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Numerical test of the semiclassical approximation to the multicurve-crossing problem: Three-state model for He$^+$ + Ne collisions*

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Transitions between adiabatic surfaces are described semiclassically via trajectories propagating about their complex intersection point. This intersection point is a branch point of the potential function and a simple pole of the nonadiabatic coupling. Thus transitions may be described without explicit introduction of the nonadiabatic coupling. This structure is independent of the total number of states, but is most easily shown for two-state systems. A three-state model of the He$^+$ + Ne collision system is solved by treating the three-state interaction as a sequence of two-state interactions. The results are in excellent agreement with accurate quantum calculations.

I. INTRODUCTION

Recently there has been considerable interest in theoretical descriptions of collison-induced electronic transitions in atom (ion)-atom and atom-diatom systems.[1-8] We have been working on a general semiclassical description of these processes based on Stueckelberg's theory of atom (ion)-atom collisions.[9] The description requires only the electronic adiabatic potential-energy surfaces of the collision system, and is based on the following features of their analytic structure. First, a complex point of degeneracy of two electronic states is a branch point of the corresponding adiabatic surfaces. Second, around the branch point, the leading term in the nonadiabatic coupling is a simple pole with residue independent of the particular electronic system. Thus transitions between states are effected by complex-valued trajectories propagating about the branch point, switching smoothly and continuously from one surface to the other. In this manner, transitions between adiabatic surfaces are described without the explicit introduction of the nonadiabatic coupling, which is responsible for the transition in a purely quantum-mechanical treatment.

Within the two-state approximation it is clear that the adiabatic surfaces exhibit the desired analytic behavior, supporting the validity of the semiclassical method. While the two-(electronic) state approximation has been reasonable for a number of collision systems, e.g., $H^+ + D_2 \rightarrow HD^+ + D$ involving transitions between the two lowest sigma states,[3,10] there are many collision systems involving significant coupling among three or more surfaces. For example, the interaction of a halogen atom (whose electronic states are split by the spin-orbit coupling into $^2P_{3/2}$ and $^2P_{1/2}$ states) with a hydrogen molecule gives rise to three electronic surfaces.[11-14] In addition, preliminary investigations into collisions in the presence of an intense laser field[15] indicate that four or more electronic-field adiabatic surfaces may often be required for an accurate description of the collision-field system.

The analytic structure of electronic adiabatic surfaces in the vicinity of their complex intersection points is independent of whether the states arise from the diagonalization of a 2×2 or a 100×100 matrix.[16] Thus, for a multistate system, we intuitively expect a straightforward generalization of the two-state result, where transitions between surfaces are localized at their complex intersection points and the local transition probability is independent of all other surfaces. Thus the scattering process can be viewed as a series of local transitions between pairs of states. Recently the semiclassical theory was formally extended to the three-state case,[17] and the simple result described above was obtained if terms containing all three nonadiabatic couplings were neglected. Hwang and Pechukas,[18] in their analysis of the problem, found a possible additional source of transition amplitude in the three-state case, but were unable to state when it might be important. We will use the straightforward approach of local two-state transitions, and compare results of this method to those of exact quantum-mechanical calculations.

In this paper we restrict ourselves to atom(ion)-atom scattering, which may be described by a single nuclear coordinate R. This allows us to focus on electronic transitions and greatly reduces the amount of computer time required to analyze any model. In particular, we wish to study the excitation

$$\mathrm{He}^+(1s) + \mathrm{Ne}(2p^6) \rightarrow \mathrm{He}^+(1s) + \mathrm{Ne}(2p^5 3s)\,, \qquad (1.1)$$

which has been of considerable interest both experimentally[19-24] and theoretically.[25-32] A three-state model of this process has been proposed recently by Cho and Eu[33] as a test of their semiclassical method. We adopt their model so that we may compare our semiclassical procedure against theirs.

In Sec. II we outline the semiclassical and quantum descriptions of atom(ion)-atom scattering. Angular and Coriolis coupling are neglected, the states coupling via radial coupling alone. In Sec. III Cho and Eu's model potential for the $He^+ + Ne$ system and the results of our calculations of transition probabilities and cross sections are presented. A discussion in Sec. IV concludes the paper.

