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ON OPTIMAL CONTROL OF A MODEL QUANTUM MECHANICAL SYSTEM

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ABSTRACT. An analysis of a model quantum mechanical system under the influence of an electric field is studied. The quantum mechanical system presented models a diatomic molecule. The purpose of this effort is to gain insight into the problem of designing an appropriate pulse to achieve a specific dissociation of desired amount in a molecule. An appropriate pulse means one that is in the range of current technology. The 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 a desired amount of dissociation in a molecule, and the mathematical difficulty inherent in the problem. The insight gained here can be of value in dealing with molecules containing more than two atoms.

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1. Inroduction

To gain understanding into the design of a realistic pulse in the infrared region that will allow to break a specific bond in a molecule leaving all other bonds as undisturbed as possible we have undertaken the analysis of a model quantum mechanical problem in detail.

In practice, a "realistic pulse" means that the duration of the pulse be in the range of hundreds of femtoseconds, the energy of the pulse not exceed $10^{11} Watt/cm^2$ and the spectrum remains localized. In other words, the pulse characteristics be in the range of current technology. Our effort here is to gain insight into the physics and mathematics that one needs to consider in designing appropriate pulse to achieve the goal.

Optimal design is achieved by the minimization of an appropriate cost functional of the electric field under appropriate constraints. Thus, an appropriate choice of the cost functional is necessary, and in the absence of explicit solution to the control problem, a numerical scheme has to be designed. For a more reliable numerical

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scheme of more complicated problems a study of a model problem for which explicit solution of the quantum mechanical system is helpful. The analysis of the current model provides insight into the complexity of the problem. By explicit calculation we are able to gain insight into the interaction of the parameters of the pulse and duration of the pulse. The insight gained here can be of value when dealing with molecules containing more than two atoms.

2. Statement of The Model Quantum Mechanical Problem

The model quantum mechanical problem is given by the equation

$$i\frac{\partial\psi}{\partial t} + \frac{\partial^2\psi}{\partial x^2} - V(x,t)\psi = 0, \tag{2.1}$$

where

$$V(x,t) = -\,|\lambda|\,\delta(x) + xE(t) \tag{2.2}$$

3. Analysis of The Problem

In this section we analyse problem (2.1)–(2.2). We consider subproblems to gain a handle on the problem.

3.1. Case of Zero Electric Field.

In (2.2) set $E(t) = 0$. In this case (2.1) becomes

$$i\frac{\partial\psi}{\partial t} + \frac{\partial^2\psi}{\partial x^2} + |\lambda|\,\delta(x)\psi(x,t) = 0 \tag{3.1}$$

By direct substitution we can verify that

$$\psi(x,t) = \sqrt{\frac{|\lambda|}{2}}e^{-\frac{|\lambda|}{2}|x|}e^{i\frac{\lambda^2}{4}t} \tag{3.2}$$

satisfies (3.1).

3.2. Case When $\lambda = 0$.

In this case (2.1) becomes

$$i\frac{\partial\psi}{\partial t} + \frac{\partial^2\psi}{\partial x^2} - xE(t)\psi = 0 \tag{3.3}$$

Taking Fourier transform we obtain from (3.1) the equation

$$i\partial_t\hat{\psi} - \xi^2\psi - iE(t)\partial_\xi\hat{\psi} = 0 \tag{3.4}$$

If we set

$$\hat{\psi} = e^{\varphi} \tag{3.5}$$

then φ satisfies the equation

$$\varphi_t - E(t)\varphi_\xi = -i\xi^2 \tag{3.6}$$

For a sufficiently smooth function of a real variable φ_H we can verify that

$$\Phi(\xi,t,t_0)=\varphi_H(\xi+\int_{t_0}^{t}E(u)du) \tag{3.7}$$

satisfies the homogeneous equation

$$\varphi_t-E(t)\varphi_\xi=0 \tag{3.8}$$

We seek a particular solution for the problem

$$\varphi_t-E(t)\varphi_\xi=-i\xi^2$$

in the form

$$\varphi_p(\xi,t)=a(t)\xi^2+b(t)\xi+c(t) \tag{3.9}$$

We can quickly verify that

$$\begin{aligned} a(t) &= -i(t-t_0)\\ b(t) &= -2i\int_{t_0}^{t}(u-t_0)E(u)du\\ c(t) &= -2i\int_{t_0}^{t}E(r)V(r,t_0)dr, \end{aligned}$$

