New method for the evaluation of the RKR potential-integrals for diatomic molecules

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Abstract. We present a new method for the evaluation of the RKR potential-integrals for diatomic molecules. This method is straightforward and fast, and the calculations can be performed to an accuracy better than any other method.

Keywords. Diatomic molecules; potential energy curve.

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1. Introduction

The classical left- and right-hand turning points, r_{min} and r_{max}, of the RKR potential-energy curve, for a diatomic molecule, are given by [1, 2]

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

where the Klein f and g integrals are defined as

$$f(\text{cm}) = \left(\frac{h}{8\pi^2 \mu c}\right)^{1/2} \int_{-\Delta}^{t} [U - E(v, J)]^{-1/2} ds \tag{1}$$

and

$$g(\text{cm}^{-1}) = \left(\frac{8\pi^2 \mu c}{h}\right)^{1/2} \int_{-\Delta}^{t} \frac{\partial E}{\partial [J(J+1)]} [U - E(v, J)]^{-1/2} ds, \tag{2}$$

where

$$s = v + \tfrac{1}{2}, \quad t = v' + \tfrac{1}{2}.$$

v is the vibrational quantum number, and v' is the vibrational quantum number of the vibrational level (with $J = 0$) for which the turning points are to be calculated. The energy of the level is given by

$$U = \sum_{i=0} Y_{i,0} t^i \tag{3}$$

and the energy of the vib-rotational levels, in a diatomic molecule, can be expressed as

$$E(v, J) = \sum_{i,j} Y_{i,j} \left(v + \frac{1}{2}\right)^i [J(J+1)]^j. \tag{4}$$

Here, h is the Planck's constant, c the speed of light, μ the reduced mass of the molecule, J the rotational quantum number and $Y_{i,j}$ are referred to Dunham coefficients. Note that the lower limit of the integrals (1) and (2), following Kaiser [3], has been taken as $-\Delta$, where Δ is the root of the equation

$$\sum_{i=0} Y_{i,0}(-\Delta)^i = 0. \tag{5}$$

For a large number of molecules, the value of the Dunham coefficient $Y_{0,0}$ is zero, and the lower limit of the integrals becomes the same (zero) as used earlier [1,2]. Using (3) and (4), the Klein integrals (1) and (2) can be expressed as

$$f(\text{cm}) = \left(\frac{h}{8\pi^2\mu c}\right)^{1/2} \int_{-\Delta}^{t} \left[\sum_{i=1}^{n} Y_{i,0}(t^i - s^i)\right]^{-1/2} ds \tag{6}$$

and

$$g(\text{cm}^{-1}) = \left(\frac{8\pi^2\mu c}{h}\right)^{1/2} \int_{-\Delta}^{t} \left[\sum_{i=0}^{n} Y_{i,1}s^i\right]\left[\sum_{i=1}^{n} Y_{i,0}(t^i - s^i)\right]^{-1/2} ds. \tag{7}$$

At the upper limit of the integrals (1) and (2) [as well as (6) and (7)], where $s = t$, $E = U$, there is obviously a singular point. A variety of methods [2, 4–16] has been used to deal with this singularity.

Here, we present a new method for dealing with this singularity. This method is straightforward and fast, and the calculations can be done to an accuracy better than any other method.

2. Some latest methods

In this section we have summarized the existing latest methods for comparison with our method to transcribe the notations for the expressions used in these papers, to conform our results.

2.1 *Dickinson* [11], *Tellinghuisen* [13] *and Le Roy* [16]

Dickinson [11], Tellinghuisen [13] and Le Roy [16] used the Gauss–Mehler quadrature for the evaluation of the Klein f and g integrals. In this method, one does not need to evaluate the integrands at the limits of the integration. For the application of the Gauss–Mehler quadrature, the first step is to transform the integration-interval $(-\Delta, t)$ onto $(-1, 1)$ by using the relation

$$s = \tfrac{1}{2}(t - \Delta) + \tfrac{1}{2}x(t + \Delta).$$

Now, the beauty of this quadrature method is that the singularity in the f and g integrals can be offset by choosing the weight function $w(x) = (1 - x)^{-1/2}$. The integral is then approximated by a sum over p points [13, 16]

$$\frac{2}{t + \Delta}\int_{-\Delta}^{t} \phi(s)ds \equiv \int_{-1}^{1} F(x)dx = \int_{-1}^{1} w(x)F_w(x)dx$$

$$\approx \sum_{i=1}^{p} H_i F_w(x_i) = \sum_{i=1}^{p} \frac{H_i F(x_i)}{w(x_i)}, \tag{8}$$

where the abscissae $[x_i]$, and the weights $[H_i]$ are chosen in such a way that the integral will be evaluated exactly when $F_w(x)$ is a polynomial of the order $2p - 1$ or lower. The abscissae $[x_i]$ and weights $[H_i]$ for $p = 1$ to 8 have been tabulated by Tellinghuisen [13], whereas $p = 16$ have been used in the programme of Le Roy [16]. One obvious point here is, to achieve a better accuracy, one should go on increasing the value of p. But the value of p cannot be taken very large because of the computational overhead, as it would be very difficult to calculate abscissae and weights for very large number of points. The accuracy of this method has been claimed to be of six-figures or seven-figures. Fortunately, the programme of Le Roy [16] is available to us. A comparison of the results obtained by this programme (see §4) with those obtained from the analytical expressions shows that the programme reproduces the analytical results up to five-figures, or sometime up to six-figures. However, the programme may reproduce the results of the other scientists up to the claimed number of figures.

