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MOLECULAR COLLISIONS. XIV. FIRST-ORDER APPROXIMATION OF THE GENERALIZED PHASE SHIFT TREATMENT OF ROTATIONAL EXCITATION: ATOM-RIGID ROTOR*

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ABSTRACT

The generalized phase shift approach to the rotational excitation problem, introduced in paper XII of this series, is applied to the atom-rigid rotor case in the lowest (first order) approximation. The treatment involves the computation of generalized action integrals over curved trajectories. Numerical results are presented to illustrate the dependence of the transition probabilities on the usual physical parameters, as well as a new parameter, ζ, which is proportional to the ratio of the moment of inertia of the van der Waals' atom-diatom system to that of the diatomic rotor (and thus to the ratio of the collision time to the diatom rotation time). In the limit $\zeta \to 0$, the development

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reduces to the sudden approximation. In the large impact parameter limit (straight-line trajectories), the deviation from the sudden approximation is described by "resonance functions" identical to those obtained implicitly by Van Kranendonk. The numerical results are presented in a manner which illustrates the deviation from each of these two limits.

The theory of rotational inelasticity in atom-diatom scattering has received considerable attention[1,2]. Although the exact (close-coupled) solution to the problem has been well formulated[3], because of the computational difficulty of its execution various approximation techniques retain their importance. A number of approximations based on either time-dependent (TD) or time-independent (TI) perturbation methods have been employed; however, relatively little attention has been devoted to the interrelationships among these schemes. A step toward providing a more unified basis for the various approximation methods was taken in paper X of this series[4]. There, the equivalence between the restricted-distorted-wave-Born (RDWB) treatment and the first-order sudden approximation (SA) in the straight-line trajectory limit was demonstrated. In the present work, considerable attention is devoted to relating the new semiclassical method under investigation to others in the hierarchy of approximation schemes.

The approximation to be evaluated represents the first-order version of the semiclassical limit of the generalized phase shift (GPS) development of paper XII of this series[5]. As noted[5], the equations arising in this treatment are amenable to interpretation in terms of certain classical dynamical features of the system. The relative translational motion is assumed to take place under the influence of the central (spherically averaged) portion of the anisotropic interaction potential (i.e., a curved but planar trajectory is assumed). To be noted is the appearance of a parameter, ξ , which is essentially

the ratio of the collision time to the diatom rotation time (τ_{coll}/τ_{rot}). Thus, since the SA is valid only in the limit $\xi \longrightarrow 0$, the GPS development provides a direct measure of the importance of deviations from the sudden limit. A completely independent (seemingly unrelated) treatment has been carried out by Van Kranendonk[6] for application to the study of pressure broadening of spectral lines. This method, however, is restricted to straight-line trajectories (i.e., the large impact parameter limit).

In the following, the first-order GPS equations for atom-diatom scattering (with an arbitrary anisotropic potential) are put into a computationally convenient form and identification of the parameter ξ is made. The relationships between the GPS development and other approximations are then discussed. In particular, it is shown that in the large impact parameter limit, the GPS and Van Kranendonk methods yield identical results[7]. Finally, a set of calculated first order GPS transition probabilities for selected values of the parameters in a model atom-diatom system are presented. Inspection of the results permits conclusions to be drawn on the importance of deviations from the SA in the curved path and straight-line trajectory treatment.

I. EQUATIONS FOR FIRST ORDER GPS TRANSITION PROBABILITIES

The most general form of the anisotropic interaction potential is the expansion of Eq. (V-5)[8] which, for the atom-diatomic case is:

$$V(r,\Theta) = V^{(0)}(r) + \sum_L v^{(1)}(L,r)\, P_L(\cos\Theta). \qquad (1)$$

Here, r is the distance from the atom to the center of mass of the diatom; Ⓗ is the angle between r and the diatom axis; and the P_L are Legendre functions.

In the first order approximation the exponential in the expression for the transition probability (Eqs. (XII-46) and (XII-72)) is expanded and only the linear term is retained. By a development only trivially different from that used in obtaining Eq. (XII-78), it is readily shown that for the potential of Eq. (1), the first order GPS expression for the probability of transition from initial rotor state $\bar{\ell}$ to ℓ for an initial relative angular momentum indexed by $\bar{\lambda}$ is

$$P(\bar{\ell};\ell;\bar{\lambda}) = \frac{M^2(2\ell+1)}{\hbar^4 \bar{k}^2} \sum_{\Delta L} \frac{1}{(2L+1)} \left| \sum_{\alpha} (-i)^{\alpha} (-1)^{\alpha} \begin{pmatrix} \ell & \bar{\ell} & L \\ 0 & \alpha & -\alpha \end{pmatrix} \right.$$

$$\times \int_{r_o}^{\infty} v^{(1)}(L,r) \left[1 - \frac{2MV^{(0)}}{\hbar^2 \bar{k}^2} - \frac{b^2}{r^2} \right]^{-1/2}$$

$$\left. \times \left[D^L(\pi, \Psi, \pi)_{0\alpha} D^L(\pi, \theta, \pi)_{\Delta 0} + D^L(\pi, 2\Psi^{(0)} - \Psi, \pi)_{0\alpha} D^L(\pi, 2\theta^{(0)} - \theta, \pi)_{\Delta 0} \right] dr \right|^2 . \tag{2}$$

Here M is the reduced mass of the atom-diatom system, L indexes the Legendre functions in Eq. (1), $v^{(1)}(L,r)$ is the radial part of the anisotropic interaction potential associated with L, and the $D^L(S)_{st}$ are the usual representation coefficients. The angles θ and Ψ are defined by Eqs. (XII-52) and (XII-56), and are given explicitly by:

$$\Theta(r) = b \int_r^\infty \frac{\alpha r}{r^2 \left[1 - \frac{2MV^{(0)}}{\hbar^2 \bar{k}^2} - \frac{b^2}{r^2}\right]^{1/2}} \tag{3}$$

and

$$\Psi(r) = \frac{M\bar{\ell}}{\bar{k} I} \left\{ r - \int_r^\infty \left\{ \left[1 - \frac{2MV^{(0)}}{\hbar^2 \bar{k}^2} - \frac{b^2}{r^2}\right]^{-1/2} - 1 \right\} \alpha r \right\}. \tag{4}$$

Here, as usual, b is the classical impact parameter ($b \cong \frac{\bar{\lambda}+\frac{1}{2}}{\bar{k}}$), $V^{(0)}$ is the orientation-averaged interaction potential, $\hbar \bar{k} = Mv$ is the initial relative (linear) momentum, and I is the moment of inertia of the diatom. The angles $\Theta^{(0)}$ and $\Psi^{(0)}$ are the values of $\Theta(r)$ and $\Psi(r)$ at $r = r_0$, the outermost zero of the square-root quantity in square brackets.

Utilizing the properties of the representation coefficients, Eq. (2) can be rewritten:

$$P(\bar{\ell}; \ell; \bar{\lambda}) = (2\ell+1) \sum_{\alpha L} \frac{1}{(2L+1)} \left| \sum_\alpha (i)^\alpha \begin{pmatrix} \ell & \bar{\ell} & L \\ 0 & \alpha & -\alpha \end{pmatrix} B_{L\alpha s} \right|^2 \tag{5}$$

where the coefficients $B_{L\alpha s}$ are defined by:

$$B_{L\alpha s} = (-1)^{s} \frac{4\pi M}{(2L+1)\hbar^2 \bar{k}} \int_{r_0}^{\infty} U^{(1)}(L,r) \left[1 - \frac{2MV^{(0)}}{\hbar^2 \bar{k}^2} - \frac{b^2}{r^2}\right]^{-1/2}$$

$$\times \left[Y_L^{\alpha}(\Psi,0)\, Y_L^{s}(\theta,0) + Y_L^{\alpha}(2\Psi^{(0)}-\Psi,0)\, Y_L^{s}(2\theta^{(0)}-\theta,0)\right] dr \tag{6}$$

and the Y^1's are spherical harmonics[9].

Eq. (5) implies that for an interaction potential of the form of Eq. (1), with only L = 1 and L = 2 terms, only $\bar{\ell} \to \bar{\ell} \pm 1$ and $\bar{\ell} \to \bar{\ell} \pm 2$ transitions are allowed. Using the properties of the 3-j symbol, for such a potential

$$P(\bar{\ell}; \bar{\ell}\pm 1; \bar{\lambda}) = (2\ell+1) \sum_{s} \frac{1}{3} \left| \sum_{\alpha} (i)^{\alpha} \begin{pmatrix} (\bar{\ell}\pm 1) & \bar{\ell} & 1 \\ 0 & \alpha & -\alpha \end{pmatrix} B_{1\alpha s} \right|^2 \tag{7}$$

and

$$P(\bar{\ell}; \bar{\ell}\pm 2; \bar{\lambda}) = (2\ell+1) \sum_{s} \frac{1}{5} \left| \sum_{\alpha} (i)^{\alpha} \begin{pmatrix} (\bar{\ell}\pm 2) & \bar{\ell} & 2 \\ 0 & \alpha & -\alpha \end{pmatrix} B_{2\alpha s} \right|^2. \tag{8}$$

As expected, for L = 1 or 2, the anisotropy of order L induces only transitions $\bar{\ell} \rightarrow \bar{\ell} \pm L$. The indices s and α in Eqs. (5) - (8) are restricted through the Y's to integer values between -L and +L. From Eq. (6) and the symmetry properties of the spherical harmonics, it follows that

$$B_{L\alpha s} = (-1)^{\alpha} B_{L-\alpha s} \; ; \; B_{L\alpha s} = (-1)^{s} B_{L\alpha -s} \; ; \; B_{L\alpha s} = (-1)^{\alpha+s} B_{L-\alpha -s} \; . \tag{9}$$

Hence,

$$P(\bar{\ell}; \bar{\ell}\pm 1; \bar{\lambda}) = \frac{(2\bar{\ell}+1)}{3} \left\{ 4 \begin{pmatrix} (\bar{\ell}\pm 1) & \bar{\ell} & 1 \\ 0 & 1 & -1 \end{pmatrix}^2 \left[2 B_{111}^2 + B_{110}^2 \right] + \begin{pmatrix} (\bar{\ell}\pm 1) & \bar{\ell} & 1 \\ 0 & 0 & 0 \end{pmatrix}^2 \left[2 B_{101}^2 + B_{100}^2 \right] \right\} \tag{10}$$

and

$$P(\bar{\ell}; \bar{\ell}\pm 2; \bar{\lambda}) = \frac{(2\bar{\ell}+1)}{5} \left\{ 4 \begin{pmatrix} (\bar{\ell}\pm 2) & \bar{\ell} & 2 \\ 0 & 2 & -2 \end{pmatrix}^2 \left[2 B_{222}^2 + 2 B_{221}^2 + B_{220}^2 \right] \right. \tag{11}$$

$$+ 4 \begin{pmatrix} (\bar{\ell}\pm 2) & \bar{\ell} & 2 \\ 0 & 1 & -1 \end{pmatrix}^2 \left[2 B_{212}^2 + 2 B_{211}^2 + B_{210}^2 \right] + \begin{pmatrix} (\bar{\ell}\pm 2) & \bar{\ell} & 2 \\ 0 & 0 & 0 \end{pmatrix}^2 \left[2 B_{202}^2 + 2 B_{201}^2 + B_{200}^2 \right]$$

$$\left. - 4 \begin{pmatrix} (\bar{\ell}\pm 2) & \bar{\ell} & 2 \\ 0 & 2 & -2 \end{pmatrix} \begin{pmatrix} (\bar{\ell}\pm 2) & \bar{\ell} & 2 \\ 0 & 0 & 0 \end{pmatrix} \left[2 B_{222} B_{202} + 2 B_{221} B_{201} + B_{220} B_{200} \right] \right\} .$$

For the limiting case of large $\bar{\ell}$, the 3-j symbols can be approximated to yield the $\bar{\ell}$ - independent limiting forms:

$$P(\bar{\ell};\bar{\ell}\pm 1;\bar{\lambda}) = \frac{1}{3}\left[2B_{111}^2 + B_{110}^2 + B_{101}^2 + \frac{1}{2}B_{100}^2\right] \tag{12}$$

and

$$P(\bar{\ell};\bar{\ell}\pm 2;\bar{\lambda}) = \frac{1}{5}\Big[\frac{1}{2}B_{222}^2 + \frac{1}{2}B_{221}^2 + \frac{1}{4}B_{220}^2 + 2B_{212}^2$$

$$+ 2B_{211}^2 + B_{210}^2 + \frac{3}{4}B_{202}^2 + \frac{3}{4}B_{201}^2 + \frac{3}{8}B_{200}^2$$

$$- \left(\frac{3}{2}\right)^{1/2}\left(B_{222}B_{202} + B_{221}B_{201} + \frac{1}{2}B_{220}B_{200}\right)\Big]. \tag{13}$$

It is noted from Eq. (6) that the needed $B_{L\alpha s}$ coefficients require spherical harmonics involving the angles ψ and $\psi^{(0)}$. For the purpose of subsequent analysis it is convenient to consider the constant multiplier in the expression (Eq. (4)) for these angles. This quantity multiplied by the impact parameter, b , forms a new parameter, say ξ , which is proportional to the ratio of the collision time to the diatom rotation time, as is seen from the following. For a rigid

rotor in the limit of high $\bar{\ell}$ (i.e., energy levels approximated by $E_{\bar{\ell}} = \bar{\ell}^2\hbar^2/2I$), the classical rotation period is given by

$$\tau_{rot} = 2\pi I/\hbar\bar{\ell}. \tag{14}$$

Utilizing this relationship, the multiplier can be put into the form

$$\frac{M\bar{\ell}}{\bar{k}I} = \frac{\tau_{coll}}{b\tau_{rot}} = \xi/b \tag{15}$$

where

$$\tau_{coll} = \frac{2\pi b}{v} \tag{16}$$

is one definition of the collision time (viz., the time required for a free particle to traverse a distance $2\pi b$). The parameter ξ proves useful in establishing the relationships between the GPS approximation and other first-order semiclassical treatments. In Section II, a more convenient and fundamental factorization of ξ is introduced.

