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The Kuramoto-Lohe Model and Collective Absorption of a Photon

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The absorption of molecular exciton states in disordered networks is studied. The main purpose of this paper is to look at how phases of the intermediate ground-excited state superposition interfere during the absorption process. How does this phase average enable, or suppress, aborption to a delocalized state? To address this question, a theory for phase oscillators is used to predict the purity of the collective excited state of the network. The results of the study suggest that collective absorption by molecular exciton states requires a sufficiently large electronic coupling between molecules in the network compared to the random distribution of transition energies at the sites, even when the molecular network is completely isolated from the environment degrees of freedom. The 'dividing line' between absorption to a mixture of, essentially, localized excited states and coherent excitation of a pure delocalized exciton state is suggested to be predicted by the threshold of phase synchronization.

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1. Introduction

When a network is formed by a group of atoms or molecules that are electronically coupled to each other, then absorption of light can reveal delocalized states known as Frenkel excitons [1–3]. What has been well-studied is how and why the delocalization of the exciton states is limited by static and dynamic energy disorder, and coupling to vibrations in the case of molecules [4–6]. The energy disorder here is the distribution of electronic transition energies that reflects the heterogenous local environments of the molecules or atoms. The well-known results for the case of static disorder (slow fluctuations of the transition energies) follow from taking an ensemble average over many networks, where each one is in a slightly different heterogenous local environment [5,7,8].

Here a very fundamental starting point is proposed regarding how to think about absorption of a photon by a single disordered network in the limit of very low temperature and negligible homogenous line broadening. In other words, the single network is characterized by a fixed assignment of transition energies to the nodes and electronic coupling between the nodes. In the main results of the paper, there is no ensemble averaging over networks. The average is taken only over the phase of the intermediate light-matter superposition. Under these ideal assumptions, if we calculate the excited states of the network the lowest energy state is going to be a pure state for any non-zero value of coupling (technically, coupling that exceeds the spectral resolution of the calculation), and a mixed state (i.e. excitation is localized on any one atom or molecule) only if the coupling is zero. This process predicts that distant, very weakly coupled, near-degenerate transitions absorb collectively.

The question addressed here is whether there is a fundamental reason that this seemingly unphysical result is avoided. Specifically, is there a threshold value of the coupling (other than ’non-zero’) to produce collective absorption of a photon by the network?

2. Absorption of a photon and ‘phase’

The absorption spectrum of a a coupled network, with Hamiltonian H, of molecules or atoms each with a transition frequency ω_n between the ground state $|0\rangle$ and excited state $|n\rangle$ is considered. It is assumed that each molecule has only a single excited state, and can host at most one excitation. That is, each molecule is a two-level system. The expression for the absorption can be written as [9,10]

$$I(\omega) = \left\langle \mathrm{Re} \sum_{m,n} \int_0^{\infty} dt e^{i\omega t} \mu_n e^{i\phi_n} \, \mathrm{Tr}_{bath} \langle n | e^{-iHt/\hbar} \mu_m e^{-i\phi_m} | m \rangle \langle 0 | \rho_{th} e^{iHt/\hbar} | 0 \rangle \right\rangle_{\epsilon,\phi} \tag{2.1}$$

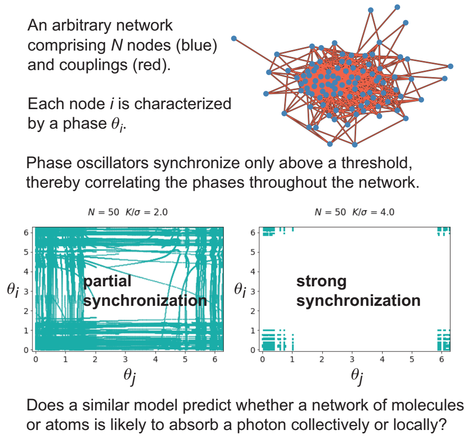
where μ_n is the dipole transition moment for molecule n, Tr_{bath} means the trace over the bath coordinates, and ρ_{th} is the bath density at thermal equilibration with the ground electronic state. The averages over ϵ and ϕ are explained below. ϵ adds a random offset to the transition energy at each site (molecule). In the first part of the paper we do not average over ϵ, but consider just a single realization of random energy offsets at each site, then average over solely the phase. In Section 5 we consider the ensemble average over ϵ .

