# Correlation Analysis of Chemical Bonds

**Terumasa Yamasaki**

*Asahi Chemical Ind. Co., Ltd., 2-1 Samejima, Fuji, Shizuoka 416, Japan*

**William A. Goddard III***

*Materials and Process Simulation Center, Beckman Institute (139-74), California Institute of Technology, Pasadena, California 91125*

*Received: October 1, 1997; In Final Form: January 5, 1998*

We present the methodology for correlation analysis of chemical bond operators (CACB) on ab initio wave functions. In CACB the wave function is analyzed in a hierarchy of quantities (charge, bond order, bond−bond correlation), where each quantity is the expectation value of an operator related to the statistical covariance of the previous quantity. CACB does not require any preconceived notion of which atoms are bonded and should be useful for reasoning about the similarity, stability, and reactivity of molecular systems. CACB does not require any special form of the wave function, but the applications here are for Hartree−Fock (HF) type wave functions. We use CACB to analyze the bonding in a number of molecules including transition states for several reactions. This analysis extracts chemically useful information without using preconcerned notations of bonding.

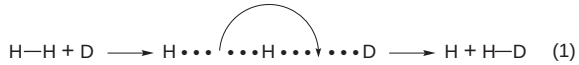
## I. Introduction

Progress in quantum chemical (QC) calculations of organic and inorganic molecules has made it practicable to calculate the structures and wave functions for very large molecules, including the transition states (TS) and reaction intermediates involved in complicated but important reactions. Indeed the structural parameters, activation energies, and other properties are rapidly approaching the point where their reliability is sufficiently high to be trusted in the absence of experimental data. However, the *interpretation* of wave functions has lagged behind these developments in extending the methods. Thus, QC papers will often discuss only structures, energies, and vibrational frequencies, with no discussion of the wave function and how it can be used to understand these properties. This is unfortunate since the possibility of interpreting the wave functions is the unique attribute of quantum chemistry. The problem is that the wave function has too much information. The difficulty is extracting a few salient parameters that provide chemical intuition useful in qualitative reasoning.

One strategy to extracting chemical information is typified by generalized valence bond (GVB) theory.[1] This utilizes a particular way to incorporate electron correlation and then extracts concepts directly from the GVB wave function. These GVB concepts are often closely related to valence bond concepts developed from empirical reasoning, and such GVB interpretations have often been useful for understanding the mechanisms of chemical reactions and the relationships between structure and energetics for various systems.[2] However, many ab initio studies involve very highly correlated wave functions not amenable to such orbital analyses. In addition, some first-principles methodology [density functional theory (DFT)] builds the electron correlation effects into a density functional that does not lead simply to GVB-like orbital interpretations. Thus, we wish to find a general way for extracting an interpretation directly from the wave function, without a preference for the particular nature of the wave function.

There have been several attempts to deduce electronic character directly from the wave function.[3] Most attempts at interpreting wave functions in terms of chemical concepts have focused on atom-centered properties (such as hybridization, valence, and partial atomic charges) or on the chemical bond (such as bond order, polarity, and bond energies). Mulliken population analysis continues to be the most popular, but new approaches such as the natural bonding orbital analysis (by Weinhold et al.)[4] and the atoms in molecules method (by Bader et al.)[5] have been developed and applied successfully to various systems. The descriptions of electronic structure produced by such approaches are generally in agreement with empirical notions about atoms and bonds in a molecule. This has allowed the molecular properties and chemical reactivities based on accurate ab initio wave functions to be discussed in terms of qualitative concepts.

Probably the most useful information to extract from such chemical concepts is the chemical reactivity. Thus, from a wave function of the molecule one would like an algorithm that would predict the relative ease of breaking various bonds and how attack on one bond might affect others. At the heart of considerations about chemical reactivity is how pairs of bonds interact with each other as bonds are distorted and exchanged during the reaction. The chemical reaction process can be viewed as in eq 1




(1)

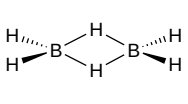
in which the arced arrow indicates how the covalent bonds *couple* or *move* during the course of the reaction. We refer to such coupling as bond*s* correlations with the plural bonds emphasizing that it is the correlation between *two* bonds that is being discussed rather than correlation within a bond. The physics underlying such bonds correlations is the Pauli principle, which for the simple Hartree−Fock (HF) wave function can be expressed as not allowing occupation of one localized molecular

* Author to whom correspondence should be addressed.

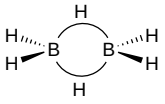
S1089-5639(97)03195-2 CCC: $15.00 
Published on Web 04/08/1998

orbital by more than two electrons. For wave functions containing electron correlation (GVB, MP2, MRCI), the Pauli principle can be expressed as allowing bond pairing (spatially symmetric or spin-singlet coupling) of no more than two electrons at a time. Thus, during a reaction the Pauli principle requires that as one bond is newly forming another bond must be breaking (generally there is not an increase in valence at the exchange center). Such considerations lead directly to selection rules whereby some reactions must necessarily have large barriers while others are allowed to have small values.[2b,6]

The implications of such bonds correlations are not limited to chemical reactions. For example, the molecules formed from the left half of the periodic table (groups 1−13) often have more valence orbitals available than electrons, leading sometimes to bonds very different than the simple two-electron bonds characteristic of columns 14−17. For example, one might think of the diborane molecule (eq 2)




(a)




(b) (2)

as either

(a) having two distinctive bonds between a bridge hydrogen and the two boron atoms (where each bond accounts for one electron) or

(b) having one three-center two-electron bond for each bridge hydrogen

In bond scheme 2a, the two bonds sharing one hydrogen are obviously *coupled* because there are only three atomic orbitals (AO) and two electrons available for these two covalent bonds. This situation becomes even more complicated for metal clusters. Thus, for icosahedral $Li_{13}^+$, there are 12 Li−Li bonds to the central Li plus 30 Li−Li bonds involving only surface atoms.[7] With just 12 valence electrons there are clearly couplings between the bonds.

In order to help clarify such dynamic bonds correlation effects, we devised an index for analyzing the degree of coupling between bond pairs. The approach, which we refer to as *correlation analysis of chemical bonds (CACB)*, is based on standard statistical methods and does not rely on any specific form of the wave function. Thus, it can be used for HF, GVB, MRCI, Meller−Plesset, and DFT wave functions. CACB provides a correlation coefficient, $\gamma_{IJ}$, between the covalent bond orders for any two bonds, *I* and *J*. This index is complementary to the atomic charge and bond order indices for characterizing the electronic structure of a molecule. The integrated formalism can be utilized in chemical similarity analyses for molecular systems.

In Section II we derive the CACB method. Although the approach is general, the specific equations developed here are for single Slater determinant wave functions. Section III reports results for various molecules and reactions and discusses some of the interpretations.

## II. Method

**A. The Covariance Hierarchy in Describing Electronic Structure.** Our approach to describing the electronic structure is a hierarchy that starts with

(i) a definition of the *atomic charge*, $Q_A$, in terms of the expectation value of an *atomic charge operator*, $\hat{q}_A$.

$$Q_A = \langle \hat{q}_A \rangle \tag{3}$$

such that the values of $Q_A$ correspond reasonably well to common concepts. A particular form of atomic charge operator is given in Section II.B.

(ii) Starting with the atomic charge operators we define the *bond order operator*, $\hat{I}_{AB}$, as the covariance form of the charge operators for centers *A* and *B*

$$\hat{I}_{AB} = \alpha(\hat{q}_A - \langle \hat{q}_A \rangle)(\hat{q}_B - \langle \hat{q}_B \rangle)$$

$$\text{where} \quad \alpha = -2 \tag{4a}$$

Here α is a multiplicative scale factor for normalizing the units. The *bond order*, $I_{AB}$, is obtained as the expectation value of the bond order operator, $\hat{I}_{AB}$

$$I_{AB} = \langle \hat{I}_{AB} \rangle \tag{4b}$$

(iii) Starting with eq 4a, we define the *bonds correlation operator*, $\gamma_{AB,CD}$, as the covariance form of the bond operators for bonds AB and CD

$$\hat{\gamma}_{AB,CD} = (\hat{I}_{AB} - \langle \hat{I}_{AB} \rangle)(\hat{I}_{CD} - \langle \hat{I}_{CD} \rangle)/\beta$$

$$\text{where} \quad \beta = [\text{cov}(\hat{I}_{AB}, \hat{I}_{AB}) \cdot \text{cov}(\hat{I}_{CD}, \hat{I}_{CD})]^{1/2} \tag{5a}$$

The *bonds correlation coefficient*, $\gamma_{AB,CD}$, is the expectation value of $\hat{\gamma}_{AB,CD}$

$$\gamma_{AB,CD} = \langle \hat{\gamma}_{AB,CD} \rangle \tag{5b}$$

The use of the coefficients for charge ($Q_A$), bond order ($I_{AB}$), and bonds correlation ($\gamma_{AB,CD}$) leads to a hierarchical description of the electronic structure for a molecule. The process is

(a) compute charges from the charge operator,

(b) combine the charge operators to obtain bond order operators from which the bond orders are obtained, and

(c) combine the bond order operators to form bonds correlation operators from which the bonds correlation coefficients are obtained.

This process could also be extended to higher order. At each step we define a multiplicative scale factor for normalizing the units so that the computed properties conform to empirical concepts about atoms, molecules, and reactions.

**B. The Atomic Charge Operator.** Once an atomic charge operator is defined, the CACB description of electronic property is unique. Here we define the atomic charge operator for atom *A* in eq 6[8]

$$\hat{q}_A = \sum_a^A a^+ \bar{a}^-, \quad \langle \hat{q}_A \rangle = Q_A \tag{6}$$

This choice for the atomic charge in eq 6 is equivalent to the Mulliken gross atomic population. Other choice for the atomic charge operator could be localized orthogonal atomic orbitals, such as natural atomic orbitals (NAO's).[4a] In eq 6, the summation runs over the atomic orbitals $\{a\}$ belonging to *A*. The brackets (⟨ ) and ( ⟩) denote ⟨HF| and |HF⟩, respectively. The creation and annihilation operators satisfy the commutation relations in eq 7

$$\left.\begin{aligned} a^+\bar{b}^+ + \bar{b}^+a^+ &= 0 \\ a^-\bar{b}^- + \bar{b}^-a^- &= 0 \\ a^+\bar{b}^- + \bar{b}^-a^+ &= \delta_{a,b} \end{aligned}\right\} \tag{7}$$

which uses a mixed covariant and contravariant basis ($\langle a|\bar{b}\rangle =$

$\delta_{ab}$) since atomic orbitals are generally nonorthogonal. For orthogonal atomic orbitals we read $a = \bar{a}$ in eqs 6 and 7.

Our representation does not distinguish between an atom and a group of atoms. Thus we can consider the charge for a group of atoms, $\langle \hat{q}_G \rangle = Q_G$, where $G$ consists of several atoms.

**C. The Bond Order Operator.** From eq 6, we construct the bond order operator as

$$\hat{I}_{AB} = -2\hat{\sigma}_{AB}$$
$$\text{where} \qquad \hat{\sigma}_{AB} = (\hat{q}_A - \langle \hat{q}_A \rangle)(\hat{q}_B - \langle \hat{q}_B \rangle) \tag{8}$$

The expectation value of $\hat{\sigma}_{AB}$ is

$$\langle \hat{\sigma}_{AB} \rangle = \langle (\hat{q}_A - \langle \hat{q}_A \rangle)(\hat{q}_B - \langle \hat{q}_B \rangle) \rangle$$
$$= \langle \hat{q}_A \hat{q}_B - Q_A \hat{q}_B - \hat{q}_A Q_B + Q_A Q_B \rangle$$
$$= \langle \hat{q}_A \hat{q}_B - Q_A Q_B \rangle = \langle \hat{q}_A \hat{q}_B \rangle - Q_A Q_B = \langle \hat{q}_A \hat{q}_B \rangle - \langle \hat{q}_A \rangle \langle \hat{q}_B \rangle \tag{9}$$

Replacing the $\langle\ \rangle$ terms with the density matrix components for a single determinant wave function, given in the Appendix, leads to the results in eq 10

$$I_{AB} = -2(\langle \hat{q}_A \hat{q}_B \rangle - \langle \hat{q}_A \rangle \langle \hat{q}_B \rangle)$$
$$= 2 \sum_{\substack{\sigma_a \\ \sigma_b}}^{\alpha,\beta} \sum_{\substack{a \in A \\ b \in B}} P_a{}^b P_b{}^a \tag{10}$$

Here

$$P_a{}^b = \sum_i^{\text{occ}} C_{i,a} C_i^b \quad \text{(spin)} \tag{11}$$

where $C_{i,a}$ and $C_i^b$ denote the covariant and contravariant coefficients, respectively, of the $i$th molecular orbital. (Note that we define $P_a{}^b$ as half of the usual bond order density matrix components.)

Equation 10 corresponds to the bond order quantity known as the Mayer bond index,[9] originally introduced by Giambiagi et. al., which is the extension of the Wiberg bond index[10] to nonorthogonal basis sets.

$$I_{AB} = 4 \sum_{\substack{a \in A \\ b \in B}}^{A,B} P_a{}^b P_b{}^a \quad \text{(closed shell)} \tag{12}$$

Giambiagi[11] and Mayer[12] have shown that $I_{AB}$ is related to the covariance form of the atomic charge operators in atoms $A$ and $B$, as in eq 8. Bond indices such as in eq 12 are known to give intuitively acceptable bond orders (approximately one for ordinary single bonds and two for ordinary double bonds). We will see below that the bond orders computed for HF wave functions give values in agreement with chemical intuition for most bonds.

The bond order in this definition may be computed for two groups of atoms as well as for two atomic centers.

