General random matrix approach to account for the effect of static disorder on the spectral properties of light harvesting systems

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We develop a random matrix model approach to study static disorder in pigment-protein complexes in photosynthetic organisms. As a case study, we examine the ring of B850 bacteriochlorophylls in the peripheral light-harvesting complex of *Rhodospirillum molischianum*, formulated in terms of an effective Hamiltonian describing the collective electronic excitations of the system. We numerically examine and compare various models of disorder and observe that both the density of states and the absorption spectrum of the model show remarkable spectral universality. For the case of unitary disorder, we develop a method to analytically evaluate the density of states of the ensemble using the supersymmetric formulation of random matrix theory. Succinct formulas that can be readily applied in future studies are provided in an appendix.

I. INTRODUCTION

Biological functions that involve electronic processes, e.g., light reception in vision or light harvesting in photosynthesis, are dominated necessarily by quantum mechanical behavior. Since living systems exist at physiological temperatures, they are subject to large disorder and ordinary, i.e., $T=0$, quantum theory cannot provide proper descriptions of such processes. The development of suitable stochastic quantum mechanics descriptions for strong disorder is a key challenge in biological physics. Meeting this challenge is of interest for life scientists who seek to analyze experimental data and improve the understanding of mechanisms underlying biological function, but it is also of interest to physicists since available theories find new relevant applications or need to be significantly extended. The present study focuses on the description of static disorder in light-harvesting complexes that have been intensely investigated both experimentally and theoretically during the past decade. We demonstrate that random matrix theory can provide a succinct formulation that describes the level densities and, hopefully also soon the optical properties, of quantum biological systems.

Compared to the light-harvesting (LH) systems of plants, bacterial light-harvesting systems exhibit a large degree of symmetry. The photosynthetic apparatus of purple bacteria contains several hundred chromophores per reaction center [1], which are organized in ringlike structures. The photosynthetic units of *Rhodospirillum (Rs.) molischianum* [2] and *Rhodopseudomonas (Rps.) acidophila* [3] contain two types of light-harvesting complexes located in the membrane. The larger of the two, LH1, directly surrounds and transmits energy to the reaction center. The reaction center is responsible for converting electronic excitation energy to a more stable charge separation across the membrane. The other protein-pigment complex, LH2, is not in direct contact with the reaction center, but rather transfers the energy it absorbs to LH1.

The LH2 exhibits an eight-fold symmetry in the case of *Rs. molischianum* and a nine-fold symmetry in the case of *Rps. acidophila*. In *Rs. molischianum*, LH2 contains 8 units, each consisting of a peptide pair, a lycopene, a B800 bacteriochlorophyll (BChl) and two B850 BChls (see Fig. 1). Each of the peptides consist of a single transmembrane helix. The BChls are named after their absorption maxima (in terms of nanometer). The eight lycopenes, eight B800 BChls, and 16 B850 BChls of LH2 all form separate concentric rings. The coupling between B800 BChls is not very strong due to their relatively large separation [4] (around 20 Å), however the B850 ring is packed closely enough (BChl separation of around 9 Å) to warrant a description in terms of an effective (16×16) Hamiltonian as introduced in Ref. [5].

In this paper we will present a random matrix model [6–8] describing such an effective Hamiltonian in the presence of an ensemble of random perturbations as a model of static disorder. The density of states and the absorption spectrum will be the main focus of our study. In addition to a numerical study of the density of states and the absorption spectrum, we will present a framework to compute the density of states analytically for Gaussian unitary disorder.

The model we study is described as the sum of a deterministic part (the noise-free effective Hamiltonian) and a random part (describing static disorder). Such deterministic plus random systems have been studied earlier by analytical methods by Pastur [9] and Zee [10] in the context of large N limits, N denoting the size of the Hamiltonian. However, the model we study has finite size ($N=16$). Therefore, for the analytical study of the density of states, we will adopt an approach by Guhr [11], based on the supersymmetric formulation of random matrix theory introduced by Efetov [12] to construct a solution in terms of the unperturbed spectrum, which is exact for any N.

In the rest of the paper we will specifically consider the effective Hamiltonian for LH2 of *Rs. molischianum*. However, the framework we present is general enough to be applied to any effective Hamiltonian description of a photosynthetic system, with or without a regular arrangement of BChls. If and when an effective Hamiltonian description be-
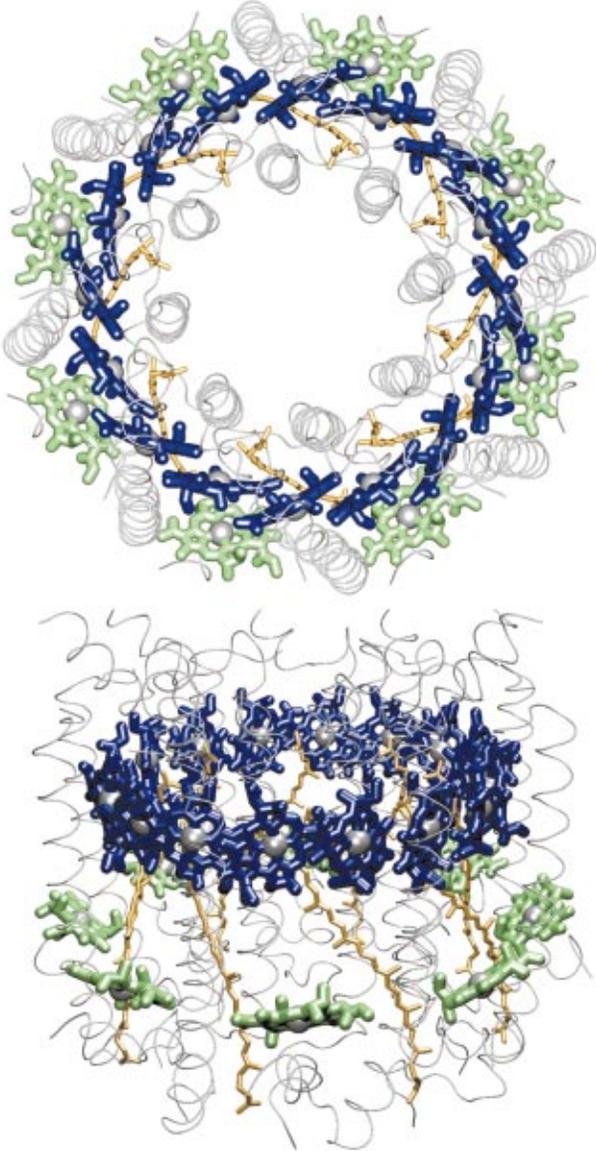
FIG. 1. (Color) The peripheral light-harvesting complex, LH2, of *Rs. molischianum*. The B850 ring is shown in blue, the B800 ring is shown in light green and the lycopenes are shown in light orange. The protein backbone is rendered in tube representation. [Figure produced with the program VMD [43].]

comes available, the cynobacterial photosystem I [13] may provide such a candidate, as well as phicobiliproteins [14,15], peridinin containing proteins of dynoflagellates [16,17], or the peripheral light-harvesting complex LHCII of green plants [18].

The organization of this paper is as follows: In the following section we will introduce the random matrix model describing static disorder in the context of effective Hamiltonians of the BChl rings in purple bacteria. In Sec. III we present four different ensembles and a numerical study of the density of states, as well as examine the implications of random matrix universality. We will also study the approach to universality by comparing ensembles of different sizes. Then, in Sec. IV, we will develop a method to analytically

evaluate the density of states in the context of Gaussian unitary disorder and express the final result in terms of the spectrum of the noise-free problem. Section V will contain a numerical study of the absorption spectrum in a similar context. Appendix A contains a number of notations and conventions we use in the paper in reference to the supersymmetric formulation of random matrix theory. In Appendix B we summarize the analytical results of Sec. IV regarding the density of states for unitary disorder for easy use.

