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SPRING COLLEGE IN MATERIALS SCIENCE
ON
"CERAMICS AND COMPOSITE MATERIALS"
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CHEMICAL BONDING
(Lecture II)

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Lecture 2

We shall discuss first a further CONCEPT of chemical bonding: that of ELECTRONEGATIVITY.

Pauling's original (1960) definition (his book!) was

'the power of an atom in a molecule to attract electrons to itself'.

Subsequent work has focussed on attempts to make 'electronegativity' fully quantitative, important work being that of Mulliken.

Electron density theory

It is through electron density theory, pioneered by Thomas (1926) and Fermi (1928), and finally completed by Hohenberg and Kohn (HK) (1964), that considerable progress has been made in the quantitative treatment of electronegativity.

To be definite, consider again a dielectric molecule: but now HETERONUCLEAR, i.e. with different atoms a and b. Now let us see how to define quantities χ_a, χ_b and χ_{ab}: related to ELECTRONEGATIVITY.

Instead of the WAVE FUNCTION VARIATION PRINCIPLE used in 1st lecture, use what Thomas, Fermi + HK found: namely that ground-state energy E of atom, molecule or solid is uniquely determined by electron density $\rho(\underline{r})$ [UNLIKE Ψ: an observable!]

Variation principle takes then the form

$$\delta[E - \chi N] = 0 \qquad \dagger$$

where the variation δ is in $\rho(\underline{r})$, which is normalised such that

$$\int \rho(\underline{r})\, d\tau = N$$ — total no. of electrons in system.

Now rewrite $\dagger$ in 'thermodynamic' form

$$\chi = \frac{\partial E}{\partial N}$$

to recognise that χ is a CHEMICAL POTENTIAL: but now of the ELECTRONIC CHARGE CLOUD $\rho(\underline{r})$.

Returning to the a, b molecule, we evidently have different χ's: χ_a and χ_b, for the different atoms, and a χ, say χ_{ab} for the molecule.

In other words, as we bring atoms a and b from infinite separation to the equilibrium molecular bond length R_e, the different χ's equalise to give χ_{ab}: characteristic of the ab MOLECULE.

This embodies the idea expressed in Sanderson's (1951) PRINCIPLE of ELECTRONEGATIVITY EQUALIZATION, in which charge flow from the less electronegative atom to the more electronegative one

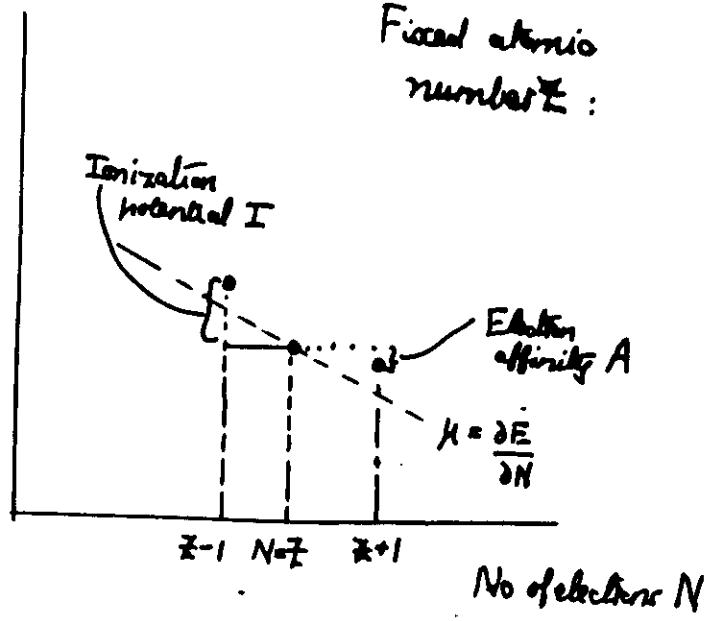
Must then discuss:

(i) Chemical potential μ for atoms (and atomic ions – to be used as FRAGMENTS in 'transferability' concept)

(ii) Chemical potential μ_{ab} for molecule.

