Functional advantages offered by many-body coherences in biochemical systems

F. J. Gómez-Ruiz,1,∗ O. L. Acevedo,2 F. J. Rodríguez,1 L. Quiroga,1 and N. F. Johnson3

1Departamento de Física, Universidad de los Andes, A.A. 4976, Bogotá D. C., Colombia
2JILA, University of Colorado, Boulder, CO 80309, U.S.A.
3Department of Physics, University of Miami, Coral Gables, FL 33124, U.S.A.

(Dated: August 14, 2017)

Quantum coherence phenomena driven by electronic-vibrational (vibronic) interactions, are being reported in many pulse (e.g. laser) driven chemical and biophysical systems. But what systems-level advantage(s) do such many-body coherences offer to future technologies? We address this question for pulsed systems of general size \( N \), akin to the LHCII aggregates found in green plants. We show that external pulses generate vibronic states containing particular multipartite entanglements, and that such collective vibronic states increase the excitonic transfer efficiency. The strength of these many-body coherences and their robustness to decoherence, increase with aggregate size \( N \) and do not require strong electronic-vibrational coupling. The implications for energy and information transport are discussed.

Many of the remarkably strong coherence phenomena that have been observed recently in pulse (e.g. laser) driven chemical and biophysical samples, appear to involve some form of quantum mechanical interference between the system’s electronic and vibrational components [1–31]. The outstanding question raised [1, 2] that we address here, is: What functional advantages do such collective coherences offer for future optoelectronic energy/information processing? While our intention is not to address the longer timescale mechanisms driving natural photosynthesis in hot, wet environments [32], we stress Kenrow et al.’s point [33] that a deeper understanding of the temporal quantum evolution in systems of general size \( N \) – as offered here – can shed new light on the early-time kinetics in real-world open systems, since this timescale is too short to couple in many of the complex degrees of freedom that will naturally exist. Most previous works examining the dynamics of quantum coherent phenomena in biochemical aggregates, produce results that are not easily scalable to the large numbers of components present in a real sample or device, and average over or truncate memory effects. For example, Ref. [7] looks at excitonic transfer in a single dimer \( N = 1 \) within a single LHCII monomer: however it is the LHCII trimer (Fig. 1(a), \( N = 3 \)) and even higher-order aggregate forms \((N > 3)\) that are naturally abundant (e.g. in green plants) [34–36].

Here we evaluate the real-time evolution of a pulse-driven system of general size \( N \), akin to LHCII aggregates found in green plants, focusing on the most naturally-abundant case: the trimer (Fig. 1(a)) [34]. We find that pulses tend to generate many-body coherences comprising particular multipartite entanglement (W-states for \( N = 3 \)), and that such vibronic states increase the collective excitonic transfer efficiency. The strength of these many-body coherences and their robustness to decoherence are both predicted to increase with \( N \). In addition

![FIG. 1. (Color online) (a) LHCII trimer in green plants (width ∼ 50Å) comprising three LHCII monomers (Γ = 1, 2, 3), adapted from Ref. [34]. Each chlorophyll is a central magnesium atom (gray) and two nitrogen atoms [34]. Green (blue) is the Chla (Chlb) nitrogen. Chlorophylls are packed together into this congested ∼ 50Å sized space. Any pair could in principle act as a dimer. Chl\(_{601}\)-Chl\(_{602}\) dimers are indicated (red ellipses). (b) Many dimers have their two excitonic levels in near-resonance with one of the background vibrational modes. The hybridized exciton energy-level splitting within the Chl\(_{601}\)-Chl\(_{602}\) dimers is \( \epsilon \approx 667\text{cm}^{-1} \), and there is a vibrational mode \( \omega_{\text{vib}} = 742\text{cm}^{-1} \) [7]. The wave-function for the higher dimer state \( |X_T\rangle \) is more localized on the chlorophyll with higher energy, and the lower dimer state \( |Y_T\rangle \) is more localized on the chlorophyll with lower energy, hence a transition \( |X_T\rangle \rightarrow |Y_T\rangle \) represents excitonic energy transfer from one chlorophyll to the other.]

* fj.gomez34@uniandes.edu.co
to their implications for device design, our results connect to the broader interest established by Thilagam in generating W states in such systems, which belong to the group characterized by two distinct Majorana spinors [1].