2.2 Fleming and Rao [12]

Fleming and Rao [12] suggested a more natural way of removing the singularity of the Klein integrals. Using the identity

$$1 \equiv \left[\sum_{i=1}^{n} Y_{i0} i t^{i-1} \right]^{-1} \left(\left[\sum_{i=1}^{n} Y_{i0} i s^{i-1} \right] + \left[\sum_{i=2}^{n} Y_{i0} i (t^{i-1} - s^{i-1}) \right] \right) \tag{9}$$

in the integrand of (6) and on solving it, they get

$$f(\text{cm}) = \left(\frac{h}{8\pi^2 \mu c} \right)^{1/2} \left[\sum_{i=1}^{n} Y_{i0} i t^{i-1} \right]^{-1} \left(2 \left[\sum_{i=1}^{n} Y_{i0} t^i + Y_{00} \right]^{1/2} \right.$$
$$\left. + \int_{-\Delta}^{t} (t-s)^{1/2} \sum_{i=2}^{n} Y_{i0} i \sum_{k=0}^{i-2} t^{i-2-k} s^k \left[\sum_{i=1}^{n} Y_{i0} \sum_{k=0}^{i-1} t^{i-1-k} s^k \right]^{-1/2} ds \right). \tag{10}$$

Now, using the identity

$$\sum_{i=0}^{n} Y_{i1} s^i \equiv \left[\sum_{i=1}^{n} Y_{i0} i t^{i-1} \right]^{-1} \left(\left[\sum_{i=0}^{n} Y_{i1} t^i \right] \left[\sum_{i=1}^{n} Y_{i0} i s^{i-1} \right] \right.$$
$$\left. + \left[\sum_{i=1}^{n} Y_{i0} i t^{i-1} \right] \left[\sum_{i=0}^{n} Y_{i1} s^i \right] - \left[\sum_{i=1}^{n} Y_{i0} i s^{i-1} \right] \left[\sum_{i=0}^{n} Y_{i1} t^i \right] \right) \tag{11}$$

in the integrand of (7) and on solving it, it follows that

$$g(\text{cm}^{-1}) = \left(\frac{8\pi^2 \mu c}{h} \right)^{1/2} \left[\sum_{i=1}^{n} Y_{i0} i t^{i-1} \right]^{-1} \left(\left[\sum_{i=0}^{n} Y_{i1} t^i \right] 2 \left[\sum_{i=1}^{n} Y_{i0} t^i + Y_{00} \right]^{1/2} \right.$$
$$+ \int_{-\Delta}^{t} (t-s)^{1/2} \left[\sum_{i=2}^{n} \sum_{j=0}^{i-2} Y_{i0} Y_{j1} i s^j t^j \sum_{k=0}^{i-j-2} t^{i-j-2-k} s^k \right.$$
$$- \sum_{i=2}^{n} \sum_{j=i}^{n} Y_{i0} Y_{j1} i s^{i-1} t^{i-1} \sum_{k=0}^{j-i} t^{j-i-k} s^k - Y_{10} \sum_{j=1}^{n} Y_{j1}$$
$$\left. \times \sum_{k=0}^{j-1} t^{j-1-k} s^k \right] \left[\sum_{i=1}^{n} Y_{i0} \sum_{k=0}^{i-1} t^{i-1-k} s^k \right]^{-1/2} ds \right). \tag{12}$$

Equations (11) and (12) are obviously free from the problem of the singularity, as the integrands of the integrals approach to zero at the upper limit of the integrals, but the final expressions are too complicated, as there are nested summations and the calculation would take a long time. Due to the same reason, the accuracy of the calculations may also be affected. Fleming and Rao [12] tested the accuracy of their method by comparing their results with those of Mantz *et al* [10]. The difference between the two sets of the values was less than 0·0000005 Å for r_{min} and less than 0·0000010 Å for r_{max}.

Before Fleming and Rao [12], Zeleznik [8] and Mantz *et al* [10] also, independently, could succeed to remove the singularity of the integrals. But since the evaluation of these methods [8, 10] was more difficult [12] than that of Fleming and Rao [12], the latter [12] was adopted for the evaluation of the RKR potential-energy curves.

