Response to ''Comment on 'On the relation between unimolecular reaction rates and overlapping resonances' '' [J. Chem. Phys. 106, 4810 (1997)]

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I. INTRODUCTION

In reply to Rotter's comment on our paper (Ref. 1) we choose to start from an apparent point of agreement: The effective microcanonical decay rate $k(E)$ of a quasibound system should saturate with increasing coupling between the quasibound states and the continuum. It is quite challenging to observe this saturation directly in experiments, since normally a change of the coupling implies also a change in energy. However, the phenomenon was illustrated theoretically for different models. The origin of the saturation is a point of dispute:

In Ref. 1 we argue and illustrate that this saturation is consistent with the ''bottle-neck'' picture of transition state theory (TST or RRKM), which relates the saturation value to the number of independent decay channels $[k_{\mathrm{eff}}(E)=N(E)/(2\pi\hbar\rho(E))]$, rather than to the widths of particular resonance states of the system.

In contrast, in Ref. 2 it is argued that the saturation is associated with a ''trapping effect'' (bifurcation of resonance widths) which relates the effective decay rate at high coupling (or high level density) to the widths of a sub-group of long-lived resonance states ($k_{\mathrm{eff}}(E)\leqslant\langle\Gamma\rangle/\hbar$).

Our previous work[1] emphasized the physical *interpretation* of the rate saturation, on the basis of a multidimensional extension of one dimensional analytic models. The detailed *mechanism* of the phenomenon was not considered in Ref. 1. Below we discuss in some detail this mechanism within the random matrix version of the optical model. We illustrate that the deviation of the simulated rate from $\langle\Gamma\rangle/\hbar$ ($\langle\Gamma\rangle$ being the average resonance width) towards the saturation region is indeed associated with a *broadening of the distribution of resonance widths*. However, this tendency is observed long before the onset of the trapping effect, i.e., *the bifurcation of the resonance widths into two distinctive groups of ''fast'' and ''slow'' ones*. Moreover, the trapping effect is associated with a *decrease* of the simulated effective decay rate which follows the saturation region, and therefore the saturation can not be attributed to this effect. We relate the nonphysical behavior associated with the trapping effect to a physically inconsistent matrix approximation of the effective Hamiltonian model.

II. THE OPTICAL MODEL AND THE TRAPPING EFFECT

In its rigorous version,[3] the optical model relates each resonance eigenstate of a decaying system to an effective Hamiltonian which depends on the particular (complex) resonance energy (E)

$$H_{\mathrm{eff}}(E)\ \ Q\psi_E=E\ \ Q\psi_E, \tag{1}$$

where

$$H_{\mathrm{eff}}(E)=QHQ+QHP\,\frac{1}{E-PHP+i\epsilon}\,PHQ. \tag{2}$$

H is the Hamiltonian and Q and P are the projection operators into the bound and continuum spaces, respectively. The solutions of Eq. (1) are the exact resonance states of the system, being the eigenstates of the Schrödinger equation in the bound (Q) space with outgoing wave boundary conditions in the continuum (P) space.[3]

It is a common *approximation* to relate a group of *different resonance states* to the eigenvalues of *the same effective Hamiltonian matrix*. Considering N quasibound states and K independent decay channels ($K<N$) in a narrow energy interval, an energy independent matrix representation of the effective Hamiltonian can be obtained, in which QHQ is a real matrix of rank N, and the residual $QHP[E-PHP+i\epsilon]^{-1}PHQ$ is a complex matrix of rank K. For sufficiently small bound continuum coupling matrix elements (PHQ) the spectrum of the effective Hamiltonian matrix consist of N complex eigenvalues whose energy shifts and widths are small with respect to the energy interval (i.e., with respect to the spectral range of the bound Hamiltonian QHQ).

As the bound-continuum coupling increases the residual matrix (of rank K) becomes dominant and eventually controls the rank of the effective Hamiltonian matrix. In such a case the spectrum splits into a group of K eigenvalues whose widths increase monotonically with increasing bound continuum coupling, and a group of $N-K$ eigenvalues whose widths become negligible with respect to the other ones. The onset of this ''bifurcation'' is the basis for the trapping effect suggested by Rotter. Clearly, this effect is an intrinsic property of *matrix approximations* of the optical model.

