Research

Cite this article: Scholes GD. 2020 Polaritons and excitons: Hamiltonian design for enhanced coherence. *Proc. R. Soc. A* **476**: 20200278.
<http://dx.doi.org/10.1098/rspa.2020.0278>

Received: 20 April 2020

Accepted: 21 September 2020

Subject Areas:

physical chemistry

Keywords:

exciton, polariton, delocalization, coherence, graph theory, synchronization

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An invited article to mark the election of the author as a fellow of the Royal Society in 2019.

Polaritons and excitons: Hamiltonian design for enhanced coherence

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The primary questions motivating this report are: Are there ways to increase coherence and delocalization of excitation among many molecules at moderate electronic coupling strength? Coherent delocalization of excitation in disordered molecular systems is studied using numerical calculations. The results are relevant to molecular excitons, polaritons, and make connections to classical phase oscillator synchronization. In particular, it is hypothesized that it is not only the magnitude of electronic coupling relative to the standard deviation of energetic disorder that decides the limits of coherence, but that the structure of the Hamiltonian—connections between sites (or molecules) made by electronic coupling—is a significant design parameter. Inspired by synchronization phenomena in analogous systems of phase oscillators, some properties of graphs that define the structure of different Hamiltonian matrices are explored. The report focuses on eigenvalues and ensemble density matrices of various structured, random matrices. Some reasons for the special delocalization properties and robustness of polaritons in the single-excitation subspace (the star graph) are discussed. The key result of this report is that, for some classes of Hamiltonian matrix structure, coherent delocalization is not easily defeated by energy disorder, even when the electronic coupling is small compared to disorder.

1. Introduction

Synchronization abounds in Nature and engineered systems [1–3]. It coerces complex systems into unified and remarkable functions. It is evident from many examples in the natural world—from the beating of a heart to plumes of flashing fireflies. At the molecular

scale, synchronization is difficult to achieve owing to stochastic fluctuations in structure and energy. Even more challenging, synchronization on the quantum scale can yield non-classical properties, but these properties predominate in fragile states that easily decompose through decoherence [4,5]. Broadly speaking, a theme underpinning recent work is the question of whether there are principles for robust synchronization that traverse the scales from macroscopic to quantum [6–12]. This report is inspired by the known robustness of systems of oscillators that are driven by a master oscillator [13], that suggests similar systems at the molecular scale might be possible, for instance, by using a cavity mode as the master oscillator [14,15]. I describe here the coherence of molecular excitons, but the approach is entirely general and can equally apply to a range of many-body systems.

At the molecular scale, the coherent superpositions of transition dipoles characteristic of molecular excitons—excited states formed by the collective delocalization of electronic excitation among two or more chromophores—have been found to show photophysical properties not achievable by molecules functioning alone [16–20]. Examples include the colour saturation of J-aggregated dyes [21–26], control of energy transfer in photosynthetic light-harvesting complexes [27–29] and singlet fission in molecular crystals [30–33]. The present study builds on reports that have asked how Hamiltonians are optimal for dynamics in multichromophoric systems [34–37].

The field of molecular excitons and their delocalization has been developing rapidly over recent years, and it has benefited from extensive feedback between theory and experiment, synthesis and measurement [38–97]. This selection of recent reports gives a sense of the ways the field is progressing. Notably, new ways of templating molecules to form excitonic systems are being developed, new experiments are being devised to detect coherent delocalization of excitons, theoretical models are now quite sophisticated and a broad range of molecular and nanoscale (Frenkel-type) excitonic systems are being studied. Some of the outstanding questions include: What is the limit of delocalization length? Are there ways to increase delocalization of excitation among many molecules at moderate electronic coupling strength? Are there ways to estimate von Neumann entropy or other coherence metrics using simple experiments? These issues will be explored in this report by studying eigenvalue distributions (i.e. density-of-states spectra) and ensemble density matrices of various structured, random matrices.

2. Loss of coherence by ensemble averaging

To set the scene and define some formalism for the next sections of this paper, consider two proximate molecules with degenerate electronic transitions. The molecules couple to each other when photoexcited [98], which produces delocalized eigenstates known as molecular exciton states [16]. Those delocalized states comprise linear combinations of site-located electronic excitations. In the case of the dimer, the symmetric and antisymmetric eigenstates are separated in energy by twice the electronic coupling.

If we include more and more molecules in this picture, concomitantly more delocalized (perfectly coherent) eigenstates are predicted for a perfect system. In reality, however, the molecules couple to an environment that produces random energy offsets to the diagonal energies in the site basis, as discussed below. This disorder leads to mixing of the pure states within the ensemble average, which breaks the delocalization—meaning coherence is reduced. The main focus of the present report is how this mixing, measured using the von Neumann entropy, depends on the structure of the Hamiltonian matrix.

The approach used here is to analyse eigenvalue distributions (i.e. density-of-states spectra) and ensemble density matrices of various structured, random matrices. This yields information about the initial photoexcited states, but not about their subsequent time evolution. The results are relevant to molecular excitons, polaritons, and I make connections to classical phase oscillator synchronization in order to motivate why the structure of the Hamiltonian matrix—or its underlying graph representation—might be interesting to study.

(a) nearest-neighbour

closely spaced states in the spectrum
 $\Rightarrow$ ensemble properties are sensitive to disorder

(b) star (polariton single excitation)

LP and UP displaced from the majority of states in the spectrum
 $\Rightarrow$ ensemble properties might be more robust to disorder

Figure 1. (a) Graph representation of the nearest-neighbour coupling model and the corresponding spectrum of eigenvalues. (b) Graph representation of the star coupling model and the corresponding spectrum of eigenvalues. Note how the spectra are quite different, motivating the hypotheses presented to the right side of the spectra. (Online version in colour.)

In particular, I examine the hypothesis that it is not only the magnitude of electronic coupling relative to the standard deviation of energetic disorder that decides the limits of coherence. I examine the possibility that the structure of the Hamiltonian—connections between sites (or molecules) made by electronic coupling—is a significant design parameter. Figure 1 summarizes the approach and motivates the main hypothesis of the report, that the ensemble average coherence (the complement to the extent of mixing evident in the density matrix) can be influenced by the Hamiltonian structure. Figure 1a shows a graph representation of the common nearest-neighbour coupling Hamiltonian. Sites are labelled $1, 2, 3, \dots, N$ and couplings between the sites are represented by a solid line. The spectrum of eigenvalues for a system with $N = 12$ and uniform coupling is shown. Figure 1b shows the star graph discussed extensively in this report. Here, each site $1, 2, 3, \dots, N$ is coupled to a central ‘master’ site, labelled c . Note how the spectrum of eigenvalues is strikingly different from that of the nearest-neighbour model.

