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A Note on the Importance of Including Monoatomic Overlap Densities in the Calculation of CNDO/2 Charge Distributions

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It is demonstrated that in the calculation of CNDO/2 charge density distributions the monoatomic overlap densities necessarily must be taken into account. Otherwise electron densities are obtained which are not invariant to molecular rotations and generally of wrong symmetry.

The valence electron density [1] of a closed shell molecule in the LCAO MO approximation is

$$\varrho = \sum_{\mu\nu} P_{\mu\nu} \phi_\mu \phi_\nu \tag{1}$$

where ϕ_μ and ϕ_ν are the valence basis AO's and $P_{\mu\nu}$ the elements of the density matrix. In the framework of the CNDO/2 method [1] (1) may be applied in two approximate forms both in accordance with the CNDO/2 normalization procedure: (i) by neglecting diatomic but retaining monoatomic overlap densities

$$\varrho = \varrho_{\mathrm{D}} + \varrho_{\mathrm{OD}}\,, \tag{2}$$

$$\varrho_{\mathrm{D}} = \sum_{\mu} P_{\mu\mu} \phi_\mu^2\,, \tag{2a}$$

$$\varrho_{\mathrm{OD}} = 2 \sum_{A} \sum_{\mu<\nu} P_{\mu\nu} \phi_\mu \phi_\nu \tag{2b}$$

where ϱ_{D} is due to the diagonal ($P_{\mu\mu}$) and ϱ_{OD} to the monoatomic off-diagonal ($P_{\mu\nu}$) matrix elements (overlap densities) and (ii) by neglecting both mono- and diatomic overlap densities

$$\varrho = \varrho_{\mathrm{D}} \tag{3}$$

In previous work [2–5] on CNDO/2 calculations of molecular multipole moments the inclusion of monoatomic overlap densities (application of (2)) was found essential for obtaining meaningfull results. However, in a recent paper [6] dealing with CNDO/2 and EH [7] charge densities Boyd applied (3) in the CNDO/2 case. In this communication we compare electron density maps of the hydrogen fluoride (HF) molecule obtained from (2) and (3). As the simple example shows the application of (3) is not allowed.

We assume the HF molecule lying in the xy plane of a Cartesian coordinate system: In case (a) with its bond axis parallel and in case (b) at an angle of 30° to the x-axis. Fig. 1 shows the density plots [8] for case (a) and Fig. 2 for case (b).

