SAPT in reactive collisions: the case of SH2+ system

The astrochemistry of sulphur is very important in the context of life formation. In particular the presence of SH+ system is important in locating the photodissociation regions in interstellar medium [1]. However, the abundances of sulphur hydrides are still not properly understood. To address this problem the kinetics of chemical reactions involving ionic and neutral sulphur hydrides should be investigated in more details. This project focuses on the interactions and dynamics in chemical reaction SH+ + H -> S+ + H2

The reactive potential energy surfaces are very difficult to obtain using the ab-initio methods based on the choice of active spaces. Their fundamental problem is a proper description of the dissociation limit, due to the lack of size consistency (the sum of energies of noninteracting subsystems is not the energy of super-system). The widely used supermolecular calculations rely on the cancellation of the errors in the dimer energy and the monomer energies, to eliminate the basis set superposition error (BSSE). Given the lack of size consistency such error cancellation do not occur. The most troublesome of the calculation of PES are the fragments corresponding to asymptotic regions, where reactants or product are far apart.

In this project we will perform the pilot calculations of most challenging parts of the potential energy surface of SH2+ system by exploiting the open-shell symmetry adapted perturbation theory (SAPT) [2]. The great advantage of SAPT method is that it precisely describes the asymptotic region of the interaction and the connection between asymptotic region and van der Waals minimum. The interaction energy is obtained with no subtraction whatsoever, hence is free from (BSSE). It properly describes the dynamic correlation effects, in particular the dispersion energy.

In the final and initial state we deal with the interaction of SH+ ion (in the $\llbracket ^3 \rrbracket$ $^-$ state) with the hydrogen atom, and the S+ (in 4S state)+ H2 reaction. Both interactions are suitable for SAPT, since they involve single reference reactants and products (H,H2, S+ and SH+). The interacting species are not very strongly polarizable; hence we predict no problems with the convergence of SAPT in the second order. The behavior of the interaction energy upon the stretching the bond of interacting monomer is rather unknown, hence we will perform some cross-comparisons with existing ab-initio methods such as MRCI or completely-renormalized coupled cluster calculations. It is particularly challenging to describe the interaction on multiple spin surfaces (in this case quartet and doublet) which happens for the case of SH+ and the hydrogen atom. Recently developed spin-flip formalism can cope with such case and will provide us invaluable information about the spin-exchange interaction.

The SAPT method was never tested for systems which react, and quite possibly one can establish more general protocol for providing the accurate parts of potential surfaces for any reactions.

In the next step we plan to perform the dynamical calculations of the SH++H collision in detail for the exchange and destruction product channels. The final state distributions for some selected initial ro-vibrational quantum number of reactant molecule will be calculated and these data will be important for astrophysical modelling of the title molecule. Total and state-to-state reaction and inelastic rate constant will be calculated in a low temperature and these data should contribute to the SH+ detection in space. For all the dynamic calculation we will implement an accurate wave packet method developed by Roncero and coworkers [3,4].

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