Comparison of positive flux operators for transition state theory using a solvable model

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Several quantum operators representing ''positive flux'' are compared for the square barrier by examining their ability to reproduce the exact transmittance when traced with the exact microcanonical density operator. They are obtained by means of the ''Weyl rule,'' the ''Rivier rule,'' by symmetrizing the product of ''flux'' and ''positive momentum projection'' operators, and by a variational technique. Explicit expressions are given for all cases. © *1996 American Institute of Physics.* [S0021-9606(96)01217-X]

I. INTRODUCTION

Classical transition state theory (CTST) provides an upper bound for the classical reaction rate,[1] in many cases an accurate one. In its simplest one dimensional version it is exact when applied at the barrier maximum. In equilibrium conditions the reactive flux, i.e., the flux due to trajectories coming from the reactants ''valley'' (on the left) which end up in the ''products'' valley (on the right) is *equal* to the positive flux, due to trajectories with positive momentum, at the top of the potential barrier. The positive flux is minimum at the barrier top and larger at other positions because there are trajectories with insufficient energy to eventually pass over the barrier.

A fully satisfactory quantum transition state theory (QTST) with all the desirable properties of its classical counterpart has not been found, even in one dimension.[2–4] Of course for realistic chemical reactions at least two dimensions have to be considered, or the effect of an external medium (e.g., a solvent), which adds to the complexity of the task. However, since some of the difficulties are already present in one dimension, we shall restrict the present discussion to this simple case. Ideally one seeks a theory that translates to the quantum case the ideas of CTST, namely a theory that gives an accurate upper bound for reaction rates for all energies and potential shapes, in particular when tunnelling is important, and which is computationally advantageous compared to the full scattering calculation of the exact rate. Even though some of these objectives are being fulfilled by various quantum approaches inspired in CTST,[3,5–9] further work on the analysis of the basic transition state theory assumption relating the rates to the positive flux is worthwhile.[4]

In one dimension the difficulties are in part due to the fact that a ''positive momentum selection,'' and ''flux'' are associated in quantum mechanics with the non commuting operators,

$$P\equiv\int_0^\infty dp|p\rangle\langle p|=\Theta(p_{\rm op}) \tag{1}$$

and

$$J_{\rm op}(x_0)=\frac{1}{2m}[p_{\rm op}\delta(x_0-x_{\rm op})+\delta(x_0-x_{\rm op})p_{\rm op}]. \tag{2}$$

(The subscript ''op'' is used for quantum operators when confusion with the corresponding expectation values or classical quantities is possible. Thus the flux per particle at x_0 is given by $J(x_0)=\mathrm{tr}[J_{\rm op}(x_0)\varrho]$, ϱ being the density operator normalized to one; Θ is the Heaviside function.)

Many quantization or ordering rules have been proposed to obtain quantum operators from classical quantities, producing in general different results since they quantize a product of classical functions in different ways.[10,11] Indeed treatises on quantum mechanics usually refer to experiment as the ultimate test for a quantization to be accepted. From this pragmatic perspective, a good quantum flux operator is in this context one which gives good transition rates. Two of the most frequently advocated rules are examined here for a solvable model, and also a different variational approach proposed by Pollak.[12] The first quantization is based on the Weyl correspondence rule. This method is equivalent to the so-called ''Wigner ansatz,'' in which one estimates the flux classically in phase space but the distribution function is taken as the Wigner function. Its use has been discussed and tested for the parabolic barrier[13] and other barriers in combination with semiclassical approximations.[14] Other aspects of the method, such as the correct coordinate representation of the operator or its bounding properties[4] have not previously been examined. The second approach is based on symmetrizing the basic operators involved. However, there is no unique symmetrization. Three different symmetrized positive flux operators are introduced here for the first time. Finally, Pollak's approach leads to an operator which has no basis in terms of some quantization rule but rather on the search for an upper bound for the exact rate.

Let us emphasize that our objective in this work is not to develop an efficient numerical scheme to approximate rate constants, but to test, using an exactly solvable model, different quantum interpretations of the basic transition state theory assumption and their validity within the quantum domain. Moreover, in order to test the fundamental TST assumption without the interference of any additional statistical averaging we shall center attention on the microcanonical ensemble.

The square barrier potential model has been chosen for two reasons: First the results can be given exactly and explicitly in terms of known functions and four different parameters (width, height, energy difference between both sides of the barrier and the position x_0 where the flux is calculated). Presumably other proposals (besides the versions for the ''positive flux'' operator discussed here) for implementing a QTST can also be expressed analytically for the square barrier, which is ideal for making comparisons with minimal computational effort. Second, the potential model, in spite of its crude shape, has a correct asymptotic form with a constant potential on both sides of the barrier, shows resonance peaks and allows for modeling of asymmetrical asymptotic states. This is in contrast with the parabolic barrier, which has been the dominant paradigm in many studies but lacks these properties. In particular the asymptotic behavior of the latter leads to unphysical divergences.[6] These two potential models may also be regarded as complementary because the parabolic barrier is highly ''classical'' in that its dynamics, expressed in Wigner function form, reduces to the classical Liouville equation, while the quantum dynamics on a square barrier is more difficult to mimic classically.[15] Thus the square barrier may be expected to be a stronger test for any version of quantum transition state theory.

II. POSITIVE FLUX OPERATORS

The ''reactive flux'' J for a trace class, normalized *stationary* state is defined as the flux due to waves with *incident* positive momentum selected out by the projector P_+,

$$J \equiv \mathrm{tr}\,[J_{\mathrm{op}}(x_0)P_+\varrho], \tag{3}$$

$$P_+ = \int_0^\infty dp|p^+\rangle\langle p^+|, \tag{4}$$

where the scattering states $|p^+\rangle$ $(p>0)$ are the eigenstates of H with eigenvalue $E_p=p^2/(2m)$ and incident plane wave $|p\rangle$. The definition of P_+ and the stationarity of ρ imply that P_+ and ϱ commute both with H and each other. In physical terms Eq. (3) amounts to selecting only waves which had positive incident momenta in the infinite past.[16]

For density operators which are not normalizible, such as $\varrho_p \equiv |p^+\rangle\langle p^+|$ physically meaningful quantities are still obtained as ratios of outgoing and ingoing fluxes. In particular the transmittance $|T|^2$ is the ratio between the reactive flux

$$J = \mathrm{tr}\,[J_{\mathrm{op}}(x_0)\varrho_p] \tag{5}$$

and the incoming flux $p/(mh)$ (note that when using delta function normalization for plane waves and scattering states the units of these quantities do not correspond to a flux. This is of course irrelevant as long as only the ratio is finally of interest),

$$|T|^2 = \frac{\mathrm{tr}\,[J_{\mathrm{op}}(x_0)\varrho_p]}{p/(mh)} = h\ \mathrm{tr}\,[J_{\mathrm{op}}(x_0)P_+\delta(E_p-H)]. \tag{6}$$

The energy delta function in Eq. (6) can be introduced because the projector P_+ selects only the state with incident positive momentum of the degenerate pair of energy eigenfunctions. The reactive flux and the transmittance are independent of x_0 in spite of the formal presence of x_0 in the flux operator as follows from the stationarity condition and the continuity equation.

In the spirit of classical transition state theory one would approximate P_+ in Eq. (6) by P. However the resulting operator $J_{\mathrm{op}}P$ for the positive flux is not Hermitian.[13] In the following subsections several possible positive flux Hermitian operators J^+_{op} are described and the accuracy of the corresponding approximations

$$|T|^2 \approx h\ \mathrm{tr}\,[J^+_{\mathrm{op}}(x_0)\,\delta(E_p-H)] \equiv \mathscr{T} \tag{7}$$

examined.

