F. LCAO-MO is a powerful idea in understanding bonding

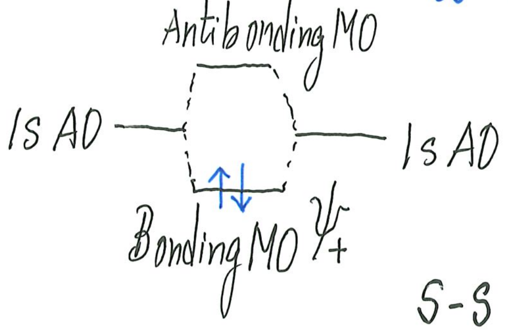
(a) H_2

- 2-electron problem
- addition $\dfrac{+e^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|}$ term in $\hat{H}_{H_2}$ (different from $\hat{H}_{H_2^+}$)

Same approach: LCAO (e.g. 1s states of atom A and atom B)

$\Rightarrow$ MO's (just like atomic orbitals)

2-electron: Apply Pauli Exclusion Principle to fill electrons into MO's to achieve lowest energy (ground state of electronic problem)



Binding energy of $H_2 = \underbrace{4.5\,\text{eV}}_{\text{relative to two neutral H-atoms}}$

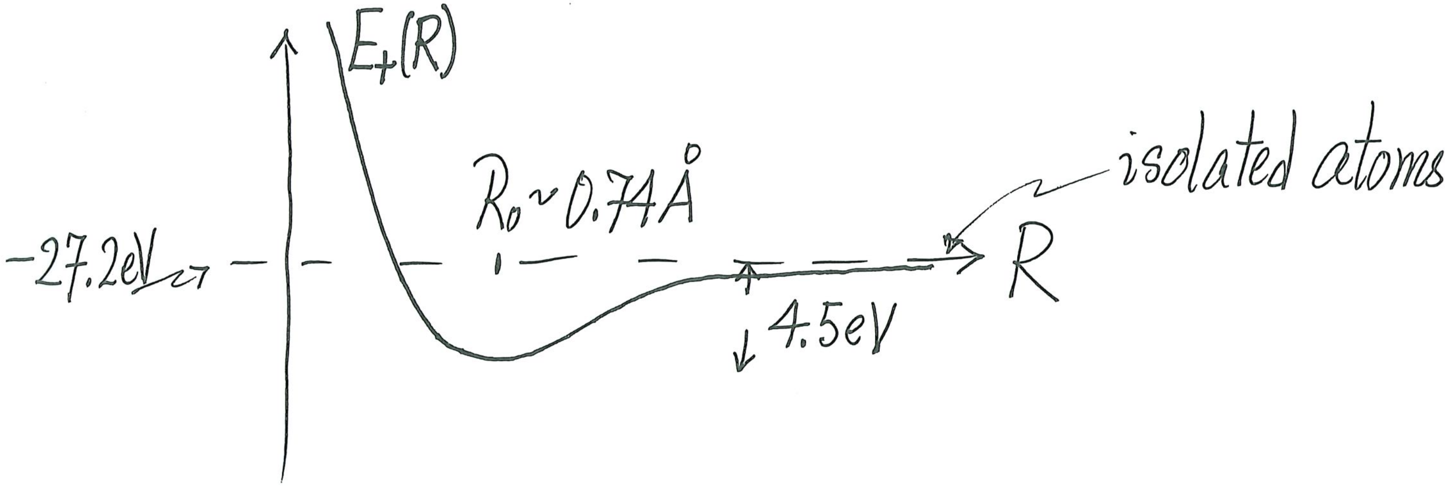
s-s σ bond

Applying knowledge from atomic physics

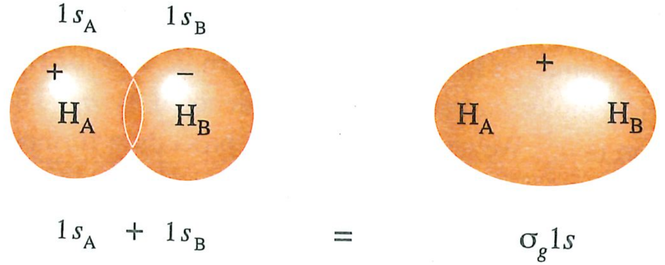
$$\psi^{H_2}_{\substack{GS \\ \text{(electronic)}}} = \underbrace{\overbrace{\psi_+(\vec{r}_1)}^{MO}\,\overbrace{\psi_+(\vec{r}_2)}^{MO}}_{\text{spatial part}} \cdot \underbrace{\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]}_{\text{spin part [singlet]}} \qquad (22)$$

[It is also possible to set up a Hartree-type calculation for $\psi_+(\vec{r})$]

