Local Orbitals for Quasi-Degenerate Systems

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A CAS-SCF algorithm based on molecular orbitals that conserve their physical character during the iterative process has been developed in our group [1,2]. The method is based on the iterative partial diagonalization of the one-body density matrix, obtained from a Configuration Interaction restricted to the space of single excitations from the CAS. When localized guess orbitals are used, the locality property is conserved for the final orbitals. This localization technique is particularly suitable for the treatment of quasi-degenerate systems, since it can be applied to those cases that cannot be correctly described at SCF level. Moreover, the use of localized orbitals for CAS-SCF or post CAS-SCF calculations permits a fine control on the *nature* of the active orbitals. In this way, it is possible to include in the active space only those orbitals that are strictly required by the nature of the studied phenomenon.

For large systems, the use of localized active orbitals leads to a huge reduction of the computational effort, and permits MR-CI treatments that would be out of the possibilities of the standard delocalized approaches. An application of this method to the study of the $Na+C_{60}$ system is presented and discussed [3].

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[3] J-V. Pitarch, S. Evangelisti, and D. Maynau, J. Mol. Strucyt (THEOCHEM) **681**, 203 (2004); J-V. Pitarch, S. Evangelisti, and D. Maynau, J. Chem. Theory and Computation, in press.