2.3 *Kirschner and Watson* [14]

The method of Kirschner and Watson [14] is as follows. Equations (6) and (7) can be written as

$$f(\text{cm}) = \left(\frac{h}{8\pi^2 \mu c}\right)^{1/2} \int_0^{E_{v'}} \frac{1}{\omega_v [E_{v'} - E_v]^{1/2}} \, dE_v \tag{13}$$

and

$$g(\text{cm}^{-1}) = \left(\frac{8\pi^2 \mu c}{h}\right)^{1/2} \int_0^{E_{v'}} \frac{B_v}{\omega_v [E_{v'} - E_v]^{1/2}} \, dE_v, \tag{14}$$

where

$$E_v = \sum_{i=0}^n Y_{i0} s^i \quad E_{v'} = \sum_{i=0}^n Y_{i0} t^i \quad \omega_v = \sum_{i=1}^n Y_{i0} i s^{i-1} \quad B_v = \sum_{i=0}^n Y_{i1} i s^i.$$

They calculated $E_{v'}$, $1/\omega_{v'}$ and $B_{v'}/\omega_{v'}$ for each value of v', and then fitted to the expressions

$$\frac{1}{\omega_{v'}} = \sum_{i=1}^\infty \alpha_n E_{v'}^n, \tag{15}$$

$$\frac{B_{v'}}{\omega_{v'}} = \sum_{i=1}^\infty \beta_n E_{v'}^n \tag{16}$$

to evaluate α_n and β_n by a least squares fit to polynomials of any degree. The degree of the polynomial was increased until the fit was satisfactory. The coefficients α_n and β_n were then inserted in the equations

$$f(\text{cm}) = \left(\frac{h}{8\pi^2 \mu c}\right)^{1/2} \sum_{n=0}^\infty \frac{n!}{(n+\frac{1}{2})(n-\frac{1}{2})\ldots\frac{1}{2}} \alpha_n E_{v'}^{n+1/2} \tag{17}$$

and

$$g(\text{cm}^{-1}) = \left(\frac{8\pi^2 \mu c}{h}\right)^{1/2} \sum_{n=0}^\infty \frac{n!}{(n+\frac{1}{2})(n-\frac{1}{2})\ldots\frac{1}{2}} \beta_n E_{v'}^{n+1/2}. \tag{18}$$

Obviously, in this procedure, it is a very difficult task to evaluate α_n and β_n for every v' from (15) and (16), respectively.

2.4 *Telle and Telle* [15]

The procedure of Telle and Telle [15] can be understood in the following manner. The expressions (6) and (7) can be rearranged as

$$f(\text{cm}) = \left(\frac{h}{8\pi^2\mu c}\right)^{1/2} \int_{-\Delta}^{t} (t-s)^{-1/2} \left[\sum_{k=1}^{n} t^{k-1} \left(\sum_{i=k}^{n} Y_{i,0} s^{i-k}\right)\right]^{-1/2} ds \quad (19)$$

and

$$g(\text{cm}^{-1}) = \left(\frac{8\pi^2\mu c}{h}\right)^{1/2} \int_{-\Delta}^{t} (t-s)^{-1/2} \left[\sum_{i=0}^{n} Y_{i,1} s^i\right]$$

$$\left[\sum_{k=1}^{n} t^{k-1} \left(\sum_{i=k}^{n} Y_{i,0} s^{i-k}\right)\right]^{-1/2} ds. \quad (20)$$

The substitution $t - s = \tau^2$, in the expressions (19) and (20), gives

$$f(\text{cm}) = 2\left(\frac{h}{8\pi^2\mu c}\right)^{1/2} \int_{0}^{\sqrt{t+\Delta}} \left[\sum_{k=1}^{n} t^{k-1} \left(\sum_{i=k}^{n} Y_{i,0} (t-\tau^2)^{i-k}\right)\right]^{-1/2} d\tau$$

$$(21)$$

and

$$g(\text{cm}^{-1}) = 2\left(\frac{8\pi^2\mu c}{h}\right)^{1/2} \int_{0}^{\sqrt{t+\Delta}} \left[\sum_{i=0}^{n} Y_{i,1}(t-\tau^2)^i\right]$$

$$\left[\sum_{k=1}^{n} t^{k-1} \left(\sum_{i=k}^{n} Y_{i,0} (t-\tau^2)^{i-k}\right)\right]^{-1/2} d\tau. \quad (22)$$

These expressions are also free from the problem of singularity. However, due to the existence of nested summations, the calculations would be slow. Furthermore, since we have to evaluate τ^2, and not the linear expression, the accuracy of these results would be affected. Nevertheless, Telle and Telle [15] claimed that the turning point of their calculations agreed to better than 1×10^{-7} Å with those of Dickinson [11], Fleming and Rao [12], and Kirschner and Watson [14].

