Fock space multireference coupled cluster method in the studies of the electronic structure of atoms and molecules

Monika Musiał

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

A generalization of the coupled cluster (CC) theory [1] to the the multireference (MR) formalism [2-4] opened a new field of the possible applications of the standard CC approach. In this communication we focus on the Fock space (FS) realization of the MR theory and its applications to studies of the electronic structure. The classic formulation of the FS-CC theory based on the Bloch equation is plagued with the divergence problems caused by the intruder states. A crucial remedy for this has been introduced by Meissner [5] by developing intermediate Hamiltonian (IH) formalism. The latter concept opened the door to using large model spaces and to inclusion of higher operators into the cluster expansion. The results obtained within the one-valence sectors (0,1) and (1,0) are equivalent to those computed with the properly defined equation-of-motion (EOM) scheme, hence they can be classified as belonging to the EOM family. So, the true MR results are connected with the solution of the FS problem in the two-valence sectors (0,2), (1,1), (2,0) and higher ones. The IH approach made it possible to obtain excitation energies for relatively large basis sets for a number of small molecules. An inclusion of the full triples both into expansion of the T and S operators in the (1,1) sector resulted in a significant improvement of the agreement of the excitation energy with the experimental data. On the the other hand, encouraging results are obtained in the studies of the dissociation of a single bond with the FS solution based on the (2,0) sector. Remarkably results are obtained also in the calculations of the potential energy curves for the alkali metal diatomics.

1. J. Cizek, *J. Chem. Phys.*, **45**, 4256 (1966).
2. B. Jeziorski, H. J. Monkhorst, *Phys. Rev. A*, **24**, 1668 (1981).
3. A. Haque, D. Mukherjee, *J. Chem. Phys.*, **80**, 5058 (1984).
4. D. Mukherjee, S. Pal, *Adv. Quantum Chem.*, **20**, 292 (1089).
5. L. Meissner, R. J. Bartlett, *J. Chem. Phys.*, **102**, 7490 (1995).