

Bonding

There are two main ways of thinking about how the electrons of a molecule are involved in bonding.

1. Valence Bond theory: regards all bonds as localized interactions involving two electrons shared between two atoms. In polyatomic molecules this leads to the use of orbital hybridization as a mathematical and pictorial procedure of manipulating the atomic orbitals to permit the bonding to be described in terms of a collection of simple ^{resonance} two-center, two-electron bonds.

2. Molecular Orbital (MO) theory: assigns electrons to molecular orbitals, which are, in general, delocalized over the entire molecule.

Which approach is better? Both are approximations.

- V.B. theory fails to explain bonding in aromatic compounds. Also fails to predict that O₂ is paramagnetic.
- MO theory is generally more consistent with the results of spectroscopic measurements.

Why do we need approximate methods? Two reasons.

- 1. exact solutions aren't possible even for H₂.
- 2. approximate methods can give insight and physical understanding into chemical bonding

M.O. theory

Born-Oppenheimer approx (We already discussed this)

Treat the nuclear and electronic motions independently.

- clamp the nuclei ; find the energies and wavefunctions.
- repeat for different nuclear positions to construct a potential energy function $U(R)$ which is a function of the nuclear coordinates.

The total energy of the "unfrozen" molecule is then

$$E_{total} = E_e + E_{vrt}$$

electronic energy (includes the total energy of the electrons in their molecular environment and the internuclear repulsion)

vibrational, rotational, and translational energy of the nuclei.

To determine the electronic energy we need to solve,
for fixed nuclear coordinates,

$$\hat{H}_e \Psi_e(\underline{r}_1, \underline{r}_2) = U(R) \Psi_e(\underline{r}_1, \underline{r}_2)$$

$$\text{or } \hat{H}_e \Psi_e(\underline{r}_1, \underline{r}_2) = E_e \Psi_e(\underline{r}_1, \underline{r}_2) \text{ at } R.$$

where we have specialized to a 2 electron system

(H₂) for simplicity.

where \hat{H}_e is the electronic Hamiltonian, which is the full Hamiltonian \hat{H} without the nuclear kinetic energy terms.

$\Psi_e(\underline{r}_1, \underline{r}_2)$ is the electronic wavefunction of the molecule with nuclear coordinates R .

This Schrödinger equation, even though we made an approx. (Born-Oppenheimer) cannot be solved.

The problem is that the electron-electron repulsion term

$$V_{12} = \frac{e^2}{4\pi\epsilon_0 r_{12}}, \quad r_{12} = |\underline{r}_1 - \underline{r}_2| \text{ depends simultaneously on both electron coordinates.}$$

Independent Electron approx

or

Orbital approx.

(81)

In this approx. we consider each electron to move in some sort of "average potential" which incorporates the interactions with the nuclei and an "averaged interaction" with the other electrons.

The electronic Hamiltonian can then be separated into two parts $\hat{H}_e = \hat{H}_1 + \hat{H}_2$ for a 2 electron system where \hat{H}_1 depends only on electron #1 and on R
 \hat{H}_2 " " " " " #2 " " "

This is a major step forward because we can now look for solutions of the form

$$\Psi_e(\underline{r}_1, \underline{r}_2) = \Psi_a(1) \cdot \Psi_b(2)$$

Molecular orbital "a" containing electron #1.

Molecular orbital "b" containing electron #2.

where $\hat{H}_1 \psi_a = E_a \psi_a$ and $\hat{H}_2 \psi_b = E_b \psi_b$
 with E_a, E_b the energy of orbital "a", "b" respectively,
 and the total electronic energy (at fixed nuclear
 coordinates R) is $E_e = E_a + E_b$, namely by the sum
 of the energies of the individual occupied molecular orbitals.

So now all we need to do is to solve the
 one-electron Schrodinger equation

$$\hat{H}_1 \psi_a = E_a \psi_a$$

effective one-electron Hamiltonian \rightarrow one electron wavefunction called a molecular orbital (MO)

The solutions are the MO wavefunctions ψ_a
 and the MO energies E_a .