2.5 *Remark*

One point to be noted here is that all these authors discussed about the accuracy of their results by comparing them with the existing values of other methods. But all of them are doing the calculations by numerical integration and the integrands in their final integrals are *quite complicated*. Therefore, the accuracy of their results may not be as good as mentioned by them. However, the accuracy of all the methods have to be almost the same. The accuracy of the quadrature method cannot be very high as the number of points cannot be taken to be very large. After comparing the results of the quadrature method with those obtained from the other methods, the accuracy has been claimed to be up to seven-figures. Unfortunately, no experimental results are available so that one could have a better estimation about the accuracy. But, fortunately, for a limited number of the Dunham coefficients, there are analytical expressions, which can play an important role for deciding about the accuracy of the results. When we compared the results of the quadrature method with those obtained from the analytical expressions (see §4), we found that the quadrature method could reproduce the

analytical results up to five-figures or sometime up to six-figures. It shows that the accuracy of all these methods may not be as good as reported by the authors, as they have compared the results of one with that of the other.

3. Present approach

Recent calculations [17] show that the Einstein A-coefficients for some vib-rotational transitions, depending on the potential-energy curve, particularly for large rotational quantum numbers J and/or large vibrational quantum numbers v, are very sensitive to the potential-energy curve. Therefore, in order to get reliable results, one should try to get the potential-energy curve as accurate as possible. In the following text, we discuss about our method for the evaluation of the RKR potential-integrals. The accuracy of this method is better than that of the other methods.

In order to have a feeling about the nature of the singularity, we considered the Dunham coefficients for $^{12}C^{16}O$ given by Farrenq *et al* [18], and plotted the arguments given by

$$f' = \left[\sum_{i=1}^{n} Y_{i,0}(t^i - s^i) \right]^{-1/2} \tag{23}$$

and

$$g' = \left[\sum_{i=0}^{n} Y_{i,1}s^i \right] \left[\sum_{i=1}^{n} Y_{i,0}(t^i - s^i) \right]^{-1/2} \tag{24}$$

of the integrals (6) and (7), for $v' = 2$, in figure 1. In the figure, the upper curve is for g', whereas the lower one is for f'. Further, we calculated the values of the integrands, and their gradients, $\partial f'/\partial s$ and $\partial g'/\partial s$, and we report here, in table 1, some values of f', g', $\partial f'/\partial s$ and $\partial g'/\partial s$, in the region near the singularity. The values in table 1, for $s = 2.5$, are calculated very close to the singularity. The figure along with table 1 shows that there is the region from $(t - \varepsilon)$ to t, where $\varepsilon \approx 10^{-2}$, in which the integrands f' and g' have enormously large gradient. The rest of the integrals, from $-\Delta$ to $(t - \varepsilon)$, can be evaluated with the help of the well-known and very accurate methods for numerical integration, e.g., Simpson method. Therefore, in the present approach, each of the Klein f and g integrals has been divided into two parts: (i) from $-\Delta$ to $(t - \varepsilon)$ and (ii) from $(t - \varepsilon)$ to t:

$$f(\text{cm}) = \left(\frac{h}{8\pi^2 \mu c} \right)^{1/2} \left[\int_{-\Delta}^{t-\varepsilon} \left[\sum_i Y_{i,0}(t^i - s^i) \right]^{-1/2} ds + F \right] \tag{25}$$

and

$$g(\text{cm}^{-1}) = \left(\frac{8\pi^2 \mu c}{h} \right)^{1/2} \left[\int_{-\Delta}^{t-\varepsilon} \left[\sum_i Y_{i,1}s^i \right] \left[\sum_i Y_{i,0}(t^i - s^i) \right]^{-1/2} ds + G \right]. \tag{26}$$

The second parts are denoted by F and G, respectively. The first part is evaluated by the Simpson method for numerical integration. The second parts are evaluated analytically in the following manner:

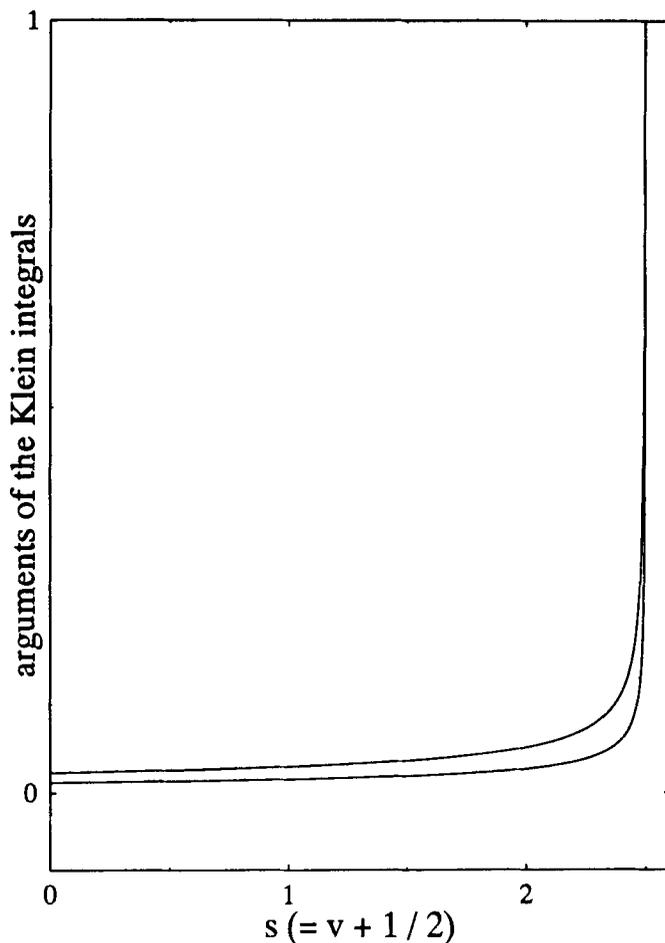$$F = \int_{t-\varepsilon}^{t} \left[\sum_i Y_{i,0}(t^i - s^i) \right]^{-1/2} ds]. \tag{27}$$

