J. Phys. Chem. A **1998,** *102,* 9577−9580

Spectral Autocorrelation Function in Weakly Open Chaotic Systems: Indirect Photodissociation of Molecules[||]

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Received: May 8, 1998; In Final Form: August 5, 1998

We derive the statistical limit of the spectral autocorrelation function and of the survival probability for the indirect photodissociation of molecules in the regime of nonoverlapping resonances. The results are derived in the framework of random matrix theory and hold more generally for any chaotic quantum system that is weakly coupled to the continuum. The "correlation hole" that characterizes the spectral autocorrelation in the bound molecule diminishes as the typical average total width of a resonance increases.

Quantum systems that are classically chaotic are believed to exhibit statistical fluctuations in their spectra and wavefunctions that are universal.[1] These universal properties are well-reproduced by the assumption that the Hamiltonians belong to an ensemble of Hamiltonians that are consistent with the underlying symmetries but are otherwise random. Such random Hamiltonians are described by random matrix theory (RMT)[2,3] and lead to level repulsion, long-range correlations in the spectrum, and Porter−Thomas statistics for the transition intensities. RMT was initially developed to explain the statistical properties of the neutron resonances in the compound nucleus.[2] However, similar statistical fluctuations are observed in a variety of molecular systems. These include fluorescence excitation spectra of polyatomic molecules, e.g., the vibrational levels and intensities of nitrogen dioxide[4,5] and pyrazine.[6] Level repulsion was observed in acetylene,[7] and statistical signatures of RMT were found in the Stark level-crossing spectra of formaldehyde at the dissociation threshold.[8] At low excitations the molecular Hamiltonian is approximately separable (though anharmonic), and the vibrational eigenstates are described by normal modes, allowing the assignment of good quantum numbers ("regular" regime). However, at higher excitations the normal modes are strongly mixed and the spectrum is better characterized in terms of its statistical properties ("chaotic" regime). A transition from regular to chaotic spectrum was observed in the vibrational levels of CS_2.[9]

Statistical measures of a spectrum include the nearest neighbors level spacing distribution and spectral rigidity (e.g., the Mehta−Dyson Δ_3 statistics). Such measures require accurate experimental determination of a complete set of levels.[5] In practice this is not always possible since the finite experimental resolution makes it difficult to determine the statistics of the small level spacings. In molecular spectroscopy it is particularly difficult to measure a complete set of levels because the density of states is very large at higher excitations.

A measure of chaos that is less sensitive to experimental resolution is the spectral autocorrelation function and its counterpart in the time domain, the survival probability.[10,11] Since the spectral autocorrelation involves the convolution of the spectrum (i.e., strength function) with itself, it is less sensitive to experimental noise. The spectral autocorrelation function is easily constructed from the experimental measurements. For example, using lasers one can excite molecules that are vibrationally and rotationally cooled and measure their absorption or fluorescence spectra (i.e., the strength function of the dipole operator). The convolution of the measured spectrum with itself is the spectral autocorrelator or the power spectrum. The corresponding quantity in the time domain, i.e., the Fourier transform of the power spectrum, is the probability that an initially prepared nonstationary state (e.g., the state generated by the operation of the dipole operator on the ground state of the molecule) remains in its initial state at a later time. For a chaotic or complex system, it was suggested that the power spectrum and the associated survival probability of the experimentally prepared state are characterized by the existence of a "correlation hole" (i.e., a pronounced local minimum) that originates in the repulsion of energy levels.[12] A correlation hole was observed in the spectrum of highly excited vibrational levels of complex molecules like methylglyoxal[12] and acetylene.[13] The correlation hole is a signature of chaos and it disappears when the dynamics of the system becomes regular.

