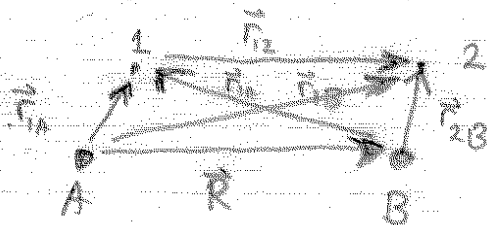


Physics 531

Lecture 18: Neutral H_2 and Diatomics

The simplest neutral molecule is diatomic hydrogen H_2 consisting of two protons and two electrons.



The electronic Hamiltonian (in a.u.)

$$H_e = \frac{\vec{P}_1^2}{2} + \frac{\vec{P}_2^2}{2} - \frac{1}{r_{1A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} - \frac{1}{r_{2B}} + \frac{1}{r_{12}} + \frac{1}{R}$$

↑
constant

As for multi-electron atoms, ^{for} multi-electron molecules we cannot solve exactly for the energy levels. There are many approaches which take into account different physically relevant effects.

MO (molecular orbitals)

Like atoms we can "build up" molecules by sequentially filling up molecular orbitals (single electron states) consistent with the Pauli exclusion principle.

We can take into account the many-electron character via a mean-field approach to obtain Hartree-Fock equations for the MO. Here we will take the simplest model to start of independent electrons.

Better approximation of H_2 is a superposition of Ψ_A and Ψ_B , both of which have $\frac{1}{\sqrt{2}}$

Define $\Psi(1,2) = \Psi_A(1,2) + c \Psi_B(1,2)$

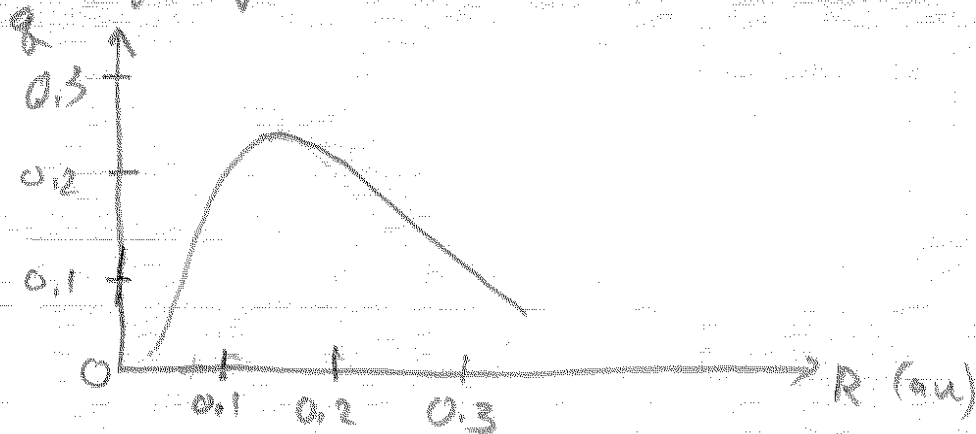
$$\Psi_B(1,2) = \frac{1}{\sqrt{2}} (-\Psi_A^{cov}(1,2) + \Psi_A^{ion}(1,2))$$

$$\Psi(1,2) = (1-c) \Psi_A^{cov} + (1+c) \Psi_A^{ion}$$

Minimize $E[c] = \frac{\langle \Psi | H_e | \Psi \rangle}{\langle \Psi | \Psi \rangle}$

One finds $R_0 = 1.42 \text{ au} = 0.75 \text{ \AA}$, $D_e = 0.147 \text{ au} = 4.0 \text{ eV}$,
a big improvement

Defining $q = \frac{1+c}{1-c}$ = ionic ratio, variational calc



Maximized at ~ 0.25 at $R_0 \approx 1.5 \text{ au}$; $q \rightarrow 0$ as $R \rightarrow \infty$

