Transition state theory, Siegert eigenstates, and quantum mechanical reaction rates

I. INTRODUCTION

The search for a rigorously based and easy to use (or, at least, systematically improvable) quantum mechanical version of transition state theory for determining reaction rate constants seems never to end. This is probably due to the fact, clearly pointed out by Pechukas,1 that the logical conclusion of such a quest must be equivalent to a full blown quantum reactive scattering calculation for the rate constant, but such a complete treatment often loses the charm of simplicity which transition state theory appears to offer. One thus continues to search for theories of reaction rates that have the simple structure of transition state theory, but which can be improved in a systematic fashion to approach the fully exact result. References 1–3 are reviews of some of the more recent efforts toward this goal.

Reactive flux correlation functions4–5 provide a rigorous (i.e., formally exact) quantum mechanical expression for reaction rates that bypasses the need of solving explicitly for all the state-to-state reactive scattering information and thus maintains a transition state look about it. Previous work6 in several groups has shown that these reactive flux rate expressions yield considerable insight into the dynamics of the reactive process, and they also show potential for allowing one to carry out rigorous calculations for rate constants in a more efficient way than an explicit quantum reactive scattering calculation.

The purpose of this paper is to describe a new way for evaluating these reactive flux rate expressions, one which provides formal insight into “quantum transition state theory” and which also, we believe, has practical utility. A particularly intriguing aspect of the present treatment is that the rate is given in terms of Siegert eigenvalues15 (and eigenfunctions) associated with the transition state. Siegert eigenvalues are normally involved with scattering resonances,14 but in the present work they are seen to determine the reactive flux through the transition state region of a potential surface. We believe that this is the first time Siegert eigenstates have appeared in this context.

The present quantum mechanical developments are an outgrowth of recent work15 involving a semiclassical transition state theory16 put forth some years ago and which is summarized in Sec. II as motivation for the quantum treatment which follows in Sec. III. This semiclassical transition state theory involves the “good” (i.e., conserved) classical action variables associated with the transition state (the saddle point region of the potential energy surface), and these “good” action variables are seen to be the semiclassical equivalent of the quantum mechanical Siegert eigenstates noted in the previous paragraph. Section IV presents the results of some calculations which illustrate the nature of these new quantum, Siegert eigenstate-based rate expressions.

To conclude Sec. I, we summarize the basic rate formulae and define various quantities that will be referred to below. In terms of the cumulative reaction probability17 N(E), the microcanonical and canonical rate constants are given by

\[ k(E) = \frac{1}{N(E)} \int_{-\infty}^{\infty} dE e^{-E} N(E), \] (1.1b)

where \( \rho_r(E) \) and \( Q_r(T) \) are the density of reactant states per unit energy and the reactant partition function, respectively. We thus focus on \( N(E) \) as the fundamental quantity which characterizes the reaction rate. One may think of \( N(E) \) as “the number of quantum states which react”? For a bimolecular reaction, for example, the expression for it in terms of the reactive scattering \( S \) matrix is

\[ N(E) = \sum_{n_p} \left| S_{n_p, n_p}(E) \right|^2, \] (1.2)

where the \( S \)-matrix elements are determined by a quantum reactive scattering calculation at energy \( E \), and \( n_p \) are the asymptotic quantum numbers of the reactants \( r \) (products \( p \)). The interpretation of \( N(E) \) as “the number of states which react” results by thinking of evaluating the sums in Eq. (1.2) in two steps: One first notes that \( P_{n_p}(E) \), defined as

\[ P_{n_p}(E) \equiv \sum_{n_p} \left| S_{n_p, n_p}(E) \right|^2, \] (1.3a)
is the total reaction probability from reactant state \( n_0 \), so that \( N(E) \) is then given by

\[
N(E) = \sum_{n} P_n(E). \tag{1.3b}
\]

If one idealized the situation by assuming that \( P_n(E) = 1 \) or 0—i.e., a given initial state \( n \), either reacts with 100% probability or not at all—then clearly \( N(E) \) from Eq. (1.3b) would be the number of states \( n \), for which \( P_n = 1 \), i.e., the number of initial states which react. One may retain this qualitative interpretation even though \( P_n(E) \) can, in general, have any value between 0 and 1.

II. REVIEW OF SEMICLASSICAL TRANSITION STATE THEORY

A formally exact semiclassical transition state theory was enunciated some years ago.\(^{16}\) (It includes as a special limit, for example, the popular "instan
t" approximation\(^{17,18}\) for transmission through a multidimensional barrier.) It requires that one first express the classical Hamiltonian (i.e., the energy \( E \)) in terms of the "good" (i.e., conserved) action variables\(^{19}\) \( (I_k), k = 1, \ldots, F \) associated with the saddle point (the transition state) of the potential energy surface, \( E(I_1, I_2, \ldots, I_F) \), where \( F \) is the number of degrees of freedom (\( F = 3N - 6 \) for a nonrotating polyatomic \( N \)-atom system). The \( F - 1 \) degrees of freedom of the activated complex, which describe bounded classical motions, are quantized in the usual semiclassical fashion,\(^{20}\)

\[
I_k = (n_k + \frac{1}{2}) \hbar, \tag{2.1}
\]

\( \{n_k\} \) being non-negative integers, for \( k = 1, \ldots, F - 1 \), while the \( F \)th action \( I_F \), which describes the unbounded reaction coordinate degree of freedom, is determined by energy conservation. That is, with the \( (F - 1) \) actions \( \{I_k\}, k = 1, \ldots, F - 1 \) quantized as in Eq. (2.1), one inverts the equation

\[
E = E(I_1, \ldots, I_{F-1}, I_F) \equiv E(n, I_I) \tag{2.2}
\]
to obtain \( I_I(n,E) \) as a function of the total energy \( E \) and the \( F - 1 \) quantum numbers \( n = (n_1, \ldots, n_{F-1}) \) of the activated complex. For real energy \( E \), the action \( I_I \) is, in general, pure imaginary,

\[
I_I(n,E) = -i\hbar \theta(n,E)/\pi, \tag{2.3}
\]

where \( \theta \) is referred to as the generalized barrier penetration integral. (In one dimension, \( \theta \) is given by the familiar WKB expression,

\[
\theta(E) = \int_{\text{barrier}} dx \sqrt{2m[V(x) - E]}/\hbar.
\]

The tunneling (or transmission) probability for state \( n = (n_1, \ldots, n_{F-1}) \) of the activated complex is then given by

\[
P(n,E) = \left[ 1 + \exp[2\theta(n,E)] \right]^{-1}, \tag{2.4a}
\]

and the cumulative reaction probability discussed in Sec. I is given by this theory\(^{16}\) as

\[
N(E) = \sum_{n} P(n,E). \tag{2.4b}
\]

Comparing Eq. (2.4b) to Eq. (1.2), one sees that the effective \( S \) matrix in Eq. (1.2) is diagonal in the quantum numbers \( n \) of the activated complex, which is consistent with the fact that these actions are constants of the motion for the classical dynamics.

