Lecture 4

THE TWO LEVEL MODEL OF BONDING

Covalent versus ionic bonding in diatoms

- Total energy of the H_2^+ molecule
- The covalent bond, H_2 molecule
- Closed shell interactions, He_2.
- The hetero nuclear bond, LiH.
- Ionization potential, electron affinity and electronegativity.
- MO picture of ionic bonds, NaCl dimer.

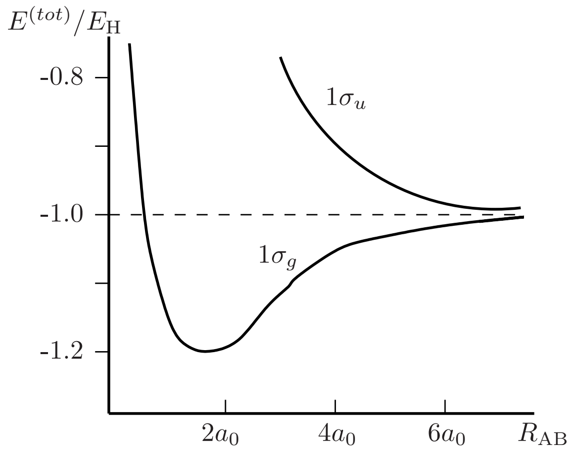
4.1: Total energy of the H_2^+ molecule

To the **orbital electronic** energy

$$E_{\sigma_\kappa} = \frac{\alpha \pm \beta}{1 \pm S} \quad \textit{where} \quad \kappa = \begin{cases} g & \textit{with} + \textit{sign} \\ u & \textit{with} - \textit{sign} \end{cases}$$

we must add the **nuclear repulsion** to obtain the **total energy**

$$E_{\sigma_\kappa}^{(tot)}(R_{AB}) = E_{\sigma_\kappa}(R_{AB}) + \frac{1}{R_{AB}}$$



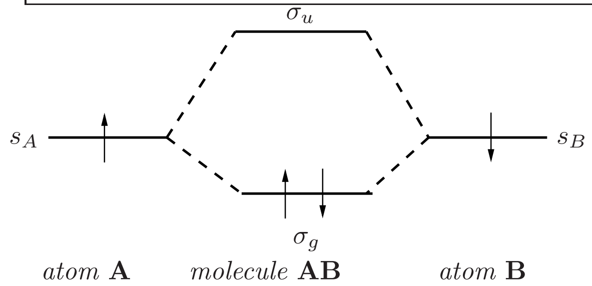
- **Short range** repulsion ($R_{AB} \to 0$).
- σ_g has a **minimum** (stable), σ_u has not (unstable)
- In the **dissociation limit**

$$R_{AB} \to \infty \quad \Rightarrow \quad E_{\sigma_\kappa}^{(tot)} \to E_{1s\mathrm{H}} = E_H$$

both curves approach the hydrogen atom energy.

4.2: Total energy of the H_2 molecule

Level diagrams correlate atomic and molecular states



Ground state:

σ_g occupied by **two** electrons, one from each atom

$$E_0^{(tot)}(R_{AB}) = 2E_{\sigma_g}(R_{AB}) + \frac{1}{R_{AB}}$$

Electronic energy doubled*

Energy curve as function of nuclear distance R_{AB}:

- **Short range** repulsion ($R_{AB} \to 0$).
- has **minimum** at equilibrium bond length.

- **Dissociates** in two atoms

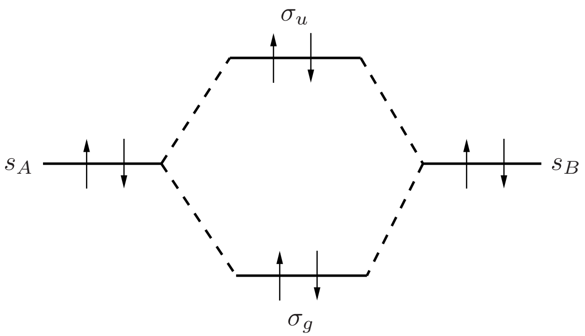
$$R_{AB} \to \infty \quad \Rightarrow \quad E_{\sigma_\kappa}^{(tot)} \to 2 \times E_H$$

