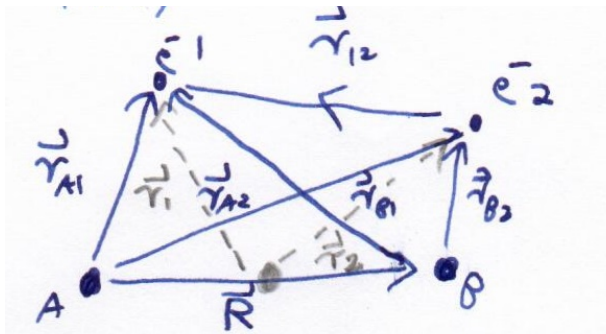PHY 402 Atomic and Molecular Physics
*Instructor: Sebastian Wüster*, IISER Bhopal, 2018

*These notes are provided for the students of the class above only. There is no warranty for correctness, please contact me if you spot a mistake.*

### 4.3.1 Hund-Mulliken Molecular Orbital (MO) Method

The next simplest molecule is $H_2$.
First let us define the co-ordinates now used:



We can then proceed by combining two molecular orbitals as in Eq. (4.9). As in Eq. (2.72), we again have spin wavefunctions:

$$|\chi_{S,m_S}\rangle = \begin{cases} \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right) & \text{S = 0, m}_S = 0 \\ \rule{6cm}{0.4pt} \\ |\uparrow\uparrow\rangle & \text{m}_S = 1 \\ \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right) & \text{S = 1, m}_S = 0 \\ |\downarrow\downarrow\rangle & \text{m}_S = \text{-1} \end{cases}$$

We need to combine this with spatial wavefunctions as in (4.9) such that the total wavefunction is anti-symmetric under 1↔2

We shall use shorthand the $\phi_g\left(1\right) = \phi_g\left(\mathbf{R}; \mathbf{r}_1\right)$

- Note: We are considering the lowest molecular electronic states only [(4.9) based on electronic ground states $\phi_{1s}$ of each separate atom].

- All states are totally antisymmetric under exchange of positions $\mathbf{r}_1 \leftrightarrow \mathbf{r}_2$ and have fixed symmetry (g or u) under $\mathbf{R}_A \leftrightarrow \mathbf{R}_B$, which is shown as subscript in the green spectroscopic label on the left (the rest of the label is defined only in section 4.4).

- Based on the example insection 4.2, the electronic state $\Phi_A$ will have lowest energy

- We can again calculate E($\mathbf{R}$) as in section 4.2 to get BO-surfaces

Let's look in more detail at $\Phi_A$ in (4.13) and insert the details of single electron orbitals from (4.9) We obtain

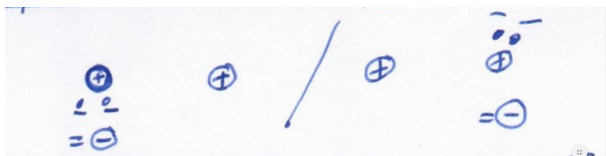$$\Phi_A = \Phi_A^{cov} + \Phi_A^{ion}, \tag{4.14}$$

where the first part represents covalent bonding

$$\Phi_A^{cov} = \frac{1}{2}\left[\phi_{1S}\left(\mathbf{r}_{A1}\right)\phi_{1S}\left(\mathbf{r}_{B2}\right) + \phi_{1S}\left(\mathbf{r}_{B1}\right)\phi_{1S}\left(\mathbf{r}_{A2}\right)\right]\left|\chi_{00}\right\rangle. \tag{4.15}$$

We see that this essentially involves the sharing of electrons. The second part,

$$\Phi_A^{ion} = \frac{1}{2}\left[\phi_{1S}\left(\mathbf{r}_{A1}\right)\phi_{1S}\left(\mathbf{r}_{A2}\right) + \phi_{1S}\left(\mathbf{r}_{B1}\right)\phi_{1S}\left(\mathbf{r}_{B2}\right)\right]\left|\chi_{00}\right\rangle, \tag{4.16}$$

is responsible for ionic bonding to do with an unequal division of charge, see sketch below.

- As in our initial discussion of Helium, the lowest order wave functions discussed here neglect $e^- - e^-$ interactions.

  They can be improved via variational principle, e.g. using the Ansatz

$$\Phi_{trial} = \Phi_A + \lambda \Phi_B \rightarrow \text{use variational principle to find best value of } \lambda \qquad (4.17)$$

  If this calculation is performed, the fraction of ionic binding in $H_2$ turns out as only 0.2 (compared to 0.5 in (4.14)).

