Random-Matrix Approach to Transition-State Theory

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To model a complex system intrinsically separated by a barrier, we use two random Hamiltonians, coupled to each other either by a tunneling matrix element or by an intermediate transition state. We study that model in the universal limit of large matrix dimension. We calculate the average probability $\langle P_{ab} \rangle$ for transition from scattering channel $a$ coupled to the first Hamiltonian to scattering channel $b$ coupled to the second Hamiltonian. Using only the assumption $\sum \nu T_{\nu \nu} \gg 1$ we find $\langle P_{ab} \rangle = P_a T_{ab} / \sum \nu T_{\nu b}$. Here $P_a$ is the probability of formation of the tunneling channel or the transition state, and the $T_{\nu}$ are the transmission coefficients for channels $b'$ coupled to the second Hamiltonian. That result confirms transition-state theory in its general form. For tunneling through a very thick barrier the condition $\sum \nu T_{\nu \nu} \gg 1$ is relaxed and independence of formation and decay of the tunneling process hold more generally.

I. INTRODUCTION

Barrier penetration and transition over a barrier play important roles in several areas of quantum physics. Since the pioneering work of Bohr and Wheeler [1], transition-state theory has been an important element in the theory of nuclear fusion [2]. It also plays a key role in physical chemistry [3]. In two recent papers, Bertsch and Hagino [4] and Hagino and Bertsch [5] have studied a statistical model for a transition-state process wherein the complete mixing of states is hindered by an internal barrier. The model consists of two uncorrelated Hamiltonians, each a member of the Gaussian Orthogonal Ensemble (GOE) of random matrices. The first random Hamiltonian is fed from some entrance channel. Penetration through the barrier separating the two Hamiltonians is due to a single channel. We believe that for transition-state theory, such a random-matrix approach is of considerable interest. Random-matrix theory is a universal tool for modeling complex quantum systems [6]. It exhibits generic features of such systems without resorting to specific dynamical assumptions. These features emerge in the limit of infinite matrix dimension which allows for a clean separation of local fluctuation properties (that are generic) and global properties (that are not).

The present paper is motivated by the fact that the model used in Refs. [4, 5] does not possess a realistic GOE limit with non-vanishing fluctuations. Actually we study two simplified versions of the model of Refs. [4, 5]. Each employs two coupled GOE Hamiltonians. In the first, the two GOE Hamiltonians are coupled by a rank-one interaction. That is a model for barrier penetration via a single channel. In the second, the two GOE Hamiltonians are coupled via a single state. That models a physical transition state located right above the barrier. In each case, we calculate the probability for the transition from the entrance channel to some final channel on the other side of the barrier. We formulate the conditions under which that probability is the product of two or three statistically uncorrelated factors. Then the decay following barrier penetration or passage through the transition state is independent of its mode of formation. Such independence is the hallmark of transition-state theory. If there are sufficiently many open channels coupled sufficiently strongly to the second Hamiltonian, we retrieve the standard expression of transition-state theory.

The two versions of our model Hamiltonian are defined in Section I. The coupling to the channels and the scattering matrix are defined in Section III. In Section IV we define the conditions of validity of transition-state theory within our model and display the results of transition probability. The special case of a thick barrier is treated in Section V. Section VI contains a brief summary. Technical details are deferred to an appendix.

II. TWO HAMILTONIANS

The tunneling Hamiltonian is

$$H_{\text{tun}} = \begin{pmatrix} H_1 & V \\ V^T & H_2 \end{pmatrix}.$$  \hspace{1cm} (1)
which carries the transition state with energy $E_0$ is

$$H_{tra} = \begin{pmatrix} H_1 V_1 & 0 \\ V_1^T E_0 V_2^T \\ 0 \ V_2 H_2 \end{pmatrix}. \quad (2)$$

Both $H_1$ and $H_2$ are coupled to the transition state by vectors $V_1$ and $V_2$, respectively. In Eqs. (1) and (7), $H_1$ and $H_2$ are GOE matrices of dimension $N \gg 1$ each, defined in two Hilbert spaces denoted as space 1 and space 2, respectively. The elements of the matrices $H_1$ and $H_2$ are uncorrelated zero-centered Gaussian random variables with second moments

$$\langle (H_1)_{\mu_1 \mu'_1} (H_1)_{\mu_2 \mu'_2} \rangle = \frac{\lambda^2}{N} (\delta_{\mu_1 \mu_2} \delta_{\mu'_1 \mu'_2} + \delta_{\mu_1 \mu'_2} \delta_{\mu'_1 \mu_2}),$$

$$\langle (H_2)_{\nu_1 \nu'_1} (H_2)_{\nu_2 \nu'_2} \rangle = \frac{\lambda^2}{N} (\delta_{\nu_1 \nu_2} \delta_{\nu'_1 \nu'_2} + \delta_{\nu_1 \nu'_2} \delta_{\nu'_1 \nu_2}). \quad (3)$$

