Accurate Excited Electronic States of The Helium Dimer Including Relativistic and Adiabatic Effects

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Background The helium dimer serves as an exemplary system for advancing our understanding of few-body physics, high-resolution laser spectroscopy, and the properties of ultracold molecules. The electronic structure of four-electron systems, like He_2, can be calculated with unparalleled accuracy. While previous *in silico* studies have attained a reasonable level of accuracy, they remain insufficient for reliably guiding and interpreting state-of-the-art experiments. The last high-accuracy calculation [1] deviates from the experimental results by approximately 1.5‰, which is still inadequate for making direct comparisons and providing meaningful insights for cutting-edge spectroscopic research. Highly accurate *ab initio* results not only allow for a direct comparison with experimental data but also guide upcoming experiments and pave the way towards the verification of the Standard Model.

Purpose This study aims to achieve benchmark-quality potential energy curves (PECs) with the highest possible accuracy for the few lowest excited states of the helium molecule. We systematically explore these states using various methods and basis sets to provide a reliable estimate of the accuracy of our computations. After incorporating relativistic and adiabatic corrections, we achieve an exceptional level of accuracy, which is essential for guiding ongoing experiments.

Method We utilize an extensive range of molecular electronic structure theory methods, including coupled cluster approaches (CCSD(T), CCSDT, EOM-CCSD, EOM-CC3) and configuration interaction (Full CI) methods. Our calculations employ basis sets developed for the He(^{1}S) + He(^{3}S) states with cardinal numbers up to 10Z, with results extrapolated to the complete basis set limit.

Results Potential energy curves (PECs) are calculated for interatomic distances up to 50 a_0. The states from the first four asymptotes are computed using the Full CI method with basis sets up to 7Z and various coupled cluster methods with basis sets up to 8Z. Additionally, a single-point calculation for the $a^3\Sigma_u^+$ and $c^3\Sigma_g^+$ states is provided in the 8Z basis set using Full CI, and in the 10Z basis set using EOM-CC3 to demonstrate convergence at the global minimum. Our calculations achieve a theoretical accuracy reaching **1.0 cm^{-1} (60-200 ppm)** at the minimum.

Conclusions The results of our calculations provide highly accurate data, enabling the calculation of Franck-Condon factors for higher Rydberg states of the helium dimer or the helium molecular ion [2]. We report that our study has achieved the highest accuracy for the helium dimer in excited electronic states.

Acknowledgments

Polish high-performance computing infrastructure PLGrid, grants no. PLG/2023/016878 & PLG/2024/017527.
European Research Council (ERC), grant no. QuantMol/101042989.
National Science Centre, Poland, grant no. 2020/38/E/ST2/00564.

References

[1] M. Pavanello, et al., *Int. J. Quantum Chem.* **108**, 2291 (2008).
[2] J. Gębala, et al., *Phys. Rev. A* **108**, 052821 (2023).