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REGULAR ARTICLE

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# Quantum Monte Carlo calculation of correlation effects on bond orders

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**Abstract** We present a computational approach, using quantum Monte Carlo, that provides some insight into the effect of electron correlation on chemical bonding between individual pairs of atoms. Our approach rests upon a recently suggested relation between the bond order and charge fluctuations with respect to atomic domains. Within the present implementation we have taken a compromise between conceptual rigour and computational simplicity. In a first step atomic domains were obtained from Hartree-Fock (HF) densities, using Bader's definition of atoms in molecules. These domains were used in a second step in quantum Monte Carlo calculations to determine bond orders for pairs of atoms. Correlation effects have been studied by comparison of HF bond orders with those obtained from pure diffusion quantum Monte Carlo calculations. We illustrate this concept for C–O and C–S bonds in different molecular environments. Our results suggest an approximate linear relation between bond order and bond length for these kinds of bonds.

**Keywords** Quantum Monte Carlo · Charge fluctuations · Bond order · Electron correlation

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## 1 Introduction

### 1.1 Analysis of chemical bonding from quantum Monte Carlo calculations

Within the last few years, *quantum Monte Carlo* (QMC) has become a versatile method for accurate electronic structure calculations, with numerous applications in quantum chemistry [1] and solid state physics [2]. Obviously, most of the work focused on the determination of measurable physical properties like binding energies, equilibrium structures, excitation energies etc. However, in quantum chemistry there is also a strong demand for quantities which provide some insight from the point of view of classical chemistry. Conventional quantum chemical methods comply to it by providing a wealth of additional information, which can be used for this purpose. We just want to mention canonical and localized orbitals, Mulliken's or Löwdin's population analysis for *Hartree-Fock* (HF) and *density functional theory* (DFT). Furthermore natural orbitals and occupation numbers as well as certain schemes for partitioning the correlation energy into contributions from orbital subspaces provide some chemical insight from correlated wavefunctions. It is a common feature of such quantities that they can be obtained with only modest additional computational effort. However, to use this information in a reasonable way requires great care due to well known conceptual shortcomings of these quantities. In contrast to this, standard QMC calculations usually offer no such information. Two novel approaches in this direction will be briefly discussed below. This shortcoming is mainly due to the fact that QMC methods operate directly in the configuration space of all electron coordinates, whereas conventional methods are based on discretization schemes using finite dimensional atomic centred basis sets. The latter greatly facilitates the decomposition of global quantities like charge and energy. From a chemist's point of view it would be highly desirable to have an interpretive tool, similar to a population analysis, available in QMC, which provides some insight into the nature of chemical bonding in molecules and solids. Such an interpretive tool has to meet a few basic requirements which are mandatory for a meaningful application in QMC calculations.

(i) Close relation to classical concepts of chemical bonding.
(ii) Consistent definition for HF and correlated wavefunctions.
(iii) Basis set independent definition.
(iv) Minor additional computational effort.

As we have already mentioned above there exist two novel approaches which provide some qualitative insight into chemical bonding from QMC calculations. The first approach by Scemama et al. [3], in the spirit of ELF, is based on an *electron pair localization function* (EPLF) [3]. This approach satisfies requirements (i) to (iii). The EPLF, however, is rather demanding from a computational point of view, since it requires the stochastic calculation of a three-dimensional function. The second approach of Savin et al. [4–7] considers the shape optimization of spatial domains in order to maximize the probability that a certain number of electrons are contained in these domains. Such kind of approach yields various domains that can be identified with atomic shells, lone pairs and covalent bonds. It satisfies requirements (i) to (iii) and has been recently applied by Scemama [4] within variational Monte Carlo calculations. The shape optimization, however, requires rather sophisticated numerical methods [6] and cannot presently be routinely applied.

### 1.2 Bond order and charge fluctuations

A useful concept in the analysis of wavefunctions are charge fluctuations with respect to certain spatial domains. The strength of this concept lays in its conceptual simplicity and great flexibility concerning the choice of the many-particle method. Charge fluctuations have been extensively studied in quantum chemistry [5,8–17] and solid-state physics [18–22] in order to get a better understanding of many-electron wavefunctions. Research in chemistry mainly focused on the effects of Fermi repulsion in HF wavefunctions, whereas a better understanding of electron correlation was the main motivation in solid state physics. These studies are either based on a direct partitioning of space into volume elements [5,8,9,15–17,20–22] or on an indirect partitioning via the underlying one-particle Hilbert space [10–12,14,18,19]. Both approaches can lead to substantially different results [13] depending on the specific choice of the basis set and wavefunction. As already mentioned above, QMC methods do not rely on a one-particle Hilbert space, therefore we do not further discuss the second approach.

Charge fluctuations with respect to spatial domains $\Omega_A \subset \mathbb{R}^3$ can be expressed in terms of the corresponding electron-number operators

$$\hat{N}_A = \sum_{i=1}^{N} \zeta_A(\mathbf{r}_i), \text{ with } \zeta_A(\mathbf{r}) = \begin{cases} 1 & \text{for } \mathbf{r} \in \Omega_A \\ 0 & \text{for } \mathbf{r} \notin \Omega_A \end{cases}, \tag{1}$$

where statistical correlations of charge fluctuations between domains are given by the covariance matrix of electron-number operators

$$\operatorname{cov}(\hat{N}_A, \hat{N}_B) = \langle \hat{N}_A \hat{N}_B \rangle - \langle \hat{N}_A \rangle \langle \hat{N}_B \rangle. \tag{2}$$