* *But no electron-electron repulsion in this non-interacting MO approximation*

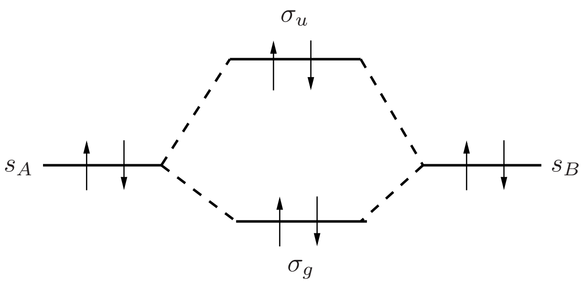
4.3: Total energy of He_2

atoms **closed shell** ⇒ *bonding and antibonding levels ocuppied*

The interaction is **non-bonding**



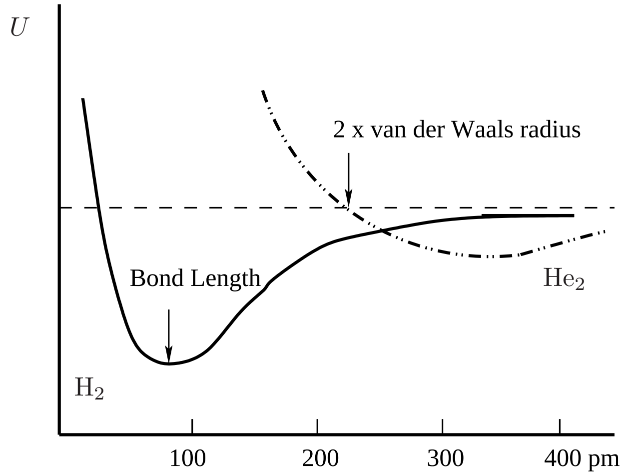
$S = 0$: levels symmetric, **no electronic interaction** energy repulsion purely nuclear ($1/R_{AB}$)



$S > 0$: net "**hard core**" **Pauli exclusion repulsion** (adding to nuclear repulsion)

Antibonding level raised more than bonding level lowered

4.4: H_2 and He_2 compared



Interaction potential

$$U(R) = E_0^{(tot)}(R) - E_0^{(tot)}(R \to \infty)$$

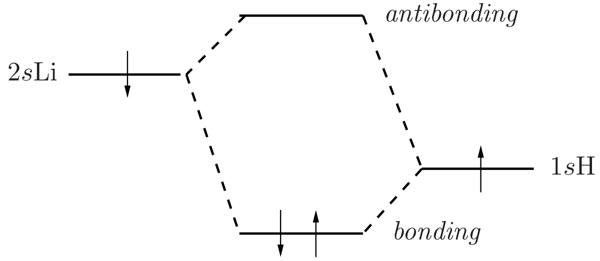
$$= E_0^{(tot)}(R) - 2E_0^{(atom)}$$

Repulsion;
H_2 : largely **nuclear** Coulomb interaction
He_2 : (non-bonding) electron exclusion (Pauli)

Attraction;
H_2 : bonding interaction
He_2 : Vander Waals (dispersive, very weak)

$$U(R) = 4\epsilon \left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6} \right]$$

4.5: Hetero-diatomic molecule LiH



Atomic levels are nolonger degenerate

Use **ionization potentials** (see later) as estimate for atomic energies

$$\begin{array}{llllll} A & = & \text{Lithium} & 2s_{\text{Li}} & : E_A = -5.4\text{eV} & = \alpha_1 \\ B & = & \text{Hydrogen} & 1s_{\text{H}} & : E_B = -13.6\text{eV} & = \alpha_2 \end{array}$$

and, hence, as estimate of Coulomb integrals in two level model

$$\mathbf{H} = \begin{pmatrix} \alpha_1 & \beta \\ \beta & \alpha_2 \end{pmatrix}$$

$$\alpha_2 \; \textit{(electronegative atom)} < \alpha_1 \; \textit{(electropositive atom)} < 0$$

Resonance integral is as usual:

$$\beta < 0$$

Overlap will be neglected for polar bonds: $S = 0$

4.5X: Binding in heteratomic diatoms

Total energy two-level system $\alpha_1 > \alpha_2$ with double groundstate occupation

$$E_0 = 2E_- \approx 2\alpha_2 - \frac{2\beta^2}{\alpha_1 - \alpha_2}$$

Electronic contribution to binding energy

$$\begin{aligned} E_0 - E_1 - E_2 &= 2E_- - (\alpha_1 + \alpha_2) \\ &\approx \alpha_2 - \alpha_1 - \frac{2\beta^2}{\alpha_1 - \alpha_2} \end{aligned}$$

As a result of electron transfer from the electropositive to the electronegative atom ($\alpha_1 > \alpha_2$) there is already binding even at negligible resonance ($\beta = 0$)

