

THE STABILITY OF THE RKR INVERSION PROCEDURE TO ERRORS IN THE SPECTROSCOPIC DATA: ORIGIN OF THE INNER-WALL RIPPLE

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The origin of the non-physical inner-wall behaviour frequently encountered in the RKR inversion procedure is discussed. The RKR procedure is found to be very sensitive to errors in the rotational data, but less demanding on the quality of the vibrational data.

1. Introduction

The RKR inversion procedure [1–3] is well established as a method for obtaining accurate potential energy curves for both intramolecular and intermolecular forces. However, in the course of inverting vibrational and rotational energy data many workers have obtained curious behaviour in the inner wall r_- of the RKR potential [4–7]. When this anomalous behaviour occurs the potential is found to contain a region in which the inner wall “bends over” and r_- increases with the vibration quantum number v . In this region the potential is double-valued and hence is non-physical. At higher values of v the inner wall may then be observed to decrease rapidly. In some work only the first anomaly has been noted, while others have observed both phenomena and the term “inner-wall ripple” has been applied in such cases [7]. We shall first consider the origins of this anomalous inner-wall behaviour, which are shown to lie in inconsistencies in the rotational and vibrational data $G(v)$ and $B(v)$ used in the inversion, and then investigate the effect of errors in the vibrational and rotational data used in the inversion on the ability of the RKR procedure to give a physically well-behaved potential.

2. The origin of the non-physical inner-wall behaviour

The Klein action integrals f and g are defined to be

$$\begin{aligned} f &= r_+ - r_- = \frac{h}{2\mu\pi^2c} \int_{v_{\min}}^v \frac{du}{[G(v) - G(u)]^{1/2}} \\ &= k \int_{v_{\min}}^v \frac{du}{[G(v) - G(u)]^{1/2}}, \\ g &= \frac{1}{r_-} - \frac{1}{r_+} = 2 \left(\frac{8\pi^2\mu c}{h} \right)^{1/2} \int_{v_{\min}}^v \frac{B(u) du}{[G(v) - G(u)]^{1/2}} \\ &= k' \int_{v_{\min}}^v \frac{B(u) du}{[G(v) - G(u)]^{1/2}}, \end{aligned}$$

where r_- and r_+ are respectively the inner and outer classical turning points of the potential at an energy $G(v)$ (when $J=0$) and μ is the reduced mass of the system and the lower limit of integration v_{\min} , is approximated here as $v_{\min} = -\frac{1}{2}$, i.e. $G(v_{\min}) = 0$. The turning points are given by

$$2r_{\pm} = (f^2 + 4f/g)^{1/2} \pm f. \quad (1)$$

Hence from a knowledge of the vibrational and rotational energies, the Klein integrals can be evaluated

and the potential function ($r_-(v), r_+(v)$) constructed.

We wish to find the condition such that the inner wall r_- is a monotonic decreasing function of v . Differentiation of (1) shows that this condition is

$$r'_- = 4/g - (4f/g^2)g'/f' + 2f - 2(f^2 + 4f/g)^{1/2} \leq 0, \quad (2)$$

where the primes indicate differentiation with respect to v .

The Klein integrals cannot in general be expressed as simple analytic functions of $G(v)$ and $B(v)$. However, we may investigate analytically the special case in which the vibrational and rotational energies are parameterized in the following way:

$$G(v) = \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2,$$

$$B(v) = B_e - \alpha_e(v + \frac{1}{2}).$$

We obtain the following results

$$f(v) = \frac{k}{(\omega_e x_e)^{1/2}} \ln \left[\frac{G'(v)}{\omega_e - 2[\omega_e x_e G(v)]^{1/2}} \right]$$

and

$$g(v) = (k'/k)f(v)(B_e - \alpha_e/2x_e) + (k'\alpha_e/\omega_e x_e)G(v)^{1/2}.$$

The condition (2) that the inner wall be a monotonic decreasing function thus becomes

$$(k'\alpha_e/g^2\omega_e x_e)[G(v)^{1/2} - f(v)dG(v)^{1/2}/df(v)] \leq \frac{1}{2}(f^2 + 4f/g)^{1/2} - \frac{1}{2}f = r_- \quad (3)$$

The lhs of this expression can be examined as a function of $(v + \frac{1}{2})$ by means of a Laurent expansion about $v = -\frac{1}{2}$. For the parameterization of $G(v)$ and $B(v)$ above we obtain

$$\frac{2}{3}(\alpha_e/k'B_e^2)[\omega_e(v + \frac{1}{2})]^{1/2}[1 + X_e(v + \frac{1}{2})(\frac{3}{10} - \frac{8}{3}F) + X_e^2(v + \frac{1}{2})^2(\frac{13}{280} - \frac{88}{15}F + \frac{16}{3}F^2) + \dots] \leq r_- \quad (4)$$

where $F = 1 - \alpha_e/2B_e X_e$, and $X_e = \omega_e x_e/\omega_e$.

