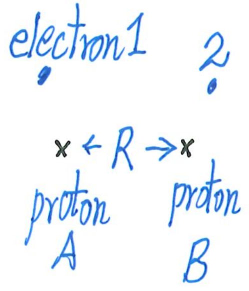
E. Electronic Part $\hat{H}_{el}\psi_{el} = E_{el}\psi_{el}$: LCAO-MO ("Step 1")

- Bad news! Even H₂ is hard to do! The H₂ problem is:



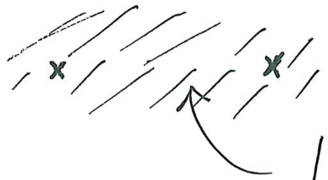
$$\Big[\underbrace{-\frac{\hbar^2}{2m}\nabla_1^2-\frac{\hbar^2}{2m}\nabla_2^2}_{\text{k.e. of electrons}}\ \underbrace{-\frac{e^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{R}_A|}-\frac{e^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{R}_B|}}_{\text{electron 1 sees nuclei}}\ \underbrace{-\frac{e^2}{4\pi\varepsilon_0|\vec{r}_2-\vec{R}_A|}-\frac{e^2}{4\pi\varepsilon_0|\vec{r}_2-\vec{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

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

- One two-electron problem for each R
- No analytic solution
- Approximate by single-electron problem + $\overbrace{\text{Anti-symmetric Wavefunction}}^{\text{Pauli Principle}}$

- H_2 is hard! Let's take a step backward.

- $\underline{H_2^+ \text{ molecular ion}}$ [2 nuclei + $\underbrace{\text{1 electron}}_{\text{single-electron (two-centered) problem}}$]



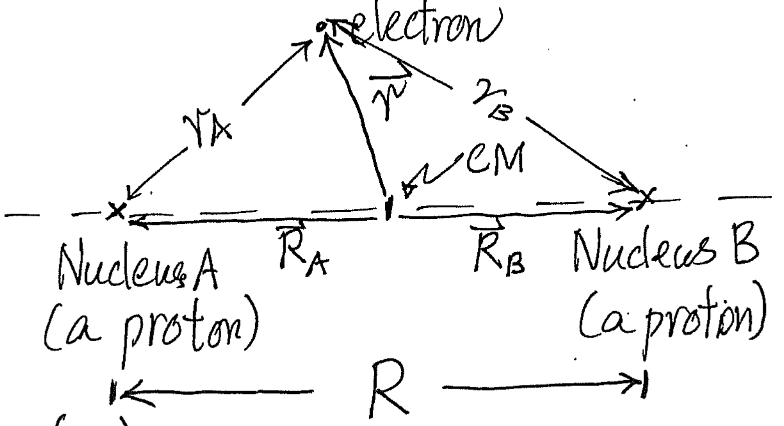
how one electron can possibly distribute itself (wavefunction) to bind two protons?

- 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)



$$\boxed{\hat{H}^{(H_2^+)}_{\text{electronic}} = \frac{-\hbar^2}{2m}\nabla^2_{\vec r} \underbrace{-\frac{e^2}{4\pi\varepsilon_0|\vec r-\vec R_A|}}_{\frac{-e^2}{4\pi\varepsilon_0 r_A}} \underbrace{-\frac{e^2}{4\pi\varepsilon_0|\vec r-\vec R_B|}}_{\frac{-e^2}{4\pi\varepsilon_0 r_B}} + \frac{e^2}{4\pi\varepsilon_0 R} \leftarrow \text{just a constant}}$$

(see fig.)

(14)

$V(\vec r ; \vec R)$ ← Given R, there is a $V(\vec r)$

$$\Rightarrow \boxed{\hat{H}_{\text{electronic}} = \frac{-\hbar^2}{2m}\nabla^2_{\vec r} + V(\vec r) + \frac{e^2}{4\pi\varepsilon_0 R}} \quad (15)$$

(an "easier" 1-electron problem)

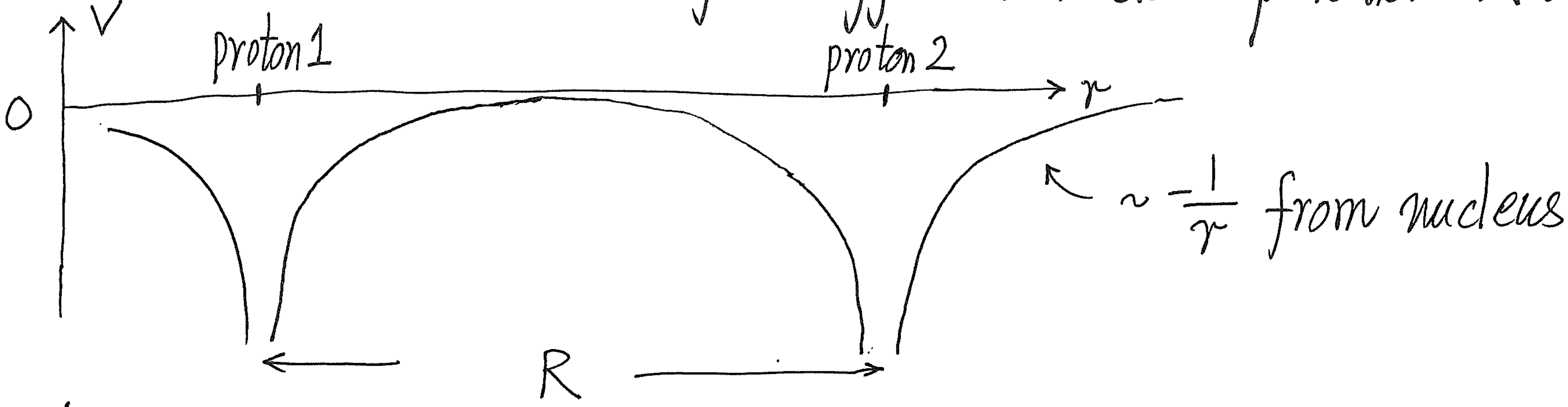
<u>Solve</u> $\hat{H}_{el}\,\psi_{el}(\vec r) = E_{el}\,\psi_{el}(\vec r)$ for given R (one problem for each R!)

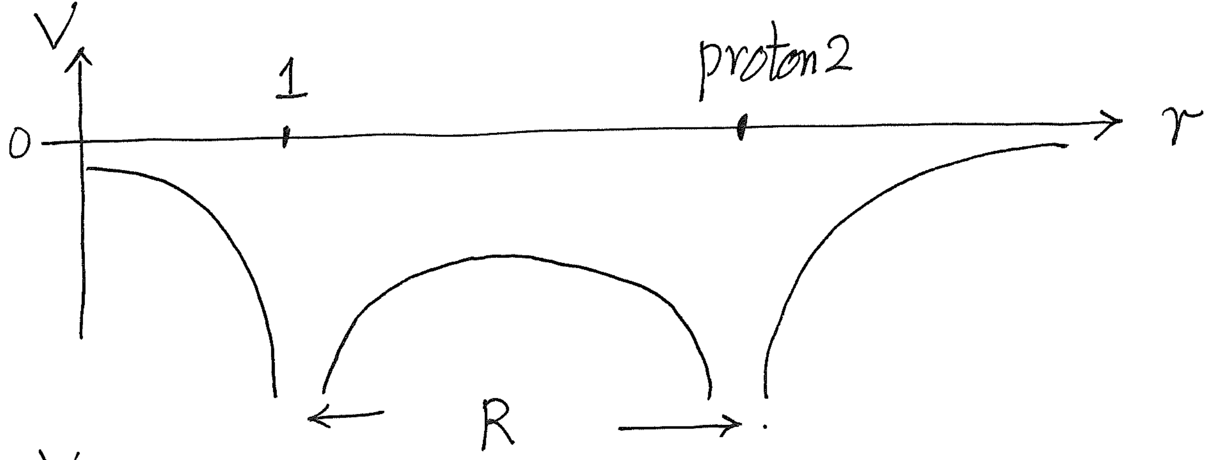
To stress that R gets into $V(\vec r)$ and thus the solutions, can write

$$\boxed{\hat{H}_{el}\,\psi^{el}_R(\vec r) = E_{el}(R)\,\psi^{el}_R(\vec r)} \quad (16)$$