We avoid typical approximations of small N, linear response and truncated memory effects in the following way. Any incident electromagnetic (light) field $\vec{E}(t)$ generates an internal polarization field $\vec{P}(\vec{r}, t)$ within the material, given exactly by Maxwell’s Equations [37, 38] (see Supplemental Material (SM)). Though nonlinear and anisotropic in general, the presence of $\partial^2/\partial t^2$ terms for both materials that a pulse in $\vec{E}$ will generate a similar pulse in $\vec{P}$, and hence a pulse in the internal electric field dynamics coupling the electronic and vibrational systems [37, 38]. Since we are not focusing on single-photon phenomena, a similar conclusion follows from a quantum-mechanical starting point (see SM and Refs. [39, 40]). This therefore motivates (see SM) a Dicke-like Hamiltonian with time-dependent electronic-vibrational coupling $\lambda(t)$, which we then integrate exactly numerically:

$$H_N(t) = \sum_{\beta} \omega_{\beta} a_{\beta}^\dagger a_{\beta} + \sum_{i=1}^{N} \sum_{\alpha_1, \alpha_2} \frac{\epsilon_{\alpha_1, \alpha_2}}{2} \sigma_{x, \alpha_i}^{\beta}(t) (a_{\beta}^\dagger + a_{\beta}) \sigma_{x, \alpha_i}^{\beta},$$

(1)

where $N$ is the number of components that respond to the pulse. Components that remain inert on such short timescales, do not need to be included. $\sigma_{x, \alpha_i}^{\beta}$ denotes the two-level Pauli operators for excitation $\alpha_i$ on each component (e.g. dimer) $i$ with $p = x, z$. The vibrational modes $\{\beta\}$ may or may not be localized, and can include relative modes [15]. Though Eq. (1) sacrifices chemical details, it allows us to explore the rich spectrum of collective vibrionic dynamics. Under the resonant conditions considered here, an $\epsilon = \omega$ pair can be retained and entangled states generated as a result of the speed of changes in $\lambda(t)$ without needing to access the strong-coupling regime [39, 41] (see SM). Many variants of Eq. (1) will give similar results due to an established universal dynamical scaling [41] and the fact that they typically generate similar types of phase diagrams and hence have similar collective states in the static $\lambda$ limit [42–45].

Figure 1(b) shows an implementation of Eq. (1) for the most abundant LHCII complex, the trimer [34] (Fig. 1(a)). Among the many possible dimer choices, many have excitonic energy-level splittings near-resonant with one of the system’s vibrational modes. The Chl$_{6001}$-Chl$_{6002}$ dimer is of greatest interest since it contributes to the fastest component of the Chl$_{6001}$-Chl$_{6002}$ interband transfer pathway that directs excitation energy towards exit sites [7, 18]. Within each dimer, there are two hybridized excitonic states $|X_T\rangle$ (higher excitonic energy state) and $|Y_T\rangle$ (lower excitonic energy state). As in a simple asymmetric double-well system, the wavefunction for the higher dimer state $|X_T\rangle$ is more localized on the chlorophyll with higher energy, and the lower dimer state $|Y_T\rangle$ is more localized on the chlorophyll with lower energy, hence a transition $|X_T\rangle \rightarrow |Y_T\rangle$ represents a spatial transfer of exciton energy from one chlorophyll to another [7]. Importantly for light-harvesting, the $|Y_T\rangle$ wavefunction is localized on the chlorophyll nearest to an energy exit site. We find (Figs. 2–3) that the excitonic transfer process can be significantly enhanced by many-body quantum coherence phenomena in two ways:

**Functional advantage 1**: Figures 2(a/b) consider the trimer starting at $t = 0$ in an excited eigenstate of Eq. (1) ($\lambda(0) = 0$) given by $W_2 = 3^{-1/2} (|X_1, X_2, Y_3\rangle + |X_1, Y_2, X_3\rangle + |Y_1, X_2, X_3\rangle) \equiv |3/2, 1/2\rangle$ where $|J, M_J\rangle$ is the angular momentum basis of Eq. (1). With high probability ($\sim 0.5$), a moderate-duration pulse (i.e. intermediate $\nu$ shown shaded) generates a non-local quantum-mechanical transfer of two excitons between chlorophylls across the trimer, ending in $|Y_1, Y_2, Y_3\rangle \equiv |3/2, -3/2\rangle$. A single dimer ($N = 1$) starting in state $|X\rangle$, would produce a final state $|Y\rangle$ with probability $\sim 0.5$, in line with simple arguments based on Rabi oscillations in a two-level system and Ref. [7]; hence for three independent dimers in the same two-excitation initial state (e.g. $|X_1\rangle|X_2\rangle|Y_3\rangle$), the corresponding probability of ending in $|Y_1\rangle|Y_2\rangle|Y_3\rangle$ is $\sim (0.5)^3 = 0.125$. Therefore the functional
advantage of the many-body quantum coherence is that it is approximately four times as efficient at transferring the excitons to chlorophylls that are closest to the exit points (i.e. to \{Y_{1}\}), and it does so non-locally across the trimer.