It is useful to illustrate the above semiclassical theory for an elementary (but commonly used) example, namely a harmonic transition state. That is, the potential energy surface is approximated by its quadratic expansion about the saddle point. In this case, the classical Hamiltonian is a linear function of the "good" actions,

\[
E(I_1, \ldots, I_F) = V_0 + \sum_{k=1}^{F} \omega_k I_k, \tag{2.5}
\]

where \( V_0 \) is the energy of the saddle point and \( \{\omega_k\} \) the normal mode frequencies at the saddle point; \( \omega_F \), the frequency for the reaction coordinate, is pure imaginary

\[
\omega_F = -i/\omega_F. \tag{2.6}
\]

With Eq. (2.7), Eq. (2.4) then gives the exactly correct (quantum) cumulative reactive probability for this case of a harmonic transition state. As simple and elementary as this result is, it underlines\(^{21}\) much of the recent work on the effects of "dissipation" on barrier transmission.

The bottleneck to application of this semiclassical theory for a general anharmonic, nonseparable potential surface is clearly the first step, being able to express the classical Hamiltonian as a function of the \( F \) "good" action variables, for so doing is tantamount to a complete solution of the classical dynamics in the saddle point region of the potential surface. Recent work,\(^{15}\) however, has shown that this can be accomplished, in general, within a perturbative approximation: The zeroth order Hamiltonian is the normal mode (i.e., harmonic) part, and cubic and quartic anharmonicities about the saddle point are included by second order perturbation theory, to yield a generalization of Eq. (2.5),

\[
E(I_1, \ldots, I_F) = V_0 + \sum_{k=1}^{F} \omega I_k + \sum_{k<k'}^{F} x_{kk'} I_k I_{k'}. \tag{2.8}
\]

The anharmonic constants \( \{x_{kk'}\} \) are given by known formulas in terms of the cubic and quartic force constants. It is then still a simple matter to implement Eqs. (2.1)-(2.4), i.e., to make the replacements

\[
I_k \rightarrow (n_k + \frac{1}{2}) \hbar, \quad k = 1, \ldots, F - 1,
\]

and then invert Eq. (2.8) to obtain \( I_I(n,E) \) and then \( N(E) \) from Eq. (2.4)]. Equation (2.8) includes the lowest order effects of anharmonicity in the reaction coordinate itself (i.e., in the barrier direction), anharmonic coupling between the various modes of the activated complex, and also coupling of the reaction coordinate (mode \( F \)) with the various modes of the activated complex (modes 1, \ldots, \( F - 1 \)).
Buoyed by the success and utility of this perturbation version of semiclassical transition state theory, one naturally becomes interested in going beyond the perturbative approximation. One could attempt higher order perturbation theory, and this might indeed be a useful approach, particularly some of the algebraic perturbation methods\(^{39}\) based on Lie algebra. An alternate to quantum perturbation theory—which is essentially identical to its classical counterpart in terms of action-angle variables—is direct diagonalization of the Hamiltonian matrix (which, in perturbation theory, is diagonalized perturbatively). Thus, consider a harmonic potential energy surface with cubic and higher anharmonicity,

\[
V(q) = V_0 + \sum_{k=1}^{F} \frac{1}{2} m \omega_k^2 q_k^2 + \sum_{k<k'} \frac{1}{3!} f_{kk'kk''} q_k q_{k'} q_{k''} + \cdots, \tag{2.10}
\]

where \(\{q_k\}\) are the normal mode coordinates for the transition state. The frequency \(\omega_F\) is pure imaginary for a saddle point, but we ignore this for the moment. It is a straightforward and simple procedure to construct the Hamiltonian matrix in the normal mode, harmonic basis

\[
H_{n',n} = \delta_{n',n} \left[ V_0 + \sum_{k=1}^{F} \hbar \omega_k (n_k + \frac{1}{2}) \right] + \text{nondiagonal anharmonic terms}, \tag{2.11}
\]

where here \(n \equiv (n_1, ..., n_F)\) denotes the full set of \(F\) quantum numbers. The perturbative treatment described in the above paragraph corresponds to diagonalizing this matrix perturbatively to obtain the eigenvalues \(E(n) = E(n_1, ..., n_F)\), noting that \(\omega_F = -i|\omega_F|\), making the replacement

\[
(n_F + \frac{1}{2})\hbar = \hat{I} \to \hat{I} \theta / \pi, \tag{2.12a}
\]

and then solving

\[
E = E(n_1, ..., n_{F-1}, \theta) \tag{2.12b}
\]

for

\[
\theta(n_1, ..., n_{F-1}, E). \tag{2.12c}
\]

To proceed non-perturbatively, we imagine diagonalizing the Hamiltonian matrix Eq. (2.11) by a direct numerical procedure. There is no difficulty in allowing the frequency \(\omega_F\) to be imaginary, \(\omega_F = -i|\omega_F|\), though we note that the Hamiltonian matrix becomes a complex symmetric matrix:

The harmonic part of the matrix, for example, has a simple imaginary part,

\[
\delta_{n,n} \left[ V_0 + \sum_{k=1}^{F} \hbar \omega_k (n_k + \frac{1}{2}) \right] + \text{nondiagonal anharmonic terms}, \tag{2.13a}
\]

and the anharmonic terms are also simple analytic expressions;\(^{33}\) e.g., the matrix elements of the term \(q_F^2\) has the factor

\[
\left( \frac{\hbar}{2m|\omega_F|} \right)^{3/2} - \left( \frac{\hbar}{-2m|\omega_F|} \right)^{3/2} = e^{2\sqrt{\omega_F}} \left( \frac{\hbar}{2m|\omega_F|} \right)^{3/2}, \tag{2.13b}
\]

and similarly for all the anharmonic matrix elements—e.g. uses the standard expressions for the matrix elements with harmonic oscillator basis functions\(^{33}\) and then makes the replacement \(\omega_F = -i|\omega_F|\) in all places where this frequency appears. The eigenvalues of this complex-symmetric (and thus non-Hermitian) matrix are complex; in the harmonic limit, for example, the complex eigenvalues are

\[
E(n) = V_0 + \sum_{k=1}^{F} \hbar \omega_k (n_k + \frac{1}{2}) = V_0 + \sum_{k=1}^{F} \hbar \omega_k (n_k + \frac{1}{2}) - i\hbar|\omega_F|(n_F + \frac{1}{2}). \tag{2.14}
\]

The distribution of these eigenvalues in the complex energy plane is indicated in Fig. 1 (a). Figure 1 (b) shows how the eigenvalues would typically be perturbed by anharmonicity in the reaction coordinate, but with no coupling to the modes \(k = 1, ..., F - 1\) of the activated complex. In general, the complex eigenvalues obtained by diagonalizing this complex-symmetric Hamiltonian matrix are the values whose semiclassical approximation corresponds to quantizing all the actions—including the \(F\) th action, that of the reaction coordinate—by the semiclassical prescription Eq. (2.1). That is, diagonalizing a Hamiltonian matrix produces eigenvalues directly, not an analytic eigenvalue function \(E(I_1, ..., I_F)\) from which one obtains eigenvalues by requiring \(I_k = (\text{integer} + 1/2)\hbar\) for all \(k\).

