New methods applicable to dissociation of the single bond based on the multireference coupled cluster theory

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It is a well known fact that the standard quantum chemical methods encounter some difficulties in the correct description of the dissociation process, i.e. in the accurate reproduction of the experimental potential energy curves (PECs). In the typical homolytic dissociation of the single bond we come upon the situations where the closed shell molecule (AB) dissociates into the open shell fragments ($AB \rightarrow A^{\bullet} + B^{\bullet}$) hence using the RHF (restricted Hartree-Fock) function as a reference in the whole range of interatomic distances is unjustified. The remedy for this is a replacement of the neutral AB molecule with its double positive (example: Li_2^{+2}) or double negative (example: F_2^{-2}) ions dissociating into the closed shell fragments.

In order to recover the wave function for the original neutral system we have to use the methods which correctly describe the process of attaching (e.g., to Li_2^{+2}) of removing (e.g., from F_2^{-2}) two electrons.

For that case we have developed the intermediate Hamiltonian (IH) Fock space (FS) coupled cluster (CC) scheme for the (2,0) and (0,2) sectors which describe double electron attached and doubly ionized states. This first scheme, (FS-CC (2,0)), is particularly advantageous in the studies of the potential energy curves for the alkali metal dimers and the second, (FS-CC (0,2)), for the interhalogen diatomics

In the current work we study the potential energy curves of the lithium dimer, F_2 and HF molecules. In all cases we were able to compute the smooth PECs for the whole range of interatomic distances from equilibrium to the dissociation limit. The other advantage of the approach is its rigorous size-extensivity allowing to reproduce the atomic excitation energies at the infinite interatomic distance.