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:

electron 1 ? electron 2

$x \leftarrow R \rightarrow x$ proton A, proton B

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

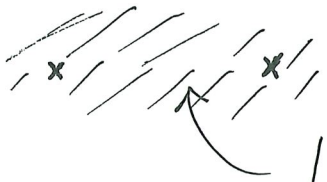
$$\left. \underbrace{+ \frac{e^2}{4\pi\varepsilon_0|\vec{r}_1 - \vec{r}_2|}}_{\text{electrons see each other}} + \underbrace{\frac{e^2}{4\pi\varepsilon_0 R}}_{\substack{\text{nuclei repulsion} \\ \text{[a constant]}}} \right] \psi_{el}(\vec{r}_1, \vec{r}_2; R) = E_{el}(R)\,\psi_{el}(\vec{r}_1, \vec{r}_2;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

(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]

single-electron (two-centered) problem

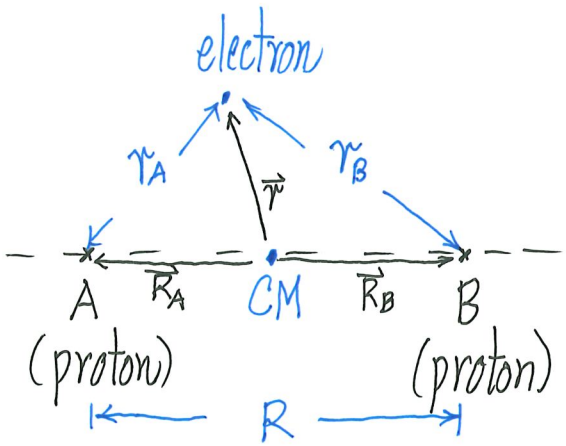


how one electron can possibly distribute itself (wavefunction) to bind two protons?

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

H_2^+ Molecular Ion : Simplest problem illustrating the physics of bonding

- Two (fixed) nuclei + 1 electron (∴ "easy" 1-electron problem)



$$\hat{H}_{electronic}^{(H_2^+)} = \frac{-\hbar^2}{2m}\nabla_{\vec{r}}^2 - \frac{e^2}{4\pi\varepsilon_0|\vec{r}-\vec{R}_A|} - \frac{e^2}{4\pi\varepsilon_0|\vec{r}-\vec{R}_B|} + \frac{e^2}{4\pi\varepsilon_0 R}$$

(just a constant)

$$= \frac{-\hbar^2}{2m}\nabla_{\vec{r}}^2 - \frac{e^2}{4\pi\varepsilon_0 r_A} - \frac{e^2}{4\pi\varepsilon_0 r_B} + \frac{e^2}{4\pi\varepsilon_0 R} \qquad (14)$$

$$= \frac{-\hbar^2}{2m}\nabla_{\vec{r}}^2 + V(\vec{r}) + \frac{e^2}{4\pi\varepsilon_0 R} \qquad (15)$$

($V(\vec{r})$: electron sees two nuclei)

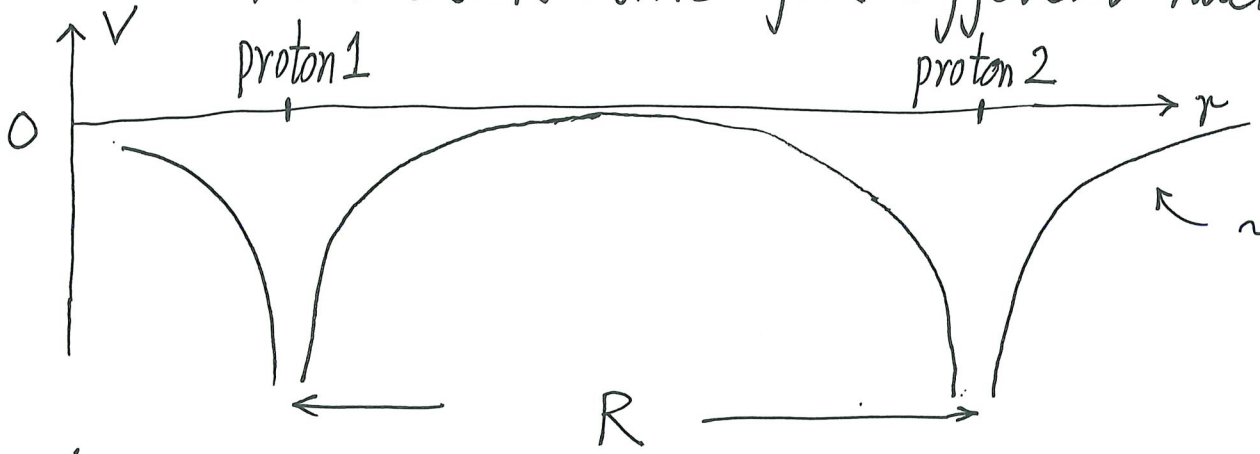
Want to solve: $\hat{H}_{el}\,\psi_{el}(\vec{r}) = E_{el}\,\psi_{el}(\vec{r})$ for a given R (each R is a problem to solve)

To emphasize that R gets in $V(\vec{r})$ and $e^2/4\pi\varepsilon_0 R$, and thus gets in the solutions:

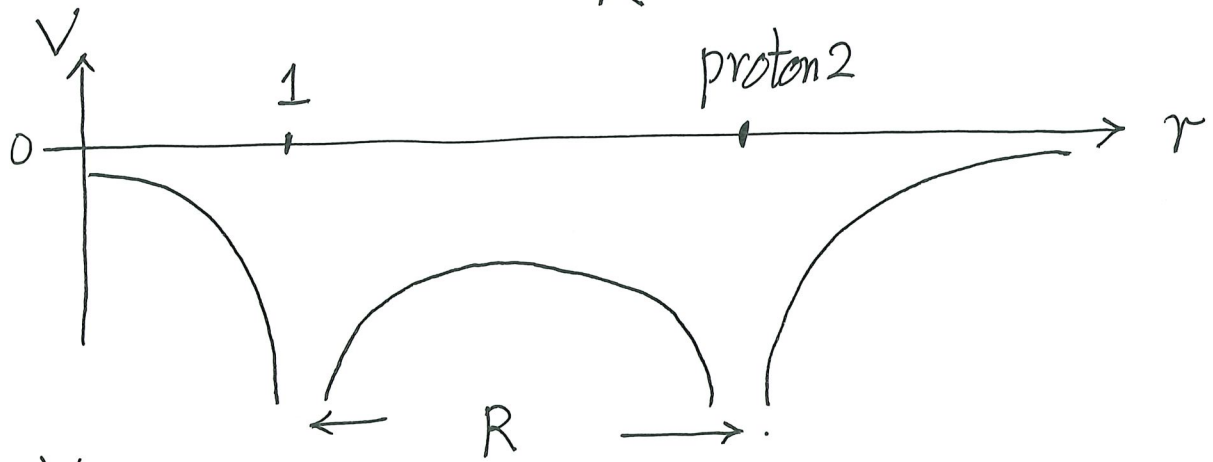
$$\hat{H}_{el}\,\psi_R^{el}(\vec{r}) = E_{el}(R)\,\psi_R^{el}(\vec{r}) \qquad (16)$$