Since this nonperturbative matrix diagonalization calculation does not produce the complex eigenvalues as an explicit function of the quantum numbers, in order to proceed semiclassically, cf. Eq. (2.12), it is necessary to "analyze the spectrum" of complex eigenvalues, i.e., for each state of the activated complex to fit the progression of complex eigenvalues in the reaction coordinate mode to an analytic function of the quantum number \(n_F\) so that the \(E(n_F)\) relation can be inverted to obtain \(n_F(E)\) and thus the generalized barrier penetration integral \(\Theta(E)\) for each state \(n = (n_1, ..., n_{F-1})\) of the activated complex.

The above discussion shows, at least conceptually, how this semiclassical transition state theory can be implemented nonperturbatively, but it also reveals its inherent limitations. Thus, consider Fig. 1. In the uncoupled, or weakly coupled case, it will be easy (for each state of the activated complex) to identify the progression of complex eigenvalues (headed primarily in the negative imaginary direction) in the reaction coordinate quantam number \(n_F\), so that one can readily fit \(E\) as a function of \(n_F\) and invert that relation to obtain \(n_F\) as a function of \(E\). For very strong coupling, however, this may not be possible. Figure 1 (c) indicates that progressions in \(n_F\) from different states of the activated complex may "collide," i.e., overlap, undergo Fermi resonance mixing, and in such cases it would not be possible to identify a function \(E(n_F)\) separately for each state of the activated complex. This is analogous to the situation for motion in a potential well (i.e., all real frequencies) when "good" action variables (invariant tori) are destroyed as the classical motion becomes chaotic. In this case, it is not possible to determine semiclassical Einstein–Brillouin–Keller (EBK) eigenvalues for the vibrational motion.\(^{20}\) The analogy which suggests itself is thus that so long as the coupling is sufficiently weak that "good" action variables exist—which in practice means that in the spectrum of complex eigenvalues, one can identify progressions in the reaction coordinate mode for
FIG. 1. Schematic depiction of the spectrum of Siegert eigenvalues in the complex $E$ plane. (a) Harmonic case, Eq. (2.4); (b) uncoupled case but anharmonic barrier; (c) strongly coupled ("chaotic") case.

The above paragraph describes one reason why we wish to go beyond the semiclassical transition state theory of Eqs. (2.1)-(2.4), i.e., in the case of strong coupling the function

$$E(I_1, ..., I_F)$$

may cease to exist (chaos). Another reason is that after one has performed a completely quantum mechanical calculation, i.e., diagonalized the complex-symmetric Hamiltonian matrix as described above, it seems "wasteful" to degrade matters by using the results of the calculation in a semiclassical theory for the reaction rate; one would like to use the results of the calculation in a fully quantum mechanical rate theory. The rest of this paper is aimed at this.

Before embarking on this fully quantum treatment, however, it is useful to identify the complex eigenvalues discussed above. To this end, it is useful to write the semiclassical transmission probability, Eq. (2.4a), in terms of the "quantum number" $n_F$,

$$I_F \equiv (n_F + \frac{1}{2}) \hbar = -i \hbar \theta / \pi,$$

i.e.,

$$2 \theta = 2 \pi i (n_F + \frac{1}{2}),$$

so that Eq. (2.4a) reads

$$P(n,E) = \{1 - \exp[-2 \pi i n_F(n,E)]\}^{-1}.$$

For real $E$, $n_F(n,E) + 1/2$ is pure imaginary, cf. Eq. (2.15a); the semiclassical approximation to the complex energy eigenvalues discussed above, however, corresponds to $n_F$ (as well as $n_1, ..., n_{F-1}$) being an integer, and Eq. (2.16) shows that the transmission probability is then singular. That is, the complex eigenvalues that have been discussed above are poles of the $S$-matrix, namely, the Siegert eigenvalues. To see the identification as Siegert eigenvalues even more concretely, consider the eigenfunctions corresponding to the complex eigenvalues that result from diagonalizing the complex-symmetric Hamiltonian matrix Eq. (2.11). The eigenfunctions will be linear combinations of the harmonic basic functions

$$\phi_n(q) = \prod_{k=1}^{F} \phi_{n_k}(q_k),$$

where $\phi_{n_k}$ is a standard one-dimensional harmonic oscillator eigenfunction. For modes $k = 1, ..., F - 1$, which have real harmonic frequencies, the functions describe bounded motion in the coordinates $\{q_k\}$, $k = 1, ..., F - 1$,

$$\phi_{n_k}(q_k) \propto \exp(-\frac{m \omega_k}{2 \hbar} q_k^2) H_{n_k} \left(\sqrt{\frac{m \omega_k}{\hbar}} q_k\right),$$

where $H_n$ is the usual Hermite polynomial. But in the reaction coordinate $(F\text{th})$ mode, one has

$$\phi_{n_F}(q_F) \propto \exp\left(\frac{im \omega_F}{2 \hbar} q_F^2\right) H_{n_F} \left(\sqrt{\frac{m \omega_F}{\hbar}} e^{-i \phi_F} q_F\right),$$

which we note is an outgoing wave in the $+$ and $-$ $q_F$ direction. The complex eigenvalues we are discussing are thus solutions to the Schrödinger equation with outgoing waves in all channels, and this is the definition of Siegert eigenvalues.
We find it fascinating that Siegert eigenvalues appear in this context having to do with reaction through the saddle point of a potential surface, for they usually arise in the topic of scattering resonances, i.e., the decay of metastable states. In this more conventional situation, one finds complex eigenvalues, \( E_{\text{real}} - i\Gamma/2 \), with small imaginary parts that give the rate \( \Gamma/\hbar \) for the decay of the metastable state. One often sees progressions, in the real energy direction, of these eigenvalues that lie slightly below the real \( E \) axis. This is completely different from the present situation, which has nothing to do with scattering resonances or metastable states, but rather quite the opposite: Transition state-like theories describe “direct” dynamics. Also, in the present case, the progressions of complex eigenvalues proceed downward in the complex \( E \) plane, in the negative imaginary direction (cf. Fig. 1). It is quite interesting to see Siegert eigenvalues arising in this new context, this first time (to our knowledge) that this has been realized.

### III. FULLY QUANTUM RATE THEORY

Equation (1.2) gives the rigorous quantum mechanical expression for the cumulative reaction probability in the framework of quantum scattering theory, but for present purposes a more useful expression is the following:

\[
N(E) = \frac{1}{i(2\pi\hbar)^2} \text{tr} \left[ \mathcal{F}\delta(E - H) \mathcal{F}\delta(E - H) \right],
\]

(3.1)

which was derived from reactive flux correlation functions and which is also formally exact. In Eq. (3.1), \( H \) is the full Hamiltonian for the system and \( \mathcal{F} \) is the symmetrized flux operator,

\[
\mathcal{F} = \frac{1}{2} \left( \mathcal{F} + i \mathcal{F}^* \right),
\]

where \( \mathcal{F} \) is the trajectory flux operator for the reaction coordinate \( q_F \),

\[
p_F = \frac{\hbar}{i \partial q_F},
\]

and where the “dividing surface” through which the flux is calculated is at position \( q_F = 0 \). (See Appendix A for a discussion of some interesting properties of the flux operator.) The microcanonical density operator which appears in Eq. (3.1) can be expressed in terms of the outgoing wave Green’s function

\[
\Delta(E) = -\pi^{-1} \text{Im} G^+(E),
\]

(3.3a)

\[
G^+(E) = \lim_{\epsilon \to 0} (E + i\epsilon - H)^{-1},
\]

