Comment on "Thermal-light-induced dynamics: Coherence and revivals in V-type and molecular Jaynes-Cummings systems"

Amro Dodin and Paul Brumer
Chemical Physics Theory Group, Department of Chemistry, and Center for Quantum Information and Quantum Control, University of Toronto, Toronto, Ontario M5S 3H6, Canada
(Received 18 August 2016; published 28 June 2017)

Recent numerical and analytical results have been obtained for the dynamics of a V-type system, and of a model molecular system, interacting with the thermal states of a cavity with a single mode or with a few discrete modes [D. Avisar and A. D. Wilson-Gordon, Phys. Rev. A **93**, 033843 (2016)]. The authors speculate that these results may be relevant to excitation with natural incoherent radiation, such as sunlight, which has a continuous spectrum. We claim that this is incorrect, as are their comments about prior work on natural incoherent radiation that does properly deal with a continuous spectrum. Specifically, while their results obtained for the Jaynes-Cummings systems may be of interest for excitation by thermal states of cavities with a few modes, the discrete nature of their field modes produces dynamics that are fundamentally different from those induced by natural sunlight. Hence, we show here that the criticisms leveled in their paper regarding prior treatments that dealt with the continuous spectrum of natural incoherent radiation, as well as their speculation that excitation with continuous-mode thermal radiation can induce long-lived molecular coherences, are incorrect.

DOI: 10.1103/PhysRevA.95.067801

I. INTRODUCTION

The recent observation of wavelike energy transfer in the multidimensional spectroscopy of photosynthetic light harvesting complexes [1,2] has motivated new studies of light-induced excitation of molecular systems [3–13]. It has been shown that the dynamics of the induced molecular coherences depend strongly on the properties of the exciting radiation [7,8,10,11,13–17]. In particular, excitation by suddenly turned on incoherent blackbody radiation generates transient noise-induced Fano coherences that differ significantly from typical laser-induced coherences in both their origin and dynamics [10–12,18]. They may be remarkably long-lived but they collapse eventually into an incoherent steady state, consistent with thermodynamic equilibrium and the Einstein rate law [10–12,14,19]. Further, slowly turned on incoherent radiation produces virtually no coherence [13].

A recent study [20] has considered the quantum dynamics of a V system interacting with the thermal state of a *single or few-mode cavity* in a Jaynes-Cummings type model. The authors observe "coherentlike" collapse and revival patterns of the V system similar to those that are well known in the dynamics of the prototypical Jaynes-Cummings model [21,22] and suggest, in disagreement with past studies [7–16], that it is possible for natural incoherent radiation to generate long-time excited-state coherences [20]. (For example, their Abstract states "... we show that multimode thermal light induces coherence in the excited material states. This is in contrast to previous studies that suggest that thermal light cannot induce coherence in material systems.") We claim here that this is incorrect: the dynamics induced by their discrete-mode bath differs fundamentally from that induced by (previously studied) continuous-mode thermal radiation such as sunlight. Specifically, while their results may be of interest for dynamics in cavities with a few discrete modes, their discrete-mode treatment is irrelevant for a continuous-mode bath, such as sunlight. Hence, their criticism of past work that dealt with continuous-mode incoherent radiation fields is incorrect. Such criticism include remarks such as the following (where the reference numbering is from [20]):

(1) "In addition, Jiang and Brumer [27] have also examined semiclassical perturbative formulation for the interaction of thermal light with a multilevel structureless material system. They concluded that no coherence between the material energy states is expected. The creation of a mixed state was also predicted by employing the von Neumann equation for the interaction of a V system with classical partially incoherent light [36]. The results we present above, both for low and high average photon numbers, contradict this conclusion (and those of subsequent studies, as is shown below)."

(2) "Based on the thermal three-mode results above for the V system, we believe that in the relevant photon number regime, that is, $\bar{n} \ll 1$, a multimode thermal light would induce excited-state coherence in the molecular system as well."

(3) "By employing a JC-type interaction model for a V-type three-level system and multimode thermal state of the light, it is shown that the thermal light does induce excited-state coherence in the material subsystem, contrary to previously stated conclusions."

