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SPECTROSCOPIC ENERGY COEFFICIENTS FOR VIBRATION–ROTATIONAL STATES OF DINUCLEAR MOLECULES

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PROGRAM SUMMARY

Title of program: YDY84C

Catalogue number: ACET

Program obtainable from: CPC Program Library, Queen's University of Belfast, N. Ireland (see application form in this issue)

Computer for which the program is designed and others on which it is operable: any computer having a FORTRAN-77 compiler and sufficient core (overlaying may be necessary but is easily effected)

Computer: Univac 1100/82; *Installation*: Computer Services Centre, Australian National University, Canberra, A.C.T. 2601, Australia

Operating system: EXEC-8 or OS1100

Programming language used: FORTRAN-77 with double precision

High speed storage required: none (16000 words was available on Univac 1100/82)

No. of bits per word: 36

Overlay structure: optional

Peripherals used: card reader or input terminal, line printer

No. of cards in combined program and test deck: 5408

Card punching code: EBCDIC

Keywords: molecular, dinuclear, potential-energy function, spectroscopic energy coefficients

Nature of physical problem
The spectroscopic energy coefficients Y_{kl} and their derivatives with respect to the parameters are calculated from a known set of the parameters: coefficients c_j ($1 \leqslant j \leqslant 10$) in the potential-energy function [1], and harmonic vibrational, ω_e, and rotational, B_e, quantities.

Method of solution
Explicit expressions for the contributions to Y_{kl} and their derivatives are used in a list scanned once in order to generate the specified quantities.

Restrictions on the complexity of the problem
The length of the program is compensated by separation of the intensive calculations into ten subroutines that can be overlaid or executed in segments. Depending on the parameters supplied, the generated values may lie within the range $10^6 - 10^{-80}$.

Typical running time
0.9 s.

Reference

[1] J.F. Ogilvie, Proc. Roy. Soc. (London) A378 (1981) 287.

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Traditionally the energies of states of neutral molecules containing two nuclei and associated electrons have been represented [1] in terms of a double summation of power series in terms of the vibrational v and total angular momentum J quantum numbers,

$$E_{v,J} = \sum_{k=0} \sum_{l=0} Y_{kl}(v+\tfrac{1}{2})^k [J(J+1) - \Lambda^2]^l, \quad (1);$$

here Λ is a quantum number for electronic angular momentum that will henceforth be omitted (as appropriate to Σ electronic states). This expression is not useful for vibration–rotational states close to the dissociation limit [2], nor where perturbations between electronic states cause irregularities of energy spacing. Most use of expression (1) has been simply as a fitting equation with no particular physical significance attributed to most the coefficients Y_{kl} [3]. It is, however, possible to relate the Y_{kl} quantities to potential-energy parameters, first achieved by Dunham [4] for a flexible form of function. Sandeman [5] extended Dunham's theory and found further expressions for contributions to the Y_{kl} in the series

$$Y_{kl} = x_{kl} + y_{kl} + z_{kl} + t_{kl} + \ldots, \quad (2),$$

where the correction terms y_{kl}, z_{kl}, t_{kl} have successively coefficients of γ^2 that usually provide for rapid convergence of the series; the reason is that γ $(= 2B_e/\omega_e)$, effectively the limiting ratio of rotational to vibrational energy internals in the one-photon spectrum, has typically values within the range 3×10^{-2}–3×10^{-4}.

Where wavenumber or frequency data exist for isotopically substituted nuclei, then a more general expression than (1) for the energies of each isotopic species is

$$E^i_{v,J} = \sum_{k=0} \sum_{l=0} Y^i_{kl}(v+\tfrac{1}{2})^k [J(J+1)]^l, \quad (3),$$

in which the quantities Y^i_{kl} may be related to a set of mass-independent quantities U_{kl} and Δ_{kl} according to the equation [6]:

$$Y^i_{kl} = \mu_i^{-(k+2l)/2} U_{kl} \left[1 + m_e\left(\Delta^a_{kl}/M_a + \Delta^b_{kl}/M_b\right)\right], \quad (4)$$