A. Positive flux operator by Weyl correspondence

The Weyl–Wigner formulation of quantum mechanics[10,17–19] is an *exact* phase space representation of standard quantum theory based on the *Weyl-transform* $A_W(x,p)$ of an operator A (expressed here in position representation)

$$A_W(x,p) \equiv \int \left\langle x-\frac{y}{2}\middle|A\middle|x+\frac{y}{2}\right\rangle e^{iyp/\hbar}\,dy. \tag{8}$$

The operator matrix elements in coordinate representation are obtained from $A_W(x,p)$ by the *inverse transformation*

$$\left\langle x-\frac{y}{2}\middle|A\middle|x+\frac{y}{2}\right\rangle = \frac{1}{h}\int A_W(x,p)e^{-iyp/\hbar}\,dp. \tag{9}$$

The quantum mechanical trace of two operators, $\mathrm{tr}(AB)$ can be written as a phase space integral of their Weyl transform

$$\mathrm{tr}(AB) = h^{-1}\int\int dp\ dx\ A_W(x,p)B_W(x,p). \tag{10}$$

In particular, the average of operator A is given by

$$\langle A\rangle = \mathrm{tr}(A\varrho) = \int\int dp\ dx\ W(x,p,t)A_W(x,p), \tag{11}$$

where $W=\varrho_W/h$ is the Wigner function, the Weyl transform of the density operator ϱ divided by h. In other words, the computation of the average value takes the same form as in classical statistical mechanics, with the Weyl transform A_W and the Wigner function W *playing the roles* of the classical function $A^{\mathrm{cl}}(x,p)$ and the classical probability distribution f^{cl}, respectively. For operators which are functions of coordinates or momenta *only*, such as $\delta(x_0-x_{\mathrm{op}})$ or p_{op}, the Weyl transform A_W agrees with the classical function A^{cl}. This is not the case in general, although in the limit $\hbar\to 0$ the classical function is obtained from A_W.[10]

If the quantum operator is not known one can apply the inverse Weyl transformation to create one by using Eq. (9)

with the classical expression $A^{\mathrm{cl}}(x,p)$ as the phase space function. This is the *Weyl-quantization rule*. Since the quantum operators do not always lead to classical functions via the Weyl transform, i.e. in general $A^{\mathrm{cl}}(x,p) \neq A_W(x,p)$, it is not guaranteed either that the classical function will produce the correct quantum operator, so this rule (as any other quantization rule) must be handled with care. For example, the classical functions $\exp(-iH^{\mathrm{cl}}t/\hbar)$, $\exp(-\beta H^{\mathrm{cl}})$, or simply the square of the energy, $(H^{\mathrm{cl}})^2$ do *not* lead to the corresponding (correct) operators $\exp(-iH_{\mathrm{op}}t/\hbar)$, $\exp(-\beta H_{\mathrm{op}})$ and H_{op}^2 via inverse Weyl transform (Weyl rule) even though $H^{\mathrm{cl}}=H_W$. In these cases the disagreement occurs because in general the Weyl transform does not preserve products, that is $(AB)_W \neq A_W B_W$. There are of course, in each case, correct phase space representations of these operators that can be obtained using Eq. (8).

The classical expression for the flux $J^{\mathrm{cl}}(x_0)=(p/m)\,\delta(x-x_0)$ is a product of position and momentum dependent functions. Nevertheless, the Weyl rule provides in this case the standard result for the flux operator, Eq. (2). In momentum representation

$$\langle p|J_{\mathrm{op}}|p'\rangle=\frac{p+p'}{2mh}e^{ix_0(p'-p)/\hbar}. \tag{12}$$

Equivalently, the Weyl transform J_W of the flux operator is the classical function J^{cl}. A natural extension of this result is to define a positive flux operator J_{op}^{+W} as the operator that the Weyl rule associates with the classical function $J^{+\mathrm{cl}}=\delta(x-x_0)\Theta(p)p/m$. This is found to be

$$\langle p|J_{\mathrm{op}}^{+W}(x_0)|p'\rangle=\frac{p+p'}{2hm}\Theta\left(\frac{p+p'}{2}\right)e^{ix_0(p'-p)/\hbar}, \tag{13}$$

$$\langle x|J_{\mathrm{op}}^{+W}(x_0)|x'\rangle=\frac{\hbar}{2\pi m}\,\delta\left[x_0-\frac{x+x'}{2}\right]\times\frac{\partial}{\partial x}\left[\mathscr{P}\left(\frac{1}{x-x'}\right)-i\pi\delta(x-x')\right]. \tag{14}$$

Note that the resulting operator is not simply the product (or even the symmetrized product as discussed further in the next section) of J_{op} and the projector selecting positive momenta associated with the classical function $P^{\mathrm{cl}}=\Theta(p)$. This latter projector is given in momentum representation by

$$\langle p|P|p'\rangle=\Theta(p)\,\delta(p-p'). \tag{15}$$

Most wave functions are given in position representation so it is useful to have the position representation of the positive flux operator,

$$\begin{aligned}\langle x|P|x'\rangle&=\int\int\langle x|p\rangle\langle p|P|p'\rangle\langle p'|x\rangle dp\,dp'\\&=\frac{1}{h}\int_0^{\infty}e^{i(x-x')p/\hbar}\,dp\\&=\frac{i}{2\pi}\left[\mathscr{P}\left(\frac{1}{x-x'}\right)-i\pi\delta(x-x')\right]\\&=\frac{i}{2\pi}\,\frac{1}{x-x'+i0}.\end{aligned} \tag{16}$$

This involves the principal part $\mathscr{P}$ of any subsequent position integral, or alternately, with the introduction of a convergence factor for carrying out the p integral, can be expressed as a quotient.

The coordinate representation (14) of the positive flux operator $J_{\mathrm{op}}^{+W}(x_0)$ had been reported before without the delta function.[13] The contribution from this term may vanish in special circumstances but is clearly required for general applications. An example is the flux for a plane wave having positive momentum. In this case both the principal part and the delta terms contribute equally, see Appendix A.

In this paper we shall calculate the positive flux using operators and the trace expression $\mathrm{tr}[J_{\mathrm{op}}^{+W}\varrho]$. It is noted that this is equivalent to using a phase space integral with the classical function for the positive flux $J^{+\mathrm{cl}}(x_0)=\Theta(p)\times(p/m)\,\delta(x-x_0)$ and the Wigner function (the "Wigner ansatz"[4]), namely,

$$\mathrm{tr}\,[J_{\mathrm{op}}^{+W}\varrho]=\int\int dp\,dx\,J^{+\mathrm{cl}}(x_0)W(x,p,t). \tag{17}$$

This popular TST approximation is usually implemented using the latter (Wigner function) representation whereas here we find it more convenient to use the equivalent operator form.

B. Positive flux operators by symmetrization

The quantization of the positive flux $J_{\mathrm{op}}^{+W}(x_0)$ due to Weyl's rule is different from the symmetrical operators $PJ_{\mathrm{op}}(x_0)P$ or $\frac{1}{2}[PJ_{\mathrm{op}}(x_0)+J_{\mathrm{op}}(x_0)P]$. They have simple expressions in momentum representation

$$\langle p|PJ_{\mathrm{op}}(x_0)P|p'\rangle=\frac{p+p'}{2mh}\Theta(p)\Theta(p')e^{ix_0(p'-p)/\hbar}, \tag{18}$$

$$\langle p|\tfrac{1}{2}[PJ_{\mathrm{op}}(x_0)+J_{\mathrm{op}}P]|p'\rangle$$

$$=\tfrac{1}{2}[\Theta(p)+\Theta(p')]\langle p|J_{op}|p'\rangle \tag{19}$$

$$=\frac{p+p'}{4mh}[\Theta(p)+\Theta(p')]e^{ix_0(p'-p)/\hbar} \tag{20}$$

that can be compared with Eq. (13). Note the different ways in which the Heaviside functions select positive momenta in the three operators.

A third symmetrical operator combining the delta function and Pp_{op} is obtained by means of *Rivier's rule of* *symmetrization*.[20] For a given classical function $g(x,p)$, this rule associates the operator G, given in coordinate representation by

$$\langle x|G|x'\rangle=\frac{1}{2h}\int e^{ip(x-x')/\hbar}[g(x,p)+g(x',p)]dp. \tag{21}$$

In particular, if g factorizes as a product of position and momentum dependent functions, $g=g_1(x)g_2(p)$, the operator is given by symmetrizing $g_1(x_{\rm op})$ and $g_2(p_{\rm op})$,

$$G=[g_1(x_{\rm op})g_2(p_{\rm op})+g_2(p_{\rm op})g_1(x_{\rm op})]/2. \tag{22}$$

This rule also allows average values tr $(G\varrho)$ to be expressed as phase space integrals where the weight function is the *Margenau-Hill function* instead of the Wigner function.[21,22] It provides the correct quantization of the square of the energy $H_{\rm cl}^2$ (in this particular application it is better than Weyl's rule) although it fails for higher powers.

