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

1. Valence Bond (VB) 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 two-center, two-electron bonds.

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. VB theory fails to explain bonding in aromatic compounds. It also fails to predict that O_2 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 are not possible even for H_2.

2. approximate methods can give insight and physical understanding into chemical bonding.

MO Theory

MO theory consistents of 3 approximations: the Born-Oppenheimer approximation, the independent electron approximation, and the linear combination of atomic orbitals (LCAO) approximation.

Born-Oppenheimer Approximation

In the BO approximation we treat the nuclear and eletronic motions independently.

∘ clamp the nuclei; find the electronic 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

$$E_{\text{total}} = E_e + E_{\text{vrt}} \tag{1}$$

where E_e is the electronic energy which includes the total energy of the electrons in their molecular environment *and* the internuclear repulsion, and where E_{vrt} represents the vibrational, rotational, and translational energy of the nuclei.

In the electronic part of the problem, there are electron-electron repulsion terms like

$$V_{12} = \frac{e^2}{r\pi\epsilon_0 r_{12}} \qquad (2)$$

where $r_{12} = |\boldsymbol{r}_1 - \boldsymbol{r}_2|$ depends simultaneously on the coordinates of two different electrons. We cannot solve the Schroedinger equation with these terms present, and so we make the

Independent Electron Approximation, also called the Orbital Approximation

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

The electronic Hamiltonian can then be separated into one-electron contributions

$$\hat{H}_e = \hat{H}_1 + \hat{H}_2 + \cdots \qquad (3)$$

where $\hat{H}_1$ depends only on electron #1 and on R. This is a major step forward because we can now look for solutions of the form

$$\psi_e(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots) = \psi_a(\boldsymbol{r}_1)\psi_b(\boldsymbol{r}_2) \cdots \qquad (4)$$

where $\psi_a(\boldsymbol{r}_1)$ stands for molecular orbital "a" containing electron #1 and where $\hat{H}_1\psi_a = E_a\psi_a$ with E_a the energy of orbital "a". The total electronic energy (at fixed nuclear coordinates R) is $E_e = E_a + E_b + \cdots$, namely the sum of the energies of the individual occupied molecular orbitals.

So now all we need to do is to solve the one-electron Schroedinger equation $\hat{H}_1\psi_a = E_a\psi_a$ where $\hat{H}_1$ is an effective one-electron Hamiltonian and ψ_a is a 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 approximation:

Linear combination of atomic orbitals (LCAO) approximation

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

$$\psi = \sum_i c_i \phi_i \qquad (5)$$

with ψ a molecular orbital, c_i a mixing coefficient, and ϕ_i an atomic orbital. In general, mixing n atomic orbitals together gives n molecular orbitals (bonding, antibonding, etc.)

Variational Principle

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

$$E_{\text{LCAO}} \geq E_{\text{exact}} \tag{6}$$

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

Proof for the ground state

The one-electron Schroedinger equation we are trying to solve is $\hat{H}_1\psi_a = E_a\psi_a$ with ground state energy $E_{a,0}$ and wavefunction $\psi_{a,0}$. We are approximating $\psi_{a,0}$ by $\sum_i c_i\phi_i$ with ϕ_i atomic orbitals. Recall that the set of eigenfunctions $\{psi_{a,n}\}_{n=0}^{n=\infty}$ 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 do not know the $\psi_{a,j}$ (or else we would not need to approximate them) but it is useful for the proof. We can thus write the approximate wavefunction as

$$\psi = \sum_i c_i(\sum_j d_j\psi_{a,j}) = \sum_k e_k\psi_{a,k} \tag{7}$$

by defining the e_k appropriately. Then, assuming ψ is normalized,

$$E_{\text{LCAO}} = \int \psi^*\hat{H}_1\psi = \int (\sum_j e_j\psi_{a,j})^*\hat{H}_1(\sum_i e_i\psi_{a,i}) \tag{8}$$

$$= \sum_{i,j} e_j^*e_i \int \psi_{a,j}^*\hat{H}_1\psi_{a,i} = \sum_{i,j} e_j^*e_i \int \psi_{a,j}^*E_{a,i}\psi_{a,i} \tag{9}$$

$$= \sum_{i,j} e_j^*e_iE_{a,i} \int \psi_{a,j}^*\psi_{a,i} = \sum_{i,j} e_j^*e_iE_{a,i}\delta_{ij} \tag{10}$$

$$= \sum_i e_i^*e_iE_{a,i} = \sum_i |e_i|^2 E_{a,i} \tag{11}$$

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

$$E_{\text{LCAO}} - E_{\text{exact}} = \sum_i |e_i|^2(E_{a,i} - E_{a,0}) \geq 0 \tag{12}$$

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which completes the proof. Note: we used the resolution of the identity as follows:

$$1 = \langle 1 \rangle = \int \psi^* 1 \psi = \int \left(\sum_j e_j \psi_{a,j} \right)^* \left(\sum_i e_i \psi_{a,i} \right) = \sum_{i,j} e_j^* e_i \int \psi_{a,j}^* \psi_{a,i} = \sum_i |e_i|^2 = 1 \quad (13)$$

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 do not want to worry about ψ being normalized, which would put restrictions on the c_i's that are inconvenient, we can write

$$E = \langle H \rangle = \frac{\int \psi^* \hat{H} \psi}{\int \psi^* \psi} \quad (14)$$

where the denominator compensates for ψ not being normalized.