**Functional advantage 2:** Figure 2(c) considers the more general case of initial eigenstate \(|Z_1, Z_2, Z_3\rangle = \left|\frac{3}{2}, -\frac{3}{2}\right\rangle\), which is the \(t = 0\) ‘ground’ state of Eq. (1) \((\lambda(0) = 0)\) comprising the lower states \(\{|Z\rangle\}\) in any three near-resonant dimers in Fig. 1(a). We stress that this ‘ground’ state is simply the lower dimer state, and hence can still be regarded as containing an exciton in each \(|Z\rangle\). After a single up-down pulse of moderate duration (i.e. intermediate \(\upsilon\)), the final state is dominated by \(W\)-states which feature high entanglement between the electronic and vibrational subsystems and comprise excitations delocalized across the trimer. The remaining weight resides essentially in the initial ground state. The dominant excited state is \(W_2\) (probability \(\sim 0.5\)) which coincides with the initial state considered in Figs. 2(a)(b) and contains two dimer excitations on \(\{|X\rangle\}\). This is followed by \(W_1\) which contains one dimer excitation on \(\{|X\rangle\}\). Hence the functional advantage that the many-body quantum coherence offers in this situation, as compared to three independent \((N = 1)\) dimers, is that multiple excitations can be simultaneously generated with far higher probability and maximally delocalized across the trimer.

Irrespective of whether biophysical systems naturally use these advantages or not, they can be exploited in future designs for energy and information processing [41, 46–59] – in particular, given the natural abundance of ready-made aggregates [34–36]. By changing the choice of dimer in Fig. 1(a), and hence the definition of lower and upper state and thus on which chromophores the excitations primarily lie, the combination of Functional Advantages 1 and 2 in principle enables multiple highly-entangled excitations to be generated by individual pulses, transferred quantum mechanically between chromophore pairs across the trimer, and reach the chromophores closest to exit sites, e.g. ‘uphill and downhill’ \(|\{Z\}\rangle \rightarrow |\{X\}\rangle \rightarrow |\{Y\}\rangle\) which exploits Functional Advantage 2 then once \((|X\rangle \rightarrow |Y\rangle = |X\rangle \rightarrow |Y\rangle\) which exploits Functional Advantage 1 twice, or any combination or subset of these. These coherence-driven functional advantages occur without the need for energy relaxation process to drive the direction of energy flow, hence the total wavefunction remains in a pure quantum state, and do not require strong electronic-vibrational coupling.

The excitations in these highly non-classical, delocalized, non-separable \(W\) states show an intrinsic robustness: if quantum coherence with one of the three dimers is lost, the state of the remaining two dimers remains entangled. Though we take \(\lambda(t)\) to be a piecewise linear up-down ramping of duration \(\upsilon^{-1}\) (i.e. the inverse ramping velocity), similar results occur for other up-down forms since the dense entanglement regime at intermediate \(\upsilon\) is generated by path interference as a result of two crossings of the quantum critical point \(\lambda_c = 0.5\) [54, 55, 60]. In particular, the shaded forms in Fig. 2(c) can be understood by averaging over the quantum oscillations generated by the up-and-down path interference in a simple two-level Landau-Zener-Stuckelberg picture: the average probability that the system ends up in the excited state manifold is \(P_e = 2P(1 - P)\), where \(P = \exp(-2\pi\Delta^2/4\upsilon)\) and \(\Delta\) is the minimum effective two-level energy gap during the pulse. Approximating \(\Delta \sim \lambda_c = 0.5\), this predicts that \(P_e\) increases monotonically as \(\upsilon\) increases from the adiabatic regime, before falling off as \(\log_2(\upsilon)\) to 0, exactly as seen in Fig. 2(c) (and also Fig. 3(a)(b)). Figures 3(a)(c) confirm that these functional advantages (Fig. 2) exploit the electronic-vibrational entanglement – and hence non-classical features of both the electronic and vibrational systems. Figure 3(b) illustrates how the many-body quantum enhancement increases in strength (darker green represents larger von Neumann entropy \(S_N\)) and occurs over a wider range of pulse durations \((\upsilon^{-1})\) as \(N\) increases (i.e. for larger aggregates).


FIG. 4. (color online) Evidence of the robustness to decoherence/losses of the many-body electronic-vibrational coherence (i.e. entanglement, witnessed by quantum logarithmic negativity) generated for two representative intermediate up-and-down pulse durations (i.e. different $v$ in left and right panels). Results shown for $N = 5$ (dashed lines) and $N = 11$ (solid lines), and various values of decoherence $\kappa$. As decoherence increases, the differences between the curves for different $N$ tend to become smaller: this hints at a possible universality in robustness with increasing $\kappa$. Inset: largest $\kappa$ value and different $v$. Increasing temperature (and hence $(n_t)$) shows broadly similar tendencies to increasing $\kappa$.