Each transition energy ω_n (in the site basis) comprises a constant mean transition energy (frequency) specific to molecule n and a fluctuating term [11,12]: $\omega_n = \epsilon_n + \delta\omega_n$. The fluctuations of transition energy are discussed more below—they are the main complication challenging the theory for spectroscopy in the case of molecular exciton states. The distribution of mean energy gaps ϵ_n, caused by the slow fluctuations, is typically ensemble averaged by performing many calculations with random, normally-distributed values of ϵ_n.

The phase offsets ϕ_n pertain to the intermediate state in the absorption process, which is a ground-excited state superposition produced by the first interaction between the light and the molecule. The phase offset indicates the quantum phase of the superposition, that is, the arbitrary complex coefficients in the intermediate state $\alpha|0\rangle + \beta|m\rangle$. This superposition is evident in Eq. 2.1 as the coherence $|m\rangle\langle 0|$ in the density matrix. When $m = n$ the phases cancel and we do not need to worry about phase at all. Otherwise, however, the phase difference does matter because it affects how efficiently the sum over $|m\rangle\langle 0|$ coherences can transition to excited state population of a delocalized state.

Finally, the fluctuating part of the transition frequency is assumed to be the same for each molecule. It is accounted for by evaluating the transition frequency correlation function using the cumulant expansion [11]. The appropriate equations are well-known for the case of an ensemble of uncoupled molecules. To calculate the absorption spectrum of a network (molecular exciton), the theory is complicated bcause we have to account for cross-correlations between molecules hand-in-hand with diagonalization of the Hamiltonian matrix to obtain the absorbing eigenstates [9,10,13,14]. Despite a number of studies, there is no exact equation we can apply to this case. As Yang notes [9], this is because there is interplay between the electron-nuclear coupling (giving the energy gap fluctations) and the intermolecular couplings, which may need to be described perturbatively.

Instead of pursuing this difficult issue of the absorption spectrum, the focus of this paper is on the phase correlations in the network. Do the phase factors cancel, like they do in the single molecule case? If not, what are the implications? The clue to answering this question is how the phase correlation is predicted to depend on the ratio of electronic coupling to the width of the distribution of molecule (or node) energy offsets. That prediction is made using well-known models for synchronization of phase oscillators, described below. The results give the qualitative picture shown in Fig. 1, that motivates the approach taken in this work.



An arbitrary network comprising N nodes (blue) and couplings (red).

Each node i is characterized by a phase θ_i.

Phase oscillators synchronize only above a threshold, thereby correlating the phases throughout the network.

Does a similar model predict whether a network of molecules or atoms is likely to absorb a photon collectively or locally?

Figure 1. Summary of the main properties of phase oscillators coupled to form a network. When coupling K exceeds a threshold, then correlations between the oscillator phases abruptly increase.

The main purpose of this paper is to look at how phases coalesce during the absorption process so that the phase differences are minimal. Or, under what conditions it is unlikely that the phases will synchronize at all, thereby fundamentally preventing aborption to a delocalized state. To address this question a theory for phase oscillators is used to predict the purity of the collective excited state of the network. The purity (defined as $\mathrm{Tr}\,\rho^2$) indicates the mixedness of a state via Kadison's inequality for positive maps on bounded linear operators on a Hilbert space.

The statistical time evolution of oscillator phases in a network of coupled oscillators has been widely studied using the Kuramoto model [15–22]. The Kuramoto model is a simple statistical model, but appropriate for predicting synchronization thresholds for a remarkable variety of systems that exhibit some kind of periodicity. The phase synchronization is modeled by the coupled differential equations

$$\dot{\theta}_i = \nu_i + \frac{K}{N}\sum_{j=1}^{N} a_{ij}\sin(\theta_j - \theta_i), \tag{2.2}$$

where ν_i is the frequency of the oscillator at node i, θ_i is the oscillator phase defined in terms of accumulated phase and an offset $\theta_i(t) = \epsilon_i t + \phi_i$, K is the coupling value, a_{ij} (with value 0 or 1) are taken from the adjacency matrix of the graph representing the node connectivities in the network [23] (assumed here to be all-to-all), and the coupling is renormalized by the factor $1/N$ so that networks are size-intensive with respect to the lowest eigenvalue. This assertion of constant all-to-all coupling, though not physical for a system of interacting molecules, does not change the physical conclusions of the work. Its main value is that it allows the numerical calculations to be compared to prior studies of phase oscillator networks.

