# Quantum control for arbitrary linear and quadratic potentials 

Frank L.H. Brown ${ }^{1}$, Robert J. Silbey *<br>Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

Received 13 April 1998


#### Abstract

We describe a theoretical framework capable of calculating optimal control fields for systems with arbitrary linear and quadratic potentials governing the nuclear degrees of freedom. Application of this method to various test cases demonstrates that quadratic coupling (between the nuclear and electronic degrees of freedom) can lead to large changes relative to models with only linear coupling. © 1998 Published by Elsevier Science B.V. All rights reserved.


## 1. Introduction

It is a long-standing goal of physical chemists to be able to influence chemistry by the application of specially designed radiation fields. Recent work, both experimental [1-7] and theoretical [8-12], has demonstrated that it is indeed possible to drive molecules toward a desired goal with laser fields. Introductions to the current state of progress in the field can be found in the recent reviews by Wilson and co-workers [6] and Zare [16] and the references therein. Without indulging in an extensive review ourselves, we comment that it would probably be unrealistic to describe the recent successes of quantum control as more than modest achievements. Experimentally, it has been difficult to achieve control for all but the simplest systems (small gas phase molecules) and although theoretical models may be a bit more advanced, they too are limited in scope because of the inherent difficulty in modeling many dimensional quantum mechanical systems. It seems clear that, for quantum control to develop into a practical science, advances will have to be made both experimentally and theoretically.

There are two possible approximate approaches one can take in attempting to model quantum systems with many degrees of freedom. In the first approach, a realistic Hamiltonian for the system of interest is employed and the dynamics are calculated by some approximate scheme. In the context of quantum control, a number of such approximate propagation schemes have been employed including: Gaussian wave packet [13,14], time-dependent Hartree [15], nearly classical [11] and stochastic bath [12] methods. In the second approach, an approximate Hamiltonian is adopted for which the dynamics may be solved exactly (i.e. quadratic potentials).

[^0]This approach has recently been pursued by Cao et al. [17] to study the problem of quantum control for a single degree of freedom coupled to a Gaussian bath. This Letter will extend the work of Cao et al. to cover the case of completely arbitrary linear and quadratic potentials via the matrix method of Balian and Brezin [2]. The formalism is quite general and has the potential to be applied to a variety of interesting control problems including the control of large molecules and control of systems in condensed phases. In the present work we consider several test cases in order to demonstrate the validity of the method. Possible extensions of these preliminary results will be discussed.

The organization of this article will be as follows. Section 2 will outline the theoretical framework for our model of quantum control. Section 3 will detail and comment upon results we have obtained by applying this model to some simple test cases. In Section 4 we will conclude with a discussion elaborating upon the possibilities for extension of this work.

## 2. Weak field control in the limit of harmonic and linear potentials

As in previous studies [11,12], we adopt the following simplified model to study the problem of quantum control. The system we desire to influence is described by a Hamiltonian

$$
\begin{equation*}
H_{\mathrm{s}}=H_{\mathrm{g}}|g\rangle\langle g|+\left(H_{\mathrm{e}}+\omega_{\mathrm{eg}}\right)|e\rangle\langle e| \tag{1}
\end{equation*}
$$

comprised of two electronic states $|g\rangle$ and $|e\rangle$ and a number of nuclear degrees of freedom whose dynamics are governed by the adiabatic Hamiltonians $H_{\mathrm{g}}$ and $H_{\mathrm{e}}$ depending upon the electronic state of the system. $\omega_{\text {eg }}$, the energy separation between the lowest nuclear eigenstate for the excited and ground electronic states, is taken to be much larger than any of the frequencies associated with nuclear motion. Coupling to the radiation field is achieved through a dipolar interaction of the form

$$
\begin{equation*}
H_{\mathrm{int}}=-\hat{\mu} \varepsilon(t) . \tag{2}
\end{equation*}
$$

For simplicity, the field is treated classically and the dipole operator is taken to be $\hat{\mu}=\mu(|g\rangle\langle e|+|e\rangle\langle g|)$, with $\mu$ a constant, so that the dipole moment is independent of the configuration of the nuclear degrees of freedom (Condon approximation). We choose to write the field

$$
\begin{equation*}
\varepsilon(t) \equiv E(t) \mathrm{e}^{-\mathrm{i} \omega_{\mathrm{eg}} t}+E^{*}(t) \mathrm{e}^{\mathrm{i} \omega_{\mathrm{eg}} t} \tag{3}
\end{equation*}
$$

in order to explicitly separate the high frequency, ( $\mathrm{e}^{-\mathrm{i} \omega_{\text {eg }} t}$ ) 'carrier', component of the field from the remaining slowly varying portion, $E(t)$, which will contain the information pertinent to control. Within the rotating wave approximation (RWA) [18], the system's dynamics are dictated by the Hamiltonian

$$
\begin{equation*}
H(t)=|g\rangle\langle g| H_{\mathrm{g}}+|e\rangle\langle e| H_{\mathrm{e}}-\mu\left(|g\rangle\langle e| E(t)+|e\rangle\langle g| E^{*}(t)\right) \tag{4}
\end{equation*}
$$

when a field is present and it is our goal to find the field, $E(t)$, which best promotes the achievement of some configuration of the system at a set time, $t_{f}$.