Want $E_{el}(R)$ and see bonding

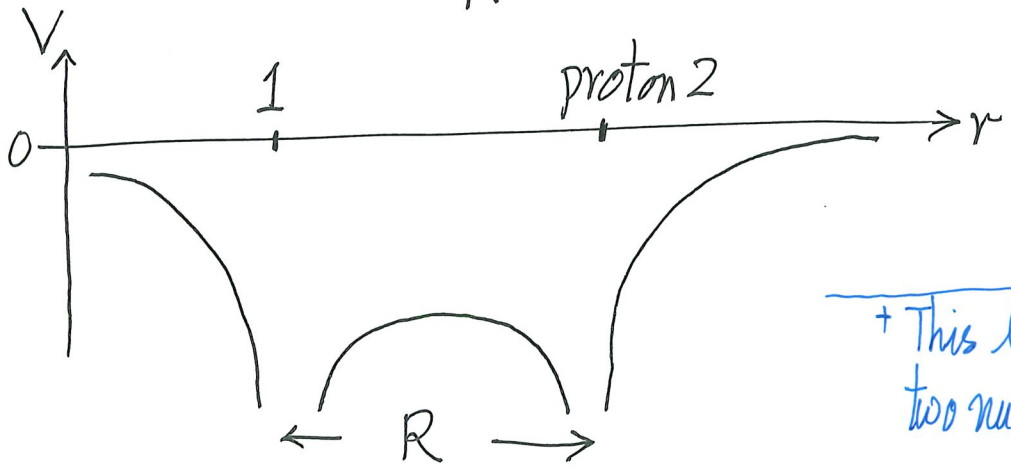
- How does $V(\vec{r})$ look like[+] for different nuclei separations R?



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



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



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

[+] This looks at $V(r)$ along a line joining the two nuclei. The full picture needs higher dimensions.

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

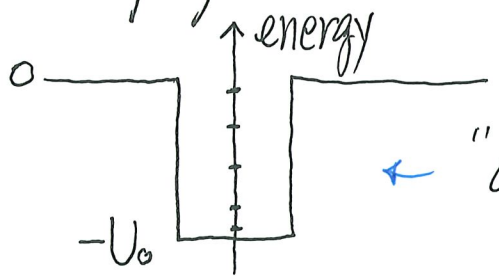
L C A O - M O

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

Molecular Orbitals

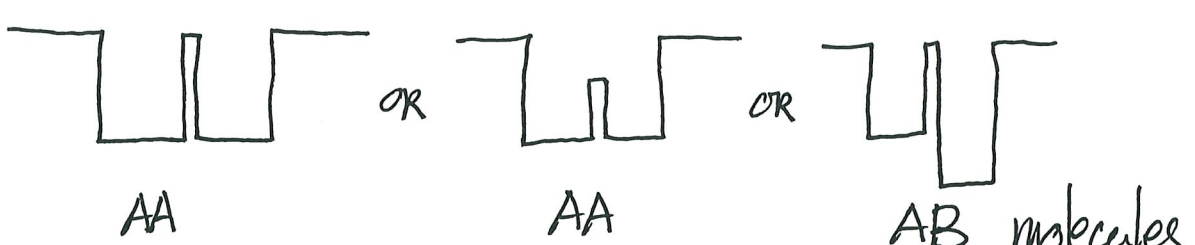
† Technical background: Variational method with $\psi_{trial} = \sum_i c_i \phi_i \Rightarrow$ Matrix Problem $(H_{ij} - \varepsilon_{el} S_{ij})$

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



← "an atom" with atomic states/orbitals

- Analogy: Molecule



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

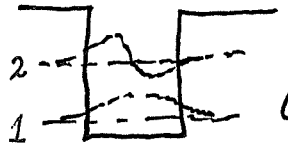
$$\hat{\mathcal{H}}_{el} = \left[\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]$$

different separations
⇓
different TISE's

How to solve the problem?

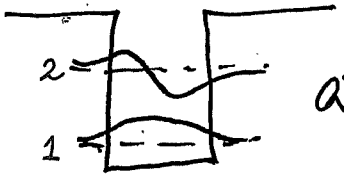
- Exactly (write down ψ and match B.C.'s), it works!

- How about expressing ψ_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 of atoms forming molecule)

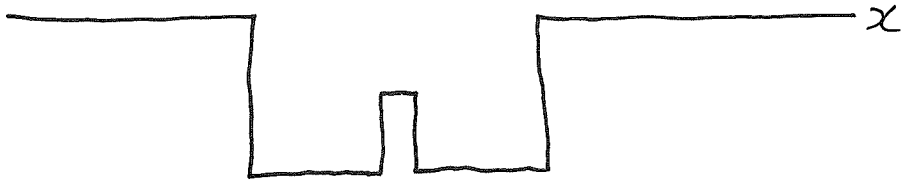
Recall:
Schrödinger Eq. becomes

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

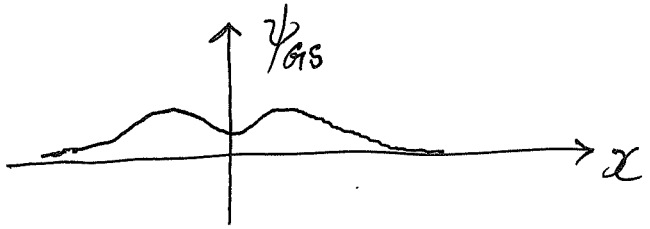
Linear Combination of Atomic Orbitals (LCAO)

- 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)

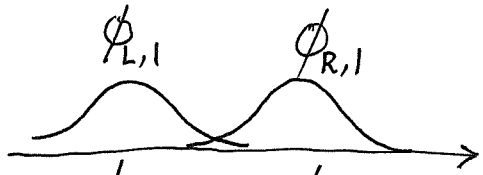
LCAO



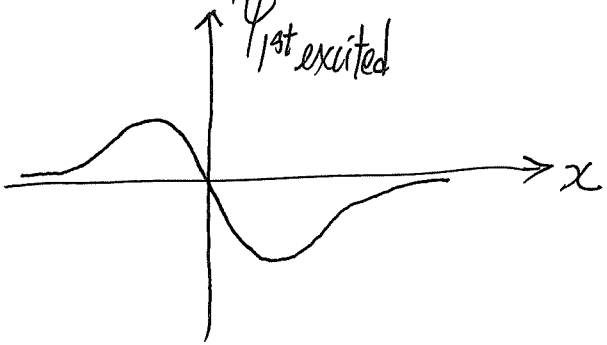
- Ground state wavefunction?



