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Covalent Bond Orders in the Topological Theory of Atoms in Molecules

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Abstract: A new definition of covalent bond orders, based on partitioning of the number of electrons within the topological theory of atoms in molecules, is proposed. Unlike the previously proposed definitions, it requires neither references to the basis sets used in the expansion of the molecular wave function nor a parameterization involving a set of standard bonds. For some conjugated molecules, the present approach affords bond orders pertinent to all relevant Lewis (resonance) structures. The new definition, which is tested on a set of several organic molecules, provides bond orders that can serve as molecular indices complementary to Bader atomic charges.

Introduction

The unprecedented progress in computational methods and the availability of high-performance hardware paved the way for a recent spurt of reliable ab initio quantum-mechanical calculations on molecules that were previously not amenable to theoretical treatment. Properties of systems involving as many as 120 atoms and 1800 basis functions can now be routinely calculated.[1] On the other hand, development of theoretical tools for interpretation of the computed wave functions has lagged considerably behind the advances in quantum-chemical methodology, despite the fact that our understanding of the electronic structure of molecules has been repeatedly demonstrated to benefit substantially from the use of such quantities as atomic charges and bond orders.

The case of bond orders serves as a typical example of how the quantities that had been developed in conjunction with the early semiempirical methods have never been brought up to the sophistication required for interpretation of ab initio wave functions. The seminal papers of Coulson[2] and Mulliken[3] on the π-electron bond orders (also known in the early literature as the "mobile" bond orders) proceeded a plethora of definitions of bond orders (or indices)[4–20] that share the common drawback of relying on a partitioning of the Hilbert space spanned by the basis functions and therefore explicitly assigning the individual basis functions to atoms. Although the sensitivity of so-defined bond orders to the choice of the basis functions varies from one approach to another, it is obvious that any quantity based on such an explicit assignment (which is completely arbitrary) cannot be expected to describe the physical reality in an unbiased way. To the best of our knowledge, there have been only two major approaches to the problem of bond orders that avoid any reference to the basis functions. In particular, Politzer has proposed a definition of bond orders[21] based on the bond lengths and the bond stretching force constants. Although such a definition is for obvious reasons clearly preferable to any of the approaches based on a Hilbert space partitioning, it is itself not completely free of arbitrariness. The ambiguity comes from the fact that the force constants are not invariant to the choice of internal coordinates. Thus, different choices of the internal coordinates lead to different values of the bond order.

The topological theory of atoms in molecules[22] offers a concise description of the electronic structure of molecules in terms of the topological properties of the electron density. The critical points at which the gradient of the electron density vanishes define bonds, rings, and cages. The magnitude of the electron density at the bond critical point (ρ_{crit}) serves as a parameter that can be used in evaluating the corresponding bond order.[23] The drawbacks of such an approach stem from the fact that one can calculate the bond order only for pairs of atoms connected by bond paths and that the correlation between ρ_{crit} and the bond order is purely empirical and therefore involves numerical parameterization. The numerical constants in the formula relating the bond order to ρ_{crit} depend on the types of atoms involved in the bond under consideration and are fitted to reproduce some "standard" bond orders (such as one for a single bond in ethane, etc.). One faces the problem of selecting a "proper" set of bonds to be used in parameterization if bond orders for a variety of different types of atomic pairs are to be evaluated.

Our interest in the development of theoretical tools for interpretation of molecular wave functions resulted in introduction of several new indices and orbital transformations that are aimed at description of the electronic structure of molecules in intuitive, yet well-defined, terms. Particular attention has been paid to assure that the proposed definitions do not involve any explicit reference to the basis sets and that they are universally applicable across the entire spectrum of quantum-chemical methods ranging from semiempirical techniques to the electron-correlated ab initio calculations. On the basis of these presumptions, a new definition of atomic charges has been proposed[24] and applied to several molecules and ions,[25–28] a rigorous definition of molecular similarity

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has been put forward,[29] and a new orbital localization technique that allows for localization of both Hartree–Fock and natural orbitals has been developed[30] together with two forms of orbital transformations that aid in the interpretation of electronic excited states.[31,32]

In this paper, we propose a new definition of the covalent bond order, which is developed along the above lines. It does not involve either reference to the basis functions or parameterization.