Following the lead of previous efforts [12,11], we define our control goal as the maximal realization of some target operator, denoted $A$, at the time $t_{f}$. Mathematically, this translates to maximizing the expectation value

$$
\begin{equation*}
A\left(t_{f}\right) \equiv \operatorname{Tr}\left\{A \rho\left(t_{f}\right)\right\} \tag{5}
\end{equation*}
$$

with respect to all possible control fields $E(t)$. For concreteness, we mention that the operator $A$ will eventually be taken to be a gaussian wave packet on the excited electronic manifold in our analysis although, to this point, there is no need to restrict $A$ to any form. In the limit of weak applied fields, it is well known how to calculate
the field, $E(t)$, which maximizes the expectation, $A\left(t_{f}\right)[11,12]$. When $A$ is purely excited in electronic character, the optimal field will satisfy the integral equation

$$
\begin{equation*}
\lambda E(t)=\int_{0}^{t_{f}} \mathrm{~d} \tau M(t, \tau) E(\tau) \tag{6}
\end{equation*}
$$

with

$$
\begin{equation*}
M\left(t_{1}, t_{2}\right)=\mu^{2} \operatorname{Tr}\left\{A_{\mathrm{e}} \mathrm{e}^{-\mathrm{i} H_{\mathrm{e}}\left(t_{f}-t_{2}\right)} \mathrm{e}^{-\mathrm{i} H_{\mathrm{g}} t_{2}} \rho(0) \mathrm{e}^{\mathrm{i} H_{\mathrm{g}} t_{1}} \mathrm{e}^{\mathrm{i} H_{\mathrm{e}}\left(t_{f}-t_{1}\right)}\right\} \tag{7}
\end{equation*}
$$

The subscript, 'e' has been appended to $A$ to remind us that the target is on the excited state surface. For calculational purposes, it is more convenient to think in terms of a discretized time representation which allows Eq. (6) to be recast as an eigenvalue equation

$$
\begin{equation*}
\lambda E_{i}=\Delta M_{i j} E_{j} \tag{8}
\end{equation*}
$$

with

$$
\begin{gather*}
E_{i} \equiv E\left(t_{i}\right) \\
M_{i j} \equiv M\left(t_{i}, t_{j}\right)  \tag{9}\\
\Delta \equiv t_{i+1}-t_{i}
\end{gather*}
$$

and it is to be understood that the timepoints, $t_{i}$, are equally spaced. Within this picture, the eigenvalue, $\lambda$, is given by:

$$
\begin{equation*}
\lambda=\frac{A\left(t_{f}\right)}{\int_{0}^{t_{f}} \mathrm{~d} t|E(t)|^{2}} \tag{10}
\end{equation*}
$$

so that we know which eigenvector corresponds to the globally optimal field. The eigenvector corresponding to the largest eigenvalue, $\lambda$, of $M_{i j}$ maximizes the value of $A\left(t_{f}\right)$ and represents the optimal field.

Eqs. (7), (8) and (10) summarize the results for weak field control with a target operator on the excited state surface. To compute the optimal $E(t)$ one has only to evaluate the response function $M$ (Eq. (7)) at a number of points corresponding to the chosen time discretization and diagonalize the resulting matrix, $M_{i j}$ (Eq. (9)). The field most capable of producing the desired target will be (in the discretized limit) the eigenvector of $M_{i j}$ corresponding to the largest eigenvalue $\lambda$ (Eq. (8)). Furthermore, we define the yield of this field to be the eigenvalue, $\lambda$, which is related to $A_{\mathrm{e}}\left(t_{f}\right)$ by Eq. (10). This yield is assumed to be an adequate measure of the achievement of our goal (target).

We stress that to this point no assumptions have been made as to the forms of $H_{\mathrm{g}}$ and $H_{\mathrm{e}}$ and that the preceding discussion has really just been a review of well-known weak field control theory [12,11]. Although the matrix formulation of Eq. (8) represents a considerable simplification over theories of control in the strong field limit [12], it remains a non-trivial matter to compute the optimal $E(t)$. The difficulty arises in the computation of the matrix $M_{i j}$. For systems with many degrees of freedom and complicated potential surfaces, exact computation of the elements of $M_{i j}$ becomes an impossibility and approximate propagation schemes (see Section 1 for a few possibilities) need to be implemented. We circumvent this difficulty by taking our potentials to be linear and quadratic functions of our coordinate degrees of freedom. Given a system with $N$ degrees of freedom we are free to write the Hamiltonian in terms of the creation and annihilation operators

$$
\begin{align*}
& a_{i}=\frac{1}{\sqrt{2}}\left(\sqrt{\frac{m_{i} \omega_{i}}{\hbar}} \hat{q}_{i}+i \sqrt{\frac{1}{m_{i} \omega_{i} \hbar}} \hat{p}_{i}\right) \\
& a_{i}^{\dagger}=\frac{1}{\sqrt{2}}\left(\sqrt{\frac{m_{i} \omega_{i}}{\hbar}} \hat{q}_{i}-i \sqrt{\frac{1}{m_{i} \omega_{i} \hbar}} \hat{p}_{i}\right) \tag{11}
\end{align*}
$$

with $i$ ranging from 1 to $N$. Our restriction to linear and quadratic potentials then translates to allowing only Hamiltonians with terms up to second order in the operators $a_{i}$ and $a_{j}^{\dagger}$.

