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An application of minimax robust optimal control theory for selective vibrational excitation in molecules

Johan G.B. Beumee and Herschel Rabitz

Department of Chemistry, Princeton University, Princeton, New Jersey 08540, USA

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In recent investigations control theory was applied to design electromagnetic fields capable of producing vibrational excitation in molecular systems. This approach has been applied to linear or non-linear classical approximations of molecular systems or to quantal systems using distributed cost functionals. Practical computations of molecular optimal control theory for large molecules especially with anharmonic potentials become difficult due to the increased dimensionality and the mixed nature of the boundary conditions. This paper proposes to approach the control design for such systems by treating a portion of the molecule containing the target and dipole bonds in full detail while the effect of the remainder of the system is modelled as a disturbance of limited energy. The optimal field *minimizes* the cost functional which is simultaneously *maximized* with respect to the disturbance. Such assumptions give rise to a robust controller akin to the H_∞ theory of robust estimation. We investigate the various field designs for truncated harmonic systems associated with different disturbance energies and demonstrate that the existence of the solution to the associated Ricatti equation ensures the existence of the equilibrium game point. In addition, in the range of physically reasonable disturbance energy the optimal field could be accurately predicted from an asymptotic expansion involving only the undisturbed reference case. As an application we show the optimal field design for a 20 atom truncated molecular chain containing both the target bond (the 5th bond) and the dipole bonds (1st and 9th) where the disturbance only affects the end bond of the system attached to the remainder of the chain. In an effort to improve on the efficiency of the bond energy deposition we investigate shortened target times and also a 40 atom truncated chain. This approach presents very conservative estimates of possible disturbances but provides insight into the sensitivity of different configurations with respect to external disturbances. The minimax approach can be generalized to non-linear molecular systems by modelling the original system as a linear system plus an energy constrained disturbance.

1. Introduction

Advances in laser technology have generated considerable interest in the selective excitation or selective vibrational motion in polyatomic molecules. Recently, control methods were applied to linear and non-linear classical approximations to molecular systems as well as fully quantum mechanical treatments for selected

examples of rotational, vibrational and electronic degrees of freedom [1,2–5,6]. The atomic motion control of large polyatomic molecules requires the use of classical mechanics for practical computational reasons, and the present paper will take this view [2–5]. Quadratic optimal control theory can readily provide explicit designs for laser pulses if the atomic motion can be approximated by a harmonic system [1,2,5] while distributed cost functionals can be employed to design control fields for fully quantal systems [4,7]. For larger molecular systems it would be desirable to be able to achieve optimal design using only the important region containing the target and dipole bonds, but the surroundings must be taken into account. Given the uncontrolled nature of the surroundings it is natural to consider their influence in a worst case scenario and model their effects as an energy constrained disturbance to the system under consideration. It is reasonable to characterize the surroundings or coupling by a mean energy so the robust optimal field is now defined as the minimum of this cost functional which has been maximized with respect to the energy constrained disturbance. This approach is akin to H_∞ theory [8–11] in the sense that it designs the controlling field for the worst possible external disturbance.

In section 2 we introduce the appropriate cost functional balancing the internal energy of a non-rotating harmonic molecule, the fluence of the optical field and an asymmetric terminal cost to ensure that the desired excitation is approached [1–3,5]. The game point for the optimal control field and the maximal disturbance are expressed in terms of the solution to the (control) Hamiltonian equations. The second variation must be calculated in order to confirm whether the solution obtained from the first variation is actually a minimax point. As in H_∞ theory, the existence of the minimax point is closely related to the solution of a particular Ricatti equation which depends on the Lagrange multiplier introduced with the energy constraint [8,10]. The disturbance parameters corresponding to minimax solutions are bounded from below and we introduce a simple algorithm to determine the lower bound. Finally we investigate the behavior of the cost functional at the minimax point as a function of the disturbance.

In section 3 we present examples of robust optimal design for the bond stretch of the 5th bond in a 20 atom truncated chain with two dipole active bonds. The disturbance affects the 19th bond (20th atom) which was originally attached to the remainder of the chain. The effectiveness of the optimal control field is discussed as a function of the disturbance energy. In addition, we discuss the similarity in optimal fields and worst case disturbances as a function of the energy constraint employing the asymptotic disturbance parameter expansion obtained in the previous section. In the presence of physically reasonable disturbances the optimal field and the disturbance field both tend to retain their temporal form in comparison with the undisturbed case, but with increased amplitude. Finally we discuss the results of the optimal control field for the same target and dipole bonds for a harmonic molecular chain truncated to 40 atoms. In the final section our conclusions will be presented and some future research indicated.

2. Formulation

In this section the robust control strategy is formulated for the bond stretch of a harmonic molecular system; extensions to anharmonic molecules can be formulated but at additional computational expense. The equations of motion are expressed in bondlength coordinates (stretch of the bonds) with the energy constrained disturbance as an inhomogeneous term and we introduce the appropriate quadratic cost functional. The optimal controlling laser field and the worst case disturbance can be presented in terms of a linear differential equation with mixed boundary conditions depending on the Lagrange parameter associated with the finite energy constraint. The existence of the minimax point is shown to be related to the existence of a continuous solution to a Ricatti equation.

Let the n bondlength displacement coordinates and their associated momenta of the truncated molecule be denoted as $q^T = (1_1(t), \ldots, q_n(t))$ and $p^T = (p_1(t), \ldots, p_n(t))$ respectively. The truncated molecule is affected by an energy constrained disturbance $w(t)$ acting on some or all of the bonds. The disturbance models the influence of the surroundings of the molecular system. The equations of motion for the complete system become

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix} q(t) \\ p(t) \end{pmatrix} = \begin{pmatrix} 0 & G_n \\ -F_n & 0 \end{pmatrix}\begin{pmatrix} q(t) \\ p(t) \end{pmatrix} + bu(t) + gw(t)\,, \tag{2.1}$$

where F_n contains the force constants and G_n is the inverse mass tensor associated with the truncated system [1]. The external optical field $u(t)$ (taken as having one component here) couples to the bonds where the input vector b (length $2n$, with the first n elements as zero) is the dipole derivative vector associated with the molecule. The matrix g of $2n$ rows is determined by the forms of the truncation and couples the appropriate bonds to outside disturbances modelled by the vector $w(t)$.

Since the disturbance $w(t)$ is of bounded energy, we will consider only disturbances such that

$$\frac{1}{2T}\int_0^T w(t)^T g^T M_w g w(t)\,\mathrm{d}t = E\,, \tag{2.2}$$

where M_w is a positive definite matrix. In keeping with past experience the natural choice for M_w is a diagonal matrix with elements taken as $(G_n)_{ii}^{-1}$. The objective is to design a minimum fluence optical field $u(t)$ which directs the reduced n coordinate system in such a fashion that at some final time T the target bonds are close to the desired configuration $(q(T)^T, p(T)^T) = \eta^T$ while a minimum energy is deposited in the remaining bonds throughout the time interval. To balance the excitation in the system, the fluence of the optical field and the cost for reaching the objective we introduce the cost functional $\Phi(u, w)$:

$$\Phi(u, w) = \tfrac{1}{2}\int_0^T [x(t)^T Q x(t) + r u(t)^2]\,\mathrm{d}t + \tfrac{1}{2}(x(T) - \eta)^T P_f (x(T) - \eta)\,, \tag{2.3}$$

where Q is some appropriate positive definite matrix (usually the entries corresponding to the position and momentum of the target bond equal zero), P_f is a positive definite matrix specifying the desired target weights, and $x(t)^T = (q(t)^T, p(t)^T)$ [1,3]. Hence, the optimal laser field is defined as the field minimizing (2.3) which has been maximized with respect to $w(t)$ under the provision of the constraint (2.2) [1–3]. This construction provides and optimal laser field assuming the worst possible disturbance $w(t)$ within the energy restraint.

