E. Electronic Part $\hat{H}_{el}\psi_{el} = E_{el}\psi_{el}$: LCAO-MO ("Step 1")

- Bad news! Even H_2 is hard to do! The H_2 problem is:

$$\left[\underbrace{-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2}_{\text{k.e. of electrons}} \underbrace{- \frac{e^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{R}_A|} - \frac{e^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{R}_B|}}_{\text{electron 1 sees nuclei}} \underbrace{- \frac{e^2}{4\pi\varepsilon_0|\vec{r}_2-\vec{R}_A|} - \frac{e^2}{4\pi\varepsilon_0|\vec{r}_2-\vec{R}_B|}}_{\text{electron 2 sees nuclei}}\right.$$

$$\left. \underbrace{+\frac{e^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|}}_{\text{electrons see each other}} + \underbrace{\frac{e^2}{4\pi\varepsilon_0 R}}_{\substack{\text{nuclei repulsion} \\ \text{[a constant]}}} \right] \psi_{el}(\vec{r}_1, \vec{r}_2; R) = E_{el}(R)\,\psi_{el}(\vec{r}_1, \vec{r}_2; R)$$

(R: [just a parameter])

- One two-electron problem for each R
- No analytic solution
- Approximate by single-electron problem + Anti-symmetric Wavefunction (Pauli Principle)

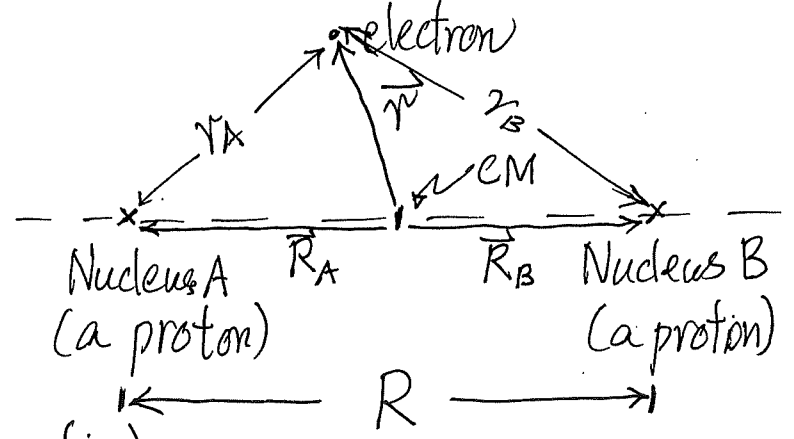
- H_2 is hard! Let's take a step backward.
- H_2^+ molecular ion [2 nuclei + 1 electron]

how one electron can possibly distribute itself (wavefunction) to bind two protons?

- What is bonding molecular orbital?
  What is anti-bonding molecular orbital?
- What is covalent bond?

H_2^+ Molecular ion: Simplest problem for learning physics of bonding

- 1 electron + two nuclei (protons)



$$\hat{H}^{(H_2^+)}_{electronic} = \frac{-\hbar^2}{2m}\nabla_{\vec{r}}^2 \underbrace{- \frac{e^2}{4\pi\varepsilon_0 |\vec{r}-\vec{R}_A|}}_{\frac{-e^2}{4\pi\varepsilon_0 r_A}} \underbrace{- \frac{e^2}{4\pi\varepsilon_0 |\vec{r}-\vec{R}_B|}}_{\frac{-e^2}{4\pi\varepsilon_0 r_B}} + \frac{e^2}{4\pi\varepsilon_0 R} \quad \text{(see fig.)} \quad (12)$$

$\leftarrow$ just a constant

$\hat{H}_{electronic}$ depends on $\vec{r}$ and $\vec{R}$: $V(\vec{r};\vec{R})$ ← Given R, there is a $V(\vec{r})$

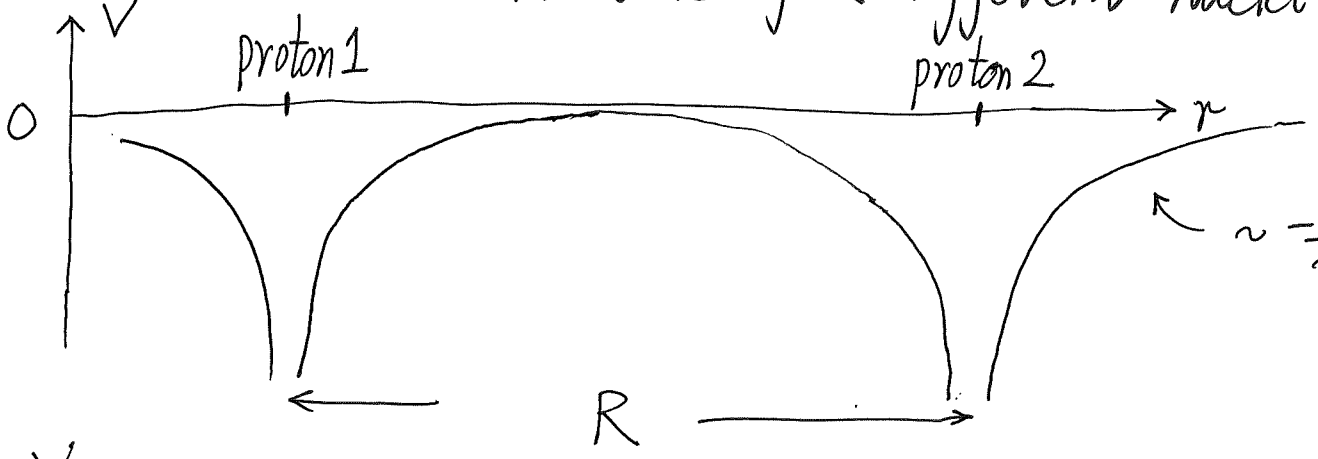
$$\Rightarrow \boxed{\hat{H}_{electronic} = \frac{-\hbar^2}{2m}\nabla_{\vec{r}}^2 + V(\vec{r}) + \frac{e^2}{4\pi\varepsilon_0 R}} \quad (13) \quad \text{(an "easier" 1-electron problem)}$$

Solve $\hat{H}_{el}\,\psi_{el}(\vec{r}) = E_{el}\,\psi_{el}(\vec{r})$ for given R (one problem for each R!)

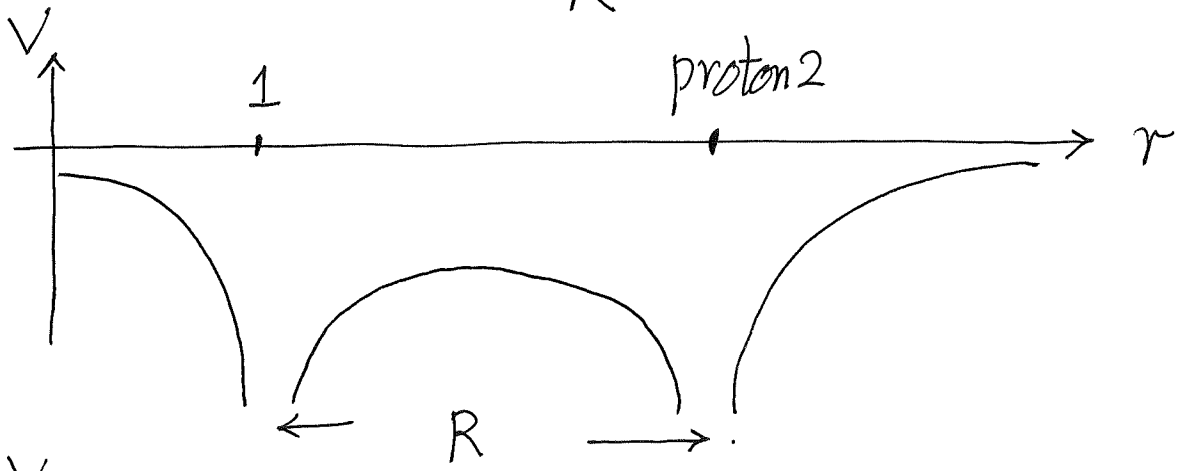
To stress that R gets into $V(\vec{r})$ and thus the solutions, can write

$$\boxed{\hat{H}_{el}\,\psi_R^{el}(\vec{r}) = E_{el}(R)\,\psi_R^{el}(\vec{r})} \quad (14) \qquad [E_{el}(R) \text{ gives bonding}]$$