Consider the vector of operators

$$
\begin{equation*}
\alpha \equiv\left(a_{1}, \cdots, a_{N}, a_{1}^{\dagger}, \cdots, a_{N}^{\dagger}\right) . \tag{12}
\end{equation*}
$$

For Hamiltonians of the form which we are discussing it is possible to write

$$
\begin{equation*}
H=\frac{1}{2} \alpha S \alpha+\lambda \tau \alpha+c \tag{13}
\end{equation*}
$$

where $\boldsymbol{S}$ is a symmetric (Hermiticity requires $\boldsymbol{S}=\tilde{\boldsymbol{S}}$ ) $2 N \times 2 N$ matrix, $\boldsymbol{\lambda}$ is a $2 N$ dimensional vector, $c$ is a constant and the $2 N \times 2 N$ matrix $\boldsymbol{\tau}$ is given by

$$
\tau=\left(\begin{array}{cc}
0 & 1  \tag{14}\\
-1 & 0
\end{array}\right)
$$

The matrix method of Balian and Brezin makes it possible to compute

$$
\begin{equation*}
\operatorname{Tr}\left\{e^{A} e^{B} e^{C} \cdots\right\} \tag{15}
\end{equation*}
$$

where $A, B, C, \ldots$ are all operators of the form Eq. (13) [23,24]. Without proof, we provide here a general formula for the multiplication of two exponentiated operators of the form Eq. (13) into a single such operator and a formula for taking the trace of a single operator of the same form. Given this machinery, it is clear that extension to Eq. (15) will follow immediately. Multiplication is accomplished via the following product law:

$$
\begin{equation*}
\mathrm{e}^{\frac{1}{2} \alpha S_{a} \alpha+\lambda_{a} \tau \alpha} \mathrm{e}^{\frac{1}{2} \alpha S_{b} \alpha+\lambda_{b} \tau \alpha}=\mathrm{e}^{\frac{1}{2} \alpha S \alpha+\lambda \tau \alpha+\nu} \tag{16}
\end{equation*}
$$

where

$$
\begin{align*}
\mathrm{e}^{\tau S}= & \mathrm{e}^{\tau S_{a}} \mathrm{e}^{\boldsymbol{\tau} S_{b}} \\
\boldsymbol{\lambda}= & \frac{\boldsymbol{\tau} \boldsymbol{S}}{\mathrm{e}^{\boldsymbol{\tau}}-1} \frac{\mathrm{e}^{\tau S_{a}}-1}{\boldsymbol{\tau} \boldsymbol{S}_{a}} \boldsymbol{\lambda}_{a}+\frac{\boldsymbol{\tau} \boldsymbol{S}}{1-\mathrm{e}^{-\boldsymbol{\tau}}} \frac{1-\mathrm{e}^{-\boldsymbol{\tau} S_{b}}}{\boldsymbol{\tau} \boldsymbol{S}_{b}} \boldsymbol{\lambda}_{b} \\
\nu= & \frac{1}{2} \boldsymbol{\lambda}_{a} \boldsymbol{\tau} \frac{\sinh \boldsymbol{\tau} \boldsymbol{S}_{a}-\boldsymbol{\tau} \boldsymbol{S}_{a}}{\left(\boldsymbol{\tau} \boldsymbol{S}_{a}\right)^{2}} \boldsymbol{\lambda}_{a}+\frac{1}{2} \boldsymbol{\lambda}_{b} \boldsymbol{\tau} \frac{\sinh \boldsymbol{\tau} \boldsymbol{S}_{b}-\boldsymbol{\tau} \boldsymbol{S}_{b}}{\left(\boldsymbol{\tau} \boldsymbol{S}_{b}\right)^{2}} \boldsymbol{\lambda}_{b}  \tag{17}\\
& -\frac{1}{2} \boldsymbol{\lambda} \boldsymbol{\tau} \frac{\sinh \boldsymbol{\tau} \boldsymbol{S}-\boldsymbol{\tau} \boldsymbol{S}}{(\boldsymbol{\tau} \boldsymbol{S})^{2}} \boldsymbol{\lambda}+\frac{1}{2} \boldsymbol{\lambda}_{a} \boldsymbol{\tau} \frac{\mathrm{e}^{\boldsymbol{\tau} S_{a}}-1}{\boldsymbol{\tau} \boldsymbol{S}_{a}} \frac{\mathrm{e}^{\tau S_{b}}-1}{\boldsymbol{\tau} \boldsymbol{S}_{b}} \boldsymbol{\lambda}_{b}
\end{align*}
$$

which is justified in the paper by Balian and Brezin [23]. The formula for the trace, given by Friesner et al. [24], is

$$
\begin{equation*}
\operatorname{Tr}\left\{\mathrm{e}^{\frac{1}{2} \boldsymbol{\alpha} S \alpha+\lambda \tau \alpha}\right\}=\mathrm{e}^{\frac{1}{2} \lambda \tau S^{-1} \tau \lambda}\left[(-1)^{N} \operatorname{det}\left(\mathrm{e}^{\tau S}-1\right)\right]^{-1 / 2} \tag{18}
\end{equation*}
$$

