A Simplified Approach to Optimally Controlled Quantum Dynamics

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Abstract

A new formalism for the optimal control of quantum mechanical physical observables is presented. This approach is based on an analogous classical control technique reported previously. Quantum Lagrange multiplier functions are used to preserve a chosen subset of the observable dynamics of interest. As a result, a corresponding small set of Lagrange multipliers needs to be calculated and they are only a function of time. This is a considerable simplification over traditional quantum optimal control theory. The success of the new approach is based on taking advantage of the multiplicity of solutions to virtually any problem of quantum control to meet a physical objective. A family of such simplified formulations is introduced and numerically tested. Results are presented for these algorithms and compared with previous reported work on a model problem for selective unimolecular reaction induced by an external optical electric field.
Different approaches and paradigms for controlling molecular motion have been proposed. \[10\] Various results indicate that the final state distribution can be controlled in many instances. Manipulating the interference between two or more routes to the same (degenerate) final state has been suggested to achieve control of the final state distribution. \[3–6\] Another approach employs the laser field to guide the wave packet motion utilizing two electronic potentials. \[7,8,28\] In addition to these particular schemes, a general optimal design formalism for the quantum control problem has been developed. \[11–13\] The capability of designing laser pulse shapes with this optimal design formalism has been demonstrated for many applications including selective excitations, \[27,32\] selective bond breaking for triatomic molecules, \[4\] control of curve-crossing reactions \[29,30\] and control of the electric susceptibility of a molecular gas. \[31\] Furthermore, it is known that multiple control solutions will likely exist for any particular system. \[33\] The multiplicity of solutions gives a range of flexibility for field design which is especially important for adaptive feedback laboratory control. \[13,9\]

The existence of these multiple optimal solutions provides the freedom to develop simplified methods to find a control field. This paper builds on this observation to present a different approach to quantum optimal control theory. The approach only requires that the feedback Lagrange variables be scalars to preserve desired observable expectation values. In contrast, the previous generic method \[2,28\] required the propagation of a typically non-linear Schrödinger type equation for the Lagrange functions causing considerable numerical complexity. The simplicity of the new approach presented here should allow for the study of molecular control of larger dynamical systems. A family of simplified approaches will be introduced. The new approaches will be applied to the selective optical dissociation of a model triatomic molecule.

The paper is organized as follows. In section II we present the general quantum control dynamics equations and the proposed simplifications. In section III we apply the theory to
a selective unimolecular reaction. The computational method to solve the control dynamics equations is presented in section IV. In section V numerical results for these methods are presented and compared to previous results. We discuss and summarize the results in section VI.

II. THE QUANTUM CONTROL PROBLEM AND ITS SIMPLIFICATION

In this section we present the quantum control dynamics equations for a molecule where the control is a laser field. The optimal control theory seeks a field pulse to steer the molecular motion from the original state to achieve a desired final objective. Consider the Hamiltonian $H$ to have the form

$$H = H_{mol}(\mathbf{z}) + H_{int}(\mathbf{R}, \epsilon(t))$$

(1)

where $H_{mol}(\mathbf{z})$ is the Hamiltonian of the undisturbed molecule, $H_{int}(\mathbf{R}, \epsilon(t))$ represents the field-molecule interaction, and $\epsilon(t)$ is the electric field vector. $\mathbf{z}$ is defined as an operator vector $\mathbf{z} = [z_1, z_2, \ldots z_{2N}] \equiv [\mathbf{R}, \mathbf{P}] \equiv [R_1, \ldots, R_N, P_1, \ldots, P_N]$ containing the coordinate $\mathbf{R}$ and conjugate momentum $\mathbf{P}$ operators of the system. $N$ is the number of degrees of freedom in the molecule. In the dipole model, the interaction Hamiltonian is

$$H_{int}(\mathbf{R}, \epsilon(t)) = -\mu(\mathbf{R}) \cdot \epsilon(t)$$

(2)

where $\mu(\mathbf{R})$ is the dipole moment vector. The control design formalism seeks the field $\epsilon(t)$.

The molecular motion evolution at time $t$ is described by $|\psi(t)\rangle$ which obeys

$$i\hbar \frac{\partial|\psi(t)\rangle}{\partial t} = H|\psi(t)\rangle$$

(3)

with the initial state being $|\psi(0)\rangle$. The knowledge of the wave function permits evaluation of any dynamical observables, and in particular $\langle \mathbf{z}(t) \rangle = \langle \psi(t)|\mathbf{z}|\psi(t)\rangle$. We will assume that the control objective can be expressed in terms of $\langle \mathbf{z}(t) \rangle$ although other expectation values (e.g., bond energy, etc.) could just as well be treated.
A. Conventional formulation of optimal control theory

In this subsection we will briefly summarize the conventional approach to optimally designing fields for molecular control. We will build on this background and some inherent design freedom to introduce alternate and simplified formulations in subsection II.B.

To design the control field $\epsilon(t)$ that best achieves the desired objective we introduce the cost functional $J[\langle z \rangle, \epsilon]$

$$J[\langle z \rangle, \epsilon] = \Phi[\langle z(T) \rangle] + \int_0^T dt [\ell_1(\langle z(t) \rangle) + \ell_2(\epsilon(t))]$$  \hfill (4)

The first part $\Phi[\langle z(T) \rangle]$ is a functional that measures the deviation from the desired physical objectives at time T. The second part involves the constraint function $\ell_1(\langle z(t) \rangle)$ that takes into account any restrictions on the variables $\langle z(t) \rangle$ over the interval $0 \leq t \leq T$ (e.g., to avoid undesired regions of phase space, or products, or in order to help guide the molecular system to the desired objective.\textsuperscript{22}) The last part, with the field cost function $\ell_2(\epsilon(t))$, expresses the desire to minimize the energy fluence or possibly introduce other biases in the field.

