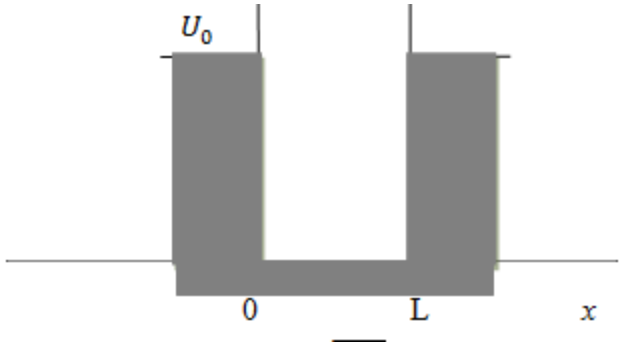
Lecture 11 Topics

- 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

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



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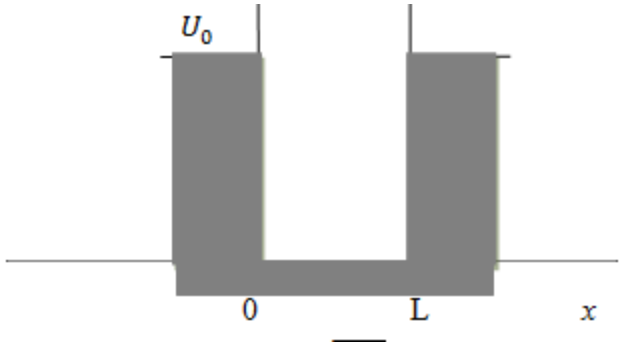

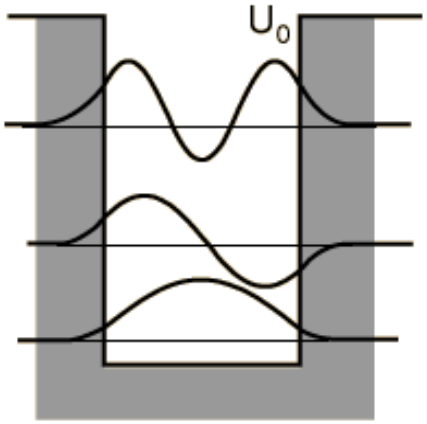

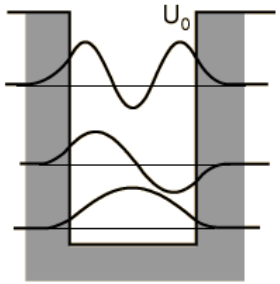
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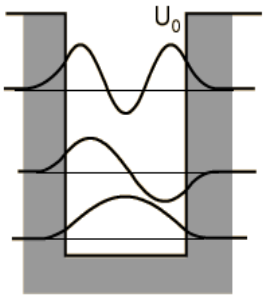
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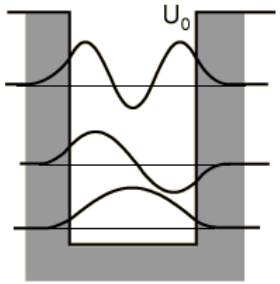
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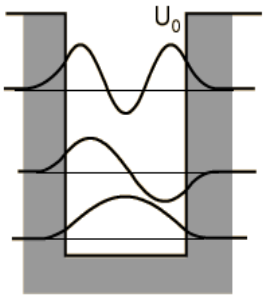
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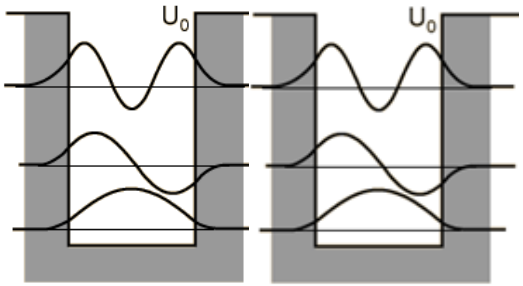
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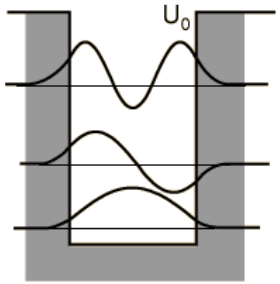
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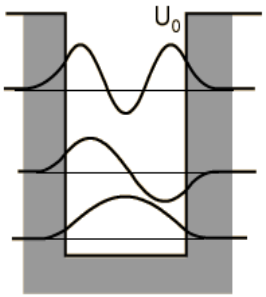
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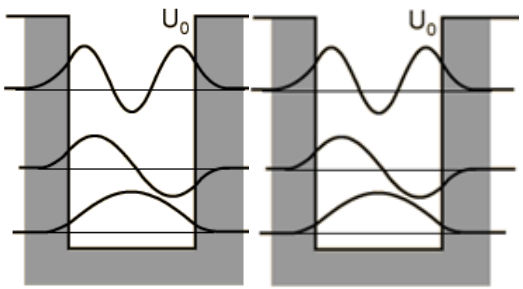
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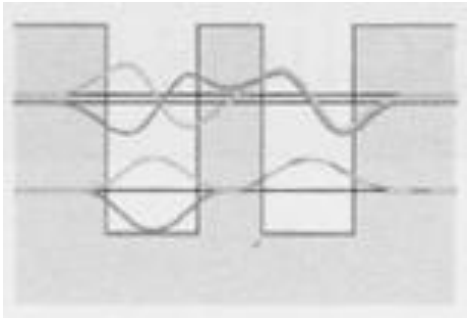

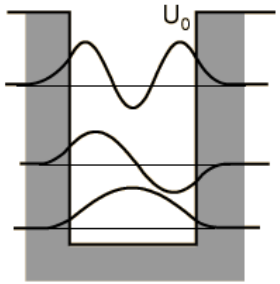
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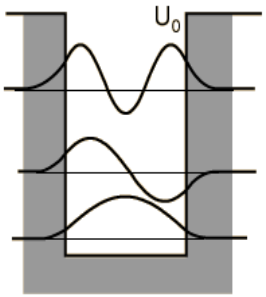
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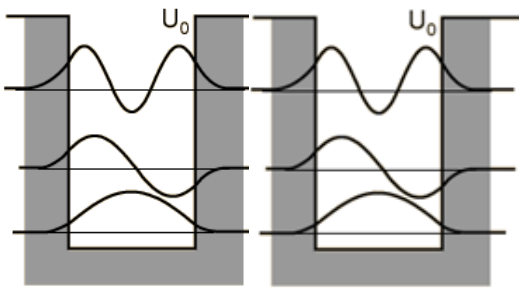
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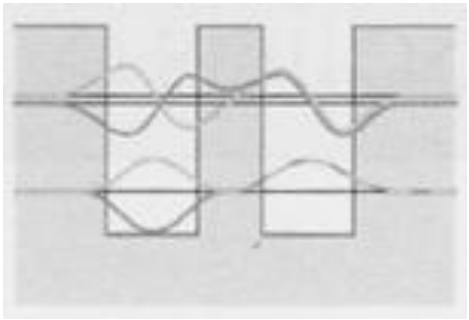

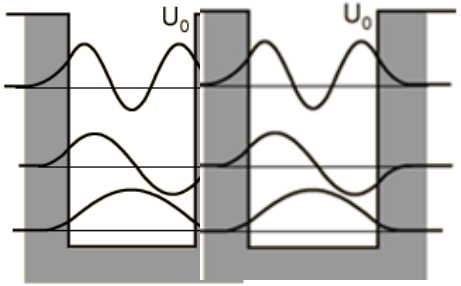
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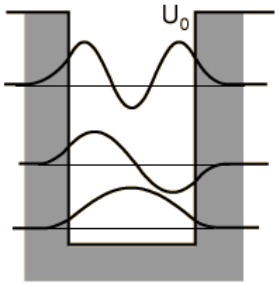
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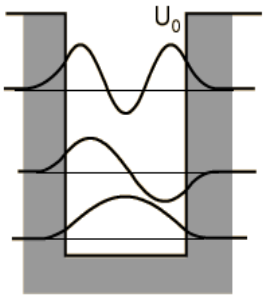
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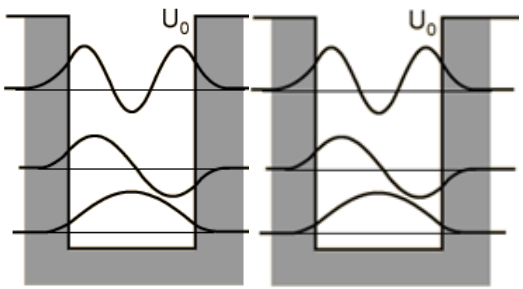
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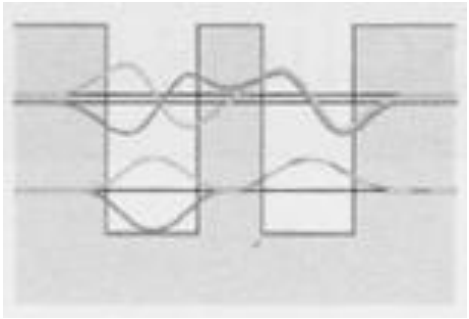

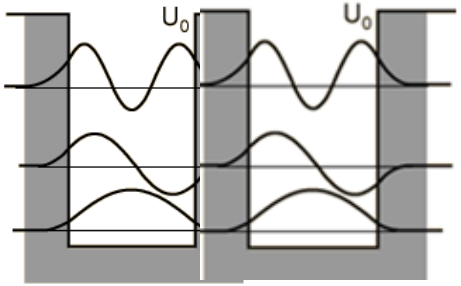
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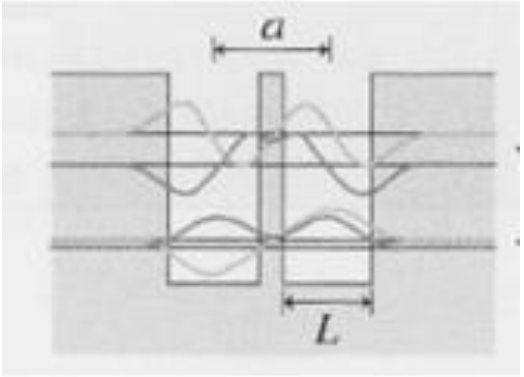
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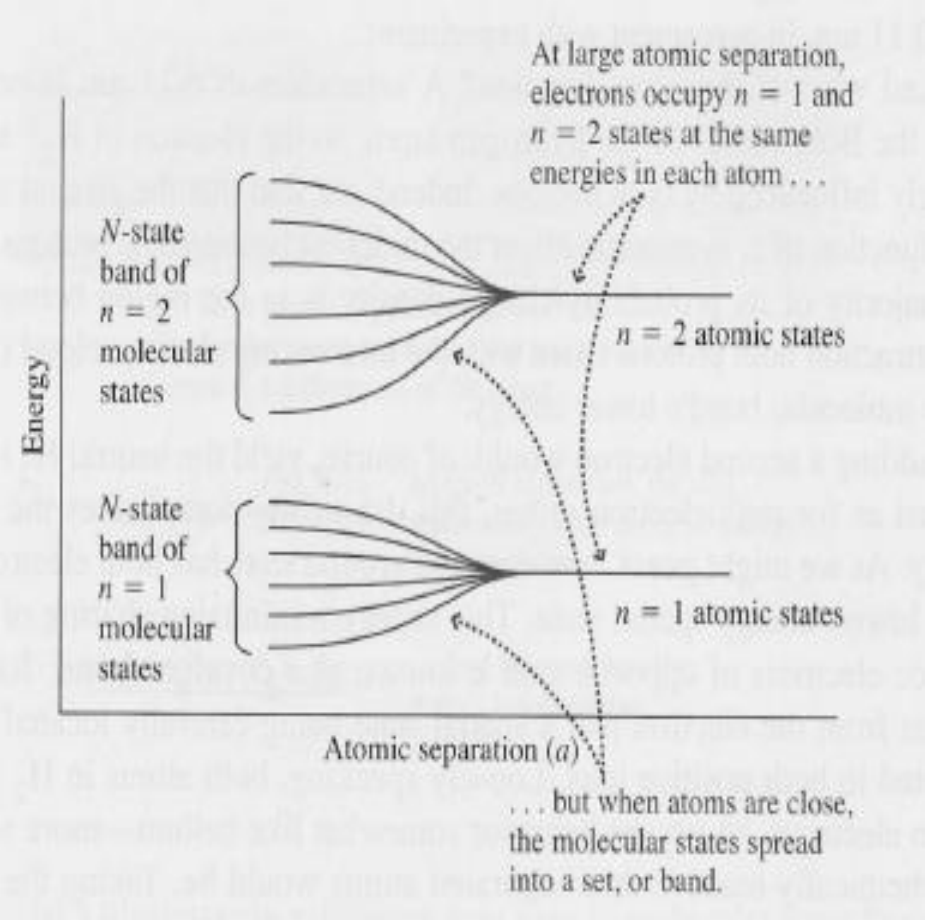
So, when atoms come together