The formulas of the preceding paragraph will prove useful in the computation of $M_{i j}$ if, in addition to the Hamiltonians $H_{\mathrm{g}}$ and $H_{\mathrm{e}}$ being of the form (13), the zero time density matrix, $\rho(0)$, and the target operator, $A_{\mathrm{e}}$ are expressible as exponentiated quadratic operators. We will always take $\rho(0)$ to be the thermally equilibrated density matrix for the system in the ground electronic state

$$
\begin{equation*}
\rho(0)=\rho_{\mathrm{eq}}=\frac{\mathrm{e}^{-\beta H_{\mathrm{g}}}}{\operatorname{Tr}\left\{\mathrm{e}^{-\beta H_{\mathrm{g}}}\right\}} \tag{19}
\end{equation*}
$$

which clearly adheres to the required form. To make contact with previous work [12,11,17], we will take our target operator, $A_{\mathrm{e}}$, to be a gaussian wave packet in the Wigner Representation [22]

$$
\begin{equation*}
A_{\mathrm{e}}(q, p)=\frac{1}{2 \pi \sqrt{W_{p} W_{q}}} \exp \left[-\frac{\left(q-q_{\mathrm{c}}\right)^{2}}{2 W_{q}}-\frac{\left(p-p_{\mathrm{c}}\right)^{2}}{2 W_{p}}\right] \tag{20}
\end{equation*}
$$

It is possible to associate with such a wave packet the operator

$$
\begin{equation*}
A_{\mathrm{e}}=2 \sinh \left(\frac{\gamma \hbar \omega_{\mathrm{A}}}{2}\right) \exp \left[-\gamma\left(\frac{\left(\hat{p}-p_{\mathrm{c}}\right)^{2}}{2 m}+\frac{m \omega_{\mathrm{A}}^{2}}{2}\left(\hat{q}-q_{\mathrm{c}}\right)^{2}\right)\right] \tag{21}
\end{equation*}
$$

where $\gamma$ and $\omega_{A}$ may be thought of as the inverse temperature and frequency associated with a fictitious oscillator whose equilibrium density matrix serves as our target for control [26]. The values of these fictitious parameters depend upon the widths of the wavepacket in the following manner:

$$
\begin{align*}
& \omega_{\mathrm{A}}=\sqrt{\frac{W_{p}}{W_{q} m^{2}}} \\
& \gamma=\frac{2 m}{\hbar} \sqrt{\frac{W_{q}}{W_{p}}} \tanh ^{-1}\left(\sqrt{\frac{\hbar^{2}}{4 W_{p} W_{q}}}\right) . \tag{22}
\end{align*}
$$

For convenience, the mass of the fictitious oscillator is taken to be the same as that of the real oscillator in the problem. Examination of Eq. (21) confirms that our target adheres to the required form as well.

In looking at $M$ (Eq. (7)) we realize that it is nothing more than a trace over many exponentiated operators of the form (13) and thus the Balian and Brezin techniques give us a simple method for its calculation. Given $M$, the calculation of $E$ requires only the comparatively simple diagonalization of a matrix. Further comments on the implementation of this formalism as well as several examples will be provided in the following sections.

## 3. Results and discussion

The results of the preceding section lay a general framework for the calculation of optimal control fields, within the limitations previously discussed. In order to demonstrate the utility of our formulation we will examine several test cases. We begin in Section 3.1 by examining the case of a single harmonic mode coupled to the electronic transition. Section 3.2 will consider the effects of coupling other modes to this primary mode as a model for dissipative dynamics.

### 3.1. Control with a single harmonic mode

A single mode of frequency $\omega_{g}$ in the ground electronic state and frequency $\omega_{e}$ in the excited state will serve as our paradigm for weak field control. In addition to the frequency shift upon excitation, the minima of the excited state potential will also be shifted relative to the ground state by an amount $d$ (see Fig. 1). For our target, we take the gaussian wave packet corresponding to the harmonic oscillator density matrix (Eq. (21))


Fig. 1. A qualitative sketch of quantum control for our simple model. The two harmonic potentials are shifted by $d$ relative to each other and in general have different frequencies in the ground and excited state. The energy, $E_{\text {eg }}$, is the difference in frequencies between the lowest vibrational eigenstate in each of the two electronic states.
centered at $q_{\mathrm{c}}=2 d$ and $p_{\mathrm{c}}=0$ with the inverse 'temperature' $\gamma$ and frequency $\omega_{A}$. The Hamiltonians, $H_{\mathrm{g}}$ and $H_{\mathrm{e}}$, and the pseudo-Hamiltonian, $H_{\mathrm{A}}$, given by

$$
\begin{align*}
& H_{\mathrm{g}}=\frac{\hat{p}^{2}}{2 m}+\frac{m \omega_{\mathrm{g}}^{2}}{2} \hat{q}^{2} \\
& H_{\mathrm{e}}=\frac{\hat{p}^{2}}{2 m}+\frac{m \omega_{\mathrm{e}}^{2}}{2}(\hat{q}-d)^{2}  \tag{23}\\
& H_{\mathrm{A}}=\frac{\hat{p}^{2}}{2 m}+\frac{m \omega_{\mathrm{A}}^{2}}{2}(\hat{q}-2 d)^{2},
\end{align*}
$$

conveniently serve to express the response function, $M$ (Eq. (7)) as

$$
\begin{gather*}
M\left(t_{1}, t_{2}\right)=N \operatorname{Tr}\left\{\mathrm{e}^{-\gamma H_{\mathrm{A}}} \mathrm{e}^{-\mathrm{i}\left(t_{f}-t_{2}\right) H_{\mathrm{c}}} \mathrm{e}^{-\left[\beta-\mathrm{i}\left(t_{1}-t_{2}\right)\right] H_{\mathrm{g}}} \mathrm{e}^{\mathrm{i}\left(t_{f}-t_{1}\right) H_{\mathrm{c}}}\right\} \\
N=4 \mu^{2} \sinh \left(\beta \hbar \omega_{\mathrm{g}} / 2\right) \sinh \left(\gamma \hbar \omega_{\mathrm{A}} / 2\right) . \tag{24}
\end{gather*}
$$