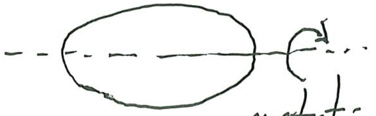
$$E_+ = \iint \psi_+^*(\vec{r}_1)\,\psi_+^*(\vec{r}_2)\,\hat{H}^{(H_2)}_{\text{electronic}}\,\psi_+(\vec{r}_1)\,\psi_+(\vec{r}_2)\,d^3r_1\,d^3r_2$$



$$\underbrace{\text{Bonding MO}}_{\psi_+ \text{ (last page)}} \sim \underset{\text{(left)}}{\psi_{1s}^{(A)}} + \underset{\text{(right)}}{\psi_{1s}^{(B)}}$$

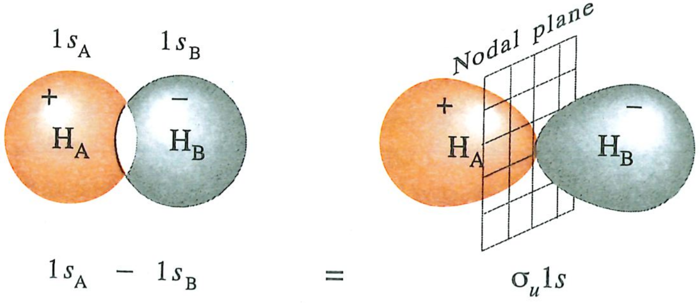


σ-bond



rotation
(nothing changed)

$$\text{Anti-Bonding MO} \sim \psi_{1s}^{(A)} - \psi_{1s}^{(B)}$$



Also σ-bond
(but anti-bonding, i.e. ss σ*)

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

Inspect spatial part of ground state wavefunction

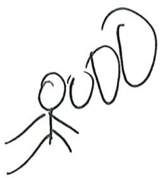
$$\psi_+(\vec{r}_1)\,\psi_+(\vec{r}_2) \propto \left[\phi_{L,1s}(\vec{r}_1)+\phi_{R,1s}(\vec{r}_1)\right]\overbrace{\left[\phi_{L,1s}(\vec{r}_2)+\phi_{R,1s}(\vec{r}_2)\right]}^{\text{LCAO-MO}}$$

Mulliken & Hund (MO Theory)

a combination of all possibilities

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

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



To do better...

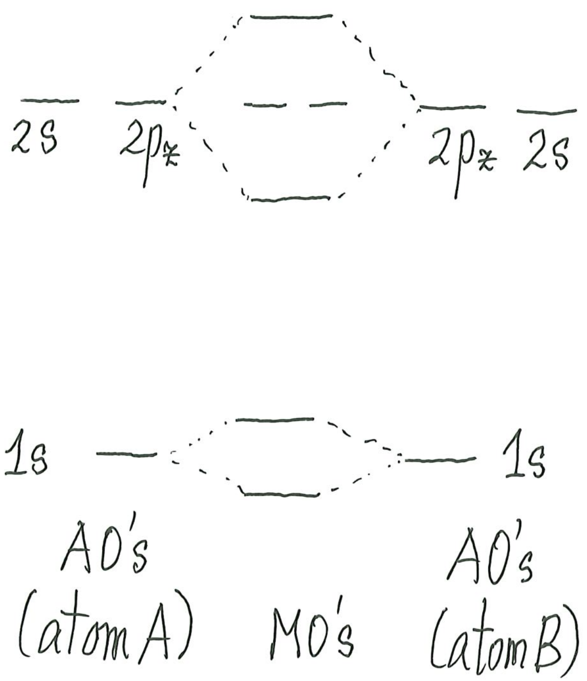
Including more atomic states from the two atoms [only 2 electrons in H_2]

e.g. $$\psi = C_1\left(\psi_{1s}^{(A)} + \psi_{1s}^{(B)}\right) + C_2\left(\psi_{2p_z}^{(A)} + \psi_{2p_z}^{(B)}\right) + C_3\left(\psi_{2s}^{(A)} + \psi_{2s}^{(B)}\right)$$

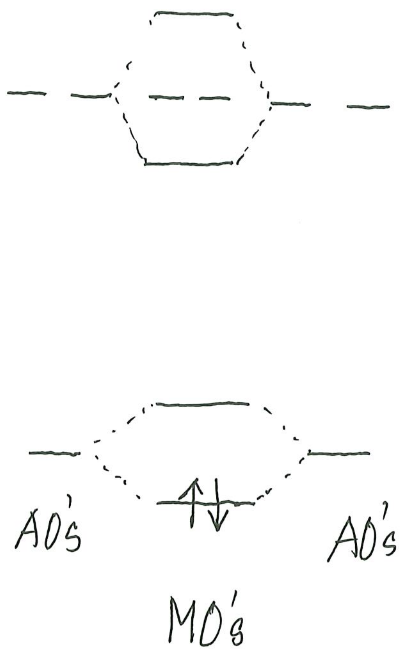
and do the (variational) calculation again. Why not?

$$\underbrace{\text{(6×6 matrix)}}_{\text{"6 in} \rightarrow \text{6 out"}}$$

Get MO's



Fill in 2 electrons



A balance between accuracy and computing workload
(need physical sense)

H_2 has a Single Bond. What does it mean?

