

Diatomic Molecules

Chem 2430

Full non-relativistic H for molecules

$$\hat{H} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \frac{\hbar^2}{2} \sum_\alpha \frac{1}{m_\alpha} \nabla_\alpha^2 + \sum_{\beta > \alpha} \frac{Z_\alpha Z_\beta e^2}{r_{\alpha\beta}} - \sum_\alpha \sum_i \frac{Z_\alpha e^2}{r_{i\alpha}} + \sum_{j > i} \frac{e^2}{r_{ij}}$$

i, j : electrons α, β : nuclei

Born-Oppenheimer approximation

Assumes that we can separate the electronic and nuclear degrees of freedom, since electrons move much faster than nuclei

For fixed nuclear positions

$$\hat{H}_{el} = \frac{-\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_\alpha \sum_i \frac{Z_\alpha e^2}{r_{i\alpha}} + \sum_{j > i} \frac{e^2}{r_{ij}}$$

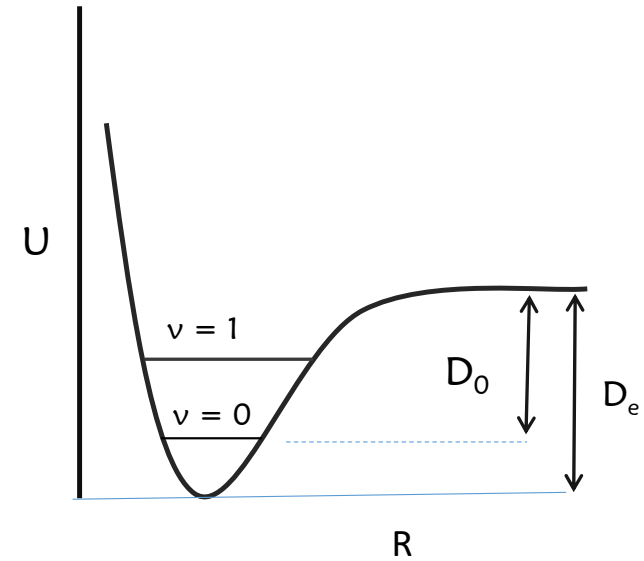
$$\hat{H}_{el} \psi_{el}^{(i)} = E_{el}^{(i)} \psi_{el}^{(i)}$$

$$U(R)^{(i)} + E_{el}^{(i)}(R) + V_{NN}(R)$$

$$\hat{H}_N = -\frac{\hbar^2}{2} \sum_\alpha \frac{1}{m_\alpha} \nabla_\alpha^2 + U(R)$$

V_{NN} represents the nuclear repulsion

Here R is used to represent the collection of all nuclear positions



Potential energy curve of a diatomic molecule

Lets revisit the nuclear part of the problem

$$\psi_{Nuc,int} = P(R) Y_\ell^m(\theta_N, \phi_N)$$

$$-\frac{\hbar^2}{2\mu} \left[P'' + \frac{2}{R} P' \right] + \frac{J(J+1)\hbar^2}{2\mu R^2} P + U(R)P = E_{int} P$$

Let $F(R) = RP(R)$

$$\rightarrow -\frac{\hbar^2}{2\mu} F'' + \left[U(R) + \frac{J(J+1)\hbar^2}{2\mu R^2} \right] F = EF$$

$$U(R) \approx U(R_e) + \frac{1}{2}k(R - R_e)^2$$

$$\frac{J(J+1)\hbar^2}{2\mu R^2} = \frac{J(J+1)\hbar^2}{2\mu(R_e + R - R_e)^2} = \frac{J(J+1)\hbar^2}{2\mu R_e^2 \left(1 + \frac{R - R_e}{R_e}\right)^2}$$

$$\approx \frac{J(J+1)\hbar^2}{2\mu R_e^2} \left[1 - \frac{2(R - R_e)}{R_e} \right]$$

$$U(R) + \frac{J(J+1)\hbar^2}{2\mu R^2} \approx U(R_e) + \frac{1}{2}k(R - R_e)^2 + \frac{J(J+1)\hbar^2}{2\mu R_e^2} - \frac{J(J+1)\hbar^2(R - R_e)\hbar^2}{\mu R_e^3}$$

If we keep only the first three terms we obtain

$$E = \tilde{U}(R_e) + \tilde{\omega}\left(v + \frac{1}{2}\right) + J(J+1)\tilde{B}_e$$

i.e., the rigid rotor plus harmonic oscillator

However, due to the last term in the Eq. for $U(R)$, the potential energy minimum is shifted from R_e .

