

Control theory applied to Quantum Chemistry: Some tracks.

Claude Le Bris *

May 25, 2000

Abstract

We present a short introduction to the models in use for the simulation of the evolution of a molecular system in the context of Quantum Chemistry. We explain how these models can provide experts at control theory with interesting topics of investigation, and how control theory can in turn be of great usefulness in the modelling of the laser control of chemical reactions. Some tracks for mathematical investigations are indicated.

1 Introduction

Quantum Chemistry aims at understanding the properties of matter through the modelling of its behaviour at the microscopic scale. It is undoubtedly a new field of investigations for applied mathematicians. The story began twenty years ago from a rather theoretical standpoint with the fundamental contributions of E.H. Lieb, B. Simon, H. Brézis and coworkers, and continued with the works of P-L. Lions. A rapid list of the most significant articles in this field should include at least the following [22, 23, 24] (For a complete list, we refer to [5, 11, 12]). To this day, it sounds reasonable to claim that most of the molecular models of Quantum Chemistry are now well understood mathematically and have been carefully analyzed¹. The focus has now turned either towards the side of the study of the condensed phase (*See* [7, 10]), or towards the side of numerical analysis (*See* [25]). However, to the best of the author's knowledge, no applied mathematician has paid attention yet to the richness and variety of problems that can arise from the interplay between control theory and Quantum Chemistry. A large amount of work in this direction has soon been accomplished by eminent chemists such as H. Rabitz and his collaborators (*See* the short review [19] on the optimal control of chemical reactions using laser beams, the works [4, 30, 32, 34, 36, 37, 38] and the references therein), but no mathematician seems to be involved in this scientific adventure. The present article has the modest goal to draw the attention of the community of experts at control theory to some relevant problems of Quantum Chemistry.

*CERMICS, Ecole Nationale des Ponts et Chaussées, 6 & 8 Av. Blaise Pascal, 77455 Champs-sur-Marne, France. lebris@cermics.enpc.fr

¹Of course, some questions (of outstanding difficulty) remain open, but a large body of work has been achieved.

Before we enter (some) technicalities, let us briefly state the problem we shall deal with. Basically, the evolution of a molecular system (all what we will say below can be adapted to more complicated microscopic systems, but for our explanatory treatment, we prefer to restrict ourselves to the simple case of a (small) molecular system) is governed by the time-dependent Schrödinger equation

$$\begin{cases} i\frac{\partial\psi}{\partial t} = H\psi, \\ \psi(0) = \psi^0, \end{cases} \quad (1)$$

where H is the Hamiltonian of the molecular system “at rest”. If we apply to this molecular system a laser field (which will play the role of the “control”), the above equation is modified into

$$\begin{cases} i\frac{\partial\psi}{\partial t} = H\psi + E(t)x_1\psi, \\ \psi(0) = \psi^0, \end{cases} \quad (2)$$

where the (scalar real) electric field $E(t)$ varies in time, the laser being fixed in the x_1 direction, say.

It is noteworthy to already mention that the characteristic length and time of this equation are the atomic ones, namely 1 Angström (10^{-10} m) and 50 femtoseconds ($50 \cdot 10^{-15}$ s).

The purpose of the control by laser can be stated as follows: design the laser field $E(t)$ in such a way that the molecular system attains (exactly, or at least approximately) some given state ψ_T at time $t = T$. In most (but not all) applications, both the initial state and the target state ψ_T are actually steady states of some hamiltonian at rest, H itself or another one (We want to “jump” from a steady state to another one). In addition, let us already make precise that the success of the enterprise is measured in practice by a criterion explicitly involving the scalar product $\langle \psi(T), \psi_T \rangle$ rather than the norm $\|\psi(T) - \psi_T\|$: indeed, we want some projection of the final state to be like this or like that, which amounts to prescribing some symmetry of the final state for instance.

On equation (2), the fundamental properties of the control problems we shall deal with already appear :

- 1** - this is a *bilinear* control problem : the state ψ is multiplied by the control $E(t)$,
- 2** - this is a *distributed-in-time* control : at the length scale of the molecular system, the laser field is seen as a homogeneous field in space, it only varies in time,
- 3** - this is (likely to be) an *open-loop* control : the characteristic time of the process is so small that (at least for today’s technology) it cannot be possible to react as fast as the molecular system (in other words the only system that can react as fast as the molecular system is the molecular system itself), the electric field is set (programmated) in advance, and then the experiment goes.

In the following sections, we shall give some details on the above statements so that the reader may make his own opinion on the feasibility of a mathematical analysis in this framework.

Before we get to the heart of the matter, we believe it is useful to give some basics on the one hand about the models in use in Quantum Chemistry (Section 2 below), and on the other hand on some technical data on laser technology that it is safe to keep in mind (Section 3). We also give there a short overview on the control theory applied to Quantum Chemistry.

In Section 4, we then introduce some time dependent models for a molecular system, and suggest in Section 5 a toy model that can be derived from it and treated as a “test case”. Finally, we draw some conclusions.

2 Basics of Quantum Chemistry

This section is to be seen as a short user’s guide for an expert at control theory that would be curious of knowing more on the models of Quantum Chemistry. A more general and comprehensive introduction can be found for instance in [13, 18, 21, 27, 29, 35]. For the theoretical background coming from Quantum Mechanics, we refer to [20, 26] e.g. We only give here a brief overview of the *stationary* models, without getting into the details nor in the rigorous foundations. The *time dependent* models will be the topic of Section 4. Let us anticipate on that by saying, somewhat formally, that to figure what a time dependent model is reading the following stationary ones is quite intuitive : just insert a partial derivative with respect to time $i\frac{\partial}{\partial t}+$ in front of the stationary operator. Of course, this will be made precise in Section 5.

