Letter

Porter-Thomas fluctuations in complex quantum systems

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(Received 10 July 2021; revised 12 September 2021; accepted 1 November 2021; published 22 November 2021)

The Gaussian orthogonal ensemble (GOE) of random matrices has been widely employed to describe diverse phenomena in strongly coupled quantum systems. In particular, it has often been invoked to explain the fluctuations in decay rates that follow the χ-squared distribution for one degree of freedom, as originally proposed by Brink and by Porter and Thomas. However, we find that the coupling to the decay channels can change the effective number of degrees of freedom from one to two. Our conclusions are based on a configuration-interaction Hamiltonian originally constructed to test the validity of transition-state theory, also known as the Rice-Ramsperger-Kassel-Marcus theory in chemistry. The internal Hamiltonian consists of two sets of GOE reservoirs connected by an internal channel. We find that the effective number of degrees of freedom depends on the control parameter $\rho\Gamma$, where ρ is the level density in the first reservoir and Γ is the level decay width. The distribution for two degrees of freedom is a well-known property of the Gaussian unitary ensemble (GUE); our model demonstrates that the GUE fluctuations can be present under much milder conditions. Our treatment of the model permits an analytic derivation for $\rho\Gamma \gtrsim 1$.

DOI: 10.1103/PhysRevE.104.L052104

Introduction. Random matrix theory was proposed by Wigner [1] and extended by Dyson [2] to model the generic features of complex quantum systems. The main idea is to consider an ensemble of Hamiltonians with matrix elements that randomly generated. The theory has been widely employed to discuss properties in a variety of systems [3] including nuclear spectra [4,5], atomic spectra [6], electrons in mesoscopic systems [7,8], unimolecular chemical reactions [9], quantum chromodynamics [10], and microwave cavity resonances [11–13]. See also Ref. [14] for a recent development of random state technology, in which the properties of random states are exploited to carry out numerical simulations for many-body systems.

Among the ensembles in random matrix theory is the Gaussian orthogonal ensemble (GOE) with Dyson index $\beta = 1$, used to simulate Hamiltonians that obey time-reversal symmetry. For our purposes the important property is that the eigenfunction amplitudes approach a Gaussian distribution in the limit of large matrix dimensions. This leads to a χ-squared distribution with one degree of freedom for the fluctuations of decay widths at fixed energy into a single channel. On the other hand, if the Hamiltonian is complex, its decay widths might follow a χ-squared distribution with two degrees of freedom, as in the Gaussian unitary ensemble (GUE) characterized by the Dyson index $\beta = 2$. Both of these distributions were proposed as possibilities in the original publication by Porter and Thomas [15], as well as in the earlier publication by Brink [16]. In the sequel, we will refer to the $\beta = 1$ distribution as the "PT distribution" and the other one by its definition, the χ-squared distribution with $\nu = 2$ degrees of freedom.[1] Since the Hamiltonian matrices governing the quantum systems are often real, it is commonly assumed that they follow the PT distribution. However, in nuclear physics, the topic has recently become controversial [17–19] and other mechanisms have been suggested to explain deviations [20–25].

In this Letter, we revisit this problem making use of a random matrix model we developed in Ref. [26]. The model was constructed to assess the validity of transition-state theory [27–34]. The internal states of the system are represented by two GOE Hamiltonians connecting with each other via bridge states. Each GOE Hamiltonian is augmented by an imaginary energy $-i\Gamma/2$ on the diagonal associated with direct decays from the states. Hamiltonians based on two interacting GOE reservoirs have been studied previously [11,35], but limited to purely real Hamiltonians. In our reaction model, the Hamiltonian also contains an explicit entrance channel that is coupled to the first GOE reservoir. Those reservoir states can decay directly or pass to the second reservoir through the bridge channel. We will show below that the decay rate from the second GOE Hamiltonian follows the PT distribution when Γ_a for the first GOE matrix is small, changing gradually to the χ-squared for two degrees of freedom as Γ_a increases. Note that the internal Hamiltonian is real, but becomes

[1]The number of degrees of freedom denoted here by the symbol ν is conventionally written k.

effectively complex due to the boundary conditions imposed by the coupling to the entrance and decay channels.

