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Semiclassical off-shell T-matrix elements for nearly coincident momenta in the classically allowed region

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Semiuniform off-shell wave functions and T-matrix elements are presented that remain valid even in the limit of equal incoming and outgoing momenta. Numerical comparisons are made with both primitive semiclassical and fully quantal predictions for scattering described by a Hulthen potential.

INTRODUCTION

Light scattering by atoms undergoing collisions can yield a wealth of information concerning interatomic interactions. Recently, a large amount of effort, both theoretical and experimental, has been devoted to the study of so-called half-collision events, such as collisional redistribution[1–4] and molecular photodissociation.[5–7] In a typical redistribution experiment, a photon, tuned far from the asymptotic free-atom transition, is absorbed, exciting a localized population deep within the collision according to the Franck-Condon principle. Information about the subsequent evolution of the collision complex, out to the final asymptotic states, is obtained by observing the polarization dependence of the resulting fluorescence close to line center,[1] or by absorption of a second photon to a higher atomic level.[8]

Lately some workers[9,10] have proposed that even more detailed information about the collisional evolution could be obtained if these experiments were generalized, so that the interaction with the second photon would also occur deep within the collision. This would allow one to isolate even smaller pieces of the collisional evolution (see Fig. 1). This kind of truncated collisional interaction is well described by the term "incomplete collisions,"[11] since, described as a scattering event, the important collisional evolution is confined to a region well removed from the asymptotic "in" and "out" scattering states. A description of these incomplete collisions can be readily couched in terms of the rather powerful formalism existent for the two-body off-the-energy-shell T operator. Although fully quantal codes for the calculation of the off-shell T-matrix elements for spherically symmetric potentials already exist,[12] one would also like to have available a reasonable semiclassical formulation, primarily because of the added physical insight such an approach provides. In particular, the concept of far-wing (quasistatic) atomic absorption is well established in terms of a semiclassical description. In fact, the semiclassical description of quasistatic absorption is often simple enough to allow for the direct inversion of experimental data to yield interatomic potential energy curves.[13] An additional advantage of developing the formalism for a semiclassical description of incomplete collisions in terms of the off-shell T operator is that one can then compare the resultant predictions directly with existing fully quantal calculations.

Recently there have been several efforts at developing such a formalism.[11,14–17] The pioneering work was a series of papers by Korsch and Möllenkamp,[14,15] in which they developed a semiclassical formula for off-shell T-matrix elements using WKB wave functions. With this approach, the start and finish of the incomplete collision appear as stationary phase points which dominate the generalized overlap integrals. Good agreement was obtained in comparison with quantal calculations of Beard and Micha[18] for H-H scattering, except for regions where the stationary phase points approached either the classical turning points of the collision, or the asymptotic region, or each other. The breakdown near the classical turning point is a familiar feature of the WKB approximation. Subsequently Burnett and Belsley[16] attempted to develop a uniform generalization of this approach based upon mapping the differential equation for the off-shell propagator onto a comparison equation for an isolated

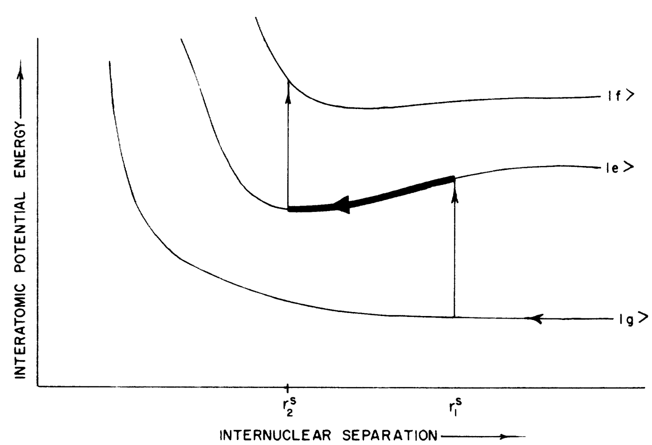

FIG. 1. A schematic diagram showing how one can create an "incomplete" collision through two photon absorption. The first photon is absorbed at the point r_1^s, where the electronic energy curves are shifted into resonance by the collisional interaction. This creates a localized population which then propagates up to the point r_2^s where it is removed via absorption to a higher-lying state.

turning point. The purpose of the present work is to explicitly develop a formula valid in the classically accessible region, even in the limit for which the incoming and outgoing momenta are equal. This is particularly important for applications employing a multiple scattering formalism, since the total off-shell T-matrix elements are often largest in the region of near elastic scattering.[18] To avoid complications due to higher-order effects, such as the coalescing of three stationary points, we will limit our treatment to a consideration of purely repulsive potentials.

After a brief introduction to the relevant notation and a description of the partial-wave expansions used in this work, we outline the techniques used in the uniform evaluation of the off-shell wave function and T-matrix elements. We then compare the predictions of our development directly against those of Korsch and Möllenkamp[15] and the fully quantal variable phase and amplitude calculation of Beard and Micha[18] for the triplet H-H scattering described by a Hulthen potential. Specific conclusions are drawn regarding the applicability of this work to more general scattering problems.

PARTIAL-WAVE DECOMPOSITION OF THE OFF-SHELL T OPERATOR

In this section the standard formalism[14–20] used to obtain the partial-wave off-shell T-matrix elements is briefly outlined. Our starting point is the Lippman-Schwinger equation[21] for the two-body off-shell T operator describing the scattering of two particles at an energy E by the interaction potential $\hat{V}$,

$$\hat{T}(E)=\hat{V}+\hat{V}\frac{1}{E-\hat{H}_0+i\epsilon}\hat{T}(E) \tag{1}$$

where $\hat{H}_0$ is the kinetic energy operator for the relative motion. It is convenient to introduce an off-shell wave operator $\hat{W}(E)$ via

$$\hat{T}(E)=\hat{V}\hat{W}(E)\ , \tag{2}$$

allowing us to rewrite (1) as

$$(E-\hat{H}_0-\hat{V})\hat{W}(E)=(E-\hat{H}_0)\ . \tag{3}$$

When this equation is projected onto a mixed coordinate-momentum representation one obtains the inhomogeneous Schrödinger equation,

$$\left[E+\frac{\hbar^2}{2m}\nabla^2-V(r)\right]\langle \mathbf{r}|\hat{W}(E)|\mathbf{p}\rangle=\left[E-\frac{p^2}{2m}\right]\langle \mathbf{r}|\mathbf{p}\rangle\ , \tag{4}$$

where m, $\mathbf{r}$, and $\mathbf{p}$ are, respectively, the reduced mass, the relative coordinate, and the relative momentum of the two particles involved in the scattering event. A reduced radial equation may then be obtained by introducing a partial-wave decomposition for the off-shell wave function,

$$\langle \mathbf{r}|\hat{W}(E)|\mathbf{p}\rangle=(2\pi)^{-3/2}\sum_l i^l(2l+1)P_l(\hat{\mathbf{r}}\cdot\hat{\mathbf{p}})w_l(r,p;E)\ . \tag{5}$$

