Pulse shaping for optimal control of molecular processes

Taiwang Cheng and Alex Brown[a)]
Department of Chemistry, University of Alberta, Edmonton, Alberta T6G 2G2, Canada

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In this paper, a new method is proposed to design optimized control fields with desired temporal and/or spectral properties. The method is based on penalizing the difference between an optimized field obtained from an iterative scheme and a reference field with desired temporal and/or spectral properties. Compared with the standard optimal control theory, the current method allows a simple, experimentally accessible field be found on the fly; while compared with parameter space searching optimization, the iterative nature of this method allows automatic exploration of the intrinsic mechanism of the population transfer. The method is illustrated by examing the optimal control of vibrational excitation of the Cl–O bond with both temporally and spectrally restricted pulses.
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I. INTRODUCTION

The use of shaped or specially designed laser pulses to control chemical processes has received much attention recently,[1–7] partly due to the fast development of pulse shaping techniques.[8] With respect to controlling quantum dynamics, optimal control theory (OCT) has been developed to effectively obtain the driving field which will induce the desired quantum process.[9–16] The optimal control investigation of a laser driven system can be viewed as an inverse problem, in which rather than knowing the field and determining the final state, we now "know" the final state, and are trying to find the field which could fulfill the desired quantum process. The goals of optimal control are twofold: first, to achieve some desired quantum process with the help of shaped laser pulses and second, to detect the properties of the system by analyzing the optimized pulse.

There have been two types of widely used strategies in OCT. One is a local control scheme, where the field is adjusted on the fly to react to the instantaneous change of the quantum system—this is often used in the theoretical investigations when the system Hamiltonian is known to some extent. However, real chemical systems are often too complex to have a theoretical description with sufficient precision, and it is very difficult in experiments to determine the state of the system in real time. Moreover, the determination of the state (measurement) will inevitably disturb the original system. This leads to the so-called closed-loop control, where completely new fields emerge after the previous control experiment is finished. The new fields are often determined from some stochastic algorithm, and one of the most important is the genetic algorithm (GA), see, for example, Ref. 17.

A challenge for theory is to design pulses that are experimentally feasible and that allow understanding and interpretation of the underlying mechanisms and dynamics leading to the successful control of molecular processes.[17–26] For local optimal control, the final fields obtained usually are very complex and difficult to be realized and explained. In light of this, efforts have been devoted to reduce the complexity of the final optimized field.[19,26–28] In this paper, a new iterative scheme using a reference field in one commonly used local control scheme[13] is introduced and utilized to obtain physically simple and well defined optimized fields. The new scheme is presented in Sec. II, and then illustrated in Sec. III by examining the optimal control of vibrational excitation of the Cl–O bond with both temporally and spectrally restricted pulses. In Sec. IV, we provide a brief conclusion and discuss further applications of the current method.

II. THEORY

The control of desired transitions between preselected initial and final states (state-to-state control)[13] is of special interest due to its potential applications ranging from chemical reaction channel selection[21] to molecular quantum computing based on rovibrational states.[3,4] One of the most used algorithms for this purpose is the one initially proposed by Zhu *et al.*[13] which is an extension of one due to Krotov.[29] The method is based on a forward-backward iterative scheme to improve the control field. It has been shown that this method exhibits quadratic and monotonic convergence and has been proven to be very efficient for state-to-state control.[19,26,30]

For the control of a state-to-state transition, within the simplest form, the goal is to maximize the following objective function:

$$J(\psi_i(T),\phi_f) = |\langle \psi_i(T)|\phi_f\rangle|^2, \tag{1}$$

in which $|\phi_f\rangle$ refers to the objective state, $|\psi_i(t)\rangle$ is the time-dependent wave function, which starts from initial state $|\phi_i\rangle$ at $t=0$, and results by applying the external field $\varepsilon(t)$. T is the duration of the interaction and is usually termed as the target time.