The constraint that the Schrödinger equation be satisfied is assured through introduction of the Lagrange multiplier vector $|\lambda(t)\rangle$ along with its complex conjugate. Thus, the full cost functional is given by

$$\bar{J}[\langle z \rangle, \epsilon] = J[\langle z \rangle, \epsilon] - \int_0^T dt \langle \lambda(t) | [i\hbar \frac{\partial |\psi(t)\rangle}{\partial t} - H |\psi(t)\rangle] - \int_0^T dt [i\hbar \frac{\partial \langle \psi(t) |}{\partial t} + \langle \psi(t) | H |\lambda(t)\rangle]$$ \hfill (5)

The minimization of $\bar{J}[\langle z \rangle, \epsilon]$ leads to a link between the objective functional and the optimal solution $\epsilon(t)$ supplied by the Lagrange multiplier vector.

The quantum variational problem is given by $\delta \bar{J}[\langle z \rangle, \epsilon] = 0$ which minimizes the cost functional $\bar{J}[\langle z \rangle, \epsilon]$ with respect to $\epsilon(t)$, $|\psi(t)\rangle$ and $|\lambda(t)\rangle$. The variation with respect to $|\lambda(t)\rangle$ gives rise to the Schrödinger equation Eq. (3). The variation with respect to $|\psi(t)\rangle$ leads to the following equation:
\[ i\hbar \frac{\partial |\lambda(t)\rangle}{\partial t} = H|\lambda(t)\rangle - \sum_{i=1}^{2N} \frac{\partial l_1}{\partial \langle z_i(t) \rangle} z_i|\psi(t)\rangle \] (6)

This equation for the Lagrange multiplier vector has the same form as the Schrödinger equation along with an inhomogeneous term. The final time condition is

\[ i\hbar |\lambda(T)\rangle = \sum_{i=1}^{2N} \frac{\partial \Phi}{\partial \langle z_i(T) \rangle} z_i|\psi(T)\rangle \] (7)

The gradient of the cost functional with respect to the field is

\[ \frac{\delta \bar{J}[(z), \epsilon]}{\delta \epsilon(t)} = \frac{d\ell_2(\epsilon(t))}{d\epsilon(t)} + 2Im\langle \lambda(t)|\frac{\partial H_{int}(R, \epsilon(t))}{\partial \epsilon(t)}|\psi(t)\rangle \] (8)

The solutions of the set of equations Eqs. (3) and (6)-(8) produces the optimal field.

In the above approach, the unconstrained cost functional \( \bar{J}[(z), \epsilon] \) was introduced to conserve the Schrödinger equation, and the control equation of motion for the Lagrange multiplier vector gives similar dynamics to that of Schrödinger’s equation. In this case the Lagrange multiplier vector takes into account the state of the molecule at each instant of time in the quantum control process. A key observation is that there are generally multiple solutions, and possibly a denumerably infinite number, to the control design equations. We will take advantage of this flexibility below. The Lagrange multiplier plays the role of guiding the dynamics to a particular solution.

**B. Simplified formulation optimal control theory**

The physical cost in equation (4) only depends on the expectation values and external interaction field and not explicitly on the wave function. We can take advantage of this observation to simplify the process of achieving control solutions. The time dependence of the expectation values is governed by the equations

\[
\frac{d\langle R_i(t) \rangle}{dt} = \langle \psi(t)|\frac{\partial H}{\partial P_i}|\psi(t)\rangle \\
\frac{d\langle P_i(t) \rangle}{dt} = -\langle \psi(t)|\frac{\partial H}{\partial R_i}|\psi(t)\rangle \quad i = 1, \ldots, N.
\] (9)

which can collectively be written as
\[
\frac{d\langle z_i(t) \rangle}{dt} = \langle \psi(t)|f_i(z, \epsilon(t))|\psi(t) \rangle \quad i = 1, \ldots, 2N
\] (10)

where the functions \( f_i(z, \epsilon(t)) \) may be readily identified as momentum or coordinate derivatives of the Hamiltonian. We may now write a new unconstrained cost functional that preserves the dynamical equation (10),

\[
- \int_0^T dt \sum_{i=1}^{2N} \lambda_i(t) \left[ \frac{d\langle z_i(t) \rangle}{dt} - \langle \psi(t)|f_i(z, \epsilon(t))|\psi(t) \rangle \right]
\] (11)

In this unconstrained functional there is an implicit dependence on the Schrödinger equation, and this point will become important below. It is significant to note that the functional in (11) retains exactly the same physical objective through \( J[\langle z \rangle, \epsilon] \) as in equation (5). Here we only alter the feedback bias towards a particular control solution by the choice of Lagrange functions.

The minimization of \( \bar{J}[\langle z \rangle, \epsilon] \) is considered with respect to \( \epsilon(t), \lambda_i(t), \) and \( \langle z_i(t) \rangle \). The variation with respect to \( \lambda_i(t) \) gives the quantum equation of motion for the expectation values, Eq. (10). The variation of \( |\psi(t)\rangle \) is not explicitly treated, but we do need to consider the interpretation of the variation \( \delta\langle \psi(t)|f_i(z, \epsilon(t))|\psi(t) \rangle \). The various alternate optimal control approaches are based on different interpretations for this variation. We introduce the variation of \( \langle \psi(t)|f_i(z, \epsilon(t))|\psi(t) \rangle \), as