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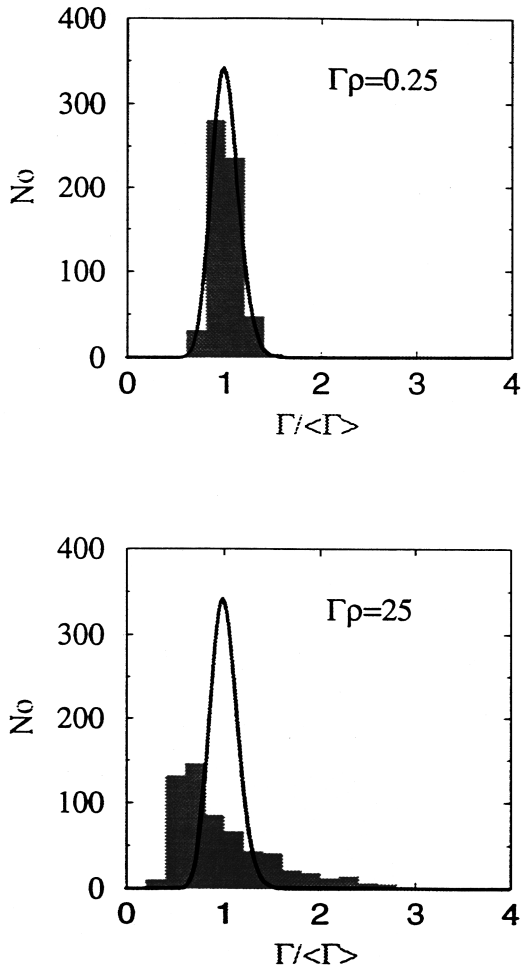

FIG. 1. Histogram: Distribution of resonance width about the average value as obtained from random matrix diagonalization with $N=600$, $K=100$, and $\rho=5$ 1/cm^{-1}. Solid: A χ^2 distribution with 100 degrees of freedom. Top: $\langle\Gamma\rangle=2\pi K\sigma^2=0.05$ cm^{-1} (weak coupling). Bottom: $\langle\Gamma\rangle=2\pi K\sigma^2=5.0$ cm^{-1} (strong coupling).

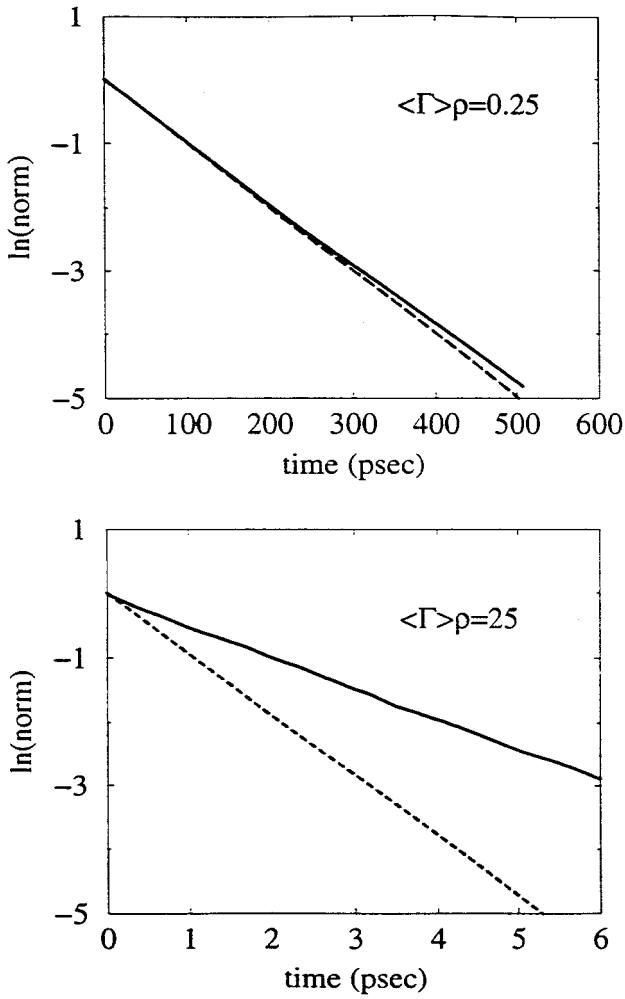

FIG. 2. Solid: $\ln(|\Phi(t)|^2)$ as a function of time as obtained from random matrix diagonalization with $N=600$, $K=100$, $\rho=5$, and (1/cm^{-1}). Dashed: $-\langle\Gamma\rangle t/\hbar$. Top: $\langle\Gamma\rangle=0.05$ cm^{-1} (weak coupling). Bottom: $\langle\Gamma\rangle=5.0$ cm^{-1} (strong coupling).

III. THE MECHANISM OF RATE SATURATION

Within the random matrix approximation, the effective $N\times N$ Hamiltonian matrix reads

$$[H_{\text{eff}}]_{m,m'}=E_m\delta_{m,m'}-i\pi\sum_{n=1}^{K}V_{m,n}V_{m',n}, \tag{3}$$

where E_m are chosen from a Wigner distribution of level spacings and $V_{m,n}$ are chosen from a normal distribution with a mean $\langle V_{m,n}\rangle=0$ and a standard deviation $\langle V_{m,n}^2\rangle=\sigma^2$. The eigenvalues of H_{eff}, $\{E_m-i/2\Gamma_m\}$ correspond to the resonance eigenstates of the system.

In Fig. 1 typical distributions of resonance widths (imaginary parts of the resonance eigenvalues) are plotted. For sufficiently small bound-continuum coupling, the widths distribution follows a χ^2 distribution with K degrees of freedom, as expected according to perturbation theory (the golden rule limit), $\Gamma_m\approx\Sigma_{n=1}^{K}V_{m,n}^2$. For larger bound-continuum coupling, a broadening of the widths distribution is observed with strong deviation from χ^2.[4] In Fig. 2 the corresponding decay curves are plotted for a uniform random vector in the *Q-space*. Clearly, in the perturbative regime, the standard relation $k=\langle\Gamma\rangle/\hbar$ is quite well fulfilled, but with increasing bound continuum coupling a strong deviation from this relation towards a smaller effective slope (k) is apparent.

