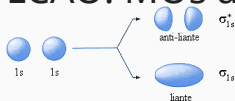# The chemical bond

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iSm2

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Three visions to compare

Lewis (1916): atoms share electrons to form a bond

LCAO: MOs are combinations of AOs

Valence Bond: Ψ is a combination of atomic centered ψ's

Lewis JACS 1916, 38, 4, 762–785

This paper opens the way to the culture of the chemical bond as a shared electron pair.

Paper in 1916 but ideas were already there in 1902 (footnote p767)

Contains 3 parts
  The cubical atom
  Molecular structure
  The color of chemical compounds

Cubical Atom

The cubical atom postulate 1

1. In every atom is an essential kernel which remains unaltered in all ordinary chemical changes and which possesses an excess of positive charges corresponding in number to the ordinal number of the group in the periodic table to which the element belongs.
→ Definition of the core electrons

The cubical atom postulate 2

2. The atom is composed of the kernel and an outer atom or shell, which, in the case of the neutral atom, contains negative electrons equal in number to the excess of positive charges of the kernel, but the number of elec- trons in the shell may vary during chemical change between 0 and 8.
$\rightarrow$ Definition of the valence electrons

The cubical atom postulate 3

3. The atom tends to hold an even number of electrons in the shell, and especially to hold eight electrons which are normally arranged symmetrically at the eight corners of a cube.
$\rightarrow$ Octet rule

The cubical atom postulate 4

4. Two atomic shells are mutually interpenetrable.
→ Importance of the overlap of the electronic clouds

5. Electrons may ordinarily pass with readiness from one position in the outer shell to another. Nevertheless they are held in position by more or less rigid constraints, and these positions and the magnitude of the constraints are determined by the nature of the atom and of such other atoms as are combined with it.

$\rightarrow$ Notion of electronegativity?

The cubical atom postulate 6

6. Electric forces between particles which are very close together do not obey the simple law of inverse squares which holds at greater distances.

→ !?

The discussion of this postulate is amazing!

The cubical atom

Cubical atoms:
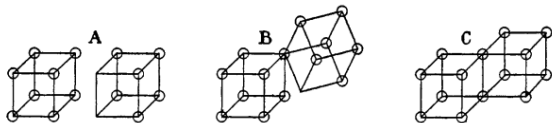

Li   Be   B   C   N   O   F

Molecular structure

Electronic structures of molecules: I₂

Molecules:

I_2 ($I_2 \rightarrow I^+ + I^-$ in solution)

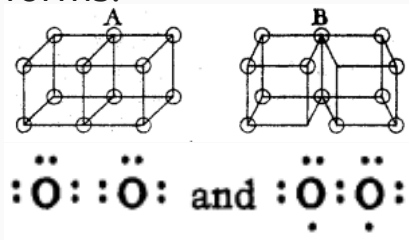A : $I^- + I^+$ ionic
B : one electron bond between ionic species
C : I_2 covalent

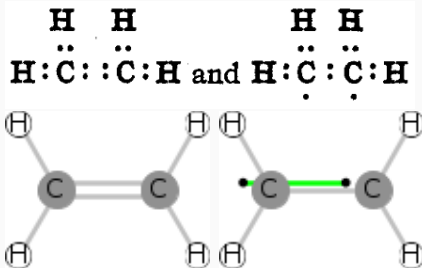# Electronic structure of molecules: O_2

Molecules:

O_2 is represented as a continuous tautomerism between the two following forms:

allowing the double bond *and* the triplet state.

Electronic structure of molecules: double bond

Molecules: ethylene

The color of chemical compounds

The color of chemical compounds

Another kind of bonding…

yellow?

