Exciton dynamics in photosynthetic complexes: excitation by coherent and incoherent light

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Abstract. In this paper, we consider the dynamics of a molecular system subjected to external pumping by a light source. Within a completely quantum mechanical treatment, we derive a general formula, which enables us to assess the effects of different light properties on the photo-induced dynamics of excitations in a molecular system. We show that, once the properties of light are known in terms of a certain two-point correlation function, the only information needed to reconstruct the system dynamics is the reduced evolution superoperator. The latter quantity is, in principle, accessible through ultrafast nonlinear spectroscopy. Considering a direct excitation of a small molecular antenna by incoherent light, we find that excitation of coherences is possible due to the overlap of homogeneous line shapes associated with different excitonic states. In Markov and secular approximations, the amount of coherence is significant only under fast relaxation, and both the populations and coherences between exciton states become static at long times. We also study the case when the excitation of a photosynthetic complex is mediated by a mesoscopic system. We find that such a case can be treated by the same formalism with a special correlation function characterizing ultrafast fluctuations of the mesoscopic system. We discuss bacterial chlorosome as an example of such a mesoscopic mediator and propose that the properties of energy-transferring chromophore–protein complexes might be specially tuned to the fluctuation properties of their associated antennae.

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1. Introduction

In recent years, the primary processes in photosynthesis have received renewed interest from a broader physical community, thanks to the experimental observation of coherent energy transfer in some photosynthetic systems. The groundbreaking coherent two-dimensional electronic spectroscopy (2D-ES) experiment of Engel et al [1] has led to a new appreciation of the role that may be played by coherent dynamics in excitation energy transfer (EET), and of the quantum mechanical nature of photosynthetic systems in general [2]. Special theoretical effort has been made to understand the role of noise [3]–[9] in the dynamics of EET and the role of coherence [10]–[14] and entanglement [15] in excitonically coupled systems. On the experimental front, the method of coherent 2D-ES [16, 17] has established itself as a tool opening a new window into the details of energy transfer dynamics in photosynthetic [18]–[23] and other molecular systems [3, 24, 25]. Coherent effects have recently been reported in different molecular systems, often biologically relevant [25, 26] and even at room temperature [27, 28]—a generality that asks for a search for a possible evolutionary advantage underlying their abundance in photosynthetic pigment–protein complexes.

The principal pigment molecules responsible for the primary processes of photosynthesis are chlorophylls (Chls) and bacteriochlorophylls (BChls) [29, 30]. They are involved in the accumulation of light energy via the EET to specific pigment–protein complexes—reaction centers. Spectral variability of photosynthetic light-harvesting pigment–protein complexes arises either from excitonic interactions between pigment molecules or from their interactions with protein surroundings. Both of these interactions are the factors determining the excitation dynamics in light harvesting [31]. Excitonic aggregates are subject to interaction with two types of environments, and they provide the means for transferring energy from one environment...
to another. The first of these environments, the radiation, is, under natural conditions, at much higher temperature than the second environment, the protein scaffold and indeed the photosynthetic chemical machinery as a whole. The excess of photons of a suitable wavelength in the radiational environment is used to excite spatially extended antenna systems that concentrate excitation energy to the reaction center, which in turn drives charge transfer processes across cellular membranes to create the transmembrane potential and the pH gradient [29].

Non-equilibrium processes occurring in photosynthetic systems during light harvesting are conveniently described by reduced density matrix (RDM) theory [31]–[33], which has the advantage of being applicable to disordered statistical ensembles that the experiments often deal with. However, with recent 2D experiments that enable us to distinguish homogeneous and inhomogeneous spectral broadenings, and with the progress in single molecular spectroscopy [34], we can gain insights into the time evolution characteristic of single molecules interacting with their environment [35, 36]. This fact enables us to return to the wavefunction formalism and to look at light harvesting from the point of view that takes the superposition principle of quantum mechanics seriously. It has been shown that such an approach yields many interesting insights into the emergence of the classical properties of the molecular system from their underlying quantum mechanical nature [37, 38]. As the light-harvesting processes seem to operate at the interface between classical and quantum worlds, it seems appropriate to look at them from the point of view of the decoherence program of Zeh, Zurek and others [39, 40]. A central role in understanding the unique properties of quantum systems is played by the notion of entanglement. Recently, entanglement of photosynthetic systems has been studied under different models of the environment by Plenio and co-workers [9]. Here, we aim to stress the central role played by entanglement of electronic degrees of freedom (DOF) with its environment in EET.

The process of light harvesting could then be described as follows. First, the system is in an ‘equilibrium’ initial state $\Psi_0$ characterized by the excitonic ground state $|g\rangle$, the state of protein (phonon) environment $|\Phi_B\rangle$ corresponding to this electronic ground state and some state of light $|X_0\rangle$, i.e.

$$|\Psi_0\rangle = |g\rangle|\Phi_B\rangle|X_0\rangle.$$  

(1)

The light harvesting occurs when the state of light is such that the time evolution of the system leads to population of higher excited states $|e_n\rangle$ of photosynthetic antenna. These states are formed from excited states of Chls and other chromophores, such as carotenoids [31]. We denote these combined excited states as excitons. In the first approximation, the photosynthetic antenna remains in the excited state until the excitation energy is transferred to the reaction center. This happens much faster than the competing process of spontaneous emission, which can therefore be neglected in our discussion. When the interaction of the antenna with light is switched on, the change occurring in the ground state portion of the total state vector after the passage of time $\Delta t$ is

$$|\Psi_0\rangle \to \alpha_{\Delta t}|g\rangle|\Phi_B\rangle|X_0\rangle + \sum_n \hat{\rho}_{\Delta t}^{(n)}|e_n\rangle|\Phi_B\rangle|X_\prime\rangle.$$  

(2)

The subsequent time evolution of the excited state portion of the state vector is independent of the ground state part, and we can thus look at it separately. Because we neglect spontaneous emission, any excitation to a higher excited state, as well as transitions between exciton states due to the light, the state vector $|X_\prime\rangle$ remains approximately unentangled with excitons and the
protein bath for the rest of the energy transfer process. It can therefore be omitted. The initial state for the energy transfer process thus reads as

$$|\Psi_e(t_0)\rangle = \sum_n \beta^{(n)}(t_0)|e_n\rangle|\Phi_B\rangle,$$

where we omitted the lower index $\Delta t$. If the basis of the states $|e_n\rangle$ is chosen so that the molecular Hamiltonian is diagonal, the energy transfer occurs only due to interaction of excitons with their surrounding environment. This interaction leads to an entanglement of excitons with the environment

$$|\Psi_e(t)\rangle = \sum_n \beta^{(n)}(t)|e_n\rangle|\Phi_B^{(n)}(t)\rangle.$$

After a sufficiently long time, the environment state vectors corresponding to different electronic states diverge maximally, and the reduced density (RDM) matrix becomes diagonal in some basis, i.e.

$$\rho(t) = \text{tr}_B[|\Psi_e(t)\rangle\langle\Psi_e(t)|] = \sum_{mn} \beta^{(m)}(t)\langle\beta^{(m)}(t)\rangle^*\langle\Phi_B^{(m)}(t)|\Phi_B^{(n)}(t)\rangle|e_n\rangle\langle e_m|.$$ (5)

Often, to a good approximation, such a preferred basis is the one in which the electronic Hamiltonian is diagonal, the so-called excitonic basis. However, notable corrections to this rule are predicted, even for weak system–bath coupling [14, 41].