II. A RANDOM MATRIX MODEL FOR THE EFFECTIVE HAMILTONIAN OF LIGHT-HARVESTING COMPLEXES

An effective Hamiltonian for the circular BChl aggregate in LH2 is expressed in terms of single BChl Q_y excitations [5]

$$
H_0 = \begin{pmatrix}
\epsilon_\alpha & v_1 & W_{13} & W_{14} & \cdots & v_2 \\
v_1 & \epsilon_\beta & v_2 & W_{24} & \cdots & W_{2N} \\
W_{31} & v_2 & \epsilon_\alpha & v_1 & \cdots & W_{3N} \\
\cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\
v_2 & W_{N2} & W_{N3} & W_{N4} & \cdots & \epsilon_\beta
\end{pmatrix}, \quad (1)
$$

where ϵ_α and ϵ_β denote the alternating site energies and v_1 and v_2 are the nearest neighbor coupling terms. The nonnearest neighbor interaction terms can be described by an induced-dipole–induced-dipole coupling given by

$$
W_{ij} = C \left(\frac{\mathbf{d}_i \cdot \mathbf{d}_j}{r_{ij}^3} - \frac{3(\mathbf{r}_{ij} \cdot \mathbf{d}_i)(\mathbf{r}_{ij} \cdot \mathbf{d}_j)}{r_{ij}^5} \right) \quad (2)
$$

where $\mathbf{d}_i$ are unit vectors along transition dipole moments from the ground state to the Q_y state of the ith BChl and $\mathbf{r}_{ij}$ are the vectors connecting BChls i and j measured along the vectors connecting the Mg atoms. The atomic positions are determined from crystallographic data [2,5]. The unit transition dipole moment vectors $\mathbf{d}_i$ are taken along the direction from N_B to Mg in the BChl [19] (see Fig. 2).

Since the distance between neighboring B850 BChls (around 9 Å) is comparable to the size of a BChl molecule [4], it is not a very good approximation to describe the nearest neighbor couplings via induced-dipole–induced-dipole interactions. In Eq. (1), $N = 2n$ is the number of BChls in the ring. For LH2, $n = 8$ or 9 for *Rs. molischianum* and for *Rps. acidophila*, respectively. Ideally this system has perfect C_n symmetry that will be broken by thermal fluctuations. Due to their similar structure, the LH1 complexes of purple bacteria can also be studied using the same framework. For example, the number of BChl molecules in LH1 of *Rs. rubrum* is determined to be 32 [20].

The five parameters describing H_0, namely, ϵ_α, ϵ_β, v_1, v_2, and C need to be determined experimentally or from quantum chemistry computations. Various such computations [4,5,19,21–24] do not agree on the values of these parameters. In an early study, using the results of such a computation [25], Hu *et al.* [5] have determined these values as follows: $\epsilon_\alpha \equiv \epsilon_\beta = 13\,362$ cm^{-1}, $v_1 = 806$ cm^{-1}, v_2
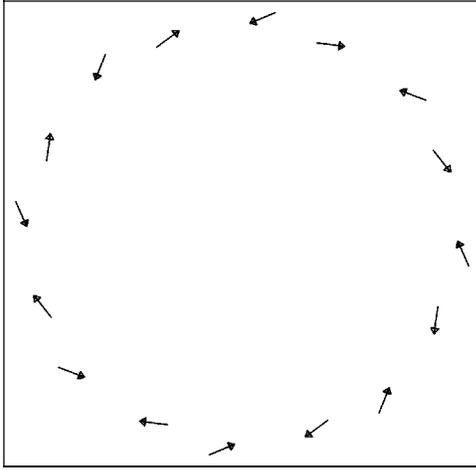
FIG. 2. The orientation of induced-dipole moment unit vectors $\mathbf{d}_i$ in the B850 ring of LH2. The induced dipole moments vectors are almost in the plane of the BChl ring and make an angle of about $7°$ out of the plane.
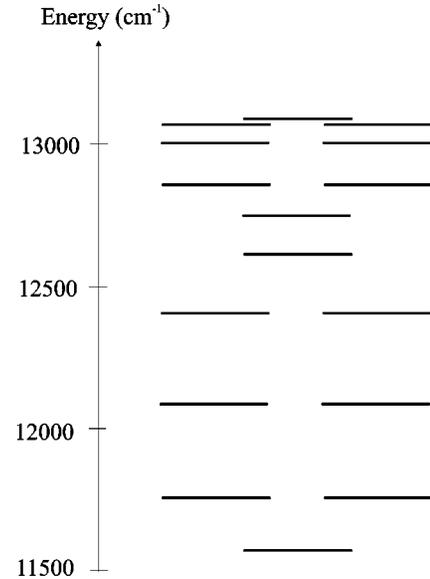

FIG. 3. The spectrum of the noise-free Hamiltonian H_0 for the parameters given in the text. The degeneracy structure is a result of the C_n symmetry.

$=377$ cm^{-1}, and $C=519\,310$ Å^3 cm^{-1}. However, it is generally considered that the values cited for nearest neighbor coupling terms, v_1 and v_2, and the difference between them is too large [19,22]. For example, Sundström *et al.* [4] suggest $v_1=339$ cm^{-1}, $v_2=336$ cm^{-1}. (For a detailed discussion regarding Hamiltonian parameters see Ref. [22].)

In the following we will be using the effective Hamiltonian parameters obtained by Tretiak and co-workers [21,22]. We take $v_1=363$ cm^{-1}, $v_2=320$ cm^{-1}, and $\epsilon_\beta-\epsilon_\alpha=166$ cm^{-1}. We would like the observed spectral maximum to coincide with the energy of the second and third energy levels of H_0, which are doubly degenerate and are known to carry all oscillator strength in the absence of noise as a result of C_n symmetry [5]. Enforcing $E_2=E_3=11\,765$ cm^{-1} [850 nm], we obtain $\epsilon_\alpha=12\,447$ cm^{-1} and $\epsilon_\beta=12\,613$ cm^{-1}. Finally, we need to determine the coupling constant C for the transition-dipole–transition-dipole interactions. This is fixed by comparing, e.g., W_{13}, to the value computed in Ref. [22], which is -102 cm^{-1}. Hence, we obtain $C=348\,000$ Å^3 cm^{-1}. The spectrum of the noise-free Hamiltonian with this choice of parameters is shown in Fig. 3. The degeneracy structure of the noise-free Hamiltonian follows from the C_n symmetry of the problem and is independent of the parameters chosen.

In the following we will study static disorder of the effective Hamiltonian given above. Static and dynamic disorder of similar light-harvesting complexes have been the focus of many studies [5,23,24,26–34]. In the present framework we will consider a thermal ensemble of LH2 effective Hamiltonians. As a description of this ensemble, we will consider the sum of the noise-free effective Hamiltonian described above and a random part representing thermal fluctuations

$$H=H_0+R. \qquad (3)$$

Here the matrix R is drawn from a certain probability distribution $P(R)$. It can be assumed that a particular choice of $P(R)$ is the correct description of thermal disorder in the

effective Hamiltonian picture. Since neither the construction nor the properties of such a distribution will be an easy matter, we will have to make some simplifying assumptions on the nature of $P(R)$. This course of action can be justified by the presence of universality in random matrix theories [8], i.e., the independence of a number of spectral properties from the choice of the random matrix distribution. Although most results on random matrix universality are based on the large-N limit, we will demonstrate below by numerical studies that remarkable spectral similarity persists for an ensemble of a finite size as small as $N=16$.

In the following section we will consider four separate ensembles from which R is chosen. In the first two ensembles R is a real symmetric matrix, in the third it is a complex Hermitian matrix, and in the fourth it is a diagonal real matrix. In Sec. IV we will choose R to be a member of the Gaussian unitary ensemble (GUE), to make an analytical computation of the density of states possible. Although the microscopic spectral quantities, such as the level spacing, are known to be strongly dependent on the symmetry class of the ensemble in question [7], the bulk of the spectrum, which we will be mainly interested in, is rather insensitive to the choice of the ensemble as long as the variance of the distribution is properly scaled. To examine the effects of random matrix universality, we also study a noninvariant distribution and a diagonal distribution of disorder.