Lewis JACS 1916, 38, 4, 762–785

Theoretical chemistry with no equation and no calculation

Use of the most modern bibliography

a paper to read every now and then

Valence Bond

Valence Bond framework: Heitler London wave function

Let a and b be the wave functions of two isolated hydrogen atoms. Let 1 and 2 be the two electrons of the system. In the VB framework on can write two wave functions:

$$\Psi_+(1,2) = N_+ \left(a(1)b(2) + a(2)b(1) \right) \quad (1)$$
$$\Psi_-(1,2) = N_- \left(a(1)b(2) - a(2)b(1) \right) \quad (2)$$

MO framework

Let σ_g be the *gerade* combination of a and b.
Let σ_u be the *ungerade* combination of a and b.

$$\sigma_g(\vec{r}) = N_g\left(a(\vec{r}) + b(\vec{r})\right) \qquad (3)$$
$$\sigma_u(\vec{r}) = N_u\left(a(\vec{r}) - b(\vec{r})\right) \qquad (4)$$
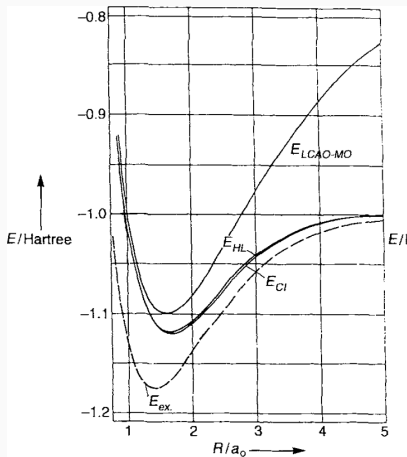
σ_g is bonding, σ_u is antibonding.

$$\Psi(1,2) = \sigma_g(1)\sigma_g(2) \qquad (5)$$

H₂ dissociation curve
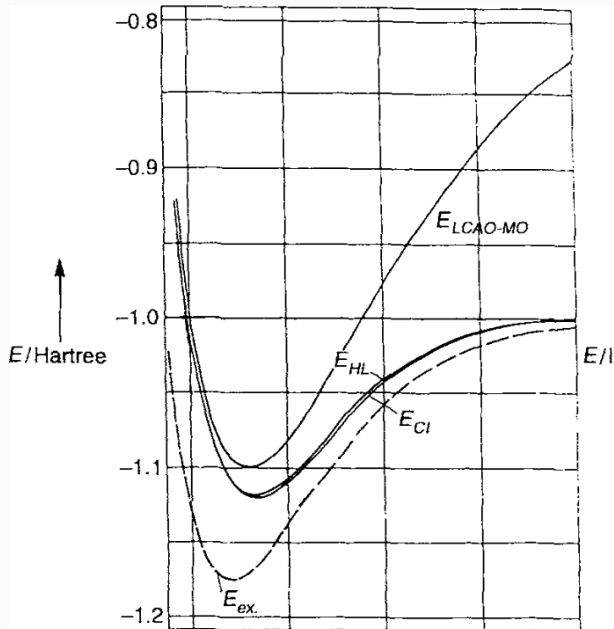
H₂ dissociation curve

MO theory fails to dissociate properly. Why?

The MO wavefunction is 50% ionic

$$\Psi(1,2) = \sigma_g(1)\bar{\sigma}_g(2) \tag{6}$$
$$= (a+b)(1)(\bar{a}+\bar{b})(2) \tag{7}$$
$$= a(1)\bar{a}(2) + a(1)\bar{b}(2) + b(1)\bar{a}(2) + b(1)\bar{b}(2) \tag{8}$$

Covalent terms: $a(1)\bar{b}(2) + b(1)\bar{a}(2)$
Ionic terms : $a(1)\bar{a}(2) + b(1)\bar{a}(2)$
Ionic terms are nonsense at large r.
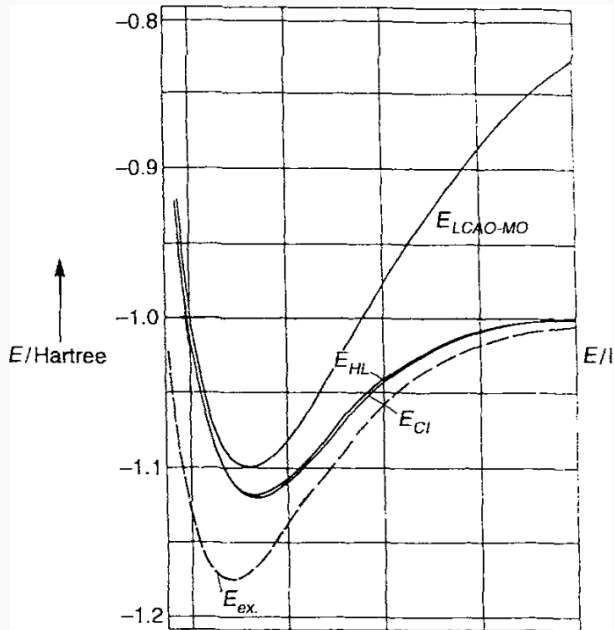
Improving the MO wavefunction