The final state of the energy transfer is the one in which just reaction centers are populated

$$|\Psi_e(t)\rangle = \sum_k \beta^{(RC_k)}(t)|e_{RC_k}\rangle|\Phi_B^{(RC_k)}(t)\rangle.$$ (6)

The last step of the energy transfer, from the antenna to the reaction center, is often slower than typical transfer times between antenna complexes, and so the final state is well localized on the reaction center, and coherences between individual reaction centers or between the reaction center and other antennae are unlikely to survive.

It is clear from the above discussion that decoherence during the energy transfer in the antenna is determined by the evolution of the environmental DOF. The decoherence from the rest of the system might be required for the localization of energy in the reaction center, but there is no obvious reason for fast decoherence during the initial steps of energy transfer in the antenna, apart from the fact that a bath formed by a completely random disordered environment would lead to just such a fast decoherence. It has been suggested before that the protein environment might play a more active role in steering and protecting electronic excitation [1, 26], and controlling the decoherence might be one of the possible pathways to a more robust EET.

There is, however, one important caveat in the above scheme. The initial condition, equation (3), has been introduced artificially into equation (2) as a result of an interaction occurring during some short time interval $\Delta t$. If the system is continuously pumped, individual contributions similar to equation (3) will interfere, possibly disabling any effect of cooperative involvement of the bath. It is even more important to consider the question of what the effects of natural sunlight are [42], i.e. whether or not the coherent scenario outlined above is plausible for the photosynthetic system in vivo. This depends strongly on the nature of the excitation...
process, whether it occurs in discrete independent jumps of the kind described by equation (2), or continuously over a long period of uncertainty interval of the photon arrival. The former view is usually held in support of the relevance of ultrafast spectroscopic findings for the in vivo function of the photosynthetic systems [13]. Below we attempt to put these ideas into a mathematical form. We derive a general formula that enables us to describe all these regimes by a unified formalism and also enables us to place the observables of ultrafast coherent spectroscopy in perspective with the dynamics under natural conditions. In a somewhat extended form, our result is also applied to another case cited in support of the utility of coherent dynamics in photosynthetic systems, a case where a small photosynthetic complex is excited through another, possibly mesoscopic, antenna [13].

This paper is organized as follows. The next section introduces a rather general model of photosynthetic aggregate and discusses the dynamics of a system excited by coherent pulsed light and the observables of the ultrafast nonlinear spectroscopy. Section 3 is concerned with the excitation of a photosynthetic system by the light from a general source. Implications of the theory for excitation by thermal and coherent light, as well as for excitation mediated by the mesoscopic system, are discussed in section 4.

2. Excitation by coherent pulsed light and nonlinear spectroscopy

Let us now consider experimental methods that provide information about the time evolution of excited states of photosynthetic systems. About the photosynthetic system we assume that it can be described by a general Hamiltonian

$$\dot{H} = H_B + H_M + H_{M-B},$$

where $H_B$, $H_M$ and $H_{M-B}$ represent thermal bath including intra-molecular vibrations, electronic DOF of the molecular system and their mutual interaction. The Hamiltonian $H_M$ is of a Frenkel exciton type [19, 31]. It has a band structure with a single ground state $|g\rangle$ and one-exciton states $|e_n\rangle$. To allow efficient EET, the radiationless relaxation from $|e_n\rangle$ states to the ground states has to be negligible on the timescale of the EET process, and the terms mediating such transitions are therefore omitted from $H_M$. Such an omission does not affect the relaxation of the excitons in the one-exciton band, which proceeds according to the detailed balance between the excitonic states. Because of the typical timescale of EET processes, spectroscopy with ultrashort time resolution is a necessary tool for its investigation. The interaction of the pulsed coherent light with the photosynthetic system is well described in semi-classical approximation [43]. The electric field of the light is then considered as an external parameter of the system Hamiltonian. Electronic DOF can be prepared very fast in an excited state, not affecting, to a good approximation, the bath DOF. Thus, in an experiment with an ideal time resolution, we would have the system prepared in the excited state, equation (3). The time evolution of the system is governed by the Schrödinger equation

$$\frac{\partial}{\partial t} |\Psi_e(t)\rangle = -\frac{i}{\hbar} (H_B + H_M + H_{M-B}) |\Psi_e(t)\rangle,$$

with $|\Psi_e(t)\rangle = 0$ for $t < t_0$. The initial condition in equation (8) is provided by an ultrafast event of the molecule–radiation interaction. The formal solution of this equation reads $|\Psi_e(t)\rangle = U_B(t) U_M(t) U_{M-B}(t) |\Psi_e(t_0)\rangle$, where we defined evolution operators $U_B(t)$, $U_M(t)$ of the bath and
the molecule, respectively, as

\[ U_B(t) = \Theta(t - t_0) \exp \left\{ -\frac{i}{\hbar} H_B(t - t_0) \right\}, \tag{9} \]

\[ U_M(t) = \Theta(t - t_0) \exp \left\{ -\frac{i}{\hbar} H_M(t - t_0) \right\}, \tag{10} \]

and the remaining interaction evolution operator as

\[ U_{M-B}(t) = \Theta(t - t_0) \exp \left\{ -\frac{i}{\hbar} \int_{t_0}^t d\tau U_B^\dagger(\tau)U_M^\dagger(\tau)H_{M-B}U_M(\tau)U_B(\tau) \right\}. \tag{11} \]

After excitation, the process of energy transfer proceeds according to the description presented in the Introduction and can be experimentally monitored.

