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BY THE RYDBERG-KLEIN-REES METHOD

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# NUMERICAL CALCULATION OF POTENTIAL-ENERGY CURVES

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## ABSTRACT

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

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## 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.<sup>1-3</sup> Klein<sup>2</sup> expressed the turning points of motion  $r_{\max}$  and  $r_{\min}$  in terms of two auxiliary functions  $f$  and  $g$ :

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

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

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

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

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

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

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

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

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

Rees<sup>3</sup> evaluated the integrals in (1) and (2) analytically for the 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<sup>4,5</sup> and others<sup>6,7</sup>. 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<sup>8</sup> this piecewise fitting can lead to errors.

The difficulty in the numerical integration of (1) and (2) is caused by the fact that the denominator of the integrands has a zero at the upper limit of integration. Jarman<sup>9</sup> circumvented this problem in an approxi-

mate 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<sup>8</sup> 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  $K$ . Introducing the notations  $x = v + 1/2$  and  $\kappa = J(J + 1)$ , we have in dimensionless form

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

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

$$A'_l(\kappa) = (U_0/E_0) - \sum_{m=0}^q Y_{lm} \kappa^m / E_0$$

In this notation the upper limit of integration  $I'$  in (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 (1) implies that the polynomial  $P(x; \kappa)$  has a zero of order one at  $x_1(\kappa)$ . If  $\kappa_0$  is a particular value of  $\kappa$ , then we can make a change in scale  $z = x/x_1(\kappa_0)$ , and the polynomial  $P$  can be written as

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

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  $\kappa$  is chosen equal to  $\kappa_0$ , then (4) takes on the simple form

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

where the subscript has been dropped from  $\kappa_0$  for convenience, and where

now  $A_l(\kappa) = x_1^l(\kappa) A'_l(\kappa)$  and  $R = \sum_{l=0}^{p-1} B_l(\kappa) z^l$ . Comparing coefficients of

like powers of  $z$  in (5) establishes the relationship between  $B_l$  and

$A_l$  as

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

Also from (5) for  $z = 1$  one can obtain  $\sum_{l=0}^p A_l(\kappa) = 0$ . Combining this

with (6) finally gives the result

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

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 (4). After the differentiation is performed,  $\kappa$  is again chosen to be equal to  $\kappa_0$ . This gives, after dropping the subscript on  $\kappa_0$ ,

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

where

$$C_l(\kappa) = x_l^2(\kappa) \partial A_l' / \partial \kappa$$

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  $E_0 = \hbar^2 / 2\mu a_0^2$ . Also, making a change in scale to the new variable  $z$  and considering the particular value  $\kappa$  that is equal to  $\kappa_0$  result in

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

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

where the subscript on  $\kappa_0$  has again been deleted for convenience.

Substituting (5) for  $P(z; \kappa)$  in (9) and (10) and performing an integration by parts give

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

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

In (11) and (12) we have achieved the objective of removing the singularity of the integrands at the upper limit. For the important case  $\kappa = 0$ , the polynomial coefficients required to evaluate the integrands of (11) and (12) have the relatively simple forms

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

No difficulties were encountered in the numerical application of (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  $H_2$  agreed to at least seven figures when using the spectroscopic constants of Weissman, Vanderslice, and Battino<sup>8</sup>.

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