It has been noted[5] in XII that in the limit ψ (or ξ) $\longrightarrow 0$ (see Eq. (4)) the first-order GPS transition probability expression, Eq. (2), reduces to that obtained from the first-order (curved trajectory) SA. Further, since the GPS expression arises from a TI development, in this limit it must also correspond identically to

the restricted distorted wave (RDW) result (if the wavefunctions are approximated by WBK semiclassical functions). A less obvious connection is the relationship between the asymptotic (large impact parameter) limit of the GPS approximation and the previously mentioned straight-line trajectory first order TD treatment of Van Kranendonk.[6] This connection is established in detail in Appendix A. In particular, it is shown that for a potential having an anisotropic portion

$$v^{(1)}(L,r) = \pm \frac{C_n}{r^n} P_L(\cos\Theta) \tag{17}$$

where $L = 1$ or 2, both methods yield identical results for the transition probabilities and the associated "resonance functions"[10] which correct for the deviation from the "sudden" character of the collision. The resonance functions obtained are given in terms of modified Bessel functions of the second kind with argument $L\xi$:

$$R(\xi) = \frac{\xi^n}{2^{n-2}\left[\Gamma(n/2)\right]^2}\left[K^2_{n/2}(\xi) + K^2_{n/2-1}(\xi)\right] \quad ; \ (L=1)$$

$$R(\xi) = \frac{1}{2^{n-2}(n^2-3n+3)\left[\Gamma\left(\frac{n-1}{2}\right)\right]^2}\left\{\frac{3}{2}(2\xi)^{n+1}K^2_{\frac{n+1}{2}}(2\xi)\right. \tag{18}$$

$$+6(2\xi)^{n+1}K^2_{\frac{n-1}{2}}(2\xi) + \frac{1}{8}\left[(n+3)(2\xi)^{\frac{n-1}{2}}K_{\frac{n-1}{2}}(2\xi)\right.$$

$$\left.\left. - 3(2\xi)^{\frac{n+1}{2}}K_{\frac{n-3}{2}}(2\xi) - 3(2\xi)^{\frac{n+1}{2}}K_{\frac{n+1}{2}}(2\xi)\right]^2\right\} \quad ; \ (L=2).$$

II. MODEL CALCULATIONS

A. Method

In the computations, the atom-diatom interaction potential was taken to be of the form

$$V(r,\Theta) = C_{12} r^{-12}\left[1 + b_1 P_1(\cos\Theta) + b_2 P_2(\cos\Theta)\right] - C_6 r^{-6}\left[1 + a_2 P_2(\cos\Theta)\right] \quad (19)$$

where a_2, b_1, and b_2 are anisotropy parameters, and $C_{12} = 4\epsilon\sigma^{12}$, $C_6 = 4\epsilon\sigma^6$, where ϵ and σ are the usual well depth and size parameters. It is convenient to introduce the usual reduced impact parameter $b^* = b/\sigma$, energy $E^* = E/\epsilon$, and de Boer quantum parameter $\Lambda^* = h/\sigma(2M\epsilon)^{1/2}$. It is also convenient to change the integration variable from r to $y = b^*\sigma/r$. Utilizing these quantities, Eqs. (3) and (4) become:

$$\theta = \int_0^{y} \frac{dy}{\left[1 - y^2 - V(y)/E\right]^{1/2}} \quad (20)$$

$$\theta^{(0)} = \int_0^{y_0} \frac{dy}{\left[1 - y^2 - V(y)/E\right]^{1/2}}$$

and

$$\psi = \xi\left\{\frac{1}{y} - \int_0^y \frac{dy}{y^2}\left\{\left[1 - y^2 - V(y)/E\right]^{-1/2} - 1\right\}\right\} \tag{21}$$

$$\psi^{(0)} = \xi\left\{\frac{1}{y_0} - \int_0^{y_0} \frac{dy}{y^2}\left\{\left[1 - y^2 - V(y)/E\right]^{-1/2} - 1\right\}\right\}$$

where

$$V(y)/E = \frac{4}{E^*}\left[\left(\frac{y}{b^*}\right)^{12} - \left(\frac{y}{b^*}\right)^{6}\right]. \tag{22}$$

Making use of the model interaction potential, Eq. (19), the $B_{L\alpha s}$ may also be rewritten:

$$B_{1\alpha s} = (-1)^{s+1}\left[\frac{16\pi^2}{3\Lambda^*\sqrt{E^*}}\right] b_1 S^{(1)}_{12,\alpha,s} \tag{23}$$

and

$$B_{2\alpha s} = (-1)^{s+1}\left[\frac{16\pi^2}{5\Lambda^*\sqrt{E^*}}\right]\left[b_2 S^{(2)}_{12,\alpha,s} - a_2 S^{(2)}_{6,\alpha,s}\right] \tag{24}$$

where the $S^{(L)}_{n,\alpha,\Delta}$ are generalized action integrals (cf. Ref. 11), here given by:

$$S^{(L)}_{n,\alpha,\Delta} = \left(\frac{1}{b^*}\right)^{n-1} \int_0^{y_0} \frac{dy\, y^{n-2}}{\left[1 - y^2 - V(y)/E\right]^{1/2}}$$

$$\times \left[Y_L^{\alpha}(\Psi,0)\, Y_L^{\Delta}(\theta,0) + Y_L^{\alpha}(2\Psi^{(*)}-\Psi,0)\, Y_L^{\Delta}(2\theta^{(*)}-\theta,0)\right], \qquad (25)$$

(Note that in the sudden limit all the $S^{(L)}_{n,\alpha,\Delta}$ integrals vanish except those for which $\alpha = 0$).

Introducing the reduced variables into the definition of ξ (Eq. (15)), it follows that

$$\xi = \frac{b^* \bar{\ell}\, \Lambda^* M\sigma^2}{2\pi\sqrt{E^* I}} = \frac{b^*}{2\pi\sqrt{E^*}}\, \zeta \qquad (26)$$

where

$$\zeta = \bar{\ell}\, \Lambda^* \frac{M\sigma^2}{I} \qquad (27)$$

is clearly a characteristic of the system under investigation. It should be noted that the quantity $M\sigma^2/I$ is essentially identical

to that used by Lester and Bernstein[12] to characterize the "strength of the coupling", namely the ratio of the moment of inertia of the atom-diatom system to that of the diatom, designated $M r_m^2 / I$.

Inspection of Eqs. (20) - (27) reveals that the first order GPS transition probabilities, Eqs. (12) and (13), are functions of E^*, b^*, Λ^*, the anisotropy parameters b_1, a_2, and b_2 and the new parameter ζ. For certain choices of the anisotropy parameters, the dependence of the transition probabilities on them and on Λ^* can be factored out. The three such cases considered here are: (1) $a_2 = b_2 = 0$, $b_1 \neq 0$ (i.e., an $r^{-12} P_1(\cos\Theta)$ repulsion); (2) $a_2 = b_1 = 0$, $b_2 \neq 0$ (an $r^{-12} P_2(\cos\Theta)$ repulsion); and (3) $b_1 = 0$, $a_2 = b_2 \neq 0$ (an $r^{-12} P_2(\cos\Theta)$ repulsion plus an $r^{-6} P_2(\cos\Theta)$ attraction with equal anisotropy coefficients). For these combinations, the transition probabilities of Eqs. (12) and (13) can be factorized in terms of "scaled transition probabilities", ρ, defined by

$$P(\bar{\ell}; \bar{\ell}\pm 1 \mid E^*, b^*, \zeta, \Lambda^*, b_1) = (\Lambda^*)^{-2} b_1^2 \rho(\bar{\ell}; \bar{\ell}\pm 1 \mid E^*, b^*, \zeta) \tag{28}$$

and

$$P(\bar{\ell}; \bar{\ell}\pm 2 \mid E^*, b^*, \zeta, \Lambda^*, a_2, b_2) = (\Lambda^*)^{-2} b_2^2 \rho(\bar{\ell}; \bar{\ell}\pm 2 \mid E^*, b^*, \zeta). \tag{29}$$

The scaled transition probabilities which are functions of only the three variables are the quantities of interest. The calculations consisted of generating values of the p's over a three dimensional grid[13] in E^*, b^*, and ζ

B. Calculations

All computations reported herein were performed on the University of Wisconsin Computing Center Univac 1108. For determination of the reduced turning points (y_o), a standard Newton-Raphson[14] algorithm was used. The angles θ, $\theta^{(o)}$, ψ, $\psi^{(o)}$, and the $S^{(L)}_{n,\alpha,s}$ integrals were evaluated by the Gauss-Chebyshev quadrature technique[15]. The considerable amount of programming required was checked in several ways. All routines were hand-checked for arithmetic accuracy on simple example problems. In addition, the y_o and $\theta^{(o)}$ calculations were checked against independently generated tables[16]. The $S^{(L)}_{n,\alpha,s}$ integrals in the limit $\zeta = 0$ were checked against independent tables[17] and analytical asymptotic expressions[11]. Finally, asymptotic transition probabilities (for various ζ) were checked against values resulting from asymptotic expressions (Eqs. (A27) and (A28)). In all cases, numerical agreement to about four significant figures was obtained.

For each of the three sets of anisotropy parameters, values of the scaled transition probability (p) were calculated over the three dimensional grid defined by $E^* = 1, 3, 10$; $b^* = 0.5, 0.9, 1.0, 1.1, 1.2, 1.3, 1.5, 2.0$ and $\zeta = 0, 10, 20, 30$. In

addition, calculations at $E^* = 30, \zeta = 30$ were also performed. The results obtained are illustrated[18] in Figure 1. As would be expected, deviations from the sudden limit ($\zeta = 0$) are most serious for large values of the parameter ζ and at low E^* . They are most pronounced for the potential with the long range attractive anisotropy (i.e., $a_2 = b_2 \neq 0$, $b_1 = 0$).

C. Analysis

In an attempt to isolate the sources of the deviations from the sudden limit, the following data analysis was performed. The ratio

$$\tilde{R}(E^*, b^*, \zeta) = \frac{p(E^*, b^*, \zeta)}{p(E^*, b^*, 0)} \tag{30}$$

gives directly a measure of the deviation of the present curved trajectory results from the first order SA in the curved trajectory treatment. It is convenient to define another ratio

$$C(E^*, b^*, \zeta) = \frac{\tilde{R}(E^*, b^*, \zeta)}{R(\zeta)} \tag{31}$$

where $R(\zeta)$ is the Van Kranendonk resonance function. This ratio represents a combined measure of the deviation from the sudden limit and the straight-line trajectory approximation. To be more

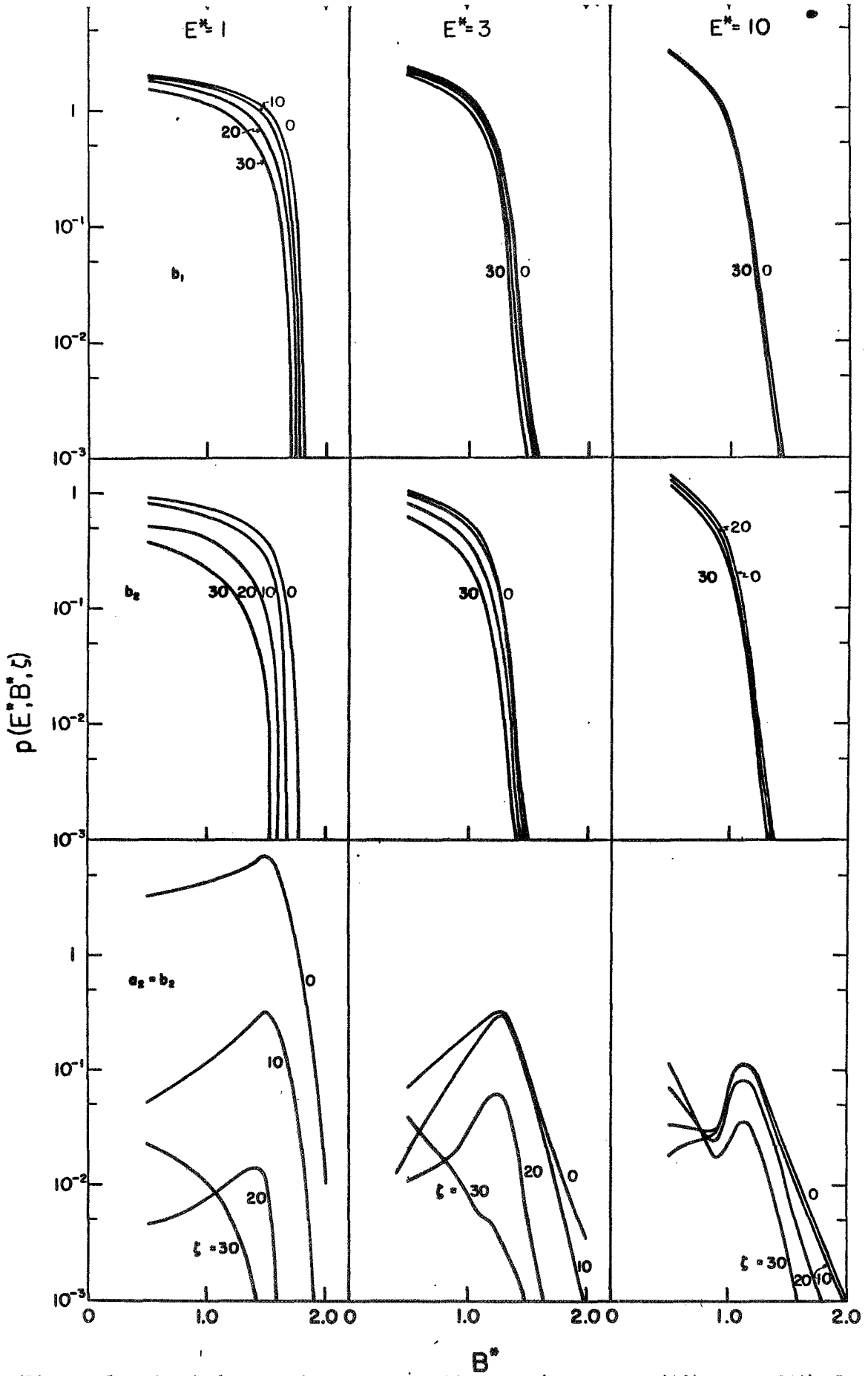

Figure 1. Scaled transition probabilities (cf. Eqs. (28) and (29)) for various E^* and ζ as functions of b^*. Each row of frames corresponds to the indicated choice of nonzero anisotropy parameters in Eq. (19).

explicit, combining Eqs. (30) and (31),

$$\rho(E^*, b^*, \xi) = C(E^*, b^*, \xi)\, R(\xi)\, \rho(E^*, b^*, 0). \tag{32}$$

Thus $C(E^*, b^*, \xi)$ represents the additional correction required to be applied to curved trajectory SA calculations after correction by the straight-line resonance function.