To obtain the minimax point under the constraint a Lagrange parameter β is employed such that we seek

$$\min_u \max_w \left[\Phi(u, w) - \frac{\beta}{2} \left(\frac{1}{T} \int_0^T w(t)^T g^T M_w g w(t) \, dt - 2E \right) \right], \tag{2.4}$$

where β (sometimes referred to as the disturbance parameter) will be chosen in such a fashion that the energy constraint (2.2) is satisfied. Notice that the optimal field becomes a function of the energy E only. A necessary condition for the minimax point is that the first variation of the constrained modified cost functional equals zero, which yields the following expressions for the field and the disturbance:

$$u(t) = -r^{-1} b^T \lambda(g), \tag{2.5a}$$

$$w(t) = \beta^{-1} (g^T M_w g)^{-1} g^T \lambda(t), \tag{2.5b}$$

where

$$\frac{d}{dt} \begin{pmatrix} x(t) \\ \lambda(t) \end{pmatrix} = \begin{pmatrix} A & \Delta_\beta \\ -Q & -A^T \end{pmatrix} \begin{pmatrix} x(t) \\ \lambda(t) \end{pmatrix}, \tag{2.6}$$

with

$$\Delta_\beta = -r^{-1} b b^T + \beta^{-1} g (g^T M_w g)^{-1} g^T, \tag{2.7}$$

and final condition $\lambda(T) = P_f(x(T) - \eta)$. The Lagrange multiplier $\lambda(t)$ ensures that the minimax solution satisfies eq. (2). It will be assumed that $x(0) = 0$ for the sake of convenience. Obviously in the case that $E = 0, \beta = \infty$ and we have $w(t) = 0$ so that the system experiences no disturbances and (2.5)–(2.7) reduce to the classical optimal control problem. The equations above are familiar in time dependent H_∞ theory [8,10,11].

For the minimax point or game point [8,12], it is required that

$$\Phi(u, w') \leqslant \Phi(u, w) \leqslant \Phi(u', w), \tag{2.8}$$

for an arbitrary optical field $u(t)'$ and disturbance $w(t)'$, if $u(t)$ and $w(t)$ are the solutions to eq. (2.5)–(2.7). However, solutions to (2.5)–(2.7) do not necessarily satisfy (2.8) for all disturbance parameters β. The value of β at the minimax point (2.8) is associated with the following Ricatti equation:

THEOREM 1

Let $\Pi(t)$ be a positive definite matrix and $\phi(t)$ a function satisfying

$$\frac{\mathrm{d}}{\mathrm{d}t}\Pi(t) + \Pi(t)A + A^T\Pi(t) + \Pi(t)\Delta_\beta\Pi(t) + Q = 0, \Pi(T) = P_f\,, \tag{2.9a}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\phi(t) + A^T\phi(t) - \Pi(t)\Delta_\beta\phi(t) = 0, \phi(T) = -P_f\eta\,, \tag{2.9b}$$

where Δ_β is defined as in (2.7). Then the state $x(t)$ and $\lambda(t)$ (costate) in (2.5)–(2.7) are related as follows:

$$\lambda(t) = \Pi(t)x(t) + \phi(t)\,, \tag{2.10}$$

so that the optimal field and disturbance can be related directly to the state $x(t)$ (feedback)

$$u(t) = -r^{-1}(\Pi(t)x(t) + \phi(t))\,, \tag{2.11a}$$

$$w(t) = \beta^{-1}(g^T M_w g)^{-1} g^T(\Pi(t)x(t) + \phi(t))\,. \tag{2.11b}$$

Proof

The proof is straightforward once expression (2.10) is substituted into (2.6).

In the absence of disturbances, in other words if $\beta = \infty$, the matrix Δ_β is negative definite which guarantees a unique solution to the Ricatti equation under very general conditions [13,14]. If disturbances are present, however, the existence of a solution to eq. (2.9a) depends on the value of β. The following theorem explains the relationship between the solution to the matrix Ricatti equation and the existence of a game point:

THEOREM 2

Assume that the constant β in (2.9) is such that there is a continuous solution $\Pi(t)$ to the matrix Ricatti equation (2.9a) subject to the final boundary condition $\Pi(T) = P_f$ and let $\phi(t)$ be the solution to (2.9b). Then for any field $u(t)$ and arbitrary disturbance $w(t)$ we have that the functional (2.3) can be written in terms of $\Pi(t)$ and $\phi(t)$:

$$\begin{aligned} 2\Phi(u,w) &= \int_0^T [x(t)^T Q x(t) + ru(t)^2]\,\mathrm{d}t + (x(T)-\eta)^T P_f(x(T)-\eta) \\ &= K(\beta) + \beta\int_0^T w(t)^T(g^T M_w g)w(t)\,\mathrm{d}t \\ &\quad + r\int_0^T [u(t) + r^{-1}b^T(\Pi(t)x(t) + \phi(t))]^2\,\mathrm{d}t - \beta\int_0^T \Delta(t)\,\mathrm{d}t\,, \end{aligned} \tag{2.12}$$

where

$$\Delta(t) = [w(t) - \beta^{-1}(g^T M_w g)^{-1} g^T(\Pi(t)x(t) + \phi(t))]^T (g^T M_w g) \times [w(t) - \beta^{-1}(g^T M_w g)^{-1} g^T(\Pi(t)x(t) + \phi(t))]$$

$$K(\beta) = \eta^T P_f \eta + x(0)^T \Pi(0) x(0) + 2x(0)^T \phi(0) - \int_0^T \phi(t)^T \Delta_\beta \phi(t)\, \mathrm{d}t. \quad (2.13)$$

Proof

Let

$$\begin{aligned} I^* &= \int_0^T \frac{\mathrm{d}}{\mathrm{d}t}[x(t)^T \Pi(t) x(t) + 2x(t)^T \phi(t)]\, \mathrm{d}t \\ &= \int_0^T [2u(t) b^T \Pi(t) x(t) + r^{-1} x(t)^T \Pi(t) b b^T \Pi(t) x(t) + 2u(t) b^T \phi(t) \\ &\quad + 2r^{-1} x(t)^T \Pi(t) b b^T \phi(t) + w(t)^T g^T \Pi(t) x(t) \\ &\quad - \beta^{-1} x(t)^T \Pi(t) g (g^T M_w g)^{-1} g^T \Pi(t) x(t) \\ &\quad - x(t)^T Q x(t) + x(t)^T \Pi(t) g w(t) + 2w(t)^T g^T \phi(t) \\ &\quad - 2\beta^{-1} x(t)^T \Pi(t) g (g^T M_w g)^{-1} g^T \phi(t)] \mathrm{d}t. \end{aligned} \quad (2.14)$$

The first four terms in this equation are equal to

$$\begin{aligned} I_1 &= r \int_0^T (u(t) + r^{-1} b^T (\Pi(t)x(t) + \phi(t))^2\, \mathrm{d}t - r \int_0^T u(t)^2\, \mathrm{d}t \\ &\quad - r^{-1} \int_0^T \phi(t)^T b b^T \phi(t)\, \mathrm{d}t, \end{aligned} \quad (2.15)$$

and the remaining terms

$$\begin{aligned} I_2 &= -\beta \int_0^T \Delta(t) \mathrm{d}t + \beta \int_0^T w(t)^T (g^T M_w g) w(t)\, \mathrm{d}t \\ &\quad + \beta^{-1} \int_0^T \phi(t)^T g (g^T M_w g)^{-1} g^T \phi(t)\, \mathrm{d}t, \end{aligned} \quad (2.16)$$

so that after some algebra

$$\begin{aligned} I^* &= I_1 + I_2 \int_0^T [r u(t)^2 + x(t)^T Q x(t)]\, \mathrm{d}t \\ &\quad - \int_0^T \phi(t)^T \Delta_\beta \phi(t)\, \mathrm{d}t + \beta \int_0^T w(t)^T g^T M_w g w(t)\, \mathrm{d}t. \end{aligned} \quad (2.17)$$

Evaluating I^* in (2.14) shows that

$$I^* = (x(T)-\eta)^T P_f(x(T)-\eta) - \eta^T P_f \eta - x(0)^T \Pi(0) x(0) - 2x(0)^T \phi(0)$$
$$= (x(T)-\eta)^T P_f(x(T)-\eta) - \eta^T P_f \eta, \tag{2.18}$$

since it was assumed that $x(0) = 0$. This combined with (2.17) yields eq. (2.12) after some algebra.