where

$$V(t,t_0)=\int_{t_0}^{t}(u-t_0)E(u)du$$

Setting

$$W(t,t_0)=\int_{t_0}^{t}E(r)V(r,t_0)dr$$

we can write the general solution of the equation

$$\varphi(\xi,t,t_0)=\Phi(\xi,t,t_0)-i(t-t_0)\xi^2-2i\xi V(t,t_0)-2iW(t,t_0) \tag{3.10}$$

Finally we have (see (3.5))

$$\hat{\psi}=e^{\Phi(\xi,t,t_0)-i(t-t_0)\xi^2-2i\xi V(t,t_0)-2iW(t,t_0)} \tag{3.11}$$

Thus,

$$\psi(x,t)=\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{\Phi(\xi,t,t_0)-i(t-t_0)\xi^2-2i\xi V(t,t_0)-2iW(t,t_0)}e^{i\xi\cdot x}d\xi. \tag{3.12}$$

Setting $t=t_0$ we see that

$$\psi(x,t)=\frac{1}{2\pi}\int_{-\infty}^{\infty}\Phi(\xi,t_0,t_0)e^{i\xi\cdot x}d\xi. \tag{3.13}$$

Thus, we must take

$$e^{\Phi(\xi,t_0,t_0)}=\hat{\psi}(\xi,t_0), \tag{3.14}$$

and

$$e^{\Phi(\xi,t,t_0)}=\hat{\psi}(\xi+\int_{t_0}^{t}E(u)du,t_0), \tag{3.15}$$

4. Solution of the problem

We now consider the equation

$$i\frac{\partial\psi}{\partial t} + \partial_x^2\psi + [|\lambda|\,\delta(x) - xE(t)]\,\psi(x,t) = 0, \tag{4.1}$$

$$\begin{aligned} E(t) &= 0, \quad t \le 0, \\ \psi(x,0) &= \sqrt{\frac{|\lambda|}{2}} e^{\frac{-|\lambda x|}{2}}. \end{aligned}$$

Taking Fourier transform we have

$$i\partial_t\hat{\psi} - \xi^2\hat{\psi} - iE(t)\partial_\xi\hat{\psi} + \frac{|\lambda|}{2\pi}\int_{-\infty}^{\infty}\hat{\psi}(p,t)dp = 0 \tag{4.2}$$

Consider the equation

$$i\partial_t\hat{\psi} - \xi^2\hat{\psi} - iE(t)\partial_\xi\hat{\psi} = \delta(t-t_0) \tag{4.3}$$

Let

$$\hat{\psi}(\xi,t,t_0) = -iH(t-t_0)e^{-i(t-t_0)\xi^2 - 2i\xi V(t,t_0) - 2iW(t,t_0)}\,. \tag{4.4}$$

where H is the Heaviside function. We can verify that the function defined in (4.4) satisfies (4.3).

Let

$$\hat{\Psi}^*(\xi,t) = -\int_{-\infty}^{\infty}\hat{\psi}(\xi,t,s)\frac{|\lambda|}{2\pi}\int_{-\infty}^{\infty}\hat{\psi}(p,s)dp\,ds \tag{4.5}$$

Let

$$\mathcal{L} = -i\partial_t - \xi^2 - iE(t)\partial_\xi \tag{4.6}$$

Then,

$$\mathcal{L}\hat{\Psi}^*(\xi,t) = -\frac{|\lambda|}{2\pi}\int_{-\infty}^{\infty}\hat{\psi}(p,t)dp\,dt \tag{4.7}$$

Taking inverse Fourier transform we have

$$\Psi^*(x,t) = \frac{i\,|\lambda|}{2\pi}\int_{t_0}^{t}\int_{-\infty}^{\infty} e^{-i(t-s)\xi^2 - 2i\xi V(t,s) - 2iW(t,s) + ix\cdot\xi}\psi(0,s)d\xi ds \tag{4.8}$$

