

# HITTING THE TRIFECTA: HOW TO SIMULTANEOUSLY PUSH THE LIMITS OF SCHRÖDINGER SOLUTION WITH RESPECT TO SYSTEM SIZE, CONVERGENCE ACCURACY, AND NUMBER OF COMPUTED STATES

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Methods for solving the Schrödinger equation have seen an explosive growth in recent years, as the importance of incorporating quantum effects in numerical simulations in order to obtain experimentally accurate data becomes increasingly recognized. In practical terms, there are just three primary factors that currently limit what can be achieved. These are: (a) SYSTEM SIZE, i.e., the number of degrees of freedom that can be treated explicitly quantum mechanically; (b) NUMERICAL ACCURACY, measured in terms of convergence with respect to ALL POSSIBLE computational parameters such as basis sizes; (c) ENERGY EXCITATION or the total number of accurately computed states. Broadly speaking, current methods can deliver on any two of these goals, but achieving all three at once remains an enormous challenge.

In this presentation, we shall describe just such a method, and demonstrate how it can be used to "hit the trifecta" in the context of molecular vibrational spectroscopy calculations.<sup>a</sup> In particular, we compute thousands of vibrational states for the 12D acetonitrile molecule (CH<sub>3</sub>CN), to a target numerical convergence of a few 10<sup>-2</sup> cm<sup>-1</sup> or better. In other words, we compute ALL vibrational states for this six-atom system in full quantum dimensionality, and throughout the entire dynamically relevant spectral range, to near spectroscopic accuracy. To our knowledge, no such vibrational spectroscopy calculation has ever previously been performed—although given the generality of the method, we anticipate there will be many more such calculations to follow.

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<sup>a</sup>J. Sarka and B. Poirier, *J. Chem. Theory Comput.* 17, 7732-7744 (2021).