The flagstone of any molecular modelling is the calculation of the ground state of the molecular system. It consists in the following minimization problem

$$U(\bar{x}_1, \dots, \bar{x}_M) = \inf \{ \langle \psi_e, H_e(\bar{x}_1, \dots, \bar{x}_M) \cdot \psi_e \rangle, \quad \psi_e \in \mathcal{H}_e, \|\psi_e\| = 1 \} \quad (3)$$

where H_e denotes the electronic Hamiltonian

$$H_e(\bar{x}_1, \dots, \bar{x}_M) = - \sum_{i=1}^N \Delta_{x_i} - \sum_{i=1}^N \sum_{k=1}^M \frac{z_k}{|x_i - \bar{x}_k|} + \sum_{1 \leq i < j \leq N} \frac{1}{|x_i - x_j|}. \quad (4)$$

In the above equation, the nuclei are fixed at positions \bar{x}_k , with charge z_k , $a \leq k \leq M$. This is the so-called Born-Oppenheimer approximation, based upon the observation that the nuclei can be treated as classical particles because they are far heavier than the electrons. At this stage, the positions \bar{x}_k are supposed to be known. So far they are only parameters of the electronic problem, but actually they will be optimized afterwards (see below). The normalized wavefunction describing the state of the N electrons typically² belongs to a subspace \mathcal{H}_e of $L_a^2(\mathbb{R}^{3N})$ (the subscript a stands for *antisymmetric* functions because of the Pauli exclusion principle).

²For simplicity, we forget the spin variable.

The above problem, which amounts to finding the smallest eigenvalue in

$$H_e \psi_e = \lambda_e \psi_e \quad (5)$$

is well understood mathematically. However, it cannot be treated in practice. The overwhelming difficulty is twofold. First, the size of the space $L^2(\mathbb{R}^{3N})$ becomes prohibitive even for a small number N of electrons. Second, the so-called bielectronic term $\sum_{1 \leq i < j \leq N} \frac{1}{|x_i - x_j|}$ in (4) increases the complexity of the computations. Consequently, approximations of this exact problem have been developed and numerically simulated.

Basically, the models of Quantum Chemistry that approximate (3)-(4) range in two classes : the class of the Density Functional Theory (DFT) models, and that of the Hartree-Fock (HF) type models.

The idea of the DFT (see [13, 21, 27, 29]) is to replace problem (3)-(4) by a problem set on the electronic density

$$\rho = N \int_{\mathbb{R}^{3(N-1)}} |\psi_e|^2(x, x_2, \dots, x_N) dx_2 \cdots dx_N, \quad (6)$$

which has the advantage to be a function of only 3 variables instead of $3N$. Next, one approximates the energy by a functional of this density ρ (whence the name of the approach). The determination of this approximated energy functional is the topic of many researches in today's theoretical chemistry. Actually, the practical implementation of the DFT resembles that of the Hartree-Fock approximation. Therefore, we shall focus henceforth on that latter approximation, keeping in mind that the mathematical and computational issues are relevant for both approaches.

The Hartree-Fock approximation (see [18, 21, 35]) consists in reducing the complexity of problem (3)-(4) by restricting the test function ψ_e to be of the form of a determinant of N functions of $L^2(\mathbb{R}^3)$ (this is the prototype of a function of $L^2_a(\mathbb{R}^{3N})$). By testing the Hamiltonian (4) on this restricted class of functions, we obtained the Hartree-Fock problem

$$I^{HF} = \inf\{E^{HF}(\varphi_1, \dots, \varphi_N), \varphi_i \in H^1(\mathbb{R}^3), \int_{\mathbb{R}^3} \varphi_i \varphi_j = \delta_{ij}\}, \quad (7)$$

$$E^{HF}(\varphi_1, \dots, \varphi_N) = \sum_{i=1}^N \int |\nabla \varphi_i|^2 - \sum_{i=1}^N \int \left(\sum_{k=1}^M \frac{z_k}{|x_i - \bar{x}_k|} \right) \varphi_i^2 + \frac{1}{2} \iint \frac{\rho(x)\rho(y)}{|x-y|} - \frac{1}{2} \iint \frac{|\rho(x,y)|^2}{|x-y|}, \quad (8)$$

where

$$\rho(x, y) = \sum_{i=1}^N \varphi_i(x)\varphi_i(y), \quad \rho(x) = \rho(x, x). \quad (9)$$

It is easy to see that the Euler-Lagrange Equations associated to (7)-(8) read as the following system of N equations, which is of the form of a (nonlinear) eigenvalue problem

$$\bar{H}_\Phi \phi_i = \lambda_i \phi_i \quad (10)$$

where \bar{H}_Φ is the Hartree-Fock Hamiltonian

$$\bar{H}_\Phi = -\Delta - \sum_{k=1}^M \frac{z_k}{|\cdot - \bar{x}_k|} + \left(\sum_{j=1}^N |\phi_j|^2 \star \frac{1}{|x|} \right) - \sum_{j=1}^N \left(\phi_j \cdot \star \frac{1}{|x|} \right) \phi_j. \quad (11)$$

This system of equations can then be attacked numerically³. Of course, some more sophisticated models⁴ might be constructed upon the basis of this model, but the essential feature is here.

