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Correlation function formulation for the state selected total reaction probability

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A correlation function formulation for the state-selected total reaction probability, $N_\alpha(E)$, is suggested. A wave packet, correlating with a specific set of internal reactant quantum numbers, α , is propagated forward in time until bifurcation is complete at which time the nonreactive portion of the amplitude is discarded. The autocorrelation function of the remaining amplitude is then computed and Fourier transformed to obtain a reactivity spectrum. Dividing by the corresponding spectrum of the original, unfiltered, wave packet normalizes the reactivity spectrum, yielding the total reaction probability from the internal state, α . The procedure requires negligible storage and just one time-energy Fourier transform for each initial reactant state, independent of the number of open channels of products. The method is illustrated numerically for the one-dimensional Eckart barrier, using both quantum-mechanical and semiclassical propagation methods. Summing over internal states of reactants gives the cumulative reaction probability, $N(E)$. The relation to the trace formula [W. H. Miller, S. D. Schwartz, J. W. Tromp, *J. Chem. Phys.* **79**, 4889 (1983)], $N(E) = \frac{1}{2}(2\pi\hbar)^2 \text{tr}(\bar{F}\delta(H-E)\bar{F}\delta(H-E))$, is established, and a new variant of the trace formula is presented. © 1998 American Institute of Physics. [S0021-9606(98)01127-1]

I. INTRODUCTION

The time-dependent approach to reactive scattering is appealing for a variety of reasons. It is conceptually simple, reflecting the temporal sequence of approach of collision partners, rearrangement of constituent atoms, and the subsequent separation of products in the course of a chemical reaction. Moreover, it simplifies the formal theory of scattering; the definition of incoming and outgoing states is most naturally cast in terms of time dependent wave packets, and, since wave packets are square integrable, there is no need to extend beyond the normal Hilbert space of bound state quantum mechanics.^{1,2} Finally, the time-dependent approach to reactive scattering in recent years has become a practical computational tool, as a result of advances in numerical methods for wave packet propagation and because of various new expressions for the scattering amplitude³⁻⁷ and reaction probability.

The complete information about the scattering is contained in the scattering matrix, $\mathbf{S}_{\beta\alpha}(E)$. The square of an element of this matrix gives the probability to obtain products with the final set of internal quantum numbers, β , in the infinite future, starting with reactants in the initial set of quantum numbers, α , in the infinite past, at total energy E . However, the complete state-to-state information is generally expensive to compute and for many purposes is much more detailed than necessary. Accordingly, several formulations have been proposed for directly computing the cumulative reaction probability, $N(E) = \sum_{\alpha\beta} |\mathbf{S}_{\beta\alpha}(E)|^2$, or the state selected total reaction probability, $N_\alpha(E) = \sum_{\beta} |\mathbf{S}_{\beta\alpha}(E)|^2$, which may then be summed to yield $N(E)$. Miller and co-

workers have suggested a variety of flux and complex absorbing potential formulations for $N(E)$.⁸⁻¹³ Attempts have been made to implement these formulations semi-classically,¹⁴ but so far numerical calculations are limited to 1D. Zhang and Light have presented an alternative formulation for $N(E)$ in terms of transition state wave packets which are the products of internal states and eigenfunctions of the flux operator.^{15,16} Neuhauser *et al.*^{17,18} and Zhang *et al.*¹⁹⁻²³ have formulated and implemented methods for calculating $N_\alpha(E)$, in three- and four-atom problems, using a time-dependent reactive flux approach, and Jäckle and Meyer have developed a complementary method which uses absorbing potentials.²⁴

In this paper we present a new formulation of the state selected total reaction probability. A wave packet, correlating with a specific set of internal reactant quantum numbers, α , is propagated forward in time until bifurcation is complete, at which time the nonreactive portion of the amplitude is discarded (if there is more than one product arrangement channel, the amplitude into all but one channel can be removed by a similar procedure). The autocorrelation function of the remaining amplitude is then computed and Fourier transformed to obtain a reactivity spectrum. Dividing by the corresponding spectrum of the original, unfiltered, wave packet normalizes the reactivity spectrum, yielding the total reaction probability from the internal state, α . No projection onto individual final states is required, and thus the storage requirements are negligible—just one correlation function and a single time-energy Fourier transform for each initial state. Moreover, the bifurcation of the wave packet is gener-

ally complete well before the wave packet has reached the asymptotic region of the potential, reducing the necessary propagation time. The method is compatible with both quantum-mechanical and semiclassical time propagation methods, as we illustrate here using the one-dimensional Eckart barrier. Summing over internal states of reactants gives the cumulative reaction probability, $N(E)$.

In Sec. II A we derive the correlation function expression for the $N_\alpha(E)$, starting from the definition of the S -matrix. The derivation, and indeed the final formula, are similar in the spirit to the correlation function formulation of individual S -matrix elements of Tannor and Weeks,³ but many new pieces come into play here. In Sec. II C we show the relation of the new expression to the trace formula for $N(E) = \frac{1}{2}(2\pi\hbar)^2 \text{tr}(\bar{F}\delta(H-E)\bar{F}\delta(H-E))$, of Miller, Schwartz, and Tromp,²⁵ and present a new variant of the trace formula. In Sec. III we implement the approach using both quantum-mechanical and semiclassical (Herman-Kluk) propagation methods to compute transmission through the one-dimensional Eckart barrier. A major surprise is the contrast between the high accuracy of the semiclassical propagation and the low accuracy of a classical criterion to define the reactive portion of the initial wave packet. This loss of accuracy can be avoided, but at considerable expense, by re-expanding the semiclassical wave function in a new set of trajectories after bifurcation is complete. Section IV is the conclusion.