The positive flux operator according to Rivier's rule, $J_{\rm op}^{+R}$, is obtained by symmetrizing the positive momentum $p_{\rm op}^{+}\equiv Pp_{\rm op}$ and position delta function $\delta(x_{\rm op}-x_0)$. In momentum representation,

$$\begin{aligned}\langle p|J_{\rm op}^{+R}|p'\rangle&=\frac{1}{2m}\langle p|(p_{\rm op}^{+}\delta(x_{\rm op}-x_0)\\&\quad+\delta(x_{\rm op}-x_0)p_{\rm op}^{+}|p'\rangle\\&=\frac{1}{2mh}e^{ix_0(p'-p)/\hbar}[\Theta(p)p+\Theta(p')p'].\end{aligned} \tag{23}$$

C. Variational approach

Pollak has proposed a positive flux operator j_+ which is given in momentum representation by[12]

$$\langle p|j_+(x_0)|p'\rangle=\frac{1}{2mh}e^{ix_0(p'-p)/\hbar}(\alpha+pp'/\alpha). \tag{24}$$

For $\alpha>0$ this is a positive operator that provides an upper bound for the absolute value of the flux, $\langle j_+(x_0)\rangle>|\langle J_{\rm op}(x_0)\rangle|$. α is then treated as a variational parameter to minimize the bound at fixed x_0.

Following this procedure the transmittance $|T(p)|^2$ is found to be bounded by

$$|T(p)|^2\leqslant hF_{\rm TST}(x_0), \tag{25}$$

where, for a microcanonical ensemble,[23]

$$\begin{aligned}F_{\rm TST}(x_0)&=\frac{\hbar}{2m}\left[\frac{1}{2}\langle x_0|\delta(E-H)|x_0\rangle\right.\\&\quad\times\frac{d^2}{dx_0^2}\langle x_0|\delta(E-H)|x_0\rangle+\frac{2m}{\hbar^2}(E-V(x_0))\\&\quad\times\langle x_0|\delta(E-H)|x_0\rangle^2]^{1/2}.\end{aligned} \tag{26}$$

It is noted that this approach does not select out a particular direction for the motion but rather approximates whether the barrier is being passed through (in either direction).

D. Time reversal and parity invariance

Some important simplifications are due to time reversal and/or parity invariance. The action of the time reversal operator θ on P and $J_{\rm op}(x_0)$ is given by $\theta P\theta=Q\equiv(1-P)$ and $\theta J_{\rm op}(x_0)\theta=-J_{\rm op}(x_0)$. If the Hamiltonian H commutes with θ the following relations are valid for any function $f(H)$ of the Hamiltonian

$$\mathrm{tr}\,[PJ_{\rm op}(x_0)Pf]=-\mathrm{tr}\,[QJ(x_0)Qf], \tag{27}$$

$$\mathrm{tr}\,[J_{\rm op}(x_0)f]=-\mathrm{tr}\,[J_{\rm op}(x_0)f]=0, \tag{28}$$

$$\mathrm{tr}\,[PJ_{\rm op}(x_0)Qf]=-\mathrm{tr}\,[QJ(x_0)Pf]. \tag{29}$$

The first two relations seem natural from a classical point of view, but the third one is non trivial since it involves quantum interference terms. A consequence of this relation is that tr $[PJ_{\rm op}(x_0)Pf]=2^{-1}$ tr $[(PJ(x_0)+J(x_0)P)f]$, i.e., *even though PJP and (PJ+JP)/2 are different operators their traces with a function of H are equal.*

The action of the parity operator r, equivalent in one dimension to a reflection about some chosen position y, on P and $J_{\rm op}(x_0)$ is given by $rPr=Q$ and $rJ_{\rm op}(x_0)r=-J_{\rm op}(2y-x_0)$. If in addition the potential is symmetric about $x=d/2$, then on choosing the reflection center as $d/2$, the Hamiltonian H commutes with r and the following relations are valid for any function $f(H)$ of the Hamiltonian:

$$\mathrm{tr}\,[PJ_{\rm op}(x_0)Pf]=-\mathrm{tr}\,[QJ_{\rm op}(d-x_0)Qf], \tag{30}$$

$$\mathrm{tr}\,[J_{\rm op}(x_0)f]=-\mathrm{tr}\,[J_{\rm op}(d-x_0)f], \tag{31}$$

$$\mathrm{tr}\,[PJ_{\rm op}(x_0)Qf]=-\mathrm{tr}\,[QJ(d-x_0)Pf]. \tag{32}$$

Combined with the time reversal symmetry (27) it follows that

$$\mathrm{tr}\,[PJ_{\rm op}(x_0)Pf]=\mathrm{tr}[PJ_{\rm op}(d-x_0)Pf]. \tag{33}$$

A special generalization of Eq. (30) is

$$\begin{aligned}&\mathrm{tr}\,[PJ_{\rm op}(x_0)P|-p^+\rangle\langle-p^+|]\\&\quad=-\mathrm{tr}\,[QJ_{\rm op}(d-x_0)Q|p^+\rangle\langle p^+|].\end{aligned} \tag{34}$$

The exact flux operator $J_{\rm op}(x_0)$ can be resolved into components in a number of different ways. One resolution of $(P+Q)J_{\rm op}(P+Q)$ is into the four components corresponding to all combinations of the projectors P and Q. The Weyl rule provides an alterative resolution into positive and negative flux contributions according to

$$\begin{aligned}J(x_0)&=\mathrm{tr}[\varrho(J_{\rm op}^{+W}+J_{\rm op}^{-W})]\\&=\int_0^\infty dp'\ W(x_0,p')p'/m\\&\quad+\int_{-\infty}^0 dp'W(x_0,p')p'/m.\end{aligned} \tag{35}$$

It is noted that no "interference terms" between positive and negative contributions arise in the resolution according to the Weyl rule whereas such quantities arise in the projector resolution. For a parity invariant potential the Wigner function $W_p(x,p')$ for the state associated with an incident (positive) momentum p, obeys the symmetry relation

$$W_p(x,-p')=W_{-p}(d-x,p'), \tag{36}$$

i.e., the positive flux (*a la Weyl*) for the states with incident negative momenta at x can be obtained as the negative flux for states with positive incident momenta at the reflected position $d-x$. Similar considerations apply for the Rivier approach.

For parity invariant potentials, or simply if $V(\infty)=V(-\infty)$,

$$\delta(E_p-H)=\frac{m}{|p|}(|p^+\rangle\langle p^+|+|-p^+\rangle\langle -p^+|). \tag{37}$$

Equations (34) and (36) allow in this case the evaluation of Eq. (7) for all momenta by considering *only* $|p^+\rangle$ states, since the contribution by $|-p^+\rangle$ can be obtained from them. This simplification will be used in the examples of Sec. III.

III. THE SQUARE BARRIER AS AN EXAMPLE

The potential for a square barrier is written as

$$V(x)=\begin{cases} 0, & -\infty<x<0 \\ V_0, & 0<x<d \\ V_1, & d<x<\infty \end{cases}. \tag{38}$$

For this potential, the scattering solution to the Schrödinger equation associated with an incoming plane wave of momentum $p=\hbar k>0$ is given by

$$\langle x|p^+\rangle=\begin{cases} h^{-1/2}[e^{ixk}+Re^{-ixk}], & -\infty<x<0 \\ h^{-1/2}[C_+e^{ixk_1}+C_-e^{-ixk_1}], & 0<x<d \\ h^{-1/2}[Te^{ixk_2}], & x>d \end{cases}, \tag{39}$$

where

$$\begin{aligned} &k\equiv(2mE)^{1/2}/\hbar, \\ &k_1\equiv[2m(E-V_0)]^{1/2}/\hbar, \\ &(k_1=i\kappa,\kappa>0, \quad \text{if } E<V_0), \\ &k_2\equiv[2m(E-V_1)]^{1/2}/\hbar, \qquad (E>V_1). \end{aligned} \tag{40}$$

In this work we restrict our attention to momenta such that both sides of the barrier are ''open channels'' so that k_2 is always real ($E>V_1$, $E>0$). The matching conditions between different potential regions require,

$$\begin{aligned} &1+R=C_++C_-; \\ &k(1-R)=k_1(C_+-C_-), \qquad \text{at } x=0 \\ &C_+e^{i\,dk_1}+C_-e^{-i\,dk_1}=Te^{i\,dk_2}; \\ &k_1(C_+e^{i\,dk_1}-C_-e^{-i\,dk_1})=k_2Te^{i\,dk_2}, \qquad \text{at } x=d. \end{aligned} \tag{41}$$

The coefficients T, R, and $C_\pm$ and the corresponding states $|-p_2^+\rangle$ with incident plane wave coming from the right are given in Appendix B.

