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Original Publication Citation

Pack, Russell T. "On Improved WKB (Uniform Asymptotic) Quantum Conditions, Dunham Corrections, the Langer Modification, and RKR Potentials." *The Journal of Chemical Physics* 57 (1972): 4612-4616.

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³³ The correlation function for \mathfrak{D} can be expressed as the sum of three exponentials whose exponents correspond to the three eigenvalues of Eq. (44). At least one of the exponentials has a negative coefficient.

³⁴ In the non-Lorentzian areas of region I, the m^4 and m^6 terms in Eq. (46) become important.

³⁵ The correlation function for \mathfrak{D} can be expressed as the sum of three exponentials, one with a negative exponent with char-

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THE JOURNAL OF CHEMICAL PHYSICS VOLUME 57, NUMBER 11 1 DECEMBER 1972

On Improved WKB (Uniform Asymptotic) Quantum Conditions, Dunham Corrections, the Langer Modification, and RKR Potentials*

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(Received 25 July 1972)

An improvement to the WKB quantum condition for the rotation-vibration levels of diatomic molecules, known empirically to give RKR potentials of increased accuracy and to account for the Dunham correction Y_{00} , is derived using uniform asymptotic methods. The role of the Langer transformation in this problem is also discussed.

I. INTRODUCTION

For the vibrational motion of a diatomic molecule in a Born-Oppenheimer potential well (Fig. 1), the ordinary first-order WKB quantum condition¹ is

$$\phi = \hbar^{-1} \int_{r_1}^{r_2} p(r) dr = (v + \frac{1}{2})\pi, \quad (1)$$

where r_1 and r_2 are, respectively, the smaller and larger classical turning points defined by $p(r_i) = 0$; $p(r)$ is given by

$$p(r) = \{(2\mu)[E(v, J) - V_J(r)]\}^{1/2}; \quad (2)$$

and the effective potential $V_J(r)$ is the intermolecular potential plus the centrifugal potential,

$$V_J(r) = V_0(r) + \hbar^2 J(J+1)/2\mu r^2. \quad (3)$$

Equation (1) says that v is an integer (0, 1, 2, ...) iff $E(v, J)$ is an eigenvalue of the associated Schrödinger equation. Inversion of this quantum condition yields the usual Rydberg-Klein-Rees (RKR) equations²

$$f = \frac{1}{2}(r_2 - r_1) = \left(\frac{\hbar^2}{2\mu}\right)^{1/2} \int_{-1/2}^v [E(v, J) - E(v', J)]^{-1/2} dv' \quad (4)$$

and

$$g = \frac{1}{2}(r_1^{-1} - r_2^{-1}) = \left(\frac{2\mu}{\hbar^2}\right)^{1/2} \int_{-1/2}^v B(v', J) \times [E(v, J) - E(v', J)]^{-1/2} dv'. \quad (5)$$

Thus, treating the experimental energy levels and rotational constant $B(v', J)$ as continuous functions of v' , one obtains the turning points and an experimental effective potential.

If f and g are evaluated accurately, the resulting potential V_J and the experimental energy levels satisfy Eq. (1) exactly. However, if that V_J is used in the radial Schrödinger equation

$$\left(\frac{-\hbar^2}{2\mu} \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + V_J(r) - E\right)R(r) = 0, \quad (6)$$

and this equation is solved exactly numerically, the resulting eigenvalues will *not* in general be exactly equal to the experimental energy levels. Dunham³ showed by a second-order WKB method (it can also be shown from quantum-mechanical perturbation theory⁴) that there are corrections to Eq. (1). The dominant correction arises because Eq. (1) implies that, at $v = -\frac{1}{2}$, $\phi = 0$; i.e., that $E(-\frac{1}{2}, 0) = -D_e$, whereas Dunham³

showed that for low energies (measured in cm^{-1} from the dissociation limit),

$$E(v, J) = -D_e + \sum_{i,j=0} Y_{ij}(v+\frac{1}{2})^i [J(J+1)]^j \quad (7)$$

$$\approx -D_e + Y_{00} + \omega_e(v+\frac{1}{2}) - \omega_e x_e(v+\frac{1}{2})^2 + \dots$$