### 2.1. Evolution superoperator

Matrix elements of the RDM of the molecule, which holds information about the population probabilities and the amount of coherence between electronic states, are given by the expectation value of projectors \(|e_n \rangle \langle e_m|\),

\[ \rho_{nm}(t) = \langle \Psi_e(t)|e_m \rangle \langle e_n|\Psi_e(t) \rangle = \text{tr}_B \{ \langle e_n|\Psi_e(t) \rangle \langle \Psi_e(t)|e_m \rangle \}
\]

\[ = \langle e_n|\text{tr}_B(U_M(t)U_{M-B}U^\dagger_B) \sum_{ab} B^{(a)}(\beta^{(b)})^* \langle a| \langle \Phi_B|U_{M-B}^\dagger U_M^\dagger(t)|e_m \rangle W_{e0} \rangle \langle b| \langle \Phi_B|U_B|e_n \rangle \}. \tag{12} \]

This can be rewritten by defining an evolution superoperator \( \mathcal{U}(t) \), which acts on the initial density matrix \( \rho_0 W_{eq} \), i.e.

\[ \rho_{nm}(t) = \text{tr}_B \{ \langle e_n|W(t)|e_m \rangle \} = \langle e_n|\mathcal{U}^{(e)}(t) \rho_0 W_{eq} |e_m \rangle. \tag{13} \]

The matrix elements of the superoperator read as

\[ \mathcal{U}^{(e)}_{abcd}(t) = \langle a|U_M(t)U_{M-B}(t)|c \rangle \ldots \langle d|U_{M-B}^\dagger U_M^\dagger(t)|b \rangle, \tag{14} \]

where the ellipsis denotes where an operator on which \( \mathcal{U}^{(e)}(t) \) acts has to be inserted. The reduced evolution operator \( \tilde{\mathcal{U}}^{(e)}(t) \) defined as

\[ \tilde{\mathcal{U}}^{(e)}(t) = \text{tr}_B \{ \mathcal{U}^{(e)}(t) W_{eq} \} \tag{15} \]

contains information about the evolution of the RDM only.

### 2.2. Nonlinear spectroscopy

In nonlinear spectroscopy, coherent laser light is used to investigate the dynamics of molecular systems by applying special sequences of pulses. Some pulses act to induce non-equilibrium dynamics (pump), and other pulses act to monitor (probe) the evolution after the pump. One of the most advanced of these methods, coherent 2D-ES [16, 44], measures the response of a system to three pulses traveling in different directions \( k_1, k_2 \) and \( k_3 \). The detection is arranged in such a way (measuring in the direction \(-k_1 + k_2 + k_3\) that the signal is predominantly of the third order, with contributions of one order per pulse [43]. Let us denote delays between the
and analogically for $U$ ground state evolution during interval $T$ sample and is usually measured in the frequency domain nonlinear signal is recorded. The signal corresponds indirectly to nonlinear polarization of the system during the time delay $	au$ and secondly, a contribution that involves evolution in the ground state

$$W_{k clergy}(t, \tau) = |\Psi_B\rangle \langle |g\rangle \langle \Psi_B| \mu \langle g| \mu \rangle.$$  

(16)

Here, we denote the pulses acting on the state vector by their corresponding wave vectors in the upper index, and the excited state or ground state bands by the lower index $g$ and $e$, respectively. For these statistical operators we can define evolution superoperators $U^{(g)}(t)$, $U^{(g)}(t)$, $U^{(ge)}(t)$ and $U^{(ge)}(t)$ in analogy with equations (13) and (14), so that

$$W_{k clergy}(t, \tau) = U^{(g)}(t)U^{(ge)}(\tau)\langle \Psi_B| \mu \langle g| \mu \rangle.$$  

(18)

and

$$W_{k clergy}(t, \tau) = U^{(g)}(t)U^{(ge)}(\tau)\langle \Psi_B| \mu \langle g| \mu \rangle.$$

(19)

The superoperator $U^{(ge)}(t)$ is the evolution superoperator of a coherence projector $\sum_n |e_n\rangle \langle g|$ and analogically for $U^{(ge)}(t)$. After a delay $T$, the third ultrafast pulse is applied and the nonlinear signal is recorded. The signal corresponds indirectly to nonlinear polarization of the sample and is usually measured in the frequency domain

$$E^{(3)}(\omega, T, \tau) \approx -\frac{\omega}{n(\omega)} \text{tr}\{\mu U^{(ge)}(\omega)\mu U^{(g)}(T)U^{(ge)}(\tau)\mu \rho_g \mu + U^{(g)}(T)U^{(ge)}(\tau)\rho_g \mu^2\} W_{eq}.\]  

(20)

Here, we denoted

$$U^{(ge)}(\omega) = \int_0^\infty dt \ e^{i\omega t} U^{(ge)}(t),\]$$

(21)

and $\rho_g = |g\rangle \langle g|$. The actual intensity of the signal depends on the intensity of the incident fields as well as the sample thickness. A detailed discussion of these dependencies can be found in e.g. [43].

In 2D coherent spectroscopy, the signal is, in addition, Fourier transformed along the time delay $\tau$, so that the spectrum is defined as

$$S_{2D}(\omega_t, T, \omega_r) = \int_{-\infty}^{\infty} d\tau \ e^{-i\omega_t \tau} E^{(3)}(\omega_t, T, \tau).$$

(22)

The spectrum defined in this way has a suitable interpretation of an absorption–absorption and absorption–stimulated emission correlation plot, with different waiting times $T$ between the two events. The 2D spectrum is, in practice, measured with finite pulses, and the measured time domain signal is thus a triple convolution of the responses to a delta pulse excitation, with the actual finite pulses [45].

From this rough sketch of the principles and the information content of the coherent 2D spectroscopy, it should be clear that 2D spectroscopy is aimed at disentangling the dynamics of the system during the time delay $T$. In the so-called Markov approximation, when the dynamics in time intervals $\tau$, $T$ and $t$ are assumed separable, and the bath is assumed stationary, the ground state evolution during interval $T$ can be neglected. Then 2D measurement essentially
accesses the reduced evolution superoperator, equation (15), and possibly also the more general superoperator

\[ \mathcal{U}^{(e)}(t, \tau) = \text{tr}_B \{ \mathcal{U}^{(e)}(t) \mathcal{U}^{(ge)}(\tau) \mathcal{W}_{\text{eq}} \}. \]  

(23)

We will show below that this superoperator, together with the light properties, determines the way in which the molecule is excited in general case, even at illumination by natural light.