This equation immediately establishes a criterion for the existence of the game point of the cost functional. Since the disturbances are restrained to energy level E, the second term on the right-hand side of eq. (2.12) reduces to $2\beta ET$ for all constrained disturbances. If we denote $u = u(t)$ and $w = w(t)$ as the solutions to (2.5)–(2.7) we see from (2.13) that

$$\Phi(u, w') \leqslant \Phi(u, w) \leqslant \Phi(u', w), \tag{2.19a}$$

$$\Phi(u, w) = K(\beta) + \beta E, \tag{2.19b}$$

where $u(t)'$ and $w(t)'$ are arbitrary input and disturbance fields, respectively. Notice that this reduces to $\Phi(u, w) = \text{const}_1 + \text{const}_2/\beta + \beta E$ for appropriate constants. For a specific energy E there may be many different solutions β and if none of these are too small the last term in this expression dominates. As a result it follows that in most circumstances the worst case disturbance satisfying the energy constraint is associated with the largest β. As in H_∞ theory the continuous solution to the Ricatti equation (2.9a) exists as long as β is larger than a specific lower bound. If $P_f = 0, \eta = 0$ the lower bound equals the H_∞ operator norm defined by the input and output relationship (2.1) [8,10,12].

In order to find the lower bound above for which all β's correspond to a continuous solution of (2.9a) we employ the following simple algorithm. First write $\Pi(t) = V(t)W(t)^{-1}$ for some matrix combination $V(t), W(t)$. Substitution into (2.9a) reduces to the following equation for $V(t)$ and $W(t)$:

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix} W(t) \\ V(t) \end{pmatrix} = \begin{pmatrix} A & \Delta_\beta \\ -Q & -A^T \end{pmatrix}\begin{pmatrix} W(t) \\ V(t) \end{pmatrix}, \tag{2.20}$$

with final condition $\Pi(T) = V(T)W(T)^{-1} = P_f$. The most convenient choice is to take $W(T) = I$, the unit matrix, and $V(T) = P_f$. A solution to eq. (2.20) always exists but the determinant of the matrix $W(t)$ is not necessarily non- zero. If the determinant vanishes on the interval $[0, T]$ clearly no continuous solution to the Ricatti equation can be obtained.

This approach allows for the following algorithm:

- Choose a value for β_u that is large so that a continuous solution to the Ricatti equation exists and a value of β_l so small that a continuous solution does not exist, for instance, $\beta_l = 0$.
- Let $\beta_2 = \frac{1}{2}(\beta_u - \beta_l)$ and determine a solution to eq. (2.20) on $[0, T]$.
- Calculate $\det[W(t)]$ on $[0, T]$ and determine whether this function stays positive. If this is the case the lower bound must be between β_l and the newly determined β_1 so we take $\beta_u = \beta_1$ and return to the previous step.

– If $\det[W(t)]$ changes sign on $[0, T]$ we take $\beta_l = \beta_1$ and return to the second step.

In this fashion the series of parameters $\beta_1, \beta_2, \ldots$ converges to the lower bound associated with the existence of the solution of the Ricatti equation. The disadvantage of this approach is obviously that the whole interval must be scanned for the values of the determinant. For large matrices the numerical values of the determinants can become very large and also the accuracy of the estimate becomes a function of the grid size on which the determinant is calculated. Some experimentation with different grid sizes suggested that our estimates of the lower bound in the examples are accurate to three decimal places.

In our examples we will find that the physically significant energies are associated with large β so it is of interest to determine the solution to (2.5)–(2.7) for asymptotically large values of the disturbance parameter. Clearly the zeroth order is the original unperturbed control problem since then $w(t) = 0$ according to (2.5b). To obtain the next order in the expansion we have the following result:

THEOREM 3

For large values of β we find

$$\begin{pmatrix} x(t) \\ \lambda(t) \end{pmatrix} = e^{H_u(t-T)} M_1 + \beta^{-1}[-e^{H_u T} M_1 + e^{H_u(t-T)} M_2] + O(\beta^{-2}), \tag{2.21}$$

where

$$M_1 = \begin{pmatrix} P_c^{-1} S_c \\ P_f(P_c^{-1} S_c - \eta) \end{pmatrix}, \tag{2.22a}$$

$$M_2 = \begin{pmatrix} P_c^{-1}(Q_c P_c^{-1} S_c - T_c) \\ P_f P_c(Q P_c^{-1} S_c - T_c) \end{pmatrix}. \tag{2.22b}$$

Here

$$P_c = [I_n 0] e^{-H_u T} \begin{pmatrix} I_n \\ P_f \end{pmatrix}, \tag{2.23a}$$

$$Q_c = [I_n 0] S(0) e^{-H_u T} \begin{pmatrix} I_n \\ P_f \end{pmatrix}, \tag{2.23b}$$

$$S_c = [I_n 0] e^{-H_u T} \begin{pmatrix} 0 \\ P_f \eta \end{pmatrix}, \tag{2.23c}$$

$$T_c = [I_n 0] S(0) e^{-H_u T} \begin{pmatrix} 0 \\ P_f \end{pmatrix}, \tag{2.23d}$$

and I_n is the unit matrix of dimension n. Also

$$S(t) = \int_0^T \mathrm{e}^{H_u(t-s)} \begin{pmatrix} 0 & g(g^T M_w g)^{-1} g^T \\ 0 & 0 \end{pmatrix} \mathrm{e}^{H_u s}\, \mathrm{d}t \tag{2.24}$$

$$H_u = \begin{pmatrix} A & -r^{-1}bb^T \\ -Q & -A^T \end{pmatrix}. \tag{2.25}$$

Proof

Separating the terms in (2.6) that depend on β it is found that

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix} x(t) \\ \lambda(t) \end{pmatrix} &= \begin{pmatrix} A & -r^{-1}bb^T \\ -Q & -A^T \end{pmatrix}\begin{pmatrix} x(t) \\ \lambda(t) \end{pmatrix} \\ &= \beta^{-1}\begin{pmatrix} 0 & g(g^T M_w g)^{-1} g^T \\ 0 & 0 \end{pmatrix}\begin{pmatrix} x(t) \\ \lambda(t) \end{pmatrix} \end{aligned} \tag{2.26}$$

so that

$$\begin{pmatrix} x(t) \\ \lambda(t) \end{pmatrix} = \mathrm{e}^{H_u(t-T)}\begin{pmatrix} x(T) \\ \lambda(T) \end{pmatrix} - \beta^{-1} S(t)\mathrm{e}^{-H_u T}\begin{pmatrix} x(T) \\ \lambda(T) \end{pmatrix} = O(\beta^{-2}), \tag{2.27}$$

where H_u is the unperturbed (control) Hamiltonian matrix (2.25) and $S(t)$ is defined in (2.24). Introducing the mixed boundary conditions $x(0) = 0$ and $\lambda(T) = P_f(x(T) - \eta)$ for the vector $(x(t)^T, \lambda(t)^T)$ it is clear that to first order

$$\begin{aligned} \begin{pmatrix} 0 \\ \lambda(0) \end{pmatrix} = \begin{pmatrix} x(0) \\ \lambda(0) \end{pmatrix} &= [I_{2n} - \beta^{-1} S(0)]\mathrm{e}^{-H_u T}\begin{pmatrix} x(t) \\ \lambda(t) \end{pmatrix} \\ &= (I_{2n} - \beta^{-1} S(0))\mathrm{e}^{-H_u T}\left[\begin{pmatrix} I_n \\ P_f \end{pmatrix} x(T) - \begin{pmatrix} 0 \\ p_f \eta \end{pmatrix}\right]. \end{aligned} \tag{2.28}$$

