Strong-Coupling Semiclassical Methods. The Average Approximation for Atom-Atom Collisions*

Merle E. Riley
Sandia Laboratories, Albuquerque, New Mexico 87115
(Received 8 March 1973)

Calculations on the $2p\sigma_u$-$2p\pi_u$ excitation in proton-hydrogen collisions demonstrate that strongly coupled radial equations may be solved using simple semiclassical approximations at the turning points. A theoretical justification of the best of these methods is based on an extension of the large-mass high-energy approximation into the turning-point region. Other model problems are solved to illustrate properties of this new average approximation.

I. INTRODUCTION

The discussion and calculations in this paper are centered around the description of an atom-atom collision as a coupled set of ordinary Schrödinger equations in which all but one degree of freedom (a radial separation coordinate) has been incorporated into a state representation by basis expansion and projection. To formulate this is difficult if one wishes to satisfy scattering boundary conditions exactly.[1] Meaningful simplifications occur through the use of known physical circumstances, such as large nuclear-to-electron-mass ratio, high collision energy, small nuclear velocity, avoided crossing structure, etc. These simplifications may seem extreme, but they are intended to be valid approximations for a given problem. The same considerations apply to the size and character of the electronic basis used; even the inclusion of all open channels is precluded in atom-atom scattering at a collision energy greater than a fraction of an atomic unit. Convergence of close-coupling methods must depend on the physics, so to speak, rather than on an arbitrary number of channels in the numerical calculation.

The following points underlie the applications of the approximations developed in this paper: (i) the relative nuclear velocity is considerably less than electron velocity, implying the use of a fixed-nuclei molecular electronic basis; (ii) static mass-polarization-type corrections are negligible compared to coupling due to nuclear motion; (iii) the total barycentric Schrödinger equation is expanded in symmetric-top rotation states and electronic fixed-nuclei states quantized on the internuclear axis[1-3] with subsequent projection onto the electronic basis, yielding a set of coupled ordinary differential equations which in general do not decouple at large separation; (iv) the computational effort is not greatly different between the partial-wave or impact-parameter pictures once suitable semiclassical approximations are known. In a previous paper[4] it was established that two simple limiting procedures exist that predict quite different semiclassical approximations in atom-atom processes; the first approximation was a large-mass limit at fixed total energy giving an adiabatic picture, while the other was a large-mass limit at fixed collision velocity (high energy) resulting in the rectilinear impact-parameter description. The aforementioned points indicate that a large-mass limit is relevant, but the collision energy appropriate for the present theory may only be as high as will ensure that nuclear velocities remain small (e.g., $E=10$, $v=0.1$ in a.u.) Strong excitation (nonadiabatic, but not necessarily diabatic) occurs in regions of near electronic degeneracy, and large scattering deflections may dominate the differential cross sections. In order to establish the notation, the two limits[4] are reviewed in the next paragraph for the equations that arise from a molecular expansion.

The coupled radial equations are assumed written in a standard form of dimension $N\times N$,

$$-\frac{\hbar^2}{2\mu}(\underline{G}''+2\underline{D}\underline{G}'+\underline{E}\underline{G})-\frac{\hbar^2}{2\mu}\underline{A}\underline{G}-\left(E-\frac{\hbar^2}{2\mu}\frac{L(L+1)}{R^2}-\underline{W}\right)\underline{G}=0\,, \quad (1)$$

where the columns of the matrix $\underline{G}$ are linearly-independent-solution vectors and the rows of $\underline{G}$ are coefficients of particular members of the expansion basis of the wave function. μ is the nuclear reduced mass, E is the barycentric energy, the prime denotes d/dR where R is the nuclear separation, $\underline{D}=-\underline{D}^T$ is the matrix of the operator d/dR between electronic states, $\underline{E}$ is the matrix of d^2/dR^2 in that basis, $\underline{A}=\underline{A}^T$ represents all angular rotation coupling matrix elements, L is the total angular momentum, and $\underline{W}$ is the diagonal matrix of eigenvalues of the

fixed-nuclei electronic Hamiltonian. The dimensionless semiclassical parameter α is introduced by replacing μ by μ/α^2 in Eq. (1) and by scaling $L(L+1)$ as P^2/α^2, $P=L+\frac{1}{2}$. Part of the angular coupling matrix $\underline{A}$, $\underline{A}_0$, should be scaled as $\underline{A}_0/\alpha$ since it contains the eigenvalues of the total angular momentum multiplied by an electronic matrix element of an angular operator.[1,3] The rest of $\underline{A}$, $\underline{A}_1$, is not scaled. Introducing this scaling into Eq. (1) and defining $K^2=2\mu E/\hbar^2$, $\underline{\lambda}=2\mu\underline{W}/\hbar^2$, there results

$$\alpha^2(\underline{G}''+2\underline{D}\underline{G}'+\underline{E}\underline{G})+\alpha\underline{A}_0\underline{G}+\alpha^2\underline{A}_1\underline{G}+(K^2-P^2/R^2-\underline{\lambda})\underline{G}=0\,. \quad (2)$$

The lowest-order solutions of Eq. (2) are the uncoupled semiclassical solutions of

$$\alpha^2\underline{\chi}''+(K^2-P^2/R^2-\underline{\lambda})\underline{\chi}=0\,. \quad (3)$$

The second-order terms $\alpha^2\underline{E}$ and $\alpha^2\underline{A}_1$ may be dropped from Eq. (2) to give the coupling through first order in α:

$$\alpha^2\underline{G}''+2\alpha^2\underline{D}\,\underline{G}'+\alpha\underline{A}_0\underline{G}+\underline{\kappa}^2\underline{G}=0\,. \quad (4)$$

The notation $\kappa^2=K^2-P^2/R^2$, $\underline{\kappa}^2=\kappa^2\underline{1}-\underline{\lambda}$ will be used for wave numbers. The isovelocity parameter[4] ϵ is introduced into Eq. (1) by replacing μ by μ/ϵ, E by E/ϵ, and $L(L+1)$ by P^2/ϵ^2 (nuclear angular momentum eigenvalues scale as $1/\epsilon$); the result is, dropping second-order terms,

$$\epsilon^2\underline{G}''+2\epsilon^2\underline{D}\underline{G}'+\epsilon\underline{A}_0\underline{G}+(\kappa^2-\epsilon\underline{\lambda})\underline{G}=0\,. \quad (5)$$

Part of the zero-order solutions of Eq. (5) are the free-wave radial solutions $\epsilon^2\chi''+\kappa^2\chi=0$, which are the equivalent in the partial-wave picture of rectilinear motion of the nuclei. The parametric structure of Eq. (5) is identical to Eq. (4) except for the smallness parameter multiplying the diagonal energy matrix. It is *solely* this difference in the limits $\epsilon\to 0$ and $\alpha\to 0$ that causes Eq. (5) to give strong coupling at zero order and Eq. (4) to predict adiabaticity. For the rest of the paper the ϵ symbolism is dropped; when necessary to develop high-energy (isovelocity semiclassical limit) properties, $\underline{\kappa}^2$ in Eq. (4) will be written $\underline{1}\kappa^2-\alpha\underline{\lambda}$, giving the identical structure in α as would have been seen in ϵ from Eq. (5).

To complete the introduction and exhibit the equations used in Sec. V, the transformations that may be carried out within the N-state basis are given; first, one may convert Eq. (4) to complete leading d/dR coupling[1,5] by the following R-dependent transforms:

$$\underline{G}=\underline{S}\underline{F}\,,\qquad \underline{S}^T\underline{S}=\underline{1}\,,$$

$$\underline{S}^T(\underline{\kappa}^2+\alpha\underline{A}_0)\underline{S}=\underline{\Lambda}=\underline{\kappa}^2+O(\alpha)\,,$$

$$(\underline{S}^T\underline{S}')_{ij}=\frac{(\underline{S}^T(\underline{\kappa}^2+\alpha\underline{A}_0)'\underline{S})_{ij}}{\Lambda_j-\Lambda_i}\,,\quad i\neq j$$

$$=0\,,\qquad i=j \quad (6)$$

where $\underline{\Lambda}$ is diagonal, giving, up to $O(\alpha^2)$,

$$\alpha^2\underline{F}''+2\alpha^2(\underline{S}^T\underline{S}'+\underline{S}^T\underline{D}\underline{S})F'+\underline{\Lambda}\,\underline{F}=0\,. \quad (7)$$

Second, Eq. (4) may be converted to complete potential coupling by[2]

$$\underline{G}=\underline{N}\underline{Y}\,,\quad \underline{N}'=-\underline{D}\underline{N}\,,\quad \underline{N}^T\underline{N}=\underline{1}\,, \quad (8)$$

giving, up to $O(\alpha^2)$,

$$\alpha^2\underline{Y}''+\underline{N}^T(\underline{\kappa}^2+\alpha\underline{A}_0)\underline{N}\underline{Y}=0\,. \quad (9)$$

The relation between Eqs. (7) and (9) is clear when one sees that $\underline{Y}=\underline{N}^T\underline{S}\underline{F}$, identifying $\underline{N}^T\underline{S}$ as the transform that converts the diabatic form of Eq. (9) to the derivative-coupling form of Eq. (7) through leading order in α.

