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### Application of quantum coherence and decoherence

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#### Abstract

Coherent phenomena in molecular chromophores interacting with a dissipative environment is addressed. We defined *coherence* by the phenomena of *decoherence* which collapses the system to pointer states. Coherent irreducible phenomena takes place in a time window before the system collapses. We describe a computational model: The Stochastic Surrogate Hamiltonian that can deal with such complex quantum systems. The conditions for coherent control are analyzed. A prerequisite for coherent phenomena is the ability to perform coherent control using shaped light sources. We show that weak field coherent control is enabled by interaction with the environment.

*Keywords:* Coherent Control, Decoherence, Surrogate Hamiltonian, Pointer states

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#### 1. Introduction

Can quantum coherent phenomena have a significant role in the dynamics of a large system at room temperature? Only a positive answer can support the claims which are at the base of quantum biology. Coherence is a manifestation of quantum phenomena which has no classical analogue. This statement is elusive and much effort has been invested for its clarification. The naive idea that quantum phenomena can only be described by employing a superposition state is basis dependent. One can always find a basis which diagonalizes the state. The consequence is that coherence can be defined only relative to a privileged basis set. Is there an objective criteria to define this privileged state? If one can impose a partition of the system to distinct sub-systems then the combined system can be described by a tensor product of the sub-systems Hilbert space. For such a partition the privileged basis set is constructed from a tensor product of the local basis functions. This choice of privileged basis sets depends on the arbitrary choice of partition. Therefore the problem of arbitrariness has been shifted to the partition.

We advocate the view that the choice of the privileged basis set depends on coupling to the environment. This viewpoint requires the general context of quantum open systems. We claim that large and complex quantum systems possess features which differ them from small model systems. These features manifest themselves in an additional fast decoherence timescale.

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For a pure state it is possible to define a measure of coherence with respect to the privileged basis set  $\{\phi\}$ . If  $\psi = \sum_j a_j \phi_j$  then the information entropy  $S_c = -\sum_j |a_j|^2 \log |a_j|^2$  is a measure of coherence.  $S_c$  is zero if  $\psi$  can be reduced to a single  $\phi_j$  and is maximum for an even superposition. For a bipartite system where the privileged basis set has a tensor product form, the entropy  $S_c$  becomes the entropy of entanglement [1, 2].

In general, the systems under study are not pure requiring a density operator description of the state and  $\hat{\rho}^2 \neq \hat{\rho}$ . Once the local structure is imposed then coherence can be defined as a state that is irreducible to a tensor product of the individual subsystems:  $\hat{\rho} \neq \hat{\rho}_1 \otimes \hat{\rho}_2 \dots$ . Such states are termed entangled. There have been many attempts to establish a measure of entanglement [3, 4, 5, 6]. For mixed states non of these measures is satisfactory.

Any mixed state  $\hat{\rho}_s$  can be purified by entangling it with an additional subsystem such that  $\hat{\rho}_s = \text{tr}_m\{\hat{\rho}_{s \otimes m}\}$  and  $\hat{\rho}_{s \otimes m}^2 = \hat{\rho}_{s \otimes m}$ . This procedure is not unique, which means that the state of a subsystem can be constructed by infinitely many entangled environments that will generate identical system observables. This freedom is the basis of the Surrogate Hamiltonian method used to simulate an open quantum system [7] (Cf. Sec 3).

Is it possible to find a less arbitrary partition of the system? Molecular systems are constantly interacting with an external environment. For example, a large chromophore of biological origin strongly coupled with its protein pocket which in turn is immersed in a water solvent. This external interaction will lead to entanglement of the system with the outer world generating a mixed state of the system. The dynamical process that leads to partial collapse of the system to this mixed state can be thought of as a weak quantum measurement where the environment constantly measures the primary system. Zurek coined the expression *Quantum Darwinism* [8] for the process where the environment selects a privileged set of states. These surviving states are termed pointer states [9]. What are these states in the context of molecular photochemistry?