Multiplying on the left and right sides of these equations with the matrix $[I_n 0]$ yields

$$[I_n 0](I_{2n} - \beta^{-1} S(0))\mathrm{e}^{-H_u T}\begin{pmatrix} I \\ P_f \end{pmatrix} x(T) = [I_n 0](I_{2n} - \beta^{-1} S(0))\mathrm{e}^{-H_u T}\begin{pmatrix} 0 \\ P_f \eta \end{pmatrix}, \tag{2.30}$$

from which $x(T)$ can be determined. This expression is equivalent to

$$(P_c - \beta^{-1} Q_c)x(T) = S_c - \beta^{-1} T_c, \tag{2.31}$$

where P_c, Q_c, S_c, T_c are defined in (2.23). Inverting the matrix $(P_c - \beta^{-1} Q_c)$ to first order in β^{-1} yields

$$x(T) = P_c^{-1}[S_c + \beta^{-1}(Q_c P_c^{-1} S_c - T_c)], \tag{2.31}$$

$$\lambda(T) = (P_f P_c^{-1} S_c - P_f \eta) + \beta^{-1} P_f (P_c^{-1} Q_c P_c^{-1} S_c - P_c^{-1} T_c) . \tag{2.32}$$

Substituting this into (2.27) and collecting the first order terms in β^{-1} then yields (2.21).

In the next section we illustrate this approach by designing robust control fields for the stretching of the 5th target bond in a 20 atom truncated linear chain. We will discuss the effects of changes in the cost functional parameters, the shortening of the target time and the change of truncation on the control field. The worst case estimate tends to be conservative and we will present a brief discussion on this issue; further details can be found in ref. [2].

3. Examples

In this section we illustrate the design of robust control fields for the bond stretch of the 5th bond in a truncated 20 atom homogeneous linear harmonic chain (all atoms are of mass $m = 10$ amu) using a balanced cost functional with a large final cost. An analogous calculation is also presented for a 40 atom truncated chain. The dipole bonds are the 1st and 9th bonds of the chain located at the same distance from the target bond. We investigate the robust optimal control field design as a function of disturbance energy, chain size and target time.

We desire to reach the above objective with a relatively small field so we choose $r = 7$ as a moderate weight on the fluence. The input dipole coupling vector b only has non- zero elements for the 1st and 9th bonds of values $b_1 = 0.295, b_9 = 0.25$. The system energy weight is chosen as $Q = I_{2n}^{5,24}\,\mathrm{diag}(F_n, G_n)$ (the diagonal matrix elements of F_n and G_n), where F_n and G_n are defined as

$$(G_n)_{ij} = \delta_{ij}(2\mu) - \delta_{i(j+1)}\mu - \delta_{i(j-1)}\mu , \tag{3.1a}$$

$$(F_n)_{ij} = \delta_{ij} k_i , \tag{3.1b}$$

for $i,j = 1,n$ where k_i are the force constants and $\mu = 1/m$. This band diagonal matrix representation for the mass tensor is due to the use of bondlength coordinates [3]. Here, $I_{2n}^{(5,24)}$ is the (2n-dimensional) unit matrix with zeros on the diagonal at entry 5 and 24, the elements in $x(t)$ that correspond to the position and momentum of the target bond. These elements are set equal to zero because our motive is to concentrate as much *energy* in the target bond as possible.

All physical quantities in our examples are expressed in terms of atomic units. The parameters in the final cost are chosen as $\eta_5 = 3.0, P_f(5,5) = 2000$ (other entries zero) to force the bond stretch of the 5th atom close to 3.0 at the target time T. Also the nth element of the vector g is $g_n = 1/m$ with all other entries equal to zero. The form of this vector is a direct result of truncation of a longer chain where the equations of motion are expressed in terms of bondlength coordinates [3]. Notice that because the bondlength coordinates were introduced before the chain

was truncated, the disturbance enters as an added momentum rather than as an additional force. If explicit external forces were considered, then force terms would appear in eq. (3.1) and not all entries g_{n+1}, g_{2n} would have vanished. A sequence of examples is given below. The parameters given above apply to all the cases except that the chain length and target bond differ in some examples.

(i) In the first example without external disturbance (i.e., $\beta = \infty$) we assume that the final time is $T = 0.2$ ps (8268 a.u.) and that the truncated system has 20 atoms ($n = 19$). Figure 1 presents the energy of the chain (in a.u.) as a function of time and bond number for the optimal control field $u(t)$ displayed in fig. 2. The cost functional for this example at the minimax point equals $\Phi(u^*, w^* = 0) = 6303$ a.u. which is mostly due to the large final cost. Since the bonds 1 and 9 are the same distance from the target bond, the main effort of the optimal field is to produce a large signal close to the final time $T = 0.2$ ps so that the pulses travelling from the two dipole bonds would combine at the target bond simultaneously. The earlier pumping phase is to position the atoms of the chain in the most favorable fashion for the final pulse close to the target time. The efficiency of the process is high in the

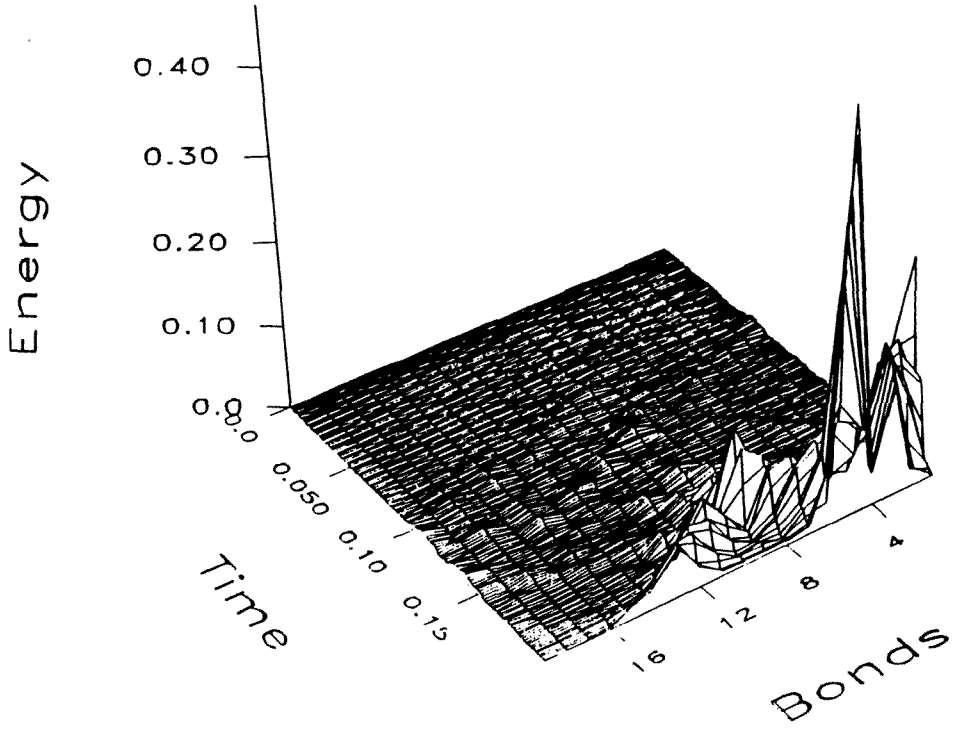

Fig. 1. Bond energy as a function of time and bond number for the system example (i) pumped by a designed optimal field in the absence of disturbances. The target bond is number 5, the dipole coefficients b_i for the ith bonds are $b_1 = 0.295, b_9 - 0.25$, the final time is $T = 0.2$ ps, the weight on the fluence equals $r = 7$, and the mean bond energy is $E_{av} = 22.8 \times 10^{-4}$ a.u. (see eq. (3.2)).