**D. The Correlation Coefficient between Bonds.** Extending the idea of the bond order operator constructed from the atomic charge operators, we use standard statistical procedures to define the *bonds correlation operator*, $\hat{\gamma}_{AB,CD}$, from the two bond operators. Thus, we construct

$$\hat{\gamma}_{AB,CD} = \frac{(\hat{I}_{AB} - \langle \hat{I}_{AB} \rangle)(\hat{I}_{CD} - \langle \hat{I}_{CD} \rangle)}{[\text{cov}(\hat{I}_{AB}, \hat{I}_{AB}) \cdot \text{cov}(\hat{I}_{CD}, \hat{I}_{CD})]^{1/2}}$$
$$= \frac{(\hat{I}_{AB} - \langle \hat{I}_{AB} \rangle)(\hat{I}_{CD} - \langle \hat{I}_{CD} \rangle)}{[\langle (\hat{I}_{AB} - \langle \hat{I}_{AB} \rangle)(\hat{I}_{AB} - \langle \hat{I}_{AB} \rangle) \rangle \langle (\hat{I}_{CD} - \langle \hat{I}_{CD} \rangle)(\hat{I}_{CD} - \langle \hat{I}_{CD} \rangle) \rangle]^{1/2}}$$
$$= \frac{4(\hat{\sigma}_{AB} - \langle \hat{\sigma}_{AB} \rangle)(\hat{\sigma}_{CD} - \langle \hat{\sigma}_{CD} \rangle)}{[4\langle (\hat{\sigma}_{AB} - \langle \hat{\sigma}_{AB} \rangle)(\hat{\sigma}_{AB} - \langle \hat{\sigma}_{AB} \rangle) \rangle 4\langle (\hat{\sigma}_{CD} - \langle \hat{\sigma}_{CD} \rangle)(\hat{\sigma}_{CD} - \langle \hat{\sigma}_{CD} \rangle) \rangle]^{1/2}}$$
$$= \frac{(\hat{\sigma}_{AB} - \langle \hat{\sigma}_{AB} \rangle)(\hat{\sigma}_{CD} - \langle \hat{\sigma}_{CD} \rangle)}{[\langle (\hat{\sigma}_{AB} - \langle \hat{\sigma}_{AB} \rangle)(\hat{\sigma}_{AB} - \langle \hat{\sigma}_{AB} \rangle) \rangle \langle (\hat{\sigma}_{CD} - \langle \hat{\sigma}_{CD} \rangle)(\hat{\sigma}_{CD} - \langle \hat{\sigma}_{CD} \rangle) \rangle]^{1/2}}$$
$$\equiv \frac{\hat{\sigma}_{ABCD}}{[\sigma_{ABAB} \cdot \sigma_{CDCD}]^{1/2}} \tag{13a}$$

Replacing the operators $\hat{\sigma}_{AB}$ and $\hat{\sigma}_{CD}$ by the definition in eq 8, the expectation value of $\hat{\gamma}_{AB,CD}$ becomes the bonds correlation coefficient

$$\gamma_{AB,CD} = \langle \hat{\gamma}_{AB,CD} \rangle = \sigma_{ABCD} / (\sigma_{ABAB} \cdot \sigma_{CDCD})^{1/2} \tag{13b}$$

where

$$\sigma_{ABCD} = \langle \hat{q}_A \hat{q}_B \hat{q}_C \hat{q}_D \rangle - \langle \hat{q}_A \hat{q}_C \hat{q}_D \rangle \langle \hat{q}_B \rangle - \langle \hat{q}_B \hat{q}_C \hat{q}_D \rangle \langle \hat{q}_A \rangle - \langle \hat{q}_A \hat{q}_B \hat{q}_D \rangle \langle \hat{q}_C \rangle - \langle \hat{q}_A \hat{q}_B \hat{q}_C \rangle \langle \hat{q}_D \rangle + \langle \hat{q}_A \hat{q}_D \rangle \langle \hat{q}_B \rangle \langle \hat{q}_C \rangle + \langle \hat{q}_B \hat{q}_D \rangle \langle \hat{q}_A \rangle \langle \hat{q}_C \rangle + \langle \hat{q}_A \hat{q}_C \rangle \langle \hat{q}_B \rangle \langle \hat{q}_D \rangle + \langle \hat{q}_B \hat{q}_C \rangle \langle \hat{q}_A \rangle \langle \hat{q}_D \rangle + 2\langle \hat{q}_C \hat{q}_D \rangle \langle \hat{q}_A \rangle \langle \hat{q}_B \rangle + 2\langle \hat{q}_A \hat{q}_B \rangle \langle \hat{q}_C \rangle \langle \hat{q}_D \rangle - \langle \hat{q}_A \hat{q}_B \rangle \langle \hat{q}_C \hat{q}_D \rangle - 4\langle \hat{q}_A \rangle \langle \hat{q}_B \rangle \langle \hat{q}_C \rangle \langle \hat{q}_D \rangle \tag{14}$$

Thus, our objective quantity $\sigma_{ABCD}$ is connected to fourth-order density matrix algebra. (Note that $\hat{q}_A = \sum_{a \in A} a^+ \bar{a}^-$.) The expectation values are computed for each $\langle\ \rangle$ term of eq 14 as given in the Appendix. Density matrix algebra for terms appearing in eq 14 were also derived by Giambiagi and coworkers.[13]

Using the abbreviations in eq 15

$$P_A = \sum_{\sigma_a}^{\alpha,\beta} \sum_a^A P_a{}^a$$
$$P_{AB} = \sum_{\sigma_a,\sigma_b}^{\alpha,\beta} \sum_{a,b}^{A,B} P_a{}^b P_b{}^a$$
$$P_{ABC} = \sum_{\sigma_a,\sigma_b,\sigma_c}^{\alpha,\beta} \sum_{a,b,c}^{A,B,C} P_a{}^b P_b{}^c P_c{}^a \tag{15}$$
$$P_{ABCD} = \sum_{\sigma_a,\sigma_b,\sigma_c,\sigma_d}^{\alpha,\beta} \sum_{a,b,c,d}^{A,B,C,D} P_a{}^b P_b{}^c P_c{}^d P_d{}^a$$

Equation 14 leads to the expressions in eq 16 with which the

correlation coefficient in eq 13 is computed

$$\sigma_{ABCD} = P_{AD}\cdot P_{BC} + P_{AC}\cdot P_{BD} - P_{ABCD} - P_{ABDC} - P_{ACBD} - P_{ACDB} - P_{ADBC} - P_{ADCB} \quad (16a)$$

$$\sigma_{ABAD} = P_{AB}\cdot P_{AD} - P_{A}\cdot P_{BD} + P_{AA}\cdot P_{BD} + P_{ABD} + P_{ADB} - 2P_{AABD} - 2P_{AADB} - 2P_{ABAD} \quad (16b)$$

$$\sigma_{ABCA} = P_{AB}\cdot P_{AC} - P_{A}\cdot P_{BC} + P_{AA}\cdot P_{BC} + P_{ABC} + P_{ACB} - 2P_{AABC} - 2P_{AACB} - 2P_{ABAC} \quad (16c)$$

$$\sigma_{ABBD} = P_{AD}\cdot P_{BB} - P_{B}\cdot P_{AD} + P_{AB}\cdot P_{BD} + P_{ABD} + P_{ADB} - 2P_{ABBD} - 2P_{ABDB} - 2P_{ADBB} \quad (16d)$$

$$\sigma_{ABCB} = P_{AC}\cdot P_{BB} - P_{B}\cdot P_{AC} + P_{AB}\cdot P_{BC} + P_{ABC} + P_{ACB} - 2P_{ABBC} - 2P_{ABCB} - 2P_{ACBB} \quad (16e)$$

$$\sigma_{ABAB} = P_{A}\cdot P_{B} - P_{AB} - P_{B}\cdot P_{AA} - P_{A}\cdot P_{BB} + P_{AB}\cdot P_{AB} + P_{AA}\cdot P_{BB} + 2P_{AAB} + 2P_{ABB} - 2P_{ABAB} - 4P_{AABB} \quad (16f)$$

$$\sigma_{ABBA} = P_{A}\cdot P_{B} - P_{AB} - P_{B}\cdot P_{AA} - P_{A}\cdot P_{BB} + P_{AB}\cdot P_{AB} + P_{AA}\cdot P_{BB} + 2P_{AAB} + 2P_{ABB} - 2P_{ABAB} - 4P_{AABB} \quad (16g)$$

The bonds correlation coefficient $\gamma_{AB,CD}$ dictates how two bonds interact with each other. Thus the sign of $\gamma_{AB,CD}$ is positive when the $A-B$ and $C-D$ bonds both form or break simultaneously, while a negative sign means that forming the $A-B$ bond is correlated with breaking of the $C-D$ bond and vice versa.

## III. Results and Discussion

We will now use the CACB descriptive scheme to discuss the electronic structure and the reactivity of molecular systems. In the following, we used Gaussian-94 for HF calculations.[14]

**A. CACB with HF Wave Functions, Basis Set Dependence.** Energetic quantities (activation barriers, bond energies) can be quite sensitive to the level of wave function and to the basis set; however, a useful interpretive analysis (charges, bond orders, bonds correlations) should be relatively insensitive to the level of wave function or the basis set. Consequently we carried out CACB on the HF wave functions using two basis sets for a number of molecular systems, with the results in Tables 1−4. Here we considered an extended basis (valence double-ζ plus polarization functions, 6-31G**) and a minimal basis (STO-3G). We find that for most systems the bonds correlation coefficients ($\gamma_{IJ}$) give similar results for minimal and extended basis.

The root-mean-square (rms) difference between minimal and extended basis in Tables 1−4 are computed to be 0.126 ($Q_A$), 0.069 ($I_{AB}$), and 0.034 ($\gamma_{IJ}$). (Multiplicity of the $Q_A$, $I_{AB}$, and $\gamma_{IJ}$ in a molecule is taken into account.) That the charge ($Q_A$) and the bond order ($I_{AB}$) are nearly independent of basis is expected since they have intrinsic significance. The observed independence in the $\gamma_{IJ}$ quantity suggests it to also be a fundamental electronic property. We note that the basis set dependence decreases in the order of $Q_A$, $I_{AB}$, and $\gamma_{IJ}$, as the electronic property becomes higher order in the covariance hierarchy.

*1. Bonds Correlations between Covalent Bonds.* Table 1 considers covalent and polar covalent bonds in molecules, while Table 2 examines the sequence $H_3C-CH_3$, $H_2C=CH_2$, and $HC\equiv CH$. The computed bond orders for such cases are mostly

**TABLE 1: CACB ($\gamma_{IJ}$) of Simple $AX_n$ Molecules with Minimal and Extended Basis Sets. Charge ($Q_A$) and Bond Order ($I_{AB}$) Values Are Also Shown**

| | STO-3G | 6-31G** |
|---|---|---|
| | (a) $AX_4$ | |
| | Methane ($CH_4$) | |
| $Q_A$(C) | 6.263 | 6.473 |
| $Q_A$(H) | 0.934 | 0.882 |
| $I_{AB}$(C−H) | 0.991 | 0.978 |
| $\gamma_{IJ}$(H−C−H) | 0.248 | 0.275 |
| | Silane ($SiH_4$) | |
| $Q_A$(Si) | 13.361 | 13.334 |
| $Q_A$(H) | 1.160 | 1.167 |
| $I_{AB}$(Si−H) | 0.943 | 0.950 |
| $\gamma_{IJ}$(H−Si−H) | 0.234 | 0.249 |
| | Tetramethylmethane (Neopentane) [$C(CH_3)_4$] | |
| $Q_A$(C) | 5.937 | 6.078 |
| $Q_A$($C_{Me}$) | 6.181 | 6.304 |
| $Q_A$(H) | 0.945 | 0.892 |
| $I_{AB}$(C−C) | 0.983 | 0.979 |
| $I_{AB}$(C−H) | 0.983 | 0.975 |
| $\gamma_{IJ}$(C−C−C) | 0.060 | 0.074 |
| $\gamma_{IJ}$(C−C−H) | 0.121 | 0.137 |
| $\gamma_{IJ}$(H−C−H) | 0.243 | 0.279 |
| $\gamma_{IJ}$(C−C, C−H; gauche) | 0.000 | 0.000 |
| $\gamma_{IJ}$(C−C, C−H; anti) | 0.001 | 0.001 |
| | (b) $AX_3$ | |
| | $BH_3$ | |
| $Q_A$(B) | 4.818 | 4.770 |
| $Q_A$(H) | 1.061 | 1.077 |
| $I_{AB}$(B−H) | 0.995 | 0.990 |
| $\gamma_{IJ}$(H−B−H) | 0.332 | 0.351 |
| | $CH_3$ | |
| $Q_A$(C) | 6.177[a] (6.180)[b] | 6.384[a] (6.392)[b] |
| $Q_A$(H) | 0.941[a] (0.940)[b] | 0.872[a] (0.869)[b] |
| $I_{AB}$(C−H) | 0.976[a] (0.986)[b] | 0.964[a] (0.973)[b] |
| $\gamma_{IJ}$(H−C−H) | 0.325[a] (0.327)[b] | 0.355[a] (0.358)[b] |
| | $NH_3$ | |
| $Q_A$(N) | 7.441 | 7.792 |
| $Q_A$(H) | 0.853 | 0.736 |
| $I_{AB}$(N−H) | 0.962 | 0.918 |
| $\gamma_{IJ}$(H−N−H) | 0.319 | 0.348 |
| | $PH_3$ | |
| $Q_A$(P) | 14.652 | 14.840 |
| $Q_A$(H) | 1.116 | 1.053 |
| $I_{AB}$(P−H) | 0.974 | 0.974 |
| $\gamma_{IJ}$(H−P−H) | 0.324 | 0.351 |
| | (c) $AX_2$ | |
| | $BeH_2$ | |
| $Q_A$(Be) | 3.909 | 3.783 |
| $Q_A$(H) | 1.046 | 1.109 |
| $I_{AB}$(Be−H) | 0.998 | 0.988 |
| $\gamma_{IJ}$(H−Be−H) | 0.499 | 0.477 |
| | Water ($H_2O$) | |
| $Q_A$(O) | 8.331 | 8.671 |
| $Q_A$(H) | 0.835 | 0.665 |
| $I_{AB}$(O−H) | 0.964 | 0.884 |
| $\gamma_{IJ}$(H−O−H) | 0.481 | 0.460 |
| | Hydrogen Sulfide ($SH_2$) | |
| $Q_A$(S) | 15.928 | 16.134 |
| $Q_A$(H) | 1.036 | 0.933 |
| $I_{AB}$(S−H) | 0.991 | 0.969 |
| $\gamma_{IJ}$(H−S−H) | 0.496 | 0.538 |
| | (d) ABA | |
| | Ozone (O′−O−O′) | |
| $Q_A$(O) | 7.860 | 7.674 |
| $Q_A$(O′) | 8.070 | 8.163 |
| $I_{AB}$(O−O′) | 1.359 | 1.353 |
| $I_{AB}$(O′−O′) | 0.500 | 0.363 |
| $\gamma_{IJ}$(O′−O−O′) | 0.081 | 0.171 |
| $\gamma_{IJ}$(O−O′, O′−O′) | −0.409 | −0.486 |
| | Sulfur Dioxide ($SO_2$) | |
| $Q_A$(S) | 15.311 | 14.925 |
| $Q_A$(O) | 8.345 | 8.538 |
| $I_{AB}$(S−O) | 1.465 | 1.741 |
| $I_{AB}$(O−O) | 0.468 | 0.115 |
| $\gamma_{IJ}$(O−S−O) | 0.094 | 0.280 |
| $\gamma_{IJ}$(S−O, O−O) | −0.419 | −0.554 |

[a] UHF results. [b] ROHF results.

