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Dr. Sonja GRUBISIC
COST-MOLIM STSM Coordinator

Subject: STSM, Dominika Viglaska

Dear Dr. Grubisic,

I would like to express my strong support to a two week long visit of Dominika Viglaska (GSMA Laboratory of Reims University (France)) to the Wigner Research Centre for Physics in March 2018.

The purpose of this visit is to develop a computer program for finding the internal axis system of molecules with asymmetric top and asymmetric frame, and to discuss and test some new and old methods for describing large amplitude internal motions of non-rigid molecules.

Sincerely,

Viktor Szalay

Budapest, 6 October 2017

October 4, 2017

Dominika Viglaska
University of Reims
France

Dear Dominika,

I suggest the we should do research in two problems which might be useful to your PhD work:

(a) Product (geometric) integration of the evolution equation determining the internal axis system (IAS) for molecules with asymmetric top and asymmetric frame. If successful it offers an alternative to the Floquet based method of determining the IAS.

(b) Numerical and analytical validation of some new ideas of constructing vibrational coordinates for molecules with large amplitude internal motions. In particular, the use of "real" LAM coordinates will be examined.

If you supervisors agree, I suggest that we should start working on the problems straight away.

Details of the projects

Work should be started by a few weeks preparation process in which earlier results are discussed, and, if needed, computer codes are written. As to project (a) the following papers will be reviewed:

- H. M. Pickett, J. Chem. Phys. **56**, 1715 (1972).
- V. Szalay and J. Origoso, J. Chem. Phys. **109**, 3911 (1998).
- V. Szalay, A. G. Császár, J Santos, and J. Ortigoso, J. Chem. Phys. **118**, 6801 (2003).

From these we learn about the general form of the ro-vibrational Hamilton operator, the existence of IAS for molecules with asymmetric top and asymmetric frame, and the evolution equation whose solution gives the rotation to the IAS as function of the LAM coordinate. Floquet method may be used to solve the evolution equation. However, it has a drawback: One must give an angular velocity like vector analytically as a function the LAM coordinate. To overcome this difficulty we should learn and implement the method of product integration:

- J. D. Dollard and C. N. Friedman, *Product integration with applications to differential equations*, Addison Wesley Publishing Company, 1979.
- J. F. Hamilton, jr. and L. S. Schulman, J. Math. Phys. **12**, 160 (1971).
- R. L. Karp, F. Mansouri, and J. S. Rno, J. Math. Phys. **40**, 6033 (1999).
- I. Kramer, Am. J. Physics, **40**, 1221 (1972).

As to project (b) a main issue is to avoid using effective LAM coordinates, since they application can become very complicated (J. Mol. Spectrosc., **52**, 439 (1974); Comp. Phys. Rep. **1**, 1 (1983); Topics in Current Chemistry Vol. 68, pp 59-102, 2006) . One of the sources of the complications is that the values of effective LAM coordinates differ from the actual values the LAM coordinates taken at distorted configurations which do not coincide with the (non-rigid) reference configuration. No general formula expressing an effective LAM coordinate in terms of the actual value of the LAM coordinate is known. The use of "real" LAM coordinates, as has been demonstrated at least partially (J. Mol. Spectrosc. **128**, 24 (1988); J. Chem. Phys. **118** , 10631 (2003)), is both general and devoid of the complications associated with effective LAM coordinates. When "real" LAM coordinates are employed

it is required that small amplitude vibrational displacements should not change the values of the LAM coordinates. Therefore the primary goal of our work is to establish a method for constructing small amplitude vibrational displacements such that do not change the values of the LAM coordinates. How this might be achieved has been described in my notes entitled "Coordinates for vibrational and large-amplitude internal motions of molecules in the Eckart frame" whose updated version is attached. To complete the development of this method it must be checked numerically and, as much as possible, analytically. In doing so we shall start with calculations on an example of a triatomic molecule with large amplitude bending motion, the water molecule, say. The calculations will follow the steps of derivations described in Section VII of my notes. While carrying out this calculations you will learn, about Wilson's **s**-vectors, orthogonalization of vectors, and block-diagonalization methods.

With best wishes,

Viktor