Theory

The topological theory of atoms in molecules[22] defines atomic basins as the regions in Cartesian space that are bordered by zero-flux surfaces in the gradient of the electron density. Such partitioning allows one to treat the resulting atoms (nuclei together with atomic basins) as quantum mechanically separate systems. The properties of atoms in molecules are calculated by integration over the atomic basins.[33] In particular, for an atom (A), the corresponding atomic basin (Ω_A), and two spin orbitals (ϕ_i and ϕ_j), the corresponding element of the atomic overlap matrix (AOM) is given by

$$\langle i|j\rangle = \int_{\Omega_A} \phi_i^*(\vec{r})\phi_j(\vec{r})\,\mathrm{d}\vec{r} \tag{1}$$

When the spin orbitals are related to the Hartree–Fock occupied spin orbitals through a unitary transformation, the elements of AOM satisfy two important conditions:

$$\sum_A \langle i|j\rangle_A = \langle i|j\rangle = \delta_{ij} \tag{2}$$

and

$$N_A = \sum_i \langle i|i\rangle_A \tag{3}$$

where N_A is the number of electrons of the atom A and

$$N = \sum_A N_A \tag{4}$$

is the total number of electrons present in the system under consideration. The difference between N_A and the atomic number of A is known as the Bader atomic charge.

Taking into account eqs 2–4, one may write

$$N = \sum_i \sum_A \sum_B \langle i|i\rangle_A \langle i|i\rangle_B \tag{5}$$

According to eq 5, the total number of electrons can be partitioned into atomic and diatomic contributions:

$$N = N_a + N_d \tag{6}$$

where

$$N_a = \sum_i \sum_A (\langle i|i\rangle_A)^2 \tag{7}$$

and

$$N_d = 2\sum_i \sum_{B>A} \langle i|i\rangle_A \langle i|i\rangle_B \geq 0 \tag{8}$$

Such a partitioning is not invariant to unitary transformations among the occupied Hartree–Fock spin orbitals. There are, however, minima in N_d (or the equivalent maxima in N_a) with respect to the orbital rotations among the occupied spin orbitals. Each of these minima corresponds to a set of localized spin orbitals.[30] More importantly, if there is a pair of corresponding bonding and antibonding spin orbitals present, minimization of N_d results in a mutual cancellation of their contributions to N_d. This is so because orbital rotations within bonding–antibonding spin orbital pairs result in spin orbitals that are localized on single atoms. This corresponds to larger values of N_a since such spin orbitals have vanishing contributions to N_d. In other words, for a hypothetical system composed only of noninteracting atoms, one would expect $N_d = 0$. The same would be true for a hypothetical molecule with only purely ionic bonds.

Let us investigate the properties of the above partitioning in more detail. The diatomic contribution (N_d) can be written as a sum of bond terms:

$$N_d = \sum_{B>A} P_{AB} \tag{9}$$

where

$$P_{AB} = 2\sum_i \langle i|i\rangle_A \langle i|i\rangle_B \tag{10}$$

According to eq 10, the contribution to P_{AB} from each doubly occupied localized orbital describing a purely covalent bond between the atoms A and B is equal to 1. The contribution from a doubly occupied localized orbital that describes a polarized bond is less than 1. The contributions from ionic bonds are equal to 0. Taking the above observations into account, we conclude that P_{AB} (eq 10), calculated with the localized spin orbitals that maximize N_a, defines a covalent bond order between the atoms A and B in the Lewis (resonance) structure described by this particular set of localized spin orbitals. Since the localized spin orbitals can have any degree of ionicity, there is usually only one maximum in N_a, even for molecules that are traditionally described by several resonating Lewis structures. For example, there is only one maximum for the formate anion ($HCOO^-$) corresponding to two equivalent localized π orbitals that describe polarized bonds between the carbon atom and the oxygens, although $HCOO^-$ is often described in terms of two resonance structures involving unequivalent C–O bonds. The same is true for the $C(CN)_3^-$ anion (see Examples section), for which there is one maximum in N_a despite the commonly used description that uses four resonance structures. However, in certain cases (such as, for example, benzenoid hydrocarbons), the localized orbitals form patterns that have lower symmetry than the corresponding (local) molecular symmetry. In such cases, there are multiple maxima in N_a, each with the corresponding set of localized spin orbitals and covalent bond orders. One should note that the localized sets of orbitals are just *different descriptions of the same wave function* and therefore do not correspond to the VB structures. Hence, it is reasonable to assume that the actual covalent bond orders in the real molecules are given by the unweighted averages of P_{AB} over all (global and local) maxima in N_a.