III. THE DENSITY OF STATES AND THE EFFECT OF UNIVERSALITY

In this section we introduce a number of random matrix ensembles, describing the disorder term R in Eq. (3). We will be specifically interested in the study of the density of states (or the spectral density, as it is sometimes called) and postpone a similar study of the absorption spectrum to Sec. V.

Below we present a numerical comparison for the density of states for different ensembles.

It is known from various studies in random matrix theory that the exact shape of the probability distribution defining the random ensemble is largely irrelevant for the behavior of a number of spectral properties. This property is referred to as universality [8]. This term is not unambiguously defined however. Within a given symmetry class (e.g., orthogonal vs unitary symmetry) microscopic spectral distributions such as two-point correlators and nearest neighbor spacing distributions are known to depend only on the second moment of the probability distribution $P(R)$ of the ensemble. However, the bulk shape of the density of states can be sensitive to the choice of $P(R)$ even when one remains within the same symmetry class, as one can ascertain by comparing Gaussian matrix ensembles with ensembles that have quartic terms in the exponent of their distribution functions. The bulk of the density of states enjoys a different kind of universality, however, as realized by Wigner's semicircle law [6,7]. When the widths of the distributions are properly scaled, all three Gaussian Dyson ensembles are known to have the same overall density of states up to $\mathcal{O}(1/N)$ effects. Below we will see the manifestation of this kind of universality for both the density of states and the absorption spectrum across different ensembles.

The density of states of an ensemble in Eq. (3), given by a probability distribution $P(R)$ is defined in terms of the ensemble average

$$\rho(\omega) = \left\langle \sum_{i=1}^{N} \delta(\omega - E_i) \right\rangle, \qquad (4)$$

where $\langle \cdots \rangle \equiv \int d[R] P(R) \ldots$ and E_i are the eigenvalues of $H = H_0 + R$.

In the first ensemble we consider, R will be a member of the Gaussian orthogonal ensemble (GOE),

$$P_1(R) = N_1 \exp\left(- \frac{1}{2\nu_{GOE}^2} \text{tr}(R^T R) \right),$$

$$= N_1 \prod_i \exp\left(- \frac{1}{2\nu_{GOE}^2} R_{ii}^2 \right)$$

$$\times \prod_{i<j} \exp\left(- \frac{1}{\nu_{GOE}^2} R_{ij}^2 \right). \qquad (5)$$

This ensemble is invariant under orthogonal transformations, namely, $P(R) = P(O^T R O)$, for an orthogonal matrix O. To examine the effects of universality we will also consider a noninvariant ensemble in which R is still real and symmetric. Following Eq. (5) we choose

$$P_2(R) = N_2 \prod_i f(\nu_{GOE}, R_{ii}) \prod_{i<j} f(\sqrt{2}\nu_{GOE}, R_{ij}), \qquad (6)$$

where

$$f(\nu, x) = \begin{cases} \dfrac{1}{2\sqrt{3}\nu}, & |x| < \sqrt{3}\nu \\ 0, & \text{otherwise} \end{cases} \qquad (7)$$

is the flat probability distribution with width ν. The distribution of individual matrix elements are chosen to have the same width as their GOE counterparts.

In the third ensemble, R will be chosen from GUE

$$P_3(R) = N_3 \exp\left(- \frac{1}{2\nu_{GUE}^2} \text{tr}(R^\dagger R) \right),$$

$$= N_1 \prod_i \exp\left(- \frac{1}{2\nu_{GUE}^2} R_{ii}^2 \right)$$

$$\times \prod_{i<j} \exp\left(- \frac{1}{\nu_{GUE}^2} ((\text{Re } R_{ij})^2 + (\text{Im } R_{ij})^2) \right), \qquad (8)$$

which will also be studied analytically in the following section.

The final ensemble we consider describes diagonal disorder. It is given by

$$P_4(R) = N_4 \prod_i \exp\left(- \frac{1}{2\nu_{diag}^2} R_{ii}^2 \right) \prod_{i<j} \delta(R_{ij}). \qquad (9)$$

Diagonal disorder in the present context has previously been studied in Ref. [5]. The relevance of diagonal disorder comes from molecular dynamics studies, where it was observed that fluctuations of the diagonal matrix elements are much larger than the interaction terms [35].

To achieve a proper comparison between different ensembles their widths have to be taken carefully into account. It is known in the case of Dyson ensembles that for a proper comparison $\Sigma_{ij} \nu_{ij}^2$ should be fixed to a constant, where ν_{ij} is the variance of the (i,j)th matrix element. Following this argument we obtain

$$\nu_{diag}^2 = \frac{N}{2} \nu_{GOE}^2 = N \nu_{GUE}^2. \qquad (10)$$

In comparison to the width of the absorption spectrum obtained in hole burning spectroscopy experiments [36], Hu *et al.* [5] have obtained a diagonal disorder width of around $\nu_{diag} = 170$ cm^{-1}. Using this value in Eq. (10) we obtain $\nu_{GOE} = 60.1$ cm^{-1} and $\nu_{GUE} = 42.5$ cm^{-1}. These values will be used throughout the rest of the paper.

We have performed numerical studies of the density of states for the ensembles introduced above. These are demonstrated in Figs. 4, 5, and 6. We first compare the density of states for the two real symmetric ensembles (5) and (6). Although universality results manifest themselves usually in the limit of large matrices, it is amazing to see (Figs. 4 and 5) that even for an ensemble of mesoscopic size such as the one studied here, the global density of states remains largely un-
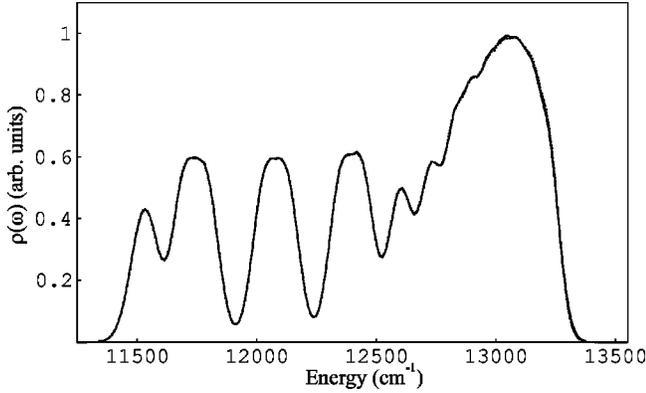
FIG. 4. The density of states for $N=2\times 8$ for an ensemble of real symmetric disorder obtained numerically. The width of the ensemble is $\nu_{GOE}=60.1$ cm^{-1}. The case where the disorder term is chosen from the Gaussian orthogonal ensemble (solid line) is barely distinguishable from an ensemble of flat distributed matrix elements with the same width (dotted line). See also Fig. 5.

changed under the change of the probability distribution of individual matrix elements. Even across different universality classes (GOE vs GUE vs diagonal disorder) defined further by Eqs. (8) and (9), remarkable spectral similarity persists, when the widths of the distributions are taken into account (see Fig. 6).

