# ON ACCURATE COMPUTATION OF RKR POTENTIALS

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We present an alternative procedure to calculate Klein's $g$ integral. The procedure is free from singularities and allows one to use any standard integrator in the computation of the Rydberg–Klein turning points. Further, we discuss the implementation of the present procedure in pocket calculators.

Accurate interatomic potential energy curves are essential ingredients to model a variety of processes such as those involving atomic and ionic collision phenomena, or in the calculation of vibrational wavefunctions needed to generate reliable band-strength parameters and Franck–Condon-type overlap integrals. In the adiabatic approximation [1] a diatomic system is completely determined by the internuclear potential curves of its several electronic states. Therefore, the determination of these potentials is amongst the most important problems of theoretical specroscopy.

Nowadays, the favorite method of generating potential energy curves for diatomic molecules is the semiclassical Rydberg–Klein–Rees (RKR) method [2–4]. In this method one constructs potential curves from the standard expressions for the vibrational and rotational energy $E=E(v, J)$, where $v$ and $J$ are the quantum numbers associated with vibration and rotation, respectively. Basically, the great advantage of the method is that the resulting curves depend directly on the experimentally determined energy levels and not on derived constants. The method does not depend either on the dissociation energy or on any assumption about the form of the curve. The RKR method is based on the semiclassical WKB approximation and, in spite of this, produces remarkably accurate potential curves, particularly for ground states [5]. An example of this is the comparison of the accurate ab initio and the RKR potential curves for the lightest molecule $H_2$ [6]. Quite often, energies obtained by numerically solving the Schrödinger equation with RKR potentials agree with the experimental values on which the potentials are based [7]. In more complicated cases, when discrepancies between measured and calculated values show up, it is possible to use iterative procedures for the calculation of corrections [8].

The basic ingredient of the RKR method is the energy $E(I, \kappa)$ of vibration and rotation, given as a function of the classical action variable $I$ and of a certain quantity $\kappa$, equal to the square of the angular momentum divided by twice the reduced mass $\mu$. From this, for every vibrational energy $U$, the method generates a pair of turning points, derived from an auxiliary function $S(U, \kappa)$. Using classical mechanics Klein [3] showed that

$$S(U,\kappa)=(2\pi^2\mu)^{-1/2}\int_0^{I'}[U-E(I,\kappa)]^{1/2}\,\mathrm{d}I\,, \qquad (1)$$

where $I'$ is the value of $I$ for which the integrand vanishes. Quantization of vibrational motion and of the angular momentum are taken into account by replacing $I$ and $\kappa$ by their quantum counterparts, namely

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$$I=(v+\tfrac{1}{2})h\,, \tag{2a}$$

$$\kappa=J(J+1)h^2/8\pi^2\mu\,, \tag{2b}$$

where $h$ is Planck's constant. As shown by Klein, the minimum ($r_-$) and maximum ($r_+$) interbarionic separation for a molecule vibrating with energy $U$ are

$$r_\pm=(f^2+f/g)^{1/2}\pm f, \tag{3}$$

where

$$f=\frac{\partial S}{\partial U},\quad g=\frac{\partial S}{\partial \kappa}. \tag{4}$$

Rotationless potential curves require

$$f=\frac{\partial S}{\partial U}\bigg|_{\kappa=0},\quad g=-\frac{\partial S}{\partial \kappa}\bigg|_{\kappa=0}. \tag{5}$$

We shall now briefly consider the practical procedures available for constructing (rotationless) potential curves. To simplify the notation we write the standard expressions for the vibrational energy $G(v)$ and the rotational constant $B(v)$ in terms of experimentally obtained spectroscopic constants $g_i$ and $b_i$ defined by

$$G(v)=\sum_{i=1}^{m} g_i(v+\tfrac{1}{2})^i\,, \tag{6}$$

$$B(v)=\sum_{i=1}^{n} b_i(v+\tfrac{1}{2})^{i-1}\,. \tag{7}$$

Instead of Klein's $U$, given vibrational level $v$ will be now characterized by the more frequently used symbol $E$ ($\equiv G(v)$).