By taking into account constraints on the external field, the optimal control can be reformulated as the problem of maximizing the following objective function:

[a)]Electronic mail: alex.brown@ualberta.ca

$$K(\psi_i(t),\psi_f(t)) = |\langle \psi_i(T)|\phi_f\rangle|^2 - \int_0^T f(\varepsilon(t))dt - 2\,\mathrm{Re}\left[\langle \psi_i|\phi_f\rangle \int_0^T \langle \psi_f(t)|\left(\frac{i}{\hbar}[H_0 - \mu\varepsilon(t)] + \frac{\partial}{\partial t}\right)|\psi_i(t)\rangle\right]. \quad (2)$$

In the right hand side of Eq. (2), the first term is the original objective of state transition J, the last term is to ensure that the time evolution follows the Schrödinger equation, while the second term represents constraints on the control field $\varepsilon(t)$, expressed as a functional f.

In the original work of Zhu *et al.*,[13] the functional $f(\varepsilon(t))=\alpha_0\varepsilon(t)^2$, where α_0 is a constant. Due to the fact that only the pulse energy is constrained, the method of Zhu *et al.* does not include explicit constraints on the pulse shape and/or spectral properties of the optimized field. Therefore, the fields obtained are often complex both in temporal shape and spectral composition. In light of this, de Vivie-Riedle and co-workers have proposed methods to reduce the temporal and spectral complexities of the optimized field.[19,26] They first introduced a pulse shaping function $s(t)$ to force the pulse to be smoothly turned on and off, i.e., $f(\varepsilon(t)) =[\alpha_0\varepsilon(t)^2]/s(t)$.[26] More recently, a subspace projection method was utilized to reduce the spectral complexity of the final field from the OCT algorithm.[19] In the direction of restricting the field strength of the final optimized field, Farnum and Mazziotti[27] have introduced a trigonometric mapping into the standard optimal control scheme and are able to restrict the field strength explicitly.

However, the above methods have one intrinsic problem as to how strongly the pulse energy should be penalized, i.e., how large the parameter α_0 should be is to some extent arbitrary. With a nonzero penalization of the total energy, the final transition objective becomes related to the penalization parameters chosen.[20,31] To overcome this difficulty, in the investigation of quantum unitary operation optimization,[4] Palao and Kosloff use a method where the difference between the field of the present iteration and the previous iteration (reference field) is penalized, i.e, $f(\varepsilon(t))=[\alpha_0(\varepsilon(t) - \epsilon_{\mathrm{ref}}(t))^2]/s(t)$, where $\epsilon_{\mathrm{ref}}(t)$ is the optimized field obtained in the previous iteration. In this scheme, the original objective of the state transition will not be affected by the second field term, as $f(\varepsilon(t))=[\alpha_0(\varepsilon(t)-\epsilon_{\mathrm{ref}}(t))^2]/s(t)$ of Eq. (2) will be zero upon convergence. However, this simple choice has the problem that the final field may be very complex and sometimes unrealistically strong, since there is no confinement regarding the field strength and spectral complexity.

To overcome the above problems, we adopt the idea that instead of choosing the field of the previous iteration as the reference field, a new reference field $\epsilon(t)$ is constructed based on the previous field, with the application of a filter function F to ensure the fulfillment of some predesigned temporal and spectral properties. For $f(\varepsilon(t))=[\alpha_0(\varepsilon(t) - \epsilon_{\mathrm{ref}}(t))^2]/s(t)$, with $\epsilon_{\mathrm{ref}}(t)$ as reference field, the solution of the optimization problem, i.e., maximizing Eq. (2) with respect to ψ_f, ψ_i, and $\varepsilon(t)$ can be readily written as

$$i\hbar\frac{\partial}{\partial t}\psi_i(t) = [H_0 - \mu\varepsilon(t)]\psi_i(t), \quad \psi_i(0) = \phi_i, \quad (3)$$

$$i\hbar\frac{\partial}{\partial t}\psi_f(t) = [H_0 - \mu\varepsilon(t)]\psi_f(t), \quad \psi_f(T) = \phi_f, \quad (4)$$

$$\frac{\alpha_0}{s(t)}(\varepsilon(t) - \epsilon_{\mathrm{ref}}(t)) = -\,\mathrm{Im}[\langle\psi_i|\psi_f\rangle\langle\psi_f|\mu|\psi_i\rangle]. \quad (5)$$

