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PARTIAL CHARGE CORRELATION FUNCTION DEFINITION OF THEORETICAL BOND
ORDER, AND ITS COMPUTATION FROM EFFECTIVE MINIMAL BASIS SETS

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Abstract

We survey previous work on quantum mechanical definitions of bond order between two atoms in a molecule and discuss how the definitions are related. We discuss a definition applicable to single-determinant *ab initio* wavefunctions. This definition has a clear physical interpretation in terms of correlated charge fluctuations. The basis set issues of previous methods such as the Wiberg and Mayer bond orders are resolved by using intrinsic atomic orbitals. A formula in terms of density matrices is given for calculating the bond order in practice. Bond orders calculated using the new definition are compared to those calculated using previous definitions.

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Chapter 1

Introduction

The ubiquitous chemical concept of bond order is correlated with bond dissociation energies and lengths of bonds[1, 2] and used to rationalize the electronic structure of molecules. Being able to properly define and calculate bond orders helps in making qualitative chemical interpretations from otherwise-opaque, quantitative molecular wave functions obtained by modern computational methods. Like other intuitively-appealing, systematizing "classical" chemical concepts such as atomic orbitals, atoms within molecules, hardness and softness, partial charges, and aromaticity,[3] bond order is not a quantum mechanical observable and has no unique definition as the expectation value of an operator. The quantum mechanical meaning of bond order is neither widely known nor agreed upon.[4, 5, 6]

The simplest definition of bond order is the usual, widely-taught one for diatomic molecules, $1/2(N_b - N_a)$ where N_b is the number of electrons in bonding orbitals and N_a is the number of electrons in anti-bonding orbitals.[7, 8] This definition cannot be used for more complicated systems.[4, 9] It relies on the assumption that each spin-orbital is either occupied or unoccupied by one electron and so does not work for molecules undergoing dissociation.

The first definition of bond order applicable to more general single-determinant electronic structure methods was given by Wiberg in a footnote to a 1968 paper. It is applicable to semi-empirical quantum chemistry methods using orthonormal atomic orbital basis sets.[10] Wiberg's definition was generalized to *ab initio* methods using non-orthogonal basis sets by Mayer in 1984, employing Mulliken population analysis.[11, 12] Population analysis methods themselves do not give bond orders of the expected multiplicity of 0 to 3.[13] Also, if an orthonormal basis is used, the Mulliken overlap population is 0. The quantitative Mayer and Wiberg definitions are likely the most often-used bond order definitions,[9, 14, 15, 16] but their physical background is not widely-recognized.[17, 4, 18, 9]

In 1985, Giambiagi *et al.* gave a more general, statistical definition of bond order, relating bond order to instantaneous correlated charge fluctuations between atoms in a molecule.[19] We propose a modification of the bond order of Giambiagi *et al.*. Their definition and physical interpretation of bond order is not often used,[20] nor is its generality widely-recognized. Any partial charge definition, one based on either real (three-dimensional, physical) space or Hilbert space (orbital) analysis, can be used in the Giambiagi bond order definition. We derive the equations for its practical evaluation from Hartree-Fock and Kohn-Sham DFT wave functions. We show that if Löwdin charges or Mulliken charges are used in the Giambiagi bond order definition, the Wiberg and Mayer bond orders, respectively, are obtained.[20]

We explain and illustrate the physical picture motivating the Giambiagi definition. The Giambiagi bond order makes apparent that the Wiberg and Mayer definitions are not arbitrary, but instead physically justified.

If partial charges calculated using Intrinsic Atomic Orbitals (IAOs)[21] are used, the basis set issues of bond order definitions that correspond to various other charge definitions with unphysical basis set dependence (such as the widely-used Mulliken or Löwdin charges) are avoided.[22] Mulliken and Löwdin charges encounter problems with diffuse and non-atom-centered basis functions or periodic systems.[23, 24, 7, 6, 25, 16, 22] These Hilbert space partition schemes assign too much physical significance to basis functions, even if they are diffuse or not atom-centered. A basis function may be centered on one atom but describe electron density on a second atom, and then this electron density will be erroneously attributed to the first atom.[23] As the basis set quality increases, the wave function should eventually no longer change qualitatively, yet the usual Mulliken and Löwdin charges may give erratic values. In contrast, IAO charges, computed with

IAOs clearly associated with each atom, remain stable as the basis set quality increases. Consequently, bond orders calculated with IAO charges are much less basis set-dependent than bond orders calculated with the usual Löwdin or Mulliken charges.

