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COMMENTS

Comment on "Chemoselectives in Acetalization, Thioacetalization, Oxathioacetalization and Azathioacetalization"

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The recent paper by Roy and co-workers[1] relies on the use of the Hirshfeld and Mulliken population analyses to obtain atom condensed Fukui functions. In eqs 6a−6c, Roy et al. express that the $p_k(N)$ and analogs for the molecular ions are the Hirshfeld populations[2] of the *k*th atom in the molecule (AIM). This commonly used approach to computing Hirshfeld based atom condensed Fukui functions is debatable and some important questions should be raised. First, the Hirshfeld AIM weight functions and thus AIM populations are arbitrary by choosing some promolecular density function. This means that when a different promolecule is chosen, other AIM populations will appear and as such another model of understanding chemical reactivity in terms of these descriptors may result. Our recent Hirshfeld-I algorithm[3,4] allows obtaining nonarbitrary self-consistent Hirshfeld charges, as originally suggested by Davidson et al.[5] The resulting charges differ substantially from classical Hirshfeld charges (see below for an example). They allow computing unique atomic charges in molecules but also molecular ions, independent of the promolecule chosen in the first step.[3,4]

Another important problem is that of using the same weight function for computing AIM populations in a neutral molecule and its ionic counterparts as done for atom condensed Fukui functions. Yang and Mortier introduced these as changes in AIM populations between the molecule and the molecular ions.[6] It is important to stress that they used the Mulliken approach, which is not a coincidence. Taking as an example eq 6a from Roy et al. and taking into account the normalization requirements of the information theory background of the Hirshfeld AIM,[7,8] one has

$$f_k^+(\mathbf{r}) = \int w_k^{\mathrm{H}}[(N+1),\mathbf{r}]\,\rho_{\mathrm{mol}}^{N+1}(\mathbf{r})\,\mathrm{d}\mathbf{r} - \int w_k^{\mathrm{H}}[N,\mathbf{r}]\,\rho_{\mathrm{mol}}^{N}(\mathbf{r})\,\mathrm{d}\mathbf{r} \qquad (1)$$

where we show explicitly that, in the Hirshfeld method, the Hirshfeld weight functions w_k^{H} *have to* depend on the normalization of the molecular (ionic) density. If not, one cannot connect the Hirshfeld AIM to information theory. The Mulliken approach, used by Yang et al. to introduce atom condensed Fukui functions does not suffer this problem,[6] because, as long as one uses the same basis set for all molecular (ionic) calculations, the projection operator over basis functions remains the same.[9] The computational implementation of eqs 6a−6c by Roy et al. apparently uses the same weight function for $p_k(N)$ and $p_k(N-1)$, which is inappropriate if one assumes validity of $p_k(N) - p_k(N-1)$ as the atom condensed f_k^- Fukui function in their eq 6b and the p_k are electronic populations obtained from integration of the AIM density.

TABLE 1: Carbonyl Carbon Atom Charges in *p*-Hydroxybenzaldehyde Using Different AIM Methods (HF/6-31G) for the Neutral Molecule (q_k^N), Cation (q_k^{N-1}), and the Atom Condensed Fukui Function $f_k^- = p_k(N) - p_k(N-1)$**

	q_k^N	q_k^{N-1}	f_k^-
Mulliken	0.4090	0.3690	−0.0400
Hirshfeld	0.1729	0.1718	−0.0011
Hirshfeld-I	0.6180	0.3919	−0.2261

As an example, we compare in Table 1 Mulliken, Hirshfeld, and Hirshfeld-I charges on the carbonyl carbon atom in *p*-hydroxybenzaldehyde (vis a vis Table 1 in Roy et al.).

The very large difference between the Hirshfeld and Hirshfeld-I charges is reminiscent of the finding of Cioslowski et al.[10] who also noticed the large differences in Bader's AIM charges in formaldehyde when computing different atomic basins in the molecule and ion or using the same basins. Given the quite large differences obtained when using properly derived, nonarbitrary Hirshfeld charges, one should take care when confronting the Mulliken and Hirshfeld techniques. These problematic aspects of the Hirshfeld approach influence strongly the chemical reactivity models in the study of Roy et al.

References and Notes

(1) Roy, R. K.; Bagaria, P.; Naik, S.; Kavala, V.; Patel, B. K. *J. Phys. Chem. A* **2006**, *110*, 2181.
(2) Hirshfeld, F. L. *Theor. Chim. Acta.* **1977**, *44*, 129.
(3) Bultinck, P. *Farad. Discuss.* **2007**, *135*, 244−246.
(4) Bultinck, P.; Van Alsenoy, C.; Ayers, P. W.; Carbó-Dorca, R. *J. Chem. Phys.*, in press.
(5) Davidson, E. R.; Chakravorty, S. *Theor. Chim. Acta* **1992**, *83*, 319.
(6) Yang, W.; Mortier, W. *J. Am. Chem. Soc.* **1986**, *108*, 5708.
(7) Nalewajski, R. F.; Parr, R. G. *Proc. Natl. Acad. Sci. U.S.A.* **2000**, *97*, 8879.
(8) Parr, R. G.; Ayers, P. W.; Nalewajski, R. F. *J. Phys. Chem. A* **2005**, *109*, 3957.
(9) Carbó-Dorca, R.; Bultinck, P. *J. Math. Chem.* **2004**, *36*, 201.
(10) Cioslowski, J.; Martinov, M.; Mixon, S. T. *J. Phys. Chem.* **1993**, *97*, 10948.

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