$$\Psi(1,2) = c_1 \sigma_g(1) \bar{\sigma}_g(2) + c_2 \sigma_u(1) \bar{\sigma}_u(2) \quad (9)$$
$$= c_1(a+b)(1)(\bar{a}+\bar{b})(2)$$
$$+ c_2(a-b)(1)(\bar{a}-\bar{b})(2) \quad (10)$$

$$= c_1(a(1)\bar{a}(2) + a(1)\bar{b}(2) + b(1)\bar{a}(2) + b(1)\bar{b}(2))$$
$$+ c_2(a(1)\bar{a}(2) - a(1)\bar{b}(2) - b(1)\bar{a}(2) + b(1)\bar{b}(2))$$
$$(11)$$

Hence, $c_1 + c_2$ is the coefficient of the ionic structures and $c_1 - c_2$ the coefficient of the covalent structures.

H₂ dissociation curve

Improving the VB wavefunction: add ionic

$$\Psi_{VB} = c_{cov}(a\bar{b} + \bar{a}b) + c_{ion}(a\bar{a} + b\bar{b}) \qquad (12)$$

One should be careful:
 same set of orbitals for ionic and covalent
 the configurations are not orthogonal

The donor acceptor bond

Let us solve

$$\hat{H}\phi_n = E_n\phi_n \qquad (13)$$

We consider that there exists a functional such that

$$\epsilon[\phi] = \frac{\int \phi^* \hat{H}\phi}{\int \phi^* \phi} \qquad (14)$$

Optimization

We know that

$$\epsilon[\phi_1 + \phi_2] \neq \epsilon[\phi_1] + \epsilon[\phi_2] \qquad (15)$$

Let us define

$$h_{12} = \frac{1}{2} \left(\epsilon[\phi_1 + \phi_2] - \epsilon[\phi_1 - \phi_2] \right) \qquad (16)$$

which is the splitting of the in-phase and out-of-phase solutions.

Optimal orbital

We are looking for the optimal orbital

$$\Phi_{opt} = c_1 \phi_1 + c_2 \phi_2 \tag{17}$$

The energy of Φ_{opt} is the solution of

$$\begin{vmatrix} \epsilon_1 - E & h_{12} \\ h_{12} & \epsilon_2 - E \end{vmatrix} \tag{18}$$

The donor acceptor model

Donor Acceptor 1/4

Let us work on a system made of a donor and an acceptor atom. They respectively carry an occupied ϕ_o and a virtual ϕ_v orbital. The solutions of 18 are:

$$E_{\pm} = \frac{\epsilon_v + \epsilon_o}{2} \pm \sqrt{\left(\frac{\epsilon_v - \epsilon_o}{2}\right)^2 + h_{ov}^2} \qquad (19)$$

We assume $\epsilon_v > \epsilon_o$ and we do the Taylor expansion of the square root.

$$E_\pm = \frac{\epsilon_v + \epsilon_o}{2} \pm \left(\frac{\epsilon_v - \epsilon_o}{2} + \frac{h_{ov}^2}{\epsilon_v - \epsilon_o} + \cdots \right) \quad (20)$$

The low energy solution is

$$E_- = \epsilon_o - \frac{h_{ov}^2}{\epsilon_v - \epsilon_o} \quad (21)$$

We call $\Delta E_{DA} = \frac{h_{ov}^2}{\epsilon_v - \epsilon_o}$.

