Quantum dynamics manipulation using optimal control theory in the presence of laser field noise

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We discuss recent advances in optimal control theory (OCT) related to the investigation of the impact of control field noise on controllability of quantum dynamics. Two numerical methods, the gradient method and the iteration method, are paid particular attention. We analyze the problem of designing noisy control fields to maximize the vibrational transition probability in diatomic quantum systems, e.g. the HF and OH molecules. White noise is used as an additive random variable in the amplitude of the control field. It is demonstrated that the convergence is faster in the presence of noise and population transfer is increased by 0.04% for small values of noise compared to the field amplitude.

Keywords: optimal control; amplitude noise; cooperative effect

1. Introduction

The subject of control of quantum phenomena has rapidly evolved in recent years, with key developments both in theory [1–6] and experiments [7–10].

Noise is inevitably present in a realistic control field and its involvement is generally destructive for achieving control of quantum dynamics [11]. The noise in the laser pulse could be associated with amplitude, frequency and phase and hence may be modeled as collecting the uncertainties in these physical quantities. Their random fluctuations include various types of correlated and uncorrelated errors, typically expected from the environment, experimental setup and nature of the molecular system. Several aspects of the effects of laser noise have been discussed in [12–17]. The impact of the noise on the quantum dynamics manipulation may be constructive [18] or destructive [15] thus improving [19] or reducing [20] the convergence rate.

In [15], the authors provide us with the strategies to correct the noise effects by studying dynamical and static noise models. For the population transfer in an anharmonic vibrational ladder, it was shown that optimal pulses are robust to white amplitude noise because the system acts as a dynamical filter. The white frequency and white phase noise were shown to affect the optimal pulses by reducing the pulse area. So, these effects can be partially compensated by pulse amplitude rescaling. However, the effect of the static noise cannot be easily corrected.

Recent theoretical [16,17] studies of the population transfer in a multi-state ladder quantum system driven by noisy control fields showed that there exists a control field which cooperates with the noise to reach the target state. For the goal of small population transfer, up to 10%, the control field can effectively cooperate with amplitude noise to drive the quantum dynamics. In such cases the deterministic field or noise acting alone would each produce a small yield, but the two acting together result in a more pronounced quantum yield.

It is nontrivial to design an optimal form of a pulse to reach a predetermined quantum yield in a system. Theoretical approaches for development of optimal laser pulses include pump–dump control [4], Brumer–Shapiro coherent control [2], stimulated Raman adiabatic passage (STIRAP) [21], also, phase modulated adiabatic control [22] and genetic algorithms [23]. A powerful tool is optimal control theory (OCT) [1,24,25]. It intrinsically accounts for the interference processes taking place in a dynamical system.

The OCT based optimization of time-dependent parameters to control the evolution of quantum systems is a long standing goal in physics. It has been applied to quantum information processing [26,27], protecting the quantum coherence [28], control of decoherence [29], control of quantum dots [30].

Methods of coherent control may have significant impact on developments in the area of quantum information processing [26,27], e.g. coherent manipulation of quantum computers. Small molecular systems are well suited to implement quantum computation processes. The quantum gate operations on the
vibrational qubits are performed using shaped ultrashort laser pulses, which are usually determined theoretically by applying the OCT [31–33].

Laser cooling [34] and Bose–Einstein condensation [35] of ultra-cold atoms have been one of the most exciting developments in physics in recent years. However, molecular cooling has proven to be much more challenging due to the complicated internal vibrational and rotational structure. Theoretical progress in the cooling of molecular internal degrees of freedom has been made recently using shaped laser pulses [36,37].

OCT has recently been introduced to NMR spectroscopy as a means to systematically design and optimize pulse sequences for applications in imaging [38], electron–nuclear interactions [39], and solid-state NMR [40].

Application of OCT in numerical calculations assumes incorporation of a toolkit of time propagation operators into the numerical algorithm to perform the optimal control of quantum dynamics in a system. Iterative schemes are used to enhance efficiency through rationally designed algorithms to reduce computational costs [41].