Finally, we have sought to capture R_0 and D_e , but not long range potential. For $H_2 \rightarrow$ van der Waals potential $\sim 1/r^6$. More later

Heitler-London (Valence bond method)

Alternative due to Heitler and London: Choose Atomic orbital, rather than molecular orbital (better for long range potential)

Ansatz: Two Hydrogen atoms $\phi_{1s}^A(\vec{r}_1) |m_{s_A}\rangle, \phi_{1s}^B(\vec{r}_2) |m_{s_B}\rangle$
at long range

⇒ For possibilities

$$\text{Singlet: } |\Sigma_g^+\rangle = \frac{1}{\sqrt{2}} \left(\phi_{1s}^A(\vec{r}_1) \phi_{1s}^B(\vec{r}_2) + \phi_{1s}^B(\vec{r}_1) \phi_{1s}^A(\vec{r}_2) \right) \chi_{00}$$

$$\text{Triplet: } |\Sigma_u^-\rangle = \frac{1}{\sqrt{2}} \left(\phi_{1s}^A(\vec{r}_1) \phi_{1s}^B(\vec{r}_2) - \phi_{1s}^B(\vec{r}_1) \phi_{1s}^A(\vec{r}_2) \right) \chi_{1, M_S}$$

$$\text{Singlet} = \frac{\Psi_{\text{cov}}}{\sqrt{2}} \quad \text{triplet} = \frac{2\Psi_{\text{cov}}}{\sqrt{2}} \quad \text{from MO}$$

In Heitler-London model

$$E_{gu} = 2E_{1s} + \frac{J}{1 \pm I^2} \pm \frac{K}{1 \pm I^2} + \frac{1}{R}$$

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

$$J = \int d^3r_1 d^3r_2 |\phi_{1s}^A(\vec{r}_1)|^2 |\phi_{1s}^B(\vec{r}_2)|^2 \left(\frac{1}{r_{12}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} \right)$$

(Coulomb)

$$K = \int d^3r_1 d^3r_2 \phi_{1s}^A(\vec{r}_1) \phi_{1s}^B(\vec{r}_2) \left(\frac{1}{r_{12}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} \right) \phi_{1s}^A(\vec{r}_2) \phi_{1s}^B(\vec{r}_1)$$

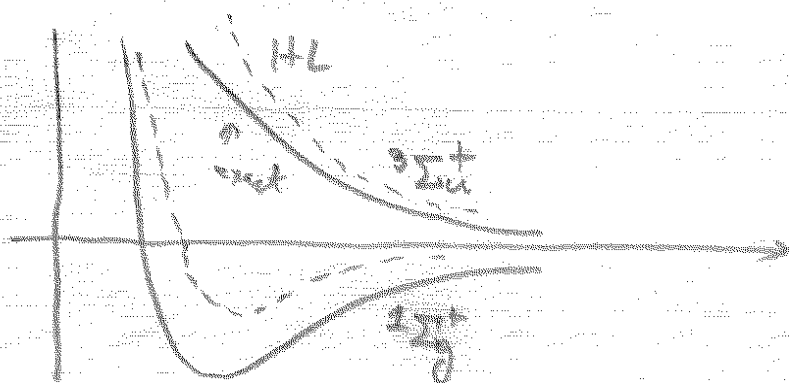
(Exchange)

One find $KCO \Rightarrow 1\Sigma_g^+$ is lower energy than $3\Sigma_u^+$

This makes sense: Electrons in singlet closer together
 \Rightarrow Excess charge density between nuclei
 \Rightarrow Bonding

In this case we find $R_0 = 1.6 \text{ au} = 0.87 \text{ \AA}$
 $D_e = 0.115 \text{ au} = 3.14 \text{ eV}$

Better than MO because that method gave equal weight to covalent and ionic bonding whereas for H_2 covalent dominates.



