Announcements

- HW3 due on Friday, 14th
- HW4 distributed today and due on Friday, 21st
- Mid-term exam 2 will be on Tues, 25th
- The class on the 20th will serve as a review session
- Piatra, Chris M, and John: meeting scheduled today
- Kevin and Gerardo: need to schedule

Grading

- 95+ A+
- 90-94=A
- 87-89=A-
- 84-86=B+
- 80-83=B
- 77-79=B-
- 74-76=C+
- 70-73=C

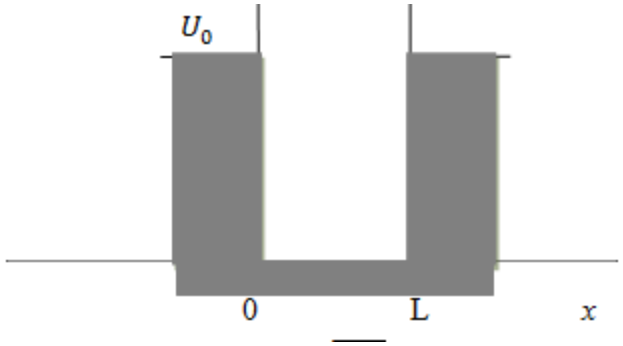
Lecture 11 Topics

- Atoms coming together
- Bonding of atoms
  - Valence bond approach
  - Molecular orbital approach
    - Bonding and antibonding states
    - Bonding types: sigma and pi and others
    - Diatomic molecules
    - Hybridized orbitals: sp3 and sp2
- Molecular energy quantization due to
  - Rotation
  - Vibration
- Molecular spectra

When atoms come together

Finite Well

$$U(x) = \begin{cases} U_0 & x \leq 0 \\ 0 & 0 < x < L \\ U_0 & x \geq L \end{cases}$$



When atoms come together

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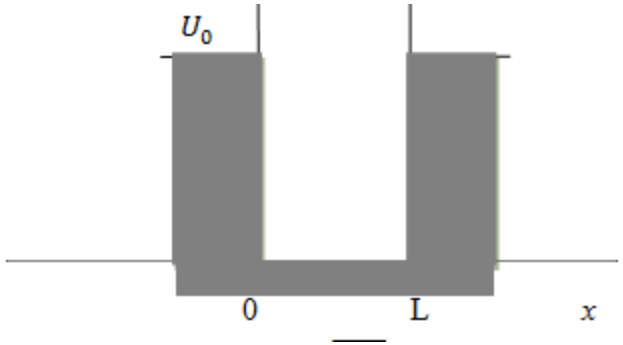

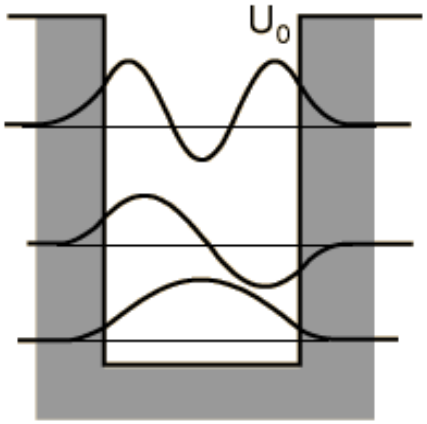

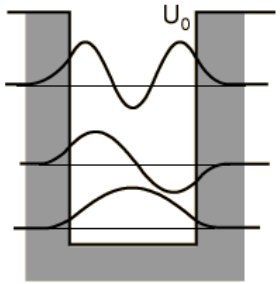
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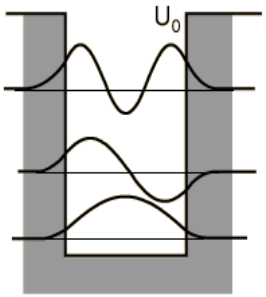
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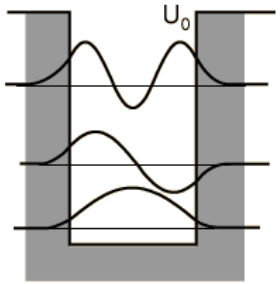
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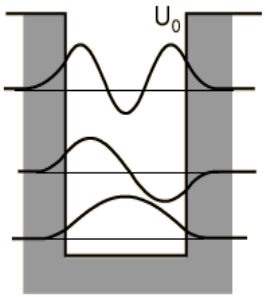
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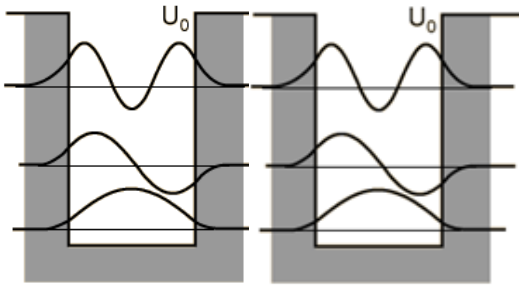
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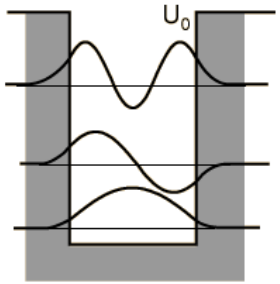
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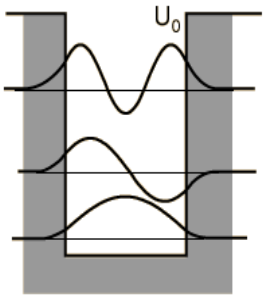
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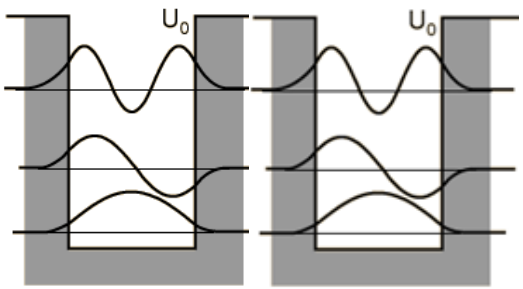
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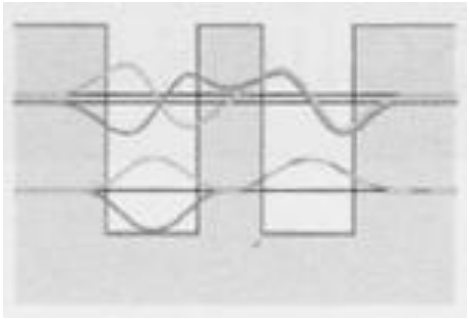

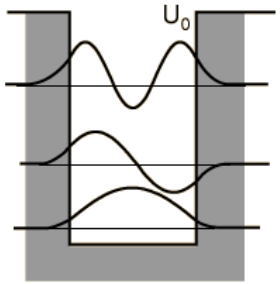
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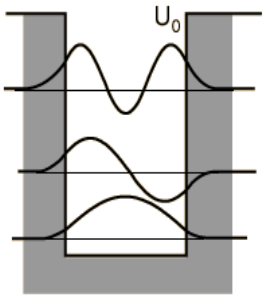
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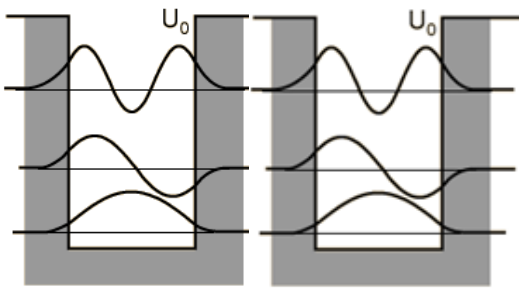
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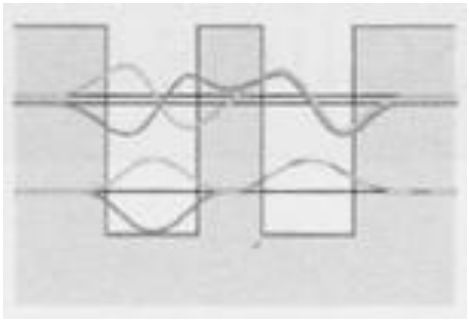

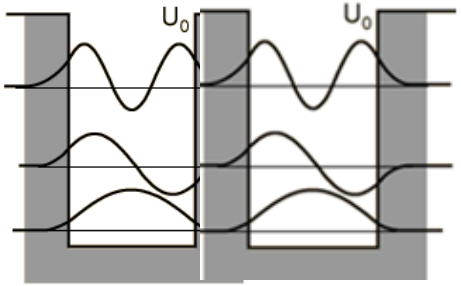
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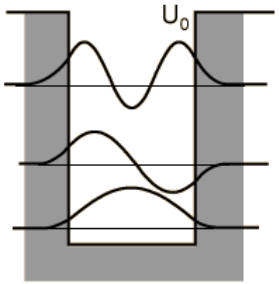
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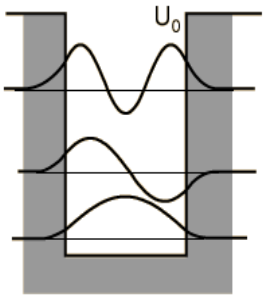
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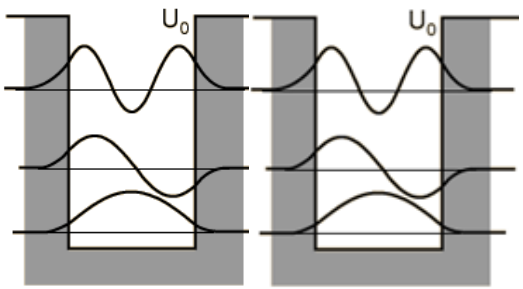
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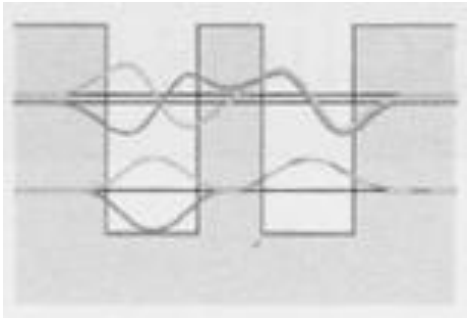