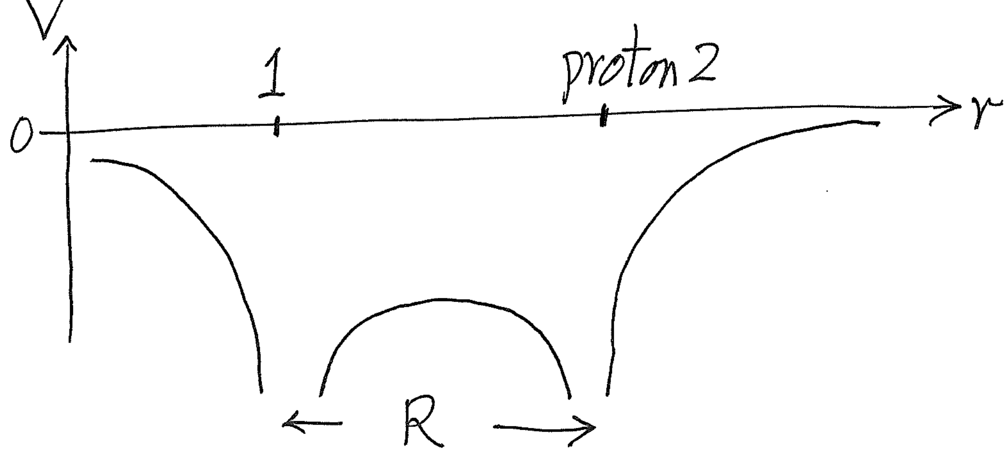
[$E_{el}(R)$ gives bonding]

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





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



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

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

But $\frac{e^2}{4\pi\varepsilon_0 R}$ is just a constant for given R

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

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

$\Rightarrow$ Solve $\boxed{\hat{\mathcal{H}}_{el}\,\psi_R^{el}(\vec{r}) = \mathcal{E}_{el}(R)\,\psi_R^{el}(\vec{r})}$ first (17)

then
$$E_{el}(R) = \mathcal{E}_{el}(R) + \frac{e^2}{4\pi\varepsilon_0 R} \qquad (18)$$

$\therefore$ Focus on solving Eq. (17)

To approximately[+] solve Eq.(17) and to understanding bonding in H_2^+, H_2 and other molecules, LCAO is an effective and physically transparent approach

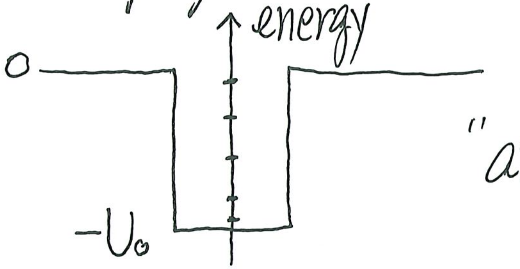
L C A O - M O

Linear Combination of Atomic Orbitals as a good approximation to the formation of (single-particle)... Molecular Orbitals

---

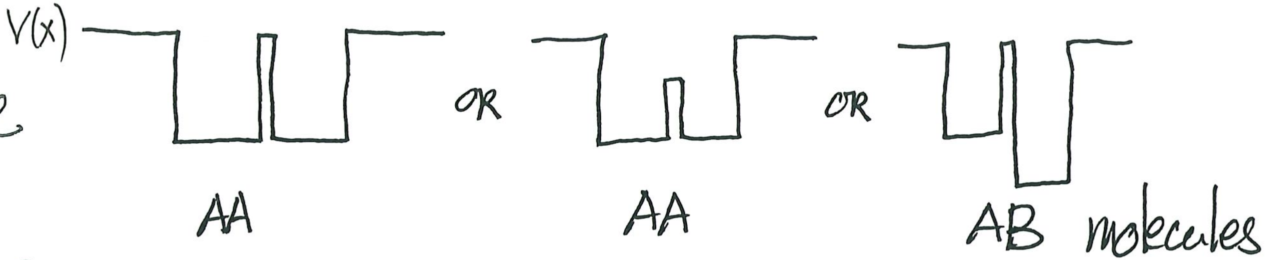
[+] Technical background: Variational method with $\psi_{trial} = \sum_i c_i \phi_i \Rightarrow$ Matrix Problem $(H_{ij} - \mathcal{E}_{el} S_{ij})$

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



"an atom" with atomic states/orbitals

- Analogy : Molecule



$$\underbrace{\hat{\mathcal{H}}_{el}}\,\psi^{el}_R(x) = \mathcal{E}_{el}(R)\,\psi^{el}_R(x)$$

↑

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]$$

↑

different separations

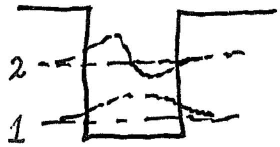
⇓

different TISE's

How to solve the problem?

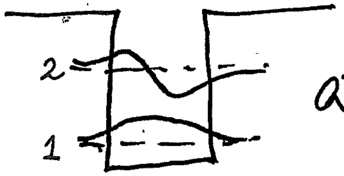
- Exactly (write down ψ and match B.C.'s), it works!

- How about expressing ψ^{el}_R 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

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

atomic orbitals of atoms forming molecule

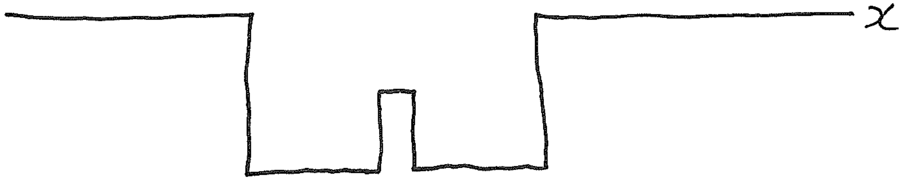
Recall:
Schrödinger Eq. becomes

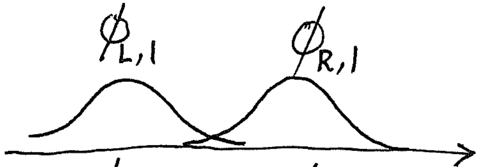
$$\underbrace{\left|\mathcal{H}_{ij} - E S_{ij}\right|}_{(ij)^{\text{th}}\text{ element}} = 0$$

Linear Combination of Atomic Orbitals (LCAO)

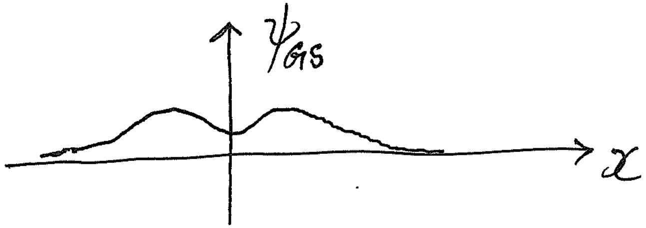
- Physically transparent picture: How atomic orbitals combine into Molecular Orbitals
- How many AO's to use? $\underbrace{\text{The more the better}}_{\text{(True in principle)}}$? $\underbrace{\text{Guided by physics}}_{\text{(in practice)}}$!