For each choice of the anisotropy parameters, the quantities $R(\xi)$ were evaluated from Eqs. (18). For the potentials with a $P_2(\cos\Theta)$ anisotropy, the Bessel functions are half integer order and, hence, may be written explicitly[19]. For two of the three cases of Sec. II-B the following expressions for the resonance functions (Eqs. (18)) result:

$$R(\xi) = \frac{e^{-2(2\xi)}}{\left[\frac{1}{2}(10395)^2 + \frac{3}{2}(2835)^2\right]} \left\{ \frac{1}{2}\left[(2\xi)^6 + 21(2\xi)^5 + 210(2\xi)^4 \right.\right.$$

$$\left. + 1260(2\xi)^3 + 4725(2\xi)^2 + 10395(2\xi) + 10395\right]^2 + 2\left[(2\xi)^6 \right.$$

$$\left. + 15(2\xi)^5 + 105(2\xi)^4 + 420(2\xi)^3 + 945(2\xi)^2 + 945(2\xi)\right]^2$$

$$+ \frac{3}{2}\left[(2\xi)^6 + 13(2\xi)^5 + 90(2\xi)^4 + 420(2\xi)^3 + 1365(2\xi)^2 \right.$$

$$\left.\left. + 2835(2\xi) + 2835\right]^2 \right\}$$

Case 2:
$(a_2 = b_1 = 0,\ b_2 \neq 0)$ (33)

$$R(\xi) = e^{-2(2\xi)}\left[\frac{2}{63}(2\xi)^6 + \frac{4}{21}(2\xi)^5 + \frac{13}{21}(2\xi)^4 + \frac{4}{3}(2\xi)^3 + 2(2\xi)^2 + 1\right]. \tag{34}$$

Case 3:
($b_1 = 0$, $a_2 = b_2 \neq 0$)

For the potential with the $P_1(\cos\Theta)$ anisotropy ($b_1 \neq 0$, $a_2 = b_2 = 0$), the K's are integer order and require computer evaluation.[20] The calculated resonance functions are presented in Figure 2.

Values obtained for the $C(E^*, b^*, \xi)$ are given in Tables 1, 2 and 3. As is evident, they ranged from order unity to very large. For the cases $E^* = 10$, $\xi = 10, 20, 30$, they are presented graphically in Figure 3.

III. SUMMARIZING DISCUSSION

The results presented here should prove useful in gauging the importance of deviations from the first order SA. In that the fundamental quantities ($S^{(L)}_{n,\alpha,a}$ integrals) depend only on characteristic parameters of the system, they are readily transferable from one situation to another. The scaled transition probabilities calculated for the three special cases give a clue as to when deviations from the SA might be expected to be large.

The present work demonstrates that the first order GPS development represents the next logical step upward from existing first-order semi-classical perturbation methods. In addition, through the parameter ξ

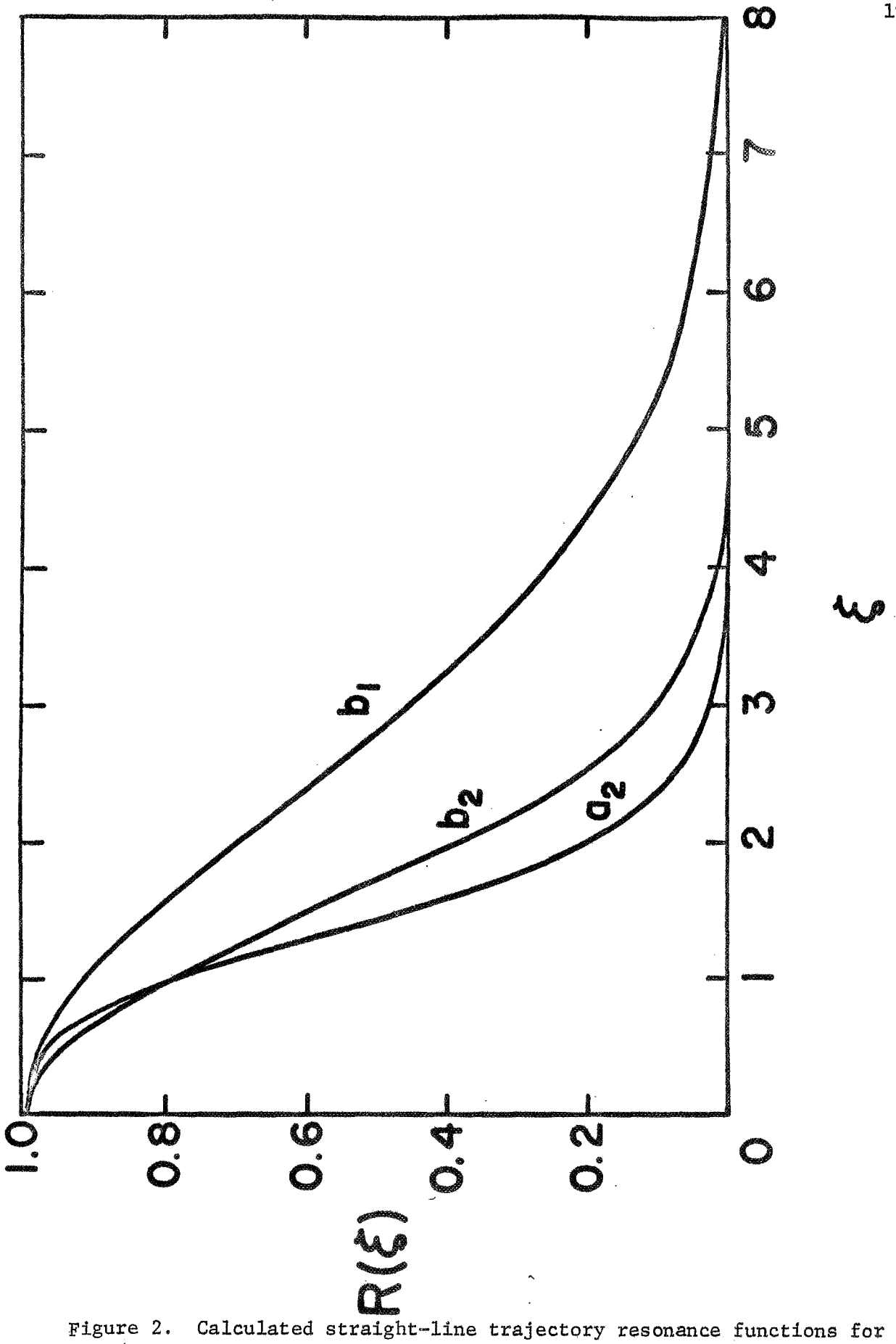

Figure 2. Calculated straight-line trajectory resonance functions for the indicated nonzero anisotropy parameters in Eq. (19).

TABLE 1[+] $C(E^*, b^*, \zeta)$ for Case 1 ($b_1 \neq 0$, $a_2 = b_2 = 0$)

$\zeta = 10$

b^* \ E^*	1	3	10
0.5	1.0209 (0)	1.0018 (0)	9.9965 (-1)
0.9	1.1460 (0)	1.0351 (0)	1.0067 (0)
1.0	1.1897 (0)	1.0441 (0)	1.0072 (0)
1.1	1.2383 (0)	1.0511 (0)	1.0058 (0)
1.2	1.2905 (0)	1.0524 (0)	1.0032 (0)
1.3	1.3443 (0)	1.0404 (0)	1.0014 (0)
1.5	1.4231 (0)	1.0039 (0)	1.0003 (0)
2.0	9.8929 (-1)	9.9991 (-1)	1.0000 (0)

$\zeta = 20$

b^* \ E^*	1	3	10
0.5	1.0934 (0)	1.0085 (0)	9.9871 (-1)
0.9	1.7180 (0)	1.1486 (0)	1.0273 (0)
1.0	1.9842 (0)	1.1887 (0)	1.0291 (0)
1.1	2.3106 (0)	1.2204 (0)	1.0236 (0)
1.2	2.7012 (0)	1.2257 (0)	1.0127 (0)
1.3	3.1469 (0)	1.1672 (0)	1.0052 (0)
1.5	3.8569 (0)	1.0042 (0)	1.0009 (0)
2.0	8.9665 (-1)	9.9602 (-1)	9.9995 (-1)

$\zeta = 30$

b^* \ E^*	1	3	10	30
0.5	1.2416 (0)	1.0229 (0)	9.9752 (-1)	9.9863 (-1)
0.9	3.3079 (0)	1.3677 (0)	1.0629 (0)	1.0124 (0)
1.0	4.4869 (0)	1.4753 (0)	1.0671 (0)	1.0097 (0)
1.1	6.1723 (0)	1.5631 (0)	1.0540 (0)	1.0052 (0)
1.2	8.5190 (0)	1.5757 (0)	1.0284 (0)	1.0023 (0)
1.3	1.1680 (1)	1.4010 (0)	1.0109 (0)	1.0010 (0)
1.5	1.7651 (1)	9.8188 (-1)	1.0013 (0)	1.0002 (0)
2.0	7.1149 (1)	9.8351 (-1)	9.9951 (-1)	9.9432 (-1)

[+]Number in parentheses represents the power of ten by which each entry is to be multiplied.

TABLE 2[+] $C(E^*, b^*, \zeta)$ for Case 2 ($b_1 = a_2 = 0$, $b_2 \neq 0$)

$\zeta = 10$

b^* \ E^*	1	3	10
0.5	1.0074 (0)	9.8080 (-1)	9.9061 (-1)
0.9	1.3731 (0)	1.0617 (0)	1.0064 (0)
1.0	1.5270 (0)	1.0866 (0)	1.0092 (0)
1.1	1.7153 (0)	1.1106 (0)	1.0116 (0)
1.2	1.9427 (0)	1.1321 (0)	1.0137 (0)
1.3	2.2130 (0)	1.1551 (0)	1.0125 (0)
1.5	2.8712 (0)	1.0969 (0)	1.0071 (0)
2.0	1.0346 (0)	1.0146 (0)	1.0019 (0)

$\zeta = 20$

b^* \ E^*	1	3	10
0.5	1.1463 (0)	9.4569 (-1)	9.6523 (-1)
0.9	4.3721 (0)	1.3495 (0)	1.0336 (0)
1.0	6.7631 (0)	1.4994 (0)	1.0461 (0)
1.1	1.0752 (1)	1.6507 (0)	1.0533 (0)
1.2	1.7379 (1)	1.7611 (0)	1.0535 (0)
1.3	2.8120 (1)	1.7249 (0)	1.0428 (0)
1.5	6.2061 (1)	1.1620 (0)	1.0211 (0)
2.0	6.3572 (-1)	1.0025 (0)	1.0041 (0)

$\zeta = 30$

b^* \ E^*	1	3	10	30
0.5	1.6494 (0)	9.3396 (-1)	9.3064 (-1)	9.7244 (-1)
0.9	3.0668 (1)	2.1977 (0)	1.1003 (0)	1.0071 (0)
1.0	7.4926 (1)	2.8074 (0)	1.1319 (0)	1.0112 (0)
1.1	1.8934 (2)	3.4729 (0)	1.1397 (0)	1.0134 (0)
1.2	4.8422 (2)	3.8759 (0)	1.1170 (0)	1.0124 (0)
1.3	1.2146 (3)	3.1903 (0)	1.0785 (0)	1.0097 (0)
1.5	5.0082 (3)	1.0473 (0)	1.0308 (0)	1.0051 (0)
2.0	1.2325 (0)	9.3452 (-1)	1.0029 (0)	1.0000 (0)

[+] Number in parentheses represents the power of ten by which each entry is to be multiplied.

