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

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Hybridization

For an atom with a valence shell containing s and p orbitals, one can classify hybridization into the following main types:

(i) Mixing one s with one p orbital (leaving the other two unchanged) one can set us 2 equivalent hybrids (sp)

(ii) Mixing one s and 2 p orbits, one can set up 3 equivalent hybrids (sp^2)

(iii) Mixing one s and all 3 p orbits, one can set up 4 equivalent hybrids (sp^3).

Solid state examples

sp hybrids appropriate for linear chain of C atoms, sp^2 for a graphite layer and sp^3 for diamond.

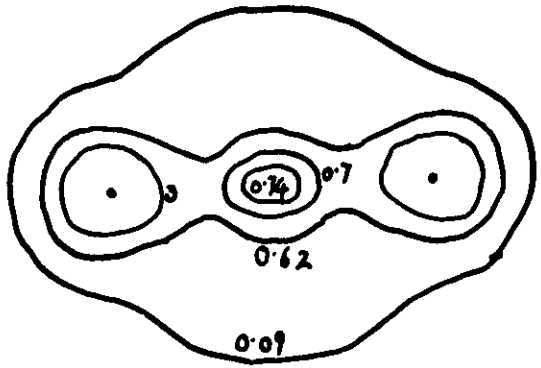
Molecular examples

Benzene is an example of sp^2 (case iii) above) while methane typifies sp^3.

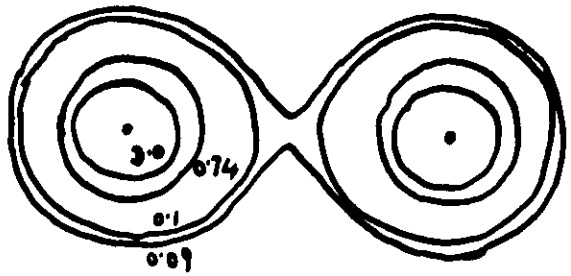
TRANSERABILITY will illustrated by using a Si-Si bond built from sp^3 hybrids to construct $\rho(r)$ in both crystalline a amorphous Si:

Effect of hybridization

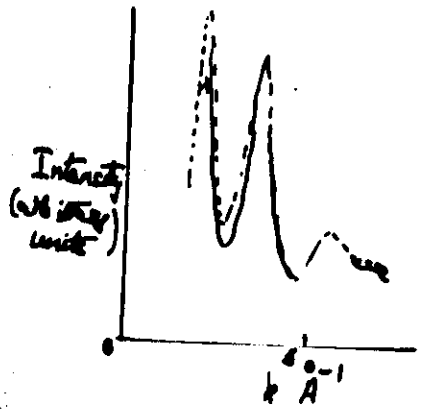
sp^3 hybridization : Si-Si bond



Superposition of isolated atom densities



X-ray intensity for amorphous silicon using transferability of Si-Si sp^3 bond



Without bonding, i.e superposition of atomic densities, 1st peak too low (indicated by X).

hkl	Same model Expt.	Crystalline Si. (units: electrons/unit cell) sp^3 bond model
000	64	64
111	39·4	38·1
220	47·4	47·2
311	31·4	31·2
222	0·26	0·25
400	40·5	40·6
331	27·7	27·4
422	36·1	36·9
333	24·5	24·3
440	32·3	32·1

Effect of d orbitals

Although in principle any number of atomic orbitals may be used in a full MO treatment of a molecule [FORMALIZED in Rayleigh-Ritz method below], those which affect most strongly the MOs that describe the valence electrons are those which belong to the valence shells of the constituent atoms.

Thus in EXAMPLE of H_2O, one builds the MOs from H 1s and O 2s and 2p atomic orbitals. REFINED work would add, say, H 2p or O 3d orbitals.

As one goes to heavier elements, other types of atomic orbitals become important. Thus the group VI element (like O) S has 3d orbital with an energy near enough to that of 3p to allow substantial mixing to occur.

TO PRESS this: this fact gives SULPHUR capacity to form a richer variety of compounds than OXYGEN: eg both the tetrafluoride SF_4 and the hexafluoride SF_6.

