Multireference Perturbation Theory: the *n*–electron Valence State Perturbation Theory Approach

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A few general considerations concerning Multireference Perturbation Theory (MRPT) approaches are firstly reported, focusing in particular on the concepts of contraction (internal and external), of quasi-degeneracy (actual and artificial), and of first order interacting space. As a particular case of MRPT method, the *n*–electron Valence State Perturbation Theory (NEVPT) is described in some details clarifying its main properties and focusing on the interpretation of the energies appearing in the perturbation denominators in terms of physical processes taking place in the active space. Finally, the problems arising in MRPT in presence of a correlation-induced relaxation of the molecular orbitals (also called Brueckner effect in the Coupled Cluster field) are shortly discussed, using the singlet $\pi \rightarrow \pi^*$ excited state of the ethylene molecule as an example.

References

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