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THE VARIATIONAL METHOD FOR ROTATION-VIBRATIONAL CALCULATIONS

JONATHAN TENNYSON
Dept. of Physics & Astronomy, University College London,
London WC1E 6BT, UK

A rigorous formulation of the nuclear motion problem will be presented starting from the full non-relativistic Hamiltonian for the problem. Both space-fixed and body-fixed approaches will be discussed: these approaches differ because while the latter identifies separate vibrational and rotational coordinates, the former does not.

Variational methods can be used to obtain high accuracy solutions for these nuclear motion Hamiltonians. Numerical tests show that both space-fixed and body-fixed approaches yield the same results. However for strongly bound molecules such as water or H_3^+ the body-fixed approach has significant advantages in terms of both the ease of computation and the interpretation of the results.

Calculations using body-fixed Hamiltonians and variational approaches have given results of near-spectroscopic accuracy for the H_3^+ system [1]. Indeed our work on this problem [2] was recently cited as only one of five solved problems in the entire area of atomic and molecular physics [3].

High quality *ab initio* calculations on the water molecule still do not reproduce the measured laboratory spectra to even near their intrinsic accuracy [4]. These residual errors are not due to the treatment of the nuclear motion, for which different codes [5,6] give essentially identical results, but due to treatment of the electronic motion and the coupling between electronic and nuclear motion.

Variational procedures can thus be regarded as giving a definitive solution to the triatomic nuclear motion problem as far as high resolution spectroscopy is concerned. As can be judged from other presentations at the meeting these methods are making a huge impact on the spectroscopy of water. Indeed these methods are now being widely used to study a whole variety of other triatomic species such as ozone [7], H_2Te [8], CO_2 [9] and H_2S [10].

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