New approximation for the third-order reduced density matrix

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There has been renewed interest in the calculation of multicenter bond indices based on reduced density matrices (RDM).[1-12] Multicenter indices have been employed in a number of situations such as the analysis of conjugation and hyperconjugation effects,[7] to identify agostic bonds,[8] to account for electron distributions in molecules[4-5] or to study aromaticity in both organic[10] and all-metal compounds.[11-12] The general formula of the multicenter index involves the intuitive *n*-order central moment of the electron population used in probability theory:[13,14]

$$D(A_1,\ldots,A_n) \sim \left\langle \left(\hat{N} - \overline{N}\right)^n \right\rangle_{A_1,\ldots,A_n},$$

which depends on the *n*-order reduced density matrix (*n*-RDM). The calculation of the *n*-RDM is overwhelmingly expensive for correlated wavefunctions and, therefore, the studies of multicenter indices available in the literature have used at most the 3-RDM. In this talk we analyze different multicenter indices suggested in the literature, which depend either on the corresponding *n*-RDM or their approximation in terms of lower-order densities. We also suggest new approximations for the *n*-RDM, which we use in the calculation of three-center bond indices.[15] Our formula for the 3-RDM provides more accurate three-center indices than the approximation suggested by Valdemoro.[16-17]

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