Mathematical tools applied to high-resolution molecular spectroscopy

Attila G. Császár[a,b]

[a] *Laboratory of Molecular Structure and Dynamics, Institute of Chemistry, Eötvös University, H-1117 Budapest, Pázmány Péter sétány 1/A, Hungary*
[b] *MTA-ELTE Complex Chemical Systems Research Group, H-1518 Budapest 112, P.O. Box 32, Hungary*

csaszar@chem.elte.hu

In the fourth age of quantum chemistry [1] there are several areas of first-principles nuclear motion theory which require significant development and these efforts can be helped greatly by various mathematical tools. A couple of related attempts, characterizing our group's research efforts, will be reviewed during the talk.

While analytic derivation of kinetic energy operators expressed in internal coordinates is certainly feasible, especially using techniques of geometric algebra, it seems more practical to rely on numerical handling of the kinetic energy operators [2,3] during the solution of the time-independent nuclear Schrödinger equation. The ensuing fully numerical handling of both the kinetic and potential energy operator parts of the Hamiltonian allows (a) the treatment of both full- and reduced-dimensional models of molecular systems within the same code for arbitrary systems, (b) the inclusion of the Eckart embedding in arbitrary nuclear motion computations, and (c) the efficient consideration of non-adiabatic effects, considerably improving the accuracy of the computation of rovibrational energy levels.

Iterative determination of a large number of eigenstates of huge Hamiltonian matrix representations is a special requirement during the solution of the time-independent nuclear Schrödinger equation. Certain results from our own experience are summarized, related to the iterative Lanczos technique and FEAST.

It is still true that quantum theory is usually unable to match the accuracy of high-resolution spectroscopic experiments. Thus, experimental determination of a large number of rovibrational energy levels is important, especially in view of the many applications which need such data. The theory of spectroscopic networks (SN) has been introduced [4] and developed in our group, providing an interesting chemical application of graph theory. Based on the concept of SNs, experimental-quality rovibrational energy levels can be derived via the Measured Active Rotational-Vibrational Energy Levels (MARVEL) approach [5].

References
1. A. G. Császár, C. Fábri, T. Szidarovszky, E. Mátyus, T. Furtenbacher, and G. Czakó, *Phys. Chem. Chem. Phys.* **14**, 1085-1106 (2012).
2. E. Mátyus, G. Czakó, and A. G. Császár, *J. Chem. Phys.* **130**, 134112 (2009).
3. C. Fábri, E. Mátyus, and A.G. Császár, *J. Chem. Phys.* **134**, 074105 (2011).
4. A. G. Császár and T. Furtenbacher, *J. Mol. Spectrosc.* **266**, 99 (2011).
5. T. Furtenbacher and A. G. Császár, *J. Quant. Spectrosc. Rad. Transfer* **113**, 929 (2012).