What is obvious in the formulation (8) (and which also applies to DFT type models) is that the price to pay to make from (3)-(4) a numerically tractable problem is *nonlinearity*. This will be one of the main difficulty, which we shall keep in our toy model of Section 5.

As announced above, once the electronic ground state is calculated, many computations remain to be done, such as the determination of the excited states, or the determination of the nuclear configuration $(\bar{x}_1, \dots, \bar{x}_M)$ that yields the minimum total energy $U(\bar{x}_1, \dots, \bar{x}_M)$ (such a process is called geometry optimization). Next, dipolar moments, polarizabilities, and a lot of other physical and chemical properties of the molecular system under study can be evaluated. We refer the reader to our bibliography.

Likewise, for extensions of the models introduced above to the case of the condensed phase, liquid or solid, we refer the reader to [28, 31]. The sequel of this article would apply, *mutatis mutandis*, to the more sophisticated class of models described therein.

3 A rapid introduction to the laser control technology: theory and experiment

The use of laser technology in chemistry goes back to the sixties. Among all the problems that were attacked through this then new technology was the challenge to break a given bond determined in advance in a given molecule. The canonical example is the linear molecule consisting say of 20 atoms, and where we want to

³From the standpoint of the control theory, let us mention that the stationary Hartree-Fock model (7)-(8) gives rise to an interesting (open) question, namely that of the *Optimized Effective Potential* problem: minimize the Hartree-Fock energy (8) over the set of eigenvectors ϕ_i of some Schrödinger operator $-\Delta + V$, and then try to find the optimal V that yields the lowest energy.

⁴Take a *sum* of determinants, ...

break, right in the middle, the ninth bond. The intuitive idea was that it was sufficient to fit the laser frequency on that of the target bond (modelled as an harmonic oscillator, which is common in that framework) to give to this bond a huge amount of energy and therefore finally make it break (such a strategy is called *mode selective chemistry*). The flaw in this argument is that the bonds are actually not independent from one another: consequently, the laser energy does not concentrate on the target bond, but rather spreads over the whole molecule, through the game of interferences. In other words, the design of the convenient laser field is not so obvious, and the intuition fails. The problem has to be set in a control theory language. In addition, the modelling of a chemical reaction can go further than the simple “stationary” image given above : in a simplified view, it is nothing else but the breakings of a few well chosen bonds, but in a more sophisticated manner, we can see it as an evolution in time. Such questions have been attacked by Rabitz and coworkers.

The consequence of the above observation is that the optimal laser field to be used is not necessarily a splendid sine function. It might be much more chaotic (see Figure 1). Typically, what is needed is an electric field that has some given shape at the scale of a few tenth of picosecond. Therefore the question arises as to know what kind of signal can technically be done by lasers. Let us briefly give some insight into this.

Today, lasers available on the commercial market commonly permits pulses whose duration is of the order of one tenth of picosecond. Current research in laboratories is directed towards building lasers that produce impulsions of one hundredth of picosecond (that is 10 femtoseconds). Of course, the shorter the impulsion, the larger the bandwidth : one cannot be too demanding on both items. In terms of power, the short term goal is the Table-Top-Terawatt (10^{12} Watt), and further the Petawatt (10^{15} Watt) in any laboratory. Here again, a compromise has to be made between power and duration: the highest power cannot be emitted during a “long” time.

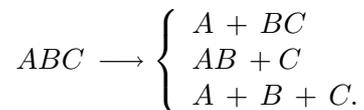
In addition to the duration, the power, and the bandwidth of the impulsion, two other technological data of importance are a) the modulation risetime, that is the time necessary to establish the given shape of the impulsion (one can play with that, for creating a moderate pulse in an extremely short time can be almost as efficient as giving to the system a “slowly” increasing more powerful impulsion) : the typical modulation risetime available today is 5 femtoseconds, b) the repetition frequency, as it is important to be able to make a lot of experiments in a short time⁵; today the frequency ranges from 10 Hertz to one kiloHertz, depending on the power.

Finally, the chemist must establish a trade-off between all these technological constraints in order to choose the most efficient way to proceed.

Experimentally, today’s state of the art of laser control of chemical reactions is still at a very early stage, to the best of the author’s knowledge. The short term

⁵Note that this is (again) a highly uncommon feature of the control theory applied to quantum chemistry : we are here in a framework where we can do plenty of experiments in a minute. This is obviously not the case in other fields of engineering sciences. And this must be taken into account.

goal is to discriminate among the possible ways of dissociation for a molecule, like in



Another goal can for instance be to prevent dissociation of a molecular system (to give it as much energy as possible, and let it release that energy in one go). So far, doing (experimentally) isotopic separation of hydrogen with laser control is possible, and current research is directed towards going further⁶.

On the theoretical side, things are more advanced.

As mentioned above, there is a lot of works devoted to the application of control theory to some models of Quantum Chemistry: [30, 32, 34, 36, 37, 38]. The mathematician will be most inspired by these works. However, some comments are in order.

- 1** - most of the works deal either with optimal control on a very simplified model, or with exact control on a finite dimensional approximation,
- 2** - there seems to be plenty of room for improvement in the mathematical proofs [30], and in the numerical analysis [37],
- 3** - there is a huge discrepancy between the sophistication of the theoretical models that are available for the simulation of the evolution of molecular systems, and the simplified models that are actually used in the theoretical arguments for control theory. Typically, either the Schrödinger equation itself is used, which is technically very limiting because only a “significant” subsystem (of very limited size) of the total system can be considered, or some very crude approximation of the Schrödinger equations is used, which in turn also dramatically reduces the scope of the study.
- 4** - what is probably partially responsible for the observation **3** - is the fact that although a large number of codes are available for the simulation of the steady state of a molecular system and for the associated physico-chemical properties, there are only a few of them whose capabilities include the simulation of time dependent phenomena⁷. In addition, these “rare” code are mostly home-made codes, rather confidential, and not commercial user-friendly worldwide known codes.