(3.3b)

and if \( \{u_j(q)\} \) is a basis set with outgoing waves in all open channels, then a variationally stable approximation to the Siegert eigenstates, and in terms of which Eq. (3.4) becomes

\[
\langle q | G^+(E) | q' \rangle = \sum_j \psi_j(q) \psi_j(q').
\]

(3.5)

Equation (3.5), together with Eq. (3.3a) and Eq. (3.1), thus give the following formally exact (in the limit of a sufficiently large basis) quantum expression for the cumulative reaction probability in terms of the Siegert eigenvalues and eigenvectors,

\[
N(E) = \frac{1}{\pi} \text{Re} \sum_{ij} \frac{\langle \psi_j | F | \psi_i \rangle^2}{(E - E_j)(E - E_i)} - \frac{\langle \psi_j^* | F | \psi_i^* \rangle^2}{(E - E_j^*)(E - E_i^*)}.
\]

(3.6)

There are some subtle difficulties involved with Eq. (3.6) as it stands, but before addressing them, several general comments are in order. First, the reader will notice that the variational approximation to \( G^+(E) \) in Eqs. (3.4) and (3.5) is a special case of the method of complex basis functions. Consider, for example, the harmonic oscillator basis functions for the reaction coordinate with imaginary frequency in Eq. (2.17c); it is clear that this complex basis function also results from the real function

\[
\phi_{n\alpha}(q_F) = \exp \left( -\frac{m|\omega_F|}{2\hbar} q_F^2 \right) \tilde{n}_n^\alpha \left( \sqrt{\frac{m|\omega_F|}{\hbar}} q_F \right)
\]

(3.7)

by the complex scaling transformation \( q_F \to e^{-ia} q_F \), here with \( \alpha = \pi/4 \). It has also been clearly discussed in past work that application of Siegert (i.e., outgoing wave) boundary conditions is closely related to complex scaling. As the referee pointed out to us, all of the complex eigenvalues \( \{E_j\} \) are actually not Siegert eigenvalues. As is well known from complex scaling theory, some of the complex eigenvalues correspond to Siegert states—they, for example, are stable with respect to increase in the size, or variation of other parameters of the basis set—but there will, in general, also be “background” eigenvalues distributed along the ray \( e^{-2i\alpha} \) in the complex \( E \) plane. They arise from the asymptotic free particle region and become increasingly dense as the basis is increased. For \( \alpha = \pi/4 \), \( e^{-2i\alpha} = -i \), so the background eigenvalues tend to fall along the negative imaginary axis in the \( E \) plane. The eigenvalues in Fig. 1(b), for example, do indeed tend toward the negative imaginary axis for increasing quantum numbers. For potential barriers of interest, however, the sums over eigenstates converge sufficiently rapidly (see applications below) that only the true Siegert eigenvalues make a significant contribution.] Second, we note that the approximation of the Green’s function in Eq. (3.4) also leads to the S-matrix Kohn variational method for carrying out quantum scattering calculations. The primary difference from this previous work is that here we do not envision using a complex basis which contains all the explicit information about the asymptotic
reactant and product channels. That is, the complex “transition state” basis in Eq. (2.17) simply imposes outgoing waves in all directions from the saddle point region, but contains no explicit information about asymptotic channel eigenstates.

Finally, it is interesting to note that this formally exact expression for the cumulative reaction probability, Eq. (3.6), is superficially similar to that obtained from scattering theory, Eq. (1.2), if the S matrix is dominated by resonances, i.e.,

$$S_{a_i a_r}(E) = \sum_{j} \frac{b_{a_i a_r}}{E - E_j}. \tag{3.8a}$$

With this form for the S matrix, Eq. (1.2) gives

$$N(E) = \sum_{j} \frac{B_{j f}}{(E - E_j)(E - E_j^*)}, \tag{3.8b}$$

with

$$A_{j f} = \sum_{a} a_{j a}^* a_{f a}, \tag{3.8c}$$

$$B_{j f} - \sum_{a} b_{j a}^* b_{f a}. \tag{3.8d}$$

The similar structure of Eq. (3.8b) and Eq. (3.6) suggests that Eq. (3.6) will be an efficient representation of the cumulative reaction probability for both the case where the reaction proceeds by formation of a collision complex (resonant scattering) or by a direct mechanism; it is all determined by where the Siegert eigenvalues lie. If they lie close to the real energy axis (i.e., have small imaginary points), then this corresponds to complex formation, but if they form progressions in which their (negative) imaginary parts increase (in absolute value) much faster than their real parts, as in Fig. 1, then this corresponds to a direct scattering mechanism.

We now turn to the practical aspects of evaluating Eq. (3.6), and it is useful first to consider explicitly the one-dimensional version of the theory, i.e., a potential barrier $V(x)$ along the real line $x = q + (0,\infty)$. It is not hard to show that the one-dimensional version of Eq. (3.6) reduces to a one-dimensional expression given previously,

$$G + (0,0;E) = \sum_{n=0}^{\infty} \frac{\psi_n(0)^2}{E - E_n}. \tag{3.10a}$$

with the Siegert eigenstate expansion, Eq. (3.5), for the various elements of the Green’s function,

$$G^+ (0,0;E) = \sum_{n=0}^{\infty} \frac{\psi_n(0)^2}{E - E_n} \tag{3.10a}$$

$$\left( \frac{\partial^2 G^+ (x,x';E)}{\partial x \partial x'} \right)_{x = x' = 0} = \sum_{n=0}^{\infty} \frac{\psi_n'(0)^2}{E - E_n} \tag{3.10b}$$

$$\left( \frac{\partial G^+ (x,0;E)}{\partial x} \right)_{x = 0} = \sum_{n=0}^{\infty} \frac{\psi_n'(0) \psi_n(0)}{E - E_n}. \tag{3.10c}$$

If the potential $V(x)$ is symmetric, then the eigenfunctions are either even or odd, so that

$$\psi_n(0) = 0 \text{ for } n \text{ odd}, \tag{3.11a}$$

$$\psi_n(0) = 0 \text{ for } n \text{ even}, \tag{3.11b}$$

and in this case, the quantity in Eq. (3.10c), and thus the second term in Eq. (3.9), is zero. Now, however, we encounter a significant difficulty: The sum over Siegert states in Eq. (3.10b), the one which results from the second derivative of the Green’s function at the dividing surface, does not converge! (Appendix B shows how this divergence is avoided in the semiclassical limit.)