TABLE 3[+] $C(E^*, b^*, \zeta)$ for Case 3 ($b_1 = 0$, $a_2 = b_2 \neq 0$)

$\zeta = 10$

b^* \ E^*	1	3	10
0.5	1.8142 (-1)	2.7901 (-1)	1.8541 (0)
0.9	4.8140 (-1)	6.5922 (-1)	1.0905 (0)
1.0	6.6458 (-1)	7.9823 (-1)	1.0497 (0)
1.1	9.4246 (-1)	9.7146 (-1)	1.0692 (0)
1.2	1.3718 (0)	1.1953 (0)	1.0795 (0)
1.3	2.0521 (0)	1.4613 (0)	1.0663 (0)
1.5	5.0121 (0)	1.3187 (0)	1.0343 (0)
2.0	1.0847 (0)	1.0400 (0)	1.0076 (0)

$\zeta = 20$

b^* \ E^*	1	3	10
0.5	3.4701 (-2)	1.9061 (-1)	4.0092 (0)
0.9	4.6047 (-2)	3.3476 (-1)	1.0338 (0)
1.0	1.0748 (0)	5.3654 (-1)	9.5520 (-1)
1.1	2.6301 (0)	8.7868 (-1)	1.0681 (0)
1.2	6.5952 (0)	1.3867 (0)	1.1349 (0)
1.3	1.6485 (1)	1.8433 (0)	1.1159 (0)
1.5	7.8000 (1)	1.2143 (0)	1.0506 (0)
2.0	3.0991 (-1)	9.7710 (-1)	1.0046 (0)

$\zeta = 30$

b^* \ E^*	1	3	10	30
0.5	7.1556 (-1)	1.0355 (0)	7.0495 (0)	1.2425 (0)
0.9	3.6446 (1)	9.4898 (-1)	1.1192 (0)	7.7031 (0)
1.0	1.0374 (2)	8.9354 (-1)	7.2443 (-1)	1.2034 (0)
1.1	2.8948 (2)	9.5042 (-1)	9.0428 (-1)	1.0790 (0)
1.2	7.6702 (2)	1.2841 (0)	1.0478 (0)	1.0437 (0)
1.3	1.8118 (3)	1.4799 (0)	1.0550 (0)	1.0278 (0)
1.5	4.0437 (3)	6.5302 (-1)	1.0082 (0)	1.0096 (0)
2.0	8.0532 (3)	7.4437 (-2)	9.8428 (-1)	9.9726 (-1)

+ Numbers in parentheses represent the power of ten by which each entry is multiplied.

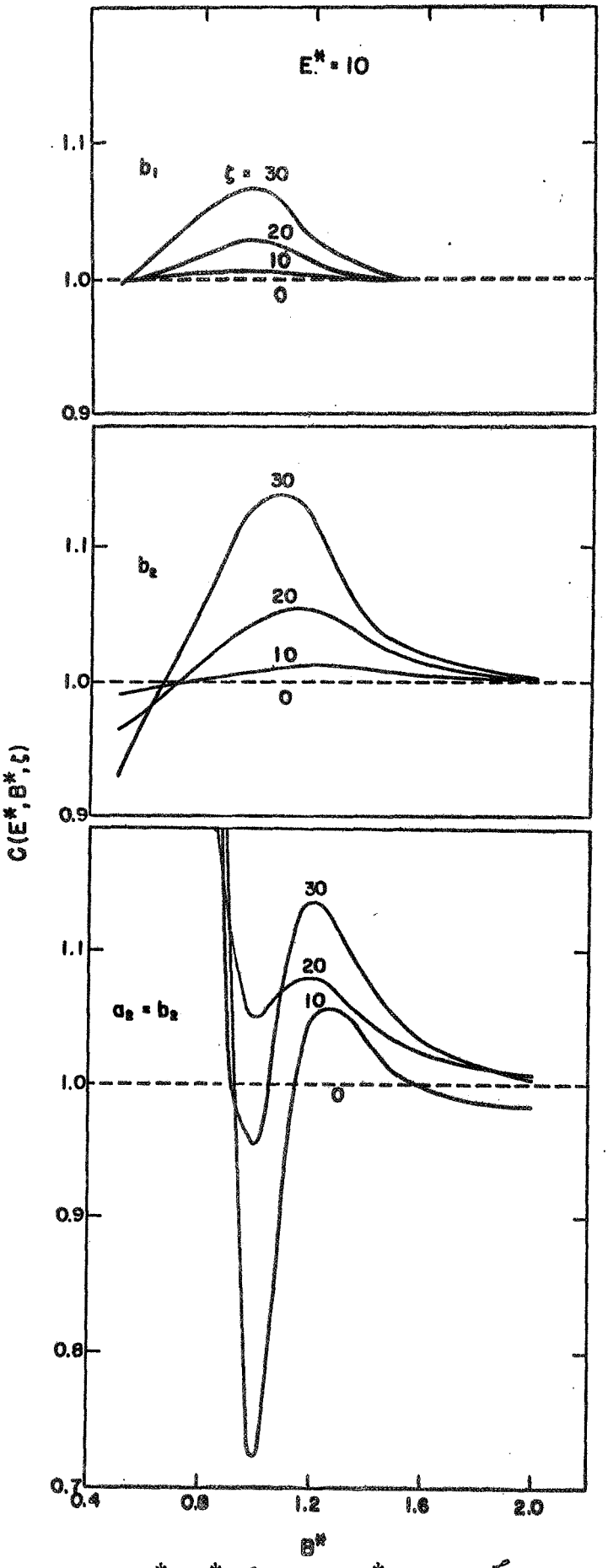

Figure 3. $C(E^*, b^*, \zeta)$ for $E^* = 10$, ~~$\zeta = 10$~~ as a function of b^*. Nonzero anisotropy parameters (Eq. (19)) are indicated in each frame.

it emphasizes the importance of the moment of inertia ratio, $M\sigma^2/I$, in determining the accuracy of the SA.

Drawing on the previously mentioned results of papers X and XII, it is now possible (in the limit of large $\bar{\ell}$) to consolidate the various first-order semiclassical perturbation treatments into the hierarchy illustrated [23] in Figure 4.

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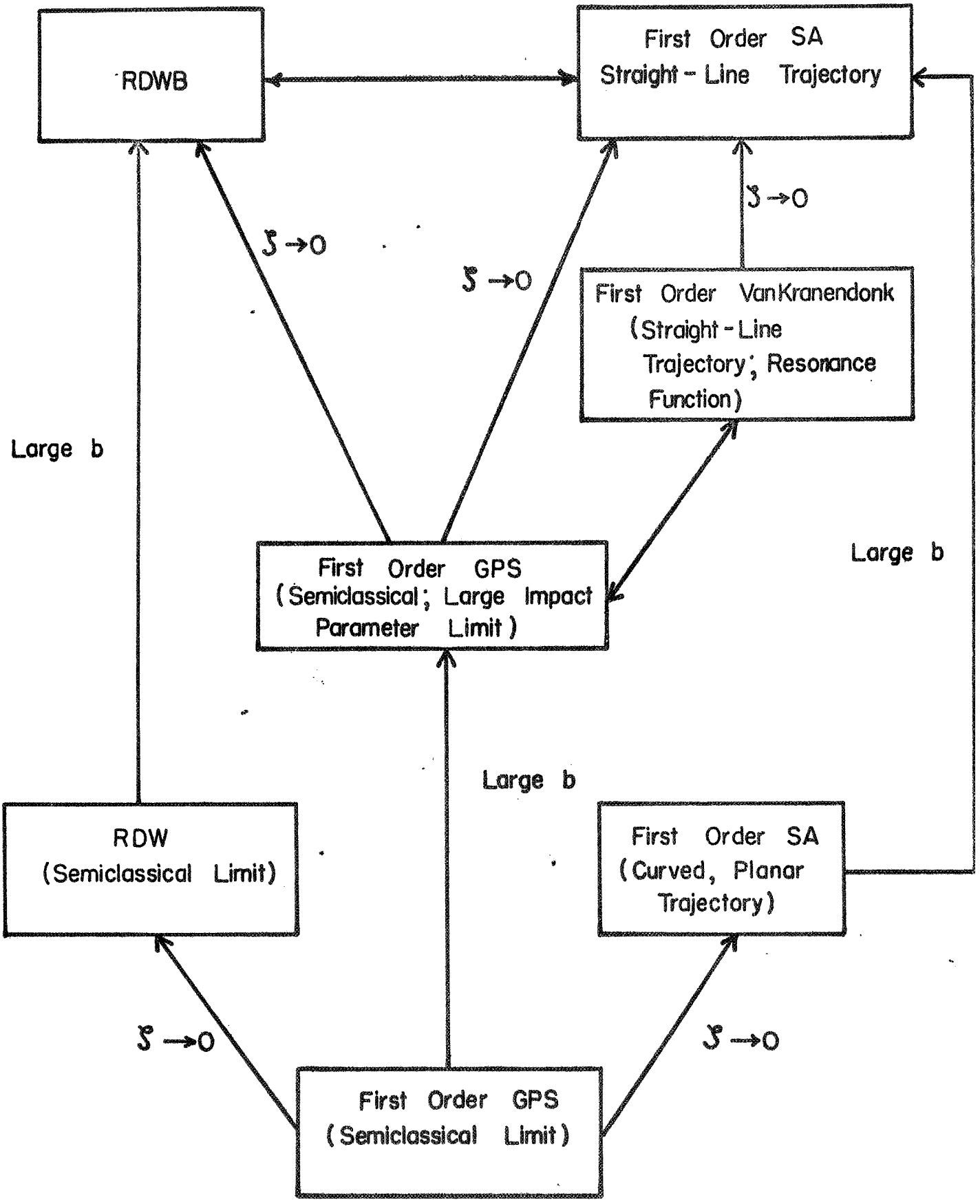

Figure 4. Hierarchy relating various first-order semiclassical treatments of rotational inelasticity (in the high $\bar{\ell}$ limit). For abbreviations, see text.

APPENDIX A

For atom-diatom scattering, the starting point for the Van Kranendonk treatment[6] is the usual first order TD perturbation formula[21] for the degeneracy-averaged probability of scattering from rotor state $\bar{\ell}$ to ℓ.

$$P(\bar{\ell};\ell;\bar{\lambda}) = \frac{1}{(2\bar{\ell}+1)} \sum_{\mu\bar{\mu}} \left| \frac{i}{\hbar} \int_{-\infty}^{+\infty} \langle \ell\mu | v^{(1)}(L,r) | \bar{\ell}\bar{\mu} \rangle e^{i\omega t} dt \right|^2 . \tag{A1}$$

Here μ and $\bar{\mu}$ are respectively the final and initial rotor orientation quantum numbers, ω is the transition frequency $((E_{\ell}-E_{\bar{\ell}})/\hbar)$, and $\langle \ell\mu | v^{(1)}(L,r) | \bar{\ell}\bar{\mu} \rangle$ is the matrix element of the L^{th} anisotropic portion of the interaction potential between the final ($\ell\mu$) and initial ($\bar{\ell}\bar{\mu}$) rotor states.

For simplicity, the potential is here assumed to have an anisotropic portion given by

$$v^{(1)}(L,r) = \pm \frac{C_n}{r^n} P_L(\cos\Theta) \tag{A2}$$

where L = 1 or 2. It is convenient to introduce the coordinate system of Bernstein and Kramer[11] and to expand the P_L Legendre function in terms of the angles θ, φ, θ', φ'. Thus,

$$v^{(1)}(L,r) = \frac{4\pi}{(2L+1)} \frac{C_n}{r^n} \sum_m Y_L^m(\theta,\varphi)^* \, Y_L^m(\theta',\varphi') \tag{A3}$$

and, from Eq. (A1),

$$P(\bar{l};\bar{l}\pm L;\bar{\lambda}) = \frac{16\pi^2 C_n^2}{(2L+1)^2(2\bar{l}+1)\hbar^2}\sum_{\mu\bar{\mu}}\left|\sum_m \langle l\mu|Y_l^m(\theta',\varphi'|\bar{l}\bar{\mu}\rangle\int_{-\infty}^{+\infty} Y_L^m(\theta,\varphi)^* e^{i\omega t}\frac{dt}{r^n}\right|^2. \tag{A4}$$

The first-order SA results from evaluating (A4) in the limit $\omega \longrightarrow 0$ (i.e., energetically degenerate rotor states). The Van Kranendonk treatment retains $\omega \neq 0$ but assumes a straight-line trajectory. Thus, introducing the usual straight-line approximations:

$$r = (b^2 + v^2t^2)^{1/2} \quad ; \quad \sin\theta = b/r \quad ; \quad \varphi = 0 \tag{A5}$$

and the new variables:

$$x = \omega b/v \quad ; \quad z = vt/b \tag{A6}$$

Eq. (A4) becomes:

$$P(\bar{l};\bar{l}\pm L;\bar{\lambda}) = \frac{16\pi^2 C_n^2}{(2L+1)^2(2\bar{l}+1)\hbar^2 b^{2n-2} v^2}\sum_{\mu\bar{\mu}}\left|\sum_m \langle l\mu|Y_L^m(\theta',\varphi')|\bar{l}\bar{\mu}\rangle \times \int_{-\infty}^{+\infty} e^{ixz}\, Y_L^m(\theta,0)\frac{dz}{(1+z^2)^{1/2}}\right|^2. \tag{A7}$$