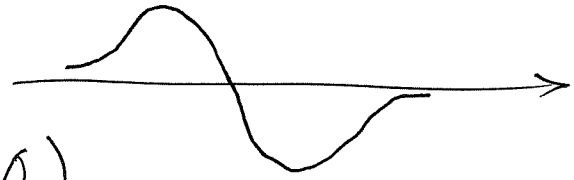
looks like $\sim \phi_{L,1} + \phi_{R,1}$



- 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!

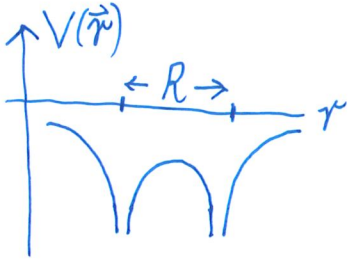
Back to H_2^+ (or H_2 after reducing to single-electron problem)

Left × Right ×

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

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

$$\hat{\mathcal{H}}_{el}\psi_{el}(\vec{r}) = \mathcal{E}_{el}(R)\,\psi_{el}(\vec{r}) \qquad (17)$$



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

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

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

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

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

"Pushing up and Pushing down"

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

(Why? Bias a side? Which side?)

---

† Think perturbation

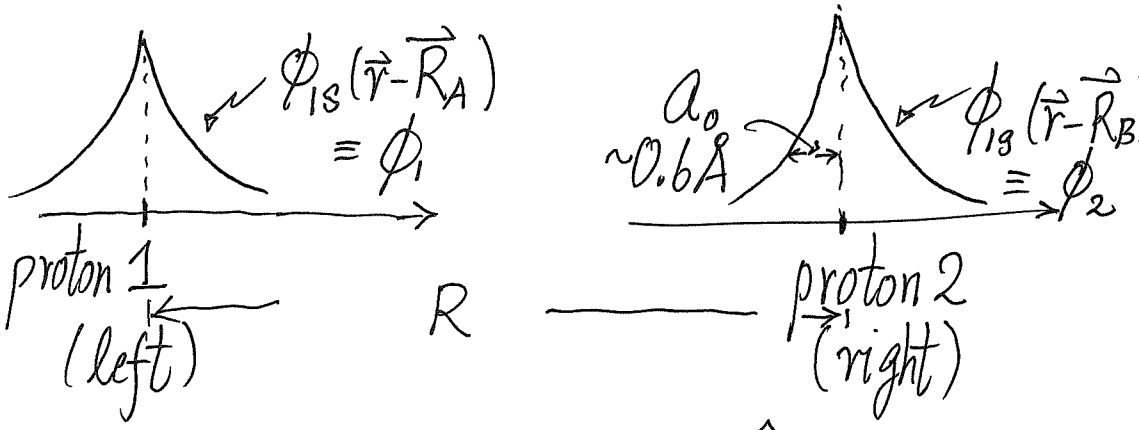
‡ Eq.(20) is an approximation, but a reasonable one.

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)

Picture



[they centered at different places]

For $R \gg a_0$ ($100\text{Å} \gg 0.6\text{Å}$),

$\hat{\mathcal{H}}_{el}\phi_1 = (-13.6\,eV)\phi_1$

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

Why?

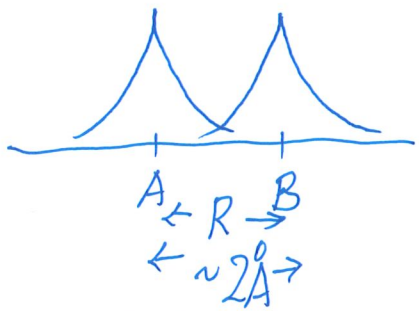
ϕ_1's tail is zero near proton 2, and vice versa

Remark:

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

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

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.

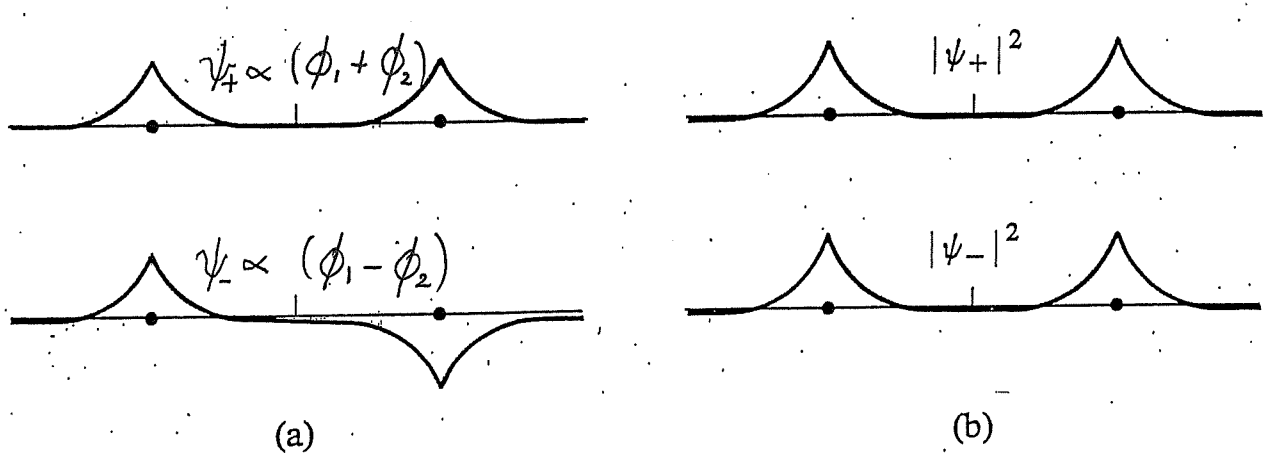
- For <u>any</u> separation R, $|\psi_{el}(\vec{r})|^2$ should be <u>symmetric about mid-point</u> between nuclei (nuclei are protons)

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

Satisfy this requirement. They are LCAO's.

Large Separation R

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



(a) 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).