Angular brackets denote the ensemble average. Greek letters $\mu, \mu', \mu_1, \rho, \rho'$ etc. range from 1 to $N$ in space 1 while $\nu, \nu', \nu_1, \sigma, \sigma'$ etc. range from $N+1$ to $2N$ in space 2. The center row and column of the matrix $\mathbf{V}$ carry the index zero. The spectra of $H_1$ and $H_2$ range from $-2\lambda$ to $+2\lambda$. For both Hamiltonians, the average level density as function of energy $E$ is given by

$$\rho(E) = \frac{N}{\pi \lambda} \left(1 - [E/(2\lambda)]^2\right)^{1/2}. \quad (4)$$

The rank-one interaction $V$ in Eq. (1) is given by

$$V_{\mu \nu} = (O_1)_{\mu N} V (O_2)_{(N+1)\nu}. \quad (5)$$

Here $V$ is a constant with dimension energy, and $(O_1)_{\mu N}$ and $(O_2)_{(N+1)\nu}$ are the elements of the $N$th column (of the first row, respectively) of two arbitrary $N$-dimensional orthogonal matrices in space 1 (space 2, respectively). Transforming

$$H_{tun} \rightarrow \begin{pmatrix} 0 & O_2^T \\ O_1 & 0 \end{pmatrix} H_{tun} \begin{pmatrix} 0 & O_2^T \\ O_1 & 0 \end{pmatrix} \quad (6)$$

and using the orthogonal invariance of the GOE leaves the ensembles $H_1$ and $H_2$ unchanged but changes $V$ into

$$V_{\mu \nu} = \delta_{\mu N} \delta_{\nu (N+1)} V. \quad (7)$$

For the Hamiltonian in Eq. (2), the vectors $V_1 = \{V_{1\mu}\}$ and $V_2 = \{V_{2\nu}\}$ are written, respectively, as $\sqrt{\sum_{\mu} V_{1\mu}^2} \{e_{1\mu}\}$ and as $\sqrt{\sum_{\nu} V_{2\nu}^2} \{e_{2\nu}\}$. Here $\{e_{1\mu}\}$ and $\{e_{2\nu}\}$ are unit vectors in $N$ dimensions. Each of these forms one column of an orthogonal $N$-dimensional matrix $O_1$ and $O_2$, respectively. Via a transformation similar to that in Eq. (6), the vectors $V_1$ and $V_2$ take the form

$$V_{1\mu} = \delta_{\mu N} V_1, \ V_{2\nu} = \delta_{\nu (N+1)} V_2. \quad (8)$$

Here

$$\frac{1}{N} V_1^2 = \frac{1}{N} \sum_{\mu} V_{1\mu}^2 = V_1^2,$$

$$\frac{1}{N} V_2^2 = \frac{1}{N} \sum_{\nu} V_{2\nu}^2 = V_2^2. \quad (9)$$

Eqs. (1) and (7) on the one hand and Eqs. (2), (8) and (9) on the other define our two Hamiltonians. Without loss of generality we assume that $V_1, V_2, V$ are positive.

In Section III, we show that to be physically meaningful, $V$ must be independent of $N$ and small compared to $\lambda$. An estimate for $V_1$ and $V_2$ is obtained by introducing the mean GOE level spacing $d = \pi \lambda/N$ at the center $E = 0$ of the GOE spectrum. Then $V_1^2/\lambda = (\pi/d) V_1^2$ and $V_2^2/\lambda = (\pi/d) V_2^2$. We use the standard expressions for the spreading widths that account for the coupling of the transition state to the states in space 1 (space 2) with mean square coupling elements $V_1^2$ ($V_2^2$, respectively),

$$\Gamma_1 = (2\pi/d) V_1^2, \ \Gamma_1 = (2\pi/d) V_2^2. \quad (10)$$

To be physically meaningful, $\Gamma_1$ and $\Gamma_2$ must be substantially smaller than the range of the GOE spectrum, and that same statement then applies to $V_1$ and $V_2$. We define dimensionless positive parameters

$$\tilde{V} = \frac{V}{\lambda}, \ \tilde{V}_1 = \frac{V_1}{\lambda}, \ \tilde{V}_2 = \frac{V_2}{\lambda} \quad (11)$$

all of which are independent of $N$ and small compared to unity. In what follows we think of the parameter $\tilde{V}$ as being determined by a semiclassical calculation of the transition probability through the barrier. The parameters $\tilde{V}_1$ and $\tilde{V}_2$ measure the strength of the coupling of the transition state to spaces 1 and 2 and can only be determined by a fit to data.

