

Overlap dispersion and overlap induction

Nicolaos D. Epiotis

Department of Chemistry, University of Washington, Seattle, Washington,
98195-9550

Abstract "Metallic" atoms combine to form molecules by two mechanisms, aside from the well familiar "ionic" mode: Overlap Dispersion and Overlap Induction. An example of the former is $\text{Ni}(\text{CO})_4$ or ferrocene and an example of the latter is $(\text{CH}_3\text{Li})_4$.

Hydrogen molecule (H_2) has two valence electrons in a bonding 1σ MO. Sodium dimer has also two valence electrons in a bonding 2σ MO. Nonetheless, the two MO's which have identical symmetry describe two entirely different bonding mechanisms as evidenced by the fact that H_2^+ radical cation has a weaker bond than H_2 but Na_2^+ has a stronger bond than Na_2 (ref. 1). After nearly half a century of preoccupation with orbital symmetry implications for chemical bonding (Huckel's Rule, Woodward-Hoffmann rules) we now realize that there is more to chemistry than orbital symmetry control: Under identical symmetry constraints, two species can exhibit completely different chemical behavior. We hold this to be the key theoretical problem of the next generation of applied quantum chemists and here we offer our own interpretation of the phenomenon by using the qualitative theoretical tool which has been developed in the last ten years: Molecular Orbital Valence Bond Theory (ref. 2,3,4). We will argue that the chemical and physical properties of a system depend jointly upon symmetry and a property called "color", that the mechanism of electron delocalization is color-dependent, and that this aspect of chemical bonding can be made transparent only by a Configuration Interaction (CI) type formalism such as the one employed in MOVV theory. In this note, we argue that there exist four types of chemical binding mechanisms: The familiar overlap ("covalent") and classical Coulomb ("ionic") mechanisms and two more: Overlap Dispersion and Ionic Overlap Induction. The latter two are responsible for the binding of the vast majority of chemical compounds other than those made up of first row "nonmetallic" atoms.

I. THEORETICAL BACKGROUND

The recipe for formally implementing MOVV theory is as follows:

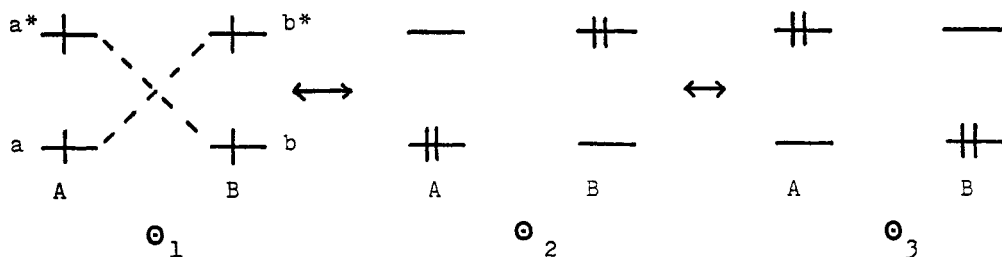
(a) A molecule in a given geometry is dissected into two fragments. The most convenient dissection choice is the one for which the local symmetry of the fragments is highest. (b) The symmetry-adapted fragment orbitals (MO's or AO's) are written from first principles or computed by using an effective one-electron Hamiltonian of the Extended HMO (EHMO) variety. (c) The electrons are distributed so as to generate the MOVV Configuration Wavefunctions (CW's), ϕ_i 's. (d) The MOVV CW's are partitioned into sets, T_m 's, and each set is diagonalized separately to generate the diabatic states, θ_{im} 's. (e) The diabatic states are, finally, diagonalized to produce the final adiabatic states, ψ_i .

The partitioning of CW's into sets is carried out in such a manner so that each θ_{m1} , the ground state resulting from diagonalizing the ϕ_i 's of T_m , represents just one way of making interfragmental bonds or antibonds. With this convention, the approximate form of the ground total wavefunction becomes:

$$\psi_1 = \sum \lambda_m \theta_{m1}$$

That is to say, higher diabatic states of appropriate symmetry (e.g., θ_{mi} 's with $i > 1$) are deemed to be relatively unimportant.