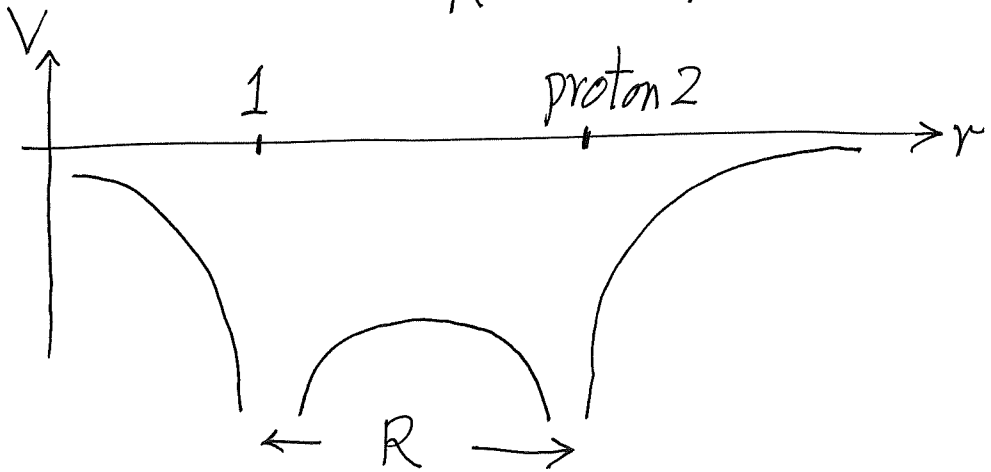
- How does $V(\vec{r})$ look like for different nuclei separations R?



$\sim -\frac{1}{r}$ from nucleus



This is what the electron sees in vicinity of two nuclei (protons)



- $V(\vec{r})$ goes into $\hat{H}_{electronic}$

- Wanted to solve $\left[\frac{-\hbar^2}{2m}\nabla_{\vec{r}}^2 - \frac{e^2}{4\pi\varepsilon_0 r_A} - \frac{e^2}{4\pi\varepsilon_0 r_B} + \frac{e^2}{4\pi\varepsilon_0 R}\right]\psi_R^{el}(\vec{r}) = E_{el}(R)\psi_R^{el}(\vec{r})$
  - $\frac{e^2}{4\pi\varepsilon_0 R}$ is just a constant for given R

$\therefore$ Solve $\left[\frac{-\hbar^2}{2m}\nabla_{\vec{r}}^2 - \frac{e^2}{4\pi\varepsilon_0 r_A} - \frac{e^2}{4\pi\varepsilon_0 r_B}\right]\psi_R^{el}(\vec{r}) = \mathcal{E}_{el}(R)\psi_R^{el}(\vec{r})$

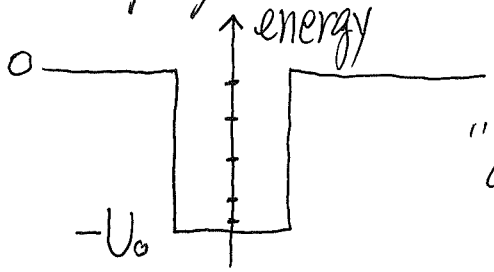
$\Rightarrow \left[\frac{-\hbar^2}{2m}\nabla_{\vec{r}}^2 + V(\vec{r})\right]\psi_R^{el}(\vec{r}) = \mathcal{E}_{el}(R)\psi_R^{el}(\vec{r})$

$\Rightarrow \boxed{\hat{\mathcal{H}}_{el}\,\psi_R^{el}(\vec{r}) = \mathcal{E}_{el}(R)\psi_R^{el}(\vec{r})}$ first (15)

then $E_{el}(R) = \mathcal{E}_{el}(R) + \frac{e^2}{4\pi\varepsilon_0 R}$ (16)

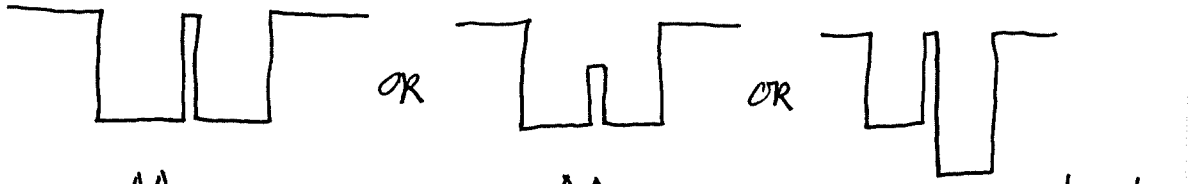
$\therefore$ Focus on solving Eq. (15)

- To help you think, recall "an atom" is like a 1D well



"an atom" with atomic states/orbitals

- Analogy: Molecule

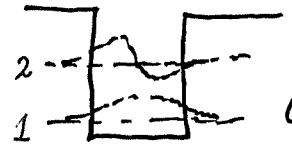


$\hat{\mathcal{H}}_{el}\psi_R^{el}(x) = \mathcal{E}_{el}(R)\psi_R^{el}(x)$

How to solve the problem?

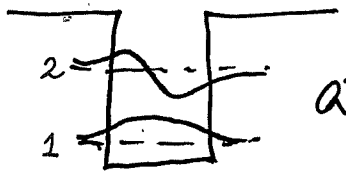
- Exactly (write down ψ and match B.C.'s), it works!

- How about expressing ψ_R^{el} as linear combination of states belonging to atom A and atom B? [Variational Method]



atomic orbitals

"Left atom"



atomic orbitals

"Right atom"

How about a variational method based on

$$\psi_{trial} = c_1\phi_{L,1} + c_2\phi_{R,1} + c_3\phi_{L,2} + c_4\phi_{R,2} \; ?$$

($\phi_{L,1}$, $\phi_{R,1}$, $\phi_{L,2}$, $\phi_{R,2}$: atomic orbitals)

Recall:

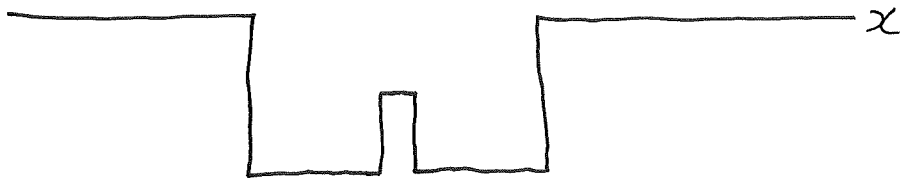
Schrödinger Eq. becomes

$$\left|\underbrace{\hat{H}_{ij} - ES_{ij}}_{(ij)^{th}\text{ element}}\right| = 0$$

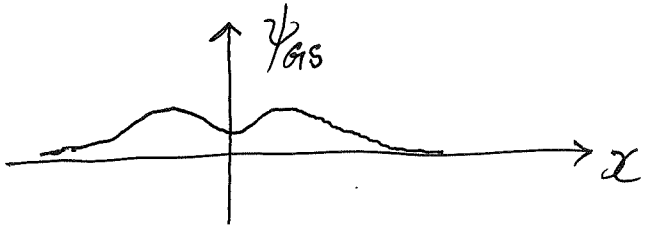
Linear Combination of Atomic Orbitals (LCAO)

- Physically transparent picture: How atomic orbitals combine into Molecular Orbitals
- How many AO's to use? The more the better? (True in principle) Guided by physics! (in practice)

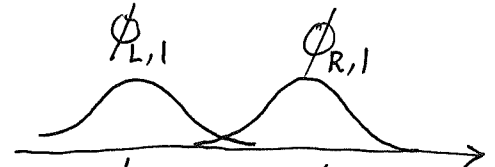
LCAO



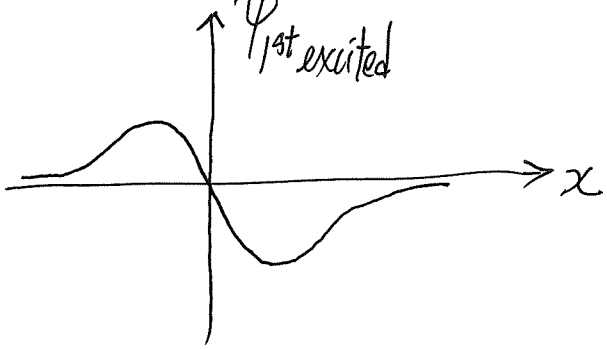
- Ground state wavefunction?



