INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION
INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
I.C.T.P., P.O. BOX 586, 34100 TRIESTE, ITALY, CABLE: CENTRATOM TRIESTE

SMR/388 - 8

**SPRING COLLEGE IN MATERIALS SCIENCE
ON
"CERAMICS AND COMPOSITE MATERIALS"
(17 April - 26 May 1989)**

CHEMICAL BONDING
(Lecture I)

N.H. MARCH
Theoretical Chemistry Department
University of Oxford
5 South Parks Road
Oxford OX1 3UB
England

These are preliminary lecture notes, intended only for distribution to participants.

CHEMICAL BONDING

by

N.H. March,
Theoretical Chemistry Department,
University of Oxford,
5 South Parks Road,
Oxford OX1 3UB,
England.

1. Introduction

The object here is first to give an introduction to the basic elements of the quantum-chemical treatment of bonding. It is natural then to start with the simplest molecule H_2. The so-called 'molecular orbital' method assigns each electron in the ground state to the same orbital belonging to the molecule as a whole. This picture is fairly satisfactory at the equilibrium bond length of H_2 but begins to fail as the protons are pulled sufficiently far apart. The reason for this is 'electron correlation', which eventually 'drives electrons back onto their own atoms'. Then one recovers the Heitler–London or valence-bond method. The breakdown of the molecular orbital method will be illustrated by means of the Coulson–Fischer (1949) variational method.

Contents

Chemical Bonding

Aims

To discuss:

CONCEPTS

and

TYPES of METHOD

used

in theory of chemical bonding.

Approach

Shall explain and then illustrate both CONCEPTS and METHODS by appeal to simplest systems available (usually small molecules: eg H_2).

Relevance to solid state emphasized at each stage: and in final lecture (as well as in notes) some examples will be taken from high

OUTLINE

CONCEPTS	TYPES of METHOD
(a) Delocalized versus localized electrons (role of electron-electron repulsion e^2/r_{ij} crucial here.)	Molecular orbital ≡ energy band theory of solids. Valence bond (Heitler-London
(b) Transferability (fragment or bond used as building block for larger systems: eg SOLIDS)	Localized approach. But even energy band theory can be written in a 'localized' form (Wannier functions)
(c) Charge transfer and electronegativity.	Electron density theory. Population analysis (Mulliken).
(d) Resonance between structures. (ring currents and possible relevance to superconductors).	Pauling resonating valence bond method. Also molecular orbital method has relevance.
(e) Hybridization (especially)	

Symmetry and spin in 'fixed nuclei' approximation

FIXED NUCLEUS approximation

Because nuclei heavy ($\sim 2000\, m_e$ at least) their motion sluggish compared with electrons. Therefore, a starting-point for electronic structure is to consider motion of electrons in field of FIXED NUCLEI.

Then, having solved for electronic ground-state energy (say) as function of (assumed given) nuclear positions $[E(\{\underset{\sim}{R}\})]$, can discuss nuclear motions as a 2^{nd} stage [Born – Oppenheimer : adiabatic approximations].

Let us note here though that 'expansion parameter' is not simply (m_e/M), where M measures nuclear mass. (In fact : later lecture : it is $\{m_e/M\}^{1/4}$).

ANTISYMMETRY of ELECTRONIC WAVE FUNCTION

For electrons (Fermions : spin ½ particles), total wave function must be ANTISYMMETRIC in interchange of coordinates (space and spin) of two electrons [Generalised

Summary on H_2 molecule ground state.

Spin function : $\alpha(1)\beta(2) - \alpha(2)\beta(1)$ (antisymm

Spatial $\Psi(1,2) = \Psi(2,1)$ (symmetric).

(Total wave fn is product of space & spin : ∴ antisymmetric).

Delocalised MO (molecular orbitals)

ELECTRONS BELONG to molecule as a WHO

$$\Psi_{mo}(1,2) = \phi_{mo}(1)\,\phi_{mo}(2)$$
$$\simeq N[\psi_a(1)+\psi_b(1)][\psi_a(2)+\psi_b(2)]$$

COVALENT + IONIC (with equal weights).

Already 'transferability' invoked!

