

Ab initio computation and representation of potentials for open shell complexes

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In 1998 John Doyle and co-workers succeeded in trapping the $\text{CaH}(^2\Sigma^+)$ molecule with the buffer gas cooling method. In this experiment the molecules were thermalized in a magnetic trap with cold ^3He to 0.4 K. The efficiency of the process depends on the elastic, rovibrationally inelastic, and spin-flipping transition rates. To model this process a three-dimensional He-CaH interaction potential was computed [1] with the partially spin restricted open shell single and double excitation method with perturbative triples [RCCSD(T)]. The application of this potential in scattering calculations will be presented in the talks of Roman Krems and Balakrishnan. Here the computation and representation of the potential will be discussed. Other systems for which the potentials were constructed by a similar approach are $\text{O}_2(X^3\Sigma_g^-)\text{-He}$ [2] and $\text{NH}(X^3\Sigma^-)\text{-He}$ [3].

When an open-shell complex involves a spatially degenerate fragment a single surface description is not adequate. It will be shown how in this case the proper expansions of the multiple diabatic potentials correlating with the degenerate fragment state can be derived from the requirement that the potential energy operator is invariant under rotation and inversion. The recently computed $\text{CO}(a^3\Pi)\text{-He}$ [4], $\text{F}(^2P)\text{-H}_2$ [5], and $\text{Cl}(^2P)\text{-HCl}$ [6] systems will be given as examples of systems that are described by multiple potential energy surfaces. To assess the accuracy of the potentials dynamical calculations are required to allow comparison with experimental data. The results of the computation of the frequencies and intensities of bound-bound and bound-free transitions in the singlet-triplet excitation spectrum of CO-He will be shown and a suggestion is made for an experiment that may detect this transition. The photodissociation of this complex can be considered as a half-collision induced by a spin-flip.

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