We assume $\Omega_A \cap \Omega_B = \emptyset$ for different domains. The calculation of the covariance matrix requires the expectation values

$$\langle \hat{N}_A \rangle = \int\limits_{\Omega_A} \rho(\mathbf{r}) \, \mathrm{d}^3 r, \tag{3}$$

$$\langle \hat{N}_A \hat{N}_B \rangle = \delta_{A,B} \int\limits_{\Omega_A} \rho(\mathbf{r}_1) \, \mathrm{d}^3 r_1 + 2 \int\limits_{\Omega_A} \int\limits_{\Omega_B} g(\mathbf{r}_1, \mathbf{r}_2) \, \mathrm{d}^3 r_1 \mathrm{d}^3 r_2, \tag{4}$$

which can be obtained from the spin-averaged electron density $\rho$ and pair density

$$g(\mathbf{r}_1, \mathbf{r}_2) = \frac{N(N-1)}{2} \sum_{s_1 \ldots s_N} \int |\Psi(\mathbf{r}_1, s_1, \ldots, \mathbf{r}_N, s_N)|^2 \, \mathrm{d}^3 r_3 \mathrm{d}^3 r_4 \ldots \mathrm{d}^3 r_N \tag{5}$$

of a HF or correlated wavefunction. These expectation values are defined in configuration space and provide a consistent definition for HF and correlated wavefunctions, satisfying requirements (ii) and (iii). We have already applied charge–number operators in QMC calculations to study chemical bonding in mercury clusters [23,24], where their computational simplicity, in accordance with requirement (iv), has been demonstrated. Since we were only interested in correlation effects, Wigner–Seitz cells were chosen for the definition of atomic domains. Within the present work we have extended our studies to covalent polar bonds. In order to take into account polarization effects more complex domains are needed. A common partitioning scheme is Bader's *atoms in molecules* (AIM) approach [8]. It requires only the electron density, where domains are defined by the so the called zero-flux surfaces. They are characterized by the requirement that the gradient of the density is at every point tangential to these surfaces. Typically zero-flux surfaces enclose regions, with a single atomic nucleus inside, that can be interpreted as atomic domains. Alternatively the *electron localization function* (ELF) [25,26] can be used along the same lines for domain decomposition. We have used the AIM approach since it allows a direct comparison of our calculations with previous results published in the literature. Furthermore, zero-flux surfaces do not seem to be very sensitive to electron correlation. This enables us to determine these surfaces using, compared with QMC, less expensive methods like HF or DFT.

Although there is general agreement on the physical and chemical relevance of charge fluctuations in the literature, their interpretation in terms of classical chemical concepts however is highly controversial. Based on previous work of

Mayer [10–12], Ángyán et al. [15] proposed the following definition

$$\mathcal{B}_{A,B} = -2\,\mathrm{cov}\,(\hat{N}_A, \hat{N}_B) = -2\left(\langle \hat{N}_A \hat{N}_B\rangle - \langle \hat{N}_A\rangle\langle \hat{N}_B\rangle\right) \tag{6}$$

of a bond order $\mathcal{B}_{A,B}$ between different atoms A and B in a molecule. The diagonal part of the covariance matrix defines atomic valence

$$\mathcal{V}_A = 2\left(\langle \hat{N}_A^2\rangle - \langle \hat{N}_A\rangle^2\right). \tag{7}$$

Bond orders and atomic valence are related by the sum rule

$$\mathcal{V}_A = \sum_{B\neq A} \mathcal{B}_{A,B}. \tag{8}$$

It should be mentioned that definition (6) agrees with Mayer's definition of bond order for HF wavefunctions. However, the generalization proposed by Mayer for correlated wavefunctions [12] differs in the sense that only the "exchange part" of the correlated pair density (5) has been taken into account. The "exchange part" corresponds to the square of the one-particle density matrix, which has been obtained from a correlated wavefunction. A peculiar feature of Mayer's definition is that the sum rule (8) for correlated wavefunctions is no more valid. Since any subdivision of the pair density has some kind of arbitrariness, we follow Ángyán's suggestion for the definition of bond orders. Mayer's argument to refuse definition (6) for correlated wavefunctions is based on considerations using a partitioning of the one-particle Hilbert space. The inconsistency found there, however disappears if a real space partitioning is used, as pointed out by Ángyán et al. [15].

The interpretation of charge fluctuations between atomic domains in terms of bond orders has been criticized by Fradera et al. [16] referring to the original work of Bader and Stephens [9]. Instead they prefer to define a delocalization index, which is identical to Ángyán's definition for the bond order (6). They rely on Lewis original definition of a bond order as the number of electron pairs that constitute a chemical bond between two atoms [27,28]. For homonuclear molecules Mayer's definition yields values very close to classical bond orders [15], whereas polar bonds yield fractional bond orders in contrast to classical assignments. In order to reconcile both definitions, Chesnut proposed some kind of renormalization procedure [29]. For correlated wavefunctions it becomes even more difficult to assign a certain number of orbitals to a chemical bond. From the authors point of view it seems to be justifiable to sacrifice agreement with classical concepts in these cases for the benefit of a consistent definition for correlated and HF wavefunctions. Another criticism of Fradera et al. concerns the appearance of non-vanishing bond orders between atoms which are not connected by a bond path in the sense of Bader's topological analysis of the electron density [8]. In our opinion, the presence of significant bond orders between classically non-bonded atoms questions the applicability of the classical model to certain kinds of chemical bonds. An appropriate criterion for the applicability of Lewis model has been already suggested by Ponec and Uhlik [30].

