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Communication

Orbital Contributions to the Molecular Charge and Energy Density Distributions in $Co_2(CO)_8$

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For $Co_2(CO)_8$, the representative of a whole class of bridged cobalt complexes, the 18-electron rule predicts a direct metal–metal bond in addition to the metal–bridge bonds. By intuition, this bond should have bent-bond character. However, it is well-known from charge density analyses that no bond critical point exists in the corresponding spatial region. Otherwise, the energy density distribution points to a certain stabilizing contribution of this local area to the total molecular energy. It is shown that a partitioning of the total charge and energy densities into orbital contributions can lead to a deeper insight into complex bonding properties.

Bader's theory of atoms in molecules (AIM)[1] has become a valuable tool for bonding analyses. These analyses are based on the molecular charge density. A necessary condition for a bond is the existence of a so-called *bond critical point* (bcp), which is characterized by the minimum of the charge density along the path of maximum charge density between two atoms. This Communication deals with the so-called bent-bond problem, which is of basic interest concerning the complex bonding properties of polynuclear transition-metal compounds. For $Co_2(CO)_8$, the representative of a whole class of bridged cobalt complexes, the 18-electron rule predicts a direct metal−metal bond in addition to the metal−bridge bonds. By intuition, this bond should have bent-bond character. However, it has been shown for $Co_2(CO)_8$, $Co_4(CO)_{12}$, and related systems that no bcp is obtained in the bent-bond region.[2−4] Thus, the charge density analysis excludes any bent bonds in these systems.

The prediction of a bent bond is connected with the existence of an occupied Co−Co bonding orbital of bent shape. This orbital is expected to accumulate charge density in the bent-bond region. The questions are, can such a charge density accumulation be demonstrated and, if so, why does it not lead to a bcp? In this Communication, we show that a bonding analysis involving orbital contributions to the total charge density can answer these questions.

On the other hand, it has been shown recently that in the bent-bond regions of $Co_2(CO)_8$ and $Co_4(CO)_{12}$ a local minimum of the total energy density $H(\mathbf{r})$ (with negative $H(\mathbf{r})$ value) is obtained.[5] This points to a certain energy-decreasing, i.e., stabilizing, contribution of this local area to the total molecular energy, in relation to neighboring areas. Also in this respect, the orbital analysis appears to be advantageous.

The method is based on the partitioning of the total densities into orbital contributions. Such a partitioning is not established strictly quantum mechanically. However, there is a pragmatic justification in the case of single-configuration wave functions (Hartree−Fock or density functional theory, DFT, methods). Then, the total molecular charge and energy densities are evaluated as the sum of the contributions from the occupied molecular orbitals (MOs). Thus, one can provide more information concerning complex bonding properties by examining in addition to the total densities also the individual contributions from specific orbitals or orbital groups. First, the large contributions originating from the core electrons that are not involved in any specific valence orbital interactions can be identified and separated. Second, one can derive which of the MOs are responsible for the accumulation or depletion of the charge density and the decrease or increase of the energy density in a certain spatial region.

We remark that, in a natural way, canonical orbitals should be used for the partitioning. However, localized orbitals could be used as well. Then, all of those orbitals that are mixed in the localization procedure should be considered as a group. Natural orbitals (with broken occupation numbers) go beyond the single-configuration wave function.

For $Co_2(CO)_8$, optimizations using common DFT techniques reproduce the molecular structure rather well. Therefore, we simply considered for our analysis an idealized structure (C_{2v}) of $Co_2(CO)_8$ (Figure 1) based on the experi-

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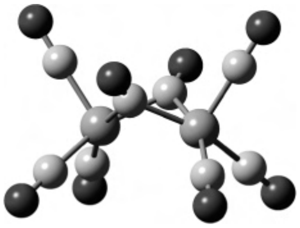

Figure 1. Structure of $Co_2(CO)_8$.

mental one[6] and applied the DFT procedure adopting the B3LYP functionals.[7] An appropriate all-electron basis set[8] for cobalt and the standard 6-31G(d) basis set[9] for the ligand atoms were used for the analyses. Some variations of these details did not change the resulting picture. The basic calculations were performed with the Gaussian03 program package,[10] the bonding analyses with the Extreme routine included in the Aimpac package of Bader.[11] From the AIM analysis, it results that only for the Co−C and C−O bonds do bcp's exist. No bcp appears in the Co−Co bent-bond region.

In Figure 2, top, the total charge density $\rho(\mathbf{r})$, its Laplacian $\nabla^2\rho(\mathbf{r})$, and the energy density $H(\mathbf{r})$ in the plane containing the 2-fold symmetry axis and the two Co centers are displayed, together with selected orbital group contributions (to be discussed below). In Figure 3, the respective density values along the 2-fold symmetry axis are given. The total charge and energy densities (Figure 3, left, full lines) have already been given recently.[3] The maximum of the total charge density along the axis, which is a minimum in the perpendicular plane, represents a *ring critical point*. According to the total charge density and its Laplacian, there is no bent bond. The total energy density shows a distinct minimum in the bent-bond region.