This is more conveniently expressed in terms of separate power series in X_e and α_e/B_e ,

$$(2/3k')(\alpha_e/B_e^2)[\omega_e(v + \frac{1}{2})]^{1/2} \times \{ [1 - \frac{71}{30}X_e(v + \frac{1}{2}) - \frac{29}{420}X_e^2(v + \frac{1}{2})^2 + \dots] + [\frac{4}{3}(\alpha_e/B_e)(v + \frac{1}{2}) + \frac{4}{3}(\alpha_e^2/B_e^2)(v + \frac{1}{2})^2 + \dots] + \text{cross-terms} \} \leq r_- \quad (5)$$

the cross-terms being of the order $(\alpha_e X_e/B_e)(v + \frac{1}{2})^2$ or higher. This equation can be used to discuss the origin of non-physical behaviour in the inner wall: we first note that the lhs of (5) changes much more rapidly with v than does the rhs, which may thus be considered (to first order) as a constant. The lhs initially increases with v at a rate which increases the larger α_e and ω_e , and the smaller B_e . If α_e/B_e is sufficiently large this increase may eventually cause the inequality to be violated leading to a bending over of the inner wall ($r'_- > 0$). At higher v the anharmonic terms $[X_e(v + \frac{1}{2})]^n$ become important and the lhs passes through a maximum and then decreases. If this decrease is sufficient the inequality (5) may again be satisfied and we obtain $r'_- < 0$ close to the top of the well.

The inner-wall behaviour can be interpreted in terms of $B(v)$ and $G(v)$: the initial bending over of the inner wall is essentially due to too large a value of α_e , i.e. the rotational energies decrease too rapidly. A simple way to interpret this is to associate a rapid decrease in $B(v)$ with a rapid movement of the mid-point of the potential $\frac{1}{2}(r_+ + r_-)$ to larger separations. This essentially "pulls" both r_+ and r_- to larger values of r .

To understand the rapid decrease in r_- at the top of the well, we note that in the region near to dissociation, when v approaches v_{\max} ,

$$\lim_{v \rightarrow v_{\max}} f = \frac{k}{(\omega_e x_e)^{1/2}} \ln \left\{ \frac{2[\omega_e x_e G(v_{\max})]^{1/2}}{G'(v_{\max})} \right\}.$$

Hence the well-width increases very rapidly at the top of the well. If now the $B(v)$ values do not decrease sufficiently rapidly the change in the potential mid-point cannot compensate for the increasing well-width, with the result that r_+ increases rapidly but also r_- decreases rapidly. Clearly the form of $B(v)$ must be very flexible if the inner wall is not to exhibit these instabilities.

3. Relationship between the parameters for physical behaviour

Eq. (4) can be examined further to give expressions showing how the parameters ω_e, X_e, B_e and α_e must be related in order that the potential obtained on RKR inversion shows a physically well-behaved inner wall $r'_- < 0$. We first expand r_- in eq. (4) as a power

series in $(v + \frac{1}{2})^{1/2}$. Substitution into (4) and collecting terms then gives

$$\begin{aligned} & \left(\frac{k}{k'B_c} \right)^{1/2} - (v + \frac{1}{2})^{1/2} \left(\frac{2}{3} \frac{\alpha_e \omega_e^{1/2}}{k'B_c^2} + \frac{k}{\omega_e^{1/2}} \right) \\ & + (v + \frac{1}{2}) \left(\frac{k}{k'B_c} \right)^{1/2} \frac{\alpha_e}{3B_c} \\ & - (v + \frac{1}{2})^{3/2} \frac{\alpha_e \omega_e^{1/2}}{9k'B_c^2} \left(\frac{8\alpha_e}{B_c} - \frac{71X_c}{5} \right) + \dots > 0. \quad (6) \end{aligned}$$

This is the inequality which must be satisfied to ensure a physical solution $r' < 0$.