We want to conclude this section with a brief discussion of some other closely related approaches to analyse chemical bonds in terms of charge fluctuations. In a series of papers Ponec and coworkers studied the compatibility of Lewis electron pair model with Bader's atoms in molecules approach [14,30–33]. They assigned chemical bonds to orbitals which minimize the sum of their individual pair fluctuations [14]. This method has been extended to correlated wavefunctions [33]. In addition they have studied the properties of a "charge-weighted" Fermi hole as a criterion for the characterization of chemical bonds [31,32] and its connection to charge fluctuations. Furthermore, we want to mention Fulton's approach [34,35] based on the square root of the one-particle density matrix, the latter has to be understood in the sense of an operator. For HF wavefunctions Fulton's and Mayer's definitions are equivalent due to the idempotency of the one-particle density matrix. However when applied to correlated wavefunctions both definitions deviate from each other. It has been stressed by Mayer that his definition of bond order is intimately related to well established concepts in semi-empirical methods like Wiberg indices, we refer to Ref. [12] for a discussion of this subject. Another approach, closely connected to charge fluctuations is the recently proposed *electron localizability indicator* (ELI) [36], based on the integral of the same-spin electron pair density over compact regions enclosing fixed charge. ELI is related to the correlation of the motion of same-spin electrons. At the HF level of theory, ELF is an approximation to ELI.

## 2 QMC calculation of charge fluctuations

We have used the *pure diffusion Monte Carlo* (PDMC) method of Caffarel and Claverie [37]. It is based on a generalization of the Feynman–Kac formula for the imaginary time Green's function, which allows importance sampling from a given trial wavefunction. The PDMC calculations have been performed using the so-called fixed-node approximation, which means, that the nodes of the trial wavefunction define Dirichlet boundary conditions for the stochastic solution of Schrödinger's equation. In contrast to the commonly employed *diffusion Monte Carlo* (DMC) method [38], weights associated with individual walkers are carried through the simulation and are not converted into branching steps. A significant advantage for our present application is that the PDMC algorithm enables an unbiased sampling of expectation values of local operators. It has been recently proofed by Assaraf et al. [39] that the PDMC algorithm becomes asymptotically unstable for a large number of accumulated weights. Within the present application this does not pose a serious problem due to the fast convergence of the quantities under consideration. We demonstrate convergence of the energy and expectation values for an explict example below. However it should be mentioned that applications to larger molecules may require a modification of the algorithm, the so called stochastic reconfiguration method [39], which is asymptotically stable.

Expectation values of the fixed-node ground state wavefunction $\Psi_{\text{fn}}$ for local operators $\hat{O}$, e.g. $\hat{O} = \hat{N}_A,\ \hat{N}_A\hat{N}_B$, can be obtained from a PDMC calculation according to the formula

$$\begin{aligned}\langle\hat{O}\rangle_{\text{fn}} &:= \frac{\langle\Psi_{\text{fn}} \mid \hat{O} \mid \Psi_{\text{fn}}\rangle}{\langle\Psi_{\text{fn}} \mid \Psi_{\text{fn}}\rangle} \\ &= \lim_{\tau\to\infty} \frac{\langle\Phi \mid \exp\left(-\frac{\tau}{2}\hat{H}\right)\hat{O}\exp\left(-\frac{\tau}{2}\hat{H}\right) \mid \Phi\rangle}{\langle\Phi \mid \exp\left(-\tau\hat{H}\right) \mid \Phi\rangle} \\ &= \lim_{\tau\to\infty}\lim_{T\to\infty} \frac{\int_0^T \mathrm{d}t\ \exp\left(-\int_t^{t+\frac{\tau}{2}} E_L(\mathbf{x}_s)\mathrm{d}s\right)\hat{O}(\mathbf{x}_{t+\frac{\tau}{2}})\exp\left(-\int_{t+\frac{\tau}{2}}^{t+\tau} E_L(\mathbf{x}_s)\mathrm{d}s\right)}{\int_0^T \mathrm{d}t \exp\left(-\int_t^{t+\tau} E_L(\mathbf{x}_s)\mathrm{d}s\right)},\end{aligned} \tag{9}$$

where $\Phi$ corresponds to a suitably chosen trial wavefunction. The right hand side of Eq. (9) has to be understood as a path integral in the sense of Feynman and Kac, where random paths in configuration space $\mathbf{x} = (\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n) \in \mathbb{R}^{3N}$ are sampled from the stochastic differential equation

$$\mathrm{d}\mathbf{x} = \frac{\nabla\Phi(\mathbf{x})}{\Phi(\mathbf{x})}\mathrm{d}t + \mathrm{d}\mathbf{G} \tag{10}$$

driven by a Wiener process $\mathbf{G}$. Approximating differentials by finite differences, each path of length $\tau = M\delta\tau$ carries an exponential weight

$$W(\mathbf{x}_i, \mathbf{x}_{i+1}, \ldots, \mathbf{x}_{i+M}) = \prod_{k=1}^{M} \exp\left[-E_L(\mathbf{x}_{i+k})\delta\tau\right] \tag{11}$$

corresponding to the local energy

$$E_L(\mathbf{x}) = \frac{\hat{H}\Phi(\mathbf{x})}{\Phi(\mathbf{x})} \tag{12}$$

evaluated along the random walk. The expectation value (9) can be approximated as the limit of averages

$$\langle\hat{O}\rangle_{\text{fn}} \approx \lim_{M\to\infty} \frac{\sum_i\ W(\mathbf{x}_i, \mathbf{x}_{i+1}, \ldots, \mathbf{x}_{i+M/2})\ \hat{O}(\mathbf{x}_{i+M/2})\ W(\mathbf{x}_{i+M/2}, \mathbf{x}_{i+1+M/2}, \ldots, \mathbf{x}_{i+M})}{\sum_i\ W(\mathbf{x}_i, \mathbf{x}_{i+1}, \mathbf{x}_{i+2}, \ldots, \mathbf{x}_{i+M})} \tag{13}$$

with respect to sums over random paths of length $\tau = M\delta\tau$. It is obvious from Eq. (9) that in the opposite limit $\tau \to 0$, expectation values for the trial wavefunction $\Phi$ can be obtained. Taking merely a HF wavefunction for $\Phi$, this provides a simple method to obtain uncorrelated charge fluctuations from a QMC calculation. We want to mention that the estimate (13) is closely related to the forward walking algorithm in DMC [40]. Combined with a PDMC calculation of the energy, the stochastic average (13) requires only minor additional computational effort. On top of it, only pointwise evaluations of the local operator $\hat{O}$ along the random walk have to performed. Within our present application a pointwise evaluation of an operator $\hat{N}_A$ just requires to count the number of electrons $\mathbf{r}_i \in \Omega_A$ of a specific configuration $\mathbf{x} = (\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n)$ which belong to an atomic domain $\Omega_A$.

