ADDITIONS AND CORRECTIONS

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Tapas Kar, János G. Ángyán, and A. B. Sannigrahi*: Comparison of ab Initio Hartree−Fock and Kohn−Sham Orbitals in the Calculation of Atomic Charge, Bond Index, and Valence

Page 9954. In Table 1, the correct value of the entry in the 4th column against HCl is 0.258.

Page 9955. The following footnote has to be added to Table 2: The four values of I_{AB} from top to bottom against each bond correspond to MPA, LPA, NPA, and AIM, respectively.

Page 9959. Equation 6 should read

$$\sum_{\mathrm{A}} N_{\mathrm{A}}^{(3)} + \sum_{\mathrm{A<B}} N_{\mathrm{AB}}^{(3)} + \sum_{\mathrm{A<B<C}} N_{\mathrm{ABC}}^{(3)} = N' + \sum_{\mathrm{A<B<C}} N_{\mathrm{ABC}}^{(3)} = N$$

Page 9961. The Appendix contains numerous typographical errors. The correct version follows:

The most general definition of atomic charge and 2c and 3c bond indices invokes the atomic population operator, $\hat{N}_{\mathrm{A}}$, corresponding to various population analysis (PA) schemes. Second quantization formalism allows us to write these operators in a particularly compact form. In the case of the orthogonal Löwdin and NAO basis sets, we can express $\hat{N}_{\mathrm{A}}$, the electronic population operator of atom A, as

$$\hat{N}_{\mathrm{A}}(\mathrm{LPA,NPA}) = \sum_{i\in\mathrm{A}} \psi_i^+ \psi_i^- \tag{8}$$

where ψ_i^+ and ψ_i^- are creation and annihilation operators for either the Löwdin or the NAO basis set. The atomic Mulliken population operator is defined as

$$\hat{N}_{\mathrm{A}}(\mathrm{MPA}) = \sum_{i\in\mathrm{A}} \chi_i^+ \tilde{\chi}_i^- \tag{9}$$

where χ_i^+ and $\tilde{\chi}_i^-$ form a pair of anticommutating creation and annihilation operators, and the biorthogonal basis $\tilde{\chi}$ is related to the original nonorthogonal AO basis set by the transformation $\tilde{\chi} = \chi S^{-1}$, where S is the AO overlap matrix. Finally, the second-quantized form of the AIM atomic population operator is

$$\hat{N}_{\mathrm{A}}(\mathrm{AIM}) = \sum_{ij} S_{ij}^{\mathrm{A}} \phi_i^+ \phi_j^- \tag{10}$$

where ϕ_i are the molecular orbitals and S_{ij}^{A} is the atomic overlap matrix.

For closed-shell molecules described by a single-determinant wave function the working expressions for atomic charge (q_{A}), 2c bond index (I_{AB}), and 3c bond index (I_{ABC}) are given by

$$q_{\mathrm{A}} = Z_{\mathrm{A}} - \sum_a D_{aa}^{\mathrm{A}} \tag{11}$$

$$I_{\mathrm{AB}} = \sum_a \sum_b D_{ab}^{\mathrm{A}} D_{ba}^{\mathrm{B}} \tag{12}$$

$$I_{\mathrm{ABC}} = \sum_a \sum_b \sum_c D_{ab}^{\mathrm{A}} D_{bc}^{\mathrm{B}} D_{ca}^{\mathrm{C}} \tag{13}$$

Here Z_{A} is the atomic number of A and D_{ab}^{A} denotes a kind of generalized atomic density matrix, which satisfies

$$\sum_{\mathrm{A}} D_{ab}^{\mathrm{A}} = D_{ab} \tag{14}$$

and is specific to the PA scheme. For the different schemes we have

$$D_{ab}^{\mathrm{A}}(\mathrm{MPA}) = \begin{cases} \sum_k P_{ak} S_{kb} & \text{if } a \in \mathrm{A} \\ 0 & \text{if } a \notin \mathrm{A} \end{cases} \tag{15}$$

$$D_{ab}^{\mathrm{A}}(\mathrm{LPA}) = \begin{cases} \tilde{P}_{ab} & \text{if } a \in \mathrm{A} \\ 0 & \text{if } a \notin \mathrm{A} \end{cases} \tag{16}$$

$$D_{ab}^{\mathrm{A}}(\mathrm{NPA}) = \begin{cases} \tilde{\tilde{P}}_{ab} & \text{if } a \in \mathrm{A} \\ 0 & \text{if } a \notin \mathrm{A} \end{cases} \tag{17}$$

$$D_{ab}^{\mathrm{A}}(\mathrm{AIM}) = \sum_k P_{ak} S_{kb}^{\mathrm{A}} \tag{18}$$

where P is the AO density matrix, S is the AO overlap matrix, $\tilde{P} = S^{1/2} P S^{1/2}$ is the density matrix in the Löwdin orthogonalized AO basis, $\tilde{\tilde{\mathrm{P}}}$ is density matrix in the (orthogonal) natural atomic orbital (NAO) basis, and S_{ab}^{A} is the atomic overlap matrix. In the case of $D_{ab}^{\mathrm{A}}(\mathrm{AIM})$ usually the molecular orbital (MO) basis is used

$$D_{ij}^{\mathrm{A}}(\mathrm{AIM}) = n_i S_{ij}^{\mathrm{A}} \tag{19}$$

Orbital valence (V_i) and orbital bond index $(I_{\mathrm{AB}})_i$ are calculated using the expanded form of the **D** matrix in eq 12 and the following relations:

$$\sum_i^{\mathrm{occ}} V_i = V_M = \frac{1}{2} \sum_{\mathrm{A}} V_{\mathrm{A}} = \frac{1}{2} \sum_{\mathrm{A}} \sum_{\mathrm{B}\neq\mathrm{A}} I_{\mathrm{AB}} \tag{20}$$

and

$$I_{\mathrm{AB}} = \sum_i^{\mathrm{occ}} (I_{\mathrm{AB}})_i \tag{21}$$

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