Physics 531

Lecture 19: Diatomic Continued

- **Pairing and valency:**

To build up larger molecules, we first note
that majority of the chemical bond is due to the
valence electrons of the constituent atoms (i.e.
those electrons not in a closed shell).
Consider, for example, the possible binding of
$He\ (1s)^2$ to $H\ (1s)$. A Heitler-London
type molecular orbital can be constructed
by writing a Slater determinant for the three
electron state $He(1s)^2 + H(1s)$

$$\Phi = N \begin{vmatrix} v_{1s}(1)|\uparrow\rangle_1 & v_{1s}(1)|\downarrow\rangle_1 & u_{1s}(1)|\uparrow\rangle_1 \\ v_{1s}(2)|\uparrow\rangle_2 & v_{1s}(2)|\downarrow\rangle_2 & u_{1s}(2)|\uparrow\rangle_2 \\ v_{1s}(3)|\uparrow\rangle_3 & v_{1s}(3)|\downarrow\rangle_3 & u_{1s}(3)|\uparrow\rangle_3 \end{vmatrix}$$

where $\begin{cases} v_{1s} \text{ is the Helium } 1s \text{ orbital} \\ u_{1s} \text{ is the Hydrogen } 1s \text{ orbital} \end{cases}$

The electronic energy of this state

$$E(R) = J(R) - K(R)$$

where $J(R) = N^2 \int d^3\vec{r}_1\, d^3\vec{r}_2\, d^3\vec{r}_3\ |v_{1s}(1)|^2 |v_{1s}(2)|^2 |u_{1s}(3)|^2\ \hat{H}_e(R)$

(Direct)

$$K(R) = N^2 \int d^3\vec{r}_1\, d^3\vec{r}_2\, d^3\vec{r}_3\ |v_{1s}(2)|^2 \left(v_{1s}(1)\, u_{1s}(3)\, \hat{H}_e(R)\, v_{1s}(3)\, u_{1s}(1) \right)$$
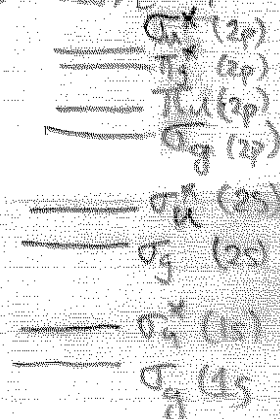
(Exchange)

We see here that the Hydrogen-1s electron can only "exchange" with a Helium-1s of the same spin, since Pauli exclusion forbids two electrons in the the Helium-1s shell with same spin. The result is that Parallel spin give a repulsive exchange energy, and no binding by this mechanism. Thus, only "unpaired" electrons can lead to covalent bonding, i.e. electrons in the valence shell. Atoms with completely filled shells are said to be chemically inert. Note: There can be weak bonding due to long range forces not included here (van der Waals) — more on that below.
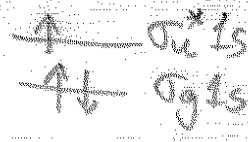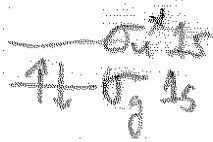
Buildup of molecule orbitals

In the same way that we "build up" multielectron atoms by successively filling atomic orbitals, we can get some coarse understanding of the nature of molecules by successively filling up the molecular orbitals. The σ-orbitals can accomodate two electrons of opposite spin; the $\lambda > 0$ orbital (e.g. π-orbitals) can accomodate four electrons ($\pm$ symmetry and spin up-down for each)

Using the separated atom MO's we found the following energy level scheme, with antibonding orbitals denoted with an asterisk.

$$\sigma_u^* \, (2p)$$
$$\pi_g^* \, (2p)$$
$$\pi_u \, (2p)$$
$$\sigma_g \, (2p)$$

$$\sigma_u^* \, (2s)$$
$$\sigma_g \, (2s)$$

$$\sigma_u^* \, (1s)$$
$$\sigma_g \, (1s)$$

First few homonuclear diatomics

H_2^+ $(\sigma_g 1s)$ H_2 $(\sigma_g 1s)^2$ He_2^+ $(\sigma_g 1s)^2 \sigma_u^* 1s$