3. Excitation by light

In order to account for the general properties of light we will consider the problem fully quantum mechanically, and assume only deterministic evolution of the system wavefunction. The Hamiltonian of the system reads as

\[ H = H_M + H_B + H_R + H_{M-B} + H_{M-S} + H_{B-S} + H_{B-R} + H_{R-S}. \]  

(24)

We have divided the system into a molecule \( H_M \), its environment or bath \( H_B \), the radiation \( H_R \) and the light-emitting body (LEB) that produces it, e.g. sun or laser medium \( H_S \). It seems reasonable to neglect a direct interaction between the molecule (together with its environment) and the molecules of the LEB. Consequently, the terms \( H_{M-S} \) and \( H_{B-S} \) can be disregarded. To make the treatment simpler we can also neglect the interaction between radiation and the molecular environment, \( H_{B-R} \). The assumption is that the energy of the molecular transition that is used to harvest light for photosynthetic purposes is much larger than any of the transitions in this environment and the two regions of the light spectrum can thus be treated separately. One can also assume that the part of the radiation spectrum that would interact with the bath is simply filtered out, and the environment is kept at a certain temperature by other means.

3.1. Radiation entangled with the LEB

An important special case is the one in which the radiation and the LEB are at equilibrium with each other so that the radiation is described by the canonical equilibrium density matrix

\[ W_R^{(eq)} = \sum_{\lambda,q} \frac{e^{-N_{\lambda,q} h \omega q / kT}}{Z_{\lambda,q}} |N_{\lambda,q}\rangle \langle N_{\lambda,q}|. \]  

(25)

Here, \( |N_{\lambda,q}\rangle \) is the \( N \)-photon state of the radiation mode with polarization vector \( e_\lambda \) and wave vector \( q \). As we have already noted above, the statistical concept of the density matrix will be replaced here with the concept of entangled states, so that we can describe the whole system by its state vector. Thus, we introduce a state vector

\[ |\Xi(t)\rangle = \sum_{\lambda,q} \sum_{N_{\lambda,q}} c_{N_{\lambda,q}}(t) |N_{\lambda,q}\rangle |\phi_{N_{\lambda,q}}(t)\rangle, \]  

(26)

in which the light is fully entangled with the states \( |\phi_{N_{\lambda,q}}(t)\rangle \) of the LEB. The LEB states have to fulfill the condition

\[ \langle \phi_{N_{\lambda,q}}(t) | \phi_{N_{\lambda',q'}}(t) \rangle = \delta_{\lambda,\lambda'} \delta_{q,q'} \delta_{N_{\lambda,q} N_{\lambda',q'}}, \]  

(27)

so that when the total density matrix of the LEB and radiation is averaged over the states of the body, we obtain equation (25). \( W_R^{(eq)} \) is recovered provided that

\[ |c_{N_{\lambda,q}}(t)|^2 = \frac{e^{-N_{\lambda,q} h \omega q / kT}}{Z_{\lambda,q}}. \]  

(28)
In the absence of the light-absorbing body, the evolution of the state \( |\Xi(t)\rangle \) is governed by the Hamiltonian
\[
H_L = H_R + H_S + H_{R-S}
\] (29)
and
\[
U_L(t) = \Theta(t-t_0) \exp \left\{ -\frac{i}{\hbar} (H_S + H_R + H_{R-S})(t-t_0) \right\}
\] (30)
is the corresponding evolution operator.

### 3.2. Excited state dynamics under pumping

For the subsequent treatment of the system dynamics, we introduce the interaction picture with respect to Hamiltonian operators \( H_M, H_B \) and \( H_L \) and work with the state vector
\[
|\Psi_1(I)\rangle(t) = U_M^\dagger(t)U_B^\dagger(t)U_L^\dagger(t)|\Psi_1(t_0)\rangle.
\] (31)
As discussed in section 2, there are no terms in the Hamiltonian connecting the ground and excited states, except for the radiative transitions. In the first order of perturbation theory, we may describe the excited state part of the state vector via a source term
\[
|S'(t)\rangle = -\frac{i}{\hbar} H_{M-R}(t)|\Psi_0\rangle.
\] (32)
The source terms are derived in appendix A. The equation of motion for the state vector, equation (31), thus reads as
\[
\frac{\partial}{\partial t}|\Psi_e^{(I)}(t)\rangle = -\frac{i}{\hbar} H_{M-B}(t)|\Psi_e^{(I)}(t)\rangle - \frac{i}{\hbar} H_{M-R}(t)|\Psi_0\rangle,
\] (33)
with the initial condition \( |\Psi_e^{(I)}(t_0)\rangle = 0 \). Next we apply the dipole approximation
\[
H_{M-R} \approx -\mu \cdot E_T(r),
\] (34)
where \( \mu \) is the transition dipole moment operator of the aggregate
\[
\mu = \sum_n d_n |e_n\rangle\langle g| + \text{h.c.}
\] (35)
and \( E_T \) is the operator of the (transversal) electric field of the radiation. Using the results of appendix B and definitions therein, the source term can be written as
\[
|S'(t)\rangle = \frac{1}{\hbar} \sum_{\lambda q} \mu_{\lambda q}(t) f_{\lambda q} a_{\lambda q}(t)|g\rangle|\Phi_B\rangle|\Xi_0\rangle.
\] (36)
With this form of the source term, we can find the state into which the molecule is weakly driven by any type of light.

So far we have treated the problem systematically using the wavefunction approach. The time evolution of the system wavefunction is governed by equation (33). To find the probabilities of creating population on and coherence between certain excitonic levels \( |e_a\rangle \), we solve equation (33) formally,
\[
|\Psi_e^{(I)}(t)\rangle = \int_{t_0}^t d\tau U_{M-B}(t-\tau)|S'(\tau)\rangle.
\] (37)
Here, we used the fact that $|\Psi_e(t)| = 0$ for $t < t_0$. Now let us evaluate the matrix element $P_{ab}(t) = \langle \Psi_e(t)|P_{ab}|\Psi_e(t)\rangle$ of a projector

$$P_{ab} = |e_a\rangle\langle e_b|,$$

which gives the probability of finding the molecule in state $|e_a\rangle$ if $a = b$, or characterizes the amount of coherence between states $|e_a\rangle$ and $|e_b\rangle$ if $a \neq b$. Note that we have removed the interaction picture, equation (31). We have

$$P_{ab}(t) = \int_0^t dt \int_0^t dt' \sum_{\lambda q, \lambda' q'} f_{\lambda q}(f_{\lambda' q'})^* \times \langle \Xi_0|\tilde{a}_{\lambda q}^\dagger(\tau)\tilde{a}_{\lambda' q'}(\tau')|\Xi_0\rangle \langle e_b|\tilde{U}(e)(t-\tau, \tau-\tau')\rho_0^{0|\lambda q, \lambda' q'}|e_a\rangle,$$  

(39)

where the evolution superoperator $\tilde{U}(e)(t-\tau, \tau-\tau')$ has been defined in equation (23).

