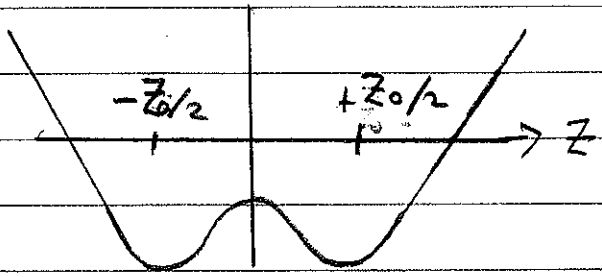
Physics 492
M. Gold

Spring 2010

Lecture 16: Covalent Bond

Approximate proton separation as fixed.
Potential seen by electrons in double-well:



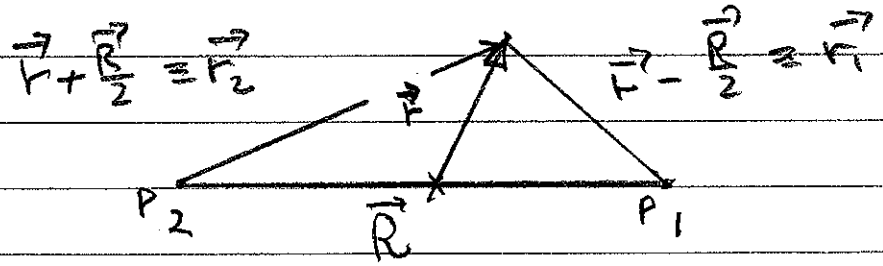
$$V(z) = \frac{m\omega^2}{2}\left(|z| - \frac{z_0}{2}\right)^2$$

Constant proton separation Z_0 justified by slow proton oscillations

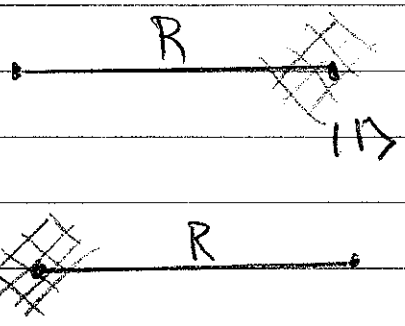
$$\frac{1}{2}m\omega^2 = \frac{1}{2}\left(\frac{m}{m_p}\right)m_p\omega^2$$

So expect $\omega_p \sim \sqrt{\frac{m}{m_p}}\,\omega$

Coordinate System:



perturbative approach: $H + p$



Exact solution for $R \gg a_0$

$$\langle \vec{r}_1 | 1 \rangle = \frac{1}{\sqrt{\pi a_0^3}} e^{-r_1/a_0}$$

$$\langle \vec{r}_2 | 2 \rangle = \frac{1}{\sqrt{\pi a_0^3}} e^{-r_2/a_0}$$

} degenerate unperturbed states

$$\hat{H} = \frac{\hat{p}^2}{2m} - \frac{e^2}{r_1} - \frac{e^2}{r_2} + \frac{e^2}{R}$$

H matrix:

$$\langle 1 | \hat{H} | 1 \rangle = \langle 2 | \hat{H} | 2 \rangle = H_{11} = H_{22} = E_0$$

$$\langle 1 | \hat{H} | 2 \rangle = \langle 2 | \hat{H} | 1 \rangle = H_{12} = H_{21} = -A$$

where $-A$ is energy due to tunneling across potential barrier separating states $|1\rangle, |2\rangle$.

Diagonalizing $[\hat{H}] = \begin{pmatrix} E_0, & -A \\ -A, & E_0 \end{pmatrix}$

solutions:

$E_I = E_0 - A$, $|I\rangle = \frac{1}{\sqrt{2}}(|1\rangle + |2\rangle)$ binding

$E_{II} = E_0 + A$, $|II\rangle = \frac{1}{\sqrt{2}}(|1\rangle - |2\rangle)$ non-binding

We have assumed $\langle 1|2\rangle = 0$ which is not correct.
Introduce overlap

$\Delta = \langle 1|2\rangle = \langle 2|1\rangle$ real, dimensionless

get (see HW)

$$E_I = \frac{1}{1+\Delta}(E_0 - A); \quad |I\rangle = \frac{1}{\sqrt{2+2\Delta}}(|1\rangle + |2\rangle)$$

$$E_{II} = \frac{1}{1-\Delta}(E_0 + A); \quad |II\rangle = \frac{1}{\sqrt{2-2\Delta}}(|1\rangle - |2\rangle)$$

Δ further lowers the ground state energy.
Following Pauling and Wilson,

$$J \equiv \int d^3r_1 \frac{e^2}{r_2} |\psi_1|1\rangle|^2 \propto \frac{e^2}{a_0}$$

with $E_1 \equiv$ H-atom ground state energy

$$\langle 1|\hat{H}|1\rangle = \langle 2|\hat{H}|2\rangle = E_1 - J + \frac{e^2}{R} = E_0$$

and

$$K \equiv \int d^3 r_1 \langle 2|r_1\rangle \frac{e^2}{r_2} \langle r_1|1\rangle$$

off diagonal (tunneling) terms are

$$\langle 2|\hat{H}|1\rangle = \Delta \cdot E_1 - K + \Delta \frac{e^2}{R} = -A$$

giving $A = K - \Delta\left(E_1 + \frac{e^2}{R}\right)$

then in terms of J, K

$$E_I = \frac{1}{1+\Delta}\left[E_1 + J + \frac{e^2}{R} - K + \Delta\left(E_1 + \frac{e^2}{R}\right)\right]$$

$$= E_1 + \frac{e^2}{R} - \left(\frac{J+K}{1+\Delta}\right)$$

$$E_{II} = E_1 + \frac{e^2}{R} - \left(\frac{J-K}{1-\Delta}\right)$$

for completeness, integrals are $\left(D \equiv \frac{R}{a_0}\right)$

$$\Delta = e^{-D}\left(1 + D + \tfrac{1}{3}D^2\right)$$

$$J = -\frac{e^2}{a_0}\left[-\frac{1}{D} + e^{-2D}\left(1 + \frac{1}{D}\right)\right]$$

$$K = \frac{e^2}{a_0} e^{-D}(1+\Delta)$$

where $\frac{e^2}{a_0} = \hbar c \alpha \left(\frac{mc\alpha}{\hbar}\right) = mc^2\alpha^2$

E_I is then a function of R and has a minimum @ R = 0.13 nm and value -15.4 eV

binding or dissociation=pulling the molecule apart into proton and hydrogen

binding energy is $-E_{bind} = E_I - E_1$

after dissociation, electron is bound to one of the protons

$E_{bind} = (-13.6\,eV) - (-15.4\,eV) = 1.8\,eV$

Exp value $R = 0.106$ nm $E_{bind} = 2.8$ eV

We have assumed wave functions are undistorted by presence of other proton.

Covalent bond is due to tunneling between degenerate states.