LCAO



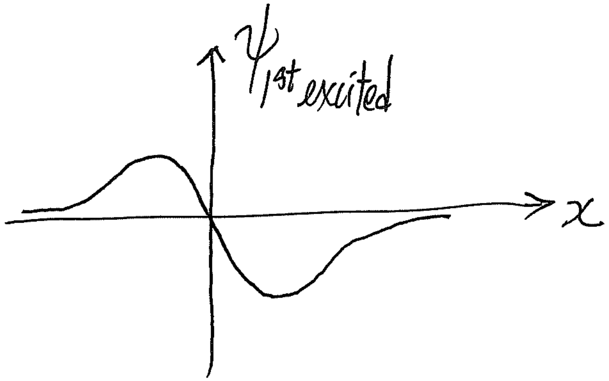


- Ground state wavefunction?

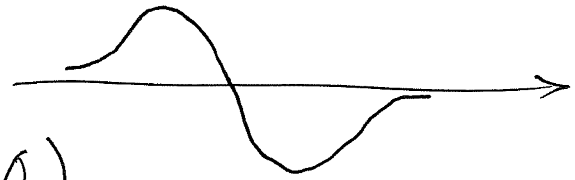


looks like $\sim \underbrace{\phi_{L,1} + \phi_{R,1}}$

- First excited state wavefunction?



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



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)

$\boxed{\text{LCAO makes Good Sense!}}$

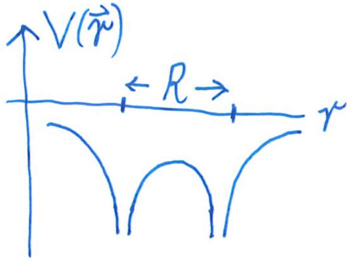
Back to H_2^+ (or H_2 after reducing to single-electron problem)

Left × Right ×

$$\boxed{\hat{\mathcal{H}}_{el}\,\psi_{el}(\vec{r}) = \varepsilon_{el}(R)\,\psi_{el}(\vec{r})} \quad (17)$$

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

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



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

$$\boxed{\psi^{(\text{molecule})}_{\text{electronic}}(\vec{r}) = \sum_{\substack{\text{atomic states}\\ \text{of Left atom}}} C_{L,i}\,\phi_{L,i} + \sum_{\substack{\text{atomic states}\\ \text{of Right atom}}} C_{R,i}\,\phi_{R,i}} \quad (19)$$

$C_{L,i}$ 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 ⇒ Not important[†] for H_2^+ Ground state]

$$\psi_{el,(GS)} = c_1 \phi_{L,1s} + c_2 \phi_{R,1s} \quad \underbrace{(\text{as simple}^{\ddagger} \text{ as that!})}_{\text{More, expect } |c_1|^2 = |c_2|^2} \quad (20)$$

(Why? Bias a side? Which side?)

$\therefore$ Just a $\underbrace{|\text{"}2\times2\text{"}| = 0}_{\text{"Pushing up and Pushing down"}}$ problem

---

[†] Think perturbation

[‡] Eq.(20) is an approximation, but a reasonable one.

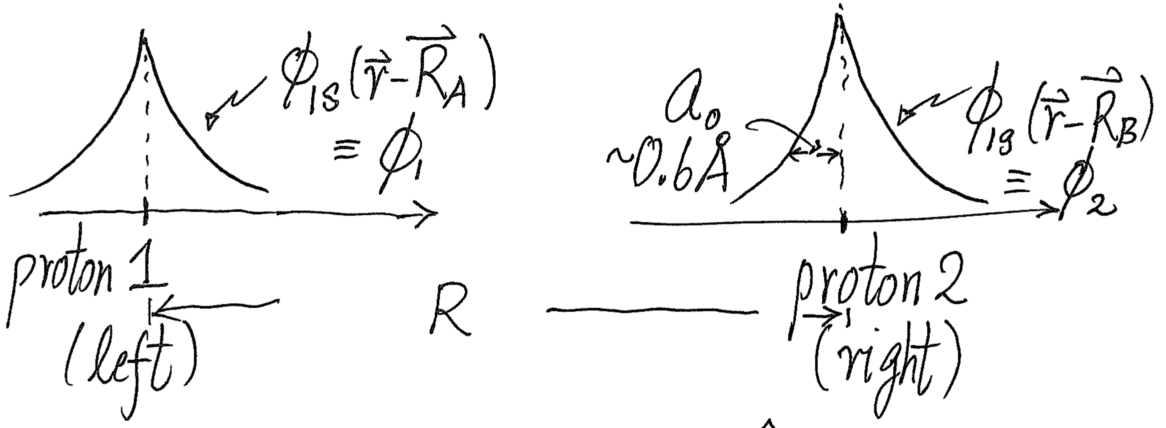
LCAO for H_2^+ without Mathematics

- $\phi_{1s}(\vec{r}) = A\, e^{-r/a_0}$ [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]

Picture



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

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

Why?

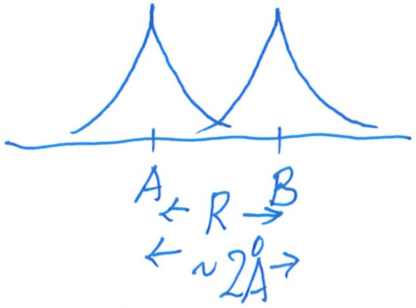
ϕ_1's tail is zero near proton 2, and vice versa

Remark:

$$\psi_{trial} = c_1 \underbrace{\phi_{1s}(\vec{r}-\vec{R}_A)}_{\text{centered at A}} + c_2 \underbrace{\phi_{1s}(\vec{r}-\vec{R}_B)}_{\text{centered at B}}$$

$S_{12} = \int \phi^*_{1s}(\vec{r}-\vec{R}_A)\, \phi_{1s}(\vec{r}-\vec{R}_B)\, d^3r$ is $\underbrace{\text{NOT zero}}_{\text{though not big}}$ in general

Small R



$S_{12} = S(R)$ Only when $R \gg a_0$, $S(R) \to 0$

This is why we set up the general matrix problem as $\begin{pmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} \\ H_{21}-ES_{21} & H_{22}-ES_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$ when we discussed variation method.

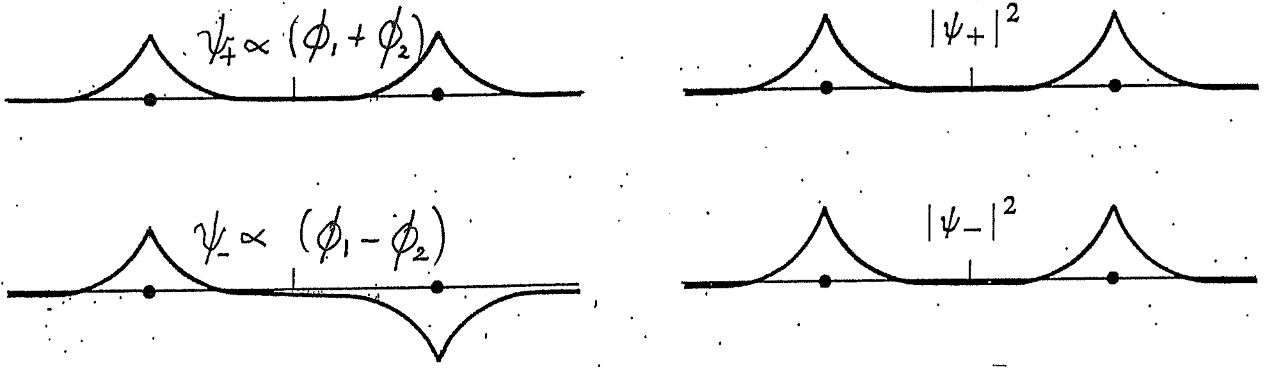
- For any separation R, $|\psi_{el}(\vec{r})|^2$ should be symmetric about mid-point between nuclei (nuclei are protons)

$$\boxed{\psi_{el,+}(\vec{r}) = C_+(\underset{(L,1s)}{\phi_1} + \underset{(R,1s)}{\phi_2}) \;;\quad \psi_{el,-}(\vec{r}) = C_-(\underset{(L,1s)}{\phi_1} - \underset{(R,1s)}{\phi_2})} \qquad (21)$$

Satisfy this requirement. They are LCAO's.

