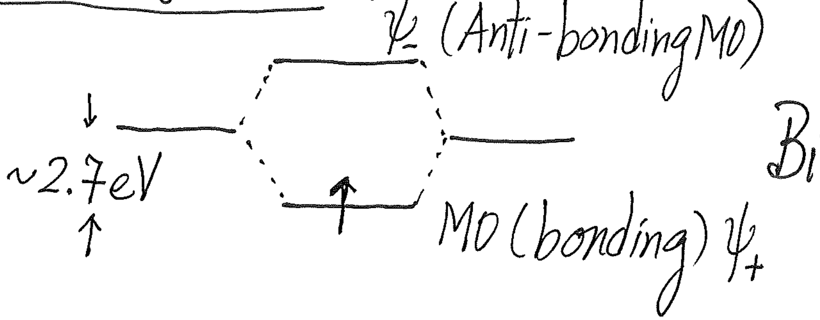
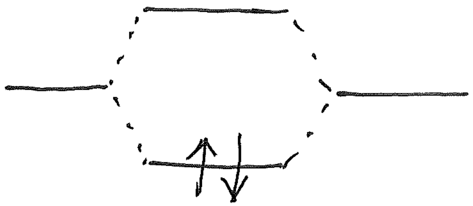
F. What about H_2?

- H_2^+



Binding energy of H_2^+ ion = 2.7eV

- If we "copy" (incorrect) the result to H_2,



Rough estimate of H_2 Binding energy ~ 2×2.7 eV
= 5.4 eV

Actual Binding Energy of H_2 = 4.5eV

∴ $\underbrace{\text{less stable}}_{\text{Make sense!}}$ than rough estimate

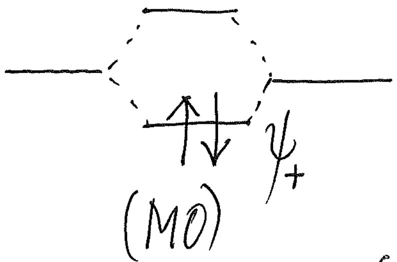
el-el repulsion $\left(+\frac{e^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|}\right)$ destablizes H_2

[one could do perturbation for this term]

- Any molecular problem [electronic part] is hard to do!

- Variational Method, Hartree-Fock, "Slater orbitals"...,
  many approaches tried to recuse the molecular orbitals picture
  [fill electrons based on Pauli Principle] AND LCAO

At the end



picture is retained
[but energies different from He^+]

($\because$ $\hat{H}^{(H_2)}_{electronic} \neq \hat{H}^{(H_2^+)}_{electronic}$)

Different QM problems

Ground state

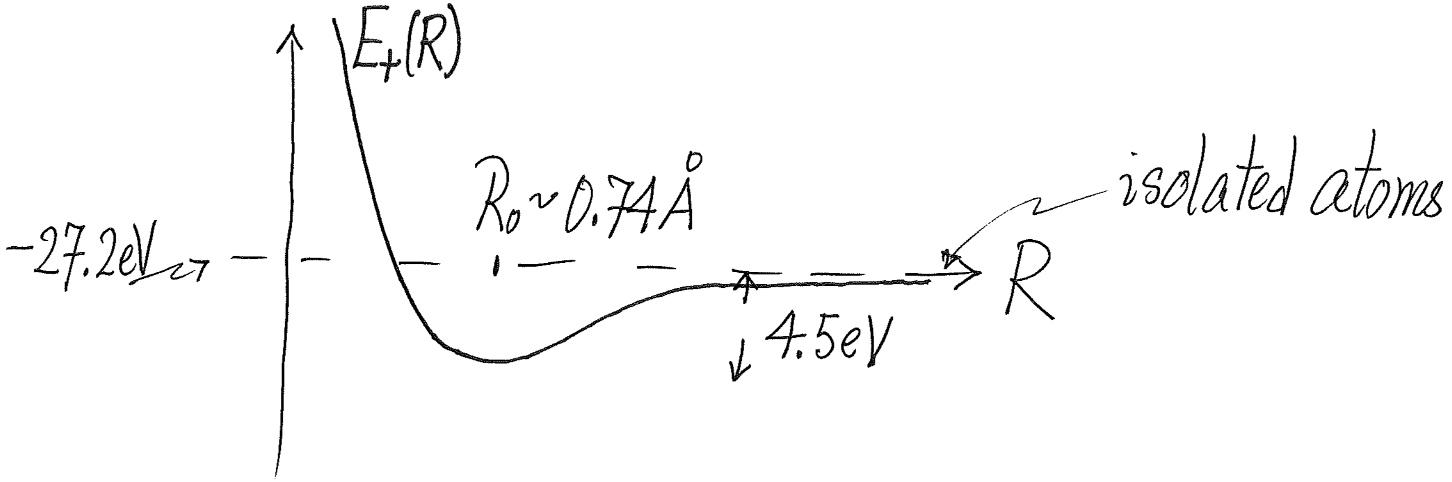
See next page for $\psi_{GS}^{(H_2)}$

- But H_2 is a two-electron system [nuclei assumed fixed]

$$\underset{\substack{\text{2-electron}\\\text{ground}\\\text{state wavefn}}}{\psi_{GS}^{(H_2)}} = \overbrace{\underset{\substack{\text{bonding}\\\text{MO}}}{\psi_+(1)}\,\underset{\substack{\text{bonding}\\\text{MO}}}{\psi_+(2)}}^{\text{spatial part}}\;\underbrace{\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2)-\beta(1)\alpha(2)\right]}_{\text{spin singlet }(S=0)} \qquad (20)$$

Anti-symmetric w.r.t. interchanging electrons' coordinates

$$E_+ = \iint \psi_+^*(\vec{r}_1)\,\psi_+^*(\vec{r}_2)\,\hat{H}^{(H_2)}_{\text{electronic}}\,\psi_+(\vec{r}_1)\,\psi_+(\vec{r}_2)\,d^3r_1\,d^3r_2 \qquad (21)$$



- What's inside $\psi_{GS}^{(H_2)}$ in LCAO-MO (Molecular Orbital Theory)?