As is well known, properly treating the interaction of an atomic or molecular system with incoherent radiation possessing a continuous spectrum can be done by tracing over the radiation field to produce the density matrix and associated master equation for the system dynamics [23,24]. In several places in the published paper [20] the authors suggest that a proper quantum treatment has not been carried out. We claim that this is incorrect: appropriate fully quantum completely positive master equation approaches (or correct averages over the radiative environment) treating the interaction of systems with weak quantized incoherent radiation with a continuous spectrum, appropriate to sunlight, have been published—e.g., their Refs. [26] and [32]. Interestingly, they do not regard their Ref. [32]—a published paper from our research group [10]—as satisfactory on the grounds that it includes "intrinsic coupling between the material excited states." However, this

is not the case; there is no such coupling in that model. These fully correct studies do not show long-lived light-induced coherences in the steady state, contrary to the authors' expectations.

To appreciate the central issue, note their statement: "Our results suggest that it should be worthwhile to reconsider the previous general conclusion, drawn in earlier studies, that thermal light should induce only a mixture of material eigenstates. In particular, our results do not indicate any fundamental restriction for excited-state coherence to be induced by thermal light." This statement fails to note that there is indeed a *fundamental* distinction in the physics resulting from irradiation with multimode light vs that of continuous-mode radiation. This is discussed in detail below.

II. DISCRETE VERSUS CONTINUOUS SPECTRA

A. Thermodynamics, recurrences, Fermi's golden rule, and master equations

Consider first the analytic results derived in Ref. [20]. The population of the material excited state driven by a single-mode bath is given by (Eq. (A7) of Ref. [20])

$$\rho_{M,ee}(t) = \rho_{M,ff}(t) = (\lambda\Delta)^2 \sum_n p_n \frac{n}{\Omega_n^2}[\cos(\sqrt{\Omega_n}t) - 1]^2 + \lambda^2 \sum_n p_n \frac{n}{\Omega_n}\sin^2(\sqrt{\Omega_n}t), \tag{1}$$

where $\Omega_n = \Delta^2 + 2\lambda^2 n$ is the generalized Rabi frequency, Δ is the energy splitting of the excited states, and λ is the interaction constant set equal for the two excited states. The thermal population of the n photon state of the single-mode excited state is given by the Boltzmann distribution as $p_n = \overline{n}^n/(1+\overline{n})^{n+1}$, where $\overline{n}$ is the mean thermal occupation and the material system is initially in the ground state. Equation (1) is even in time and shows short-time dynamics that are quadratic in time. This quadratic time dependence is characteristic of excitation by a discrete bath and disagrees with Fermi's golden rule prediction of linear time dependence for times longer than the bath coherence time (1.3 fs for sunlight) for the population of excited states driven by a continuous-mode bath.

Further, Eq. (1) shows no long-time limit, a result which is at odds with thermodynamic considerations of a system interacting with a continuous-mode thermal bath, which predicts a final incoherent equilibrium state at the bath temperature. This feature is a fundamental limitation of discrete-bath approximations to continuous baths that affects all of the calculations in Ref. [20], since any discrete quantum system will show Poincaré recurrences and not display the irreversible dynamics required for thermalization.

B. Correlation functions and explicit dynamics

The origin of the fundamental discrepancy between a proper continuous-bath treatment of thermal radiation and their discrete-mode treatment is readily displayed from the basic underlying dynamics. Consider the exact dynamics of a V system interacting with an arbitrary multimode bath under a Jaynes-Cummings type Hamiltonian:

$$H = H_S + H_B + H_I, \tag{2a}$$

$$H_S = (\hbar\omega_0 - \Delta)|e_1\rangle\langle e_1| + (\hbar\omega_0 + \Delta)|e_2\rangle\langle e_2|, \tag{2b}$$

$$H_B = \sum_{\boldsymbol{k},\lambda} \hbar\omega_k a^\dagger_{\boldsymbol{k},\lambda} a_{\boldsymbol{k},\lambda}, \tag{2c}$$

$$H_I = \sum_i (|e_i\rangle\langle g| + |g\rangle\langle e_i i|)\boldsymbol{\mu}_{e_i g} \sum_{\boldsymbol{k},\lambda} \boldsymbol{\epsilon}_{\boldsymbol{k},\lambda} E_k (a_{\boldsymbol{k},\lambda} - a^\dagger_{\boldsymbol{k},\lambda}), \tag{2d}$$

where ω_0 is the splitting between the ground- and excited-state manifold, Δ is the excited-state splitting, and ω_k is the frequency of the field mode with wave vector $\boldsymbol{k}$. The single-photon field strength of a photon with wave vector $\boldsymbol{k}$ and polarization λ is given by E_k, the polarization vector by $\boldsymbol{\epsilon}_{\boldsymbol{k}\lambda}$, and the creation and annihilation operators by $a^\dagger_{\boldsymbol{k},\lambda}$ and $a_{\boldsymbol{k},\lambda}$, respectively. The transition dipole moment of the $|g\rangle \leftrightarrow |e_i\rangle$ transition is given by $\boldsymbol{\mu}_{e_i g}$.