This formalism is sufficient to allow a study of semiclassical close-coupling methods and numerical testing on relevant problems. It should be noted that no particular electronic behavior is assumed in the diabatic representation. The electronic basis functions are the fixed-nuclei solutions, and the distinction between adiabatic and diabatic will only enter through semiclassical approximations for nuclear motion.

The remainder of the paper is arranged as follows: Section II gives the mechanics of treating coupled systems of equations containing a limiting parameter. The discussion is similar to well-known methods in the literature, and it forms the basis for the new approximation developed for distorted-wave theory in Sec. III and for close coupling in Sec. IV. Additional numerical studies are contained in Sec. V.

II. SEMICLASSICAL APPROXIMATIONS BY REFERENCE FUNCTIONS

At high energy, $\underline{\kappa}^2$ in Eq. (9) and $\underline{\Lambda}$ in Eq. (7) both are equal to $\underline{1}\kappa^2+O(\alpha)$. This shows that the largest terms in either equation are the diagonal ones which are all equal to $\alpha^2 d^2/dR^2+\kappa^2$. If $\underline{\kappa}^2\neq\underline{1}\kappa^2+O(\alpha)$, the diagonal of Eq. (7) is still the largest part, as expressed in Eq. (3), but the diagonal of Eq. (9) is not special. Since the procedures to be described make use of solutions to the diagonal part of the coupled system, neither the pure adiabatic equation (7) or the pure diabatic equation (9) is used, but an equation with both forms:

$$\alpha^2\underline{G}''+2\alpha^2\underline{D}\underline{G}'+(\underline{\kappa}^2-\alpha\underline{U})\underline{G}=0\,. \quad (10)$$

The reason that Eq. (10) is distinguished from the original equation (4) is that $\underline{U}$ in Eq. (10) could

contain diabatic potential coupling obtained from the removal of d/dR radial motion coupling. $\underline{D}$ is off-diagonal, and the diagonal part of $\underline{U}$ is included in $\underline{\kappa}^2$. Numerical integration of Eq. (10) is difficult for small α since the derivaties of $\underline{G}$, $\underline{G}^{(n)}$, generally behave in magnitude as α^{-n}. As in asymptotic methods[4,6] where the essential singularity in α is factored from the whole solution, $\underline{G}$ is written as a linear combination of two linearly independent diagonal solutions of the lowest-order part of the differential equation, $\alpha^2 d^2/dR^2 + \underline{\kappa}^2$.[7-10] These diagonal solutions,[11] called reference functions here, incorporate the leading part of the essentially singular behavior in α. Since they need not be exact, but are usually asymptotic approximations such as JWKB or uniform[6,12] solutions, a diagonal $\underline{\Theta}$ matrix is used as a measure of their accuracy[12]:

$$\begin{aligned} &\alpha^2 \underline{\chi}_i'' + \underline{\kappa}^2 \underline{\chi}_i = \alpha^2 \underline{\Theta} \underline{\chi}_i , \\ &\underline{\chi}_1 \underline{\chi}_2' - \underline{\chi}_1' \underline{\chi}_2 = \underline{1} W_{12} . \end{aligned} \tag{11}$$

Thus $\underline{G}$ is written as

$$\underline{G} = \underline{\chi}_1 \underline{C}_1 + \underline{\chi}_1 \underline{C}_2 , \tag{12}$$

which does not yet uniquely determine $\underline{C}_1$ and $\underline{C}_2$. The usual linear constraint relation to use in conjunction with Eq. (12) is[7-10]

$$\begin{aligned} &\underline{G}' = \underline{\chi}_1' \underline{C}_1 + \underline{\chi}_2' \underline{C}_2 , \\ &\underline{\chi}_1 \underline{C}_1' + \underline{\chi}_2 \underline{C}_2' = 0 , \end{aligned} \tag{13}$$

which necessarily must allow a well-behaved determination of $\underline{C}_1$ and $\underline{C}_2$:

$$\begin{aligned} \underline{C}_1 &= (1/W_{12})(\underline{\chi}_2' \underline{G} - \underline{\chi}_2 \underline{G}') , \\ \underline{C}_2 &= -(1/W_{12})(\underline{\chi}_1' \underline{G} - \underline{\chi}_1 \underline{G}') . \end{aligned} \tag{14}$$

In place of Eq. (13), one can use[13]

$$\begin{aligned} &\underline{G}' = \underline{\chi}_1' \underline{C}_1 + \underline{\chi}_2' \underline{C}_2 - \underline{D} \underline{G} , \\ &\underline{\chi}_1 \underline{C}_1' + \underline{\chi}_2 \underline{C}_2' = -\underline{D} \underline{G} , \end{aligned} \tag{15}$$

which affords a more symmetrical treatment of derivative coupling. Combining Eqs. (11), (12), and (15) with Eq. (10), one derives

$$\begin{aligned} \underline{C}_1' = (1/\alpha W_{12}) &[\underline{\chi}_2 (\alpha \underline{\Theta} - \underline{U})(\underline{\chi}_1 \underline{C}_1 + \underline{\chi}_2 \underline{C}_2) \\ &+ \underline{\chi}_2 \alpha \underline{D} (\underline{\chi}_1' \underline{C}_1 + \underline{\chi}_2' \underline{C}_2) - \underline{\chi}_2' \alpha \underline{D} (\underline{\chi}_1 C_1 + \underline{\chi}_2 \underline{C}_2)] ; \end{aligned} \tag{16}$$

$\underline{C}_2'$ is the above expression with the 1 and 2 indices interchanged. The normalization choice for $\underline{\chi}_1$ and $\underline{\chi}_2$ will either involve the real regular and irregular solutions

$$\begin{aligned} &\underline{\chi}_r \sim \underline{K}^{-1/2} \sin(\underline{K} R/\alpha - \tfrac{1}{2} L\pi + \underline{\eta}) \quad \text{as } R \to \infty , \\ &\underline{\chi}_i \sim \underline{K}^{-1/2} \cos(\underline{K} R/\alpha - \tfrac{1}{2} L\pi + \underline{\eta}) \quad \text{as } R \to \infty , \\ &W_{ri} = -1/\alpha , \qquad \underline{\kappa} \sim \underline{K} \qquad \text{as } \underline{R} \to \infty , \end{aligned} \tag{17}$$

or the complex incoming and outgoing irregular forms

$$\begin{aligned} &\underline{\chi}_\pm = \underline{\chi}_i \pm i \underline{\chi}_r \underset{R \to \infty}{\sim} \underline{K}^{-1/2} \exp[\pm i(\underline{K} R/\alpha - \tfrac{1}{2} L\pi + \underline{\eta})] , \\ &W_{+-} = -2i/\alpha . \end{aligned} \tag{18}$$

If uniform approximations are used for $\underline{\chi}_r$ and $\underline{\chi}_i$, $\underline{\Theta}$ is bounded for all R[12] and may be rigorously dropped from Eq. (16) as a higher-order term. With suitable boundary conditions at small R (e.g., $\underline{C}_r = \underline{1}$, $\underline{C}_i = 0$) system (16) may be numerically integrated; this semiclassical uniform approximation (SCUNF) integrates as rapidly as expected for a system that is not in-out decoupled anywhere. The derivatives of the dependent variables are of order α^{1-n} rather than α^{-n}. The Airy functions were calculated by the algorithm of Gordon[9] and the N quantities,

$$Q_i(R) = \frac{(\frac{3}{2} | \int_{T_i}^{R} \kappa_i(x)\, dx |)^{2/3}}{|\kappa_i^2(R)|} ,$$

were spline fitted for fast reference on the significant range of integration. The uniform $\underline{\chi}$ are evaluated at any R as

$$\begin{aligned} (\underline{\chi}_r)_n &= (\sqrt{\pi}) Q_n^{1/4} \mathrm{Ai}(-\kappa_n^2 Q_n) , \\ (\underline{\chi}_i)_n &= (\sqrt{\pi}) Q_n^{1/4} \mathrm{Bi}(-\kappa_n^2 Q_n) , \\ (\underline{\chi}_r')_n &= -(\sqrt{\pi}) Q_n^{-1/4} \mathrm{Ai}'(-\kappa_n^2 Q_n) , \\ (\underline{\chi}_i')_n &= -(\sqrt{\pi}) Q_n^{-1/4} \mathrm{Bi}'(-\kappa_n^2 Q_n) . \end{aligned}$$

Integration was carried out by the Bulirsch-Stoer method[14] which has some ability for "walking" over the high-frequency structure if such amplitudes are small compared to the automatic error control.