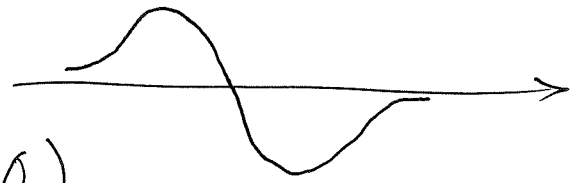
looks like $\sim \phi_{L,1} + \phi_{R,1}$



- First excited state wavefunction?



looks like $\sim \phi_{L,1} - \phi_{R,1}$



Note: V(x) is symmetric about center

$\Rightarrow$ Prob. ($\sim|\psi|^2$) should not bias one side (c.f. H_2^+, H_2, O_2)

LCAO makes Good Sense!

Back to H_2^+ (or H_2 after reducing to single-electron problem)

Left × Right ×

Left $(1s, 2s, 2p_x, 2p_y, 2p_z, 3s, 3p_x, 3p_y, 3p_z, \cdots)$ $\{\phi_{L,i}\}$

Right $(1s, 2s, 2p_x, 2p_y, 2p_z, 3s, 3p_x, 3p_y, 3p_z, \cdots)$ $\{\phi_{R,i}\}$

$$\hat{\mathcal{H}}_{el}\psi_{el}(\vec{r}) = \mathcal{E}_{el}(R)\,\psi_{el}(\vec{r}) \quad (15)$$

LCAO $\Rightarrow$ $\psi_{el}(\vec{r})$ formally can be expressed as

$$\psi_{electronic}^{(molecule)}(\vec{r}) = \sum_{\substack{\text{atomic states}\\ \text{of Left atom}}} C_{L,i}\,\phi_{L,i} + \sum_{\substack{\text{atomic states}\\ \text{of Right atom}}} C_{R,i}\,\phi_{R,i} \quad (17)$$

$C_{L,i}$ and $C_{R,i}$ are coefficients to be determined

- Often, a few atomic orbitals from each atom suffice
- Can be extended to Polyatomic Molecules readily

Ground state of H_2^+

Physical sense: Hard to imagine $\phi_{L,3d}$ and $\phi_{R,3d}$ would have much effect!

Most important: $\phi_{L,1s}$ and $\phi_{R,1s}$

[ϕ_{2s}, ϕ_{2p} are ~10eV up in AO's $\Rightarrow$ Not important† for H_2^+ Ground state]

$$\psi_{el,(GS)} = c_1 \phi_{L,1s} + c_2 \phi_{R,1s} \quad \text{(as simple}^{\ddagger}\text{ as that!)} \quad (18)$$

$\therefore$ Just a $|\text{"}2\times 2\text{"}| = 0$ problem

"Pushing up and Pushing down"

More, expect $|c_1|^2 = |c_2|^2$

(Why? Bias a side?)

---

† Think perturbation

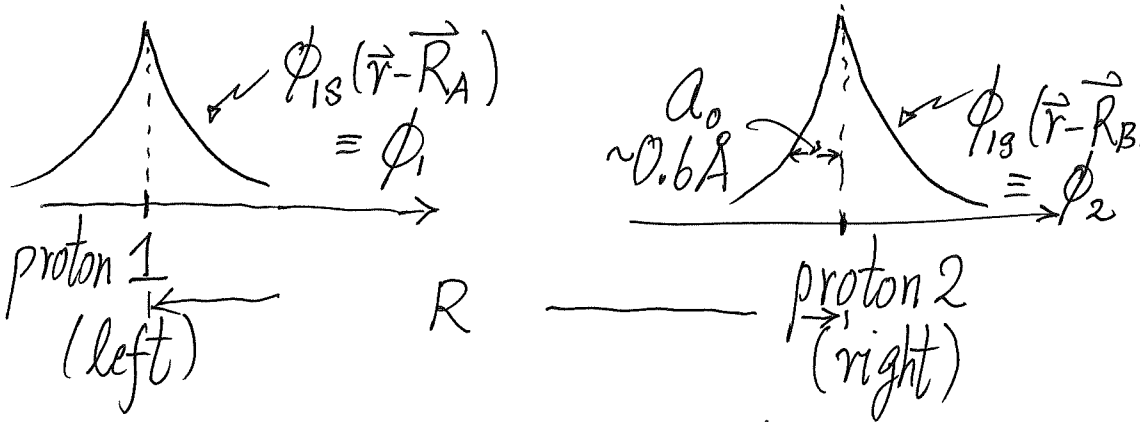
‡ Eq.(18) is an approximation, but a reasonable one.

LCAO for H_2^+ without Mathematics

- $\phi_{1s}(\vec{r}) = A e^{-r/a_0}$ [when nucleus is located at (0,0,0)] (atom)
- Nucleus at $\vec{R}_A$: $\phi_{1s}(\vec{r}-\vec{R}_A) = A e^{-|\vec{r}-\vec{R}_A|/a_0} \equiv \phi_1$ (for simplicity)

  Nucleus at $\vec{R}_B$: $\phi_{1s}(\vec{r}-\vec{R}_B) = A e^{-|\vec{r}-\vec{R}_B|/a_0} \equiv \phi_2$ (for simplicity)

  [they centered at different places]



For $R \gg a_0$ (100Å $\gg$ 0.6Å), $\hat{\mathcal{H}}_{el}\phi_1 = (-13.6\,eV)\phi_1$

$\hat{\mathcal{H}}_{el}\phi_2 = (-13.6\,eV)\phi_2$

Why? ϕ_1's tail is zero near proton 2, and vice versa

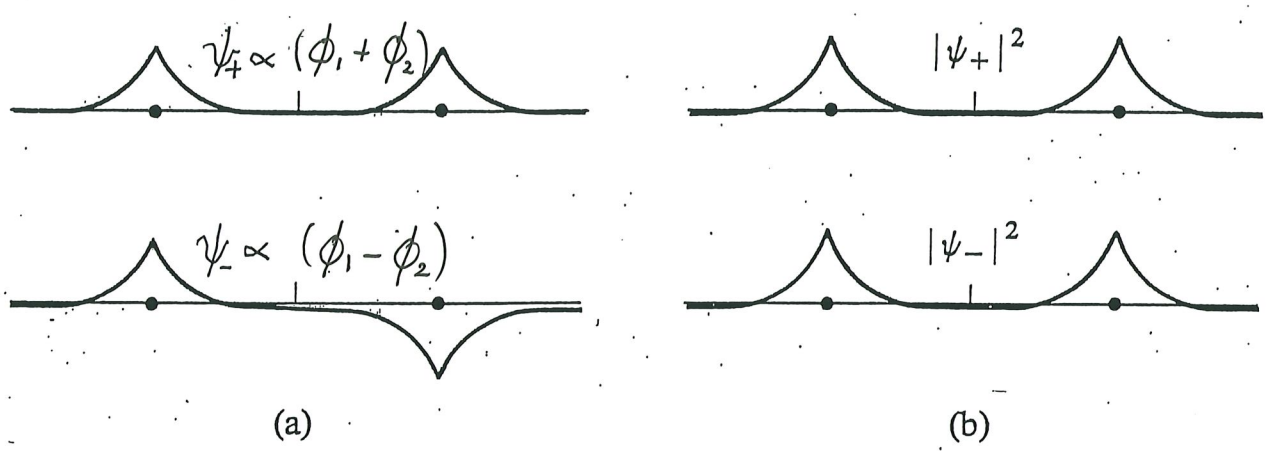
- For any separation R, $|\psi_{el}(\vec{r})|^2$ should be symmetric about mid-point between nuclei (nuclei are protons)

$$\psi_{el,+}(\vec{r}) = C_+(\underbrace{\phi_1}_{(L,1s)} + \underbrace{\phi_2}_{(R,1s)}) \; ; \quad \psi_{el,-}(\vec{r}) = C_-(\underbrace{\phi_1}_{(L,1s)} - \underbrace{\phi_2}_{(R,1s)}) \qquad (19)$$