We now give an illustration of our approach by showing the bond diagrammatic representation of $A=B$. According to the "drawing convention" of MOVV theory, dashed



lines connecting orbitals belonging to the same irreducible representation denote the set of configurations which can be generated by shifting electrons along them starting from the parent configuration "projected" by the diagram itself. The approximate total wavefunction is simply a linear combination of these three "bonding schemes", i.e., these three bond diagrams.

$$\Psi = \lambda_1 \theta_1 + \lambda_2 \theta_2 + \lambda_3 \theta_3$$

In fact, for ground state $A=B$

$$\Psi \approx \theta_1$$

This is so because θ_2 and θ_3 , being antibonds, lie much higher in energy than two bonds. In general, either the "best" or the two leading bond diagrams will be sufficient for most qualitative analyses we shall attempt.

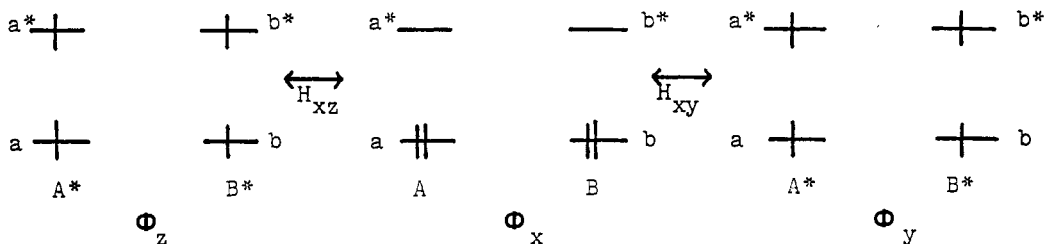
Two important results of MOVb theory are:

(a) The Periodic Table can be viewed as classification of atoms according to their capacity to generate strong overlap interaction (bonding or antibonding) through their AO's. We call this property "color". H, B, C, N, O, and F are black atoms with the characteristic property that their valence AO's extend equally in space and are equally available for overlap with the orbitals of some other atom. Green atoms differ to the extent that their valence orbitals do not extend equally in space, e.g., the 3s is contracted relative to the 3p AO in Si, etc. The same thing is true of all red atoms, but, in addition, those tend to be much more electro-positive. As a result, green and red atoms can only generate weak bonds through "spin-pairing" [DET bonds] because the overlap of one set of valence AO's is constrained to be small if the overlap of the other set of valence AO's is optimized and also because the more electro-positive an atom is the weaker the bond generated by overlap.

(b) The atomic constitution of two fragments which combine to form a molecule uniquely determines the type of electron delocalization, SET or CET. Specifically, SET (= Single Electron Transfer) is expected to be the principal mechanism when two fragments are connected by strong DET bonds with CET (= Correlated Electron Transfer) replacing it as the delocalization mechanism of choice when the two fragments are connected by modest DET bonds. CET delocalization is tantamount to a new mechanism of chemical binding: Overlap Dispersion.

II. WHAT IS OVERLAP DISPERSION?

The way in which overlap dispersion stabilizes a system can be illustrated by reference to our prototypical $A=B$ system in which two fragments, A and B, each having two orbitals of different spatial symmetry and two electrons, combine to form the composite system. The Configuration Interaction (CI) that generates Overlap Dispersion is shown below.

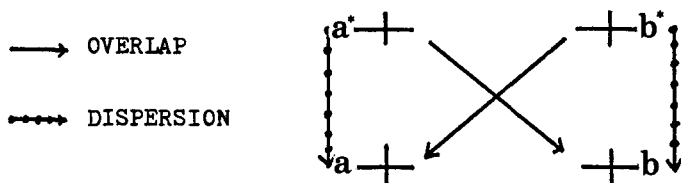


The following aspects of the CI are noteworthy:

(a) In Φ_y , each fragment is an open shell species in which the two electrons have half of the time parallel spins and benefit from exchange correlation. The two open shell species combine to form two interfragmental DET bonds. By contrast, in Φ_z , the two electrons of each fragment have always anti-parallel spin, something which generates severe interelectronic repulsion. Furthermore, the two open shell species combine to form two interfragmental DET antibonds.

(b) Each configuration differs from the one with which it interacts by two occupied spin orbitals and each interaction matrix element represents a two-electron hop. Now, each matrix element is the difference of two terms which have opposite signs: One term is an overlap term, W , and it represents formation of two CET bonds and the other term is a bielectronic repulsion integral, Z , which represents the interaction of two transition dipoles. As a result, each matrix element leads to strong configuration interaction by combining in-phase Overlap and Dispersion. Hence, the name of the bonding type is Overlap Dispersion.