II. CORRELATION FUNCTION FORMULATION FOR $N_\alpha(E)$ USING THE PROJECTION OPERATOR

A. Derivation from the S -matrix definition

Consider the scattering process of a reactive system with internal degrees of freedom. The Hamiltonian H governs the dynamics of the system. It can be written as a sum of the asymptotic Hamiltonian of reactants H_α^0 or products H_β^0 and interaction potentials vanishing when the reactants and products are far apart

$$H = H_\alpha^0 + V_\alpha = H_\beta^0 + V_\beta.$$

There are two alternative sets of eigenstates of H , $\{\psi_{\alpha,E}^+\}$ and $\{\psi_{\beta,E}^-\}$, which describe the reaction. Labels α and β refer to the sets of internal quantum numbers, including arrangement channels, for the reactants and products, respectively. The wave function $|\psi_{\alpha,E}^+\rangle$ correlates, i.e., is equivalent in the asymptotic region, to the eigenstate of H_α^0 of the same energy with internal quantum numbers α . Similarly, $|\psi_{\beta,E}^-\rangle$ correlates with the eigenstate of H_β^0 with internal quantum numbers β . The two sets of eigenfunctions are related to each other through the S -matrix, $S_{\beta\alpha}$,

$$S_{\beta\alpha}(E) = \langle \psi_{\beta,E}^- | \psi_{\alpha,E}^+ \rangle = S_{\beta\alpha}(E) \delta(E - E'). \quad (1)$$

The reaction probability from the initial state with internal quantum numbers α to a specific final state of the reactants with the internal quantum numbers β is proportional to

$$S_{\beta\alpha}^*(E) \delta(E - E') S_{\beta\alpha}(E'') \delta(E' - E'') \\ = \langle \psi_{\alpha,E}^+ | \psi_{\beta,E'}^- \rangle \langle \psi_{\beta,E'}^- | \psi_{\alpha,E''}^+ \rangle. \quad (2)$$

Integration over E' and summation over all β of the product channel gives

$$\sum_\beta S_{\beta\alpha}^*(E) S_{\beta\alpha}(E'') \delta(E - E'') \\ = \langle \psi_{\alpha,E}^+ | \left(\sum_\beta \int dE' |\psi_{\beta,E'}^- \rangle \langle \psi_{\beta,E'}^-| \right) | \psi_{\alpha,E''}^+ \rangle \\ = \langle \psi_{\alpha,E}^+ | \hat{P}^+ | \psi_{\alpha,E''}^+ \rangle, \quad (3)$$

where \hat{P}^+ denotes the projection operator for products

$$\hat{P}^+ \equiv \sum_\beta \int |\psi_{\beta,E'}^- \rangle \langle \psi_{\beta,E'}^-| dE'. \quad (4)$$

Throughout the paper the integration over energy goes from $E=0$ to $E=\infty$. The lower limit of the integration over time is $t=-\infty$ and the upper limit of the integration over time is $t=+\infty$. Henceforth, limits of the integration will be omitted. In the spirit of the derivation of Tannor and Weeks,³ we express the energy eigenfunction for a specific internal quantum number α and incoming momentum, $|\psi_{\alpha,E}^+\rangle$, in terms of an integral over the time evolution of a wave packet $|\Phi_\alpha^+\rangle$,

$$|\psi_{\alpha,E}^+\rangle = \frac{(2\pi\hbar)^{-1}}{\eta_\alpha(E)} \int dt e^{-(i/\hbar)Ht} |\Phi_\alpha^+\rangle e^{(i/\hbar)Et}. \quad (5)$$

The wave packet $|\Phi_\alpha^+\rangle$ is defined such that in the infinite past it is localized in the asymptotic region of the reactants, and is given as a direct product of the eigenstate of the internal Hamiltonian with quantum numbers α and an incoming wave packet in the translational degree of freedom. The function $\eta_\alpha(E)$ represents the energy expansion coefficients, defined as $|\Phi_\alpha^+\rangle = \int dE \eta_\alpha(E) |\psi_{\alpha,E}^+\rangle$. Substituting Eq. (5) into Eq. (3) we have

$$\sum_\beta S_{\beta\alpha}^*(E) S_{\beta\alpha}(E'') \delta(E - E'') \\ = \frac{(2\pi\hbar)^{-2}}{\eta_\alpha^*(E) \eta_\alpha(E'')} \int dt \langle \Phi_\alpha^+ | e^{(i/\hbar)Ht} e^{-(i/\hbar)Et} \hat{P}^+ \\ \times \int d\tau e^{-(i/\hbar)H\tau} |\Phi_\alpha^+\rangle e^{(i/\hbar)E''\tau} \\ = \frac{(2\pi\hbar)^{-2}}{\eta_\alpha^*(E) \eta_\alpha(E'')} \\ \times \int dt \int d\tau \langle \Phi_\alpha^+ | e^{(i/\hbar)Ht} \hat{P}^+ e^{-(i/\hbar)H\tau} | \Phi_\alpha^+ \rangle \\ \times e^{-(i/\hbar)(Et - E''\tau)}. \quad (6)$$

Since the projection operator \hat{P}^+ and the Hamiltonian H commute we can reverse their order in Eq. (6). Changing variables to $t^+ = t + \tau$, $t^- = \tau - t$ and introducing the new parameters $E^+ = (E + E'')/2$ and $E^- = (E'' - E)/2$, Eq. (6) becomes

$$\begin{aligned}
& \sum_{\beta} S_{\alpha\beta}^*(E) S_{\beta\alpha}(E'') \delta(E-E'') \\
&= \frac{1}{2} \frac{(2\pi\hbar)^{-2}}{\eta_{\alpha}^*(E) \eta_{\alpha}(E'')} \\
&\quad \times \int dt^+ \int dt^- \langle \phi_{\alpha}^+ | \hat{P}^+ e^{-(i/\hbar)Ht^-} | \Phi_{\alpha}^+ \rangle \\
&\quad \times e^{(i/\hbar)(E^- t^+ + E^+ t^-)}. \quad (7)
\end{aligned}$$

Integration over t^+ gives $4\pi\hbar\delta(E''-E)$, and replacing the dummy variable t^- by t we get

$$\begin{aligned}
& \sum_{\beta} S_{\beta\alpha}(E) S_{\beta\alpha}^*(E'') \delta(E-E'') \\
&= \frac{(2\pi\hbar)^{-1}}{\eta_{\alpha}^*(E) \eta_{\alpha}(E'')} \\
&\quad \times \int dt \langle \Phi_{\alpha}^+ | \hat{P}^+ e^{-(i/\hbar)Ht} | \Phi_{\alpha}^+ \rangle e^{(i/\hbar)E^+ t} \delta(E-E''). \quad (8)
\end{aligned}$$

