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A Numerical Simplification and Alternative to the RKR Method for Diatomic Molecules

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A new transformation of the Klein integrands is introduced so as to avoid the unnecessary inconvenience of having the integration variable different from that provided by experiment. As an alternative to the Rydberg-Klein-Rees equations, the simplification of Singh and Jain is extended to eliminate all reference to rotation and Klein's troublesome g function: not only do numerical integrations disappear, but WKB results are reduced to their bare essentials. Application of this extension to the fourteenth vibrational level of normal molecular hydrogen, which energy corresponds to 98 % of the way toward dissociation, reveals an error of only 0.41 % in the maximum turning point.

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INTRODUCTION

The Rydberg-Klein-Rees technique,[1-3] hereafter called RKR, is a method for constructing diatomic potential energy curves directly from spectroscopic

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data without the prior assumption of an analytic force law. Renewed interest in the procedure occurred about 1959 when Vanderslice, et al,[4] applied the equations to hydrogen for the ultimate purpose of calculating atom-atom collision cross sections and high-temperature gas transport coefficients; other computations followed immediately and have been summarized by Zeleznik.[5]

Perhaps the most distinguishing feature of much of this work, especially the earlier papers, is the persistent adherence to Rees' integral evaluations for energy levels containing no higher than second-order vibrational contributions. Molecular states for which the experimental data could not be represented over the entire range by a single quadratic were, instead, piecewise fitted over smaller intervals and correspondingly integrated. This procedure, being open to question even at the lower levels, could yield quite substantial errors near the dissociation limit. The only other strictly analytic approach of note is Jarmain's series development,[6] wherein the set of vibrational levels is expressed in the form of an unrestricted polynomial and Dunham's potential[7] is inverted for the classical turning points.

After a brief discussion of the validity of WKB and RKR methods, the remaining purposes of this paper are three-fold as follows: to remove singularities from Klein integrands, to develop a substitute formulation in which such integrals disappear from the working equations, and to compare results with more rigorous calculations in the case of ground-state molecular hydrogen near its dissociation limit.

KLEIN-DUNHAM POTENTIALS

Nearly all semi-empirical schemes for computing diatomic force laws originate from the slightly modified Bohr-Sommerfeld (first-order WKB) quantum condition

$$\oint p\,d\xi = h(v+\tfrac{1}{2})r_e^{-1}; \quad \xi = r_e^{-1}\,(r-r_e), \tag{1}$$

where r_e is the equilibrium separation between nuclei and v is the vibrational quantum number. It is possible to solve this equation either directly for the classical turning points of an arbitrarily chosen vibrational energy, as did Rydberg and Klein, or by assuming various series expansions for the potential and its first derivative with respect to ξ. Using

$$V = a_0\xi^2\,(1+a_1\,\xi+a_2\,\xi^2+\dots), \tag{2}$$

$$V' = \pm A_1\,V^{1/2} + A_2\,V \pm A_3\,V^{3/2} + \dots, \text{ and} \tag{3}$$

$$(V')^{-1} = A_1^{-1}\,V^{-1/2}\,(\pm 1 + B_1 V^{1/2} \pm B_2\,V + \dots), \tag{4}$$

Dunham[8] evaluated the phase integral and obtained

$$G_v\left[1 + \sum_{n=1}^{\infty} \frac{1\cdot3\cdot5\cdots(2n-1)}{(2\cdot4\cdot6\cdots2n)(n+1)}\,B_{2n}G_v^{\,n}\right] = \frac{A_1 h(v+\frac{1}{2})}{2\pi(2\mu)^{1/2}r_e} \tag{5}$$

for the energy level G_v.

Since both the RKR and Dunham expressions derive from the WKB approximation, and since that approximation regards h as an expansion parameter, neither theory is *a priori* valid to first order except for high vibrational quantum numbers and correspondingly large displacements from equilibrium of the classical turning points. It thus follows that since the comparatively limited supply of such high energy levels may provide but a small fraction of the number of coefficients in Eq. (2) needed to precisely describe the true potential at that height, the resulting truncated series may fit very poorly in ~~other~~ certain domains of ξ. The danger would be especially great near the potential minimum, because the omission of low energies in Eq. (5) discriminates against that location.