Equations (3)–(5) can be solved iteratively with an initial guess field with a method similar to that of Ref. 13, i.e.,

$$i\hbar\frac{\partial}{\partial t}\psi_i^0(t) = [H_0 - \mu\varepsilon^{\mathrm{guess}}(t)]\psi_i^0(t), \quad \psi_i(T) = \phi_i, \quad (6)$$

$$i\hbar\frac{\partial}{\partial t}\psi_f^k(t) = [H_0 - \mu\varepsilon_f^k(t)]\psi_f^k(t), \quad \psi_f(T) = \phi_f, \quad (7)$$

$$\varepsilon_f^k(t) = \epsilon_{\mathrm{ref},f}^k(t) - \frac{s(t)}{\alpha_0}\mathrm{Im}[\langle\psi_i^{k-1}(t)|\psi_f^k(t)\rangle\langle\psi_f^k(t)|\mu|\psi_i^{k-1}(t)\rangle], \quad (8)$$

$$i\hbar\frac{\partial}{\partial t}\psi_i^k(t) = [H_0 - \mu\varepsilon_i^k(t)]\psi_i^k(t), \quad \psi_i^k(0) = \phi_i, \quad (9)$$

$$\varepsilon_i^k(t) = \epsilon_{\mathrm{ref},i}^k(t) - \frac{s(t)}{\alpha_0}\mathrm{Im}[\langle\psi_i^k(t)|\psi_f^k(t)\rangle\langle\psi_f^k(t)|\mu|\psi_i^k(t)\rangle]. \quad (10)$$

Our goal in this paper is to find an optimized pulse with its spectral components within a predefined regime $\mathcal{S}$, and the maximum field amplitude to be less than some preselected value ε_0. Thus, we define the functional F as $F(\varepsilon(t)) =F_2(F_1(\varepsilon(t))$, in which F_1 is the spectral filtering,

$$F_1(f(t)) = \int_{\omega\in\mathcal{S}} \mathcal{F}_\omega(f(t))\exp(-i\omega t)dt, \quad (11)$$

where $\mathcal{F}_\omega(f(t))$ is the Fourier amplitude of $f(t)$ at frequency ω. And F_2 is defined

$$F_2(f(t)) = f(t), \quad \forall\ \max(f(t)) < \varepsilon_0,$$
$$F_2(f(t)) = \epsilon_0 f(t)/\max(f(t)), \quad \forall\ \max(f(t)) > \varepsilon_0, \quad (12)$$

where $\max(f(t))$ is the maximum of $f(t)$.

For our purpose of obtaining an optimized field with special temporal and spectral properties, a natural choice for the reference field would be $\epsilon_{\mathrm{ref},f}^k(t)=F(\varepsilon_i^{k-1}(t))$ and $\epsilon_{\mathrm{ref},i}^k(t) =F(\varepsilon_f^k(t))$. However, by performing a similar analysis to that in Eqs. (15)–(21) of Ref. 32, we find that the quadratic and monotonic convergence of the original scheme does not in general hold for any choice of F, i.e., the objective function is not guaranteed to increase after each iteration. However, it can be proven that the quadratic and monotonic convergence does hold for two special cases: (1) when $F=I$, i.e., the reference field is identical to the field from the previous iteration, this corresponds to the Kosloff scheme;[4] and (2) when the reference field is a fixed field independent of the iteration number k.