The average survival probability and power spectrum in chaotic systems were evaluated in a closed form using RMT for the various classes of Gaussian ensembles,[14] and in the framework of a scattering model.[15] Similar expressions can be obtained by considering discrete time evolution for the circular Dyson ensembles.[16] The survival probability (and the associated power spectrum) carries information on both spectral and eigenvector statistics.[11] The derivation was restricted to systems that are closed and have discrete spectra. However, in many physical situations we are interested in the spectrum at high excitations, where the eigenstates are coupled to the continuum and become resonances. The coupling of the quantum system to the continuum is expected to diminish the correlation hole. Experimentally one usually observes a quenched correlation

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[||] Dedicated to Raphy Levine on the occasion of his 60th birthday. Y.A. would like to express his gratitude to Raphy for having been on outstanding Ph.D. advisor and for many years of inspiring conversations and collaborations. This paper grew out of an earlier work with Prof. Levine (ref 14).

10.1021/jp9821836 CCC: $15.00

hole, an effect attributed to unobserved good quantum numbers[13] and/or the transition to regular dynamics.[17,18] However, since the correlation hole can also be affected by the coupling of the closed system to its environment, it is important to derive the correlation hole quantitatively in this more general situation.

An important class of processes where coupling to the continuum is important is the photodissociation of molecules. In particular we are interested in indirect photodissociation that proceeds through resonances of the excited molecular complex.[19] A light pulse excites the molecule to a higher electronic state at energies above the dissociation threshold but where a potential barrier hinders the immediate dissociation of the molecule. The barrier is usually formed because of the avoided crossing of two diabatic electronic potential surfaces (one that is binding and one that is repulsive). Vibrational excitations (below and above the barrier) become resonances whose widths depend on the coupling between the binding and repulsive manifolds. Such resonances can also be populated in molecular reactions that proceed through an excited molecular complex.

Recently, the universal correlator for the bound-to-continuum strength function was derived for any degree of openness of the quantum system,[20] by using the method of the supersymmetric nonlinear σ model.[21,22] However, the general expression turned out to be rather complicated. Here we show that in the regime of isolated resonances (i.e., weak coupling) a much simpler closed form can be derived by using random matrix techniques. This regime of nonoverlapping resonances corresponds to indirect photodissociation at energies where the corresponding vibrational resonances lie below the barrier in the excited electronic potential surface. The width of such resonances is smaller than a typical separation between vibrational states by a factor of up to several thousand. The derivation in this paper is accomplished in the time domain where the survival probability of the experimentally prepared nonstationary state is averaged over the ensemble. This derivation is analogous to that used in ref 14 for closed systems. However, in the case of an open quantum system, it is necessary to take into account the decay of the system into the continuum. The probability for an open chaotic system (that is initially bound) to remain bound at a later time was calculated in ref 23. The coupling of the system to the continuum is described by the average partial widths of the system to decay into each of the open dissociation channels. The spectral correlator derived in this paper in the quantum ergodic limit (see eqs 16 and 15 below) depends only on these average partial "dissociation" widths (and the symmetry class of the Hamiltonian) but is otherwise universal. We find that the correlation hole diminishes when the partial widths of the resonances become larger or when the number of open channels increases.

An open system is described by an effective Hamiltonian $H_{\mathrm{eff}} = H - i\Gamma/2$, where H is the Hamiltonian of the system when it is uncoupled from the continuum and Γ is a matrix describing the coupling of the system to external open channels.[22,24,25] In indirect dissociation, H represents that part of the Hamiltonian that includes the "binding" potential energy surface only, while the open channels describe the possible dissociative states of the molecule. The eigenstates $|n\rangle$ of H_{eff} have complex eigenvalues $E_n - i\Gamma_n/2$, describing resonances with energies E_n and widths Γ_n. Bound-to-continuum transitions that proceed through resonance states are described by the strength function of the corresponding transition operator T:[19]

$$\sigma(E) = \sum_n |\langle n|T|g\rangle|^2 \frac{\Gamma_n/2}{(E-E_n)^2 + {\Gamma_n}^2/4} \tag{1}$$