To make explicit contact with the notation of the previous section, we note that the Hamiltonians (Eq. (23)) may be written in the form

$$
\begin{equation*}
H=\frac{1}{2} \boldsymbol{\alpha} \boldsymbol{S} \boldsymbol{\alpha}+\boldsymbol{\lambda} \boldsymbol{\tau} \boldsymbol{\alpha}+\nu \tag{25}
\end{equation*}
$$

where $\boldsymbol{\alpha} \equiv\left(a, a^{\dagger}\right)$ with $a$ and $a^{\dagger}$ taken to be the creation and annihilation operators for the ground state Hamiltonian such that

$$
\begin{equation*}
H_{\mathrm{g}}=\left(a^{\dagger} a+\frac{1}{2}\right) \hbar \omega_{\mathrm{g}} \tag{26}
\end{equation*}
$$

The relevant matrices, vectors and constants are:

$$
\begin{align*}
& S_{\mathrm{g}}=\left(\begin{array}{cc}
0 & \hbar \omega_{\mathrm{g}} \\
\hbar \omega_{\mathrm{g}} & 0
\end{array}\right) ; \lambda_{\mathrm{g}}=(0,0) ; \nu_{\mathrm{g}}=0 \\
& S_{\mathrm{e}}=\left(\begin{array}{cc}
\frac{\hbar}{2 \omega_{\mathrm{g}}}\left(\omega_{\mathrm{e}}^{2}-\omega_{\mathrm{g}}^{2}\right) & \hbar \omega_{\mathrm{g}}+\frac{\hbar}{2 \omega_{\mathrm{g}}}\left(\omega_{\mathrm{e}}^{2}-\omega_{\mathrm{g}}^{2}\right) \\
\hbar \omega_{\mathrm{g}}+\frac{\hbar}{2 \omega_{\mathrm{g}}}\left(\omega_{\mathrm{e}}^{2}-\omega_{\mathrm{g}}^{2}\right) & \frac{\hbar}{2 \omega_{\mathrm{g}}}\left(\omega_{\mathrm{e}}^{2}-\omega_{\mathrm{g}}^{2}\right)
\end{array}\right) \\
& \lambda_{\mathrm{e}}=\sqrt{\frac{\hbar m}{2 \omega_{\mathrm{g}}} \omega_{\mathrm{e}}^{2} d(-1,1) ; \nu_{\mathrm{e}}=\frac{m \omega_{\mathrm{e}}^{2} d^{2}}{2}}  \tag{27}\\
& S_{\mathrm{A}}=\left(\begin{array}{cc}
\frac{\hbar}{2 \omega_{\mathrm{g}}}\left(\omega_{\mathrm{A}}^{2}-\omega_{\mathrm{g}}^{2}\right) & \hbar \omega_{\mathrm{g}}+\frac{\hbar}{2 \omega_{\mathrm{g}}}\left(\omega_{A}^{2}-\omega_{\mathrm{g}}^{2}\right) \\
\hbar \omega_{\mathrm{g}}+\frac{\hbar}{2 \omega_{\mathrm{g}}}\left(\omega_{\mathrm{A}}^{2}-\omega_{\mathrm{g}}^{2}\right) & \frac{\hbar}{2 \omega_{\mathrm{g}}}\left(\omega_{\mathrm{A}}^{2}-\omega_{\mathrm{g}}^{2}\right)
\end{array}\right) \\
& \lambda_{\mathrm{A}}=\sqrt{\frac{\hbar m}{2 \omega_{\mathrm{g}}} \omega_{\mathrm{A}}^{2} d(-2,2) ; \nu_{\mathrm{A}}=2 m \omega_{\mathrm{A}}^{2} d^{2}}
\end{align*}
$$

as may be verified by the rewriting of Eq. (23) in terms of creation and annihilation operators (Eq. (11) with $\omega_{i}=\omega_{g}$ ). Although it would be possible to proceed analytically, since our matrices are of dimension two, the resulting formulae will be complicated and not particularly insightful as can be seen for the linearly displaced oscillator model studied by Yan et al. [12]. Instead, we opt for numerical calculation of $M$ via repeated application of Eq. (16) followed by use of formula (18) to evaluate the trace. The only inconvenience of our formalism stems from the square root in Eq. (18). As it is unclear which branch to select for given $t_{1}$ and $t_{2}$, we are forced to analytically continue our results from the point $t_{1}=t_{2}=0$ in the manner described by Friesner et al. [24].

