

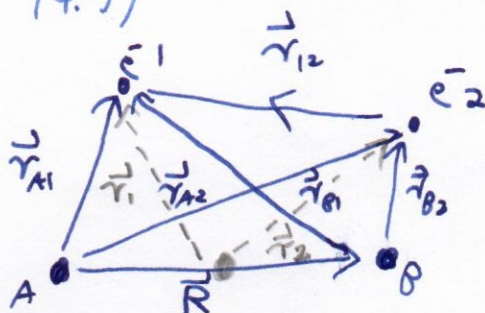
10

# HUND-MULLIKEN / MOLECULAR ORBITAL (MO) METHOD

The next simplest molecule is  $H_2$ .

We can proceed by combining two molecular orbitals as in (4.9)

Diagram:



As in (2.27) we again have spin wavefunctions:

$$|X_{S, m_s}\rangle = \begin{cases} \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) & S=0, m_s=0 \\ |\uparrow\uparrow\rangle & m_s=1 \\ \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) & S=1, m_s=0 \\ |\downarrow\downarrow\rangle & m_s=-1 \end{cases}$$

Need to combine this with spatial wave-functions as in (4.9) such that total wavefunction is anti-symmetric under  $1 \leftrightarrow 2$

We shall use shorthand  $\phi_g(1) = \phi_g(\vec{r}_1, \vec{r}_1)$ .

Out of (4.9), four combinations are possible for two-electron states ( $H_2$  molecular electronic states)

$$\begin{aligned} {}^1\Sigma_g^+ \Phi_A(\vec{r}_1, \vec{r}_2) &= \phi_g(1) \phi_g(2) |X_{00}\rangle & g \\ {}^1\Sigma_g^+ \Phi_B(\vec{r}_1, \vec{r}_2) &= \phi_u(1) \phi_u(2) |X_{00}\rangle & g \\ {}^1\Sigma_u^+ \Phi_C(\vec{r}_1, \vec{r}_2) &= \frac{1}{\sqrt{2}} [\phi_g(1) \phi_u(2) + \phi_g(2) \phi_u(1)] |X_{00}\rangle & u \\ {}^3\Sigma_u^+ \Phi_D(\vec{r}_1, \vec{r}_2) &= \frac{1}{\sqrt{2}} [\phi_g(1) \phi_u(2) - \phi_g(2) \phi_u(1)] |X_{1m_s}\rangle & u, m_s=0, \pm 1 \end{aligned} \quad (4.10)$$

- Note: We are considering the lowest molecular electronic states only [(4.9) based on  $\phi_{1s}$ ]
- all are total-antisymmetric under  $\vec{r}_1 \leftrightarrow \vec{r}_2$  and have fixed symmetry (g or u) under  $R_A \leftrightarrow R_B$
- Based on example in 4.2,  $\Phi_A$  will have lowest energy
- Can again calculate  $E[\vec{R}]$  as in 4.2 to get BO-surfaces



Let's look in more detail at  $\Phi_A$  in (4.10) and insert (4.9)

We obtain

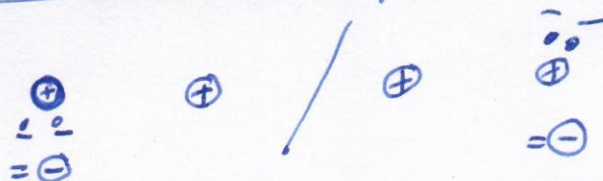
$$\Phi_A = \Phi_A^{\text{cov}} + \Phi_A^{\text{ion}}, \quad \text{where}$$

$$\Phi_A^{\text{cov}} = \frac{1}{2} \left[ \phi_{1s}(\vec{r}_{A1}) \phi_{1s}(\vec{r}_{B2}) + \phi_{1s}(\vec{r}_{A2}) \phi_{1s}(\vec{r}_{B1}) \right] |\chi_{00}\rangle \quad (4.11)$$

↳ covalent bonding = electron sharing

$$\Phi_A^{\text{ion}} = \frac{1}{2} \left[ \phi_{1s}(\vec{r}_{A1}) \phi_{1s}(\vec{r}_{A2}) + \phi_{1s}(\vec{r}_{B1}) \phi_{1s}(\vec{r}_{B2}) \right] |\chi_{00}\rangle \quad (4.12)$$

↳ ionic bonding = unequal division of charge:



• As in our discussion of Helium, the lowest order wavefunctions discussed ~~here can be improved~~ here neglect  $e^- - e^-$  interactions.

