

SEMICLASSICAL ASYMPTOTIC APPROACH TO OPTIMAL CONTROL OF A QUANTUM DYNAMICS

N. G. MEDHIN

Department of Mathematics, North Carolina State University
Raleigh, NC 27695-8205

ABSTRACT. An approach to the analysis of a control problem of a model quantum mechanical system under the influence of an electric field is studied via asymptotic method. The quantum mechanical system presented deals with a linear tri-atomic molecule. The purpose of this effort is to gain insight into the problem of designing an appropriate pulse to break a specific bond while leaving the other minimally disturbed. The asymptotic analysis of the model provides an opportunity to analyze and gain some insight into the interplay between the constituent parameters of the field and duration of the pulse as well the energy required to achieve the desired objective, and the mathematical difficulty inherent in the problem. The asymptotic method is used in constructing an appropriate multiobjective control problem to stretch/break the stronger bond while minimally disturbing the weaker bond with minimum energy.

MSC: 34K25, 49J20

Key Words: Asymptotic method, Fourier integral operator, Multiobjective control

1. Introduction

The practical problem motivating this effort is the study of the design of a realistic laser pulse in the infrared region to break a specific bond inside a molecule, leaving all the other bonds as undisturbed as possible. In practice “realistic” means that the duration of the pulse be in the range of hundreds of femtoseconds, and the energy of the pulse does not exceed $10^{11} \text{ Watt/cm}^2$ and that the spectrum remains localized. In other words that the pulse characteristics be in the range of the present time technology. Our effort here is to understand the physics and mathematics that one needs to deal with in designing appropriate pulse to achieve such a goal, and the study of optimal control problems governed by quantum dynamics.

Quantum calculations made on the linear molecule $H - C \equiv N$ [3] have shown that a good approximation can be achieved in describing this system classically. For that reason, we have used Pontryagin maximum principle. To get a more detailed insight we have opted to use classical asymptotic method. The asymptotic method was pursued due to the fact it gives a very good insight when applied to a quantum

mechanical problem modeling a diatomic molecule. In fact one can explicitly see the relationship between the separation between the atoms and the control, which is the applied electric field. At the end of the paper we have added a brief section relating to this model problem. If we know how to design the control to break the bond in the model problem, then the next step is to design the control in such a way to break a specific bond while minimally affecting other bonds in a molecule with more than two atoms. Of course, the next simple case is a tri-atomic linear molecule. Thus, we consider the tri-atomic linear molecule HCN. We follow [3] for the potential approximation of HCN. We have changed the potential slightly by adding a cross term. This is done not to simplify but rather to see the effect of the cross term. Of course, there is no claim that the cross term here represents the real situation perfectly.

Optical pulse design is achieved by minimization of a cost functional which depends on the control (electric field) used to break a specific bond. The cost functional should include physical constraints and governing equations of motion that must be satisfied. Among the physical constraints we shall consider as most important, we have: reduction of unwanted molecular motion for the bonds not to be broken, peak intensity of the laser pulse, maximum energy of the electric field and broadness of the pulse. To accomplish these conflicting goals one could consider multiobjective control problem.

The asymptotic method we follow employs global Fourier integral operators following Laptev and Sigal [5]. Finally, we set up an extremum problem on the basis of the asymptotic result. We are led to a multiobjective control problem. We have used classical Pontryagin maximum principle and the steepest descent method to numerically solve the control problem. [3].

To be specific, we shall consider the dissociation of the linear molecule $H-C \equiv N$. The easy case corresponds to



while



This is best understood by noting that the energy of $-C \equiv N$ bond is very near $11eV$ while the energy of the $H - C \equiv$ bond is very near to $5.7eV$. It is clear that in the uncontrolled molecular dissociation the weaker bond will be broken. So, what we wish to do is, study the problem of stretching/breaking the stronger bond while minimally affecting the weaker bond.

2. The Hamiltonian for $H - C \equiv N$ molecule

The Hamiltonian for this molecule, a linear rotation-less molecule, is the sum of its kinetic energy

$$T = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + \frac{p_3^2}{2m_3} \quad (2.1)$$

where $p_3 = C$ and $m_3 = M_C$ are the momentum and mass of the Carbon atom, $p_1 = p_N$ and $m_1 = M_N$ are the momentum and mass of the Nitrogen atom and $p_2 = H$ and $m_2 = M_H$ are the momentum and mass of the Hydrogen atom. The Carbon atom is singled out by the fact that the potential energy of the Nitrogen bond is supposed to depend only on the distance $r_1 - r_3$ of the Nitrogen atom to the Carbon atom and the potential energy of the Hydrogen bond is also supposed to depend only the distance $r_2 - r_3$ of the Hydrogen atom to the Carbon atom. Therefore we can write

$$H = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + \frac{p_3^2}{2m_3} + V_1(r_1 - r_3) + V_2(r_2 - r_3) + U(r_1 - r_3, r_2 - r_3) \quad (2.2)$$

where the potential energy $U(r_1 - r_3, r_2 - r_3)$ is a small residual mixed interaction at least one order of magnitude smaller than the smaller of the two interactions.

The equations of motion are given by the Hamilton's canonical equations

$$\begin{aligned} \frac{d}{dt}r_i &= \frac{\partial}{\partial p_i}H(r_i, p_i) \\ \frac{d}{dt}p_i &= -\frac{\partial}{\partial r_i}H(r_i, p_i) \end{aligned} \quad (2.3)$$

We look for a transformation such that the center of mass motion is uncoupled and each term of the potential depends only on one of the new variables.

Let $M = m_1 + m_2 + m_3$ be the total mass of the system, the transformation for the spatial variables is

$$\begin{aligned} R_1 &= r_1 - r_3 \\ R_2 &= r_2 - r_3 \\ R_3 &= R = \frac{m_1r_1 + m_2r_2 + m_3r_3}{M} \end{aligned} \quad (2.4)$$

The matrix corresponding to this transformation is

$$\begin{pmatrix} 1 & 0 & -1 \\ 0 & 1 & -1 \\ \frac{m_1}{M} & \frac{m_2}{M} & \frac{m_3}{M} \end{pmatrix}$$

We write

$$R = Lr \quad (2.5)$$

In the same way, we seek a matrix Λ such that

$$P = \Lambda p \quad (2.6)$$

We shall require that this transformation (L, Λ) be canonical. This means that the transformed Hamiltonian, $H(R_i, P_i)$ is that

$$\begin{aligned}\frac{d}{dt}R_i &= \frac{\partial}{\partial P_i}H(R_i, P_i) \\ \frac{d}{dt}P_i &= -\frac{\partial}{\partial R_i}H(R_i, P_i)\end{aligned}\quad (2.7)$$

