Journal of the Physical Society of Japan **93**, 064003 (2024)
https://doi.org/10.7566/JPSJ.93.064003

Microscopic Derivation of Transition-state Theory for Complex Quantum Systems

Kouichi Hagino[1] and George F. Bertsch[2]

[1]*Department of Physics, Kyoto University, Kyoto 606-8502, Japan*
[2]*Department of Physics and Institute for Nuclear Theory, University of Washington, Box 351560, Seattle, DC 98915, U.S.A.*

(Received December 9, 2023; revised February 18, 2024; accepted April 22, 2024; published online May 24, 2024)

The decay of quantum complex systems through a potential barrier is often described with transition-state theory, also known as RRKM theory in chemistry. Here we derive the basic formula for transition-state theory based on a generic Hamiltonian as might be constructed in a configuration-interaction basis. Two reservoirs of random Hamiltonians from Gaussian orthogonal ensembles are coupled to intermediate states representing the transition states at a barrier. Under the condition that the decay of the reservoirs to open channels is large, an analytic formula for reaction rates is derived. The transition states act as independent Breit–Wigner resonances which contribute additively to the total transition probability, as is well known for electronic conductance through resonant tunneling states. It is also found that the transition probability is independent of the decay properties of the states in the second reservoir over a wide range of decay widths.

1. Introduction

Transition-state theory is ubiquitous in physics and chemistry to calculate reaction and decay rates for many-particle systems in the presence of a barrier.[1–5] The assumptions in the theory are clear in classical dynamics but less so in the quantum regime. For fermionic systems of equal-mass particles, the Hamiltonian is often formulated in a configuration-interaction (CI) representation. This motivates considering models that exhibit the barrier dynamics in the CI framework to understand conditions to support transition-state approximations.

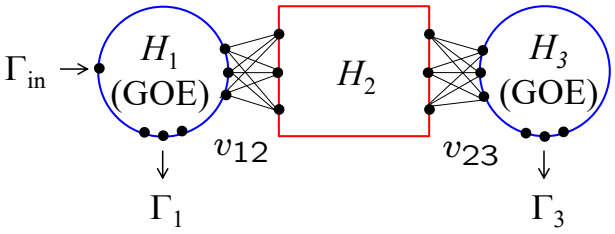

Fig. 1. (Color online) Schematic structure of the model Hamiltonian composed of two reservoirs connected by a bridge Hamiltonian and open to three sets of external channels.

2. Model Hamiltonian

Following previous recent work, we consider here a Hamiltonian composed of three sets of states. The states in the barrier region are represented in the Hamiltonian H_2. Their precise structure is not specified, but we have in mind a set of configurations with the ground states and their quasiparticle excitations determined by constrained Hartree–Fock or density-functional theory. The other two sets of states contained in Hamiltonians H_1 and H_2 are statistical reservoirs, with their Hamiltonians constructed from the matrices of the Gaussian orthogonal ensemble GOE.[6] For this Hamiltonian, one may think about, e.g., a decay from a highly excited configuration, so that the both the pre-saddle and the post-saddle configurations can be treated statistically.[7–10] It is important to note that the GOE Ansatz is the only statistical input, and the ensemble is microcanonical rather than canonical. The full Hamiltonian reads

$$H = \begin{pmatrix} H_1 & V_{12} & 0 \\ V_{12}^T & H_2 & V_{32}^T \\ 0 & V_{32} & H_3 \end{pmatrix}, \tag{1}$$

where V_{12} and V_{23} are matrices of the coupling interaction between the reservoir states and the states in the bridge Hamiltonian. This model is generalization of the of the model in Ref. 11, which assumes that H_2 has a single state at the barrier top. See also Ref. 12 for a similar generalization.

To complete a model for reactions, one also needs the coupling matrix elements between H and the reaction channels. With those ingredients the S-matrix for transitions from one channel to another can be computed by standard linear algebra manipulations. If one is only interested in reaction probabilities, the linear algebra can be collapsed to a compact formula[13–18] for the transition probability from channel a to channel b given by

$$T_{ab} = |S_{ab}(E)|^2 = {\rm Tr}(\Gamma_a G(E) \Gamma_b G^\dagger(E)). \tag{2}$$

