

# The molecular Hamiltonian

## The Extended Hückel method

Let us consider a heuristic, non rigorous, argument. Imagine that the Hamiltonian to be used in presence of two nuclei or potential boxes  $A$  and  $B$  which are placed in distant places of space

$$\hat{\mathcal{H}}^A = -\frac{\hbar^2 \nabla^2}{2m} + V(r - r_A)$$
$$\hat{\mathcal{H}}^B = -\frac{\hbar^2 \nabla^2}{2m} + V(r - r_B)$$

and can be solved independently.

$$\langle \alpha | \hat{\mathcal{H}}^A | \alpha \rangle = E_\alpha^A \text{ and } \langle \beta | \hat{\mathcal{H}}^B | \beta \rangle = E_\beta^B$$

Now we want to solve the SE in presence of the two potentials  $V_{AB} = V(r - r_A) + V(r - r_B)$  is the **sum** two parts, each one operating in the region of the corresponding atomic orbitals. For example we could use a function  $Q(|r - r_A|)$  that is 1 in the zone around the potential well and zero out side.

$$\hat{\mathcal{H}}^A \simeq -Q(|r - r_A|) \frac{\hbar^2 \nabla^2}{2m} + V(r - r_A)$$
$$\hat{\mathcal{H}}^B \simeq -Q(|r - r_B|) \frac{\hbar^2 \nabla^2}{2m} + V(r - r_B)$$

Hence we could write

$$\hat{\mathcal{H}}^{AB} \simeq \hat{\mathcal{H}}^A + \hat{\mathcal{H}}^B$$

In that case we could evaluate the matrix elements using these properties which leads to:

$$\begin{aligned} H_{\alpha,\beta}^{AB} &= \langle \alpha | \hat{\mathcal{H}}^{AB} | \beta \rangle \simeq \langle \alpha | \hat{\mathcal{H}}^A | \beta \rangle + \langle \alpha | \hat{\mathcal{H}}^B | \beta \rangle \\ &= E_\alpha^A \langle \alpha | \beta \rangle + \langle \alpha | \beta \rangle E_\beta^B \\ &= g \frac{E_\alpha^A + E_\beta^B}{2} S_{\alpha\beta} \end{aligned}$$

with  $g = 2$  and  $S_{\alpha\beta} = \langle \alpha | \beta \rangle$  the overlap matrix element. This expression was developed by Roald Hoffmann in 1963. Since it extends a previous argument used by Hückel to describe bonds in carbon compounds it is called the *Extended Hückel method*. Typically what one does is to use the measured molecular distance as inputs. Similarly, for  $E_\alpha^A$  and  $E_\beta^B$  the experimental ionization energies while the overlaps are calculated from the wave function obtained from an atomic calculation such a Hartree-Fock. Using this prescription, a typical value that fits better the experimental values is  $g=1.75$ . The difference from 2 is attributed to the non-orthogonality of the states. Hence it is a semiempirical method, in contrast with the ab-initio methods that only use the atomic numbers as inputs.

The most important fact to learn from this formula is to recognize that symmetry (or

geometry) is the origin of different signs in the matrix elements and the source of selection rules for the bonding interactions.

In order to deal with the non-orthogonality of two atomic basis we write the eigenvalue equation:

$$\widehat{\mathcal{H}}^{AB} [u_{\alpha,\varepsilon}|\alpha\rangle + u_{\beta,\varepsilon}|\beta\rangle] = \varepsilon [u_{\alpha,\varepsilon}|\alpha\rangle + u_{\beta,\varepsilon}|\beta\rangle].$$

multiplying it alternatively by  $\langle\alpha|$  and by  $\langle\beta|$  one gets two equations for the components  $u_{\alpha,\varepsilon}$  and  $u_{\beta,\varepsilon}$  of the eigenvector  $\vec{u}_\varepsilon$ . Since the states are non-orthogonal we will have coefficients of the form  $\langle\alpha|\beta\rangle = S_{\alpha\beta}$  which we identify as components of the **overlap matrix S**. This leads the actual eigenvalue equation:

$$[\mathbf{H}^{AB} - \varepsilon\mathbf{S}]\vec{u}_\varepsilon = 0$$

used in the extended Hückel package.

### Non-orthogonal states

It is not quite unusual to we have a basis, where states, although normalized are not orthogonal to each other. Hence

$$S_{i,j} = \langle i|j\rangle \text{ with } S_{i,i} = 1$$

the Hamiltonian matrix elements still can be evaluated in this basis

$$H_{i,j} = \langle i|\mathcal{H}|j\rangle$$

we want to know the eigenenergies and eigenvector. One possible procedure is first to find the an orthonormal basis, for example with the Gram-Schmidt procedure and then rewrite the the Hamiltonian in this new basis. Equivalently, one could apply a variational principle using the trial function:

$$|\psi\rangle = \sum_i c_i|i\rangle$$

$$\varepsilon = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{\sum_{ij} c_j^* c_i H_{ji}}{\sum_{ij} c_j^* c_i S_{ji}}$$

$$\begin{aligned} \frac{\partial\varepsilon}{\partial c_k} &= \frac{\sum_j c_j^* H_{jk} + \sum_i c_i H_{ki}}{\sum_{ij} c_j^* c_i S_{ji}} - \frac{\left(\sum_{ij} c_j^* c_i H_{ji}\right)\left(\sum_j c_j^* S_{jk} + \sum_i c_i S_{ki}\right)}{\left(\sum_{ij} c_j^* c_i S_{ji}\right)^2} \\ &= \frac{\sum_j c_j^* H_{jk} + \sum_i c_i H_{ki}}{\sum_{ij} c_j^* c_i S_{ji}} - \frac{\varepsilon\left(\sum_j c_j^* S_{jk} + \sum_i c_i S_{ki}\right)}{\sum_{ij} c_j^* c_i S_{ji}} \\ &= \frac{\sum_j c_j^* (H_{jk} - \varepsilon S_{jk}) + \sum_i c_i (H_{ki} - \varepsilon S_{ki})}{\sum_{ij} c_j^* c_i S_{ji}} \end{aligned}$$

Roothaan showed that the eigen-energies can be obtained from the roots of the linear equation.

$$\det|\mathbf{H} - \epsilon\mathbf{S}| = 0$$

which is often called the Roothaan's equation in the name of who deduced it a Hartree-Fock method.