We can immediately check that for the transformation to be canonical the matrix Λ for the momenta transformation must be such that $\Lambda L^T = I$. Thus, we have

$$\Lambda = \begin{pmatrix} \frac{m_2+m_3}{M} & \frac{-m_1}{M} & \frac{-m_1}{M} \\ \frac{m_2}{M} & \frac{m_1+m_3}{M} & \frac{-m_2}{M} \\ 1 & 1 & 1 \end{pmatrix}$$

Thus, we get

$$\begin{aligned}P_1 &= p_1 - \frac{m_1}{M}(p_1 + p_2 + p_3) \\ P_2 &= p_2 - \frac{m_2}{M}(p_1 + p_2 + p_3) \\ P_3 &= P = p_1 + p_2 + p_3\end{aligned}\quad (2.8)$$

The inverse transform is given by

$$\Lambda^{-1} = \begin{pmatrix} 1 & 0 & \frac{m_1}{M} \\ 0 & 1 & \frac{m_2}{M} \\ -1 & -1 & \frac{m_3}{M} \end{pmatrix}$$

Thus,

$$\begin{aligned}p_1 &= P_1 - \frac{m_1}{M}(p_1 + p_2 + p_3) \\ p_2 &= P_2 - \frac{m_2}{M}(p_1 + p_2 + p_3) \\ p_3 &= \frac{m_3}{M}p_1 - P_1 - P_2\end{aligned}\quad (2.9)$$

The kinetic energy is therefore

$$\begin{aligned}T &= \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + \frac{p_3^2}{2m_3} \\ &= \frac{P^2}{2M} + \frac{P_1^2}{2\mu_1} + \frac{P_2^2}{2\mu_2} - \frac{P_1P_2}{m_3} \\ \mu_i &= \frac{m_i m_3}{m_i + m_3}\end{aligned}\quad (2.10)$$

Working in the center of mass frame the Hamiltonian is given by

$$H_{mol} = \frac{P_1^2}{2\mu_1} + \frac{P_2^2}{2\mu_2} - \frac{P_1P_2}{M_C} + U_1(R_1) + U_2(R_2) + U(R_1, R_2)$$

where

$$\frac{1}{\mu_1} = \frac{1}{M_C} + \frac{1}{M_N}$$

$$\frac{1}{\mu_2} = \frac{1}{M_C} + \frac{1}{M_H} \quad (2.11)$$

2.1. The Hamiltonian of Interaction. The interaction between the $H - C \equiv N$ molecule and the laser field is described by the dipole moment function. Previous work [3] showed that in sufficiently intense laser fields the linear molecule tends to align in the direction of the field. Therefore we shall write the interaction as

$$H_{int} = -\mu(R)\epsilon(t) \quad (2.12)$$

where $\epsilon(t)$ is the electric field amplitude of the laser pulse as a function of time t , and $\mu(R)$ is the molecule electric dipole that depends on the position of each bond. In this specific example, we shall choose it following Rabitz ([3]).

$$\mu(R) = \mu_e[\mu(R_1) - \mu(R_2)] \quad (2.13)$$

Then,

$$H_{int} = -\mu_e[\mu(R_1) - \mu(R_2)]\epsilon(t) \quad (2.14)$$

2.2. The Total Hamiltonian. The total Hamiltonian of the system now reads

$$\begin{aligned} H = H_{mol} + H_{int} &= \frac{P_1^2}{2\mu_1} + \frac{P_2^2}{2\mu_2} - \frac{P_1 P_2}{M_C} + U_1(R_1) + U_2(R_2) \\ &+ U(R_1, R_2) - \mu_e[\mu(R_1) - \mu(R_2)]\epsilon(t) \end{aligned} \quad (2.15)$$

3. Statement of The Model Quantum Mechanical Problem

Following the discussion above we consider the quantum mechanical problem given by the equation

$$\begin{aligned} i\hbar \frac{\partial \psi}{\partial t} &= -\hbar^2 \left(\frac{1}{2\mu_1} \frac{\partial^2}{\partial x_1^2} + \frac{1}{2\mu_2} \frac{\partial^2}{\partial x_2^2} + \frac{1}{\mu_c} \frac{\partial}{\partial x_1} \frac{\partial}{\partial x_2} \right) \psi \\ &+ (V_1(x_1) + V_2(x_2) + W(x_1, x_2) - \mu_e[\mu(x_1) - \mu(x_2)]E(t))\psi \end{aligned}$$

Let

$$\begin{aligned} \alpha &= \hbar, \\ h(t, x, \xi) &= \frac{1}{2\mu_1} \xi_1^2 + \frac{1}{2\mu_2} \xi_2^2 + \frac{1}{\mu_c} \xi_1 \xi_2 \\ &+ V_1(x_1) + V_2(x_2) + W(x_1, x_2) - \mu_e[\mu(x_1) - \mu(x_2)]E(t). \end{aligned} \quad (3.1)$$

Later, when we present an extremum problem connected with our problem, we will specify V_1, V_2, W in (3.1).

4. Analysis of The Problem

Thus, we set

$$\begin{aligned} H_\alpha(t)f(t, x) &= h(t, x, \alpha D_x)f(t, x) \\ &= (2\pi\alpha)^{-2} \int \int h(t, x, \xi) e^{\frac{i(x-y)\cdot\xi}{\alpha}} f(y) dy d\xi \end{aligned}$$

Now consider the equation

$$\begin{aligned} \alpha i \frac{\partial}{\partial t} U(t, s) &= H_\alpha(t)U(t, s) \\ U(s, s) &= I. \end{aligned} \tag{4.1}$$

Let

$$\begin{aligned} \frac{dx}{dt} &= \frac{\partial h}{\partial \xi} \\ \frac{d\xi}{dt} &= -\frac{\partial h}{\partial x} \\ x(0) &= y \\ \xi(0) &= \eta \end{aligned} \tag{4.2}$$

Set

$$S(t, y, \eta) = \int_0^t \left(\xi^T \frac{dh}{d\xi} - h(s, x(s), \xi(s)) \right) ds \tag{4.3}$$

Next, let

$$\phi(t, x, y, \eta) = S(t, y, \eta) + (x - x(t))^T \xi(t) + \frac{i}{2} (x - x(t))^T B (x - x(t)) \tag{4.4}$$

where B is a function of t, y , and η .