Satisfy this requirement. They are LCAO's.

Large Separation R

$|\psi_+|^2$ and $|\psi_-|^2$ show little difference



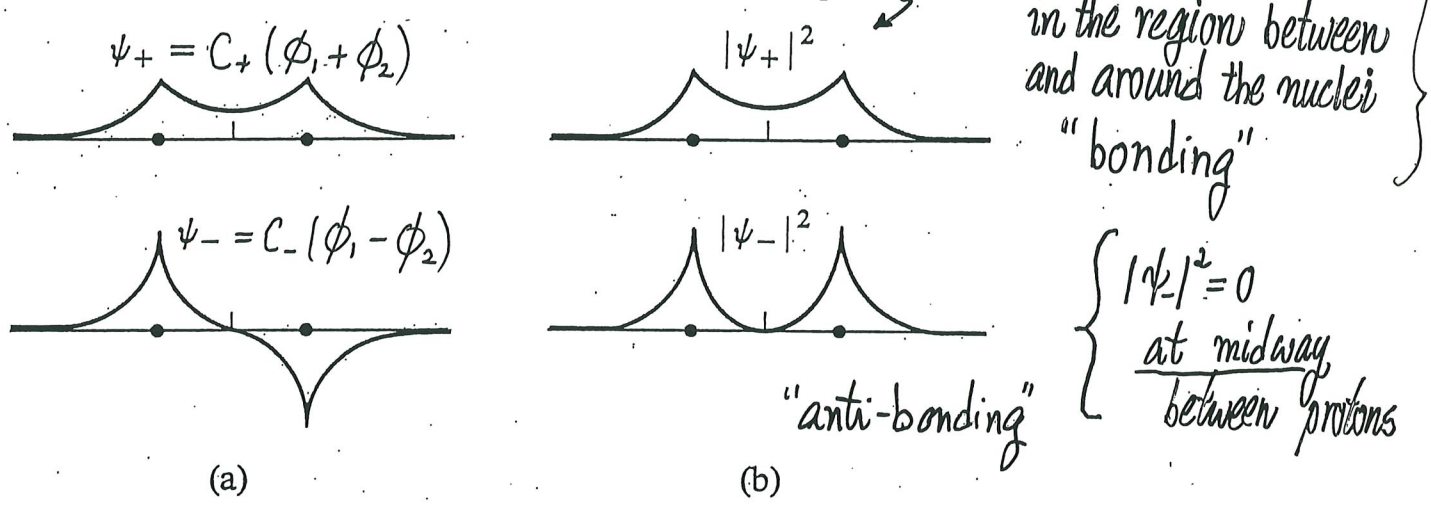
(a) The wave functions ψ_+ and ψ_- for the electron in H_2^+, when the two protons are far apart. The plots show values of $\psi_\pm$ along the internuclear axis. **(b)** Corresponding plots of the electron's probability density $|\psi_\pm|^2$ (which are identical as long as the protons are far apart).

When protons get closer : $R \sim 1\text{-}2$ Å

$\psi_{el} = c_1 \underset{(L,1s)}{\phi_1} + c_2 \underset{(R,1s)}{\phi_2}$ as trial wavefunction will give

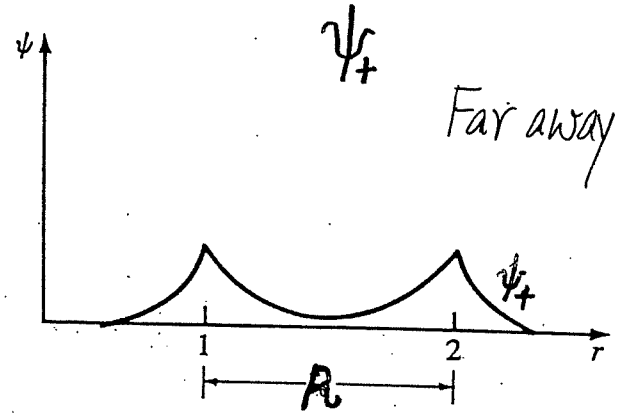
$\psi_{el,+}$ and $\psi_{el,-}$ as solutions [no choice due to $|\psi_{el}|^2$ symmetry]

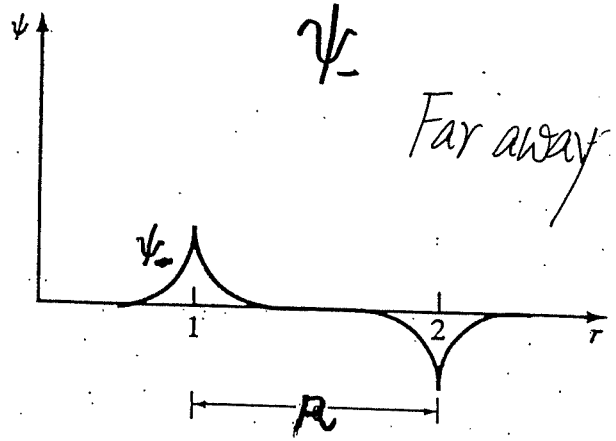
Small Separation R

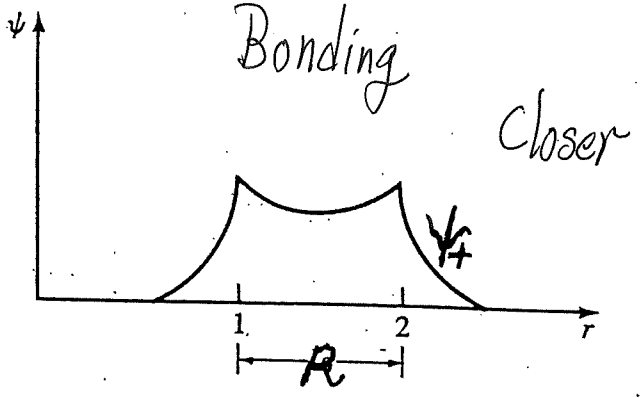


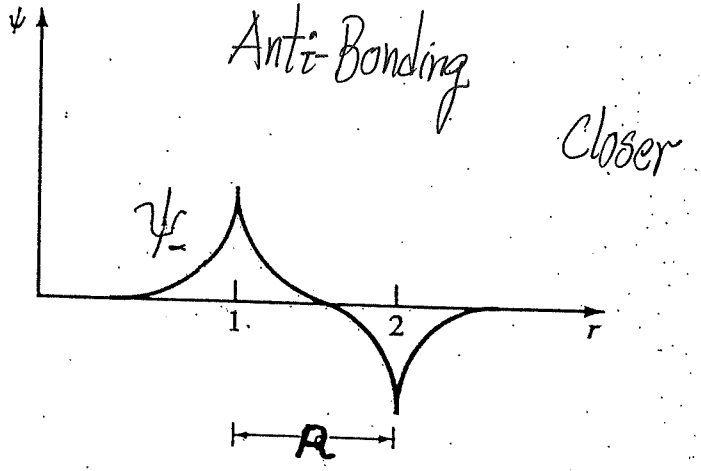
(a) Sketch of the wave functions ψ_+ and ψ_- for the electron in the H_2^+ molecule, once the distance R between the two protons is comparable to the size of an H atom. At the origin, ψ_+ is larger than either ψ_1 or ψ_2, whereas ψ_- is exactly zero. (The factors C_+ and C_- are normalization constants; C_- is a little larger than C_+ and this is why the peaks of ψ_- are a little taller than those of ψ_+.) **(b)** The corresponding probability densities.

