New Developments in the Multireference Brillouin-Wigner Coupled Cluster Method

Jiří Pittner

J. Heyrovský Institute of Physical Chemistry,
Academy of Sciences of the Czech Republic,
Dolejškova 3, 18223 Prague 8, Czech Republic

The MRBWCCSD method has been shown to yield reasonably accurate results for systems where the static correlation plays a role [1,2]. However, in order to obtain quantitative agreement with experiment, more accurate treatment of dynamic correlation is mandatory. Analogously to the single-reference case, this can be achieved by extension of the cluster operator to include connected triples. Since the full iterative state-specific MRBWCCSDT method is computationally prohibitive for all except smallest systems, we have recently developed a non-iterative approximation, analogous to the single-reference CCSD(T), which reduces the scaling to n^7 in a single step. The inclusion of connected triples is performed via corrections to matrix elements of the effective Hamiltonian similarly as in the state-universal MR CCSD(T) approach by Balková and Bartlett [3]. The MRBWCCSD(T) method has been assessed on the low-lying electronic states of the oxygen molecule, yielding very similar values of spectroscopic constants as the full iterative one. We have also applied the method to larger, chemically interesting systems, previously treated at the MRBWCCSD level.

The MRBWCC method has so far been limited by the requirement of complete model space. Recently, Li and Paldus [4] have proposed how to generalize the state-universal Hilbert space MRCC to an incomplete model space. Since we have shown previously [5] that the Brillouin-Wigner and "traditional" Rayleigh-Schrödinger Hilbert space MRCC formalism may be related to one another by a continuous transformation, it turns out that the technique of C-conditions [4] can also be exploited in the Brillouin-Wigner MRCC method. We have implemented the MRBWCCSD method for general incomplete model space within the ACES2 program and made numerical tests on small molecules. Employing the C-conditions, the MRBWCC methods preserve their important properties, valid in the complete model space [5], also in the general (incomplete) model space. In particular, with the iterative size-extensivity correction the energy is additive for a system composed of non-interacting subsystems. However, the effective Hamiltonian still contains disconnected terms, and the method thus does not fulfill the "generalized extensivity" requirement as formulated by Nooijen and Mukherjee [7].

In analogy to the Method of Moments (MM) approach suggested by Kowalski and Piecuch for MR RSCC [8], and employing the continuous transition between RSCC and BWCC [5], we have formulated the MM correction for the MRBWCC method, which, in principle, can recover the FCI energy from the MRBWCC one [9]. Based on a formula for MRCC moments derived in [8], we have found an equivalence between two related formulations of the Hilbert space MRCC at the Rayleigh-Schroedinger limit [9].

[1] Pittner J., Nachtigall P., Čársky P., Hubač I.: J. Phys. Chem. **A 105**, 1354–1356 (2001)
[2] Čársky P., Hubač I, Mach P., Pittner J., Wilson S.: *Brillouin-Wigner expansions in quantum chemistry* in Progress in theoretical chemistry and physics vol. 12, Advanced topics in theoretical chemical physics, pp. 71–118, Kluwer (2003) and references therein
[3] Balkova A., Bartlett R.J., *J. Chem. Phys.*, **101**, 8972 (1994).
[4] Li X., Paldus J.: *J. Chem. Phys.*, **119**, 5320 (2003); **120**, 5890 (2004).
[5] Pittner J., *J. Chem. Phys.*, **118**, 10876 (2003).
[6] Pittner J., Li X., Paldus J.: *Mol. Phys.*, **103**, 2239 (2005).
[7] Nooijen M., Shamasundar K., Mukherjee D.: *Mol. Phys.*, **103**, 2277 (2005)
[8] Kowalski K. and Piecuch P., *J. Mol. Struct.* **547**, 191 (2001).
[9] Pittner J., Kowalski K., and Piecuch P.: to be published.