Figure 1. Variation of the arguments f' and g' (eqs (23) and (24)) for $v' = 2$, for $^{12}C^{16}O$, using the Dunham coefficients of Farrenq *et al* [18]. The upper curve is for g', whereas the lower one is for f'.

Table 1. Integrands and their gradients.

s	f'	g'	$\partial f'/\partial s$	$\partial g'/\partial s$
2·450	9·7492E − 02	0·1841	0·9752	1·840
2·455	0·1028	0·1941	1·142	2·155
2·460	0·1090	0·2058	1·363	2·572
2·465	0·1165	0·2200	1·665	3·142
2·470	0·1259	0·2376	2·098	3·959
2·475	0·1379	0·2603	2·758	5·205
2·480	0·1542	0·2910	3·855	7·274
2·485	0·1780	0·3361	5·934	11·20
2·490	0·2180	0·4116	10·90	20·58
2·495	0·3083	0·5820	30·83	58·20
2·500	1·2366E + 05	2·3342E + 05	1·9890E + 18	3·7543E + 18

Using $r = t - s$, (27) can be rearranged as

$$F = \int_0^\varepsilon r^{-1/2} [A - rB + r^2 C - r^3 D + r^4 E]^{-1/2} dr, \tag{28}$$

where

$$A = Y_{10} + 2tY_{20} + 3t^2 Y_{30} + 4t^3 Y_{40} + 5t^4 Y_{50} + 6t^5 Y_{60} + 7t^6 Y_{70}$$
$$+ 8t^7 Y_{80} + 9t^8 Y_{90} + \ldots$$

$$B = Y_{20} + 3tY_{30} + 6t^2 Y_{40} + 10t^3 Y_{50} + 15t^4 Y_{60} + 21t^5 Y_{70} + 28t^6 Y_{80}$$
$$+ 36t^7 Y_{90} + \ldots$$

$$C = Y_{30} + 4tY_{40} + 10t^2 Y_{50} + 20t^3 Y_{60} + 35t^4 Y_{70} + 56t^5 Y_{80} + 84t^6 Y_{90} + \ldots$$

$$D = Y_{40} + 5tY_{50} + 15t^2 Y_{60} + 35t^3 Y_{70} + 70t^4 Y_{80} + 126t^5 Y_{90} + \ldots$$

$$E = Y_{50} + 6tY_{60} + 21t^2 Y_{70} + 56t^3 Y_{80} + 126t^4 Y_{90} + \ldots$$

Here, we have taken the terms up to r^4 and it can be easily extended to higher powers of r, depending upon the requirement of the accuracy of the results. Equation (28) can be written as

$$F = \int_0^\varepsilon r^{-1/2} A^{-1/2} \left[1 - \frac{rB - r^2 C + r^3 D - r^4 E}{A} \right]^{-1/2} dr. \tag{29}$$

Using the relation

$$(1 - x)^{-1/2} = 1 + \frac{1}{2}x + \frac{3}{8}x^2 + \frac{5}{16}x^3 + \frac{35}{128}x^4 + \ldots$$

in (29) and retaining the terms up to r^4 only, on integration we get

$$F = \frac{\varepsilon^{1/2}}{A^{1/2}} \left[2 + \varepsilon \left[\frac{B}{3A} \right] + \frac{2}{5}\varepsilon^2 \left[\frac{3B^2}{8A^2} - \frac{C}{2A} \right] + \frac{2}{7}\varepsilon^3 \left[\frac{5}{16}\frac{B^3}{A^3} - \frac{3}{4}\frac{BC}{A^2} + \frac{D}{2A} \right] \right.$$
$$\left. + \frac{2}{9}\varepsilon^4 \left[\frac{35}{128}\frac{B^4}{A^4} - \frac{15}{16}\frac{B^2 C}{A^3} + \frac{3}{4}\frac{BD}{A^2} + \frac{3}{8}\frac{C^2}{A^2} - \frac{E}{2A} \right] \right]. \tag{30}$$

Now,

$$G = \int_{t-\varepsilon}^t \left[\sum_i Y_{i,1} s^i \right] \left[\sum_i Y_{i,0} (t^i - s^i) \right]^{-1/2} ds. \tag{31}$$