Example: application to LiH (energies in eV)

$$\begin{aligned} E_{\text{Li H}} - E_{\text{Li}} - E_{\text{H}} &\approx E_{\text{H}} - E_{\text{Li}} - \frac{2\beta^2}{E_{\text{Li}} - E_{\text{H}}} \\ &= -13.6 - (-5.4) - \frac{2\beta^2}{-5.4 - (-13.6)} \\ &= -8.2 - \frac{2\beta^2}{8.2} = -8.2 - 0.24\,\beta^2 \end{aligned}$$

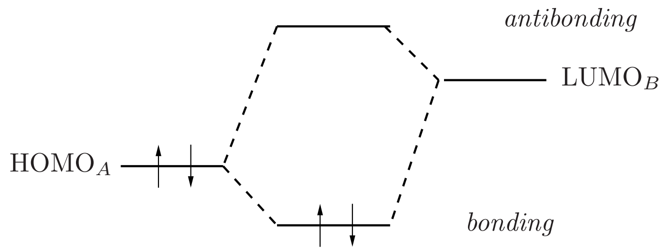
4.6: HOMO-LUMO interaction

Another illustration level repulsion:

HOMO : **Highest Occupied** Molecular Orbital
LUMO : **Lowest Unocupied** Molecular Orbital.

A doubly occupied (A) and empty orbital (B) can interact

provided **energy gap** $E_{\text{LUMO}} - E_{\text{HOMO}}$ *is not too large*



Lowering HOMO_A level by mixing (resonance) with LUMO_B

Example: **nucleophilic attack**

HOMO : non-bonded p orbital of H_2O, **nucleophile**
LUMO : π^* orbital of carbonyl group **electrophile**

4.7: The MO picture of the diatomic bond : summary

Total energy

$$E_0^{(tot)}(R_{AB}) = \sum_i^{\text{occ.}} n_i E_i(R_{AB}) + \frac{1}{R_{AB}}$$

Hetero-nuclear bonds stabilized by

- **Resonance** (covalent bonding)
- **Charge transfer** (ionic bonding) $\Rightarrow$ dipole moment

in various degrees depending on difference between α's.

4.8: How to estimate orbital energies?

Outer shell (HOMO): Use **Ionization potential** I

$$\text{X}(g) \rightarrow \text{X}^+(g) + e^-$$

$$I = E_{\text{X}^+} - E_{\text{X}} > 0$$

I = **Minimum energy** *required to remove an electron*

Inner shells: from Photo-Electron-Spectroscopy (**PES**)

$$\text{X}(g) + h\nu \rightarrow \text{X}^+(g) + e^-$$

$$h\nu = I + \frac{1}{2}mv^2$$

I = *difference energy of* **absorbed photon** *and kinetic energy of* **ejected electron**

Orbital energy estimated as

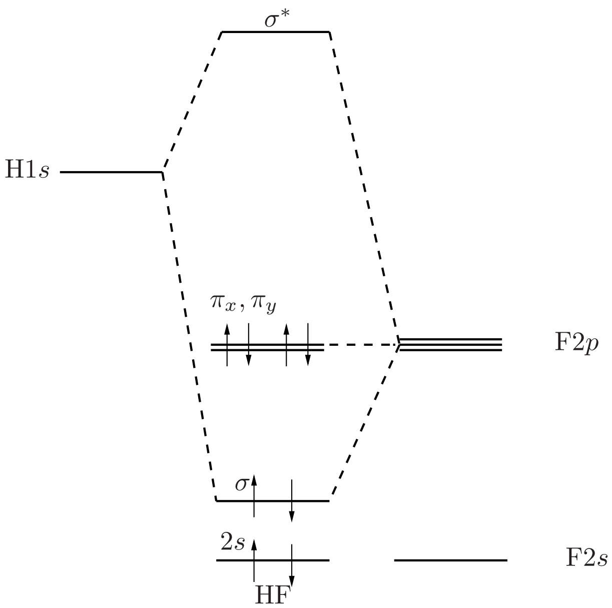
$$E_{\text{orbital}} \approx -I \quad \textit{Note change of sign}$$

4.9: Valence Orbital Ionization Energies

Experimental values in eV:

Atom	$1s$	$2s$	$2p$	$3s$	$3p$
H	13.6	-	-	-	-
He	24.6	-	-	-	-
Li	-	5.4	-	-	-
Be	-	9.3	-	-	-
B	-	14.0	8.3	-	-
C	-	19.4	10.6	-	-
N	-	25.6	13.2	-	-
O	-	32.3	15.8	-	-
F	-	40.2	18.6	-	-
Ne	-	48.5	21.6	-	-
Na	-	-	-	5.1	-
Mg	-	-	-	7.6	-
Al	-	-	-	11.3	5.9
Si	-	-	-	14.9	7.7
P	-	-	-	18.8	10.1
S	-	-	-	20.7	11.6
Cl	-	-	-	25.3	13.7
Ar	-	-	-	29.2	15.8

