

principles of chemistry
 BROOKS/COLE
 CENGAGE Learning

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Chapter 8 Covalent Bonding

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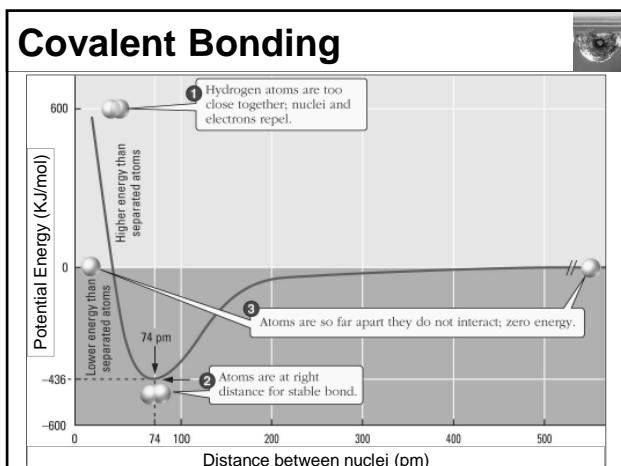
Covalent Bonding

G.N. Lewis (1916):

- Some atoms share e^- to form bonds.

Attraction Stable bond Repulsion

- Number of bonds = Number shared e^- pairs.
- Shared e^- molecules are covalent compounds with covalent bonds.



Single Covalent Bonds

Lewis structures: dot = 1 e^- . Line = 1 pair of e^-

$H \cdot \cdot H$ $H - H$

Single bond: one shared pair of e^- .

Octet rule
 To form bonds, elements gain, lose, or share e^- to achieve 8 **valence** e^-
 (doesn't apply to H)

Single Covalent Bonds

Bonding pairs = e^- pairs shared between atoms.

Lone pairs = unshared e^- pair.

$H \cdot \cdot O \cdot \cdot H$ $H - O - H$

Single Covalent Bonds

$2F = 2(7) = 14$ valence e^- .
 Share 2 e^- to form octets.

$O + 2H = 6 + 2(1) = 8$ val. e^- .
 Two O-H bonds.

$H \cdot \cdot O \cdot \cdot H$

$H \cdot \cdot N \cdot \cdot H$ $N + 3H = 5 + 3(1) = 8$ val. e^- .
 3 N-H bonds.

H

Single Covalent Bonds

Group	# of valence e ⁻	# of e ⁻ shared to form an octet (8 - A group#)	Example	
4A	4	4	C in CH ₄	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H} \end{array}$
5A	5	3	N in NF ₃	$\begin{array}{c} \text{:}\ddot{\text{F}}-\ddot{\text{N}}-\ddot{\text{F}}\text{:} \\ \\ \text{:}\ddot{\text{F}}\text{:} \end{array}$
6A	6	2	O in H ₂ O	$\text{H}-\ddot{\text{O}}-\text{H}$
7A	7	1	F in HF	$\text{H}-\ddot{\text{F}}\text{:}$

Guidelines for Writing Lewis Structures

- Count the valence e⁻ in the molecule.
- Draw a skeleton structure. Join atoms with single lines (pairs of e⁻).
- Add e⁻ pairs to form octets (except H). Start with terminal atoms.

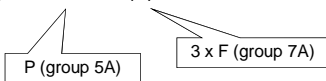
Extra e⁻? Place around the central atom.

Too few e⁻? Convert lone pairs into multiple bonds.

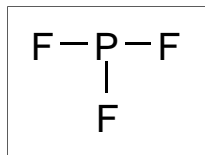
Guidelines for Writing Lewis Structures

Phosphorus trifluoride, PF₃

- PF₃ = 5 + 3(7) = 26 valence e⁻

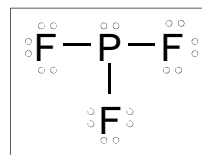


- Skeleton (X is central in XY_n).



Guidelines for Writing Lewis Structures

- Build octets – start with terminal atoms.



