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A study of the quantal time delay matrix in collinear reactive scattering

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The Eisenbud–Wigner time delay matrix is used to study the dynamics of reaction close to vibrationally adiabatic barrier energies. Maxima in the time delay are predicted and are found to be in excellent agreement with vibrationally adiabatic barrier energies determined by quantized pods. The actual time spent in the vicinity of the barriers is estimated by separating out the free particle time. This "real time" is then used to analyze the validity of the adiabatic and sudden approaches to reactive scattering in the 3D H + H_2 and D + H_2 reactions.

I. INTRODUCTION

In classical mechanics it is very easy to define the duration of a collisional event. One measures the time it takes the particles to move from one point in space to another. In quantum mechanics, the uncertainty principle prevents such a simple determination. Using a wave packet analysis Bohm,[1] Eisenbud,[2] and Wigner[3] have shown that one may extract a time delay associated with energy derivatives of the S matrix. Smith[4] has pointed out that the time operator in quantum mechanics is just $-i\hbar(d/dE)$ thus formally justifying the wave packet analysis. The time delay is just the excess (positive or negative) time spent by the colliding particles due to the interaction potential.

The time delay has been studied extensively for atom–molecule reactions. Levine and Wu[5] used the time delay as an analytic tool to prove the existence of quantal resonances in collinear reactive scattering. If a resonance exists one should observe a large time delay in the vicinity of the resonance energy. Kuppermann and co-workers[6] have studied the energy dependence of the eigenvalues of the Smith time delay matrix. They showed that quantal resonances may be understood in terms of maxima in the eigenvalues. These numerical studies of resonances and their delay times have recently been applied to three dimensional systems. Wyatt and co-workers[7] have used a j_z conserving approximation, Baer, Kouri, and co-workers[8] a sudden approximation, and Walker and Hayes[9] an adiabatic approach. All these studies have documented, via time delay analysis, the existence of resonances in quantal 3D reactive scattering.

Time delays have also been studied within a semiclassical framework. Connor and co-workers[10] have ana-lyzed resonances using the semiclassical S matrix and find good agreement with exact quantal results. The formal theory has also been studied extensively by Brumer, Osborne, and others.[11] Brumer and co-workers[12] also studied the classical time delay in collinear reactive scattering.

The purpose of this paper is also to use the time delay as a diagnostic tool, but our emphasis will be on the time delay in the vicinity of barriers to reaction. Our interest in this problem was stimulated by several different sources. One of the unsolved problems in quantum mechanics is the seemingly innocuous question—how long does it take to tunnel through a potential barrier.[13] Most studies trying to answer this question have dealt with square barrier potentials.[13,14] For such systems, in the deep tunneling regime the time delay diverges and is independent of the length of the barrier. This seemingly unphysical behavior has led various researchers to devise new definitions for time in scattering theory.[13,14] Of course, most chemical systems do not have square barrier potentials, rather, they are "smooth" barrier potentials. Thus it is of interest to study the properties of the time delay to see whether the "unphysical" behavior persists also for Eckart like potential barriers. If one is guided by classical mechanics then one would expect the quantal passage time to be zero at the energetic threshold, to have a maximum at the barrier energy and go down again to zero as the energy becomes infinite.

One of the popular approximations in molecular reactive scattering is vibrationally adiabatic transition state theory, developed by Truhlar and co-workers[15] and by Pollak.[16] If our hypothesis that the quantal time for crossing a barrier has a maximum at the barrier energy is correct then just as with resonances one should be able to use a time delay analysis to identify and confirm vibrationally adiabatic barrier energies.

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Not only is the location of the time delay maxima of interest. The magnitude of the delay may be of important significance. Mayne *et al.*[17] have pointed out, using classical trajectories, that a large delay time in the vicinity of a barrier to reaction may allow direct spectroscopic detection of the barrier energy. Intuitively we expect the quantal traversal time to be shorter than the classical time which is infinite precisely at the barrier energy.

Finally, the magnitude of the time spent in the vicinity of the barrier should be an important factor in understanding the transition from adiabatic to sudden dynamics in reactive scattering.[18] In quantal transition state theory[19] it has always been assumed that at threshold energies one should quantize the energy of the internal degrees of freedom which are perpendicular to the reaction coordinate. Specifically, in the 3D hydrogen exchange reaction, Kuppermann[6] and Schatz[20] have shown that the quantal threshold to reaction is indeed the adiabatic threshold—that is, it is the sum of the zero point energies of the internal vibrational *and* bend degrees of freedom. Comparison of the infinite order sudden approximation[21] (IOSA) cross sections with exact quantal results show that at threshold the IOSA cross sections are too large. However at post threshold energies the IOSA agrees very well with the exact quantal computation. Schatz[20] has roughly estimated that the time spent in the vicinity of the barrier is much shorter than a bend period. This has led him to question the adiabatic hypothesis. He then concludes[20] that the underlying justification for quantizing the bend motion is an "uncertainty principle constraint." Thus it is of interest to take a careful look at the magnitude of the time spent in the barrier region, and compare it with the bend period to see whether the adiabatic hypothesis is indeed invalid in the H + H$_2$ reaction.

In Sec. II we study the semiclassical time delay matrix for a one dimensional barrier potential. In Sec. III, we analyze the time delay matrix of the collinear H + H$_2$ and D + H$_2$ exchange reactions on the LSTH[22] potential energy surface. In Sec. IV we discuss the implications of our study on the transition from adiabatic to sudden dynamics in reactive scattering.

II. A BARRIER IN ONE DIMENSION

In this section we will study the time delay matrix for a one mathematical dimensional Hamiltonian

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) \tag{1}$$

whose potential $V(x)$ is assumed to have the following properties:

$$V(x) \sim \begin{cases} 0 & x \to -\infty \\ V_0 - m\tilde{\omega}^2\frac{x^2}{2} & x \simeq 0. \\ -V_\infty & x \to +\infty \end{cases} \tag{2}$$

Here V_0 is the barrier height, V_∞ the reaction exoergicity, and $\tilde{\omega}$ the imaginary frequency at the top of the barrier.

