

# An intruder-free Fock-space multireference coupled cluster method in studies of the dissociation of chemical bond

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A main difficulty in the correct description of a homolytic dissociation of the bond is the fact that the considered system is well represented by a single-determinantal reference around the equilibrium but requires a multi-determinantal approach in the dissociation limit. A desired treatment would be a possibility to redefine the reference in such a way that both the equilibrium and bond-stretched situations would correspond to the closed-shell structure. The ideal candidate for such a solution seems to be the Fock space (FS) coupled cluster approach. Why?

Because this size-extensive scheme has a built-in capability to provide - by selecting a proper FS sector - the correlated results for altered (with respect to the Hartree-Fock (HF) reference) number of electrons. E.g., the FS( $m,0$ ) sector produces results pertaining to the system with  $m$  electrons added to the HF function. Assuming that we take the neutral molecule as a HF reference these results would correspond to the  $m$ -tuply negative anion. We may take advantage of this capability of the FS approach to choose - at the HF level - such a reference which will have a convenient property to dissociate into the closed shell fragments and to generate a smooth curve in the whole region of interatomic distances, keeping in mind that by selecting a proper sector of Fock space we will recover the original structure which we want to study.

Focusing on the potential energy curves generated with the (1,0), (2,0) and/or (3,0) sector of FS we may indicate a number of diatomics which upon removal of two or three electrons from a neutral structure dissociating into the closed shell fragments. The precise knowledge of the interatomic potential for diatomics composed of alkali and alkaline-earth metal elements is crucial, e.g., in the design of the synthesis of molecules in the ultra-low temperatures.

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