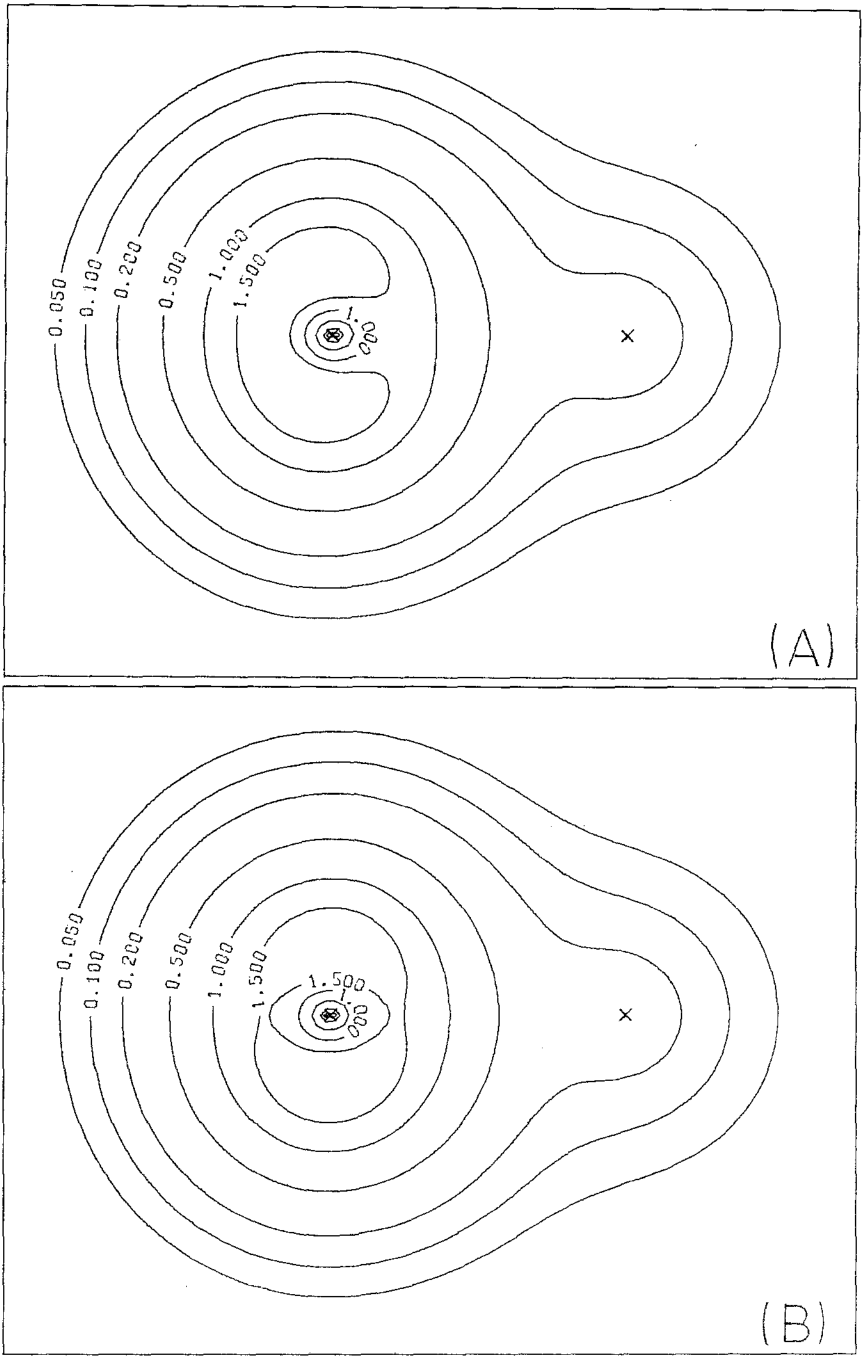

Fig. 1. Plots of the CNDO/2 densities [in a.u.] for the HF molecule lying with its molecular axis parallel to the x-axis (case (a) of the text). Map (A) was obtained from Eq. (2) (neglecting diatomic but retaining monatomic overlap densities) and map (B) from Eq. (3) (neglecting both mono- and diatomic overlap densities)

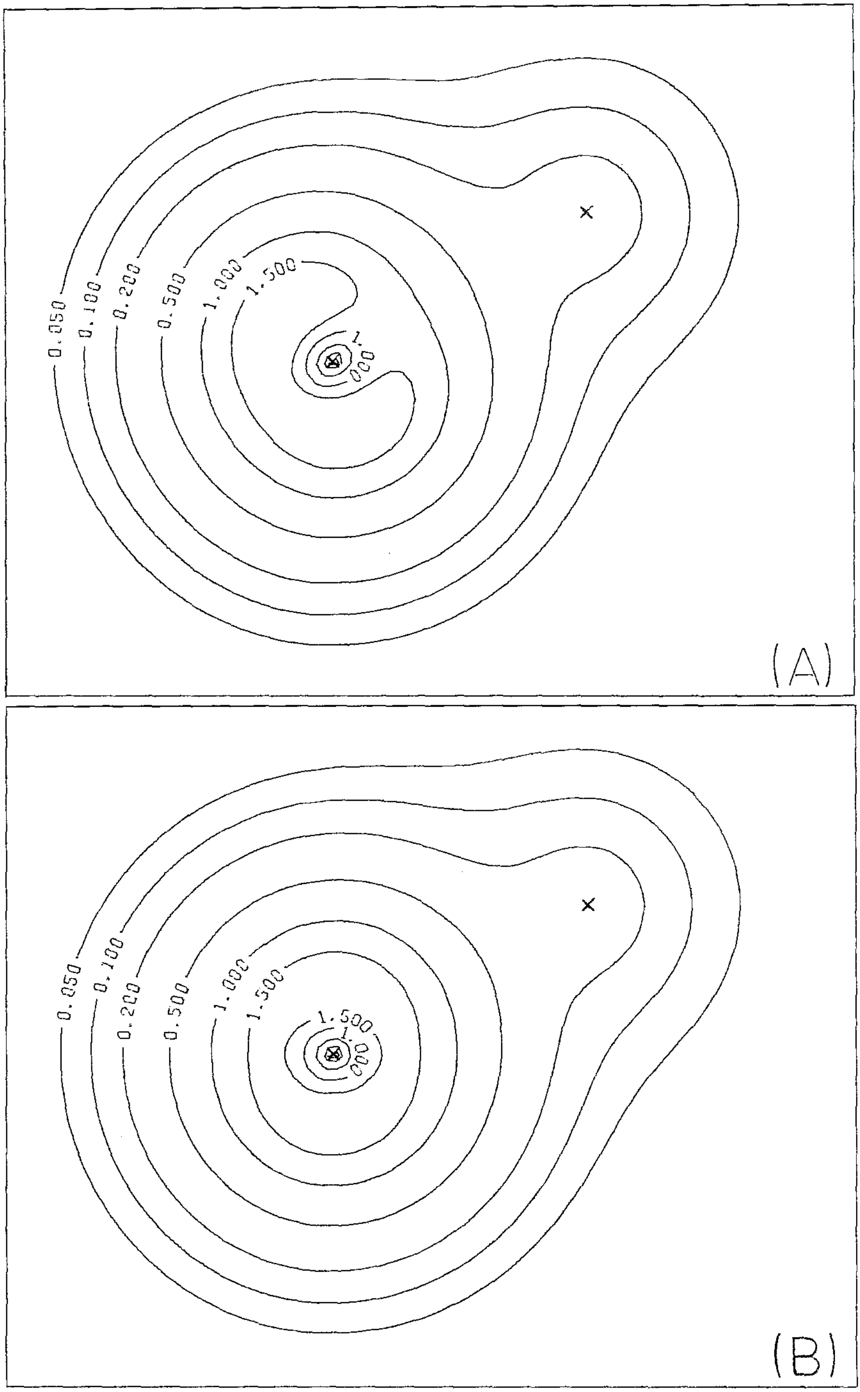

Fig. 2. Plots of the CNDO/2 densities [in a.u.] for the HF molecule lying at an angle of 30° to the x-axis (case (b) of the text). Maps (A) and (B) refer to the densities computed from Eqs. (2) and (3), respectively

As we see the density obtained from (3) is – opposite to the density obtained from (2) – not invariant to the molecular rotation and in the case (b) not symmetric to the molecular axis. Hence by neglecting monoatomic overlap densities wrong (physically unsound) CNDO/2 electron densities are produced.

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8. The density plots have been obtained with a CALCOMP-Plotter in conjunction with the TR 4 Computer of the Zentrale Rechenanlage der Philipps-Universität, Marburg/Lahn. For the method for computing and plotting contour lines, see: Hahn, H., Radloff, J.: Elektron. Rechenanl. **14**, 128 (1972).

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