Then,

$$\begin{aligned} \phi_x &= \xi(t) + iB(x - x(t)) \\ \phi_{x\eta} &= \xi_\eta - iBx_\eta + i(B_{\eta_1}(x - x(t)), B_{\eta_2}(x - x(t))) \end{aligned} \tag{4.5}$$

$$\begin{aligned} Z(t, y, \eta) &= \xi_\eta - iBx_\eta \\ Z(0, y, \eta) &= \xi_\eta(0) - iBx_\eta(0) = I \end{aligned} \tag{4.6}$$

In (4.6) we are defining $Z(t, y, \eta)$ by the right hand side of the equation. We will see later the role it plays in dealing with the Fourier integral (4.7). Now we proceed to look for an α -Fourier integral operator given by

$$U_N(t) = (2\pi\alpha)^{-2} \int e^{\frac{i\phi}{\alpha}} u_N(t, y, \eta, \alpha) d\eta \tag{4.7}$$

$$\begin{aligned} (\alpha i \partial_t - H_\alpha(t))U_N(t) &= (2\pi\alpha)^{-2} \int e^{\frac{i\phi}{\alpha}} (\partial_t \phi u_N + \alpha i \partial_t u_N) \\ &\quad - h(t, x, \phi_x(t, x, y, \eta)) u_N \end{aligned}$$

$$-\frac{\alpha}{2}(\mu_1^{-1}b_{11} + \mu_2^{-1}b_{22} + 2\mu_c^{-1}b_{12})u_N)d\eta \quad (4.8)$$

We have

$$\begin{aligned} h(t, x(t), \phi_x) &= h(t, x(t)\xi(t)) + iB(x - x(t)) \\ &= h(t, x(t)\xi(t)) + h_x^T(x, x(t), \xi(t))(x - x(t)) \\ &\quad + ih_\xi(t, x(t), \xi(t))^T B(x - x(t)) \\ &\quad + \frac{1}{2}(x - x(t))^T h_{xx}(x - x(t)) \\ &\quad + \frac{1}{2}iB(x - x(t))^T G_2 iB(x - x(t)), \end{aligned}$$

where

$$G_2 = \begin{pmatrix} \frac{1}{\mu_1} & \frac{1}{\mu_c} \\ \frac{1}{\mu_c} & \frac{1}{\mu_2} \end{pmatrix}.$$

$$\begin{aligned} (\alpha i \partial_t - H_\alpha(t))U_N(t) &= (2\pi\alpha)^{-2} \int e^{\frac{i\phi}{\alpha}} \left\{ -\frac{i}{2}(x - x(t))^T \dot{B}(x - x(t)) \right. \\ &\quad - \frac{1}{2}(x - x(t))^T G_1(x - x(t)) \\ &\quad - \frac{1}{2}[i(B(x - x(t)))^T G_2 i(B(x - x(t)))]u_N \\ &\quad \left. \alpha i \partial_t u_N - \frac{\alpha}{2}(\mu_1^{-1}b_{11} + \mu_2^{-1}b_{22} + 2\mu_c^{-1}b_{12})u_N \right\} d\eta \\ &= (2\pi\alpha)^{-2} \int e^{\frac{i\phi}{\alpha}} \left\{ -\frac{1}{2}(x - x(t))^T [i\dot{B} + G_1 - B^T G_2 B](x - x(t))u_N \right. \\ &\quad \left. \alpha i \partial_t u_N - \frac{\alpha}{2}(\mu_1^{-1}b_{11} + \mu_2^{-1}b_{22} + 2\mu_c^{-1}b_{12})u_N \right\} d\eta \quad (4.9) \end{aligned}$$

Since

$$\frac{\partial}{\partial \eta} e^{i\frac{\phi}{\alpha}} = \frac{i}{\alpha} e^{i\frac{\phi}{\alpha}} Z(x - x(t))$$

we have

$$-i\alpha Z^{-1} \frac{\partial}{\partial \eta} e^{i\frac{\phi}{\alpha}} = e^{i\frac{\phi}{\alpha}}(x - x(t))$$

Now, setting

$$G = i\dot{B} + G_1 - B^T G_2 B$$

we have, using (4.8)

$$\begin{aligned} &(2\pi\alpha)^{-2} \int e^{\frac{i\phi}{\alpha}} \left\{ -\frac{1}{2}(x - x(t))^T G(x - x(t))u_N \right\} d\eta \\ &= (2\pi\alpha)^{-2} \int \frac{i\alpha}{2}(x - x(t))^T G Z^{-1} \frac{\partial}{\partial \eta} e^{\frac{i\phi}{\alpha}} u_N d\eta \quad (4.10) \end{aligned}$$

We have

$$\begin{aligned} \text{tr} \left(i\frac{\alpha}{2} x_\eta^T G Z^{-1} e^{i\frac{\phi}{2}} \right) &= -\text{tr} i\frac{\alpha}{2} [\dot{Z} + iZBh_{\xi\xi}] Z^{-1} e^{i\frac{\phi}{\alpha}} \\ &= -\text{tr} i\frac{\alpha}{2} Z^{-1} [\dot{Z} + iZBh_{\xi\xi}] e^{i\frac{\phi}{\alpha}} \end{aligned}$$

$$= -tr i \frac{\alpha}{2} [Z^{-1} \dot{Z} + iBh_{\xi\xi}] e^{i\frac{\phi}{\alpha}}$$

Thus we have, using (4.10)

$$(\alpha i \partial_t - H_\alpha(t)) U_N(t) = (2\pi\alpha)^{-1} \int e^{i\frac{\phi}{\alpha}} \left\{ i \frac{\partial}{\partial t} u_N - \frac{i}{2} (tr Z^{-1} \dot{Z}) u_N + \frac{\alpha}{2} \Gamma \right\} d\eta \quad (4.11)$$

where

$$\Gamma = \sum_{ijk} \{ \partial^2_{\eta_k \eta_i} R_{ij} (Z^{-1})_{jk} + (\partial \eta_i R_{ij}) \partial \eta_k (Z^{-1})_{jk} \}, \quad (4.12)$$

and

$$R = [i\dot{B} + G_1 - B^T G_2 B] Z^{-1}$$

Setting

$$u_N = u_N^0 + \alpha u_N^1 + \alpha^2 u_N^2 + \alpha^3 u_N^3 + \alpha^4 u_N^4 + \alpha^5 u_N^5 + \dots \quad (4.13)$$

we use (4.11) to determine u_N^k , $k = 0, 1, \dots$ from the following recursive system of equations

$$\begin{aligned} i \frac{\partial}{\partial t} u_N^0 - \frac{i}{2} (tr Z^{-1} \dot{Z}) u_N^0 &= 0, \quad u_N^0 = 1 \\ i \frac{\partial}{\partial t} u_N^k - \frac{i}{2} (tr Z^{-1} \dot{Z}) u_N^k &= \Gamma u_N^{k-1}, \quad k = 1, 2, 3, \dots \end{aligned}$$