To actually do this we make one final approx:
 the linear combination of atomic orbitals (LCAO) approx.

where we construct MOs from linear combinations of
 atomic orbitals on individual atoms

$$\psi = \sum_i c_i \phi_i$$

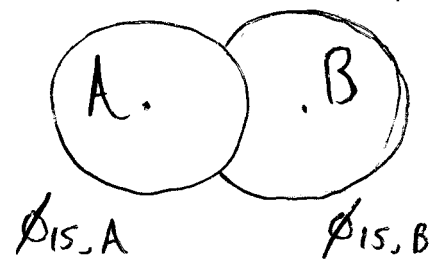
MO \rightarrow ϕ_i atomic orbitals
 c_i mixing coefficients

In its simplest form a MO may be constructed from a summation of one orbital on one atom, and a second orbital on a different atom.

ex hydrogen H₂.

Each hydrogen atom has a single valence atomic orbital \Rightarrow the 1s orbital. Two molecular orbitals may be ~~constructed~~ formed by the constructive and destructive overlap of these two AO:

1s + 1s



Constructive overlap gives the bonding MO

$\Psi_+ = C + \phi_{1s,A} + C + \phi_{1s,B} = C + (\phi_{1s,A} + \phi_{1s,B})$

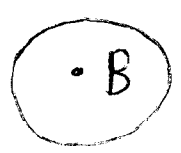
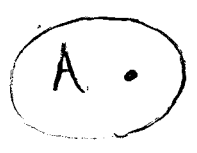


1s_g = 1s_g

lots of electron density between the atoms

Destructive overlap gives the antibonding MO

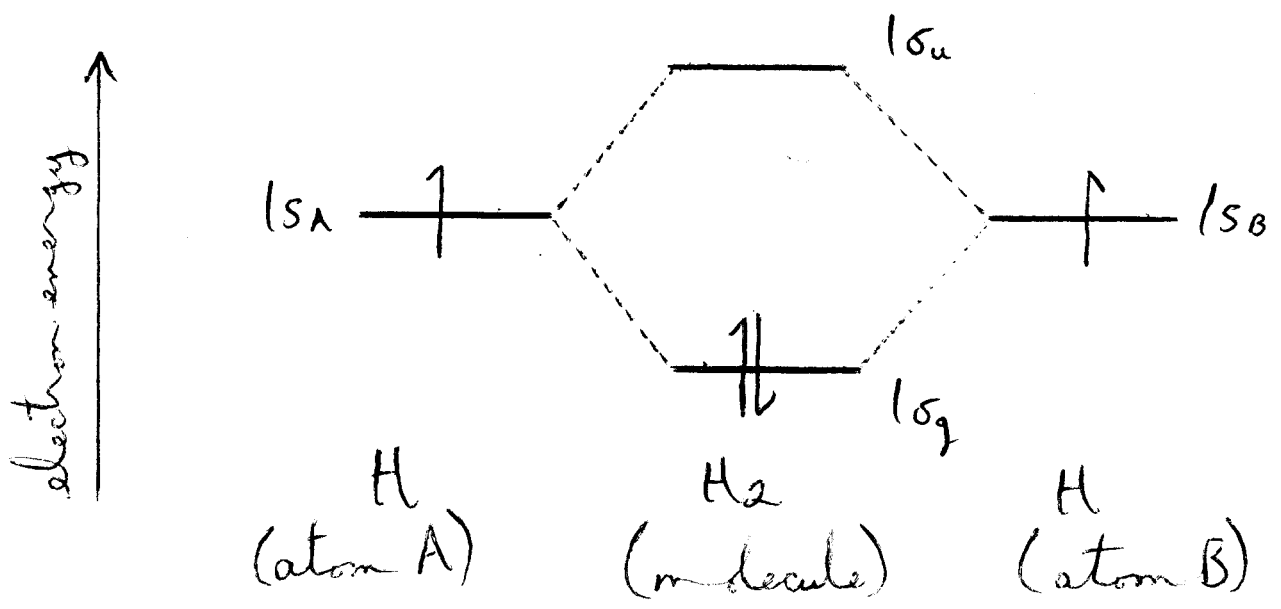
$\Psi_- = C - \phi_{1s,A} - C - \phi_{1s,B} = C - (\phi_{1s,A} - \phi_{1s,B})$