II. THEORY

A. Semiclassical

The semiclassical method as applied to two-state models of atom(ion)-atom scattering is well documented.[4,34] Transitions between adiabatic curves are localized at their complex intersection (branch) points. Thus a typical trajectory propagates on an initial surface from a large internuclear separation until it reaches the real part of a complex intersection point. At this point it may either switch to the other surface [with a local probability $p=\exp(-2\,\mathrm{Im}\phi)$, where ϕ is the phase accumulated in propagating about the branch point], or it may stay on the same curve (with a probability $1-p$). The classical trajectory then continues, making the choice of switching or not switching at each intersection point, until the nuclei are again well separated. S-matrix elements, connecting an initial state n with a final state m, must include the contributions from all possible paths connecting those states and can be written as

$$S_{mn}=\sum_j P_j e^{i\Phi_j}\,, \tag{2.1}$$

where P_j is a product of all probability factors for the particular trajectory to either make or not make a transition at the branch points, Φ_j is the real phase accumulated along the trajectory, and the sum is over all classical trajectories starting on curve n and ending on curve m.

The enumeration of all possible paths in a complicated potential system could be tedious and error-prone if done by inspection. A matrix formulation of the propagator, an appropriate product of local propagators,[35] yields a correct enumeration of paths as outlined below. A similar representation has been presented by Child[36] for the two-state case. The elements of the local propagators are of the form $\gamma e^{i\phi}$, where $\phi=\int k\,dR$, $k=(2\mu[E-W_i(R)])^{1/2}/\hbar$, and γ is a preexponential factor. Transitions are localized at the complex intersection points and involve only two states. Thus, if we consider this propagation near an intersection point of curves 1 and 2, no phase will be accumulated on the third curve, and the matrix representation of the local propagator is

$$\underline{G}_{12}^{\mp}=\begin{pmatrix}(1-p)^{1/2} & \mp p^{1/2}e^{\mp i\chi} & 0\\ \pm p^{1/2}e^{\pm i\chi} & (1-p)^{1/2} & 0\\ 0 & 0 & 1\end{pmatrix}, \tag{2.2}$$

where

$$p=\exp(-2\,\mathrm{Im}\phi)\,, \tag{2.3}$$

$$\chi=\mathrm{Re}\phi+\delta\,, \tag{2.4}$$

$$\phi=\int_{R_0}^{R_*}(k_1-k_2)\,dR\,, \tag{2.5}$$

$$k_i=(2\mu[E-W_i(R)])^{1/2}/\hbar\,, \tag{2.6}$$

$i=\sqrt{-1}$, R_* is the complex intersection point of adiabatic curves W_1 and W_2, δ is a constant phase factor, R is the internuclear separation, and the upper (lower) sign corresponds to the incoming (outgoing) portion of the trajectory. The subscripts on $\underline{G}$ denote the pair of adiabatic curves which intersect.

In regions devoid of intersection points, the propagator is simply

$$F^{\mp}(R_1,R_2)=\begin{bmatrix}\exp\left(\mp i\int_{R_1}^{R_2}k_1\,dR\right) & 0 & 0\\ 0 & \exp\left(\mp i\int_{R_1}^{R_2}k_2\,dR\right) & 0\\ 0 & 0 & \exp\left(\mp\int_{R_1}^{R_2}k_3\,dR\right)\end{bmatrix}, \tag{2.7}$$

where again the upper (lower) sign corresponds to propagation on the incoming (outgoing) segment of the trajectory. The total propagator is an appropriate set of such matrices, as determined by the potential system. Consider the potential system sketched in Fig. 1 which is the model of the $He^+ + Ne$ system. R_{01} (R_{02}) is the real part of intersection point R_{*1} (R_{*2}) between adiabatic curves W_2

