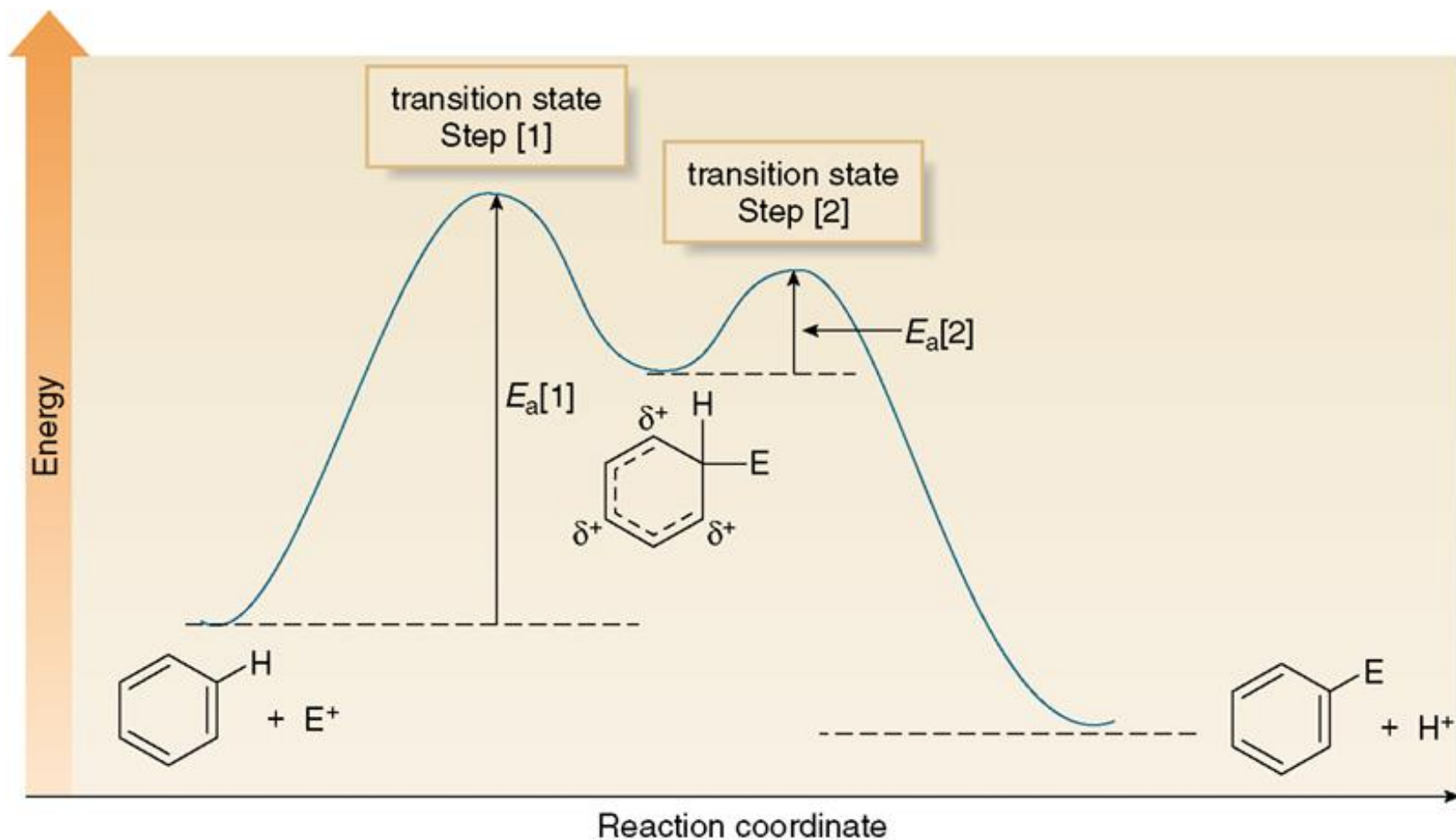


KIMIA ORGANIK FISIK

Edy Cahyono



Apakah kimia organik fisik itu?

PHYSICAL ORGANIC CHEMISTRY^{1,2}

BY ROBERT W. TAFT, JR., NORMAN C. DENO, AND PHILLIP S. SKELL

Department of Chemistry, Pennsylvania State University, University Park, Pennsylvania

A reasonable definition of the domain of *Physical Organic Chemistry* was given seventeen years ago by L. P. Hammett, in his inspiring book by this title, as one concerned with investigations of organic chemistry by quantitative and mathematical methods. The chief directions of the field were given as (a) mechanisms of reactions, and (b) the effects of structure and environment on reaction rates and equilibria.

The amount of significant research reported during the current year which falls within these confines has been so enormous that it early became apparent to us that to cover such an area would scarcely enable us to prepare a running list of titles. Consequently we have chosen for detailed review only four admittedly narrow topics within the realm. In so doing it is our hope that our modest efforts at review will provide something of use to those interested in our topics. No claims are made as to the relative merits of topics considered or not considered, and we trust that it will be possible for subsequent reviews under this title to pick up many of the important contributions which we have neglected. Inasmuch as the previous review of this area was devoted to reaction mechanisms, we have devoted much of our attention to the second of the chief directions of the field.

KIMIA ORGANIK FISIK

1. Review:
Hibridisasi, resonansi, konjugasi, hiperkonjugasi (1).
2. Reaksi dasar organik, kinetika, energetika, stereokimia, dan mekanisme reaksi (2).
3. Mekanisme Substitusi (3,4).
4. Mekanisme Eliminasi (5).
5. Faktor-faktor yang menentukan mekanisme reaksi (6)
6. Mekanisme reaksi radikal bebas (7).
7. Mid semester (8).
8. Reaksi adisi pada alkena (9,10,11)
9. Reaksi adisi pada gugus karbonil (12, 13)
10. Reaksi perisiklik (14)
11. Reaksi polimerisasi (15)

Sumber belajar:

Peter Sykes, Penuntun mekanisme reaksi organik, hal 1-100

Fessenden, Kimia Organik I, Bab Alkil halida

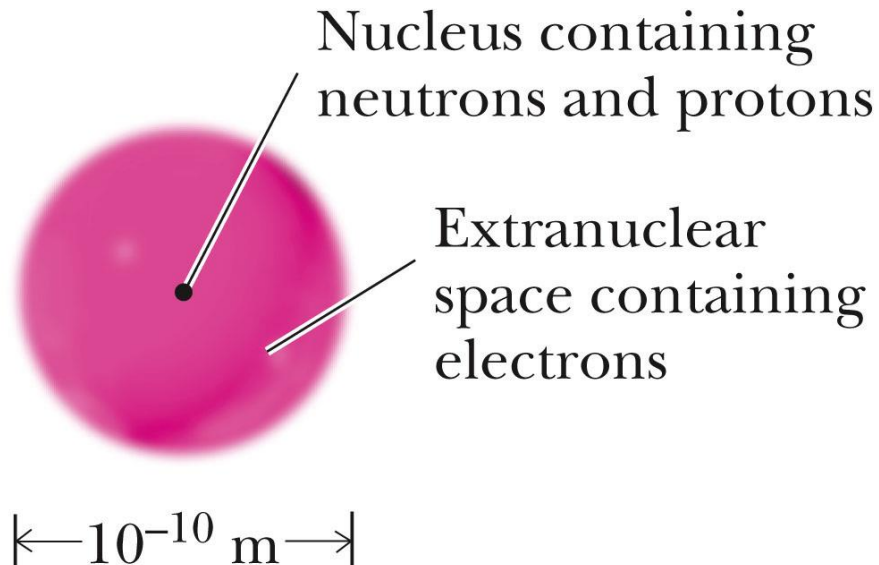
Chapter 1 Bonding and Geometry

Organic Chemistry

- The study of the compounds of carbon.
- Over 10 million compounds have been identified.
 - About 1000 new ones are identified each day!
- C is a small atom.
 - It forms single, double and triple bonds.
 - It is intermediate in electronegativity (2.5).
 - It forms strong bonds with C, H, O, N, and some metals.

Schematic View of an Atom

- A small dense nucleus, diameter 10^{-14} - 10^{-15} m, which contains positively charged protons and most of the mass of the atom.
- An extranuclear space, diameter 10^{-10} m, which contains negatively charged electrons.



Lewis Dot Structures

- Gilbert N. Lewis
- **Valence shell:**
 - The outermost occupied electron shell of an atom.
- **Valence electrons:**
 - Electrons in the valence shell of an atom; these electrons are used to form chemical bonds and in chemical reactions.
- **Lewis dot structure:**
 - The symbol of an element represents the nucleus and all inner shell electrons.
 - Dots represent electrons in the valence shell of the atom.

Lewis Dot Structures

- Table 1.4 Lewis Dot Structures for Elements 1-18

1A	2A	3A	4A	5A	6A	7A	8A
H •							He ••
Li •	Be ••	B ••	C ••	N ••	O ••	F ••	Ne ••
Na •	Mg ••	Al ••	Si ••	P ••	S ••	Cl ••	Ar ••

Lewis Model of Bonding

- Atoms interact in such a way that each participating atom acquires an electron configuration that is the same as that of the noble gas nearest it in atomic number.
 - An atom that gains electrons becomes an **anion**.
 - An atom that loses electrons becomes a **cation**.
 - The attraction of anions and cations leads to the formation of **ionic solids**. This ionic interaction is often referred to as an **ionic bond**.
 - An atom may share electrons with one or more atoms to complete its valence shell; a chemical bond formed by sharing electrons is called a **covalent bond**. Bonds may be partially ionic or partially covalent; these bonds are called **polar covalent bonds**

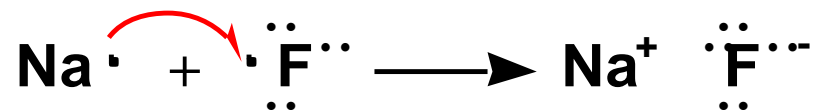
Electronegativity

- **Electronegativity:**
 - A measure of an atom's attraction for the electrons it shares with another atom in a chemical bond.
- **Pauling scale**
 - Generally increases left to right in a row.
 - Generally increases bottom to top in a column.

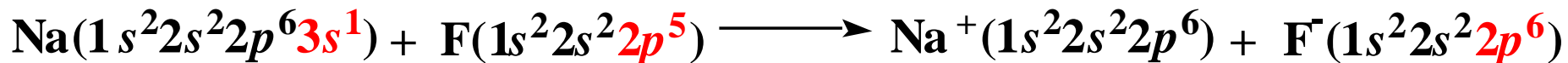
Formation of Ions

A rough guideline:

- Ions will form if the difference in electronegativity between interacting atoms is 1.9 or greater.
- Example: sodium (EN 0.9) and fluorine (EN 4.0)
- We use a single-headed (barbed) curved arrow to show the transfer of one electron from Na to F.



- In forming Na^+F^- , the single 3s electron from Na is transferred to the partially filled valence shell of F.



Covalent Bonds

- The simplest covalent bond is that in H₂
 - The single electrons from each atom combine to form an electron pair.