(c) The H_{xy} (and H_{xz}) matrix element can be represented by using arrows to indicate the motion of electrons within Φ_y (and Φ_z) that generates the additive overlap and dispersion terms.



Unlike other representations with which the reader may be familiar, we now need two pairs of arrows which indicate the two different paths by which a pair of electrons can be relocated from one to another pair of orbitals. The picture shown above embodies the concept of Overlap Dispersion.

We are now prepared to provide a very explicit description of the way a metal binds organic molecules to form a coordination compound, e.g., ferrocene (ref. 5). We proceed as follows: (a) We view ferrocene as "iron metal plus cyclopentadiene dimer", i.e., as "Fe plus Cp_2 ". (b) We write the symmetry orbitals of Fe and Cp_2 and we allocate the electrons so that, with minimal excitation of the two fragments, we accomplish the following: (1) We make the maximum number of DET bonds by coupling the odd electrons of the two fragments. (2) We match the maximum number of electron pairs of one fragment with high energy holes of the second fragment. (3) We minimize the number of four-electron antibonds. This is the recipe for generating the dominant configuration, Φ_1 , which will be the parent of the principal bond diagram. (c) The principal bond diagram, Φ_1 , is produced by connecting the orbitals of the same symmetry with dashed lines. This is now a representation of the optimal linear combination of all configurations that can be generated by moving electrons along the dashed lines.

The principal bond diagram of ferrocene is shown in Figure 1. In the parent configuration "projected" by the bond diagram as written, each Cp ring is in its ground state electronic configuration while Fe is excited to the extent that it has been forced to have a d^0 configuration with all electrons paired. Now, the important thing is that the bonding of ferrocene is due to the fact that two DET bonds connect the two fragments but, equally important, there is Overlap Dispersion produced by the simultaneous delocalization of one electron from Fe to Cp_2 and one from Cp_2 to Fe. SET delocalization does make a contribution to the extent that we can have CET delocalization starting with a parent configuration that differs from Φ_1 of Figure 1 by a single metal \rightarrow ligand electron transfer. This new parent configuration is contained within the original bond diagram.