More general diatomics

We can construct electronic states of diatomics using, e.g. the filling of MO

Simplified model. $\Phi_{g,u}(i) = N_{g,u} [\psi_a^{(A)}(r_1) + \psi_b^{(B)}(r_2)]$

This is known as the separated atom orbital, good for $R \rightarrow \infty$

We write the $H_e = H_0(1) + H_0(2) + \frac{1}{r_{12}} - \frac{1}{R}$

where $H_0(i) = \frac{\vec{p}_i^2}{2} - \frac{1}{r_{hi}} - \frac{1}{r_{bi}} + \frac{1}{R}$

(single electron in the field to 2-nuclei + nuclear repulsion)

The one electron orbitals satisfy

$$H_0(i) \Phi_{g,u}(R) = E_{g,u}(R) \Phi_{g,u}(R)$$

Based on the "separated-atom" asymptote, we found gerade and ungerade orbitals connecting to 1s hydrogen

$$\Phi_{g,u}(R) = N_{g,u}(R) (\phi_{1s}^A \pm \phi_{1s}^B) = \sigma_g 1s, \sigma_u^* 1s$$

↑ normalization constant

There are 4 possible configurations consistent with the Pauli exclusion principle

$$\left\{ \begin{aligned} \Psi_A(1,2) &= \Phi_g(1) \Phi_g(2) \chi_{0,0}^{(1,2)} \rightarrow \left(\frac{1\uparrow 1\downarrow - 1\downarrow 1\uparrow}{\sqrt{2}} \right) \text{ (singlet)} \\ \Psi_B(1,2) &= \Phi_u(1) \Phi_u(2) \chi_{0,0}(1,2) \\ \Psi_C(1,2) &= \frac{1}{\sqrt{2}} (\Phi_g(1) \Phi_u(2) + \Phi_g(2) \Phi_u(1)) \chi_{0,0}(1,2) \\ \Psi_D(1,2) &= \frac{1}{\sqrt{2}} (\Phi_g(1) \Phi_u(2) - \Phi_g(2) \Phi_u(1)) \chi_{1,0}^{(1,2)} \text{ (triplet)} \end{aligned} \right.$$

The overall parity of multi-electron molecule is the product of the parities associated with each electron. The value of $\Lambda = |M_L|$ where $M_L = m_{l_1} + m_{l_2} = 0$ for all states.

Also, because atomic s-orbitals are spherically symmetric, they are all reflection symmetric.

→ $\begin{cases} \Psi_A \text{ and } \Psi_B \text{ are } 1 \Sigma_g^+ \text{ states} \\ \Psi_C \text{ is a } 1 \Sigma_u^+ \text{ state} \\ \Psi_D \text{ is a } 3 \Sigma_u^+ \text{ state} \end{cases}$

As Ψ_g is the binding state, Ψ_A is the lowest energy

$$\rightarrow E_A(R) = \langle \Psi_A | \hat{H}_e | \Psi_A \rangle = 2E_g(R) + \int d^3r_1 d^3r_2 \frac{|\phi_g(r_1)|^2 |\phi_g(r_2)|^2}{|\vec{r}_1 - \vec{r}_2|} - \frac{1}{R}$$

Using the simplest separated-atom orbitals one finds the equilibrium separation of H_2 , $R_0 = 1.5 \text{ au} = 0.8 \text{ \AA}$ and a dissociation energy of

$$D_c = 2E_{1s} - E_A(R_0) = 0.01 \text{ au} = 2.68 \text{ eV}$$

The experimental values: $R_0 = 1.4 \text{ au} = 0.74 \text{ \AA}$, $D_c = 0.175 \text{ au} = 4.75 \text{ eV}$

