the attraction between positively polarized hydrogens and electron pairs on negatively polarized **oxygens**.



An **oxygen** can form two hydrogen bonds, represented by dotted lines.

Hydrogen bond
between chains



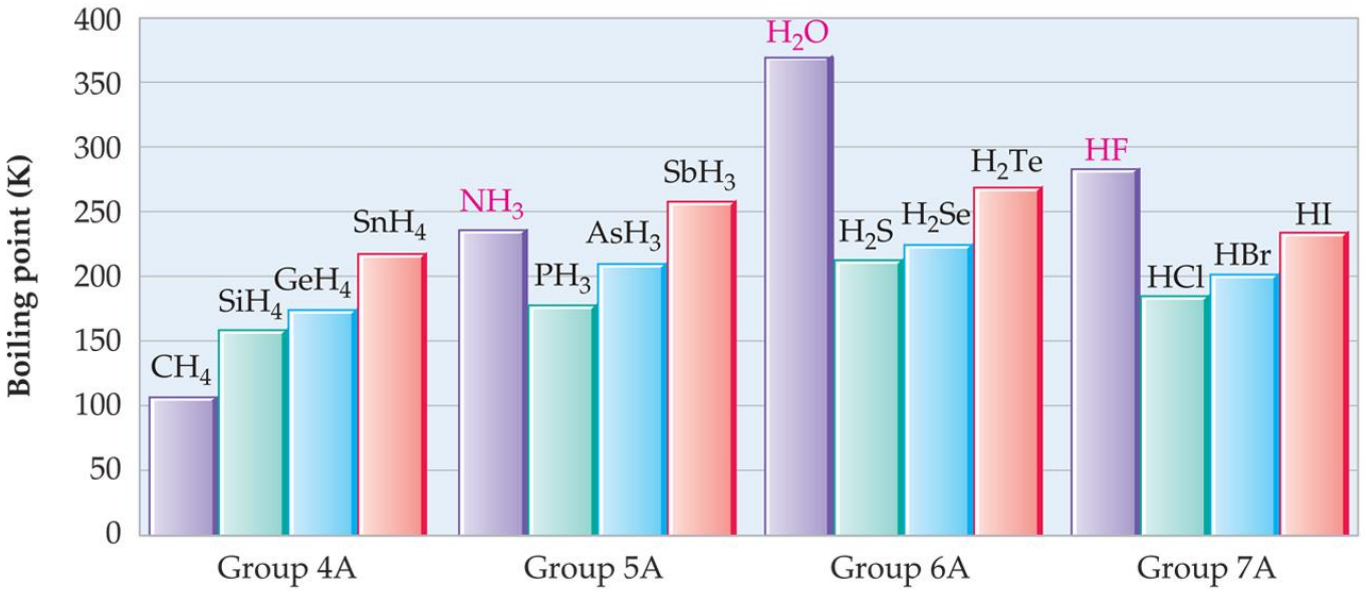


A short segment
of DNA

Intermolecular Forces

Hydrogen Bond

TABLE 8.6 Boiling Points of the Covalent Binary Hydrides of Groups 4A, 5A, 6A, and 7A



The boiling points generally increase with increasing molecular weight down a group of the periodic table, but the hydrides of nitrogen **(NH_3)**, oxygen **(H_2O)**, and fluorine **(HF)** have abnormally high boiling points because these molecules form hydrogen bonds.

Intermolecular Forces

TABLE 8.7 A Comparison of Intermolecular Forces

Force	Strength	Characteristics
Ion–dipole	Highly variable (10–70 kJ/mol)	Occurs between ions and polar molecules
Dipole–dipole	Weak (3–4 kJ/mol)	Occurs between polar molecules
London dispersion	Weak (1–10 kJ/mol)	Occurs between all molecules; strength depends on size, polarizability
Hydrogen bond	Moderate (10–40 kJ/mol)	Occurs between molecules with O—H, N—H, and F—H bonds