The S matrix at energy E is defined by the boundary conditions from the incident ($x \to -\infty$) and final ($x \to +\infty$) channels:

$$\psi_i \sim \begin{cases} \frac{1}{\sqrt{k}} e^{ikx} + \frac{1}{\sqrt{k}} S_{ii}e^{-ikx} & x \to -\infty \\ \frac{1}{\sqrt{k'}} S_{if}e^{ik'x} & x \to +\infty \end{cases} ,$$

$$\psi_f \sim \begin{cases} \frac{1}{\sqrt{k'}} e^{-ik'x} + \frac{1}{\sqrt{k'}} S_{ff}e^{ik'x} & x \to +\infty \\ \frac{1}{k} S_{fi} e^{-ikx} & x \to -\infty \end{cases} \tag{3}$$

Here the wave numbers k, k' obey the relationship

$$E = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 k'^2}{2m} - V_\infty. \tag{4}$$

The S matrix is unitary and symmetric, these properties may be summarized without loss of generality by writing the S-matrix elements in the following form:

$$S_{if} = S_{fi} = T^{1/2} \exp\left[\frac{i}{\hbar}(\theta_i + \theta_f - \phi)\right],$$

$$S_{ii} = R^{1/2} \exp\left[\frac{i}{\hbar}\left(2\theta_i - \phi - \frac{\pi\hbar}{2}\right)\right],$$

$$S_{ff} = R^{1/2} \exp\left[\frac{i}{\hbar}\left(2\theta_f - \phi - \frac{\pi\hbar}{2}\right)\right],$$

$$R = |S_{ii}|^2 = |S_{ff}|^2, \quad T = |S_{if}|^2, \quad R + T = 1. \tag{5}$$

Here the phases θ_i, θ_f, ϕ are real functions of the energy.

The time delay matrix may be defined in two different forms. The Eisenbud–Wigner matrix[2,3] denoted as τ has elements τ_{ij} defined by the relationship

$$\tau_{ij} = \text{Re}\left[-i\hbar(S_{ij})^{-1} \frac{dS_{ij}}{dE}\right]. \tag{6}$$

It is easy to see that for the one dimensional problem at hand the matrix τ may be written as

$$\tau = \begin{bmatrix} \frac{d}{dE}(2\theta_i - \phi) & \frac{d}{dE}(\theta_i + \theta_f - \phi) \\ \frac{d}{dE}(\theta_i + \theta_f - \phi) & \frac{d}{dE}(2\theta_f - \phi) \end{bmatrix}. \tag{7}$$

The Smith lifetime matrix,[4] denoted as $\mathbf{Q}$ is defined by

$$\mathbf{Q} = -i\hbar\left(\frac{d\mathbf{S}}{dE}\right)\mathbf{S}^\dagger. \tag{8}$$

It is a matter of simple manipulation to see that the elements q_{ij} of $\mathbf{Q}$ are

$$q_{11} = \frac{d}{dE}(\theta_i + \theta_f - \phi) + R\frac{d}{dE}(\theta_i - \theta_f),$$

$$q_{12} = (RT)^{1/2}e^{(i/\hbar)(\theta_i-\theta_f)}\left[\frac{\hbar}{2}\frac{d}{dE}\ln\left(\frac{T}{R}\right) + i\frac{d}{dE}(\theta_f - \theta_i)\right]. \tag{9}$$

$$q_{21} = (RT)^{1/2}e^{-(i/\hbar)(\theta_i-\theta_f)}\left[\frac{\hbar}{2}\frac{d}{dE}\ln\left(\frac{T}{R}\right) - i\frac{d}{dE}(\theta_f - \theta_i)\right]$$

$$q_{23} = \frac{d}{dE}(\theta_i + \theta_f - \phi) - R\frac{d}{dE}(\theta_i - \theta_f)$$

It is well known that the matrices $\mathbf{Q}$ and τ are not equivalent; however, as shown by Smith[4] there is a relationship between them. Thus

$$q_{ll} = R \cdot \tau_{ll} + T\tau_{if}, \quad l = i, f \tag{10}$$

and

$$\text{Tr } \mathbf{Q} = \text{Tr } \tau = 2 \frac{d}{dE} (\theta_i + \theta_f - \phi). \tag{11}$$

To proceed we find the semiclassical estimate of the S matrix. Using the connection formulas developed by Connor[23] and Child[24] one obtains the following results. For $E \leq V_0$ one has two turning points $x_+ > 0$, $x_- < 0$ for which $V(x_\pm) = E$. The phase functions θ_i and θ_f are connected with the classical action of the trajectory impinging on the barrier from the left and from the right:

$$\theta_i(E) = \lim_{x \to -\infty} \left(\int_x^{x_-} \{2m[E - V(x)]\}^{1/2} dx + \hbar k x \right), \tag{12}$$

$$\theta_f(E) = \lim_{x \to +\infty} \left(\int_{x_+}^{x} \{2m[E - V(x)]\}^{1/2} dx - \hbar k' x \right). \tag{13}$$

Note that $\hbar k' x$ and $-\hbar k x$ are just the classical action of a free particle with momentum $\hbar k'(\hbar k)$ traversing from $x = 0$ to x (from x to $x = 0$). Thus the phase functions θ_i and θ_f are the excess action to the right and left of the barrier due to the interaction potential. The phase function ϕ^{23} is the "quantum correction function" and is given as

$$(1/\hbar)\phi(\epsilon) = \epsilon + \arg \Gamma(\tfrac{1}{2} + i\epsilon) - \epsilon \ln|\epsilon|, \tag{14}$$

where ϵ is the (reduced) imaginary action

$$\epsilon = -\frac{1}{\pi\hbar} \int_{x_-}^{x_+} \{2m(V(x) - E)\}^{1/2} dx, \quad E \leq V_0. \tag{15}$$

