Abstract

Description of the electronic states of the KH and RbH molecules and of their molecular ions based on the multiference coupled-cluster method

The aim of the dissertation is an accurate description of the electronic states for the alkali hydrides and their molecular ions using *ab initio* methods with all electrons correlated. The molecules KH, RbH and their ions: KH^+, RbH^+, KH^-, RbH^- were studied. These systems are interesting also for the experimental research conducted in the ultralow temperatures. However, this kind of experiments requires an access to the accurate potential energy curves. The latter allow to describe vibrational structure, mechanism of the bond breaking and molecular properties.

The studied molecules dissociate into open-shell parts, while their ions are open-shell systems. This could be an issue, when it comes to choosing a computational method. Consistent calculations of the molecular energy in the wide range of internuclear distances would require using the UHF (Unrestricted Hartree-Fock) method with its well known disadvantages such as a spin contamination or problems with the convergence both at the HF level as well as at the post-HF ones (especially for the large values of R). A solution which allows to use restricted Hartree-Fock (RHF) scheme and to avoid problems generated by the UHF method, is proposed in the current work. Namely, a doubly ionized molecule MeH^{2+} was adopted as a reference followed by using the multireference Coupled Cluster (CC) method formulated in the (2,0) sector of the Fock space (FS). The latter scheme provides results for the system with additional two electrons added to the reference. If as a reference we adopt a neutral system then the FS (2,0) results refer to the double electron affinity. On the other hand, if the reference is a doubly positive ion then the FS (2,0) sector provides results for the neutral molecule. For alkali hydrides the doubly ionized molecule MeH^{2+} dissociates into a cation of alkali metal and a proton. Therefore, the main obstacle to using the closed-shell computational formalism has been removed.

The potential energy curves for cations of the studied hydrides are obtained as results of the calculation within the (1,0) sector. The FS (1,0) sector applies to the situation where a single electron is added to the reference which in the standard approach (when the reference is a neutral molecule) provides the (single) electron affinity. In the current calculations when the double positive ion MeH^{2+} is adopted as a reference the FS (1,0) calculations result in the description of the MeH^+ cation.

Additionally, calculations of the ground state for the negative ions of the studied molecules were also performed with the assumption that the reference system in this case is a double anion MeH^{2-}. In order to obtain the results referring to the single anion MeH^- the (0,1) sector of the Fock space

must be used. Similarly as in the cases of neutral molecules and single cations such a strategy made possible to use the RHF function in the whole range of the interatomic distances.

It is important to realize that when treating the heavier alkali metals, like potassium or rubidium, the relativistic effects are not negligible. Therefore, the latter were taken into account in computations by the DK3 (Douglas-Kroll third order) and/or IOTC (Infinite-Order Two-Component) methods. Method FS-CCSD (2,0), used in the current work for molecules KH and RbH, is a module built-in into the local version of the ACES II and GAMESS computational packages.

It is important to emphasize, that for the studied molecules and their cations the new basis functions were obtained with *even tempered* method. Quality of the latter was tested by calculations of the energy of electronic excitations for potassium, rubidium and hydrogen atoms.

To sum up, for the first time in the literature, the calculations of the potential energy curves for molecules KH, RbH and ions: KH^+, RbH^+, KH^-, RbH^- were done using the multireference coupled cluster method performed within the three sectors of the Fock space: (2,0), (1,0) and (0,1). The nonstandard approach to these calculations allowed to obtain potential energy curves in whole range of internuclear distances and to compute selected spectroscopic constants using RHF function as a reference and avoiding problems with convergence and spin contamination.