- The shared pair functions in two ways simultaneously; it is shared by the two atoms and fills the valence shell of each atom.
- The number of shared pairs
 - One shared pair forms a single bond
 - Two shared pairs form a double bond
 - Three shared pairs form a triple bond

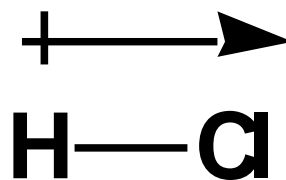
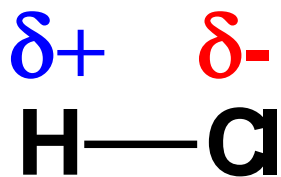
Polar and Nonpolar Covalent Bonds

- Although all covalent bonds involve sharing of electrons, they differ widely in the degree of sharing.
- We divide covalent bonds into nonpolar covalent bonds and polar covalent bonds.

Difference in Electronegativity Between Bonded Atoms	Type of Bond
Less than 0.5	Nonpolar covalent
0.5 to 1.9	Polar covalent
Greater than 1.9	Ions form

Polar and Nonpolar Covalent Bonds

- An example of a polar covalent bond is that of H-Cl.
- The difference in electronegativity between Cl and H is $3.0 - 2.1 = 0.9$.
- We show polarity by using the symbols $\delta+$ and $\delta-$, or by using an arrow with the arrowhead pointing toward the negative end and a plus sign on the tail of the arrow at the positive end.



Polar Covalent Bonds

Bond dipole moment (μ):

- A measure of the polarity of a covalent bond.
- The product of the charge on either atom of a polar bond times the distance between the two nuclei.
- Table 1.7

Bond	Bond Dipole (D)	Bond	Bond Dipole (D)	Bond	Bond Dipole (D)
$\text{H}-\text{C}$	0.3	$\text{C}-\text{F}$	1.4	$\text{C}-\text{O}$	0.7
$\text{H}-\text{N}$	1.3	$\text{C}-\text{Cl}$	1.5	$\text{C}=\text{O}$	2.3
$\text{H}-\text{O}$	1.5	$\text{C}-\text{Br}$	1.4	$\text{C}-\text{N}$	0.2
$\text{H}-\text{S}$	0.7	$\text{C}-\text{I}$	1.2	$\text{C}\equiv\text{N}$	3.5

Lewis Structures

- To write a Lewis structure
 - Determine the number of valence electrons.
 - Determine the arrangement of atoms.
 - Connect the atoms by single bonds.
 - Arrange the remaining electrons so that each atom has a complete valence shell.
 - Show a bonding pair of electrons as a single line.
 - Show a nonbonding pair of electrons (a lone pair) as a pair of dots.
 - In a **single bond** atoms share one pair of electrons, in a **double bond** they share two pairs of electrons and in a **triple bond** they share three pairs of electrons.

Lewis Structures - Table 1.8

$\text{H}-\ddot{\text{O}}-\text{H}$	$\text{H}-\ddot{\text{N}}-\text{H}$ H	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H} \end{array}$	$\text{H}-\ddot{\text{Cl}}:$
H_2O (8) Water	NH_3 (8) Ammonia	CH_4 (8) Methane	HCl (8) Hydrogen chloride
$\begin{array}{c} \text{H} & & \text{H} \\ & \backslash & / \\ & \text{C}=\text{C} \\ & / & \backslash \\ \text{H} & & \text{H} \end{array}$	$\text{H}-\text{C}\equiv\text{C}-\text{H}$	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}=\ddot{\text{O}} \\ \\ \text{H} \end{array}$	$\begin{array}{c} & & \text{:}\ddot{\text{O}}\text{:} \\ & & \\ \text{H}-\ddot{\text{O}} & - & \text{C} & - & \ddot{\text{O}}-\text{H} \\ & & & & \text{:}\ddot{\text{O}}\text{:} \end{array}$
C_2H_4 (12) Ethylene	C_2H_2 (10) Acetylene	CH_2O (12) Formaldehyde	H_2CO_3 (24) Carbonic acid

- In neutral molecules
 - hydrogen has one bond.
 - carbon has 4 bonds and no lone pairs.
 - nitrogen has 3 bonds and 1 lone pair.
 - oxygen has 2 bonds and 2 lone pairs.
 - halogens have 1 bond and 3 lone pairs.

Formal Charge

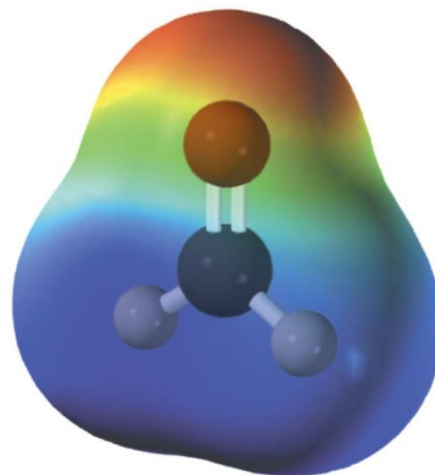
- **Formal charge:** The charge on an atom in a molecule or a polyatomic ion.
- To derive formal charge
 1. Write a correct Lewis structure for the molecule or ion.
 2. Assign each atom all its unshared (nonbonding) electrons and one-half its shared (bonding) electrons.
 3. Compare this number with the number of valence electrons in the neutral, unbonded atom.

$$\text{Formal charge} = \text{Number of valence electrons in the neutral, unbonded atom} - \left(\text{All unshared electrons} + \text{One half of all shared electrons} \right)$$

4. The sum of all formal charges is equal to the total charge on the molecule or ion.

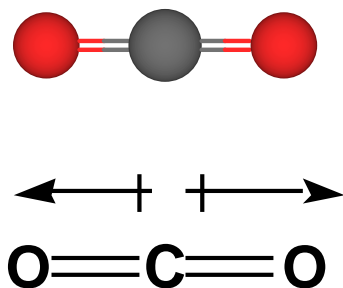
Electrostatic Potential (elpot) Maps

- In electrostatic potential maps (elpots)
 - Areas of relatively high calculated electron density are shown in red.
 - Areas of relatively low calculated electron density are shown in blue.
 - Intermediate electron densities are represented by intermediate colors.

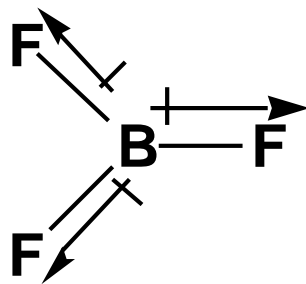
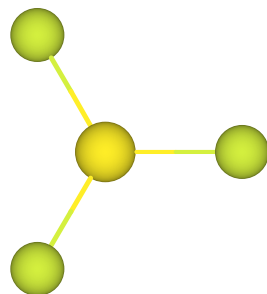


Polar and Nonpolar Molecules

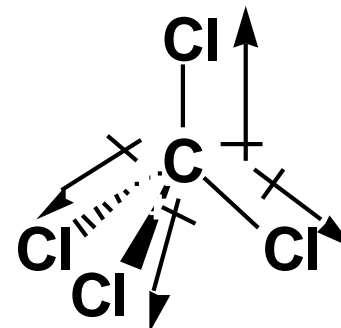
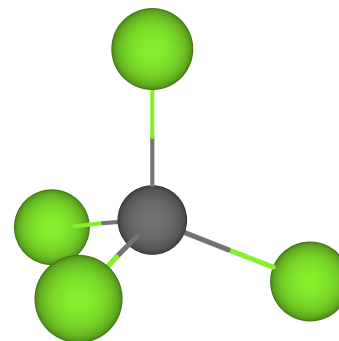
- These molecules have polar bonds, but each molecule has a zero dipole moment.



Carbon dioxide
 $\mu = 0 \text{ D}$



Boron trifluoride
 $\mu = 0 \text{ D}$

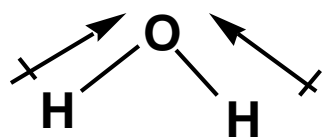


Carbon tetrachloride
 $\mu = 0 \text{ D}$

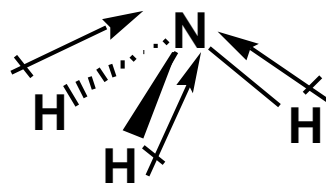
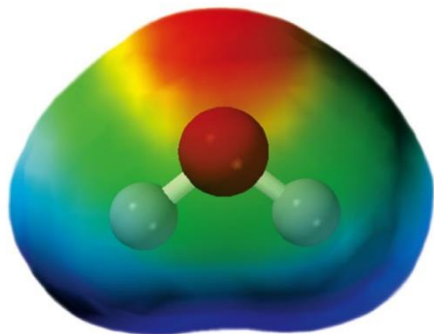
Polar and Nonpolar Molecules

- These molecules have polar bonds and are polar molecules.

direction
of dipole
moment ↑

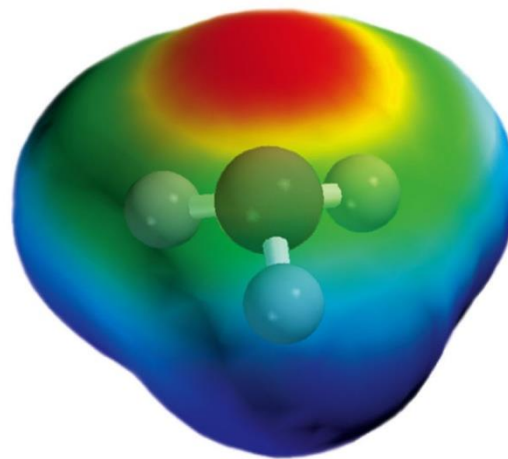


Water
 $\mu = 1.85\text{D}$



direction
of dipole
moment ↑

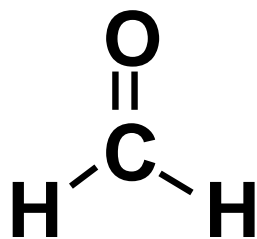
Ammonia
 $\mu = 1.47\text{D}$



Polar and Nonpolar Molecules

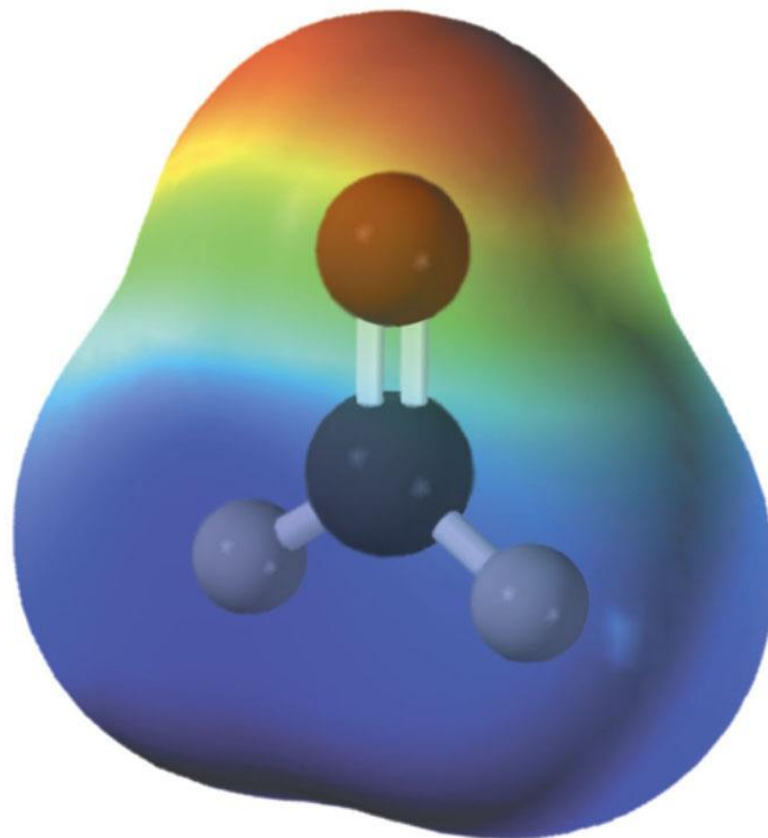
- Formaldehyde has polar bonds and is a polar molecule.