For $E > V_0$ one substitutes x_- and x_+ by $x = 0$ in Eqs. (12) and (13) while x_- and x_+ in Eq. (15) are taken to be the imaginary turning points of the potential $V(x)$. The function $\phi(\epsilon)$ is well behaved, it is an odd function of ϵ, it goes to zero at $\epsilon = 0$, ∞ and has a single maximum in between. The reflection and transmission probabilities are given by the familiar expressions

$$T = (1 + e^{-2\pi\epsilon})^{-1}, \tag{16}$$

$$R = e^{-2\pi\epsilon} \cdot T. \tag{17}$$

To obtain the quantal time delays one needs the derivative with respect to energy of the phase functions θ_i, θ_f, and ϕ. It is easy to see that

$$\frac{\partial \theta_i}{\partial E} = t_i - t_i^{\text{fp}}, \quad \frac{\partial \theta_f}{\partial E} = t_f - t_f^{\text{fp}}. \tag{18}$$

Here $t_i(t_f)$ is the time it takes a classical trajectory originating at $x = -\infty$ ($x = \infty$) with energy E to reach the turning point $x_-(x_+) \cdot t_i^{\text{fp}}(f_f^{\text{fp}})$ is the time it would take a free particle originating at $-\infty(\infty)$ to reach $x = 0$. Thus the energy derivative of the phase functions gives a time delay—the excess time spent by a classical particle in the interaction region due to the interaction potential. To obtain the derivative of $\phi(\epsilon)$ we first note that

$$\frac{d\epsilon}{dE} = \frac{1}{\pi\hbar} t_{\text{Im}}, \tag{19}$$

where t_{Im} is the time it takes a classical particle to go from x_- to x_+ on the *inverted* potential energy surface.[25] t_{Im} is the semiclassical imaginary time associated with tunneling. Accordingly

$$\frac{d\phi(\epsilon)}{dE} = \frac{1}{\pi} t_{\text{Im}}[F(\epsilon) - \ln|\epsilon|], \tag{20}$$

where the function $F(\epsilon)$ may be shown to be[26]

$$F(\epsilon) \equiv \psi\left(\frac{1}{2}\right) + G(\epsilon)$$

$$= \psi\left(\frac{1}{2}\right) + \epsilon^2 \sum_{n=0}^{\infty} \frac{1}{(n + \frac{1}{2})[\epsilon^2 + (\frac{1}{2} + n)^2]}. \tag{21}$$

Here $\psi(\frac{1}{2})$ is a number $\psi(\frac{1}{2}) = -1.963\,51. \ldots$ The function $G(\epsilon)$ is plotted in Fig. 1. Note that for $\epsilon \to \infty$, $F(\epsilon) - \ln|\epsilon| \sim 1/\epsilon^2$ so that for large ϵ, $d\phi/dE \to 0$.

Thus far our treatment has been general. In the following we will restrict ourselves to the inverse harmonic oscillator potential shown in Fig. 2. This will enable us to provide simple analytic results and so give more insight into the qualitative behavior of the time delays. For this model one only needs to integrate from $x_<$, $x_>$ instead of $(-\infty, \infty)$ and one obtains the following expressions:

$$\epsilon = \frac{E - V_0}{\hbar\tilde{\omega}},$$

$$t_i = \frac{1}{2\tilde{\omega}} \ln \frac{\sqrt{V_0} + \sqrt{E}}{|\sqrt{V_0} - \sqrt{E}|},$$

$$t_f = \frac{1}{2\tilde{\omega}} \ln \frac{\sqrt{V_0 + V_\infty} + \sqrt{E + V_\infty}}{|\sqrt{V_0 + V_\infty} - \sqrt{E + V_\infty}|},$$

$$t_i^{\text{fp}} = \frac{1}{\tilde{\omega}} \sqrt{\frac{V_0}{E}}, \quad t_f^{\text{fp}} = \frac{1}{\tilde{\omega}} \frac{\sqrt{V_0 + V_\infty}}{\sqrt{E + V_\infty}}. \tag{22}$$
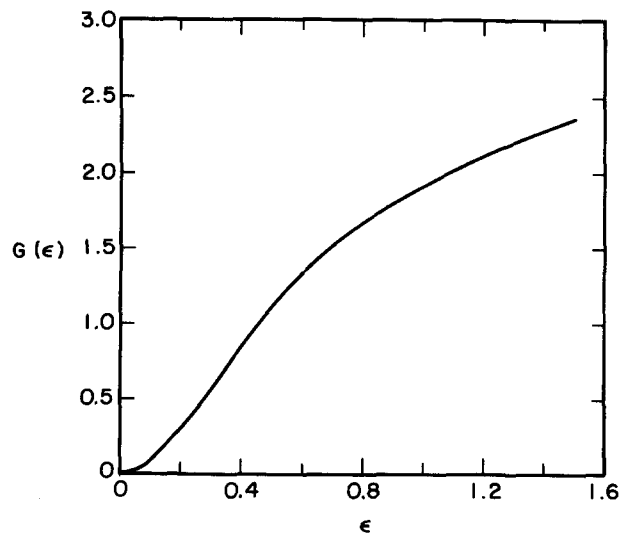
FIG. 1. A plot of the function $G(\epsilon)$ [cf. Eq. (21)]. For $\epsilon \geq 1.5$, $G(\epsilon)$ is excellently approximated as

