



Quantum control of the coupled motion of electrons and nuclei

Samrit Mainali

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Quantum control of the coupled motion of electrons and nuclei

Contrôle quantique des dynamiques couplées électrons-noyaux

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Titre : Contrôle quantique des dynamiques couplées électrons-noyaux

Mots clés : Contrôle laser, Intersections coniques, Cohérence, Molécules polyatomiques, Relaxation, MCTDH

Résumé : Les processus ultra rapides comme le transfert non-radiatif et la photodissociation ont un fort impact sur la redistribution de l'énergie dans les molécules après irradiation par la lumière. Ces processus d'une importance fondamentale impliquent souvent une intersection conique (le cas extrême de la situation hors Born-Oppenheimer), comme dans le système qui nous intéresse, la pyrazine, une molécule complexe avec 24 modes de vibration. Ainsi, le paquet d'ondes une fois excité se scinde en deux (ou plus) composantes selon le nombre d'états électroniques impliqués dans cette intersection (ici deux). Notre objectif est d'utiliser des lasers pour guider et même visualiser les paquets d'ondes, c'est-à-dire l'évolution quantique du système, dans les directions préférentielles. L'impact de l'intersection conique est également très important en chimie traditionnelle et dans les réactions biologiques pour déclencher des processus très import-

ants tels que la vision ou la photosynthèse. Nous utilisons une approche variationnelle basée sur des paquets d'ondes implémentée dans le logiciel appelé MCTDH (Multi Configuration Time Dependent Hartree) que nous utilisons. Cet algorithme, développé par nos collègues allemands, peut servir d'outil essentiel pour comprendre la dynamique moléculaire sous-jacente à de nombreux phénomènes physiques se produisant à une échelle de temps ultra-rapide. Partant d'un simple hamiltonien impliquant 2 modes normaux, la robustesse et l'efficacité de différentes stratégies de contrôle du transfert d'énergie à travers l'intersection conique ont été vérifiées par une augmentation systématique de la dimension: 4 modes normaux et une comparaison finale avec des simulations à 24 modes normaux. Nous simulons les populations et les cohérences électroniques.

Title : Quantum control of the coupled motion of electrons and nuclei

Keywords : Laser control, Conical Intersections, Coherence, Polyatomic molecules, Relaxation, MCTDH

Abstract :

The ultra fast processes like radiation-less transfer and photo dissociation have a strong impact on energy redistribution after irradiation of molecules by light. These processes of fundamental importance often involve a conical intersection (the extreme case of non Born-Oppenheimer situation), like in our system of interest, pyrazine, a complex molecule with 24 vibrational modes. Thus, the wave packet once excited is bifurcated into two (or more) components depending on the number of electronic states involved in this intersection (here two). Our goal is to use lasers to guide and indeed, visualize the wave packets, i.e. the quantum evolution of the system, in the preferred directions. The impact of conical intersection is also very important in traditional chemistry and in biological reactions to trigger very important processes such as vision or photosynthesis. We use a variational approach of

wavepackets implemented in the software called MCTDH (Multi Configuration Time Dependent Hartree) we are using. This algorithm, developed by our German colleagues, could serve as an essential tool for understanding the molecular dynamics underlying many physical phenomena occurring in an ultrafast time scale. Started with a simple Hamiltonian involving 2 normal modes, the robustness and efficiency of different strategies of control of the energy transfer through the conical intersection have been verified by systematic increase of dimensions to 4 normal modes and a final comparison to 24 normal modes. We simulate the electronic populations and coherences.

Abstract:

The main objective of this study is to numerically simulate, and control different molecular processes at their natural time scales. To do this, we solve the time-dependent Schrödinger equation, including the electronic and nuclear degrees of freedom. Those coupled equations become extremely difficult to solve, even for small molecular systems: Curse of dimensionality. Here, the idea is to go well beyond this problem. It is thus, a question of high dimensionality. Why ? It is because we wish to see if we always have a good amount of quantum effects (like coherence, interference etc.) preserved or not. What role, will successively added modes play, in our model? What about the dissipation and decoherence ? These quantum effects are not possible to deal with classical simulations, the reason why we rely on quantum simulation. Since the beginning of laser, it has been a dream of the scientists in the field of atomic and molecular physics, to be able to control these molecular processes of fundamental interest (for instance, the chemical reaction and the transfer of charge(s) from one end to the other large molecules such as proteins). For this, one possibility is to use laser pulses that are short enough to act on the system before the products begin to form.

In the first part, we are interested in studying, and controlling the ultrafast transfer effect linked to a particular geometrical structure: Conical Intersection, which manifests itself with an energy difference between the electronic states (in our case, there is a strong coupling between the two excited states S_1 and S_2). This structure is also present in biological systems, where it plays a vital role. Our objective is to make the simulation starting by two normal modes, which form this conical intersection, and to subsequently increase the number of normal modes, in order to observe, whether we preserve the quantum effect. This allows us to model, and have an insight to understand the mechanism like energy storage in photovoltaic panels, as well as to model the quantum effects in large and complex systems like DNA.

The molecule under study, called Pyrazine, is a prototype molecule, and commonly studied in the community of MCTDH (Multi Configuration Time Dependent Hartree), a numerical algorithm developed by our German colleagues. The algorithm is based on Dirac-Frenkel variational principle, and here, we propagate our time-dependent wave packet in a spatial grid.

In this molecule, it turns out that there are two possibilities to populate S_1 (low energy state): either, passing through S_2 and leaving the conical intersection to play its role of transfer, or directly exciting S_1 , which is very difficult with a direct field because there is no permanent transition dipole moment. This study considers the first possibility. As soon as the wave packet propagates in state S_2 , it passes into S_1 , thanks to the coupling via the conical intersection. It is therefore, sought to manipulate this bifurcation by using several delayed laser pulses. By optimizing the delay between these pulses, it is possible to populate (in an indirect way) S_1 in a maximum and stable manner.

The second part of this study consists in visualizing a quantum phase transition in a system considered to be a unidimensionally aligned set of rotors. For this, we compare two numerical methods: ML-MCTDH (Multi-Layer Multi Configuration Hartree) and DMRG (Density Matrix Renormalization Group), a tool used by our Canadian colleagues, who were able to calculate this transition. Here, we increase the size of our system from $N = 10$ to $N = 50$, that is to say, 100 degrees of freedom, and we look, if there are particular changes related to this increase in size. The two methods are compared for different observables (energy, entropy, computation time, memory, etc.), and the results are presented. This study helps us to better understand phenomena like spin transition in magnetic materials, super conductivity, and also phase transition in Bose-Einstein condensates.

Résumé:

L'objectif principal de cette étude est de simuler numériquement, et de contrôler les différents processus moléculaires à leurs échelles naturelles de temps. Pour ce faire, on résout l'équation de Schrödinger dépendante du temps, en incluant les degrés de libertés électroniques et nucléaires. Les équations couplées deviennent extrêmement difficiles à résoudre, même pour des petits systèmes moléculaires. Ici, l'idée est de dépasser ce problème. On passe donc en haute dimensionnalité. Pour quelle raison est-ce si important? C'est parce qu'on veut regarder si les effets quantiques (comme la cohérence, les phénomènes d'interférence etc.) sont préservés ou pas dans les grands systèmes. Quel rôle joueront des modes qui s'ajoutent successivement dans notre modèle de calcul ? Il n'est pas possible de traiter ces effets quantiques avec des approches. Un rêve des scientifiques dans le domaine de la physique atomique et moléculaire a toujours aussi été de pouvoir contrôler ces processus moléculaires au niveau le plus élémentaire où les phénomènes quantiques dominent (par exemple, la réaction chimique et le transfert de(s) charge(s) d'une extrémité à l'autre des molécules de grande taille comme les protéines). Pour y arriver, une possibilité est d'utiliser des impulsions lasers suffisamment brèves pour agir sur le système avant que les produits ne commencent à se former.

Dans la première partie, nous nous intéressons à étudier, et à contrôler, l'effet de transfert ultrarapide lié à une structure géométrique appelée Intersection Conique, qui se manifeste lorsque des états excités électroniques sont dégénérés en énergie (dans notre cas, cela induit un fort couplage entre deux états électroniques, S1 et S2). Cette structure est présente également dans les systèmes biologiques, où elle joue un rôle essentiel. Notre objectif est de faire des simulations en partant de deux modes normaux, qui forment cette intersection conique, et d'augmenter successivement le nombre de modes normaux, afin d'observer si l'on préserve les effets quantiques lorsqu'il y a un transfert de population via cette intersection conique. Cela ouvre la possibilité de modéliser et de bien comprendre le fonctionnement et le stockage d'énergie dans les panneaux photovoltaïques, ainsi que voir l'effet dans un système large et complexe comme l'ADN.

La molécule de notre étude, la Pyrazine, est une molécule prototype, et communément étudiée dans la communauté MCTDH (Multi Configuration Time Dependent Hartree), un algorithme numérique développé par nos collègues Allemands. Avec cet algorithme, basé sur le principe variationnel de Dirac-Frenkel, on propage

un paquet d'onde dépendent du temps dans l'espace des configurations de la molécule.

Dans cette molécule, il s'avère qu'il y ait deux possibilités pour peupler S_1 (état électronique le plus bas en énergie) : soit, en passant par S_2 et de laisser l'intersection conique jouer son rôle de transfert, ou alors exciter directement S_1 , ce qui est très difficile avec un champ direct car il n'y a pas de moment dipôle de transition permanent important. Cette étude considère la première possibilité. Dès que le paquet d'onde se propage dans l'état S_2 , il passe en partie dans S_1 . On cherche donc à manipuler cette bifurcation en utilisant plusieurs impulsions laser. En optimisant le délai entre ces impulsions, on peut peupler (de manière indirecte) S_1 de façon maximale et stable.

La deuxième partie de cette étude consiste à visualiser une transition de phase quantique dans un système constitué par un ensemble de rotateurs alignés uni-dimensionnellement. Pour cela, on compare deux méthodes numériques : ML-MCTDH (Multi-Layer Multi Configuration Hartree) et DMRG (Density Matrix Renormalisation Group), un outil utilisé par nos collègues Canadiens, qui ont pu décrire cette transition. Ici, on augmente la taille de notre système de $N = 10$ à $N = 50$, c'est-à-dire, 100 degrés de libertés, N étant le nombre de rotateurs, et on regarde, s'il y a des changements particuliers liés à cette augmentation de taille. Les deux méthodes sont comparées à travers différentes observables (énergie, entropie, temps de calcul, mémoire, etc.), et les résultats sont présentés dans le manuscript. Cette étude nous aide à mieux comprendre les phénomènes similaires à ceux de transition de spin dans les matériaux magnétiques, de supra conductivité, et également la transition de phase dans les condensats de Bose-Einstein.

DECLARATION

I declare hereby, via the following statement, that the thesis entitled “Quantum Control of the Coupled Motion of Electrons and Nuclei” submitted by me to the *Université Paris Saclay*, for an honour of *Doctor of Philosophy* is an original work carried out under the supervision of Dr. Fabien Gatti and Emeritus Dr. Osman Atabek in *Institut des Sciences Moléculaires d’Orsay*.

I further declare that, this work has not been and shan’t be submitted elsewhere, partially or fully, for obtention of any other degrees or diplomas accredited by any other institutions or universities.

21/02/2022, Orsay, France

An experiment is something which everyone believes except the one who did it. A theory is something which nobody believes except the one who did it !!!

- Albert Einstein

Acknowledgements

Ah A huge sigh of relief finally. When I was just at the beginning of my high school, I accidentally happened to drop some hydrochloric acid in my apron. I was very badly and cunningly scolded by the lab assistant at that time insisting that I might be welcoming my premature death. My reply to him was very clear, that even death does not have the right to take me away before I have obtained my Ph.D. Today, it has come true; although not in the same way as I had wished it to be. I survived two massive earthquakes of April 2015, saw (and survived again) the devastating damage done by the flood in France in June 2016 (which was itself historical) and recently the Covid-19. The virus never considered me as an eligible candidate to welcome in its preternatural world. None of these events took my life and I fucking feel sad. This would just have been the end of the story.

First and foremost, I would like to thank myself for being able to tolerate the whooping 3 (and even more, thanks to the beloved virus) years, staring hours and hours in front of the screen of the computer. Secondly, my family members who are so far, on the other side of the world. I hardly saw them once during my stay here in France. Their contribution in my personal and scientific development is irreplaceable and unexpressable in words. Countless number of days have they passed without having proper food to eat, just to be able to buy a book for me. Their dedication is immense. I owe them for everything I have (or become) today.

My gratitude to Dr. Fabien Gatti, who as a supervisor, was very nice. It would have been impossible to finish everything in very fine detail without his continuous support and belief on me. He always let me enough time to do the calculations and discussions with him were clearly understandable and helpful. I am also beholden to Emeritus Dr. Osman Atabek for his explanation when it comes to physics. I would knock his door several times a day and we would then discuss for hours and hours. He left me most of the time in my own world, which is freaking nice. I had to myself figure out all the papers that were necessary for me. May be I was sometimes (or most of the time) out of track? I am particularly thankful to Mme. Lise Didillon for her help regarding the technical difficulties I encountered during this PhD.

The online question and answer platform *Quora* has been quite helpful too. I was

able to know the real first hand experience of many fellow PhD students from all over the world. Not only that, I could also know their struggle to survive in the program.

I also express my gratitude to all of my friends (I am not just naming anyone, as I might forget to include the names of some of them) that I have met during my stay here. I have spent some really memorable days of my life with you guys. We will continue doing that and cheer up. Let's just wait for those beautiful sunny days. Whilst at the lab, I have met some good people who were ready to help me open-heartedly every time; never were they bothered. A big shoutout to them.

I was also able to participate in some conferences as well as professional training and exchange ideas with the scientists working in my domain. This was enriching, although I had wanted more and this was limited by the budget we had. Nevertheless, this was something fruitful and outreaching for me.

Finally, my sincere excuses to all the staffs and faculties whom I had to deal with. I guess I was sometimes (or every time ???) hard to handle.

I shall now peacefully die as Dr. Mainali.

Somewhere in France

Mr. Mainali

Acronyms

CI: Conical Intersection

CMF: Constant Mean Field

DFT: Density Functional Theory

DMRG: Density Matrix Renormalization Group

DoF: Degrees of Freedom

FC: Franck Condon

FF: Force Fields

GA: Genetic Algorithm

GS: Ground State

IC: Internal Conversion

IVR: Intramolecular Vibrational Energy Redistribution

MCTDH: Multi Configuration Time Dependent Hartree

ML-MCTDH: Multi Layer Multi Configuration Time Dependent Hartree

MLPF: Multi Layer Pot Fit

MM: Molecular Mechanics

OCT: Optimal Control Theory

PBS: Primitive Basis Set

PES: Potential Energy Surface

PIMD: Path Integral-Molecular Dynamics

RBM: Restricted Boltzmann Machines

SPF: Single Particle Function

TDM: Transition Dipole Moment

TD-DFT: Time Dependent-Density Functional Theory

TDSE: Time Dependent Schrödinger Equation

TISE: Time Independent Schrödinger Equation

TS: Transition State

VMF: Variable Mean Field

List of symbols

E : Electric field amplitude of the laser

R : Electronic coordinate

r : nuclear coordinate

μ : Transition Dipole Moment

P_i : Population of the i^{th} state

p : Contrast

τ : Delay between the pulse(s)

T : Pulse duration

W_{12} : Coupling parameter

H : Heaviside function

δ : Kronecker delta

Publications:

1. Comparison of the multi-layer multi-configuration time-dependent Hartree (ML-MCTDH) method and the density matrix renormalization group (DMRG) for ground state properties of linear rotor chains, J. Chem. Phys. **154**, 174106 (2021)
2. Laser control strategies in full dimensional funneling dynamics: The case of pyrazine (submitted)

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Chapter 1

Introduction

Life is very difficult. One of the most ancient of religious ideas that emerges everywhere, I would say, is that life is essentially suffering.

- Dr. Jordan B. Peterson

1.1 The problem itself

It is now well-established that the numerous chemical reactions are impacted by strong quantum-mechanical effects involving both the electrons and nuclei. In particular, when a molecule is excited by absorption of light in the ultraviolet-visible region, it can release its excess energy and return to the electronic ground state through light emission. However, in many cases, this light emission is quenched by a faster radiationless process due to the presence of a non-Born-Oppenheimer coupling between several electronic states. This “non-adiabatic” coupling [1–5] is often due to the presence of a so-called *conical intersection* [2, 3, 6]. The understanding of conical intersection is, thus, very important as it is the point of degeneracy between different electronic states which gives rise to fast ultrafast processes [7]. More than

that, there is a violation of what is known as *Born - Oppenheimer Approximation* (see the upcoming chapters and also [8, 9] for more details). This thus, gives rise to a nonadiabatic transfer with interference effects involving both the electrons and nuclei like, *geometric phase effect*. This latter is because, the wavefunction, although moving on a coupled surface, has to preserve its singularity. A transfer through a conical intersection corresponds to a fast change in the electronic wavefunction: we shall see that it is believed that there are some ultrafast photo physical and photo chemical processes that occur upon passing through this geometrical structure with good efficiency, thanks to their unique funnel shaped structure, thus enhancing the very fast transfer from the higher to lower coupled electronic states without any radiative emission.

We will discuss in the upcoming sections and chapters, in a precised form, what conical intersection is, what has been done in the past to study the effects it could bring in the reaction dynamics, methods and approaches used by the scientists to control it, and the mathematical background.

Now, let us consider an example: a molecular system with a ground electronic state and two excited electronic states (see fig.1.1). It is then possible that these excited states, at some point in the region of space, intersect with each other. In a multidimensional system, this point is rather a surface extended along a region of space, thus forming a cone shaped structure at the point of bifurcation; hence, the name conical intersection (see fig.2.2, chapter 2). In polyatomic molecules, their presence is rather ubiquitous [2, 3].

‘V’ in fig.1.1 represents the “diabatic” (we will see the definition of the diabatic states in detail in chapter 2) potential energy surface, while Q_i is an ensemble of nuclear degrees of freedom (e.g. the normal modes of the molecule). We shall have detailed explanation in the upcoming chapters.

Mathematically, it can be understood as the following (taken from [10, 11]). Let us consider two excited electronic states (say S_1 and S_2). Their potential energy along with the coupling term can then be written as:

$$\begin{bmatrix} V_{11}^{dia} & V_{12}^{dia} \\ V_{21}^{dia} & V_{22}^{dia} \end{bmatrix} \quad (1.1)$$

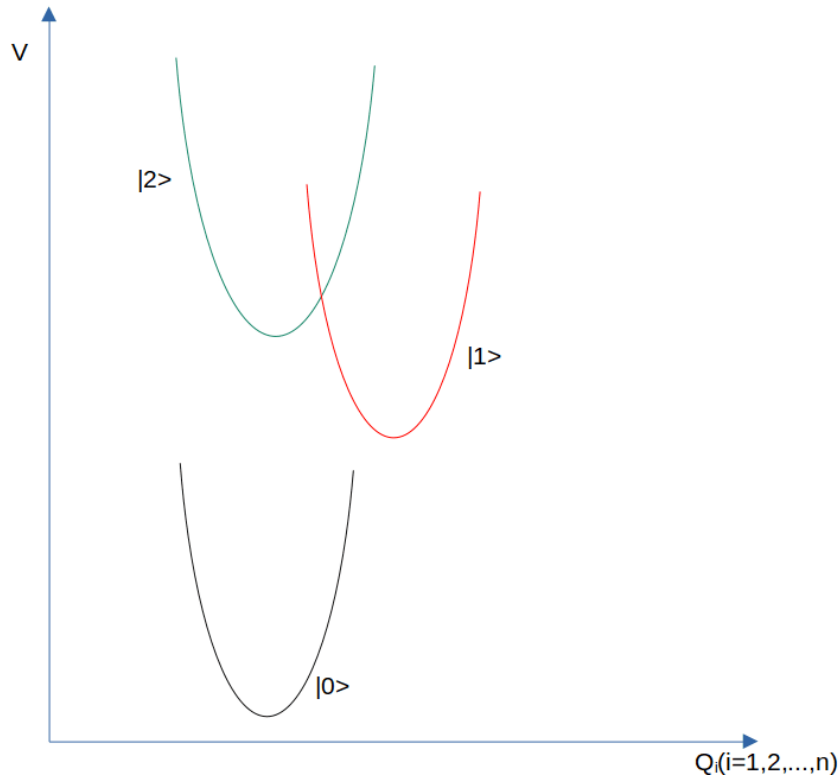


Figure 1.1: An ensemble of molecular electronic levels with ground and two excited states (like in the pyrazine molecule studied in this thesis): for each state, there is a potential energy surface that contains the electronic energy as a function of the nuclear degrees of freedom. On the figure, we see three cuts of the three potential energy surface through one nuclear coordinate only, the other being fixed. We chose a parabolic form for the sake of simplicity.

where, V_{nn} is the potential energy for the diabatic electronic states and V_{mn} is the coupling term that couples the two excited electronic states S_1 and S_2 .

For a conical intersection to persist, the following equations should be satisfied:

$$V_{11}^{dia} = V_{22}^{dia} \quad (1.2)$$

$$V_{12}^{dia} = V_{21}^{dia} = 0 \quad (1.3)$$

One can then solve eq.1.1 to get their eigen energies as below:

$$2E_1 = V_{11}^{dia} = V_{22}^{dia} + \sqrt{(V_{11}^{dia} - V_{22}^{dia})^2 + 4V_{12}^2} \quad (1.4)$$

$$2E_2 = V_{11}^{dia} = V_{22}^{dia} - \sqrt{(V_{11}^{dia} - V_{22}^{dia})^2 + 4V_{12}^2} \quad (1.5)$$

Here, E_1 and E_2 represent the “adiabatic” potential energy surfaces (see chapter 2 for more details) for the states S_1 and S_2 respectively. Since the potential energy surface is a function of $3N - 6$ nuclear coordinates and since we have two mathematical conditions to obtain a conical intersection, given by the equations 1.2 and 1.3, the latter is an hyper surface with $3N - 8$ nuclear degrees of freedom [2, 3, 11] (discussed more precisely in chapter 2) formed at the nuclear coordinate space of a molecule containing N atoms [12]. Thus, a conical intersection corresponds to a special topographic feature that occurs in potential energy surfaces at many geometries where two electronic states are degenerate. Note that conical intersections do not exist in diatomic systems.

There are many systems in nature that involve the presence of conical intersection; proving its essence and necessity. This funnel is an efficient means of ultrafast population transfer (or inversion) between different electronic states in the molecular system [7]. One can basically find two different types of processes: *Photoreactivity* [13, 14] and *Photostability* [15, 16]. Let us have a look at some exemplifications of the importance of conical intersection more figuratively now.

If we look at the potential energy surface corresponding to human DNA base pair, we see that there are two local minima. The energy of the rays (or photon) of the sun absorbed by the molecules, though able to penetrate (or tunnel) through the first minima, cannot pass through the second one, thus preventing the damage of our skin and ultimately the skin cancer. As shown by Domcke and coworkers [17], the non-adiabatic relaxation in complex molecules like DNA base pairs is probably what prevents us from the disease. Hence, the energy of the rays of the sun stabilises itself within these minima. This is called *photostability*, where the population decays back to the initial ground state non radiatively [2, 7, 16].

The other example of conical intersection can be seen during the initiation of our vision process. The light entering our eyes triggers the active region of *rhodopsin* protein found in the retina of our eyes. In doing so, there is what we call *11 cis-trans isomerization* of the retinal molecule. This process happens very fast in nature

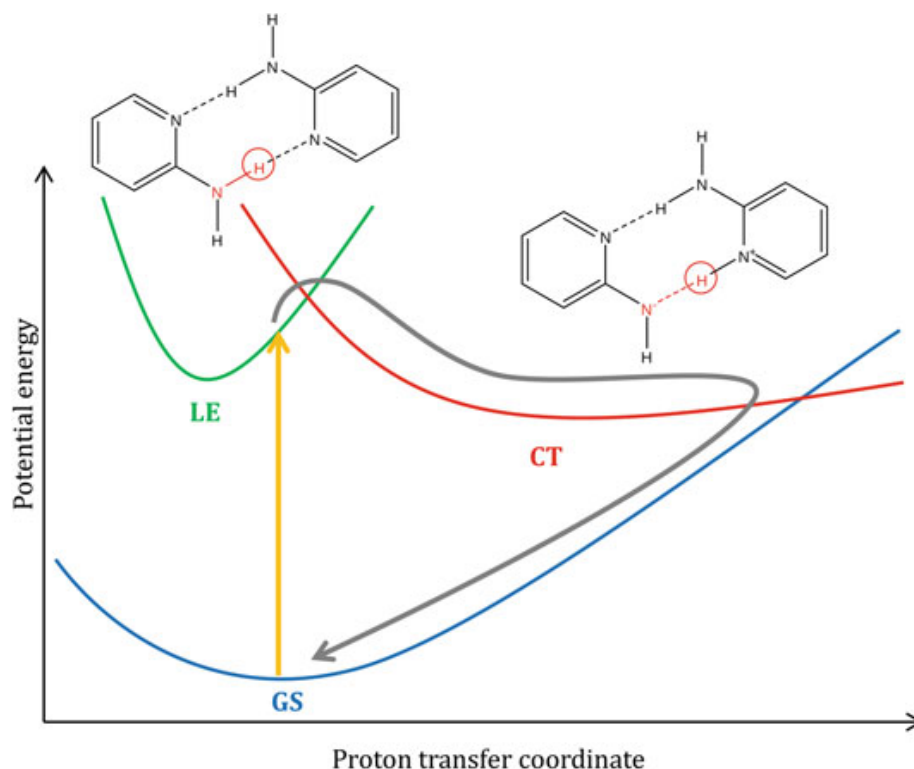


Figure 1.2: Conical Intersection in human DNA base pair: The case of photostability. Reprinted with permission from [11] Springer Nature, copyright 2017.

(within the scale of about 200fs). The initially excited molecule is changed to its isomeric state via the amount of energy that has been deposited in the excited state (see also the ring opening in benzopyrane [18]). This triggers the process of vision. This is the case of *photoreactivity* [13, 14].

The other example of this kind of system is *photosynthesis*, where it is believed that a conical intersection [19] plays a role in the absorption of light leading to the creation of a charge separation. The reaction center in bacteria, algae and other plants contain conical intersection [20, 21], which could be studied to understand their food making process and bio luminescence. More than that, it is also very important in biochemistry (or biophysics). The understanding of folding mechanisms, transition from open shape to closed shape or even any other conformational changes induced by the use of external means like laser field is of huge importance [20, 21].

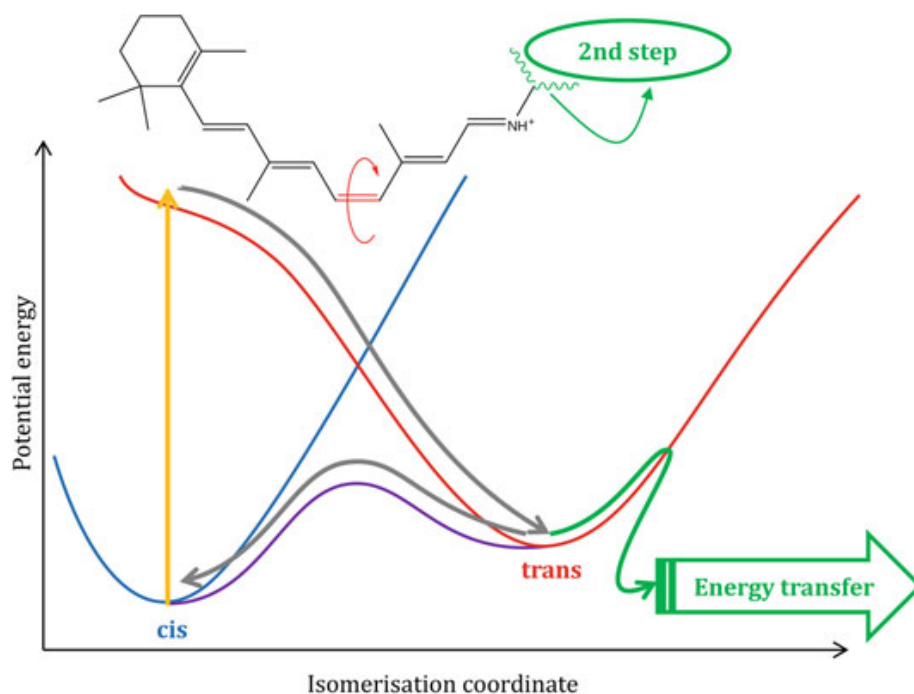


Figure 1.3: Retinal Conical Intersection: The case of photoreactivity. Reprinted with permission from [11] Springer Nature, copyright 2017.

Apart from the natural existence of conical intersection, as shown by Cederbaum and coworkers, it is also possible to create it artificially through a laser, in particular in diatomic molecules, where they do not exist in nature; it is called ‘Laser Induced Conical Intersection’(LICI) [22, 23]. It is also possible that we have conical intersection involving more than 2 excited electronic states [24, 25]. In that case, the coupled equations to solve become even more difficult. The reaction path and the branching plane (see chapter 2) to be described will then be even difficult as more degrees of freedom (e.g. the rotational degrees of freedom) will be involved.

The role of a conical intersection in photochemistry can be compared to that of a transition state in thermochemistry [11, 26]. Consider a chemical reaction shown in Fig.1.4.

Here, the two reactants A and B at the end of a chemical reaction could give two different results, depending on the properties of transition state $(AB)^*$. From a theoretician’s point of view, what is then important is to see how the landscape of potential energy of these two products are formed and how they drive the transition

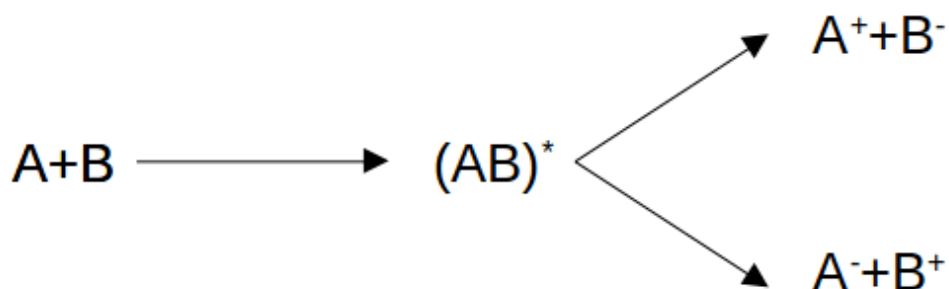


Figure 1.4: A traditional biomolecular chemical reaction involving reactants and different products; intermediate state is also shown.

state towards them [27, 28]. What s/he wishes to understand is to see how the chemical evolution of the system happens, so as to see, for instance, the bond breaking (and formation), charge transfer and so on [7]. It is the topographical structure of conical intersection that determines the fundamental properties of photochemical reactions (like what products are to be formed, decay rate, life time and so on) [4].

What is shown in fig.1.5 is the interatomic potential as a function of a reaction coordinate. The left panel shows two minima Min_R and Min_P corresponding to that of the reactants and the products respectively, and a transition state, TS , the passage responsible for formation of the product(s) via the reactant(s). In the right panel, we see the minima of an excited state Min_{ES} , the transition state TS , and conical intersection, CI . Each of these points in the energy landscape have to be properly characterized so as to understand a chemical reaction. Conical intersection thus plays an important role in photochemistry, like transition states in thermochemistry, by working as a channeling between different photo products that could be formed as one passes through the very unstable state.

This traditional sketch (fig.1.4) involves many physical parameters to be mastered

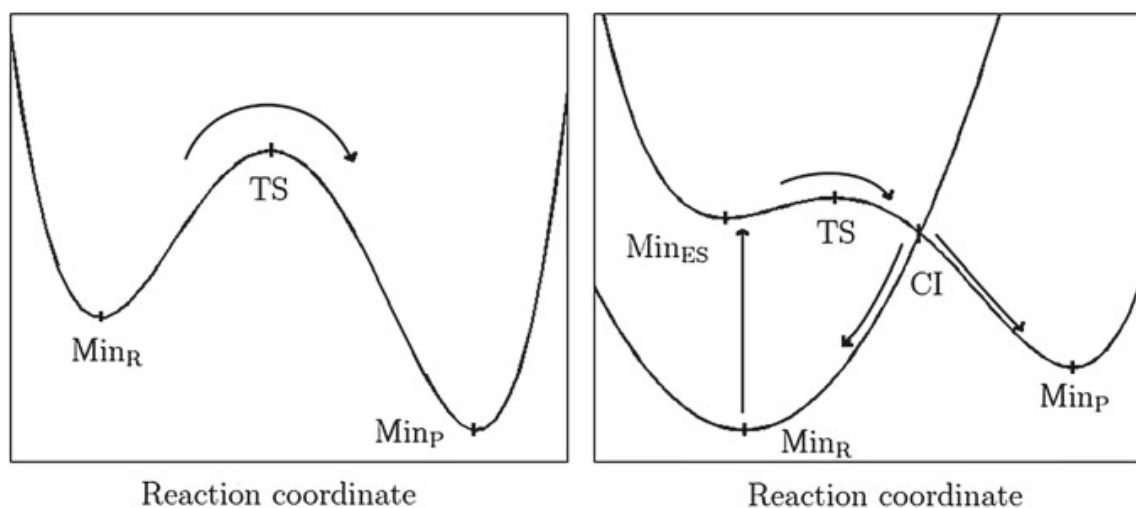


Figure 1.5: Illustration of a thermal reaction (left) and a photochemical reaction (right) in terms of the PES. The product is on the right side whereas the reactant on the left (their minima are represented as Min_R and Min_P respectively). Min_{ES} , TS and CI denote the local minimum of the excited state, the transition state and the conical intersection. Reprinted with permission from [29] Springer, copyright 2016.

[30]: pressure, temperature, kinetic energy and so on [31]. The risk of producing the unwanted products is also very high, thus arising the question of safety and environmental hazards. Here, the passage is via unstable state i.e. transition state or conical intersection. The questions that chemists (and chemical physicists in the domain of atomic and molecular physics) are interested in are: Is it possible to increase the time of formation of this unstable product so as to explore the potential energy surface? Does the potential energy surface of this product infer the final state? How can the yield of the final state be changed for example, by using a laser? How can the ratio of kinetic to thermodynamic limit be changed to enhance (or suppress) the relaxation pathways[32, 33]?

Commonly, the formation of products via the reactants is accelerated by the use of catalysis. These catalysis are the chemical compounds (or molecules), which alter the rate of chemical reaction. After the rapid advancement of lasers, this process could be done by them too [28]. This is known as *mode selective chemistry* [34]. The use of femtosecond laser pulses to study the chemical reaction was proposed by Ahmed Zewail in mid 90s and he was rewarded the Nobel Prize (1999) in Chemistry for this beautiful technique [27, 35].

Different techniques have been applied in the past to study these kind of mechanisms. STIRAP (Stimulated Rapid Adiabatic Passage) [36, 37], Stark Shift [38, 39], Coherent Control (i.e interference between the several possible routes) [40–44], Optimal Control Theory (OCT) [45, 46] and so on (see the upcoming sections of this chapter for more details).

The following thesis aims to understand, by using a series of ultrashort laser pulses, the possibility of controlling different physical observables in the context of the coherent control of the energy transfer through a conical intersection. The quantum dynamical observable under study in our case is the *electronic population* (mainly diabatic). One could, in simple words, understand this as a wavepacket being partitioned into different components corresponding to the different electronic states coupled by the conical intersection. As said previously, the conical intersection could be formed by the intersection of several excited electronic states (two in our case) and not necessarily with the same symmetry (the two excited electronic states in our system have two different symmetries).

The primary goal of the following thesis is thus, to understand (and verify) the possibility of controlling the product channels of a chemical reaction involving the large molecules (or, molecules with “huge” dimensionality). This is a challenging job because the increase in number of nuclear coordinates make it extremely difficult to direct a chemical reaction towards the desired channel (or, path), as there is an absorption via other nuclear coordinates, which results in loss of yield of an observable we wish to control. The other potential application of this study, particularly in the case of molecules like Pyrazine, is the control of flow of energy between the coupled excited states such that this energy could be used for some useful purposes later on. In brief, what we want to achieve at the end of the simulation is all the population from S_0 to S_2 to end at S_1 . This is not an easy task as there is no direct way to populate S_1 (absence of a strong permanent dipole moment).

The rapid advancement of laser has made it possible even to visualise the electronic motion to an attosecond scale [47–53], thus making it possible to follow the dynamical processes described before in real time (recently, the shortest pulse of 43 attoseconds have been generated by the group of prof. Hans Jacob Worner, in ETH Zurich [54]). One can then observe and even guide not only the nuclear motion, but also the electronic motion in the direction s/he wishes: in particular, it will be probably possible to visualize soon all the interference effects when an energy transfer occurs through a conical intersection. In this context, it is worth noting that the

presence of highly sensitive detectors make it experimentally possible to visualize the photo electron angular distribution (i.e. by which angle or direction the electron has been kicked) and these photo electron spectra can capture all the most subtle interference effects that we have mentioned. In the following work, we are more interested in understanding how this furnace shapes the final states and how could they be controlled by the lasers. One can think of the experimental possibility (or feasibility) of deployment of the intense lasers and also their commercial availability that could be used to exploit our findings.

1.2 Study of pyrazine and it's motivation

The molecule that we consider for our study is *Pyrazine*. Pyrazine is exactly like a benzene molecule, whose two of the carbon atoms (attached to the hydrogen atom) are being replaced by that of nitrogen. The chemical formula is thus $C_4H_4N_2$ and has 24 normal modes (calculated by the formula $3N - 6$, where $N = 10$ is the number of atoms).

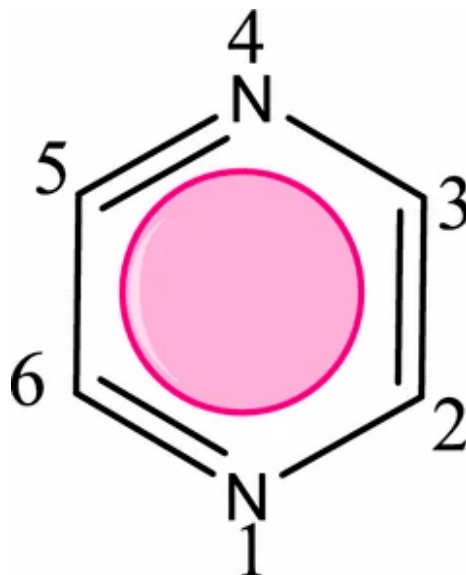


Figure 1.6: The chemical structure of Pyrazine molecule (the numbers 1, 2, ..., 6 represent the positioning of either 'N' or 'C' atoms) . Reprinted with permission from [55] Springer 'Journal of Bio- and Tribo-Corrosion', copyright 2018.

Here are some of the importance of this molecule:

1. The solvation effect when mixing the molecule with aqueous environment has been considerably studied. The electronic transition properties around the region of conical intersection changes as it changes the polarization of the molecule. However, it has very little effect on the electronic states that are not polar (see chapter 12 of [11]).
2. Recently, the molecule has also been studied to understand the ionic coherence in photoionisation and the pre-determination of the subsequent chemical product of a given species (see the introductory section of [56]).
3. One of the potential applications of the molecules with this kind of configuration is *light harvesting* [57, 58]. The energy that is transferred from higher to lower energy state (this behavior is known as *funneling dynamics*, see [58]) can be gathered and driven towards some specific location(s) and also be used for later purpose [57]. The energy gradient between several electronic states of the biomolecular systems could be hence, used for other fruitful purposes.
4. Being aromatic molecule, it has also been widely studied in computational and medicinal chemistry to understand the interaction with proteins to create drugs of higher efficiency [59].

The vibronic coupling is very strong in pyrazine and the conical intersection, being close to the Frank-Condon factor, is easily accessible [56]. Other associated physical and chemical properties can be found elsewhere (see [60] for instance).

1.3 Laser control strategies: State of art

The core understanding of the photo chemical events by the use of light is the central goal of photochemistry [61]. However, the problem with the polyatomic molecules like pyrazine is that the landscape of the potential energy surface, when all the normal modes are included is seemingly complex [61]. The use of laser technology, which implies the use of electromagnetic field, is in itself a field of physics with long history and is vastly growing [61].

For this, different schemes have been developed so as to control the evolution of the propagated wavepackets in the coupled energy surfaces of the polyatomic molecules. They include basically a coherent source of light, a laser, with its radiative coupling, that could be considered as aforementioned catalyst or reagent.

The problem of decoherence [33] is one of the major issues when it comes to the control of a quantum system. Even kept isolated, they would dissipate very fast to other degrees of freedom through Intramolecular Vibrational Energy Redistribution (IVR). This decreases also the efficiency of a quantum control [33]. Thus, what we want in the present day chemistry is to be fast enough to control the dynamics before it leads to decoherence. To do so, one of the possibilities is *Quantum Control*, where different chemical and physical properties could be manipulated in their natural timescale, which by other means would seem impossible. We, thus, play with different quantum effects in this study.

Since the historical advent of lasers in 60s, the adventure of it has driven the scientists towards various processes in atomic scale and their manual control. The earlier attempts were rather to identify certain vibrational frequencies responsible for the utmost part of the molecular dynamics and use a laser pulse with that frequency in the hope that the selected bond breaking will occur in the molecule under study. However, there were only unsuccessful stories of this strategy [62–65]. The idea of using laser as a coherent source of light and creating the interference effect, to have higher level of control (for example, splitting of products in a chemical reaction) and efficiency to steer the chemical reaction was in its infancy till the early 80s [66, 67].