We now define the pointer states of a system as states which are the most robust with respect to the dynamics induced by the system bath interaction. In large complex systems we expect that the dynamics will lead to the system to collapse to a pointer state in a very short timescales. At a longer timescale, termed the kinetic timescale, these pointer states will reach a stationary equilibrium state. Complete quantum simulation on the combined system and bath could in principle identify these pointer states empirically by projecting on the system subspace. Their elusive nature is partially the result of the difficulty of performing such simulations and the necessity to use approximations. Pointer states can be identified in reduced models of open quantum systems. It has been found that states with a minimal uncertainty with respect to the operators composing the system-bath coupling have minimal purity decay rates. These states have been termed "generalized coherent states" [10]. Pure dephasing is a primary example. It is caused by fluctuations of the systems energy due the interaction with the bath. This will eventually collapse the system to one of the energy eigenstates which in this case form the pointer states. At a longer timescale Boltzmann equilibrium will be reached. For a large system local interactions which do not commute with the total Hamiltonian, will lead to pointer states which are products of semi-local states. For a position dependent interaction with a thermal environment coherent states are candidates for pointer states. Superpositions of coherent states will collapse very fast to a mixture. Individual coherent states will decay on a different timescale to a thermal state. The choice of the privileged basis set is context dependent. Each scenario needs careful analysis to figure out the mechanism and timescale of decoherence.

To summarize: An individual complex molecular system coupled to an environment eventually will first collapse to one of the pointer states before reaching equilibrium. An ensemble described initially as a pure state will collapse to mixture of pointer states. We will now use the environmentally defined pointer states as the privileged basis set. Coherent dynamics will be one that progresses through a superposition of pointer states before this superposition collapses. *The coherence is then defined by the process of decoherence.*

## 2. Decoherence processes

Decoherence is relevant if its timescale matches the timescale of the free unitary molecular dynamics. Very fast decoherence leads to a classical-like dynamical evolution. Slow decoherence can be approximated by pure quantum unitary dynamics. Decoherence is defined as a dynamical process which generates loss of purity:  $\mathcal{P}(t) < \mathcal{P}(0)$ , where purity is defined as:  $\mathcal{P} = \text{tr}\{\hat{\rho}^2\}$ . Unitary evolution preserves the eigenvalues of  $\hat{\rho}$  and will therefore preserve the trace of any function of  $\hat{\rho}$ , which includes  $f(\hat{\rho}) = \hat{\rho}^2$  and  $f(\hat{\rho}) = -\hat{\rho} \ln \hat{\rho}$ . As a result, the purity as well as the von Neumann entropy  $S_{VN} = -\text{tr}\{\hat{\rho} \ln \hat{\rho}\}$ , are constant under unitary evolution.

A change in purity requires a non unitary evolution of a system coupled to the environment. The most studied model is of a system bath combination initially uncorrelated

$$\hat{\rho}_{SB}(0) = \hat{\rho}_S \otimes \hat{\rho}_B .$$

The joint system-bath dynamics is considered to be unitary  $\hat{U}(t) = \exp(-\frac{i}{\hbar}\hat{H}_T t)$ . The dynamics is generated by the combined system-bath Hamiltonian:

$$\hat{H}_T = \hat{H}_S + \hat{H}_B + \hat{H}_{SB} .$$

The reduced state of the system at a later time is described as:  $\rho_S(t) = \text{tr}_B\{\hat{U}(t)\hat{\rho}_{SB}(0)\hat{U}^\dagger(t)\}$ . Concentrating on the subsystem dynamics it has the form of a completely positive map:

$$\hat{\rho}_S(t) = \sum_{\alpha} \hat{K}_{\alpha} \hat{\rho}_S(0) \hat{K}_{\alpha}^{\dagger}$$

and  $\hat{K}$  which are known as Kraus operators [11] obey:

$$\sum_{\alpha} \hat{K}_{\alpha} \hat{K}_{\alpha}^{\dagger} = \hat{I} .$$

If initially  $\hat{\rho}_S$  was pure, a completely positive map always decreases purity i.e. generating decoherence.