When $H_1$ and $H_2$ each range over the orthogonal ensemble, the tunneling matrix element $\mathcal{V}$ becomes distributed uniformly over the states in space 1 and space 2. That follows from Eq. (6) as then the matrices $O_1$ and $O_2$ independently range over the set of orthogonal matrices in $N$ dimensions. Therefore, tunneling is equally likely from any state $\mu$ in space 1 to any state $\nu$ in space 2. Pictorially speaking, in the model Hamiltonian (11) the tunneling barrier is replaced by a wall of uniform thickness that extends over the entire GOE spectrum. In an actual physical situation, the tunneling barrier has more or less the shape of an inverted parabola. Tunneling becomes ever more likely as the energy of the system approaches the top of the barrier from below. For the Hamiltonian (11) we simulate that feature by keeping the system’s energy fixed at the center $E = 0$ of the GOE spectrum and increasing $V$. The top of the barrier is approached for very large $V$. The Hamiltonian (11) continues that physical picture to energies above the barrier where the transition process is enhanced by a resonance at energy $E_0$.

### III. SCATTERING MATRIX AND TRANSITION PROBABILITY

In the construction of the scattering matrix we follow Ref. [8]. The open channels labeled $a, a', \ldots \ (b, b', \ldots)$ are coupled, respectively, to states in space 1 (in space 2)
by real coupling matrix elements \( W_{ab} \) (\( W_{ba} \)). Because of
the normalization of the scattering wave functions, these
matrix elements have dimension (energy)\(^{1/2}\). The num-
ber of channels coupled to either space 1 or space 2 is
finite. It is held fixed as we take the limit \( N \to \infty \) of
infinite matrix dimension in the following Sections. In
spaces 1 and 2 we define the finite-rank width matrices
\( \Gamma_1 \) and \( \Gamma_2 \) with elements

\[
(\Gamma_1)_{\mu\nu} = 2\pi \sum_{a,a'} W_{a\mu} W_{a'a\nu},
\]

\[
(\Gamma_2)_{\mu\nu'} = 2\pi \sum_b W_{b\nu} W_{b\nu'}. \tag{12}
\]

For the Hamiltonians \( H_{\text{tun}} \) and \( H_{\text{tra}} \) we define, respect-
ively,

\[
\Gamma_{\text{tun}} = \begin{pmatrix} \Gamma_1 & 0 \\ 0 & \Gamma_2 \end{pmatrix}, \quad \Gamma_{\text{tra}} = \begin{pmatrix} \Gamma_1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \Gamma_2 \end{pmatrix}. \tag{13}
\]

The elements for scattering from channel \( a \) to channel \( b \)
of the scattering matrix \( S \) are

\[
S_{ab} = -2i\pi \sum_{\mu\nu} W_{a\mu} (D^{-1})_{\mu\nu} W_{b\nu}, \tag{14}
\]

with \( D \) given by

\[
D_{\text{tun}} = E - H_{\text{tun}} + (i/2)\Gamma_{\text{tun}},
\]

\[
D_{\text{tra}} = E - H_{\text{tra}} + (i/2)\Gamma_{\text{tra}}. \tag{15}
\]

Eqs. \(13, 15\) are completely general. In applications,
however, the incident channel \( a \) consists of two fragments,
each in its ground state. The final channels \( b \) consist of
all pairs of fragments either in their ground or in excited
states. In the converse reaction \( b \to a \), channel \( b \) consists
of two fragments, each in its ground state. The final
channels \( a \) consist of all pairs of fragments either in their
ground or in excited states.

We expand \( D_{\text{tun}}^{-1} \) in powers of \( \mathcal{V} \). The resulting series
is odd in \( \mathcal{V} \). We separate the first or the last factor \( \mathcal{V} \).
The remaining series containing even powers of \( \mathcal{V} \) can be
resummed. We expand \( D_{\text{tra}}^{-1} \) in powers of the elements
in rows and columns labeled zero, respectively and proceed
analogously. The resulting element \( S_{ab} \) of the scattering
matrix is the product of three dimensionless factors,

\[
S_{ab} = -i \left( \sum_\mu W_{a\mu} [(E - H_1 + (i/2)\Gamma_1)^{-1}]_{\mu N} \sqrt{2\pi} \lambda \right)
\times \mathcal{A}(\sqrt{2\pi} \lambda \sum_\nu [(E - H_2 + (i/2)\Gamma_2)^{-1}]_{(N+1)\nu} W_{\nu b}), \tag{16}
\]

with

\[
\mathcal{A}_{\text{tun}} = \mathcal{V} \left( 1 - \xi_2 \mathcal{V} \xi_1 \mathcal{V} \right)^{-1},
\]

\[
\mathcal{A}_{\text{tra}} = \frac{\lambda}{E - E_0 - V_1 \xi_1 \mathcal{V} - V_2 \xi_2 \mathcal{V}} \mathcal{V} \mathcal{V}. \tag{17}
\]