They can be improved via variational principle, e.g.

$$\Phi_T = \Phi_A + \lambda \Phi_B \quad \rightarrow \text{find } \lambda.$$

In that case the fraction of ionic binding in  $H_2$  is only 0.2

• Instead of first assembling molecular orbitals (4.9) ~~and then~~ ~~from those~~ out of atomic orbitals, and then from MO create molecular electronic states (4.10), we can also skip (4.9) and directly write guess/variational Ansatz for molecular electronic states in terms of atomic orbitals

↳ Heitler-London / Valence Bond Method

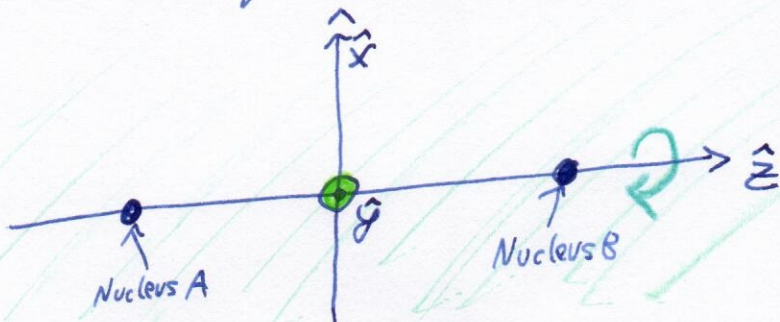
• Even more sophisticated methods for molecular electronic states: Hartree-Fock & DFT as discussed for atoms.



# 4.4. Symmetries in homo-nuclear di-atomic molecules

We are anyway focussing on this type of molecule. Here we list all symmetries and resulting classifications of electronic states

Diagram:



Body-fixed-frame:  
defined by nuclei  
≠  
Laboratory frame

■ Around atomic nucleus: Spherical symmetry, classify states via  $\hat{H}, \hat{L}^2, \hat{L}_z$

• Here, only cylindrical symmetry around  $z$

classify states via  $\hat{H}, \hat{L}_z$  only

• Electronic states satisfy  $\hat{L}_z \phi_0 = \hbar M_L \phi_0 = \pm \hbar L \phi_0$   $L = |M_L|$   
 $L = 0, 1, 2, \dots$

Code Letters:  $L = 0, 1, 2, 3$

$\Sigma$	$\Pi$	$\Delta$	$\Phi$
(Greek capital)	S	P	D
	$\pi$	$\delta$	$\phi$

[For single electron in MO:  $\sigma, \pi, \delta, \phi, \dots$ ]

■ System symmetric under reflection off  $x, z$  plane:  
swaps  $M_L \rightarrow -M_L$  for fixed  $L$ ,  $\Rightarrow$  each  $L$  (approx)  
two-fold degenerate. (L-doubling)

For  $\Sigma$  we write  $\Sigma^+, \Sigma^-$  for symmetric (anti-symmetric)  
states under swap  $y \rightarrow -y$ .

■ System symmetric under reflection through origin • (point-reflection)  
(for this homo-nuclear is crucial)  
 $\Rightarrow$  Wavefunction symmetric or anti-symmetric under this  $\Rightarrow$  g (grade)  
u (ungerade)  
labels (see (4.9))

Molecular state label:

Spin multiplicity

2S+1  
e.g. 3

$L$  code - letter

symmetry over  $x, z$

$\Sigma_u^+$   
g, u

(4.13)

(Now re-check (4.10))



