Thermal-Light-Induced Coherent Dynamics in Atoms and Molecules – an Exact Quantum Mechanical Treatment

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(Dated: May 4, 2015)

The question of whether sunlight induces coherent dynamics in biological systems is under debate. Here we show, on the basis of an exact fully quantum mechanical treatment, that thermal light induces excited-state coherences in matter similar to those induced by a coherent state. We demonstrate the phenomenon on a V-type model system and a two-state Born-Oppenheimer molecular system. Remarkably, wavepacket-like dynamics is induced in the excited molecular potential-energy surface.

PACS numbers: 33.80.-b, 42.50.-p, 42.50.Ct, 42.50.Md

Coherence is a fundamental and central theme in quantum mechanics and is manifested in light–matter interaction through a variety of unique phenomena [1], including quantum control [2], storage and retrieval of information [3], and quantum state reconstruction [4, 5]. In recent years, there has been a lively debate on whether sunlight-induced chemical reactions in biological systems evolve coherently and consequently exhibit extremely efficient energy transfer. Experimental evidence for vibrational and electronic coherence in such systems has been reported in several studies [6–14]. However, it has been argued that since such studies employ coherent laser pulses rather than sunlight (so-called thermal or chaotic light) to initiate material dynamics, the results obtained cannot establish conclusively that sunlight-induced biological processes evolve coherently [14].

Theoretical studies of the excitation of atomic and molecular systems by thermal light have reached contradictory conclusions as to whether the induced dynamics is coherent. Most of these studies are approximate in some sense, as they involve either semiclassical or perturbative treatments, and some of them rely on the presence of an intrinsic coupling between the material excited states, such as vacuum- or decay-induced coherence [15–22]. Others, treat the material system only following an assumed coherent excitation [23]. None of these studies employ an exact and fully quantum mechanical treatment of the interaction of thermal light with matter without such limiting constraints. Interestingly, the entanglement (correlations) between separated material sites has also been studied in this context [24, 25].

Since the interaction of thermal light with matter is a fundamental issue of enormous potential implications, the need for a definite conclusion on whether thermal light can induce coherent material dynamics is of primary importance and significance. In order to reach a definite conclusion, we treat the problem starting from basic considerations which, to the best of our knowledge, has never been done before.

We employ an exact (non-perturbative) dynamical treatment for the interaction of a material system (atomic and molecular) with a thermal state of the electromagnetic field, where both the material and light subsystems are quantized. Concretely, we treat the light–matter system as a bipartite composite system whose subsystems interact via a Jaynes-Cummings-type [26] interaction model. We thus express the initial system by its density matrix, \( \rho(0) = \rho_F(0) \otimes \rho_M(0) \) (where \( F \) and \( M \) stand for ‘field’ and ‘material’, respectively), and fully propagate it in time according to \( \rho(t) = U(t) \rho(0) U^\dagger(t) \), where \( U(t) \) is the system propagator. In the case we consider, the material subsystem is initially in its ground state, while the field is in a single-mode statistical mixture of Fock states.

As we describe below in detail, we apply the interaction model to a three-level V-type system as a basic model, and, for the first time to the best of our knowledge, to a two-state Born-Oppenheimer molecular system for which we propagate the full density matrix, represented in the electronic \( \otimes \) bond-coordinate \( \otimes \) photon-Fock product space. To conform with the conditions of a natural process in our simulations, we consider the weak-field regime and initial average photon number characteristic of sunlight (about 500nm wavelength at 6000 K, [27]). We find that thermal light induces excited-state coherent dynamics in both the atomic and molecular subsystems, as it also does in the regime of strong field and high average photon number. We compare this result with that obtained for the interaction of the material systems with a coherent-state. Remarkably, we find that both scenarios exhibit almost identical excited-state coherence features. On the other hand, in contrast to a coherent-state, thermal light does not induce coherence between the material ground and excited states.