Finally we have also examined the approach to universality as a function of the matrix size defining the ensemble. This has been accomplished by comparing the density of states for Eqs. (5) and (6) in the case of a 32×32 and an 8×8 ensemble of matrices. For these new ensembles, the noise-free part of the Hamiltonian H_0 has been constructed by artificially extrapolating the structure of the B850 ring in LH2 as introduced in Sec. II, to one with 32 BChls and another one with eight BChls, respectively. Although a 32 BChl ring is relevant for a study of LH1, the eight BChl ring is artifical from a biological point of view. The results of this study, shown in Fig. 7, are in accordance with the expectation that the universality becomes more manifest with increasing matrix size. However, even in the case of the 8×8 ensemble the difference between density of states is remarkably small.
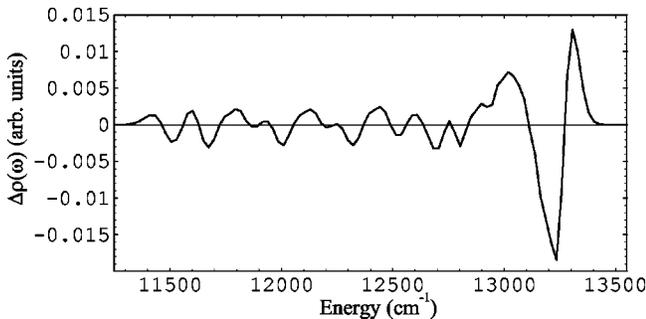

FIG. 5. The difference in numerically obtained density of states for Gaussian orthogonal disorder and an ensemble of flat distributed matrix elements as in Fig. 4 obtained by diagonalizing 360 000 000 matrices from each ensemble. The scale is identical to that of Fig. 4, hence the difference is generally within two percent of the maximum of the density of states.
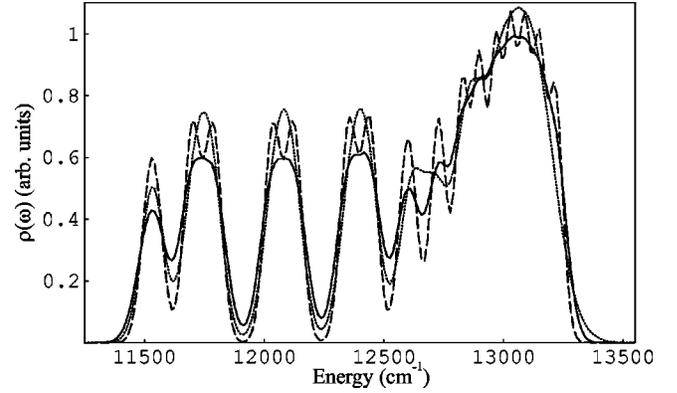

FIG. 6. The numerically obtained density of states for three different universality classes with properly chosen widths (see text for the determination of the widths): Gaussian orthogonal disorder with width $\nu_{GOE}=60.1$ cm^{-1} (solid line), Gaussian unitary disorder with width $\nu_{GUE}=42.5$ cm^{-1} (dashed line) and diagonal disorder with width $\nu_{diag}=170$ cm^{-1} (dotted line). The individually pronounced peaks occurring for Gaussian unitary disorder can be understood in terms of the strong level repulsion present in unitary ensembles given by Mehta. The level repulsion (and, therefore, the separation) is not as strong for orthogonal or diagonal disorder.

IV. ANALYTICAL COMPUTATION OF THE DENSITY OF STATES

In this section we present an analytical calculation of the density of states (4) of the ensemble (3), where the random part R is a complex Hermitian matrix drawn from the probability distribution

$$P(R)=N_R \exp\left(-\frac{1}{2\nu^2}\mathrm{tr}(R^\dagger R)\right), \qquad (11)$$

where the normalization constant is given by

$$N_R=\frac{2^{N(N-1)/2}}{(2\pi\nu^2)^{N^2/2}}. \qquad (12)$$

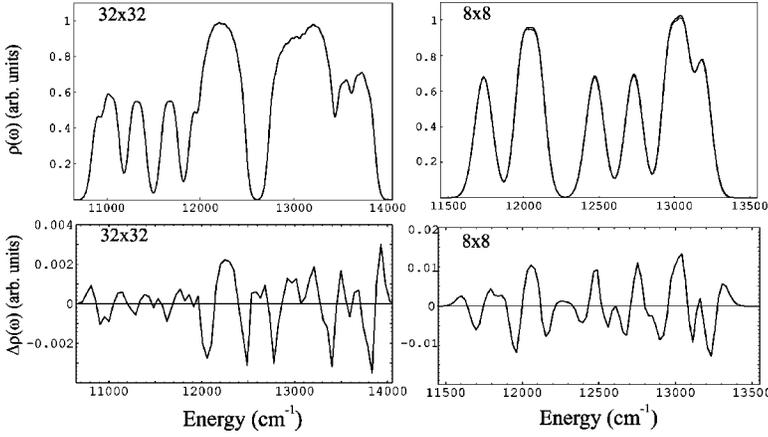We will proceed by applying a Hubbard-Stratonovitch transformation to reduce the ensemble average to an integral over a space of $(1+1)\times(1+1)$ supermatrices. Our notational conventions can be found in Appendix A.

The density of states (4) can be expressed as

$$\rho(\omega)=\frac{1}{\pi}\mathrm{Im}\left\langle \mathrm{tr}\frac{1}{\omega^- -(H_0+R)}\right\rangle, \qquad (13)$$

where we have used $\delta(x)=(1/\pi)\mathrm{Im}(1/(x-i\epsilon))$ with $i\epsilon$ being a small imaginary increment. In Eq. (13) and below, ω^- denotes that ω has a small negative imaginary increment, which is used to decide the sign of corresponding principal value integrals.

At this point it can be seen that, for an invariant probability distribution $P(R)=P(U^\dagger R U)$, $U\in U(N)$, such as Eq. (11), H_0 can be replaced by its diagonal part $\Gamma=\mathrm{diag}(\gamma_1,\ldots,\gamma_N)$, where

FIG. 7. The approach to universality: The density of states (top) and their differences (bottom) for Gaussian orthogonal disorder and an ensemble with flat distributed matrix elements (compare to Figs. 4 and 5) for a 32×32 ensemble (left) and an 8×8 ensemble (right). The results are obtained by diagonalizing 10 000 000 matrices for the 8×8 case and 20 000 000 matrices for the 32×32 case. The scales for the top and bottom figures are identical.

$$H_0 = U_0^\dagger \Gamma U_0, \quad U_0 \in U(N), \tag{14}$$

since the Jacobian of the transformation $R \to U_0 R U_0^\dagger$ is unity. The unperturbed eigenvalues γ_i are obtained by directly diagonalizing H_0 and are given in Fig. 3.

Finally, using the identity

$$\mathrm{tr}\frac{1}{A} = \frac{1}{2}\frac{\partial}{\partial j}\bigg|_{j=0}\frac{\det(A+j)}{\det(A-j)}, \tag{15}$$

we can express the density of states in terms of a partition function

$$\rho(\omega) = \frac{1}{2\pi}\frac{\partial}{\partial j}\bigg|_{j=0} \mathrm{Im}\, \mathcal{Z}(j), \tag{16}$$

$$\mathcal{Z}(j) = \int d[R]P(R)\frac{\det[\omega^- - (\Gamma+R)+j]}{\det[\omega^- - (\Gamma+R)-j]}. \tag{17}$$

The ratio of determinants in Eq. (17) can be converted to Gaussian integrals using Eqs. (A3) and (A4) from the Appendix A

$$\mathcal{Z}(j) = \int d[\phi]d[\chi]$$

$$\times \exp\left[i\begin{pmatrix}\phi\\\chi\end{pmatrix}^\dagger \cdot \begin{pmatrix}\omega^- - \Gamma - j & 0\\0 & \omega^- - \Gamma + j\end{pmatrix} \cdot \begin{pmatrix}\phi\\\chi\end{pmatrix}\right]$$

$$\times I_R, \tag{18}$$

where the R integral is now of Gaussian form

$$I_R = \int d[R]N_R \exp\left(-\frac{1}{2\nu^2}\mathrm{tr}\,R^2\right)$$

$$\times \exp(-i\phi^\dagger \cdot R \cdot \phi - i\chi^\dagger \cdot R \cdot \chi). \tag{19}$$

