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Semiclassical normalization of a path integral for a multichannel scattering problem

A. P. Penner and R. Wallace
Department of Chemistry, University of Manitoba, Winnipeg, Manitoba, Canada
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The evaluation of a Feynman path integral is discussed for a scattering problem in which some degrees of freedom of the system are treated classically, while others are treated quantum mechanically. The path integral is of the type $K(0,t'';0,t')$, and is of interest in a multichannel semiclassical collision theory previously developed by Pechukas. It is shown that this path integral can be evaluated precisely in practice, despite the presence of noncausal terms in the integrand.

I. INTRODUCTION

The discussion of (electronically inelastic) atomic collisions can often be simplified through the use of impact-parameter theory or eikonal theory, especially in those cases where the impact energy is so high that one does not have to worry too much about the exact details of the nuclear motion during the collision.[1] For low-energy collisions, however, the situation is somewhat more complex. If the impact energy is so low that an electronic rearrangement during the collision will significantly perturb the nuclear motion, then it is quite difficult to derive a semiclassical theory for this process. With regard to the validity of impact parameter and eikonal theories in this case, the statement has been made[2]: "There remains a general collision problem which has not yet been satisfactorily solved by either treatment: the problem of how to carry out calculations if the classical trajectories in the initial and final states differ markedly." In certain situations, such as resonant charge exchange and Landau-Zener curve-crossing problems, it has been possible to develop specialized techniques to overcome this problem at low energies,[3,4] but the general solution is still rather elusive.

A significant step towards this general solution has recently been formulated by Pechukas,[5] using a time-dependent semiclassical approximation to the Feynman path integral which characterizes this problem.[6] The theory which results from this procedure is, admittedly, rather difficult to work with in practice, but it has considerable intuitive appeal since the nuclear trajectories which it yields automatically possess the appropriate long-range behavior before and after the collision. In addition to this, they satisfy a stationary-phase constraint (analogous to the principle of least action used in single-channel problems), which means that the relationship between the semiclassical theory and the original quantum-mechanical theory can be spelled out quite clearly. It can also be shown that the theory satisfies detailed balancing,[6] and that the equations are invariant under a transformation of the electronic basis set (e.g., from diabatic to adiabatic). However, as noted by Delos and Thorson,[7] it is not yet clear just how generally valid the equations are, because of the complexity of the path-integral derivation which is used. We would therefore like to discuss one aspect of this derivation in more detail than was previously given.

The derivation of this theory consists of two distinct steps, the first of which concerns the classical nuclear trajectories themselves, while the second deals with the normalization of the path integral assuming that these trajectories are known. In a previous discussion of this theory we restricted our attention to the nuclear trajectories themselves and showed that these trajectories can be calculated precisely in practice, even though the classical equations of motion are "noncausal."[8] Concerning the normalization constant for that problem, we simply borrowed a result derived by Pechukas. We will now derive an expression for this normalization constant which, to the best of our knowledge, is new. The practical implications of this result are probably not very great, but it serves to put the formal theory on what we hope will be a more solid footing.

II. THEORY

For the sake of simplicity we consider a one-dimensional problem. The path integral of interest is[8]

$$K_{\beta\alpha}(x'', t''; x', t') = \int_{x't'}^{x''t''} \underline{U}_{\beta\alpha}(t'', t')\, e^{i S_0[x(t)]}\mathfrak{D}x(t). \tag{1}$$

This is a quantum-mechanical probability amplitude for an event in which the relative nuclear position moves from x' to x'' while the electrons make the transition from state α to β. The functional $S_0[x(t)]$ is given by

$$S_0[x(t)] = \int_{t'}^{t''} \tfrac{1}{2} m \dot{x}^2 \, dt .$$

Within the diabatic representation, $\underline{U}(t, t')$ satisfies a matrix equation of the type

$$\frac{d}{dt} \underline{U}(t, t') = -i \underline{H}(x(t)) \underline{U}(t, t') .$$