Definition

$$\text{Number of Bonds (between 2 atoms)} = \text{Bond Order} = \frac{\left(\#\text{ electrons in Bonding MO's}\right) - \left(\#\text{ electrons in Anti-bonding MO's}\right)}{2}$$

H_2 Bond order $= \dfrac{2-0}{2} = 1$ $\underbrace{\text{“single bond”}}_{\text{a QM concept!}}$

How about H_2^+? Bond order $= \dfrac{1-0}{2} = 1/2$ half-a-bond

$$\left.\begin{array}{l}\text{“Double Bond”: Bond order} = 2\\ \text{“Triplet Bond”: Bond order} = 3\end{array}\right\rangle \text{Need to involve } p \text{ AO's and } \underbrace{\pi \text{ bonds}}_{\text{“non } \sigma\text{- bond”}}$$

(b) pp σ (bonding & Antibonding) and pp π (bonding & Antibonding)

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

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

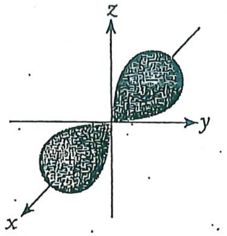
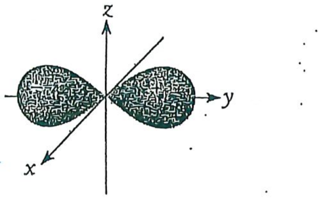
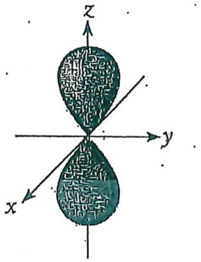
p orbitals $\Rightarrow \underbrace{l=1}$

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

$\leftarrow p_z$

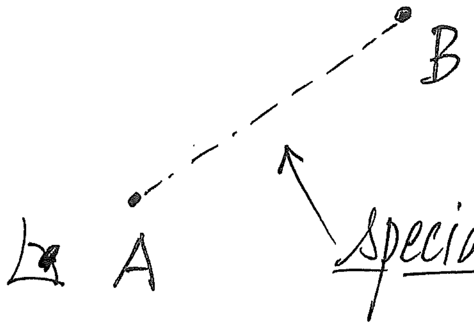
[$\because$ $r\cos\theta = z$ in spherical coordinates]

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

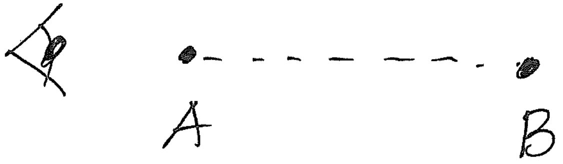
	n	l	m_l	
p_x	2,3,4, ...	1	±1	
p_y	2,3,4, ...	1	±1	
p_z	2,3,4, ...	1	0	

But for one lonely atom, there is NO SENSE about what x, y, z directions are!

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

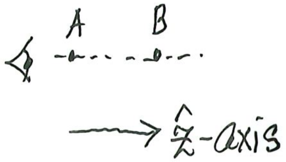


<u>special</u> direction (may call it x, or y, or z)

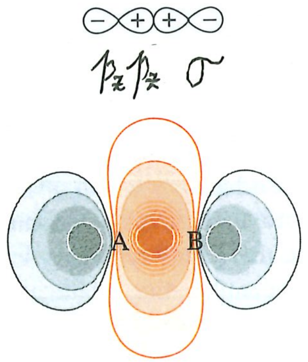


- σ and π bonds[†] are defined w.r.t. rotation about the axis connecting the two nuclei
- σ bond : symmetric w.r.t. rotation about axis
- π bond : Not so