The Hubbard-Stratonovitch transformation consists of converting this integral over an $N \times N$ matrix to an integral over a $(1+1) \times (1+1)$ supermatrix. The Gaussian integral in Eq. (19) can be easily evaluated by completing the squares,

$$I_R = \exp\left(-\frac{1}{2}\nu^2\,\mathrm{tr}(\phi\phi^\dagger - \chi\chi^\dagger)^2\right),$$

$$= \exp\left[-\frac{1}{2}\nu^2\,\mathrm{str}\begin{pmatrix}(\phi^\dagger\cdot\phi) & (\chi^\dagger\cdot\phi)\\(\phi^\dagger\cdot\chi) & (\chi^\dagger\cdot\chi)\end{pmatrix}^2\right],$$

$$= \int d[\sigma]N_\sigma \exp\left(-\frac{1}{2\nu^2}\mathrm{str}\,\sigma^2\right)$$

$$\times \exp\left\{-i\,\mathrm{str}\left[\sigma\cdot\begin{pmatrix}(\phi^\dagger\cdot\phi) & (\chi^\dagger\cdot\phi)\\(\phi^\dagger\cdot\chi) & (\chi^\dagger\cdot\chi)\end{pmatrix}\right]\right\}. \tag{20}$$

Here, σ is a $(1+1) \times (1+1)$ Hermitian supermatrix. The normalization constant N_σ is equal to 1, since $\int d[\sigma]\exp(-(2\nu^2)^{-1}\mathrm{str}\,\sigma^2) = 1$ due to the supersymmetric nature of the integral: the bosonic and fermionic contributions cancel each other.

Now the ϕ and χ integrals in Eq. (18) can be performed by another completion of squares and using Eq. (A5). This reduces the partition function to

$$\mathcal{Z}(j) = \int d[\sigma]\exp\left(-\frac{1}{2\nu^2}\mathrm{str}\,\sigma^2\right)$$

$$\times \prod_{i=1}^{N}\mathrm{sdet}^{-1}\left[\begin{pmatrix}\omega^- - \gamma_i - j & 0\\0 & \omega^- - \gamma_i + j\end{pmatrix} - \sigma\right]. \tag{21}$$

To further simplify the partition function we will make a change of variables to

$$\sigma \to \sigma + Q,$$

$$Q = \begin{pmatrix}\omega^- - j & 0\\0 & \omega^- + j\end{pmatrix}, \tag{22}$$

and superdiagonalize σ as $\sigma = uSu^\dagger$, where $u \in U(1|1)$ and $S = \mathrm{diag}(s_0, is_1)$ contains the eigenvalues of σ. In these new variables the integration measure can be written as

$$d[\sigma] = d\mu(u)d[S]B^2(S), \tag{23}$$

where $d\mu(u)$ is the Haar measure of the superunitary group, $U(1|1)$, and $d[S] = ds_0 ds_1$. The integrals over the eigenvalues s_0 and s_1 run along the real axis. The Jacobian of the transformation is given in terms of the Berezinian, $B(S) = 1/(s_0 - i s_1)$. Thus, the expression for the partition function becomes

$$\mathcal{Z}(j) = \int d[S] B^2(S) \prod_{i=1}^N \text{ sdet}^{-1}(S + \gamma_i) \mathcal{I}_u(S),$$

$$\mathcal{I}_u(S) = \int d\mu(u) \exp\left(-\frac{1}{2\nu^2} \text{str}[u S u^\dagger + Q]^2\right). \quad (24)$$

The last integral can be recognized as an Itzykson-Zuber-Harish-Chandra integral [11,37,38], which can be evaluated by solving for the kernel of the heat equation in the space of the underlying superunitary group. The final result is given in Ref. [11]

$$\mathcal{I}_u(S) = \frac{1}{2\pi\nu^2} \frac{\exp\left(-\frac{1}{2\nu^2} \text{str}(S+Q)^2\right)}{B(S) B(-Q)} + \Phi. \quad (25)$$

Here Φ is a boundary contribution known as an Efetov-Wegner term, which is proportional to $[1 - \chi(j)]$ where

$$\chi(j) = \begin{cases} 0, & \text{if } j = 0, \\ 1, & \text{otherwise.} \end{cases} \quad (26)$$

We shall neglect Φ below, since it does not contribute to the density of states $\rho(\omega)$ after the derivative with respect to the source term j in Eq. (16).

After noting that, $B(-Q) = 1/(2j)$, the expression for the density of states (16) reduces to

$$\rho(\omega) = \frac{1}{2\pi^2\nu^2} \text{Im} \int d[S] B(S) \prod_{i=1}^N \text{ sdet}^{-1}(S + \gamma_i)$$

$$\times \exp\left(-\frac{1}{2\nu^2} \text{str}(S + \omega^-)^2\right). \quad (27)$$

To separate the bosonic and fermionic eigenvalue integrals we employ a "Feynman trick" to rewrite $B(S)$ as

$$B(S) = \frac{1}{s_0 - i s_1} = \int_0^\infty d\alpha \exp[-\alpha(s_0 - i s_1)] \quad (28)$$

and using the definition of a superdeterminant from Appendix A we obtain

$$\text{sdet}^{-1}(S + \gamma_i) = \frac{i s_1 + \gamma_i}{s_0 + \gamma_i}. \quad (29)$$

A final expression for the density of states, valid for any finite sized ensemble described by a fixed Hamiltonian plus a random part from GUE, is thus obtained as

$$\rho(\omega) = \frac{1}{\pi} \int_0^\infty d\alpha \, \mathcal{A}_0 \mathcal{A}_1, \quad (30)$$

$$\mathcal{A}_0 = \frac{1}{\pi} \text{Im} \int_{-\infty}^\infty d\xi e^{-\xi^2} \prod_{i=1}^N \frac{1}{\xi - i\epsilon - \frac{1}{\sqrt{2}\nu}(\omega + \nu^2\alpha - \gamma_i)},$$

$$\mathcal{A}_1 = \int_{-\infty}^\infty d\eta e^{-\eta^2} \prod_{i=1}^N \left(i\eta - \frac{1}{\sqrt{2}\nu}(\omega + \nu^2\alpha - \gamma_i)\right),$$

where we have explicitly substituted the imaginary increment $i\epsilon$ where it would contribute.

The expression (30) for the density of states can be evaluated by realizing that $\mathcal{A}_0$ yields δ functions at the poles using the identity

$$\frac{1}{\pi} \text{Im} \prod_{i=1}^N \frac{1}{x - i\epsilon - s_i} = \sum_{i=1}^N \delta(x - s_i) \prod_{j \neq i}^N \frac{1}{x - s_j}, \quad (31)$$

and that $\mathcal{A}_1$ is just the integral of a Gaussian times a polynomial.

The application of Eq. (30) to the spectrum of the ensemble defined by Eq. (1) is a laborious task because the N eigenvalues γ_i of the deterministic part enter as parameters in the analytical expression. This is best carried out with the help of a symbolic algebra program such as MATHEMATICA [39] and is outlined in Appendix B. A final formula for the density of states is given by Eq. (B9). In Sec. IV A we perform some consistency checks on Eq. (30) for various limits.