In eq 1 each transition intensity (to a state imbedded in the continuum) is weighted by a Lorentzian centered at the resonance energy. In indirect photodissociation, the photoabsorption spectrum is proportional to eq 1 where T is the dipole operator of the molecule. In the following we consider only weakly coupled systems that are characterized by nonoverlapping and narrow resonances (relative to their mean spacing). In this case $|n\rangle$ are just the eigenstates of the closed system Hamiltonian H, E_n are the eigenvalues of H (to leading order we ignore shifts in eigenvalues), and the widths are given by

$$\Gamma_n = \sum_{n=1}^{\Lambda} \Gamma_{nc} \tag{2}$$

where $\Gamma_{nc} = |\gamma_{nc}|^2$ is the partial width of a resonance level n to decay into an open channel c (γ_{nc} is the partial width amplitude). We assume that there are Λ open channels. In the R-matrix formulation of reaction theory it is possible to express the partial width amplitude as an overlap integral of the eigenstate n and the corresponding channel wave function at the interface of the internal "interaction" region and the external asymptotic region.[26]

The total strength satisfies the sum rule[14]

$$\int \sigma(E)\,\mathrm{d}E = \sum_n |\langle n|T|g\rangle|^2 = \langle g|T^{\dagger}T|g\rangle \tag{3}$$

so that the experimentally prepared state $T|g\rangle$ can be normalized by defining $|\alpha\rangle \equiv T|g\rangle/\sqrt{\langle g|T^{\dagger}T|g\rangle}$. The normalized strength function $\tilde{\sigma}(E) = \sigma(E)/\int\sigma(E')\,\mathrm{d}E'$ can then be rewritten as

$$\tilde{\sigma}(E) = \sum_n |\langle n|\alpha\rangle|^2 \frac{1}{\pi} \frac{\Gamma_n/2}{(E-E_n)^2 + {\Gamma_n}^2/4} \tag{4}$$

In the following we shall simply use $\sigma(E)$ to denote the normalized strength function.

The spectral autocorrelation function $G(\omega)$ is defined in terms of the strength function by[11]

$$G(\omega) = \int_{-\infty}^{\infty} \sigma(E)\sigma(E+\omega)\,\mathrm{d}E \tag{5}$$

In the time domain we can define $C(t)$ as the Fourier transform of $\sigma(E)$, $C(t) = \int_{-\infty}^{\infty} \exp(-iEt)\sigma(E)\,\mathrm{d}E$. Using eq 4 we find

$$C(t) = \sum_n |\langle n|\alpha\rangle|^2 \mathrm{e}^{-iE_nt - \Gamma_n|t|/2} = \langle\alpha|\alpha(t)\rangle \tag{6}$$

where $|\alpha(t)\rangle \equiv \exp(-iH_{\mathrm{eff}}t)|\alpha\rangle$ is the state at time t that evolves from the experimentally prepared nonstationary initial state $|\alpha\rangle$ under the effective Hamiltonian H_{eff}. Thus the Fourier transform of the spectral autocorrelation $G(\omega)$ is just the survival probability $P(t) = |C(t)|^2$, i.e., the probability at time t that the system remains at its initially prepared state. Notice that for an open system, decay (into the continuum) is included in the time evolution. By use of eq 6, the survival probability can be expressed as

$$P(t) = \sum_n |\langle n|\alpha\rangle|^4\, \mathrm{e}^{-\Gamma_n|t|} + \sum_{n\neq m} |\langle n|\alpha\rangle|^2 |\langle m|\alpha\rangle|^2\, \mathrm{e}^{i(E_n-E_m)t} \times \mathrm{e}^{-|t|(\Gamma_n+\Gamma_m)/2} \tag{7}$$

