Journal of Quantitative Spectroscopy & Radiative Transfer 186 (2017) 158–166

Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

journal homepage: www.elsevier.com/locate/jqsrt

RKR1: A computer program implementing the first-order RKR method for determining diatomic molecule potential energy functions

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ARTICLE INFO

Article history:
Received 10 January 2016
Received in revised form
22 March 2016
Accepted 22 March 2016
Available online 8 April 2016

ABSTRACT

This paper describes computer program **RKR1**, which implements the first-order semi-classical Rydberg–Klein–Rees procedure for determining the potential energy function for a diatomic molecule from a knowledge of the dependence of the molecular vibrational energies G_v and inertial rotation constants B_v on the vibrational quantum number v. **RKR1** allows the vibrational energies and rotational constants to be defined in terms of: (i) conventional Dunham polynomial expansions, (ii) near-dissociation expansions (NDE's), or (iii) the mixed Dunham/NDE "MXR" functions introduced by Tellinghuisen [J Chem Phys 2003; 118: 3532]. Internal convergence tests ascertain and report on the precision of the resulting turning points. For cases in which only vibrational data are available, **RKR1** also allows an overall potential to be constructed by combining directly-calculated well widths with inner turning points generated from a Morse function. It can also automatically smooth over irregular or unphysical behavior of the steep inner wall of the potential.

1. Introduction

The Rydberg [1,2]–Klein [3]–Rees [4] (RKR) method is a widely used first-order semiclassical inversion procedure for calculating the pointwise potential energy curve of a diatomic molecule from a knowledge of the dependence of its vibrational level energies G_v and inertial rotation constants B_v upon the vibrational quantum number v. Within the first-order semiclassical, or WKB, approximation [5], this method yields a unique potential energy function that *exactly* reflects the input functions representing the v-dependence of G_v and B_v. This paper describes a computer program, **RKR1**, for performing such calculations.

In spite of its later ubiquitous use, the success of the RKR method was slow in coming. Rydberg's 1931 publication [1] of the original graphical trial-and-error version of this procedure was followed promptly by Klein's derivation [3] of the integral expressions that are at the core of the method as we know it today [6]. However, while the method did see some use [2], during the two decades following its introduction it was largely ignored. This was likely due to the remarkable success of Dunham's 1932 derivation [7,8] of exact (within the third-order WKB approximation) analytic expressions relating the coefficients of a power series expansion for the potential energy function to the coefficients of the conventional expansion for vibrational–rotational energies as a double power series in $\left(v+\frac{1}{2}\right)$ and $[J(J+1)]$, namely,

$$E(v,J)=\sum_{m=0}\sum_{l=0}Y_{l,m}\left(v+\frac{1}{2}\right)^{l}[J(J+1)]^{m}, \quad (1)$$

in which v and J, respectively, are the vibrational and rotational quantum numbers. By the end of the 1940s, however, the practical limitations of the Dunham

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http://dx.doi.org/10.1016/j.jqsrt.2016.03.030
0022-4073/

approach, particularly its practical restriction to the lower part of the potential well, began to make themselves felt.

In 1947, Rees led subsequent work on this problem by turning his attention to the integral expressions for the turning points derived by Klein [4]. Followed by a number of other workers over the next decade and a half, he devised analytic expressions for these integrals based upon truncated or approximate local representations for the vibrational energies and rotational constants. However, what really changed the situation was Jarmain's 1961 proposal that these integrals should simply be evaluated numerically [9], and Hurley's formal proof that the RKR and first-order Dunham procedures were equivalent [10]. In the early 1960s a number of numerical techniques for evaluating the Klein integrals were proposed and saw service. In particular, Zare's development and generous distribution of his computer program [11,12] effectively made it the de facto standard for a number of years, and contributed immensely to the infectious spread of the method throughout the spectroscopy and molecular physics communities. Moreover, the insightful study by Mantz et al. in 1971 [13] showed that even for a 'moderately light' diatomic such as CO, level energies and B_v constants calculated quantum-mechanically from an RKR potential could be in remarkably good agreement (G_v discrepancies of $\lesssim$0.15 cm^{-1}, B_v discrepancies of $\lesssim$0.003%) with the analytic G_v and B_v functions used to generate that RKR potential, up to over half the well depth. However, as with virtually all methods in use before 1972, Zare's code was based on a relatively crude treatment of the (integrable) singularities in the integrands of the Klein integrals (see below), and thus was incapable of yielding results of high precision.