As a prototype for a molecular system, we consider a three-level V-type model system interacting with a single mode of the radiation field. The Jaynes-Cummings-type
The state of each subsystem is obtained by tracing \(\rho(t)\) over the space of the other subsystem; that is,

\[
\rho_A(t) = \text{Tr}_B \left[ \rho(t) \right].
\]

In the supplemental material, we give an analytical expression for \(\rho(t)\) for the \(V\) system, as well as for the coherence element of the material subsystem for the fully resonant case where \(\omega - \omega_{e,f} = 0\). Furthermore, we compare the analytical and numerical calculations in order to justify the numerical simulations presented here.

We now compare the \(V\) system dynamics induced by a coherent state with that induced by a thermal state. For both scenarios, the energy separation between the \(|e\rangle\) and \(|f\rangle\) states is set to 250 cm\(^{-1}\), and the field frequency is tuned between them. We set \(\lambda_{e,f} = 10^{-4}\), and \(\bar{n} = 0.008\) (obtained for 495.9 nm and temperature 6000 K for the field mode). We construct the initial states of the light with the first ten Fock states. In Fig. 1 we show the material excited states populations (top panel), the real and imaginary parts of the material excited states coherence element, \(\rho_{M,e,f}(t)\) (middle panel), and the trace of the material (and field) reduced density matrix, \(\text{Tr}[\rho_{M,e,f}(t)]\), and of its square, \(\text{Tr}[\rho_{M,e,f}^2(t)]\) (bottom panel), as obtained for the interaction with the coherent state. In Fig. 2 we present the same dynamical measures for the interaction of the \(V\) system with thermal light; in the lower panel, however, we show only \(\text{Tr}[\rho_{M,e}^2(t)]\) and \(\text{Tr}[\rho_{F}^2(t)]\) which are generally different for a mixed state.

Figures 1 and 2 show striking similarity between the material populations and, most remarkably, the excited state coherence for the coherent and thermal light scenarios. In this context, it is interesting to refer to the similarity in the interaction of a coherent and thermal states with a two-level system as noted by Cummings [28]. In contrast, \(\text{Tr}[\rho_{M,e}^2(t)]\) and \(\text{Tr}[\rho_{F}^2(t)]\) show different behavior. In the mixed state scenario (interaction with the thermal light), the two oscillate out-of-phase (as if purity is exchanged between the subsystems), while in the pure scenario (interaction with the coherent state) both are identical, as is well known for a pure system. We note that throughout the interaction of the thermal light with the \(V\) system, \(\rho_F(t)\) remains diagonal as we show analytically in the supplemental material.

Another major difference between thermal and coherent state of the light is that while the latter induces coherence between the material ground and excited states, the former does not. (We derive this result analytically in the supplemental material). We explain this phenomenon...
Thermal light, is obtained through an exact quantum thermal state, as noted elsewhere \[30\].

The material ground and excited states (since they share common photon states), and also among the excited states themselves. Note that a Schrödinger cat they share common photon states), and also among the excited states. Such couplings were introduced in a number of previous studies, and were necessary to allow the material excited-state coherence. Our exact treatment proves such coherence is obtained naturally via the interaction with thermal light, similarly to that obtained in the interaction with a coherent state. In the supplemental material we show that similar dynamical characteristics are obtained for the interaction of a the system with two-mode thermal (and coherent) state.

A realistic molecular system is by far more significant for understanding matter interaction with thermal light. We therefore apply a similar fully exact quantum mechanical treatment to a molecular system of two Born-Oppenheimer potential energy surfaces (PESs). Specifically, the field is represented in Fock space, and the molecular system is spanned by the two-dimensional electronic space and the continuous coordinate space for the nuclei separation. Thus the state of the system is given by the tensor product of these three spaces.