Basic equations of the optimal control theory are developed in Section 2 together with a brief description of numerical methods for the solution of OCT equations. Section 3 is devoted to applications of OCT to design robust laser pulses possessing noise to maximize the transition probability in quantum systems, e.g., in diatomics HF and OH. A brief summary is given in Section 4.

### 2. Optimal control theory

OCT [1,24,25] is a valuable tool for finding an optimal solution to a given problem. It has been applied to various physical and chemical problems, e.g., control of photoinduced reactions, or manipulation with state population and coherence, and also to multiple engineering problems, e.g., to design trajectories for satellites and space probes.

The theory is based on the definition of the cost functional $K[\epsilon(t)]$ which must have an optimal value when the desired dynamical transformation is successfully achieved by the laser pulse. The optimization procedure is based on variational principle and strongly depends on the choice of the $K[\epsilon(t)]$. Usually, the cost functional reads

$$K[\epsilon(t)] = \left| (\psi_0(T)\phi_0(T)) \right|^2 - \int_0^T \alpha(t)|\epsilon(t)|^2 \, dt - 2 \Re \left[ \int_0^T \langle \chi(t) | \phi_0(T) \rangle \left( \frac{\partial}{\partial t} + \frac{1}{\hbar} \hat{H} \right) \psi_0(t) \, dt \right].$$

The first term in Equation (1), known as the objective, is chosen such that, for the maximal value of the cost functional, the system initial state $\psi_0(T)$ has maximum overlap with the desired product state $\phi_0(T)$ at the terminal time $T$.

The second term in Equation (1), known as the penalty term, determines a restriction on the strength of the field $\epsilon(t)$. The factor $\alpha$ is a time-dependent positive parameter used to adjust the contribution of the radiation energy to the functional. It reads

$$\alpha = \alpha(t) = \frac{\alpha_0}{s(t)},$$

where $s(t)$ is a pulse envelope function.

If the laser–molecule interaction contains contributions mostly from the molecular polarizability, as in the case of homo-nuclear diatomic molecules, then the appropriate penalty term is $\int_0^T |\epsilon(t)|^2 \, dt$, [3]. Or, if it is required for a particular state $\psi_0(t)$ to be minimally populated during the control process, then the state-dependent penalty term may be chosen in the form of $\int_0^T (\psi_0(t)|\psi_0(t)) \, dt$ [12,28,42]. This choice is good for the molecular systems subject to processes implying loss of coherence such as ionization and predissociation.

The third term in Equation (1) is known as the dynamical constraint. Here it is written in the form different from the traditional one through the presence of the term $\langle \psi_0(t)|\phi_0(T) \rangle$ [43]. The choice is of significance since it decouples the boundary conditions for $\psi_0(t)$ and $\chi_0(t)$. The second integral involves the Schrödinger equation which should be followed explicitly during the time evolution of a system. The function $\chi_0(t)$ is a Lagrange multiplier. The Hamiltonian, $\hat{H}$, written in the dipole approximation [44], is defined as

$$\hat{H} = \hat{H}_0 + \hat{V} - \hat{\mu}[\epsilon(t) + \eta(t)],$$

where $\hat{H}_0$ is the kinetic energy, $\hat{V}$ is the potential energy, $\hat{\mu}$ is the transition dipole moment, and $\eta(t)$ is the noise term, which is equal to zero for the deterministic case.

Each of these terms depends explicitly or implicitly on the unknown driving field $\epsilon(t)$. The goal is to determine $\epsilon(t)$ by demanding the cost functional variation to be zero. Varying the cost functional with respect to the Lagrange multiplier $\chi_0(t)$, the wave function $\psi_0(t)$ and the electric field $\epsilon(t)$ leads to the following set of coupled equations:

$$i\hbar \frac{\partial \psi_0(t)}{\partial t} = \hat{H} \psi_0(t); \quad \psi_0(0) = \phi_0(0),$$

$$i\hbar \frac{\partial \chi_0(t)}{\partial t} = \hat{H} \chi_0(t); \quad \chi_0(T) = \phi_0(T),$$

$$\epsilon(t) = \frac{s(t)}{\alpha_0 \hbar} \Im \left( \langle \psi_0(t) | \chi_0(t) \rangle \langle \chi_0(t) \left| \frac{\partial \hat{H}}{\partial \epsilon(t)} \right| \psi_0(t) \rangle \right).$$
Equations (4) and (5) give the time evolving initial and final states which are used in Equation (6) to calculate the electric field. These coupled differential equations are solved iteratively due to their non-linear nature.