In equation (39), the light is represented by a first-order correlation function

$$I_{\lambda q, \lambda' q}(\tau, \tau') = f_{\lambda q}(f_{\lambda' q'})^*(\Xi_0|\tilde{a}_{\lambda q}^\dagger(\tau)\tilde{a}_{\lambda' q'}(\tau')|\Xi_0)$$

(40)

(see e.g. [46]), which comprises all its relevant properties. We also denoted

$$\rho_{\lambda q, \lambda' q} = \frac{1}{\hbar^2}\langle \mu_{\lambda q}|g\rangle\langle g|\mu_{\lambda' q'}.$$

(41)

The quantities $P_{ab}(t)$ are the matrix elements of the RDM ($P_{ab}(t) = \langle e_b|\rho(t)|e_a\rangle$) of the system, which reads as

$$\rho(t) = \int_0^t dt \int_0^t dt' \tilde{U}(e)(t-\tau, \tau-\tau') \sum_{\lambda q, \lambda' q'} \rho_{\lambda q, \lambda' q}^{0}I_{\lambda q, \lambda' q}^{(1)}(\tau, \tau').$$

(42)

For a weakly driven system, equation (42) has a very wide range of applicability. We will discuss its application to thermal light and pulsed coherent light in the following section.

4. Discussion

A thorough discussion of excitation dynamics in molecular systems excited by incoherent light was given in [42]. Molecular systems were considered without the bath effect, which is, however, significant for light harvesting. Equation (42) contains reduced evolution superoperator of the molecular system so that the state of the system created by the incident light depends on its reduced dynamics. To fully utilize equation (42) one needs to consider non-Markov effects in the excitation process, i.e. the dependence of the relaxation dynamics on delay $\tau - \tau'$. For many molecular systems of practical importance, the superoperator $\tilde{U}(e)$ will have to be evaluated in some low (2nd) order of perturbation theory with respect to system–bath interaction. Such theories are able to account for most of the effects of coherence [47]. The study of the general properties of the RDM $\rho(t)$, such as entanglement evolution [8], is then complicated by the fact that $\rho(t)$ approximated in lower order system–bath theory might not be completely positive. However, by combination of simulations and nonlinear spectroscopic experiments, it might be possible to obtain $\tilde{U}(e)$ with sufficient confidence to allow quantitative studies of both energy transfer efficiency and its mode (coherent versus incoherent) under different excitation conditions. Since it is not possible to consider the general case of such dynamics analytically, we will commit ourselves to some simple cases.
In the so-called secular and Markov approximations (see e.g. [32]), matrix elements of the evolution superoperator governing the coherences take a very simple form. First, it is possible to separate the two time arguments in the superoperator $\tilde{U}^{(e)}(t, \tau)$ so that

$$\tilde{U}^{(e)}(t, \tau) = \tilde{U}^{(e)}(t)\tilde{U}^{(e)}(\tau).$$  \hspace{1cm} (43)

Since each coherence is independent of the population dynamics and of other coherences, the one-argument superoperator elements read as

$$\tilde{U}^{(e)}_{abab}(t) = e^{-i\omega_{ab}t - (\Gamma_a + \Gamma_b)t}$$  \hspace{1cm} (44)

and

$$\tilde{U}^{(eg)}_{agag}(t) = e^{-i\omega_{ag}t - \Gamma_at}.$$  \hspace{1cm} (45)

Here the dephasing rate

$$\Gamma_a = \gamma_0 + \frac{1}{2} K_a$$  \hspace{1cm} (46)

comprises the pure dephasing rate $\gamma_0$ and the rate $K_a$ of depopulation, i.e. the sum of transition rates from state $|e_a\rangle$ to other states. A simplified treatment of the populations is possible for the states that are only depopulated, i.e. no contributions to the population can be attributed to the transfer from other levels. They are found at the top of the energetic funnel of the antenna. For these states we have

$$\tilde{U}^{(e)}_{aaaa}(t) = e^{-K_at}.$$  \hspace{1cm} (47)

Equations (44)–(47) neglect all coherence transfer effects as well as possible coupling between the dynamics of population and coherence.

4.1. Excitation of coherences by thermal light

For an equilibrium thermal light the correlation function $I^{(1)}_{\lambda q, \lambda' q'}(\tau, \tau')$ depends only on the difference between the times $\tau$ and $\tau'$. As discussed above, $|\Xi_0\rangle$ represents the equilibrium of the system described by Hamiltonian $H_L$. The equilibrium density matrix is stationary, i.e.

$$U_L(0)|\Xi_0\rangle\langle \Xi_0|U_L^\dagger(t) = |\Xi_0\rangle\langle \Xi_0|,$$  \hspace{1cm} (48)

so we can write

$$I^{(1)}_{\lambda q, \lambda' q'}(\tau, \tau') = |f_{\lambda q}|^2 \langle \Xi_0|a_{\lambda q}^\dagger(\tau - \tau')a_{\lambda q}(0)|\Xi_0\rangle e^{i\omega_{\lambda q}(\tau - \tau')}\delta_{\lambda\lambda'}\delta_{qq'}$$

$$\equiv |f_{\lambda q}|^2 (\bar{I}_{\lambda q}(\tau - \tau')\delta_{\lambda\lambda'}\delta_{qq'}).$$  \hspace{1cm} (49)

It can be shown that

$$\bar{I}_{\lambda q}(-t) = \bar{I}_{\lambda q}^*(t).$$  \hspace{1cm} (50)

Assuming some simple form of a light correlation function, e.g.

$$\bar{I}_{\lambda q}(t) = \tilde{I}_{\lambda q}^0 e^{-(|t|/\tau_L) + i\omega_q t},$$  \hspace{1cm} (51)

we obtain for the populations

$$\rho_{aa}(t) = 2Re \sum_{\lambda q} \tilde{I}_{\lambda q}^0 [\rho_{\lambda q}]_{aa} \int_0^t d\tau \int_0^\tau d\tau' e^{i\omega_q(\tau - \tau')} e^{-\Gamma_a(\tau - \tau') - (\tau - \tau')/\tau_L - i(\omega_q - \omega_q)(\tau - \tau')}.$$  \hspace{1cm} (52)