The Hamiltonian of the entire system is

\[ H_{\text{mol}} = \sum_{i=g,e} H_i(r)|i\rangle\langle i| + \omega(a^\dagger a + \frac{1}{2}) + \lambda(|e\rangle\langle g| + |g\rangle\langle e| a^\dagger), \]

where \( H_i(r) = V_i(r) + T \) is the nuclear Hamiltonian of the ground and excited electronic states (\(|g\rangle\) and \(|e\rangle\)), with the PES \( V_i(r) \) and the kinetic energy operator \( T = -\frac{1}{2m} \nabla^2 \). The parameter \( m \) is the molecular reduced mass. We denote the (vibrational) eigenstates of \( H_i(r) \) by \( \psi_{i,\nu}(r) \), where \( \nu \) is the vibrational quantum number. In writing the Hamiltonian of Eq. \[4\] we invoke the dipole, Condon, and rotating-wave approximations.

We examine the molecular dynamics induced by excitation with both thermal and coherent states, as before. The initial molecular (ground) state is \( \rho_{\text{M}}(0) = |g\rangle\langle g| \psi_{g,0}\rangle\langle \psi_{g,0}| \) and the initial state of the field \( \rho_{\text{F}}(0) \) is either a coherent or thermal state, as described above. The initial state of the system is \( \rho(0) = \rho_{\text{F}}(0) \otimes \rho_{\text{M}}(0) \), and its state at any time in the course of interaction is

\[ \rho(t + \Delta t) = e^{-iH_{\text{mol}}\Delta t}\rho(t)e^{iH_{\text{mol}}\Delta t}. \]

It is convenient to employ the “split operator” method \[31\] in propagating \( \rho \), and split the kinetic energy term of the Hamiltonian from the rest of the terms. Thus, for each time-step the propagator is \( e^{-iH_{\text{mol}}\Delta t} \approx e^{-iT\Delta t}e^{-i\tilde{H}_{\text{mol}}\Delta t} \), where \( \tilde{H}_{\text{mol}} \) is the full Hamiltonian of Eq. \[4\] without \( T \). In practice, we simulate the interaction of thermal light with a two-state Born-Oppenheimer model system of two one-dimensional Morse-type PESs, \( V_i(r) = D_i(1 - e^{-b_i(r-r_i)})^2 + T_i \) (the potentials parameters, based on these of the Li\(_2\) molecule, are given in the supplemental material). The frequency

\[ \omega = \frac{\hbar}{\sqrt{2m\lambda}. \]

in the following way. According to our model, the interaction of a single Fock state, say \(|n\rangle\), with the material ground-state \(|g\rangle\) produces the general superposition \( a|g, n\rangle + (b|e\rangle + c|f\rangle)|n-1\rangle \), which in the material subspace (that is, after tracing over the field subspace) corresponds to a mixed state of the material ground and excited states. However, the material excited-states are in a coherent superposition with coherences between them. Thermal light is a statistical mixture of single Fock states and, therefore, induces only excited-state coherences in the material subsystem. The absence of coherence between the ground and excited states is related to the vanishing of the material dipole moment in this scenario as pointed out in \[29\]. In contrast, since a coherent state is a coherent superposition of Fock states, its interaction with the material ground-state will generate coherence between the material ground and excited states (since they share common photon states), and also among the excited states themselves. Note that a Schrödinger cat (coherent) state \[27\] is expected to behave just like a thermal state, as noted elsewhere \[30\].

The material excited-state coherence, induced by the thermal light, is obtained through an exact quantum mechanical treatment without any intrinsic coupling between the excited states. Such couplings were introduced in a number of previous studies, and were necessary to allow the material excited-state coherence. Our exact treatment proves such coherence is obtained naturally via the interaction with thermal light, similarly to that obtained in the interaction with a coherent state. In the supplemental material we show that similar dynamical characteristics are obtained for the interaction of a the system with two-mode thermal (and coherent) state.

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The material excited-state coherence, induced by the thermal light, is obtained through an exact quantum
of the exciting field is tuned between the third and fourth vibrational eigenstates of the excited state. The initial state $\rho_F(0) = \sum_n p_n |n\rangle\langle n|$ is constructed with the first seven Fock states. We set $\lambda = 10^{-4}$, and $\bar{n} = 0.0072$ (obtained for 486.1 nm at 6000 K for the field mode).