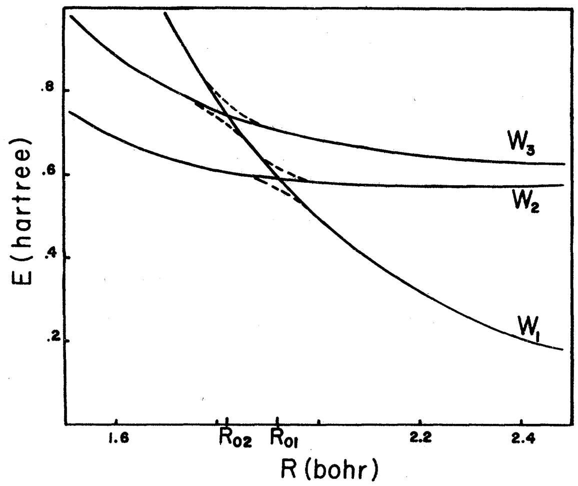

FIG. 1. Potential-energy system: Diabatic potentials chosen for the He$^+$ + Ne system are the solid curves, and adiabatic potentials W_1, W_2, and W_3 are the dashed lines. E and R are in atomic units.

and W_1 (W_3). For this system, the propagator is

$$\underline{K} = \underline{F}^-(R_a, R_{01})\underline{G}_{12}^-\underline{F}^-(R_{01}, R_{02})\underline{G}_{23}^-\underline{F}^-(R_{02}, \mathrm{TP}) \times \underline{F}^+(\mathrm{TP}, R_{02})\underline{G}_{23}^+\underline{F}^+(R_{02}, R_{01})\underline{G}_{12}^+\underline{F}^+(R_{01}, R_a)\,, \tag{2.8}$$

where TP collectively represents the turning points of the curves and R_a is large. Equation (2.8) is valid for energies high enough that R_{02} is classically accessible on all curves. Evaluation of the matrix multiplications leads to

$$K_{11} = ((1-p_1)\exp[2i(A_1+B_1)] + p_1\mathfrak{F})\exp(2iG_1)\,, \tag{2.9}$$

$$K_{12} = [p_1(1-p_1)]^{1/2}(\exp\{i[2(A_1+B_1)+F_1]\} - \mathfrak{F}) \times \exp[i(G_1+G_2)]\,, \tag{2.10}$$

$$K_{13} = [p_1p_2(1-p_2)]^{1/2}\exp[i(A_2+A_3-F_1)] \times\{\exp[i(2B_3-F_2)] - \exp[i(2B_2+F_2)]\} \times\exp[i(G_1+G_3)]\,, \tag{2.11}$$

where

$$\mathfrak{F} = \exp[2i(A_2-F_1)]\{(1-p_2)\exp[2iB_2] + p_2\exp[2i(B_3-F_2)]\}\,, \tag{2.12}$$

$$A_i = \int_{R_{02}}^{R_{01}} k_i\,dR\,, \tag{2.13}$$

$$B_i = \int_{TP_i}^{R_{02}} k_i\,dR\,, \tag{2.14}$$

$$G_i = \int_{R_{01}}^{R_a} k_i\,dR\,, \tag{2.15}$$

$$p_1 = \exp[-2\,\mathrm{Im}(C_1-C_2)]\,, \tag{2.16}$$

$$p_2 = \exp[-2\,\mathrm{Im}(D_2-D_3)]\,, \tag{2.17}$$

$$F_1 = \mathrm{Re}(C_1-C_2)+\delta_1\,, \tag{2.18}$$

$$F_2 = \mathrm{Re}(D_2-D_3)+\delta_2\,, \tag{2.19}$$

$$C_i = \int_{R_{01}}^{R_{*1}} k_i\,dR\,, \tag{2.20}$$

$$D_i = \int_{R_{02}}^{R_{*2}} k_i\,dR\,, \tag{2.21}$$

and δ_1 and δ_2 are constant phase factors.

These phase factors, although associated with individual isolated transitions, are dependent on the overall dynamics of the collision process. In this sense, we can define a value to the total phase factor $\delta = \delta_1 + \delta_2$, which is determined by the behavior of the diabatic curves, analagous to the two-state case.[4] For low energies, R_{02} is classically inaccessible, and hence $\delta = \delta_1 = \frac{1}{4}\pi$. For higher energies such that R_{02} is classically accessible, the choice $\delta_1 = 0$, $\delta_2 = \frac{1}{4}\pi$ yields excellent agreement with the quantum results. Thus the crossing point at the highest energy appears to be the most important. (Various authors[36-39] have proposed analytic forms for the phase factor δ associated with two-state transitions, but for our present study we found the constant phase factors to yield better agreement with exact quantum results than these analytic forms.)

