Chapter 3

Coordination of Carbon Dioxide to Nickel

An Alternative Theoretical Model

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An alternative to the molecular orbital description of CO_2 bonding to a transition metal is proposed here. The new description is based on ab initio calculations which include important electronic correlation effects neglected in molecular orbital theory. The resulting valence bond picture, which includes "bent-bonds" for CO_2 rather than σ and π bonds, has striking similarities to the description given in qualitative discussions by Pauling many years ago.

In the last two to three decades molecular orbital theory has become the paradigm for discussing bonding in molecules. It has had many impressive successes and has contributed greatly to our understanding of the electronic structure of molecules. However, one must not lose sight of the fact that molecular orbital theory totally neglects electronic correlation effects, which may have important consequences for bonding.

Here, we investigate the effect of electronic correlation on our understanding of chemical bonding for the case of the CO_2 molecule and the coordination of this molecule to a nickel atom. We employ ab initio calculations based on the generalized valence bond (GVB) method (1) to study the CO_2 molecule, both as an isolated entity and coordinated to Ni. By analogy to transition metal complexes, three different coordination geometries for the CO_2 molecule are considered: pure carbon coordination (I), pure oxygen coordination (II) and mixed carbon-oxygen coordination (III).

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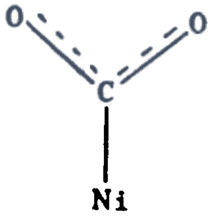
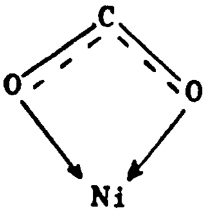


(I)



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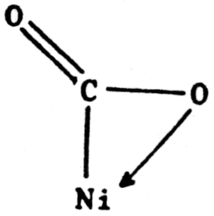

(III)

In all cases studied, the bonding between the CO_2 moiety and the metal atom is described best as a CO_2^- anion interacting with a Ni cation. On the basis of the calculations, several features of the interaction of CO_2 and metal surfaces can be discussed. Before discussing these results for coordinated CO_2 in more detail, we consider the isolated CO_2 molecule.

The CO_2 Molecule and Bent-Bonds

It has recently been demonstrated (2) that if correlated wave functions are used in the description of the CO_2 molecule and the orbitals are not forced to be symmetry orbitals, then one obtains a lower energy for multiple "bent-bonds" (Ω-bonds) than for the traditional σ and π bonds. Figure 1 shows contour plots of the Ω-bonds for one of the double bonds of CO_2. In panel A two orbitals which overlap to form a C-O bond are shown. On the left is an orbital more localized on the oxygen atom and on the right one which is more localized on the carbon atom; they can be thought of as overlapping, variationally determined atomic-like hybrids. Panel B shows the orbitals which make up the other half of the double bond; they are clearly symmetry-related to those in panel A. In panel C, contour plots of one of the oxygen lone pairs are shown. One can clearly see the "in-out" correlation exhibited by the pair of electrons, in which one orbital (at the right) is closer to the oxygen nucleus, while the other orbital (at the left) is more extended. Panel D shows the orbitals making up the second lone pair on the same oxygen atom; they are equivalent by symmetry to the pair in panel C. In Figure 2a, a schematic representation of the many-electron wave function is presented. The dots denote the number of electrons in each orbital and the lines denote which orbitals overlap to form bonds. The bonds labeled A and B in Figure 2a are composed of the orbitals in panels A and B of Figure 1, respectively. The computational details are described elsewhere (2).

The perfect-pairing (PP) orbitals of this wave function clearly show the "lone-pairs" and "bond pairs" which are part of the language of the experimental chemist. This is in contrast to the molecular orbital description or to the GVB description with $\sigma-\pi$ restrictions where the lone pairs and "π" bonds are not discernable from contour plots of the orbitals (2). It is somewhat reassuring that the wave function which gives the lowest variational energy (that of Figures 1 and 2a) also most closely coincides with the experimental chemist's traditional view of the bonding (3).