Model. The Hamiltonian in our model is a matrix acting on states in a discrete-basis representation. The bridge channel consists of two states that are connected to each other and to the sets of GOE reservoir states. The Hamiltonian is defined as

$$\mathbf{H} = \begin{bmatrix} \ddots & \ddots & & & & & \\ \ddots & 0 & t_1 & 0 & 0 & 0 & 0 \\ & t_1 & 0 & \boldsymbol{v}_2^T & 0 & 0 & 0 \\ & 0 & \boldsymbol{v}_2 & H_a^{\rm goe} - i\Gamma_a/2 & \boldsymbol{v}_3 & 0 & 0 \\ & 0 & 0 & \boldsymbol{v}_3^T & 0 & t_2 & 0 \\ & 0 & 0 & 0 & t_2 & 0 & \boldsymbol{v}_4^T \\ & 0 & 0 & 0 & 0 & \boldsymbol{v}_4 & H_b^{\rm goe} - i\Gamma_b/2 \end{bmatrix}. \tag{1}$$

The ellipses and first two explicit entries in the vector space are associated with states in the entrance channel; the parameter t_1 is a hopping matrix element connecting adjacent states in the channel. The entries in the fourth and fifth rows and columns apply to the bridge states. The third and sixth rows and columns represent $N_g \times N_g$ subblocks containing the GOE Hamiltonians with $g = a$ or b. The matrix elements in the $H_g^{\rm goe}$ submatrices are taken from the GOE ensemble [4],

$$\langle i|H_g^{\rm goe}|j\rangle = \langle j|H_g^{\rm goe}|i\rangle = r_{ij} v_g (1+\delta_{i,j})^{1/2}. \tag{2}$$

Here, r_{ij} is a random number from a Gaussian distribution of unit dispersion, $\langle r_{ij}^2\rangle = 1$, and v_g is the root-mean-square value of the matrix elements. The vectors $\boldsymbol{v}_k$ connect the channels to the GOE states, and we assume that their matrix elements are given as $\boldsymbol{v}_k(i) = r_i v_k$, where r_i is random with $\langle r_i^2\rangle = 1$ and v_k is an overall scaling factor. It will be convenient to parametrize the derived analytic formulas in terms of the GOE level density $\rho_{0g} = N_g^{1/2}/\pi v_g$ at the center of the spectrum and the limiting eigenvalues $E_{mg} = \pm 2 N_g^{1/2} v_g$.

As described in Ref. [26] and in the Supplemental Material [36], the GOE states can be treated implicitly in a reduced Hamiltonian, leaving only the four channel amplitudes explicit:

$$H_{\rm red} = \begin{bmatrix} 0 & t_1 & 0 & 0 \\ t_1 & w_{22} & w_{23} & 0 \\ 0 & w_{23} & w_{33} & t_2 \\ 0 & 0 & t_2 & w_{44} \end{bmatrix}. \tag{3}$$

We have left out the couplings marked by ellipses in the previous equation because they are treated implicitly in the derived expressions for reaction rates. The $w_{kk'}$ in Eq. (3) are self-energies associated with the states in the channels. They are given by

$$w_{kk'} = \boldsymbol{v}_k \cdot \left(E - H_g^{\rm goe} + i\Gamma_g/2\right)^{-1} \cdot \boldsymbol{v}_{k'}, \tag{4}$$