Similarly, in the Ni atom, the 3d, 4s and 4p levels all lie within about 4eV of each other and there again one can expect HYBRIDIZATION mixing d, s and p orbitals

Pauling (1931) was the first to show that, by suitable combination of d, s and p orbitals, very STRONGLY directed hybrids could be formed, giving coordination numbers and valence angles QUITE DIFFERENT from those expected using s, p or d type atomic orbitals separately.

In studying CONSEQUENCES of admitting the participation of d orbitals: AGAIN POSSIBLE to define PRINCIPAL TYPES: i.e sets of 2, 3, 4, 5 and 6 hybrids appropriate to specific highly symmetrical molecules and again, with SLIGHT DISTORTION, these can be used to describe LESS symmetrical molecules.

Table on NEXT transparency summarises the most important types of hybridization involving s, p and d orbitals, IRRESPECTIVE of principal quantum number, provided they lie fairly close in energy.

Important types of hybridization

Coordination number of hybrids	Atomic orbitals used	Resultant hybrids
2	sp	Linear
	dp	Linear
	sd	Bent
3	sp^2	Trigonal plane
	dp^2	Trigonal plane
	d^2s	Trigonal plane
	d^2p	Trigonal pyramid
4	sp^3	Tetrahedral
	d^3s	Tetrahedral
	dsp^2	Tetragonal plane
5	dsp^3	Trigonal bipyramid
	d^3sp	Trigonal bipyramid
	d^4s	Tetragonal pyramid
	d^2sp^3	Octahedral
	d^4sp	Trigonal prism

Example

Octahedral hybrids (d^2sp^3). The terminology d^2sp^3 means mixing 2 of the d orbitals with the s and 3 p orbitals.

An octahedral set of hybrids comprises 6 atomic directed nucleiues pointing along the +ve and -ve x, y and z axes: it is obtained by mixing $d_{x^2-y^2}$ and d_{z^2} atomic orbitals with s, p_x, p_y and p_z atomic orbitals.

[eg (in a.u)

$$\psi_{3d_{x^2-y^2}} = N_{3d}\,\tfrac{1}{2}\sqrt{3}\,(x^2-y^2)\exp(-Zr/3)$$

$$\psi_{3d_{z^2}} = N_{3d}\,\tfrac{1}{2}\,(3z^2-r^2)\exp(-Zr/3)$$

are hydrogen-like 3d atomic orbitals].

Molecular orbitals as linear combination: Rayleigh – Ritz method

Particular form of variation method in which a trial wave function ψ (ϕ) is compounded out of n functions $\phi_1, \phi_2 \ldots \phi_n$ in form of a linear combination

$$\psi\,(\phi) = c_1\phi_1 + c_2\phi_2 + \ldots + c_n\phi_n$$

is especially tractable. Developed long before wave mechanics to solve wide variety of problems in classical mechanics and wave motion, it is known as the Rayleigh – Ritz method. For just two functions we set 'trial energy $\mathcal{E}$' as

$$\mathcal{E}(\phi) = \frac{c_1^2\int\phi_1 H\phi_1\,d\tau + 2c_1c_2\int\phi_1 H\phi_2\,d\tau + c_2^2\int\phi_2 H\phi_2\,d\tau}{c_1^2\int\phi_1^2\,d\tau + 2c_1c_2\int\phi_1\phi_2\,d\tau + c_2^2\int\phi_2^2\,d\tau}$$

Here we have used fact that $\int\phi_1 H\phi_2\,d\tau = \int\phi_2 H\phi_1\,d\tau$, characteristic of the operators used in quantum mechanics.

