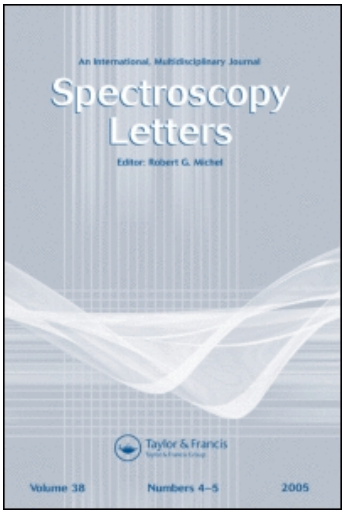

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Energy Levels of Asymmetric Rotors: An Improved Computational Procedure

C. S. C. Chung[a]
[a] Department of Chemistry, Iowa State University, Ames, Iowa

To cite this Article Chung, C. S. C.(1973) 'Energy Levels of Asymmetric Rotors: An Improved Computational Procedure', Spectroscopy Letters, 6: 10, 617 — 620
To link to this Article: DOI: 10.1080/00387017308060851
URL: http://dx.doi.org/10.1080/00387017308060851

SPECTROSCOPY LETTERS, 6(10), 617-620 (1973)

ENERGY LEVELS OF ASYMMETRIC ROTORS: AN IMPROVED COMPUTATIONAL PROCEDURE

KEY WORDS: Microwave Spectroscopy, Asymmetric Rotor Energy Levels

C. S. C. Chung

Department of Chemistry
Iowa State University
Ames, Iowa 50010

The microwave band spectra[1] of asymmetric top molecules have $2J + 1$ distinct rotational energy sublevels for each value of rotational quantum number J. Through application of group theory, the stationary states of rigid asymmetric rotors can be classified by the irreducible representations or by the symmetry species of the $V(D_2)$ point group (the Four-group). When performing a Wang symmetrizing transformation[2] on the original energy matrix $\mathbf{E}(\kappa)$ where κ is the Ray's asymmetry parameter[3], a new energy matrix $\mathbf{E}'(\kappa)$ may be readily obtained.

$$\mathbf{E}'(\kappa) = \mathbf{X}^{-1}\mathbf{E}(\kappa)\mathbf{X} = \mathbf{E}^{+}(\kappa) + \mathbf{O}^{+}(\kappa) + \mathbf{E}^{-}(\kappa) + \mathbf{O}^{-}(\kappa)^{\dagger} \qquad (1)$$

The energy levels for any value of J can then be obtained as functions of the eigenvalues of the above four submatrices (i.e., the four secular equations), their dimensions being ½ J or

† $\mathbf{E}$ and $\mathbf{O}$ refer to the parity of the quantum number K which superscripts + and - refer to the parity of $(J + \gamma)$ where γ is an auxiliary quantum number having the values of 0 or 1, depending upon the choice of a particular representation.

½J + 1 (J even) and ½(J ± 1) (J odd). The submatrices may be expressed in the following convenient form:

$$\mathbf{E}^{\pm}(\kappa), \quad \mathbf{O}^{\pm}(\kappa) = \begin{Vmatrix} \alpha_1 & \beta_1 & 0 & \cdots & 0 & 0 \\ 1 & \alpha_2 & \beta_2 & \cdots & 0 & 0 \\ 0 & 1 & \alpha_3 & \cdots & 0 & 0 \\ & & & \ddots & & \\ 0 & 0 & 0 & \cdots & \alpha_{n-1} & \beta_{n-1} \\ 0 & 0 & 0 & \cdots & 1 & \alpha_n \end{Vmatrix} \tag{2}$$

There are several common numerical methods available for determining the roots of the above submatrices, the most common being the iterative continued-fraction expansion method of Swalen and Pierce[4] and the Ritishauser quotient-difference method by Bennett, Ross and Wells.[5]

We wish to point out the applicability of an improved computational procedure which can be readily adapted to existing comprehensive asymmetric rotor computer programs with only minor modifications. This procedure consists of two steps. The original real, continuant and tridiagonal (quasi-symmetric with non-negative elements above and below the diagonal elements) matrix is first transformed to a symmetric tridiagonal matrix by means of a similarity transformation with a non-singular diagonal matrix.[6] The resulting symmetric tridiagonal matrix is then diagonalized by applying the QL algorithm with implicit shift.[#7,8,9] The QL