Inspect spatial part of ground state wavefunction

$$\psi_+(\vec{r}_1)\,\psi_+(\vec{r}_2) \propto \left[\phi_{L,1s}(\vec{r}_1)+\phi_{R,1s}(\vec{r}_1)\right]\left[\phi_{L,1s}(\vec{r}_2)+\phi_{R,1s}(\vec{r}_2)\right]$$

Mulliken & Hund
(MO Theory)

$$= \underbrace{\Big[\underbrace{\phi_{L,1s}(\vec{r}_1)\,\phi_{L,1s}(\vec{r}_2)}_{\text{electrons on left}} + \underbrace{\phi_{R,1s}(\vec{r}_1)\,\phi_{R,1s}(\vec{r}_2)}_{\text{electrons on right}}\Big]}_{\underline{\text{Ionic character}}} + \underbrace{\underbrace{\Big[\phi_{R,1s}(\vec{r}_1)\,\phi_{L,1s}(\vec{r}_2)+\phi_{L,1s}(\vec{r}_1)\,\phi_{R,1s}(\vec{r}_2)\Big]}_{\text{"one electron on each side, but can't tell which electron is on which side"}}}_{\underline{\text{"Valence Bond"}}\text{ character}}$$

[1927 Heilter and London used only VB terms to explain bonding in H_2 with success]

G. Some more complicated Molecules

- H_2^+ or H_2 : s-s (σ) bond
- What about s-p bonds? What are single/double/triple bonds?
  What are π bonds?
- Same physics: LCAO to get MO's, fill electrons into MO's
  by Pauli Principle
- Atoms Bind to lower energy
  - Why He_2 doesn't exist?
- Bonding governed by $\underbrace{\text{outermost electrons}}_{\text{called "valence electrons" (價電子)}}$ in atom

- Fluorine atom : $1s^2\ 2s^2\ \underbrace{2p^5}$

  $2p_x^2\ \ 2p_y^2\ \ 2p_z^1$

  (Hund's rule)

  unpaired electron (one) ready to form bond (Valence 1)

  - e.g. HF , F_2

- Oxygen atom : $1s^2\ 2s^2\ \underbrace{2p^4}$

  $2p_x^2\ \ 2p_y^1\ \ 2p_z^1$

  unpaired electrons (two) ready to form bonds (Valence 2)

  e.g. H_2O , $\underbrace{O_2}$

  double bond (What is it?)

- Nitrogen atom : $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$

  unpaired electrons (three) ready to form bonds (Valence 3)

  e.g. $\underbrace{NH_3}$, $\underbrace{N_2}$

  special structure

  triple bond (What is it?)

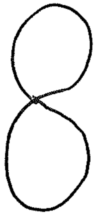
Directionality of atomic orbitals ⇒ directional properties of covalent bonds

Recall: For atoms, $V(\vec{r}) = V(|\vec{r}|) = V(r)$ spherically symmetric

then $\psi(r,\theta,\phi) \sim R_{n\ell}(r)\, \underbrace{Y_{\ell m}(\theta,\phi)}_{\text{spherical harmonics}}$

p orbitals $\Rightarrow \underbrace{\ell = 1}$

$$\underbrace{Y_{10}(\theta,\phi)}_{\underbrace{\sim \cos\theta}},\quad \underbrace{\underbrace{Y_{11}(\theta,\phi)}_{\sim +\sin\theta e^{i\phi}},\quad \underbrace{Y_{1-1}(\theta,\phi)}_{\sim +\sin\theta e^{-i\phi}}}$$

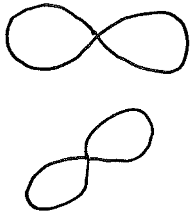


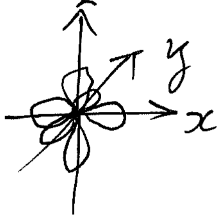
← p_z

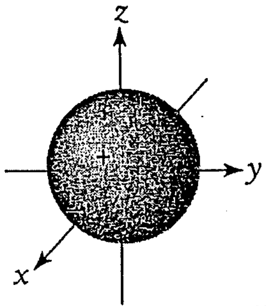
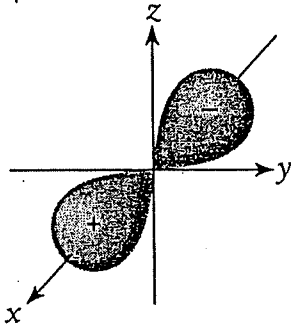
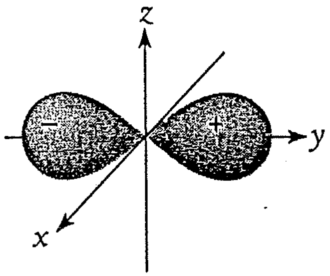
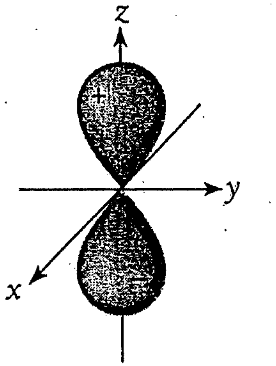
[∵ $r\cos\theta = z$ in spherical coordinates]

$$\boxed{\begin{aligned} p_x &\sim Y_{11} + Y_{1-1} \\ p_y &\sim Y_{11} - Y_{1-1} \end{aligned}}$$