A. Consistency checks for the analytical expression for the density of states

As a first test we consider the deterministic limit, $\nu \to 0$, where the density of states (30) should coincide with the spectrum of the deterministic part,

$$\rho_D(\omega) = \sum_{i=1}^N \delta(\omega - \gamma_i). \quad (32)$$

Without loss of generality we will assume that the eigenvalues γ_i are nondegenerate. Using Eq. (31) one can rewrite the bosonic contribution $\mathcal{A}_0$ as

$$\mathcal{A}_0 = (\sqrt{2}\nu)^{N-1} \sum_{i=1}^N \exp\left[-\frac{1}{2\nu^2}(\omega + \nu^2\alpha - \gamma_i)^2\right] \prod_{j \neq i}^N \frac{1}{\gamma_j - \gamma_i},$$

$$= (\sqrt{2}\nu)^{N-1} \sqrt{2\pi}\nu \sum_{i=1}^N \delta(\omega - \gamma_i) e^{-\alpha(\omega - \gamma_i)}$$

$$\times \prod_{j \neq i}^N \frac{1}{\gamma_j - \gamma_i}, \quad (33)$$

where we have used the Gaussian representation of a δ function and the limit of small ν to rewrite

$$\exp\left[-\frac{1}{2\nu^2}(\omega+\nu^2\alpha-\gamma_i)^2\right]$$

$$=\sqrt{2\pi}\nu\delta(\omega-\gamma_i)e^{-\alpha(\omega-\gamma_i)}e^{-O(\nu^2)}. \quad (34)$$

Similarly, the fermionic contribution $\mathcal{A}_1$ can be rewritten as

$$\mathcal{A}_1=\frac{\sqrt{2\pi}\nu}{(\sqrt{2}\nu)^{N+1}}\int_{-\infty}^{\infty}dy\,e^{i\alpha(y-i\omega)}\delta(y-i\omega)\prod_{i=1}^{N}(iy+\gamma_i). \quad (35)$$

The remaining integrals in Eq. (30) are then easily evaluated by utilizing the δ functions, reducing to the expression (32) for the noise-free density of states.

As another consistency check, we consider the case where the deterministic part is a multiple of the identity matrix $\Gamma=\gamma\mathbf{1}$, hence all $\gamma_i=\gamma$. Since γ only shifts the eigenvalues, ω, we can set it to zero. Then the density of states should coincide with the well known result [7] for the GUE,

$$\rho_{GUE}(\omega)=\frac{1}{\sqrt{2}\nu}\sum_{j=0}^{N-1}\varphi_j^2\left(\frac{\omega}{\sqrt{2}\nu}\right), \quad (36)$$

$$\varphi_j(x)=\frac{1}{\sqrt{2^j j!}\sqrt{\pi}}e^{-x^2/2}H_j(x),$$

where $H_j(x)$ are the Hermite polynomials and $\varphi_j(x)$ are the oscillator wave functions.

In order to proceed we will use the identity

$$\frac{1}{\pi}\mathrm{Im}\frac{1}{(x_i-i\epsilon-s)^N}=\frac{(-1)^{N-1}}{(N-1)!}\left(\frac{\partial}{\partial x}\right)^{N-1}\delta(x-s), \quad (37)$$

and rewrite $\mathcal{A}_0$ as

$$\mathcal{A}_0=\frac{1}{(N-1)!}\left(\frac{\partial}{\partial x}\right)^{N-1}e^{-x^2}\Bigg|_{x=(\omega+\nu^2\alpha)/(\sqrt{2}\nu)}, \quad (38)$$

where we have evaluated the derivatives of the δ function by integration by parts.

The fermionic contribution $\mathcal{A}_1$ is given by

$$\mathcal{A}_1=\int_{-\infty}^{\infty}d\eta\,e^{-\eta^2}\left(i\eta-\frac{1}{\sqrt{2}\nu}(\omega+\nu^2\alpha)\right)^N. \quad (39)$$

Both $\mathcal{A}_0$ and $\mathcal{A}_1$ can be represented by Hermite polynomials using the identities

$$H_n(x)=(-1)^n e^{x^2}\left(\frac{\partial}{\partial x}\right)^n e^{-x^2}=\frac{2^n}{\sqrt{\pi}}\int_{-\infty}^{\infty}d\eta\,e^{-\eta^2}(x-i\eta)^n. \quad (40)$$

After some algebra the density of states (30) can be expressed in terms of the oscillator wave functions

$$\rho(\omega)=\frac{\sqrt{N}}{\nu}\int_0^{\infty}dt\,\varphi_{N-1}\left(\frac{\omega}{\sqrt{2}\nu}+t\right)\varphi_N\left(\frac{\omega}{\sqrt{2}\nu}+t\right). \quad (41)$$

One arrives at the expression (36) for the Gaussian unitary ensemble using the following identity [11]:

$$\int_0^{\infty}dt\,\varphi_{N-1}(x+t)\varphi_N(x+t)=\frac{1}{\sqrt{2N}}\sum_{j=0}^{N-1}\varphi_j^2(x). \quad (42)$$

V. THE ABSORPTION SPECTRUM

The absorption spectrum measures the optical response of the system as a function of the frequency. The average absorption spectrum can be formulated in a way similar to the average density of states [40]. Let us label the localized excitations at individual sites by $|m\rangle$, and the eigenstates of the system by $|\tilde{i}\rangle=\sum_m c_i(m)|m\rangle$. Then the transition dipole moments for each of the eigenstates can be written as

$$\mathbf{D}_i=\sum_m c_i(m)\mathbf{d}_m, \quad (43)$$

where $\mathbf{d}_m$ are unit vectors along the direction of the induced dipole moments of individual sites.

The directionally and ensemble averaged absorption spectrum can be written as

$$\alpha(\omega)=\frac{4\pi^2\omega n}{3c}\left\langle\sum_i|\mathbf{D}_i^2|\delta(\omega-E_i)\right\rangle, \quad (44)$$

where E_i are the energy eigenvalues and $\langle\cdots\rangle$ once again denotes the ensemble average.

Unlike the density of states (4) however, the absorption spectrum cannot be expressed solely as an average involving the energy eigenvalues of the system, since the transition dipole moments $\mathbf{D}_i$ depend on the expansion coefficients of the eigenstates. We find it impossible to carry out the analytical computation of the preceding section for the case of the absorption spectrum. Therefore the absorption spectrum will be treated only numerically.

As explained in Sec. II, the transition dipole moments $\mathbf{d}_m$ used in Eq. (44) are determined using the structure data of the LH2 of *Rs. molischianum* [2].

In a manner parallel to Sec. III, we first compare ensembles within the same symmetry class, namely, Gaussian orthogonal disorder (5) and a similar ensemble with flat distributed matrix elements (6). The results of such a comparison is given in Figs. 8 and 9, where it can be seen that universality is even more strongly manifest than in the case of the density of states. This is naturally due to the averaging with respect to oscillator strengths in Eq. (44). In the absence of disorder all of the oscillator strength is at the second and third energy levels $E_2=E_3$ [5]. When the disorder term is turned on, other states, especially the first energy level, give nonzero contributions to the absorption spectrum. However, the absorption spectrum still remains dominated by the now nondegenerate second and third energy levels. A similar comparison across universality classes is given in Fig. 10.
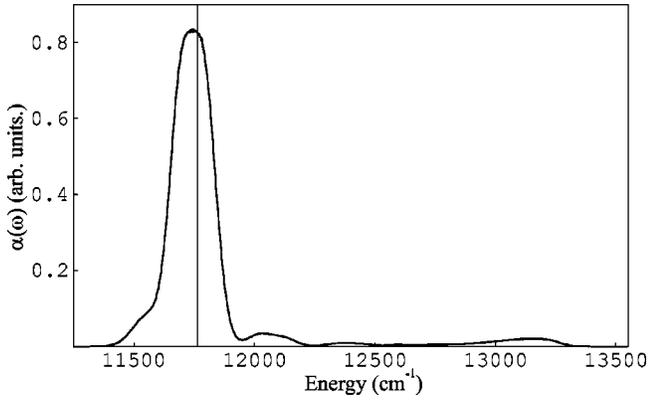
FIG. 8. The numerically obtained absorption spectrum for an ensemble of real symmetric disorder. The width of the ensemble is the same as in Fig. 4. Once again, the Gaussian orthogonal ensemble (solid line) is virtually indistinguishable from an ensemble of flat distributed matrix elements with the same width (dotted line). See also Fig. 9. The vertical line denotes the 850 nm [11 765 cm^{-1}] line.

