

## Lecture 22

Last time, applied variational method to He atom

Today look at  $H_2^+$  molecular ion

Compare: He:  $2e^-$ , 1 proton

$H_2^+$ :  $1e^-$ , 2 proton

Similar 3-body situation, but mass difference significant

Hamiltonian: Protons at  $\vec{R}_1, \vec{R}_2$  mass  $M$   
 electron at  $r$  mass  $m$

$$H = -\frac{\hbar^2}{2M} (\nabla_{\vec{R}_1}^2 + \nabla_{\vec{R}_2}^2) - \frac{\hbar^2}{2m} \nabla_r^2 - \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{|\vec{r}-\vec{R}_1|} + \frac{1}{|\vec{r}-\vec{R}_2|} - \frac{1}{|\vec{R}_1-\vec{R}_2|} \right)$$

We haven't normally worried about QM of nuclear motion

$$M \approx 2000 m$$

$\Rightarrow$  momentum much larger

$\Rightarrow R_1, R_2$  better localized via  $\Delta x \Delta p \approx \hbar$

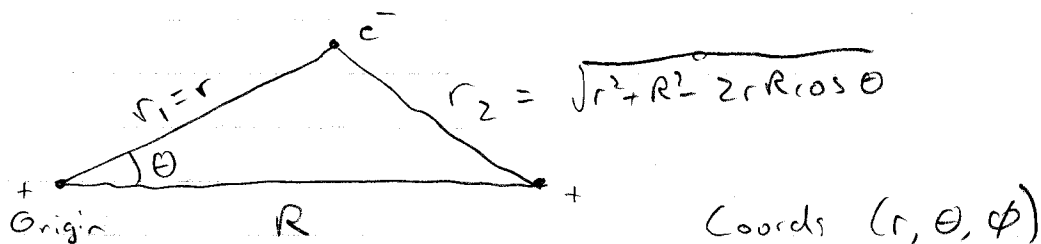
So assume nuclei at definite positions  $R_1, R_2$

Only treat electron using QM

Still need to know what  $R_1, R_2$  are

Specifically,  $H$  depends on  $R = |\vec{R}_1 - \vec{R}_2|$

$$H \rightarrow -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{r_1} + \frac{1}{r_2} - \frac{1}{R} \right)$$



Idea: treat  $R$  as variational parameter

Need trial  $\psi$

If  $R \gg a$ , expect  $\psi_{gs} \sim \psi_{100}(r) = \psi_0(r) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}$

But  $e^-$  could be on other proton, so use

$$\psi = A [\psi_0(r_1) + \psi_0(r_2)]$$

Step 1: Normalize

$$\begin{aligned} 1 &= \int |\psi|^2 d^3r \\ &= |A|^2 \int |\psi_0(r_1)|^2 + |\psi_0(r_2)|^2 + 2\psi_0(r_1)\psi_0(r_2) d^3r_1 \end{aligned}$$

Know  $\int |\psi_0(r_1)|^2 d^3r_1 = \int |\psi_0(r_2)|^2 d^3r_2 = 1$

3rd term gives overlap integral

$$\begin{aligned} I &\equiv \int \psi_0(r_1)\psi_0(r_2) d^3r_1 \\ &= \frac{1}{\pi a^3} \int e^{-(r_1+r_2)/a} d^3r_1 \\ &= \frac{1}{\pi a^3} \int e^{-r/a} e^{-\frac{1}{a}\sqrt{r^2+R^2-2rR\cos\theta}} r^2 \sin\theta dr d\theta d\phi \end{aligned}$$

Problem has several integrals like this

Book does this one, get

$$I = e^{-R/a} \left[ 1 + \frac{R}{a} + \frac{1}{3} \left( \frac{R}{a} \right)^2 \right]$$

We'll show you a different one shortly

We get normalization  $A = \frac{1}{\sqrt{2(I+1)}}$

Step 2: Calculate  $\langle \psi | H | \psi \rangle$

as usual, use tricks to make it easier

$$\begin{aligned} H\psi &= A \left[ -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{r_1} + \frac{1}{r_2} - \frac{1}{R} \right) \right] [\psi_0(r_1) + \psi_0(r_2)] \\ &= A \left\{ \left[ E_1 - \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{r_2} - \frac{1}{R} \right) \right] \psi_0(r_1) + \left[ E_1 - \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{r_1} - \frac{1}{R} \right) \right] \psi_0(r_2) \right\} \\ &= \left( E_1 + \frac{e^2}{4\pi\epsilon_0} \frac{1}{R} \right) \psi - A \frac{e^2}{4\pi\epsilon_0} \left[ \frac{1}{r_2} \psi_0(r_1) + \frac{1}{r_1} \psi_0(r_2) \right] \end{aligned}$$

$$\begin{aligned} \text{So } \langle H \rangle &= E_1 + \frac{e^2}{4\pi\epsilon_0} \frac{1}{R} - A \frac{e^2}{4\pi\epsilon_0} \left[ \langle \psi | \frac{1}{r_2} | \psi_0(r_1) \rangle \right. \\ &\quad \left. + \langle \psi | \frac{1}{r_1} | \psi_0(r_2) \rangle \right] \end{aligned}$$