A version of the Kuramoto model that can be applied to systems characterized by non-Abelian algebra, such as quantum nodes (two-level systems) has been proposed by Lohe [24],

$$i\hbar\dot{U}_i U_i^\dagger = H_{ii} + \frac{iK}{2N}\sum_{j=1}^{N} a_{ij}(U_j U_i^\dagger - U_i U_j^\dagger), \tag{2.3}$$

where H_{ii} incorporates the frequency offset (relative to the mean) $\epsilon_i/\hbar$ of node i, and U_i is an $n \times n$ unitary matrix that associates node i with an element of the unitary group $U(n)$ or one of its subgroups, such as $SU(n)$. The matrix represents the quantum phase of node i. This equation has also been well studied [25–27]. If we associate $U_i = e^{-i\theta_i}$, then the Kuramoto equation is recovered. As described below, this simplified case is appropriate for a network of molcules that are fixed in position relative to each other.

The key finding of the Kuramoto-Lohe equations is that phase synchronization is a threshold phenomenon. That is, phases spontaneously correlate only once the threshold value of coupling (K) relative to the standard deviation of energy offsets ϵ_i of nodes in the network (σ_E) is surpassed. Here it is hypothesized that such a threshold also exists for collective absorption of a photon by an isolated network. To test that idea, we will study here whether purity of the synchronized state of the network can be defined and that it measures mixedness, as it should. Note that the Kuramoto-Lohe model predicts solely the synchronized state of the network, which is the single emergent state [28], whose eigenvalue is distinguished from the main density of states. The motivation and approach of the paper are summarizd in Fig. 1.

How does phase potentially matter? It is well known that energy inhomogeneity increases the mixedness of an exciton state (e.g. [23] and references cited therein). Similarly, an average over the unknown phase distribution of the intermediate states in the absorption process—the ground-excited state superpositions—may introduce mixedness to the absorbing state.

3. Formalism and methods

The systems we will examine in this paper are networks comprising N coupled quantum nodes (that can represent two-level systems, atoms, molecules, etc). The energy gap of node i, obtained from expectation values of the zeroth-order Hamiltonian H_0, is ϵ_i. The site excitation energies ϵ_i of the ensemble of nodes i are disordered and normally distributed with standard deviation σ_E about the mean. In the numerical work, once the set of ϵ_i are assigned, they are fixed. That is, a single representative network is being consided in each calculation. The networks studied in the numerical computations comprise between 100 and 2000 nodes with standard deviation of energy off-sets $\sigma_E = 10$ in the same relative units as K.

The nodes are coupled to each other by an interaction Hamiltonian H_I 'all-to-all', which is standard for the models inspiring this work, but any other coupling scheme could be assumed.

We make the abstraction that all the node-node coupling matrix elements of H_I, H_{ij}, are equal:

$$H_{ij} = K a_{ij}/N \tag{3.1}$$

In the Kuramoto-Lohe model, the operator for each node acts on the Hilbert space $\mathcal{H}_i$ for node i taken over $\mathbb{C}^2$ with respect to the basis vector ψ_i. An arbitrary intermediate state (coherence) during light absorption is an element of $SU(2)$

$$|\psi_i\rangle = \alpha_i|0\rangle + \beta_i|1\rangle \tag{3.2}$$

with $\alpha_i, \beta_i \in \mathbb{C}$ and $|\alpha_i|^2 + |\beta_i|^2 = 1$. The phase state of the network comprising N nodes in the single excitation subspace has the form

$$\begin{aligned}\Phi(t) &= \bigotimes_{i=1}^{N}(\alpha_i|0\rangle_i + \beta_i|1\rangle_i) \\ &\approx \sum_i \alpha_1|0\rangle_1\alpha_2|0\rangle_2\ldots\beta_i|1\rangle_i\ldots\alpha_N|0\rangle_N\end{aligned} \tag{3.3}$$

Quantum phase is defined by the complex coefficients for the state of each node [29], and, for one node, can be viewed as a point on the 3-sphere $\mathbb{S}^3$, or a normalized quaternion, $\mathbf{x}_i = x_i + \mathbf{i}y_i + \mathbf{j}z_i + \mathbf{k}w_i$. The quantum phase of the product state is a point on the $3N$-torus. However, by defining a phase relative to $\alpha_1\alpha_2\ldots\alpha_N$, the relative phase of the product state is reduced a point on $\mathbb{S}^3$.