We have verified [26] that in the limit of $\omega_{\mathrm{g}}=\omega_{\mathrm{e}}$ the method just described gives results identical to those previously obtained [11]. In addition, however, our method allows for the computation of optimal fields when $\omega_{\mathrm{g}} \neq \omega_{\mathrm{e}}$. To demonstrate the importance of quadratic coupling we consider a model with a relatively simple coordinate system consisting of: $m=1, \beta=1, d=5, t_{f}=5, \mu=1$ and $\gamma=6.91$ ( $\gamma$ value corresponds to $W_{p}=W_{q}=0.501$ in Eq. (20) and a density operator corresponding to better than $99.9 \%$ ground state occupation - for all practical purposes this value of $\gamma$ gives rise to a minimum uncertainty target). The values taken for the ground, excited and target frequencies will be varied between 0.8 and 1.2. Table 1 lists the yields for several

Table 1
Yields (Eq. (10)) for various combinations of harmonic frequencies

| $\omega_{\mathrm{g}}$ | $\omega_{\mathrm{e}}$ | $\omega_{\mathrm{A}}$ | Yield |
| :--- | :--- | :--- | :--- |
| 1.0 | 1.0 | 1.0 | 0.3243 |
| 1.0 | 1.0 | 0.8 | 0.3045 |
| 1.0 | 1.0 | 1.2 | 0.3391 |
| 1.0 | 0.8 | 1.0 | 0.5041 |
| 1.0 | 1.2 | 1.0 | 0.2257 |
| 0.8 | 1.0 | 1.0 | 0.2711 |
| 1.2 | 1.0 | 1.0 | 0.3708 |

different $\omega_{\mathrm{g}}, \omega_{\mathrm{e}}$ and $\omega_{\mathrm{A}}$ combinations. All other parameters are the same as previously discussed. The time, $t_{f}$, is short enough to insure that our optimal field profile consists of a single pulse so that we need not be concerned with coherence effects as discussed by Yan et al. [12]. We observe three clear trends within the table.

1. Increase of $\omega_{\mathrm{A}}$ while keeping the other frequencies fixed corresponds to a gain in yield.
2. Increase of $\omega_{\mathrm{e}}$ while keeping the other frequencies fixed corresponds to a loss of yield.
3. Increase of $\omega_{\mathrm{g}}$ while keeping the other frequencies fixed corresponds to a gain in yield.

We interpret these findings as follows. Since we have taken our dipole moment to be constant and we have a limited choice of excitation frequencies to choose from due to the constant level spacing within the harmonic oscillator model, the profile of excited population will be more or less determined by the Franck-Condon overlap factors between the ground and excited state oscillator levels. We argue that the easiest way to control the population on the excited surface under these conditions will be in modulation of amplitude of the applied field over time. The best control of shape of the excited wave packet will be given by a ground state with the most spatially constrained initial population ( $\omega_{\mathrm{g}}$ high), so as to give the narrowest profile upon initial excitation, and an excited state with the lowest slope at $q=0$ ( $\omega_{\mathrm{e}}$ low), so that the excited population evolves away from the vertical transition site slowly thus giving the field more time to adjust. The weak yield dependence upon $\omega_{\mathrm{A}}$ suggests that although it may not be possible to create a wave packet in perfect agreement with the goal, it will be possible to create a packet with appreciable probability at $q=2 d$ at the target time. A narrow target will lead to higher yield even if the fit is reasonably poor because of the high overlap right at $q=2 d$ whereas a broad target would require quite a good fit to get a correspondingly good yield.

### 3.2. Multiple modes and dissipative effects

The true strength in our harmonic treatment lies in the ease of treating a number of quantum mechanical degrees of freedom exactly. In principle this ability could be exploited to examine quantum control on rather large gas phase molecules - a possibility we will not consider here. Instead, we demonstrate this ability by examining and generalizing a model recently discussed by Cao et al. [17]. The system we consider is basically the same as that detailed in the preceding section, but with the addition of several oscillators coupled to the primary coordinate. The coupling of the primary coordinate to other modes serves as a model for dissipation (assuming we examine times short enough to avoid Poincare recurrences due to the finite size of our bath) and is of interest as a means to mimic intermolecular interactions in condensed phases.

The Hamiltonians in the ground and excited state for our dissipative system are taken as:

$$
\begin{align*}
& H_{\mathrm{g}}=\frac{\hat{p}^{2}}{2 m}+\frac{m \omega_{\mathrm{g}}^{2}}{2} \hat{q}^{2}+\sum_{i=1}^{N}\left[\frac{\hat{p}_{i}^{2}}{2 m_{i}}+\frac{m_{i} \omega_{i}^{2}}{2}\left(\hat{q}_{i}-\frac{c_{i}}{m_{i} \omega_{i}^{2}} \hat{q}\right)^{2}\right]  \tag{28}\\
& H_{\mathrm{e}}=\frac{\hat{p}^{2}}{2 m}+\frac{m \omega_{\mathrm{e}}^{2}}{2}(\hat{q}-d)^{2}+\sum_{i=1}^{N}\left[\frac{\hat{p}_{i}^{2}}{2 m_{i}}+\frac{m_{i} \omega_{i}^{2}}{2}\left(\hat{q}_{i}-\frac{c_{i}}{m_{i} \omega_{i}^{2}} \hat{q}\right)^{2}\right]
\end{align*}
$$

where $\tilde{q}$ and $\tilde{p}$ are the position operators for the primary coordinate whereas the $\tilde{q}_{i} \mathrm{~s}$ and $\tilde{p}_{i} \mathrm{~s}$ are the operators for the bath modes with the associated frequencies, $\omega_{i}$, and masses, $m_{i}$. The coupling constants, $c_{i}$, allow for linear coupling between the coordinates of the primary oscillator and the bath. To be fully general we could also allow for the possibility of differing bath frequencies and coupling constants depending upon the electronic state of the system, but in this preliminary study we restrict our Hamiltonian to this simpler form. Calculation of the optimal field proceeds formally identically to the treatment of the last section. Spatial constraints (and common sense) preclude us from attempting to display the matrices $\mathbf{S}_{g}$, etc., for a multiple mode model, but generalization of the steps leading up to Eq. (27) should be transparent.