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

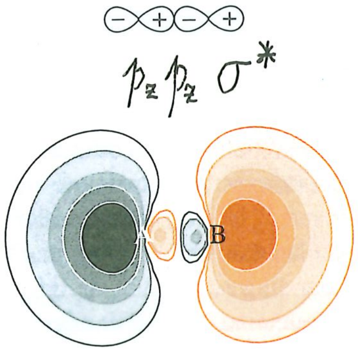


pp σ



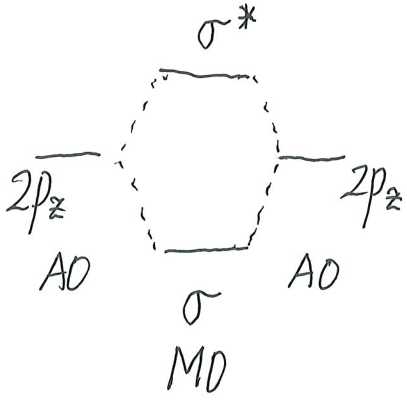
$p_z p_z\ \sigma$

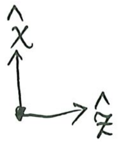
bonding



$p_z p_z\ \sigma^*$

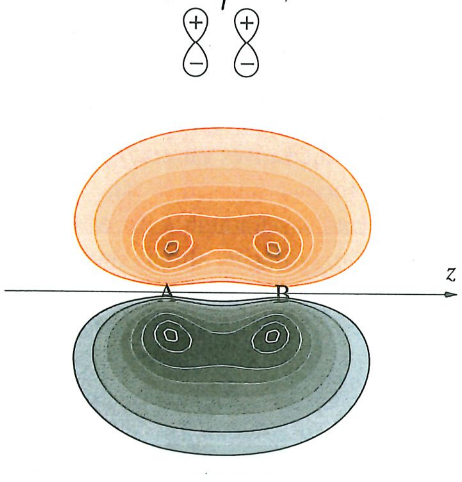
Anti-bonding





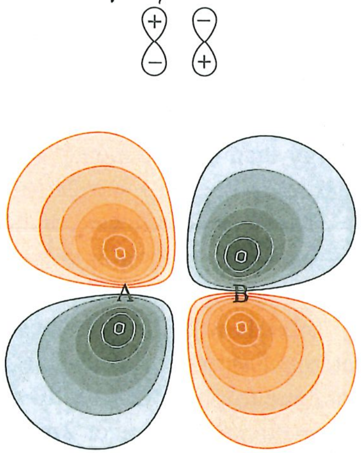
pp π

$p_x\ p_x\ \pi$

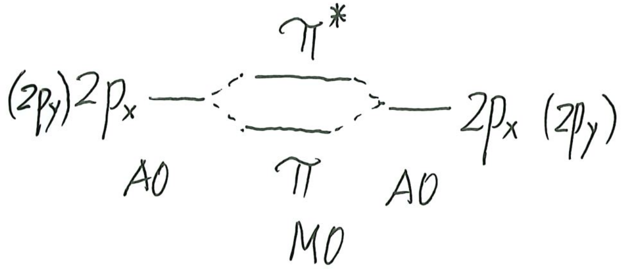


bonding

$p_x\ p_x\ \pi^*$

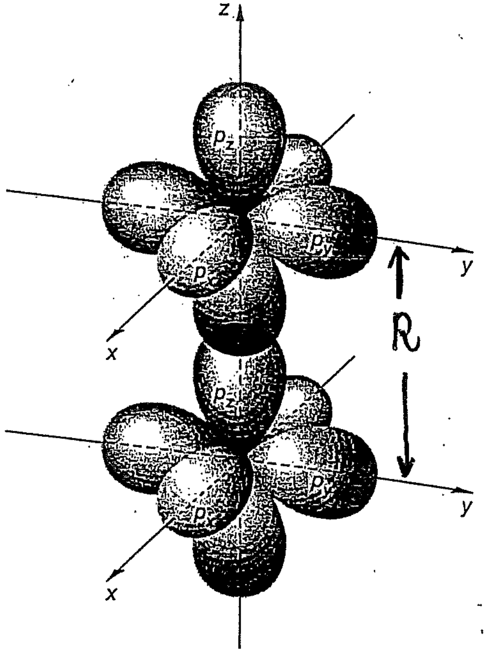


anti-bonding



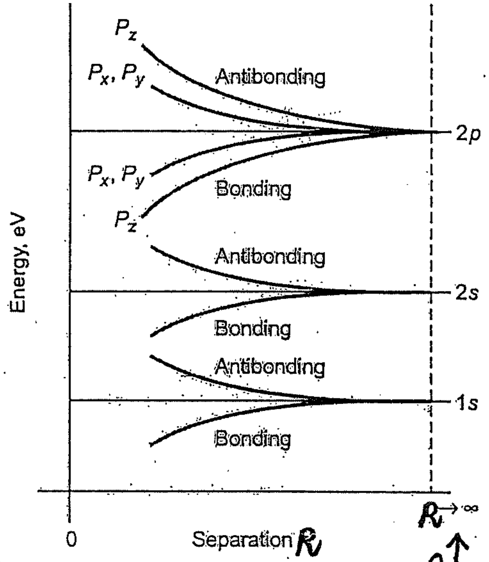
(Same for $p_y p_y \pi$)