The star graph has the same Hamiltonian matrix as that for the single-exciton subspace of the Tavis–Cummings Hamiltonian for an ensemble of atoms or molecules coupled to a cavity mode [99–103]. The spectrum is labelled accordingly, showing the lower polariton (LP) state and the upper polariton (UP) state and the remaining eigenstates (the dark states) that have eigenvalues at 0 frequency in figure 1. The UP and LP states, split off from the dark states by $\pm V\sqrt{N}$, comprise 50% amplitude of the central oscillator and superpositions of the other N states. In most of this paper, I make the star model general, and label the central site 1 or N instead of c , which means the splitting is $\pm V\sqrt{N-1}$.

The calculations reported below are averages over energy disorder in the diagonal terms of the Hamiltonian matrix, and the physical basis for this model will now be justified. In a condensed phase environment, for example, the interacting chromophores are aggregated, and each of these aggregates might comprise tens to hundreds of molecules, possibly dispersed in a solvent. The transition energies of the molecules comprising each aggregate fluctuate. The fluctuations—usually assumed to be independent for each chromophore—are caused by fluctuations of the chromophore–solvent interactions (solvatochromism) that, in turn, are due to stochastic fluctuations of the solvent molecules [104]. As a consequence, the exciton states fluctuate in energy and composition (i.e. the coefficients of each wave function fluctuate) [105,106]. A significant consequence is the loss of coherence of the exciton states so that photoexcitation localizes to a few, or only a single, chromophores. If the fluctuation amplitude (approx. equal to $(\lambda kT)^{1/2}$ where λ is the reorganization energy, k is the Boltzmann constant and T is temperature) is of the same order

as the electronic coupling, then the phases of the exciton eigenstates become randomized upon averaging, the phase that maintains exciton coherence is lost, and photoexcitation is localized on one of the chromophores.

In the present work I do not model these dynamics, though it is straightforward to extend the calculations to stochastic energy gap fluctuations. Instead, I focus on the nature of the initial photoexcited states. Their properties are well approximated by considering the distribution of frequencies that produces line broadening as a distribution of the ensemble, rather than via the stochastic fluctuations of each chromophore. Thereby, random matrix theory [107–110] can be used to calculate eigenvalue distributions that represent the spectrum of the density-of-states of the initially photoexcited ensemble of states. These same calculations yield also density matrices that are averaged over the ensemble and can be analysed to estimate the delocalization of the ensemble of states that interact with the excitation light.

The loss of phase in an ensemble with diagonal disorder is illustrated in figure 2, calculated using the methods described below. I consider here a 4×4 Hamiltonian with the mean diagonal value of zero and unit values of off-diagonal couplings according to the nearest-neighbour coupling model. This is the adjacency matrix for the corresponding graph, described later in the paper. Random offsets to the four site energies are added for each copy of the system before each matrix is diagonalized. The phase of each eigenstate, a superposition of the four basis states, is represented by a double vector. These arrows (generated by Matplotlib using quiver) show direction, not magnitude, of the coefficient in order to emphasize the phase of eigenstates. Two examples are given in figure 2a. For an eigenstate $\psi = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + c_4\phi_4$, the two arrows have directions from the origin given by $\mathbf{u} = (c_1, c_2)$ and $\mathbf{v} = (c_3, c_4)$.

There are two ways the phase of eigenstates becomes lost by averaging. The first is evident in figure 2b, by focusing on only one eigenstate (that with lowest eigenvalue for each system in the ensemble). The tight cluster of quivers that depicts the ensemble distribution of eigenstate coefficients for small disorder becomes spread out and randomized when disorder is larger than the electronic coupling. Note that this plot is merely a way to illustrate the ensemble of eigenvector coefficients, it is not a phase factor analogous to the order parameter for the classical phase oscillators discussed in the following section. The eigenstates must be orthogonal, so each ensemble retains a symmetry and does not completely randomize, as evident in figure 2c.

The second way phase is lost in the ensemble average is by the eigenvalue dispersion, which means that different eigenstates can lie in the same energy band around E , $[E, E + \varepsilon]$, where ε defines the (small) bandwidth (figure 2d). The principle of the dephasing is similar to the idea of the eigenstate thermalization hypothesis and related theories [111–114]. Note that in the left panel in figure 2d, the ordered eigenvalues, denoted by the colour scheme, are more-or-less lined up vertically, which shows the eigenvalues and hence eigenstates are similar throughout the ensemble. By contrast, there is more disorder in the eigenvalues (colours) in any vertical direction, i.e. spectral band, in the right panel in figure 2d.

Owing to the arguments presented above, it is generally understood that delocalization of excitons is limited by the ratio of electronic coupling to the standard deviation of energy disorder in the ensemble, V/σ . When $\sigma > V$, the system is more likely to be localized than delocalized. Indeed, aside from examples where electronic coupling is especially large, molecular excitons are typically found to be quite localized. It appears that V/σ imposes a frustrating limit on coherence lengths. In the remaining sections of this paper, I will discuss how this limit can be defeated by changing the way electronic coupling connects the chromophores, or, more profoundly, when the molecules are coupled to a ‘master oscillator’—the central vertex in the star graph model.

3. Methods

Real, symmetric Hamiltonian matrices are constructed corresponding to each graph. The off-diagonal elements are zero unless there is a connection from site m to n , in which case electronic coupling matrix elements $V_{nm} = V_{mn} = V$ are included. The mean diagonal matrix elements are identical, with the value being arbitrary. To account for random energy gap fluctuations,

Figure 2. (a) Double vector representation of the four-state superposition corresponding to an eigenstate of the 4×4 Hamiltonian. (b) An ensemble of eigenstates generated with different magnitude of diagonal disorder, as indicated by the ratio of electronic coupling (V) to standard deviation of disorder about a zero mean (σ). Note that the phase space (constrained by symmetry of the eigenstate) is filled as disorder increases. (c) Similar to above, but showing the phase distributions for each of the four eigenstates. (d) Plot of phases of 10 eigenstates randomly selected. Each quiver is centred on its corresponding eigenvalue. Each set of four eigenstates is indexed on the y-axis. The eigenstates, in order of eigenvalues, are coloured green, purple, red and yellow. (Online version in colour.)

as discussed above, a random offset taken from a Gaussian distribution with zero mean and standard deviation σ is added to each site energy for each copy of the system before each matrix is diagonalized. This standard approach is described elsewhere [115].