⁶More precisely, the chemists usually classify the techniques of control in experimental quantum chemistry into three categories : those of *optimal control* (works by Rabitz and collaborators, these are the ones we focus on), those of *coherent control* (use of more than one single laser in order to create constructive interferences and lead the molecule where desired, works by Brumer and collaborators [4]), and those of *nonlinear control* (use of very intense laser beams, works by Bandrauk and collaborators).

⁷Time-dependent phenomena are mostly approached through the determination of frequencies, and not as such.

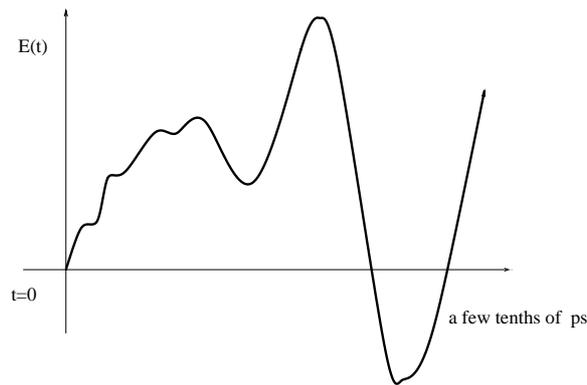


Figure 1: **A typical output of optimal control theory applied to the evolution of a molecular system: the laser field to be used in order to approach the target state.**

5 - apparently, connections seem to be missing between chemists doing the theoretical works and chemists doing the experiments. The fact that oversimplified models are used in the theoretical works and the numerical simulations seem to play some role here, because they are likely to make difficult the comparison between experiment and numerical simulation. Using more sophisticated models could help in that respect.

For all the above reasons, it seems that we mathematicians could try to do something in this field. Of course, the author does not pretend that a mathematical approach (what is more if made by him) will succeed where the chemical somewhat pragmatic approach has failed. But at least it can do no harm.

Before we suggest a way to proceed, let us emphasize the following fact.

In view of the technological data recalled above, there is a legitimate question that can be asked. When we define our mathematical model (2) for the laser control, we shall need to prescribe a class of admissible controls $E(t)$. Then

- 1 - should we stick to reality and consider in our class of mathematical admissible fields $E(t)$ only fields that are feasible by today's state of the art of the laser technology (indeed, this is often a critics made to the theoretician that he must take into account the constraints of the real life), or
- 2 - should we extend the class of admissible controls to electric fields that we definitely know to be unrealistic today ?

It turns out that both choices are correct and useful. As it might seem unclear for the second choice, let us emphasize that one useful output of a theoretical control approach in this context could be a significant help in the design of the next generation of lasers, or more generally on the next generation of devices used in laser technology. Indeed, it is somewhat difficult, without disposing of any concrete need and without formulating it in precise statements, to give directions and anticipate for the need of lasers. Saying "for the application we have in mind, we would need

to generate an electric field of the following shape, within the following risetime” would therefore provide some help in that respect.

In other words, the situation is such that we can feel free on the theoretical side, and this is good news.

4 Towards more sophisticated models: Approximations of the time-dependent Schrödinger equation for molecular systems

We consider a chemical system consisting of M nuclei and of N electrons. Denoting by m_k the mass of the k -th nucleus and z_k its charge, the “exact” non-relativistic Hamiltonian reads

$$\begin{aligned}
 H = & - \sum_{k=1}^M \frac{1}{m_k} \Delta_{\bar{x}_k} - \sum_{i=1}^N \Delta_{x_i} - \sum_{i=1}^N \sum_{k=1}^M \frac{z_k}{|x_i - \bar{x}_k|} \\
 & + \sum_{1 \leq i < j \leq N} \frac{1}{|x_i - x_j|} + \sum_{1 \leq k < l \leq M} \frac{z_k z_l}{|\bar{x}_k - \bar{x}_l|}.
 \end{aligned} \tag{12}$$

The first term in the Hamiltonian H represents the kinetic energy of the nuclei, the second term that of the electrons, the third term the attraction between electrons and nuclei, the fourth and the fifth terms the interelectronic and the internuclear repulsions respectively. To write this Hamiltonian, all the physical constants have been set to one for simplicity. The space of the physical states is a tensor product of the subspaces \mathcal{H}_n and \mathcal{H}_e of the nuclear and electronic wave functions. For chemical systems made up of more than two or three particles, the problem of solving directly equation (1) with the Hamiltonian H given by (12) is of too much a large size to be directly tackled by standard numerical methods and it is then necessary to approximate it.