Using $r = t - s$, (31) can be rearranged as

$$G = \int_0^\varepsilon r^{-1/2} [a - rb + r^2 c - r^3 d + r^4 e][A - rB + r^2 C - r^3 D + r^4 E]^{-1/2} dr, \tag{32}$$

where

$$a = Y_{01} + tY_{11} + t^2 Y_{21} + t^3 Y_{31} + t^4 Y_{41} + t^5 Y_{51} + t^6 Y_{61} + t^7 Y_{71}$$
$$+ t^8 Y_{81} + t^9 Y_{91} + \ldots$$

$$b = Y_{11} + 2tY_{21} + 3t^2 Y_{31} + 4t^3 Y_{41} + 5t^4 Y_{51} + 6t^5 Y_{61} + 7t^6 Y_{71}$$
$$+ 8t^7 Y_{81} + 9t^8 Y_{91} + \ldots$$

$$c = Y_{21} + 3tY_{31} + 6t^2 Y_{41} + 10t^3 Y_{51} + 15t^4 Y_{61} + 21t^5 Y_{71} + 28t^6 Y_{81}$$
$$+ 36t^7 Y_{91} + \dots$$

$$d = Y_{31} + 4tY_{41} + 10t^2 Y_{51} + 20t^3 Y_{61} + 35t^4 Y_{71} + 56t^5 Y_{81} + 84t^6 Y_{91} + \dots$$

$$e = Y_{41} + 5tY_{51} + 15t^2 Y_{61} + 35t^3 Y_{71} + 70t^4 Y_{81} + 126t^5 Y_{91} + \dots$$

Here also, we have taken the terms up to r^4. One can consider more terms, depending on the requirement of the accuracy of the results. Following the above mentioned procedure, the final expression for G can be obtained as

$$G = \frac{\varepsilon^{1/2}}{A^{1/2}} \left[2a + \frac{2}{3}\varepsilon \left[\frac{Ba}{2A} - b \right] + \frac{2}{5}\varepsilon^2 \left[\frac{3B^2 a}{8A^2} - \frac{Ca}{2A} - \frac{Bb}{2A} + c \right] \right.$$

$$+ \frac{2}{7}\varepsilon^3 \left[\frac{5}{16}\frac{B^3 a}{A^3} - \frac{3}{4}\frac{BCa}{A^2} + \frac{Da}{2A} - \frac{3B^2 b}{8A^2} + \frac{Cb}{2A} + \frac{Bc}{2A} - d \right]$$

$$+ \frac{2}{9}\varepsilon^4 \left[\frac{35}{128}\frac{B^4 a}{A^4} - \frac{15}{16}\frac{B^2 Ca}{A^3} + \frac{3}{4}\frac{BDa}{A^2} + \frac{3}{8}\frac{C^2 a}{A^2} - \frac{Ea}{2A} \right.$$

$$\left. \left. - \frac{5}{16}\frac{B^3 b}{A^3} + \frac{3}{4}\frac{BCb}{A^2} - \frac{Db}{2A} + \frac{3}{8}\frac{B^2 c}{A^2} - \frac{Cc}{2A} - \frac{Bd}{2A} + e \right] \right]. \tag{33}$$

These expressions for F and G look a bit bulky, but they are very simple from the computation point of view. The expressions for F and G, for the given value of v', have to be evaluated one time only, and not on several points taken in the numerical integration. The integrands of the integrals in (25) and (26) are very simple in comparison to the integrands of the methods discussed in the previous section. Thus, the present method is very fast in comparison to the other methods.

The accuracy of the first part of the integrals, here, can be enhanced to any required value by reducing the step-size in the numerical integration. Obviously, the present approach would face less problem of computation time, by reducing the step-size, than the others, as the integrands in the present approach are the simplest ones. The accuracy of the second part of the integrals can be increased by including higher powers of r in (28) and (32). Since the expressions for F and G, for the given value of v', have to be evaluated one time only, the inclusion of the higher powers of r, would not affect the speed of the method.

4. Test for the accuracy

For the limited number of Dunham coefficients, $Y_{0,0}, Y_{1,0}, Y_{2,0}, Y_{0,1}$, and $Y_{1,1}$, Klein f and g integrals can be solved analytically. The analytical expressions are

$$f(\text{cm}) = \left(\frac{h}{8\pi^2 \mu c(-Y_{2,0})} \right)^{1/2} \ln \left[\frac{\sqrt{l^2 - m}}{\sqrt{l^2 + k} - \sqrt{m + k}} \right] \tag{34}$$

and

$$g(\text{cm}^{-1}) = \left(\frac{8\pi^2 \mu c}{h(-Y_{2,0})} \right)^{1/2} (-Y_{1,1})$$

$$\left(\sqrt{m + k} - (l - n)\ln \left[\frac{\sqrt{l^2 - m}}{\sqrt{l^2 + k} - \sqrt{m + k}} \right] \right), \tag{35}$$

where

$$k = \frac{Y_{0,0}}{(-Y_{2,0})}, \quad l = \frac{Y_{1,0}}{2(-Y_{2,0})}, \quad m = \frac{U - Y_{0,0}}{(-Y_{2,0})} \quad \text{and} \quad n = \frac{Y_{0,1}}{(-Y_{1,1})}.$$