It has already been mentioned that the PDMC method is plagued with an asymptotic instability in the limit $\tau\to\infty$. Therefore, it is important to study carefully the convergence of each individual expectation value. For good trial wavefunctions, corrections are typically small and convergence can be achieved before asymptotic instability becomes noticeable. This is illustrated in Fig. 1 for formaldehyde. The convergence of Eq. (9) with respect to the parameter $\tau$ is shown for electron-number operators (1), bond-orders (6) and for comparison for the total energy. It can be seen that all quantities converge quite well and remain stable over a fairly long range of the parameter $\tau$. As anticipated from our previous work [41], the total energy requires only half the value of $\tau$ for convergence than the other operators. It has also been observed that bond orders converge slightly faster than the electron-number operators. Furthermore, the convergence behaviour of sulphur compounds seems to be better than for their oxygen analogues. This can be understood from the underlying charge density, which is smoother around the sulfur atoms due to the pseudopotential employed.

## 3 Computational details

We have used standard trial wavefunctions, consisting of a Jastrow factor [42] times HF wavefunction, in our PDMC calculations. The parameters of the Jastrow factor have been optimized by minimizing the variance of the local energy. For oxygen (sulphur) compounds, the Jastrow factors recovered between 70 and 83% (84–88%) of the PDMC correlation energy. In order to ensure unbiased results, a fairly small time step ($\delta\tau = 0.004$ hartree$^{-1}$) has been employed in the PDMC calculations. Throughout our calculations, we have used semilocal pseudopotentials [43,44] with 1, 4, 6, and 6 valence electrons for Na, C, O, and S, respectively. For the HF part of the trial wavefunctions we have chosen uncontracted standard basis sets [43,44], where we have added at each atom three $d$-type polarization functions from VQZ basis sets [45,46] and four $s$-type basis functions with large

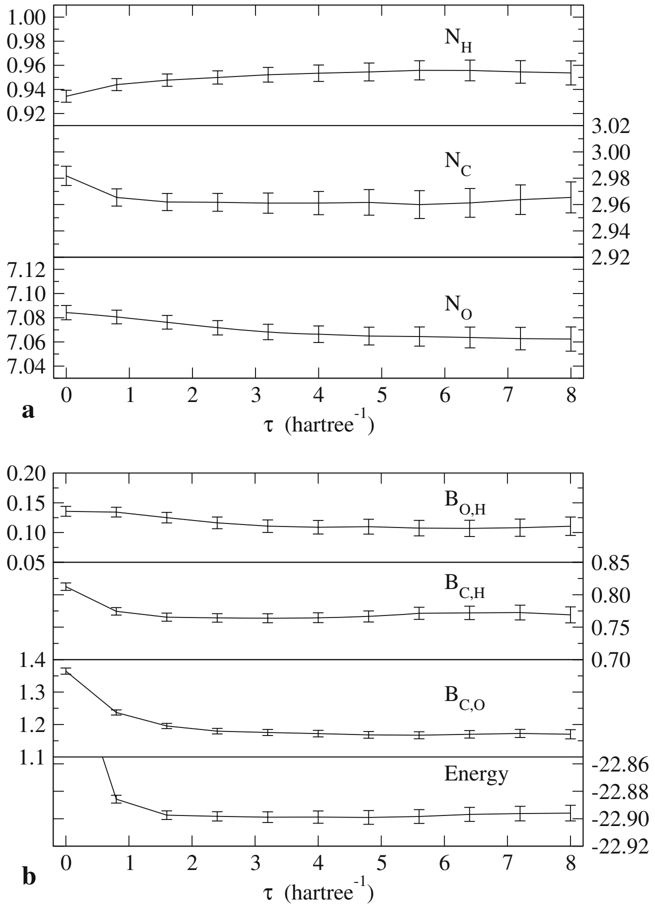

**Fig. 1** Convergence of PDMC expectation values with respect to the parameter $\tau$ for electron-number operators $\hat{N}_A$, bond-orders $\mathcal{B}_{AB}$ and the total energy (hartree) of formaldehyde

exponents. The latter have been added to improve the behaviour of the trial wavefunction near the electron-nuclear cusps. For the same reason we have chosen a large $(11\,s,1\,p)$ basis set on hydrogen with exponents taken from Ref. [47]. In the following we refer to these basis sets as the standard bases. We have used equilibrium structures determined from experiments [48] in our calculations, except for dithioformic acid and the two sodium complexes where the structures have been optimised using *coupled cluster with single and double excitations* (CCSD) and the standard basis sets. Furthermore we have performed CCSD and CCSD(T) calculations using uncontracted $(12s6p3d2f1g)$ (C,O), $(16s11p3d2f1g)$ (S), and $(6s3p2d1f)$ (H) basis sets with exponents taken from aug-cc-VQZ basis sets [45,46]. In the following we refer to these basis sets as the benchmark bases. These calculations provide benchmarks for the quality of our PDMC calculations. All of our HF, CCSD and CCSD(T) calculations have been performed using the MOLPRO package of *ab initio* programs [49].

The electron densities for Bader's analysis were calculated with Gaussian 98 [50] using 6-311G basis sets. Herewith, discrete representations of electron densities were generated on an equidistant grid [51]. On this discrete scalar field, the density basins, i.e., regions enclosed by surfaces of zero-flux in the electron density gradient, were determined [52].

