NASA TECHNICAL NOTE

NASA TN D-2526

c. 1

NASA TN D-2526

NUMERICAL CALCULATION OF POTENTIAL-ENERGY CURVES BY RYDBERG-KLEIN-REES METHOD

by Frank J. Zeleznik

Lewis Research Center
Cleveland, Ohio

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • DECEMBER 1964

NUMERICAL CALCULATION OF POTENTIAL-ENERGY CURVES BY RYDBERG-KLEIN-REES METHOD

By Frank J. Zeleznik

Lewis Research Center
Cleveland, Ohio

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

For sale by the Office of Technical Services, Department of Commerce,
Washington, D.C. 20230 -- Price $0.50

NUMERICAL CALCULATION OF POTENTIAL-ENERGY CURVES BY RYDBERG-KLEIN-REES METHOD

by Frank J. Zeleznik

Lewis Research Center

SUMMARY

A technique is presented for the numerical evaluation of the integrals occurring in the Rydberg-Klein-Rees method of calculating potential energy curves.

INTRODUCTION

The potential-energy curves for the bound states of diatomic molecules can be obtained from spectroscopic constants by using the Rydberg-Klein-Rees method (refs. 1 to 3). Klein (ref. 2) expressed the turning points of motion r_{max} and r_{min} in terms of two auxiliary functions f and g:

$$r_{max} = \left(f^2 + \frac{f}{g}\right)^{1/2} + f$$

$$r_{min} = \left(f^2 + \frac{f}{g}\right)^{1/2} - f$$

Both of the functions f and g depend parametrically on the potential energy U and an additional parameter $K = J(J + 1)\hbar\ /2\mu$ where J is the rotational quantum number and μ is the reduced mass. The functions f and g are defined as

$$f = \frac{1}{2\pi(2\mu)^{1/2}} \int_0^{I'} \frac{dI}{[U - E(I,K)]^{1/2}} \tag{1}$$

$$g = \frac{1}{2\pi(2\mu)^{1/2}} \int_0^{I'} \frac{\frac{\partial E}{\partial K}}{[U - E(I,K)]^{1/2}} dI = \frac{-1}{2\pi(2\mu)^{1/2}} \int_0^{I'} \frac{\frac{\partial[U - E(I,K)]}{\partial K}}{[U - E(I,K)]^{1/2}} dI \tag{2}$$

Here $E(I,K)$ represents the vibrational-rotational energy levels, and $I = h(v + 1/2)$ with v representing the vibrational quantum number. From spectroscopic data, the energy levels are generally expressible in the form

$$E(I,K) = \sum_{l=0}^{p} \sum_{m=0}^{q} Y_{lm}\left(v + \frac{1}{2}\right)^{l} [J(J + 1)]^{m} \tag{3}$$

where Y_{lm} are the usual spectroscopic constants. The upper limits of integration in equations (1) and (2) are obtained from $E(I',K) - U = 0$.

Rees (ref. 3) evaluated the integrals of equations (1) and (2) analytically for special cases where $E(I,K)$ was either quadratic or cubic in I. The results in the cubic case were not in a very convenient form for computation. The results in the quadratic case, however, have been used as the basis for rather extensive calculations by Vanderslice and coworkers (refs. 4 and 5) and others (refs. 6 and 7). Molecules, whose data could not be adequately represented over the entire range by a quadratic, were treated by piecewise fitting of quadratics to the energy levels. As pointed out by Weissman, Vanderslice, and Battino (ref. 8), this piecewise fitting can lead to errors.

The difficulty in the numerical integration of equations (1) and (2) is caused by the fact that the denominator of the integrands has a zero at the upper limit of integration. Jarmain (ref. 9) circumvented this problem in an approximate manner by fitting $[U - E(I,K)]^{1/2}$ to an expression of the form $c(I' - I)^{-d}$. The constants c and d were evaluated by using two points very close to the upper limit of integration. Similarly, $\partial E/\partial K$ was fitted to a quadratic in $I' - I$. These approximations were then analytically integrated to evaluate the contributions to f and g from regions close to I'. More recently, Weissman, Vanderslice, and Battino (ref. 8) introduced a new integration variable $x = [U - E(I,K)^{1/2}$ in order to eliminate the singularity from the integrands. Although correct, this procedure produces some unnecessary numerical inconvenience since the integrands are available as expressions in I and not the integration variable x. Thus, in numerical evaluation of the integrals one cannot use arbitrarily selected increments of x but rather must select increments of I and calculate increments of x as

$$\Delta x = [U - E(I + \Delta I,K)]^{1/2} - [U - E(I,K)]^{1/2}$$

The technique that will be described here does not require the fitting of the integrand near the upper limit, and further, it essentially retains the original integration variable. It is based on the fact that the singularities in the integrands of f and g can be easily removed by an integration by parts.