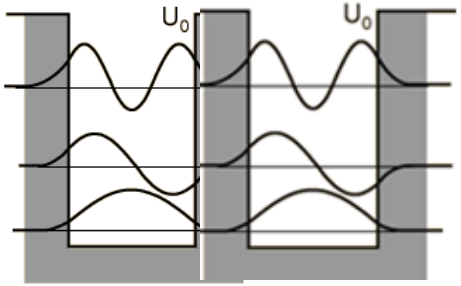
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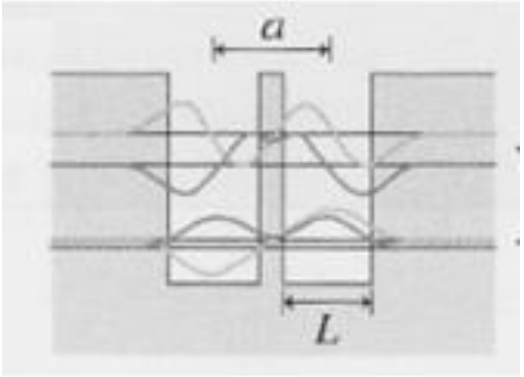
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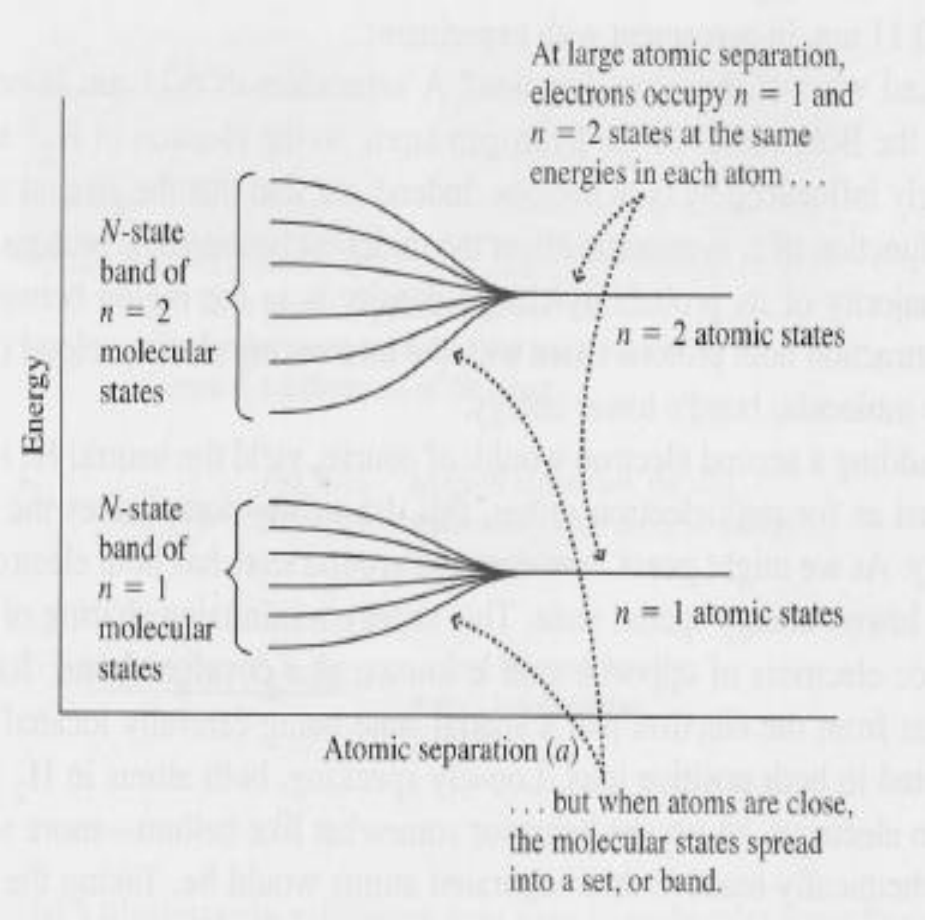
So, when atoms come together



Molecules

- Two or more atoms together
- A molecule forms when it gives a more stable arrangement than individual atoms
- Bonded via valence electrons
  - Inner electrons are relatively stable
- Two approaches
  - Valence bond approach
  - Molecular orbital approach

Valence bond approach

- Each bond consists of two electrons of opposite spins; each electron is provided by an atom in the molecule.
- The bond is called covalent bond.
- Use dots or lines to represent a bond.
- Hund's rule allows the availability of unpaired valence electrons in each atom for bonding.

Valence band approach

Element	*Atomic number*	*Atomic structure*	*Occupancy of orbitals* 1s	2s	$2p_x$	$2p_y$	$2p_z$	*Unpaired electrons*	*Molecular structure*	*Bond energy,*
Hydrogen, H	1	$1s$	↑					1 (1s)	H—H	4.72
Helium, He	2	$1s^2$	↑↓					0	No molecule	
Lithium, Li	3	$1s^2 2s$								
Beryllium, Be	4	$1s^2 2s^2$								
Boron, B	5	$1s^2 2s^2 2p$								
Carbon, C	6	$1s^2 2s^2 2p_x^2$								
Nitrogen, N	7	$1s^2 2s^2 2p^3$								
Oxygen, O	8	$1s^2 2s^2 2p^4$								
Fluorine, F	9	$1s^2 2s^2 2p^5$								
Neon, N	10	$1s^2 2s^2 2p^6$								

Valence band approach

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Helium, He	2	$1s^2$	↑↓					0	No molecule	
Lithium, Li	3	$1s^2 2s$	↑↓	↑				1 (2s)	Li—Li	1.03
Beryllium, Be	4	$1s^2 2s^2$								
Boron, B	5	$1s^2 2s^2 2p$								
Carbon, C	6	$1s^2 2s^2 2p_x^2$								
Nitrogen, N	7	$1s^2 2s^2 2p^3$								
Oxygen, O	8	$1s^2 2s^2 2p^4$								
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Helium, He	2	$1s^2$	↑↓					0	No molecule	
Lithium, Li	3	$1s^2 2s$	↑↓	↑				1 (2s)	Li—Li	1.03
Beryllium, Be	4	$1s^2 2s^2$	↑↓	↑↓				0	No molecule	
Boron, B	5	$1s^2 2s^2 2p$	↑↓	↑↓	↑			1 (2p)	B—B	3.0
Carbon, C	6	$1s^2 2s^2 2p_x^2$	↑↓	↑↓	↑	↑		2 (2p)	C=C	6.5
Nitrogen, N	7	$1s^2 2s^2 2p^3$								
Oxygen, O	8	$1s^2 2s^2 2p^4$								
Fluorine, F	9	$1s^2 2s^2 2p^5$								
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Valence band approach

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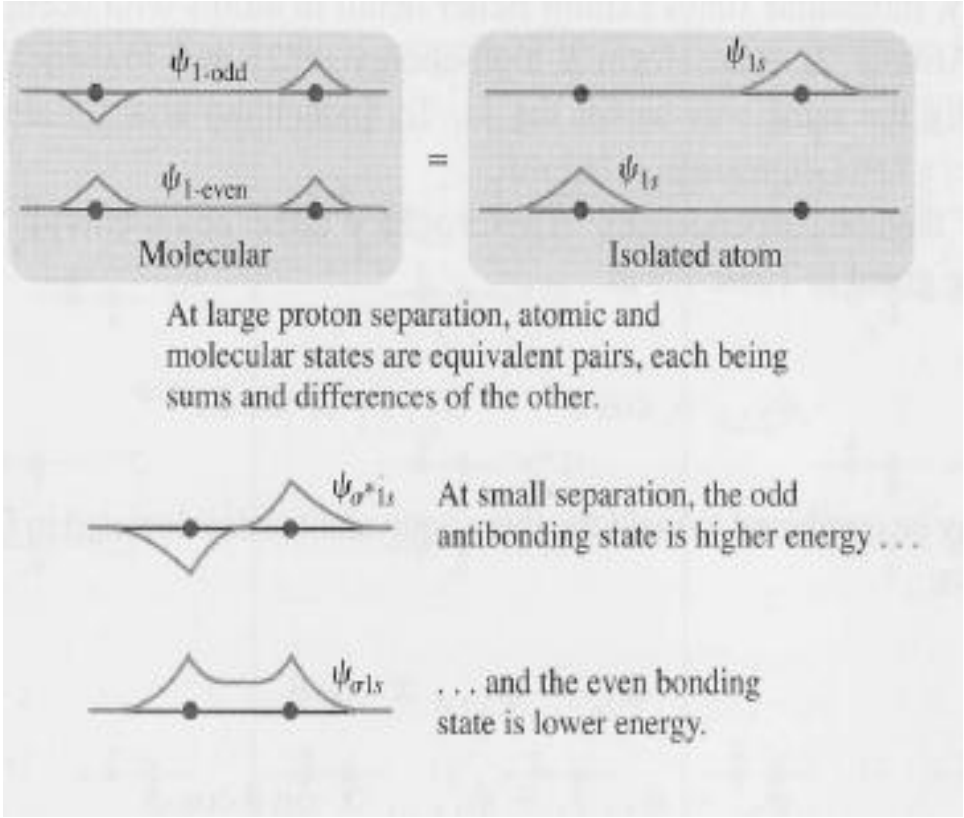
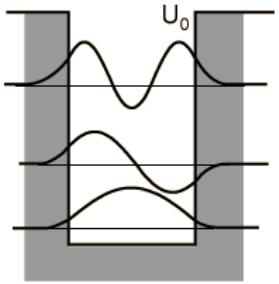
Helium, He	2	$1s^2$	↑↓					0	No molecule	
Lithium, Li	3	$1s^22s$	↑↓	↑				1 (2s)	Li—Li	1.03
Beryllium, Be	4	$1s^22s^2$	↑↓	↑↓				0	No molecule	
Boron, B	5	$1s^22s^22p$	↑↓	↑↓	↑			1 (2p)	B—B	3.0
Carbon, C	6	$1s^22s^22p_x^2$	↑↓	↑↓	↑	↑		2 (2p)	C=C	6.5
Nitrogen, N	7	$1s^22s^22p^3$	↑↓	↑↓	↑	↑	↑	3 (2p)	N≡N	9.8
Oxygen, O	8	$1s^22s^22p^4$	↑↓	↑↓	↑↓	↑	↑	2 (2p)	O=O	5.1
Fluorine, F	9	$1s^22s^22p^5$	↑↓	↑↓	↑↓	↑↓	↑	1 (2p)	F—F	1.6
Neon, N	10	$1s^22s^22p^6$	↑↓	↑↓	↑↓	↑↓	↑↓	0	No molecule	