One of the methods explored in the past and widely used experimentally is the *Dynamic Stark Control* [38, 39, 68]. This method describes the possibility of controlling a chemical reaction by modifying the potential energy barriers without giving rise to any real electronic transitions [68]. That is to say, by the use of very long and non-resonant pulse(s) as control source, we can modify the position of a conical intersection in a given molecule; thus also playing with the observables (see [29, 39] for more details). This is similar to having a solvent effect, that could manifest a change in the topography around the conical intersection. What happens is that, the conical intersection is shifted in position by the presence of a polar solvent and this could modify the non-adiabatic transfer.

We shall now see the other possibilities for such control.

1.3.1 Coherent Control

Although the wave-particle duality was introduced during the infancy of quantum dynamics, it was not till 80s, that the scientist thought of the quantum dynamical processes as the wave processes and one could thus, have both constructive and destructive interference arising from the interfering amplitude of these waves [69].

The experimental feasibility of exploration of different quantum mechanical observables depends on the waveform of the electrical field chosen. Consider the following:

$$\epsilon_x(t) = \text{Re}(\sum_i A_i(t) \exp[i\omega_i(t)t + \phi_i(t)]). \quad (1.6)$$

This equation explicitly includes three essential parameters: amplitude modulation $[A_i(t)]$, phase modulation $[\phi_i(t)]$ and frequency modulation $[\omega_i(t)]$. By the proper combination of two of these parameters, required control can be achieved [69] (for instance, the control parameter in our theoretical model is the time delay, where the rest of the parameters remain constant). This equation, in essence, shows that, we can play with either:

1. Time Delay

The selectivity of the final products of any chemical reaction can be governed by modulating the interference pathways with a variable time delay. For instance, in a three level system, one creates a replica of a ground state wavefunction (via pulse excitation) in the state with higher energy and let it evolve in the coupled potential energy surface. The second wavefunction, which is phase locked compared to the first one, is then again excited from the ground state (irrespective of the excited states now) with some delay. This control parameter, delay (noted as τ hereafter), can induce sufficient overlap between the wavepackets, leading to the constructive interference (or vice versa, the process then would lead to destructive interference) [70].

2. Phase Delay

An alternative approach would be to play with the phase involving the transitions [70]. This is not the case in the present study (see for instance [61],

where the authors used some shaped ultrafast lasers with phase delay in their experiments, to study the dynamics).

As the transition dipole moment from S_0 to S_1 is very small for the molecule under study (see fig 1.1), the interference between the two possible excitation pathways, initially cited elsewhere in the literature [70–73], is not possible here. Three regimes have been identified: weak, intermediate and strong. In the case of weak field, a light source can be used to create an artificial wavepacket, that can then be moved towards or away from the seam (or, point of intersection) so as to play with the probability of the final outcome, without affecting the landscape of the Potential Energy Surfaces (PESs) [74]. For the fields with intermediate strength, the light pulse can be used as a catalyst, which can distort the energy landscape by shifting the position of conical intersection and the shape of the seams too [68]. This is the case of a Stark effect. In the case of strong field, it is where the removal of electrons can occur (leading to ionization or dissociation) [75].

If one allows sufficient time after the irradiation of molecule by the first laser, we could see the post pulse dynamics and then, we could use the second laser pulse. In the following thesis, we have tried to analyze the population in different time windows: *symptotic* [46-78]fs, *intermediate* [110-200]fs and *asymptotic* [400-500]fs. These time frames were arbitrarily chosen; an aim to understand the dynamical behaviour under the influence of laser(s) and also long after the laser(s) are turned off. The experimental analogue of this would be to plot branching ratios of quasi-dark state and bright state as a function of the coupling parameter used in system bath interaction.

The calculation was started with a simple 2D model, with further addition of normal modes. This subsequent rise goes up to 4D. Literature studies show that 4D models, in comparison to 24D models, are often enough for short dynamics [76] (see chapter 3 and results presented therein). A final calculation with 24D has, however, been performed to confirm this for our strategies of control. In the following study, N sine squared pulses with a sequence of delay have been used. In the literature, one could find the same study done by using the Gaussian pulse [71]. Similar studies regarding the control has also been studied by the use of trapezoidal pulse [77].

1.3.2 Optimal Control

(This is not the goal of the present thesis. However, it is discussed in brief below.)

The other well known control strategy is the *optimal control* [78–80]; which has been widely used to study the problem of dynamical systems. Here, an external time dependant parameter is used, known as cost functional. The idea then is to maximize the observable while minimizing the cost functional. One thus, plays within the compromisation of these 2 factors. Various algorithms exist for doing so. The authors in [81–83] have extensively used this technique to study the molecular photofragmentation, orientation and dissociation using pulse shaping techniques.

One of the possible algorithms in this approach is the *genetic algorithm*. If the objective is to maximize the observable (for instance, the population, or energy or control time of the pulse used), then the solution to the problem becomes much more easier. This is an *inverse problem*, where the knowledge of quantum mechanical equation and the goal is enough, as we then will have enough parameters to play with. This results with several choices of the laser field [70]. The computer aided field, designed as such, might, however not be as robust as needed to minimize the errors coming from the Hamiltonian as well as the uncertainties induced in the laboratory [66].

The feedback learning mechanism can also be used to understand the complexity of the molecular Hamiltonian, which otherwise would be very difficult for the molecules of large size as the dependency related to the normal modes increases and one needs to have insightful knowledge of all these modes and their controllability: that is, the capacity to drive the system to a desired state (see refs [66, 69] and the references therein). This has been the dream of scientists since then.

1.4 The problem of Rotors

The other issue that has been described in this manuscript is the ground state energy of a one dimensional linear rotor chain (maximum size = 50, so the total no. of degrees of freedom = 100). This, by using DMRG (Density Matrix Renormal-

ization Group) [84–86], is also a very recent calculation [84] and since MCTDH (Multi-Configuration Time Dependent Hartree) is considered to be the standard for the dynamics involving wavepacket propagation [87–89], the idea here is to benchmark the results obtained via DMRG. For this, ML-MCTDH (Multi-Layer Multi-Configuration Time Dependent Hartree), an extended version of MCTDH, has been used.

We mimic what has been reproduced already in [84], by taking into account the fact that the interaction between the rotors could be of two types: *neighbour* and *all*. Moreover, we are also interested in understanding different physical properties like entanglement entropy (otherwise called *Shanon* entropy), orientational correlation (to see the effects on the ground state energy when they do not have same orientation or alignment; this is difficult to understand because this depends exclusively on the system size under consideration), the difference in the memory taken by these two methods, wall time and so on. This is a published work [90] and has been dealt exclusively in chapter 5.

In the future works, one can also add FT (Finite Temperature) condition in the Hamiltonian operator to see the effects [91].

1.5 Method: State of art

One of the major problems in molecular quantum dynamics is the mixing of the electrons and nuclei. Their movement is intermingled and the only way to get rid of it is to try to treat their dynamics separately, using different approximations (we will see in chapter 2). In the case of the conical intersection, this separation is not possible, but, in all cases, we split the molecular problems into two steps: first, the electronic dynamics, second the nuclear dynamics. The electronic part is separated as much as possible from the nuclear one. In our study, we focus on the nuclear dynamics, but this assumes that the electronic part has already been treated, and that we have the electronic potential energy surfaces.

If we look in fig.1.7, we see that the electronic structure theory could be aborted by many methods like *ab initio*, DFT, force fields, and so on. They are more or less accurate and the choice of the method depends on the size of the system and

the accuracy one needs or can reach. For many cases, one could treat the nuclei classically; this is the field of *molecular dynamics*.

Fig.1.7 shows different methods available to solve the electronic part: (i) the most accurate and, thus the most expensive, are the ab initio methods or the “many body methods”, that solve the quantum many body problem; (ii) Density Functional Theory (DFT) is often less accurate, but allows to treat larger systems; (iii) semi-empirical methods are often used to treat even larger systems : some of the parameters are fitted to reproduce the experimental results; (iv) for extremely large systems, the classical motion of the nuclei is driven by force fields (molecular mechanics). Also, the problem we deal is basically dependent on what we wish to achieve at the end: the more precise results, i.e the better converged ones will require methods like DFT (Density Functional Theory), TD-DFT (Time-Dependent Density Functional Theory) or many body methods (involving even the electron correlation). Remember, that the problem of nuclei is not included quantum mechanically in fig.1.7.

But, the classical treatment of the nuclei is not enough in our case because of the presence of several Nuclear Quantum Effects (NQEs)[92], which is important to understand the structure and dynamics of the system (pyrazine, for instance). To capture an essential part of quantum physics, quantum-chemistry calculations must be combined with a quantum approach for the nuclei: this is now possible even for relatively large systems with methods such as MCTDH. We thus, introduce a theoretical algorithm (MCTDH), which can feasibly treat systems like pyrazine on a full quantum mechanical ground. A major problem in computational chemistry is of course, the increase in wall time when increasing the system dimension. At some point, it becomes so saturated that the algorithm no longer supports the calculation. This is known as the *curse of dimensionality*. This is not totally solved, but avoided to some extent in algorithms like MCTDH (discussed in chapter 2).

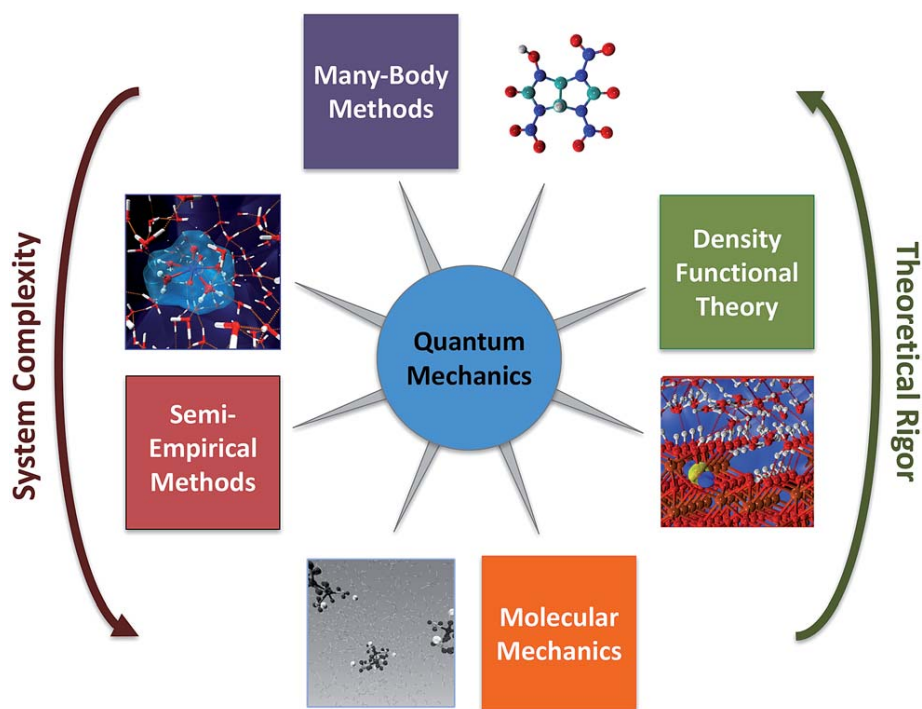


Figure 1.7: Different computational approaches in Quantum mechanics (Reproduced from [93] with permission from the *Royal Society of Chemistry*)

1.6 Similarities of the two studies

As a tool extremely useful to do molecular dynamics in excited state, we use this advantage to study the phase transition resulting from the breaking of rotational symmetry in linear rotor chains (chapter 5).

Both the problems (*rotors* and *pyrazine*) are a N-body problem: that is to say, involve many degrees of freedom. Using MCTDH is really fruitful because both of these problems have an important no. of degrees of freedom, which we be difficult to solve otherwise.

The advantage of using ML-MCTDH (the Multi-Layer variant of MCTDH, where the compact wavefunction can be re-expressed as a function of different combination

of basis sets; it is described in detail in chapter 2) is that the large systems can be easily explored within considerable amount of time [90, 94–96]. In MCTDH, the wavepacket propagation takes its exact form [88, 89], thus considered as an important tool to study the underlying physical processes in ultrafast timescale, whereas DMRG (Density Matrix Renormalization Group) is an algorithm in electronic structure theory [84], a time independent one and used particularly in the field of condensed matter physics [85, 86].

The calculation of the ground state properties of a linear chain of rotors by ML-MCTDH and comparison with DMRG (see the forthcoming chapters for better understanding) is inspired by the fact that there has not been much common work between these two communities till now. This could be a very good initial step to perform same calculations by several methods for various reasons (see in detail in chapter 5). The MCTDH algorithm has also been extensively developed to treat bosons (MCTDH-B) and fermions (MCTDH-X). Here are the major reasons of this common study:

1. To see the limit of all the codes in existence.
2. To have a better simulation. In doing an overall comparison between various existing codes, one can not only see the limits, but also include the improvements on the upcoming version. For the users then, will be a range of numerical algorithms to choose upon his/her need(s).

Chapter 2

Mathematical formulation

If there is a meaning in life at all, then there must be a meaning in suffering. Suffering is an ineradicable part of life, even as fate and death. Without suffering and death, human life cannot be complete.

- Viktor E. Frankl

The mathematical formulation explained here comes mostly from the references [10, 11, 97].

2.1 Basic Concepts

2.1.1 The Molecular Schrödinger Equation

To explain different physical phenomena in molecular physics occurring in their natural timescale, one has to make simulations with some preset assumptions. To do

so, depending on the resources available and modeling objective(s), one could make a compromise. The biophysicists, for instance, are more interested in understanding the protein dynamics and thus, the classical treatment of the system under study via the Force Fields suffices; we are hence, solving Newton's second law of motion. However, if one is to study the quantum mechanical properties and the observables associated with, like the charge migration or the electronic coherence, then there is no other choice than doing the quantum mechanical calculation. Quantum mechanically, the only way to simulate a model is to solve the time-dependent Schrödinger equation. It is discussed hereafter in brief.

Let us consider a multidimensional molecular system (say pyrazine, the molecule in our case) with R , noted as the nuclear coordinates and r , noted as the electronic coordinates. In the field free case (that is to say when there is no presence of an oscillating field), the total Hamiltonian acting on this system is the sum of the following forces:

$$H_{pyr} = T_{nu}(R) + H_{el}(r, R), \quad (2.1)$$

where, $T_{nu}(R)$ is the nuclear kinetic energy at a given geometrical configuration. The electronic Hamiltonian $H_{el}(r, R)$ for a fixed nuclear co-ordinate can be re-written as following:

$$H_{el}(r, R) = V_{el-el}(r) + V_{nu-nu}(R) + V_{nu-el}(r, R) + T_{el}(r). \quad (2.2)$$

The direct solution of this molecular Hamiltonian is rarely useful since it is computationally very expensive [98].

In the expression 2.2, $V_{el-el}(r)$ is the electrostatic repulsive potential between all the electrons in the molecule. $V_{nu-nu}(R)$ is the electrostatic repulsive potential between all the nuclei. $V_{nu-el}(r, R)$ is the attractive coulomb potential between the electrons and the nuclei. $T_{el}(r)$ is the kinetic energy associated with the electrons. In the Hamiltonian state in eq.2.1, the kinetic energy of nuclei $T_{nu}(R)$ is already separated from the total molecular Hamiltonian. The electronic Hamiltonian in this equation is also known as *clamped nucleus* Hamiltonian. As the ratio of masses of

nuclei to electrons is 1836, the classical approach of this clamping indicates that the rapidly oscillating electron clouds will ultimately, after some time frame, follow the path of slow moving nuclei.

Each of the terms of eqs.2.1 and 2.2 can be re-written as the following:

$$T_{nu}(R) = - \sum_{\alpha}^{N_{Nu}} \frac{\hbar^2}{2M_{\alpha}} \nabla_{\alpha} \cdot \nabla_{\alpha}, \quad (2.3)$$

$$T_{el}(r) = - \sum_i^{N_{el}} \frac{\hbar^2}{2M_e} \nabla_i \cdot \nabla_i, \quad (2.4)$$

$$V_{el-el}(r) = \sum_i^{N_{el}} \sum_{j>i}^{N_{el}} \frac{e^2}{4\pi\epsilon_0 |r_j - r_i|}, \quad (2.5)$$

$$V_{Nu-Nu}(R) = \sum_{\alpha}^{N_{Nu}} \sum_{\beta>\alpha}^{N_{Nu}} \frac{Z_{\alpha}Z_{\beta}e^2}{4\pi\epsilon_0 |R_{\alpha} - R_{\beta}|}, \quad (2.6)$$

$$V_{Nu-el}(R) = \sum_{\alpha}^{N_{Nu}} \sum_i^{N_{el}} \frac{Z_{\alpha}e^2}{4\pi\epsilon_0 |R_{\alpha} - r_i|}, \quad (2.7)$$

with α and β being 2 nuclei at a fixed position R_{α} and R_{β} respectively.

In our study, we are solving the time dependent Schrödinger equation for the nuclei in the electronic potential given by the time independent Schrödinger equation solved for the electrons (see below). Then, for the given nuclear geometries, the TDSE (for the nuclei) is solved to understand the transfer of population between the excited electronic states (the same applies for other observables).

The time independent schrödinger equation for the molecular Hamiltonian of eq.2.1 is given by:

$$H_{pyr}\varphi_{pyr}(r, R) = E_n\varphi_{pyr}(r, R) . \quad (2.8)$$

Here, $\varphi_{pyr}(r, R)$ represents the total wavefunction. This wavefunction can be re-expressed in a complete basis set as follows:

$$\psi_{pyr}(r, R) = \sum_n \chi_n(R)\phi_n(r, R) , \quad (2.9)$$

where, $\chi_n(R)$ will then be the corresponding nuclear wavefunction.

The eigenfunctions for the adiabatic electronic states are denoted as $\psi_l^{el/ad}(r, R)$. The equation to solve is the following:

$$H_{el}(r, R)\psi_l^{el/ad}(r, R) = E_l^{el}(R)\psi_l^{el/ad}(r, R) , \quad (2.10)$$

where, $V_{nn} = E_n$ and $V_{nm} = 0$ for $n \neq m$ (n and m correspond to the labelling of the electronic states).

In other form:

$$V_{nm}^{ad} = \langle \psi_n^{el/ad}, R | H^{el}(R) | \psi_m^{el/ad}, R \rangle_r = \delta_{nm} E_m^{el}(R) . \quad (2.11)$$

where, $E_m^{el}(R)$ is the adiabatic electronic energy for state m at a given nuclear geometry R . This gives rise to the concept of potential energy surface (see upcoming sections in this chapter).

The system of coupled equations is then the following:

$$\sum_m [T_{nm}^{ad}(R) + \delta_{nm} E_m^{el}(R)] \psi_m^{ad}(R, t) = i\hbar \frac{\partial \psi_m^{ad}(R, t)}{\partial t} \quad (2.12)$$

which can be re-expressed in the matrix form as:

$$\begin{bmatrix} T_{11}^{ad} + E_1 & T_{12}^{ad} \\ T_{21}^{ad} & T_{22}^{ad} + E_2 \end{bmatrix} \begin{bmatrix} \varphi_1^{Nu/ad}(R, t) \\ \varphi_2^{Nu/ad}(R, t) \end{bmatrix} = i \frac{\partial}{\partial t} \begin{bmatrix} \varphi_1^{Nu/ad}(R, t) \\ \varphi_2^{Nu/ad}(R, t) \end{bmatrix}. \quad (2.13)$$

In eq.2.13 above, the coupling term T_{nm}^{ad} between the different electronic states is still present. The nuclear wavefunction, which no more depends on the electron coordinates r is propagated in the adiabatic electronic states. In adiabatic regime, only the potential energy operator for nuclei is diagonal while the kinetic part is not [97].

The adiabatic electronic basis sets are frequently used in molecular physics and quantum chemistry [97]. However, it is not adapted to treat features like conical intersection [99]. This is because, the nonadiabatic coupling matrix is difficult to obtain computationally [97].

The time dependent version of the Schrödinger equation is the following:

$$H_{pyr} \varphi_{pyr}(r, R, t) = i\hbar \frac{\partial \varphi_{pyr}(r, R, t)}{\partial t}. \quad (2.14)$$

This equation provides information about how the molecular wave-function is evolving in different time regime. The difficulty in solving an exact solution of these equations gives rise to the separation of electronic and nuclear motion.

Once again, the molecular wavefunction can be written as a following linear combination:

$$\varphi_{pyr}(r, R, t) = \sum_m \varphi_m(R, t) \phi_m^{el}(r, R), \quad (2.15)$$

$\phi_m^{el}(r, R)$ in the above equation should be complete and orthogonal. Also, we see that the time dependency of the molecular Hamiltonian is only with the nuclear part

of the wavefunction. Thus, the quantum mechanical treatment of a molecular system is a two-step process: First, we solve the time independent schrödinger equation for the electrons for the given nuclear geometries (fixed). Doing so will give us the potential energy surface of each of the electronic states involved. Then, we solve the time dependent Schrödinger equation for the nuclei in the perimeter of the obtained potential energy surface. This could be a problem if we have very huge number of electronic states and many more coupling terms between these states.

Multiplying eq.2.14 with $\phi_n^{el*}(r, R)$ and integrating over all the electron coordinates gives the following:

$$\sum_m \langle \phi_n^{el}; R | H_{pyr}(R) \varphi_m(R, t) | \phi_m^{el}; R \rangle = i\hbar \sum_m \langle \phi_n^{el}; R | \phi_m^{el}; R \rangle \frac{\partial \varphi_m(R, t)}{\partial t}. \quad (2.16)$$

Applying the following orthonormality condition:

$$\int \varphi_m^{el*}(r; R) \varphi_n^{el}(r; R) dr = \langle \varphi_m^{el}; R | \varphi_n^{el}; R \rangle_r = \delta_{mn}, \quad (2.17)$$

on eq.2.16 gives the following sets of coupled equations:

$$\sum_m \langle \phi_n^{el}; R | H_{pyr}(R) \varphi_m(R, t) | \phi_m^{el}; R \rangle \varphi_m(R, t) = i\hbar \frac{\partial \varphi_n(R, t)}{\partial t}. \quad (2.18)$$

Substituting the expression of the Hamiltonian of 2.2 in the above equation gives us the time dependent schrödinger equation in the form of coupled differential equations as written below:

$$\sum_m (T_{nm}(R) + V_{nm}(R)) \varphi_m(R, t) = i\hbar \frac{\partial \varphi_n(R, t)}{\partial t}, \quad (2.19)$$

where, the indices n and m correspond to the electronic states n and m respectively.

For the sake of simplicity, let's consider two electronic states 1 and 2. The total molecular Hamiltonian in these states is then the following:

$$\varphi_{pyr}(r, R, t) = \varphi_1(R, t)\phi_1^{el}(r, R) + \varphi_2(R, t)\phi_2^{el}(r, R). \quad (2.20)$$

The time dependent schrödinger equation then is the following:

$$\begin{bmatrix} T_{11}(R) + V_{11}(R) & T_{12}(R) + V_{12}(R) \\ T_{21}(R) + V_{11}(R) & T_{22}(R) + V_{22}(R) \end{bmatrix} \begin{bmatrix} \phi_1(R, t) \\ \phi_2(R, t) \end{bmatrix} = i\hbar \frac{\partial}{\partial t} \begin{bmatrix} \phi_1(R, t) \\ \phi_2(R, t) \end{bmatrix}. \quad (2.21)$$

The molecular eigenfunction $\varphi_l^{pyr}(r, R)$ for an electronic state with energy E_l can be made separate in terms of nuclear and electronic coordinates. Their expansion is the following:

$$\varphi_l^{pyr}(r, R) = \sum_m \sum_\lambda d_{\lambda,l}^m \varphi_\lambda^{nu}(R) \phi_m^{el}(r, R). \quad (2.22)$$

Lastly, we obtain the following:

$$\begin{bmatrix} T_{11}(R) + V_{11}(R) & T_{12}(R) + V_{12}(R) \\ T_{21}(R) + V_{11}(R) & T_{22}(R) + V_{22}(R) \end{bmatrix} \begin{bmatrix} \psi_1^l(R) \\ \psi_2^l(R) \end{bmatrix} = E_l \begin{bmatrix} \psi_1^l(R) \\ \psi_2^l(R) \end{bmatrix}. \quad (2.23)$$

2.1.2 Born-Oppenheimer Approximation

The time dependent nuclear wavefunction, presented in the previous section, sees an effective potential provided by the electrons. This is known as Potential Energy Surface (PES) and is given by the quantum chemistry packages involving very sophisticated calculations behind (we shall see this in detail in the upcoming sections). The nuclei has the possibility (and is indeed, what happens in the adiabatic picture) to move on a single PES created by the electrons, which move much faster than them [100]. However, if we have multiple PESs corresponding to different electronic states, then the nuclear wavefunction, while moving around those surfaces that may intersect (known as Conical Intersection, CI), has to adapt consequently to preserve the singularity. This is one of the many quantum mechanical effects occurring around

the vicinity of a conical intersection. It is also, via the conical intersection that the efficient transition between the nonadiabatic states occur [100].

Here, one speaks about the fast and slow motion, describing respectively the electrons and nuclei. In this approximation, it is assumed that the nuclei remains intact during the time when the electron interacts with the external potential [101]. In doing so, the electrons adapt easily with the nuclear motion. This approximation is known as Born-Oppenheimer Approximation and is valid as long as the gap between the energy levels is sufficiently large [102].

Mathematically speaking,

$$\frac{\partial \varphi_l^{el/ad}(r, R)}{\partial R} \approx 0; \frac{\partial^2 \varphi_l^{el/ad}(r, R)}{\partial R^2} \approx 0. \quad (2.24)$$

Then:

$$T_{Nu} \varphi_l^{Nu}(R, t) \varphi_l^{el}(r, R) \approx \varphi_l^{el}(r, R) T_{Nu} \varphi_l^{Nu}(R, t). \quad (2.25)$$

By definition, the electronic Hamiltonians are diagonal (comes from the quantum chemistry packages). Thus, the following holds true:

$$\begin{bmatrix} T_{Nu} + E_1 & 0 \\ 0 & T_{Nu} + E_2 \end{bmatrix} \begin{bmatrix} \phi_1^{Nu/ad}(R, t) \\ \phi_2^{Nu/ad}(R, t) \end{bmatrix} = i \frac{\partial}{\partial t} \begin{bmatrix} \phi_1^{Nu/ad}(R, t) \\ \phi_2^{Nu/ad}(R, t) \end{bmatrix}. \quad (2.26)$$

The eigenstates can be written as a product below:

$$\varphi_l^{el}(r; R) \times \phi_m^{vib1}(R), \quad (2.27)$$

with:

$$(T_{Nu} + E_1) \phi_m^{vib1} = E_m^{vib1} \phi_m^{vib1}(R). \quad (2.28)$$

Thus, in Born-Oppenheimer Approximation, the electronic motion is completely separated from that of the nuclei. We first solve for the electronic eigenvalues at given nuclear geometries, followed by the nuclear dynamics in the electronic potential [97].

Physically, it means that the nuclear motion, which is relatively slow, will lead just to the deformation of the electronic states (in terms of energy level), but is not able to lead to the transition between the electronic states. The electronic wavefunction, on the other hand, is capable of deforming rapidly enough to follow the nuclear motion [97].

There are some particular cases, where the approximation is violated. If we look at the conical intersection (crossing point of adiabatic potentials), the following relation holds true:

$$T_{12}^{ad} \propto \frac{1}{E_1 - E_2}. \quad (2.29)$$

If $E_1(R) \approx E_2(R)$, then T_{12}^{ad} will diverge. This is precisely the reason why we need the diabatic states. On the other hand, if the two energy levels are close to each other but no presence of conical intersection (for instance, due to some symmetry reasons), the approximation is no longer valid. This is known as *avoided crossing*. For polyatomic molecules like pyrazine, the occurrence of conical intersection is very probable and is very strong in terms of the effects generated [101].

If the approximation is no longer valid, then the eigenstates are no longer a product. For a system with two coupled electronic states, this becomes the following:

$$\varphi_1^{el}(r; R) \times \phi_m^{vib1}(R) + \varphi_2^{el}(r; R) \times \phi_m^{vib2}(R). \quad (2.30)$$

The matrix representation of the Hamiltonian in the adiabatic basis sets with the approximation is reduced to the following:

$$\begin{bmatrix} T_{11}^{ad} + E_1 & T_{12}^{ad} \\ T_{21}^{ad} & T_{22}^{ad} + E_2 \end{bmatrix} \begin{bmatrix} \phi_m^{vib1}(R) \\ \phi_m^{vib2}(R) \end{bmatrix} = E_m^{vibronic} \begin{bmatrix} \phi_m^{vib1}(R) \\ \phi_m^{vib2}(R) \end{bmatrix} \quad (2.31)$$

whereas in the diabatic (we will see in the next section) representation, it becomes the following:

$$\begin{bmatrix} T^{nu}(R) + V_1^{dia}(R) & V_{12}^{dia}(R) \\ V_{21}^{dia}(R) & T^{nu}(R) + V_2^{dia}(R) \end{bmatrix} \begin{bmatrix} \varphi_1^{dia}(R, t) \\ \varphi_2^{dia}(R, t) \end{bmatrix} = i\hbar \frac{\partial}{\partial t} \begin{bmatrix} \varphi_1^{dia}(R, t) \\ \varphi_2^{dia}(R, t) \end{bmatrix} \quad (2.32)$$

2.1.3 Diabatic representation

We shall now switch to the diabatic representation. The nonadiabatic coupling matrix element, being difficult to calculate, we start the problem from the diabatic representation [11, 97]. This is because, this coupling matrix diverges when the energy difference between the two excited electronic states becomes zero (see eq. 2.29) and this divergence cannot be treated numerically properly. Here, the electronic wavefunction for a fixed nuclear geometry R_0 is solved by the following equation:

$$[H(r) + V_{eN}(r, R_0)]\phi_n(r, R_0) = \epsilon_n(R_0)\phi_n(r, R_0) \quad (2.33)$$

The total molecular wavefunction can be expanded as a linear combination of the basis set functions $\phi_n(r, R_0)$. The basis set is known as crude adiabatic basis.

$$\psi(r, R) = \sum_n \chi_n^0(R)\phi_n(r, R_0) \quad (2.34)$$

Where, $V_{eN}(r, R_0)$ is the interaction potential between the electrons and the nuclei. This crude adiabatic basis representation can be substituted in eq.2.8 and integrated over the electronic wavefunction. This then gives the coupled electronic in diabatic representation for the nuclear wavefunction as:

$$T_N \chi_m^0(R) + \sum_N U_{mn}(R) \chi_n^0(R) = E \chi_m^0(R) \quad (2.35)$$

All the coupling between the electronic terms comes from the electronic Hamiltonian and the matrix of the nuclear kinetic energy in this basis set is diagonal: this

defines a diabatic basis set.

However, the problem of the basis expressed in eq.2.34 is that one needs a huge number of functions to describe the dynamics even in the electronic ground state, as obtained within the Born-Oppenheimer approximation. This gives rise to the need of a quasi diabatic representation: a basis set that minimizes as much as possible the coupling coming from the nuclear kinetic energy operator. The definition of this quasi diabatic basis set is not unique and the diabatic criteria,

$$U^{dia\dagger}(q)U^{dia}(q) = U^{dia}(q)U^{dia\dagger}(q) = 1 \quad (2.36)$$

is not achievable everywhere ([11], chapter 4). Eq.2.35 is often referred as the time independent Schrödinger equation written in a diabatic basis. U_{mn} is a diagonal term in the potential energy operator and is commonly known as diabatic potential.

Equation 2.35 can be written in the matrix form as:

$$T_{mn}(R) = T_N \delta_{mn} \quad (2.37)$$

One of the ways to get the diabatic states are simply by minimizing T_{mn} . The kinetic energy operator is supposed diagonal whereas the potential energy operator is not. The non-diagonal coupling is due to the electron-nuclear interaction $V_{eN}(r, R)$. However, this approach is very expensive and possible only for small systems.

A more approximate approach is adopted here. This is a procedure called *diabatization by ansatz*. The Hamiltonian matrix (discussed in the upcoming sections in the diabatic basis set) H_q^{dia} is a simple and smooth function of q . We choose a simple expression for the diabatic states with the parameters to be found. The way to obtain the most precise values of different parameters in this Hamiltonian is by a fitting procedure in such a way that H_q^{dia} has its eigenvalues as close as those obtained by ab initio adiabatic energies over a wide range of molecular geometries.

As we will see later on in the upcoming sections, one of the ways to choose the ansatz for H_q^{dia} is to make a Taylor expansion around the Franck-Condon point; this is

so called linear (first order) or quadratic (second order) vibronic Hamiltonian model.

For a complete electronic basis set, the diabatic and adiabatic expansion of a given molecular wavefunction should be identical. That is to say:

$$\psi(r, R) = \sum_n \chi_n(R) \phi_N(r|R) = \sum_n \chi_n^0(R) \phi_N(r|R_0) \quad (2.38)$$

We can then integrate the molecular wavefunction over all the electronic coordinates. This will give the correspondence of the nuclear wavefunction expressed in adiabatic and diabatic representations.

$$\chi_m(R) = \sum_n D_{mn}(r|R_0) \chi_n^0(R) \quad (2.39)$$

The transformation matrix D_{mn} is given by the following relation:

$$D_{mn}(r|R_0) = \langle \phi_m(R) | \phi_n(R_0) \rangle = \int \phi_m^*(r|R) | \phi_n(r|R_0) dr \quad (2.40)$$

The calculation of this transformation matrix is not obvious as it involves the calculation of adiabatic eigenfunction $\phi_n(R_0)$. The way to avoid this is to start by the diabatic representation stated in eq.2.35 so as to have the diabatic coupling matrix $\mathbf{U}(R)$. The one to one transformation relation between the diabatic and adiabatic potential is then given by the following relation:

$$\mathbf{V}(R) = \mathbf{D}^\dagger(r|R_0) \mathbf{U}(R) \mathbf{D}(r|R_0) \quad (2.41)$$

One can thus, simply opt for a solution of the diabatic wavefunction $\chi^0(R)$ first and make a transformation to get the adiabatic wavefunction $\chi(R)$ when needed. This is much more simple than directly solving the nonadiabatic problems by taking the nonadiabatic representation [97].

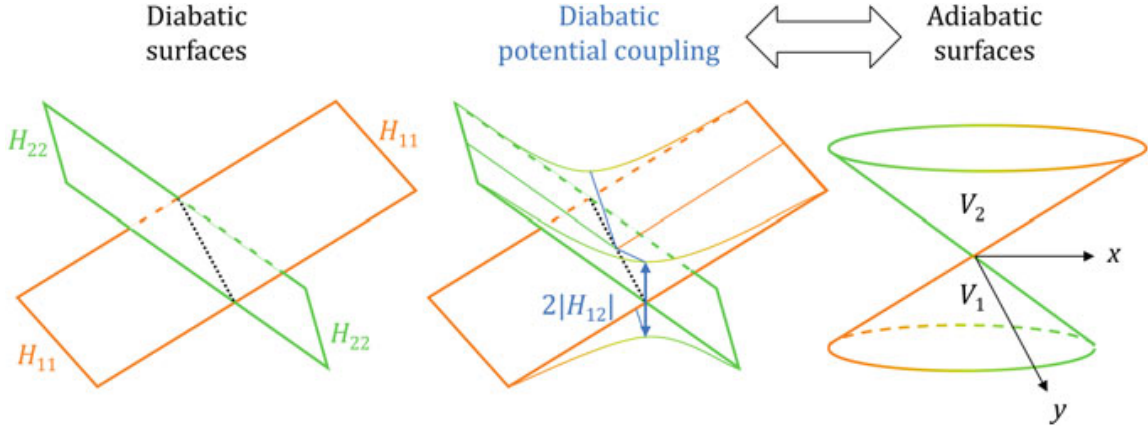


Figure 2.1: Diabatic and adiabatic surfaces: H_{ij} ($i, j = 1, 2$) represent two diabatic electronic energy surfaces whereas V represents the adiabatic one spanned over the two coordinates x and y . Reprinted with permission from [11] Springer Nature copyright 2017 (see chapter 4 of [11] for more details).

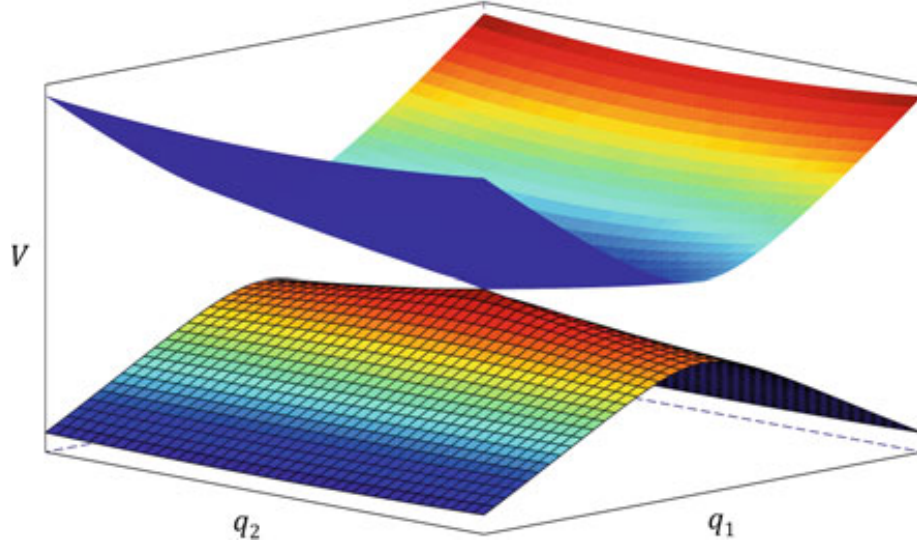


Figure 2.2: A simplified pictorial illustration of a conical intersection involving two surfaces V_1 (lower) and V_2 (upper). The intersection lies exactly at the origin $(0,0)$ and the two cones formed at this point are then spanned over the coordinates q_1 and q_2 . The plane (q_1, q_2) is known as *branching plane*. Reprinted with permission from [11] Springer Nature copyright 2017 (see chapter 4 of [11] for more details).

As seen in fig.2.2, once we move far from the point of the formation of cone, the slope of the cone starts to increase linearly, thus increasing also the energy difference between the two electronic states. It then becomes evident that one has to work with the diabatic representation rather than with the adiabatic one. The only way to

merge the two representations is to work within the vicinity of a conical intersection. This plane of bifurcation is known as *branching plane* or *branching space* (branching plane is a tangent to the branching space at the conical intersection). Formed in an adiabatic potential, the branching space shown in the fig.2.2 is a result of eqs.1.2 and 1.3 stated in chapter 1. These two mathematical requirements describe two linearly independent directions, intersecting at ($q_1 = 0$, $q_2 = 0$).

2.1.4 Exploration of the Potential Energy Surfaces

Potential energy surface can be understood as a graphical representation of the potential energy as a function of nuclear coordinates (when only one coordinate is involved, then it simply is a potential energy curve, see chapter 7 of [103]). It is therefore, the effective potential seen by the nuclei in the electronic configuration and is important to know its value at each geometry, as it gives us insight into the formation of different products from a given transition state [103] (see fig.1.5). Moreover, for a given molecule, it tells us how the potential energy changes when the nuclear coordinates involved in a chemical reaction are varied. Thus, understanding this behavior is a central issue if one wants to apprehend the chemical kinetics [103].

Obtaining a potential energy surface is a very hefty task and is a bottleneck in computational chemistry [104, 105]. Involving more and more atoms means that many coordinates are added. This, thus, defines a multidimensional surface. However, visualising this is a constraint and the reduction of dimensionality in such a way that all the active coordinates responsible for the dynamics in the study is the only way to overcome them [103]. One might obtain a complete potential energy surface also by repeating the calculation at several nuclear geometries [103]. There are, however, some other ways to explore it directly by the code ([106–108]).

2.2 Quantum Dynamics Simulation and MCTDH

Before entering into the details of understanding of the basics of MCTDH, let's see what the standard expansion method implies in molecular quantum dynamics.

According to the standard method, the total time dependent wavefunction can be

re-written as a function of time independent basis sets, expressed as shown below:

$$\psi(q_1, q_2, \dots, q_f, t) = \sum_{j_1=1}^{n_1} \dots \sum_{j_f=1}^{n_f} C_{j_1 \dots j_f}(t) \chi_{j_1}^{(1)}(q_1) \dots \chi_{j_f}^{(f)}(q_f) \quad (2.42)$$

where, $q_1, q_2, \dots, q_f$ are the nuclear degrees of freedom (or, nuclear coordinates), n_k is the number of basis functions used for the k^{th} degree of freedom. Similarly, χ_j are the orthonormal basis functions (for instance, they could be harmonic oscillators, Legendre polynomials, plane waves etc).

The problem with this method is that it has to employ huge no. of basis sets to reach the convergence, which then would not only increase the computational cost, but also the equation to be solved. Thus, the standard method suffers the exponential increase with increasing number of degrees of freedom, which is a real bottleneck for solving the Schrödinger equation numerically. More than that, only the coefficients C_{j_k} are optimized.

One of the ways to overcome this problem is to use the MCTDH ansatz (discussed in the upcoming section). It is a very powerful algorithm in existence since the early 90s, where we solve the time dependent Schrödinger equation with several wavepackets at the same instant of time [88, 89].

2.2.1 Primitive Basis Sets

The electronic wavefunction in quantum chemistry has to be re-expressed as a combination of some other basis functions. One of the well known problems here is that increasing the no. of degrees of freedom (or, the dimensionality) means also increasing the no. of primitive functions. In MCTDH, this problem is minimized by the use of what we call single particle functions, spfs (see in the upcoming sections) that evolve in the same manner as that of the electronic wavefunction. These contracted wavefunctions in MCTDH are such that $n_1, \dots, n_f$ (see eq.2.42), the no. of basis functions for spfs are smaller than $N_1, \dots, N_f$, the no. of basis functions for the primitive basis sets (for more about different possibilities regarding the choice of primitive basis sets, see the documentation file of MCTDH).