When evaluating the response of $\underline{U}(t'', t')$ to a change in the nuclear trajectory it will be convenient to use the representation

$$\underline{U}(t'', t') = \lim_{N\to\infty} \prod_{j=0}^{N} [\underline{1} - i\epsilon \underline{H}(x_j)], \quad (2)$$

where $x_i = x(ti)$, $N\epsilon = t'' - t'$, and t_0 (t_N) equals t' (t''). We reexpress Eq. (1) in the form

$$K_{\beta\alpha}(x'', t''; x', t') = \int_{x't'}^{x''t''} |\underline{U}_{\beta\alpha}(t'', t')| \, e^{i S_0[x(t)] + i\phi} \mathfrak{D}x(t),$$

where $\phi = \operatorname{Im} \ln \underline{U}_{\beta\alpha}(t'', t')$. We now wish to develop a second-order Volterra expansion of ϕ about the classical path given by $\bar{x}(t)$,[9] where

$$m\ddot{\bar{x}}(t) = -\operatorname{Re}\left(\frac{[\underline{U}(t'', t)[\partial/\partial\bar{x}(t)]\underline{H}(x)\underline{U}(t, t')]_{\beta\alpha}}{\underline{U}_{\beta\alpha}(t'', t')} \right) \quad (3)$$

and $\bar{x}(t') = x'$, $\bar{x}(t'') = x''$.[8] We ignore variations in $|\underline{U}_{\beta\alpha}(t'', t')|$ as the path varies about $\bar{x}(t)$, and factor $|\underline{U}^{\text{cl}}_{\beta\alpha}(t'', t')|$ out of the path integral, where $|\underline{U}^{\text{cl}}_{\beta\alpha}(t'', t')|$ is evaluated along the path $\bar{x}(t)$. The phase ϕ is approximated by

$$\phi \sim \operatorname{Im} \ln \underline{U}^{\text{cl}}_{\beta\alpha}(t'', t') + \phi^{(1)}[y(t)] + \phi^{(2)}[y(t)],$$

where $\phi^{(1)}[y(t)]$ and $\phi^{(2)}[y(t)]$ are linear and quadratic in $y(t) = x(t) - \bar{x}(t)$. From the definition of $\bar{x}(t)$ in Eq. (3) we can readily show that $\phi^{(1)}[y(t)]$ will cancel with a term linear in $y(t)$ which comes from $S_0[\bar{x}(t) + y(t)]$. The semiclassical approximation to the path integral in Eq. (1) is now given by

$$K^{\text{cl}}_{\beta\alpha}(x'', t''; x', t') = \underline{U}^{\text{cl}}_{\beta\alpha}(t'', t') e^{i S_0[\bar{x}(t)]} K(0, t''; 0, t'), \quad (4)$$

where $K(0, t''; 0, t')$ is the "normalization constant":

$$K(0, t''; 0, t') = \int_{0t'}^{0t''} e^{i S_0[y(t)] + i\phi^{(2)}[y(t)]} \mathfrak{D}y(t). \quad (5)$$

We note that the semiclassical approximation, as defined here, consists of ignoring all variations in the magnitude of the integrand of Eq. (1) (and taking account of variations in the phase only to second order) as the path varies about the classical path. [It is perhaps worthwhile noting that $K(0, t''; 0, t')$ is actually a functional of the path $\bar{x}(t)$, although the notation does not show this dependence.[9]]

The problem is now one of calculating $K(0, t''; 0, t')$. We assume that the path $\bar{x}(t)$ is known and concentrate instead on the independent variable $y(t)$. $\phi^{(2)}[y(t)]$ is expressible as[9]

$$\phi^{(2)}[y(t)] = \tfrac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{\partial}{\partial \bar{x}_i} \frac{\partial}{\partial \bar{x}_j} [\operatorname{Im} \ln \underline{U}_{\beta\alpha}(t'', t')] y_i y_j , \quad (6)$$

where the time interval $(t'' - t')$ has been broken up into N steps of length ϵ (with N arbitrarily large), and where $\underline{U}(t'', t')$ is given by Eq. (2). It is convenient to distinguish three cases in Eq. (6), namely, $j < i$, $j = i$, and $j > i$, in order to avoid confusion in the time ordering of operators. After some manipulation we obtain