Notation Put

$$H_{rs} = \int\phi_r H\phi_s\,d\tau \;:\; S_{rs} = \int\phi_r\phi_s\,d\tau$$

and note that $H_{rs} = H_{sr}$ and $S_{rs} = S_{sr}$ to get

$$\mathcal{E} = \frac{c_1^2H_{11} + 2c_1c_2H_{12} + c_2^2H_{22}}{c_1^2S_{11} + 2c_1c_2S_{12} + c_2^2S_{22}}.$$

Now minimize w.r.t c_1 & c_2:

$\frac{\partial\mathcal{E}}{\partial c_1} = 0$: $\frac{\partial\mathcal{E}}{\partial c_2} = 0$: set what are known

$$\left.\begin{aligned} c_1(H_{11}-\mathcal{E}S_{11}) + c_2(H_{12}-\mathcal{E}S_{12}) &= 0 \\ c_1(H_{12}-\mathcal{E}S_{12}) + c_2(H_{22}-\mathcal{E}S_{22}) &= 0 \end{aligned}\right\} * \quad (9$$

Here, $\mathcal{E}$ has been written for E because for these values of c_1 and c_2 $\mathcal{E}$ is closest approx. to the energy. Eqns * can be solved to determine $\mathcal{E}$ and also RATIO of coefficients c_1/c_2.

Generalisation to n component functions

If $\psi = c_1\phi_1 + c_2\phi_2 + \cdot \quad + c_n\phi_n$, there are n secular eqns generalizing *:

$$c_1(H_{11}-\mathcal{E}S_{11}) + c_2(H_{12}-\mathcal{E}S_{12}) + \cdots + c_n(H_{1n}-\mathcal{E}S_{1n}) = 0$$
$$c_1(H_{12}-\mathcal{E}S_{12}) + c_2(H_{22}-\mathcal{E}S_{22}) + \cdots + c_n(H_{2n}-\mathcal{E}S_{2n}) = 0$$
$$\cdots\cdots\cdots$$
$$c_1(H_{1n}-\mathcal{E}S_{1n}) + c_2(H_{2n}-\mathcal{E}S_{2n}) + \cdots + c_n(H_{nn}-\mathcal{E}S_{nn}) = 0.$$

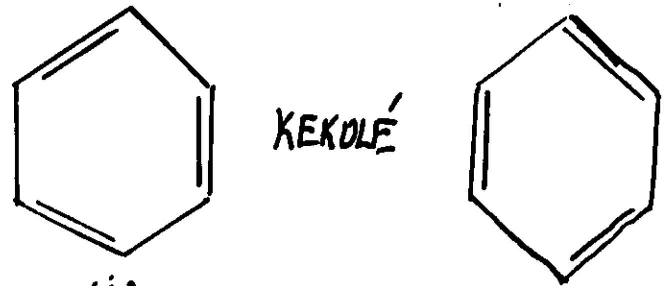
In case of only two functions * can be used to eliminate c_1 + c_2 to get:

$$\begin{vmatrix} H_{11}-\mathcal{E}S_{11} & H_{12}-\mathcal{E}S_{12} \\ H_{12}-\mathcal{E}S_{12} & H_{22}-\mathcal{E}S_{22} \end{vmatrix} = 0$$

where LHS is det. of coeffs of c_1 + c_2 in *. Gives quadratic eqn in $\mathcal{E}$ with two (real) roots $\mathcal{E}_1$ + $\mathcal{E}_2$. These roots are APPROXS. to the energy of the ground and the first excited state. FACT that an excited state energy + wave fns come as BYPRODUCTS of the ground-state calculation is ...

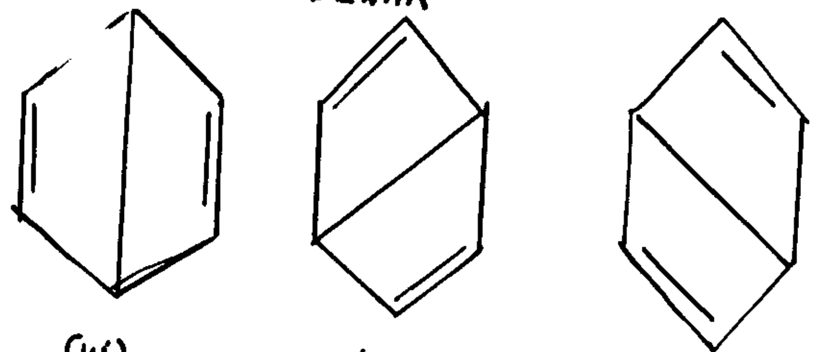
Resonance between structures: illustrative example of benzene (10

In benzene, 5 structures form a complete set of valence bond functions. Though the 2 Kekulé structures (i) and (ii) below are the most important, one really should add structures with long bonds (iii–v), termed Dewar structures.