If in addition Markovian dynamics is imposed on the subsystem  $\dot{\hat{\rho}} = \mathcal{L}(\hat{\rho})$  then the generator of the dynamics has the form [12, 13]:

$$\mathcal{L}(\hat{\rho}) = -\frac{i}{\hbar} [\hat{H}_S, \hat{\rho}] + \sum_k \hat{V}_k \hat{\rho} \hat{V}_k^{\dagger} - \frac{1}{2} \{ \hat{V}_k \hat{V}_k^{\dagger}, \hat{\rho} \} ,$$

where  $H_S$  and  $\hat{V}$  are system operators.

The dynamics of completely positive maps is characterized by a decreasing distance to the invariant state of the dynamics  $\mathcal{L}(\hat{\rho}_{eq}) = 0$  [14, 15]. This is a manifestation of a monotonic approach to equilibrium. Pointer states are expected in the intermediate timescale before equilibrium is reached. This is because the pointer states are the slowest to relax to equilibrium.

The system-bath setup of completely positive maps has been criticized on the basis that typically one cannot decouple the system from the bath, therefore the initial state  $\hat{\rho}_{SB}(0) = \hat{\rho}_S \otimes \hat{\rho}_B$  cannot be realized [16]. In large complex systems, typically the system and bath are entangled even in equilibrium. Experimentally the dynamics is studied by initiating a non stationary state by an impulsive pump pulse. This pulse perturbs the system generating a non stationary correlated initial state. After a time delay the combined system-bath is measured by the probe. If the timescale of the pump is sufficiently fast the pump will generate coherence with respect to the pointer states. Such a superposition will display an oscillatory decay first to a mixture of pointer states and finally back to equilibrium. We advocate a computational method that is able to follow such a scenario. It is important therefore that in the initial state the system and bath are correlated. In addition the dynamics should include different types of system bath couplings. Markovian approximation could be harmful in describing the fast timescale where we can expect coherent superpositions of pointer states.

### 3. Surrogate Hamiltonian

The surrogate Hamiltonian is a quantum dynamical modeling approach designed to simulate large and complex dynamical systems. It is based on a Hamiltonian description of the system bath interaction where the actual bath is replaced by a surrogate reduced subsystem [17, 18]. Convergence is obtained by increasing the number of bath modes. The exponential growth of the computation effort with the number of modes is checked by adding a stochastic outer layer. This construction is employed to study light induced coherent dynamics in large complex systems.

Specifically, we consider a molecular system coupled to a radiation field. The molecular system is subject to dissipative forces due to coupling to a primary bath. In turn the primary bath is subject to interactions with a secondary bath:

$$\hat{H}_T = \hat{H}_S + \hat{H}_B + \hat{H}_{B'} + \hat{H}_{SB} + \hat{H}_{BB'} ,$$

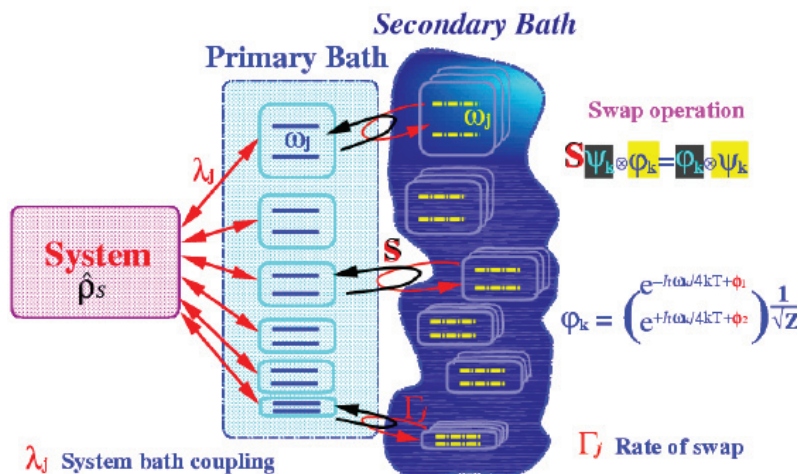


Figure 1: Flowchart of energy currents between the primary system, the primary bath and the secondary bath. The system and the primary bath are coupled via the Hamiltonian interaction represented by the interaction  $\lambda_j$ . The primary bath and the secondary bath interact via the swap operation  $\hat{S}$ .