It is thus clear that in any parameterization of energy-level data, the coefficients in the $(v + \frac{1}{2})$ expansion are not free to vary in an unrestricted manner but must lie within certain limits to ensure the RKR potential obtained on inversion has a physically well-behaved inner wall. Note that for the model considered the value of X_c is not bounded in either the first- or second-order approximations. The non-physical behaviour of the inner wall thus depends much more strongly on the value of α_e than $\omega_e X_c$, i.e. on $B'(v)$ than $G'(v)$.

When we come to consider real systems, the exact variables $G(v)$, $B(v)$, $G'(v)$ and $B'(v)$ must naturally satisfy the above inequalities. However, when analysing experimental data it is possible that errors in measuring these variables, or in fitting them to a functional form, will make the data used in the RKR inversion intrinsically "non-physical" in the sense discussed above. We shall now consider the sensitivity of the RKR inversion to such errors.

4. Stability of the RKR inversion to errors in experimental data

It has been shown above that for certain sets of $G(v)$ and $B(v)$ data the RKR procedure can lead to anomalous behaviour in the inner wall r_- of the potential obtained on inversion and in such cases we may classify the inversion procedure as unstable with respect to this set of data. The stability of the RKR inversion scheme is defined here in terms of the behaviour of the inner wall. The inversion is said to be stable if the potential produced on inversion has a monotonically decreasing inner wall $r'_- < 0$.

To study the effect of errors in the vibrational and rotational energies on the stability of the RKR inversion we chose a model system in which these levels are given by the following equation:

$$\begin{aligned} G(v) &= \sum_{i=1}^5 Y_{i0} (v + \frac{1}{2})^i, \\ B(v) &= \sum_{i=0}^4 Y_{i1} (v + \frac{1}{2})^i, \end{aligned}$$

where $Y_{10} = 125.69708$; $Y_{20} = -7.64244 \times 10^{-1}$; $Y_{30} = -1.77598 \times 10^{-3}$; $Y_{40} = -7.37943 \times 10^{-5}$; $Y_{50} = 1.0306 \times 10^{-6}$; $Y_{01} = 2.90387 \times 10^{-2}$; $Y_{11} = -1.5819 \times 10^{-4}$; $Y_{21} = -3.36318 \times 10^{-7}$; $Y_{31} = -4.77727 \times 10^{-8}$; $Y_{41} = 3.26287 \times 10^{-10}$ and $\mu = 63.5$. Such a parameterization has been proposed by Barrow and Yee for the $B^3\Pi$ state of I_2 [8]. The stability of the RKR inversion to the introduction of both systematic and random errors into this data was investigated.

The effect of random errors in the rotational levels $B(v)$ was first considered. The model rotational data calculated according to the parameterization above was taken and modified by adding a random error to each $B(v)$ point. These random errors were drawn from a gaussian distribution whose standard deviation was chosen to reflect the typical magnitude of errors encountered experimentally by Barrow and Yee when measuring rotational energies [8]. For levels $v = 0$ to $v = 41$ the standard deviation was $2 \times 10^{-6} \text{ cm}^{-1}$ and for levels $v = 42$ to $v = 77$ the standard deviation was $1 \times 10^{-5} \text{ cm}^{-1}$. The model $G(v)$ data was left unmodified. Fig. 1 compares the inner wall r_- of the potential obtained on inversion of the model data with that obtained on inversion of the data modified by random errors. This shows clearly the stability of the RKR inversion to such random errors. To emphasize this point we show in fig. 2 the results for the case where the standard deviations were increased to five times those in fig. 1. Again the inversion shows remarkable stability. This instability is probably due to the structure of the inversion, which involves integration from the bottom of the well to the level of interest, thus implicitly introducing a smoothing procedure into the method.

The effect of random errors in the vibrational data was also studied. The inversion procedure again showed great stability to such errors.

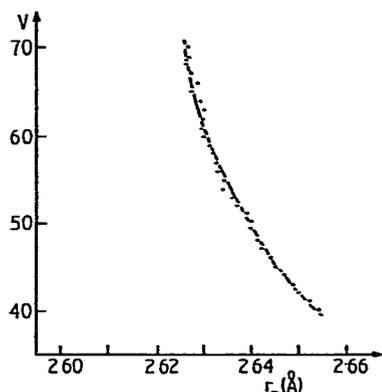


Fig. 1. The sensitivity of the RKR inversion to random errors in $B(v)$. The full line shows the inner wall of the potential obtained from the model data. The points are the values of r_- obtained from the data modified by random errors in $B(v)$. The standard deviation of the error distribution is $2 \times 10^{-6} \text{ cm}^{-1}$ for $v = 0$ to $v = 41$ and $1 \times 10^{-5} \text{ cm}^{-1}$ for $v = 42$ to $v = 77$.