4.1 The adiabatic approximation

A standard approximation method is the so-called adiabatic approximation. Briefly speaking, it consists in getting rid of the fast dynamics of the electrons by assuming that at any time the electrons are in the electronic ground state, which of course depends on the time *via* the nuclear coordinates. In some cases, the adiabatic approximation means that the electrons remain in the k -th excited state, k being independent of time, but for simplicity, we shall only deal here with the ground state. More precisely, the nuclei are assumed to interact with the electrons through the potential

$$U(\bar{x}_1, \dots, \bar{x}_M) = \inf \{ \langle \psi_e, H_e(\bar{x}_1, \dots, \bar{x}_M) \cdot \psi_e \rangle, \psi_e \in \mathcal{H}_e, \|\psi_e\| = 1 \} \tag{13}$$

where H_e denotes the electronic Hamiltonian

$$H_e(\bar{x}_1, \dots, \bar{x}_M) = - \sum_{i=1}^N \Delta_{x_i} - \sum_{i=1}^N \sum_{k=1}^M \frac{z_k}{|x_i - \bar{x}_k(t)|} + \sum_{1 \leq i < j \leq N} \frac{1}{|x_i - x_j|}. \quad (14)$$

Next, the nuclear motion is treated either as a quantum problem

$$i \frac{\partial \psi_n}{\partial t} = H_n \psi_n \quad (15)$$

with

$$H_n = - \sum_{k=1}^M \Delta_{\bar{x}_k} + U(\bar{x}_1, \dots, \bar{x}_M) + \sum_{1 \leq k < l \leq M} \frac{z_k z_l}{|\bar{x}_k - \bar{x}_l|}, \quad (16)$$

or as a semi-classical problem, or also, which is most frequently the case, as a classical problem. In the latter case, the system reads

$$\begin{cases} m_k \frac{d^2 \bar{x}_k}{dt^2}(t) = -\nabla_{\bar{x}_k} \left(U(\bar{x}_1(t), \dots, \bar{x}_M(t)) + \sum_{1 \leq l < m \leq M} \frac{z_l z_m}{|\bar{x}_l - \bar{x}_m|} \right) \\ U(\bar{x}_1, \dots, \bar{x}_M) = \inf \{ \langle \psi_e, H_e(\bar{x}_1, \dots, \bar{x}_M) \cdot \psi_e \rangle, \quad \psi_e \in \mathcal{H}_e, \|\psi_e\| = 1 \} \end{cases} \quad (17)$$

The adiabatic approximation is in fact the generalization of the Born-Oppenheimer approximation to a time-dependent setting.

In practice, the minimization problem (13) has to be approximated, as in the time-independent case, by one of the standard (Hartree-Fock [18] or Density Functional [13]) method. The quantum nature of the problem is completely enclosed in the potential U . The rest of the problem is a matter of classical dynamics for the nuclei moving along the hypersurface of energy (see the connected theory of chemical reaction paths in [14]). However, problem (17) remains very time-consuming since a time-independent minimization problem has to be solved for each time step in order to compute ∇U . A possibility is to make an additional approximation first introduced by Car and Parrinello [9]: it consists in replacing the minimization problem by a fictitious (non-physical) electronic dynamics which makes the electronic wave function evolve in the neighbourhood of the adiabatic state. From a mathematical point of view, the Car-Parrinello method is investigated in [3]. All the models described so far can be attacked in a control theory approach. Nevertheless, we prefer to concentrate on another type of models, to which we now turn.

4.2 A non-adiabatic approximation

Unfortunately, the adiabatic approximation is not always valid. When a time-dependent electric field is turned on, the electrons do not stay in a well-defined Born-Oppenheimer energy surface, for this perturbation induces *a priori* transitions in the electronic spectrum. Adaptations of the adiabatic models can indeed be made, but in order to deal with such situations, the following approximation method is often used. Firstly, the nuclei are considered as classical point particles. In the sequel, this is referred to as the point nuclei approximation. Like that of the Born-Oppenheimer approximation, the physical justification of the point nuclei approximation comes from the fact that nuclei are much heavier than electrons. Consequently, the quantum nature of the nuclei can be neglected with good reason in most applications⁸. The point nuclei approximation is almost always valid in Chemistry: the state of the system is then described at time t by

$$\left(\left\{ \bar{x}_k(t), \frac{d\bar{x}_k}{dt}(t) \right\}_{1 \leq k \leq M}, \psi_e(t) \right) \in \mathbb{R}^{6M} \times \bigwedge_{i=1}^N L^2(\mathbb{R}^3, \mathbb{C}^2), \quad (18)$$

where $\bar{x}_k(t)$ and $\frac{d\bar{x}_k}{dt}(t)$ denote respectively the position and the speed of the k -th nuclear at time t and where $\psi_e(t)$ denotes the electronic wave function at time t . The motion of the electrons is controlled by the electronic Schrödinger equation

$$i \frac{\partial \psi_e}{\partial t} = H_e(t) \psi_e, \quad (19)$$

where the electronic Hamiltonian reads

$$H_e(t) = - \sum_{i=1}^N \Delta_{x_i} - \sum_{i=1}^N \sum_{k=1}^M \frac{z_k}{|x_i - \bar{x}_k(t)|} + \sum_{1 \leq i < j \leq N} \frac{1}{|x_i - x_j|} \quad (20)$$

Note that $H_e(t)$ acts on the electronic variables only; the nuclear coordinates $\bar{x}_k(t)$ are parameters. Chemical reactions are then described by the system consisting of (19) together with

$$m_k \frac{d^2 \bar{x}_k}{dt^2}(t) = -\nabla_{\bar{x}_k} W(t; \bar{x}_1(t), \dots, \bar{x}_M(t)) \quad (21)$$

where

$$W(t; \bar{x}_1, \dots, \bar{x}_M) = - \sum_{k=1}^M \int_{\mathbb{R}^3} \frac{z_k \rho(t, x)}{|x - \bar{x}_k|} dx + \sum_{1 \leq k < l \leq M} \frac{z_k z_l}{|\bar{x}_k - \bar{x}_l|}. \quad (22)$$

⁸Again, not *all* applications, but we need to be schematic.

and

$$\rho(t, x) = N \int_{\mathbf{R}^{3(N-1)}} |\psi_e|^2(t, x, x_2, \dots, x_N) dx_2 \cdots dx_N$$

denotes the electronic density. The above two equations mean that each nucleus moves according to the Newton dynamics in the electrostatic potential created by the other nuclei and by the mean electronic density ρ .