Thus, p_x, p_y, p_z





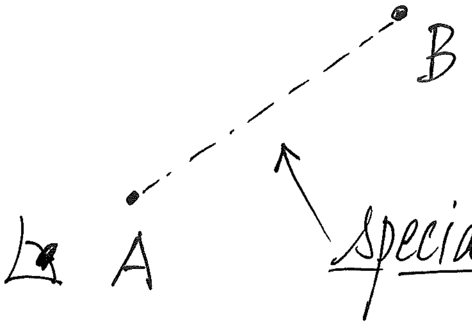
Orbital	n	l	m_l	
s	1,2,3, …	0	0	
p_x	2,3,4, …	1	±1	
p_y	2,3,4, …	1	±1	
p_z	2,3,4, …	1	0	

Boundary surface diagrams for s and p atomic orbitals. Each orbital can "contain" two electrons. There is a high probability of finding an electron described by one of these orbitals in the shaded regions. The sign of the wave function in each lobe is indicated.

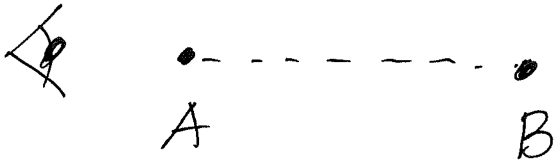
Recall that p_x, p_y are linear combinations† of Y_{11} and Y_{1-1} states

For one lonely atom, there is however no sense about what are x, y, z directions!

Only when atoms come closer to form molecule, there is a special direction



special direction (may call it x, or y, or z)

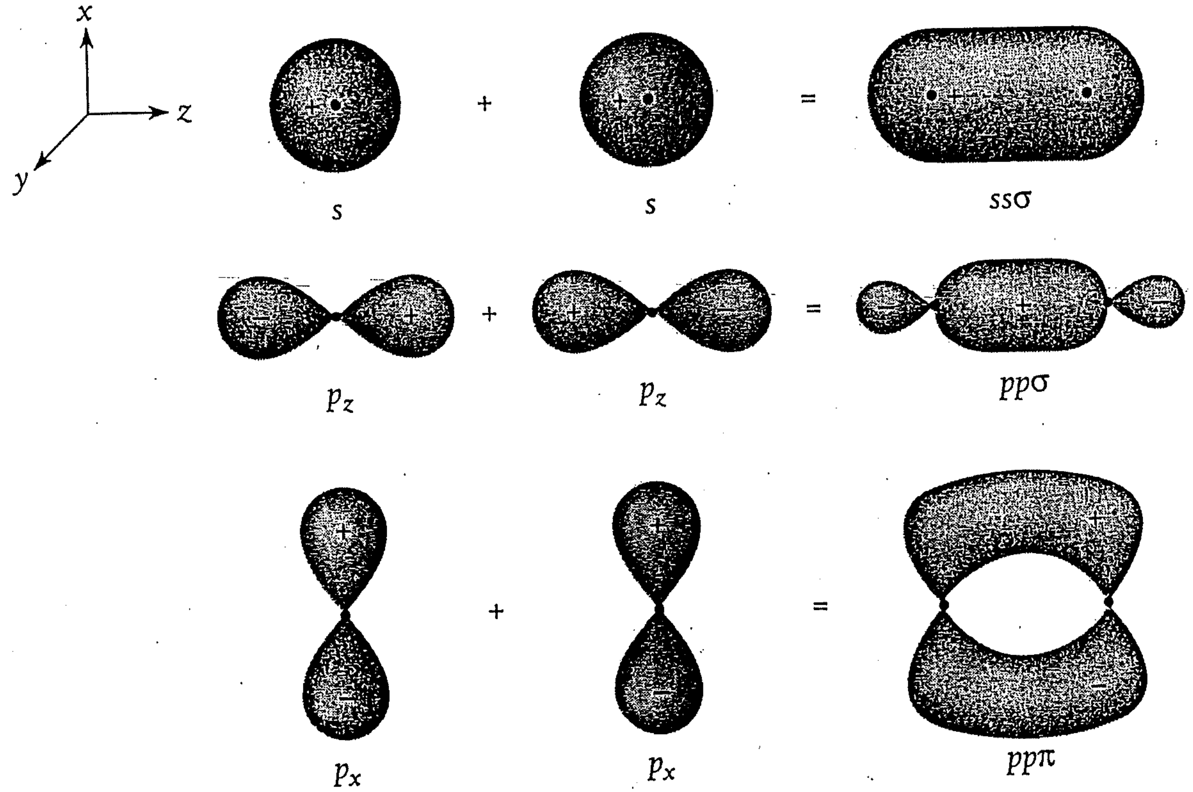


- σ and π bonds[†] are defined w.r.t. rotation about the axis connecting the two nuclei
- σ bond : symmetric w.r.t. rotation about axis
- π bond : Not so

[†] The labels σ and π were first introduced by Hund.

