Application and development on the internally contracted Multireference Coupled-Cluster Theory

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INTRODUCTION

The internally contracted multireference coupled-cluster method (icMRCC) is a promising tool to describe chemical systems with strong static correlation effects with the accuracy of an exponential *ansatz*. However, due to the complexity of the working equations, only recently this method became feasible. In the present work we show the application of the icMRCC method to the F + HCl reaction and the development of a multi-state extension of the theory.

METHODS

The icMRCC method is based on the *ansatz* $|\Psi\rangle = e^T \sum_\mu c_\mu |\Phi_\mu\rangle = e^T |\Psi_0\rangle$. The reference wave function, $|\Psi_0\rangle = \sum_\mu c_\mu |\Phi_\mu\rangle$, is of a CAS type for a selected electronic state, upon which the cluster operator, T, acts. The equations are obtained by a procedure similar to the single-reference case, but an orthogonalization procedure is needed to eliminate linear dependencies in the excitation manifold. This process is the main difficulty of the method and a procedure that leads to a size extensive theory was proposed by our group[1].

The implementation of the icMRCC approach is carried out using the *General Contraction Code* (GeCCo) to automated generate the equations. The orbitals and required integrals are calculated with the DALTON and Molpro codes.

RESULTS AND DISCUSSION

The application of the icMRCC theory to the reaction F + HCl showed a much better agreement to experimental values for the exothermicity and transition state energy than the MRCI method[2]. This leads us to the development of a potential energy surface for this reaction, obtained scaling an MRCI-based PES to reproduce the transition state geometry and energy calculated with icMRCC. Contrary to the original PES, the newly developed surface is able to correctly describe the experimental vibrational distribution for the products of this reaction.

We also propose a multi-state extension of the icMRCC theory, able to describe situations of quasi-degeneracy. The current approach treats each state in a separate calculation, controlling the target state through the reference wave function. This makes the convergence of the equations for excited states very difficult in near-degeneracy situations. The developed approach deals with this problem solving the coupled residual equations for several states. The results show that accuracy can be obtained without relaxing the reference coefficients, what is not true for the state-specific case.

CONCLUSIONS

Among the several multireference coupled-cluster theories, the icMRCC method keeps the desired features from the single reference case and it has been showing very accurate results. The present work shows the application of this theory on a system whose chemical dynamics is not satisfactorily described by standard methods. A large effort is also being done on extensions of the current approach and a multi-state procedure is being developed.

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[1] M. Hanauer and A. Köhn, J. Phys. Chem. A, 134, 204111 (2011);
[2] A. Li, H. Guo, Z. Sun, J. Kłos and M. H. Alexander, Phys. Chem. Chem. Phys., 15, 15347 (2013).