where  $\hat{H}_S$  represents the system,  $\hat{H}_B$  represents the primary bath,  $\hat{H}_{B'}$  the secondary bath  $\hat{H}_{SB}$  the system-bath interaction and  $\hat{H}_{BB'}$  the primary/secondary bath interaction. The system Hamiltonian  $\hat{H}_S$  describes a ground electronic state and coupled excited electronic states:

$$\hat{H}_S = \begin{pmatrix} \hat{H}_g & \hat{\mu}_{gb}\epsilon(t) & 0 & \cdot \\ \hat{\mu}_{bg}\epsilon^*(t) & \hat{H}_b & \hat{V}_{ba} & \cdot \\ 0 & \hat{V}_{ab} & \hat{H}_a & \cdot \\ \cdot & \cdot & \cdot & \cdot \end{pmatrix}$$

where the operators are functions of the nuclear coordinates:

$\hat{H}_k = \frac{\hat{p}_k^2}{2m} + \hat{V}_k$  is the surface Hamiltonian, and  $\hat{V}_k$  is the ground (g), bright (b) or acceptor (a) potential.

$\hat{V}_{ba}$  represents the non-adiabatic coupling between the excited surfaces.

$\hat{\mu}$  represents the transition dipole operator which is chosen to couple only the ground and the bright excited state.

$\epsilon(t)$  represents the time dependent electromagnetic field. Typically, a Gaussian excitation pulse is used:  $\epsilon(t) = \Omega_0 \exp[-\frac{t^2}{2\tau_0^2} + i\omega_0 t]$  where  $\Omega_0$  is the light intensity, and  $\tau_0$  the temporal pulse width. For coherent control applications this pulse is shaped.

A quantum formulation is used for the bath. We envision a primary part directly interacting with the system. A secondary bath interacts with the primary bath generating decoherence. As a result, the primary bath decays to its pointer states eliminating recurrence. The primary bath Hamiltonian is composed of a collection of two-level-systems:

$$\hat{H}_B = \sum_j \omega_j \hat{\sigma}_j^+ \hat{\sigma}_j + \sum_{jk} \kappa_{jk} \hat{\sigma}_j^+ \hat{\sigma}_k$$

The energies  $\omega_j$  represent the spectrum of the bath and  $\kappa_{jk}$  the mode-mode interaction. The system-bath interaction  $\hat{H}_{SB}$  can be chosen to represent different physical processes [19, 20, 17, 18]. Single and binary spin interactions should be also included in the system-bath interaction [19]. The addition of spin-spin interactions allows the bath dynamics to become universal meaning that any other quantum bath can be simulated. This is in analogy to the universality class of one and two qbit operation in generating an arbitrary unitary operation.

The surrogate Hamiltonian is employed to study weak field coherent control in open system dynamics. For this

task a system bath interaction leading to vibrational relaxation is required:

$$\hat{H}_{SB} = f(\hat{R}_s) \otimes \sum_j^N \lambda_j (\hat{\sigma}_j^\dagger + \hat{\sigma}_j),$$

where  $f(\hat{R}_s)$  is a dimensionless function of the system coordinate  $\hat{R}_s$ .  $\lambda_j$  is the system-bath coupling frequency of bath mode  $j$ . When the system-bath coupling is characterized by a spectral density  $J(\omega)$  (units of frequency) then  $\lambda_j = \sqrt{J(\omega_j)}/\rho_j$  and  $\rho_j = (\omega_{j+1} - \omega_j)^{-1}$  is the density of bath modes.

The secondary bath is also composed of noninteracting two-level-systems (TLS) at temperature  $T$  with the same frequency spectrum as the primary bath. At random times the states of primary and secondary bath modes of the same frequency are swapped at a rate  $\Gamma_j$  [17, 18, 19, 21]. The swap operator  $\hat{S}$  is defined as:

$$\hat{S}\psi_{B_j} \otimes \phi_{B_j} = \phi_{B_j} \otimes \psi_{B_j}.$$

In a full swap operation the primary bath mode is reset to a state  $\phi$  with thermal amplitudes and random phases:

$$\phi_j = \frac{1}{\sqrt{2 \cosh[\frac{\hbar\omega_j}{2k_B T}]}} \begin{pmatrix} e^{-\frac{\hbar\omega_j}{4k_B T} + i\theta_1} \\ e^{+\frac{\hbar\omega_j}{4k_B T} + i\theta_2} \end{pmatrix}$$

where  $\theta_1, \theta_2$  are random phases.