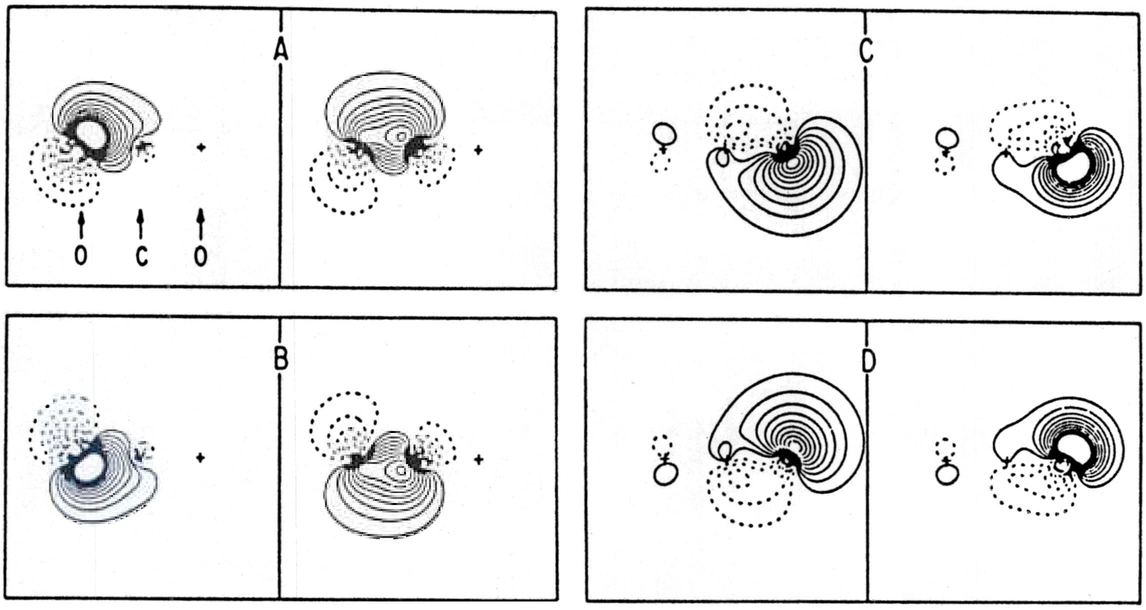

Figure 1. GVB-perfect pairing orbitals for the ground state of CO_2: A and B show the orbitals of the Ω-bonds for one of the CO double bonds; C and D show the orbitals of the two lone pairs on one of the oxygen atoms.

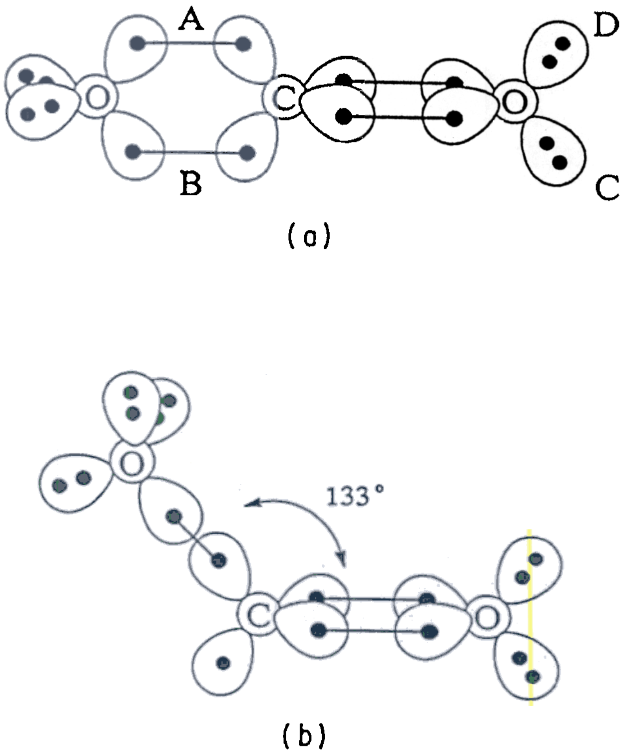

Figure 2. Schematic representations of the many-electron wave functions for: (a) the CO_2 ground state; (b) the CO_2^- anion.