- The point here is that, using the symmetry that the nuclei are identical,

  (electron won't bias one side ("∵ electron can't distinguish left nucleus from right nucleus, because they are the same")

  $|C_1|^2 = |C_2|^2$ (without calculation)

  - Either $C_1 = C_2 = C_+$ (even about mid-point)

    OR $C_1 = -C_2 = C_-$ (odd about mid-point)

    [Normalization condition then determines C_+, C_-]

- But for AB ($A \neq B$) molecule

  A B

  - no symmetry argument
  - use $\psi_{el} = C_1 \phi_{atomic}(\vec{r} - \vec{R}_A) + C_2 \phi_{atomic}(\vec{r} - \vec{R}_B)$ as trial wavefunction

    $\Rightarrow$ (2×2) problem

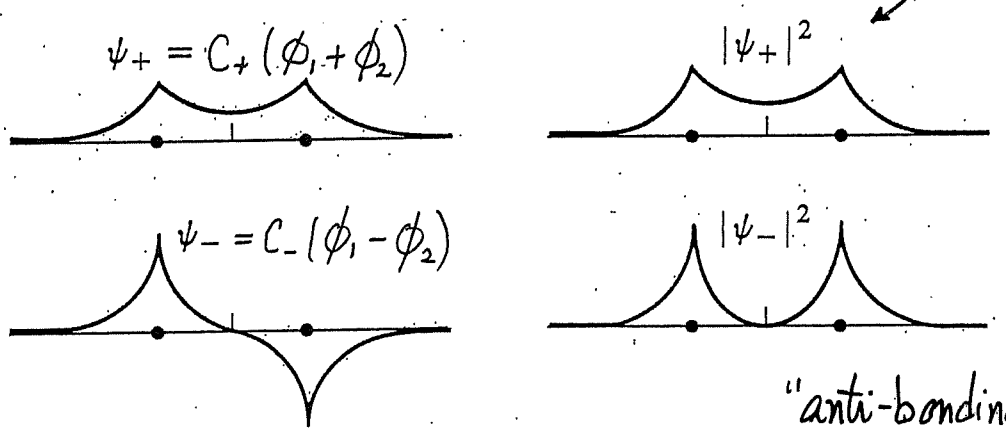
When protons get closer : $R \sim 1\text{-}2$ Å

$\psi_{el} = c_1 \phi_1 + c_2 \phi_2$ as trial wavefunction will give

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

ϕ_1 : (L, 1S) $\quad \phi_2$: (R, 1S)

Small Separation R



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

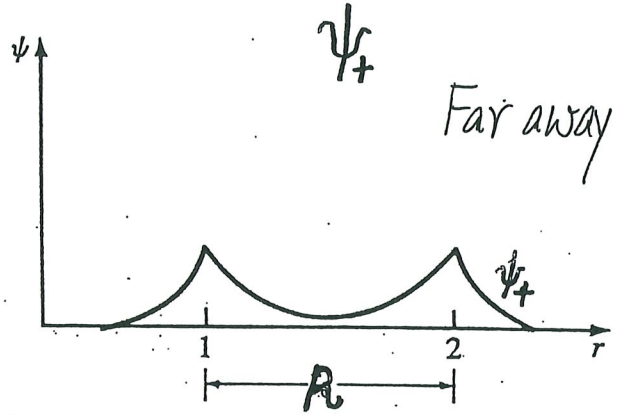
This is what you learned as covalent bond before

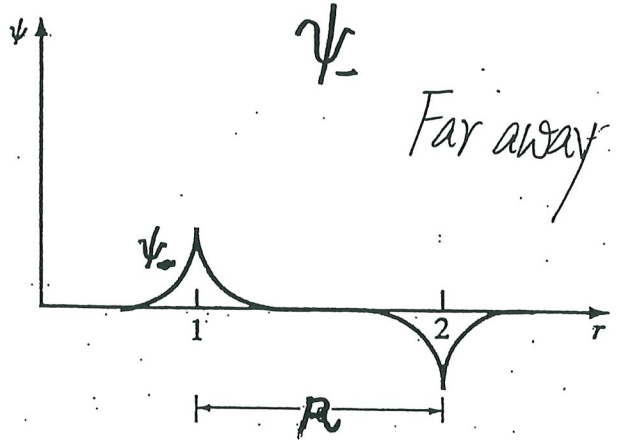
"anti-bonding"

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

(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.

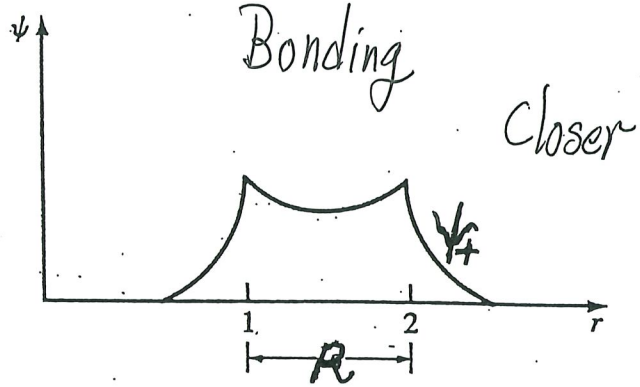
LCAO $\psi_\pm \propto \phi_{L,1S} \pm \phi_{R,1S}$ for H_2^+ ion

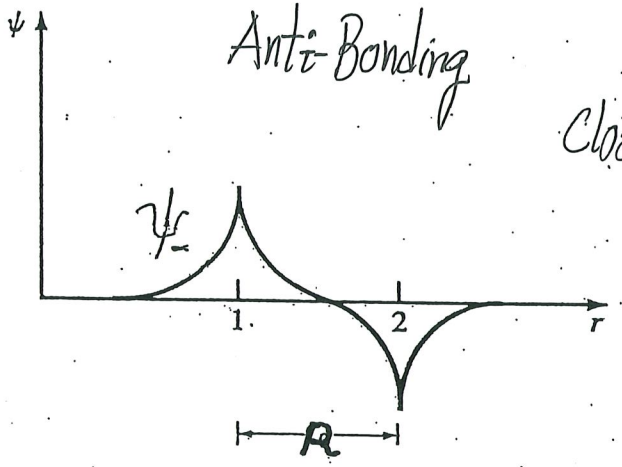




Far away

$|\psi_+|^2$ and $|\psi_-|^2$ do not differ by much





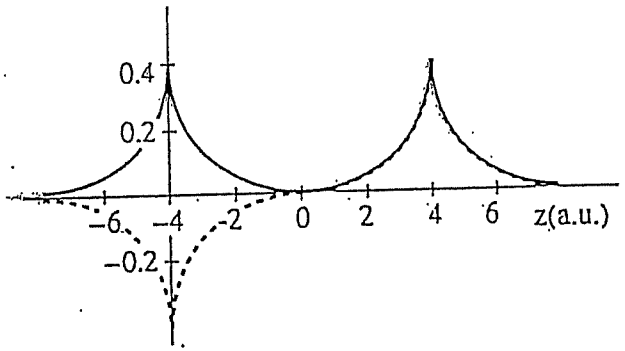
Closer

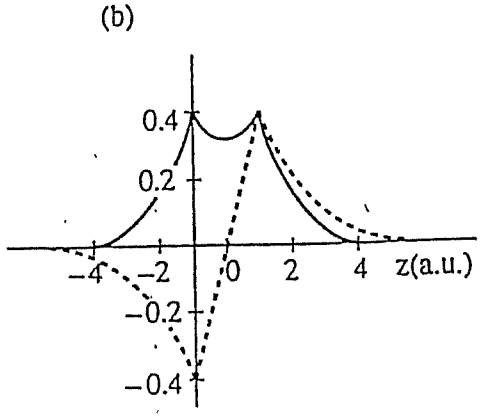
$|\psi_+|^2$ and $|\psi_-|^2$ are very different (energies are also different)

