

# Physics 472 Lecture 17

## The $H_2^+$ Ion (simplest molecule)

$$H = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{|\vec{r} - \vec{R}_1|} - \frac{e^2}{|\vec{r} - \vec{R}_2|} + \frac{e^2}{|\vec{R}_1 - \vec{R}_2|}$$

The Schrödinger equation can be solved using elliptical coordinates, but let us use the variational approach, which is more instructive.

Trial wave function

$$\Psi(\vec{r}) = c_1 \overbrace{\Psi_{100}(\vec{r} - \vec{R}_1)}^{\Psi_1(\vec{r})} + c_2 \overbrace{\Psi_{100}(\vec{r} - \vec{R}_2)}^{\Psi_2(\vec{r})}$$

$\Psi_{100}(\vec{r}) =$  Hydrogenic ground state

$$= \sqrt{\frac{1}{\pi a_0^3}} e^{-|\vec{r}|/a_0}$$

Since the potential is symmetric } 2  
under reflection about a plane  
perpendicular to the molecular axis,  
passing through the midpoint  
 $\frac{1}{2}(\vec{R}_1 + \vec{R}_2)$ , more appropriate  
trial functions are those that  
reflect this symmetry, namely,  
even- and odd-parity combinations  
of  $\psi_1$  and  $\psi_2$ :

$$\psi_{\pm}(\vec{r}) = C_{\pm} [\psi_1(\vec{r}) \pm \psi_2(\vec{r})]$$

This defines a molecular orbital,  
which is a linear combination  
of atomic orbitals (LCAO).

The normalization factors are  $\sqrt{3}$

$$\langle \psi_{\pm} | \psi_{\pm} \rangle = |C_{\pm}|^2 (\langle 111 \rangle + \langle 212 \rangle \pm 2 \langle 112 \rangle)$$

since  $\langle 112 \rangle = \langle 112 \rangle^* \in \mathbb{R}$ .

$$\langle \psi_{\pm} | \psi_{\pm} \rangle = |C_{\pm}|^2 (2 \pm 2S(R)),$$

where  $R \equiv |\vec{R}| = |\vec{R}_1 - \vec{R}_2|$  and

$$S = \langle 112 \rangle = \frac{1}{\pi a_0^3} \int d^3r e^{-\frac{|\vec{r}|}{a_0} - \frac{|\vec{r} - \vec{R}|}{a_0}}$$

is the overlap integral. This

integral is most easily calculated

using elliptical coordinates

$\rho, \sigma, \phi$ :

$$\rho = \frac{1}{R} (|\vec{r}| + |\vec{r} - \vec{R}|)$$

$$\sigma = \frac{1}{R} (|\vec{r}| - |\vec{r} - \vec{R}|)$$

$$\int d^3r = \int_1^\infty \rho \, d\rho \int_{-1}^1 \sigma \, d\sigma \int_0^{2\pi} d\phi \frac{R^3}{8} (\rho^2 - \sigma^2)$$

(see advanced calculus text)

$$\Rightarrow S = \frac{1}{8\pi} \frac{R^3}{a_0^3} \int_1^\infty e^{-\frac{R}{a_0} \rho} \rho \, d\rho \int_{-1}^1 (\rho^2 - \sigma^2) d\sigma \int_0^{2\pi} d\phi$$

$$= \left[ 1 + \frac{R}{a_0} + \frac{R^2}{3a_0^2} \right] e^{-R/a_0}$$

$$\langle H \rangle = \frac{1}{2 \pm 2S} \left[ \langle 1|H|1 \rangle + \langle 2|H|2 \rangle \pm 2 \langle 1|H|2 \rangle \right]$$

$$\langle H \rangle = \frac{\langle 1 | H | 1 \rangle \pm \langle 1 | H | 2 \rangle}{1 \pm S} \quad [5]$$

$$\langle 1 | H | 1 \rangle = \int d^3r \psi_1^*(\vec{r}) \left[ -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{|\vec{r}|} - \frac{e^2}{|\vec{r}-\vec{R}|} + \frac{e^2}{R} \right] \psi_1(\vec{r})$$

$$= E_1 + \frac{e^2}{R} - e^2 \int d^3r \frac{|\psi_1(\vec{r})|^2}{|\vec{r}-\vec{R}|}$$

$$\frac{1}{\pi a_0^3} \int d^3r \frac{e^{-\frac{2|\vec{r}|}{a_0}}}{|\vec{r}-\vec{R}|} = \frac{1}{R} \left[ 1 - e^{-\frac{2R}{a_0}} \left( 1 + \frac{R}{a_0} \right) \right]$$

