On the *n*-mode representation of the rotation-vibration Hamiltonian in curvilinear internal coordinates and the Eckart frame

A. Yachmenev[a], S. N. Yurchenko[a]

[a] Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK

Accurate variational solutions of the fully-coupled rotational-vibrational Schrödinger equation for small molecules with more than four atoms represent the current state of the art of the theoretical rovibrational spectroscopy. One of the biggest obstacles of such calculations is the essentially exponential scaling of the number of wave functions with the number of degrees of freedom (number of atoms). While there are powerful methods that conquer this problem employing various types of basis set contractions, the choice of the coordinates and thus the form of the Taylor-made Hamiltonian becomes a key consideration for their successful application. The use of the curvilinear internal coordinates along with the Eckart frame is becoming widely appreciated as the most optimal choice of the coordinate system. The need to select the coordinates and construct the rovibrational Hamiltonian afresh for each specific problem has initiated a number of recent developments toward the black-box type approaches for numerical construction of the rovibrational Hamiltonian for arbitrary molecule [1-3]. Due to the lack of an analytical solution for the Eckart coordinate frame, all approaches can be divided into two major classes depending on how the kinetic energy operator (KEO) is constructed. The first class of approaches is based on the point-wise representation of the KEO and use of the quadratures for the integration, and is usually called an *exact kinetic energy operator* approach [1,2]. In the second class of approximations, the analytical representation of KEO is constructed in the form of a truncated Taylor series expansion in terms of curvilinear coordinates, where all required derivatives are calculated numerically using finite differences [3].

In this work we explore a new method for analytical construction of the Eckart-embedded Hamiltonian in the form of an *n*-mode expansion in terms of curvilinear internal coordinates. We overcome the problem of the absence of a closed analytical Eckart solution by computing all derivatives required for an *n*-mode expansion recursively, from a set of differentiated Eckart equations. The *Automatic Differentiation* technique, as implemented in the Rapsodia library [4], is employed to compute the derivatives at the machine precision. The present work can be regarded as an extension of the TROVE methodology [3] toward an accurate machine-precision Taylor series representation of the rovibrational Hamiltonian. These improvements allow us to employ more sophisticated forms of curvilinear coordinates and expansions of higher orders, which are otherwise inaccessible due to the errors in numeric differentiation.

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