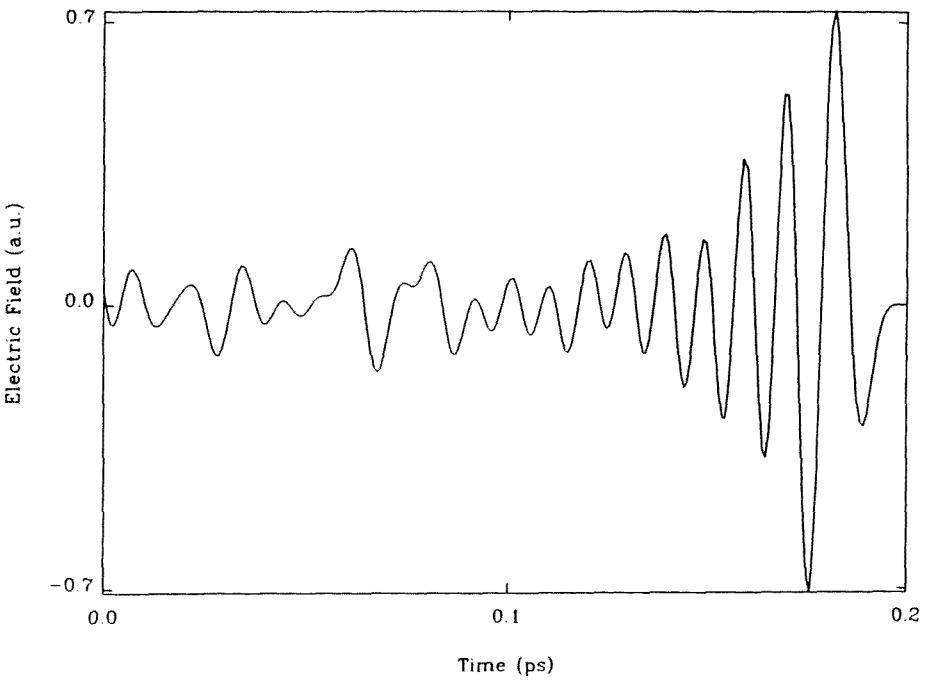

Fig. 2. The designed optimal field for the time interval $T = 0.2$ ps without disturbances for the case in fig. 1.

sense that the amount of energy concentrated in the target bond at the final time is high in comparison with energy located elsewhere in the chain. To relate the disturbance energy constraint in the subsequent calculations to the motion of the unperturbed system we have taken as a reference the mean energy per bond that travels through the chain as the field manipulates the dipole bonds. In our example this equals

$$E_{\mathrm{av}} = \frac{m}{19T}\int_0^T \left[\frac{\mathrm{d}}{\mathrm{d}t}q(t)^T\right]\frac{\mathrm{d}}{\mathrm{d}t}q(t)\,\mathrm{d}t = 22.8 \times 10^{-4}\ \text{a.u.} \tag{3.2}$$

In the present case this equals about 350 cm^{-1}, which is rather small due to the fact that the chain is weakly perturbed most of the time. The larger pulses are produced close to the end of the time interval and do not contribute much to the integral. In the examples that follow we compare (3.2) with the disturbance energy constraint.

(ii) Figure 3 refers to the bond energy as a function of time and bond number and figs. 4 and 5 present the optimal control field and the worst disturbance field for the case that $\beta = 1600$. In fig. 3 we see that the energy disturbances in the chain in the 1st and 3rd bonds almost equal the energy concentration at the target bond 5 at time $T = 0.2$ ps. In this case $E_{\mathrm{av}} = 1.9 \times 10^{-4}$ a.u. which corresponds to a dis-

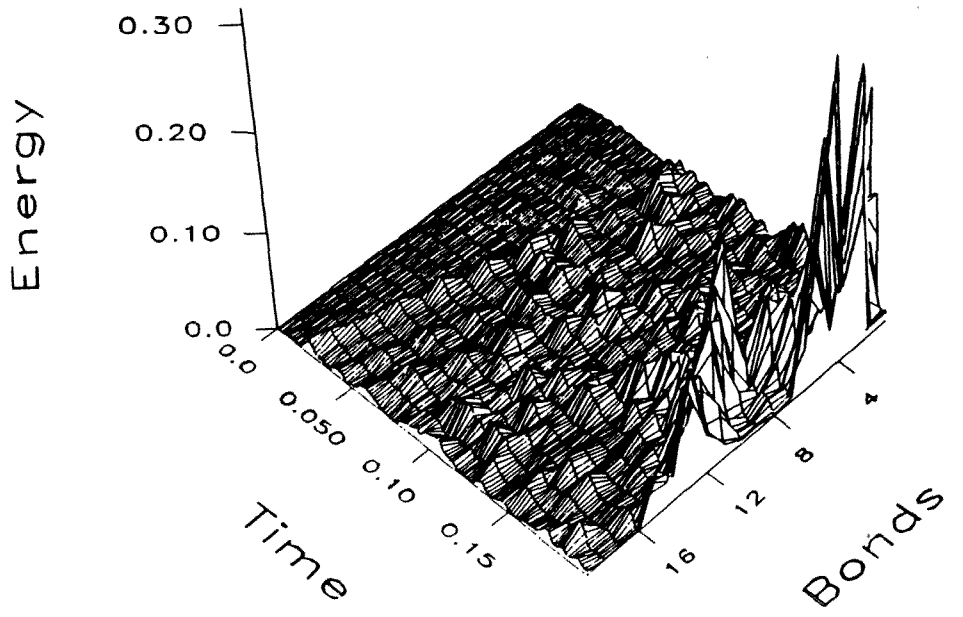

Fig. 3. Bond energy as a function of time and bond number for the system example (ii) pumped by a designed optimal field in the presence of a worst case disturbance constrained to an energy of 1.94×10^{-4} a.u. (9% of the mean bond energy, $\beta = 1600$). The physical system is the same as for fig. 1 except now with the disturbance.

turbance energy that equals approximately 9% of the average bond energy of the reference case. The cost functional evaluated at the minimax point increased by almost 30%, the fluence more than doubled and the final cost of the stretch increased by about 22% in comparison with the reference case. This case has reached the point where allowing more intense disturbances will produce larger energy fluctuations throughout the chain rather than in the target bond and further calculations with a smaller disturbance parameter β confirmed this. Comparing fig. 4 and fig. 2 we see that the optimal fields are quite similar but not exactly alike as can be seen from the structure of both fields around 0.1 ps. Notice that the largest disturbance in fig. 5 occurs at the very beginning of the time interval and there is a large pulse at 0.14 ps that obviously intends to interfere with the 9th dipole bond. This latter pulse reduces the final bond stretch and therefore enlarges the final term in the cost functional. The purpose of the large disturbance pulse in the beginning is probably to create a large disturbance in the chain and increase the system energy term in the cost functional. In addition, this disturbance has time to reach bond 1 and affect the coherence generated by $u(t)$ at that bond.