Despite the common origin of Klein (RKR) and Dunham potentials, several misconceptions have developed since the original work: It is often stated,[9] for example, that the semiclassical foundations of the RKR method render it untenable at low v, whereas Dunham's first approximation is accurate near potential minima. Perhaps the difficulty arises from looking too closely at the form of Eq. (2) without recognizing the role played by WKB theory in determining the coefficients as functions of spectroscopic constants. In any event, the distinction is somewhat academic for many molecular states because corrections to (1) of order $\hbar^2$ and higher are completely negligible; hence no consideration of the classical limit is necessary and all restrictions on v may be removed. Accordingly, both the Klein and Dunham potentials will suffice over the entire range in certain cases - but to the extent that either fails near the minimum, so also must the other.

A CONVENIENT TRANSFORMATION

The RKR equations for a nonrotating molecule are listed as follows:

$$r_{max,min} = (f^2 + g^{-1} f)^{1/2} \pm f, \tag{6}$$

$$f = \left(\frac{h}{8\pi^2 \mu c}\right)^{1/2} \int_{-1/2}^{v} (G_v - G_{v'})^{-1/2}\, dv', \quad \text{and} \tag{7}$$

$$g = \left(\frac{8\pi^2 \mu c}{h}\right)^{1/2} \int_{-1/2}^{v} B_{v'}\, (G_v - G_{v'})^{-1/2}\, dv', \tag{8}$$

where G_v and $B_v\, J(J+1)$ are the pure vibrational and first-order rotational energies, respectively, each measured in inverse centimeters, and h is Planck's constant in erg-seconds. Other parameters include the reduced mass μ, the speed of light c, and the vibrational quantum number v corresponding to that energy G_v for which the classical turning points r_{max} and r_{min} are required.

With the assumption now that G_v is an analytic function of v, the integrand of Eq. (7) may be written

$$(G_v - G_{v'})^{-1/2} = (G'_v)^{-1/2}\, (v-v')^{-1/2} \left[\sum_{k=1} \frac{(-1)^{k-1} G_v^{(k)}}{k!\; G'_v} (v-v')^{k-1}\right]^{-1/2}, \tag{9}$$

where the primes and superscripts on G_v all refer to differentiations of various orders with respect to v. Suggested immediately by (9) is the simple transformation from v' to $x = (v-v')^{1/2}$, according to which Klein's f and g functions become

$$f = \left(\frac{h}{2\pi^2 \mu c G'_v}\right)^{1/2} \int_{0}^{(v+\frac{1}{2})^{1/2}} \left[\sum_{k=1} \frac{(-1)^{k-1} G_v^{(k)}}{k!\; G'_v}\, x^{2(k-1)}\right]^{-1/2} dx \tag{10}$$

and

$$g = \left(\frac{32\pi^2 \mu c}{hG_v'}\right)^{1/2} \int_0^{(v+1/2)^{1/2}} B(v,x) \left[\sum_{k=1} \frac{(-1)^{k-1} G_v^{(k)}}{k!\,G_v'} x^{2(k-1)}\right]^{-1/2} dx \qquad (11)$$

with

$$B(v,x) = B_e - \alpha_e(v-x^2+\tfrac{1}{2}) + \gamma_e(v-x^2+\tfrac{1}{2})^2 + \text{-----}. \qquad (12)$$

Several advantages of ~~equations~~ Eq. (10) and (11) over (7) and (8) are obvious: No longer do integrand singularities exist, only the properties of the G_v curve at the chosen level are required, and x is a convenient variable of integration. This last advantage becomes evident when comparison is made with Weissman's substitution[10] of x for $(G_v - G_{v'})^{1/2}$ to obtain

$$\int_{-1/2}^{v} (G_v - G_{v'})^{-1/2}\, dv' = 2\int_0^{(G_v-G_{-1/2})^{1/2}} \left(\frac{dG_{v'}}{dv'}\right)^{-1} dx. \qquad (13)$$

Numerical evaluation of (13) introduces an unnecessary inconvenience: Since the integrand is available in v' rather than x, only increments of the former may be selected arbitrarily and those of the latter then calculated from $\Delta x = (G_v - G_{v'+\Delta v'})^{1/2} - (G_v - G_{v'})^{1/2}$.