This problem can be seen most simply by considering the case of a free particle. Starting with real particle-in-a-box eigenfunctions for the interval $(-a,a),$

$$\phi_n(x) = a^{-1/2} \sin\left[ n \pi (x + a) / 2a \right], \tag{3.12a}$$

the general complex scaling transformation gives complex eigenfunctions

$$\psi_n(x) = e^{-i \alpha a} - 1/2 \sin(n \pi x / 2a + n \pi / 2) \tag{3.12b}$$

and eigenvalues

$$E_n = e^{-2i \alpha} \frac{\hbar^2}{2m} \left( \frac{n \pi}{2a} \right)^2 \tag{3.13}$$

for $n = 1, 2, \ldots$. (Here $n = 1, 3, \ldots$ correspond to even functions, and $n = 2, 4, \ldots$ to odd functions.) The two sums in Eqs. (3.10a) and (3.10b) thus become

$$G^+ (0,0;E) = \sum_{n=0}^{\infty} \frac{\psi_n(0)^2}{E - E_n}$$

$$= e^{-i \alpha a} - 1 \sum_{n=0,3}^{\infty} \left[ E - e^{-2i \alpha} \frac{\hbar^2}{2m} \left( \frac{n \pi}{2a} \right)^2 \right]^{-1} \tag{3.14a}$$

and

$$\left( \frac{\partial^2 G^+ (x,x';E)}{\partial x \partial x'} \right)_{x = x' = 0}$$

$$= e^{-i \alpha a} - 1 \sum_{n=0,3}^{\infty} \left[ \frac{n \pi}{2a} \right]^2 \left[ E - e^{-2i \alpha} \frac{\hbar^2}{2m} \left( \frac{n \pi}{2a} \right)^2 \right]^{-1} \tag{3.14b}$$

It is clear that though the sum in Eq. (3.14a) converges (because the summand decreases as $1/n^2$ as $n \to \infty$), that in Eq. (3.14b) does not (because the summand becomes constant as $n \to \infty$), regardless of the choice of the complex rotation angle $\alpha$. This problem is not special for the free particle, but was discovered initially in applications to realistic one-dimensional barrier potentials.

What is the source of the problem? These quantities certainly exist for the correct Green’s function; e.g., for the free particle one has

$$\text{Im} G^+ (x,x';E) = \frac{m}{\hbar^2 k} \cos[k(x - x')], \tag{3.15a}$$

where $k = \sqrt{2m E / \hbar^2}$, so that
\[ \text{Im} \, G^+(0,0;E) = \frac{m}{\hbar^2}, \quad (3.15b) \]
\[ \text{Im} \left( \frac{\partial^2 G^+(x,x';E)}{\partial x \partial x'} \right)_{x=x'=0} = -\frac{mk}{\hbar^2}, \quad (3.15c) \]
and Eq. (3.9) then gives \( N(E) = 1 \), the correct result for a free particle. Recall, however, the general theorem for approximating matrix elements of \( G^+(E) \) with a complex scaled basis:25-27 A matrix element of the form

\[ \langle \phi | G^+(E) | \chi \rangle = \int dx \int dx' \phi(x) G^+(x,x';E) \chi(x') \]

is variationally approximated with \( G^+(E) \) given by Eqs. (3.4) or (3.5) provided that \( \phi(x) \) and \( \chi(x) \) are square integrable functions. The quantities we desire in Eq. (3.10), however, correspond to

\[ \phi(x) = \chi(x) = \delta(x) \quad (3.17a) \]

for Eq. (3.10a), and

\[ \phi(x) = \chi(x) = \delta'(x) \quad (3.17b) \]

for Eq. (3.10b). In neither case are \( \phi(x) = \chi(x) \) square integrable; we escape disaster for the case Eq. (3.17a), but not for the more singular case Eq. (3.17b).

A way out of this dilemma is to consider the time-dependent analog of Eq. (3.5). (This was suggested to us in trying to evaluate time-dependent flux correlation functions with these Siegert eigenstates, and it is also considered explicitly in the work of McCurdy et al.28) The outgoing wave Green's function and the time evolution operator are related to each other by the well-known quantum expressions

\[ G^+(E) = (i\hbar)^{-1} \int_0^t dt \, e^{iE t/\hbar} e^{-iHt/\hbar}, \quad (3.18a) \]
\[ e^{-iHt/\hbar} = \left( -2ui \right)^{-1} \int_{-\infty}^\infty \, dE \, e^{-iE t/\hbar} G^+(E), \quad (3.18b) \]

so that the expansion for the time evolution operator that results from Eq. (3.5) is

\[ \langle x' | e^{-iHt/\hbar} | x \rangle = \sum_n \psi_n(x') \psi_n(x) e^{-iE_n t/\hbar} \quad (3.19a) \]

for \( t > 0 \). Since \( \text{Im} \, E_n < 0 \), this expansion for the propagator is rapidly convergent for all \( t > 0 \), as we have tested with a variety of potentials and as shown by McCurdy et al.25 The specific quantities of interest to us with regard to Eq. (3.10) are

\[ \langle 0 | e^{-iHt/\hbar} | 0 \rangle = \sum_n \psi_n(0)^2 e^{-iE_n t/\hbar} \quad (3.19b) \]
\[ \left( \frac{\partial^2}{\partial x \partial x'} \langle x | e^{-iHt/\hbar} | x' \rangle \right)_{x=x'=0} = \sum_n \psi_n'(0)^2 e^{-iE_n t/\hbar}. \quad (3.19c) \]

Though both of these sums converge with excellent efficiency for \( t > 0 \), for \( t = 0 \), the sum in Eq. (3.19c) diverges sufficiently strongly that its time integral, to give the Green's function element in Eq. (3.10b) [via Eq. (3.18a)], also diverges.

A solution to the problem is to divide the time integral in Eq. (3.18a) into two parts,
so that Eq. (3.22c) becomes
\[ \left( \frac{\partial^2 G^+ (x,x';E)}{\partial x \partial x'} \right)_{x=x'=0} = 2 \frac{m}{\hbar^2} \left( \frac{m}{2\pi i\hbar} \right)^{1/2} \left( -\frac{1}{2}e^{i(E-V_0)t/\hbar} - \frac{i}{\hbar} (E-V_0) \right) \times \int_0^\tau dt t - \frac{1}{2}e^{i(E-V_0)t/\hbar} + \sum_{n=0}^\infty \psi_\epsilon'(0)^2 e^{i(E-E_n)t/\hbar}, \]

(3.22d)

the desired result for this short-time corrected matrix element. For completeness, we note that the short-time free particle correction for the matrix element involving only one derivative of the Green's function, Eq. (3.10c), vanishes.

To summarize, the short time-corrected Green's function elements which replace those in Eq. (3.10) [for use in Eq. (3.9)] are as follows:

\[ G^+ (0,0;E) = \sum_{n=0}^\infty \psi_\epsilon(0)^2 \frac{E-E_n}{E-E_n} e^{i(E-E_n)t/\hbar} + (i\hbar)^{-1} \int_0^\tau dt K_\epsilon(t), \]

(3.23a)

\[ \left( \frac{\partial^2 G^+ (x,x';E)}{\partial x \partial x'} \right)_{x=x'=0} = \sum_{n} \psi_\epsilon(0)^2 e^{i(E-E_n)t/\hbar} + 2m \frac{1}{\hbar^2} \times \left[ K_\epsilon(t) + (E-V_0)(i\hbar)^{-1} \int_0^\tau dt K_\epsilon(t) \right], \]

(3.23b)

\[ \left( \frac{\partial G^+ (x,0;E)}{\partial x} \right)_{x=0} = \sum_{n} \psi_\epsilon(0) \psi_\epsilon'(0) e^{i(E-E_n)t/\hbar}, \]

(3.23c)

where \( K_\epsilon(t) \) is

\[ K_\epsilon(t) = \left( \frac{m}{2\pi i\hbar} \right)^{1/2} \frac{e^{i(E-V_0)t/\hbar}}{\hbar}. \]

(3.23d)

[The integral of \( K_\epsilon(t) \) that appears in Eqs. (3.23a) and (3.23b) can be expressed in terms of the error function of complex argument, i.e., combinations of Fresnel integrals.30] Since \( \text{Im} E_n < 0 \), the finite value of \( \tau \) insures that all the sums over Siegert states in Eq. (3.23) converge. It is actually possible to neglect the short time corrections for \( G^+ (0,0;E) \) and \( \partial G^+ (x,0;E)/\partial x \) at \( x=0 \), i.e., to set \( \tau = 0 \) in Eq. (3.23a), and (3.23c) though it is more accurate not to do so, but it is clear that one cannot do so for the second derivative matrix element, Eq. (3.23b); i.e., the second term in (3.23b), \( K_\epsilon(t) \), is singular at \( \tau = 0 \), and this is necessary to cancel the corresponding singularity in the first term (the sum over Siegert states) at \( \tau = 0 \).