The similarity between the optimal control fields in fig. 2 and fig. 4 is due to the rather large size of the disturbance parameter β as can be shown as follows. In eq. (2.21) we obtained the behavior of the solution to (2.5)–(2.7) in the form of an

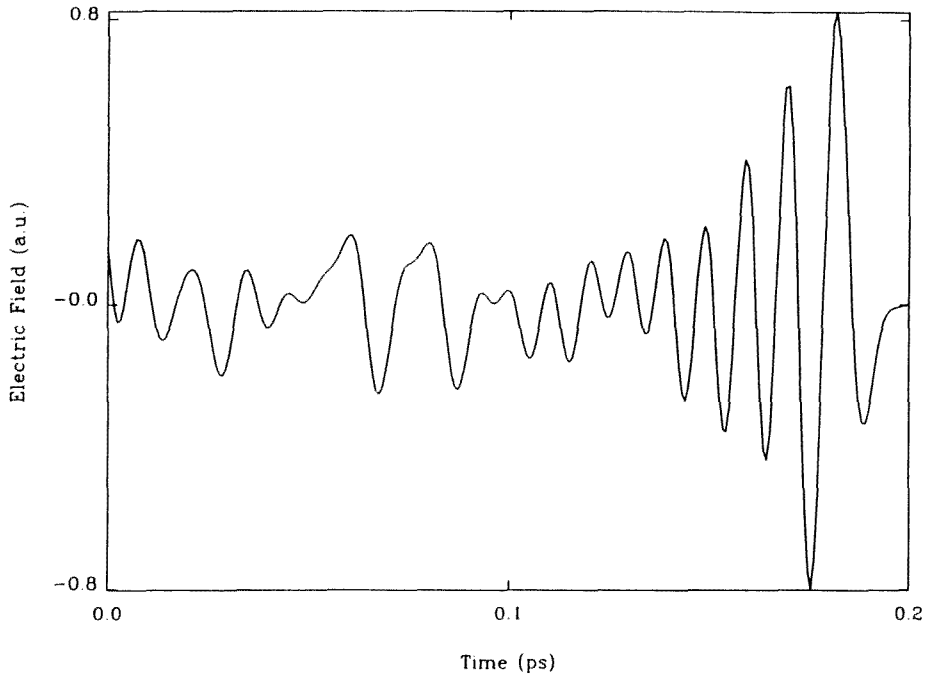

Fig. 4. The designed optimal field for the time interval $T = 0.2$ ps for the worst case corresponding to fig. 3. The field is similar in form to the optimal field presented in fig. 2, but more intense.

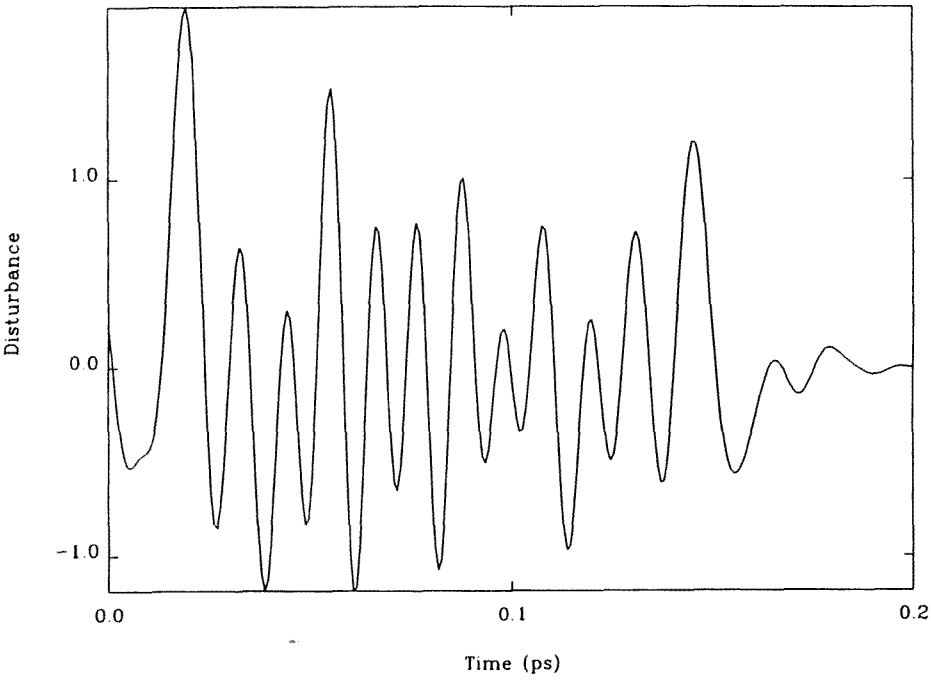

Fig. 5. The worst case disturbance under the constraint that the energy equals 1.94×10^{-4} a.u. (i.e. the case of fig. 3).

asymptotic expansion in β^{-1}, assuming a large disturbance parameter. If, for example, in (2.21) the matrices M_2 and $S(t)$ were proportional to the unit matrix then in the regime where β is sufficiently large we have that $x(t)$ and $\lambda(t)$ scale directly with $1 + \text{const}/\beta$ so that the optimal field and the disturbance field are proportional to $e^{H_u(t-T)}[1 + \text{const}/\beta]$ and $(1/\beta)e^{H_u(t-T)}[1 + \text{const}/\beta]$, respectively. For the optimal field $u(t)$ this is exactly the unperturbed solution times a scale factor. According to this expression the intensity of the disturbance changes proportional to β^{-1} (first order) and the optimal field scales with $1 + \text{const}/\beta$. This assumption is easily tested and we modeled the maximum intensity of the optimal fields and disturbance fields for various different β's in a second order approximation for the disturbance field and a first order approximation for the optimal control field as indicated above. As a result we were able to make predictions with 2–5% accuracy of the maximum intensities of both. This behavior may confirm the plausibility of the assumptions on M_2 and $S(t)$, although other relations amongst the matrices of (2.21) will also give the same scaling results.

The approximate scaling between the competing fields $u(t)$ and $w(t)$ in the two cases has some interesting physical implications. This suggests that for a mildly disturbed system the control field for reaching a molecular objective is approximately a more intense version of the field obtained for the reference case. Hence the intuition of "trying harder" by increasing the intensity of the laser field is to first order a correct approach. The changes in the (control) Hamiltonian in (2.6) as a function of β generally are responsible for the change of shape of the fields (rather than its scale) and clearly for such large β values the Hamiltonian does not change enough to significantly alter the shape of the field and disturbance. In different harmonic systems for different objectives it may not be possible to find such convenient scaling laws. Since the explicit expressions are known to second order and can be obtained to higher order with a certain amount of perseverance, it can be determined beforehand whether or not it is valid to use the scaled up version of the unperturbed control field. If scaling were valid, a simple law will then provide the optimal control fields countering any disturbances that are present. For ultimate experimental purposes this may be of considerable significance.

To determine the parameter β as a function of the disturbance energy we have to solve $(1/mT)\int_0^T w(t)^2\,\mathrm{d}t = E$ and if there are multiple solutions for β the solution with the largest cost functional corresponds to the minimax point. However, the behavior of the disturbance energy as a function of β can be very complicated. Figure 6 shows the disturbance energy $(1/mT)\int_0^T w(t)^2\,\mathrm{d}t$ as a function of β in the case where the dipole bond is the first bond and the target is the 10th bond of the chain. In the region where β is sufficiently large the energy is a monotonically decreasing function of β, and in the vicinity of 1240 the value of the energy increases dramatically while the figure shows a peak around 1180 as well. Going to smaller values of β showed a rather dense array of peaks while the function never drops below 0.169×10^{-4} a.u. The slowly varying lower bound to all the peaks has some variation around 1050 and 280 and then as the point 0.67 is approached the