First term:

$$\begin{aligned} \langle \psi | \frac{1}{r_2} | \psi_0(r_1) \rangle &= A \left[ \langle \psi_0(r_1) | \frac{1}{r_2} | \psi_0(r_1) \rangle \right. \\ &\quad \left. + \langle \psi_0(r_2) | \frac{1}{r_2} | \psi_0(r_1) \rangle \right] \\ &= A \left[ \langle \psi_0(r_1) | \frac{1}{r_2} | \psi_0(r_1) \rangle + \langle \psi_0(r_1) | \frac{1}{r_1} | \psi_0(r_2) \rangle \right] \end{aligned}$$

Symmetry  $r_1 \leftrightarrow r_2$

$$= \frac{A}{a} [D + X]$$

$$\text{for } D = a \langle \psi_0(r_1) | \frac{1}{r_2} | \psi_0(r_1) \rangle$$

$$X = a \langle \psi_0(r_1) | \frac{1}{r_1} | \psi_0(r_2) \rangle$$

For 2<sup>nd</sup> term in  $H$ , have

$$\langle \psi | \frac{1}{r_1} | \psi_0(r_2) \rangle$$

$$= A [\langle \psi_0(r_1) | \frac{1}{r_1} | \psi_0(r_2) \rangle + \langle \psi_0(r_2) | \frac{1}{r_1} | \psi_0(r_2) \rangle]$$

$$\hookrightarrow = \langle \psi_0(r_1) | \frac{1}{r_2} | \psi_0(r_1) \rangle$$

$$= \frac{A}{a} [X + D]$$

So

$$\langle H \rangle = E_1 + \frac{e^2}{4\pi\epsilon_0 R} - 2A^2 \frac{e^2}{4\pi\epsilon_0 a} (D + X)$$

$$\langle H \rangle = E_1 \left( 1 - \frac{2a}{R} + 2 \frac{D+X}{1+I} \right)$$

Recall  $I = e^{-x} \left( 1 + x + \frac{x^2}{3} \right)$   $x = \frac{r}{R}$

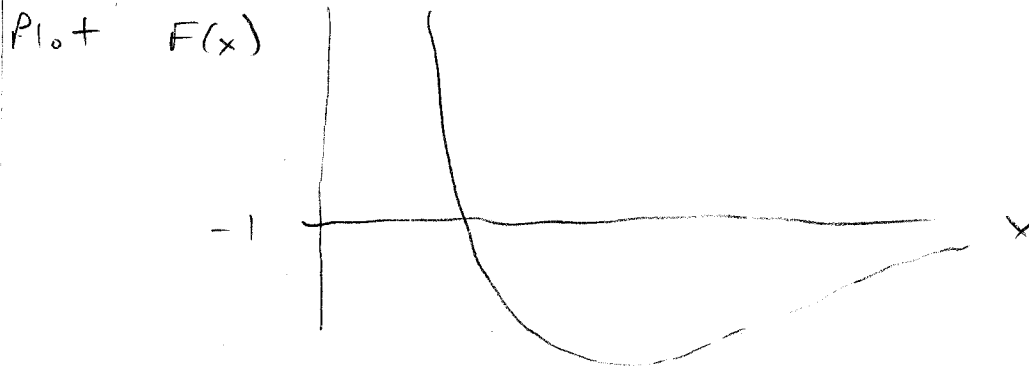
Find  $D = \frac{1}{x} - \left( 1 - \frac{1}{x} \right) e^{-2x}$

$$X = e^{-x} (1+x)$$

Joe will show calculation of  $D$

Write  $\langle H \rangle = -E_1 F(x)$

$$F(x) = -1 + \frac{2}{x} \left[ \frac{(1 - \frac{2}{3}x^2)e^{-x} + (1+x)e^{-2x}}{1 + (1+x + \frac{1}{3}x^2)e^{-x}} \right]$$



Get minimum numerically  $X_{min} = 2.4a$   
 $E_{min} = E_1 - 1.8eV$

So molecular binding energy is 1.8eV

Experimentally, find  $X_{min} = 2.0a$   
 $E_{min} = E_1 - 2.8eV$

Not great agreement, but calculation does prove that bound state should exist

Call plot of  $\langle H \rangle$  vs  $R$  = "molecular potential"

Use it to think about molecular dynamics as well  
 use  $\langle H \rangle(R) = V(R)$  = potential for nuclear motion

Can even quantize  $e$ , and treat nuclei with QM after all, but separately from  $e^-$  motion

Idea:  $e^-$  moves much faster than protons

To electron, protons seem to sit still

To protons,  $e^-$  instantaneously adjusts to give  $U(R)$

Approach called Born-Oppenheimer approximation  
underpinning of quantum chemistry