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A Computer Program Implementing the First-Order RKR Method for Determining Diatomic Molecule Potential Energy Functions

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Chemical Physics Research Report

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This manual describes program **RKR1**, which utilizes the first-order semiclassical Rydberg-Klein-Rees procedure to determine a diatomic molecule potential energy function from from a knowledge of its vibrational level energies G_v and inertial rotation constants B_v . **RKR1** allows the vibrational energies and rotational constants to be defined by conventional Dunham expansions, by near-dissociation expansions (NDE's), or by the "MXS" form of Tellinghuisen's [*J. Chem. Phys.* **118**, 3532 (2003)] mixed Dunham/NDE functions. For a case in which only vibrational data are available, it 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 behaviour of the steep inner wall of the potential.

I. INTRODUCTION

The Rydberg[1,2]-Klein[3]-Rees[4] or RKR method is an extremely widely used first-order semiclassical inversion procedure for determining diatomic molecule potential energy curves from a knowledge of vibrational level energies G_v and inertial rotation constants B_v. Within the first-order semiclassical or WKB approximation,[5] this method yields a unique potential energy function which *exactly* reflects the input functions representing the v-dependence of G_v and B_v. This manual describes the use of program **RKR1** for performing such calculations.

In spite of its now 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 which are at the core of the method as we know it today (indeed his procedure had such elegant appeal that it was inadvertently re-invented some 4 decades later[6]). However, while the method did see some use,[2] for the next two decades it was largely ignored. This oversight was probably mainly due to the startling success of Dunham's 1932 derivation 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 $(v+\frac{1}{2})$ and $[J(J+1)]$. By the early 1950's, however, the practical limitations of the Dunham approach, particularly its 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 host of other workers over the next decade and a half, he devised analytic expressions for these integrals based on 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 simply be evaluated numerically,[7] and the formal proof that the RKR and first-order Dunham procedures were equivalent.[8] In the early 1960's 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 program effectively made it the *de facto* standard,[9,10] and contributed immensely to the infectious spread of the method throughout the spectroscopy and molecular physics communities. However, as with virtually all methods in use before 1972, his code was based on a relatively crude treatment of the (integrable) singularities in the integrands of the Klein integrals (see below), and was incapable of yielding results of high precision.

Finally, a single 1972 issue of the *Journal of Molecular Spectroscopy* contained three papers reporting accurate and efficient new procedures for evaluating the Klein integrals.[11–13] Of these, the method of Tellinghuisen[13,14] has proved most durable, probably because of it's 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 near dissociation, (ii) an automatic procedure for smoothing to remove the unphysical behaviour 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 procedure introduced by Tellinghuisen[15]), and (iv) provision of upper bounds on the numerical precision of the calculations.

The current version of the (thoroughly commented) source code for **RKR1** may be obtained by filling in the form accessible from the "**RKR1**" link from the "Computer Programs" link on the www page *http://leroy.UWaterloo.ca*; a PDF file of this manual is also available there. While, there are no charges associated with distribution or use of this program, its use should be acknowledged in publications through reference to this report using a citation such as that of Ref. 16. Users are also requested *not* to distribute the program themselves, but to refer other prospective users to the above web site or to the author. I would also appreciate having users inform me of any apparent errors or instabilities in the code, and of additional features which might appear desirable for future versions.

II. METHODOLOGY

A Background Theory

The theory underlying the RKR method is discussed in the literature and in a number of monographs.[1–6,8,17–21] For the interested reader, a full derivation of the basic equations is presented in Appendix A. The key result of this theory consists of the two Klein integrals on which the RKR method is based:

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

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

where $r_1(v)$ and $r_2(v)$ are the inner and outer classical turning points of the potential 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 point are in Å, so the constant $\mathbb{C}_\mathrm{u} = \hbar^2/2 = 16.857\,629\,09$ [amu Å^2 cm^{-1}]. Program **RKR1** defines μ as Watson's charge-modified reduced mass $\mu = \mu_W \equiv M_A\,M_B/(M_A + M_B - Q\,m_\mathrm{e})$,[22] in which M_A and M_B are the normal atomic isotope masses, m_e is the electron mass, and Q is the integer net charge on the molecule. The numerical values of $\mathbb{C}_\mathrm{u}$ and m_e used in the program are based on the current recommended physical constants,[23] while the masses of all stable atomic isotopes (provided in the program by a data subroutine) are taken from the 1993 compilation.[24] Rearrangement of Eqs. (1) and (2) gives the final expressions:

$$r_1(v) \;=\; \sqrt{f^2 + f/g} \;-\; f \tag{3}$$

$$r_2(v) \;=\; \sqrt{f^2 + f/g} \;+\; f \tag{4}$$

It is important to remember that although the semiclassical quantization condition maps integer values of v onto the quantized vibrational energy levels, within the semiclassical approach v may be treated as a continuous variable. 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 $v_\mathrm{min} = -\,\frac{1}{2}$, while in higher-order semiclassical treatments it is a real number close to $-\,\frac{1}{2}$. More generally, it means that turning points may be calculated at either integer or non-integer values of v. This is an important point, since if turning points could only be calculated for integer values of v one would have a relatively sparse set of points to define the potential, which in turn would make them difficult to use for precise numerical calculations. For this reason program **RKR1** allows a user to specify different vibrational intervals at which turning points are to be calculated in different regions of the potential well.

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 usually agree with the experimentally determined input G_v and B_v functions to within the experimental uncertainties. On the other hand, for hydrides one often finds significant discrepancies 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,[19,25,26] but none has (yet!) been implemented in a robust, documented, publicly available code.

In spite of the above, an approximate way of attempting to go beyond the first-order semiclassical method is implemented as an option in **RKR1**. First introduced in 1970 by E.W. Kaiser,[27] it is based on the fact that within the third-order semiclassical quantization condition[5,19,26,28] the value of v associated with the the potential minimum is (approximately)

$$v_{\min} \;=\; -\,\tfrac{1}{2} - Y_{0,0}/Y_{1,0} \tag{5}$$

where $Y_{1,0} \equiv dG_v/dv|_{v=-\frac{1}{2}}$ and[29,30]

$$Y_{0,0} \;=\; \frac{Y_{0,1}+Y_{2,0}}{4} - \left(\frac{Y_{1,1}\,Y_{1,0}}{12\,Y_{0,1}}\right) + \frac{1}{Y_{0,1}}\left(\frac{Y_{1,1}\,Y_{1,0}}{12\,Y_{0,1}}\right)^2 \tag{6}$$

and the $Y_{l,m}$ constants for $\{l,m\} \neq \{0,0\}$ are defined by the normal Dunham power series expressions for G_v and B_v (see below), or more generally by the appropriate derivatives of the vibration-rotation energy with respect to v and $[J(J+1)]$, 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 (unpublished student exercises in a U. Waterloo grad course) indicate that its use does not necessarily yield a potential curve whose quantum-calculated vibrational level spacings and B_v values are in better 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 the fact that the Kaiser correction effectively assumes that contributions to the quantization condition from the higher-order phase integrals are constant, independent of v, which is certainly not true in general.[31] 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[32] to examine whether or not its use actually improved the level of agreement with the G_v and B_v functions used to generate the potential.

In any case, independent 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 (e.g., see Appendix C).

B 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, where the choice of representation for any particular case is specified by parameters in the input data file.

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:[29,30]

$$G_v \;=\; \sum_{l=1} Y_{l,0}\,(v+\tfrac{1}{2})^l \;=\; \omega_e(v+\tfrac{1}{2}) - \omega_e x_e(v+\tfrac{1}{2})^2 + \omega_e y_e(v+\tfrac{1}{2})^3 + ... \tag{7}$$

$$B_v \;=\; \sum_{l=0} Y_{l,1}\,(v+\tfrac{1}{2})^l \;=\; B_e - \alpha_e(v+\tfrac{1}{2}) + \gamma_e(v+\tfrac{1}{2})^2 + ... \tag{8}$$

2. Near-Dissociation Expansions (NDE's).

The second type of functional representation allowed by **RKR1** is pure "near-dissociation expansions" (NDE's), which incorporate the theoretically-known limiting near-dissociation behaviour of G_v or B_v into an expression which includes empirical parameters to be determined from the experimental data.[33–39] Just as conventional Dunham expressions are expansions about the limiting case of harmonic-oscillator/rigid-rotor behaviour at the potential minimum, NDE's are expansions about the theoretically-known limiting functional behaviour near dissociation, and hence are much more effective for extrapolating to high v beyond the range of observed data[37,38,40] and/or compactly representing data sets spanning a large fraction of the potential well.[36,39] The rest of this subsection describes the NDE expressions and their parameterization in program **RKR1**; users not familiar with this approach may wish to review some of the associated theory and review papers[26,33–35,38,41–43] and illustrative applications of this approach.[37,39,44–47]

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 properties of such levels depend mainly on the shape of the potential energy function near their outer turning points.[33,34] As a result, their v-dependence is mainly determined by the limiting asymptotic behaviour of the intermolecular potential, which usually has the simple attractive inverse-power form

$$V(r) = \mathfrak{D} - C_n/r^n \tag{9}$$

where $\mathfrak{D}$ 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,[34,42] 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

$$\begin{aligned} G_v &= \mathfrak{D} - K_0^\infty(v) \times \mathcal{F}_0(v_\mathfrak{D} - v) && (10)\\ B_v &= K_1^\infty(v) \times \mathcal{F}_1(v_\mathfrak{D} - v) && (11)\end{aligned}$$

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

$$K_m^\infty(v) \;=\; X_m(n, C_n, \mu) \times (v_\mathfrak{D} - v)^{[2n/(n-2)]-2m} \tag{12}$$

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.[26,34,35]

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

$$\mathcal{F}_m(v_\mathfrak{D} - v) \;=\; \left(\frac{1 \,+\, \sum_{i=t}^{L}\, p_i^m\,(v_\mathfrak{D} - v)^i}{1 \,+\, \sum_{j=t}^{M}\, q_j^m\,(v_\mathfrak{D} - v)^j}\right)^{\mathcal{S}} \tag{13}$$

$$\mathcal{F}_m(v_\mathfrak{D} - v) \;=\; \exp\left\{\sum_{i=t}^{L} p_i^m\,(v_\mathfrak{D} - v)^i\right\} \tag{14}$$

In the rational polynomial expression of Eq. (13) 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 of the power t of the leading expansion is often known from theory.[43,48]

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 behaviour of vibrational energies and other properties, they are much more reliable for extrapolating to predict the dissociation energy and the number, energies and properties of unobserved high vibrational levels. This means that they allow the calculation of realistic and reasonable 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 for them even the turning points calculated for the highest observed levels may not be reliable.[49]
- 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 which yield equivalent quality fits, since the dense manifold of levels near dissociation is represented by a relatively small number of empirical expansion parameters.

3. *"MXS" Mixed Near-Dissociation/Dunham Expansions.*

In spite of their numerous advantages, applications of NDE representations to states with 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.[50,51] In particular, his "MXS" mixed representation functions use

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

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

$$F_s(v) \;=\; \left\{1 + \exp\left(\frac{v - v_s}{\delta v_s}\right)\right\}^{-1} \tag{15}$$

to yield the MXS expressions

$$G_v^{\rm MXS} \;=\; F_s(v)\, G_v^{\rm Dun} \;+\; [1 - F_s(v)]\, G_v^{\rm NDE} \tag{16}$$

$$B_v^{\rm MXS} \;=\; F_s(v)\, G_v^{\rm Dun} \;+\; [1 - F_s(v)]\, B_v^{\rm NDE} \tag{17}$$

Thus, to specify an MXS expansion it is necessary to input the number and values of the Dunham coefficients, the physical ($\mathfrak{D}$ and $v_{\mathfrak{D}}$) and empirical parameters defining the NDE function, and the values of the parameters v_s and δv_s defining the switching function. Note too that because of the sensitivity of the function to their values, the input values of $v_{\mathfrak{D}}$, v_s and δv_s should all be input using floating point "d" format (e.g., $v_s = 27.0\mathrm{d}0$).

Note that the type of representation **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, the same must be true for B_v ; if G_v is represented by an NDE function, B_v may be represented by either a Dunham or an NDE function; if G_v is represented by an MXS function, B_v may be represented using any of the three type of functions.

C Evaluating the f and g Integrals

As mentioned above, early applications of the Klein inversion integrals Eqs. (1) and (2) had difficulty dealing with the (integrable) integrand singularity at the upper end of the range of integration. Tellinghuisen pointed out[13,14] that this problem is completely removed by use of the Gauss-Mehler quadrature formula,[52,53] as its points and weights implicitly take account of this behaviour. In particular, the f integral of Eq. (1) is readily rearranged to the form:

$$f \;=\; \sqrt{\mathbb{C}_{\rm u}/\mu}\int_{v_{\rm min}}^{v} \frac{[v-v']^{1/2}}{[G_v-G_{v'}]^{1/2}}\,\frac{dv'}{[v-v']^{1/2}} \;=\; \sqrt{\mathbb{C}_{\rm u}/\mu}\int_{v_{\rm min}}^{v} p(v')\,\frac{dv'}{[v-v']^{1/2}} \qquad (18)$$

where 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.[53]

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.[13,14] 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 becoming unacceptably large. Moreover, many applications require (or at least desire) potentials which are smooth to virtually machine precision. Thus, there is a need for an enhanced procedure which can yield both higher accuracy and some indication of the precision of the resulting turning points.

The most obvious way of increasing the the accuracy of any integration procedure is to simply increase the number of quadrature points used. However, for a Gaussian-type procedure whose points and weights are not readily generated analytically, it can be very inconvenient to attempt to make ever-higher-order quadrature formulae available for testing and improving the accuracy of a desired result. The present program takes an alternate approach which is based on use of 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.

Since the singularities in the integrands in Eqs. (1) and (2) lie at the upper end of the range, dividing the interval in half will yield two types of subintervals: in the first, $[v_{\rm min}\,,\ (v_{\rm min}+v)/2]$, the integrand is everywhere well behaved, so the ordinary Gauss-Legendre quadrature formula will suffice (See § 25.4.30 of Ref. 52); in the second, $[(v_{\rm min}+v)/2\,,\ v]$, the integrand has the same singular behaviour as when the whole interval is treated as one, and the Gauss-Mehler procedure is again appropriate. If one repeatedly bisects all subintervals, after the m^{th} stage of subdivision the first (2^m-1) subintervals may be treated using the ordinary Gauss-Legendre procedure, while only the last one requires use of the 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 $1/2^{N-2}$ 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 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 (1) and (2). The interval is then divided in half, the appropriate quadrature schemes applied in the two parts, and the results summed. The relative 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. (35) and (34) and printed out, together with the final values of `tst(f)` and `tst(g)` and the total number of subintervals used in the final iteration cycle, NDIV $= 2^m$. Thus, turning points generated by the present program are accompanied by estimated upper bounds to their numerical error.

In a procedure such as this, the convergence criterion TOLER would usually 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 is based on a relative convergence test of TOLER $= 10^{-\mathrm{KCONV}}$, where the value of KCONV (currently $= 10$) is set in line 60 of the code (and may be modified by the user). If this criterion is made too demanding (say, KCONV $= 16$), 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 virtually 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 behaviour are found in the illustrative cases discussed in Appendices B and C. We note that 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 uncertainties 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 are deemed an tolerable irritation.