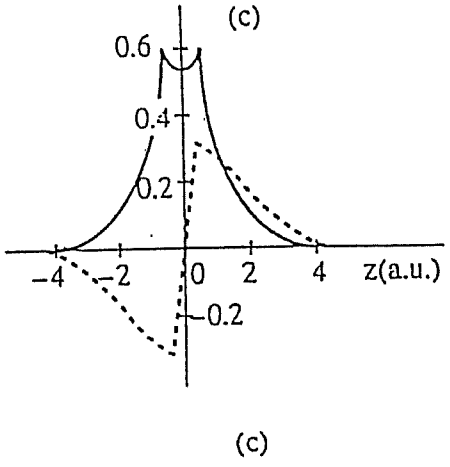
One can solve $\hat{\mathcal{H}}_{el}\,\psi_{el}(\vec{r}) = \mathcal{E}_{el}(R)\,\psi_{el}(\vec{r})$ numerically (exactly)

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

(3 separations)







Just like $\psi_{\pm}^{\circ}$

∴ LCAO makes good physical sense AND Works!

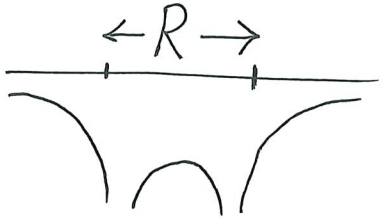
$\psi_{\pm}$: good agreement with exact solution

- 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

(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 $\mathcal{E}_-(R)$

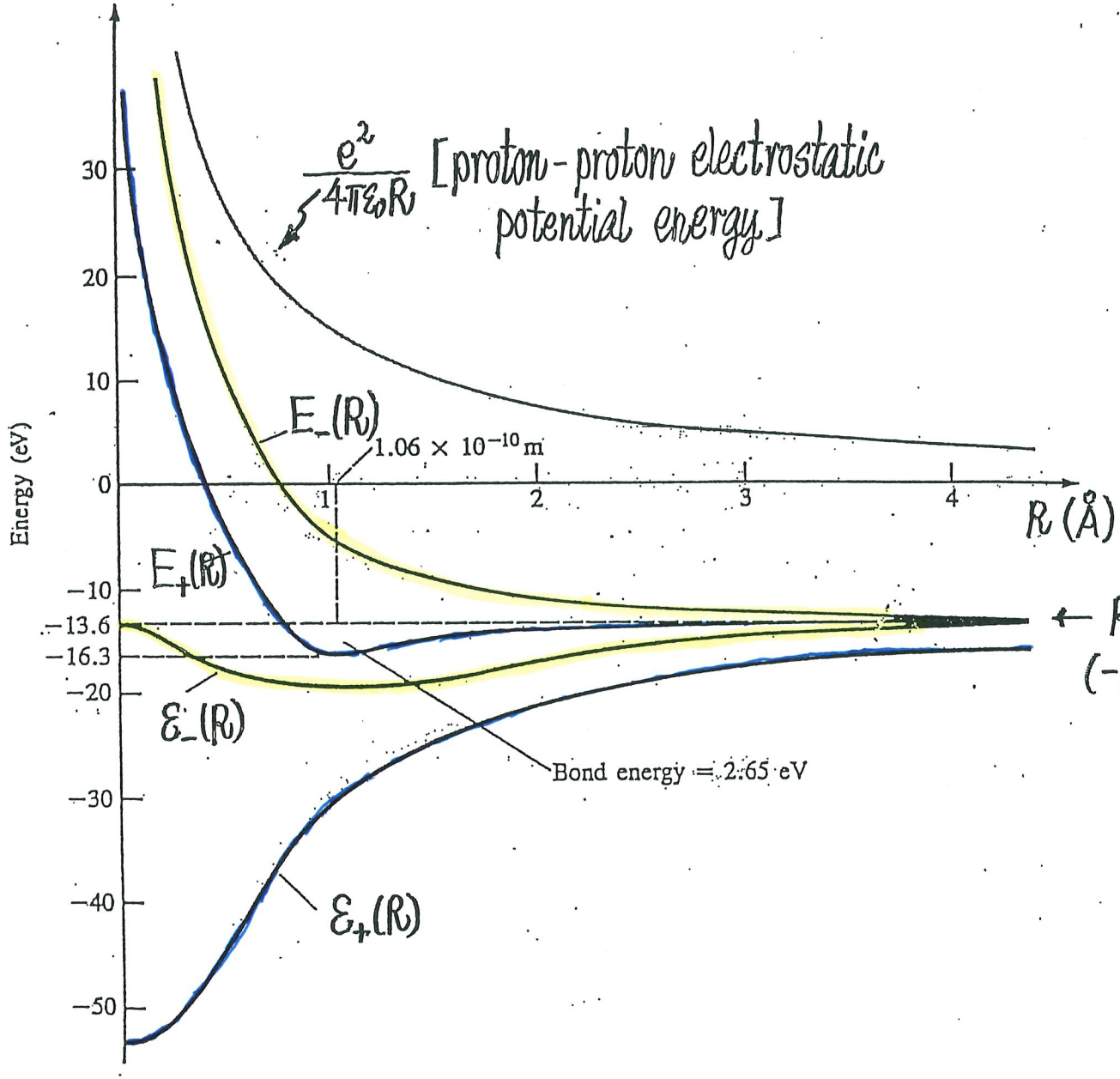
(ii) Expectation Value of $\hat{\mathcal{H}}$ w.r.t. ψ_+ and ψ_-

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

($\psi_\pm$ assumed normalized)

Same results [of course]

$$E_+(R) = \mathcal{E}_+(R) + \frac{e^2}{4\pi\varepsilon_0 R} \quad \text{and} \quad E_-(R) = \mathcal{E}_-(R) + \frac{e^2}{4\pi\varepsilon_0 R} \quad \text{(Eq. (18))} \quad \text{for } H_2^+ \text{ ion}$$



$\leftarrow R \to \infty$ (−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