A. Weyl approximation

The positive flux according to the Weyl correspondence can be calculated in different ways, depending on whether Eq. (14) is written as the single factor $1/(x_0-x+i0)$ or resolved into principal and delta function parts, and whether an integration by parts is used to reflect the derivative onto the wave functions. Some alternate ways of expressing the relevant formula are

$$\begin{aligned} J^{+W}(x_0)&=\mathrm{tr}[J_{\mathrm{op}}^{+W}(x_0)|\psi\rangle\langle\psi|] \\ &=\frac{-h}{4\pi m}\int dy\left[\mathscr{P}\left(\frac{1}{y}\right)+i\pi\delta(y)\right]\frac{d}{dy}(\langle x_0+y|\psi\rangle \\ &\quad\times\langle\psi|x_0-y\rangle) \\ &=\lim_{\epsilon\to 0}\frac{-\hbar}{4\pi m}\int du\,\frac{\langle\psi|x_0+u\rangle\langle x_0-u|\psi\rangle}{(u+i\varepsilon)^2}, \end{aligned} \tag{42}$$

with similar expressions for the negative flux. (It is also possible to represent the trace as a double integral in phase space and work with the Wigner function[24] but the present route appears to be simpler.) By symmetry of each of these equations, the integrals need be carried out only for positive y or u and twice the real part of the result taken. The evaluation of either of these integrals is relatively straightforward with the aid of the equations of Appendix B but lengthy. The integrand depends on the wave function at two different positions. Because the two wave functions in Eq. (42) change their functional form at different x values [the critical points are $\pm x_0$ and $\pm(d-x_0)$], the integral has to be separated into five different pieces. It is also necessary to distinguish between the cases $0<x_0<d/2$ and $d/2<x_0<d$ and whether $E>V_0$ or $E<V_0$, corresponding to whether the dynamics is classically allowed or whether tunneling occurs.

$J^{+W}(x_0)$ is separated into two types of terms, $J^{+W}(x_0)=J_1+J_2$. The structure of J_1 is common to both cases:

$$\begin{aligned} J_1=&|T|^2p_2/(2mh)+\frac{1}{4\pi^2m}\Im\mathrm{m}\{T(k+k_2)e^{ix_0(k_2-k)}E_1[-i(k_2+k)(d-X)]+TR^*(k_2-k)e^{i(k+k_2)x_0}E_1[-i(k_2-k)(d-X)]\} \\ &+\frac{1}{4\pi^2m}\{\Theta(E-V_0)(|C_+|^2+|C_-|^2)k_1[2\Im\mathrm{m}E_1(2iXk_1)+\pi]-\Theta(V_0-E)2\kappa(E_1(2X\kappa)+E_i(2X\kappa))\Re(C_+C_-^*)]\}, \end{aligned} \tag{43}$$

where $X=\min(x_0,d-x_0)$. In addition, for $0<x_0<d/2$,

$$J_2=\frac{1}{4\pi^2 m}\Im\mathrm{m}\{C_+ e^{ix_0(k_1-k)}(k+k_1)[E_1(-ix_0(k+k_1))-E_1(-i(d-x_0)(k+k_1))]+C_+R^* e^{ix_0(k_1+k)}(k_1-k)$$
$$\times[E_1(-ix_0(k_1-k))-E_1(-i(d-x_0)(k_1-k))]+C_- e^{-ix_0(k_1+k)}(k-k_1)[E_1(ix_0(k_1-k))-E_1(i(d-x_0)(k_1-k))]$$
$$-C_-R^* e^{-ix_0(k_1-k)}(k_1+k)[E_1(ix_0(k_1+k))-E_1(i(d-x_0)(k_1+k))]\} \tag{44}$$

while for $d/2<x_0<d$,

$$J_2=\frac{1}{4\pi^2 m}\Im\mathrm{m}\{TC_+^* e^{ix_0(k_2-k_1^*)}(k_2+k_1^*)[E_1(-i(k_2+k_1^*)(d-x_0))-E_1(-i(k_2+k_1^*)x_0)]$$
$$+TC_-^* e^{ix_0(k_2+k_1^*)}(k_2-k_1^*)[E_1(-i(k_2-k_1^*)(d-x_0))-E_1(-i(k_2-k_1^*)x_0)]\}. \tag{45}$$

B. Symmetrization approximations

The positive flux associated with a wave function ψ and operator $PJ_{\mathrm{op}}P$ is given by the trace

$$\mathrm{tr}\,[PJ_{\mathrm{op}}(x_0)P|\psi\rangle\langle\psi|]$$
$$=\mathrm{tr}\,[J_{\mathrm{op}}(x_0)P|\psi\rangle\langle\psi|P]$$
$$=-\frac{\hbar}{m}\Im\mathrm{m}\left[\langle x_0|P|\psi\rangle\frac{d}{dx_0}\langle\psi|P|x_0\rangle\right]. \tag{46}$$

This is recognized as the standard expression for the flux associated with the wave function $\langle x_0|P|\psi\rangle$. By definition this wavefunction is given by

$$\langle x_0|P|\psi\rangle=\int\langle x_0|P|x\rangle\langle x|\psi\rangle dx$$
$$=\frac{i}{2\pi}\int\frac{1}{x_0-x+i0}\langle x|\psi\rangle dx$$
$$=\frac{1}{2\pi i}\int\left[\mathscr{P}\left(\frac{1}{x-x_0}\right)+i\pi\delta(x-x_0)\right]\langle x|\psi\rangle dx. \tag{47}$$

Using Eq. (39) the projected wave function for the square barrier is explicitly evaluated with the aid of the formulas given in Appendix C in terms of exponential integrals.[25] Restricted to positions x_0 within the barrier ($d>x_0>0$), the result is

$$\langle x_0|P|p^+\rangle=\frac{1}{2\pi i h^{1/2}}\{-e^{ix_0k}E_1(ix_0k)-Re^{-ikx_0}E_1(-ikx_0)$$
$$+C_+e^{ix_0k_1}[E_1(ix_0k_1+i0)-E_1(-i(d-x_0)k_1)$$
$$+2i\pi]+C_-e^{-ix_0k_1}[E_1(-ix_0k_1)$$
$$-E_1(i(d-x_0)k_1+i0)]+Te^{ix_0k_2}$$
$$\times E_1[-i(d-x_0)k_2]\}. \tag{48}$$

The derivative of the complex conjugate of this wave function can be directly carried out. In doing so the derivatives of the exponential integrals lead to terms involving $1/x_0$ and $1/(d-x_0)$. Inherently these can lead to divergences, however, on explicit calculation it can be shown that the matching conditions (41) result in these various terms canceling each other. The final result for the (complex conjugate) derivative is thus

$$\frac{d}{dx_0}\langle p^+|P|x_0\rangle=\frac{1}{2\pi h^{1/2}}\{-ke^{-ikx_0}E_1(-ix_0k)+R^*ke^{ix_0k}E_1(ix_0k)+C_+^*k_1^*e^{-ix_0k_1^*}[E_1(-ix_0k_1^*-i0)-E_1(i(d-x_0)k_1^*)$$
$$-2i\pi]-C_-^*k_1^*e^{ix_0k_1}[E_1(ix_0k_1^*)-E_1(-i(d-x_0)k_1^*-i0)]+T^*k_2e^{-ix_0k_2}E_1[i(d-x_0)k_2]\}, \tag{49}$$

again restricted to $d>x_0>0$.