In numerical calculations, the optimization methods such as conjugate gradient method [3,45] and iterative methods proposed by Zhu and Rabitz [46], and Tannor and co-workers [43] can be applied to find the control field by maximizing the cost functional in Equation (1). These iterative methods are based on a forward–backward iterative scheme to improve the control field. At each iteration, the methods guarantee to increase the magnitude of the cost functional, \( K \), and to produce constructive changes in the field. Convergence of these iterative methods is much faster than that of gradient-type methods [31,43]. A more detailed description of the schemes is given in Appendix 1.

3. Applications: role of the noise in the optimal control of quantum systems

Noise plays an important role in optimal control of quantum systems. Defined as fluctuations of a physical quantity about the mean deterministic stationary value, it affects most physical measurements. Noise is generally associated with inaccuracies in measurements or impurities in signals. Presence of noise in real systems is unavoidable and becomes more and more prominent as one moves from macroscopic to microscopic scales. Theoretical investigations of noisy phenomena help the understanding of the role played by the noise on controllability of molecular dynamics. There are two main contributions of noise into the problem of laser control of molecules: through the field and through the molecular environment. Environmental noise arises, for example, from the fast dynamics of other degrees of freedom, such as rotational and electronic degrees of freedom or from the non-zero temperature of a system (thermal noise). In this paper we focus on the noise of the field. Through theoretical modeling of the field noise we understand the molecular dynamics induced by noisy fields and learn the extent to which noise is tolerable without a loss of controllability.

Various models may be used to study the effect of laser noise on the dynamics of quantum systems [15]. Noise could be additive or multiplicative in different pulse parameters. It can be introduced as a random parameter, \( \delta A \), \( \delta \omega \) or \( \delta \theta \) in the deterministic field amplitude \( A_0 \), frequency \( \omega_0 \) and phase \( \theta_0 \), respectively. A laser pulse in the presence of additive noise reads

\[
\epsilon(t) = (A_0 + \delta A) \cos \left( (\omega_0 + \delta \omega)t + (\theta_0 + \delta \theta) \right).
\]

The additive noise is generally chosen in the form of the white noise. It is defined by the following properties of the moments of stochastic variable \( X \):

\[
\mathbb{E}[X(t)] = 0, \\
\mathbb{E}[X(t_1)X(t_2)] = \delta(t_1 - t_2),
\]

i.e. it is a zero mean process for all time and has infinite power at zero time shift, e.g. its autocorrelation function is the delta function.

The source of white noise can be attributed to any process that causes fast random fluctuations in the pulse parameters, during the generation or amplification of the laser radiation. In order to explore the effects of noise on the dynamics one can also consider other noise models such as white Gaussian noise and shot-to-shot static noise in different pulse parameters [15]. In our optimization problem, we chose white noise with a flat power spectral density as the most difficult case for deduction of the noise effect.

White noise may be generated using the random number generator. Noise contributes to the field at every time step during the propagation of Equations (4)–(6) using the Hamiltonian in Equation (3) with implementation of, e.g. the Rabitz iterative scheme.

If the value of the functional has changed by less than or equal to the convergence criterion \( \gamma \) for two consecutive iterations, the process may be considered as converged:

\[
\Delta K^j = \left| \frac{K^j - K^{j-1}}{K^j} \right| \leq \gamma.
\]

The convergence criterion, \( \gamma \), on the objective functional is sufficient to be \( 1 \times 10^{-6} \). We illustrate the effect of the noise on the control objective on an example of vibrational excitation of diatomics HF and OH. Similar diatomic molecules are chosen for comparative studies of the effect of noise on optimization dynamics and quantum yield. The Schrödinger equation for HF and OH is solved using the Fourier grid Hamiltonian (FGH) method to obtain vibrational bound state eigenvalues and eigenfunctions.