The total cross section for an inelastic process is

$$\sigma_{i\leftarrow j} = \frac{\pi}{k_j^2(R_a)}\sum_{l=0}^{\infty}(2l+1)\,|S_{ij}(l)|^2\,, \tag{2.22}$$

where l is the partial-wave index. The partial-wave expansion adds a centrifugal term to the potential, yielding the effective potentials

$$W_i(R) = W_i(R) + \frac{(l+\frac{1}{2})^2}{2\mu R^2}\,. \tag{2.23}$$

Here, the Langer correction[40] has been incorporated. As l increases, the centrifugal barrier increases and the turning points become larger. As the turning points approach the vicinity of R_{02} and R_{01}, the simple formulas (2.9)–(2.12) must be modified. One must keep in mind that the semiclassical theory is based on a Feynman path-integral representation of the propagator. This integral is evaluated by the method of stationary phase, and when the paths of stationary phase are well separated, the results (2.9)–(2.12), the so called primitive semiclassical results, are valid. However, as the paths of stationary phase begin to coalesce, more sophisticated methods are required to evaluate the path integral.[4,34] As the turning point on the upper surface approaches the real part of the inner intersection point, the following uniform expressions are needed:

$$S_{11}=\{(1-p_1)\exp(2iA_1)+p_1\exp[2i(A_2-F_1)] \times(1-\kappa^2)^{1/2}\}\exp(2iG_1)\,, \tag{2.24}$$

$$S_{12}=[p_1(1-p_1)]^{1/2} \times\{\exp[i(2A_1+D_1)]-\exp[i(2A_2-F_1)](1-\kappa^2)^{1/2}\} \times\exp[i(G_1+G_2)]\,, \tag{2.25}$$

$$S_{13}=(p_1)^{1/2}\kappa\exp[i(A_2+A_3+G_1+G_3-D_1)]\,, \tag{2.26}$$

$$\kappa=[p_2(1-p_2)]^{1/2}2\pi^{1/2}z^{1/4}\mathrm{Ai}(-z)\,, \tag{2.27}$$

$$z=[\tfrac{3}{2}(B_2-B_3)]^{2/3}\,. \tag{2.28}$$

These formulas are used when $|z|<5$. For larger l, or smaller E, R_{02} is classically inaccessible on both W_2 and W_3, $|z|>5$ and $\kappa=\exp[i(D_2-D_3-B_2-B_3)]$. As l increases further, transitions between W_1 and W_3 become negligible, and TP_2 becomes closer to R_{01}. Thus it is necessary to make the $1\rightarrow 2$ transition uniform in a manner analogous to (2.24)–(2.28) for the $2\rightarrow 3$ transition.

This formulation ignores second-order effects predicted in formal developments of the three-state theory.[17,18] The neglect of these terms yields a straightforward formalism that can easily be extended to the general N-state system.

B. Quantum

An inelastic collision between an atom (ion) and an atom is described in the coupled-channel representation by a set of simultaneous equations which may be written in matrix form as

$$\left[\left(-\frac{\hbar^2}{2\mu}\nabla^2_{\vec{R}}-E\right)\underline{1}+\underline{V}(\vec{R})\right]\underline{\psi}(\vec{R})=0\,, \tag{2.29}$$

where $\underline{\psi}$ is a matrix of indexed probability-amplitude functions ψ_{ji} related to the electronic state transitions $\phi_i\rightarrow\phi_j$, and where $\underline{V}$ is the matrix representation of the potential

$$V_{ij}(\vec{R})=\langle\phi_i|V(\vec{R},\vec{r})|\phi_j\rangle\,. \tag{2.30}$$

$V(\vec{R},\vec{r})$ contains the electronic kinetic energy as well as the Coulombic potential terms. If the potential matrix $\underline{V}$ depends only upon the radial coordinate, i.e., no angular coupling, we can expand the wave functions in terms of spherical coordinates and obtain