Integration of Eq. (8) over E'' gives

$$\begin{aligned}
& \sum_{\beta} |S_{\beta\alpha}(E)|^2 \equiv N_{\alpha}(E) \\
&= \frac{(2\pi\hbar)^{-1}}{|\eta_{\alpha}(E)|^2} \int dt \langle \Phi_{\alpha}^+ | \hat{P}^+ e^{-(i/\hbar)Ht} | \Phi_{\alpha}^+ \rangle \\
&\quad \times e^{(i/\hbar)Et}. \quad (9)
\end{aligned}$$

Equation (9) expresses $N_{\alpha}(E)$ as the cross-correlation function of the reactive wave function $\hat{P}^+ \Phi_{\alpha}^+$ with the unfiltered, incoming wave function Φ_{α}^+ ; in practice either one of these wave functions can be propagated in time, or the propagation can be partitioned between the two. The correlation function expression and the whole approach is closely related to the formulation for the S -matrix elements of Tannor and Weeks,^{3,4}

$$S_{\beta\alpha}(E) = \frac{(2\pi\hbar)^{-1}}{\eta_{\beta}^*(E) \eta_{\alpha}(E)} \int dt \langle \Phi_{\beta}^- | e^{-(i/\hbar)Ht} | \Phi_{\alpha}^+ \rangle e^{(i/\hbar)Et}, \quad (10)$$

where the wave packet $|\Phi_{\beta}^- \rangle = \int dE \eta_{\beta}(E) |\psi_{\beta,E}^- \rangle$ is such that in the infinite future it is localized in the asymptotic region of the products, and is given as a direct product of the β eigenstate of the internal Hamiltonian and an outgoing wave packet in the translational degree of freedom.

B. Alternative expressions for $N_{\alpha}(E)$

Using the properties of the projection operator $\hat{P}^{+2} = \hat{P}^+$ and $\hat{P}^{+*} = \hat{P}^+$, we can rewrite Eq. (9) in a symmetrized way

$$N_{\alpha}(E) = \frac{(2\pi\hbar)^{-1}}{|\eta_{\alpha}(E)|^2} \int dt \langle \hat{P}^+ \Phi_{\alpha}^+ | e^{-(i/\hbar)Ht} | \hat{P}^+ \Phi_{\alpha}^+ \rangle e^{(i/\hbar)Et}. \quad (11)$$

The right-hand side of Eq. (11) is manifestly real since it involves the Fourier transform of the autocorrelation function, and for any autocorrelation function $C(-t) = C^*(t)$.

One can use the identities $\hat{P}^+ = \hat{1} - \hat{Q}^+$ and $\hat{Q}^{+2} = \hat{Q}^+$ and Eq. (15) to find the total reaction probability through the nonreactive part of the wave function $|\hat{Q}^+ \Phi_{\alpha}^+ \rangle$,

$$\begin{aligned}
N_{\alpha}(E) &= 1 - \frac{(2\pi\hbar)^{-1}}{|\eta_{\alpha}(E)|^2} \\
&\quad \times \int dt \langle \hat{Q}^+ \Phi_{\alpha}^+ | e^{-(i/\hbar)Ht} | \hat{Q}^+ \Phi_{\alpha}^+ \rangle e^{(i/\hbar)Et} \\
&= 1 - \frac{(2\pi\hbar)^{-1}}{|\eta_{\alpha}(E)|^2} \int dt \langle \hat{Q}^+ \Phi_{\alpha}^+ | e^{-(i/\hbar)Ht} | \Phi_{\alpha}^+ \rangle e^{(i/\hbar)Et}. \quad (12)
\end{aligned}$$

We can proceed further by recalling that $\Phi_{\alpha}^+(r, R) = \Omega_+^{\alpha}(\chi_{\alpha}^+(r) \times g(R))$. Here, $\chi_{\alpha}(r)$ is an eigenstate of the internal degrees of freedom, $g(R)$ is an arbitrary incoming wave packet in the translational coordinate and Ω_+^{α} is the reactant Møller operator defined as

$$\Omega_+^{\alpha} = \lim_{t \rightarrow -\infty} e^{(i/\hbar)Ht} e^{-(i/\hbar)H_0 t}. \quad (13)$$

As shown in Ref. 3, the energy expansion coefficients $\eta_{\alpha}(E)$ can be found through the Fourier transform of $g(R)$,

$$\eta_{\alpha}(E) = (|p_{\alpha}|)^{-1/2} \int dR g(R) e^{(i/\hbar)p_{\alpha}R}, \quad (14)$$

where $p_{\alpha} = \sqrt{2m(E-E_{\alpha})}$. Alternatively, it is possible to express the absolute value of the energy expansion coefficients in terms of the Fourier transform of the autocorrelation function of $|\Phi_{\alpha}^+ \rangle$,

$$|\eta_{\alpha}(E)|^2 = \frac{1}{2\pi\hbar} \int dt \langle \Phi_{\alpha}^+ | e^{-(i/\hbar)Ht} | \Phi_{\alpha}^+ \rangle e^{(i/\hbar)Et}. \quad (15)$$

Expression (15) can be used even if the wave packet $|\Phi_{\alpha}^+ \rangle$ is in the interaction region and distorted from the separable product form, as long as the state *correlates* with a single set of internal quantum numbers, i.e., evolves into a state with a single set of internal reactant quantum numbers in the infinite past.

Combining Eqs. (11) and (15) yields

$$N_{\alpha}(E) = \frac{\int dt \langle \hat{P}^+ \Phi_{\alpha}^+ | e^{-(i/\hbar)Ht} | \hat{P}^+ \Phi_{\alpha}^+ \rangle e^{(i/\hbar)Et}}{\int dt \langle \Phi_{\alpha}^+ | e^{-(i/\hbar)Ht} | \Phi_{\alpha}^+ \rangle e^{(i/\hbar)Et}}. \quad (16)$$

This expression, Eq. (16), is the central result of this paper. It expresses the state-selected total reaction probability as a ratio of two spectra, that of the reactive wave packet divided by that of the initial wave packet, which has both reactive and nonreactive components. The latter spectrum normalizes the former, ensuring that the total reaction probability is between 0 to 1 and that the result at each energy is independent of the choice of energy distribution in the initial translational wave packet.