For simplicity, consider the case where the two transition dipole moments $\boldsymbol{\mu}_{e_i,g}$ are parallel. In this case, define an interaction weighted field as

$$E' = \sum_{\boldsymbol{k},\lambda} E'_{\boldsymbol{k},\lambda}(a_{\boldsymbol{k},\lambda} - a^\dagger_{\boldsymbol{k},\lambda}), \tag{3}$$

where the interaction-weighted field strength is given by $E'_{\boldsymbol{k},\lambda} = E_k(\boldsymbol{\mu}_{\boldsymbol{e_i g}} \cdot \boldsymbol{\epsilon}_{\boldsymbol{k},\lambda})/\mu_{e_i g}$. Due to the parallel transition dipole moment this definition is the same for both excited states. Using the interaction-weighted field the interaction Hamiltonian from Eq. (2d) can be rewritten as the tensor product

$$H_I = \left(\sum_i S_i\right) \otimes E', \tag{4}$$

where $S_i = \mu_{e_i g}(|e_i\rangle\langle g| + |g\rangle\langle e_i|)$ is the scalar polarization operator for the $|e_i\rangle \leftrightarrow |g\rangle$ transition.

Transforming to the interaction picture with interaction Hamiltonian H_I, define $H_0 = H_S + H_B$ as the "bare" Hamiltonian and the interaction-free propagator from t_0 to t as

$$U_0(t,t_0) = \exp\left[-\frac{i}{\hbar}H_0(t-t_0)\right] = \exp\left[-\frac{i}{\hbar}H_S(t-t_0)\right] \otimes \exp\left[-\frac{i}{\hbar}H_B(t-t_0)\right]. \tag{5}$$

The interaction Hamiltonian in the interaction picture is given by

$$V(t) = U_0^\dagger(t,t_0) H_I U_0(t,t_0). \tag{6}$$

Suppose that the material and radiation field are initially in a separable state $\rho_I(t_0) = \rho_S(t_0) \otimes \rho_B(t_0)$, where $\rho_S(t_0) = |g\rangle\langle g|$ and $\rho_B(t_0)$ is the thermal state of the multimode bath at temperature T. The von Neuman equation in the interaction picture then gives the dynamics of the interaction picture density operator

$$\rho_I(t) = \rho_I(t_0) - i\int_{t_0}^{t} dt_1 [V(t_1), \rho_I(t_1)]. \tag{7}$$

Iteratively substituting Eq. (7) into itself yields the following asymptotic series:

$$\rho_I(t) = \rho_I(t_0) - i\int_{t_0}^{t} dt_1[V(t_1),\rho_I(t_0)] - \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2[V(t_1),[V(t_2),\rho_I(t_0)]] + \cdots . \quad (8)$$

Upon tracing over the bath coordinates to obtain the reduced material system dynamics, each term in Eq. (8) gives a multiple-time correlation function of the interaction-weighted field.

Consider then the correlation function of a field with a few discrete modes vs that of a continuous-mode field such as natural sunlight. To illustrate their considerable difference consider, as an example, the (unnormalized) first-order correlation function of the field that arises in the second-order terms of the asymptotic series Eq. (8):

$$G'^{(1)}(t_2,t_1) = \langle E'(t_1)E'(t_2)\rangle = -\sum_{\boldsymbol{n}}\sum_{\boldsymbol{k}\lambda} |E'_{\boldsymbol{k}\lambda}|^2 e^{-i\omega_k(t_1-t_2)} p_{\boldsymbol{n}-\boldsymbol{e}_{\boldsymbol{k},\lambda}}, \quad (9)$$

where $\boldsymbol{n}$ is a vector of occupation numbers for each mode of the field, and $p_{\boldsymbol{n}-\boldsymbol{e}_{\boldsymbol{k},\lambda}}$ is the Boltzmann probability of $n_{\boldsymbol{k}',\lambda'}$ photons in each mode $(\boldsymbol{k}',\lambda') \neq (\boldsymbol{k},\lambda)$ and $n_{\boldsymbol{k},\lambda} - 1$ photons in the the $(\boldsymbol{k},\lambda)$ mode of the field.