Finally, a single issue of the *Journal of Molecular Spectroscopy* in 1972 contained three papers reporting accurate and efficient new procedures for evaluating the Klein integrals [14–16]. Of these, the method of Tellinghuisen [16,17] has proved most durable, probably because of its simplicity and very high potential accuracy. The present program is based on the quadrature procedure suggested by Tellinghuisen, but incorporates a number of enhancements not included in other codes. These include: (i) an improved ability to yield accurate results for levels lying very near dissociation, (ii) an automatic smoothing procedure to remove the unphysical behavior sometimes found in the upper part of the inner wall of directly calculated RKR potentials, (iii) the ability to generate complete potentials when only vibrational energies are available (another innovation introduced by Tellinghuisen [18]), and (iv) provision of upper bounds on the numerical precision of the calculations.

The current version of the (thoroughly commented) source code for **RKR1** is included in the Supplementary Material associated with this paper, together with a Manual (presented as Appendices in that Supplementary Material) that provides a detailed description of the nature of the input data files, as well as sample input files and listings of the resulting output.

2. Methodology

2.1. Background theory

The theory underlying the RKR method is discussed in the literature and in a number of monographs [1–5,10,19–24]. For the interested reader, a full derivation of the basic equations is presented in Appendix D in the Supplementary Material associated with this paper. The key result of this theory consists of the two Klein integrals on which the RKR method is based, specifically

$$r_2(v)-r_1(v)=2\sqrt{\mathbb{C}_u/\mu}\int_{v_{min}}^{v}\frac{dv'}{[G_v-G_{v'}]^{1/2}}=2f, \tag{2}$$

$$\frac{1}{r_1(v)}-\frac{1}{r_2(v)}=2\sqrt{\mu/\mathbb{C}_u}\int_{v_{min}}^{v}\frac{B_{v'}\,dv'}{[G_v-G_{v'}]^{1/2}}=2g, \tag{3}$$

in which $r_1(v)$ and $r_2(v)$ are the inner and outer classical turning points respectively on the potential energy function for vibrational level v with energy G_v, B_v is the inertial rotational constant for that vibrational level, and v_{min} is the non-integer effective value of the vibrational quantum number at the potential minimum. In this expression G_v and B_v are assumed to have units cm^{-1}, the reduced mass μ is in amu, and the turning points are in Å, and hence the constant $\mathbb{C}_u=\hbar^2/2=16.857629206$ amu Å^2 cm^{-1} [25]. Program **RKR1** defines μ as Watson's charge-modified reduced mass [26]

$$\mu=\mu_W\equiv\frac{M_AM_B}{M_A+M_B-Qm_e}, \tag{4}$$

in which M_A and M_B are the normal atomic isotope masses, m_e is the electron mass, and $Q\equiv$ CHARGE is the integer net charge on the molecule. The numerical values of $\mathbb{C}_u$ and m_e used in the program are based upon the current recommended physical constants [25], while the most recent values for the masses of all stable atomic isotopes [27] are included in a program data subroutine. Rearrangement of Eqs. (2) and (3) gives the final expressions:

$$r_1(v)=\sqrt{f^2+f/g}-f, \tag{5}$$

$$r_2(v)=\sqrt{f^2+f/g}+f. \tag{6}$$

It is important to remember that although the semiclassical quantization condition maps integer values of v onto the quantized vibrational energy levels, v may be treated as a continuous variable within the semiclassical approach. This is illustrated by the fact that within the first-order RKR method the lower bound of integration, defined by the potential minimum, is associated with $v_{min}=-\frac{1}{2}$, while in higher-order semiclassical treatments it is a real number that is close to, but not identical to $-\frac{1}{2}$. More generally, it means that turning points may be calculated for either integer or non-integer values of v. This is an important point, since turning points calculated only for integer values of v would provide a relatively sparse grid for defining the potential, thereby making it difficult to rely on for precise numerical calculations. For this reason program **RKR1** allows the user to specify multiple

vibrational intervals within which turning points may be calculated using different mesh sizes.

Finally, it is also important to remember that the normal RKR inversion procedure is only exact within the first-order semiclassical or WKB approximation. This approximation is sufficiently accurate that for 'heavy' (large-reduced-mass) molecules, quantum mechanical level spacings and B_v values calculated (numerically) from the resulting potentials normally agree fairly well with the experimentally determined input G_v and B_v functions (i.e., with discrepancies close to the experimental uncertainties). However, both for hydrides and for heavier species (e.g., CO [13]) significant discrepancies are often found between such results and the 'exact' experimental values of those quantities defined by those input functions. More accurate RKR-type methods based on higher-order semiclassical quantization conditions have been reported [22,28,29], but none has (yet!) been implemented in a robust, documented, and publicly available code.

