Internally Contracted Multi-Reference Coupled-Cluster Theory

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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_2O_2 and the ring-opening reaction of azirines.

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[2] see e.g. Jeziorski, Monkhorst, *Phys. Rev. A* 24, 1668 (1981), Mahapatra, Datta, Mukherjee, *J. Chem. Phys.* 110, 6171 (1999), Hanrath, *J. Chem. Phys.* 123, 084102 (2005); Nooijen, Shamasundar, *Collect. Czech Chem. Comm.* 70, 1082 (2005); Evangelista, Gauss, *J. Chem. Phys.* 133, 044101 (2010); for a recent review, see Lyakh, Musiał, Lotrich, Bartlett, *Chem. Rev.* 112, 182 (2012)

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