ALTERNATE METHOD FOR NUMERICAL EVALUATION

The quantity $U - E$ that appears in the integrands of f and g is a polynomial of order p in the variable I with coefficients that depend on K. By introducing the notations $x = v + 1/2$ and $\kappa = J(J + 1)$, the following dimensionless form is obtained:

$$\frac{U - E}{E_0} \equiv P(x;\kappa) = \sum_{l=0}^{p} A_l'(\kappa)x^l$$

where E_0 is a constant with the dimensions of energy and where the coefficients in the polynomial P have the explicit form

$$A_l'(\kappa) = \frac{U\delta_{l0} - \sum\limits_{m=0}^{q} Y_{lm}\kappa^m}{E_0}$$

In this notation the upper limit of integration I' in equations (1) and (2) corresponds to $hx_1(\kappa)$ where $x_1(\kappa)$ is the smallest, real, positive root of $P(x;\kappa)$.

If the existence of the improper integral f is assumed, then equation (1) implies that the polynomial $P(x;\kappa)$ has a zero of order one at $x_1(\kappa)$. If κ_0 is a particular value of κ, then a change in scale $z = x/x_1(\kappa_0)$ can be made, and the polynomial P can be written as

$$P(z;\kappa) = \sum_{l=0}^{p} A_l(\kappa)z^l = (1 - z)R(z;\kappa) - \left[1 - \frac{x_1(\kappa)}{x_1(\kappa_0)}\right]R(z;\kappa) \qquad (4)$$

where $A_l(\kappa) = x_1^l(\kappa_0)A_l'(\kappa)$ and where $R(z;\kappa)$ is a polynomial in z of order $p - 1$. If κ is chosen equal to κ_0, then equation (4) takes on the simple form

$$P(z;\kappa) = \sum_{l=0}^{p} A_l(\kappa)z^l = (1 - z)R(z;\kappa) \qquad (5)$$

where the subscript has been dropped from κ_0 for convenience, and where now

$$A_l(\kappa) = x_1^l(\kappa)A_l'(\kappa)$$

$$R = \sum_{l=0}^{p-1} B_l(\kappa)z^l$$

Comparing coefficients of like powers of z in equation (5) establishes the relation between B_l and A_l as

$$B_l(\kappa) = \begin{cases} \sum_{n=0}^{l} A_n(\kappa) & l = 0, 1, \cdot \cdot \cdot, p - 2 \\ -A_p(\kappa) & l = p - 1 \end{cases} \tag{6}$$

Also from equation (5), for $z = 1$ one can obtain

$$\sum_{l=0}^{p} A_l(\kappa) = 0$$

Combining this with equation (6) finally gives the result

$$B_l(\kappa) = -\sum_{j=l+1}^{p} A_j(\kappa) \qquad l = 0, 1, \ldots, p - 1 \tag{7}$$

The numerator of the integrand of g is essentially $\partial P/\partial\kappa$. This partial derivative is most conveniently evaluated by using the first equality in equation (4). After the differentiation is performed, κ is again chosen to be equal to κ_0. This gives, after dropping the subscript on κ_0,

$$\frac{\partial P}{\partial \kappa} \equiv Q(z;\kappa) = \sum_{l=0}^{p} C_l(\kappa) z^l \tag{8}$$

where

$$C_l(\kappa) = x_1^l(\kappa) \frac{\partial A_l'}{\partial \kappa}$$

The integrals for f and g can be written in dimensionless form by using the Bohr radius a_0 as a unit of length and $E_0 = \hbar^2/2\mu a_0^2$ as a unit of energy. Also, making a change in scale to the new variable z and considering the particular value κ that is equal to κ_0 result in

$$F \equiv \frac{f}{a_0\left(v' + \frac{1}{2}\right)} = \int_0^1 \frac{dz}{P^{1/2}(z;\kappa)} \tag{9}$$

$$G \equiv \frac{-a_0 g}{\left(v' + \frac{1}{2}\right)} = \int_0^1 \frac{\frac{\partial P}{\partial \kappa}}{P^{1/2}(z;\kappa)} dz = \int_0^1 \frac{Q(z;\kappa)}{P^{1/2}(z;\kappa)} dz \tag{10}$$

where the subscript on κ_0 has again been deleted for convenience. Substituting equation (5) for $P(z;\kappa)$ into equations (9) and (10) and performing an integration by parts give

$$F = \frac{2}{R^{1/2}(0,\kappa)} - \int_0^1 \frac{(1 - z)^{1/2}}{R^{3/2}(z;\kappa)} \frac{\partial R(z;\kappa)}{\partial z} dz \tag{11}$$

$$G = 2 \frac{Q(0,\kappa)}{R^{1/2}(0,\kappa)} + 2 \int_0^1 (1 - z)^{1/2} \frac{d}{dz}\left[\frac{Q(z;\kappa)}{R^{1/2}(z;\kappa)}\right] dz \tag{12}$$

In equations (11) and (12) the objective of removing the singularity of the integrands at the upper limit has been achieved.