In Fig. 3 we show snapshots of the excited-state material reduced density matrix, $\rho_{M,ee}(t)$. In the left column we show $\rho_{M,ee}(t)$ in the coordinate representation, while in the right column we show its projection onto the first 15 excited vibrational eigenstates. The clear observation that emerges from these snapshots is that thermal light induces excited-state vibrational coherent dynamics. An almost identical coherence fea-

![Figure 3](image_url)

**FIG. 3:** (color online). Snapshots of $\rho_{M,ee}(t)$ for thermal light interacting with two-state Born-Oppenheimer molecule. The left column shows $\rho_{M,ee}(t)$ in coordinate space (with the time specified in femtoseconds), and the right column shows its projection onto the vibrational eigenstates of the molecular excited-state.
light. On the basis of recent studies \cite{21}, we expect that the interaction of the system with environment would not eliminate the induced coherence. In addition, based on our two-mode calculations, we expect that a continuous-mode of thermal light, interacting with matter, should induce similar type of coherences.

The results we present in this Letter may suggest a significant role that a statistical source of modes can have in coherent dynamics, as was pointed out in a similar context \cite{23}. Consequently, our results may have direct impact on the understanding the dynamical characteristics of sunlight-induced biological processes.

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SUPPLEMENTARY MATERIAL

Analytical dynamical expressions for the interaction of the V system

In the interaction picture, the Hamiltonian for the V-type three-level system, assuming $\omega - \omega_{ef} = 0$ and a common parameter $\lambda$, is given by

$$ H_I = \lambda \sum_{i=e,f} (\langle i | (g\hat{a} + |g\rangle \langle i | \hat{a}^\dagger) $$

Employing Taylor expansion, we get the following matrix for the propagator $e^{-iH_I t}$ in the three-dimensional material space

$$ e^{-iH_I t} = \begin{pmatrix} \hat{C}_f(t) & \hat{C}_{ef}(t) & \hat{S}_{fg}(t) \\ \hat{C}_{ef}(t) & \hat{C}_e(t) & \hat{S}_{eg}(t) \\ \hat{S}_{fg}(t) & \hat{S}_{eg}(t) & \hat{C}_g(t) \end{pmatrix}, $$

with the matrix elements given by

$$ \hat{C}_f(t) = \hat{C}_e(t) = \frac{1}{2} \left[ \cos(\sqrt{2\alpha t} \lambda t) + 1 \right] $$

$$ \hat{C}_{ef}(t) = \frac{-i}{\sqrt{2}} \sin(\sqrt{2\alpha t} \lambda t) \hat{a}^\dagger $$

$$ \hat{S}_{fg}(t) = \hat{S}_{eg}(t) = \frac{-i}{\sqrt{2}} \sin(\sqrt{2\alpha t} \lambda t) \hat{a}^\dagger $$

$$ \hat{C}_g(t) = \cos(\sqrt{2\alpha t} \lambda t). $$

The operations of each of the propagator matrix elements on Fock states are then

$$ \hat{C}_f(t)|n\rangle = \frac{1}{2} \left[ \cos(\sqrt{2(n+1)} \lambda t) + 1 \right] |n\rangle \equiv C_{fn}(t)|n\rangle $$

$$ \hat{C}_{ef}(t)|n\rangle = \frac{-i}{\sqrt{2}} \sin(\sqrt{2(n+1)} \lambda t) |n\rangle \equiv C_{efn}(t)|n\rangle $$

$$ \hat{S}_{fg}(t)|n\rangle = \frac{-i}{\sqrt{2}} \sin(\sqrt{2n} \lambda t) |n-1\rangle \equiv S_{fgn}(t)|n-1\rangle $$

$$ \hat{S}_{eg}(t)|n\rangle = \frac{-i}{\sqrt{2}} \sin(\sqrt{2(n+1)} \lambda t) |n+1\rangle \equiv S_{egn}(t)|n+1\rangle $$

$$ \hat{C}_g(t)|n\rangle = \cos(\sqrt{2n} \lambda t) |n\rangle \equiv C_{gn}(t)|n\rangle. $$