Molecular Orbital Theory: The Hydrogen Molecule

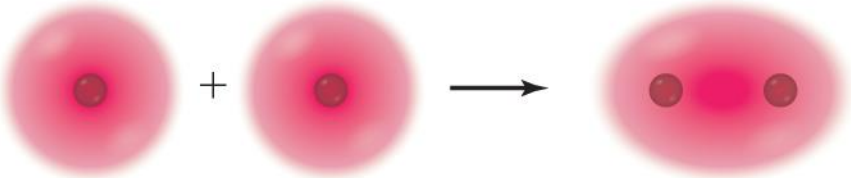
Atomic Orbital: A wave function whose square gives the probability of finding an electron within a given region of space *in an atom*

Molecular Orbital: A wave function whose square gives the probability of finding an electron within a given region of space *in a molecule*

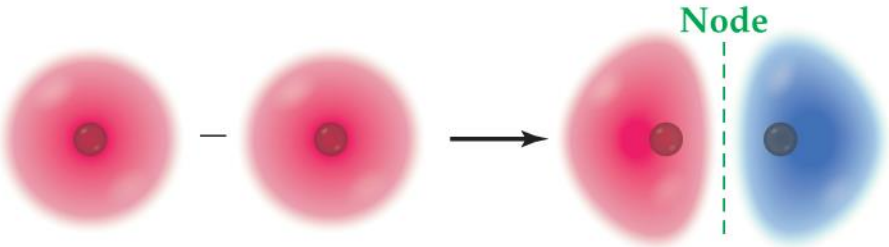
Molecular Orbital Theory: The Hydrogen Molecule

σ bonding orbital

The additive combination of atomic 1*s* orbitals forms a lower-energy, **bonding molecular orbital**, σ.



The subtractive combination of atomic 1*s* orbitals forms a higher-energy, **antibonding molecular orbital**, σ*, that has a **node** between the nuclei.



σ* antibonding orbital

Molecular Orbital Theory: The Hydrogen Molecule

σ bonding orbital

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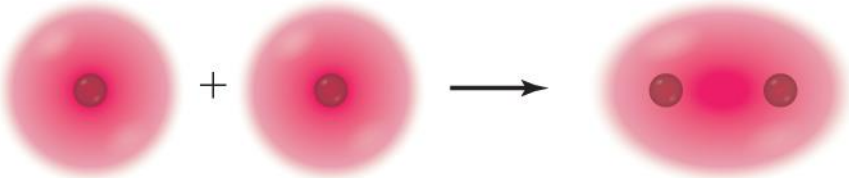

