An efficient intruder-free Fock space multireference coupled cluster method in the studies of excited states

Monika Musiał

University of Silesia in Katowice, Institute of Chemistry,
Szkolna 9, 40-006 Katowice, Poland

In the current work we focus on the Fock space (FS) realization of the multireference (MR) coupled cluster (CC) theory and its application in the studies of the electronic structure. The key point is the Intermediate Hamiltonian (IH) formulation [1] which offers an easy way to replace the iterative solution of the standard Bloch equation by the direct diagonalization of the properly constructed matrix ('dressed' $\bar{H}$ called IH) within the CBE (Canonical Bloch Equation) scheme [2]. Thanks to this we can omit all problems with the so-called intruder states which for years have blocked the wider application of this method. The new concept [2] opened the door to use large model spaces and to include higher operators into the cluster expansion. Majority of the results are connected with the solution of the FS problem in the two-valence sectors [3]. Developing and having access to various realizations of the FS-CC approaches (EE - excitation energy, IP - ionization potential, EA - electron affinity, DIP - double ionization potential, DEA - double electron affinity, TEA - triple electron affinity, etc.) we propose a new computational strategy to calculate excited states of systems (AB), i.e. we adopt one of the uncharged or charged analogues (AB, AB^-, AB^+, AB^{2-}, AB^{2+}, AB^{3+}, ...) as a reference, which form a closed-shell system, avoiding the UHF (Unrestricted Hartree-Fock) reference. This strategy offers a very simple route for calculations of EEs for the open-shell systems.

References

[1] L. Meissner, *J. Chem. Phys.*, **108**, 9227 (1998); M. Musiał, L. Meissner, S. A. Kucharski, R. J. Bartlett, *J. Chem. Phys.*, **122**, 224110 (2005).

[2] M. Musiał, R. J. Bartlett, *J. Chem. Phys.*, **129**, 134105 (2008).

[3] M. Musiał, R. J. Bartlett, *J. Chem. Phys.*, **129**, 044101 (2008); M. Musiał, *J. Chem. Phys.*, **136**, 134111 (2012).