The exciton wave functions indexed by j , Ψ^j , with a basis of N single-molecule excitation states $|n\rangle = \varphi_1 \varphi_2 \dots \varphi'_n \dots \varphi_N$ (where the primed molecular wave function denotes the electronic excited state at site n), are

$$\Psi^j = \sum_{n=1}^N a_n^j |n\rangle. \quad (3.1)$$

The delocalization of excitation in an ensemble of multichromophore arrays can be quantified by the inverse participation ratio (IPR) [116], which is an effective measure for simulations where exciton wave functions are ensemble-averaged [117–119]. IPR characterizes the variance of probabilities within a wave function delocalized among N molecule-local sites. Each Ψ^j has an associated eigenvalue of ε_j .

The IPR for exciton state j , I_j , is defined in terms of the site amplitudes by

$$I_j = \sum_{n=1}^N |a_n^j|^4. \quad (3.2)$$

Note that each I_j is associated with an eigenvalue ε_j . In the calculations reported below, we use the (ε_j, I_j) tuples to determine the spectrum of $1/I_j$ for an ensemble of structurally identical molecule aggregates by plotting a histogram of I_j versus frequency. The inverse of the ensemble average IPR spectrum, $1/\langle I_j(\varepsilon_j) \rangle$, indicates the average delocalization length of the exciton ensemble in units of sites or molecules. For a linear aggregate with nearest-neighbour coupling, then the delocalization length is given by $3/(2 \times I_j)$ [116].

When reporting delocalization length for the star graph, I include in the calculation only the exterior vertices of the graph (not the central, master oscillator). The eigenstates are renormalized after removing the central, multiply connected vertex, then IPR is calculated. The idea is to measure the delocalization of the sites connected to the periphery by removing the bias from the large amplitude of the wave function at the central site. This allows comparison of the IPR to that estimated for other graphs, like the nearest-neighbour model. Essentially, we are asking, how delocalized is the wave function that is spread over the periphery because of the way the central chromophore hosts all the interactions?

Ensemble properties are estimated using simple Monte Carlo sampling. Each independent realization of an exciton is constructed by adding random energy offsets to the diagonal elements of the Hamiltonian matrix [115]. These energies are taken from a Gaussian random distribution with a specified standard deviation σ . The density-of-states spectrum is plotted as the number of eigenvalues in an energy interval $[E, E + r]$, where the resolution of the spectrum r is determined by the frequency axis range. Owing to the different ranges of the various plots presented here, the y -axis values for the density-of-states plots vary, but in all cases, the units are states per frequency interval.

Ensemble density matrix operators are defined in the molecular site basis from equation (3.1) according to

$$\rho_{mn}^j = \langle a_m^j a_n^j \rangle_M, \quad (3.3)$$

where the angle brackets indicate that an average of the density matrix is taken over M realizations of the ensemble. In this work, j denotes the index of the eigenstate according to the ordering of the corresponding eigenvalue. For instance, when the ρ_{mn} for $j=1$ is reported, the density matrix average is taken over eigenstates that correspond in each realization of the ensemble to the lowest eigenvalue, which, for the large ensembles considered here, is similar to calculating the density matrix for states in a narrow energy band $[(\varepsilon_j) - \varepsilon, (\varepsilon_j) + \varepsilon]$, where the angle brackets mean ensemble average of ε_j and the magnitude of ε depends on the variance of the disorder. In some calculations, I use the nearest integer to $j = N/2$ in order to study eigenstates associated with the middle eigenvalue of each spectrum in the ensemble. I use this method because it gives a reasonable estimate of the relevant density matrices provided the spectral bands are reasonably separated. The calculation approximately integrates over a spectral band and will yield a lower limit for the von Neumann entropy.

The phase defines the coherence of an exciton state because it locks the transition densities of molecules in the system in step and thereby causes excitation to delocalize. This phase, or coherence, is evident in off-diagonal elements of the system's density matrix. The way that ensemble averaging washes away these off-diagonal elements is illustrated in figure 3. The density matrix for the exciton state at the centre of the spectrum is plotted as a function of averaging over various numbers of manifestations of the system randomly selected from an ensemble. The first snapshot is that of a randomly selected pure state. Note how the off-diagonal contributions to the density matrix are diminished even after only a few systems are included in the average.

The loss of exciton delocalization of eigenstate j , that is, its degree of mixed character in the ensemble average [120–124], is estimated from the corresponding density matrix ρ with elements

Figure 3. The density matrix for the exciton state at the centre of the spectrum for a 12×12 Hamiltonian (nearest-neighbour coupling), $V/\sigma = 1$. The density matrix is plotted as a function of averaging over various numbers of manifestations of the system randomly selected from an ensemble. The number of systems included in the average increase from (a) to (f) as 1, 5, 10, 20, 50, 100. (Online version in colour.)

ρ_{mn} using the von Neumann entropy S_j :

$$S_j = -\text{Tr}(\rho \log_2 \rho). \quad (3.4)$$

The von Neumann entropy has a value for 0 for a pure state, and $\log_2 N$ for an ensemble density matrix that is fully mixed. Recall that the ensemble comprises N molecular aggregates that are identical except for the random site energy offsets. How the system is averaged will depend on the way it is observed, which in turn depends on the experimental approach. Here, I examine averages of eigenstates according to the energy ordering of their eigenvalues, which is emphasized by the subscript j .

Quantifying coherence, especially for the investigation of possible useful non-classical correlations in the quantum information field, has been recently pursued [125]. Relative entropy of coherence has been proposed as a rigorous measure that satisfied a set of axioms [126]. Here, I focus on comparative measures of mixing, using the von Neumann entropy, and do not attempt to elucidate non-classical correlations compared to classical correlations.