Large Separation R

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



(a) (b)

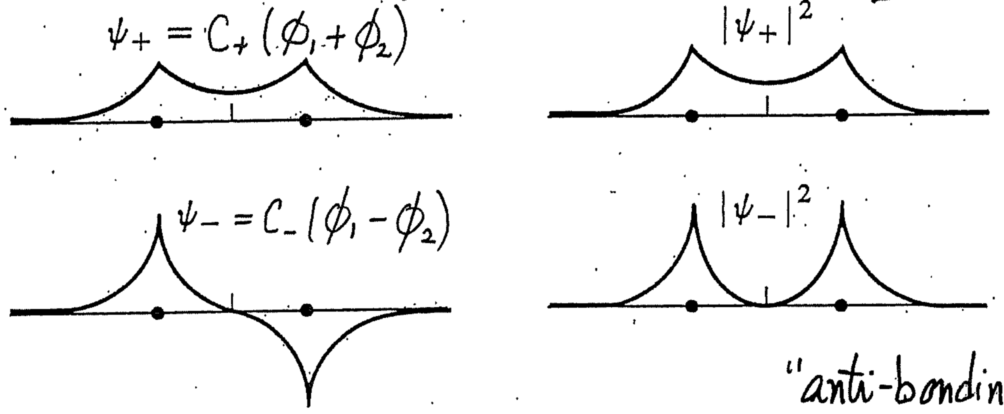
(a) The wave functions ψ_+ and ψ_- for the electron in H_2^+, when the two protons are far apart. The plots show values of $\psi_\pm$ along the internuclear axis. **(b)** Corresponding plots of the electron's probability density $|\psi_\pm|^2$ (which are identical as long as the protons are far apart).

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

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

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

Small Separation R



(a) (b)

Note: $|\psi_+|^2$ concentrates in the region between and around the nuclei "bonding"

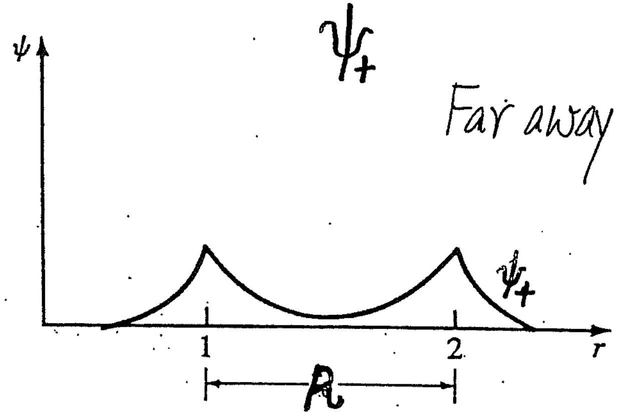
This is what you learned as covalent bond before

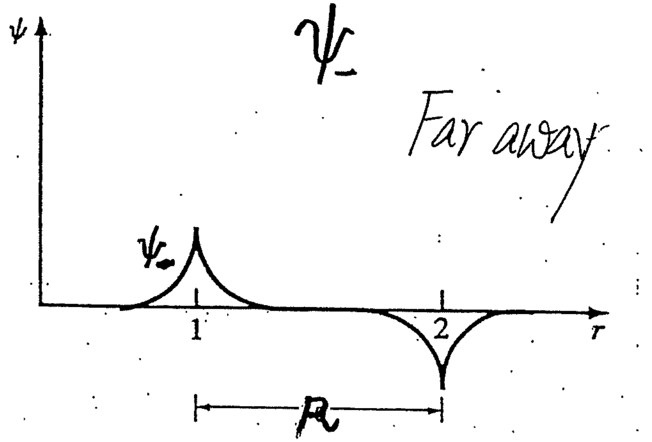
$|\psi_-|^2 = 0$ at midway between protons

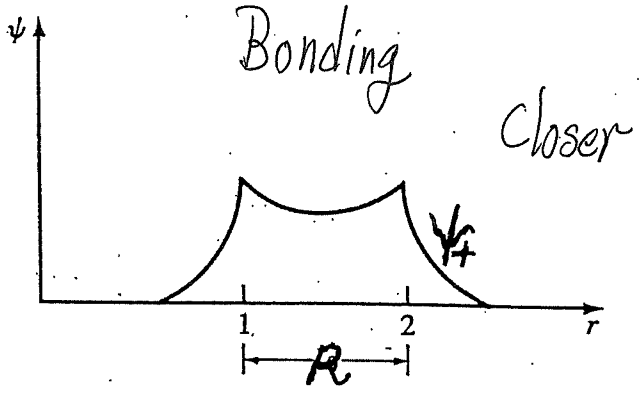
"anti-bonding"

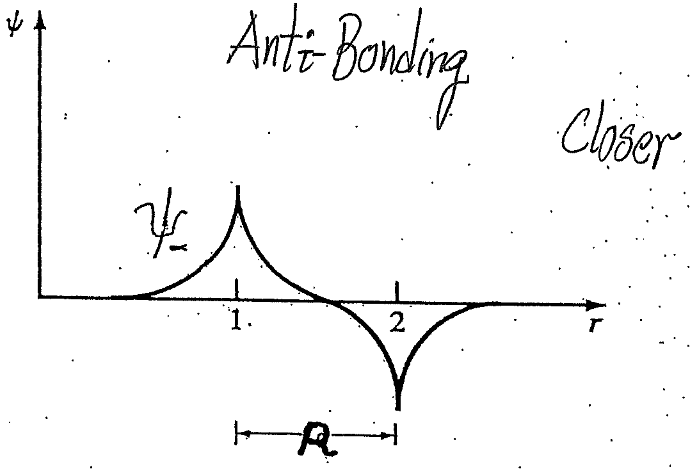
(a) Sketch of the wave functions ψ_+ and ψ_- for the electron in the H_2^+ molecule, once the distance R between the two protons is comparable to the size of an H atom. At the origin, ψ_+ is larger than either ψ_1 or ψ_2, whereas ψ_- is exactly zero. (The factors C_+ and C_- are normalization constants;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







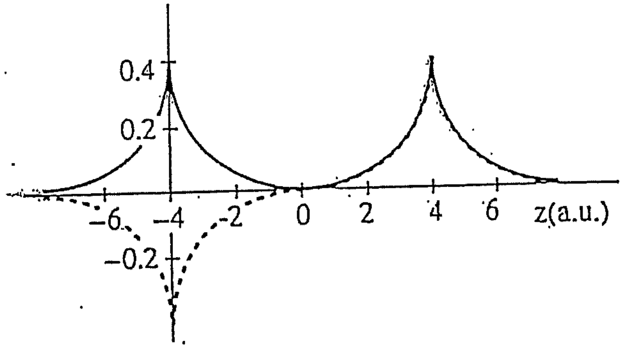


One can solve $\hat{\mathcal{H}}_{el}\,\psi_{el}(\vec{r}) = \mathcal{E}_{el}(R)\,\psi_{el}(\vec{r})$ numerically (exactly)

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

(3 separations)

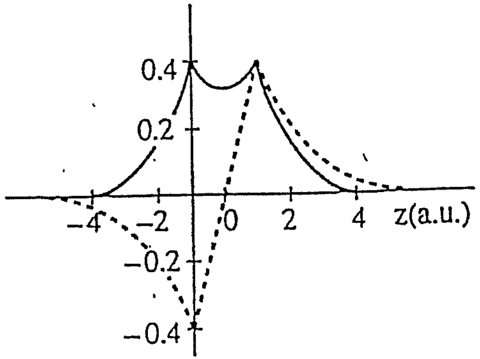
(a)



Just like $\psi_\pm$

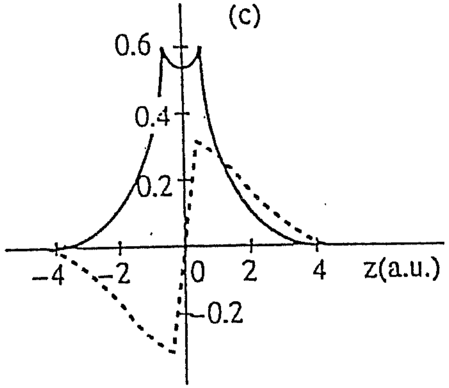
$\therefore$ LCAO makes good physical sense AND Works!