The swapping procedure permits description of both dephasing and energy relaxation. The final results are obtained by averaging the stochastic realizations. The swap makes the bath effectively infinite. Each swap operation eliminates the quantum correlation between the system and remaining bath with the mode swapped. This loss of entanglement leads to dephasing.

At each instant the reduced density operator of the system  $\hat{\rho}_s$  can be reconstructed by taking the partial trace over all bath degrees of freedom and averaging over the stochastic realizations:

$$\hat{\rho}_s = \frac{1}{L} \sum_k^L \text{tr}_B \{ |\Psi_{S \otimes B}(k)\rangle \langle \Psi_{S \otimes B}(k)| \}$$

where  $L$  is the number of stochastic realizations and  $\Psi_{S \otimes B}(k)$  is the many body system bath wavefunction of realization  $k$ .

The stochastic surrogate Hamiltonian approach is a complete quantum treatment of system-bath dynamics. The method is based on a wavefunction construction where the dynamics is generated by a coupled system bath Hamiltonian. The results is a non Markovian description of the primary system. The system and bath are initially correlated, the initial state is the combined thermal state generated by propagating with the Boltzmann operator using the coupled system-bath Hamiltonian:

$$\Psi_{S \otimes B}(\beta) = Z^{-1/2} e^{-\beta/2 \hat{H}_T} \Psi_{S \otimes B}(R)$$

where  $\Psi_{S \otimes B}(R)$  is the even amplitude random phase combined system-bath wavefunction [22]. Additional entanglement is generated by the dynamics.

Convergence of the model can be verified by increasing the number of bath modes and the number of stochastic realizations. Typically very fast convergence was obtained for large systems. In the cases studied seven bath modes were sufficient for convergence with approximately 20 to 30 realizations. The convergence was found to be faster when the size of the Hilbert space increases [22]. This phenomena is a manifestation of self averaging of large systems. This self averaging is also responsible to the collapse of the system to pointer states.

#### 4. Coherent control

Coherent control is a stringent test of coherent processes. The main idea is to manipulate the coherence with the purpose to steer the system to a desired outcome [23, 24, 25]. For isolated molecules the energy eigenstates are

the privileged basis set. For pure initial and final states the method can be termed *state-to-state* coherent control. A generalization is steering simultaneously a set of initial pure states to a set of final states, i.e. controlling a unitary transformation. Such an application sets the foundation for a quantum gate operation [26, 27, 28]. Three basic questions address feasibility of coherent control. The first, for a preset initial and target state: Does a control field exist? This is the problem of controllability. The second: Synthesis deals with constructively finding the field that leads to the target. Finally: Optimizing the field that carries out this task. This is the problem of Optimal Control Theory [29, 30, 31]. Experimentally, there has been a remarkable success in constructing devices able to generate arbitrary control fields [32, 33, 34]. Nevertheless, in practice controllability is hard to achieve even for small quantum systems [35, 36, 37].

The issue of controllability of a closed quantum system has been addressed by Tarn and Clark [38]. The theorem states that if the control operators and the unperturbed Hamiltonian of a finite dimensional closed quantum system generate Lie-algebra of all Hermitian operators of the system, it is *completely controllable*. This means that an arbitrary unitary transformation of the system can be realized by an appropriate application of the controls [39]. Complete controllability implies *state-to-state controllability*. The main idea is that each commutator defines a new direction in the control landscape. If all possible directions are covered then the system is completely controllable. For open quantum systems the issue of controllability is more subtle [40]. On the one hand, the dissipative operator represents a new control direction, but in addition a dissipative systems is contracting which means that the control space is lost.

These contradicting effects allow a small window of opportunity where decoherence can be exploited before the control landscape contracts to its assembly of pointer states.

## 5. Weak field coherent control

Naturally occurring photochemical reactions driven by sunlight are single photon events. The excitation density is such that only a single excitation event is possible. Nevertheless the solar spectrum is broad which means it can be decomposed to an ensemble of short pulses with a random spectral phase. Can the broad bandwidth of the excitation pulse under sunlight conditions induce coherent processes?