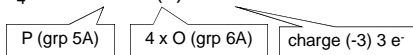
6 e⁻ used in 3 bonds,
20 e⁻ remain (10 pairs)

$$6 + 20 = 26 \text{ e}^-$$

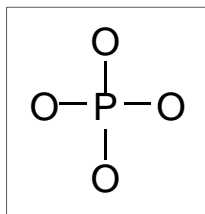
Guidelines for Writing Lewis Structures

Phosphate ion, PO₄³⁻

- PO₄³⁻ = 5 + 4(6) + 3 = 32

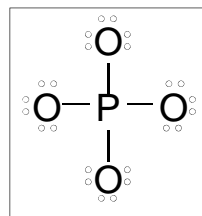


- Skeleton. P is central.



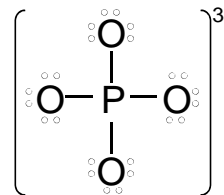
Guidelines for Writing Lewis Structures

- Add e⁻ pairs:



8 e⁻ used in 4 bonds,
24 e⁻ remain (12 pairs)
32 e⁻ used.

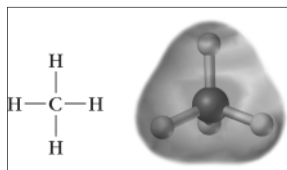
Add brackets and overall charge to show this is an ion.



Single Covalent Bonds in Hydrocarbons

Alkanes = hydrocarbons with C-C single bonds.

Methane:

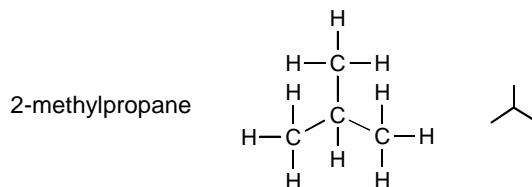
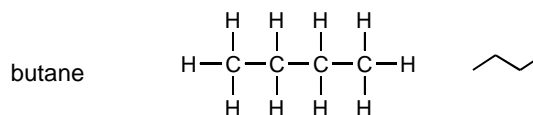


e^- density: red = high density ; blue = low density

Saturated hydrocarbons each C is bonded to its maximum number of H.

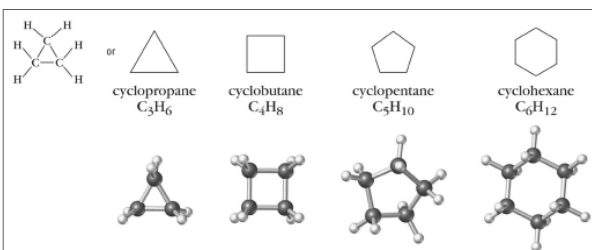
Single Covalent Bonds in Hydrocarbons

Larger alkanes:



Single Covalent Bonds in Hydrocarbons

Cyclic alkanes:



Multiple Covalent Bonds

Too few "dots" to complete all the octets?
Convert lone pairs to shared pairs.

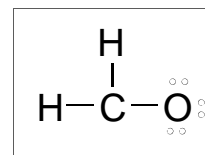
Example methanal (formaldehyde) H_2CO

1. Valence $e^- = 2(1) + 4 + 6 = 12$

2. Skeleton.

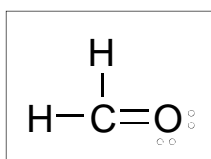
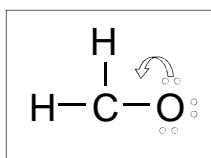
3. 6 e^- in bonds. Add the other 3 pairs to O (outer atom).

- Each H shares 2 e^-
- C only "has" 6 e^- .



Multiple Covalent Bonds

Convert lone pairs to bond pairs.



Each H shares 2 e^-
C shares 8.
O shares 8.

Multiple Covalent Bonds

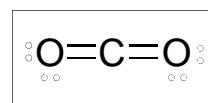
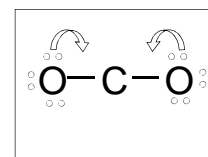
Example carbon dioxide CO_2

1. $4 + 2(6) = 16 e^-$

2. Skeleton

3. 4 e^- in bonds. Add 3 pairs to each O.