The choice of the basis set in expanded wavefunction is governed by several factors like the physics one wants to describe, the volume element, the boundary conditions and the presence of singularities in the nuclear kinetic energy operator. The number N for most of the numerical applications is a finite one and this representation is thus, known as Finite Basis Representation (FBR) [109]. Some of the examples of this are spherical harmonics (see also, chapter 5 of this manuscript), Hermite functions, the particle-in-a-box eigenfunctions and so on.

However, while doing simulation(s), for instance in a computer, the wavefunction ψ has to be represented by a discrete vector especially to calculate the action of the potential on the wavefunction. This is known as DVR (or, Discrete Variable Representation), where the wavefunction is expressed on a grid of points [110, 111]. The mathematical details and the one to one correspondence of FBR and DVR has been explained elsewhere (see [11], chapter 8 for instance or [112–115]). For each FBR, there is an associated DVR with an unitary transformation between the two.

In practice, the wavefunction in MCTDH is expressed in the DVR (in other words, the “primitive” basis set is a DVR) and one switches to the FBR only to apply the derivative operators in the kinetic energy.

2.2.2 MCTDH and ML-MCTDH

The MCTDH wavefunction ansatz is given by the following relation [11, 116–119]:

$$\psi(q_1, q_2, \dots, q_f, t) = \sum_{j_1=1}^{n_1} \dots \sum_{j_f=1}^{n_f} A_{(j_1 \dots j_f)}(t) \prod_{k=1}^f \psi_{j_k}^{(k)}(q_k, t) \quad (2.43)$$

$$\psi_{j_k}^{(k)}(q_k, t) = \sum_{i_k=1}^{N_k} C_{i_k j_k}^{(k)}(t) \chi_{i_k}^{(k)}(q_k) \quad (2.44)$$

Here, both the coefficients $A_{(j_1 \dots j_f)}(t)$ and the basis set functions $\psi_{j_k}^{(k)}(q_k, t)$ are optimized functions by using Variational Principle [87, 89, 120, 121] (see the upcoming

sections). The functions $\psi_{j_k}^{(k)}(q_k, t)$ are known as Single Particle Functions (SPFs) in the terminology of MCTDH. As they evolve with time in the same way as does the nuclear wavefunction, the exponential limit is somehow reduced. However, the question of curse of dimensionality is still present. Apart from that, the q_k 's here can be combined (known as *Mode Combination*, see the upcoming sections). This, when properly combined, will also reduce our computational time.

These functions can again be re-written as a linear combination of some time independent basis sets, known as primitive basis sets or DVR grids. As the expansion coefficients of both spfs and Primitive Basis Set depend on time, this allows us to have enough flexibility in the effort related to the computational time, which otherwise increases exponentially. The contracted basis is built within the space of primitive basis, but is much smaller when it comes to the size [122]. As they are optimized, the numbers $n_1, n_2, \dots, n_k$ become smaller as compared to $N_1, N_2, \dots, N_k$; this will allow more flexibility. Hence, we can study the dynamics of larger molecular systems like pyrazine with smaller number of equation of motions.

Not only this, there is still a possibility of rewriting the time dependent basis functions as a linear combination of several layers of time independent basis sets. This procedure is known as ML-MCTDH [123–125].

The recently introduced variant of MCTDH is ML-MCTDH [123–127] (Multi-Layer MCTDH), which can solve even the problems related to higher dimensionality [124, 125, 127]. The idea here is to re-express the MCTDH ansatz as many times as one wills, so as to create a series of layers which are interconnected by the time-dependent basis functions. Hence, one allows a very high flexibility not only in the MCTDH ansatz, but also in the choice of layers, which ultimately influences the final results (will be shown in the later sections). The last layer is then time independent. The concept of ML-MCTDH was used for the very first time by H. Wang in 2003 [128–130]. Since then, the group in Heidelberg has incorporated this idea in the MCTDH ansatz.

The basic equations for ML-MCTDH are stated below with a representative example.

$$\psi(q_1, q_2, q_3, t) = \sum_{j_{12}=1}^{n_{12}} \dots \sum_{j_3=1}^{n_3} A_{j_{12}, j_3}(t) \varphi_{j_{12}}^{(12)}(q_1, q_2, t) \varphi_{j_3}^{(3)}(q_3, t) \quad (2.45)$$

$$\varphi_{j_{12}}^{(12)}(q_1, q_2, t) = \sum_{k_1=1}^{n_1} \sum_{k_2=1}^{n_2} B_{k_1, k_2}^{(12, j_{12})}(t) \xi_{k_1}^{(1)}(q_1, t) \xi_{k_2}^{(2)}(q_2, t) \quad (2.46)$$

$$\xi_{k_1}^{(1)}(q_1, t) = \sum_{j_1=1}^{N_1} C_{i_1}^{(1, k_1)}(t) \chi_{i_1}^{(1)}(q_1) \quad (2.47)$$

$$\xi_{k_2}^{(2)}(q_2, t) = \sum_{j_2=2}^{N_2} C_{i_2}^{(1, k_2)}(t) \chi_{i_2}^{(2)}(q_2) \quad (2.48)$$

We see clearly the main difference with standard MCTDH: in eq.2.46, the spf functions are themselves expressed in terms of new spf functions and not in terms of the time-independent basis set functions: this constitutes a new layer. The corresponding “tree” of the above mathematical ML-MCTDH ansatz is depicted in fig. 2.3. Thus, ML-MCTDH exploits the possibility of re-defining the basis sets (or configuration). As we can see (eqs.2.47 and 2.48), the last layer is time independent and as in MCTDH, all the coefficients involved are optimized by using the variational principle: this allows one to have a very compact form of the wavepacket and to treat up to hundreds of thousands of nuclear degrees of freedom.

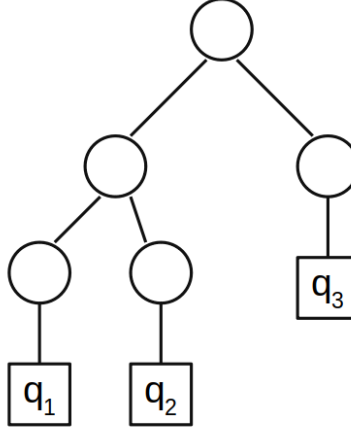


Figure 2.3: ML-MCTDH representation of a 2 layer Tree for 3D (see also chapter 5).

2.2.3 Dirac Frenkel Variational Principle

(See the appendix A of [121] for more details)

One can obtain the approximate solution of TDSE by using the variational principle. This assures that the parameters of the wavefunction are such that its solution is as close as possible to the one (which is exact) given by the TDSE.

The time-dependent Schrödinger equation is the following:

$$H\varphi = i\hbar \frac{\partial \varphi}{\partial t} \quad (2.49)$$

The Dirac Frenkel principle is used, where one can essentially write:

$$\left\langle \partial \varphi \left| H - i \frac{\partial}{\partial t} \right| \varphi \right\rangle = 0 \quad (2.50)$$

where, $\partial \varphi$ takes into account the variation of the wavefunction that are generated by varying different parameters given by:

$$\delta\varphi = \sum \frac{\partial\varphi}{\partial\lambda_k} \delta\lambda_k \quad (2.51)$$

where, λ_k s are the parameters of the wavefunction. In MCTDH, the parameters to be varied are the coefficients $A_{j_1} \dots A_{j_f}$ and the single particle functions $\psi_{j_k}^{(k)}$. Using variational principle, one conserves both the energy and norm.

2.2.4 MCTDH Equations of Motion (MCTDH-EOM):

(Presented in detail in [11])

The MCTDH ansatz as stated in eq.2.43 is the following:

$$\begin{aligned} \psi(q_1, q_2, \dots, q_f, t) &= \sum_{j_1=1}^{n_1} \dots \sum_{j_f=1}^{n_f} A_{j_1 \dots j_f}(t) \varphi_{j_1}^{(1)}(q_1, t) \dots \varphi_{j_f}^{(f)}(q_f, t) \\ &= \sum_j A_j \Phi_j \\ &= \sum_{j=1}^{n_k} \varphi_j^{(k)} \psi_j^{(k)}, \end{aligned} \quad (2.52)$$

which is true for any k going from 1 to f . The derivative of the above stated time dependent wavefunction with respect to A coefficients and SPFs is:

$$\frac{\delta\psi}{\delta A_j} = \Phi_j, \quad (2.53)$$

and,

$$\frac{\delta\psi}{\delta \varphi_j^{(k)}} = \psi_j^{(k)}. \quad (2.54)$$

And, the time differentiation is:

$$\dot{\psi} = \sum_j \dot{A}_j \Phi_j + \sum_{k=1}^n \sum_{j=1}^{n_k} \dot{\varphi}_j^{(k)} \psi_j^{(k)}. \quad (2.55)$$

First, we look only at the variation with respect to the coefficients. For δA_j , this is the following:

$$\langle \delta \psi | H | \psi \rangle = \langle \Phi_j | H | \psi \rangle = \sum_L \langle \Phi_j | H | \Phi_L \rangle A_L \quad (2.56)$$

$$i \langle \delta \psi | \dot{\psi} \rangle = i \langle \Phi_j | \dot{\psi} \rangle = i \dot{A}_j + i \sum_k \sum_l (-i g_{j_k l}^{(k)}) A_{J_l^k}. \quad (2.57)$$

The Dirac Frenkel Principle sets eqs.2.53 and 2.54 equal. Now, if we solve for $\dot{A}$, we get the following:

$$g_{j_k l}^{(k)} \equiv \langle \varphi_j^{(k)} | g^{(k)} | \varphi_l^{(k)} \rangle = \langle \varphi_j^{(k)} | \dot{\varphi}_l^{(k)} \rangle, \quad (2.58)$$

Thus:

$$i \dot{A}_j = \sum_L \langle \Phi_j | H | \Phi_L \rangle A_L - i \sum_{k=1}^f \sum_{l=1}^{n_k} g_{j_k l}^{(k)} A_{j_k^l}. \quad (2.59)$$

Similarly, with respect to SPFs, the variation is the following:

$$\langle \delta\psi | H | \psi \rangle = \left\langle \psi_j^{(k)} | H | \psi \right\rangle = \left\langle \psi_j^{(k)} | H | \sum_l \psi_l^{(k)} \varphi_l^{(k)} \right\rangle = \sum_{l=1}^{n_k} \langle H \rangle_{jl}^{(k)} \psi_l^{(k)} \quad (2.60)$$

$$i \left\langle \delta\psi | \dot{\psi} \right\rangle = i \underbrace{\sum_L \left\langle \psi_j^{(k)} | \Phi_L \right\rangle \dot{A}_L}_{part1} + i \underbrace{\sum_L \left\langle \psi_j^{(k)} | \sum_{\nu=1}^f \sum_{l=1}^{n_\nu} \dot{\varphi}_l^{(\nu)} \psi_l^{(\nu)} \right\rangle}_{part2}. \quad (2.61)$$

Setting $g^{(k)} \equiv 0$, gives the following:

$$i \dot{A}_L = \sum_L \langle \Phi_L | H | \psi \rangle A_L = \sum_k \langle \Phi_L | H | \Phi_K \rangle A_K, \quad (2.62)$$

and, part 1 of eq.2.59 becomes:

$$i \sum_L \left\langle \psi_j^{(k)} | \Phi_L \right\rangle \dot{A}_L = \sum_L \left\langle \psi_j^{(k)} | \Phi_L \right\rangle \langle \Phi_L | H | \psi \rangle, \quad (2.63)$$

which, with,

$$\Phi_L = \Phi_{L^k} \psi_{l_k}^{(k)}, \quad (2.64)$$

and,

$$\psi_j^{(k)} = \sum_{j^k} A_{J_j}^{(k)} \Phi_{j^k}, \quad (2.65)$$

can be turned to the following:

$$(part1) = \sum_{L^k, l_k} A_{L_j^k}^* \left| \psi_{l_k}^{(k)} \right\rangle \langle \Phi_{L^k} | H | \psi \rangle = P^{(k)} \left\langle \psi_j^{(k)} | H | \psi \right\rangle, \quad (2.66)$$

with the following MCTDH projector,

$$P^{(k)} = \sum_{j=1}^{n_k} \left| \psi_j^{(k)} \right\rangle \left\langle \psi_j^{(k)} \right|. \quad (2.67)$$

The final solution for part 1 is then the following:

$$i \sum_L \left\langle \psi_j^{(k)} | \Phi_L \right\rangle \dot{A}_L = P^{(k)} \left\langle \psi_j^{(k)} | H | \psi \right\rangle = P^{(k)} \langle H \rangle_{jl}^{(k)} \varphi_l^{(k)}. \quad (2.68)$$

For part 2:

$$i \left\langle \psi_j^{(k)} | \sum_{\nu=1}^f \sum_{l=1}^{n_\nu} \dot{\varphi}_l^{(\nu)} \psi_l^{(\nu)} \right\rangle = i \left\langle \psi_j^{(k)} | \sum_l \dot{\varphi}_l^{(k)} \psi_l^{(k)} \right\rangle = i \sum_l \rho_{jl}^{(k)} \dot{\psi}_l^{(k)}. \quad (2.69)$$

with,

$$\left\langle \psi_j^{(k)} | \dot{\psi}_l^{(k)} \right\rangle = 0. \quad (2.70)$$

this holds for any j and l as we assumed $g^{(k)} \equiv 0$.

$$\sum_{l=1}^{n_k} \langle H \rangle_{jl}^{(k)} \varphi_l^{(k)} = P^{(k)} \langle H \rangle_{jl}^{(k)} \varphi_l^{(k)} + i \sum_l \rho_{jl}^{(k)} \dot{\psi}_l^{(k)}, \quad (2.71)$$

or,

$$i\dot{\psi}_j^{(k)} = \sum_{k,l} (\boldsymbol{\rho}^{(k)})_{jk} (1 - P^{(k)}) \langle H \rangle_{kl}^{(k)} \psi_l^{(k)}. \quad (2.72)$$

$$i\dot{\mathbf{A}}_J = \sum_L \langle \Phi_J | H | \Phi_L \rangle A_L, \quad (2.73)$$

$$i\dot{\psi}_j^{(k)} = (1 - P^{(k)}) \sum_{k,l=1}^{n_k} (\boldsymbol{\rho}^{(k)})_{jk} \langle H \rangle_{kl}^{(k)} \psi_l^{(k)}. \quad (2.74)$$

2.2.5 Electronic States

The wavefunction can be propagated on several (possibly coupled) electronic states. As such, the wavefunction expansion will be the following:

$$|\psi\rangle = \sum_{j_1}^{n_1} \dots \sum_{j_f}^{n_f} \sum_{\alpha=1}^{n_s} A_{j_1 \dots j_f \alpha} \varphi_{j_1}^{(1)}(q_1, t) \dots \varphi_{j_f}^{(f)}(q_f, t) |\alpha\rangle \quad (2.75)$$

This is called *single-set* formalism, because all the electronic states have one (and, the same) set of SPFs. On the contrary, the *multi-set* formulation can also be used, where the sets of SPFs are different for each state concerned.

$$|\psi\rangle = \sum_{\alpha=1}^{n_s} \varphi_{\alpha}(q_1, \dots, q_f, t) |\alpha\rangle \quad (2.76)$$

The component ψ_{α} can then be written in MCTDH form as follows:

$$\varphi_{\alpha}(q_1, \dots, q_f, t) = \sum_{j_1^{\alpha}}^{n_1^{\alpha}} \dots \sum_{j_f^{\alpha}}^{n_f^{\alpha}} A_{j_1^{\alpha} \dots j_f^{\alpha}}^{\alpha}(t) \varphi_{j_1^{\alpha}}^{1,\alpha}(q_1, t) \dots \varphi_{j_f^{\alpha}}^{f,\alpha}(q_f, t) \quad (2.77)$$

2.2.6 Other Existing Approaches and the Advantages of MCTDH

As said previously, the exploration of a potential energy surface is a very challenging work and the essence of methodological and computational developments of analytical tools lies in this aspect since most of the chemistry is described by it [131]. Theoretically, the understanding of the underlying phenomena in molecular quantum dynamics is done via the simulation. For this, several codes (or, algorithms or, packages) are in existence [132–135]. The common goal, however, of all these methods is to predict, hypothesize, understand, describe and control the dynamics at an elementary level [122]. In the field of molecular dynamics, these different approaches serve in calculating various properties requiring either the exact quantum mechanical description (small systems) or the approximate statistical methods (large systems). Further simplification is provided by the BO separation; thus, the study of nuclear effects in large systems (with several hundreds of atoms) is possible both classically and quantum mechanically. Depending on what one wishes to have, they could be exploited.

The table below summarizes different methods (or, approaches) used in the field of computational chemistry (see introductory section of ref [10] and also chapter 1 of the current manuscript, where in fig.1.7, we describe the approaches and simulation methods commonly used).

Table 2.1: methods (or, approaches) in the field of molecular dynamics, reprinted with permission from [10], Wiley, copyright 1997.

Description	Dynamics	Potential
Quantum	Coupled eqs., coupled wavepackets	Full
Semi-classical	Trajectories, Gaussian wavepackets	
	coupled equations	Full
Classical	Trajectories	Full
Reaction path	Wavepackets, trajectories	Restricted
Transition state	Counting of states, reactive flux	Restricted
Phase space/statistical	Counting of states	Restricted

Molecular quantum dynamics is a borderline of quantum physics and chemistry [122]. In molecular quantum dynamics, we solve the time dependent Schrödinger equation for nuclei. This is preceded by the time independent Schrödinger equation for the electrons, where the nuclei is treated as a point charge. Here, the nuclei is a particle moving in a manifold of the coupled potential energy surfaces [131].

The challenges we have in our study are the following [136]:

1. The transition between the electronic states should be approached quantum mechanically or quasi-classically using methods like surface hopping.
2. The conical intersection, as it depends on the nuclear geometry, could change due to the strong coupling among different nuclear coordinates. Thus, the true understanding will not result from the low dimensional calculations.
3. We thus require accurate calculations for high dimensional systems capable of tackling structures like conical intersection. This is the bottleneck; hence, different approaches are introduced in the literature ([40, 137, 138]) to treat this problem, one of them being MCTDH.

The only way to overcome these issues is by the use of quantum mechanical description for a molecular system and to do so, we need methods like MCTDH. The equations of motion, derived by variational principle (see section 2.2.5), come from very flexible wavefunction ansatz. The optimally small basis sets in the wavefunction representation can be gradually increased depending on the level of convergence we want to achieve.

Now, let's see some of the advantages of MCTDH with respect to the traditional standard propagation methods while considering the complete quantum approach for treating the system. Note that, the same can be done even with the techniques like surface hopping [139] or even by density matrix [140, 141]. The gain (compared to the standard method) in terms of memory is given by the following relation:

$$gain(memory) \approx \frac{1}{4} \left(\frac{N}{n} \right)^f \quad (2.78)$$

Similarly, the gain in terms of CPU time is given by the following relation:

$$gain(CPU) \approx \frac{1}{2s} \left(\frac{N}{n} \right)^{f+1} \quad (2.79)$$

where, N and n is the size of spf functions and primitive basis sets respectively. f is the f^{th} degree of freedom. MCTDH has also been applied to density matrix

methods to include the effect of temperature and also the environment and its impact on quantum decoherence[94].

2.2.7 Improved Relaxation: Few Words

(Principally taken from [11])

Although primarily designed for time dependent calculations, one can also do time independent calculations with MCTDH. In doing so, one obtains the quantum eigenstates and quantum resonances with pretty good accuracy [11, 142]. *Relaxation* in quantum mechanics is a method of propagating the wavepacket in negative imaginary time. In doing so, we calculate the ground state energy of the system (see, chapter 5 of this manuscript, for instance), which otherwise, with the evolution operator, will calculate the excited states.

The Schrödinger equation with $t = -i \times t$ can be written as following:

$$\dot{\varphi} = -H\varphi \quad (2.80)$$

The φ in the equation above can be written in terms of the eigenstates. We then get:

$$\varphi(t) = \sum_n a_n e^{-E_n t} \varphi_n \quad (2.81)$$

The above equation shows that the final wavefunction contains the term, which is exponentially decaying. In doing so, we damp our system to the ground state. As it is based on the variational principle, the energy goes on decreasing with respect to time.

There is a conservation of norm; which essentially is one of the factors to verify the convergence of our calculation. The Schrödinger equation can then be re-written as following:

$$\dot{\varphi} = -(H - E(t))\varphi(t) \quad (2.82)$$

with:

$$E(t) = \langle \varphi(t) | H | \varphi(t) \rangle \quad (2.83)$$

Thus,

$$\left\langle \varphi(t) | \dot{\varphi}(t) \right\rangle = 0 \quad (2.84)$$

$$\frac{d\|\varphi^2\|}{dt} = 0 \quad (2.85)$$

This shows that the term $E(t)$ was just introduced to preserve the constancy of the norm of our wavefunction. Classically, it is the Lagrange parameter introduced to minimise the action. Differentiating E with respect to time gives:

$$\dot{E} = -2 \left\langle \varphi(t) | (H - E(t))^2 | \varphi(t) \right\rangle \quad (2.86)$$

Eq.2.86 shows that the energy decreases with time and for $H = E(t)$, becomes zero. In this case, the wavefunction will become an exact eigenstate of H . This is what happens for the ground state. Relaxation is convincing when the initial guess of the wavefunction ψ has sufficient overlap with the ground state.

If we wish to calculate the excited states, it is still possible by what is known as *improved relaxation* method (discussed below). Here, we combine relaxation with diagonalization of the Hamiltonian operator (this is how the A-vector is determined).

One uses then, the time independent variational principle given by the following relation:

$$\delta \{ \langle \varphi | H | \varphi \rangle - constraints \} = 0 \quad (2.87)$$

That is:

$$\delta \left\{ \langle \varphi | H | \varphi \rangle - E \left(\sum_j A_j^* A_j - 1 \right) - \sum_{k=1}^f \sum_{j,l=1}^{n_k} \epsilon_{jl}^{(k)} \left(\left\langle \varphi_j^{(k)} | \varphi_l^{(k)} \right\rangle \delta_{jl} \right) \right\} = 0 \quad (2.88)$$

The constraints can be attributed to the Lagrange parameter. We optimize all the parameters because the number of Lagrange multipliers here is very large than those used in standard methods. E is the first Lagrange parameter in the above equation and it ensures the normalization of A vectors, while $\epsilon_{jl}^{(k)}$ ensures the orthonormality of the SPFs used.

With two states j and k , the Hamiltonian can be written as:

$$H_{jk} = \langle \Phi_j | H | \Phi_k \rangle \quad (2.89)$$

Varying A_j^* gives the secular equation as follows:

$$\sum_k H_{jk} A_k = E A_j \quad (2.90)$$

By diagonalizing the above equation, we can get A , which are the eigenvectors of the Hamiltonian matrix of eq.2.90. For the SPFs, we use the relation below:

$$\langle \varphi | H | \varphi \rangle = \left\langle \sum_j \Psi_j^{(k)} \varphi_j^{(k)} | H | \sum_l \Psi_l^{(k)} \varphi_l^{(k)} \right\rangle = \sum_{j,l} \left\langle \varphi_j^{(k)} \left| \langle H \rangle_{jl}^{(k)} \right| \varphi_l^{(k)} \right\rangle \quad (2.91)$$

And, Varying $\left\langle \varphi_l^{(k)} \right|$ gives:

$$\sum_{l=1}^{n_k} \langle H \rangle_{jl}^{(k)} \varphi_l^{(k)} = \sum_{l=1}^{n_k} \epsilon_{jl}^{(k)} \varphi_l^{(k)} \quad (2.92)$$

One can project the above equation to $\varphi_k^{(k)}$. This leads to:

$$\epsilon_{jk}^k = \sum_l \left\langle \varphi_k^{(k)} \left| \langle H \rangle_{jl}^{(k)} \right| \varphi_l^{(k)} \right\rangle \quad (2.93)$$

Thus, it follows that:

$$(1 - P^{(k)}) \sum_{l=1}^{n_k} \langle H \rangle_{jl}^{(k)} \varphi_l^{(k)} = 0 \quad (2.94)$$

This is a general equation and holds true for any j . In the same way, the equation remains valid for any linear combination of j too. If we derive the above equation, we get the equations of motion for MCTDH.

$$\dot{\varphi}_j^{(k)} = -(1 - P^{(k)}) \sum_{k,l} (\rho^{(k)})^{-1} \langle H \rangle_{jl}^{(k)} \varphi_l^{(k)} = 0 \quad (2.95)$$

With:

$$\dot{\varphi} = \frac{\partial \varphi}{\partial t}, \tau = it \quad (2.96)$$

One can thus explain improved relaxation in very simple words as follows: First, we define an initial state by a guess. This guessed state should have reasonable overlap with the target state. Then, we build the matrix representation for the Hamiltonian, H_{jk} of the system and then diagonalize it. Thus, the mean fields are built and the SPFs are then relaxed in those mean fields, until their time derivatives become sufficiently small. After this, the H_{jk} is then built in the space of new SPFs and again, the whole process is iterated until one reaches new level of convergence. This iterative process, which gives us the eigen energies of our system, is very helpful because it eliminates the components of space that are higher in energy. In doing so, the quality of the basis function is, indeed, improved.

2.2.8 Integration Schemes

In the Heidelberg package, we assume that we have an Hamiltonian operator as a sum of products of low-dimensional operators. This allows one to avoid large integrals. In all the systems studied in this work, the operator had the proper form. If not, many methods have been devised to re-express the operators (mainly the potential operator) in this form [143–147]. In addition, we have to solve numerically the equations of motion of MCTDH.

The MCTDH equations of motion are a set of coupled, non-linear differential equations. There are different integration schemes available, which build the mean field matrices H_{jl}^k and ϵ_{jk}^k in every time step of propagation.

The analytical expression of the time-evolution of a wavepacket is given by:

$$\psi(t) = \sum_n a_n \varphi_n e^{-iE_n t} \quad (2.97)$$

This wavefunction of the time independent Schrödinger equation,

$$H\psi_n = E\psi_n \quad (2.98)$$

has an oscillating term $e^{-iE_n t}$. To integrate $e^{-iE_n t}$, the following condition has to be satisfied:

$$\Delta t \leq \frac{1}{|E_n|} \quad (2.99)$$

This means that the time step of propagation is limited by the absolute largest eigenvalue of the Hamiltonian matrix.

The MCTDH equations of motion are solved numerically: one never calculates the eigenfunctions explicitly and never uses eq.2.97. Many integrators have been developed to solve the time-dependent Schrödinger equation [148]. In MCTDH, two different integrators are used : one for the A coefficients, the Short Iterative Lanczos (SIL) integration scheme [149] and the Bulirsch-Stoer (BS) extrapolation integrator for the SPFs [150].

We also use the Constant Mean Field approach (CMF): the idea in CMF is to set the mean-fields constant over a large update time step τ and to integrate the A-vectors and SPFs of the MCTDH wavefunction with much smaller time steps [150].

2.3 Laser Molecule Interaction

2.3.1 Full Picture of the Hamiltonian Used

After having defined the general form of the molecular Hamiltonian in the earlier sections, we now move to the Hamiltonian operator defined for the molecule of pyrazine. This is a very well studied molecule in the community of chemical physics. We are using here the so-called “linear vibronic coupling” model, which can be seen as a linear Taylor expansion of the diabatic potentials in terms of the dimensionless normal coordinates of the electronic ground state [6, 151, 152]. The linear (and quadratic) coupling model has been used successfully to reproduce the experimental UV absorption of pyrazine [153, 154].

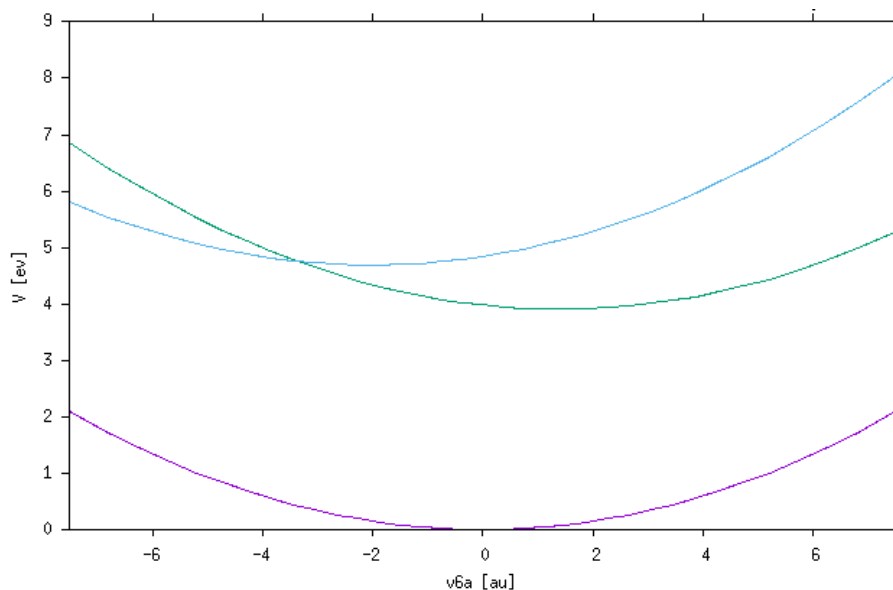


Figure 2.4: Cut of the potential energy surface along Q_{6a} (tuning mode)

The total Hamiltonian of the system is a sum of ‘Free Hamiltonian’ (or molecular Hamiltonian, or system Hamiltonian) and the ‘Interaction Hamiltonian’. This can be written in the matrix form as stated below:

$$H_{mol} = \begin{pmatrix} T + V_0 & 0 & 0 \\ 0 & T + V_1 & V_{12} \\ 0 & V_{21} & T + V_2 \end{pmatrix} \quad (2.100)$$

Where, T is the nuclear kinetic energy operator and V_0 , V_1 and V_2 are the corresponding potential energies for the electronic states S_0 (ground state), S_1 (quasi-dark state, optically difficult to reach) and S_2 (bright state, possibility of direct excitation) respectively (see fig.1.1). The molecule (pyrazine) itself has a D_{2h} point group symmetry. All these states have different symmetries given by ^1A_g , $^1B_{3u}$ and $^1B_{2u}$ respectively [155]. In brief, it contains three planes that are mutually perpendicular with each other, thus a center of symmetry. Around this point, the mirror symmetry of inversion can also be seen. Each of the terms in eq.2.100 is described hereafter.

The nuclear kinetic energy operator for a model with f vibrational modes is the following:

$$T = - \sum_{j=1}^f \frac{\omega_j}{2} \frac{\partial^2}{\partial q_j^2} \quad (2.101)$$

q_j is the dimensionless nuclear coordinate for j^{th} normal mode of the electronic ground state (we have 24 in total, in our case).

The potential energy term for the ground state in the harmonic approximation is the following:

$$V_0 = \sum_{j=1}^f \frac{\omega_j}{2} q_j^2 \quad (2.102)$$

In the linear vibronic coupling model, for the excited states, the diabatic potentials are written as[153, 154]:

$$V_1 = E_1 + \sum_{j=1}^f \frac{\omega_j}{2} q_j^2 + \sum_{j=1}^{f-1} \kappa_j^{(1)} q_j \quad (2.103)$$

$$V_2 = E_2 + \sum_{j=1}^f \frac{\omega_j}{2} q_j^2 + \sum_{j=1}^{f-1} \kappa_j^{(2)} q_j \quad (2.104)$$

Where, E_1 and E_2 are the vertical excitation energies. $V_{12} = V_{21}$ is the coupling term that couples S_1 and S_2 . It is expressed as:

$$V_{12}(= V_{21}) = W_{12}Q_f \quad (2.105)$$

W_{12} is a coupling parameter and is supposed to be a function of a single normal coordinate (ν_{10a}) in our case, labeled f in the previous equations. ω_j s are the harmonic oscillator frequencies and κ_j s are the parameters describing the displacements of the excited states with respect to the equilibrium position of the ground state. The electronic states considered are the diabatic ones and coincide with the adiabatic ones at the equilibrium geometry of the ground state $q_0 = 0$. All these parameters are given by the quantum chemistry packages. Their proper derivation has been given in [11, 156]. The normal modes of the pyrazine molecule, is given in fig.2.5 below.

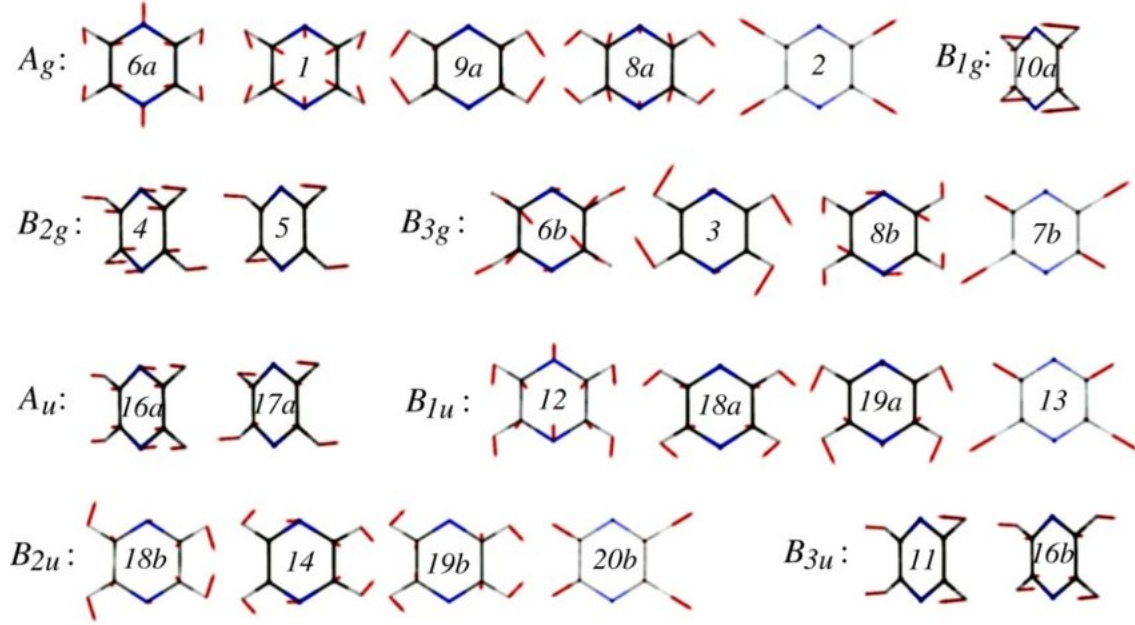


Figure 2.5: All 24 normal modes of Pyrazine, reprinted with permission from [157].

In the upcoming chapters, we shall use three models:

- the 2 dimensional (2D) model that includes q_{6a} and q_{10a} ,
- the 4 dimensional model (4D) including q_{6a} , q_{10a} , q_{9a} and q_1 ,

- and the full dimensional model (24D), with all the normal modes.

It has been shown [153, 154] that q_{6a} and q_{10a} are the two most important coordinates to reproduce the absorption spectrum, that the 4D model is almost enough to reproduce this spectrum quantitatively and that the other 20 modes play a less important role for this spectrum (they are often called the “bath”).

Before entering into the details of the interaction part our Hamiltonian, let's see in brief, what *diabatisation by ansatz* means. Describing the topography of a conical interaction is an essential task, because it contains an information about the non-adiabaticity and how diabatic the states are. Let us first consider only a 2D model for the sake of simplicity and see the meaning of all the terms involved.

$$\mathbf{H}^{dia}(q_1, q_2) = \left(\frac{\hbar\omega_1}{2} q_1^2 + \frac{\hbar\omega_2}{2} q_2^2 \right) \mathbf{1} + \begin{bmatrix} E_1 & 0 \\ 0 & E_2 \end{bmatrix} + \begin{bmatrix} \kappa^{(1)} q_1 & \lambda q_2 \\ \lambda q_2 & \kappa^{(2)} q_2 \end{bmatrix} \quad (2.106)$$

Equation 2.106 is known as vibronic-coupling Hamiltonian model [155, 158, 159] for a two state (1 and 2), two mode (q_1 and q_2) system. In this equation, different parameters have to be calculated. They can be obtained as follows:

$$\mathbf{H}^{dia}(0, 0) = \begin{bmatrix} E_1 & 0 \\ 0 & E_2 \end{bmatrix} \quad (2.107)$$

$$\left(\frac{\partial \mathbf{H}^{dia}}{\partial q_1} \right)_0 = \begin{bmatrix} \kappa^{(1)} & 0 \\ 0 & \kappa^{(2)} \end{bmatrix}, \left(\frac{\partial \mathbf{H}^{dia}}{\partial q_2} \right)_0 = \begin{bmatrix} 0 & W_{12} \\ W_{12} & 0 \end{bmatrix} \quad (2.108)$$

$$\left(\frac{\partial^2 \mathbf{H}^{dia}}{\partial q_1^2} \right)_0 = \hbar\omega_1 \mathbf{1}, \left(\frac{\partial^2 \mathbf{H}^{dia}}{\partial q_2^2} \right)_0 = \hbar\omega_2 \mathbf{1}, \left(\frac{\partial^2 \mathbf{H}^{dia}}{\partial q_1 \partial q_2} \right)_0 = 0 \quad (2.109)$$

For $\kappa^1 = \kappa^2 = 0$, we will obtain two identical parabola with harmonic frequencies ω_1 and ω_2 respectively. $E_2 - E_1$ is the vertical transition energy calculated at the

origin. Remember that, Eq. (2.106) gives the explicit expression of Eq. (2.100) for our model.

In eq.2.106, another approach is adopted: one diagonalizes analytically the matrix of the potential. The eigenvalues are, by definition, the adiabatic potential surfaces. The adiabatic potentials are the energies given by the quantum chemistry softwares. Thus, in eq.2.106, many adiabatic energies are calculated for different geometries and the parameters in the vibronic coupling models are fitted to be as close as possible to the ab initio values of the potential. In the 24 model, these analytical eigenvalues are given by the following relation [160]:

$$V_{1,2} = \frac{E_1 + E_2}{2} + \frac{1}{2} \sum_{i=1}^f \omega_i q_i^2 + \frac{1}{2} \sum_{i \in G_1}^{f-1} [\kappa_i^{(1)} + \kappa_i^{(2)}] q_i + \\ \pm \left[\frac{1}{2} [E_2 - E_1 + \sum_{i \in G_1}^{f-1} [\kappa_i^{(2)} - \kappa_i^{(1)}] q_i]^2 + 4 \sum_{i \in G_3} \lambda_i q_i \right]^{1/2} \quad (2.110)$$

where, V_1 is for minus sign and V_2 for plus sign. G_i takes the modes corresponding to different symmetry groups. Note that, if it is easy to fit the adiabatic potentials, this is a very good criterion to know if the initial ansatz for the diabatic potentials was sufficient. In other words, we had built quasidiabatic potentials, for which the kinetic coupling can be neglected.

Since we add external pulses in our simulations, the interaction Hamiltonian (or, the Hamiltonian for the field-matter interaction) is written in dipole approximation. With the consideration, of a classical electric field, this is given by:

$$H_{int} = \vec{\mu} \cdot \vec{E}(t) \quad (2.111)$$

Where, $\vec{\mu}$ is the radiative transition dipole moment (see in the appendix for its explicit expression in our case) and E is the electric field amplitude of the laser pulse. The explicit expression of E is provided in chapter 3. Here, we will assume that the molecule is ideally aligned: the vectors will disappear and we take the norm of the

vector [39]. All the terms are expressed in atomic units (a.u.). In matrix form, the eq.2.111 is the following:

$$H_{mol} = \begin{bmatrix} 0 & \mu_{01}(q) & \mu_{02}(q) \\ \mu_{01}(q) & 0 & 0 \\ \mu_{02}(q) & 0 & 0 \end{bmatrix} . E(t) \quad (2.112)$$

The respective forms of $\mu_{01}(q)$ and $\mu_{02}(q)$ and all the associated numerical constants are given in [39]. We shall also give the values of some of the important numerical parameters of our Hamiltonian in the upcoming chapters.

The total Hamiltonian then becomes:

$$H = H_{mol} + H_{int} \quad (2.113)$$

The interaction part consists of a Hamiltonian with an external laser field described classically and the remaining part of the Hamiltonian (i.e system) quantum mechanically. Thus, our Hamiltonian (or, even the model) is a quantum semi-classical one. For the molecular part of the Hamiltonian, different models have been proposed in the past [158, 161–163]. In the present study, the necessary numerical parameters are taken from [39]. All the constants are calculated using the *ab initio* methods. As shall be shown (and discussed in detail) later, the most essential four modes were retained and included in the initial calculations. The remaining 20 modes are weakly coupled to the system and act only as a reservoir (or bath) [155, 164].

Chapter 3

Results and Discussion: Interference

The greatest wealth is to live content with little.

- Plato

The overall idea of the following PhD project is to develop a laser control strategy for molecules of intermediate size like pyrazine. The two excited states S_1 and S_2 (see fig.3.1) are coupled due to the presence of a conical intersection; hence leading to a natural flow of population from S_2 towards S_1 . Our goal is to have the maximum of population deposited in S_1 , which could then be readily used for practical applications like light harvesting, photovoltaic cells and solar panels. This is completely a different strategy than what has been suggested by the authors of [46, 165], where they have identified a way to prevent this internal conversion by limiting the population only in S_2 via some locally stable eigenstates in a dense manifold of vibrational levels.

3.1 Strategies Employed

We have identified two different strategies, notably interference and kicks (to be discussed in chapter 4). We start our simulation with a 2D model and, increase gradually the no. of modes. The laser parameters that are used in this calculation are the ones obtained for 4D simulation, thus practically suitable for 24D too.