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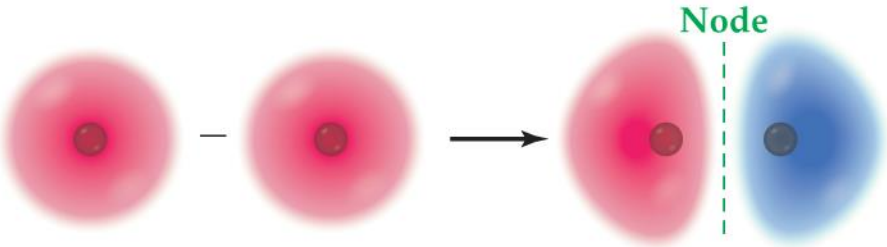
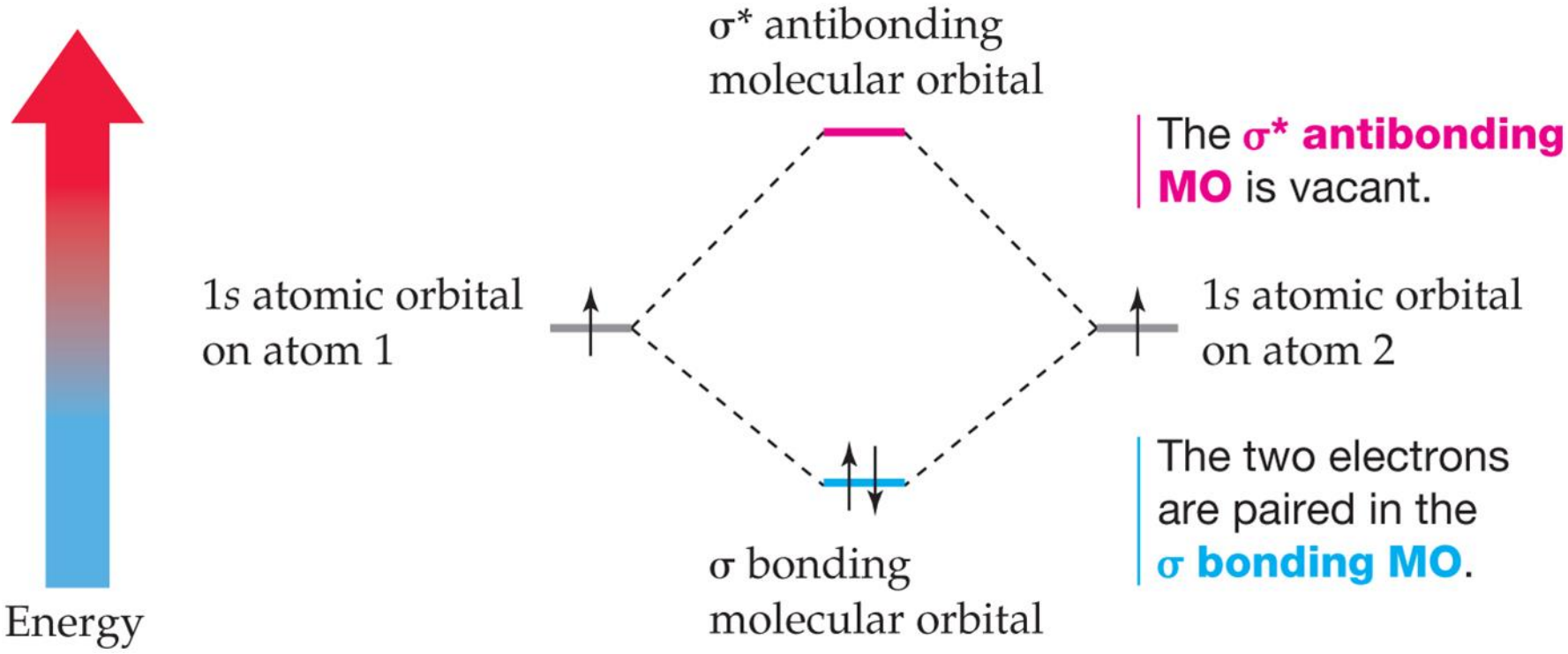


σ* antibonding orbital

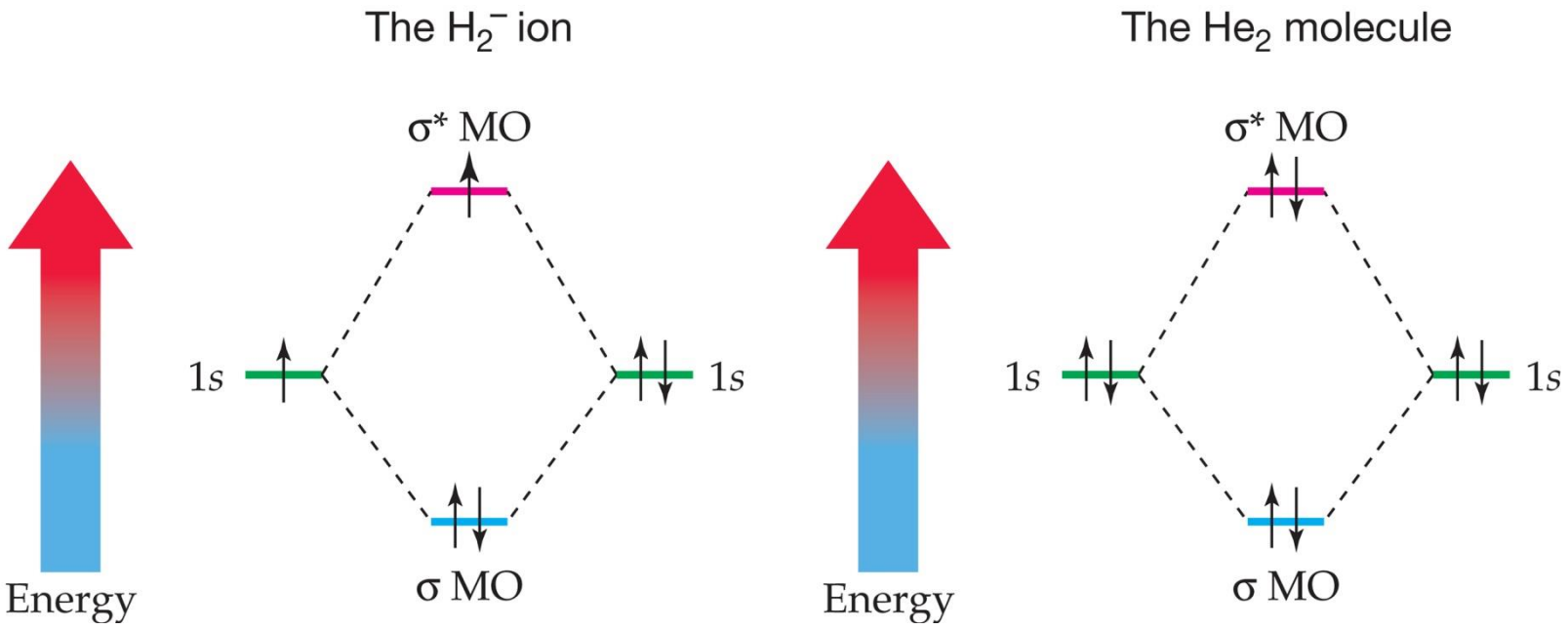
$$\text{Bond order} = \frac{(\#\ \text{bonding } e^- - \#\ \text{antibonding } e^-)}{2}$$