In (4) the mass dependence is mostly incorporated into the factors of reduced mass $\mu_i = M_a M_b/(M_a + M_b)$, M_a and M_b being the masses of the separated neutral atoms a and b, but residual mass effects appear in the small (m_e = rest mass of the electron) correction terms involving the elemental mass coefficients $\Delta^{a,b}_{kl}$ (that are of order unity). The latter correction terms $\Delta^{a,b}_{kl}$ not only include implicitly the Dunham corrections y_{kl}, z_{kl}, $t_{kl}, \ldots$, but also take partial account of the failure of the Born–Oppenheimer approximation of separation of electronic and nuclear motions. Thus, it has proved possible to represent the wavenumbers and frequencies of ≈ 1200 lines of vibration–rotational transitions of various species of $^{1,2,3}H^{35,37}Cl$ by the combination of only 19 U_{kl} and 7 $\Delta^{H,Cl}_{kl}$ (that have statistically significant values); the accuracy attained in this reduction was $\approx \pm 1$ m^{-1} or the experimental inaccuracy of the measured values [7].

To ascribe a physical meaning to the Y_{kl} or U_{kl} quantities is possible if these can be related to a function that expresses how the potential energy V depends upon internuclear separation R. By this means for instance, the 19 U_{kl} of HCl were related [7] to R_e, the equilibrium internuclear separation and nine coefficients a_j, $0 \leqslant j \leqslant 8$, of the Dunham function for potential energy [4]. Recently a new flexible formulation [8] has been developed to yield in principle an accurate representation of potential energy over the entire range of separations pertinent to molecular existence. Thereby the new function avoids the fundamental invalidity of the Dunham function for $R > 2R_e$ [9]. The new function is also of the form of a polynomial, in argument $z = 2(R - R_e)/(R + R_e)$, truncated as required by a limited amount of experimental (or other) data:

$$V(z) = c_0 z^2 \left(1 + \sum_{j=1}^{n} c_j z^j\right). \quad (4)$$

By computational methods described elsewhere [10], it has proved possible to determine some 84 expressions for Y_{kl} in terms of the harmonic vibrational parameter ω_e, the rotational parameter B_e, and the coefficients c_j in (4), $1 \leqslant j \leqslant 10$, with $c_0 = \omega_e^2/4B_e$. Of these Y_{kl} expressions, 49 are the primary contributions (x_{kl} of Sandeman [5]) with

$(2k+l) \leqslant 12$; 25 are the secondary contributions (y_{kl}) with $(2k+l) \leqslant 8$; 9 are the tertiary contributions (z_{kl}) with $(2k+l) \leqslant 4$, and the other is $t_{0,0}$. Together they comprise all the possible expressions that contain terms not beyond c_1^{10}, c_{10}, etc. The expressions like $Y_{2,8}$ contain 139 terms, such as $11053360440 c_1^8 c_2$ (multiplied by $96B_e^{17}/\omega_e^{16}$); thus, more complicated expressions containing terms in c_1^{11}, c_{11}, etc., would probably be too cumbersome to be useful. Such a collection of Y_{kl} should suffice to describe accurately the vibration–rotational energy states that are below about 0.7 of the dissociation limit; beyond this energy the convergence of the representation (1) is suspect, and alternative representations are preferred [11].

The coefficients c_j are usually determined by means of an iterative procedure [8] from the Y_{kl}, although the coefficients a_j of the Dunham formulation of potential energy have on occasion been determined directly from the line wavenumbers [3]. In fact a proper merging procedure [7], with due account taken of the statistical weighting factors and correlation, would be entirely equivalent to the direct procedure [3]. Either the iterative or the merging procedure requires determination of the derivatives of the Y_{kl} quantities with respect to the parameters c_j, B_e and ω_e for the purpose of assessment of error propagation from the line wavenumbers to the ultimate potential-energy coefficients. Analytic expressions for these derivatives of Y_{kl} have also been obtained [10].