To ensure that the study here is intuitive, this phase problem is reduced from a point on $\mathbb{S}^3$ one phase angle ϕ_i, a point on $\mathbb{S}^1$ by putting $U_i = e^{i\theta_i}$. This is appropriate when the physical structure of the network restricts the phase. For example, consider that the two states of the node can be ground and excited electronic states of a molecule. Further, consider each node (i.e. molecule) to be located at position $\vec{R}_i$, and the transition dipole moment $\vec{\mu}_i$ at each site has a fixed orientation. Then each phase is constrained relative to this structure because it represents the unknown phase associated solely with each vector $\vec{\mu}_i$. With this simplification, the synchronized, or emergent, phase state predicted by Eq. 2.3 is

$$\Phi(t) = \frac{1}{\sqrt{N}}\sum_{i=1}^{N} e^{i\theta_i}|0\rangle_1|0\rangle_2\ldots|1\rangle_i\ldots|0\rangle_N. \tag{3.4}$$

The Kuramoto model is a statistical theory, so we are really using it to calculate densities by averaging over initial phases. For example, a good way of thinking about Eq. 2.3 is to associate $U_iU_j^\dagger$ to the statistical density operator element $\rho_{ij} = |i\rangle\langle j|$. Eq. 3.4 captures this idea if we use it to define the phase density operator $\rho_\theta = |\Phi(t)\rangle\langle\Phi(t)|$, calculated by ensemble averaging over phase. This appropriately represents the statistical average of synchronization trajectories starting from different values of the initial phase distribution. Below it is established that the mixedness of the synchronized state is indeed estimated using the purity, Tr ρ_θ^2.

4. A connection between synchronization and mixedness

The order parameter indicates the extent of phase synchronization. It is defined [15] as the real part, r, of the sum of complex phases:

$$re^{i\psi} = \frac{1}{N}\sum_{i=1}^{N} e^{i\theta_i}. \tag{4.1}$$

Fig. 2a shows two representative trajectories, quantified by the order parameter, for an ensemble of phase oscillators with the initial condition of a partially random phase distribution. Below the threshold value of K relative to σ_E the phases do not synchronize and the order parameter equilibrates to zero, as seen in the trajectory for $K = 14$. When the order parameter is zero it means the phases of the nodes θ_i are uncorrelated. In such a case, the phase trajectories are sensitive to the initial phase distribution. For example, see how the phases evolve in the two panels of Fig. 2b, where all the parameters in the two simulations are identical, except that the initial phase distributions are different. The 'zig-zag' form of the phase indicates that phase accumulates with time ($\epsilon_i t$) when it is not synchronized by, essentially, zeroing out the ϵ_i contribution to θ_i because of the coupling. The 'zig-zag' shape comes about because θ_i mod(2π) is plotted.

In the case that K exceeds the threshold value, then the order parameter is not zero, as seen in the trajectory with $K = 25$. A high order parameter indicates that correlations increase because the phases coalesce owing to autonomous optimization of the phase offsets in θ_i, Fig. 2c. Notice now that all the θ_i lock to near zero (or, equivalently, multiples of 2π).