We would like to calculate the ensemble average of $P(t)$. In RMT, the eigenvalues and eigenvectors are statistically independent. This implies that $|\langle n|\alpha\rangle|^2$ and Γ_n (which are determined by the eigenfunctions) are statistically independent from the spectrum E_n. Moreover, we assume that the prepared state $|\alpha\rangle$ has no overlap with the channels, so that the projection of the eigenstate $|n\rangle$ on $|\alpha\rangle$ and on the channels (i.e., partial width amplitudes) are also statistically independent. We conclude that all three quantities, $|\langle n|\alpha\rangle|^2$, Γ_n, and E_n, appearing in eq 7, are statistically independent. Consequently, the ensemble average on the right-hand side of eq 7 can be taken over each factor separately. In RMT, the eigenvector components are distributed randomly on the N-dimensional sphere, and thus one finds for a fixed normalized vector $|\alpha\rangle$:

$$\frac{\overline{|\langle n|\alpha\rangle|^2\,|\langle m|\alpha\rangle|^2}}{\overline{|\langle n|\alpha\rangle|^4}} = \frac{\beta}{\beta+2} \tag{8}$$

$$N\overline{|\langle n|\alpha\rangle|^4} = \frac{\beta+2}{N\beta+2}$$

Here β is a constant that depends on the corresponding Gaussian ensemble. For systems that conserve time-reversal symmetry, the relevant ensemble is the Gaussian orthogonal ensemble (GOE) and $\beta = 1$, while systems that break time-reversal symmetry are characterized by the Gaussian unitary ensemble (GUE) and $\beta = 2$. Chaotic nuclear and molecular systems always have $\beta = 1$. The partial width amplitudes can be shown to have a joint Gaussian distribution[27]

$$P(\gamma) \propto (\det M)^{-(\beta/2)} e^{-(\beta/2)\gamma^{\dagger}M^{-1}\gamma} \tag{9}$$

where $M_{cc'} \equiv \overline{\gamma^*_c\gamma_{c'}}$ is the channel correlation matrix and $\boldsymbol{\gamma}$ is a column vector of the partial width amplitudes γ_c (all γ_c refer to the same level n). Equation 9 follows from RMT using the fact that the partial widths can be described as the projection of the internal wave function (of the closed system) on the open channels. In the following we assume, without loss of generality, that all the Λ channels are uncorrelated. Otherwise, it is always possible to transform to the set of eigenchannels. The eigenvalues of M are just the average partial widths $\bar{\Gamma}_c$ of the eigenchannels. Using $\Gamma_n = \sum_{c=1}^{\Lambda} |\gamma_{nc}|^2$ and the known distribution (eq 9) of the partial width amplitudes γ_{nc}, it is possible to derive the total width distribution $P(\Gamma_n)$.[24,27] Such distributions were observed, for example, in the measured decay rates of highly excited vibrational states of formaldehyde in its ground electronic states S_0.[8,24] They were also reproduced in numerical simulations of a two-dimensional model chaotic cavity.[27] For the ensemble average of the decay factor in eq 7 we then find

$$\overline{e^{-(\Gamma_n/2)|t|}} = \det\left(1 + \frac{|t|}{\beta}M\right)^{-\beta/2} = \prod_c \frac{1}{(1 + (|t|/\beta)\bar{\Gamma}_c)^{\beta/2}} \tag{10}$$

To leading order in $1/N$, Γ_n and Γ_m $(n \neq m)$ are statistically independent so that $\overline{\exp[-|t|(\Gamma_n+\Gamma_m)/2]} = [\overline{\exp(-|t|\Gamma_n/2)}]^2$. From the known RMT spectral statistics we also have

$$(N-1)\overline{e^{i(E_n - E_m)t}} = \delta\left(\frac{t}{t_{\mathrm{H}}}\right) - b_{2,\beta}\left(\frac{t}{t_{\mathrm{H}}}\right) \tag{11}$$

where $t_{\mathrm{H}} \equiv 2\pi\bar{\rho}$ ($\bar{\rho}$ is the average level density) is the Heisenberg time. $b_{2,\beta}(\tau)$ is the two-level form factor, defined as the Fourier transform of the two-point cluster function $Y_{2,\beta}(s)$. The form factor is known analytically for both the GOE and GUE ensembles[3]

$$b_{2,\beta}(\tau) = \begin{Bmatrix} [1 - 2\,|\tau| + |\tau|\ln(1 + 2|\tau|)]\,\theta(1 - |\tau|) + \left[|\tau|\ln\left(\frac{2|\tau|+1}{2|\tau|-1}\right) - 1\right]\theta(|\tau| - 1) & (\beta = 1) \\ (1 - |\tau|)\,\theta(1 - |\tau|) & (\beta = 2) \end{Bmatrix} \tag{12}$$