It is further noted that the upper limits to the summations in Eqs. (9)-(11) ~~(10, (11)~~ are, at most, the degree of the highest polynomial with which the spectroscopic data on G_v can be fitted, i.e., the number of observed vibrational levels. In addition, because of the relative unimportance of higher derivatives as compared with the first, such polynomials ordinarily may be considerably truncated by least squares methods and no significant error is expected from the appearance of successive slopes of experimental measurements.

Zeleznik[11] has recently developed a new method for evaluating the Klein integrals that ~~also~~ essentially retains the original integration variable. He removed the singularities with an integration by parts and expressed the remaining integrands in terms of polynomial expansions containing derivatives with respect to v'. No particular gain is apparent, however, over Eqs. (10) and (11) in which such derivatives at all points below the chosen v are specifically eliminated. Other, more approximate procedures involving analytic curve fitting only near the upper limits of Eqs. (7) and (8) with numerical integrations over the rest have been applied by several investigators,[12-14] as has the technique of Gaussian integration[15] near the singularities.

THE MORSE POTENTIAL

As a preliminary to our alternative to the RKR method, it is convenient to point out the simplifications inherent in the Morse potential[16]

$$V = D\left\{1 - \exp\left[-a(r-r_e)\right]\right\}^2, \tag{14}$$

the differentiation of which yields

$$A_1 = 2ar_eD^{1/2};\ B_{2n} = D^{-n} \tag{15}$$

for substitution into Dunham's expression (5). Since

$$\sum_{n=1}^{\infty} \frac{1\cdot 3\cdot 5\cdots(2n-1)}{(2\cdot 4\cdot 6\cdots 2n)(n+1)}\, x^{n} = \frac{2}{x}\left[1 - (1-x)^{1/2}\right] - 1, \tag{16}$$

the solution of Eqn. (5) may be written in closed form as follows:

$$\begin{aligned} G_v &= \omega(v+\tfrac{1}{2}) - \omega x(v+\tfrac{1}{2})^2 \\ &= \left(\frac{ha^2D}{2\pi^2\mu c}\right)^{1/2}(v+\tfrac{1}{2}) - \left(\frac{ha^2}{8\pi^2\mu c}\right)(v+\tfrac{1}{2})^2; \end{aligned} \tag{17}$$

accordingly,

$$a = \left(\frac{8\pi^2\mu c\omega x}{h}\right)^{1/2}; \quad D = \frac{\omega^2}{4\omega x}. \tag{18}$$

Davidson and ~~Pines~~ Price[17] apparently were the first to recognize that rigorous Morse energy levels are identical (apart from half-integral quantum numbers) with those predicted by the Bohr-Sommerfeld quantum condition, a fact which also follows from the vanishing of first and higher corrections to (5). In spite of the support it grants to Dunham and RKR methods, this agreement seems to have been overlooked in the more recent literature.

Verification of the above statement in the case of Klein's f function proceeds just as smoothly. Substitution of the energy (17) into Eq.(10) yields

$$f = \left(\frac{h}{32\pi^2\mu c\omega x}\right)^{1/2} \ln\left[\frac{\omega + 2(\omega x G_v)^{1/2}}{\omega - 2(\omega x G_v)^{1/2}}\right], \tag{19}$$

which result concurs with the direct solution of (14) for the separate turning points

$$r_{max,min} = r_e - \left(\frac{h}{8\pi^2 \mu c \omega x}\right)^{1/2} \ln\left[\frac{\omega \mp 2(\omega x G_v)^{1/2}}{\omega}\right]. \qquad (20)$$

Corresponding agreement does not prevail, on the other hand, between the f functions of a rotating Morse molecule.

It is thus anticipated that a full-scale RKR treatment (f and g both) will not be so successful as (19) and (20) because of the somewhat artificial concept of rotation introduced through Eq. (11); more precisely, since the WKB energy condition (1) can reveal at most the difference~~s~~ between classical turning points at a specified level, Klein's g function must be regarded as a clever artifice for extending the theory and providing additional (but less reliable) information. Failure of Eqs. (10) and (11) to attain complete accuracy for r_{max} and r_{min} individually for a Morse potential cannot, therefore, be attributed to any failure *per se* of the WKB method. One of our goals, then, is to eliminate as nonessential all reference to rotation in analyses of nonrotating diatomic molecules.

