Optimal pump-dump control: Linearization and symmetry relation

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(Received 24 January 1997; accepted 28 May 1997)

A generalized eigenequation is derived for the optimal pairs of phase-unlocked pump-dump fields in the control of pure state molecular systems in the weak response regime. The associated eigenvalues are further correlated to the yields of pump-dump control, thus the globally optimal pair of phase-unlocked pump-dump fields is identified unambiguously. Presented is also a hierarchy of reduction from the general Liouville-space density matrix control formulation in the strong response regime to various linearized control equations in the weak response regime. Application to the control of a molecular ro-vibronic level in the ground electronic surface reveals a novel symmetry relation between the optimal pump field and its counterpart of the optimal dump field. © *1997 American Institute of Physics.* [S0021-9606(97)00933-1]

I. INTRODUCTION

Optimal control theory[1–8] provides a solid background for using tailored laser fields to manipulate molecular motion and chemical reactivity. In principle, the optimal control formulation is capable of incorporating all molecular aspects and experimental considerations in a coherent manner. As a general mathematical tool for searching the functional maximum, the optimal control theory leads usually to a complicated nonlinear equation which requires a numerically expensive approach to solve. The resulting fields are however not only locally optimal but also too complicated to be experimentally realizable. To facilitate this problem, there has been considerable effort on arriving a linearized version of control formalism.[7–16] The simplest linearizable system is the control of one-photon achievable target.[7–11] In this case, the optimal control in the weak response regime can be reduced to an eigen-problem of a second order control response function, whose eigenfunction and eigenvalue give the optimal field and yield, respectively.[7,8] The globally optimal field in the one-photon control scenario can thus be unambiguously identified. Moreover, we have found, at least for the systems of study, that the globally optimal field is reasonably simple and robust, and retains as a good control field as its intensity scales up to a moderately strong level.[17] An example which successfully correlates theory[8,18] and experiment[19] is the control of wave packet focusing on the I_2 B potential surface. The globally optimal field in the weak response regime serves as an ideal starting point to investigate the general but more complicated optimal control fields in the strong response regime.

The linearization to control formulation beyond one-photon accessible targets, such as the pump-dump scheme proposed by Tannor and Rice,[1] may also be achieved under certain experimental conditions.[12–16] In their original work,[1] Tannor and Rice considered the control with a pair of phase-unlocked weak fields and derived a linear equation for the optimal dump field with respect to a given pump field in the weak response regime. Yan[13,14] has extended Tannor-Rice's original idea and arrived at a pair of coupled quasi-linear optimal pump-dump equations in the weak response regime. This is done by expanding the pump (or dump) control kernel to the first order in the pump (or dump) field and the resulting control response function depends on its counterpart field.[13,14] This approach can be generalized to reduce a phase-unlocked n-field (n-photon) control formulation into n coupled quasi-linear control equations.[15,16] Recently, we have further derived the general density matrix formulation for the optimal pump-dump control with two phase-unlocked coherent fields in the strong response regime.[14]

The remaining of this paper is organized as follows. In Sec. II, we summarize our recent development[14] on the general density matrix formulation of optimal phase-unlocked pump-dump control. The key result of this paper is in Sec. III where our previous general formulation[14] is further reduced to a standard eigenvalue problem in the pure state control in the weak response regime [cf. Eq. (27)]. This result is very similar to recent work by Dubov and Rabitz[12] in which a different but related eigenequation was derived for the phase-locked two-photon control of pure state in the weak response regime. The detailed comparison between the phase-unlocked pump-dump control and its phase-locked counterpart will be presented elsewhere.[20] In Sec. III, we also connect the control yield to the eigenvalue in the optimal equation. Thus, the *globally* optimal pair of phase-unlocked pump-dump fields can be identified in the pure state weak control response regime. In Sec. IV, we apply the pump-dump control eigenequation developed in Sec. III to the optimal stimulated Raman pumping in which both the initial system and the final target are in the molecular ro-vibronic levels on the ground electronic surface. In this case, a novel symmetry relation between the optimal pump field and its joint optimal dump field is rigorously established [cf. Eqs. (33) and (34)]. Included in Sec. IV is also a numerical example to demonstrate the underline control process. Finally, we summarize our result in Sec. V.

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II. GENERAL THEORY OF OPTIMAL PUMP-DUMP CONTROL

In this section, we shall present the general formulation, developed in Ref. 14, for the optimal phase-unlocked pump-dump control of a molecular system involving two electronic surfaces, the ground g and an excited e. The molecular Hamiltonian is assumed to be the form of $H=H_g|g\rangle\langle g|+H_e|e\rangle\langle e|$. The total Hamiltonian in the presence of a pair of pump-dump fields, $E(t;\theta)=E_1(t)+e^{-i\theta}E_2(t)$ that is locked at the specific relative phase $\theta=\theta_2-\theta_1$, is given by

$$H_T(t;\theta)=H-D_+E(t;\theta)-D_-E^*(t;\theta). \tag{1}$$

Here, we adopted the electronic rotating wave approximation.[14] In the above equation, $D_+=\mu|e\rangle\langle g|$ and $D_-=D_+^\dagger=\mu|g\rangle\langle e|$ are two components of electronic transition dipoles. As $D_+|g\rangle=\mu|e\rangle, D_-|e\rangle=\mu|g\rangle$ and $D_+|e\rangle=D_-|g\rangle=0$, these two transition dipole components can also be viewed as the exciton creation and annihilation operators, respectively. In the following derivation, we shall introduce the auxiliary Liouville-space dipole operators, $\mathscr{D}_\pm^{l,r}$, defined by their action on an arbitrary operator $\hat{O}$ as[14]