\[
\delta\langle \psi(t)|f_i(z, \epsilon(t))|\psi(t) \rangle \approx \sum_{j=1}^{2N} \langle \psi(t)|\frac{\partial f_i(z, \epsilon(t))}{\partial z_j} \delta z_j|\psi(t) \rangle \\
\approx \sum_{j=1}^{2N} \langle \psi(t)|\frac{\partial f_i(z, \epsilon(t))}{\partial z_j} |\psi(t) \rangle \langle \delta z_j(t) \rangle
\] (12)

where \( \langle \delta z_j(t) \rangle \) is

\[
\langle \delta z_j(t) \rangle = \langle \psi(t)|\delta z_j|\psi(t) \rangle
\] (13)

and \( |\psi(t)\rangle \) satisfies equation (3). Thus, in employing the functional in Eq. (11) an important point is that the Schrödinger equation for \( |\psi(t)\rangle \) is not approximated so that the true molecular dynamics is fully retained. Secondly, the original cost functional \( J[\langle z \rangle, \epsilon] \)
in equation (11) is retained, implying that any control solution \( \epsilon(t) \) obtained through this alternate formulation is just as valid as obtained the conventional way in section II.A. Thus, the variation in equation (12) should be thought of as guiding the design process from one valid solution to another equally valid one. The only question at this point is whether this new approach can guide the process to achieve designs \( \epsilon(t) \) that produce quality control. The computations in section III will show that the approach can achieve excellent results.

Considering the above arguments we have the full variation of \( \bar{J}(\langle z \rangle, \epsilon) \), as

\[
\delta \bar{J}(\langle z \rangle, \epsilon) = \sum_{i=1}^{2N} \left[ \frac{\partial \Phi(\langle z(T) \rangle)}{\partial \langle z_i(T) \rangle} - \lambda_i(T) \right] \delta z_i(T)
\]  

(14a)

\[
+ \int_0^T dt \sum_{i=1}^{2N} \left[ \frac{d\lambda_i(t)}{dt} \frac{\partial f_i(z, \epsilon(t))}{\partial z_i} \psi(t) \psi(t) \right.
\]

\[
+ \left. \frac{\partial \ell_1(\langle z(t) \rangle)}{\partial \langle z_i(t) \rangle} \right] \delta z_i(t) \]  

(14b)

\[
+ \int_0^T dt \frac{d\ell_2(\epsilon(t))}{d\epsilon(t)} + \sum_{i=1}^{2N} \lambda_i(t) \psi(t) \left[ \frac{\partial f_i(z, \epsilon(t))}{\partial \epsilon(t)} \psi(t) \right] \delta \epsilon(t).
\]  

(14c)

The boundary conditions at time \( T \),

\[
\lambda_i(T) = \frac{\partial \Phi(\langle z(T) \rangle)}{\partial \langle z_i(T) \rangle} \quad i = 1, ..., 2N,
\]  

(15)

are obtained through the Eq. (14a). As, we require \( \delta \bar{J}(\langle z \rangle, \epsilon) = 0 \), the second equation derived from Eq. (14b) is

\[
\int_0^T dt \sum_{i=1}^{2N} \left[ \frac{d\lambda_i(t)}{dt} \frac{\partial f_i(z, \epsilon(t))}{\partial z_i} \psi(t) \right.
\]

\[
+ \left. \frac{\partial \ell_1(\langle z(t) \rangle)}{\partial \langle z_i(t) \rangle} \right] \delta z_i(t) = 0,
\]  

(16)

and the gradient with respect to the field is

\[
\frac{\delta \bar{J}(\langle z \rangle, \epsilon)}{\delta \epsilon(t)} = \frac{d\ell_2(\epsilon(t))}{d\epsilon(t)} + \sum_{i=1}^{2N} \lambda_i(t) \psi(t) \left[ \frac{\partial f_i(z, \epsilon(t))}{\partial \epsilon(t)} \psi(t) \right].
\]  

(17)

The Lagrange multipliers are chosen to obey the following equations
\[
\frac{d\lambda_i(t)}{dt} = -\sum_{j=1}^{2N} \lambda_j(t) \langle \psi(t) | \frac{\partial f_j(\mathbf{z}, \epsilon(t))}{\partial z_i} | \psi(t) \rangle - \frac{\partial \ell_1(\langle \mathbf{z}(t) \rangle)}{\partial \langle z_i(t) \rangle}
\]

\[i = 1, ..., 2N \quad (18)\]

The control dynamics equations to solve the quantum control problem are given by Eqs. (3), (18) and (17) with the final conditions for the Lagrange multipliers given by Eq. (15). The results based on this approach will be called method I.

The fundamental distinction between solving these equations and those of the standard treatment in Eqs. (3), (6)-(8) lies in the nature of the Lagrange multipliers. Equation (6) is a partial differential equation, while Eq. (18) is a much simpler ordinary differential equation. A key point is that the control \(\epsilon(t)\) generated from the new formulation should be fully acceptable physically, despite the simplified form in Eq. (18), since the Schrödinger equation is not approximated. The new formulation takes advantage of the multiplicity of solutions to steer the design process from one possible field to another. In some cases the control might even be similar to that found with the full conventional control formulation (this is the case in the examples of Section III). In other cases the control field may be different, but importantly retention of the original cost functional assure a proper test of the achieved results.

It is worthwhile to explore if further simplified formulations for the Lagrange multipliers can also be successfully introduced. One may replace Eq. (18) by the following:

\[
\frac{d\lambda_i(t)}{dt} \approx -\sum_{j=1}^{2N} \lambda_j(t) \frac{\partial f_j(\langle \mathbf{z}(t) \rangle, \epsilon(t))}{\partial \langle z_i(t) \rangle} - \frac{\partial \ell_1(\langle \mathbf{z}(t) \rangle)}{\partial \langle z_i(t) \rangle}
\]

\[i = 1, ..., 2N \quad (19)\]

This is a classical like formulation for \(\lambda_i(t)\), but quantum mechanics is still fully retained in solving for \(|\psi(t)\rangle\) and \(\langle z_i(t)\rangle\). Using this formulation the control dynamics equations to solve are: Eqs. (3), (19), (17) with the boundary conditions Eq. (15). This approach will be called method II.