Here G is the Green's function of the Hamiltonian in presence of entrance or decay channels c at reaction energy E,[20]

$$G(E) = \left(H - i \sum_c \Gamma_c/2 - E \right)^{-1}. \tag{3}$$

In general the Γ_c are rank-one matrices (of the same dimension as H) but for the present model they have only one entry on the diagonal and a block structure given by

$$\Gamma_{\rm in} = \begin{pmatrix} \tilde{\Gamma}_{\rm in} & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad \Gamma_1 = \begin{pmatrix} \tilde{\Gamma}_1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix},$$
$$\Gamma_3 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \tilde{\Gamma}_3 \end{pmatrix} \tag{4}$$

depending on which subblock the channel c connects to. The full Hamiltonian with its coupling to external channels is depicted in Fig. 1. In general, one is interested in the reaction probability T_{a3} from an entrance channel ($a = {\rm in}$) to all possible decay channels in the second reservoir,

$$T_{\mathrm{in},3} = \sum_{c\in \text{block } 3} |S_{\mathrm{in},c}|^2. \tag{5}$$

Due to the block structures of H and Γ_c we only need the G_{13} block of the Green's function

$$G = \begin{pmatrix} G_{11} & G_{12} & G_{13} \\ G_{21} & G_{22} & G_{23} \\ G_{31} & G_{32} & G_{33} \end{pmatrix} \tag{6}$$

in Eq. (2). As derived in Appendix A, the submatrix G_{13} reduces to

$$G_{13} = G_1 V_{12} G_2 V_{32}^T G_3, \tag{7}$$

where G_1, G_3, and G_2 are given by

$$G_1 = (H_1 - i\tilde{\Gamma}_{\mathrm{in}}/2 - i\tilde{\Gamma}_1/2 - E)^{-1}, \tag{8}$$

$$G_3 = (H_3 - i\tilde{\Gamma}_3/2 - E)^{-1}, \tag{9}$$

$$G_2 = (H_2 - V_{12}^T G_1 V_{12} - V_{32}^T G_3 V_{32} - E)^{-1}. \tag{10}$$

Substituting Eq. (7) into Eq. (2), the transmission coefficient is obtained as

$$T_{\mathrm{in},3}(E) = \mathrm{Tr}[\tilde{\Gamma}_{\mathrm{in}}(G_1 V_{12} G_2 V_{32}^T G_3)\tilde{\Gamma}_3 (G_3^\dagger V_{32} G_2^\dagger V_{12}^T G_1^\dagger)], \tag{11}$$

$$= \mathrm{Tr}[(V_{12}^T G_1^\dagger \tilde{\Gamma}_{\mathrm{in}} G_1 V_{12}) G_2 (V_{23} G_3 \tilde{\Gamma}_3 G_3^\dagger V_{32}) G_2^\dagger]. \tag{12}$$

We write the elements of the two GOE Hamiltonians as

$$(H_k)_{ij} = (H_k)_{ji} = v_k \sqrt{1+\delta_{ij}}\, r_{ijk}, \tag{13}$$

where r_{ijk} is a random number from a Gaussian distribution of unit dispersion, $\langle r_{ijk}^2 \rangle = 1$. Then the average level density ρ_k at $E = 0$ at the centers of the GOE Hamiltonians is given by

$$\rho_k = \frac{N_k^{1/2}}{\pi v_k}, \tag{14}$$

where N_k is the dimension of H_k. We set $E = 0$ for the rest of this paper. Each state in H_2 is assumed to couple to specific states in the GOE reservoirs. We parameterize the couplings as[21)]

$$(V_{12})_{ij} = v_{12} N_1^{1/2} \delta_{ij}, \quad (V_{32})_{ij} = v_{32} N_3^{1/2} \delta_{ij}. \tag{15}$$

This parameterization is not as restrictive as it may seem. Due to the GOE invariance, the couplings can be to arbitrary orthogonal vectors in the GOE spaces. The specific form of the coupling is such that the average matrix element is independent of the dimension N_k.