The integrals over $\hat{z}$ for m = - L, - L + 1, ... , + L are easily evaluated[22] in terms of modified Bessel functions of the second kind in the variable x (which will be shown to be closely related to ξ of Eq. (15)), and

$$\langle \ell\mu | Y_L^m(\theta',\varphi') | \bar{\ell}\bar{\mu} \rangle = \left[\frac{(2L+1)(2\ell+1)(2\bar{\ell}+1)}{4\pi}\right]^{1/2} \begin{pmatrix} \ell & L & \bar{\ell} \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell & L & \bar{\ell} \\ -\mu & m & \bar{\mu} \end{pmatrix}. \tag{A8}$$

Thus, after simplification, making use of the orthogonality properties of the 3-j symbols and invoking the large $\bar{\ell}$ limit:

$$P(\bar{\ell};\bar{\ell}\pm 1;\bar{\lambda}) = \frac{\pi C_n^2 X^n}{3\hbar^2 2^{n-1} b^{2n-2} v^2 \left[\Gamma\left(\frac{n+1}{2}\right)\right]^2} \left[K^2_{n/2}(X) + K^2_{\frac{n}{2}-1}(X)\right] \tag{A9}$$

$$P(\bar{\ell};\bar{\ell}\pm 2;\bar{\lambda}) = \frac{3\pi C_n^2}{10\hbar^2 b^{2n-2} v^2 2^n n^2 \left[\Gamma\left(\frac{n}{2}\right)\right]^2} \left\{ \frac{3}{2} X^{n+1} K^2_{\frac{n+1}{2}}(X) \right.$$

$$+ 6 X^{n+1} K^2_{\frac{n-1}{2}}(X) + \frac{1}{8}\left[(n+3) X^{\frac{n-1}{2}} K_{\frac{n-1}{2}}(X) \right. \tag{A10}$$

$$\left. \left. - 3 X^{\frac{n+1}{2}} K_{\frac{n-3}{2}}(X) - 3 X^{\frac{n+1}{2}} K_{\frac{n+1}{2}}(X)\right]^2 \right\}.$$

As noted previously, the first order SA is obtained in the limit ω (or X) $\longrightarrow$ 0 . For small x ,

$$K_n(x) \sim \frac{2^{n-1}}{x^n}\,\Gamma(n), \tag{A11}$$

so that

$$P(\bar{\ell};\bar{\ell}\pm 1;\bar{\lambda})_{x=0} = \frac{\pi C_n^2}{6\hbar^2 b^{2n-2} v^2}\left[\frac{\Gamma(n/2)}{\Gamma(\frac{n+1}{2})}\right]^2 \tag{A12}$$

and

$$P(\bar{\ell};\bar{\ell}\pm 2;\bar{\lambda})_{x=0} = \frac{3\pi C_n^2}{40\hbar^2 b^{2n-2} v^2}\left[\frac{n^2-3n+3}{n^2}\right]\left[\frac{\Gamma(\frac{n-1}{2})}{\Gamma(n/2)}\right]^2. \tag{A13}$$

Thus, for the potential (A2), the Van Kranendonk "resonance functions" which measure the deviation from the SA in the straight-line trajectory approximation are:

$$R(x) = \frac{P(\bar{\ell};\bar{\ell}\pm 1;\bar{\lambda})}{P(\bar{\ell};\bar{\ell}\pm 1;\bar{\lambda})_{x=0}} = \frac{x^n}{2^{n-2}\left[\Gamma(\frac{n}{2})\right]^2}\left[K^2_{\frac{n}{2}}(x) + K^2_{\frac{n}{2}-1}(x)\right] \quad ; (L=1) \tag{A14}$$

and

$$R(x) = \frac{P(\bar{l};\bar{l}\pm 2;\bar{\lambda})}{P(\bar{l};\bar{l}\pm 2;\bar{\lambda})_{x=0}} = \frac{1}{2^{n-2}(n^2-3n+3)\left[\Gamma\left(\frac{n-1}{2}\right)\right]^2}\left\{\frac{3}{2}x^{n+1}K^2_{\frac{n+1}{2}}(x)\right.$$
$$\left. + 6\,x^{n+1}K^2_{\frac{n-1}{2}}(x) + \frac{1}{8}\left[(n+3)x^{\frac{n-1}{2}}K_{\frac{n-1}{2}}(x) - 3x^{\frac{n+1}{2}}K_{\frac{n-3}{2}}(x) - 3x^{\frac{n+1}{2}}K_{\frac{n+1}{2}}(x)\right]^2\right\}. \quad \text{(A15)}$$

$$(L=2)$$

(These expressions are believed to be new; previously published resonance functions[6,21] refer to dipole-dipole potentials.)

It will now be shown that expressions identical to Eqs. (A9) - (A15) result from the asymptotic (large impact parameter) limit of the GPS development. From Eqs. (2) and (A2), in the limit of large b,

$$P(\bar{l};\bar{l}\pm L;\bar{\lambda}) = \frac{16\pi^2 M^2 C_n^2 (2\bar{l}\pm L+1)}{(2L+1)^3 \hbar^4 k^2}\sum_{\alpha}\left|\sum_{\alpha}(i)^{\alpha}\begin{pmatrix}(\bar{l}\pm L) & \bar{l} & L\\ 0 & \alpha & -\alpha\end{pmatrix} I_L(\alpha,\alpha)\right|^2 \quad \text{(A16)}$$

where

$$I_L(\alpha,\alpha) = \int_{r_0}^{\infty}\frac{\alpha\, r}{r^{n-1}(r^2-b^2)^{1/2}}\left[Y_L^{\alpha}(\Psi,0)\,Y_L^{\alpha}(\theta,0) + Y_L^{\alpha}(2\Psi^{(0)}-\Psi,0)\,Y_L^{\alpha}(2\theta^{(0)}-\theta,0)\right]. \quad \text{(A17)}$$

By expanding the sum over α in Eq. (A16), evaluating the 3-j symbols in the high $\bar{l}$ limit, and making use of the properties of the spherical harmonics, one finds:

$$P(\bar{\ell};\bar{\ell}\pm 1;\bar{\lambda}) = \frac{16\pi^2 M^2 C_n^2}{27\hbar^4\bar{k}^2}\left\{\left[I_1(1,0)\right]^2 + \left[I_1(0,1)\right]^2\right\} \tag{A18}$$

and

$$P(\bar{\ell};\bar{\ell}\pm 2;\bar{\lambda}) = \frac{4\pi^2 M^2 C_n^2}{125\hbar^4\bar{k}^2}\left\{2\left[\left(\tfrac{3}{2}\right)^{1/2} I_2(0,2) - I_2(2,2)\right]^2\right.$$

$$\left. + \left[\left(\tfrac{3}{2}\right)^{1/2} I_2(0,0) - I_2(2,0)\right]^2 + 8\left[I_2(1,1)\right]^2\right\}. \tag{A19}$$

For large b (small angles of deflection $\chi = \pi - 2\theta^{(0)}$) the angles, Eqs. (3) - (6), can be evaluated to yield:

$$\theta = \frac{\pi}{2} - \cos^{-1}\left(\frac{b}{r}\right) \quad ; \quad \theta^{(0)} = \frac{\pi}{2} \tag{A20}$$

and

$$\psi = \frac{\xi}{b}\left(r^2 - b^2\right)^{1/2} \quad ; \quad \psi^{(0)} = 0. \tag{A21}$$

Utilizing these limiting forms in Eq. (A17), it is readily shown that

$$I_1(1,0) = \frac{3\,\xi^{n/2}}{\sqrt{\pi}\, b^{n-1}\, 2^{\frac{n+3}{2}}\,\Gamma\left(\frac{n+1}{2}\right)} K_{\frac{n}{2}-1}(\xi) \tag{A22}$$

$$I_1(0,1) = \frac{3\xi^{n/2}}{\sqrt{\pi}\, b^{n-1} 2^{\frac{n+3}{2}} \Gamma\left(\frac{n+1}{2}\right)} K_{\frac{n}{2}}(\xi) \tag{A23}$$

$$\left[\left(\frac{3}{2}\right)^{1/2} I_2(0,2) - I_2(2,2)\right] = \frac{15(2\xi)^{\frac{n+1}{2}}}{\sqrt{\pi}\, b^{n-1} 2^{\frac{n+7}{2}} \Gamma\left(\frac{n+2}{2}\right)} K_{\frac{n+1}{2}}(2\xi) \tag{A24}$$

$$\left[\left(\frac{3}{2}\right)^{1/2} I_2(0,0) - I_2(2,0)\right] = \frac{5\sqrt{3}}{\sqrt{\pi}\, b^{n-1} 2^{\frac{n+3}{2}}} \left[\frac{(2\xi)^{\frac{n-1}{2}}}{\Gamma\left(\frac{n}{2}\right)} K_{\frac{n-1}{2}}(2\xi) - \frac{3(2\xi)^{\frac{n+1}{2}}}{8\Gamma\left(\frac{n+2}{2}\right)} \times K_{\frac{n+1}{2}}(2\xi)\right] \tag{A25}$$

and

$$I_2(1,1) = \frac{15(2\xi)^{\frac{n+1}{2}}}{\sqrt{\pi}\, b^{n-1} 2^{\frac{n+7}{2}} \Gamma\left(\frac{n+2}{2}\right)} K_{\frac{n-1}{2}}(2\xi). \tag{A26}$$

Inserting these into Eqs. (A18) and (A19), it is found after simplification that,

$$P(\ell; \bar{\ell}\pm 1; \bar{\lambda}) = \frac{\pi M^2 C_n^2 \xi^n}{3\hbar^4 k^2 2^{n-1} b^{2n-2} \left[\Gamma\left(\frac{n+1}{2}\right)\right]^2} \left[K^2_{\frac{n}{2}}(\xi) + K^2_{\frac{n}{2}-1}(\xi)\right] \tag{A27}$$

$$P(\bar{\ell};\bar{\ell}\pm 2;\bar{\lambda}) = \frac{3\pi M^2 C_n^2}{10\hbar^4\bar{k}^2 b^{2n-2} 2^n n^2\left[\Gamma\left(\frac{n}{2}\right)\right]^2}\left\{\frac{3}{2}(2\xi)^{n+1}K^2_{\frac{n+1}{2}}(2\xi)\right.$$

$$+6(2\xi)^{n+1}K^2_{\frac{n-1}{2}}(2\xi)+\frac{1}{8}\left[(n+3)(2\xi)^{\frac{n-1}{2}}K_{\frac{n-1}{2}}(2\xi)\right.$$

$$\left.\left.-3(2\xi)^{\frac{n+1}{2}}K_{\frac{n-3}{2}}(2\xi)-3(2\xi)^{\frac{n+1}{2}}K_{\frac{n+1}{2}}(2\xi)\right]^2\right\}. \qquad \text{(A28)}$$

Noting that $V^2 = \hbar^2\bar{k}^2/M^2$ and, in the high $\bar{\ell}$ limit, $X = (\ell-\bar{\ell})\,\xi$, it is seen that Eqs. (A27) and (A28) are identical, respectively, to Eqs. (A9) and (A10).

APPENDIX B

Tables of $S^{(L)}_{n,\alpha,A}$ Integrals

(Defined in Eq. (25))

$S^{(1)}_{12,1,1}$

ZETA = 0

E* / B*	1	3	10	30
.50	.00000	.00000	.00000	.00000
.90	.00000	.00000	.00000	.00000
1.00	.00000	.00000	.00000	.00000
1.10	.00000	.00000	.00000	.00000
1.20	.00000	.00000	.00000	.00000
1.30	.00000	.00000	.00000	.00000
1.50	.00000	.00000	.00000	.00000
2.00	.00000	.00000	.00000	.00000

ZETA = 10

E* / B*	1	3	10	30
.50	.01564	.02210	.02591	
.90	.02299	.02051	.01322	
1.00	.02252	.01559	.00611	
1.10	.02043	.00897	.00090	
1.20	.01629	.00176	-.00054	
1.30	.00985	-.00290	-.00029	
1.50	-.00715	-.00043	-.00003	
2.00	-.00001	-.00000	-.00000	

ZETA = 20

E* / B*	1	3	10	30
.50	-.00021	.03136	.04833	
.90	.01603	.03501	.02563	
1.00	.02119	.02776	.01188	
1.10	.02447	.01643	.00174	
1.20	.02359	.00320	-.00103	
1.30	.01624	-.00502	-.00054	
1.50	-.01099	-.00065	-.00006	
2.00	-.00001	-.00000	-.00000	

ZETA = 30

E* / B*	1	3	10	30
.50	-.01381	.02309	.06431	.08846
.90	-.00883	.03987	.03650	.02182
1.00	.00030	.03428	.01700	.00520
1.10	.01141	.02139	.00246	.00007
1.20	.01980	.00413	-.00142	-.00027
1.30	.01808	-.00599	-.00074	-.00011
1.50	-.01089	-.00061	-.00007	-.00001
2.00	-.00000	-.00000	-.00000	-.00000

$S^{(1)}_{12,1,0}$

ZETA = 0

B* \ E*	1	3	10	30
.50	.00000	.00000	.00000	.00000
.90	.00000	.00000	.00000	.00000
1.00	.00000	.00000	.00000	.00000
1.10	.00000	.00000	.00000	.00000
1.20	.00000	.00000	.00000	.00000
1.30	.00000	.00000	.00000	.00000
1.50	.00000	.00000	.00000	.00000
2.00	.00000	.00000	.00000	.00000

ZETA = 10

B* \ E*	1	3	10	30
.50	.04090	.05118	.05287	
.90	.02397	.01708	.00938	
1.00	.01797	.00956	.00433	
1.10	.01176	.00444	.00266	
1.20	.00609	.00303	.00176	
1.30	.00227	.00469	.00078	
1.50	.00908	.00069	.00014	
2.00	.00002	.00001	.00001	