- 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

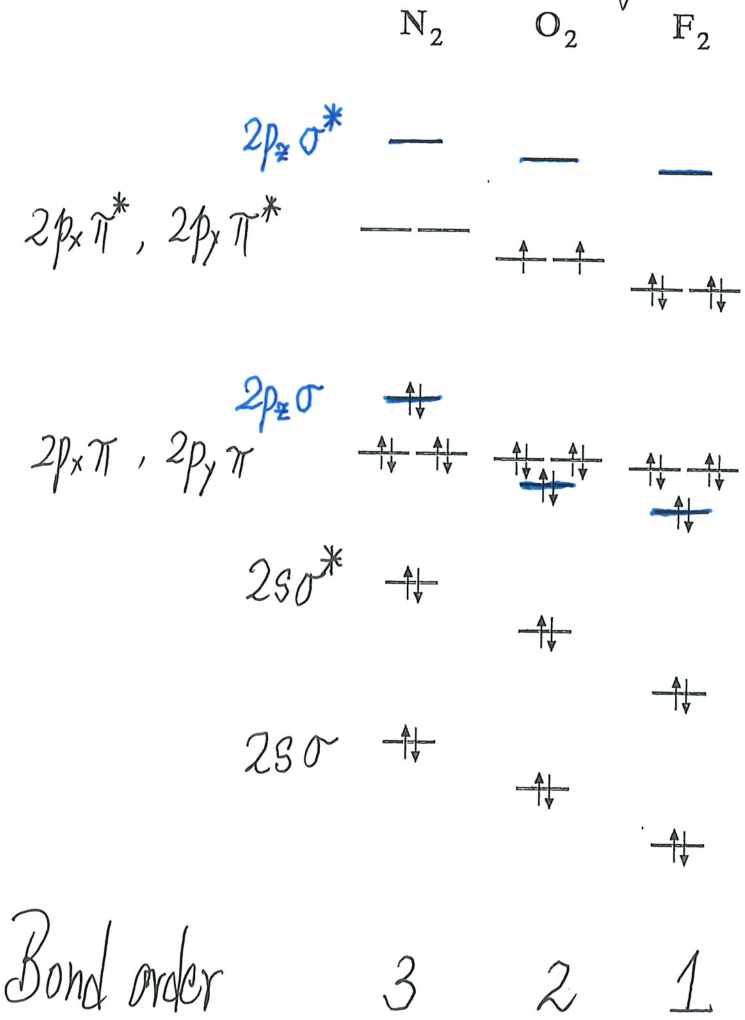
← From overlap of 1s orbitals (as discussed in H_2^+)

↑ far away

↑ Fill electrons into molecular orbitals according to the Pauli exclusion principle and Hund's rules

Can be used to consider existence and bonding in N_2, O_2, F_2

Each case is defined by $\underbrace{\text{its own Hamiltonian}}_{\text{different QM problems}}$



Fill electrons in: Pauli Principle + Hund's rules

Molecular Orbital Theory predicts O_2 is paramagnetic [Correct experimentally!]

Final Remark

- Does He_2 exist?

[MO Theory predicts zero bond order, thus predicts no He_2]

The weakest bond: Experimental observation of helium dimer

Fei Luo, George C. McBane, Geunsik Kim, Clayton F. Giese, and W. Ronald Gentry
Chemical Dynamics Laboratory, University of Minnesota, 207 Pleasant Street SE, Minneapolis, Minnesota 55455

(Received 9 November 1992; accepted 11 December 1992)

Helium dimer ion was observed after electron impact ionization of a supersonic expansion of helium with translational temperature near 1 mK. The dependence of the ion signal on source pressure, distance from the source, and electron kinetic energy was measured. The signal was determined to arise from ionization of neutral helium dimer.

Journal of Chemical Physics <u>98</u>, 3564 (1993)

Loosely binded He_2 } Binding energy ~ 0.01 $J \cdot mol^{-1}$
~ 1 mK ~ 8.6×10^{-8} eV [weak!]