The matrices for the decay widths are assumed to be diagonal with elements

$$(\tilde{\Gamma}_1)_{ij} = \gamma_1\, \delta_{i,j}, \quad (\tilde{\Gamma}_3)_{ij} = \gamma_3\, \delta_{i,j}, \tag{16}$$

except for the entrance channel $a = \mathrm{in}$, which couples to a single state $i = 1$ in the first reservoir,

$$(\tilde{\Gamma}_{\mathrm{in}})_{ij} = \gamma_{\mathrm{in}}\, \delta_{i,1}\delta_{j,1}. \tag{17}$$

Without loss of generality, the only requirement on $\tilde{\Gamma}_{\mathrm{in}}$ is that it has rank one within the space of H_1, as in the "Büttiker probes" of semiconductor transport theory.[22–24)]

3. Transition-state Theory

We now examine how the average reaction probability depends on the parameters of the model. Since transition-state theory deals with fluxes into or from a statistical reservoir, it is convenient to define a transmission coefficient $\mathcal{T}_{ck}$ of a channel c in the second block into the reservoir k

$$\mathcal{T}_{ck} = 2\pi\rho_k\gamma_k \tag{18}$$

and its sum over channels,

$$\mathcal{T}_k = \sum_{c\in k} \mathcal{T}_{ck}. \tag{19}$$

For small values of $\mathcal{T}_{ck}$ it has the physical significance of the transmission probability from the channel c into the statistical reservoir. As shown in Ref. 11, it is straightforward to carry out the statistical averaging for Eq. (2) in the limit that $\mathcal{T}_k/N_k \gg 1$ for both reservoirs. We first examine the Green's function G_2 and the coupling terms $V_{k2}^T G_k V_{k2}$ in it. The averages of G_k $(k = 1, 3)$ at $E = 0$[25)] including the decay-width matrices are given by[11,26–28)]

$$\langle G_k \rangle_{ij} = i\frac{\pi\rho_k}{N_k}\delta_{ij}. \tag{20}$$

The standard deviation of the fluctuations is

$$SD(G_k)_{ij} = \frac{\pi\rho_k}{N_k}(1+i)\left(\frac{2(1+\delta_{i,j})N_k}{\mathcal{T}_k}\right)^{1/2}. \tag{21}$$

The fluctuations go to zero in the limit $\mathcal{T}_k/N_k \gg 1$ so these terms in G_2 can be replaced by $i\pi v_{k2}^2\rho_k$ times the unit matrix. Thus the correlations between G_2 and the other terms in Eq. (12) vanish, allowing it to be evaluated as

$$\bar{G}_2 = (H_2 - V_{12}^T\langle G_1\rangle V_{12} - V_{32}^T\langle G_3\rangle V_{32} - E)^{-1}. \tag{22}$$

The two terms in parentheses in Eq. (12) are independent of each other so can also be replaced by their ensemble averages.

$$\langle (V_{12}^T G_1 \tilde{\Gamma}_{\mathrm{in}} G_1^\dagger V_{12})_{ij}\rangle = \frac{\gamma_{\mathrm{in}}}{N_1\gamma_1} 2\pi v_{12}^2\rho_1\delta_{ij}, \tag{23}$$

$$\langle (V_{32}^T G_3 \tilde{\Gamma}_3 G_3^\dagger V_{32})_{ij}\rangle = 2\pi v_{32}^2\rho_3\delta_{ij}, \tag{24}$$

in the limit $\mathcal{T}_k/N_k \gg 1$ (see Appendix B).

We can cast the formulas in a more transparent notation by defining decay widths of the transition states to the right-hand and left-hand reservoirs as

$$\Gamma_R = 2\pi v_{32}^2\rho_3 \tag{25}$$

and

$$\Gamma_L = 2\pi v_{12}^2\rho_1. \tag{26}$$

Using Eq. (B·8) in Appendix B, one obtains

$$\langle T_{\mathrm{in},3}\rangle = \frac{\mathcal{T}_{\mathrm{in}}}{\mathcal{T}_1}\Gamma_L\Gamma_R \sum_{i,j}\langle |(G_2)_{ij}|^2\rangle \sum_{b\in 3}\left(\frac{T_b}{\sum_{b'\in 3} T_{b'}}\right)$$

$$= \frac{\mathcal{T}_{\mathrm{in}}}{\mathcal{T}_1}\Gamma_L\Gamma_R \sum_{i,j}\langle |(G_2)_{ij}|^2\rangle, \tag{27}$$

where $\mathcal{T}_{\mathrm{in}} = 2\pi\Gamma_{\mathrm{in}}\rho_1/N_1$. It is remarkable that the ensemble average of the transmission coefficient is independent of Γ_3, and thus the insensitive property[7,26,29)] is realized.