4. Coupled classical oscillators and the Kuramoto model

Synchronization of oscillator populations has been widely studied and has motivated this report by showing how synchronization is affected by the way the phase oscillators are coupled (*vide infra*). It has been found that quite rich phase behaviour is predicted by simple mathematical models, most notably the Kuramoto model [3,127–132]. It is found that relatively weak coupling K between pairs of oscillators in a large system of many phase oscillators—each with different frequency according to a Gaussian random distribution with standard deviation σ and disparate initial phase—can spontaneously synchronize when K is comparable to σ . The entrained system can be understood through models for phase oscillators, for example, by starting from the van der Pol model [132]

$$\ddot{x} + \omega_0^2 x = \mu f(x, \dot{x}), \quad (4.1)$$

where x is the oscillator coordinate, ω_0 is the oscillator frequency and μ is a parameter encompassing the nonlinearity. The problem is solved by writing equation (4.1) as a system of

coupled first-order differential equations

$$\begin{aligned}\dot{x} &= y \\ \dot{y} &= -\omega_0^2 x + \mu f(x, \dot{x}).\end{aligned}\quad (4.2)$$

Here, μ is a small parameter, and in the limit when $\mu = 0$ the system reduces to the harmonic oscillator. The time-dependent amplitude of the oscillator maps onto a point rotating around a circle of radius ρ (interpreted as the oscillator amplitude) on the (x, y) plane

$$\begin{aligned}x &= \rho \cos(\omega_0 t + \theta) \\ y &= -\rho \omega_0 \sin(\omega_0 t + \theta).\end{aligned}\quad (4.3)$$

Such that the angle θ defines the oscillator phase in the rotating frame. We can find similar solutions when $\mu \neq 0$, but small. An example is the Kuramoto model for many oscillators (N), with respective phases θ_j (in the rotating frame), pairwise coupled by a uniform coupling K . The mean-field solution turns out to be [133]

$$\dot{\theta}_i = \omega_i + \frac{K}{N} \sum_{j=1}^N \sin(\theta_j - \theta_i). \quad (4.4)$$

The coupling is a source of feedback that provides nonlinearities so that oscillators speed up and slow down during a period of motion in order to lock to the ensemble phase.

By taking the sum of the complex exponential of each phase, Kuramoto defined a complex order parameter in terms of a global phase ψ , where $r(t)$ indicates the coherence of the phases

$$r \exp(i\psi) = \frac{1}{N} \sum_{j=1}^N \exp(i\theta_j). \quad (4.5)$$

At any time t in the calculation, the order parameter $r(t)$ takes values in the closed interval $[0, 1]$. Its value indicates the degree of phase correlation in the oscillator ensemble; it is, therefore, a measure of phase oscillator ensemble coherence. Strogatz [133] describes the complex order parameter as ‘the collective rhythm produced by the whole population’.

The Kuramoto model has been employed to gain insight into a range of phenomena [134–138], and it has been studied primarily for the case of ‘all-to-all’ coupling, where the Hamiltonian matrix corresponds to a complete graph (see the following section). It has also been examined for nearest-neighbour coupling models and for driven systems [13, 139, 140], where the Hamiltonian matrix corresponds to the star graph described below. In figure 4, calculations of order parameter as a function of time are shown. The initial phase in the simulations is dispersed, indicated by the low initial order parameter, and the oscillators synchronize with time to various extents. Comparing these simulations for different Hamiltonian structures supports the idea that synchronization improves with connectivity of the coupling model [141–143].

The structure of the Kuramoto model is analogous to that of the exciton systems described above in that the system comprises N coupled oscillators competing with disorder in the frequencies of each site. In previous work [144], I have shown that this analogy provides physical insight and, in particular, the order parameter for the nearest-neighbour Hamiltonian is quantitatively comparable to the quantum-mechanical delocalization length, $1/I_j$. Synchronization of phase oscillators is not the same as delocalization of excitons, but the similarity of these two parameters is interesting—it comes from common properties of two analogous systems, not from them being the same measure, but in different guise, of one system. That is, there does not appear to be a way of obtaining the Kuramoto-type order parameter by transforming the IPR. The Kuramoto order parameter reflects a different averaging from the IPR because it relates to a complex, isolated, system of phase oscillators that has equilibrated, whereas the IPR comes averaging over snapshots of the ensemble.

Previous work has explored how the onset of synchronization of phase oscillators is influenced by the structure of the Hamiltonian matrix [141–143]—the topology of the underlying graph. That previous work motivates the next section of this paper.

Figure 4. Order parameter, equation (4.5), as a function of time for three-phase oscillator models: (a) nearest-neighbour coupling; (b) all-to-all coupling (the usual Kuramoto model), where the inset shows the final phase distribution, see (d) for details of the plot; (c) star graph (one-to-all coupling). In each case $N = 200$ oscillators, $K = 50 \text{ cm}^{-1}$, and $\sigma = 25 \text{ cm}^{-1}$. The calculations all use the same coupling, that is, it is not rescaled to make the calculations size-invariant (e.g. in the Kuramoto, all-to-all, model equation (4.4) K/N is changed to K). (d) (i) The initial phase of the oscillators for the calculation of the star graph, shown on a radial axis with radial coordinate r arbitrary and angular coordinate θ the oscillator phase (in the rotating phase). (ii) The final time step in the simulation. (Online version in colour.)

5. Hamiltonian design for coherence

Figure 2 shows a physical picture for how eigenstate phases randomize in an ensemble as a consequence of diagonal energy disorder. Electronic coupling produces an ensemble of uniform, stable delocalized eigenstates, while disorder undoes this delocalization by randomly distorting the eigenstate coefficients for each realization of the ensemble [145]. This macroscopic phase correlation in the coefficients of the eigenstates throughout the ensemble is reminiscent of the synchronization of phase oscillators, as discussed above. In classical phase oscillator systems, attractions among the oscillators introduce a nonlinearity that speeds up or slows down the oscillators to synchronize their phases, despite the distribution of the frequencies of oscillators in the system. Studies in that field suggest that, in addition to the magnitude of electronic coupling, the structure of the connections between sites that indicate couplings can have a significant effect on synchronization. In other words, the network of interactions matters. An analogous idea, but in the context of Hamiltonians for molecular excitons, is explored in this section.

By exploiting the fact that a matrix, such as a Hamiltonian matrix, can be represented as a graph [146,147], we can examine more deeply how the structure and connectivity of chromophores affect coherent delocalization of excitons. In particular, I conclude some principles for Hamiltonian design that enable the apparent limit for coherence, presented by the relative magnitude of electronic coupling compared to that of spectral line broadening (V/σ), to be overcome. Graphs are helpful, too, because they correspond physically to how chromophores may be arranged and coupled in space, as I touch on at the end of this section.