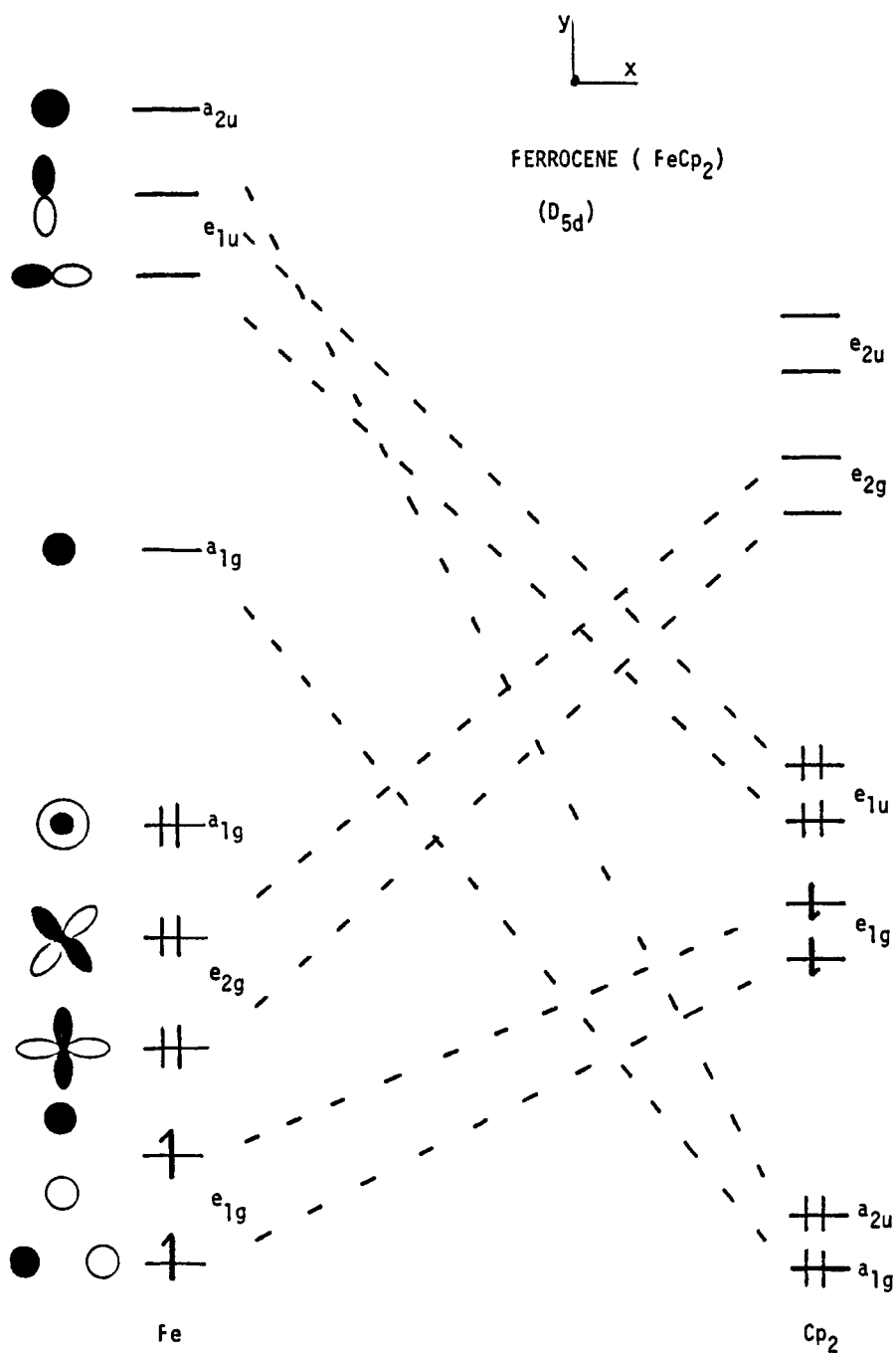
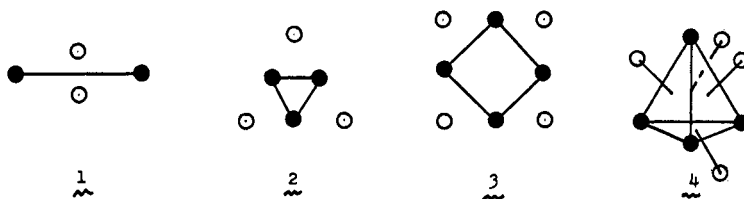


FIGURE 1

III. WHAT IS IONIC OVERLAP INDUCTION?

Consider the smallest (RLi)_n polymer 1 in which n = 2.

Scheme 1



If Li is thought of as an H analogue, i.e., if Li is thought of as having only a 2s AO and no 2p AOs and that this pseudo-Li binds by an overlap mechanism, then the stable geometry of $(\text{RLi})_2$ should be two RLi molecules separated by infinite distance. The reason is that the two symmetry MO's of R_2 and the two symmetry MO's of pseudo Li_2 match only in a linear but not a bridged geometry and if $(\text{RLi})_2$ is conceived as the product of the union of triplet Li_2 and triplet R_2 , then union should occur at infinite Li—Li distance at which triplet pseudo Li_2 has its minimum. So, deletion of the 2p AOs of Li and enforcement of overlap binding predicts that RLi should be a monomer much like RH.

The next choice is to delete the 2p AOs of Li but replace overlap by ionic binding in which case we predict a cyclic structure, A, in which the charges



alternate and this is consistent with the fact that $(\text{RLi})_2$ is computed to have a bridged geometry (ref. 6). Now, what we will argue is that the mechanism of binding of $(\text{RLi})_2$ clusters is neither overlap nor ionic but one that we will call Ionic Overlap Induction, an analogue of Overlap Dispersion. This bonding mechanism critically depends on the presence of the Li 2p AOs and it leads to a Lewis description of the bridged $(\text{RLi})_2$ species as indicated by formula B. In this molecule, the R_2 unit has accepted one electron from the Li_2 unit with the following results:

(a) Li_2^+ is bound by induction. This means that one electron "glues" electrostatically two Li cations. This electron is called an interstitial electron.