To approximate $|T|^2$ according to Eq. (7) and expression (34) the negative flux associated with the operator $QJ_{\mathrm{op}}Q$ is also required. It is obtained along similar lines.

The positive flux for a state ψ according to Rivier's rule is given by

$$\mathrm{tr}[J_{\mathrm{op}}^{+R}(x_0)|\psi\rangle\langle\psi|]=-\frac{\hbar}{m}\Im\mathrm{m}\left[\langle x_0|\psi\rangle\frac{d}{dx_0}\langle\psi|P|x_0\rangle\right], \tag{50}$$

requiring the use of Eq. (49) for its evaluation.

C. Pollak's Bound

In the case of a symmetrical square barrier (i.e., $V_1=0$), a remarkable simplification of Eqs. (25) and (26) can be found. It is convenient to write first the diagonal matrix elements appearing in Eq. (26) as

$$\langle x_0|\pm p^+\rangle\langle\pm p^+|x_0\rangle = \frac{2}{\pi\hbar}\,\frac{k^2k_1^2+k^2k_0^2\sin^2[k_1(x_0-d/2\mp d/2)]}{4k^2k_1^2+k_0^4\sin^2(k_1d)}, \tag{51}$$

where $k_0=(2mV_0)^{1/2}/\hbar$. (In all equations of this section x_0 is limited to the barrier region, $0\leqslant x_0\leqslant d$.) These expressions are valid for all k. Substituting them in Eq. (37) and then in Eq. (26) one finds

$$F_{\rm TST}(x_0)=\frac{1}{h}|T|^2\xi(x_0,k), \qquad 0\leqslant x_0\leqslant d, \tag{52}$$

where $|T(k)|^2$ is the transmittance,

$$|T(k)|^2=\left[1+\frac{k_0^4\,\sin^2(k_1d)}{4k^2k_1^2}\right]^{-1}, \tag{53}$$

and the factor $\xi(x_0,k)$ is given by

$$\xi(x_0,k)=\frac{1}{2kk_1}\{[2k^2-k_0^2(\sin^2\,k_1x_0+\sin^2\,k_1(x_0-d))] \times[2k^2-k_0^2(\cos^2\,k_1x_0+\cos^2\,k_1(x_0-d)]\}^{1/2}. \tag{54}$$

From these equations it can be readily seen that for $k>k_0$ and $k_1d=(2n+1)\pi/2$ $(n=0,\pm1,\pm2,\ldots)$, $F_{\rm TST}(x_0)$ becomes independent of x_0 and takes the value

$$F_{\rm TST}(x_0)|_{k_1d=(2n+1)\pi/2}=\frac{1}{h}|T(k)|=\frac{2kk_1}{h(k^2+k_1^2)}. \tag{55}$$

But in general $F_{\rm TST}(x_0)$, $0<x_0<d$, depends on x_0. For any value of k, $F_{\rm TST}(x_0)$ has a minimum at $x_0=d/2$. This is the only minimum for $k<k_0$. For $k>k_0$ there are also minima at $x_n=d/2+n\pi/(2k_1)$, $n=0,\pm1,\pm2,\ldots$. Since $F_{\rm TST}$ takes the same value in all these points it is convenient to consider only the point $x_0=d/2$ (it is the only position that provides a minimum for any k).

Substituting $x_0=d/2$ in Eq. (54) one finds after some algebra the simple result

$$F_{\rm TST}\left(\frac{d}{2}\right)=\frac{1}{h}|T(k)|. \tag{56}$$

Pollak's bound reduces in this case to the inequality

$$|T(k)|^2\leqslant|T(k)|. \tag{57}$$

Thus the bound is exact at resonance, when $|T|=1$, and in general gives an accurate estimate in the limit of transparent barriers, i.e., when $|T|\approx1$. The relative error is

$$\Delta\equiv\frac{|T|-|T|^2}{|T|^2}=\left(\frac{1}{|T|}-1\right). \tag{58}$$

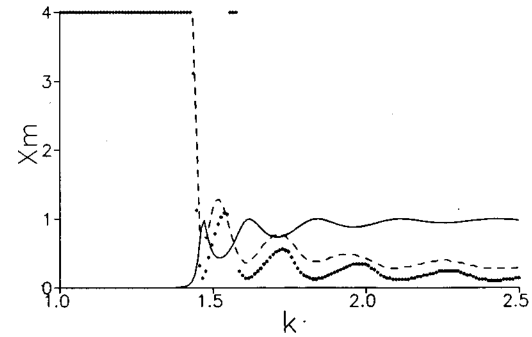

FIG. 1. Position of minimum positive flux, x_m, vs k for a barrier of height $V_0=1$ and width $d=8$. Stars: Weyl rule; Dashed line: PJP symmetrization. The transmittance is also shown for comparison (solid line).

This is larger than 100% when $|T|^2<1/4$, and grows without limit as $|T|^2\to0$. From Eqs. (53) and (58) the simple criterion

$$\frac{k_0^4\,\sin^2\,k_1d}{4k^2k_1^2}<1 \tag{59}$$

provides an estimate for the usefulness of the bound.

IV. COMPARISON

Using the above explicit equations, the approximations due to the Weyl rule, the symmetrization rules (PJP and Rivier), and Pollak's bound to the transmittance [$\mathscr{T}_W,\mathscr{T}_{PJP},\mathscr{T}_R$, and $\mathscr{T}_P$ respectively, or generically $\mathscr{T}$, see Eq. (7)], are compared with the exact result in Figs. 1–9 for the symmetric potential case ($k_2=k, V_1=0$). (In all figures atomic units are used and $m=1$.) Attention is paid to the momenta below the classical threshold $k_0=(2mV_0)^{1/2}/\hbar$ (tunneling) and also immediately above, where it is expected that a one dimensional $QTST$ may disagree with the exact result, and to values of x_0 within the barrier ($0<x_0<d$).

The main findings are:

(i) For all definitions of the positive flux used in the present work the microcanonical QTST approxima-

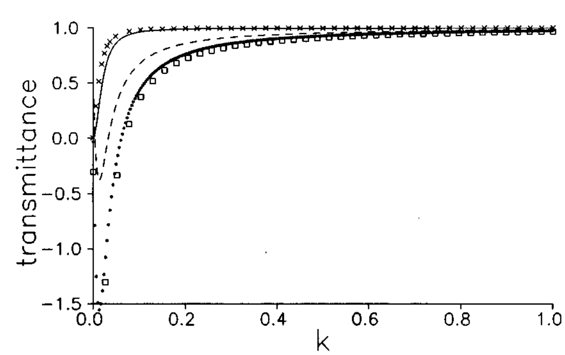

FIG. 2. Transmittance (solid line) vs k for $d=0.2$, $V_0=0.1$ and $x_0=x_m=0.1$. Stars: Weyl rule approximation; Dashed line: PJP symmetrization; Crosses: Pollak's bound; Squares: Rivier's rule.

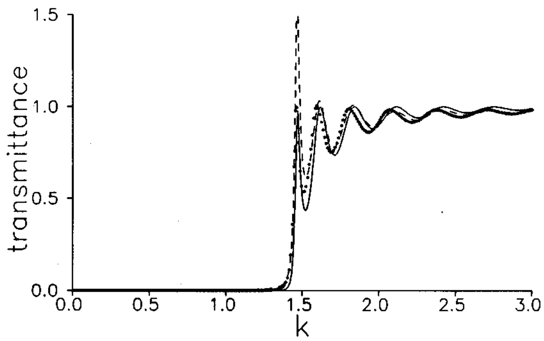

FIG. 3. Transmittance (solid line) vs k for the same barrier used in Fig. 1. Stars: Weyl rule approximation at x_m; Dashed line: PJP symmetrization at x_m.