Summing up, calculation of the covalent bond order involves the following steps: (1) finding the extrema of the electron density and constructing the atomic boundaries, (2) computing the elements of the AOM by integrating the orbital products over atomic basins (eq 1), (3) finding a unitary transformation among the occupied spin orbitals that maximizes N_a (this can be accomplished by using a sequence of 2 × 2 Jacobi rotations[34] or by employing more sophisticated second-order methods[35]), (4) calculating the covalent bond orders (eq 10), with use of the localized orbitals, and (5) repeating steps 3 and 4 to find all the maxima in N_a and averaging the covalent bond orders over all these maxima.

To complete this section, three observations about the above definition should be added.

First, our extensive computational testing reveals that, for the molecules that are adequately described by just one Lewis structure, there is always only one maximum in N_a.

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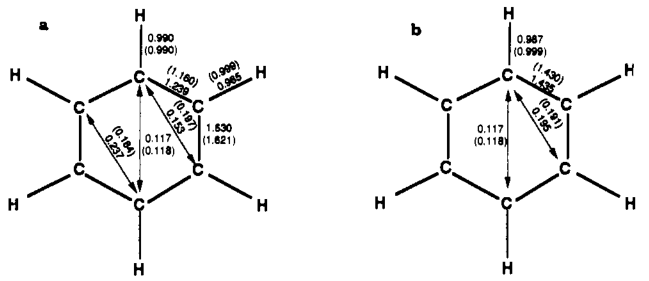

Figure 1. The calculated HF/6-31G* (HF/6-31++G** in parentheses) covalent bond orders in the benzene molecule: a, one of the two resonance structures; b, the real molecule.

Second, the definition can be easily generalized to correlated wave functions by replacing the Hartree–Fock spin orbitals by the natural ones and using the more general equations

$$N_a = \sum_i \sum_A \nu_i^2(\langle i|i\rangle_A)^2 \qquad (11)$$

and

$$P_{AB} = 2\sum_i \nu_i^2 \langle i|i\rangle_A \langle i|i\rangle_B \qquad (12)$$

where ν_i is the occupation number of the ith natural spin orbital, in place of eqs 7 and 10. In fact, maximization of so-defined N_a has been recently proposed as a means for localizing Hartree–Fock as well as natural orbitals.[30] To accomplish this, the unitary transformations of orbitals have to be replaced by the more general isopycnic transformations.[30] The contributions to bond orders from individual types of orbitals (such as the σ- and π-electron bond orders) can be easily calculated by restricting the summation in eq 10 (or eq 12) to those orbitals.

Third, there are some similarities between the present definition of the covalent bond order and the bond index of Wiberg.[5] Like Wiberg's, our derivation of P_{AB} is based on partitioning of the total number of electrons into atomic and diatomic terms and interpreting the latter as bond orders (or indices). The resulting P_{AB}'s are nonnegative in both definitions. Due to a proper cancellation of the contributions from the bonding and antibonding orbitals, both indices give the value of 0 for the bond orders between noninteracting pairs of atoms, although some misleading (and obviously incorrect) criticism concerning this property of Wiberg's bond index was published in the chemical literature.[16,20] However, we should emphasize that, unlike Wiberg's, our definition does not rely on assigning basis functions to individual atoms and therefore is equally valid for, for example, numerical orbitals.[36]

Examples

All the calculations reported in this sections were performed at either the HF/6-31G* or the HF/6-31++G** level with the HF/6-31G*-optimized geometries. The computations were carried out with the GAUSSIAN 88 suite of programs[37] running either on a VAX 3540 workstation or a CRAY Y-MP supercomputer. The AOMs were calculated with the programs EXTREM and PROAIM.[33] The localization of orbitals and evaluation of the covalent bond orders were carried out by using a program (BONDER) available from J.C. upon request. The calculated bond orders are displayed in Table I and Figures 1 and 2.