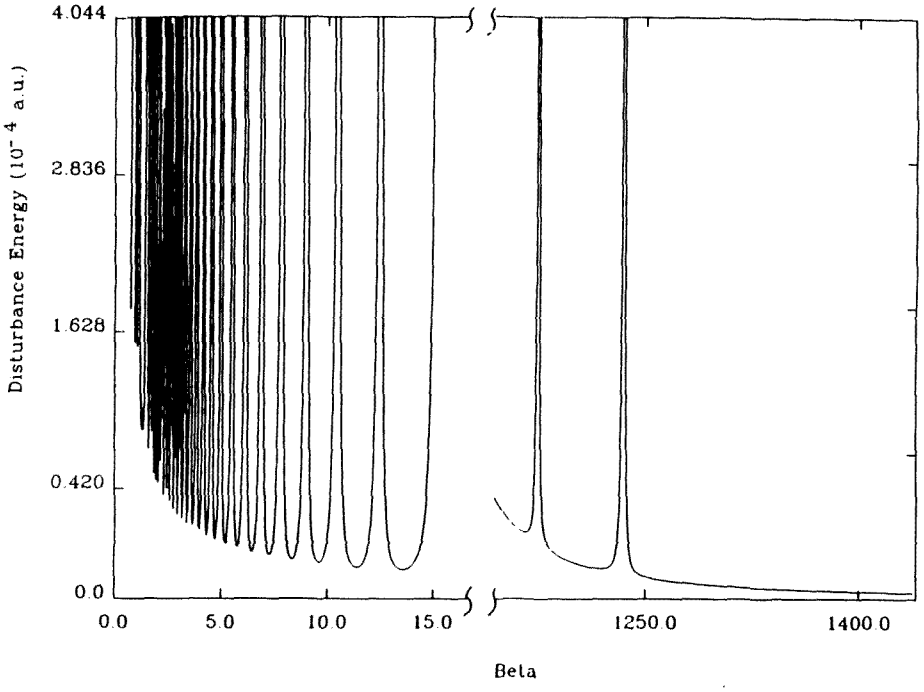

Fig. 6. The disturbance energy $(1/mT)\int_0^T w(t)^2\,dt$ as a function of the disturbance parameter β for the intervals 0.67–17 and 1125–1450. At a higher value of energy there are clearly multiple values of β with only one corresponding to the minimax value.

lower bound starts to rise and the number of peaks increase rapidly. In all the 20 atom truncation examples the physically reasonable energies only had one solution for β but this is not true for the 40 atom truncation case we investigated. For a further discussion on this topic see [15]. Our calculations also showed that in all the 20 atom truncated chain examples above in general the very worst case, i.e. the largest cost functional, corresponds with the largest β. In fact, a careful consideration of the function $K(\beta)$ in (2.19b) shows that $\Phi(u^*, w^*) = \text{const}_1 + \text{const}_2/\beta + \beta E$. If the multiple solutions for β are all sufficiently large it is clear that $\Phi(u, w)$ is maximized for the largest β for a given energy E.

Finally in an attempt to limit the effect of the disturbance, the target time was reduced to $T = 0.06$ ps. Although the optimal control strategy for pumping was slightly different from the field presented in fig. 4, the same level of relative disturbance (approximately 9%) once again caused a significant effect in the molecule. At $T = 0.06$ ps there is still sufficient time for the disturbance to propagate inward and affect the target bond.

(iii) In the next example we improved the bond site energy deposition efficiency by truncating the chain at the 40th bond rather than at the 20th while the target still

resides at bond 5. The disturbance directly affects only the 40th bond and is not capable of reaching the 9th bond in the short target time of $T = 0.06$ ps. The bond energy distribution of the reference case with $\beta = \infty$ was similar to that in fig. 1 with an optimal field similar in form to the *last* 0.06 ps of $u(t)$ in fig. 2. One difference is the lack of time for any rebound energy off of bond 40 and back to the target bond. Choosing the parameter $\beta = 401.35$ corresponds to a disturbance with an energy equal to 50% of the mean bond energy and fig. 7 shows the corresponding bond energy as a function of time and bond number. The disturbance upsets the system in the sense that it pumps a large energy pulse into the system as soon as possible. The cost functional increases 25% as a result entirely due to an increase in system energy. The energy fluctuations generated by the disturbance in fig. 8 are now as large as the concentration of energy in the target bond. This disturbance pulse, however, is not capable of reaching the final bond stretch nor the outer dipole 9th bond, and the intensity of the energy in the target bond is exactly the same as in the reference case. There is no difference between the optimal fields in this case and the one in the reference case in shape or in intensity (see fig. 9). Since the disturbance cannot communicate with the part of the chain that is being controlled by the optical field, then the form of the field does not change. This example

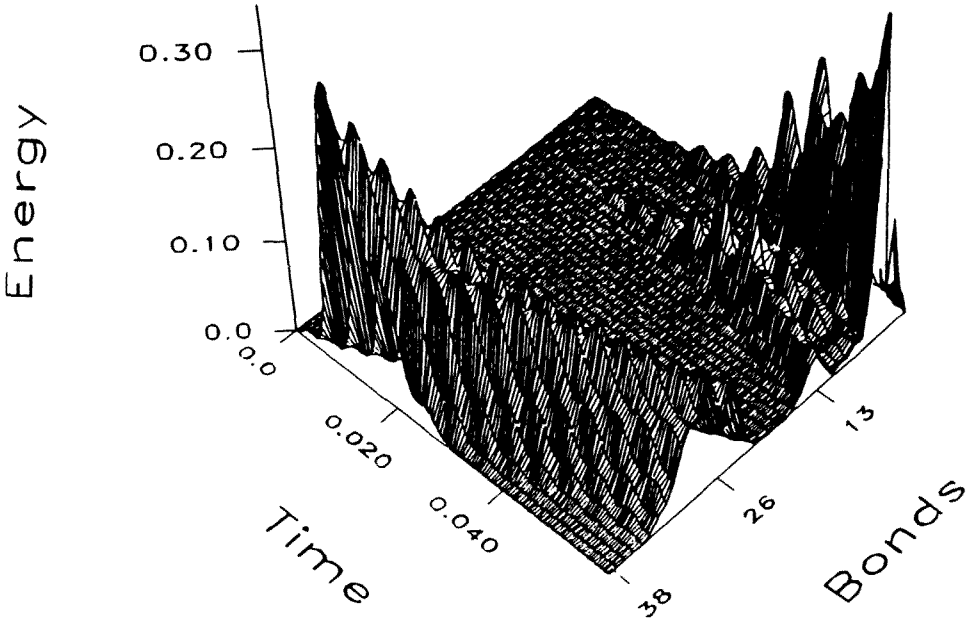

Fig. 7. Bond energy as a function of time and bond number for the 40 atom system example (iii) pumped by a designed optimal field in the presence of a worst case disturbance constrained to an energy of 1.33×10^{-4} a.u. There is not sufficient time for the disturbance to affect the dipole or target regions, but the aft end of the molecule is influenced by the disturbance.

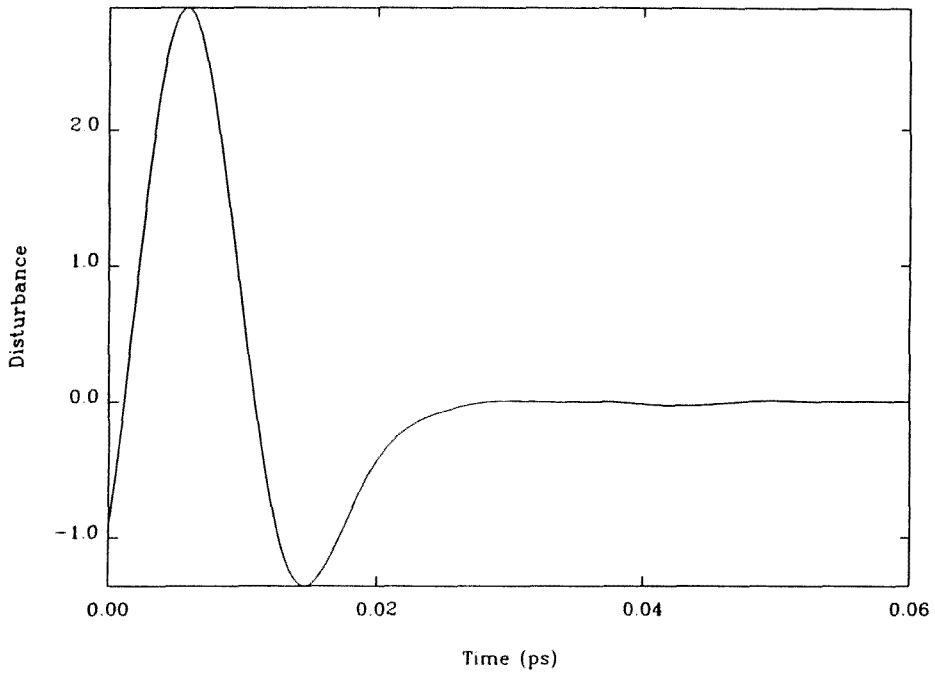

Fig. 8. The worst case disturbance for a 40 atom system in example (iii) for a final time $T = 0.06$ ps under the constraint that the energy equals 1.33×10^{-4} a.u. (i.e. the case of fig. 7).