The dimensionless random variables \( \xi_1, \xi_2 \) are defined as

\[
\xi_1 = \lambda [(E - H_1 + (i/2)\Gamma_1)^{-1}]_{NN}, \quad \xi_2 = \lambda [(E - H_2 + (i/2)\Gamma_2)^{-1}]_{(N+1)(N+1)}. \tag{18}
\]

For the transition probability \( P_{ab} \) from channel \( a \) to channel \( b \), Eq. \(16\) gives

\[
P_{ab} = \left| \sum_\mu W_{a\mu} [(E - H_1 + (i/2)\Gamma_1)^{-1}]_{\mu N} \sqrt{2\pi} \lambda \right|^2 \mathcal{A}^2 \times \left| \sum_\nu \sqrt{2\pi} \lambda [(E - H_2 + (i/2)\Gamma_2)^{-1}]_{(N+1)\nu} W_{\nu b} \right|^2. \tag{19}
\]

For both Hamiltonians \(1\) and \(2\), the first (last) of the three factors gives the probability to enter (leave) the
tunneling process or the transition state. The factor \( \mathcal{A}_{\text{tun}} \) in the first of Eqs. \(17\) accounts for tunneling, with
the denominator accounting for repeated tunneling events,
and correspondingly for the factor \( \mathcal{A}_{\text{tra}} \) in the second
of Eqs. \(17\) which accounts for passage through the transition
state.

Each of the three factors in Eq. \(19\) is a random variable
depending, in that order, on \( H_1 \), on both \( H_1 \) and
\( H_2 \), and on \( H_2 \). Therefore, the three factors are corre-
lated. The probability of decay, given by the last factor,
is not independent of the mode of formation of the tun-
neling process (or of the transition state). Averaging \( P_{ab} \)
over the two ensembles does not help because the aver-
dge does not factorize. That shows that the standard
assumption of transition-state theory does not hold in
general. Transition-state theory holds if and only if the
fluctuations of either \( \xi_1 \) or \( \xi_2 \) or both in the second factor
in Eq. \(19\) are negligible in which case at least one of the
three factors in Eq. \(19\) becomes uncorrelated with the
rest. We now investigate the conditions for that to be
the case.

IV. ASYMPTOTIC RESULTS

We determine the fluctuations of \( \xi_1 \) and \( \xi_2 \) by calculating
mean values and variances\(^1\) of these quantities in the
limit of infinite matrix dimension \( N \). Eqs. \(18\) show that
\( \xi_1 \leftrightarrow \xi_2 \) by simultaneously interchanging \( N \leftrightarrow N + 1 \),
\( H_1 \leftrightarrow H_2 \) and \( \Gamma_1 \leftrightarrow \Gamma_2 \). Therefore, we confine ourselves
to \( \xi_1 \). We use the close formal similarity of \( \xi_1 \) to the
S-matrix describing scattering by the GOE Hamiltonian
\( H_3 \) coupled to channels \( a, a' \). That matrix is defined by \(3\)

\[
S_{aa'} = \delta_{aa'}, \tag{20}
\]

\[
-2i\pi \sum_{\mu\mu'} W_{a\mu} [(E - H_1 + (i/2)\Gamma_1)^{-1}]_{\mu\mu'} W_{\mu a'}. \]

\(^1\) We use the term variance for the expression \( \langle |\xi - \langle \xi \rangle|^2 \rangle \).
The central piece of $S_{aa''}$ is the propagator $(E - H_1 + (i/2)\Gamma_1)^{-1}$. That same propagator defines $\xi_1$ in the first of Eqs. (13). In Ref. 8 mean value and variance of $S_{aa''}$ were calculated analytically for $N \rightarrow \infty$ with the help of the supersymmetry approach. Adopting that calculation to the present case we obtain explicit expressions for average and variance of $\xi_1$. Details are given in the Appendix. For the sake of completeness we mention that combining results of Refs. 10 and 11 yields an analytic expression for the full distribution of $\xi_1$.

