Nonadiabatic relativistic and QED corrections to rovibrational energy levels of the $X^1\Sigma_g^+$ state of hydrogen molecule istopologues

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Recent advancements in spectroscopic techniques have enabled sub-MHz (1 MHz $\approx 3.3 \cdot 10^{-5}$ cm⁻¹) accuracy for selected rovibrational transitions in H₂ and its isotopologues [1–6]. This new level of precision has revealed minor yet significant differences between measurements and theoretical predictions, presenting a new and severe challenge for theoretical models.

To attain similar accuracy in quantum-mechanical computations, it is essential to fully account for interparticle correlation and finite nuclear mass (recoil) effects in the nonrelativistic, relativistic, and quantum-electrodynamic (QED) energy components. In this communication, we report on the results of such calculations, which have been made possible by the recent discovery of new classes of four-particle integrals [7]. Calculations were performed using the direct nonadiabatic (DNA) approach and the four-body nonadiabatic James-Coolidge (naJC) wave function. The naJC wave function includes coupling between the nuclei's rotational angular momentum and the electronic angular momentum. An effective method for reducing the angular dependence of matrix elements facilitated its use in rotationally and vibrationally excited states [8]. Successful incorporation of recoil effects in the principal energy components resulted in reducing the discrepancies between theoretical predictions and experimental findings.

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