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

Element	*Atomic number*	*Atomic structure*	*Occupancy of orbitals* 1s	2s	$2p_x$	$2p_y$	$2p_z$	*Unpaired electrons*	*Molecular structure*	*Bond energy,*
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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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Valence band approach

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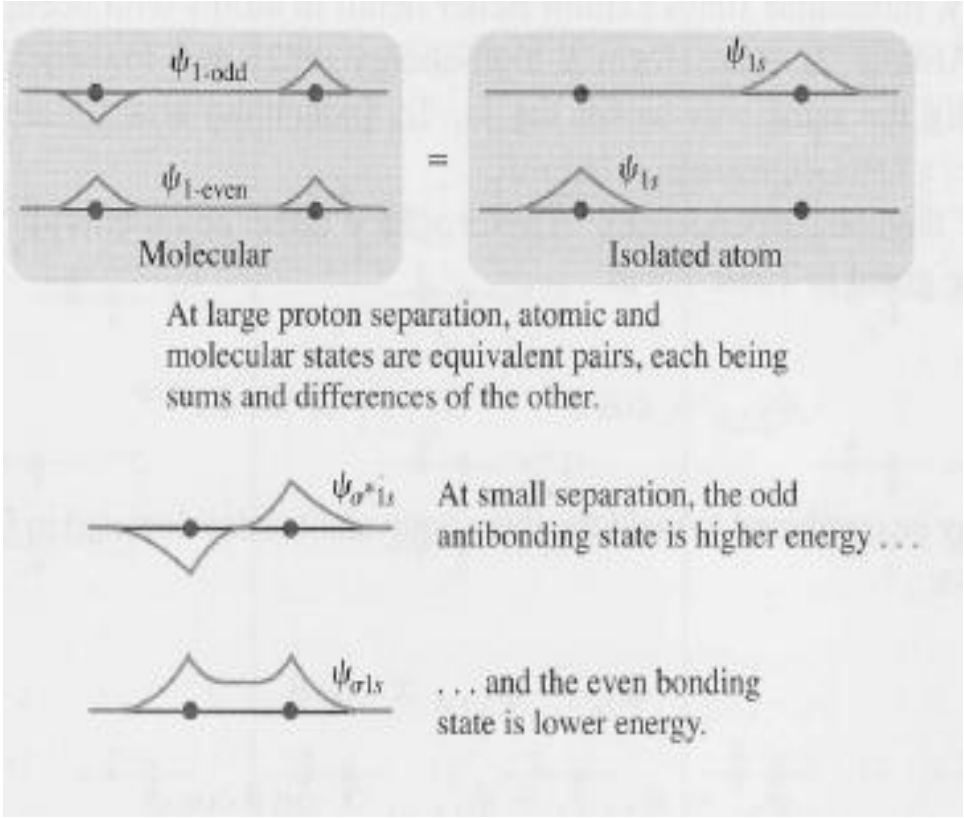
Helium, He	2	$1s^2$	↑↓					0	No molecule	
Lithium, Li	3	$1s^2 2s$	↑↓	↑				1 (2s)	Li—Li	1.03
Beryllium, Be	4	$1s^2 2s^2$	↑↓	↑↓				0	No molecule	
Boron, B	5	$1s^2 2s^2 2p$	↑↓	↑↓	↑			1 (2p)	B—B	3.0
Carbon, C	6	$1s^2 2s^2 2p_x^2$	↑↓	↑↓	↑	↑		2 (2p)	C=C	6.5
Nitrogen, N	7	$1s^2 2s^2 2p^3$								
Oxygen, O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

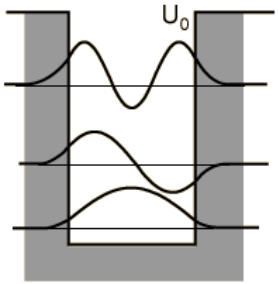
Valence band approach

Element	Atomic number	Atomic structure	Occupancy of orbitals 1s	2s	$2p_x$	$2p_y$	$2p_z$	Unpaired electrons	Molecular structure	Bond energy, e
Hydrogen, H	1	$1s$	↑					1 (1s)	H—H	4.72
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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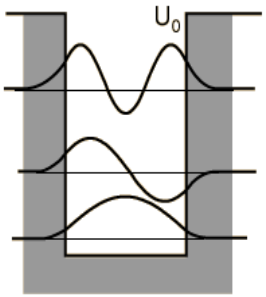
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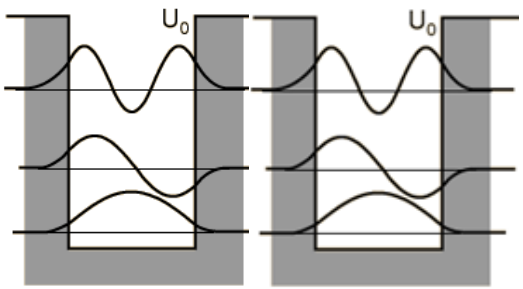
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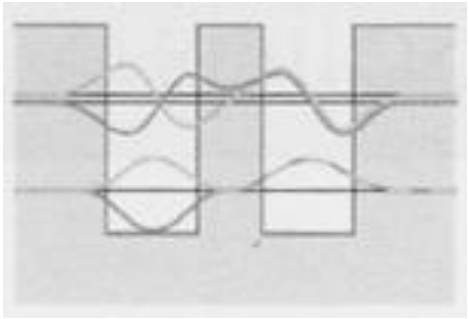

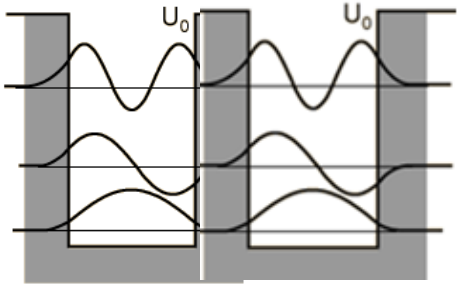
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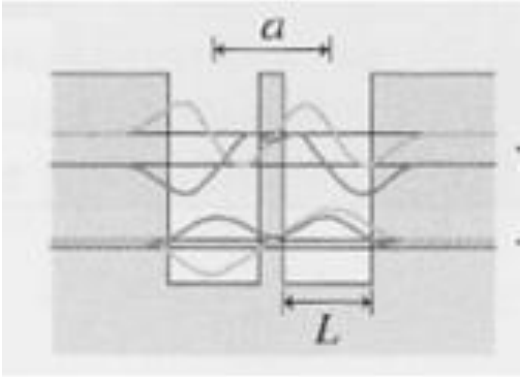
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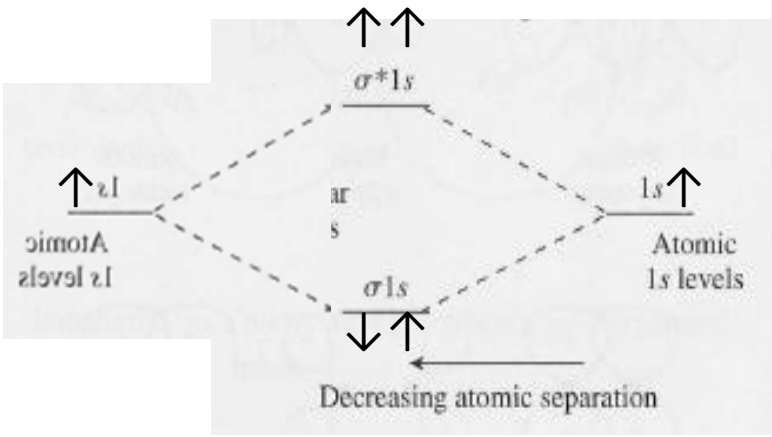
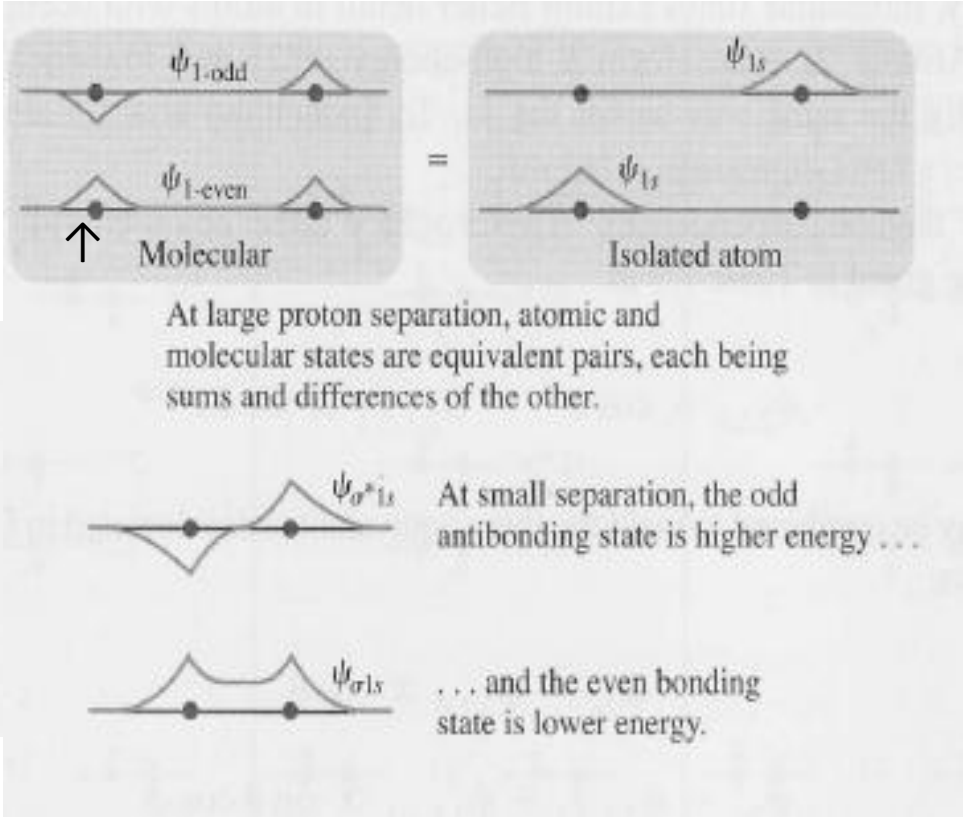
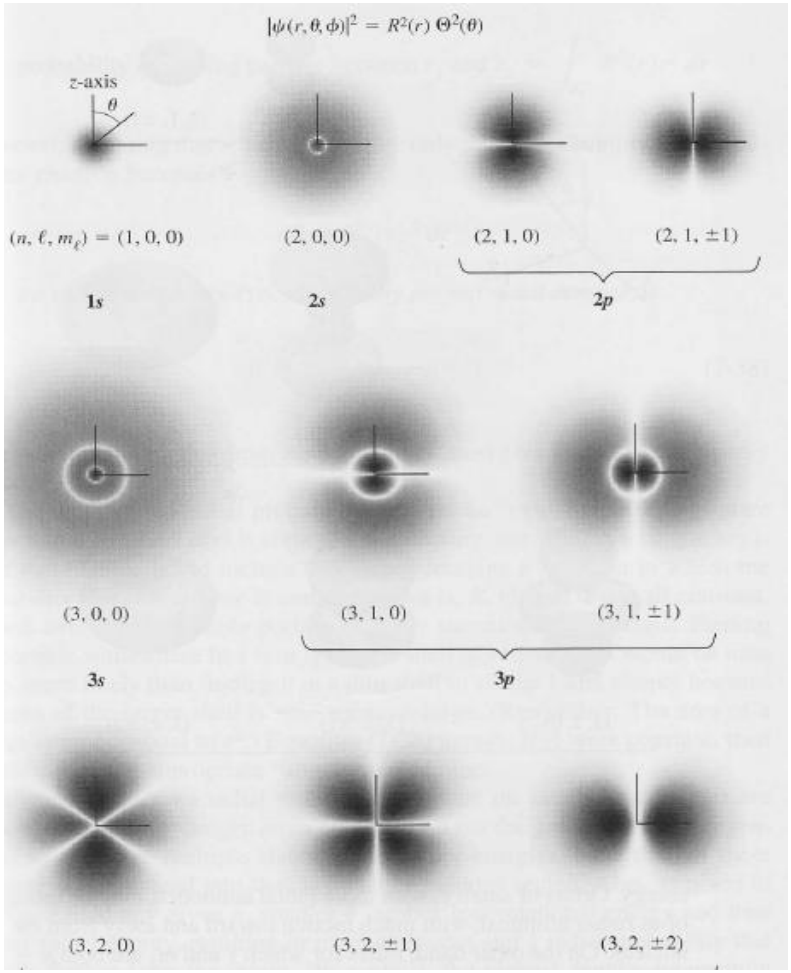
Molecular orbital approach