The average, given by

$$\langle \xi_1 \rangle = -i \, ,$$

has magnitude unity and is independent of $\Gamma_1$. The variance of $\xi_1$ does depend upon $\Gamma_1$ and is given by the threefold integral in Eq. (38) that involves the transmission coefficients

$$T_a = 1 - |\langle S_{aa'} \rangle|^2 \, .$$

These are defined in terms of the average diagonal elements of the GOE scattering matrix (20) and measure the strength of the coupling of channel $a$ to space 1. For a single open channel with transmission coefficient $T_a$ the variance diverges like $1/T_a$ for $T_a \rightarrow 0$. That is in contrast to the variance of $S_{aa''}$ in Eq. (21) which is bounded from above by unitarity. The variance of $\xi_1$ decreases as the number of channels and the strength of their couplings to space 1 increase. If the sum of the transmission coefficients $\sum_{a'} T_{a'} \gg 1$ we may use the asymptotic expansion of the threefold integral in inverse powers of $\sum_{a'} T_{a'}$ given in Ref. 12. As shown in the Appendix, the term of leading order is

$$\langle |\xi_1|^2 \rangle - 1 = \frac{2}{\sum_{a'} T_{a'}} \text{ for } \sum_{a'} T_{a'} \gg 1 \, .$$

If the inequality in Eq. (23) applies, $\xi_1$ in Eqs. (17) may be replaced by $|\xi_1|$, and transition-state theory applies. In practice, the fluctuations of $\xi_1$ are sufficiently small if the number of open channels with transmission coefficients of order unity coupled to $H_1$ is of order 10 or bigger.

If the inequality in Eq. (23) holds, the first factor on the right-hand side of Eq. (19) is not correlated with the rest. It is then meaningful to calculate mean value and variance of the amplitude (the expression under the absolute sign). Using the same steps as for $\xi_1$ we show in the Appendix that the mean value of the amplitude vanishes and that for $\sum_{a'} T_{a'} \gg 1$ the variance, given by the leading term in the asymptotic expansion in inverse powers of $\sum_{a'} T_{a'}$, is equal to

$$2\pi \left\langle \sum_{\mu} W_{a\mu}[(E - H_1 + (i/2)\Gamma_1)^{-1}]_{\mu N} \sqrt{\lambda} \right|^2 \right\rangle = \frac{T_a}{\sum_{a'} T_{a'}} \, .$$

Using Eqs. (22) and (24) and the corresponding results for $\xi_2$, we can now give the asymptotic forms of the average transition probability. We distinguish three cases.

(i) The inequality $\sum_{a'} T_{a'} \gg 1$ holds, the variance of $\xi_2$ is small compared to unity but the variance of $\xi_1$ is not. Then

$$A_{\text{tan}} = \frac{\tilde{V}}{1 + i\xi_1\tilde{V}} \, ,$$

$$A_{\text{tra}} = \frac{\lambda}{\tilde{V}_1 - \xi_1\tilde{V}_1 + (i/2)\Gamma_1^2 + \lambda} \tilde{V}_2 \, .$$

We define

$$P_a = \left\langle \left| A \right|^2 \right\rangle = \left\langle \left| \sqrt{2\pi} \sum_{\mu} W_{ab}[(E - H_1 + (i/2)\Gamma_1)^{-1}]_{\mu N} \sqrt{\lambda} \right|^2 \right\rangle \, .$$

Here $A$ stands for either $A_{\text{tan}}$ or $A_{\text{tra}}$ defined in Eq. (25) as the case may be. Then

$$\langle P_{ab} \rangle = \frac{P_a T_b}{\sum_{a'} T_{a'} \, .} \right\rangle \, .$$

The ensemble-averaged probability $P_a$ of formation of the transition channel or transition state is not accessible analytically and can only be calculated numerically. The normalized decay probability into channel $b$ is given by $T_b/\sum_{a'} T_{a'}$ and is independent of the mode of formation of the transition channel or transition state.

(ii) The inequality $\sum_{a'} T_{a'} \gg 1$ holds, the variance of $\xi_1$ is small compared to unity but the variance of $\xi_2$ is not. Then

$$A_{\text{tan}} = \frac{\tilde{V}}{1 + i\xi_2\tilde{V}} \, ,$$

$$A_{\text{tra}} = \frac{\lambda}{\tilde{V}_1 - \xi_2\tilde{V}_1 + (i/2)\Gamma_1^2 + \lambda} \tilde{V}_2 \, .$$

We define

$$P_b = \left\langle \left| A \right|^2 \right\rangle = \left\langle \left| \sqrt{2\pi} \sum_{\nu} \sqrt{\lambda}[(E - H_2 + (i/2)\Gamma_2)^{-1}]_{(N+1)\nu} W_{ab} \right|^2 \right\rangle \, .$$