Let Eq. (16) be written in the in-out reference function decomposition:

$$\begin{aligned} \underline{C}_\pm' = \mp (1/2i) &[\underline{\chi}_\mp (\alpha \underline{\Theta} - \underline{U})(\underline{\chi}_+ \underline{C}_+ + \underline{\chi}_- \underline{C}_-) \\ &+ \underline{\chi}_\mp \alpha \underline{D} (\underline{\chi}_+' \underline{C}_+ + \underline{\chi}_-' \underline{C}_-) \\ &- \underline{\chi}_\mp' \alpha \underline{D} (\underline{\chi}_+ \underline{C}_+ + \underline{\chi}_- \underline{C}_-)] . \end{aligned} \tag{19}$$

Away from the turning points T_i of the reference functions, JWKB approximations may be used for $\underline{\chi}_\pm$:

$$\begin{aligned} (\underline{\chi}_\pm)_n &= \kappa_n^{-1/2} \exp\left(\pm i \int_{T_n}^{R} \kappa_n(x)\, dx/\alpha \pm \tfrac{1}{4} i\pi \right) , \\ (\underline{\chi}_\pm')_n &= \pm (i \kappa_n^{1/2}/\alpha) \exp\left(\pm i \int_{T_n}^{R} \kappa_n(x)\, dx/\alpha \pm \tfrac{1}{4} i\pi \right) . \end{aligned} \tag{20}$$

If $\kappa_i + \kappa_j \gg |\kappa_i - \kappa_j|$ (always true in the high-energy limit), the high-frequency approximation is invoked[15] in which all $\underline{\chi}_\mp \underline{U} \underline{\chi}_\mp$, $\underline{\chi}_\mp' \underline{D} \underline{\chi}_\mp$, and $\underline{\chi}_\mp \underline{D} \underline{\chi}_\mp'$ terms are dropped from Eq. (19), concurrent with the use of JWKB reference functions inward

to the turning points and a neglect of $\underline{\Theta}$ which is not bounded or integrable at the T_i. This system of equations

$$\underline{C}'_{\pm} = \mp(1/2i)[-\underline{\chi}_{\mp}\underline{U}\underline{\chi}_{\pm} + \underline{\chi}_{\mp}\alpha\underline{D}\underline{\chi}'_{\pm} - \underline{\chi}'_{\mp}\alpha\underline{D}\underline{\chi}_{\pm}]\underline{C}_{\pm} \quad (21)$$

is required by guess to satisfy uncoupled boundary conditions at each T_i, which establishes a connection between the in and out parts of the solution. This was introduced as a computational procedure by Berson[16] for potential coupling; the basic idea was well known, however.[15] The method is to integrate the $\underline{C}_-$ equation inward $[\underline{C}_-(\infty) = \underline{1}]$ until a turning point T_n is encountered; from there inward the nth row of $\underline{C}_-$ is dropped from the coupled equations and values of $(\underline{C}_-)_{ni}$, $i = 1, \cdots, N$, are saved. An outward integration restores the coupling at each T_n, using $(\underline{C}_+)_{ni} = -(\underline{C}_-)_{ni}$, so that $(\underline{G})_{ni} = (\underline{\chi}_+)_n(\underline{C}_+)_{ni} + (\underline{\chi}_-)_n(\underline{C}_-)_{ni} \approx 2i\kappa_n^{-1/2}\sin(\frac{1}{4}\pi + \int_{T_n}^{R}\kappa_n/\alpha)(\underline{C}_+)_{ni}$ for $R \approx T_n$. In practice, only outward integration was used and boundary conditions set up at the T_i such that $\underline{C}_+(R) = \underline{C}^{\pm}(R)$. This procedure, referred to here as SCJWKB, is an attempt to enforce a global high-frequency approximation, or in-out decoupling, on strongly coupled equations with no special treatment of turning points.

In perspective, one sees that the conditions $\kappa_i + \kappa_j \gg |\kappa_i - \kappa_j|$ are only ensured at high energy except at certain avoided crossing points or degeneracies. Since this occurs generally in the high-energy isovelocity limit,[4] the following expansions are introduced into Eq. (21) to complete that limit:

$$\underline{\kappa} = \underline{1}\kappa + O(\alpha),$$
$$\int_{T_i}^{R}\frac{\kappa_n(x)\,dx}{\alpha} = \int_{P/K}^{R}\frac{\kappa(x)\,dx}{\alpha} - \int_{P/K}^{R}\frac{\lambda_n(x)}{2\kappa(x)}\,dx + O(\alpha). \quad (22)$$

This gives the zero-order (α-*independent*) coupled system

$$\underline{C}'_{\pm} = \underline{M}_{\pm}\underline{C}_{\pm},$$
$$(\underline{M}_{\pm})_{nm} = \left(\pm\frac{1}{2i\kappa}U_{nm} - D_{nm}\right)\exp\left(\pm i\int_{P/K}^{R}\frac{\lambda_n - \lambda_m}{2\kappa}\,dx\right), \quad (23)$$

whose turning points (or in-out connection points) have all coalesced to P/K. System (23) is the partial-wave analog of the rectilinear impact-parameter equation. As is well known, the integration coordinate transforms:

$$[1/\kappa(R)]\,dR = \pm(1/K)\,dZ,$$
$$R^2 = (P/K)^2 + Z^2, \quad (24)$$
$$\frac{d}{dR} = \frac{R}{Z}\frac{d}{dZ},$$

so that system (23) may be written as a Z-dependent integration:

$$\frac{d}{dZ}\underline{C} = \underline{M}\underline{C},$$
$$[\underline{M}(Z)]_{nm} = \left(\frac{1}{2iK}U_{nm} - \frac{Z}{R}D_{nm}\right) \times \exp\left(\frac{i}{2K}\int_{-\infty}^{Z}(\lambda_n - \lambda_m)\,dZ'\right), \quad (25)$$

providing one connects $\underline{C}_+$ to $\underline{C}_-$ at $R = P/K$, $Z = 0$, by defining $\underline{C}_- = -\underline{C}$ for $Z < 0$, $\underline{C}_+ = \underline{C}$ for $Z > 0$.[10]

III. SEMICLASSICAL DISTORTED-WAVE METHODS

The preceding section contained no new theory except for the inclusion of a well-defined parametrization; this and the following section will make use of the parameter to develop a new approximation. Distorted-wave theory is not generally useful for the types of coupled problems being investigated here; however, some of the consequences of semiclassical approximations are present in the distorted-wave approximation and are easier to study.

Bates and Crothers[10] demonstrated an extremely useful property of JWKB-type approximations for coupled problems. That is, one can cancel out a considerable part of the nonuniform turning-point error by artificially coalescing the turning points of the zero-order solutions and simultaneously dropping the high-frequency terms. Consider the matrix element

$$I(\alpha) = \int_0^{\infty} dR\,\chi_1(R,\alpha)U_{12}(R)\chi_2(R,\alpha), \quad (26)$$

which is evaluated using the regular solutions:

$$\left(\alpha^2\frac{d^2}{dR^2} + \kappa_i^2(R)\right)\chi_i(R,\alpha) = 0,$$
$$\chi_i(R,\alpha) \sim K_i^{-1/2}\sin(K_iR/\alpha + \eta_i) \quad \text{as } R \to \infty, \quad (27)$$
$$\kappa_i^2 = K^2 - P^2/R^2 - \lambda_i(R) \sim K_i^2 \quad \text{as } R \to \infty,$$

where the semiclassical large-mass parameter α is explicitly retained. In the $\alpha \to 0$ limit, $I(\alpha)$ will be of high order in α unless a crossing occurs in λ_1 and λ_2. Bates and Crothers consider a diabatic model with an actual crossing point R_x, in which case the stationary-phase evaluation of $I(\alpha)$ at R_x shows $I(\alpha)$ to be $O(\alpha^{1/2})$:

$$I(\alpha) \approx \pi^{1/2}\alpha^{1/2}U_{12}(R_x)\kappa_1^{-1/2}(R_x) \times |\lambda_2'(R_x) - \lambda_1'(R_x)|\cos\phi_x. \quad (28)$$