(b) One R radical makes an overlap bond with the Li_2^+ unit. The remaining R^- anion is attached to RLi_2^+ by ionic bonding.

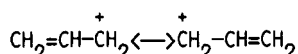
(c) The $(\text{RLi})_2$ dimer is really a composite of R_2^- radical anion and Li_2^+ radical cation covalently bound. The important thing is that a covalent bond is formed which is directed from an atom (C of R^*) to the midpoint of the line connecting two other much more electropositive atoms. We call such bonds interstitial bonds and this mechanism of binding Ionic Overlap Induction.

In Figure 2a, we show the principal bond diagrams for $(\text{RLi})_2$ in a D_{2h} (bridged) geometry, with $\text{HT} = \text{NS} = \text{Li}_2$ and $\text{GT} = R_2$ (ref. 7). Note the following:

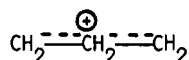
(a) The $(\text{RLi})_2$ dimer is represented by two principal bond diagrams, θ_1 and θ_2 , each one having one multicenter bond connecting host HT with guest GT fragment.

(b) In each of θ_1 and θ_2 , one electron has been transferred from the host to the guest fragment and this is why N or S has one electron and GT has three electrons.

Recall now the fact that organic chemists represent a molecule either by drawing resonance structures or by drawing the corresponding resonance hybrid. For example:



is equivalently represented by



In a completely analogous fashion, the resonance bond diagram θ_R (formerly called the "detailed bond diagram"), shown in Figure 2b is equivalent to the two individual bond diagrams of Figure 2a plus the "extrinsic configurations" not contained in θ_1 and θ_2 (ref. 2,3,4)

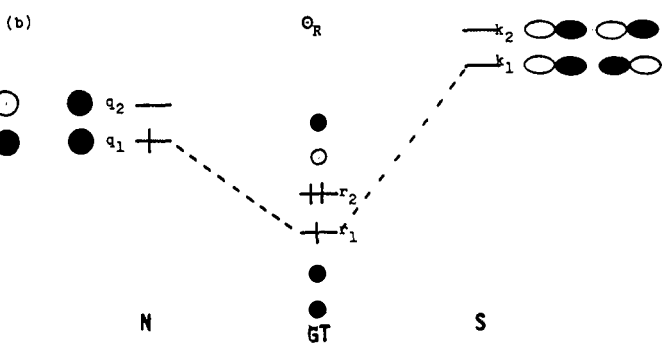
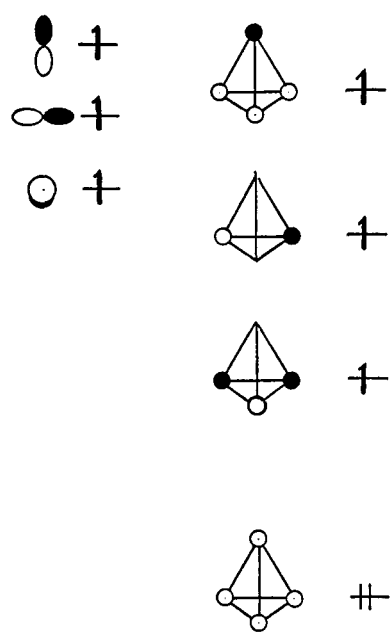
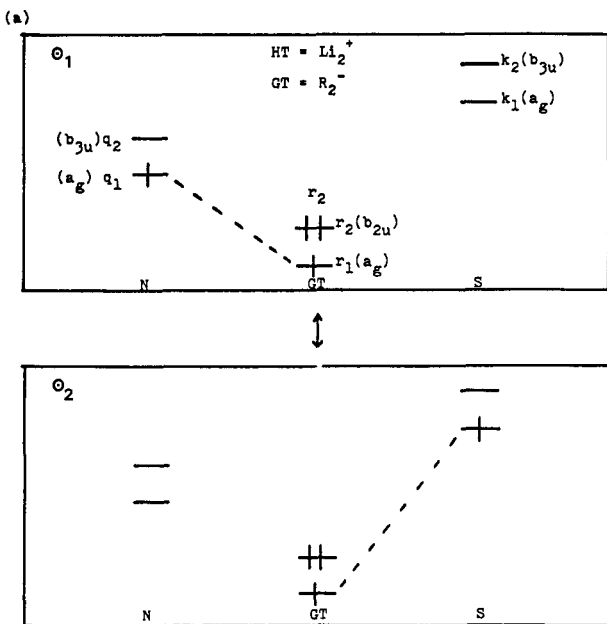
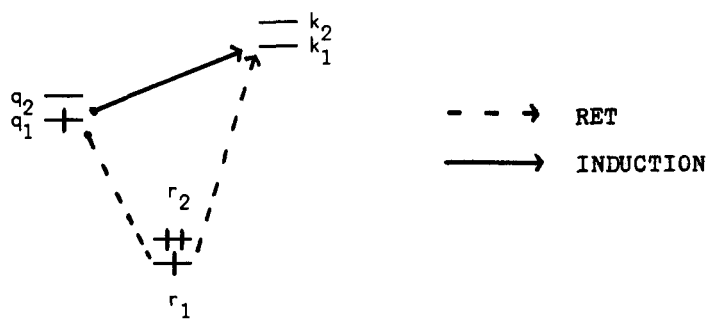