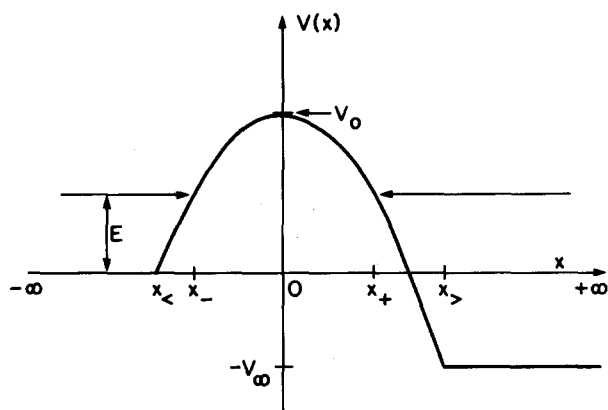$$-\psi\left(\frac{1}{2}\right) + \ln|\epsilon| - \frac{1}{24\epsilon^2}\left(1 + \frac{7}{60\epsilon^2}\right).$$

FIG. 2. Schematic diagram of an inverse harmonic oscillator potential. x_-, x_+ are the turning points at energy E. $x_<$, $x_>$ are the limits of the potential—beyond them one has a free particle potential. V_0 is the barrier height and V_∞ the exoergicity of the reaction.

It is then easy to see that

$$\text{Tr } \mathbf{Q} = 2 \frac{d}{dE} (\theta_i + \theta_f - \phi)$$

$$= \frac{2}{\tilde{\omega}} \left[\ln \frac{(\sqrt{V_0} + \sqrt{E})(\sqrt{V_0 + V_\infty} + \sqrt{E + V_\infty})}{\hbar \tilde{\omega}} \right.$$

$$\left. - F(\epsilon) \right] - 2(t_i^{\text{fp}} + t_f^{\text{fp}}) = 2(t_{\text{i.h.o}} - t_{\text{fp}}). \tag{23}$$

Equation (23) is the central result of this section. Note that in contrast to the square barrier potential, the quantal time $t_{\text{i.h.o.}}$ it takes to cross the barrier does not diverge at any energy! In fact, for $E \to \infty$, $t_{\text{i.h.o.}} \to 0$, for $E \to 0$ $t_{\text{i.h.o.}}$ is small but finite. One may also show that $t_{\text{i.h.o.}}$ has a maximum at an energy very close to the barrier height, but slightly larger. Note that although $F(\epsilon)$ is a symmetric function of ϵ, $t_i + t_f$ is not. Classically one spends more time in the barrier region when $\epsilon > 0$. However for most potentials the asymmetry is small. For a symmetric potential ($V_\infty = 0$) one finds from Eqs. (21) and (23) that the shift in the maximum (ΔE) from V_0 is well approximated by

$$\Delta E \sim 2.971 \times 10^{-2} \frac{(\hbar \tilde{\omega})^2}{V_0} \tag{24}$$

so that unless the barrier is extremely thin, the delay time will have a maximum at the barrier energy. Equation (23) also implies that in contrast to the square barrier, even in the deep tunneling region $t_{\text{i.h.o.}}$ *is* very much dependent on the shape of the barrier. The flatter the barrier, the smaller $\tilde{\omega}$ and the larger is $t_{\text{i.h.o.}}$.

One may convince oneself that in the semiclassical limit the qualitative features found for the i.h.o. remain valid for any smooth barrier potential. The tunneling time through the barrier may be attributed solely to the contribution arising from the quantum correction function [Eq. (20)] which may be used as a definition of the tunneling time. For deep tunneling, ϵ is large so that $d\phi/dE$ is finite but small. It is not clear whether in an exact quantal treatment the tunneling time actually remains finite at threshold. But the semiclassical limit analysis

does indicate that the tunneling time does not diverge as in the case of a square barrier. This implies that one must be very careful before reaching conclusions based only on analysis of square barrier potentials.[13,14] The small tunneling time at threshold is also significant in relation to the adiabatic-sudden transition which will be discussed in Sec. IV.

Equation (23) simplifies for a symmetric barrier. Using the "reduced" notation

$$e \equiv \frac{\epsilon}{\hbar \tilde{\omega}}, \quad v_0 = \frac{V_0}{\hbar \tilde{\omega}}, \quad \theta \equiv \tilde{\omega} t_{\text{i.h.o.}} \tag{25}$$

one finds that

$$\theta(e, v_0) = 2 \ln(\sqrt{e} + \sqrt{v_0}) - F(e - v_0). \tag{26}$$

In Fig. 3 we plot $\theta(e, v_0)$ as a function of e for v_0 values of 0.1, 1, and 10. Note that Eq. (24) predicts the maximum of θ very accurately over this whole range. Note also the negative time for the thin barrier around threshold. This is probably due to the breakdown of the semiclassical approximation for this extreme case. Finally note that the maximal value of θ is an increasing function of v_0. The larger v_0 the thicker the barrier and the longer it takes to cross it. In fact it is easy to see from Eq. (26) that the maximal time delay increases logarithmically with v_0.

Thus far we have analyzed in detail the trace of the lifetime matrices τ and $\mathbf{Q}$. As is evident from Eqs. (7) and (8) one may analyze a variety of elements and definitions for the time delay. One may look at the eigenvalues of the matrices or the diagonal elements or each element separately. It is though not very clear what the physical significance of each such element is. Instead of making an attempt at providing a detailed analysis, we prefer to take a more pragmatic approach. Our main objective is to identify barriers in reaction dynamics. From our analysis it is clear that the function $(d/dE)(\theta_i + \theta_f - \phi)$ is suitable for this purpose. Inspection of Eq.
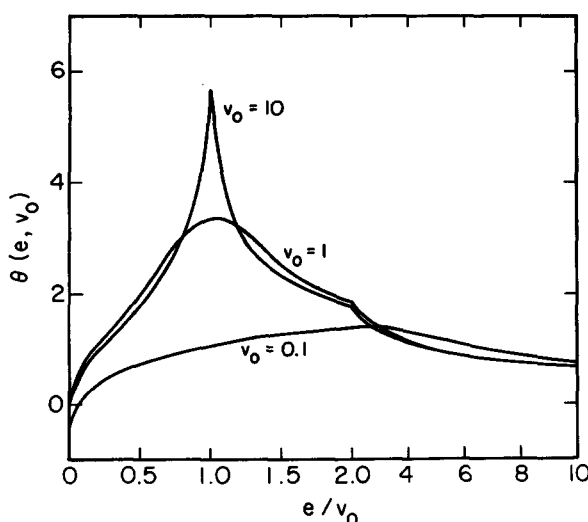

FIG. 3. Reduced traversal time (θ) for a symmetric inverted harmonic oscillator potential as a function of the reduced energy (e) and reduced barrier height v_0. Note that for $v_0 = 1$, 10, θ peaks very close to the barrier height. For further details see the text.