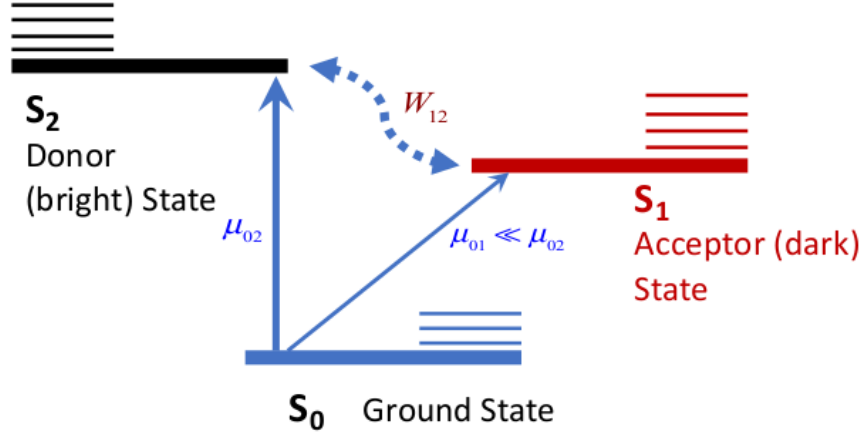


Figure 3.1: 3 level molecular representation of pyrazine

Fig.3.1 is a simplified 3-level diagram illustrating the electronic states in pyrazine. S_1 (thick red line) and S_2 (thick black line) are the two excited electronic states commonly called as donor and acceptor state, and S_0 (thick blue line), the ground electronic state. μ_{02} and μ_{01} are the transition dipole moments for the transitions $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_1$ respectively, whereas W_{12} is a coupling parameter as a result of the conical intersection between S_1 and S_2 . This is a simplified diagram since the molecule possesses 24 nuclear degrees of freedom and, thus, in each electronic state, many vibrational states are present.

There are two ways to populate S_1 . The first possibility (we hereby call it pump pulse) is to populate S_1 via S_2 . This is given by the following mathematical relation:

$$T_1 = \left\langle S_1 \left| W_{12} \frac{1}{E_{S_1} - E_{S_2} - \hbar\omega} \mu_{02} E_1 \right| S_0 \right\rangle. \quad (3.1)$$

Where, T_1 is the transition probability amplitude. Here, we go from S_0 to S_2

initially via the radiative coupling given by the product of μ_{02} and E_1 . Once in S_2 , the population will be transferred naturally to S_1 via the coupling W_{12} , i.e. via the conical intersection. μ_{02} is the matrix element of the radiative transition dipole moment μ responsible for the transfer of population from S_0 to S_2 . E_1 in the above equation represents the electric field amplitude for the pump pulse.

The other possible route to populate S_1 is by direct excitation. This is given by the following relation:

$$T_2 = \langle S_1 | \mu_{01} E_2 | S_0 \rangle. \quad (3.2)$$

The ground state wavepacket in this case is launched directly to S_1 by the use of radiative coupling, which, here, is the product of μ_{01} , the matrix element of μ giving rise to the transfer from S_0 to S_1 and E_2 , the other electric field amplitude for probe pulse (different than E_1).

When using pump probe strategy with a variable delay, the total transition probability amplitude is then the sum of eqs.3.1 and 3.2. Thus:

$$P_1 = |T_1 + T_2 \exp^{-iE\tau/\hbar}|^2. \quad (3.3)$$

with $E = E_{S_0} + \hbar\omega$. This, then, is the interference process where the delayed laser pulses create the wavepackets which could overlap with each other while moving back and forth in the coupled potential energy surface. So, in interference, roughly speaking, you make a Franck-Condon launching of the first wavepacket in S_2 , which then will evolve in time while moving back and forth in S_2 and with some transfer to S_1 . After some time, one then launches the second wavepacket in the same way as previous. In doing so, the two wavepackets will interfere each other since there is a natural coupling between S_1 and S_2 .

What has been shown in the past is somehow different (see [40, 43, 72, 73] for detailed understanding). The two excitation pathways are completely different in these studies. That is to say, the two delayed lasers take different routes (for instance one from S_0 to S_1 and the other from S_0 to S_2 , or the reverse) and then, the wavepackets created in the excited states from the laser excitation will overlap (or interfere) with each other while moving back and forth. However, for this to happen, the following relation must hold true:

$$\mu_{02} \times E_1 = \mu_{01} \times E_2. \quad (3.4)$$

Since, in the particular case of pyrazine, μ_{02} is much larger than μ_{01} (approximately 10 times, see [39]), we need to have E_2 very large than E_1 . This is the difficulty we have in our study (see appendix E) as some secondary effects like ionization or dissociation damage of the molecule could occur. This is something we wish to avoid: we thus work with rather weak fields and T_2 will be neglected from hereon. So, for physical reasons linked to the nature of the molecule of pyrazine, the alternative path was chosen, which is described by the equation below and that retains only route 1.

$$P_1 = |T_1 + T_1 \exp^{-iE\tau/\hbar}|^2. \quad (3.5)$$

Repeated with another delayed laser, the generalized equation for transition probability amplitude is given by eq.3.5. In other words, we are going to use at least two lasers, but all following route 1 only.

The basics of our methods is described in brief below:

Interference mechanism: It is created by the delay parameter (τ) in our transition probability amplitude. In short, the first resonant pulse launches a wavepacket from S_0 to S_2 , which then has a possibility to move back and forth in the coupled electronic potential energy surface of S_2 and S_1 . After a while, the second wavepacket can be launched in S_2 . This then creates a situation where the part of first wavepacket overlaps (or, interferes) with that of the second one if the delay between the two pulses is adequately chosen.

Kicks mechanism: The pulses used are very short; we thus, are not giving enough time for the wavepackets to evolve much. Just immediately after the excitation via the first pulse, we are suddenly exciting the system multiple no. of times (5 in our case, see chapter 4 for more details). Doing so, the molecule is kicked by each laser. The ground state is depleted more and more, while maximizing the amount of population in S_2 and then the energy deposited in S_1 , favored by the coupling parameter W_{12} . Resonance condition is not necessary in this strategy.

We have different parameters for both the system and laser. In interference, intensity and the pulse duration is fixed, while the delay is varied. On the other hand, for kicks, the delay between the pulses is fixed and rather the pulse duration is varied. Both of these strategies will be discussed in detail in the forthcoming chapters.

It should be emphasized that the situation we are dealing with, i.e. no possible direct excitation of an electronic state (here S_1), and the necessity to populate S_1 only by populating of another electronic state (here S_2), that is coupled to the targeted electronic state through a conical intersection, has a general character. This situation appears in some very important biological systems (see, for instance chapter 2, part I of [3], where the authors have shown some particular examples of electron and proton transfer facilitated by the presence of conical intersection. One of the particular examples of this is the photosynthesis. See also [166], where the authors studied the DNA bases and the photostability. In chapter 7 of [122], the ionization potential of benzene and other chemical substances have also been discussed). It is like the antenna that captures the light energy necessary for a chemical process. This is the reason why devising general strategies of control for a model system, pyrazine, can lead to many applications. In our case, S_1 does not trigger a chemical process, but for systems of (bio)chemical relevance S_1 , may be a reservoir of energy leading to a chemical process.

We will now discuss the results obtained for interference mechanism, which shall subsequently be followed by the kicks mechanism in chapter 4.

Experimentally, interference is exactly the pump-dump scheme proposed by Rabitz and co-workers [167], where the control is indeed achieved by a delay (τ) between the two successive femtosecond laser pulses [167–169]. So, what happens in this process is the following: the wavepacket is propagated in the excited surface S_2 . Note that after around 70fs (first vibrational period) the wavepacket revisits the FC region. Then, after some time, another wavepacket of the same form is again created by the second laser and propagated (to be discussed in detail later). In doing so, they overlap (or, not) to create constructive (or, destructive) interference. This is how the branching ratio between the two (or, more) pathways is manipulated in this strategy, so as to increase (or, decrease) the probability of outcome of certain species in a chemical reaction.

n	q	$\epsilon^{(n)}$ (eV)	$\omega_q^{(n)}$ (eV)	$\kappa_q^{(n)}$ (eV)
(0)	6a	0	0.074	0
	10a		0.094	0
	9a		0.157	0
	1		0.127	0
(1)	6a	3.91	<i>id</i>	-0.096
	10a			0
	9a			0.159
	1			0.047
(2)	6a	4.84	<i>id</i>	0.119
	10a			0
	9a			0.048
	1			0.201

Table 3.1: Diagonal elements of the system Hamiltonian H^{dia} . The off-diagonal coupling term $W_{12} = 0.1825$ eV is along the mode 10a and couples S_2 with S_1 . Parameters taken from [170]. The energetic positioning of S_2 is given by [162, 171].

n	q'_1	q'_2	q'_3	q'_4	q'_5	q'_6	q'_7	q'_8
(0)	10	10	4	4	4	4	4	4
(1)	28	28	4	4	4	4	4	4
(2)	28	28	4	4	4	4	4	4

Table 3.2: Number of single particle functions used in 24D calculation for interference mechanism. Their notation is as follows: $q'_1 = (q_{6a}, q_{10a})$, $q'_2 = (q_1, q_{9a}, q_{8a})$, $q'_3 = (q_2, q_4, q_5)$, $q'_4 = (q_{6b}, q_3, q_{8b})$, $q'_5 = (q_{7b}, q_{16a}, q_{17a})$, $q'_6 = (q_{12}, q_{18a})$, $q'_7 = (q_{19a}, q_{13}, q_{18b}, q_{14})$ and $q'_8 = (q_{19b}, q_{20b}, q_{16b}, q_{11})$. They are defined in multi-set formalism (see [172] for details). The numerical values are taken from [161].

As seen in table 3.2, the number of single particle functions associated with q'_1 and q'_2 are very large compared to other modes as they essentially combine the ones involved essentially in the dynamics.

3.2 Electric Field and Renormalization of the Laser Intensity

The electric field for the first pulse is given by the relation below:

$$E_1(t) = \sqrt{I} \sin^2 \left(\pi \frac{t}{T} \right) \cos(\omega t) H(T - t) \quad (3.6)$$

Here, T is the laser pulse duration and H is the Heaviside (or step) function, so as to limit the pulse within the given duration. It is defined in the following way for the first pulse.

$$\begin{cases} t < T & H = 1 \\ t > T & H = 0 \end{cases} \quad (3.7)$$

As one can see, we have the sine-squared form for the envelope and a pulsating (or, oscillating) term given by $\cos(\omega t)$.

For the delayed (or, second) pulse, the electric field takes the form as:

$$E_2(t, \tau) = \sqrt{I} \sin^2 \left[\pi \frac{(t - \tau)}{T} \right] \cos[\omega(t - \tau)] H(t - \tau) H(T + \tau - t) \quad (3.8)$$

Where, τ is the time delay between the two successive pulses. The Heaviside function for this pulse is then the following:

$$\begin{cases} t < T & H(t - \tau) = 0 \\ t > T & H(T + \tau - t) = 0 \end{cases} \quad (3.9)$$

What we wish now is to separate the effects coming from the strong laser pulses and the interference mechanism. To do so, we need to inject the same amount of energy to our system in each time of excitation by the train of pulses. For this, the parameter to be calculated is the total flux. The flux entering in the molecular system should always be equal; regardless of the delay and the no. of pulses introduced [173]. This is given by the following quantity:

$$A = \int_0^t E^2(t) dt \quad (3.10)$$

Let us consider the case of two identical pulses $E_1 = E_2 = \epsilon$, then,

$$A = a \int_0^t \epsilon^2(t) dt. \quad (3.11)$$

Our fields are normalized so as to provide the same total electromagnetic energy: this is done by dividing the intensities I by a , or, the electric field by $\sqrt{a}$. Fig.3.2 shows the variation of the normalization factor with respect to the delay between the pulses. This variation is rather smooth; decreases continuously from 4 to 2.

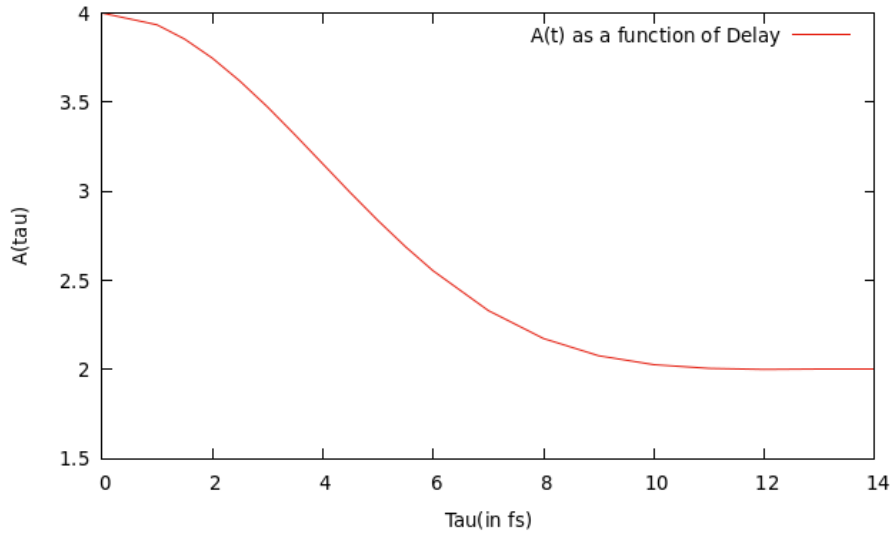


Figure 3.2: Envelope of our pulse including the normalization factor.

We limit the time to 14fs in fig 3.2 as it will remain constant after the pulse duration.

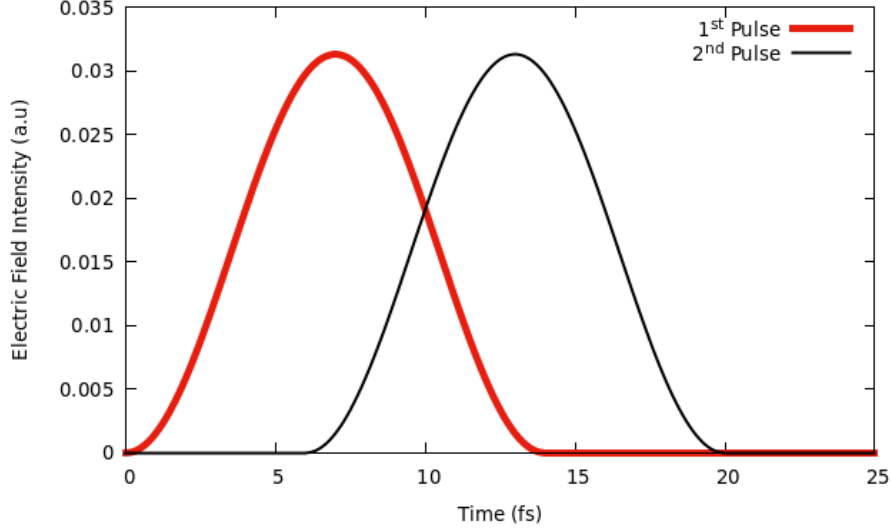


Figure 3.3: Envelopes of the two pulses used in our strategies. The two pulses, as represented by solid black and red lines respectively, have a duration of 14fs each, and the delay shown in this figure is 6fs.

Fig 3.3 shows an example of two pulses (after renormalization) that are used in our strategies. For this particular case, two pulses of duration $T = 14\text{fs}$ and intensity $I = 8.8 \times 10^{13}\text{W}/\text{cm}^2$ were chosen.

3.2.1 Weak Field vs Strong Field

The variation of population of S_2 as a function of laser intensity is shown in fig 3.4 (see below). The red dashed curve is for a single pulse and the thick black line is for two delayed pulses (the delay is taken to be 13fs for this particular calculation). This was obtained for a calculation involving 4 normal modes; the changes when including all the 24 degrees of freedom are very minor (see the upcoming sections).

To understand whether the intensity chosen is within the limit of weak or strong field, certain things have to be verified. If, for instance, the observable, the population P_2 increases (almost) linearly while increasing the intensity, this means that we are in

the weak field limit[69], like here for $I = \times 10^{13} \text{W/cm}^2$. The strong field regime shows non-linear behavior: a saturation in S_2 population around $I = 2 \times \times 10^{13} \text{W/cm}^2$ and a decrease up to $I = 7 \times \times 10^{13} \text{W/cm}^2$.

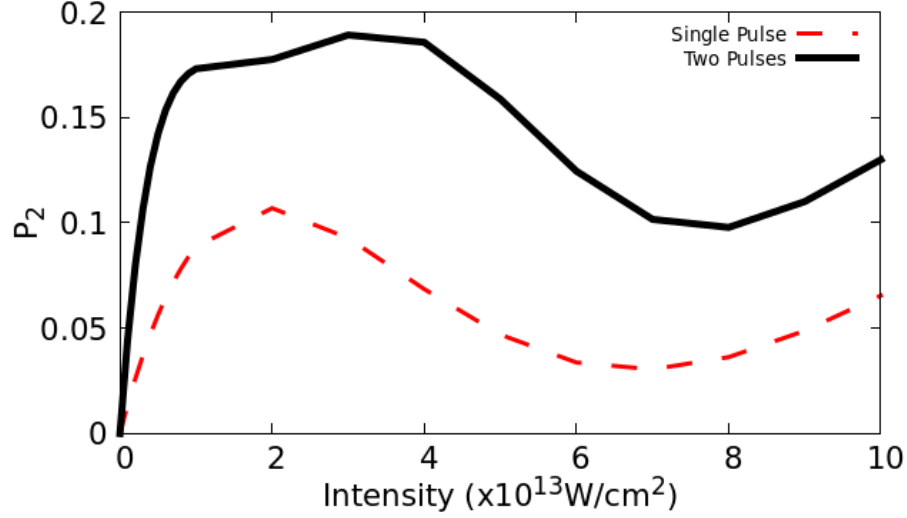


Figure 3.4: Population of S_2 as a function of laser intensity ($\times 10^{13} \text{W/cm}^2$). Black solid line and red dashed line denote respectively, two pulses and a single pulse situation, with $\tau = 12 \text{fs}$

However, in the case of strong field, this is not possible: the physics is more complicated. There is no such simple scaling relation, because the laser pulses generate a complex behavior resulting from the higher order terms of the radiative coupling. This, in turn, means that the depletion of the ground state is very strong (more than 50% generally speaking)[69]. In the upcoming sections, we shall see the calculations for 3 different regimes.

3.3 Observable under study

The observable calculated in this study is the following:

$$p(t) = \frac{P_1(t) - P_2(t)}{P_0(t)} \quad (3.12)$$

We name this quantity *contrast*, where $P_0(t)$, $P_1(t)$, $P_2(t)$ are the time-dependent populations of the electronic states 0, 1 and 2 respectively. We wish to maximize this quantity. To do so, the following things should be kept in mind:

1. Maximize the population in the excited state S_2 , which could result only from the minimization of the population in S_0 .
2. Maximum difference of the population between S_1 and S_2 , that is to say have maximum of the population in S_1 .

This indirectly also means the maximization of population in S_1 , which is the goal of the current study.

The observable in eq.3.12 is a function of t . Rather than calculating the value of this observable at a particular point, we choose several relevant regions during and after the pulse, so as to carefully analyze the dynamical behavior not only when the lasers are still on, but also when they are turned off and the populations in each electronic states are towards the verge of stabilization. These values for different time windows are indeed, compared. So, the new terminology for our observable then becomes the following:

$$p = \frac{1}{t_{max} - t_{min}} \int_{t_{min}}^{t_{max}} p(t) dt = \frac{1}{t_{max} - t_{min}} \int_{t_{min}}^{t_{max}} \frac{P_1(t) - P_2(t)}{P_0(t)} dt \quad (3.13)$$

where, t_{min} and t_{max} correspond to two ranges: [46-78]fs for the part corresponding to the maximum of contrast (mainly the the first vibrational pattern) and [400-500]fs

corresponding to the *asymptotic* domain. This quantity p is thus, purely a scalar. We repeat that the goal of this study is to maximize p .

$P_i(t)$, the electronic state population is defined as the following:

$$P_i(t) = \sum_i |\langle i | \psi(t) \rangle|^2 \quad (3.14)$$

Hence, $P_i(t)$ is the projection of the wavefunction in a given electronic state $|i\rangle$. The time-dependent wavefunction $\psi(t)$ can be reformulated as:

$$|\psi(t)\rangle = U(t) |\psi(0)\rangle \quad (3.15)$$

Where, $U(t)$ is the evolution operator defined as:

$$U(t) = e^{-iHt/\hbar} \quad (3.16)$$

Moreover, the other observables like the ratio of the population in the two excited states [$P_1(t)/P_2(t)$ or the reverse] could indeed, be calculated. However, the inconvenience of doing this is that no information of P_0 is necessary (or provided). Thus, this can be for both weak field and strong field. This does not make any sense as it does not help us to identify the weak field limit that we are interested in.

3.4 Field-free dynamics

In order to control the mechanism of transfer from S_2 to S_1 , it is important to understand the natural dynamics, i.e. without any strategy of control. The system is excited here with a single pulse and we analyze in detail the following dynamics increasing the dimensionality step by step.

The numerical simulation is started with 2D to analyze the $S_2 \rightarrow S_1$ population transfer. Remember that, our 2D simulation includes the modes q_{6a} and q_{10a} .

These two modes describe the branching plane over which the conical intersection in pyrazine is spanned. What we do in this calculation is the following: the vibrationless ($v = 0$) ground state wavefunction is launched to S_2 . This is done in the lowest intensity regime ($5 \times 10^{12} \text{W/cm}^2$) with a laser of duration $T = 14 \text{fs}$.

As shown in fig.3.5, for the first 14fs, the population of S_2 increases and reaches up to a value of about 0.37. During this time, the population in S_1 is almost unchanged. It is after this 14fs that the coupling W_{12} comes into play. This is demonstrated by the increase in population of S_1 . This feature is then forever preserved in the system. The explanation of the typical behavior seen in the fig.3.5 is the following: there are revival structures, which are repeated several times. This is particularly a signature of 2D, as there are no other modes where the population could possibly go onto decay (we will see in the upcoming sections that they are not preserved when increasing the dimension). These structures could be re-expressed in terms of vibrational periods T_1 and T_2 corresponding to that of the states S_1 and S_2 respectively. Moreover, the funneling time (or, the characteristic time corresponding to the conical intersection) can also be observed where the population is shared equally between S_1 and S_2 : this is W_{12}^{-1} . The physical parameters used in this study are taken from [170]. T_1 corresponds to the S_1 vibrational period: after $T_1 = 56 \text{fs}$, the system reflects on the outer right turning point, returns back to CI with a partial transfer to S_1 . T_2 corresponds to the vibrational period of $T_2 = 44 \text{fs}$. The combination of the two oscillations gives rise to a recursive pattern in the population dynamics that is periodically repeated as shown in Fig. 3.5.

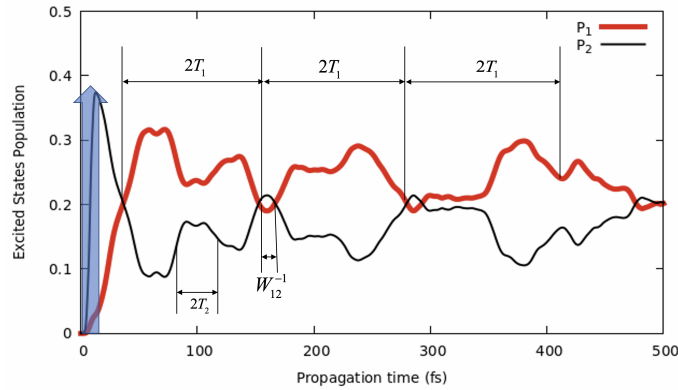


Figure 3.5: Excited states population as a function of propagation time, limited to 500fs (2D; $I = 5 \times 10^{12} \text{W/cm}^2$). Here, P_1 and P_2 correspond to the population of the excited states 1 and 2 and, are represented by thick red line and thin black line respectively. The characteristic vibrational periods $T_1 = 56 \text{fs}$ and $T_2 = 44 \text{fs}$ are also shown in the figure. W_{12}^{-1} is a characteristic time of coupling strength. The vertical blue line at $t = 0$ is the vertical launching of the ground state wavefunction.

Although the physics in 2D is rich and complex, it is however, not sufficient to guaranty that the model constructed is valid while increasing the dimension. Hence, we will now proceed to the calculations with 4D and 24D. This will also ensure the robustness and efficiency of our theoretical model. 2D calculations are the most simplest ones and take about 10 minutes in average (for single pulse).

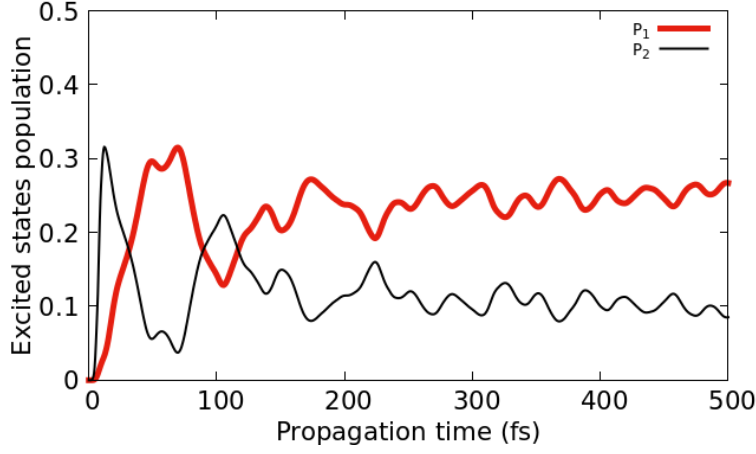


Figure 3.6: Excited states population as a function of propagation time (4D; $I = 5 \times 10^{12} \text{W/cm}^2$). Same notations as in fig.3.5.

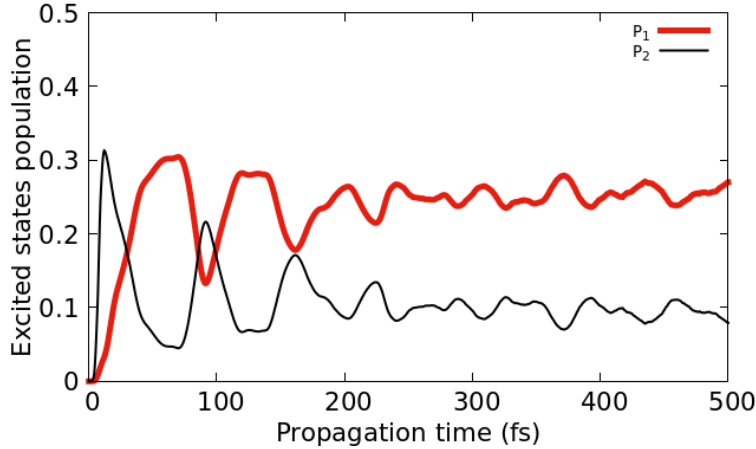


Figure 3.7: Excited states population as a function of propagation time (24D; $I = 5 \times 10^{12} \text{W/cm}^2$). Same notations as in fig.3.5.

The inclusion of additional degrees of freedom dramatically increases the density of vibrational states and thus, the specificity of the T_1 and T_2 , vibrational periods seen in 2D model is lost. In figs.3.6 and 3.7 are presented the electronic states population as a function of propagation time, respectively for 4D and 24D. These two figures

resemble a lot. However, the main difference compared to the 2D calculation is the loss of specificity regarding the number of revival structures present in the dynamics. Here, we see that typically after about 250fs, these structures are suppressed and the population in S_1 and S_2 moves towards the stability. This is also the characteristic time of decoherence for large molecules.

3.5 Results with the interference mechanism

We now begin this section with the results obtained for 4D calculations, followed by 24D. In fig.3.5, we can see the post-pulse evolution of the electronic populations. Two interference mechanisms can be envisioned: one concerning the early dynamics with $t < 80$ fs (80fs corresponds to about $2T_2$ in fig.3.5) and, the other for the longer times $t > 80$ fs (when the wavepacket in S_2 revisits the FC region).

3.5.1 4D

The 4D simulations were launched by taking into account the four normal modes: q_{6a} , q_{10a} , q_{8a} and q_1 (see fig.2.5).

We have calculated our observable, the contrast for three different intensities notably considering them as weak, intermediate and strong ones (as it turns out so for pyrazine). The asymptotic 4D contrast is shown in the fig.3.9.

Fig.3.9 is a plot of contrast as a function of delay (τ). We have identified 3 regimes of laser pulse: weak ($I = 5 \times 10^{12} \text{W/cm}^2$, blue dotted dashed line), intermediate ($I = 10^{13} \text{W/cm}^2$, red dashed line) and strong ($I = 8.8 \times 10^{13} \text{W/cm}^2$, black solid line). In a very short time, let's say within the first 14 fs, we see that the contrast is varying a lot for each of these intensities. These oscillations (or, variations) are the signature of a strong interference mechanism. This is the case for all the three intensities chosen. The contrast is seen increasing when increasing the intensity. For weak field regime, the maximum for the contrast obtained is about 0.3. This value increases to 0.8 and 1.6 respectively for intermediate and strong regime. For the blue and red curve, the form of the contrast is basically the same. As there is a factor of 2 between these two intensities, we are still in weak field limit (this can also be verified

from the fig 3.4). However, the black curve has a shape completely different with respect to the rest. This is a high intensity. We also see that, for this intensity, there is another optimal contrast at $\tau = 75$ fs, the time when the wavepacket launched from S_2 to S_1 is stabilized and the system gains an organizational restructuring. In the upcoming section, the 24D calculations are shown.

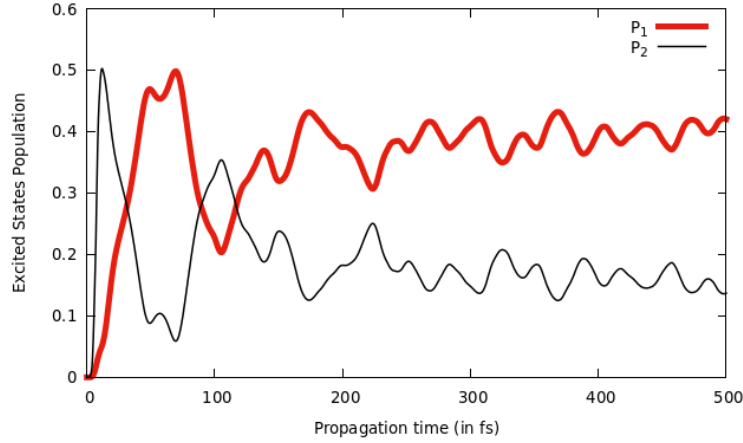


Figure 3.8: Same as fig.3.6 for $I = 10^{13} \text{ W/cm}^2$

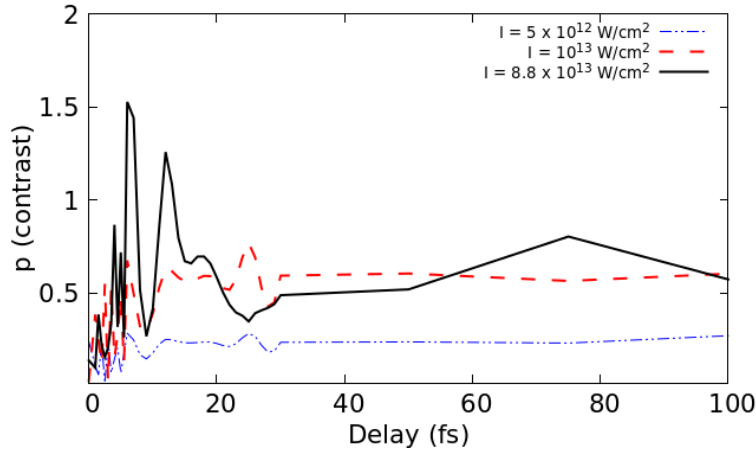


Figure 3.9: Asymptotic contrast as a function of delay for two pulses calculated with different intensities (4D model). The dotted dashed blue line represents weak field regime ($I = 5 \times 10^{12} \text{ W/cm}^2$), the dashed red an intermediate regime ($I = 10^{13} \text{ W/cm}^2$), and the solid black line the strong field regime ($I = 8.8 \times 10^{13} \text{ W/cm}^2$).

The 4D calculations with single pulse take an hour in average while with delayed pulses take about 18 hours in average (in a local desktop and without any parallelization). Below, we show the electronic states populations for three particular delays:

6fs, 9fs and 75fs.

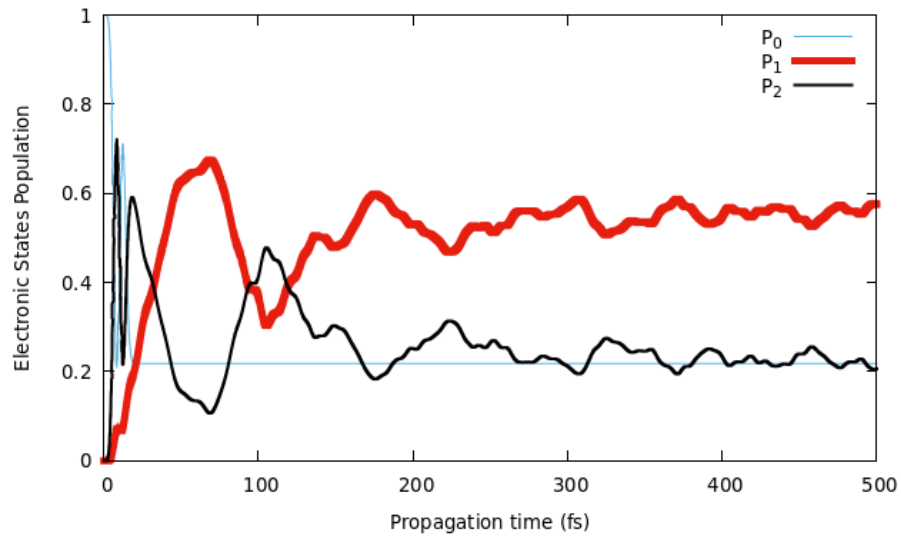


Figure 3.10: Electronic State Populations for 4D ($I = 8.8 \times 10^{13} \text{ W/cm}^2$, $\tau = 6 \text{ fs}$).

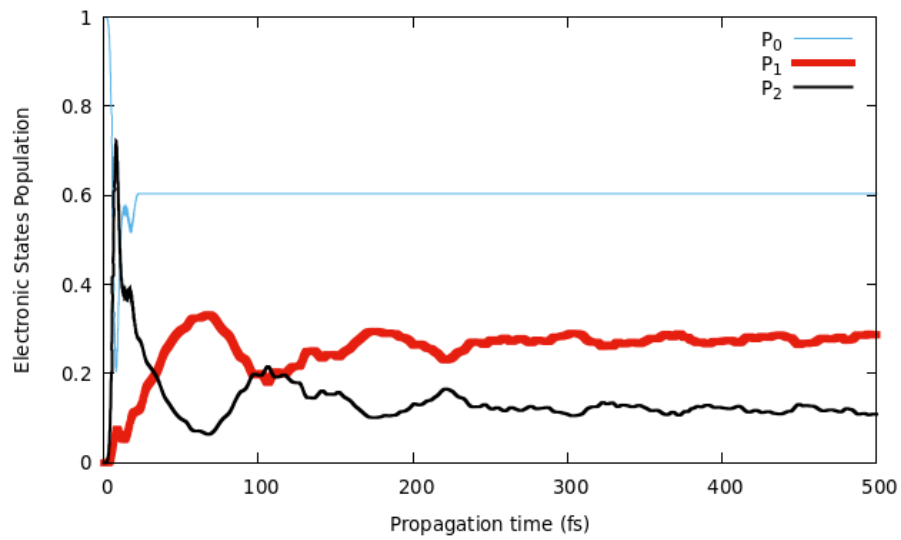


Figure 3.11: Electronic State Populations for 4D ($I = 8.8 \times 10^{13} \text{ W/cm}^2$, $\tau = 9 \text{ fs}$).

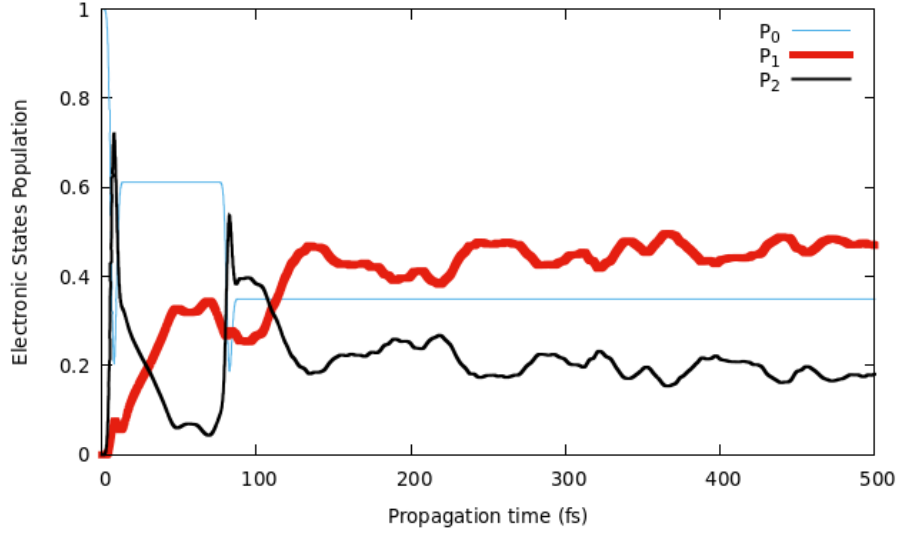


Figure 3.12: Electronic State Populations for 4D ($I = 8.8 \times 10^{13} \text{ W/cm}^2$, $\tau = 75\text{fs}$).

3.5.2 24D

The 24D simulation consists of a 4D system (discussed previously) and treats the rest of the normal modes as bath [131, 174]. Theoretically, researchers in the University of Heidelberg [87, 131, 174] have already made a comparison between the theoretical and experimental absorption spectrum by taking into account all the 24 normal modes present in the molecular system under study. More than that, their studies have also shown that the 4D model is sufficient to reproduce the experimental spectrum. This simply not only reduces the number of terms in the Hamiltonian, but also makes the calculation faster.

To further reduce the computational time, this can (and has been done in the literature, see [96, 123, 125]) be equally done with the other form of MCTDH, i.e ML-MCTDH (see chapter 2 for mathematical details; we will present our work using this form for other calculation in chapter 5). For calculations with single pulse, it took about 33 hours without parallelization and 14 hours after parallelization (16 processors).

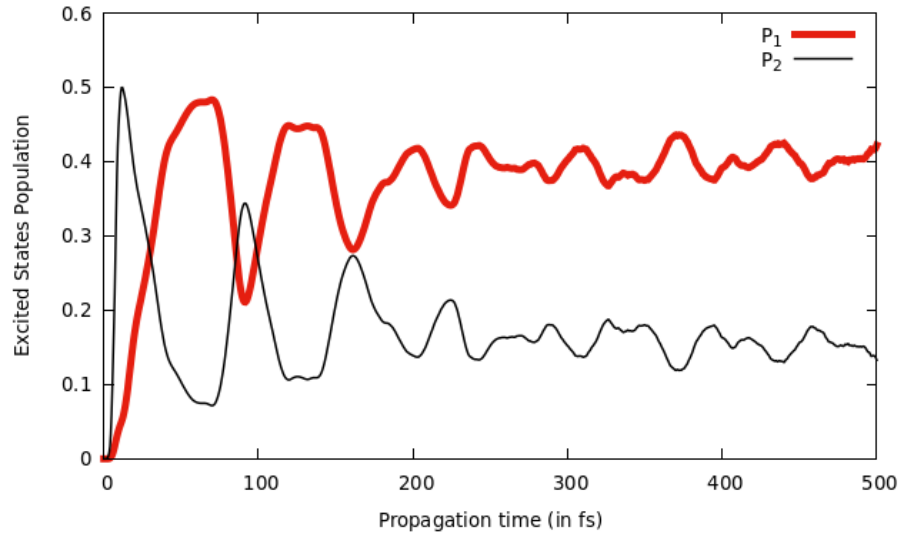


Figure 3.13: Same as fig.3.7 for $I = 10^{13} \text{W/cm}^2$.

For 24D calculation, certain particular delays were retained. This is defined by the maxima and minima from the fig.3.9. The delayed calculations were done in Mésolum with 16 processors and took 32 hours in average. Without the parallelization, it was an average of 120 hours. It is thus, a significant gain.