(b)



(b).

(c)



(c)

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

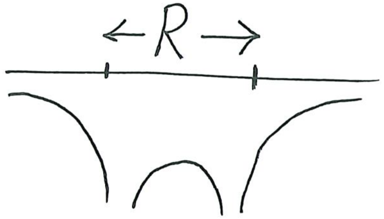
- To see bonding (or why the name anti-bonding), need the energies $\mathcal{E}_+(R)$ [for ψ_+] and $\mathcal{E}_-(R)$ [for ψ_-]

Two Ways

Same results [of course]

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

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



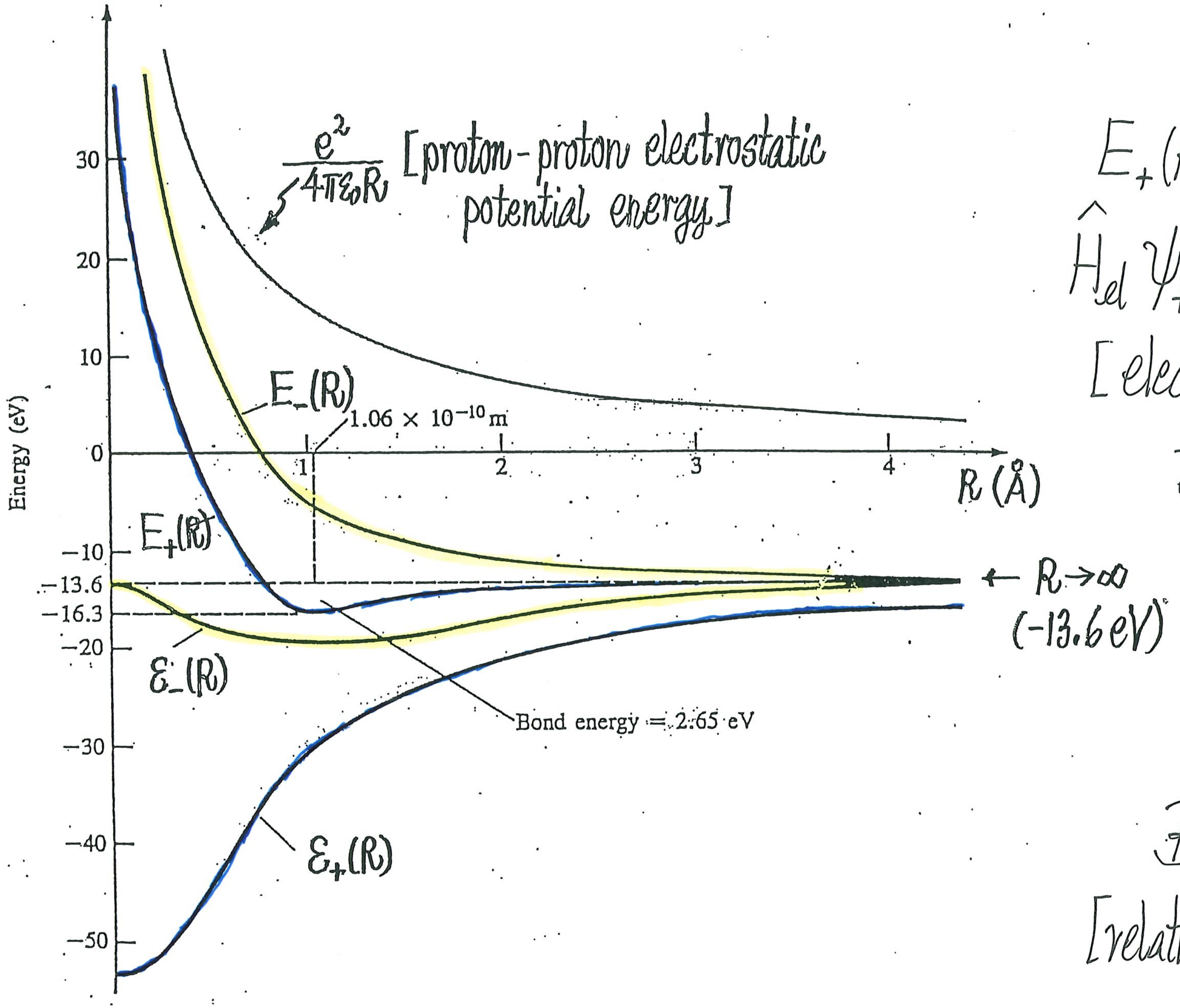
$\Rightarrow$ Two values of $\mathcal{E}$ corresponding to $\mathcal{E}_+(R)$ and $\mathcal{E}_-(R)$

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

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

assumed normalized

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



$E_+(R)$ is the energy in

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

[electronic part]

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

Minimum at

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

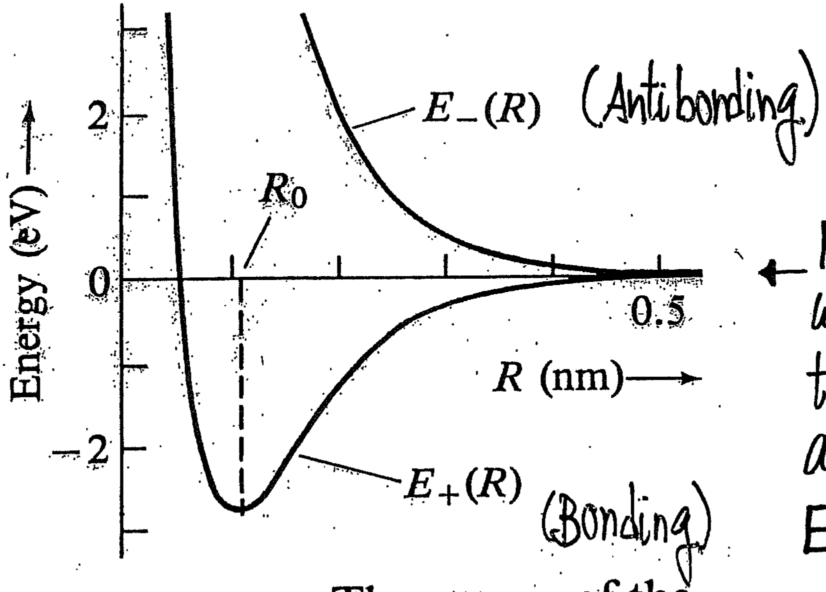
$= 1.06$ Å

$\mathcal{B} = 2.65\,eV$

[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_-.