AN ALTERNATE FORMULATION

As a substitute for the above introduction of rotational parameters, we now propose a compromise between the RKR ideal of no predetermined analytic potential and those formulations that do so begin. Since most analytic potentials, the Morse included despite its obvious deficiencies at small separations, are quite adequate over considerable portions of their inner or repulsive legs, it seems reasonable to apply such a function to those regions only and subsequently combine with the RKR formula (10) for determination of the attractive part. Good repulsive branches also are available in many instances from the reduction of high energy scattering data.

Our second simplification is related, though rather loosely because of their retention of the g function, to an approximate technique devised by Singh and Jain.[18] A critical analysis of that method is therefore desirable and we start with the diagram

$$\begin{tikzcd}
V\left[r_{max,min}(v)\right] \arrow[rr, "(1)"] & & f_v(V) \\
G_v^a \arrow[u, dashed, "(3)"] \arrow[d, "(4)"] \arrow[rr, "(2)"] & & f_v^a\,(\mathrm{RKR}) \arrow[d, dash, dotted, "(6)"] \\
V_m \arrow[rr, "(5)"] & & f_v^m\,(V_m)
\end{tikzcd} ,$$

where the subscripts and superscripts a and m refer to analytic and Morse, respectively.

The various paths are explained as follows:

Path (1): The only argument stated explicitly by Singh and Jain reduces to the fact that a good description of V, though perhaps only within a very narrow Δv about the chosen quantum number, trivially guarantees good f values in that range.

Path (2): Their actual procedure, on the other hand, is to start with good vibrational energies, as depicted by some analytic G_v^a within the same v limits, and then apply Klein's f integral to compute f_v^a (RKR).

Path (3): Unless, of course, values of G_v that are guaranteed acceptable only within Δv automatically ensure correspondingly acceptable $V[r_{max,min}(v)]$, the argument for path (1) is entirely irrelevant and additional proof for path (2) is required. No such evidence is discussed.

Path (2) continued: It is desirable, therefore, to establish a convincing reason for direct coupling between accurate energy levels and reliable f (RKR) values, all within some specified Δv range. One such argument, though very crude and in apparent conflict with the indication from Eq. (7) that lower levels cannot be ignored, develops from the fact that a substantial portion of Klein's f integral is contributed by levels fairly close to the chosen energy. Accordingly, that neighborhood is by far the best narrow region in which to require a good description of G_v. Since Morse energies are seldom very poor, even for a single application over the entire range of v, and since the greatest errors accompanying a fit of Eq. (17) to Δv nearly always arise where they count the least, we may hopefully assert a reasonable accuracy for the corresponding evaluation of f at any level.

Path (4): If the intention of Singh and Jain is to simplify the more rigorous calculation, path (2) cannot be applied conveniently to a least squares fit of G_v with a polynomial higher than second degree. Path (4) merely associates this quadratic with the Morse potential $(s = m)$ that best defines it according to Eqs. (14), (17), and (18), whereas the equilibrium separation r_e is provided from

$$r_e = \left(\frac{h}{8\pi^2 \mu c B_e}\right)^{1/2} . \tag{21}$$

Path (5): The equation $V_m(r_{max,min}) = G_v^m$ is solved directly to yield, as in the case of (20) above, the quantity $f_v^m\,(V_m)$. Since the latter specifies two of the three Morse parameters, only r_e is required to reverse this path back toward V_m.

Path (6): Because of the property of first-order WKB theory to reproduce exactly a Morse potential, it is clear that $f_v^m\,(\mathrm{RKR}) \equiv f_v^m\,(V_m)$; consequently, there is no advantage to solving Klein's f integral with G_v^m.

What Singh and Jain evidently fail to recognize is that quadratic energy levels are synonomous with a Morse potential. Their sequence of path (2) plus the introduction of Klein's g function is identical, exclusive of additional approximations related to rotation, with the much simpler and far more direct route of path (4). As an almost equivalent replacement for the Singh and Jain formulation, we therefore adopt the following expressions:

$$r_{min} = r_e - \left(\frac{h}{8\pi^2 \mu c \omega x}\right)^{1/2} \ln \frac{\omega + 2(\omega x G_v^m)^{1/2}}{\omega} , \tag{22}$$

$$f = \frac{1}{2}\,(r_{max}-r_{min}) = \left(\frac{h}{32\pi^2\mu c\omega x}\right)^{1/2} \ln \left[\frac{\omega+2(\omega x G_v^m)^{1/2}}{\omega-2(\omega x G_v^m)^{1/2}}\right], \tag{23}$$

and

$$G_v^m = \omega(v+\tfrac{1}{2}) - \omega x(v+\tfrac{1}{2})^2 , \tag{24}$$

where ω and ωx are determined from a least squares fit of the four observed vibrational levels closest to the one chosen. One need not, of course, ~~both~~ bother with f at all, but it is a convenient quantity for comparison with rigorous RKR calculations.