$$+ B_e J(J+1) - \alpha_e(v+\frac{1}{2})J(J+1) + \dots, \quad (8)$$

where Y_{00} , given in terms of the other spectroscopic constants by

$$Y_{00} \approx \frac{1}{2} B_e + (\alpha_e \omega_e / 12 B_e) + [(\alpha_e \omega_e)^2 / 144 B_e^3] - \frac{1}{4} (\omega_e x_e), \quad (9)$$

is *not* zero in general. Hence, one has

$$E(-\frac{1}{2}, 0) = -D_e + Y_{00} \neq -D_e. \quad (10)$$

To obtain RKR potentials which account properly for the Dunham correction Y_{00} , one can go to a second-order RKR procedure,⁵ but that is more complicated and usually involves iterative calculations. A much simpler semiempirical approach has been taken by Kaiser⁶ and by Mantz *et al.*,⁷ who replaced Eq. (1) by the modified quantum condition

$$\phi = (v + \frac{1}{2} + \delta)\pi, \quad (11)$$

where δ was chosen so that, when $J=0$ and $v = -(\frac{1}{2} + \delta)$, $E = -D_e$. From Eq. (8) this gives

$$\delta \approx Y_{00} / \omega_e, \quad (12)$$

or to a better (but usually unnecessary) approximation,

$$\delta = [-\omega_e + (\omega_e^2 + 4\omega_e x_e Y_{00})^{1/2}] / (2\omega_e x_e). \quad (13)$$

Beginning from (11) and going through the derivation of the RKR equations, one gets exactly Eqs. (4) and (5) except that the lower limits of integration are replaced by $-(\frac{1}{2} + \delta)$. These modified RKR equations were applied^{6,7} to ground state HCl, DCl, and CO. The (numerically calculated) energy levels of the resulting potentials were much better than those of the usual RKR potentials. [As Stwalley has noted,⁸ these authors should also have determined the equilibrium internuclear distance r_e from $B(-\frac{1}{2} - \delta)$ rather than from the usual $B_e = B(-\frac{1}{2})$ in order to maintain consistent accuracy; however, the effect is small on HCl and DCl and negligible for CO.]

In the next section we justify Eq. (11) by deriving it via a uniform asymptotic approximation. In Sec. III the role of the Langer modification [replacement of $J(J+1)$ by $(J+\frac{1}{2})^2$] in this method is discussed, and the last section summarizes the results of the paper.

II. UNIFORM ASYMPTOTIC QUANTUM CONDITION

In this section we summarize the uniform asymptotic methods of Miller and Good⁹ and Dingle¹⁰ and use them to derive the modified quantum condition.

We let $\mathcal{R}(r) = \psi(r)/r$ in Eq. (6) and write the re-

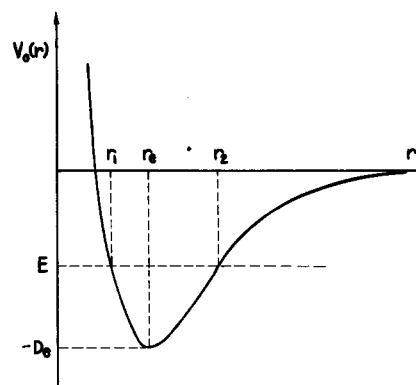


FIG. 1. Sketch of a typical interatomic potential V_0 . D_0 is the dissociation energy, r_e the equilibrium internuclear distance, and r_1 and r_2 the turning points at energy E .

sulting equation in the form

$$[(d^2/dr^2) + p^2(r)/\hbar^2]\psi(r) = 0, \quad (14)$$

where p is defined by Eq. (2), and V_0 is the true (known or unknown) potential. To proceed, one chooses some other "comparison equation"

$$[(d^2/dR^2) + P^2(R)/\hbar^2]\Psi(R) = 0, \quad (15)$$

where $P^2(R) = W - U(R)$, and $U(R)$ is chosen to be some potential function which has the same *qualitative* behavior as V_0 but whose exact eigenvalues W and eigenfunctions $\Psi(R)$ are known. One then transforms Eq. (14) into (15) by writing

$$\psi(r) = (dR/dr)^{-1/2} \Psi(R). \quad (16)$$

Upon substitution, the function $R(r)$ is found to be determined by the equation

$$(dR/dr)^2 P^2(R) = p^2(r) + (dR/dr)^{1/2} (d^2/dr^2) (dR/dr)^{-1/2}. \quad (17)$$