## 4 Effect of electron correlation on CO and CS bonds

The conventional bond order of CO bonds in molecules varies between 1 to 3 depending whether the classical Lewis structure corresponds to a single, double or triple bond. However, even on the classical level this concept has to be softened due to the appearance of resonance structures that yield fractional bond orders for certain molecules. For a detailed discussion of these aspects of CO bonds we refer to the monograph [28]. In Table 1 we have listed bond orders $\mathcal{B}_{A,B}$ according to the definition of Mayer and Ángyán (6) for selected small molecules containing varies types of CO bonds. The underlying atomic domains have been determined from HF electron densities. Below we briefly discuss the effect of electron correlation on atomic domains which turned out to be rather small. Before we enter into a discussion of bond orders, let us first consider the average number of valence electrons $\mathcal{N}_A$ in the atomic domains $\Omega_A$. According to our observations this quantity is rather insensitive to electron correlation. Therefore we have listed only the correlated results from PDMC calculations in Table 1. It turns out that the corresponding atomic charges are in good agreement with the uncorrelated results reported in Ref. [28]. We want to mention, however, that due to discretization errors in our numerical scheme for the determination of zero-flux surfaces, the remaining uncertainty for $\mathcal{N}_A$ is $\approx 0.1$ electrons. While the average number of valence electrons in domains of O atoms remains almost constant between 7.0 and 7.3, the domains of C atoms show large variations ranging between 1.5 for $CO_2$ up to 3.0 for formaldehyde. These numbers already indicate the strong polarity of CO bonds. The polarity of covalent bonds is further reflected by the bond orders of these molecules.

Uncorrelated calculations yield for the typical C–O single bond in formic acid a bond order of 0.84, which has to be compared with a bond order of 1.5 for C=O double bonds in this molecule and formaldehyde. Although polarity causes substantial deviations from integer values the ratio between the bond orders is close to two. Contrary to the classical Lewis structure, where a triple bond has been assigned to the CO molecule, we observe a bond order very close to typical double bonds. Placing a $Na^+$ ion on the side of the C atom reduces the polarity of the bond and causes a slight increase of the bond order. Another case where the calculated bond order is lower than conventionally expected is the $CO_2$ molecule. Instead of a double bond we obtained a bond order of 1.2 that is halfway between a single and double bond. In accordance with the qualitative theory of charge fluctuations, incorporation of electron correlation always reduce bond orders. We refer to Fulde's monograph [18] for a detailed discussion of the subject. Single bonds are reduced by $\approx 0.13$ orders whereas double bonds are affected much

**Table 1** Correlation effects on CO and neighbouring bonds for selected small molecules

| Molecule | Atom | $\langle \hat{N}_A \rangle_{\text{PDMC}}$ | Pair | $\mathcal{B}^{\text{HF}}_{A,B}$ | $\mathcal{B}^{\text{PDMC}}_{A,B}$ | $\Delta\mathcal{B}_{A,B}$ |
|---|---|---|---|---|---|---|
| $H_2CO$ | H | 0.99(1) | H,C | 0.90(1) | 0.76(1) | 0.14(2) |
| | C | 2.96(1) | C,O | 1.51(1) | 1.17(1) | 0.34(2) |
| | O | 7.06(1) | | | | |
| HCOO′H′ | H | 0.86(1) | C,H | 0.86(1) | 0.71(1) | 0.15(2) |
| | C | 2.56(1) | C,O | 1.48(1) | 1.14(1) | 0.34(2) |
| | | | C,O′ | 0.84(1) | 0.72(1) | 0.12(2) |
| | O | 6.98(1) | | | | |
| | O′ | 7.16(1) | O′,H′ | 0.66(1) | 0.57(1) | 0.09(2) |
| | H′ | 0.45(1) | | | | |
| $CO_2$ | C | 1.51(2) | C,O | 1.20(1) | 1.04(3) | 0.16(4) |
| | O | 7.25(2) | | | | |
| CO | C | 2.67(1) | C,O | 1.56(1) | 1.28(1) | 0.28(2) |
| | O | 7.33(1) | | | | |
| $Na^+$ CO | C | 2.91(1) | C,O | 1.71(1) | 1.40(1) | 0.31(2) |
| | O | 7.05(1) | | | | |

Average number of valence electrons in atomic domains $\langle \hat{N}_A \rangle_{\text{PDMC}}$ and bond orders between pairs of atoms $\mathcal{B}^{\text{PDMC}}_{A,B}$ have been obtained from PDMC calculations. The correlation effects on the bond order $\Delta\mathcal{B}_{A,B}$ have been obtained by comparison with corresponding HF bond orders $\mathcal{B}^{\text{HF}}_{A,B}$. Statistical errors on the last digit are given in parenthesis

**Table 2** Same as Table 1 but for small molecules containing C and S atoms

| Molecule | Atom | $\langle \hat{N}_A \rangle_{\text{PDMC}}$ | Pair | $\mathcal{B}^{\text{HF}}_{A,B}$ | $\mathcal{B}^{\text{PDMC}}_{A,B}$ | $\Delta\mathcal{B}_{A,B}$ |
|---|---|---|---|---|---|---|
| $H_2CS$ | H | 0.96(1) | H,C | 0.98(1) | 0.82(2) | 0.16(3) |
| | C | 4.58(1) | C,S | 2.08(1) | 1.44(1) | 0.64(2) |
| | S | 5.50(1) | | | | |
| HCSS′H′ | H | 0.87(1) | H,C | 0.93(1) | 0.76(1) | 0.17(2) |
| | C | 4.59(1) | C,S | 1.88(2) | 1.34(2) | 0.54(4) |
| | | | C,S′ | 1.28(2) | 0.95(2) | 0.33(4) |
| | S | 5.70(1) | | | | |
| | S′ | 5.78(1) | S′,H′ | 1.07(1) | 0.90(2) | 0.17(3) |
| | H′ | 1.05(1) | | | | |
| $CS_2$ | C | 5.36(1) | C,S | 2.05(2) | 1.49(3) | 0.56(5) |
| | S | 5.32(2) | | | | |
| CS | C | 4.84(1) | C,S | 2.81(3) | 1.87(2) | 0.94(5) |
| | S | 5.16(1) | | | | |
| $Na^+$ CS | C | 4.77(1) | C,S | 2.74(2) | 1.83(2) | 0.91(4) |
| | S | 5.14(1) | | | | |

stronger and decrease by ≈ 0.32 orders. Again a noticeable exception is the $CO_2$ molecule where the correlation effect is comparatively weak.