where E is the total energy of the reaction. These are evaluated with $(H_g^{\rm goe}, \Gamma_g) = (H_a^{\rm goe}, \Gamma_a)$ for w_{22}, w_{23}, and w_{33}, and with $(H_g^{\rm goe}, \Gamma_g) = (H_b^{\rm goe}, \Gamma_b)$ for w_{44}. Since the spectrum of $H_g^{\rm goe}$ is purely real, the inverse matrix expression (4) always exists. The reaction cross section $\sigma_{k\ell}$ associated with an entrance channel k leading to an exit channel ℓ may be computed as a kinematic cross section for the entrance channel multiplied by a transmission factor $T_{k\ell}$,

$$\sigma_{k\ell} = \sigma_k T_{k\ell}. \tag{5}$$

Our model has only one entrance channel and we drop the index k in the formulas below. There are many exit channels associated with the imaginary decay widths; we add together all the contributions passing through states in reservoir a to define T_a and similarly for reservoir b. The total inelastic transmission factor T is then given by $T = T_a + T_b$. Notice that T and T_b are proportional to Φ_{12} and Φ_{34}, respectively, where Φ_{ij} expresses the probability flux from channel site i to j. Formulas for T and T_a expressing their dependence on the Hamiltonian parameters are derived in the Supplemental Material.

A particularly interesting physical observable is the probability P_b of the reaction producing products from the b reservoir,

$$P_b = \frac{T_b}{T}. \tag{6}$$

This is closely related to the branching ratio $B_r = T_b/T_a$ discussed in Ref. [26]. As derived in the Supplemental Material, P_b can be expressed in terms of the Hamiltonian parameters as

$$P_b = \frac{t_2^2 |w_{23}|^2 \,{\rm Im}(w_{44})}{{\rm Im}(w_{22})|s|^2 - {\rm Im}(w_{23}^2 w_{44} s^*)}, \tag{7}$$

where $s = w_{33}w_{44} - t_2^2$.

Fluctuation statistics. We derived the transition-state formula in Ref. [26] by estimating the mean value of B_r from the statistical properties of the self-energies. For that estimate we evaluated the expectation values of the diagonal self-energies and their off-diagonal squares $|w_{23}|^2$ and w_{23}^2. The results are shown in Table I, together with additional statistical properties needed in the present context. See Refs. [37,38] and the Supplemental Material for their derivation.

In assessing how the statistical properties of the self-energies affect P_b, we first note that w_{23}^2 is small compared to the other terms in the denominator of Eq. (7). This is due to its inverse dependence on E_{mg}, since that energy is large compared to all other energy scales. Also, the fluctuation in the diagonal self-energy can be neglected for large GOE spaces since it varies as $N_g^{-1/4}$ times its expectation value. Thus, the entire fluctuation in P_b can be attributed to its dependence on $|w_{23}|^2$. From Table I we see that its standard deviation

TABLE I. Expectation values and standard deviations $\mathrm{SD}(x) = \sqrt{\langle x^2\rangle - \langle x\rangle^2}$ of self-energy expressions appearing in Eq. (7). The statistical properties have been evaluated at $E = 0$ in the limits of large N_g and $(\rho_{0g})^{-1} \ll \Gamma_g \ll E_{mg}$. It is assumed that $k \neq k'$ in the entries with subscript kk'.

x	$\langle \mathrm{Re}\, x\rangle$	$\langle \mathrm{Im}\, x\rangle$	$\mathrm{SD}(\mathrm{Re}\, x)$	$\mathrm{SD}(\mathrm{Im}\, x)$
w_{kk}	0	$-\pi v_k^2 \rho_{0g}$	$(\frac{2\pi v_k^4 \rho_{0g}}{\Gamma_g})^{1/2}$	$(\frac{2\pi v_k^4 \rho_{0g}}{\Gamma_g})^{1/2}$
$w_{kk'}$	0	0	$(\frac{\pi v_k^2 v_{k'}^2 \rho_{0g}}{\Gamma_g})^{1/2}$	$(\frac{\pi v_k^2 v_{k'}^2 \rho_{0g}}{\Gamma_g})^{1/2}$
$\lvert w_{kk'}\rvert^2$	$\frac{2\pi v_k^2 v_{k'}^2 \rho_{0g}}{\Gamma_g}$		$\frac{2\pi v_k^2 v_{k'}^2 \rho_{0g}}{\Gamma_g}$	
$w_{kk'}^2$	$-\frac{\pi v_k^2 v_{k'}^2 \rho_{0g}}{E_{mg}}$	0	$\frac{2\pi v_k^2 v_{k'}^2 \rho_{0g}}{\Gamma_g}$	$\frac{2\pi v_k^2 v_{k'}^2 \rho_{0g}}{\Gamma_g}$