To our best knowledge, all presently available procedures to obtain $f$ and $g$ involve evaluation of the improper integrals

$$f=k\int_{v_{\min}}^{v}[E-G(x)]^{-1/2}\,\mathrm{d}x\,, \tag{8}$$

$$g=\frac{1}{k}\int_{v_{\min}}^{v}B(x)[E-G(x)]^{-1/2}\,\mathrm{d}x\,, \tag{9}$$

where

$$k=(h/8\pi^2c\mu)^{1/2}\,, \tag{10}$$

$c$ being the speed of light. The above integrals are improper because they are clearly singular at the upper limit of integration. The lower limit $v_{\min}$ is the value of $v$ corresponding to the potential minimum. As is trivial to see from eqs. (1) and (2a), $v_{\min}=-1/2$. However, it was later found [9, 10] that an improvement of the potential curve could be obtained by taking [11,12]

$$v_{\min}=-\tfrac{1}{2}-Y_{00}/g_1\,, \tag{11}$$

where

$$Y_{00}=\tfrac{1}{4}(g_2+b_1)-\tfrac{1}{12}g_1b_2/b_1+\tfrac{1}{144}(g_1b_2)^2/b_1^3\,. \tag{12}$$

When using this $v_{\min}$ the energy level is given by $E=G(v)+Y_{00}$ instead of $G(v)$.

As discussed in a plethora of papers, the crucial point in calculating RKR potential curves has been the evaluation of the improper integrals $f$ and $g$. The reason for this is the aforementioned singularity. To overcome this problem a variety of methods has been developed (for specific references see ref. [13]; more recent works are quoted by Kaminsky [14]). In essence, these methods are based on effectively removing the singularities from the integrands. In this task the quadrature method of Gauss proved very effective because it does not require evaluation of the integrand at the limits of integration. In fact, nowadays two widely used programs to generate RKR potential curves are based on gaussian quadrature. One of them is the program of Zare [15] which uses the Gauss–Legendre quadrature. The other widely used program is that of Tellinghuisen [12], who found $w(x)=(1-x)^{-1/2}$ to be a better weight function than $w(x)=1$ used by Zare. Both programs are based on suitable particular cases of the general quadrature known as Gauss–Mehler quadrature [12,16].

While all practical procedures available today to obtain $f$ and $g$ are based on evaluating singular integrals, a case can be made that the original formulation of Klein involves only one integral, given by eq. (1), which is not at all singular. The partial differentiation of, say, a function $P(E)$ with respect to a parameter $E$ can be approximated by

$$\frac{\partial P}{\partial E}=\frac{P(E+\epsilon)-P(E)}{\epsilon}\,, \tag{13}$$

where $\epsilon$ is a small number. The approximation will be quite a good one if $P(E)$ is sensitive to slight variations of $E$. Anyone who tries to use Klein's eqs. (4) or (5) in conjunction with eq. (13) to get $f$ and $g$ soon learns that it generates very accurate $f$ but very poor $g$ values. This might perhaps explain the general preference for first performing analytically the parametric derivates, even at the price of having to deal with singular integrals.

The purpose of this letter is to point out that by introducing another non-singular auxiliary function (similar to $S$ in eq. (1)) it is possible to calculate $g$ from a different parametric derivative than that originally proposed by Klein. In contrast to the formula of Klein, our equation produces accurate $g$ values and can be used as an alternative and efficient method to generate accurate potential curves. The biggest advantage of working with parametric derivatives is that one deals with non-singular integrals, being therefore *free to use any quadrature method in the computation of $f$ and $g$*. Thus, instead of having to worry about proper weight functions and to compute and/or store weights and abscissae, one can use any standard integration routine as, e.g. those commonly available in computer libraries. In calculations to be discussed below, we use Simpson's rule to achieve results of similar accuracy to those reported by Tellinghuisen [12]. Another application to be discussed below is the implementation of the present method in programmable pocket calculators.

