Internally Contracted Multi-Reference Coupled-Cluster Theory

M. Hanauer, A. Köhn
Institut für Physikalische Chemie, Universität Mainz, 55099 Mainz, Germany

For single-reference systems, coupled-cluster theory provides a hierarchy of methods with systematically increasing accuracy and is hence one of the keystones for quantitative quantum chemistry [1]. However, the generalization of the coupled-cluster ansatz to multi-reference systems (e.g. biradicals, transition metal compounds) is still an open question and to date no agreement on the most promising route has been reached [2].

The internally contracted multi-reference coupled-cluster (icMRCC) approach was originally suggested by Banerjee and Simons in the early 80s[3], but was only implemented and tested for the special case of commuting cluster operators. Recently, the approach has been further investigated by several groups [4,5]. Modern tools like automated implementation schemes help to deal with the rather complex set of equations of the full ansatz and allow a rigorous analysis of its capabilities. In particular, our implementation scheme [5] shows the correct scaling with system size and allows for applications to ‘real-life’ examples.

In this contribution, I will shortly review some technical aspects (orbital invariance, construction of the operator manifold, approximation schemes, see also [5,6]) and show how to arrive at an icMRCCSD(T) method [7]. The use of the scheme is demonstrated for a set of sample calculations, including ozone, Ni$_2$O$_2$ and the ring-opening reaction of azirines.