$$\mathscr{D}_\pm^{\,l}\hat{O}\equiv D_\pm\hat{O}, \tag{2a}$$

$$\mathscr{D}_\pm^{\,r}\hat{O}\equiv-\hat{O}D_\pm. \tag{2b}$$

Physically, $\mathscr{D}_+^{\,l}$ (or $\mathscr{D}_-^{\,r}$) and $\mathscr{D}_-^{\,l}$ (or $\mathscr{D}_+^{\,r}$) are responsible for the electronic pumping and dumping, respectively, from the ket (or bra) side. The control target, which can generally be represented by an operator $\hat{A}$, is chosen to be a certain nuclear dynamic event in the ground electronic state. The goal of control is to find the optimal phase-unlocked pair of pump-dump fields, $\{E_1,E_2\}$, so that they maximize the expectation value of the target $\hat{A}$ at a given target time t_f,

$$A(t_f)=\langle\mathrm{Tr}[\hat{A}\rho_T(t_f;\theta)]\rangle=\langle\mathrm{Tr}[\hat{A}\mathscr{G}_T(t_f,t_0;\theta)\rho(t_0)]\rangle, \tag{3}$$

under certain experimental constraints that will further be specified in the following. In Eq. (3), $\mathscr{G}_T(\tau,t_0;\theta)$ is the Liouville-space propagator associating with the total Hamiltonian $H_T(t;\theta)$ [Eq. (1)] in the presence of θ phase-locked pump-dump fields; Tr denotes the trace over both the electronic and nuclear degrees of freedom in the molecular system, while $\langle\cdots\rangle$ stands for the statistic average over the random distribution of relative phase θ between the pump and the dump fields.

In this paper, we shall consider the optimal pump-dump control under the following three constraints. The first one is the phase-unlocked experimental condition as stated earlier, in which θ is assumed to be an evenly distributed random variable within $[0,2\pi)$. The second constraint is that the roles of E_1 and E_2 in their interactions with the optical medium can be distinct as pump and dump, respectively. This is the conventional pump-dump control scenario in which the power spectra of the two fields are separated away from each other. In this case, the phase-lock may be neither experimentally easy nor physically important to the control of target dynamics. The third constraint is the requirement of the finite incident energy from each of the fields, $j=1$ and 2,

$$I_j=\int_{t_0}^{t_f}d\tau|E_j(\tau)|^2. \tag{4}$$

Under these three constraints, we have derived[14] the following general coupled self-consistent control equations:

$$K_j(\tau;t_f)=\lambda_jE_j(\tau);\ \text{ with } j=1 \text{ and } 2, \tag{5}$$

for a pair of optimal pump-dump fields $\{E_1,E_2\}$. In Eq. (5), $\tau\in[t_0,t_f]$ and λ_j is a Lagrange multiplier for the finite incident energy constraint in Eq. (4). The inclusion of two independent Lagrange multipliers, λ_1 and λ_2, is consistent with the condition of the complete random phase θ. The key quantities in Eq. (5) are the pump control kernel K_1 and the dump control kernel K_2. They are formally given by[14]

$$K_1(\tau;t_f)=\langle(i/\hbar)\mathrm{Tr}[\hat{A}_T(\tau;t_f,\theta)\mathscr{D}_-^{\,r}\rho_T(\tau;\theta)]\rangle \equiv\langle K_+^*(\tau;t_f,\theta)\rangle, \tag{6a}$$

$$K_2(\tau;t_f)=\langle(i/\hbar)\mathrm{Tr}[\hat{A}_T(\tau;t_f,\theta)\mathscr{D}_-^{\,l}\rho_T(\tau;\theta)]e^{i\theta}\rangle \equiv\langle K_-(\tau;t_f,\theta)e^{i\theta}\rangle. \tag{6b}$$

Recall that the auxiliary Liouville-space dipole operators, $\mathscr{D}_-^{\,r}$ and $\mathscr{D}_-^{\,l}$ [Eq. (2)], are responsible for the pump and the dump processes respectively. Similarly, the control kernels, K_1 and K_2 [Eq. (6)], are for the pump control and the dump control processes, respectively. $K_\pm(\tau;t_f,\theta)$, defined in the second identities in Eq. (6), are the two components of theconventional single-field (or phase-locked) control kernel.[7,14,17] They can be equivalently recast in terms of Hilbert-space operators only:[7,14,17] [cf. Eqs. (2) and (6)]

$$K_\pm(\tau;t_f,\theta)=(i/\hbar)\mathrm{Tr}[\hat{A}_T(\tau;t_f,\theta)D_\pm\rho_T(\tau;\theta)]. \tag{7}$$

In Eqs. (6) and (7), $\rho_T(\tau;\theta)\equiv\mathscr{G}_T(\tau,t_0;\theta)\rho(t_0)$ is the density matrix propagated forward from the initial t_0 to τ, while $\hat{A}_T(\tau;t_f\theta)=\hat{A}\mathscr{G}_T(t_f,\tau;\theta)=\mathscr{G}_T(\tau,t_f;\theta)\hat{A}$ is the target operator propagated backward from the final t_f to τ. Since the propagator is controlled by the total Hamiltonian $H_T(t,\theta)$ which depends on both the pump E_1 and the probe E_2 fields, the control kernel K_j [Eq. (6)] will also be functional of both control fields. The control equations in Eq. (5) with $j=1$ and 2 should therefore be solved jointly and iteratively. The resulting pump-dump fields are only locally optimal and are often also too complicated and unrobust to be experimentally realizable.