Here $A$ stands for either $A_{\text{tan}}$ or $A_{\text{tra}}$ defined in Eq. (28) as the case may be. Then

$$\langle P_{ab} \rangle = \frac{T_a P_b}{\sum_{a'} T_{a'} \, .} \right\rangle \, .$$

The ensemble-averaged decay probability $P_b$ in Eq. (29) is not available analytically and can only be calculated numerically. Therefore, Eq. (30) does not provide a useful parametrization of the reaction $a \rightarrow b$. It does, however, usefully parametrize the converse reaction $b \rightarrow a$ defined below Eq. (15). For that reaction, the normalized probability to populate final channel $a$ is given by $T_a/\sum_{a'} T_{a'}$, irrespective of the mode of formation of the transition channel or transition state.
(iii) The inequalities \( \sum_{a'} T_{a'} \gg 1 \) and \( \sum_{b'} T_{b'} \gg 1 \) both hold, the variances of \( \xi_1 \) and \( \xi_2 \) are both small compared to unity. Then

\[
A_{\text{tun}} = \frac{\tilde{V}}{1 + \tilde{V}^2}, \quad \quad A_{\text{tra}} = \frac{\tilde{V}_1 - \tilde{V}_2}{E - E_0 + (i/2)\Gamma_1 + (i/2)\Gamma_2} \tilde{V}_2
\]

(31)

and

\[
\langle P_{ab} \rangle = \frac{T_a}{\sum_{a'} T_{a'}} |A|^2 \frac{T_b}{\sum_{b'} T_{b'}} \langle \text{tun} \rangle.
\]

(32)

Here \( A \) stands for either \( A_{\text{tun}} \) or \( A_{\text{tra}} \) defined in Eq. (31) as the case may be. The normalized decay probability into channel \( b \) is given by \( T_b/\sum_{b'} T_{b'} \) and is independent of the mode of formation of the transition channel or transition state. The same statements apply to the converse reaction defined below Eq. (15). In contrast to Eqs. (27) and (30), Eq. (32) gives an explicit expression for the probability of both, the reaction \( a \to b \) and the converse reaction \( b \to a \).

V. THICK BARRIER

A special case is tunneling through a thick barrier. Then \( \tilde{V} \ll 1 \), suggesting that \( \xi_2 \tilde{V} \xi_1 \tilde{V} \) in the denominator of \( A_{\text{tun}} \) in the first of Eqs. (17) may be neglected. For that to be the case, the square roots of the variances of \( \xi_1 \) and \( \xi_2 \) must be small in magnitude compared to \( 1/\tilde{V} \). Since \( 1/\tilde{V} \gg 1 \) that is a much weaker condition than imposed in Section IV where the square roots had to be small compared to unity. The condition is fulfilled already when only few channels are coupled to \( H_1 \) and to \( H_2. \) In that case the asymptotic expressions in Section IV do not apply, and the variances of \( \xi_1 \) and \( \xi_2 \) must be obtained by direct calculation of the threefold integral in Eq. (33). If \( \xi_2 \tilde{V} \xi_1 \tilde{V} \) is indeed negligible, lowest-order perturbation theory in \( \tilde{V} \) is appropriate,

\[
A_{\text{tun}} = \tilde{V}
\]

(33)

does not fluctuate, \( P_{ab} \) in Eq. (19) is the product of three statistically uncorrelated factors, and transition-state theory holds. For \( \langle P_{ab} \rangle \) we find

\[
\langle P_{ab} \rangle = \frac{\langle \text{tun} \rangle^2}{\sum_{a'} T_{a'}} \times \left\langle \left| \sqrt{2\pi} \sum_{\mu} W_{\mu} [(E - H_1 + (i/2)\Gamma_1)^{-1}]_{\mu N} \sqrt{\lambda} \right|^2 \right\rangle
\]

\[
\times \left\langle \left| \sqrt{2\pi} \sum_{\nu} \sqrt{\lambda} [(E - H_2 + (i/2)\Gamma_2)^{-1}]_{(N+1)\nu} W_{\nu b} \right|^2 \right\rangle.
\]

(34)

Formation and decay of the tunneling channel are independent processes. The associated probabilities, given by the ensemble averages in Eq. (34), can be calculated using the threefold integral (40) and its analogue for channel \( b. \) The formal symmetry of Eq. (34) with respect to the interchange \( a \leftrightarrow b \) reflects the symmetry of the scattering matrix in Eq. (14).