LCAO $\psi_{\pm} \propto \phi_{L,1S} \pm \phi_{R,1S}$ for H_2^+ ion







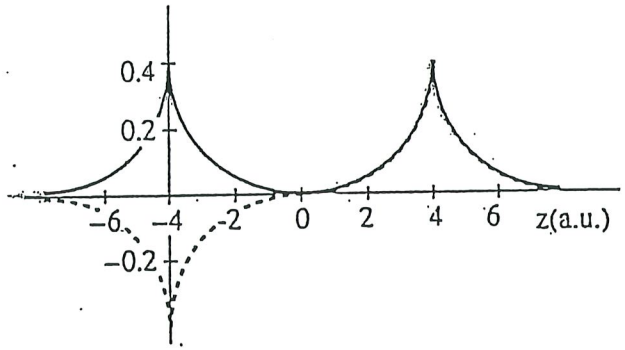


One can solve $\hat{\mathcal{H}}_{el}\,\psi_{el}(\vec{r}) = \mathcal{E}_{el}(R)\,\psi_{el}(\vec{r})$ numerically (exactly)

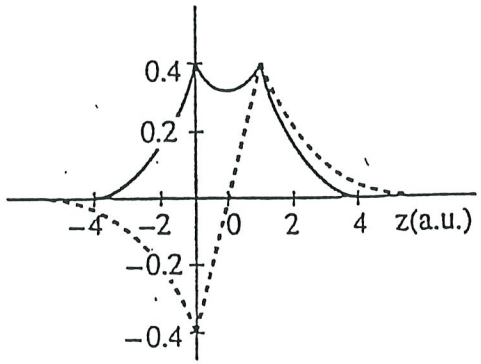
Compare with Exact Solution [J.C. Slater, "Quantum Theory of Matter"]

(3 separations)

(a)

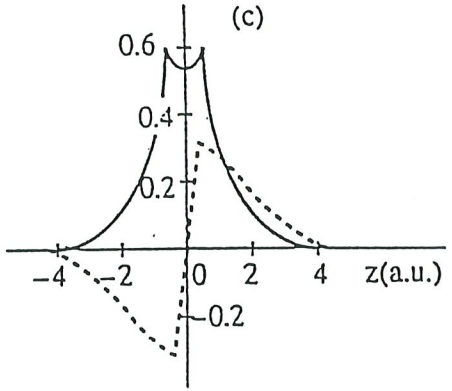


(b)



(b)

(c)



(c)

$\therefore$ LCAO makes good physical sense AND Works!

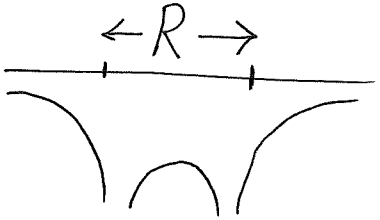
$\psi_{\pm}$: good agreement with exact solution

- To see bonding (or why the name anti-bonding), need the energies $\mathcal{E}_+(R)$ [for ψ_+] and $\mathcal{E}_-(R)$ [for ψ_-]

Two Ways (Same results [of course])

(i) $$\begin{vmatrix} \mathcal{H}_{11} - \mathcal{E}S_{11} & \mathcal{H}_{12} - \mathcal{E}S_{12} \\ \mathcal{H}_{21} - \mathcal{E}S_{21} & \mathcal{H}_{22} - \mathcal{E}S_{22} \end{vmatrix} = 0$$

$$\hat{\mathcal{H}} = \frac{-\hbar^2}{2m}\nabla_{\vec{r}}^2 + \underbrace{V(\vec{r})}$$



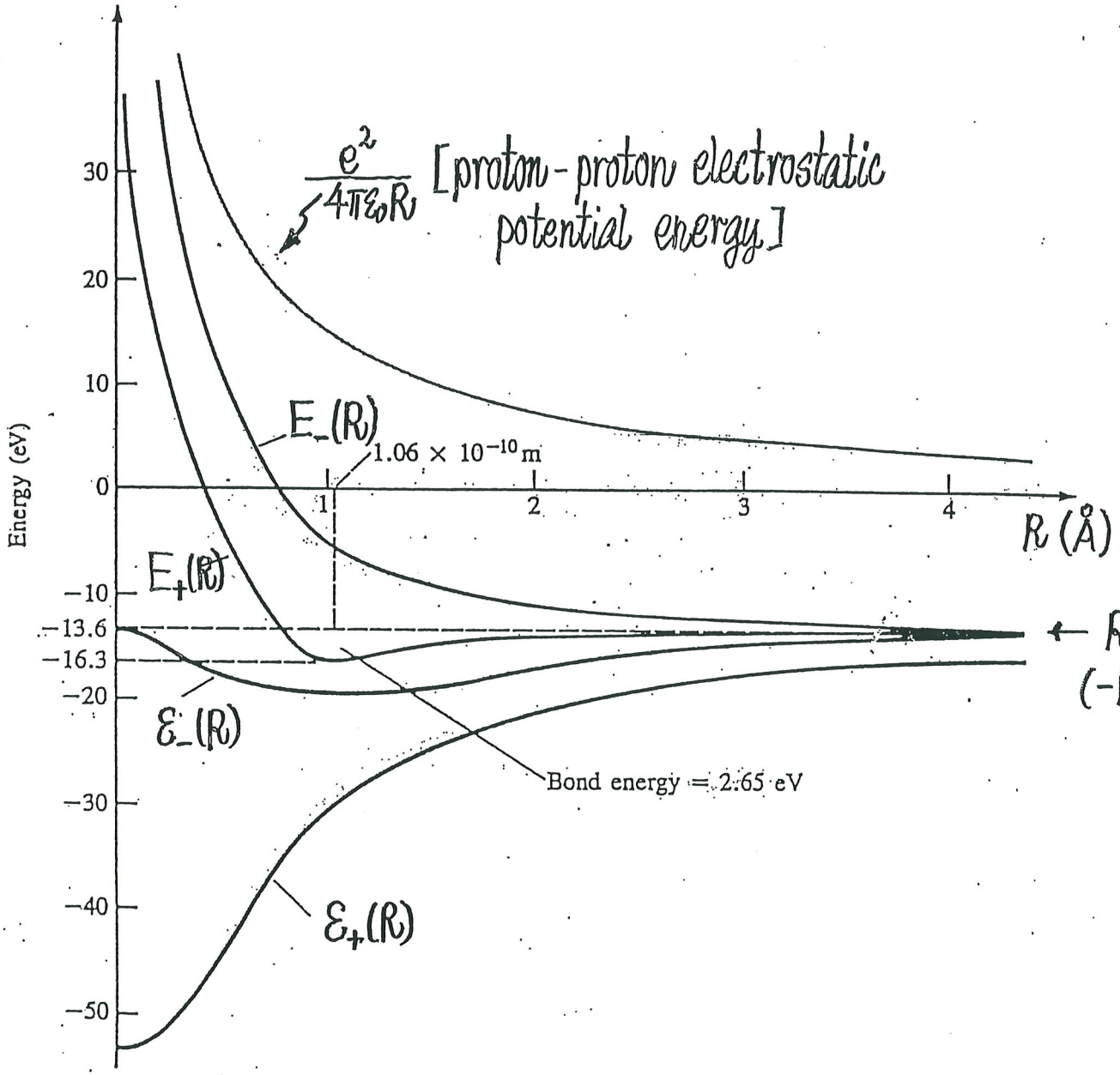
$\Rightarrow$ Two values of $\mathcal{E}$ corresponding to $\mathcal{E}_+(R)$ and $\mathcal{E}_-(R)$