Notice that G_2 in Eq. (10) can be written

$$G_2 = (H_2 - i(\Gamma_L/2 + \Gamma_R/2)\mathbb{1})^{-1}. \tag{28}$$

Table I. Comparison of transmission probability calculated by the trace formula Eq. (2) and by the $\mathcal{T}_k/N_k \gg 1$ reduction, Eq. (27). The parameter values in the reservoir Hamiltonians are $(v_k, v_{k2}, \gamma_k, N_k) = (0.1, 0.1, 0.1, 100)$. The H_2 matrix contains N_2 transition states at energies $E_i = 0$, and the partial width of the entrance channel is $\gamma_{\rm in} = 0.01$. The ensemble average in Eq. (2) was carried out with 10000 samples; the statistical uncertainties are of the order 1%.

N_2	$\mathcal{T}_k/N_k \gg 1$	Eq. (2)
1	0.0010	0.00079
2	0.0020	0.00148

Then if H_2 is diagonal[30] with matrix elements $(H_2)_{ij} = E_i\delta_{i,j}$, the transmission coefficient becomes

$$\langle T_{\rm in,3}\rangle = \frac{\mathcal{T}_{\rm in}}{\mathcal{T}_1}\sum_i \frac{\Gamma_L\Gamma_R}{E_i^2 + (\Gamma_L+\Gamma_R)^2/4}. \tag{29}$$

This is a well-known formula for electron transport through intermediate resonances.[31,32] It agrees with an underlying assumption in transition-state models, that the contributions of the individual transition states are additive in the total transmission probability.[33]

The formula also shows that the contribution to the transmission coefficient is suppressed when the energy of a bridge state is outside the range of $\pm(\Gamma_L + \Gamma_R)/2$ around the incident energy. This is marked contrast to models in which the transition state is an internal channel that remains open at all energies above the threshold. To maintain the correspondence to the CI formulation, one would have to include highly excited configurations that carry momentum along a collective coordinate. At some point the model would break down because the coupling matrix element would become small compared to v_k, the coupling strength of the configurations within the GOE's.

3.1 Numerical examples

Equations (21)–(23), and (29) are valid in limit $\mathcal{T}_k/N_k \gg 1$. It is of interest to see how their accuracy is degraded at finite values of these parameters, as well as the sensitivity to other assumptions in the model.[34] Table I shows two aspects of the model Hamiltonian and its reduction to the $\mathcal{T}_k/N_k \gg 1$ limit. First, one sees that reduction is accurate only to a 20% level despite the seeming large value for $\mathcal{T}_k/N_k = 20$. The slow convergence can be traced to the r.m.s. fluctuation exhibited in Eq. (21), dying off only as $N_k^{-1/2}$. The table also demonstrates for $N_2 = 1$ and 2 that the transmission probability scales quite well with the number of transition states at the same energy, given that their couplings are orthogonal and have the same strength. This is implicit in the reduction to Eq. (29).

Next we examine the sensitivity to the decay matrix elements. The dependence on $\gamma_{\rm in}$ is trivial as it contributes quadratically when it is small compared to other widths. The exit decay is independent of γ_3 in the reduced formula. This is tested in Table II, varying γ_3 and keeping the other parameters fixed. One sees that the dependence is quite flat within the boundaries $\rho_3^{-1} < \gamma_3 < \sqrt{N_3}v_3$.

It is also interesting to see how the formula breaks down when the condition $\mathcal{T}_k/N_k \gg 1$ is no longer satisfied. When the direct decay of the first reservoir becomes small, more of the probability flux crosses the barrier and $T_{\rm in,3}$ only competes with elastic scattering. Table III shows a comparison of the analytic reduction with the full trace evaluation in Eq. (2). One sees that the analytic reduction becomes quite inaccurate for the smaller values of $\mathcal{T}_1/N_1$.

Table II. Dependence of transmission probability on the parameter γ_3. The other parameters are the same as in the caption to Table I for the $N_2 = 1$ Hamiltonian.

γ_3	Eq. (2)
0.05	0.00074
0.1	0.00079
0.2	0.00083
0.4	0.00085

Table III. Dependence of transmission probability on $\mathcal{T}_1/N_1$ varying the parameter γ_1. The other parameters are the same as in the caption to Table I for the $N_2 = 1$ Hamiltonian. The column R shows the ratio of the analytic reduction Eq. (27) to value obtained with Eq. (2) taking 10000 samples of the GOE's. The statistical errors decrease from 2% for the first entry to 1% for the last one.