The working equations of the present approach are based on the identity

$$\int_{\alpha}^{\beta} a(x)[E-b(x)]^{-1/2}\,\mathrm{d}x = 2\frac{\partial}{\partial E}\int_{\alpha}^{\beta} a(x)[E-b(x)]^{1/2}\,\mathrm{d}x\,. \tag{14}$$

This trivial identity allows one to cast $f$ and $g$ as

$$f = 2k\partial P/\partial E,\quad g=(2/k)\partial Q/\partial E\,, \tag{15}$$

where

$$P(E)=\int_{v_{\min}}^{v}[E-G(x)]^{1/2}\,\mathrm{d}x\,, \tag{16}$$

$$Q(E)=\int_{v_{\min}}^{v}B(x)[E-G(x)]^{1/2}\,\mathrm{d}x\,. \tag{17}$$

These equations are the main results of the present paper. The basic difficulty with Klein's formula for $g$ is that $\partial S/\partial\kappa$ is practically constant for small variations of $\kappa$. An accurate determination of $\partial S/\partial\kappa$ therefore requires a knowledge of $S$ with an exceedingly large number of significant digits for the difference in eq. (13) to give reliable results. Being a function of the energy, our $\partial Q/\partial E$ can be evalutated much more easily.

In table 1 we compare turning points $r_-$ and $r_+$ obtained by using eq. (15) with the corresponding $r_{\min}$ and $r_{\max}$ calculated by Tellinghuisen [12] for the B state of $I_2$ and the X state of CO. For $I_2$ the numbers basically agree to 5 significant digits while for CO 4 digit accuracy is easily achieved. In calculating our turning points we used the same spectroscopic constants as Tellinghuisen. Accordingly, the $Y_{00}$ correction was taken into account for CO and omitted for $I_2$. Although the nuclear masses of both molecules are given by Tellinghuisen with no less than 6 digits, the exact value of $k$ used by him (cf. eq. (10)) remains unknown to us since the actual numerical constants involved were not given and we do not have a copy of his program. Following our previous work [17], we took $h/8\pi c=16.8575$ giving $k=(16.8575/63.45220)^{1/2}$ for $I_2$ and $k=(16.8575/6.85621)^{1/2}$ for CO. The integrals $P(E)$ and $Q(E)$ were evaluated using Simpson's rule with a double precision version of the routine SIMP of Davis and Rabinowitz [18], setting the error tolerance parameter to $10^{-11}$. All calculations were done in double precision (16 significant digits) on an IBM 4341 at the University of Florianopolis. The numbers in table 1 were obtained with $\epsilon=10^{-8}$ in eq. (13), although roughly the same values are obtained using $\epsilon=10^{-7}$ or $10^{-6}$. These values of $\epsilon$ are quite modest and can be used for calculations in the majority of computers available today. More accurate results are to be expected for calculations with smaller values of $\epsilon$ on front-line computers like the CRAY, for instance, or from extrapolations to the limit $\epsilon\to 0$. In table 1 it is also important to observe that for $v=85$ the numbers given by Tellinghuisen for $I_2$ are values for which the algorithm of integra-

Table 1
Comparison of the Rydberg–Klein turning points $r_\pm$ as obtained from eqs. (3), (13) and (15) with $r_{\text{max}}$ and $r_{\text{min}}$ calculated by Tellinghuisen [12]. The upper part of the table ($v$=0–85) refers to $I_2$ while the lower part refers to CO.