Molecular orbital approach

- Electrons can be shared in two ways:
  - Bonding state
  - Antibonding state

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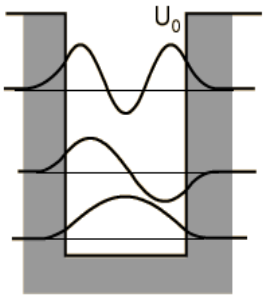
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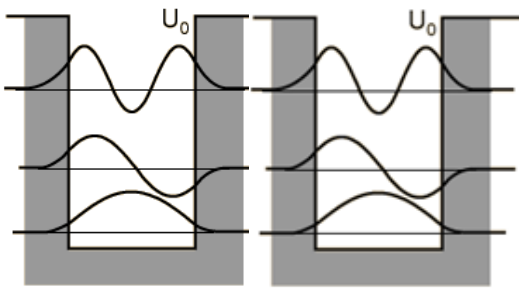
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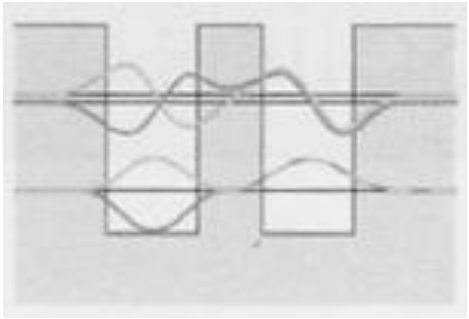

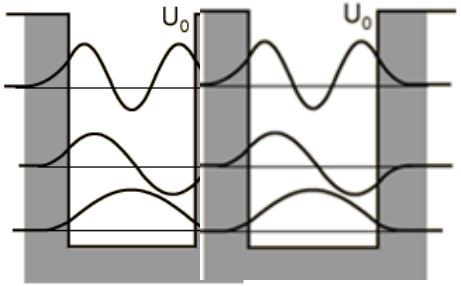
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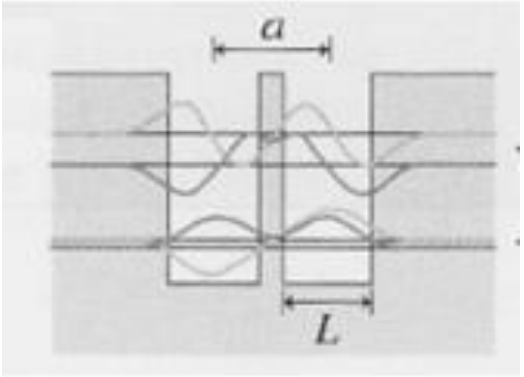
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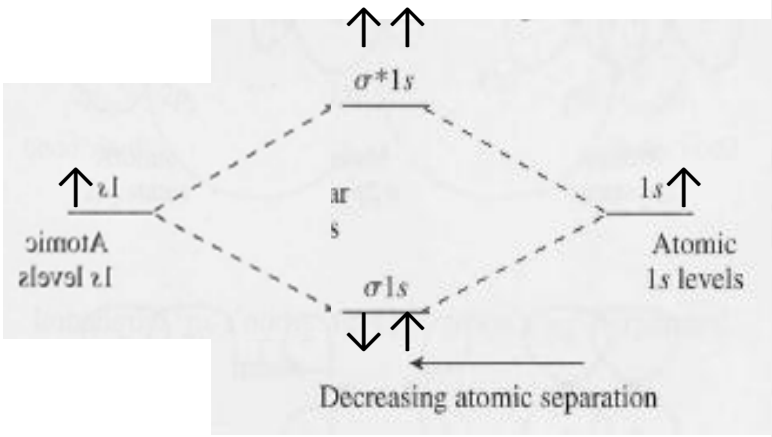
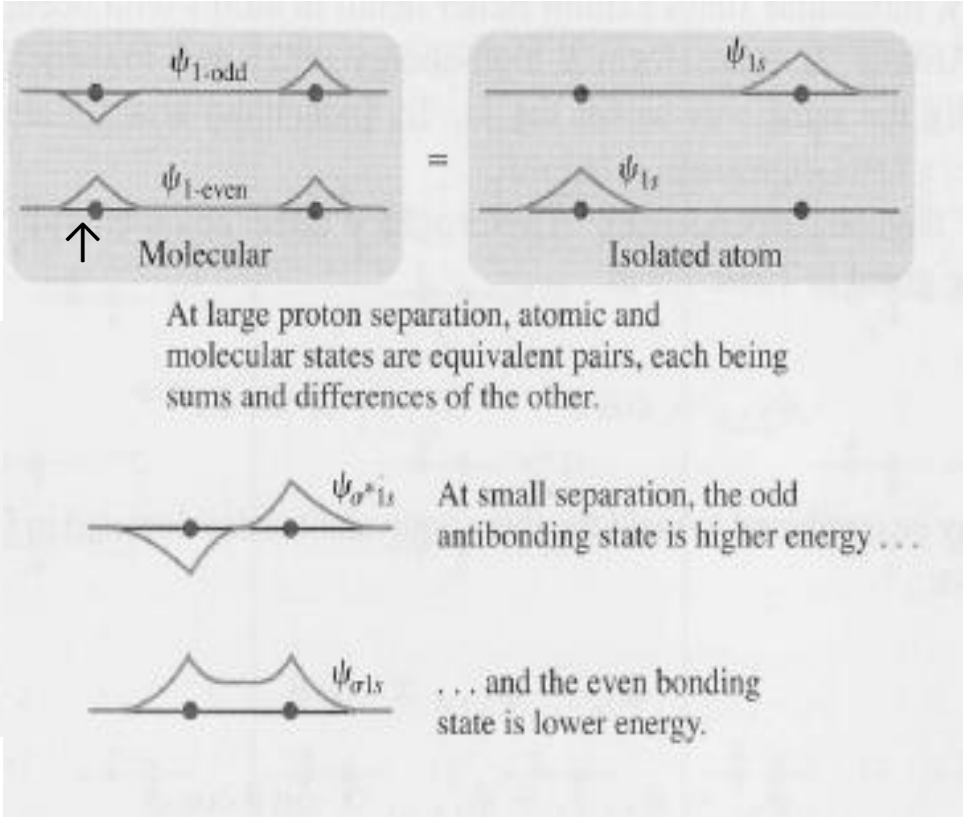
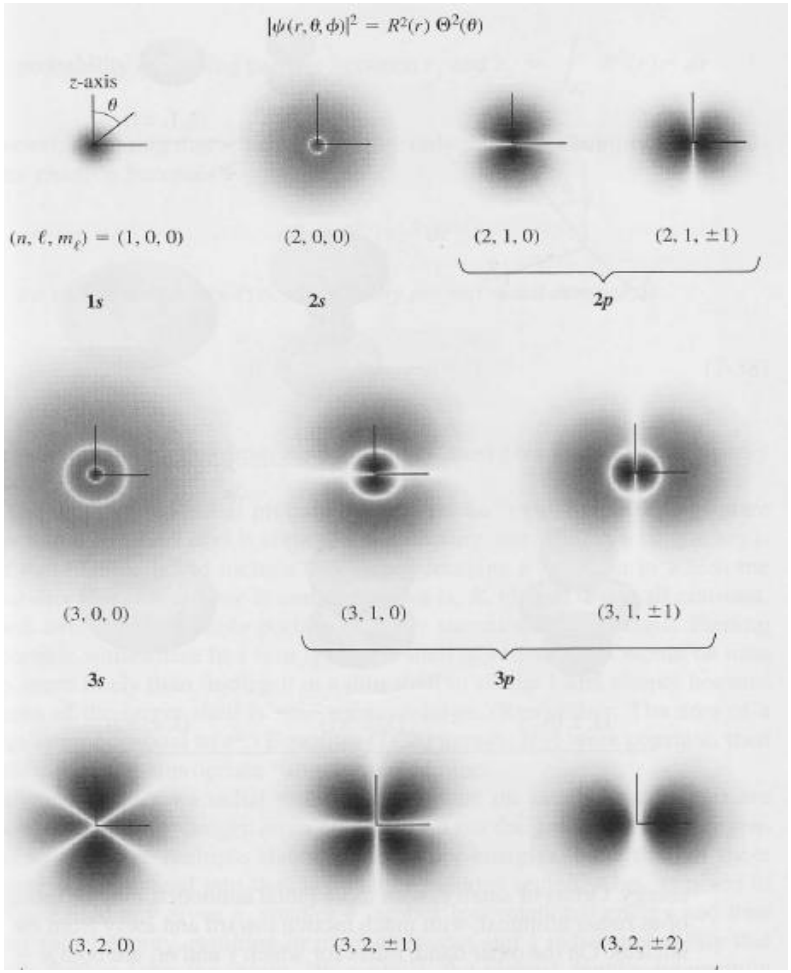
Molecular orbital approach