Molecular Orbital Theory: The Hydrogen Molecule



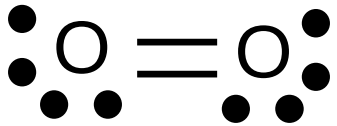
$$\text{Bond order} = \frac{2 - 0}{2} = 1$$

Molecular Orbital Theory: The Hydrogen Molecule



Bond order: $\frac{2-1}{2} = 2$ $\frac{2-2}{2} = 0$

Molecular Orbital Theory: Other Diatomic Molecules

O_2 

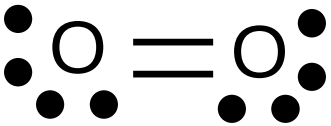
Diamagnetic: All electrons are spin-paired. Diamagnetic substances are weakly repelled by magnetic fields.

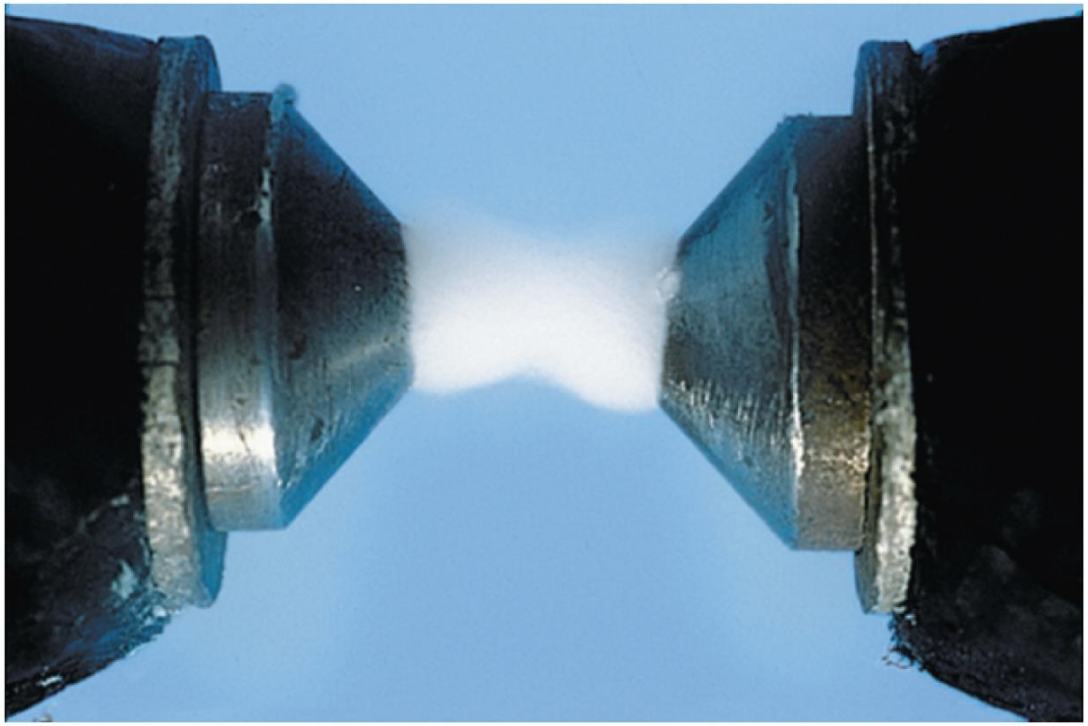
Paramagnetic: There is at least one unpaired electron. Paramagnetic substances are weakly attracted by magnetic fields.