D 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 behaviour in this region. For example, rather than have a (negative) slope and slowly varying positive curvature, this inner wall may pass through an inflection point and take on negative curvature, or the wall may even turn outward with increasing energy, with the algebraic sign of the slope becoming positive. Occasional papers in the literature have accepted behaviour 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 usually merely reflects inadequacies of the molecular constants used in the calculation.[54–57]

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 behaviour of the inner wall of an RKR potential is usually attributed to inadequacies in the latter.[54,56] (Indeed, minimization of such irregularities has been proposed as a means of improving otherwise poorly-known rotational constants.[54]) However, whatever the source of the problem, a modest degree of inappropriate behaviour of either the G_v or B_v function will give rise to non-physical behaviour of the 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 obvious 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. (1), 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[58]) then yields a 'best' estimate of the upper portion of the potential yielded by the available data. 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 behaviour, 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

$$V_{\rm inner}(r) \;=\; A + B\, e^{-C\, r} \tag{19}$$

and the value of the resulting exponent parameter $C \equiv \texttt{C}(exp)$ 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 vary slowly from one level to the next. However, if the wall passes through a point of inflection `C`(exp) will change sign, while if the wall begins to double over outward, it will grow rapidly and become quite large before the slope becomes positive. Thus, the behaviour of `C`(exp) is the required indicator of the onset of non-physical behaviour (see sample outputs in Appendix C).

To correct for such irregular behaviour 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 § IV). Examination of the behaviour 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. (19) 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) of the directly calculated turning points which yield the desired smoothing of the directly-calculated value of RMIN $= r_1(v)$. Examples of this type of correction are found in the sample output listings in Appendix C.

E 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. (2) may not be evaluated. However, directly calculated values of the f integral of Eq. (1) may be combined with an assumed inner potential wall and used to generate a realistic overall potential. Following an approach recommended by Tellinghuisen for this type of situation,[15] the present program can automatically generate the inner potential wall from a Morse function

$$V_{\rm Morse}(r) \;=\; \mathfrak{D}_e[e^{-\beta(r-r_e)} - 1]^2 \tag{20}$$

and generate the corresponding outer turning points by adding values of $2f$ calculated from Eq. (1) 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 which define the Morse function which will then be used to generate the required inner turning point values at the specified energies.

III. USING RKR1: 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 mentioned earlier, the electron and atomic masses and the physical constants used to define the constant $\mathbb{C}_\mathrm{u}$ appearing in Eqs. (1) and (2) were taken from the most recent compilations.[23,24] For all stable isotopes of all atoms, the masses are found in the data subroutine MASSES, so all a user need specify in the input is the atomic number and mass number of each atom of each isotopomer considered in the analysis.

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 20. However, a user may readily change this by making appropriate modifications to the array dimensions in lines 36, 37, 40 and 44 of the source code.

RKR1 reads the input data file in free format on channel–5 (e.g., READ(5,*) ...). The structure of the requisite data file and precise definitions of the various program options are presented below in § IV. 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 on 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 not convenient for use as input to 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 $v = v_\mathrm{min}$, arranged in order of increasing distance. In addition, to facilitate use of the resulting potential array for making plots or for numerical calculations, when appropriate, five additional inner extrapolated points are generated from Eq. (19) and included as the innermost points in that channel–7 output array.

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's 'bin' directory:

```
# UNIX shell ‘rrkr’ to execute the compiled version of program RKR1 named
#   rkr.x, which 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
```

where `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
```

where `molec.5` is the data file containing the instructions regarding the type of fit to be performed, and `molec` is a filename which 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.

IV. DATA FILE STRUCTURE AND INPUT PARAMETER DEFINITIONS

The logical structure and read statements defining the channel–5 input data file describing the system to be treated, and providing all necessary system-specific parameters, is shown below. The following subsection then provides a detailed description of the nature of and/or options associated with each of the input variables.

```
#1      READ(5,*,END=99) IAN1, IMN1, IAN2, IMN2, CHARGE, NDEGv, NDEBv
#2a     IF((IAN1.LE.0).OR.(IAN1.GT.109) READ(5,*) NAME1, MASS1
#2b     IF((IAN2.LE.0).OR.(IAN2.GT.109) READ(5,*) NAME2, MASS2
#3      READ(5,*) TITLE
        IF((NDEGv.EQ.0).OR.(NDEGv.EQ.2)) THEN
#4          READ(5,*) LMAXGv
#5          READ(5,*) (YL0(L),L= 1,LMAXGv)
            ENDIF
#6      IF(NDEGv.GE.2) READ(5,*) VS, DVS, DLIM
        IF(NDEGv.GE.1) THEN
#7          READ(5,*) NLR, ITYPE, IZP0, IZQ0, NP0, NQ0, VD, XCN0
#8          IF(NP0.GT.0) READ(5,*) (P0(I),I= 1,NP0)
#9          IF(NQ0.GT.0) READ(5,*) (Q0(I),I= 1,NQ0)
            ENDIF
#10     IF(NDEBv.LT.0) READ(5,*) Req
        IF((NDEBv.EQ.0).OR.(NDEBv.EQ.2)) THEN
#11         READ(5,*) LMAXBv
#12         IF(LMAXBv.GE.0) READ(5,*) (YL1(L),L= 0,LMAXBv)
            ENDIF
        IF(NDEBv.GE.1) THEN
#13         READ(5,*) ITYPB, IZP1, IZQ1, NP1, NQ1, XCN1
#14         IF(NP1.GT.0) READ(5,*) (P1(I),I= 1,NP1)
#15         IF(NQ1.GT.0) READ(5,*) (Q1(I),I= 1,NP1)
            ENDIF
#16     READ(5,*)  Kaiser, NSV, VEXT
        DO  J= 1,NSV
#17         READ(5,*) V1(I), DV(I), V2(I)
            ENDDO
```

Definitions and Descriptions of Input File Data

Read integers identifying the molecule or system.

#1. `READ(5,*) IAN1, IMN1, IAN2, IMN2, CHARGE, NDEGv, NDEBv`

IAN1 & IAN2 : integer atomic numbers of the atoms/particles #1 & 2 forming the molecule. If both are positive and ≤ 109, atomic masses from the tabulation in subroutine MASSES will generate the reduced mass of the system. If either is ≤ 0 or > 109, the mass of that particle must be input via READ statement #2.

IMN1 & IMN2 : integer mass numbers of the atoms #1 & 2 forming the molecule. For a normal stable atomic isotope, the mass is taken from the tabulation in subroutine MASSES; if IMN1 or IMN2 lies outside the range for the normal stable isotopes of that atom, the abundance-averaged atomic mass is used.

CHARGE : ± integer for the total charge on the molecule. Used to generate Watson's charge-modified reduce mass for neutral or ionic molecules:[22] $\mu = \mu_W = M_A\, M_B/(M_A + M_B - m_e \times$ CHARGE$)$.

NDEGv : specifies whether G_v for this state is to be represented: a) by the Dunham expansion of Eq. (7) when NDEGv $= 0$, b) by the NDE expressions of Eqs. (10) and (12) - (14), when NDEGv $=1$, or c) by the Tellinghuisen-type MXS "mixed" representation of Eq. (16) when NDEGv $= 2$.

NDEBv : specifies whether B_v for this state is to be represented: a) by the Dunham expansion of Eqs. (8) when NDEBv $= 0$, b) by the NDE expressions of Eqs. (11) and (12) - (14), when

NDEBv$=1$, or c) by the Tellinghuisen-type MXS "mixed" representation of Eq. (17) when NDEBv≥ 2. If no rotational data are available and a potential is to be generated using a Morse function inner wall (see § II.E), one should set NDEBv$=-1$. Note than necessarily NDEBv $\leq$ NDEGv.

In the special case when IAN1 and/or IAN2 is either ≤ 0 or > 109, we read in a two-character alphanumeric name for that particle and its mass (in amu). This facilitates the treatment of model systems or of exotic species such as muonium or positronium "molecules".

#2.a `IF((IAN1.LE.0).OR.(IAN1.GT.109)) READ(5,*) NAME1, MASS1`
#2.b `IF((IAN2.LE.0).OR.(IAN2.GT.109)) READ(5,*) NAME2, MASS2`

NAME1 & NAME2 : a two-character alphanumeric name for the particle whose mass is being read, enclosed in single quotes, as in ′mu′.

MASS1 & MASS2 : the masses (in amu) of the particles.

Read a title or output header for the calculation, consisting of up to 78 characters on a single line enclosed between single quotes: e.g., ′title of problem′.

#3. `READ(5,*) TITLE`

Representation for the vibrational energies G_v

READ statements #$4-9$ are concerned with the three possible ways of representing G_v: #4 & 5 are used for a pure Dunham function, #$7-9$ for a pure NDE function, and all of #$4-9$ are used for an MXS function.

If Dunham or MXS expansions are used for G_v (NDEGv$=0$ or 2), read in the (integer) order of the G_v vibrational polynomials, LMAXGv, and values of the Dunham coefficients $Y_{l,0}$, starting with $l=1$.

#4. `READ(5,*) LMAXGv`
#5. `READ(5,*) (YLO(L), L= 1,LMAXGv)`

If an MXS mixed representation is to be used for G_v (NDEGv$=2$), read in the *real number* values of VS $=v_s$, the value of v at which the Dunham/NDE switching function Eq. (15) is centred, and of DVS $=\delta v_s$, the width parameter for that switching function. Because of the sensitivity of the calculation to their values, VS and DVS should be read in floating point "d" format (e.g., $v_s = 55.0\text{d}0$).
For an MXS function, the absolute value of DLIM $\equiv [G(v=v_{\mathfrak{D}})-G(v=-1/2)]$ must also be specified.

#6. `READ(5,*) VS, DVS, DLIM`

If an NDE or MXS functions is used for G_v (NDEGv≥ 1), read in parameters characterizing the NDE function to be used.

#7. `READ(5,*) NLR, ITYPE, IZP0, IZQ0, NP0, NQ0, vD, XCN0`

NLR : is the integer power of the asymptotically-dominant inverse-power term in the long-range potential of Eq. (9).

ITYPE : is an integer specifying the type of NDE expression to be used for G_v:

- ITYPE$=1$ for an "outer" rational polynomial expansion using Eq. (13) with $\mathcal{S}=1$.
- ITYPE$=2$ for an "inner" rational polynomial expansion using Eq. (13) with $\mathcal{S}=2n/(n-2)$.
- ITYPE$=3$ uses the exponential NDE function of Eq. (14).

IZP0 & IZQ0 : are the values of the integer t specifying the leading term in the polynomial expansions in, respectively, the numerator and denominator of Eq. (13) for ITYPE$=1$ or 2, while for ITYPE$=3$ IZP0 specifies the power of the leading term in the exponent expansion of Eq. (14) and IZQ0 is a dummy variable.

NP0 & NQ0 : are the (integer) number of coefficients in, respectively, the numerator and denominator polynomials of Eq. (13) for ITYPE = 1 or 2, while for ITYPE = 3 NP0 is the number of terms in the exponent polynomial of Eq. (14) and NQ0 is a dummy variable which should be set ≤ 0: NP0 = $L + 1 - t$ and NQ0 = $M + 1 - t$.

vD : is the non-integer effective vibrational index at dissociation $v_{\mathfrak{D}}$, and should be read in floating point "d" format (e.g., $v_{\mathfrak{D}} = 64.41\mathrm{d}0$).

XCN0 : is the numerical value of the ND-theory coefficient $X_0(n, C_n, \mu)$ of Eq. (12) for $m = 0$.

Now read in the actual values of the NDE expansion coefficients `P0(`i`)` $= p^0_{i-t+1}$ and `Q0(`j`)` $= q^0_{j-t+1}$ required to define the particular NDE function.

#8. `READ(5,*) (P0(i), i=1, NP0)`
#9. `READ(5,*) (Q0(j), j=1, NQ0)`

Representation for the intertial rotational constants B_v

If no reliable B_v function is available for this state and one wishes to utilize the approach described in § II.E to generate an approximate potential, one should have NDEBv = -1 and read in here a value of Req = r_e to specify the position of the minimum of the Morse function for this case.

#10. `READ(5,*) Req`

If a Dunham or MXS expansion is used for B_v (NDEBv = 0 or 2), read in the order of the B_v vibrational polynomial LMAXBv and the values of the expansion coefficients YL1(l) = $Y_{l,1}$ for $l = 0 -$ LMAXBv.

#11. `READ(5,*) LMAXBv`
#11. `IF(LMAXBv.GE.0) READ(5,*) (YL1(L), L= 0,LMAXBv)`

If an NDE or MXS functions is used for B_v, read the parameters defining the type of NDE function and the values of the associated expansion parameters. The function types and definitions of the parameters are precisely analogous to those for the vibrational case: see description of READs #7 – 9.

#13. `READ(5,*) ITYPB, IZP1, IZQ1, NP1, NQ1, XCN1`
#14. `READ(5,*) (P1(I), I=1, NP1)`
#15. `READ(5,*) (Q1(J), J=1, NQ1)`

Finally, specify the sophistication of the calculation and define the set(s) of v values for which turning points are to be calculated.

#16. `READ(5,*) Kaiser, NSV, VEXT`

Kaiser : is an integer which specifies whether (Kaiser ≥ 1) or not (Kaiser = 0) the "Kaiser correction" of § II.A is to be applied.

NSV : is an integer specifying the number of different mesh sizes Δv are to be used in specifying the set of v values for which turning points are to be calculated.

VEXT : is a real number whose value controls the option which allows the program to correct unphysical behaviour of the upper part of the inner potential wall defined by the input G_v and B_v functions, as described in § II.D. For VEXT ≤ 0.0, no inner-wall smoothing is performed, but if VEXT > 0.0, for $v >$ VEXT inner turning points $r_1(v)$ are generated from Eq. (19) using values of the coefficients A, B & C define by fitting this function to the inner turning points for the three largest v values with $v \leq$ VEXT, while the outer turning points are defined as the sum of these analytic value plus the calculated quantity $2f$.

For each of NSV cases, read in (floating point) variables V1(i), DV(i) & V2(i) to specify the set of v values running from V1(i) to V2(i) in steps of DV(i) = Δv, at which turning points are to be calculated. If necessary, the program internally corrects the input values of V2(i) to ensure that when NSV > 1, necessarily V1(i) $\leq$ V2(i+1). A reasonable example would be to set NSV = 2 and to then input

$$\{\text{V1(i), DV(i), V2(i)}\} \;=\; \{-0.4\text{d0}, 0.2\text{d0}, 1.6\text{d0}\} \quad \text{and} \quad \{2.0\text{d0}, 0.5\text{d0}, \text{v}_{\text{max}}\} \quad \text{for} \quad \text{i} = 1 \;\&\; 2$$

where v_{max} is the highest vibrational level for which turning points are desired. It is usually best to set V1(1) ≥ -0.4d0.

#17. `READ(5,*) V1(i), DV(i), V2(i)`

V. PROGRAM UPDATES

The current version[16] of **RKR1** incorporates a number of modifications and extensions not present in the previous one.[59] In particular:

- Instead of reading in explicit atomic masses in amu, the new version reads in the integer atomic number and mass number of the component atoms and retrieves the appropriate atomic mass from an internal data subroutine whose contents are taken from the most recent atomic mass determination.[24]
- In addition to allowing for use of Dunham or pure NDE functions to represent the v–dependence of G_v and B_v, the new version also allows for use of Tellinghuisen's "MXS" mixed representations.
- The NDE functions used to represent B_v in either pure NDE or MXS representations may now be based on either Eq. (13) or (14), rather than only on the latter.
- The input defining the mesh of v values at which turning points are to be calculated is input in a more convenient manner which obviates a need to explicitly count out the number of turning point pairs to be associated with each of the NSV chosen mesh Δv values.
- The compact channel–7 output turning point listing includes the value of r_e associated with the value of B_v at the potential minimum $v = v_{\text{min}}$, plus five additional extrapolated inner-wall points generated from Eq. (19) to provide a turning point array which can more readily be used for plotting purposes.

Moreover, the present program manual contains substanially more discussion of details of the method and sample results than did the earlier edition.

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APPENDIX: DERIVATION, AND ILLUSTRATIVE DATA & OUTPUT FILES

A. Derivation of the RKR Equations

The first formal derivation of what is now known as the "RKR" method was due to O. Klein,[3] and a version of it is outlined here. Starting from the first-order JWKB or Bohr-Sommerfeld quantization condition

$$v + \tfrac{1}{2} \;=\; \frac{1}{\pi}\sqrt{\frac{2\mu}{\hbar^2}} \int_{r_1}^{r_2} [E - V(r)]^{1/2}\, dr \tag{21}$$

For the purpose of this derivation it is notationally convenient to start by replacing v by v' and E by E'. We then take the derivative of this expression with respect to energy E', and divide the range of integration into two parts to separate the repulsive and attractive regions:

$$\frac{dv'}{dE'} \;=\; \frac{1}{2\pi}\sqrt{\frac{2\mu}{\hbar^2}} \left\{ \int_{r_1}^{r_e} \frac{dr}{[E' - V(r)]^{1/2}} \;+\; \int_{r_e}^{r_2} \frac{dr}{[E' - V(r)]^{1/2}} \right\} \tag{22}$$

For a well-behaved single minimum potential, on each of the intervals $[r_1, r_e]$ and $[r_e, r_2]$ there is a unique monotonic relationship between the distance variable r and the value of the potential energy function, $u = V(r)$. We can therefore re-write Eq. (22) with u replacing r as the independent variable in the two integrals:

$$\begin{aligned}\frac{dv'}{dE'} &= \frac{1}{2\pi}\sqrt{\frac{2\mu}{\hbar^2}} \left\{ \int_{E'}^{0} \frac{1}{[E' - u]^{1/2}}\, \frac{dr_1(u)}{du}\, du \;+\; \int_{0}^{E'} \frac{1}{[E' - u]^{1/2}}\, \frac{dr_2(u)}{du}\, du \right\} \\ &= \frac{1}{2\pi}\sqrt{\frac{2\mu}{\hbar^2}} \int_0^{E'} \left(\frac{dr_2(u)}{du} - \frac{dr_1(u)}{du} \right) \frac{du}{[E' - u]^{1/2}}\end{aligned} \tag{23}$$

We now introduce a mathematical gimmick (sometimes called an Abelian transformation[3]), which involves premultiplying both sides of Eq. (23) by the factor $dE'/[E - E']^{1/2}$ and integrating E' from 0 to E:

$$\begin{aligned}\int_0^{E} \frac{(dv'/dE')\, dE'}{[E - E']^{1/2}} &= \int_{v_{min}}^{v(E)} \frac{dv'}{[E(v) - E(v')]^{1/2}} \\ &= \frac{1}{2\pi}\sqrt{\frac{2\mu}{\hbar^2}} \int_0^{E} dE' \left\{ \int_0^{E'} \left(\frac{dr_2(u)}{du} - \frac{dr_1(u)}{du} \right) \frac{du}{[(E - E')(E' - u)]^{1/2}} \right\}\end{aligned} \tag{24}$$

in which $v_{min} = v(E\!=\!0)$ is the (non-integer) effective vibrational quantum number index associated with the potential minimum. If we then change the order of the double integration, and utilize the standard mathematical identity

$$\int_a^b \frac{dx}{[(b - x)(x - a)]^{1/2}} \;=\; \pi \tag{25}$$

we obtain

$$\begin{aligned}\int_{v_{min}}^{v(E)} \frac{dv'}{[E(v) - E(v')]^{1/2}} &= \frac{1}{2\pi}\sqrt{\frac{2\mu}{\hbar^2}} \int_0^{E} du \left\{ \left(\frac{dr_2(u)}{du} - \frac{dr_1(u)}{du} \right) \int_u^{E} \frac{dE'}{[(E - E')(E' - u)]^{1/2}} \right\} \\ &= \frac{1}{2}\sqrt{\frac{2\mu}{\hbar^2}} \left\{ \int_0^{E} \frac{dr_2(u)}{du}\, du \;-\; \int_0^{E} \frac{dr_1(u)}{du}\, du \right\} \\ &= \frac{1}{2}\sqrt{\frac{2\mu}{\hbar^2}} \left\{ \int_{r_e}^{r_2(E)} dr \;-\; \int_{r_e}^{r_1(E)} dr \right\} \\ &= \frac{1}{2}\sqrt{\frac{2\mu}{\hbar^2}}\; [r_e(E(v)) - r_1(E(v))]\end{aligned} \tag{26}$$

Rearranging this expression yields the first or “vibrational” RKR equation

$$r_2(v)\;-\;r_1(v)\;=\;2\sqrt{\frac{\hbar^2}{2\mu}}\int_{v_{min}}^{v}\frac{dv'}{[E(v)-E(v')]^{1/2}}\;=\;2f \tag{27}$$

The derivation of the second or “rotational” RKR equation proceeds in the same way, except that we first have to perform some manipulations to obtain the appropriate starting equation. The starting point is the recognition that for a rotating molecule $J>0$ and the effective centrifugally-distorted potential appearing in the quantization condition of Eq. (21) is actually

$$V_J(r)\;=\;V(r)+\frac{\hbar^2}{2\mu}\,\frac{[J(J+1)]}{r^2} \tag{28}$$

so the quantization condition may be re-written as

$$v(E,J)+\tfrac{1}{2}\;=\;\frac{1}{\pi}\sqrt{\frac{2\mu}{\hbar^2}}\int_{r_1}^{r_2}\left[E-V(r)-\frac{\hbar^2}{2\mu}\,\frac{[J(J+1)]}{r^2}\right]^{1/2}dr \tag{29}$$

For a given value of J, Eq. (29) tells us that there exists a unique mapping between v and E, and the chain rule of calculus tell us that in ths case, for any function $\mathfrak{F}(E,J)$,

$$\left(\frac{\partial\mathfrak{F}(E,J)}{\partial[J(J+1)]}\right)_E\;=\;\left(\frac{\partial E}{\partial[J(J+1)]}\right)_v\left(\frac{\partial\mathfrak{F}}{\partial E}\right)_J \tag{30}$$

Applying this chain rule relationship to Eq. (29) then yields

$$\left(\frac{\partial v}{\partial[J(J+1)]}\right)_E\;=\;\left(\frac{\partial E}{\partial[J(J+1)]}\right)_v\left(\frac{\partial v}{\partial E}\right)_J\;=\;-\frac{1}{2\pi}\sqrt{\frac{\hbar^2}{2\mu}}\int_{r_1}^{r_2}\frac{dr}{r^2\left[E-V(r)-\frac{\hbar^2}{2\mu}\frac{[J(J+1)]}{r^2}\right]^{1/2}} \tag{31}$$

From the standard definition of the inertial rotational constant, we know that $\left.\frac{\partial E(v,J)}{\partial[J(J+1)]}\right|_{J=0}\equiv B_v$, so for $J=0$ Eq. (31) becomes

$$B_v\times\frac{dv}{dE}\;=\;-\frac{1}{2\pi}\sqrt{\frac{\hbar^2}{2\mu}}\int_{r_1}^{r_2}\frac{dr}{r^2\,[E-V(r)]^{1/2}} \tag{32}$$

in which the partial derivative has been replaced by an exact derivative, since when J is fixed (at $J=0$) there in only one independent variable.

Equation (32) provides a starting point which is the precise analog of Eq. (22) in the derivation of the RKR “f integral” result of Eq. (27). Proceeding precisely as before: (i) replace variable names E and v with E' and v', respectively, (ii) split the range of integration into two parts at r_e, (iii) change the variable of integration from r to $u=V(r)$, (iv) multiply by $dE'/(E-E')^{1/2}$ and integrate E' from 0 to E, (v) change the order of integration and apply the identity of Eq. (25), and (vi) rearrange the result appropriately, then yields the second or “rotational” RKR equation:

$$\frac{1}{r_1(v)}\;-\;\frac{1}{r_2(v)}\;=\;2\sqrt{\frac{2\mu}{\hbar^2}}\int_{v_{min}}^{v}\frac{B_{v'}\;dv'}{[E(v)-E(v')]^{1/2}}\;=\;2g \tag{33}$$

Combining Eqs. (27) and (33) then yields the final turning point expressions

$$r_2(v)=\;\left(f^2+f/g\right)^{1/2}+f \tag{34}$$

$$r_1(v)=\;\left(f^2+f/g\right)^{1/2}-f \tag{35}$$

Thus, for any case in which we have smooth functions which accurately describe the dependence on v of the vibrational energy and inertial rotational constant B_v, Eqs. (27) and (27)-(35) may be used to generate the potential energy function in a pointwise manner.

B. Illustrative Data Files and Commentary

The section presents sample data files for seven cases, and discusses some features of the results illustrated by the associated channel-6 output files listed in Appendix C. Note that in the sample data files shown below, the "`%`" symbol appearing on most lines after the last parameter associated with that READ statement and any following text are merely comments, and are ignored by the program. It is often convenient to include such comments on the input files to remind one which parameter is which.

Cases (i) & (ii): Standard Dunham-Representation Applications

The first two sample data files shown below are for the common case in which pure Dunham polynomials in $(v+\frac{1}{2})$ are used for both G_v and B_v. The experimental data on which these Dunham polynomials were based stops at $v = 82$, so the turning point calculation also stops there. The input data files for these cases are shown below.