To find the new minimum calculate dU/dR

$$\frac{dU}{dR} = k(R - R_e) - \frac{J(J+1)\hbar^2}{\mu R_e^2} = 0$$

$$R_{\min} = R_e + \frac{J(J+1)\hbar^2}{\mu R_e^3 k}$$

Substituting back into the rotational terms gives

$$\frac{J(J+1)\hbar^2}{2\mu R_e^2} - \frac{J^2(J+1)^2\hbar^4}{2(\mu R_e^3)^2 k} \leftarrow \text{Centrifugal distortion}$$

If we keep the next term (quadratic in $R-R_e$) in the series expansion of the rotational, this leads to a modified force constant for the vibration, and leads to vibrational-rotational coupling:

$$\frac{3\hbar^2}{\omega\mu^2 R_e^4} \left(v + \frac{1}{2} \right) J(J+1)$$

Actually the coefficient of the $(v + 1/2)J(J+1)$ is supposed to be negative

There is another contribution which arises from the cubic term in the potential

The vibrational/rotational coupling can be interpreted as a v -dependent rotational constant, B

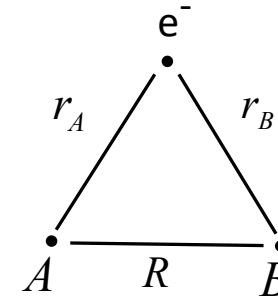
$$B_v = B_e - \alpha_e \left(v + \frac{1}{2} \right)$$

H_2^+ : Simplest one electron diatomic

$$H_{el} = -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{e^2}{r_A} - \frac{e^2}{r_B} \quad \left| \text{To get U we add } \frac{1}{R} \text{ to } E_{el}(R) \right.$$

In a minimal basis set LCAO approach for the ground state we would have $\psi = c_1 1s_A + c_2 1s_B$

where $1s_A$ and $1s_B$ are functions centered on atoms A and B, respectively



With this basis set the energies are given by

$$\begin{vmatrix} H_{AA} - \lambda & H_{AB} - S_{AB}\lambda \\ H_{BA} - S_{BA}\lambda & H_{BB} - \lambda \end{vmatrix} = 0$$

and the orbitals are determined by symmetry

$$E_+ = \frac{H_{AA} + H_{AB}}{1 + S_{AB}}, \quad E_- = \frac{H_{AA} - H_{AB}}{1 - S_{AB}}, \quad \psi_+ = \frac{1s_A + 1s_B}{\sqrt{2(1 + S_{AB})}}, \quad \psi_- = \frac{1s_A - 1s_B}{\sqrt{2(1 - S_{AB})}}$$

$$H_{AA} = \langle 1s_A | H | 1s_A \rangle \quad H_{BB} = \langle 1s_B | H | 1s_B \rangle$$

$$H_{AB} = \langle 1s_A | H | 1s_B \rangle \quad S_{AB} = \langle 1s_A | 1s_B \rangle$$

$$\text{For } \text{H}_2^+ \quad H_{AA} = H_{BB}$$

$$\text{Let } 1s_A = \sqrt{\frac{k^3}{\pi}} e^{-kr_A}, \quad 1s_B = \sqrt{\frac{k^3}{\pi}} e^{-kr_B}$$

$$S_{AB} = e^{-kR} \left(1 + kR + \frac{1}{3} k^2 R^2 \right)$$

$$H_{AA} = \frac{1}{2} k^2 - k - \frac{1}{R} + e^{-2kR} (k + R^{-1})$$

$$H_{AB} = -\frac{1}{2} k^2 S_{AB} - k(2-k)(1+kR)e^{-kR}$$

(if we were considering HeH^{2+} , $H_{AA} \neq H_{BB}$)