1s* = 1s_u

Zero electron density between the atoms

These interactions of atomic orbitals may be represented in the form of an orbital energy diagram which shows the relative energies of the orbitals.



The 2 atomic orbitals gave us 2 MOs. In general n atomic orbitals give n MOs

Variational Principle

The LCAO approximation can be made as accurate as possible by using the variational principle:

$$E_{LCAO} \geq E_{exact}$$

Hence the best approximate solution is obtained by finding the LCAO which minimizes the energy.

Proof for the ground state

The one-electron Schrodinger equation we are trying to solve is $\hat{H}_1 \Psi_a = E_a \Psi_a$

with ground state energy $E_{a,0}$ and wavefun $\Psi_{a,0}$.

We are approximating $\Psi_{a,0}$ by $\sum_i c_i \phi_i$ atomic orbitals

Recall that the set of eigenfunctions $\{E_{a,n}\}$ form an orthonormal basis. A consequence of this is that any wavefunction, say ϕ_i , can be expressed as a linear combination of these eigenfunctions $\phi_i = \sum_j d_j \Psi_{a,j}$

This is not useful in practice because we don't know the $\Psi_{a,j}$ (or else we wouldn't need to approx. them) but it is useful for the proof.

We can thus write the approx. wavefunction as

$$\phi = \sum_i c_i \left(\sum_j d_j \psi_{a,j} \right) = \sum_k e_k \psi_{a,k} \text{ by defining } e_k \text{ appropriately}$$

Then $E_{LCAO} = \int \phi^* \hat{H}_1 \phi$ assuming ϕ is normalized.

~~to show~~
for

$$= \int \left(\sum_j e_j \psi_{a,j} \right)^* \hat{H}_1 \left(\sum_i e_i \psi_{a,i} \right)$$

$$= \int \sum_{i,j} e_j^* e_i \int \psi_{a,j}^* \hat{H}_1 \psi_{a,i} = \sum_{i,j} e_j^* e_i \int \psi_{a,j}^* E_{a,i} \psi_{a,i}$$

$$= \sum_{i,j} e_j^* e_i E_{a,i} \int \psi_{a,j}^* \psi_{a,i} = \sum_{i,j} e_j^* e_i E_{a,i} \delta_{ij} \begin{matrix} 1 \text{ if } i=j \\ 0 \text{ if } i \neq j \end{matrix}$$

$$= \sum_i e_i^* e_i E_{a,i} = \sum_i |e_i|^2 E_{a,i}$$

Now subtract $E_{a,0} = E_{\text{exact}}$ from both sides:

$$E_{LCAO} - E_{\text{exact}} = \sum_i |e_i|^2 (E_{a,i} - E_{a,0}) \geq 0 \quad \blacksquare$$

We used

$$1 = \langle 1 | 1 \rangle = \int \phi^* 1 \phi = \int \left(\sum_j e_j \psi_{a,j} \right)^* \left(\sum_i e_i \psi_{a,i} \right)$$

$$= \sum_{i,j} e_j^* e_i \int \psi_{a,j}^* \psi_{a,i} = \sum_i |e_i|^2 = 1.$$

How do we make use of this principle?

1. Choose which atomic orbitals ϕ_i to include, giving $\Psi = \sum_i c_i \phi_i$ where the c_i are undetermined.

2. Write an expression for E_{LCAO} . If we don't want to worry about Ψ being normalized, which would put a restriction on the c_i 's that are inconvenient, we can write

$$E = \langle H \rangle = \frac{\int \Psi^* \hat{H} \Psi}{\int \Psi^* \Psi}$$

compensates for Ψ not being normalized.