In order to see how it works consider a simple case of a two dimensional space the two states  $|A\rangle$  and  $|B\rangle$  which are linearly independent and properly normalized  $\langle A|A\rangle = 1$  and  $\langle B|B\rangle = 1$  but not orthogonal i.e.  $\langle A|B\rangle = S \neq 0$ . This is expressed in the overlap matrix

$$\mathbf{S} = \begin{bmatrix} 1 & S \\ S & 1 \end{bmatrix}.$$

We know the energy matrix elements in this basis are

$$\mathbf{H} = \begin{bmatrix} E_A & -V \\ -V & E_B \end{bmatrix},$$

the solution can be worked out in Maple to obtain:

$$\frac{\frac{1}{2}(E_A + E_B) + SV \mp \sqrt{(\frac{1}{2}(E_A + E_B) + SV)^2 + (1 - S)^2(V^2 - E_A E_B)}}{(1 - S^2)}$$

and which can be expanded as a series in the overlap:

$$E^\mp \simeq \frac{1}{2}(E_A + E_B) \mp \sqrt{(\frac{1}{2}(E_A - E_B))^2 + V^2} + S \left[ V - \frac{(E_A + E_B)}{\sqrt{(E_A + E_B)^2 + 4V^2}} V \right] + \mathcal{O}(S^2)$$

There is an **energy increase** in both levels **proportional** to  $SV$ . This has an important consequence that one can not increase the coupling just by decreasing the distance since the energies will diverge. For  $s$  and  $p$  orbitals both the overlap and the bonding term diverge as  $1/d^2$  hence one would expect that the energy would blow up as  $1/d^4$ .

In the simple example of two approaching boxes, the same physics can be seen just as an effect of uncertainty principle as the lowest energy has to blow up as  $1/d^2$

This still seems quite a mess, let's still go to a simpler case

$$E_0 = E_A = E_B$$

$$V_{AB} = -V \quad \text{with } V > 0$$

the secular equation becomes

$$(E_0 - \epsilon)^2 - (-V - \epsilon S)^2 = 0$$

which can be rewritten as

$$[(E_0 - \varepsilon) - (-V - \varepsilon S)][(E_0 - \varepsilon) + (-V - \varepsilon S)] = 0$$

either the first bracket is zero or the second one is zero. This provides the two eigenvalues:

$$\varepsilon_+ = \frac{E_0 + V}{1 - S}$$

$$\varepsilon_- = \frac{E_0 - V}{1 + S}$$

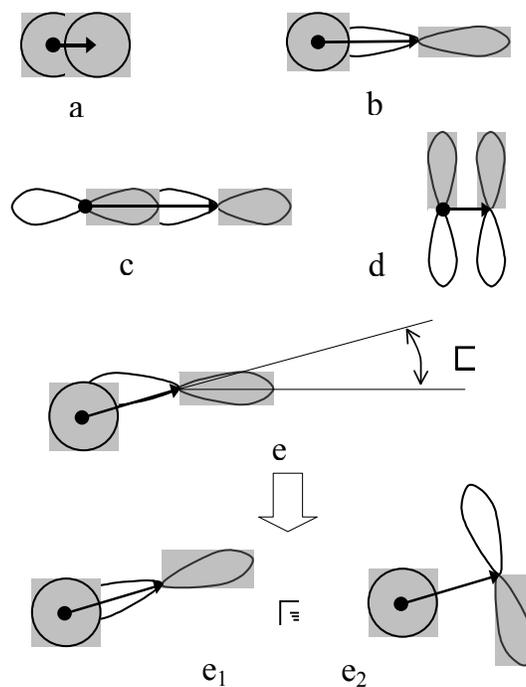
Typically, the overlaps tend to be positive we see that the bonding state is even deeper in energy by effect of the overlap while the antibonding tends to be higher in energy.

In the rest of these notes, we will use the Hamiltonian above within the **“tight-binding”** approximation which keeps only nearest neighbors interactions and neglects overlaps. In quantum chemistry this approximation is called *Completely Neglected Differential Overlaps* (CNDO).

## Tight Binding: The Harrison’s parameters

To evaluate a matrix element  $\langle \alpha | \hat{H} | \beta \rangle$  between orbitals at different atoms, we construct the vector  $\mathbf{a}$  from the atom at which  $\langle \alpha |$  is centered to the atom of  $|\beta\rangle$ , the right atom.

The  $z$ -axis is constructed, in both atoms along the direction of  $\mathbf{a}$ . The polar and azimuthal angles being  $\theta$  and  $\phi$  respectively. The angular part of the orbitals are then  $Y_{l,m}(\theta, \phi)$  and  $Y_{l',m'}(\theta', \phi)$ . The angular factors depending upon  $\phi$  combine to give the factor  $e^{i(m-m')\phi}$ . Therefore, this integral will be zero unless  $m = m'$  and  $V$  can be unambiguously denoted with three subindexes. The indexes used in the matrix elements follow the convention of Slater and Koster (1954). Then, the matrix elements are labeled  $\sigma$ ,  $\pi$  and  $\delta$  for  $m = 0$ , 1 and 2 respectively. For example the matrix element  $V_{sp\sigma}$  corresponds to  $l = 0$ ,  $l' = 1$  and  $m = 0$ .