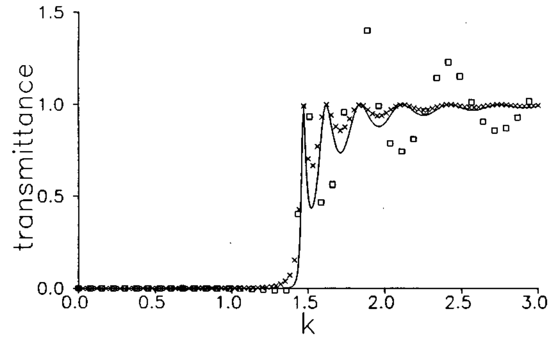

FIG. 5. Transmittance (solid line) vs k for the same barrier used in Fig. 1. Squares: Rivier's rule approximation at $x_0=d/2$; Crosses: Pollak's bound at $x_0=d/2$.

tion to $|T|^2$, Eq. (7), depends on the position x_0 chosen within the barrier. [An exceptional case has been pointed out in Eq. (55).] The position x_m where the minimum positive flux is found is at the center of the barrier, $x_m=d/2$, when $E<V_0$ (except for the Rivier rule). For the Weyl rule and the symmetrical PJP approach x_m is displaced from the center for momenta larger than a momentum threshold (which is slightly above the classical threshold $p_0 \equiv \hbar k_0$), see Fig. 1. Since the positive flux is symmetrical with respect to $d/2$, only the first half of the barrier, $0<x<d/2$, is depicted in Fig. 1. x_m is minimum (i.e. the ''bottleneck'' or transition state is displaced maximally from the center) at the resonance energies. The minimum of Pollak's bound stays at $d/2$ for $E>V_0$ as discussed in the previous section.

(ii) Only $\mathscr{T}_P$ provides an upper bound for the exact value of $|T|^2$. In fact the other approaches can give plainly absurd results such as values smaller than zero (especially the Weyl and Rivier rules for very thin barriers), see Fig. 2, or larger than one, see e.g. Fig. 3.

(iii) The *absolute error* is of $O(1)$ or smaller, and is negligible in many cases, in particular in the tunnelling region (well below threshold) and for large k, see Figs. 3–5.

(iv) For $\mathscr{T}_W$ and $\mathscr{T}_{PJP}$ above the barrier and close to threshold there is a significant difference between the results obtained at x_m or at the center of the barrier $x_0=d/2$, compare Figs. 3 and 4. Above threshold the approximations to $|T|^2$ at the barrier center, Fig. 4, essentially bound the exact result (on close inspection of the numerical data it is found that the bound is not a rigorous one) which is not clearly the case when x_m is chosen, see Fig. 3. Also the approximations obtained at $x_0=d/2$ converge better to the exact result than the calculations at x_m in the high momentum limit. Rivier rule gives the worst results at $x=d/2$, see Fig. 5. They do not improve by using x_m (not shown).

(v) For $E>V_0$ there is no clear winner concerning relative or absolute errors, all methods (except Rivier's) giving similar results, see, e.g., Figs. 3 and 5. Pollak's bound has the merit of locating the resonance peaks exactly and giving the correct value at these points ($|T|^2=1$), although in the valley between resonances the bound is too large. The Weyl rule, when the position for the minimum flux x_m is chosen, systematically shifts the momenta of the resonances to lower values. The symmetrization PJP locates the resonances better, an example is provided in Fig. 3. Rivier's method misses half of the resonance peaks, see Fig. 5.

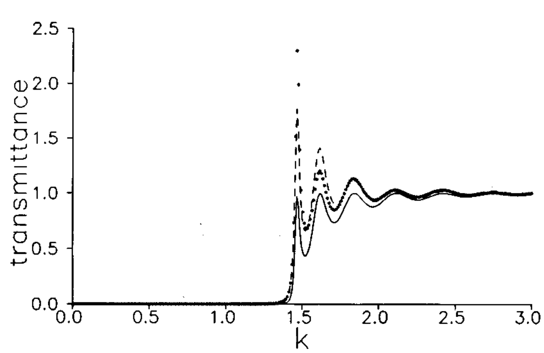

FIG. 4. Transmittance (solid line) vs k for the same barrier used in Fig. 1. Stars: Weyl rule approximation at $x_0=d/2$; Dashed line: PJP symmetrization at $x_0=d/2$.

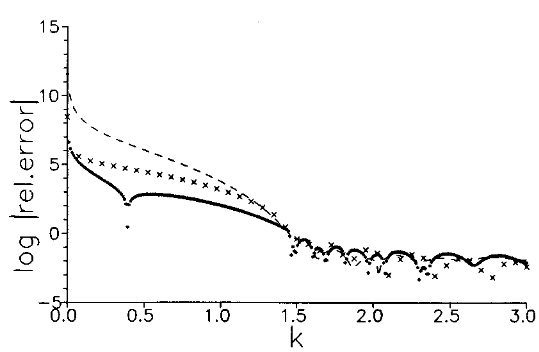

FIG. 6. $\log_{10}$ of the absolute value of the relative error $\Delta=(|T|^2-\mathscr{T})/|T|^2$ vs k, where $\mathscr{T}$ is $\mathscr{T}_W$ (stars) at x_m; $\mathscr{T}_{PJP}$ (dashed line) at x_m; and $\mathscr{T}_P$ (crosses). Same barrier as Fig. 1.

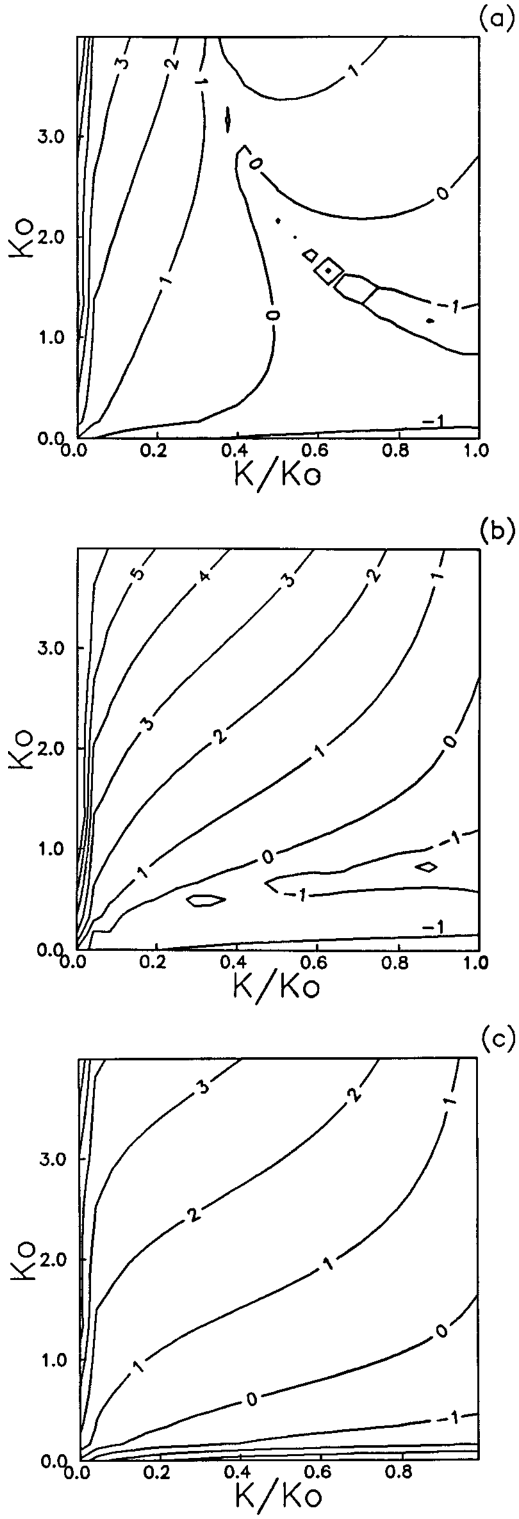

FIG. 7. Contour plots of $\log_{10}(|\Delta|)$ for tunneling momenta; $d=2$ (a) Weyl rule; (b) PJP; (c) Pollak's bound.