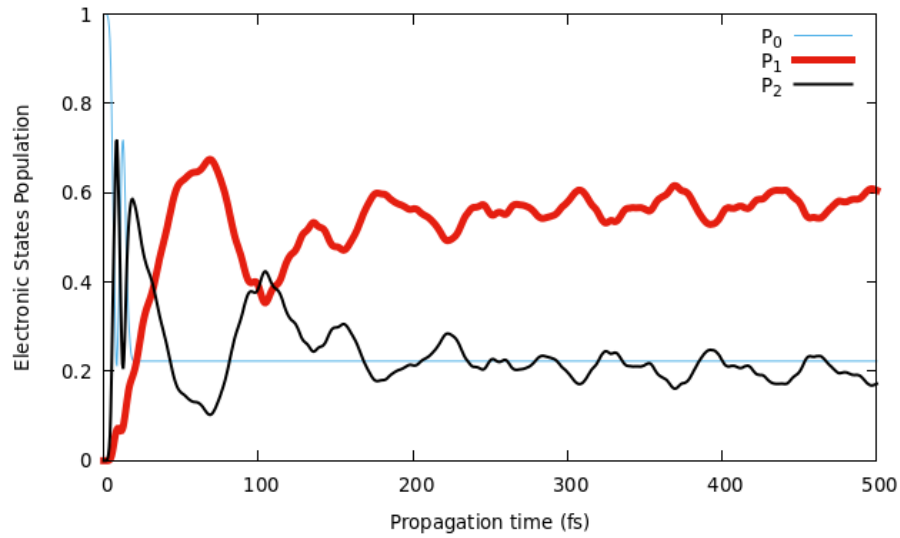


Figure 3.14: Electronic State Populations for 24D ($I = 8.8 \times 10^{13} \text{W/cm}^2$, $\tau = 6\text{fs}$)

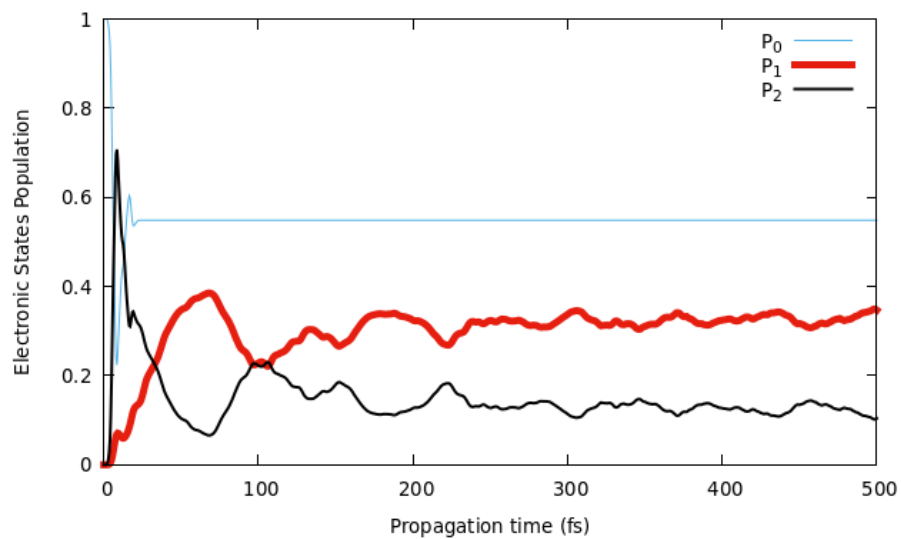


Figure 3.15: Electronic State Populations for 24D ($I = 8.8 \times 10^{13} \text{ W/cm}^2$, $\tau = 9\text{fs}$)

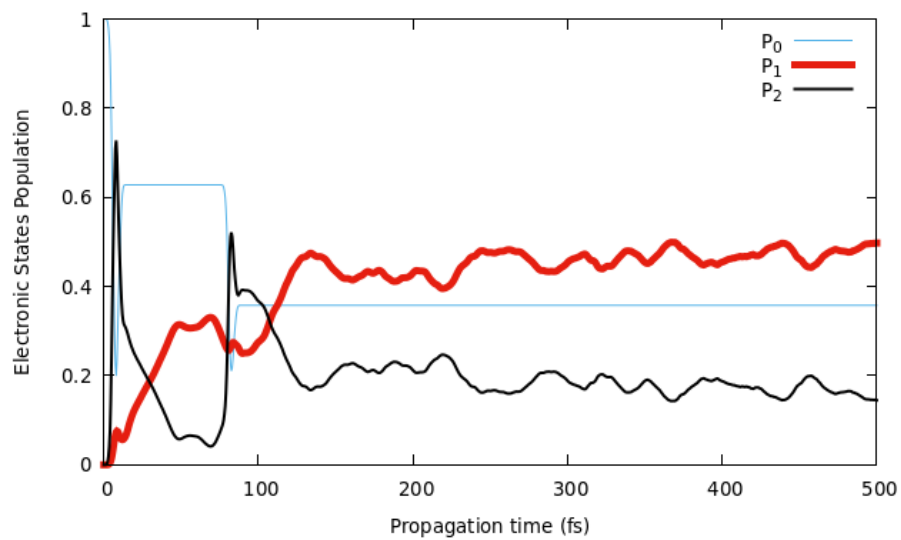


Figure 3.16: Electronic State Populations for 24D ($I = 8.8 \times 10^{13} \text{ W/cm}^2$, $\tau = 75\text{fs}$)

3.6 4D vs 24D: Autocorrelation Function

We are not limited only to the contrast as an observable. The auto correlation function and power spectrum has also been calculated between 4D and 24D, they resemble quite a lot (see the references for literature understanding).

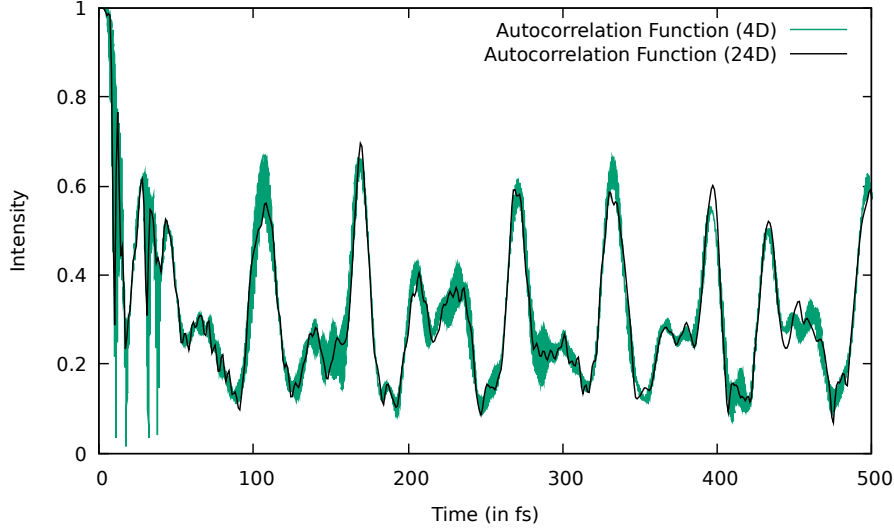


Figure 3.17: Autocorrelation Function, $\langle C(t)|C(0) \rangle$ (4D vs 24D) calculated at $\tau = 10\text{fs}$

The Fourier transform of this autocorrelation function (see above) is the power spectrum; which has been calculated elsewhere [11, 164]. The study of an ensemble of these observables provides an insight that 4D is enough to understand the dynamics. Moreover, the similarity between the 4D and 24D simulations indicate that the quantum effects are still well preserved in our calculation and, the decoherence almost has no impact.

3.7 Conclusion

The contrast calculated in the interference mechanism hugely increases when we switch the calculations from one pulse to two. This means that the method used is very efficient. Most importantly, the same quantum effect is still preserved on

going from 4D to 24D. Surprisingly, the contrast is significantly even better for 24D compared to that of 4D!

We also see that the contrast is varying a lot while going from weak (or even intermediate) to strong field regime. They are sometimes increased even by a factor of 10. The strong field regime offers much better contrasts by depleting more the ground state population. The optimal result obtained for an early dynamics control scheme, leads to a population $P_2 = 0.6$ in S_1 . In other words, it means that 60 % of the ground state initial population is transferred to the acceptor S_1 , while only 18 % remains in the donor S_2 .

Chapter 4

Results and Discussion: Kicks

There is no greater agony than bearing an untold story inside you.

- Maya Angelou

As shown in fig.3.1 and also in the introductory section, there are two possible strategies (three actually, one is discussed briefly in the appendix E) to populate S_1 (this state is considered as an optically quasi-dark state in the literature). Here, we shall focus on the *kicks* mechanism. This is a very well documented strategy when it comes to molecular alignment and rotation in free space, optical trapping of ultracold atoms [61, 175–177]. The physical description of this mechanism is the following:

One takes a laser with pulse duration so short that s/he is able to cover certain bandwidth in the excited energy region of the molecule. Hence, whether one is on-resonant or off-resonant is really not a concern as one plays with very short laser, and the mechanism that it could trigger in the ultrafast time scale following the excitation. Particularly, what has grabbed the utmost interest among the theoreticians and the experimentalists is the fact that an intense, linearly polarized laser field either resonant or near-resonant is realisable and the control observables with good efficacy is achievable [176, 178]. The main advantage of this method is its simplicity.

Instead of using a single (or 2 lasers), one uses multiple identical lasers where the idea is to kick the system once the population of S_2 (the electronic state with higher energy level, refer to fig.3.1) starts to decrease. As seen from our observation (we will see in the figures later), there is a cost to pay for that. So, instead of that, we rather played with P_0 (or state S_0). What we are basically seeing in each of these figures (see the upcoming sections) is the enough depletion of the ground state and also a good mixture of S_2 and S_1 , which ultimately results in the flow of population towards S_1 . This is actually the goal of our study. Thus, one can consider this as a pump-pump process, repeated several times with the identical short pulse(s). The ground state wave-packet is propagated in S_2 electronic potential energy surface and subsequently relaunched several times (5 in our case). The natural flow from S_2 to S_1 is governed by the coupling parameter W_{12} .

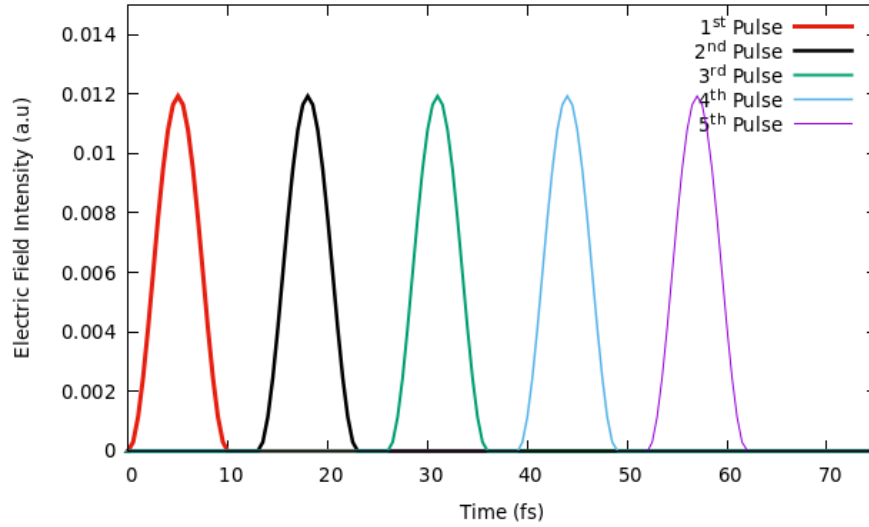


Figure 4.1: Envelope of the laser pulses used for this study (presented here are the pulses with duration of 10fs). 5 identical pulses with $I = 5 \times 10^{12} \text{W/cm}^2$ were used.

For this mechanism,

1. The number of kicks we took are limited to 5. More than this could be also difficult to manipulate experimentally. The time delay (τ) between subsequent pulses is the same for all the pulses.
2. We deal with two control parameters, the pulse duration and the delay (τ).

n	q'_1	q'_2	q'_3	q'_4	q'_5	q'_6	q'_7	q'_8
(0)	18	18	4	4	4	4	4	4
(1)	34	34	4	4	4	4	4	4
(2)	30	30	4	4	4	4	4	4

Table 4.1: Number of single particle functions used in 24D calculation for kicks mechanism. The notation of the combined modes is identical to the one stated in table 3.2. Compared to table 3.2, we see in table 4.1 that we need even more single particle functions for q'_1 and q'_2 since we use five and not two pulses here.

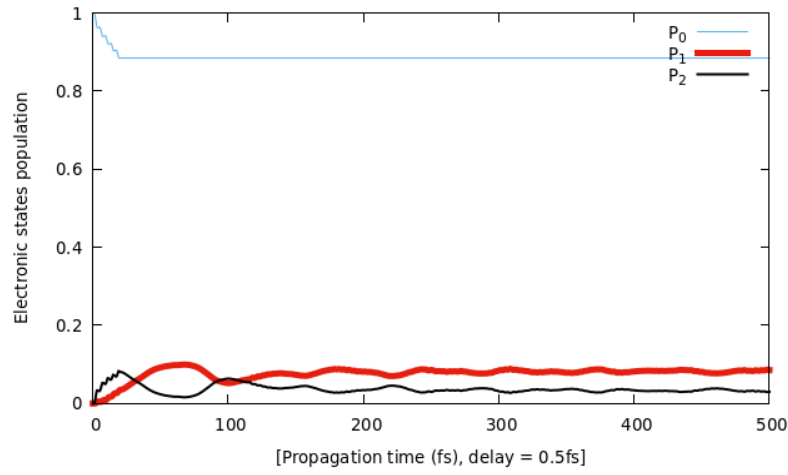
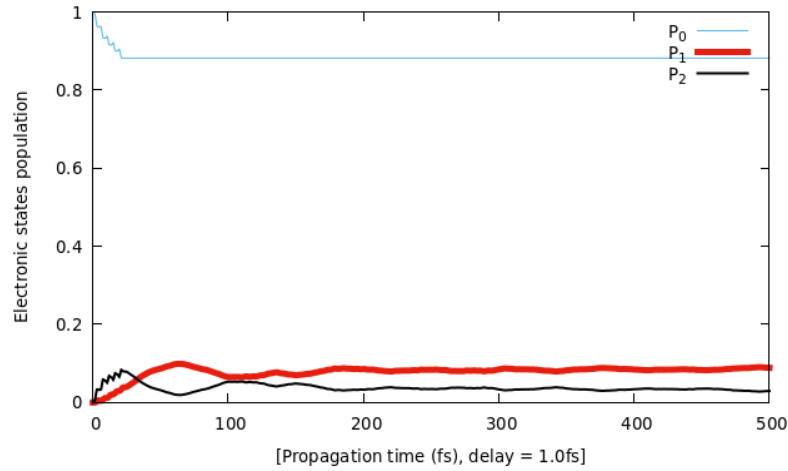
Mathematically, it then is the repetition of eq.3.5 several times, but with sudden kicks.

Several calculations with different pulse durations ($T = 3.5\text{fs}$, 7fs , 10fs and 14fs) have been performed. Finally, we conclude the work by calculating the contrast in both symptotic and asymptotic region (they are shown in figs.4.23 and 4.24). All these calculations were performed with the same intensity ($I = 5 \times 10^{12} \text{ W/cm}^2$). At the end, a final calculation is shown including all the 24 normal modes so as to have a comparison with that of the 4D; they are almost similar and the contrast calculated are quite comparable. This part of the study was directly started by using the 4 normal modes q_{10a} , q_{6a} , q_1 and q_8 (see fig. 2.5 for normal modes of pyrazine). The rest are introduced later (for 24D calculations) on, that essentially act as bath to our system.

In the upcoming sections, we will briefly present the results obtained for different pulse durations and different delays. The goal is to screen our observable along this delay, the sole control parameter in our study.

4.1 4D

We now proceed to discuss the results obtained with various pulse durations. We shall demonstrate the results obtained with a reduced (4D) simulation in this section, which shall then be followed by a full dimensional (24D) results in the next section.

4.1.1 $T = 3.5\text{fs}$ Figure 4.2: Electronic states population with 5th kick for pulse duration of 3.5fs and delay of 10.5fs.Figure 4.3: Electronic states population with 5th kick for pulse duration of 3.5fs and delay of 11fs.

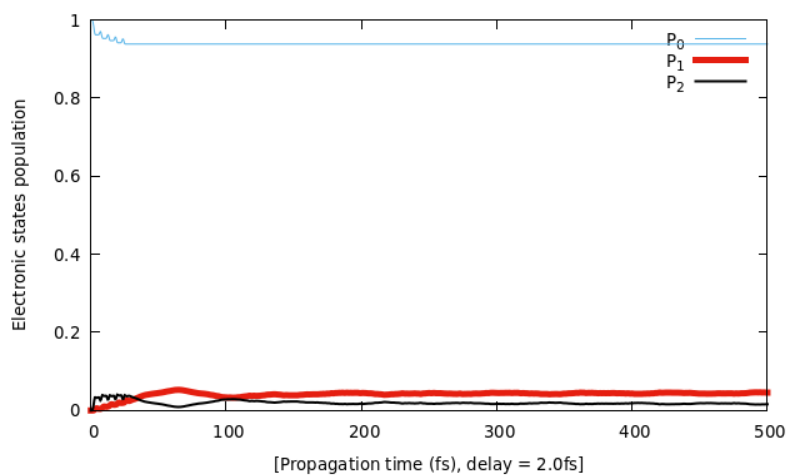


Figure 4.4: Electronic states population with 5th kick for pulse duration of 3.5fs and delay of 12fs.

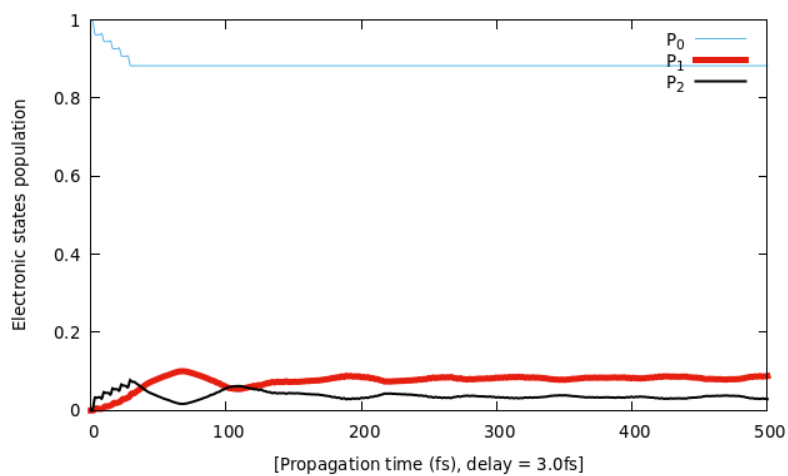


Figure 4.5:
Electronic states population with 5th kick for pulse duration of 3.5fs and delay of 13fs.

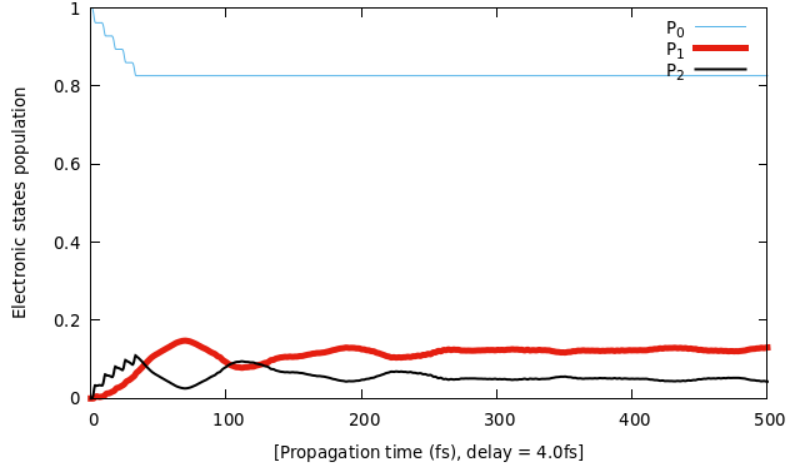
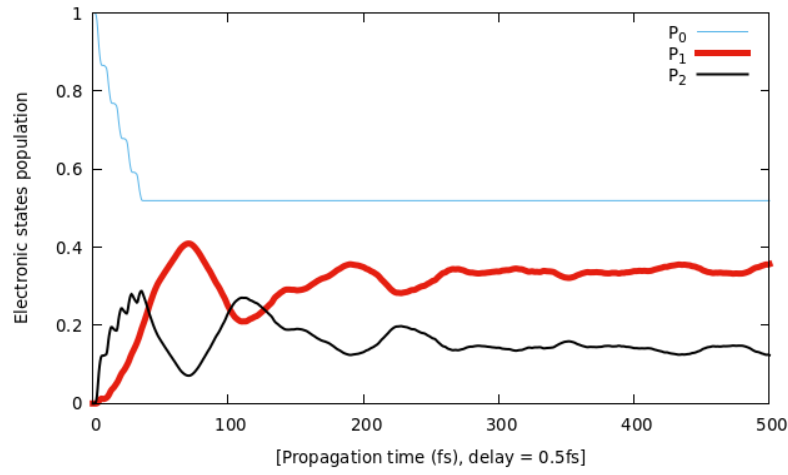
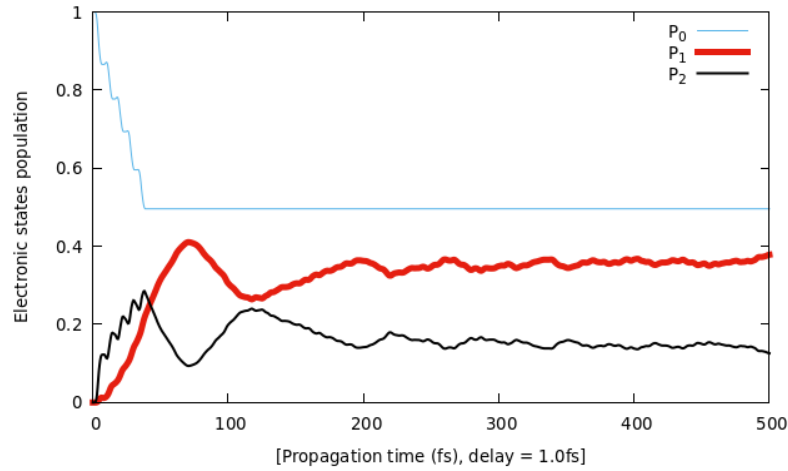


Figure 4.6: Electronic states population with 5th kick for pulse duration of 3.5fs and delay of 14fs.

As one can observe, when using a pulse as short as 3.5fs, the final population in the ground state even after the fifth kick is very high. What has been shown is the population of the electronic states at the end of the fifth pulse for different delays (τ) with fixed pulse duration (T). The final time of propagation is always limited to 500fs here.

There is a systematic pattern that we observe here: for $T = 3.5$ fs, not only the population of the ground state is decreasing (which is obvious), but the population of the state S_2 is increasing each time when kicked by a new laser pulse (we see it at the very beginning in black). This is true for all the delays chosen in our study. This gives rise to a better mixing between S_2 and S_1 ; however, the populations of both S_2 and S_1 remain very low at the long run. If we make an average over this time, this is indeed constant. Although it remains extremely small, the contrasts change with delay (will be shown in figs.4.23 and 4.24). This shows that our control parameter (i.e. τ) has an important role.

4.1.2 $T = 7.0\text{fs}$ Figure 4.7: Electronic states population with 5th kick for pulse duration of 7fs and delay of 10.5fs.Figure 4.8: Electronic states population with 5th kick for pulse duration of 7fs and delay of 11fs.

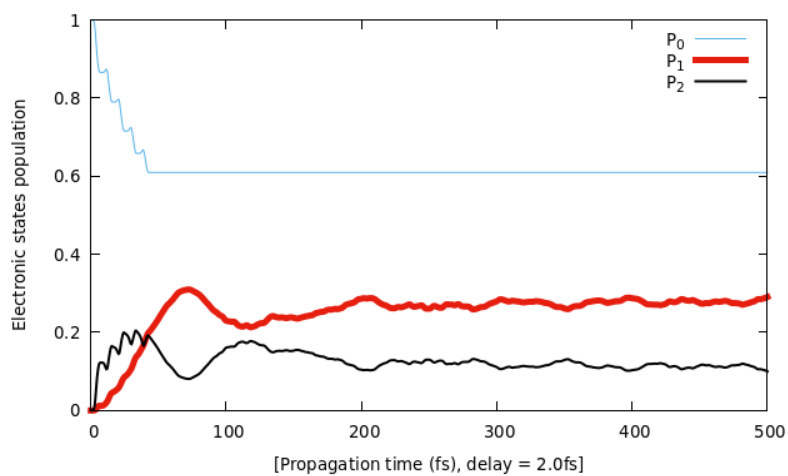


Figure 4.9: Electronic states population with 5th kick for pulse duration of 7fs and delay of 12fs.

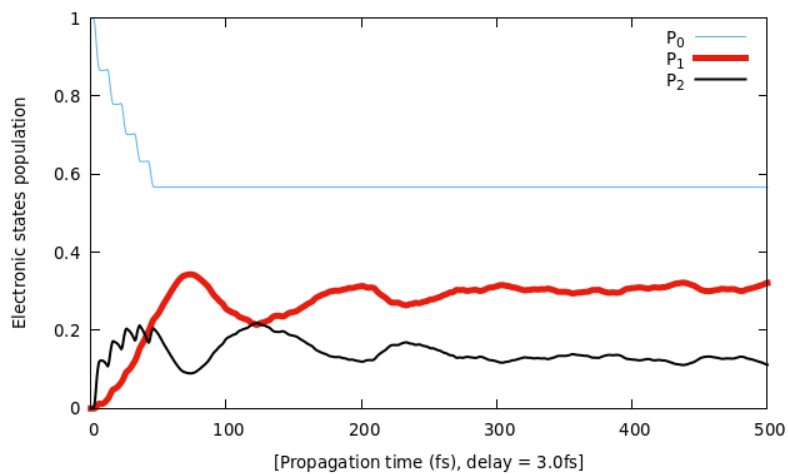


Figure 4.10: Electronic states population with 5th kick for pulse duration of 7fs and delay of 13fs.

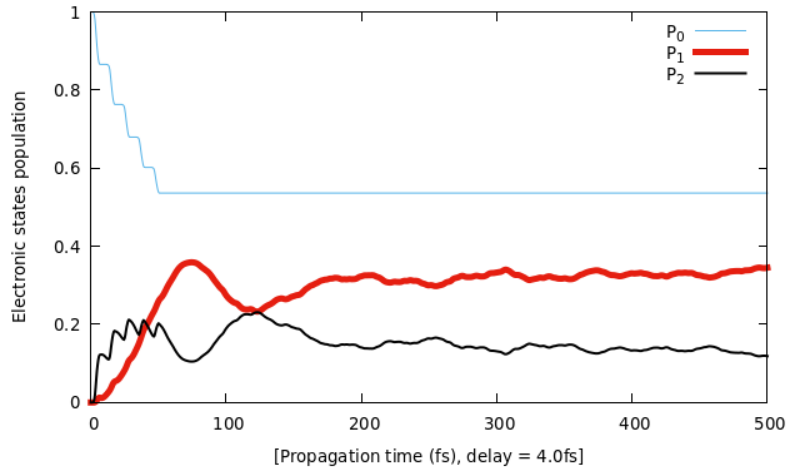
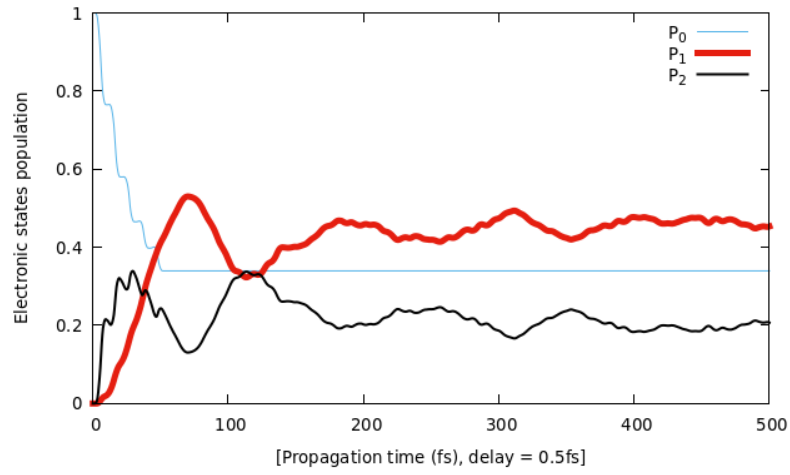
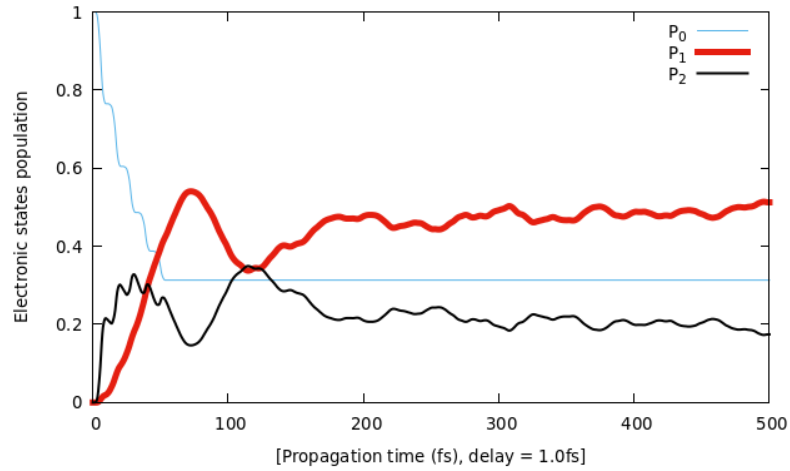


Figure 4.11: Electronic states population with 5th kick for pulse duration of 7fs and delay of 14fs.

Let us focus now on the calculations performed with $T = 7$ fs for different delays between the pulses (10.5fs, 11fs, 12fs, 13fs and 14fs respectively in figs.4.7, 4.8, 4.9, 4.10 and 4.11). At the end of excitation by the fifth kick for each of these delays, we see that the population of the ground state has been depleted by around 50% for some delays (contrary to what we observe for 3fs). Moreover, if we look at the contrast it looks much better. Not only that, the population of S_2 is not always increasing. This general trend, if we analyze precisely, is lost for $\tau \geq 2$ fs for $T = 7$ fs.

In addition to this, the quantum mechanical mixing of the population between S_2 and S_1 is also not always so pronounced (contrary to what we saw for interference mechanism). It is because, we are not giving our wavepacket enough time to deform itself. It doesn't have sufficient time to move back and forth in the coupled potential energy surface. The sudden kicks, applied in a very short interval of time, thus, do not let the wavepacket to evolve in a proper sense, but rather impart their momenta to the molecular system.

What is interesting is to see the final population in S_2 and S_1 . What we see in each of these figures is that we have about 40% (at max.) of population in S_1 . This, which is forever localised in the potential energy surface of S_1 , can then be used as an extra amount of energy for some potential applications like light harvesting (see [179–181] for more details).

4.1.3 $T = 10.0\text{fs}$ Figure 4.12: Electronic states population with 5th kick for pulse duration of 10fs and delay of 10.5fs.Figure 4.13: Electronic states population with 5th kick for pulse duration of 10fs and delay of 11fs.

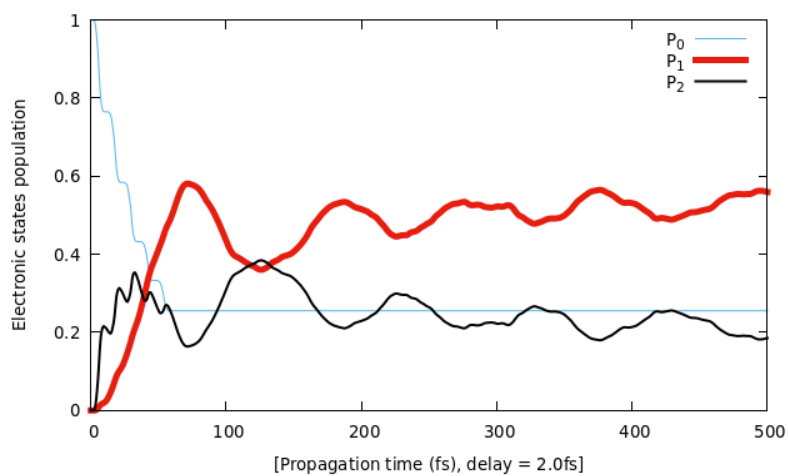


Figure 4.14: Electronic states population with 5th kick for pulse duration of 10fs and delay of 12fs.

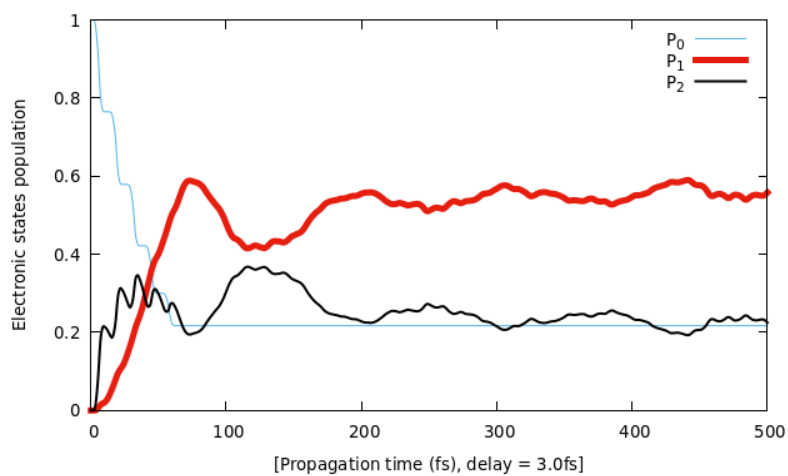


Figure 4.15: Electronic states population with 5th kick for pulse duration of 10fs and delay of 13fs.

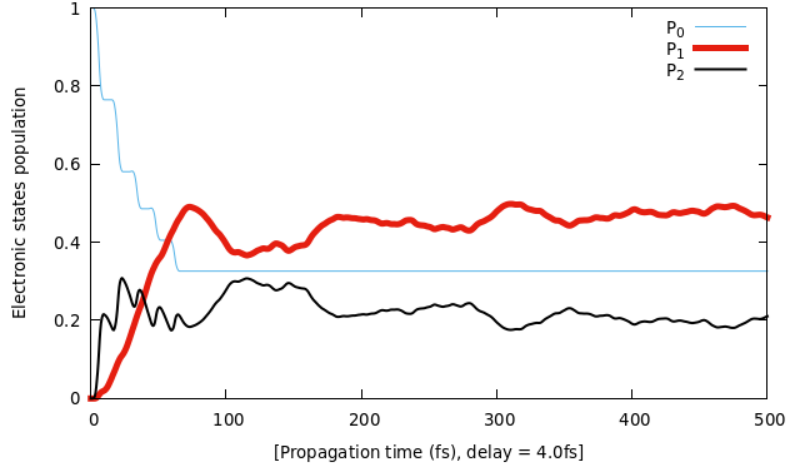
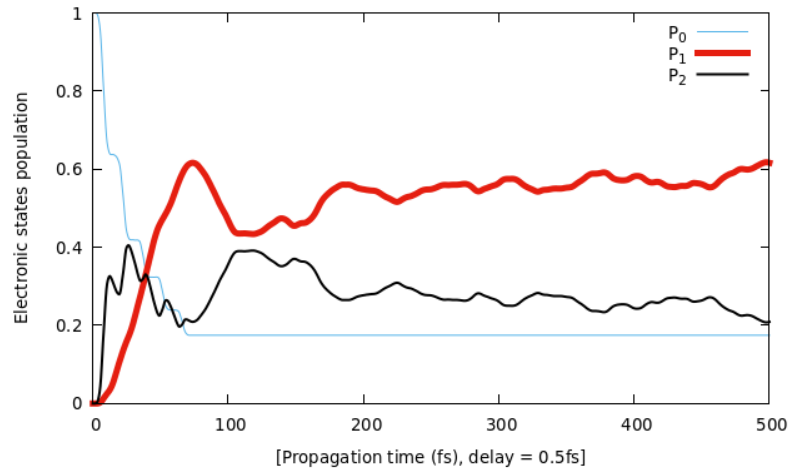
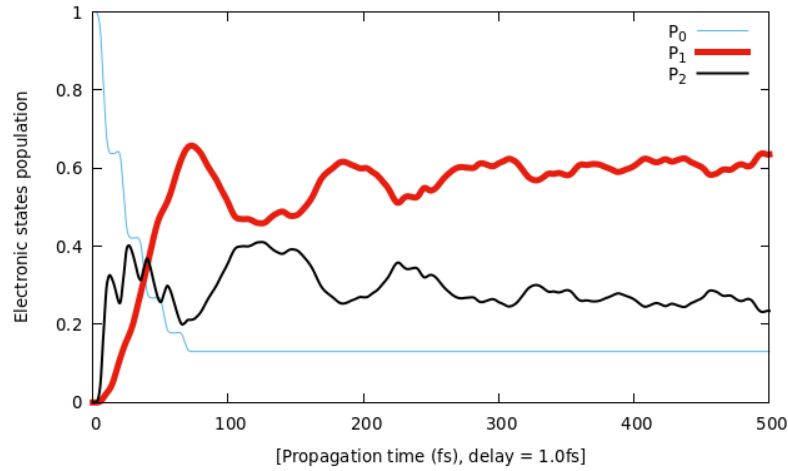


Figure 4.16: Electronic states population with 5th kick for pulse duration of 10fs and delay of 14fs.

Here, for all the delays, we see that the level of ground state depletion is about 70% (on average). After the third pulse, the population in S_2 decreases whereas that of S_1 is always increasing from the beginning. With different delays, the mixing (which actually never prevails in the system after about 120fs) is better as is also the final population in S_1 . That, at the end, is indeed, our objective.

Also, the amount of depletion caused by each laser is not the same. The first laser depletes more than 20%, while the rest do even less than 10%. This efficiency of depletion, as seen in these figures (see above), show that we might actually need huge number of pulses to have cent percent depletion of the ground state. However, it still doesn't suffice to tell that all the population will eventually go to S_1 . If we calculate the contrast at the end of each pulse, we will clearly see the difference (see the upcoming section). This difference is an indirect indication of efficiency of each kick.

4.1.4 $T = 14.0\text{fs}$ Figure 4.17: Electronic states population with 5^{th} kick for pulse duration of 14fs and delay of 10.5fs.Figure 4.18: Electronic states population with 5^{th} kick for pulse duration of 14fs and delay of 11fs.

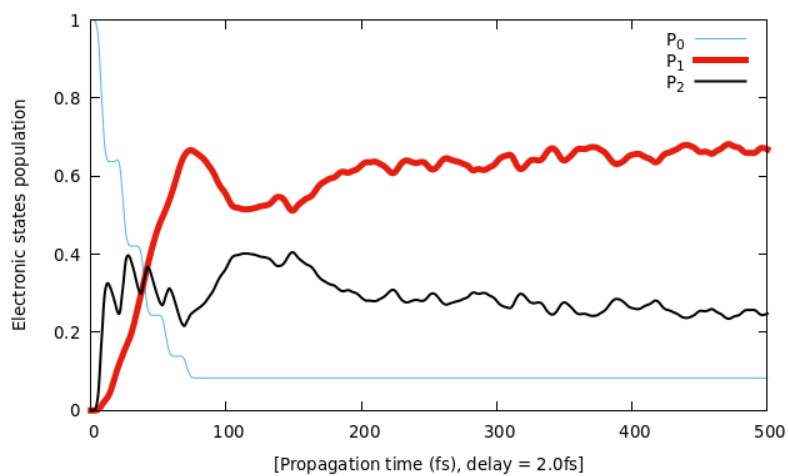


Figure 4.19: Electronic states population with 5th kick for pulse duration of 14fs and delay of 12fs.

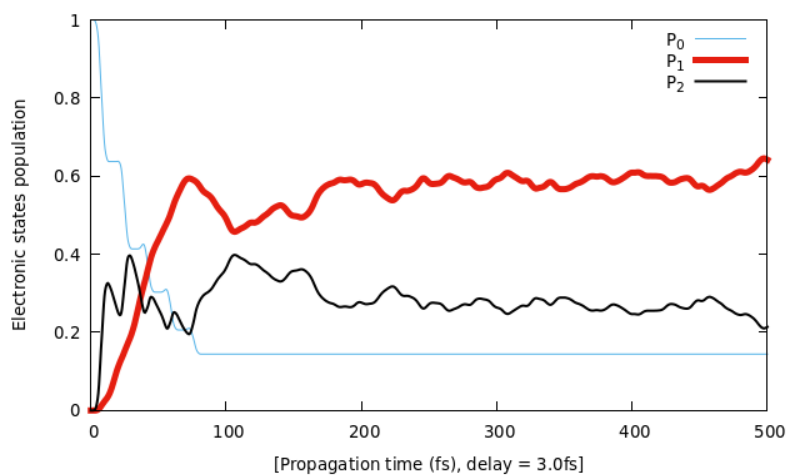


Figure 4.20: Electronic states population with 5th kick for pulse duration of 14fs and delay of 13fs.

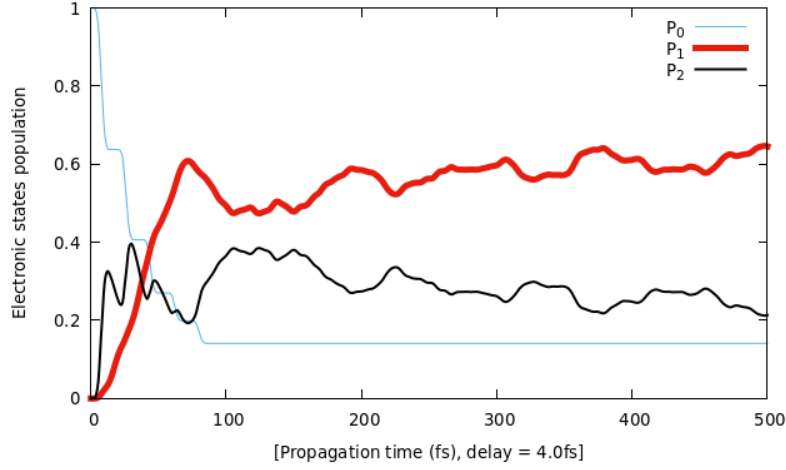


Figure 4.21: Electronic states population with 5th kick for pulse duration of 14fs and delay of 14fs.

With $T = 14$ fs, the maximum we could have in S_1 is about 70%. What has to be understood is the fact that this is not during the pulse, but in a post pulse situation as long as 500fs. Our intuition is that, naturally, this will be the case even afterwards, when other normal modes start to come into play. This is actually a good achievement.

4.2 24D

For this part, we only did one specific calculation to have a comparison with our 4D model shown in the previous section. As we will see later, the contrast in the asymptotic region is more important.

What is interesting after the inclusion of 24D calculation is that the population transfer remains very similar even after adding all the modes (both ‘bath’ and ‘active’). This, on the other hand, is even more efficient than what has been shown in [46, 165], where the authors were successful to fight against the radiationless transfer, but only during the time when the laser was turned on. Moreover, their calculations proved to be efficient only for 2D.