While a lot of quantitative numerical work now exists in these areas, we'll use here a VERY INTUITIVE APPROACH very close to ideas of Mulliken.

ATOMIC IONS



Description of charge transfer in molecules

Start with two neutral atoms. Since

$$\mu = \left.\frac{\partial E}{\partial N}\right|_Z = \mu(Z, N) \qquad \#$$

write

$$\mu_a = \mu(Z_a, Z_a) \; ; \; \mu_b = \mu(Z_b, Z_b).$$

Then regard ab molecule as made up of FRAGMENTS which are, in general, FRACTIONALLY CHARGED atomic ions. The fractional charges evidently arise from the electron redistribution which brings chemical potential of ab molecule to its (constant) equilibrium value μ_{ab}.

Applying eqn # to an atomic ion with nuclear charge Z and N^* electrons leads then to

$$\mu(Z_a, N_a^*) = \mu(Z_b, N_b^*) \qquad \S$$

where N_a^* and N_b^* are the (non-integral) numbers of electrons of atomic ions a and b comprising the molecule (the TRANSFERABLE FRAGMENTS here).

Evidently TOTAL CHARGE neutrality means

$$N_a^* - Z_a = -(N_b^* - Z_b). \qquad +$$

THESE 2 eqns § and + can be exploited to calculate the AMOUNT of electronic charge transferred between the two atoms.

[illegible] can compare with [illegible]

Procedure

(i) Taylor expand $\mu(Z, N^*)$ around neutral atom limit $N^* = Z$:

$$\mu(Z, N^*) = \mu(Z, Z) + (N^* - Z)\mu' + \ldots .$$

Hence get

$$\mu(Z_a, Z_a) + \mu'_a Q_a = \mu(Z_b, Z_b) + \mu'_b Q_b ,$$

where $Q_i = N_i^* - Z_i \; (i = a, b)$. Since $Q_a = -Q_b = Q$ say we finish for charge transfer

$$Q = (\mu_b - \mu_a)/(\mu'_b + \mu'_a).$$

Use 'finite-difference' approximation to $\mu = \left(\frac{\partial E}{\partial N}\right)_v$ is get

$$\bar{\mu}(Z, Z) = -\tfrac{1}{2}(I + A)$$

which is just the negative of Mulliken's electronegativity

Same finite difference approach yields (hardness)