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

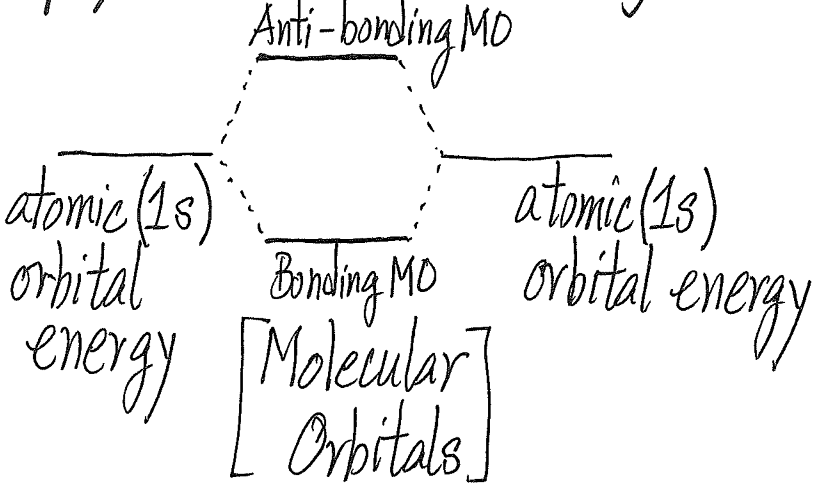
R_0 = equilibrium separation $\cong$ 0.11 nm (bond length)

B = binding energy = 2.65 eV

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

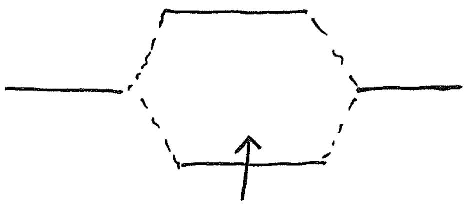
$\psi_+(\vec{r})$ for $R=R_0$ is a Bonding Molecular Orbital

This is the physics behind the following picture in chemistry books



- Electron(s) fills (fill) into MO's according to <u>Pauli Exclusion Principle</u>

H_2^+ ion

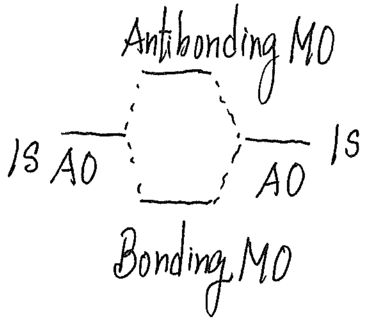


↓↑ gain energy compared with

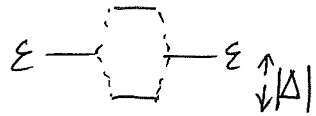
$$\underbrace{\underbrace{H}_{\text{neutral atom}} + \underbrace{p}_{\text{a proton far away}}}_{\approx -13.6\ \text{eV}}$$

$$\therefore \underbrace{H_2^+ \text{ can be formed}}_{\text{true! An exp'tal fact}}$$

Chemical Bonding is Quantum Business : Make connection with 2x2 matrix



"pushing down" & "pushing up" looks like $\begin{pmatrix}\varepsilon & \Delta \\ \Delta^* & \varepsilon\end{pmatrix}$ physics (and it is!)



Think like a physicist

Formally,

$$\begin{pmatrix} \mathcal{H}_{11} - ES_{11} & \mathcal{H}_{12} - ES_{12} \\ \mathcal{H}_{21} - ES_{21} & \mathcal{H}_{22} - ES_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

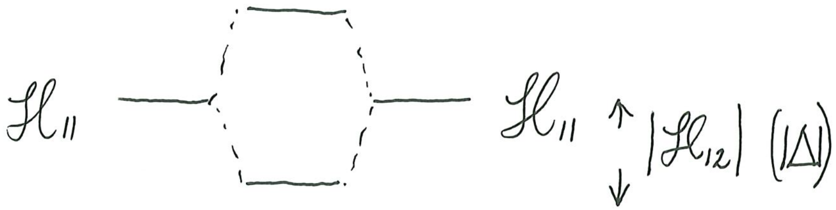
But it is "too serious" for applied purposes!

$S_{12} \neq 0$ in general ("  " integral), but not big.

So $S_{12} \approx 0 \approx S_{21}$. $\mathcal{H}_{11} = \mathcal{H}_{22}$ (due to "AA" type molecule)

[$S_{11} = S_{22} = 1$ (normalized AO's)]

$$\begin{pmatrix} \mathcal{H}_{11}-E & \mathcal{H}_{12} \\ \mathcal{H}_{21}^{*} & \mathcal{H}_{11}-E \end{pmatrix}\begin{pmatrix}C_1\\C_2\end{pmatrix}=0 \Rightarrow \underbrace{\begin{pmatrix}\mathcal{H}_{11} & \mathcal{H}_{12}\\ \mathcal{H}_{21}^{*} & \mathcal{H}_{11}\end{pmatrix}}_{\text{want to get eigenvalues } E}\begin{pmatrix}C_1\\C_2\end{pmatrix}=E\begin{pmatrix}C_1\\C_2\end{pmatrix}$$



$\therefore$ It is $\underbrace{\mathcal{H}_{12}}_{\uparrow\ \text{responsible for lowering Bonding MO energy}}$ doing the pushing

"What is $\mathcal{H}_{12}$?"

$$\psi_{trial} = C_1 \overbrace{\phi_{1s}(\vec{r}-\underset{\substack{\uparrow \\ \text{left-side nucleus}}}{\vec{R}_A})}^{\text{"1"}} + C_2 \overbrace{\phi_{1s}(\vec{r}-\underset{\substack{\uparrow \\ \text{right-side nucleus}}}{\vec{R}_B})}^{\text{"2"}}$$

$$\hat{H}_{electronic} = \hat{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0|\vec{r}-\vec{R}_A|} - \frac{e^2}{4\pi\varepsilon_0|\vec{r}-\vec{R}_B|} + \frac{e^2}{4\pi\varepsilon_0 R}$$

$$\mathcal{H}_{12} = \int \phi_{1s}^{*}(\vec{r}-\vec{R}_A)\ \hat{H}\ \phi_{1s}(\vec{r}-\vec{R}_B)\, d^3r$$

complicated! (many terms)

different centers

Focus on selected term in $\mathcal{H}_{12}$, one term[+] is

$$\int \phi_{1s}^{*}(\vec{r}-\vec{R}_A)\left[\frac{-e^2}{4\pi\varepsilon_0|\vec{r}-\vec{R}_B|} + \frac{e^2}{4\pi\varepsilon_0 R}\right]\phi_{1s}(\vec{r}-\vec{R}_B)\, d^3r$$

it does <u>NOT</u> have classical EM interpretation (<u>entirely quantum!</u>)

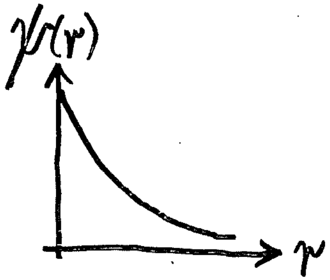
"More quantum" than simply needed the Schrödinger Equation

this appeared in $\mathcal{H}_{12}$ (or Δ), which is doing the pushing!

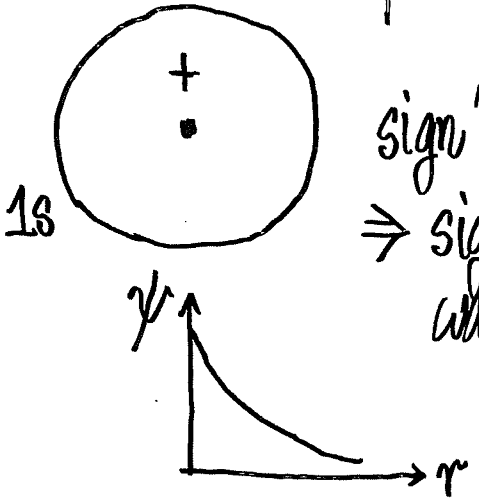
[+] <u>Note</u>: Don't see factors like $e\,\phi_{1s}^{*}(\vec{r}-\vec{R}_A)\,\phi_{1s}(\vec{r}-\vec{R}_A) = e|\phi_{1s}(\vec{r}-\vec{R}_A)|^2$ here (charge density)!

