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Theoretical studies of charge recombination reactions

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Abstract:

This thesis is based on theoretical studies that have been done for low-energy reactions involving small molecular systems. It is mainly focusing on mutual neutralization of oppositely charged ions and dissociative recombination of molecular ions. Both reactions involve highly excited electronic states that are coupled to each other. Employing electronic structure methods, the electronic states relevant to the reactions are computed. It is necessary to go beyond the Born-Oppenheimer approximation and include non-adiabatic effects. This non-adiabatic behaviour plays a crucial role in driving the reactions. Schemes on how to go about and include these coupling elements are discussed in the thesis, which include computations of non-adiabatic and electronic couplings of the resonant states to the ionisation continuum.

The nuclear dynamics are studied either semi-classically, using the Landau-Zener method or quantum mechanically, employing the time-independent and time-dependant Schr̈odinger equations. Reactions studied here are mutual neutralization in collision of H^++H^-, where both the semi-classical and quantum mechanical methods are employed. Total and differential cross sections are computed for all hydrogen isotopes. We also perform quantum mechanical studies of mutual neutralization in the collision of He^++H^-. For this system not only the non-adiabatic couplings among the neutral states have to be considered, but also the electronic coupling to the ionization continuum. Worth noting in the two systems is that reactants and the final products belong to different electronic states, which a coupled together, hence for the reaction to take place there must be non-adiabatic transition.

Lastly, the direct mechanism of dissociative recombination of H_2O^+ is studied. Here time-dependant quantum mechanical methods are employed and the dissociation cross section is computed.