Before proceeding with calculations we must specify the full set of masses, frequencies and coupling constants for the bath. Although we restrict our set of bath modes to be some finite number for calculational
purposes, the presence of these modes serves as a model for an infinite bath. It is known, both from classical studies [19] and quantum mechanical path integral methods [20,25], that the effect of a harmonic bath upon a system it is linearly coupled to may be completely specified if the spectral density, defined by

$$
\begin{equation*}
J(\omega)=\frac{\pi}{2} \sum_{i=1}^{N} \frac{c_{i}^{2}}{m_{i} \omega_{i}} \delta\left(\omega-\omega_{i}\right) \tag{29}
\end{equation*}
$$

is known. This suggests a convenient scheme for picking the set of bath constants [21]. A functional form for $J(\omega)$ is selected as is a finite set of modes with equally spaced frequencies. The coupling constants are then constrained by Eq. (29) to be given by

$$
\begin{equation*}
c_{i}^{2}=\frac{2}{\pi} m \omega_{i} J\left(\omega_{i}\right) \Delta \omega \tag{30}
\end{equation*}
$$

where we have taken the masses, $m_{i}$, to be equal to the mass of the primary coordinate, for convenience, and $\Delta \omega$ represents the discretized frequency increment. Mathematically, the functional form of $J(\omega)$ is unrestricted, but for physical problems a suitable form must be chosen. To make contact with the work of Cao et al. [17] we will consider two different forms for $J(\omega)$ :

1. $J(\omega)=\eta_{0} \omega$; we will refer to this form ohmic friction.
2. $J(\omega)=D \eta_{0} \omega / \omega^{2}+D^{2}$; we will refer to this form as non-ohmic friction.

The dissipative model we will study first is similar to the model studied by Cao et al. [17], and our interest in it is purely in proving the validity of our treatment. We take the parameters of the primary coordinate to be


Fig. 2. Plots of the yield (Eq. (10)) vs. friction strength, $\eta_{0}$, for a single harmonic mode coupled to a 'bath' of harmonic modes (see text). The functional forms for the spectral density for each of the two types of friction are described in Section 3.2.


Fig. 3. Three plots of yield (Eq. (10)) vs. (non-ohmic) friction strength. The convergence of the three plots suggests that dissipation has a more severe effect on the oscillators with longer periods of vibration.
identical to those of the preceding section with $\omega_{\mathrm{g}}=\omega_{\mathrm{e}}=\omega_{\mathrm{A}}=1$ and $t_{f}=5$. The target is taken to be the same minimum uncertainty wavepacket centered at $q=2 d$. The bath is modeled by 11 modes with frequencies evenly spaced between 0.5 and 1.5 and coupling constants dictated by Eq. (30). This narrow range of frequencies is expected to be acceptable as the primary coordinate will only couple effectively to those modes nearly in resonance with it. The value of $\eta_{0}$ will be varied and in the case of our non-ohmic form (case 2) $D$ will be set equal to 1 . The bath is assumed to be in equilibrium with the primary oscillator so that $\beta=1$ will be used in the initial density matrix.

In Fig. 2 the yield (Eq. (10)) is plotted against the friction strength, $\eta_{0}$ for the case of ohmic and non-ohmic friction (cases 1 and 2 above). In both cases, increasing the friction is seen to significantly reduce the yield and the decrease in yield is seen to be most severe for the ohmic case. This loss of yield reflects the loss of energy from the primary mode to the bath. Such a loss of energy makes it impossible for the wavepacket to get all the way to $2 d$ and hence the overlap with the target suffers accordingly. The relative severity of the loss of yield for the ohmic case is attributable to the fact that Eq. (30) dictates coupling constants for the modes near frequency 1 to be larger than those in the non-ohmic case. Our plot is in agreement with the treatment of Cao et al. [17]. What is surprising is that we are able to achieve this agreement with only 11 bath modes whereas the analytical technique of Cao takes an infinite number of modes into consideration. The generality of our method allows for extension of the model beyond the analytically solvable ( $\omega_{\mathrm{g}}=\omega_{\mathrm{e}}=1$ ) case and in Fig. 3 we present results for varied excited state frequencies in the case of non-ohmic dissipation. Note that as the excited state frequency is decreased that the loss of yield, induced by increasing the friction constant, goes up. This effect may be attributed to the longer vibrational period associated with smaller frequencies which means a longer exposure to dissipation on the way to the target.

## 4. Conclusion

We have demonstrated that the method of Balian and Brezin [23] is easily applied to the problem of quantum control and that it exhibits advantages over methods previously implemented. In particular, the method allows for exact solutions to control problems with arbitrary quadratic and linear potentials for the adiabatic surfaces. Previously implemented exact methods were capable of describing only linear coupling between the ground and excited electronic states. Inspection of Table 1 demonstrates that the even the simplest manifestation of quadratic coupling can lead to large effects in yield and should not be ignored. Furthermore, Fig. 3 demonstrates the importance of quadratic coupling in the presence of dissipation. We concede that none of the test cases discussed in this work would be impossible to solve by other methods, but we believe that the extension of the present work to more complicated systems is immediate and has the potential to look at problems which would otherwise be difficult to consider. The application which immediately comes to mind is that of a many atom molecule with changes in frequency of all harmonic modes on making the ground to excited electronic transition. It would also be possible to consider a system with several primary modes coupled to a bath. Such a model would be useful in assessing the feasibility of control for a complicated molecule in a condensed phase.