Eq. (34) does not require that either \( \sum_{a'} T_{a'} \gg 1 \) or \( \sum_{b'} T_{b'} \gg 1 \) or both. It suffices that the square roots of both sums are substantially bigger than \( \tilde{V} \), the (small) dimensionless tunneling matrix element through the barrier. That weaker constraint may be useful in some practical cases. Indeed, barrier penetration is small for energies far below the barrier. The number of open channels in either fragment decreases with decreasing excitation energy, reducing both \( \sum_{a'} T_{a'} \) and \( \sum_{b'} T_{b'} \). A likely result is \( 1 \approx \left[ \langle \sum_{a'} T_{a'} \rangle^{1/2}, \langle \sum_{b'} T_{b'} \rangle^{1/2} \right] \gg \tilde{V}. \)

VI. SUMMARY

To model a system intrinsically separated by a barrier, we have used two GOE Hamiltonians (each coupled to open channels) that are coupled to each other either by a tunneling matrix element, or by an intermediate transition state. We have studied that model in the universal limit of large matrix dimension of random-matrix theory. The transition probability \( P_{ab} \) connecting an incoming channel \( a \) that feeds the first GOE Hamiltonian to an outgoing channel \( b \) coupled to the second Hamiltonian, is the product of three statistically correlated factors. These account, respectively, for formation of, passage through, and decay of the transition channel or transition state.

A sufficient condition for transition-state theory to hold in its standard form is that the sum of the transmission coefficients \( T_{b'} \) accounting for decay of the second Hamiltonian into channels \( b' \) obeys \( \sum_{b'} T_{b'} \gg 1 \). Then the third of the above-mentioned factors becomes uncorrelated with the first two, the average transition probability factorizes, the decay of the transition channel or transition state is independent of its mode of formation, and the ensemble-averaged transition probability is

\[
\langle P_{ab} \rangle = \frac{P_a T_b}{\sum_{b'} T_{b'}}.
\]

(35)

The probability \( P_a \) of formation of the transition channel or transition state is a parameter that is analytically available only if for the entrance channels \( a' \) the analogous condition \( \sum_{a'} T_{a'} \gg 1 \) holds as well.

Our formulation is symmetric with regard to the interchange \( a \leftrightarrow b \). Therefore, the average probability for the converse reaction \( b \to a \) is given by

\[
\langle P_{ba} \rangle = \frac{P_b T_a}{\sum_{a'} T_{a'}}
\]

(36)

provided that \( \sum_{a'} T_{a'} \gg 1 \).

The conditions \( \sum_{b'} T_{b'} \gg 1 \) for the reaction \( a \to b \) and \( \sum_{a'} T_{a'} \gg 1 \) for the converse reaction \( b \to a \) are sufficient for the transition-state formulas (34) and (36), respectively, to hold. The weaker conditions \( \langle \sum_{a'} T_{a'} \rangle^{1/2} \gg \tilde{V}, \langle \sum_{b'} T_{b'} \rangle^{1/2} \gg \tilde{V} \) suffice for tunneling through a thick
barrier with dimensionless tunneling matrix element $\tilde{V} \ll 1$. Then the average probability for the reaction $a \to b$ factorizes. The probabilities for formation and decay of the tunneling channel given in Eq. (22) do not have the simple form $T_{a'}/\sum_{a'} T_{a'}$ but are available in terms of the threefold integral in Eq. (10).

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APPENDIX: MEAN VALUES AND VARIANCES

We follow Ref. [9], referring to equations in Ref. [9] by a prefix $V$. For the average $\langle \xi_1 \rangle$ we use the steps leading to Eq. (V.7.7). That gives Eq. (21). For the calculation of the variance of $\xi_1$, we sketch the important steps. According to Eqs. (V.2.3) and (V.2.4) with $H \to H_I$ we have $\xi_1 = \lambda D^{-1}_{NN}$. For the variance of $\xi_1$ we use Eq. (V.3.16c) with $E_1 = E_2$ and $\mu(1) = \mu(1) = N = \mu(2) = \nu(2)$. The ensemble average of the generating function $Z$ is given in Eq. (V.7.10) where $\varepsilon = 0$, $c = 1$, $\alpha = 0$. The graded matrix $J$ equals $\{J_{NN}(1)I(1), J_{NN}I(2)\}$, with $I(1)$ and $I(2)$ defined below Eq. (V.7.12). In the limit $N \to \infty$, the graded matrix $\rho$ in Eq. (V.7.11) tends to the unit matrix. We use Eq. (V.5.41) for $\sigma_G$ and Eq. (V.5.29) for $T_0$. Following the steps that lead to Eq. (V.7.23) we obtain for the variance of $\xi_1$

$$
\langle |\xi_1|^2 \rangle - 1 = \frac{1}{16} \int d\mu(t) \left\{ \text{trg} (\alpha_1 I(1)) \text{trg} (\alpha_2 I(2)) \right. \\
+ 8 \text{trg} (t_{21}(1 + (1/2)\alpha_1)^{1/2}I(1)t_{12}(1 + (1/2)\alpha_2)^{1/2}I(2)) \left. \right\} \\
\times \exp \left\{ - (1/2) \sum_{a'} \text{trg} \ln (1 + (1/2)T_{a'}\alpha_1) \right\}.
$$