For comparison we have also studied bond orders for CS bonds where an analogous set of molecules with O replaced by S has been considered. The polarity of the bonds is reversed in this case as can be seen from the number of valence electrons in the atomic domains of C and S atoms listed in Table 2. Within the atomic domains of C atoms we found between 4.6 and 5.4 electrons, whereas between 5.1 and 5.8 electrons could be assigned to S atoms. This means that the absolute atomic charges are much smaller than in the corresponding O containing molecules.

Due to the weak polarity of the CS bonds, the Mayer and Ángyán definition of bond order is much closer to its classical counterpart. The calculated uncorrelated bond order of 1.3 for the C–S single bond in dithioformic acid is somewhat larger, while the bond order of 2.8 for a triple bond in the CS molecule is slightly smaller than the bond orders derived from the classical Lewis structures. For double bonds almost perfect agreement between the calculated uncorrelated and classical bond orders has been observed. In contrast to $CO_2$, the bonds in the $CS_2$ molecule behave like ordinary double bonds. Taking into account electron correlation we obtain much stronger effects on the bond orders than for the corresponding molecules containing O atoms. For thioformaldehyde and dithioformic acid the reduction of the bond order for CS bonds, due to electron correlation, is almost twice as large as for the CO bonds in formaldehyde and formic acid. The reduction of bond order for the $CS_2$ molecule is in agreement with their characterization as double bonds in the uncorrelated calculations. Even three times larger is the reduction of bond order for CS compared to CO molecules. These observations indicate the importance of an accurate treatment of electron correlation. In order to demonstrate the high accuracy of our PDMC calculations, we have shown in Fig. 2, the total amount of correlation energy recovered from PDMC calculations compared with CCSD and CCSD(T) correlation energies obtained with the benchmark basis sets discussed in Sect. 3.

Within the present work, Bader's analysis has been performed for HF electron densities which means that we neglected possible effects of electron correlation on the shape of atomic domains. This is owing to technical difficulties to calculate accurate correlated electron densities and their gradients with QMC or other many-particle methods. In principle DFT provides exact electron densities, however, in practice there exists a whole zoo of functionals and the qualitiy of the corresponding electron densities are hard to guess.

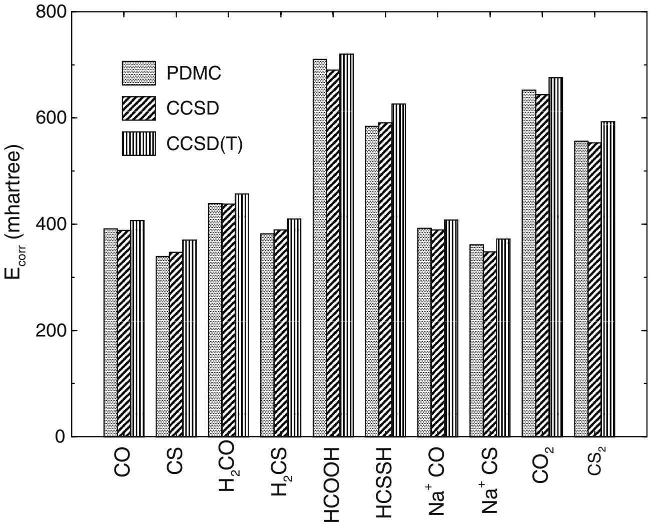

**Fig. 2** Comparison of correlation energies from CCSD, CCSD(T) and PDMC calculations. Absolute values of the correlation energy $E_{\text{corr}}$ (mhartree) are shown for various molecules under consideration. The CCSD and CCSD(T) calculations have been performed with the benchmark bases

In order to get an idea about the magnitude of this correlation effect, we have studied the CO and CS molecule with atomic domains from DFT electron densities using the B3LYP exchange-correlation functional. It is well known that electron correlation plays an important part in the chemical bonding of these molecules. The number of electrons assigned to the C atom is slightly increased by $\approx 0.2$ electrons, which indicates that the zero-flux surface is shifted towards the O (S) atom for these molecules. Concerning the bond order we observed only a minor increase of $\approx 0.1$ orders for both molecules. This is considerably smaller than the total effect of electron correlation which is $\approx 0.3$ and 0.9 orders for CO and CS, respectively.

As we have already mentioned in Sect. 1.2, a main objection against the definition of bond order via charge fluctuations [16] is the presence of non-vanishing bond orders between classically non-bonded atoms. Some of these non-classical bond orders are shown in Fig. 4 for formaldehyde, formic acid and their sulphur analogous. Indirect exchange paths via intermediate atoms perhaps give rise to these non-classical bond orders. In contrast to bond orders between classically bonded atoms, these bond orders are in some cases slightly enhanced through electron correlation. Concerning their magnitude, there seems to be almost no difference between the oxygen and sulfur compounds. The largest non-classical contributions appear in $CO_2$ and $CS_2$, where correlated bond orders of 0.25 have been observed between the two oxygen and sulfur atoms.