4. Convert lone pairs to bond pairs.

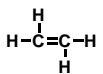


Multiple Covalent Bonds in Hydrocarbons

Alkenes: hydrocarbons with C=C bonds.

- -ene ending.
- C_nH_{2n} (unless cyclic)
- Unsaturated (can add more H)

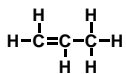
ethene C_2H_4



(ethylene)



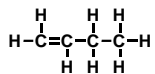
propene C_3H_6



(propylene)



butene C_4H_8



(1 isomer shown)

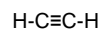


Multiple Covalent Bonds in Hydrocarbons

Alkynes: hydrocarbons with $C\equiv C$ bonds.

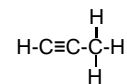
- -yne ending.
- C_nH_{2n-2}
- Unsaturated

ethyne (acetylene)



C_2H_2

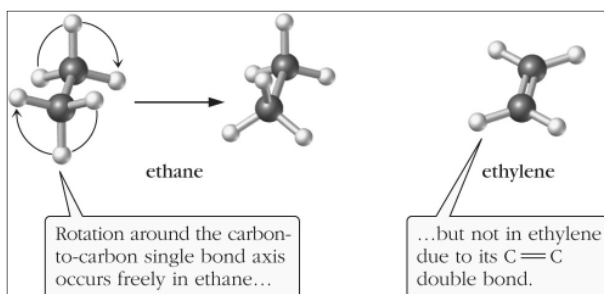
propyne



C_3H_4

Double Bonds and Isomerism

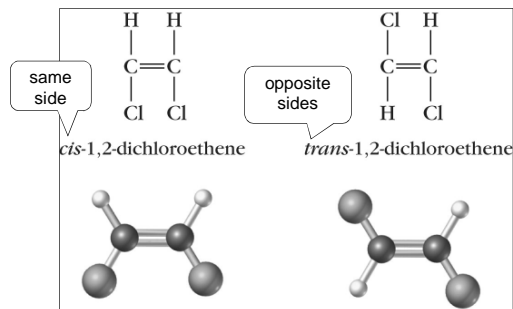
Bond rotation:



$\text{CHCl}=\text{CHCl}$ is "locked" - Two isomers occur.

Double Bonds and Isomerism

1,2-dichloroethene (Cl on carbon 1 and 2)

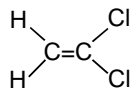
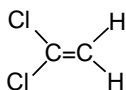


m.p. = -81°C , b.p. = 60°C

m.p. = -50°C , b.p. = 48°C .

Double Bonds and Isomerism

1,1-dichloroethene does not have isomeric forms. (both Cl on carbon 1)

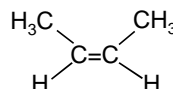


2,2-dichloroethene? NO!
Same molecule
(lowest numbers used)

Double Bonds and Isomerism

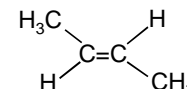
Unsubstituted alkenes can have *cis-trans* isomers.

2-butene ($C=C$ starts on carbon 2)



cis-2-butene

Methyls on the same side.
m.p. = -139°C , b.p. = 4°C .

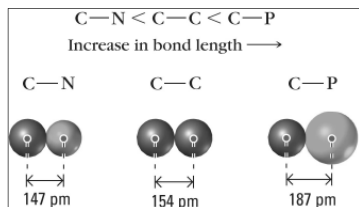


trans-2-butene

Methyls on opposite sides.
m.p. = -106°C , b.p. = 1°C .