$$\frac{d^2}{dR^2}\underline{\chi}(R)=\underline{W}(R)\underline{\chi}(R)\,, \tag{2.31}$$

where

$$W_{ij}(R)=-\frac{2\mu}{\hbar^2}\left[\left(E-\frac{l(l+1)}{2\mu R^2}\right)\delta_{ij}-V_{ij}(R)\right]\,, \tag{2.32}$$

$$\chi_i(R)=\psi_i(R)/R\,. \tag{2.33}$$

The set of N second-order coupled differential equations is first rewritten as a set of $2N$ first-order coupled differential equations. In matrix notation, this is

$$\frac{d}{dR}\underline{\psi}(R)=\begin{pmatrix}\underline{0} & \underline{1}\\ \underline{W} & \underline{0}\end{pmatrix}\underline{\psi}(R)\,, \tag{2.34}$$

where

$$\underline{\psi}(R)=\begin{pmatrix}\underline{\chi}\\ d\underline{\chi}/dR\end{pmatrix}\,. \tag{2.35}$$

For a short interval d, the solution of Eq. (2.33) may be written

$$\underline{\psi}(R+\tfrac{1}{2}d)=\exp\left[d\begin{pmatrix}\underline{0} & \underline{1}\\ \underline{W}(R) & \underline{0}\end{pmatrix}\right]\underline{\psi}(R-\tfrac{1}{2}d)\,. \tag{2.36}$$

This is the lowest order of the Magnus approximation[41] and was used in our calculations. The propagator for a large distance, $\underline{A}$, is a product of short-interval solutions, where the size of these intervals, d, is chosen such that

$$d\lesssim\left(144\alpha\,\frac{\sum_i|\lambda_{ii}|^2}{\sum_i[W'_{ii}]^2}\right)^{1/4}\,, \tag{2.37}$$

where λ^2_{ii} are the eigenvalues of $\underline{W}(R)$. In our calculations, we choose $\alpha\simeq 7\times 10^{-7}$.

The propagation is initiated at small R_0, buried far below the potential barrier, such that the initial conditions $\underline{\chi}=\underline{0}$ and $\underline{\chi}'=\underline{1}$ are satisfied. As one propagates in the classically forbidden region, exponential growth of the solution matrix is encountered. Left unchecked, it would soon overflow the computer. A number of remedies for this problem have been proposed,[41-44] of which we use a modification of the Riley[44] method. Under the barrier the propagator is stabilized every few steps and is restarted with appropriately revised initial conditions. The propagation is continued to large internuclear separation R_a, where

$$\underline{\psi}(R_a)=\underline{A}\,\underline{\psi}(R_0)=\begin{pmatrix}\underline{I}\underline{X}-\underline{O}\underline{Y}\\ \underline{I}'\underline{X}-\underline{O}'\underline{Y}\end{pmatrix}, \tag{2.38}$$

where $\underline{I}$ ($\underline{O}$) is the diagonal matrix of the incoming (outgoing) waves and $\underline{X}$ and $\underline{Y}$ are their coefficients. The boundary conditions can also be expressed as

$$\underline{\psi}(R_a) \sim \begin{pmatrix} \underline{I} - \underline{O}\,\underline{k}^{1/2}\underline{S}\,\underline{k}^{-1/2} \\ \underline{I}' - \underline{O}'\underline{k}^{1/2}\underline{S}\,\underline{k}^{-1/2} \end{pmatrix}, \tag{2.39}$$

where $\underline{k}$ is the (diagonal) matrix of channel momenta and $\underline{S}$ is the S matrix. A comparison of these equations yields

$$\underline{S} = \underline{k}^{-1/2}\underline{Y}\,\underline{X}^{-1}\underline{k}^{1/2}, \tag{2.40}$$

where $\underline{X}$ and $\underline{Y}$ are obtained from Eq. (2.38). The $\underline{S}$ matrix obtained via this procedure is unitary to at least eight places. The step-size parameter α, and the initial (R_0) and final (R_a) points of propagation were chosen conservatively to yield converged results. The calculation of transition probabilities at a single value of l, the partial-wave index, took 4–5 sec of CPU time on a CDC 6600.