Each $N > 3$, the final states are dominated by increasingly higher entangled $N > 3$ equivalents of $W$ states (i.e. Functional Advantage 2) which can then be exploited for efficient transfer (i.e. Functional Advantage 1). Given the naturally-occurring availability of $N > 3$ aggregates [34–36], this increase in functional enhancement with increasing $N$ may inspire new device designs. The lower bound $v_{\text{min}}$ does not depend on the maximum value of $\lambda(t)$ reached. The scaling $v_{\text{min}} \propto N^{-1}$ that emerges, comes from a relation for the minimal energy gap at the critical threshold [55]. The upper bound $v_{\text{max}}$ does not depend on system size, and is instead dictated by the $\log_2(v) \rightarrow 0$ drop-off of $P^c$. Figure 3(c) confirms that the coherence is fundamentally non-classical. Purely quantum features appear in the Wigner functions of both the vibrational and electronic subsystems (e.g. negative values shown as red). Though our results consider ramping up to the modest value of $\lambda(t) \approx 1$ and back, similar results occur for smaller maximum values and hence weaker pulses as long as maximum $\lambda(t) \geq 0.5$. For maximum $\lambda(t) < 0.5$, the system does not feel the quantum critical point and hence there is essentially no quantum coherence, in line with empirical observations that coherence effects are primarily found beyond the weak perturbative driving field regime. The presence of decoherence/losses to the environment, does not change our main conclusions, as illustrated in Fig. 4. Since $S_N$ is no longer a good entanglement witness in an open system, we use the closely related quantity quantum negativity [61] $\mathcal{N}(\rho) = \frac{1}{2} \| \rho^{\pi} - \rho \|_1$ where $\rho^{\pi}$ is the partial transpose of $\rho$ with respect to the matter subsystem, and $\| \cdot \|_1 \equiv \text{tr} \{ \sqrt{\rho^\dagger \rho} \}$ is the trace norm. It gives essentially the same results as $S_N$ for small decoherence since both measures represent essentially the same information [39]. The electronic-vibrational density matrix $\rho(t)$ evolves as [62]:

$$\dot{\rho} = -i[H, \rho] + 2\kappa (\bar{n} + 1) D(\rho; \bar{a}) + 2\kappa \bar{n} D(\rho; a^\dagger)$$

where $\kappa$ is the damping rate and $\bar{n}$ is the thermal mean photon number. The Lindblad superoperator $D$ is defined as $\dot{A} \rho A^\dagger - \frac{1}{2} \{ A^\dagger \dot{A}, \rho \}$ ($\{,\}$ is the anti-commutator). Not only do our main results survive well with increasing decoherence $\kappa$, the strength and robustness of the many-body coherence both increase with $N$. (For very large $N$, other system-level decoherence mechanisms may set in). Different temperatures are simulated by varying the average number of phonons $\bar{n}$, choosing values typical of the low temperatures in most experimental realizations, and including a thermal distribution in the initial density matrix [55]. Again our main conclusions are qualitatively unchanged.

Our findings point to new coherence-driven, systems-level functional advantages for energy-harvesting and quantum information device design in terms of transferring excitonic energy and information throughout an $N$-body system, and without requiring strong electronic-vibrational coupling. Our also findings warn that models focused on $N \rightarrow 1$ will miss these features, despite perhaps appearing as more realistic in terms of chemical details.

Acknowledgments

F.J.G-R., F.J.R., and L.O. acknowledge financial support from Facultad de Ciencias through UniAndes-2015 project Quantum control of nonequilibrium hybrid systems-Part II. O.L.A. acknowledges support from NSF-PHY-1521080, JILA-NSF-PFC-1125844, ARO, AFOSR, and MURI-AFOSR. N.F.J. acknowledges support from the National Science Foundation (NSF) under grant CNS 1522693 and the Air Force under AFOSR grant FA9550-16-1-0247. The views and conclusions contained herein are solely those of the authors and do not represent official policies or endorsements by any of the entities named in this paper.