Combining eqs 8, 10, and 11 and measuring time in units of the Heisenberg time ($\tau = t/t_{\mathrm{H}}$), we find for the ensemble average of the survival probability

$$N\overline{P(\tau)} = \delta(\tau) - b_{2,\beta}(\tau)\prod_c \frac{1}{(1 + |\tau|T_c/\beta)^{\beta}} + \frac{\beta+2}{\beta}\prod_c \frac{1}{(1 + 2|\tau|T_c/\beta)^{\beta/2}} \tag{13}$$

where we have used the transmission coefficients T_c. For a weakly coupled system, the average partial width $\bar{\Gamma}_c$ is related to the transmission coefficient T_c in channel c by $\bar{\Gamma}_c = T_c/2\pi\bar{\rho}$.[22] In the limit of closed system $T_c = 0$ for all channels and eq 13 reduces to eq 12 of ref 14.

The ensemble average of the spectral autocorrelation $G(\omega)$ is found by taking the inverse Fourier transform of eq 13. Defining the reduced spectral autocorrelation function $g(\omega) \equiv [\overline{\sigma(E)\sigma(E+\omega)} - (\overline{\sigma(E)})^2]/(\overline{\sigma(E)})^2 = [(\bar{\rho}/N)G(\omega) - (\overline{\sigma(E)})^2]/(\overline{\sigma(E)})$,[2] we find the following universal form:

$$g_\beta(\omega) = 2\left[\frac{\beta+2}{\beta}\int_0^\infty \mathrm{d}\tau \cos(2\pi\omega\tau)\prod_c \frac{1}{(1 + (2/\beta)T_c\tau)^{\beta/2}} - \int_0^\infty \mathrm{d}\tau \cos(2\pi\omega\tau) b_{2,\beta}(\tau)\prod_c \frac{1}{(1 + (1/\beta)T_c\tau)^{\beta}}\right] \tag{14}$$

By defining a function $F_\beta(\omega)$ in the energy domain

$$F_\beta(\omega) = 2\int_0^\infty \mathrm{d}\tau \cos(2\pi\omega\tau)\prod_c \frac{1}{(1 + (2/\beta)T_c\tau)^{\beta/2}} \tag{15}$$

we can rewrite the reduced spectral autocorrelation in the form

$$g_\beta(\omega) = \frac{\beta+2}{\beta}F_\beta(\omega) - \int_{-\infty}^{\infty}\mathrm{d}\tilde{\omega}\; Y_{2,\beta}(\tilde{\omega})F_{2\beta}(\omega - \tilde{\omega}) \tag{16}$$

There are two interesting limits for eq 16. In the limit of a closed system all transmission coefficients vanish ($T_c = 0$), and eq 14 reduces to[14]

$$g_\beta(\omega) = \frac{\beta+2}{\beta}\delta(\omega) - Y_{2,\beta}(\omega) \tag{17}$$

The second term in eq 17 gives rise to the correlation hole discussed in the introduction. Another limit for Λ equivalent open channels ($T_c = T$ for all c) is the limit $\Lambda \to \infty$ such that $\Lambda T = \kappa$ is kept constant. This is equivalent to taking the limit of a large number of equivalent channels while keeping the total average width $\bar{\Gamma}$ of the level constant. In this limit the integrand in eq 14 becomes $e^{-\kappa|\tau|}$ and $F_\beta(\tau) = (\kappa/2)\,[(\pi\omega)^2 + (\kappa/2)^2]^{-1}$ is a Lorentzian which is independent of β. Thus we obtain[20]