- Instead of first assembling molecular orbitals (MOs) (4.9) out of atomic orbitals and then from MOs create molecular electronic states (4.13), we can also skip (4.9) and directly write a guess or variational Ansatz for molecular electronic states in terms of the original atomic orbitals.
  $\hookrightarrow$ This is called Heitler - London / Valence Bond Method.

- Some even more sophisticated methods for the calculation of molecular electronic states are the Hartree-Fock and DFT methods that we already discussed for atoms in section 2.4.4.

## 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.
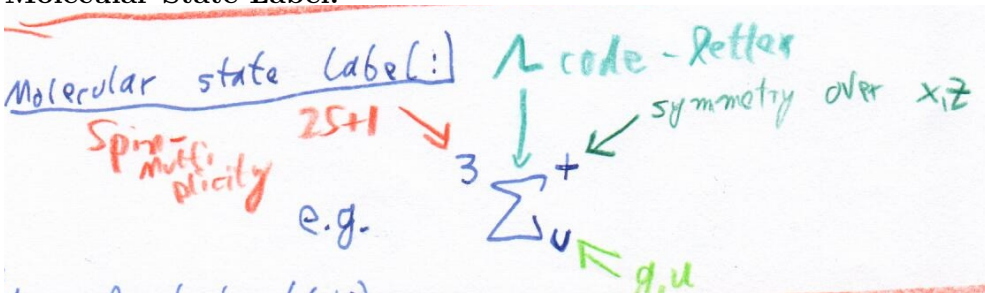Diagram:
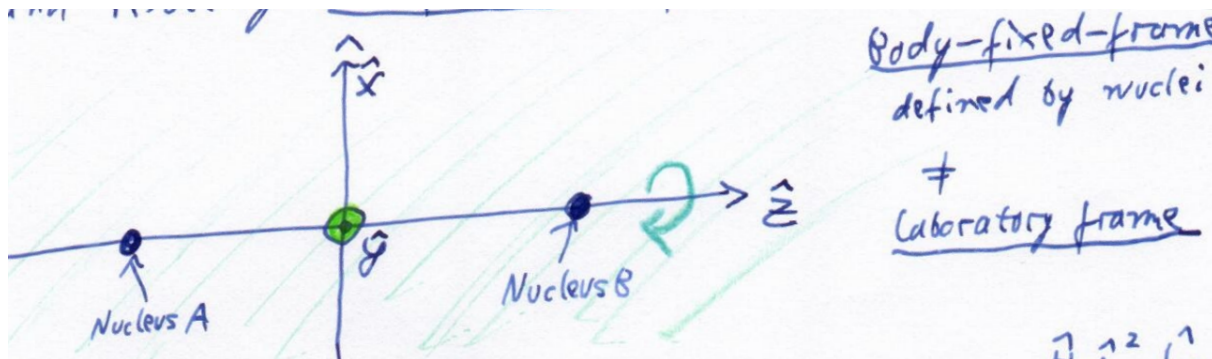


- - Earlier around an atomic nucleus we had a spherical symmetry and could classify states via the operators $\hat{H}$, $\hat{L}^2$, $\hat{L}_z$

  - Here, we can only use the cylindrical symmetry around the $z$ axis, indicated by the green circular arrow above. We thus classify states via $\hat{H}$ and $\hat{L}_z$ only.

  - Thus all electronic states of a di-atomic molecule satisfy $\hat{L}_z |\phi_s\rangle = \hbar M_L |\phi_s\rangle = \pm\hbar\Lambda |\phi_s\rangle$, where we de: $|M_L| = 0, 1, 2, ......$ According to this, molecular states are then given the code letters shown in green, and a single electron in a molecular orbital the ones in red

| Code Letters: $\Lambda =$ | 0, | 1, | 2, | 3 |
|---|---|---|---|---|
| | $\Sigma$ | $\Pi$ | $\Delta$ | $\Phi$ |
| (= Greek Capital for | S | P | D | F...) |
| (For single e$^-$ in MO | $\sigma$ | $\pi$ | $\delta$ | $\phi$) |

- 
  - The system is also symmetric under reflection off $x$, $z$ plane, shown as green shade above: This swaps $M_L \to -M_L$ for fixed $\Lambda \Rightarrow$ each quantum number $\Lambda$ is two-fold degenarate. This is called  (Λ-doubling)
  - For a molecular state with label $\Sigma$ we thus write $\Sigma^+$, ($\Sigma^-$) for symmetric (antisymmetric) states under the swap $y \to -y$.