Here, $[\rho]_{ab} \equiv \langle e_a|\rho|e_b\rangle$. We utilized equation (51) and the fact that, by definition (see equations (40) and (41)), the time $\tau$ corresponds to the action of the dipole moment operator from the left,
whereas time $\tau'$ corresponds to the same action from the right. At long times $t - t_0 \to \infty$, this yields

$$
\rho_{aa}^{\infty} = \sum_{\lambda q} 2 \frac{(\Gamma_a + \frac{1}{\tau_a}) I_{a q}^{0} [\rho_{a q}^{0}]_{a a}}{K_a (\omega_{a g} - \omega_q)^2 + (\Gamma_a + \frac{1}{\tau_a})^2}.
$$

(53)

However, neglecting the influence of environment as in [42] yields

$$
\rho_{aa}^{\text{long}}(t - t_0) = \sum_{\lambda q} \frac{\tau_a^{-1} 2 I_{a q}^{0} [\rho_{a q}^{0}]_{a a}(t - t_0)}{(\omega_{a g} - \omega_q)^2 + \frac{1}{\tau_a}},
$$

(54)

which grows linearly with time.

For coherences we have

$$
\rho_{ab}^{\infty} = 2 \sum_{\lambda q} I_{\lambda q}^{0} [\rho_{\lambda q}^{0}]_{a b} \frac{1}{i\omega_{a b} + (\Gamma_a + \Gamma_b)} \left[ \frac{1}{i(\omega_{a g} - \omega_q) + \Gamma_a + \frac{1}{\tau_a}} + \frac{1}{-i(\omega_{b g} - \omega_q) + \Gamma_b + \frac{1}{\tau_b}} \right],
$$

(55)

which turns into equation (53) for $a = b$ (with the additional assumption $K_a = 2\Gamma_a$). In case of no dephasing, the first fraction in equation (55) yields a delta function $\delta(\omega_{a b})$ [42]. Thus, for slow or non-existent relaxation due to interaction with the environment, the system is excited predominantly into a state represented by a diagonal RDM, as all coherence terms are negligible compared to the linearly growing population. For fast relaxation, the coherences may be of the same order of magnitude as the populations.

The case of very fast relaxation is particularly interesting. It was suggested previously that coherent dynamics can be relevant for the in vivo case, because the fluctuating light from the sun corresponds to a train of ultrafast spikes [13]. The relaxation of the antenna must be in such a case fast enough to prevent averaging over many such spikes. Equations (53) and (55) with large $K_a$ describe just such a situation. The RDM created by incoherent light resembles in a certain sense the one created by ultrafast pulses; it represents a linear combination of excitons. The coherences in equation (55) are, however, static at long times.

In our demonstration, we concentrated on a simple model assuming both Markov and secular approximations to be valid. The presence or absence of coherences has no effect on the population dynamics and thus on the transfer efficiency in such a case. More involved theories of the RDM dynamics [10, 11, 14] have to be used to investigate the role of coherences in energy transfer processes by equation (42).

4.2. Coherent pulsed light

In derivation of equation (42), we assumed a certain initial state $|Xi_0\rangle$ of the system composed of the light and its source. The condition that the light is in a stationary state, fully entangled with its source, has only been used to simplify the correlation function $I_{\lambda q, \lambda' q'}^{(1)}(\tau, \tau')$ for the case of the thermal light. In the general case, $|Xi_0\rangle$ will not represent an equilibrium state. It can indeed describe even systems such as a laser producing coherent Gaussian light pulses with some carrier frequency $\omega_0$ and a width parameter $\Delta$. If we, in addition, assume that the light is described by a single polarization, and that the dynamics after one such pulse are centered at time $t = \tau_0$, the light is described as

$$
\sum_{\lambda q, \lambda' q'} I_{\lambda q, \lambda' q'}^{(1)}(\tau, \tau') \equiv I_0 e^{-(\tau - \tau_0)^2/\Delta^2 - (\tau' - \tau_0)^2/\Delta^2}.
$$

(56)
The coherence element created by such light reads as

\[ \rho_{ba}(t) = e^{i\omega_{bg}t} \int_{t_0}^{t} dt \int_{t_0}^{t} dt' e^{-i(\omega_{bg}-\omega_g)t} e^{i(\omega_{bg}-\omega_g)t'} \times e^{-\Gamma_a(t-t')-\Gamma_b(t-t')} I_0 e^{-(t-t_0)^2/\Delta^2-(t'-t_0)^2/\Delta^2} 0 \rho_{ba}, \]  

(57)

where \( \rho_{ba} = \frac{1}{\sqrt{\pi}} \langle e_b|\mu|g \rangle \langle g|\mu|e_a \rangle \). In the limit of ultrashort pulses when \( e^{-(t-t_0)^2/\Delta^2} \rightarrow \alpha \delta(t-t_0) \), the pulse creates a pure state at \( \tau_0 \), which then dephases as

\[ \rho_{ba}(t) = \Theta(t-t_0) e^{-(\Gamma_a(t-t_0)+i\omega_0(t-t_0))} \rho_{ba}^0 I_0 \alpha^2. \]  

(58)

In the case of a finite pulse and no dephasing, our results coincide with those found in [42].

4.3. Mediated excitation

The major difference between excitation by the thermal light and a coherence pulse is in the occurrence of a sudden event which populates a nearly pure state of the excited state band. Clearly, a single molecule interacting with an ideal continuum of radiation modes in equilibrium does not experience such sudden events. Rather, its interaction with light corresponds to a continuous pumping, and the suddenness of the photon arrival is the consequence of our ability to register only classical outcomes. In order to register them we have to interact with the system and become entangled with it. Our experience is that macroscopic systems interacting with low-intensity light can be used to detect single photons, and certain more or less definite times can be attributed to their arrivals. Interaction of a photon with a macroscopic detector yields a temporal localization of the arrival event. A mesoscopic system may play the role of such a detector (mediator) that provides its fluctuations to be harvested by a dedicated nano-sized antenna. Green photosynthetic bacteria, from which the photosynthetic complex FMO was isolated, collect light mainly by means of the so-called chlorosomes [29, 48]. The chlorosome is a self-assembled aggregate of \( \sim 10^5 \) BChls and carotenoids with very little protein. The typical dimensions of the chlorosome are of the order of 100 nm [48]. It does not seem to be organized as an energy funnel [49, 50], and the energy transfer time between its main body and the base plate to which FMO complexes are attached is of the order of 120 ps [51], i.e. rather slow. The excitation in such a mesoscopic system may have enough time to become localized through interaction with the large number of the system’s DOF and arrive at the FMO complex in a particle-like, i.e. also temporally localized, fashion.

