TOWARD COMPLETENESS AND HIGH ACCURACY FROM ADVANCED COMPUTATIONAL METHODS: A REVIEW

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The spectral characterization of various planetary atmospheres, brown dwarfs, etc. makes the computational modelling of the rotation-vibration molecular states very challenging. Because of their completeness, extensive first-principles quantum mechanical calculations are generally preferred to those based on empirically-fitted effective spectroscopic models for planetary and astrophysical applications. The first necessary ingredient in variational calculations is the construction of accurate intra-molecular potential energy and dipole moment surfaces in a large range of nuclear displacements. The second one lies in the development of efficient computational methods using adapted coordinates to solve the Schroedinger equation for medium-sized molecules (say \( N \leq 8 \)). This talk will be essentially focused on the second point and will review different computational methods.

The first part will concern the treatment of semirigid molecules in the framework of the Eckart-Watson (EW) approach. A series reduction and compression methods will be described to compute highly excited molecular states involved in hot spectra calculations. To overcome the limitations of the normal mode approach, a rigorous procedure will be explained to transform EW into its curvilinear counterpart. The second part of this talk will be focused on molecules possessing at least one large amplitude motion. To this end, a systematic derivation of the Hougen-Bunker-Johns (HBJ) Hamiltonian will be discussed, on the one hand, and its formulation in terms of symmetry-adapted curvilinear coordinates will be presented, on the other hand. Finally, we will see how (W) and (HBJ) can be linked together as well as with other existing models.

Symmetry will be exploited at all stages of the calculation where the group-theoretically based methods are implemented in the computer code TENSOR for all Abelian and non-Abelian groups.

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5M. Rey, submitted
7D. Viglaska, M. Rey, V. Tyuterev, to be submitted
8M. Rey, D. Viglaska, to be submitted