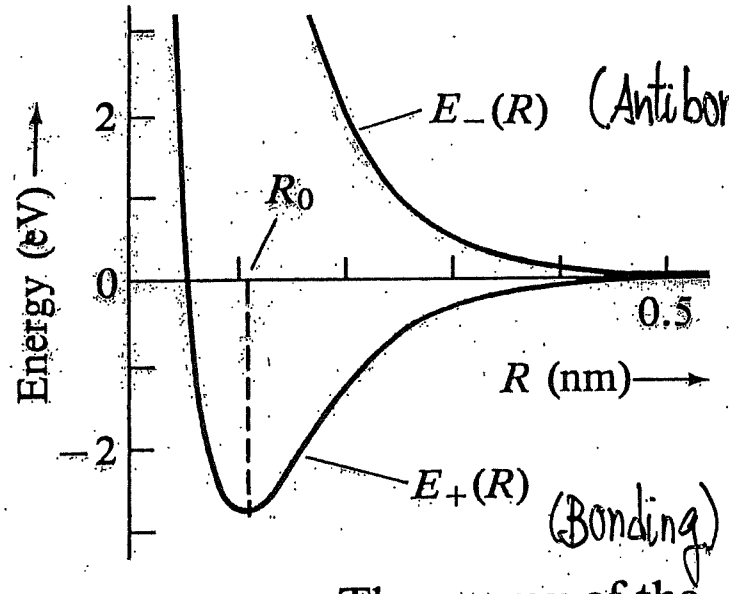
$= 1.06$ Å

$B = 2.65$ eV

[relative to well separated case]

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

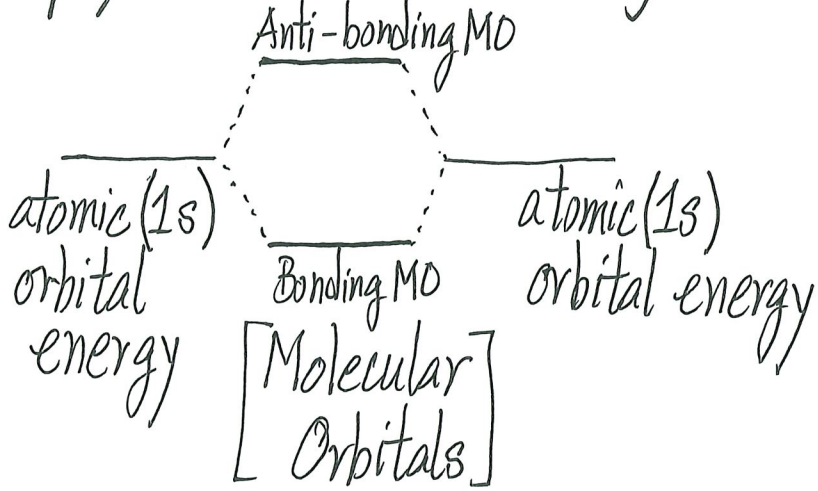
← Note: we shifted the energy axis so that $E(R\to\infty)=0$

- 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>"
- <u>the name</u> carries over to cases <u>beyond</u> H_2^+ ion and H_2 molecule

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

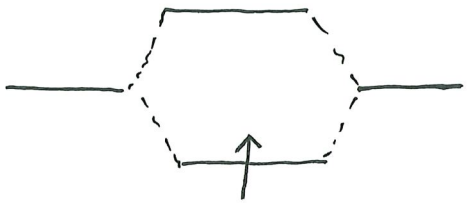
Bonding MO

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
(only 1 electron)



↓
↑ Gain energy compared with

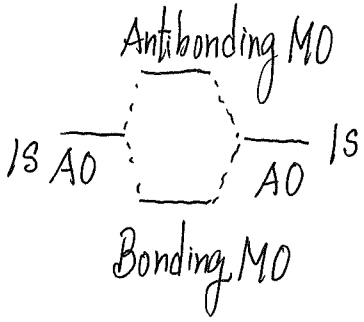
$\underbrace{H}_{\text{neutral atom}} + \underbrace{p}_{\text{a proton far away}}$

≈ -13.6 eV

$\therefore$ H_2^+ can be formed

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!) ε — ε $\updownarrow |\Delta|$

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 ("$\wedge\wedge$" integral), but not big.

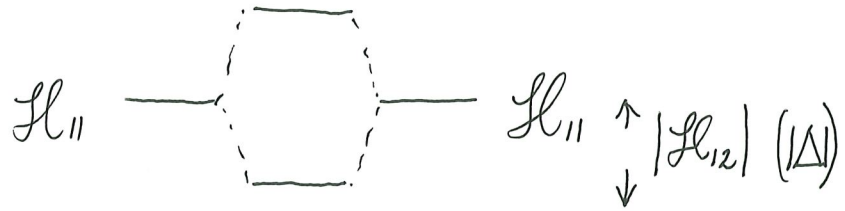
So $S_{12} \approx 0 \approx S_{21}$. $\mathcal{H}_{11} = \mathcal{H}_{22}$ (due to "AA" type molecule)

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

Good

$$\begin{pmatrix} \mathcal{H}_{11} - E & \mathcal{H}_{12} \\ \mathcal{H}_{21}^{*} & \mathcal{H}_{11} - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \Rightarrow \underbrace{\begin{pmatrix} \mathcal{H}_{11} & \mathcal{H}_{12} \\ \mathcal{H}_{21}^{*} & \mathcal{H}_{11} \end{pmatrix}}_{\text{want to get eigenvalues } E} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

Δ : $\mathcal{H}_{12}$; Δ^{*} : $\mathcal{H}_{21}^{*}$



∴ It is $\mathcal{H}_{12}$ doing the pushing (mixing)

↑ responsible for lowering Bonding MO energy

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

$$\psi_{trial} = c_1 \overbrace{\phi_{1s}(\vec{r} - \vec{R}_A)}^{\text{"1"}} + c_2 \overbrace{\phi_{1s}(\vec{r} - \vec{R}_B)}^{\text{"2"}}$$

"1": left-side nucleus; "2": right-side nucleus

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

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

different centers

complicated! (many terms)

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 NOT have classical EM interpretation (entirely quantum!)

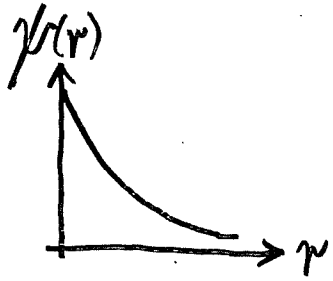
"More quantum" than simply needed the Schrödinger Equation

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

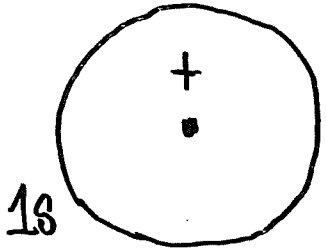
† Note: Don't see factors like $e\phi_{1S}^{*}(\vec{r}-\vec{R}_A)\phi_{1S}(\vec{r}-\vec{R}_A) = e|\phi_{1S}(\vec{r}-\vec{R}_A)|^2$ here (charge density)!