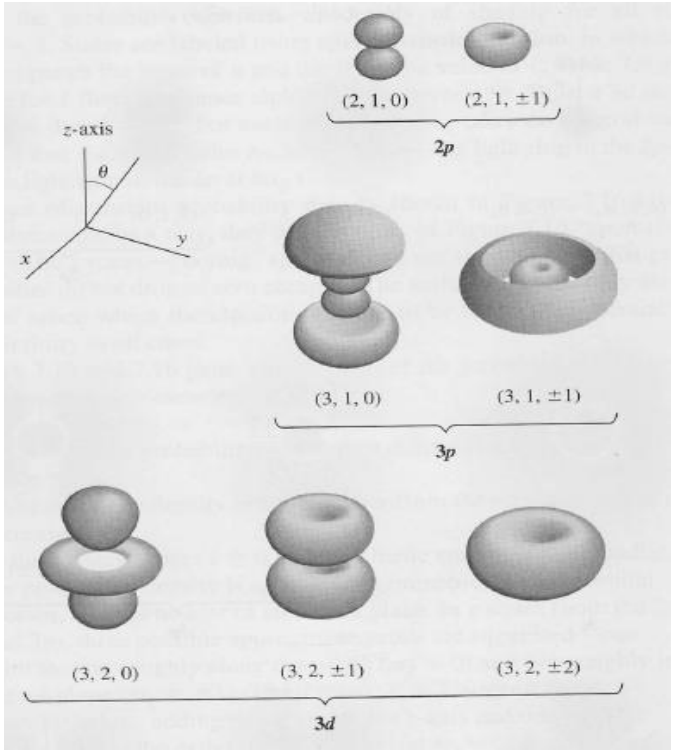
- Electrons can be shared in two ways:
  - Bonding state
  - Antibonding state





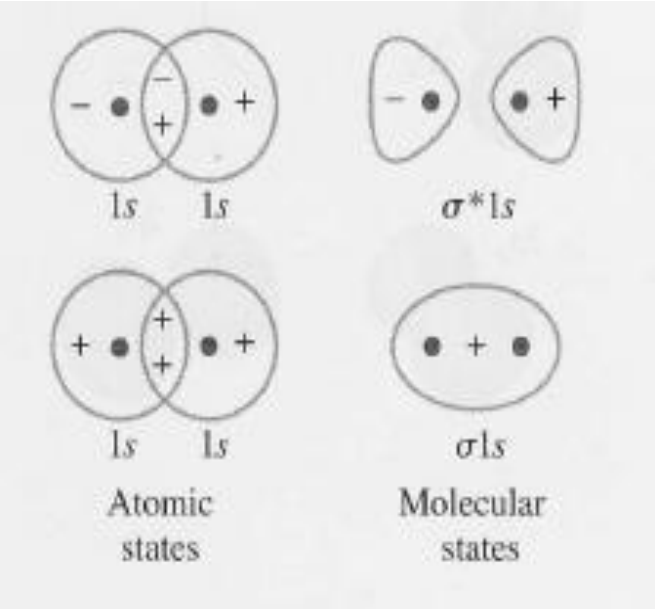
Using atomic orbitals to add up

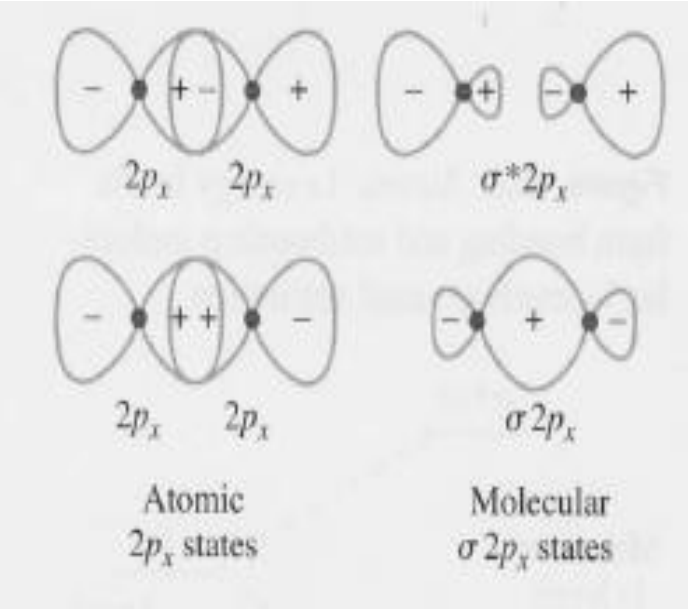




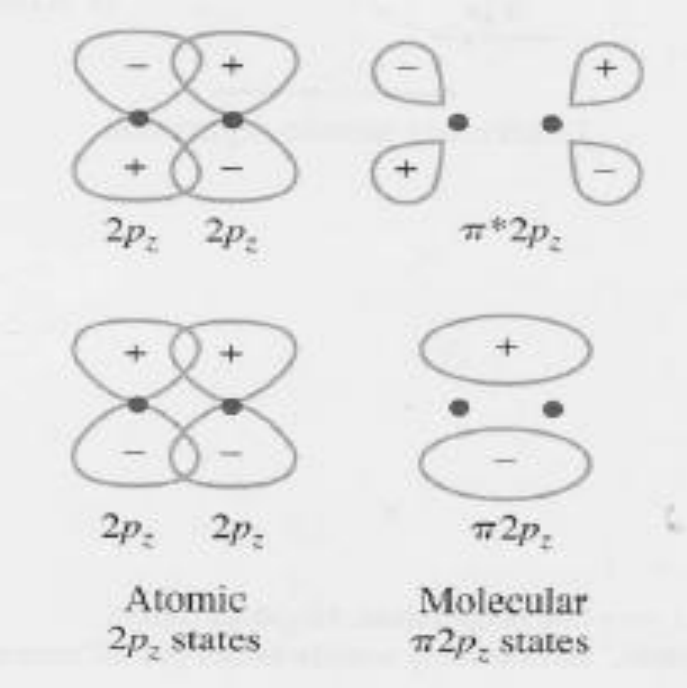
Which atomic orbitals can bond together?

Sigma (σ) Bonding/antibonding

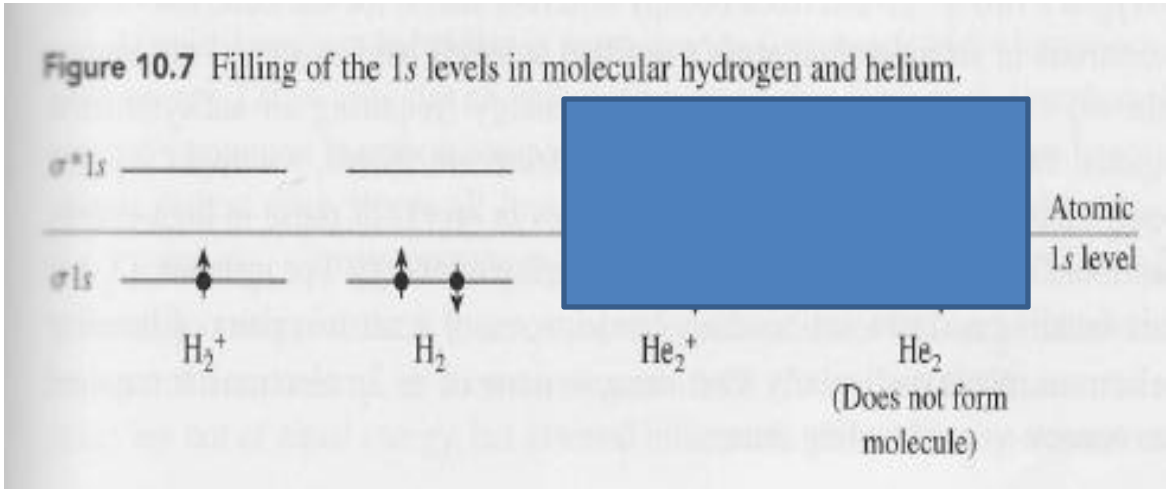




Pi Bonding/antibonding (π)

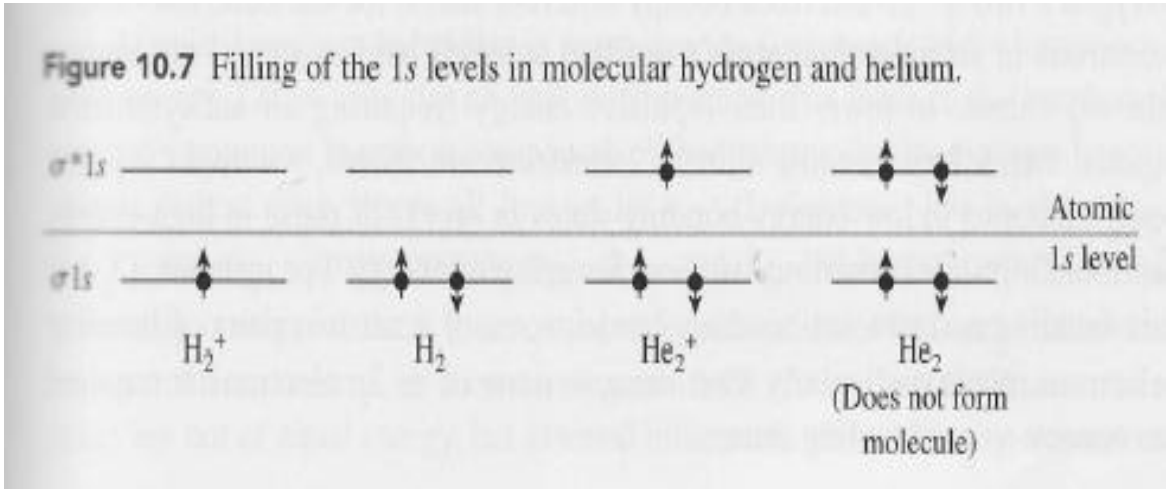


Fill up molecular orbitals



- 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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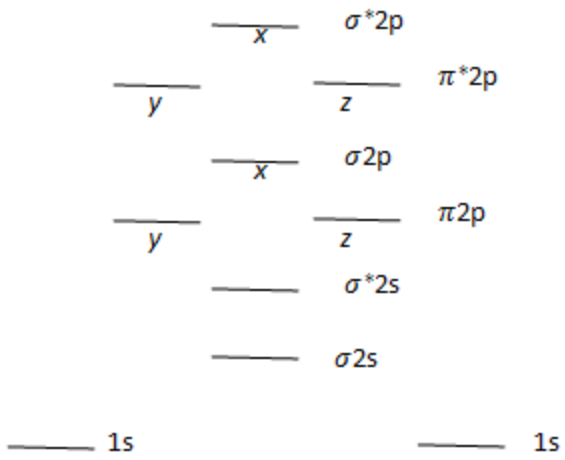
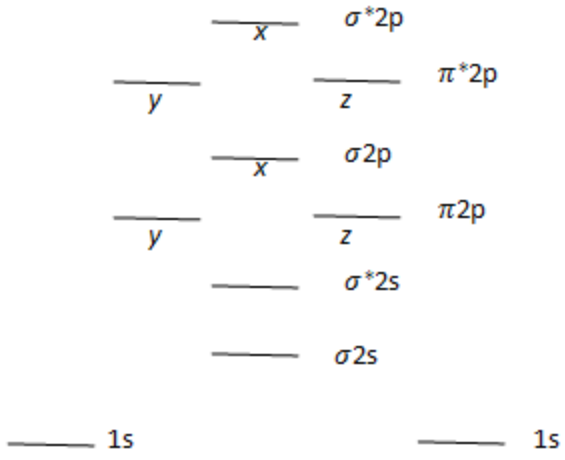