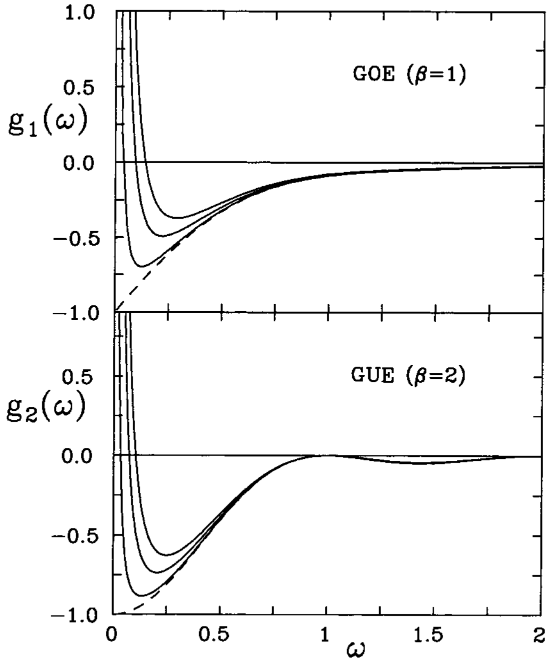

Figure 1. Reduced spectral autocorrelation function $g(\omega)$ vs ω for $\Lambda = 1$, 5, and 10 equivalent channels, each with a transmission coefficient of $T = 0.01$ (solid lines). The minimum of $g(\omega)$ ("correlation hole") becomes shallower as the number of channels increases. For reference we also show by dashed line $g(\omega)$ for a closed system (without the δ function at $\omega = 0$). Top, GOE statistics ($\beta = 1$); bottom, GUE statistics ($\beta = 2$).

$$g_\beta(\omega) = \frac{\beta + 2}{\beta}\frac{\kappa/2}{(\pi\omega)^2 + (\kappa/2)^2} - \int_{-\infty}^{\infty} d\tilde{\omega} Y_{2,\beta}(\tilde{\omega}) \frac{\kappa/2}{\pi^2(\omega - \tilde{\omega})^2 + (\kappa/2)^2} \quad (18)$$

Equations 16 and 15 provide a closed expression for the universal spectral autocorrelation in weakly open chaotic systems, and is the main result of this paper. In Figure 1 we compare the GOE and GUE reduced spectral autocorrelators for an open system coupled to $\Lambda = 1$, 5, and 10 equivalent channels with a partial transmission coefficient of $T = 0.01$ in each channel. For reference, we show by a dashed line the spectral correlator for a closed system (not including the δ function at $\omega = 0$). As the number of channels increases, the correlation hole shrinks. It is seen that for the same number of open channels, the GOE correlation hole is shallower than the GUE hole. Thus the GOE hole disappears faster when opening the system to more channels. This could be explained by the stronger level repulsion in the GUE case. A similar effect (not shown here) is observed for a fixed number of channels as the transmission coefficient increases. Generally, we observe a shallower hole as the total mean resonance width increases.[20]

In conclusion, we have derived in closed form the spectral autocorrelation function and survival probability for bound-to-continuum transitions that proceed through a regime of isolated resonances. The correlator is universal and depends only on the symmetry class (i.e., conserved or broken time-reversal symmetry), and the partial dissociation widths (or transmission coefficients) for the open channels. The correlation hole, a signature of chaos in both the power spectrum and survival probability, disappears gradually as more channels are opened, and it does so faster in systems that conserve time-reversal symmetry. It would be interesting to compare our prediction for the correlation hole in open systems (for the case of time-reversal symmetry) with actual measurements or numerical simulations of indirect photodissociation spectra of complex molecules.

Acknowledgment. This work was supported in part by the U.S. Department of Energy Grant No. DE-FQ-0291-ER-40608 and by SFB237 "Unordnung und grosse Fluktuationen".

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