The CO_2^- anion is unstable in the gas phase, but the dimer anion $(CO_2)_2^-$ which can be thought of as composed of a neutral molecule (somewhat polarized of course) and a carbon dioxide anion, is stable (4). We have investigated the CO_2^- anion using this geometry and find the many-electron wave function to be of the form shown schematically in Figure 2b. The lone pair and bond pair orbitals of CO_2^- are found to be nearly identical to those of CO_2 (Figure 1), supporting the intuitive notion of transferability of such entities between similar systems. One can think of the wave function of CO_2^- (Figure 2b) as arising from that of CO_2, when an additional electron is accepted by the latter in an orbital of an oxygen atom (the oxygen orbital of bond B, for example). The extra electron on oxygen (due to its higher electron affinity) results in the breaking of a carbon-oxygen bond and the formation of another oxygen lone pair. The anion can lower its energy by allowing the remaining bond (A in Figure 2a) to increase the overlap of its component orbitals (and decrease the Pauli repulsion between the new lone pair and the singly occupied orbital on carbon), resulting in the wave function of Figure 2b. This provides a simple and natural alternative explanation for the geometry of CO_2^- to that given by Walsh's rules.

Coordinated CO_2

We now turn to a discussion of the bonding between CO_2 and a Ni atom. A complete description of theoretical and computational details and the relationship of the results to the chemisorption of CO_2 on metal surfaces has been presented elsewhere (5); here we focus strictly on those aspects related to the bonding. However, before we discuss the bonding for the three individual coordination geometries (I), (II) and (III) on the basis of the PP-orbitals, it is appropriate to comment on a general result which is independent of the geometry. That is, all the orbitals localized on the CO_2 moiety in the $NiCO_2$ complexes have the same shapes as the orbitals of CO_2^- with the exception of those orbitals directly interacting with the Ni atom which are modified as described in the following discussion. This general result suggests that it is indeed appropriate to consider the bonding in Ni-CO_2 by focusing on the interaction of CO_2^- and Ni^+.

Pure Carbon Coordination (I)

For the case of the pure carbon coordination (I), it is obvious that the single electron on the CO_2^- forms a covalent bond with the unpaired d-electron on the Ni atom in its d^9 configuration. The GVB pair forming this bond is shown in Figure 3a. Although the results of a Mulliken population analysis can only be regarded as a qualitative indicator of the actual charge distribution, a calculated electron transfer of 0.53e from the Ni atom to the CO_2 moiety supports the view expressed above regarding the substantial ionic nature of the interacting species. Figure 3b shows a schematic representation of the many electron wave function; the bond whose orbitals are given in Figure 3a, is labeled A. The stabilization of (I) with respect to the infinitely separated parts is 7.79 eV. This stabilization is due both to the formation of a covalent bond and the coulombic interaction. An upper