**TABLE 2: CACB ($\gamma_{IJ}$) of $C_2H_n$ Molecules with Minimal and Extended Basis Sets. Charge ($Q_A$) and Bond Order ($I_{AB}$) Values Are Also Shown**

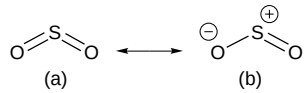
| | STO-3G | 6-31G** |
|---|---|---|
| (a) Ethane ($C_2H_6$) | | |
| $Q_A$(C) | 6.175 | 6.335 |
| $Q_A$(H) | 0.942 | 0.888 |
| $I_{AB}$(C−C) | 1.009 | 0.966 |
| $I_{AB}$(C−H) | 0.984 | 0.977 |
| $\gamma_{IJ}$(C−C−H) | 0.124 | 0.138 |
| $\gamma_{IJ}$(H−C−H) | 0.244 | 0.281 |
| $\gamma_{IJ}$(C−H, C−H; gauche) | 0.000 | 0.000 |
| $\gamma_{IJ}$(C−H, C−H; anti) | 0.003 | 0.003 |
| (b) Ethylene ($C_2H_4$) | | |
| $Q_A$(C) | 6.121 | 6.254 |
| $Q_A$(H) | 0.940 | 0.873 |
| $I_{AB}$(C═C) | 2.012 | 1.969 |
| $I_{AB}$(C−H) | 0.976 | 0.975 |
| $\gamma_{IJ}$(C═C−H) | 0.232 | 0.251 |
| $\gamma_{IJ}$(H−C−H) | 0.238 | 0.274 |
| $\gamma_{IJ}$(C−H, C−H; cis) | 0.003 | 0.000 |
| $\gamma_{IJ}$(C−H, C−H; trans) | 0.006 | 0.004 |
| (c) Acetylene ($C_2H_2$) | | |
| $Q_A$(C) | 6.109 | 6.233 |
| $Q_A$(H) | 0.891 | 0.767 |
| $I_{AB}$(C≡C) | 3.000 | 3.190 |
| $I_{AB}$(C−H) | 0.985 | 0.893 |
| $\gamma_{IJ}$(C≡C−H) | 0.317 | 0.272 |
| $\gamma_{IJ}$(C−H, C−H) | 0.002 | 0.007 |

close to the formal bond orders. For such cases, each $\gamma_{IJ}$ is generally positive with relatively large coefficients for bonds that share a center. $\gamma_{IJ}$ assesses the dependence between bonds in a molecule, reflecting the nature of the underlying wave function. The sequence $CH_4$, $NH_3$, $OH_2$ leads to $\gamma_{IJ}$(H−X−H) = 0.275, 0.348, 0.460, while $SiH_4$, $PH_3$, $SH_2$ leads to 0.249, 0.351, 0.538. This effect is due to the difference in the orbital space contributing to each bond order. Polar bonds have bond orbital spaces that are less exclusive of each other (in terms of the interaction through the *density matrices*) than for covalent bonds. This is supported by comparing $CH_4$ and $C(CH_3)_4$: between the central CC bonds of $C(CH_3)_4$, $\gamma_{IJ}$(C−C−C) = 0.074 indicating little correlation. However, the methyl groups for $C(CH_3)_4$ lead to $\gamma_{IJ}$(H−C−H) = 0.279 which is comparable to the $\gamma_{IJ}$(H−C−H) = 0.275 for $CH_4$ [the bond orders are similar: 0.978 in $CH_4$ and 0.979 in $C(CH_3)_4$]. Similarly $SiH_4$ leads to $\gamma_{IJ}$(H−Si−H) = 0.249 [closer to the $\gamma_{IJ}$(H−C−H) = 0.275 for $CH_4$ even though $Q_A$(H; $CH_4$) = 0.882 while $Q_A$(H; $SiH_4$) = 1.167].

Small bonds correlations are observed between nonadjacent bonds in hydrocarbons (Table 2). Thus, for ethylene, C−H bonds on different centers lead to small values [$\gamma_{IJ}$(C−H, C−H; cis) = 0.000 and $\gamma_{IJ}$(C−H, C−H; trans) = 0.004], whereas bonds at one center are positive [$\gamma_{IJ}$(H−C−H) = 0.274]. For C−H bonds on different centers of $C_2H_2$, $C_2H_4$, and $C_2H_6$ we find that $|\gamma_{IJ}$(C−H, C−H)| < 0.01 for all cases.

Tables 1 and 2 show that bonds correlations decrease to zero as there are additional bonds between them. Thus, although a molecule with $N$ bonds has $N(N+1)/2$ bonds correlation pairs, the number of nonzero coefficients is of order $N$.

*2. $SO_2$ versus $O_3$.* An exception to the basis set invariance of the bond orders is $SO_2$. Here the $I_{AB}$(S−O) bond order changes from 1.465 to 1.741 between the two basis sets. This suggests that the d functions included with the extended basis set lead to a fundamental change in the character of $SO_2$. Thus, one can visualize $SO_2$ as a resonance between




But the a structure requires d character on the S missing in the minimal basis. This is supported by the analysis for ozone ($O_3$), which can only involve the b description. For $O_3$ the central bond orders change from 1.359 to 1.353 as the basis is extended, indicating that d functions are not essential.

In $O_3$ and $SO_2$ molecules, the bonding in the $\pi$ system leads to partial bonding between the two end oxygens. This results in a very large negative correlation to the central bonds [$\gamma_{IJ}$(O−O′, O′−O′) = −0.486 for $O_3$ and $\gamma_{IJ}$(S−O, O−O) = −0.554 for $SO_2$]. Thus, CACB leads to a bonding scheme very different than $BeH_2$ or $H_2O$ even though each has an *ABA* structure.

The basis set dependence for the bond order between the terminal oxygens is also large in $SO_2$. Thus, as the basis is extended in $SO_2$, $I_{AB}$(O−O) changes from 0.468 to 0.115. In contrast, for $O_3$ the increase in basis changes $I_{AB}$(O′−O′) from 0.500 to 0.363.

**B. Hydrogen and Donor−Acceptor Bonds.** Bonding interactions involving hydrogen bonds and donor−acceptor (DA) (Lewis base−Lewis acid) bonds are given in Table 3.

*1. Water Dimer.* For a hydrogen-bonded system such as water dimer, the hydrogen bond order is small and changes little (0.054 to 0.056) as the basis is extended. The hydrogen bond has very small correlations (0.02 to 0.03) to adjacent O−H bonds. A similar tendency is observed for DA bonds (vide infra).

*2. Donor−Acceptor Bonds.* For typical DA complexes, such as $BH_3$−$NH_3$ or $AlH_3$−$PH_3$ in Table 3, the DA bonds are much stronger than a hydrogen bond, with $I_{AB}$(B−N) = 0.453 and $I_{AB}$(Al−P) = 0.279. The DA bond orders decrease significantly upon extending the basis (0.561 to 0.453 for B−N and 0.336 to 0.279 for Al−P). This may arise from the basis set superposition error (BSSE) expected for MO's in such systems. For DA bonds the correlation to adjacent bonds is positive (0.08 and 0.05) but smaller than ordinary intramolecular bonds correlations (0.2 to 0.3). The basis set dependence is also negligible.

*3. Diborane.* In diborane (Table 3) the bridge bonds are best described as a three-center two-electron bond (B−$\mu$H−B′). Indeed the partial bond order between the boron atoms is significant, $I_{AB}$(B−B) = 0.47 compared to (B−$\mu$H) = 0.48. This suggests that the four electrons are involved in multicentered bonds involving both boron atoms and both bridge-hydrogen atoms.

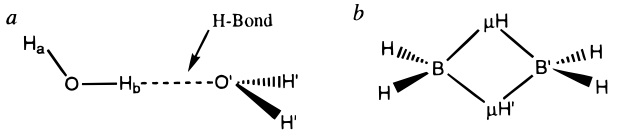
Alternatively, we can consider diborane as a resonance of two bonding configurations, one with bonds B−$\mu$H and B′−$\mu$H′ the other with B−$\mu$H′ and B′−$\mu$H. This would lead to average bond orders of $I_{AB}$(B−$\mu$H) = 0.48, as observed. In this view each BH bond can interact with the empty in-plane $\pi$ orbital of the adjacent $BH_3$, as in $NH_3$−$BH_3$. This leads to the bond order of 0.73 for each B [$I_{AB}$(B−$\mu$H) plus half of $I_{AB}$(B−B)], stronger than the DA bond of $I_{AB}$ = 0.45 for $NH_3$−$BH_3$.

In DA complexes such as $NH_3$−$BH_3$ and diborane, the sum of the bond orders in Table 3 (6.042 for $BH_3$−$NH_3$ and 6.346 for diborane) exceeds the value of 6.0 expected for two isolated molecules. This difference arises from the extra DA bonding. The nitrogen lone pair of $NH_3$ or the B−H bond of $BH_3$ forms a partial covalent bond with the boron vacant orbital of $BH_3$. This partial covalent bond contribute to a total bond order exceeding the sum of formal bond orders.

**TABLE 3: CACB ($\gamma_{IJ}$) of Molecular Complexes with Donor/Acceptor Bonds and Hydrogen Bonds. Charge ($Q_A$) and Bond Order ($I_{AB}$) Values Are Also Shown**

| | STO-3G | 6-31G** |
|---|---|---|
| (a) $H_2O$ Dimer[a] ($H_aOH_b-O'H'_2$) | | |
| $Q_A(O)$ | 8.383 | 8.716 |
| $Q_A(H_a)$ | 0.859 | 0.675 |
| $Q_A(H_b)$ | 0.804 | 0.637 |
| $Q_A(O')$ | 8.333 | 8.671 |
| $Q_A(H)$ | 0.811 | 0.650 |
| $I_{AB}(H_a-O)$ | 0.972 | 0.892 |
| $I_{AB}(O-H_b)$ | 0.899 | 0.833 |
| $I_{AB}(O'-H')$ | 0.954 | 0.873 |
| $I_{AB}(H_b-O')$ (H-bond) | 0.054 | 0.056 |
| $\gamma_{IJ}(H_a-O-H_b)$ | 0.456 | 0.440 |
| $\gamma_{IJ}(H'-O'-H')$ | 0.456 | 0.440 |
| $\gamma_{IJ}(O-H_b-O')$ | −0.024 | 0.016 |
| $\gamma_{IJ}(H_b-O'-H')$ | 0.025 | 0.027 |
| (b) $BH_3-NH_3$ | | |
| $Q_A(B)$ | 4.936 | 4.792 |
| $Q_A(H_B)$ | 1.134 | 1.157 |
| $Q_A(N)$ | 7.390 | 7.715 |
| $Q_A(H_N)$ | 0.758 | 0.674 |
| $I_{AB}(B-H)$ | 0.976 | 0.978 |
| $I_{AB}(N-H)$ | 0.921 | 0.885 |
| $I_{AB}(B-N)$ (DA bond) | 0.561 | 0.453 |
| $\gamma_{IJ}(H-B-H)$ | 0.275 | 0.300 |
| $\gamma_{IJ}(H-N-H)$ | 0.257 | 0.290 |
| $\gamma_{IJ}(H-B-N)$ | 0.083 | 0.078 |
| $\gamma_{IJ}(B-N-H)$ | 0.080 | 0.078 |
| $\gamma_{IJ}$(B−H, N−H; anti) | 0.002 | 0.001 |
| (c) $AlH_3-PH_3$ | | |
| $Q_A(Al)$ | 12.230 | 12.452 |
| $Q_A(H_{Al})$ | 1.324 | 1.233 |
| $Q_A(P)$ | 14.618 | 14.789 |
| $Q_A(H_P)$ | 1.060 | 1.020 |
| $I_{AB}(Al-H)$ | 0.862 | 0.926 |
| $I_{AB}(P-H)$ | 0.970 | 0.966 |
| $I_{AB}(Al-P)$ (DA bond) | 0.336 | 0.279 |
| $\gamma_{IJ}(H-Al-H)$ | 0.259 | 0.289 |
| $\gamma_{IJ}(H-P-H)$ | 0.284 | 0.316 |
| $\gamma_{IJ}(H-Al-P)$ | 0.050 | 0.046 |
| $\gamma_{IJ}(Al-P-H)$ | 0.053 | 0.047 |
| $\gamma_{IJ}$(Al−H, P−H; anti) | 0.001 | 0.001 |
| (d) Diborane[b] ($B_2H_6$) | | |
| $Q_A(B)$ | 4.910 | 4.870 |
| $Q_A(\mu H)$ | 1.018 | 1.028 |
| $Q_A(H)$ | 1.036 | 1.051 |
| $I_{AB}(B-H)$ | 0.988 | 0.993 |
| $I_{AB}(B-\mu H)$ | 0.483 | 0.476 |
| $I_{AB}(B-B)$ | 0.506 | 0.470 |
| $\gamma_{IJ}(H-B-H)$ | 0.282 | 0.301 |
| $\gamma_{IJ}(H-B-\mu H)$ | 0.137 | 0.148 |
| $\gamma_{IJ}(H-B-B)$ | 0.075 | 0.078 |
| $\gamma_{IJ}(\mu H-B-\mu H')$ | 0.039 | 0.045 |
| $\gamma_{IJ}(B-\mu H-B')$ | −0.148 | −0.146 |
| $\gamma_{IJ}(B-B-\mu H)$ | −0.205 | −0.211 |

*a* *b*

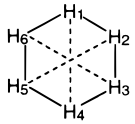



CACB shows some bonds correlations of diborane to be negative, namely, the bond correlations between the B−$\mu$H bonds [$\gamma_{IJ}$(B−$\mu$H−B′) = −0.146] and between the B−$\mu$H bond and the B−B bond [$\gamma_{IJ}$(B−B−$\mu$H) = −0.211]. This effect is typical for interrelated bonds. The Pauli principle causes an interdependence between such bonds so that the increase in the bond order of one bond leads to a decrease in the bond order of the other (correlated) bond.