(7) shows that this corresponds to the element τ_{if} in the Wigner–Eisenbud matrix τ. Thus in the next section we will analyze only this time delay.

III. THE COLLINEAR H_3 SYSTEM

The vibrationally adiabatic barriers of the collinear H_3 system have been well characterized by various methods.[27-29] Invariably though, the question how important are these barriers was answered by comparing adiabatic reaction probabilities or rate constants with exact quantal results. Pollak and Pechukas[30] and Ashton et al.[31] have shown that classical trajectories usually are vibrationally adiabatic from the barrier outwards towards the entrance or exit channel. In this section we provide a different test of the adiabatic assumption. Using the results of the previous section, we look for maxima in the quantal time delays of the H_3 system and correlate them with known vibrationally adiabatic barrier heights.

The collinear vibrationally adiabatic barrier energies of the HHH and DHH systems on the LSTH potential energy surface are given in Table I. In Fig. 4 we plot the quantal time delay obtained for the $n = 0 \rightarrow n = 0$ and $n = 1 \rightarrow n = 1$ reactive transitions using the Eisenbud–Wigner methodology—Eq. (6). There are two notable features in these time delays; one at $E \sim 0.55$ eV, the other at $E \sim 0.89$. The former correlates excellently with the $n = 0$ adiabatic barrier energy, the latter with the lowest quantal resonance of the system.[6] Qualitatively, we already find for $n = 0$ good agreement between the time and the adiabatic barrier height. For $n = 1$, the barrier is masked by the prominent resonance feature.

One of the "hard" problems in any time delay analysis is separation of the free particle contribution to obtain the "true" time spent by the system in the interaction region. However, the analysis of the previous section suggests that for deep tunneling the true time is actually very small, implying that the large negative time delays observed in the threshold region are primarily due to the free particle contribution. If the potential has a finite range as in the inverse harmonic oscillator than the free particle contribution is proportional to $E_T^{-1/2}$. In Fig. 5 we plot the two time delays shown in Fig. 4 as functions of $1/\sqrt{E_T}$. Note the linearity in the threshold region. From the slope one may extract an effective length (L_{fp}^{nn}) for the interaction region by assuming that

FIG. 4. Time delays of the H + H_2 exchange reaction. τ_{if}^{00} and τ_{if}^{11} are the Eisenbud–Wigner time delays for the reactive transitions from initial vibrational state $n = 0$ to final state $n = 0$ and $n = 1$ to $n = 1$, respectively. The energy is relative to the bottom of the asymptotic H_2 well.

$$\tau_{fp}^{nn} = \frac{2L_{fp}^{nn}}{(2E_T/\mu)^{1/2}}, \tag{27}$$

where μ is the atom–diatom reduced mass. From Fig. 5 we find $L_{fp}^{00} = 4.78$ bohr, $L_{fp}^{11} = 5.19$ bohr. Both of these numbers are reasonable when one considers that the $n = 0$ adiabatic barrier is found at (atom to center of mass of diatom distance) 2.64 bohr[23] and the $n = 1$ adiabatic barrier at 3.35 bohr.[32] At high energies one expects the free particle time to go to zero. Thus in principle, if the potential is of finite range then the straight lines shown in Fig. 5 should intercept the τ axis at $\tau = 0$. This is not so for the lines of Fig. 5. Actually, one does expect the effective length of the interaction region to decrease with energy. In the limit of very high energy it should be the sum of the radii of two H atoms, thus the straight line

TABLE I. Vibrational adiabatic barrier heights[a] of the H_3 system.

System	n	E_n	$E_n^{\ddagger b}$
H + HH	0	0.270	0.548
	1	0.787	0.897
D + HH	0	0.270	0.530
	1	0.787	0.895
H + HD	0	0.235	0.530
	1	0.685	0.819

[a] All energies are in eV relative to the bottom of the asymptotic HH well.
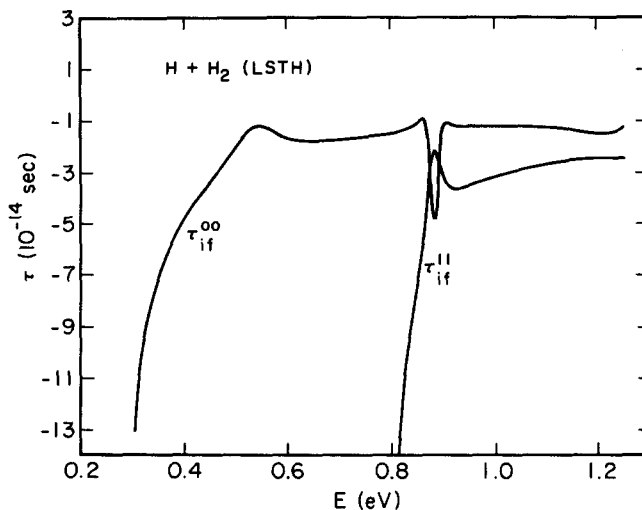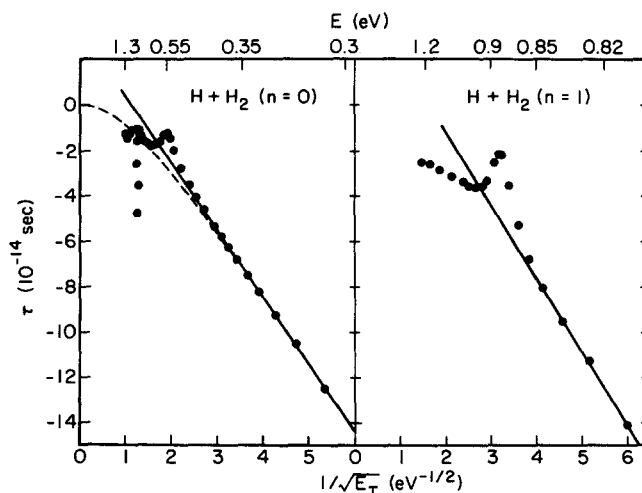[b] Based on evaluation by quantized pods (Refs. 27 and 32).