3. Determine the values c_1, c_2, \dots which minimize E . Then the LCAO wavefunction is $\Psi = \sum_i c_i \phi_i$ and the orbital energy is E_{min} .

Overlap of Two atomic Orbitals

Consider just two orbitals: M.O. is then $\Psi = c_1 \phi_1 + c_2 \phi_2$ on 2 different atoms

$$E = \frac{\int \Psi^* \hat{H} \Psi}{\int \Psi^* \Psi} = \frac{\int (c_1 \phi_1 + c_2 \phi_2) \hat{H} (c_1 \phi_1 + c_2 \phi_2)}{\int (c_1 \phi_1 + c_2 \phi_2)^2}$$

assume Ψ is real from now on.

Numerator: $c_1^2 \int \phi_1 \hat{H} \phi_1 + 2c_1 c_2 \int \phi_1 \hat{H} \phi_2 + c_1 c_2 \int \phi_2 \hat{H} \phi_1 + c_2^2 \int \phi_2 \hat{H} \phi_2$

α_1
energy of an electron in atomic orbital 1 (in the molecular environment)

β_{12}, β_{21}
a measure of the strength of the bonding interaction between ϕ_1 and ϕ_2 .

$= c_1^2 \alpha_1 + 2c_1 c_2 \beta_{12} + c_2^2 \alpha_2$

since $\beta_{12} = \beta_{21}$ → it can show this but we will just take it without proof.

Denominator:

$c_1^2 \int \phi_1^2 + 2c_1 c_2 \int \phi_1 \phi_2 + c_2^2 \int \phi_2^2$

we will assume the atomic orbitals are normalized.

$S = \text{overlap integral} > 0$

$= c_1^2 + c_2^2 + 2c_1 c_2 S$

Summarizing, $E = \frac{c_1^2 \alpha_1 + 2c_1 c_2 \beta_{12} + c_2^2 \alpha_2}{c_1^2 + c_2^2 + 2c_1 c_2 S}$

Need to minimize E by varying c_1, c_2 .

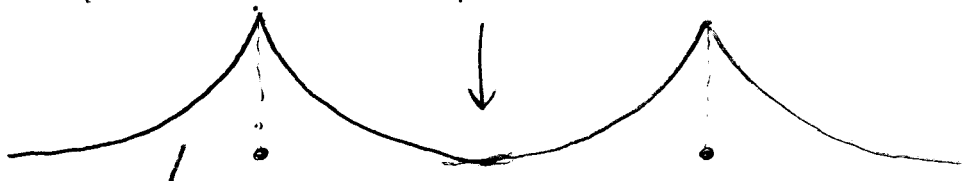
α : Coulomb integral < 0 , energy of an electron in A.O.

β : resonance integral < 0 for bonding orbitals: strength of bonding interaction between orbitals 1, 2.

S : overlap integral > 0 but $\ll 1$. Measures orbital overlap

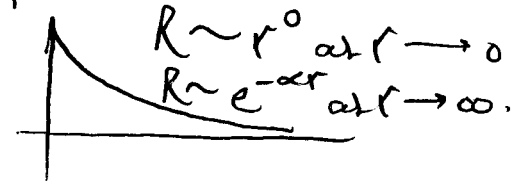
Illustration of S for two $1s$ orbitals:

$$S = \int \phi_1 \phi_2$$



Why have I drawn this shape?

Recall the $1s$ radial wavefunction



Move the nuclei closer together so they intersect:



Minimize E by varying c_1, c_2

We have $E(c_1^2 + c_2^2 + 2c_1c_2S) = c_1^2\alpha_1 + 2c_1c_2\beta_{12} + c_2^2\alpha_2$.

To find extrema, set $\frac{\partial E}{\partial c_1} = \frac{\partial E}{\partial c_2} = 0$.