For the initial state $\rho(0) = |g\rangle \langle g| \otimes \rho_F(0)$ of the composite system, the density matrix at any time $t$ of the evolution, in the interaction picture, is

$$ \rho_I(t) = \begin{pmatrix} \hat{S}_{fg}\rho_F(0)\hat{S}_{ge} & \hat{S}_{fg}\rho_F(0)\hat{C}_g \\ \hat{S}_{fg}\rho_F(0)\hat{S}_{eg} & \hat{S}_{fg}\rho_F(0)\hat{C}_g \end{pmatrix}, $$

where we have omitted, for convenience, the explicit time dependence of the matrix elements of $\rho_I$.

First we derive an expression for the coherence element between the ground and excited state for the case of a coherent state of the field. We then show that this element is identically zero for the thermal state of the field. Let us consider the element $-\hat{C}_g\rho_F(0)\hat{S}_{ge}$. For the coherent state of the field we plug $\rho_F(0) = |\alpha\rangle \langle \alpha|$ into this element and trace over the field space. As a result, we get

$$ \rho_{M,fg}(t) = \text{Tr}_F \left[ -\hat{C}_g(t)|\alpha\rangle \langle \alpha| \hat{S}_{ge}(t) \right] = -\langle \alpha|\hat{S}_{ge}(t)\hat{C}_g(t)|\alpha\rangle $$

$$ = -\langle \alpha|\hat{S}_{ge}(t)\hat{C}_g(t)|\alpha\rangle $$

$$ = \frac{e^{-|\alpha|^2}}{2} \sum_n \frac{\alpha^n(\alpha^*)^{n+1}}{\sqrt{n!(n+1)!}} \sin(\sqrt{2(n+1)} \lambda t) \cos(\sqrt{2n} \lambda t). $$

If we plug into $-\hat{C}_g\rho_F(0)\hat{S}_{ge}$ the expression for the thermal state of the field, $\sum_n p_n|n\rangle \langle n|$, and trace over the field space, the coherence element $\rho_{M,fg}(t)$ is identically zero (as well as for the $eg$ element):

$$ \rho_{M,fg}(t) = \text{Tr}_F \left[ -\hat{C}_g(t) \sum_n p_n|n\rangle \langle n| \hat{S}_{ge}(t) \right] = -\sum_{n,m} p_n m |\alpha\rangle \langle \alpha| \hat{S}_{ge}(t)(m) $$

$$ = -\sum_{n,m} p_n m |\alpha\rangle \langle \alpha| \hat{S}_{ge}(t)\hat{C}_g(t)|n\rangle = 0 $$

The coherence element $\rho_{M,fe}(t)$ is obtained by tracing over the field subspace of the matrix element $\rho_{I,fe}(t)$:

$$ \rho_{M,fe}(t) = \text{Tr}_F \left[ -\hat{S}_{fg}(t)\rho_F(0)\hat{S}_{ge}(t) \right] $$

$$ = -\sum_m |\alpha\rangle \langle \alpha| \hat{S}_{fg}(t)\rho_F(0)(m). $$

For a coherent state, we plug $\rho_F(0) = |\alpha\rangle \langle \alpha|$ (with $|\alpha| = e^{-\frac{1}{2}|\alpha|^2} \sum_n \frac{\alpha^n}{\sqrt{n!}} |n\rangle$) into Eq. 13 and get the following expression for the excited-state coherence element

$$ \rho_{M,fe}(t) = \frac{1}{2} e^{-|\alpha|^2} \sum_n \frac{|\alpha|^2 n^n}{n!} \sin^2(\sqrt{2n}\lambda t) $$

$$ = \frac{1}{2} e^{-\bar{n}} \sum_n \frac{\bar{n}^n}{n!} \sin^2(\sqrt{2\lambda t}). $$