We can reformulate another cost functional based on replacing Eq. (11) with

\[
\frac{d\langle z_i(t) \rangle}{dt} \approx f_i(\langle \mathbf{z}(t) \rangle, \epsilon(t))
\]

\[i = 1, ..., 2N \quad (20)\]

This equation signifies that the time dependence of the expectation values (the quantum
motion behavior) resembles one classical trajectory in the $2N$ dimensional quantum phase space. The cost functional may be now rewritten as

$$\tilde{J}[\langle z \rangle, \epsilon] = J[\langle z \rangle, \epsilon] - \int_0^T dt \sum_{i=1}^{2N} \lambda_i(t) \left[ \frac{d\langle z_i(t) \rangle}{dt} - f_i(\langle z(t) \rangle, \epsilon(t)) \right]$$  \hspace{1cm} (21)

The variations of $\tilde{J}[\langle z \rangle, \epsilon]$ with respect to $\langle z_i(t) \rangle$, $\epsilon(t)$ and $\lambda(t)$ produce the control equations. The variations with respect to $\lambda_i(t)$ give Eq. (20). The variations with respect to $\langle z_i(t) \rangle$ gives the same boundary condition as Eq. (15). The equations of motion for the Lagrange multipliers are identical to Eq. (19). However, the gradient of the cost functional with respect to electric field is different,

$$\frac{\delta \tilde{J}[\langle z \rangle, \epsilon]}{\delta \epsilon(t)} = \frac{d\ell_\epsilon(t)}{d\epsilon(t)} + \sum_{i=1}^{2N} \lambda_i(t) \frac{\partial f_i(\langle z(t) \rangle, \epsilon(t))}{\partial \epsilon(t)}$$  \hspace{1cm} (22)

These control of equations are coupled to the Schrödinger equation. This approach will be referred to as method III below. To solve this system of non-linear differential equations we need to know the expectation value for each observable in phase space. The quantum control feedback equations (15), (19) and Eq. (22) are identical to classical feedback dynamics with a single trajectory, the average trajectory; a comparison between these quantum and classical control dynamics equations will be reported elsewhere.

To summarize, the conventional approach in II.A and methods I, II and III in II.B should be viewed as providing alternate routes to equivalent control field designs consistent with the proper quantum dynamics of the molecule and the physical objectives.

**III. SELECTIVE CONTROL OF A UNIMOLECULAR REACTION**

The conventional quantum optimal control dynamics equations Eqs. (3), (6), (7) and (8) in section II.A has been applied to a variety of problems including selective bond breaking through infrared excitation. In order to compare with the approaches described in Section II.B, we treat the same model expressed previously. The selective dissociation of one bond in a linear triatomic molecule is studied. The molecule is modeled as a pair of kinetically coupled Morse oscillators. The molecular Hamiltonian in internal coordinates is
\[
H_{\text{mol}} = \frac{P_1^2}{2\mu_1} + \frac{P_2^2}{2\mu_2} - \frac{1}{M_C}P_1P_2 + V(R_1) + V(R_2)\text{mol} \tag{23}
\]

where

\[
V(R_i) = D_i[1 - \exp(-\alpha_i R_i)]^2, \tag{24}
\]

\(R_1, R_2\) are the displacement operators of the bonds from their equilibrium positions, \(P_1, P_2\) are the conjugate momentum operators corresponding to \(R_1\) and \(R_2\), the reduced masses (amu) are \(\frac{1}{\mu_1} = \frac{1}{12} + \frac{1}{19}, \frac{1}{\mu_2} = \frac{1}{12} + \frac{1}{33.45},\) \(M_C = 12\text{amu},\) and

\[
D_1 = 0.1976\text{au}, \quad D_2 = 0.13705\text{au},
\]

\[
\alpha_1 = 0.9217\text{au} \quad \text{and} \quad \alpha_2 = 1.02725\text{au}.
\]

The dipole function of the molecule has the form

\[
\mu(R_1, R_2) = \mu_e[(R_1 + R_o) \exp(-\beta R_1) - (R_2 + R_o) \exp(-\beta R_2)] \tag{25}
\]

where the parameters are \(\mu_e = 0.3934\text{au},\) \(R_o = 2\text{au}\) and \(\beta = 1\text{au}.\) The polarization of the external field \(\epsilon(t)\) is along the axis of the molecule.

The model treats the selective dissociation of bond 1 at a minimum disturbance of the non selected bond 2 along with a minimum fluence of the electric field. Following the early studies (Ref. [2]) we choose the objective function to be

\[
\Phi[\langle z(T) \rangle] = \frac{1}{2}[\langle R_1(T) \rangle - \gamma]^2 P_{f1} + \frac{1}{2}\langle P_1(T) \rangle^2 h[-\langle P_1(T) \rangle] P_{f3} \tag{26}
\]

where \(\gamma\) is the “target stretch”, \(P_{f1}, P_{f3}\) are positive constant weights and \(h(x)\) is the Heaviside function

\[
h(x) = \begin{cases} 1, & \text{if } x \geq 0 \\ 0, & \text{if } x < 0. \end{cases} \tag{27}
\]

The constraint function \(\ell_1(z(t))\) is chosen as

\[
\ell_1(z(t)) = \frac{1}{2}[\langle R_2(t) \rangle - \langle R_2(0) \rangle]^2 W_2 + \frac{1}{2}[\langle P_2(t) \rangle - \langle P_2(0) \rangle]^2 W_4 \tag{28}
\]
where $W_2, W_4$ are positive weights. This function biases the dynamics such that bond 2 remains minimally excited and $\langle R_2(t) \rangle$ does not move far away from its initial value. The last function $\ell_2(\epsilon(t))$, is chosen to minimize the intensity of the laser pulse

$$\ell_2(\epsilon(t)) = \frac{1}{2} \omega_e \epsilon^2(t) \tag{29}$$

where $\omega_e$ is a positive weight.