Chapter 2

Charge Fluctuations and Covalent Bonds

Correlated charge fluctuations from the mean *define* covalent bonding.[4, 26] If electron density increases on one atom, it must decrease on the other bonded atom. The strength of this correlation indicates the bond order. The Giambiagi bond order is based upon this physical picture.[19] The concept is illustrated most simply in the H_2 molecule, containing the ideal covalent bond. We show this here for illustration and discuss the mathematical generalization to arbitrary molecules and basis sets in the next section. We employ a minimal basis set at the Hartree-Fock level. Given an orthonormal, minimal basis set of two 1s AOs χ_1 and χ_2 , the bonding spatial MO ϕ is $\frac{1}{\sqrt{2}}(\chi_1 + \chi_2)$. Then the H_2 wave function can be written as the determinant

$$|\phi(1)\bar{\phi}(2)\rangle = \frac{1}{\sqrt{2}}(\phi(1)\bar{\phi}(2) - \bar{\phi}(1)\phi(2))$$

where ϕ , $\bar{\phi}$ indicate spin-up and spin-down spin-orbitals, respectively. Inserting ϕ in terms of the AOs, we obtain

$$|\phi(1)\bar{\phi}(2)\rangle = \frac{1}{2}(|\chi_1(1)\bar{\chi}_1(2)\rangle + |\chi_1(1)\bar{\chi}_2(2)\rangle + |\chi_2(1)\bar{\chi}_1(2)\rangle + |\chi_2(1)\bar{\chi}_2(2)\rangle).$$

Hence the covalent wave function is a linear combination of two ionic ($|\chi(1)\bar{\chi}(1)\rangle$, $|\chi(2)\bar{\chi}(2)\rangle$) and two radical ($|\chi(1)\bar{\chi}(2)\rangle$, $|\chi(2)\bar{\chi}(1)\rangle$) determinants (Figure 2.1), all four with equal weights. The covalent wave function includes instantaneous, correlated charge fluctuations. In contrast, in an ionic configurations, both electrons simply remain at one center. So ionic or non-bonding character is characterized by average charge, while covalent bonding is characterized by correlated charge fluctuation from the mean. Arguments similar to the one for the H_2 bond can be made for arbitrary two-center bonds in any molecule described by a single determinant.

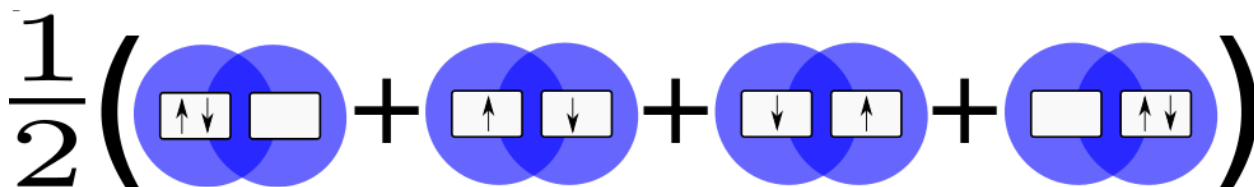


Figure 2.1: H_2

Chapter 3

Statistical Covariance Bond Order

3.1 Statistical Covariance Formulation

Most single-determinant wave functions cannot be efficiently decomposed in the pictorial fashion described in the previous section. Instead, a numerically-evaluable definition of bond order consistent with the correlated charge fluctuation picture was given by Giambiagi et al. as the covariance of charge on atoms A and B,

$$I_{AB} = -2 \langle (\hat{q}^A - \langle \hat{q}^A \rangle) (\hat{q}^B - \langle \hat{q}^B \rangle) \rangle \quad (3.1)$$

where \hat{q}^I is some charge operator. This bond order indicates the strength of correlation of charge fluctuations away from the average partial charges on atoms A and B.[19] Giambiagi and coworkers did not prescribe how to calculate their bond order in practice, specify the charge operator, provide test calculations, or relate their bond order to pre-existing bond order definitions. We investigate these neglected points here.