Equation (3.9), with the Green's function elements of Eq. (3.23), gives the correct quantum result for \( N(E) \) in the limit that \( \tau \) is sufficiently small; i.e., \( \tau \) must be small enough to insure that the free particle approximation for the propagator is accurate for the time interval \((0,\tau)\). For the sums over Siegert eigenstates to converge as rapidly as possible, however, one would like \( \tau \) to be as large as possible (because of the damping factor \( \exp(-\tau |\text{Im} E_n/\hbar|) \) in the summand). The balance between these competing considerations must be investigated by actual calculation, and this is the subject of Sec. IV.

It is also possible to use better short time approximations for the \((0,\tau)\) time interval than the free particle approximation, Eq. (3.21). Better short time approximations allow one to take \( \tau \) larger so that the sums over Siegert eigenstates in Eq. (3.23) will converge more rapidly. One rather obvious choice would be to use the propagator for a harmonic potential, i.e., a parabolic barrier for one dimension, \( V(x) = V_0 - 1/2m\omega_n^2 x^2 \), where \( \omega_n = |\omega_F| \); the free particle propagator of Eq. (3.21) is then replaced by

\[ \langle x'| e^{-iH\tau/\hbar} | x \rangle = \left( \frac{m\omega_n}{2\pi i\hbar \sinh(\omega_n\tau)} \right)^{1/2} \exp \left[ \frac{i}{\hbar} \left( -V_0 \tau + \frac{(x^2 + x'^2) \cosh(\omega_n \tau) - 2xx'}{2 \sinh(\omega_n \tau) / m\omega_n} \right) \right]. \]

(3.24)

Calculations analogous to those in Eq. (3.22) can be carried out with this improved short time approximation. Equations (3.23a) and (3.23c) are unchanged, except that the function \( K_\epsilon(t) \) is now given by

\[ K_\epsilon(t) = \left( \frac{m\omega_n}{2\pi i\hbar \sinh(\omega_n\tau)} \right)^{1/2} \frac{e^{i(E-V_0)t/\hbar}}{\hbar}, \]

(3.25a)

but Eq. (3.25b) has the additional term

\[ \frac{m\omega_n}{\hbar^2} \int_0^\tau dt K_\epsilon(t) \tanh \left( \frac{\omega_n \tau}{2} \right). \]

(3.25b)

IV. EXAMPLES

As noted in Sec. III, use of the complex reaction coordinate basis functions with imaginary frequency is completely equivalent to the complex scaling transformation \( q_F \rightarrow q_F e^{i\alpha} \) for this degree of freedom (with \( \alpha = \pi/4 \)). For a general potential energy surface \( V(q) = V(q_1,...,q_F) \); therefore, the complex symmetric Hamiltonian matrix in the harmonic transition state basis can be constructed via the complex-scaling procedure, giving

\[ H_{n'\epsilon,n} = \sum_{k=1}^F \delta_{n'\epsilon,n}^{(k)} t^{(k)} \]

+ \( \int dq \left( \sum_{k=1}^F \phi_{n'\epsilon,n}^*(q_F) \phi_{n\epsilon,n}(q_F) \right) V(q_1,...,q_{F-1},e^{i\alpha}q_F), \]

(4.1)

where \( \delta_{n'\epsilon,n}^{(k)} \) is a product of Kronecker delta's for all modes except the \( k \) th one,

\[ \delta_{n'\epsilon,n}^{(k)} = \sum_{j=1}^F \delta_{n'\epsilon,n}^{(j)} j \neq k, \]

(4.1) is the one-dimensional kinetic energy matrix for the \( k \) th degree of freedom.
1.0

\( t_{n_k n_k} = \frac{\hbar \omega_b}{4} \left[ (2n_k + 1) \delta_{n_k n_k} - \sqrt{n_k (n_k - 1)} \delta_{n_k + 2, n_k} - \sqrt{(n_k + 1) (n_k + 2)} \delta_{n_k - 2, n_k} \right], \)

(recall that \( \omega_F = -i |\omega_F| \)), and the reaction coordinate basis functions \( \phi_{n_k}(q_F) \) and \( \phi_{n_k}(q_F) \) in the potential energy term are the (normalized) real oscillator functions of Eq. (3.7). To calculate Siegert eigenvalues and eigenfunctions, it is, of course, not necessary to use this harmonic basis with \( \alpha = \pi/4 \), but this is the one that makes direct contact with the perturbative analysis discussed in Sec. II.

We now present the results of some calculations to illustrate the behavior of the cumulative reaction probability of Eq. (3.9), with the Green's function elements given by Eqs. (3.23) and (3.25).

A. Parabolic barrier

It is useful to test the short time corrections to the Siegert expansion for the Green's function, Eq. (3.23), first with the parabolic barrier potential,

\( V(x) = V_0 - \frac{1}{2} m \omega_b^2 x^2, \)

(4.2a)

where \( \omega_b = |\omega_b| \), because here the Siegert eigenvalues and eigenfunctions are known exactly,

\( E_n - V_0 = -i \hbar \omega_b (n + \frac{1}{2}), \)

(4.2b)

\( \phi_n(x) = e^{-i \frac{\omega_b}{\hbar} (n + \frac{1}{2})} \left( \frac{m \omega_b}{\hbar} \right)^{1/2} \times e^{i x^2 m \omega_b^2 / 2 \hbar} H_n \left( \sqrt{\frac{m \omega_b}{\hbar}} e^{-i \pi/4} \right). \)

(4.2c)

Eq. (3.23) thus gives

\( G^{+}(0,0;E) = e^{-i \pi/4} \frac{e^{i \omega_b \tau}}{\pi \hbar \omega_b} \left( \frac{m \omega_b}{\hbar} \right)^{1/2} \times \sum_{n = 0, 2, ...} \frac{\Gamma(n/2 + \frac{1}{2})}{\Gamma(n/2 + 1)} \frac{e^{-\omega_b \tau} (n + \frac{1}{2})}{\epsilon + i(n + \frac{1}{2})} + \text{STC}, \)

(4.3a)

\( \frac{\partial^2 G^{+}(x,x';E)}{\partial x \partial x'} \bigg|_{x = x' = 0} = 4 e^{-i \pi/4} \frac{e^{i \omega_b \tau}}{\pi \hbar \omega_b} \left( \frac{m \omega_b}{\hbar} \right)^{1/2} \times \sum_{n = 1, 3, ...} \frac{\Gamma(n/2 + 1)}{\Gamma(n/2 + \frac{1}{2})} \frac{e^{-\omega_b \tau} (n + \frac{1}{2})}{\epsilon + i(n + \frac{1}{2})} + \text{STC}, \)