We now consider the individual orbital contributions of which the total densities are composed (Figures 2 and 3). We refer to the MO scheme given in Figure 4.

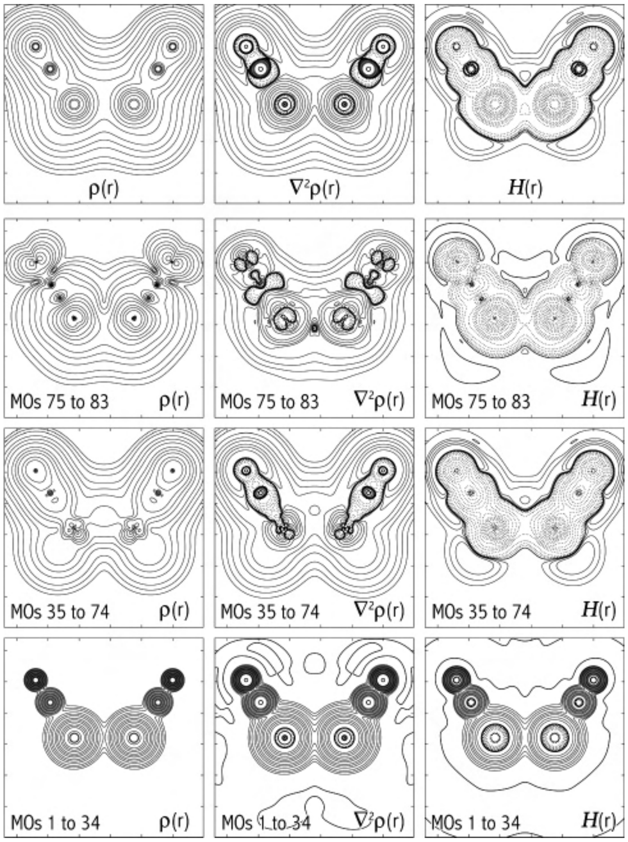

Figure 2. Total density maps (top) and selected orbital group contributions (below) to the total densities in the plane containing the 2-fold axis, the two Co centers, and two terminal CO's (compare Figure 1).

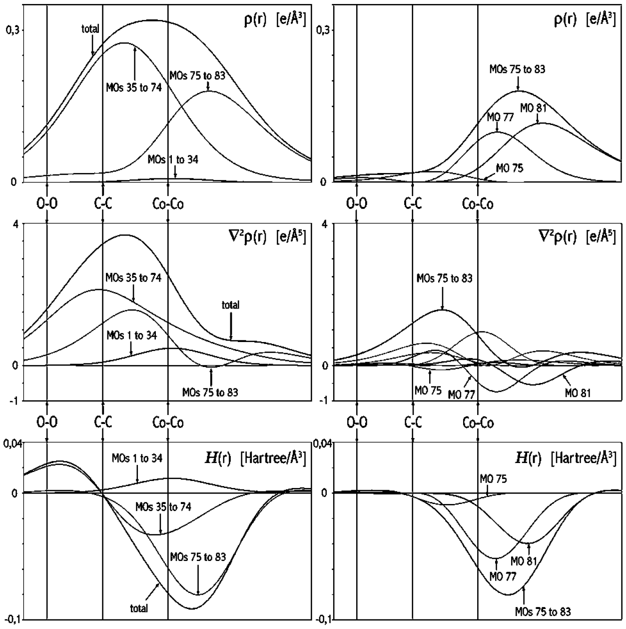

Figure 3. Total density values (left, full lines) and selected orbital or orbital group contributions to the total densities along the 2-fold axis. The positions of the Co−Co, C(br)−C(br), and O(br)−O(br) connecting vectors are indicated (compare Figure 1).

There are 83 doubly occupied orbitals. The MOs 1−34 correspond to the inner-shell electrons with vanishing charge density contributions along the central 2-fold axis (Figure 3, left, top). Positive values for the Laplacian of the charge density and the energy density indicate the repulsive interac-