III. MODEL CALCULATION

The excitation process shown in Eq. (1.1) has been analyzed by a number of theoretical techniques.[28-33] In most cases a two-state model has been invoked, and the potential parameters have been adjusted to mimic selected experimental results. The excited state of Ne lies approximately 16.8 eV above the ground state, and is split into ${}^2P_{3/2}$ and ${}^2P_{1/2}$ components, which are separated by 0.178 eV.[45] In this calculation, a set of potentials which correlate asymptotically to $\mathrm{He}^+(1s) + \mathrm{Ne}(2p^6)$ and $\mathrm{He}^+(1s) + \mathrm{Ne}(2p^5 3s, {}^2P_{3/2,1/2})$ were used. The diabatic potentials,

$$V_{11} = (33.1/R)e^{-R/0.57}, \tag{3.1}$$

$$V_{22} = (18.1/R - 10.1)e^{-R/0.57} + 0.6128, \tag{3.2}$$

$$V_{33} = (18.1/R - 6.9)e^{-R/0.57} + 0.6194, \tag{3.3}$$

are the solid curves sketched in Fig. 1. The coupling potentials are

$$V_{12} = V_{21} = 0.178e^{-R/0.667}, \tag{3.4}$$

$$V_{13} = V_{31} = 0.050e^{-R/0.667}, \tag{3.5}$$

$$V_{23} = V_{32} = 0, \tag{3.6}$$

where all parameters are in atomic units. This potential system was introduced by Cho and Eu,[33] and we adopt it to compare our approach with theirs. The adiabatic curves are represented by the dashed curves in Fig. 1 and vary little from the diabatic curves. The real parts of the complex intersection points differ little from the crossing points of the diabatic curves and are shown on Fig. 1. In the following calculations any rotational or Coriolis coupling is ignored.

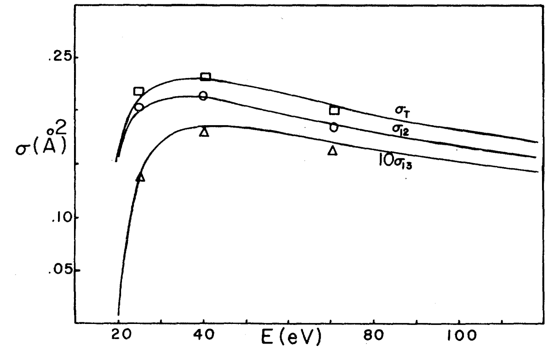

FIG. 2. Total cross sections: The solid lines are the accurate quantum results and ○, △, and □ represent σ_{12}, $10 \times \sigma_{13}$, and $\sigma_T = \sigma_{12} + \sigma_{13}$, respectively, as calculated by our semiclassical method.

The S-matrix and transition probabilities as a function of partial-wave index l were calculated for center-of-mass collision energies in the range 20–100 eV. These probabilities were then summed by the prescription of Eq. (2.22) to yield total inelastic cross sections. As experiments have not been set up to distinguish the spin-orbit states of Ne, the total inelastic cross section $\sigma_T = \sigma_{12} + \sigma_{13}$ was also calculated. The results of these calculations are drawn in Fig. 2. The solid lines represent the accurate quantum results, and the ○, △, and □ represent the semiclassical σ_{12}, σ_{13}, and σ_T results, respectively. The σ_{13} results have been multiplied by 10. The semiclassical results show excellent agreement with the quantum cross sections. However, as those represent a sum over a large number of partial waves (typically 300), the agreement could be fortuitous.