Li_2


σ*2p
x
π*2p
y
z
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π2p
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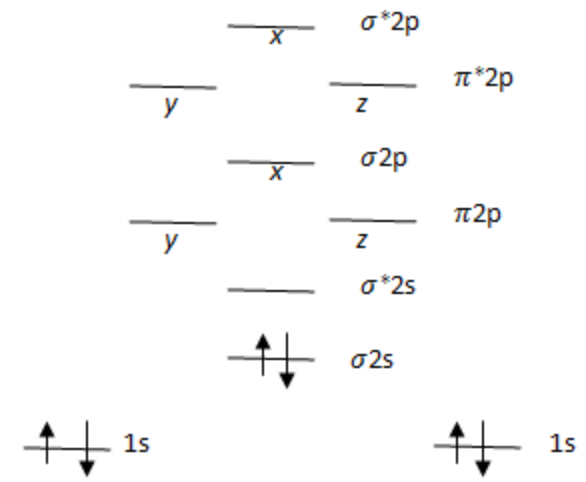
z
σ*2s
σ2s
1s
1s

Li_2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σ2s
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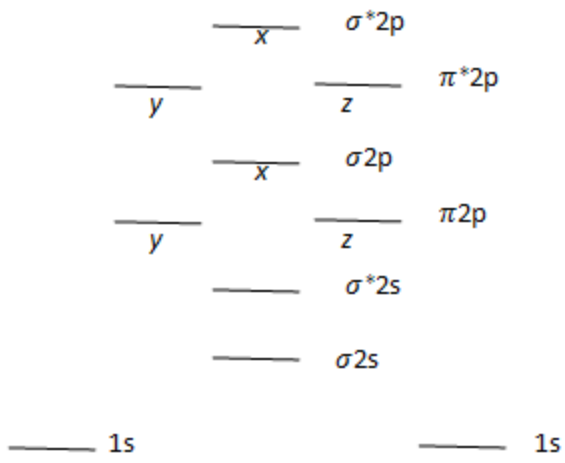
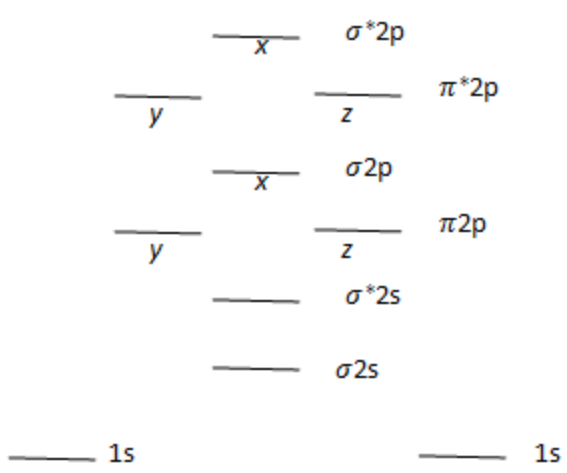
1s