(using elliptical coordinates)

$$\Rightarrow \langle 1 | H | 1 \rangle = E_1 + \frac{e^2}{R} \left( 1 + \frac{R}{a_0} \right) e^{-\frac{2R}{a_0}}$$

$$= \langle 2 | H | 2 \rangle = \text{"direct integral"}$$

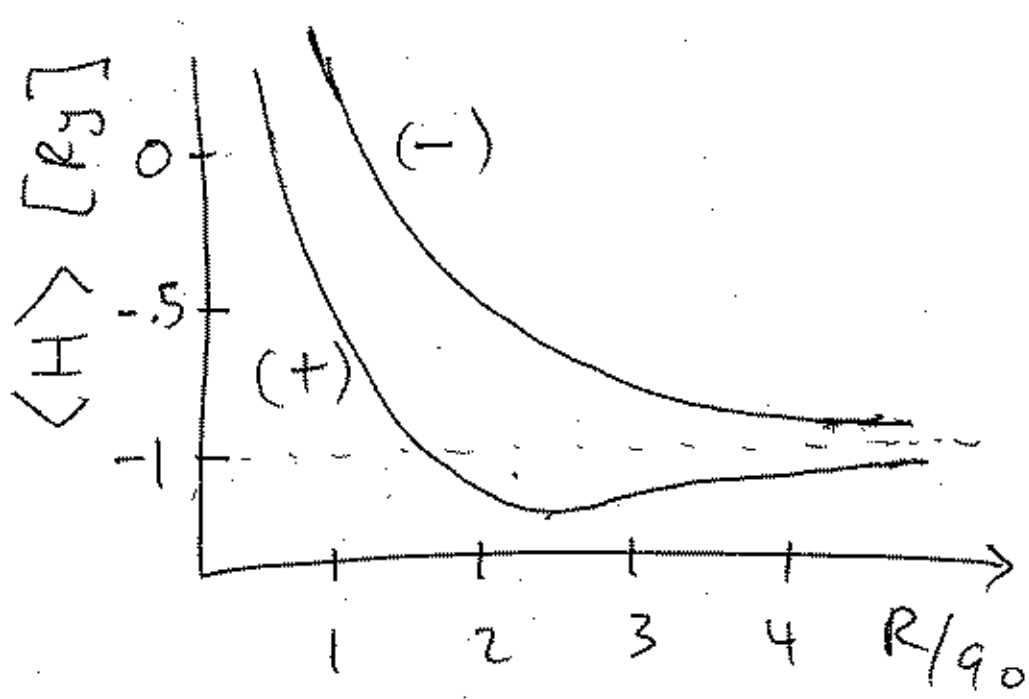
$$\langle 11 | H | 22 \rangle = \left( E_1 + \frac{e^2}{R} \right) S$$

$$- e^2 \int d^3r \frac{\psi_1^*(\vec{r}) \psi_2(\vec{r})}{|\vec{r} - \vec{R}|}$$

"exchange integral"

$$= \left( E_1 + \frac{e^2}{R} \right) S - \frac{e^2}{a_0} \left( 1 + \frac{R}{a_0} \right) e^{-R/a_0}$$

Combining all the terms, we find



The even state has a minimum 7  
1.8 eV below  $E_1$ , occurring when

$$R = 2.4 a_0 = 1.3 \text{ \AA}.$$

On the other hand, the odd state has no minimum. The

even state is referred to as

the bonding orbital and

the odd state as the

antibonding orbital. The

antibonding orbital has a node

$$\text{at } \vec{r} = \frac{1}{2}(\vec{R}_1 + \vec{R}_2) \text{ and the}$$

force between the two protons

is repulsive:

$$F_{-} = - \frac{\partial \langle H \rangle}{\partial R} > 0$$

in the even state

on the other hand, the force between the two protons is attractive for  $R > 1.3 \text{ \AA}$ , with a short-range repulsion, leading to a bound state, the  $\text{H}_2^+$  molecular ion.

It is a covalent bond, with the electron shared equally by both protons.



Note that the experimental value of the binding energy is  $2.8 \text{ eV}$ , greater than the  $1.8 \text{ eV}$  resulting from our variational calculation. This

is not surprising, since a variational calculation overestimates the ground state energy.

Nonetheless, the variational calculation correctly predicts the existence of a bound state for a symmetric wavefunction.

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