$\mathcal{T}_k/N_k$	R
1	2.75
2	2.00
6	1.45
10	1.30
20	1.25

4. Summary

While transition-state theory for decay of quantum complex systems is usually derived with a statistical approach, we have successfully derived it starting from a matrix Hamiltonian as is commonly used in configuration-interaction formulations. To this end, we considered two reservoirs described by random matrices. One of the configurations in the first reservoir undergoes transitions to configurations in the second reservoir through bridge configurations between them. A potential barrier may exist for the bridge configurations. This generalizes a model with a single barrier configuration that was discussed by Weidenmüller.[11]

As in Ref. 11, we have shown that the average transmission coefficient from the entrance configuration to configurations in the second reservoir can be factorized into a product form of the formation and the decay probabilities of transition channels, in the limit of $\mathcal{T}_3/N_3 \gg 1$. This is also a consequence of the usual starting point of transition state theory, that once the system passes the barrier, it never comes back.

If the condition $\mathcal{T}_1/N_1 \gg 1$ is also satisfied, the transmission coefficient is further simplified to a product of the population probability of the first reservoir, the transmission coefficient over the barrier, and the decay probability of the configurations in the second reservoir. In that case the transmission coefficient can be expressed in terms of Breit–Wigner resonance decays, as has been long known in nuclear physics and in the field of electron transport.

Transition-state theory is a landmark framework for decays of quantum complex systems, but conditions for transition-state theory to work have not yet been well clarified. The microscopic derivation based on the random matrix approach

shown in this paper provides a necessary condition for transition-state theory to work. Such consideration would be important in the decay of complex systems at energies close to barrier tops.

Acknowledgments We thank Hans Weidenmüller for useful discussions. This work was supported in part by JSPS KAKENHI Grant Numbers JP19K03861 and JP23K03414.

Appendix A: The Green's Function for a Block-tridiagonal Hamiltonian

We invert the matrix

$$H - i\tilde{\Gamma}_{\rm in}/2 - i\tilde{\Gamma}_1/2 - i\tilde{\Gamma}_3/2 - E = \begin{pmatrix} \tilde{H}_1 & V_{12} & 0 \\ V_{12}^T & \tilde{H}_2 & V_{23} \\ 0 & V_{23}^T & \tilde{H}_3 \end{pmatrix}, \tag{A·1}$$

where $\tilde{H}_i$ are defined as

$$\tilde{H}_1 \equiv H_1 - i\Gamma_{\rm in}/2 - i\Gamma_1/2 - E, \tag{A·2}$$

$$\tilde{H}_2 \equiv H_2 - E, \tag{A·3}$$

$$\tilde{H}_3 \equiv H_1 - i\Gamma_3/2 - E. \tag{A·4}$$

The Green's function (6) satisfies the relation,

$$\begin{pmatrix} \tilde{H}_1 & V_{12} & 0 \\ V_{12}^T & \tilde{H}_2 & V_{32}^T \\ 0 & V_{32} & \tilde{H}_3 \end{pmatrix} \begin{pmatrix} G_{11} & G_{12} & G_{13} \\ G_{21} & G_{22} & G_{23} \\ G_{31} & G_{32} & G_{33} \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \tag{A·5}$$

from which one finds

$$\tilde{H}_1 G_{13} + V_{12} G_{32}^T = 0, \tag{A·6}$$

$$V_{12}^T G_{13} + \tilde{H}_2 G_{23} + V_{23} G_{33} = 0, \tag{A·7}$$

$$V_{32} G_{23} + \tilde{H}_3 G_{33} = 1. \tag{A·8}$$

From Eqs. (A·6) and (A·8), G_{13} and G_{33} read

$$G_{13} = -\tilde{H}_1^{-1} V_{12} G_{23}, \tag{A·9}$$

and

$$G_{33} = \tilde{H}_3^{-1} - \tilde{H}_3^{-1} V_{32} G_{23}, \tag{A·10}$$

respectively. Substituting these into Eq. (A·7), one obtains

$$G_{23} = -(\tilde{H}_2 - V_{12}^T \tilde{H}_1^{-1} V_{12} - V_{32}^T \tilde{H}_3^{-1} V_{32})^{-1} V_{32}^T \tilde{H}_3^{-1}. \tag{A·11}$$

Combining Eqs. (A·9) and (A·11), one finally obtains Eq. (7).