Finally, using (3.12), and (4.8) we can give the solution of (4.1) by

$$\begin{aligned} \psi(x,t) &= \frac{1}{2\pi}\int_{-\infty}^{\infty}\hat{\psi}\left(\xi + \int_{t_0}^{t}E(u)du, t_0\right)e^{-i(t-t_0)\xi^2 - 2i\xi V(t,t_0) - 2iW(t,t_0)}e^{ix\cdot\xi}d\xi \\ &\quad + \frac{i\,|\lambda|}{2\pi}\int_{t_0}^{t}\int_{-\infty}^{\infty} e^{-i(t-s)\xi^2 - 2i\xi V(t,s) - 2iW(t,s) + ix\cdot\xi}\psi(0,s)d\xi ds \end{aligned} \tag{4.9}$$

In the problem at hand $t_0 = 0$ and $t_0 = 0$ henceforth.

We use analytic continuation in Fourier-inverting the second integral in (4.9) to rewrite (4.9) as

$$\begin{aligned}\psi(x,t) &= \frac{1}{\sqrt{4\pi\, it}}e^{-2iW(t,0)}\int_{-\infty}^{\infty} e^{\frac{i}{4t}(x-y-2V(t,0))^2}e^{-iy\int_0^t E(u)du}\psi(y,0)dy \\ &\quad + \frac{i\,|\lambda|}{\sqrt{4\pi i}}\int_0^t e^{\frac{i}{4(t-s)}\cdot x^2 - i\frac{V(t,s)}{t-s}\cdot x + i\frac{V^2(t,s)}{t-s} - 2iW(t,s)}\frac{\psi(0,s)}{\sqrt{(t-s)}}ds \qquad (4.10)\end{aligned}$$

We note that $\hat{\psi}(\zeta,0)$ is the Fourier transform of $\sqrt{\frac{|\lambda|}{2}}e^{\frac{-|\lambda|}{2}|x|}$.

If we set $x=0$ in (4.10) we obtain

$$\begin{aligned}\psi(0,t) &= \frac{1}{\sqrt{4\pi\, it}}e^{-2iW(t,0)}\int_{-\infty}^{\infty} e^{\frac{i}{4t}(y+2V(t,0))^2}e^{-iy\int_0^t E(u)du}\psi(y,0)dy \\ &\quad + \frac{i\,|\lambda|}{\sqrt{4\pi i}}\int_0^t e^{i\frac{V^2(t,s)}{t-s} - 2iW(t,s)}\frac{\psi(0,s)}{\sqrt{(t-s)}}ds \qquad (4.11)\end{aligned}$$

Set

$$\mathcal{Q}_\psi(x,t) = \frac{1}{\sqrt{4\pi\, it}}e^{-2iW(t,0)}\int_{-\infty}^{\infty} e^{\frac{i}{4t}(x-y-2V(t,0))^2}e^{-iy\int_0^t E(u)du}\psi(y,0)dy \qquad (4.12)$$

The equation in (4.11) is a Volterra integral equation for $\psi(0,t)$. To simplify our notation we rewrite (4.11) as

$$\psi(0,t) = \mathcal{Q}_\psi(0,t) + \frac{i\,|\lambda|}{\sqrt{4\pi i}}\int_0^t e^{i\frac{V^2(t-s)}{t-s} - 2iW(t,s)}\frac{\psi(0,s)}{\sqrt{(t-s)}}ds \qquad (4.13)$$

At this point we remark that $\psi(y,0)$ in (4.10) equals $\sqrt{\frac{|\lambda|}{2}}e^{\frac{-|\lambda|}{2}|y|}$.

Let $\mathcal{R}(t,s;\lambda)$ be the resolvent kernel for the integral equation (4.13). Then,

$$\psi(0,t) = \mathcal{Q}_\psi(0,t) + \int_0^t \mathcal{R}(t,s;\lambda)\mathcal{Q}_\psi(0,s)ds \qquad (4.14)$$

Now, we see that from (4.10) and (4.14) that $\psi(x,t)$ is completely determined from $\psi(x,0)$.