First we discuss the trends in the covalent bond orders in selected diatomic molecules. The magnitude of P_{AB} for the single bond in HF is more than twice that in either LiH or LiF. This is in agreement with the degrees of ionicity of these bonds. A similar trend is apparent in the isoelectronic series consisting of the N_2, CN^-, and CO molecules. One arrives at the value of P_{AB} close to 3 for the triple bond in the nitrogen molecule. This is reduced to ca. 2.1 in the CN^- ion and to ca. 1.5 in the CO molecule. These values, which follow the differences in the electronegativities of the atoms involved in bonding, are quite insensitive to the choice of the basis set. In the hydrogen cyanide molecule, the calculated covalent bond order of the C–N bond is close to that in the cyanide anion. The covalent bond order of the C–H is close to 1, due to the small difference in the electronegativities of the carbon and hydrogen atoms. This is changed radically in the hydrogen isocyanide molecule. Both the N–H and C–N covalent bond orders are much smaller than the C–H and C–N ones in the HCN molecule. This is not surprising taking into account the increased ionicities of the bonds in the HNC molecule. Since both HCN and HNC are triatomic molecules, one can also calculate P_{AB} for

Table I. Covalent Bond Orders in Selected Molecules and Anions

system[a]	bond	covalent bond order 6-31G*	 6-31++G**[b]
HF	H–F	0.506	0.433
LiF	Li–F	0.167	0.160
LiH	Li–H	0.207	0.210
N_2	N–N	3.038	3.045
CN^-	C–N	2.051	2.115
CO	C–O	1.509	1.524
HCN	H–C	0.922	0.922
	C–N	2.241	2.232
	H–N	0.073	0.089
HNC	H–N	0.653	0.641
	N–C	1.692	1.719
	H–C	0.021	0.023
$H_aC_aC_bH_a$	H_a–C_a	0.990	1.015
	C_a–C_b	2.920	2.897
	H_a–C_b	0.050	0.061
	H_a–H_b	0.003	0.003
$H_aH_bC_aC_bH_cH_d$	H_a–C_a	1.005	1.013
	C_a–C_b	1.958	1.918
	H_a–H_b	0.028	0.035
	C_a–H_c	0.059	0.097
	H_a–H_c	0.005	0.010
$H_aH_bH_cC_aC_bH_dH_eH_f$	H_a–C_a	0.984	0.982
	C_a–C_b	1.047	1.018
	H_a–H_b	0.035	0.044
	C_a–H_d	0.044	0.048
CHF_3	H–C	0.865	0.867
	C–F	0.570	0.572
	H–F	0.066	0.065
	F–F	0.171	0.171
CF_3^-	C–F	0.598	0.617
	F–F	0.168	0.178

[a] Lettered subscripts added wherever necessary to distinguish between different bonds. [b] At the HF/6-31G*-optimized geometries.

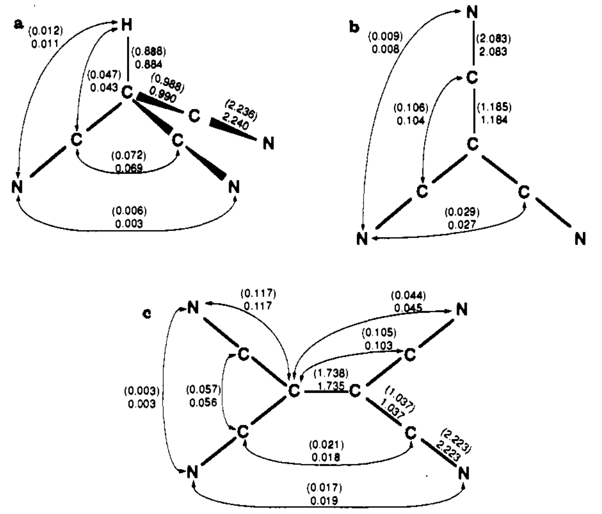

Figure 2. The calculated HF/6-31G* (HF/6-31++G** in parentheses) covalent bond orders: a, the $CH(CN)_3$ molecule; b, the $C(CN)_3^-$ anion; c, the $C_2(CN)_4$ molecule.

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the pairs of atoms not directly involving in bonding. As expected, these bond orders are quite small.

The covalent bond orders in the acetylene, ethylene, and ethane molecules follow the expectations based on chemical intuition. All the C–H bonds have their P_{AB}'s close to 1, whereas the covalent bond orders of the bonds between the carbon atoms are close to 3, 2, and 1, respectively. The bond orders between the nonbonded pairs of atoms (including the vicinal hydrogen atoms) are again small.

In the course of bond order calculations reported in this paper, we found only one maximum of N_a per molecule, with the obvious exception of the benzene molecule. In accordance with the number and the character of the Kekulé structures, for the benzene molecule, we obtained two identical maxima, with the pattern of covalent bond orders exhibiting symmetry reduced from D_{6h} to D_{3h} (Figure 1). The C–C bonds have the bond orders of ca. 1.2 and 1.6, which averages to ca. 1.4 in the real molecule. The C–H bond orders are close to 1 in both the individual resonance structures and the molecule itself.