**direction
of dipole
moment**



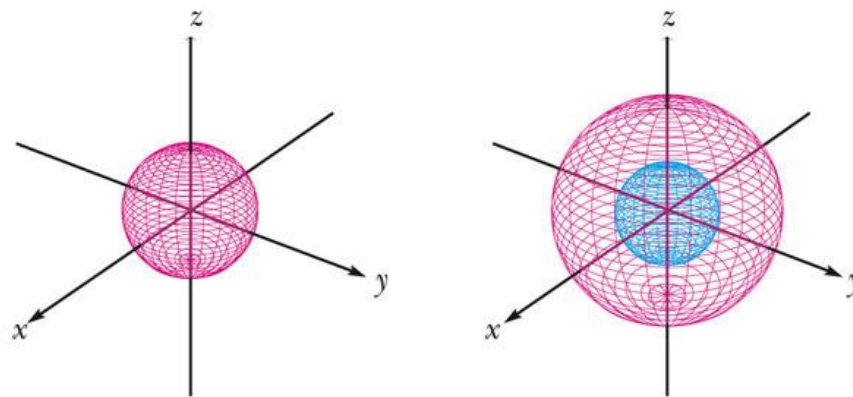
Formaldehyde

$$\mu = 2.33 \text{ D}$$

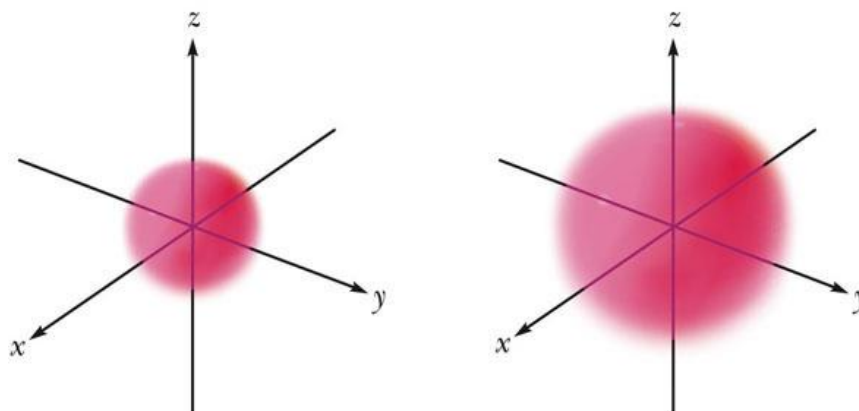


Shapes of Atomic s and p Orbitals

- All s orbitals have the shape of a sphere with the center of the sphere at the nucleus.



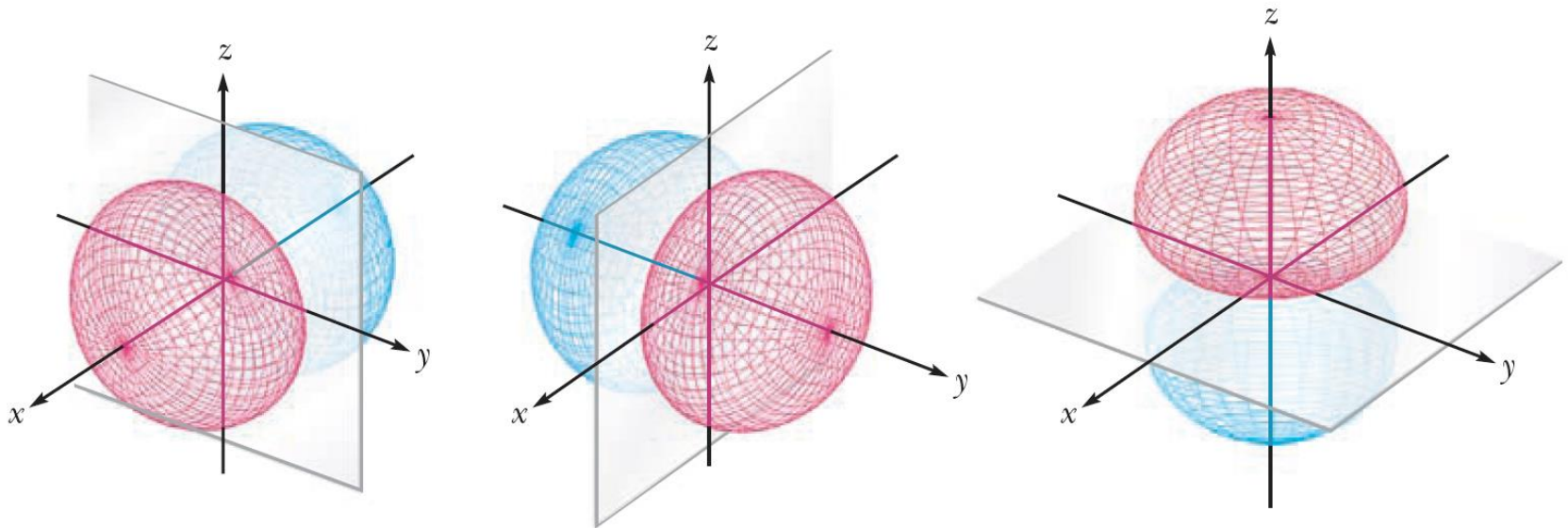
(a) $1s$ and $2s$ orbitals computed using the Schrödinger equation



(b) Cartoon representations of $1s$ and $2s$ orbitals

Shapes of Atomic s and p Orbitals

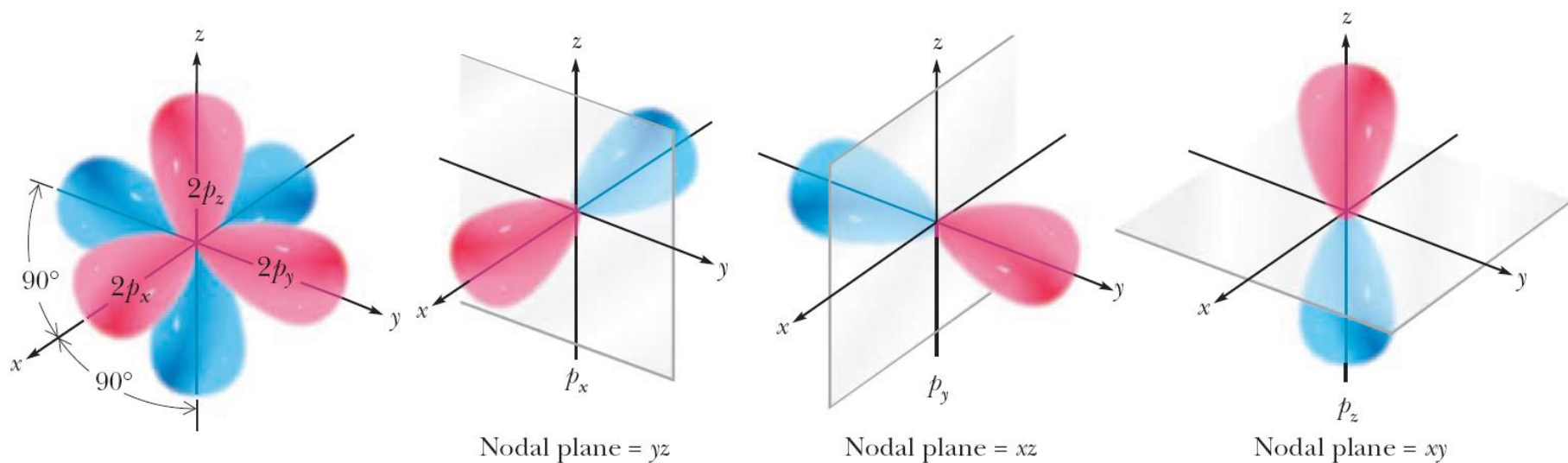
- Figure 1.9 (a) 3D representations of the $2p_x$, $2p_y$, and $2p_z$ atomic orbitals including nodal planes.



(a) $2p$ Orbitals computed using the Schrödinger equation

Shapes of Atomic s and p Orbitals

- Figure 1.9(b) Cartoon representations of the $2p_x$, $2p_y$, and $2p_z$ atomic orbitals.



(b) Cartoon representations of $2p$ orbitals

Molecular Orbital Theory

- MO theory begins with the hypothesis that electrons in atoms exist in atomic orbitals and electrons in molecules exist in molecular orbitals.