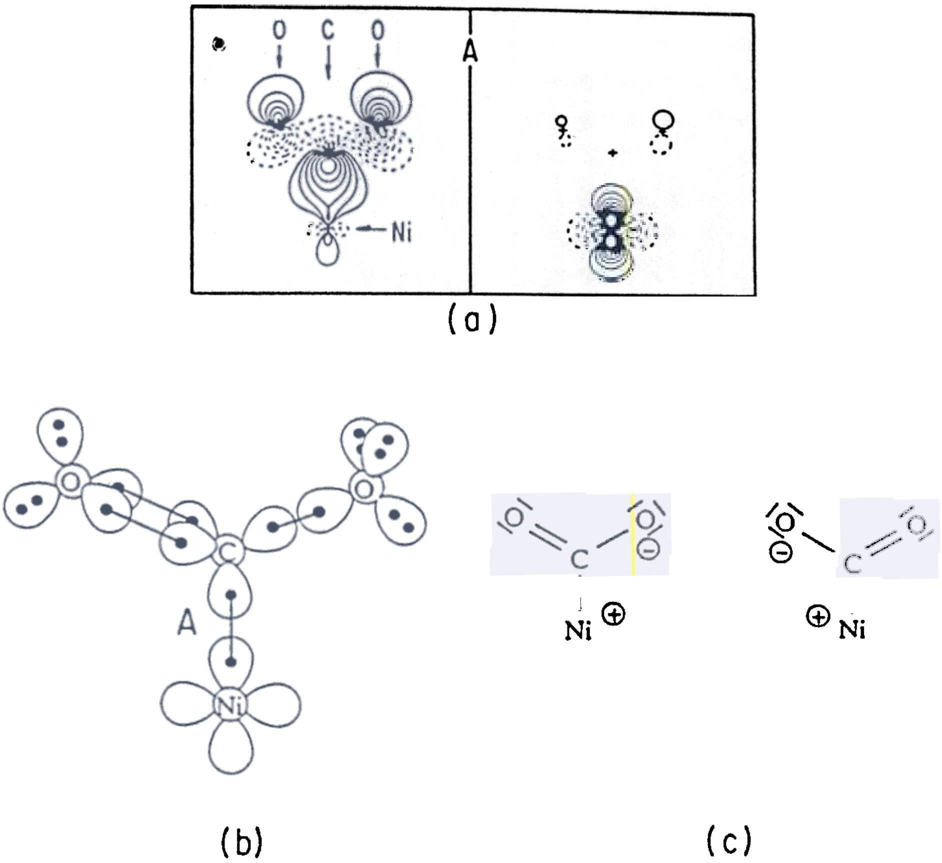

Figure 3. Coordination of CO_2 to Ni via carbon coordination: (a) orbitals forming the Ni-C covalent bond; (b) schematic diagram of the many-electron wave function; (c) classical "resonance" structures.

limit to the latter contribution can be estimated from the Mulliken atomic charges of the separated systems to be 5.65 eV, which is 73% of the total stabilization energy. Note that the corresponding energy using the Hartree-Fock (molecular orbital) wave function is only 5.68 eV, i.e., close to the pure coulomb interaction energy. However, the proper reference for the total energy of the system is not $Ni^+ + CO_2^-$ but rather $Ni + CO_2$. With respect to this reference point (I) is unbound by 1.72 eV. At the Hartree-Fock level it is unbound by 3.57 eV. As discussed elsewhere (5), this analysis with respect to the separated neutral species using calculated total energies needs to include corrections for errors made in the calculated electron affinity of CO_2 and the calculated ionization potential of the Ni atom. To correct for these errors we need to add 0.86 eV (HF: 1.02 eV) to the calculated binding energy with respect to the neutral species. Even including this correction, however, leaves (I) unbound by 0.86 eV (HF: 2.55 eV) with respect to $Ni + CO_2$. Although two resonance structures (Figure 3c) should be taken into account for a proper description of the ground state wave function, the resonance stabilization will mainly arise on the CO_2^- moiety, and therefore be similar to that in uncoordinate CO_2^-. Thus we expect only little influence of resonance on the bond energy of (I). Therefore, we conclude that the pure carbon coordination is unfavorable for CO_2 bonding to Ni.

Pure Oxygen Coordination (II)

If we place the Ni atom on the opposite side of the CO_2 moiety as compared to (I), the Ni atom has a pure oxygen coordination, (II). We have chosen the Ni-O distance to be consistent with the bond lengths found in molecular complexes (6,7). The panels (A, A', B and C) of Figure 4a show the orbitals which are non-trivially modified as a result of the Ni-CO_2 bonding interaction. The system has two unpaired electrons, coupled to form a triplet state. One electron resides on the CO_2^- moiety pointing away from the Ni atom (panel A), and the other is a *d*-electron on the Ni atom (panel A'). The former has the same shape as the orbital of the unpaired electron in free CO_2^-. The two lone pairs which establish two dative bonds to the Ni atom are shown in panels B and C of Figure 4a. The bonds are formed by the lone pairs donating into somewhat diffuse, unoccupied hybrid orbitals (of s and p character) on the Ni atom. Due to the choice of the contours in the plotted orbitals (increment of 0.05 a.u.) the bonding interaction between the oxygen lone pairs and the diffuse Ni orbitals shows up as an indentation in the contours of the in-out correlated lone pairs which is not present in the isolated system (Figure 1). A schematic representation of the wave function is given in Figure 4b. A charge transfer similar to that for (I) is found, however the stability of (II) has drastically improved over that of (I). With respect to the separated ions, namely Ni^+ and CO_2^-, we calculate a stabilization energy of 9.23 eV. With respect to the separated neutrals, (II) is unbound by 0.28 eV. This results in a bound state by 0.58 eV, once the correction for the electron affinity of CO_2 and the ionization potential of Ni are taken into account.