One approximate way of attempting to go beyond the first-order semiclassical method has been implemented as an option in **RKR1**. First introduced in 1970 by Kaiser [30], this procedure is based upon the fact that within the third-order semiclassical quantization condition [5,22,29,31], the value of v associated with the potential minimum may be written approximately as

$$v_{\min} = -\frac{1}{2} - \frac{Y_{0,0}}{Y_{1,0}}, \tag{7}$$

in which $Y_{0,0}$ is given by [8,32]

$$Y_{0,0} = \frac{Y_{0,1}+Y_{2,0}}{4} - \left(\frac{Y_{1,1}\,Y_{1,0}}{12Y_{0,1}}\right) + \frac{1}{Y_{0,1}}\left(\frac{Y_{1,1}\,Y_{1,0}}{12Y_{0,1}}\right)^2, \tag{8}$$

and the $Y_{l,m}$ constants for $\{l,m\} \neq \{0,0\}$ are defined by appropriate derivatives of the vibration–rotation energy with respect to v and $[J(J+1)]$ (see Eq. (1)), evaluated at $v = -\frac{1}{2}$ and $J = 0$. This "Kaiser correction" has often been used when calculating RKR potentials, especially for small-reduced-mass species, such as hydrides, for which values of $Y_{0,0}$ tend to be relatively large.

Use of the Kaiser correction would superficially appear to be 'obviously' better than a basic first-order treatment, in that it takes at least some account of higher-order semiclassical effects. However, detailed numerical studies [33] indicate that its use sometimes/often yields a potential curve whose quantum-calculated vibrational level spacings and B_v values are in *worse* agreement with the input G_v and B_v functions than are those obtained from a 'basic' first-order calculation. The reason for this is that the Kaiser correction effectively assumes that contributions to the quantization condition from the higher-order phase integrals are independent of v, which is not true in general [34]. Thus, a user of **RKR1** who chooses to invoke the Kaiser correction to try to obtain highly accurate results would be advised to perform quantum calculations on the resulting potential [35,36] to check whether or not its use actually improves the level of agreement with the G_v and B_v functions employed to generate the potential.

In any case, independently of whether or not the Kaiser correction is used, the zero of energy for turning points generated by **RKR1** is the energy associated with the value of $v_{\min} \equiv$ `v00` shown in the program output (see Appendix C of the Supplementary Material).

2.2. Representations for G_v and for B_v

RKR1 offers a user three possible ways of representing the v-dependence of the vibrational energies G_v and the inertial rotational constants B_v, with the choice of representation for the particular case being specified by parameters in the input data file.

2.2.1. Dunham expansions

The first type of representation for G_v and B_v is the conventional power series in $(v+\frac{1}{2})$ associated with Dunham: [8,32],

$$G_v = \sum_{l=1} Y_{l,0}\left(v+\frac{1}{2}\right)^l = \omega_e\left(v+\frac{1}{2}\right) - \omega_e x_e\left(v+\frac{1}{2}\right)^2 + \omega_e y_e\left(v+\frac{1}{2}\right)^3 + \cdots \tag{9}$$

$$B_v = \sum_{l=0} Y_{l,1}\left(v+\frac{1}{2}\right)^l = B_e - \alpha_e\left(v+\frac{1}{2}\right) + \gamma_e\left(v+\frac{1}{2}\right)^2 + \cdots \tag{10}$$

2.2.2. Near-dissociation expansions (NDE's)

The second type of functional representation allowed by **RKR1** is pure "near-dissociation expansions" (NDE's), functions that incorporate the theoretically-known [37–39] limiting near-dissociation behavior of G_v or B_v within expressions that include empirical parameters to be determined from the experimental data [40–45]. Just as the conventional Dunham expressions are expansions about the limiting case of harmonic-oscillator/rigid-rotor behavior at the potential minimum, NDE's are expansions about the theoretically-known limiting functional behavior near dissociation, and hence they are much more effective for extrapolating to large values of v, i.e., to values of v lying beyond the range of observed data [41,42,44] and/or for compactly representing data sets spanning a large fraction of the potential well [40,43,45–47]. The rest of this subsection describes the NDE expressions and their parameterization in program **RKR1**: users who are not familiar with this approach may wish to review some of the associated theory and review papers [29,37–39,42,48,49], and illustrative applications of this approach [41,43,45–47,50–52].