The simplest linearized version of Eq. (5) can be obtained by considering the optimal control in either the weak pump or/and the weak dump response regime.[13,14] This can be done by considering, at any given $E_k\neq E_j$, the perturbative expansion of the control kernel K_j [Eq. (6)] to the first order in the control field E_j. In this case, Eq. (5) reduces to the following form:[13,14]

$$\int_{t_0}^{t_f}d\tau' M_j(\tau,\tau';\{E_k\})E_j(\tau')=\lambda_jE_j(\tau);\quad \text{with } j\neq k=1,2. \tag{8}$$

In Eq. (8), the E_k-dressed control response function M_j is Hermitian with respect to their two time arguments and formally given by[14] ($\tau \geqslant \tau'$)

$$M_1(\tau,\tau';\{E_2\}) = M_1^*(\tau',\tau;\{E_2\}) = (i/\hbar)^2 \mathrm{Tr}[\hat{A}_2(\tau;t_f)\mathscr{D}^r_- \mathscr{G}_2(\tau,\tau')\mathscr{D}^l_+ \rho_2(\tau')], \tag{9a}$$

$$M_2(\tau,\tau';\{E_1\}) = M_2^*(\tau',\tau;\{E_1\}) = (i/\hbar)^2 \mathrm{Tr}[\hat{A}_1(\tau;t_f)\mathscr{D}^l_- \mathscr{G}_1(\tau,\tau')\mathscr{D}^r_+ \rho_1(\tau')]. \tag{9b}$$

In these equations, the Green function $\mathscr{G}_k(\tau,\tau')$ is defined by the molecular Hamiltonian in the presence of the external field E_k only,[13,14]

$$H_k(t) = H - D_+ E_k(t) - D_- E_k^*(t). \tag{10}$$

It also governs the forward propagated density matrix, $\rho_k(\tau') = \mathscr{G}_k(\tau',t_0)\rho(t_0)$, and the backward propagated target, $\hat{A}_k(\tau;t_f) = \hat{A}\mathscr{G}_k(t_f,\tau) = \mathscr{G}_k(\tau,t_f)\hat{A}$, in Eq. (9). In deriving Eq. (9), we included the random phase θ average.[14] As a result, all the phase-sensitive terms that contain explicitly either two D_-'s or two D_+'s do not contribute to the control response function M_j. We have also made use of the condition that E_1 and E_2 are distinct for the pump and the dump, respectively, as they interact with the optimal medium.[14] Therefore, M_1 [Eq. (9a)] that contains $\mathscr{D}^l_+$ and $\mathscr{D}^r_-$ describes the second-order pump response in which both the ket and the bra are excited by the E_1 field [cf. Eq. (2)]. Similarly, M_2 [Eq. (9b)] that contains $\mathscr{D}^r_+$ and $\mathscr{D}^l_-$ describes the second-order dumping process in which both the ket and bra are de-excited by the E_2 field. In fact, M_j is the E_k-dressed molecular response function for the control expectation value $A(t_f)$ [cf. Eq. (3)] to the second order in the E_j field. That is,[13,14]

$$A_j^{(2)}(t_f) = \int_{t_0}^{t_f} d\tau \int_{t_0}^{t_f} d\tau' M_j(\tau,\tau';\{E_k\}) E_j^*(\tau) E_j(\tau'). \tag{11}$$

Substituting Eqs. (4) and (8) into Eq. (11), we obtain $A_j^{(2)}(t_f) = \lambda_j I_j$. The eigenvalue λ_1 in Eq. (8) is therefore the optimal pump control yield $A_1^{(2)}(t_f)$ with respect to the incident weak pump energy I_1 at the given dump field E_2. Similarly, the eigenvalue λ_2 is the weak dump control yield at the given pump field. We can therefore identify,[13,14] for any given $E_k \neq E_j$, the globally optimal weak E_j control field as the eigenfunction of Eq. (8) that corresponds to the largest eigenvalue λ_j. The above analysis is based on the viewpoint of single-photon pump (dump) control[7] in the presence of an arbitrary given dump (pump) field.[13,14] In order to find the optimal pair of pump-dump fields $\{E_1,E_2\}$, Eq. (8) with $j=1$ and 2 should be solved jointly and iteratively.[14] In this case, both fields should also be retained in the weak response regime. At each step of the iteration, the globally optimal field E_j can be obtained with respect to the given counterpart field $E_k \neq E_j$. However, whether the globally optimal pair of pump-dump field $\{E_1,E_2\}$ can be obtained or not is yet to be identified. In the next section, we shall consider the control of pure state systems in which the globally optimal pair of pump-dump fields can be identified unambiguously in the weak response regime.