It is straightforward to recognize the relation between the broadening of the widths distribution and the decrease of the effective decay rate with respect to $\langle\Gamma\rangle/\hbar$, eventually leading to the saturation (as observed in Ref. 1). The asymmetry of the broadened distribution in Fig. 2 suggests that a *small group* of widths above average is balanced by a *large group* of widths below average. The majority of states are therefore decaying with a rate slower than $\langle\Gamma\rangle/\hbar$. Although this simple explanation neglects possible interference effects between different resonance states, a reasonable explanation is given for the observed saturation tendency.

The deviation of the rate from $\langle\Gamma\rangle/\hbar$ occurs long before the onset of the trapping effect, i.e., long before the resonance widths bifurcate into two distinctive groups of ''large'' and ''small'' widths (see the distributions in Fig. 1). It is quite arbitrary (and thus *meaningless*) in this situation to

relate the observed decay rate to a particular group of slow resonance states, and to ignore the others. In contrast, our TST interpretation in Ref. 1 which does not relate the simulated rate to particular resonance widths still applies.

IV. THE TRAPPING EFFECT PREVENTS SATURATION WITHIN RANDOM MATRIX SIMULATIONS

When the ''bifurcation'' occurs and two time scales are well separated the simulated decay rate is dominated by the long-lived states, while the short lived states contribute only at initial times as explained by Rotter. It is an implicit property of the random matrix approximation (see Sec. II) that with increasing coupling, the $N-K$ small widths become smaller. In this situation the decay is in fact dominated by *nonoverlapping resonances*(!). Consequently, the simulated decay rate is related to the $N-K$ small widths by the standard relation for non overlapping resonances ($k=\langle\Gamma\rangle/\hbar$), which implies that not only the widths, but also *the effective decay rate decreases with increasing coupling, i.e., does not saturate*. This decrease of the effective rate was confirmed in ours and in Rotter's random matrix simulations.[1,2]

Thus within the random matrix version of the optical model, the onset of the trapping (bifurcation) effect as the coupling increases corresponds to the onset of the *decrease* of the effective rate with increasing coupling, not with its saturation. This contradicts physical intuition i.e., TST, analytical models, and random matrix simulations *before* the bifurcation region (see Fig. 3 in Ref. 1). This nonphysical decrease is consistent, however, with the failure to approximate the exact resonances of the system with a single effective Hamiltonian matrix when the bound-continuum coupling is too large. In Ref. 1 we pointed out the condition for breakdown of the random matrix approximation and related it to a sampling error which allows for some resonance widths to exceed the entire energy interval. More generally, the sampling error implies that the spectral domain (real or imaginary parts) of the residual operator exceeds the spectral range of QHQ. Note that this limitation of the random matrix model does not contradict its application to overlapping resonances. The condition for overlap (i.e., that resonance widths are larger than the typical level spacings ΔE) is met long before the model limitation is reached (i.e., when resonance widths are larger than the energy interval, $N\times\Delta E$).

V. CONCLUSIONS

The effective energy-dependent decay rate of a system saturates with increasing bound-continuum coupling. This saturation is consistent with a TST interpretation of the optical model as presented in Ref. 1, but not with the onset of two different time scales as suggested in Ref. 2. At least according to our random matrix simulations the saturation tendency, i.e., $k<\langle\Gamma\rangle/\hbar$, is associated with a broadening of the widths distribution long before the bifurcation of the resonance widths into two different groups. It is meaningless in this situation to associate the effective decay rate with a sub-group of widths and to ignore the others. Moreover, when the onset of bifurcation is reached, the effective decay rate *decreases* with increasing bound continuum coupling, and not saturates. We relate the onset of this nonphysical behavior to a sampling error which violates the condition for applicability of the matrix approximation of the optical model.

The exact limit beyond which the random matrix approximation to the effective Hamiltonian ceases to be physically meaningful is the subject of ongoing investigation and scrutiny, and may vary for different applications. For unimolecular reactions, the regime of small to moderate resonance overlap (or bound-continuum coupling) appears to be most relevant, and this regime is removed from the onset of the bifurcation. Our results within the random matrix approximation show that even in this regime saturation of the rates is approached, and comparing this behavior with that obtained in other model potentials (see Ref. 1) we give this saturation trend an interpretation based on transition state theory.

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[1] U. Peskin, H. Reisler, and W. H. Miller, J. Chem. Phys. **101**, 9672 (1994).
[2] I. Rotter, J. Chem. Phys. **106**, 4810 (1997), preceding paper.
[3] H. Feshbach, *Theoretical Nuclear Physics: Nuclear Reactions* (Wiley, New York, 1991).
[4] V. Peskin, W. H. Miller, and H. Reisler, J. Chem. Phys. **102**, 8874 (1995).