Table 1 lists grid parameters and other details needed for the solution of the time-dependent Schrödinger equation. The parameter \( \omega_0 = \omega_{01} - \omega_{02} \) in Table 1 corresponds to the transition frequency from initial state to the target state. For HF it is equal to \( 3966 \text{ cm}^{-1} \), for OH \( \omega_{01} = 3784 \text{ cm}^{-1} \). The termination time is \( T = 3 \times 10^4 \hbar/E_{\text{h}} \approx 0.725 \text{ ps} \), which is on the order of a vibrational period.

3.1. Vibrational excitation: HF(v=0) \( \rightarrow \) HF(v=1)

Hydrogen fluoride has been broadly investigated with a large amount of theoretical and experimental data,
providing relevant information and allowing the validation of the results obtained [31,47].

Optimal fields are designed using white noise as an additive random variable in the field amplitude (see Equations (3) and (7)) for the vibrational excitation of HF from the ground vibrational state to the first excited vibrational state in its ground electronic configuration.

A Morse potential model is used for the anharmonic interaction potential with the following parameters [48]: dissociation energy, \(D_e = 0.225E_h\) (\(E_h = \hbar^2/(m_e a_0^2)\)), equilibrium internuclear distance, \(x_0 = 1.7329a_0\) and \(\beta = 1.17d_0^{-1}\), where \(a_0\) is the Bohr radius. The potential reads

\[
V(x) = D_e[1.0 - \exp(-\beta(x - x_0))]^2 - D_e.
\]

The dipole moment used is [49]

\[
\mu(x) = \mu_0 x \exp(-\xi x^4),
\]

where \(\mu_0 = 0.4535e\) and \(\xi = 0.0064a_0^{-4}\).

The initial state, \(\psi(t)\), and the Lagrange multiplier, \(\chi(t)\), are propagated in time using the second order split-operator method. The magnitude of the deterministic field peak amplitude (DFPA) is chosen to be 0.005\(E_h/a_0\) for this transition. This value was obtained in [31] and it provides an optimal, almost complete, population transfer from the ground to first excited vibrational state in the HF molecule. Different values of white noise amplitude relative to DFPA are used for designing the optimal fields. The percentage ratio is labeled as \(Q\).

Let's discuss the impact of the noise amplitude on the solution for a field that provides full population transfer between vibrational states in the HF molecule. Figure 1 shows the number of iteration steps needed for convergence of the optimization process as a function of the ratio \(Q\). The number of iteration steps first decreases and then increases with increasing value of \(Q\). The convergence to the desired dynamical goal is faster in the presence of noise having small intensities, within 10% of the field amplitude. Further increase in noise intensities makes convergence harder to achieve. Thus, small values of noise play a constructive role in the control dynamics. In the presence of noise, the field improves faster at each time step as compared to the deterministic case leading to a significant decrease in the number of iteration steps.

Figure 2 shows the dependence of the population of the first excited vibrational state in the HF molecule as a function of noise parameter \(Q\). For values of \(Q\) from zero to four this dependence is shown in the insert with the fine resolution. It is seen that the population of the target state \((v = 1)\) first increases and then starts decreasing for increasing values of \(Q\). For values of noise parameter from \(Q = 1\) to \(Q = 3\), noise appears to have a constructive role in achieving the population in the target state (even though, there is no significant increase in population compared to population of the target state for the deterministic case). There is 0.01% increase in population for \(Q = 2\) compared to \(Q = 0\), i.e. without noise. The increase in the population for low target yields in the presence of amplitude noise has been described also in [16], which is in agreement with our results.