- σ bond and π bond (differ by symmetry w.r.t. rotation about axis)

(see figure) $(\underbrace{ss\sigma}_{\text{a sigma bond results from overlap of two s-atomic orbitals}},\ pp\sigma,\ pp\pi,\ sp\sigma)$



$ss\sigma$ ← $|\psi|^2$ OR charge distribution symmetrical w.r.t. rotation about axis joing two nuclei

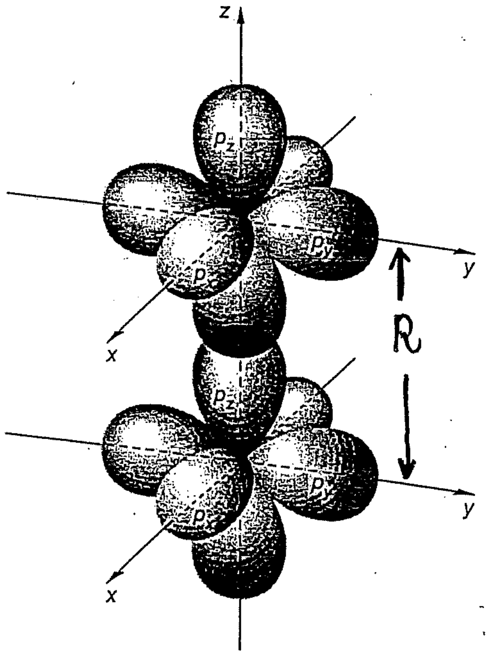
$pp\sigma$ ←

$pp\pi$ ← Not so

The formation of $ss\sigma$, $pp\sigma$, and $pp\pi$ bonding molecular orbitals. Two p_y atomic orbitals can combine to form a $pp\sigma$ molecular orbital in the same way as shown for two p_x atomic orbitals but with a different orientation.

- When 1s-orbitals from two atoms come closer → anti-bonding MO / → bonding MO
- Same for 2s orbitals

- How about p orbitals?



Observe

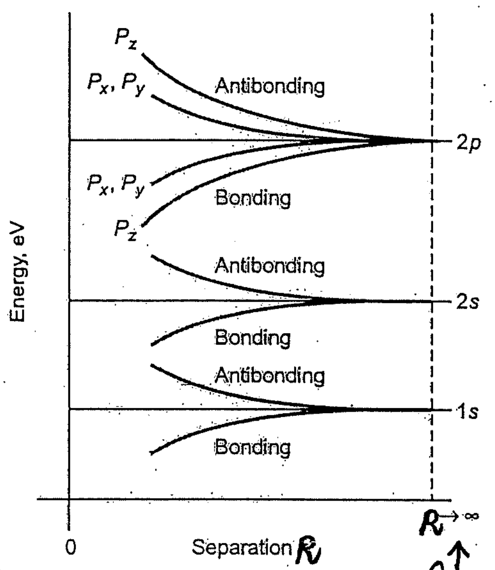
p-p σ

and

p-p π

Energy of molecular orbitals (Physical Picture)

(schematic)



} From overlap of 2p orbitals

← From overlap of 2s orbitals

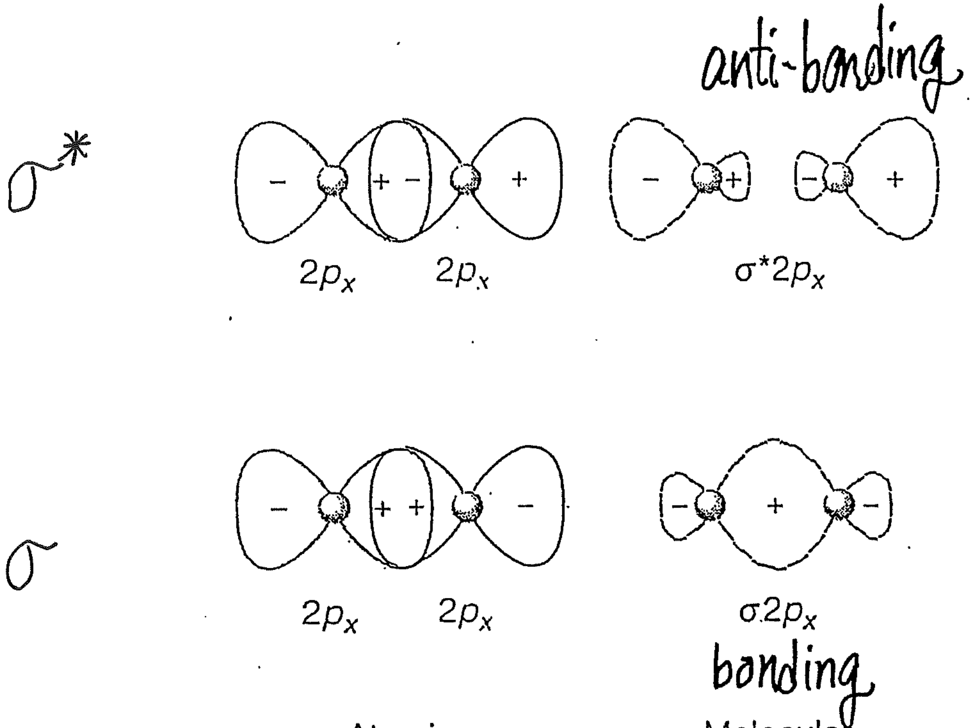
← From overlap of 1s orbitals (as discussed in H_2^+)

↑ far away

↑ Fill electrons into molecular orbitals according to the Pauli exclusion principle.