It is true that a harmonic model misses a large part of the richness associated with a general anharmonic potential, but current theoretical and computational limitations defeat any hope of exactly solving a many dimensional anharmonic quantum mechanical time dependent problem. Perhaps it would be possible to incorporate the methods described here for a number of degrees of freedom while allowing other degrees of freedom to move on anharmonic surfaces. Such a hybrid approach has been discussed previously by Cao et al. [21] in a more limited context. We also note that the Balian and Brezin method is completely portable to the case of control on the ground state surface (i.e. a pump-dump experiment), but since such an experiment requires two photons and hence higher orders of perturbation theory, the matrix formulation of Eq. (8) breaks down. The additional computational expense of iteratively solving for the optimal field for such a pump-dump type experiment represents an appreciable hurdle and we have chosen not to pursue such a lofty goal at this point. Finally, we mention that although the models we have considered are relatively crude, they appear to demonstrate the same qualitative features associated with more complex treatments. It seems clear, for instance, that control of molecular dynamics makes sense only to the extent that you choose a sensible target. It will never be possible to fully realize a target which corresponds to conserving energy for the excited wave packet when dissipation is present. Perhaps, through detailed study and understanding of such simple models, it will become possible to realistically assess the potential of quantum control as a means to influence chemistry.

## Acknowledgements

This work was supported in part by a grant to RJS from the National Science Foundation. We would like to thank Jianshu Cao for helpful discussions.

## References

[1] S.A. Rice, Science 258 (1992) 412.
[2] D.J. Tannor, S.A. Rice, J. Chem. Phys. 83 (1985) 5013.
[3] W.S. Warren, H. Rabitz, M. Dahleh, Science 259 (1993) 1581.
[4] P. Brumer, M. Shapiro, Faraday Disc. Chem. Soc. 82 (1986) 177.
[5] P. Brumer, M. Shapiro, Annu. Rev. Phys. Chem. 43 (1992) 257.
[6] B. Kohler, J. Krause, F. Raksi, K.R. Wilson, R.M. Whitnell, V.V. Yakovlev, Y.J. Yan, Acc. Chem. Res. 28 (1995) 133.
[7] B. Kohler, V.V. Yakovlev, J. Che, J.L. Krause, M. Messina, K.R. Wilson, N. Schwentner, R.M. Whitnell, Y.J. Yan, Phys. Rev. Lett. 74 (1995) 3360.
[8] D.J. Tannor, R. Kosloff, S.A. Rice, J. Chem. Phys. 85 (1986) 5805.
[9] R. Kosloff, S.A. Rice, P. Gaspard, S. Tersigni, D.J. Tannor, Chem. Phys. 139 (1989) 201.
[10] R.S. Judson, H. Rabitz, Phys. Rev. Lett. 68 (1992) 1500.
[11] J.L. Krause, R.M. Whitnell, K.R. Wilson, Y.J. Yan, in: J. Manz, L. Woste (Eds.), Femtosecond Chemistry, Springer, Weinheim, 1995, p. 743.
[12] Y. Yan, R.E. Gillian, R.M. Whitnell, K.R. Wilson, S. Mukamel, J. Phys. Chem. 97 (1993) 2320.
[13] M. Messina, K.R. Wilson, Chem. Phys. Lett. 241 (1995) 502.
[14] J. Che, M. Messina, K.R. Wilson, V.A. Apkarian, Z. Li, C.C. Martens, R. Zadoyan, Y.J. Yan, J. Phys. Chem. 100 (1996) 7873.
[15] M. Messina, K.R. Wilson, J.L. Krause, J. Chem. Phys. 104 (1996) 173.
[16] R.N. Zare, Science 279 (1998) 1875.
[17] J. Cao, M. Messina, K.R. Wilson, J. Chem. Phys. 106 (1997) 5239.
[18] L. Allen, J. Eberly, Optical Resonance and Two-Level Atoms, Dover, New York, 1987.
[19] R. Zwanzig, J. Stat. Phys. 9 (1973) 215.
[20] A.J. Leggett, S. Chakravarty, A.T. Dorsey, M.P.A. Fisher, A. Garg, W. Zwerger, Rev. Mod. Phys. 59 (1987) 1.
[21] J. Cao, L.W. Ungar, G.A. Voth, J. Chem. Phys. 104 (1996) 4189.
[22] S. Mukamel, Principles of Nonlinear Optical Spectroscopy, Oxford, New York, 1995.
[23] R. Balian, E. Brezin, Nuevo Cimento B 64 (1969) 37.
[24] R. Friesner, M. Pettitt, J.M. Jean, J. Chem. Phys. 82 (1983) 2918.
[25] R.P. Feynman, F.L. Vernon, Ann. Phys. 24 (1963) 118.
[26] F.L.H. Brown, Ph.D. Thesis, Massachusetts Institute of Technology, Boston, MA, 1998.


[^0]:    * Corresponding author. E-mail: silbey@mit.edu
    ${ }^{1}$ Present address: Department of Chemistry and Biochemistry, University of California at San Diego, La Jolla, CA 93093-0339, USA.