Utilizing the above criteria for the cost functional Eq. (11), where $z_i = [z_1, z_2, z_3, z_4]$ represent the coordinate and momentum operators, we obtain the corresponding set of equations (18) for the Lagrange multipliers of approach I

$$\frac{d\lambda_1(t)}{dt} = \lambda_3(t) \left[ \langle \psi(t) | V''(z_1) | \psi(t) \rangle - \mu_e \langle \psi(t) | \mu''(z_1) | \psi(t) \rangle \epsilon(t) \right] \tag{30a}$$

$$\frac{d\lambda_2(t)}{dt} = \lambda_4(t) \left[ \langle \psi(t) | V''(z_2) | \psi(t) \rangle + \mu_e \langle \psi(t) | \mu''(z_2) | \psi(t) \rangle \epsilon(t) \right]$$

$$- W_2 [\langle z_2(t) \rangle - \langle z_2(0) \rangle] \tag{30b}$$

$$\frac{d\lambda_3(t)}{dt} = - \frac{\lambda_1(t)}{\mu_1} + \frac{1}{M} \lambda_2(t) \tag{30c}$$

$$\frac{d\lambda_4(t)}{dt} = - \frac{\lambda_2(t)}{\mu_2} + \frac{1}{M} \lambda_1(t) - W_4 [\langle z_4(t) \rangle - \langle z_4(0) \rangle] \tag{30d}$$

where the prime denotes the derivative with respect to $z_i$, e.g. $V''(z_i) \equiv \frac{\partial^2 V(z_i)}{\partial z_i^2}$. The boundary conditions Eq. (15) are

$$\lambda_1(T) = P_{f1} [\langle z_1(T) \rangle - \gamma] \tag{31a}$$

$$\lambda_2(T) = 0 \tag{31b}$$

$$\lambda_3(T) = P_{f3} \langle z_3(T) \rangle h(-\langle z_3(T) \rangle) + \frac{P_{f3}}{2} \langle z_3(T) \rangle^2 \delta(-\langle z_3(T) \rangle) \tag{31c}$$

$$\lambda_4(T) = 0 \tag{31d}$$

and the gradient of the cost functional $\bar{J}[\langle z \rangle, \epsilon]$ with respect of the field in Eq. (17) is

$$\frac{\delta \bar{J}[\langle z \rangle, \epsilon]}{\delta \epsilon(t)} = \omega_e \epsilon(t) + \mu_e [\lambda_3(t) \langle \psi(t) | \mu'(z_1) | \psi(t) \rangle - \lambda_4(t) \langle \psi(t) | \mu'(z_2) | \psi(t) \rangle] \tag{32}$$
The minimization condition \( \frac{\delta \bar{J}[\langle z \rangle, \epsilon]}{\delta \epsilon(t)} = 0 \) gives

\[
\epsilon_I(t) = -\frac{\mu_e}{\omega_e} [\lambda_3(t)\langle \psi(t) | \mu'(z_1) | \psi(t) \rangle - \lambda_4(t)\langle \psi(t) | \mu'(z_2) | \psi(t) \rangle]
\] (33)

The electric field depends on the two Lagrange multipliers \( \lambda_3(t) \) and \( \lambda_4(t) \) and the average value of the dipole function derivative. Equation (33) links the Lagrange multipliers with the Schrödinger equation of motion.

Also for method II we treat the Lagrange multipliers in the same manner as in Eq. (19). These equations are

\[
\frac{d\lambda_1(t)}{dt} \approx \lambda_3(t) \left[ V''(\langle z_1(t) \rangle) - \mu e \mu''(\langle z_1(t) \rangle) \epsilon(t) \right]
\] (34a)

\[
\frac{d\lambda_2(t)}{dt} \approx \lambda_4(t) \left[ V''(\langle z_2(t) \rangle) + \mu e \mu''(\langle z_2(t) \rangle) \epsilon(t) \right] - [\langle z_2(t) \rangle - \langle z_2(0) \rangle]W_2
\] (34b)

\[
\frac{d\lambda_3(t)}{dt} = -\frac{\lambda_1(t)}{\mu_1} + \frac{1}{M} \lambda_2(t)
\] (34c)

\[
\frac{d\lambda_4(t)}{dt} = -\frac{\lambda_2(t)}{\mu_2} + \frac{1}{M} \lambda_1(t) - [\langle z_4(t) \rangle - \langle z_4(0) \rangle]W_4
\] (34d)

The control equations Eq. (34) have the same boundary conditions Eq. (31) and the same gradient of the cost functional with respect to electric field in Eq. (32). In this approach II the Lagrange multipliers will differ from those of the previous approach I and therefore the minimum solutions \( \epsilon_I(t) \) and \( \epsilon_{II}(t) \) are expected to be different.

