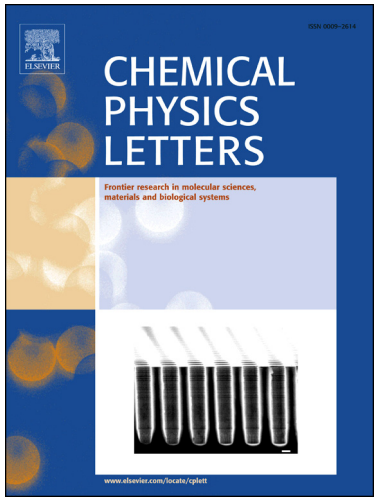

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Atom-Triatom Rigid Rotor Inelastic Scattering with the MultiConfiguration Time Dependent Hartree approach

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Abstract

The inelastic scattering between a rigid rotor triatomic molecule and an atom is described within the frame of the MultiConfiguration Time dependent Hartree (MCTDH) method. Sample calculations are done on the H_2O-Ar system for which a flexible 6D PES (used here in the rigid rotor approximation) has been recently computed in our group and will be presented separately. The results are compared with corresponding time independent calculations using the Arthurs and Dalgarno approach and confirm as expected the equivalence of the two methods.

Keywords: Quantum dynamics, Inelastic scattering, Time-Dependent, Close-coupling

1. Introduction

Collisional (vibrational and rotational) energy transfer has a central role in chemical and physical studies of atomic and molecular species. From a fundamental standpoint, scattering studies are often used concurrently with spectroscopy to identify signatures of atoms and molecules in various environments. Scattering dynamics govern transport processes and both reactive and non-reactive scattering are important in kinetics. The importance of vibrational energy transfer[1] is well known for processes such as combustion, laser operation, photochemical reactions and even surface etching. Rotational energy transfer is a key process in many astrophysical environments, competing with radiative processes in the interstellar medium, interstellar clouds, and cool planetary atmospheres. Energy transfer mechanisms control the processes of collisional stabilization/activation, maintenance of thermal equilibrium and even pyrolysis, all of which are important to chemical reactivity[2].

The most rigorous approach to obtain information on energy transfer mechanisms is via solution of the quantum mechanical Schrödinger equation for the atom(s) and/or molecule(s) involved in the process. Within the Born Oppenheimer approximation, one usually solves the electronic Schrödinger equation to provide the potential energy surface (PES) on which the dynamics of the nuclei are studied. While for small systems, the electronic structure part is generally solved quantum mechanically, the dynamics of the nuclei are often treated more approximately (classically or semi-classically). A major issue for quantum dynamics calculations is what is known as 'the curse of dimensionality', or very poor scaling. Quantum dynamics calculations of inelastic collisions are typically very computationally costly, and as a result most of the calculations that have been reported for 'heavy-heavy' collisions (beyond the lightest few-electron systems) were only done fully quantum mechanically either for diatomic systems or for polyatomics at very low energy. Most other calculations made use of mixed quantum/classical, semi-classical or even classical approaches to study collisions at higher energies. In this respect, there has recently been a revival of quantum/classical approaches[3] (where the collisional coordinate is treated classically while the internal modes of the collision partners are described quantum mechanically) to study inelastic collisions, aiming to provide reliable estimates of cross-sections and rates for a large range of systems that have not been feasible because of computational limitations. Babikov's results[3] are very impressive even for some light systems that one might assume would require a fully quantum treatment. However, there are still some limitations to mixed quantum/classical methods particularly when resonances are important. The work presented here explores a fully quantum mechanical approach to providing inelastic cross-sections and rates using alternate methods with improved efficiency to describe systems that have been difficult to study because of the computational cost[4].