It may be shown in general that the *error* in the matrix element produced by using JWKB approximations with real-axis integration over the turn-

ing-point singularities is about $O(\alpha^{1/2})$[17]:

$$|\Delta I(\alpha)| \approx \alpha^{1/2}(0.40)U_{12}(T_2)|\chi_1(T_2)|[-U_2'(T_2)]^{-1/2},$$
$$U_2(R) = P^2/R^2 + \lambda_2(R), \tag{29}$$

from the outer turning point at T_2. Since the matrix element and the JWKB error are of the same magnitude, the real-axis JWKB method[18] is not of general use as an approximation in the large-mass fixed-energy limit. If one considers the use of JWKB solutions at high energy and large mass, the error comparison is quite different. $I(\alpha)$ is of leading order α^0 and the turning-point error introduced by the JWKB solutions remains localized in a small region about the turning points and contributes (roughly) only order $\alpha^{1/2}$. If the contributions to the JWKB element $I^{\mathrm{JWKB}}(\alpha)$ from inside the turning points are dropped and the high-frequency terms are dropped outside, leaving[15]

$$I^{\mathrm{HFA,JWKB}}(\alpha) = \int_{T_>}^{\infty} dR \frac{1}{2(\kappa_1\kappa_2)^{1/2}} U_{12} \times \cos\left(\int_{T_1}^{R} \frac{\kappa_1}{\alpha} - \int_{T_2}^{R} \frac{\kappa_2}{\alpha}\right), \tag{30}$$

the errors behave much the same as $I^{\mathrm{JWKB}}(\alpha)$, neither systematically better nor worse, as confirmed by direct numerical evaluation of Eq. (30) for the problem of Bates and Crothers. The insight of their forced-common-turning-point method was that most of the error in $I^{\mathrm{HFA,JWKB}}$ came from the end point of the integration, $T_>$, where the integrand is singular and the phase of the cos term is $\int_{T_1}^{T_2}\kappa_1$, which might never receive matching oscillatory cancellation from the rest of the integral. The magnitude of this error may be examined by considering a simpler model problem which is representative of the outer-turning-point region. This is done now.

In Eq. (27) let $s = R - T_>$ and expand all potentials and phases about $T_> = T_2$:

$$\begin{aligned}
&\kappa_2^2 = Ds + O(s^2), \quad D = -U_2'(T_2),\\
&\kappa_1^2 = \kappa_1^2(T_2) + O(s),\\
&(\kappa_1\kappa_2)^{-1/2} = D^{-1/4}s^{-1/4}/[\kappa_1(T_2)]^{1/2} + O(s^{3/4}),\\
&\int_{T_1}^{R}\kappa_1 = \int_{T_1}^{T_2}\kappa_1 + O(s) = \varphi + \kappa_1(T_2)s + O(s^2),\\
&\int_{T_2}^{R}\kappa_2 = \tfrac{2}{3}s^{3/2}D^{1/2} + O(s^{5/2}),\\
&U_{12} = U_{12}(T_2) + O(s).
\end{aligned} \tag{31}$$

If all of the higher-order terms in s are dropped, then one has a model crossing problem consisting of

$$\begin{aligned}
&\chi_1 = k^{-1/2}\sin[(\varphi + ks)/\alpha],\\
&\chi_2 = \pi^{1/2}(\alpha D)^{-1/6}\,\mathrm{Ai}(-D^{1/3}s/\alpha^{2/3}),\\
&U_{12} = (\mathrm{const}), \quad k = \kappa_1(T_2),
\end{aligned} \tag{32}$$

where the normalization of χ_2 was obtained from the uniform solution as defined in Eq. (27). $I(\alpha)$ may be evaluated for the wave functions in Eq. (32) if the lower limit of the integration is extended to minus infinity:

$$\begin{aligned}
I(\alpha) &= U_{12}\int_{-\infty}^{\infty} ds\,\chi_1\chi_2\\
&= \alpha^{1/2}U_{12}\left(\frac{\pi}{kD}\right)^{1/2}\sin\left(\frac{\varphi + k^3/3D}{\alpha}\right).
\end{aligned} \tag{33}$$

Let Ai be replaced by the leading term of its asymptotic series for $s>0$ in Eqs. (32) and (33) and the high-frequency term dropped to give the special case of Eq. (30):

$$I^{\mathrm{HFA,JWKB}}(\alpha) = \tfrac{1}{2}U_{12}\int_0^{\infty} ds\,k^{-1/2}(sD)^{-1/4} \times \cos\left(\frac{\pi}{4} - \frac{\varphi}{\alpha} + \frac{2}{3}\frac{D^{1/2}s^{3/2}}{\alpha} - \frac{ks}{\alpha}\right). \tag{34}$$

The stationary-phase approximation to Eq. (34) at the point $s = k^2/D$ gives the value of $I(\alpha)$ as written in Eq. (33). The exact evaluation of Eq. (34), however, has an end-point contribution from the lower limit as is seen upon transforming to integration variable $s = t^{4/3}$:

$$\int_0^{\infty} dt\cos\left(\frac{\pi}{4} - \frac{\varphi}{\alpha} + \frac{2}{3}\frac{D^{1/2}t^2}{\alpha} - \frac{kt^{4/3}}{\alpha}\right), \tag{35}$$

where the derivative of the cos argument is zero at both $t = k^{3/2}/D^{3/4}$ ($s = k^2/D$) and $t = 0$. The size of the end-point contribution may be estimated from the area of the first half-wave and is of order $\alpha^{3/4}$. It should be pointed out that the relative phase-shift term $\frac{1}{4}\pi - \varphi/\alpha$ is not the sole cause of the end-point contribution.

If one examines the Bates-Crothers method, it is evident that their procedure removes end-point contributions. If $I(\alpha)$ is replaced by their forced-common-turning-point integral and the integration variable transformed to $t = \sqrt{s}$, where s is the distance from the common turning point, the distorted-wave integral behaves as

$$I^{\mathrm{BC}}(x) \propto b\int_0^{x} dt\cos\frac{at}{\alpha} = \frac{b\alpha}{a}\sin\frac{ax}{\alpha} \tag{36}$$

as a function of the upper limit for small x. The integral is oscillatory about zero and therefore is canceled to leading order without any residual end-point effect. In fact, all that is necessary to avoid a residual contribution from the lower limit in the integral

$$I(x)=\int_0^x ds\, s^{-\mu}\cos(as^{\nu}) \tag{37}$$

is that $\mu+\nu\leq 1$. Bates and Sprevak[19] have demonstrated that the forced-common-turning-point procedure performs well for close-coupling problems, as expected, since the residual end-point-contribution arguments also apply at the beginning of integration of the in-out decoupled equation for the local S matrix[7]

$$\underline{S}'=(1/2i)(\underline{\chi}_-\underline{U}\underline{\chi}_+\underline{S}+\underline{S}\underline{\chi}_+\underline{U}\underline{\chi}_-)\,, \tag{38}$$

where, near the beginning of integration of channel n, $S_{ni}\approx\delta_{ni}$, and the coupling develops like the distorted-wave integral near its lower limit.

The distorted-wave average approximation is now developed; this new approximation is conceptually and computationally simpler than the Bates-Crothers method and appears to be as useful in application. If the high-energy expansions defined by Eq. (22) are introduced into Eq. (30), one has the radial equivalent of the impact-parameter method,

$$\lim_{\alpha\to 0} I(\alpha)=\int_{P/K}^{\infty} dR\,\frac{1}{2K}\,U_{12}(R)\cos\left(\int_{P/K}^{R}\frac{\lambda_2-\lambda_1}{2K}\,dx\right), \tag{39}$$

which illustrates the point that the high-energy limit itself makes the radial turning points coalesce to P/K. Consider the wave-number difference away from the turning points, using the high-energy parametrization:

$$\begin{aligned}\kappa_1-\kappa_2&=(\kappa^2-\alpha\lambda_1)^{1/2}-(\kappa^2-\alpha\lambda_2)^{1/2}\\&=\alpha\frac{\lambda_2-\lambda_1}{2K}+\alpha^2\frac{\lambda_2^2-\lambda_1^2}{8K^3}+\cdots\,.\end{aligned} \tag{40}$$

If, instead of expanding directly in a series in α, one expands in the differences of λ_1 and λ_2 from a common unspecified potential $\overline{U}$:

$$\begin{aligned}&[\kappa^2-\alpha\overline{U}-\alpha(\lambda_1-\overline{U})]^{1/2}-[\kappa^2-\alpha\overline{U}-\alpha(\lambda_2-\overline{U})]^{1/2}\\&\quad=\alpha\frac{\lambda_2-\lambda_1}{2(\kappa^2-\alpha\overline{U})^{1/2}}+\alpha^2\frac{(\lambda_2-\overline{U})^2-(\lambda_1-\overline{U})^2}{8(\kappa^2-\alpha\overline{U})^{3/2}}+\cdots\,,\end{aligned} \tag{41}$$

the second term will be identically zero for all R if $\overline{U}$ is chosen to be[20]

$$\overline{U}=\tfrac{1}{2}(\lambda_1+\lambda_2)\,. \tag{42}$$

The expansion of the JWKB amplitude term

$$[(\kappa^2-\alpha\lambda_1)(\kappa^2-\alpha\lambda_2)]^{-1/4}=\kappa^{-1/2}+O(\alpha) \tag{43}$$

is likewise correct through first order in α if expanded about the differences from the average potential defined above:

$$[(\kappa^2-\alpha\lambda_1)(\kappa^2-\alpha\lambda_2)]^{-1/4}=(\kappa^2-\alpha\overline{U})^{-1/2}+O(\alpha^2)\,.$$