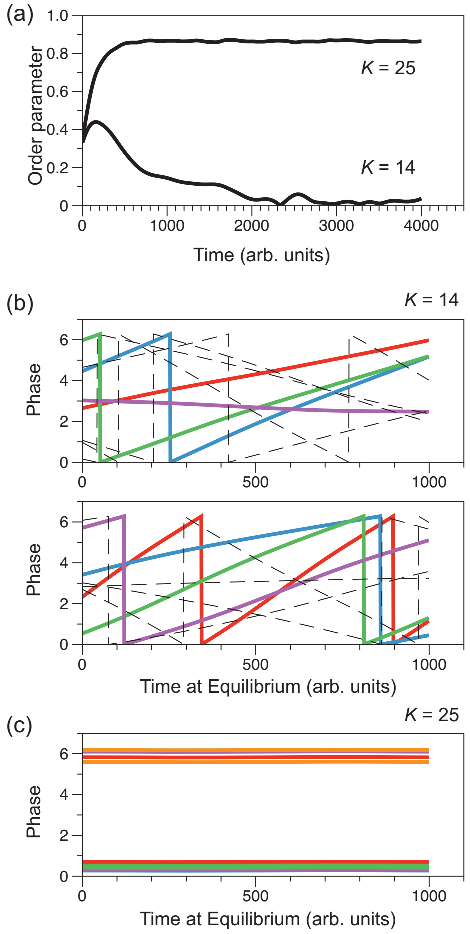


Figure 2. (a) Order parameter versus time in trajectories. (b) Phases (in the rotating frame modulus 2π) for 10 randomly selected nodes, calculated with $K = 14$. The two panels show two calculations of exactly the same network, but different initial phases. The time range is the last quarter of the trajectory shown in part (a). (c) Phases (in the rotating frame) for 10 randomly selected nodes, calculated with $K = 25$. These phase trajectrories are insensitive to the initial phase distribution.

The increase in order parameter, and hence phase correlation, can be measured by the distribution of phase in the equilibrium part of the trajectories. Variance and standard deviation of a distribution on the circle is 'directional' because of the way the distribution wraps around the circumferance. So, we need to be careful analyze the phase distribution appropriately. The phase distributions are therefore quantified by their circular standard deviations, using the definition in Ref. [30]. The method is implemented in the Astrostatistics library for Python.

The circular standard deviation for the phases in each calculation, σ_θ, are plotted in Fig. 3. Notice that narrowing of the phase distribution mirrors the increase in order, with the abrupt transition from unsynchronized phase oscillators (phase distribution that is effectively uniform), to synchronized phase oscillators with a narrow phase distribution. The phase distributon narrows because the synchronized phase oscillators will be found in a small interval containing the fixed point, or attractor [21].

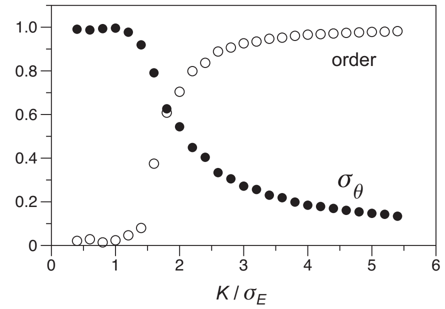


Figure 3. Order parameter as a function of the ratio of coupling strength to energy standard deviation calculated for a network with $N = 2000$.

The issue to consider is whether the complex phases in Eq. 3.4 can be used to construct the density operator $\rho_\theta = |\Phi(t)\rangle\langle\Phi(t)|$ that, in turn, measures mixedness, caused by phase disorder, of the absorbing state of the network. The mixedness is measured by $\mathrm{Tr}\,\rho_\theta^2$, which will have a value of $1/N$ for a fully mixed state and a value of 1 for a pure state.

We can see that this does work out by first explicitly writing an arbitrary average over phases of the phase density operator. Here the system comprises N nodes and the average is taken over M realizations. The complex phase for successive samples in the average is indicated by a prime.

$$\rho_\theta = \frac{1}{N^2 M^2} \begin{bmatrix} M & e^{i\theta_{12}} + e^{i\theta'_{12}} + \dots & e^{i\theta_{13}} + e^{i\theta'_{13}} + \dots & \cdots \\ e^{-i\theta_{12}} + e^{-i\theta'_{12}} + \dots & M & & \\ e^{-i\theta_{13}} + e^{-i\theta'_{13}} + \dots & & M & \\ \vdots & & & \ddots \end{bmatrix} \tag{4.2}$$

We then obtain

$$\mathrm{Tr}\,\rho_\theta^2 = \frac{1}{N^2 M}\left[N M^2 + 2\sum_{j>i} (e^{i\theta_{ij}} + e^{i\theta'_{ij}} + \dots)(e^{-i\theta_{ij}} + e^{-i\theta'_{ij}} + \dots) \right] \tag{4.3}$$