For the case, $Y_{0,0} = 0$, these expressions are the same as derived by Rees [2], which have been used as the basis for rather extensive calculations by a number of research-groups and can play an important role for checking the accuracy of the present approach. Fortunately, the programme of Le Roy [16] is available to us. We calculated the classical turning points for the Dunham coefficients, $Y_{1,0}$, $Y_{2,0}$, $Y_{0,1}$, and $Y_{1,1}$ for $^{12}C^{16}O$, given by Farrenq *et al* [18], by using (i) the programme for the quadrature method [16], (ii) the analytical expressions (34) and (35) and (iii) the present method (eqs (25) and (26)). (The Dunham coefficient $Y_{0,0}$ for $^{12}C^{16}O$ is zero.) The values of the turning points are given in table 2.

Table 2 shows that the present method reproduces the analytical results atleast up to seven-figures. For some values of v', it reproduces up to eight-figures. The accuracy of the present method, obviously, can be enhanced by including higher powers of r in (28) and (32), and by reducing the step-size in the numerical integration. Nevertheless, in the present form, the accuracy of the present method is better than that of the other methods. Moreover, here we are deciding about the accuracy by comparing our results with those obtained from the analytical expressions.

Table 2. Turning points for the Dunham coefficients $Y_{1,0}$, $Y_{2,0}$, $Y_{0,1}$ and $Y_{1,1}$.

v'	Quadrature technique		Analytical		Present	
	r_{min}	r_{max}	r_{min}	r_{max}	r_{min}	r_{max}
0	1·08330749	1·17877144	1·08331168	1·17876726	1·08331165	1·17876723
2	1·03421758	1·24989222	1·03421947	1·24989035	1·03421944	1·24989032
4	1·00710030	1·29954077	1·00710172	1·29953937	1·00710169	1·29953933
6	0·98719792	1·34249955	0·98719910	1·34249839	0·98719907	1·34249834
8	0·97123407	1·38207159	0·97123511	1·38207057	0·97123508	1·38207053
10	0·95782732	1·41966713	0·95782827	1·41966621	0·95782824	1·41966616
12	0·94624181	1·45605321	0·94624268	1·45605236	0·94624266	1·45605232
14	0·93603079	1·49171041	0·93603160	1·49170962	0·93603157	1·49170957
16	0·92689885	1·52697092	0·92689963	1·52697018	0·92689960	1·52697013
18	0·91863839	1·56208251	0·91863913	1·56208181	0·91863910	1·56208176
20	0·91109649	1·59724198	0·91109719	1·59724131	0·91109717	1·59724126
22	0·90415626	1·63261440	0·90415693	1·63261376	0·90415691	1·63261371
24	0·89772546	1·66834501	0·89772611	1·66834439	0·89772608	1·66834434
26	0·89172928	1·70456716	0·89172991	1·70456656	0·89172989	1·70456651
28	0·88610551	1·74140798	0·88610613	1·74140740	0·88610610	1·74140735
30	0·88080115	1·77899270	0·88080175	1·77899214	0·88080172	1·77899209
32	0·87576998	1·81744825	0·87577056	1·81744771	0·87577053	1·81744765
34	0·87097076	1·85690652	0·87097133	1·85690599	0·87097131	1·85690593
36	0·86636581	1·89750747	0·86636637	1·89750695	0·86636634	1·89750689
38	0·86191980	1·93940243	0·86192035	·93940192	0·86192033	1·93940186
40	0·85759884	1·98275772	0·85759938	1·98275722	0·85759936	1·98275716

5. Computer programme

The computer programme developed for the present method is available on request from the first author. In the programme one has to put (1) the data for the atomic masses (in atomic units), AMASS(1) and AMASS(2), of the atoms of the diatomic molecule; (2) the Dunham coefficients $Y_{i,0}$ and $Y_{i,1}$ (in cm^{-1}). The indices of the Dunham coefficients is increased by 1, for example, $Y(3,2)$ is used for $Y_{2,1}$.

In the programme, we have used the Dunham coefficients for the CO molecule, given by Farrenq *et al* [18]. The output of the programme is given in Appendix 1, where the Klein integrals F (in cm) and G (in cm^{-1}), the turning points RMIN and RMAX (in Å), and the potential energy (POTENE) (in cm^{-1}) are given for the vibrational quantum number V up to 40.