It is possible to construct the initial wave packet $|\Phi_\alpha^+\rangle$ by projecting an arbitrary wave packet $|\Phi\rangle$ onto the specific internal state α using Eq. (15) for the energy coefficients, $|\Phi_\alpha^+\rangle = \hat{P}_\alpha |\Phi\rangle$. The total reaction probability can then be written as

$$N_\alpha(E) = \frac{\int dt \langle \hat{P}^+ \hat{P}_\alpha \Phi^+ | e^{-(i/\hbar)Ht} | \hat{P}^+ \hat{P}_\alpha \Phi^+ \rangle e^{(i/\hbar)Et}}{\int dt \langle \hat{P}_\alpha \Phi^+ | e^{-(i/\hbar)Ht} | \hat{P}_\alpha \Phi^+ \rangle e^{(i/\hbar)Et}}. \quad (17)$$

It is worth noting that all the expressions for the state selected total reaction probability can be reversed to treat the case of a single well-defined internal state of products, summed over all internal states of reactants. To do so, the labels α and β must be interchanged, the projection operator must be redefined to project onto reactants as the final wave packet (which is separable into the outgoing wave packet in the translational coordinate and internal eigenstate β of the product internal Hamiltonian as $t \rightarrow \infty$) is propagated back in time.

C. Derivation of the trace formula from $N_\alpha(E)$

1. Preliminaries

The trace formula of Miller, Schwartz, and Tromp^{25,26} reads

$$N(E) = \frac{(2\pi\hbar)^2}{2} \text{tr}(\bar{F} \delta(E-H) \bar{F} \delta(E-H)), \quad (18)$$

with the flux operator defined via the commutator of the full Hamiltonian H and the Heaviside function $h(s)$,

$$\bar{F} = \frac{1}{2} \left(\delta(s) \frac{p}{m} + \frac{p}{m} \delta(s) \right) = \frac{i}{\hbar} [H, h(s)], \quad (19)$$

with s being the reaction coordinate. The direction of the reaction is such that $s = -\infty$ corresponds to the reactants and $s = \infty$ corresponds to the products. The Heaviside function, defined as

$$h(s) = \begin{cases} 1 & \text{if } s > 0 \\ 0 & \text{if } s < 0 \end{cases} \quad (20)$$

projects onto reactants. It is a part of one of the alternative expressions of the projection operator for products

$$\hat{P}^+ = \lim_{t \rightarrow \infty} e^{(i/\hbar)Ht} h(s) e^{-(i/\hbar)Ht}. \quad (21)$$

The operator \hat{P}^+ projects onto the states that are on the product side in the infinite future. Another projection operator is

$$\hat{P}^- = \lim_{t \rightarrow -\infty} e^{(i/\hbar)Ht} h(s) e^{-(i/\hbar)Ht}, \quad (22)$$

which projects onto products in the infinite past. Its action on the incoming wave packet is trivial, $\hat{P}^- |\Phi_\alpha^+\rangle = 0$. A useful relation between the projection and flux operators is

$$\begin{aligned} \int dt e^{(i/\hbar)Ht} \bar{F} e^{-(i/\hbar)Ht} &= \int dt e^{(i/\hbar)Ht} \frac{i}{\hbar} [H, h(s)] e^{-(i/\hbar)Ht} \\ &= \int dt \left(\frac{d}{dt} e^{(i/\hbar)Ht} h(s) e^{-(i/\hbar)Ht} \right) \\ &= \lim_{t \rightarrow \infty} e^{(i/\hbar)Ht} h(s) e^{-(i/\hbar)Ht} \\ &\quad - \lim_{t \rightarrow -\infty} e^{(i/\hbar)Ht} h(s) e^{-(i/\hbar)Ht} \\ &= \hat{P}^+ - \hat{P}^-. \end{aligned} \quad (23)$$

We now rearrange a part of Eq. (18) using Eq. (23),

$$\begin{aligned} (2\pi\hbar)^2 \delta(E-H) \bar{F} \delta(E-H) &= \int dt e^{(i/\hbar)(H-E)t} \bar{F} \int d\tau e^{(i/\hbar)(-H+E)\tau} \\ &= \int dt^- \int dt e^{(i/\hbar)Ht} \frac{i}{\hbar} [H, h(s)] \\ &\quad \times e^{-(i/\hbar)Ht} e^{-(i/\hbar)(H-E)t^-} \\ &= \int dt \frac{d}{dt} \left\{ e^{(i/\hbar)Ht} h(s) e^{-(i/\hbar)Ht} \right\} \int dt^- e^{-(i/\hbar)(H-E)t^-} \\ &= \left(\lim_{t \rightarrow \infty} e^{(i/\hbar)Ht} h(s) e^{-(i/\hbar)Ht} \right. \\ &\quad \left. - \lim_{t \rightarrow -\infty} e^{(i/\hbar)Ht} h(s) e^{-(i/\hbar)Ht} \right) 2\pi\hbar \delta(E-H) \\ &= 2\pi\hbar (\hat{P}^+ - \hat{P}^-) \delta(E-H). \end{aligned} \quad (24)$$

In the intermediate steps of the derivation we made the substitution $t^- = \tau - t$. Thus, Eq. (18) can be rewritten as

$$N(E) = \pi\hbar \text{tr}(\bar{F} \delta(E-H) (\hat{P}^+ - \hat{P}^-)), \quad (25)$$

which is an interesting alternative expression for the cumulative reaction probability.

2. Getting the trace expression for $N(E)$

We now return to the correlation function expression, Eq. (11), and manipulate it into a form closely resembling Eq. (25),

$$N_\alpha(E) = \frac{(2\pi\hbar)^{-1}}{|\eta_\alpha(E)|^2} \int dt \langle \Phi_\alpha^+ | \hat{P}^+ e^{-(i/\hbar)Ht} \hat{P}^+ | \Phi_\alpha^+ \rangle e^{(i/\hbar)Et}$$

$$= \frac{(2\pi\hbar)^{-1}}{|\eta_\alpha(E)|^2} \int dt \langle \Phi_\alpha^+ | (\hat{P}^+ - \hat{P}^-) \times e^{-(i/\hbar)Ht} (\hat{P}^+ - \hat{P}^-) | \Phi_\alpha^+ \rangle e^{(i/\hbar)Et} \quad (26)$$

$$= \frac{(2\pi\hbar)^{-1}}{|\eta_\alpha(E)|^2} \int dt \langle \Phi_\alpha^+ | \left(\int d\tau e^{(i/\hbar)H\tau} \bar{F} e^{-(i/\hbar)H\tau} \right) \times e^{-(i/\hbar)Ht} (\hat{P}^+ - \hat{P}^-) | \Phi_\alpha^+ \rangle e^{(i/\hbar)Et} \quad (27)$$

$$= \frac{(2\pi\hbar)^{-1}}{|\eta_\alpha(E)|^2} \int dt^+ \int d\tau \langle \Phi_\alpha^+ | e^{(i/\hbar)(H-E)\tau} \times \bar{F} (\hat{P}^+ - \hat{P}^-) e^{-(i/\hbar)(H-E)t^+} | \Phi_\alpha^+ \rangle \quad (28)$$

$$= 2\pi\hbar \langle \psi_{\alpha,E}^+ | \bar{F} (\hat{P}^+ - \hat{P}^-) | \psi_{\alpha,E}^+ \rangle. \quad (29)$$