$$\phi^{(2)}[y(t)] = g(0, t''; 0, t'), \quad (7)$$

where $g(0, t''; 0, t')$ is a special case of the functional

$$\begin{aligned} g(y, t; 0, t') = & -\tfrac{1}{2} \operatorname{Re} \int_{t'}^{t} \frac{ds\, \underline{F}^{(2)}_{\beta\alpha}(s) y(s)^2}{\underline{U}^{\text{cl}}_{\beta\alpha}(t'', t')} \\ & - \tfrac{1}{2} \operatorname{Im} \int_{t'}^{t} ds \int_{t'}^{s} \frac{dr\, \underline{F}_{\beta\alpha}(s, r) y(s) y(r)}{\underline{U}^{\text{cl}}_{\beta\alpha}(t'', t')} \\ & - \tfrac{1}{2} \operatorname{Im} \int_{t'}^{t} ds \int_{s}^{t} \frac{dr\, \underline{F}_{\beta\alpha}(r, s) y(s) y(r)}{\underline{U}^{\text{cl}}_{\beta\alpha}(t'', t')} \\ & + \tfrac{1}{2} \operatorname{Im} \left\{ \left[\int_{t'}^{t} \frac{ds\, \underline{F}^{(1)}_{\beta\alpha}(s) y(s)}{\underline{U}^{\text{cl}}_{\beta\alpha}(t'', t')} \right]^2 \right\}. \end{aligned} \quad (8)$$

The notation $g(y, t; 0, t')$ implies that the path $y(s)$ has end points $y(t) = y$, $y(t') = 0$. The $\underline{F}$ matrices are given by

$$\underline{F}^{(1)}(t) = \underline{U}^{\text{cl}}(t'', t) \frac{\partial \underline{H}(x)}{\partial \bar{x}(t)} \underline{U}^{\text{cl}}(t, t'),$$

$$\underline{F}^{(2)}(t) = \underline{U}^{\text{cl}}(t'', t) \frac{\partial^2 \underline{H}(x)}{\partial \bar{x}(t)^2} \underline{U}^{\text{cl}}(t, t'),$$

$$\underline{F}(s, t) = \underline{U}^{\text{cl}}(t'', s) \frac{\partial \underline{H}(x)}{\partial \bar{x}(s)} \underline{U}^{\text{cl}}(s, t) \times \frac{\partial \underline{H}(x)}{\partial \bar{x}(t)} \underline{U}^{\text{cl}}(t, t'), \quad (s > t).$$

The definition of $\phi^{(2)}[y(t)]$ in Eq. (7) is to be compared with Eq. (3.5) of Pechukas.[5]

There are two distinct types of contributions to $\phi^{(2)}[y(t)]$. The first type is contained within a single integral in Eq. (8), and has been taken account of in the previous normalization of this path integral.[5] This type of term has a fairly well-defined single-channel analog.[10] The second type is due to double integrals in Eq. (8) and has no single-channel analog. It represents coupling between two first-order deviations from classical motion, occurring at different times, and is a reflection of the noncausal nature of the theory. This type of coupling is due to the fact that the potential energy which controls the nuclear motion cannot be expressed in the form $V(\overline{x}, t)$, but must instead be regarded as a functional of the entire path $\overline{x}(s)$. The presence of such coupling terms in a closely related problem has been noted by Feynman and the remarks made at the end of Sec. 3–10 of Ref. 6 apply here. In particular, we note that it is not possible to define a WKB-type wave function for the translational motion of the nuclei, and that we are therefore quite unable to observe the "classical nature" of the nuclei during the course of the collision. It should, however, be possible to define this type of wave function long before, or long after, the collision if the net effect of the noncausal terms is constant in these regions.

Despite the conceptual difficulties associated with the double-integral contributions, it is possible to evaluate the normalizing integral exactly in practice. One possible approach would be to try to find a change of variable from $y(t)$ to $z(\tau)$ such that the definition of $\phi^{(2)}[z(\tau)]$ in terms of $z(\tau)$ would contain only single integrals. The relationship between $z(\tau)$ and $y(t)$ would have to be of the type

$$z(\tau)=\int_{t'}^{t''} A(\tau, t)y(t)\,dt.$$

In this way the noncausal contributions would be temporarily hidden within the definition of $z(\tau)$ and the treatment of them could be postponed until later in the derivation. An approach similar to this has been used by Friedrichs and Shapiro,[11] and is probably more amenable to a rigorous treatment than our approach. We use a method similar to that of Pechukas.[10]

Consider the quantity $K(0, t; 0, t')$, satisfying the constraint that $K(0, t; 0, t') \to K(0, t''; 0, t')$ as $t \to t''$. $K(0, t; 0, t')$ is not uniquely specified by this constraint and we arbitrarily choose a definition which yields the simplest possible dependence on t. Define $K(0, t; 0, t')$ as the limit as $y \to 0$ of

$$K(y, t; 0, t')=\int_{0t'}^{yt} e^{iS_0(y,t;0,t')+ig(y,t;0,t')}\mathfrak{D}y(t), \tag{9}$$