The approach III has the same Lagrange multiplier equations as in the approach II in (34) and the gradient of the cost functional Eq. (21) with respect to the electric field is

\[
\frac{\delta \bar{J}[\langle z \rangle, \epsilon]}{\delta \epsilon(t)} = \omega_e \epsilon(t) + \mu_e [\lambda_3(t)\mu'(\langle z_1(t) \rangle) - \lambda_4(t)\mu'(\langle z_2(t) \rangle)]
\] (35)

The minimization condition \( \frac{\delta \bar{J}[\langle z \rangle, \epsilon]}{\delta \epsilon(t)} = 0 \) gives

\[
\epsilon_{III}(t) = -\frac{\mu_e}{\omega_e} [\lambda_3(t)\mu'(\langle z_1(t) \rangle) - \lambda_4(t)\mu'(\langle z_2(t) \rangle)]
\] (36)
Note that these equations are identical to those reported previously \[1\] for molecular classical optimal control evaluated over the average trajectory. These set of quantum control equations Eq. (34), (35) with the boundary conditions Eq. (31) can be treated consistently with the Schrödinger equation. Solving the Schrödinger equation directly, the trajectory of the expectation values \(\langle z_i(t) \rangle\) are obtained and are then utilized to solve the coupled set of equations Eq. (34), (35). This is the basis for the self consistency of this approach.

In the following section we explain the computational method used to solve the equations leading to \(\epsilon_I(t), \epsilon_{II}(t), \epsilon_{III}(t)\).

**IV. COMPUTATIONAL METHOD**

To explain the computational methodology first consider the approach I. The set of control dynamics equations to solve are Eqs. (3), (30), (32) with the boundary conditions Eq. (31). An iterative scheme is adopted with the aim of finding \(\epsilon_I(t)\) at a minimum cost while meeting the desired objective. The control algorithm used in this paper is the following:

a) Make an initial guess for the field \(\epsilon_I(t)\).

b) Integrate Schrödinger’s equation Eq. (3) and calculate the quantum average trajectory and other expectation values necessary to integrate Eq. (30).

c) Calculate the probability of dissociation for each of the channels and evaluate the cost functional.

d) Integrate Eq. (30) for the Lagrange multipliers \[34\] backward in time.

e) Calculate of the gradient of the cost functional with respect to the electric field.

f) Update a new field from the last step.

The steps (b) to (f) are repeated until a converged solution is obtained.
Similar algorithms can be constructed for the two other approaches II and III. In order to improve the form of $\epsilon(t)$ on each iteration we use the conjugate gradient algorithm. [20]

The Schrödinger equation was integrated using the split operator method. [15,14] This requires the propagator

$$
U(t + \delta t, t) \approx \exp\left(\frac{-i}{2} \int_{t}^{t + \delta t} [V(R) + H_{\text{int}}(R, \epsilon(t'))]dt' / \hbar\right) \exp\left(-iK\delta t / \hbar\right)
$$

which evolves the wave function $\delta t$ in time. The number of grid points chosen for the two coordinates $(R_1, R_2)$ was 256 × 128. The range of values for $R_1$ and $R_2$ was [-1,12]au and [-1,5]au, respectively. The time step $\delta t = 16.1au$ was used to propagate the wave function over a time interval of 0.1ps, and for times larger than 0.1ps, $\delta t = 0.5au$ was selected.

An optical potential was introduced to absorb flux in the boundary region. The new Hamiltonian is

$$
H = H_{\text{mol}} + H_{\text{int}} - iV_{\text{opt}}(R)
$$

where the optical potential is chosen to be

$$
V_{\text{opt}}(R_i) = \begin{cases} 
V_o, & \text{if } a \leq R_i \leq b; \\
0, & \text{otherwise.}
\end{cases}
$$

The parameters for the first bond are $V_o = 2a.u.$, $a = 11.5a.u.$, $b = 12.0a.u.$ and those for the second bond are $V_o = 1a.u.$, $a = 4.5a.u.$, $b = 5.0a.u.$.

With this scheme, we can define the dissociation probability in various ways. The most straightforward approach is simply to compute the probability as

$$
P_i(t) = \int_{0}^{t} dt' \int_{a_i}^{b_i} dR_d \mathcal{J}_i(R_d, t')
$$

where the $\mathcal{J}_i(R_d, t)$ is the flux defined as

$$
\mathcal{J}_i(R_d, t) = \frac{\hbar}{\mu_i} \text{Im} \langle \psi(t) | \hat{n} \cdot \nabla_i | \psi(t) \rangle
$$

The spatial integral in Eq. (40) is over the flux dividing line between two points in the surface $a_i$ and $b_i$, and $\hat{n}$ is the local unit vector normal to the dividing line. The gradient
in Eq. (11) is with respect to \( R_1, R_2 \) and the index \( i \) refers to a specific channel in the photodissociation process. We can get four different channels in the process of dissociation,

\[
ABC \rightarrow \begin{cases} 
A + BC & \text{dissociate bond 1} \\
AB + C & \text{dissociate bond 2} \\
A + B + C & \text{full break up} \\
ABC & \text{no dissociation}
\end{cases}
\]  

(42)

where each process has a distinct probability of occurrence. In order to calculate the probability for each channel, we choose the following values: \( P_1 \equiv A + BC \) for the flux through the line [6,-1] to [6,4]; \( P_2 \equiv AB + C \) for [-1,4] to (6,4); \( P_3 \equiv A + B + C \) for [7,4] to [6,5] (all of these values are in a.u.). The probability for \( P_4 \equiv ABC \) was calculated as

\[
P_4(t) = 1 - \sum_{i=1}^{3} P_i(t).
\]  

(43)

V. NUMERICAL RESULTS

In Fig. 1 we show the optimal laser pulse and its corresponding power spectrum, utilizing the standard quantum control equations Eqs. (3), and (6) to (8) of section II.A. The optimal laser pulse is identical to that in Ref.[2]. The power spectrum of the field has only one dominant peak at 1334 cm\(^{-1}\), which is higher than the two fundamental frequencies \( \omega_1^0 = 1098 \text{ cm}^{-1} \) and \( \omega_2^0 = 923 \text{ cm}^{-1} \) of both Morse oscillators. The second peak at 667 cm\(^{-1}\) plays a less important role.