FIG. 5. Time delays of the H_3 system as functions of $E_T^{-1/2}$. The top scale shows the total energy. The dots are the actual time delays, the straight solid lines show the linear dependence of the time delay on $E_T^{-1/2}$ in the threshold region. The dashed line is a qualitative estimate of the true free particle time at all energies. For further details see the text.

should curve as shown schematically by the dashed line in Fig. 5. However, in the threshold region, this curvature is hopefully not very large so that a *reasonable* estimate of the actual time spent by the system in the barrier region may be obtained by subtracting the free particle time estimated by extrapolating the threshold behavior. The net result for the $n = 0$ barrier is shown in Fig. 6. Here the dots are the net time while the solid line is an inverse harmonic oscillator *prediction* based on Eq. (23) and on the adiabatic barrier height (cf. Table I) and the known imaginary frequency[22] ($\hbar\tilde{\omega} = 0.1848$ eV) of the LSTH surface. Note that the location of the maximum and magnitude of the time spent at the barrier maximum are well accounted for by the inverse harmonic oscillator prediction. Since v_0 is ~ 1.5, Eq. (24) predicts a negligible (~ 0.004 eV) shift of the maximum relative to the barrier height. Note also that had we used the dashed line shown in Fig. 5 as the background contribution, agreement with the i.h.o. model would have been better.

In summary, we have seen that at least for the ground state hydrogen exchange reaction, the qualitative features of the quantal time delay may be understood with the aid of the inverse harmonic oscillator analysis of the previous section. However, for excited states the quantal resonances mask out any delay arising from vibrationally excited adiabatic barriers. Therefore we will also study the time delay in a system which does not exhibit resonance structure—the $D + H_2 \rightarrow DH + H$ exchange reaction on the LSTH potential energy surface.

The 0–0 and 1–1 reactive time delays of the $D + H_2$ system are plotted in Fig. 7. Consider first the 0–0 time delay. There are three noticeable bumps. The first one corresponds to the $n = 0$ adiabatic barrier energy. The next two correspond to the HD $n = 1$ and $n = 2$ adiabatic barrier energies in the *exit* channel. Two qualitative features are noteworthy. The last two bumps are a

FIG. 7. Time delays of the $D + H_2$ exchange reaction. The arrows denote the vibrationally adiabatic barrier heights in the entrance (HH) and exit (HD) channels as obtained from quantized pods (cf. Table I). All other notation is as in Fig. 4. The dashed line is a qualitative estimate of the background—see the text.

result of vibrationally nonadiabatic interactions and so cannot be analyzed with the simple model of Sec. II. More importantly, the HH ($n = 1$) entrance channel barrier has no effect on the 0–0 time delay.

Since the $D + H_2$ system is asymmetric one has to work a bit harder on extracting the background. As is evident from the matrix in Eq. (7), the background of a reactive element is the average of the backgrounds of the nonreactive elements. Therefore in Fig. 8 we plot the two 0–0 unreactive time delays as functions of $1/\sqrt{E_T}$. Again we find the expected linear dependence in the threshold regions. The slopes of the lines give free particle lengths [cf. Eq. (27)] of 4.70 bohr for the entrance ($D + H_2$) channel and 5.03 bohr for the exit (H + HD) channel, both results are in reasonable agreement with the length found for $H + H_2$. Using these slopes one obtains an average background for the reactive transition which is subtracted from the time delay shown in Fig. 7. The net time spent at the $D + H_2$ $n = 0$ barrier for the reactive channel is shown in Fig. 9. The time peaks at $E = 0.515$ eV in good agreement with the pods estimate. Note, that as predicted by the pods (and as might be expected from
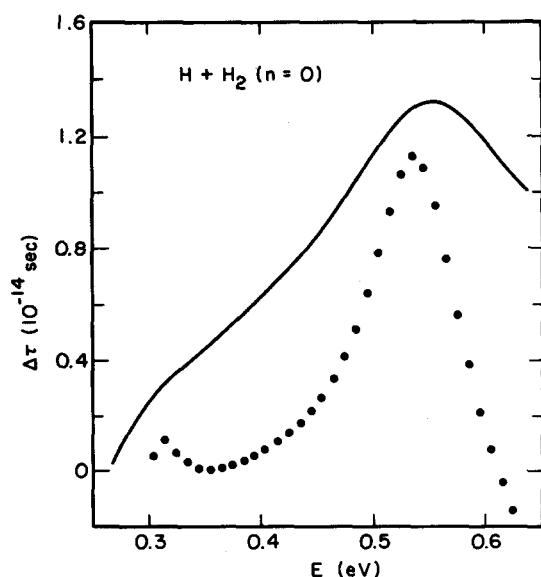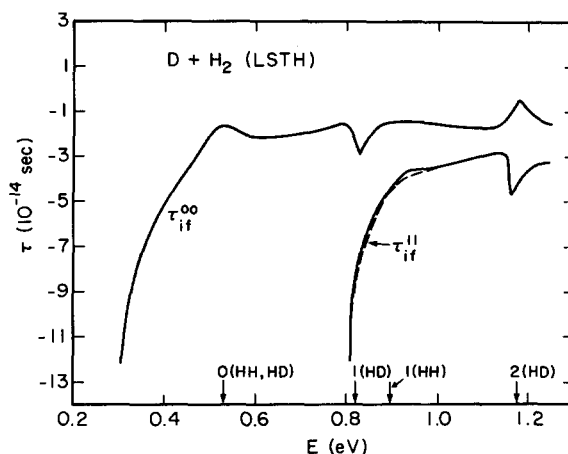