Other Pictorial Representations and Notations

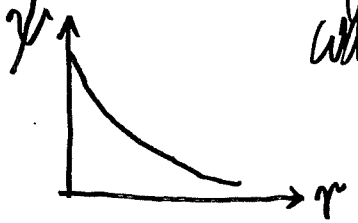
Recall 1s state: $\psi(r,\theta,\phi) \sim e^{-r/a_B}$ — no θ,ϕ dependence (ψ is spherically symmetric)



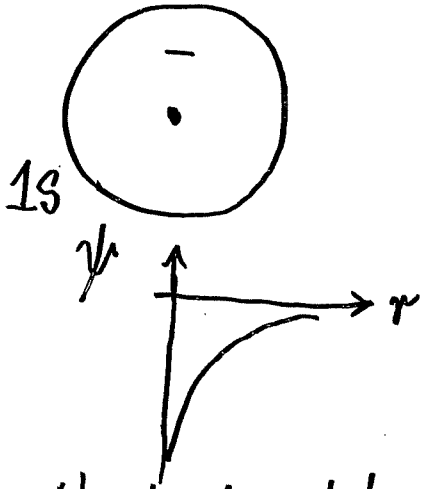
Since it is spherically symmetric, we can represent it as:



sign "+" ⇒ sign of wavefunction



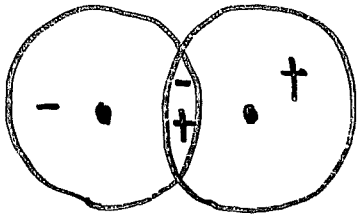
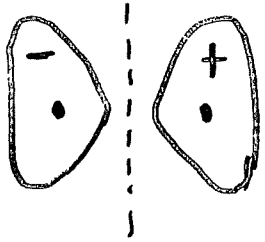
Atomic 1s states



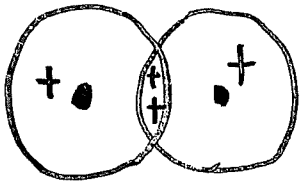
Atomic 1s states

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

nodal plane

$\psi_- \propto \phi_1 - \phi_2$ Anti-bonding   $\sigma^* 1s$

"*" - anti-bonding

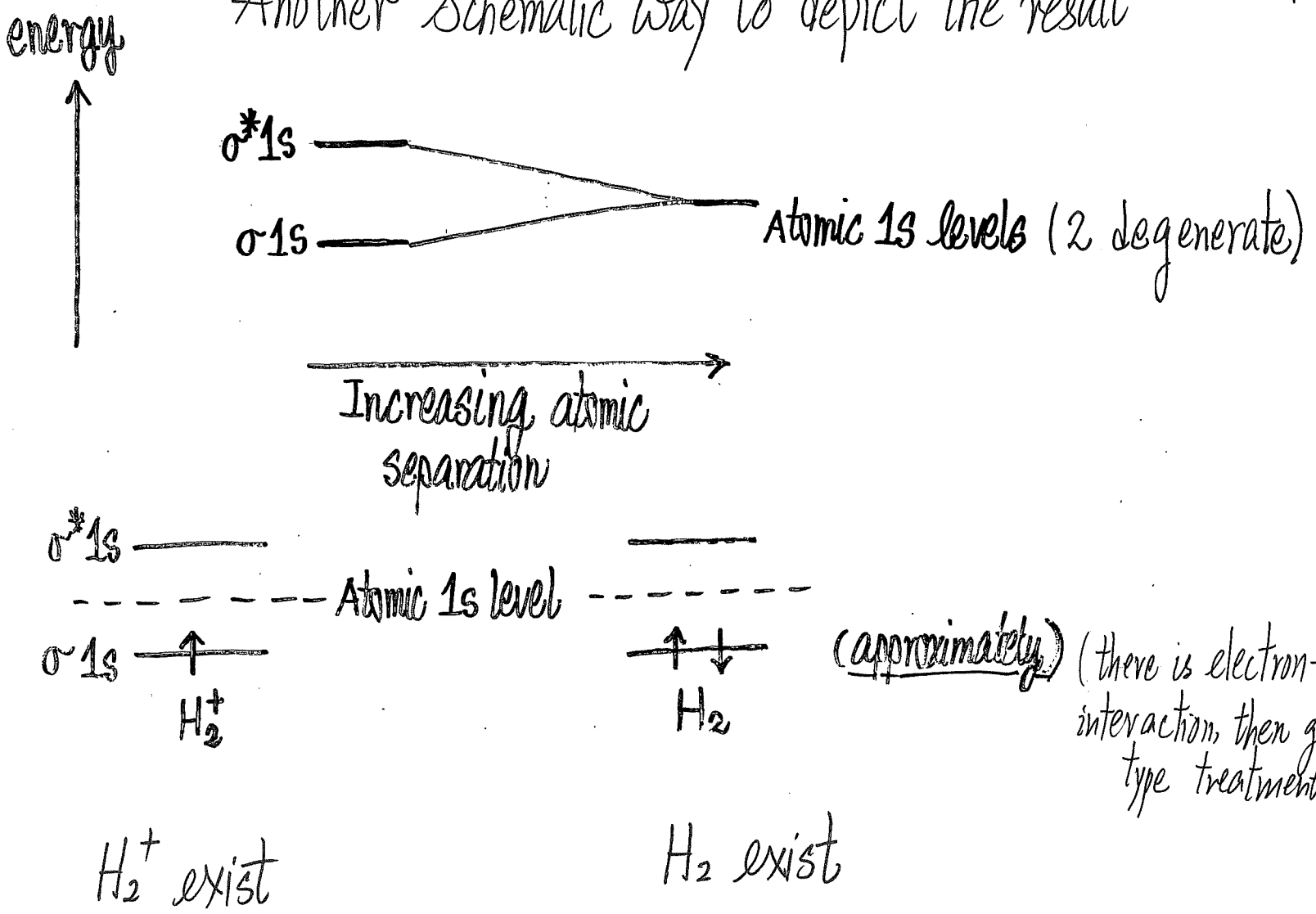
$\psi_+ \propto \phi_1 + \phi_2$ Bonding   $\sigma 1s$

In terms of Atomic 1s states | Molecular states | Notation

σ-bond: What is it in QM?

- a bond connects two nuclei $\Rightarrow$ 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



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!