In Fig. 2 we show the optimal pulses obtained from the three different algorithms I, II and III proposed where the guessed input field was zero. The optimal pulse I is produced from the solution of the control dynamics equations (3), (30) and (32) with the boundary condition Eq. (31). The optimal solution II is obtained with the Lagrange multiplier given by Eq. (34). The result III in Fig. 2 is based on the control dynamics equations calculated over one quantum trajectory utilizing Eqs. (3), (34), (35) and Eq. (31). In all three cases the optimal solutions for the electric field selectively dissociate bond 1. All three fields \( \epsilon_I, \epsilon_{II} \) and \( \epsilon_{III} \) are strikingly similar and also closely like that in Fig. 1. The power spectra of
\(\epsilon_I, \epsilon_{II}\) and \(\epsilon_{III}\) are also similar to that in Fig. 1, except that the small low frequency peak near \(700cm^{-1}\) is missing.

Figure 3 shows the temporal evolution of the quantum expectation values for the approximate bond energy, bond lengths, momenta and total molecular energy in the presence of the optimal field of Fig. 1. The analogous results for the field \(\epsilon_I\) of Fig. 2 is shown in Fig. 4 (the results of applying \(\epsilon_{II}\) and \(\epsilon_{III}\) are almost the same as \(\epsilon_I\)). The desired dissociation event ABC\(\rightarrow\) A + BC is clearly evident. The approximate energy for each bond (this energy is approximate because the kinetic coupling between the two bonds is not taken into account) shows high excitation in bond 1 (the dissociation energy is \(0.197a.u\)) much in contrast to bond 2 (the dissociation energy is \(0.137a.u\)). The time evolution of the expectation values for the positions and the momenta for the two bonds also indicate selective dissociation of bond 1. The expectation values of the interaction energy and the total energy of the molecule as a function of time are shown in Fig. 5 for the conventional field in Fig. 1 and the approach I (the results of II and III are essentially the same as the latter case). We observe that the interaction energy has its maximum value around the time \(t = 0.055ps\) in all the cases.

Table 1 shows the probability for the four reaction channels using the four optimal pulses of Figs. 1 and 2. More than of 50% of the dissociation occurs for the desired channel ABC\(\rightarrow\) A+BC with less than 1% for the channel ABC\(\rightarrow\) C+AB in all cases. The low values for the dissociation probabilities for the reactions ABC\(\rightarrow\) C+AB and ABC\(\rightarrow\) A+B+C demonstrates the high degree of control achieved for the new approaches to designing controls over quantum motion. The number of iterations to achieve the same level of convergence with the various methods is essentially the same as shown in table 2. However, the computational saving of methods I, II or III over that of conventional quantum control is nearly a factor of two as the overhead is very small for solving the Lagrange multiplier equations with the new methods. The potential for further computational saving will be discussed in the conclusion section.
VI. CONCLUSIONS

In this work we have presented a new general formalism for the control of quantum observables. Illustrations were carried out to compare a family of related methods. The conventional reference approach standardly utilizes a full Lagrange multiplier state vector introduced to preserve the Schrödinger equation. The Lagrange multipliers in the new approach are scalars introduced to preserve the average dynamics. A family of related approaches I, II, III was presented, where each member corresponded to a distinct treatment of the Lagrange multiplier equations.

The four algorithms presented in this work were applied to a triatomic molecule model studied previously. The numerical results demonstrate the selective dissociation of the stronger bond 1, while bond 2 remains only weakly excited. The approximate bond energy and the temporal evolution of the bond length and momentum expectation values demonstrate selective dissociation for each of the optimal fields. We also compared the expectation values of the total molecular energy with the interaction energy as a measure of the efficiency of the control process. From these observations we deduce that the three new algorithms I, II, III proposed here give excellent and very similar results. The dissociation probability of the desired bond 1 was more than 50%, while for bond 2 the dissociation was less than 1%.

With these excellent results in evidence, a central question is why such a serious alteration of the Lagrange multiplier equations is successful. Three factors are operative here:

1. The proper quantum dynamics of the molecule through $|\psi(t)\rangle$ is fully retained.

2. The cost functional retains the goal of achieving the original target objective.

3. There are typically multiple (if not an infinite number) of possible control solutions in any physically well posed molecular control problem.

The role of the Lagrange multipliers is to provide feedback and guide the dynamics to an acceptable solution. Considering the three points above, the alternative formulations we
introduced for $|\lambda(t)\rangle$ just serve to take us from one acceptable solution to another. The striking similarity of the reference pulse and those of methods I, II and III also suggests that the field minimization space of the cost functional is not locally distorted to a significant degree. The ultimate saving with the new methods resides in their simplification of the traditional strongly coupled two point boundary value problem for $|\psi(t)\rangle$ and $|\lambda(t)\rangle$.

The alternate methods for $|\lambda(t)\rangle$ greatly reduce the complexity of this task. The different dynamics for $\lambda(t)$ in methods I, II and III give almost the same fields (actually, fields II and III are numerically the same) which in turn are very similar to that of the conventional approach. This strong similarity may not always occur in other problems, but its presence here clearly indicates the wide latitude in treating the feedback process in control field design. Capitalizing on this flexibility, by the approaches suggested here or other related ones, could greatly simplify the molecular control design process.

