Fifteen years of Quantum Control: from concept to experiment

1 Preamble

In this paper I wish to give an account of the seminal contributions of Mohammed Dahleh to the field of quantum molecular control. Prior to the recognition of the laser field design problem as a control problem, physicists and physical chemists had attempted to design laser fields based on physical intuition. However, due to the complex dynamics of molecules which are most accurately modeled by the Schrodinger equation, it is difficult if not impossible to arrive at intuitive field designs that will achieve the desired objective. By 1985 little progress had been made on the field design process. At that time I was an Applied Mathematics graduate student in the Program in Applied and Computational Mathematics at Princeton University and was working for a physical chemist, Hersch Rabitz, on reaction diffusion problems on catalytic surfaces. From Hersch I became aware of the laser field design problem and discussed this problem with Mohammed, who was a fellow student in the Applied Mathematics Program. Mohammed immediately recognized this problem as a control problem and we agreed to collaborate on a project to formulate the quantum molecular control problem as an optimal control problem, to explore issues of existence of controllers, and to validate the field designs by means of numerical experiments. This project culminated in the publication of our first paper using optimal control in the design of laser fields for quantum molecular control [8]. There followed a plethora of papers which make use of this methodology in the design of more complex molecules than those considered in the initial paper as well as a variety of cost functionals.

Being a control theorist, Mohammed was plagued by the fact that the bilinearity of the control problem, which is legislated by the way in which the laser field acts on the state in the Schrodinger equation, ruled out the possibility of exploiting the results of linear systems theory - which by that time had reached a high level of maturity and sophistication. In addition, having the instincts of a control engineer, Mohammed was alarmed that the only control fields that could be envisaged at the time were of the open loop variety - given that the desired molecular dynamics was expected to be

complete in hundreds of femtoseconds while observation and feedback on this time-scale was impossible. Having ruled out the possibility of feedback design, Mohammed and I proceeded to investigate the possibility of designing open loop controllers that are robust to uncertainties in the molecular Hamiltonian and to perturbations in initial conditions (see [3]). Mohammed also championed an investigation of the controllability of finite level quantum systems using Lie Group methods (see [9]) and proceeded to stimulate an interest in this area in a number of his students (see [2]).

In section 2 I outline the objectives of molecular control and in section 3 describe some of the earlier pre-control attempts at field design. In section 4 I briefly summarize the initial control formulation in which Mohammed's contribution was vital and demonstrate this design procedure for the case of a diatomic molecule - similar to the initial numerical experiments we performed. In section 5 I discuss the extension of this methodology to the design of fields that are robust to variations in initial conditions or to parameter fluctuations. In section 6 I describe a closed-loop design scheme and refer to some of the initial laboratory experiments that have made use of optimal control. I make some concluding remarks in section 7.

2 Molecular control

Since the beginning of alchemy one of the primary goals of chemists has been to stimulate chemical reactions to form desired products. Traditionally these stimuli were applied by changing the global thermodynamic variables such as the temperature and the pressure or by adding the appropriate combination of reagents to achieve desired products. In stimulating such chemical reactions it often happens that only a certain fraction of the reagents combine to form the desired products while the remaining reagents may combine to form a number of unwanted by-products. In addition, there are products that cannot be produced by varying such global control variables. It is, therefore, desirable to search for alternative, more selective, and perhaps more efficient ways to stimulate chemical reactions.

Neighboring atoms within molecules frequently have net opposite charges on them (the water molecule is a typical example), and the dipoles formed by such pairs of atoms act as microscopic "handles" on the molecules. Using applied electric fields it is possible to try to excite the molecules in a desired way. Another possible way to effect chemical reactions is to use stimulated molecular emission to prepare large quantities of molecules in selected states which are inaccessible by simple absorption. Although these new modes of stimuli offer the possibility of more selective excitation, their success depends on being able to determine the correct field to apply in order to achieve the desired objective.