In (4.10) we can verify that

$$\int_{-\infty}^{\infty}|\psi(x,t)|^2dx = 1. \qquad (4.15)$$

5. Feasibility of dissociation

In this section we investigate the problem of dissociation and the design of corresponding control.

Using (4.10) set

$$U(x,t) = \frac{1}{\sqrt{4\pi\, it}}e^{-2iW(t,0)}\int_{-\infty}^{\infty} e^{\frac{i}{4t}(x-y-2V(t,0))^2}e^{-iy\int_0^t E(u)du}\psi(y,0)dy \qquad (5.1)$$

Next, set

$$\Phi(x,z,t) = e^{-i(z-2V(t,0))\int_0^t E(u)du}\psi(z-2V(t,0)+x,0) \qquad (5.2)$$

Referring to (3.2) let

$$f(x) = \psi(x,0) = \sqrt{\frac{|\lambda|}{2}} e^{-\frac{|\lambda|}{2}|x|}$$

We would like to see what happens to f as a result of the electric field excitation. Using the stationary phase formula we have

$$\begin{aligned} U(x,t) &\sim e^{2iW(t,0)} e^{-i(x-2V(t,0))\int_0^t E(u)du} f(x-2V(t,0)) \\ &\quad + e^{2iW(t,0)} \sum_{k=1}^{\infty} \frac{t^k}{k!} i^k \partial_z^{2k} \Phi(x,z,t))|_{z=0} \end{aligned} \tag{5.3}$$

where $\Phi(x,z,t)$ is given in (5.2). The second integral in (4.10)is bounded by $const.\sqrt{t}$, and when $x \neq 0$, it decreases to zero fast as t tends to zero. To minimize its contribution we have to make t small. Then, to get a shift of the order of 1 we must consider $E(t) \sim \frac{1}{t^2}$. We see this from (5.3) and the fact that

$$V(s,0) = \int_0^s uE(u)du$$

In (5.3) the sum can be explicitly calculated and tends to zero as $t \longrightarrow 0$. We also see from (5.3) that the function f is translated by $2V(t,0)$. Thus, our problem becomes design of the electric field to translate f by a desired amount while minimizing the energy required. Thus, recalling that

$$V(s,0) = \int_0^s uE(u)du$$

we have the following extremum problem

$$\min \int_0^t E^2(s)ds$$

subject to

$$\int_0^t sE(s)ds| \geq \frac{\delta}{2} \tag{5.4}$$

where δ is the desired amount of displacement or separation between the atoms. We notice from (5.4) that the electric field has to be large to achieve the desired displacement. Accepting that reality we would like to do the best we can, i.e., minimize the energy. From the constraint in (5.4) we see that

$$\int_0^t s|E(s)|ds \geq \frac{\delta}{2}$$

Thus

$$\int_0^t E(s)ds \geq \frac{\delta}{2t}$$

Thus, we see that a choice of

$$E(s) = \frac{\delta}{t^2},\ 0 \leq s \leq t \tag{5.5}$$

would accomplish the displacement

$$\int_0^t uE(u)du = \frac{\delta}{2}$$

in the time interval t. Any other electric field $\tilde{E}$ is such that $\tilde{E}^2 > E^2$ somewhere in the interval $(0, t)$. Therefore there should be a mechanism to generate a stronger electric field. Next, using (5.5), we have

$$\int_0^t E^2(s)ds = \frac{\delta^2}{t^3} \tag{5.6}$$

Thus an enormous amount of energy is required to effect a significant displacement of the initial wave distribution in a short time. With E given by (5.5) we note that

$$W(t, 0) = \frac{\delta^2}{6t} \tag{5.7}$$

Thus, the wave function after the application of the electric field $E(s) = \frac{2\delta}{s^2},\ 0 < s \leq t$ for the time interval $(0, t]$, should be moved by an amount approximately equal to δ.

In the following figures the first one (Figure 1) shows the shifting of the modulus of the original wave.