If this were solved exactly for $R(r)$, the transformation and solution would be exact. That is not usually possible. However, if dR/dr is nearly constant, a uniform asymptotic approximation is obtained by neglecting the last term in (17). Then, $R(r)$ is determined by the quadrature

$$\int_{R_1}^{R(r)} P(R) dR = \int_{r_1}^r p(r) dr, \quad (18)$$

where the turning points are thus required to match; i.e., $R(r_i) = R_i$. The quantum condition is given by

$$\phi = \hbar^{-1} \int_{r_1}^{r_2} p(r) dr = \hbar^{-1} \int_{R_1}^{R_2} P(R) dR, \quad (19)$$

where the integral over R is simply evaluated using the known W and $U(R)$.

The quantum condition obtained here depends on the choice of comparison function, and it is clear that the more closely U resembles V_0 the more accurate

(19) will be. However, even very crude choices can give reasonable results. The use of $P^2(R) = \pm 1$ leads to the usual WKB result; choosing $U(R) = \pm R$ leads to the Airy function¹¹ uniform asymptotic approximation commonly used for single turning point problems¹² but whose use here requires fitting two solutions together and gives a quantum condition which is neither flexible nor accurate.¹³ Letting $U(R) = \frac{1}{2}R^2$ gives simple harmonic oscillator comparison functions^{9,10} which automatically fit the boundary conditions but give

$$U(R) = D_e \{ (1 - \epsilon^2) \exp[-2\gamma(R - R_e)] - 2(1 - \epsilon) \exp[-\gamma(R - R_e)] \} / \{ 1 - \epsilon \exp[-\gamma(R - R_e)] \}^2. \quad (20)$$

This potential satisfies the conditions $U'(R_e) = 0$ and $U(R_e) = -D_e$. If we let $\gamma = \gamma_0(1 - \epsilon)$ and $\gamma_0 = (\mu/2D_e)^{1/2}\omega_e$ (in a consistent set of units), then $U''(R_e) = \mu\omega_e^2$. To make U similar to V_0 , we choose these parameters to match V_0 (or experiment) and let ϵ be arbitrary at the moment. (If $\epsilon = 0$, this potential reduces to a Morse potential.)

Letting $x = R - R_e$, we follow Tietz¹⁵ to obtain an exact solution of (15) with this potential on $-\infty < x < \infty$. (This relaxation of the boundary conditions is discussed in the next section.) Let $y = \epsilon \exp(-\gamma x)$, and Eq. (15) becomes

$$\{ y^2 (d^2/dy^2) + y(d/dy) - \kappa^2 - [(\alpha y^2 - \beta y)/(1 - y)^2] \} \Psi = 0, \quad (21)$$

where

$$\kappa = (-2\mu W/\hbar^2\gamma^2)^{1/2}, \quad (22)$$

$$\alpha = 2\mu D_e(1 - \epsilon)(1 + \epsilon)/(\epsilon^2\hbar^2\gamma^2), \quad (23)$$

and

$$\beta = 4\mu D_e(1 - \epsilon)/(\epsilon\hbar^2\gamma^2). \quad (24)$$

We distinguish two cases: If $\epsilon > 0$, then the potential has a singularity and $0 \leq y \leq 1$; if $\epsilon < 0$, $-\infty < y \leq 0$. In what follows the upper sign gives the formulas for $\epsilon > 0$, the lower sign those for $\epsilon < 0$. In either case the well-behaved solutions of (21) are given by

$$\Psi = y^a(1 - y)^t F(a, b; c; y), \quad (25)$$

where F is a hypergeometric function,¹⁶

$$t = \frac{1}{2} \pm (\alpha - \beta + \frac{1}{4})^{1/2}, \quad (26)$$

$$c = 2\kappa + 1, \quad (27)$$

$$a = \kappa + p \mp (\alpha + \kappa^2)^{1/2}, \quad (28)$$

and

$$b = \kappa + p \pm (\alpha + \kappa^2)^{1/2}. \quad (29)$$

If $\epsilon > 0$, the F diverges at $y = 1$ unless a is a negative integer, $a = -v$; if $\epsilon < 0$, the asymptotic behavior of Ψ as $y \rightarrow -\infty$ also requires that $a = -v$. Thus, in either case one has

$$\kappa = [\alpha - (t + v)^2]/2(t + v) \quad (30)$$

and energies $W(v) = -\hbar^2\gamma^2\kappa^2/(2\mu)$.