is equal to its expectation value. In the χ-squared family of distributions, the standard deviation of the PT distribution is twice its expectation value while the distribution for two degrees of freedom is equal to the expectation value. One can also infer that the fluctuations in $w_{kk'}$ have two independent degrees of freedom by noting that the cross-correlation $\langle(\mathrm{Re}\, w_{kk'})(\mathrm{Im}\, w_{kk'})\rangle$ vanishes in the limit considered above. Thus the real and imaginary parts can be considered separate degrees of freedom. This is our analytic evidence that the fluctuations in transition-state theory follow the corresponding χ-squared distribution in the overlapping resonance region, $\rho_{0a}\Gamma_a \gtrsim 1$.

For the remainder of the Letter we explore numerically the distribution for a range of $\rho_{0a}\Gamma_a$ extending well into the isolated resonance region,[2] $\rho_{0a}\Gamma_a \ll 1$. Figure 1 shows the distribution of P_b for the Hamiltonian parameters given in the caption. One can see that the numerically sampled distribution agrees well with the χ-squared distribution for two degrees of freedom. To understand the deviation from the PT distribution, Fig. 2 shows the distribution of the probability P_b for several values of Γ_a, setting $t_2 = -(10\Gamma_a)^{1/2}$ and keeping the other parameters the same as in Fig. 1. We wish to keep the expectation value $\langle P_b\rangle$ constant as Γ_a is varied. This is achieved in the transition-state formula Eq. (38) of Ref. [26] by changing t_2 as described. The two curves in each panel show the fits to the two distributions. When Γ_a is much smaller than v_g and Γ_b, as in Fig. 2(a), the distribution is consistent with the PT distribution. As Γ_a increases, it gradually deviates from that, and eventually comes close to the distribution for two degrees of freedom. We have checked that the calculated distribution is insensitive to the decay widths in the second reservoir over a broad range of the parameter $\rho_{0b}\Gamma_b$.

[2]The Green's function for the isolated resonance region has also been studied analytically [39].

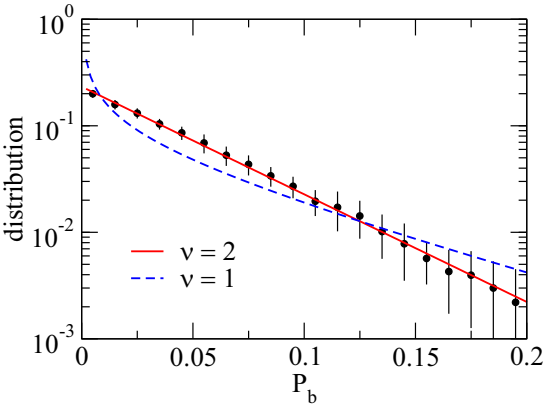

FIG. 1. Distribution of numerically sampled decay probabilities P_b (black circles) compared with the PT distribution (dashed line) and χ-squared distribution for two degrees of freedom (dashed line). The dimensions of the two GOE spaces are $N_g = 100$ and their Hamiltonian parameters $v_g, v_k, v_{k'}, \Gamma_g$ are set to 0.1. The hopping matrix elements in the channel spaces are taken as $t_i = 1$. The mean values and the root-mean-square (rms) deviations for the numerical sampling are calculated for 50 histogrammed runs, each of which is constructed for 500 samples.