$$\bar{\mu}' = I - A$$

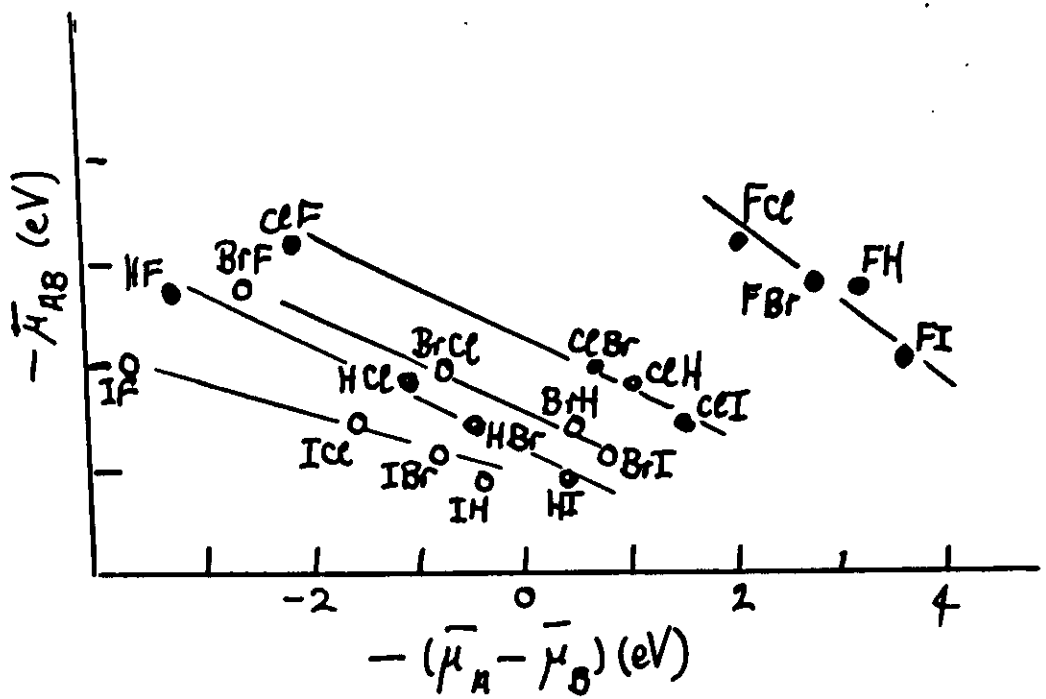
and hence

$$Q = -\tfrac{1}{2}(I_b + A_b - I_A - A_a)/(I_b - A_b + I_a - A_a)$$

Can compare with (crude) estimation of Q from experimental electric dipole moment (D) data

$$D = Q_{\text{E}} R_{\text{equil}}.$$

Good results for mixed halides BrCl, IBr, ClF, ICl and BrF but not much other checks available as yet. But PROMISING.



Valence bond theory : reformulation as an important tool for crystals

The high T_c ceramic oxides are known:

(i) To be near to the metal-insulator transition we discussed during Coulson-Fischer treatment of H_2 in 1st lecture. Electron correlation evidently very important in this regime : ∴ must TRANSCEND simple MO & energy band theory.

(ii) To have a phase diagram involving states which exhibit LONG-RANGE magnetic order.

These motivate how the reformulation of VALENCE bond theory in terms of electron spins : the main TOOL is the so-called HEISENBERG HAMILTONIAN, to be discussed below.

Valence bond method : H_2 : singlet and triplet states

Singlet spin function $\alpha(1)\beta(2) - \alpha(2)\beta(1)$ demanded SYMMETRIC SPACE FUNCTION

$$\Psi_s(1,2) = \psi_a(1)\psi_b(2) + \psi_b(1)\psi_a(2)$$

Triplet (symmetric) spin fns

$$\left.\begin{array}{l}\alpha(1)\alpha(2)\\ \beta(1)\beta(2)\\ \alpha(1)\beta(2)+\alpha(2)\beta(1)\end{array}\right\}$$

demand antisymmetric space function

$$\Psi_a(1,2) = \psi_a(1)\psi_b(2) - \psi_b(1)\psi_a(2)$$

In other words, the corresponding ORBITAL parts of the wave functions are SYMMETRICAL for total spin $S=0$ (ground state of H_2 which was treated in 1st lecture) and ANTISYMMETRICAL for $S=1$.

Aim To demonstrate that this situation can be represented as a STRONG coupling between spins $\underset{\sim}{s}_1$ and $\underset{\sim}{s}_2$ of the two individual electrons.

Proof If one measures the spin angular momentum vectors $\underset{\sim}{s}_1$ and $\underset{\sim}{s}_2$ of the two electrons in units of $\hbar$, then, as seen above, the allowed values $S=0$ and 1 correspond to:

ALLOWED VALUES of $(\underset{\sim}{s}_1+\underset{\sim}{s}_2)^2$ are $S(S+1)$: $S=0$ or 1.