Numerically, we find that if we set $\epsilon^k_{\mathrm{ref},f}(t)=F(\varepsilon^{k-1}_i(t))$ and $\epsilon^k_{\mathrm{ref},i}(t)=F(\varepsilon^k_f(t))$, the objective function starts to decrease after a relatively large number of iterations. A careful examination shows that this problem cannot be fully resolved in the current iterative scheme. In the current implementation, we utilize a numerical procedure to ensure the improvement of population transfer. We start from a guess field $\varepsilon^{\mathrm{guess}}(t)$ in Eq. (6), then $\epsilon^k_{\mathrm{ref},f}(t)=\varepsilon^{k-1}_i(t)$ and $\epsilon^k_{\mathrm{ref},i}(t)=\varepsilon^k_f(t)$ are used to do the iterations in Eqs. (7)–(10). After each iteration, we test the final optimized field by calculating the population transfer with the field $F(\varepsilon^k_i(t))$. If the population transfer improves compared with that from $F(\varepsilon^{k-1}_i(t))$, then we proceed to the next step. However, if the population transfer decreases in the kth iteration, we go back one step and use the filtered optimized field in $(k-1)$th iteration $F(\epsilon^{k-1}_i(t))$ as the new guess field. In the new forward step [Eq. (6)], the penalty parameter α_0 is increased to be $2\alpha_0$ to perform a finer search. The process is repeated until a desired convergence criterion is achieved.

In this paper, the results are considered converged when α_0 increases from its initial value of 1 to over 16 within ten iterations. One iteration corresponds to a successful step in Eqs. (7)–(10) such that the population transfer with the filtered field is improved. In our calculations, we also reset α_0 to be the intial value (here $\alpha_0=1$) after ten iterations to take advantages of the large change of field in parameter space when α_0 is small, see Eqs. (8) and (10). The large change in parameter space has two advantages: first is to increase the convergence rate if the change is within one local peak, and the second is to allow the field to (possibly) move from one local maximum to another local maximum in parameter space.

III. RESULTS

To test the above scheme, we consider the optimal control of vibrational excitation in chlorine monoxide (ClO). The ground electronic state potential energy surface, dipole moment, and the vibrational states are obtained with an *ab initio* calculation.[33] Due to the fact the ClO vibrational ladder is quite harmonic, and has quite strong overtone transitions, this system is a reasonable benchmark problem for testing different optimal control algorithms. In this paper, we use the lowest 22 vibrational levels out of 42 total bound states to represent the ClO system, with the vibrational quantum number ranging from 0 to 21. We have tested that increasing the number of levels or using the potential explicitly does not affect the results shown here significantly. The objective considered is to transfer the population initially in the vibrational ground state $\nu=0$ to vibrational excited state $\nu=10$.

In Fig. 1(a), we present the optimized field $\varepsilon(t)$ obtained from setting the reference field $\epsilon(t)=0$, i.e., we use the original objective function suggested by Zhu *et al.*[13] The penalty parameter α_0 is chosen to be 0.05.[34] The initial guess field here, and in all subsequent optimization, is $\varepsilon^{\mathrm{guess}}_i=\varepsilon_0 \sin(\omega_0 t)$, with $\omega_0=(E_{10}-E_0)/10$ and $\varepsilon_0=0.01$ a.u. The

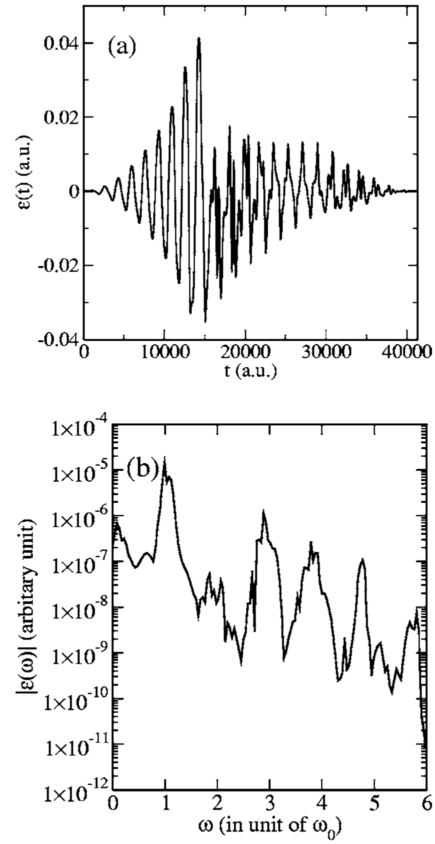

FIG. 1. Optimized field (a) and corresponding spectrum (b) with the reference field $\epsilon(t)=0$. The population transfer is 79.1%.