Explicit expressions for the 84 contributions to the Y_{kl} quantities and their non-zero derivatives with respect to c_j $(1 \leqslant j \leqslant 10)$, B_e and ω_e have been coded in FORTRAN-77 statements that, with requisite declarations and identifying comments, occupy 5364 lines of text separated into ten subroutines in the program YDY84C. These subroutines require to be passed, through COMMON storage, values of c_j $(1 \leqslant j \leqslant 10)$, B_e and ω_e, and in turn generate the YE(N), $1 \leqslant \mathrm{N} \leqslant 84$, values of the contributions to Y_{kl}, and the ZE(N, I), derivatives of these YE(N) with respect to the parameters c_I $(1 \leqslant \mathrm{I} \leqslant 10)$, B_e (I = 11) and ω_e (I = 12). The identifying comments indicate the relation of the YE(N) and ZE(N, I) to the Y_{kl} quantities, and a third index p indicates a x_{kl}, y_{kl}, z_{kl} or t_{kl} contribution ($p = 1,2,3,4$, respectively). A sample driver routine is supplied that within 44 lines provides for test purposes values of the parameters for an exponential type of potential-energy function [12]

$$V(x) = 6.25 c_0^2 (1 - e^{-2.5x})^2, \tag{5}$$

in which $x = 2z/(2-z)$. Despite the density of much of the code, the program takes less than one second of CPU time to execute on a Univac 1100/82 computer in double-precision FORTRAN-77. The output consists simply of a list of supplied values of ω_e, B_e and c_j $(1 \leqslant j \leqslant 10)$, and then 84 pairs of lines, each pair containing the identifying index N, YE(N) and the 12 ZE(N, I). If instead of ω_e and B_e there are supplied to the subroutines values of $U_{1,0}$ $(= \omega_e/\mu^{1/2})$ and $U_{0,1}$ $(= B_e/\mu)$, then the quantities returned as YE and ZE will be U_{kl} and their derivatives; in this case the YE(N) and ZE(N, I) with N > 49 (in the latter five subroutines) should be ignored. In the following test run output, sample portions of the results are shown for demonstration purposes.

For this exponential type of potential-energy function, all the contributions to $Y_{k,0}$ should be identically zero (proved by analytic substitution) except $Y_{1,0}$ ($x_{1,0}$) and $Y_{2,0}$ ($x_{2,0}$). That the typical values of the other contributions to $Y_{k,0}$ are in fact less than 4×10^{-15} of the magnitude of $Y_{2,0}(x_{2,0})$ is an indication of the numerical precision attained on the Univac 1100/82, but this factor may be expected to be dependent on machine.

By means of another potential-energy function, one can check that the expressions for the Y_{kl} produce the correct values. The function

$$V(x) = \frac{\omega_e^2}{4B_e}\left(\frac{x}{x+1}\right)^2 \tag{6}$$

has the special set of coefficients $c_j, j > 0$, given [8] by the relations:

$$c_j = (j+1)/2^j + \sum_{k=1}^{j+1} \frac{(j+1)!(-1)^{j-k}}{k!(j-k)!2^k}. \tag{7}$$

In this case the analytic expressions for the Y_{kl}, quite simple in form, have been given by Sandeman [5], and the user of YDY84C can thus easily check that the numerical values of the quantities

YE(N) produced by this program correspond to those of the appropriate Y_{kl} from Sandeman's formulae, within the precision of the machine. Although the derivatives cannot be similarly checked, the YE(N) can be differentiated by inspection to check the formulae given in the statements for the ZE(N, I).

One obvious application of these expressions for Y_{kl} and their derivatives is the determination of the potential-energy coefficients c_j in the course of a spectroscopic analysis, in order to be assured of the internal consistency and physical significance of the energy coefficients Y_{kl} or U_{kl}. Conversely, if points of E(R) are found in the clamped-nuclei procedure of a quantum computation (molecular orbital or similar method) then fitting the energy points of a polynomial in z will permit determination of the coefficients c_j that can in turn be used to generate values of U_{kl} or Y_{kl} directly through these analytic expressions in YDY84C, rather than by numerical (perturbation) methods. Equivalently any other method of generating a potential-energy function that can be transformed to $V(z)$ [8] can also lead to a spectral line prediction through the Y_{kl} or U_{kl} in YDY84C. For these or other applications, the ten subroutines of YDY84C can be simply appended to whatever other routines and subroutines are required for the user's purposes.