ZETA = 20

B* \ E*	1	3	10	30
.50	-.00220	.07128	.09810	
.90	.01493	.02825	.01795	
1.00	.01518	.01632	.00828	
1.10	.01253	.00767	.00506	
1.20	.00756	.00523	.00330	
1.30	.00287	.00750	.00145	
1.50	.01157	.00093	.00025	
2.00	.00001	.00001	.00001	

ZETA = 30

B* \ E*	1	3	10	30
.50	-.03598	.04991	.12934	.15972
.90	-.01126	.03036	.02506	.01621
1.00	-.00242	.01877	.01157	.00808
1.10	.00355	.00910	.00702	.00440
1.20	.00452	.00627	.00446	.00200
1.30	.00201	.00795	.00191	.00086
1.50	.00913	.00074	.00032	.00018
2.00	.00000	.00001	.00001	.00001

$S^{(1)}_{12,0,1}$

ZETA = 0

B* \ E*	1	3	10	30
.50	.02252	.04594	.10845	.25705
.90	.03588	.06388	.11405	.18312
1.00	.03792	.06267	.09167	.11020
1.10	.03918	.05766	.05916	.05037
1.20	.03945	.04740	.02786	.01994
1.30	.03839	.03030	.01073	.00797
1.50	.02932	.00346	.00178	.00154
2.00	.00010	.00007	.00006	.00006

ZETA = 10

B* \ E*	1	3	10	30
.50	-.00013	.03314	.10172	
.90	.01308	.05594	.11181	
1.00	.01870	.05755	.09050	
1.10	.02472	.05497	.05845	
1.20	.03031	.04587	.02739	
1.30	.03402	.02853	.01050	
1.50	.02509	.00309	.00173	
2.00	.00006	.00006	.00006	

ZETA = 20

B* \ E*	1	3	10	30
.50	-.02104	.00257	.08253	
.90	-.02375	.03486	.10527	
1.00	-.01683	.04364	.08710	
1.10	-.00550	.04758	.05638	
1.20	.00920	.04172	.02604	
1.30	.02333	.02389	.00984	
1.50	.01541	.00219	.00159	
2.00	.00001	.00004	.00005	

ZETA = 30

B* \ E*	1	3	10	30
.50	.00050	-.02751	.05366	.22186
.90	-.02711	.00754	.09497	.17634
1.00	-.03094	.02463	.08174	.10651
1.10	-.02663	.03720	.05314	.04826
1.20	-.01134	.03596	.02396	.01890
1.30	.01094	.01794	.00885	.00748
1.50	.00571	.00126	.00138	.00142
2.00	.00000	.00002	.00004	.00005

$S^{(1)}_{12,0,0}$

ZETA = 0

B* \ E*	1	3	10	30
.50	.05892	.10428	.21336	.44359
.90	.03676	.04789	.05770	.05904
1.00	.02919	.03016	.02180	.01130
1.10	.02077	.01218	.00007	-.00095
1.20	.01149	-.00391	-.00370	-.00096
1.30	.00133	-.01224	-.00149	-.00034
1.50	-.02149	-.00116	-.00013	-.00003
2.00	-.00002	-.00000	-.00000	-.00000

ZETA = 10

B* \ E*	1	3	10	30
.50	-.00166	.07383	.19914	
.90	.01185	.04065	.05590	
1.00	.01280	.02654	.02111	
1.10	.01151	.01075	-.00001	
1.20	.00735	-.00401	-.00356	
1.30	.00006	-.01064	-.00141	
1.50	-.01579	-.00085	-.00012	
2.00	-.00000	-.00000	-.00000	

ZETA = 20

B* \ E*	1	3	10	30
.50	-.05494	.00204	.15871	
.90	-.02625	.02191	.05071	
1.00	-.01562	.01707	.01914	
1.10	-.00630	.00705	-.00024	
1.20	-.00110	-.00423	-.00316	
1.30	-.00242	-.00681	-.00119	
1.50	-.00511	-.00022	-.00009	
2.00	.00000	-.00000	-.00000	

ZETA = 30

B* \ E*	1	3	10	30
.50	.00426	-.06634	.09838	.37702
.90	-.02619	-.00113	.04271	.05444
1.00	-.02373	.00502	.01613	.01012
1.10	-.01611	.00238	-.00058	-.00091
1.20	-.00741	-.00439	-.00257	-.00084
1.30	-.00425	-.00270	-.00087	-.00029
1.50	.00278	.00023	-.00006	-.00003
2.00	.00000	.00000	-.00000	-.00000

$S^{(2)}_{12,2,2}$

ZETA = 0

B* \ E*	1	3	10	30
.50	.00000	.00000	.00000	.00000
.90	.00000	.00000	.00000	.00000
1.00	.00000	.00000	.00000	.00000
1.10	.00000	.00000	.00000	.00000
1.20	.00000	.00000	.00000	.00000
1.30	.00000	.00000	.00000	.00000
1.50	.00000	.00000	.00000	.00000
2.00	.00000	.00000	.00000	.00000

ZETA = 10

B* \ E*	1	3	10	30
.50	.00922	.00996	.00645	
.90	.02112	.01082	.00336	
1.00	.02090	.00751	.00180	
1.10	.01807	.00410	.00109	
1.20	.01271	.00225	.00069	
1.30	.00641	.00226	.00033	
1.50	.00472	.00046	.00007	
2.00	.00003	.00001	.00000	

ZETA = 20

B* \ E*	1	3	10	30
.50	.00100	.02027	.02238	
.90	.01274	.03103	.01245	
1.00	.02047	.02315	.00668	
1.10	.02683	.01315	.00400	
1.20	.02634	.00718	.00248	
1.30	.01647	.00671	.00118	
1.50	.01108	.00111	.00025	
2.00	.00004	.00003	.00001	

ZETA = 30

B* \ E*	1	3	10	30
.50	.00778	.01270	.03957	.03467
.90	.00793	.04075	.02479	.00997
1.00	.00681	.03497	.01339	.00546
1.10	.01254	.02168	.00793	.00304
1.20	.02249	.01198	.00476	.00147
1.30	.02123	.01010	.00218	.00068
1.50	.01308	.00137	.00044	.00017
2.00	.00004	.00003	.00002	.00001

$S^{(2)}_{12,2,1}$

ZETA = 0

B* \ E*	1	3	10	30
.50	.00000	.00000	.00000	.00000
.90	.00000	.00000	.00000	.00000
1.00	.00000	.00000	.00000	.00000
1.10	.00000	.00000	.00000	.00000
1.20	.00000	.00000	.00000	.00000
1.30	.00000	.00000	.00000	.00000
1.50	.00000	.00000	.00000	.00000
2.00	.00000	.00000	.00000	.00000

ZETA = 10

B* \ E*	1	3	10	30
.50	.03375	.03267	.01884	
.90	.03112	.01332	.00361	
1.00	.02380	.00704	.00139	
1.10	.01516	.00281	.00017	
1.20	.00728	.00025	-.00024	
1.30	.00220	-.00223	-.00014	
1.50	-.00678	-.00041	-.00002	
2.00	-.00001	-.00000	-.00000	

ZETA = 20

B* \ E*	1	3	10	30
.50	.00364	.06437	.06468	
.90	.01629	.03602	.01304	
1.00	.02010	.02003	.00497	
1.10	.01899	.00800	.00059	
1.20	.01196	.00047	-.00084	
1.30	.00371	-.00577	-.00045	
1.50	-.01327	-.00075	-.00005	
2.00	-.00001	-.00000	-.00000	

ZETA = 30

B* \ E*	1	3	10	30
.50	.02847	.03775	.11248	.08983
.90	.01259	.04340	.02494	.00879
1.00	.00715	.02709	.00940	.00217
1.10	.00731	.01124	.00103	-.00005
1.20	.00749	.00021	-.00148	-.00019
1.30	.00263	-.00728	-.00075	-.00008
1.50	-.01321	-.00069	-.00008	-.00001
2.00	-.00001	-.00000	-.00000	-.00000

$S^{(2)}_{12,2,0}$

ZETA = 0

B* \ E*	1	3	10	30
.50	.00000	.00000	.00000	.00000
.90	.00000	.00000	.00000	.00000
1.00	.00000	.00000	.00000	.00000
1.10	.00000	.00000	.00000	.00000
1.20	.00000	.00000	.00000	.00000
1.30	.00000	.00000	.00000	.00000
1.50	.00000	.00000	.00000	.00000
2.00	.00000	.00000	.00000	.00000

ZETA = 10

B* \ E*	1	3	10	30
.50	.04355	.03658	.01788	
.90	.00222	-.00148	-.00082	
1.00	-.00528	-.00290	-.00067	
1.10	-.00888	-.00206	-.00036	
1.20	-.00809	-.00088	-.00012	
1.30	-.00441	.00053	-.00005	
1.50	.00230	.00004	-.00002	
2.00	-.00002	-.00001	-.00000	

ZETA = 20

B* \ E*	1	3	10	30
.50	.00489	.06839	.06027	
.90	-.00152	-.00682	-.00345	
1.00	-.00815	-.01058	-.00271	
1.10	-.01576	-.00752	-.00151	
1.20	-.01854	-.00354	-.00060	
1.30	-.01229	-.00049	-.00028	
1.50	-.00015	-.00030	-.00008	
2.00	-.00002	-.00002	-.00001	

ZETA = 30

B* \ E*	1	3	10	30
.50	.03653	.03618	.10166	.07021
.90	.00218	-.01302	-.00803	-.00325
1.00	-.00182	-.01859	-.00606	-.00204
1.10	-.00791	-.01379	-.00343	-.00098
1.20	-.01671	-.00689	-.00158	-.00045
1.30	-.01637	-.00304	-.00075	-.00022
1.50	-.00299	-.00063	-.00019	-.00006
2.00	-.00002	-.00002	-.00001	-.00000

$S^{(2)}_{12,1,2}$

ZETA = 0

B* \ E*	1	3	10	30
.50	.00000	.00000	.00000	.00000
.90	.00000	.00000	.00000	.00000
1.00	.00000	.00000	.00000	.00000
1.10	.00000	.00000	.00000	.00000
1.20	.00000	.00000	.00000	.00000
1.30	.00000	.00000	.00000	.00000
1.50	.00000	.00000	.00000	.00000
2.00	.00000	.00000	.00000	.00000

ZETA = 10

B* \ E*	1	3	10	30
.50	.00016	.02088	.03487	
.90	.01673	.03793	.02864	
1.00	.02357	.03187	.01366	
1.10	.02864	.01953	.00210	
1.20	.02859	.00413	-.00103	
1.30	.02008	-.00497	-.00056	
1.50	-.01121	-.00068	-.00006	
2.00	-.00001	-.00000	-.00000	

ZETA = 20

B* \ E*	1	3	10	30
.50	-.00011	.00304	.05262	
.90	-.01908	.03904	.05102	
1.00	-.01775	.04074	.02466	
1.10	-.00642	.02856	.00370	
1.20	.01171	.00599	-.00176	
1.30	.02034	-.00634	-.00091	
1.50	-.00966	-.00053	-.00009	
2.00	-.00000	-.00000	-.00000	

ZETA = 30

B* \ E*	1	3	10	30
.50	-.00003	-.01628	.04570	.11780
.90	.01069	.01018	.06317	.04569
1.00	-.00092	.02669	.03136	.01083
1.10	-.01451	.02630	.00454	.00021
1.20	-.01056	.00570	-.00204	-.00049
1.30	.00962	-.00476	-.00099	-.00020
1.50	-.00333	-.00019	-.00009	-.00002
2.00	-.00000	-.00000	-.00000	-.00000

$S^{(2)}_{12,1,1}$

ZETA = 0

B* \ E*	1	3	10	30
.50	.00000	.00000	.00000	.00000
.90	.00000	.00000	.00000	.00000
1.00	.00000	.00000	.00000	.00000
1.10	.00000	.00000	.00000	.00000
1.20	.00000	.00000	.00000	.00000
1.30	.00000	.00000	.00000	.00000
1.50	.00000	.00000	.00000	.00000
2.00	.00000	.00000	.00000	.00000

ZETA = 10

B* \ E*	1	3	10	30
.50	-.00078	.06619	.09821	
.90	.02189	.04232	.02745	
1.00	.02366	.02580	.01305	
1.10	.02049	.01245	.00793	
1.20	.01275	.00827	.00499	
1.30	.00483	.01062	.00218	
1.50	.01644	.00138	.00039	
2.00	.00002	.00002	.00002	

ZETA = 20

B* \ E*	1	3	10	30
.50	.00153	.00556	.14512	
.90	-.02719	.03771	.04687	
1.00	-.02130	.02803	.02239	
1.10	-.00929	.01493	.01342	
1.20	.00017	.01044	.00804	
1.30	.00107	.01091	.00334	
1.50	.00925	.00079	.00054	
2.00	.00000	.00001	.00002	

ZETA = 30

B* \ E*	1	3	10	30
.50	-.00204	-.05248	.12008	.29010
.90	.01762	.00181	.05405	.04518
1.00	.00287	.01186	.02629	.02260
1.10	-.00880	.00971	.01551	.01184
1.20	-.00745	.00833	.00859	.00518
1.30	-.00266	.00610	.00329	.00217
1.50	.00052	.00016	.00047	.00044
2.00	.00000	.00000	.00001	.00002