3 Design by intuition

The idea of using electric or optical fields to achieve selective chemistry was not new when Mohammed first learned of the problem in 1985. Indeed, a great deal of research in this area had been done over the previous thirty years. Unfortunately, prior to the application of control theory by Mohammed, the field designs, which were often based on intuition, were largely unsuccessful. For example, if there was a need to break a particular bond within a molecule, then simple intuition would indicate that excitation at the frequency associated with that bond could induce a resonance which would ultimately break the bond. However, due to the coupling between the bond in question and the remainder of the molecule, it is extremely difficult to localize the energy imparted to the molecule within the bond. It is clear that the complicated dynamics and interference structure of the molecule have to be incorporated and perhaps even exploited in the field-design process. These initial attempts were largely unsuccessful in all but the simplest of objectives. Indeed, inspection of the complex structure of the required laser field designs, constructed using control theory, clearly illustrate the limitations of the intuitive field designs - akin to attempting to play a complicated piano concerto with a single finger.

4 The optimal control formulation

By 1985 the field of molecular control was ripe for the introduction of techniques from systems theory. Mohammed's contribution was vital to the introduction of the optimal control formalism in the field of molecular control. In this section I outline the initial formulation that was used in our 1988 paper [3].

Let the spatial domain be $\Omega \in \mathbf{R}^n$ and consider control on a finite time horizon $[0, T]$. Let $X = L_2(\Omega)$, $X_t = L_2(\Omega, [0, T])$, and X_{HS} = the Hilbert Space of Hilbert-Schmidt Operators. The optimal control problem is prescribed by minimizing the following cost functional:

$$J[U] = \left\langle \psi(\cdot, T) - \hat{\psi}(\cdot), Q\left(\psi(\cdot, T) - \hat{\psi}(\cdot)\right)\right\rangle_X + \beta \int_0^T \langle U, U\rangle_{HS}\, ds$$

subject to the dynamics of the Schrodinger equation with a molecular Hamiltonian H_0 :

$$\frac{d\psi}{dt} = -\frac{i}{\hbar}(H_0 + U)\psi, \quad \text{with } \psi(x, 0) = \psi_0(x)$$

over all $U \in X_{HS}$.Here $\hat{\psi} \in X$ is a specified reference state to which we wish to push the final wavefunction $\psi(x, T)$, and $H_0 = -\frac{\hbar}{2m}\nabla^2 + V_0$, and

$U\psi = \int\limits_{\Omega} u(x,x',t)\psi(x',t)dx'$. Introducing the Lagrange Multiplier function $p(x,t)$ we minimize the Lagrangian:

$$L[U;\psi,p] = J[U] + \mathrm{Re}\left\{ \int\limits_0^T \int\limits_{\Omega} p\left(\dot{\psi} + \frac{i}{\hbar}(H_0+U)\psi\right)^* dxdt \right\}$$

where $()^*$ denotes the complex conjugate. By taking Frechet derivatives of $L[U;\psi,p]$ with respect to p, ψ, and U we obtain the following necessary conditions for a minimum:

$$\begin{aligned} IVP: \frac{d\psi}{dt} &= -\frac{i}{\hbar}(H_0+U)\psi, \quad \text{with } \psi(x,0) = \psi_0(x) \\ FVP: \frac{dp}{dt} &= -\frac{i}{\hbar}(H_0+U)p, \quad \text{with } p(x,T) = 2\left\{\hat{\psi}(x) - \psi(x,T)\right\} \quad (1) \\ Gradient: 0 &= \int\limits_0^T \int\limits_{\Omega} \left(2\beta U - \mathrm{Re}(p\frac{i}{\hbar}\psi^*)\right)\delta U dxdt \end{aligned}$$

The initial-final value problems (1) form the basis for a numerical gradient numerical search procedure to locate a minimum. A monotonically convergent algorithm due to Krotov [10] is typically used to search for a minimum.

By exploiting the lower semicontinuity of the norm, the weak closure of the unit ball in L_2, and the regularity of the solution it is possible to prove the following theorem (see [8]):

Theorem 1 *There exists a solution $U \in L_2(X_{HS};[0,T])$ and a corresponding $\psi \in X_t$ that solves the optimization problem.*

