EXPLICITLY CORRELATED METHODS FOR SPECTROSCOPIC-ACCURACY CALCULATIONS IN HEH^+ AND HE_2^+

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High-precision molecular calculations require a consistent treatment of electronic correlation, finite nuclear-mass effects, and higher-order relativistic and QED contributions across multiple spatial and energy scales. In this contribution, we present recent methodological developments in explicitly correlated approaches designed for spectroscopic-accuracy calculations in few-electron molecular systems. The presented framework combines variational explicitly correlated basis expansions with asymptotically adapted representations that enable stable treatment of competing correlation length scales over the full range of internuclear separations. Particular attention is devoted to the construction of hybrid variational spaces incorporating both fully correlated molecular sectors and separable asymptotic components, significantly improving numerical stability in the dissociation regime [1]. The methodology is demonstrated for molecular ions such as HeH^+ and He_2^+, which constitute important benchmark systems for precision spectroscopy, nonadiabatic theory, and molecular quantum electrodynamics. In particular, HeH^+, as the simplest heteronuclear two-electron molecular ion with unequal nuclear charges, represents a qualitatively different physical system from the isoelectronic H_2 molecule. The broken inversion symmetry, asymmetric dissociation channel, and strong coupling between different correlation and mass scales make HeH^+ a sensitive testing ground for high-accuracy treatments of nonadiabatic, relativistic, and QED effects at near-spectroscopic precision. The availability of high-resolution spectroscopic data further makes these systems particularly suitable for validating explicitly correlated computational frameworks [2,3].

The presented methodology provides a general framework for precision molecular calculations and can be extended to broader classes of molecular systems relevant to computational spectroscopy, molecular modeling, and mathematical chemistry.

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REFERENCES

[1] M. Puchalski and M. Siłkowski, *to be published soon*

[2] M. Siłkowski, J. Komasa, and M. Puchalski, JPC A 129(49) (2025)

[3] M. Siłkowski, P. Czachorowski, J. Komasa, and M. Puchalski, PRA **113**, 032803 (2026)