But

$$(\underset{\sim}{s}_1+\underset{\sim}{s}_2)^2 = \underset{\sim}{s}_1^2 + \underset{\sim}{s}_2^2 + 2\,\underset{\sim}{s}_1\cdot\underset{\sim}{s}_2 .$$

It follows that for $S=0$ (i.e $(\underset{\sim}{s}_1+\underset{\sim}{s}_2)^2=0$) since $\underset{\sim}{s}_1^2+\underset{\sim}{s}_2^2 = \frac{1}{2}(\frac{1}{2}+1)+$ same for $s_2=\frac{3}{2}$:

and therefore

$$\underset{\sim}{s}_1\cdot\underset{\sim}{s}_2 = -\frac{3}{4} \quad : \quad S=0.$$

For $S=1$: $(\underset{\sim}{s}_1+\underset{\sim}{s}_2)^2 = S(S+1)$

$$\underset{\sim}{s}_1^2+\underset{\sim}{s}_2^2 = S(S+1) - 2\,\underset{\sim}{s}_1\cdot\underset{\sim}{s}_2$$

$$\text{or } \frac{3}{2}-2 = -2\,\underset{\sim}{s}_1\cdot\underset{\sim}{s}_2$$

$$\text{or } \underset{\sim}{s}_1\cdot\underset{\sim}{s}_2 = \frac{1}{4} \quad : \quad S=1.$$

THUS this difference between spin coupling $\underset{\sim}{s}_1\cdot\underset{\sim}{s}_2$ can be used, as will be seen below, to characterize a Hamiltonian representing the two-electron system.

Now wave functions in variational principle

$$\mathcal{E} = \frac{\int \Psi H \Psi \, d\tau_1 d\tau_2}{\int \Psi H \Psi \, d\tau_1 d\tau_2} \quad \text{with } H = H_0 + V_{12}$$

(V_{12}: electron–electron interaction)

Suppose energy is W_0 in absence of V_{12}.

One can then write the energy for Ψ_{sym} and Ψ_{anti} in the forms

$$E_S = W_0 + K_{12} + J_{12}$$

$$E_A = W_0 + K_{12} - J_{12}$$

Without writing out K & J explicitly, important point to emphasize is that expectation value of V_{12} is
$K_{12}+J_{12}$ — symmetric wave fn
$K_{12}-J_{12}$ — antisymmetric wave fn

One can as a result of the values of $\underset{\sim}{s}_1\cdot\underset{\sim}{s}_2$ derived above : namely $\underset{\sim}{s}_1\cdot\underset{\sim}{s}_2 = -\frac{3}{4}$: $S=0$

and $\underset{\sim}{s}_1\cdot\underset{\sim}{s}_2 = \frac{1}{4}$: $S=1$: WRITE

$$V_{12} = \Lambda_{12} - \tfrac{1}{2} J_{12} - 2 J_{12}\, \underset{\sim}{S}_1 \cdot \underset{\sim}{S}_2$$

which gives back $K_{12} + J_{12}$ for $S=0$ (with $\underset{\sim}{S}_1 \cdot \underset{\sim}{S}_2 = -\frac{3}{4}$)

and $K_{12} - J_{12}$ for $S=1$ (with $\underset{\sim}{S}_1 \cdot \underset{\sim}{S}_2 = \frac{1}{4}$)

CONCLUSION

The two electrons behave as though there were a strong coupling between their two spins which, apart from an (unimportant) additive constant, is proportional to the SCALAR product of those spin angular momenta, or to the cosine of the angle between the two spin vectors [cf $\underset{\sim}{M}_1 \cdot \underset{\sim}{M}_2 / r^3$ term appearing in mutual potential energy between two magnetic dipoles].

NOT to SAY, of course, that there is a real magnetic coupling: the STRONG direct coupling here between the SPINS is solely because the EXCLUSION PRINCIPLE requires one type of orbital solution when spins $\uparrow\uparrow$ and another when they are antiparallel.

HEISENBERG HAMILTONIAN

Formalism in theory of magnetism in crystals:

$$H_{\text{Heisenberg}} = -2 \sum J_{kl}\, \underset{\sim}{S}_k \cdot \underset{\sim}{S}_l$$

where the coupling constant J_{kl} (exchange integral) will depend on states assumed to be occupied by those 2 electrons k, l...