(i) (ii)

DEWAR



(iii) (iv) (v)

Denoting corresponding wave fns by Ψ^i, total VB wave fn is written

$$\Psi_{VB} = c_1(\Psi^i + \Psi^{ii}) + c_2(\Psi^{iii} + \Psi^{iv} + \Psi^{v})$$

One can now use the Rayleigh – Ritz variational method just outlined to determine c_1/c_2 and the energies in this approximation.

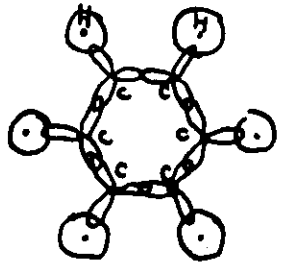
The lowest energy obtained by solving the secular equation corresponds to the ground state: as explained earlier the Rayleigh – Ritz method has the merit that the other solutions correspond to electronically excited states.

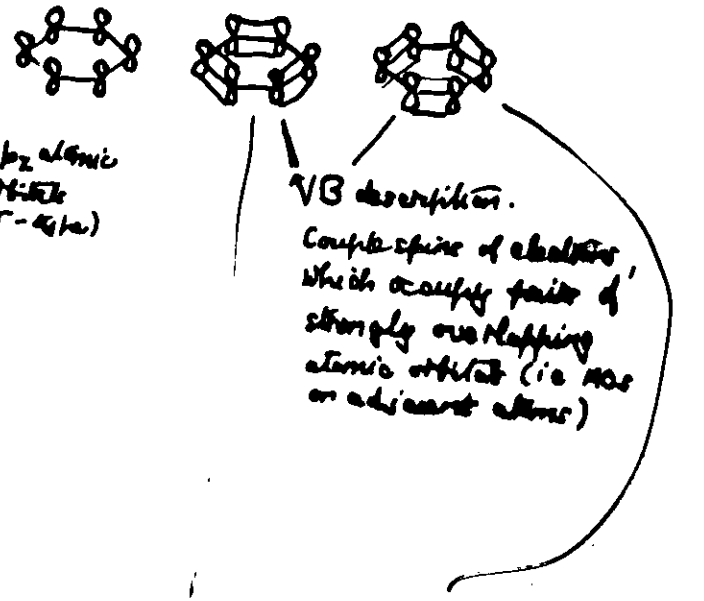
Definition of resonance energy

It should be emphasized that the difference between the ground-state energy and that of the Kekulé structure is defined as the resonance energy.

Trigonal hybrids in benzene (sp^2)

σ-bonds may be described either in MO or VB schemes: essential character same in both.





Some brief summary of work on high T_c ceramic oxides

Two aspects are related to CONCEPTS and METHODS used in chemical bonding:

(i) Electronic structure: LCAO-MO → energy bands

(ii) Connection with resonating structures.

Briefly as to (i) Matthews (L.F) (Phys. Rev. Lett 58, 1028, 1987) presents electronic structure calculations for tetragonal La_2CuO_4.

O 2p orbitals form strong σ bonds with neighbouring Cu atoms.

Of 17 bands in the Cu(3d) – O(2p) manifold[2] are of special importance. They both arise from strong nearest-neighbour (pdσ) interactions between Cu 3d orbitals with x^2-y^2 symmetry (illustrated above for H) (ie pointing towards the oxygens) and neighbouring O 2p orbitals that are directed along the Cu-O bond axes in the xy plane. The antibonding subband is half filled: obviously ∴ intersecting the Fermi level.

ESSENTIAL feature can be understood in terms of a 2-dimensional LCAO band.

Similar results and conclusions reached independently by A. J. Freeman

Other quantum chemical calculations relevant to high T_c ceramic oxides

In the lecture notes, some further details are recorded on chemical bonding in Cu–O planes in the high T_c ceramic oxides, following Fu and Freeman (1987) and Z.Q. Qi et al (ICTP Report IC/88/265, 1988).