### Geometry of matrix elements

The figure above shows the geometry associated to the matrix elements. The positive parts of the wave function are shaded while negative parts are white. Figure **a**) shows two  $s$  orbitals at a distance **a**. Their overlap leads to the matrix element  $V_{ss\sigma}$ . Part **b**) shows the overlap originating  $V_{sp\sigma}$ , a matrix element which has different sign than  $V_{ss\sigma}$ . Part **c**) schematizes orbitals interacting with  $V_{pp\sigma}$  and **d**) with a  $V_{pp\pi}$ . Finally, a general orientation of the orbitals respective to the internuclear vector as depicted in **e**) would lead to a matrix element of the form  $V_{sx} = \langle s | \hat{H} | x \rangle = V_{sp\sigma} \cos \theta + V_{sp\pi} \sin \theta$ . Where  $V_{sp\pi} \equiv 0$  by symmetry as can be inferred from the part **e**<sub>2</sub>).

A practical estimation of the matrix elements is provided by Harrison and is based in a paper by Froyen and Harrison (1979). A brief idea of its logic underlying his proposal will be discussed below. For the moment let us say that it is clear that the interaction terms should be bigger (in magnitude) for shorter distances and since they account for the energy won by delocalization, we expect that

$$V_{l'l'm} = \eta_{l'l'm} \hbar^2 / (md^2), \text{ for } l, l' = 0, 1$$

where the values of the coefficient are given in the table below:

Coefficient	Theoretical Values		Adjusted
	Simple cubic structure	Tetrahedral	
$\eta_{ss\sigma}$	$-\frac{\pi^2}{8} = -1.23$	$\frac{9\pi^2}{64} = -1.39$	-1.40
$\eta_{sp\sigma}$	$\frac{\pi}{2} \sqrt{\frac{\pi^2}{4} - 1} = 1.90$	$\frac{9\pi^2}{32} \sqrt{1 - \frac{16}{3\pi^2}} = 3.24$	1.84
$\eta_{pp\sigma}$	$\frac{3\pi^2}{8} = 3.70$	$\frac{21}{64} \pi^2 = 3.24$	3.24
$\eta_{pp\pi}$	$-\frac{\pi^2}{8} = -1.23$	$-\frac{3\pi^2}{32} = -0.93$	-0.81

In a similar way the homonuclear parameters coupling the d orbitals are evaluated connecting the  $d$  orbitals are

$$V_{ll'm} = \eta_{ll'm} \hbar^2 r_d^3 / (md^5), \text{ for } l, l' = 2$$

where the atomic radius  $r_d^3$  is tabulated

$$Ti \rightarrow 1.03 \text{ \AA}$$

$$Fe \rightarrow 0.74 \text{ \AA}$$

$$Cu \rightarrow 0.69 \text{ \AA}$$

and

$$\eta_{dd\sigma} = -\frac{45}{\pi}$$

$$\eta_{dd\pi} = \frac{30}{\pi}$$

$$\eta_{dd\delta} = -\frac{15}{2\pi}$$

Finally the interaction that fits the narrow bands associated with the f localizes orbitals can be seen to scale with distance  $d$  as.

$$V_{ffx} = \eta_{ffx} \hbar^2 r_f^5 / (md^7)$$

The fact that we want to rescue is that the scaling laws of the homonuclear coupling matrix elements with the distance depends on the angular momentum.

We are not going to use these parameters in this course but they are given just for completeness to estimate the values if needed. However, one must remember that the above parameters only account for the kinetic energy, and for both  $d$  and  $f$  orbital the Coulomb interactions play a most relevant role.

ref. W. A Harrison, *Elementary Electronic Structure*, World Scientific, Singapore (1999)

## Polarity and covalency

The simplest Hamiltonian that describe the molecular interaction between two orbitals belonging to different atoms  $A$  and  $B$  is:

$$\mathbf{H} = \begin{bmatrix} E_A & V_2 \\ V_2 & E_B \end{bmatrix}$$

Let us define:

$$V_3 = \frac{1}{2}(E_B - E_A) > 0$$

and typical  $V_2 < 0$ .

The polarity parameter is defined by Harrison as

$$\alpha_P = \frac{V_3}{\sqrt{|V_2|^2 + |V_3|^2}}.$$

The bonding state becomes

$$u_{1g} = \sqrt{\frac{1 + \alpha_P}{2}} \quad \text{and} \quad u_{2g} = \sqrt{\frac{1 - \alpha_P}{2}}$$

Analogously, the ungerade or antibonding amplitudes are:

$$u_{1u} = \sqrt{\frac{1 - \alpha_P}{2}} \quad \text{and} \quad u_{2u} = -\sqrt{\frac{1 + \alpha_P}{2}}$$

Let's call  $|+\rangle$  the bonding state. The probability to find the electron in atom  $A$  is:

$$P_A = \frac{|\langle A|+\rangle|^2}{|\langle A|+\rangle|^2 + |\langle B|+\rangle|^2} = \frac{1 + \alpha_P^2}{2}$$

Similarly, the probability to find the electron in  $B$  is

$$P_B = \frac{|\langle B|+\rangle|^2}{|\langle A|+\rangle|^2 + |\langle B|+\rangle|^2} = \frac{1 - \alpha_P^2}{2}$$

Hence  $\alpha_P^2$  accounts for the charge transfer towards  $A$  which gives rise to a dipolar moment. Accordingly, the coefficient  $\alpha_P$ , defined with equation

$$\alpha_P^2 = \frac{V_3^2}{V_3^2 + V_2^2}$$

is called **polarity**.