(4.3b)

where STC indicates the "short time corrections" in Eqs. (3.23a) and (3.23b), and \( \epsilon \) is the reduced energy,

\( \epsilon = \frac{(E - V_0)}{\hbar \omega_b}. \)

(4.4a)

Since for large \( n \),

\( \frac{\Gamma \left( \frac{n}{2} + \frac{1}{2} \right)}{\Gamma \left( \frac{n}{2} + \frac{1}{2} \right)} \sim \left( \frac{2}{n} \right)^{1/2}, \)

(4.5)

we note that the summands in Eq. (4.3) have the asymptotic form \( n^{-1/2} e^{-\omega_b \tau} \) for Eq. (4.3a), and \( n^{-1/2} e^{-\omega_b \tau} \) for Eq. (4.3b), again showing that the former sum will converge (though very slowly) even with \( \tau = 0 \), but that the latter one will not.

Figures 2-5 show the results obtained for \( N(E) \) from Eqs. (3.9) and (4.3), with the short time corrections as in Eq. (3.23), for a sequence of values of \( n_{\text{max}} \), the largest "vibrational" quantum number retained in the Siegert sums; \( n_{\text{max}} + 1 \) is thus the total number of Siegert states included,
half of them even and half odd. The results in Figs. 2–5 are
given for several values of the short time parameter \( \tau \) (actu-
ally the dimensionless short time parameter \( \tilde{\tau} \equiv \omega_b \tau \)), and in
all cases compared to the exact result for the parabolic bar-

\[
N_{PB}(E) = \left( 1 + e^{-2\pi \epsilon} \right)^{-1}.
\]  
(4.4b)

Figure 2 shows that reasonable results are obtained even
with \( n_{max} = 1 \), i.e., only one even and one odd Siegert state,
and that \( N(E) \) is quite quantitative by the time \( n_{max} \) is as
large as 7 (Fig. 5). For small \( n_{max} \), the results are more
sensitive to the short time parameter \( \tau \), but this sensitivity
diminishes as \( n_{max} \) increases. To see this feature more clear-

\[ V(x) = V_0 \text{sech}^2(x/a) \]  
(4.6)

provides a more realistic reaction barrier to test the rate
expression of Sec. III. The parameters \( V_0 = 0.0156 \) a.u.,
\( a = 0.734 \) a.u., and the mass \( m = 1061 \) a.u. are chosen so
that the barrier height (\( V_0 \)) and barrier frequency
\( \omega_b = \sqrt{(2V_0/ma^2)} \) correspond approximately to the
\( \text{H} + \text{H}_2 \) reaction. The Siegert eigenvalues and eigenfunc-
tions were calculated by diagonalizing the complex symmet-
ric Hamiltonian matrix in the harmonic basis, Eq. (4.1).

The dimensionless short time parameter \( \tilde{\tau} \) was chosen to
be energy dependent

\[
\tilde{\tau} = \begin{cases} 
(E - V_0)\tau/\hbar, & E > V_0 (1 + \delta) \\
\delta V_0 \tau/\hbar, & E < V_0 (1 + \delta), 
\end{cases}
\]  
(4.7)

with \( \delta \approx 1 \). \( \tilde{\tau} \) is held fixed for the entire energy range, so that
the short time interval \((0, \tau)\) is shorter the higher energy,
which seems quite reasonable. The parameter \( \delta \) is intro-
duced so that \( \tau \) is always positive.

Figures 7 and 8 show the cumulative reaction probabili-
ity \( N(E) \) for various size harmonic basis sets, compared to
the exact result\(^{11}\) for the Eckart barrier,

\[
N_{EB}(E) = \left( 1 + \left[ \cosh(c)/\sinh(b) \right] \right)^{-1} \]  
(4.8)

with

\[
b = 2\pi \left( V_0 E / (\hbar \omega_b) \right)^{1/2},
\]
\[
c = 2\pi \left( V_0 / (\hbar \omega_b) \right)^{1/2}.
\]
The results in Fig. 7 are with the free particle short time correction of Eq. (3.23), and those in Fig. 8 with the parabolic barrier short time correction of Eq. (3.25); as expected, the latter short time correction is a significant improvement, i.e., good results are obtained with smaller size basis sets. Figure 8 shows that quite good results are obtained with only four basis functions.

Finally, Fig. 9 shows the results of Fig. 8 with four basis functions for various choices of the reduced short time parameter $\tilde{\tau}$. As before, this dependence on $\tilde{\tau}$ will diminish as the size of the basis is increased, but it is clear that the results are not unduly sensitive to the precise choice for $\tilde{\tau}$ even with only four basis functions.

V. CONCLUDING REMARKS

The discussion in Sec. II showed that the "good" action variables associated with the transition state of a potential surface, on which semiclassical transition state theory relies, are actually the semiclassical counterpart to the Siegert eigenvalues of the system. Being able to express the energy as a function of the "good" action variables (i.e., quantum numbers) requires that the spectrum of Siegert eigenvalues be "regular," i.e., assignable. If it is, then one can apply semiclassical transition state theory; this is analogous to the situation for a potential well for which semiclassical (EBK) eigenvalues are obtainable when the spectrum is "regular," and which corresponds to quasiperiodic classical motion. If the spectrum of Siegert eigenvalues is unassignable, then semiclassical transition state theory cannot be applied (because there exist no "good" action variables); this is analogous to the eigenvalue case that the classical motion is chaotic and the EBK invariant tori do not exist.

Section III showed how the Siegert eigenvalues (and eigenfunctions) can be used in a rigorous quantum framework to obtain a fully quantum mechanical result for the reaction rate. A short time correction is needed to obtain convergence of the Siegert eigenstate expansions, and two simple choices for this were considered and illustrated by the test calculations presented in Sec. IV. More sophisticated and accurate short time corrections are possible and worth investigating. The better the short time correction, the fewer basis functions are required in the Siegert expansions.

A potentially useful and intriguing aspect of the quantum rate expressions of Sec. III is that they are applicable
also for reactions which proceed via formation of a long-lived collision complex, and not only for "direct" reaction dynamics for which transition state theory is most appropriate. It would be interesting for future work to consider application of these approaches to problems that indeed involve complex formation.

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APPENDIX A: EIGENVALUES OF THE FLUX OPERATOR IN A REAL FINITE BASIS

This Appendix is somewhat of an aside with regard to the present paper, but it is nevertheless a useful observation to make. In a series of papers on evaluating reactive flux correlation functions, Park and Light* noted that the matrix of the flux operator, Eq. (3.2a), in a real finite basis (of arbitrary size),

\[ (F)_{n,m} = \frac{\hbar}{2iM} [\phi_n(0)\phi'_m(0) - \phi'_n(0)\phi_m(0)] \]

has only two nonzero eigenvalues, and furthermore that the eigenvalues are the negatives of each other and the corresponding eigenvectors the complex conjugates of each other. This was discovered empirically, i.e., by diagonalizing the matrix \( F \) in various basis sets, and the point of this Appendix is to give a simple proof of these facts.