III. PUMP-DUMP CONTROL OF PURE STATE SYSTEMS

The general Liouville space control formulation presented in the previous section serves as the common background for quantum, classical and semiclassical numerical implementations. In this section, we shall use the Hilbert space dynamics and consider the pump-dump control in which both the initial system $\rho(t_0)$ and the final target $\hat{A}$ are in the pure states. Let us denote them as

$$\rho(t_0) = |\psi(t_0)\rangle\langle\psi(t_0)|, \tag{12a}$$

$$\hat{A} = |\phi\rangle\langle\phi|. \tag{12b}$$

For completeness, we shall start with the general control kernels, K_1 and K_2 [Eq. (6)] in the strong response regime. For simplicity, let us focus on the auxiliary kernels, $K_\pm(\tau;t_f,\theta)$ of Eq. (7). In the pure state case, the propagated density matrix and target in Eq. (7) at time $\tau \in [t_0,t_f]$ are given by:

$$\rho_T(\tau;\theta) = |\psi_T(\tau;\theta)\rangle\langle\psi_T(\tau;\theta)|, \tag{13a}$$

$$\hat{A}_T(\tau;t_f,\theta) = |\phi_T(\tau;t_f,\theta)\rangle\langle\phi_T(\tau;t_f,\theta)|. \tag{13b}$$

Here, $\psi_T(\tau;\theta) \equiv G_T(\tau,t_0;\theta)\psi(t_0)$ and $\phi_T(\tau;t_f,\theta) \equiv G_T(\tau,t_f;\theta)\phi$ are the forward propagated and the backward propagated Hilbert space wave functions for the system and the target, respectively. The Hilbert space time propagator, $G_T(\tau,\tau';\theta)$, is governed by the total Hamiltonian $H_T(t;\theta)$ of Eq. (1) at the given value of the relative phase θ. Substituting Eq. (13) into Eq. (7), we obtain[14]

$$K_\pm(\tau;t_f,\theta) = c^*(t_f;\theta) f_T^\pm(\tau;t_f,\theta). \tag{14}$$

Here,

$$c(t_f;\theta) = \langle\phi|\psi_T(t_f;\theta)\rangle, \tag{15}$$

is the amplitude of the target yield if the control is performed under the phase-locked pump-dump scenario, and

$$f_T^\pm(\tau;t_f,\theta) = (i/\hbar)\langle\phi_T(\tau;t_f,\theta)|D_\pm|\psi_T(\tau;\theta)\rangle. \tag{16}$$

The final phase-unlocked pure state control kernels, K_1 and K_2, are then obtained by substituting Eq. (14) for Eq. (6).

We now turn to the field-dressed control response function, M_j [Eq. (9)] in the weak pump or the weak dump response regime. In the pure state case, we have: [cf. Eq. (9)]

$$\rho_k(\tau') = |\psi(\tau';\{E_k\})\rangle\langle\psi(\tau';\{E_k\})|, \tag{17a}$$

$$\hat{A}_k(\tau;t_f) = |\phi(\tau;t_f,\{E_K\})\rangle\langle\phi(\tau;t_f,\{E_k\})|. \tag{17b}$$

Both the forward propagation in the system wave function $\psi(\tau';\{E_k\})$ and the backward propagation in the target $\phi(\tau;t_f,\{E_k\})$ are governed by the E_k-dressed Hamiltonian H_k of Eq. (10). Substituting Eq. (17) into Eq. (9), and further

making use of the definitions of Liouville-space operators, $\mathscr{D}_{\pm}^{l,r}$ of Eq. (2) and $\mathscr{G}_k(\tau,\tau')\hat{O}=G_k(\tau,\tau')\hat{O}G_k^{\dagger}(\tau,\tau')$, we can arrive at the following equations:[14]

$$M_1(\tau,\tau';\{E_2\})=f_+^*(\tau;t_f,\{E_2\})f_+(\tau';t_f,\{E_2\}), \quad (18a)$$

$$M_2(\tau,\tau';\{E_1\})=f_-(\tau;t_f,\{E_1\})f_-^*(\tau';t_f,\{E_1\}). \quad (18b)$$

Here, $f_{\pm}$ has the similar form as $f_T^{\pm}$ [Eq. (16)] and is given by

$$f_{\pm}(\tau;t_f,\{E_k\})=(i/\hbar)\langle\phi(\tau;t_f,\{E_k\})|D_{\pm}|\psi(\tau;\{E_k\})\rangle. \quad (19)$$

Equation (18) describes the unique feature for the pure state pump-dump control case in which the field dressed-response function M_j with two time variables can be factorized as a product of two single time variable functions. This feature greatly reduces the computational effort on the evaluation of the pump-dump control response function M_j. In the case of control a thermal equilibrium system, the right-hand-sides of Eq. (18) should include the Boltzmann canonical ensemble summation over all populated states. Upon substituting Eq. (18) into [Eq. (8)] and followed by applying the phase-unlocked condition that allows the removal of an arbitrary constant phase factor, we obtain the following two simplified control equations:[14]

$$f_+^*(\tau;t_f,\{E_2\})=\lambda_1' E_1(\tau), \quad (20a)$$

$$f_-(\tau;t_f,\{E_1\})=\lambda_2' E_2(\tau). \quad (20b)$$

The constant λ_j' in Eq. (20) relates to the original Lagrange multiplier, i.e. the eigenvalue λ_j in Eq. (8), as[14]

$$\lambda_1'=\lambda_1\Big|\int_{t_0}^{t_f}d\tau' f_+(\tau';t_f,\{E_2\})E_1(\tau')\Big|^{-1}=(\lambda_1/I_1)^{1/2}, \quad (21a)$$

$$\lambda_2'=\lambda_2\Big|\int_{t_0}^{t_f}d\tau' f_-^*(\tau';t_f,\{E_1\})E_1(\tau')\Big|^{-1}=(\lambda_2/I_2)^{1/2}. \quad (21b)$$