Bond Length ~ 6000 pm ~ 6 nm ~ $\underbrace{60\,\text{Å}}_{\text{very long}}$

VOLUME 85, NUMBER 11, p.2284 PHYSICAL REVIEW LETTERS 11 SEPTEMBER 2000

Determination of the Bond Length and Binding Energy of the Helium Dimer by Diffraction from a Transmission Grating

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Max-Planck-Institut für Strömungsforschung, Bunsenstraße 10, 37073 Göttingen, Germany

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(Received 5 June 2000)

A molecular beam consisting of small helium clusters is diffracted from a 100 nm period transmission grating. The relative dimer intensities have been measured out to the 7th order and are used to determine the reduction of the effective slit width resulting from the finite size of the dimer. From a theoretical analysis of the data which also takes into account the van der Waals interaction with the grating bars, the bond length (mean internuclear distance) and the binding energy are found to be $\langle r \rangle = 52 \pm 4$ Å and $|E_b| = 1.1 + 0.3/ - 0.2$ mK.

Binding energy ~ 1.1 mK ~ 9.48×10^{-8} eV , Bond length ~ $\underbrace{52\,\text{Å}}_{\text{very long distance between the helium atoms}}$

- Believe what QM says
- Be cautious with approximations

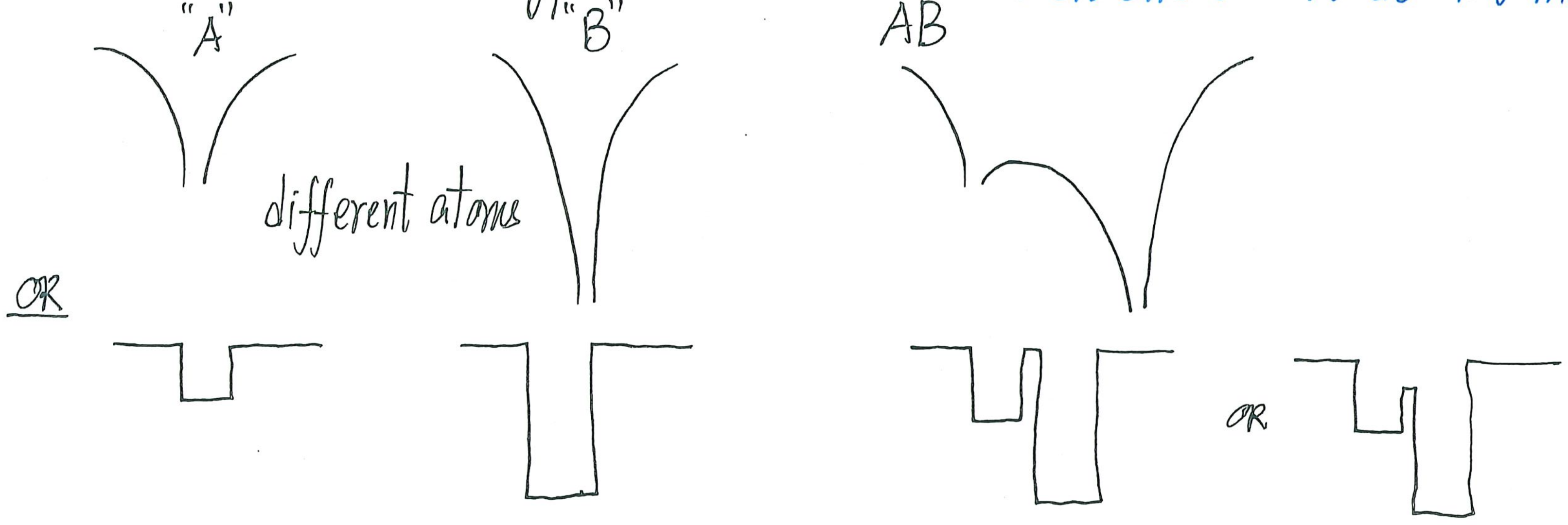
[but MO theory works very well, He_2 is so weakly binded]

(c) sp σ-bond (e.g. HF)

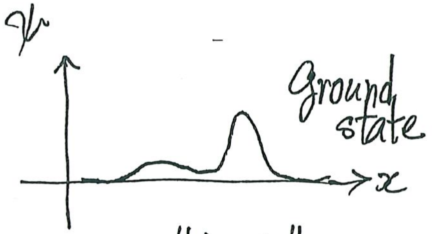
F $1s^2\ 2s^2\ 2p^5$

[$\underbrace{\text{one 2p AO has 1 electron}}_{\text{which one? it doesn't matter}}$, others (1s, 2s, 2p) are full]

HF is the type "AB"



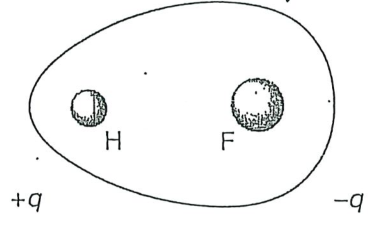
Rough analogy:



"ionic"

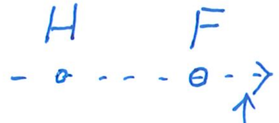
electron tends to be found on one side (high. prob)

HF sp σ-bond



A polar covalent bond.

