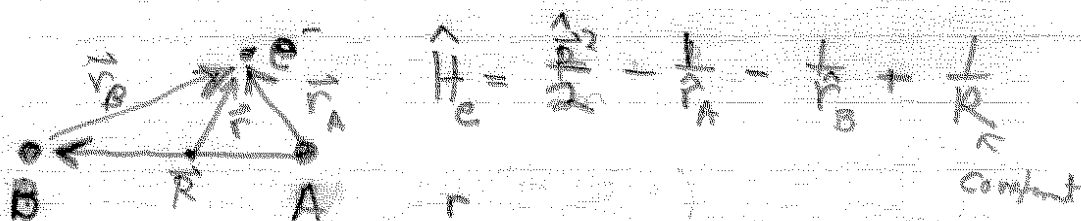


Physics 531

Lect 17: Molecular Hydrogen Ion

In order to understand the nature of molecular structure we begin with the simplest case: the molecular hydrogen ion consisting of two nuclei (protons) and one electron.



We seek the Born-Oppenheimer potential which can bind the nuclei into a molecule. It's one of the great triumphs of quantum mechanics that this can happen at all.

In order to gain a physical understanding of the mechanism for binding we will consider a succession of models.

Model 1: Neutral hydrogen perturbed by a proton. Though an asymmetric model, this will highlight some important physical mechanisms.

$$\hat{H}_e = \hat{H}_0 + \hat{H}_1, \quad \hat{H}_0 = \frac{\hat{p}^2}{2} - \frac{1}{r_A}$$

$$\hat{H}_1 = -\frac{1}{r_B} + \frac{1}{R}$$

Perturbation to ground-state $\begin{cases} E_H^{(0)} = -\frac{1}{2} \text{ a.u.} \\ \phi_H^{(0)} = \frac{1}{\sqrt{\pi}} e^{-r} \end{cases}$

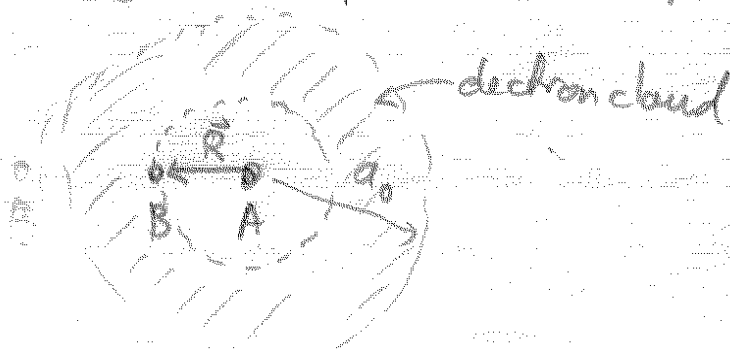
$$\Rightarrow E_{H-P^+}^{(1)} = E_H^{(0)} + \underbrace{\langle \phi_A^{(0)} | -\frac{1}{r_B} | \phi_A^{(0)} \rangle}_{\equiv J} + \frac{1}{R}$$

$$J = \int d^3r \left(\frac{-1}{|\vec{r} - \frac{\vec{B}}{2}|} \right) |\phi_H^{(0)}(\vec{r} + \frac{\vec{B}}{2})|^2$$

$$\Rightarrow J = \left[-\frac{1}{R} + e^{-2R} \left(1 + \frac{1}{R} \right) \right]$$

$$\Rightarrow \boxed{E_{H-P^+}^{(1)} = -\frac{1}{2} + \underbrace{e^{-2R} \left(1 + \frac{1}{R} \right)}_{\text{purely repulsive}}}$$

The electron cloud around proton-A is spherically symmetric:



The charge distribution outside R does not contribute. Inside R, shielding cannot produce attraction greater than ~~at~~ repulsion of nucleus \Rightarrow No binding in this model. Need covalent bonding component (electron "shared" between two nuclei)

Model 2: LCAO molecular orbitals.

Clearly model 1 was flawed from the get-go in that it treated nucleus A & B asymmetrically. We seek the R-dependent orbital (and eigenvalue) for a single electron in the field of two protons. This is known as a "molecular orbital" for an electron. For the case of a single electron we can in principle solve the Schrödinger equation numerically, with the help of a separation of variables in elliptical coordinates: (ξ, η, ϕ)

$$\xi = \frac{1}{R}(r_A + r_B), \quad \eta = \frac{1}{R}(r_A - r_B)$$

$$\Rightarrow \Psi(\xi, \eta, \phi) = F(\xi) G(\eta) e^{im\phi}$$

ODE's for $F(\xi)$ and $G(\eta)$.