Considering only the summation over the length of the wave vector k for each fixed direction $\boldsymbol{k}/k$ and polarization λ in Eq. (9), it is easy to see that, in accordance with the Wiener-Khinchin theorem, the interaction-weighted correlation function is simply a geometrically weighted inverse Fourier transform of the power spectral density of the field. Hence, the modal structure of the field, captured by the power spectral density, dictates the dynamics it produces. In particular, any field with a discrete-modal structure will be quasiperiodic, as is known for discrete Fourier series. By contrast, for a continuous-mode field, such as sunlight, irreversible decay of the correlation function is possible, enabling the proper approach to a thermal equilibrium discussed in Sec. II A. Analogous arguments hold for higher-order correlation functions contribution to Eq. (9), and for multilevel systems.

III. CONCLUSION

Hence, contrary to the claims in Ref. [20], the discrete-mode Jaynes-Cummings model tells us nothing about the physics of sunlight-induced system dynamics. Their single- and few-mode bath studies do not show irreversible dynamics nor do they produce a canonical thermal equilibrium state as a quasiequilibrium state at intermediate times. The minimal requirement to properly model sunlight is a continuous spectrum, which their discrete-bath model fails to provide. Further, their statement that proper quantum studies of excitation with weak natural incoherent light, appropriate to sunlight, are nonexistent does not take account of satisfactory treatments in the literature (e.g., Refs. [8,10]). Finally, and significantly, prior conclusions [7–16] that excitation with incoherent sunlight produces a steady state that is devoid of molecular coherences, challenged in Ref. [20] are, in fact, correct.

[1] G. S. Engel, T. R. Calhoun, E. L. Read, T. K. Ahn, T. Mancal, Y. C. Cheng, R. E. Blankenship, and G. R. Fleming, Nature (London) **446**, 782 (2007).

[2] E. Collini, C. Y. Wong, K. E. Wilk, P. M. Curmi, P. Brumer, and G. D. Scholes, Nature (London) **463**, 644 (2010).

[3] Y. C. Cheng and G. R. Fleming, Annu. Rev. Phys. Chem. **60**, 241 (2009); L. A. Pachon and P. Brumer, Phys. Chem. Chem. Phys. **14**, 10094 (2012).

[4] A. Chenu and G. D. Scholes, Annu. Rev. Phys. Chem. **66**, 69 (2015).

[5] N. Lambert, Y.-N. Chen, Y.-C. Cheng, C.-M. Li, G.-Y. Chen, and F. Nori, Nat. Phys. **9**, 10 (2013).

[6] R. J. León-Montiel, I. Kassal, and J. P. Torres, J. Phys. Chem. B **118**, 10588 (2014).

[7] X-P. Jiang and P. Brumer, J. Chem. Phys. **94**, 5833 (1991).

[8] P. Brumer and M. Shapiro, Proc. Natl. Acad. Sci. USA **109**, 19575 (2012).

[9] J. Olšina, A. G. Dijkstra, C. Wang, and J. Cao, arXiv:1408.5385.

[10] T. V. Tscherbul and P. Brumer, Phys. Rev. Lett. **113**, 113601 (2014).

[11] T. V. Tscherbul and P. Brumer, J. Chem. Phys. **142**, 104107 (2015).

[12] A. Dodin, T. V. Tscherbul, and P. Brumer, J. Chem. Phys. **144**, 244108 (2016).

[13] A. Dodin, T. V. Tscherbul, and P. Brumer, J. Chem. Phys. **145**, 244313 (2016).

[14] T. Grinev and P. Brumer, J. Chem. Phys. **143**, 244313 (2015).

[15] T. Mancal and L. Valkunas, New J. Phys. **12**, 065044 (2010).

[16] I. Kassal, J. Yuen-Zhou, and S. Rahimi-Keshari, J. Phys. Chem. Lett. **4**, 362 (2013).

[17] G. C. Hegerfeldt and M. B. Plenio, Phys. Rev. A **47**, 2186 (1993).

[18] G. S. Agarwal, *Quantum Statistical Theories of Spontaneous Emission and their Relation to Other Approaches* (Springer-Verlag, Berlin, 1974).

[19] G. S. Agarwal and S. Menon, Phys. Rev. A **63**, 023818 (2001).

[20] D. Avisar and A. D. Wilson-Gordon, Phys. Rev. A **93**, 033843 (2016).

[21] F. W. Cummings, Phys. Rev. **140**, A1051 (1965).

[22] J. H. Eberly, N. B. Narozhny, and J. J. Sanchez-Mondragon, Phys. Rev. Lett. **44**, 1323 (1980).

[23] G. S. Agarwal, *Quantum Optics* (Cambridge University Press, New York, 2013).

[24] Z. Ficek and S. Swain, *Quantum Interference and Coherence* (Springer, New York, 2005).