The second identities in Eqs. (21) were obtained by making use of Eq. (20), together with the definition of I_j in Eq. (4) for the total incident energy from the jth control field. A similar result to Eq. (20b) was previously derived by Tannor and Rice [cf. Eq. (6) of Ref. 1] using the perturbation expansion of f_- [cf. Eq. (19)] to the first order in the field E_1. In their original work,[1] the dump field is optimized for a given weak pump field. Eq. (20) shows that the Tannor-Rice pump-dump scheme can be readily extended to a joint optimization of a pair of correlated optimal pump-dump fields.[14] As we discussed earlier, either Eq. (20a) or Eq. (20b) can be used independently to find the optimal weak field E_j in the presence of the given $E_k\neq E_j$ with arbitrary form and intensity. This is done by propagating $\psi(\tau;\{E_k\})$ forward and $\phi(\tau;\{E_k\})$ backward respectively, followed by evaluating the dipole overlap to obtain $f_{\pm}$ [Eq. (19)], and thus the optimal control field E_j [cf. Eq. (20)].

To find the pair of optimal pump-dump fields, Eqs. (20a) and (20b) shall be solved jointly and iteratively.[14] By doing that we shall also retain both of the control fields in the weak response regimes.[14] Furthermore, the above analysis assures only that, at each step of iteration, the unique (therefore also the globally) optimal field E_j be obtained with respect to a given counterpart field $E_k\neq E_j$. However, whether the globally optimal pair of pump-dump field $\{E_1,E_2\}$ can be obtained or not is yet to be identified.

In the following, we shall explicitly consider the weak pump-dump response regime and identify unambiguously the globally optimal pair of control fields in this case. To do this, we can start either with $f_T^{\pm}$ [Eq. (16)] or $f_{\pm}$ [Eq. (19)], followed by the explicit first order expansion of the relevant quantity to the field it depends on. The former approach[20] is similar to the one used by Dubov and Rabitz[12] where the phase-locked pump-dump control was considered. In this paper, let us consider the latter approach. By carrying out the trace over the electronic degrees freedom, followed by the perturbation expansion of the relevant Schrödinger wave functions to the lowest order in the control field, we can recast Eq. (19) in the following form:

$$\begin{aligned} f_+(\tau;t_f,\{E_2\}) &= (i/\hbar)\langle\phi_e(\tau;t_f,\{E_2\})|\mu|\psi_g(\tau;\{E_2\})\rangle \\ &\approx (i/\hbar)\langle\phi_e^{(1)}(\tau;\{E_2\})|\mu|\psi_g^{(0)}(\tau)\rangle \\ &\equiv \int_{\tau}^{t_f}d\tau' B(\tau',\tau)E_2^*(\tau'), \end{aligned} \quad (22a)$$

$$\begin{aligned} f_-(\tau;t_f,\{E_1\}) &= (i/\hbar)\langle\phi_g(\tau;t_f,\{E_1\})|\mu|\psi_e(\tau;\{E_1\})\rangle \\ &\approx (i/\hbar)\langle\phi_g^{(0)}(\tau)|\mu|\psi_e^{(1)}(\tau;\{E_1\})\rangle \\ &\equiv \int_{t_0}^{\tau}d\tau' B(\tau,\tau')E_1(\tau'). \end{aligned} \quad (22b)$$

Here, $B(\tau,\tau')$ can be viewed as the Hilbert-space two-photon control response function, defined by $(\tau\geqslant\tau')$

$$B(\tau,\tau')=\langle\phi_g^{(0)}(\tau)|\hat{T}(\tau-\tau')|\psi_g^{(0)}(\tau')\rangle, \quad (23)$$

with

$$\hat{T}(t)\equiv(i/\hbar)^2\mu e^{-iH_e t/\hbar}\mu, \quad (24)$$

being the dipole transition operator. In Eq. (23), $|\psi_g^{(0)}(\tau')\rangle=e^{-iH_g(\tau'-t_0)/\hbar}|\psi_g(t_0)\rangle$ is the free forward propagation of the initial system wave function, and $\langle\phi_g^{(0)}(\tau)|=\langle\phi_g(t_f)|e^{-iH_g(t_f-\tau)/\hbar}$ the free backward propagation of the final target wave function in the ground electronic state. The final coupled eigenequations for a pair of optimal pump-dump control fields in the weak response regime can then be obtained by substituting Eq. (22) into Eq. (20).

Before presenting the final eigenequations, we shall re-examine the physical meaning of the eigenvalue λ_j' [cf. Eq. (21)] in the weak pump-dump response regime. Let us first introduce the joint yield for pump-dump control as

$$\lambda^2=y(t_f)\equiv\frac{A(t_f)}{I_1 I_2}. \quad (25)$$

Since $\lambda_j=A(t_f)/I_j$ corresponds to the optimal yield with respect to the weak E_j response regime in the presence of any given $E_k\neq E_j$ field, the relation $\lambda^2=\lambda_1/I_2=\lambda_2/I_1$ will be

valid for the joint optimal pair of weak pump-dump fields. Combined with Eq. (21), we have that $\lambda_1'(I_1/I_2)^{1/2}=\lambda_2'(I_2/I_1)^{1/2}=\lambda$. In the weak pump-dump response regime, however, the incident energies from the optimal fields act as scaling factors. Without losing the generality of the pump-dump control in the weak response regime, we can choose $I_1=I_2$ and thus obtain

$$\lambda_1'=\lambda_2'=\lambda \tag{26}$$

as the square root of the joint control yield [Eq. (25)]. We have therefore arrived at the following generalized control eigenequations [cf. Eqs. (20)–(26)] for the optimal pairs of phase-unlocked pump-dump fields in the weak response regime,

$$\int_\tau^{t_f} d\tau' B^*(\tau',\tau)E_2(\tau')=\lambda E_1(\tau), \tag{27a}$$

$$\int_{t_0}^{\tau} d\tau' B(\tau,\tau')E_1(\tau')=\lambda E_2(\tau). \tag{27b}$$