The point nuclei approximation enables one to deal with the nuclear part of the system. Now, as in the time-independent setting, the electronic Schrödinger equation cannot be solved directly and additional approximations are necessary.

A possibility we shall focus on is to use the Hartree-Fock approximation: it consists in forcing the wave function to move on the manifold

$$\mathcal{A} = \left\{ \psi_e(x_1, \dots, x_n) = \frac{1}{\sqrt{N!}} \det(\phi_i(x_j)), \phi_i \in H^1(\mathbf{R}^3, \mathbf{C}), \int_{\mathbf{R}^3} \phi_i \cdot \phi_j^* = \delta_{ij} \right\} \quad (23)$$

of \mathcal{H}_e and in replacing equation (19) by the stationarity condition for the action

$$\int_0^T \langle \psi_e(t), (i\partial_t \psi_e(t) - H_e(t)\psi_e(t)) \rangle dt. \quad (24)$$

The associated Euler-Lagrange equations [26] read

$$i \frac{\partial \phi_i}{\partial t} = \bar{H}_\Phi \phi_i + \sum_{j=1}^N \lambda_{ij} \phi_j \quad (25)$$

with

$$\bar{H}_\Phi = -\Delta - \sum_{k=1}^M \frac{z_k}{|\cdot - \bar{x}_k|} + \left(\sum_{j=1}^N |\phi_j|^2 \star \frac{1}{|x|} \right) - \sum_{j=1}^N \left(\phi_j^* \cdot \star \frac{1}{|x|} \right) \phi_j. \quad (26)$$

We draw the reader's attention on the fact that, again, this approximation has created nonlinearity.

The system under study couples the electronic Hartree-Fock evolution equation with the nuclear dynamics and reads⁹:

⁹Let us notice that in calculations on large biological systems, the chemical system under consideration is sometimes split into two parts, the first one being computed with Quantum Mechanics, the other one with Classical Mechanics. The system obtained then is of the same form as (27).

$$\left\{ \begin{array}{l} i \frac{\partial \phi_i}{\partial t} = -\Delta \phi_i - \sum_{k=1}^M \frac{z_k}{|\cdot - \bar{x}_k(t)|} \phi_i + \left(\sum_{j=1}^N |\phi_j|^2 \star \frac{1}{|x|} \right) \phi_i - \sum_{j=1}^N \left(\phi_j^* \phi_i \star \frac{1}{|x|} \right) \phi_j \\ m_k \frac{d^2 \bar{x}_k}{dt^2}(t) = -\nabla_{\bar{x}_k} W(t; \bar{x}_1(t), \dots, \bar{x}_M(t)) \\ \phi_i(0) = \phi_i^0, \quad \bar{x}_k(0) = \bar{x}_k^0, \quad \frac{d\bar{x}_k}{dt}(0) = \bar{v}_k^0. \end{array} \right. \quad (27)$$

with

$$W(t; \bar{x}_1, \dots, \bar{x}_M) = - \sum_{k=1}^M \sum_{i=1}^N \langle \phi_i(t) | \frac{z_k}{|\cdot - \bar{x}_k|} | \phi_i(t) \rangle + \sum_{1 \leq k < l \leq M} \frac{z_k z_l}{|\bar{x}_k - \bar{x}_l|}. \quad (28)$$

Incidentally, let us mention that a lot of theoretical work remains to be done concerning the rigorous foundations of the time-dependent models above. Although, we have plenty of information at our disposal (mainly asymptotic limits) to understand to which extent the stationary models of Quantum Chemistry approximate the stationary Schrödinger equation, we miss such results in the time dependent setting.

5 A toy model

Taking only one electronic wavefunction and one nucleus in the above system (27) leads to the following simpler system:

$$\left\{ \begin{array}{l} i \frac{\partial \phi}{\partial t}(t, x) = -\Delta \phi(t, x) + V(x - \bar{x}(t)) \phi(t, x) + \left(|\phi|^2 \star \frac{1}{|x|} \right) (t, x) \phi(t, x) \\ m \frac{d^2 \bar{x}}{dt^2}(t) = \langle \phi(t) | \nabla V(\cdot - \bar{x}(t)) | \phi(t) \rangle \\ \phi(0, \cdot) = \phi^0, \quad \bar{x}(0) = \bar{x}^0, \quad \frac{d\bar{x}}{dt}(0) = \bar{v}^0, \end{array} \right. \quad (29)$$

where $V(x) = -\frac{Z}{|x|}$ (Z being given).