Here P_l are the Legendre polynomials. A similar decomposition can be given[21] for the coordinate-momentum overlap in terms of the Ricatti-Bessel functions, $j_l(pr/\hbar)$. The resulting reduced radial equation is

$$\left[\hbar^2\frac{d^2}{dr^2}+\left[E-V(r)-\frac{\hbar^2 l(l+1)}{2mr_2^2}\right]\right]w_l(r,p;E)=(p_E^2-p^2)j_l(pr/\hbar)\ , \tag{6}$$

with $p_E=\sqrt{E/2m}$. Using Eq. (2), the matrix elements of the off-shell T operator can then be obtained from the off-shell wave function. In terms of a partial-wave decomposition,

$$\langle \mathbf{p}_2|T(E)|\mathbf{p}_1\rangle=\frac{1}{4\pi}\sum_{l=0}^{\infty}(2l+1)t_l(p_2,p_1;E)P_l(\hat{\mathbf{p}}_2\cdot\hat{\mathbf{p}}_1)\ , \tag{7}$$

the T-matrix element for an initial momentum p_1, and final momentum p_2, is

$$t_l(p_2,p_1;E)=\frac{2}{\pi\hbar p_1p_2}\int_0^\infty dr_2 j_l\left[\frac{p_2r_2}{\hbar}\right]\times V(r_2)w_l(r_2,p_1;E) \tag{8}$$

where, in general, the momenta are off shell, i.e., $p_1\neq p_2\neq p_E$.

THE OFF-SHELL WAVE FUNCTION

As in a previous paper,[16] our approach will be to develop an expression for the off-shell wave function in terms of a Green's-function solution to the homogeneous Schrödinger equation, i.e.,

$$\left[\hbar^2\frac{d^2}{dr_2^2}+\left[E-V(r_2)-\frac{\hbar^2 l(l+1)}{2mr_2^2}\right]\right]g_l(r_2,r_1;E)=\hbar\delta(r_1-r_2)\ . \tag{9}$$

Given $g_l(r_2,r_1;E)$ we can write a solution to (7) in the form

$$w_l(r_2,p_1;E)=\frac{p_E^2-p_1^2}{2m\hbar}\int_0^\infty dr_1 g_l(r_2,r_1;E)j_l\left[\frac{p_1r_1}{\hbar}\right] \tag{10}$$

for $p_E^2\neq p_1^2$. The partial-wave T-matrix element can then be written as

$$t_l(p_2,p_1;E)=\frac{p_E^2-p_1^2}{\pi\hbar^2p_1p_2m}\times\int_0^\infty dr_2\int_0^\infty dr_1 j_l\left[\frac{p_2r_2}{\hbar}\right]V(r_2)\times g_l(r_2,r_1;E)j_l\left[\frac{p_1r_1}{\hbar}\right]\ . \tag{11}$$

We now go on to develop a simple WKB approximation to the Green's-function propagator. Although it is possible to develop a uniform version of the propagator, valid for arbitrary r_1 and r_2, our interest is in describing incomplete collisions properly in the limit for which the incoming and outgoing momenta are nearly equal. For simplicity we assume that these are both well within the classical region so that we need not consider complications due to the classical turning point. While this restricts the validity of our development, for the description of incomplete optical collisions this restriction is rather weak in practice; the vast majority of collisions in a thermal environment have Condon points (stationary phase points) for absorption that are well separated from the classical turning point of the motion.[13] This allows one to use primitive WKB solutions to the homogeneous Schrödinger equation in constructing the propagator. Our first step is to make the usual Langer substitution[22] for the angular momentum in Eq. (9) to give

$$\left[\hbar^2\frac{d^2}{dr_2^2}+\left[\frac{E-V(r_2)-\hbar^2(1+\frac{1}{2})^2}{2mr_2^2}\right]\right]g_l(r_2,r_1;E)=\hbar\delta(r_1-r_2)\ . \quad (12)$$

We will need solutions both for outgoing wave ψ^+ and standing wave ψ^0 boundary conditions at $r=\infty$. These may easily be shown to be

$$\psi^+(r)=\left[\frac{p_E}{p_l(r)}\right]^{1/2}\exp\left[\frac{i}{\hbar}\int_{r_0}^{r}dr'p_l(r')+\frac{i\pi}{4}\right] \quad (13)$$

and

$$\psi^0(r)=\left[\frac{p_E}{p_l(r)}\right]^{1/2}\sin\left[\frac{1}{\hbar}\int_{r_0}^{r}dr'p_l(r')+\frac{\pi}{4}\right]\ . \quad (14)$$