**Problem:** Take an electric field  $E$  along the axis of a  $H_2$  molecule. If the s-states of the two orbitals are separated by  $d$ , this will make an energy difference between the two atomic orbitals of  $eEd$ , making the molecule polar. This will also shift the average occupation of each atomic orbital from the original  $u_i^2 = 1/2$  with no field. Calculate the dipole  $p = \alpha E$  that arises in first order in the field (two electrons in the bonding state) to obtain the polarizability  $\alpha$  is related to the polarity coefficient  $\alpha_P$ . Magnitudes are enough.

A complementary quantity, the **covalency** coefficient  $\alpha_C$ , is defined through the relation:

$$\alpha_C^2 = 1 - \alpha_P^2 = \frac{V_2^2}{V_3^2 + V_2^2}$$

This justifies the identification calling  $V_2$  a **covalent energy** and to  $V_3$  a **polar energy**.

## A simple case of Ligand Field

We are going to consider the H – Li molecule where the electronic structure of each atom is Li[ $1s^2 2s^1$ ] and H[ $1s^1$ ]. Obviously, each atom would like to receive an electron to complete its energy shell, so they share.

Since the energy of the Lithium  $1s^2$  orbital lies well below the 13.5 eV of the Hydrogen  $1s^1$  orbital, the only relevant matrix elements are:

$$\begin{aligned} V_{s,s} &= V_{ss\sigma} < 0 \\ V_{p_z,s} &= V_{ps\sigma} < 0 \\ V_{p_y,s} &= V_{p_x,s} \equiv 0. \end{aligned}$$

The matrix representation of the Hamiltonian is:

$$\begin{bmatrix} & \begin{matrix} {}_1s \text{ H} & {}_2s \text{ Li} & {}_{2p_z} \text{ Li} & {}_{2p_x} \text{ Li} & {}_{2p_y} \text{ Li} \end{matrix} \\ \begin{matrix} {}_1s \\ {}_2s \\ {}_{2p_z} \\ {}_{2p_x} \\ {}_{2p_y} \end{matrix} & \begin{bmatrix} E_{1s} & V_{ss\sigma} & V_{ps\sigma} & \cdot & \cdot \\ V_{ss\sigma} & E_{2s} & \cdot & \cdot & \cdot \\ V_{ps\sigma} & \cdot & E_{2p} & \cdot & \cdot \\ \cdot & \cdot & \cdot & E_{2p} & \cdot \\ \cdot & \cdot & \cdot & \cdot & E_{2s} \end{bmatrix} \end{bmatrix}$$

where we represent the null elements with a dot instead of a 0 to facilitate the visualization of the structure taken by the non-zero elements. Notice that the convention of indices indicates that the H approaches the Li from above. Once a convention is adopted, one should keep it in all the matrix elements. This is essential to get signs in the interactions providing a consistence between energies and molecular orbitals. There are two elements of the same order that mix both atoms. Which one of the Li orbitals will bind the H? Since  $V_{ss\sigma} \simeq V_{ps\sigma} \simeq V$  the answer is both! The presence of the nucleus of the Hydrogen breaks the symmetry that produced the degeneracy of the Li levels. The situation is similar to what happen when a Li atom is placed in an electric field. Hence, we do a transformation within the Li orbitals

$$\begin{aligned} |sp^+\rangle &= \frac{1}{\sqrt{2}}(|2s\rangle + |2p_z\rangle) \\ |sp^-\rangle &= \frac{1}{\sqrt{2}}(|2s\rangle - |2p_z\rangle) \end{aligned}$$

which were discussed in the context of the Stark effect. In the new basis, it is easy to evaluate the matrix elements

$$\begin{aligned}\langle sp^+ | \hat{H}^{\text{Li}} | sp^\pm \rangle &= \frac{1}{2} (\langle 2s | + \langle 2p_z |) \hat{H}^{\text{Li}} (|2s\rangle \pm |2p_z\rangle) \\ &= \frac{1}{2} [E_{2s} + 0 \pm E_{2p} + 0]\end{aligned}$$

The calculation of the other matrix elements follows the same procedure.

$$\begin{aligned}\langle sp^+ | \hat{H}^{\text{Li}} | sp^+ \rangle &= \frac{1}{2} [E_{2s} + E_{2p}] = E_2 \\ \langle sp^+ | \hat{H}^{\text{Li}} | sp^- \rangle &= -\frac{1}{2} [E_{2p} - E_{2s}] = V_1 \\ \langle sp^- | \hat{H}^{\text{Li}} | sp^- \rangle &= \frac{1}{2} [E_{2s} + E_{2p}] = E_2\end{aligned}$$

For reasons that will become more clear below  $V_1$  is frequently called a **metallic or banding energy** term.

The most important term is

$$\begin{aligned}\langle sp^\mp | \hat{V}^{\text{H-Li}} | 1s \rangle &= \frac{1}{\sqrt{2}} \{ \langle 2s | \pm \langle 2p_z | \} \hat{V}^{\text{H-Li}} (|1s\rangle) \\ &= \frac{1}{\sqrt{2}} (V_{ss\sigma} \pm V_{sp\sigma}) \\ &= \begin{cases} \sqrt{2} V = V_\sigma < 0 \\ \simeq 0 \end{cases}\end{aligned}$$

Notice the  $\sqrt{2}$  factor which reinforces the covalent interaction with the hybrid orbital. In the new basis the Hamiltonian is written as

$$\mathbf{H}_{\text{H-Li}} = \begin{bmatrix} \text{H}_{1s} & \text{Li}_{2sp^-} & \text{Li}_{2sp^+} & \text{Li}_{2px} & \text{Li}_{2py} \\ \text{H}_{1s} & E_{1s} & \sqrt{2} V & \cdot & \cdot & \cdot \\ \text{Li}_{2sp^-} & \sqrt{2} V & E_2 & V_1 & \cdot & \cdot \\ \text{Li}_{2sp^+} & \cdot & V_1 & E_2 & \cdot & \cdot \\ \text{Li}_{2px} & \cdot & \cdot & \cdot & E_{2p} & \cdot \\ \text{Li}_{2py} & \cdot & \cdot & \cdot & \cdot & E_{2p} \end{bmatrix}$$

Notice that  $V_1 < 0$  implies that in case of atoms far apart, the atomic orbitals would be recovered. At atomic distances in this species  $|\sqrt{2} V| \gg |V_1|$ . Actually, the value  $|V_1| = E_{2p} - E_{2s} \simeq 2\text{eV}$  for Li increases regularly in the period up to approximately 27eV for Ne.