Understanding the mathematical properties of this latter system is enough to completely understand that of the original system (27). A complete study of the Cauchy problem for (29) has been given in [6]. The case when the molecular system is subjected to an electric field has also been studied, therefore preparing the groundwork for a study of the laser control in this setting. In fact, system (29) may be further simplified into

$$\left\{ \begin{array}{l} i \frac{\partial \phi}{\partial t}(t, x) = -\Delta \phi(t, x) - \frac{Z}{|x|} \phi(t, x) + \left(|\phi|^2 \star \frac{1}{|x|} \right) (t, x) \phi(t, x) \\ \phi(0, \cdot) = \phi^0, \end{array} \right. \quad (30)$$

where we get rid of the moving nucleus and replace it by a fixed one at the origin. Although system (29) and system (30) do not exactly exhibit the same mathematical properties (the conservation law for energy is slightly different), we believe it is enough for a first step to understand the control problem on the toy model (30). In [8], we therefore investigate the following optimal control problem that we formulate somewhat vaguely here : let us be given some final time T , some constant $\alpha > 0$, some initial state $\psi^0(\cdot)$ and some target state $\psi_T(\cdot)$, both living, at least, in $L^2(\mathbb{R}^3)$,

$$\begin{aligned} &\text{Find some electric field } E(t), \text{ minimizing} \\ &\inf\{\|\psi(t = T, \cdot) - \psi_T(\cdot)\|^2 + \alpha\|E(\cdot)\|^2\} \end{aligned} \tag{31}$$

where $\psi(t = T, \cdot)$ is value at time $t = T$ of the solution to

$$\begin{cases} i\frac{\partial\phi}{\partial t}(t, x) = -\Delta\phi(t, x) - \frac{Z}{|x|}\phi(t, x) + \left(|\phi|^2 \star \frac{1}{|x|}\right)(t, x)\phi(t, x) \\ \phi(0, \cdot) = \phi^0. \end{cases} \tag{32}$$

$$+E(t)x_1\phi(t, x)$$

One may find in equation (32) the general difficulties of the type of problems we consider : the equation is nonlinear, nonlocal, and features a potential that is both locally singular and long ranged. We therefore believe that a complete study of this question will give some valuable insight into the more general problem of control. Needless to say, other simplified “model” problems could as well be considered.

6 Conclusion

In our opinion, Quantum Chemistry is an unexplored field for experts at Control Theory that is worthwhile investigating.

Having in mind the applications related to the laser control of chemical reactions, we have given a short (not exhaustive) list of time dependent models, concentrating on the time-dependent Hartree-Fock model, that seems to us the most interesting. However, in this list and in the models mentioned in the numerous references we have given¹⁰, the reader can pick out any model and study it from the control theory standpoint : such a study will certainly give some precious insight into the whole hierarchy of models. Anyhow, the community of applied mathematicians can benefit from the studies made by chemists on these topics.

In the variety of models that can be used to simulate the evolution of a molecular system (or more generally the interaction of molecular systems through chemical reactions), it is crucial to understand questions such as the following one. Should we *approximate* the “exact” Schrödinger equation by some numerically tractable theoretical model, *then* apply the machinery of control theory to this model, and finally get into the numerics, or should we proceed the other way round, applying the

¹⁰why not use a molecular dynamics model like those of [15, 17, 33], coupled with a quantum model for the reactive part of the system, if necessary?

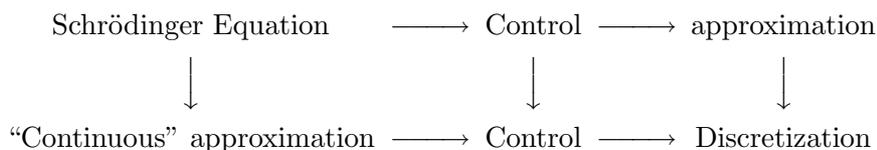


Figure 2: Some possible ways to proceed, amongst others.

control theory to the *exact* Schrödinger equation, and *next* try to approximate things, continuously and then numerically¹¹ (See Figure 2)? Of course, many intermediate ways can alternatively be followed ...

We have concentrated on purpose on the theoretical aspects of control theory applied to quantum chemistry. However, a companion article could be written, the focus being this time on the computational aspects. Indeed, the numerical optimization problems are numerous and interesting in Quantum Chemistry. They are not all issued from an optimization related to an optimal control problem for the laser control of chemical reaction: they also arise in other contexts. In any case, they exhibit some very peculiar features, that can be either advantages or disadvantages from the practical viewpoint. To mention just one feature, let us say that in Quantum Chemistry, the gradient of the energy with respect to some parameters of the problem (like the positions of nuclei) often admits an explicit analytic expression, which rarely occurs in the everyday life of engineering sciences ! Special algorithms have to be used or designed, taking benefit of such a feature, and of other ones of the same peculiarity. This makes Quantum chemistry also a rich field of investigation for researchers interested by such computational issues.

In addition, we have concentrated on the *optimal* control problem, mainly because we believe the exact controllability question to be too difficult. Even in the most “simple” cases [1], bilinear control is quite an achievement. However, there may be some simplified problems, for instance corresponding to finite dimensional approximations of the PDE, where that question could be tractable.

Likewise, other questions of interest such as robustness issues (*See* [38]) may be addressed.

The author strongly encourages the interested reader to contact him. Any suggestion or comment is welcome and will receive his best attention.

Acknowledgements : In the preparation of this work, the author has greatly benefited from enlightening discussions with J.-M. Coron, O. Kaviani, J.-P. Puel, and E. Zuazua.

References

- [1] J. M. Ball & M. Slemrod, *Feedback stabilization of distributed semilinear control system*, Appl. Math. Optim., 5, pp 169-179, 1979.

¹¹Obviously, we prefer the first strategy which we suspect to be more efficient...

