On nuclear motions in H_n^+ systems (n = 2, 3, 5)

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Abstract

The new algorithms, methods, and codes developed in quantum dynamics [1] allow to address interesting and occasionally strange phenomena related to the motions of the nuclei of molecules exhibiting large-amplitude motions perhaps over several minima. The motions and the related high-resolution spectroscopy of the H_n^+ systems are simple enough from an electronic structure point of view but are still interesting from a quantum dynamical point of view.

A central question related to the nuclear motion of diatomic molecules is how non-adiabatic effects, the last true hurdle in the way of achieving spectroscopic accuracy in quantum dynamics computations, should be handled. The H_2^+ system offers some insight into this problem via the adiabatic Jacobi corrections (AJC) approach [2,3].

For the parent and the partially deuterated isotopologues of the triatomic molecule H_3^+ an outstanding question is whether for this two-electron system quantum chemistry could provide rovibrational energy levels which would be close in accuracy to the not extremely accurate high-resolution measurements. The answer is not a clear yes but more like a maybe [4,5,6] and the results and the remaining difficulties are discussed.

Finally, H_5^+ and its deuterated isotopologues serve as an example of molecules exhibiting several strongly coupled large amplitude motions [7]. It is shown how to handle such situations effectively and what are the difficulties one faces and how one can attempt to solve them.

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