We first examine these issues by studying the prospects of coherent control of a molecular system employing a weak broadband pulse. If coherent control becomes possible, then the prospects of naturally occurring coherent processes is strengthened. The basic control Hamiltonian is of the form:

$$\hat{H} = \hat{H}_0 + \hat{\mu} \cdot \epsilon(t) .$$

Let us consider the control of a state to state transition from the stationary eigenvalues of the molecular Hamiltonian  $\hat{H}_0$  by a light field  $\epsilon(t)$  generated by the dipole operator  $\hat{\mu}$  for an isolated molecule. The probability of transition from an initial to a final state can be calculated from first order time dependent perturbation theory leading to:

$$P_{i \rightarrow f}(t) = \frac{1}{\hbar^2} |\langle f | \hat{\mu} | i \rangle|^2 \left| \int_0^t e^{-i\omega_{if}t'} \epsilon(t') dt' \right|^2 .$$

For large  $t$  the probability depends only on the spectral component of  $\tilde{\epsilon}(\omega)$  in the transition frequency  $\omega_{if}$ . It is clear from this description that the state to state transition probability is independent of the phase of the excitation field  $\epsilon$ . This finding can be extended to any control target that commutes with  $\hat{H}_0$  [25]. It is therefore not possible to exceed the optimal outcome obtained by energetically selecting the best CW transition determined by Franck-Condon overlap between the initial state and the final target state [41, 42].

A different scenario of coherent control is a two photon pump-dump scheme where the first pulse transfers amplitude to the electronic excited state and the second pulse, after an appropriate time delay, stabilizes the state in the desired conformer [43, 44]. Many variants of this mechanism are possible which include both shaping the pump and the dump pulses [30, 29]. It is clear from the description that this mechanism requires at least two interactions with the control field to set up the necessary interference [45]. Do these considerations rule out naturally occurring coherent excitation processes?

Can coherent control of a single weak shaped pulse become possible when the molecule is immersed in a condensed phase environment? Recently there have been experimental reports of weak field control of large molecules



## Model system for weak field control phase only control

Target: change the branching ratio on the excited state

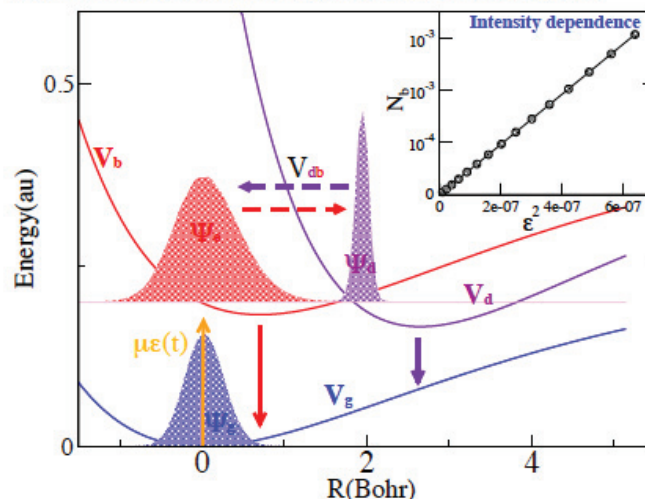


Figure 2: The model for weak field coherent control. The system is composed from a ground state and two excited states: a bright and dark state. The target of control could be the branching ratio of the photochemical reaction. This ratio is determined experimentally by the ratio of spontaneous emission at the bottom of the potential wells (Red and purple arrows). The insert shows the linear dependence of excitation on the pulse intensity. Superimposed on the potential are the ground state probability density and transient wavepackets on the excited potential energy surfaces.

in solution [46, 47, 48]. The main feature of the control pulses employed is a negative chirp. The amount of control reported varies from a few percent to a factor of 1.5 [48]. These findings were criticized on the basis that weak field control is impossible [49, 50]. A clue to explain these results can be found in the study of van der Walle et. al. [48]. In this experiment first the optimal pulse was established for a dye molecule in a specific solvent, then the same pulse was applied to a series of different solvents. As a result the target of control, the branching ratio, varied significantly. The only possible mechanism of control consistent with these experiments is one that is enabled by the environment [41, 51].