We note that

$$u_N^0 = \sqrt{\det Z} \quad (4.14)$$

Taking

$$f(y) = \rho(y) e^{\frac{iy^T \eta_0}{\alpha}} \quad (4.15)$$

Setting

$$I = (2\pi\alpha)^{-2} \int e^{i\psi(t,x,y,\eta)/\alpha} u_N(t,y,\eta) \rho(y) d\eta dy, \quad (4.16)$$

where

$$\psi(t,x,y,\eta)/\alpha = \phi(t,x,y,\eta) + y \cdot \eta_0$$

We use stationary phase method to obtain

$$\begin{aligned} I &= \rho(\bar{y}(t,x,\eta_0)) e^{i\bar{y}(t,x,\eta_0)^T \eta_0} e^{iS(t,\bar{y},\eta_0)/\eta_0} \cdot \\ &\cdot e^{i\frac{\pi}{2} m(t,\bar{y},\eta_0)} |\det x_y(t,\bar{y},\eta_0)|^{\frac{-1}{2}} + O(\alpha) \end{aligned} \quad (4.17)$$

where $m(t,\bar{y},\eta)$ is the Morse index of the trajectory $x(s;y,\eta)$, $0 \leq s \leq t$ and $\bar{y} = \bar{y}(t,x,\eta_0)$ is the unique solution of the equation

$$x^t(y,\eta_0) = x \quad (4.18)$$

Note that

$$\begin{aligned} \dot{x}_\eta &= h_{\xi\xi} \cdot \xi_\eta \\ \dot{\xi}_\eta &= -h^T_{xx} \cdot x_\eta \end{aligned} \quad (4.19)$$

$$h_{\xi\xi} = \begin{pmatrix} \frac{1}{\mu_1} & \frac{1}{\mu_c} \\ \frac{1}{\mu_c} & \frac{1}{\mu_2} \end{pmatrix} \quad (4.20)$$

$$h_{xx} = \begin{pmatrix} V_1'' - \mu_e \mu''(x_1)E + W_{11} & W_{12} \\ W_{21} & V_2'' - \mu_e \mu''(x_2)E + W_{22} \end{pmatrix} \quad (4.21)$$

5. Extremum Problem

In what follows we take specific potentials V_1 and V_2 . In particular, we take

$$V_1(x_1) = V_1(1 - e^{\alpha_1 x_1})^2 \quad (5.1)$$

$$V_2(x_2) = V_2(1 - e^{\alpha_2 x_2})^2 \quad (5.2)$$

We have

$$V_1'(x_1) \approx 2\alpha_1^2 V_1 x_1 \quad (5.3)$$

$$V_2'(x_2) \approx 2\alpha_2^2 V_2 x_2 \quad (5.4)$$

Next,

$$\mu_e \mu(x_1) = \mu_e(x_1 + x_0)e^{-\tilde{\alpha}x_1} E(t) \quad (5.5)$$

Thus,

$$\mu_e \mu'(x_1) \approx \mu_e E(t)(1 - \tilde{\alpha}x_0) - \mu_e \tilde{\alpha}(2 - \tilde{\alpha}x_0)E(t)x_1 \quad (5.6)$$

$$\mu_e \mu'(x_2) \approx \mu_e E(t)(1 - \tilde{\alpha}x_0) - \mu_e \tilde{\alpha}(2 - \tilde{\alpha}x_0)E(t)x_2 \quad (5.7)$$

$$W_{x_1} \approx \epsilon x_1, \quad W_{x_2} \approx \epsilon x_2 \quad (5.8)$$

Let

$$\Lambda_1 = 2\alpha_1^2 V_1 - \mu_e \tilde{\alpha}(2 - \tilde{\alpha}x_0)E \quad (5.9)$$

$$\Lambda_2 = 2\alpha_2^2 V_2 - \mu_e \tilde{\alpha}(2 - \tilde{\alpha}x_0)E \quad (5.10)$$

$$\tilde{\mu}_e = \mu_e(1 - \tilde{\alpha}x_0) \quad (5.11)$$

Now we have the system

$$\begin{aligned} \frac{dx_1}{dt} &= \frac{1}{\mu_1} \xi_1 + \frac{1}{\mu_c} \xi_2 \\ \frac{dx_2}{dt} &= \frac{1}{\mu_2} \xi_2 + \frac{1}{\mu_c} \xi_1 \\ \frac{d\xi_1}{dt} &= \tilde{\mu}_e - \Lambda_1(t)x_1 - \epsilon x_2 \\ \frac{d\xi_2}{dt} &= -\tilde{\mu}_e - \Lambda_2(t)x_2 - \epsilon x_1 \end{aligned} \quad (5.12)$$

Corresponding to (5.12) we have the second order system

$$\begin{aligned} \frac{d^2 x_1}{dt^2} &= \frac{1}{\mu_1}(\tilde{\mu}_e E - \Lambda_1(t)x_1 - \epsilon x_2) - \frac{1}{\mu_c}(\tilde{\mu}_e E - \Lambda_2(t)x_2 - \epsilon x_1) \\ \frac{d^2 x_2}{dt^2} &= \frac{1}{\mu_2}(\tilde{\mu}_e E - \Lambda_2(t)x_2 - \epsilon x_1) + \frac{1}{\mu_c}(\tilde{\mu}_e E - \Lambda_1(t)x_1 - \epsilon x_2) \end{aligned} \quad (5.13)$$

Let

$$L(t) = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ -\left(\frac{\Lambda_1}{\mu_1} + \frac{\epsilon}{\mu_c}\right) & -\left(\frac{\Lambda_2}{\mu_c} + \frac{\epsilon}{\mu_1}\right) & 0 & 0 \\ -\left(\frac{\Lambda_1}{\mu_c} + \frac{\epsilon}{\mu_2}\right) & -\left(\frac{\Lambda_2}{\mu_2} + \frac{\Lambda_2}{\mu_c}\right) & 0 & 0 \end{pmatrix} \quad (5.14)$$

