Variational solutions of the nuclear motion problem - from rovibrational calculations to protonic densities

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The nuclear motion problem lies at the heart of molecular spectroscopy and dynamics. While approximate methods such as vibrational perturbation theory (VPT2) have become indispensable tools in computational chemistry, their reliability ultimately rests on comparison against rigorous reference data. Variational approaches occupy a special role in this landscape: employing the exact kinetic energy operator, they provide solutions that converge systematically toward the exact answer for a given potential energy surface. Upon convergence, all remaining discrepancies with experiment can be unambiguously attributed to errors in the surface itself — making variational calculations not only a benchmark for approximate vibrational methods, but also a sensitive probe of the underlying ab initio electronic structure methods.

This talk traces how variational nuclear motion calculations have guided research across different regimes. Starting from high-resolution rovibrational spectroscopy, where variational calculations have helped interpret and predict experimental observations, their application to the emerging nuclear-electronic orbital (NEO) framework will then be discussed — in which electrons and select nuclei, typically protons, are treated quantum mechanically on equal footing. Here, variational protonic densities offer a stringent and transparent benchmark for approximate NEO methods, shedding new light on the quality of protonic basis sets and the physical content of these approaches.