We can understand the short comings of our ansatz by expanding the molecular orbital in terms of atomic ones

$$\begin{aligned}\Psi_A(1,2) &= \frac{1}{2} [\phi_{1s}^A(\vec{r}_1) + \phi_{1s}^B(\vec{r}_1)] [\phi_{1s}^A(\vec{r}_2) \pm \phi_{1s}^{(2)}(\vec{r}_2)] \chi_{00} \\ &= \frac{1}{\sqrt{2}} (\Psi_A^{\text{cov}}(1,2) + \Psi_A^{\text{ion}}(1,2))\end{aligned}$$

$$\begin{cases} \Psi_A^{\text{cov}}(1,2) = \frac{1}{2} (\phi_{1s}^A(\vec{r}_1) \phi_{1s}^B(\vec{r}_2) + \phi_{1s}^B(\vec{r}_1) \phi_{1s}^A(\vec{r}_2)) \chi_{00} \\ \Psi_A^{\text{ion}}(1,2) = \frac{1}{\sqrt{2}} (\phi_{1s}^A(\vec{r}_1) \phi_{1s}^A(\vec{r}_2) + \phi_{1s}^B(\vec{r}_1) \phi_{1s}^B(\vec{r}_2)) \chi_{00} \end{cases}$$

The state Ψ_A^{cov} corresponds to each nucleus having one electron in superposition with each electron being on the opposite nucleus. This is covalent bonding.
As $R \rightarrow \infty$ $\Psi_A^{\text{cov}} \rightarrow \text{H}(1s) + \text{H}(1s)$ two neutral hydrogen in 1s

In contrast, the state Ψ_A^{ion} corresponds to each nucleus containing both electrons

As $R \rightarrow \infty$ $\Psi_A^{\text{ion}} \rightarrow \text{H}^-(1s)^2 + \text{proton}$

The non-equal distribution of charge between the nuclei leads to ionic bonding.

This model fails for two reasons

- (i) Each contribution of covalent & ionic bonding
- (ii) H^- ground state \neq doubly occupied neutral hydrogen orbitals

As $R \rightarrow 0$, should approach "united atoms".

Molecular Orbital found from

$$H_e = H_0 + H_1$$

$$H_0 = \frac{p^2}{2} - \left(\frac{Z_A + Z_B}{r} \right)$$

$$H^* = \frac{Z_A + Z_B}{r} - \frac{Z_A}{|r^2 - R^2|} - \frac{Z_B}{|r^2 - R^2|}$$

Two notations:

Separated atom λ (nl)sep

united atom (nl)unite λ_{gu} where $\begin{cases} g & \text{if } l \text{ even} \\ u & \text{if } l \text{ odd} \end{cases}$

Consider homonuclear (e.g. H_2)

Separated ns \rightarrow MO σ_g or σ_u^*

Separated np \rightarrow MO $\sigma_g, \sigma_u, \pi_g, \pi_u$

For separated σ_g (ns) bonding σ_u^* (ns) antibonding

We saw this by examining the charge density (probability) of the electron between the nuclei.

Consider the separated np MO. The p-orbitals have negative parity w.r.t. their center

$$\psi_{\lambda=nlm}(\vec{r}) = \frac{1}{\sqrt{2}} \left(\phi_{np,lm}(\vec{r} - \frac{\vec{R}}{2}) \pm \phi_{np,lm}(\vec{r} + \frac{\vec{R}}{2}) \right)$$

$$\Rightarrow \psi_{\lambda=nlm}(\vec{r}) = \frac{1}{\sqrt{2}} \left(\phi_{np,lm}(-\vec{r} - \frac{\vec{R}}{2}) \pm \phi_{np,lm}(-\vec{r} + \frac{\vec{R}}{2}) \right)$$

$$\begin{aligned} \Phi_{\lambda=|m_l|}(\vec{r}) &= -\frac{1}{\sqrt{2}} \left(\phi_{np, m_l}(\vec{r} + \frac{\vec{R}}{2}) \pm \phi_{np, m_l}(\vec{r} - \frac{\vec{R}}{2}) \right) \\ &= \mp \frac{1}{\sqrt{2}} \left(\phi_{np, m_l}(\vec{r} - \frac{\vec{R}}{2}) \pm \phi_{np, m_l}(\vec{r} + \frac{\vec{R}}{2}) \right) \end{aligned}$$