If the column vectors \( \mathbf{v} \) and \( \mathbf{d} \) are the basis functions and their derivatives evaluated at the dividing surface,

\[ (\mathbf{v})_n = \phi_n(0), \]
\[ (\mathbf{d})_n = \phi'_n(0), \]

then the matrix \( F \) of Eq. (A1) can be written in dyadic form as

\[ F = \frac{\hbar}{2iM} (\mathbf{v}\mathbf{d}^T - \mathbf{d}\mathbf{v}^T), \]

where \( T \) denotes transpose and thus changes a column vector into a row vector. The finite eigenvalue problem for the flux matrix,

\[ Fc = \lambda c, \]

thus becomes

\[ \frac{\hbar}{2iM} [\mathbf{v}(\mathbf{d}^T\mathbf{c}) - \mathbf{d}(\mathbf{v}^T\mathbf{c})] = \lambda c, \]

which shows that the eigenvector \( c \) must be a linear combination of the two (known) vectors \( \mathbf{v} \) and \( \mathbf{d} \). Writing

\[ c = a\mathbf{v} + b\mathbf{d} \]

and substituting this expansion into Eq. (A5), leads to the following linear homogeneous equations for the expansion coefficients \( a \) and \( b \),

\[ \begin{pmatrix} dv \cos \theta - \frac{2iM}{\hbar} \lambda, & d^2 \\ v^2, & dv \cos \theta + \frac{2iM}{\hbar} \lambda \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = 0, \]

where

\[ v^2 = \mathbf{v}^T\mathbf{v}, \]
\[ d^2 = \mathbf{d}^T\mathbf{d}, \]
\[ d^\mathbf{v} - dv \cos \theta, \]

\[ \lambda, \quad (A8) \]

(i.e., \( \theta \) is the angle between vectors \( \mathbf{d} \) and \( \mathbf{v} \)). The determinant of the \( 2 \times 2 \) matrix in Eq. (A7) must thus be zero (the secular equation), and this gives a quadratic equation for the eigenvalue \( \lambda \) with the following roots,

\[ \lambda = \pm \frac{\hbar}{2M} dv \sin \theta = \lambda_\pm. \]

The normalized eigenvectors \( c_\pm \) corresponding to these eigenvectors are also easily found,

\[ c_\pm = (-e^{\pm i\theta} + \mathbf{d})/(\sin \theta \sqrt{2}), \]

where \( \mathbf{v} \) and \( \mathbf{d} \) are the unit vectors

\[ \mathbf{v} = \mathbf{v}/v, \]
\[ \mathbf{d} = \mathbf{d}/d. \]

Equations (A9) and (A10) demonstrate the observations of Light et al.* We also note that \( \theta = \pi/2 \) if the basis has even-odd symmetry at the dividing surface, and that \( \mathbf{v} \) and \( \mathbf{d} \) become infinitely large as the basis is increased, so that \( \lambda_\pm \to \pm \infty \) in the limit of an infinite basis.

APPENDIX B: SEMICLASSICAL APPROXIMATION FOR THE SUM OVER SIEGERT STATES

It is shown here how Eqs. (3.9) and (3.10) reduce to the correct semiclassical result with appropriate approximations. We consider the symmetric barrier case in the tunneling regime (\( E \ll V_{\text{barrier}} \)), and in the usual semiclassical spirit, the sums over quantum states in Eq. (3.10) are replaced by integrals,

\[ \sum_{n=1,3,5} \frac{\psi_n(0)^2}{E - E_n} \approx -\frac{1}{2} \int_{E - E} dn - \frac{\psi_n(0)^2}{E - E(n)} \]

\[ = -\frac{1}{2} \int dE \left( \frac{dE}{dn} \right)^{-1} \psi_n(0)^2 \frac{1}{E - E}, \]

\[ \sum_{n=1,3,5} \frac{\psi_n(0)^2}{E - E_n} \approx -\frac{1}{2} \int_{E - E} dn - \frac{\psi_n(0)^2}{E - E(n)} \]

\[ = -\frac{1}{2} \int dE \left( \frac{dE}{dn} \right)^{-1} \psi_n(0)^2 \frac{1}{E - E}, \]

where the integrals over quantum number \( n \) have been changed to those over \( E = E(n) \); \( \psi_{E,e} \) and \( \psi_{E,o} \) are the even and odd eigenfunctions, respectively, for energy \( E \). Integrating over real values of \( n \) implies that the integral over \( E \) is along a contour in the complex energy plane (cf. Fig. 1), but we now distort this contour to lay infinitesimally below the real energy axis. The wave functions are then real, and

\[ \text{Im}(E - E)^{-1} = -\pi\delta(E - E), \]

so that from Eq. (B1a) one has

\[ \text{Im} \sum_n \frac{\psi_n(0)^2}{E - E_n} \approx -\frac{1}{2} \left( \frac{dE}{dn} \right)^{-1} \psi_{E,e}(0)^2, \]
and then Eq. (3.9) gives the cumulative reaction probability as

\[ N(E) = \left( \frac{\beta^2}{2m} \right)^{1/2} \int \left[ \exp \left( -\int_{x_0}^{x} dx' \kappa(x') \right) \right] \psi_{E_{kn}}(0) \psi_{E_{kn}}(0), \]  

With a WKB approximation for the wave functions in the tunneling region (normalized as though they were a bound state wave function),

\[ \psi_{E_{kn}}(x) = \frac{2m}{\beta^2 \pi \hbar^2} \left[ \exp \left( -\int_{x_0}^{x} dx' \kappa(x') \right) \right] \psi_{E_{kn}}(0), \]  

where \( x_0 \) is the classical turning point and \( \kappa(x) = \sqrt{2m(V(x) - E)}/\hbar^2 \), one has

\[ \psi_{E_{kn}}(0)^2 = \frac{2m}{\beta^2 \pi \hbar^2} \frac{dE}{dn} e^{-\theta/\kappa(0)}, \]  

\[ \psi_{E_{kn}}(0)^2 = \frac{2m}{\beta^2 \pi \hbar^2} \frac{dE}{dn} e^{-\theta/\kappa(0)}, \]  

where \( \theta = 2 \int_{x_0}^{x} dx' \kappa(x') = \int_{-x_0}^{x} dx' \kappa(x') \), so that Eq. (B3) gives

\[ N(E) = e^{-2\theta(E)}, \]  

the correct semiclassical result in the tunneling region. The divergence problems discussed in the text are avoided in the semiclassical limit because the sum over Siegert eigenstates is replaced by an integral,

\[ \sum_{n} \int dx_n, \]  

and the integral over \( n \) is distorted so that the new integration variable (the energy) \( \tilde{E} \equiv E(n) \) is infinitesimally close to the real axis. The “imaginary part,” Eq. (B2), then requires \( \tilde{E} \) to be on the energy shell, so that the complex Siegert eigenvalues \( E(n) \) are only needed at the complex “quantum number” \( n \) for which \( E(n) = \tilde{E} \), just as in the case for the general semiclassical theory summarized in Sec. II. These manipulations are obviously not possible in the fully quantum case, so that explicit sums over complex Siegert eigenvalues must be retained in a rigorous quantum evaluation.