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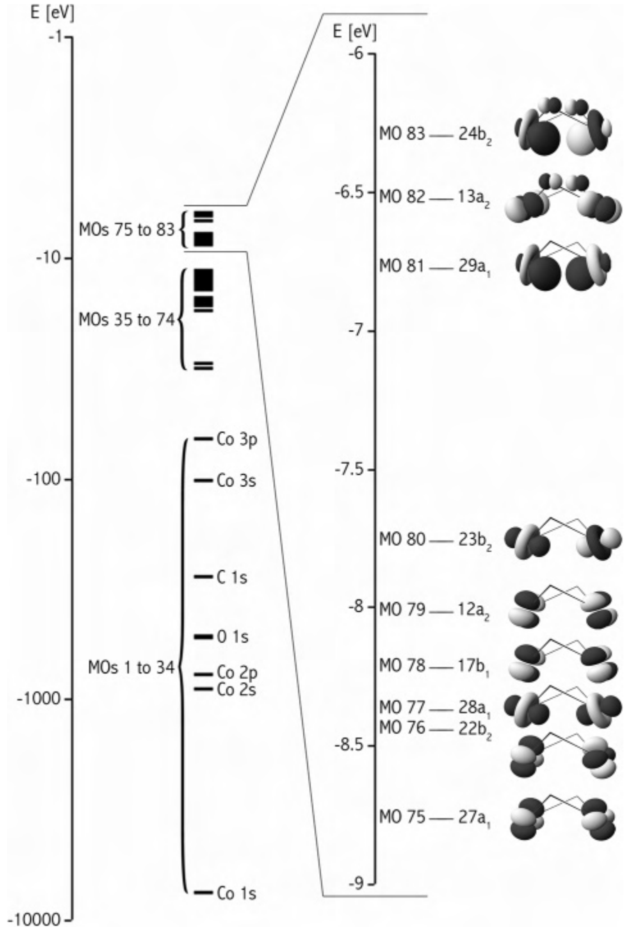

Figure 4. Molecular orbital scheme of $Co_2(CO)_8$.

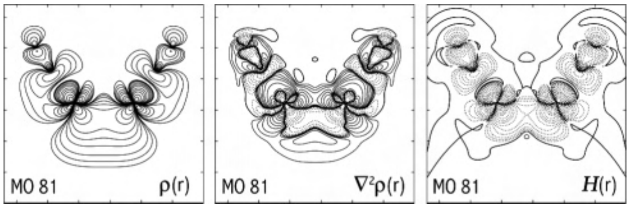

Figure 5. Density maps for the bent-bond MO.

tion between the two metal cores (below). The MOs 35−74 include (besides the terminal metal−ligand and intraligand orbitals with negligible contributions in this area) the bridge-to-metal donor orbitals and the orbitals of the bridging ligands. They give rise to large charge density values at the "center" of the puckered Co_2C_2 moiety (Figure 3, left, top). This charge density has a repulsive effect between the two bridging carbonyls and a stabilizing one in the center of the Co_2C_2 moiety; see the sign of the corresponding energy density (bottom).

The remaining MOs, the frontier orbitals 75−83, represent the in-phase and out-of-phase combinations of the formally nonbonding "t_{2g}" orbitals of the pseudo-octahedrally coordinated Co centers (75−80) as well as the metal-to-bridge π-acceptor orbitals (82 and 83) and the formal bent-bond orbital (81). They give rise to remarkable charge density contributions connected with negative values of the energy density in the bent-bond region.

Further splitting (Figure 3, right) shows that from the latter orbital group only those of a_1 symmetry give nonvanishing charge and energy density contributions along the 2-fold axis. For the other orbitals, this axis lies in at least one nodal plane. From the two formally nonbonding a_1 orbitals, one (75) has small density values opposite to the bent-bond region, whereas the other one (77) has larger values in that region. It is striking that the formal bent-bond orbital (81) leads to significant contributions to the charge density at a rather strongly bent position, which is also demonstrated by the two-dimensional plots (Figure 5).

The density partitioning demonstrates that the formal bent-bond orbital, as expected, causes a certain charge density accumulation in the bent-bond region. However, as can be seen from Figure 3, top, this effect is overcompensated by the contributions originating from the orbitals 35−74. The latter dominate the total charge density. The contribution of the bent-bond orbital remains completely hidden if only the total charge density is considered. Consequently, the charge density analysis excludes the existence of a bent bond.

The result of the partitioning is related to the conclusion of Macchi and Sironi that the strong electron delocalization in metal−carbonyl compounds is an essential reason for the nonexistence of a M−M bcp. More information concerning the charge density distribution can be provided from Figure 3, top. On the one hand, the accumulation of charge density originating from the bent-bond orbital is too small, surely because of the weak overlap between the metal orbitals. On the other hand, the contributions originating from the metal−bridge bonding orbitals are too large, considering the close vicinity of the respective spatial regions.

The Laplacian of the charge density, which involves both bonding and antibonding interactions, is more sensitive (Figure 3, middle). A distinct shoulder in the bent-bond region is obtained, originating from the contributions of the orbitals 75−83. For the whole frontier orbital group, a certain accumulation of charge density is indicated. Nevertheless, the Laplacian of the total density remains dominated by the contributions from the other orbitals.

In contrast, the total energy density along the 2-fold axis is determined by the contributions from the frontier orbitals, whereas the orbitals related to the metal−bridge bonds are less important. It is especially the formal bent-bond orbital that dominates the energy density in the bent-bond region, resulting in the obtained minimum of the total energy density with negative density value, which indicates a certain stabilizing contribution of this local area to the total molecular energy, although no bond is indicated by the charge density.

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