Bond Properties: Bond Length

Atom size and bond type are important:



Bond	Bond length (pm)
C—O	143 pm
C=O	
C≡O	122 pm
C—O	113 pm
C=O	

Bond Length

Table 8.1 Some Average Single and Multiple Bond Lengths (in picometers, pm)*

Single Bonds											
	I	Br	Cl	S	P	Si	F	O	N	C	H
H	161	142	127	132	138	145	92	94	98	110	74
C	210	191	176	181	187	194	141	143	147	154	
N	205	184	169	174	180	187	134	136	140		
O	199	180	165	170	176	183	130	132			
F	197	178	163	168	174	181	128				
Si	250	251	216	221	227	254					
P	243	224	209	214	220						
S	237	218	205	208							
Cl	232	215	200								
Br	217	228									
I	266										

Multiple Bonds			
N=N	120	C=C	134
N=N	110	C=C	121
C=N	127	C=O	122
C=N	115	C=O	113
O=O (in O ₂)	112	N=O	108
N=O	115		

*1 pm = 10⁻¹⁰ m.

Bond Enthalpies

Bond Enthalpy (*D*) Shorter bond = stronger bond.

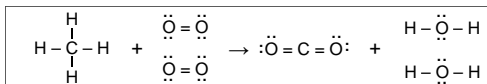
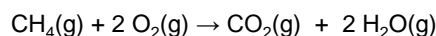
Table 8.2 Average Bond Enthalpies (in kJ/mol)*

Single Bonds											
	I	Br	Cl	S	P	Si	F	O	N	C	H
H	299	366	431	347	322	323	566	467	391	416	436
C	213	285	327	272	264	301	486	336	285	356	
N	—	—	193	—	—200	335	272	201	160		
O	201	—	205	—	—340	368	190	146			
F	—	—	255	326	490	582	158				
Si	254	310	391	226	—	226					
P	184	264	519	—	209						
S	—	213	255	226							
Cl	209	217	242								
Br	180	193									
I	151										

Multiple Bonds			
N=N	418	C=C	598
N=N	946	C=C	813
C=N	616	C=O (as in CO ₂ , O=C=O)	803
C=N	866	C=O (as in H ₂ C=O)	695
O=O (in O ₂)	498	C=O	1073

Bond Enthalpies

Estimate ΔH for the following reaction from bond *E*.



$$\begin{aligned} \Delta H &= \{\text{sum of bonds broken}\} - \{\text{sum of bonds formed}\} \\ &= \{4 D_{\text{C-H}} + 2 D_{\text{O=O}}\} - \{2 D_{\text{C=O}} + 4 D_{\text{H-O}}\} \\ &= \{4(416) + 2(498)\} - \{2(803) + 4(467)\} \\ &= -814 \text{ kJ} \end{aligned}$$

(experimental value is -802 kJ)

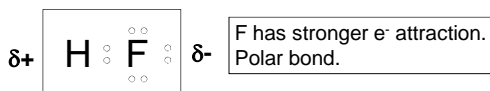
Bond Polarity and Electronegativity

Bonding pairs are not always **equally** shared.

Nonpolar = equally shared (identical atoms).



Polar = unequal sharing (different attraction for e⁻)

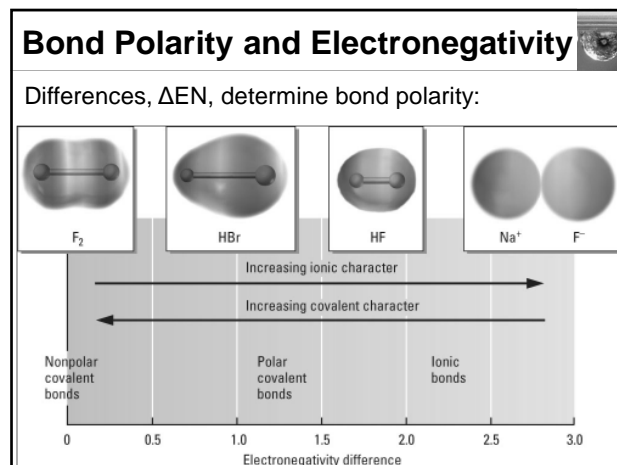
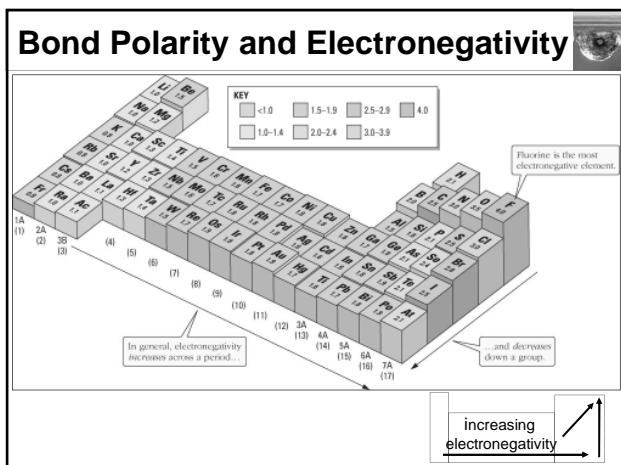