It is tempting to study possible correlations between bond orders and bond lengths for these molecules. In Fig. 3 we have plotted bond orders versus bond lengths for CO and CS bonds. For both kinds of bonds a linear dependence between bond order and bond length seems to reproduce the data reasonably well except the $CO_2$ molecule. This can be seen from Fig. 4 where straight lines are fitted to our data excluding the $CO_2$ molecule. Inclusion of electron correlation seems to improve somewhat the linear fit, whereby a slight flattening of the straight lines can be observed. In order to be taken serious, these correlations, however, require further studies on much larger sets of molecules.

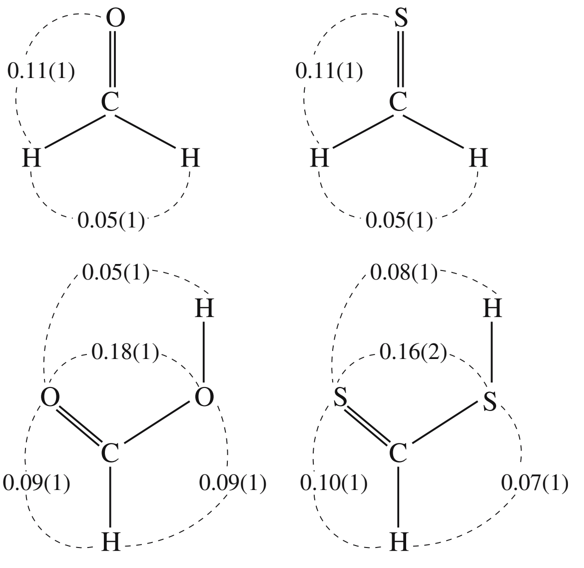

**Fig. 3** Bond orders between classically non-bonded atoms from PDMC calculations. Statistical errors on the last digit are given in *parenthesis*

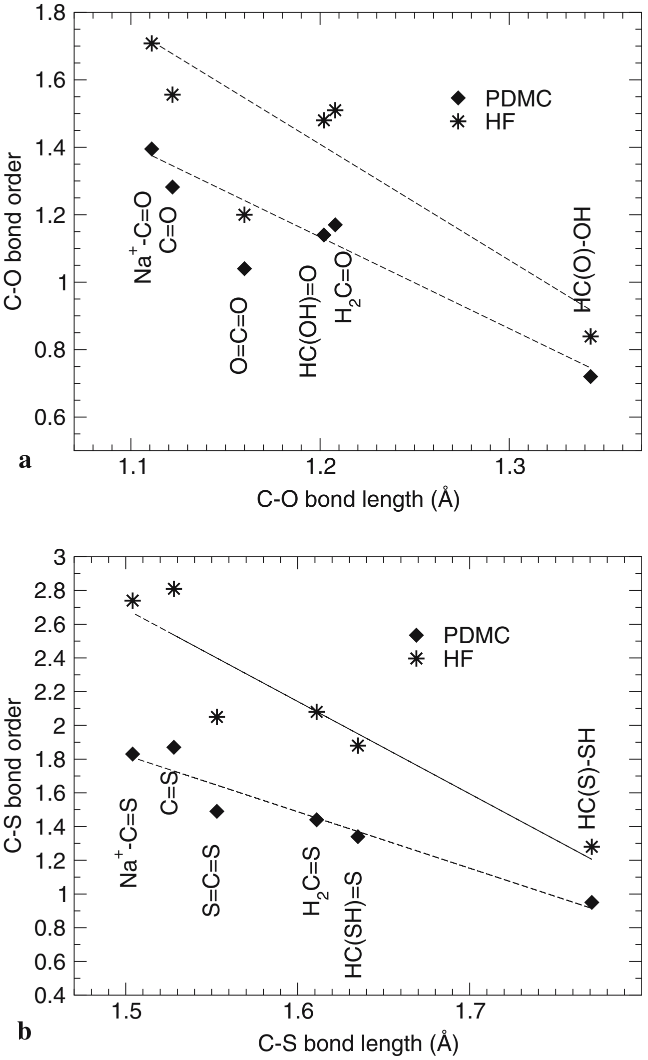

**Fig. 4** Bond order of CO and CS bonds versus equilibrium bond length for selected small molecules. The correlated bond orders have been obtained from PDMC calculations. *Straight lines* are fitted to the correlated and uncorrelated bond orders. The $CO_2$ molecule has been excluded from the fits

## 5 Conclusions

The usefulness of Lewis structures is due to the fact that they provide a simple interpretation of experimental data, e.g. bond lengths, vibrational frequencies or mean bond enthalpies, in terms of single, double and triple bonds. However, correlations between bond order and these properties have only qualitative character. They are further obscured by an obvious ambiguity of the model, i.e. if several resonance structures are required for the description of a chemical bond. More quantitative models avoid possible ambiguities for systems with several resonance structures and are in good agreement with the classical Lewis model for system that can be described by a single Lewis formula. An obvious drawback of such models is the loss of simplicity compared with Lewis structures that leads to a considerable computational effort. In order to study the suitability of a quantitative model it is important to perform calculations with the highest possible accuracy. However, the prospect to obtain refined and possibly quantitative correlations between bond order and experimental data outweigh this disadvantage. Within the present work we focused on a concept of bond order based on charge fluctuations with respect to atomic domains. The model requires the computation of expectation values with respect to complicated spatial domains. QMC offers the possibility to calculate these expectation values for highly accurate correlated wavefunctions with reasonable computational costs. Our results emphasize the significance of an accurate treatment of electron correlation. This has been demonstrated for CO and CS bond orders, the latter are in nice agreement with the Lewis model on the HF level of theory. Incorporation of electron correlation reduces these bond orders on the average by 18 and 30%, respectively. Contrary to this, bond orders between classically non-bonded atoms are partly enhanced by electron correlation. We have studied possible correlations between our calculated bond orders and bond lengths. It turned out that an almost linear dependency can be observed for these bonds, which actually improves by incorporation of electron correlation.