**TABLE 4: CACB Analysis for the Transition States of Simple Reactions. Values Are Shown for Minimal and Extended Basis Sets**

| | STO-3G | 6-31G** |
|---|---|---|
| (a) $[H\cdots H_c\cdots H]^-$ | | |
| $Q_A(H_c)$ | 0.920 | 0.841 |
| $Q_A(H)$ | 1.540 | 1.597 |
| $I_{AB}(H_c-H)$ | 0.497 | 0.501 |
| $I_{AB}(H-H)$ | 0.211 | 0.115 |
| $\gamma_{IJ}(H-H_c-H)$ | −0.330 | −0.196 |
| $\gamma_{IJ}(H-H_c, H-H)$ | −0.198 | −0.277 |
| (b) $[H\cdots H_c\cdots H]$ | | |
| $Q_A(H_c)$ | 0.999[a] (0.999)[b] | 1.079[a] (1.082)[b] |
| $Q_A(H)$ | 1.001[a] (1.001)[b] | 0.961[a] (0.959)[b] |
| $I_{AB}(H_c-H)$ | 0.461[a] (0.500)[b] | 0.439[a] (0.441)[b] |
| $I_{AB}(H-H)$ | 0.130[a] (0.250)[b] | 0.051[a] (0.050)[b] |
| $\gamma_{IJ}(H-H_c-H)$ | −0.300[a] (−0.333)[b] | −0.173[a] (−0.169)[b] |
| $\gamma_{IJ}(H-H_c, H-H)$ | −0.144[a] (−0.218)[b] | −0.229[a] (−0.239)[b] |
| (c) $[H\cdots H_c\cdots H]^+$ (Linear) | | |
| $Q_A(H_c)$ | 1.101 | 1.301 |
| $Q_A(H)$ | 0.449 | 0.349 |
| $I_{AB}(H_c-H)$ | 0.495 | 0.455 |
| $I_{AB}(H-H)$ | 0.202 | 0.122 |
| $\gamma_{IJ}(H-H_c-H)$ | −0.329 | −0.294 |
| $\gamma_{IJ}(H-H_c, H-H)$ | −0.192 | −0.138 |
| (d) $H_3^+$ (Trigonal $D_{3h}$) | | |
| $Q_A(H)$ | 0.667 | 0.667 |
| $I_{AB}(H-H)$ | 0.444 | 0.444 |
| $\gamma_{IJ}(H-H-H)$ | −0.286 | −0.286 |
| (e) $[F\cdots CH_3\cdots F]^-$ | | |
| $Q_A(C)$ | 5.901 | 5.836 |
| $Q_A(H)$ | 1.053 | 0.886 |
| $Q_A(F)$ | 9.469 | 9.753 |
| $I_{AB}(C-H)$ | 0.920 | 0.974 |
| $I_{AB}(C-F)$ | 0.590 | 0.359 |
| $\gamma_{IJ}(F-C-F)$ | −0.056 | −0.045 |
| $\gamma_{IJ}(H-C-F)$ | 0.105 | 0.146 |
| $\gamma_{IJ}(H-C-H)$ | 0.213 | 0.289 |
| (f) $[H_6]$[c] $D_{6h}$ | | |
| $Q_A(H)$ | 1 | 1 |
| $I_{AB}(H_1-H_2)$ | 0.444 | 0.465 |
| $I_{AB}(H_1-H_4)$ | 0.111 | 0.069 |
| $\gamma_{IJ}(H_1-H_2, H_3-H_4)$ | 0.148 | 0.138 |
| $\gamma_{IJ}(H_1-H_2-H_3)$ | 0.000 | 0.018 |
| $\gamma_{IJ}(H_1-H_2, H_3-H_6)$ | 0.296 | 0.329 |
| $\gamma_{IJ}(H_1-H_2, H_4-H_5)$ | −0.037 | −0.048 |

[a] UHF results. [b] ROHF results. *c*




[c] $D_{6h}$ symmetric transition state. Only representative values are shown.

**C. Chemical Reactions and Transition States (TS).** Bonding schemes for the TS of some simple reactions are shown in Table 4.

*1. Three-Centered Exchange.* The reaction, $H_2 + D \rightarrow H + HD$, is the simplest one-bond exchange process. (Here D is used to discriminate the reactant and product.) At the TS the bond orders for the central to terminal bonds are 0.44 for $H_3$ (neutral), 0.50 for $H_3^-$, and 0.46 for linear $H_3^+$. The two end hydrogens are partially bonding (as in $O_3$ and $SO_2$), with bond orders of 0.05, 0.12, and 0.12 for $H_3$, $H_3^-$, and $H_3^+$ (linear), respectively. The $\gamma_{IJ}$ is negative for the two interchanging bonds in all three cases: −0.17 for $H_3$, −0.20 for $H_3^-$, and −0.29 for linear $H_3^+$. The interchanging bonds also have negative correlations against the terminal H−H bonds: −0.23 (−0.24) for

$H_3$, −0.28 for $H_3^-$, and −0.14 for linear $H_3^+$. Letting $H_3^+$ relax to the $D_{3h}$ minimum energy (equilateral triangle) leads to negligible changes: to $I_{AB}$(H−H) from 0.46 to 0.44 and $\gamma_{IJ}$(H−H−H) from −0.29 to −0.29.

Similar results are obtained for the TS for the $S_N2$ inversion process $[F\cdots CH_3\cdots F]^-$. However, $\gamma_{IJ}$(F−C−F) is small (−0.045), presumably because of the enhanced ionic nature of bonds being exchanged.

*2. Six-Centered Exchange.* The $2_s + 2_s + 2_s$ exchange

$$H_2 + D_2 + T_2 \rightarrow HD + DT + TH$$

represents a simple example of a symmetry-allowed multibond exchange process.[6] (Here D and T are used to discriminate atoms.) Assuming that all three bonds are interchanged simultaneously, the TS has a symmetric $D_{6h}$ geometry. At the RHF level, we calculate the TS to be at 91.7 kcal/mol above the initial state. Clearly a higher level of theory is required to account for the stabilization in the simultaneous exchange of three bonds. Despite the inadequacy of HF, we will analyze the bonding in analogy to other stable molecules and favorable TS. There are six interchanging H−H bonds (with $I_{AB} = 0.465$) and three very weak diagonal bonds (with $I_{AB} = 0.069$). Adjacent bonds do not couple [e.g., $\gamma_{IJ}(H_1-H_2-H_3) = 0.018$], while second neighbor bonds couple positively [e.g., $\gamma_{IJ}(H_1-H_2, H_3-H_4) = 0.138$]. On the other hand, diagonal bonds (e.g., $H_3-H_6$) couple strongly with parallel bonds [e.g., $\gamma_{IJ}(H_1-H_2, H_3-H_6) = 0.329$], but parallel bonds couple slightly [e.g., $\gamma_{IJ}(H_1-H_2, H_4-H_5) = -0.048$]. Thus, CACB analysis at HF level indicates that the electronic structure of $H_6$ resembles that of a stable molecule. It does not possess a strong bonds-interchanging nature. Such multibond exchange processes are studied further in Section III.E.

**D. Basis Set Dependence and Charge Operator.** Although CACB is a general formalism, the particular choice used in this paper is only on the Mulliken-type charge operator as in eq 6 (referred to as the Mulliken charge operator). The results in Tables 1−4 show that the basis set dependence of charge, bond order, and bonds correlation is not very significant. However it is known that Mulliken population analyses can give unrealistic values for highly extended basis sets.[15] Also the Mulliken charge operator is non-Hermite and be problematic in calculating the bonds orders and bonds correlations.

One approach to avoiding this problem is to use a localized orthogonal atomic orbital set. An appropriate choice will be the natural atomic orbitals (NAO) of Weinhold et al.,[4a] which we briefly analyze here. We write the NAO charge operator as

$$\hat{q}_A = \sum_c^{\text{core}} c_A^+ c_A^- + \sum_v^{\text{valence}} v_A^+ v_A^- + \sum_r^{\text{rydberg}} r_A^+ r_A^- \qquad (17)$$

with the associated first-order density matrix

$$\rho^{(1)}(\mathbf{r}) = \sum_A^{\text{Mol}} \left[ \sum_c^{\text{core}} c_A(\mathbf{r}) n_{c_A} c_A(\mathbf{r}) + \sum_v^{\text{valence}} v_A(\mathbf{r}) n_{v_A} v_A(\mathbf{r}) + \sum_r^{\text{rydberg}} r_A(\mathbf{r}) n_{r_A} r_A(\mathbf{r}) \right] \qquad (18)$$

where $n_i$ denotes the occupation number of $i$th NAO. (For RHF, $n_c \approx 2$, $0 \le n_v \le 2$, $n_r \approx 0$; for UHF, $n_c \approx 1$, $0 \le n_v \le 1$, $n_r \approx 0$.)

The important terms in the charge operator, eq 17, are those with nonzero occupation numbers in eq 18, i.e., the core and valence atomic orbital terms. These terms interact through the first- and higher-order density matrices and contribute expectation values. If such finite occupied atomic orbitals are well-localized at each atom and consistent (transferable) between different basis sets, we obtain physically meaningful consistent results with CACB formalism.

*1. Mulliken versus NAO Charge Operator.* Table 5 shows the charge, bond order, and bonds correlation properties for selected molecules in Tables 1−3 calculated using the NAO charge operator, eq 17, with highly extended basis sets, such as cc-pVTZ and AUG-cc-pVTZ. These results are compared with those using the Mulliken charge operator, eq 6, for $SO_2$ molecule. In this example, the charge and bond properties are still similar between different basis sets. However, the CACB properties are much less sensitive to basis for NAO, eq 17, than for Mulliken, eq 6. For example, with Mulliken the bond order $I_{AB}$(O−O) is large (0.51) in minimal basis and small (0.03−0.15) in extended basis, whereas with NAO it is 0.22 for nonminimal basis sets. Also, the Mulliken charge operator leads to a nonmonotonic change in the bond order as the basis is extended. It decreases from 0.12 to 0.03 upon adding diffuse s and p functions to the 6-31G** basis set but increases to 0.15 for the highly extended basis, AUG-cc-pVTZ. The bonds correlation coefficients also show particular deviation in the 6-31$^{++}$G** case.

The NAO charge operator gave quite consistent results for these quantities with double-$\zeta$ and highly extended basis sets. Thus for the extended basis (6-31G** through AUG-cc-pVTZ), the largest deviation is 1.9% in $\gamma_{IJ}$(O−S−O) of AUG-cc-pVTZ.

In addition, we also evaluated those properties with natural minimal basis (NMB) in AUG-cc-pVTZ.[4a] NMB includes the same number of atomic orbitals as the minimal basis set (e.g., STO-3G), but each atomic orbital is determined on the basis of the NAO procedure with HF/AUG-cc-pVTZ. We also considered NMB(d), in which an extra d function NAO is included in the NMB. Here we see that NMB leads to both the sulfur charge and sulfur−oxygen bond order that differ from the full-basis results. Including the first-shell d functions in NAO, which have non-negligible occupancies (0.006−0.040), leads to the charge and bond order closer to the full-basis results. This shows the importance of d function for $SO_2$ (as discussed in Section III.B.2). Including the next shell s function NAO to NMB(d), [i.e., NMB(sd)], $Q_A$(S) leads to 14.126 and $I_{AB}$(S−O) to 1.428 in much better agreement with full-basis results.

The NAO results for $BH_3-NH_3$ are also given in Table 5. Computed properties are consistent among the extended basis sets. The largest deviation is 4.8% in $Q_A(H_N)$ of AUG-cc-pVTZ. The DA bond order (0.56−0.59) increases slightly as the basis is extended from 6-31G** to AUG-cc-pVTZ. Here NMB gives results quite similar to the full basis.

For both $SO_2$ and $BH_3-NH_3$, the STO-3G results are quite different from the extended basis set results. Thus the STO-3G basis is inadequate with too limited freedom to properly define the atomic orbital space and HF density.