Bond Polarity and Electronegativity

Polar bond: one atom is more electronegative.

Electronegativity = ability of an atom in a covalent bond to attract shared e⁻ to itself.

- Linus Pauling developed the first scale
- Based on bond energies.
- Pauling's scale: F = 4.0 (arbitrary).
- Unitless.



Bond Polarity and Electronegativity

Consider the bond pairs (i) Cl-F & Br-F and (ii) Si-Br & C-Br. Which bond is more polar in each pair? Show $\delta+$ and $\delta-$.

ClF vs BrF
 $EN_F > EN_{Cl} > EN_{Br}$
 In each case F is $\delta-$, the other end is $\delta+$.

ΔEN (F and Br) $>$ ΔEN (F and Cl)
 BrF is more polar than ClF.

(Electronegativities: Br = 2.8, Cl = 3.0, F = 4.0)

increasing electronegativity

Bond Polarity and Electronegativity

(ii) Si-Br & C-Br. More polar? $\delta+$ and $\delta-$?

SiBr vs CBr
 $EN_{Si} < EN_C < EN_{Br}$. Si is $\delta+$ in SiBr, C is $\delta+$ in CBr.

Largest ΔEN between Si and Br
 SiBr is more polar than SiC.

(Electronegativities: Si = 1.8, C = 2.5, Br = 2.8)

increasing electronegativity

Formal Charge

Used to study charge distribution in a molecule.

Method

- Find the number of e^- assigned to each atom:
 e^- "on" an atom = (lone pair e^-) + $\frac{1}{2}$ (bonding e^-)
- Formal charge of each atom
 $= (\# \text{ of valence } e^-) - (e^- \text{ "on" the atom})$.

Note: sum of formal charges = charge on species

Formal Charge

	O	C	N
Valence e^-	6	4	5
Lone pair e^-	6	0	2
$\frac{1}{2}$ shared e^-	1	4	3
Formal Charge	-1	0	0

Check: Σ (formal charges) = ion charge = -1

Formal Charge

Given a choice between Lewis structures:

- Smaller formal charges are favored.
- Negative formal charges should be on the most EN atoms
- Like charges should **not** be on adjacent atoms

Example

Which N_2O structure is preferred?



Formal charges: -1 +1 0 0 +1 -1
Preferred. $EN_O > EN_N$

Formal Charge

Which ClO_2^- structure is preferred?



Formal charges: -1 0 0 -1 +1 -1

Preferred
(Smaller charges)

Lewis Structures and Resonance

Ozone has 2 equivalent structures:



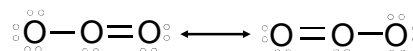
Both:

- obey the octet rule
- have the same number and types of bonds
- have the same formal charges

Experiments show that the OO bonds are identical.

Lewis Structures and Resonance

Resonance structures are used to show O_3 is a mixture of both:



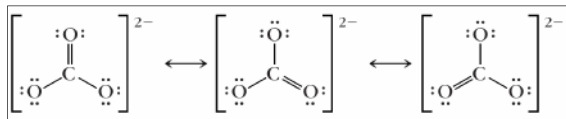
- They differ only in e⁻ pair positions.
- Atom positions must not change.

Resonance hybrids are also used: $O \text{---} O \text{---} O$

Each is $1\frac{1}{2}$ bonds. O_3 does NOT "flip" back & forth.