FIGURE 2

(c) The resonance diagram, θ_R , of Figure 2b tells us that there is one HT electron which may occupy either q_1 of N or k_1 of S. This is the interstitial electron and the interfragmental multicenter bond linking N and S to GT is the interstitial bond.

We now show that the type of bonding described by θ_R is Ionic Overlap Induction, the mono-electronic analogue of Overlap Dispersion (ref. 8).

The principal contributor to θ_1 is configuration ϕ and the principal contributor to θ_2 is configuration X_1 , each projected by the corresponding θ_i . We can write an arrow representation of the interaction matrix element $\langle \phi | H | X \rangle$, much as we did for the case of Overlap Dispersion, as shown below. Note how an electron from q_1 ends up in k_1 by two different mechanisms ("routes") which operate "in-phase". The two-solid-arrow path represents RET (= Relay Electron Transfer) and the single dotted-arrow path represents induction.



In summary, we read the resonance bond diagram θ_R as implying that there is one electron permanently transferred from HT to GT so that it generates an electric field responsible for overlap induction which manifests itself by one interstitial electron and one interstitial bond. Induction-assisted RET bonding involving q_1 and k_1 is equivalent to DET bonding now involving an interstitial orbital, p , located at the midpoint of the line connecting the two Li centers.

IV. IMPLICATIONS OF IONIC OVERLAP INDUCTION

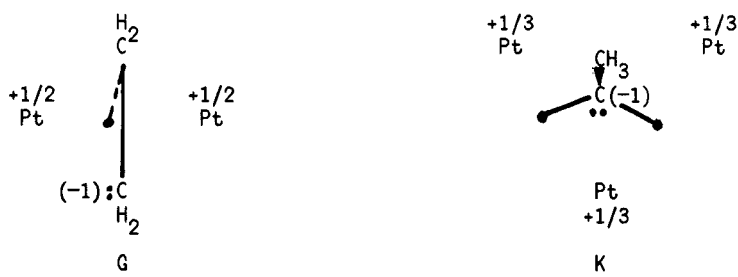
(a) If tetrahedral $(RLi)_4$ is viewed as $(Li)_4^+(X)^-$ where $X^- = R_4^-$ (structure 4 in Scheme 1) (ref. 9), then Figure 3 shows that ${}^4R_4^-$ is isosynaptic to ground ${}^4C^-$! That is to say, both ground ${}^4R_4^-$ and ground ${}^4C^-$ have three singly occupied MO's which precisely match the three singly occupied t_2 MO's of the Li_4^+ tetrahedron in defining three interstitial bonds. Hence, we predict that tetrahedral CLi_4 is neither covalent (like CH_4) nor ionic (e.g. $C^+Li_4^+$). In other words, the correct electronic structure of the "simple" molecule CLi_4 is not the one implied by conventional Lewis structures. Rather, CLi_4 must be regarded as a tetrahedral Li_4^+ cluster with three interstitial electrons shared by the four faces of the tetrahedron (t_2 interstitial electrons) which are being used to form three interstitial bonds with the singly occupied carbon 2p AO's of ground C^- . So, with respect to Li_4^+ , C^- does from "inside" what R_4^- does from the "outside". This analysis has direct and immediate bearing on the electronic structures of inorganic guest-host complexes, the electronic basis of intercalation and the nature of bridging in organometallic complexes.