[1] A. Thilagam, J. Math. Chem. 53, 466 (2015).
[2] G. D. Scholes, G. R. Fleming, L. X. Chen, A. Aspuru-Guzik, A. Buchleitner, D. F. Coker, G. S. Engel, R. van Grondelle, A. Ishizaki, D. M. Jonas, J. S. Lundeen, J. K. McCusker, S. Mukamel, J. P. Ogilvie, A. Olaya-Castro, M. A. Ratner, F. C. Spano, K. B. Whaley, and X. Zhu, Nature 543, 647 (2017).
[3] E. Cassette, R. D. Pensack, B. Mahler, and G. D. Sc-
holes, Nat. Commun. 6, 6086 (2015).
[4] Y. Fujihashi, G. R. Fleming, and A. Ishizaki, J. Chem. Phys. 142, 212403 (2015).
[5] A. Olaya-Castro, C. F. Lee, F. F. Olsen, and N. F. Johnson, Phys. Rev. B 78, 085115 (2008).
[6] A. W. Chin, J. Prior, R. Rosenbach, F. Caycedo-Soler, S. F. Huelga, and M. B. Plenio, Nat. Phys. 9, 113 (2012).
[7] E. J. O’Reilly and A. Olaya-Castro, Nat. Commun. 5, 3012 (2014).
[8] F. Dubin, R. Melet, T. Barisien, R. Grousset, L. Legrand, M. Schott, and V. Voiotios, Nat. Phys. 2, 32 (2006).
[9] G. D. Scholes, G. R. Fleming, A. Olaya-Castro, and R. van Grondelle, Nat. Chem. 3, 763 (2011).
[10] J. A. Kenrow, K. E. Sayed, and C. J. Stanton, Phys. Rev. Lett. 78, 4871 (1997).
[11] Z. Liu, H. Yan, K. Wang, T. Kuang, J. Zhang, L. Gui, X. An, and W. Chang, Nature 428, 287 (2004).
[12] D. Bartlomiej, W.-B. Mariam, K. Y. Sathish, F.-S. Aljica, F. Fabricia, J. B. Egbert, and C. Roberta, Biochimica et Biophysica Acta (BBA) - Bioenergetics 1837, 63 (2014).
[13] P. Lambrev, Z. Varkonyi, S. Krumova, L. Kovacs, Y. Miloslavina, A. Holzwarth, and G. Garab, Biochimica et Biophysica Acta (BBA) - Bioenergetics 1767, 847 (2007).
[14] C. Li, Nonlinear Optics: Principles and Applications (Springer, Berlin, 2017) p. 25.
[15] M. Schroter, Dissipative Exciton Dynamics in Light-Harvesting Complexes (Springer, Berlin, 2015) p. 40.
[16] F. J. Rodríguez, L. Quiroga, C. Tejedor, M. D. Martin, L. Vina, and R. Andre, Phys. Rev. B 78, 035312 (2008).
[17] G. D. Scholes and G. R. Fleming, J. Phys. Chem. A 110, 6086 (2011).
[18] G. D. Scholes, G. R. Fleming, A. Olaya-Castro, and R. van Grondelle, Nat. Chem. 3, 763 (2011).
[19] J. A. Kenrow, K. E. Sayed, and C. J. Stanton, Phys. Rev. Lett. 78, 4871 (1997).
[20] Z. Liu, H. Yan, K. Wang, T. Kuang, J. Zhang, L. Gui, X. An, and W. Chang, Nature 428, 287 (2004).
[21] D. Bartlomiej, W.-B. Mariam, K. Y. Sathish, F.-S. Aljica, F. Fabricia, J. B. Egbert, and C. Roberta, Biochimica et Biophysica Acta (BBA) - Bioenergetics 1837, 63 (2014).
[22] P. Lambrev, Z. Varkonyi, S. Krumova, L. Kovacs, Y. Miloslavina, A. Holzwarth, and G. Garab, Biochimica et Biophysica Acta (BBA) - Bioenergetics 1767, 847 (2007).
[23] C. Li, Nonlinear Optics: Principles and Applications (Springer, Berlin, 2017) p. 25.
[24] M. Schroter, Dissipative Exciton Dynamics in Light-Harvesting Complexes (Springer, Berlin, 2015) p. 40.
[25] F. J. Rodríguez, L. Quiroga, C. Tejedor, M. D. Martin, L. Vina, and R. Andre, Phys. Rev. B 78, 035312 (2008).
[26] O. L. Acevedo, L. Quiroga, F. J. Rodríguez, and N. F. Johnson, Phys. Rev. Lett. 112, 030403 (2014).
[27] C. F. Lee and N. F. Johnson, Europhysics Letters 81, 37004 (2008).
[28] T. C. Jarrett, C. F. Lee, and N. F. Johnson, Phys. Rev. B, Rapid Communications 74, 121301 (2006).
[29] C. F. Lee and N. F. Johnson, Phys. Rev. Lett. 93, 083001 (2004).
[30] T. C. Jarrett, A. Olaya-Castro, and N. F. Johnson, Europhysics Letters 77, 34001 (2007).
[31] A. Osterloh, L. Amico, G. Falci, and R. Fazio, Nature 416, 608 (2002).
[32] L.-A. Wu, M. S. Sarandy, and D. A. Lidar, Phys. Rev. Lett. 93, 250404 (2004).
[33] J. Reslen, L. Quiroga, and N. F. Johnson, Europhys. Lett. 69, 8 (2005).
[34] O. L. Acevedo, L. Quiroga, F. J. Rodríguez, and N. F. Johnson, New J. Phys. 17, 093005 (2015).
[35] O. L. Acevedo, L. Quiroga, F. J. Rodríguez, and N. F. Johnson, Phys. Rev. A 92, 032330 (2015).
[36] F. J. Rodríguez, J. J. Mendoza-Arenas, F. J. Rodríguez, C. Tejedor, and L. Quiroga, Phys. Rev. B 93, 035441 (2016).
[37] J. Vidal and S. Dusuel, Europhys. Lett. 74, 817 (2006).
[38] O. Castaños, E. Nahmad-Achar, R. López-Peña, and J. G. Hirsch, Phys. Rev. A 84, 013819 (2011).
[39] O. Castaños, E. Nahmad-Achar, R. López-Peña, and J. G. Hirsch, Phys. Rev. A 86, 023814 (2012).
[40] F. J. Gómez-Ruiz, O. L. Acevedo, L. Quiroga, F. J. Rodríguez, and N. F. Johnson, Entropy 18, 319 (2016).
[41] G. Vidal and R. F. Werner, Phys. Rev. A 65, 032314 (2002).
[42] H. P. Breuer and F. Petruccione, The Theory of Open Quantum Systems (Oxford University Press, Oxford, 2007).
SUPPLEMENTAL MATERIAL (SM)