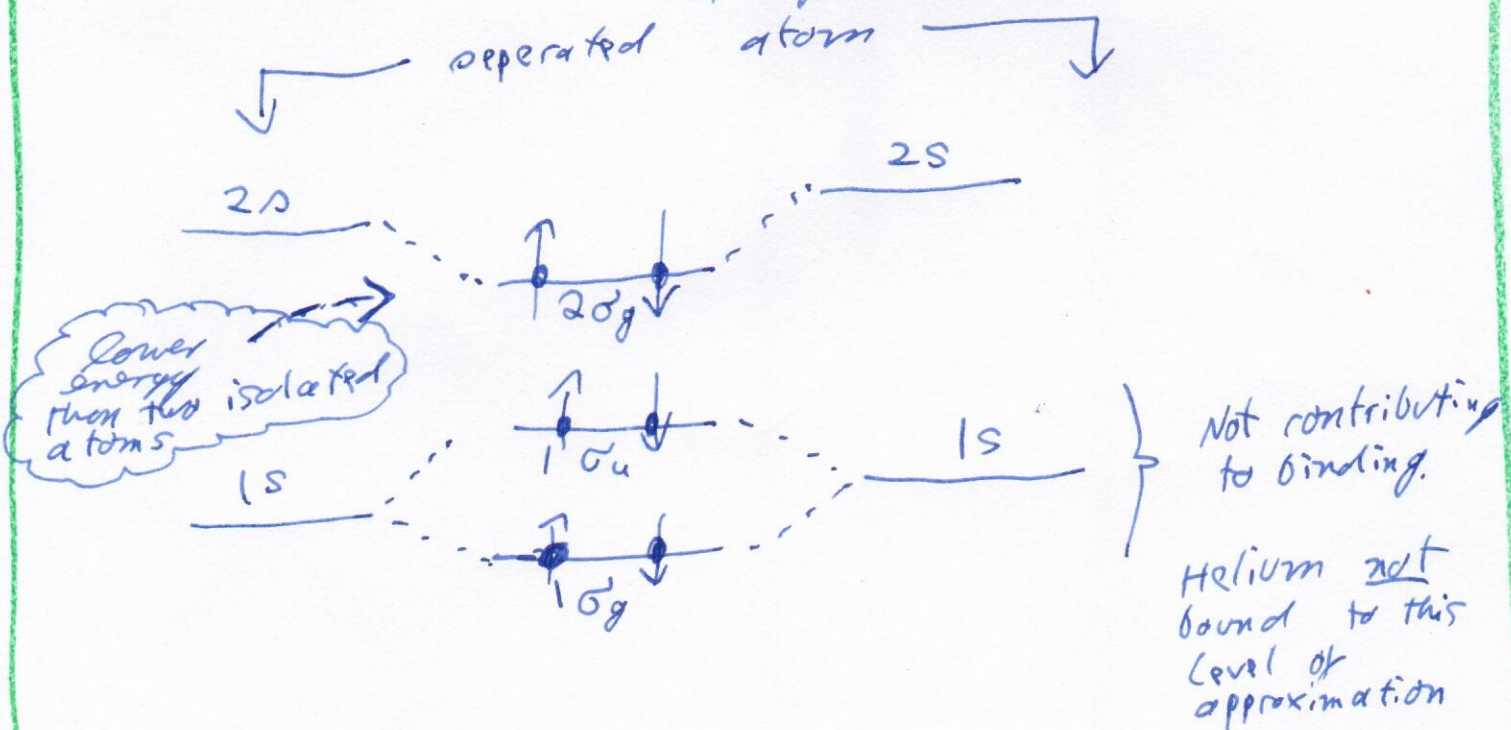
# Example for section 4.4: $\text{Li}_2$ molecule:

•  $\text{Li } Z=3 \Rightarrow$  We have a total of 6 electrons to distribute  
 For atoms we were following:

- Construct atomic states similar to Hydrogen
- Understand differences to hydrogen
- Fill from low to high energy, respecting Pauli principle.

For Molecules

- Construct Molecular states based on atoms (Eq. 4.10)
- Understand differences to atoms ( $E_g < E_u$ )
- Fill from low to high energy, respecting Pauli-principle.



• Can write electron configuration of molecule

$$\text{Li}_2: \Sigma_g^+ = (1\sigma_g)^2 (1\sigma_u)^2 (2\sigma_g)^2$$

~~excited states~~

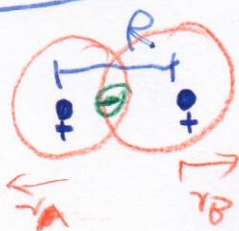


# 4.5. More general overview of chemical bonds

- Mathematical all bonds arise the same:  
Solve (4.2) [electronic TISE] as a function of nuclear co-ordinates  $\vec{R}$ . If some  $E_q(\vec{R})$  has a local minimum, there may be a bond.
- In practice, the physical interpretation ~~is~~ [based on  $\phi_q(\vec{R}, \vec{r}_1, \dots, \vec{r}_n)$ ] may vary:

## Chemical bonds:

### Covalent:



Nuclei share electrons.  
 $\hookrightarrow$  larger  $\ominus$ 've charge density in-between

size of atom A  
 $R < r_a + r_b$   
 inter nuclear distance  
 electron clouds overlap  
 at slightly larger R  
 $R \approx r_a + r_b$

### Ionic:



Nuclei transfer electrons  
 $\hookrightarrow$  excess  $\oplus$  on one, excess  $\ominus$  on other  $E \sim \frac{1}{R}$

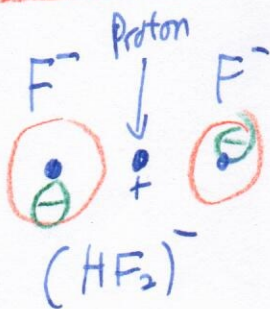
### Van-der-Waals



Atoms polarize each other, dipole moments (or their fluctuations)  
 attract  $E \sim \frac{1}{R^6}$   
 $R > r_a + r_b$

### More peculiar:

- Hydrogen bonding  
 [charge reverse of covalent]



e.g. DNA-strands bind like this

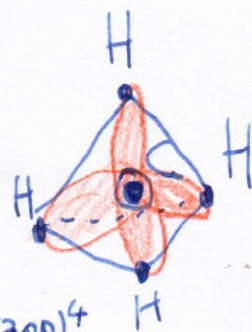
- s-p hybrid  
 $MO = |s\rangle + |p\rangle$



(compare section 3.4.1)

electron is shifted in a specific direction

CH<sub>4</sub>:



3D picture

Carbon:  $(1s)^2 (2s)^2 (2p)^2$