BULL. AUSTRAL. MATH. SOC.
VOL. 29(1984), 159-160.

A FINITE ELEMENT APPROACH TO MOLECULAR VIBRATION

M. J. HAMILTON

The thesis is concerned with the computation of vibration energy levels of small molecules, in particular H_3^+ and D_3^+, which had previously been studied by Carney and Porter (1980) in a series of papers.

The computational problem can be divided into the following stages:

(a) the computation of an ab initio potential at sufficient points in the vibration co-ordinate space to permit the vibration calculation to proceed

(b) the representation of the potential surface by some type of analytic approximation which faithfully represents the ab initio points and is free of spurious minima and turning points

(c) the computation of the vibration energy levels using the analytic potential. For the molecules in question the co-ordinate space is three dimensional (when centre of mass motion and rotations are removed). To make this computation, the vibration wave function is written as a linear combination of products of eigenfunctions of projections of the three dimensional operator along the co-ordinate axes. The one dimensional eigenfunctions are approximated by Hermite cubics.

Results are presented for two different sets of ab initio potential

Received 22 May 1984. Thesis submitted to University of Wollongong, November 1983. Degree approved February 1984. Supervisor: Dr. G. Doherty.

values. A variety of functional forms for the potential surface have been investigated, for goodness of fit using the singular value decomposition, and for physical plausibility. A method for dealing with the Watson term which arises in the quantum calculations from attempts to separate the rotation and vibration has been developed. Different numerical integration schemes for the three dimensional potential integrals have been investigated. The effects of different mesh subdivisions and of truncation of the eigenfunction expansion with different selection criteria have been documented. Finally, a set of theoretical assignment predictions for H_3^+ and D_3^+ are presented which incorporate the improvements resulting from the above investigations, using the previously unpublished potential of Burton et al (1984).

References

[1] P. G. Burton, E. von Nagy-Felsobuki, G. Doherty and M. Hamilton, "The vibration spectrum of H_3^+ : A PNO-CI ab initio potential surface and its analytical representation"(to appear).

[2] G. D. Carney and R. N. Porter, "Ab initio prediction of the rotation vibration spectrum of H_3^+ and D_3^+ ", *Phys. Lett. Rev.* 45 (1980), 537.

Department of Mathematics,
University of Wollongong,
Wollongong,
New South Wales 2500,
Australia.