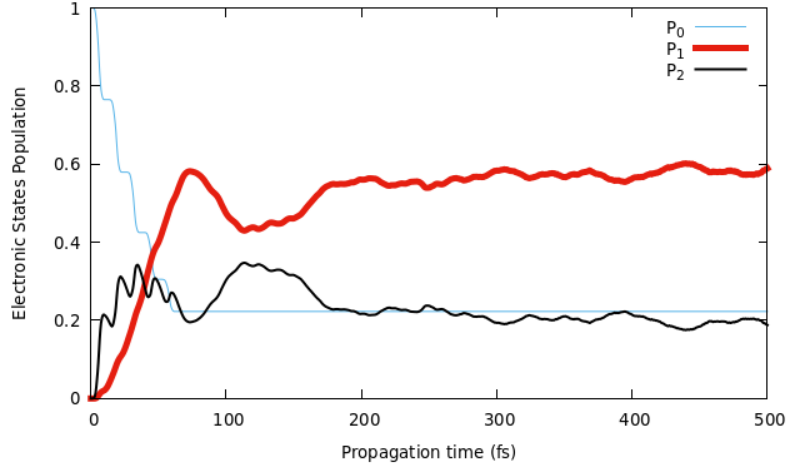


Figure 4.22: Electronic states population with 5th kick for pulse duration of 10fs and delay of 13.0fs for 24D.

The 4D calculations were run on a simple desktop, without parallelization. This takes about 3 hours of time, which is affordable. Once the intensity, pulse duration and delay between the pulse sequences were finalized, we then launched 24D calculations with the following parameters:

Intensity (I) = $5 \times 10^{12} \text{ W/cm}^2$

Delay (τ) = 3 fs

Pulse Duration (T) = 10 fs

Number of pulses (N) = 5

The 24D calculation was performed in *Fusion*, the computing platform of *Centrale Supélec* (we thank them for letting us run our calculations). Following is the computer specification [182](the details can be found in the reference cited):

Intel Xenon CPU E5 - 2695V2@2.40 GHz

GPU reference Nvidia Tesla K40m

Intel compilers/17.0.4

We see that the full dimensional calculation (24D) resembles very much with the

calculation of reduced dimensionality (4D). This also holds true while calculating other experimental observables such as absorption spectrum [124, 183, 184]. 24D calculations in this study took about 55 hours in average to converge.

Below, we present the contrast that has been calculated for different pulse durations and different delays (the same quantity has also been calculated for the intermediate regime of the dynamics and is shown in the appendix).

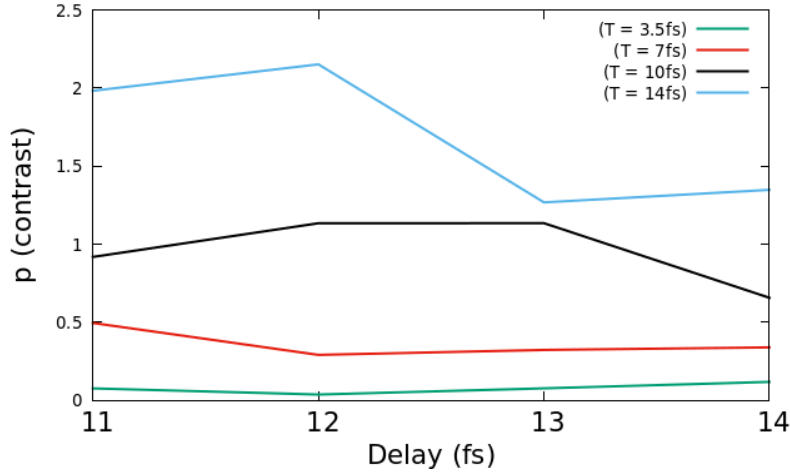


Figure 4.23: *Symptotic* contrasts for different pulse durations (calculated at $\tau = 13$ fs).

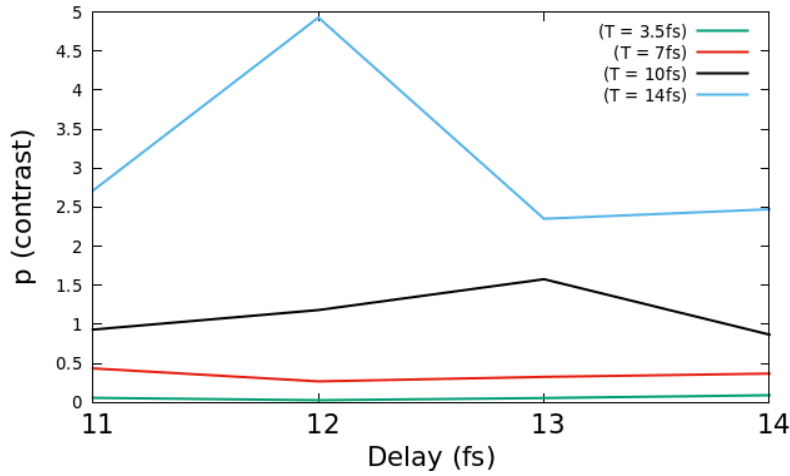


Figure 4.24: Asymptotic contrasts for different pulse durations (calculated at $\tau = 13$ fs).

The behavior, as seen, is not always the same. For instance, the maximum for $T = 10$ fs at $\tau = 3$ fs is actually the minimum for $T = 14$ fs at $\tau = 3$ fs. This shows

that, there is a tendency where it (the contrast) changes while changing the laser parameter (pulse duration in our case) and the delay (τ). Even within a single T , we see that p , the contrast varies with τ , the delay.

In the asymptotic region, we see that p is even larger. This is remarkable because it corresponds to the situation when the lasers are off. That is to say, this contrast prevails forever in the system.

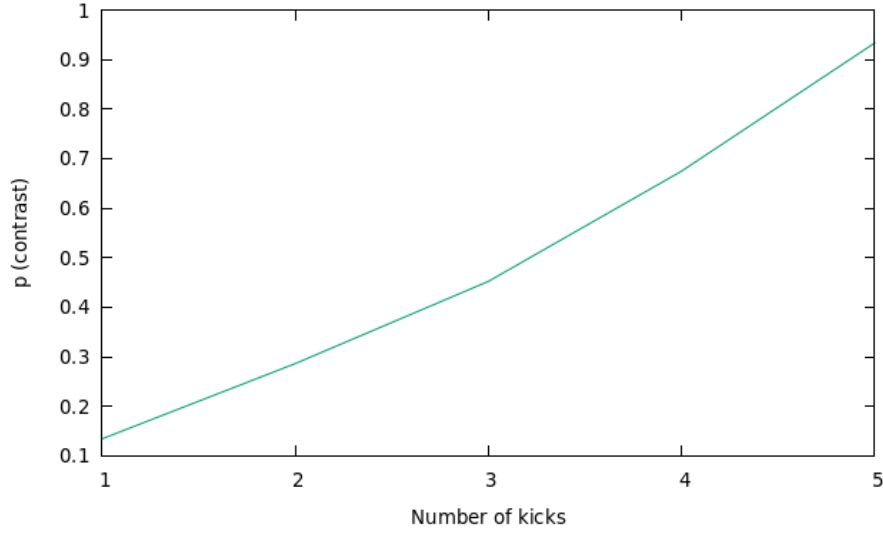


Figure 4.25: Asymptotic contrasts for different kicks (calculated at $\tau = 11\text{fs}$ for $T = 10\text{fs}$).

If we look at the fig.4.25, we see that the contrast is gradually increasing while increasing the number of kicks. This means that even better contrast could be achieved while increasing the number of kicks applied in the system. The same could be expected for other delays too. The contrast $p = 1.74$, calculated for 24D, is actually a good one for kicks mechanism.

4.3 Conclusion

The sudden kicking of molecular systems reported in this chapter is done with the laser intensity of $5 \times 10^{12} \text{W/cm}^2$. One has to be indeed, careful when choosing the laser intensity so as not to induce the processes like dissociation and ionization, which

are a direct signature of an intense pulse [42, 176, 185].

As seen in the figures presented in this chapter, the population of S_2 is not always increasing (on the contrary, the population of S_0 is always decreasing). This means that we are putting more and more population of S_0 in S_2 and it thus, allows us to prepare better mixing of S_2 and S_1 . On the long run (after the laser has been turned off), we see that the average of population in S_2 and S_1 remains constant. This phenomenon, with 24D, is even more obvious as we will have other normal modes that come into play.

What we see from these figures is also that on increasing the pulse duration, we have more depletion of the ground state and better exchange between the excited states. For instance, if we look for $T = 3.5\text{fs}$, we see that even with the fifth kick, we are not really transporting enough population from S_0 to S_2 . Whereas, this phenomenon gets better while increasing the pulse duration. The form of the post pulse dynamics is always the same. This means that the dynamics of the molecule is not changed with the laser parameters. Within the experimental constraints (or limit) of the pulse, what have been obtained in our calculations is really an interesting result. As mentioned by the authors in [40], the short pulses are indeed, capable of transferring significantly from S_0 to S_2 and from S_2 to S_1 via IC (Internal Conversion).

We have identified two regions to calculate the contrast during and after the pulse (more or less). For $T = 14\text{fs}$, the contrast is even better in the asymptotic region. Contrast greater than 1 is actually obtained here by pulses which are not very intense. For $T = 10\text{fs}$ and $T = 14\text{fs}$, we see that increasing the no. of kicks resulted in better contrast. The number of kicks, as said in the introduction of this chapter, is limited to 5 by taking into account the experimental difficulties one has to deal with a lot of lasers.

Chapter 5

Ground State Properties of Rotor Chains

Today's scientists have substituted mathematics for experiments, and they wander off through equation after equation, and eventually build a structure which has no relation to reality.

- Nikola Tesla

The following chapter deals with the work that has been published as a joint collaboration between the teams of Canada (Prof. P.N Roy and D. Iouchtchenko, University of Waterloo) and Germany (Prof. Emeritus H. D. Meyer, University of Heidelberg).

We compare, for a system of one dimensional linear rotor chains, the physical observables obtained via our algorithm, ML-MCTDH, the Multi-Layer variant of MCTDH (see chapter 2 for further explanation) and DMRG (Density Matrix Renormalization Group, see the upcoming sections). The convergence criterion has been verified by both algorithms and the results are briefly discussed (see also [90]). Remember that, ML-MCTDH is essentially an algorithm for molecular quantum dynamics [88, 120] and thus for the time-dependent Schrödinger equation. Whereas, DMRG [84] solves the time-independent Schrödinger equation, and is primarily an algorithm developed for this kind of problems with several optimization strategies:

the calculation of the ground state of a one dimensional chain of rotors. However, as already stated in chapter 2, we can also solve time independent Schrödinger equation by MCTDH to calculate the eigenstates of a system: the ground state can be obtained by a propagation of a wavepacket in negative imaginary time and the “improved relaxation” method allows one to calculate excited eigenstates. Here, since the improved relaxation approach has not been implemented yet for ML-MCTDH, we have simply done relaxation to obtain the ground state for one-dimensional rotor chains. A more systematic comparison of the two methods is appealing and could lead to important improvements for the simulations of molecular quantum systems[186]. Hence, via the following study, we aim to compare the calculated rotational ground states between ML-MCTDH and DMRG and to promote cross-pollination of the theory and implementation between ML-MCTDH and DMRG in the context of quantum molecular dynamics.

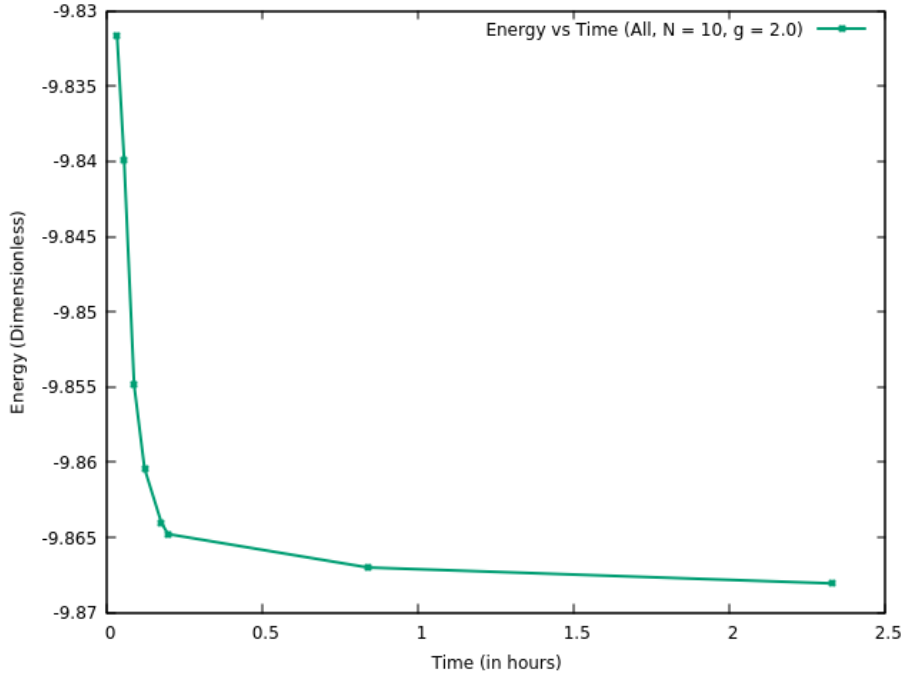


Figure 5.1: Relaxation calculation (unpublished) for $N = 10$, $g = 2.0$ and interaction type = ‘All’ (detailed in the upcoming sections)

The above picture shows the relaxation calculation performed: the energy is plotted as a function of the CPU time in hours in the case of 10 rotors and for a coupling between the rotors with $g = 2.0$ (see below for the precise definition of g). Here, one starts with a very small spf basis set, performs a propagation and stops it (for each

dot on the figure) and, goes on increasing each time the size of the spf basis set so as to have better convergence. Meanwhile, the primitive basis set always remains the same and has been chosen previously to guarantee high convergence). As ML-MCTDH is based on variational principle, we see that the energy is decreasing. Once the plateau is reached, we are convinced that it is more or less the most accurate and the best converged results we could get by ML-MCTDH.

This work has the following three motivations:

1. To know the numerical limitations of each of the algorithms. This helps to implement new techniques in each of these algorithms for future works.
2. For ML-MCTDH, validity of the algorithm when it comes to systems that have not been previously explored : here, a second order quantum phase transition.
3. The overlap between the studies could serve as a reference (or benchmark) for further use (to our knowledge, it is the very first calculation between the two communities). In particular, we plan to study the time-evolution of systems and observe a quantum phase with ML-MCTDH in the case of high dimensionality: a problem that may be much more difficult for DMRG.

Only the results that are interesting to the scientific community has been included in the following chapter.

5.1 Introduction

The simulation of quantum systems to understand the molecular and material response is very essential; thus leading to their efficient performance (for instance, the molecular simulation of photo-voltaic cells). The novelty of molecular quantum dynamical simulation is in the essence that we could solve the Schrödinger equation[187] so as to understand different phenomenon happening in the elementary level. MCTDH [87, 89, 120, 121, 131] has been seemingly used by the scientists all over the world to study different photochemical and photophysical processes, laser guided control of chemical reaction [42, 188], optimal control [45, 46], alignment and orientation of polyatomic molecules [185] and so on. Some examples of the application include the computation of absorption spectrum of the two excited electronic

states of Pyrazine molecule involving all the 24 different normal modes (4 modes as a system + 20 other modes as a bath) [161], the infrared absorption spectrum of the zundel cation $H_5O_2^+$ [174, 189].

The idea of the following study is to use the Heidelberg MCTDH package and DMRG [190] so as to compare the results of these two different algorithms. The motivation for the following study comes from the ref [84]. As there are not yet enough comparisons between the two communities, our expectation is that this could even serve as a benchmark calculation for other groups interested.

In this study, the first step of our common work was to take into account a multidimensional system of rotors as a reference and see the low-lying ground state properties. As we are dealing with a system which could, for instance take more than 50 rotors, this inherently proves the essence of our algorithm. However, keep in mind that DMRG is essentially exploited for these systems, thus superior to MCTDH in every aspect, at least for the ground state (see [84, 90] and the references therein). The next step of our collaboration (not performed yet) would be then to understand the excited state(s) dynamics with a proper model; with probably an addition of temperature effect and also other degrees of freedom (translational and vibrational) rather than taking only the rotational degrees of freedom in spherical coordinates. Thus, our work is very appealing and of fundamental importance as we lack the overlapping of different algorithms, which is primarily our motivation. This indeed, not only validates our model, but also helps us to see individually the positive and negative aspects of each of the algorithms used. We now move directly to the explanation of DMRG.

5.2 DMRG

(The following section is a re-phrased version of our article [90]. See also [84] for more detailed understanding).

Another well known tensor based approach is the DMRG (Density Matrix Renormalization Group), that has considerably gathered interests to study the physics at low energy for quantum many body systems with high accuracy. Originally introduced by White in 1992 [191], the method since then has been used suc-

cessfully in condensed matter physics[192, 193], quantum chemistry[194–196], and molecular physics[197]. Although commonly applied to systems with several spatial dimensions[198] and to real time evolution[199–201], the nature of the method is such that it primarily well captures the underlying physics of the ground states of a long, one dimensional system with huge degrees of freedom. Both of these methods are based on the tensor network; however the overlap has been very little.

The authors in [202] have used DMRG to compute the ground states of rotor chains that describe endofullerene “peapod” nanomolecular assemblies (NMAs). They are the carbon nanotubes that enclose fullerene atoms or molecules inside. These cages were treated as a rigid 1D system, which then simplifies the study and visualisation of these trapped molecules. Via this approach has also been achieved, the benchmarking of the Path Integral Ground State (PIGS) method for the computation of Rényi entanglement entropies in rotor chains using the replica trick [203], and also to train neural network representations of the many-body states of interacting rotors using Restricted Boltzmann Machines (RBMs)[204]. In the ref [84], the Hamiltonian has been taken to be inherently linear for a system size up to $N = 100$. In the present study, we limit ourselves to $N = 50$. Similar calculations are expected for higher N in the near the future.

DMRG uses a “tree” different than the one(s) introduced for ML-MCTDH in previous chapters: it makes use of tensor network states that allow to have a direct link between all the neighbors, which is not the case in the hierarchical decomposition of the tree tensor network in ML-MCTDH. This is also one of the reasons why DMRG is very well adapted to describe linear chains where the neighbors are strongly coupled, but may be less efficient to describe strong correlations between distant particles. In addition, DMRG uses many optimized algorithms to converge the ground state.

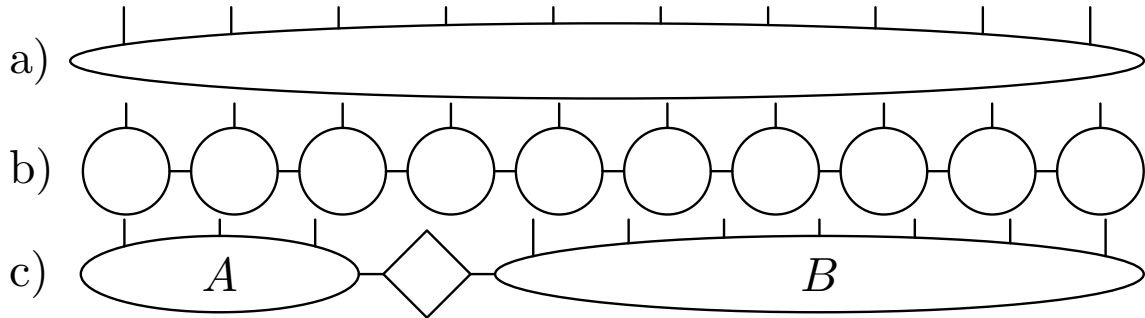


Figure 5.2: Full tensor (top panel), its corresponding matrix (middle panel) and Schmidt decomposition (bottom panel). Reprinted with permission from [90] AIP, copyright 2021.

Let us see what it means mathematically. The complex wavefunction of the many-body system can be re-expressed as a product of matrix states, known as MPSs (Matrix Product States). In a finite basis, the wavefunction can be represented as a vector $C_n = \langle n | \psi \rangle$ with multi-index $\vec{n} = (n_1, n_2, \dots, n_N)$.

This vector for N rotors can be re-written as:

$$\langle n | \psi \rangle = \underline{A}^{(1),n_1} \underline{A}^{(2),n_2} \dots \underline{A}^{(N),n_N} \quad (5.1)$$

Where, $\underline{A}^{(k)}$ is a set of matrix and n_k is the labelling associated with k , the physical site.

The bond dimension (or, bond length) is the size between $\underline{A}^{(k),n_k}$ and $\underline{A}^{(k+1),n_{k+1}}$. Illustratively, it is a length between the two points where our rotors situate. This length indeed can be decreased, which decreases the system size. In doing so, one decreases equally the entanglement entropy and the associated accuracy because there is a sweep of basis functions between the physical sites and the iteration, unlike in ML-MCTDH, which is just limited to some steps.

The exact solution of eq.5.1 gives rise to exponential scaling. To avoid this situation, the idea then would be to play with the system size while preserving the entanglement among the rotors. Thus, a compromise is made between accuracy and preservation of entropy.

The entanglement entropy of a system is a sum of entropy between each states. Sometimes, they are same, which means that they are more correlated. In that case, the solution would be rather easier as the system size grows linearly with N . However, it is not always the case. So, what is done with the DMRG is the following: the Hilbert space is splitted into two halves (not necessarily equal) with some coefficients. See the equation below:

$$|\psi\rangle = \sum i\sqrt{\lambda_i} |\phi_i^A\rangle \left| \bigotimes \phi_i^B \right\rangle \quad (5.2)$$

where, $\mathcal{H}_A$ and $\mathcal{H}_B$ are the splitted Hilbert spaces and $|\phi_i^A\rangle$ and $|\phi_i^B\rangle$ are respectively, the orthonormal sets in those Hilbert spaces. λ_i is a positive number and in ML-MCTDH, is a natural population in each orbital.

5.3 Hamiltonian

One can rewrite the Hamiltonian of an ideal system consisting N identical rotors with the rotational constant B and the dipole moment μ , which is given by the following relation (we took it granted for our study here, hence the proof could be consulted elsewhere):

$$\hat{H} = \frac{B}{\hbar^2} \sum_{i=1}^N \hat{l}_i^2 + \frac{\mu^2}{4\pi\epsilon_0} \sum_{i=2}^N \sum_{j=1}^{i-1} \frac{\hat{V}_{ij}}{(i-j)^3} \quad (5.3)$$

Where, the term r_{ij} is the distance between the rotors i and j , regardless of their position and $\hat{l}_i$ the angular momentum of the i^{th} rotor.

Now, since we wish to describe an ensemble of carbon nanotube assembly structured in an one-dimensional array, we could fix, in principle, the linear motion along only one axis: let's say along the z axis. As such, the inter-atomic potential can be expressed as a function of Cartesian coordinates:

$$\hat{V}_{ij}^{(z)} = \hat{x}_i \hat{x}_j + \hat{y}_i \hat{y}_j - 2\hat{z}_i \hat{z}_j \quad (5.4)$$

With $(\hat{x}_i, \hat{y}_i, \hat{z}_i)$ being the unit vectors of i^{th} rotor.

Rewriting eq.5.3 gives:

$$\frac{\hat{H}}{B} = \sum_{i=1}^N \frac{\hat{l}_i^2}{\hbar^2} + \frac{\mu^2}{4\pi\epsilon_0 B r^3} \sum_{i=2}^N \sum_{j=1}^{i-1} \frac{V_{ij}^{(z)}}{(i-j)^3} \quad (5.5)$$

$$= \sum_{i=1}^N \frac{\hat{l}_i^2}{\hbar^2} + g \sum_{i=2}^N \sum_{j=1}^{i-1} \frac{V_{ij}^{(z)}}{(i-j)^3} \quad (5.6)$$

Where,

$$g = \frac{\mu^2}{4\pi\epsilon_0 B r^3} = \frac{1}{R^3} \quad (5.7)$$

The transformation of the Cartesian coordinates into the spherical coordinates is made and hence, the rotation of each of these rotors is assumed along θ_i and ϕ_i for the i^{th} rotor (and same for the j^{th} rotor).

5.4 DVR used in the calculation

Before entering into the discussion and the results obtained for this study, let's see the DVR used.

The spfs of the MCTDH wavefunction are represented in a grid as some mathematical functions. In our study, the ML-MCTDH basis set is a finite representation of two dimensional Legendre polynomial. The two angles θ and ϕ describe the rotational motion and the basis functions are the L^2 normalized associated Legendre functions given by:

$$\chi_{l-m+1}(\theta) = \sqrt{\frac{2l+1}{2} \frac{(l-m)!}{(l+m)!}} P_l^m(\cos\theta) \quad (5.8)$$

where, $P_l^m(\cos\theta)$ are the corresponding eigenfunctions of the angular momentum

operator $\hat{l}^2$. m is the magnetic quantum number and is fixed while l goes from m to $m + N - 1$, i.e. $m \leq l \leq m + N - 1$.

The function P_l^m is given by the following polynomial:

$$P_l^m(x) = \frac{(-1)^m}{2^l l!} (1 - x^2)^{m/2} \frac{d^{l+m}}{dx^{l+m}} (x^2 - 1)^l \quad (5.9)$$

with $0 \leq m \leq l$.

They are not to be expressed mathematically and explicitly as is already incorporated in the algorithm. Below is the typical example of primitive basis section from our calculations:

```
-----
theta1 PLeg 5 all
phi1 exp 5 2pi
theta2 PLeg 5 all
phi2 exp 5 2pi
-----
```

The number 5 indicates the no. of basis functions (or, grid points) used and *all* or *2pi* indicates the angular value limit for θ and ϕ . Depending on the no. of rotors, the no. of angles vary. This two dimensional DVR has `PLeg`, which is a keyword corresponding to the Legendre polynomial and combining the angular modes θ and ϕ .

5.5 Results

The solution of this physical problem is given by eq.5.6. As stated in [84], there is a quantum phase transition occurring at around $g = 1.0$. This happens due to the breaking of the rotational symmetry [205]. It is believed that this breaking

is due to the quantum fluctuations in the system. This quantum phase transition differentiates ordered and disordered states. As it happens at $T = 0K$, it cannot be described classically. For N even, this happens exactly at the midpoint of an ensemble of the system ($N = 10$ and 50). However, for $N = 25$, this happens at the 12^{th} and 13^{th} node, thus the system possesses more disorderness. So, we identify the two interesting regimes given by g : $g > 1$ and $g < 1$. This parameter is known as *order parameter* and identifies the orientation of a system with respect to a certain value. This could be compared with the classical analogue of Curie temperature T_c , which apparently changes the spin of the system by the application of magnetic or electric field [206, 207].

The Von Neumann entanglement entropy of the system can be defined as:

$$S_{vN} = - \sum_j \lambda_j \ln \lambda_j \quad (5.10)$$

Similarly, the Orientational Correlation (OC) is calculated as:

$$\frac{2}{N(N-1)} \sum_{i=2}^N \sum_{J=1}^{i-1} \mathbf{e}_i \mathbf{e}_j \quad (5.11)$$

The orientational correlation gives us information about the relative orientation of the rotors with respect to the position of each other. The highly converged values of these observables have been provided also in [90] (see tables I and II). These results have very high level of precision obtained using DMRG and could essentially serve as a benchmark for the numerical improvements and technical implementation of ML-MCTDH for rotors. We shall now move towards the results obtained via this common study.

The same calculation has partly been done in [84], where the authors performed the calculation for all pair interaction and for very high level of accuracy. Here, both neighboring and all pair wise interaction are studied (with slightly lower level of convergence, see also [90]).

Table 5.1: DMRG parameters, results, and corresponding computational effort for systems with nearest-neighbor interactions (NN). Wall-times are given in hours “h”, minutes “m”, and seconds “s”. Maximum memory usage and ground state MPS size are reported in MB. Reprinted from [90] with permission AIP copyright 2021

N	g	l_{max}	ε	E	S_{vN}	OC	Time	Memory	Size
10	0.5	5	10^{-14}	-0.3781091744	0.069105639	0.00533842	12m30s	54	1
	1.0	6	10^{-14}	-1.5597054109	0.2456055	0.03695576	42m59s	261	2
	1.5	7	10^{-14}	-3.7909948650	0.61805	0.184790	2h41m25s	1036	4
	2.0	8	10^{-14}	-7.383621680	0.7724429	0.369532	4h41m11s	1500	6
25	0.5	5	10^{-14}	-1.009392863	0.06910577	0.0023572	39m18s	55	2
	1.0	6	10^{-14}	-4.184455427	0.24657055	0.0187613	3h14m17s	370	6
	1.5	7	10^{-14}	-10.491188621	0.786916	0.2467871	22h18m29s	2398	25
	2.0	8	10^{-14}	-20.775486204	0.77801316	0.41543072	23h15m03s	1861	23
50	0.5	5	10^{-14}	-2.061532344	0.06910577	0.00121253	1h26m 23s	57	3
	1.0	6	10^{-14}	-8.559041298	0.24657259	0.0100223	7h33m51s	431	14
	1.5	7	10^{-13}	-21.73364018	0.8213455	0.2788758	43h19m25s	2259	43
	2.0	8	10^{-14}	-43.103080319	0.778014411	0.430220817	60h58m57s	2059	52

Table 5.2: DMRG parameters, results, and corresponding computational effort for systems with all pairwise interactions (All). Wall-times are given in hours “h”, minutes “m”, and seconds “s”. Maximum memory usage and ground state MPS size are reported in MB. Reprinted from [90] with permission AIP copyright 2021

N	g	l_{max}	ε	E	S_{vN}	OC	Time	Memory	Size
10	0.5	5	10^{-14}	-0.398960623	0.079905618	0.00969951	24m35s	441	2
	1.0	7	10^{-14}	-1.800214523	0.3963543	0.09268385	3h40m56s	3958	9
	1.5	8	10^{-14}	-5.065659016	0.74355776	0.334380701	9h30m29s	9930	17
	2.0	8	10^{-14}	-9.869695663	0.744232934	0.447721340	9h28m06s	8838	16
25	0.5	6	10^{-14}	-1.071398284	0.08016462	0.004763804	4h32m37s	1613	11
	1.0	7	10^{-14}	-5.036369456	0.5578798	0.1100315	58h48m22s	13271	80
	1.5	8	10^{-14}	-15.219922215	0.748988662	0.39127903	102h11m09s	17940	93
	2.0	8	10^{-14}	-29.04624326	0.741768134	0.48826618	76h55m59s	14742	75
50	0.5	5	10^{-14}	-2.19213100	0.080169146	0.0025307	6h29m22s	1175	23
	1.0	7	10^{-13}	-10.48545272	0.712649	0.1319925	162h36m00s	16952	167
	1.5	7	10^{-14}	-32.2218434	0.74856170	0.409262540	158h38m18s	15255	204
	2.0	8	10^{-13}	-61.1002505	0.74150944	0.50184354	109h29m11s	8055	95

Despite the layered form of the wavefunction in ML-MCTDH being complex in terms of representation, one can have several possibilities regarding the choice of layers (however, one should be aware that we will not end up with the same results for different layers, especially for parameter like entropy; the requirements of no. of spfs will be very large for convergence. We have indeed, performed some calculations with asymmetric tree. However, the entropy and the OC obtained is very far from the realistic values obtained via DMRG; lest the cpu times are more comparable. As the system under study is symmetric, we need to have also symmetric layers. We will below illustrate this by two examples taken for our calculation (we show the tree for $N = 10, 25$ and 50 for different g 's). For N being even, the choice of our tree is, in fact, simple.

Let us have a look at fig.5.3 below. It is a four layer wavefunction (just count the number of circles for the number of layers). We split the first layer into two equal halves: with ten coordinates on each side. These layers contain 16 spfs (see the number next to the leg) each. They are splitted again into two symmetric halves with 20 and 56 spfs on each groups. Then, they are again splitted into three groups with the no. of spfs 13, 16 and 16 on each groups. They are further splitted into two groups, which ultimately take two coordinates. The last layer is time independent whereas all the other layers are time dependent. Remember that the tree is mirror symmetric (or translationally symmetric). Hence, the number of spfs used is also equal. This is at least the case for $N = 10$ (for $N = 25$ and 50 , different spfs have been used while increasing system size and g). This gives rise to the fact that the system is ordered by construction (theoretical) and we have equal entropy on both the halves.

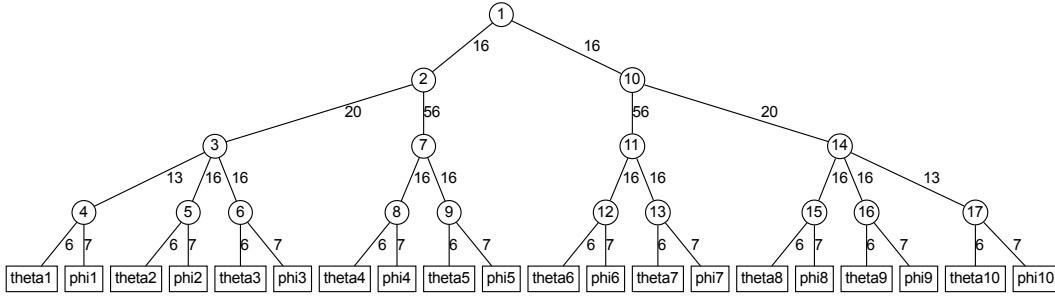


Figure 5.3: ML-MCTDH tree for $N = 10$ and $g = 2.0$

Here, since $N = 25$ is odd, the rotational symmetry is more difficult to preserve. More than that, as seen from the fig.5.4 and 5.5, it is evident that the entropy, which is a signature of disorder in the system, might also differ since the left splitting and right splitting is not the same thing.

Let us have a look for $N = 50$ now. The tree structure of the ML-MCTDH wavefunction is shown in the figs.5.6 and 5.7. This is a six layer wavefunction. The top layer is divided into two sub layers of 50 coordinates with 48 spfs on each. These layers are again divide subsequently on different subgroups and so on. The calculations were performed with different sets of DVR functions: from 5 to 9 and 19 (not reported here). It happens that ML-MCTDH (and MCTDH also in general) is not very responsive with respect to the size and the comparable results can be obtained by taking only 5 DVR functions even for high accuracy (minimum 10^{-6} for the (dimensionless) energy). However, a compromise has been made between the choice regarding the no. of spf functions and the cpu time so as to obtain comparable results.

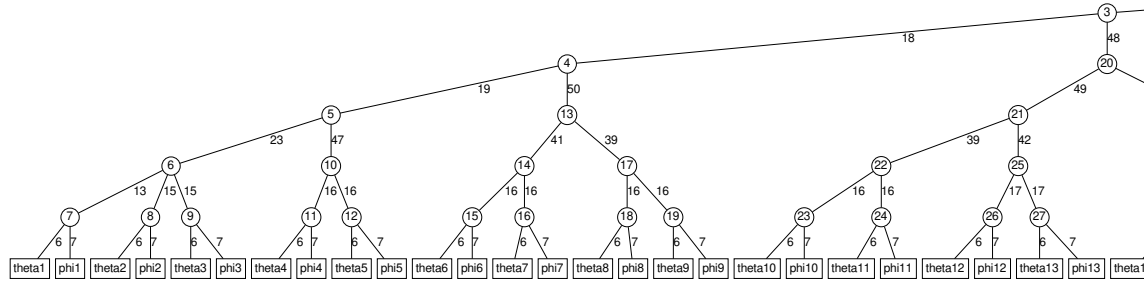


Figure 5.6: Left part of the ML-MCTDH tree for $N = 50$ & $g = 2.0$; the tree is splitted into two halves for better resolution.

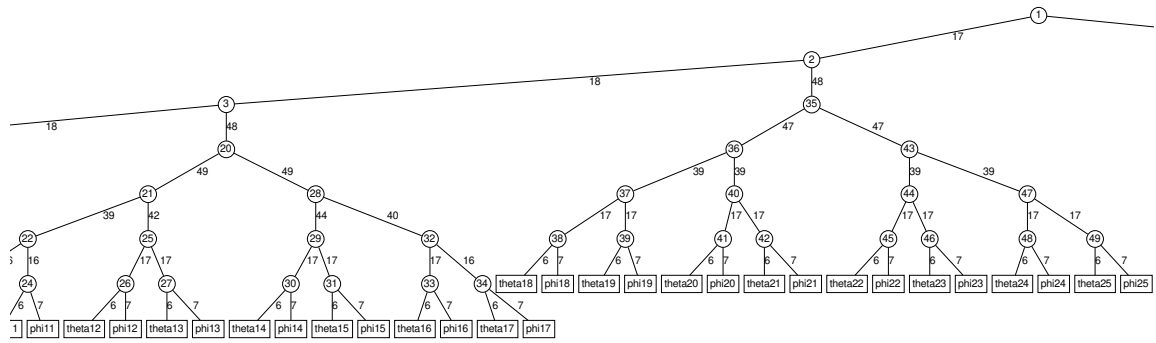


Figure 5.7: Same as fig.5.6, the remaining side of the left part of the tree

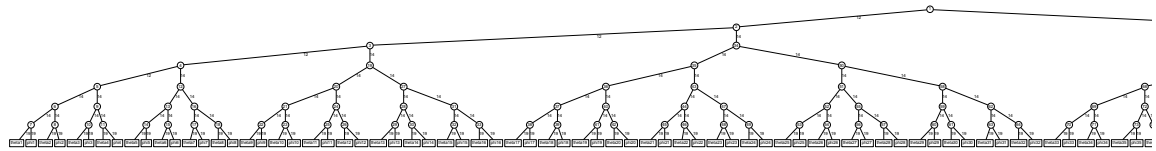


Figure 5.8: Left part of the ML-MCTDH tree for $N = 50$ and $g = 2.0$, partitioned unequally

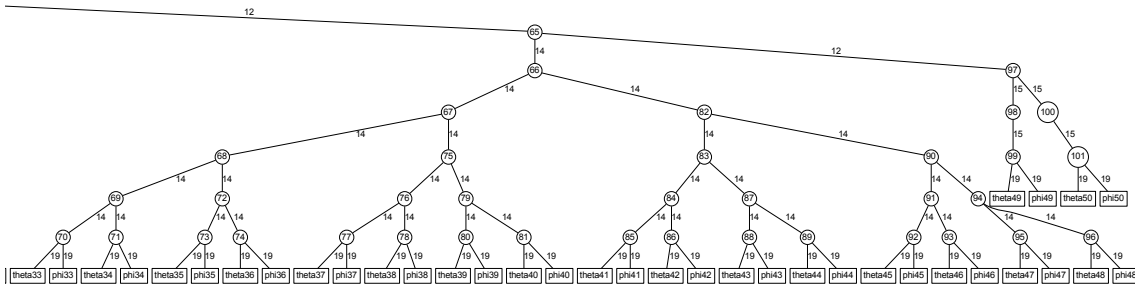


Figure 5.9: Right part of the ML-MCTDH tree for $N = 50$ and $g = 2.0$, partitioned unequally

With ML-MCTDH, the ground states have been obtained by a “simple” propagation in imaginary time. As it is time dependent and, also depends on the basis size we are choosing, we see the exponential (or inverse) behavior with decrease in energy (see fig.5.1). The 5 digits (or even 6 digits for some calculations) accuracy have been obtained between DMRG and ML-MCTDH. The results are presented for two cases: ‘All’ and ‘NN’. ‘All’ denotes the interaction among all the rotors, irrespective of their position while ‘NN’ denotes the interaction between the neighboring rotors only.

5.5.1 System dependent Properties

The system dependent properties are methodologically intrinsic, that is to say, their physical properties remain same irrespective of the numerical algorithms used for simulation.

Energy

In the table below (see table 5.3), we compare the ground state energy (dimensionless) of a system for different N s and the constant g s. In the left part of the table, we indicate the coupling between the neighboring rotors; whereas in the right, the coupling takes all pair wise interaction. This coupling, as seen from the eq.5.7, is proportional to $1/R^3$ with R being the inter-rotor distance. As said in [90], so as to have more comparable figures, the values for DMRG are calculated at lower level of accuracy (or convergence) than what they can achieve. As seen from the table 5.1, it is proven that these two numerical algorithms give the same results. Even for the

most difficult ones (i.e. $g = 1.0$ and interaction type = ‘All’), ML-MCTDH is able to converge within considerable amount of time. It is even more interesting to note that the underlying physics is well captured by ML-MCTDH. We know from the other literature (see the chemical potentials shown in [84], for instance) that the quantum phase transition occurs at around $g = 1.0$ (we do not know the exact value) and thus, the calculations for $g = 1.0$ are the most difficult ones.

Table 5.3: (Dimensionless) energies given by eq.5.6 obtained with (a) ML-MCTDH and (b) DMRG for $N = 10, 25$ and 50 rotors with $g = 0.5, 1.0, 1.5$ and 2 .

g	NN			All		
	$N = 10$	$N = 25$	$N = 50$	$N = 10$	$N = 25$	$N = 50$
$0.5^{(a)}$	-0.3781	-1.0093	-2.0611	-0.3989	-1.0713	-2.1912
$0.5^{(b)}$	-0.3781	-1.0093	-2.0614	-0.3989	-1.0713	-2.1919
$1.0^{(a)}$	-1.5597	-4.1836	-8.5573	-1.8002	-5.0351	-10.480
$1.0^{(b)}$	-1.5597	-4.1844	-8.5590	-1.8002	-5.0362	-10.485
$1.5^{(a)}$	-3.7908	-10.490	-21.726	-5.0654	-15.219	-32.218
$1.5^{(b)}$	-3.7905	-10.489	-21.729	-5.0656	-15.213	-32.222
$2.0^{(a)}$	-7.3836	-20.774	-43.095	-9.8696	-29.045	-61.096
$2.0^{(b)}$	-7.3836	-20.775	-43.103	-9.8695	-29.046	-61.099

Entropy

Table 5.4: Von Neumann entanglement entropies, given by eq.5.10 obtained with (a) ML-MCTDH and (b) DMRG for $N = 10, 25$ and 50 rotors with $g = 0.5, 1.0, 1.5$ and 2 .

g	NN			All		
	$N = 10$	$N = 25$	$N = 50$	$N = 10$	$N = 25$	$N = 50$
$0.5^{(a)}$	0.0691	0.0691	0.0688	0.0799	0.0800	0.0793
$0.5^{(b)}$	0.0691	0.0691	0.0691	0.0799	0.0801	0.0801
$1.0^{(a)}$	0.246	0.245	0.246	0.396	0.542	0.660
$1.0^{(b)}$	0.246	0.247	0.247	0.396	0.558	0.712
$1.5^{(a)}$	0.618	0.782	0.818	0.743	0.749	0.748
$1.5^{(b)}$	0.618	0.787	0.821	0.744	0.749	0.749
$2.0^{(a)}$	0.772	0.777	0.776	0.744	0.742	0.741
$2.0^{(b)}$	0.772	0.778	0.778	0.744	0.742	0.742

Here again, the two calculations are giving basically the same values. The entropy in ML-MCTDH is the sum of λ_j s (this is the occupancy number associated with each orbital). As the top node in ML-MCTDH is mirror symmetric, the entropy given by each branch is basically the same. This calculated entropy is responsible

for the orderliness of our system. Since the entropy depends on the heat and the temperature, it could be interesting to introduce the temperature effect in our next calculation.