~~Set~~ Take $\frac{\partial E}{\partial c_1}$ on both sides

$$\frac{\partial E}{\partial c_1} (c_1^2 + c_2^2 + 2c_1c_2S) + E(2c_1 + 2c_2S) = 2c_1\alpha_1 + 2c_2\beta_{12}$$

~~Set~~ Set $\frac{\partial E}{\partial c_1} = 0$ to get $2Ec_1 + 2Ec_2S = 2c_1\alpha_1 + 2c_2\beta_{12}$

Similarly for $\partial/\partial c_2$:

$$E(2c_2 + 2c_1 S) = 2c_1 \beta_{12} + 2c_2 \alpha_2$$

$$\text{or } 2Ec_2 + 2Ec_1 S = 2c_2 \alpha_2 + 2c_1 \beta_{12}$$

$$\text{Rearrange to get } \left\{ \begin{aligned} c_1(E - \alpha_1) + c_2(ES - \beta_{12}) &= 0 \\ \text{and } c_1(ES - \beta_{12}) + c_2(E - \alpha_2) &= 0 \end{aligned} \right\} (*)$$

E in these equations is E_{extremum} since we imposed $\frac{\partial E}{\partial c_1} = \frac{\partial E}{\partial c_2} = 0$.

~~$$\begin{bmatrix} E - \alpha_1 & ES - \beta_{12} \\ ES - \beta_{12} & E - \alpha_2 \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$$~~

$$\begin{bmatrix} E - \alpha_1 & ES - \beta_{12} \\ ES - \beta_{12} & E - \alpha_2 \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \text{ Matrix form}$$

For useful solutions (namely not $c_1 = c_2 = 0$) we need

$$\det \begin{bmatrix} E - \alpha_1 & ES - \beta_{12} \\ ES - \beta_{12} & E - \alpha_2 \end{bmatrix} = 0 \text{ where } \det \begin{vmatrix} a & b \\ c & d \end{vmatrix} = ad - cb$$

Why? Try solving these equations and it becomes clear:

Eliminate c_2 from $*$:

$$c_1(E - \alpha_1)(E - \alpha_2) + c_2(E - \alpha_2)(ES - \beta_{12}) = 0$$

$$c_1(ES - \beta_{12})^2 + c_2(E - \alpha_2)(ES - \beta_{12}) = 0$$

$$c_1 \left((E - \alpha_1)(E - \alpha_2) - (ES - \beta_{12})^2 \right) = 0 = \begin{vmatrix} \alpha_1 & \alpha_2 & ES - \beta_{12} \\ E - \alpha_1 & & \\ ES - \beta_{12} & & E - \alpha_2 \end{vmatrix}$$

Case 1 Overlap of Two Identical Orbitals

$\alpha_1 = \alpha_2$ since ϕ_1, ϕ_2 are the same.

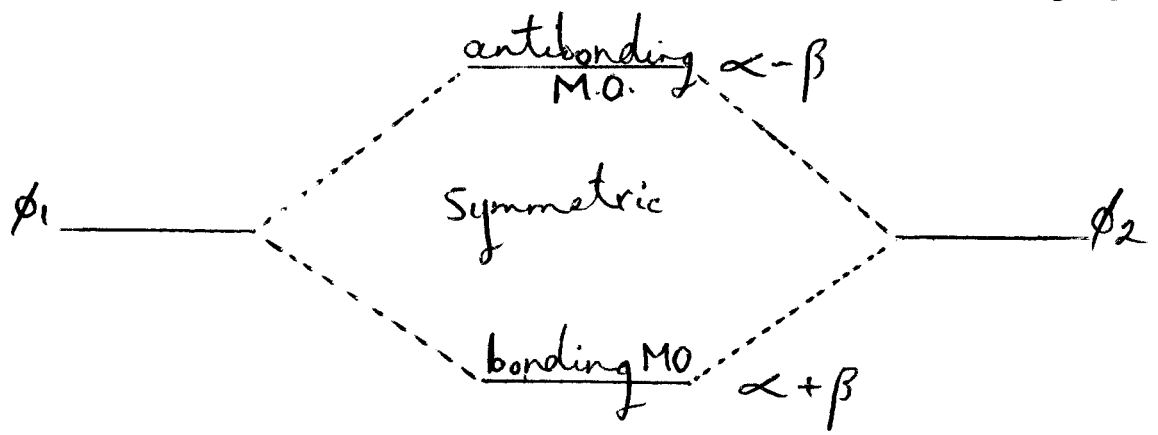
Represent ϕ_2 by β .