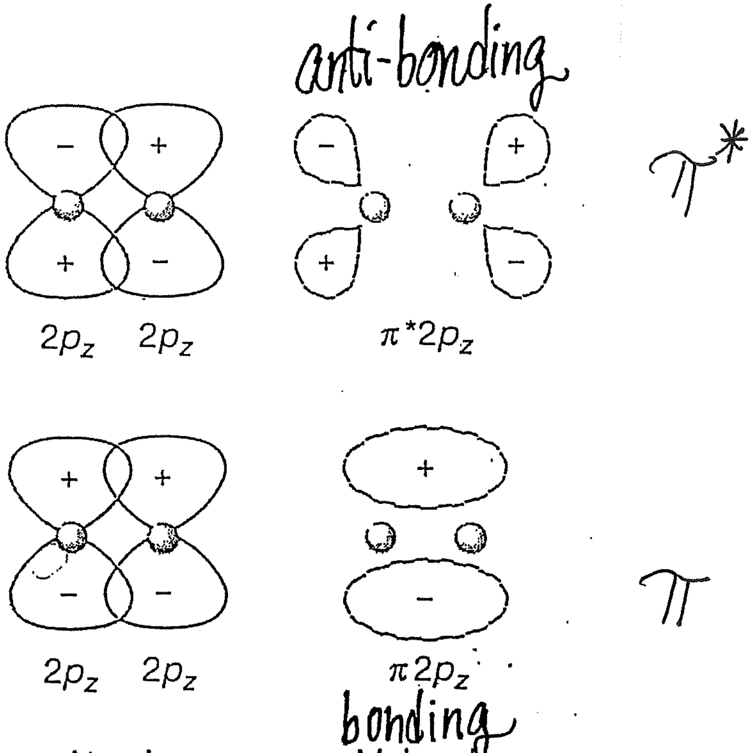
$$\psi \sim \psi_{2p_x}^{(L)} \pm \psi_{2p_x}^{(R)}$$

$$\psi \sim \psi_{2p_{y,z}}^{(L)} \pm \psi_{2p_{y,z}}^{(R)}$$



Atomic $2p_x$ states

Molecular $\sigma 2p_x$ states



Atomic $2p_z$ states

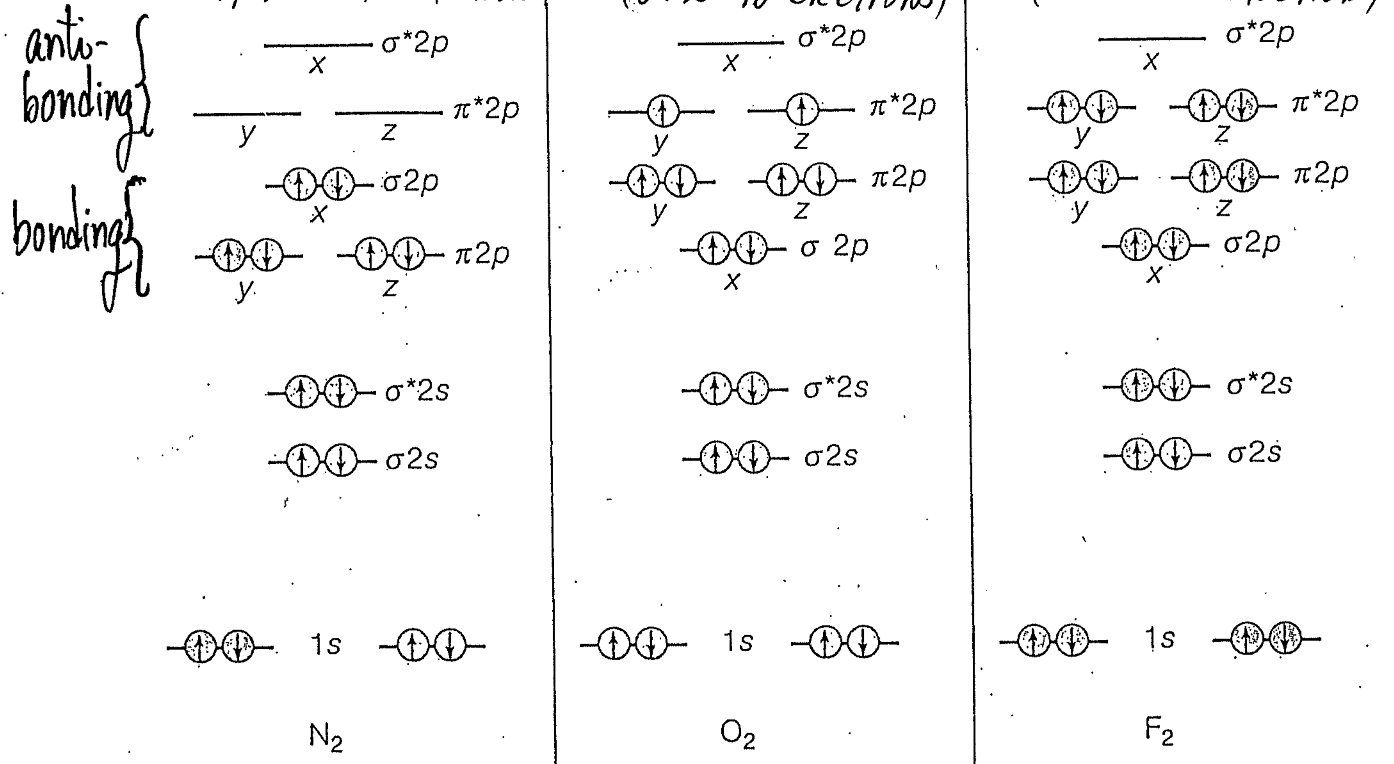
Molecular $\pi 2p_z$ states

Formation of 2p bonding and antibonding states

† x-direction is the line joining two nuclei

Each molecule is a new QM problem ⇒ Each molecule has its own MO alignments

N_2 ($7 \times 2 = 14$ electrons) | O_2 ($8 \times 2 = 16$ electrons) | F_2 ($9 \times 2 = 18$ electrons)



Counting all : 10 in bonding, 4 in anti-bonding | 10 in bonding, 6 in anti-bonding | 10 in bonding, 8 in anti-bonding