Next, let

$$\begin{aligned} \theta(t) &= \begin{pmatrix} 0 \\ 0 \\ \frac{\mu_c - \mu_1}{\mu_1 \mu_c} \tilde{\mu}_e E(t) \\ \frac{\mu_2 - \mu_c}{\mu_c \mu_2} \tilde{\mu}_e E(t) \end{pmatrix}, \\ \tilde{\theta}(t) &= \begin{pmatrix} \frac{\mu_c - \mu_1}{\mu_1 \mu_c} \tilde{\mu}_e E(t) \\ \frac{\mu_2 - \mu_c}{\mu_c \mu_2} \tilde{\mu}_e E(t) \end{pmatrix} \end{aligned} \quad (5.15)$$

and

$$\begin{aligned} z_1 &= x_1 \\ z_2 &= x_2 \\ z_3 &= \frac{dx_1}{dt} \\ z_4 &= \frac{dx_2}{dt} \end{aligned} \quad (5.16)$$

and

$$z = \begin{pmatrix} z_1 \\ z_2 \\ z_3 \\ z_4 \end{pmatrix} \quad (5.17)$$

Then,

$$\frac{dz}{dt} = L(t)Z + \theta(t) \quad (5.18)$$

Let $\Phi(t, s)$ be the solution of the equation

$$\begin{aligned} \frac{d}{dt}\Phi(t, s) &= L(t)\Phi(t, s) \\ \Phi(s, s) &= I \end{aligned} \quad (5.19)$$

Then,

$$z(t) = \Phi(t, 0) \begin{pmatrix} y \\ \eta \end{pmatrix} + \int_0^t \Phi(t, s)\theta(s)ds \quad (5.20)$$

Then,

$$\begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = \begin{pmatrix} z_1 \\ z_2 \end{pmatrix} = \Phi_{11}(t, 0)y + \Phi_{12}(t, 0)\eta + \int_0^t \Phi(t, s)\tilde{\theta}(s)ds \quad (5.21)$$

Let

$$\mathcal{M}^{-1} = \begin{pmatrix} \frac{1}{\mu_1} & \frac{1}{\mu_2} \\ \frac{1}{\mu_c} & \frac{1}{\mu_2} \end{pmatrix} \tag{5.22}$$

Then

$$\begin{pmatrix} \frac{dx_1}{dt} \\ \frac{dx_2}{dt} \end{pmatrix} = \Phi_{21}(t, 0)y + \Phi_{22}(t, 0)\mathcal{M}^{-1}\eta + \int_0^t \Phi_{22}(t, s)\tilde{\theta}(s)ds \tag{5.23}$$

We note that

$$\begin{pmatrix} \xi_1 \\ \xi_2 \end{pmatrix} = \mathcal{M} \begin{pmatrix} \frac{dx_1}{dt} \\ \frac{dx_2}{dt} \end{pmatrix} \tag{5.24}$$

Thus,

$$\begin{pmatrix} \xi_1 \\ \xi_2 \end{pmatrix} = \mathcal{M}\Phi_{21}(t, 0)y + \mathcal{M}\Phi_{22}(t, 0)\mathcal{M}^{-1}\eta + \int_0^t \mathcal{M}\Phi_{22}(t, s)\tilde{\theta}(s)ds \tag{5.25}$$

We note from (5.21) that

$$|\det x_y| = |\det \Phi_{11}(t, 0)|^{-1/2} \tag{5.26}$$

Let

$$\zeta(x) = \Phi_{11}^{-1}(t, 0)[x - \Phi_{12}(t, 0)\eta - \int_0^t \Phi_{12}(t, s)\tilde{\theta}(s)ds] \tag{5.27}$$

Next, let

$$\begin{aligned} \psi(t, x) &= \rho(\zeta(x))e^{i\zeta(x)^T\eta_0}e^{iS(t, \zeta(x), \eta_0)/\alpha}u_N^0(t, \zeta(x), \eta_0) \\ &\quad \cdot e^{i\frac{\pi}{2}m(t, \zeta(x), \eta_0)}|\det x_y(t, \bar{y}, \eta)|^{-1/2} \end{aligned}$$

We recall from (4.6) and (4.14) that

$$\begin{aligned} Z(t, y, \eta) &= \xi_\eta - iBx_\eta, \\ u_N^0 &= \sqrt{\det Z}. \end{aligned}$$

and

$$|\psi(t, x)| = |\rho(\zeta(x))||\det x_y(t, \bar{y}, \eta)|^{-1/2} \tag{5.28}$$

Below, we take specific values for our parameters in (5.1)-(5.8) as follows

$$\mu_1 = 11860, \quad \mu_2 = 282, \quad \mu_c = -524.5764, \quad \mu_e = .3924$$

$$V_1 = .1976, \quad V_2 = .137, \quad \alpha_1 = .9217, \alpha_2 = .137, \quad x_0 = 2, \tilde{\alpha} = 1, \quad \epsilon = .01$$

In our optimal control computation we use atomic mass units (au) [3]. The hydrogen mass is $1836 m_e$, where m_e is electron mass. The carbon mass is $12 * 1836 m_e = 22032 m_e$, and the nitrogen mass is $14 * m_e$. We just write $1836 au$ for the hydrogen mass, and $22032 au$ for the carbon mass. For example, the reduced mass of $-C \equiv N$ bond is $11860 au$. The energy of $-C \equiv N$ bond is very near $11ev$, and that of the

$H - C \equiv$ bond is very near 5.7 ev . We can now approximately calculate the $-C \equiv N$ bond length to be about 2.18 au , and that of the $H - C \equiv$ bond to be about 2.008 au . Magnitude of the momentum for the nitrogen bond $-C \equiv N$ can be approximated by 98.2 au , and for hydrogen bond $H - C \equiv$ by 10.2 au . We use the bond lengths and the momenta in y and η (see (4.2)) in the second objective functional of the control problem below. In the same objective functional $x^* = (x_1^*, x_2^*)$ is what we would like $(x_1(T), x_2(T))$ to be close too. We choose (x_1^*, x_2^*) so that the stronger bond length x_1 gets stretched and the weaker bond length remains close to what it was before applying the electric field. In this way we get the numerical inputs we need to proceed with our numerical computation.

Below we compute the control (electric field $E(t)$) and corresponding states using the maximum principle. The results are plotted below. We note that the strong bond has actually been stretched in each case while the weaker bond shrunk. In Figure 2 we see that stronger bond is stretched and the weaker bond is minimally affected.