The second term on the square brackets comprises $N(N-1)/2$ terms, each made up of M^2 products. These M^2 products, when multiplied out, give a total of $(M-1)$ 'squared' terms and $M(M-1)$ 'cross' terms. These cross terms can be collected into $M(M-1)/2$ groups that pair them up:

$$2\sum_{j>i} (e^{i\theta_{ij}} + e^{i\theta'_{ij}} + \dots)(e^{-i\theta_{ij}} + e^{-i\theta'_{ij}} + \dots) \tag{4.4}$$

$$= \underbrace{e^{i\theta_{ij}} e^{-i\theta_{ij}} + \dots}_{N(M-1)\ \mathrm{terms}} + \underbrace{e^{i\theta_{ij}} e^{-i\theta'_{ij}} + e^{i\theta'_{ij}} e^{-i\theta_{ij}} + \dots}_{(N-1)^2 M(M-1)/2\ \mathrm{groups}} \tag{4.5}$$

Now each of the groups can be written in terms of the cosine of a difference in phase differences that compares terms in the distribution. That is, if we index the pairs by k and collect the phase differences into each χ_{ij}^k, they have the form

$$e^{i\theta_{ij}}e^{-i\theta'_{ij}} + e^{i\theta'_{ij}}e^{-i\theta_{ij}} = 2\cos\chi_{ij}^k \tag{4.6}$$

So we end up with

$$\mathrm{Tr}\,\rho_\theta^2 = \frac{1}{N^2M^2}[NM^2 + (M-1)N + \underbrace{\sum_{j>i}\cos\chi_{ij}^k}_{(N-1)N\times M(M-1)\text{ terms}}]. \tag{4.7}$$

Now taking the limit $M \to \infty$, it is evident that $\mathrm{Tr}\,\rho_\theta^2$ takes values ranging from $1/N$ to 1 as required.

We can also see this result in a more general way. The ensemble average in the phase basis produces the state that is a mixture of unitary transformations of a pure reference state with density operator ρ, so that $\rho_\theta = \sum \frac{1}{N}U_i^\dagger\rho U_i$, and $\mathrm{Tr}\,\rho_\theta = 1$ by linearity of the trace and the cyclic permutation $U^\dagger AU = AUU^\dagger = A$. However, $\mathrm{Tr}\,\rho_\theta^2$ comprises two sets of terms:

$$\mathrm{Tr}\,\rho_\theta^2 = \left\{\begin{array}{ll} \frac{1}{N^2}\Big[(U_1^\dagger\rho U_1)^2 + (U_2^\dagger\rho U_2)^2 + \ldots & \text{squared terms} \\ +U_1^\dagger\rho U_1 U_2^\dagger\rho U_2 + \ldots\Big] & \text{cross terms} \end{array}\right. \tag{4.8}$$

The N squared terms, each equal to unity, sum to $1/N$. The cross terms do not reduce to unity because, while the trace is invariant under cyclic permutations, arbitrary permutations are not allowed. The cross-terms average to zero when $\sigma_\theta = 1$, and then $\mathrm{Tr}\,\rho_\theta^2 \to 1/N$.

The limiting values of $\mathrm{Tr}\,\rho_\theta^2$ as a function of N are illustrated by numerical calculations presented in Fig. 4. To carry these out, a random matrix theory approach has been used [23] as described in the following section. This procedure yields the results shown in Figure 4 for $\sigma_\theta = 1$. Notice that $\mathrm{Tr}\,\rho_\theta^2$ tends to $1/N$ in each as the number of samples M in the average becomes very large.

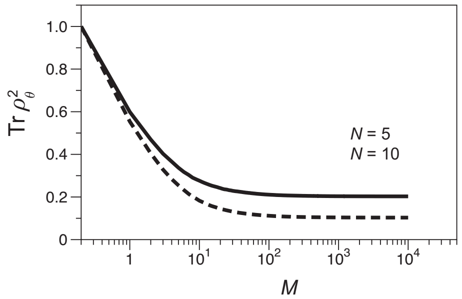


Figure 4. RMT phase-basis calculations of mixing of states as a function of the number of realizations of the ensemble included in the average. The anymptotic values $1/N$ are evident. M is the number of samples taken in the average.

In Fig. 5, the mixedness of the synchonized eigenstate of the network is plotted as a function of K. The mixedness is assessed by $\mathrm{Tr}\,\rho_\theta^2$, where the average has been taken over the initial phase distribution. A transition, as a function of K, from a mixed state to a pure state with respect to the phase basis is evident. The threshold occurs at the same value as the threshold for synchronization, see Figure 3. For this isolated network, after the synchronization threshold is passed as a function of K, the states converge quickly to pure states. The pure exciton state is the result we expect for optical absorption an isolated, single network. The results indicate that, as hypothesized, absorption of light does not coherently excite the entire network for smaller values of K because absorption 'events' (light-matter coupling) in the site basis are unsynchronized. The electronic coupling K plays a key role synchronizing the light-matter coupling to populate a coherent (delocalized) exciton state.