```
 53 127  53 127  0  0 0               % IAN1 IMN1 IAN2 IMN2 CHARGE NDEGv NDEBv
'(i) Dunham Calculation with Gerstenkorn constants for I2(B)    (VEXT = 0)'
 16                                   % LMAXGv
  1.256643430002D+2 -7.475284960242D-01 -5.016833169864D-3  3.788414181699D-4
 -4.983773834286D-5  4.200565944860D-06 -2.462699605029D-7  1.035559345644D-8
 -3.168784847369D-10 7.099055257498D-12 -1.159685360751D-13 1.361205680478D-15
 -1.115309496593D-17 6.046170833273D-20 -1.947198245975D-22 2.820031243526D-25
 15                                   % LMAXBv
  2.900080684844D-2 -1.496203558218D-04 -1.122999681016D-6 -8.598750387065D-9
 -3.993514191186D-9  7.442705931721D-10 -7.729114740147D-11 4.998660579762D-12
 -2.157393379080D-13 6.436910217056D-15 -1.347501253707D-16 1.977227945639D-18
 -1.994896518940D-20 1.320031684314D-22 -5.162433698190D-25 9.047632057664D-28
  0  2  0.d0                          % Kaiser NSV VEXT
  -0.4d0  0.2d0  1.6d0                %(1) V1 DV V2
   2.0d0  1.0d0  82.d0                %(2) V1 DV V2

 53 127  53 127  0  0 0               % IAN1 IMN1 IAN2 IMN2 CHARGE NDEGv NDEBv
'(ii) Dunham Calculation with Gerstenkorn constants for I2(B)    (VEXT > 0)'
 16                                   % LMAXGv
  1.256643430002D+2 -7.475284960242D-01 -5.016833169864D-3  3.788414181699D-4
 -4.983773834286D-5  4.200565944860D-06 -2.462699605029D-7  1.035559345644D-8
 -3.168784847369D-10 7.099055257498D-12 -1.159685360751D-13 1.361205680478D-15
 -1.115309496593D-17 6.046170833273D-20 -1.947198245975D-22 2.820031243526D-25
 15                                   % LMAXBv
  2.900080684844D-2 -1.496203558218D-04 -1.122999681016D-6 -8.598750387065D-9
 -3.993514191186D-9  7.442705931721D-10 -7.729114740147D-11 4.998660579762D-12
 -2.157393379080D-13 6.436910217056D-15 -1.347501253707D-16 1.977227945639D-18
 -1.994896518940D-20 1.320031684314D-22 -5.162433698190D-25 9.047632057664D-28
  0  2  45.d0                         % Kaiser NSV VEXT
  -0.4d0  0.2d0  1.6d0                %(1) V1 DV V2
   2.0d0  1.0d0  82.d0                %(2) V1 DV V2
```

Case (i) is a calculation performed with the input value of $\mathrm{VEXT} = 0$, so no inner-wall extrapolation is performed. However, the rapid growth of the value of `C`(exp) above $v \sim 45$ and the warning message printed at $v = 63$ shows that the inner-wall unreliability discussed in § II.D is a problem here. Case (ii) therefore repeats exactly the same calculation, but with the input value $\mathrm{VEXT} = 45$, so that for $v > 45$ the inner wall is defined by Eq. (19) and the outer turning points adjusted accordingly. As shown by the resulting values of `d`(RMIN) in the last column of the output for Case (ii), the smoothing for this case requires only very modest displacements of the turning points.

The various warning messages " `*** STOP ITERATION:   At   NDIV= ...` " appearing in both output files for $v = 70$ and $v \geq 76$ illustrate the type of convergence problem discussed at the end of § II.C. At high v the higher-order terms in the Dunham polynomial yield large contributions of alternating sign, and a substantial amount of numerical cancellation occurs when they are combined to give the overall values of G_v, $G_{v'}$ and $B_{v'}$ appearing in the integrands of Eq. (1) and (2). This loss of significant digits introduces "numerical noise" into the calculation, and prevents the specified degree of numerical convergence being achieved. Precisely the same problem sometimes occurs at low v when using high-order pure NDE functions, because of the high powers of $(v_{\mathfrak{D}} - v)$ involved. This problem usually has nothing to do with the RKR procedure itself, but rather is a precision problem associated with the type of G_v and/or B_v representation being used. In this case the best way of avoiding them would be to use MXS representations, as relatively lower-order polynomials (than for pure Dunham or NDE functions) would be required for both the Dunham and NDE components, so the introduction of numerical noise due to cancellation of significant digits would be greatly reduced.

Cases (iii) & (iv): Pure NDE *G_v and B_v Functions*

The two following data file are based on NDE functions reported for the $1\,{}^3\Sigma_g^-$ state of Na_2.[47] These two cases again differ only in that one uses $\mathrm{VEXT} = 0$ and the other $\mathrm{VEXT} = 35$, with the value of VEXT used in Case (iv) being having been selected based on the trends in the values of `C(exp)` seen in the output for Case (iii) in Appendix C. The output for Case (iii) shows three different types of warning messages associated with inner-wall misbehaviour, but from the output for Case (iv) we see that the turning point adjustments required to give a smooth inner wall are also quite modest for this case, especially relative to the magnitude of the turning point differences `[RMAX(v) - RMIN(v)]`. Note too that in contrast to Cases (i) and (ii), these Na_2 calculations apply the Kaiser correction, so the lower bound on the integrals in Eqs. (1) and (2) is `v00` $= v_{\min} = -0.5018267\ldots$.