In particular, Qi et al have studied the electronic structures of clusters (related to simulate crystal structure of $YBa_2Cu_3O_7$):

(i) a Cu_4O_{16} cluster

(ii) CaO_7

(iii) Cu_2O_{12}

by electronic density theory [$V = V_{Hartree} + \frac{\delta E_{xc}}{\delta \rho(r)}$] (From homogeneous electron gas.)

In this way, they have been able to calculate CHARGE TRANSFER: both within plane charge transfer (actually driven by oxygen stretching motions) and interplane charge transfer [Mulliken populations which were discussed in 1st lecture were also calculated].

So far, widespread use made of ceramic oxides of (i) LCAO ≡ tight-binding energy band calculation

(ii) Electron density theory

(New terms to VG)

In MO ≡ energy band calculations on solids, including high T_c ceramic oxides, ELECTRON DENSITY CONCEPTS are invoked. Therefore, of interest to summarise method here. Roughly speaking, the chemical potential μ $\left(= \frac{\partial E}{\partial N}\right)$ is given also by

$$\mu = \underbrace{\frac{p_F^2(r)}{2m}}_{\text{Kinetic piece}} + \underbrace{V(r)}_{\substack{\text{one-body periodic} \\ \text{potential to use in} \\ \text{energy band study.}}}$$

But what is form of V?

Answer lies in writing

$$E = \underbrace{T_s(\rho)}_{\substack{\text{single-particle} \\ \text{kinetic}}} + \int \rho V_N \, d\tau + \tfrac{1}{2}\int \rho V_e \, d\tau + \underbrace{E_{xc}(\rho)}_{\substack{\text{exchange+} \\ \text{correlation}}}$$

Use $\delta(E - \mu N) = 0$ as in second lecture, to get

$$\mu = \frac{\delta T_s}{\delta \rho(r)} + V_N + V_e + \frac{\delta E_{xc}(\rho)}{\delta \rho}$$

One-electron Euler eqn: $V(r) = V_{Hartree} + V_{xc}(r)$

↑ In this use LOCAL DENSITY APPROX

Is now the most widely used method in

The valence bonds important in high T_c superconductors?

Following Pauling's pioneering work [Nature 161, 1019 (1948); Proc. Roy. Soc A196, 343 (1949)], on a 'resonating valence bond' theory of metals, P. W. Anderson (Science 235, 1196, 1987) and R. P. Messmer (Solid State Commun. 63, 405, 1987) have argued for such a theory in high T_c superconductors.

Much of this work is highly technical, and here only possible, based largely on the discussion of benzene given above, to mention a few of the salient points.

At the outset, one should again stress:

(i) The stabilisation of benzene below the Kekulé structure by the resonance energy. Could this be the origin of the gap in the superconducting spectrum?

(ii) Quantum chemists (led again by Pauling) have discussed

Following all this, Messmer has argued for

(i) Accurate description of C_6H_6 correlated many-electron ground state wave fn. in terms of a superposition of the two Kekulé structures we drew above. (ie for neglect of Dewar structures)

(ii) Because of the nature of the correlated orbitals making up one of the Kekulé structures, Messmer proposes that a benzene molecule in the xy plane can be represented by a ground state to be thought of as a superposition of the coherent motion of electron pairs about the z-axis in the clockwise and counter-clockwise directions.

While in absence of magnetic field there is no net current, in presence of magnetic field ring currents, and again these consistent with large diamagnetism of benzene.

Messmer writes 'it is proposed that a related mechanism is operative in new oxide high T_c materials' ||

Messmer notes a number of aspects that emerge from RESONATING valence bonds: some of which have already been mentioned:

(i) Stabilization or resonance energy is responsible for energy gap in superconducting state.

(ii) It seems that there may be two different energies to consider: resonance energy in (i) and pair-breaking energy.

(iii) BCS type electron-phonon interaction not responsible for pairing

(iv) The resonance energy stabilizes a symmetric structure against alternative symmetry lowering distortions (of benzene).

Most of these aspects unlikely to be of consequence for ordinary metals and alloys, where BCS theory works!

CONCLUSION Whatever may or may not stand the test of time out of this debate on high T_c ceramic oxides, IT IS CLEAR that the CONCEPTS of chemical bonding will play a major role in any final definitive understanding of the high T_c ceramic oxide superconductors.