where $g(y, t; 0, t')$ is defined by Eq. (8) and where

$$S_0(y, t; 0, t')=\int_{t'}^{t} \tfrac{1}{2}m\dot{y}^2\,dt. \tag{10}$$

We are interested in the time dependence of $K(0, t; 0, t')$, but it is convenient to first consider the dependence of $K(y, t; 0, t')$ on y. To determine this dependence we consider the particular path which makes the phase of the integrand of Eq. (9) stationary with respect to first-order variations in the path. This path [denoted by $\overline{y}(s)$] will move between the space-time points $(0, t')$ and (y, t), and can be shown to satisfy the integro-differential equation

$$m\ddot{\overline{y}}(s)=-f[\overline{y}(s)], \quad t'<s<t$$

where

$$\begin{aligned}f[z(s)]=\mathrm{Re}\left\{\frac{\underline{F}^{(2)}_{\beta\alpha}(s)z(s)}{\underline{U}^{\mathrm{cl}}_{\beta\alpha}(t'', t')}\right\}&+\mathrm{Im}\int_{t'}^{s}\frac{\underline{F}_{\beta\alpha}(s, r)z(r)\,dr}{\underline{U}^{\mathrm{cl}}_{\beta\alpha}(t'', t')}\\&+\mathrm{Im}\int_{s}^{t}\frac{\underline{F}_{\beta\alpha}(r, s)z(r)\,dr}{\underline{U}^{\mathrm{cl}}_{\beta\alpha}(t'', t')}\\&-\mathrm{Im}\left\{\frac{\underline{F}^{(1)}_{\beta\alpha}(s)}{\underline{U}^{\mathrm{cl}}_{\beta\alpha}(t'', t')}\int_{t'}^{t}\frac{\underline{F}^{(1)}_{\beta\alpha}(r)z(r)\,dr}{\underline{U}^{\mathrm{cl}}_{\beta\alpha}(t'', t')}\right\}.\end{aligned} \tag{11}$$

Because $K(y, t; 0, t')$ has an "action" which is quadratic in $y(s)$ we can perform an exact quadratic expansion of $K(y, t; 0, t')$ about the path $\overline{y}(s)$ in terms of the variable $\eta(s)=y(s)-\overline{y}(s)$ to obtain

$$K(y, t; 0, t')=K(0, t; 0, t')e^{i\theta}, \tag{12}$$

where $\theta=S_0(y, t; 0, t')+g(y, t; 0, t')$, and θ is evaluated using the path $\overline{y}(s)$ in Eqs. (8) and (10). In Eq. (12), $K(0, t; 0, t')$ is defined using the variable $\eta(s)$, but is identical to $K(0, t; 0, t')$ defined as the limit of Eq. (9) as $y(t) \to 0$. Furthermore, $K(0, t; 0, t')$ has no dependence on the path $\overline{y}(s)$. Because θ is evaluated along a path of stationary phase, we have

$$\frac{\partial\theta}{\partial y(t)}=m\dot{\overline{y}}(t).$$

The quantity $\partial^2\theta/\partial y^2(t)$ is also of interest and can be reexpressed as

$$\frac{\partial^2\theta}{\partial y^2(t)}=m\frac{d}{dt}\ln u(t),$$

where

$$u(t)=\left(\frac{\partial\overline{y}(t)}{\partial\dot{\overline{y}}(t')}\right)_{\overline{y}(t')},$$

and where $u(t)$ is a solution of the equation

$$m\ddot{u}(s)=-f[u(s)], \tag{13}$$

which is solved between the times t' and t, with $f[u(s)]$ given by Eq. (11) and with $u(t')=0$, $\dot{u}(t')=1$.

We note that $u(t)$ does not depend on the path $\bar{y}(s)$ and that θ is therefore a quadratic function of the end point $y(t)$. We consider a Taylor-series expansion of θ about the point $y(t)=0$ and note that it can be truncated to second order without introducing any error. In order to determine the zeroth- and first-order coefficients in the expansion it is necessary to find the path $\bar{y}(s)$ between the points $(0, t')$ and $(0, t)$. A solution of the equation of motion for $\bar{y}(s)$, subject to these end-point constraints, is the path $\bar{y}(s)=0$. The "action" developed along this path and the momentum $m\dot{\bar{y}}(t)$ are both zero. Therefore, the first two terms of the expansion do not contribute and we find

$$\theta = \tfrac{1}{2}m\left[\frac{d}{dt}\ln u(t)\right]y^2 . \tag{14}$$

The dependence of $K(y, t; 0, t')$ on y is therefore known exactly.