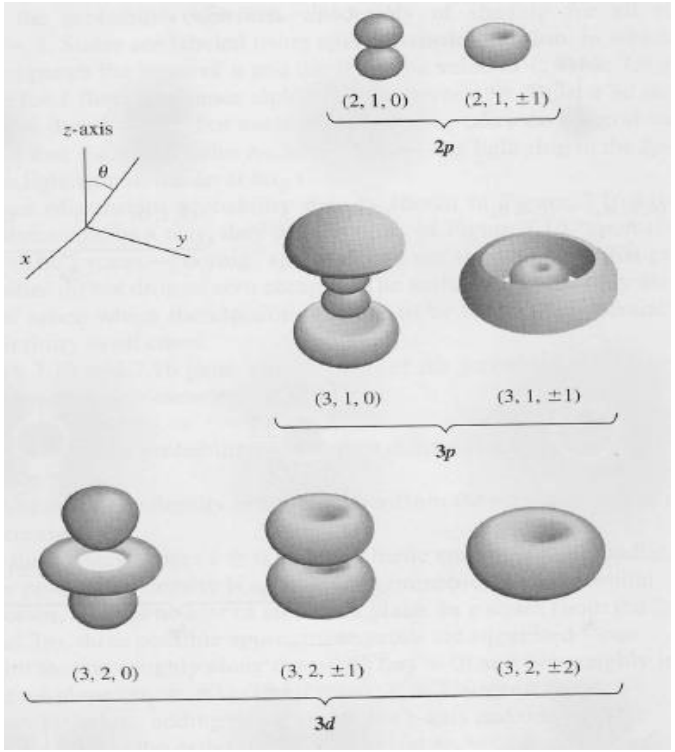
- Electrons can be shared in two ways:
  - Bonding state
  - Antibonding state





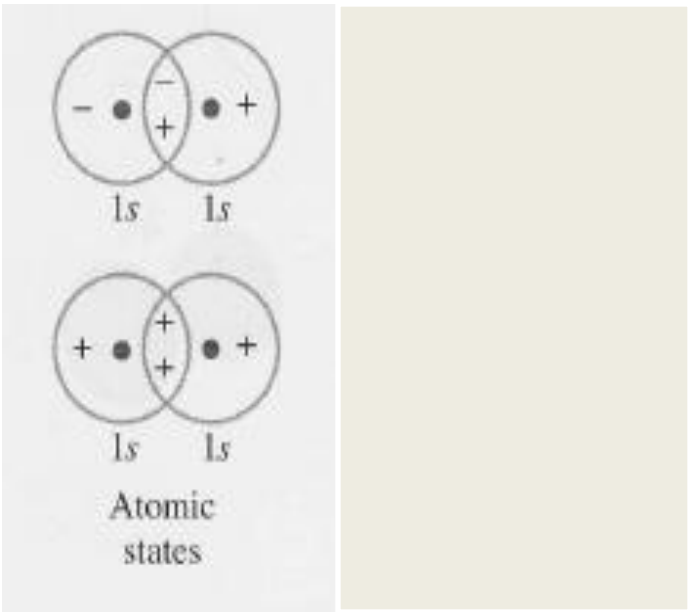
Using atomic orbitals to add up

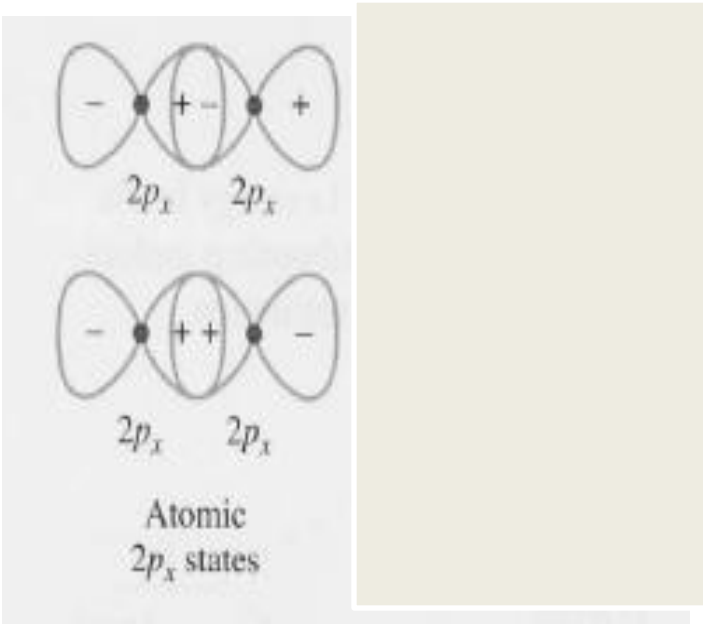




Which atomic orbitals can bond together?

Sigma (σ) Bonding/antibonding





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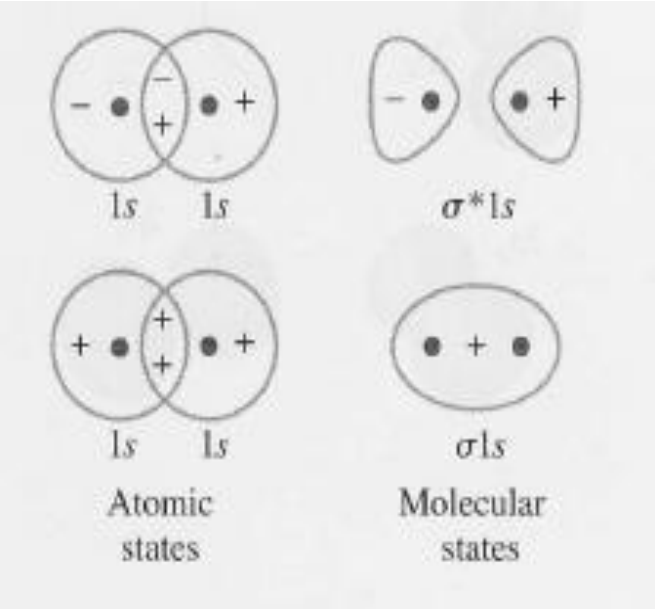
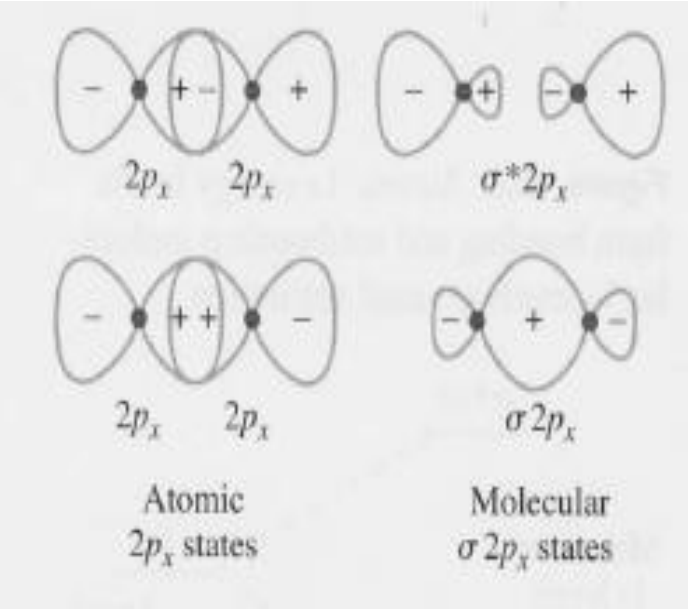
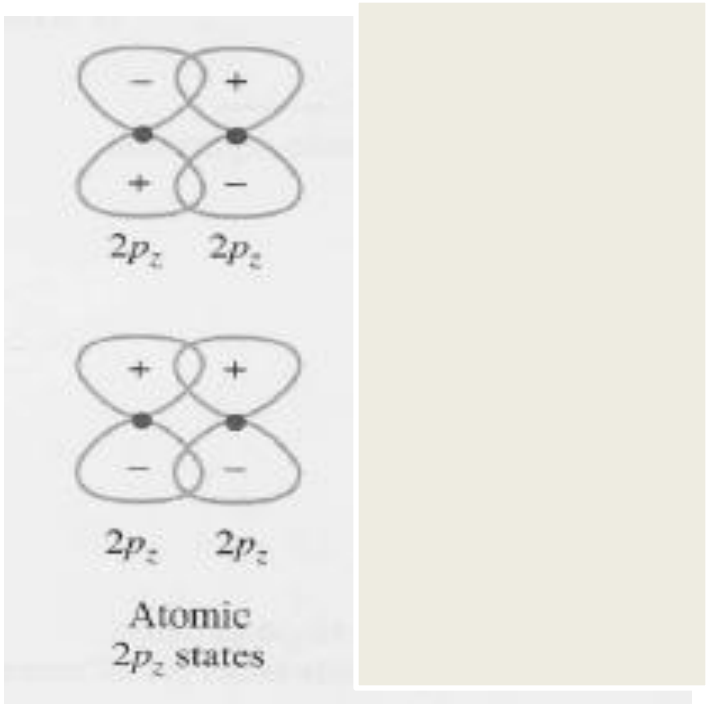
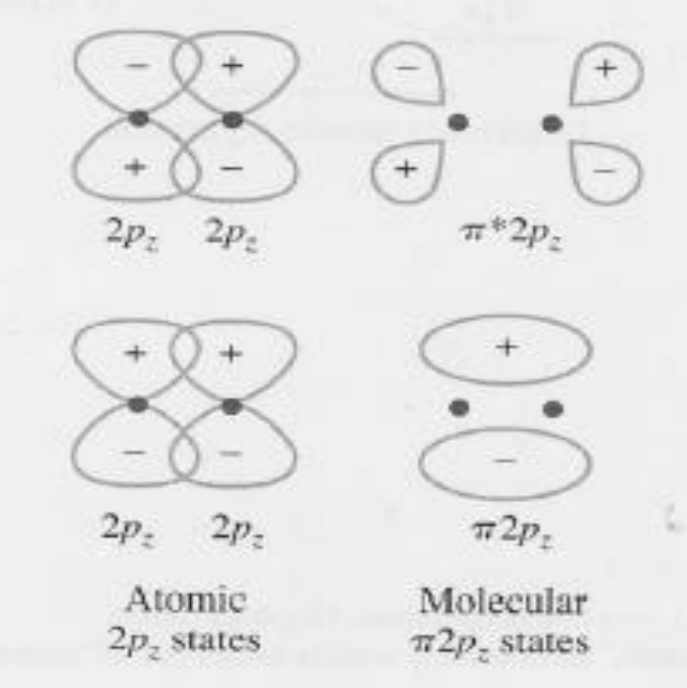