Substituting $W(v)$ into (29) and evaluating the

$\delta = 0$. Similarly, if $U(R)$ is the Morse potential, one gets exactly $\delta = 0$.^{3,14} Hence, an even more realistic and flexible exactly soluble comparison function is needed.

The most appropriate potential we have found is one of several that have been proposed by Tietz.¹⁵ It is flexible enough near the minimum to give either positive or negative Y_{00} (but not flexible enough to give a negative anharmonicity). It can be written in the form

phase integral exactly using partial fractions, one obtains the quantum condition (11)

$$\phi = (v + \frac{1}{2} + \delta)\pi,$$

with

$$\delta = \pm [(\alpha - \beta + \frac{1}{4})^{1/2} - (\alpha - \beta)^{1/2}]. \quad (31)$$

We note that (in centimeter-gram-seconds or atomic units)

$$\begin{aligned} \alpha - \beta &= 2\mu D_e(1 - \epsilon)^2/(\hbar^2\gamma^2\epsilon^2) \\ &= 2\mu D_e/(\hbar^2\gamma_0^2\epsilon^2) \\ &= (2D_e/\hbar\omega_e\epsilon)^2. \end{aligned} \quad (32)$$

For most molecules $\alpha - \beta$ is very large, and (31) reduces to

$$\delta = \pm [8(\alpha - \beta)^{1/2}]^{-1} = \hbar\omega_e\epsilon/(16D_e). \quad (33)$$

Thus, given a potential V_0 , one can fit a Tietz potential to it near its minimum (where the ordinary WKB method is inaccurate) to determine ϵ and get the corrected quantum condition from (33) and (11). Or given the energy spectrum of an unknown potential one can determine δ as discussed below and use the RKR equations with the modified lower limit of integration to get an accurate potential.

The simplest way to determine δ from spectroscopic data is with Eqs. (12) or (13). Values of this δ for a few molecules are listed in Table I. This should usually be adequate. However, for highly anharmonic shallow potential wells, the Dunham expansion (7) for the energy is not convergent. In such a case, another possible way to proceed is to choose the Tietz potential to fit some of the vibrational levels (if the dissociation energy D_0 is at least approximately known) as follows: let $S(v) = [W(v)/W(0)]^{1/2}$, where $W(v)$ is the observed energy of the v th vibrational level measured from dissociation. Then, from (22) one has $\kappa(v)/\kappa(0) = S(v)$. Using Eq. (30) and $S(v)$ for two nonzero values of v , one gets a pair of equations in α and t . After elimination of α and some rearrangement, one obtains a quadratic for t

$$\begin{aligned} 2[v_2 - v_1 + v_1 S(v_2) - v_2 S(v_1)]t^2 \\ + \{v_2^2 - v_1^2 + v_1^2 S(v_2) - v_2^2 S(v_1) + 2v_2 v_1 [S(v_2) - S(v_1)]\}t \\ + v_2 v_1 [v_1 S(v_2) - v_2 S(v_1)] = 0. \end{aligned} \quad (34)$$

TABLE I. Quantum condition corrections δ determined from spectroscopic constants and Eq. (12). All energies are in cm^{-1} .

Molecular state	ω_e	$\omega_e x_e$	B_e	α_e	Y_{00}	δ	Ref.
$\text{H}_2(X^1\Sigma_g^+)$	4395.24	117.995	60.809	2.993	9.0758	0.002065	14
$\text{CO}(X^1\Sigma^+)$	2169.81801	13.2906899	1.93126515	0.0175054229	0.19005	0.0000876	7
$\text{HCl}(X^1\Sigma^+)$	2990.946	52.8186	10.59070	0.30706	1.575	0.000527	6
$\text{LiH}(A^1\Sigma^+)$	234.413	-28.9474	2.8186	-0.78305	12.964	0.05530	a

^a F. H. Crawford and T. Jorgensen, Phys. Rev. **47**, 358, 932 (1935); **49**, 745 (1936).