Oxygen, O_2, is predicted to be *diamagnetic* by electron-dot structures and valence bond theory.

Molecular Orbital Theory: Other Diatomic Molecules

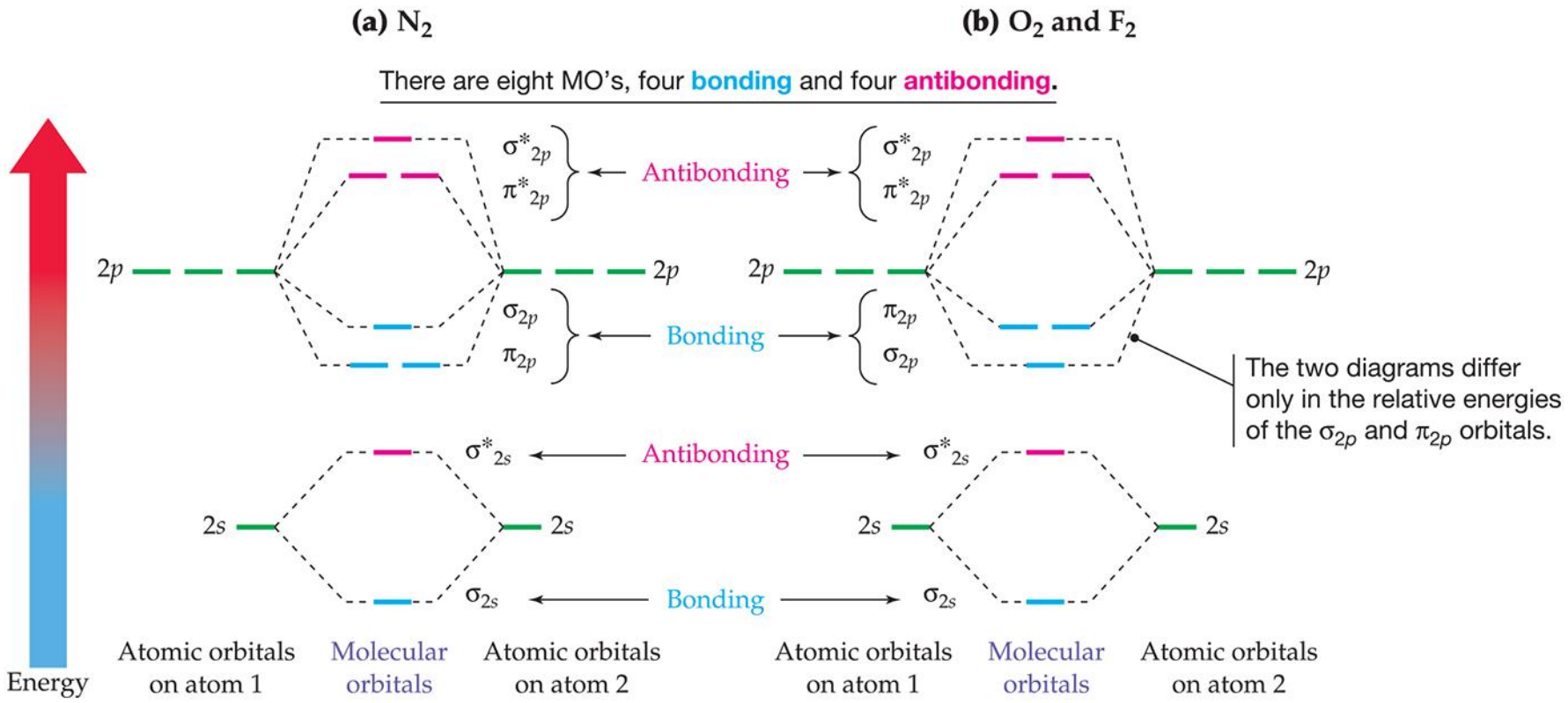