6. Conclusions

On the basis of the facts mentioned in the previous sections, we can conclude that the present method for the evaluation of the RKR potential-integrals for diatomic molecules is straightforward and fast, and the calculations can be performed to a better accuracy than that of the other methods. In the approach, the accuracy can be enhanced (i) by considering the higher powers of r in (28) and (32) and (ii) by reducing the step-size in the numerical integration of the first part. However, the achievement of the accuracy is limited by the accuracy of the computer used.

Appendix 1

ATOMIC MASSES ARE: 12·00000   15·99491

VIBRATIONAL DUNHAM COEFFICIENTS ARE:

2169·812670	$- 13·28787634$	$1·0411066470E - 02$
$6·9366407560E - 05$	$1·6793523060E - 07$	$2·0592515760E - 09$
$- 8·4881457070E - 10$	$1·2397720130E - 11$	$- 8·2337372780E - 14$

ROTATIONAL DUNHAM COEFFICIENTS ARE:

1·931280985	$- 1·7504392290E - 02$	$7·1739170070E - 07$
$- 2·1463545860E - 08$	$4·4354039090E - 09$	$- 1·3610694500E - 10$
$1·2457857150E - 12$	$- 2·1251234150E - 14$	

V	F	G	RMIN	RMAX	POTENE
0	$4·77277D - 10$	$3·73757D + 06$	1·083312	1·178767	1081·5857
1	$8·30935D - 10$	$6·46760D + 06$	1·053423	1·219610	3224·8568
2	$1·07832D - 09$	$8·34185D + 06$	1·034222	1·249886	5341·6478
3	$1·28258D - 09$	$9·86103D + 06$	1·019395	1·275911	7432·0247
4	$1·46202D - 09$	$1·11710D + 07$	1·007114	1·299518	9496·0550
5	$1·62496D - 09$	$1·23386D + 07$	0·996547	1·321539	11533·8078

V	F	G	RMIN	RMAX	POTENE
6	1·77605D − 09	1·34011D + 07	0·987231	1·342441	13545·3543
7	1·91816D − 09	1·43819D + 07	0·978880	1·362513	15530·7670
8	2·05325D − 09	1·52966D + 07	0·971300	1·381951	17490·1202
9	2·18270D − 09	1·61567D + 07	0·964355	1·400896	19423·4901
10	2·30754D − 09	1·69703D + 07	0·957942	1·419451	21330·9539
11	2·42855D − 09	1·77439D + 07	0·951986	1·437696	23212·5907
12	2·54636D − 09	1·84826D + 07	0·946424	1·455697	25068·4807
13	2·66147D − 09	1·91904D + 07	0·941210	1·473505	26898·7056
14	2·77430D − 09	1·98706D + 07	0·936302	1·491162	28703·3478
15	2·88517D − 09	2·05261D + 07	0·931670	1·508704	30482·4908
16	2·99440D − 09	2·11590D + 07	0·927285	1·526164	32236·2189
17	3·10222D − 09	2·17714D + 07	0·923124	1·543568	33964·6167
18	3·20887D − 09	2·23651D + 07	0·919168	1·560941	35667·7691
19	3·31452D − 09	2·29414D + 07	0·915398	1·578303	37345·7608
20	3·41936D − 09	2·35018D + 07	0·911802	1·595674	38998·6766
21	3·52354D − 09	2·40472D + 07	0·908364	1·613072	40626·6001
22	3·62719D − 09	2·45789D + 07	0·905074	1·630513	42229·6144
23	3·73045D − 09	2·50976D + 07	0·901923	1·648013	43807·8009
24	3·83344D − 09	2·56041D + 07	0·898899	1·665587	45361·2396
25	3·93626D − 09	2·60993D + 07	0·895996	1·683249	46890·0081
26	4·03903D − 09	2·65838D + 07	0·893207	1·701012	48394·1814
27	4·14183D − 09	2·70582D + 07	0·890524	1·718890	49873·8318
28	4·24478D − 09	2·75231D + 07	0·887941	1·736896	51329·0276
29	4·34795D − 09	2·79789D + 07	0·885454	1·755044	52759·8334
30	4·45144D − 09	2·84262D + 07	0·883057	1·773345	54166·3090
31	4·55534D − 09	2·88654D + 07	0·880745	1·791814	55548·5091
32	4·65974D − 09	2·92970D + 07	0·878515	1·810464	56906·4825
33	4·76473D − 09	2·97212D + 07	0·876363	1·829310	58240·2716
34	4·87040D − 09	3·01386D + 07	0·874286	1·848365	59549·9117
35	4·97683D − 09	3·05494D + 07	0·872279	1·867645	60835·4299
36	5·08413D − 09	3·09540D + 07	0·870341	1·887167	62096·8449
37	5·19239D − 09	3·13527D + 07	0·868468	1·906946	63334·1657
38	5·30171D − 09	3·17458D + 07	0·866659	1·927001	64547·3909
39	5·41220D − 09	3·21336D + 07	0·864909	1·947350	65736·5076
40	5·52398D − 09	3·25164D + 07	0·863219	1·968015	66901·4905

Acknowledgements

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