The determinant condition is $\begin{vmatrix} E - \alpha & ES - \beta \\ ES - \beta & E - \alpha \end{vmatrix} = 0$

If we neglect the overlap integral $S \approx 0$ we get

$$\begin{vmatrix} E - \alpha & \beta \\ \beta & E - \alpha \end{vmatrix} = 0 \implies (\alpha - E)^2 = \beta^2$$
$$\implies E = \alpha \pm \beta$$

Since $\beta < 0$, $E_+ = \alpha + \beta \implies$ the ^{energy of the} bonding orbital,
 $E_- = \alpha - \beta \implies$ the energy of the antibonding orbital



If we do not neglect S (more realistic) we have

$$(E - \alpha)^2 = (ES - \beta)^2 \text{ from the determinant condition}$$

The solution is

$$E_+ = \frac{\alpha + \beta}{1 + S}$$

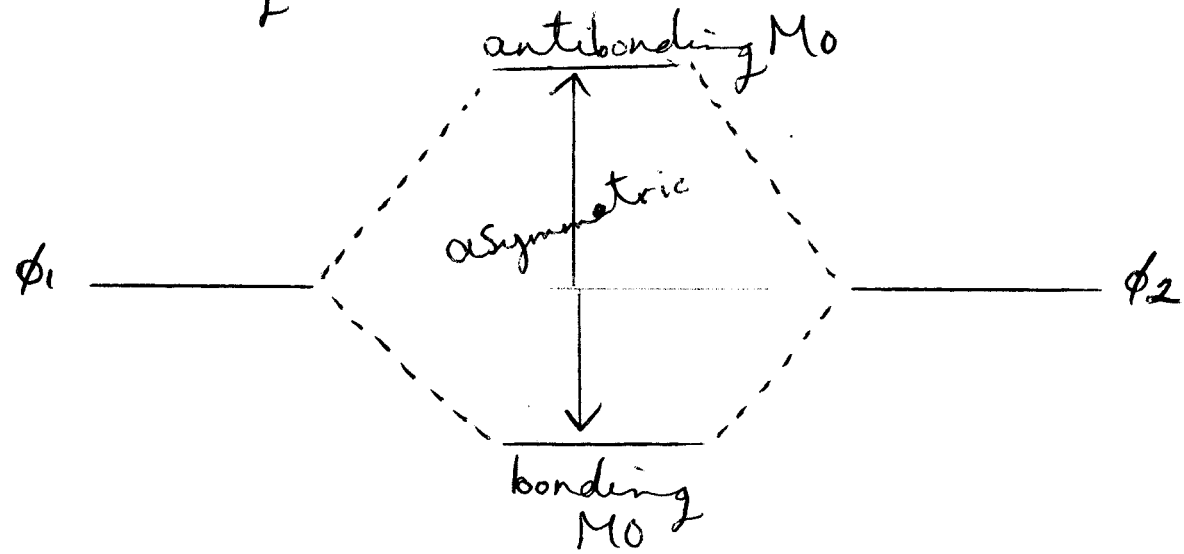
and

$$E_- = \frac{\alpha - \beta}{1 - S}$$

bonding orbital energy

antibonding orbital energy

Analyzing these expressions, we find that the bonding and antibonding orbital energies are now not symmetric: the antibonding orbital is higher in energy than the stabilizing energy decrease of the bonding orbital



One consequence of this asymmetry is that He_2 is not a stable molecule. By this I mean:

