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Communication: Conditions for one-photon coherent phase control in isolated and open quantum systems

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Coherent control of observables using the phase properties of weak light that induces one-photon transitions is considered. Measurable properties are shown to be categorizable as either class A, where control is not possible, or class B, where control is possible. Using formal arguments, we show that phase control in open systems can be environmentally assisted. © 2010 American Institute of Physics. [doi:10.1063/1.3491366]

I. INTRODUCTION

The essential principal of the coherent control of atomic and molecular processes is the creation of multiple interfering pathways to the same final state.¹ Manipulation of laboratory parameters that induce these pathways then allows direct control over the associated interference, and hence control over the relative cross sections involved in the process.

A longstanding result in coherent control states that control over relative product cross sections using one-photon excitation is not possible.² That proof deals with gas-phase photofragmentation of isolated molecules, with a focus on the long time limit at fixed energy in a degenerate continuum. However, a recent experiment on weak-field shaped-pulse cis/trans isomerization of retinal,³ as well as computational studies on model systems,⁴ claims a demonstration of one-photon control of long-time isomerization yields by varying the relative phases of components of the incident radiation. In both cases, the system isomerization takes place within an open dissipative environment, where the earlier proof does not apply. Motivated by these results, we here generalize the previous proof focusing on control by varying relative laser phase (“coherent phase control”) in either isolated and open quantum systems. In particular, we obtain strict conditions under which one-photon phase control is possible.

II. ONE-PHOTON INDUCED ELECTRONIC EXCITATION

For simplicity we focus on one-photon induced transitions between two electronic states and consider measurements of the excited state dynamics. Consider a quantum system with Hamiltonian $\hat{H}_0$, eigenenergies $\{E_n\}$, and eigenstates $\{|\phi_n\rangle\}$, where the labels n denote all quantum numbers needed to specify the state (e.g., vibrational numbers, rota-

tional numbers, electronic state). The system is irradiated with a weak laser pulse whose frequency spectrum is given by

$$A(\omega) = |A(\omega)|e^{i\varphi_s(\omega)}, \quad (1)$$

where $\varphi_s(\omega)$ is the spectral phase, a quantity central to the present study. With the system initially in a pure state n_0 of the ground electronic state, the excited wave function following one-photon absorption is given in first order perturbation theory by

$$|\Psi\rangle = \sum_n \mu_{nn_0} A(\omega_{nn_0}) |\phi_n\rangle, \quad (2)$$

where $\mu_{nm} = \langle \phi_n | \hat{\mu} | \phi_m \rangle$ are the dipole transition matrix elements and $\omega_{nm} = (E_n - E_m)/\hbar$. The expectation value $\langle \hat{O}(t) \rangle$, corresponding to an arbitrary measurement of the system property $\hat{O}$ at some later time t on the excited electronic state, is given by

$$\begin{aligned} \langle \hat{O}(t) \rangle = & \sum_n O_{nn} |\mu_{nn_0}|^2 |A(\omega_{nn_0})|^2 \\ & + \sum_{n \neq m} O_{nm} \mu_{mn_0} \mu_{nn_0}^* A(\omega_{mn_0}) A^*(\omega_{nn_0}) e^{i\omega_{nm}t}, \end{aligned} \quad (3)$$

where $O_{nm} = \langle \phi_n | \hat{O} | \phi_m \rangle$. The dependence of $\langle \hat{O}(t) \rangle$ on the laser phase $\varphi_s(\omega)$ can be made more explicit by writing Eq. (3) as

$$\begin{aligned} \langle \hat{O}(t) \rangle = & \sum_n O_{nn} |\mu_{nn_0}|^2 |A(\omega_{nn_0})|^2 \\ & + \sum_{n \neq m} |O_{nm} \mu_{mn_0} \mu_{nn_0} A(\omega_{mn_0}) A(\omega_{nn_0})| \\ & \times \cos[\omega_{nm}t + \theta_{nm} + \varphi_s(\omega_{mn_0}) - \varphi_s(\omega_{nn_0})], \end{aligned} \quad (4)$$

where the hermiticity of $\hat{O}$ was used, θ_{nm} is the phase of the matrix element ($O_{nm} = |O_{nm}|e^{i\theta_{nm}}$), and μ_{nm} is assumed real. In the case where the initial state is described by a density matrix $\hat{\rho}(0) = \sum_{n_0} w_{n_0} |\phi_{n_0}\rangle \langle \phi_{n_0}|$, Eq. (4) is replaced by a w_{n_0} -weighted sum over the right hand side of the equation. In the case of a continuous spectrum all sums become integrals.⁵

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Equation (4) displays the effect of the laser phase $\varphi_s(\omega)$ on observables after one-photon induced state preparation. The first sum in Eq. (4) represents the incoherent contribution to the observable arising from level populations, and is both time-independent and $\varphi_s(\omega)$ -independent. By contrast, the second sum, which is the coherent interference term, is both time-dependent and $\varphi_s(\omega)$ -dependent. Interest is in the control achievable through changes in laser phase since varying laser intensity, which affects the $|A(\omega)|$, constitutes passive control associated with changing the laser power spectrum. By contrast, the $\varphi_s(\omega)$ terms explicitly alter the interference contribution.