Given this result, it is now possible to relate $K(0, t+\epsilon; 0, t')$ and $K(0, t; 0, t')$:

$$K(0, t+\epsilon; 0, t') = \int_{-\infty}^{\infty}\frac{dz}{A}\int_{0t'}^{zt} e^{iS_0(0,t+\epsilon;0,t')+ig(0,t+\epsilon;0,t')}\mathfrak{D}y(s) \tag{15}$$

where $A=(2\pi i\epsilon/m)^{1/2}$.[6] From Eq. (10) we find

$$S_0(0, t+\epsilon; 0, t') = S_0(z, t; 0, t') + m z^2/2\epsilon . \tag{16}$$

The relationship between $g(0, t+\epsilon; 0, t')$ and $g(z, t; 0, t')$ is not as simple as Eq. (16), because the difference of these two quantities is itself a functional of the path $y(s)$ between $(0, t')$ and (z, t). However, it is possible to show that

$$g(0, t+\epsilon; 0, t') = g(z, t; 0, t') + \epsilon z h[y(s)], \tag{17}$$

where $h[y(s)]$ is a linear functional of the path $y(s)$. Because the second term in Eq. (17) is of order ϵ (and because it is linear in z), one might expect it to contribute only negligibly. We substitute Eqs. (16) and (17) into Eq. (15) and make use of the definition of $K(z, t; 0, t')$ in Eq. (9) to obtain

$$K(0, t+\epsilon; 0, t') = \int_{-\infty}^{\infty}[K(z, t; 0, t') + \epsilon z\tilde{h}(z, t)] \times e^{imz^2/2\epsilon}\frac{dz}{A},$$

where $\tilde{h}(z, t)$ is the leading term due to $h[y(s)]$ in Eq. (17). Using Eqs. (12) and (14) to specify the z dependence of $K(z, t; 0, t')$, and integrating over z, we obtain

$$K(0, t+\epsilon; 0, t') = K(0, t; 0, t')\left[1+\epsilon\frac{d}{dt}\ln u(t)\right]^{1/2} + O(\epsilon^{3/2}).$$

In the limit as $\epsilon\to 0$ this becomes

$$\frac{d}{dt}K(0, t; 0, t') = -\tfrac{1}{2}K(0, t; 0, t')\frac{d}{dt}\ln u(t)$$

and integration yields

$$K(0, t; 0, t') = Cu^{-1/2}(t),$$

where C is a constant. The expression obtained here for $K(0, t; 0, t')$ is comparable to Eq. (A4) of Pechukas,[10] except that in our case $u(t)$ is determined by an integro-differential equation, Eq. (13), instead of an initial-value differential equation.

We now consider the limit as $t\to t''$. In the limit we find that $K(0, t''; 0, t')$ is determined by $[\partial\bar{y}(t'')/\partial\dot{\bar{y}}(t')]_{\bar{y}(t')}$. Since this quantity is known to be independent of the path $\bar{y}(t)$, we anticipate that it may be uniquely determined by the path $\bar{x}(t)$. In particular, it can be shown that

$$\left(\frac{\partial\bar{x}(t'')}{\partial\dot{\bar{x}}(t')}\right)_{\bar{x}(t')} = \left(\frac{\partial\bar{y}(t'')}{\partial\dot{\bar{y}}(t')}\right)_{\bar{y}(t')} . \tag{18}$$

The left-hand side of Eq. (18) is obtained by differentiating Eq. (3) with respect to $\dot{\bar{x}}(t')$ and deriving an integro-differential equation of motion for $[\partial\bar{x}(t)/\partial\dot{\bar{x}}(t')]_{\bar{x}(t')}$, taking account of the fact that $\underline{U}(t'', t)$, $\underline{U}(t, t')$, and $\underline{U}(t'', t')$, as well as $\partial\underline{H}(x)/\partial\bar{x}(t)$, are all functions of $\dot{\bar{x}}(t')$; for example,

$$\frac{\partial\underline{U}(t, t')}{\partial\dot{\bar{x}}(t')} = -i\int_{t'}^{t}\underline{U}(t, s)\frac{\partial\underline{H}(x)}{\partial\bar{x}(s)}\underline{U}(s, t')\left(\frac{\partial\bar{x}(s)}{\partial\dot{\bar{x}}(t')}\right)_{\bar{x}(t')}ds .$$