(ii) Expectation Value of $\hat{\mathcal{H}}$ w.r.t. ψ_+ and ψ_-

$$\mathcal{E}_{\pm}(R) = \int \psi_{\pm}^{*}(\vec{r})\, \hat{\mathcal{H}}\, \psi_{\pm}(\vec{r})\, d^3r$$

assumed normalized

$E_+(R) = \mathcal{E}_+(R) + \frac{e^2}{4\pi\varepsilon_0 R}$ and $E_-(R) = \mathcal{E}_-(R) + \frac{e^2}{4\pi\varepsilon_0 R}$ (Eq. (14)) for H_2^+ ion



← $R \to \infty$ (−13.6 eV)

$E_+(R)$ is the energy in

$\hat{H}_{el}\,\psi_+(\vec{r}) = E_{el(+)}(R)\,\psi_+(\vec{r})$

[electronic part]

for $\psi_+ = C_+[\phi_{L,1S} + \phi_{R,1S}]$

Minimum at

$R_0 = 1.06 \times 10^{-10}$ m

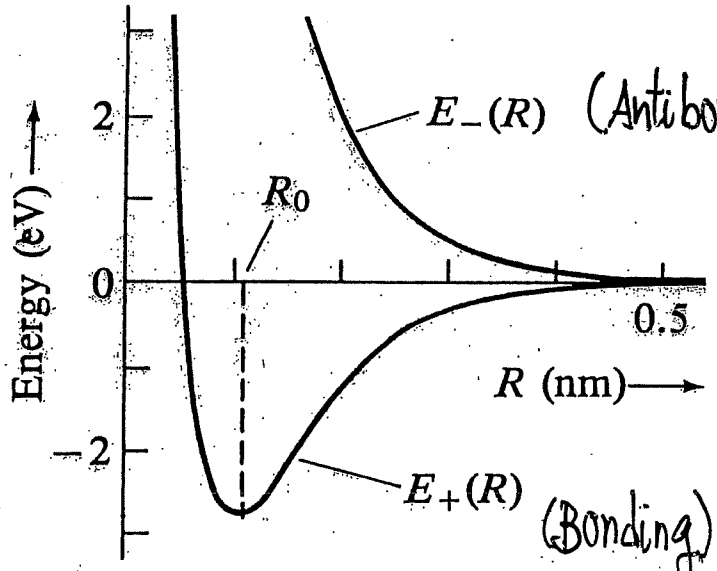
$= 1.06$ Å

$\mathcal{B} = 2.65$ eV

[relative to well separated nuclei]

Summary

$$\hat{H}_{el}\,\psi_{\pm}(\vec{r}) = E_{\pm}(R)\,\psi_{\pm}(\vec{r})$$



The energy of the H_2^+ molecule as a function of the distance R between the two protons. The curve $E_+(R)$ is the energy of the "bonding state" ψ_+; and $E_-(R)$ is that of the "antibonding state" ψ_-.

R_0 = equilibrium separation $\cong$ 0.11 nm (bond length)

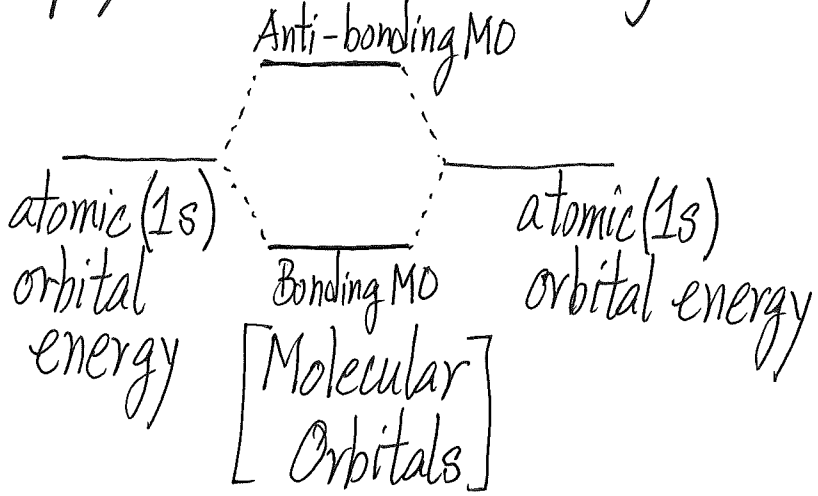
B = binding energy = 2.65 eV

← Note: we shifted the energy axis so that $E(R\to\infty)=0$

- Note that $E_-(R)$ is always ABOVE energy of well separated nuclei
- It does <u>not</u> encourage bonding (in H_2^+ ion)
- So the name "<u>anti-bonding</u>"
- the name carries over to cases beyond H_2^+ ion and H_2 molecule

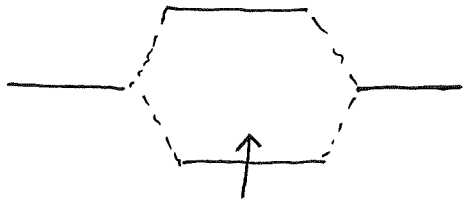
$\psi_+(\vec{r})$ for $R=R_0$ is a <u>Bonding Molecular Orbital</u>

This is the physics behind the following picture in chemistry books



- Electron(s) fills (fill) into MO's according to Pauli Exclusion Principle

H_2^+ ion



∴ H_2^+ can be formed

true! An exp'tal fact

↓ ↑ gain energy compared with

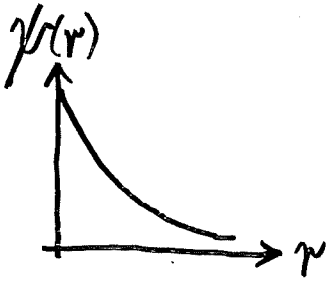
H + p

neutral atom a proton far away

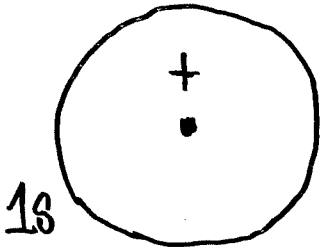
≈ -13.6 eV

Other Pictorial Representations and Notations

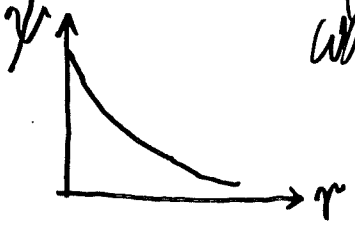
Recall 1s state: $\psi(r,\theta,\phi) \sim e^{-r/a_B}$ — no θ,ϕ dependence (ψ is spherically symmetric)



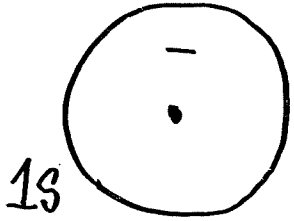
Since it is spherically symmetric, we can represent it as:

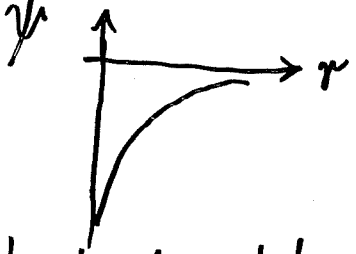


sign "+" ⇒ sign of wavefunction



Atomic 1s states

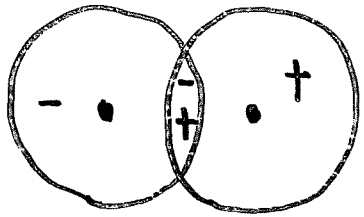


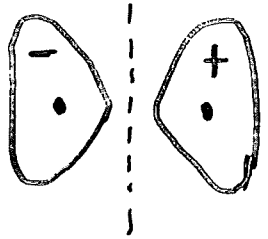


Atomic 1s states

[No problem with negative ψ as it is $|\psi|^2$ that matters]