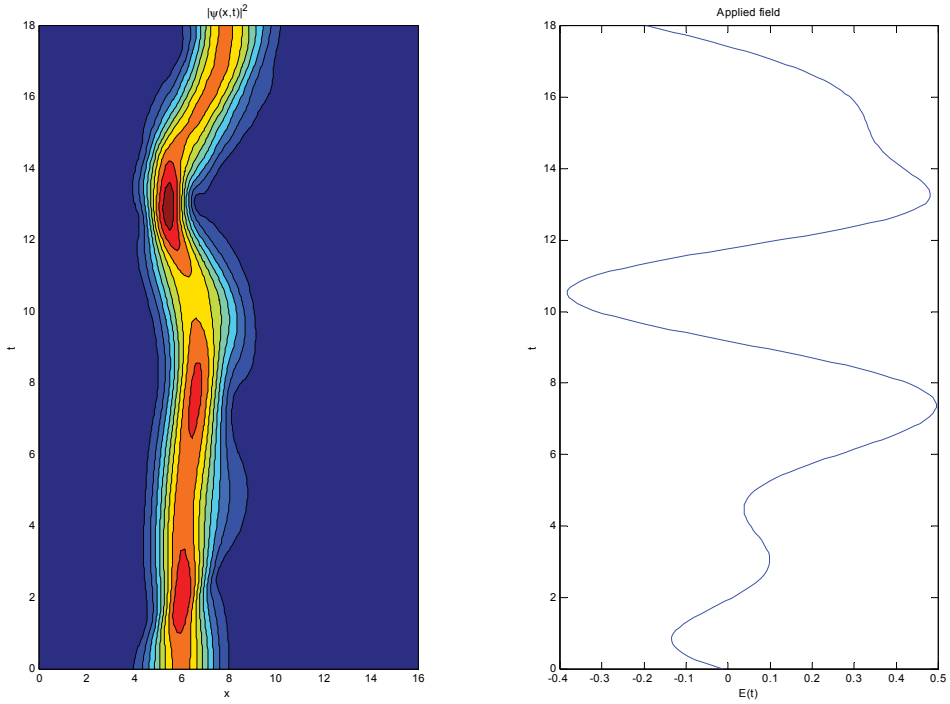
In the following example we demonstrate the control design process for a simple diatomic molecule in which the molecular potential is assumed to be given by the Morse Potential:

$$V_0(x) = D(1 - e^{-\gamma(x-x_0)})^2$$

We assume that $\hbar = 1$, $m = 2$, $D = 10, \gamma = 1/\sqrt{10}$, $T = 18$ and that the initial wavepacket is a Gaussian of unit width centered at $x_0 = 6$ and that the target wavepacket is a Gaussian having the same shape but centered at $\hat{x} = 8$, i.e.:

$$\psi(x,0) = g(x,6,1) \text{ and } \hat{\psi}(x,T) = g(x,8,1) \text{ where } g(x,x',l) = \pi^{-\frac{1}{4}} l^{-\frac{1}{2}} \exp(-\frac{(x-x')^2}{2l^2})$$

In this experiment we assumed that the laser field was of the form $u(x,t) = E(t)B(x) = E(t)(x-x_0)$ so that the dipole moment function $B(x)$ is assumed to be linear.