Functional advantages offered by many-body coherences in biochemical systems

F. J. Gómez-Ruiz$^1$, O. L. Acevedo$^2$, F. J. Rodríguez$^3$, L. Quiroga$^1$, and N. F. Johnson$^3$

$^1$Departamento de Física, Universidad de los Andes, A.A. 4976, Bogotá D. C., Colombia.
$^2$JILA, University of Colorado, Boulder, CO 80309, U.S.A.
$^3$Department of Physics, University of Miami, Coral Gables, FL 33124, U.S.A.

I. TEMPORAL COUPLING $\lambda(t)$ FROM DRIVING FIELD

Here we discuss from a quantum mechanical starting point, the fact that memory effects can arise in the exciton-vibration (XV) dynamics due to the interaction with a (controllable) exterior field – and hence justify the use of a time-dependent $\lambda(t)$ in Eq. (1) of the paper. For quantum systems embedded in complex environments, where extra degrees of freedom modulate the interaction between the quantum system of interest and a large reservoir, effective non-Markovian behaviors in the quantum system dynamics arise even though the reservoir itself can be described within a Markovian approximation [A. Budini and H.J. Schomerus, Phys. A: Math. and Gen. 38, 9251 (2005)]. In our model, the memory effects are due to the parametric pulsed coupling between the exciton and the vibration modes which is represented by the time-dependent XV coupling. Consequently, although it is true that the phase imprinted by the excitation laser is lost during the first steps of electron-exciton relaxation from the high energy sector to the XV region, this is not a sufficient reason to exclude any coherent-like behavior in the relaxing XV dynamics. Indeed it can be shown that for a wide class of phase-mixed states of the pump modes, results for the signal population can be obtained that are identical to those for a coherent population of those modes. In order to clarify this critical point, we now show that our basic premise is justified for a variety of reasons. According to the extensive literature concerning light-matter Hamiltonians, in the classical limit the system can be considered as equivalent to two coupled harmonic oscillators. This information is enough to gain analytical insight into the solution of the resulting quadratic system. The driven system in this limit is described by two coupled harmonic oscillators with a time-dependent coupling frequency. Consequently for this purpose, we will consider a simplified model for the parametric process that contains just 3 boson modes (for the sake of simplicity we describe now the $N$ dimer subsystem in the low excitation limit as an effective boson $b$ mode), as described by the Hamiltonian:

$$\hat{H} = \omega_a \hat{a}^\dagger \hat{a} + \chi \left( \hat{a}^\dagger \hat{a} \right)^2 + \omega_b \hat{b}^\dagger \hat{b} + \omega_c \hat{c}^\dagger \hat{c} + g \left( \hat{a}^\dagger \hat{b}^\dagger \hat{c} + \hat{a} \hat{b} \hat{c}^\dagger \right)$$

(S1)

where the operators $\hat{a}$, $\hat{b}$ and $\hat{c}$ correspond to the vibration, exciton and high energy controllable exciton modes, where we allow for anharmonic terms of strength $\chi$ for the vibration mode. We now consider the effect of the pump state on the dynamics of this simple, but representative, model. In particular, we consider the excitation of high energy electron states, which indirectly feeds (through relaxation process) an effective pump reservoir which follows the applied radiation pulse shape. We assume in Eq. (S1) that $\left( \hat{a}^\dagger \hat{b}^\dagger \hat{c} + \hat{a} \hat{b} \hat{c}^\dagger \right) = h(t)(\hat{a}^\dagger \hat{b} + \hat{a} \hat{b}^\dagger)$ where $h(t)$ represents the applied pulse shape. It is usually argued that the expectation value $\langle \hat{c}^\dagger \rangle$ is different from zero only if the high energy reservoir states have coherent populations. Since the laser pulse excites electrons at a higher energy, the excess energy might be expected to relax into the exciton region giving rise to a coherent interaction. However this is not necessarily the case: after non-resonant excitation, the phase imprinted by the excitation laser is generally lost. The appearance of a well-defined phase is often regarded as the true characteristic feature of a coherent state. However, a careful analysis of unitary dynamics from mixed states, such as those produced by incoherent relaxation processes, shows that coherent-like behaviors can often be obtained. In order to justify this last claim we compute the time evolution of XV observables under two kind of pump initial states: (i) A pure initial state like $|\Psi\rangle = |0_a\rangle |0_b\rangle |\alpha_c\rangle$, denoting the vacuum state for both XV modes, and a pump coherent state. (ii) A statistical mixed state with no phase information at all, given by a density matrix $\hat{\rho}_P = \int_0^{2\pi} d\theta P(\theta) \hat{\Pi}_p(\theta)|\Psi\rangle\langle\Psi| \hat{\Pi}_p^{-1}(\theta)$, where $\hat{\Pi}_p(\theta) = e^{i\hat{N}\theta}$, with $\hat{N} = \hat{a}^\dagger \hat{a} + \hat{b}^\dagger \hat{b} + \hat{c}^\dagger \hat{c}$, denotes a phase smearing operator, given the fact that it takes a pump coherent state $|\alpha_c\rangle$ to a different phase coherent state $|e^{i\theta} \alpha_c\rangle$, leaving the XV modes in the vacuum state. The function $P(\theta)$ fixes the pump phase smearing effect with $P(\theta) \geq 0$ and $\int_0^{2\pi} d\theta P(\theta) = 1$. Since $[\hat{H}, \hat{N}] = 0$, it follows that the time-evolution operator $\hat{U}(t) = e^{-i\hat{H}t}$ commutes with the phase smearing operator $\hat{\Pi}_p(\theta)$. It is now an easy task to obtain for any XV observable like $\hat{a} \hat{a}^\dagger$, the time-evolution as