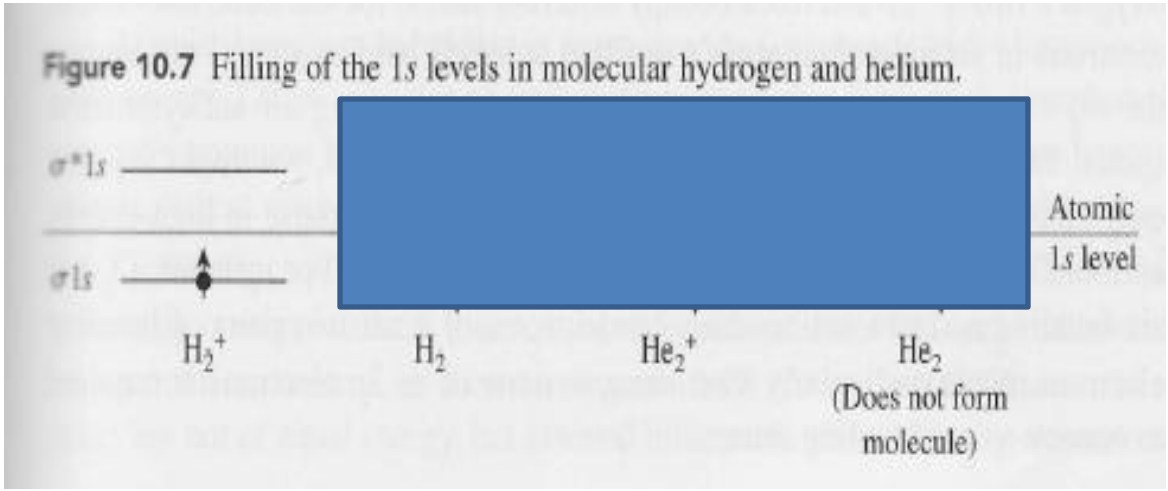
Pi Bonding/antibonding (π)



Pi Bonding/antibonding (π)

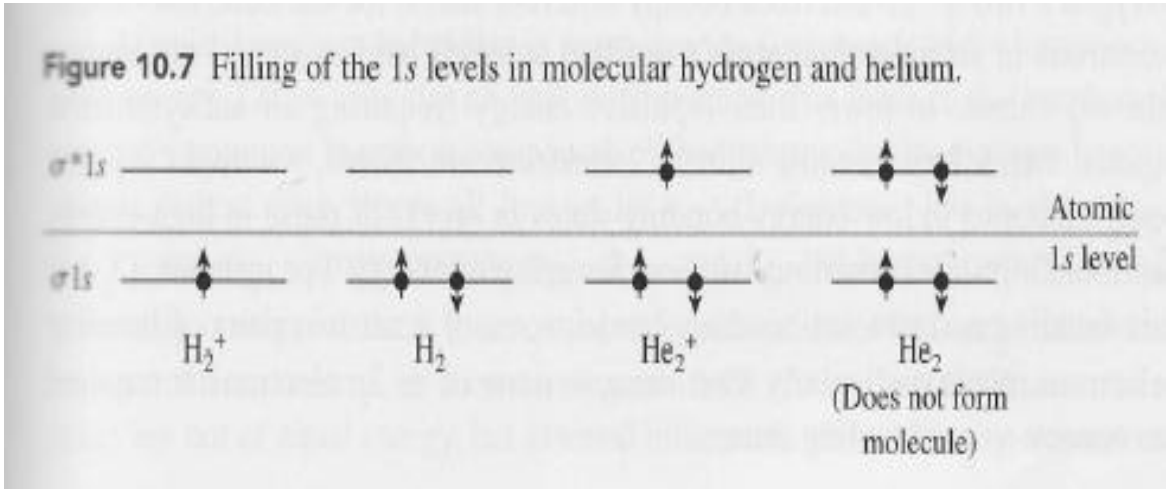


Fill up molecular orbitals



- From lower energy states to higher energy states
- Spreading electrons when degeneracies exist
- Bonding states are lower in energy than antibonding states, thus fill them first

Fill up molecular orbitals



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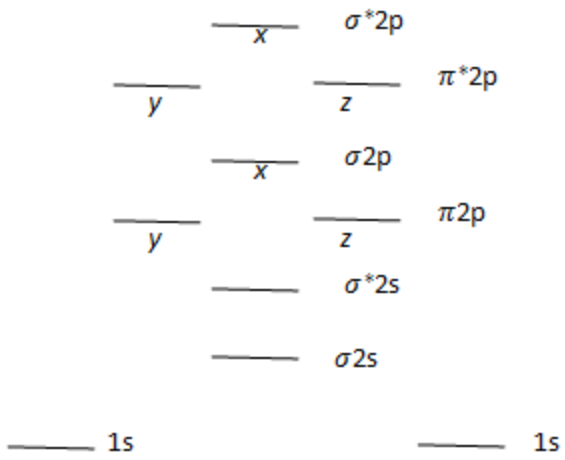
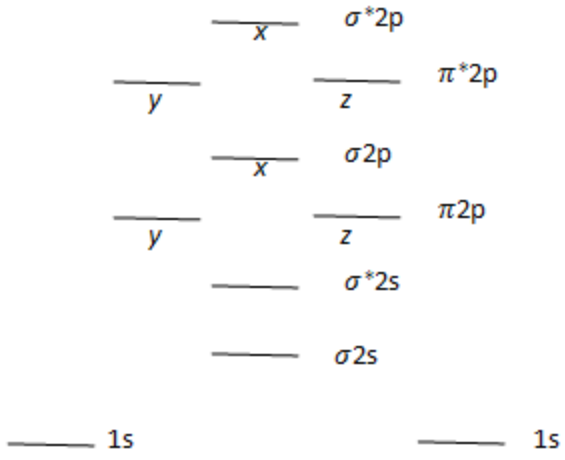
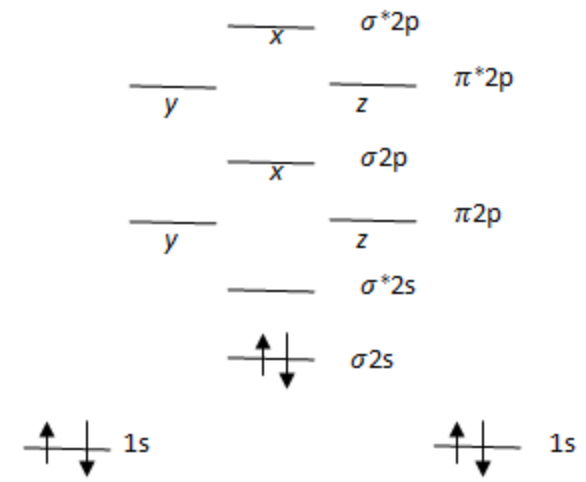