Thus, instead of allowing the high-energy approximation for $I(\alpha)$ to go to zero order in the isovelocity semiclassical limit [Eq. (39)], $I(\alpha)$ is kept correct through first order in α in terms of the JWKB theory by the average approximation

$$\begin{aligned}&I^{\mathrm{av}}(\alpha)=\int_{\overline{T}}^{\infty} dR\,U_{12}(R)\frac{1}{2\overline{\kappa}(R,\alpha)}\cos\left(\int_{\overline{T}}^{R}\frac{\lambda_2-\lambda_1}{2\overline{\kappa}(x,\alpha)}\,dx\right),\\&\overline{\kappa}(R,\alpha)=[\kappa^2-\tfrac{1}{2}\alpha(\lambda_2+\lambda_1)]^{1/2}\,,\\&\overline{\kappa}(\overline{T},\alpha)=0\,,\end{aligned} \tag{44}$$

which possesses all the necessary end-point cancellation properties discussed previously in this section. A numerical study of the average approximation for both values of the coupling parameter of the model problem of Bates and Crothers confirmed that the method gives total cross sections accurately (fractions of a percent error) and partial cross sections accurately for large L.[21] The low-L partial cross sections are out of phase as a function of L because of an accumulated difference in the two phase expressions:

$$\frac{\int_{T_1}^{R}\kappa_1-\int_{T_2}^{R}\kappa_2}{\alpha}-\int_{\overline{T}}^{R}\frac{\lambda_2-\lambda_1}{2\overline{\kappa}}\,. \tag{45}$$

The same difficulty arises in the Bates-Crothers method, except that the phase error is not as large for low L because their "averaging" is switched off as P^2/R^2 decays out at large R.

IV. AVERAGE APPROXIMATION FOR CLOSE COUPLING; TESTING ON THE $2p\sigma_u$-$2p\pi_u$ TRANSITION IN H^+ ON H

There are several ways of developing the average approximation for close-coupling; the simplest is to begin with system (21) and require that the essentially singular part in α of the coupling be restructured consistent with the introduction of the high-energy condition $\kappa_i-\kappa_j=O(\alpha)$:

$$\underline{C}'_{\pm}=\underline{M}_{\pm}\underline{C}_{\pm}\,,$$

$$(\underline{M}_{\pm})_{nm}=\left\{\pm\frac{1}{2i(\kappa_n\kappa_m)^{1/2}}\,U_{nm}-\frac{1}{2}\left[\left(\frac{\kappa_m}{\kappa_n}\right)^{1/2}+\left(\frac{\kappa_n}{\kappa_m}\right)^{1/2}\right]D_{nm}\right\}\exp\left(\mp i\int_{T_n}^{R}\frac{\kappa_n\,dx}{\alpha}\right)\exp\left(\pm i\int_{T_m}^{R}\frac{\kappa_m\,dx}{\alpha}\right). \tag{46}$$

Equations (22) and (23) give the full $\alpha\to 0$ limit; it is possible, however, to expand $\underline{M}_{\pm}$ in a series whose leading term is correct through first order in α, as discussed in Sec. III. Suppose the phase difference is

expanded in an α series:

$$\varphi_{nm}(R,\alpha)=\int_{T_n}^{R}\frac{\kappa_n\,dx}{\alpha}-\int_{T_m}^{R}\frac{\kappa_m\,dx}{\alpha}$$
$$=\int_{T}^{R}\frac{\lambda_m-\lambda_n}{2\kappa}\,dx+\frac{\alpha}{2}\left(\frac{\lambda_n(T)\lambda_n(R)-\lambda_m(T)\lambda_m(R)}{2\omega'(T)\kappa(R)}\right.$$
$$+\frac{1}{\omega'(T)}\int_{T}^{R}\frac{\lambda_n(T)\lambda_n(x)\omega'(x)-\lambda_n^2(x)\omega'(T)-\lambda_m(T)\lambda_m(x)\omega'(x)+\lambda_m^2(x)\omega'(T)}{4\kappa^3(x)}\,dx$$
$$\left.-\frac{1}{\omega'(T)}\int_{T}^{R}\frac{\lambda_n(T)\lambda_n'(x)-\lambda_m(T)\lambda_m'(x)}{2\kappa(x)}\,dx\right)+\cdots, \tag{47}$$

where

$$\kappa_i^2(x,\alpha)=\kappa^2(x)-\alpha\lambda_i(x),$$
$$\omega(x)=\kappa^2(x), \tag{48}$$
$$\kappa_i^2(T_i(\alpha),\alpha)=0,\quad \omega(T)=0.$$

If in Eq. (48) one makes the replacement,

$$\kappa^2(x)=\kappa^2(x)-\alpha\overline{U},\quad \lambda_i(x)=\lambda_i(x)-\overline{U}, \tag{49}$$

and inserts these new definitions into the phase expansion in Eq. (47), the whole second term is identically zero for all R if $\overline{U}=\frac{1}{2}(\lambda_n+\lambda_m)$. Thus

$$\varphi_{nm}(R,\alpha)=\int_{T_{nm}}^{R}\frac{\lambda_m-\lambda_n}{2\kappa_{nm}(x,\alpha)}\,dx+O(\alpha^2),$$
$$\kappa_{nm}(x,\alpha)=[\kappa^2(x)-\tfrac{1}{2}\alpha(\lambda_n+\lambda_m)]^{1/2} \tag{50}$$
$$\kappa_{nm}(T_{nm}(\alpha),\alpha)=0.$$

Expansion (50) incorporates a coalescence of the turning points into the crude JWKB theory consistent with the high-energy limit. The JWKB amplitude factors are also expanded about the pairwise average:

$$(\kappa_i\kappa_i)^{-1/2}=1/\kappa_{ij}+O(\alpha^2),$$
$$\tfrac{1}{2}[(\kappa_i/\kappa_j)^{1/2}+(\kappa_j/\kappa_i)^{1/2}]=1+O(\alpha^2), \tag{51}$$

where the $O(\alpha^2)$ term is not bounded for all R; it is the leading term of a divergent series for $|R-T_{ij}(\alpha)|=O(\alpha)$; the same applies to Eq. (50). The full average approximation consists in replacing in Eq. (46):

$$(\underline{M}_{\pm})_{nm}=\left(\pm\frac{1}{2i\kappa_{nm}}U_{nm}-D_{nm}\right)$$
$$\times\exp\left(\pm i\int_{T_{nm}}^{R}\frac{\lambda_n-\lambda_m}{2\kappa_{nm}}\,dx\right). \tag{52}$$

Each coupling has been replaced with an average to incorporate the first-order term exactly. One can further approximate Eq. (46) by

$$(\underline{M}_{\pm})_{nm}=\left(\pm\frac{1}{2i\overline{\kappa}}U_{nm}-D_{nm}\right)$$
$$\times\exp\left(\pm i\int_{\overline{T}}^{R}\frac{\lambda_n-\lambda_m}{2\overline{\kappa}}\,dx\right),$$
$$\overline{\kappa}=(\kappa^2-\alpha\overline{U})^{1/2}, \tag{53}$$
$$\overline{\kappa}(\overline{T})=0,$$

using a common potential for all channels. In atom-atom collisions, it would seem reasonable to choose this common potential to be a screened nuclear repulsion. Boundary conditions for the average approximation are slightly complicated by the presence of $\frac{1}{2}N(N-1)$ "notch" points T_{ij}, as opposed to N turning points. The computational procedure is as follows: (i) the diagonal potentials λ_i and the coupling terms U_{ij} and/or D_{ij} are spline fitted or used as functional forms if known; (ii) for each L all turning points and notch points are found by grid search and the method of false position; (iii) the JWKB phase shifts are determined and all T_{ij} ordered; (iv) outward numerical integration of system (46) containing the averaged coupling is completed between adjacent notch points, dropping coupling between channels whose notch points are outside the current interval; (v) the average phases, as defined in Eq. (50), are computed as the system is integrated; (vi) only the + equations are solved, using the unitarity property $\underline{C}_{\pm}^{\dagger}\underline{C}_{\pm}=1$ and $\underline{C}_{-}=\underline{C}_{+}^{*}$, $\underline{C}_{+}=-i\underline{1}$ as $R\to 0$, to evaluate the partial-wave $\underline{S}$ matrix, defined by

$$\underline{G}=\underline{K}^{-1/2}[\exp(-i\underline{K}R/\alpha+\tfrac{1}{2}iL\pi)$$
$$-\exp(i\underline{K}R/\alpha-\tfrac{1}{2}iL\pi)\underline{S}]\quad\text{as } R\to\infty,$$
$$\underline{S}=-\exp(i\underline{\eta}^{\mathrm{JWKB}})\underline{C}_{+}\underline{C}_{+}^{T}\exp(i\underline{\eta}^{\mathrm{JWKB}}), \tag{54}$$
$$\underline{S}^{T}=\underline{S},\quad \underline{S}^{\dagger}\underline{S}=1.$$

The integration coordinate outside any particular notch point T_{ij} is transformed from R to Y:

$$Y=(R-T_{ij})^{1/2},$$
$$\frac{d}{dR}=\frac{1}{2Y}\frac{d}{dY}, \tag{55}$$

to remove the $(R-T_{ij})^{-1/2}$ singularity at the beginning of each integration interval.