$$\langle \hat{a} \hat{a}^\dagger \rangle_P = Tr(\hat{a} \hat{a}^\dagger \hat{\rho}_P(t)) = \int_0^{2\pi} d\theta P(\theta) Tr(\hat{U}^{-1}(t) \hat{\Pi}_p^{-1}(\theta) \hat{a} \hat{a}^\dagger \hat{\Pi}_p(\theta) \hat{U}(t)|\Psi\rangle\langle\Psi|) .$$

(S2)
an internal polarization field \( \vec{P} \) and \( \vec{E} \) paper, the equation describing the time-domain behavior in a general, anisotropic and nonlinear medium subject to vibrational population are indeed meaningful. Hence the replacement of \( \hat{c} \) class of coherent pump-plus-relaxation process conditions, our main results on the non-Markovian evolution of the system can therefore be captured by this simple 3-mode Hamiltonian. Therefore we can conclude that for a wide probability \( P \) lossless then electromagnetic theory (e.g. \( \vec{\epsilon} \) which consequently yields a time-dependent XV coupling strength \( \lambda(t) \) – is justified. Also, the range of validity of our assumption is the same as the usual one for the parametric approximation which requires a highly populated coherent state, \( |\alpha_c| \gg 1 \), and short times, \( gt \ll 1 \). These conditions are precisely identical to those under which we show our model fits with previous studies of XV coherence generation: high excitation and a rapid relaxation dynamics. Therefore, there is indeed a formal justification for reducing the last terms in Eq. (S1) to \( gh(t)(\hat{a}^\dagger \hat{b}^\dagger + \hat{a} \hat{b}) \) where \( h(t) \) represents the applied pulse shape – hence justifying the time-dependent interaction \( \lambda(t) \sim gh(t) \) in Eq. 1 of the main paper.

Next we discuss the parallel statement in the main paper, that any incident electromagnetic (light) field \( \vec{E} \) generates an internal polarization field \( \vec{P} \) within the material, given exactly by Maxwell’s Equations. Following Ref. 37 of the paper, the equation describing the time-domain behavior in a general, anisotropic and nonlinear medium subject to a general time and position-dependent light field \( \vec{E} \) is given by:

\[
\nabla \times \nabla \times \vec{E} + \mu_0 \sigma \frac{\partial \vec{E}}{\partial t} + \mu_0 \frac{\partial^2 \vec{E}}{\partial t^2} \cdot \vec{E} = -\mu_0 \frac{\partial^2 \vec{P}}{\partial t^2}
\]

which is Eq. (2.1.17) from Ref. 37 of the paper, in which the standard symbols have their well-known meaning from electromagnetic theory (e.g. \( \vec{\epsilon} \) is a complex second-order tensor). Following Ref. 37 of the paper, if the medium is lossless then \( \sigma = 0 \) and so this equation can be rewritten as:

\[
[\nabla \times (\nabla \times) + \frac{1}{\epsilon_0 c^2} \frac{\partial^2}{\partial t^2} \vec{E}] = -\frac{1}{\epsilon_0 c^2} \frac{\partial^2 \vec{P}}{\partial t^2}
\]

which is Eq. (2.1.18) from Ref. 37 of the paper, and also Eq. (2.130) of Ref. 38 of the paper. Though nonlinear and anisotropic in general, the presence of \( \partial^2 / \partial t^2 \) terms for \( \vec{E} \) and \( \vec{P} \) in both equations means that a pulse in \( \vec{E} \) will generate a similar pulse in \( \vec{P} \), and hence a pulse in the internal electric field dynamics coupling the electronic and vibrational systems (i.e. a pulse in \( \lambda(t) \)).