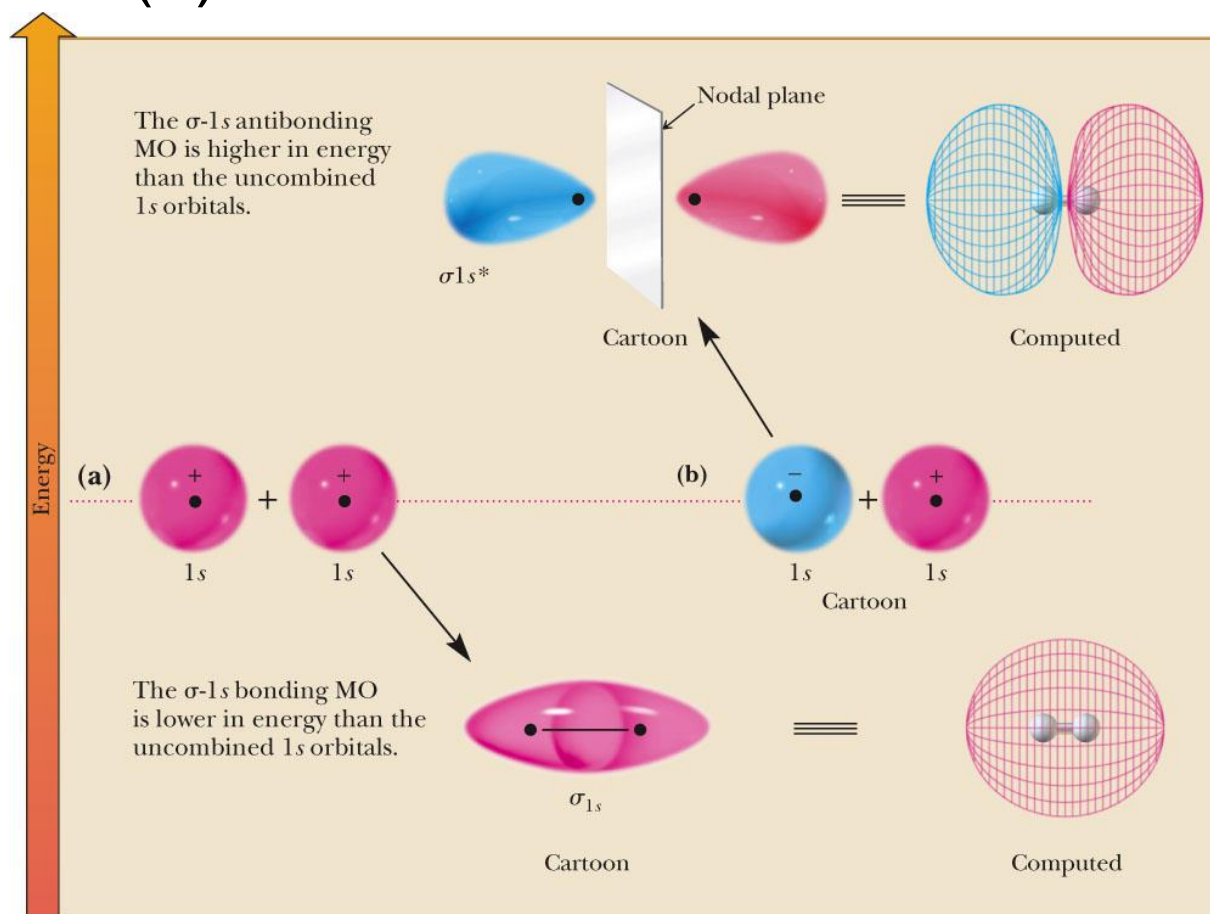
Molecular Orbital Theory

Rules:

- Combination of n atomic orbitals gives n MOs.
- MOs are arranged in order of increasing energy.
- MO filling is governed by the same rules as for atomic orbitals:
 - **Aufbau principle: fill beginning with LUMO**
 - **Pauli exclusion principle: no more than $2e^-$ in a MO**
 - **Hund's rule: when two or more MOs of equivalent energy are available, add $1e^-$ to each before filling any one of them with $2e^-$.**

Molecular Orbital Theory

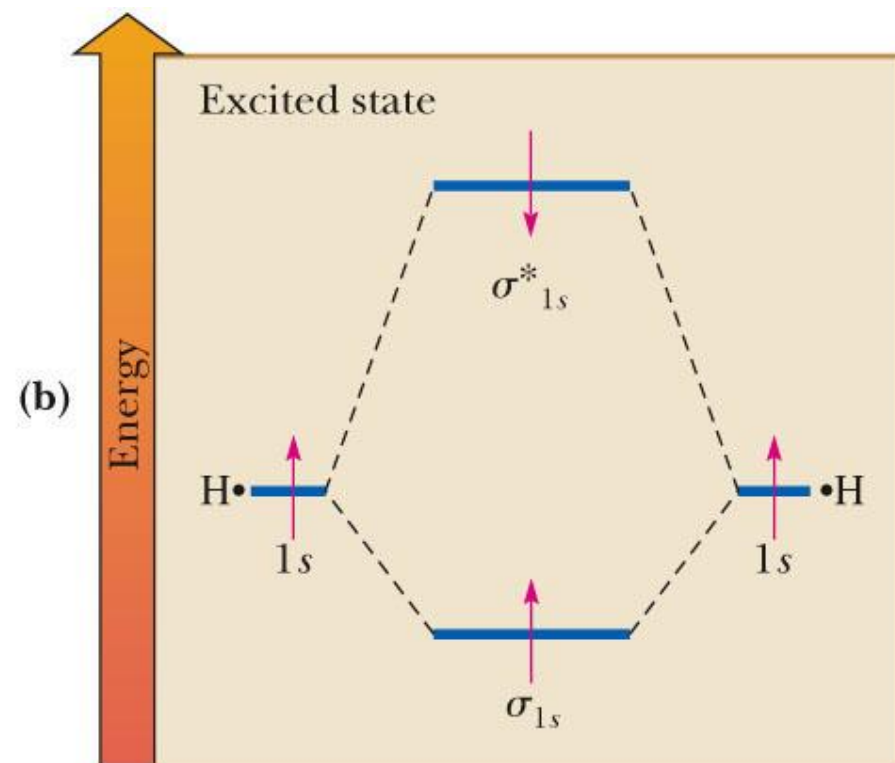
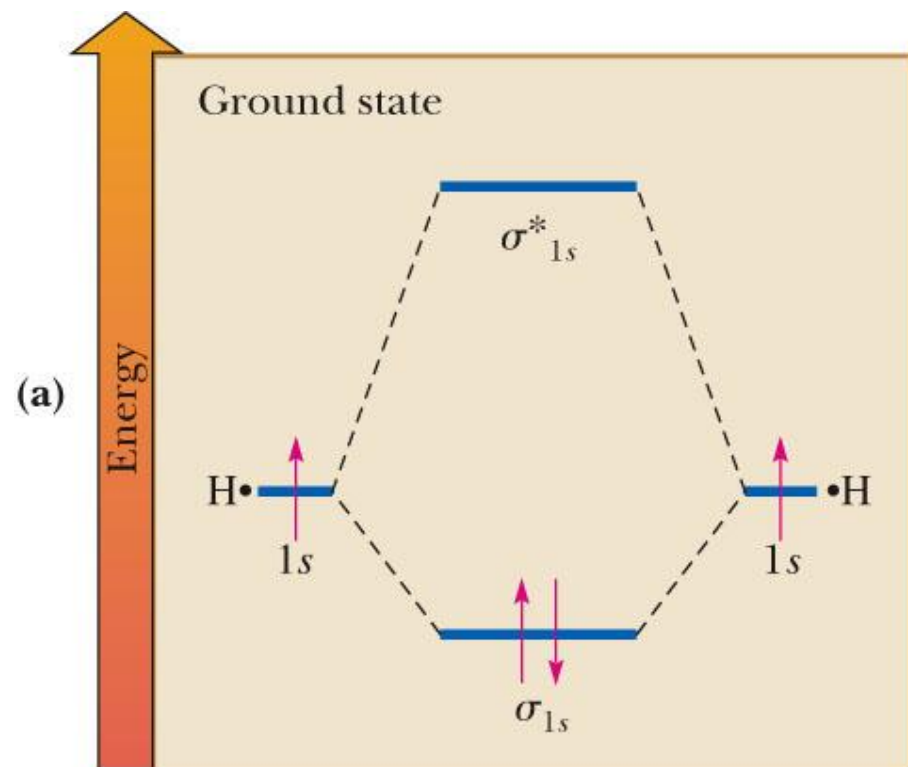
- Figure 1.10 MOs derived from combination by (a) addition and (b) subtraction of two $1s$ atomic orbitals.



Covalent Bonding-Combined VB & MO

- **Bonding molecular orbital:** A MO in which electrons have a lower energy than they would have in isolated atomic orbitals.
- **Sigma (σ) bonding molecular orbital:** A MO in which electron density is concentrated between two nuclei along the axis joining them and is cylindrically symmetrical.

Covalent Bonding-Combined VB & MO



Covalent Bonding-Combined VB & MO

- **Antibonding MO:** A MO in which electrons have a higher energy than they would in isolated atomic orbitals.

VB: Hybridization of Atomic Orbitals

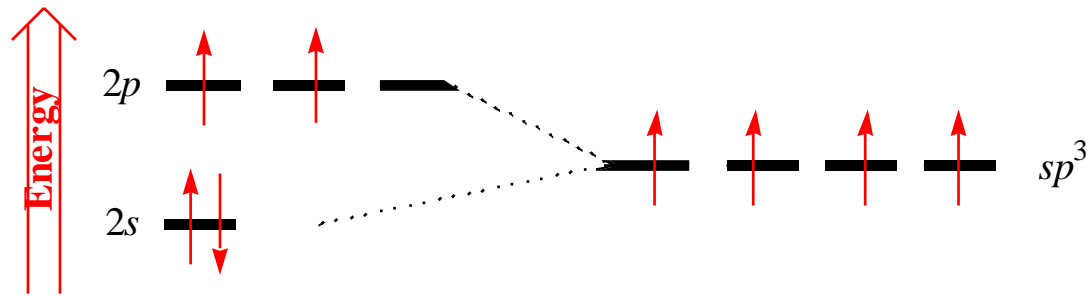
- A principle of VB theory is that bonds are created by the overlap of atomic orbitals.
 - Therefore in VB theory, bonds are localized between adjacent atoms rather than delocalized over several atoms as in MO theory.
 - The VB model correlates with Lewis pictures where two electrons are visualized between atoms as a bond.
 - However, localization of bonds between atoms presents the following problem.
 - In forming covalent bonds, atoms of C, N, and O use $2s$ and $2p$ atomic orbitals.
 - If these atoms used these orbitals to form bonds, we would expect bond angles of approximately 90° .
 - However, we rarely observe these bond angles.

VB: Hybridization of Atomic Orbitals

- Instead, we find bond angles of approximately 109.5° in molecules with only single bonds, 120° in molecules with double bonds, and 180° in molecules with triple bonds.
- Linus Pauling proposed that atomic orbitals for each atom combine to form new atomic orbitals, called **hybrid orbitals**, which form bonds by overlapping with orbitals from other atoms.
- Hybrid orbitals are formed by combinations of atomic orbitals by a process called hybridization.

VB: Hybridization of Atomic Orbitals

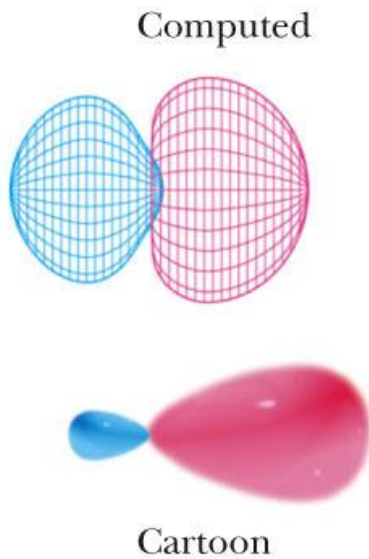
- The number of hybrid orbitals formed is equal to the number of atomic orbitals combined.
- Elements of the 2nd period form three types of hybrid orbitals, designated sp^3 , sp^2 , and sp .
- The mathematical combination of one $2s$ atomic orbital and three $2p$ atomic orbitals forms four equivalent sp^3 hybrid orbitals.