A good test of a strong-coupling semiclassical method is to solve a problem whose transitions arise from the turning-point region. This occurs in rotational coupling in atom-atom collisions where the electronic fixed-nuclei eigenvalues are tending toward a near or exact united-atom degeneracy and the $\underline{A}_0$ potential-like coupling [Eq. (5)] is large as $R\to 0$. H^+ on H has been studied extensively by Knudson and Thorson[5] and their results are used as a benchmark for the study here. Rotational coupling occurs between the $2p\sigma_u$ and $2p\pi_u$ electronic fixed-nuclei states of the H_2^+ molecule[5]:

$$\begin{aligned}
&G_{1i}''+\kappa_1^2 G_{1i}=U_{12}G_{2i},\\
&G_{2i}''+\kappa_2^2 G_{2i}=U_{21}G_{1i},\\
&\kappa_i^2=(2\mu/\hbar^2)(E-V_i)-(L+\tfrac{1}{2})^2/R^2,\\
&U_{12}=U_{21}=-(\sqrt{2}\,)[L(L+1)]^{1/2}\langle L_+\rangle/R^2,
\end{aligned} \tag{56}$$

where

$$\begin{aligned}
V_1=W_{2p\sigma_u}&\sim 1/R-0.5+O(R^2) && \text{as } R\to 0\\
&\sim -0.5+O(1/R^4) && \text{as } R\to\infty,\\
V_2=W_{2p\pi_u}&\sim 1/R-0.5+O(R^2) && \text{as } R\to 0\\
&\sim -0.125+O(1/R^3) && \text{as } R\to\infty,\\
\langle L_+\rangle=\langle 2p\sigma_u|L_+|2p\pi_u\rangle&\sim(2)^{1/2}+O(R^2) && \text{as } R\to 0\\
&\sim(2/3)^4 R && \text{as } R\to\infty,
\end{aligned} \tag{57}$$

in a.u.[22,23] Solutions by SCUNF (see Eq. (16) and *et seq.*) and the hybrid quantum-JWKB method of Knudson and Thorson agreed to several figures for this problem as they should. Since SCUNF was of the same computational speed and avoided the test of where to join solutions, it is used as the "exact" result for all semiclassical comparisons.

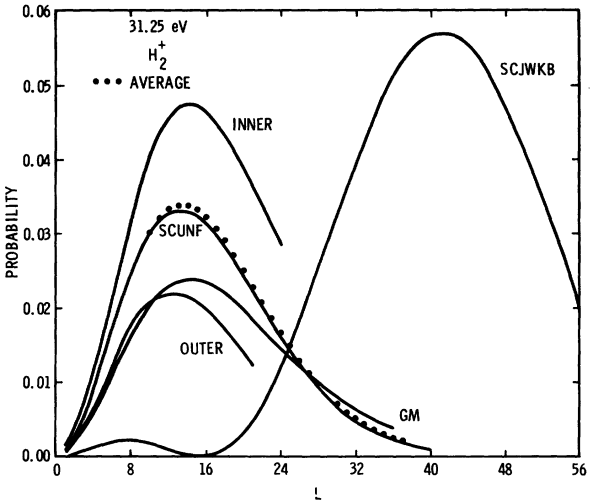

FIG. 1. Comparison of six semiclassical approximations for the $2p\sigma_u$ - $2p\pi_u$ rotational excitation in H^+ on H scattering as a function of nuclear rotation quantum number. "Inner" and "outer" refer to the use of V_1 or V_2 as a common potential and GM refers to the geometric-mean-velocity method.

Figure 1 presents an L-dependent study of the probability of excitation for six semiclassical methods at a relative collision energy of 31.25 eV for the lowest state ($E=0.6485$ a.u.): (i) the uniform reference function method, SCUNF, which is essentially exact; (ii) the average approximation; (iii) the use of V_1 as a common potential; (iv) the use of V_2 as a common potential; (v) the JWKB reference function method, SCJWKB; and (vi) the geometric-mean-velocity method advocated by Lawley and Ross.[24] The average approximation is clearly superior and demonstrates that the turning-point region is treated adequately by the procedure. Bates and Sprevak have shown that their method has almost exactly the same relative error for this problem.[19]

Figure 2 demonstrates that at a higher collisional energy, 250 eV relative kinetic energy in lowest

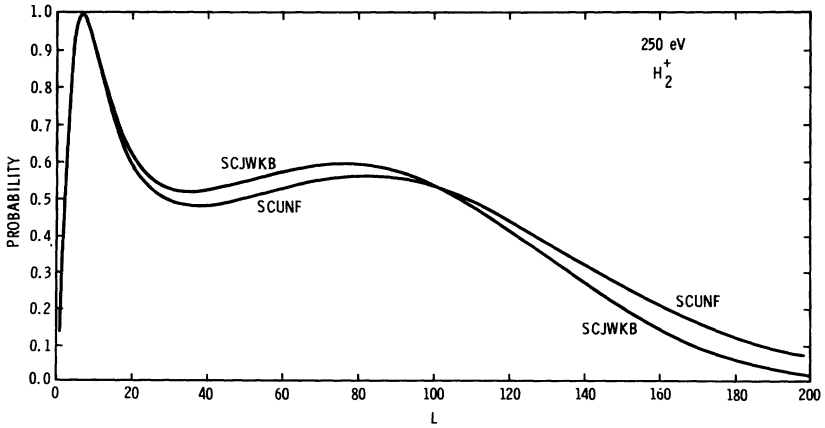

FIG. 2. Comparison of the semiclassical JWKB close-coupling approximation with the uniform method at a higher energy for the $2p\sigma_u$ -$2p\pi_u$ excitation in H^+ on H.

state ($E=8.6879$ a.u.), the SCJWKB method can give a more reasonable global picture of the excitation probabilities. The average approximation is coincident to graphical accuracy with SCUNF, and either the V_1 or V_2 common potential would work well as known from Knudson and Thorson's study of V_1.[5] The straight-line impact-parameter results are still in error for small L, though, so they completely miss the inner peak which contributes to large-angle scattering; the impact-parameter study for this excitation process is contained in Ref. 5. This general trend of approximations at high energy is to be expected.

V. TESTING OF AVERAGE APPROXIMATION ON OTHER PROBLEMS

This section contains the numerical study of several model problems which seem to be of special interest in testing of semiclassical approximations.

The rotational coupling of Sec. IV acted between molecular states which were degenerate at $R=0$. It is of interest to compare the methods pictured in Fig. 1 for coupling between nondegenerate molecular states, with the coupling potential still weighted towards the turning points. In particular, for a given energy, the turning points are further apart and the transition probability is much smaller. Figure 3 presents a study of an "artificial problem" generated by using the coupling U_{12} of Eq. (56) and V_2 of Eq. (57), but replacing $V_1=W_{2p\sigma_u}$ with $W_{1s\sigma_g}$, which has the properties:

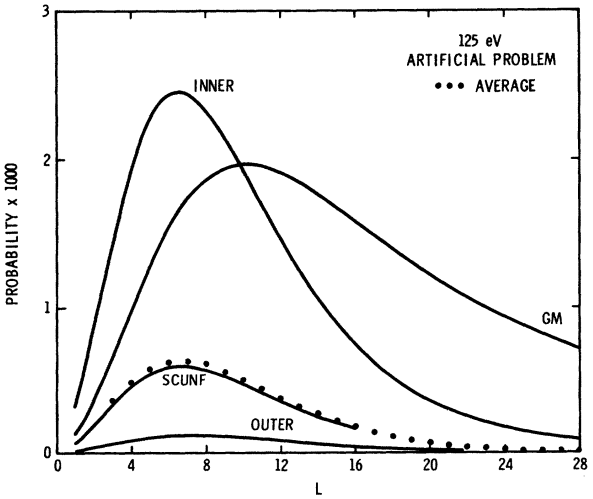

FIG. 3. Comparison of semiclassical approximations for the artificial problem defined in the text. The coupling arises from the turning-point region, but the diagonal potentials are not degenerate at $R=0$. "Inner" and "outer" refer to the use of the lower or higher interaction as a common potential and GM refers to the geometric-mean-velocity method.