Lewis Structures and Resonance

Resonance in CO_3^{2-}



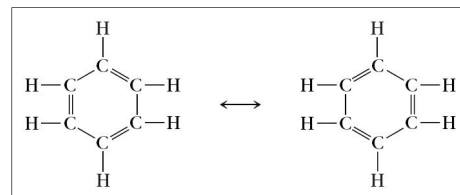
Experiment: All three CO bonds = 129 pm.

Typical bond lengths:

C-O 143 pm
C=O 122 pm

Lewis Structures and Resonance

Benzene, C_6H_6 , is a ring compound best described using resonance ideas:



Experimental: All C-C bonds are identical.

Lewis Structures and Resonance

Benzene is often represented by line-angle structures:



or



Where a circle shows:

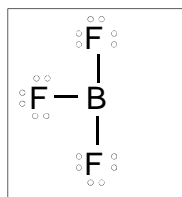
- The C=C π bond e^- are delocalized.
- The π e^- spread out around the ring.

Exceptions to the Octet Rule

Fewer than 8 valence electrons: Be and B compounds:



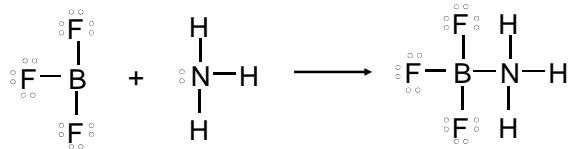
$$2 + 2(1) = 4 \text{ valence } e^-$$



$$3 + 3(7) = 24 \text{ valence } e^-$$

Fewer than Eight Valence Electrons

Often very reactive:

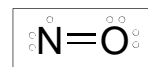


Odd Number of Valence Electrons

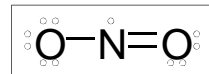
Some stable molecules have an odd number of e^- .

Examples

$$\text{NO} \quad 5 + 6 = 11 \text{ valence } e^-$$



$$\text{NO}_2 \quad 5 + 2(6) = 17 \text{ valence } e^-$$



Free radical = atom or molecule with unpaired e^- .

Very reactive. Most stable molecules have paired e^- .

More Than Eight Valence Electrons

"Expanded octets" are relatively common.

Low-lying d orbitals can accept extra e^-
(only 3rd period and beyond).

Examples

- 5 bonds (5 e^- pairs) around P in PF_5
 - NF_5 does not exist
- 4 bonds and 1 lone-pair (5 e^- pairs) around S in SF_4
 - OF_4 does not exist.

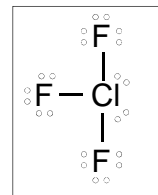
More Than Eight Valence Electrons

$$\text{ClF}_3 \quad 7 + 3(7) = 28 \text{ val. } e^-$$

Make octets on F.

24 e^- used, 4 remain.

[bonds (3 x 2); Lone pairs (3 x 6)]



Add 2 lone pairs to Cl – the 3rd period element.

Molecular Orbital Theory

Bond formation by overlap of atomic orbitals and e⁻-pair sharing is called valence bond theory.

It works well, but it fails to reliably predict magnetic properties.

- O₂ prediction: :Ö=Ö: (all e⁻ paired = diamagnetic).
- Experiment: O₂ is paramagnetic.

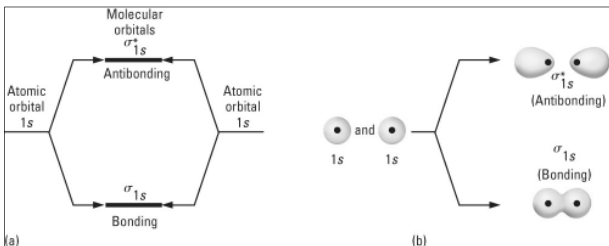
Molecular orbital (MO) theory corrects this problem.

Molecular Orbital Theory

- Valence atomic orbitals (AOs) are combined to form MOs.
- MOs can extend over an entire molecule.
- They are **not** confined to pairs of atoms.
- *Number of AOs mixed = number of MOs formed*
- Valence e⁻ fill the MOs following the Pauli exclusion principle.
- Hund's rule is obeyed.

