Non-adiabatic, relativistic, and QED corrections to the rovibrational intervals of He_2 ($a\ ^3\Sigma_u^+$) and He_2^+ ($X^+\ ^2\Sigma_u^+$)

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Spectroscopists have been interested in the low-lying electronically excited states of He_2 (the lowest being $^3\Sigma_u^+$, denoted as a) and their cation (ground state $^2\Sigma_u^+$, denoted as X^+) for decades. These excited states are strongly bound compared to the $^1\Sigma_g^+$ ground state and, therefore, have much richer rovibrational spectra. The accuracy of the experiment has improved drastically over the years for this system [1, 2], the uncertainty of measured rotational intervals or vibrational spacings being on the order of $\sim 10^{-4}$ cm^{-1} or even less. At the same time, theoretical predictions lag behind in many respects. While there are recent computations for the rotational-vibrational levels of the cation [3], only older results are available for He_2 a, which show a non-negligible discrepancy with experiment [4, 5, 6].

I present the joint effort of our group towards the accurate computation of rovibrational and fine-structure levels of He_2 a, and improved computations for He_2^+ X^+. Using an explicitly correlated Gaussian basis representation, we computed variationally the non-relativistic Born-Oppenheimer potential energy curves (PEC). Along each PEC, diagonal Born-Oppenheimer correction and non-adiabatic mass corrections [7] were computed, as well as accurate leading-order relativistic and quantum-electrodynamical (QED) corrections using regularization techniques [8, 9, 10, 11, 12]; higher-order QED corrections and nuclear finite size effects were approximately taken into account. Accurate rotational-vibrational energies were found by solving the Schrödinger equation of the nuclei with the corrected PEC. In the case of He_2 a, the magnetic dipole interaction gives rise to zero-field splitting and the fine-structure splitting of rotational energy levels. This splitting was also obtained by computing the relativistic and QED couplings between the $M_S = -1, 0, +1$ components of the He_2 a state.

Our work improves significantly on previous theoretical results for the rotational intervals, as well as the vibrational spacings.When QED corrections are properly taken into account, the computed fine-structure intervals are in similarly excellent agreement with available experimental data [13, 14].

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