Furthermore, if $\{E_1,E_2\}$ is the eigenfunction to Eq. (27) associating with the eigenvalue λ, then $\{-E_1,E_2\}$ or $\{E_1,-E_2\}$ is also the eigenfunction associating with the eigenvalue of $-\lambda$. However, these pairs of fields are the same in this paper in which the relative phase θ between E_1 and E_2 is considered to be completely random. We shall therefore consider only the solutions of Eq. (27) with positive eigenvalues, $\lambda=[A(t_f)/(I_1I_2)]^{1/2}$ [cf. Eq. (25)], which are also the square roots of the control yields with respect to the product of incident field energies I_1I_2 [cf. Eq. (4)]. Therefore, the *globally optimal pair* of pump-dump fields in the weak response regime can be obtained as the eigenfunction of Eq. (27) associating with the largest positive eigenvalue λ. In order to see that Eq. (27) are indeed the joint eigenequations for solving the optimal pair of pump-dump $\{E_1,E_2\}$ fields, let us consider the time-grid representation in the region $[t_0,t_f]$. In this case, each of $E_1(t)$ and $E_2(t)$ is a vector of N elements, while $B(\tau,\tau')$ is a lower-trigonal $N\times N$ matrix, defined as

$$\mathbf{B}_{jk}=\begin{cases} 0 & \text{for } j<k \\ B(t_j,t_k) & \text{for } j\geqslant k \end{cases}. \tag{28}$$

Equations (27) can thus be recast in the form of two standard $N\times N$ Hermitian matrix eigenequations:

$$\mathbf{B}^\dagger\mathbf{B}E_1=\lambda^2E_1, \tag{29a}$$

$$\mathbf{B}\mathbf{B}^\dagger E_2=\lambda^2E_2. \tag{29b}$$

Equations (27) [or Eq. (29)] together with the above physical argument on the eigenvalue λ [Eq. (25)] constitute the major theoretical result of this paper. In this formulation, the optimal pair of pump-dump control fields in the weak response regime can be obtained as an eigenequation problem and the solution is non-iterative. Furthermore, the globally optimal pair of pump-dump fields can be identified unambiguously.

IV. OPTIMAL STIMULATED RAMAN PUMPING IN THE WEAK RESPONSE REGIME

In this section, we shall limit our investigation to the case where both the initial system and the final target wave functions are in ro-vibronic levels on the ground electronic surface, i.e., $|\psi_g(t_0)\rangle=|i\rangle$ and $|\phi_g(t_f)\rangle=|f\rangle$, with corresponding eigenenergies of ϵ_i and ϵ_f, respectively. In this case, the weak pump-dump control response function B of Eq. (23) assumes the following form:

$$B(\tau,\tau')=e^{-i\epsilon_f(t_f-\tau)/\hbar}T_{fi}(\tau-\tau')e^{-i\epsilon_i(\tau'-t_0)/\hbar}. \tag{30}$$

Here, $T_{fi}(t)=\langle f|\hat{T}(t)|i\rangle$ [cf. Eq. (24)], is the well-known T-matrix elements for the Raman [more precisely the stimulated emission pumping[21] (SEP) or the stimulated Raman pumping[22] (STIRAP)] $f\leftarrow i$ transition amplitude.[23,24] Since both the pump-dump control and the SEP or STIRAP spectroscopic processes describe the same two-photon dynamics that excite the initial $|i\rangle$ level to the final $|f\rangle$ level on the ground surface via the intermediate excited electronic state, it is not surprising that they share the same dynamical quantity. The possibility of using the control formulation developed in this section to design the optimal SEP or STIRAP spectroscopic measurements or to extract the dynamic information from the spectroscopic signals for the control feedback will be investigated in future.

To proceed, let us introduce the following auxiliary field functions:

$$x_1(t)=e^{-i\epsilon_i t/\hbar}E_1(t), \tag{31a}$$

$$x_2(t)=e^{-i\epsilon_f t/\hbar}E_2(t). \tag{31b}$$

In this case, Eq. (27) reduces to

$$\int_\tau^{t_f} d\tau' T_{fi}^*(\tau'-\tau)x_2(\tau')=\lambda x_1(\tau), \tag{32a}$$

$$\int_{t_0}^{\tau} d\tau' T_{fi}(\tau-\tau')x_1(\tau')=\lambda x_2(\tau). \tag{32b}$$

For simplicity, we have removed the constant phase factor in the above equations, since the relative phase between the two control fields is anyhow unlocked. Equations (32a) and (32b) are in fact not independent. By changing the time argument of x_1 to t_0+t and that of x_2 to t_f-t, we can see that the above two equations are just complex conjugate to each other. We have therefore $x_1^*(t_0+t)=x_2(t_f-t)$. This identity leads to the following symmetry relation between the optimal pump field and its counterpart of optimal dump field [cf. Eq. (31)]:

$$e^{i\epsilon_i(t_0+t)/\hbar}E_1^*(t_0+t)=e^{-i\epsilon_f(t_f-t)/\hbar}E_2(t_f-t). \tag{33}$$

