Numerically constructed kinetic energy operators in computational molecular spectroscopy

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Rotational-vibrational transitions of N-atomic molecules have been traditionally described in quantum mechanics by replacing the $3N$ laboratory-fixed Cartesian coordinates with $3N$-6 internal coordinates, 3 orientation angles of a frame fixed to the body, and 3 Cartesian coordinates of the center of mass of the nuclei. This replacement of the coordinates is motivated both by the physical-chemical intuition and by the possible gain in the computational effort. At the same time, the kinetic energy operator of the resulting internal-coordinate Hamiltonian can have a very complicated analytic form, which is different for the different sets of coordinates and the different molecules.

Instead of the development of tailor-made algorithms and computer codes for every single coordinate system and molecule, one might ask if the development of a universally applicable approach is possible. In my talk I explain that such a universal approach is based on the numerical representation of the kinetic energy operator on a grid. I review the development of the idea and the various existing implementations for (ro)vibrational computations. I also present our algorithm and computer program developed, named GENIUSH, applicable for the quasi-variational solution of the time-independent rovibrational Schrödinger equation using arbitrary sets of internal coordinates and body-fixed frames [1,2].

Such a universal treatment is an essential theoretical and computational development toward a black-box-type approach for the solution of the nuclear motion problem. It is logical to ask however, whether we can expect anything more from the numerical construction than just a practical automatization procedure. I finish my talk with recent applications, which benefit from this numerical construction [3].

[1] E. Mátyus, G. Czakó, and A. G. Császár, *J. Chem. Phys.* **2009**, *130*, 134112.
[2] Cs. Fábri, E. Mátyus, and A. G. Császár, *J. Chem. Phys.* **2011**, *134*, 074105.
[3] Cs. Fábri, E. Mátyus, and A. G. Császár, *Spectrochim. Acta A* **2013**, in press.