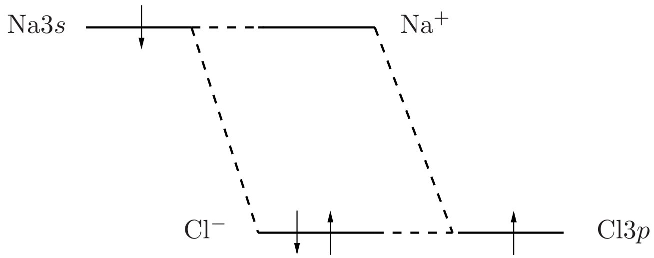
4.10: Energy level diagram of HF



Note

- $2p$ levels of fluor atom below $1s$ level of hydrogen.
- Only F$2p_z$ orbital mixes with the H$1s$ forming σ.
- F$2p_x$ and $2p_y$ become π type non-bonding. orbitals

4.11: Questions regarding ionic bonding



Does the MO picture work for strongly **ionic** bonds?

For example

Is this the level diagram of an ionic dimer such as NaCl?

Bonding entirely due to electron transfer ($\beta = 0$), hence

$$\begin{aligned} \Delta E &= E_{\text{NaCl}} - E_{\text{Na}} - E_{\text{Cl}} \\ &= 2\alpha_{\text{Cl}} - \alpha_{\text{Na}} - \alpha_{\text{Cl}} = \alpha_{\text{Cl}} - \alpha_{\text{Na}} \end{aligned}$$

Using the valence orbital ionization energy table

$$\begin{aligned} \Delta E &= -I_{3p\text{Cl}} - (-I_{3s\text{Na}}) \\ &= -13.7 + 5.1\text{eV} = -8.6\text{eV} \end{aligned}$$

Experimentally $\Delta E = -4.25$eV. **Something is wrong**

Electrons are added to Cl: So, should we have used the **electron affinity** *instead of the ionization potential for the electro-negative element (Cl)?*

4.12: Electron affinity and ionization potentials

Electron affinity A

$$\text{X}(g) + e^- \rightarrow \text{X}^-(g)$$

$$A = E_{\text{X}} - E_{\text{X}^-} \geq 0$$

$$\boxed{A = \textit{Binding energy electron added with zero kinetic energy}}$$

comparing to definition ionization potential I

$$\mathrm{X}(g) \;\rightarrow\; \mathrm{X}^+(g) + e^-$$

$$I = E_{\mathrm{X}^+} - E_{\mathrm{X}} > 0$$

$$\boxed{I = \textit{Minimum energy required to remove an electron}}$$

we see that

$$A_{\text{atom}} = I_{\text{anion}}$$

Electron affinities are positive (or zero) and moreover

$$I = E_{\mathrm{X}^+} - E_{\mathrm{X}} > E_{\mathrm{X}} - E_{\mathrm{X}^-} = A$$

4.13: Electronegativity

Mulliken defined (absolute) **electronegativity** as

$$\chi = \frac{I + A}{2}$$

Tendency of atoms to attract electrons in bond formation = average of energy for adding and removing electrons

Motivation for this particular definition: Consider gasphase equilibrium

$$\mathrm{Y}^+(g) + \mathrm{Z}^-(g) \;\rightleftharpoons\; \mathrm{YZ} \;\rightleftharpoons\; \mathrm{Y}^-(g) + \mathrm{Z}^+(g)$$

Energy difference between products on the right and the left

$$(I_{\mathrm{Z}} - A_{\mathrm{Y}}) - (I_{\mathrm{Y}} - A_{\mathrm{Z}}) = 2\,(\chi_{\mathrm{Z}} - \chi_{\mathrm{Y}})$$

*Charge distribution (**polarity**) in molecule is similar to the partioning of charge in the more stable dissociation product*

If Z is the more negative element

$$\chi_{\mathrm{Z}} > \chi_{\mathrm{Y}} \;\Rightarrow\; \textit{dominant prod.}\ \mathrm{Y}^+ + \mathrm{Z}^- \;\Rightarrow\; \mathrm{Y}^+\mathrm{Z}^-\ \textit{polarity in mol.}$$

If Y is the more negative element

$$\chi_{\mathrm{Z}} < \chi_{\mathrm{Y}} \;\Rightarrow\; \textit{dominant prod.}\ \mathrm{Y}^- + \mathrm{Z}^+ \;\Rightarrow\; \mathrm{Y}^-\mathrm{Z}^+\ \textit{polarity in mol.}$$