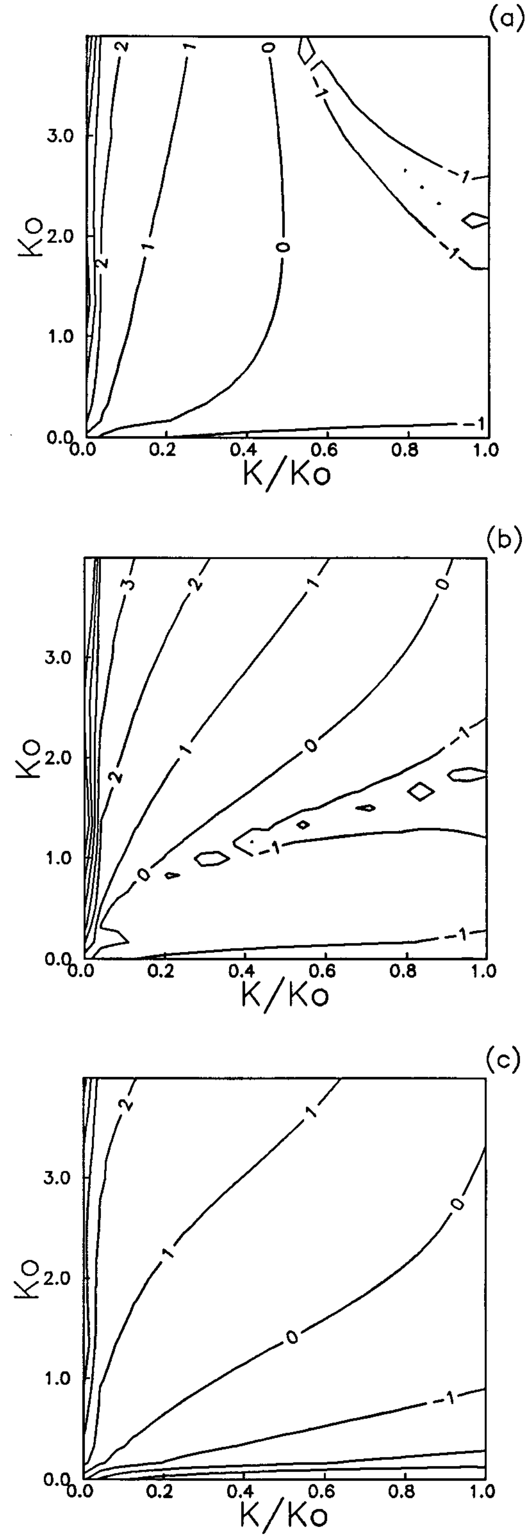

FIG. 8. Contour plots of $\log_{10}(|\Delta|)$ for tunneling momenta; $d=1$ (a): Weyl rule; (b) PJP; (c) Pollak's bound.

(vi) As a general trend the *relative error* decreases with k. It is large for tunneling energies, see Fig. 6.

(vii) Contour maps showing the logarithm ($\log_{10}$) of the (absolute value of the) relative error with respect to k_0 and k/k_0 at various values of d are shown for tunnelling energies in Figs. 7–9. Note that in these figures the contour 0 means that the relative error is 100%; -1 implies a 10% error, etc. In summary, the range of parameters (d,k_0,k) where the approximations are valid (say, $\log|\Delta|<-1$) is very limited. For fixed barrier width d the Weyl rule performs better

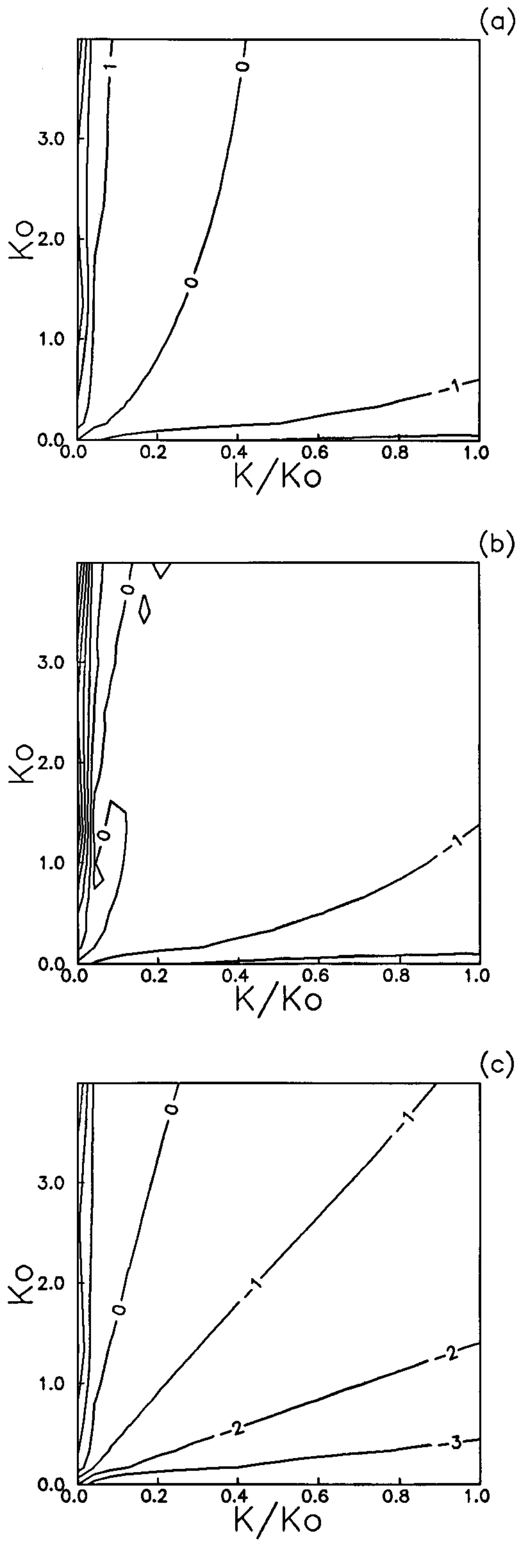

FIG. 9. Contour plots of $\log_{10}(|\Delta|)$ for tunneling momenta; $d=0.2$ (a) Weyl rule; (b) PJP; (c) Pollak's bound.

than the other methods for high (opaque) barriers, the symmetrical operator PJP gives the best results for intermediate barriers, and Pollak's approach for small (transparent) barriers. Rivier's approach is never better than the other three methods. All these approximations are poor at very low momenta. As expected, for extremely thin (almost transparent) barriers Pollak's method improves significantly.

V. DISCUSSION

In a realistic application of quantum transition state theory to a chemical system a number of additional approximations are generally involved, both formal (such as separability of the Hamiltonian at the transition state) and numerical (e.g., in the calculation of integrals using a finite basis set) that can make unclear the actual origin of the disagreement with exact results.[14] This has motivated the present study where the ''chemical system'' is reduced to the bare bones of a one dimensional barrier, where the averaging has been reduced by considering only the microcanonical ensemble, and where all quantities can be obtained exactly and explicitly in terms of known functions.

At this level of simplification the fundamental TST assumption to be tested is whether or not the quantum positive flux provides an accurate transmittance. Unfortunately the meaning of ''quantum positive flux'' is not obvious, so the test has to be performed on different implementations (operators) of this concept. In this work we have examined for the square barrier two old candidates, one based on Weyl's rule and one based on a variational approach, together with two new candidates, each of which is based on a (different) symmetrization of the basic operators involved. Examples have been provided of their behavior for several barriers and energy ranges. For tunneling energies the relative errors are only small in very limited regions of the parameter space of the system.

Other positive flux operators could also be investigated. A positive flux operator has been proposed[26,27] using the fact that in a finite real square integrable basis the flux operator J_{op} has only two eigenvectors with (nonzero) eigenvalues of opposite sign. Selecting only the positive eigenvalue and its eigenvector provides seemingly a natural definition for a positive flux operator. Unfortunately, as the basis is increased the eigenvalue tends to infinity, a problem already noted by McLafferty and Pechukas.[28] A detailed examination of the convergence properties or usefulness of this procedure could be analyzed with the aid of the present potential model.

As it occurs for many problems involving noncommuting observables,[29] it is difficult to justify from first principles a particular quantization of the positive flux. In fact there is no universally valid principle in quantum mechanics that selects one operator in particular, and every application requires a separate study. In the context of transition state theory there is at least the advantage that it is known what a ''good operator'' should do. However, it is not at all evident that the fundamental hypothesis in terms of a positive flux and the ideal objective are entirely compatible. After all, the initial motivation for a quantum transition state theory is simply the success of its classical counterpart. But, regarding the classical rate constant as an approximation to the exact quantum rate, all that CTST may provide is a good aproximation to the classical rate which is in turn only an approximation to the true quantum rate.