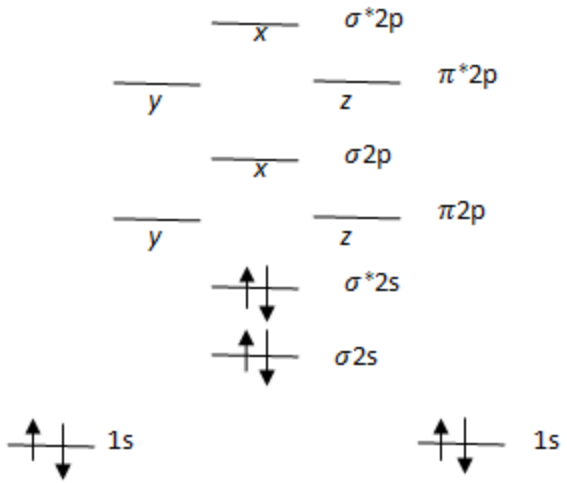
Li_2



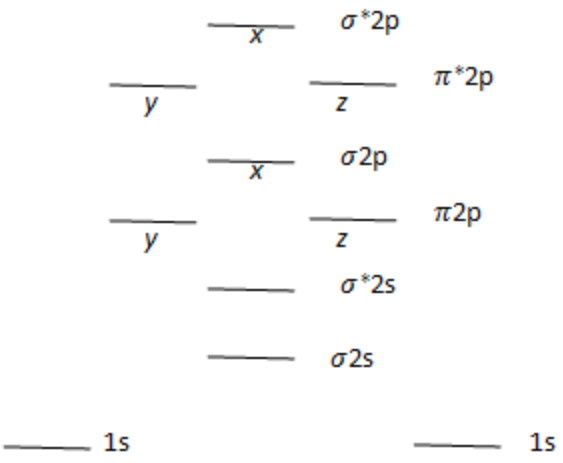
Be_2


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

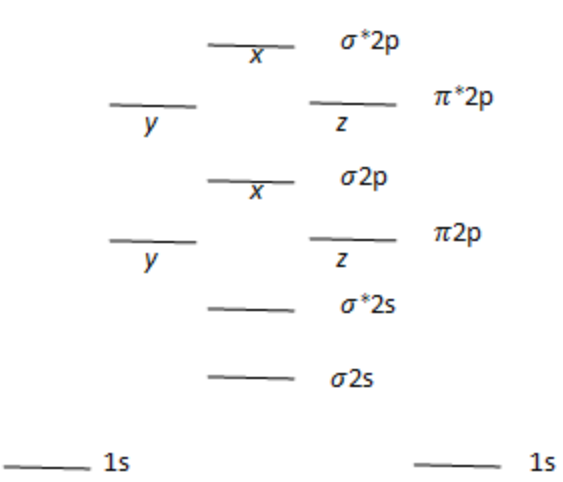
Be_2


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

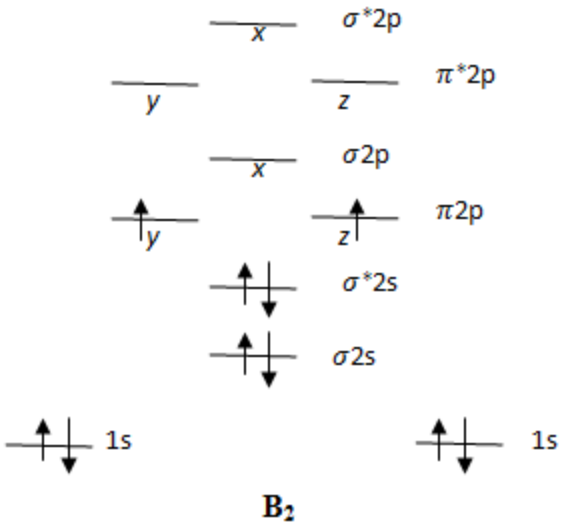
Be_2



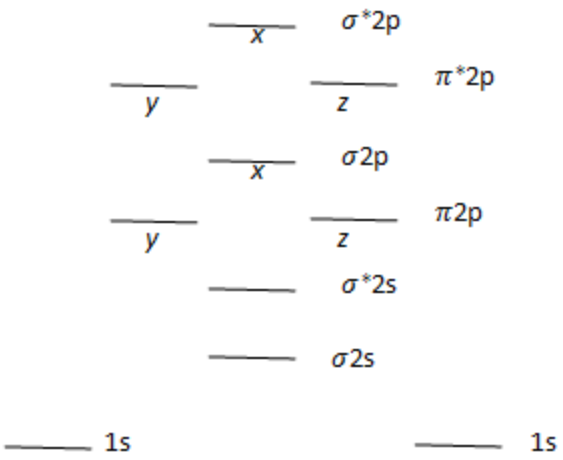
B_2


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

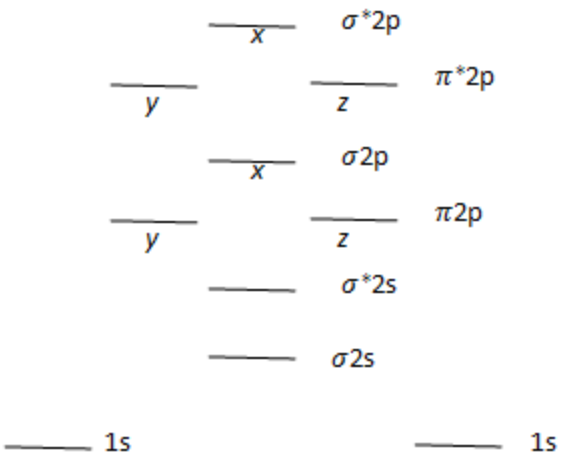
B_2


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

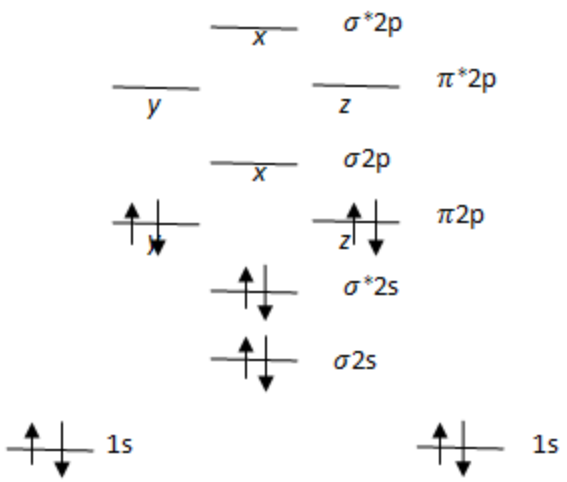
B_2



C_2

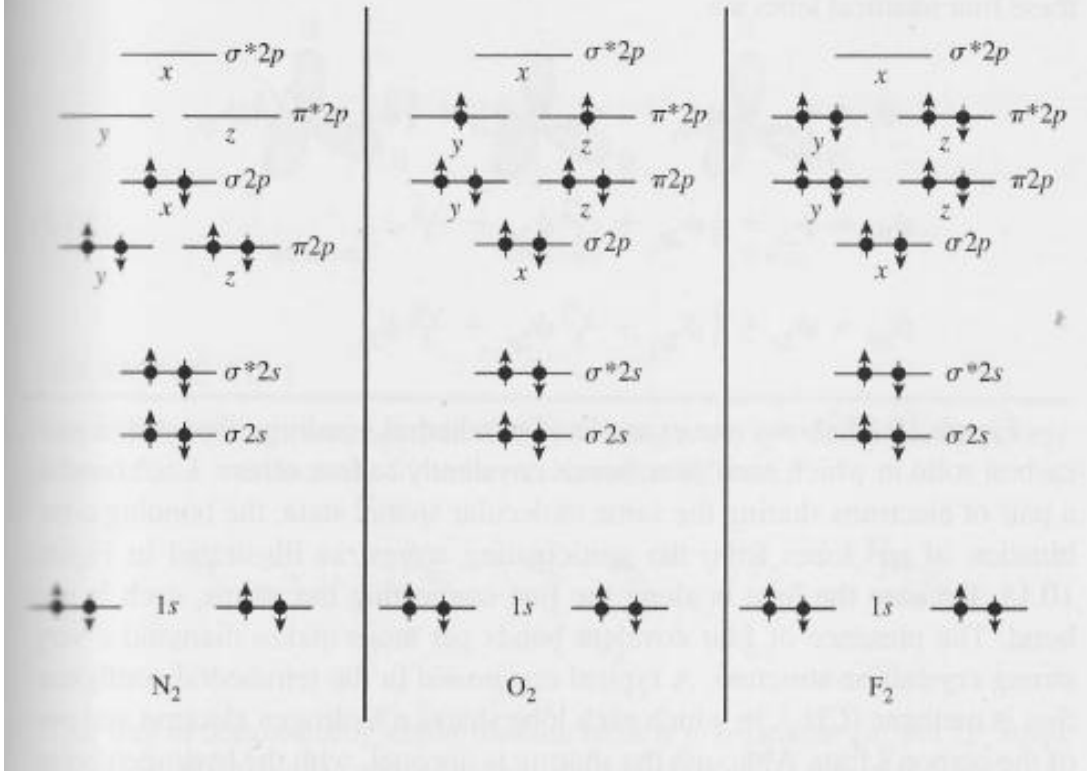

σ*2p
x
π*2p
y
z
σ2p
x
π2p
y
z
σ*2s
σ2s
1s
1s

C_2

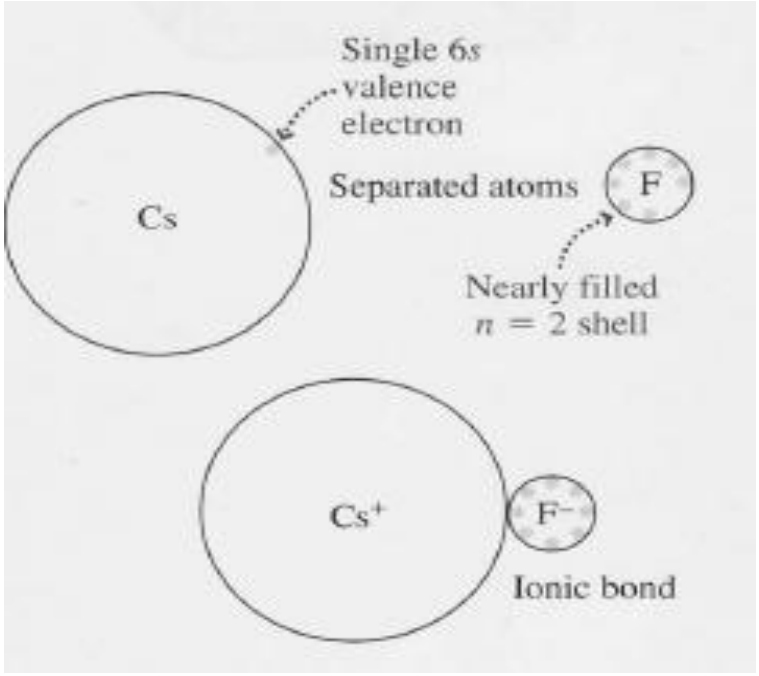

σ*2p
x
π*2p
y
z
σ2p
x
π2p
y
z
σ*2s
σ2s
1s
1s

C_2

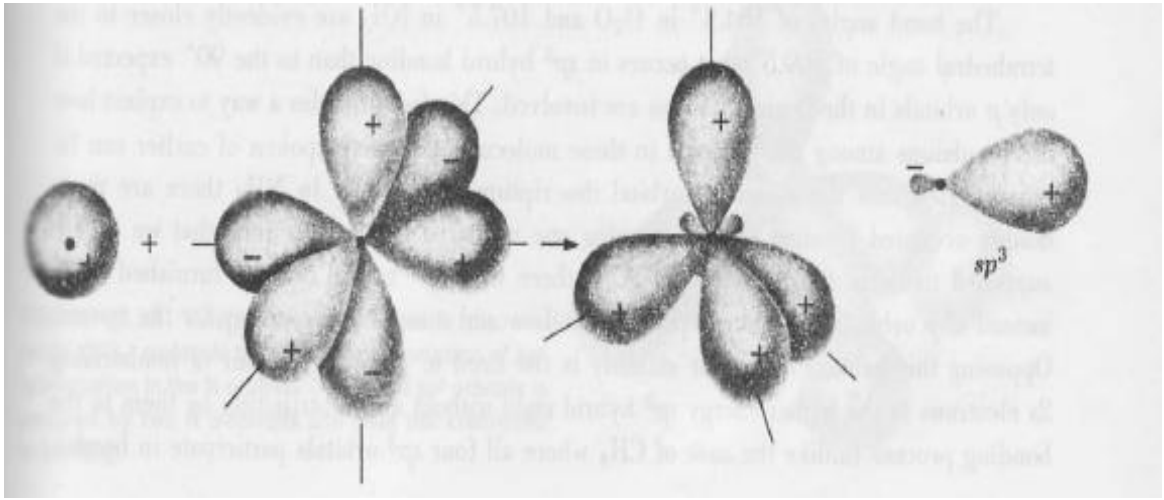
Figure 10.10 Molecular energy levels in nitrogen, oxygen, and fluorine.



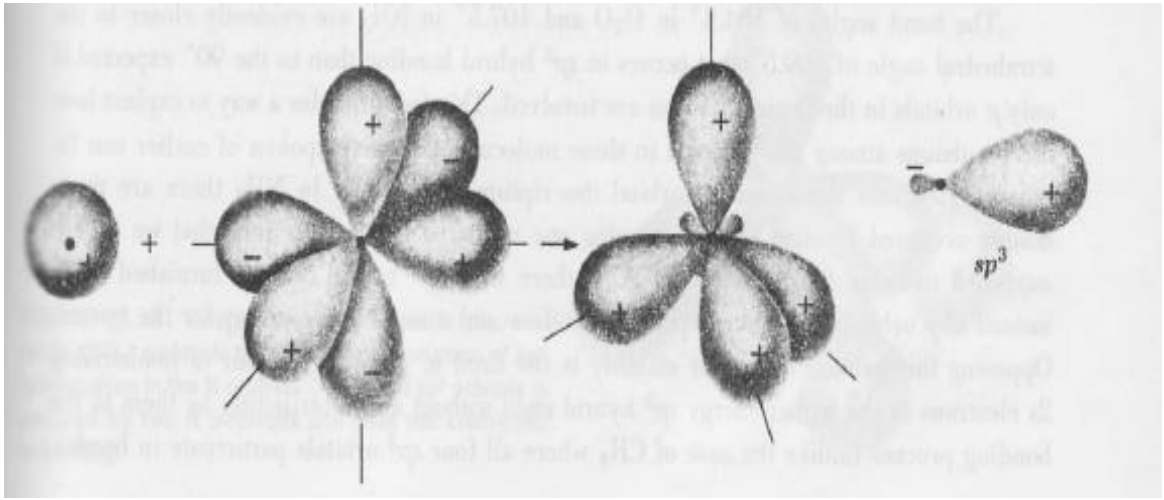
Ionic Bond

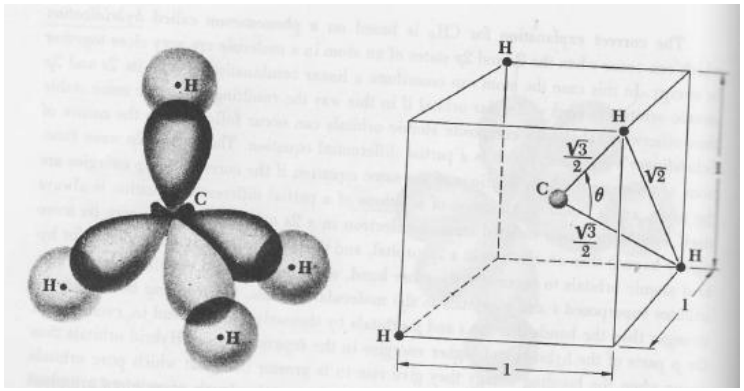

Single 6s
valence
electron
Separated atoms
F
Cs
Nearly filled
n = 2 shell
Cs+
F−
Ionic bond

sp3 hybridized orbital

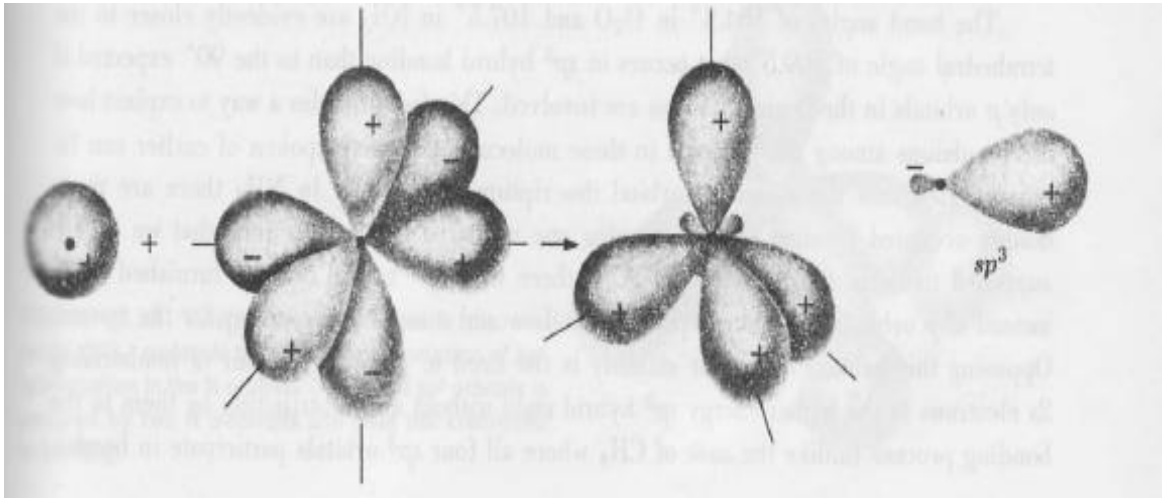


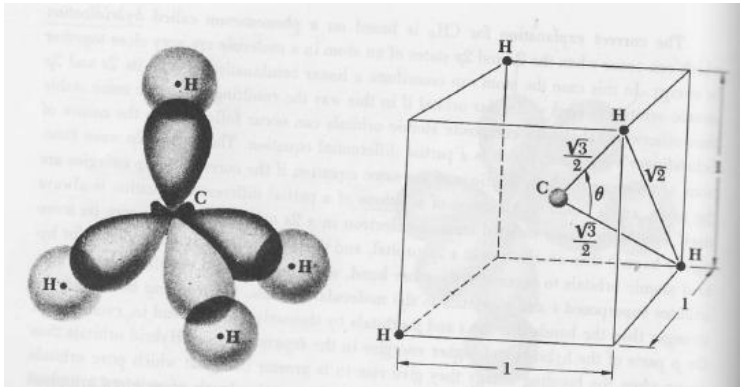
sp3 hybridized orbital





sp3 hybridized orbital





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

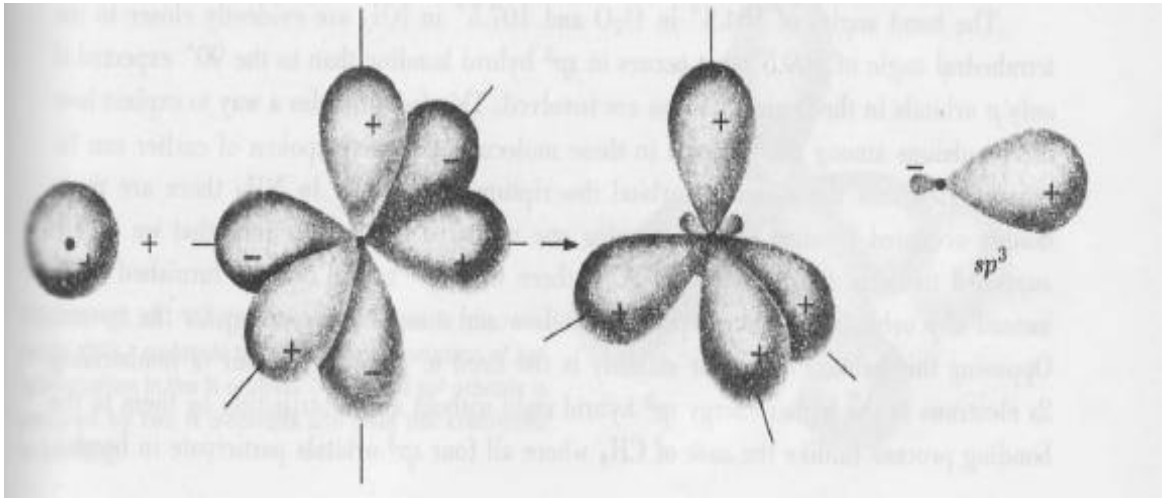
$$\psi_{II} = \psi_{2s} + \frac{1}{3}\psi_{2p_z} - \frac{\sqrt{8}}{3}\psi_{2p_z}$$