In this section, we will generalize our result, equation (42), for the case when the excitation of the photosynthetic systems occurs by transfer from another system. We will therefore assume that our molecule does not interact directly with light but is pumped in a similar fashion by another system. The source term, equation (36), is then generalized as

\[ |S'(t)\rangle = \frac{i}{\hbar} A(t)|g \rangle |\Phi_B \rangle \left( \sum_n \alpha_n(t) |\xi_n \rangle |\phi_n(t) \rangle \right). \]  

(59)

Here, \( A = \sum_{\alpha,n} |e_n \rangle |\xi_\alpha \rangle \langle \xi_\alpha | \langle g | + \text{h.c.} \) is the molecule–mediator interaction Hamiltonian and the time dependence results from the interaction picture

\[ A(t) = U_M^\dagger(t)U_A^\dagger(t)AU_A(t)U_M(t). \]  

(60)
We denoted the ground and excited states of the mediator by $|\xi_g\rangle$ and $|\xi_n\rangle$, respectively. The state of the molecule at long times is in analogy with equation (42)

$$\rho(t) = \int_{t_0}^{t} d\tau \int_{t_0}^{t} d\tau' U^{(e)}(t - \tau, \tau - \tau') \sum_{nn'} \alpha^*_n(\tau) \alpha_{n'}(\tau) \times \langle \xi_n | A(\tau) A(\tau') | \xi_{n'} \rangle \langle \phi_n(\tau) | \phi_{n'}(\tau') \rangle.$$  

(61)

The complicated two-point correlation function in equation (61) results from the pumping of the mediator similarly to the direct pumping of the molecule in equation (42). A mesoscopic system, especially when excited will, however, always exhibit fluctuations that will prevent the correlation function from having a simple smooth dependence without recurrences. Such recurrences can temporally localize the excitation events of the molecule. In such an excitation regime, when coherent dynamics from different excitation times do not interfere, optimization of the FMO’s energy channeling capability for the case of initially coherent states would be an advantage.

4.4. Outlook

More research into specific forms of both the light correlation function for different situations that may occur in vivo and the analogical interaction of systems like FMO with mesoscopic antennae is clearly needed. Ultrafast spectroscopic experiments play a pivotal role in this research by yielding information about the system’s response to light. To conclude on the utility of coherent dynamics for the function of the photosynthetic system is, however, only possible by taking into account the properties of light in natural conditions, for which the results of this paper provide the means. If the coherent dynamics observed in some photosynthetic chromophore–protein complexes has significance for their light-harvesting efficiency and these systems evolved to optimize it for their corresponding ecological situation, it can be expected that the properties of at least some parts of the photosynthetic machinery would be tuned to the fluctuation properties of their source of excitation. For plants and some bacteria, this may be sunlight; others, like FMO complexes, could be expected to be tuned to the properties of their associated chlorosomes.

To quantify the utility of coherent dynamics under the excitation scheme, equation (42), one would use quantitative estimates of the transfer efficiency into a trapping state that can be a part of the excited system, as e.g. in [7]. To evaluate the presence and the effect of the coherence under different excitation schemes, one would use a measure of coherence or entanglement recently developed in [8, 52]. Since incoherent light cannot address individual sites of excitonic systems, measurement of the mode entanglement [8] seems to be more appropriate than the site entanglement. An investigation of particular molecular systems under particular light conditions based on the formulation presented in this paper will be presented elsewhere.

5. Conclusions

In this paper, we have discussed the dynamics of a molecular system subjected to external pumping by a light source. With a completely quantum mechanical treatment, we have derived a general formula that enables us to study the effect of different light properties on the photo-induced dynamics of molecular systems. This formula naturally contains the system–environment interaction contribution to the excitation process which enters via the
appearance of the RDM dynamics. We show that, once the properties of light are known in terms of a certain two-point correlation function, the only information needed to reconstruct the system’s dynamics is the reduced evolution superoperator, which is in principle accessible through ultrafast nonlinear spectroscopy. This conclusion applies to any type of light and thus makes the results of ultrafast spectroscopic experiments universally relevant. Considering a direct excitation of a multilevel electronic system with secular relaxation, we found that excitation of coherences is possible due to overlap of homogeneous line shapes associated with different excitonic states. These coherences are, however, static and correspond to a change to the preferred basis set into which the system relaxes from the one defined by the bath only to the one defined by the action of both the light and the bath. When an excitation of a photosynthetic complex mediated by a larger, possibly mesoscopic, system is considered, our formalism predicts that the complex can harvest fluctuations originating from the non-equilibrium state of the mediator. Fluctuations of the mesoscopic system, such as chlorosomes, may time localize excitation events of the energy channeling complex, and excite the adjacent energy channeling complex coherently. It is likely that in such a case the properties of energy channeling complexes, like the well-known FMO complex, would be specially tuned to the fluctuation properties of their associated chlorosomes.

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Appendix A. Equations of motion with pumping terms

In this appendix, we derive equations of motion for the state vector, equation (31). The interaction picture Hamiltonian reads as

\[ H^{(i)}(t) = H_{M-B}(t) + H_{M-R}(t), \] (A.1)

where

\[ H_{M-B}(t) = U_M^\dagger(t) U_B^\dagger(t) H_{M-B} U_B(t) U_M(t) \] (A.2)

and

\[ H_{M-R}(t) = U_M^\dagger(t) U_L^\dagger(t) H_{M-R} U_L(t) U_M(t). \] (A.3)

The solution of the equation of motion for the state vector, equation (31), can be found formally as

\[ |\Psi^{(i)}(t)\rangle = \exp\left\{ -\frac{i}{\hbar} \int_{t_0}^{t} d\tau (H_{M-B}(\tau) + H_{M-R}(\tau)) \right\} |\Psi_0\rangle. \] (A.4)

We will assume that the system is initially in the state \( |\Psi_0\rangle \) of equation (1). With this choice we have

\[ H_{M-B}(t) |\Psi_0\rangle = 0. \] (A.5)
Assuming weak interaction with the radiation, so that it can be described by linear theory, we need to collect all terms in the expansion of equation (A.4) that include one occurrence of $H_{M-R}(t)$. Thanks to equation (A.5), however, all terms where $H_{M-R}(t)$ is not on the far right of the expression are equal to zero. Equation (A.4) therefore simplifies to a series

$$|\Psi^{(i)}(t)\rangle = |\Psi_0\rangle - \frac{i}{\hbar} \int_{t_0}^t d\tau H_{M-R}(\tau) |\Psi_0\rangle$$

$$- \frac{1}{\hbar^2} \int_{t_0}^t d\tau \int_{t_0}^\tau d\tau' H_{M-B}(\tau) H_{M-R}(\tau') |\Psi_0\rangle + \cdots .$$  \hspace{1cm} (A.6)