The theory underlying NDE expressions for vibrational energies, rotational constants and other properties of vibrational levels lying near dissociation is based on the fact that these properties depend mainly on the shape of the potential energy function near the outer turning points [37]. As a result, their v-dependence is mainly determined by the limiting asymptotic behavior of the intermolecular potential, which has the simple attractive inverse-power form

$$V(r) = \mathfrak{D} - \frac{C_n}{r^n}, \tag{11}$$

in which $\mathfrak{D}$ is the energy at the dissociation limit, the (known) power n is determined by the nature of the electronic states

of the atoms formed when the given molecular state dissociates [37,39], and reliable values of the limiting long-range coefficient C_n are often known from theory.

The NDE expressions for G_v and B_v are usually written as [43,45]

$$G_v = \mathfrak{D} - K_0^{\infty}(v) \times \mathcal{F}_0(v_{\mathfrak{D}} - v), \tag{12}$$

$$B_v = K_1^{\infty}(v) \times \mathcal{F}_1(v_{\mathfrak{D}} - v), \tag{13}$$

in which $v_{\mathfrak{D}}$ is the (non-integer) effective vibrational index at dissociation and the $\mathcal{F}_m(v_{\mathfrak{D}} - v)$ are empirically determined expressions that are required to approach unity in the limit $v \to v_{\mathfrak{D}}$. The theoretical limiting near-dissociation behavior of $[\mathfrak{D} - G_v]$ and B_v incorporated into these functions is given by

$$K_m^{\infty}(v) = X_m(n, C_n, \mu)(v_{\mathfrak{D}} - v)^{[2n/(n-2)]-2m}, \tag{14}$$

in which $X_m(n, C_n, \mu) = \overline{X}_m(n)/[(\mu)^n (C_n)^2]^{1/(n-2)}$ and $\overline{X}_m(n)$ is a known numerical factor depending only on the physical constants and the value of the integer n [29,37,38].

The empirically-determined functions $\mathcal{F}_m(v_{\mathfrak{D}} - v)$ used by **RKR1** have one of the forms

$$\mathcal{F}_m(v_{\mathfrak{D}} - v) = \left(\frac{1 + \sum_{i=t}^{L} p_i^m (v_{\mathfrak{D}} - v)^i}{1 + \sum_{j=t}^{M} q_j^m (v_{\mathfrak{D}} - v)^j} \right)^{\mathcal{S}} \tag{15}$$

or

$$\mathcal{F}_m(v_{\mathfrak{D}} - v) = \exp\left\{ \sum_{i=t}^{L} p_i^m (v_{\mathfrak{D}} - v)^i \right\}. \tag{16}$$

In the rational polynomial expression of Eq. (15) the exponent power $\mathcal{S}$ is either $\mathcal{S} = 1$, yielding what is called an "outer" expansion, or $\mathcal{S} = 2n/(n-2)$, yielding an "inner" expansion, and the most appropriate choice for the power t of the leading expansion term is often known from theory [49,53].

While they are somewhat more complicated to use, NDE expressions have two particular advantages over Dunham expansions.

- Because they explicitly incorporate the theoretically-known limiting near-dissociation behavior of vibrational energies and other properties, they are much more reliable for the extrapolated prediction of the dissociation energy and of the number, energies and properties of unobserved high vibrational levels. This means that NDE expressions allow the calculation of realistic and reasonably reliable turning points in the region between the highest observed vibrational level and the dissociation limit. In contrast, as with all polynomial functions, Dunham expansions are notoriously unreliable for performing extrapolations, and even the turning points for the highest observed levels may not be reliable [54].
- For systems in which the experimental data span a large fraction of the potential well, NDE's tend to be more compact than Dunham expansions that yield fits of equivalent quality, as the dense manifold of levels near dissociation is represented accurately by a very small number of empirical NDE expansion parameters.

2.2.3. "MXR" mixed near-dissociation/Dunham expansions

In spite of their numerous advantages, applications of NDE representations to states with very large numbers of vibrational levels tend to encounter difficulties. Tellinghuisen has shown that these problems could be resolved by using mixed representations consisting of Dunham-type power series for levels spanning the lower part of the potential energy well and NDE expansions for levels lying near dissociation [46,55,56]. In particular, his "MXR" mixed representation functions use

- a normal Dunham polynomials in $(v+\frac{1}{2})$ for $v \lesssim v_s$, and
- a near-dissociation expansion for $v \gtrsim v_s$,

and merges them at a chosen switch-over point $v = v_s$ using the switching function

$$F_s(v) = \left\{ 1 + \exp\left(\frac{v - v_s}{\delta v_s} \right) \right\}^{-1} \tag{17}$$

to yield the MXR expressions

$$G_v^{\mathrm{MXR}} = F_s(v) G_v^{\mathrm{Dun}} + [1 - F_s(v)]\, G_v^{\mathrm{NDE}}, \tag{18}$$

and

$$B_v^{\mathrm{MXR}} = F_s(v) G_v^{\mathrm{Dun}} + [1 - F_s(v)]\, B_v^{\mathrm{NDE}}. \tag{19}$$