```
 11 23  11 23  0  1  1                 % IAN1 IMN1 IAN2 IMN2 CHARGE NDEGv NDEBv
'(iii) Liu et al. JCP 111, 3494 (1999) NDE functions for Na2:  VEXT = 0'
 6  1  1 1  3 2   61.41d0  4.4867d-2   % NLR ITYPE IZP0 IZQ0 NP0 NQ0 VD XCN0
 0.436636d0  -3.529d-3  1.54d-5
 4.8d-2  1.366d-2
 3  1 0  7 0  3.0921d-3                % ITYPB IZP1 IZQ1 NP1 NQ1 XCN1
 0.1341d0  -1.6863d-2  9.2d-4  -2.810837d-5  4.924d-7  -4.61952d-9  1.8d-11
 1  2   0.d0                           % Kaiser NSV VEXT
  -0.4d0  0.2d0  1.6d0                 %(1) V1 DV V2
   1.d0   1.0d0 61.d0                  %(2) V1 DV V2
```

```
 11 23  11 23  0  1  1                 % IAN1 IMN1 IAN2 IMN2 CHARGE NDEGv NDEBv
'(iv) Liu et al. JCP 111, 3494 (1999) NDE functions for Na2:  VEXT > 0'
 6  1  1 1  3 2   61.41d0  4.4867d-2   % NLR ITYPE IZP0 IZQ0 NP0 NQ0 VD XCN0
 0.436636d0  -3.529d-3  1.54d-5
 4.8d-2  1.366d-2
 3  1 0  7 0  3.0921d-3                % ITYPB IZP1 IZQ1 NP1 NQ1 XCN1
 0.1341d0  -1.6863d-2  9.2d-4  -2.810837d-5  4.924d-7  -4.61952d-9  1.8d-11
 1  2   35.d0                          % Kaiser NSV VEXT
  -0.4d0  0.2d0  1.6d0                 %(1) V1 DV V2
   1.d0   1.0d0 61.d0                  %(2) V1 DV V2
```

Case (v): No Rotational Data: Morse Inner Wall

This data set illustrates the type of situation discussed in § II.E, a case for which one has vibrational data but little or no rotational data. As discussed in § II.E, the program uses the vibrational data to determine Morse parameters $\mathfrak{D}_e$ and β, which are then combined with a read-in value of r_e and used to generate the inner-wall turning points. The regular RKR calculation of Eq. (1) is then used to define the outer wall of the potential. Although the molecular species in this example is a hydride (ArH^+), for which one might normally expect to use the Kaiser correction, the uncertainty associated with the inner wall makes such niceties pointless for this case.

```
 20 40  1 1  0  1 -1                   % IAN1 IMN1 IAN2 IMN2 CHARGE NDEGv NDEBv
'(v) NDE-based potential for Ar-H(+):  Morse Inner Wall Extrapolation'
 4 1  2 2  3 1  33.2D0  0.146D0        % NLR ITYPE IZP0 IZQ0 NP0 NQ0 VD XCN0
 -0.396754604292D-4  0.456933925968D-5  -0.392256864315D-7
  0.414470068478D-2
```

```
 1.28066d0                             % r_e  Morse minimum
  0  2  11.1d0                         % Kaiser NSV VEXT
  -0.4d0  0.2d0  1.6d0                 %(1) V1 DV V2
   2.0d0  1.0d0  32.d0                 %(2) V1 DV V2
```

Cases (vi) & (vii): MXS *Function for G_v With a Pure Dunham or an* MXS *Expression for B_v*

These two cases illustrate the data file setup associated with use of an MXS representation for G_v, combined with either a Dunham or an MXS representation for B_v. In the output for both cases we see that there are some convergence problems as $v \to v_{\mathfrak{D}}$ because of significant digit cancellation in the integrand argument $[G_v - G_{v'}]$. This cannot be avoided unless the whole calculation is performed in quadruple precision, but since no real additional physical accuracy would be attained, it would not be worth the trouble to do that. Note too that both these examples use $\mathrm{VEXT} > 0$, which indicates that a prior $\mathrm{VEXT} = 0$ calculation was used to determine an appropriate value for VEXT for each.

```
3 7  3 7  +0  2  0                       % IAN1 IMN1 IAN2 IMN2 CHARGE NDEGv NDEBv
’(vi) For Li2(A): MXS function for Gv  &  Dunham for Bv’
  9                                      % LMAXGv
  2.554976991440D+02 -1.591528931916D+00 4.320069610295D-03 -1.297800483407D-04
  5.126092802711D-06 -3.043543008425D-07 9.142950968846D-09 -1.496898654541D-10
  9.980517130870D-13
  55.d0  1.d0  9352.11494d0              % VS DVS DLIM
 3  1  2 2  7 0 113.2817653490D0 2.577D-08 % NLR ITYPE IZP0 IZQ0 NP0 NQ0 VD XCN0
  1.910501922487D-03 -3.893923351925D-04 2.334546248943D-05 -6.987656722521D-07
  1.155836220945D-08 -1.015514433411D-10 3.720613823813D-13
   17                                    % LMAXBv
  4.974826807719D-01 -5.451871858525D-03 -2.310449795574D-06 9.775126360220D-06
 -2.425290834207D-06 3.831066457326D-07 -4.243945514918D-08 3.342936415566D-09
 -1.887782854700D-10 7.703531741973D-12 -2.287056796063D-13 4.954101341163D-15
 -7.802622660609D-17 8.821305429325D-19 -6.966209130239D-21 3.645524469475D-23
 -1.135472319430D-25 1.593096618270D-28
 1  2   45.d0                            % Kaiser NSV VEXT
  -0.4d0  0.2d0  1.6d0                   %(1) V1 DV V2
   1.d0   1.0d0 113.d0                   %(2) V1 DV V2

 3 7  3 7  +0  2  2                      % IAN1 IMN1 IAN2 IMN2 CHARGE NDEGv NDEBv
’(vii) For Li2(A): MXS function for both Gv  &  Bv’
  9                                      % LMAXGv
  2.554976991440D+02 -1.591528931916D+00 4.320069610295D-03 -1.297800483407D-04
  5.126092802711D-06 -3.043543008425D-07 9.142950968846D-09 -1.496898654541D-10
  9.980517130870D-13
  55.d0  1.d0  9352.11494d0              % VS DVS DLIM
 3  1  2 2  7 0 113.2817653490D0 2.577D-08 % NLR ITYPE IZP0 IZQ0 NP0 NQ0 VD XCN0
  1.910501922487D-03 -3.893923351925D-04 2.334546248943D-05 -6.987656722521D-07
  1.155836220945D-08 -1.015514433411D-10 3.720613823813D-13
   8                                     % LMAXBv
  4.974956434974D-01 -5.487758555749D-03 2.648227703650D-05 -1.139866232979D-06
  7.141138262611D-08 -4.445710119333D-09 1.443419023131D-10 -2.497993558364D-12
  1.725383416037D-14
 3  0 0  6 0  4.263D-08                  % ITYPB IZP1 IZQ1 NP1 NQ1 XCN1
  2.114415071744D-01 -2.929745145298D-02 1.369881187153D-03 -3.136194459560D-05
  3.563240597730D-07 -1.610153741067D-09
 1  2   49.d0                            % Kaiser NSV VEXT
  -0.4d0  0.2d0  1.6d0                   %(1) V1 DV V2
   1.d0   1.0d0 114.d0                   %(2) V1 DV V2
```

C. Channel-6 “Standard” Output for the Cases Considered in Appendix C

Cases (i): Standard Dunham-Representation Application with VEXT $= 0$

```
(i) Dunham Calculation with Gerstenkorn constants for I2(B)    (VEXT = 0)
************************************************************
RKR potential for  I(127)- I(127)   with   Charge= 0
Reduced mass   ZMU= 63.45223400000   and constant   C_u/ZMU =  0.265674319363
    from atomic masses: 126.9044680000  &  126.9044680000(u)

Seek relative quadrature convergence 1.0D-10.   Bisect interval up to  5 times.
    performing 16-point Gaussian quadrature in each segment

The 16 Dunham  Gv  expansion coefficients are
       1.2566434300D+02 -7.4752849602D-01 -5.0168331699D-03  3.7884141817D-04
      -4.9837738343D-05  4.2005659449D-06 -2.4626996050D-07  1.0355593456D-08
      -3.1687848474D-10  7.0990552575D-12 -1.1596853608D-13  1.3612056805D-15
      -1.1153094966D-17  6.0461708333D-20 -1.9471982460D-22  2.8200312435D-25

The 16 Dunham  Bv  expansion coefficients are
       2.9000806848D-02 -1.4962035582D-04 -1.1229996810D-06 -8.5987503871D-09
      -3.9935141912D-09  7.4427059317D-10 -7.7291147401D-11  4.9986605798D-12
      -2.1573933791D-13  6.4369102171D-15 -1.3475012537D-16  1.9772279456D-18
      -1.9948965189D-20  1.3200316843D-22 -5.1624336982D-25  9.0476320577D-28

At  v00= -0.50000   Gv=  0.00000000   dG/dv= 125.6643   (1/2)d2G/dv2= -0.747528
                    Bv=  0.02900081   { ==>   Req= 3.026702587(A) }
                    alpha_e = 0.000149620

Calculate turning points at the  92 v-values
  -0.40  -0.20   0.00   0.20   0.40   0.60   0.80   1.00   1.20   1.40   1.60
   2.00   3.00   4.00   5.00   6.00   7.00   8.00   9.00  10.00  11.00  12.00
  13.00  14.00  15.00  16.00  17.00  18.00  19.00  20.00  21.00  22.00  23.00
  24.00  25.00  26.00  27.00  28.00  29.00  30.00  31.00  32.00  33.00  34.00
  35.00  36.00  37.00  38.00  39.00  40.00  41.00  42.00  43.00  44.00  45.00
  46.00  47.00  48.00  49.00  50.00  51.00  52.00  53.00  54.00  55.00  56.00
  57.00  58.00  59.00  60.00  61.00  62.00  63.00  64.00  65.00  66.00  67.00
  68.00  69.00  70.00  71.00  72.00  73.00  74.00  75.00  76.00  77.00  78.00
  79.00  80.00  81.00  82.00

Resulting Turning Points:
    v        E(v)    dE(v)/dv       B(v)          RMIN(v)        RMAX(v)   NDIV  tst(f)   tst(g)    C(exp)       d(RMIN)
*************************************************************************************************************************
 -0.40     12.5590   125.5147   0.0289858336   2.9982686459   3.0564581070   2  1.9D-15  1.8D-15
 -0.20     37.6319   125.2145   0.0289558194   2.9782446305   3.0791322611   2  6.6D-15  6.7D-15
  0.00     62.6447   124.9132   0.0289257146   2.9648302088   3.0952061881   2  8.9D-16  8.9D-16  24.136902
  0.20     87.5971   124.6109   0.0288955185   2.9541434528   3.1085618932   2  3.3D-16  0.0D+00  18.743521
  0.40    112.4890   124.3076   0.0288652304   2.9450561836   3.1203276364   2  2.2D-15  0.0D+00  16.187465
  0.60    137.3201   124.0033   0.0288348494   2.9370523609   3.1310195425   2  3.3D-15  0.0D+00  14.589502
  0.80    162.0902   123.6980   0.0288043746   2.9298446852   3.1409249984   2  4.4D-16  0.0D+00  13.464354
  1.00    186.7992   123.3919   0.0287738052   2.9232537557   3.1502234944   2  1.8D-15  0.0D+00  12.615397
  1.20    211.4469   123.0849   0.0287431401   2.9171586793   3.1590360152   2  1.4D-15  0.0D+00  11.944830
  1.40    236.0331   122.7771   0.0287123783   2.9114734225   3.1674486871   2  8.9D-16  0.0D+00  11.397566
  1.60    260.5577   122.4684   0.0286815190   2.9061341912   3.1755253986   2  4.4D-16  0.0D+00  10.939821
  2.00    309.4212   121.8487   0.0286195034   2.8963088821   3.1908562445   2  2.8D-15  0.0D+00  10.441069
  3.00    430.4899   120.2854   0.0284626875   2.8753681168   3.2257437218   2  1.1D-15  0.0D+00   9.702227
  4.00    549.9855   118.7026   0.0283032399   2.8579347599   3.2573947782   2  1.8D-15  0.0D+00   8.895459
  5.00    667.8885   117.1000   0.0281410524   2.8428708827   3.2869596105   2  1.2D-15  0.0D+00   8.178077
...........................................................................................................
.................................. delete 35 intermediate lines of output ................................
...........................................................................................................
 41.00   3681.1924    47.2736   0.0194400086   2.6537025244   4.3732707639   2  2.3D-13  0.0D+00   5.192286
 42.00   3727.4605    45.2666   0.0190953193   2.6519001036   4.4195058946   2  2.7D-13  0.0D+00   5.224621
 43.00   3771.7343    43.2856   0.0187450476   2.6501912657   4.4675140226   2  2.6D-13  0.0D+00   5.274020
 44.00   3814.0412    41.3331   0.0183893231   2.6485728093   4.5174035981   2  3.4D-13  0.0D+00   5.347653
 45.00   3854.4110    39.4118   0.0180282757   2.6470416619   4.5692911140   2  2.8D-13  0.0D+00   5.453391
 46.00   3892.8760    37.5240   0.0176620329   2.6455948697   4.6233023232   2  1.2D-12  0.0D+00   5.599118
 47.00   3929.4709    35.6718   0.0172907158   2.6442295846   4.6795736761   2  9.2D-14  0.0D+00   5.791764
 48.00   3964.2321    33.8570   0.0169144365   2.6429430468   4.7382540058   2  9.3D-13  0.0D+00   6.036134
 49.00   3997.1980    32.0814   0.0165332948   2.6417325641   4.7995064979   2  6.8D-13  0.0D+00   6.333526
 50.00   4028.4084    30.3464   0.0161473763   2.6405954908   4.8635109804   2  8.8D-13  0.0D+00   6.680356
 51.00   4057.9046    28.6531   0.0157567507   2.6395292057   4.9304665782   2  4.0D-13  0.0D+00   7.067007
 52.00   4085.7289    27.0026   0.0153614704   2.6385310949   5.0005947807   2  3.8D-12  0.0D+00   7.477323
 53.00   4111.9244    25.3958   0.0149615706   2.6375985389   5.0741429799   2  1.7D-12  0.0D+00   7.889415
 54.00   4136.5351    23.8333   0.0145570694   2.6367289097   5.1513885469   2  9.5D-14  0.0D+00   8.278745
 55.00   4159.6059    22.3158   0.0141479701   2.6359195786   5.2326435303   2  6.8D-12  0.0D+00   8.624812
 56.00   4181.1819    20.8439   0.0137342632   2.6351679364   5.3182600792   2  1.2D-11  0.0D+00   8.923187
 57.00   4201.3091    19.4181   0.0133159311   2.6344714271   5.4086367194   2  9.0D-12  0.0D+00   9.204982
 58.00   4220.0337    18.0390   0.0128929531   2.6338275935   5.5042256461   2  9.1D-12  0.0D+00   9.566795
 59.00   4237.4027    16.7071   0.0124653122   2.6332341308   5.6055412466   2  7.1D-12  0.0D+00  10.213564
 60.00   4253.4639    15.4232   0.0120330036   2.6326889442   5.7131701232   2  4.6D-12  0.0D+00  11.519225
 61.00   4268.2654    14.1880   0.0115960442   2.6321902021   5.8277829769   2  3.4D-11  0.0D+00  14.112796
 62.00   4281.8564    13.0023   0.0111544832   2.6317363743   5.9501488226   2  3.3D-11  0.0D+00  18.999250
*** CAUTION *** inner wall exponent parameter becomes very large so skip converging it.
 63.00   4294.2868    11.8670   0.0107084144   2.6313262452   6.0811521635   2  1.9D-11  0.0D+00  27.731911
 64.00   4305.6074    10.7830   0.0102579875   2.6309588868   6.2218139674   2  7.7D-12  0.0D+00  42.728016
 65.00   4315.8701     9.7512   0.0098034201   2.6306335816   6.3733175872   2  7.3D-11  0.0D+00  67.687148
 66.00   4325.1275     8.7726   0.0093450080   2.6303496808   6.5370411895   2  9.2D-11  0.0D+00 108.374812
 67.00   4333.4333     7.8480   0.0088831328   2.6301063921   6.7145988856   2  5.3D-11  0.0D+00 173.796741
 68.00   4340.8418     6.9782   0.0084182663   2.6299024984   6.9078936101   4  2.8D-11  0.0D+00 277.902359
 69.00   4347.4081     6.1636   0.0079509683   2.6297360142   7.1191861948   2  6.3D-11  0.0D+00 440.777359
*** STOP ITERATION:  At  NDIV= 32   tst(f)/(previous)= 4.8D-10/1.8D-10   tst(g)/(previous)= 0.0D+00/0.0D+00
 70.00   4353.1875     5.4046   0.0074818794   2.6296038088   7.3511870356  32  4.8D-10  0.0D+00 684.406781
 71.00   4358.2357     4.7012   0.0070117035   2.6295012375   7.6071800042   2  1.7D-11  0.0D+001001.070502
 72.00   4362.6083     4.0531   0.0065411828   2.6294218561   7.8911930896   4  4.4D-11  0.0D+001227.613180
```

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 73.00  4366.3602      3.4598   0.0060710625   2.6293572889   8.2082388420   8  6.9D-11  0.0D+00 740.914685
 74.00  4369.5458      2.9203   0.0056020488   2.6292973602   8.5646611076   2  9.2D-11  0.0D+00***********
 75.00  4372.2184      2.4334   0.0051347613   2.6292305250   8.9686494197   4  7.1D-11  0.0D+00***********
*** STOP ITERATION:  At  NDIV=  8   tst(f)/(previous)= 8.6D-09/4.6D-09   tst(g)/(previous)= 0.0D+00/0.0D+00
 76.00  4374.4295      1.9973   0.0046696885   2.6291445320   9.4310264483   8  8.6D-09  0.0D+00***********
*** STOP ITERATION:  At  NDIV=  8   tst(f)/(previous)= 4.8D-09/7.7D-10   tst(g)/(previous)= 0.0D+00/0.0D+00
 77.00  4376.2292      1.6102   0.0042071562   2.6290269317   9.9664981783   8  4.8D-09  0.0D+00***********
*** STOP ITERATION:  At  NDIV= 16   tst(f)/(previous)= 1.0D-08/4.5D-09   tst(g)/(previous)= 0.0D+00/0.0D+00
 78.00  4377.6655      1.2700   0.0037473247   2.6288642234  10.5957276302  16  1.0D-08  0.0D+00***********
*** STOP ITERATION:  At  NDIV= 16   tst(f)/(previous)= 2.2D-08/6.1D-10   tst(g)/(previous)= 0.0D+00/0.0D+00
 79.00  4378.7840      0.9744   0.0032902410   2.6286369902  11.3489510075  16  2.2D-08  0.0D+00***********
*** STOP ITERATION:  At  NDIV= 16   tst(f)/(previous)= 8.1D-09/2.0D-09   tst(g)/(previous)= 0.0D+00/0.0D+00
 80.00  4379.6283      0.7211   0.0028359793   2.6283048004  12.2726821336  16  8.1D-09  0.0D+00***********
*** STOP ITERATION:  At  NDIV=  8   tst(f)/(previous)= 9.3D-09/3.0D-09   tst(g)/(previous)= 0.0D+00/0.0D+00
 81.00  4380.2397      0.5082   0.0023849172   2.6277675077  13.4430895058   8  9.3D-09  0.0D+00***********
*** STOP ITERATION:  At  NDIV=  8   tst(f)/(previous)= 3.8D-08/2.6D-08   tst(g)/(previous)= 0.0D+00/0.0D+00
 82.00  4380.6576      0.3339   0.0019382124   2.6267751713  14.9951678534   8  3.8D-08  0.0D+00***********
**************************************************************************************************************************
```