II. MULTI-COMPONENT RESONANCE

Our focus in the paper is on near resonant conditions since these are the most favorable for generating large coherences. We only consider one such resonance for simplicity, however this can be generalized by matching up different excitation energies \( \epsilon' \), \( \epsilon'' \), etc. to the nearest vibrational energies \( \omega' \), \( \omega'' \) etc. and then solving Eq. 1 of the main paper in the same way for each subset \( \epsilon' \), \( \epsilon'' \) etc. For example, if the \( N \) components are partitioned into \( n \) subpopulations, where each subpopulation has the same resonant energy and vibrational mode but where these values differ between subpopulations, the total Hamiltonian will approximately decouple into \( H^{(1)} \oplus H^{(2)} \oplus H^{(3)} \cdots \oplus H^{(N)} \). Any residual coupling between these subpopulations can then be treated as noise.

III. CALCULATION DETAILS

For each time \( t \) starting at \( t = 0 \), we obtain numerically the instantaneous state \( |\psi(t)\rangle \). The accuracy of our numerical solutions was checked by extending the expansion basis beyond the point of convergence [F.J. Rodríguez, and N.F. Johnson, Phys. Rev. A. 92, 032330 (2015); O.L. Acevedo, L. Quiroga, F.J. Rodríguez, and N.F. Johnson, New J. Phys. 17, 093005 (2015); F.J. Gómez-Ruiz, O.L. Acevedo, L. Quiroga, and F.J. Rodríguez, and N.F. Johnson, Entropy 9, 319 (2016)]. Given a subsystem \( A \), the von Neumann entropy:

\[
S_N = -\text{tr} \{ \rho_A \log (\rho_A) \} , \quad \rho_A = \text{tr}_B \{ |\psi\rangle \langle \psi| \}
\]
where $B$ is the complementary subsystem and the total system is in a total state $|\psi\rangle$ that is pure. When the total system is in such a pure state, the entropy of subsystem $A$ is equal to the entropy of its complementary subsystem $B$, and this quantity $S_N$ is a measure of the entanglement between both subsystems. The natural choice in our system for such a bipartition is where one subsystem is the vibrational mode and the other subsystem is the molecular excitonic subsystem. Since this is a closed system (i.e., a pure global quantum state with an unitary evolution), the increase of $S_N$ in each subsystem is synonymous with an interchange of information between the vibrations and molecular components during the cycle, hence providing a more direct thermodynamical interpretation for the memory effects of the cycle.

Finally, we stress the following general points about our calculations and results:

1. Our focus is on the question of collective coherence in any setting where there is some pulsed perturbation of the system, in order to explore better the idea of how excitations (e.g., excitons) may ‘ride a wave’ of coherence. However, the external profile $\vec{E}(t)$ and hence $\lambda(t)$ can be general. It need not be a pulse. Also the application of Eq. (1) could be to transport experiments as well as optical experiments, or any combination of these.

2. There are two ways in which Eq. 1 of the paper can be applied: (i) We assume that incident light has already created excitons in our system, hence the initial ground state in Eq. 1 is one in which each of $N$ dimers is in the lower excited state, i.e. $|J,M_J = -N/2\rangle$. An initial excited state in Eq. 1 is one in which one or more of the $N$ dimers is in the upper excited state, i.e. $|J,M_J > -N/2\rangle$. Our model then calculates what additional many-body coherence is generated by a pulse. (ii) We can alternatively assume that the system starts in a true ground state with no excitations. The same analysis follows. It is case (i) that we are interested in here for the particular setting of the LHII trimer, since it is the energy separation of each dimer’s two hybridized excitonic states $|Y\rangle$ and $|X\rangle$ that is quasi-resonant with a vibrational mode.

3. The pulse $\lambda(t)$ is a consequence of the internal polarization $\vec{P}(t)$ due to an external pulse of light $\vec{E}(t)$. Maxwell’s Equations give a nonlinear, exact equation that relates $\vec{P}(t)$ to $\vec{E}(t)$, and as a result of the mathematical form (see above) a pulse in $\vec{E}(t)$ will generate a pulse in $\vec{P}(t)$. This can also be established starting from a full quantum picture (see above).

4. The effect of finite temperature is treated when discussing the losses/decoherence, by including the finite numbers of phonons consistent with temperature distributions. We find that these do not change our main conclusions for reasonably low temperatures. Even for higher temperatures, the effects that we discuss have not disappeared.

5. Recent papers (e.g., Ref. 33 of the paper) make the point that a deeper understanding of the temporal quantum evolution in systems of general size $N$ – as our paper tries to offer – may shed light on the early-time kinetics in real-world open systems, since this timescale is too short to couple in many of the complex degrees of freedom that will naturally exist in a hot, wet environment.

6. Overall, we believe our model provides a firm framework for exploring the generation/diffusion of collective coherence across multisite vibronic systems excited by different kinds of fields – and can even include those introduced by entangled photon sources.