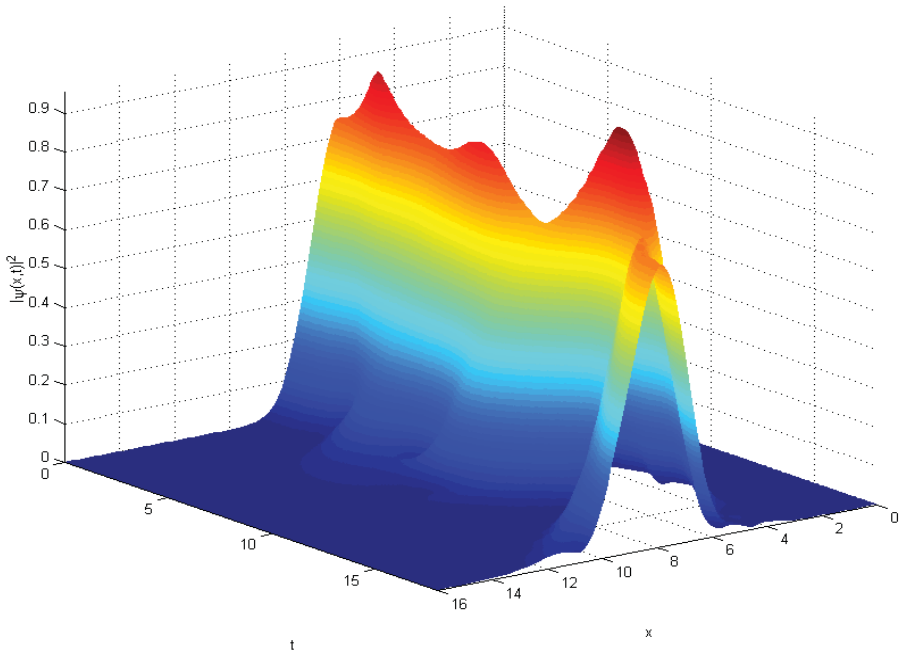


In figure 1 we provide a space-time contour plot of the probability density of the wavepacket $|\psi(x,t)|^2$ juxtaposed with the corresponding electric field $E(t)$:

We observe the complex structure of the field $E(t)$ as well as the corresponding dynamics of the wavepacket as it makes its way to the target state. In figure 2 we provide a 3D plot of the same probability function which is close to the target Gaussian at time $T = 18$.

This formalism was adopted by many subsequent researchers as they endeavoured to design fields to control more complex molecules. Many researchers also used this initial optimal control framework to explore molecular control using semi-classical and even classical molecular models. In principle, this formalism should be adequate to design laser fields for molecules containing any number of atoms. Unfortunately, the number of space dimensions n required in the solution of the Schrodinger equation grows with the number of atoms in a molecule. Thus field designs are severely limited by the computing resources required to solve the initial and final value problems.

x



5 Uncertainty and robust design

Due to the fact that the molecular Hamiltonians for large complex molecules are not known precisely there are likely to be considerable uncertainties in the molecular models used in the design process. Because of these uncertainties and the restriction to open-loop controllers, Mohammed was a strong protagonist for establishing a robust design methodology. In this section I briefly outline the extension of the previous optimal control framework to achieve robust field designs.

One drawback of the optimal design approach used in the work described above is that these controllers are likely to be sensitive to uncertainties in the molecular Hamiltonian and in the initial state of the system. In order to achieve more robust field designs, averaged cost functionals corresponding to those described in the previous section have been considered (see [3]). In particular the optimal control problem involves minimizing the following cost functional:

$$J[U] = E_{\alpha,\psi_0}\left[\left\langle \psi(\cdot,T) - \hat{\psi}(\cdot), Q\left(\psi(\cdot,T) - \hat{\psi}(\cdot)\right)\right\rangle_X\right] + \beta \int_0^T \langle U, U\rangle_{HS}\, ds$$

subject to:

$$\frac{d\psi}{dt} = -\frac{i}{\hbar}(H_0(\alpha) + E(t)B(\alpha))\psi, \quad \text{with } \psi(x,0) = \psi_0(x)$$

Here $E_{\alpha,\psi_0}[\cdot]$ represents the expectation operator. It is possible to define a family of cost propagator operators which make it possible to perform explicit averaging of the cost functionals. These averaged cost functionals do indeed lead to field designs that are demonstrably less sensitive to perturbations in initial conditions or to fluctuations in the parameters of the molecular Hamiltonian.

6 Experiments and closed loop design

At the time of our initial control paper in 1988, the laser fields that could be prepared in the laboratory could only vary on time-scales of tens of picoseconds whereas our calculations indicated that the pulses required to effect the laser control had to vary on time-scales involving tens of femtoseconds. Thus at the time laboratory realization of laser fields to control molecular reactions seemed a remote goal awaiting the development of new technology. However, it did not take very long for the required technology to develop to the point that optimized femtosecond pulses were used to control molecular motion (see [5]).

In a more recent development, laser controllers have been designed by various classes of evolutionary algorithms, which exploit the fact that millions of experiments can be performed in nanoseconds. In these search algorithms, more successful candidate fields are maintained within the candidate population and allowed to share their characteristics with other "more fit" laser fields to yield offspring fields for the next generation (see [4]). In particular a laser field of the following form is assumed:

$$E(t) = Ae^{-\frac{1}{2}(t-\bar{t})^2/\Gamma^2}e^{-i\Phi(t)}, \text{ where } \Phi(t) = \bar{\Phi} + \omega(t-\bar{t}) + \frac{1}{2}b(t-\bar{t})^2 + \dots$$

The unknown parameters in this family of fields $\Gamma, \bar{t}$, ω, b are sought via a genetic or evolutionary algorithm that exploits the huge number of experiments that can be performed without having to model or even characterize the precise dynamics of the molecules.