pulse shaping function is chosen in this paper as $s(t)=\sin^2(t\pi/T)$. E_i is the energy for ith vibrational level. The target time T is hereafter chosen to be 1 ps, as was used in a previous study of controlled vibrational excitation in ClO.[35] The optimized population transfer is determined to be 79.1%. The corresponding power spectrum $|\varepsilon(\omega)|$ is shown in Fig. 1(b). There is a predominant peak around the one-photon resonance with several small peaks around the overtone transitions.

We now apply the scheme described in Sec. II to find an optimized field with restrictions both in spectral bandwidth and maximum field strength. The frequency regime $\mathcal{S}$ in Eq. (11) is first set to be $[0.7\omega_0, 1.1\omega_0]$, which includes all the frequencies corresponding to adjacent level transitions in this 22 level system. The field amplitude is limited by setting the maximum field strength to be $\epsilon_0=0.05$ a.u. Thus, the field will be rescaled according to Eq. (12) if its maximum amplitude exceeds this value. We note that the frequency filtering in Eq. (11) introduces abrupt turn on and off of the field and to avoid this, we have applied $\sin^2$ filters in the initial and final 10 fs of the pulse. The resulting field is shown in Fig. 2. The population to the target level after interaction with the optimized field is 95.7%. Although we have set the maximum allowed field strength to be 0.05 a.u., the maximum value of final field is less than 0.04 a.u. This maximum field strength is comparable with that from a previous study,[35] but the population transfer there is only 83.3%.

The improvement of population transfer by using the new iterative algorithm is quite impressive. We note that we

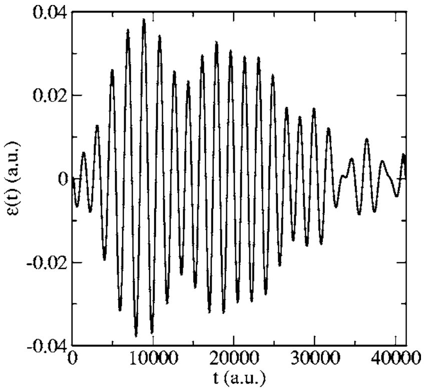

FIG. 2. Optimized field with spectrum limited to $[0.7\omega_0, 1.1\omega_0]$ and maximum field strength confined to be less than 0.05 a.u. The population transfer is 95.7%.

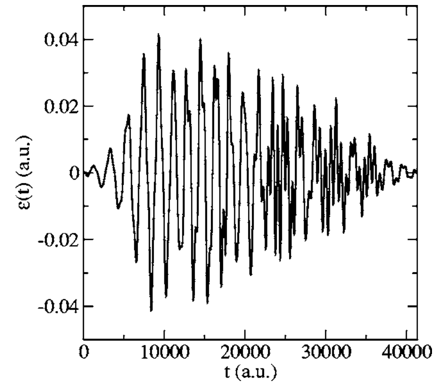

FIG. 4. Optimized field with spectrum limited to $[0.7\omega_0, 1.1\omega_0]$ and $[2.2\omega_0, 3.2\omega_0]$, and maximum field strength confined to be less than 0.05 a.u. The population transfer is 99.0%.

could decrease the penalty parameter α_0 further to obtain better population transfer when there is no reference field, $\epsilon(t)=0$. However, a very small α_0 indicates that there is little restriction on the pulse energy. Therefore, with a small penalty parameter α_0, the iterative algorithm may result in a very strong field, since the change of field in each iteration depends inversely on α_0, see Eqs. (8) and (10). Also, in the above discussion, we have chosen to explicitly constrain the maximum field strength, but there would be no difficulty to constrain the total pulse energy.