Counting MO's from 2p orbitals : 6 in bonding, 0 in anti-bonding | 6 in bonding, 2 in anti-bonding | 6 in bonding, 4 in anti-bonding

[R_0 ~ 0.11 nm, B ≅ 9.8 eV] | [R_0 ~ 0.12 nm, B ~ 5.1 eV] | [R_0 ~ 0.14 nm, B ~ 1.6 eV]

Single, Double, Triple, half-a-bond: Bond Order

$$\boxed{\text{Number of Bonds} = \text{Bond Order} = \frac{\begin{pmatrix}\text{\# electrons in}\\ \text{Bonding MO's}\end{pmatrix} - \begin{pmatrix}\text{\# electrons in}\\ \text{Anti-Bonding MO's}\end{pmatrix}}{2}} \quad (22)$$

[a bond must connect two atoms]

$\therefore$ N_2: Number of bonds $= \frac{10-4}{2} = \frac{6-0}{2} = 3$ [Triple Bond]

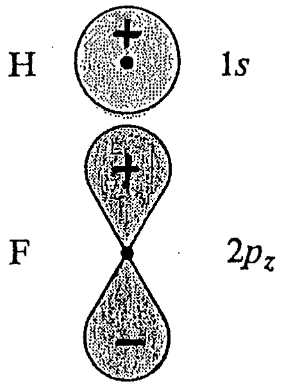
O_2: Double Bond

F_2: Single Bond

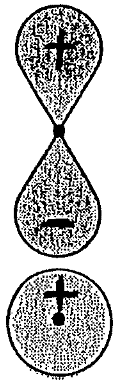
H_2: Single Bond

H_2^+: Number of Bonds $= \frac{1-0}{2} = 1/2$ [half-a-bond]

HF molecule [spσ]



(a) Bonding



(b) Antibonding

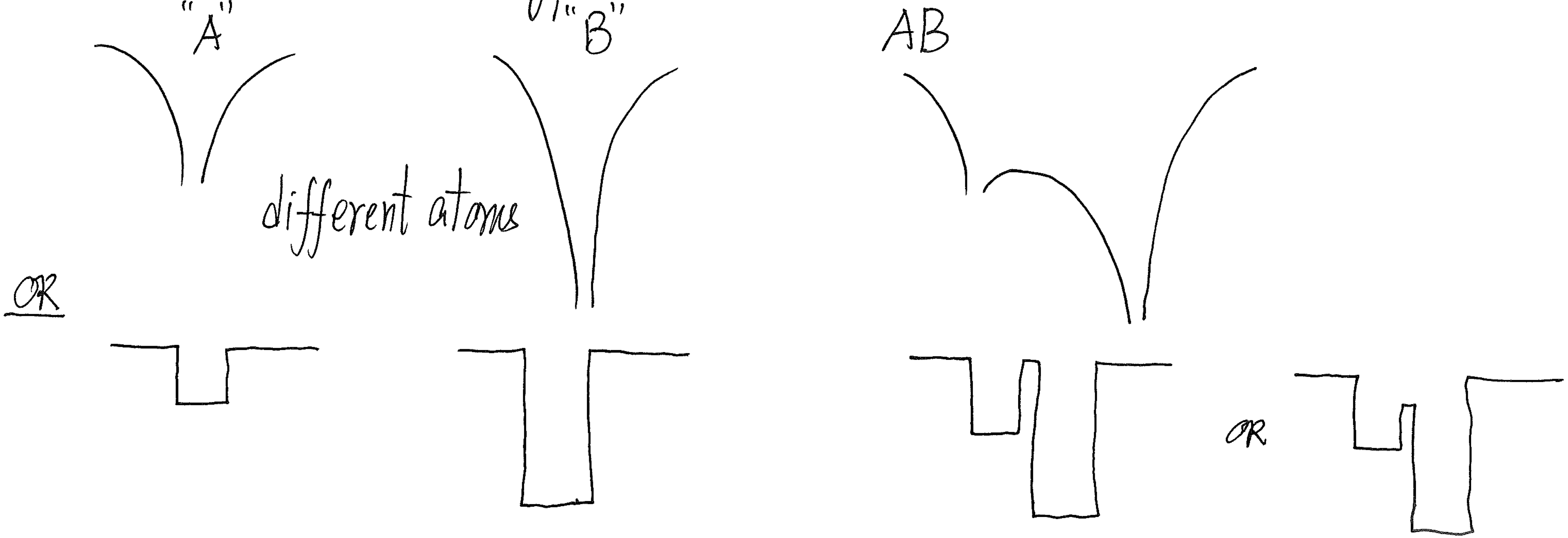
Wave functions for the HF molecule. **(a)** We obtain the bonding orbital by adding the wave functions for the 1*s* electron in H and the $2p_z$ electron in F, *provided* that the H atom approaches the positive lobe of the $2p_z$ function. (The $2p_z$ wave function in F is shown here as a figure of eight to emphasize that both lobes belong to a single atomic wave function.) **(b)** If the H atom approaches from the opposite direction, then adding the two wave functions gives an antibonding orbital. For clarity the two atoms are shown with their wave functions not yet overlapping.

[LCAO]

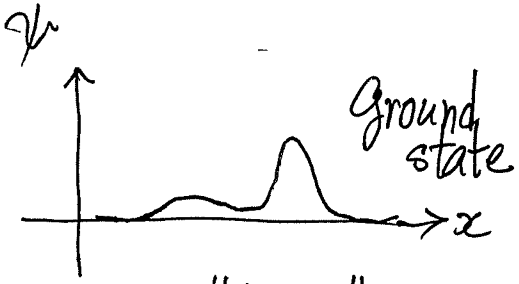
$$\psi^{MO} \sim c_1 \psi_{H,1s} + c_2 \psi_{F,2p}$$

[Mathematically, we are forming a linear combination of an s-orbital from one atom and a p-orbital from another atom.]