Other Pictorial Representations and Notations

Recall 1s state: $\psi(r,\theta,\phi) \sim e^{-r/a_B}$ $\quad \underbrace{\text{no } \theta,\phi \text{ dependence}}_{\left(\psi \text{ is spherically symmetric}\right)}$

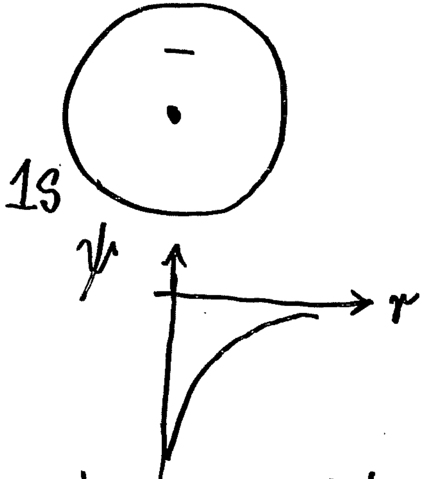


Since it is spherically symmetric, we can represent it as:



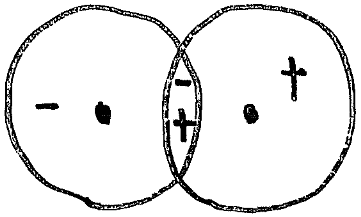
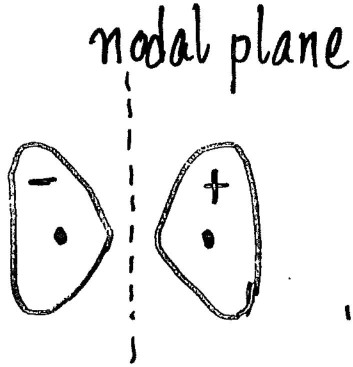
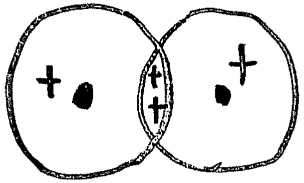
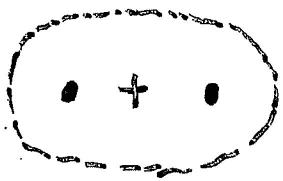
sign "+"
⇒ sign of wavefunction

Atomic 1s states



Atomic 1s states

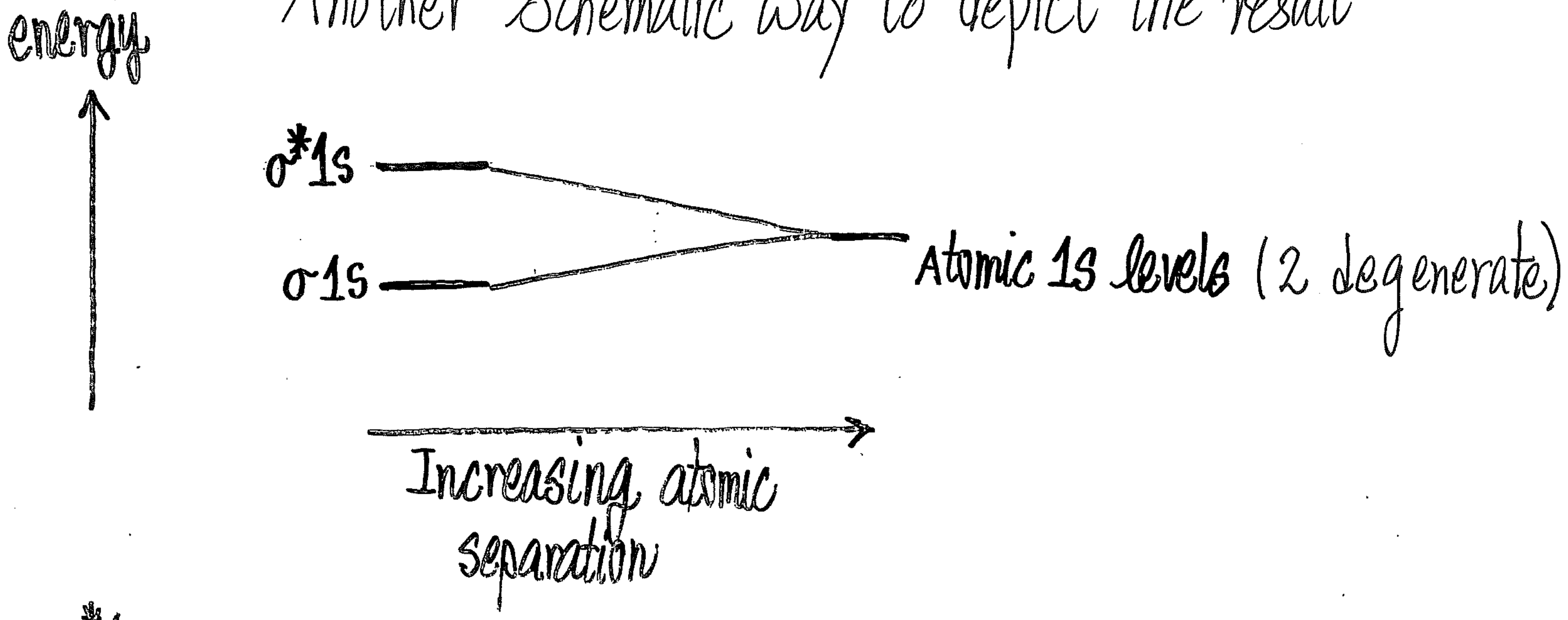
[No probem with negative ψ
as it is $|\psi|^2$ that matters]

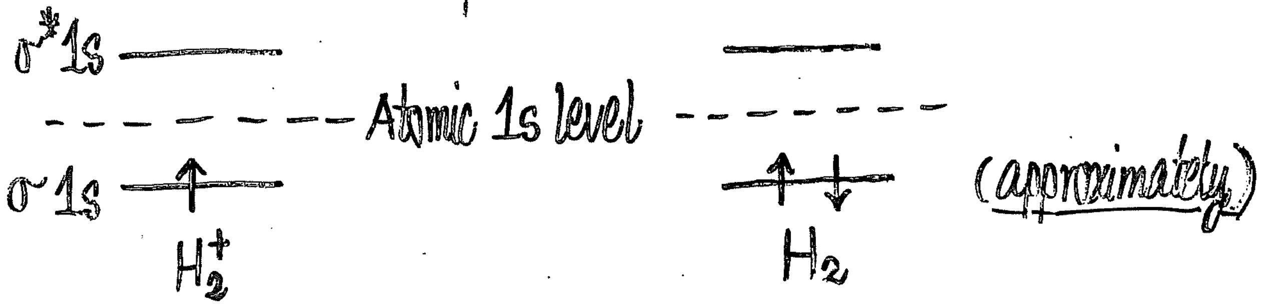
		In terms of Atomic 1s states	Molecular states	Notation
$\psi_- \propto \phi_1 - \phi_2$	Anti-bonding			$\sigma^* 1s$ "*"- anti-bonding
$\psi_+ \propto \phi_1 + \phi_2$	Bonding			$\sigma 1s$

σ-bond: What is it in QM?

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

Another Schematic way to depict the result





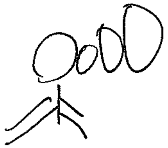
H_2^+ exist

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 <u>four</u> Molecular Orbitals (see fig. next page)

- # AO's in LCAO ⇒ 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!