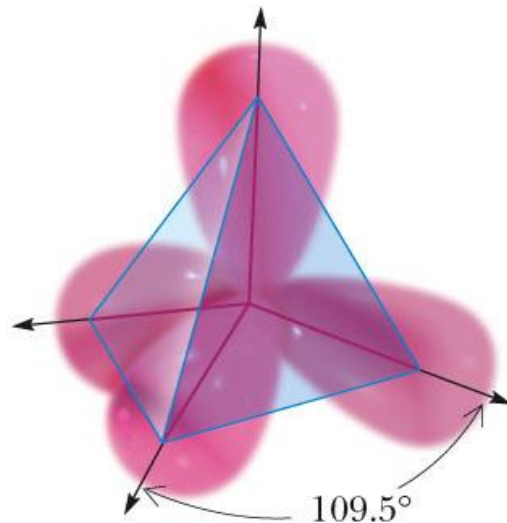
sp^3 Hybridization, with electron population for carbon to form four single bonds

VB: Hybridization of Atomic Orbitals

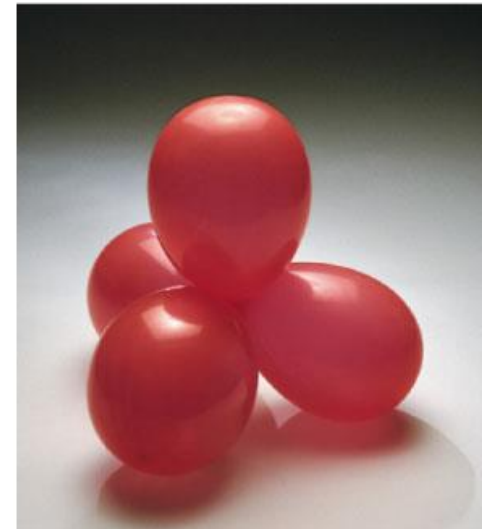
- Figure 1.12 sp^3 Hybrid orbitals. (a) Computed and (b) cartoon three-dimensional representations. (c) Four balloons of similar size and shape tied together, will assume a tetrahedral geometry.



(a) An sp^3 orbital



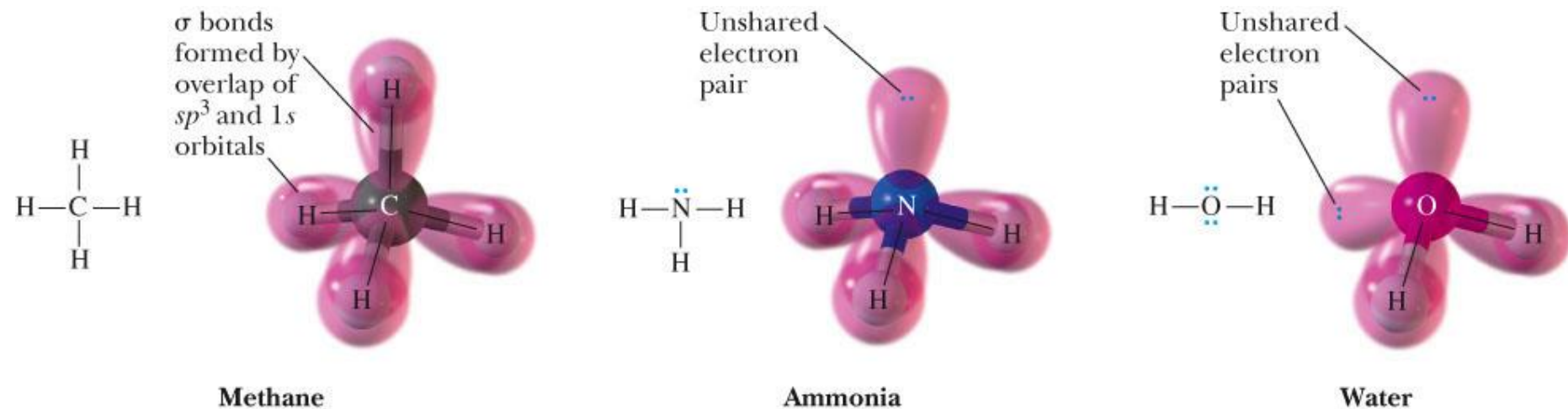
(b) Four sp^3 orbitals in a tetrahedral arrangement



(c)

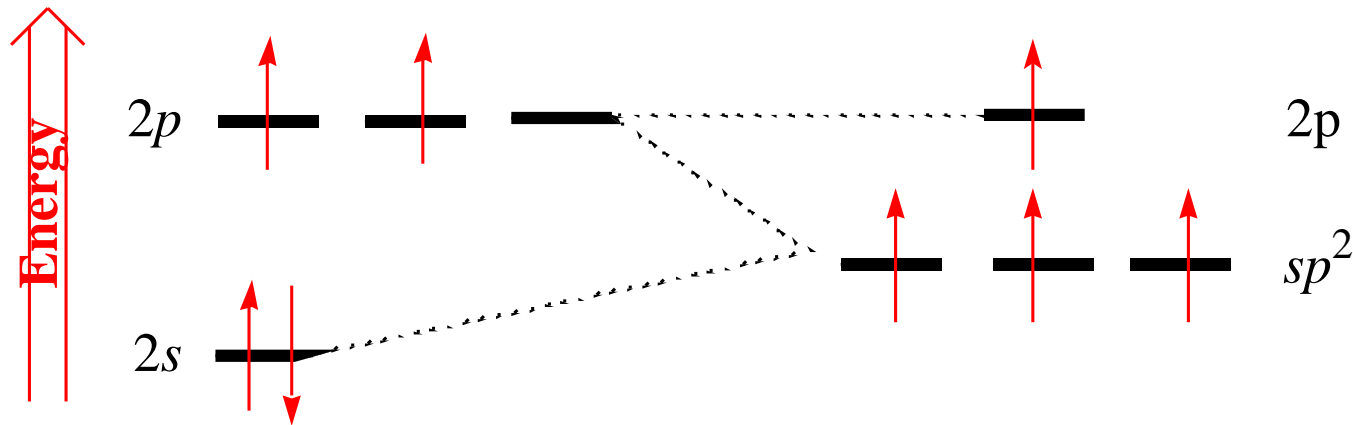
VB: Hybridization of Atomic Orbitals

- Figure 1.13 Orbital overlap pictures of methane, ammonia, and water.



VB: Hybridization of Atomic Orbitals

- The mathematical combination of one $2s$ atomic orbital wave function and two $2p$ atomic orbital wave functions forms three equivalent sp^2 hybrid orbitals.

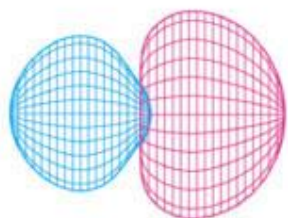


sp^2 Hybridization, with electron population for carbon to form double bonds

VB: Hybridization of Atomic Orbitals

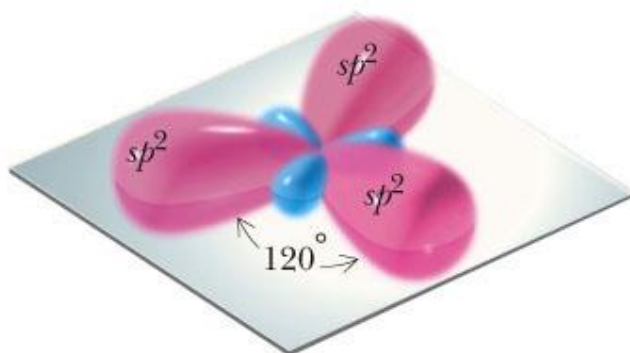
- Figure 1.14 sp^2 Hybrid orbitals and a single $2p$ orbital on an sp^2 hybridized atom.

Computed

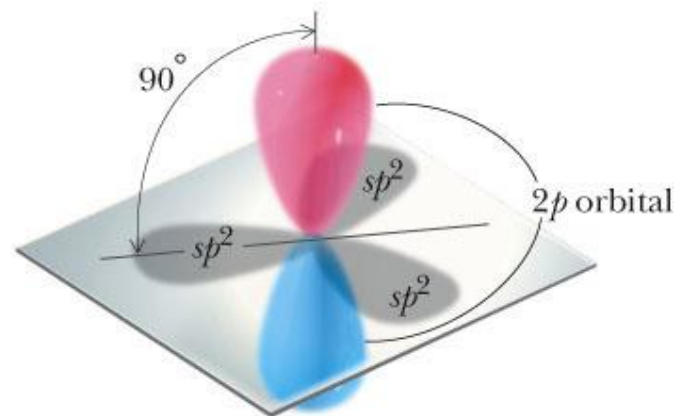


Cartoon

(a) An sp^2 orbital



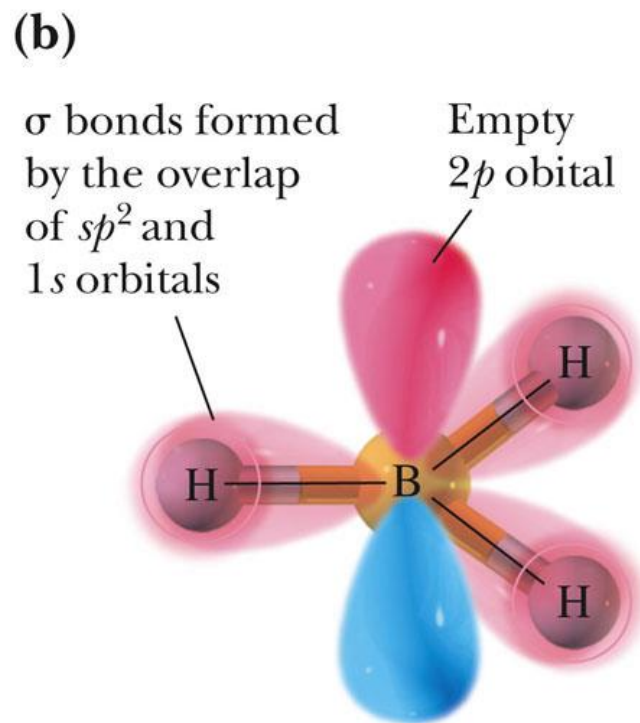
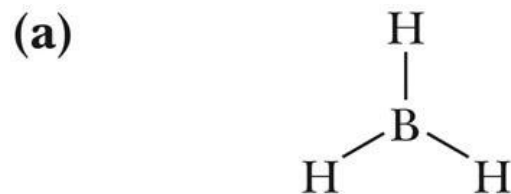
(b) Three sp^2 orbitals



(c) A $2p$ orbital perpendicular to three sp^2 orbitals.

VB: Hybridization of Atomic Orbitals

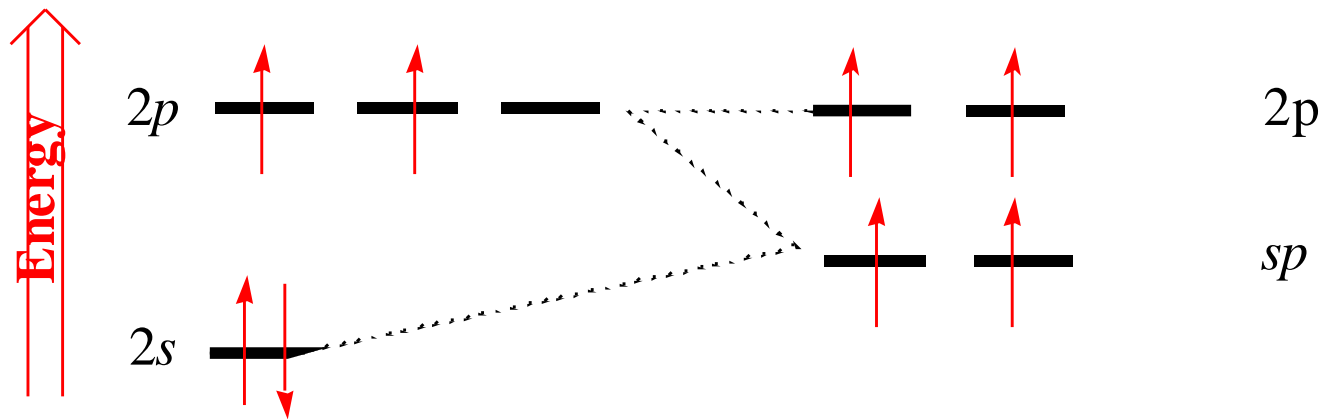
- VSEPR tells us that BH_3 is trigonal planar, with 120° H-B-H bond angles. In BH_3 the unhybridized 2p orbital is empty.



