PHYS 4410

Quantum Mechanics 2

Spring 2023

Lecture 23

The Born-Oppenheimer approximation

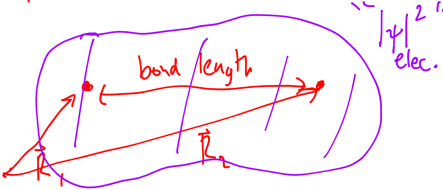
March 15

Today: covalent bond / hybrid orbitals

Eg. H_2^- (hydrogen molecule ion):

$$H = \underbrace{\frac{\vec{P}_1^{\,2}}{2M} + \frac{\vec{P}_2^{\,2}}{2M}}_{\text{proton: mass } M} + \frac{e^2}{4\pi\varepsilon_0 |\vec{R}_1 - \vec{R}_2|} + \underbrace{\frac{\vec{p}^{\,2}}{2m}}_{\substack{\text{mass } m \\ \text{of electron}}} - \frac{e^2}{4\pi\varepsilon_0 |\vec{r} - \vec{R}_1|} - \frac{e^2}{4\pi\varepsilon_0 |\vec{r} - \vec{R}_2|}$$

Expect: e^- is "shared" btwn two protons



Key idea:

large dimensionless ...

$$\frac{M}{m} \sim 1800$$

$\boxed{2}$ If $M \to \infty$ ... then

$$H_{el} = \frac{e^2}{4\pi\epsilon_0|\vec{R}_1-\vec{R}_2|} + \frac{\vec{p}^2}{2m} - \frac{e^2}{4\pi\epsilon_0|\vec{r}-\vec{R}_1|} - \frac{e^2}{4\pi\epsilon_0|\vec{r}-\vec{R}_2|}$$

H_{el} does not depend on $\vec{P}$:

simultaneously diagonalize $\left\{ \begin{array}{l} [H_{el}, \vec{R}_1] = [H_{el}, \vec{R}_2] = 0 \\ [\vec{R}_1, \vec{R}_2] = 0. \end{array} \right.$

$\vec{R}_1, \vec{R}_2$: fixed constants.

Born-Oppenheimer approximation:

Step 1:

$$E_{eff}(\vec{R}_1,\vec{R}_2)\,\underbrace{\psi_{el}(\vec{r};\vec{R}_1,\vec{R}_2)} = H_{el}(\vec{R}_1,\vec{R}_2)\,\psi_{el}(\vec{r};\vec{R}_1,\vec{R}_2)$$

$(\vec{R}_1,\vec{R}_2)$
$\downarrow$

Step 2:

$$H = \frac{\vec{P}_1^{\,2}}{2M} + \frac{\vec{P}^2}{2M} + H_{el} \ldots$$

$$\psi_{tot}(\vec{r},\vec{R}) = \psi_{ion}(\vec{R})\,\psi_{el}(\vec{r};\vec{R})$$

$$H[\psi_{ion}\psi_{el}] = \left[E_{eff}(\vec{R})\,\psi_{el}\right]\psi_{ion} + \left[\frac{\vec{P}_1^{\,2}}{2M} + \frac{\vec{P}^2}{2M}\psi_{ion}\right]\psi_{el}$$

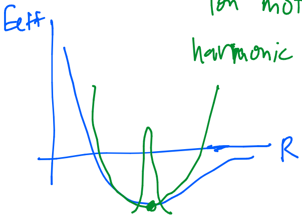
$$\cancel{+\ \psi_{ion}\left[\frac{\vec{P}_1^{\,2}}{2M} + \frac{\vec{P}_2}{2M}\right]\psi_{el}} \rightarrow \left[\frac{\partial}{\partial R}\psi_{el}\right]\frac{1}{M} \sim \frac{1}{a_B}\frac{1}{M} \sim \frac{m}{M} \ll 1$$