After this is solved for t , δ is obtained (to a good approximation) from

$$\delta = [8(t - \frac{1}{2})]^{-1}. \quad (35)$$

Values of δ obtained in this way are listed for a few molecular states in Table II. Since this method requires the comparison potential to fit the true potential for higher vibrational states, it may no longer fit well near the minimum (where the usual WKB approximation most needs improving); hence, determination of δ via Eq. (12) is usually to be preferred.

III. THE LANGER MODIFICATION

Many arguments have been given both for¹⁷ and against^{18,19} the wholesale use of the Langer modification [replacement of $J(J+1)$ by $(J+\frac{1}{2})^2 = J(J+1) + \frac{1}{4}$] in Eq. (1) for potential wells of the type (Fig. 1) considered here. None of these is conclusive. In this section we consider the relationship between δ and the Langer transformation and add some more (inconclusive) arguments.

First, let us note that use of the Langer transformation is equivalent to (but less general than) use of quantum condition (11). For example, if one uses the Kratzer potential,^{5b}

$$U_0(R) = D_e [(R_e/R)^2 - 2(R_e/R)], \quad (36)$$

as the comparison potential in the previous section, he obtains $\delta=0$ with the Langer modification and

$$\delta = [D_e B_e^{-1} + (J + \frac{1}{2})^2]^{1/2} - [D_e B_e^{-1} + J(J+1)]^{1/2} \quad (37)$$

without it. For the Kratzer potential, the only correction to Eq. (1) is the Langer modification. However, this is not true of most potentials. For the Morse potential one has $\delta=0$ without the Langer modification; if one used the modification, he would need to use $\delta = -B_e(4\omega_e)^{-1}$ to get reasonably accurate energy levels.

The first term ($B_e/4$) in Eq. (9) for Y_{00} looks very much as if it had been contributed by the Langer modification, but if Dunham's³ formulas are used to write Y_{00} in terms of the potential, it becomes

$$Y_{00} = (B_e R_e^2 / 32) [(U^{IV} / U^{II}) - (7/9)(U^{III} / U^{II})^2], \quad (38)$$

where U^{II} is the second derivative of the potential at its minimum, etc., so that Y_{00} appears to be determined by the shape of the potential rather than by any Langer transformation.

Langer's¹¹ original justification of the modification is based on boundary condition arguments. The exact solution $\psi(r)$ of Eq. (14) must approach zero at least as fast as r as r goes to zero, but the usual WKB solutions simply decrease exponentially as r moves left of r_1 (see Fig. 1) toward zero. If $V_J \rightarrow \infty$ faster than r^{-2} as $r \rightarrow 0$, those WKB solutions also satisfy the exact boundary condition; otherwise, they do not. If $V_J \rightarrow \infty$ as r^{-1} or r^{-2} as $r \rightarrow 0$, Langer⁹ showed that via the transformation $r = e^r$ one obtains a new Schrödinger equation whose WKB solutions do satisfy the exact boundary conditions. Expression of the resulting quantum condition in terms of r gives Eq. (1) except that $J(J+1)$ gets replaced by $(J+\frac{1}{2})^2$.

Now let us consider the Tietz potential. Since the

TABLE II. Quantum condition corrections δ determined by direct fit of lowest vibrational levels, via Eqs. (34) and (35). Energies are in cm^{-1} relative to dissociation.

Molecular state	$W(0)$	$W(1)$	$W(2)$	δ	Ref.
$\text{H}_2(X^1\Sigma_g^+)$	-36 117.5	-31 955.4	-28 028.8	-0.000685	a
$\text{CO}(X^1\Sigma^+)$	-89 594.1	-87 450.8	-85 334.1	+0.000048	7, 14
$\text{LiH}(B^1\Pi^-)$	-180.5	-49.8	-3.9	+0.031	b
$\text{Ar}_2(X^1\Sigma_g^+)$	-84.0	-58.4	-38.0	+0.0035	c

^a R. J. LeRoy, University of Wisconsin Theoretical Chemistry Institute Report WIS-TCI-387, 1971; J. Chem. Phys. **54**, 5433 (1971).