For derivation see
<http://www2.chem.umd.edu/groups/alexander/chem691/Chap3.pdf>

$$E_{\pm} = -\frac{1}{2}k^2 + \frac{k^2 - k - \frac{1}{R} + \frac{1}{R}(1+kR)e^{-2kR} \pm k(k-2)(1+kR)e^{-kR}}{1 \pm e^{-kR} \left(1 + kR + \frac{k^2 R^2}{3}\right)}$$

As $R \rightarrow \infty$, $E_{\pm} \rightarrow -\frac{1}{2}k^2 + k^2 - k$

$$= \frac{1}{2}k^2 - k$$

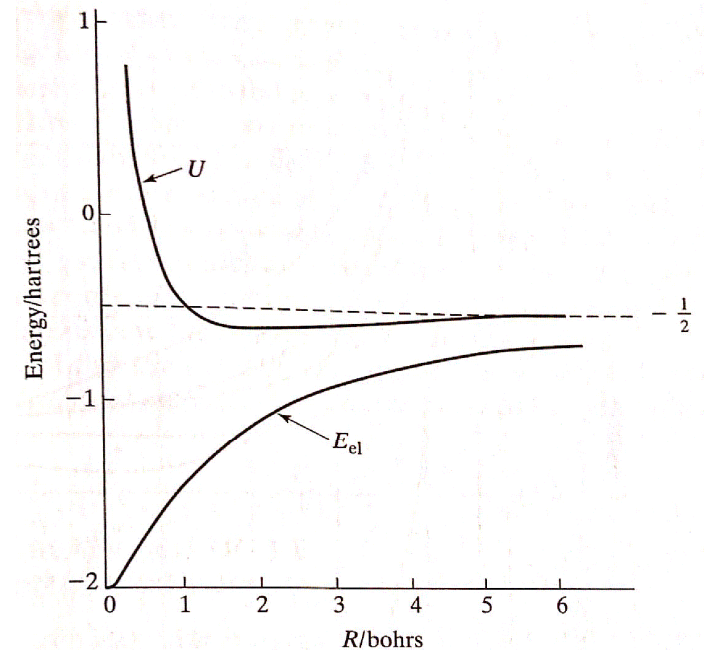
Note if $k = 1$, $E = -\frac{1}{2}$
which is just the energy of an
H atom

For E_{+} k goes from 1 at $R = \infty$ to 2
at $R = 0$

at R_e (~ 2.0 Bohrs) $k = 1.24$

$k = 2$ in the $R \rightarrow 0$ limit
from the above eq.

$$U_{\pm} = E_{\pm} + \frac{1}{R}$$



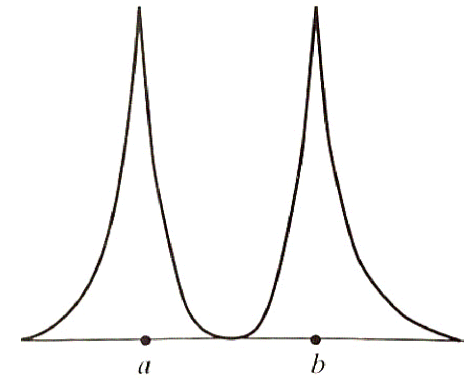
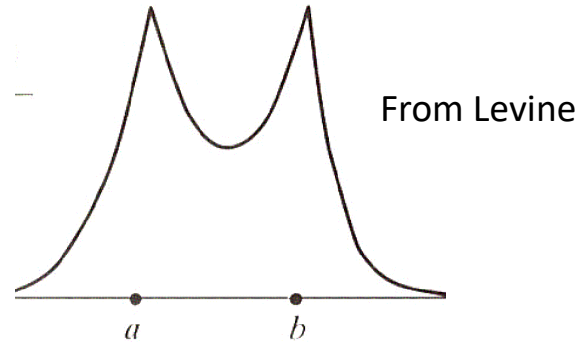
U and E_{el} for the ground state of H_2^+
(from Levine)

$$H_2^+ \quad R_e = 2 \text{ Bohrs}$$

$$E(R_e) = -15.96 \text{ eV} \quad (D_e = 2.36 \text{ eV})$$

$$\text{True answer } E(R_e) = -16.39 \text{ eV} \quad (D_e = 2.79 \text{ eV})$$

$$\phi_+^2 = \frac{1s_A^2 + 1s_B^2 + 21s_A 1s_B}{2(1 + S_{AB})}$$



More charge at the middle of the bond than obtained from $1s_A^2 + 1s_B^2$

But the simple interpretation that the bonding comes from this build-up of charge is not fully correct