This method not very generalizable, but useful here.

More generally one employs a method constructing molecular orbitals from a linear combination of atomic orbitals (LCAO) and then use the variation method to solve for the correct superposition.

Simple first ansatz for molecular ground state

$$\Psi(\vec{r}) = C_A \phi_{1s}(\vec{r}_A) + C_B \phi_{1s}(\vec{r}_B)$$

Electron in superposition of hydrogen 1s states

$$E[\psi] = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{(c_A^2 + c_B^2) \langle A | \hat{H} | A \rangle + 2c_A c_B \langle A | \hat{H} | B \rangle}{c_A^2 + c_B^2 + 2c_A c_B \langle A | B \rangle}$$

where $|A\rangle = |\phi_{1s}^A\rangle$ $|B\rangle = |\phi_{1s}^B\rangle$

$$\frac{\partial E[\psi]}{\partial c_A} = \frac{\partial E[\psi]}{\partial c_B} = 0$$

$$\Rightarrow [c_A^2 + c_B^2 + 2c_A c_B \langle A | B \rangle] (2c_A H_{AA} + 2c_B H_{AB}) - [c_A^2 + c_B^2] H_{AA} + 2c_A c_B H_{AB} (2c_A + 2c_B \langle A | B \rangle) = 0$$

$$\Rightarrow \boxed{c_A = \pm c_B}$$

two possible solutions

$$\phi_{\sigma_g} = N_g (\phi_{1s}^A(\vec{r}) + \phi_{1s}^B(\vec{r}))$$

$$\phi_{\sigma_u} = N_u (\phi_{1s}^A(\vec{r}) - \phi_{1s}^B(\vec{r}))$$

Symmetric / Antisymmetric combination

g = gerade u = ungerade

Both have (+) reflection symmetry

$$E_g = \frac{H_{AA} + H_{AB}}{1+S}, \quad E_u = \frac{H_{AA} - H_{AB}}{1-S}$$

H_{AA} is the result of model 1

$$= E_{1s} + \frac{e^2}{R} + J = E_{1s} + e^{-2R} \left(1 + \frac{1}{R}\right)$$

$$H_{AB} = \int d^3r \phi_{1s}(\vec{r}_A) (\hat{H}_e \phi_{1s}(\vec{r}_B))$$

$$= E_{1s} + \frac{e^2}{R} + K$$

$$J = \int d^3r \phi_{1s}(\vec{r}_A) \left(\frac{1}{r_B}\right)$$

Coulomb-integral

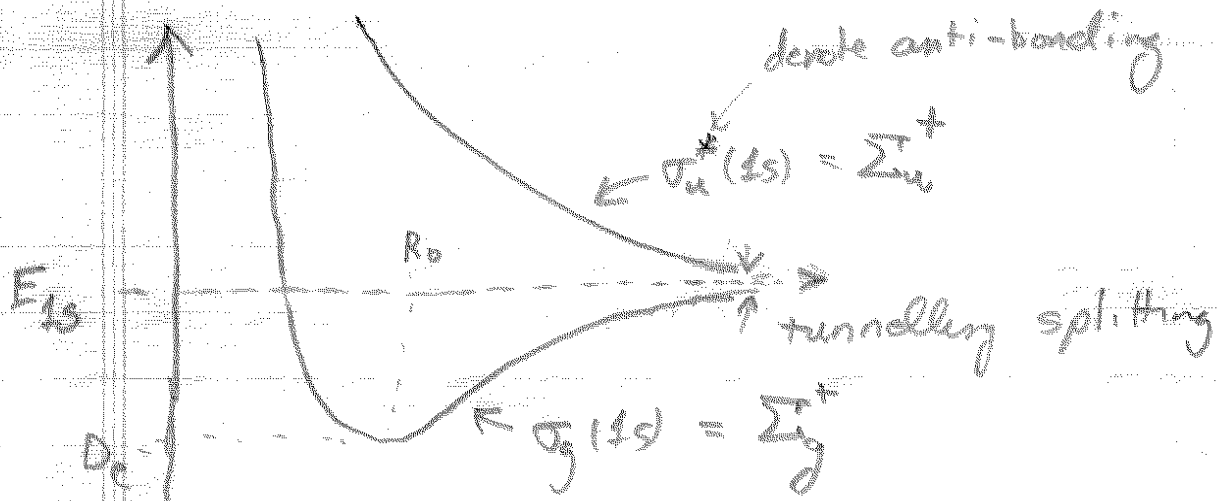
$$K = \int d^3r \phi_{1s}(\vec{r}_A) \phi_{1s}(\vec{r}_B) \left(-\frac{1}{r_B}\right)$$