Here,

$$p_l(r)=\{2m[E-V(r)]-[(\hbar)(l+\tfrac{1}{2})/r]^2\}^{1/2} \quad (15)$$

is the relative radial momentum of the reduced scattering particle and r_0 is the classical turning point of the motion, i.e., $p_l(r_0)=0$. One can then show by direct substitution into Eq. (9) that the propagator obeying outgoing boundary conditions, consistent with the $+i\epsilon$ prescription in Eq. (1), is simply

$$g_l(r_2,r_1;E)=-\frac{2m}{p_E}\psi^0(r_<)\psi^+(r_>)\ , \quad (16)$$

or

$$g_l(r_2,r_1;E)\simeq-\frac{2m}{[p_l(r_1)p_l(r_2)]^{1/2}}\times\exp\left[\int_{r_0}^{r_>}p_l\frac{(r)dr}{h}+\frac{\pi}{4}\right]\times\sin\left[\int_{r_0}^{r_<}p_l\frac{(r)dr}{h}+\frac{\pi}{4}\right]\ , \quad (17)$$

where $r_>=\max(r_1,r_2)$ and $r_<=\min(r_1,r_2)$. Under these same restrictions we can obtain a WKB approximation for the Ricatti-Bessel functions,

$$j_l\left[\frac{p_ir}{h}\right]\simeq\left[\frac{p_i}{p_i^j(r)}\right]^{1/2}\sin\left[\int_{r_{i0}^j}^{r}\frac{p_i^j(r)dr}{h}+\frac{\pi}{4}\right] \quad (18)$$

with

$$p_i^j(r)=\{p_i^2-[\hbar(l+\tfrac{1}{2})/r]^2\}^{1/2}$$

and r_{i0}^j defined by (19)

$$p_i^j(r_{i0}^j)=0,\ i=1,2\ .$$

Substituting these equations into the above expression for the partial-wave decomposition of the off-shell wave function and writing out the terms explicitly, we obtain the expression

$$w_1(r_2,p_1;E)=-\frac{p_E^2-p_1^2}{2i\hbar[p_l(r_2)]^{1/2}}\left[\exp\left[\frac{i}{\hbar}\int_{r_0}^{r_2}p_l(r)dr+\frac{i\pi}{4}\right]\int_{r_0}^{\infty}dr_1\left[\frac{p_1}{p_l(r_1)p_1^j(r_1)}\right]^{1/2}\times\sin\left[\frac{1}{\hbar}\int_{r_{10}^j}^{r_1}[p_1^j(r)dr]+\frac{\pi}{4}\right]\times\exp\left[\frac{i}{\hbar}\int_{r_0}^{r_1}p_l(r)dr+\frac{i\pi}{4}\right]-\int_{r_0}^{\infty}dr_1\left[\frac{p_1}{p_l(r_1)p_1^j(r_1)}\right]^{1/2}\sin\left[\frac{1}{\hbar}\int_{r_{10}^j}^{r_1}[p_1^j(r)dr]+\frac{\pi}{4}\right]\times\exp\left[\frac{i}{\hbar}\int_{r_0}^{r_>}p_l(r)dr-\frac{i}{\hbar}\int_{r_0}^{r_<}p_l(r)dr\right]\right]\ . \quad (20)$$

The first integral in this expression can easily be evaluated using the standard methods of stationary phase. The integral is dominated by the contribution near the stationary point r_1^s defined by the relation

$$p_E^2-p_1^2=2mV(r_1^s)\ . \quad (21)$$

In the language of a semiclassical description[11,14] r_1^s is the localized point signifying the start of the incomplete col-

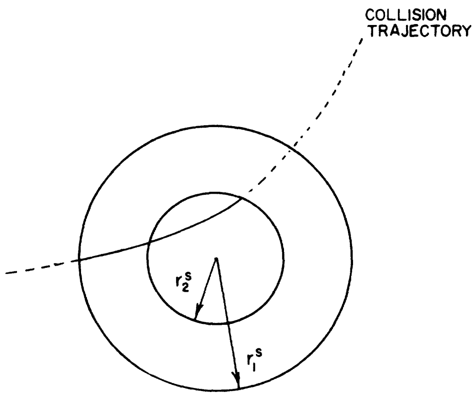

FIG. 2. One contribution to the off-shell T matrix comes from trajectories for which the start and finish of the incomplete collision are separated by the classical turning point. Shown here is the situation for $p_1 > p_2$.

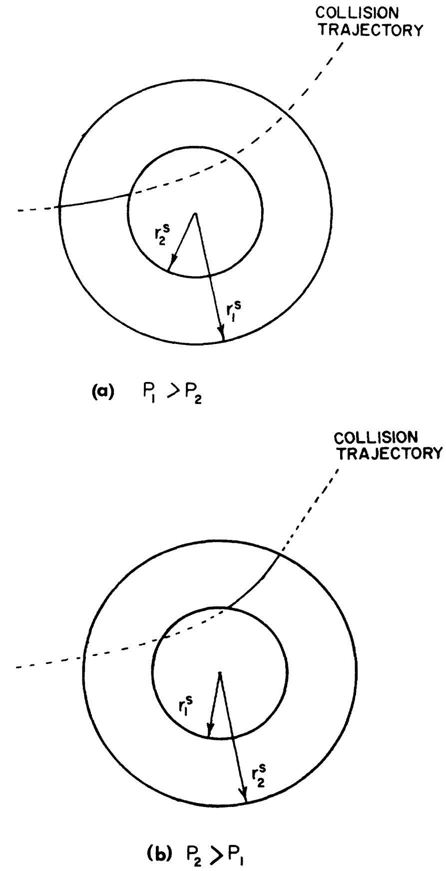

FIG. 3. A second contribution to the off-shell T matrix comes form trajectories for which the start and finish occur on the same side of the classical turning point. The interference between this contribution and that from Fig. 2 is what gives rise to the oscillatory structure of the T matrix in the classically allowed region.

lision. Similarly the stationary point in the r_2 integral will represent the end of the incomplete collision. Since there is no restriction on the relation between r_1^s and r_2, this first integral represents the contribution to the scattering process in which the start of the collision occurs "on the way in," while the finish takes place "on the way out" of the collision volume (see fig. 2).