For the important case $\kappa = 0$, the polynomial coefficients required to evaluate the integrands of equations (11) and (12) have the relatively simple forms

$$\left.\begin{aligned} B_n(0) &= \sum_{m=n+1}^{p} \left(v' + \frac{1}{2}\right)^m \frac{Y_{m,0}}{E_0} \qquad n = 0, 1, \cdot \cdot \cdot, p - 1 \\ C_n(0) &= - \left(v' + \frac{1}{2}\right)^n \frac{Y_{n,1}}{E_0} \qquad n = 0, 1, \cdot \cdot \cdot, p \end{aligned}\right\} \tag{13}$$

No difficulties were encountered in the numerical application of equations (11), (12), and (13) to the calculation of potential-energy curves for several diatomic molecules by using standard integration techniques. In fact, the results of single and double precision calculations for the ground state of hydrogen agreed to at least seven figures when using the spectroscopic constants of Weissman, Vanderslice, and Battino (ref. 8).

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio, September 18, 1964

REFERENCES

1. Rydberg, R.: Graphic Representation of Results of Band Spectroscopy. Zs. Phys., vol. 73, nos. 5-6, Dec. 10, 1931, pp. 376-385.

2. Klein, O.: Calculation of Potential Curves for Diatomic Molecules with Help of Spectral Terms. Zs. Phys., vol. 76, nos. 3-4, May 31, 1932, pp. 226-235.

3. Rees, A. L. G.: The Calculation of Potential-Energy Curves from Band-Spectroscopic Data. Proc. Phys. Soc. (London), vol. 59, Nov. 1947, pp. 998-1008.

4. Vanderslice, J. T., Mason, E. A., Maisch, W. G., and Lippincott, E. R.: Ground State of Hydrogen by the Rydberg-Klein-Rees Method. Jour. Molecular Spectroscopy, vol. 3, no. 1, Feb. 1959, pp. 17-29. (See also errata, vol. 5, no. 1, July 1960, p. 83.)

5. Fallon, Robert J., Vanderslice, Joseph T., and Cloney, Robert D.: Potential Curves and Rotational Perturbations of CN. Jour. Chem. Phys., vol. 37, no. 5, Sept. 1, 1962, pp. 1097-1100.

6. Verma, R. D.: Ultraviolet Resonance Spectrum of the Iodine Molecule. Jour. Chem. Phys., vol. 32, no. 3, Mar. 1960, pp. 738-749.

7. Singh, N. L., and Jain, D. C.: The Rydberg-Klein-Rees Method of Constructing the True Potential Energy Curves of Diatomic Molecules. Proc. Phys. Soc. (London), vol. 79, Feb. 1962, pp. 274-278.

8. Weissman, Stanley, Vanderslice, Joseph T., and Battino, Rubin: On the Recalculation of the Potential Curves for the Ground States of I_2 and H_2. Jour. Chem. Phys., vol. 39, no. 9, Nov. 1, 1963, pp. 2226-2228.

9. Jarmain, W. R.: Transition Probabilities of Molecular Band Systems. XX. Tabulated Klein-Dunham Potential Energy Functions for Ten States of C_2(4), O_2(2), OH(2), and SiO(2). Sci. Rep. 8, Univ. Western Ontario (Canada), July 1, 1961.

NASA-Langley, 1964 E-2606

> *"The aeronautical and space activities of the United States shall be conducted so as to contribute . . . to the expansion of human knowledge of phenomena in the atmosphere and space. The Administration shall provide for the widest practicable and appropriate dissemination of information concerning its activities and the results thereof."*
>
> —NATIONAL AERONAUTICS AND SPACE ACT OF 1958

NASA SCIENTIFIC AND TECHNICAL PUBLICATIONS

TECHNICAL REPORTS: Scientific and technical information considered important, complete, and a lasting contribution to existing knowledge.

TECHNICAL NOTES: Information less broad in scope but nevertheless of importance as a contribution to existing knowledge.

TECHNICAL MEMORANDUMS: Information receiving limited distribution because of preliminary data, security classification, or other reasons.

CONTRACTOR REPORTS: Technical information generated in connection with a NASA contract or grant and released under NASA auspices.

TECHNICAL TRANSLATIONS: Information published in a foreign language considered to merit NASA distribution in English.

TECHNICAL REPRINTS: Information derived from NASA activities and initially published in the form of journal articles.

SPECIAL PUBLICATIONS: Information derived from or of value to NASA activities but not necessarily reporting the results of individual NASA-programmed scientific efforts. Publications include conference proceedings, monographs, data compilations, handbooks, sourcebooks, and special bibliographies.

Details on the availability of these publications may be obtained from:

SCIENTIFIC AND TECHNICAL INFORMATION DIVISION

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Washington, D.C. 20546