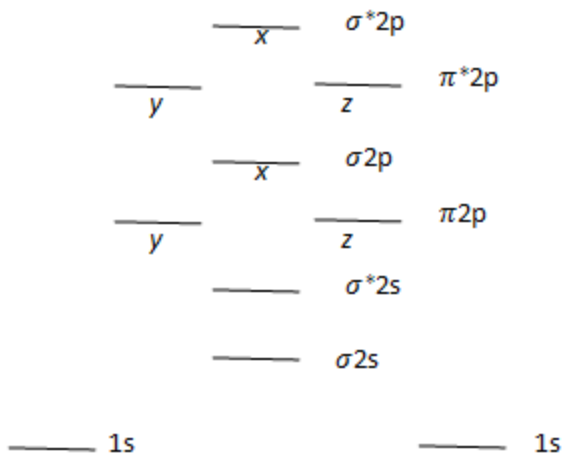
Li_2


σ*2p
x
π*2p
y
z
σ2p
x
π2p
y
z
σ*2s
σ2s
1s
1s

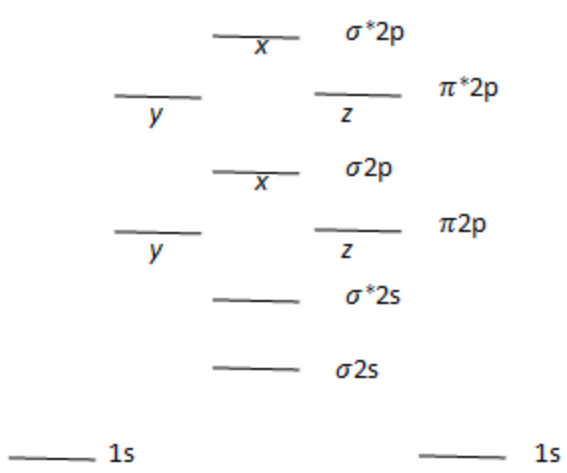
Li_2


σ*2p
x
π*2p
y
z
σ2p
x
π2p
y
z
σ*2s
σ2s
1s
1s

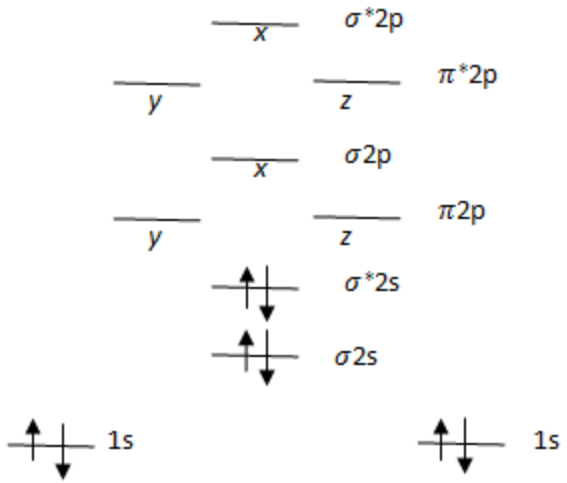
Li_2



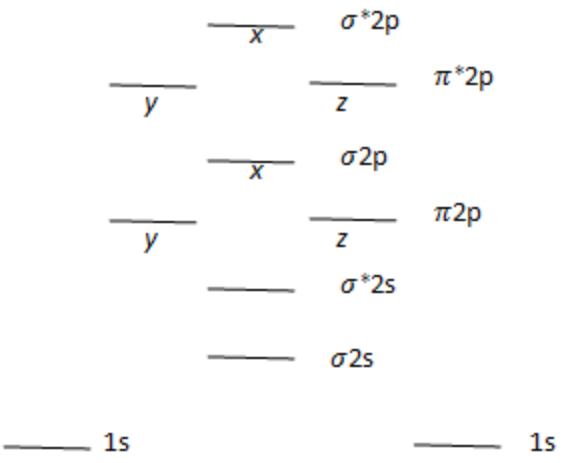
Be_2


σ*2p
x
π*2p
y
z
σ2p
x
π2p
y
z
σ*2s
σ2s
1s
1s

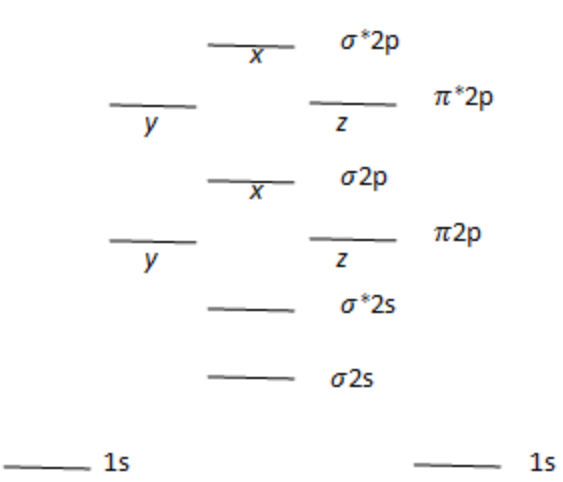
Be_2


σ*2p
x
π*2p
y
z
σ2p
x
π2p
y
z
σ*2s
σ2s
1s
1s

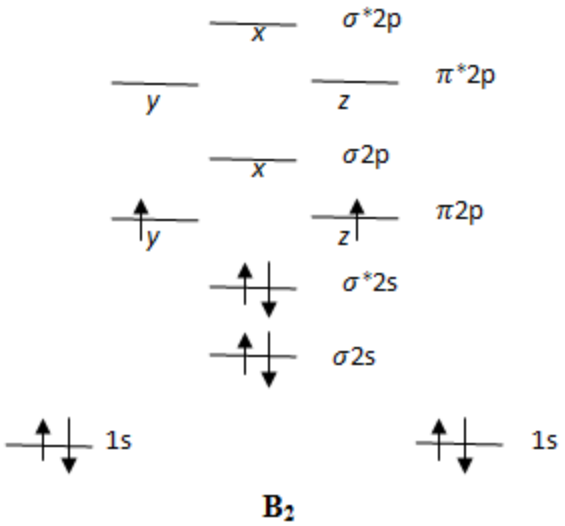
Be_2



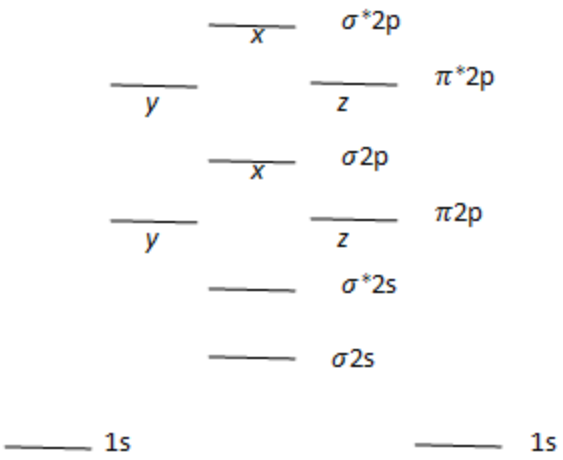
B_2


σ*2p
x
π*2p
y
z
σ2p
x
π2p
y
z
σ*2s
σ2s
1s
1s

