

On the Representation of ZDO MO Electron Densities with Correct Nodal Properties

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It is shown that ZDO MO electron densities (including monoatomic differential overlap or not) have incorrect nodal properties. This deficiency is overcome by taking diatomic overlap densities into account which implies renormalization of the MOs.

The one electron density of a LCAO MO ψ_i ,

$$\psi_i = \sum_{\mu} c_{i\mu} \Phi_{\mu} \quad (1)$$

in general is

$$\rho_i = \sum_A \rho_i^A + \sum_{A \neq B} \rho_i^{AB} \quad (2)$$

with

$$\rho_i^A = \sum_{\mu} c_{i\mu}^2 \Phi_{\mu}^2 + \sum_{\mu \neq \nu} c_{i\mu} c_{i\nu} \Phi_{\mu} \Phi_{\nu} \quad (3)$$

and

$$\rho_i^{AB} = \sum_{\mu} \sum_{\nu} c_{i\mu} c_{i\nu} \Phi_{\mu} \Phi_{\nu}. \quad (4)$$

ρ_i^A and ρ_i^{AB} are the density contributions from atom A and atom pair AB, respectively. $\Phi_{\mu}(c_{i\mu})$ and $\Phi_{\nu}(c_{i\nu})$ refer to valence basis AOs (AO expansion coefficients).

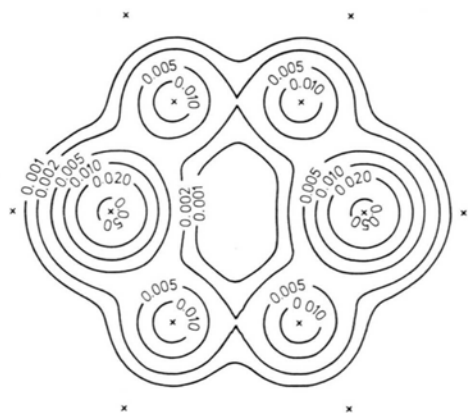


Fig. 1. Plot of the CNDO/2 density [in a.u.] (neglecting diatomic overlap) of one of the two highest occupied π MOs of benzene. Contours are drawn in a plane parallel to the molecular plane and 0.615 a.u. above it.

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In a previous paper¹ we showed that in calculating ZDO valence electron densities the monoatomic overlap densities [contained in the second term of (3)] must be retained; otherwise the produced densities are not rotationally invariant. Below we demonstrate that diatomic overlap densities [contained in (4)], too, must be taken into account; otherwise MO densities with incorrect nodal properties are obtained.

Figure 1 shows the CNDO/2² density of one member of the degenerate highest occupied π MO pair of benzene. Obviously the node does not appear. This can be seen immediately: The only contributions to the π MO density are the (positive) π AO densities of the C-atoms [see first sum in (3)].

This deficiency should be overcome by taking into account all terms of the squared MO, that means not only the monoatomic overlap terms in (3) but also the diatomic overlap terms in (4): A node in the MO, then of course, would appear in its density, too [due to negative terms in (4)].

The inclusion of diatomic overlap, however, implies — opposite to the inclusion of monoatomic overlap only — a renormalization of the ZDO MOs. A suitable method for renormalization — used on the CNDO/2 (INDO) level by several authors^{3–6} — is the Löwdin transformation⁷. Figure 2 displays the electron density of the Löwdin transformed π MO including diatomic overlap. As expected the node now does appear.

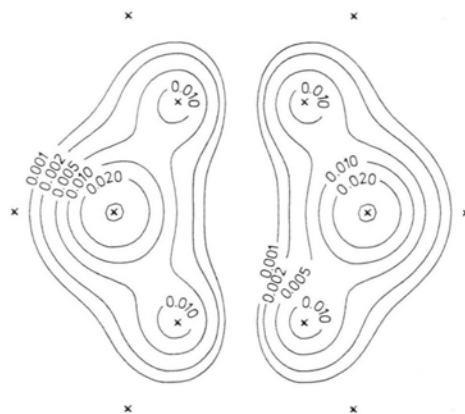


Fig. 2. Plot of the CNDO/2 density [in a.u.] after renormalization by the Löwdin transformation (including diatomic overlap) of one of the highest occupied π MOs of benzene. Contours are drawn in a plane parallel to the molecular plane and 0.615 a.u. above it.

Acknowledgements

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