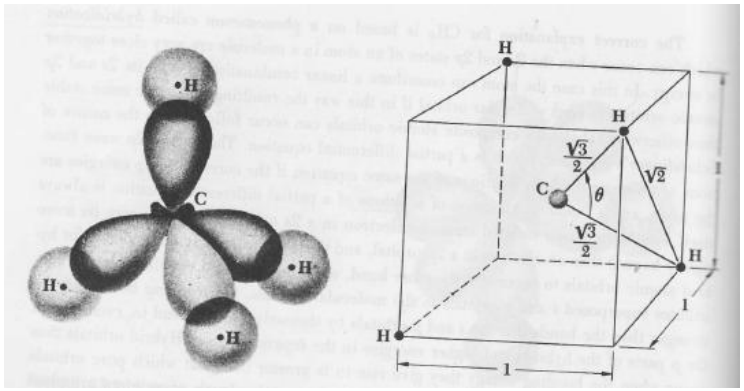
$$\psi_{III} = \psi_{2s} + \frac{1}{3}\psi_{2p_z} + \frac{\sqrt{2}}{3}\psi_{2p_x} - \frac{\sqrt{6}}{3}\psi_{2p_y}$$

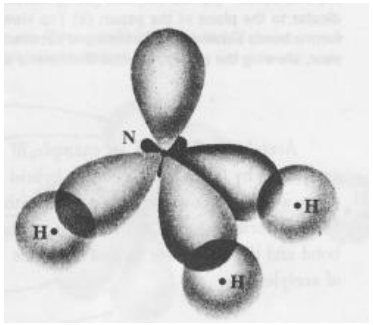
$$\psi_{IV} = \psi_{2s} + \frac{1}{3}\psi_{2p_z} + \frac{\sqrt{2}}{3}\psi_{2p_x} + \frac{\sqrt{6}}{3}\psi_{2p_y}$$

$$\theta = 109.5^\circ$$

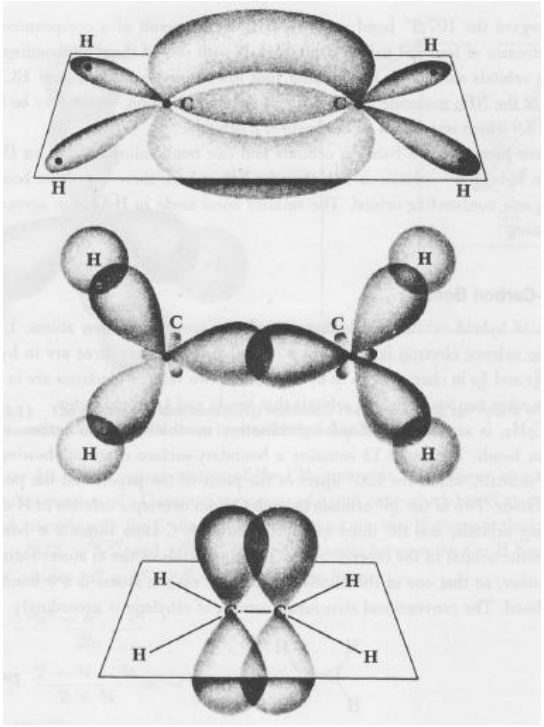
sp3 hybridized orbital







sp2 hybridized orbital



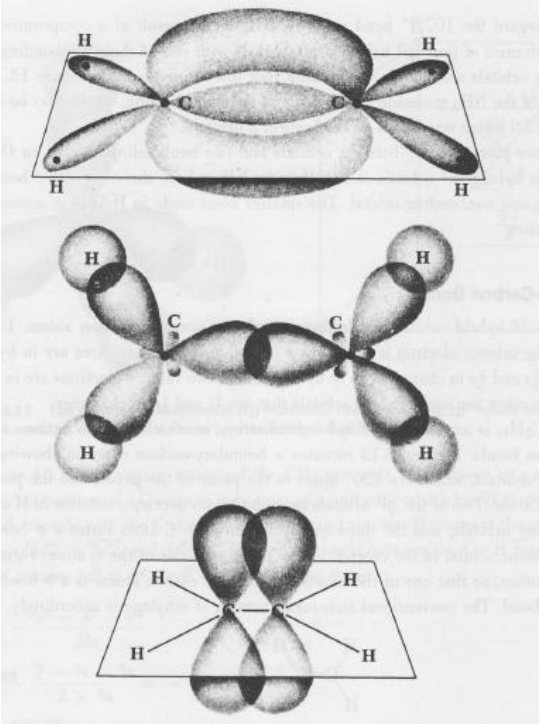
sp2 hybridized orbital

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

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

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

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



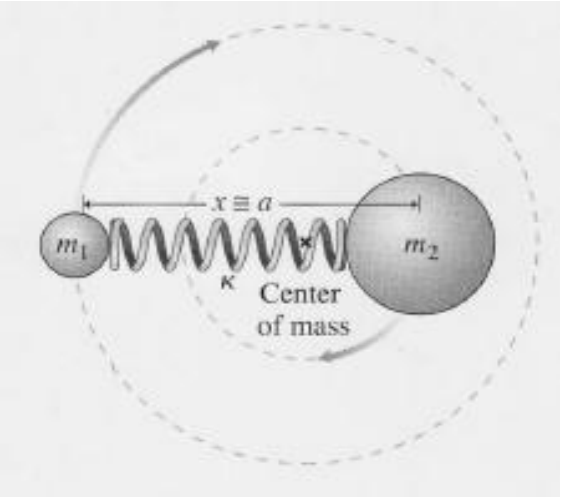
Energies in molecules

- Energy levels electrons occupy in their molecular orbitals (order of greater than 1eV)
- Rotations (order of .001 eV)
- Vibrations (order of .1 eV)

Diatomic Molecule

m_1, m_2

$$a = r_1 + r_2$$



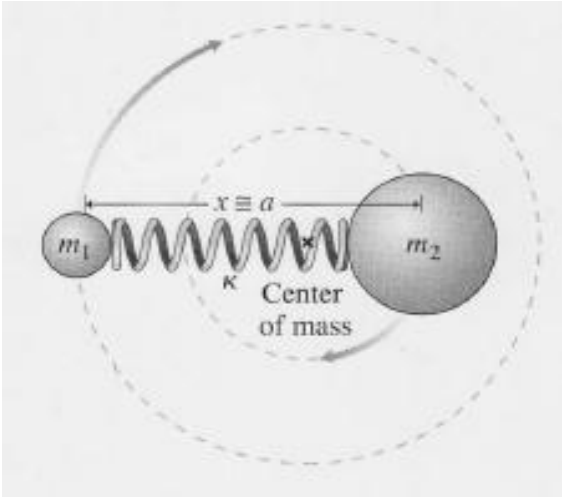
Diatomic Molecule

m_1, m_2

$$a = r_1 + r_2$$

$$I = m_1 r_1^2 + m_2 r_2^2$$

$$m_1 r_1 = m_2 r_2$$



Diatomic Molecule

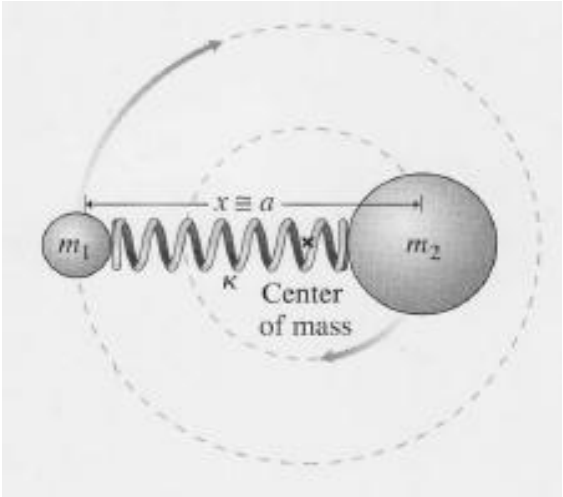
m_1, m_2

$$a = r_1 + r_2$$

$$I = m_1 r_1^2 + m_2 r_2^2$$

$$m_1 r_1 = m_2 r_2$$

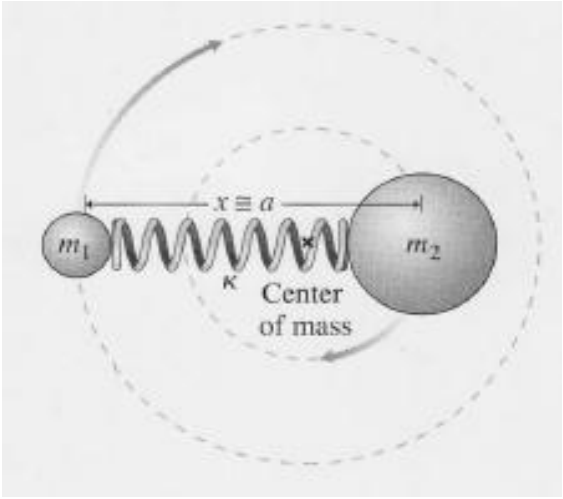
$$I = \left(\frac{m_1 m_2}{m_1 + m_2}\right)(r_1 + r_2)^2 = \mu a^2$$



Diatomic Molecule

m_1, m_2

$$a = r_1 + r_2$$



$$I = m_1 r_1^2 + m_2 r_2^2$$

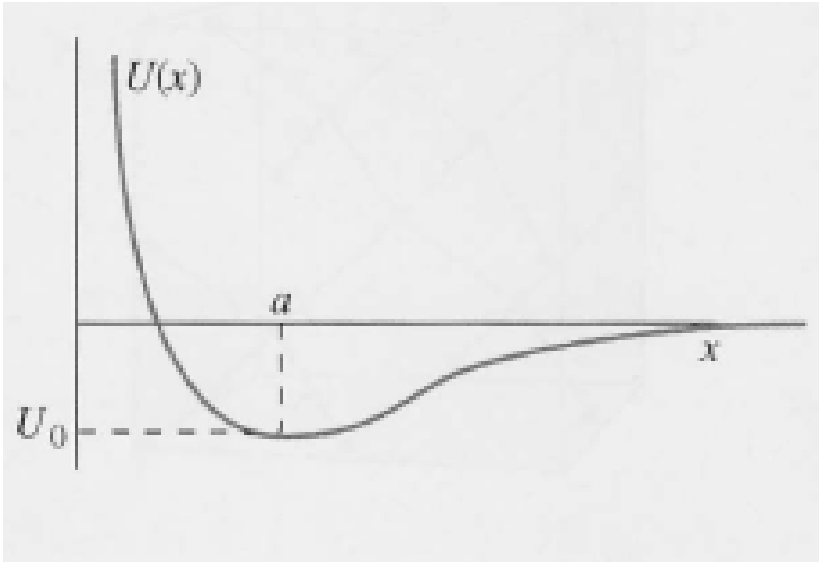
$$m_1 r_1 = m_2 r_2$$

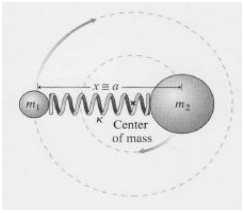
$$I = \left(\frac{m_1 m_2}{m_1 + m_2}\right)(r_1 + r_2)^2 = \mu a^2$$

$$\left(\frac{m_1 m_2}{m_1 + m_2}\right) \equiv \mu \text{ (Reduced mass)}$$

$m_2 \gg m_1$, μ becomes simply m_1

Diatomic molecule: Potential





Molecular energy quantization

$$E_{n(vib),l(rot)} = E_{vib} + E_{rot}$$

Molecular energy quantization

$$E_{n(vib),l(rot)} = E_{vib} + E_{rot}$$

$$= \hbar\left(n + \frac{1}{2}\right)\sqrt{\frac{k}{\mu}} + \frac{\hbar^2 l(l+1)}{2\mu a^2} \qquad \begin{cases} n = 0, 1, 2 \dots \\ l = 0, 1, 2 \dots \\ m_l = 0, \pm 1, \dots \pm l \end{cases}$$