These experiments suggest that weak field broad band coherent control is possible provided the chromophore is subject to dissipation by the environment. To gain insight on this issue we set a minimal computational model. Figure 2 shows the general scheme employed for weak field coherent control of a molecular system.

We chose control scenarios where only phase control of the pulse was employed [18]. The simplest choice is a chirped pulse. The pulse is set in the frequency domain where the Fourier transform the electric field  $\epsilon(t)$  becomes [52, 53]:

$$\tilde{\epsilon}(\omega) = \tilde{\Omega}_0 \exp \left[ -\frac{(\omega - \omega_0)^2}{2\Gamma^2} + i\bar{\chi} \frac{(\omega - \omega_0)^2}{2} \right],$$

where  $\bar{\chi}$  is the chirp, and  $\Omega_0$  is the TL peak field.  $\omega_0$  is the spectral center of the pulse and  $\Gamma$  the spectral band width. Linear weak field optical manipulations do not change the frequency bandwidth. In the time domain the pulse has the following shape:

$$\epsilon(t) = \Omega_0 \exp \left[ -\frac{(t - t_0)^2}{2\tau^2} + i\bar{\chi} \frac{(t - t_0)^2}{2} + i\omega_0 t \right],$$

where  $\tau$  is the pulse duration given by  $\tau = \Gamma^{-2}(1 + \chi^2\Gamma^4)$  and the chirp rate  $\bar{\chi} = \chi\Gamma^4/(1 + \chi^2\Gamma^4)$ .

In view of the experiments, the target of control was chosen as the asymptotic population ratio of the bright and dark excited states  $N_d/N_b$ , where  $N_b, N_d$  represent the population on the bright/dark states. Experimentally this ratio is extracted from the accumulated long time spontaneous emission emerging from the bottom of the bright and dark potential wells.

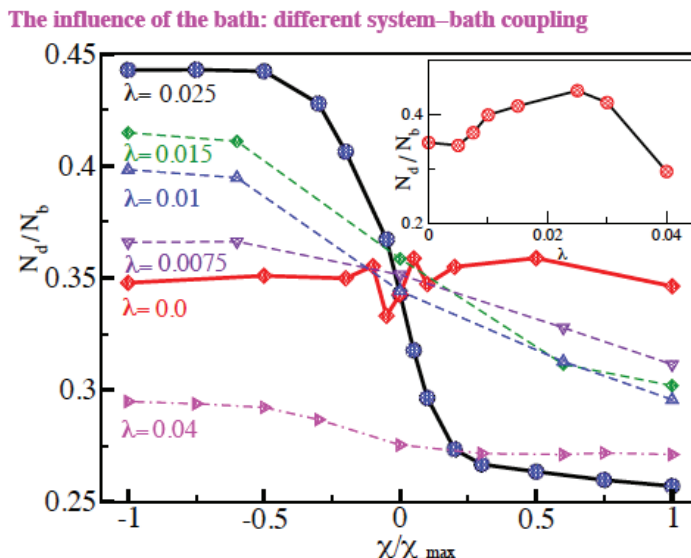


Figure 3: Branching ratio between the bright and dark state as a function of the chirp rate  $\bar{\chi}/\bar{\chi}_{max}$ , ( $\chi_{max} = 0.0184 \text{ fsec}^{-2}$ ). The branching ratio is defined as the ratio of population  $N_d/N_b$  on each state at 7 psec. Each line corresponds to a different system-bath coupling value characterized by  $\lambda$  the system bath coupling parameter. The solid red line corresponds to the reference free system. The insert shows the branching ratio between dark and bright states for  $\chi/\chi_{max} = -1.0$  for different system-bath coupling parameter  $\lambda$ .