(b) NMR experiments have revealed that there is ${}^{13}C - {}^7Li$ but there is not ${}^6Li - {}^7Li$ spin-spin coupling in $(CH_2Li)_4$ (ref. 10,11). The presence of the former is the result of the interstitial overlap bond while the absence of the latter is the result of induction (non-overlap) binding of Li and Li^+ . Second, the principal configuration of the resonance bond diagram of $(RLi)_2$, i.e., the "picture" obtained by removing the dashed lines from θ_R in Figure 2b, has a vacant q_2 MO in Li_2^+ and a half-occupied r_1 MO in R_2^- . Hence, sequential delivery of two electrons will place the first in the vacant q_2 (which is delocalized over the two Li's) and the second in the singly occupied r_1 thus creating an odd unpaired electron in q_1 . Had the bonding of $(RLi)_2$ been completely ionic, the single configuration $R_2^-Li_2^+$ representing the system would have two equivalent holes in Li_2^+ . Hence, $(RLi)_2$ should display two different reduction potentials if it is bound by Ionic Overlap Induction but only one (or, better, two having the same value) reduction potential if it is bound by "classical" coulomb forces (ionic bonding limit). Indeed, the analogous system $(CuOR)_2^{+2}$ has been found to exhibit behavior sometimes consistent with Ionic Overlap Induction and other times consistent with ionic bonding (ref. 12).

(c) Addition of H_2 to ethylene over Pt (ref. 13) may plausibly involve the following steps.

1. Ethylene is adsorbed on one Pt atom via Overlap Dispersion and this complex is electronically very similar to the Pt-Ethylene gas phase complex.

2. One Pt atom transfers one electron to ethylene (E) and the resulting radical anion, E^- , is coordinated to a Pt_2^+ unit in a manner completely analogous to the case of $(RLi)_2$, i.e., the E plays the role of R_2^- and Pt_2^+ , with two active 6s electrons, plays the role of Li_2^+ .

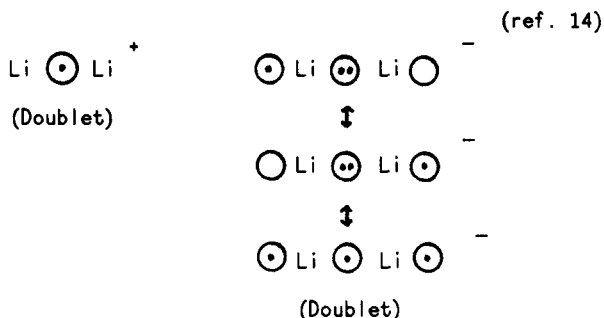


3. G^- rearranges to K^- which is now completely analogous to $(RLi)_3$, i.e., 2

in Scheme 1. R_3^- within $R_3^-Li_3^+$ is isosynaptic to CH_3-C^- within $CH_3C^-Pt_3^+$. Pt is analogous to Li_3 because both have an ns odd electron in their ground configurations. We propose that K^- is the correct electronic structure of the observed ethylidyne

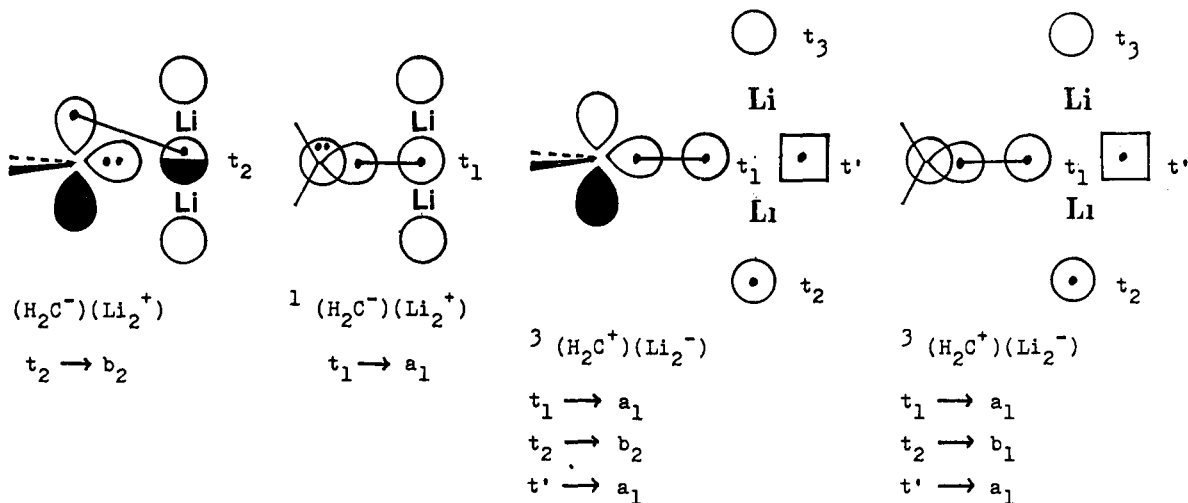
intermediate observed in the heterogeneous reaction of ethylene and hydrogen over Pt metal which chemists represent by conventional Lewis structures.