The above symmetry relation can be recast in the frequency domain as

$$e^{-i\omega(t_0+t_f)}\hat{E}_2(\omega)=\hat{E}_1^*(\omega+\omega_{fi}), \tag{34}$$

where $\hat{E}_j(\omega)$ is the Fourier transform of $E_j(t)$:

$$\hat{E}_j(\omega)=\int_{-\infty}^{\infty} d\ t e^{i\omega t}E_j(t)\equiv|\hat{E}_j(\omega)|e^{i\varphi_j(\omega)}. \tag{35}$$

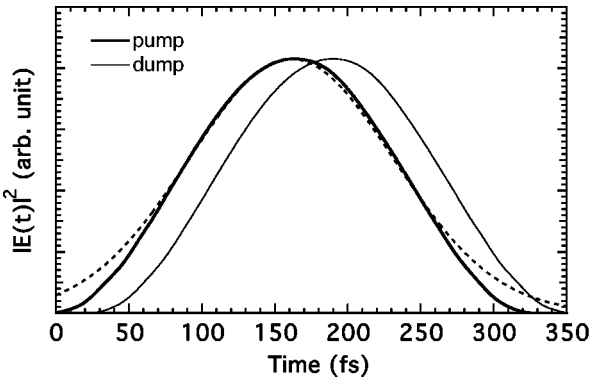

FIG. 1. Globally optimal pair pump-dump fields for the target of $\nu = 14$ in I_2 X surface. The molecule begins at $\nu = 0$. The fitted Gaussian pump pulse is also included in the dashed line.

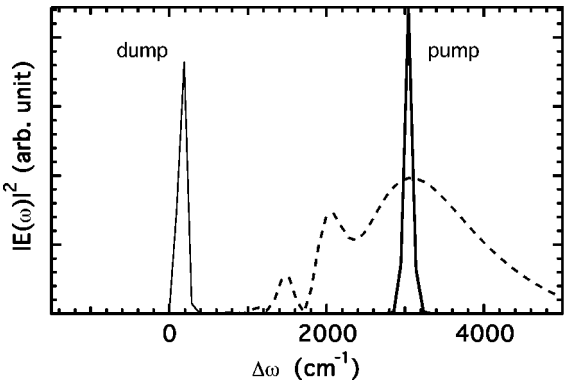

FIG. 2. Globally optimal pair pump-dump fields as the same as Fig. 1. Included in the dashed line is also the Raman excitation profile defined in Eq. (36).

Note that the n^{th} order frequency chirp of field E_j is defined by $c_j^{(n)} = d^{n+1}\varphi_j(\omega=\overline{\omega_j})/d\omega^{n+1}$, where $\overline{\omega_j}$ is its central frequency. Equations (33) and (34) lead therefore to the following conclusions for the optimal pair of pump-dump fields, $\{E_1, E_2\}$: (i) their frequency chirps are of the same value but opposite in signs; (ii) their temporal spectra, $|E_j(t)|^2$, are symmetric about the center, i.e. $(t_0+t_f)/2$, of the interaction region $[t_0, t_f]$; (iii) the power spectrum of the optimal dump field, $|\hat{E}_2(\omega)|^2$, is red (Stoke) shifted by $\omega_{fi} = (\epsilon_f - \epsilon_i)/\hbar$ compared with that of the pump field, $|\hat{E}_1(\omega)|^2$. The above three properties of optimal pair of pump-dump fields hold for the control of eigenstate in the absence of dephasing and relaxation processes.

As an example of implementation the formalism developed in this section, let us consider the pump-dump control of vibrational excitation in the iodine molecule. The molecule begins in its ground X state which is coupled to the excite B state via pump or dump field interaction. For simplicity, we assume that the molecule begins at the vibronic ground $\nu = 0$ level in X and neglect the effects of molecular rotation. The potential functions for I_2 vibration in the electronic ground X state and in the electronic excited B state are chosen as the same as those used in Ref. 18. The target is chosen to be the $\nu = 14$ vibronic level in X, and the target time is set to be $t_f = 350$ fs. The Raman frequency between the final target and the initial vibronic level is $\omega_{fi} = 2876\ \text{cm}^{-1}$. Shown in Fig. 1 and Fig. 2 are, respectively, the temporal and spectral profiles of the globally optimal pair of pump-dump fields evaluated by using Eqs. (27) with Eq. (30). Each field in this globally optimal pump-dump pair consists of a nearly transform-limited pulse with the temporal FWHM of 165 fs. The globally optimal pump field has the temporal center at 161 fs and the spectral center at $\omega_1 = 3030\ \text{cm}^{-1} + \omega_{eg}$ (i.e., the excess carrier frequency of $3030\ \text{cm}^{-1}$). As the symmetry relation [Eqs. (33) or (34)], the corresponding dump field centers at 189 fs (i.e., $t_f - 161$ fs) with the carrier frequency of $\omega_2 = \omega_1 - \omega_{fi}$. In order to understand the physical meaning of the carrier frequency of the globally pump field, we also include in Fig. 2 a dashed curve for the finite-time Raman excitation profile signal, defined by (assuming $t_0 = 0$)

$$S_R(\omega; t_f) = \left| \int_0^{t_f} dt\ e^{i(\omega+\epsilon_i/\hbar)t} T_{fi}(t) \right|^2 . \tag{36}$$