Therefore, in the LiH molecule, the important matrix to obtain the energy levels is

$$\begin{bmatrix} E_{1s}^H & V_\sigma \\ V_\sigma & E_2^{\text{Li}} \end{bmatrix}$$

with  $E_2^{\text{Li}} - E_{1s}^H > 0$  and the discussion of the preceding subsection concerning the polarity will apply.

## Hybrid orbitals

We already discussed the appearance of the  $sp$  hybrid orbitals in the context of the Stark effect and the  $\text{HLi}$  molecule. When we are dealing with methane ( $\text{CH}_4$ ) we see that the H would need to be placed as much symmetrically as possible around the C. This is the tetrahedral symmetry.

### The $sp^3$

The  $sp^3$  family which provides states with tetrahedral symmetry on the space. These were first defined by Koster and Slater as:

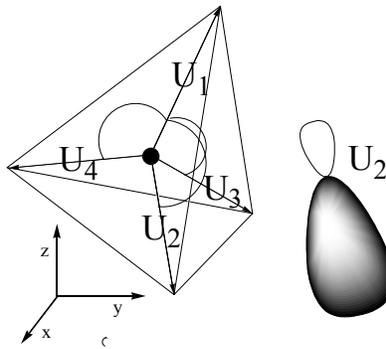
$$|U_1\rangle = \frac{1}{2}(|s\rangle + |p_x\rangle + |p_y\rangle + |p_z\rangle) \text{ with orientation } [111]$$

$$|U_2\rangle = \frac{1}{2}(|s\rangle + |p_x\rangle - |p_y\rangle - |p_z\rangle) \text{ with orientation } [1\bar{1}\bar{1}]$$

$$|U_3\rangle = \frac{1}{2}(|s\rangle - |p_x\rangle + |p_y\rangle - |p_z\rangle) \text{ with orientation } [\bar{1}1\bar{1}]$$

$$|U_4\rangle = \frac{1}{2}(|s\rangle - |p_x\rangle - |p_y\rangle + |p_z\rangle) \text{ with orientation } [\bar{1}\bar{1}1]$$

These orbitals can be plotted in the form



Koster and Slater  $sp^3$  orbitals

We then evaluate the matrix elements:

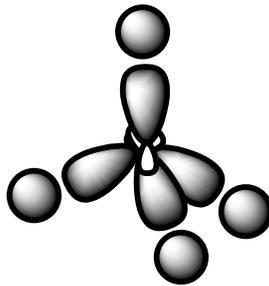
$$\begin{aligned} \langle U_1 | \hat{H}^{\text{atom}} | U_1 \rangle &= \frac{1}{4} (\langle s | + \langle p_x | + \langle p_y | + \langle p_z |) \hat{H}^{\text{atom}} (|s\rangle + |p_x\rangle + |p_y\rangle + |p_z\rangle) \\ &= \frac{1}{4} (E_s + 3E_p) = \langle U_n | H^{\text{atom}} | U_n \rangle \end{aligned}$$

this is called the **hybrid energy**. While the mixing term will be:

$$\begin{aligned}
\langle U_1 | \hat{H}^{\text{atom}} | U_2 \rangle &= \frac{1}{4} (\langle s | + \langle p_x | + \langle p_y | + \langle p_z | ) \hat{H}^{\text{atom}} ( |s\rangle + |p_x\rangle - |p_y\rangle - |p_z\rangle ) \\
&= \frac{1}{4} (E_s - E_p) = V_1 \\
&= \langle U_1 | \hat{H}^{\text{atom}} | U_3 \rangle = \langle U_1 | \hat{H}^{\text{atom}} | U_4 \rangle = \langle U_2 | \hat{H}^{\text{atom}} | U_4 \rangle \dots
\end{aligned}$$

Simple molecules:  $CH_4$  and  $C_2H_6$

Having analyzed the possible states of an atom, let's see the structure of the **methane** ( $CH_4$ ) molecule. We know that it has the structure of a tetrahedral pyramid, with the C-H bonds forming angles of  $109.5^\circ$  to each other.



The electronic Hamiltonian in the  $sp^3$  basis for the C atom is

$$H = \begin{bmatrix}
& H_{1s} & H_{2s} & H_{3s} & H_{4s} & c_{U_1} & c_{U_2} & c_{U_3} & c_{U_4} \\
H_{1s} & E_{1s}^H & \cdot & \cdot & \cdot & V_2 & \cdot & \cdot & \cdot \\
H_{2s} & \cdot & E_{1s}^H & \cdot & \cdot & \cdot & V_2 & \cdot & \cdot \\
H_{3s} & \cdot & \cdot & E_{1s}^H & \cdot & \cdot & \cdot & V_2 & \cdot \\
H_{4s} & \cdot & \cdot & \cdot & E_{1s}^H & \cdot & \cdot & \cdot & V_2 \\
c_{U_1} & V_2 & \cdot & \cdot & \cdot & E_2^C & V_1 & V_1 & V_1 \\
c_{U_2} & \cdot & V_2 & \cdot & \cdot & V_1 & E_2^C & V_1 & V_1 \\
c_{U_3} & \cdot & \cdot & V_2 & \cdot & V_1 & V_1 & E_2^C & V_1 \\
c_{U_4} & \cdot & \cdot & \cdot & V_2 & V_1 & V_1 & V_1 & E_2^C
\end{bmatrix}$$

