

Annotatio

Comment on a Paper by Stout and Politzer

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Stout and Politzer [1] presented an analysis of atomic charges in molecules using various definitions of the charge on an atom, one of which (labeled the Modified Mulliken definition) was

$$Q_r = \sum_k N_k \left[\sum_m \left(C_{km}^2 + \sum_{n \neq m} 2F_{mnk} C_{km} C_{kn} S_{mn} \right) \right], \quad (1)$$

where

$$F_{mnk} = C_{km}^2 / (C_{km}^2 + C_{kn}^2).$$

The claim is also made that for this definition of F_{mnk} , (1) reduces to a definition for Q_r given by Ros and Schuit [2],

$$Q_r = \sum_k N_k \left[\sum_m \left(C_{km}^2 / \sum_n C_{kn}^2 \right) \right], \quad (2)$$

where the index n runs through all orbitals of the basis set.

It can be shown by simple but lengthy matrix arguments that:

a) Q_r as given by (1) is invariant neither to unitary transformations among degenerate molecular orbitals nor to unitary transformations of basis orbitals on r , and is thus not useful as a definition of atomic charge.

b) (1) does not reduce to (2), which does possess the desired invariance properties.

The tables presented by Stout and Politzer used formula (2) for the Modified Mulliken entries [3], so the tables stand as published if it is understood that the Modified Mulliken definition refers to (2) rather than (1).

References

1. Stout, E. W., Jr., Politzer, P.: Theoret. chim. Acta (Berl.) **12**, 379 (1968).
2. Ros, P., Schuit, G. C. A.: Theoret. chim. Acta (Berl.) **4**, 1 (1966).
3. Politzer, P.: Private communication.

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