Case (ii): Standard Dunham-Representation Application with $\mathrm{VEXT} > 0$

```
(ii) Dunham Calculation with Gerstenkorn constants for I2(B)    (VEXT > 0)
************************************************************
RKR potential for  I(127)- I(127)   with   Charge= 0
Reduced mass   ZMU= 63.45223400000   and constant   C_u/ZMU =  0.265674319363
    from atomic masses: 126.9044680000  &  126.9044680000(u)

Seek relative quadrature convergence 1.0D-10.   Bisect interval up to  5 times.
    performing 16-point Gaussian quadrature in each segment

The 16 Dunham  Gv  expansion coefficients are
       1.2566434300D+02 -7.4752849602D-01 -5.0168331699D-03  3.7884141817D-04
      -4.9837738343D-05  4.2005659449D-06 -2.4626996050D-07  1.0355593456D-08
      -3.1687848474D-10  7.0990552575D-12 -1.1596853608D-13  1.3612056805D-15
      -1.1153094966D-17  6.0461708333D-20 -1.9471982460D-22  2.8200312435D-25

The 16 Dunham  Bv  expansion coefficients are
       2.9000806848D-02 -1.4962035582D-04 -1.1229996810D-06 -8.5987503871D-09
      -3.9935141912D-09  7.4427059317D-10 -7.7291147401D-11  4.9986605798D-12
      -2.1573933791D-13  6.4369102171D-15 -1.3475012537D-16  1.9772279456D-18
      -1.9948965189D-20  1.3200316843D-22 -5.1624336982D-25  9.0476320577D-28

At  v00= -0.50000   Gv=  0.00000000   dG/dv= 125.6643   (1/2)d2G/dv2= -0.747528
                    Bv=  0.02900081   { ==>   Req= 3.026702587(A) }
                    alpha_e = 0.000149620

Above   v =  45.000   extrapolate inner wall with exponential
        fitted to last 3 points ( & shift  RMAX  accordingly)

Calculate turning points at the  92 v-values
  -0.40  -0.20   0.00   0.20   0.40   0.60   0.80   1.00   1.20   1.40   1.60
   2.00   3.00   4.00   5.00   6.00   7.00   8.00   9.00  10.00  11.00  12.00
  13.00  14.00  15.00  16.00  17.00  18.00  19.00  20.00  21.00  22.00  23.00
  24.00  25.00  26.00  27.00  28.00  29.00  30.00  31.00  32.00  33.00  34.00
  35.00  36.00  37.00  38.00  39.00  40.00  41.00  42.00  43.00  44.00  45.00
  46.00  47.00  48.00  49.00  50.00  51.00  52.00  53.00  54.00  55.00  56.00
  57.00  58.00  59.00  60.00  61.00  62.00  63.00  64.00  65.00  66.00  67.00
  68.00  69.00  70.00  71.00  72.00  73.00  74.00  75.00  76.00  77.00  78.00
  79.00  80.00  81.00  82.00

Resulting Turning Points:
    v        E(v)    dE(v)/dv       B(v)          RMIN(v)        RMAX(v)   NDIV  tst(f)   tst(g)    C(exp)       d(RMIN)
**************************************************************************************************************************
 -0.40    12.5590    125.5147   0.0289858336   2.9982686459   3.0564581070   2  1.9D-15  1.8D-15
 -0.20    37.6319    125.2145   0.0289558194   2.9782446305   3.0791322611   2  6.6D-15  6.7D-15
  0.00    62.6447    124.9132   0.0289257146   2.9648302088   3.0952061881   2  8.9D-16  8.9D-16  24.136902
  0.20    87.5971    124.6109   0.0288955185   2.9541434528   3.1085618932   2  3.3D-16  7.8D-16  18.743521
  0.40   112.4890    124.3076   0.0288652304   2.9450561836   3.1203276364   2  2.2D-15  2.3D-15  16.187465
  0.60   137.3201    124.0033   0.0288348494   2.9370523609   3.1310195425   2  3.3D-15  3.3D-15  14.589502
  0.80   162.0902    123.6980   0.0288043746   2.9298446852   3.1409249984   2  4.4D-16  4.4D-16  13.464354
  1.00   186.7992    123.3919   0.0287738052   2.9232537557   3.1502234944   2  1.8D-15  1.3D-15  12.615397
  1.20   211.4469    123.0849   0.0287431401   2.9171586793   3.1590360152   2  1.4D-15  1.4D-15  11.944830
  1.40   236.0331    122.7771   0.0287123783   2.9114734225   3.1674486871   2  8.9D-16  6.7D-16  11.397566
  1.60   260.5577    122.4684   0.0286815190   2.9061341912   3.1755253986   2  4.4D-16  6.7D-16  10.939821
  2.00   309.4212    121.8487   0.0286195034   2.8963088821   3.1908562445   2  2.8D-15  2.7D-15  10.441069
  3.00   430.4899    120.2854   0.0284626875   2.8753681168   3.2257437218   2  1.1D-15  1.7D-15   9.702227
  4.00   549.9855    118.7026   0.0283032399   2.8579347599   3.2573947782   2  1.8D-15  1.8D-15   8.895459
  5.00   667.8885    117.1000   0.0281410524   2.8428708827   3.2869596105   2  1.2D-15  1.0D-15   8.178077
...........................................................................................................
................................. delete 35 intermediate lines of output ..................................
...........................................................................................................
 41.00  3681.1924     47.2736   0.0194400086   2.6537025244   4.3732707639   2  2.3D-13  1.9D-13   5.192286
 42.00  3727.4605     45.2666   0.0190953193   2.6519001036   4.4195058946   2  2.7D-13  2.3D-13   5.224621
 43.00  3771.7343     43.2856   0.0187450476   2.6501912657   4.4675140226   2  2.6D-13  2.2D-13   5.274020
 44.00  3814.0412     41.3331   0.0183893231   2.6485728093   4.5174035981   2  3.4D-13  2.9D-13   5.347653
 45.00  3854.4110     39.4118   0.0180282757   2.6470416619   4.5692911140   2  2.8D-13  2.3D-13   5.453391
 46.00  3892.8760     37.5240   0.0176620329   2.6455945570   4.6233020105   2  1.2D-12  0.0D+00   5.453391  -0.0000003127
 47.00  3929.4709     35.6718   0.0172907158   2.6442283317   4.6795724232   2  9.2D-14  0.0D+00   5.453391  -0.0000012529
 48.00  3964.2321     33.8570   0.0169144365   2.6429399227   4.7382508818   2  9.3D-13  0.0D+00   5.453391  -0.0000031241
 49.00  3997.1980     32.0814   0.0165332948   2.6417263632   4.7995002970   2  6.8D-13  0.0D+00   5.453391  -0.0000062010
 50.00  4028.4084     30.3464   0.0161473763   2.6405847803   4.8635002700   2  8.8D-13  0.0D+00   5.453391  -0.0000107104
...........................................................................................................
................................. delete 15 intermediate lines of output ..................................
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 66.00   4325.1275     8.7726   0.0093450080   2.6300725746   6.5367640833   2  9.2D-11  0.0D+00    5.453391  -0.0002771062
 67.00   4333.4333     7.8480   0.0088831328   2.6297868147   6.7142793081   2  5.3D-11  0.0D+00    5.453391  -0.0003195774
 68.00   4340.8418     6.9782   0.0084182663   2.6295323006   6.9075234123   4  2.8D-11  0.0D+00    5.453391  -0.0003701978
 69.00   4347.4081     6.1636   0.0079509683   2.6293070169   7.1187571975   2  6.3D-11  0.0D+00    5.453391  -0.0004289973
*** STOP ITERATION:  At  NDIV= 32   tst(f)/(previous)= 4.8D-10/1.8D-10   tst(g)/(previous)= 0.0D+00/0.0D+00
 70.00   4353.1875     5.4046   0.0074818794   2.6291089572   7.3506921839  32  4.8D-10  0.0D+00    5.453391  -0.0004948516
 71.00   4358.2357     4.7012   0.0070117035   2.6289361304   7.6066148971   2  1.7D-11  0.0D+00    5.453391  -0.0005651071
 72.00   4362.6083     4.0531   0.0065411828   2.6287865671   7.8905578006   4  4.4D-11  0.0D+00    5.453391  -0.0006352890
 73.00   4366.3602     3.4598   0.0060710625   2.6286583288   8.2075398819   8  6.9D-11  0.0D+00    5.453391  -0.0006989601
 74.00   4369.5458     2.9203   0.0056020488   2.6285495164   8.5639132638   2  9.2D-11  0.0D+00    5.453391  -0.0007478438
 75.00   4372.2184     2.4334   0.0051347613   2.6284582803   8.9678771751   4  7.1D-11  0.0D+00    5.453391  -0.0007722447
*** STOP ITERATION:  At  NDIV=  8   tst(f)/(previous)= 8.6D-09/4.6D-09   tst(g)/(previous)= 0.0D+00/0.0D+00
 76.00   4374.4295     1.9973   0.0046696885   2.6283828296   9.4302647459   8  8.6D-09  0.0D+00    5.453391  -0.0007617024
*** STOP ITERATION:  At  NDIV=  8   tst(f)/(previous)= 4.8D-09/7.7D-10   tst(g)/(previous)= 0.0D+00/0.0D+00
 77.00   4376.2292     1.6102   0.0042071562   2.6283214407   9.9657926872   8  4.8D-09  0.0D+00    5.453391  -0.0007054911
*** STOP ITERATION:  At  NDIV= 16   tst(f)/(previous)= 1.0D-08/4.5D-09   tst(g)/(previous)= 0.0D+00/0.0D+00
 78.00   4377.6655     1.2700   0.0037473247   2.6282724645  10.5951358713  16  1.0D-08  0.0D+00    5.453391  -0.0005917589
*** STOP ITERATION:  At  NDIV= 16   tst(f)/(previous)= 2.2D-08/6.1D-10   tst(g)/(previous)= 0.0D+00/0.0D+00
 79.00   4378.7840     0.9744   0.0032902410   2.6282343315  11.3485483488  16  2.2D-08  0.0D+00    5.453391  -0.0004026587
*** STOP ITERATION:  At  NDIV= 16   tst(f)/(previous)= 8.1D-09/2.0D-09   tst(g)/(previous)= 0.0D+00/0.0D+00
 80.00   4379.6283     0.7211   0.0028359793   2.6282055525  12.2725828857  16  8.1D-09  0.0D+00    5.453391  -0.0000992479
*** STOP ITERATION:  At  NDIV=  8   tst(f)/(previous)= 9.3D-09/3.0D-09   tst(g)/(previous)= 0.0D+00/0.0D+00
 81.00   4380.2397     0.5082   0.0023849172   2.6281847157  13.4435067139   8  9.3D-09  0.0D+00    5.453391   0.0004172080
*** STOP ITERATION:  At  NDIV=  8   tst(f)/(previous)= 3.8D-08/2.6D-08   tst(g)/(previous)= 0.0D+00/0.0D+00
 82.00   4380.6576     0.3339   0.0019382124   2.6281704758  14.9965631578   8  3.8D-08  0.0D+00    5.453391   0.0013953044
***************************************************************************************************************************

Note that for   v .GE. 45.00  inner wall extrapolated as:   V(R) =   -1000.5391 + 0.90235927D+10*exp(-  5.45339142*R)
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Case (iii): Pure NDE Functions for G_v *and* B_v $\mathrm{VEXT} = 0$

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(iii) Liu et al. JCP 111, 3494 (1999) NDE functions for Na2:  VEXT = 0
************************************************************
RKR potential for Na( 23)-Na( 23)   with   Charge= 0
Reduced mass   ZMU= 11.49488483000   and constant   C_u/ZMU =  1.466533099662
    from atomic masses:  22.9897696600  &   22.9897696600(u)

Seek relative quadrature convergence 1.0D-10.   Bisect interval up to  5 times.
    performing 16-point Gaussian quadrature in each segment

NDE for  Gv  is an  (NP= 3/NQ= 2)  OUTER Pade  expansion in  (vD-v)  with
       X0(n=6)= 4.4867000D-02  and leading num. and denom. powers  1  &   1
       vD=   61.4100    D-G(v=-1/2)=   3432.458368
    Numerator coefficients are:  4.366360000000D-01 -3.529000000000D-03
             1.540000000000D-05
    Denominator coefficients :   4.800000000000D-02  1.366000000000D-02

NDE for  Bv  is an  (NP= 7/NQ= 0) Exponential  expansion in  (vD-v)  with
       X1(n=6)= 3.0921000D-03  and leading num. and denom. powers  1  &   0
    Numerator coefficients are:  1.341000000000D-01 -1.686300000000D-02
             9.200000000000D-04 -2.810837000000D-05  4.924000000000D-07
            -4.619520000000D-09  1.800000000000D-11

Calculate   Y00=  0.171244236    v(cor)= -0.0018267047    v(min)= -0.5018267047
    using    we=  93.7441    wexe= 0.451924    Be=  0.118327    ae= 0.00188162
    and corrected effective   De=  3432.629612 (after adding Y00)

At  v00= -0.50183   Gv=  0.00000000   dG/dv=  93.7457   (1/2)d2G/dv2= -0.451924
                    Bv=  0.11833058   { ==>   Req= 3.520443964(A) }
                    alpha_e = 0.001881624

Calculate turning points at the  67 v-values
  -0.40  -0.20   0.00   0.20   0.40   0.60   1.00   2.00   3.00   4.00   5.00
   6.00   7.00   8.00   9.00  10.00  11.00  12.00  13.00  14.00  15.00  16.00
  17.00  18.00  19.00  20.00  21.00  22.00  23.00  24.00  25.00  26.00  27.00
  28.00  29.00  30.00  31.00  32.00  33.00  34.00  35.00  36.00  37.00  38.00
  39.00  40.00  41.00  42.00  43.00  44.00  45.00  46.00  47.00  48.00  49.00
  50.00  51.00  52.00  53.00  54.00  55.00  56.00  57.00  58.00  59.00  60.00
  61.00

Resulting Turning Points:
    v       E(v)    dE(v)/dv       B(v)          RMIN(v)        RMAX(v)   NDIV  tst(f)   tst(g)    C(exp)       d(RMIN)
***************************************************************************************************************************
 -0.40      9.5411    93.6537   0.1181411455   3.4433774831   3.6030899250   2  3.7D-12  3.7D-12
 -0.20     28.2538    93.4731   0.1177817356   3.3910255327   3.6662176475   2  4.5D-13  4.3D-13
  0.00     46.9304    93.2926   0.1174382433   3.3563298755   3.7114568080   2  5.8D-13  5.9D-13    9.540879
  0.20     65.5709    93.1123   0.1171096782   3.3288990060   3.7492108023   2  5.6D-14  0.0D+00    7.535556
  0.40     84.1753    92.9322   0.1167950997   3.3056943386   3.7825296865   2  7.1D-14  0.0D+00    6.547257
  0.60    102.7438    92.7521   0.1164936143   3.2853252312   3.8128151640   2  1.2D-13  0.0D+00    5.901498
  1.00    139.7727    92.3924   0.1159265724   3.2502928119   3.8671290476   2  7.9D-14  0.0D+00    5.307723
  2.00    231.7160    91.4946   0.1146836989   3.1817425861   3.9811207866   2  4.0D-14  0.0D+00    4.541315
  3.00    322.7622    90.5979   0.1136272512   3.1278016425   4.0774161199   2  3.4D-14  0.0D+00    3.770565
  4.00    412.9118    89.7012   0.1126941968   3.0821210595   4.1632698873   2  4.0D-14  0.0D+00    3.145085
  5.00    502.1641    88.8032   0.1118369435   3.0419588892   4.2421563194   2  4.1D-14  0.0D+00    2.770094
............................................................................................................
................................. delete 25 intermediate lines of output ...................................
............................................................................................................
 31.00   2475.5535    60.8194   0.0853376407   2.5748002973   5.8987370001   2  5.7D-15  0.0D+00    2.494313
 32.00   2535.6636    59.3943   0.0839351846   2.5660411322   5.9710693371   2  3.0D-15  0.0D+00    2.557118
 33.00   2594.3287    57.9291   0.0824882473   2.5576787204   6.0454464448   2  5.3D-15  0.0D+00    2.572445
 34.00   2651.5077    56.4219   0.0809967870   2.5496940239   6.1220841546   2  6.7D-16  0.0D+00    2.516015
 35.00   2707.1579    54.8708   0.0794609787   2.5420647559   6.2012201307   2  2.4D-15  0.0D+00    2.361046
```

```
 36.00    2761.2341    53.2737   0.0778809883   2.5347654982   6.2831191877   2  4.1D-15  0.0D+00   2.080646
 37.00    2813.6893    51.6284   0.0762566898   2.5277681497   6.3680801273   2  2.2D-15  0.0D+00   1.651688
 38.00    2864.4740    49.9324   0.0745873285   2.5210427320   6.4564444856   2  2.2D-16  0.0D+00   1.060115
 39.00    2913.5363    48.1832   0.0728711368   2.5145585742   6.5486077108   2  1.3D-15  0.0D+00   0.307079
*** CAUTION ***  Inner potential wall has negative curvature and requires smoothing for   VEXT .ge.  40.00
 40.00    2960.8217    46.3779   0.0711049093   2.5082858923   6.6450334682   2  1.7D-15  0.0D+00  -0.585320
 41.00    3006.2725    44.5136   0.0692835503   2.5021977695   6.7462720275   2  4.4D-15  0.0D+00  -1.570285
 42.00    3049.8281    42.5869   0.0673996069   2.4962725339   6.8529840661   2  2.7D-15  0.0D+00  -2.575856
 43.00    3091.4244    40.5943   0.0654428122   2.4904965103   6.9659717804   2  4.9D-15  0.0D+00  -3.507648
 44.00    3130.9935    38.5319   0.0633996671   2.4848670988   7.0862200463   2  2.7D-15  0.0D+00  -4.252501
 45.00    3168.4635    36.3954   0.0612531062   2.4793960957   7.2149516703   2  2.2D-15  0.0D+00  -4.677874
 46.00    3203.7583    34.1806   0.0589823104   2.4741131226   7.3537028255   2  8.9D-16  0.0D+00  -4.618253
 47.00    3236.7971    31.8829   0.0565627497   2.4690689637   7.5044280716   2  1.1D-15  0.0D+00  -3.832715
 48.00    3267.4950    29.4981   0.0539665741   2.4643385315   7.6696498268   2  1.6D-15  0.0D+00  -1.897550
 49.00    3295.7631    27.0227   0.0511634986   2.4600231041   7.8526764784   2  2.2D-16  0.0D+00   2.069065
 50.00    3321.5095    24.4547   0.0481223659   2.4562514269   8.0579297293   2  2.2D-16  0.0D+00  10.203665
*** CAUTION *** inner wall exponent parameter becomes very large so skip converging it.
 51.00    3344.6420    21.7955   0.0448135876   2.4531793245   8.2914517940   2  1.3D-15  0.0D+00  28.503162
 52.00    3365.0721    19.0516   0.0412126675   2.4509877706   8.5617204229   2  5.7D-14  0.0D+00  79.410279
 53.00    3382.7221    16.2389   0.0373049516   2.4498801811   8.8810152590   2  2.8D-13  0.0D+00 292.309499
*** WARNING ***  inner wall becomes unstable at   v = 54.00  where  RMIN  turns!
 54.00    3397.5369    13.3878   0.0330916168   2.4500815522   9.2678267882   2  1.7D-12  0.0D+00
 55.00    3409.5017    10.5499   0.0285966481   2.4518458455   9.7513731752   2  1.1D-11  0.0D+00
 56.00    3418.6677     7.8065   0.0238741458   2.4554852846  10.3807552860   2  7.8D-11  0.0D+00
 57.00    3425.1846     5.2741   0.0190147352   2.4614486411  11.2455145113   4  7.5D-14  0.0D+00
 58.00    3429.3359     3.1019   0.0141491994   2.4705000254  12.5288253204   4  1.5D-12  0.0D+00
 59.00    3431.5617     1.4483   0.0094468833   2.4840954343  14.6775185059   8  4.2D-13  0.0D+00
 60.00    3432.4448     0.4276   0.0051062558   2.5051464812  19.1825152839   8  1.7D-11  0.0D+00
 61.00    3432.6260     0.0272   0.0013357077   2.5396186784  37.5136881941  32  8.5D-11  0.0D+00
****************************************************************************************************************************
```