Compare zero-point vib vs. rot energies

- Estimate the temperature where the rot E is 1/10 of the zero-point vib E in a system of the HD molecule

$$\frac{1}{10} = \frac{No.\ of\ molecules\ with\ energy\ E_{01}}{No.of\ molecules\ with\ energy\ E_{00}} = \frac{3e^{-E_{01}/k_BT}}{e^{-E_{00}/k_BT}} = 3e^{-(E_{01}-E_{00})/k_BT}$$

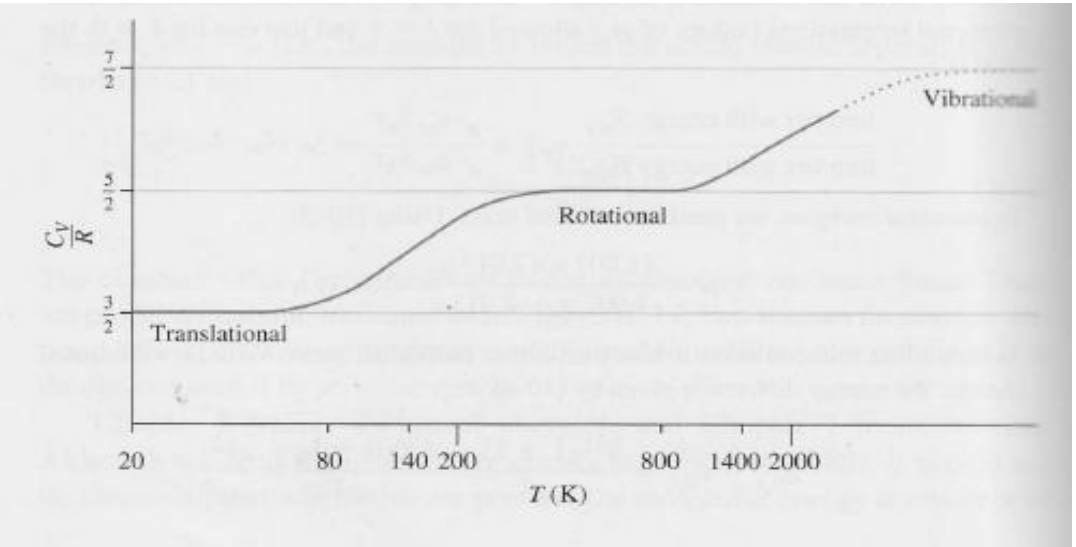
$$E_{01} - E_{00} = \frac{\hbar^2}{2\mu a^2}(1x2 - 0x1) = \frac{\hbar^2}{\mu a^2}$$

$$\left(\frac{m_1 m_2}{m_1 + m_2}\right) \equiv \mu = \frac{(1.007u)(2.013u)}{1.007u + 2.013u} = 0.671u$$

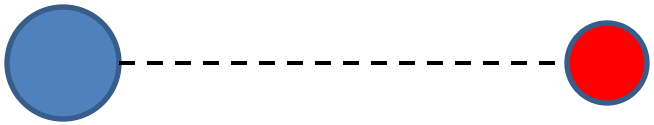
$$E_{01} - E_{00} = 0.011eV$$

This gives $T = 40K$

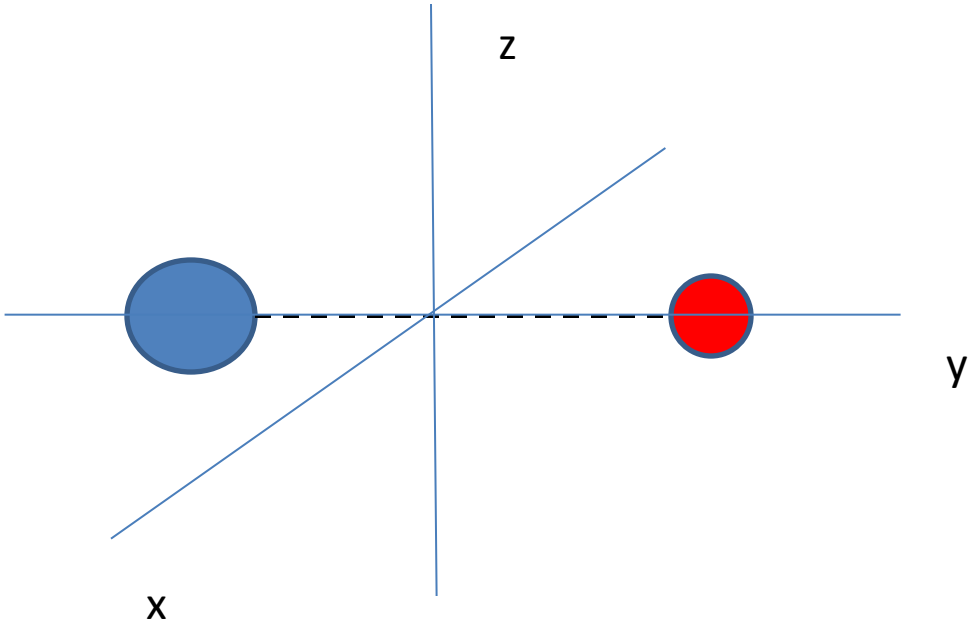
Heat capacity of the H_2



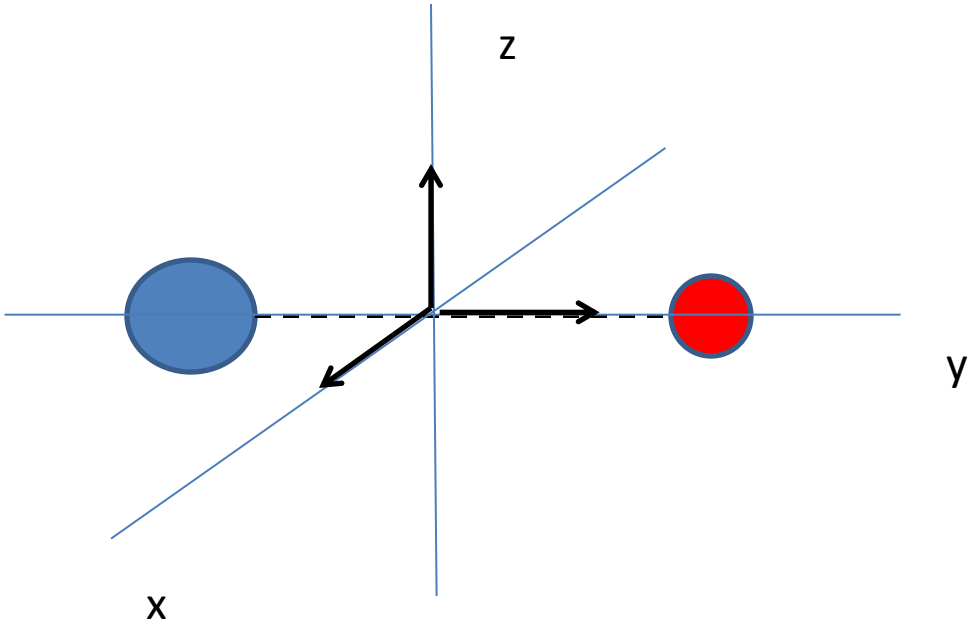
Degrees of freedom in a diatomic molecule



Degrees of freedom in a diatomic molecule

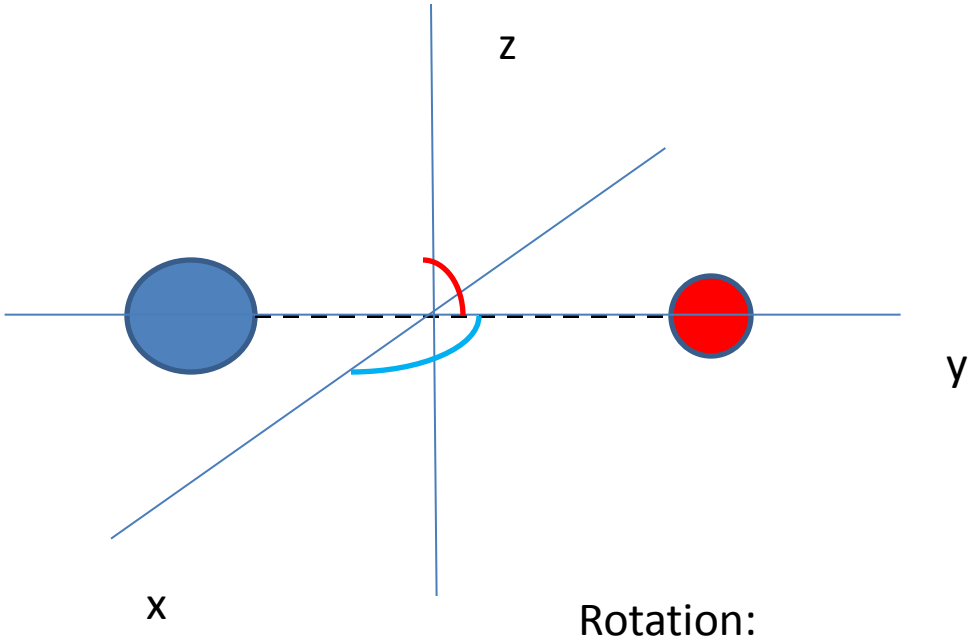


Degrees of freedom in a diatomic molecule



Translation: center of mass moving in three directions

Degrees of freedom in a diatomic molecule

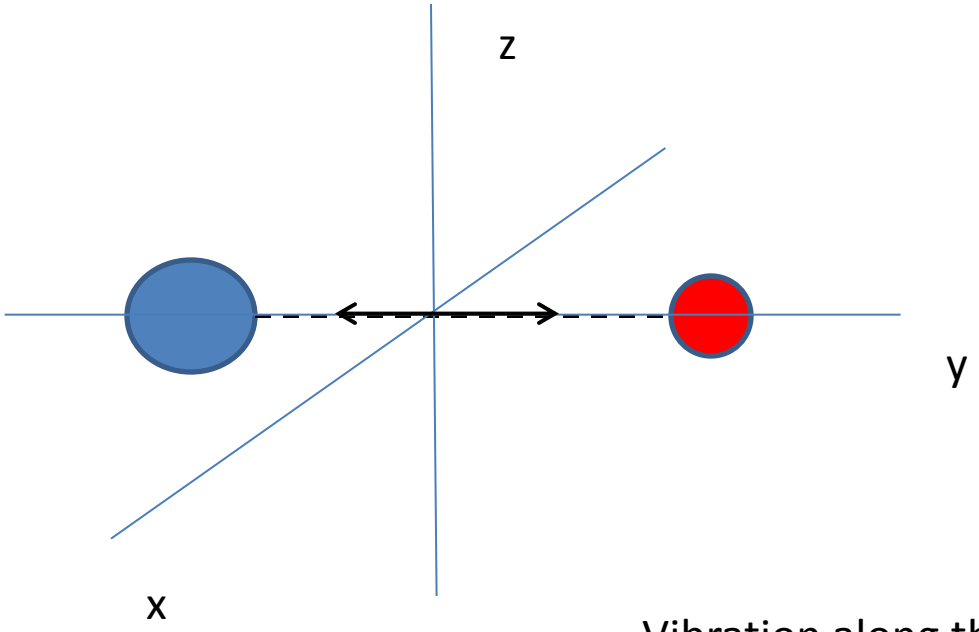


Rotation:

-rotating on the x-y plane (ϕ)