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

$\boxed{\text{Overlap of two atomic orbitals}}$

Consider just two orbitals on two different atoms: the MO is then $\psi = c_1 \phi_1 + c_2 \phi_2$

$$E = \frac{\int \psi^* \hat{H} \psi}{\int \psi^* \psi} = \frac{\int (c_1 \phi_1 + c_2 \phi_2) \hat{H} (c_1 \phi_1 + c_2 \phi_2)}{\int (c_1 \phi_1 + c_2 \phi_2)^2} \quad (15)$$

where we will assume ψ is *real* from now on.

Numerator:

$$c_1^2 \underbrace{\int \phi_1 \hat{H} \phi_1}_{\alpha_1} + c_1 c_2 \underbrace{\int \phi_1 \hat{H} \phi_2}_{\beta_{12}} + c_1 c_2 \underbrace{\int \phi_2 \hat{H} \phi_1}_{\beta_{21}} + c_2^2 \underbrace{\int \phi_2 \hat{H} \phi_2}_{\alpha_2} \quad (16)$$

where α_1 is the energy of an electron in atomic orbital 1 (in the molecular environment) and $\beta_{12} = \beta_{21}$ is a measure of the strength of the bonding interaction between ϕ_1 and ϕ_2.

Denominator:

$$c_1^2 \underbrace{\int \phi_1^2}_{1} + 2 c_1 c_2 \underbrace{\int \phi_1 \phi_2}_{s} + c_2^2 \underbrace{\int \phi_2^2}_{1} \quad (17)$$

where s is the overlap integral and where we will assume that the atomic orbitals are normalized.

Illustration of the overlap s for two 1s orbitals: $s = \int \phi_1 \phi_2$ Recall that the 1s radial wavefunction looks like $R(r) \sim r^0$ as $r \to 0$ and $R(r) \sim e^{-\alpha r}$ as $r \to \infty$. (figure here)

Summarizing:

α: Coulomb integral. The energy of an electron in an AO (< 0)

β: resonance integral. The strength of the bonding interaction between AO's (< 0)

s: overlap integral. Measures the AO overlap (> 0 but $\ll 1$)

$$E = \frac{c_1^2 \alpha_1 + 2c_1 c_2 \beta + c_2^2 \alpha_2}{c_1^2 + c_2^2 + 2c_1 c_2 s} \tag{18}$$

Our task is to minimize E by varying c_1, c_2.

We have

$$E(c_1^2 + c_2^2 + 2c_1 c_2 s) = c_1^2 \alpha_1 + 2c_1 c_2 \beta + c_2^2 \alpha_2 \tag{19}$$

To find the extrema, set

$$\frac{\partial E}{\partial c_1} = \frac{\partial E}{\partial c_2} = 0 \tag{20}$$

We will implicitly differentiate by taking $\frac{\partial}{\partial c_1}$ on both sides, and then by setting $\frac{\partial E}{\partial c_1}$ we obtain

$$2Ec_1 + 2Ec_2 s = 2c_1 \alpha_1 + 2c_2 \beta \tag{21}$$

Similarly for $\frac{\partial}{\partial c_2}$ we obtain

$$2Ec_2 + 2Ec_1 s = 2c_2 \alpha_2 + 2c_1 \beta \tag{22}$$

We can rearrange to obtain the pair of equations

$$
\begin{aligned}
c_1(E - \alpha_1) + c_2(Es - \beta) &= 0 \\
c_1(Es - \beta) + c_2(E - \alpha_2) &= 0
\end{aligned}
\tag{23}
$$

or in matrix form

$$\begin{bmatrix} E - \alpha_1 & Es - \beta \\ Es - \beta & E - \alpha_2 \end{bmatrix} = \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \tag{24}$$

For non-trivial solutions we need

$$\det \begin{bmatrix} E - \alpha_1 & Es - \beta \\ Es - \beta & E - \alpha_2 \end{bmatrix} = 0 \tag{25}$$

where

$$\det \begin{bmatrix} a & b \\ c & d \end{bmatrix} = ad - cb \tag{26}$$

Case 1: overlap of two identical orbitals

In this case $\alpha_1 = \alpha_2 = \alpha$ since ϕ_1 and ϕ_2 are the same. The determinant condition is

$$\det \begin{bmatrix} E - \alpha & Es - \beta \\ Es - \beta & E - \alpha \end{bmatrix} = 0 \tag{27}$$

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

$$\det \begin{bmatrix} E - \alpha & -\beta \\ -\beta & E - \alpha \end{bmatrix} = 0 \Rightarrow (\alpha - E)^2 = \beta^2 \Rightarrow E = \alpha \pm \beta \tag{28}$$

Since $\beta < 0$, $E_+ = \alpha + \beta$ is the energy of the bonding orbital, and $E_- = \alpha - \beta$ is the energy of the antibonding orbital.

(orbital energy diagram here)

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

$$(E - \alpha)^2 = (Es - \beta)^2 \tag{29}$$

from the determinant condition, whose solution is

$$E_+ = \frac{\alpha + \beta}{1 + s} \quad \text{and} \quad E_- = \frac{\alpha - \beta}{1 - s} \tag{30}$$

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

(orbital energy diagram here)

One consequence of this asymmetry is that He_2 is not a stable molecule.