O_2



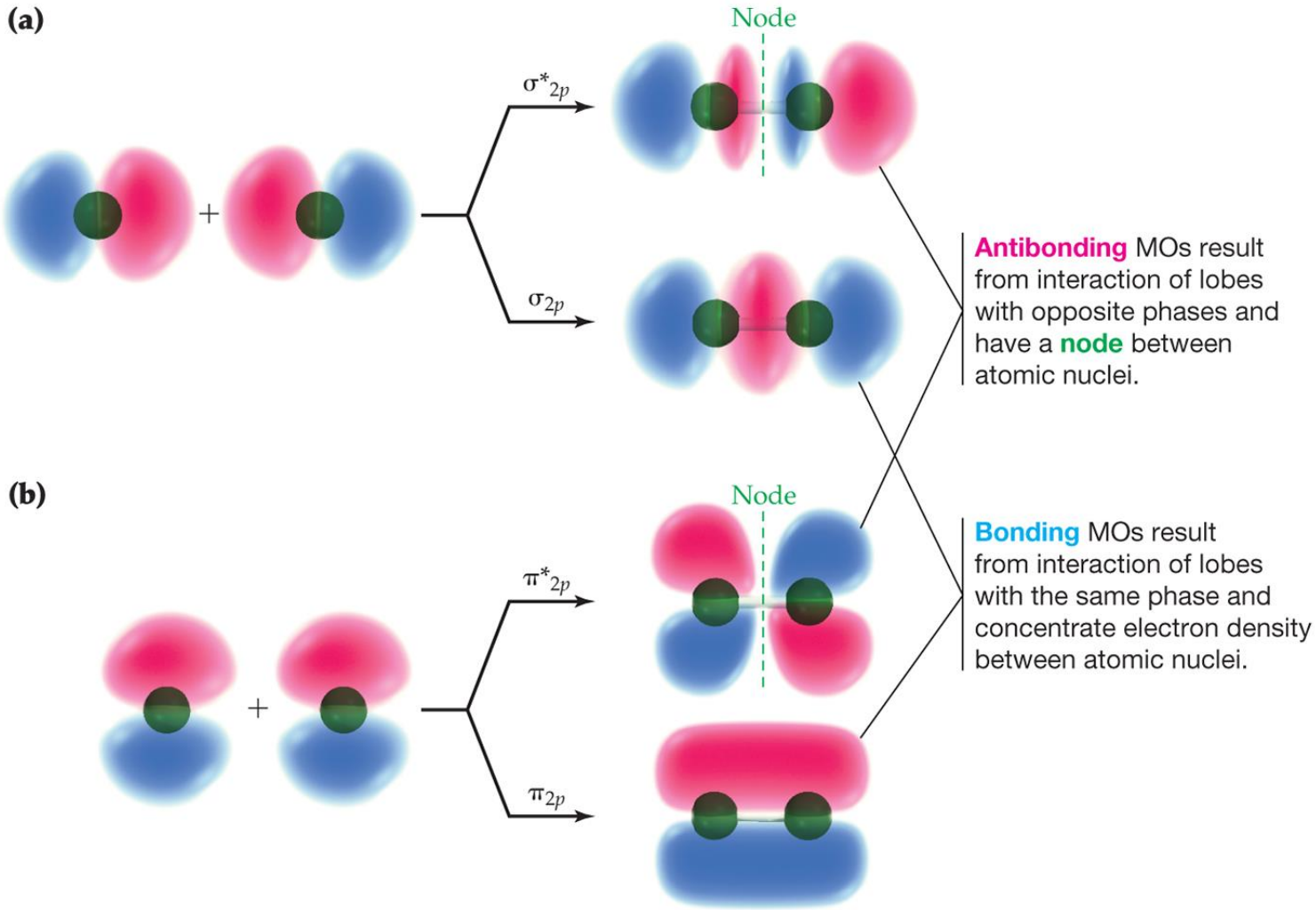


However, it is known to be *paramagnetic.*

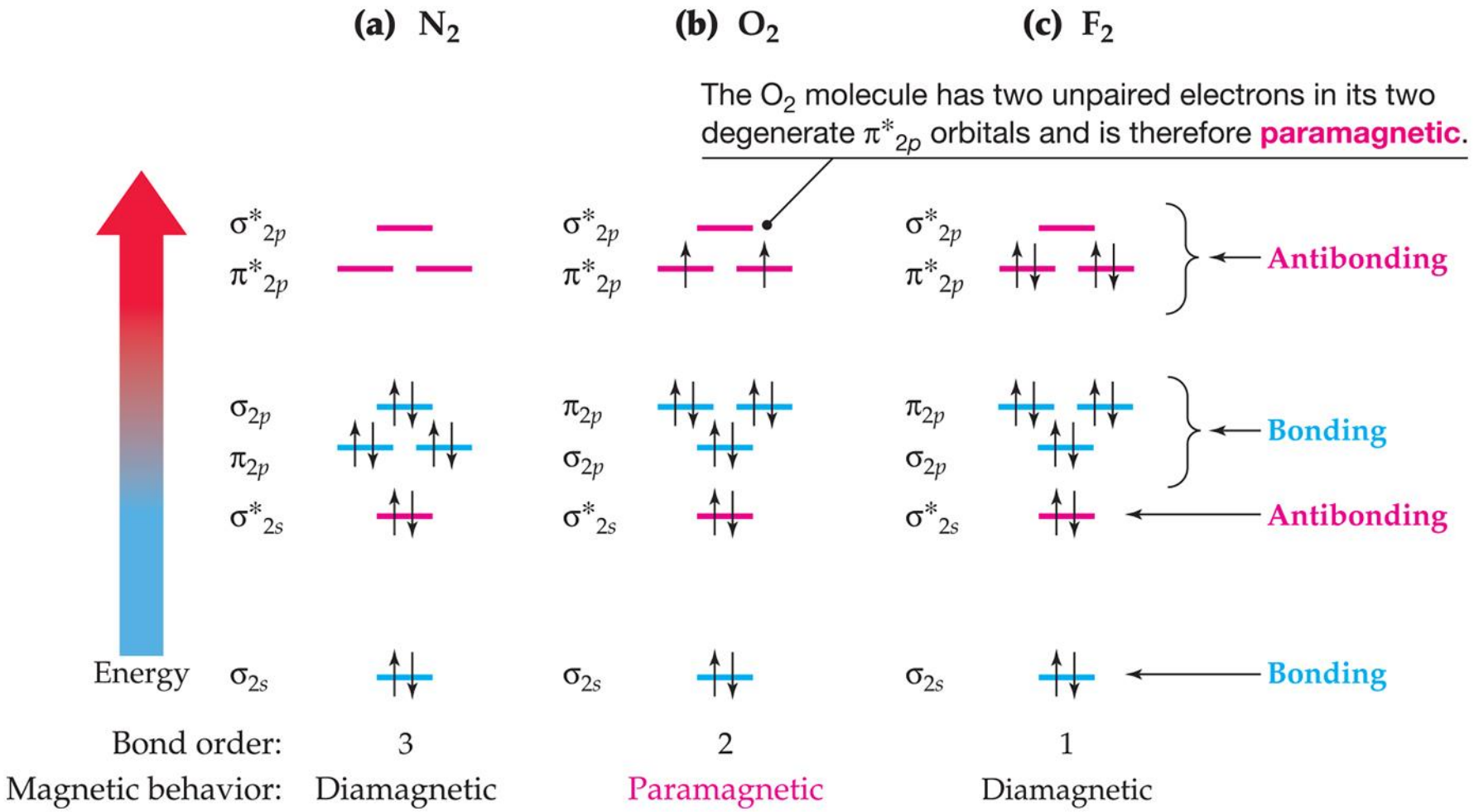
Molecular Orbital Theory: Other Diatomic Molecules



Molecular Orbital Theory: Other Diatomic Molecules



Molecular Orbital Theory: Other Diatomic Molecules



Combining Valence Orbital Theory and Molecular Orbital Theory