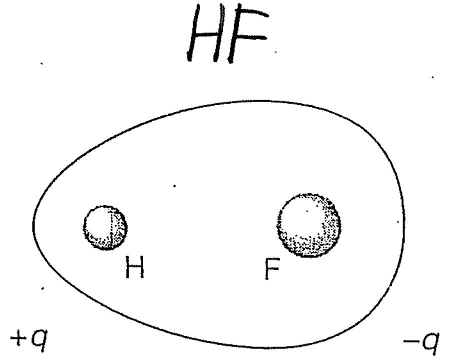
HF is the type "AB"



different atoms



"ionic"



A polar covalent bond.

electron tends to be found on one side (high. prob.)

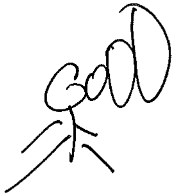
"HF" : Think like an applied physicist

- Relevant atomic orbitals : H(1s) , F(one 2p) (say $2p_z$)

LCAO $\psi = c_1 \psi_{1s}^{(H)} + c_2 \psi_{2p_z}^{(F)}$

It follows that
$$\begin{pmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

<u>Don't</u> think too formally on how to evaluate H_{ij} & S_{ij}

- 

H_{11} and H_{22}? Dominated by the respective <u>atomic state energy</u> ("on-site" energy)

∴ Put $H_{11} = \varepsilon_{1s}^{(H)}$; $H_{22} = \varepsilon_{2p}^{(F)}$

- $\underbrace{S_{11}}$ and $\underbrace{S_{22}}$? Atomic orbitals are normalized

$$\therefore \quad S_{11} = 1, \quad S_{22} = 1$$

- $\underbrace{S_{12}}$ and $\underbrace{S_{21}}$? Overlap of atomic states from <u>different</u> <u>atoms</u>

[<u>NOT</u> to be big!] Put $S_{12} = S_{21}^* \approx 0$

- H_{12} and H_{21}? Important for forming Bonds

[Don't need to evaluate it explicitly for understanding Bonding]

Put $H_{12} = \Delta$, $H_{21} = \Delta^*$

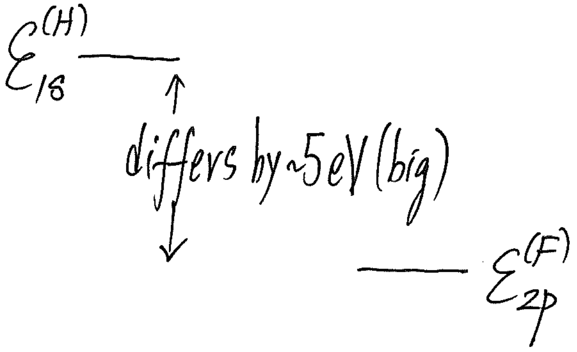
Done!
$$\begin{pmatrix} \varepsilon_{1s}^{(H)} - E & \Delta \\ \Delta^* & \varepsilon_{2p}^{(F)} - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \qquad (23)$$

Non-Trivial Solutions

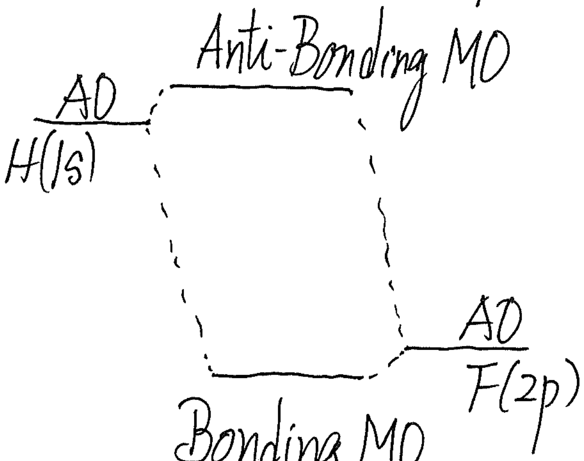
$$\begin{vmatrix} \mathcal{E}_{1s}^{(H)} - E & \Delta \\ \Delta^* & \mathcal{E}_{2p}^{(F)} - E \end{vmatrix} = 0$$

(2x2 math)

- $\mathcal{E}_{1s}^{(H)}$ [-13.6eV] much higher energy than $\mathcal{E}_{2p}^{(F)}$



- $|\Delta| \ll \mathcal{E}_{1s}^{(H)} - \mathcal{E}_{2p}^{(F)}$
-



$\underbrace{\text{Bonding MO}}$

almost like $\psi_{2p}^{(F)}$

[e.g. use 1st order perturbation]