Case (iv): Pure NDE Functions for G_v *and* B_v VEXT > 0

```
(iv) Liu et al. JCP 111, 3494 (1999) NDE functions for Na2:  VEXT > 0
*************************************************************
RKR potential for Na( 23)-Na( 23)   with   Charge= 0
Reduced mass   ZMU= 11.49488483000   and constant   C_u/ZMU =  1.466533099662
    from atomic masses:  22.9897696600  &   22.9897696600(u)

Seek relative quadrature convergence 1.0D-10.   Bisect interval up to  5 times.
    performing 16-point Gaussian quadrature in each segment

NDE for  Gv  is an  (NP= 3/NQ= 2)  OUTER Pade  expansion in  (vD-v)  with
       X0(n=6)= 4.4867000D-02  and leading num. and denom. powers  1  &   1
       vD=   61.4100    D-G(v=-1/2)=   3432.458368
    Numerator coefficients are:  4.366360000000D-01 -3.529000000000D-03
             1.540000000000D-05
    Denominator coefficients :   4.800000000000D-02  1.366000000000D-02

NDE for  Bv  is an  (NP= 7/NQ= 0) Exponential  expansion in  (vD-v)  with
       X1(n=6)= 3.0921000D-03  and leading num. and denom. powers  1  &   0
    Numerator coefficients are:  1.341000000000D-01 -1.686300000000D-02
             9.200000000000D-04 -2.810837000000D-05  4.924000000000D-07
            -4.619520000000D-09  1.800000000000D-11

Calculate   Y00=  0.171244236    v(cor)= -0.0018267047    v(min)= -0.5018267047
    using    we=  93.7441    wexe= 0.451924    Be=  0.118327    ae= 0.00188162
    and corrected effective   De=  3432.629612 (after adding Y00)

At  v00= -0.50183   Gv=  0.00000000   dG/dv=  93.7457   (1/2)d2G/dv2= -0.451924
                    Bv=  0.11833058   { ==>   Req= 3.520443964(A) }
                    alpha_e = 0.001881624

Above   v =  35.000   extrapolate inner wall with exponential
        fitted to last 3 points ( & shift  RMAX  accordingly)

Calculate turning points at the  67 v-values
  -0.40  -0.20   0.00   0.20   0.40   0.60   1.00   2.00   3.00   4.00   5.00
   6.00   7.00   8.00   9.00  10.00  11.00  12.00  13.00  14.00  15.00  16.00
  17.00  18.00  19.00  20.00  21.00  22.00  23.00  24.00  25.00  26.00  27.00
  28.00  29.00  30.00  31.00  32.00  33.00  34.00  35.00  36.00  37.00  38.00
  39.00  40.00  41.00  42.00  43.00  44.00  45.00  46.00  47.00  48.00  49.00
  50.00  51.00  52.00  53.00  54.00  55.00  56.00  57.00  58.00  59.00  60.00
  61.00

Resulting Turning Points:
    v        E(v)    dE(v)/dv       B(v)          RMIN(v)        RMAX(v)   NDIV  tst(f)   tst(g)    C(exp)       d(RMIN)
****************************************************************************************************************************
 -0.40       9.5411    93.6537   0.1181411455   3.4433774831   3.6030899250   2  3.7D-12  3.7D-12
 -0.20      28.2538    93.4731   0.1177817356   3.3910255327   3.6662176475   2  4.5D-13  4.3D-13
  0.00      46.9304    93.2926   0.1174382433   3.3563298755   3.7114568080   2  5.8D-13  5.9D-13   9.540879
  0.20      65.5709    93.1123   0.1171096782   3.3288990060   3.7492108023   2  5.6D-14  6.3D-14   7.535556
  0.40      84.1753    92.9322   0.1167950997   3.3056943386   3.7825296865   2  7.1D-14  8.6D-14   6.547257
  0.60     102.7438    92.7521   0.1164936143   3.2853252312   3.8128151640   2  1.2D-13  1.4D-13   5.901498
  1.00     139.7727    92.3924   0.1159265724   3.2502928119   3.8671290476   2  7.9D-14  8.0D-14   5.307723
............................................................................................................
................................ delete 30 intermediate lines of output ....................................
............................................................................................................
 32.00    2535.6636    59.3943   0.0839351846   2.5660411322   5.9710693371   2  3.0D-15  2.2D-16   2.557118
 33.00    2594.3287    57.9291   0.0824882473   2.5576787204   6.0454464448   2  5.3D-15  9.3D-15   2.572445
 34.00    2651.5077    56.4219   0.0809967870   2.5496940239   6.1220841546   2  6.7D-16  6.7D-16   2.516015
 35.00    2707.1579    54.8708   0.0794609787   2.5420647559   6.2012201307   2  2.4D-15  2.0D-15   2.361046
 36.00    2761.2341    53.2737   0.0778809883   2.5347806271   6.2831343166   2  4.1D-15  0.0D+00   2.361046   0.0000151289
 37.00    2813.6893    51.6284   0.0762566898   2.5278325674   6.3681445450   2  2.2D-15  0.0D+00   2.361046   0.0000644177
```

```
 38.00   2864.4740    49.9324  0.0745873285   2.5212126519   6.4566144055   2  2.2D-16  0.0D+00   2.361046   0.0001699200
 39.00   2913.5363    48.1832  0.0728711368   2.5149140417   6.5489631782   2  1.3D-15  0.0D+00   2.361046   0.0003554675
 40.00   2960.8217    46.3779  0.0711049093   2.5089309366   6.6456785124   2  1.7D-15  0.0D+00   2.361046   0.0006450443
.........................................................................................................
................................ delete 15 intermediate lines of output .................................
.........................................................................................................
 56.00   3418.6677     7.8065  0.0238741458   2.4549913497  10.3802613511   2  7.8D-11  0.0D+00   2.361046  -0.0004939349
 57.00   3425.1846     5.2741  0.0190147352   2.4542710724  11.2383369426   4  7.5D-14  0.0D+00   2.361046  -0.0071775687
 58.00   3429.3359     3.1019  0.0141491994   2.4538128985  12.5121381934   4  1.5D-12  0.0D+00   2.361046  -0.0166871270
 59.00   3431.5617     1.4483  0.0094468833   2.4535674352  14.6469905068   8  4.2D-13  0.0D+00   2.361046  -0.0305279991
 60.00   3432.4448     0.4276  0.0051062558   2.4534700877  19.1308388903   8  1.7D-11  0.0D+00   2.361046  -0.0516763935
 61.00   3432.6260     0.0272  0.0013357077   2.4534501120  37.4275196277  32  8.5D-11  0.0D+00   2.361046  -0.0861685664
************************************************************************************************************************

Note that for   v .GE. 35.00  inner wall extrapolated as:   V(R) =    -410.1832 + 0.12600573D+07*exp(-  2.36104609*R)
************************************************************************************************************************
```