The Hartree-Fock calculation for (II) yields a stabilization energy with respect to the separated atoms which is nearly identical to the GVB-PP calculation, and taking the appropriate correction into

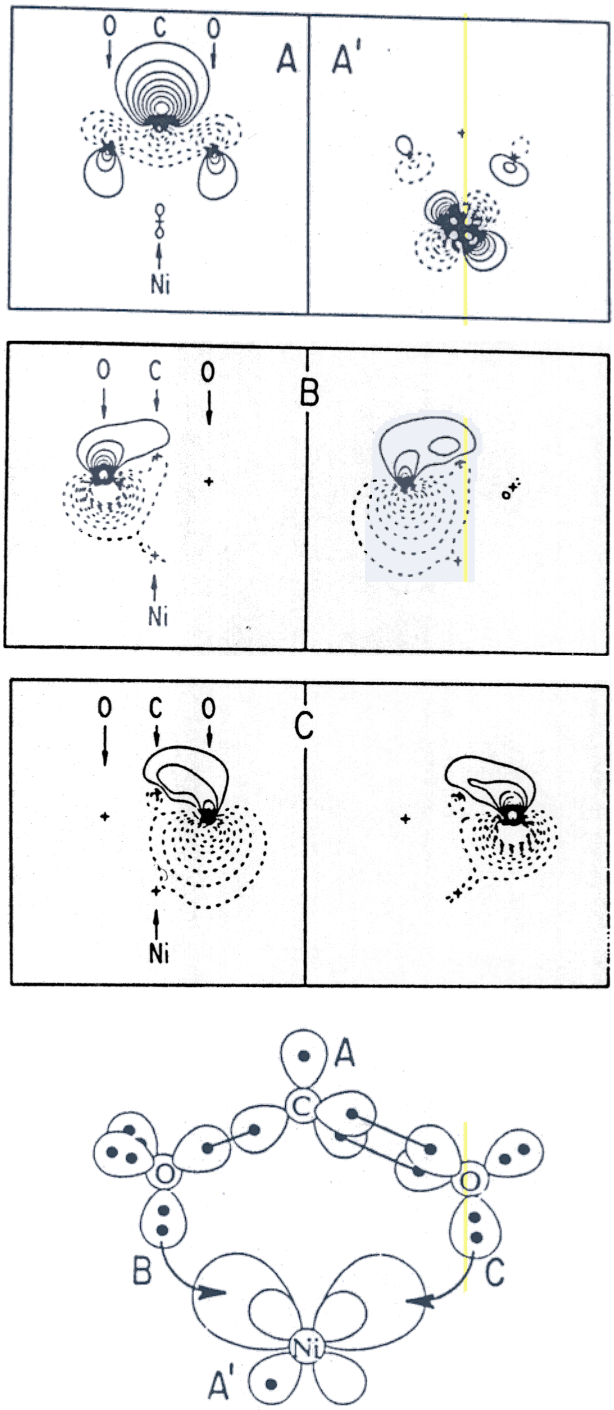

Figure 4. Coordination of CO_2 to Ni via pure oxygen coordination: (a) triplet coupled orbitals (A and A'); oxygen lone pairs forming dative bonds to Ni (panels B and C); (b) schematic diagram of the many-electron wave function.

account (see above) the system is stable with respect to dissociation into CO_2 and Ni. Thus, as far as the calculated stabilization energy is concerned, electron correlation does not seem to be crucial in this case, because the amount of covalent bonding is smallest, and the electrostatic interaction largest, of the three geometries considered. The extra coulombic stabilization experienced in (II) as compared to the pure carbon coordination (I) is sufficient to account for the higher stability of (II). Thus, our calculations indicate that the pure oxygen coordination represents a favorable coordination geometry for the Ni-CO_2 interaction. It should be mentioned that Jordan (8) has predicted a corresponding structure for $LiCO_2$ on the basis of Hartree-Fock calculations. The structure of the Li-salts have recently been investigated using vibrational spectroscopy (9) and the results seem to be consistent with Jordan's prediction.