Thus, to specify an MXR expansion it is necessary to input values for the Dunham coefficients ($\{Y_{l,m}\}$), values of the physical ($\mathfrak{D}$, $v_{\mathfrak{D}}$ and X_m) and empirical ($\{p_i^m\}$ and $\{q_j^m\}$) parameters defining the NDE function, and values of the parameters v_s and δv_s defining the switching function. Because of the sensitivity of the function to the values of $v_{\mathfrak{D}}$, v_s and δv_s, they should all be input precisely using floating point "d" format (e.g., v_s=27.50d0).

Note that the type of representation that **RKR1** uses for B_v need not be the same at that used for G_v; however, the former cannot be more sophisticated than the latter. In particular: if G_v is represented by a Dunham expansion, then so must B_v; if G_v is represented by an NDE function, then B_v may be represented either by a Dunham or an NDE function; if G_v is represented by an MXR function, then B_v may be represented by any of the three types of function.

2.3. Evaluating the f and g integrals

As mentioned above, early applications of the Klein inversion integrals Eqs. (2) and (3) had difficulty dealing with the (integrable) integrand singularity at the upper end of the range of integration. Tellinghuisen pointed out [16,17] that this problem is completely removed by use of the Gauss–Mehler quadrature formula [57,58] as its points and weights implicitly take account of such behavior. In particular, the f integral of Eq. (2) is readily rearranged into the form:

$$f = \sqrt{\frac{\mathbb{C}_{\mathrm{u}}}{\mu}} \int_{v_{\min}}^{v} \frac{[v - v']^{1/2}}{[G_v - G_{v'}]^{1/2}} \frac{dv'}{[v - v']^{1/2}} \tag{20}$$

$$= \sqrt{\frac{\mathbb{C}_{\mathrm{u}}}{\mu}} \int_{v_{\min}}^{v} p(v') \frac{dv'}{[v - v']^{1/2}},$$

in which the function $p(v')=[(v-v')/(G_v-G_{v'})]^{1/2}$ is well behaved (smooth, with no singularities) on the entire interval; this is precisely the form required by the Gauss–Mehler quadrature formula [58].

Tellinghuisen showed that for vibrational levels extending 80% of the way to dissociation, use of the Gauss–Mehler formula with only four quadrature points typically yields f and g integrals with an accuracy of better than 1 part in 10^7 [16,17]. However, he also showed that the error grows rapidly for the higher vibrational levels, and it is important to ensure that these errors do not become unacceptably large. Moreover, many applications require (or at least desire) potentials that are smooth virtually to machine precision. Thus, there is a need for an enhanced procedure that can yield both higher accuracy and some indication of the precision of the resulting turning points.

The most obvious way of increasing the accuracy of any integration procedure is simply to increase the number of quadrature points used. However, for a Gaussian quadrature procedure, whose points and weights are not readily generated analytically, it can be very inconvenient to attempt to invoke ever-higher-order quadrature formulae for testing and improving the accuracy of a desired result. Following an approach introduced by Tellinghuisen [16,17] the present program uses a fixed number of quadrature points in the numerical integration procedure(s), but with the overall integration interval being repeatedly subdivided into smaller intervals until the total integral converges. In particular, since the singularities in the integrands in Eqs. (2) and (3) lie at the upper end of the range, dividing the interval in half will yield two types of sub-intervals: in the first sub-interval, $[v_{\min},(v_{\min}+v)/2]$, the integrand is everywhere well behaved, so the ordinary Gauss–Legendre quadrature formula will suffice (See Section 25.4.30 of Ref. [57]); in the second sub-interval, $[(v_{\min}+v)/2,v]$, the integrand has the same singular behavior found when the whole interval is treated as a single unit, and the Gauss–Mehler procedure is again appropriate. If one repeatedly bisects all sub-intervals, then following the mth stage of subdivision, the first (2^m-1) sub-intervals may be treated using the ordinary Gauss–Legendre procedure, while only the last sub-interval requires use of Gauss–Mehler points and weights. Consideration of the error term associated with the ordinary Gauss–Legendre quadrature scheme indicates that if an N–point quadrature is being performed on each subinterval, the overall error decreases by a factor of $1/2^{2n}$ with each stage of subdivision. For $N=16$, this corresponds to an increase in accuracy by more than four orders of magnitude at each bisection, while only one set of points and weights (of each type) needs to be introduced and stored. Thus, both rapid convergence and programming simplicity are achieved.