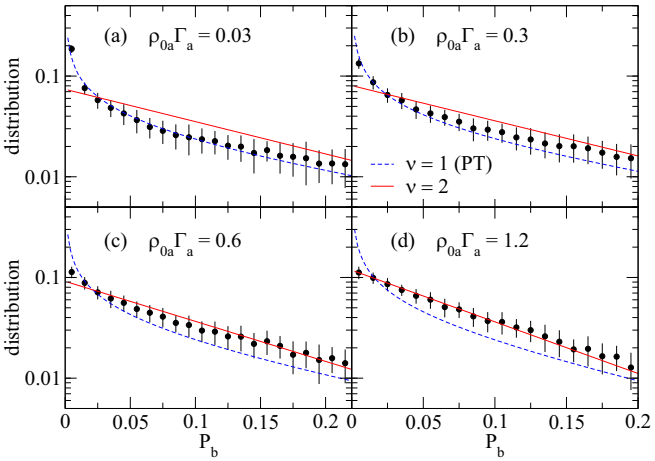

FIG. 2. The distribution of the transmission probability for the second reservoir, P_b, for several values of Γ_a and $t_2 = -(10\Gamma_a)^{1/2}$ as explained in the text. The dots with error bars were calculated with 50 histogrammed samplings as in Fig. 1. The dashed and the solid curves denote the PT distribution and the χ-squared distribution for two degrees of freedom, respectively.

We also carried out a least-squared fit of number of degrees of freedom in a χ-squared distribution to the histogrammed data with results shown in Fig. 3. It comes out close to one for small control parameter $\rho_{0a}\Gamma_a$ and close to two for moderate and large $\rho_{0a}\Gamma_a$. We have also plotted on the figure the function $\nu(y) = (1 + 8.28y^2)/(1 + 3.81y^2)$ with $y = \rho_{0a}\Gamma_a$ as a purely phenomenological description of fitted ν parameters.

Summary. Making use of random-matrix theory, we have applied a Hamiltonian model to fluctuations in reactions of complex quantum systems. The model had been previously proposed to find the limits of validity of the transition-state theory of averaged reaction quantities. It is common wisdom that fluctuations in decay rates associated with a transition state in a time-reversal-invariant Hamiltonian follow the PT distribution for one degree of freedom. However, the effective Hamiltonian is complex when boundary conditions arising from other channels are taken into account. When those decay widths are comparable or larger than the average level spacing, the fluctuations approach the χ-square distribution

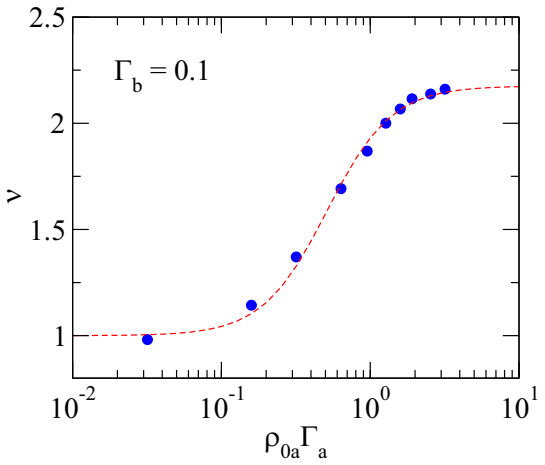

FIG. 3. Fitted values to the number of degrees of freedom ν as a function of the control parameter $\Gamma_a\rho_{0a}$. The Hamiltonians are defined in the same way as in Fig. 2. The dashed line shows an empirical fit, $\nu(y) = (1 + 8.28y^2)/(1 + 3.81y^2)$ with $y = \rho_{0a}\Gamma_a$. Note that the ν exceeds 2 in the asymptotic region $\rho_{0a}\Gamma_a \gg 1$. This may be a finite-size effect, but we have not examined this possibility.

for two degrees of freedom. In the model, the key quantity responsible for fluctuations is the quantity w_{23} which depends on Green's function for the Hamiltonian of the first reservoir. For real Green's functions the fluctuations are also real, corresponding to a single degree of freedom. However, if the states in the reservoir can decay directly into continuum channels, the Green's function is complex and the fluctuations approach those of a complex quantity with independent variations in the real and imaginary parts. This behavior leads to reaction rates that follow a distribution with two degrees of freedom.