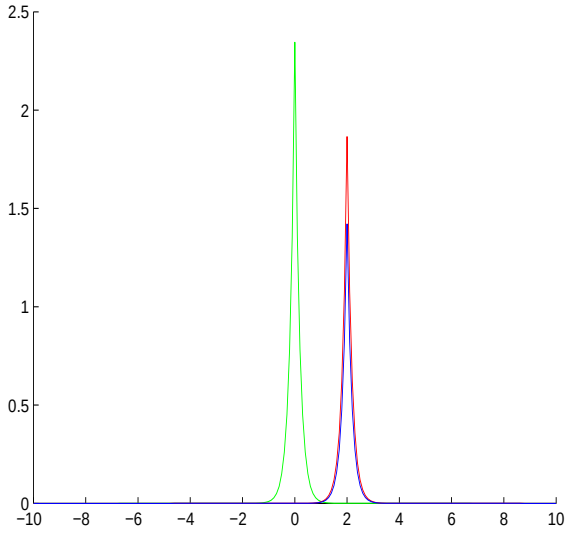

FIGURE 1. Shifting The Original Wave

6. Setting up a corresponding control problem

We saw above that we wish to accomplish the following

$$\min \int_0^t E^2(s)ds$$

subject to

$$\int_0^t sE(s)ds| \geq \frac{\delta}{2}$$

Note that

$$\int_0^t sE(s)ds = tx_1(t) - x_2(t)$$

where

$$x_1(t) = \int_0^t E(s)ds, \quad x_2(t) = \int_0^t x_1(s)ds$$

Note that $x_1(0) = 0$ and $x_2(0) = 0$. This is used in the control problem we consider next. Now we consider the following multiobjective problem

$$\min \int_0^{t_f} E^2(s)ds, \quad \& \quad \min(t_f x_1(t_f) - x_2(t_f) - \delta/2)^2$$

subject to

$$\begin{aligned} \frac{dx_1}{dt} &= E(t) \\ \frac{dx_2}{dt} &= x_1(t) \end{aligned}$$

where $\delta/2$ is the desired displacement of the initial wave function. In the control problem above we have two objective functionals. We create one objective functional by adding them. This control problem is solved by the method steepest descent and the plots of the control $E(t)$ and the Hamiltonian of the control problem J (Figure 2) and displacement of the initial wave function (Figure 3) are shown below. We remark that $E(t)^2$ represents the energy contained in the electric field. In Figure 2 we note that the Hamiltonian J decreases. The Hamiltonian J includes the square of the electric field.

To do a control problem such as the one we have here for a particular diatomic molecule we work in atomic mass units. We need the mass of the atoms, thus the reduced mass, the energy of the bond from which we can approximate the bond length and momentum of the reduced mass.

7. A related abstract problem

Here we present an abstract problem that is related to the problem we just presented. In this abstract formulation we note that the discontinuous potential represents the excitation of the molecule. How can one deal with the discontinuity without losing critical information in an abstract reformulation? We note from the objective function of this abstract formulation it is required to move a wave function to a desired location with a minimal amount of excitation energy. Thus, it is the same problem we presented above. The discontinuous input control in the abstract formulation is handled by introducing operator valued measures. The above detailed