From this perspective the approach of QTST trying to quantize a secondary approximation to the exact rate seems somewhat convoluted, and a direct route based on approximating directly the exact quantum rate, regardless of what may or may not work in the classical case appears to be more natural. Indeed many approaches to evaluate the reaction rate, which retain in some cases a strong TST flavor, are primarily based on direct approximations of the exact quantum expression.[6,7,30] It is thus not strange that reviews on QTST have reflected some degree of pessimism or even exasperation.[2–4] In spite of the drawbacks, the quantum translation of the TST idea remains an appealing objective, in part because there is so much to gain, and in part because there are so many avenues yet to be explored. Clearly the different quantizations that have been proposed for the positive flux do not exhaust all possibilities, and surely much remains to be done in trying to find operators that bound accurately the exact rate.[12,28] (An additional reason for investigating these operators is a proposed relation between the lifetime of resonances and the flux directed in the outgoing direction.[31]) The square barrier provides a severe test for these attempts and can readily show ranges of validity or limitations. It offers analytical expressions and a relative flexibility due to the possible variation of four parameters: width, height, energy difference between ‘‘reactants’’ and ‘‘products’’ potential energies, and location within the barrier.

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APPENDIX A: THE WEYL POSITIVE FLUX FOR A PLANE WAVE

The Wigner function for the density operator representing a plane wave $\varrho_p \equiv |p\rangle\langle p|$ is given by

$$W(p',x) = h^{-1}\delta(p-p'). \tag{A1}$$

The corresponding flux takes the form

$$\begin{aligned} J(x_0) &= \mathrm{tr}[\varrho_p J_{\mathrm{op}}(x_0)] \\ &= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dx dp \frac{1}{h}\delta(p-p')\frac{p'}{m}\delta(x-x_0) \\ &= \frac{p}{hm} \end{aligned} \tag{A2}$$

Because of the delta function $\delta(p-p')$ the momentum integral does not change by shifting the lower limit to 0 when $p>0$. In this case $J(x_0)$ is equal to the positive flux $J^{+W}(x_0)$, but if $p<0$ the positive flux vanishes. These results can also be obtained in coordinate representation using the expression (14) for the positive flux operator. The positive flux is separated into the two terms associated with the delta function and the principal part in Eq. (14): $J^{+W} = J^+_\delta + J^+_{\mathscr{P}}$

$$\begin{aligned} J^+_\delta &= \frac{1}{4\pi m i}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dx\ dx'\ e^{-ip(x-x')/\hbar}\delta \\ &\quad\times\left[x_0 - \frac{x+x'}{2}\right]\frac{\partial}{\partial x}\delta(x-x'). \end{aligned} \tag{A3}$$

For the integration of the delta functions it is convenient to introduce the new variables $s=(x+x')/2, y=x-x'$ and then integrate by parts on y to give

$$\begin{aligned} J^+_\delta &= \frac{1}{4\pi m i}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} ds\ dy\ e^{-ipy/\hbar}\delta(x_0-s)\delta'(y) \\ &= \frac{p}{2mh}. \end{aligned} \tag{A4}$$

The same change of variables and integration by parts for the principal part term lead to

$$\begin{aligned} J^+_{\mathscr{P}} &= \frac{1}{4\pi^2 m}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dx dx' e^{-ip(x-x')/\hbar}\delta \\ &\quad\times\left[x_0 - \frac{x+x'}{2}\right]\frac{\partial}{\partial x}\mathscr{P}\left(\frac{1}{x-x'}\right) \\ &= \frac{ip}{2\pi m h}\mathscr{P}\int_{-\infty}^{\infty} dy \frac{e^{-ipy/\hbar}}{y} \\ &= \frac{p}{2\pi m h}\int_{-\infty}^{\infty} dy \frac{\sin(py/\hbar)}{y} = \frac{|p|}{2mh}. \end{aligned} \tag{A5}$$

This route shows the importance of keeping both the delta and principal part terms in Eq. (14). The final result, $J^{+W} = \Theta(p)p/(hm)$, can also be obtained without explicit separation into the two terms by using the formula

$$\frac{1}{x-x'+i0} = \mathscr{P}\left(\frac{1}{x-x'}\right) - i\pi\delta(x-x'), \tag{A6}$$

changing to s and y variables in

$$\begin{aligned} J^{+W}(x_0) &= \frac{1}{4\pi^2 m}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dx\ dx' e^{-ip(x-x')/\hbar}\delta \\ &\quad\times\left[x_0 - \frac{x+x'}{2}\right]\frac{\partial}{\partial x}\frac{1}{x-x'+i\epsilon} \\ &= \frac{-1}{4\pi^2 m}\int_{-\infty}^{\infty} dy \frac{e^{-ipy/\hbar}}{(y+i\varepsilon)^2} = \frac{p}{mh}\Theta(p), \end{aligned} \tag{A7}$$

and taking the limit $\epsilon \to 0$ after the final y integral is carried out by closing the contour above (when $p<0$) or below (when $p>0$) in the complex y plane.

APPENDIX B: INCIDENT NEGATIVE MOMENTA

The state $|-p_2^+\rangle$ corresponding to incident negative momentum $-p_2<0$ has the following coordinate representation:

$$\langle x|-p_2^+\rangle=\begin{cases} h^{-1/2}\hat{T}e^{-ixk}, & -\infty<x<0\\ h^{-1/2}[\hat{C}_+e^{-ixk_1}+\hat{C}_-e^{ixk_1}], & 0<x<d\\ h^{-1/2}[e^{-ixk_2}+\hat{R}e^{ixk_2}], & x>d\end{cases} \tag{B1}$$

The coefficients in Eqs. (39) and (B1) are given by the following expressions

$$C_+=2F^{-1}k(k_1+k_2)e^{-idk_1}, \tag{B2}$$

$$C_-=2F^{-1}k(k_1-k_2)e^{idk_1}, \tag{B3}$$

$$T=4F^{-1}kk_1e^{-idk_2}, \tag{B4}$$

$$R=F^{-1}[e^{-ik_1d}(k_2+k_1)(k-k_1) +e^{idk_1}(k_1-k_2)(k+k_1)], \tag{B5}$$

$$\hat{C}_+=2F^{-1}k_2(k_1+k)e^{-idk_2}, \tag{B6}$$

$$\hat{C}_-=2F^{-1}k_2(k_1-k)e^{-idk_2}, \tag{B7}$$

$$\hat{T}=4F^{-1}k_1k_2e^{-idk_2}, \tag{B8}$$

$$\hat{R}=F^{-1}[e^{-ik_1d}(k+k_1)(k_2-k_1) +e^{i\,dk_1}(k_1-k)(k_2+k_1)]e^{-2idk_2}, \tag{B9}$$

where

$$F=e^{idk_1}(k_1-k_2)(k-k_1)+e^{-idk_1}(k+k_1)(k_1+k_2). \tag{B10}$$

APPENDIX C: EXPONENTIAL INTEGRALS

The two basic exponential integrals used in the text are

$$E_1(z)=\int_z^\infty \frac{e^{-Y}}{Y}dY, \qquad |\arg z|<\pi, \tag{C1}$$

where the contour does not cross the negative real axis, and

$$E_i(x)=-\mathscr{P}\int_{-x}^\infty \frac{e^{-Y}}{Y}dY, \qquad x>0. \tag{C2}$$

Their numerical evaluation is readily available through library subroutines based on a combination of Taylor series, asymptotic series and continued fractions.[32] They are related by

$$E_1(-x\pm i0)=-E_i(x)\mp i\pi. \tag{C3}$$

By contour deformation it is possible to reduce the integrals arising in Sec. III to combinations of exponential integrals. In particular, for $a,b>0$,

$$\int_a^\infty \frac{e^{iY}}{Y}dY=E_1(-ia), \tag{C4}$$

$$\mathscr{P}\int_{-a}^b \frac{e^{iY}}{Y}dY=E_1(ia)-E_1(-ib)+i\pi, \tag{C5}$$

$$\mathscr{P}\int_{-a}^b \frac{e^{-Y}}{Y}dY=-E_i(a)-E_1(b), \tag{C6}$$

$$\int_z^\infty \frac{e^{-Y}}{Y^2}dY\equiv\frac{E_2(z)}{z^2}=\frac{e^{-z}}{z}-E_1(z). \tag{C7}$$

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