Towards a multireference coupled-cluster method based on a unitary transformation

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The application of a unitary transformation to be able to describe a set of strongly interacting real particles as a set of weakly interacting quasi-particles is a frequently used tool in the many-body theory. Our aim is to adapt such a transformation in the multireference coupled-cluster (MRCC) framework. The main idea behind the new method is to use a unitary transformation which allows to describe a set of orthogonal basis functions – showing multirefence (MR) character – by single determinants. The elements of the MR basis are defined by the solutions of complete active space (CAS) problems and one element of the MR basis is the reference CAS function itself. Using this unitary transformation quasi-particle operators ($\hat{Q}$) are defined. These operators allow us to represent the CAS reference function or any other elements of the MR basis in a determinant-like form, $|\Phi_{\mathrm{CAS}}\rangle = \hat{Q}_n^+ \ldots \hat{Q}_2^+ \hat{Q}_1^+ |\rangle$, where the quasi-particle creation and annihilation operators satisfy the fermion anti-commutation relations. On the basis of these quasi-particles a possible generalization of the normal ordered operator products for MR problem can be introduced.

As a consequence of the formal simplicity of the reference function, the definition of an MRCC approach on the unitary transformed basis is straightforward and this approach retains several beneficial properties of the single reference CC approach. On the other hand we have to handle two obvious difficulties, namely the ambiguity of the definition of the unitary transformation and the more than two particle nature of the Hamiltonian expressed through the quasi-particles.

Test results for small systems are presented using a pilot implementation of our method. The results are compared to the MRCC theory originally published by Oliphant and Adamowicz [J. Chem. Phys 94 (1991) 1229] and later generalized by Piecuch and co-workers [J. Chem. Phys 99 (1993) 1875 , J. Chem. Phys 110 (1999) 6103], which is reminiscent of our approach in the sense that in both methods the single reference CC framework is applied in the MRCC context.