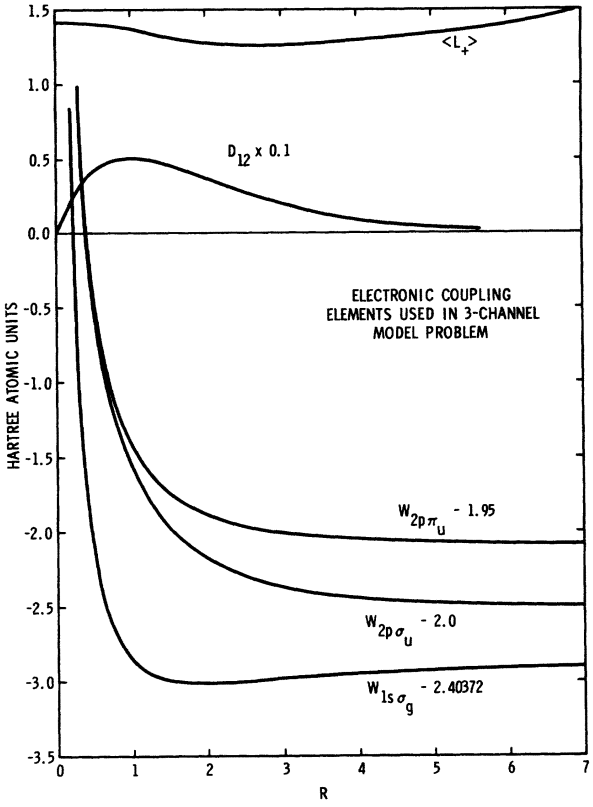

FIG. 4. Diagonal potentials and coupling elements used in the three-channel problem. The H_2^+ energies are scaled to resemble the lower states of HeH^+. $\langle L_+\rangle$ is the matrix element used in the $2p$ united atom coupling of H_2^+.

$$W_{1s\sigma_g} \sim 1/R - 2 + O(R^2) \quad \text{as } R \to 0,$$
$$\sim -0.5 + O(1/R^4) \quad \text{as } R \to \infty. \tag{58}$$

This study was done at a relative kinetic energy of 125 eV for the lower state ($E=4.0940$ a.u.). SCJWKB is grossly in error and not shown.

Many-channel calculations are specifically of interest at higher energies where transitions arise from coupling between energetically well-separated fixed-nuclei electronic states. Although such calculations cannot be expected to mean much without plane-wave factors,[1,4] nothing prevents testing of the semiclassical close-coupling methods on them. From the three H_2^+ potentials and the H_2^+ rotational coupling function, a model is constructed with three states, energetically like HeH^+:

$$V_1 = W_{1s\sigma_g} - 2.40372,$$
$$V_2 = W_{2p\sigma_u} - 2.0,$$
$$V_3 = W_{2p\pi_u} - 1.95,$$
$$D_{12} = 5Re^{1-R},$$

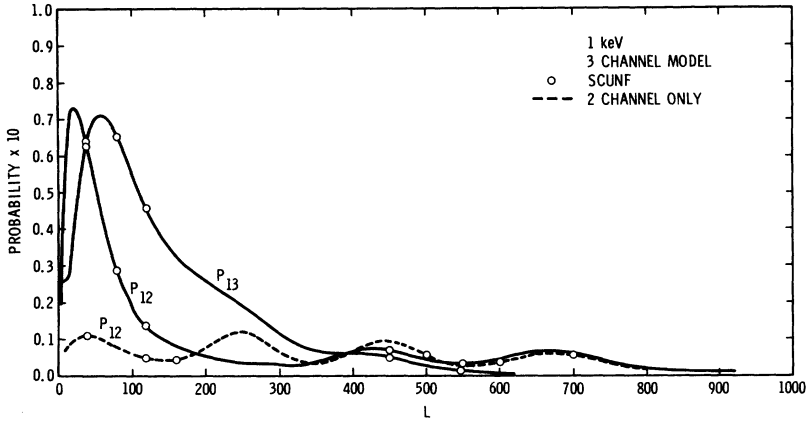

FIG. 5. A comparison of the average approximation with the more precise uniform method for a three-channel problem at 1 keV. The interactions for this problem are displayed in Fig. 4 and the masses used were those of HeH^+. Note the enhanced excitation at low L owing to the third channel.

$$U_{23} = -(\sqrt{2})[L(L+1)]^{1/2} < L_+ > /R^2 . \quad (59)$$

The relevant behavior of these is plotted in Fig. 4, and the results of two-channel and three-channel solutions displayed in Fig. 5 at 1-keV relative kinetic energy in channel 1 ($E = 33.848$ a.u.). The "angular" coupling between 2 and 3 has a curious effect on the 1 to 2 excitation probability. SCUNF confirms that the average approximation was as good as expected at this relatively high energy with no spurious results. The other semiclassical methods (common potential, impact parameter) are undoubtedly well into their domain of accuracy, but were not calculated for this rather fictitious problem.

Figure 6 presents a study of a problem designed to show the primary defect of the average approximation. The situation is a two-channel potential-coupling problem with a crossing (diabatic coupling) of the diagonal energy curves:

$$\begin{aligned} V_1 &= W_{2p\sigma_u} + 1/R^2 , \\ V_2 &= W_{2p\pi u} , \\ U_{12} &= (2\mu/\hbar^2)(0.03)(\tfrac{1}{2}R)e^{1-R/2} . \end{aligned} \quad (60)$$

The crossing occurs around $R = 2$ where V_{12} is about 0.03 a.u. The effect of the accumulated average phase error [Eq. (45)] is evident in the interference oscillation pattern at low L. The $L = 0$ turning points are at approximately 0.89 and 1.37 and the average potential turning point (notch point) is at 1.20 where the integration starts. By the time the integration reaches $R = 2$, the average phase difference [Eq. (45)] would appear from Fig. 6 to be $\frac{1}{2}\pi$ rad in error. The inelastic differential cross section in the center-of-mass frame shows that the $L = 60$ peak contributes to 40° scattering with a maximum of $4a_0^2$, where a_0 is the Bohr radius, and that the region of L less than 15 contributes to scattering greater than 120° with a magnitude less than $0.3a_0^2$. Thus, for this problem, the phase error as indicated in Fig. 7 is a large-angle effect and not too significant over-all.

The last problem investigated is based on the atom-diatomic molecule vibrational-excitation model of Secrest and Johnson,[25] which is a well-known problem in the field. For that reason, only the scaled input parameters are given here. Figure 7 compares two-channel coupling as a function of energy for a weak-coupled system and a strong-coupled system with a smaller mass parameter. The channels are the lowest two harmonic-oscillator states of the target and the barycentric energy is measured in units of $\frac{1}{2}\hbar\omega$.[25] The average

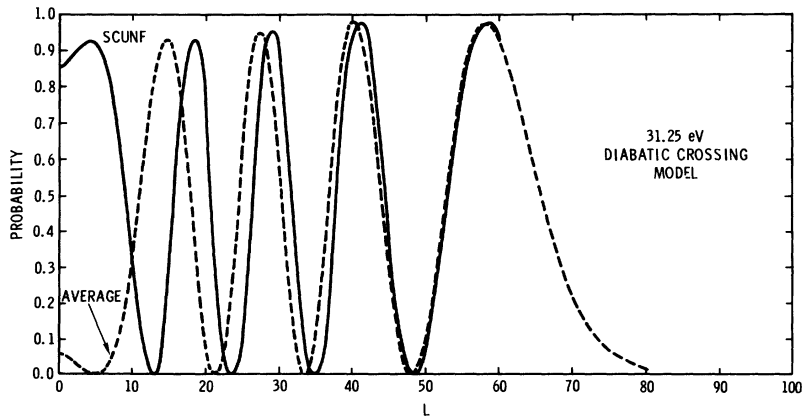

FIG. 6. A low-energy crossing model which displays the accumulated phase error in the average approximation. The diabatic coupling at the turning region is treated correctly (correct envelope), but the average phase between the crossing and the turning region is only correct through first order. The reduced mass is that of H_2^+ and the coupling is given in the text.