The stability of the inversion to systematic errors in both the rotational and vibrational levels was then investigated. This was done by taking the model data characterized by the parameterization above and modifying these systematically by changing the values of ω_e and α_e . For such a system we might expect the

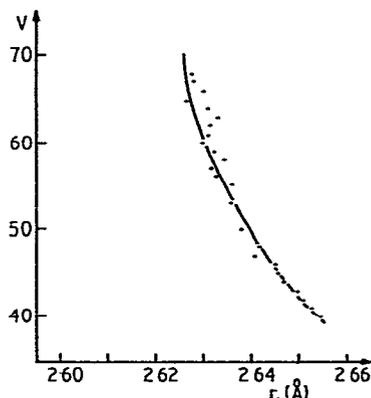


Fig. 2. The sensitivity of the RKR inversion to random errors in $B(v)$. The full line shows the inner wall of the potential obtained from the model data. The points are the values of r_- obtained from the data modified by random errors in $B(v)$. The standard deviation of the error distribution is $1 \times 10^{-5} \text{ cm}^{-1}$ for $v = 0$ to $v = 41$ and $5 \times 10^{-5} \text{ cm}^{-1}$ for $v = 42$ to $v = 77$.

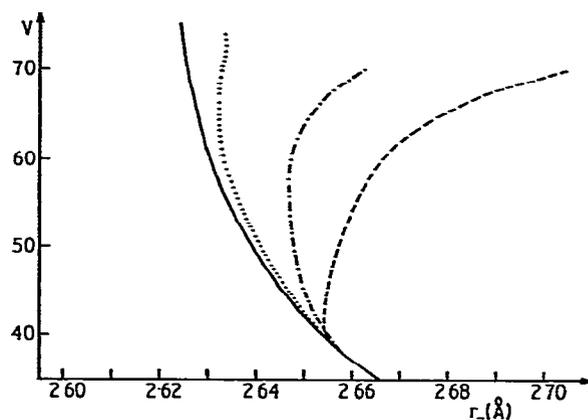


Fig. 3. The sensitivity of the RKR inversion to systematic error in $B(v)$. The full line shows the inner wall of the potential obtained from the model data with the α_e value given in the paper. The other plots refer to the inversion of data obtained using a value α'_e , where $\alpha'_e = \alpha_e - \text{error}$. (···) error = 10^{-6} cm^{-1} ; (- - -) error = $5 \times 10^{-6} \text{ cm}^{-1}$; (- - -) error = $1 \times 10^{-5} \text{ cm}^{-1}$.

following uncertainties in ω_e and α_e when parameterizing experimental results [8]:

$$\delta\omega_e \approx 4 \times 10^{-2} \text{ cm}^{-1}, \quad \delta\alpha_e \approx 2 \times 10^{-5} \text{ cm}^{-1}.$$

The model data was thus modified systematically by changing ω_e and α_e by amounts in accord with these "experimental" uncertainties. The results are shown in figs. 3 and 4 which compare the inner wall r_- of the

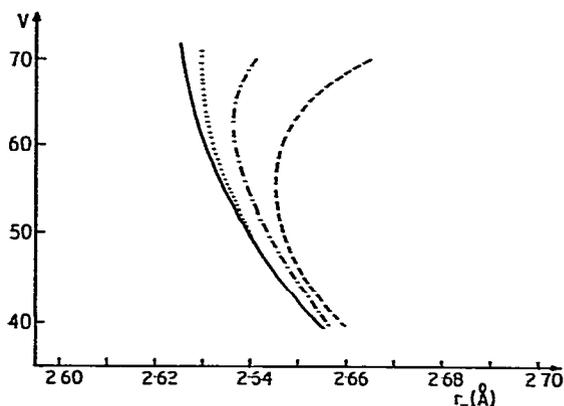


Fig. 4. The sensitivity of the RKR inversion to systematic error in $G(v)$. The full line shows the inner wall of the potential obtained from the model data with the ω_e value given in the paper. The other plots refer to the inversion of data using a value ω'_e , where $\omega'_e = \omega_e + \text{error}$. (···) error = 0.1 cm^{-1} ; (- - -) error = 0.5 cm^{-1} ; (- - -) error = 1.0 cm^{-1} .