*2. Bonds Correlation and Covalency.* In Table 5, we also compare the NAO results for methane and neopentane. Here we are particularly interested in the bonds correlation effect for very covalent (C−C) and partially covalent (C−H) bonds. Using the NAO charge operator, we obtain $\gamma_{IJ}$(C−C−C) = 0.06 for neopentane, much smaller value than for any other adjacent bonds correlation coefficients. ($\gamma_{IJ}$(H−C−H) is 0.23−0.25 in both molecules.) This indicates that the bond orbital spaces are exclusive with each other for covalent bonds in neopentane

**TABLE 5: Basis Set Dependency of the CACB Analysis from Highly Extended Basis Sets.[a,b] The Results of Using the Mulliken Charge Operator [Eq 6] and the NAO Charge Operator [Eq 17] Are Compared**

| | STO-3G | 6-31G** | 6-31++G** | AUG-cc-pVTZ | NMB[c] | NMB(d)[d] | NMB(sd)[e] |
|---|---|---|---|---|---|---|---|
| | | | Mulliken Charge Operator | | | | |
| | | | Sulfur Dioxide ($SO_2$) | | | | |
| $Q_A$(S) | 15.064[a] | 14.925 | 14.925 | 14.803 | | | |
| $Q_A$(O) | 8.468 | 8.538 | 8.537 | 8.599 | | | |
| $I_{AB}$(S−O) | 1.461 | 1.741 | 1.587 | 1.790 | | | |
| $I_{AB}$(O−O) | 0.507 | 0.115 | 0.027 | 0.148 | | | |
| $\gamma_{IJ}$(O−S−O) | 0.057 | 0.280 | 0.346 | 0.275 | | | |
| $\gamma_{IJ}$(S−O, O−O) | −0.392 | −0.554 | −0.631 | −0.531 | | | |
| | | | NAO Charge Operator | | | | |
| | | | Sulfur Dioxide ($SO_2$) | | | | |
| $Q_A$(S) | 15.053 | 14.144 | 14.133 | 14.150 | 13.952 | 14.077 | 14.126 |
| $Q_A$(O) | 8.473 | 8.928 | 8.933 | 8.925 | 8.859 | 8.859 | 8.859 |
| $I_{AB}$(S−O) | 1.469 | 1.459 | 1.456 | 1.470 | 1.288 | 1.394 | 1.428 |
| $I_{AB}$(O−O) | 0.488 | 0.220 | 0.222 | 0.216 | 0.197 | 0.197 | 0.197 |
| $\gamma_{IJ}$(O−S−O) | 0.066 | 0.153 | 0.152 | 0.157 | 0.093 | 0.137 | 0.148 |
| $\gamma_{IJ}$(S−O, O−O) | −0.398 | −0.445 | −0.443 | −0.447 | −0.414 | −0.438 | −0.445 |
| | | | $BH_3$−$NH_3$ | | | | |
| $Q_A$(B) | 4.818 | 5.041 | 5.034 | 5.026 | 5.017 | | |
| $Q_A$($H_B$) | 1.183 | 1.093 | 1.097 | 1.104 | 1.100 | | |
| $Q_A$(N) | 7.364 | 7.983 | 7.953 | 7.826 | 7.806 | | |
| $Q_A$($H_N$) | 0.756 | 0.566 | 0.574 | 0.612 | 0.609 | | |
| $I_{AB}$(B−H) | 0.959 | 0.983 | 0.983 | 0.980 | 0.975 | | |
| $I_{AB}$(N−H) | 0.936 | 0.802 | 0.809 | 0.839 | 0.833 | | |
| $I_{AB}$(B−N) (DA bond) | 0.601 | 0.559 | 0.563 | 0.588 | 0.581 | | |
| $\gamma_{IJ}$(H−B−H) | 0.286 | 0.275 | 0.275 | 0.271 | 0.270 | | |
| $\gamma_{IJ}$(H−N−H) | 0.263 | 0.236 | 0.238 | 0.242 | 0.239 | | |
| $\gamma_{IJ}$(H−N−N) | 0.087 | 0.087 | 0.087 | 0.088 | 0.081 | | |
| $\gamma_{IJ}$(B−N−H) | 0.087 | 0.079 | 0.079 | 0.082 | 0.087 | | |
| $\gamma_{IJ}$(B−H, N−H; gauche) | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | | |
| $\gamma_{IJ}$(B−H, N−H; anti) | 0.001 | 0.002 | 0.002 | 0.002 | 0.002 | | |

| | 6-31G** | cc-pVTZ |
|---|---|---|
| | Methane ($CH_4$) | |
| $Q_A$(C) | 6.880 | 6.718 |
| $Q_A$(H) | 0.780 | 0.820 |
| $I_{AB}$(C−H) | 0.951 | 0.968 |
| $\gamma_{IJ}$(H−C−H) | 0.243 | 0.245 |
| | Tetramethylmethane (Neopentane) [$C(CH_3)_4$] | |
| $Q_A$(C) | 6.050 | 5.969 |
| $Q_A$($C_{Me}$) | 6.641 | 6.515 |
| $Q_A$(H) | 0.782 | 0.831 |
| $I_{AB}$(C−C) | 0.997 | 0.999 |
| $I_{AB}$(C−H) | 0.940 | 0.957 |
| $\gamma_{IJ}$(C−C−C) | 0.060 | 0.059 |
| $\gamma_{IJ}$(C−C−H) | 0.120 | 0.119 |
| $\gamma_{IJ}$(H−C−H) | 0.233 | 0.235 |
| $\gamma_{IJ}$(C−C, C−H; gauche) | 0.000 | 0.000 |
| $\gamma_{IJ}$(C−C, C−H; anti) | 0.002 | 0.003 |

[a] The 6-31G** optimized geometry was used for all calculations. For this reason, $SO_2$ results for STO-3G are different from those in Table 1. [b] Basis set notations are those in Gaussian-94 program (ref 14). STO-3G: 1s (H), 2s/1P (2nd row), 3s/2p (3rd row). 6-31G**: 2s/1p (H), 3s/2p/1d (2nd row), 4s/3p/1d (3rd row). 6-31++G**: 3s/1p (H), 4s/3p/1d (2nd row), 5s/4p/1d (3rd row). cc-pVTZ: 3s/2p/1d (H), 4s/3p/2d/1f (2nd row), 5s/4p/2d/1f (3rd row). AUG-cc-pVTZ: 4s/3p/2d (H), 5s/4p/3d/2f (2nd row), 6s/5p/3d/2f (3rd row). [c] Natural minimal basis set (NMB) in AUG-cc-pVTZ NAO. [d] NMB in AUG-cc-pVTZ supplemented one d NAO function. [e] NMB in AUG-cc-pVTZ supplemented one d and one s NAO functions.

interacting less in underlying wave function (as discussed in Section III.A.1)

**E. CACB Description of Multibond Exchange Reactions.** We applied CACB to selected reactions with the results in Figure 1. These structures correspond to the intermediates and TS for the simultaneous exchange of two bonds. Thus, there are four electrons involved in a total number of four bonds. The structures in Figure 1 were obtained assuming $C_s$ point symmetry. In (a), the hydrogen molecule inserts into the Ti−H bond of $Cl_2TiH^+$, and in (d), the ethylene molecule inserts into the Zr−C bond. (b) and (c) correspond to the model metathesis reaction in which ethylene cyclo-adds to the Ti═C bond. The CACB description of bond correlations is quite similar for each of these TS's. In (a), (b), and (d) negative correlation coefficients were obtained for the $\gamma_{IJ}$(1, 2) and $\gamma_{IJ}$(3, 4) interactions. An extra diagonal bonding interaction, bond 5, has a negative correlation to the other four bonds.

For the metathesis case, the intermediate (c) and TS (b) optimize to similar four-membered structures. Geometric parameters (in Å) for R(1), R(2), R(3), R(4), and R(5) are 2.286, 1.381, 2.471, 1.876, and 2.492 for the TS, and 1.959, 1.575, 1.575, 1.959, and 2.392 for the intermediate state, respectively. However, the electronic structure descriptions

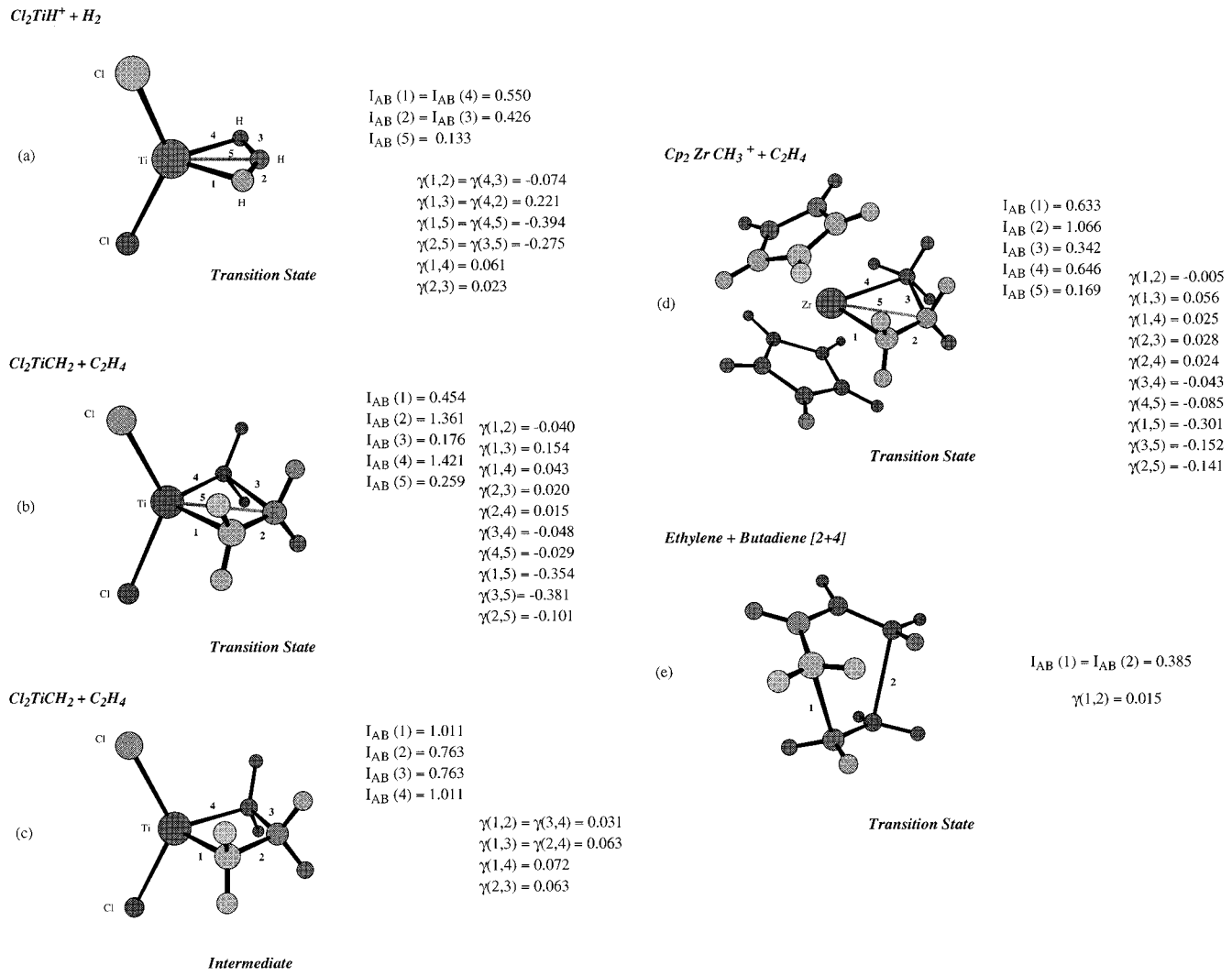



**Figure 1.** CACB on two bond exchange reactions. Structures are optimized at the RHF level with the Hay−Wadt ECP + DZ basis (LANL1DZ) for (a), (b), (c), and (d) and 6-31G** for (e). $C_s$ point symmetry was assumed for all cases. Structure (a) optimized to $C_{2v}$ symmetry.

by bond orders and bonds correlations are very different. Thus, in the intermediate state, the extra bonding interaction (bond 5 in TS) is negligibly small ($I_{AB} = 0.025$) and $\gamma_{IJ}$ values are all positive. At the TS, bond 5 has a bond order of 0.259 and the bonds correlations are similar to other TS cases (a) and (d).

Figure 1e shows the Diels Alder [$2_s + 4_s$] cycloaddition reaction. There has been some controversy about this reaction concerning whether the bond exchange takes place synchronously via a symmetric TS or favors the two-step process via a biradical intermediate state.[16] The structure in (e) corresponds to the synchronous pathway (the structure was optimized with symmetry constraints). The CACB shows a positive coupling, $\gamma_{IJ}(1, 2) = 0.015$, between the two forming bonds. This is similar to the nonadjacent bond correlations in ethane and ethylene molecules (Table 2). This indicates some synchronicity in the bond formation; i.e., the formation of one bond has the effect of slightly accelerating the formation of the other bond. The synchronicity of the overall process depends on how much the bond energies in the breaking bonds are compensated by those in forming bonds.

**F. Similarity in Chemical Reactivity.** To further study the similarity in the chemical reactivity, we considered insertion reactions depicted in Figure 1. These results are shown in Table 6.

The three reactions (19a, b, c)

$$Cl_2TiH^+ + D_2 \rightarrow Cl_2TiH^+/D_2 \rightarrow Cl_2TiH(D_2)^+ \quad (19a)$$

$$Cl_2TiCH_2 + C_2H_4 \rightarrow Cl_2TiCH_2/C_2H_4 \rightarrow Cl_2TiCH_2(C_2H_4) \rightarrow Cl_2Ti(CH_2)_3 \quad (19b)$$

$$Cp_2ZrCH_3^+ + C_2H_4 \rightarrow Cp_2ZrCH_3^+/C_2H_4 \rightarrow Cp_2ZrCH_3(C_2H_4)^+ \quad (19c)$$

correspond to Figure 1a−d. These belong to the generic class of reaction with formula

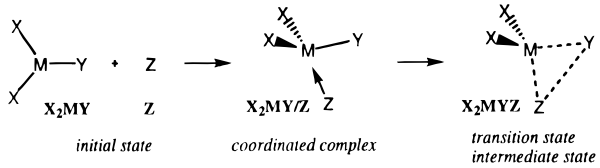
$$X_2MY + Z \text{ (initial)} \rightarrow X_2MY/Z \text{ (coordinated)} \rightarrow X_2MYZ \text{ (TS or intermediate)} \quad (19)$$

where M = Ti, Zr; X = Cl, Cp; Y = H, $CH_2$, $CH_3$; Z = $D_2$, $C_2H_4$.

In eq 19, the second species is the coordinated complex and the third species is the TS of the reaction. In eq 19b the reaction proceeds to the stable metallacycle butane intermediate (fourth species), which is compared to the TS step.