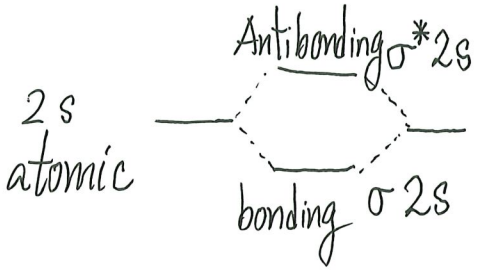
Including 1s, 2s AO's from left and right atoms

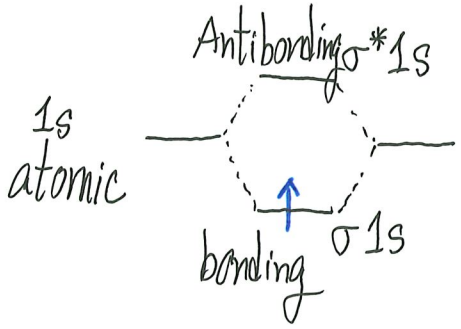
$$\psi_{trial} = C_{1s,L}\phi_{1s,L} + C_{2s,L}\phi_{2s,L} + C_{1s,R}\phi_{1s,R} + C_{2s,R}\phi_{2s,R}$$

$\Rightarrow$ 4 x 4 matrix problem

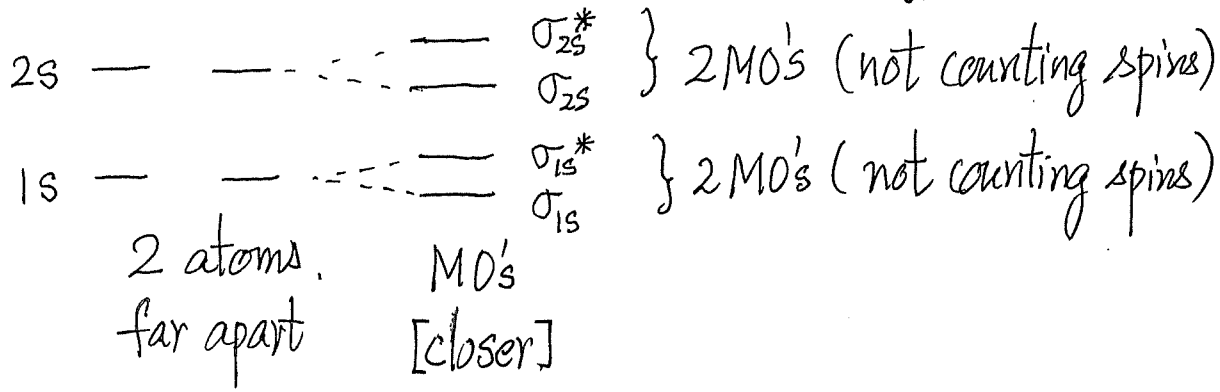
$\Rightarrow$ 4 eigenvalues

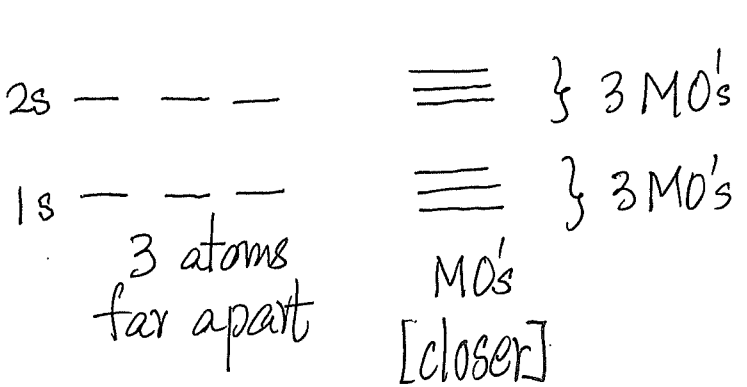
H_2^+

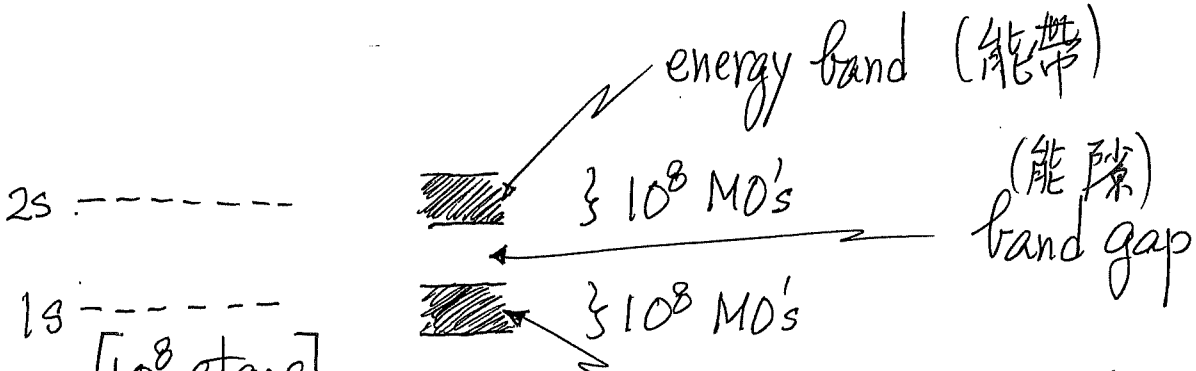




From MO's in Molecules to Energy Bands in Solids







come together

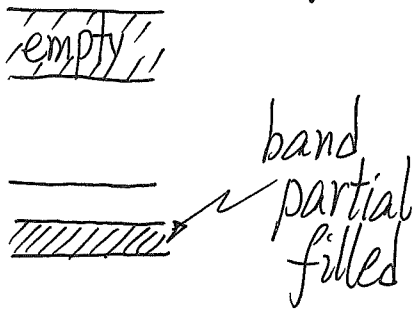
⇒ Solid state physics

↳ 10^{23} atoms/cm^3

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

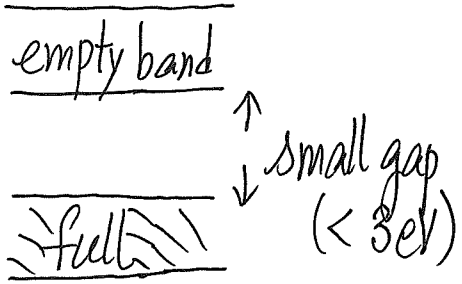
- Big Consequences from little new physics
- Solids: 10^{23} electrons (per cm^3) to fill into <u>electronic states</u> in bands

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



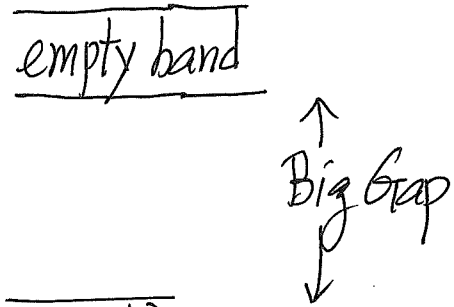
<u>Conductor (Metal)</u>

(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!