Borane

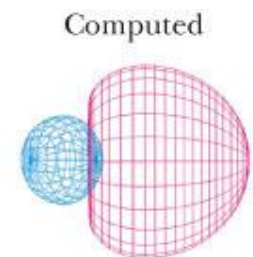
VB: Hybridization of Atomic Orbitals

- The mathematical combination of one $2s$ atomic orbital and one $2p$ atomic orbital gives two equivalent sp hybrid orbitals.

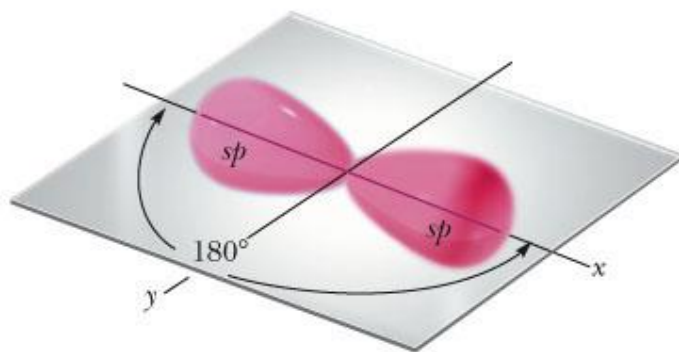


sp Hybridization, with electron population for carbon to form triple bonds

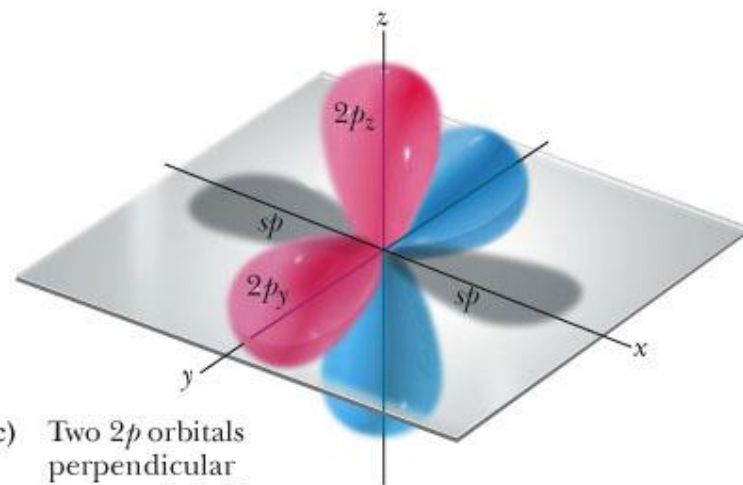
VB: Hybridization of Atomic Orbitals



(a) An sp orbital



(b) Two sp orbitals



(c) Two $2p$ orbitals perpendicular to the sp hybrid orbitals

Combining VB & MO Theories

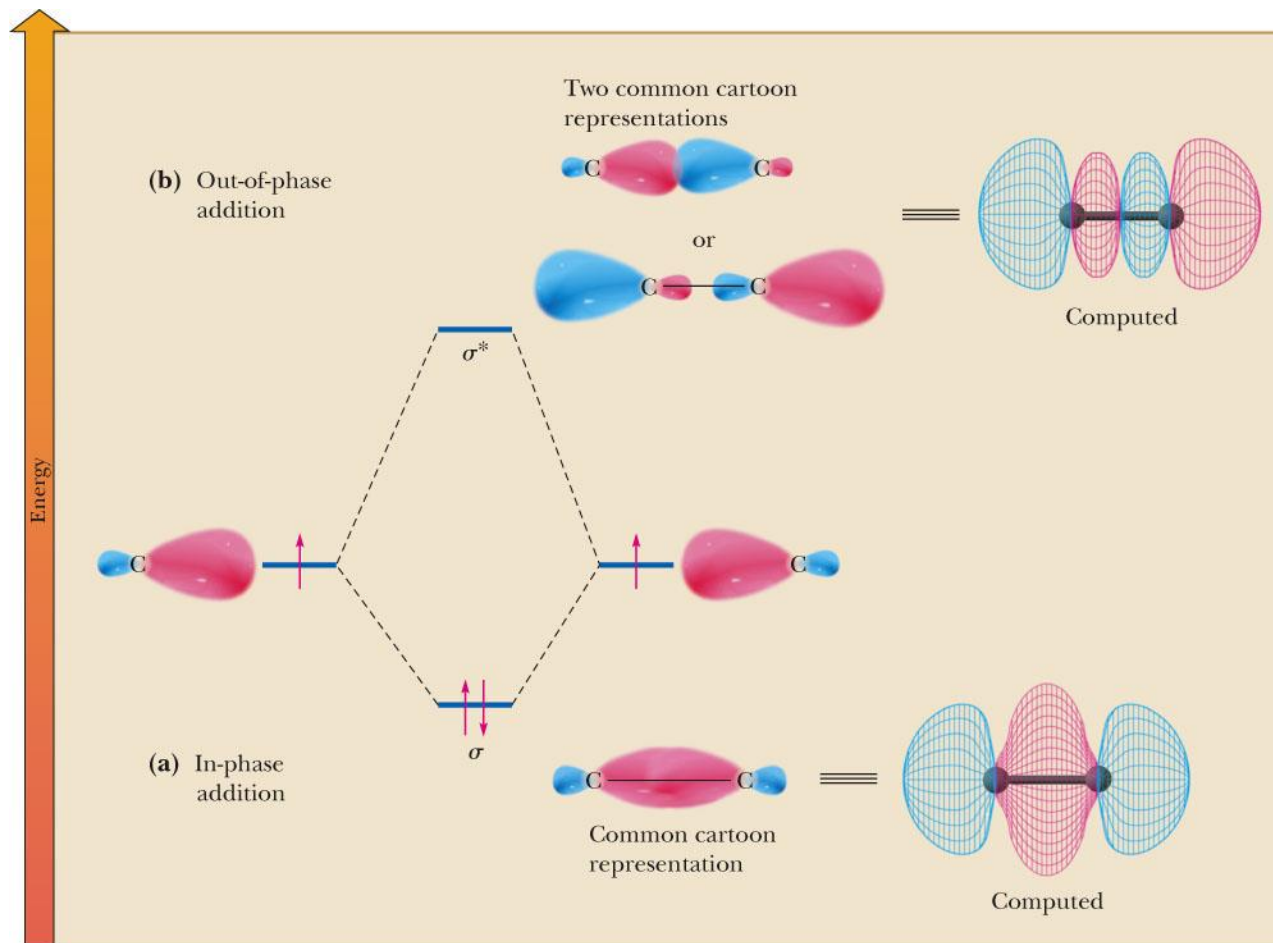
- VB theory views bonding as arising from electron pairs localized between adjacent atoms. These pairs create bonds.
- Further, organic chemists commonly use atomic orbitals involved in three hybridization states of atoms (sp^3 , sp^2 , and sp) to create orbitals to match the experimentally observed geometries.
- How do we make orbitals that contain electrons that reside between adjacent atoms? For this, we turn back to MO theory.

Combining VB & MO Theories

- To create orbitals that are localized between adjacent atoms, we add and subtract the atomic orbitals on the adjacent atoms, which are aligned to overlap with each other.
- Consider methane, CH_4 . The sp^3 hybrid orbitals of carbon each point to a $1s$ orbital of hydrogen and, therefore, we add and subtract these atomic orbitals to create molecular orbitals.
- As with H_2 , one resulting MO is lower in energy than the two separated atomic orbitals, and is called a bonding σ orbital. The other is higher in energy and is antibonding.

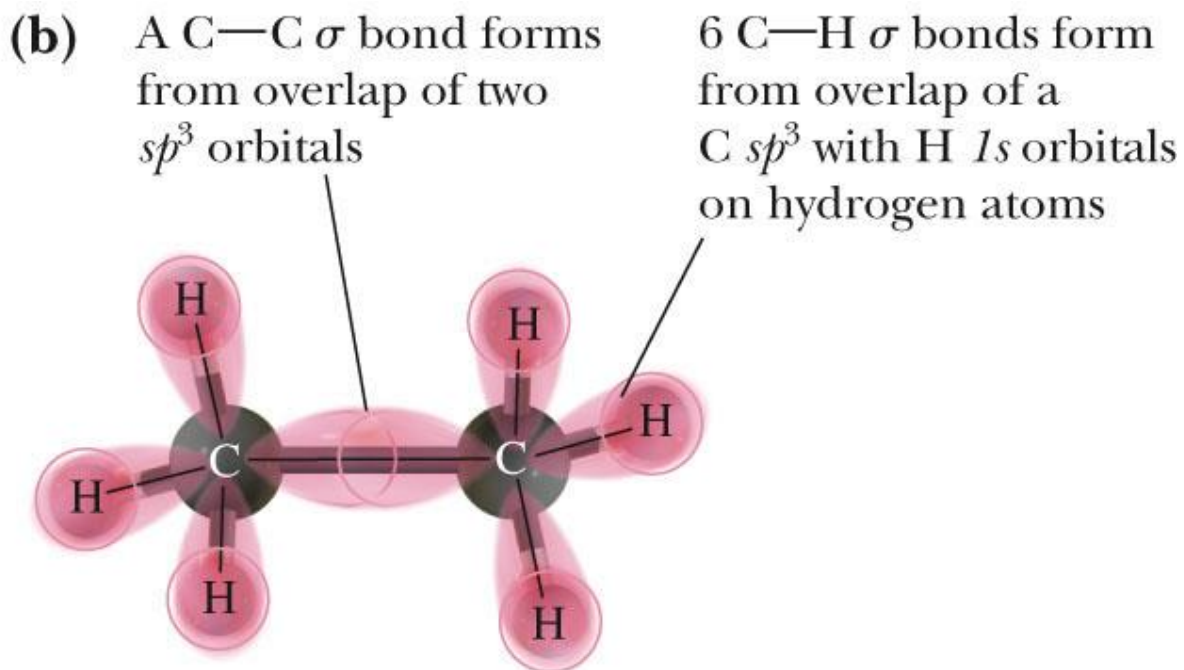
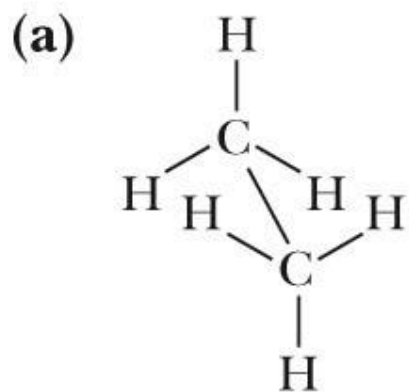
Combining VB & MO Theories

- Figure 1.17 Molecular orbital mixing diagram for creation of any C-C σ bond.