A proper evaluation of the second integral requires more care.[23] In essence it is really two distinct integrals, depending on whether r_1 is greater or less than r_2. In these integrals the end point r_2 can come arbitrarily close to the stationary point in r_1, prohibiting one from considering the contribution from the end point separately from that due to the stationary phase point. These two terms represent contributions for collisions which both start and end, either on the way in ($r_1 > r_2$), or on the way out ($r_2 > r_1$), as shown in Fig. 3. The evaluation of oscillatory integrals for which the end point can lie arbitrarily close to the stationary point is a standard problem that has been treated by many authors.[24–26]

To illustrate the method we consider explicitly a portion of the second integral in w_1,

$$I(r_2)=\int_{r_0}^{r_2} dr_1 \left[\frac{p_1}{p_l(r_1)p_1^j(r_1)}\right]^{1/2} \times \exp\left[\frac{i}{\hbar}\int_{r_{10}^j}^{r_1}[p_1^j(r)dr]+\frac{i\pi}{4}\right] \times \exp\left[-\frac{i}{\hbar}\int_{r_0}^{r_1}p_l(r)dr-\frac{i\pi}{4}\right] . \quad (22)$$

A uniform approximation to this integral can be developed by mapping it onto the simplest comparison integral with the same qualitative features, namely, the Fresnel integral,

$$J(\Lambda)=\int_{-\infty}^{\Lambda(r_2,r_1^s)} dx \exp\left[\frac{i\beta(x^2)}{2}\right] \quad (23)$$

where $\Lambda(r_2,r_1^s)$ is a mapping function which provides a measure of the proximity of the end point r_2 to the stationary phase point r_1^s. The parameter β is equal to ± 1, depending on whether r_1^s corresponds to a minimum or a maximum of the phase. Using this technique we can evaluate Eq. (21), obtaining

$$I(r_2)=\left[\frac{\hbar p_1}{p_l(r_1^s)|mV(r_1^s)|}\right]^{1/2} \exp[-i\eta_1(r_1^s)]\int_{-\infty}^{\Lambda(r_2,r_1^s)} dx \exp\left[-\frac{i(x^2)}{2}\right] - i\hbar\left[\left[\frac{p_1}{p_l(r_2)p_1^j(r_2)}\right]^{1/2}\frac{1}{p_l(r_2)-p_1^j(r_2)}-\frac{1}{\Lambda(r_2,r_1^s)[p_l(r_1^s)|mV(r_1^s)|]^{1/2}}\right]\exp[i\eta_1(r_1^s)-i\eta_1(r_2)] . \quad (24)$$

Here we have introduced the notation

$$\eta_1(r)=\frac{1}{\hbar}\int_{r_0}^{r}p_l(r')dr'-\frac{1}{\hbar}\int_{r_{l0}^{j}}^{r}p_1^j(r')dr' \tag{25}$$

while

$$\Lambda(r_2,r_1^s)=\pm\{2[\eta_1(r_2)-\eta_1(r_2^s)]\}^{1/2},\quad \pm \text{ for } r_2\gtrless r_1^s\ . \tag{26}$$

Since r_1^s is a minimum of η_1, Λ is strictly real.

Because these terms are to be substituted back into the expression for t_l and integrated over r_2 it is convenient to rewrite the Fresnel integral in terms of the auxillary Fresnel functions f and g,[27]

$$\int_{-\infty}^{\Lambda(r_2,r_1^s)}dx\,\exp\left[\frac{\pm i(x^2)}{2}\right]=\sqrt{2\pi}\exp\left[\frac{\pm i\pi}{4}\right]\Theta(r_2-r_1^s)-\sqrt{\pi}\,\mathrm{sgn}(r_2-r_1^s)\left[g\left(\left|\frac{\Lambda(r_2,r_1^s)}{\sqrt{\pi}}\right|\right)\pm if\left(\left|\frac{\Lambda(r_2,r_1^s)}{\sqrt{\pi}}\right|\right)\right]\exp\left[-\frac{i(\Lambda^2(r_2,r_1^s))}{2}\right]. \tag{27}$$

Here Θ is the Heaviside step function, which is equal to 1 if its argument is positive, 0 if negative. In this manner, since f and g are slowly varying functions of their arguments, all of the rapidly varying phase dependence is expressed as the argument of an exponential. This makes explicit the phase dependence of the Fresnel integral, allowing one to again use the generalized stationary phase procedure to evaluate the r_2 integral.

It is instructive to group the auxiliary Fresnel functions together with the uniform end-point contribution in $I(r_2)$,

$$\begin{aligned}I(r_2)=&\left[\frac{2\pi\hbar p_1}{p_l(r_1^s)|mV(r_1^s)|}\right]^{1/2}\exp[-i\eta_1(r_1^s)]\Theta(r_2-r_1^s)\\&-i\hbar\left\{\left[\frac{p_1}{p_l(r_2)p_1^j(r_2)}\right]^{1/2}\frac{1}{p_l(r_2)-p_1^j(r_2)}\right.\\&-\frac{1}{[p_l(r_1^s)|mV(r_1^s)|]^{1/2}}\\&\left.\times\left\{\frac{1}{\Lambda(r_2,r_1^s)+i\sqrt{\pi}\,\mathrm{sgn}(r_2-r_1^s)}\left[g\left(\left|\frac{\Lambda(r_2,r_1^s)}{\sqrt{\pi}}\right|\right)+if\left(\left|\frac{\Lambda(r_2,r_1^s)}{\sqrt{\pi}}\right|\right)\right]\right\}\right\}\exp[i\eta_1(r_1^s)-i\eta_1(r_2)]\ .\end{aligned} \tag{28}$$

Written in this way the uniform stationary phase approximation can be interpreted in terms of a pure stationary phase term represented by the first term in Eq. (28) plus a uniform end-point contribution. The pure stationary phase contribution turns on sharply if the integration interval contains the stationary phase point. Due to the Heaviside step function the stationary term is present only if the integration interval contains the stationary phase point. The primary contribution to the uniform end-point term comes from the pole [the second line of Eq. (28)]. This pole term represents the isolated end-point contribution and is usually obtained by a simple integration by parts. Near the region for which the end point r_2 coincides with the stationary point r_1^s, the divergence due to the pole is canceled by the term involving the mapping function Λ, and the sum remains finite. The auxiliary Fresnel terms then smooth the sharp turn on of the stationary phase contribution. In the opposite limit when the end point is well separated from the stationary point, one would expect the uniform end-point contribution to reduce to that of an isolated end point. Indeed, under these circumstances, one can show that the auxiliary Fresnel terms can be written as

$$i\sqrt{\pi}\,\mathrm{sgn}(r_2-r_1^s)\left[g\left(\left|\frac{\Lambda}{\sqrt{\pi}}\right|\right)+if\left(\left|\frac{\Lambda}{\sqrt{\pi}}\right|\right)\right]=i\,\mathrm{sgn}(r_2-r_1^s)\exp\left[-\frac{i(\Lambda^2)}{2}\right]\int_{|\Lambda|}^{\infty}\exp\left[\frac{i(x^2)}{2}\right]\to-\frac{1}{\Lambda}\ \text{ for } |\Lambda|\gg 1\ . \tag{29}$$