3.2 Equations for Single-Determinant Wave Functions

We derive a practical formula for the covariance bond order in terms of density matrices of single-determinant wave functions. Let $\mu\nu\rho\sigma$ denote a possibly non-orthogonal basis set. We use "mixed" second quantization for a non-orthogonal basis.[11, 19, 20, 27]

We have the general charge operator $\langle \hat{q}^I \rangle = \sum_{\rho\sigma} \langle \hat{E}_\sigma^\rho \rangle n_{\rho\sigma}^I$, and $\hat{E}_\nu^\mu = \hat{\chi}_\mu^\dagger \hat{\chi}_\nu = \hat{\chi}_\mu^\dagger (S^{-1})_{\nu\rho} \hat{\chi}_\rho$ so that $[\hat{\chi}_\mu^\dagger, \hat{\chi}_\nu] = \delta_{\mu\nu}^+$. Then

$$\begin{aligned} I_{AB} &= -2 \langle (\hat{q}^A - q^A) (\hat{q}^B - q^B) \rangle = -2 (\langle \hat{q}^A \hat{q}^B \rangle - q^A q^B) \\ &= -2 \sum_{\rho\sigma\tau\nu} \langle \hat{E}_\sigma^\rho \hat{E}_\nu^\tau \rangle n_{\rho\sigma}^A n_{\tau\nu}^B - \langle \hat{E}_\sigma^\rho \rangle n_{\rho\sigma}^A \langle \hat{E}_\nu^\tau \rangle n_{\tau\nu}^B \\ &= -2 \sum_{\rho\sigma\tau\nu} n_{\rho\sigma}^A n_{\tau\nu}^B (\delta_\sigma^\tau - \langle \hat{E}_{\nu\sigma}^{\rho\tau} \rangle - \langle \hat{E}_\sigma^\rho \rangle \langle \hat{E}_\nu^\tau \rangle) \\ &= -2 \sum_{\rho\sigma\tau\nu} n_{\rho\sigma}^A n_{\tau\nu}^B (\delta_\sigma^\tau - (\langle E_\nu^\rho \rangle \langle E_\sigma^\tau \rangle - \langle E_\sigma^\rho \rangle \langle E_\nu^\tau \rangle) - \langle \hat{E}_\sigma^\rho \rangle \langle \hat{E}_\nu^\tau \rangle) \\ &= -2 \sum_{\rho\sigma\tau\nu} n_{\rho\sigma}^A n_{\tau\nu}^B (\delta_\sigma^\tau - \langle E_\nu^\rho \rangle \langle E_\sigma^\tau \rangle) \\ & (= 2 \sum_{\rho\sigma\tau\nu} n_{\rho\sigma}^A n_{\tau\nu}^B \langle E_\nu^\rho \rangle \langle E_\sigma^\tau \rangle) \end{aligned}$$

if $A \neq B$.

3.3 Relationship to Wiberg/Mayer Definitions

It has been shown previously that the Mayer bond order is a special case of the Giambiagi one.[20, 28] Also, the Wiberg definition is a special case of the Mayer definition.[11] For the

Mayer bond order, we use the Mulliken charge operator definition in a non-orthogonal basis. For the Wiberg bond order, we use the Löwdin charge operator definition in a symmetrically orthogonalized basis. Proofs are given here to emphasize the generality of the correlated charge fluctuation bond order definition.

$$\begin{aligned}
I_{AB} &= -2 \sum_{\mu\nu\rho\sigma} n_{\rho\sigma}^A n_{\tau\nu}^B \gamma^{\rho\nu} \eta^{\tau\sigma} \\
&= -2 \sum_{\rho,\nu \in B, \sigma, \tau \in A} S_{\rho\sigma} S_{\tau\nu} \gamma^{\rho\nu} \eta^{\tau\sigma} \\
& (= 2 \sum_{\nu \in B, \sigma \in A} [\gamma \cdot S]_{\sigma}^{\nu} [\gamma \cdot S]_{\nu}^{\sigma} \text{ for Mayer/Wiberg}) \\
& (= 2 \sum_{\nu \in B, \sigma \in A} \gamma_{\sigma}^{\nu} \gamma_{\nu}^{\sigma} \text{ for Wiberg})
\end{aligned}$$