There are experimentally observed phenomena wherein noise has been found to aid certain physical processes constructively. Most widely described as the phenomenon of the stochastic resonance, the addition of noise to a system is found to enhance its response to an external weak periodic force [50]. Our results show that an enhancement in achieving the population in the target state is achieved by addition of the weak noise up to a threshold value. Noise is found to improve the convergence rate. This situation of a cooperative interplay between the field and noise resulting in improvement of the control results can be related to stochastic resonance phenomenon when noise acquires

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha_0)</td>
<td>1</td>
</tr>
<tr>
<td>Number of grid points</td>
<td>256</td>
</tr>
<tr>
<td>Number of time steps (N)</td>
<td>8192</td>
</tr>
<tr>
<td>Shape function</td>
<td>(s(t) = \sin^2(\pi t/T))</td>
</tr>
<tr>
<td>Initial guess field</td>
<td>(\epsilon(t) = 0.005 \sin(\alpha_0 t))</td>
</tr>
</tbody>
</table>

Figure 1. The number of iteration steps needed for the optimization process versus the ratio of the noise to deterministic field peak amplitude \(Q\) for the transition \(v = 0 \rightarrow v = 1\) in the HF molecule.
a degree of coherence with the deterministic field at its own maximum.

Robust optimal fields with enhanced control can be designed for values of $Q$ from 1 to 10. The amount of noise up to 10% of the field amplitude is useful in the control field. Further increase in the noise amplitude plays a destructive role.

Figure 3 shows a time-dependent profile of the optimal pulse in the presence of white noise for $Q = 2$. The respective power spectrum is shown in the insert with the main peak centered at 3966 cm$^{-1}$ corresponding to the $v = 0 \rightarrow v = 1$ transition in the HF molecule.

3.2. Vibrational excitation: $OH(v=0) \rightarrow OH(v=1)$

The described above methodology was applied to study the dynamics in the OH radical subject to interaction with the noisy field. The ground vibrational state in the ground electronic configuration is chosen as the initial state and the first excited vibrational state as the target state to be reached at the terminal time $T$.

Morse potential is used for the OH radical with the following parameters: dissociation energy, $D_e = 0.1994 \text{E}_h$, equilibrium internuclear distance, $x_e = 1.821 a_0$ and $\beta = 1.189 a_0^{-1}$ [51]. The dipole moment is [51]

$$\mu(x) = \mu_0 x \exp(-x/x_0),$$

where $\mu_0 = 3.088 e$ and $x_0 = 0.6 a_0$.

We study the constructive role of the field noise in the molecular dynamics by analyzing the convergence process as a function of the parameter $Q$, which is the ratio of the noise to deterministic field peak amplitude (DFPA). The value of DFPA was equal to $0.0053 \text{E}_h/\text{ea}_0$. Figure 4 shows the number of iteration steps needed for the convergence of the optimization as a function of $Q$. A pronounced decrease in the number of iterations is observed for small values of $Q$ up to $Q = 10$, similar to the results for the HF molecule. Figure 5 shows population of the target state $v = 1$ as a function of parameter $Q$ in the OH diatomic. A trend similar to the HF molecule is observed for population increase as a function of $Q$, reaching 0.04% of the almost total population transfer obtained by the deterministic field.

The optimized electric field has a temporal profile analogous to that for the HF molecule. The respective power spectrum features the major peak around 3784 cm$^{-1}$ which matches the transitional frequency between the ground and the first excited states of the OH diatomic.
Figure 5. Population of $v=1$ state plotted as a function of $Q$ for the transition $v=0 \rightarrow v=1$ in the OH radical.

A comparison of the results for the HF and OH diatomics shows that the relative increase and, then, decrease in the excited state population with the increase of the parameter $Q$ is faster in the HF molecule than in the OH radical. This is due to the larger value of the transition dipole moment that the HF molecule possesses in comparison to that of the OH. The larger value of the dipole moment leads to a more pronounced interaction with the external electric field. The constructive role of the noise is demonstrated to be very similar for both diatomics with an increase in relative population transfer and improvement of convergence process.

In [16,17], the authors identify the conditions when the control field cooperates with the field noise for the population transfer in a multi-state ladder quantum system. For low target yields, it effectively cooperates with the amplitude noise. In our results, we also observed a cooperative behavior of the amplitude noise and uncover the noise amplitude value which leads to designing the robust field.