In constructing the model, we assumed that the diagonal energies of the entrance channel, the bridge channels, and the centers of the two GOE reservoirs are equal. In fact, the conclusions remain under less restrictive conditions. The equality of the two bridge-state energies is implicit in the definition of a channel. Also, the interest is only in fluctuations associated transmission through open channels; this requires the channel energy to be close to that of the bridge channel. The center energies of the two GOE reservoirs are not required to be the same. Displacements of the center energies result in an offset of the real part of the w_{kk}, which can be subsumed into the construction of the channel Hamiltonian. Turning to the off-diagonal w_{23}, its crucial role in the fluctuations is due to the fact that its expectation value is zero. This comes about because of the structure of the matrix element with the uncorrelated vectors v_2 and v_3 rather than the details of the reservoir Hamiltonian.

A crossover from one to two degrees of freedom has also been studied in random matrix models [8,40], interpolating between the GOE and the GUE ensembles. However, it is not clear from such studies how to relate the complex matrix elements to physical quantities when the underlying Hamiltonian is purely real.

The present model might be useful in the methodology for determining the effective number of channels in transition-state theory. In Ref. [41] the effective number of channels in a unimolecular reaction was estimated from a formula based on the PT distribution [9],

$$\nu_{\rm eff} = 2\langle\Gamma\rangle^2/(\langle\Gamma^2\rangle - \langle\Gamma\rangle^2). \tag{8}$$

The authors found that their theoretical calculations were a factor of 2 off. Depending on the direct decay widths of the initial molecule, the explanation might be the factor of 2 difference between the variances of the two distributions.

Previously, it has been shown in nuclear physics that a coupling to continuum states could narrow the distribution, leading to a fitted number of degrees of freedom smaller than one [22]. This was not realized in our model, as the fit gave values between 1 and 2. In any case, it would be interesting if the deviation from the Porter-Thomas distribution discussed in that paper could be observed experimentally.

Acknowledgments. We thank Yoram Alhassid for linking the distribution for two degrees of freedom to the fluctuations of w_{23} in the complex plane. We also thank him, Yan Fyodorov, and Hans Weidenmüller for additional comments on the manuscript. This work was supported in part by JSPS KAKENHI Grants No. JP19K03861 and No. JP21H00120.

[1] E. Wigner, Ann. Math. **52**, 548 (1955).
[2] F. J. Dyson, J. Math. Phys. **3**, 140 (1962).
[3] T. Guhr, A. Müller-Groeling, and H. A. Weidenmüller, Phys. Rep. **299**, 189 (1998).
[4] H. A. Weidenmüller and G. E. Mitchell, Rev. Mod. Phys. **81**, 539 (2009).
[5] V. Zelevinsky, B.A. Brown, N. Frazier, and M. Horoi, Phys. Rep. **276**, 85 (1996).
[6] P. Naubereit, D. Studer, A. V. Viatkina, A. Buchleitner, B. Dietz, V. V. Flambaum, and K. Wendt, Phys. Rev. A **98**, 022506 (2018).
[7] C. W. J. Beenakker, Rev. Mod. Phys. **69**, 731 (1997).
[8] Y. Alhassid, Rev. Mod. Phys. **72**, 895 (2000).
[9] W. H. Miller, R. Hernandez, C. B. Moore, and W. F. Polik, J. Chem. Phys. **93**, 5657 (1990).
[10] J. Verbarrschot and T. Wettig, Annu. Rev. Nucl. Part. Sci. **50**, 343 (2000).
[11] H. Alt, C. I. Barbosa, H. D. Graf, T. Guhr, H. L. Harney, R. Hofferbert, H. Rehfeld, and A. Richter, Phys. Rev. Lett. **81**, 4847 (1998).
[12] B. Dietz and A. Richter, Chaos **25**, 097601 (2015).
[13] B. Dietz, T. Guhr, H. L. Harney, and A. Richter, Phys. Rev. Lett. **96**, 254101 (2006).
[14] F. Jin, D. Willsch, M. Willsch, H. Lagemann, K. Michielsen, and H. De Raedt, J. Phys. Soc. Jpn. **90**, 012001 (2021).
[15] C. E. Porter and R. G. Thomas, Phys. Rev. **104**, 483 (1956).
[16] D. M. Brink, Some aspects of the interaction of light with matter, Ph.D. thesis, Oxford University, 1955, https://ora.ox.ac.uk/objects/uuid:334ec4a3-8a89-42aa-93f4-2e54d070ee09.