Some examples of graphs, each comprising 12 chromophores (the vertices), are shown in figure 5. Together with each graph G , I show the corresponding adjacency matrix $A(G)$ and

Figure 5. Examples of various graphs and corresponding adjacency matrices (that show the structure of the corresponding Hamiltonian). The plots show the spectra of these graphs. Graphs (c–f) were taken from [148] (available at <http://hog.grinvin.org>) and correspond to HoG graph id 36, 33088, 1024 and 32806, respectively. (Online version in colour.)

the spectrum of $A(G)$. The adjacency matrix provides the core structure for a corresponding Hamiltonian matrix by laying out the locations of off-diagonal terms, the electronic coupling matrix elements. The spectrum of $A(G)$ displays its eigenvalues—and spectral graph theory has established relationships between graph structure, properties and spectra [146,147].

It is obvious from figure 5 that different graphs have distinct spectra. What intuition do these graph spectra provide about Hamiltonian design for exciton delocalization and coherence? A first hypothesis is that dephasing of coherently delocalized states by the interplay of electronic coupling and energy disorder is affected by spacing of the eigenvalues for each system from the ensemble, figure 1. For instance, if eigenvalues are closely spaced, like in the nearest-neighbour graph B, then a narrower distribution of disorder may disrupt the phase of eigenstates because their ordering is less robust to disorder than a graph with larger spacing of the lower eigenvalues, such as any other graph shown in figure 5. This mechanism is what I described as the second way averaging destroys exciton ensemble phase, figure 2.

This hypothesis regarding eigenvalue spacing was tested by calculating ensemble density matrices for each graph, with a range of different values of the ratio V/σ , table 1. The von Neumann entropy quantifies the mixing caused by averaging over the ensemble of eigenstates with the lowest eigenvalues for each Hamiltonian structure. Comparison of these data generally supports the hypothesis. Solely on the basis of eigenvalue spacing, we would anticipate that the sensitivity of the 12-vertex graphs to disorder should decrease approximately as E (note the fivefold degenerate lowest eigenstate), D, B, C, F, A. Indeed, the calculated von Neumann entropy (table 1) for $V/\sigma = 1, 2$, decreases in the same order. When disorder is dominant, for example, $V/\sigma = 0.25$, the coherence not lost by mixing, gauged by the von Neumann entropy, is about the same for each graph.

The spread of eigenvalues of the adjacency matrix is decided by the maximum vertex degree of the corresponding graph, d . Adjacency eigenvalues lie within the range $[-d, d]$. For example, in the case of the nearest-neighbour graph, where $d = 2$, it is known that the electronic bandwidth spans up to $4V$. Different graphs can have different values of d , which, in turn, means the limit for the range of the eigenvalue spectrum is determined by how the graph is connected, not only by the magnitude of those connections (i.e. the electronic coupling V).

Table 1. Analysis of coherence for the various graphs shown in figure 5.

graph	$\lambda_2(G)$	von Neumann entropy				density matrix ($V/\sigma = 1$)
		$V/\sigma = 1/4$	$V/\sigma = 1/2$	$V/\sigma = 1$	$V/\sigma = 2$	
A	1	3.20	2.06	0.61	0.15
B	0.07	3.38	3.05	2.36	1.52
C	0.26	3.29	2.50	1.07	0.35
D	0.47	3.32	2.98	2.53	2.19
E	2	3.30	3.01	2.68	2.47
F	2	2.91	1.75	0.65	0.20

In the context of the classical model for synchronization of phase oscillators, it has been conjectured [141] that the coupling needed to synchronize an array of oscillators is inversely proportional to the smallest non-zero eigenvalue of the Laplacian matrix of the corresponding graph $L(G)$. The Laplacian matrix of a graph G is defined as

$$L(G) = D(\text{deg}) - A(G), \quad (5.1)$$

where $D(\text{deg})$ is the diagonal matrix that contains the degree of each vertex. The eigenvalues of $L(G)$ are greater than 0 and are ordered $\lambda_1 = 0 \leq \lambda_2 \leq \lambda_3 \dots$.

The smallest positive eigenvalue of $L(G)$, known as the algebraic connectivity λ_2 , indicates how well G is connected [149,150]. This is because λ_2 is related to the isoperimetric constant [151,152] of G . The isoperimetric constant is a measure of the degree of connectedness of a graph, which in turn can be related to the number of bottlenecks. Values of λ_2 for each graph are collected in table 1, and these values are seen to correlate inversely with the von Neumann entropy, more or less. That is, better graph connectivity lowers the von Neumann entropy (and thus reduces mixing). The cuboctahedral graph E appears to be an outlier, likely owing to the fivefold degeneracy of its lowest $A(G)$ eigenstate, which makes it highly susceptible to ensemble dephasing.

The star graph A is a special case—star graphs of any size N have $\lambda_2 = 1$. However, the star graph has an exceptional number of zero eigenvalues of $L(G)$, $N - 2$ in fact. The number of zero eigenvalues of $L(G)$ quantifies the number of connections in a graph and it has been used to assess robustness and synchronizability of networks [153,154].

In figure 6, the size-scalings of the von Neumann entropy for four selected graph types, with $V/\sigma = 1$, are plotted. The λ_2 values of four graphs of similar size are indicated together with representative $L(G)$ and $A(G)$ spectra. In figure 6b, the upper limit for von Neumann entropy of a fully mixed state is shown by the dashed line. The classical information scales linearly with the x -axis scale given by $\log_2 N$, which indicates the maximum classical information that can be encoded in each size system.

The highly connected circulant graphs are clearly more robust to size and disorder than the nearest-neighbour and cuboctahedral graphs. That observation is consistent with the eigenvalue structure of the corresponding $A(G)$ spectra. The star graph is extraordinary—it becomes more robust as N increases, despite the entropic penalty (see [144] for a discussion of entropic limits on delocalization). This property of star graphs is discussed elsewhere [155]. A key factor in the stability of the lowest (and highest) eigenstates of the star graph is given by a property of the arrowhead matrix [156]; the lowest and highest eigenvalues are split off from the other $N - 2$ zero-valued eigenvalues, and that splitting scales as $\sqrt{N}$. That fact is exploited in polariton systems.

The influence of disorder is more closely examined by comparing nearest-neighbour, star and circulant graphs for two different size systems ($N = 17, 85$), figure 7. Here $V/\sigma = 1$. All plots show the von Neumann entropy associated with the ensemble of states with the lowest eigenvalue for each system in the ensemble (i.e. Ψ_1 when the eigenstates are ordered by eigenvalue) and the delocalization length predicted by the IPR. For the star graphs, those quantities are also listed for the ensemble of eigenstates $\Psi_{\text{int}(N/2)}$, where int means closest integer value. For the plots with $N = 85$, the order parameter obtained from the Kuramoto model of corresponding (classical) phase oscillators is listed, as is the Laplacian matrix eigenvalue λ_2 .