In the present version of program **RKR1**, N has been set at 16, and the necessary Gauss–Legendre and Gauss–Mehler quadrature points and weights are prepared (in subroutine WGHT) on first entering the program. At each energy G_v for which turning points are desired, the program begins by using a single $N=16$ point Gauss–Mehler quadrature to evaluate the integrals of Eqs. (2) and (3). The interval is then divided in half, the appropriate quadrature schemes applied in the two parts, and the results summed. The fractional changes in the two integrals `tst(f)` and `tst(g)` are then calculated and compared with an internally specified convergence criterion, `TOLER`. This iterative subdivision is then repeated until the convergence criterion is satisfied. When it is, the turning points are calculated from Eqs. (5) and (6) and printed out, together with the final values of `tst(f)` and `tst(g)` and the total number of sub-intervals used in the final iteration cycle, $\mathrm{NDIV}=2^m$. Thus, turning points generated by the present program are accompanied by estimated upper bounds to their numerical errors.

In a procedure such as this, the convergence criterion `TOLER` would normally be set at a small number, such as 1×10^{-10}. For many computers, however, optimum convergence is achieved by simply requiring the iteration cycle to continue until the accumulative effect of numerical truncations causes the magnitude of `tst(f)` or `tst(g)` to *increase* from its value for the preceding cycle. Both of these convergence tests are used in **RKR1**. The first test is based on a relative convergence test of $\mathrm{TOLER}=10^{-10}$, which is set in line 60 of the code (and may be modified by the user). If this criterion is made too demanding for ordinary double-precision arithmetic (say, $\mathrm{TOLER}=10^{-16}$), the relative truncation error criterion takes over.

The approach described above is implemented in **RKR1**, and it provides a reliable and stable integration procedure for essentially all cases. The only situations in which complete numerical convergence is not achieved are those in which a substantial loss of significant digits occurs in the calculation of $[G_v-G_{v'}]$ or B_v, either because the level whose turning points are being calculated lies very close to the dissociation limit or to the potential minimum, or because of a loss of significant digits when adding large terms of opposite sign. Examples of such behavior are found in the illustrative cases presented in the Supplementary Materials associated with this paper. These anomalies could be removed by the use of quadruple precision (`REAL*16`) arithmetic in the program. However, the loss of accuracy due to these problems is not significant relative to the error in the first-order RKR method itself, and a `REAL*16` implementation of the code would inhibit its use by some researchers, so printout of occasional warning messages due to this problem is deemed to be a tolerable irritation.

2.4. Smoothing over an irregular inner potential wall

Inadequacies in the experimentally-derived functions characterizing G_v and B_v will, of course, give rise to errors in calculated RKR turning points. Since the repulsive inner wall of the potential is very steep, especially at high vibrational energies, these errors sometimes manifest themselves as non-physical behavior in this region. For example, rather than have a negative slope and positive curvature that increases slowly with energy, this inner wall may pass through an inflection point and take on negative curvature, or the inner turning points obtained from Eq. (5) may even turn outward with increasing energy, with the algebraic sign of the slope becoming positive. Occasional papers in the literature have accepted behavior such as inflection and negative curvature or

"wiggling" of the inner wall as being real, and attempted to explain it in terms of potential curve crossings or related effects. However, it normally merely reflects inadequacies of the molecular constants used in the calculation [59–62].

Except for the zero-point level of the ground state, whose properties may sometimes be determined by microwave spectroscopy, experimental data often define the G_v function with greater relative accuracy than the B_v function. For this reason, irregular behavior of the inner wall of an RKR potential may normally be attributed to inadequacies in the latter [59,61]. (Indeed, minimization of such irregularities has been proposed as a means of improving otherwise poorly-known rotational constants [59].) However, whatever the source of the problem, a modest degree of inappropriate behavior of either the G_v or B_v function will give rise to non-physical behavior of the steep inner wall of the potential, since the expected monotonic increase in slope with energy makes even very small errors in the f and/or g integrals manifestly evident there. At the same time, while small relative errors in the f or g integral would make the curvature or slope of the inner wall at high energy change in an unacceptable non-physical manner, the rapid growth of the f integral with increasing G_v means that the width of the potential $[r_2(v)-r_1(v)]$ as a function of energy may still be relatively well defined by Eq. (2), even when the directly-calculated inner potential wall is unreliable. Thus, combining this directly-calculated well-width function with a reasonable extrapolated inner potential wall (a procedure first introduced by Verma [63]) should yield a 'best' estimate of the upper portion of the potential obtainable from the available G_v and B_v functions. Program **RKR1** incorporates the following automatic procedure for doing this.