Here we see that we might split the problem in 4 identical  $2 \times 2$  matrices that represent the CH coupling

$$\begin{bmatrix}
E_{1s}^H & V_2 \\
V_2 & E_2^C
\end{bmatrix}$$

with eigenvalues:

$$E_u^{C-H} = \frac{1}{2}(E_{1s}^H + E_2^C) + \sqrt{\frac{1}{4}(E_{1s}^H - E_2^C)^2 + V_2^2}$$

$$E_g^{C-H} = \frac{1}{2}(E_{1s}^H + E_2^C) - \sqrt{\frac{1}{4}(E_{1s}^H - E_2^C)^2 + V_2^2}$$

with eigenstates of the form

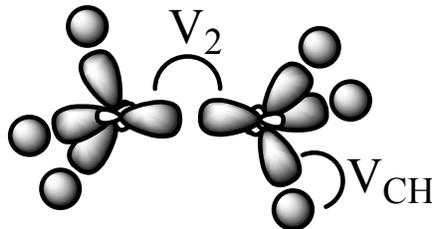
$$b^{C-H} =$$

The problem is almost solved. However we might still want to see what happens with the four degenerate bonding states that hold the eight electrons shared in the  $CH_4$  bond. Coming back to the intra-atomic mixing term in the carbon, that we neglected before, we would get a Hamiltonian of the form

$$H_g^{C-H} = \begin{bmatrix} E_g^{C-H} & \frac{1}{2}V_1 & \frac{1}{2}V_1 & \frac{1}{2}V_1 \\ \frac{1}{2}V_1 & E_g^{C-H} & \frac{1}{2}V_1 & \frac{1}{2}V_1 \\ \frac{1}{2}V_1 & \frac{1}{2}V_1 & E_g^{C-H} & \frac{1}{2}V_1 \\ \frac{1}{2}V_1 & \frac{1}{2}V_1 & \frac{1}{2}V_1 & E_g^{C-H} \end{bmatrix}$$

The interaction will break the four fold degeneracy of the bonding state into a lower  $s$ -like state of energy  $E_g^{C-H} - 3\frac{1}{2}|V_1|$  and three degenerate  $p$ -like states with energy  $E_g^{C-H} + \frac{1}{2}|V_1|$ . Since the trace of the matrix is constant, and all the states are filled it **will not change the total electronic energy!** Therefore, we see that it is correct to neglect this interaction. A similar situation will occur with the empty anti-bonding states.

The evaluation of the electronic structure of **ethane** ( $C_2H_6$ ) follows a similar procedure.



Ethane

The C-H bonds are very strong and each one leads to a corresponding  $2 \times 2$  bonding matrix that provides the bonding states that will hold 2 electrons. Hence they go out of the calculation. We are only left with sigma C-C bond. This is easier represented in a graphic energy representation than in matrix form.

From the Harrison book we extract typical interaction matrix elements which, being obtained from the crystalline structure apply to homo-atomic bindings:

	Metallic energy	Covalent Energy
Element	$V_1[\text{eV}]$	$V_2[\text{eV}]$
C	2.13	6.94
Si	1.76	2.94
Ge	2.01	2.76
Sn	1.64	2.10

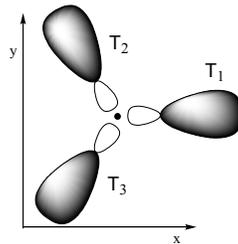
When dealing with other carbon compounds one has to resort to the **the  $sp^2$**

Other hybrid orbitals are the  $sp^2$  family in the  $xy$  plane:

$$|T_1\rangle = \frac{1}{\sqrt{3}} (|s\rangle + \sqrt{2}|p_x\rangle)$$

$$|T_2\rangle = \frac{1}{\sqrt{3}} (|s\rangle - \sqrt{\frac{1}{2}}|p_x\rangle + \sqrt{\frac{3}{2}}|p_y\rangle)$$

$$|T_3\rangle = \frac{1}{\sqrt{3}} (|s\rangle - \sqrt{\frac{1}{2}}|p_x\rangle - \sqrt{\frac{3}{2}}|p_y\rangle)$$



Set of  $sp^2$

The energies of these orbitals are

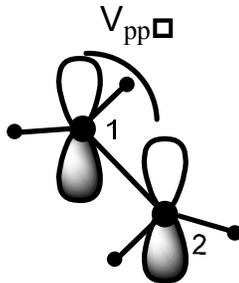
$$\begin{aligned} \langle T_1 | H^{\text{atom}} | T_1 \rangle &= \frac{1}{3} (\langle s | + \sqrt{2} \langle p_x |) H^{\text{atom}} (|s\rangle + \sqrt{2}|p_x\rangle) \\ &= \frac{1}{3} (E_s + 2E_p) \\ &= \langle T_2 | H^{\text{atom}} | T_2 \rangle = \langle T_3 | H^{\text{atom}} | T_3 \rangle. \end{aligned}$$

Since these hybrid orbitals are not eigenfunctions of the atom they will have matrix elements

$$\begin{aligned} \langle T_1 | H^{\text{atom}} | T_{2(3)} \rangle &= \frac{1}{3} (\langle s | + \sqrt{2} \langle p_x |) H^{\text{atom}} (|s\rangle - \sqrt{\frac{1}{2}}|p_x\rangle \pm \sqrt{\frac{3}{2}}|p_y\rangle) \\ &= \frac{1}{3} (E_s - E_p) = -V_1 \\ &= \langle T_2 | H^{\text{atom}} | T_{1(3)} \rangle = \langle T_3 | H^{\text{atom}} | T_{1(2)} \rangle. \end{aligned}$$

## Molecules with double bonds: $C_2H_4$ and $C_4H_6$

$\pi$  bonds in ethylene ( $C_2H_4$ ).