The He_2^+ molecular ion consists of two binding and one antibinding orbitals, leading to a net weak binding. This must be due to slight ionizing since He itself is inert (closed shell)

- Neutral He_2 $\quad$ No binding in this level of approx.
$(\sigma_g 1s)^2 (\sigma_u^* 1s)^2$
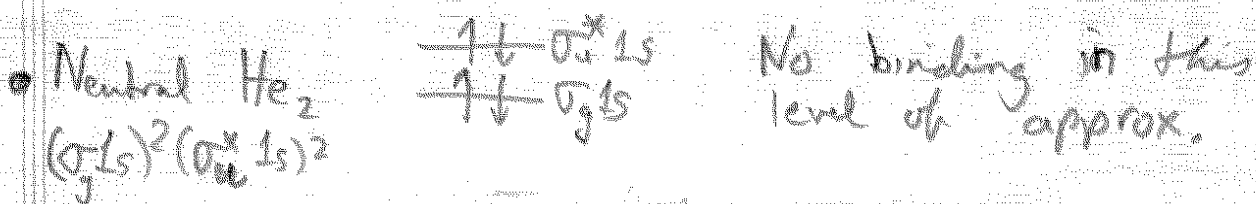
$\qquad$ Experimentally, we find $^4He_2$ weakly bound (bound-length ~ 50 Å) by van der Waals

- Neutral Li_2:   Each Li atom configuration $(1s)^2 (2s)$
The inner core $(1s)^2$ plays little role in chemical binding, valence electron dominates
⇒ Ground State configuration $(\sigma_g 2s)^2$
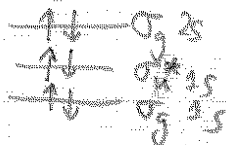
- Neutral Be_2: $(\sigma_g 2s)^2 (\sigma_u^* 2s)^2$ not bound

- Neutral B_2: Each Boron $(1s)(2s)^2 2p$; Only 2p contributes to binding
$\qquad$ Configuration $(\sigma_g 2p)^2$ bound

- Neutral C_2 Carbon atom $(1s)(2s)^2(2p)^2$
$\qquad$ Configuration $(\sigma_g 2p)^2 (\pi_u 2p)^2$;   bound

- Neutral N_2:   Nitrogen $(1s)(2s)^2(2p)^3$

       Configuration: $(\sigma_g 2p)^4 (\pi_u 2p)^2$ bound

- Neutral O_2:   Oxygen $(1s)(2s)^2(2p)^4$

       Configuration: $(\sigma_g 2p)^4 (\pi_u 2p_x)^2 (\pi_u 2p_y)^2 (\pi_g^* p_x)(\pi_u^* p_y)$

       <u>bound</u>

                         not obvious why not two in same orbital

Terms:

Like atoms, given a "configuration" of filled orbitals (calculated in a Hartree-Fock calculation, for example), electron-electron interaction breaks up an energy level into a set of terms specified by $\Lambda = |M_L|$, $\pm$ reflection (for $\Lambda = 0$), and g,u for homonuclear, and $2S+1$ multiplicity for the total spin.

For neutral dimers, MO are typically filled in pairs so spin $S=0 \Rightarrow$ Singlet (for ground state)

A closed shell with $S=0 \Rightarrow |M_L|=0 \Rightarrow$ typically ground molecule ${}^1\Sigma_g^+$
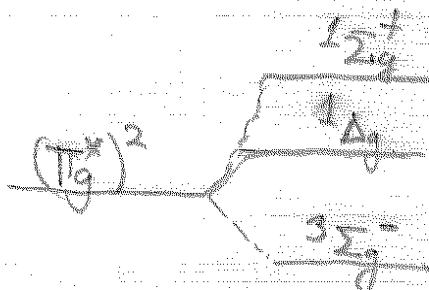
Exception: O_2 Consider Slater Table for $(\pi_g^* 2p)^2$

m_{ℓ_1}	m_{ℓ_2}	m_{s_1}	m_{s_2}	M_L	M_S
1	1	$\frac{1}{2}$	$-\frac{1}{2}$	2	0
1	-1	$\frac{1}{2}$	$\frac{1}{2}$	0	1
1	-1	$\frac{1}{2}$	$-\frac{1}{2}$	0	0
1	-1	$-\frac{1}{2}$	$\frac{1}{2}$	0	0
1	-1	$-\frac{1}{2}$	$-\frac{1}{2}$	0	-1
1	-1				