For the case of thermal field, with $\rho_F(0) = \sum_n p_n|n\rangle \langle n|$, we get

$$ \rho_{M,fe}(t) = \frac{1}{2} \sum_n p_n \sin^2(\sqrt{2n}\lambda t) $$

$$ = \frac{1}{2} \sum_n \frac{\bar{n}^n}{(1+\bar{n})^{n+1}} \sin^2(\sqrt{2\lambda t}). $$
In addition, we can also show that during the interaction of the thermal light with the $V$ system, the reduced density matrix of the light, $\rho_F(t)$, remains diagonal. To show that we trace $\rho_I(t)$ of Eq. 10 over the material subspace, and use the the equalities of Eq. 9. The result obtained is

$$\rho_F(t) = \text{Tr}_M[\rho_I(t)] = \sum_i \langle i | \rho_I(t) | i \rangle$$

$$= -2 \hat{S}_{fg}(t) \rho_F(0) \hat{S}_{ge}(t) + \hat{C}_g(t) \rho_F(0) \hat{C}_g(t)$$

$$= \sum_n p_n \sin^2(\sqrt{2n\lambda t}) \langle n-1 | n \rangle$$

$$+ \sum_n p_n \cos^2(\sqrt{2n\lambda t}) \langle n | n \rangle,$$

which represents a diagonal reduced density matrix $\rho_F(t)$.

We use the above analytical expressions for the excited states coherence to compare with our numerical results and verify our numerical simulations for the density matrix dynamics. In Fig. 4 we show the real part of the excited state coherence element of the density matrix $\rho_{M,fe}(t)$, obtained for the field initially in a coherent state. In blue is the result obtained from the numerical propagation, whereas in red is the result obtained using Eq. 14. In Fig. 5, we show the comparison of the analytical (following Eq. 15) and numerical calculation for the excited state coherence obtained for the thermal field. Note the remarkable similarity of the results obtained for the coherent state of the light and the thermal state! Figures 4 and 5 confirm unequivocally our numerical propagation for the density matrix.

**Interaction of $V$ system with two-mode field.**

Here we show that, similar to the interaction of a single-mode states of the light, the interaction with two-mode states of a coherent state and thermal state, induce excited-state coherence.

In Fig. 6 we show the dynamical measures, as discussed.
in the main text, of the interaction of a $V$ system with two-mode of a coherent state. In Fig. 7 we show the same dynamical measures obtained for the interaction of a $V$ system with two-mode thermal state of the light.

Spectrum of the excited-state coherent dynamics

In Fig. 8 we show the spectrum obtained by Fourier-transform of the excited-state correlation function $C(t) = \text{Tr} \left[ \rho_{M,gg}(0) \rho_{M,ee}(t) \right]$. The spectrum reveals the harmonics of the energy difference between the excited-state vibrational eigenstates $\omega_{ex} \approx 0.0011$ a.u.

FIG. 7: (color online.) Populations (top), coherences (middle) and partial traces (bottom) obtained for the interaction of a two-mode thermal light with $V$ system.

FIG. 8: (color online). The spectrum obtained by Fourier-transform of the excited-state molecular auto-correlation function $C(t) = \text{Tr} \left[ \rho_{M,gg}(0) \rho_{M,ee}(t) \right]$.

Potentials parameters

Below are the potentials parameters used for the two-state Born-Oppenheimer molecular dynamics. The PESs are essentially the $X$ and $A$ states of the Li$_2$ molecule, but only with the $A$ state shifted in energy [1].

TABLE I: The parameters, in atomic units, for PESs used for the molecular simulations.

|   | $V_g$   | $V_e$   |
|---|---------|---------|
| $D$ | 0.0378492 | 0.0426108 |
| $b$ | 0.4730844 | 0.3175063 |
| $r_0$ | 5.0493478 | 5.8713786 |
| $T$ | 0       | 0.0911267 |

[1] G. Herzberg, in *Molecular Spectra and Molecular Structure; I. Spectra of Diatomic Molecules*, Krieger Publishing Company, Malabar, Florida, (1950).