As a first step, it is necessary to determine whether or not the directly-calculated inner potential wall displays irregular behavior, and if it does, to locate its onset. **RKR1** accomplishes this in the following way. The turning-point calculation normally starts near the potential minimum and proceeds monotonically to successively higher energies. On completion of the calculation for each value of v, the program fits the inner turning point for that case and those for the two closest smaller v values to the function

$$V_{\rm inner}(r) = A + Be^{-Cr}, \tag{21}$$

and the value of the resulting exponent parameter $C \equiv$ C(exp) is printed with the turning points in the main output file. If the inner wall is well-behaved, the resulting values of C(exp) will be positive and will increase slowly from one level to the next. However, if the directly-calculated repulsive inner wall passes through a point of inflection, then C(exp) will change sign, while if that directly-calculated wall begins to double over outward, C(exp) will grow rapidly, become quite large (and negative) and approach a singularity just before the slope becomes positive. Thus, the behavior of C(exp) is the required indicator of the onset of non-physical behavior (see illustrative output files in the Supplementary Material).

To correct for such irregular behavior by imposing a smooth inner wall on the potential in the affected region, the user must first perform an RKR calculation while setting input parameter VEXT ≤ 0 (see READ statement #16 in Appendix B). Examination of the behavior of the C(exp) values listed in the program output then allows one to determine whether there exists some energy above which the directly-calculated inner potential wall can no longer be trusted. If so, the program should be re-run with the value of VEXT set equal to the vibrational index associated with that energy. When this is done, inner turning points for levels $v \geq$ VEXT will be calculated from Eq. (21) using the values of the constants A, B and C associated with the three largest v values for which $v \leq$ VEXT, and the corresponding outer turning points obtained by adding $2f$ to the associate inner turning point. When this is done, the program also prints the values of the displacements d(RMIN) from the directly-calculated turning points RMIN $= r_1(v)$ that yield the desired smoothing of the inner wall. Examples of this type of correction are found in the sample illustrative output files in the Supplementary Material.

2.5. Determining a potential in the absence of rotational constants

If no experimental B_v values are available for the system of interest, the g integrals of Eq. (3) may not be evaluated. However, directly calculated values of the f integral of Eq. (2) may still be combined with some assumed inner potential wall and used to generate a realistic overall potential. Following an approach recommended by Tellinghuisen for this type of situation [18], program **RKR1** can automatically generate the inner potential wall from a Morse function

$$V_{\rm Morse}(r) = \mathfrak{D}_e[e^{-\beta(r-r_e)} - 1]^2 \tag{22}$$

and generate the corresponding outer turning points by adding values of $2f$ calculated from Eq. (2) to the Morse-function inner turning point at each specified energy.

This option is invoked in **RKR1** by setting input parameter NDEBv $= -1$ and reading in a value for the Morse potential equilibrium distance r_e (Å). The program then uses the first two derivatives of the vibrational energy at the potential minimum ($Y_{1,0} = \omega_e$ and $Y_{2,0} = -\omega_e x_e$) to determine the apparent well depth $\mathfrak{D}_e$ and exponent parameters β that define the Morse function that will then be employed to generate the required inner turning point values at the specified energies.

3. Technical details: units, array dimensions and input/output

All input or output quantities associated with program **RKR1** are either dimensionless or have units with energy in cm^{-1} and lengths in Å. As was mentioned earlier, the electron and atomic masses and the physical constants used to define the constant $\mathbb{C}_u$ appearing in Eqs. (2) and (3) were taken from the most recent compilations [27,25]. For all stable isotopes of all atoms, the masses are found in the data subroutine MASSES, so all a user need to specify in the input is the atomic number and mass number of each atom of the molecular isotopolog considered in the

analysis although, if desired, other non-standard masses can be read in.

In the current version of the program, the array dimensioning allows for the calculation of pairs of turning points for up to 500 vibrational levels, and for Dunham or NDE polynomial expansions of order up to 25. However, a user may readily change this by making appropriate modifications to the array dimensioning `PARAMETER` statements in lines 19 and 600 of the source code.

Program **RKR1** reads the input data file in 'free format' on Channel-5 (e.g., READ(5,*), etc.). The structure of the requisite data file and precise definitions of the various program options are presented in Appendices A and B of the Supplementary Material. The program writes standard output to Channel-6, and a supplementary output file to Channel-7. The standard output written to Channel-6 presents a complete description of the input data and lists the calculated turning points and upper bounds to the precision of the calculated f and g integrals.