$\boxed{3}$

$$H\psi_{el}\psi_{ion} = \underbrace{\left[\frac{\vec{P}_1^2+\vec{P}_2^2}{2M}\psi_{ion}\right]\cdot\cancel{\psi_{el}} + \left(E_{eff}(\vec{R})\psi_{ion}\right)\cdot\cancel{\psi_{el}} = E\,\psi_{ion}\cancel{\psi_{el}}}_{\text{equations for just ions!}}$$

Because ions have large M...

ion motion ≈ harmonic oscillation



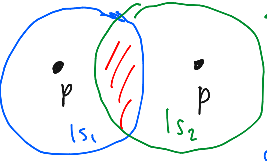
Interesting dynamics / ψ is associated to ψ_{el}

Main problem: $H_{el}\,\psi_{el} = E_{eff}(\vec{R})\,\psi_{el}$

classical problem: find minima of $E_{eff}(\vec{R})$

$\boxed{4}$ Even H_{el} can't be solved exactly...

Common ansatz: Linear Combo of Atomic Orbitals (LCAO)



$\psi_{1s_2} = \psi_{100}(\vec{r}-\vec{R}_2)$

$$|\sigma_\pm\rangle = A_\pm\Big[\,|1s_1\rangle \pm |1s_2\rangle\,\Big]$$

$\psi_{1s_1} = \psi_{\underset{n\,l\,m}{100}}(\vec{r}-\vec{R}_1)$ ← closed form...

Caveat: $A_\pm \neq 1/\sqrt{2}$ b/c $\langle 1s_1 | 1s_2\rangle \neq 0$.

Variational methods: $E_{\pm,\text{eff}}(R) = \langle \sigma_\pm | H_{el} | \sigma_\pm \rangle$

[analytically done in Tong... follow lec 2]

negative energy... stable

covalent bond

$\boxed{5}$ What happens if $H_2^- \longrightarrow H_2$ (2 protons / 2 el)?

Proceed w/ variational calculation:

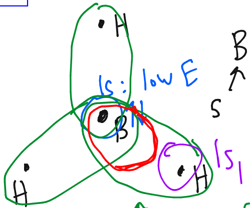
$$|\psi\rangle = |\sigma_+ \sigma_+\rangle \otimes \frac{|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle}{\sqrt{2}}$$

pick best value of R

true: ≈ -0.17 eV

Calculate $\langle\psi|H_{el}|\psi\rangle \approx \underbrace{-0.1 \text{ eV}}_{\text{more stable to have } H_2 \text{ rather than } H + H} - 2 \cdot 13.6 \text{ eV}$

$\boxed{6}$ Much of quantum chemistry ... follows from these ideas.



$\underset{S}{B}\,\underset{3\cdot 1}{H_3}$

$6 = 3\cdot 2$

$\cancel{8}$ unpaired electrons...

$$\frac{|p_x\rangle \pm i|p_y\rangle}{\sqrt{2}} = |\overset{n}{2}\ \overset{\ell}{1}\ \overset{m}{\pm 1}\rangle$$

Goal: find LCAO ansatz for 3 covalent bonds.

Theory of symmetry:
"sp^2 hybrid orbital"

$$\begin{cases} |2sp^2_1\rangle = a_1|2s\rangle + a_2|2p_x\rangle \\ |2sp^2_{2,3}\rangle = a_1|2s\rangle + a_2\left[\pm\frac{\sqrt{3}}{2}|2p_y\rangle - \frac{1}{2}|2p_x\rangle\right] \end{cases}$$

Like before: $|\sigma_{1,2,3}\rangle = A_1\,|2sp^2_{1,2,3}\rangle + A_2\,|1s_{1,2,3}\rangle$

Lowest energy trial: $|\psi\rangle \sim$ antisymmetric... $[|1s_B\uparrow\rangle \otimes |1s_B\downarrow\rangle$

$\otimes|\sigma_1\uparrow\rangle \otimes |\sigma_1\downarrow\rangle \otimes|\sigma_2\uparrow\rangle \otimes|\sigma_2\downarrow\rangle \otimes|\sigma_3\uparrow\rangle \otimes|\sigma_3\downarrow\rangle$