- [2] F. A. Bornemann, P. Nettersheim and Ch. Schütte, *Quantum-classical molecular dynamics as an approximation to full quantum dynamics*, J. Chem. Phys. 105 (1996) 1074-1083
- [3] F.A. Bornemann and Ch. Schütte, *A mathematical investigation of the Car-Parrinello method*, Konrad-Zuse-Zentrum für Informationstechnik Berlin, Preprint SC 96-19 (1996)
- [4] P. Brumer and M. Shapiro, *Laser control of chemical reactions*, Scientific American, March 1995, 34-39.
- [5] E. Cancès, M. Defranceschi & C. Le Bris, *Some recent mathematical contributions to Quantum Chemistry*, International Journal of Quantum Chemistry, 74, pp 553-557, 1999.
- [6] E. Cancès and C. Le Bris, *On the time-dependent Hartree-Fock equations coupled with a classical nuclear dynamics*, Mathematical Models and Methods in Applied Sciences, 9, 7, pp 963-990, 1999.
- [7] E. Cancès, *Simulation moléculaire et effets d'environnement : une perspective mathématique et numérique*, Thèse de l'Ecole Nationale des Ponts et Chaussées, 1998.
- [8] E. Cancès, C. Le Bris & M. Pilot, work in preparation.
- [9] R. Car and M. Parrinello, *Unified approach for molecular dynamics and density functional theory*, Phys. Rev. Letters 55 (1985) 2471-2474
- [10] I. Catto, C. Le Bris & P-L. Lions, *Mathematical Theory of Thermodynamic Limits : Thomas-Fermi type models*, Oxford University Press, 1998.
- [11] M. Defranceschi & C. Le Bris, *Computing a molecule : A mathematical viewpoint.*, J. Math. Chem., 21, 1997, pp 1-30.
- [12] M. Defranceschi & C. Le Bris, *Computing a molecule in its environment : A mathematical viewpoint.*, Int. J. Quant. Chem., 71, pp 227-250, 1999.
- [13] R.M. Dreizler and E.K.U. Gross, **Density functional theory**, Springer-Verlag, 1990.
- [14] M. J. Field, *The simulation of chemical reactions*, in **Computer simulations of biomolecular systems**, vol.2, W.F. van Gunsteren et al. Eds., ESCOM, 1993.
- [15] D. Frenkel & B. Smit, **Understanding molecular simulation**, Academic Press, 1996.
- [16] G.A. Hagedorn, *A time-dependent Born-Oppenheimer approximation*, Commun. Math. Phys. 77 (1980) 77-93
- [17] J. M. Haile, **Molecular dynamics simulation**, Wiley, 1992.
- [18] W.J. Hehre, L. Radom, P.v.R. Schleyer and J.A. Pople, **Ab initio molecular orbital theory**, J. Wiley and Sons, 1986

- [19] Mei Kobayashi, *Mathematics make molecules dance*, SIAM NEWS, 24, November 1998.
- [20] L. Landau and E. Lifchitz, **Quantum Mechanics: non-relativistic theory**, 3rd edition, Pergamon Press, 1977
- [21] I.N. Levine, **Quantum Chemistry**, 4th edition, Prentice Hall, 1991.
- [22] E.H. Lieb and B. Simon, *The Hartree-Fock theory for Coulomb systems*, Commun. Math. Phys. 53 (1977) 185-194
- [23] E. H. Lieb, *Thomas-Fermi and related theories of atoms and molecules*, Rev. Mod. Phys., 53, 4, 1981, pp 603-641.
- [24] P.L. Lions, *Solutions of Hartree-Fock equations for Coulomb systems*, Comm. Math. Phys., 109 (1987), p 33-97.
- [25] Y. Maday & G. Turinici, work in progress.
- [26] R. McWeeny, **Methods of molecular quantum mechanics**, 2nd edition, Academic Press, 1992
- [27] N.H. March, **Electron density theory of atoms and molecules**, Academic Press, New-York, 1989.
- [28] G. Naray-Szábo and A. Warshet, **Computational approaches to biochemical reactivity**, Kluwier 1997.
- [29] R.G. Parr & W. Yang, **Density-functional theory of atoms and molecules**, Oxford University Press, Oxford & New York, 1989.
- [30] A. Peirce, M. Dahleh & H. Rabitz, *Optimal control of quantum mechanical systems: existence, numerical approximations and applications*, Phys. Rev. A, 37, p 4950, 1988.
- [31] C. Pisani (Ed.), **Quantum Mechanical Ab Initio Calculation of the properties of crystalline materials**, 67, Lecture Notes in Chemistry, Springer, 1996.
- [32] V. Ramakrishna, et al. *Controllability of molecular systems*, Phys. Rev. A, 51, 2, p 960-966, 1995.
- [33] D.C. Rapaport, **The art of molecular dynamics simulation**, Cambridge University Press, 1995.
- [34] S. Shi, A. Woody, H. Rabitz, *Optimal control of selective vibrational excitation in harmonic linear chain molecules*, J. Chem. Phys, 88, pp 6870-6883, 1988.
- [35] A. Szabo & N.S. Ostlund, **Modern quantum chemistry: an introduction to advanced electronic structure theory**, Macmillan, New-York, 1982.
- [36] W.S. Warren, H. Rabitz and M. Dahleh, *Coherent control of quantum dynamics: the dream is alive*, Science 259 (1993) 1581-1589

- [37] W. Zhu & H. Rabitz, *A rapid monotonically convergent iteration algorithm for quantum optimal control over the expectation value of a positive definite operator*, J. Chem. Phys., 109, 2, p 385-391, 1998.
- [38] H. Zhang & H. Rabitz, *Robust optimal control of quantum molecular systems in the presence of disturbances and uncertainties*, Phys. Rev. A, 49, 4, p 2241-2254, 1994.