FIG. 6. The time spent at the barrier for the $H + H_2$ ($n = 0$) reaction. The dots are the difference between the time delay and the background contribution as estimated from Fig. 5. The solid line is an inverse harmonic oscillator estimate. For further details see the text.
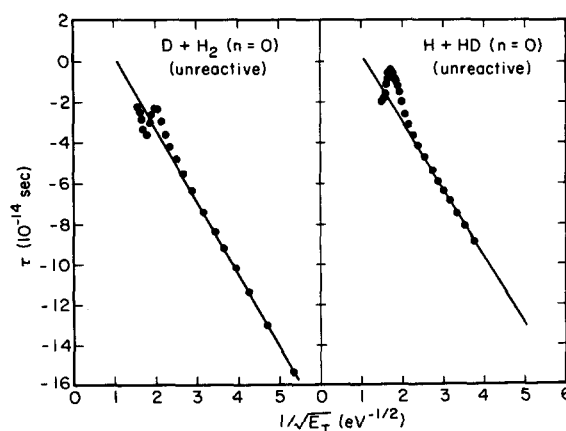

FIG. 8. Unreactive ground vibrational state time delays of the $D + H_2$ system as functions of $E_T^{-1/2}$. Other notation is as in Fig. 5.
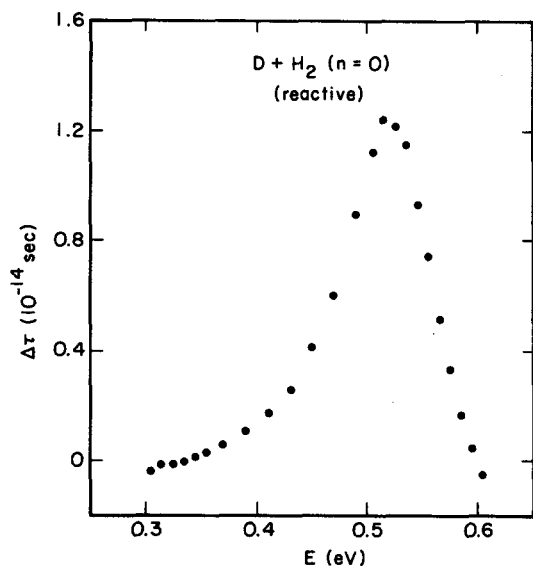
FIG. 9. The time spent at the barrier for the D + H_2 (n = 0) reaction. For further details see the text.

the heavier mass of the D atom) the barrier here is lower in energy than the H + H_2 (n = 0) barrier. Except for this slight shift, the ground state times for H + H_2 and D + H_2 are very similar.

The 1–1 reactive time delay shown in Fig. 7 is a bit surprising. Both the entrance and exit channel n = 1 adiabatic barrier are barely noticeable. With a bit of imagination (the dashed line) one does notice a slight delay at the barrier energies but the delay is in any case very small. The n = 2 HD barrier is though very noticeable, again this is a vibrationally nonadiabatic effect.

IV. DISCUSSION

The analysis of the previous sections has established two facts. Time delays may be used to identify vibrationally adiabatic barriers to reaction. Secondly, in contrast to square barriers, for smooth barriers, a particle tunnels through a large barrier very rapidly; the particle is delayed significantly only if its energy is of the order of the barrier energy. As a result the threshold time delays are just the free particle traversal time. This gives us a tool with which to estimate the real time spent by the particle as it passes through the barrier.

One of the major purposes of our study was to understand the threshold behavior of 3D reactive cross sections. In the H + H_2 system,[20] both for the ground and first excited vibrational states the 3D thresholds seem to be determined adiabatically with respect to the vibrational and the bending motion. Thus the 3D thresholds are given by the sum of the collinear vibrationally adiabatic barrier heights and the zero point bend energy at the barrier. In the following we will study in detail whether the separation of time scales necessary to justify the adiabatic result really exists.

To do so we must first decide on a quantitative criterion with which to judge whether one is in the adiabatic limit. It is very suggestive to use the dimensionless product of the frequency ω of the internal degrees of

freedom and the net time $\Delta\tau$ spent at the barrier. Surely if $\omega\Delta\tau \gg 1$ one is in the adiabatic limit, if $\omega\Delta\tau \ll 1$ the sudden limit is obtained. Note that this criterion implies that internal motion at the barrier will be quantized if the period of the internal motion is at least $(1/2\pi)\Delta\tau$—seemingly one does not have to stay a long time in the vicinity of the barrier before quantization of the internal motion sets in. A qualitative justification for this criterion has been given by Miller based on semiclassical analysis of resonances.[33]

Consider first the "simpler" vibrational problem. Both for H + H_2 and D + H_2 the vibrational frequency of the pods at the n = 0 and n = 1 barriers is of the order of 2000 and 3500 cm^{-1}, respectively.[16] The criterion $\omega\Delta\tau \geq 1$ implies that the time $\Delta\tau$ spent at the barrier must be at least 0.26×10^{-14} and 0.15×10^{-14} s for n = 0 and n = 1, respectively. Inspection of Figs. 6 and 9 shows that for n = 0 this criterion implies that vibrational adiabaticity is justified at translational energies that are ~0.1 eV less than the barrier height. At such energies the reaction probability is already so low ($\leq 5 \times 10^{-4}$) so it is not surprising that the threshold to reaction is the vibrationally adiabatic threshold. For n = 1, the picture is not as clear; however, the conclusion is similar. For the H + H_2 system it is evident from Fig. 5 that already at 0.05 eV less than the n = 1 barrier energy $\omega\Delta\tau$ = 1. Although it is difficult to determine separately the resonance contribution and the barrier contribution it is plausible that at least 10% of $\Delta\tau$ is contributed by the barrier, this is enough to justify quantization of the vibrational motion at the barrier. For D + H_2 (n = 1) the same is true if one is willing to believe the dashed line as a good estimate of the background.