$$E_\pm = \frac{\epsilon_v + \epsilon_o}{2} \pm \left(\frac{\epsilon_v - \epsilon_o}{2} + \frac{h_{ov}^2}{\epsilon_v - \epsilon_o} + \cdots \right) \quad (22)$$

The low energy solution is

$$E_- = \epsilon_o - \frac{h_{ov}^2}{\epsilon_v - \epsilon_o} \qquad (23)$$

We call $\Delta E_{DA} = \frac{h_{ov}^2}{\epsilon_v - \epsilon_o}$.

Donor Acceptor 4/4

It can be shown that the solutions are of the
form

$$E_- = \epsilon_o - \Delta E_{DA} \qquad (24)$$
$$E_+ = \epsilon_v + \Delta E_{DA} \qquad (25)$$

with ΔE_{DA} depending only on the magnitude
of h_{ov}.

Donor Acceptor: occupation

The solutions associated with E_- and E_+ are:

$$\Phi_- = c_o \phi_o + c_v \phi_v \qquad (26)$$

$$\Phi_+ = c'_o \phi_o + c'_v \phi_v \qquad (27)$$

As their energy splitting depends essentially on h_{ov}, the four electrons system is non bonding.

Donor Acceptor: hamiltonian

The lowering is generic *i.e.* it does not depend on the details of $\hat{H}$: ΔE_{DA} depends on the magnitude of h_{ov}, not its sign.

The solutions are due to the superposition of ϕ_o and ϕ_v.

Hence, it is misleading to rationalize the chemical bond by classical concepts without reference to superposition.

Donor Acceptor: mixing

It is remarkable that mixing an orbital of low energy ϕ_o with another orbital of higher energy ϕ_v, one obtains a solutions of lower energy than the initial low energy orbital.

$$\Phi_- = c_o\phi_o + c_v\phi_v$$
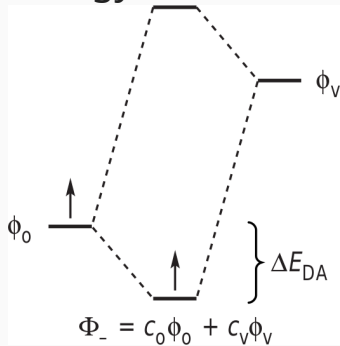
Back to H$_2$

Interactions

Let us write Φ_- as:

$$\Phi_- = \cos(\theta)\phi_o + \sin(\theta)\phi_v \qquad (28)$$

The extend of mixing is given by:

$$\tan(\theta) = -\frac{\Delta E}{h_{ov}} \qquad (29)$$

Note that $\tan(\theta) = 1$, $c_o = c_v$, $\epsilon_o = \epsilon_v$ and $\Delta E = |h_{ov}|$

$H + H^+ \rightarrow H_2^+$

At large separations, the electron is on H :

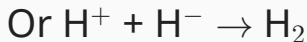$$c_o >> c_v \qquad\qquad h_{ov} \text{ small}$$

At smaller separations, when h_{ov} increases, the total symmetric solution becomes optimal. This corresponds to the σ orbital:

$$\sigma_{AB} = \frac{1}{\sqrt{2}} \left(1s_A + 1s_B \right) \qquad (30)$$

H + H → H_2

The H + H → H_2 case can be seen as two H + H^+ → H_2^+ cases, one for α and another for β electrons.

$$\phi_o^A \to \phi_v^B \qquad \bar{\phi}_o^B \to \bar{\phi}_v^A \qquad \text{covalent}$$

Or H^+ + H^- → H_2

$$\phi_o^A \to \phi_v^B \qquad \bar{\phi}_o^B \to \bar{\phi}_v^A \qquad \text{dative}$$

We are back to the ionic/covalent description of the chemical bond

The end

Simple models are full of insights
100 years articles are extremely rich
Calculations are not always required
No functional was harmed during this
slideshow

- THE END

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Disc Producer : David Rubinson

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