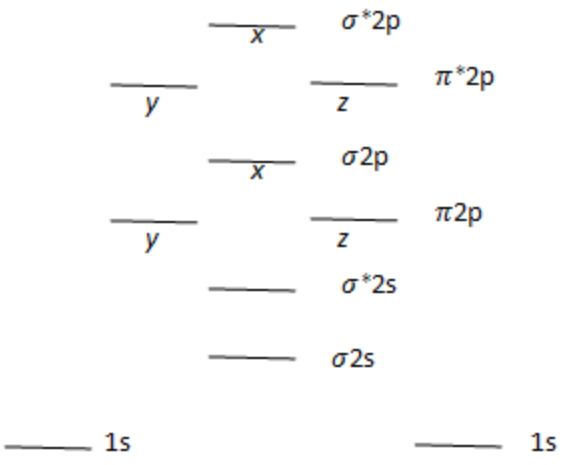
B_2


σ*2p
x
π*2p
y
z
σ2p
x
π2p
y
z
σ*2s
σ2s
1s
1s

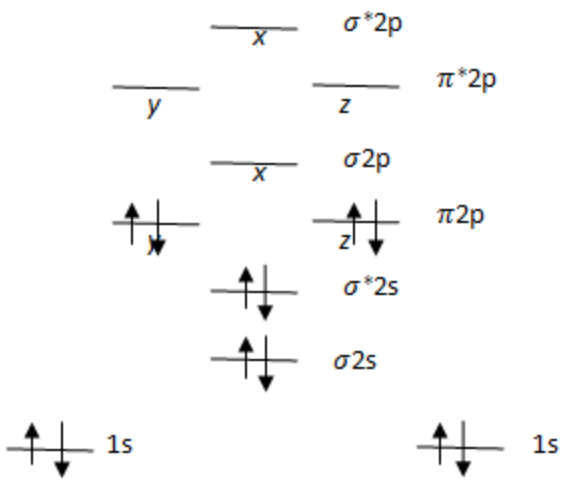
B_2



C_2

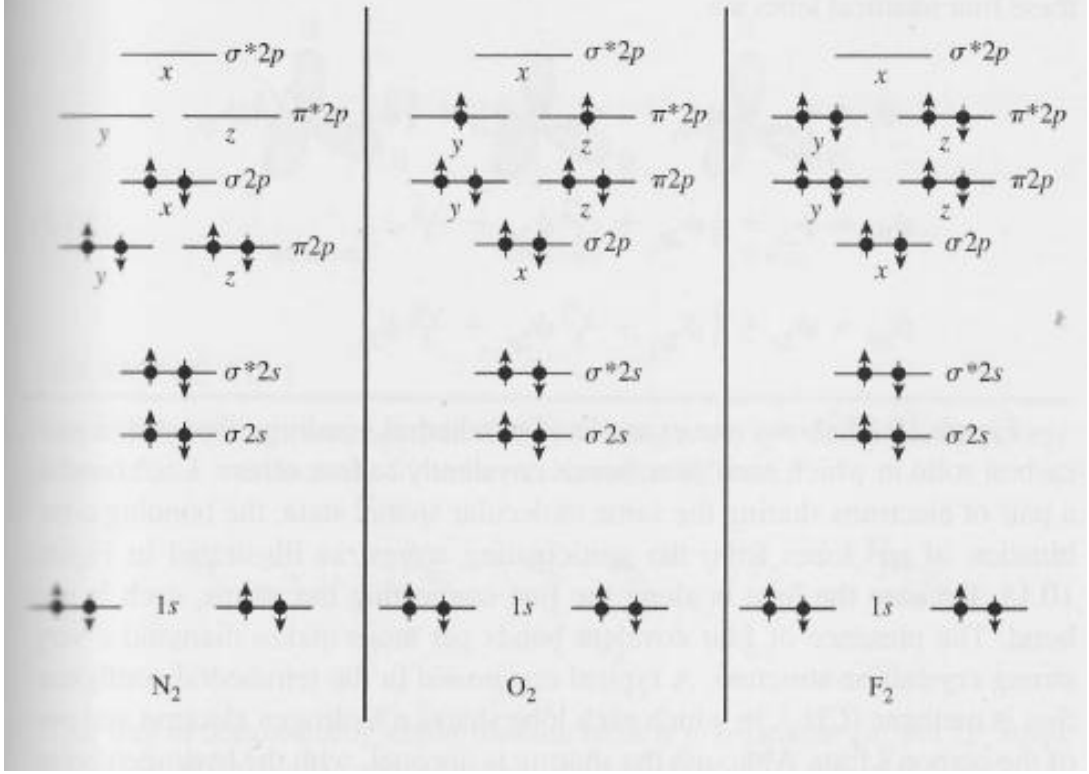

σ*2p
x
π*2p
y
z
σ2p
x
π2p
y
z
σ*2s
σ2s
1s
1s

C_2

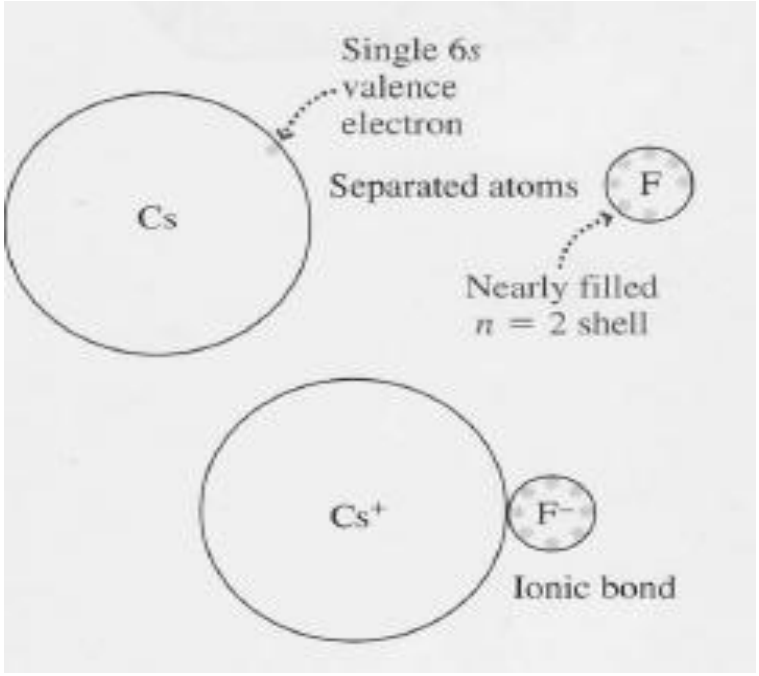

σ*2p
x
π*2p
y
z
σ2p
x
π2p
y
z
σ*2s
σ2s
1s
1s

C_2

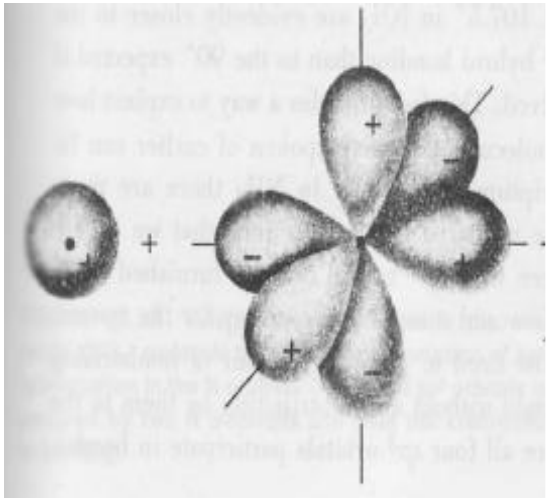
Figure 10.10 Molecular energy levels in nitrogen, oxygen, and fluorine.



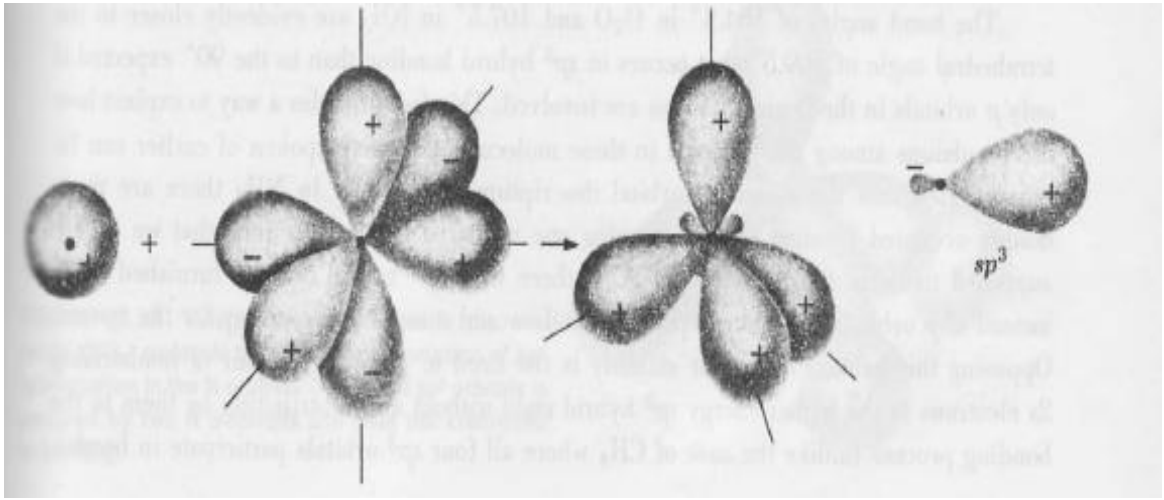
Ionic Bond


Single 6s
valence
electron
Separated atoms
F
Cs
Nearly filled
n = 2 shell
Cs+
F−
Ionic bond