*1. Insertion of Molecular Hydrogen into a Ti−H Bond (Reaction 19a).* First we analyze the reactions separately. For

**TABLE 6: Similarity in Insertion Reactions of General Scheme**




where M = Ti, Zr; X = Cl, Cp, Y = H, $CH_2$, $CH_3$, Z = $D_2$, $C_2H_4$

(a) Initial State

| $X_2MY$ | $Cl_2TiH^+$ | $Cl_2Ti(CH_2)$ | $Cp_2Zr(CH_3)^+$ | st. dev. ($\sigma$)[a] |
|---|---|---|---|---|
| $Q_M$ | 2.690[b] (1.310)[c] | 3.111(0.889) | 2.975(1.025) | 0.215(0.215) |
| $Q_Y$ | 1.036 (−0.036) | 7.972(0.028) | 9.227(−0.227) | 4.412(0.133) |
| $Q_X$ | 7.137 (−0.137) | 7.459(−0.459) | 34.899(0.101) | 15.936(0.281) |
| $Q_X$ | 7.137 (−0.137) | 7.459(−0.459) | 34.899(0.101) | 15.936(0.281) |
| | | | | $\langle\sigma(Q_A)\rangle_{Atom}$[d] = 9.125(0.227) |
| | | | | $\langle\sigma(Q_A)\rangle_N$[e] = 0.888(0.480) |
| $I_{MY}$ | 0.928 | 1.157 | 0.982 | 0.120 |
| $I_{MX}$ | 1.328 | 0.949 | 1.665 | 0.358 |
| $I_{MX}$ | 1.328 | 0.949 | 1.665 | 0.358 |
| | | | | $\langle\sigma(I_{AB})\rangle_{Bond}$ = 0.239 |
| | | | | $\langle\sigma(I_{AB})\rangle_N$ = 0.555 |
| $\gamma_{XM,MY}$ | 0.212 | 0.219 | 0.209 | 0.005 |
| $\gamma_{XM,MY}$ | 0.212 | 0.219 | 0.209 | 0.005 |
| $\gamma_{XM,MX}$ | 0.155 | 0.141 | 0.213 | 0.038 |
| | | | | $\langle\sigma(\gamma_{IJ})\rangle_{Corr}$ = 0.016 |
| | | | | $\langle\sigma(\gamma_{IJ})\rangle_N$ = 0.098 |

(b) Coordinated Complex

| $X_2MY/Z$ | $Cl_2TiH^+/D_2$ | $Cl_2Ti(CH_2)/(C_2H_4)$ | $Cp_2Zr(CH_3)^+/(C_2H_4)$ | st. dev ($\sigma$) |
|---|---|---|---|---|
| $Q_M$ | 2.940(1.060) | 3.208(0.792) | 3.223(0.777) | 0.159(0.159) |
| $Q_Y$ | 0.965(0.035) | 8.015(−0.015) | 9.189(−0.189) | 4.448(0.118) |
| $Q_X$ | 7.125(−0.125) | 7.451(−0.451) | 34.912(0.088) | 15.950(0.271) |
| $Q_X$ | 7.125(−0.125) | 7.451(−0.451) | 34.912(0.088) | 15.950(0.271) |
| $Q_Z$ | 1.845(0.155) | 15.876(0.124) | 15.765(0.235) | 8.069(0.057) |
| | | | | $\langle\sigma(Q_A)\rangle_{Atom}$ = 8.915(0.175) |
| | | | | $\langle\sigma(Q_A)\rangle_N$ = 0.867(0.370) |
| $I_{MY}$ | 0.909 | 1.455 | 0.981 | 0.297 |
| $I_{MX}$ | 1.364 | 0.964 | 1.679 | 0.358 |
| $I_{MX}$ | 1.364 | 0.964 | 1.679 | 0.358 |
| $I_{MZ}$ | 0.273 | 0.420 | 0.410 | 0.082 |
| | | | | $\langle\sigma(I_{AB})\rangle_{Atom}$ = 0.274 |
| | | | | $\langle\sigma(I_{AB})\rangle_N$ = 0.636 |
| $\gamma_{XM,MY}$ | 0.192 | 0.211 | 0.214 | 0.012 |
| $\gamma_{XM,MY}$ | 0.192 | 0.211 | 0.214 | 0.012 |
| $\gamma_{XM,MX}$ | 0.177 | 0.128 | 0.222 | 0.047 |
| $\gamma_{YM,MZ}$ | 0.093 | 0.092 | 0.123 | 0.018 |
| $\gamma_{XM,MZ}$ | 0.098 | 0.115 | 0.138 | 0.020 |
| $\gamma_{XM,MZ}$ | 0.098 | 0.115 | 0.138 | 0.020 |
| | | | | $\langle\sigma(\gamma_{IJ})\rangle_{Corr}$ = 0.021 |
| | | | | $\langle\sigma(\gamma_{IJ})\rangle_N$ = 0.131 |

(c) TS

| $X_2MYZ$ | $Cl_2TiH(D_2)^+$ (TS) | $Cl_2Ti(CH_2)(C_2H_4)$ (TS) | $Cl_2Ti(CH_2)(C_2H_4)$ (Intermediate) | $Cp_2Zr(CH_3)(C_2H_4)^+$ (TS) | st. dev. ($\sigma$) |
|---|---|---|---|---|---|
| $Q_M$ | 2.857(1.143) | 3.202(0.798) | 3.026(0.974) | 3.464(0.536) | 0.259(0.259) |
| $Q_Y$ | 0.980(0.020) | 8.022(−0.022) | 8.150(−0.150) | 9.032(−0.032) | 3.738(0.073) |
| $Q_Z$ | 1.862(0.138) | 15.910(0.090) | 16.044(−0.044) | 15.751(0.249) | 7.021(0.121) |
| $Q_X$ | 7.150(−0.150) | 7.433(−0.433) | 7.390(−0.390) | 34.877(0.123) | 13.777(0.256) |
| $Q_X$ | 7.150(−0.150) | 7.433(−0.433) | 7.390(−0.390) | 34.877(0.123) | 13.777(0.256) |
| | | | | | $\langle\sigma(Q_A)\rangle_{Atom}$ = 7.714(0.193) |
| | | | | | $\langle\sigma(Q_A)\rangle_N$ = 0.750(0.408) |
| $I_{MY}$ | 0.550 | 1.437 | 1.032 | 0.735 | 0.387 |
| $I_{MX}$ | 1.321 | 0.986 | 1.021 | 1.762 | 0.359 |
| $I_{MX}$ | 1.321 | 0.986 | 1.021 | 1.762 | 0.359 |
| $I_{MZ}$ | 0.683 | 0.721 | 1.149 | 0.804 | 0.213 |
| $I_{YZ}$ | 0.400 | 0.144 | 0.678 | 0.342 | 0.220 |
| | | | | | $\langle\sigma(I_{AB})\rangle_{Bond}$ = 0.308 |
| | | | | | $\langle\sigma(I_{AB})\rangle_N$ = 0.715 |

**TABLE 6 (Continued)**

(c) TS (continued)

| $X_2MYZ$ | $Cl_2TiH(D_2)^+$ (TS) | $Cl_2Ti(CH_2)(C_2H_4)$ (TS) | $Cl_2Ti(CH_2)(C_2H_4)$ (Intermediate) | $Cp_2Zr(CH_3)(C_2H_4)^+$ (TS) | st. dev. ($\sigma$) |
|---|---|---|---|---|---|
| $\gamma_{XM,MY}$ | 0.119 | 0.194 | 0.135 | 0.179 | 0.036 |
| $\gamma_{XM,MY}$ | 0.119 | 0.194 | 0.135 | 0.179 | 0.036 |
| $\gamma_{XM,MX}$ | 0.141 | 0.123 | 0.124 | 0.209 | 0.041 |
| $\gamma_{YM,MZ}$ | −0.303 | 0.041 | −0.202 | −0.188 | 0.145 |
| $\gamma_{XM,MZ}$ | 0.132 | 0.135 | 0.142 | 0.165 | 0.015 |
| $\gamma_{XM,MZ}$ | 0.132 | 0.135 | 0.142 | 0.165 | 0.015 |
| $\gamma_{MY,YZ}$ | −0.350 | −0.307 | −0.323 | −0.329 | 0.018 |
| $\gamma_{MZ,ZY}$ | −0.003 | −0.389 | −0.253 | −0.138 | 0.164 |
| $\gamma_{XM,YZ}$ | 0.009 | 0.002 | 0.010 | −0.009 | 0.009 |
| $\gamma_{XM,YZ}$ | 0.009 | 0.002 | 0.010 | −0.009 | 0.009 |
| | | | | | $\langle\sigma(\gamma_{IJ})\rangle_{Corr} = 0.049$ |
| | | | | | $\langle\sigma(\gamma_{IJ})\rangle_{N} = 0.296$ |

[a] Standard deviation for each row. [b] Total charge for each atom or fragment. [c] Net atomic or fragment charge. [d] Step-averaged standard deviation for the property $P = Q_A$ ($Q_A^{net}$), $I_{AB}$, $I_{AB}$, $\gamma_{IJ}$. [e] Ratio of step-averaged versus total standard deviations for $P = Q_A$ ($Q_A^{net}$), $I_{AB}$, $\gamma_{IJ}$.

$Cl_2TiH^+$ the net charges in the initial state are $Q_{Ti} = 1.31$, $Q_{Cl} = -0.14$, and $Q_H = -0.04$, while the bond orders are $I_{TiH} = 0.93$ and $I_{TiCl} = 1.33$ and the bonds correlations are $\gamma_{ClTi,TiH} = 0.21$ and $\gamma_{ClTi,TiCl} = 0.16$. (This covalent character of such Ti−H bonds was originally pointed out by Steigerwald and Goddard.[2d]) Coordination with the $D_2$ leads to a net charge $Q_{D_2} = 0.16$ and a change in $Q_H$ by +0.07. As a result $Q_{Ti}$ decreases by 0.25. The net bond order is $I_{TiD_2} = 0.27$, which is accompanied by an increase of 0.04 in the $I_{TiCl}$ and a decrease of 0.02 in $I_{TiH}$. The $D_2$ has a similar bonds correlation of 0.1 with the Ti−Cl and Ti−H bonds. Going to the TS leads to a slight increase (0.08) in $Q_{Ti}$. At the TS $Q_{Cl}$ and $I_{TiCl}$ return toward the values of the metal complex as does $\gamma_{ClTi,TiCl}$. At the TS $Q_H = 0.02$ while $Q_{D_2} = 0.14$. Since the D next to the Ti must have $Q_D = 0.02$, this leaves $Q_D = 0.12$ for the far D. The bond order $I_{TiH}$ drops from 0.91 to 0.55 while $I_{Ti(D_2)}$ increases from 0.27 to 0.68. Given $I_{TiD} = 0.55$ for the near D bond leaves $I_{TiD} = 0.13$ for the far TiD bond order. The bond orders of $I_{TiH} = I_{TiD} = 0.55$ and $I_{HD} = I_{DD} = 0.43$ (see Figure 1a) agree with the covalent character of this reaction as deduced from GVB calculations by Steigerwald and Goddard.[2d]

*2. Insertion of Ethylene into a Zr−C Bond (Reaction 19c).* Next we consider the $Cp_2ZrCH_3^+ + C_2H_4$ reaction,[2j] a prototype of metallocene-catalyzed polymerization. For the initial state we find charges of $Q_{Cp} = 0.10$ while $Q_{Zr} = 1.03$ and $Q_{CH_3} = -0.23$. The bond orders are $I_{ZrCp} = 1.67$ and $I_{ZrCH_3} = 0.98$. This supports the idea that the metal methyl bond is covalent.[2j] It also suggests that the bonding between the Zr and Cp involves more than one pair of electrons. Coordinating one olefin to the Zr leads to a charge of $Q_{C_2H_4} = +0.24$ on the olefin while the charge on the Zr changes by $\delta Q_{Zr} = -0.25$. This corresponds to a Lewis base−Lewis acid bond with the bond order $I_{Zr,C_2H_4} = 0.41$ that compares well to the bond order $I_{BN} = 0.45$ in $BH_3NH_3$. However, the bonds correlation of $\gamma_{CH_3Zr,ZrC_2H_4} = 0.12$ is larger than the $\gamma_{BH,BN} = 0.08$ for $BH_3$-$NH_3$. This indicates a stronger coupling to the Zr−$CH_3$ by the bonding of $C_2H_4$ to Zr. Going from coordinated $C_2H_4$ to the TS for insertion, there is no change in the charge on the $C_2H_4$ ($\delta Q_{C_2H_4} = 0.01$) but the Zr becomes less positive ($\delta Q_{Zr} = -0.24$) while the $CH_3$ becomes more positive ($\delta Q_{CH_3} = 0.16$). Similarly the bond order $I_{ZrCH_3}$ decreases from 0.98 to 0.74 while $I_{Zr(C_2H_4)}$ increases from 0.41 to 0.80 and $I_{CH_3(C_2H_4)}$ increases from 0 to 0.34 [the $I_{ZrCp}$ stays constant ($\delta I_{ZrCp} = +0.08$)]. Of course the internal double bond in $C_2H_4$ decreases from 1.97 to 1.07 (see Figure 1d). The $\gamma_{CH_3Zr,ZrC_2H_4} = -0.19$, which is large and negative like $\gamma_{HTi,TiD_2} = -0.30$ in reaction 19a. Similarly $\gamma_{ZrCH_3,CH_3(C_2H_4)} = -0.33$ for reaction 19c, and $\gamma_{TiH,H(D_2)} = -0.35$ in 19a. These negative bonds correlations indicate strong competitive couplings between the bonds.