4.14: Thermochemistry of NaCl formation

Will the Cl^- electron affinity solve the NaCl dimer problem?:

Consider the gas phase formation of NaCl

$$\mathrm{Na}(g) + \mathrm{Cl}(g) \rightarrow \mathrm{NaCl}(g) \qquad \Delta H = -4.25\mathrm{eV}$$

An example of an almost pure ionic reaction

Resolve the reaction

- in an **electron transfer** at "infinite" separation

$$\mathrm{Na}(g) + \mathrm{Cl}(g) \rightarrow \mathrm{Na}^+(g) + \mathrm{Cl}^-(g)$$

- followed by an **association reaction** of ionic products

$$\mathrm{Na}^+(g) + \mathrm{Cl}^-(g) \rightarrow \mathrm{NaCl}(g)$$

4.15: Thermochemistry of NaCl formation (cont'd)

Energetics

- $\mathrm{Na}(g) + \mathrm{Cl}(g) \rightarrow \mathrm{Na}^+(g) + \mathrm{Cl}^-(g)$ determined by **ionization potentials**

$$\begin{aligned} \mathrm{Na}(g) &\;\rightarrow\; \mathrm{Na}^+(g) + e^-, & \Delta E = I_{\mathrm{Na}} &= 5.14\mathrm{eV} \\ \mathrm{Cl}(g) + e^- &\;\rightarrow\; \mathrm{Cl}^-(g) & \Delta E = -A_{\mathrm{Cl}} &= -3.61\mathrm{eV} \end{aligned}$$

giving for the transfer reaction energy

$$\Delta E_t = 5.14 - 3.61 = 1.53\mathrm{eV} \quad \textit{Reaction is exothermic!}$$

- $\mathrm{Na}^{+}(g) + \mathrm{Cl}^{-}(g) \rightarrow \mathrm{NaCl}$ determined by **Coulomb attraction**

$$E_c = -\frac{1}{R_{\mathrm{NaCL}}} = -6.04\mathrm{eV}$$

Hence, for the combined reaction

$$\Delta E = I_{\mathrm{Na}} - A_{\mathrm{Cl}} - \frac{1}{R_{\mathrm{NaCl}}} = -4.51\mathrm{eV}$$

very close to the experimental reaction energy of -4.25eV.

Coulomb energy stabilizes ionic bonds **not** *the electron affinity of the electro-negative element*

4.16: MO picture of ionic bonding

One thing that is wrong is that we forgot the Coulomb term in α

$$E_{-} = \alpha_2 = E_B - \int d\mathbf{r}\, \frac{[\psi_B(\mathbf{r})]^2}{|\mathbf{r} - \mathbf{R}_A|}$$

i.e. interaction of an electron on B with nucleus A. Using

$$[\psi_B(\mathbf{r})]^2 \approx \delta(\mathbf{r} - \mathbf{R}_B) \quad \textit{point charge approximation}$$

this becomes (recall we use atomic units)

$$E_{-} = \alpha_2 = E_B - \frac{1}{R_{AB}}$$

There are two electrons on B and none on A, giving

$$E_0^{tot} = 2E_{-} + \frac{1}{R_{AB}} = 2E_B - \frac{1}{R_{AB}}$$

and hence we find for the formation energy of the dimer

$$\Delta E = E_0^{(tot)} - E_A - E_B = E_B - E_A - \frac{1}{R_{AB}}$$

4.17: Application to the NaCL dimer

If we now set

$$E_A = -I_A \quad \textit{with } A = \mathrm{Na} \quad \textit{the electropositive atom}$$
$$E_B = -A_B \quad \textit{with } B = \mathrm{Cl} \quad \textit{the electronegative atom}$$

the result from thermochemical arguments is recovered

$$\Delta E = I_{\mathrm{Na}} - A_{\mathrm{Cl}} - \frac{1}{R_{\mathrm{NaCl}}}$$

Be very careful however with ionic systems: The real origin of these inconsistencies is the neglect of **electron-electron interaction** *in MO total energy*

$$E_{tot} = \sum_{I}^{occ} n_i E_i + \Delta E_{ee}$$

A striking illustration: Compare energies of an atom to its cation

- Total energy of a cation is higher (ionization potentials are positive)

$$E_{tot}^{\mathrm{cation}} > E_{tot}^{\mathrm{atom}}$$

- However energy levels are lower (attraction to nucleus stronger)

$$E_{i}^{\mathrm{cation}} < E_{i}^{\mathrm{atom}}$$