The relative phases of the nodes encode their correlations in the network. When the phases are uncorrelated, the corresponding equilibrium state is fully mixed. This is not intuitive. One would think that if ϵ_i is specified for each node, and the pairwise coupling among nodes $H_{ij} \neq 0$, then the eigenstate of the emergent, synchronized state must be a pure state. However, if the phase for each node is uncorrelated with phase at any other node, it is a random variable taken from the uniform circular distribution because the phase of the intermediate superposition state at each node is unknowable—and thus the state produced by light absorption is fully mixed. This fully mixed state is simply the statistical average of the excitation being at any one of the nodes in the network.

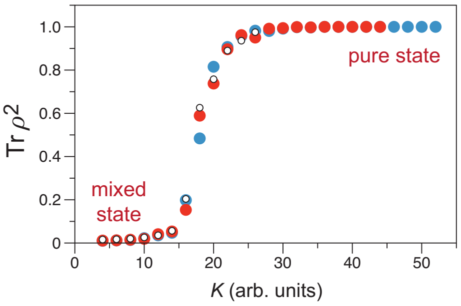


Figure 5. Mixedness of the isolated state as a function of K. The blue dots correspond to results for a network with $N = 500$, the red dots for $N = 1000$, and black open circles for $N = 2000$.

5. Comparison to random matrix theory

The phase distribution discussed in the previous sections is related to the energy gap distribution on the network. Here we examine that idea by comparing ensemble averages taken over phase with those taken over energy offsets (ϵ_i). To calculate these averages, a form of random matrix theory is used. Random matrix theory [23] is a simple way to calculate ensemble properties of a disorded system. We study the method here in order to put the phase oscillator model into the context of a well known theory for calculating the excited states of disordered molecular exciton systems.

The approach for the phase random matrix theory (RMT$_\theta$) involves using the phase distribution σ_θ associated to each K, shown in Figure 3. We then solve the eigenvalue problem for an $N \times N$ Hamiltonian matrix in the site basis, with phase disorder constrained by σ_θ:

$$H_{ij} = \begin{cases} -\frac{K}{N} a_{ij} e^{i(\theta_j - \theta_i)} & \forall i \neq j \\ 0 & \text{when } i = j \end{cases} \tag{5.1}$$

Instead of an average over energies, the system is ensemble-averaged over the distribution of random phase variables θ_i drawn from a normal circular distribution with standard deviation σ_θ. We obtain an eigenvalue spectrum equivalent to that of the adjacency matrix $\mathbf{A}$ with elements a_{ij}. The eigenvector of the state with lowest eigenvalue in each realization of the ensemble—the synchronized state—is used to construct the density matrix in the phase basis ρ_θ.

Analogous calculations using the usual Hamiltonian matrix elements (i.e. amplitude as well as phase information) were carried out, RMT$_E$, using the methods previously described [23] and Hamiltonian matrix elements

$$H_{ij} = \begin{cases} -\frac{K}{N} a_{ij} & \forall i \neq j \\ \epsilon_i & \text{when } i = j \end{cases} \tag{5.2}$$

where ϵ_i is a random variable drawn from a normal distribution with standard deviation σ_E. The ensemble average gives the spectrum of density of (singly-excited) states. The eigenvector of the sychronized state at each realization of the ensemble in the RMT$_E$ calculation is identified as the eigenvector with the lowest inverse participation ratio (i.e. the most delocalized states). That state is used to construct the density matrix in the energy basis ρ_E.

Now we compare calculations using RMT$_\theta$ to analogous calculations using the RMT$_E$ method to show: (a) the relationship between phase oscillator models and random matrix theory methods; (b) to thereby reveal two sources of decoherence in large, isolated quantum networks, which clarifies the size-scaling of mixedness of a quantum state.