(d) We can represent Li_2^\bullet by one VB structure which immediately tells us that Li_2^\bullet is a building block with one interstitial electron residing in an Interstitial Orbital (IO) placed between the two atomic nuclei. Now, by using a conceptual minimal IO basis set, we can represent doublet Li_2^- in a similar fashion as illustrated below, each circle representing an IO.



A warning of utmost importance: All analyses should be made using the symmetry adapted y , MO's and then translated into IO (t_i) language. Failure to do so and unwarranted simplification (e.g., assigning one spherical IO per Li atom in an Li_n cluster) is bound to lead to erroneous conclusions regarding molecular electronic structure. The following discussion respects these restrictions.

Consider triplet methylene and singlet Li_2 put together to make dilithio-methane₃ by the MOVVB procedure: We argue that one electron will be transferred from Li_2 to $^3\text{CH}_2$ so that coupling of the two resulting radical ions will yield a molecule which can be represented by the formula shown below. The predicted shape is a highly distorted tetrahedron with a large LiCLi angle or a planar structure with a much smaller LiCLi angle. In the tetrahedral geometry, the two radical ion fragments are joined by a b_2 interstitial bond. In the planar geometry, the interstitial bond has a₁ symmetry. The notation $t_1 \rightarrow a_1$ means " t_1 upon symmetry adaption yields an a_1 MO".



What will be the structure of the lowest energy triplet state? To make the ground singlet state we obeyed the wishes of the electropositive Li_2 to be transformed to interstitial Li_2^+ by donating one electron to $^3\text{CH}_2$ so that ultimately interstitial bond formation joining the resulting radical ions produces the most stable species. To make the ground triplet state the direction of charge transfer is simply reversed: We now transfer one electron from $^3\text{CH}_2$ to Li_2 to generate the stable interstitial Li_2^- which needs comparatively small energy to be promoted to the interstitial Li_2^+ having the configuration $2\sigma_g 2\sigma_u 1\pi_u \dots$. Coupling of $^3\text{CH}_2^+$ and $^4\text{Li}_2^-$ by one interstitial bond results in the formation of a molecule which can be represented by the formula shown below. The predicted shape is either a distorted tetrahedron or a distorted planar system with the remarkable property that the Li_2 unit is negatively charged against all intuitive ideas based upon the notion of ionic bonding. In both geometries, there is one a_1 interstitial bond.

We say that singlet as well triplet CH_2Li_2 is bound by Overlap Induction, i.e., induction "interstitializes" the electrons of the ion metallic fragment and these are then used to form covalent interstitial bonds with the second nonmetallic or semimetallic fragment. These ideas are consistent with the computational results of Laidig and Schaefer concerning the electronic structure of CH_2Li_2 (ref. 15).

A final word of caution: MOVb theory is tailored for the human mind. Generalized VB (GVB) theory (ref. 16) is tailored for the computer. The former makes transparent how symmetry orchestrates bonding while the latter cannot do so (though it does contain symmetry control). Hence, GVB theory cannot serve as a basis for a conceptual approach to chemistry. Recently, the Goddard group has performed calculations of clusters departing from an IO basis (ref. 17). The fact that the selection of the IO's has been intuitive and with disregard to operative symmetry constraints and the "perfect pairing approximation", which leads to a qualitatively incorrect perception of bonding in metallic systems, leads us to suspect that many of the results obtained in this way will turn out to be erroneous when compared to full-scale computations.

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