We used the fact that $\hat{P}^- | \Phi_\alpha^+ \rangle = 0$ to obtain Eq. (26). Then we used Eq. (23), relating projection operators to the flux operator, to get Eq. (27). Substituting $t^+ = t + \tau$, changing variables of integration from (t, τ) to (t^+, τ) and using the commutativity of the projection operator with the Hamiltonian we get Eq. (28). Finally, the expression for the energy eigenfunction was used to arrive at Eq. (29).

Summing over α for the cumulative reaction probability,

$$N(E) = \sum_\alpha N_\alpha(E) = \sum_\alpha 2\pi\hbar \langle \psi_{\alpha,E}^+ | \bar{F} (\hat{P}^+ - \hat{P}^-) | \psi_{\alpha,E}^+ \rangle$$

$$= 2\pi\hbar \sum_\alpha \int dE' \langle \psi_{\alpha,E'}^+ | \bar{F} (\hat{P}^+ - \hat{P}^-) \times \delta(E - E') | \psi_{\alpha,E'}^+ \rangle \quad (30)$$

$$= 2\pi\hbar \sum_\alpha \int dE' \langle \psi_{\alpha,E'}^+ | \bar{F} \delta(E - H) (\hat{P}^+ - \hat{P}^-) | \psi_{\alpha,E'}^+ \rangle. \quad (31)$$

Integration over the energy E' is introduced to approach the trace form and the order of \hat{P}^+ and $\delta(E - H)$ is changed since they commute. Now Eq. (31) resembles Eq. (25), evaluated in the energy eigenfunction basis set, except that the set $\{\psi_{\alpha,E}^+\}$, as defined by Eq. (5) is not complete. This set describes just the pure outgoing waves in the product channel. There is another set of the energy eigenfunctions $\{\psi_{\alpha,E}^*\}$ which are orthogonal to $\{\psi_{\alpha,E}^+\}$ and describe pure incoming waves in the product channel and are complex conjugates (or time reversed) of the eigenfunctions $\{\psi_{\alpha,E}^+\}$. Functions $\{\psi_{\alpha,E}^*\}$ form the subspace where the operator \hat{P}^- acts non-trivially, but $\hat{P}^+ | \psi_{\alpha,E}^* \rangle = 0$. We now add these terms to complete the trace evaluation in the complete set of the energy eigenfunctions. We can rewrite Eq. (30) to make it explicitly real

$$2\pi\hbar \sum_\alpha \langle \psi_{\alpha,E}^+ | \bar{F} (\hat{P}^+ - \hat{P}^-) | \psi_{\alpha,E}^+ \rangle$$

$$= 2\pi\hbar \sum_\alpha \langle \psi_{\alpha,E}^+ | \bar{F} \left(\int dt e^{(i/\hbar)Ht} \bar{F} e^{-(i/\hbar)Ht} \right) | \psi_{\alpha,E}^+ \rangle \quad (32)$$

$$= 2\pi\hbar \sum_\alpha \langle \psi_{\alpha,E}^+ | \bar{F} \left(\int dt e^{(i/\hbar)(H-E)t} \right) \bar{F} | \psi_{\alpha,E}^+ \rangle$$

$$= (2\pi\hbar)^2 \sum_\alpha \langle \psi_{\alpha,E}^+ | \bar{F} \delta(H - E) \bar{F} | \psi_{\alpha,E}^+ \rangle \quad (33)$$

$$= (2\pi\hbar)^2 \sum_\alpha \frac{1}{2} (\langle \psi_{\alpha,E}^+ | \bar{F} \delta(H - E) \bar{F} | \psi_{\alpha,E}^+ \rangle$$

$$+ \langle \psi_{\alpha,E}^* | \bar{F} \delta(H - E) \bar{F} | \psi_{\alpha,E}^* \rangle). \quad (34)$$

Above we used Eq. (23) once again. In Eq. (34) we added the term

$$\langle \psi_{\alpha,E}^* | \bar{F} \delta(H - E) \bar{F} | \psi_{\alpha,E}^* \rangle$$

$$= (\langle \psi_{\alpha,E}^+ | \bar{F} \delta(H - E) \bar{F} | \psi_{\alpha,E}^+ \rangle)^*$$

$$= \langle \psi_{\alpha,E}^+ | \bar{F} \delta(H - E) \bar{F} | \psi_{\alpha,E}^+ \rangle,$$

which is the complex conjugate of the real expression (33), divided by a factor of 2. Thus, we can rewrite Eq. (29) as

$$N(E) = \pi\hbar \sum_\alpha \int dE' (\langle \psi_{\alpha,E'}^+ | \bar{F} \delta(E - H) (\hat{P}^+ - \hat{P}^-) | \psi_{\alpha,E'}^+ \rangle$$

$$+ \langle \psi_{\alpha,E'}^* | \bar{F} \delta(E - H) (\hat{P}^+ - \hat{P}^-) | \psi_{\alpha,E'}^* \rangle)$$

$$= \pi\hbar \text{tr}(\bar{F} \delta(E - H) (\hat{P}^+ - \hat{P}^-))$$

$$= \frac{(2\pi\hbar)^2}{2} \text{tr}(\bar{F} \delta(E - H) \bar{F} \delta(E - H)), \quad (35)$$

where, using Eq. (25), we have finally arrived to the trace expression (18).