- Finally the system is also symmetric under reflection through the origin shown as ● (point-reflection). For this symmetry the feature <u>homo-nuclear</u> is crucial. $\Rightarrow$ The wavefunction will also be symmetric or anti-symmetric under this operation $\Rightarrow$ This gives rise to the g(gerade), u(ungerade) labels, as before in section 4.3.

All this information is summarized in

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**Molecular State Label:**



Examples of these labels were found in (4.13) before.         (4.18)

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**Example for section 4.4: Li$_2$ Molecule:**

- Li Z=3 $\Rightarrow$ We have total of 6 electrons to distribute

| For <u>atoms</u> we were following: | ▶ Construct atomic states similar to Hydrogen |
| --- | --- |
| | ▶ Understand Differences to Hydrogen |
| | ▶ Fill from low to high energy, respecting the Pauli principle. |
| For <u>Molecules</u>: | ▶ Construct Molecular states based on <u>atoms</u> (4.13) |
| | ▶ Understand differences compared to atoms ($E_g < E_u$) |
| | ▶ Fill from low to high energy, respecting the Pauli principle |

- We can write an <u>electron configuration</u> of molecules, similar to what we did for atoms

$$\text{Li}_2 : {}^1\Sigma_g^+ = (1s\sigma_g)^2 \, (1s\sigma_u)^2 \, (2s\sigma_g)^2 \tag{4.19}$$

## 4.5 More General overview of chemical bonds

- Mathematically all bonds arise the same manner: We solve Eq. (4.2) (the electronic Schrödinger equation) as a function of static nuclear nuclear co-ordinates $\mathbf{R}$. If some resulting Born-Oppenheimer surface $E_q(\mathbf{R})$ has a local minimum, there <u>may</u> be a bond, depending on its depth.

- However the physical <u>interpretation</u> for the reason of the bond may vary, depending on the underlying electronic <u>quantum state</u> $\phi_q(\mathbf{R}; \mathbf{r}_1, \ldots, \mathbf{r}_n)$.

**Chemical bonds:**

**Covalent:**
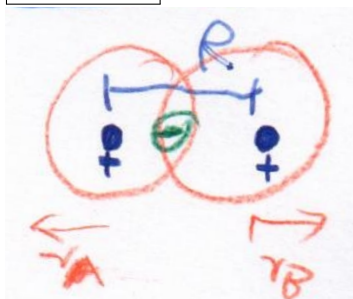


**left:** Nuclei <u>share</u> electrons: $\rightarrow$ larger negative charge density in the spatial area <u>between</u> the nuclei. As in the sketch this is typically important when $R < r_a + r_b$, where $R$ is the inter-nuclear distance and $r_{a/b}$ would be the size of the individual unbound atoms. In that case the electron clouds of individual atoms strongly overlapp.

**Ionic:**



**left:** Nuclei <u>transfer</u> electrons from one to another→ this causes excess positive charge $\oplus$ on one of them, and excess negative charge $\ominus$ on the other. Overall we obtain the usual Coulomb attraction with $V \sim 1/R$. This becomes more important at slightly larger separations than for covalent bonding, when $R \geq r_a + r_b$.

**Van-der Waals:**



**left:** Essentially individual atoms can polarise each other, the resulting dipole moments (their fluctuations) then attract, which gives rise to a potential $V \sim 1/R^6$. This will be dominant at even larger distances $R \gg r_a + r_b$, but an also lead to binding.
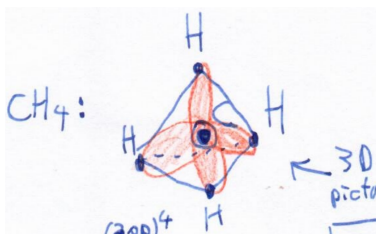
**Some more peculiar bond types:**

- 
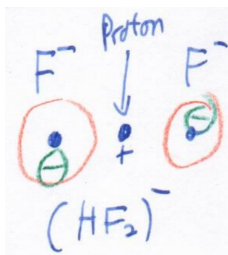
  **left:** Hydrogen bonding [$\approx$ charge reverse of a covalent bond], e.g. DNA strands bind like this

- 

  **left:** s-p hybrid molecular orbital $= |s\rangle + |p\rangle$. As first sketched in section 3.6.1, in such a superposition the electron on one atom is shifted into a <u>specific direction</u>. Many such orbitals can be nicely formed in Carbon: $(1s)^2 (2s)^2 (2p)^2 \rightarrow (1s)^2 (2sp)^4$.



**left:** Carbon can thus shift its four valence electron into four specific directions, for example in Methane