Case (v): No Rotational Data: Morse Inner Wall

```
(v) NDE-based potential for Ar-H(+):  Morse Inner Wall Extrapolation
*************************************************************
RKR potential for Ca( 40)- H(  1)   with   Charge= 0
Reduced mass   ZMU=  0.98303369736   and constant   C_u/ZMU = 17.148577027645
    from atomic masses:  39.9625912000  &    1.0078250319(u)

Seek relative quadrature convergence 1.0D-10.   Bisect interval up to  5 times.
    performing 16-point Gaussian quadrature in each segment

NDE for  Gv  is an  (NP= 3/NQ= 1)  OUTER Pade  expansion in  (vD-v)  with
       X0(n=4)= 1.4600000D-01  and leading num. and denom. powers  2  &   2
       vD=   33.2000    D-G(v=-1/2)=  35609.923120
    Numerator coefficients are: -3.967546042920D-05  4.569339259680D-06
           -3.922568643150D-08
    Denominator coefficients :   4.144700684780D-03

NO rotational constants input, so inner wall of potential is Morse function.
  Input   Req= 1.280660(Angst)   plus   we= 2710.952  &  wexe= 61.66771 [cm-1]
  yields Morse with  De= 29793.805 [cm-1]   and   beta= 1.896334 [1/Angst.]

At  v00= -0.50000   Gv=  0.00000000   dG/dv=2710.9524   (1/2)d2G/dv2=-61.667709
                    Bv= 10.45587538   { ==>   Req= 1.280660000(A) }
                    alpha_e = 0.345659441

Calculate turning points at the  42 v-values
  -0.40  -0.20   0.00   0.20   0.40   0.60   0.80   1.00   1.20   1.40   1.60
   2.00   3.00   4.00   5.00   6.00   7.00   8.00   9.00  10.00  11.00  12.00
  13.00  14.00  15.00  16.00  17.00  18.00  19.00  20.00  21.00  22.00  23.00
  24.00  25.00  26.00  27.00  28.00  29.00  30.00  31.00  32.00

Resulting Turning Points:
    v        E(v)   dE(v)/dv       B(v)          RMIN(v)        RMAX(v)   NDIV  tst(f)   tst(g)    C(exp)       d(RMIN)
************************************************************************************************************************
 -0.40    270.4791  2698.6344  10.4558753821   1.2326671604   1.3334617169   2  2.3D-12  0.0D+00
 -0.20    807.7496  2674.0913  10.4558753821   1.2002812029   1.3755279841   2  2.4D-13  0.0D+00
  0.00   1340.1238  2649.6715  10.4558753821   1.1792317644   1.4063398848   2  1.4D-13  0.0D+00
  0.20   1867.6263  2625.3741  10.4558753821   1.1628329913   1.4325826462   2  1.0D-13  0.0D+00
  0.40   2390.2815  2601.1982  10.4558753821   1.1491474879   1.4561934677   2  2.6D-13  0.0D+00
  0.60   2908.1136  2577.1429  10.4558753821   1.1372913397   1.4780563096   2  1.8D-15  0.0D+00
  0.80   3421.1467  2553.2073  10.4558753821   1.1267736204   1.4986623086   2  5.4D-14  0.0D+00
  1.00   3929.4045  2529.3905  10.4558753821   1.1172884796   1.5183176490   2  6.0D-14  0.0D+00
  1.20   4432.9107  2505.6914  10.4558753821   1.1086302686   1.5372284122   2  5.9D-14  0.0D+00
  1.40   4931.6888  2482.1091  10.4558753821   1.1006529499   1.5555411520   2  2.4D-14  0.0D+00
  1.60   5425.7621  2458.6426  10.4558753821   1.0932484604   1.5733645202   2  2.2D-15  0.0D+00
  2.00   6399.8859  2412.0524  10.4558753821   1.0798454827   1.6078583065   2  4.4D-14  0.0D+00
  3.00   8754.4466  2297.5257  10.4558753821   1.0522601543   1.6896839677   2  7.8D-15  0.0D+00
.........................................................................................................
................................ delete 25 intermediate lines of output .................................
.........................................................................................................
 29.00  35567.6034    38.9271  10.4558753821   0.8912713112   8.1742294726   2  2.4D-12  0.0D+00
 30.00  35595.2410    17.9773  10.4558753821   0.8911643690  10.2996571510   2  1.1D-12  0.0D+00
 31.00  35606.5707     6.0350  10.4558753821   0.8911205477  14.3471635421   4  4.4D-12  0.0D+00
 32.00  35609.6222     1.0001  10.4558753821   0.8911087469  25.1222213607   8  1.4D-13  0.0D+00
************************************************************************************************************************
```

Case (vi): MXS Function for G_v Combined With a Pure Dunham Expansion for B_v

```
(vi) For Li2(A): MXS function for Gv  &  Dunham for Bv
************************************************************
RKR potential for Li(  7)-Li(  7)   with   Charge= 0
Reduced mass   ZMU=  3.50800205000   and constant   C_u/ZMU =  4.805478685510
    from atomic masses:   7.0160041000  &    7.0160041000(u)

Seek relative quadrature convergence 1.0D-10.   Bisect interval up to  5 times.
    performing 16-point Gaussian quadrature in each segment

Represent  Gv’s  by Tellinghuisen-type MXS mixed representation:
================================
   9’th order Dunham for  v .le. VS   &   NDE for  v > VS,   with   VS= 55.0000
   with switching function   F_s = 1/[1 + exp{(v-VS)/DVS}]   with   DVS= 1.0000
    and a   sympotote energy (dissociation limit)   DLIM=  9352.1149 [cm-1]
```

```
The  9 Dunham  Gv  expansion coefficients are
       2.5549769914D+02 -1.5915289319D+00  4.3200696103D-03 -1.2978004834D-04
       5.1260928027D-06 -3.0435430084D-07  9.1429509688D-09 -1.4968986545D-10
       9.9805171309D-13

NDE for  Gv  is an  (NP= 7/NQ= 0)  OUTER Pade  expansion in  (vD-v)  with
       X0(n=3)= 2.5770000D-08  and leading num. and denom. powers  2  &   2
       vD=  113.2818    D-G(v=-1/2)=   9352.114940
    Numerator coefficients are:  1.910501922487D-03 -3.893923351925D-04
             2.334546248943D-05 -6.987656722521D-07  1.155836220945D-08
            -1.015514433411D-10  3.720613823813D-13

The 18 Dunham  Bv  expansion coefficients are
       4.9748268077D-01 -5.4518718585D-03 -2.3104497956D-06  9.7751263602D-06
      -2.4252908342D-06  3.8310664573D-07 -4.2439455149D-08  3.3429364156D-09
      -1.8877828547D-10  7.7035317420D-12 -2.2870567961D-13  4.9541013412D-15
      -7.8026226606D-17  8.8213054293D-19 -6.9662091302D-21  3.6455244695D-23
      -1.1354723194D-25  1.5930966183D-28

Calculate   Y00=  0.069258147    v(cor)= -0.0002710711    v(min)= -0.5002710711
    using    we= 255.4977    wexe= 1.591529    Be=  0.497483    ae= 0.00545187
    and corrected effective   De=  9352.184198 (after adding Y00)

At  v00= -0.50027   Gv=  0.00000000   dG/dv= 255.4986   (1/2)d2G/dv2= -1.591529
                    Bv=  0.49748416   { ==>   Req= 3.107983465(A) }
                    alpha_e = 0.005451872

Above   v =  45.000   extrapolate inner wall with exponential
        fitted to last 3 points ( & shift  RMAX  accordingly)

Calculate turning points at the 119 v-values
  -0.40  -0.20   0.00   0.20   0.40   0.60   1.00   2.00   3.00   4.00   5.00
   6.00   7.00   8.00   9.00  10.00  11.00  12.00  13.00  14.00  15.00  16.00
  17.00  18.00  19.00  20.00  21.00  22.00  23.00  24.00  25.00  26.00  27.00
  28.00  29.00  30.00  31.00  32.00  33.00  34.00  35.00  36.00  37.00  38.00
  39.00  40.00  41.00  42.00  43.00  44.00  45.00  46.00  47.00  48.00  49.00
  50.00  51.00  52.00  53.00  54.00  55.00  56.00  57.00  58.00  59.00  60.00
  61.00  62.00  63.00  64.00  65.00  66.00  67.00  68.00  69.00  70.00  71.00
  72.00  73.00  74.00  75.00  76.00  77.00  78.00  79.00  80.00  81.00  82.00
  83.00  84.00  85.00  86.00  87.00  88.00  89.00  90.00  91.00  92.00  93.00
  94.00  95.00  96.00  97.00  98.00  99.00 100.00 101.00 102.00 103.00 104.00
 105.00 106.00 107.00 108.00 109.00 110.00 111.00 112.00 113.00

Resulting Turning Points:
    v        E(v)    dE(v)/dv       B(v)          RMIN(v)        RMAX(v)   NDIV  tst(f)   tst(g)    C(exp)       d(RMIN)
**************************************************************************************************************************
 -0.40     25.6031   255.1795   0.4969374800   3.0234371089   3.1972364033   2  1.1D-15  1.1D-15
 -0.20     76.5754   254.5439   0.4958471565   2.9645028124   3.2655732754   2  1.1D-15  1.1D-15
  0.00    127.4208   253.9093   0.4947572489   2.9252415954   3.3142559945   2  5.9D-15  5.9D-15   8.335775
  0.20    178.1392   253.2757   0.4936680686   2.8941027582   3.3548343809   2  3.1D-15  2.8D-15   6.542694
  0.40    228.7311   252.6431   0.4925798647   2.8677257784   3.3906682381   2  6.7D-16  8.9D-16   5.697028
  0.60    279.1965   252.0114   0.4914928338   2.8445729297   3.4232947125   2  4.2D-15  4.0D-15   5.170596
  1.00    379.7488   250.7506   0.4893228659   2.8048359201   3.4820274749   2  5.9D-15  6.0D-15   4.714860
  2.00    628.9293   247.6138   0.4839253904   2.7279074651   3.6067168586   2  5.3D-15  5.0D-15   4.178674
...........................................................................................................
................................. delete 40 intermediate lines of output ..................................
...........................................................................................................
 43.00   8062.0241   102.0111   0.2412555800   2.0485434778   7.1373524453   2  4.0D-15  7.3D-14   2.575810
 44.00   8161.4881    96.9039   0.2324814935   2.0439677236   7.2771485827   2  1.7D-14  2.9D-13   2.616591
 45.00   8255.8092    91.7289   0.2234973505   2.0396767315   7.4254973941   2  1.3D-14  1.2D-13   2.518026
 46.00   8344.9314    86.5106   0.2143347759   2.0356644184   7.5833042914   2  6.7D-16  0.0D+00   2.518026   0.0000048059
 47.00   8428.8260    81.2792   0.2050337064   2.0319241366   7.7515235865   2  3.3D-15  0.0D+00   2.518026   0.0000207800
 48.00   8507.4973    76.0703   0.1956415038   2.0284484460   7.9311393873   2  1.2D-14  0.0D+00   2.518026   0.0000542433
 49.00   8580.9874    70.9239   0.1862115850   2.0252289113   8.1231385570   2  1.1D-16  0.0D+00   2.518026   0.0001093876
 50.00   8649.3802    65.8830   0.1768016272   2.0222559517   8.3284767587   2  4.2D-15  0.0D+00   2.518026   0.0001860396
...........................................................................................................
................................. delete 40 intermediate lines of output ..................................
...........................................................................................................
 91.00   9349.9208     0.5433   0.0043654185   1.9930208941  52.7914063130  16  2.9D-12  0.0D+00   2.518026   0.0024226820
 92.00   9350.4146     0.4468   0.0043678740   1.9930010257  57.0230301833  16  1.9D-13  0.0D+00   2.518026   0.0020612915
 93.00   9350.8188     0.3637   0.0081788543   1.9929847656  61.8154949905  16  1.2D-11  0.0D+00   2.518026   0.0344420865
 94.00   9351.1461     0.2927   0.0211356402   1.9929716000  67.2840583830  16  4.5D-12  0.0D+00   2.518026   0.1662928645
 95.00   9351.4078     0.2325   0.0532459063   1.9929610696  73.5769426792  16  7.9D-12  0.0D+00   2.518026   0.4821751393
 96.00   9351.6143     0.1819   0.1221249565   1.9929527639  80.8871455165  16  9.0D-12  0.0D+00   2.518026   0.9560123018
 97.00   9351.7746     0.1399   0.2573510113   1.9929463169  89.4694647127  16  2.3D-12  0.0D+00   2.518026   1.4016998047
 98.00   9351.8967     0.1055   0.5067819126   1.9929414038  99.6655697000  16  3.2D-11  0.0D+00   2.518026   1.6929583242
 99.00   9351.9879     0.0778   0.9455438757   1.9929377378 111.9418033860  16  8.8D-11  0.0D+00   2.518026   1.8477776097
100.00   9352.0542     0.0558   1.6886134727   1.9929350682 126.9476946642  16  7.5D-12  0.0D+00   2.518026   1.9233260861
101.00   9352.1012     0.0389   2.9081746778   1.9929331783 145.6092456814   8  7.7D-11  0.0D+00   2.518026   1.9593706439
102.00   9352.1334     0.0261   4.8572546941   1.9929318835 169.2827628491  16  7.6D-11  0.0D+00   2.518026   1.9766193774
*** STOP ITERATION:  At  NDIV= 16   tst(f)/(previous)= 2.0D-10/1.3D-10   tst(g)/(previous)= 0.0D+00/0.0D+00
103.00   9352.1546     0.0168   7.9015366608   1.9929310302 200.0186077996  16  2.0D-10  0.0D+00   2.518026   1.9849609294
*** STOP ITERATION:  At  NDIV= 16   tst(f)/(previous)= 5.1D-10/1.3D-10   tst(g)/(previous)= 0.0D+00/0.0D+00
104.00   9352.1680     0.0103  12.5617284597   1.9929304931 241.0345549613  16  5.1D-10  0.0D+00   2.518026   1.9890364583
*** STOP ITERATION:  At  NDIV= 32   tst(f)/(previous)= 7.4D-10/1.9D-10   tst(g)/(previous)= 0.0D+00/0.0D+00
105.00   9352.1759     0.0059  19.5694488444   1.9929301732 297.6128540392  32  7.4D-10  0.0D+00   2.518026   1.9910407175
*** STOP ITERATION:  At  NDIV= 32   tst(f)/(previous)= 1.3D-09/4.5D-10   tst(g)/(previous)= 0.0D+00/0.0D+00
106.00   9352.1803     0.0032  29.9402950271   1.9929299953 378.9163296103  32  1.3D-09  0.0D+00   2.518026   1.9920273470
*** CAUTION: 32 interval incomplete convergence:  tst(f) & tst(g)= 5.0D-10 0.0D+00  while  TOLER= 1.0D-10
107.00   9352.1826     0.0015  45.0685981148   1.9929299044 501.9793549911  32  5.0D-10  0.0D+00   2.518026   1.9925101038
*** STOP ITERATION:  At  NDIV= 16   tst(f)/(previous)= 4.4D-09/3.7D-09   tst(g)/(previous)= 0.0D+00/0.0D+00
108.00   9352.1836     0.0006  66.8493802887   1.9929298629 701.4484332249  16  4.4D-09  0.0D+00   2.518026   1.9927427801
*** STOP ITERATION:  At  NDIV= 16   tst(f)/(previous)= 1.2D-08/3.6D-09   tst(g)/(previous)= 0.0D+00/0.0D+00
109.00   9352.1840     0.0002  97.8342234679   1.99292984661056.9199760441  16  1.2D-08  0.0D+00   2.518026   1.9928518808
*** STOP ITERATION:  At  NDIV= 16   tst(f)/(previous)= 8.5D-08/6.7D-09   tst(g)/(previous)= 0.0D+00/0.0D+00
```

```
110.00   9352.1842     0.0001 141.4291794378   1.99292984141786.3831882618  16  8.5D-08  0.0D+00   2.518026   1.9929007150
*** STOP ITERATION:  At  NDIV= 16   tst(f)/(previous)= 3.9D-07/1.9D-07   tst(g)/(previous)= 0.0D+00/0.0D+00
111.00   9352.1842     0.0000 202.1445232172   1.99292984033679.6494191046  16  3.9D-07  0.0D+00   2.518026   1.9929208980
*** STOP ITERATION:  At  NDIV= 32   tst(f)/(previous)= 2.4D-05/3.0D-06   tst(g)/(previous)= 0.0D+00/0.0D+00
112.00   9352.1842     0.0000 285.9081210720   1.9929298401***************  32  2.4D-05  0.0D+00   2.518026   1.9929280629
*** STOP ITERATION:  At  NDIV= 16   tst(f)/(previous)= 4.8D-02/1.3D-02   tst(g)/(previous)= 0.0D+00/0.0D+00
113.00   9352.1842     0.0000 400.4564901612   1.9929298401***************  16  4.8D-02  0.0D+00   2.518026   1.9929297870
**************************************************************************************************************************

Note that for   v .GE. 45.00  inner wall extrapolated as:   V(R) =    -520.9673 + 0.14922924D+07*exp(-  2.51802625*R)
**************************************************************************************************************************
```