"HF" : Think like an applied physicist



call this z-direction

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

Background "Variational Method"

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

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

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

-

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

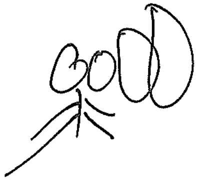
∴ Put $H_{11} = \varepsilon_{1s}^{(H)}$; $H_{22} = \varepsilon_{2p}^{(F)}$

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

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

$S_{\underbrace{12}}$ and $S_{\underbrace{21}}$? Overlap of atomic states from <u>different</u> <u>atom</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 $H_{12}=\Delta$, $H_{21}=\Delta^{*}$

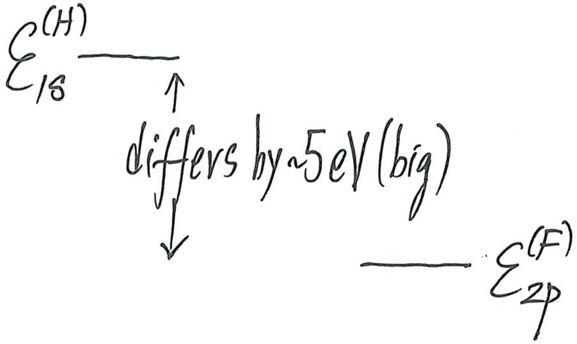
Done!

$$\begin{pmatrix} \varepsilon_{1s}^{(H)}-E & \Delta \\ \Delta^{*} & \varepsilon_{2p}^{(F)}-E \end{pmatrix}\begin{pmatrix} C_1 \\ C_2 \end{pmatrix}=0 \qquad (23)$$

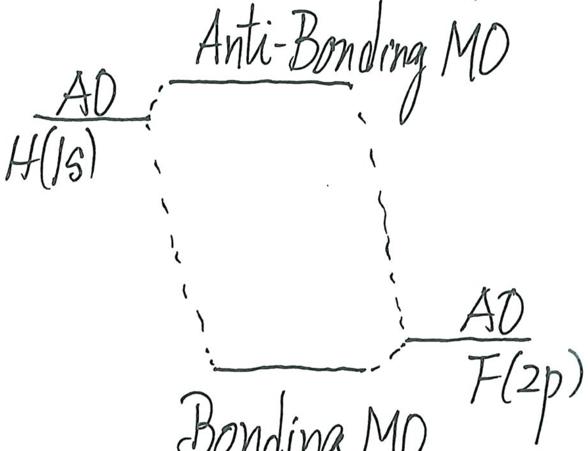
Non-Trivial Solutions

$$\begin{vmatrix} \varepsilon_{1s}^{(H)} - E & \Delta \\ \Delta^* & \varepsilon_{2p}^{(F)} - E \end{vmatrix} = 0 \qquad (2\times 2 \text{ math})$$

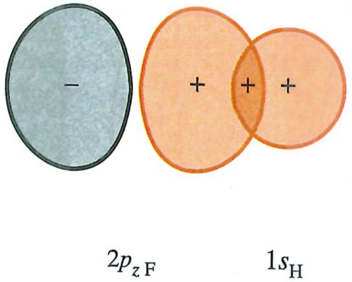
- $\varepsilon_{1s}^{(H)}$ [−13.6 eV] much higher energy than $\varepsilon_{2p}^{(F)}$



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

- 

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



- Fill 2 electrons into MO's

Bonding MO

Strong ionic character

ψ_{bonding} ? Bonding MO closer in energy to F(2p) AO

$$\therefore \psi_{\text{bonding}} = \underbrace{C_F}_{\uparrow\ \text{big}} \phi_{2p}^{(F)} + \underbrace{C_H}_{\uparrow\ \text{small}} \phi_{1s}^{(H)} \qquad \text{(2x2 matrix math)}$$

$$\underbrace{\text{has much character of } \phi_{2p}^{(F)} \text{ and a little bit of } \phi_{1s}^{(H)}}$$

$$\therefore \underbrace{|\psi_{\text{bonding}}|^2 \text{ bias the Florine side}}_{\text{like } F^-}$$

(ionic character)

This is deep physics without (much) Math!

Ex: Why don't we include 1s AO of Florine?

Why don't we include $2p_x$, $2p_y$ AO's of Florine?