Fig. 3 displays the branching ratio  $N_d/N_b$  as a function of the chirp parameter  $\chi$ . When the bath is absent as expected the chirp has no influence on the branching ratio. Once relaxation is set the population on each excited state stabilizes. The results of Fig. 3 demonstrate that when there is sufficient system-bath coupling, phase only control is possible. Positive chirp suppresses the dark state while negative chirp enhances with respect to the transform limit pulse (no chirp) which is similar to free propagation ratio  $N_d/N_b \sim 0.35$ . The maximum effect is obtained when the timescale of energy relaxation matches the oscillation period bright/dark population transfer. When the system-bath coupling further increases a turnover is observed and the ratio  $N_d/N_b$  decreases (Cf. insert of Fig 3). In addition the control is lost. In this case the strong dissipation destroys coherence and stabilizes the product in the first bright well. The turnover is reminiscent of phenomena observed in electron transfer [54, 19, 55].

Pure dephasing cannot enable control. Formally, weak field phase only control is possible provided the target operator, in this case the projection on the excited state, does not commute with the total field free Hamiltonian. In the combined system-bath scenario control is provided by the system bath coupling which does not commute with the target operator which commutes with the system Hamiltonian. Pure dephasing commutes with the systems Hamiltonian and therefore does not enable control. When the intensity is increased to at least two photon interaction, negative chirp leads to minimum population transfer. This phenomena has been well studied both theoretically and experimentally [56, 53, 57, 58, 59, 60, 61, 62].

In this complex molecular photo-system what is the privileged basis set? The environment first leads to a loss of phase between the ground and excited electronic manifolds. This loss of electronic phase does not enable weak field control since it commutes with  $\hat{H}_0$ . On the contrary, it will hamper control of population transfer between different electronic states. Another timescale is associated with vibrations settling to localized coherent states. We therefore speculate that the pointer states are tensor products of electronic and coherent vibrational states. The window of opportunity for coherent control to be applied is the period before the system collapsed to the pointer states. This sets the timescale to be intermediate between electronic dephasing and vibrational relaxation, typically 100 to 1000 fsec for room temperature molecules in solution.



## 6. Discussion

Can coherent dynamics be employed in large and complex quantum systems? We use the paradigm of coherent control which is based on interference as a test for the existence of such processes. Strong fields coherent control can be enabled by dynamically decoupling the system from its environment. Therefore, only weak field coherent control can serve as an indicator of coherent processes in large complex quantum systems.

Our major finding is that phase only coherent control is possible in weak field conditions. This requires that the trio of time scales to match: The internal molecular timescale, the external environmentally induced energy relaxation timescale and the control timescale. Coherent control engineers the control pulse to match these natural timescales. A random search through pulse shapes can also be employed [48] identifying a control timescale of the order of 100 fsec to 1 psec for a dye molecule in solution. How can these timescales be matched? Chemical synthetic approaches can tune the low frequency vibrational timescale of a molecule by modifying the molecule. In addition the interaction with the environment can be altered by changing solvents [48]. If such coherence is important in biology then natural selection can lead to timescale matching.

The optimization of the control yield with respect to these three parameters leads to the phenomena of turnover [63, 54, 19, 55]. The control process shows an optimum as a function of all dynamical parameters. Increasing the system bath coupling for example will first enable control and then with further increase will disable it. This behavior is typical of the quantum Zeno effect [64]. As a conjecture we can expect that naturally occurring coherent processes have to match the vibrational, electronic and decoherence timescales.

What is the extent of the coherence which enables control? For this task we invoke the idea of pointer states as the privileged basis set. These states are the most immune to the environment. If an individual system completely collapses to one pointer state then no coherence is left and the dynamics is best described by an ensemble of stochastic trajectories. Each trajectory represents the dynamics of an individual pointer state. For systems exhibiting strong nonlinearities such as bifurcations, coherence is generated. Classically such dynamics would lead to chaotic motion. In analogue quantum systems the bifurcation leads to the generation of new coherence. In these cases it is necessary to describe the dynamics of the system as a superposition of pointer states [65]. The size of this superposition is expected to be quite small. In addition it is expected to be independent of the total system's size [66].

## 7. Conclusions

Coherent control under weak field conditions of complex molecular systems was verified experimentally and computationally. Interacting with an environment is a prerequisite for observing such phenomena. This phenomena may be an indication that solar driven coherent processes could become possible. The prerequisite is a balanced interplay of the timescales of electronic, vibrational and environmental dynamics.

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