The CHF_3 molecule, in which the C–H covalent bond order is considerably smaller than in the unsubstituted hydrocarbons, illustrates nicely the influence of substituents on the ionicity of adjacent bonds. In the CF_3^- anion, the C–F covalent bond orders are slightly larger than in CHF_3.

Our recent calculations on the $CH(CN)_3$ and $C(CN)_3^-$ systems[38] confirmed that, in the latter, the electron delocalization results in stronger C–C bonds and weakened C–N bonds. This conclusion has been drawn from the changes in the optimized bond lengths and the electron densities at the relevant critical points accompanying deprotonation of $CH(CN)_3$. The computed covalent bond orders, displayed in Figure 2a,b, provide even more a transparent manifestation of this effect. In the $CH(CN)_3$ molecule, the C–C bond orders have values close to 1, whereas the magnitudes of the C–N bond orders are very close to those in the HCN molecule. On the other hand, in the $C(CN)_3^-$ anion, the values of P_{AB}'s increase for the C–C bonds and decrease by almost the same amount for the C–N bonds. Quite similar but less dramatic changes are observed in the $C_2(CN)_4$ (TCNE) molecule (Figure 2c) as compared to ethylene. In this case, the electron-withdrawing CN substituents lower the covalent bond order of the central C–C bond considerably.

Conclusions

The proposed definition of the covalent bond order has several advantages over the previously known ones.

First, it does not rely on an explicit assignment of the basis functions to individual atoms. Numerical values of the computed bond orders are quite insensitive to the choice of the basis set, provided the particular basis set is capable of providing an accurate description of the electron distribution in the molecule in question. One should remark that the minimal basis sets (such as STO-3G) are usually inadequate for this purpose as reflected by large errors in the calculated dipole moments and GAPT charges.[24] The covalent bond orders are expected to converge smoothly with increasing number of basis functions to a limit independent of the nature of these functions (multicenter functions, one-center functions, bond functions, ghost orbitals, numerical orbitals, etc.).

Second, the definition follows from a simple partitioning of the total number of electrons present in the molecule under consideration. Minimization of the diatomic term leads to localization of the spin orbitals. The contribution of each localized spin orbital to each atomic pair is then assessed by means of calculating a weighted product of the relevant atomic overlap matrix (AOM) elements. This yields bond orders for individual Lewis (resonance) structures represented by localized spin orbitals. If more than one of such structures exist, a simple averaging provides the covalent bond orders of the real molecule.

Such a prescription results in covalent bond orders that are physically significant, quite easy to calculate, and transparent to interpretation. The presented examples demonstrate that the computed bond orders follow the expectations based on chemical intuition, reproducing for instance the inductive and resonance effects of substituents. The proposed covalent bond orders can be therefore used as companion indices to the Bader atomic charges.

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Ab Initio Study of the Insertion Reaction of Mg into the Carbon–Halogen Bond of Fluoro- and Chloromethane

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Abstract: Theoretical calcuations using self-consistent field (SCF) and Moller–Plessett perturbation theory, up to fourth order (MP4), have been carried out on the gas-phase $Mg + CH_3X \rightarrow CH_3MgX$ Grignard reaction surface for X = F and Cl. The transition-state energies, geometries, and vibrational frequencies for both reactions are presented and compared to the smaller $Mg + HX \rightarrow HMgX$ reaction. The transition states for both X = F and X = Cl are found to possess C_s symmetry and to be almost identical in structure. The activation energy for the Mg + fluoromethane reaction is found to be 31.2 kcal·mol^{-1}, while that for the chloromethane reaction is substantially higher, at 39.4 kcal·mol^{-1}, calculated at the MP4SDTQ level by using the 6-311G(d,p) basis. The intrinsic reaction coordinate has been followed down from the transition state toward both reactants and product for the $Mg + CH_3F \rightarrow CH_3MgF$ reaction, confirming the connection of these points on the potential surface.

Introduction

The reaction of magnesium with fluorocarbons such as tetrafluoroethylene (TFE) has received interest due to its pyrotechnic applications. Formulations involving Mg dispersed in solid TFE burn readily and contain many advantageous characteristics as rocket motor igniters and flares.[1-5] The mechanism of the combustion reaction is not entirely clear,[6,7] and attention is being

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