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## References

1. Lüchow A, Anderson JB (2000) Annu Rev Phys Chem 51:501
2. Foulkes WMC, Mitas L, Needs RJ, Rajagopal G (2001) Rev Mod Phys 73:33
3. Scemama A, Chaquin P, Caffarel M (2004) J Chem Phys 121:1725
4. Scemama A (2005) J Theor Comp Chem 4:397
5. Savin A (2002) In: Sen KD (ed) Reviews of modern quantum chemistry: a celebration of the contributions of Robert G. Parr. World Scientific, Singapore, p 43
6. Cancès E, Keriven R, Lodier F, Savin A (2004) Theor Chem Acc 111:373
7. Gallegos A, Carbó-Dorca R, Lodier F, Cancès E, Savin A (2005) J Comp Chem 26:455
8. Bader RFW (1995) Atoms in molecules, a quantum theory. Oxford University Press, Oxford
9. Bader RFW, Stephens ME (1975) J Am Chem Soc 97:7391
10. Mayer I (1983) Int J Quantum Chem 23:341
11. Mayer I (1983) Chem Phys Lett 97:270
12. Mayer I (1986) Int J Quantum Chem 29:73
13. Ángyán JG, Loos M, Mayer I (1994) J Phys Chem 98:5244
14. Ponec R (1998) Int J Quantum Chem 69:193
15. Ángyán JG, Rosta E, Surján PR (1999) Chem Phys Lett 299:1
16. Fradera X, Austen MA, Bader RFW (1999) J Phys Chem A 103:304
17. Chamorro E, Fuentealba P, Savin A (2003) J Comput Chem 24:496
18. Fulde P (1993) Electron correlations in molecules and solids, 2nd edn. Springer, Berlin Heidelberg New york
19. Mödl M, Dolg M, Fulde P, Stoll H (1996) J Chem Phys 105:2353
20. Ziesche P (1999) In: Gonis A, Kioussis N, Ciftan M (eds) Electron correlations and materials properties. Kluwer/Plenum, New York, p 361
21. Ziesche P, Tao J, Seidl M, Perdew JP (2000) Int J Quantum Chem 77:819
22. Ziesche P (2000) J Mol Struct (Theochem) 527:35
23. Schautz F, Flad H-J, Dolg M (1998) Theor Chem Acc 99:231
24. Wang Y, Flad H-J, Dolg M (2000) Phys Rev B 61:2362
25. Becke AD, Edgecombe KE (1990) J Chem Phys 92:5397
26. Savin A, Nesper R, Wengert S, Fässler TF (1997) Angew Chem Int Ed Engl 36:1808
27. Lewis GN (1916) J Am Chem Soc 38:762
28. Gillespie RJ, Popelier PLA (2001) Chemical bonding and molecular geometry: from Lewis to electron densities. Oxford University Press, Oxford
29. Chesnut DB (2001) Chem Phys 271:9
30. Ponec R, Uhlik F (1997) J Mol Struct (Theochem) 391:159
31. Ponec R, Duben AJ (1999) J Comput Chem 20:760
32. Ponec R, Roithová J (2001) Theor Chem Acc 105:383
33. Ponec R, Carbó-Dorca R (1999) Int J Quantum Chem 72:85
34. Fulton RL (1993) J Phys Chem 97:7516
35. Fulton RL, Mixon ST (1993) J Phys Chem 97:7530
36. Kohout M (2004) Int J Quantum Chem 97:651
37. Caffarel M, Claverie P (1988) J Chem Phys 88:1088; ibid 88:1100
38. Hammond BL, Lester WA Jr, Reynolds PJ (1994) Monte Carlo methods in ab initio quantum chemistry. World Scientific, Singapore
39. Assaraf R, Caffarel M, Khelif A (2000) Phys Rev E 61:4566
40. Langfelder P, Rothstein SM, Vrbik J (1997) J Chem Phys 107:8525
41. Schautz F, Flad H-J (1999) J Chem Phys 110:11700
42. Flad H-J, Savin A (1995) J Chem Phys 103:691
43. Fuentealba P, Preuss H, Stoll H, v Szentpaly L (1982) Chem Phys Lett 89:418
44. Bergner A, Dolg M, Kuechle W, Stoll H, Preuss H (1993) Mol Phys 80:1431
45. Dunning TH Jr (1989) J Chem Phys 90:1007
46. Woon DE, Dunning TH Jr (1993) J Chem Phys 98:1358
47. Peterson KA, Woon DE, Dunning TH Jr (1994) J Chem Phys 100:7410
48. Linde DR (ed) (1996) Handbook of chemistry and physics, 77th edn. CRC, Boca-Raton
49. Werner H-J, Knowles PJ, Amos RD, Bernhardsson A, Berning A, Celani P, Cooper DL, Deegan MJO, Dobbyn AJ, Eckert F, Hampel C, Hetzer G, Korona T, Lindh R, Lloyd AW, McNicholas SJ, Manby FR, Meyer W, Mura ME, Nicklass A, Palmieri P, Pitzer R, Rauhut G, Schütz M, Schumann U, Stoll H, Stone AJ, Tarroni R, Thorsteinsson T. MOLPRO is a package of ab initio programs
50. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JA Jr., Stratmann RE, Burant JC, S. Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Cioslowski J, Ortiz JV, Baboul AG, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Gonzalez C, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Andres JL, Gonzalez C, Head-Gordon M, Replogle ES, Pople JA (1998) Gaussian 98, Revision A.7, Gaussian Inc., Pittsburgh
51. Program DGrid, version 2.3, Max Planck Institute for Chemical Physics of Solids, Dresden (2002)
52. Program Basin, version 2.3, Max Planck Institute for Chemical Physics of Solids, Dresden (2002)