III. NUMERICAL IMPLEMENTATION

A. General considerations

The correlation function expressions, Eqs. (9) and (11), formally require three time propagations:

- (1) Propagation of the wave packet $|\Phi_\alpha^+\rangle$ forward in time into the infinite future followed by the projection onto the products.
- (2) Propagation back in time up to $t=0$ to complete the construction of the $|\hat{P}^+ \Phi_\alpha^+\rangle$.
- (3) Calculation of the correlation function $C(t) = \langle \Phi_\alpha^+(0) | \hat{P}^+ \Phi_\alpha^+(t) \rangle$, or the autocorrelation function $C_a(t) = \langle \hat{P}^+ \Phi_\alpha^+(0) | \hat{P}^+ \Phi_\alpha^+(t) \rangle$ for $t = [-\infty, \infty]$.

In practice, some of the steps can be combined. The maximal propagation time T in the first step can be determined from the approaching of the norm of the wave function in the product region $\int_0^\infty ds |\Phi_\alpha^+(s, t)|^2$ to a constant value (s is a reaction coordinate). This happens before the wave packet

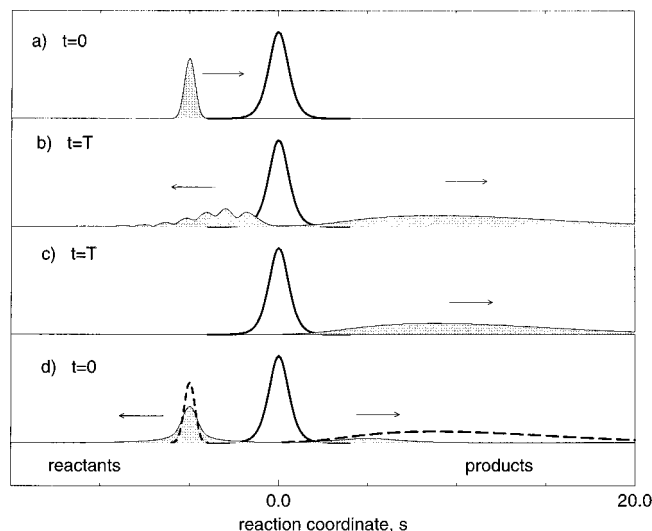


FIG. 1. Scattering on a one-dimensional barrier; (a) at $t=0$ an initial wave packet $|\Phi(0)\rangle$ (shaded) starts moving towards the barrier (solid line on all panels); (b) at time $t=T$ the wave packet $|\Phi(T)\rangle$ (shaded) is split into two parts: the reactive part is on the right side of the barrier and the nonreactive part is on the left side; (c) the nonreactive part of the wave packet is discarded since the transport of the amplitude towards the product region is stopped, $\hat{P}|\Phi(T)\rangle$; (d) the reactive part of the wave packet $|\hat{P}\Phi(T)\rangle$ (shaded) is propagated back in time from $t=T$ to $t=0$ and its autocorrelation $\langle \hat{P}\Phi(T) | \hat{P}\Phi(T-t) \rangle$ (long dashed line $-|\hat{P}\Phi(T)\rangle$) or the correlation with the initial wave packet (short dashed line) $\langle \Phi(0) | \hat{P}\Phi(T-t) \rangle$ is computed.

reaches the asymptotic region, while transitions between different internal states of products can still be happening. The projection onto the products consists of simply multiplying the wave function by the Heaviside function (20). The autocorrelation function of the initial wave packet can be calculated as part of the first step, if Eq. (15) is used for the energy expansion coefficients $\eta(E)$. However, the second step, the propagation back to $t=0$, is not necessary. One can start computing the autocorrelation function of the projected wave function $C_a(t) = \langle \hat{P}^+ \Phi_\alpha^+(T) | e^{-(i/\hbar)Ht} | \hat{P}^+ \Phi_\alpha^+(T) \rangle$. Propagation just forward or just backward in time will be sufficient since $C_a(-t) = C_a^*(t)$. Propagation back seems to be more practical because it requires a smaller grid than the further propagation forward. Moreover, using Eq. (9), one can calculate the cross-correlation function of the projected wave function and the initial wave packet $C_c(T+t) = \langle \Phi_\alpha^+(0) | e^{-(i/\hbar)Ht} | \hat{P}^+ \Phi_\alpha^+(T) \rangle$ for times $t=[T,0]$. This correlation function $C_c(t)$ also satisfies the property $C_c(-t) = C_c^*(t)$, since Eqs. (9) and (11) are equivalent.

Figure 1 illustrates this procedure for a scattering on a barrier in one dimension.

B. Using the quantum-mechanical propagator

We applied Eqs. (9) and (11) with operators \hat{P}^+ and \hat{P}^{+2} for a one-dimensional test problem, the Eckart barrier scattering. The parameters of the potential, $V(s) = 16 \cosh^{-2}(1.1243s)$, correspond to the parameters for the hydrogen exchange reaction and the mass is unity. The initial wave packet has the Gaussian form

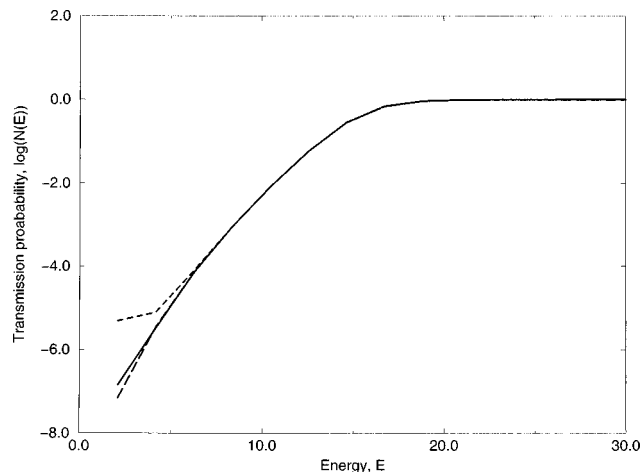


FIG. 2. Transmission probability $N(E)$ for the Eckart barrier, $V(x) = 16 \cosh^{-2}(1.3214x)$, obtained quantum-mechanically using Eq. (9) with one projection operator \hat{P} (short dashed line), using Eq. (11) with two projection operators \hat{P}^2 (long dashed line), and analytical result (solid line). $N(E)$ is plotted on a logarithmic scale.