These data support the conjectures proposed earlier in this report. It is apparent that connectivity (indicated by large relative values of λ_2) is important, but it is especially significant for robust synchronization in the Kuramoto model. The most important consideration for maximizing coherent delocalization of excitons by suppressing mixing (minimizing the von Neumann entropy) is the separation of the eigenvalue of the lowest eigenstate (Ψ_1) from the next closest eigenstates. This is the reason that the von Neumann entropy of the circulant graph $N = 85$ is higher than that of the star graph, despite the better connectivity and higher order parameter—the lowest eigenstate of the circulant graph is doubly degenerate.

Figure 6. Coherence properties of graphs. (a,b) Size-scaling of the von Neumann entropy of four selected graph types, with $V/\sigma = 1$. Here, the cuboctahedral graphs are, from [148] (available at <http://hog.grinvin.org>), HoG graph id 1024 ($N = 12$), 1319 ($N = 24$) and 1124 ($N = 48$). The circulant graphs are, from [148], HoG graph id 32806 ($N = 12$), 30395 ($N = 17$), 26998 ($N = 61$), 27002 ($N = 85$) and 27000 ($N = 103$). (c) The Laplacian matrix $L(G)$ spectra and (d) adjacency matrix $A(G)$ spectra for three graphs. The nearest-neighbour graph has $N = 48$. The cuboctahedral graph ([148] HoG graph id = 1124) is $N = 48$. The circulant graph ([148] HoG graph id = 26998) is $N = 61$. (Online version in colour.)

The reduction in von Neumann entropy of the ensemble of lowest eigenstates of the star graph as N increases is remarkable. For context, in a recent paper [144] I pointed out, for a system with nearest-neighbour coupling, how energy lowering of the lowest eigenstate becomes successively smaller as the size of the system (N) increases. I then pointed out that the entropy of delocalization in a 1000-molecule system must, therefore, be an important consideration. Specifically, there is only one way to perfectly delocalize the exciton, but there are 901! ways of delocalizing the exciton over 100 molecules in that aggregate and of those, approximately 990 involve delocalization over 100 consecutive molecules. Given that the energy difference between the lowest eigenstate of the 1000-molecule systems and a 100-molecule system is very small, I suggested that the entropy of mid-sized delocalization within a large molecular aggregate must predominate and limit delocalization length, even at low temperature.

In the case of the star graph system, the key difference is that the lowest eigenstate energy is lowered as N increases (recall the lowest eigenvalue is $V\sqrt{(N+1)}$), which protects the lowest energy eigenstate by separating it from the manifold of dark states. This enables incredible delocalization of the polariton state, at least for photoexcitation. The large entropy difference between the LP state and the dark states is likely an important consideration for the mechanism of

Figure 7. Comparison of the density of states and coherence metrics for nearest-neighbour, star and circulant graphs for two different size systems. See figure 6 for details of the graphs. (Online version in colour.)

Figure 8. Comparison of the density of states for three star graphs (i.e. single-excitation polariton manifolds) with different sizes, $N = 50, 100$ and 500 . Note that as N increases, the UP and LP bands split further apart and the density of dark states increases. In these calculations, $V = \sigma = 25 \text{ cm}^{-1}$. (Online version in colour.)

relaxation dynamics after photoexcitation, as proposed elsewhere [155]. The splitting of the lower exciton state from the manifold of dark states as a function of N is shown in figure 8.

As noted earlier, adjacency eigenvalues lie in the range $[-d, d]$, meaning the energy of the lowest eigenvalue is bounded by Vd . In the case of a system with nearest-neighbour coupling, d is a constant ($d = 2$), so as N increases, the lowest eigenstate ψ_1 is asymptotically lowered in

energy and the density of states close to it increases. Whereas, for the star graph $d = N - 1$, so the lower bound for Ψ_1 is lowered with N and the density of states increases around zero eigenvalue (known as the ‘dark states’)—well separated, for large N by approximately $V\sqrt{N}$, from Ψ_1 . This is evident in figure 7, note the very low von Neumann entropy of the ensemble of Ψ_1 compared to a value close to a fully mixed state for the dark states at zero eigenvalue.

How might these graphs be translated into the design of molecular exciton systems? The main challenge is to achieve sufficiently strong interchromophore electronic couplings. The graphs inform how to connect molecules. Obviously, some are impractical, like the complete graph, but others are feasible, like the cuboctahedral graphs, requiring a network of molecules each connected to four others. As discussed below, the star graph is realized in systems where a cavity promotes strong light–matter coupling. In the entirely molecular setting, however, there may be ways of producing star networks by, for example, linking many molecular chromophores to a single nanoscale system like a carbon nanotube.

6. Multi-excitation states and delocalization estimates

So far in this report, I have discussed single-excitation states and their delocalization. One of the experimental challenges in the field is to work out effective ways of measuring delocalization. Spectroscopic methods typically involve comparing one-excitation and two-excitation states using pump–probe spectroscopy [119,157–159] or comparing vibronic transitions [160–162] in the single-excitation manifold. Other methods include various interferometric approaches [38,49,163,164]. Here, I examine multi-excitation manifolds of the star graph, which are relevant to the rapidly emerging area of strong light–matter coupling in molecular systems [101,102,165–175].

The ultrafast dynamics and nonlinear spectroscopy of molecular polaritons have been studied quite widely [176–184]. Multi-exciton states in the Tavis–Cummings model [99,100] for polaritons are well known and such states for molecular systems have recently been studied by a combination of theory and experiment [184]. Polariton multi-excitation states can be photoexcited only indirectly from the ground state, by pump–probe techniques, multiphoton absorption or nonlinear spectroscopy. By leveraging the special structure of star-graph spectra, can we discover ways that these manifolds provide internal references enabling information about coherence to be extracted?

The Hamiltonian matrices for one-excitation, two-excitation and three-excitation systems building on the one-excitation star graph (collectively, the Tavis–Cummings model for polaritons) are given in appendix A in the electronic supplementary material. Note that the graph changes with excitation number, in particular, the vertex connectivity changes. In addition, the size of the (finite) vector space changes according to the binomial theorem, from dimension 7 in the single-excitation system, to dimension 22 in the two-excitation system, to dimension 42 in the three-excitation system. It is, therefore, anticipated that there will be entropic differences between these spaces.