It is clear that the globally optimal pump field carries the frequency ω_1 at which the Raman excitation profile reaches its global maximum. For comparison, we consider also the pair of Gaussian pulses whose temporal and spectral centers, and temporal FWHM's are set to be those of the globally optimal pump-dump fields pair. Shown in the dashed curve in Fig. 1 is the temporal profile of the fitted Gaussian pump pulse. The corresponding fitted Gaussian dump field is not plotted since it can be obtained by the symmetry relation of Eq. (33). Figure 3 presents the control yield, $A(t)/(I_1 I_2)$ with respect to λ^2_{max} [Eq. (25)] as a function of time. The solid line is for the globally optimal pump-dump pair while the dashed line is for the fitted Gaussian pump-dump pair [cf. the dashed curve in Fig. 1], which reaches about 90% of the globally optimal result. In order to investigate the key factors in the present control system of study, we also shift the temporal centers of both the pump and dump pulses to 175 fs, the center of the control interaction interval, while remain the optimal carrier frequencies untouched. The resulting yield in this case reduces only slightly further. The above analysis implies that the key factor in the present control

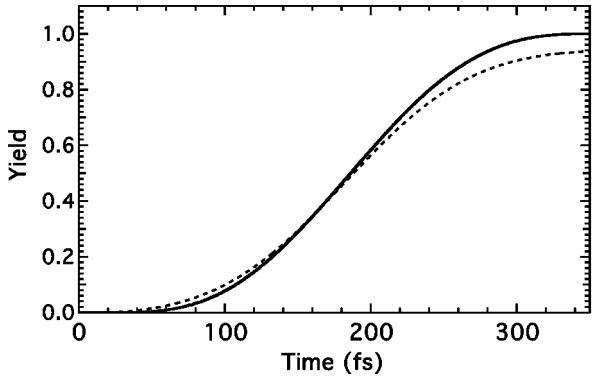

FIG. 3. Relative control yield $y(t)$ [cf. Eq. (25)] with respect to λ^2_{max} for both the globally optimal pair of pump-dump fields (solid) and the fitted pair of Gaussian fields (dashed).

system is the spectral components of the control fields. This is in consistent with the simple physical intuition of the stimulated Raman pump-dump control.

V. SUMMARY AND CONCLUSION

In this paper, we systematically investigated the general theory of the optimal phase-unlocked pump-dump control. We presented a hierarchy of reduction from the general Liouville-space density matrix control formulation in the strong response regime and arrived at the generalized eigenequation [Eq. (27) with Eq. (23)], which is applicable in the pure state weak control response regime. Besides the novel eigenequation [Eq. (27)] for the optimal pump-dump control, this work has also acclaimed the following accomplishments.

We showed that the square of the eigenvalue [λ in Eq. (27)] is the pump-dump control yield, $A(t_f)$, with respect to the incident pump-dump field energies product, $I_1 I_2$ [cf. Eq. (25) and the comments followed]. Therefore, the globally optimal pair of phase-unlocked pump-dump control fields in the pure state and weak response regime is identified as the eigenfunction of Eq. (27) associating with the largest positive eigenvalue λ. Discussed and further demonstrated were the numerical implementation of the eigenequation based on the time-grid representation [cf. Eqs. (28) and (29)]. The implementation based on the expansion of the fields on a set of basis functions can also be carried out without major difficulty.

We further investigated the weak response optimal stimulated Raman pumping control in which both the initial system and the final target state are molecular eigenstates on the ground electronic surface (cf. Sec. IV). In this case, we derived the novel symmetry relation, i.e. Eqs. (33) and (34) and the discussion followed, between the optimal pump field and its counterpart dump field. Noted that the symmetry relation described by Eqs. (33) and (34) holds rigorously only for the control of eigenstate in non-dissipative systems. We may however expect certain qualitative properties will retain in the other types of control systems. In a recent numerical example in which we considered the control of a highly excited I_2 stretching wave packet localized in both coordinate and momentum in the ground X electronic state, the optimal pump-dump pair fields are shown to be of opposite signs in the chirps.[14] The key quantity, $T_{fi}(t)$ [cf. Eqs. (24) and (30)], in the optimal stimulated Raman pumping control processes is the same as that in the Raman spectroscopic measurement.[23,24] This property may lead to the possibility of using the control formulation developed in this paper to device the optimal SEP or STIRAP spectroscopic measurements or to extract the dynamic information from the optical signals to the control feedback. The simple numerical example presented in Sec. IV suggested a such kind of strong correlation.

In conclusion, this work constitutes a systematic theory of the optimal control with two phase-unlocked fields that are physically distinct as the pump and the dump fields. This is consistent with the well known Tannor-Rice control scenario.[1] The method developed here can be readily applied to study the phase-unlocked pump-pump control processes.[12,13] The theoretical framework in this paper provides a clear interplay of the variety of two-field control formulations in the strong response regime and in weak response regime, in terms of Liouville-space density matrix dynamics and in the Hilbert-space wave function representation. Comparison of the phase-unlocked two-field control scenario with its phase-locked counterpart[2,12] will be made elsewhere.[20]

ACKNOWLEDGMENT

The support of the Research Grants Council of the Hong Kong Government is gratefully acknowledged.

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