*3. Insersion of Ethylene into a Ti═C Bond (Reaction 19b).* For $Cl_2Ti(CH_2)$ the net charges are $Q_{Cl} = -0.46$, $Q_{Ti} = 0.89$, and $Q_{CH_2} = 0.03$. Thus, the Ti−$CH_2$ bond is covalent. However, the bond orders are $I_{TiCl} = 0.95$ and $I_{TiCH_2} = 1.16$ implying that the metal carbene bond is not nearly the double bond implied by the GVB orbitals.[2f] The $I_{TiCH_2}$ can be partitioned into $\sigma$ and $\pi$ contributions in canonical MO with $I_{TiCH_2}(\sigma) = 0.48$ and $I_{TiCH_2}(\pi) = 0.50$. Electrons in each MO are decomposed to $Q_{Ti}(\sigma) = 0.31$, $Q_{CH_2}(\sigma) = 1.55$, $Q_{Ti}(\pi) = 1.48$, and $Q_{CH_2}(\pi) = 0.34$. Thus, there are two bonds but each is partially polar. Covalent complexing with $C_2H_4$ leads to a net charge of $Q_{C_2H_4} = 0.12$ with $\delta Q_{Ti} = -0.10$ and $\delta Q_{CH_2} = -0.04$. Here the bond orders increase, $I_{TiC_2H_4} = 0.42$ (compare to the 0.41 for $I_{ZrC_2H_4}$ in reaction 19b) with $I_{TiCH_2} = 1.46$ (an increase of 0.30). The bonds correlations are $\gamma_{CH_2Ti,TiC_2H_4} = 0.09$ (equal to $\gamma_{HTi,TiH_2}$ for reaction 19a) and $\gamma_{ClTi,TiC_2H_4} = 0.12$ (between the values of 0.10 and 0.14 for reactions 19a and 19c). Going from the $Cl_2TiCH_2/C_2H_4$ complex to the TS leads to little change in the charges (ca. 0.03 in $C_2H_4$) but big changes in bond orders. Thus, $I_{TiC_2H_4}$ increases from 0.42 to 0.72 while $I_{CH_2,C_2H_4}$ increases from 0 to 0.14. Finally we form the metallacycle butane stable intermediate[2g] with net charges of $Q_{Ti} = 0.97$, $Q_{Cl} = -0.39$, $Q_{CH_2} = -0.15$, and $Q_{C_2H_4} = -0.04$. At this point the bond orders (see Figure 1c) are $I_{TiC} = 1.01$ (two cases) and $I_{CC} = 0.76$ [whereas the group bond orders (Table 6) are $I_{TiCH_2} = 1.03$ and $I_{(CH_2)(CH_2)} = 0.68$]. Here there are three strong negative bond correlations: $\gamma_{TiCH_3,CH_3C_2H_4} = -0.32$, $\gamma_{TiC_2H_4,C_2H_4CH_3} = -0.25$, and $\gamma_{CH_3Ti,TiC_2H_4} = -0.20$, which are also negative for the TS of 19a and 19b.

*4. Comparisons of Reactions.* Overall these analyses of the HF wave functions for the three reactions in eq 19 give the description of a 2s + 2s cycloaddition, as derived from early GVB calculations.[2d,f−h] However, the CACB analysis can be done for a wave function using the delocalized MOs from a HF or DFT wave function. In addition, CACB provides a qualitative measure of the character.

Previous electronic structure calculations on reaction 19 suggest that there are many similarities in these reactions. We want now to examine how well the CACB electronic structure descriptors would identify the similarities between these three reactions with charge ($Q_A$), net atomic charge ($Q_A^{net}$), bond order ($I_{AB}$), and bonds correlation coefficient ($\gamma_{IJ}$) shown in Table 6 for each step. The similarity of these reactions was evaluated by computing average standard deviations [$\langle\sigma(P, \text{Step})\rangle$] for each

descriptor

$$P = Q_A, Q_A^{\text{net}}, \quad I_{AB}, \quad \text{or} \quad \gamma_{IJ} \quad \text{and}$$

$$\text{Step} = \text{Initial, Coordinated, TS, and Intermediate}$$

We also computed the standard deviations of each descriptor over the elements and reaction steps [$\sigma(P)$]. These are $\sigma(Q_A) = 10.279$, $\sigma(Q_A^{\text{net}}) = 0.474$, $\sigma(I_{AB}) = 0.431$, and $\sigma(\gamma_{IJ}) = 0.164$, which indicate the distribution of parameter values.

Obviously, the charge ($Q_A$) comparison is valid only when similar atoms or fragments are compared. The net atomic charge ($Q_A^{\text{net}}$) seems to be a transferable descriptor, with standard deviations for steps ($\langle\sigma(Q_A^{\text{net}})\rangle_{\text{Atom}}$) of 0.227 (initial), 0.175 (coordinated), and 0.193 (TS and intermediate). These values are smaller than the total standard deviation $\sigma(Q_A^{\text{net}}) = 0.474$, showing some similarities among three reactions within the current data set. The ratios of $\langle\sigma(P)\rangle_{\text{Atom}}/\sigma(P)$ are also shown in Table 6, denoted by $\langle\sigma(P)\rangle_N$. These are computed to be 0.480 (initial), 0.370 (coordinated), and 0.408 (TS and intermediate).

The comparison of bond order descriptors is valid only when the bond orders are equivalent. They differ here because the M−Y bond could be a single bond (M−H or M−$CH_3$) or a double bond (M═$CH_2$). Also the Zr−Cp bond is of double-bond nature, while the Zr−Cl bonds are single bonds and the Ti−Cl bond is in between. Similarity of reactivity will be compared by the bond order index only when formal bond orders to be matched are consistent. Computed standard deviations for the $I_{AB}$ descriptor are less than the total standard deviation of $I_{AB}$, but the ratio is somewhat higher than in the net atomic charge descriptor.

The bonds correlation descriptor seems to be a good similarity measure. Thus, the ratio $\langle\sigma(\gamma_{IJ})\rangle_N$ shows the smallest values for all reaction steps. The decrease in sensitivity of descriptor as $Q_A > I_{AB} > \gamma_{IJ}$ reflects the hierarchy in the electronic description. The most sensitive descriptor, $Q_A$, discriminates very similar molecules and reactivities, while the least sensitive descriptor ($\gamma_{IJ}$) can be used to determine class invariance properties.

In Table 6 we note that by grouping atoms into fragments as in eq 19, the intermediate state of eq 19b resembles other TS with negative $\gamma_{IJ}$. This contrasts with the results in Figure 1 where the electronic structure descriptions are very different between the intermediate state and the TS species.

## IV. Conclusion

We present a new approach for analyzing the chemical bond character in molecular systems. The CACB method describes the interaction between two bonds through the fourth-order density matrix. This correlation is positive for interactions between stable bonds and shows negative values for multicentered bonds in chemical reactions and nonclassical molecules.

In order to facilitate the use of these concepts to analyze wave functions, we have made available on the Internet the free use of our current analysis programs.[17] We ask that users send us summaries of their results and any improvements they make in the program.

**Acknowledgment.** This research was supported by Asahi Chemical Industry and by National Science Foundation (CHE 95-22179). The facilities of the MSC are also supported by grants from Chevron Petroleum Technology, Aramco, Exxon, Owens-Corning, Chevron Chemical Co., Asahi Glass, Chevron Research and Technology Co., Hercules, Avery Dennison, BP Chemical, and the Beckman Institute.

## Appendix. Derivation of the Contracted Density Operators

**A.1. Definitions.** This appendix presents the contractions of density operators required in the calculation of bond−bond correlation coefficients.[9] We consider here only single Slater determinant wave functions (i.e., RHF and UHF).

The atomic charge operator is defined by,

$$\hat{q}_A = \sum_a^A a^+ \bar{a}^- \tag{A1}$$

where $a$ and $\bar{a}$ are covariant and contravariant basis, respectively, and satisfy the following commutation rules.

$$\left.\begin{aligned} a^+\bar{b}^+ + \bar{b}^+a^+ &= 0 \\ a^-\bar{b}^- + \bar{b}^-a^- &= 0 \\ a^+\bar{b}^- + \bar{b}^-a^+ &= \delta_{a,b} \end{aligned}\right\} \tag{A2}$$

Required density components are computed by applying commutation rule and summing over occupied orbitals in the single determinant wave function[9]

$$\langle\hat{q}_A\rangle = \sum_a^A \langle a^+\bar{a}^-\rangle = \sum_{\sigma_a}^{\alpha,\beta}\sum_a^A P_a{}^a \equiv P_A$$

$$\text{where} \quad P_a{}^b = \sum_i^{\text{occ}} C_{i,a}C_i^b \tag{A3}$$

We will use the abbreviations in eq A4

$$P_A = \sum_{\sigma_a}^{\alpha,\beta}\sum_a^A P_a{}^a$$

$$P_{AB} = \sum_{\sigma_a,\sigma_b}^{\alpha,\beta}\sum_{a,b}^{A,B} P_a{}^b P_b{}^a$$

$$P_{ABC} = \sum_{\sigma_a,\sigma_b,\sigma_c}^{\alpha,\beta}\sum_{a,b,c}^{A,B,C} P_a{}^b P_b{}^c P_c{}^a \tag{A4}$$

$$P_{ABCD} = \sum_{\sigma_a,\sigma_b,\sigma_c,\sigma_d}^{\alpha,\beta}\sum_{a,b,c,d}^{A,B,C,D} P_a{}^b P_b{}^c P_c{}^d P_d{}^a$$

For the closed-shell case, the $P$ terms can be simplified to

$$P_A = 2\sum_a^A P_a{}^a$$

$$P_{AB} = 2\sum_{a,b}^{A,B} P_a{}^b P_b{}^a$$

$$P_{ABC} = 2\sum_{a,b,c}^{A,B,C} P_a{}^b P_b{}^c P_c{}^a \tag{A5}$$

$$P_{ABCD} = 2\sum_{a,b,c,d}^{A,B,C,D} P_a{}^b P_b{}^c P_c{}^d P_d{}^a$$

Higher-order components are obtained as follows. We

express the general form of

$$\langle \hat{q}_A \hat{q}_B \hat{q}_C \ldots \rangle \tag{A6}$$

in terms of density matrix components. First eq A6 is transformed by use of commutation rules into the terms of form

$$\langle \hat{q}_A \hat{q}_B \hat{q}_C \ldots \rangle = \sum_{a,b,c,\ldots}^{A,B,C,\ldots} \langle a^+ \bar{a}^- b^+ \bar{b}^- c^+ \bar{c}^- \ldots \rangle$$

$$= \sum_{a,b,c,\ldots}^{A,B,C,\ldots} \langle a^+ b^+ c^+ \ldots \bar{c}^- \bar{b}^- \bar{a}^- \rangle + \delta_{AB} \sum_{a,c,\ldots}^{A,C,\ldots} \langle a^+ c^+ \ldots \bar{c}^- \bar{a}^- \rangle + \ldots \tag{A7}$$

where *A*, *B*, *C*, ... denote atoms. Expanding atomic orbitals by canonical molecular orbitals

$$|a\rangle = \sum_{i}^{\text{occ+vir}} |i\rangle C_a^i = \sum_{i}^{\text{occ+vir}} |i\rangle C_{i,a} \tag{A8}$$

($C_a^i = C_{i,a}$ as $|i\rangle$ is orthonormal), we obtain for each term of eq A7 that

$$\sum_{a,b,\ldots}^{A,B,\ldots} \langle a^+ b^+ \ldots \bar{b}^- \bar{a}^- \rangle = \sum_{a,b,\ldots}^{A,B,\ldots} \sum_{i,j,\ldots}^{\text{occ+vir}} C_{i,a} C_{j,b} \ldots C_k^b C_l^a \langle i^+ j^+ \ldots m^+ n^- \ldots k^- l^- \rangle$$

$$= \sum_{a,b,\ldots}^{A,B,\ldots} \sum_{i,j,\ldots}^{\text{occ+vir}} C_{i,a} C_{j,b} \ldots C_k^b C_l^a \langle \text{HF}' | \text{HF}'' \rangle \tag{A9}$$

where $\langle \text{HF}' | = \langle \text{HF} | i^+ j^+ \ldots m^+$ and $|\text{HF}'' \rangle = n^- \ldots k^- l^- |\text{HF}\rangle$

In eq A9, $\langle \text{HF}' | \text{HF}'' \rangle \neq 0$ requires that the set of creation operators $\{i^+, j^+, \ldots, m^+\}$ must correspond to the set of annihilation operators $\{l^-, k^-, \ldots, n^-\}$. Thus, the surviving terms in eq A9 corresponds to all possible permutations of ($i^-, j^-, \ldots, m^-$)

$$\langle \text{HF} | a^+ b^+ \ldots r^+ \bar{s}^- \ldots \bar{c}^- \bar{d}^- | \text{HF} \rangle$$

$$= \sum_{i,j,\ldots}^{\text{occ+vir}} C_{i,a} C_{j,b} \ldots C_k^c C_l^d \langle \text{HF} | i^+ j^+ \ldots m^+ n^- \ldots k^- l^- | \text{HF} \rangle$$

$$= \sum_{i,j,\ldots}^{\text{occ+vir}} C_{i,a} C_{j,b} \ldots C_k^c C_l^d \delta_{il} \delta_{jk} \ldots \langle \text{HF} | i^+ j^+ \ldots m^+ \times (\sum_P \epsilon_P P(m^- \ldots j^- i^-)) | \text{HF} \rangle \tag{A10}$$

$$= \sum_{i,j,\ldots}^{\text{occ+vir}} C_{i,a} C_{j,b} \ldots C_k^c C_l^d \delta_{il} \delta_{jk} \ldots (\sum_P \epsilon_P n_i n_j \ldots)$$

$$= \sum_P \epsilon_P \sum_{i,j,\ldots}^{\text{occ}} C_{i,a} C_{j,b} \ldots C_j^c C_i^d = \sum_P \epsilon_P P_a{}^d P_b{}^c \ldots$$

where $P$ and $\epsilon_P$ denote a permutation operator and the parity of the permutation, respectively. The $n_i$ is the occupation number, either 0 or 1, of the $i$th state. The parity of necessary permutations are given in Table 7. This sort of derivation is straightforward but tedious to do by hand for higher-order terms. We used symbolic programming techniques to generate the computer codes in Fortran or C.[18]

**A2. First-Order Term.**

$$\langle \hat{q}_A \rangle = \sum_{a}^{A} \langle a^+ \bar{a}^- \rangle = \sum_{\sigma_a}^{\alpha,\beta} \sum_{a}^{A} P_a{}^a \equiv P_A \tag{A11}$$