In figure 9, the density of states spectra of the lowest multi-excitation manifolds of the 6-molecule system are plotted. The absorption spectra from the ground state are overlaid for the single-excitation case. The absorption bands are calculated by using the standard method described in [115], where each molecule has an identical and oriented transition dipole. In addition to those one-photon allowed transitions from the ground state, transitions are possible between manifolds. For instance, in recent work [184], we identified strong optical transitions from the single-excitation polariton bands to two-excitation bands.

Analyses of the data from figure 9 are summarized in table 2. The number of configurations in the vector space scales steeply with excitation state, meaning the maximum classical information and, therefore, von Neumann entropy is higher in the eigenstate ensembles of the multi-excitation subspaces than those of the single-excitation subspace. For the parameters used in these calculations, the dark states have approximately 80% of the von Neumann entropy value that is predicted to be the maximum, while the von Neumann entropy is considerably lower in

Figure 9. Comparison of the density of states spectra for multi-excitation states of the star graph (polariton) with $N = 6$. The spectra of transition dipole allowed one-photon transitions from the ground state are overlaid in red. In these calculations, $V = 100 \text{ cm}^{-1}$ and $\sigma = 50 \text{ cm}^{-1}$. (Online version in colour.)

Table 2. von Neumann entropies (bits) from data plotted in figure 9.

	configurations	S_{class}^a	$S(\lambda_1), \sigma_1^b$	$S(\lambda_d), \sigma_d$	$S(\lambda_1)/S_{\text{class}}$	$S(\lambda_d)/S_{\text{class}}$
1-excitation	7	2.81	0.19 (5.3)	2.36 (23)	0.068	0.84
2-excitation	22	4.46	0.31 (6.3)	3.43 (27)	0.070	0.77
3-excitation	42	5.39	0.39 (5.2)	3.93 (24)	0.072	0.73

^aMaximum classical entropy ($\log_2 N$), where N is the total number configurations.

^bStandard deviation of a Gaussian fit to the density-of-states lineshape.

the LP band (denoted λ_1). Notably, the von Neumann entropy for λ_1 increases as the number of excitations in the subspace increases.

It is well known that any effect (in this case coherent exciton delocalization) that allows a system to average over configurations of energy disorder on a timescale faster than the measurement of the lineshape will narrow the absorption lineshape [185]—a phenomenon often exploited in magnetic resonance spectroscopy. Intuitively, the spectral linewidth narrowing with energy disorder is consistent with the diminished von Neumann entropy. In an early theoretical study of the lineshapes in absorption spectra of molecular aggregates, Knapp [186] predicted the ratio of linewidths of a linear or cyclic aggregate compared to a monomer spectrum linewidth to be

$$\left(\frac{\sigma_{\text{aggregate}}}{\sigma_{\text{monomer}}} \right) = \frac{1}{\sqrt{N}}. \quad (6.1)$$

Here I hypothesize that the structure of the star graph spectrum enables a way to measure delocalization by comparing the lineshape of the LP band, specifically its standard deviation σ_1 , with that of the dark state, σ_d . The dark state band could be that of the single-excitation manifold (if it can be measured), but the dark state of the two-excitation manifold is likely more convenient, and it can be detected using transient absorption spectroscopy [184]. It turns out that the value of σ_d for the parameters studied here is equivalent to the standard deviation of disorder, σ , input into the calculation.

Calculations were performed for star graph (polariton) Hamiltonians in the single-excitation subspace for a range of the number of molecules N and various values of electronic coupling V and standard deviations of disorder, σ . For each calculation, the LP (λ_1) lineshape in the density-of-states spectrum was fitted to a Gaussian lineshape to estimate the standard deviation σ_1 . A typical fitting is shown in figure 10*a*. In addition, the von Neumann entropies of λ_1 and the dark states were calculated. I label these entropies S_1 and S_d , respectively. It was confirmed that the results of the analysis below depend only on the relative values of V and σ , so that, for example, $V = 50 \text{ cm}^{-1}$ and $\sigma = 25 \text{ cm}^{-1}$ give identical results to $V = 100 \text{ cm}^{-1}$ and $\sigma = 50 \text{ cm}^{-1}$.

Knapp's prediction [186] for an idealized system suggests that the ratio of the spectra line widths can be used to estimate the coherent delocalization length of the excitation. In the calculations reported here, the LP band is completely delocalized over all N molecules (as

Figure 10. (a) Zoomed-in view of the LP (λ_1) band in a spectrum (blue dots), with the fitted Gaussian overlaid (pink solid line). (b) Plots of linewidth ratios versus N for various parameters. (c) Plots of von Neumann entropy ratios versus N for various parameters. (d) Empirically rescaled plots of von Neumann entropy ratios versus N . In these calculations, the values of V and σ are indicated on each plot and by the marker shapes. (Online version in colour.)

established earlier in this report); therefore, I examine the relation $(\sigma_d/\sigma_1)^2 \approx aN$. The applicability of this relationship is strikingly evident in the trend of the data from all sets of calculations, plotted in figure 10b. The fit of the representative dataset where $V=50 \text{ cm}^{-1}$ and $\sigma=25 \text{ cm}^{-1}$ yields $a=3.8$. There is an important difference between the system studied here, the star graph, and that examined by Knapp—that is, the coupling for the star graph scales with N , being effectively $V\sqrt{N}$, for large N , which likely contributes to the steep scaling law that is observed.

To compare with the line shape analysis, the ratio of von Neumann entropies S_d/S_1 is plotted in figure 10c. The green line is the fitted line representative of the linewidth data shown in figure 10b. These data also scale linearly with N , but the gradient of each plot depends on the V and σ parameters. For $V/2\sigma < 1$, the gradient of the S_d/S_1 plot is lower than that of the linewidth ratio plots, then the gradient becomes greater than that of the linewidth ratio plots when V is more significantly greater than σ . Indeed, a remarkable empirical relationship is evident; all the S_d/S_1 plots overlay, figure 10d, when each dataset is multiplied by its corresponding $(\sigma/V)^2$. Fitting of these data indicates the empirical trend

$$\left(\frac{S_d}{S_1}\right) \approx 0.8N \left(\frac{V}{\sigma}\right)^2. \quad (6.2)$$

A qualitative explanation for this relationship is offered below. Equation (6.2) might inspire a way of estimating the von Neumann entropy of the delocalized LP state if the line broadening is dominated by inhomogeneous broadening.