Hence in this limit the auxiliary Fresnel terms cancel the $1/\Lambda$ term, leaving only the pole contribution. The same general procedures can be followed to evaluate the remaining integrals in Eq. (20). Collecting all of the resulting terms yields the following expression:

$$w_l(r_2,p_1;E)=\frac{p_E^2-p_1^2}{2m(\hbar)}\Bigg\{-\left[\frac{2\pi\hbar}{p_l(r_1^s)|mV'(r_1^s)|}\right]^{1/2}\exp[-i\eta_1(r_1^s)]$$
$$\times\int_{r_1^s}^{\infty}\frac{dr_1V(r_2)}{[p_l(r_2)p_2^j(r_2)]^{1/2}}\exp\left[\frac{i}{\hbar}\int_{r_0}^{r_2}p_l(r)dr\right]\sin\left[\frac{1}{\hbar}\int_{r_{20}^j}^{r_2}p_2^j(r)dr+\frac{\pi}{4}\right] .$$
$$+\left[\frac{2\pi\hbar}{p_l(r_1^s)|mV'(r_1^s)|}\right]^{1/2}\exp[i\eta_1(r_1^s)]$$
$$\times\int_{r_0}^{r_1^s}\frac{dr_2V(r_2)}{[p_l(r_2)p_2^j(r_2)]^{1/2}}\exp\left[-\frac{i}{\hbar}\int_{r_0}^{r_2}p_l(r)dr\right]\sin\left[\frac{1}{\hbar}\int_{r_{20}^j}^{r_2}p_2^j(r)dr+\frac{\pi}{4}\right]$$
$$-i\hbar\int_{r_0}^{\infty}\frac{dr_2V(r_2)}{[p_1^j(r_2)p_2^j(r_2)]^{1/2}}\sin\left[\frac{1}{\hbar}\int_{r_{20}^j}^{r_2}p_2^j(r)dr+\frac{\pi}{4}\right]$$
$$\times\Bigg[\exp\left[\frac{i}{\hbar}\int_{r_{10}^j}^{r_2}p_1^j(r)dr+\frac{i\pi}{4}\right]$$
$$\times\left[\frac{2}{p_l^2(r_2)-p_1^{2j}(r_2)}-\left[\frac{p_1^j(r_2)}{p_l(r_2)p_l(r_1^s)|mV'(r_1^s)|}\right]^{1/2}\right.$$
$$\left.\times\left\{\frac{1}{\Lambda(r_2,r_1^s)}-\mathrm{sgn}(r_2-r_1^s)\sqrt{\pi}\left[f\left(\left|\frac{\Lambda(r_2,r_1^s)}{\sqrt{\pi}}\right|\right)+ig\left(\left|\frac{\Lambda(r_2,r_1^s)}{\sqrt{\pi}}\right|\right)\right]\right\}\right]+\text{c.c.}\Bigg]\Bigg\}. \tag{30}$$

THE PARTIAL-WAVE OFF-SHELL T-MATRIX ELEMENTS

To obtain the off-shell T-matrix elements the above expression for the off-shell wave function is inserted into Eq. (8). The evaluation of the resulting integrals can be accomplished using either an integration by parts (when no stationary points exist) or the uniform stationary phase approximation as is appropriate. Eventually one arrives at the following form for the off-shell partial-wave T-matrix elements:

$$t_l(p_2,p_1;E)=-\frac{(p_E^2-p_1^2)(p_E^2-p_2^2)}{m\hbar[p_1p_l(r_1^s)|2mV'(r_1^s)|p_2p_l(r_2^s)|2mV'(r_2^s)|]^{1/2}}\exp\left[i\eta_>(r_>^s)-\frac{i\pi}{4}\right]\sin\left[\eta_<(r_<^s)-\frac{\pi}{4}\right]$$
$$+\frac{p_E^2-p_1^2}{2\pi\hbar(p_1p_2)^{1/2}}\mathrm{Re}\Bigg[\int_{r_0}^{\infty}dr_2\frac{V(r_2)}{[p_1^j(r_2)p_2^j(r_2)]^{1/2}}\exp[i\eta_2(r_2)-i\eta_1(r_2)]$$
$$\times\left[\frac{2}{p_l^2(r_2)-p_1^{2j}(r_2)}-\left[\frac{p_1^j(r_2)}{p_l(r_2)p_lr_1^s|mV'(r_1^s)|}\right]^{1/2}\right.$$
$$\left.\times\left\{\frac{1}{\Lambda(r_2,r_1^s)}-\mathrm{sgn}(r_2-r_1^s)\sqrt{\pi}\left[f\left(\left|\frac{\Lambda(r_2,r_1^s)}{\sqrt{\pi}}\right|\right)+ig\left(\left|\frac{\Lambda(r_2,r_1^s)}{\sqrt{\pi}}\right|\right)\right]\right\}\right]\Bigg]$$
$$+\frac{p_E^2-p_1^2}{[\pi\hbar p_1p_2p_l(r_1^s)|2mV'(r_1^s)|]^{1/2}}$$
$$\times\mathrm{Re}\Bigg[\exp\left[i\eta_2(r_1^s)-i\eta_1(r_1^s)-\frac{i\pi}{4}\right]$$
$$\times\left[\frac{V(r_1^s)}{[p_l(r_1^s)p_2^j(r_1^s)]^{1/2}}\frac{1}{p_l(r_1^s)-p_2^j(r_1^s)}\right.$$
$$-\frac{V(r_2^s)}{[p_l(r_2^s)|mV'(r_1^s)|]^{1/2}}$$
$$\left.\times\left\{\frac{1}{\lambda(r_1^s,r_2^2)}-\sqrt{\pi}\,\mathrm{sgn}(p_1-p_2)\left[\left[f\left|\frac{\lambda(r_1^s,r_2^s)}{\sqrt{\pi}}\right|\right]+ig\left[\left|\frac{\lambda(r_1^s,r_2^s)}{\sqrt{\pi}}\right|\right]\right]\right\}\right]\Bigg]. \tag{31}$$