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TEST RUN OUTPUT

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  0  .3000000000+006  .1000000000+004  -.1500000000+001  .6458333333+000  .1354166667+000  -.9982638889-001  -.4036458333-001
     .6739056333-002  .9431707778-002   .2353621111-002 -.7929456667-003 -.8331408889-003
 TEST DATA SET WITH MORSE FUNCTION PARAMETERS TO SIMULATE HCL APPROXIMATELY.
W AND BE ARE IN RECIPROCAL METRES.
OUTPUT GIVES NUMBER N OF EXPRESSION AS IN THE SUBROUTINES, VALUE OF YE(N)
AND VALUES OF ZF(N,I) WHICH ARE THE DERIVATIVES OF YE WITH RESPECT TO C(I) FOR I=1 TO 10
AND TO BE AND W FOR I=11 AND 12 RESPECTIVELY.  AM=2.5  .
  1  .3000000000+006  .0000000000       .0000000000      .0000000000      .0000000000      .0000000000       .0000000000
     .0000000000      .0000000000       .0000000000      .0000000000      .0000000000      .1000000000+001
  2  .1000000000+004  .0000000000       .0000000000      .0000000000      .0000000000      .0000000000       .0000000000
     .0000000000      .0000000000       .0000000000      .0000000000      .1000000000+001  .0000000000
  3 -.4444444444-001  .0000000000       .0000000000      .0000000000      .0000000000      .0000000000       .0000000000
     .0000000000      .0000000000       .0000000000      .0000000000     -.1333333333-003  .2962962963-006
  4 -.3000000000+002  .2000000000+002   .0000000000      .0000000000      .0000000000      .0000000000       .0000000000
     .0000000000      .0000000000       .0000000000      .0000000000     -.6000000000-001  .1000000000-003
  5  .9876543210-006  .1975308642-005   .0000000000      .0000000000      .0000000000      .0000000000       .0000000000
     .0000000000      .0000000000       .0000000000      .0000000000      .4938271605-008 -.1316872428-010
  6 -.6250000000+004  .7125000000+004   .1500000000+004  .0000000000      .0000000000      .0000000000       .0000000000
     .0000000000      .0000000000       .0000000000      .0000000000     -.6250000000+001  .0000000000
  7 -.2407407407-003  .3333333333-002   .1777777778-002  .0000000000      .0000000000      .0000000000       .0000000000
     .0000000000      .0000000000       .0000000000      .0000000000     -.9629629630-006  .2407407407-006
  8 -.8047553727-010  .6584762140-010   .8779149520-010  .0000000000      .0000000000      .0000000000       .0000000000
     .0000000000      .0000000000       .0000000000      .0000000000     -.5633287609-012  .1609510745-014
  9  .0000000000      .5312500000+003   .3750000000+003  .0000000000      .0000000000      .0000000000       .0000000000
     .0000000000      .0000000000       .0000000000      .0000000000      .0000000000      .0000000000
 10 -.1527777778+000  .1931944444+001   .1300000000+001  .3333333333+000  .0000000000      .0000000000       .0000000000
     .0000000000      .0000000000       .0000000000      .0000000000     -.4583333333-003  .1018518519-005
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 48 -.1762961981-034  .5438523908-033   .3596314644-033  .2086634542-033  .1168724019-033  .5508956709-034   .2682230341-034
     .9366487790-035  .3997106789-035   .7815186047-036  .2977213732-036 -.3525923962-036  .1116542588-038
 49 -.3660567751-042  .9536616547-041   .5729760036-041  .2784753737-041  .1395694871-041  .5270862925-042   .2322978069-042
     .6290241135-043  .2492149542-043   .3675572509-044  .1336571821-044 -.8419304907-044  .2684416057-046
 50 -.1250041737-010  .5312500000+003   .3750000000+003  .0000000000      .0000000000      .0000000000       .0000000000
     .0000000000      .0000000000       .0000000000      .0000000000     -.1250041737-013  .0000000000
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 83  .4860171278-017  .1490549417-015   .4709750357-015  .7308192303-015  .9664796933-015  .9959203663-015   .9989809393-015
     .7533573812-015  .6288103948-015   .2757963745-015  .2112482853-015  .5346188406-019 -.1620057093-021
 84  .4703738801-014  .3593224973-005  -.6835437761-005 -.1994518260-004 -.2917693574-004 -.2633590070-004  -.5498815466-005
     .2869405864-004  .7310655382-004   .7519531250-004  .1002604167-003  .2351869401-016 -.6271651735-019
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