Alternatively, if $\gamma^{\mu\nu}$ is the 1-particle density matrix, $\eta^{\rho\sigma} = 2S^{\rho\sigma} - \gamma^{\rho\sigma}$, the 1-hole density matrix, $S^{\rho\sigma} = [\vec{S}^{-1}]_{\rho\sigma}$ is an inverse overlap matrix, and $q_{\mu\rho}^A = S_{\mu\rho} \Big|_{\rho \in A}$, then we obtain the Wiberg definition bond order:

$$W_{AB} = \sum_{\nu \in A} \sum_{\rho \in B} \left(\sum_{\mu} \gamma^{\mu\nu} S_{\mu\rho} \right) \left(\sum_{\sigma} \eta^{\rho\sigma} S_{\nu\sigma} \right) \quad (3.2)$$

$$= \sum_{\nu \in A} \sum_{\rho \in B} \gamma_{\rho}^{\nu} \gamma_{\nu}^{\rho} \quad (3.3)$$

Table 3.1 and Table 3.2 support the claim made in Chapter 1 that when partial charges are computed using IAOs instead of the original basis set, the charges are independent of basis set quality, as are the bond orders. Given that the calculations with larger basis sets produce almost quantitatively-correct wave functions, differences in charge and bond order values for different basis sets have no physical meaning. The drastic differences in charge and bond order values between basis sets only occur when the Löwdin/Mulliken charge definitions are used with the original basis set and not IAOs. All bond orders were computed using the Giambiagi bond order definition with Löwdin or Mulliken charge operators.

basis set	Löwdin	Mulliken	IAO (Löwdin)	IAO (Mulliken)
def2-SV(P)	-0.459	-0.065	-0.089	-0.245
def2-SVP	-0.173	0.218	-0.106	-0.271
def2-TZVP	-0.539	-0.073	-0.115	-0.294
def2-TZVPP	-0.156	0.039	-0.116	-0.296
def2-QZVP	0.029	0.024	-0.116	-0.296
def2-QZVPP	0.029	0.024	-0.116	-0.296
cc-pVDZ	-0.252	0.157	-0.116	-0.293
cc-pVTZ	-0.069	-0.011	-0.117	-0.297
cc-pVQZ	0.017	0.116	-0.116	-0.296
cc-pV5Z	0.071	0.206	-0.116	-0.296
aug-cc-pVDZ	-0.140	0.883	-0.118	-0.299
aug-cc-pVTZ	0.156	-0.626	-0.117	-0.297
aug-cc-pVQZ	0.461	-0.396	-0.116	-0.297
aug-cc-pV5Z	0.593	-0.336	-0.116	-0.297

Table 3.1: Basis set dependence of partial charge on C in CH₃OH for Löwdin, Mulliken, IAO-Löwdin, and IAO-Mulliken definitions

basis set	Löwdin (Wiberg)	Mulliken (Mayer)	IAO (Löwdin)	IAO (Mulliken)
def2-SV(P)	1.175	0.849	0.973	0.819
def2-SVP	1.129	0.862	0.973	0.817
def2-TZVP	1.593	0.840	0.966	0.799
def2-TZVPP	1.405	0.846	0.966	0.799
def2-QZVP	1.543	0.828	0.965	0.796
def2-QZVPP	1.544	0.828	0.965	0.796
cc-pVDZ	1.143	0.943	0.973	0.809
cc-pVTZ	1.299	0.928	0.967	0.801
cc-pVQZ	1.482	0.923	0.965	0.798
cc-pV5Z	1.582	0.951	0.965	0.796
aug-cc-pVDZ	1.508	0.538	0.966	0.797
aug-cc-pVTZ	1.628	0.619	0.964	0.796
aug-cc-pVQZ	1.704	0.646	0.964	0.796
aug-cc-pV5Z	1.731	0.888	0.964	0.796

Table 3.2: Basis set dependence of C-O bond order in CH₃OH using Giambiagi bond order and Löwdin, Mulliken, IAO-Löwdin, and IAO-Mulliken charges

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