CALCULATIONS ON $H_2(X^1\Sigma_g^+)$

Ground-state hydrogen is especially suited for a check of the above method for three reasons: In the first place, Morse's potential is known to be a poorer fit for this than for most diatomic molecules; secondly, reliable data is available up to the dissociation limit; thirdly, Weissman, et al,[10] have provided good RKR turning points. In order to make the test even more stringent, we further single out the fourteenth vibration level ($v = 13$), which energy is roughly 98% of that of dissociation and therefore lies in the region least adaptable to an overall analytic curve-fit and most subject to the errors discussed in the preceding section.

Morse potentials were employed in several different ways in the present calculation. The third and fifth columns of Table I were obtained from known values of D and G_o, each potential extending over the entire range of v but with the applications differing according to whether G^m_{13} or G^s_{13} (spectroscopic data) was used in Eqs. (19) and (20), and the spectroscopic constants were computed from

$$\omega = 4D\left[1-(1-D^{-1}G_o)^{1/2}\right]; \quad \omega x = 4D\left[1-(1-D^{-1}G_o)^{1/2}\right]^2. \qquad (25)$$

Column four also represents a single potential over the entire range, only this time with the spectroscopic constants determined from a least squares fit of all 15 observed levels. Again G^m_{13} was used and D was deduced from Eq. (18).

As expected, the best results are associated with the last column, where the procedure was identical with the fourth except for the use only of the top four energies in the least squares determination of ω and ωx. Though they differ slightly (within 1%) from those of Tobias and Vanderslice,[19] Weissman's calculations were regarded as exact in all cases. It is interesting to note that despite the fact that a better potential would have yielded a smaller error in r_{min}, that discrepancy is in the right direction to actually increase the reliability of r_{max} from Eq. (23); the same would have been accomplished automatically, however, from the r_{max} form of (20) in conjunction with the same G^m_{13} and independently of r_{min}.

SUMMARY

Two new methods, one of which involves a transformation that simultaneously removes the upper-limit singularities of Klein integrands and establishes a single integration variable throughout, have been introduced for finding diatomic potentials more or less directly from spectroscopic data. The other is an alternate procedure that effectively replaces the RKR integrals, while at the same time deriving a sort of semi-rigorous support from that formulation. Numerical calculations on normal hydrogen revealed a discrepancy of less than 0.5 % for the attractive branch of the potential; accordingly, the alternate technique, together with Heitler-London type approximations at large separations,[20] should provide an adequate representation for many collision problems - including those concerned with transport and other nonequilibrium phenomena in dilute gases. Because of the ease of calculation without electronic computers, the alternate treatment might aptly be termed a "poor man's RKR."

Table I. Classical turning points for H_2 ($X^1\Sigma_g^+$; G_{13} = 0.98D).

Quantity	Best RKR[a]	Eqs. (19), (20), and (25)	Eqs. (22) - (24), least squares (v = 0-14)	Eqs. (19), (20), and (25), using C_{13}^s	Eqs. (22) - (24), least squares (v = 11-14)
D, cm^{-1}	38,274[b,c]	38,274	40,625	38,274	38,895
f, Å	1.131	1.116	1.051	1.358	1.139
% error	0	-1.33	-7.07	20.1	0.71
r_{min}, Å[c]	0.413	0.393	0.386	0.389	0.408
% error	0	-4.84	-6.54	-5.81	-1.21
r_{max}, Å	2.675	2.625	2.488	3.104	2.686
% error	0	-1.87	-6.09	16.0	0.41

[a] Weissman, et al, reference 10.

[b] D_e^o, where $D = D_e^o + G_o$, was taken from G. Herzberg, Spectra of Diatomic Molecules (D. Van Nostrand, Inc., Princeton, New Jersey, 1950), 2nd ed., p. 530.

[c] G_o and r_e from G. Herzberg and L. L. Howe, Can.J. Phys. 37,636 (1959).

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