Finally, as in Sec. III, we examine the approach to universality for the absorption spectrum. Once again it is seen that for an ensemble of larger sized matrices the universality is more strongly manifest (see Fig. 11) and even in the 8×8 case the difference between Gaussian and flat ensembles remains within about a percent. One can also observe that by moving to a higher number of components the absorption spectrum shifts to the red and becomes narrower, as expected for such aggregates [40].

VI. CONCLUSIONS

We have developed a random matrix model to study effective Hamiltonians of light-harvesting complexes and applied our framework to the peripheral light-harvesting complex, LH2, of *Rs. molischianum*. In addition to an analytical study of the density of states in the case of Gaussian unitary disorder, we have examined the effects of random matrix universality on the density of states and the absorption spectrum of the photosynthetic effective Hamiltonians. We observe that despite the small size of the matrices in question,
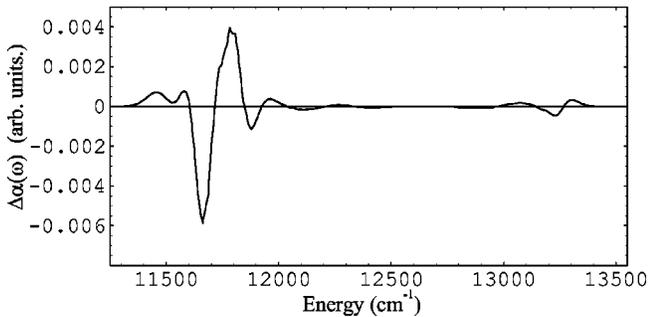

FIG. 9. The difference in absorption spectra for a Gaussian orthogonal ensemble and an ensemble of flat distributed matrix elements as in Fig. 8. The scale is identical to that of Fig. 8, hence the difference is generally within half a percent of the maximum of the absorption spectrum.
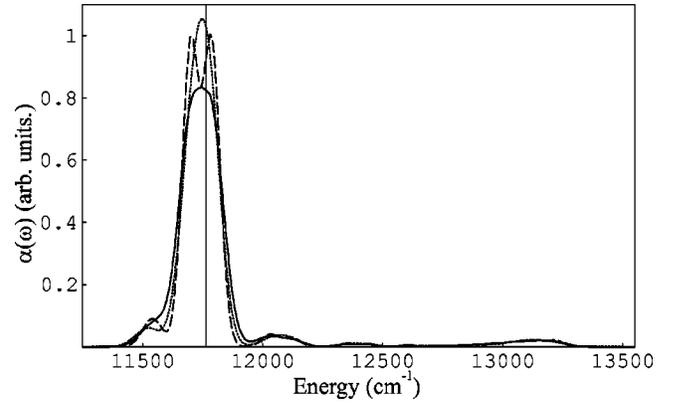

FIG. 10. The absorption spectra for three different universality classes with widths given in Fig. 6: Gaussian orthogonal disorder (solid line), Gaussian unitary disorder (dashed line), and diagonal disorder (dotted line). The pronounced double peak occurring for Gaussian unitary disorder can again be understood in terms of the strong level repulsion in unitary ensembles. Namely, the degenerate second and third eigenvalues get rapidly separated from each other due to noise, but maintain their high oscillator strengths.

signs of universality are strongly present even across symmetry classes. The framework developed in this paper can be applied to many similar systems described by an effective Hamiltonian under the effect of thermal disorder.

ACKNOWLEDGMENTS

APPENDIX A: NOTATION AND CONVENTIONS

In this appendix we outline our notation and conventions for superanalysis, which parallel those found in Ref. [41]. The reader is referred to Berezin's work [42] for a detailed introduction to superanalysis.

We denote the N generators of a complex Grassmann algebra by χ_k which satisfy $\chi_j \chi_k = -\chi_k \chi_j$. We will adopt the conjugation of the second kind where $(\chi_k^*)^* = -\chi_k$. and $(\chi_k \chi_l)^* = \chi_k^* \chi_l^*$.

A (p,q) supervector

$$\Phi = \begin{pmatrix} \phi \\ \chi \end{pmatrix}$$

has p commuting components ϕ_k and q anticommuting components χ_l. A (p,q) supermatrix

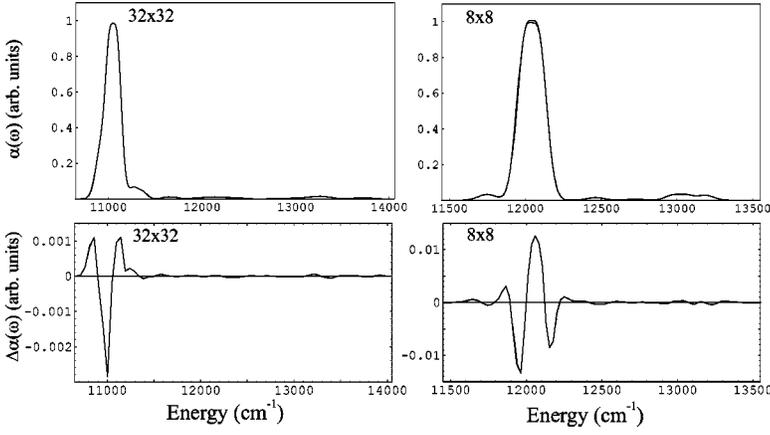$$F = \begin{pmatrix} a & \sigma \\ \rho & b \end{pmatrix}$$

FIG. 11. The approach to universality: The absorption spectra (top) and their differences (bottom) for Gaussian orthogonal disorder and an ensemble with flat distributed matrix elements (compare to Figs. 8, 9, and 7) for a 32×32 ensemble (left) and an 8×8 ensemble (right). The scales for the top and bottom figures are identical.

acts on the space of (p,q) supervectors, where a and b are $p \times p$ and $q \times q$ commuting matrices and σ and ρ are $p \times q$ and $q \times p$ anticommuting matrices, respectively. Transposition is defined as in

$$F^T = \begin{pmatrix} a^T \rho^T \\ -\sigma^T b^T \end{pmatrix}, \qquad (A1)$$

so that $(F\Phi)^T = \Phi^T F^T$. The Hermitian conjugation is defined naturally as $F^\dagger = (F^T)^*$, so that for any supervector Φ, $(\Phi\Phi^\dagger)^\dagger = \Phi\Phi^\dagger$ and for any supermatrix F, $(F^\dagger F)^\dagger = F^\dagger F$ as in the case of ordinary vectors and matrices.

The supertrace and the superdeterminant of a supermatrix are defined as $\mathrm{str} F \equiv \mathrm{tr}\, a - \mathrm{tr}\, b$ and $\mathrm{sdet}\, F \equiv \det(a - \sigma b^{-1} \rho)(\det b)^{-1}$, respectively. This ensures that they satisfy the relation, $\mathrm{sdet}\, F = \exp(\mathrm{str}\ln F)$, along with many other familiar identities for traces and determinants.

Unitary matrices, diagonalization, and Lie groups have their corresponding natural superanalogues [42], so that for any super-Hermitian matrix, H, $H = U^\dagger \Lambda U$, where $\Lambda = \mathrm{diag}(\lambda_b, i\lambda_f)$ for U being a superunitary matrix and λ_b and λ_f ordinary diagonal real matrices. The eigenvalues in λ_b are called bosonic whereas the ones in λ_f are called fermionic. Even some results in harmonic analysis over unitary groups generalize rather naturally to superunitary groups as in the case of Itykson-Zuber-Harish-Chandra integrals [11,37,38] that we employ in Sec. III.

Differentiation of Grassmann numbers are introduced in the natural way $(\partial/\partial\chi_k)\chi_l = \delta_{kl}$. This implies, together with the nilpotency of Grassmann generators, that the Taylor expansion of any Grassmann valued function truncates after a finite number of terms. The integration of Grassmann numbers are defined according to $\int d\chi = 0$ and $\int d\chi \chi = 1/\sqrt{2\pi}$. The prefactor is choosen in such a way as to satisfy

$$\int d\phi^* d\phi d\chi^* d\chi \exp(i\phi^*\phi + i\chi^*\chi) = 1, \qquad (A2)$$

where ϕ is an ordinary complex number and χ a Grassmann number.