In the present paper the new Lagrange variable acted to preserve the dynamics for the molecular bond length and momentum expectation values. The same logic could also be applied to preserve additional or distinctly different observable expectation values besides $\langle z_i(t) \rangle$. Analogous problems of this type also arise in more traditional engineering applications of control theory, and it would be interesting to apply these reduced Lagrange multiplier concepts in such cases.

The ultimate significance of the findings in this paper is suggested by considering the work in the context of the analogous classical study \cite{1} and recent tracking control studies. \cite{16,17} Tracking is relevant here, as it operationally replaces the feedback role of the Lagrange multiplier by an expression for the control field explicitly in terms of the system wave function. In essence, the present paper introduces what may appear to be serious approximations for the feedback Lagrange multipliers; but, in fact, the resultant control is well-achieved, and in some cases, the field is strikingly similar to that obtained by the full traditional feedback approach. Similarly, the operations of tracking would appear to create a drastic modification of traditional feedback, yet tracking encompasses traditional optimal control solutions, as well as others. All of this work points to the observation that there is
considerable freedom for introducing approximations and direct physical guidance into the feedback aspects of quantum control. This feedback can be compactly expressed as

$$i\hbar \frac{\partial |\psi(t)\rangle}{\partial t} = [H_{\text{mol}} + \mu \epsilon(t, \langle O \rangle, |\psi(t)\rangle)] |\psi(t)\rangle$$

(44)

where the field is shown to possibly depend on time explicitly, the expectation value $\langle O \rangle$ of target observable operator $O$ and the state $|\psi(t)\rangle$ of the system. Tracking control has this form of feedback, and a formal solution to the Lagrange multiplier equations also leads to a similar form of feedback. In the simplest case, Eq. (44) only needs to be integrated once to achieve a design. The ultimate savings from these overall simplified approaches could be a factor of two, or up to many times that magnitude, when iteration is eliminated as in tracking and other direct feedback approaches (i.e. for tracking the factor of savings is $\sim 2N$ where $N$ is the nominal number of optimal control iterations and typically $N \gg 10$). The insight gained from the present body of work suggests that focusing on the physical and numerical content of the feedback should be a very fruitful direction in molecular control theory.

This new approach may be conveniently combined with methods that compute the potential surface as the dynamics proceeds. [39–43] The Lagrange multiplier logic has now been applied to classical mechanics [1,24–26] and quantum mechanics in the present paper. The same control concepts may also be applied for semiclassical wave packet propagation [44–46] and mixed quantum/classical molecular dynamics. [35–38]

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FIGURES

FIG. 1. The optimal electric field and power spectrum for selective dissociation using the traditional approach of Eqs. (3), (6), (7) and Eq. (8). The system is in the ground state at $t = 0$. The parameters in the control dynamics equations are $\gamma = 5$, $P_{f_1} = 400D_1\alpha_1^2$, $P_{f_3} = \frac{200}{\mu_1}$, $W_2 = 2D_2\alpha_2^2$, $W_4 = \frac{1}{\mu_2}$. The pulse duration time was 0.1ps. These parameters also apply to the following figures.

FIG. 2. Optimal electric fields: Method I using the Eqs. (30) to (32); Method II using the Lagrange multiplier in Eq. (34); Method III using the Eqs. (34) and (35) with the same boundary conditions. The results of methods II and III are numerically identical.

FIG. 3. Time dependence of the quantum expectation values of the approximate bond energy, bond length and momentum for each bond for the optimal pulse of the Fig. 1.

FIG. 4. The same as Fig. 3 for the optimal pulse I of Fig. 2. The results from the pulse II and III are similar to those of pulse I.

FIG. 5. Time dependence of the quantum expectation value of the total molecular Hamiltonian $\langle E_T \rangle$ and the interaction term $\langle E_{int} \rangle$. a) for the reference pulse in Fig. 1; b) for the pulse I of Fig. 2. The results from the pulse II and III are very similar to that of pulse I.
TABLES

TABLE I. Convergent value of the dissociation probability $P_i$ for the four reaction channels. The four channels are: $P_1$ for $\text{ABC} \rightarrow \text{A} + \text{BC}$; $P_2$ for $\text{ABC} \rightarrow \text{C} + \text{AB}$; $P_3$ for $\text{ABC} \rightarrow \text{B} + \text{A} + \text{C}$ and $P_4$ means no dissociation. CM means the conventional method (the pulse of the Fig. 1). For the approaches II and III we obtain almost the same dissociation probability as that in approach I.

| Method | $P_1$  | $P_2$ | $P_3$  | $P_4$  |
|--------|--------|--------|--------|--------|
| CM     | 0.560  | 1.8×10^{-3} | 1×10^{-3} | 0.437  |
| I      | 0.628  | 7.3×10^{-3} | 2.7×10^{-3} | 0.362  |

TABLE II. Number of iterations for the four different methods in order to find the optimal pulse field in Fig. 1 and Fig. 2.

| Method | Number of Iteractions |
|--------|-----------------------|
| CM     | 17                    |
| I      | 18                    |
| II     | 19                    |
| III    | 15                    |
Figure 1

Electric Field (a.u.)

Time (ps)

Power Spectrum

Frequency (cm$^{-1}$)
Figure 2
Figure 3

![Graphs of \(< E_1 >\), \(< E_2 >\), \(< P_1 >\), \(< P_2 >\), \(< R_1 >\), and \(< R_2 >\) vs. Time (ps).]
Figure 4

- $< E_1 >$
- $< E_2 >$
- $< P_1 >$
- $< P_2 >$
- $< R_1 >$
- $< R_2 >$

Time (ps)
Figure 5

\[ \langle E_T \rangle \]

\[ \langle E_{int} \rangle \]

\( \langle E_i(t) \rangle \) (a.u.)

Time (ps)