| $v$ | $2f$ | $r_-$ | $r_{\text{min}}-r_-$ | $20g$ | $r_+$ | $r_{\text{max}}-r_+$ |
|---|---|---|---|---|---|---|
| 0 | 0.13018 | 2.96304 | 0.00004 | 0.14204 | 3.09322 | 0.00005 |
| 5 | 0.44403 | 2.84399 | 0.00004 | 0.47484 | 3.28802 | 0.00005 |
| 10 | 0.63228 | 2.78859 | 0.00004 | 0.66281 | 3.42087 | 0.00005 |
| 15 | 0.79460 | 2.74977 | 0.00002 | 0.81529 | 3.54438 | 0.00003 |
| 20 | 0.94984 | 2.72038 | 0.00004 | 0.95133 | 3.67022 | 0.00005 |
| 25 | 1.10775 | 2.69777 | −0.00001 | 1.07900 | 3.80552 | 0.00001 |
| 30 | 1.27584 | 2.68023 | 0.00003 | 1.20327 | 3.95607 | 0.00005 |
| 35 | 1.46141 | 2.66685 | 0.00000 | 1.32742 | 4.12826 | 0.00002 |
| 40 | 1.67291 | 2.65662 | 0.00003 | 1.45446 | 4.32952 | 0.00006 |
| 45 | 1.92117 | 2.64897 | 0.00001 | 1.58694 | 4.57014 | 0.00004 |
| 50 | 2.22135 | 2.64320 | 0.00007 | 1.72760 | 4.86455 | 0.00013 |
| 55 | 2.59625 | 2.63910 | 0.00003 | 1.87908 | 5.23535 | 0.00013 |
| 60 | 3.08287 | 2.63627 | −0.00000 | 2.04472 | 5.71914 | 0.00009 |
| 65 | 3.74661 | 2.63447 | 0.00002 | 2.22870 | 6.38108 | 0.00015 |
| 70 | 4.71851 | 2.63330 | 0.00008 | 2.43730 | 7.35181 | 0.00018 |
| 75 | 6.31120 | 2.63140 | 0.00001 | 2.68202 | 8.94260 | 0.00027 |
| 80 | 9.52926 | 2.62294 | −0.00003 | 2.98962 | 12.15219 | 0.00042 |
| 85 | 18.77917 | 2.62208 | 0.00011 | 3.34650 | 21.40126 | 0.00173 |
| | | | | | | |
| 0 | 0.09546 | 1.08330 | 0.00003 | 0.74758 | 1.17877 | −0.00002 |
| 2 | 0.21566 | 1.03422 | 0.00002 | 1.66836 | 1.24989 | 0.00002 |
| 4 | 0.29239 | 1.00708 | 0.00005 | 2.23425 | 1.29947 | 0.00007 |
| 6 | 0.35521 | 0.98722 | 0.00003 | 2.68029 | 1.34243 | 0.00004 |
| 8 | 0.41065 | 0.97127 | 0.00005 | 3.05948 | 1.38192 | 0.00006 |
| 10 | 0.46149 | 0.95794 | 0.00003 | 3.39401 | 1.41943 | 0.00006 |
| 12 | 0.50923 | 0.94642 | 0.00004 | 3.69635 | 1.45565 | 0.00009 |
| 14 | 0.55483 | 0.93628 | 0.00007 | 3.97418 | 1.49111 | 0.00010 |
| 16 | 0.59886 | 0.92727 | 0.00007 | 4.23185 | 1.52613 | 0.00010 |
| 18 | 0.64175 | 0.91916 | 0.00008 | 4.47300 | 1.56091 | 0.00011 |
| 20 | 0.68382 | 0.91176 | 0.00013 | 4.70051 | 1.59558 | 0.00019 |
| 22 | 0.72539 | 0.90527 | −0.00009 | 4.91396 | 1.63066 | −0.00003 |
| 24 | 0.76657 | 0.89916 | −0.00013 | 5.11813 | 1.66573 | −0.00001 |
| 26 | 0.80782 | 0.89312 | 0.00023 | 5.31766 | 1.70094 | 0.00023 |
| 28 | 0.84939 | 0.88824 | −0.00014 | 5.50326 | 1.73763 | −0.00056 |

tion did not converge. This might perhaps explain the relatively large differences at this level, specially between $r_{\text{max}}$ and $r_+$. Part of the remaining differences for all other levels could perhaps be explained as due to the uncertainty in $k$ as discussed above.

Being free to use any integrator, we calculated the same RKR turning points using the built-in integrator of an HP-15C programmable pocket calculator. This calculator has a 10-digit display and, unfortunately, the user's manual does not mention what type of integrator it uses. Fixing the display to 6 significant digits (thereby fixing a compromise between accuracy and time limit for the calculations) we have been able to generate one value of $f$ or $g$ every 2.5 to 3.5 minutes of calculation. In this way it was possible to achieve an accuracy of basically three significant digits wit almost no more additional effort than needed to compute $G(v)$ and $B(v)$. We find this quite remarkable. This means that some future generation of scientific *pocket* calculator, operating a little bit faster and with more significant digits, will make the computation of RKR curves not much more difficult than the evaluation of a polynomial and a square root.

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