potential obtained on inversion of the model data with those obtained on inversion of the data modified by systematic errors. The graphs clearly show that with respect to systematic error in the rotational energy, an error within the "experimental" limit is sufficient to cause substantial non-physical behaviour in the potential obtained on inversion. With respect to systematic error in the vibrational energy, an error of an order of magnitude greater than that typically encountered experimentally is required before non-physical behaviour is observed. The RKR inversion procedure is thus highly sensitive to systematic error in the determination of rotational energies, but sensitivity to systematic error in the vibrational energy is less pronounced.

It is possible to quantify the effect δr_- on the inner wall due to small errors δG and δB in the vibrational and rotational energies: such errors will cause the Klein integrals to change thus

$$\delta f = (f'/G')\delta G, \quad \delta g = (g'/G')\delta G + (g'/B')\delta B.$$

The primes again indicating differentiation with respect to v . To first order in δ , the change in the value of the inner wall is then

$$\delta r_- = C_G \delta G + C_B \delta B,$$

where

$$C_G = -f'/2G', \quad C_B \approx -(f^2 + 4f/g)^{1/2} (f/g^2)g'/B'.$$

The coefficients C_G and C_B are rapidly varying functions of v , but we may give as orders of magnitude for our model system

$$\delta r_- (\text{\AA}) \approx -10^{-4} \delta G (\text{cm}^{-1}) + 10^2 \delta B (\text{cm}^{-1}).$$

This equation can be used to describe the effect on the inner wall when $\delta(G, B)$ refers to either random or systematic error in the vibrational-rotation data: For the case of random errors, if we consider errors in the rotational levels only then, for the inner wall to be smooth to within 10^{-3} \AA, we require $B(v)$ values to be accurate to within 10^{-5} cm^{-1} . Alternatively, considering only random $G(v)$ error, δG would have to be accurate to within 10 cm^{-1} to ensure the inner wall was smooth to within 10^{-3} \AA. This again shows the greater sensitivity of the inner-wall behaviour to errors in the rotational levels.

To discuss the effect of systematic error in $G(v)$ and $B(v)$ on the behaviour of the inner wall, we

consider the following systematic errors due to incorrect parameterization of the vibration-rotation data:

$$\delta G = (v + \frac{1}{2})\delta\omega_e, \quad \delta B = -(v + \frac{1}{2})\delta\alpha_e.$$

Substitution into (6) then gives

$$\delta r_- \approx 10^{-4}(v + \frac{1}{2})\delta\omega_e - (v + \frac{1}{2})10^2\delta\alpha_e,$$

lending quantitative support to the observations above that a systematic error in $B(v)$ caused by a small error in the parameterization of the rotational levels can lead to many large changes in the behaviour of the inner wall, while errors in the parameterization of $G(v)$ due to an error in ω_e are less strongly manifested in inner-wall behaviour.

The great sensitivity of the inner wall of the potential to small systematic changes in the vibration-rotation levels shows that the RKR procedure requires data of extremely high accuracy if the inner wall is to be determined with confidence. When data of sufficient accuracy has not been available, or when the data has been incomplete, interpolation or extrapolation has often been used to predict the energy levels [6,7]. Non-physical behaviour $r'_- > 0$ may then be observed, and it has often been the practice to smooth the non-physical, or uncertainly determined region using a Morse curve or some similar potential [7]. Such procedures have recently been investigated in some depth by Tellinghuisen and Henderson [9].

5. Conclusions

It is the structure of the RKR inversion, involving the simultaneous solution of equations involving $(r_+ - r_-)$ and $(1/r_- - 1/r_+)$ which makes the procedure rather unstable to small, systematic errors in the experimental data. These instabilities are due to inconsistencies in the behaviour of the vibrational and rotational energy levels and are made manifest by a non-physical behaviour $r'_- > 0$ in the inner wall. The RKR procedure is thus highly demanding of the quality of the $B(v)$ data if the inner wall is to be determined accurately, but less sensitive to the quality of $G(v)$ data. This implies that the energy levels calculated from a potential are relatively insensitive to the details of the inner wall. It is thus possible, when non-physical behaviour is observed, to modify the inner-wall by a Morse curve or similar empirical form and still obtain

a potential which is essentially consistent with the experimental data.

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