Here,

$$\eta_2(r)=\frac{1}{\hbar}\int_{r_0}^{r} p_l(r')dr'-\frac{1}{\hbar}\int_{r_{20}^{j}}^{r} p_2^{j}(r')dr' . \quad (32)$$

$r_>^s$ corresponds to $\max(r_1^s,r_2^s)$ while

$$\lambda(r_1^s,r_2^s)=\operatorname{sgn}(r_1^s-r_2^s)\{2[\eta_2(r_1^s)-\eta_2(r_2^s)]\}^{1/2} \quad (33)$$

is a measure of the proximity of the end point r_1^s to the stationary point in r_2.

The expression for the partial-wave off-shell T-matrix elements in Eq. (31) represents the main result of this work. The first term in this expression coincides with the formula of Korsch[14] in the classically accessible region. As such it represents the contribution from isolated stationary phase points. Although continuous near $p_1=p_2$, this term give rise to a discontinuous first derivative due to the sharp switch between $\eta_>$ and $\eta_<$ in this region. Right at $p_1=p_2$ Korsch and Möllenkamp[15] suggested adding an inhomogeneous contribution,

$$u_l(p_1,p_2;E)=\frac{2\hbar^2}{\pi p_1 p_2}(p_E^2-p_1^2) \times \mathrm{P}\int_0^\infty dr\frac{j_l\left[\frac{p_2 r}{\hbar}\right]V(r)j_l\left[\frac{p_1 r}{\hbar}\right]}{p_E^2-p_1^2-2mV(r)} , \quad (34)$$

to $t_l(p_1,p_2{:}E)$. No justification was given for interpreting this integral as a Cauchy principle-part-type integral.

In the present formulation the discontinuous behavior near coincident momenta is smoothed by the presence of two uniform end-point contribution terms [the two terms containing a Re part designation in Eq. (31)], the first associated with the integral over r_1, which must be subsequently integrated over r_2, and the second associated with the r_2 integral over the stationary phase terms in r_1.

Each of these end-point terms contains the subtle cancellation effects as mentioned above. In addition, there is a strong cancellation between these two end-point terms. This can be most readily seen by considering the contribution from the auxiliary Fresnel functions, for values of p_1 not too close to p_2, to the integral over r_2 [the first Re part term in Eq. (31)]. The auxiliary Fresnel function term possesses a sharp discontinuity when $r_2=r_1^s$. Hence one might expect that a reasonable approximation to their contribution in the integral over r_2 could be obtained through an integration by parts with the integration interval broken up at the point of discontinuity. If such a procedure is carried out one obtains a term which exactly cancels the pole in the last term of Eq. (31). One could further argue that the main impact of the $1/\Lambda$ term within the integral over r_2 is to cancel the divergence in the isolated end-point term when r_2 is near r_1^2. Similarly the $1/\lambda$ term in the second Re part term of Eq. (31) serves to cancel the divergence of the pole associated with it near $r_1^s=r_2^s$ (or $p_1=p_2$), which is when an integration by parts for the auxiliary Fresnel function term in the integral over r_2 becomes suspect. It follows then that the combined contribution of the uniform end-point terms could be reasonably approximated by a Cauchy principle-part integral over r_2 of the pole term.[28] This leads to the following simplified expression:

$$\begin{aligned} t_l(p_{1,}p_{2;E})=&\frac{(p_E^2-p_1^2)(p_E^2-p_2^2)}{2m\hbar[p_1 p_l(r_1^s)|2mV'(r_1^s)|p_2 p_l(r_2^s)|2mV'(r_2^s)|]^{1/2}} \\ &\times\Bigg[\exp[i\eta_1(r_1^s)+i\eta_2(r_2^s)] \\ &+\exp\left[i\eta_1(r_1^s)-i\eta_2(r_2^s)-\frac{i\pi}{4}\right]\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\lambda(r_1^s,r_2^s)}dx\exp\left[-\frac{i(x^2)}{2}\right] \\ &-\exp\left[-i\eta_1(r_1^s)+i\eta_2(r_2^s)+\frac{i\pi}{4}\right]\frac{1}{\sqrt{2\pi}}\int_{\lambda(r_1^s,r_2^s)}^{\infty}dx\exp\left[\frac{i(x^2)}{2}\right]\Bigg] \\ &+\frac{p_E^2-p_1^2}{\pi(\hbar)(p_1p_2)^{1/2}}\mathrm{P}\int_{r_0}^{\infty}dr_2\frac{V(r_2)}{[p_1^j(r_2)p_2^j(r_2)]^{1/2}}\frac{\exp[i\eta_2(r_2)-i\eta_1(r_2)]}{p_l^2(r_2)-p_1^j(r_2)} . \end{aligned} \quad (35)$$

This form is almost identical to the form of the semiclassical off-shell T-matrix elements proposed by Korsch and Möllenkamp with the inclusion of the inhomogeneous contribution of Eq. (34). The sole difference is a smoothing of the sharp turn on of the stationary phase terms in their expression by the Fresnel integrals. However, this difference is crucial to obtaining a smooth dependence near the region of equal incoming and outgoing momenta.

COMPARISON CALCULATIONS FOR THE HUTHEN POTENTIAL

In this section we follow closely the original test used by Korsch and Möllenkamp for their formulation through a comparison with the exact quantal results due to Beard and Micha,[18] for the Hulthen potential,

$$V(r)=V_0\frac{\exp(-r/\alpha)}{1-\exp(-r/\alpha)} . \quad (36)$$

We use the same potential parameters, $\alpha=0.9422$ a.u. and $V_0=1.469$ a.u., as did Korsch and Möllenkamp. These parameters give a good description of the triplet interaction of the H-H collisional system. We restrict ourselves to the region of validity for our formulation, that of the classically accessible region. This region is defined by the limits placed on p_1 and p_2 for a given value of the collision energy E. The minimum value for the momenta is given by the value of the momenta at the classical turning point, r_0, i.e.,

$$p_{\min}=\frac{\hbar(1+\frac{1}{2})}{r_0} ,$$

while the maximum value of the momenta is p_E. We note that only the real parts of both Eqs. (31) and (35) differ from the Korsch and Möllenkamp[15] results. Hence in what follows we focus our attention on the real part of $t_l(p_1,p_2;E)$.