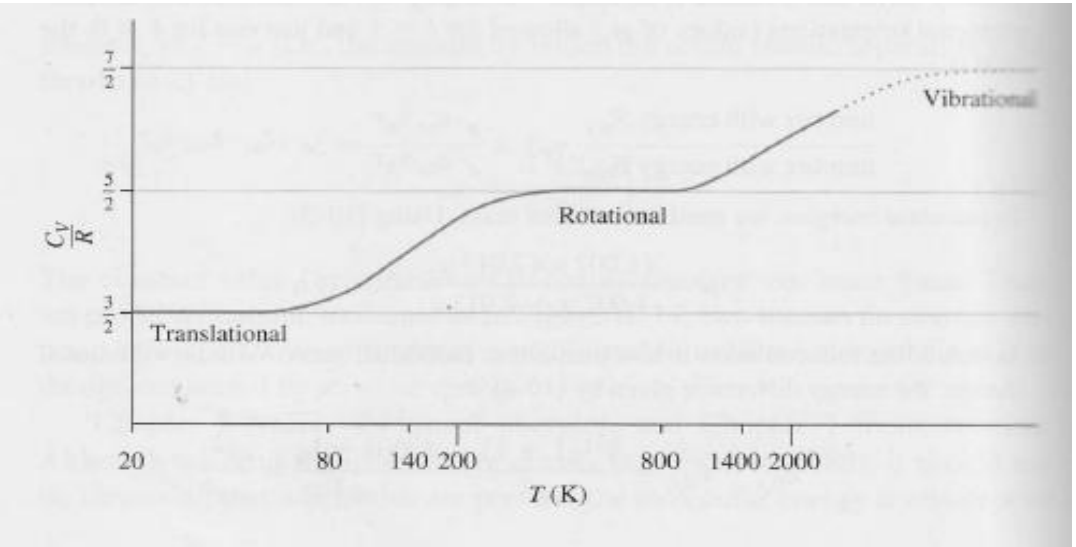
-rotating on the y-z plane ($\boldsymbol{\theta}$)

Degrees of freedom in a diatomic molecule



Vibration along the y-axis
-displacement from equilibrium position (x2-x1)
-momentum

Heat capacity of the H_2



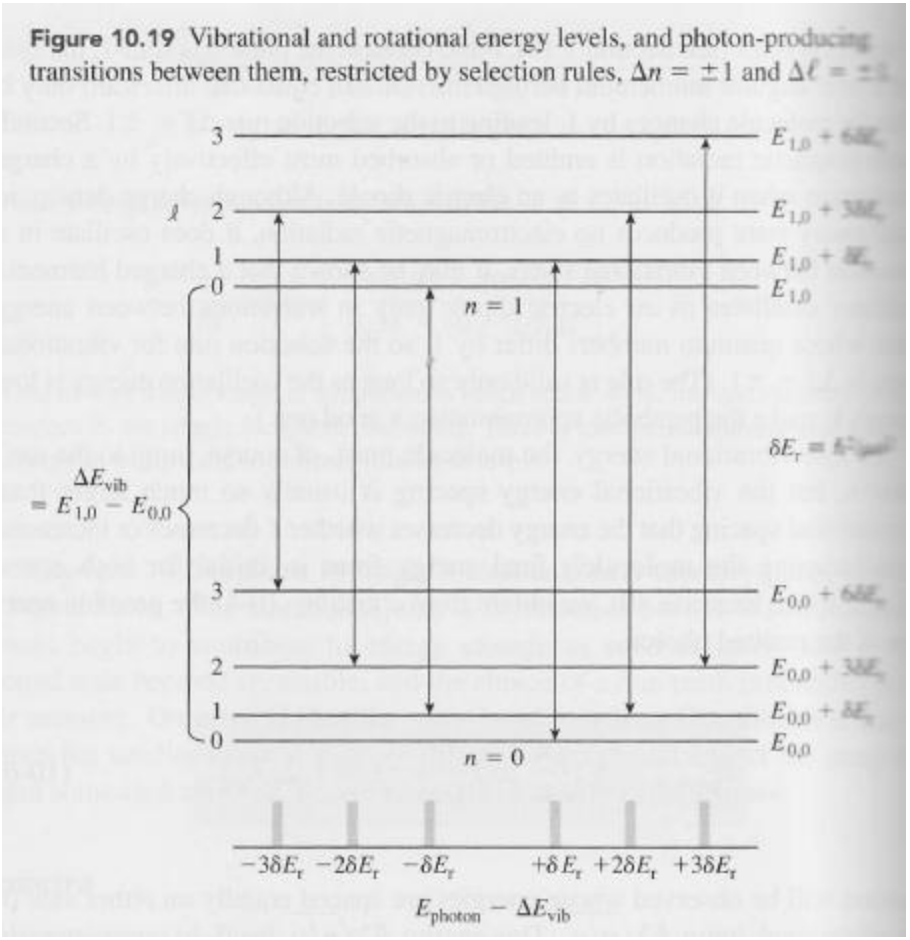
Molecular spectra

$$\text{Vibration: } \Delta n = \pm 1$$

$$\text{Rotation: } \Delta l = \pm 1$$

$$E = \hbar\left(n + \frac{1}{2}\right)\sqrt{\frac{k}{\mu}} + \frac{\hbar^2 l(l+1)}{2\mu a^2}$$

$$E_{higher} - E_{lower} = E_{n,l} - E_{n-1,l\pm1}$$



Molecular spectra

$$\text{Vibration: } \Delta n = \pm 1$$

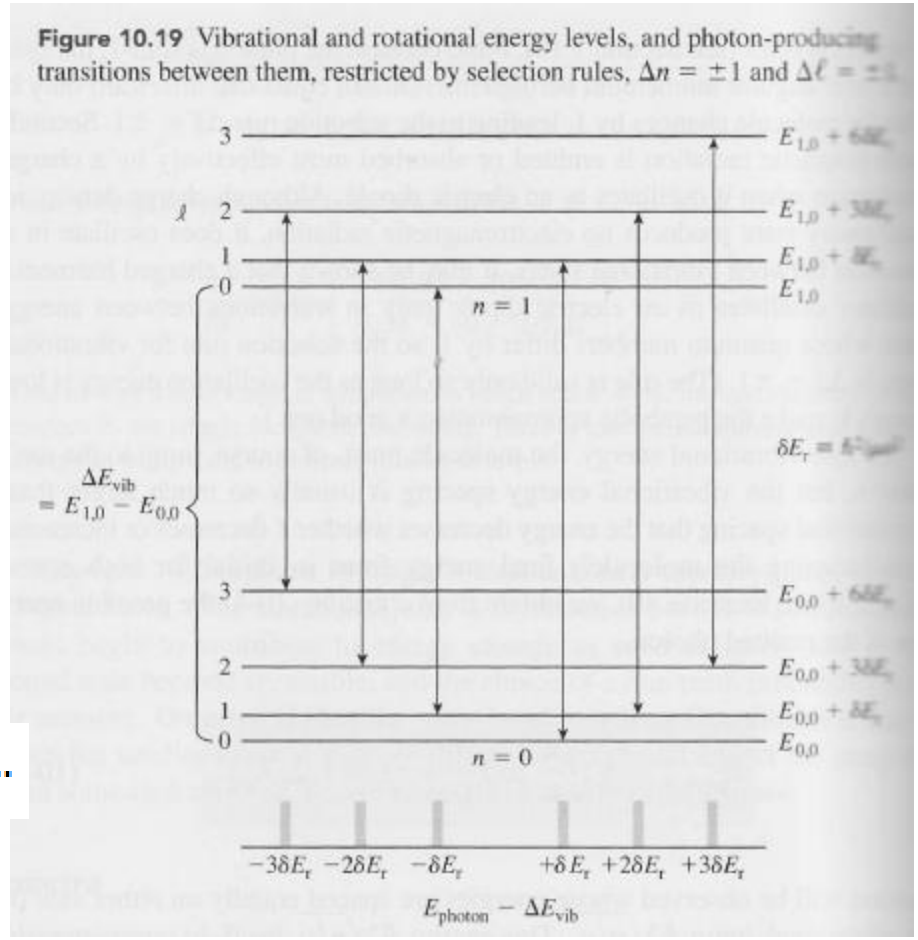
$$\text{Rotation: } \Delta l = \pm 1$$

$$E = \hbar\left(n + \frac{1}{2}\right)\sqrt{\frac{k}{\mu}} + \frac{\hbar^2 l(l+1)}{2\mu a^2}$$

$$E_{higher} - E_{lower} = E_{n,l} - E_{n-1,l\pm1}$$

$$= \hbar\sqrt{\frac{k}{\mu}} \pm \frac{\hbar^2}{\mu a^2} I$$

Where $I = 1,2,3 \ldots$



Molecular spectra

Vibration: $\Delta n = \pm 1$

Rotation: $\Delta l = \pm 1$

$$E_{higher} - E_{lower} = E_{n,l} - E_{n-1,l\pm1}$$

$$= \hbar\sqrt{\frac{k}{\mu}} \pm \frac{\hbar^2}{\mu a^2} I$$

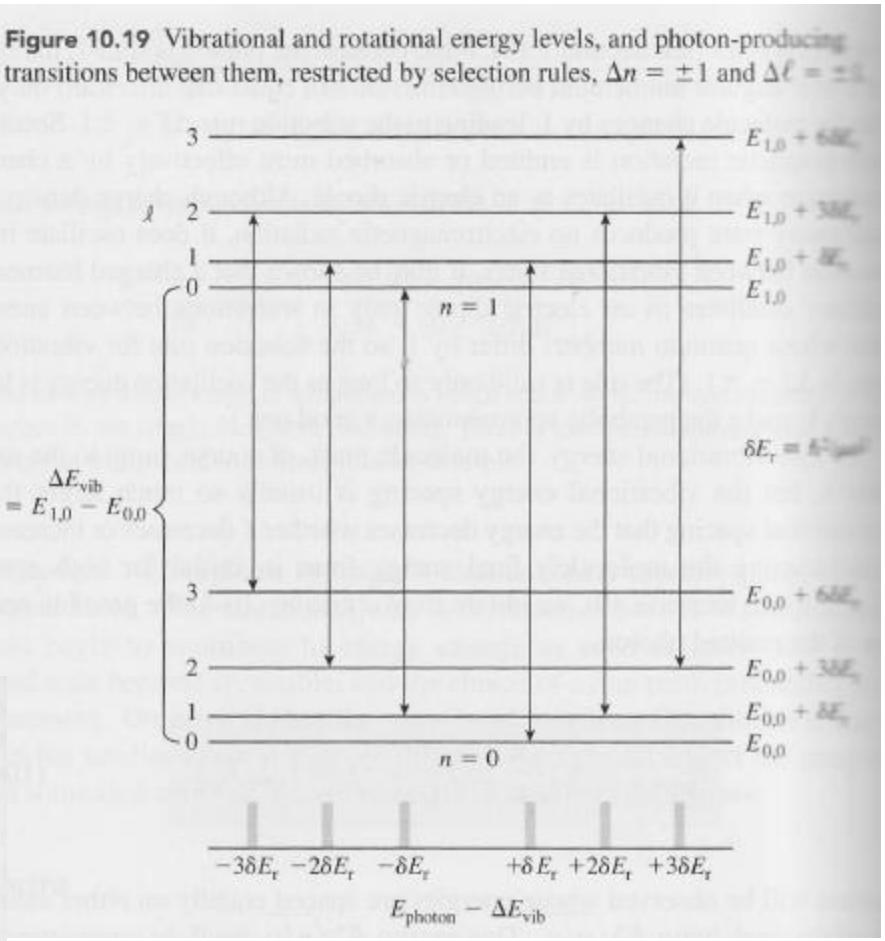


Figure 10.19 Vibrational and rotational energy levels, and photon-producing transitions between them, restricted by selection rules, $\Delta n = \pm 1$ and $\Delta \ell = \pm 1$.

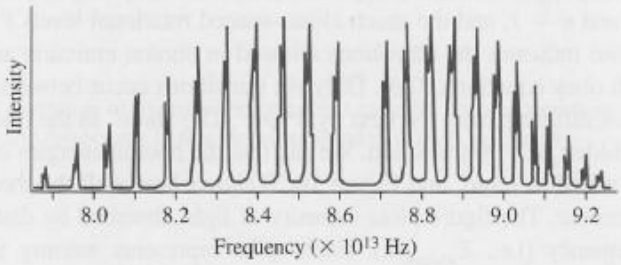


Figure 10.20 Vibration/rotation absorption spectrum of HCl. The "hole" in the middle is due to the forbidden $\Delta \ell = 0$ transition.

Molecular energy levels