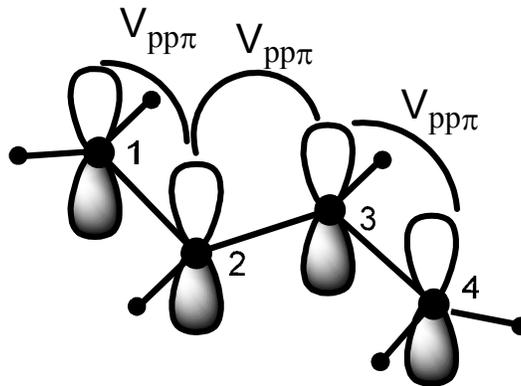


Ethylene

We remember that, when the atoms are approaching along the  $x$  direction, the interaction term between two  $p_z$  orbitals is called  $V_{pp\pi}$

$$H^{C-C} = \begin{bmatrix} E_{2p_z} & V_{pp\pi} \\ V_{pp\pi} & E_{2p_z} \end{bmatrix},$$

from now on we call them simply  $V$ . This leads to the energy levels shown in the figure (**Falta**).



We now consider the **butadiene** molecule ( $C_4H_6$ ), whose structure is shown in the figure

$$\begin{bmatrix} E_{2p_z} & V & . & . \\ V & E_{2p_z} & V & . \\ . & V & E_{2p_z} & V \\ . & . & V & E_{2p_z} \end{bmatrix} \begin{bmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \end{bmatrix} = \varepsilon \begin{bmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \end{bmatrix}$$

Clearly, there is no reason to expect that the probability amplitudes at site 1 and 4 be different. The same is for sites 2 and 3. With this assumption

$$\begin{cases} u_4 = u_1 \\ u_3 = u_2 \end{cases} \quad \text{or} \quad \begin{cases} u_4 = -u_1 \\ u_3 = -u_2 \end{cases}$$

from the node counting or oscillation theorem we know that the first condition will provide the ground state and the second state as only 0 or 1 nodes would be allowed from such selection. The second only affords states with two or three nodes which would become the 3rd and 4th energy states.

Let us try the first two equations:

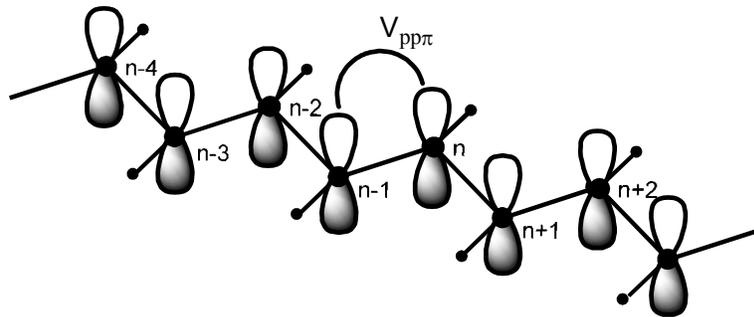
$$\begin{aligned} E_p u_1 + V u_2 &= \epsilon u_1 \\ + V u_1 + E_p u_2 + V u_2 &= \epsilon u_2 \end{aligned}$$

the third repeats the second one and the fourth equation the first. Hence the matrix to be solved is

$$\det \begin{vmatrix} \epsilon - E_p & -V \\ -V & \epsilon - V - E_p \end{vmatrix} = 0$$

which leads to the solution.

**Problem.** finish this calculation.



### Polyacetylene

From the above calculations we see the structure that would result in posing the problem of a general polyene molecule





$$\begin{bmatrix}
 \ddots & A_{(n-1)} & A_{(n)} & A_{(n+1)} & A_{(n+2)} & \dots & B_{(n-1)} & B_{(n)} & B_{(n+1)} \\
 A_{(n-1)} & E_2 - V_2 & \frac{1}{2} V_1 & \cdot & \cdot & \vdots & \frac{1}{2} V_1 & \cdot & \cdot \\
 A_{(n)} & \frac{1}{2} V_1 & E_2 - V_2 & \frac{1}{2} V_1 & \cdot & \vdots & \cdot & \frac{1}{2} V_1 & \cdot \\
 A_{(n+1)} & \cdot & \frac{1}{2} V_1 & E_2 - V_2 & \frac{1}{2} V_1 & \vdots & \cdot & \cdot & \frac{1}{2} V_1 \\
 A_{(n+2)} & \cdot & \cdot & \frac{1}{2} V_1 & E_2 - V_2 & \vdots & \cdot & \cdot & \cdot \\
 \vdots & \vdots & \vdots & \vdots & \vdots & \ddots & \dots & \dots & \dots \\
 B_{(n-1)} & \frac{1}{2} V_1 & \cdot & \cdot & \vdots & \vdots & E_2 + V_2 & \frac{1}{2} V_1 & \cdot \\
 B_{(n)} & \cdot & \frac{1}{2} V_1 & \cdot & \vdots & \vdots & \frac{1}{2} V_1 & E_2 + V_2 & \frac{1}{2} V_1 \\
 B_{(n+1)} & \cdot & \cdot & \frac{1}{2} V_1 & \vdots & \vdots & \cdot & \frac{1}{2} V_1 & E_2 + V_2
 \end{bmatrix}$$

Clearly, this gives a band of width  $2|V_1|$  around the bonding energy  $E_2 + V_2$  and a band of width  $2|V_1|$  around the anti-bonding energy  $E_2 - V_2$ . This suggests that we can look at the more complex situation of networks in the space.