$S^{(2)}_{12,1,0}$

ZETA = 0

B* \ E*	1	3	10	30
.50	.00000	.00000	.00000	.00000
.90	.00000	.00000	.00000	.00000
1.00	.00000	.00000	.00000	.00000
1.10	.00000	.00000	.00000	.00000
1.20	.00000	.00000	.00000	.00000
1.30	.00000	.00000	.00000	.00000
1.50	.00000	.00000	.00000	.00000
2.00	.00000	.00000	.00000	.00000

ZETA = 10

B* \ E*	1	3	10	30
.50	-.00339	.07026	.08769	
.90	-.00169	-.00996	-.01118	
1.00	-.00906	-.01611	-.00691	
1.10	-.01673	-.01246	-.00146	
1.20	-.02033	-.00391	-.00012	
1.30	-.01567	-.00102	.00001	
1.50	-.00027	.00004	.00001	
2.00	.00001	.00000	.00000	

ZETA = 20

B* \ E*	1	3	10	30
.50	.00533	-.00064	.12462	
.90	-.00035	-.01628	-.02195	
1.00	.00408	-.02456	-.01345	
1.10	.00102	-.02028	-.00274	
1.20	-.01035	-.00593	.00006	
1.30	-.01680	.00174	.00016	
1.50	.00547	.00038	.00003	
2.00	.00000	.00000	.00000	

ZETA = 30

B* \ E*	1	3	10	30
.50	-.00600	-.05620	.09378	.20518
.90	.00285	-.01142	-.03093	-.02070
1.00	.00375	-.02043	-.01881	-.00522
1.10	.00999	-.02071	-.00362	-.00043
1.20	.00707	-.00586	.00045	.00006
1.30	-.00828	.00319	.00038	.00004
1.50	.00415	.00024	.00005	.00001
2.00	.00000	.00000	.00000	.00000

$S^{(2)}_{12,0,2}$

ZETA = 0

B* \ E*	1	3	10	30
.50	.01558	.03539	.09224	.23727
.90	.04195	.08111	.15304	.25213
1.00	.04794	.08468	.12737	.15339
1.10	.05259	.08064	.08231	.06976
1.20	.05511	.06611	.03828	.02754
1.30	.05441	.04032	.01472	.01101
1.50	.03696	.00462	.00246	.00213
2.00	.00013	.00010	.00009	.00009

ZETA = 10

B* \ E*	1	3	10	30
.50	-.00701	.01100	.07644	
.90	-.00979	.05460	.14481	
1.00	-.00327	.06628	.12296	
1.10	.00834	.07061	.07965	
1.20	.02399	.06060	.03659	
1.30	.03870	.03477	.01390	
1.50	.02541	.00350	.00228	
2.00	.00005	.00006	.00008	

ZETA = 20

B* \ E*	1	3	10	30
.50	.01312	-.01426	.03743	
.90	.01075	.00510	.12254	
1.00	-.00220	.02798	.11100	
1.10	-.01313	.04842	.07251	
1.20	-.00941	.04852	.03220	
1.30	.01405	.02388	.01183	
1.50	.00981	.00190	.00185	
2.00	.00003	.00003	.00005	

ZETA = 30

B* \ E*	1	3	10	30
.50	-.00349	.00428	-.00468	.15235
.90	.02253	-.01872	.09231	.22770
1.00	.03127	-.00098	.09456	.14001
1.10	.02187	.02754	.06290	.06232
1.20	.00002	.03676	.02662	.02395
1.30	.00240	.01557	.00937	.00933
1.50	.00492	.00126	.00139	.00172
2.00	.00003	.00003	.00004	.00006

$S^{(2)}_{12,0,1}$

ZETA = 0

B* \ E*	1	3	10	30
.50	.05696	.11181	.25164	.56621
.90	.05980	.08370	.10507	.10871
1.00	.05120	.05569	.04044	.02059
1.10	.03854	.02297	.00014	-.00169
1.20	.02207	-.00717	-.00646	-.00170
1.30	.00256	-.02015	-.00258	-.00060
1.50	-.03398	-.00189	-.00022	-.00006
2.00	-.00003	-.00001	-.00000	-.00000

ZETA = 10

B* \ E*	1	3	10	30
.50	-.02570	.03179	.20550	
.90	-.01644	.05107	.09622	
1.00	-.00709	.03844	.03704	
1.10	.00140	.01609	-.00029	
1.20	.00423	-.00778	-.00586	
1.30	-.00283	-.01469	-.00224	
1.50	-.01738	-.00089	-.00018	
2.00	-.00000	-.00000	-.00000	

ZETA = 20

B* \ E*	1	3	10	30
.50	.04804	-.04586	.09320	
.90	.01988	-.00453	.07313	
1.00	.00197	.00663	.02826	
1.10	-.00798	.00338	-.00132	
1.20	-.00722	-.00831	-.00441	
1.30	-.00651	-.00602	-.00147	
1.50	-.00147	-.00006	-.00010	
2.00	-.00001	-.00000	-.00000	

ZETA = 30

B* \ E*	1	3	10	30
.50	-.01278	.01933	-.02388	.34618
.90	.02896	-.02260	.04398	.08719
1.00	.03368	-.01068	.01741	.01527
1.10	.02063	-.00455	-.00240	-.00157
1.20	.00372	-.00769	-.00282	-.00123
1.30	-.00389	-.00232	-.00074	-.00039
1.50	-.00162	-.00021	-.00004	-.00003
2.00	-.00001	-.00000	-.00000	-.00000

$S^{(2)}_{12,0,0}$

ZETA = 0

B* \ E*	1	3	10	30
.50	.07363	.11855	.21347	.37901
.90	.00224	-.02646	-.08415	-.16325
1.00	-.01492	-.04900	-.08682	-.10555
1.10	-.02923	-.05695	-.05648	-.04672
1.20	-.03877	-.04594	-.02439	-.01816
1.30	-.04102	-.02001	-.00925	-.00726
1.50	-.00897	-.00236	-.00160	-.00142
2.00	-.00008	-.00006	-.00006	-.00006

ZETA = 10

B* \ E*	1	3	10	30
.50	-.03305	.02894	.16966	
.90	-.00319	-.02284	-.08215	
1.00	-.00198	-.04190	-.08519	
1.10	-.00747	-.05192	-.05560	
1.20	-.01894	-.04378	-.02410	
1.30	-.03023	-.02131	-.00912	
1.50	-.01461	-.00246	-.00156	
2.00	-.00004	-.00005	-.00005	

ZETA = 20

B* \ E*	1	3	10	30
.50	.06164	-.04898	.06584	
.90	.00597	-.00975	-.07570	
1.00	.00504	-.02309	-.08018	
1.10	.00937	-.03852	-.05279	
1.20	.00663	-.03728	-.02291	
1.30	-.01091	-.01882	-.00855	
1.50	-.00859	-.00161	-.00139	
2.00	-.00002	-.00003	-.00004	

ZETA = 30

B* \ E*	1	3	10	30
.50	-.01586	.02993	-.03555	.20704
.90	-.00311	.00543	-.06448	-.15530
1.00	-.01045	-.00346	-.07197	-.10054
1.10	-.00985	-.02317	-.04807	-.04431
1.20	.00215	-.02906	-.02052	-.01706
1.30	-.00091	-.01255	-.00741	-.00673
1.50	-.00163	-.00082	-.00113	-.00127
2.00	-.00002	-.00002	-.00003	-.00005

$S^{(2)}_{6,2,2}$

ZETA = 0

B* \ E*	1	3	10	30
.50	.00000	.00000	.00000	.00000
.90	.00000	.00000	.00000	.00000
1.00	.00000	.00000	.00000	.00000
1.10	.00000	.00000	.00000	.00000
1.20	.00000	.00000	.00000	.00000
1.30	.00000	.00000	.00000	.00000
1.50	.00000	.00000	.00000	.00000
2.00	.00000	.00000	.00000	.00000

ZETA = 10

B* \ E*	1	3	10	30
.50	.01332	.01161	.00560	
.90	.03227	.01718	.00615	
1.00	.03339	.01500	.00537	
1.10	.03130	.01230	.00488	
1.20	.02591	.01067	.00428	
1.30	.01883	.01069	.00338	
1.50	.01565	.00653	.00201	
2.00	.00263	.00160	.00072	

ZETA = 20

B* \ E*	1	3	10	30
.50	.00429	.02253	.01851	
.90	.02345	.04211	.02041	
1.00	.03303	.03770	.01753	
1.10	.04111	.03059	.01576	
1.20	.04233	.02591	.01355	
1.30	.03398	.02540	.01033	
1.50	.02784	.01251	.00564	
2.00	.00280	.00235	.00167	

ZETA = 30

B* \ E*	1	3	10	30
.50	.01010	.01650	.03123	.02012
.90	.01840	.05075	.03614	.01798
1.00	.02038	.04956	.03058	.01578
1.10	.02761	.04173	.02697	.01316
1.20	.03757	.03501	.02250	.01013
1.30	.03798	.03248	.01645	.00761
1.50	.03027	.01384	.00832	.00444
2.00	.00281	.00243	.00213	.00145

$S^{(2)}_{6,2,1}$

ZETA = 0

B* \ E*	1	3	10	30
.50	.00000	.00000	.00000	.00000
.90	.00000	.00000	.00000	.00000
1.00	.00000	.00000	.00000	.00000
1.10	.00000	.00000	.00000	.00000
1.20	.00000	.00000	.00000	.00000
1.30	.00000	.00000	.00000	.00000
1.50	.00000	.00000	.00000	.00000
2.00	.00000	.00000	.00000	.00000

ZETA = 10

B* \ E*	1	3	10	30
.50	.04782	.03974	.01771	
.90	.04845	.02420	.00739	
1.00	.03986	.01647	.00394	
1.10	.02894	.00904	.00074	
1.20	.01762	.00137	-.00102	
1.30	.00771	-.00701	-.00099	
1.50	-.01601	-.00431	-.00032	
2.00	-.00059	-.00014	-.00002	

ZETA = 20

B* \ E*	1	3	10	30
.50	.01466	.07037	.05642	
.90	.02817	.05087	.02319	
1.00	.03032	.03433	.01204	
1.10	.02755	.01768	.00196	
1.20	.01877	.00089	-.00326	
1.30	.00697	-.01539	-.00289	
1.50	-.02461	-.00587	-.00082	
2.00	-.00050	-.00014	-.00004	

ZETA = 30

B* \ E*	1	3	10	30
.50	.03603	.04661	.09069	.05615
.90	.02652	.05256	.03767	.01493
1.00	.02012	.03736	.01889	.00506
1.10	.01640	.01874	.00258	-.00008
1.20	.01212	-.00079	-.00505	-.00096
1.30	.00371	-.01648	-.00406	-.00068
1.50	-.02294	-.00503	-.00101	-.00021
2.00	-.00050	-.00013	-.00004	-.00001

$S^{(2)}_{6,2,0}$

ZETA = 0

B* \ E*	1	3	10	30
.50	.00000	.00000	.00000	.00000
.90	.00000	.00000	.00000	.00000
1.00	.00000	.00000	.00000	.00000
1.10	.00000	.00000	.00000	.00000
1.20	.00000	.00000	.00000	.00000
1.30	.00000	.00000	.00000	.00000
1.50	.00000	.00000	.00000	.00000
2.00	.00000	.00000	.00000	.00000

ZETA = 10

B* \ E*	1	3	10	30
.50	.06177	.05000	.02111	
.90	.00675	.00440	.00225	
1.00	-.00415	.00031	.00162	
1.10	-.01053	-.00034	.00246	
1.20	-.01140	.00263	.00327	
1.30	-.00732	.01124	.00250	
1.50	.01582	.00417	.00099	
2.00	-.00084	-.00021	.00016	

ZETA = 20

B* \ E*	1	3	10	30
.50	.01956	.07538	.06135	
.90	-.00248	-.00352	.00246	
1.00	-.01239	-.01105	.00041	
1.10	-.02219	-.01094	.00226	
1.20	-.02632	-.00519	.00403	
1.30	-.02026	.00479	.00250	
1.50	.00486	-.00116	.00015	
2.00	-.00113	-.00101	-.00036	

ZETA = 30

B* \ E*	1	3	10	30
.50	.04638	.04345	.08926	.05530
.90	.00419	-.01393	-.00290	.00262
1.00	-.00437	-.02230	-.00556	.00270
1.10	-.01410	-.02099	-.00291	.00341
1.20	-.02400	-.01338	-.00038	.00252
1.30	-.02407	-.00401	-.00121	.00141
1.50	.00011	-.00350	-.00195	.00028
2.00	-.00113	-.00114	-.00084	-.00020

$S^{(2)}_{6,1,2}$

ZETA = 0

B* \ E*	1	3	10	30
.50	.00000	.00000	.00000	.00000
.90	.00000	.00000	.00000	.00000
1.00	.00000	.00000	.00000	.00000
1.10	.00000	.00000	.00000	.00000
1.20	.00000	.00000	.00000	.00000
1.30	.00000	.00000	.00000	.00000
1.50	.00000	.00000	.00000	.00000
2.00	.00000	.00000	.00000	.00000

ZETA = 10

B* \ E*	1	3	10	30
.50	.00177	.02340	.02723	
.90	.02446	.04663	.02898	
1.00	.03339	.04139	.01642	
1.10	.04008	.02805	.00396	
1.20	.04036	.00865	-.00160	
1.30	.02979	-.00700	-.00175	
1.50	-.01495	-.00372	-.00052	
2.00	-.00015	-.00010	-.00003	

ZETA = 20

B* \ E*	1	3	10	30
.50	-.00107	.00554	.04006	
.90	-.01858	.04187	.04814	
1.00	-.01651	.04408	.02717	
1.10	-.00497	.03256	.00605	
1.20	.01282	.00868	-.00279	
1.30	.02138	-.00839	-.00269	
1.50	-.01102	-.00205	-.00070	
2.00	-.00000	-.00002	-.00003	