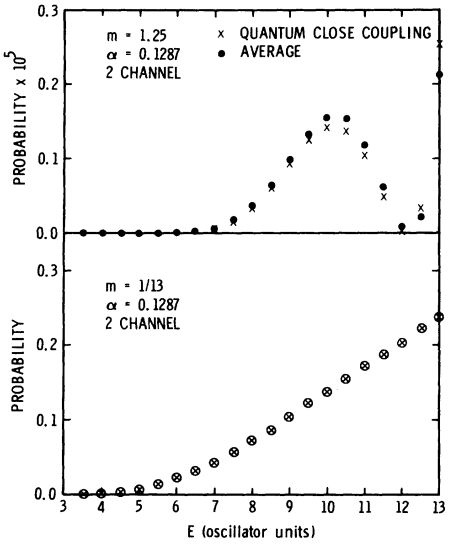

FIG. 7. Comparison of two-channel average and full-quantum calculations for the atom on diatom vibrational-excitation problem (Ref. 25). These results are identical in potential-coupling or derivative-coupling pictures.

approximation was compared to full quantum close-coupling results[13] since SCUNF was slow and not of sensible use. Table I presents a series of calculations for a six-channel problem, including the full quantum results (which include one closed channel, and are inaccurate in the last significant figure). Several facts are evident: (i) the excitation probabilities of the average approximation in the potential-coupling representation [see Eq. (9)] are not equivalent to those of the average approximation in the derivative-coupling representation [see Eq. (7)] for more than a two-channel problem; (ii) for this problem, the derivative-coupling average is superior; (iii) the two-channel result for the average agrees with the quantum two-channel calculation (Fig. 7) showing that this failure of the potential-coupling average method is a many-channel effect.

VI. DISCUSSION

In the many-channel case, the use of a common potential with in-out decoupling has always been appealing because of the classical trajectory interpretation of the equations.[15] Its utility really is the inherent necessity of making the radial turning points coalesce to avoid the real axis JWKB turning-point contributions as explained by Bates and Crothers. In the case of a two-channel problem, the average approximation has a simple common potential interpretation whereas the Bates-Crothers method does not. For two channels, the average approximation gives the same transition probability in either the potential or derivative coupling pictures. This is because the average potential is just one-half the trace of the coupling matrix, which is invariant to the transform that converts between the two representations [Eqs. (6)–(9)]. The many-channel average approximation does not have this property.

Computational speeds are nebulous things to compare, but any of the in-out decoupled semiclassical methods discussed here are more than an order of magnitude faster than the SCUNF procedure, which is fast itself in the semiclassical limit.

Phases of the S matrix have not been reported here explicitly; in general, they are of the same quality as the modulus for all of the methods. Neither did the calculational testing report the use of a SCJWKB method in the derivative coupling picture. This procedure, which would seem the theory of choice for low-energy collisions based on a large-mass fixed-energy limit with in-out decoupling, is considerably better than SCJWKB in the potential-coupling picture, but not generally better than the common-potential methods for the H_2^+ problem of Sec. IV or the artificial problem of Sec. V.

In conclusion, it seems that the average approx-

TABLE I. Comparison of potential- and derivative-coupling average approximations with full quantum results for the six open-channel Secrest-Johnson problem (Ref. 25) defined by $E = 12.8365$, $\alpha = 0.1287$, $m = \frac{1}{13}$, all in their scaled oscillator units. The columns represent the probability of excitation from the ground state of the target diatomic molecule, labeled as 1.

Final state	Quantum	Potential-coupling average	Derivative-coupling average
1	0.632	0.711	0.630
2	0.317	0.247	0.318
3	0.0485	0.0358	0.0490
4	0.0025	0.0057	0.0026
5	3.3×10^{-5}	9.5×10^{-4}	3.9×10^{-5}
6	0.5×10^{-7}	1.2×10^{-4}	1×10^{-7}

imation is the best of all simple common potentials to use for two-channel coupling. The multichannel average loses this common-potential aspect, but the method is obviously advantageous if one considers close coupling among two individually degenerate manifolds of states, e.g., the $2p$ and $3p$, $3d$ united-atom levels. At high energies the common potential is useful[5] and eventually the impact-parameter method will suffice[5] to describe the major features for all problems. It might also be added that the first derivations of the average approximation for close-coupling made direct use of the simple expansion techniques of Ref. 4 rather than the reference-function procedure used here. The original results gave the two-channel average approximation and a common-potential method for many channels. The reference-function procedure seems to afford an adequate generalization to the many-channel problem.

Note added in proof. The average approximation for the He^+Ne system studied by R. E. Olson and F. T. Smith [Phys. Rev. A 3, 1607 (1971)] reveals about a 10% peak-to-peak phase error at low L and a total cross section of 0.693 a.u. at 70.9 eV. CDC-6600 computation time was 1 min.

ACKNOWLEDGMENT

The author gratefully acknowledges many discussions with Thomas A. Green.

*Work supported by the U. S. Atomic Energy Commission.

[1]W. R. Thorson, J. Chem. Phys. **42**, 3878 (1965).
[2]F. T. Smith, Phys. Rev. **179**, 111 (1969).
[3]W. Kolos and L. Wolniewicz, Prog. Met. Phys. **35**, 473 (1963).
[4]M. E. Riley, Phys. Rev. A 7, 626 (1973).
[5]S. K. Knudson and W. R. Thorson, Can. J. Phys. **48**, 313 (1970).
[6]W. Wasow, *Asymptotic Expansions for Ordinary Differential Equations* (Interscience, New York, 1965).
[7]F. Calorgero, *Variable Phase Approach to Potential Scattering* (Academic, New York, 1967)
[8]R. J. Cross, J. Chem. Phys. **51**, 5163 (1969).
[9]R. G. Gordon, J. Chem. Phys. **51**, 14 (1969).
[10]D. R. Bates and D. S. Crothers, Proc. R. Soc. A **315**, 465 (1970).
[11]The reference-functions decomposition need not be restricted to diagonal solutions. Consider $G'' + MG = 0$, $M = P + Q$, $P^T = P$, $Q^T = Q$. In terms of two fundamental matrix solutions of $F_i'' + PF_i = 0$, $i = 1,2$, one can show that $W_{ji} = F_i^{T\prime}F_j - F_i^T F_j'$ is constant, which is all that is needed to establish $C_1 = W_{12}^{-1}(F_2^{T\prime}G - F_2^T G')$, $C_2 = W_{21}^{-1}(F_1^{T\prime}G - F_1^T G')$, if $W_{11} = W_{22} = 0$ and $C'_1 = W_{12}^{-1}F_2^T QG$, $C'_2 = W_{21}^{-1}F_1^T QG$. Other relations can be developed, but because of computational restrictions the general method does not seem useful.
[12]R. Langer, Phys. Rev. **51**, 669 (1937).
[13]E. J. Shipsey (private communication).
[14]R. Bulirsch and J. Stoer, Numer. Math. **8**, 1 (1965).
[15]Considerable literature exists concerning the high-frequency approximation: See Refs. 1, 5, 8, 10, and the recent papers of Delos: J. B. Delos, W. R. Thorson, and S. K. Knudson, Phys. Rev. A **6**, 709 (1972); J. B. Delos and W. R. Thorson, Phys. Rev. A **6**, 720 (1972).
[16]I. Berson, in *The Seventh International Conference on the Physics of Electronics and Atomic Collisions, Amsterdam, 1971*, edited by L. M. Branscomb *et al.* (North-Holland, Amsterdam, 1972).
[17]M. E. Riley, J. Chem. Phys. **55**, 1606 (1971). The error is $O(\alpha^{3/4})$ due to the rapid oscillation of χ_1 in Eq. (26) when the T_i are not near R_x.
[18]Integration over the nonuniform JWKB functions should be distinguished from a more elaborate analysis: R. T. Pack and J. S. Dahler, J. Chem. Phys. **50**, 2397 (1969); W. D. Smith and R. T. Pack, J. Chem. Phys. **52**, 1381 (1970).
[19]D. R. Bates and D. Sprevak, Chem. Phys. Lett. **10**, 428 (1971).
[20]E. E. Nikitin has discussed the importance of using a common potential (trajectory) such that the first-order term is exact {Opt. Spektrosk. 11, 452 (1961) [Opt. Spectrosc. 11, 246 (1961)]}.
[21]These calculations were done by T. A. Green and will be reported in a future publication.
[22]A tabular array of the H_2^+ eigenvalues were kindly supplied by Dr. J. M. Peek of Sandia Laboratories.
[23]Professor Thorson kindly gave a rational-fraction fit to $\langle L_x \rangle$ for use in comparing to the results in Ref. 4.
[24]K. P. Lawley and J. Ross, J. Chem. Phys. **43**, 2930 (1965).
[25]D. Secrest and B. R. Johnson, J. Chem. Phys. **45**, 4556 (1966).