**A3. Second-Order Terms.** When *A* and *B* are different ($A \neq B$) atoms, we obtain

$$\langle \hat{q}_A \hat{q}_B \rangle = \sum_{a,b}^{A,B} \langle a^+ \bar{a}^- b^+ \bar{b}^- \rangle = \sum_{\sigma_a,\sigma_b}^{\alpha,\beta} \sum_{a,b}^{A,B} (P_a{}^a P_b{}^b - P_a{}^b P_b{}^a) \equiv P_A P_B - P_{AB} \tag{A12}$$

When *A* and *B* are the same ($A = B$) atoms, we obtain

$$\langle \hat{q}_A \hat{q}_B \rangle = \langle \hat{q}_A \rangle + \text{eq A12} \tag{A13}$$

Thus, together we have

$$\langle \hat{q}_A \hat{q}_B \rangle = \delta_{AB} \langle \hat{q}_A \rangle + \text{eq A12} \tag{A14}$$

**A4. Third-Order Terms.** When *A*, *B*, and *C* are all different ($\neq \{A, B, C\}$) atoms, we obtain

$$\langle \hat{q}_A \hat{q}_B \hat{q}_C \rangle = \sum_{a,b,c}^{A,B,C} \langle a^+ b^+ c^+ \bar{c}^- \bar{b}^- \bar{a}^- \rangle = P_A P_B P_C - P_A P_{BC} - P_B P_{AC} - P_C P_{AB} + P_{ABC} + P_{ACB} \tag{A15}$$

When *A* and *B* are the same but different than *C* ($A = B \neq C$) atoms, we obtain

$$A = B \neq C$$

$$\langle \hat{q}_A \hat{q}_B \hat{q}_C \rangle = \langle \hat{q}_A \hat{q}_C \rangle + \text{eq A15} \tag{A16}$$

Similarly,

$$A = C \neq B$$

$$\langle \hat{q}_A \hat{q}_B \hat{q}_C \rangle = \langle \hat{q}_B \hat{q}_C \rangle + \text{eq A15} \tag{A17}$$

$$B = C \neq A$$

$$\langle \hat{q}_A \hat{q}_B \hat{q}_C \rangle = \langle \hat{q}_A \hat{q}_B \rangle + \text{eq A15} \tag{A18}$$

$$A = B = C$$

$$\langle \hat{q}_A \hat{q}_B \hat{q}_C \rangle = \langle \hat{q}_A \rangle + \langle \hat{q}_A \hat{q}_B \rangle + \langle \hat{q}_B \hat{q}_C \rangle + \langle \hat{q}_C \hat{q}_A \rangle + \text{eq A15} \tag{A19}$$

**TABLE 7: Parity of Permutations Up to Fourth Order**

| permutation | $P$ | $\epsilon_P$ |
|---|---|---|
| | First Order | |
| $(i)$ | () | 1 |
| | Second Order | |
| $(i, j)$ | () | 1 |
| $(j, i)$ | $((i, j))$ | −1 |
| | Third Order | |
| $(i, j, k)$ | () | 1 |
| $(i, k, j)$ | $((j, k))$ | −1 |
| $(j, i, k)$ | $((i, j))$ | −1 |
| $(j, k, i)$ | $((i, j), (j, k))$ | 1 |
| $(k, i, j)$ | $((i, k), (j, k))$ | 1 |
| $(k, j, i)$ | $((i, k))$ | −1 |
| | Fourth Order | |
| $(i, j, k, l)$ | () | 1 |
| $(i, j, l, k)$ | $((k, l))$ | −1 |
| $(i, k, j, l)$ | $((j, k))$ | −1 |
| $(i, k, l, j)$ | $((j, k), (k, l))$ | 1 |
| $(i, l, j, k)$ | $((j, l), (k, l))$ | 1 |
| $(i, l, k, j)$ | $((j, l))$ | −1 |
| $(j, i, k, l)$ | $((i, j))$ | −1 |
| $(j, i, l, k)$ | $((i, j), (k, l))$ | 1 |
| $(j, k, i, l)$ | $((i, j), (j, k))$ | 1 |
| $(j, k, l, i)$ | $((i, j), (j, k), (k, l))$ | −1 |
| $(j, l, i, k)$ | $((i, j), (j, l), (k, l))$ | −1 |
| $(j, l, k, i)$ | $((i, j), (j, l))$ | 1 |
| $(k, i, j, l)$ | $((i, k), (j, k))$ | 1 |
| $(k, i, l, j)$ | $((i, k), (j, k), (k, l))$ | −1 |
| $(k, j, i, l)$ | $((i, k))$ | −1 |
| $(k, j, l, i)$ | $((i, k), (k, l))$ | 1 |
| $(k, l, i, j)$ | $((i, k), (j, l))$ | 1 |
| $(k, l, j, i)$ | $((i, k), (j, l), (k, l))$ | −1 |
| $(l, i, j, k)$ | $((i, l), (j, l), (k, l))$ | −1 |
| $(l, i, k, j)$ | $((i, l), (j, l))$ | 1 |
| $(l, j, i, k)$ | $((i, l), (k, l))$ | 1 |
| $(l, j, k, i)$ | $((i, l))$ | −1 |
| $(l, k, i, j)$ | $((i, l), (j, k), (k, l)$ | −1 |
| $(l, k, j, i)$ | $((i, l), (j, k))$ | 1 |

Thus, together we have

$$\langle \hat{q}_A \hat{q}_B \hat{q}_C \rangle = \delta_{ABC}\langle \hat{q}_A \rangle + \delta_{BC}\langle \hat{q}_A \hat{q}_B \rangle + \delta_{AC}\langle \hat{q}_B \hat{q}_C \rangle + \delta_{AB}\langle \hat{q}_A \hat{q}_C \rangle + \text{eq A15} \quad \text{(A20)}$$

**A5. Fourth-Order Terms.** When $A$, $B$, $C$, and $D$ are all different ($\neq\{A,B,C,D\}$) atoms, we obtain

$$\langle \hat{q}_A \hat{q}_B \hat{q}_C \hat{q}_D \rangle = \sum_{a,b,c,d}^{A,B,C,D} \langle a^+ b^+ c^+ d^+ \bar{d}^- \bar{c}^- \bar{b}^- \bar{a}^- \rangle$$

$$= P_A P_B P_C P_D - P_A P_B P_{CD} - P_A P_D P_{BC} - P_A P_C P_{BD} - P_C P_D P_{AB} - P_B P_D P_{AC} - P_B P_C P_{AD} + P_A P_{BCD} + P_A P_{BDC} + P_B P_{ACD} + P_B P_{ADC} + P_C P_{ABD} + P_C P_{ADB} + P_D P_{ABC} + P_D P_{ACB} + P_{AB} P_{CD} + P_{AC} P_{BD} + P_{AD} P_{BC} - P_{ABCD} - P_{ABDC} - P_{ACDB} - P_{ACBD} - P_{ADCB} - P_{ADBC} \quad \text{(A21)}$$

For fourth-order terms, we may further constrain $A \neq B$, $C \neq D$, because bond orders are always defined between different centers (remember $I_{AB}$, $A \neq B$)

$$A = C, \neq\{A,B,D\}$$

$$\langle \hat{q}_A \hat{q}_B \hat{q}_C \hat{q}_D \rangle = \langle \hat{q}_A \hat{q}_B \hat{q}_D \rangle + \text{eq A21} \quad \text{(A22)}$$

$$A = D, \neq\{A,B,C\}$$

$$\langle \hat{q}_A \hat{q}_B \hat{q}_C \hat{q}_D \rangle = \langle \hat{q}_A \hat{q}_B \hat{q}_C \rangle + \text{eq A21} \quad \text{(A23)}$$

$$B = C, \neq\{A,B,D\}$$

$$\langle \hat{q}_A \hat{q}_B \hat{q}_C \hat{q}_D \rangle = \langle \hat{q}_A \hat{q}_B \hat{q}_D \rangle + \text{eq A21} \quad \text{(A24)}$$

$$B = D, \neq\{A,B,C\}$$

$$\langle \hat{q}_A \hat{q}_B \hat{q}_C \hat{q}_D \rangle = \langle \hat{q}_A \hat{q}_B \hat{q}_C \rangle + \text{eq A21} \quad \text{(A25)}$$

$$A = C, B = D$$

$$\langle \hat{q}_A \hat{q}_B \hat{q}_C \hat{q}_D \rangle = \langle \hat{q}_A \hat{q}_B \hat{q}_D \rangle + \langle \hat{q}_A \hat{q}_B \hat{q}_C \rangle + \langle \hat{q}_A \hat{q}_B \rangle + \text{eq A21} \quad \text{(A26)}$$

$$A = D, B = C$$

$$\langle \hat{q}_A \hat{q}_B \hat{q}_C \hat{q}_D \rangle = \langle \hat{q}_A \hat{q}_B \hat{q}_C \rangle + \langle \hat{q}_A \hat{q}_B \hat{q}_D \rangle + \langle \hat{q}_A \hat{q}_B \rangle + \text{eq A21} \quad \text{(A27)}$$

Thus, together we obtain (including all cases)

$$\langle \hat{q}_A \hat{q}_B \hat{q}_C \hat{q}_D \rangle = \delta_{ABCD}\langle \hat{q}_A \rangle + \delta_{ABC}\langle \hat{q}_A \hat{q}_D \rangle + \delta_{ABD}\langle \hat{q}_A \hat{q}_C \rangle + \delta_{ACD}\langle \hat{q}_A \hat{q}_B \rangle + \delta_{BCD}\langle \hat{q}_A \hat{q}_B \rangle + \delta_{AC}\delta_{BD}\langle \hat{q}_A \hat{q}_B \rangle + \delta_{AD}\delta_{BC}\langle \hat{q}_A \hat{q}_B \rangle + \delta_{AB}\delta_{CD}\langle \hat{q}_A \hat{q}_C \rangle + \delta_{AB}\langle \hat{q}_A \hat{q}_C \hat{q}_D \rangle + \delta_{AC}\langle \hat{q}_A \hat{q}_B \hat{q}_D \rangle + \delta_{AD}\langle \hat{q}_A \hat{q}_B \hat{q}_C \rangle + \delta_{BC}\langle \hat{q}_A \hat{q}_B \hat{q}_D \rangle + \delta_{BD}\langle \hat{q}_A \hat{q}_B \hat{q}_C \rangle + \delta_{CD}\langle \hat{q}_A \hat{q}_B \hat{q}_C \rangle + \text{eq A21} \quad \text{(A28)}$$

## References and Notes


(1) (a) Goddard, W. A., III; Dunning, T. H., Jr.; Hunt, W. J.; Hay, P. J. *Acc. Chem. Res.* **1973**, *6*, 368. (b) Bobrowicz, F. W.; Goddard, W. A., III. *Mod. Theor. Chem.* **1977**, *3*, (*Methods Electron. Struct. Theory*), 79.

(2) (a) Goddard, W. A., III. *J. Am. Chem. Soc.* **1970**, *92*, 7520. (b) Goddard, W. A., III. *J. Am. Chem. Soc.* **1972**, *94*, 793. (c) Wilson, C. W., Jr.; Goddard, W. A., III. *J. Chem. Phys.* **1969**, *51*, 716. (d) Steigerwald, M. L.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1984**, *106*, 308. (e) Goddard, W. A., III; Harding, L. B. *Annu. Rev. Phys. Chem.* **1978**, *29*, 363. (f) Rappé, A. K.; Goddard, W. A., III. *Potential Energy Surfaces and Dynamics Calculations*; Truhlar, D. G., Ed.; Plenum Press: New York, 1981; pp 661−684. (g) Rappé, A. K.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1982**, *104*, 297. (h) Rappé, A. K.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1982**, *104*, 448. (i) Steigerwald, M. L.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1985**, *107*, 5027. (j) Bierwagen, E. P.; Bercaw, J. E.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1994**, *116*, 1481.

(3) Bachrach, S. M. *Rev. Comput. Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; VCH: New York, 1993; Vol. 5, p 171.

(4) (a) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735. (b) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899 and references therein.

(5) Bader, R. F. W. *Atoms in Molecules*; Clarendon Press: Oxford, 1994 and references therein.

(6) (a) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Academic Press: New York, 1970. (b) Goddard, W. A., III. *J. Am. Chem. Soc.* **1970**, *92*, 7520.

(7) (a) McAdon, M. H.; Goddard, W. A., III. *Phys. Rev. Lett.* **1985**, *55*, 2563. (b) McAdon, M. H.; Goddard, W. A., III. *J. Phys. Chem.* **1986**, *91*, 2607.

(8) For the general reference to the second quantization and operator algebra, refer to, for instance: (a) Surjan, P. R. *Second Quantized Approach to Quantum Chemistry*; Springer-Verlag: Berlin Heidelberg, 1989. (b) Jorgensen, P.; Simons, J. *Second Quantization-Based Methods in Quantum Chemistry*; Academic Press: New York, 1981.

(9) (a) Giambiagi, M.; de Giambiagi, M. S.; Grempel, D. R.; Heymann, C. D. *J. Chim. Phys.* **1975**, *72*, 15. (b) Mayer, I. *Chem. Phys. Lett.* **1983**, *97*, 270.

(10) Wiberg, K. A. *Tetrahedron* **1968**, *24*, 1083.

(11) Giambiagi, M. S.; Giambiagi, M.; Jorge, F. E. *Theor. Chim. Acta* **1985**, *68*, 337.

(12) Mayer, I. *Int. J. Quantum Chem.* **1986**, *29*, 73.

(13) Mundim, K. C.; Giambiagi, M.; de Giambiagi, M. S. *J. Phys. Chem.* **1994**, *98*, 6118.

(14) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Peterson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewsku, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian 94, Revision D.1; Gaussian, Inc.: Pittsburgh, PA, 1995.

(15) Weinhold, F.; Carpenter, J. E. *Theochem.* **1988**, *165*, 189.

(16) (a) Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 209. (b) Li, Yi; Houk, K. N. *J. Am. Chem. Soc.* **1993**, *115*, 7478.

(17) The URI is http://www.wag.caltech.edu.

(18) We developed Prolog and Mathematica (c) program for the derivation (unpublished). See, for example: Gotoh, M.; Mori, K.; Ito, R. *Int. J. Quantum Chem.* **1995**, *56*, 163.