6. Use of Pontryagin's Maximum Principle

In this section we show how we use the Pontryagin's maximum principle. If the actual initial wave function is $\chi(y, \eta)$ we use (see 4.16)

$$I = (2\pi\alpha)^{-2} \int e^{i\phi(t,x,y,\eta)/\alpha} u_N(t, y, \eta) \chi(y, \eta) d\eta dy$$

where u_N comes from the asymptotic expansion (4.13), (4.14) and (4.14). Also see (4.14). Of course, to first order in α , which is really Planck's constant, we only need (4.14), which is known explicitly (see (4.14)). In employing the maximum principle we use as initial wave function, $\rho(y)e^{\frac{iy^T \eta_0}{\alpha}}$ introduced in (4.15). A rational for doing so is that we could approximate the actual initial wave function $\chi(y, \eta)$ by $\sum_{m,n} \rho_m(y) e^{i\epsilon_n y^T \eta/\alpha}$. Thus, if we carry out the control problem for initial wave functions of the form $\rho_m(y) e^{i\epsilon_n y^T \eta/\alpha}$ we can approximate the result for the actual wave function by adding the results we get using initial wave function of these simpler forms. With $\rho(y) e^{iy^T \eta_0/\alpha}$ we use stationary phase formula to get (4.17). Thus, we consider the following three objective functionals at the same time.

$$\min \int_0^T E^2(t) dt,$$

$$\min \left\{ |x^* - [\Phi_{11}(T, 0)y + \Phi_{12}(T, 0)\eta + \int_0^T \Phi_{12}(T, s)\tilde{\theta}(s) ds]| \right\},$$

and

$$\max |I| = |\rho(\bar{y}(T, x, \eta_0))| |\det x_y(T, \bar{y}, \eta_0)|^{-1/2},$$

where $|I|$ comes from (4.16) subject to (5.12). To include the contribution of $|\det x_y(t, \bar{y}, \eta_0)|$ we supplement (5.12) by

$$\begin{aligned}
 \frac{dx_{11}}{dt} &= \frac{1}{\mu_1}\xi_{11} + \frac{1}{\mu_c}\xi_{21} \\
 \frac{dx_{12}}{dt} &= \frac{1}{\mu_1}\xi_{12} + \frac{1}{\mu_c}\xi_{22} \\
 \frac{dx_{21}}{dt} &= \frac{1}{\mu_2}\xi_{21} + \frac{1}{\mu_c}\xi_{11} \\
 \frac{dx_{22}}{dt} &= \frac{1}{\mu_2}\xi_{22} + \frac{1}{\mu_c}\xi_{12} \\
 \frac{d\xi_{11}}{dt} &= -\Lambda_1(t)x_{11} - \epsilon x_{21} \\
 \frac{d\xi_{12}}{dt} &= -\Lambda_2(t)x_{12} - \epsilon x_{22} \\
 \frac{d\xi_{21}}{dt} &= -\Lambda_1(t)x_{21} - \epsilon x_{11} \\
 \frac{d\xi_{22}}{dt} &= -\Lambda_2(t)x_{22} - \epsilon x_{12} \\
 x_{ij}(0) &= \delta_{ij} \\
 \xi_{ij}(0) &= 0
 \end{aligned} \tag{6.1}$$

Thus, we have to solve a multiobjective control problem. The control is the electric field $E(t)$, and $E^2(t)$ is the energy contained in the electric field. We note that three objective functionals constitute the multiobjective control problem. The first objective functional (COST1) is designed to minimize the energy needed. The goal to be accomplished is to stretch the stronger bond length, i.e., break it, while affecting the weaker bond minimally. The second objective functional (COST2) is designed for this purpose. The third objective functional (COST3) localizes the wave function, which is needed to increase the probability our goal of affecting the bonds is realized sharply. Our objective functional that we want to minimize is now $\alpha_1 \cdot COST1 + \alpha_2 \cdot COST2 + \alpha_3 \cdot (-COST3)$ subject to the dynamics (5.12) and (6.1). The constants $\alpha_1, \alpha_2, \alpha_3$ are positive constants that we can choose. In our case we chose them to be .5, 25, 25. We tried various choices without much difference. Introducing scalarization parameters is normal in dealing with multiobjective control problems. In multiobjective problems one might choose the scalarizing parameters emphasizing which of the various competing objective functions is important. We remind the reader that x_1 is the bond length for the $-C \equiv N$ bond, and x_2 is the bond length for the $H - C \equiv$ bond. The stronger bond is the $-C \equiv N$ bond, and that is what we would like stretched. That is, we would like x_1 increased from its original value, while x_2 is kept the same, or affected minimally. We use Pontryagin's maximum principle and the method of steepest descent [4] to look for the best

control. The method of steepest descent is a numerical procedure to look for the best control using the hamiltonian in Pontryagin's maximum principle. The resulting control ($E(t)$), corresponding Hamiltonian J , and states are shown below for three different maximum levels of the control. Figure 1 and Figure 2 correspond to case (a): $|E| \leq 200$. Figure 3 and Figure 4 correspond to case (b): $|E| \leq 25$. Figure 5 and Figure 6 correspond to case (c): $|E| \leq 3$. We note that among the results shown below, in the plots for the states, Figure 2 perfectly fits our goal. That is, x_1 increased from its original value, while x_2 is affected minimally. In Figure 4 and Figure 6 the stronger bond is also stretched as we wanted. However, the weaker bond did not quite stay near where it initially was. It was shortened. That is, in both cases x_1 increased, while x_2 decreased. In Figure 1, Figure 3, and Figure 5 the Hamiltonian J of the control problem decreases. The Hamiltonian J includes the square of the electric field.

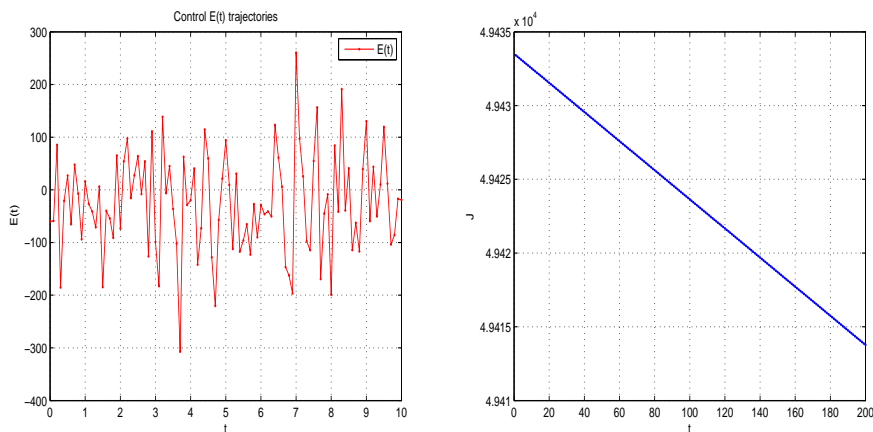


FIGURE 1. Control and Hamiltonian J : case(a).