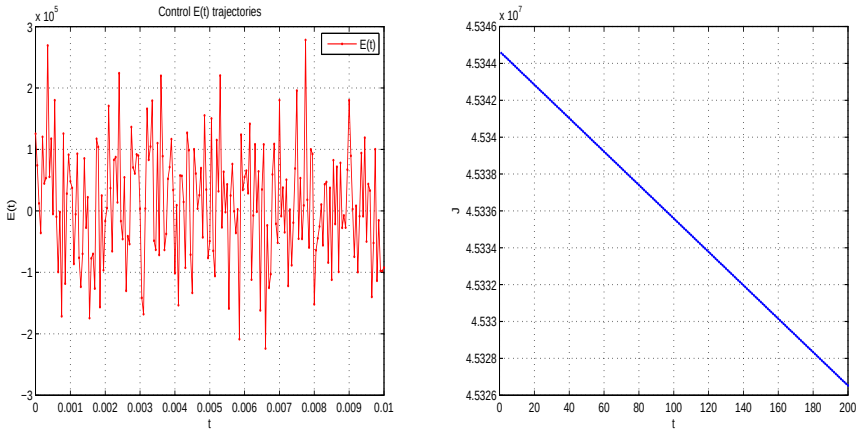

FIGURE 2. Control and corresponding Hamiltonian J

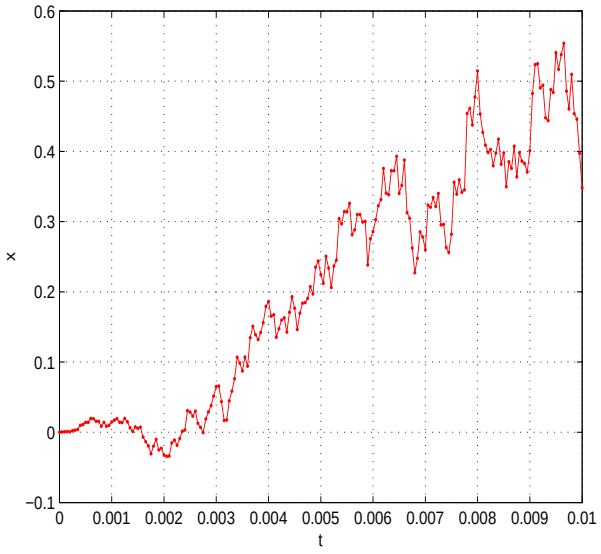

FIGURE 3. Corresponding Size of Shift inThe Original Wave

concrete analysis gives insight into what it takes to deal with the general abstract problem in detail in specific situation, and to what extent the objective in the abstract problem is met. That is, from the concrete problem above we see how the control is related to the excitation energy and what should be the constraints on the size of the control to accomplish a meaningful shift. Equipped with these observations the abstract problem can be formulated even more precisely. The abstract problem we have in mind is dealt with in ([1]) where existence and necessary conditions are established. The verification that best control exists in the abstract formulation assures us the concrete problem is well posed and we just have to make the effort to

get to it.

$$\begin{aligned} i\frac{\partial \phi}{\partial t} &= H_0\phi + v(t)\chi_\Gamma\phi \\ \phi(0,\xi) &= \phi_0(\xi),\ (t,\xi) \in I \times \Omega,\ \ \Gamma \subset \Omega \\ i(d\phi) &= H_0\phi dt + V_0(dt)\phi,\ \phi(0) = \phi_0(\cdot),\ t \in I. \end{aligned}$$

Writing the real and imaginary parts of the wave function $\phi = \phi_1 + i\,\phi_2$ we can model the differential equation on $L_2(\Omega) \times L_2(\Omega)$ as

$$dx = \mathcal{A}xdt + \mathcal{M}(dt)x,\ x(0) = x_0 = (\phi_{0,1},\, \phi_{0,2})$$

$$\mathcal{A} = \begin{pmatrix} 0 & H_0 \\ -H_0 & 0 \end{pmatrix}$$

$$\mathcal{M}(\sigma) = \begin{pmatrix} 0 & V_0(\sigma) \\ -V_0(\sigma) & 0 \end{pmatrix}$$

$$J(\mathcal{M}) = \frac{1}{2}(Q[x(T) - x_d],\, [x(T) - x_d]) + \Phi(\mathcal{M})$$

8. Conclusion

The motion of a diatomic molecule can be separated into a center of mass part and an equivalent one particle part with a reduced mass. The center of mass contribution to the total kinetic energy can be ignored, since it only represents a shift in the total energy of the system. The potential energy depends only upon the separation distance between the atoms.

We can thus consider a one-dimensional equation to represent the motion of a diatomic molecule. In this paper we see precisely, using asymptotic method, how much the original wave function is shifted and the exact relationship with the control and the energy. In addition we saw the asymptotic method was used to set up a control problem that was solved by the method of steepest method. Thus, this model problem gives insight in problems where we have more than two atoms and we want to break a specific bond minimally affecting other bonds. In addition it provides insight into the details of abstract problems of the same spirit.

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