Given Eq. (4), two distinct classes of measurements can be identified:

Class A: Measurements of properties $\hat{O}$ where $[\hat{H}_0, \hat{O}] = 0$, that is, operators $\hat{O}$ that are constants of the motion under laser-free system evolution. In this case $O_{nn} = 0$ so that $\langle \hat{O}(t) \rangle$ then only involves the first sum in Eq. (4) and does not depend on $\varphi_s(\omega)$.

Class B: Measurements whose corresponding operators $\hat{O}$ do not commute with $\hat{H}_0$: $\langle \hat{O}(t) \rangle$ then involves the second sum in Eq. (4) and depends on $\varphi_s(\omega)$.

Hence, class A observables cannot be coherently phase controlled via a one-photon transition, while one-photon coherent phase control of class B observables is possible. Since class A measurements rigorously lead to time-independent results, any observables exhibiting a time-dependence must fall into class B and can therefore be sensitive to $\varphi_s(\omega)$. In the remainder of the paper, we examine important examples in each class.

A. Isolated molecules

Consider first the case of isolated molecules. A relevant example is that treated in Ref. 2. There, one-photon photofragmentation of an isolated molecule was considered, and the observable was the ratio of the photodissociation products. Such product states $|\mathbf{n}\rangle$ are eigenstates of $\hat{H}_0$.⁶ Hence, the operator

$$\hat{\mathcal{P}}_\alpha = \sum_{\mathbf{n} \in \alpha} |\mathbf{n}\rangle \langle \mathbf{n}| \quad (5)$$

corresponding to measurements of product populations, where the sum includes eigenstates corresponding to a particular product channel α at fixed energy E , is diagonal in the energy basis. The ratio of populations of two different product channels

$$\mathcal{R}(\alpha, \beta) = \langle \hat{\mathcal{P}}_\alpha \rangle / \langle \hat{\mathcal{P}}_\beta \rangle \quad (6)$$

examined in Ref. 2 is therefore of class A and is independent of $\varphi_s(\omega)$, as well as independent of laser intensity in the one-photon limit. One-photon control is therefore not possible.

Many additional class A measurements clearly exist. For example, they also include all time-averaged quantities $\bar{O}$, with

$$\bar{O} = \lim_{T \rightarrow \infty} \left(\frac{1}{T} \right) \int_0^T dt \langle \hat{O}(t) \rangle = \sum_{\mathbf{n}} O_{nn} |\mu_{n n_0}|^2 |A(\omega_{nn_0})|^2. \quad (7)$$

Consider, by contrast, class B cases for isolated molecules, i.e., all measurements whose corresponding operators are time dependent under laser-free evolution. A particular example of interest among the large class of such measurements is that of spatially distinct measurements, such as that of cis versus trans molecular isomers. Since the associated measurement operator, constituting a projection onto a subspace of the full configuration space, does not commute with $\hat{H}_0$, it constitutes a class B measurement, and we expect that coherent control is indeed possible in this case. Note that such control does not require an open system environment.

B. Nonisolated systems

As a second, more general type of class B measurements, consider the case where a subsystem of an overall system is measured. The component of the total system that is measured is termed the subsystem, and the component that is not measured is termed the environment. The latter can be of any size.⁷ The full Hamiltonian is given by