^b R. Velasco, Can. J. Phys. **35**, 1204 (1957).

^c Y. Tanaka and K. Yoshino, J. Chem. Phys. **53**, 2012 (1970); R. J. LeRoy, J. Chem. Phys. **57**, 573 (1972).

exact solutions of the previous section satisfy WKB rather than exact boundary conditions, let us see what contribution to δ is due to this approximate boundary condition. If $\epsilon = \epsilon' \equiv \exp(-\delta r_e)$, this potential has an r^{-2} singularity at the origin. However, for any $\epsilon < \epsilon'$, it is nonsingular there, and WKB-like solutions satisfying the exact boundary conditions can be constructed by taking the solutions for $r < r_1$ to be of the form²⁰

$$\psi = \frac{A}{2q^{1/2}} \exp\left(-\int_r^{r_1} q dr\right) + \frac{B}{2q^{1/2}} \exp\left(\int_r^{r_1} q dr\right), \quad (39)$$

where $q = (-p^2)^{1/2}$, $B = -A \exp(-2\chi)$, and

$$\chi = \int_0^{r_1} q dr, \quad (40)$$

rather than setting $B = 0$ as in the usual WKB approximation. This leads to the quantum condition

$$\cot\phi = \frac{1}{2} \exp(-2\chi). \quad (41)$$

Use of Eq. (11) gives as the contribution δ_b due to the boundary conditions

$$\delta_b \approx (2\pi)^{-1} \exp(-2\chi). \quad (42)$$

For $\epsilon = 0$ (Morse limit) for ground state H_2 this δ_b is always less than 10^{-19} and is hence completely negligible. (The contribution to δ of the Langer transformation would be about 4×10^{-3} here.) Furthermore, as $\epsilon \rightarrow \epsilon'$, $\delta_b \rightarrow 0$. By contrast, the actual δ for this potential, Eq. (33), *increases* smoothly with ϵ . By proper choice of ϵ the repulsive wall of the Tietz potential can be made to be a very good model of a true effective potential.²¹ Therefore, we conclude that *for the bound states of interatomic potentials, the Langer modification, if justified at all, is not justified by boundary considerations.* This conclusion is further strengthened by the fact that Y_{00} [Eq. (38)] is determined solely by the behavior of the potential near its minimum and not by its small r behavior. It is also in agreement with the observed fact that the results of numerical integration of Eq. (14) are insensitive to the precise nature of the small r boundary condition. Indeed, all the popular accurate numerical methods of which the author is aware satisfy the usual WKB boundary condition rather than the exact one!

In conclusion, it is the opinion of the author that the Langer modification should not be used for WKB or RKR treatments of the bound levels of diatomic molecules. If, however, one wished to use it, he could still obtain accurate results by choosing $\delta = \delta'$ in Eq. (11) such that $E(-\frac{1}{2} - \delta', -\frac{1}{2}) = -D_e$. This gives $\delta' \approx (Y_{00} - \frac{1}{4} B_e) / \omega_e$.

IV. DISCUSSION

With the methods described in this paper, it should be possible to obtain improved RKR potentials accurate to within experimental error as easily as one obtains standard RKR potentials, at least for the low v and J for which RKR potentials are usually constructed. However, the exact δ is probably a slowly varying function of v and J , and a different δ may be needed near dissociation. In any event, it is recommended that *any* RKR potential constructed be checked by comparing its numerically calculated energy levels with experiment.

ACKNOWLEDGMENTS

It is a pleasure to thank Professor William C. Stwalley for suggesting this problem and him and Dr. Robert J. LeRoy for helpful suggestions.

* Research supported by a grant from Brigham Young University.

¹ See, for example, J. L. Powell and B. Craseman, *Quantum Mechanics* (Addison-Wesley, Reading, Mass., 1961), p. 140, or almost any quantum mechanics text.

² See E. A. Mason and L. Monchick, *Advan. Chem. Phys.* **12**, 329 (1967), and references therein.

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