

Abstract

Multireference coupled cluster method applied to the description of dissociation processes of selected alkali and alkaline earth metal diatomics

Grzegorz Skrzyński, M.Sc.

This doctoral dissertation presents comprehensive theoretical studies of potential energy curves and spectroscopic constants for four diatomic systems composed of alkali metals and/or alkaline earth metals, namely: the *LiRb* molecule and the molecular cations *LiRb*⁺, *LiMg*⁺, and *NaMg*⁺. Describing the dissociation processes of such systems poses computational challenges due to the open-shell nature of the dissociating fragments. Typically, it is not possible to use computational methods based on the spin-restricted Hartree-Fock (RHF) function, while alternative approaches employing the unrestricted Hartree-Fock (UHF) function or the spin-restricted open-shell Hartree-Fock (ROHF) function may lead to problems with convergence.

The main part of the study employs an advanced computational strategy based on the multireference intermediate hamiltonian Fock-space coupled cluster method (IH-FS-CC) formalism in the (1,0) and (2,0) sectors. By adopting as the reference system a multiply positively ionized molecule and then applying the formalism used in the calculations of electron affinity, it becomes possible to obtain closed-shell fragments upon dissociation and to use the RHF reference function across the entire range of internuclear distances. This approach ensures high accuracy due to the size-extensive nature of the IH-FS-CC method, eliminates the problem of intruder states, and allows to describe a large number of electronic states with correlating all electrons. The study includes relativistic effects for the calculated spectroscopic constants by employing Douglas-Kroll third-order (DK3) scalar relativistic corrections.

For the *LiRb*⁺ molecular cation, the ground state and the 10 lowest-lying excited states were analyzed. For the neutral *LiRb* molecule, 22 lowest-energy electronic states were investigated. For the molecular cations *LiMg*⁺ and *NaMg*⁺, 15 and 20 lowest-lying electronic states were determined, respectively. The potential energy curves for each of the computed states are smooth and continuous throughout the entire range of internuclear distances – from equilibrium distances up to dissociation limits.

For all four studied systems for the first time the accurate potential energy curves and spectroscopic constants have been determined for such a large number of electronic states including full electron correlation and without the use of pseudopotentials. The studies on *LiMg*⁺ and *NaMg*⁺ represent the first IH-FS-CC calculations for molecular cations composed of elements of the groups 1 and 2.

The obtained results confirm the effectiveness and adaptability of the IH-FS-CC method in studying diatomic systems composed of alkali and alkaline earth metals – both neutral molecules and molecular cations.