"Resonance"

$$= -e^{-R} (1+R)$$

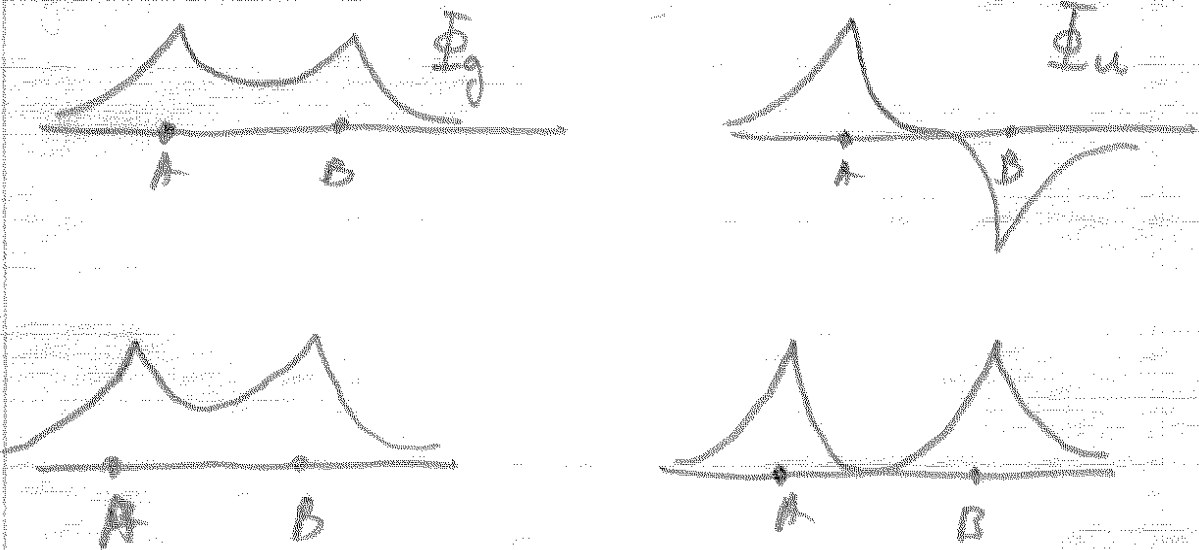
$$E_g = E_{1s} + \frac{1}{R} + \frac{J+K}{1+S}$$

$$= E_{1s} + \frac{1}{R} \frac{(1+R)e^{-2R} \pm (1-2R^2/2)e^{-R}}{1 \pm (1+R + \frac{R^2}{3})e^{-R}}$$



The σ_g orbital leads to a bonding configuration
 σ_u^* " " " " anti-bonding configuration

Wave function (along inter-nuclear axis)



Excess of electron charge between nuclei binds them together.

Covalent mechanism: Electron is "shared" between protons tunnelling

- Binding energy in this model:

Energy from min of B-O potential to E_{1s}

$$D_c^{\text{model}} = 0.065 \text{ au} = 1.77 \text{ eV}$$

• True value $D_c = 0.103 \text{ au} = 2.79 \text{ eV}$

- Equilibrium separation $R_0^{\text{model}} = 2.49 \text{ au} = 1.32 \text{ \AA}$

True value $R_0^{\text{true}} = 1.06 \text{ \AA}$

Break down of model

Limit $R \rightarrow 0$, united atom = He^+ .

We can take this into account by taking the effective nuclear charge to vary with R .

$$\text{Trial } \phi_{1s}(z(R), \vec{r}) = \sqrt{\frac{z(R)}{\pi}} e^{-z(R)r}$$

At each R , minimize w.r.t z

⇒ Excellent results (see Cohen-Tannoudji
Complement
G3E)