While the main Channel-6 output file contains both the numerical results and a detailed description of the input data file, the turning points are listed there in pairs as a function of v, a format that is not convenient for use as input to most other programs. The Channel-7 output file therefore provides a compact listing of those turning points, supplemented by the value of r_e defined by the value of B_v at $v = v_{\min}$, arranged in order of increasing distance. In addition, to facilitate use of the resulting potential array for making plots or for numerical calculations, the inner wall is extrapolated by including in the Channel-7 output array five additional points generated from the version of from Eq. (21) associated with the highest vibrational levels for which turning points have been generated.

The source code was written in the Fortran language, and has been tested using the SUN Fortran-77 and Fortran-90 compilers, as well as the public domain gfortran compilers.

If one is executing **RKR1** in a UNIX or Linux operating system environment, it may be convenient to do so using a shell (named, say, `rrkr`) such as that shown below, which may be stored in the system or user 'bin' directory

```
# UNIX shell 'rrkr' to execute the compiled version of program RKR1 named
#   rkr.x, that is stored in the directory /userpath/.  The Channel-5 input
#   data file  $1.5  and the output files  $1.6 & $1.7 are all assumed to be
#   in the current directory.  For an input datafile named  molec.5  this
#   shell causes the Channel--6 and 7 output to be written to files
#   molec.7  and molec.7
time  /userpath/rkr.x  < $1.5 > $1.6
mv fort.7 $1.7 >& /dev/null
```

in which `userpath` is a path specifying the location of the executable file `rkr.x` on the user's computer. This shell allows the program to be executed using the input file '`molec.5`' with the simple command:

```
rrkr molec
```

in which `molec.5` is the data file containing the instructions regarding the type of fit to be performed, and `molec` is a filename that may be chosen arbitrarily by the user. In this case the standard output to Channel-6 will be written to file `molec.6` and the Channel-7 output to file `molec.7` in the same directory as the `molec.5` Channel-5 input data file.

4. Concluding remarks

As a final point, one may well ask: what is the utility of the first-order semiclassical RKR method in an era in which it is increasingly common to use fully quantum mechanical "Direct Potential Fit" (DPF) methods (see Ref. [64] and references therein) to reduced large experimental data sets to sophisticated, fully-analytic potential energy functions? There are two answers to this question. First of all, for many applications, workers may not consider it worth the extra effort to determine a closed-form potential, and much of the time, the RKR-based quantum properties (e.g., band constants and Franck–Condon factors) will be adequate. However, Dunham description of the spectroscopic constants often will not suffice, so the NDE and MXR options are important.

A second answer to this question lies the very sophistication of the potential function forms used in such DPF analyses. Their analytic complexity makes it difficult to generate the sets of realistic initial-trial-parameter values that are required to initiate those non-linear least-squares fits. As a result, the most common approach is to start with a classical analysis involving fits of assigned data to some variant of Eq. (1), with G_v represented by one of Eqs. (9), (12), or (18), and B_v represented by one of (10), (13), or (19) (see, e.g., Ref. [65]). This is then followed by an RKR calculation using a code such as the one described herein. Fits to the resulting potential function points using a specialized code, such as program **dParFit**, which is described in another paper in this issue [66], then yield the set of trial parameter values required to initiate the DPF analysis. Thus, a classical analysis culminating in the performance of an RKR calculation is also a crucial part of a modern DPF analysis.

5. Supplementary materials

The Supplementary materials associated with this paper consist of: (i) a plain text ASCII file containing the full Fortran source code for program **RKR1**, (ii) a plain text ASCII file containing copies of the sample data files described in Appendix C, (iii) a Pdf document containing: *Appendix A.* "Input Data File Structure", *Appendix B.*

"Definitions and Descriptions of the Input File Data", *Appendix C*. "Illustrative Data and Output Files, and Commentary", and *Appendix D*. "Derivation of the RKR Equations". Anyone who wishes to be Registered with the author as a user of this code, eligible to be sent any future bug fixes or updates, should fill in the online form at the www address "http://scienide2.uwaterloo.ca/~rleroy/RKR16".

Acknowledgments

I am pleased to acknowledge the foresight and stimulation provided by the late Professor George Burns of the University of Toronto, who instigated my work with this type of novel (at the time) computational research tool back in 1966, and the inspiration and assistance provided by R.N. Zare's seminal 1964 Franck–Condon and RKR programs [11,12]. I am also grateful to Professor G. McBane and Dr. A.J. Ross for suggestions regarding improvements to the code and its documentation, and to Professor F.R.W. McCourt for a meticulously careful reading of the manuscript. This work has been supported by the Natural Sciences and Engineering Research Council of Canada.

Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.jqsrt.2016.03.030

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