Figures 3 and 4 show the transition probabilities $|S_{13}|^2$ and $|S_{12}|^2$, respectively, as a function of

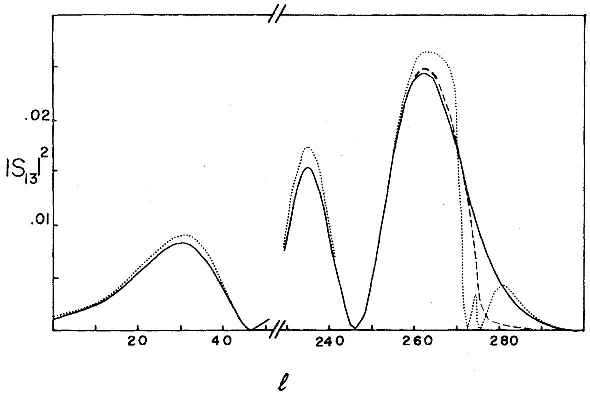

FIG. 3. $|s_{13}|^2$ versus l, the partial-wave index: The solid, dashed, and dotted curves represent quantum, our semiclassical, and Cho and Eu's semiclassical results, respectively. For l between 50 and 230 these curves oscillate 12 times; all are in excellent agreement.

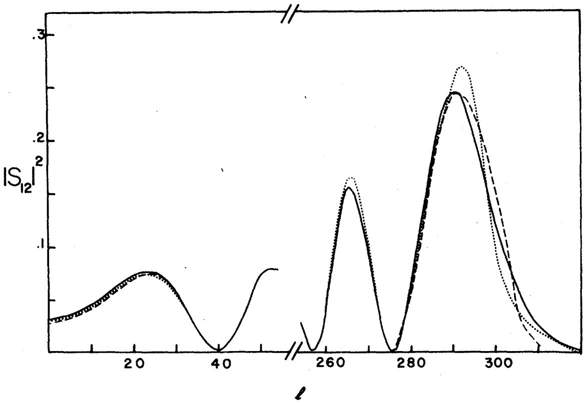

FIG. 4. $|s_{12}|^2$ vs l: The curves are labeled as in Fig. 3. Between $l = 50$ and $l = 260$ these curves oscillate 17 times; all methods are in excellent agreement.

partial wave index l at a collision energy 2.605 hartree (70.9 eV). In both figures the solid curve represents the accurate quantum results, and the dashed (dotted) curves represent our (Cho and Eu's) semiclassical results. A large range of l values are excluded in each case where all methods are in excellent agreement. Only two trajectories contribute to S_{13} [see Eq. (2.11)] such that it has the general structure of the well-known two-state result,[34] with a preexponential factor $\sqrt{p_1}$ and some phase factors due to the presence of W_1. Thus it is no surprise that our result is in such excellent agreement with the quantum results, as can be seen from Fig. 3. At large l, the turning points on W_2 and W_3 coalesce with R_{02}, and the uniform procedures cannot completely duplicate the quantum results. The disagreement is over a very small range of partial-wave index and has a small effect on the total cross section.

S_{12} is a more severe test of our semiclassical theory, as three trajectories contribute, and phase differences among all curves determine the probability. However, we again find (Fig. 4) excellent agreement with the quantum results by following the prescription of Sec. II A. Our results appear somewhat better than those of Cho and Eu, but both are in excellent agreement with the accurate quantum results.

IV. DISCUSSION

In the Introduction we asserted that the branch-point structure at degeneracies of adiabatic electronic surfaces was independent of the total number of surfaces. This allowed us to treat transitions between adiabatic surfaces locally, by the same procedure as in the two-state case. Any possible corrections due to the presence of the third surface[17,18] were ignored. As can be seen from Figs. 2–4, for this model potential system, these additional corrections were unnecessary.

This procedure may readily be extended to larger numbers of adiabatic surfaces. The matrix methods outlined in Sec. II A can be used to enumerate all possible paths, once the complex intersection points are located. S-matrix elements may be written as in Eq. (2.1) with all quantities calculated using analogies to two-surface results.

Although in this paper we have restricted ourselves to atom-(ion) atom scattering, the formalism is not restricted to this case and may easily be generalized to atom-diatom three-dimensional scattering. This is most easily visualized within the decoupling approximation,[46] where the transition probabilitity is calculated locally by integrating in the complex plane over the nuclear coordinate which couples most strongly to the electronic transition. In addition to the conceptual simplicity of the decoupling procedure, substantial computational savings result since the potential-energy surfaces need to be analytically continued locally rather than globally. In multistate applications of the semiclassical theory, we expect the decoupling approximation to be valuable.

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