7. Asymptotic Expansion On a Model Problem

In this section we will briefly present a problem that would give some insight and motivation for the asymptotic approach that was done above. We consider a quantum mechanical model of a diatomic molecule. Using classical asymptotic method one can see how to design an appropriate pulse/electric field to achieve a dissociation of desired amount in the molecule. The analysis of the model provides an insight into the interplay between the constituent parameters of the field and duration of the electric pulse required to achieve a desired amount of dissociation in a molecule, and the mathematical difficulty inherent in the problem. The insight gained in dealing with this problem is useful in dealing with molecules containing more than two atoms. In the figure below (Figure 7) we see the original wave function shifted, verifying a separation between the atoms has been achieved. The relationship of the separation

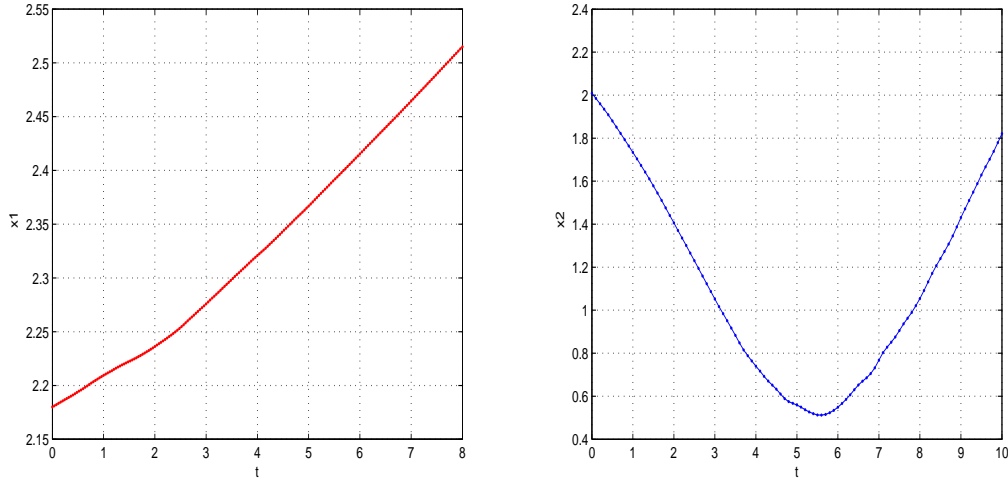


FIGURE 2. State1 and State 2 corresponding to Control and Hamiltonian J: case (a).

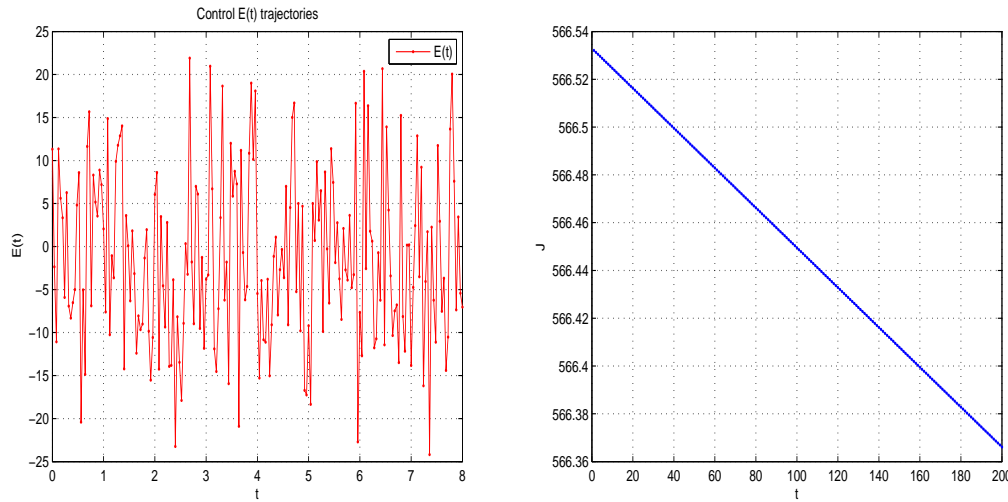


FIGURE 3. Control and Hamiltonian J: case(b).

amount to the applied control can be gotten from the asymptotic formula. The model equation is

$$i\frac{\partial\psi}{\partial t} + \frac{\partial^2\psi}{\partial x^2} - V(x, t)\psi = 0, \tag{7.1}$$

where

$$V(x, t) = -|\lambda|\delta(x) + xE(t) \tag{7.2}$$

The following gives the solution to (7.1)

$$\begin{aligned} \psi(x, t) = & \frac{1}{2\pi} e^{i[-2W(t,0) + \int_0^t E(u)du(t \int_0^t E(u)du + 2V(t,0) - x)]} \cdot \\ & \int_{-\infty}^{\infty} e^{i[t\zeta^2 - 2(t \int_0^t E(u)du - V(t,0))\zeta]} e^{i\zeta \cdot x} \hat{\psi}(\zeta, 0) d\zeta \end{aligned}$$

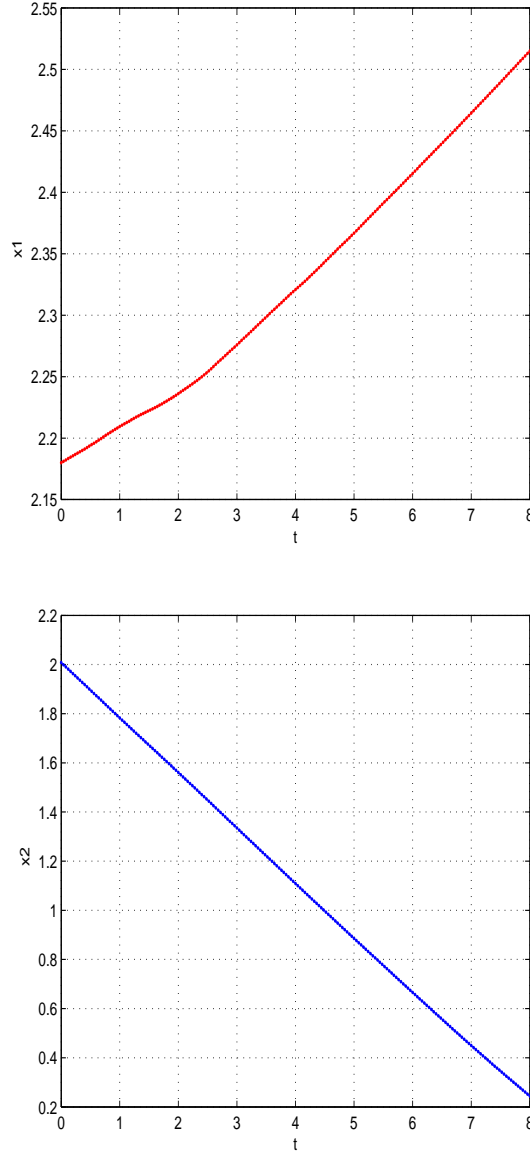


FIGURE 4. State 1 and State 2 corresponding to Control and Hamiltonian J: case(b).