Here, a comment on the values of the peak field amplitudes obtained using OCT is relevant. The simplest laser pulse which leads to the population inversion in a two-level system is known to be a $\pi$ pulse and the population inversion condition can be written as

$$A_0 \mu_{ij} \frac{1}{\hbar} \int_0^T s(t) \, dt = \pi,$$  \hspace{1cm} (13)

where $A_0$ is the peak field amplitude and $\mu_{ij}$ is the transition dipole moment connecting the two states of interest. Equation (13) is well known as the pulse area theorem. Analytically calculated values of $A_0$ for the $v=0 \rightarrow v=1$ transition of the HF and OH diatomics are 0.00538 and 0.00564$E_h/ea_0$, respectively. They were obtained using the expression $A_0 = 2\pi/T \mu_{01}$ for $T = 3 \times 10^4 h/E_h$. These values are very close to the values of $A_0$ (0.0051$E_h/ea_0$ for the HF molecule and 0.0052$E_h/ea_0$ for the OH radical) obtained using the optimal control formalism.

To calculate pulse area of the optimal pulses obtained for the HF and OH diatomics, we used the absolute value of $\epsilon(t)$ for $A_0s(t)$. In the limit of large number of oscillations, the two integrals will be equal. The values of pulse area are 1.8585 for $Q=2$ for HF and 1.8424 for $Q=4$ for OH, respectively. It is pertinent to mention here that the two-level system is an idealization and it is known that the pulse area can be different from $\pi$ for realistic simulations [52] involving multiple levels. How close one comes to $\pi$ is a question of choice of the penalty parameter $\alpha_0$. Cheng and Brown stated that unless $\alpha_0 = 0$, the optimal pulse will never be the $\pi$ pulse [32].

4. Summary

We have discussed the OCT for designing the control field to manipulate the quantum dynamics in the presence of the field noise. The results of numerical calculation of the OCT equations aiming to design the noisy control field and understanding the effect of the laser noise on controllability are discussed in more detail. The vibrational excitation of the HF molecule and the OH radical is investigated. Different values of the noise intensity are considered relative to the optimal magnitude of the deterministic peak field amplitude. Robust noisy control fields are obtained for the noise-to-field ratio ranging from 1 to 10. The results demonstrate that convergence is faster in the presence of small amplitudes of noise in both molecules, i.e. noise cooperates with the field, presumably, following the stochastic resonance mechanism. For larger values of the noise-to-field ratio, noise plays a destructive role, it decreases the population of the target state and increases the number of iteration steps involved in the optimization process. These observations are consistent with data in [16,17] and uncover a cooperative role of the amplitude noise in the control field to drive the dynamics effectively. The results of calculations of lowest vibrational states excitation in diatomics HF and OH may be useful for studies of optimal control in multi-level systems using the cooperative effect of the laser field noise.

References

Appendix 1.

Conjugate gradient method

For given terminal time $T$, the number of time steps $N$ ($t_i = i \times \Delta t$, where $i = 0, 1, 2, \ldots, N$ and $N\Delta t = T$), and the method for the wavepacket propagation, the conjugate-gradient method involves the following steps to obtain the optimal field:

Step 1: Guess an initial electric field $\epsilon_0(t)$.

Step 2: Set $j = 1$ and $\epsilon_j(t) = \epsilon_0(t)$.

Step 3: Propagate $\psi_j^T(0) = \phi(0)$ forward in time using $\epsilon_j(t)$ according to Equation (4) to obtain $\psi_j^T(T)$.

Step 4: Evaluate the cost functional $K^j$ according to Equation (1) and compare it with the convergence threshold, $\gamma$. If $\Delta K^j \leq \gamma$, then stop the iteration and declare that the optimal pulse has been obtained.

Step 5: If $j \geq 2$, compute $\Delta K^j$ according to Equation (9) and compare it with the convergence threshold, $\gamma$. If $\Delta K^j \leq \gamma$, then stop the iteration and declare that the optimal pulse has been obtained.

Step 6: Set $x_j^T(T) = \phi(T)$. Propagate $x_j^T(T)$ and $\psi_j^T(T)$ backward in time using field $\epsilon_j(t)$ to obtain $x_j^T(0)$ and $\psi_j^T(0)$.