[17] P. E. Koehler, F. Becvar, M. Krticka, J. A. Harvey, and K. H. Guber, Phys. Rev. Lett. **105**, 072502 (2010).
[18] P. E. Koehler, Phys. Rev. C **84**, 034312 (2011).
[19] J. F. Shriner, Jr., C. A. Grossmann, and G. E. Mitchell, Phys. Rev. C **62**, 054305 (2000).
[20] A. Volya, H. A. Weidenmüller, and V. Zelevinsky, Phys. Rev. Lett. **115**, 052501 (2015).
[21] E. Bogomolny, Phys. Rev. Lett. **118**, 022501 (2017).
[22] G. L. Celardo, N. Auerbach, F. M. Izrailev, and V. G. Zelevinsky, Phys. Rev. Lett. **106**, 042501 (2011).
[23] A. Volya, Phys. Rev. C **83**, 044312 (2011).
[24] H. A. Weidenmüller, Phys. Rev. Lett. **105**, 232501 (2010).
[25] Y. V. Fyodorov and D. V. Savin, Europhys. Lett. **110**, 40006 (2015).
[26] G. F. Bertsch and K. Hagino, J. Phys. Soc. Jpn. **90**, 114005 (2021).
[27] N. Bohr and J. A. Wheeler, Phys. Rev. **56**, 426 (1939).
[28] D. G. Truhlar, B. C. Garrett, and S. J. Klippenstein, J. Phys. Chem. **100**, 12771 (1996).
[29] D. G. Truhlar, W. L. Hase, and J. T. Hynes, J. Phys. Chem. **87**, 2664 (1983).
[30] G. Mills and H. Jónsson, Phys. Rev. Lett. **72**, 1124 (1994).
[31] W. H. Miller, J. Chem. Phys. **61**, 1823 (1974).
[32] K. J. Laidler and M. C. King, J. Phys. Chem. **87**, 2657 (1983).
[33] R. A. Marcus and O. K. Rice, J. Phys. Colloid Chem. **55**, 894 (1951).
[34] R. A. Marcus, J. Chem. Phys. **20**, 359 (1952).
[35] H.-L. Harney, A. Richter, and H. A. Weidenmüller, Rev. Mod. Phys. **58**, 607 (1986).
[36] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevE.104.L052104 for derivations for the decay probability and the variances of self-energy quantities.
[37] O. I. Lobkis, R. L. Weaver, and I. Rozhkov, J. Sound Vib. **237**, 281 (2000).
[38] S. B. Fedeli and Y. V. Fyodorov, J. Phys. A: Math. Theor. **53**, 165701 (2020).
[39] I. Rozhkov, Y. V. Fyodorov, and R. L. Weaver, Phys. Rev. E **69**, 036206 (2004).
[40] Y. Alhassid, J. N. Hormuzdiar, and N. D. Whelan, Phys. Rev. B **58**, 4866 (1998).
[41] W. F. Polik *et al.*, J. Chem. Phys. **92**, 3471 (1990).