Now we introduce a projector $P_e$ that excludes the excitonic ground state $|g\rangle P_e = \sum_n |e_n\rangle \langle e_n|$. Applying this projector to equation (A.6) has only the effect of eliminating the first term of the series. Introducing abbreviations

$$|S(t)\rangle = -\frac{i}{\hbar} \int_{t_0}^t d\tau H_{M-R}(\tau) |\Psi_0\rangle$$ \hspace{1cm} (A.7)

$$|\Psi_e^{(i)}(t)\rangle = P_e |\Psi^{(i)}(t)\rangle ,$$ \hspace{1cm} (A.8)

we can write

$$|\Psi_e^{(i)}(t)\rangle = |S(t)\rangle - \frac{i}{\hbar} \int_{t_0}^t d\tau H_{M-B}(\tau) |S(\tau)\rangle$$

$$- \frac{1}{\hbar^2} \int_{t_0}^t d\tau \int_{t_0}^\tau d\tau' H_{M-B}(\tau) H_{M-B}(\tau') |S(\tau')\rangle + \cdots .$$ \hspace{1cm} (A.9)

It is possible to verify easily that this series is a solution of the equation

$$\frac{\partial}{\partial t} |\Psi_e^{(i)}(t)\rangle = -\frac{i}{\hbar} H_{M-B}(t) |\Psi_e^{(i)}(t)\rangle + \frac{\partial}{\partial t} |S(t)\rangle ,$$ \hspace{1cm} (A.10)

with the initial condition $|\Psi_e^{(i)}(t_0)\rangle = 0$.

**Appendix B. Pumping source terms**

Equation (A.10) is an equation of motion for the excited states of an excitonic aggregate pumped by a source term

$$|S'(t)\rangle = \frac{\partial}{\partial t} |S(t)\rangle = -\frac{i}{\hbar} H_{M-R}(t) |\Psi_0\rangle .$$ \hspace{1cm} (B.1)

The Hamiltonian $H_{M-R}$ will be assumed in the dipole approximation, equation (34), and the transverse field operator has the form

$$E_T(r) = -i \sum_{l \neq q} (e_{l-q} f_q(r) a_{lq}^\dagger - e_{s_q} f_q(r) a_{sq}),$$ \hspace{1cm} (B.2)

with

$$f_q(r) = \frac{\sqrt{\hbar\omega_q}}{2\epsilon_0 \Omega} e^{i q \cdot r} .$$ \hspace{1cm} (B.3)

Here, $\Omega$ is a quantization volume.
We consider a molecule much smaller than the wavelength of the light, so that \( e^{i \mathbf{q} \cdot \mathbf{r}} \) is constant in the volume of the molecule. The origin of the coordinates can thus be conveniently put into the molecule, yielding \( e^{i \mathbf{q} \cdot \mathbf{r}} \approx 1 \). The interaction Hamiltonian in equation (B.1) then reads as

\[
H_{M-R}(t) = i \sum_{\lambda q} \mu_{\lambda q}(t) f_{\lambda q}(0)a_{\lambda q}^\dagger(t) - i \mu_{\lambda q}(t) f_{\lambda q}(0)a_{\lambda q}(t),
\]  

(4.4)

where the creation and annihilation operators of the field are in the interaction picture with respect to Hamiltonian \( H_L \), i.e.

\[
a_{\lambda q}^\dagger(t) = U_{L}^\dagger(t) a_{\lambda q}^\dagger U_L(t), \quad (B.5)
\]

\[
a_{\lambda q}(t) = U_{L}^\dagger(t) a_{\lambda q} U_L(t). \quad (B.6)
\]

The transition dipole moment operator projected on the polarization vector of a mode \( \lambda q \) appears in the interaction picture with respect to Hamiltonian \( H_M \),

\[
\mu_{\lambda q}(t) = U_M^\dagger(t) \mathbf{\mu} \cdot \mathbf{e}_{\lambda q} U_M(t). \quad (B.7)
\]

The evolution operator \( U_L(t) \), equation (30), can be rewritten as

\[
U_L(t) = U_S(t) U_R(t) U_{R-S}(t), \quad (B.8)
\]

where

\[
U_{R-S}(t) = \Theta(t-t_0) \exp \{ -i \frac{\bar{\hbar}}{\hbar} \int_{t_0}^t d\tau U_S^\dagger(\tau) U_R^\dagger(\tau) H_{R-S} U_R(\tau) U_S(\tau) \}. \quad (B.9)
\]

Since Hamiltonian \( H_S \) commutes with the radiation operators and

\[
U_R(t) a_{\lambda q} U_R(t) = e^{-i\omega_{\lambda q} t} a_{\lambda q}, \quad (B.10)
\]

we have

\[
a_{\lambda q}^\dagger(t) = \tilde{a}_{\lambda q}^\dagger(t) e^{i\omega_{\lambda q} t}, \quad (B.11)
\]

and

\[
a_{\lambda q}(t) = \tilde{a}_{\lambda q}(t) e^{-i\omega_{\lambda q} t}. \quad (B.12)
\]

Here, we introduced slow oscillating envelopes

\[
\tilde{a}_{\lambda q}^\dagger(t) = U_{R-S}^\dagger(t) a_{\lambda q}^\dagger U_{R-S}(t), \quad (B.13)
\]

and

\[
\tilde{a}_{\lambda q}(t) = U_{R-S}^\dagger(t) a_{\lambda q} U_{R-S}(t). \quad (B.14)
\]

Inserting these expressions into equation (B.4), we can distinguish two terms associated with the transition from the ground state \( |g\rangle \) to an excited state \( |e_{\alpha}\rangle \) with respective phase factors \( e^{i(\omega_{\alpha} - \omega_{\lambda q}) t} \) and \( e^{-i(\omega_{\alpha} + \omega_{\lambda q}) t} \). While the first one will lead to a resonance excitation around \( \omega_{\lambda q} \approx \omega_{\alpha} \), the latter term is oscillating fast and will therefore contribute very little compared to the former one. Thus, we drop the fast oscillating part and obtain the source term in the form of equation (36).
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