But doesn't determine unique answer : thus

Heitler – London (valence bond)

$$\Psi_{HL}(1,2) = N[\psi_a(1)\psi_b(2) + \psi_b(1)\psi_a(2)]$$

NO IONIC CONFIGURATIONS.

ELECTRON density ($S = \int \psi_a(1)\psi_b(1)\,d\tau_1$ overlap integral)

$$\rho_{MO}(\underset{\sim}{r}) = \underbrace{\frac{1}{1+S}[\psi_a^2(1)+\psi_b^2(1)]}_{\text{'atomic'}} + \underbrace{\frac{2}{1+S}\psi_a(1)\psi_b(1)}_{\text{'Bonding'}}$$

$$\rho_{HL}(\underset{\sim}{r}) = \frac{1}{1+S^2}[\psi_a^2(1)+\psi_b^2(1)] + \frac{2S}{1+S}\psi_a(1)\psi_b(1)$$

SO ANSWER depends SOMEWHAT on JUST HOW one

Molecular-orbital versus valence-bond theory of H_2 molecule

The ground-state wave function of the H_2 molecule has the singlet form

$$\Psi = \psi(r_1\, r_2)\Big[\alpha(1)\beta(2) - \alpha(2)\beta(1)\Big] \qquad (1.1)$$

with α and β denoting the usual spin wave functions. From the antisymmetry of the total wave function Ψ it follows that the spatial part of $\psi(r_1 r_2) \equiv \psi(1,2)$ must be symmetric and it is customary to write this in molecular orbital theory as the product

$$\psi(1,2) = \phi_m(1)\phi_m(2) \qquad (1.2)$$

with both electrons, since they have opposed spins according to (.1), placed in the same molecular orbital ϕ_m, which embraces both nuclei a and b and can therefore be said to belong to the molecule as a whole. Evidently, one could invoke the variation principle

$$\varepsilon = \int \psi(1,2) H \psi(1,2) d\underset{\sim}{r}_1 d\underset{\sim}{r}_2 \Big/ \int \psi^2(1,2) d\underset{\sim}{r}_1 d\underset{\sim}{r}_2 \geq E_0 \qquad (1.3)$$

with H the total Hamiltonian and E_0 the ground-state energy, to determine the 'best' molecular orbital ϕ_m. Generally, however, ϕ_m is approximated in quantum chemical calculations by a linear combination of atomic orbitals (LCAO) approximation. The simplest limit of this procedure is to write

$$\phi_m = \phi_a + \phi_b \qquad (1.4)$$

where ϕ_a and ϕ_b denote hydrogen 1s wave functions centred on nuclei a and b respectively. Using this in the trial form (.2) and calculating $\varepsilon(R)$ with R the internuclear separation gives a fair account of the equilibrium properties of the molecule.

Range of validity of molecular orbital description

Coulson and Fischer (1949) now considered the range of validity of the molecular orbital method by proceeding as follows. They formed 'asymmetric' orbitals $\phi_a + \lambda\phi_b$, $\lambda(R) \leq 1$ centred on proton a and $\phi_b + \lambda(R)\phi_a$ centred on nucleus b. Their spatial trial function ψ was then taken as

$$\psi(1,2) = [\phi_a(1) + \lambda\phi_b(1)][\phi_b(2) + \lambda\phi_a(2)] \qquad (1.5)$$

and again the variational principle was employed to calculate this time $\lambda(R)$. Denoting the equilibrium bond length by R_e, their remarkable finding was that, over the range $0 < R < 1.6R_e$, $\lambda(R)$ was identically equal to unity, but that for larger R, λ decreased rapidly to zero with increasing R. Roughly speaking, one is seeing here, when the nuclei are separated by more than $1.6R_e$, interelectronic repulsion driving the electrons back onto their own atoms.

It is necessary to add here, however, that eqn (.5) is not symmetric with respect to the interchange of electrons 1 and 2, as can be seen from the fact that as $\lambda \to 0$, $\psi(1,2) = \phi_a(1)\phi_b( )$ which is only one component of the correct Heilter–London function $\phi_a(1)\phi_b(2) + \phi_b(1)\phi_a(2)$ in the large R limit. Nevertheless, the Coulson–Fischer calculation is surely giving an important criterion displaying the range of validity of molecular orbital theory.