Here $T_{a'}$ is the transmission coefficient in channel $a'$ defined in Eq. (22). Integration over the saddle-point manifold as in Section 8 of Ref. [9] gives

$$
\langle |\xi_1|^2 \rangle - 1 = \frac{1}{2} \int_0^\infty d\lambda_1 \int_0^\infty d\lambda_2 \int_0^1 d\lambda \ \mu(\lambda_1, \lambda_2, \lambda) \\
\times \prod_{a'} \frac{(1 - T_{a'}\lambda)}{(1 + T_{a'}\lambda)^{1/2}(1 + T_{a'}\lambda)^{1/2}} \\
\times \left( \frac{\lambda_1(1 + \lambda_1)}{(1 + T_0\lambda_1)} + \frac{\lambda_2(1 + \lambda_2)}{(1 + T_0\lambda_2)} + 2\lambda(-1 - \lambda_1) \right). \quad (38)
$$

The integration measure in Eq. (38) is given by

$$
\mu(\lambda_1, \lambda_2, \lambda) = \frac{(1 - \lambda_1\lambda_2\lambda)(\lambda + \lambda_1)^2(\lambda + \lambda_2)^2}{(1 + \lambda_1\lambda_2\lambda)(\lambda + \lambda_1)(\lambda + \lambda_2)^2}. \quad (39)
$$

For an isolated system (all $T_{a'} = 0$) the integrals in Eq. (38) diverge. That is because for $\lambda_1, \lambda_2 \gg 1$ the leading part of the integrand is $|\lambda_1 - \lambda_2|^{-1} - \lambda_2^{-1}$ times a factor given by either $\lambda_1^2$ or $\lambda_2^2$ or $\lambda_1\lambda_2$. Either of the first two factors yields a diverging integral. To cure the divergence it suffices that $H_I$ be coupled to a single open channel $a$ as that gives rise to an additional factor $T_{a}^{-1}(1 + \lambda_1\lambda_2)^{(-1/2)}$. However, for the single-channel case the factor $T_{a}^{-1}$ and with it, the variance of $\xi_1$ may be arbitrarily large. More factors of the form $T_{a}^{-1}(1 + \lambda_1\lambda_2)^{(-1/2)}$ arise as the number of open channels increases, showing that the variance decreases with the number of open channels. That is confirmed when we apply the asymptotic expansion in inverse powers of $\sum_{a'} T_{a'}$ of the GOE scattering matrix in Section 4 of Ref. [12] to our case. For the right-hand side of Eq. (38), Eq. (4.8) of that paper yields, in leading order, Eq. (23).

We turn to the amplitude of formation of the tunneling channel or transition state. The ensemble average of that amplitude vanishes for $N \to \infty$. That is seen by following the steps that lead to Eq. (V.7.7). The calculation of the variance proceeds along the lines that lead to Eq. (35). It does not seem necessary to give the steps in detail. We find

$$
2\pi \left\{ \sum_{\mu} W_{a\mu} [E - H_I + (i/2)\Gamma_1]^{-1} \right\} \mu N \sqrt{\lambda} = \frac{T_a}{2} \int_0^\infty d\lambda_1 \int_0^\infty d\lambda_2 \int_0^1 d\lambda \ \mu(\lambda_1, \lambda_2, \lambda) \\
\times \prod_{a'} \frac{(1 - T_{a'}\lambda)}{(1 + T_{a'}\lambda)^{1/2}(1 + T_{a'}\lambda)^{1/2}} \\
\times \left( \frac{\lambda_1(1 + \lambda_1)}{(1 + T_0\lambda_1)} + \frac{\lambda_2(1 + \lambda_2)}{(1 + T_0\lambda_2)} + 2\lambda(-1 - \lambda) \right). \quad (40)
$$

If $\sum_{a'} T_{a'} \gg 1$, we approximate the right-hand side of Eq. (40) by the first term of the asymptotic expansion in inverse powers of $\sum_{a'} T_{a'}$. Eq. (4.8) of Ref. [12] then gives Eq. (24). Corresponding expressions hold for the last factor on the right-hand side of Eq. (19).
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