Step 7: The gradient $g_j(t)$ of the cost functional $K^j$ defined in Equation (1) with respect to the variation of $\epsilon_j(t)$ at time $t$ is given by

$$g_j(t) = \frac{\delta K^j}{\delta \epsilon_j(t)}$$

$$= -2\left[\epsilon_j(t) - \frac{s(t)}{\hbar \epsilon_0} \text{Im}(\langle \psi_j^T(t)|x_j^T(t)\rangle |x_j^T(t) \rangle \frac{\partial \hat{H}}{\partial \epsilon_j(t)} |\psi_j^T(t)\rangle)\right].$$

(14)

The Polak–Ribiere–Polyak search direction can be calculated using Equation (14) as

$$d_j(t) = g_j(t) + \zeta_j d_{j-1}(t),$$

(15)

where

$$\zeta_j = \frac{g_j(t)}{g^{j-1}(t) g^{j-1}(t)};$$

(16)

$j = 2, 3, \ldots, d_j(t) = g_j(t)$. The function $\zeta_j$ is the conjugate gradient update parameter and $g_j(t)^T$ is the transpose of $g_j(t)$. A line search is then performed along this direction to determine the maximum value of the cost functional.

Step 8: The electric field for the $(j+1)$ iteration is taken as

$$\epsilon^{j+1}(t) = \epsilon_j(t) + \lambda \cdot d_j(t),$$

(17)

where $\lambda$ is determined by the line search, which makes $\epsilon^{j+1}(t)$ generate the maximum value of $K$.

Iterative method

The iterative method of Rabitz and co-workers [51] involves the following steps to find the optimal value of the control field:

Step 1: Guess an initial electric field $\epsilon_0(t)$. Set $j = 1$ and $\epsilon_0(t) = \epsilon_j(t)$.

Step 2a: System target state $x_j^T(T) = \phi(T)$ is propagated backward in time using $\epsilon_j(t)$ to obtain $x_j^T(0)$ using Equation (5).

Step 2b: Propagate $\psi_j^T(0) = \phi(0)$ forward in time using the new field $\epsilon_j(t)$ given by Equation (18) according to Equation (4) to obtain $\psi_j^T(T)$.

$$\epsilon_j(t) = \frac{s(t)}{\hbar \epsilon_0} \text{Im}(\langle \psi_j^T(t)|x_j^T(t)\rangle |x_j^T(t) \rangle \frac{\partial \hat{H}}{\partial \epsilon_0(t)} |\psi_j^T(t)\rangle).$$

(18)

Step 3: Evaluate the cost functional $K^j$ according to Equation (1).

Step 4: If $j \geq 2$, compute $\Delta K^j$ according to Equation (9) and compare it with the convergence threshold, $\gamma$. If $\Delta K^j \leq \gamma$, then stop the iteration and declare that the optimal pulse has been obtained.

Step 5a: System target state $x^{j+1}_j(T) = \phi(T)$ is propagated backward in time using the new electric field $\epsilon^{j+1}(t)$ in Equation (19) to obtain $x^{j+1}_j(0)$.

$$\epsilon^{j+1}(t) = \frac{s(t)}{\hbar \epsilon_0} \text{Im}(\langle \psi^{j+1}_j(t)|x^{j+1}_j(t)\rangle |x^{j+1}_j(t) \rangle \frac{\partial \hat{H}}{\partial \epsilon_0(t)} |\psi^{j+1}_j(t)\rangle).$$

(19)

Step 5b: Propagate $\psi^{j+1}_j(0) = \phi(0)$ forward in time using the new field $\epsilon^{j+1}(t)$ calculated by Equation (20) to obtain $\psi^{j+1}_j(T)$.

$$\epsilon^{j+1}(t) = \frac{s(t)}{\hbar \epsilon_0} \text{Im}(\langle \psi^{j+1}_j(t)|x^{j+1}_j(t)\rangle |x^{j+1}_j(t) \rangle \frac{\partial \hat{H}}{\partial \epsilon_0(t)} |\psi^{j+1}_j(t)\rangle).$$

(20)