An important caveat for these results is they pertain to inhomogeneously broadened lines, so the relationships will be compromised by homogeneous line broadening in molecular, condensed phase, systems. Nevertheless, it appears that the dark states of the polariton spectra provide a convenient internal reference of a strongly mixed state that can be compared to the delocalized LP band using, for instance, nonlinear spectroscopy, to estimate a bound on delocalization length or mixing. The relationships can be tested for systems where inhomogeneous line broadening dominates homogeneous line broadening.

Figure 11. (a) Some representative characteristic polynomials for the matrix of the nearest-neighbour graph with $N = 4$ and diagonal disorder, $V = 1, \sigma = 0.1$. (b) The same, but with $V = 1, \sigma = 0.5$. (c) Some representative characteristic polynomials for the matrix of the star graph with $N = 8$ and diagonal disorder, $V = 1, \sigma = 0.2$. (d) The same, but with $V = 1, \sigma = 0.5$. (Online version in colour.)

7. Comparison of random polynomials

A lot of information can be gathered by studying distributions of eigenvalues from random matrices. Are there additional insights embedded in the matrix determinants that yield those eigenvalues? This can be achieved by studying appropriate random polynomials [187]. As a reminder, the eigenvalues t of a matrix $\mathbf{A}$ can be found using the relation

$$\det(\mathbf{A} - t\mathbf{I}) = 0, \quad (7.1)$$

where $\det$ means determinant and $\mathbf{I}$ is the unit matrix. Equation (7.1) shows that the eigenvalues are the roots of a characteristic polynomial, and I hypothesize that studying those characteristic polynomials for the pseudo-random matrices that predict the density-of-states spectra gives some insight into the different ways that electronic coupling and disorder interplay.

For example, representative characteristic polynomials for the nearest-neighbour graph with $N=4$ are shown in figure 11*a,b*, with parameters $V=1$, $\sigma=0.1$ and $\sigma=0.5$ (arb. units), respectively. Note that when σ is small compared to V , the four eigenvalues of the ensemble are decided by the zeros of a reasonably tight distribution of quadratic functions, figure 11*a*. However, when σ takes even moderate values, figure 11*b*, there is considerable disorder in the polynomials and consequently their roots (the eigenvalues). As expected from the discussions above, the nearest-neighbour graph is sensitive to the ratio V/σ .

Studying the star graph in more detail, the characteristic polynomials for the general matrix equation (7.2) can be found, where the electronic couplings are labelled by column or row to show

the result more clearly. In the calculations $V_2 = V_3 = \dots V_N = V$. Random offsets to the diagonal energies are labelled $a_1, a_2, \dots, a_N$:

$$\begin{vmatrix} a_1 - t & V_2 & V_3 & \dots & V_N \\ V_2 & a_2 - t & & & 0 \\ V_3 & & a_3 - t & & \\ \vdots & 0 & & \ddots & \\ V_N & & & & a_N - t \end{vmatrix} = 0. \quad (7.2a)$$

That is,

$$(a_1 - t)(a_2 - t) \dots (a_N - t) - V_2^2(a_3 - t)(a_4 - t) \dots (a_N - t) - (a_2 - t)V_3^2(a_4 - t) \dots (a_N - t) - \dots - (a_2 - t)(a_3 - t) \dots (a_{N-1} - t)V_N^2 = 0. \quad (7.2b)$$

If all random energy offsets are set to zero, the characteristic polynomial simplifies to $t^{(N-2)}(t^2 - V^2(N-1))$, which has roots at $t=0, \pm V\sqrt{N-1}$, as expected. Note that this analysis includes the central vertex in the count of N molecules. In a polariton system, that vertex would represent the radiation field and we may choose to exclude it from N . In that case, too, we would set $a_1 = 0$. Note that in equation (7.2b), aside from the terms from the first line, the coefficients of the other terms of the polynomial comprise the product of V^2 and products random energy offsets. This structure of the polynomial probably yields the $(V/\sigma)^2$ scaling factor discovered in the analysis of figure 10c,d.

The characteristic polynomials for the star graphs, figure 11c, show a special structure, that reflects the spectrum of eigenvalues. The region around 0 closely approaches 0 and is affected by the higher order terms in t in equation (7.2b)—it is also easily influenced by disorder. The UP and LP eigenvalues are each pinned in a tight cluster by the steep gradient of the polynomial. It is evident that that these polynomials are more robust to disorder than the corresponding nearest-neighbour characteristic polynomials, e.g. compare figure 11b with figure 11d. These qualitative observations can likely be quantified in a general setting by analysing distributions of distances between eigenvalues for matrices corresponding to different graphs. Theorems regarding the lower bounds on polynomial root separation are well studied [188]. The present topic would benefit from studies of distributions of separations of the root with lowest eigenvalue from the other roots.

8. Conclusions

The central question investigated in this report was: Are there ways to increase delocalization of excitation among many molecules at moderate electronic coupling strength? From past work, there appears to be a frustrating limit to delocalization that stems from the simple ratio of electronic coupling to disorder (or, more generally, line broadening). Inspired by studies of synchronization in systems of phase oscillators and results from spectral graph theory, it was found that the structure of the Hamiltonian for molecular exciton systems—connections between sites (or molecules) made by electronic coupling—is a significant design parameter that can overcome the V/σ limit imposed on systems described by nearest-neighbour Hamiltonians. An important property of robust Hamiltonian structures is large energy separation of the lowest eigenstate from the next higher-lying states. The star graph—the Hamiltonian structure of the one-excitation polariton subspace—has special delocalization properties and robustness. Thus, there appear to be ways to defeat entropy, at least for the light-absorbing states, in particular by using the property of the star graph where the effective electronic coupling increases with the size of the system. It seems likely that molecules in a Fabry–Perot cavity can interact coherently with radiation on length scales corresponding to many hundreds of thousands of molecules. This leads to a key result of this report: for some classes of Hamiltonian matrix structure, coherent delocalization is not easily defeated by energy disorder, even when the electronic coupling is

small compared to disorder (i.e. $V/\sigma < 1$)—a result in contrast with current expectations in the field.

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.

Funding. Financial support was provided jointly by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, of the US Department of Energy through grant no. DE-SC0015429 and the W. M. Keck Foundation through award no. 1005586.

Acknowledgements. I thank Prof. D. Beratan for discussion and many helpful suggestions. Gregory Scholes is a CIFAR Fellow in the Bio-Inspired Energy Program.

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