Following a similar procedure, one can also derive

$$G_{11} = G_1 + G_1 V_{12} G_2 V_{12}^T G_1. \tag{A·12}$$

Appendix B: Ensemble Average of $VG\tilde{\Gamma}G^\dagger V^T$

In this Appendix, we evaluate the ensemble average of a matrix $VG\tilde{\Gamma}G^\dagger V^T$, where the elements of V are Gaussian-distributed random numbers with $\langle v_{ij}^2 \rangle = v^2$, $\tilde{\Gamma}$ is a constant times the unit matrix $\tilde{\Gamma}_{ij} = \gamma\delta_{i,j}$, and G is the Green's function $G = (H - i\tilde{\Gamma}/2)^{-1}$. Here H is a sample of the $N \times N$ GOE with a level density ρ_0 in the center of its spectrum. We follow Refs. 26 and 29 to carry out the ensemble averaging. We first express the elements of the Green's function as

$$G_{ij} = \sum_\lambda \frac{\phi_i^\lambda \phi_j^\lambda}{E_\lambda - i\gamma/2}, \tag{B·1}$$

where E_λ are the eigenvalues of the Hamiltonian H and ϕ^λ are the corresponding eigenfunctions.

The ij element of $VG\tilde{\Gamma}G^\dagger V^T$ then reads,

$$(VG\tilde{\Gamma}G^\dagger V^T)_{ij} = \sum_{i'j'mm'\lambda\lambda'} \frac{V_{ii'}\phi_{i'}^\lambda \phi_m^\lambda \tilde{\Gamma}_{mm'} \phi_{m'}^{\lambda'} \phi_{j'}^{\lambda'} V_{j'j}}{(E_\lambda - i\gamma/2)(E_{\lambda'} + i\gamma/2)}. \tag{B·2}$$

The sum over m' is evaluated as

$$\sum_{m'} \tilde{\Gamma}_{mm'} \phi_{m'}^{\lambda'} = \gamma \phi_m^{\lambda'}, \tag{B·3}$$

since $\tilde{\Gamma}$ is assumed to be proportional to the unit matrix. Next the orthogonality of the eigenvectors λ and λ' permits the sum over λ' to be dropped with replacement λ' by λ. Then Eq. (B·2) reduces to

$$(VG\tilde{\Gamma}G^\dagger V^T)_{ij} = \gamma \sum_{i'j'} \sum_\lambda \left(\frac{V_{ii'} V_{jj'} \phi_{i'}^\lambda \phi_{j'}^\lambda}{E_\lambda^2 + \gamma^2/4} \right). \tag{B·4}$$

Next we take the ensemble average of the factor in parentheses. One of the properties of the GOE is that fluctuations about the average level densities are small, so the ensemble averages of the numerator and denominator are uncorrelated. The denominator average is[26,29]

$$\left\langle \sum_\lambda \frac{1}{E_\lambda^2 + \gamma^2/4} \right\rangle = 2\pi \frac{\rho_0}{\gamma}. \tag{B·5}$$

For the numerator, we first notice that the dot products $\boldsymbol{V}_i \cdot \boldsymbol{\phi}_\lambda \equiv \sum_{i'} V_{ii'} \phi_{i'}^\lambda$ are Gaussian distributed with $\boldsymbol{V}_i \cdot \boldsymbol{\phi}_\lambda = v\, r_{i\lambda}$, where $r_{i\lambda}$ is a random number satisfying $\langle r_{i\lambda} \rangle = 0$ and $\langle r_{i\lambda} r_{i'\lambda'} \rangle = \delta_{i,i'}\delta_{\lambda\lambda'}$. One thus obtains

$$\langle (\boldsymbol{V}_i \cdot \boldsymbol{\phi}_\lambda)(\boldsymbol{V}_j \cdot \boldsymbol{\phi}_\lambda) \rangle = v^2 \delta_{i,j}, \tag{B·6}$$

which leads to

$$\langle (VG\tilde{\Gamma}G^\dagger V^T)_{ij} \rangle = 2\pi v^2 \rho_0\, \delta_{i,j}. \tag{B·7}$$

We also need the ensemble average of $VG\tilde{\Gamma}_{\rm in}G^\dagger V^T$ with $G = (H - i\tilde{\Gamma}/2 - i\tilde{\Gamma}_{\rm in}/2)^{-1}$, where $\tilde{\Gamma}_{\rm in}$ is given by Eq. (17). In this case, the sum over m is restricted to a single state in Eq. (B·2). Due to the invariance of the averages under unitary transformations, the sum over m, m' becomes $\langle \phi_{\lambda,{\rm in}} \phi_{\lambda',{\rm in}} \rangle = \delta_{\lambda,\lambda'}/N$. The final result is

$$\langle (VG\tilde{\Gamma}_{\rm in}G^\dagger V^T)_{ij} \rangle = \frac{\Gamma_{\rm in}}{N\gamma} 2\pi v^2 \rho_0\, \delta_{i,j}. \tag{B·8}$$

