New stringent conditions for the cumulant matrix

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In this work we suggest new conditions that the second-order cumulant matrix of a molecular system should fulfill. These conditions are easy to compute and provide a means to check the spin structure of the cumulant matrix and, therefore, of the reduced second-order density matrix. To this aim, we use the decomposition of the local spin, previously developed in our laboratory,[1-2] and the number of electrons shared at the dissociation limit of homonuclear diatomic molecules to provide stringent conditions that the cumulant part of the pair density should attain. These new conditions are tested on a series of natural orbital functionals known as Piris natural orbital functionals (PNOF).[3-8] Despite PNOF cumulants fulfills Q, P and G conditions and provide the correct total $\langle S^2 \rangle$ value, no PNOF cumulant attains the newly developed conditions. These new stringent conditions can be used to guide the construction of natural orbital functionals as well as other functionals based on the second-order cumulant matrix.

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