A comparison of the resulting equation for $[\partial\bar{x}(t'')/\partial\dot{\bar{x}}(t')]_{\bar{x}(t')}$ with Eq. (13) will yield the equality in Eq. (18). We therefore find that

$$K(0, t''; 0, t') = \left\{m\left[2\pi i\left(\frac{\partial\bar{x}(t'')}{\partial\dot{\bar{x}}(t')}\right)_{\bar{x}(t')}\right]^{-1}\right\}^{1/2},$$

where the proportionality constant is determined by the free-particle limit, and where the phase may undergo discontinuous changes at turning points of the nuclear motion.[10] For a scattering problem this result can be rewritten as[10]

$$K(0, t''; 0, t') = \left\{m\left[2\pi i(t''-t')\left(\frac{\partial\bar{x}(t'')}{\partial\bar{x}(t')}\right)_{\dot{\bar{x}}(t')}\right]^{-1}\right\}^{1/2}, \tag{19}$$

where t'' is a time just after the scattering has occurred and t' is a time in the far past. With t'' and t' defined in this way it can be seen that the partial derivative in Eq. (19) is given by the ratio of the final momentum over the initial momentum.

A generalization to three dimensions is also possible,[10] in which case the partial derivative in Eq. (19) becomes a Jacobian determinant of a final position with respect to an initial position. The expression for $K(0t'', 0t')$ in a three-dimensional problem will therefore contain the quantity $d\Omega/d\sigma$, which yields the classical expression for the differential cross section.

III. DISCUSSION

The form of the result we have obtained for the normalization constant is identical to that obtained in Eq. (3.9) of Pechukas[5] in the sense that both normalizations are determined by the response of the end point of a classical trajectory to a change in the initial position, but the way in which this response is calculated in practice in the two cases is quite different. To evaluate the normalization constant derived by Pechukas[5] one must perform a single trajectory calculation with a particular set of initial conditions, parametrize the resulting energy surface to have the form $V(\bar{x}, t)$, and subsequently constrain the energy surface to retain this form as the response of the trajectory to a change in the initial conditions is evaluated. To evaluate our result for the normalization we would perform two entirely independent classical trajectory calculations, with slightly different initial conditions, and the partial derivative which is required would be evaluated numerically using these two trajectories. In this case it is clear that no constraints are being imposed on the "response" of the energy surface to a change in initial conditions. The difference between these two methods of determining the normalization is due precisely to the presence of double integrals in the expression for $\phi^{(2)}[y(t)]$ in Eq. (7). To some extent, this result has been anticipated by Pechukas,[5] but we are not aware of any previous derivation of it.

It is of some interest to consider situations in which the two definitions of the normalization yield different numerical results. To do this, it is necessary to consider a three-dimensional problem since the normalization for a one-dimensional problem is determined entirely by the long-range behavior of the energy surface and will therefore be the same regardless of which definition is used. In a three-dimensional calculation we find that $K(0, t''; 0, t')$ is related to $d\Omega/d\sigma = \sin\theta\, d\theta/b\, db$. The quantity $d\theta/db$ is of particular interest, since the two procedures described above for the calculation of this type of derivative will yield different answers. The actual energy surface for the collision can be put into the form $V_{\beta\alpha}(R, t, E, b)$, where E and b are the total impact energy and impact parameter, respectively. The difference between the two methods of evaluating $d\theta/db$ will be due to the dependence of the energy surface on the impact parameter b. (For an example of a situation in which this dependence is rather pronounced, see Fig. 2 of Penner and Wallace.[8])

The present discussion of the "normalizing integral" was undertaken in order to define more precisely how the differential cross section should be calculated, after the trajectory problem has been solved. Previously, we were not sure that the procedure used by Penner and Wallace[8] to define the cross section was the correct one. We now find that it is, provided that $d\theta/db$ is evaluated numerically with no constraints imposed on the response of the energy surface to a change in b. (We therefore believe that the lack of agreement between the elastic differential cross section of Penner and Wallace[8] and the experimental results is due predominantly to the fact that a single-trajectory theory does not adequately describe nuclear motion inside the interaction region for this type of curve-crossing problem; the success achieved by Olson and Smith[4] using a multitrajectory theory seems to support this statement. This failure of our theory is closely related to the breakdown of the assumption that $|\underline{U}_{\beta\alpha}(t'', t')|$ does not change significantly as the path varies about the classical path.) If improvements in the theory were desired it would probably be necessary to consider the effects of variations in $|\underline{U}_{\beta\alpha}(t'', t')|$ or, possibly, to develop more specialized versions of this theory instead of the general theory discussed here.

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