ZETA = 30

B* \ E*	1	3	10	30
.50	.00053	-.01187	.03430	.05999
.90	.00763	.01130	-.05390	.03501
1.00	-.00165	.02440	.03049	.01133
1.10	-.01188	.02391	.00618	.00070
1.20	-.00821	.00600	-.00300	-.00101
1.30	.00795	-.00507	-.00250	-.00073
1.50	-.00327	-.00044	-.00054	-.00020
2.00	-.00000	-.00000	-.00001	-.00001

$S^{(2)}_{6,1,1}$

ZETA = 0

B* \ E*	1	3	10	30
.50	.00000	.00000	.00000	.00000
.90	.00000	.00000	.00000	.00000
1.00	.00000	.00000	.00000	.00000
1.10	.00000	.00000	.00000	.00000
1.20	.00000	.00000	.00000	.00000
1.30	.00000	.00000	.00000	.00000
1.50	.00000	.00000	.00000	.00000
2.00	.00000	.00000	.00000	.00000

ZETA = 10

B* \ E*	1	3	10	30
.50	.00109	.07361	.08097	
.90	.02723	.05943	.04435	
1.00	.02981	.04546	.03593	
1.10	.02751	.03498	.03366	
1.20	.02110	.03470	.02921	
1.30	.01568	.04100	.02074	
1.50	.03587	.01593	.00963	
2.00	.00052	.00172	.00220	

ZETA = 20

B* \ E*	1	3	10	30
.50	.00017	.00780	.11135	
.90	-.02664	.03735	.06314	
1.00	-.02251	.03235	.04935	
1.10	-.01278	.02575	.04451	
1.20	-.00358	.02606	.03624	
1.30	.00123	.02556	.02363	
1.50	.01113	.00466	.00928	
2.00	.00000	.00024	.00141	

ZETA = 30

B* \ E*	1	3	10	30
.50	-.00083	-.03954	.08486	.15459
.90	.01424	-.00227	.05867	.06793
1.00	.00346	.00727	.04490	.05666
1.10	-.00633	.01055	.03869	.04450
1.20	-.00753	.01340	.02848	.03054
1.30	-.00357	.00893	.01658	.02011
1.50	.00003	.00049	.00538	.00910
2.00	.00000	.00002	.00052	.00168

$S^{(2)}_{6,1,0}$

ZETA = 0

E* / B*	1	3	10	30
.50	.00000	.00000	.00000	.00000
.90	.00000	.00000	.00000	.00000
1.00	.00000	.00000	.00000	.00000
1.10	.00000	.00000	.00000	.00000
1.20	.00000	.00000	.00000	.00000
1.30	.00000	.00000	.00000	.00000
1.50	.00000	.00000	.00000	.00000
2.00	.00000	.00000	.00000	.00000

ZETA = 10

E* / B*	1	3	10	30
.50	-.00802	.07866	.08255	
.90	-.00868	-.00479	.00152	
1.00	-.01698	-.01361	-.00079	
1.10	-.02540	-.01361	-.00240	
1.20	-.02937	-.01010	-.00408	
1.30	-.02479	-.01237	-.00259	
1.50	-.00537	-.00141	-.00050	
2.00	.00020	.00004	-.00001	

ZETA = 20

E* / B*	1	3	10	30
.50	.00733	-.00741	.09853	
.90	.00047	-.02246	-.00952	
1.00	.00238	-.02870	-.00857	
1.10	-.00218	-.02453	-.00482	
1.20	-.01331	-.01088	-.00292	
1.30	-.01941	.00239	-.00099	
1.50	.00847	.00242	.00003	
2.00	.00000	.00003	.00001	

ZETA = 30

E* / B*	1	3	10	30
.50	-.00586	-.04277	.05721	.12263
.90	.00349	-.01683	-.02282	-.00235
1.00	.00518	-.02273	-.01651	-.00151
1.10	.00929	-.02147	-.00595	-.00153
1.20	.00545	-.00759	-.00028	-.00088
1.30	-.00746	.00478	.00095	-.00034
1.50	.00480	.00079	.00037	-.00003
2.00	.00000	.00000	.00001	.00000

$S^{(2)}_{6,0,2}$

ZETA = 0

B* \ E*	1	3	10	30
.50	.02551	.04609	.08453	.14676
.90	.07380	.12397	.19268	.26230
1.00	.08670	.13928	.19182	.22005
1.10	.09835	.14692	.16497	.15706
1.20	.10739	.14113	.11907	.10365
1.30	.11182	.11553	.07784	.06846
1.50	.09429	.04563	.03466	.03249
2.00	.00916	.00795	.00761	.00752

ZETA = 10

B* \ E*	1	3	10	30
.50	-.00713	.01764	.07080	
.90	-.00524	.08189	.17761	
1.00	.00491	.10254	.17867	
1.10	.02169	.11680	.15302	
1.20	.04393	.11500	.10859	
1.30	.06570	.08935	.06955	
1.50	.05596	.02965	.02975	
2.00	.00272	.00402	.00586	

ZETA = 20

B* \ E*	1	3	10	30
.50	.01499	-.00910	.03920	
.90	.01636	.02083	.14268	
1.00	.00578	.04693	.14887	
1.10	-.00234	.07198	.12637	
1.20	.00370	.07768	.08588	
1.30	.02858	.05331	.05255	
1.50	.02608	.01498	.02085	
2.00	.00229	.00220	.00352	

ZETA = 30

B* \ E*	1	3	10	30
.50	.00078	.00567	.00803	.09747
.90	.02872	-.00034	.10416	.21825
1.00	.03677	.01788	.11692	.18140
1.10	.03072	.04470	.09891	.12483
1.20	.01537	.05538	.06396	.07884
1.30	.01878	.03596	.03755	.04981
1.50	.02014	.01172	.01429	.02161
2.00	.00229	.00200	.00240	.00398

$S^{(2)}_{6,0,1}$

ZETA = 0

B* \ E*	1	3	10	30
.50	.09024	.14034	.221	.33578
.90	.10049	.12079	.12	.10371
1.00	.08789	.08539	.055	.02644
1.10	.06778	.03821	.00023	-.00334
1.20	.03986	-.01343	-.01730	-.00557
1.30	.00477	-.04699	-.01170	-.00324
1.50	-.06601	-.01530	-.00273	-.00081
2.00	-.00164	-.00041	-.00011	-.00004

ZETA = 10

B* \ E*	1	3	10	30
.50	-.02689	.04300	.17823	
.90	-.01820	.06151	.10500	
1.00	-.00976	.04505	.04585	
1.10	-.00311	.01606	-.00157	
1.20	-.00330	-.01679	-.01481	
1.30	-.01411	-.02982	-.00928	
1.50	-.02680	-.00475	-.00194	
2.00	-.00018	-.00006	-.00006	

ZETA = 20

B* \ E*	1	3	10	30
.50	.05433	-.03203	.08342	
.90	.03149	-.00382	.06632	
1.00	.01361	.00129	.02600	
1.10	.00029	-.00509	-.00457	
1.20	-.00611	-.01561	-.00931	
1.30	-.01229	-.00930	-.00462	
1.50	-.00571	-.00092	-.00073	
2.00	-.00041	-.00007	-.00001	

ZETA = 30

B* \ E*	1	3	10	30
.50	.00200	.02618	-.00053	.19825
.90	.03552	-.00796	.03085	.06714
1.00	.03861	-.00611	.00923	.01404
1.10	.02762	-.00771	-.00608	-.00313
1.20	.01017	-.01149	-.00493	-.00321
1.30	-.00433	-.00662	-.00177	-.00158
1.50	-.00980	-.00299	-.00025	-.00030
2.00	-.00041	-.00010	-.00001	-.00001

$S^{(2)}_{6,0,0}$

ZETA = 0

B* \ E*	1	3	10	30
.50	.11733	.15016	.19069	.22971
.90	.00646	-.03253	-.08771	-.13795
1.00	-.02201	-.06744	-.10519	-.11663
1.10	-.04662	-.08425	-.08429	-.07676
1.20	-.06365	-.07196	-.05184	-.04896
1.30	-.06760	-.02908	-.03309	-.03243
1.50	.00095	-.01240	-.01593	-.01565
2.00	-.00370	-.00375	-.00369	-.00367

ZETA = 10

B* \ E*	1	3	10	30
.50	-.03396	.02768	.13899	
.90	-.01006	-.04331	-.09323	
1.00	-.01186	-.06820	-.10914	
1.10	-.02083	-.08343	-.09031	
1.20	-.03573	-.07840	-.05985	
1.30	-.04968	-.05660	-.03921	
1.50	-.03781	-.02262	-.01836	
2.00	-.00164	-.00322	-.00408	

ZETA = 20

B* \ E*	1	3	10	30
.50	.06941	-.03449	.04040	
.90	.01254	-.02391	-.09372	
1.00	.00834	-.04036	-.10620	
1.10	.00775	-.05746	-.08981	
1.20	.00083	-.05925	-.06171	
1.30	-.01797	-.04081	-.03920	
1.50	-.01094	-.00956	-.01631	
2.00	-.00093	-.00127	-.00281	

ZETA = 30

B* \ E*	1	3	10	30
.50	.00372	.04372	-.02794	.09426
.90	-.00379	.00159	-.08061	-.14436
1.00	-.01130	-.01282	-.09157	-.12324
1.10	-.01208	-.03283	-.07716	-.08510
1.20	-.00485	-.03919	-.05089	-.05513
1.30	-.00865	-.01926	-.03012	-.03589
1.50	.00067	-.00382	-.01116	-.01633
2.00	-.00092	-.00096	-.00163	-.00318

FOOTNOTES

1. K. Takayanagi, Advan. At. Mol. Phys., 1, 146 (1965).
2. See, e.g., (a) C. F. Curtiss and R. B. Bernstein, J. Chem. Phys., 50, 1168 (1969), (b) R. W. Fenstermaker, C. F. Curtiss and R. B. Bernstein, J. Chem. Phys., 51, 2439 (1969); papers IX and X of this series; and references cited therein.
3. (a) G. Gioumousis and C. F. Curtiss, J. Chem. Phys., 29, 996 (1958); paper I of this series; (b) A. M. Arthurs and A. Dalgarno, Proc. Roy. Soc. (London) A256, 540 (1960).
4. Ref. (2b). It should be noted that in Eqs. (21) and (22) of this paper, the high j limit has been taken, but this need not be invoked.
5. C. F. Curtiss, J. Chem. Phys., 52, 4832 (1970); paper XII of this series.
6. J. Van Kranendonk, Can. J. Phys., 41, 433 (1963). See also R. J. Cross, Jr., Ph.D. Dissertation, Harvard University (1965).
7. Arguments presented in this work are restricted throughout to the case of a "high" initial diatom rotor state ($\bar{\ell}$), such that $\bar{\ell}(\bar{\ell}+1)$ can be well approximated by $\bar{\ell}^2$.
8. Eq. (V-5) is used to indicate Eq. (5) of paper V of this series, etc..
9. We use the definition of the spherical harmonics given in J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, Molecular Theory of Gases and Liquids, Wiley, New York, 1964.
10. As defined by Van Kranendonk (Ref. 6), the resonance function is the ratio of the transition probability calculated for a given ξ to that for $\xi = 0$.

11. R. B. Bernstein and K. H. Kramer, J. Chem. Phys., 44, 4473 (1966).

12. W. A. Lester, Jr. and R. B. Bernstein, J. Chem. Phys., 53, 11 (1970).

13. Of course, the fundamental quantities calculated are the $S^{(L)}_{n,\alpha,a}$ integrals; the transition probabilities, either scaled or unscaled, are simply linear combinations of these quantities. Tables of all $S^{(L)}_{n,\alpha,a}$ calculated are given in Appendix B. Frequent convergence checks established the validity of these values certainly to four and usually to five decimal digits.

14. F. B. Hildebrand, Introduction to Numerical Analysis, McGraw-Hill, New York, 1956. p. 447.

15. A. Ralston, A First Course in Numerical Analysis, McGraw-Hill, New York, 1965. p. 98.

16. R. B. Bernstein and K. H. Kramer, Technical Note WIS-TCI-91, Theoretical Chemistry Institute, University of Wisconsin, 13 July 1965.

17. See Ref. 11, footnote 13.

18. For brevity, the scaled transition probabilities defined via Eqs. (28) and (29) are henceforth denoted simply by $P(E^*, b^*, S)$.

19. M. Abramowitz and I. A. Stegun (eds.), Handbook of Mathematical Functions, National Bureau of Standards, Washington, D. C., 1964.

20. The authors thank Dr. H. A. Rabitz for the use of his Bessel function subroutine.

21. See, e.g., R. J. Cross, Jr., and R. G. Gordon, J. Chem. Phys., 45 3571 (1966).

22. I. S. Gradshtyn and I. M. Ryzhik, Tables of Integrals, Series and Products, Academic Press, New York, 1965, p. 429.

23. An incidental benefit of the present work is that the straight-line trajectory resonance functions, Eqs. (18), can be applied directly to improve the RDWB results given in paper X (Ref. 2(b)) for an inverse power potential (n > 2). For a specific system, given Λ^*, M, $\bar{l}$, and σ at a designated E^*, for any b^* the value of ξ and hence $R(\xi)$ can be calculated. $R(\xi)$ then enters as a multiplicative correction to the b^*-dependent RDWB transition probabilities (Eq. (X-21)).