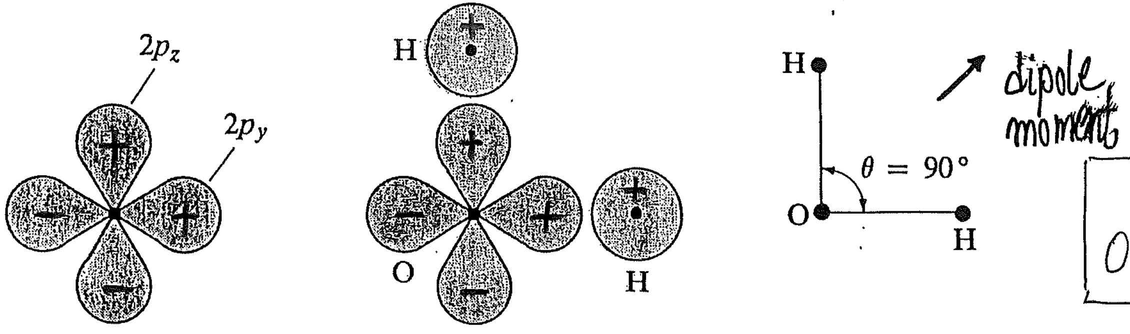
Nothing wrong about including them, but ...

(d) Water Molecule: H_2O

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

↑ ↑ for Bonding

Schematic



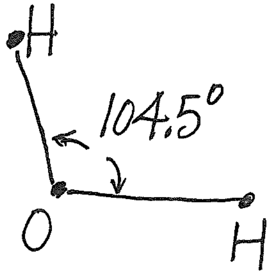
(a) (b) (c)

(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.)

LCAO

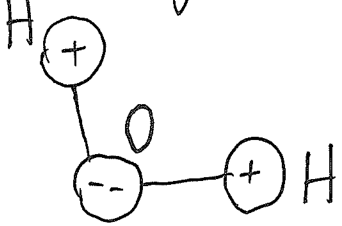
O: $2p_y$, $2p_z$, H1: 1s, H2: 1s

Actual



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

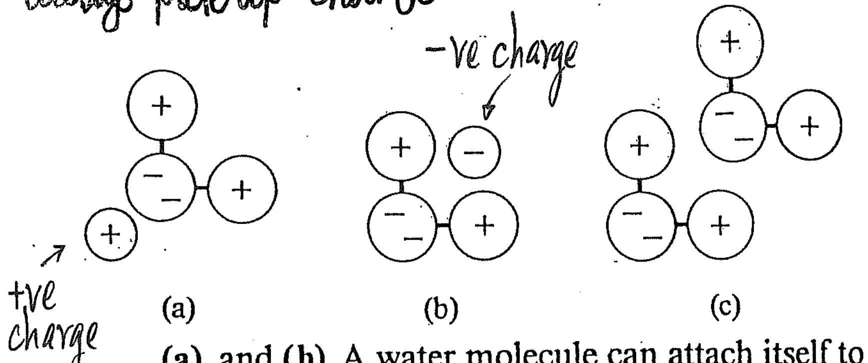
- Small −ve charge near O and small positive charge near the two H



⇒ electric dipole moment
and
a good solvent

Water molecule can easily pick up charges

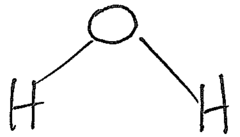
Properly aligned water molecules attract one another



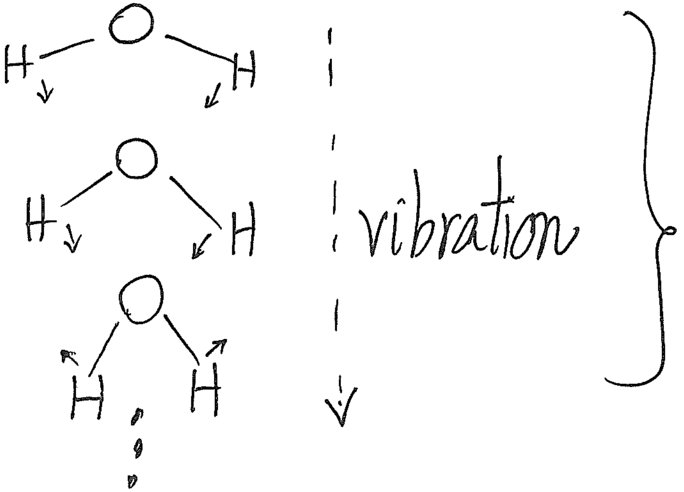
(a) and **(b)** A water molecule can attach itself to a positive OR negative charge. **(c)** Water molecules tend to align and attract one another.

[dipole-dipole]

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



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



$\Rightarrow$ $\boxed{\vec{\mu} \text{ changes as } H_2O \text{ molecule vibrates in bending mode}}$ $\Rightarrow$ Absorb EM waves at frequency of this mode [greenhouse gas]