$$\Phi^+(s,0) = (2a/\pi)^{1/4} \exp\left(-a(s-s_0)^2 + \frac{i}{\hbar} p_0(s-s_0)\right) \quad (36)$$

with $a=6$, $s_0=3.5$, $p_0=6$ in the units of $\hbar=1$, $m=1$. The initial wave packet was propagated up to time $T=6$ with the time step $dt=0.006$ using the FFT method.²⁷ Then, $\Phi^+(s,t)$ was multiplied by the Heaviside function (20), $\Phi_\rho^+(s,T) = h(s)\Phi^+(s,T)$, and propagated back in time until $t=0$. At the same time, the function $C(T+t) = \langle \Phi^+(0) | \Phi_\rho^+(t) \rangle$, to use in Eq. (9), or the function $C(t) = \langle \Phi_\rho^+(T) | \Phi_\rho^+(T+t) \rangle$ to use in Eq. (11), was calculated. The propagation time T was determined by the desired resolution of the Fourier transform. The total amplitude of the wave function in the product region stopped changing for times greater than $t_0=3$, according to the criterion

$$\left| \int_0^\infty |\Phi^+(s,t+dt)|^2 ds - \int_0^\infty |\Phi^+(s,t)|^2 ds \right| < 10^{-8}. \quad (37)$$

The time of the projection need not be the same as the propagation time T ; in principle, the projection can be performed at t_0 and the correlation function computed by propagating the wave function backwards in time from t_0 to $t=0$ and forwards in time from t_0 to time T , with the total time long enough to obtain the desired resolution in $N(E)$. The quantum transmission probabilities are presented in Fig. 2. As one can see, a single wave packet gives a good description of the dynamics from energies in the tunneling regime to those far above the barrier energy.

C. Using the semiclassical propagator of Herman and Kluk

Semiclassical wave packet propagation methods, pioneered by Heller,^{28,29} are the natural companion to the time dependent approach to scattering. To calculate the correlation function here we use semiclassical propagator of Her-

man and Kluk (HK),^{30,31} that has been rederived by Kay^{32–34} and successfully applied to a number of problems.^{35–40} The HK propagator is a superposition of the contributions from classical trajectories (in one dimension),

$$K^{\text{sc}}(s', t; s, 0) = \int \int \frac{dp_i dq_i}{2\pi\hbar} R_{qpt} e^{iS_{qpt}/\hbar} g_\gamma(q_t, p_i, s') g_\gamma^*(q_i, p_i, s), \quad (38)$$

$$g_\gamma(q_t, p_t, s) = \left(\frac{\gamma}{\pi}\right)^{1/4} \exp\left(-\frac{\gamma}{2}(s - q_t)^2 + \frac{i}{\hbar} p_t(s - q_t)\right), \quad (39)$$

$$R_{qpt} = \sqrt{\det\left(\frac{1}{2}\left(\frac{\partial p_t}{\partial p_i} + \frac{\partial q_t}{\partial q_i} - \frac{i\gamma}{\hbar} \frac{\partial q_t}{\partial p_i} + \frac{i}{\hbar\gamma} \frac{\partial p_t}{\partial q_i}\right)\right)}, \quad (40)$$

and q_t and p_t are the coordinates and momenta at time t of a classical trajectory started with initial conditions q_i and p_i at time zero. The sign in Eq. (40) has to be chosen such that R_{qpt} is a continuous function of time.³² S_{qpt} is the classical action,

$$S(q, p, t) = \int_0^t (p_{t'} \dot{q}_{t'} - H(p_{t'}, q_{t'}, t')) dt'. \quad (41)$$

The integration goes over all initial values (q_i, p_i) . In general, γ is a parameter. Here we chose it to be dependent on the width of the wave function (36) to be propagated, $\gamma = 2a$. Thus, the correlation function is a sum over the trajectories

$$C^{\text{sc}}(t) = \int \int ds ds' \Phi^{+*}(s', 0) K^{\text{sc}}(s', t; s, 0) \Phi^+(s, 0) = \sum_{qp} C_{qpt}.$$

It is natural, in the context of semiclassical propagation, to try to replace the quantum projection operator procedure by a classical reactivity criterion, in which the contribution of reactive trajectories to the correlation function is kept, and that of nonreactive trajectories is discarded, i.e.,

$$C^{\text{cl}}(t) = \langle \Phi^+(0) | \hat{P}^{\text{cl}} \Phi^+(t) \rangle = \sum_{qp} C_{qpt} \theta_{qp}, \quad (42)$$

with θ_{qp} defined as

$$\theta_{qp} = \begin{cases} 1 & \text{if } q(q_i, p_i, t \rightarrow -\infty) < 0 \text{ and } q(q_i, p_i, t \rightarrow \infty) > 0 \\ 0 & \text{if } q(q_i, p_i, t \rightarrow -\infty) < 0 \text{ and } q(q_i, p_i, t \rightarrow \infty) < 0 \end{cases} \quad (43)$$

For the one-dimensional case this criterion is equivalent to keeping only trajectories started from the reactant side with momentum towards the barrier and with energy greater than the barrier top. We used this idea in Eq. (9), for the same test problem and parameters as described in Sec. III B (Gaussian wave packet in the Eckart potential). Unfortunately, the agreement with the quantum results was poor (Fig. 3). It turns out that the classical reactivity criterion is applicable only when the reactive and nonreactive trajectories become spatially separated. For earlier times the interference between trajectories is crucial and classically reactive trajectories do

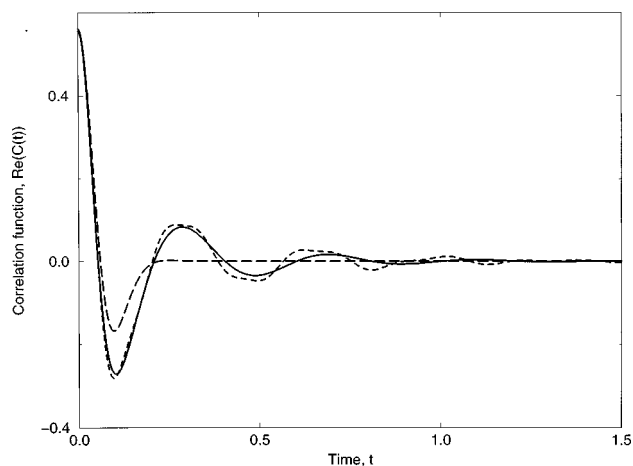


FIG. 3. Comparison of the autocorrelation function $C(t)$ of the projected wave function for the Eckart barrier used in Eq. (11), obtained semiclassically with the Herman-Kluk propagator (short dashed line), semiclassically with the classical reactivity criterion (long dashed line) and quantum-mechanically (solid line). The real part of $C(t)$ is plotted.