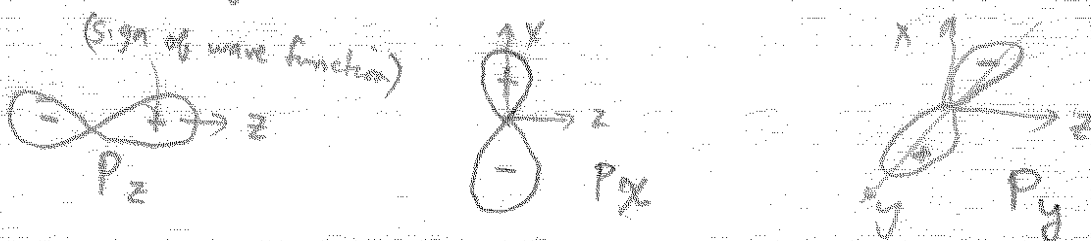
⇒ gerade and ungerade arise from antisymmetric and symmetric combinations of p-orbitals

Graphically: Recall P_x, P_y, P_z orbitals

$$P_z = Y_{00} \propto \cos\theta = \frac{z}{r}$$

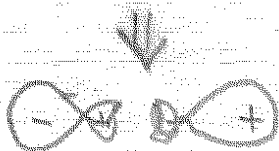
$$P_x = -Y_{1+1} + Y_{1-1} \propto \sin\theta \cos\phi = \frac{x}{r}$$

$$P_y = -Y_{1+1} - Y_{1-1} \propto \sin\theta \sin\phi = \frac{y}{r}$$



$\sigma(np)$ MO formed from separated np_z orbitals

$\sigma_u(np_z)$: antibonding

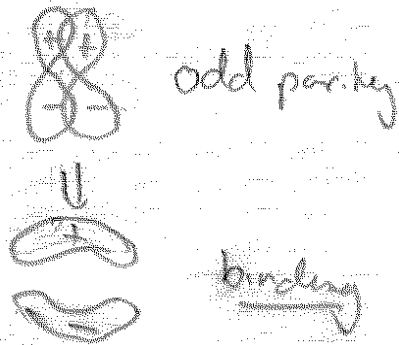


$\sigma_g(np_z)$: bonding

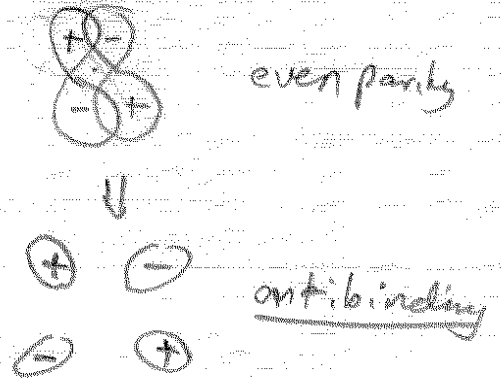


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$\Pi_u(np_x \text{ or } np_y)$: bonding



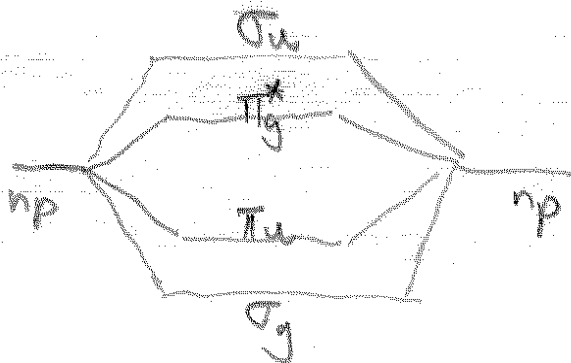
$\Pi_g(np_x \text{ or } np_y)$: antibonding



Note: The Π orbitals are doubly degenerate, here described by possible separated atomic orbitals np_x or np_y . In fact, we see that $\Pi(np_x) = \Pi^+$, $\Pi(np_y) = \Pi^-$ by reflection symmetry. We typically don't denote the reflection parity for $\lambda > 0$.