Include p_z basis function on each atom: get $D_e \approx 2.73 \text{ eV}$

For the ground state of H_2^+

$$R \rightarrow \infty \quad H^+ + H \quad E = -\frac{1}{2} \quad U = -\frac{1}{2}$$

$$R \rightarrow 0 \quad He^+ \quad E = -2 \quad U = \infty$$

$$E \text{ at minimum} = -1.1033\text{au}$$

$$U \text{ at minimum} = -0.6026\text{au} \quad (D_e = 2.79\text{eV})$$

in the separated atom limit

$$1\sigma_g \text{ bonding} \longrightarrow 1s_A + 1s_B$$

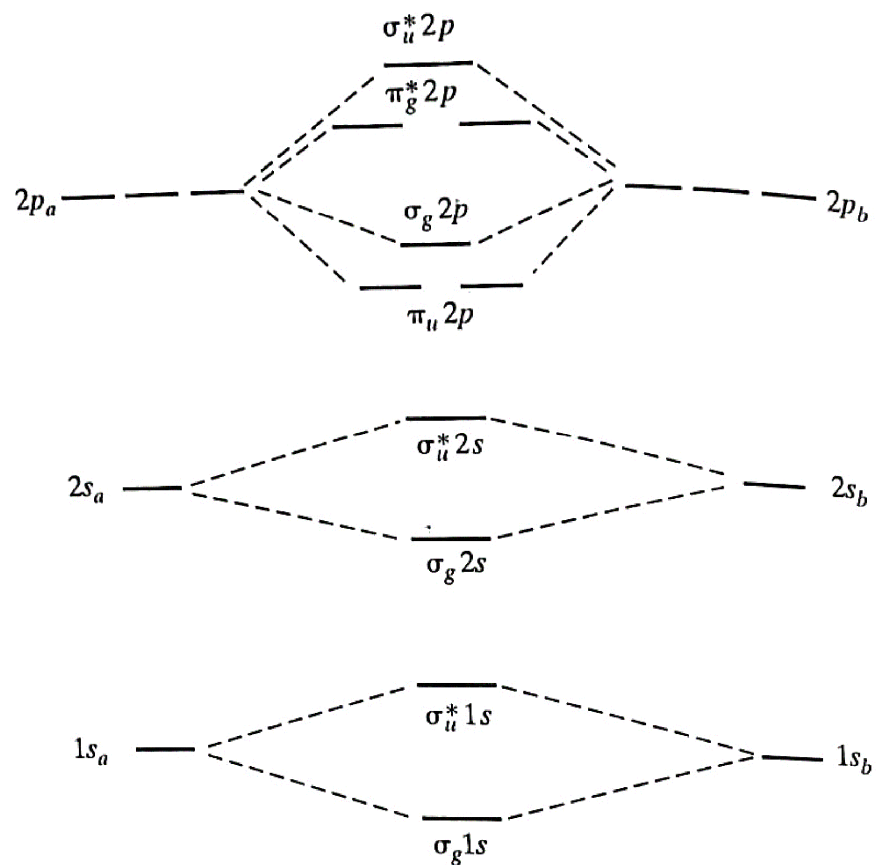
$$1\sigma_u \text{ anti-bonding} \longrightarrow 1s_A - 1s_B$$

in the united atom limit

$$1\sigma_g \longrightarrow He^+(1s)$$

$$1\sigma_u \longrightarrow He^+(2p)$$

Low-lying MO's from AOs



United atom to separated atom orbital correlation diagram