$$\hat{H} = \hat{H}_0 + \hat{V}_L, \quad (8)$$

where

$$\hat{H}_0 = \hat{H}_s + \hat{H}_e + \hat{H}_{se}, \quad (9)$$

$\hat{H}_s$ is the subsystem Hamiltonian, $\hat{H}_e$ is the environment Hamiltonian, $\hat{H}_{se}$ is the subsystem-environment coupling, and $\hat{V}_L = \hat{\mu}E(t)$ is the laser interaction driving the one-photon transition. We define the subsystem space to be that on which the measurement operators $\hat{O}$ act. For $\hat{O}$ to be a class B measurement, and hence controllable via a one-photon transition, requires that $[\hat{O}, \hat{H}_0] \neq 0$. This condition can be achieved in two ways. First, if $[\hat{O}, \hat{H}_s] \neq 0$, as in the example above, then $[\hat{O}, \hat{H}_0] \neq 0$ immediately follows. Alternatively, if $[\hat{O}, \hat{H}_s] = 0$ (which would imply that $\langle \hat{O} \rangle$ is not phase controllable if $\hat{H}_s$ were a closed system), $\langle \hat{O} \rangle$ can still be phase controllable in an open system if $[\hat{O}, \hat{H}_{se}] \neq 0$ and the coupling $\hat{H}_{se}$ is dissipative (i.e., the subsystem can exchange energy with the environment, which implies that $[\hat{H}_{se}, \hat{H}_s] \neq 0$). Note that virtually⁸ any $\hat{O}$ that commutes with $\hat{H}_s$ will not commute with $\hat{H}_{se}$.

The generality of this statement, and the ubiquitous presence of dissipative open systems, make this result one of considerable importance.⁹ That is, it implies that *in an open system, virtually every subsystem property can, in principle, be coherently phase controlled via a one-photon transition*. Note, in particular that in the case where $[\hat{O}, \hat{H}_s] = 0$, such control would be *environmentally assisted*. Whether such control is significant in practice depends upon the nature of the O_{nn} matrix elements in Eq. (3), where $|\phi\mathbf{n}\rangle$ and $|\phi\mathbf{m}\rangle$ are eigenstates of the full (subsystem+environment) Hamiltonian.

Finally, we note that demonstrating one-photon phase control appears to require a careful treatment of both the laser preparation and the dynamics of the total system. For example, our efforts¹⁰ to computationally demonstrate one-photon phase control on a model open system using both secular and nonsecular Redfield theory,¹¹ as well as our detailed study of model bacteriorhodopsin isomerization using a TDSCF approach¹² failed to show one-photon phase control.¹³ By contrast, Katz *et al.*⁴ have successfully shown one-photon phase control in a computation that models the full subsystem+environment dynamics. Further work on obtaining a detailed understanding of conditions for quantitatively demonstrating significant phase control is hence necessary and is in progress.

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⁴G. Katz, M. A. Ratner, and R. Kosloff, *New J. Phys.* **12**, 015003 (2010); One clarification regarding this computation is necessary. In accord with the idea of phase control, the authors' intention is to vary $\varphi_s(\omega)$ without changing $|A(\omega)|$. They proposed to do so by varying the chirp parameter χ in the laser field $\epsilon(t)$ [their Eq. (8)]. However, computing $A(\omega)$ from their $\epsilon(t)$ shows that it depends upon $|\chi|^2$. Hence, dynamical effects in their Fig. 4 that result from changing the *sign* of χ are indeed evidence for phase control. However, dynamical effects resulting from varying $|\chi|$ are a result of changes to both the relative phases and to $|A(\omega)|$, and are hence not evidence of phase control. Alternate computations showing phase control have been obtained as well (R. Kosloff, private communication).

⁵Additional terms with a similar relationship between time dependence and laser phase appear in the case where excitation is not between different electronic surfaces.

⁶J. R. Taylor, *Scattering Theory: The Quantum Theory of Nonrelativistic Collisions* (Wiley, New York, 1972).

⁷J. Gong and P. Brumer, *Phys. Rev. A* **68**, 022101 (2003).

⁸Consider the case of $[\hat{O}, \hat{H}_s] = 0$. Then (in the basis of $\hat{H}_s$) $\hat{O} = \sum_n O_n |n\rangle\langle n|$ and $\hat{H}_{se} = \sum_{m,m'} A_{m,m'} |m\rangle\langle m'|$, where $A_{m,m'}$ operates on the space of the environment. It follows that $[\hat{O}, \hat{H}_{se}] = \sum_{m,m'} [O_m - O_{m'}] A_{m,m'} |m\rangle\langle m'|$. Barring unusual cases involving degeneracies of $\hat{O}$ exactly canceling the off-diagonal components of $\hat{H}_{se}$ (such as cases where the system dependence of $\hat{H}_{se}$ is solely a function of $\hat{O}$), this shows that in general $[\hat{O}, \hat{H}_{se}] \neq 0$.

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¹³Interestingly, in model systems studied with a Redfield approach we found that we could generally construct different wavepackets "by hand" on an excited potential energy surface that displayed the desired phase dependent control behavior. However, these wavepackets could not be obtained via one-photon excitation from the ground state.