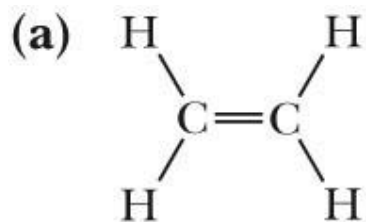
Combining VB & MO Theories

- This approach is used to create C-H σ bonds.
- CH_3CH_3 contains 1 C-C σ bond and 6 C-H σ bonds.

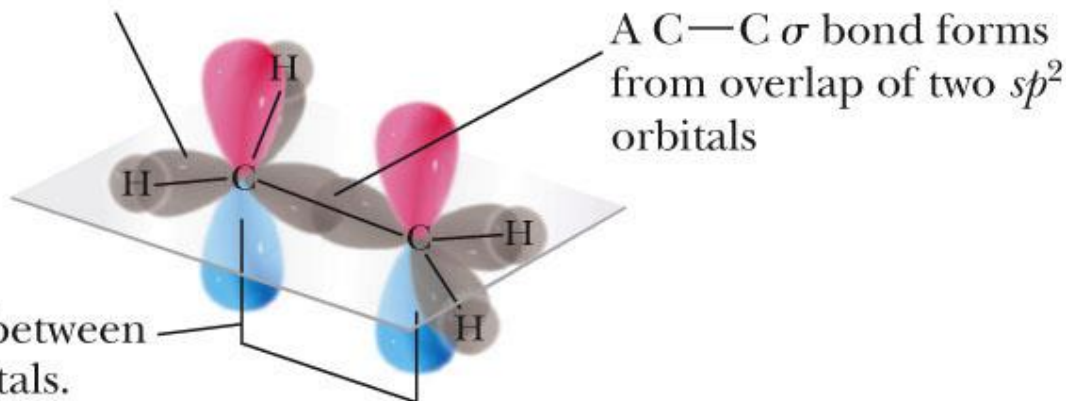


Combining VB & MO Theories

- A double bond uses sp^2 hybridization.
- In ethylene, C_2H_4 . Carbon uses a combination of sp^2 hybrid orbitals and the unhybridized $2p$ orbital to form double bonds.

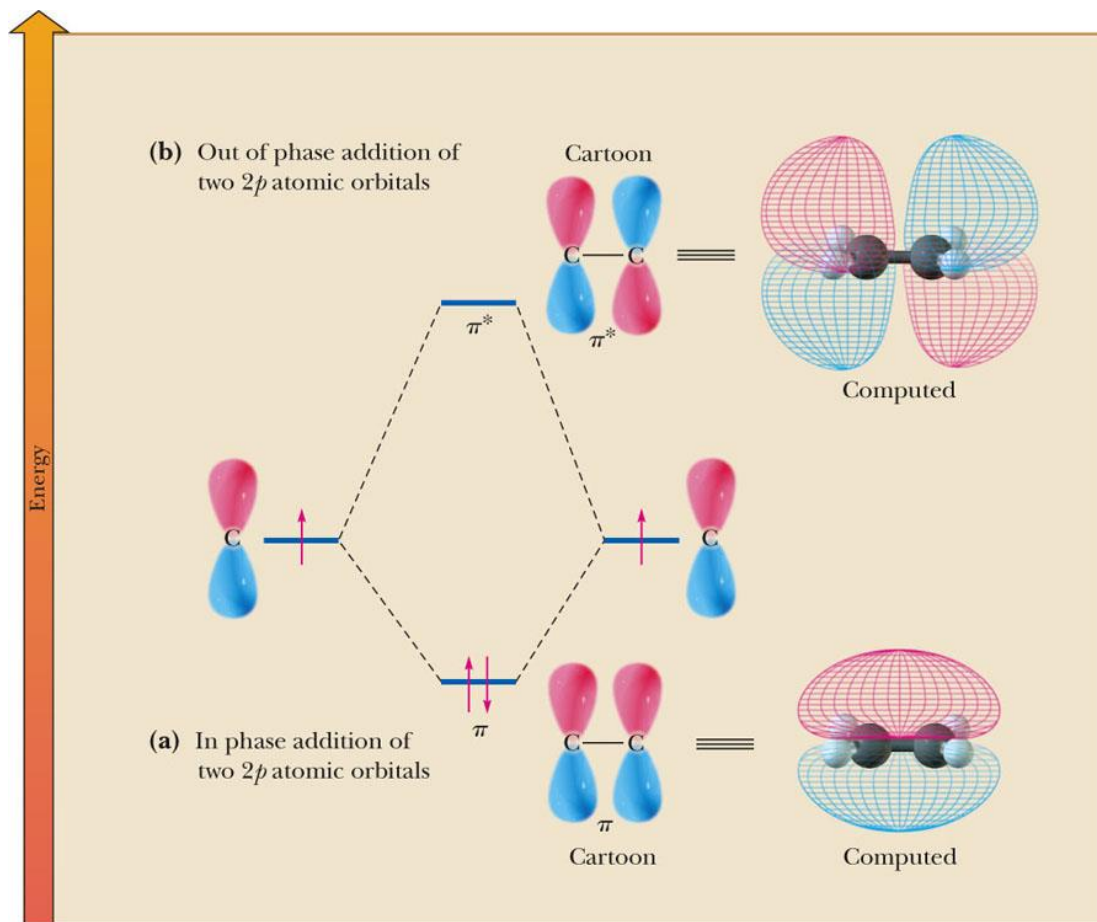


(b) Four C—H σ bonds form from overlap of a C sp^2 and a H $1s$ orbital. See one here.



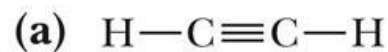
Combining VB & MO Theories

- Figure 1.21 MO mixing diagram for the creation of any C-C π bond.



Combining VB & MO Theories

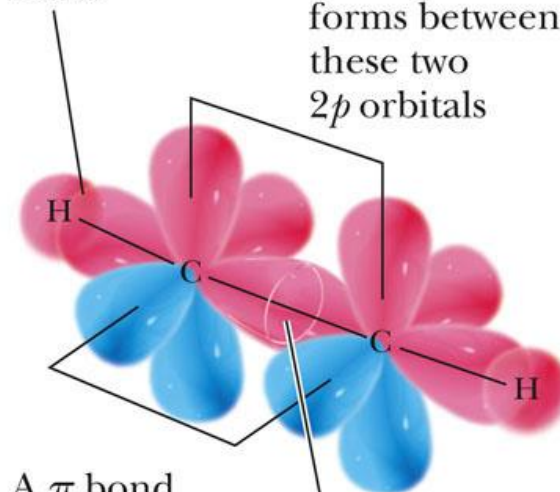
- A carbon-carbon triple bond consists of one σ bond formed by overlap of sp hybrid orbitals and two π bonds formed by the overlap of parallel $2p$ atomic orbitals.



(b)

Two C—H σ bonds form from overlap of a C sp and a H $1s$ orbital. See one here.

A π bond forms between these two $2p$ orbitals

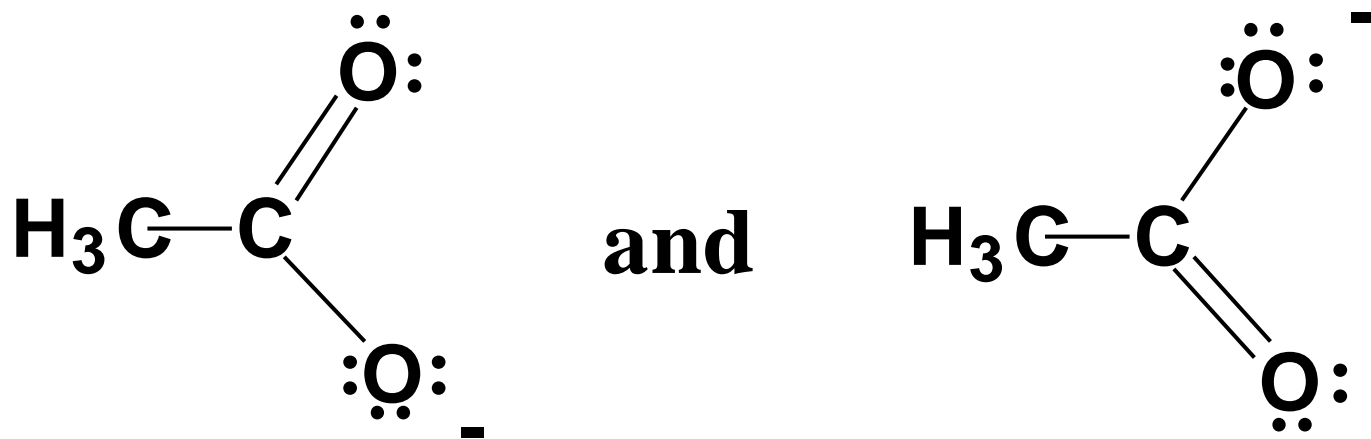


A π bond forms between these two $2p$ orbitals

A C—C σ bond forms from overlap of two sp orbitals

Resonance

- For many molecules and ions, no single Lewis structure provides a truly accurate representation.



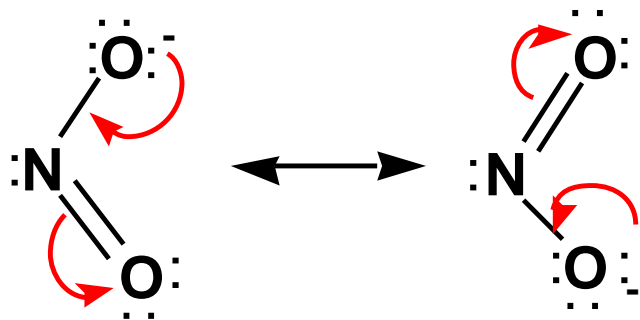
**Ethanoate ion
(acetate ion)**

Resonance

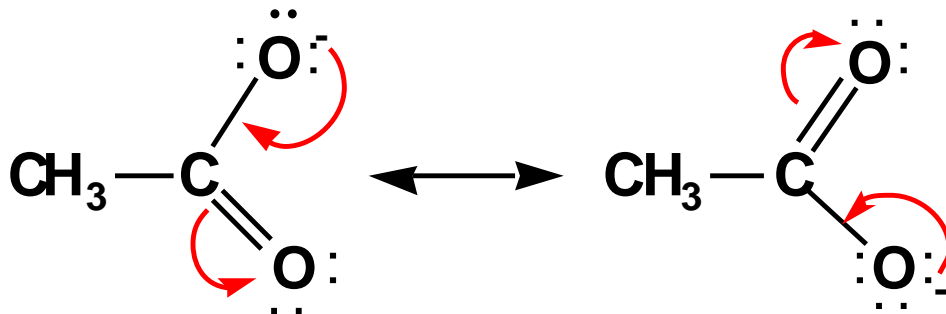
- Linus Pauling - 1930s
 - Many molecules and ions are best described by writing two or more Lewis structures.
 - Individual Lewis structures are called contributing structures.
 - Connect individual contributing structures by double-headed (resonance) arrows.
 - The molecule or ion is a hybrid of the various contributing structures.