The power of the supersymmetry method comes from the ability to express ratios of determinants in terms of Gaussian integrals. With our conventions it follows

$$\int d[\phi^*] d[\phi] \exp(i\phi^\dagger H \phi) = \frac{1}{\det(H/2\pi)}, \qquad (A3)$$

$$\int d[\chi^*] d[\chi] \exp(i\chi^\dagger H \chi) = \det(H/2\pi), \qquad (A4)$$

for any Hermitian matrix H, and bosonic and fermionic vectors ϕ and χ. Similarly,

$$\int d[\Phi^*] d[\Phi] \exp(i\Phi^\dagger F \Phi) = \frac{1}{\mathrm{sdet}(F)}, \qquad (A5)$$

for a supervector, Φ, and a Hermitian supermatrix, F.

APPENDIX B: THE DENSITY OF STATES FOR UNITARY DISORDER

In this appendix we summarize the results from Sec. IV regarding the analytical formulation of the density of states of effective Hamiltonians in the case of Gaussian unitary disorder.

We consider an ensemble of finite sized matrices $H = H_0 + R$ where the deterministic part H_0 is a fixed matrix and the probability distribution for the disorder term R is given by Eq. (11). The density of states of this ensemble is then given by

$$\rho(\omega) = \frac{1}{\pi} \int_0^\infty d\alpha \, \mathcal{A}_0 \mathcal{A}_1, \qquad (B1)$$

$$\mathcal{A}_0 = \frac{1}{\pi} \mathrm{Im} \int_{-\infty}^{\infty} d\xi \, e^{-\xi^2} \prod_{i=1}^{N} \frac{1}{\xi - i\epsilon - \dfrac{1}{\sqrt{2}\nu}(\omega + \nu^2\alpha - \gamma_i)},$$

$$\mathcal{A}_1 = \int_{-\infty}^{\infty} d\eta \, e^{-\eta^2} \prod_{i=1}^{N} \left(i\eta - \frac{1}{\sqrt{2}\nu}(\omega + \nu^2\alpha - \gamma_i) \right),$$

where γ_i are the eigenvalues of the deterministic part, H_0, ν is the width of the distribution and N is the size of the matrices, which we will assume to be even. Although the derivation of Eq. (B1) requires advanced mathematics, the result can be utilized with basic calculus and the help of a symbolic

algebra program. Below we will simplify Eq. (B1) as much as possible, but due to the presence of N parameters, the eigenvalues, γ_i, of the unperturbed effective Hamiltonian, the final expressions are best evaluated using a symbolic algebra program such as MATHEMATICA [39].

In order to evaluate the density of states (B1) we note that $\mathcal{A}_0$ results in δ functions at the poles and $\mathcal{A}_1$ is the integral of a Gaussian times a polynomial. Without loss of generality we will work with the case of nondegenerate γ_i. The degeneracies can be treated by taking the proper limits at the end. Also we will work in energy units, where $\sqrt{2}\nu = 1$.

The "bosonic part" $\mathcal{A}_0$ of Eq. (B1) can be evaluated with the help of the identity

$$\frac{1}{\pi} \mathrm{Im} \prod_{i=1}^{N} \frac{1}{x - i\epsilon - s_i} = \sum_{i=1}^{N} \delta(x - s_i) \prod_{j \neq i}^{N} \frac{1}{x - s_j}. \quad (B2)$$

Integrating the δ functions results in

$$\mathcal{A}_0 = \sum_{i=1}^{N} e^{-[(1/2)\alpha + (\omega - \gamma_i)]^2} \prod_{j \neq i}^{N} \frac{1}{\gamma_j - \gamma_i}. \quad (B3)$$

For the evaluation of the "fermionic part" $\mathcal{A}_1$ we introduce the following constants:

$$I_k \equiv \int_{-\infty}^{\infty} d\eta\, e^{-\eta^2} \eta^{2k} = \frac{(2k-1)!!\sqrt{\pi}}{2^k}. \quad (B4)$$

Then $\mathcal{A}_1$ can be written as a polynomial in α, ω, and γ_i

$$\mathcal{A}_1 = (-1)^{N/2} \sum_{k=0}^{N/2} I_{(N/2)-k}(-1)^k$$

$$\times \sum_{\sigma \in S_{T_N}^{2k}} \prod_{p=1}^{2k} \left(\frac{1}{2}\alpha + (\omega - \gamma_{\sigma_p}) \right), \quad (B5)$$

where S_T^n is the set of n-element subsets of the finite set T and $T_N \equiv \{1, \ldots, N\}$. In order to write Eq. (B5), we have used the identity

$$\prod_{i=1}^{N} (\eta + s_i) = \sum_{j=0}^{N} \eta^{N-j} \sum_{\sigma \in S_{T_N}^j} \prod_{p=1}^{j} s_{\sigma_p}, \quad (B6)$$

and that $\int_{-\infty}^{\infty} d\eta\, e^{-\eta^2} \eta^k$ vanishes for odd k.

After a shift of integration variables the density of states can be written as

$$\rho(\omega) = \frac{(-1)^{(N/2)+1}}{\pi} \sum_{i=1}^{N} \int_{2(\omega - \gamma_i)}^{\infty} d\alpha\, e^{-[(1/2)\alpha]^2}$$

$$\times \prod_{j \neq i}^{N} \frac{1}{\gamma_j - \gamma_i} \sum_{k=0}^{N/2} I_{(N/2)-k}(-1)^k$$

$$\times \sum_{\sigma \in S_{T_N}^{2k}} \prod_{p=1}^{2k} \left(\frac{1}{2}\alpha + (\gamma_i - \gamma_{\sigma_p}) \right). \quad (B7)$$

This expression can be recognized as polynomial terms in ω and γ_i. The remaining integration yields prefactors of the form

$$J_k(A) = 2 \int_A^{\infty} dt\, e^{-t^2} t^k$$

$$= \begin{cases} 2\Gamma\left(\dfrac{k+1}{2}\right) - \Gamma\left(\dfrac{k+1}{2}, A^2\right), & k \text{ even}, \quad A < 0, \\[2ex] \Gamma\left(\dfrac{k+1}{2}, A^2\right), & \text{otherwise}, \end{cases}$$

$$(B8)$$

where $\Gamma(n,x)$ is the incomplete gamma function. The formula for the density of states (now free of any integrations) can then be written as a combinatorial expression

$$\rho(\omega) = \frac{(-1)^{(N/2)+1}}{\pi} \sum_{i=1}^{N} \prod_{j \neq i}^{N} \frac{1}{\gamma_j - \gamma_i}$$

$$\times \sum_{k=0}^{N/2} I_{(N/2)-k}(-1)^k \sum_{\sigma \in S_{T_N}^{2k}} \sum_{m=0}^{2k} J_{N-m}(\omega - \gamma_i)$$

$$\times \sum_{\rho \in S_\sigma^m} \prod_{q=1}^{m} (\gamma_i - \gamma_{\sigma_{\rho_q}}). \quad (B9)$$

The reader is invited to repeat this calculation at least for the case of 2×2 random Gaussian unitary matrices (with $\gamma_1 = \gamma_2 = 0$) and compare it to the well known result for GUE, namely, $\rho(\omega) = (1/\sqrt{\pi}) e^{-\omega^2} (1 + 2\omega^2)$. It should be noted that the combinatorial load of this computation increases dramatically with N. This formulation can also be utilized to examine the functional behavior of the density of states in an interval containing a small group of eigenvalues as part of a larger spectrum, if one treats the eigenvalues outside this interval in a "mean field" setting. This will be the subject of a further study.

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