We first investigate the momentum dependence of $t_l(p_1,p_2;E)$ on p_2. To begin, we choose a value for p_1 of 4.0 a.u., while for E we take 0.01 a.u., which gives $p_E=4.27$ a.u. This choice is somewhat unfavorable for a semiclassical formulation since p_1 is nearly on shell where the stationary phase evaluation breaks down. We also choose to focus on the $l=0$ partial wave which often presents difficulties for semiclassical formulations. One expects then that these values will provide a good test of our formulation.

Figure 4 displays the results of the three different formulations. As expected, far from the point at which $p_2=p_1$ our results coincide with those of Korsch and Möllenkamp. The closeness of the uniform semiclassical results to those of Korsch and Möllenkamp in this region is a measure of the degree of cancellation present between the two uniform end-point terms in Eq. (31). As noted by Korsch and Möllenkamp,[15] the agreement with the quantal variable phase and amplitude (VPA) results is fair, and in particular the agreement in phase is very good. Near the point of equal momenta our results reproduce the quantal result quite nicely. Away from this point the semiclassical amplitudes tend to be too large. This may be due in part to the use of a WKB propagator, which diverges for portions of the collision trajectory near the classical turning point. In principle this question could be resolved by replacing the WKB propagator used in our development by a uniform Airy version,[16]

$$g_l(r_2,r_1;E)=-2m\pi\left[\frac{x(r_2)}{p_l^2}(r_2)\right]^{1/4}\left[\frac{x(r_1)}{p_l^2}(r_1)\right]^{1/4}$$
$$\times[\mathrm{Bi}(-x(r_>))+i\,\mathrm{Ai}(-x(r_>))]$$
$$\times\mathrm{Ai}(-x(r_<)) . \qquad (37)$$

However, to follow the development in this paper using such a propagator one would need to develop functions analogous to the auxiliary Fresnel functions f and g for the incomplete Airy integral.

In Fig. 5 we present a comparison between the various formulations for equal incoming and outgoing momenta as a function of incident energy, again for the $l=0$ partial wave. Right at the point of equal incoming and outgoing momenta the purely stationary phase version of the Korsch and Möllenkamp formulation can be patched up

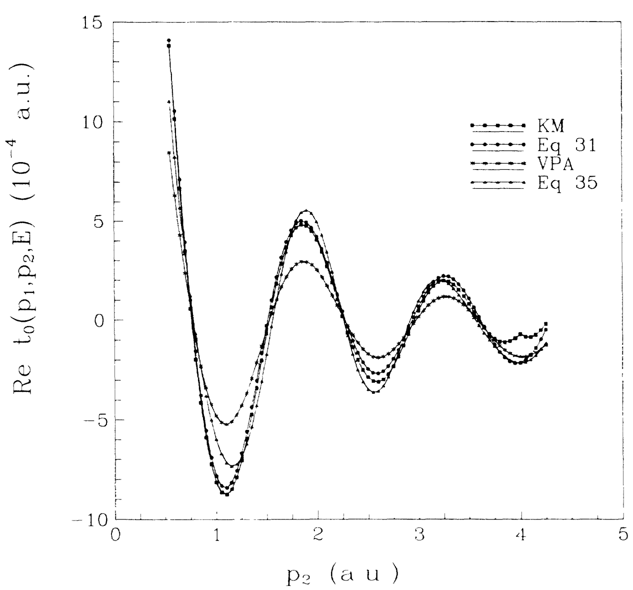

FIG. 4. The real part of $t_0(p_1,p_2;E)$ for the triplet H-H Hulthen potential with $E=0.01$ a.u. and $p_1=4.0$ a.u. The primitive semiclassical approximation due to Korsch and Möllenkamp (labeled KM) breaks down for both $p_2=p_E=4.27$ a.u. and for $p_2\simeq p_1$. Both semiuniform approximations smooth the singularity present at $p_2=p_1$. The curve labeled VPA is the fully quantal variable phase and amplitude results due to Beard and Micha.

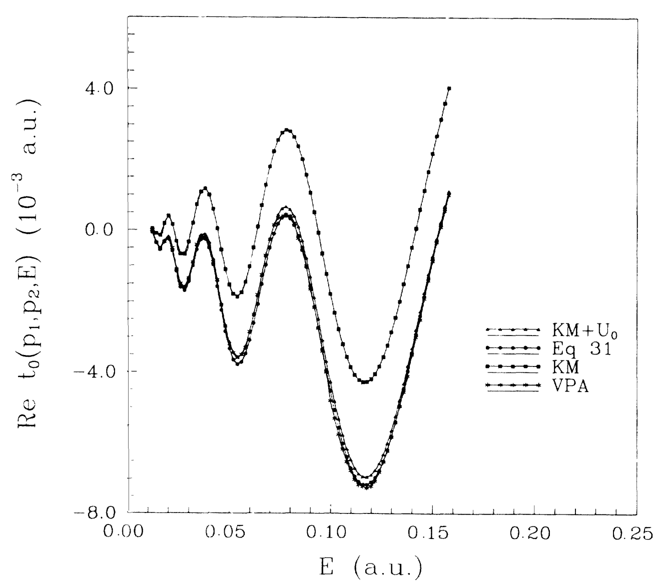

FIG. 5. A study of the diagonal term of the off-shell partial-wave T-matrix elements as a function of the energy with $p_1=p_2=4.5$ a.u. The primitive semiclassical curve can be improved by adding the inhomogeneous contribution u_0 from Eq. (38).

by adding the inhomogeneous contribution of Eq. (34). For the Hulthen potential the $l=0$ partial-wave contribution of this term can be evaluated analytically, giving

$$u_0(p,p;E)=-\frac{U_0\hbar^2\alpha}{2m\pi p^2}\left[1+U_0\frac{}{p_E^2-p^2}\right]^{-1}\times\ln\left[\frac{U_0}{p_E^2-p^2}\right]. \tag{38}$$