The choice of frequency in Fig. 2 is based on only including adjacent level transitions, which is intuitively the most important mechanism. To find the most important mechanisms beyond this, we use the field in Fig. 2 as the initial guess field, and perform the iteration in Eqs. (7)–(10) once, with reference field set as $\epsilon^k_{\text{ref},f}(t)=\varepsilon^{k-1}_i(t)$ and $\epsilon^k_{\text{ref},i}(t)=\varepsilon^k_f(t)$. This should automatically introduce the most significant mechanism other than that in the reference field. The spectrum of this field is illustrated in Fig. 3, and it can be seen that the most important Fourier component outside the range $[0.7\omega_0, 1.1\omega_0]$ is a peak around $2.6\omega_0$. This peak corresponds to the second-order overtone transitions, i.e., $|\nu\rangle \rightarrow |\nu+3\rangle$.

In order to assess the effects of including spectral components corresponding to high-order transitions, we perform

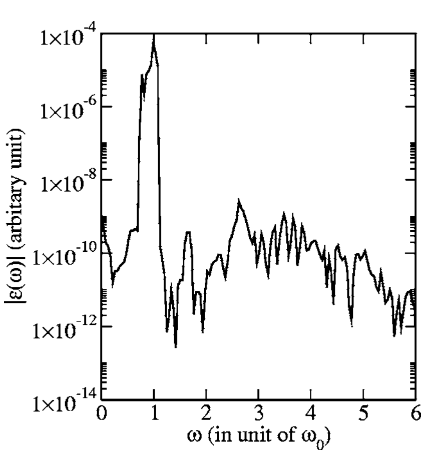

FIG. 3. The spectrum of the optimized field after one iteration with the field in Fig. 2 as guess field, see text for details.

another similar calculation, but redefine $\mathcal{S}$ to be $[0.7\omega_0, 1.1\omega_0]$ plus $[2.2\omega_0, 3.2\omega_0]$. These spectral ranges include both the $|\nu\rangle \rightarrow |\nu+1\rangle$ and $|\nu\rangle \rightarrow |\nu+3\rangle$ transitions. The maximum field strength is kept unchanged as $\epsilon_0=0.05$ a.u. The final field is shown in Fig. 4. The final optimized field has a slightly larger maximum field strength and it looks more complex than that in Fig. 2, but the population transfer from $|0\rangle$ to $|10\rangle$ is now 99.0% compared to 95.7% when including only one-photon transitions.

IV. CONCLUSIONS AND DISCUSSIONS

In conclusion, the above results demonstrate that the scheme used here can obtain optimized fields with desired properties. Since the choice of the function F is arbitrary, it could be generalized to other problems. For example, in Fig. 4, the optimized field has frequency components in two ranges. However, if we reduce the two ranges to be two points in Fourier space, then it would correspond to using two fields with fixed frequencies to control the system. If one could introduce the relative phase between these two frequency components into the optimal control algorithm, then the above scheme could be used to investigate coherent control problems[36] in complex systems. Work in this direction is underway.

We note that other schemes have been proposed to obtain optimized pulse with both spectral and fluence constraints. In a recent paper,[28] both frequency filtering and a maximum field strength limitation have been introduced in a conjugate gradient maximization procedure. Spectral and fluence constraints have also been introduced with an adaptive penalty parameter α_0.[37]

The present results also demonstrate that achieving high population transfer in complex systems with simple laser fields may be feasible, as we have achieved 95.7% population transfer from $|0\rightarrow|10\rangle$ for the very harmonic ClO system with a simple and not too strong field, as shown in Fig. 2. As Rabitz *et al.* have shown in their optimal control transition landscapes investigations,[6] all optimal control scenarios are perfect if there is no limitation imposed on the form of the field. The principal idea of obtaining optimized pulses in this paper is to use the unrestricted search, i.e., use the field from a previous iteration as the reference field, to find the optimized field in a restricted parameter space. Numerical results indicate that this search algorithm works very well. The theoretical foundation of optimal control transition landscapes in restricted parameter spaces and its relationship to the optimal control transition landscapes in the unrestricted parameter space would be an interesting topic to investigate in the future.

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