Nonadiabatic investigations of rovibrational frequencies within the systems \( H_2^+ \), \( H_2 \), and \( H_3^+ \): Use of distance-dependent effective masses

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For small hydrogenic systems the discrepancy between theoretical and experimental studies of rovibrational spectra is mostly related to the neglect of adiabatic and nonadiabatic effects on the rovibrational eigenvalues. In case of \( H_3^+ \) and its isotopomers detailed investigations of low lying ro-vibrational excitations have been performed. Using gaussian geminals an absolute accuracy of the Born-Oppenheimer potential energy surface (PES) by \( \sim 0.02 \text{ cm}^{-1} \) was reached. Of similar quality are calculations of relativistic effects and diagonal adiabatic contributions. Non-adiabaticity can be simulated by using atomic masses for vibrational motion and nuclear masses for rotational motion, so that the deviation to experiment can be reduced to a few hundredths of a wavenumber [1].

 Recently, a rigorous non-adiabatic theory in terms of a single potential energy surface had been developed and was tested numerically for \( H_2^+ \) and \( H_2 \) [2]. Within this new non-adiabatic theory distance-dependent effective nuclear masses have to be used. Our main interest is to use these new ideas for taking into account the effects of non-adiabaticity on the rovibrational spectrum of \( H_3^+ \) and its isotopomers. Within a perturbative approach we investigate the influence of the operator of nuclear kinetic energy of a triatomic molecule on the electronic wavefunction. For the asymptotic arrangement of a nearly separated atom - diatomic system we can calculate numerically with high accuracy the distance-dependent effective nuclear masses for \( H_2^+ \) and \( H_2 \). The kinetic energy operator for a triatomic molecule describing ro-vibrational motion has many different terms, where different effective masses have to be taken into account. Within the present work for \( H_2^+ \), the distance-dependent effective mass for the diatomic motion part, using Jacobi coordinates, will be presented.