Mixed Carbon-Oxygen Coordination (III)

The final coordination geometry considered is (III). We have chosen the geometry such that the carbon-Ni and oxygen-Ni bonds lengths are consistent with those of (I) and (II). Figure 5a shows the orbitals involved in the bonding between Ni and CO_2. In view of the discussion above, it is almost unnecessary to note that all other orbitals are basically identical to the non-interacting fragments Ni^+ and CO_2^-. Panel A of Figure 5a shows the GVB pair represening the carbon-Ni bond. Except for the asymmetry induced by the chosen geometry, the bond is very similar to the one shown in panel A of Figure 3a for the case of pure carbon coordination. Panel B shows the oxygen lone pair donation into the diffuse s/p hybrid orbitals of Ni as indicated by the indentation of the lone pair contours. Clearly, this unsymmetric coordination involves both covalent and dative bonding modes. A schematic view of the many-electron wave function is shown in Figure 5b. The stability of this coordination mode is nearly as great as the pure oxygen coordination (II). Similar to the situation for (I), the present geometry is unbound for the uncorrelated Hartree-Fock calculations even after accounting for the appropriate corrections. Thus, correlation effects for (III) are crucial in obtaining a bound system, unlike the situation for (II).

Summary

Our results for the three coordination modes considered here indicate that the CO_2 molecule prefers to adopt either a mixed carbon-oxygen coordination (III) or a pure coordination (II) to the metal center, while a pure carbon coordination (I) appears to be unfavorable. Further, the results suggest a rather weak CO_2 - transition metal bond consistent with the low stability of adsorbed CO_2 and CO_2 in molecular complexes.

We have attempted to summarize some qualitative aspects of bonding obtained from recent quantitative calculations which include important electronic correlation effects ignored in molecular orbital theory. The resulting valence bond concepts derived from the calculations, which have long been ignored as only qualitative and without sound theoretical foundation, are made quantitative and computationally accessible through the generalized valence bond theory. The concept of bent-bonds (Ω-bonds), much discussed in the chemical

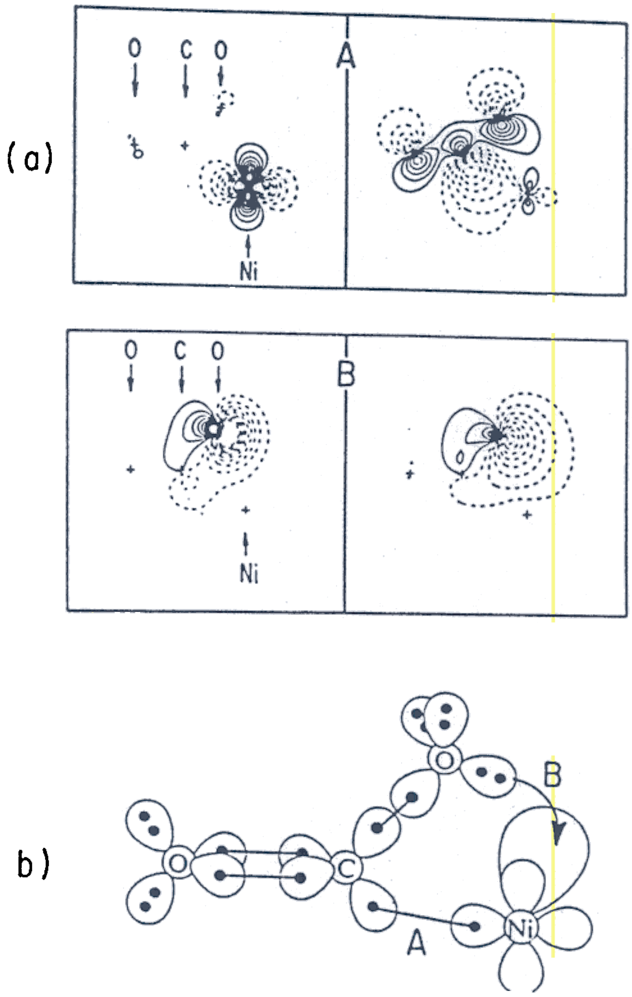

Figure 5. Coordination of CO_2 to Ni via mixed carbon and oxygen coordination: (a) orbitals forming a covalent bond between Ni and C (panel A); orbitals of a oxygen lone pair forming a dative bond to Ni (panel B); (b) schematic diagram of the many-electron wave function.

literature for decades has been demonatrated for the first time (2) to be the energetically favored description of bonding in CO_2. The Ω-bonds description is not only found for double bonds, but for triple bonds and conjugated bonds as well (Messmer, R. P. and Schultz, P. A. Physical Review Letters, in press). Hence, it appears that a natural language for the discussion of electronic correlation effects in bonding is a modified version of the valence bond approach long used by chemists as a useful empirical method to organize their vast experimental experience.

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