Case (vii): MXS Functions for G_v and for B_v

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(vii) For Li2(A): MXS function for both Gv  &  Bv
***********************************************************
RKR potential for Li(  7)-Li(  7)   with   Charge= 0
Reduced mass   ZMU=  3.50800205000   and constant   C_u/ZMU =  4.805478685510
    from atomic masses:   7.0160041000  &    7.0160041000(u)

Seek relative quadrature convergence 1.0D-10.   Bisect interval up to  5 times.
    performing 16-point Gaussian quadrature in each segment

Represent  Gv's  by Tellinghuisen-type MXS mixed representation:
================================
   9'th order Dunham for  v .le. VS   &   NDE for  v > VS,   with   VS= 55.0000
   with switching function   F_s = 1/[1 + exp{(v-VS)/DVS}]   with   DVS= 1.0000
    and a   sympotote energy (dissociation limit)   DLIM=  9352.1149 [cm-1]

The  9 Dunham  Gv  expansion coefficients are
       2.5549769914D+02 -1.5915289319D+00  4.3200696103D-03 -1.2978004834D-04
       5.1260928027D-06 -3.0435430084D-07  9.1429509688D-09 -1.4968986545D-10
       9.9805171309D-13

NDE for  Gv  is an  (NP= 7/NQ= 0)  OUTER Pade  expansion in  (vD-v)  with
       X0(n=3)= 2.5770000D-08  and leading num. and denom. powers  2  &   2
       vD=  113.2818    D-G(v=-1/2)=   9352.114940
    Numerator coefficients are:  1.910501922487D-03 -3.893923351925D-04
             2.334546248943D-05 -6.987656722521D-07  1.155836220945D-08
            -1.015514433411D-10  3.720613823813D-13

Represent  Bv's  by Tellinghuisen-type MXS mixed representation:
================================
   8'th order Dunham for  v .le. VS   &   NDE for  v > VS,   with   VS= 55.0000

The  9 Dunham  Bv  expansion coefficients are
       4.9749564350D-01 -5.4877585557D-03  2.6482277037D-05 -1.1398662330D-06
       7.1411382626D-08 -4.4457101193D-09  1.4434190231D-10 -2.4979935584D-12
       1.7253834160D-14

NDE for  Bv  is an  (NP= 6/NQ= 0) Exponential  expansion in  (vD-v)  with
       X1(n=3)= 4.2630000D-08  and leading num. and denom. powers  0  &   0
    Numerator coefficients are:  2.114415071744D-01 -2.929745145298D-02
             1.369881187153D-03 -3.136194459560D-05  3.563240597730D-07
            -1.610153741067D-09

Calculate   Y00=  0.072227980    v(cor)= -0.0002826947    v(min)= -0.5002826947
    using    we= 255.4977    wexe= 1.591529    Be=  0.497496    ae= 0.00548776
    and corrected effective   De=  9352.187168 (after adding Y00)

At  v00= -0.50028   Gv=  0.00000000   dG/dv= 255.4986   (1/2)d2G/dv2= -1.591529
                    Bv=  0.49749719   { ==>   Req= 3.107942744(A) }
                    alpha_e = 0.005487759

Above   v =  49.000   extrapolate inner wall with exponential
        fitted to last 3 points ( & shift  RMAX  accordingly)

Calculate turning points at the 119 v-values
  -0.40  -0.20   0.00   0.20   0.40   0.60   1.00   2.00   3.00   4.00   5.00
   6.00   7.00   8.00   9.00  10.00  11.00  12.00  13.00  14.00  15.00  16.00
  17.00  18.00  19.00  20.00  21.00  22.00  23.00  24.00  25.00  26.00  27.00
  28.00  29.00  30.00  31.00  32.00  33.00  34.00  35.00  36.00  37.00  38.00
  39.00  40.00  41.00  42.00  43.00  44.00  45.00  46.00  47.00  48.00  49.00
  50.00  51.00  52.00  53.00  54.00  55.00  56.00  57.00  58.00  59.00  60.00
  61.00  62.00  63.00  64.00  65.00  66.00  67.00  68.00  69.00  70.00  71.00
  72.00  73.00  74.00  75.00  76.00  77.00  78.00  79.00  80.00  81.00  82.00
  83.00  84.00  85.00  86.00  87.00  88.00  89.00  90.00  91.00  92.00  93.00
  94.00  95.00  96.00  97.00  98.00  99.00 100.00 101.00 102.00 103.00 104.00
 105.00 106.00 107.00 108.00 109.00 110.00 111.00 112.00 113.00

Resulting Turning Points:
    v        E(v)    dE(v)/dv       B(v)          RMIN(v)        RMAX(v)   NDIV  tst(f)   tst(g)    C(exp)       d(RMIN)
**************************************************************************************************************************
 -0.40     25.6061    255.1795   0.4969471313   3.0233986323   3.1972079980   2  3.3D-15  2.9D-15
 -0.20     76.5784    254.5439   0.4958516691   2.9644779293   3.2655542160   2  5.8D-15  6.0D-15
  0.00    127.4237    253.9093   0.4947582466   2.9252260088   3.3142449225   2  8.9D-16  6.7D-16   8.337849
  0.20    178.1422    253.2757   0.4936668143   2.8940938619   3.3548293028   2  1.3D-15  1.3D-15   6.543549
  0.40    228.7341    252.6431   0.4925773248   2.8677215946   3.3906674239   2  2.2D-15  1.8D-15   5.696890
  0.60    279.1995    252.0114   0.4914897331   2.8445719144   3.4232967471   2  2.0D-15  1.8D-15   5.169724
  1.00    379.7518    250.7506   0.4893200731   2.8048379029   3.4820320728   2  1.8D-15  1.6D-15   4.713391
  2.00    628.9323    247.6138   0.4839263400   2.7279072064   3.6067186320   2  2.7D-15  2.4D-15   4.176945
..........................................................................................................
................................. delete 40 intermediate lines of output .................................
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 43.00   8062.0271    102.0111   0.2412589816    2.0486529072   7.1374624423    2  1.8D-15  1.1D-15    2.082971
 44.00   8161.4911     96.9039   0.2325109768    2.0440506931   7.2772321162    2  1.3D-14  9.3D-15    2.100804
 45.00   8255.8122     91.7289   0.2235482561    2.0397275717   7.4255487952    2  9.3D-15  6.9D-15    2.121922
 46.00   8344.9344     86.5106   0.2143966102    2.0356792150   7.5833196458    2  1.5D-14  1.2D-14    2.143082
 47.00   8428.8290     81.2792   0.2050918461    2.0319002973   7.7515003022    2  2.9D-14  2.3D-14    2.153211
 48.00   8507.5003     76.0703   0.1956805490    2.0283840142   7.9310755081    2  2.8D-14  1.2D-14    2.124768
 49.00   8580.9904     70.9239   0.1862199849    2.0251215470   8.1230317429    2  7.8D-16  5.0D-14    2.004384
 50.00   8649.3832     65.8830   0.1767764544    2.0221044119   8.3283257668    2  3.6D-14  0.0D+00    2.004384   0.0000026832
...............................................................................................................
.................................. delete 40 intermediate lines of output .....................................
...............................................................................................................
 91.00   9349.9237      0.5433   0.0054828749    1.9922074225  52.7905933683   16  2.2D-13  0.0D+00    2.004384   0.0107413154
 92.00   9350.4176      0.4468   0.0048343858    1.9921869662  57.0222166506   16  5.2D-12  0.0D+00    2.004384   0.0132731106
 93.00   9350.8218      0.3637   0.0042447604    1.9921702247  61.8146809772   16  5.8D-12  0.0D+00    2.004384   0.0161634248
 94.00   9351.1490      0.2927   0.0037078430    1.9921566693  67.2832439790   16  1.1D-12  0.0D+00    2.004384   0.0194191920
 95.00   9351.4108      0.2325   0.0032181566    1.9921458271  73.5761279630   16  9.6D-12  0.0D+00    2.004384   0.0230387198
 96.00   9351.6173      0.1819   0.0027709805    1.9921372754  80.8863305535   16  5.8D-12  0.0D+00    2.004384   0.0270095533
 97.00   9351.7776      0.1399   0.0023624202    1.9921306374  89.4686495599   16  2.3D-11  0.0D+00    2.004384   0.0313061498
 98.00   9351.8997      0.1055   0.0019894625    1.9921255787  99.6647544012   16  3.9D-11  0.0D+00    2.004384   0.0358874912
 99.00   9351.9908      0.0778   0.0016500049    1.9921218042 111.9409879905   16  1.5D-12  0.0D+00    2.004384   0.0406948594
100.00   9352.0572      0.0558   0.0013428443    1.9921190555 126.9468791764   32  4.9D-11  0.0D+00    2.004384   0.0456501251
101.00   9352.1042      0.0389   0.0010676020    1.9921171096 145.6084301443    8  9.3D-11  0.0D+00    2.004384   0.0506550630
*** CAUTION: 32 interval incomplete convergence:  tst(f) & tst(g)= 1.1D-10 0.0D+00  while  TOLER= 1.0D-10
102.00   9352.1364      0.0261   0.0008245605    1.9921157765 169.2819472668   32  1.1D-10  0.0D+00    2.004384   0.0555923788
103.00   9352.1576      0.0168   0.0006143927    1.9921148979 200.0177922226    8  1.3D-11  0.0D+00    2.004384   0.0603292831
*** STOP ITERATION:  At  NDIV=  8   tst(f)/(previous)= 3.8D-10/1.2D-10   tst(g)/(previous)= 0.0D+00/0.0D+00
104.00   9352.1709      0.0103   0.0004377745    1.9921143448 241.0337393271    8  3.8D-10  0.0D+00    2.004384   0.0647244857
*** STOP ITERATION:  At  NDIV= 16   tst(f)/(previous)= 3.3D-10/1.3D-10   tst(g)/(previous)= 0.0D+00/0.0D+00
105.00   9352.1789      0.0059   0.0002949042    1.9921140155 297.6120385123   16  3.3D-10  0.0D+00    2.004384   0.0686393081
106.00   9352.1833      0.0032   0.0001849888    1.9921138323 378.9155144481   32  7.2D-11  0.0D+00    2.004384   0.0719530285
*** STOP ITERATION:  At  NDIV= 16   tst(f)/(previous)= 4.9D-09/2.8D-09   tst(g)/(previous)= 0.0D+00/0.0D+00
107.00   9352.1856      0.0015   0.0001058115    1.9921137387 501.9785405388   16  4.9D-09  0.0D+00    2.004384   0.0745814315
*** STOP ITERATION:  At  NDIV= 32   tst(f)/(previous)= 1.9D-08/2.5D-09   tst(g)/(previous)= 0.0D+00/0.0D+00
108.00   9352.1866      0.0006   0.0000535269    1.9921136960 701.4476102169   32  1.9D-08  0.0D+00    2.004384   0.0764957225
*** STOP ITERATION:  At  NDIV= 16   tst(f)/(previous)= 8.4D-09/7.9D-09   tst(g)/(previous)= 0.0D+00/0.0D+00
109.00   9352.1870      0.0002   0.0000228278    1.99211367921056.9191687147   16  8.4D-09  0.0D+00    2.004384   0.0777366851
*** STOP ITERATION:  At  NDIV= 16   tst(f)/(previous)= 5.8D-08/6.3D-09   tst(g)/(previous)= 0.0D+00/0.0D+00
110.00   9352.1871      0.0001   0.0000075505    1.99211367391786.3821355100   16  5.8D-08  0.0D+00    2.004384   0.0784169107
*** CAUTION: 32 interval incomplete convergence:  tst(f) & tst(g)= 8.9D-08 0.0D+00  while  TOLER= 1.0D-10
111.00   9352.1872      0.0000   0.0000016323    1.99211367273679.6483059296   32  8.9D-08  0.0D+00    2.004384   0.0787037348
*** STOP ITERATION:  At  NDIV= 32   tst(f)/(previous)= 2.5D-05/3.2D-06   tst(g)/(previous)= 0.0D+00/0.0D+00
112.00   9352.1872      0.0000   0.0000001442    1.9921136725***************   32  2.5D-05  0.0D+00    2.004384   0.0787795026
*** STOP ITERATION:  At  NDIV= 16   tst(f)/(previous)= 6.1D-02/1.3D-02   tst(g)/(previous)= 0.0D+00/0.0D+00
113.00   9352.1872      0.0000   0.0000000003    1.9921136725***************   16  6.1D-02  0.0D+00    2.004384   0.0787927230
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Note that for   v .GE. 49.00  inner wall extrapolated as:   V(R) =   -2694.1259 + 0.65309251D+06*exp(-  2.00438369*R)
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