$\psi_- \propto \phi_1 - \phi_2$ Anti-bonding

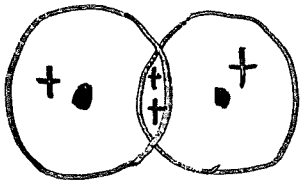




$\sigma^* 1s$

"*" - anti-bonding

$\psi_+ \propto \phi_1 + \phi_2$ Bonding



$\sigma 1s$

In terms of Atomic 1s states

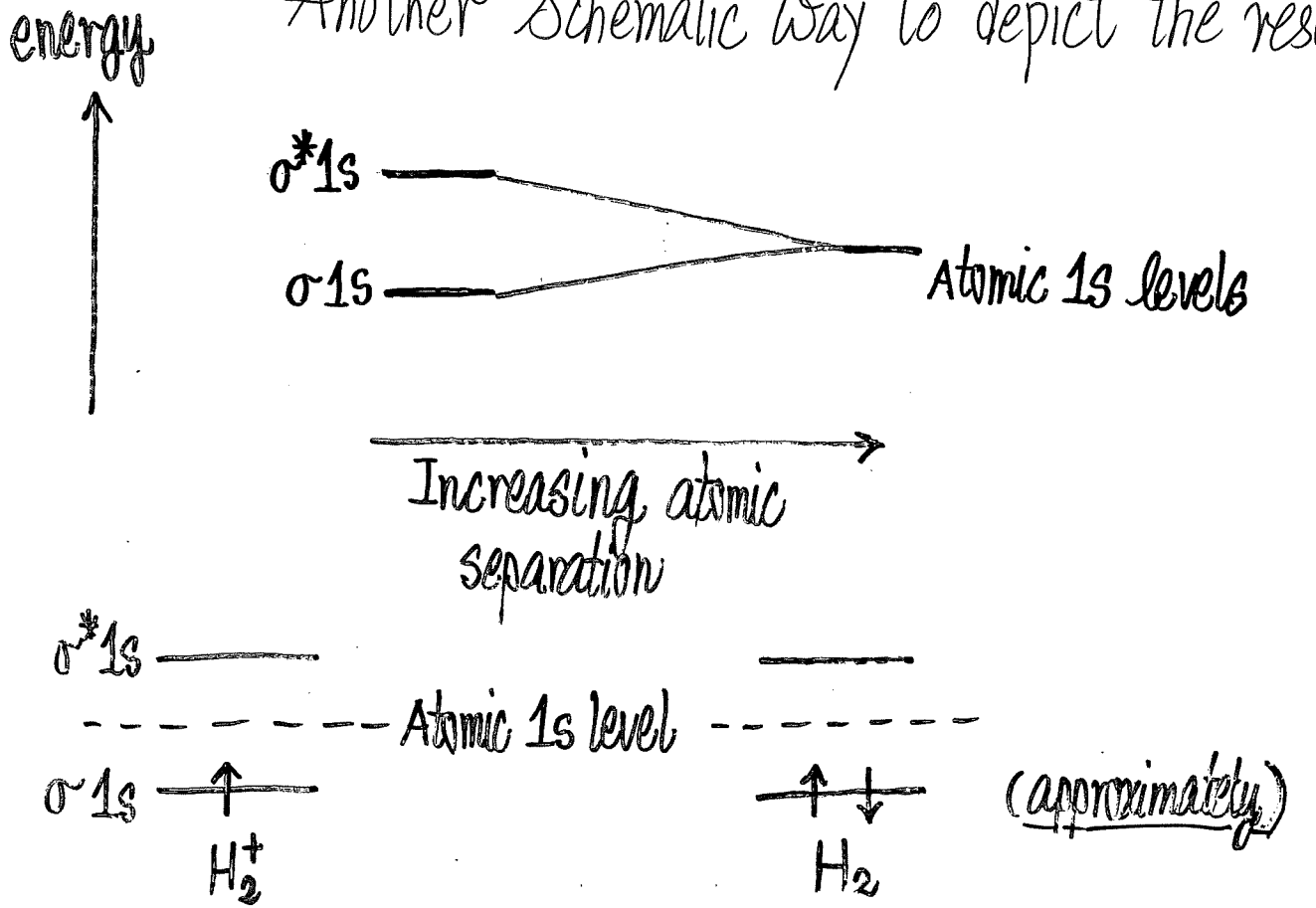
Molecular states

Notation

σ-bond?

- a bond connects two nuclei ⇒ <u>an axis</u> joining two nuclei
- electron density is <u>symmetric on rotation</u> about axis joining two nuclei
- If not so, π-bond

Another Schematic way to depict the result



H_2^+ exist

H_2 exist

Appreciation: Bonding is a Quantum effect and it can only be understood by Quantum Mechanics!

Points for Extension / Discussion

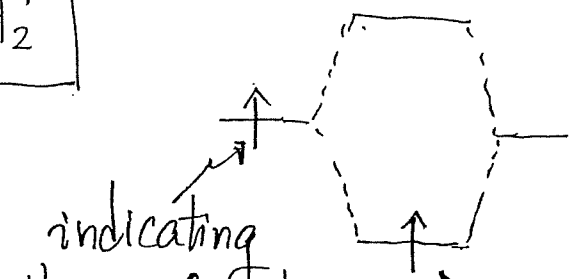
- Why do $[\psi_{L,1S}(\vec{r}) \pm \psi_{R,1S}(\vec{r})]$ work so well?
- What if we start with $\psi_{el} = C_{L,1S}\phi_{L,1S} + C_{R,1S}\phi_{R,1S} + C_{L,2S}\phi_{L,2S} + C_{R,2S}\phi_{R,2S}$?

$|4\times4| = 0$ Get four Molecular Orbitals (see fig. next page)

- # AO's in LCAO $\Rightarrow$ same # MO's as output
- What if molecule is heteronuclear? (formed by different atoms?)
- What if polyatomic molecules? (formed by many atoms)
- What if it is formed by $\sim 10^{23}$ atoms (i.e., a solid)?

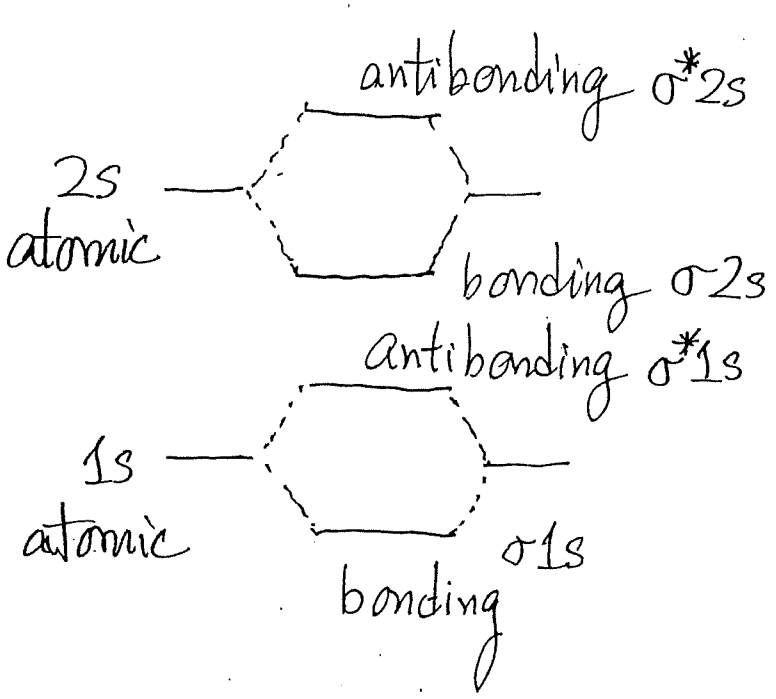
LCAO works!