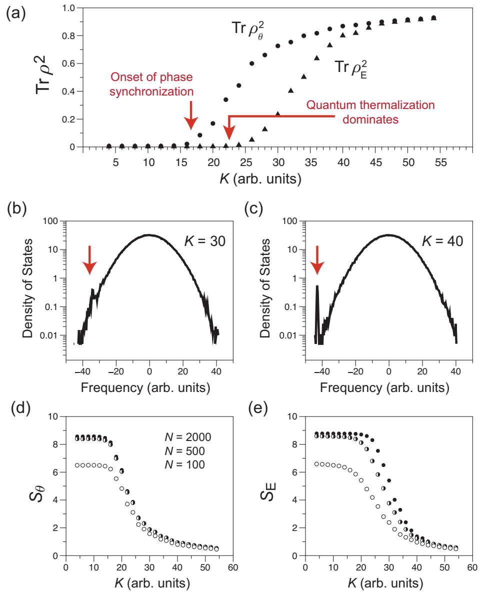


Figure 6. (a) Comparison of mixing as a function of coupling strength K for RMT$_\theta$ calculations versus RMT$_E$ calculations. (b) Density of excited states predicted by RMT$_E$ with the synchronized state indicated by an arrow. Here eigenstate thermalization mixes the synchronized state with the background density of states. (c) Same as (b), but here the synchronized state is distinguished from the background density of states. (d) Von Neumann entropies calculated from RMT$_\theta$ calculations. (e) Von Neumann entropies calculated from RMT$_E$ calculations.

The analysis of ρ_θ obtained from random matrix theory calculations based on the estimates of σ_θ for each K are compared to analysis of ρ_E in Fig. 6. It is evident that mixedness of the synchronized state in the phase-RMT, quantified by Tr ρ_θ^2 or von Neumann entropy S_θ, decreases with a similar trend to the decrease in σ_θ and increase in order parameter. These results are compared with their analogs, Tr ρ_E^2 or von Neumann entropy S_E, highlighting the trends as a function of N. The RMT$_\theta$ and RMT$_E$ calculations are in qualitative agreement because RMT$_\theta$ captures a key source of mixing in disordered systems, which is the loss of phase coherence by averaging.

The notable difference between the $K-$dependence of mixedness estimated from analysis of ρ_θ versus ρ_E, is that the onset of synchronization (rapid reduction of mixedness) happens at higher K in the energy-RMT calculations than predicted using the phase-RMT. The reason for this is that mixing in ρ_θ caused solely by phase decoherence, but mixing in ρ_E is caused by both phase decoherence and the zero-temperature regime of eigenstate 'thermalization' [31,32]. When the synchronized state is embedded in the density of other states, Fig. 6b, then the synchronized state (indicated by the arrow) mixes with the quasi-degenerate background states; by convexity of the state, any linear combination of these quasi-degenerate state is also a valid eigenstate. This source of mixing is eigenstate thermalization. It appears to be significant in the regime when $K < 2\sigma_E$. When the synchronized state is sufficiently separated from the density of other states, Fig. 6c, phase synchronization is the dominant mixing mechanism and consequently the mixing predicted by the models in the phase-RMT and energy-RMT are in close agreement.

6. Conclusion

This study considered absorption of a photon by a single disordered network in the limit of very low temperature and negligible homogenous line broadening. In other words, the single network is characterized by a fixed assignment of transition energies to the nodes and electronic coupling between the nodes. Under these ideal assumptions, if we calculate the excited states of the network by diagonalizing the Hamiltonian matrix in the usual way, the lowest energy state is going to be a pure state for any non-zero value of coupling, and a mixed state (i.e. excitation is localized on any one atom or molecule) only if the coupling is zero. This process leads to the unfortunate result that distant, very weakly coupled, near-degenerate transitions absorb collectively. The question addressed here was whether there is a fundamental reason that this seemingly unphysical result is avoided. Specifically, is there a threshold value of the coupling (other than 'non-zero') to produce collective absorption of a photon by the network? The results of the study suggest that collective absorption by (isolated) molecular exciton states does require a sufficiently large electronic coupling between molecules in the network compared to the random distribution of transition energies at the sites. The 'dividing line' between absorption to a mixture of, essentially, localized excited states and coherent excitation of a pure delocalized exciton state was suggested to be predicted by the threshold of phase synchronization.

Data Accessibility. The data are all calculated and can be reproduced using the methods described in the paper.

Competing Interests. I declare I have no competing interests.

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