The picture becomes more interesting when considering the bend motion. For both reactions the bend frequencies ω_B for n = 0, 1 are ~900 and 650 cm^{-1}, respectively.[20,22,32,34] The criterion $\omega_B\Delta\tau \geq 1$ implies that $\Delta\tau \geq 0.6 \times 10^{-14}$ and 0.8×10^{-14} s for the ground and first excited vibrational states, respectively. For the ground state reactions, this implies that quantization of the bend may be justified at least very close to the barrier energy but beyond ±0.05 eV of the barrier energy the time delay does not justify an adiabatic approach to the bend motion. For D + H_2 (n = 1) the problem is even more severe. It is clear that for all energies in the barrier region $\omega_B\Delta\tau \ll 1$.

To summarize, thus far we have seen that the time delay analysis justifies an adiabatic approach to vibrational motion. However, in contrast to exact quantal calculations, one should not expect the bending degree of freedom to behave adiabatically. As noted in Ref. 20 this poses a fundamental problem—why do the exact quantal 3D results show adiabatic behavior for the bend degree of freedom?

Beyond a time scale argument, adiabatic dynamics will also occur if the system is separable. Consider for example the vibrational degree of freedom for D + HH (n = 1). The vibrational frequency at the vibrationally adiabatic barrier is only slightly less than the asymptotic H_2 frequency. Here the vibrational degree of freedom is

almost separable so that it is really not surprising that the exact collinear quantal results are vibrationally adiabatic in the threshold region. The bend motion is however *not* separable. Asymptotically, the bend motion turns into a free rotation. There is a large variation in the bend potential along the reaction coordinate.

One may always criticize our analysis by noting that we have only studied collinear scattering. Surely the adiabatic bend potential may alter the true 3D time delays. Although we do not claim that the time delay in 3D will be the same as in 1D it is plausible to assume that the same qualitative features will remain. That is, in the deep tunneling and post barrier energy ranges, the time delay analysis does not justify quantization of the bend degrees of freedom.

Schatz[20] has argued that quantization of the internal degrees of freedom at a barrier is a basic law of nature, as a result of the uncertainty principle. Here we should point out that the sudden approximation to the bend motion does not violate the uncertainty principle. The proof, although trivial, is given in detail in the Appendix, so as to remove all doubt. Of course in the sudden limit, motion of internal degrees of freedom need not be quantized and in fact is not quantized at the transition state.

If so, the question persists, why do exact 3D quantal results show adiabatic behavior with respect to the bend motion? One may suggest a few alternatives. One is the possibility that the time delay is not the "only" time scale; this point is currently being investigated intensively.[35,36] Another possibility is that in fact the true behavior of the 3D system is actually not adiabatic.[37] Here it should be noted, that in agreement with our present time delay analysis, a recent study by Pollak and Wyatt[18] shows that at translational energies ~ 0.05 eV above the barrier, exact quantal scattering results are sudden-like in nature and not adiabatic. It is also well known that the sudden approximation is very useful for predicting inelastic scattering cross sections.[38] Consider the threshold region of the H + H$_2$ ($n = 0$) system. At low translational energies a sudden approach is assumed reasonable for rotationally inelastic scattering again in agreement with our time delay analysis. Could it be that the solution of the paradox is simply that most systems will behave suddenly with respect to the bend motion rather than adiabatically?

APPENDIX: THE UNCERTAINTY PRINCIPLE IS NOT VIOLATED IN THE SUDDEN LIMIT

Let $\hat{q}$ and $\hat{p}$ be the quantal position and momentum operators. Let $\psi(\hat{q})$ denote a quantal wave function. Let $\langle \hat{O} \rangle$ denote the mean of operator $\hat{O}$:

$$\langle \hat{O} \rangle = \frac{\langle \psi | \hat{O} | \psi \rangle}{\langle \psi | \psi \rangle}. \tag{A1}$$

The uncertainty principle may be stated as[39]

$$U \equiv \langle \Delta \hat{q} \rangle \langle \Delta \hat{p} \rangle \geq \hbar/2, \tag{A2}$$

where

$$\langle \Delta \hat{O} \rangle \equiv \langle (\hat{O} - \langle \hat{O} \rangle)^2 \rangle. \tag{A3}$$

Consider now the sudden limit. Here one freezes a coordinate γ and finds the exact quantal wave function $\psi_s(q'; \gamma)$ for a γ-dependent Hamiltonian. By definition then for each fixed γ, the sudden wave function ψ_s obeys the uncertainty principle

$$U_s(\gamma) \equiv \langle \Delta \hat{q}' \rangle_\gamma \langle \Delta \hat{p}' \rangle_\gamma \geq \hbar/2. \tag{A4}$$

Here the notation $\langle \ \rangle_\gamma$ serves to remind us that the expectation value is taken over the sudden wave function and the prime denotes all coordinate and momentum operators other than γ and p_γ. Within the sudden approximation, the global uncertainty is obtained by averaging $U_s(\gamma)$ over all angles

$$U \equiv \frac{\int_0^\pi U_s(\gamma) \sin \gamma \, d\gamma}{\int_0^\pi \sin \gamma \, d\gamma} \geq \frac{\hbar}{2}, \tag{A5}$$

where the inequality is obtained by putting Eq. (A4) explicitly in the numerator. Thus, the sudden limit is internally consistent and obeys the uncertainty principle.

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