## Frontier orbitals theory for chemical reactions

The basic idea of the Theory of frontier orbitals that led to the 1981 Nobel prize of Roald Hoffman and Kenichi Fukui, can be rationalized from a simple energy diagram of the reactants A and B to form the product AB in a single (concerted) step. The analysis is simplified using the names introduced by Fukui :

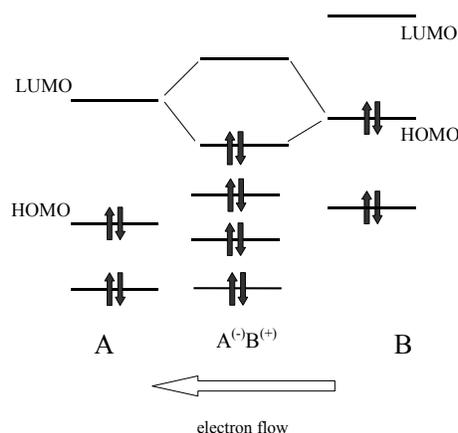
HOMO: Highest occupied molecular orbital.

LUMO: Lowest unoccupied molecular orbital.

As two molecules collide, two categories of processes can be identified.

1) Electrostatic interactions that cause that the occupied orbitals repel each other through an electrostatic mechanism. Similarly, regions with positive charge in one molecule attracts regions of negative charge on the other.

2) The quantum mechanics would act in two competing ways represented in the diagram.



### Frontier Orbitals for $A + B \rightarrow AB$

On first order it appears a repulsion between the occupied states. This is the effect of the overlap in the Schrödinger equation. The proximity of the nuclei tries to force the electrons to occupy the same physical space. This is not allowed by the exclusion principle and will have a weak antibonding effect. On the opposite, kinetic terms favor the delocalization of the electrons towards space regions previously inaccessible. This decreases the energy by increasing the localization uncertainty.

The lessons we learn from this diagram are:

- When a complex activated complex is formed, there must be non-vanishing matrix element (a net positive overlap in the extended Hückel theory).
- The electrons flow from the HOMO of one specie towards the LUMO of the other and viceverse. For hetero-molecular reactions, this could lead to a net charge transfer.
- Since we know the order of magnitude of the overlap matrix elements is a few eV, for these to be effective the energies must be close ( $\leq 6\text{eV}$ ). The closest the energies, the fastest the reaction.
- The flow of electrons from the HOMO of the nucleophile specie to the LUMO of the electrophile molecule also must lead to the breaking of the bonds and the formation of the products. If this is not the case one could not be certain of the occurrence of the reaction.
- HOMO-HOMO and LUMO-LUMO couplings do not contribute to the binding energy. On the contrary, they contribute to the molecular repulsion.

Now we are going to see how this works in some specific examples.

Example 1:  $H_2 + I_2 \rightarrow 2HI$

Example 2:

The discussed examples allow us to understand the empirical cycloaddition rules:

If a molecule with  $m$  electrons  $\pi$  is added to a molecule with  $n$  electrons of the  $\pi$  type, the reaction:

- Is **thermally** allowed if  $m + n = 4q + 2$
- Is **photochemically** activated if  $m + n = 4q$

Example. The reaction 2 ethylene  $\rightarrow$  cyclobutene which is naturally hindered can be

photochemically activated through diradicals.

Example. the reactions of the Diels and Alder (Nobel 1950) type are those of the form  $m + n = 4q + 2$  type are thermally concerted.

The quantitative evaluation of the energy associated to a reaction can be done with the Klopman Theorem. (Klopman, J. Am. Chem. Soc. 90, 223 (1968). also a paper by Salem). It states that the binding energy can be obtained just from a perturbation theory evaluation:

$$\Delta E = + \frac{Q_A Q_B}{\epsilon R_{AB}} + \sum_{a,b} (f_a + f_b) V_{ab} S_{ab} + \left( \sum_{\substack{k \\ \text{occupied}}} \sum_{\substack{l \\ \text{unocc.}}} - \sum_{\substack{l \\ \text{occupied}}} \sum_{\substack{k \\ \text{occupied}}} \right) \frac{(\sum_{ab} u_{ak} u_{bl} V_{ab})^2}{E_k - E_l} + \text{solv.}$$

The first term is a simple electrostatic term where the  $Q_A$  and  $Q_B$  are the total charges of the species, and  $R_{AB}$  is their distance. This term is usually very similar for any direction of attack. It is obviously important to describe polar molecules. The second and third terms have quantum origin. The second is the repulsion among the closed shell states. It is evaluated in first order perturbation theory. Here

$$f_a = \sum_{\substack{k \\ \text{occupied}}} |u_{ak}|^2$$

Since  $u_{ak}$  is the amplitude of the atomic orbital  $a$  in the occupied molecular orbital  $k$  with energy  $E_k$ ,  $|u_{ak}|^2$  is the electron occupation of atomic orbital  $a$ . The individual contribution can be quite directional, but the overall effect of this term could be quite unpredictable.

Finally, the last term is the second order quantum contribution to the bond. It describes the transfer from the occupied into the unoccupied states. Clearly the HOMO and the LUMO provide the most important contribution among them. This is generally the most important contribution to explain differential reactivity among different pathways or processes.

Further analysis of the reaction would require the unwritten term dubbed **solvation**, which could include: the **entropy** of activation. Also important in the analysis would be the **strain** of the network, and the **steric** factors.

#### Some references:

After this notes were prepared I noticed that

- *Molecular Quantum Mechanics*

P. W. Atkins and R. S. Friedman (Oxford U. P. 3rd Ed.),

in their sections 11.11-11.16 extends these lectures. It is recommended as complementary reading.