- Fill 2 electrons into MO's

Bonding MO

Strong ionic character

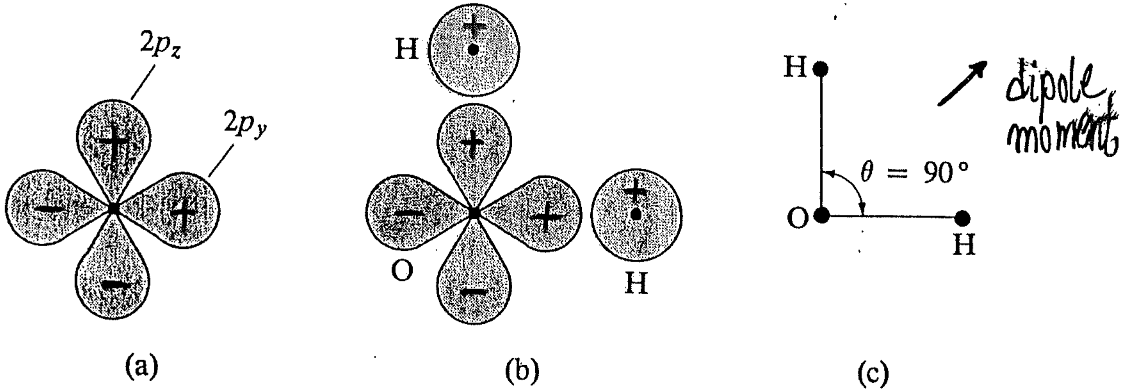
Water Molecule: H_2O

$O: 1s^2\ 2s^2\ 2p_x^2\ \underbrace{2p_y^1}\ \underbrace{2p_z^1}$

↑ ↑

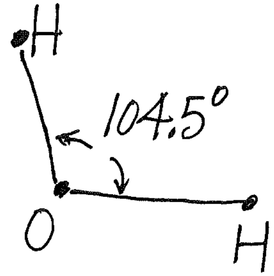
for Bonding

Schematic



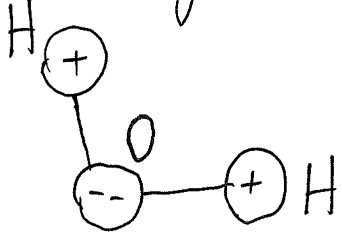
(a) The two unpaired electrons in an O atom occupy the $2p_y$ and $2p_z$ orbitals. **(b)** A water molecule can form if the two H atoms approach the positive lobes of these two orbitals. **(c)** The centers of the atoms in the resulting molecule form an "L" with angle $\theta = 90°$ between the arms. (The experimental value is $\theta \approx 105°$, as explained in the text.)

Actual



$\theta > 90°$ due to mutual repulsion between H nuclei

- Small −ve charge near O and small positive charge near the two H



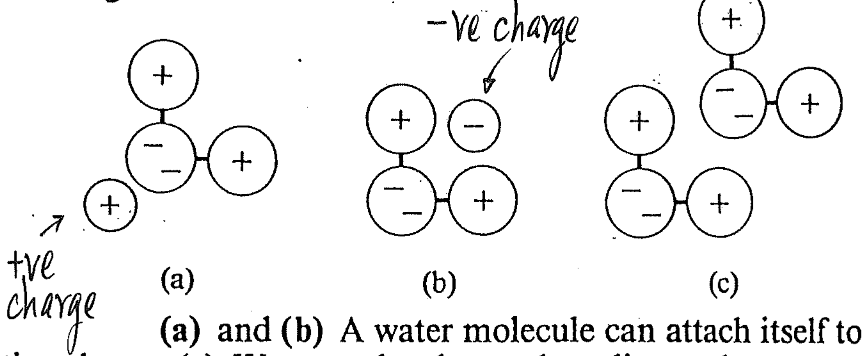
⇒ electric dipole moment
and
a good solvent

Water molecule can easily pick up charges

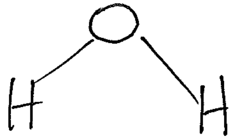
Properly aligned water molecules attract one another

[dipole-dipole]

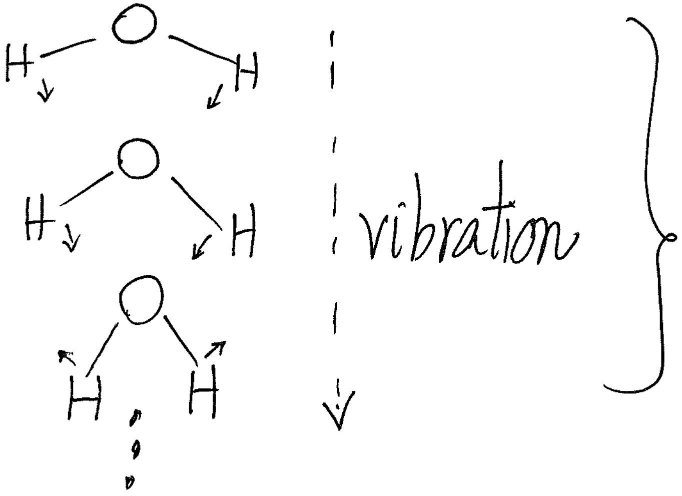
- hydrogen bond binding energy ~0.5 eV/molecule (weak)



(a) and (b) A water molecule can attach itself to a positive OR negative charge. (c) Water molecules tend to align and attract one another.



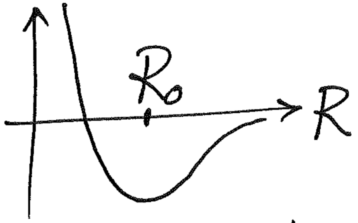
⇒ $\downarrow \vec{\mu}$ (electric dipole moment)



⇒ $\vec{\mu}$ changes as H_2O molecule vibrates in bending mode

⇒ Absorb EM waves at frequency of this mode [greenhouse gas]

Summary

- Molecular TISE is hard to solve
- Electronic part (assuming fixed nuclei) could give bonding
- LCAO combines AOs of different atoms to form Molecular Orbitals (MOs)
- MOs are to be filled in by electrons according to Pauli Exclusion Principle
- Bonding (from electrons) gives 

bond length and $\underbrace{\text{spring constant}}_{[2^{nd}\text{ derivative}]}$
- $\dfrac{\#\text{ electrons in bonding MOs} - \#\text{ electrons in anti-bonding MOs}}{2}$ = bond order
- Single, double, triple bonds and σ, π bonds
- Still need to consider nuclei motions (vibrational and rotational)