H_2^+



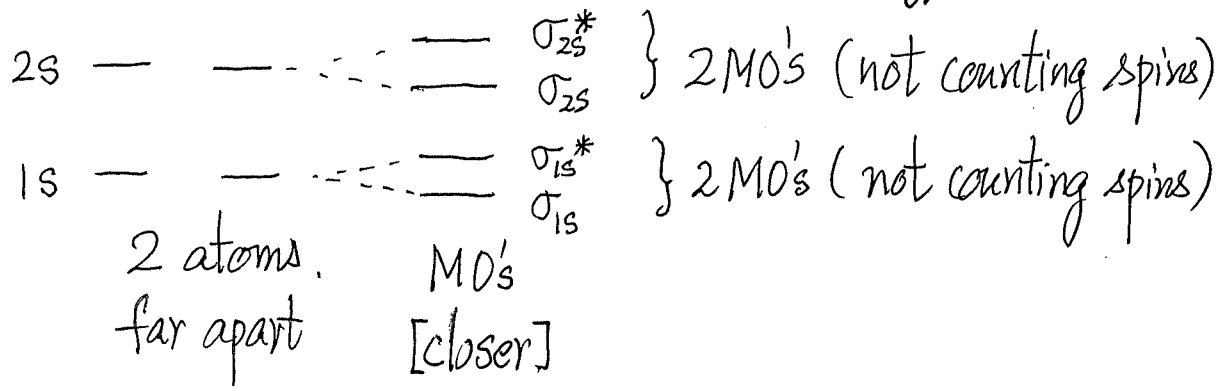
[Using 1s in each atom Only]

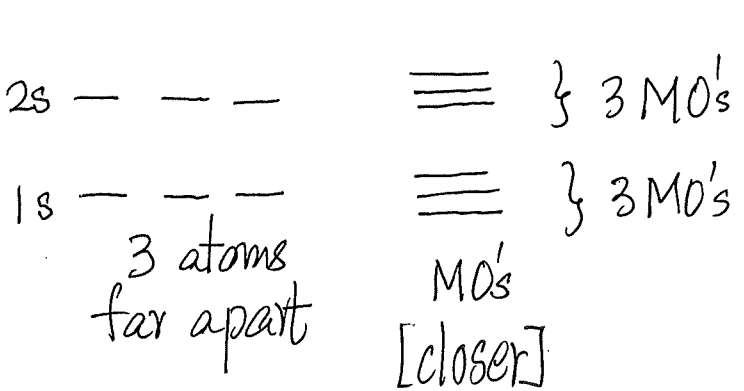
If we include 1s, 2s

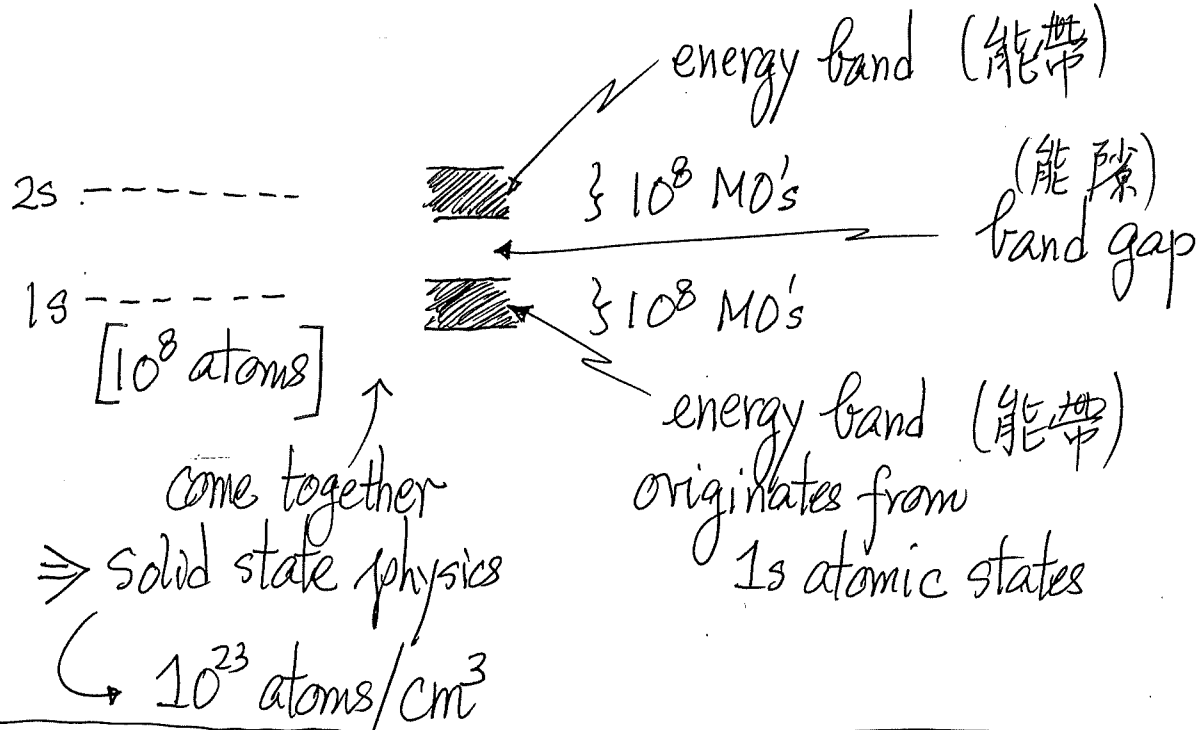


Ordering is Schematic

From MO's in Molecules to Energy Bands in Solids



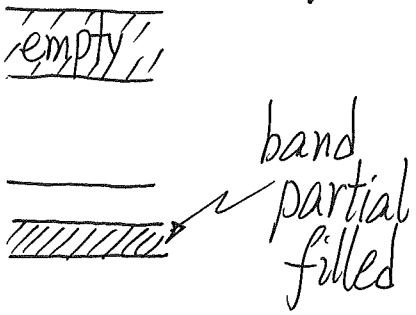




Energy Bands Formation in Solids is the problem equivalent to MO formation in molecules!

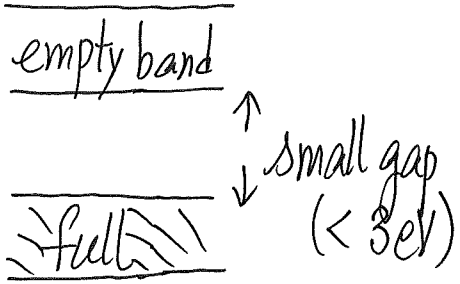
- Big Consequences from little new physics
- Solids: 10^{23} electrons (per cm^3) to fill into <u>electronic states</u> in bands

No new physics! <u>Pauli Exclusion Principle!</u> (Fermi-Dirac Distribution)



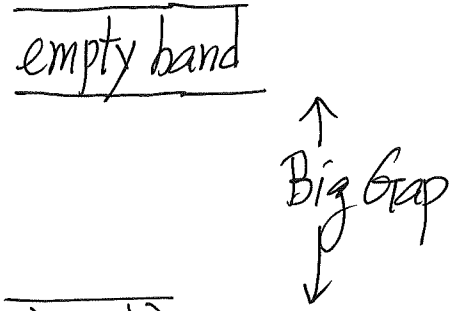
<u>Conductor (Metal)</u>

(e.g. Na, K, Cu)



<u>Semiconductor</u>

(e.g. Si gap ~ 1.1eV)



<u>Insulator</u>

(e.g. Diamond/Carbon, gap ~ 7eV)

This is 1/3 of a solid state physics course!