At the heart of the success of this process, which is termed "learning control", is an elementary form of feedback loop in the design process. Making use of this methodology, numerous experiments have been performed on relatively simple molecules (see [1]) and more recently on complex organic molecules (see [6]). We see that Mohammed's instincts as a control theorist were correct. He believed that a practical control methodology, that would be experimentally viable, would have to incorporate some form of feedback loop. It is interesting that this form of feedback loop does not appear in the standard form associated with classical system theory in which real-time observation of the state is possible.

7 Concluding remarks

Today Quantum Control is an exploding field. This year there were more than five international conferences in Quantum Control. The field has developed along the path originally charted by pioneers like Mohammed. Indeed, the optimal design methodology is still being used to design laser fields for more complex molecules. Optimal controllers have been successfully employed in laboratory experiments. But it is interesting that many of the fundamental questions that Mohammed asked when he entered the field remain open problems today: e.g. a complete characterization of controllability for quantum systems; an input-output description that will make the system more amenable to analysis; a more comprehensive robust design methodology.

The possible technological benefits of this research include: molecular scale surgery to create new molecules; purification of semiconductor materials by selective removal of impurities; super fast computer memory; unprecedented resolution of molecular scale dynamical processes for the extraction of fundamental forces between atoms; high density encoding

and decoding of solid state electron wavepackets for transport of information; and more recently, the use of quantum control to construct the basic building-blocks for quantum computers.

Mohammed's insight provided the spark at the inception of this new area of application of control theory. Mohammed was quick to recognize the major hurdles to progress such as the bilinearity of the control problem, robustness, and open-loop designs. In his inimitable way he stimulated many others to become interested in the topic including some of his students who proceeded to develop many of the theoretical underpinnings of the field. The field is much richer for his profound insights and multiple contributions.

8 Bibliography

9 References

[1] C.J. Bardeen, V.V. Yakovlev, K.R. Wilson, S.D. Carpenter, P.M. Weber and W.S.Warren, "Feedback Quantum Control of Molecular Electronic Population Transfer",Chemical Physics Letters, 280, 151-158 (1997).

[2] D. D'Alessandro and M. Dahleh, "Optimal control of two-level quantum systems", IEEE Transactions on Automatic Control, Vol. 46, No. 6, June 2001, pg. 866-876.

[3] M. Dahleh, A. Peirce, and H. Rabitz, "Optimal Control of Uncertain Quantum Systems", Physical Review A, Vol. 42, No. 3, pp. 1065-1079, August, 1990.

[4] R.S. Judson and H. Rabitz,"Teaching Lasers to Control Molecules", Phys. Rev. Lett., 68, 1500 (1992).

[5] B. Kohler, V.V. Yakovlev, J. Che, J.L. Krause, M. Messina, K. Wilson, N. Schwentner, R.M. Whitnell, Y. Yan, "Quantum control of wave packet evolution with tailored femtosecond pulses", Physical Review Letters, 74, No. 17, 3360-3363, 1995.

[6] R.J. Levis and H. Rabitz, "Closing the Loop on Bond Selective Chemistry Using Tailored Strong Field Laser Pulses", J. Phys. Chem. A, 106, 6427-6444 (2002).

[7] Y. Maday and G.Turiniciy, "New formulations of monotonically convergent quantum control algorithms", 2002 (preprint).

[8] A. P. Peirce, M. Dahleh and H. Rabitz, "Optimal Control of Quantum Mechanical Systems: Existence, Numerical Approximations and Applications", Physical Review A, Vol. 37, No. 12, pp. 4950-4964, 15 June, 1988.

[9] V. Ramakrishna, M. Salapaka, M. Dahleh, H. Rabitz, and A. Peirce, "Controllability of Molecular Systems," Physical Review A, Vol. 51, No. 2, pp. 960-966, 1995.

[10] D. Tannor, V. Kazakov, and V. Orlov, in Time Dependent Quantum Molecular Dynamics, edited by Broeckhove J. and Lathouwers L. (Plenum, 1992), pp. 347{360).