A COMPLETE CONSIDERATION OF NON-ADIABATIC EFFECTS (UP TO ORDER M^{-2}, M=REDUCED NUCLEAR MASS) IN A TRIATOMIC MOLECULE: INFLUENCE ON THE ROVIBRATIONAL ENERGIES OF H_3^+.

RALPH JAQUET, *Theoretical Chemistry, University Siegen, 57068 Siegen, Germany*

For a triatomic molecule (like H_3^+) it is already problematic to calculate with spectroscopy accuracy *all* rovibrational transitions < 16000 cm^{-1}.

Our main focus is the investigation of the influence of non-adiabaticity on the rovibrational bound states of H_3^+. For this purpose a full configuration interaction (FCI) treatment using Gaussian basis functions is applied to calculate the energies of the electronic states as well as all couplings between them caused by the nuclear motion.

These *'derivative couplings'* were evaluated up to second order by means of a perturbation treatment using the 'some-over-states'-strategy. While this has been possible already for diatomics, e.g. H_2^+, H_2, etc., nothing equivalent has been available for H_3^+. The present work [1] is an extension of the investigation of earlier non-adiabatic investigations based on first derivative couplings of electronic states that led to the *concept of geometry-dependent effective nuclear masses* [2] needed for only *one single potential energy surface* [3, 4, 5, 6]. Our new implementation allows to include for the first time also for H_3^+ all non-adiabatic effects (*coupling of second-derivatives, and second-derivatives with first-derivatives*) up to the order of μ^{-2}, μ being the reduced nuclear mass.

These new inclusions of all nonadiabatic effects could reduce also for H_3^+ the deviations to experimental data for most rovibrational levels (< 16000 cm^{-1}) to less than 0.1 cm^{-1} without any empirically adjustable parameters. For H_3^+, the accuracy is slightly improved when also *relativistic and QED effects* are taken into account [7]. For some questionable assignments of observed transitions in H_3^+ we propose a new labeling. In future investigations we are going to analyse non-adiabaticity for triatomics with more than 2 electrons.

[1] R. Jaquet, J. Mol. Spectr., 384, 111585 (2022).
[2] R.M. Herman, A. Ashgarian, J. Mol. Spectr. 19, 305 (1966).
[3] R. Jaquet, M. Khoma, J. Phys. Chem. A, 121, 7016 (2017).
[4] M. Khoma, R. Jaquet, J. Chem. Phys., 147, 114106 (2018).
[5] R. Jaquet, M. Khoma, J. Mol. Phys., 116, 3507 (2018).
[6] M. Khoma, R. Jaquet, J. Math. Chem., 57, 701 (2019).
[7] R. Jaquet, M. Lesiuk, J. Chem. Phys., 152, 104109 (2020).

p-number: p189 **Submitted on Thu, 15 Jun 2023 15:44:13 +0200**