1) P. Hänggi, P. Talkner, and M. Borkovec, Rev. Mod. Phys. **62**, 251 (1990).
2) D. G. Truhlar, B. C. Garrett, and S. J. Klippenstein, J. Phys. Chem. **100**, 12771 (1996).
3) U. Weiss, *Quantum Dissipative Systems* (World Scientific, Singapore, 2012) 4th ed.
4) N. Bohr and J. A. Wheeler, Phys. Rev. **56**, 426 (1939).
5) R. A. Marcus and O. K. Rice, J. Phys. Chem. **55**, 894 (1951).
6) H. A. Weidenmüller, Rev. Mod. Phys. **81**, 539 (2009).
7) G. F. Bertsch and K. Hagino, Phys. Rev. C **107**, 044615 (2023).
8) W. F. Polik, D. R. Guyer, W. H. Miller, and C. B. Moore, J. Chem. Phys. **92**, 3471 (1990).
9) W. H. Miller, R. Hernandez, C. B. Moore, and W. F. Polik, J. Chem. Phys. **93**, 5657 (1990).
10) R. Hernandez, W. H. Miller, C. B. Moore, and W. F. Polik, J. Chem. Phys. **99**, 950 (1993).
11) H. A. Weidenmüller, Phys. Rev. E **105**, 044143 (2022).
12) H. A. Weidenmüller, Phys. Rev. E **109**, 034117 (2024).
13) P. S. Damle, A. W. Ghosh, and S. Datta, Phys. Rev. B **64**, 201403

(2001).
14) S. Datta, *Electronic Transport in Mesoscopic Systems* (Cambridge University Press, Cambridge, U.K., 1995) Eq. (e3.5.20).
15) W. H. Miller, Acc. Chem. Res. **26**, 174 (1993).
16) H. Haug and A.-P. Jauho, *Quantum Kinetics in Transport and Optics of Semiconductors* (Springer, Berlin, 2008) Eq. (12.37).
17) Y. Alhassid, G. F. Bertsch, and P. Fanto, Ann. Phys. **424**, 168381 (2021).
18) The formula had been used earlier as well[19] in the theory of electrical conductivity.
19) Y. Meir and N. S. Wingreen, Phys. Rev. Lett. **68**, 2512 (1992), Eq. (7).
20) It is implicitly assumed in Eq. (3) that the Γ_c are independent of energy.
21) We implicitly assume $N_k > N_2$ for both reservoirs.
22) M. Büttiker, Phys. Rev. Lett. **57**, 1761 (1986).
23) R. Venugopal, M. Paulsson, S. Goasguen, S. Datta, and M. S. Lundstrom, J. Appl. Phys. **93**, 5613 (2003).
24) S. Datta, *Quantum Transport: Atom to Transistor* (Cambridge University Press, Cambridge, U.K., 2005).
25) We note that there are mild restrictions on the ranges of the parameters in Eq. (20). In practice, the widths associated with the individual channels should be large compared to the level spacing in the GOE but small with respect to the boundaries of its eigenspectrum.
26) K. Hagino and G. F. Bertsch, Phys. Rev. E **104**, L052104 (2021).
27) O. I. Lobkis, R. L. Weaver, and I. Rozkhov, J. Sound Vib. **237**, 281 (2000).
28) S. B. Fedeli and Y. V. Fyodorov, J. Phys. A **53**, 165701 (2020).
29) G. F. Bertsch and K. Hagino, J. Phys. Soc. Jpn. **90**, 114005 (2021).
30) In fact, this restriction is not necessary. The matrix H_2 can always be diagonalized by an orthogonal transformation which has no effect on the ensemble average.
31) G. F. Bertsch, arXiv:1407.1899 [nucl-th].
32) Y. Alhassid, Rev. Mod. Phys. **72**, 895 (2000).
33) This may not be the case for the probability fluxes through the individual transition states.
34) (Supplemental Material) Computer programs to generate the tables in this subsection are provided in the Supplementary Material.