It should be noted that the performance of the QL method without implicit shift, in determining the eigenvectors and eigenvalues of the above submatrices (without additional centrifugal distortion terms), is almost equivalent to that of the QL method with implicit shift. When the magnitude of successive row sums of any symmetric matrix varies to a large degree, then the latter method will excel the former method. For the sake of convenience, the latter method should be adopted.

method is a procedure whereby a sequence of symmetric tridiagonal matrices, unitarily similar to the original symmetric tridiagonal matrix, is formed which converges to a diagonal matrix. The shift at the mth iteration is defined as $\rho^{(m)}$, $\{s_n^{(m)}; n = 2.....i\}$ are subdiagonal elements and $\{d_n^{(m)}; n = 1.....i\}$ are diagonal elements of the tridiagonal matrix. At the mth iteration, the shift is chosen to be the eigenvalue of the bottom 2 X 2 principal minor which is closer to the diagonal element of this minor $d_i^{(m)}$. When $s_j^{(m)}$ is considered negligible, $d_i^{(m)}$ is taken as an eigenvalue and the order i of the matrix is reduced by one (by neglecting the last row and column). This process is repeated on the successively reduced matrices until the entire matrix is diagonalized. The eigenvalues are then sorted, ranked and compared with published asymmetric rotor energy level tables ($J \leq 40$).[10,11,12]

We have performed the above calculations for values of κ = -1.....0.....+1. (in steps of +0.05 with values of J up to 100 on both IBM 360/65 (real memory) and IBM 370/145 (virtual memory) with double precision arithmetic. Our results using the implicit QL method are accurate to at least ten decimal places, numerically stable, reliable, efficient$^{\neq}$ (i.e., converging in less than ten iterations while never converging to undesired roots), economical in storage requirements (for a matrix of order i, two one-dimensional arrays of i locations are required for the diagonal and subdiagonal elements of the symmetric tridiagonal matrix and

$\neq$ CPU times of 0.284 second and 0.922 second are required to diagonalize submatrices of order 25 (when J = 50) and 50 (when J = 100) respectively of Equation (2) (based on the IBM 360/65 at Iowa State University). Practically none of the above CPU time is used on the similarity transformation of the first step.

only one large array is involved in the iterative process)[8] and economical in the number and in the extent of virtual memory sweeps.[13]

Note: Listings of the FORTRAN IV subroutines to perform the above diagonalization procedures are available upon request from the author.

Acknowledgment: I wish to thank Prof. G. A. Russell, Iowa State University, for his encouragement and financial support.

References

[1] For a recent review on Microwave Spectroscopy: Flygare, W. H., Chapter V, Physical Methods of Chemistry Part III A, Weissberger and Rossiter, editors, Wiley, page 439, (1972).

[2] Wang, S. C., Phy. Rev., 34, 243 (1929).

[3] Ray, B. S., Feits. f. Physik, 78, 74 (1932).

[4] Swalen, J. D. and Pierce, L., J. Math. Phy., 2, 736 (1961).

[5] Bennett, J. M., Ross, I. G., and Wells, E. J., J. Mol. Spectrosc., 4, 342 (1960).

[6] Wilkinson, J. H., The Algebraic Eigenvalue Problem, Clarendon Press, Oxford, Page 335, (1965)

[7] Bowdler, H., Martin, R. S., Reinsch, C., Wilkinson, J. H., Num. Math., 11, 293 (1968).

[8] Martin, R. S., Wilkinson, J. H., Num. Math., 12, 377 (1968).

[9] Dubrulle, A., Num. Math., 15, 450 (1970).

[10] King, G. W., Hainer, R. M., and Cross, P. C., J. Chem. Phy., 11, 27 (1943).

[11] Erlandsson, G., Archiv Fysik, 10, 65 (1956).

[12] Allen, A. C., and Cross, P. C., Molecular Vib-rotors, Wiley, New York, page 22, (1963).

[13] Moler, C. B., Communication ACM, 15, No. 4, April (1972).

Received August 27, 1973
Accepted September 10, 1973