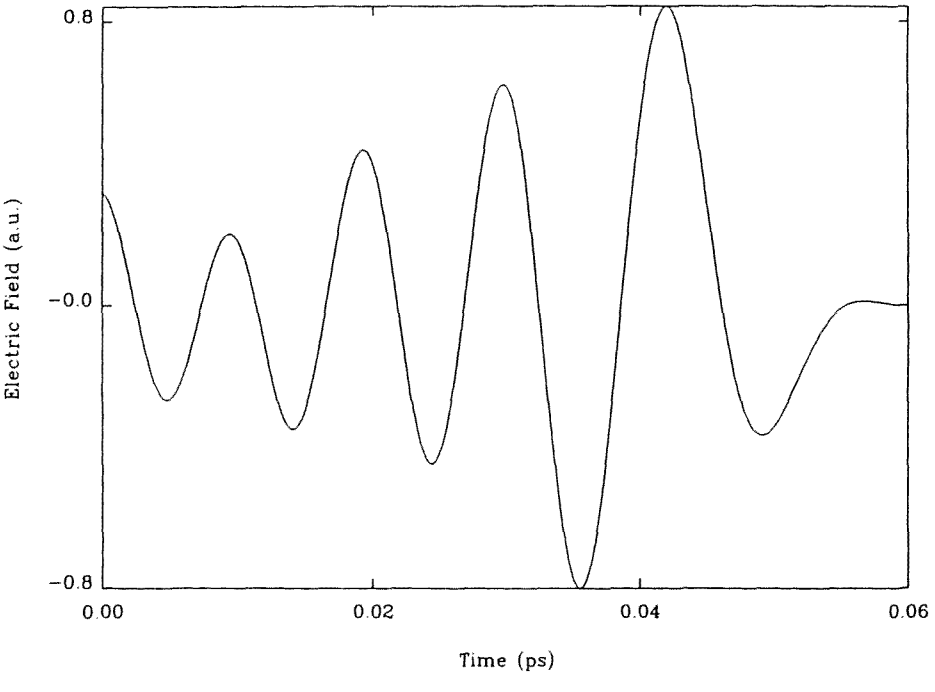

Fig. 9. The designed optimal field for the time interval $T = 0.06$ ps for a worst case disturbance constrained to an energy of 1.33×10^{-4} a.u.

supports the intuition that it is favourable to choose the important target and dipole bonds as isolated as possible from regions of molecular control uncertainty. This can be done, in principle, by creating a larger physical distance between target and the disturbance or in some cases shortening the control time interval. The latter approach in general, however, will necessitate a more intense field if the same target goal is to be achieved.

4. Conclusions

This paper proposed a robust control method in the form of a minimax problem to design optical laser pulses for molecular control objectives of a truncated molecule affected by disturbance elements. It was assumed that all physical system uncertainties and non-linear terms beyond the core harmonic system are represented as an energy bounded disturbance and the basic elements of H_∞ theory are employed to design robust laser pulses for the molecular objectives in the truncated subsystem. The equations for the solution to this minimax problem were obtained using a Lagrange parameter for the energy constraint. Sufficiency for the existence of minimax solutions was shown to be related to the existence of a continuous solution to a Ricatti equation that depended on the Lagrange parameter. We introduced a straightforward algorithm for finding the lower bound of the disturbance parameters and discovered a scaling law for small disturbances using the asymptotic expression for large disturbance parameters. As an example the robust optimal control field was obtained for stretching the 5th bond in a truncated molecular chain where the effects of the remainder of the chain are modelled as disturbances. Only the 1st and 9th bond in the chain interacted with the optical field and the disturbance energies in the examples were compared with the mean bond kinetic energies calculated from the reference case where no disturbance field was present.

Clearly the worst case disturbance is a very conservative estimate of the influence the surroundings can have on the molecular objectives. One aim of this study was to show how sensitive certain configurations of target and dipole bonds can be with respect to the effect of the disturbance. A molecular system is never entirely isolated so in designing control laser pulses it is important to understand what part of the system must be modeled in order to obtain adequate fields. The minimax analysis provides an answer to the question of which and how many atoms must be entered into the model before the surroundings can be neglected and suggests how the optimal field must be changed if a disturbance of specified energy affects the system.

In the case where $T = 0.2$ ps for a 20 atom truncated chain sensitive to outside disturbances, with the target bond at the 5th bond of the chain we found that the system could reasonably sustain disturbances up to 10% of the original mean bond energy of the reference case before the magnitude of the disturbances became so large that individual disturbances elsewhere in the chain dominated the energy con-

centration in the target bond. The optimal optical field in the 10% disturbance case looked very similar to the field obtained in the reference case. This demonstrates that the asymptotic expression for the optimal field and disturbance obtained in section 2 is valid in the physically reasonable disturbance energy regime. Our experience with many other examples of truncated 20 atom chains with different objectives and dipole bond configurations showed that the asymptotic expressions tend to be quite accurate in the physically relevant regime. Some experimentation with shortening the target time in the example above to $T = 0.06$ ps showed no improvement in efficiency in the sense that again approximately 10% of the mean bond energy created energy fluctuations in the bonds that were of the same intensity as the energy concentrated at the target. In this case the disturbance could reach only the 9th dipole bond but not directly the 5th target bond in the time interval, but nevertheless, the objective is significantly influenced to decrease the final stretch at the target time. When we truncated this same chain at 40 atoms instead of 20 atoms for the same final time the disturbance could not reach the final stretch or any of the dipole bonds. Consequently the cost functional increased due to the change in overall system energy but the bond stretch at the final time did not change. This is in complete accordance with intuition and suggests that the truncation of a large system should be done in such a fashion that the disturbance be kept as far as possible from the important target and dipole bonds.

The scaling rule in this paper was based on the asymptotic formula for large β and suggests that the most efficient way of countering a disturbance is by simply increasing the intensity of the controlling field. This rule seems appropriate for all the 20 atom chains examples we investigated for various objectives and dipole configurations, but it is not clear whether it is applicable in general. We tested the expression on the peak intensity of the optical field and the disturbance field of various examples and found that second order approximations actually predict the peak intensities to a few percent accuracy.

If the subsystem under consideration has been obtained from linearization of a non-linear, larger system, then the coupling matrices may well be time dependent which will necessitate a time dependent approach to the minimax problem [8,11]. Control field designs for quantum mechanical systems are non-linear but could be linearized to yield distributed systems where once again the non-linear parts could be modelled as disturbances. Some research in this direction is in progress. Another way of treating the robust quantal problem of control design is to use a classical approximation and assume that the quantal effects are modeled as disturbances to the underlying classical system. One final point that has not been touched upon in this paper is that in the case of truncation one must intelligently specify the energy content of the disturbance. Further study needs to be done on this matter. A combination of included disturbances expected during the control process and the minimax design forms a powerful tool for the control of microphysical processes.

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