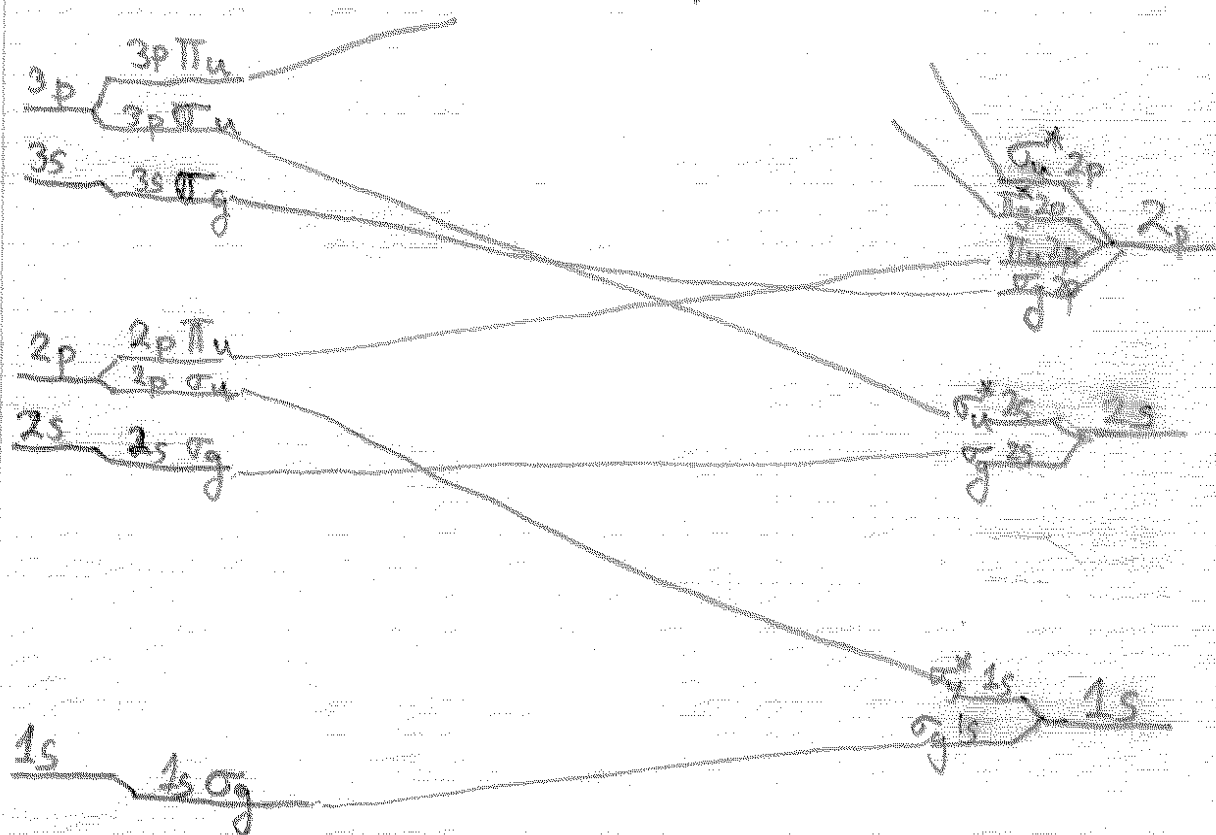
Note: Because of the charge distribution in these orbitals σ_g is more tightly bound than Π_u .

Thus the molecular orbitals forming from separate atomic p orbitals



Given the MO for separated and united atoms, we can find draw a "correlation diagram" to see how the nature of the MO changes as a function of R . An important guide is that the Born-Oppenheimer potentials of the same symmetry λ_g, λ_u cannot cross

For homonuclear diatomic, \dots



United
Atom
($R \rightarrow 0$)

Separated
Atom
($R \rightarrow \infty$)