The quantum entropy measured here is different to classical one in a sense that it is a change of response with respect to the order parameter whereas classically, it is a measure of change in macroscopic property of the system [208]. More than that, it is also similar to ‘Shanon entropy’ observed in quantum information theory.

Orientational Correlation (OC)

Table 5.5: Orientational Correlation, given by eq.5.11 obtained with (a) ML-MCTDH and (b) DMRG for $N = 10, 25$ and 50 rotors with $g = 0.5, 1.0, 1.5$ and 2 .

g	NN			All		
	$N = 10$	$N = 25$	$N = 50$	$N = 10$	$N = 25$	$N = 50$
$0.5^{(a)}$	0.00534	0.00235	0.00121	0.009692	0.00477	0.00250
$0.5^{(b)}$	0.00534	0.00235	0.00121	0.009689	0.00476	0.00253
$1.0^{(a)}$	0.0369	0.0183	0.0100	0.0926	0.110	0.118
$1.0^{(b)}$	0.0370	0.0188	0.0100	0.0927	0.110	0.132
$1.5^{(a)}$	0.183	0.244	0.279	0.334	0.391	0.409
$1.5^{(b)}$	0.185	0.246	0.279	0.334	0.391	0.409
$2.0^{(a)}$	0.369	0.415	0.430	0.448	0.488	0.502
$2.0^{(b)}$	0.370	0.415	0.430	0.448	0.488	0.502

This parameter measures the degrees of correlation between the rotors i and j . The way how they are aligned with respect to each other is addressed by this quantity. Looking at the values shown in table 5.5, both the methods are proven to be rather comparable.

5.5.2 Method dependent Properties

The method dependent properties are described in the subsequent subsections. They are specific of the methods used and differ in a significant basis.

CPU Time

Table 5.6: Wall times (expressed in hours ‘h’, minutes ‘m’ and seconds ‘s’ obtained with (a) ML-MCTDH and (b) DMRG for $N = 10, 25$ and 50 with $g = 0.5, 1.0, 1.5$ and 2 .

g	NN			All		
	$N = 10$	$N = 25$	$N = 50$	$N = 10$	$N = 25$	$N = 50$
$0.5^{(a)}$	0m32s	4m36s	7m25s	2m25s	1h11m	4h32
$0.5^{(b)}$	0m37s	1m44s	3m21s	0m39s	2m21s	4m41s
$1.0^{(a)}$	2m06s	9m22s	1h09m	11m34s	5h00m	69h38m
$1.0^{(b)}$	2m32s	7m11s	15m46s	3m09s	12m24s	40m52s
$1.5^{(a)}$	2m48s	51m07s	2h08m	12m26s	12h09m	87h23m
$1.5^{(b)}$	3m10s	10m56s	28m16s	9m27s	28m50s	1h07m
$2.0^{(a)}$	11m19s	48m49s	1h56m	40m21s	12h49m	60h10m
$2.0^{(b)}$	7m08s	25m09s	52m29s	8m57s	32m35s	1h09m

Although the calculations regarding the ML-MCTDH have been performed on several computing platforms (e.g. Fusion [182], Mésolum), we provide in the table below, the simulation results obtained by Prof. Dieter (see also [90]). Almost all the calculations (except $g = 1.0, 1.5, 2.0$ and interaction type = all; these calculations, after having launched for some integrated steps were extrapolated as it would take enormous amount of time otherwise) were performed in his local (personal) desktop using 4 processors. The DMRG calculations were done without any parallelization. From the table 5.6, it is evident that DMRG provides the results in better timescale (faster) as compared to ML-MCTDH. Having said that, getting the calculations terminated with the wall times indicated above is already something reasonable for ML-MCTDH. This huge disparity of CPU times in ML-MCTDH calculations could be explained by several reasons as follows:

1. A ’s are complex. As such, to calculate these A vectors takes twice the time in normal calculations. There is a way to get rid of this by MLPF (Multi-Layer Potfit) method [106], recently developed and not yet officially included in the

available MCTDH packages.

2. Relaxation is not a good way to do it. The calculations has been done by CMF and VMF scheme. CMF seems slightly faster (the results are not shown here).

Calculations With Mésolum

Table 5.7: Wall times (expressed in hours ‘h’, minutes ‘m’ and seconds ‘s’) obtained with ML-MCTDH using different no. of cores in ‘Mésolum’ for $N = 10$

g	NN			All		
	8 Cores	4 Cores	Single Core	8 Cores	4 Cores	Single Core
0.5	0m49s	1m31s	2m58s	3m31s	4m53s	17m31s
1.0	2m46s	4m56s	10m18s	12m32s	17m18s	1h02m20m
1.5	4m39s	5m33s	14m53s	18m10s	34m05s	1h29m18s
2.0	17m	19m45s	48m12s	58m36s	1h17m39s	4h46m02m

Table 5.8: Wall times (expressed in hours ‘h’, minutes ‘m’ and seconds ‘s’) obtained with ML-MCTDH using different no. of cores in ‘Mésolum’ for $N = 25$

g	NN			All		
	8 Cores	4 Cores	Single Core	8 Cores	4 Cores	Single Core
0.5	5m07s	10m33s	23m42s	1h11m40s	2h06m	8h55m55s
1.0	15m27s	22m27s	52m19s	2h18m08s	5h04m35s	19h39m02s
1.5	1h18m31s	1h54m04s	4h26m02s	20h28m24s	29h42m30s	110h56m11s
2.0	1h14m35s	1h48m18s	4h14m18s	19h30m04s	26h24m53s	111h44m24s

Table 5.9: Wall times (expressed in hours ‘h’, minutes ‘m’ and seconds ‘s’) obtained with ML-MCTDH using different no. of cores in ‘Mésolum’ for $N = 50$

g	NN			All		
	8 Cores	4 Cores	Single Core	8 Cores	4 Cores	Single Core
0.5	11m14s	12m28s	39m06s	6h43m49ss	12h39m46s	38h53m41s
1.0	1h21m37s	1h48m55s	7h48m5s	51h45m25s	108h55m7s	358h06m36s
1.5	2h46m56s	4h28m10s	14h54m42s	104h54m32s	315h27m	697h07m12s
2.0	1h55m23s	3h58m19s	10h31m43	95h38m45s	214h34m12s	537h36s

Separately, the calculations with 8 cores, 4 cores and single core has been reported in tables 5.7, 5.8 and 5.9. Although the efficiency of the parallelization is seen while increasing the no. of cores, this increase in performance is not linear. Moreover, our results with 8 cores calculation are even worse than what is shown in the table above.

Calculations With Fusion

An additional calculation for $N = 10, 25$ and 50 with 24 cores is shown (coming from Fusion [182]). There is not much difference in the values obtained with Mésolum and Fusion.

Table 5.10: Wall times (expressed in hours ‘h’, minutes ‘m’ and seconds ‘s’) obtained with with ML-MCTDH using 24 cores in ‘Fusion’

g	NN			All		
	$N = 10$	$N = 25$	$N = 50$	$N = 10$	$N = 25$	$N = 50$
0.5	0m55s	8m26s	7m01s	1m28s	22m37s	2h16
1.0	2m49s	8m47ss	59m12s	4m52s	49m05s	23h10m
1.5	3m46s	50m25ss	1h33m10s	6m59s	5h25m11s	50h12m
2.0	12m48s	51m19ss	1h43m29s	22m17s	4h44m29s	37h27m36s

As seen from the tables 5.7, 5.8 and 5.9, the calculations are still possible in our local computing platform, Mésolum too. However, it takes long time. The same is seen in ‘Fusion’, the only difference being that we could launch our calculations with 24 processors.

Memory and SizeTable 5.11: Memory (in MB) obtained with (a) ML-MCTDH and (b) DMRG for $N = 10, 25$ and 50 rotors with $g = 0.5, 1.0, 1.5$ and 2 .

g	NN			All		
	$N = 10$	$N = 25$	$N = 50$	$N = 10$	$N = 25$	$N = 50$
$0.5^{(a)}$	29	94	149	30	100	198
$0.5^{(b)}$	18	17	17	26	30	32
$1.0^{(a)}$	64	142	448	65	165	555
$1.0^{(b)}$	28	29	31	73	141	2523
$1.5^{(a)}$	64	275	536	65	281	595
$1.5^{(b)}$	32	60	72	172	428	2843
$2.0^{(a)}$	145	278	548	147	292	619
$2.0^{(b)}$	66	78	77	174	194	210

Table 5.12: Size (in MB) obtained with (a) ML-MCTDH and (b) DMRG for $N = 10, 25$ and 50 rotors with $g = 0.5, 1.0, 1.5$ and 2 .

g	NN			All		
	$N = 10$	$N = 25$	$N = 50$	$N = 10$	$N = 25$	$N = 50$
$0.5^{(a)}$	1.4	4.3	6.4	1.4	4.3	6.4
$0.5^{(b)}$	0.06	0.1	0.2	0.07	0.3	0.6
$1.0^{(a)}$	3.1	6.8	21.4	3.1	7.6	24.3
$1.0^{(b)}$	0.1	0.4	0.9	0.3	2.1	64
$1.5^{(a)}$	3.1	13.5	25.7	3.1	13.5	25.8
$1.5^{(b)}$	0.2	1.2	3.1	0.7	7.6	72
$2.0^{(a)}$	7.2	13.6	25.9	7.2	14.1	27.1
$2.0^{(b)}$	0.4	1.4	3.2	0.7	2.4	5.3

In the tables above (5.11 and 5.12), we show the size of the wavefunction used and also the amount of space (called “memory” here) required so as to store all the final eigenstates. Although DMRG seems more interesting (or, less consuming) here, we are sure that while increasing the system size, ML-MCTDH will prove to be more efficient. This is the essence of ML-MCTDH [96, 123, 125].

5.6 Summary and Outlook

The coupling constant introduced here can be compared with a classical analogue: the Curie temperature, T_c in solid state physics. The orientational correlation gives us information about whether the system is oriented or not (this depends on some pre-defined value on the basis of which we define the relative orientation). This is similar to what happens in solid state physics: depending on the temperature one can change the spin of the system from paramagnetic to ferri-magnetic or any other [206–208].

The only problem with ML-MCTDH is to find a suitable combination of layers. It is also important to note that ML-MCTDH calculations are not so much affected by the higher values of primitive basis sets (we have performed a series of calculation with higher primitive basis sets and it happens that it only increases the computational time by some hours). As the basis sets used are very flexible, we could also see that the memory demand is not very huge. Since DMRG could obtain the excited states [84], it could also be fruitful to have a comparison regarding the calculation for those excited states.

It is also possible to do the same calculation using *Quantum Ising model* (see chapter 1 of [208]). The ground state Hamiltonian used here depends only on the dimensionless coupling g and two interesting regimes were identified: $g < 1$ and $g > 1$. We, indeed, observed the second order phase transition resulting from the quantum fluctuations. They are qualitatively the change in the correlation terms between the rotors in ground state.

As seen previously, by using ML-MCTDH, we are able to produce the second order quantum phase transition as highlighted by DMRG. However, since DMRG is especially a numerical algorithm for these kinds of problems, we see that it outperforms ML-MCTDH in every scale. This is not surprising: the network is adapted to chains. On the other hand, the ML-MCTDH tree separate some rotors that are neighbors and that are thus strongly coupled. In addition, ML-MCTDH is originally a time-dependent method and DMRG is optimized to converge the ground state. Just to give one example: to perform the propagation in imaginary time, we use complex numbers while DMRG works with real numbers. This alone multiply by a factor two the necessary memory and by a factor four the speed of the calculation. In this context, it is remarkable that ML-MCTDH can correctly reproduce the quantum phase

transition and could be used to describe the time-evolution of a quantum phase in more than one dimension such as CO molecules of a surface of NaCl [209].

Chapter 6

Conclusion and perspectives

I want to leave, to go somewhere where I should be really in my place, where I would fit in ... but my place is nowhere; I am unwanted.

— *Jean-Paul Sartre, Nausea*

As presented in the earlier chapters (see chapter 3 and 4 for more details), our idea in the following study (in part) was to use a series of laser pulses, with sufficient time delay between them so as to provide the molecule with some organisational time frame, and which are intense enough to diverge the channeling (or passage) from one potential energy surface to the other to have sufficient amount of quantum mechanical mixing. As the laser is a coherent source of light, we were able to create the coherent superposition between different eigenstates. In doing so, we could indeed guide the electronic motion via some selective eigenstates, while suppressing the rest. It was also verified from several calculation whether the intensity chosen is in the weak field or strong field limit.

Shortly, one could also state the differences between weak field and strong field limit [210, 211]. The advantage of weak field regime is that we are sure about not creating some additional physical processes like ionization in the molecule (this

could be even further verified by what we call the ‘Keldysh Parameter’, see [212] for instance). More than that, it is not necessary to create some intermediate states; thus a single resonant pulse is enough to start the excitation. This is however, not the case with strong field limit.

In chapter 3, the well-known strategy, interference was discussed. In chapter 4, the kicks mechanisms was discussed. It is one of the mechanisms to control the physical observable of a molecule in an excited state [82, 213]. The questions to be addressed while using this method are the mastering (in case if we use different delays between the pulses) and the possibility of experimental feasibility (the limit of availability of the laser intensity to be used). The contrast was calculated between 4D and 24D in each of these strategies. With kicks mechanism, we see that the better contrast can be achieved even by laser with an intensity as small as $5 \times 10^{12} W/cm^2$.

The mathematical framework of the results presented in the earlier chapters are basically based on the following three pillars [10]:

1. B.O. approximation and beyond.
2. Construction of the PESs: in our case, we have used a linear coupling model theorized by the researchers of University of Heidelberg.
3. Dynamical Calculations: here, we used the Heidelberg MCTDH code.

The molecule we studied is already large for conventional numerical approaches (see [214], for example). Moreover, we are adding also the laser-molecule interaction, which complexify even more the dynamics. There are several parameters that play a vital role, for instance [10]:

- Intensity of the pulse
- Shape of the pulse used
- Laser pulse duration

It has been shown from this thesis that the method of quantum control we are using is quite effective. However, several aspects have not been studied and could be interesting for further works, for instance:

- The exploitation of the other route (i.e. transition from S_0 to S_1) irrespective of the laser intensity and the damage induced could be verified out. This forms a basis for pump-probe interference process.
- The effect of alignment and orientation could also be studied. The commercially available intense laser pulse could prove fruitful in that case.
- The conical intersection is a seam of $3N-8$ degrees of freedom: several strategies can be devised to target several regions of the seam that display different topographies and may lead to different behaviors (photo-reactivity or photostability) [215, 216].

This work has a more general scope than the study of pyrazine. The latter has been used only as a model to describe funneling dynamics, which is a key mechanism in artificial light-harvesting processes, biological antennas and organic photovoltaic devices, among others, [217–223]. Transfer from an initial donor that absorbs light efficiently (acceptor) to a donor that may be almost dark (as is the case in pyrazine) is driven by a non-adiabatic process through a conical intersection. One of the very important points shown in this thesis is the fact that we could devise strategies of coherent control with a simple 4D model of pyrazine and that the extension to full dimensionality (24D) does not alter the efficiency of the control. This supports, modestly, the assumption that such situations may occur in larger biological systems: it has been indeed assumed that a small number of active modes guide the dynamics one wishes to control in important biological processes and that the others are rather spectators. Under these conditions, it has been claimed that quantum coherence may play a role and could be exploited to guide these biological processes [217–222].

In this work, we have used the MCTDH method as an essential tool to simulate the quantum dynamics of the nuclei. In this context, one other important aspect of this thesis has been the first comparison between MCTDH (more precisely ML-MCTDH) and the very promising DMRG method (chapter 5). We have calculated the ground state of a chain of rotors including up to 100 degrees of freedom. Unsurprisingly, DMRG turned out to be more efficient for this system (DMRG has been optimized to solve this kind of problems). It was, however, satisfying to verify that MCTDH can very correctly reproduce the quantum phase transition observed by changing the parameter in the model (basically the strength of the coupling between the rotors). In addition, ML-MCTDH could be used to study of the time-dependent evolution of a quantum phase of system of rotors such as molecules of CO on a surface of NaCl and the present work can be seen as a first step in this direction. It is proposed

that the molecules of CO may display a process of synchronization like the famous metronome synchronization process [209]. To prove this, it may be necessary to use a more complex model that includes the internal motion of the molecules and, more importantly, the motions of the center-of-mass of the molecules. This can be done by using the Ising Model of Rotors [208, 224]. The inclusion of all degrees of freedom (rotational, vibrational, translational) is more challenging and perhaps more adapted to ML-MCTDH than DMRG [84, 205]. This is mandatory to check that the quantum phase is not destroyed by them (especially the translation of the molecules).

Appendices

Chapter A

Impact of the Step Size on MCTDH Calculations

While doing propagation of the wavefunction, the equations of motions have to be solved. The impact of the laser has to be correctly described. Different integration schemes (see MCTDH documentation) are implemented in the Heidelberg MCTDH package. In particular, we often use the Short Iterative Lanczos (SIL) integration scheme [149] for the A coefficients and the Bulirsch-Stoer (BS) extrapolation integrator for the SPFs [150]. Here, we discuss only the error tolerance: this is very important since the laser oscillates very fast and we must check that the integrators can describe correctly the impact of those oscillations.

Following is an example of an integrator section used in one of the calculations:

```
#####  
INTEGRATOR-SECTION  
CMF/var = 0.5, 1.0d-06  
BS/spf = 7 , 1.0d-06 , 2.5d-05  
SIL/A = 5 , 1.0d-06  
end-integrator-section  
#####
```

Here, CMF integration scheme is used. The initial step size of this calculation is 0.5fs and the error tolerance is 10^{-6} . This error tolerance automatically adjusts the step size at each time of the propagation that is thus adapted and hence, the integration error [225]. The other parameters of this integration scheme has been discussed elsewhere [150]. Here, CMF stands for Constant Mean Field, meaning that the mean fields, density matrices and the Hamiltonian matrix elements are kept constant for some time, instead of re-evaluating in each integration step for the SPFs: CMF is often efficient since generally the SPFs move faster than the A coefficients. This is the primary difference with VMF scheme [150].

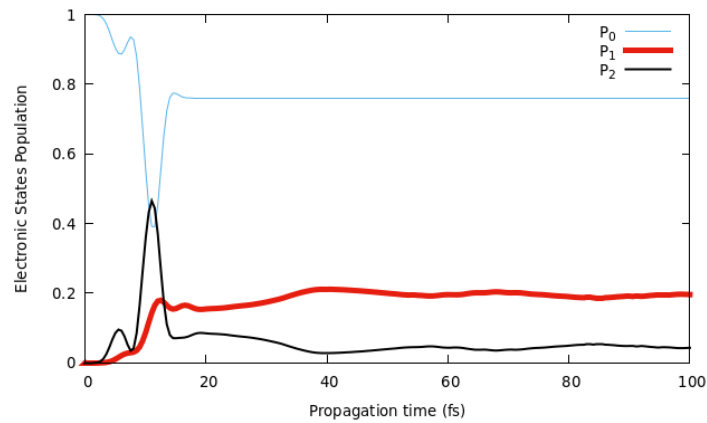


Figure A.1:
Electronic States Population (Error Tolerance: 1d-06)

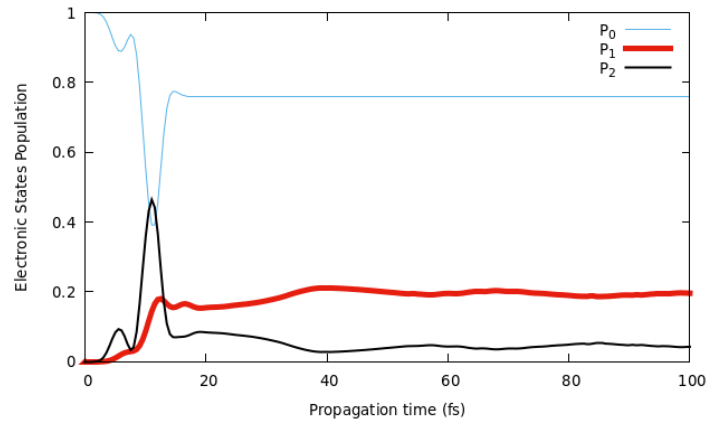


Figure A.2:
Electronic States Population (Error Tolerance: 1d-07)

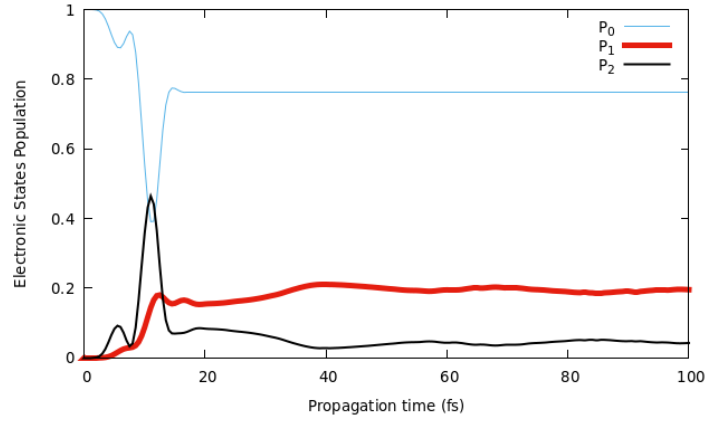


Figure A.3:
Electronic States Population (Error Tolerance: 1d-08)

From the figures above, we see that the difference is rather negligible, which proves that our integrators can correctly describe the action of the laser. However, in terms of wall time, it could be of huge importance to consider this effect as they could even differ by an order of magnitude sometimes (we increase by a factor of 3 on going from a tolerance of 10^{-6} to 10^{-8}).

Chapter B

Transition Dipole Moments

The interaction part of the Hamiltonian used in our study has been briefly discussed in chapter 2 (see section 2.3). Their explicit explanation with each of the terms involved is described in this appendix.

The matrix elements of the interaction Hamiltonian is given by the following relation [226]:

$$V_E = \vec{\mu} \cdot \vec{E} \quad (\text{B.1})$$

where, $\vec{\mu} = \sum_n q_n \vec{r}_n$ is the transition dipole moment and $\vec{E}$ is the electric field amplitude. q_n and r_n in B.1 represent respectively, the charge and the position for the n^{th} particle. The summation is over all the electrons and nuclei present in the system.

The permanent dipole moment for an electronic transition is given by the following relation:

$$\vec{d} = \langle \psi_i | \vec{\mu} | \psi_i \rangle \quad (\text{B.2})$$

where, $|\psi_i\rangle$ is an electronic state (3 in our case). We then take the norm of the dipole transition vectors.

The dipole moments used in this study are taken from [39]. The detailed description can be consulted therein (see supplementary material).

$$\mu_{01}^d(q) = \xi_{10a}^{(01)} q_{10a} \quad (\text{B.3})$$

$$\mu_{02}^d(q) = \mu^{(02)}(0) + \sum_k \xi_k^{(02)} q_k + \frac{1}{2} \rho_{10a}^{(02)} q_{10a}^2 \quad (\text{B.4})$$

where, $\mu^{(02)}(0)$ is the transition dipole moment from S_0 to S_2 calculated at the Franck-Condon geometry. The symbol d corresponds to the diabatic states. For symmetry arguments, $\mu_{02}^d(q)$ is much larger than $\mu_{01}^d(q)$. The consequence of this then would be to use lasers with very high intensity should one consider the excitation path from S_0 to S_1 (see fig. 1.1).

The numerical values of all these parameters along with the procedure to calculate these matrices can be found in the same reference cited above.

Chapter C

Interference *Mechanism: Intermediate Contrast*

In chapter 3 of the following thesis, we discussed our observable: p , the contrast. There, we calculated p for several delays while restricting ourselves within the asymptotic time window $[400, 500]$ fs. During this time frame, our lasers are completely off and we see the stabilisation of the population in all the electronic states.

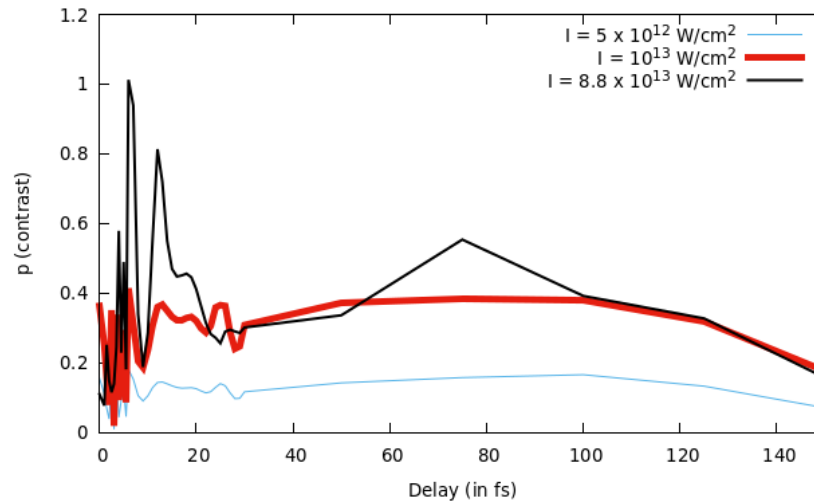


Figure C.1: 4D asymptotic contrast (*Interference*) in the intermediate region as a function of delay τ for different laser intensities. Same notation as in fig.3.9.

However, one could also choose several other time windows. One of the possibilities is the intermediate time frame: $[110, 200]$ fs. The starting point of this time frame is chosen from the point where the degeneracy is obtained after the wavepacket has made a complete cycle in the mixed potential well. That is to say, after one complete cycle in 4D dynamics.

Conclusively, if we compare fig.C.1 with fig.3.9, where the asymptotic contrast as a function of delay for different laser intensities is plotted, we see that this function maintains its shape. The better contrast is obtained with a laser of highest intensity and during the time when the two pulses are superimposed. However, the values are quite different. It is because, the populations are not yet stabilised in this window.

Chapter D

Kicks Mechanism: Intermediate Contrast

In chapter 4 of the manuscript is discussed the 4D asymptotic contrast for kicks. As said in appendix C, we were also interested to see the contrast in intermediate time frame. Shown below is such illustration for kicks.

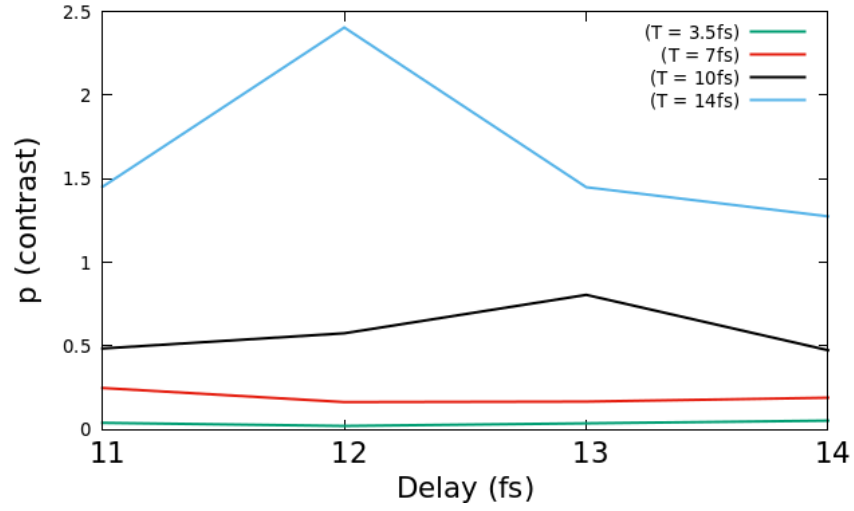


Figure D.1: 4D asymptotic contrasts (*Kicks*) in the intermediate region for different pulse durations (calculated at $\tau = 13\text{fs}$).

Fig.D.1 shows the contrast as a function of delay (constant) between several pulses and for different pulse durations. Those durations vary from 3.5fs to 14fs. Like stated in the former appendix for interference mechanism, the function maintains well its shape in this case too (a simple comparison between the figures D.1 and 4.23 suffices).

What could be said in brief about this figure is the following: the blue line, illustrating the pulse duration of 3.5fs is not very interesting as it covers huge density of states that are not at all responsive to the laser effect. So, the contrasts obtained are rather small. Compared to what has been seen in fig.4.24, the contrast obtained is always smaller irrespective of the pulse duration. While increasing the pulse duration resulted in better contrast, this is not the objective of kicks mechanism as the necessity of use of ultrashort pulses then vanishes.

Chapter E

Transfer from S_0 to S_1

In the results presented in chapter 3 and 4, the excitation path chosen was always from S_0 to S_2 (see the equations shown in appendix B to see the obvious reason, coming from the presence of a permanent dipole for this excitation route). However, it is still possible to excite the system via the other route.i.e S_0 to S_1 .

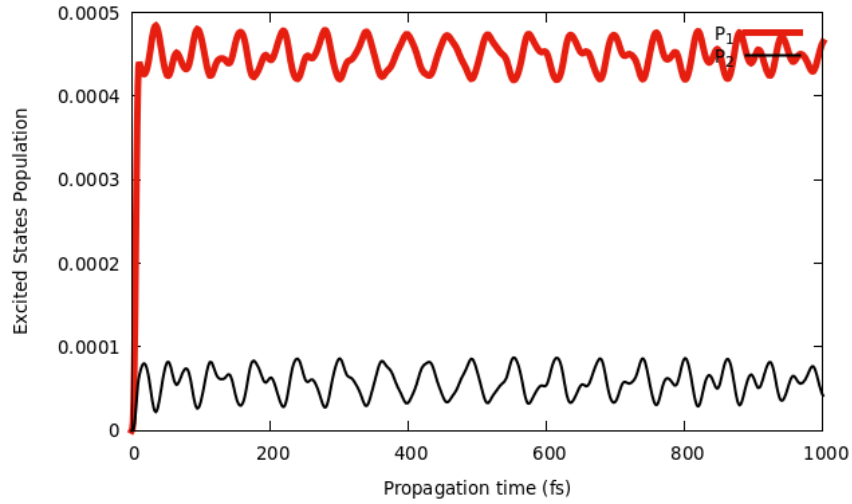


Figure E.1: Excited states population (2D)

In fig.E.1 is shown the excited states population in 2D with a resonant frequency for state S_1 ($E_1 = 3.91eV$) and a laser with an intensity of $5 \times 10^{12}W/cm^2$. We see that most of the populations, once excited from S_0 , remain localized forever in S_1 . It is because the resonant energy is well below the position of the conical intersection, and also that since the transition dipole moment for excitation via this route is negligible, we would need very intense lasers to excite the same amount of population as done by the laser for the transfer from S_0 to S_2 . This is the reason why this route hasn't been considered in our study.

Chapter F

Effect of the coupling parameter (W_{12})

For all the calculations demonstrated in chapters 3 and 4, the value of the coupling strength is chosen to be 0.1825 eV . This corresponds to the characteristic time of about 20fs.

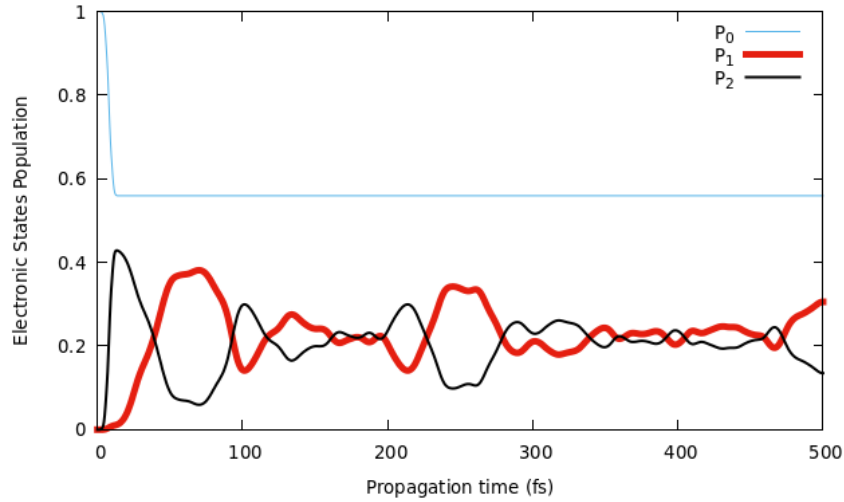


Figure F.1: Electronic states population (2D, $W_{12} = 0.131 \text{ eV}$)

However, we also performed some additional simulations for a single pulse (2D,

$I = 5 \times 10^{12} \text{W/cm}^2$) with different values of W_{12} to see the changes inferred in the dynamics. What we observe is that the form of the transfer between the excited states is same; however, the percentage of transfer is varying. W_{12} 's are changed; so are the characteristic time of mixing (or, the periodicity). While increasing (or, decreasing) this parameter, we see that there is evidently also a change in no. of recursive patterns observed.

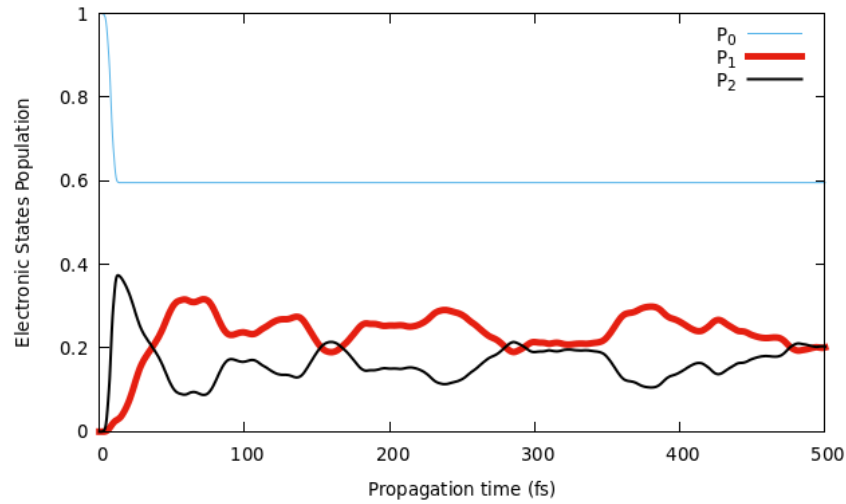


Figure F.2: Electronic states population (2D, $W_{12} = 0.262 \text{eV}$)

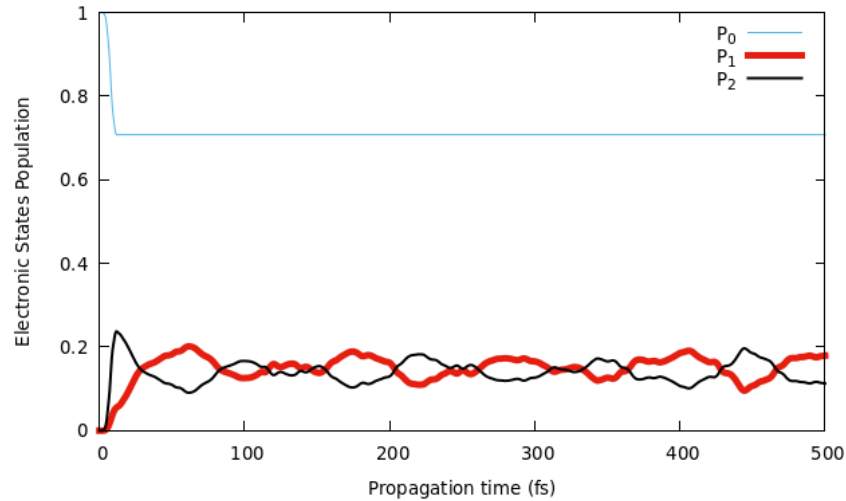


Figure F.3: Electronic states population (2D, $W_{12} = 0.524 \text{eV}$)

Bibliography

- [1] Basile FE Curchod and Federica Agostini. On the dynamics through a conical intersection. *The journal of physical chemistry letters*, 8(4):831–837, 2017.
- [2] Wolfgang Domcke, David Yarkony, and Horst Köppel. *Conical intersections: electronic structure, dynamics & spectroscopy*, volume 15. World Scientific, 2004.
- [3] Wolfgang Domcke, David R Yarkony, and Horst Köppel. *Conical intersections: theory, computation and experiment*, volume 17. World Scientific, 2011.
- [4] Camille A Farfan and Daniel B Turner. A systematic model study quantifying how conical intersection topography modulates photochemical reactions. *Physical Chemistry Chemical Physics*, 22(36):20265–20283, 2020.
- [5] Benjamin G Levine and Todd J Martínez. Isomerization through conical intersections. *Annu. Rev. Phys. Chem.*, 58:613–634, 2007.
- [6] H. Köppel and W. Domcke. Vibronic dynamics in polyatomic molecules. In P. v. R. Schleyer, N. L. Allinger, T. Clark, J. Gasteiger, P. A. Kollman, H. F. Schaefer III, and P. R. Schreiner, editors, *Encyclopedia of Computational Chemistry*, pages 3166–3182, New York, 1998. John Wiley and Sons.
- [7] Martial Boggio-Pasqua. Computational mechanistic photochemistry: The central role of conical intersections, 2015.
- [8] Peter Hamm and Gerhard Stock. Vibrational conical intersections as a mechanism of ultrafast vibrational relaxation. *Physical review letters*, 109(17):173201, 2012.

- [9] L. S. Cederbaum. Born-oppenheimer approximation and beyond. In W. Domcke, D. R. Yarkony, and H. Köppel, editors, *Conical Intersections*, pages 3–40, Singapore, 2004. World Scientific Co.
- [10] Gert Due Billing, Kurt V Mikkelsen, and Kurt W Mikkelsen. *Advanced molecular dynamics and chemical kinetics*. Wiley-Interscience, 1997.
- [11] Fabien Gatti, Benjamin Lasorne, Hans-Dieter Meyer, and André Nauts. *Applications of Quantum Dynamics in Chemistry*, volume 98. Springer, 2017.
- [12] Terry A Miller. Holding computations of conical intersections to a gold standard. *Quantum Dynamics at Conical Intersections*, 2004.
- [13] Luis Seidner and Wolfgang Domcke. Microscopic modelling of photoisomerization and internal-conversion dynamics. *Chemical physics*, 186(1):27–40, 1994.
- [14] Luis Seidner, Gerhard Stock, and Wolfgang Domcke. Nonperturbative approach to femtosecond spectroscopy: General theory and application to multidimensional nonadiabatic photoisomerization processes. *The Journal of chemical physics*, 103(10):3998–4011, 1995.
- [15] Benjamin Lasorne, Graham A Worth, and Michael A Robb. Excited-state dynamics. *Wiley Interdisciplinary Reviews: Computational Molecular Science*, 1(3):460–475, 2011.
- [16] Michael A Robb. *Theoretical chemistry for electronic excited states*, volume 12. Royal Society of Chemistry, 2018.
- [17] T. Schultz, E. Samoylova, W. Radloff, I. V. Hertel, A. L. Sobolewski, and W. Domcke. Efficient deactivation of a model base pair via excited-state hydrogen transfer. *Science*, 306:1765, 2004.
- [18] Mohamad Saab, Loïc Joubert Doriot, Benjamin Lasorne, Stéphane Guérin, and Fabien Gatti. A quantum dynamics study of the benzopyran ring opening guided by laser pulses. *Chemical Physics*, 442:93–102, 2014.
- [19] G. A. Worth and L. S. Cederbaum. Mediation of ultrafast electron transfer in biological systems by conical intersections. *Chem. Phys. Lett.*, 338:219–223, 2001.
- [20] Gloria Olaso-González, Manuela Merchan, and Luis Serrano-Andrés. Ultrafast electron transfer in photosynthesis: Reduced pheophytin and quinone interaction mediated by conical intersections. *The Journal of Physical Chemistry B*, 110(48):24734–24739, 2006.