This gives good agreement with the calculations of Beard and Micha[18] and is almost indistinguishable from our semiuniform equation (31). While there is little difference between these two semiclassical versions exactly at $p_1=p_2$, we believe that the smooth nature of our version [Eq. (31)] throughout a small region encompassing this point is a significant calculational advantage. This is especially critical for multiple scattering applications as the total off-shell T matrix summed over the partial waves tends to be largest near the region of small momentum transfer[18] for a fixed energy. Because of the oscillatory nature of the integrand it is somewhat time consuming to numerically evaluate the integral contained in (31). However, the region near the pole does not present any special problems. Near the pole the integrand can be expanded in a Taylor series. Due to the presence of the $1/\Lambda$ term the integrand remains finite in this region and the integral can be evaluated using a simple Gaussian quadrature integration package.[29]

The smooth nature of the semiuniform solution represented by Eq. (31) is emphasized in Fig. 6 where we show the real part of $t_0(p_1,p_2;E)$ for $E=0.01$ a.u. and $p_1=2.0$ a.u. These values are well within the classically allowed region so that the semiclassical results are expected to be close to the exact results.

Finally in Fig. 7 we investigate the half-shell behavior of Eqs. (31) and (35). The half-shell matrix elements represent the limit of the fully off-shell matrix elements as one of the momenta becomes on shell. Here we let $p_2\to p_E$. In principle our formulation should break down in this limit since the stationary point r_2^s is not well localized. Still both equations compare reasonably well to the primitive semiclassical formula obtained independently of the fully off-shell formula by solving the homogeneous version of Eq. (6),[14,15] i.e.,

$$t_l(p_1,p_E;E)=(\hbar)^{3/2}\frac{p_1^2-p_E^2}{m\{[\pi p_1 p_E|p_l(r_1^s)2mV'(r_1^s)|]\}^{1/2}}\times\exp\left[\frac{i}{\hbar}\int_{r_0}^{\infty}(p_l(r)-p_E)dr-\frac{p_E r_0}{\hbar}+\frac{(l+\frac{1}{2})\pi}{2}\right]\sin\left[\eta_1(r_2^s)-\frac{\pi}{4}\right]. \tag{39}$$

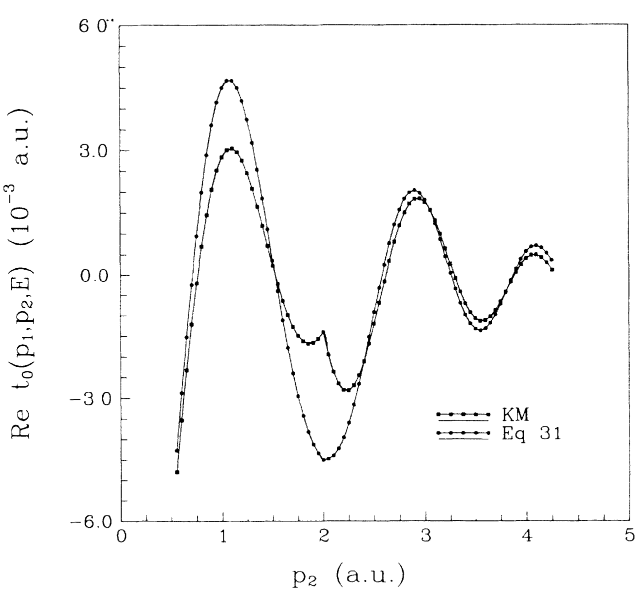

FIG. 6. The real part of $t_0(p_1,p_2;E)$ for $E=0.01$ a.u. and $p_1=2.0$ a.u. The smoothing due to the uniform end-point contributions is particularly evident.

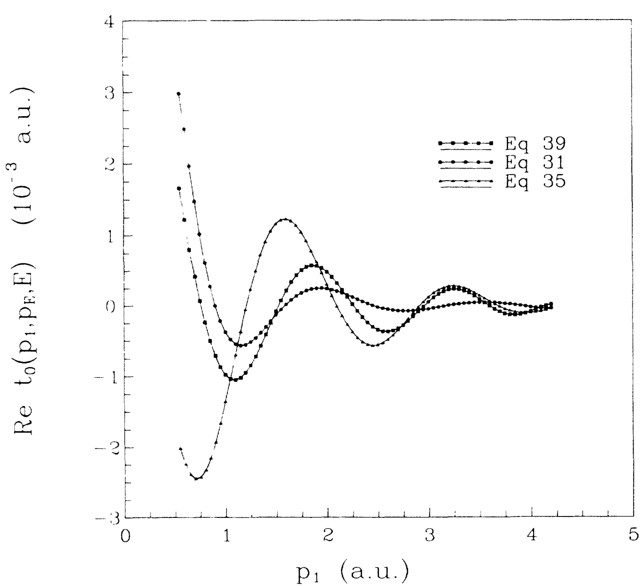

FIG. 7. The half-shell T-matrix elements $t_0(p_1,p_E;E)$ for $E=0.01$ a.u. as a function of p_1. The semiclassical curve due to Korsch [Eq. (39)] is plotted for comparison.

In fact for values of p_1 large compared to $p_{\min}$ formula (35) is almost identical to the above expression. This suggests that it may be possible to develop a semiuniform approximation which is valid, both in the region of equal incoming and outgoing momenta, as well as near the half-shell limit. The discrepancy near $p_1 = p_{\min}$ is most likely due once again to the breakdown of both formulations near the classical turning point as commented on above. A formulation which is based upon a uniform propagator as in Eq. (37) should be able to resolve this point.

In conclusion we have presented a development of a semiuniform semiclassical formulation for fully off-shell partial-wave T-matrix elements. Our formulas remain valid in the limit of equal incoming and outgoing momenta, but suffer from the usual breakdown of primitive semiclassical formulations for momenta close to values of the radial momentum at the classical turning point of the motion. Future work will be focused on attempts to extend this general procedure to uniformly valid forms of the propagator.

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