$$+ \frac{i|\lambda|}{\sqrt{4\pi i}} \int_0^t e^{\frac{i}{4(t-s)} \cdot x^2 - i\frac{V(t,s)}{t-s} \cdot x + i\frac{V^2(t,s)}{t-s} - 2iW(t,s)} \psi(0, s) ds \quad (7.3)$$

where

$$W(t, 0) = \int_0^t E(r)V(r, 0)dr$$

Using asymptotic method one can see that the initial wave function will be displaced by $2V(t, 0)$ in time t and $V(t, 0) = \int_0^t uE(u)du$ where $E(t)$ is the control. This model problem of a diatomic molecule shows, using asymptotic method, how much the original wave function is shifted and the exact relationship with the shift,

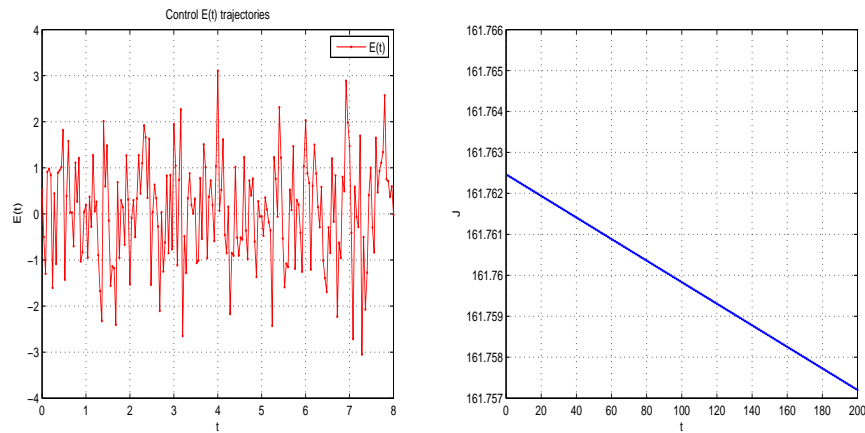


FIGURE 5. Control and Hamiltonian J: case(c).

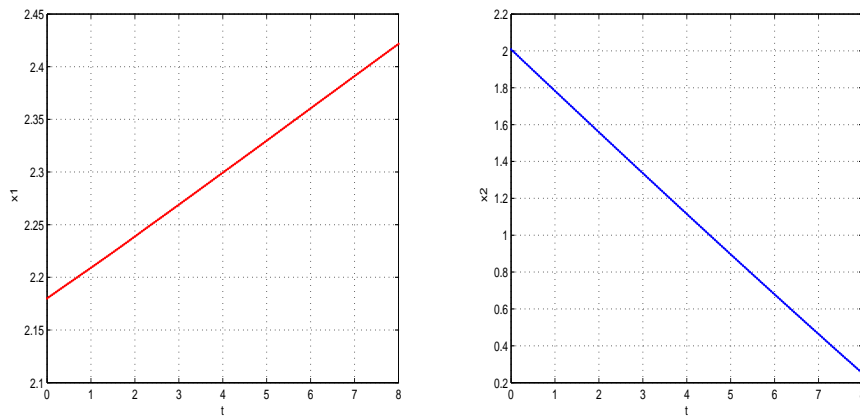


FIGURE 6. State1 and State 2 corresponding to Control and Hamiltonian J : case(c).

control electric field and the energy. Thus, one would conclude it may be beneficial to consider asymptotic methods to deal with problems where we have more than two atoms and we want to break a specific bond while minimally affecting other bonds. This is precisely the motivation for what was done above.

8. Conclusion

We have demonstrated how we can use classical asymptotic procedure to gain insight into the relationship between the applied control (electric field) and its effect on the original wave function. We have demonstrated how one would set up a classical control problem where it is required to break the stronger bond while affecting the weaker less. We note from the above computations that the stronger bond is in fact stretched, while the weaker is not, and the energy is minimized. In Figure 2 the state corresponding to the stronger bond is stretched while the state corresponding

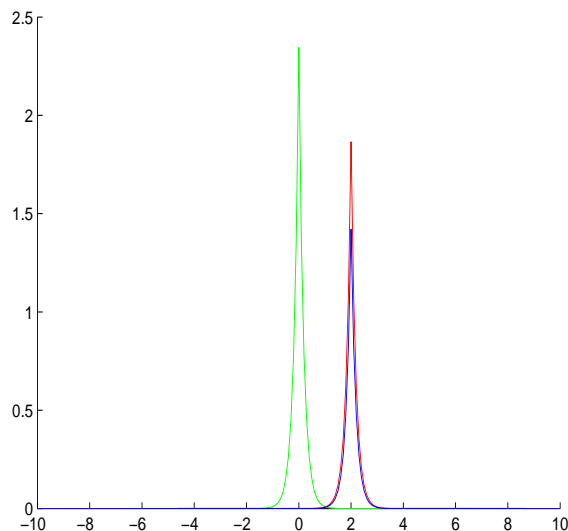


FIGURE 7. Shifting The Original Wave (diatomic model.)

to the weaker bond is not disturbed much. In Figure 4 and Figure 6 the stronger bond is stretched while the weaker bond is actually shortened. We can say that we have managed to construct a model in a mathematically satisfactory way where the stronger bond is stretched while the weaker bond is minimally disturbed or shrunk. The control problems were numerically solved using the steepest descent method. The result of the asymptotic method on the model problem suggests that the asymptotic method is in fact a good approach. It sheds light on what is really involved in optimal control problems governed by quantum dynamics.

REFERENCES

- [1] C. Bardeen et al., Feedback quantum control of molecular electronic population transfer, *Chem. Phys. Lett.* 280(1997), pp. 151–158.
- [2] E. Brown and H. Rabitz, Some mathematical and algorithmic challenges in the control of quantum dynamics phenomena, *J. of Mathematical Chem.*, Vol. 31, No. 1, pp. 17(2002).
- [3] Jair Botina, Herschel Rabitz, Naseem Rahman A simplified approach to optimally controlled quantum dynamics, *J. Chem. Phys.* 104(11) pp. 4031–4040.
- [4] Donald Kirk Optimal Control Theory, PRENTICE-HALL, INC., Englewood Cliffs, New Jersey, 1970.
- [5] A. Laptev, I. M. Segal, A. Laptev and I. M. Segal, Global Fourier Integral Operators and Semiclassical Asymptotics, *Rev. Math. Phys.* 12(2000) pp. 749–766.
- [6] R.J. Levis, G.M. Menkir and H. Rabitz, Selective bond dissociation and rearrangement with optimally tailored, strong-field laser pulses, *Science* 292(2001) pp. 709–713.
- [7] W. S. Warren, H. Rabitz, and M. Dahleh, Coherent Control of Quantum Dynamics: The Dream is alive, *Science* 259(1993), pp. 1581–1589.