Resonance

- **Examples:** equivalent contributing structures.



Nitrite ion
(equivalent contributing
structures)



Acetate ion
(equivalent contributing
structures)

Resonance

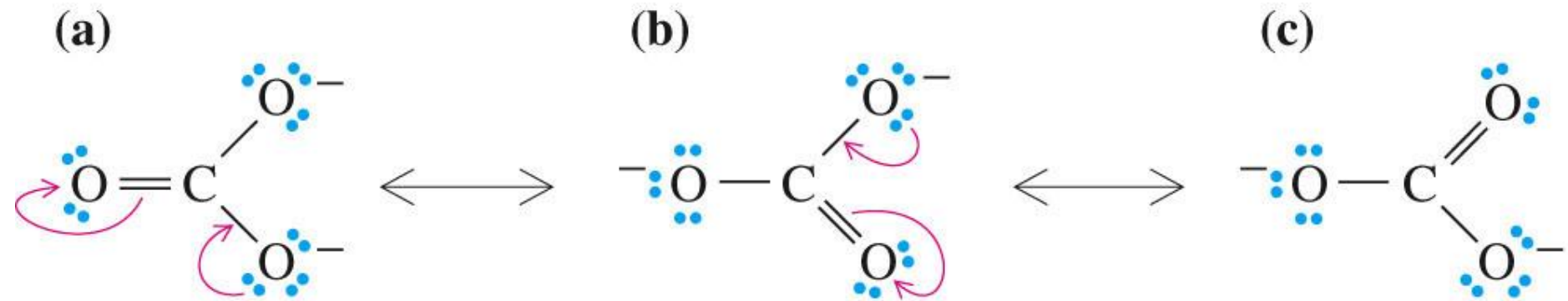
- **Curved arrow:** A symbol used to show the redistribution of valence electrons.
- In using curved arrows, there are only two allowed types of electron redistribution:
 - from a bond to an adjacent atom.
 - from a lone pair on an atom to an adjacent bond.
- Electron pushing is critical throughout organic chemistry.

Resonance

- All contributing structures must
 1. have the same number of valence electrons.
 2. obey the rules of covalent bonding:
 - no more than 2 electrons in the valence shell of H.
 - no more than 8 electrons in the valence shell of a 2nd period element.
 3. differ only in distribution of valence electrons; the position of all nuclei must be the same.
 4. have the same number of paired and unpaired electrons.

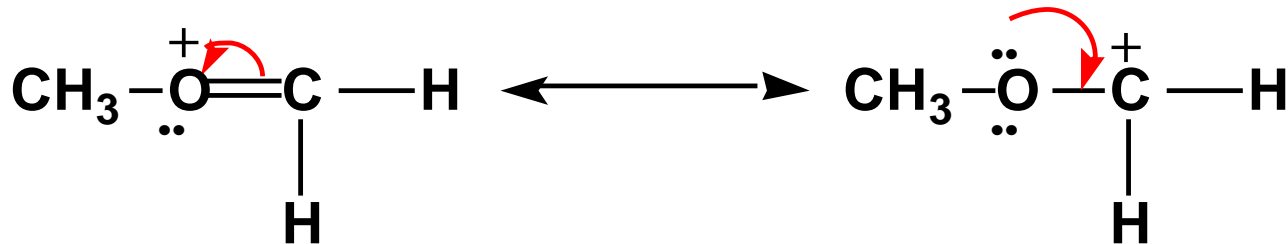
Resonance

- The carbonate ion
 - Is a hybrid of three equivalent contributing structures.
 - The negative charge is distributed equally among the three oxygens.



Resonance

- **Preference 1:** filled valence shells
 - Structures in which all atoms have filled valence shells contribute more than those with one or more unfilled valence shells.

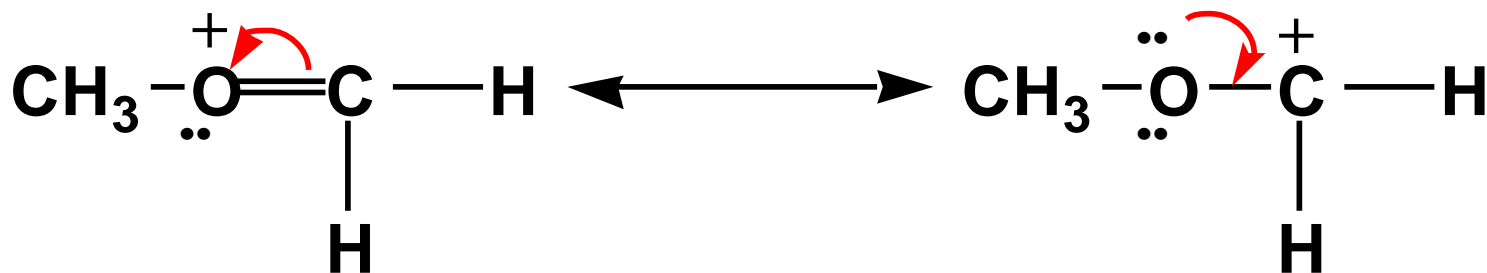


Greater contribution;
both carbon and oxygen have
complete valence shells

Lesser contribution;
carbon has only 6 electrons
in its valence shell

Resonance

- **Preference 2:** maximum number of covalent bonds
 - Structures with a greater number of covalent bonds contribute more than those with fewer covalent bonds.

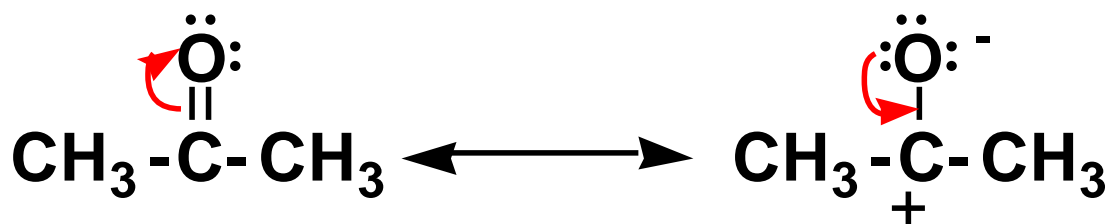


**Greater contribution
(8 covalent bonds)**

**Lesser contribution
(7 covalent bonds)**

Resonance

- **Preference 3:** least separation of unlike charge
 - Structures with separation of unlike charges contribute less than those with no charge separation.

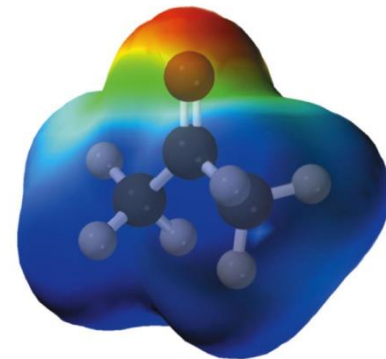
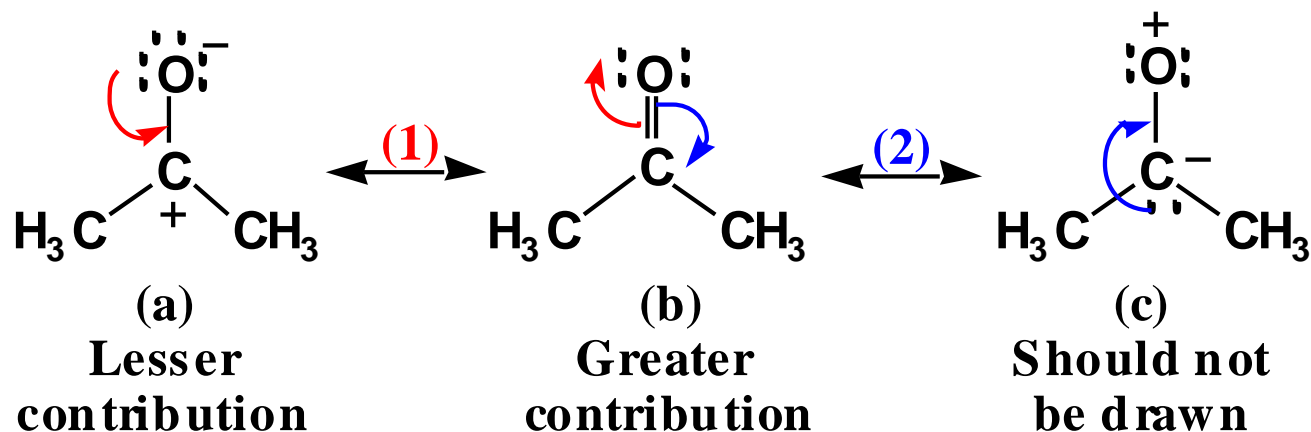


Greater contribution
(no separation of
unlike charges)

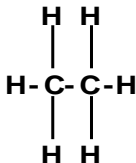
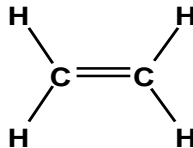
Lesser contribution
(separation of unlike
charges)

Resonance

- **Preference 4:** negative charge on the more electronegative atom.
 - Structures that carry a negative charge on the more electronegative atom contribute more than those with the negative charge on a less electronegative atom.



Bond Lengths and Bond Strengths

Name	Formula	Bond	Orbital Overlap	Bond Length (pm)
Ethane		C-C	sp^3-sp^3	153.2
		C-H	sp^3-1s	111.4
Ethene		C-C	$sp^2-sp^2, 2p-2p$	133.9
		C-H	sp^2-1s	110.0
Ethyne	H-C \equiv C-H	C-C	$sp-sp, \text{ two } 2p-2p$	121.2
		C-H	$sp-1s$	109.0

1.10: Bond Lengths and Strengths

- Alkyne C-C shorter than Alkene C-C
- Alkene C-C shorter than Alkane C-C
- Alkyne C-H shorter than Alkene C-H
- Alkene C-H shorter than Alkane C-H

- Shorter bonds are stronger
- But sigma bonds are stronger than pi

FAKTOR-FAKTOR YANG MENENTUKAN DENSITAS ELEKTRON DALAM MOLEKUL ORGANIK

- Efek Induksi
- Mesomeri/delokalisasi elektron
- Resonansi
- Polarisabilitas
- Sterik/Ruang

PEMAKSAPISAHAN

- Homolitik: menghasilkan radikal
- Heterolitik: menghasilkan karbokation dan karboanion

KAJIAN MEKANISME REAKSI

Chemistry 30A
Introduction to Organic Chemistry
Spring 2009

MWF 12-12:50 CS50

Instructor: Dr. Arif Karim

Office: 3077D Young Hall

Office Hours: M 3-5 and by appointment

Email: akarim@chem.ucla.edu