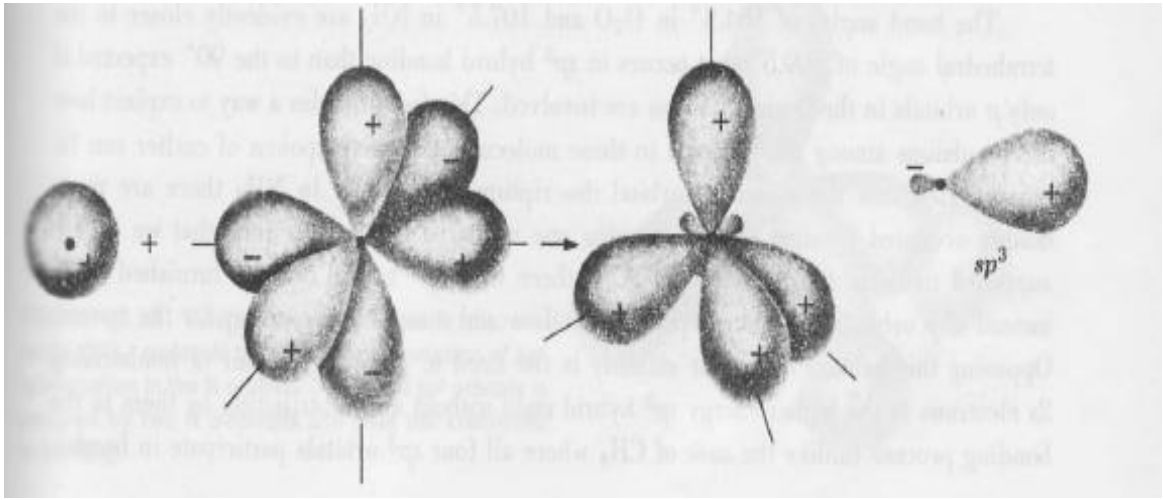
sp3 hybridized orbital

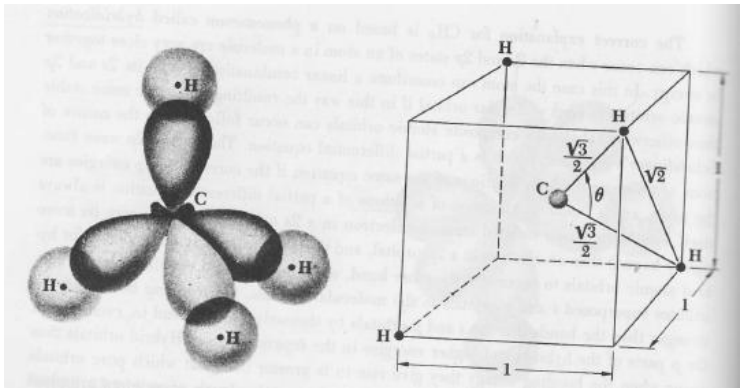


sp3 hybridized orbital

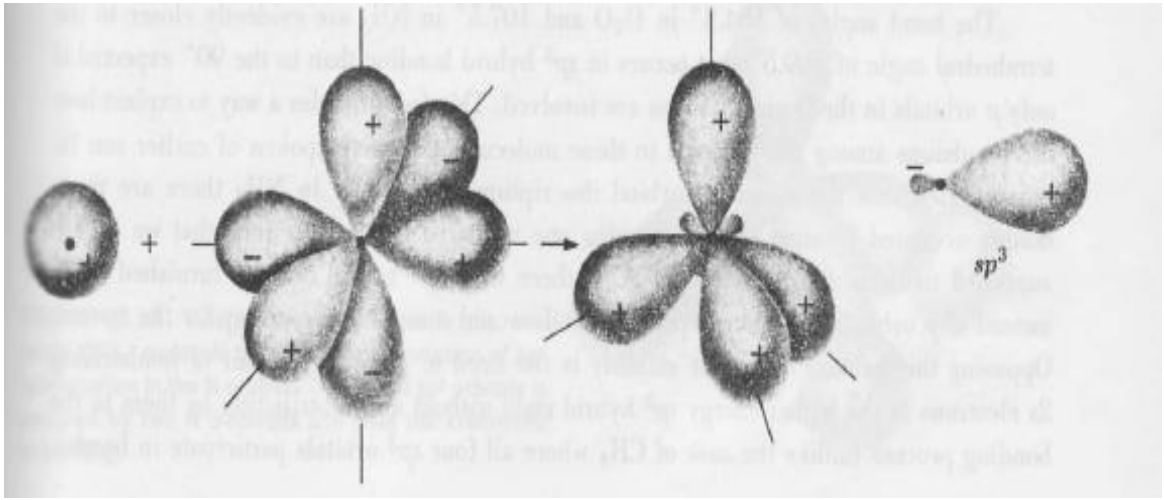


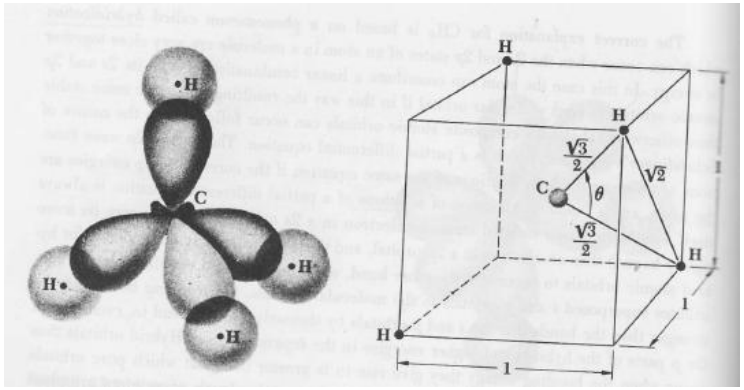
sp3 hybridized orbital





sp3 hybridized orbital





$$\psi_I = \psi_{2s} - \psi_{2p_z}$$

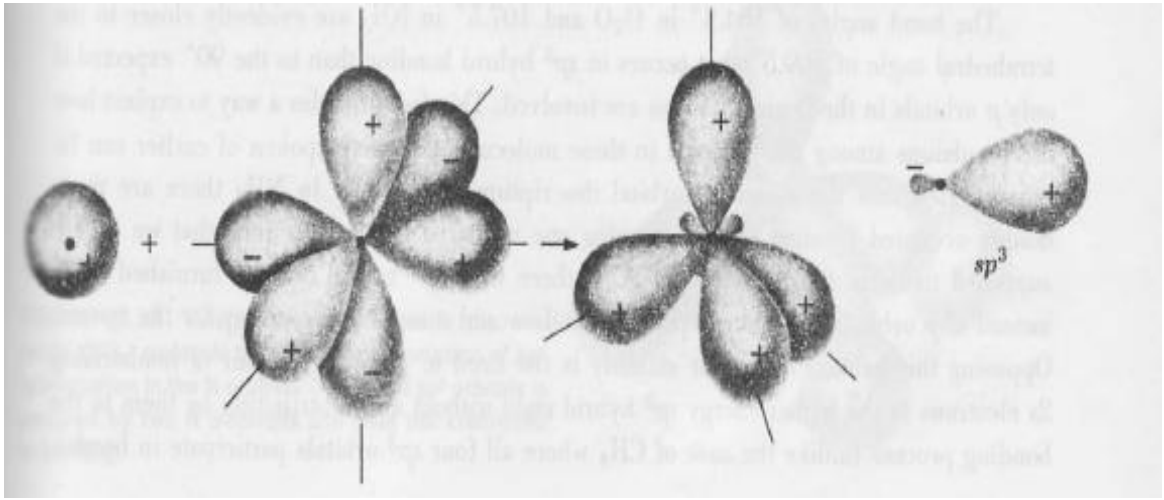
$$\psi_{II} = \psi_{2s} + \frac{1}{3}\psi_{2p_z} - \frac{\sqrt{8}}{3}\psi_{2p_z}$$

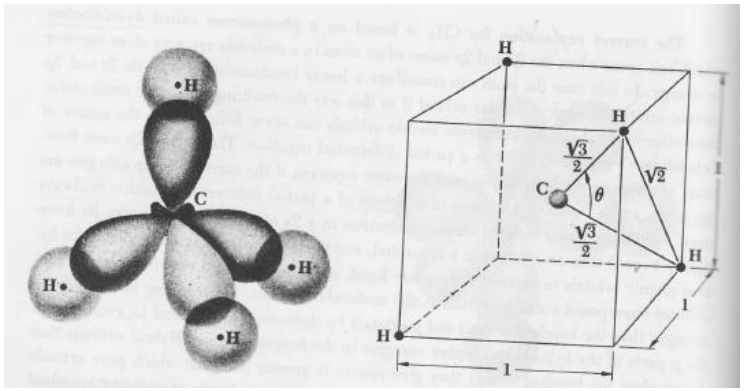
$$\psi_{III} = \psi_{2s} + \frac{1}{3}\psi_{2p_z} + \frac{\sqrt{2}}{3}\psi_{2p_x} - \frac{\sqrt{6}}{3}\psi_{2p_y}$$

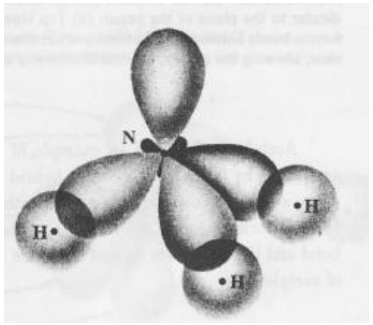
$$\psi_{IV} = \psi_{2s} + \frac{1}{3}\psi_{2p_z} + \frac{\sqrt{2}}{3}\psi_{2p_x} + \frac{\sqrt{6}}{3}\psi_{2p_y}$$

$$\theta = 109.5^\circ$$

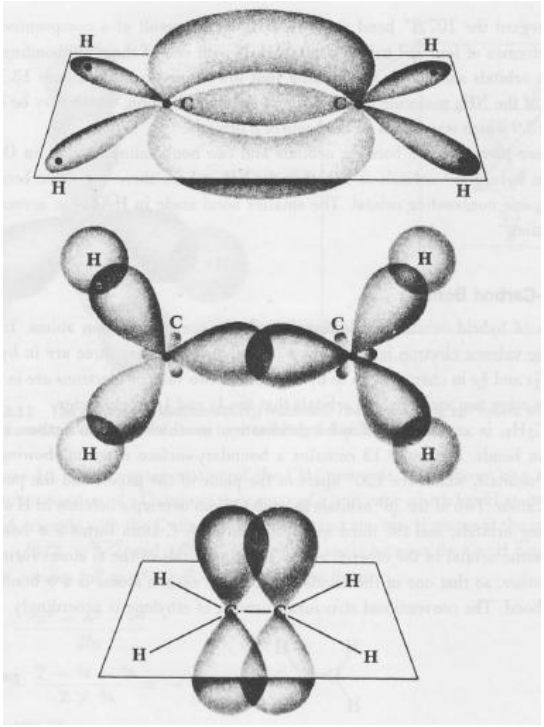
sp3 hybridized orbital







sp2 hybridized orbital



sp2 hybridized orbital

$$\psi_I = \psi_{2s} + \sqrt{2}\psi_{2p_x}$$

$$\psi_{II} = \psi_{2s} - \sqrt{\frac{1}{2}}\psi_{2p_x} + \sqrt{\frac{3}{2}}\psi_{2p_y}$$

$$\psi_{II} = \psi_{2s} - \sqrt{\frac{1}{2}}\psi_{2p_x} - \sqrt{\frac{3}{2}}\psi_{2p_y}$$

$$\theta = 120\,^{\circ}$$