We can now assign subshells to terms

M_L	M_S	Term
2	0	$\left.\vphantom{\begin{array}{c}1\\2\end{array}}\right\}$ $^1\Delta_g$
-2	0	
0	1	$\left.\vphantom{\begin{array}{c}1\\2\\3\end{array}}\right\}$ $^3\Sigma_g^-$
0	0	
0	-1	
0	0	$\}$ $^1\Sigma_g^+$

reflection symmetry follows from details of consistent Atomic orbitals

By Hund's rules:

$(\pi_g^*)^2$

$^1\Sigma_g^+$

$^1\Delta_g$

$^3\Sigma_g^-$

The triplet is lowest state since electrons avoid each other spatially $\Rightarrow$ Less coulomb repulsion

Thus O_2 has a permanent magnetic dipole moment
$\Rightarrow$ Paramagnetic

From Separated Atomic Terms to Molecular Terms

We found molecular terms by building up molecular orbitals. We can see which molecular terms connect to Multielectron atomic terms. These are known as Wigner-Witmer rules

(see Herzberg, "Spectra of Diatomic Molecules"

Heteronuclear Molecules

Unlike the homonuclear case, there is no inversion symmetry, so we are unlikely to see _tunnelling resonances_ of electrons between the two nuclei, with MO approximated well by single local atomic orbitals.

For two nuclei which are not too different, we might have near degeneracy, in which two local atomic orbitals dominate the contribution to the MO.

$$\Phi = \alpha \, u_A(\vec{r}) + \beta \, v_B(\vec{r})$$

where $u_A(\vec{r})$, $v_B(\vec{r})$ are atomic orbitals associated with (and centered at) atom-A and atom-B. The resulting electronic energy using near-degeneracy perturbation theory

$$E_{\pm} = \frac{1}{2}\left(H_{AA} + H_{BB}\right) \pm \frac{1}{2}\sqrt{\left(H_{AA} - H_{BB}\right)^2 + 4\left(H_{AB} - S_{AB}E\right)}$$

where $S = \langle u_A | v_B \rangle$

- If $|H_{AA} - H_{BB}| \gg 2|H_{AB} - S_{AB}E| \Rightarrow \begin{cases} E_+ = H_{AA}, & \Phi_+ \approx u_A \\ E_- = H_{BB}, & \Phi_- \approx v_B \end{cases}$

In this case, the electrons are highly localized on one or the other nucleus, leaving the other nucleus reduced by one. The result is ~~there~~ a large contribution of ionicity in the MO.

- If $|H_{AA} - H_{BB}| \ll 2|H_{AB} - S_{AB}E|$, covalent dominates.

Hybrid Orbitals

Because there are not necessarily tunnelling resonances for heteronuclear molecules, having just one local atomic orbital for each nucleus is not a good approximation. This is especially true for situations where two atomic orbitals of different nl are near degenerate; superpositions of these will strongly contribute to the MO. These superpositions of local atomic orbitals with different nl are known as "hybrid orbital".

An important example is the mixing of ns an np_z orbitals. We already saw this mixing in the Stark effect of hydrogen.

s p_z sp_z atom hybrid

For example, consider LiH. From separated atom MO.

An important contribution to the ground state is formed by the superposition of the Li hybrid $(2s)(2p_z)$ orbital with H $(1s)$. Because of the asymmetry, the electron is not equally distributed between the nuclei. The result a permanent electric dipole moment in the molecule.