Molecular Orbitals for Diatomics

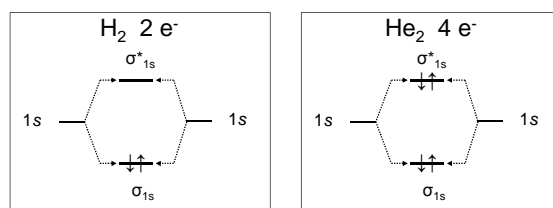
MOs produced by combining 1s AOs:



- Bonding MOs are more stable (lower E) than the original AOs.
- Antibonding (*) MOs are less stable.

Molecular Orbitals for Diatomics

Add valence e⁻ (obey Pauli):



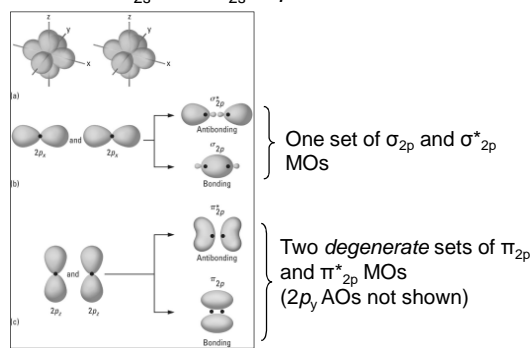
Bond order = $\frac{1}{2} \{(\text{bonding } e^-) - (\text{antibonding } e^-)\}$

$$\text{H}_2: = \frac{1}{2} \{2 - 0\} = 1 \text{ bond}$$

He₂ does not exist! (It would have $\frac{1}{2} \{2 - 2\} = 0$ bond)

Molecular Orbitals for Diatomics

2s AOs form σ_{2s} and σ_{2s}^* . 2p AOs form:



Molecular Orbitals for Diatomics

MO predictions:

Molecular orbitals	Occupancy of Orbitals							
	σ_{2s}	σ_{2s}^*	π_{2p}	π_{2p}	σ_{2p}	π_{2p}^*	π_{2p}^*	σ_{2p}^*
Li ₂	(↑↓)							
Be ₂	(↑↓)	(↑↓)						
B ₂	(↑↓)	(↑↓)	(↑)	(↑)				
C ₂	(↑↓)	(↑↓)	(↑↓)	(↑↓)				
N ₂	(↑↓)	(↑↓)	(↑↓)	(↑↓)	(↑↓)			
O ₂	(↑↓)	(↑↓)	(↑↓)	(↑↓)	(↑↓)	(↑)	(↑)	
F ₂	(↑↓)	(↑↓)	(↑↓)	(↑↓)	(↑↓)	(↑↓)	(↑↓)	
Ne ₂	(↑↓)	(↑↓)	(↑↓)	(↑↓)	(↑↓)	(↑↓)	(↑↓)	(↑↓)

Degenerate (Equal E) Degenerate (Equal E)

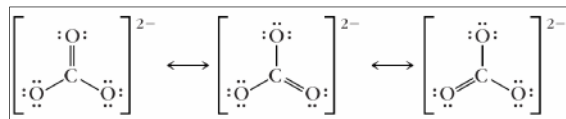
Molecular Orbitals for Diatomics

	Predicted Properties		Observed Properties	
	Unpaired e ⁻	Bond Order	Unpaired e ⁻	Bond E (kJ/mol)
Li ₂	0	1	0	105
Be ₂	0	0	0	Unstable
B ₂	2	1	2	289
C ₂	0	2	0	598
N ₂	0	3	0	946
O ₂	2	2	2	498
F ₂	0	1	0	158
Ne ₂	0	0	0	Nonexistent

Polyatomics; Delocalized π -Electrons

Consider CO₃²⁻

Lewis dot + resonance view:



MO view of CO₃²⁻

- The skeleton involves three σ bonds.
- A delocalized π MO holds the 4th e⁻ pair.