not adequately describe the semiclassical reactive wave function. We found that to obtain satisfactory accuracy we had to re-expand the propagated-projected wave function at the “infinite future” in a new set of trajectories and propagate it back in time, calculating the overlap with the initial reactant wave function. The new set of trajectories covered a big section of the phase space, since the wave function at the infinite future is spread; the re-expansion weighting coefficients for every new trajectory were calculated once at $t = T$. An alternative is to calculate the autocorrelation function shifted in time by T , in which case the initial set of trajectories can be reused, but summation over two sets of trajectories needs to be performed at every time step to compute $C_a^{\text{sc}}(t)$. If we use the explicit expression for the semiclassical propagator, Eq. (38), and a Gaussian for the initial wave function, Eq. (36), we have

$$C_a^{\text{sc}}(t) = \langle \hat{P}^+ \Phi_a^+(T) | \hat{P}^+ \Phi_a^+(T+t) \rangle = (2\pi\hbar)^{-1} \sum_{uvqp} f(q_i, p_i, s_0, p_0) f(u_i, v_i, q_T, p_T) \times f^*(u_t, v_t, q_T, p_T) e^{(i/\hbar)(S_{uvt} - S_{qpt})} R_{qpt}^* R_{uvt} \theta_{qp} \theta_{uv}, \quad (44)$$

where

$$f(q, p, u, v) = \exp\left(-\frac{\gamma}{4}(q-u)^2 - \frac{1}{4\hbar^2\gamma}(p-v)^2 + \frac{i}{2\hbar}(q-u)(p+v)\right).$$

In practice, this means that a set of trajectories $\{q_i, p_i\}$ sampling the initial wave packet $\Phi_a^+(0)$ is propagated until time T , when the bifurcation of the wave packet is complete; at this point all the information about the trajectories at time T is stored. Now the trajectories $\{q_T, p_T\}$ are relabeled as $\{u_i, v_i\}$ and propagated further forward in time. Since in Eq. (44) we propagate both bra and ket up to time T we have two

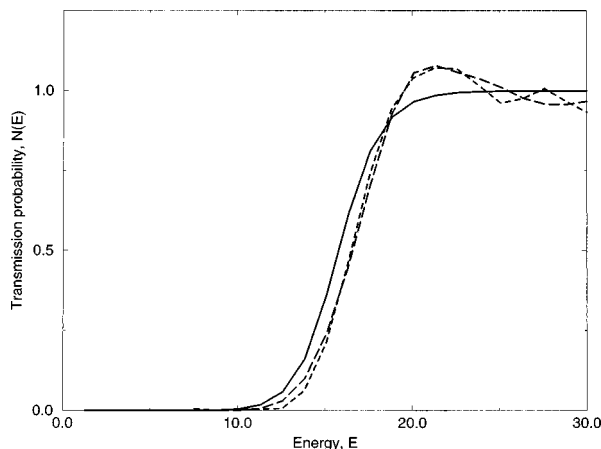


FIG. 4. Transmission probability $N(E)$ for the Eckart barrier, obtained semiclassically using Eq. (9) with one projection operator \hat{P} (short dashed line), using Eq. (11) with two projection operators \hat{P}^2 (long dashed line), and the analytical result (solid line).

summations over the set $\{q, p\}$, one describing the stationary wave packet $\Phi(T)$, and the other over the set $\{u, v\}$, describing the further evolution of $\Phi(T+t)$ in time. Due to the Heaviside functions, the nonzero contribution comes only from the reactive trajectories. At time T the bifurcation is already complete and there can be no interference between reactive and nonreactive trajectories. Thus, we can write just θ_{qp} or θ_{uv} in Eq. (44) instead of their product. This is equivalent to the statement that after time T the property $P^{+2} = P^+$ is fulfilled. Semiclassically, propagation forward in time into the asymptotic region is convenient since there is no concern about the grid size and the propagation is simpler in the asymptotic region. Here we used 1000 classical trajectories, equally spaced in position q and distributed in momentum p as $p^2 = 2V_0 + p_0^2$ with equally spaced p_0 . The semiclassical correlation function is shown in Fig. 3. The semiclassical transmission probability is shown in Fig. 4 and compared with the analytical result. The two semiclassical (HK) calculations are about of the same accuracy, giving the correct general picture but underestimating tunneling and deviating slightly from unity in the high energy region.

IV. CONCLUSIONS

In this paper we derived a correlation function expression for the initial-state-selected total reactive probability, $N_\alpha(E)$, which contains a projection operator for products. We showed how this formula, summed over initial states, gives the well-known trace formula of Miller *et al.* for the cumulative reaction probability. Our approach has the advantage of negligible storage and just a single Fourier transform, which is important in many dimensions. This approach does not require calculation of the product eigenstates; moreover, the propagation time may be significantly shorter than that required for the calculation of state-to-state S -matrix elements since it is not necessary to propagate all the way to the product asymptotic region. This is especially important if the potential is long range or if the number of product channels is significantly greater than the number of reactant channels. The method can be implemented quite efficiently with

quantum-mechanical propagation methods. We demonstrated it on the scattering from the one-dimensional Eckart barrier, using the quantum-mechanical propagator. We then implemented the correlation function expression semiclassically, using the Herman–Kluk propagator, and achieved results of the same accuracy as with the Tannor–Weeks formulation for the S -matrix reported earlier.³ However, we found that a semiclassical criterion for the reactive wave function, keeping only the contribution from classically reactive trajectories, cannot be substituted for the quantum projection operator on the wave function; we had to propagate the semiclassical wave function until bifurcation was complete, project in position space, and then propagate forwards to calculate the autocorrelation function. This procedure requires calculating cross overlaps of a large number of Gaussians at each time step, and is computationally expensive. Alternatively, we found that the semiclassical method was accurate if the reactive wave function was re-expanded in a new set of classical trajectories after the projection step, propagated backwards, and overlapped with the initial Gaussian incoming state; the re-expansion is done only once, but again requires cross overlaps between a large number of Gaussians. The number of overlaps is prohibitive in more than one dimension; for example, on the order of $(10^5 - 10^6)^2$ for the hydrogen exchange reaction.³⁹ Finally, we note that quantum mechanically or semiclassically, the method is not expected to be efficient for problems with narrow resonances, which inherently involve long time propagation at the transition state.

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