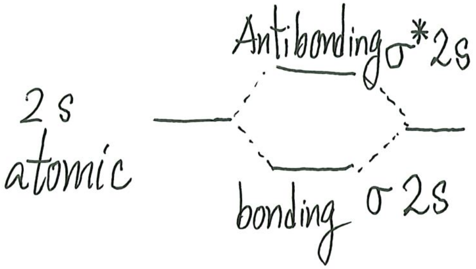
Including 1s, 2s AO's from left and right atoms

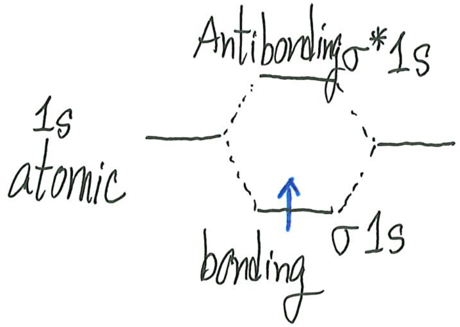
$$\psi_{trial} = C_{1s,L}\,\phi_{1s,L} + C_{2s,L}\,\phi_{2s,L} + C_{1s,R}\,\phi_{1s,R} + C_{2s,R}\,\phi_{2s,R}$$

$\Rightarrow$ 4 x 4 matrix problem

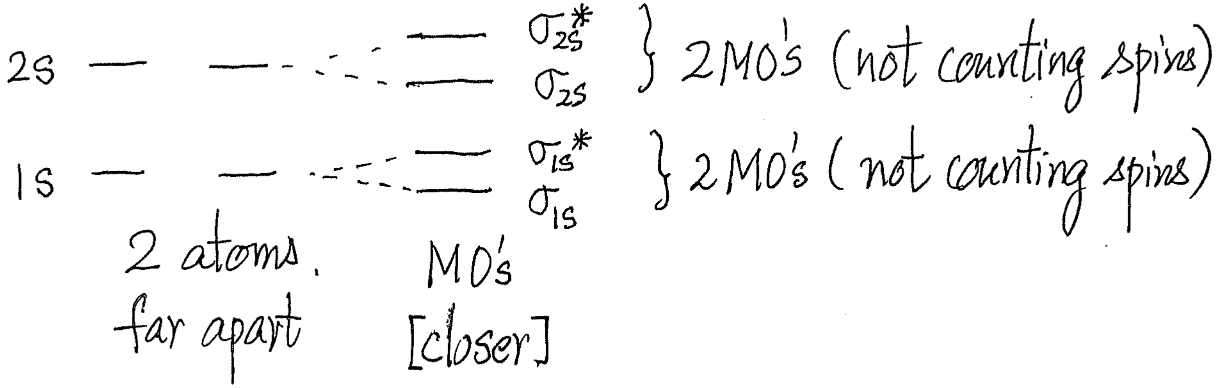
$\Rightarrow$ 4 eigenvalues

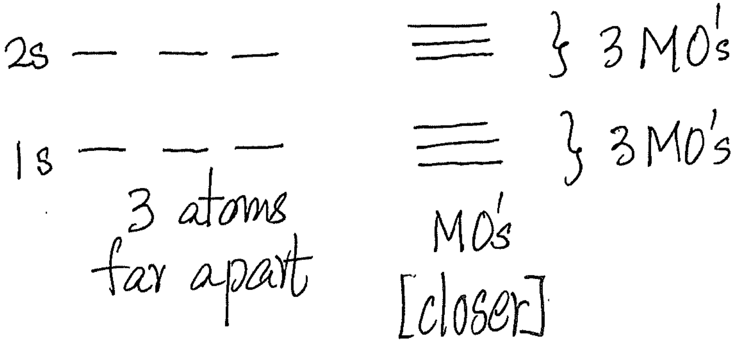
H_2^+

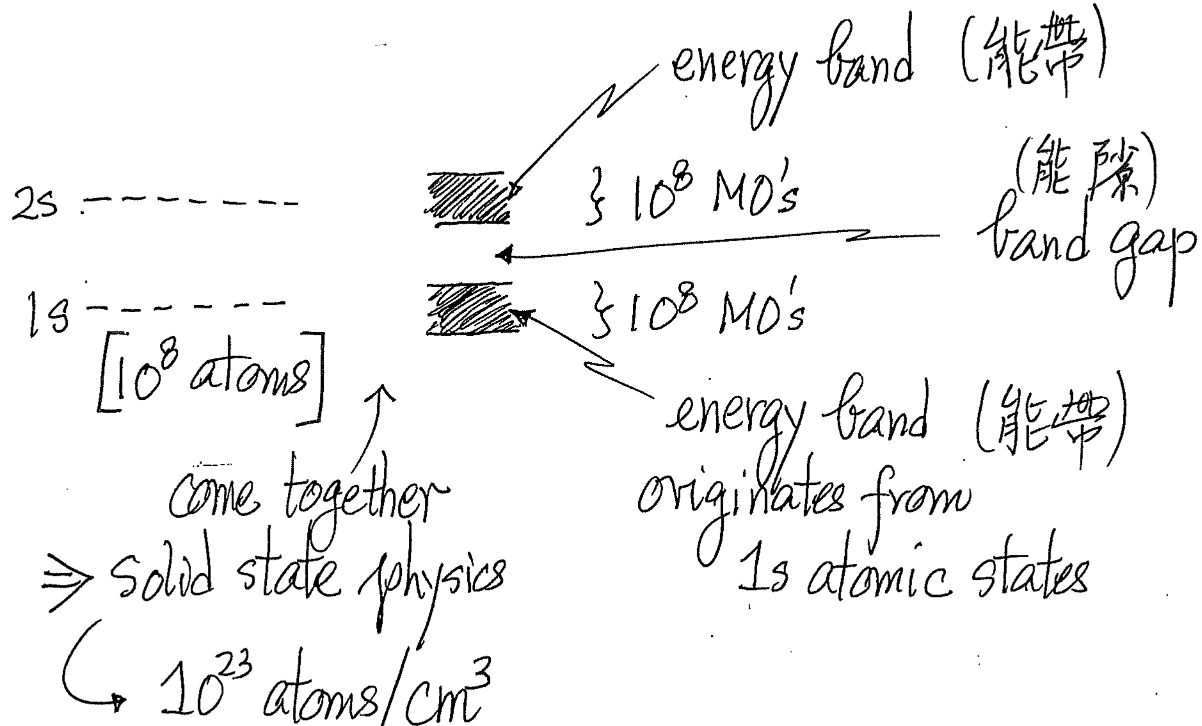




From MO's in Molecules to Energy Bands in Solids



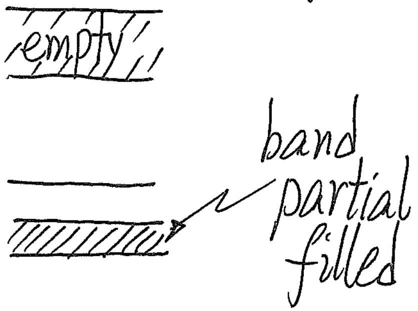




Energy Bands Formation in Solids is the problem equivalent to MO formation in molecules!

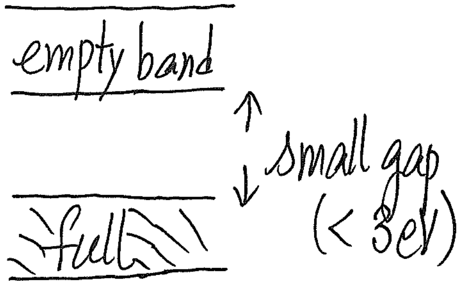
- Big Consequences from little new physics
- Solids: 10^{23} electrons (per cm^3) to fill into <u>electronic states</u> in bands

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



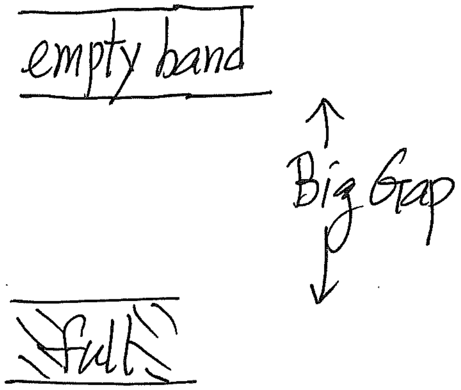
<u>Conductor (Metal)</u>

(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!