- [21] Cong Hou, Ya-Jun Liu, Nicolas Ferré, and Wei-Hai Fang. Understanding bacterial bioluminescence: a theoretical study of the entire process, from reduced flavin to light emission. *Chemistry—A European Journal*, 20(26):7979–7986, 2014.
- [22] Nimrod Moiseyev, Milan Šindelka, and Lorenz S Cederbaum. Laser-induced conical intersections in molecular optical lattices. *Journal of Physics B: Atomic, Molecular and Optical Physics*, 41(22):221001, 2008.
- [23] Gábor J Halász, Ágnes Vibók, Milan Šindelka, Nimrod Moiseyev, and Lorenz S Cederbaum. Conical intersections induced by light: Berry phase and wavepacket dynamics. *Journal of Physics B: Atomic, Molecular and Optical Physics*, 44(17):175102, 2011.
- [24] Seungsuk Han and David R Yarkony. Nonadiabatic processes involving three electronic states. i. branch cuts and linked pairs of conical intersections. *The Journal of chemical physics*, 119(10):5058–5068, 2003.
- [25] Spiridoula Matsika and David R Yarkony. Conical intersections of three electronic states affect the ground state of radical species with little or no symmetry: pyrazolyl. *Journal of the American Chemical Society*, 125(41):12428–12429, 2003.
- [26] Martial Boggio-Pasqua. Computational mechanistic photochemistry: The central role of conical intersections.
- [27] ED Potter, JL Herek, S Pedersen, Q Liu, and AH Zewail. Femtosecond laser control of a chemical reaction. *Nature*, 355(6355):66–68, 1992.
- [28] Shaul Mukamel and Kaiyu Shan. On the selective elimination of intramolecular vibrational redistribution using strong resonant laser fields. *Chemical physics letters*, 117(5):489–494, 1985.
- [29] Matthieu Sala. *Quantum dynamics and laser control for photochemistry*. Springer, 2016.
- [30] Fabien Gatti. Molecular dynamics simulated by photons, 2018.
- [31] Charles R Hickenboth, Jeffrey S Moore, Scott R White, Nancy R Sottos, Jerome Baudry, and Scott R Wilson. Biasing reaction pathways with mechanical force. *Nature*, 446(7134):423–427, 2007.
- [32] Reaction mechanisms: nature of reactants, intermediates, and products.

- [33] Luis GC Rego, Lea F Santos, and Victor S Batista. Coherent control of quantum dynamics with sequences of unitary phase-kick pulses. *Annual review of physical chemistry*, 60:293–320, 2009.
- [34] TC Weinacht, JL White, and PH Bucksbaum. Toward strong field mode-selective chemistry. *The Journal of Physical Chemistry A*, 103(49):10166–10168, 1999.
- [35] Ahmed H Zewail. Femtochemistry: recent progress in studies of dynamics and control of reactions and their transition states. *Atomic and Molecular Beams*, pages 415–476, 1996.
- [36] Bruce W Shore. Pre-history of the concepts underlying stimulated raman adiabatic passage (stirap). *Acta Physica Slovaca*, 63(6):361–481, 2013.
- [37] Klaas Bergmann, Nikolay V Vitanov, and Bruce W Shore. Perspective: Stimulated raman adiabatic passage: The status after 25 years. *The Journal of chemical physics*, 142(17):170901, 2015.
- [38] Mohamad Saab, Matthieu Sala, Benjamin Lasorne, Fabien Gatti, and Stéphane Guérin. Full-dimensional control of the radiationless decay in pyrazine using the dynamic stark effect. *The Journal of chemical physics*, 141(13):134114, 2014.
- [39] Matthieu Sala, Mohamad Saab, Benjamin Lasorne, Fabien Gatti, and Stéphane Guérin. Laser control of the radiationless decay in pyrazine using the dynamic stark effect. *The Journal of chemical physics*, 140(19):194309, 2014.
- [40] Ioannis Thanopoulos, Xuan Li, Paul Brumer, and Moshe Shapiro. Time-dependent partitioning theory of the control of radiationless transitions in 24-mode pyrazine. *The Journal of chemical physics*, 137(6):064111, 2012.
- [41] National Research Council et al. *Controlling the quantum world: the science of atoms, molecules, and photons*, volume 2. National Academies Press, 2007.
- [42] MF Kling, Ch Siedschlag, Aart J Verhoef, JI Khan, Martin Schultze, Th Uphues, Yicheng Ni, Matthias Uiberacker, M Drescher, Ferenc Krausz, et al. Control of electron localization in molecular dissociation. *Science*, 312(5771):246–248, 2006.
- [43] Zhan Hu, Sima Singha, Youbo Zhao, Grant E Barry, Tamar Seideman, and Robert J Gordon. Coherent control of the photoionization of pyrazine. *The Journal of Physical Chemistry Letters*, 3(19):2744–2748, 2012.

- [44] Audrey Dell Hammerich, Ronnie Kosloff, and Mark A Ratner. Chemistry in strong laser fields: An example from methyl iodide photodissociation. *The Journal of chemical physics*, 97(9):6410–6431, 1992.
- [45] Luxia Wang, Hans-Dieter Meyer, and Volkhard May. Femtosecond laser pulse control of multidimensional vibrational dynamics: Computational studies on the pyrazine molecule. *The Journal of chemical physics*, 125(1):014102, 2006.
- [46] Maxim Sukharev and Tamar Seideman. Optimal control approach to suppression of radiationless transitions. *Physical review letters*, 93(9):093004, 2004.
- [47] J. Zanghellini, M. Kitzler, C. Fabian, T. Brabec, and A. Scrinzi. An MCTDHF approach to multi-electron dynamics in laser fields. *Laser Phys.*, 13:1064, 2003.
- [48] J. Caillat, J. Zanghellini, and A. Scrinzi. Parallelization of the MCTDHF code. *AURORA Technical Reports*, 19:1, 2004.
- [49] Jeremie Caillat, Jürgen Zanghellini, Markus Kitzler, Othmar Koch, Wolfgang Kreuzer, and Armin Scrinzi. Correlated multielectron systems in strong laser fields - an MCTDHF approach. *Phys. Rev. A*, 71:012712, 2005.
- [50] T. Kato and H. Kono. Time-dependent multiconfiguration theory for electronic dynamics of molecules in an intense laser field. *Chem. Phys. Lett.*, 392:533, 2004.
- [51] M. Nest, T. Klamroth, and P. Saalfrank. The multiconfiguration time-dependent Hartree-Fock method for quantum chemical calculations. *J. Chem. Phys.*, 122:124102, 2005.
- [52] D. Hochstuhl, S. Bauch, and M. Bonitz. Multiconfigurational time-dependent Hartree-Fock calculations for photoionization of one-dimensional helium. *J. Phys.: Conf. Ser.*, 220:012019, 2010.
- [53] D. J. Haxton, K. V. Lawler, and C. W. McCurdy. Multiconfiguration time-dependent Hartree-Fock treatment of electronic and nuclear dynamics in diatomic molecules. *Phys. Rev. A*, 83:063416, 2011.
- [54] Joachim Schnabl. The world’s shortest laser pulse, 2017.
- [55] IB Obot, Ikenna B Onyeachu, and SA Umoren. Pyrazines as potential corrosion inhibitors for industrial metals and alloys: a review. *Journal of Bio-and Tribo-Corrosion*, 4(2):1–13, 2018.
- [56] Marco Ruberti. Quantum electronic coherences by attosecond transient absorption spectroscopy: ab initio b-spline rcs-adc study. *Faraday Discussions*, 2021.

- [57] Philip Ball. <https://www.chemistryworld.com/features/light-harvesting/3004665.article>.
- [58] Joonsuk Huh, Semion K Saikin, Jennifer C Brookes, Stephanie Valleau, Takatoshi Fujita, and Alan Aspuru-Guzik. Atomistic study of energy funneling in the light-harvesting complex of green sulfur bacteria. *Journal of the American Chemical Society*, 136(5):2048–2057, 2014.
- [59] Martin Juhás and Jan Zitko. Molecular interactions of pyrazine-based compounds to proteins. *Journal of medicinal chemistry*, 63(17):8901–8916, 2020.
- [60] Pyrazine properties, 2021.
- [61] Robert J Gordon, Zhan Hu, Tamar Seideman, Sima Singha, Maxim Sukharev, and Youbo Zhao. Coherent phase control of internal conversion in pyrazine. *The Journal of chemical physics*, 142(14):144311, 2015.
- [62] VS Letokhov. Laser isotope separation. *Nature*, 277(5698):605–610, 1979.
- [63] VS Letokhov. Laser-induced chemistry. *Nature*, 305(5930):103–108, 1983.
- [64] Nicolaas Bloembergen and Eli Yablonovitch. Infrared-laser-induced unimolecular reactions. *Phys. Today*, 31(5):23–31, 1978.
- [65] Ahmed H Zewail. Femtochemistry: atomic-scale dynamics of the chemical bond using ultrafast lasers (nobel lecture). *Angewandte Chemie International Edition*, 39(15):2586–2631, 2000.
- [66] Richard S Judson and Herschel Rabitz. Teaching lasers to control molecules. *Physical review letters*, 68(10):1500, 1992.
- [67] Herschel Rabitz, Regina de Vivie-Riedle, Marcus Motzkus, and Karl Kompa. Whither the future of controlling quantum phenomena? *Science*, 288(5467):824–828, 2000.
- [68] Benjamin J Sussman, Dave Townsend, Misha Yu Ivanov, and Albert Stolow. Dynamic stark control of photochemical processes. *Science*, 314(5797):278–281, 2006.
- [69] Warren S Warren, Herschel Rabitz, and Mohammed Dahleh. Coherent control of quantum dynamics: the dream is alive. *Science*, 259(5101):1581–1589, 1993.
- [70] Ronnie Kosloff. Time dependent approach to femtosecond laser chemistry. In *AIP Conference Proceedings*, volume 295, pages 152–170. American Institute of Physics, 1993.

- [71] Timur Grinev, Moshe Shapiro, and Paul Brumer. Coherent quantum control of internal conversion: in pyrazine via weak field excitation. *Journal of Physics B: Atomic, Molecular and Optical Physics*, 48(17):174004, 2015.
- [72] Moshe Shapiro and Paul Brumer. *Principles of the quantum control of molecular processes*. John Wiley & Sons, 2003.
- [73] Paul Brumer and Moshe Shapiro. Coherence chemistry: controlling chemical reactions [with lasers]. *Accounts of Chemical Research*, 22(12):407–413, 1989.
- [74] D Geppert and R de Vivie-Riedle. Velocity control of ultrafast reactions: manipulation of the nuclear wave packets momentum with phase-sensitive optimal control theory. *Chem. Phys. Lett*, 404:289, 2005.
- [75] David Mendeive-Tapia, Morgane Vacher, Michael J Bearpark, and Michael A Robb. Coupled electron-nuclear dynamics: Charge migration and charge transfer initiated near a conical intersection. *The Journal of chemical physics*, 139(4):044110, 2013.
- [76] I Burghardt, K Giri, and GA Worth. Multimode quantum dynamics using gaussian wavepackets: The gaussian-based multiconfiguration time-dependent hartree (g-mctdh) method applied to the absorption spectrum of pyrazine. *The Journal of chemical physics*, 129(17):174104, 2008.
- [77] Suk Kyoung Lee, Arthur G Suits, H Bernhard Schlegel, and Wen Li. A reaction accelerator: Mid-infrared strong field dissociation yields mode-selective chemistry. *The journal of physical chemistry letters*, 3(18):2541–2547, 2012.
- [78] Steffen J Glaser, Ugo Boscain, Tommaso Calarco, Christiane P Koch, Walter Köckenberger, Ronnie Kosloff, Ilya Kuprov, Burkhard Luy, Sophie Schirmer, Thomas Schulte-Herbrüggen, et al. Training schrödinger’s cat: quantum optimal control. *The European Physical Journal D*, 69(12):1–24, 2015.
- [79] Christiane P Koch, Mikhail Lemesko, and Dominique Sugny. Quantum control of molecular rotation. *Reviews of Modern Physics*, 91(3):035005, 2019.
- [80] Ugo Boscain, Mario Sigalotti, and Dominique Sugny. Introduction to the pontryagin maximum principle for quantum optimal control. *PRX Quantum*, 2(3):030203, 2021.
- [81] Dominique Sugny, Stéphane Vranckx, Mamadou Ndong, Nathalie Vaeck, Osman Atabek, and Michèle Desouter-Lecomte. Control of molecular dynamics with zero-area fields: Application to molecular orientation and photofragmentation. *Physical Review A*, 90(5):053404, 2014.

- [82] Dominique Sugny, Arne Keller, Osman Atabek, David Daems, CM Dion, Stéphane Guérin, and Hans-Rudolf Jauslin. Reaching optimally oriented molecular states by laser kicks. *Physical Review A*, 69(3):033402, 2004.
- [83] Dominique Sugny, Stéphane Vranckx, Mamadou Ndong, Osman Atabek, and Michèle Desouter-Lecomte. External constraints on optimal control strategies in molecular orientation and photofragmentation: role of zero-area fields. *Journal of Modern Optics*, 61(10):816–821, 2014.
- [84] Dmitri Iouchtchenko and Pierre-Nicholas Roy. Ground states of linear rotor chains via the density matrix renormalization group. *The Journal of chemical physics*, 148(13):134115, 2018.
- [85] Ulrich Schollwöck. The density-matrix renormalization group. *Reviews of modern physics*, 77(1):259, 2005.
- [86] Ulrich Schollwöck. The density-matrix renormalization group in the age of matrix product states. *Annals of physics*, 326(1):96–192, 2011.
- [87] Hans-Dieter Meyer and Graham A Worth. Quantum molecular dynamics: propagating wavepackets and density operators using the multiconfiguration time-dependent hartree method. *Theoretical Chemistry Accounts*, 109(5):251–267, 2003.
- [88] Uwe Manthe, H-D Meyer, and LS Cederbaum. Multiconfigurational time-dependent hartree study of complex dynamics: Photodissociation of no2. *The Journal of chemical physics*, 97(12):9062–9071, 1992.
- [89] H-D Meyer, Uwe Manthe, and Lorenz S Cederbaum. The multi-configurational time-dependent hartree approach. *Chemical Physics Letters*, 165(1):73–78, 1990.
- [90] Samrit Mainali, Fabien Gatti, Dmitri Iouchtchenko, Pierre-Nicholas Roy, and Hans-Dieter Meyer. Comparison of the multi-layer multi-configuration time-dependent hartree (ml-mctdh) method and the density matrix renormalization group (dmrg) for ground state properties of linear rotor chains. *The Journal of Chemical Physics*, 154(17):174106, 2021.
- [91] Amit Dutta and JK Bhattacharjee. Phase transitions in the quantum ising and rotor models with a long-range interaction. *Physical Review B*, 64(18):184106, 2001.
- [92] Mariana Rossi. Progress and challenges in ab initio simulations of quantum nuclei in weakly bonded systems. *The Journal of Chemical Physics*, 154(17):170902, 2021.

- [93] Paul G Tratnyek, Eric J Bylaska, and Eric J Weber. In silico environmental chemical science: properties and processes from statistical and computational modelling. *Environmental Science: Processes & Impacts*, 19(3):188–202, 2017.
- [94] David Mendive-Tapia, Etienne Mangaud, Thiago Firmino, Aureélien de la Lande, Michèle Desouter-Lecomte, Hans-Dieter Meyer, and Fabien Gatti. Multidimensional quantum mechanical modeling of electron transfer and electronic coherence in plant cryptochromes: The role of initial bath conditions. *The Journal of Physical Chemistry B*, 122(1):126–136, 2018.
- [95] Haobin Wang and Hans-Dieter Meyer. On regularizing the ml-mctdh equations of motion. *The Journal of chemical physics*, 149(4):044119, 2018.
- [96] Qingyong Meng and Hans-Dieter Meyer. A multilayer mctdh study on the full dimensional vibronic dynamics of naphthalene and anthracene cations. *The Journal of chemical physics*, 138(1):18908, 2013.
- [97] John Zeng Hui Zhang. *Theory and application of quantum molecular dynamics*. World Scientific, 1998.
- [98] Benjamin Lasorne. Nonadiabatic dynamics current methods and challenges, 2019.
- [99] A. T. Le and C. D. Lin. Diabatization: A simple way to get to highly excited states, 2014-04-14.
- [100] David R Yarkony. Diabolical conical intersections. *Reviews of Modern Physics*, 68(4):985, 1996.
- [101] Caroline Arnold, Oriol Vendrell, Ralph Welsch, and Robin Santra. Towards attochemistry: Control of nuclear motion through conical intersections and electronic coherences. *arXiv preprint arXiv:1808.06872*, 2018.
- [102] Franck Lépine, Misha Y Ivanov, and Marc JJ Vrakking. Attosecond molecular dynamics: fact or fiction? *Nature Photonics*, 8(3):195–204, 2014.
- [103] Jeffrey I Steinfeld, Joseph Salvatore Francisco, and William L Hase. *Chemical kinetics and dynamics*. Prentice Hall Upper Saddle River, NJ, 1999.
- [104] J Espinosa-Garcia, M Monge-Palacios, and JC Corchado. Constructing potential energy surfaces for polyatomic systems: Recent progress and new problems. *Advances in Physical Chemistry*, 2012.
- [105] Tak-San Ho and Herschel Rabitz. A general method for constructing multidimensional molecular potential energy surfaces from ab initio calculations. *The Journal of chemical physics*, 104(7):2584–2597, 1996.

- [106] Frank Otto. Multi-layer potfit: an accurate potential representation for efficient high-dimensional quantum dynamics. *The Journal of chemical physics*, 140(1):014106, 2014.
- [107] Hans-Dieter Meyer. Potfit and multigrid potfit. transforming general multi-potential energy surfaces to product form. applications to h3o2-. 2013.
- [108] Benjamin C Shepler, Bastiaan J Braams, and Joel M Bowman. Quasiclassical trajectory calculations of acetaldehyde dissociation on a global potential energy surface indicate significant non-transition state dynamics. *The Journal of Physical Chemistry A*, 111(34):8282–8285, 2007.
- [109] S. Carter and N. C. Handy. A variational method for the calculation of ro-vibronic levels of any orbitally degenerate (renner-teller) triatomic molecule. *Mol. Phys.*, 52:1367–1391, 1984.
- [110] Z. Bačić and J. C. Light. Highly excited vibrational levels of “floppy” triatomic molecules: A discrete variable representation – Distributed Gaussian approach. *J. Chem. Phys.*, 85:4594, 1986.
- [111] Z. Bačić and J. C. Light. Accurate localized and delocalized vibrational states of HCN/HNC. *J. Chem. Phys.*, 86:3065, 1987.
- [112] M. J. Bramley, J. W. Tromp, T. Carrington Jr., and R. C. Corey. Efficient calculation of highly excited vibrational energy levels of floppy molecules: The band origins of H_3^+ up to $35\,000\text{ cm}^{-1}$. *J. Chem. Phys.*, 100:6175, 1994.
- [113] G. C. Corey and D. Lemoine. Pseudospectral method for solving the time-dependent Schrödinger equation in spherical coordinates. *J. Chem. Phys.*, 97:4115, 1992.
- [114] G. C. Corey, J. W. Tromp, and D. Lemoine. Fast pseudospectral algorithm in curvilinear coordinates. In C. Cerjan, editor, *Numerical Grid Methods and Their Application to Schrödinger’s Equation*, pages 1–23, Netherlands, 1993. Kluwer Academic Publishers.
- [115] M. J. Bramley and T. Carrington, Jr. A general discrete variable method to calculate vibrational energy levels of three- and four-atom molecules. *J. Chem. Phys.*, 99:8519, 1993.
- [116] H.-D. Meyer, U. Manthe, and L. S. Cederbaum. The multi-configurational time-dependent Hartree approach. *Chem. Phys. Lett.*, 165:73–78, 1990.
- [117] U. Manthe, H.-D. Meyer, and L. S. Cederbaum. Wave-packet dynamics within the multiconfiguration Hartree framework: General aspects and application to NOCl. *J. Chem. Phys.*, 97:3199–3213, 1992.

- [118] M. H. Beck, A. Jäckle, G. A. Worth, and H.-D. Meyer. The multi-configuration time-dependent Hartree (MCTDH) method: A highly efficient algorithm for propagating wave packets. *Phys. Rep.*, 324:1–105, 2000.
- [119] H.-D. Meyer, F. Gatti, and G. A. Worth, editors. *Multidimensional Quantum Dynamics: MCTDH Theory and Applications*. Wiley-VCH, Weinheim, 2009.
- [120] Uwe Manthe, H-D Meyer, and Lorenz S Cederbaum. Wave-packet dynamics within the multiconfiguration hartree framework: General aspects and application to nocl. *The Journal of chemical physics*, 97(5):3199–3213, 1992.
- [121] Michael H Beck, Andreas Jäckle, Graham A Worth, and H-D Meyer. The multiconfiguration time-dependent hartree (mctdh) method: a highly efficient algorithm for propagating wavepackets. *Physics reports*, 324(1):1–105, 2000.
- [122] Fabien Gatti. *Molecular quantum dynamics: from theory to applications*. Springer, 2014.
- [123] Haobin Wang and Michael Thoss. Multilayer formulation of the multiconfiguration time-dependent hartree theory. *The Journal of chemical physics*, 119(3):1289–1299, 2003.
- [124] Oriol Vendrell and Hans-Dieter Meyer. Multilayer multiconfiguration time-dependent hartree method: Implementation and applications to a henon–heiles hamiltonian and to pyrazine. *The Journal of chemical physics*, 134(4):044135, 2011.
- [125] Haobin Wang. Multilayer multiconfiguration time-dependent hartree theory. *The Journal of Physical Chemistry A*, 119(29):7951–7965, 2015.
- [126] Uwe Manthe. A multilayer multiconfigurational time-dependent hartree approach for quantum dynamics on general potential energy surfaces. *The Journal of chemical physics*, 128(16):164116, 2008.
- [127] Uwe Manthe and Thomas Weike. On the multi-layer multi-configurational time-dependent hartree approach for bosons and fermions. *The Journal of chemical physics*, 146(6):064117, 2017.
- [128] H. Wang and M. Thoss. Multilayer formulation of the multiconfiguration time-dependent Hartree theory. *J. Chem. Phys.*, 119:1289–1299, 2003.
- [129] H. Wang and M. Thoss. Theoretical study of ultrafast photoinduced electron transfer processes in mixed-valence systems. *J. Phys. Chem. A*, 107:2126–2136, 2003.

- [130] Haobin Wang, David E Skinner, and Michael Thoss. Calculation of reactive flux correlation functions for systems in a condensed phase environment: A multilayer multiconfiguration time-dependent hartree approach. *The Journal of chemical physics*, 125(17):174502, 2006.
- [131] Hans-Dieter Meyer, Fabien Gatti, and Graham A Worth. *Multidimensional quantum dynamics: MCTDH theory and applications*. John Wiley & Sons, 2009.
- [132] Hans-Joachim Werner, Peter J Knowles, Frederick R Manby, Joshua A Black, Klaus Doll, Andreas Heßelmann, Daniel Kats, Andreas Köhn, Tatiana Korona, David A Kreplin, et al. The molpro quantum chemistry package. *The Journal of chemical physics*, 152(14):144107, 2020.
- [133] Mark James Abraham, Teemu Murtola, Roland Schulz, Szilárd Páll, Jeremy C Smith, Berk Hess, and Erik Lindahl. Gromacs: High performance molecular simulations through multi-level parallelism from laptops to supercomputers. *SoftwareX*, 1:19–25, 2015.
- [134] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox. Gaussian~16 Revision C.01, 2016. Gaussian Inc. Wallingford CT.
- [135] P Giannozzi, O Andreussi, T Brumme, O Bunau, M Buongiorno Nardelli, M Calandra, R Car, C Cavazzoni, D Ceresoli, M Cococcioni, N Colonna, I Carnimeo, A Dal Corso, S de Gironcoli, P Delugas, R A DiStasio Jr, A Ferretti, A Floris, G Fratesi, G Fugallo, R Gebauer, U Gerstmann, F Giustino, T Gorni, J Jia, M Kawamura, H-Y Ko, A Kokalj, E Küçükbenli, M Lazzeri, M Marsili, N Marzari, F Mauri, N L Nguyen, H-V Nguyen, A Otero de-la Roza, L Paulatto, S Poncé, D Rocca, R Sabatini, B Santra, M Schlipf, A P Seitsonen, A Smogunov, I Timrov, T Thonhauser, P Umari, N Vast, X Wu, and S Baroni.

- Advanced capabilities for materials modelling with quantum espresso. *Journal of Physics: Condensed Matter*, 29(46):465901, 2017.
- [136] Till Westermann and Uwe Manthe. Decoherence induced by conical intersections: Complexity constrained quantum dynamics of photoexcited pyrazine. *The Journal of chemical physics*, 137(22):22A509, 2012.
- [137] PS Christopher, Moshe Shapiro, and Paul Brumer. Overlapping resonances in the coherent control of radiationless transitions: Internal conversion in pyrazine. *The Journal of chemical physics*, 123(6):064313, 2005.
- [138] PS Christopher, M Shapiro, and P Brumer. Quantum control of internal conversion in 24-vibrational-mode pyrazine. *The Journal of chemical physics*, 125(12):124310, 2006.
- [139] Uwe Müller and Gerhard Stock. Surface-hopping modeling of photoinduced relaxation dynamics on coupled potential-energy surfaces. *The Journal of chemical physics*, 107(16):6230–6245, 1997.
- [140] Yuki Kurashige. Matrix product state formulation of the multiconfiguration time-dependent hartree theory. *The Journal of chemical physics*, 149(19):194114, 2018.
- [141] A Raab and H-D Meyer. A numerical study on the performance of the multiconfiguration time-dependent hartree method for density operators. *The Journal of Chemical Physics*, 112(24):10718–10729, 2000.
- [142] Hans-Dieter Meyer, Frédéric Le Quéré, Céline Léonard, and Fabien Gatti. Calculation and selective population of vibrational levels with the multiconfiguration time-dependent hartree (mctdh) algorithm. *Chemical physics*, 329(1-3):179–192, 2006.
- [143] A. Jäckle and H.-D. Meyer. Product representation of potential energy surfaces. *J. Chem. Phys.*, 104:7974, 1996.
- [144] A. Jäckle and H.-D. Meyer. Product representation of potential energy surfaces II. *J. Chem. Phys.*, 109:3772, 1998.
- [145] F. Gatti and H.-D. Meyer. Intramolecular vibrational energy redistribution in Toluene: A nine dimensional quantum mechanical study using the MCTDH algorithm. *Chem. Phys.*, 304:3–15, 2004.
- [146] D. Peláez and H.-D. Meyer. The multigrid POTFIT (MGPF) method: Grid representations of potentials for quantum dynamics of large systems. *J. Chem. Phys.*, 138:014108, 2013.

- [147] M. Schröder. Transforming high-dimensional potential energy surfaces into a canonical polyadic decomposition using Monte Carlo methods. *J. Chem. Phys.*, 152:024108, 2020.
- [148] C. Leforestier, R. H. Bisseling, C. Cerjan, M. D. Feit, R. Friesner, A. Guldenberg, A. Hammerich, G. Jolicard, W. Karrlein, H.-D. Meyer, N. Lipkin, O. Roncero, and R. Kosloff. A comparison of different propagation schemes for the time dependent Schrödinger equation. *J. Comp. Phys.*, 94:59, 1991.
- [149] T. J. Park and J. C. Light. Unitary quantum time evolution by iterative Lanczos reduction. *J. Chem. Phys.*, 85:5870, 1986.
- [150] M. H. Beck and H.-D. Meyer. An efficient and robust integration scheme for the equations of motion of the multiconfiguration time-dependent Hartree (MCTDH) method. *Z. Phys. D*, 42:113–129, 1997.
- [151] H. Köppel, W. Domcke, and L. S. Cederbaum. Multimode molecular dynamics beyond the Born-Oppenheimer approximation. *Adv. Chem. Phys.*, 57:59, 1984.
- [152] H. Köppel, W. Domcke, and L. S. Cederbaum. The multi-mode vibronic-coupling approach. In W. Domcke, D. R. Yarkony, and H. Köppel, editors, *Conical Intersections*, pages 323–367, Singapore, 2004. World Scientific Co.
- [153] G. A. Worth, H.-D. Meyer, and L. S. Cederbaum. The effect of a model environment on the S₂ absorption spectrum of pyrazine: A wavepacket study treating all 24 vibrational modes. *J. Chem. Phys.*, 105:4412, 1996.
- [154] A. Raab, G. Worth, H.-D. Meyer, and L. S. Cederbaum. Molecular dynamics of pyrazine after excitation to the S₂ electronic state using a realistic 24-mode model Hamiltonian. *J. Chem. Phys.*, 110:936–946, 1999.
- [155] Graham A Worth, H-D Meyer, Horst Köppel, LS Cederbaum, and Irene Burghardt. Using the mctdh wavepacket propagation method to describe multimode non-adiabatic dynamics. *International Reviews in Physical Chemistry*, 27(3):569–606, 2008.
- [156] GA Worth, HD Meyer, LS Cederbaum, W Domcke, D Yarkony, and H Köppel. Multidimensional dynamics involving a conical intersection: Wavepacket calculations using the mctdh method. *Conical intersections: Electronic structure, dynamics and spectroscopy*, pages 583–617, 2004.
- [157] Toshinori Suzuki. Ultrafast internal conversion of aromatic molecules studied by photoelectron spectroscopy using sub-20 fs laser pulses. *Molecules*, 19(2):2410–2433, 2014.

- [158] H Köppel, Wolfgang Domcke, and Lorenz S Cederbaum. Multimode molecular dynamics beyond the born-oppenheimer approximation. *Advances in chemical physics*, 57:59–246, 1984.
- [159] Graham A Worth and Lorenz S Cederbaum. Beyond born-oppenheimer: molecular dynamics through a conical intersection. *Annu. Rev. Phys. Chem.*, 55:127–158, 2004.
- [160] Chr Cattarius, Graham A Worth, H-D Meyer, and LS Cederbaum. All mode dynamics at the conical intersection of an octa-atomic molecule: Multi-configuration time-dependent hartree (mctdh) investigation on the butatriene cation. *The Journal of chemical physics*, 115(5):2088–2100, 2001.
- [161] A Raab, Graham A Worth, H-D Meyer, and LS Cederbaum. Molecular dynamics of pyrazine after excitation to the s 2 electronic state using a realistic 24-mode model hamiltonian. *The Journal of chemical physics*, 110(2):936–946, 1999.
- [162] Clemens Woywod, Wolfgang Domcke, Andrzej L Sobolewski, and Hans-Joachim Werner. Characterization of the s_1 – s_2 conical intersection in pyrazine using ab initio multiconfiguration self-consistent-field and multireference configuration-interaction methods. *The Journal of chemical physics*, 100(2):1400–1413, 1994.
- [163] L Seidner, W Domcke, and W Von Niessen. $\tilde{X}^2a_g$ – $\tilde{A}^2b_1$ conical intersection in the pyrazine cation and its effect on the photoelectron spectrum. *Chemical physics letters*, 205(1):117–122, 1993.
- [164] GA Worth, MH Beck, Andreas Jäckle, and Hans-Dieter Meyer. The mctdh package, version 8.2,(2000). h. *D. Meyer, version*, 8, 2002.
- [165] Maxim Sukharev and Tamar Seideman. Optical control of nonradiative decay in polyatomic molecules. *Physical Review A*, 71(1):012509, 2005.
- [166] Andrzej L Sobolewski and Wolfgang Domcke. The chemical physics of the photostability of life. *Europhysics News*, 37(4):20–23, 2006.
- [167] Herschel Rabitz. Shaped laser pulses as reagents. *Science*, 299(5606):525–527, 2003.
- [168] Chantal Daniel, Jürgen Full, Leticia González, Cosmin Lupulescu, Jörn Manz, Andrea Merli, Štefan Vajda, and Ludger Wöste. Deciphering the reaction dynamics underlying optimal control laser fields. *Science*, 299(5606):536–539, 2003.

- [169] Matthias Roth, Laurent Guyon, Jonathan Roslund, Véronique Boutou, Francois Courvoisier, Jean-Pierre Wolf, and Herschel Rabitz. Quantum control of tightly competitive product channels. *Physical review letters*, 102(25):253001, 2009.
- [170] Graham A Worth, H-D Meyer, and LS Cederbaum. Relaxation of a system with a conical intersection coupled to a bath: A benchmark 24-dimensional wave packet study treating the environment explicitly. *The Journal of chemical physics*, 109(9):3518–3529, 1998.
- [171] R Schneider, W Domcke, and H Köppel. Aspects of dissipative electronic and vibrational dynamics of strongly vibronically coupled systems. *The Journal of chemical physics*, 92(2):1045–1061, 1990.
- [172] G. A. Worth, M. H. Beck, A. Jäckle, and H.-D. Meyer. The Heidelberg MCTDH Package: A set of programs for multi-dimensional quantum dynamics. User’s Guide, Version 8, 2000
(The User’s Guide can be downloded from the URL: <http://mctdh.uni-hd.de/>).
- [173] Rick Trebino. Ultrashort laser pulses i.
- [174] Oriol Vendrell, Fabien Gatti, and Hans-Dieter Meyer. Dynamics and infrared spectroscopy of the protonated water dimer. *Angewandte Chemie International Edition*, 46(36):6918–6921, 2007.
- [175] Monika Leibscher, I Sh Averbukh, and Herschel Rabitz. Enhanced molecular alignment by short laser pulses. *Physical Review A*, 69(1):013402, 2004.
- [176] Jakob Juul Larsen, Kasper Hald, Nis Bjerre, Henrik Stapelfeldt, and Tamar Seideman. Three dimensional alignment of molecules using elliptically polarized laser fields. *Physical review letters*, 85(12):2470, 2000.
- [177] Niels E Henriksen. Molecular alignment and orientation in short pulse laser fields. *Chemical Physics Letters*, 312(2-4):196–202, 1999.
- [178] Wei Kong and Jaap Bulthuis. Orientation of asymmetric top molecules in a uniform electric field: Calculations for species without symmetry axes. *The Journal of Physical Chemistry A*, 104(5):1055–1063, 2000.
- [179] Alexander Pieper, Manuel Hohgardt, Maximilian Willich, Daniel Alexander Gacek, Nour Hafi, Dominik Pfennig, Andreas Albrecht, and Peter Jomo Walla. Biomimetic light-harvesting funnels for re-directioning of diffuse light. *Nature communications*, 9(1):1–9, 2018.

- [180] Marcel M Willich, Lucas Wegener, Johannes Vornweg, Manuel Hohgardt, Julia Nowak, Mario Wolter, Christoph R Jacob, and Peter Jomo Walla. A new ultrafast energy funneling material harvests three times more diffusive solar energy for gainp photovoltaics. *Proceedings of the National Academy of Sciences*, 117(52):32929–32938, 2020.
- [181] Mike Reppert and Paul Brumer. Quantumness in light harvesting is determined by vibrational dynamics. *The Journal of chemical physics*, 149(23):234102, 2018.
- [182] Ruche hardware configuration.
- [183] Dmitrii V Shalashilin and Mark S Child. Real time quantum propagation on a monte carlo trajectory guided grids of coupled coherent states: 26d simulation of pyrazine absorption spectrum. *The Journal of chemical physics*, 121(8):3563–3568, 2004.
- [184] Dmitrii V Shalashilin. Nonadiabatic dynamics with the help of multiconfigurational ehrenfest method: Improved theory and fully quantum 24d simulation of pyrazine. *The Journal of chemical physics*, 132(24):244111, 2010.
- [185] Henrik Stapelfeldt and Tamar Seideman. Colloquium: Aligning molecules with strong laser pulses. *Reviews of Modern Physics*, 75(2):543, 2003.
- [186] H.R. Larsson. Computing vibrational eigenstates with tree tensor network states (TTNS). *J. Chem. Phys.*, 151:204102, 2019.
- [187] Graham R Fleming and Mark A Ratner. Grand challenges in basic energy sciences. *Phys. Today*, 61(7):28, 2008.
- [188] Constantin Brif, Raj Chakrabarti, and Herschel Rabitz. Control of quantum phenomena. *Advances in Chemical Physics*, 148:1, 2012.
- [189] Oriol Vendrell, Fabien Gatti, and Hans-Dieter Meyer. Full dimensional (15-dimensional) quantum-dynamical simulation of the protonated water dimer. ii. infrared spectrum and vibrational dynamics. *The Journal of chemical physics*, 127(18):184303, 2007.
- [190] Steven R White. Density matrix formulation for quantum renormalization groups. *Phys. Rev. Lett.*, 69(19):2863, 1992.
- [191] S.R. White. Density matrix formulation for quantum renormalization groups. *Phys. Rev. Lett.*, 69:2863, 1992.
- [192] Ulrich Schollwöck. The density-matrix renormalization group. *Rev. Mod. Phys.*, 77:259, 2005.

- [193] U. Schollwöck. The density-matrix renormalization group in the age of matrix product states. *Ann. Phys.*, 326:96, 2011.
- [194] S. R. White and R. L. Martin. Ab initio quantum chemistry using the density matrix renormalization group. *J. Chem. Phys.*, 110(9):4127–4130, 1999.
- [195] Garnet Kin-Lic Chan and Sandeep Sharma. The density matrix renormalization group in quantum chemistry. *Ann. Rev. Phys. Chem.*, 62:465–481, 2011.
- [196] Corinne Duperrouzel, Paweł Tecmer, Katharina Boguslawski, Gergely Barcza, Örs Legeza, and Paul W Ayers. A quantum informational approach for dissecting chemical reactions. *Chem. Phys. Lett.*, 621:160–164, 2015.
- [197] Alberto Baiardi and Markus Reiher. The density matrix renormalization group in chemistry and molecular physics: Recent developments and new challenges. *J. Chem. Phys.*, 152:040903, 2020.
- [198] E. M. Stoudenmire and S. R. White. Studying two-dimensional systems with the density matrix renormalization group. *Annu. Rev. Condens. Matter Phys.*, 3:111–128, 2012.
- [199] J. Haegeman, C. Lubich, I. Oseledets, B. Vandereycken, and F. Verstraete. Unifying time evolution and optimization with matrix product states. *Phys. Rev. B*, 94:165116, 2016.
- [200] Y. Kurashige. Matrix product state formulation of the multiconfiguration time-dependent Hartree theory. *J. Chem. Phys.*, 149:194114, 2018.
- [201] S. Paeckel, T. Höhler, A. Swoboda, S. R. Mammanna, U. Schollwöck, and C. Hubig. Time-evolution methods for matrix-product states. *Ann. Phys.*, 411:167998, 2019.
- [202] D. Iouchtchenko and P.-N. Roy. Ground states of linear rotor chains via the density matrix renormalization group. *J. Chem. Phys.*, 148:134115, 2018.
- [203] Tapas Sahoo, Dmitri Iouchtchenko, CM Herdman, and Pierre-Nicholas Roy. A path integral ground state replica trick approach for the computation of entanglement entropy of dipolar linear rotors. *J. Chem. Phys.*, 152:184113, 2020.
- [204] Isaac J. S. De Vlugt, Dmitri Iouchtchenko, Ejaaz Merali, Pierre-Nicholas Roy, and Roger G. Melko. Reconstructing quantum molecular rotor ground states. *Phys. Rev. B*, 102:035108, 2020.

- [205] B P Abolins, R E Zillich, and K B Whaley. A ground state Monte Carlo approach for studies of dipolar systems with rotational degrees of freedom. *J. Low Temp. Phys.*, 165(5-6):249–260, 2011.
- [206] W AshcroftNeil, Neil W Ashcroft, N David Mermin, and N David Mermin. *Solid state physics*, volume 3. Cengage Learning, 1976.
- [207] Charles Kittel, Paul McEuen, and Paul McEuen. *Introduction to solid state physics*, volume 8. Wiley New York, 1996.
- [208] Subir Sachdev. *Quantum Phase Transitions*. Cambridge University Press, second edition, 2011.
- [209] Li Chen, Jascha A Lau, Dirk Schwarzer, Jörg Meyer, Varun B Verma, and Alec M Wodtke. The sommerfeld ground-wave limit for a molecule adsorbed at a surface. *Science*, 363(6423):158–161, 2019.
- [210] André D Bandrauk. Molecules in laser fields. In *Frontiers of Chemical Dynamics*, pages 131–150. Springer, 1995.
- [211] Spencer L Horton, Yusong Liu, Pratip Chakraborty, Philipp Marquetand, Tamás Rozgonyi, Spiridoula Matsika, and Thomas Weinacht. Strong-field-versus weak-field-ionization pump-probe spectroscopy. *Physical Review A*, 98(5):053416, 2018.
- [212] Turker Topcu and Francis Robicheaux. Dichotomy between tunneling and multiphoton ionization in atomic photoionization: Keldysh parameter γ versus scaled frequency ω . *Physical Review A*, 86(5):053407, 2012.
- [213] I Sh Averbukh, M Leibscher, R Arvieu, and H Rabitz. Kicking atoms and molecules by non-resonant fields: from molecular alignment to atom lithography. In *12th International Laser Physics Workshop LPHYS’03*, 2003.
- [214] Niels Kristian Madsen, Mads Böttger Hansen, Graham A Worth, and Ove Christiansen. Mr-mctdh [n]: Flexible configuration spaces and nonadiabatic dynamics within the mctdh [n] framework. *Journal of Chemical Theory and Computation*, 16(7):4087–4097, 2020.
- [215] L. Blancafort, F. Gatti, and H.-D. Meyer. Quantum dynamics study of fulvene double bond photoisomerization: The role of intramolecular vibrational energy redistribution and excitation energy. *J. Chem. Phys.*, 135:134303, 2011.
- [216] S. Ruiz-Barragan and L. Blancafort. Photophysics of fulvene under the non-resonant stark effect. shaping the conical intersection seam. *Faraday Discuss.*, 163:497, 2013.

- [217] E. Collini, Cathy, Y. Wong, K. E. Wilk, P. M. G. Curmi, P. Brumer, and G. D. Scholes. Coherently wired light-harvesting in photosynthetic marine algae at ambient temperature. *Nature*, 463:644, 2010.
- [218] J. L. Herek, W. Wohlleben, R. J. Cogdell, D. Zeidler, and M. Motzus. Quantum control of energy flow in light harvesting. *Nature*, 417:533, 2002.
- [219] C. A. Rozzi, S. M. Falke, N. Spallanzani, A. Rubio, E. Molinari, D. Brida, M. Maiuri, G. Cerullo, H. Schramm, J. Christophers, and C. Lienau. Quantum coherence controls the charge separation in a prototypical artificial light-harvesting system. *Nat. Commun.*, 4:1603, 2013.
- [220] G. D. Scholes, G. R. Fleming, A. Olaya-Castro, and R. van Grondelle. Lessons from nature about solar light harvesting. *Nat. Chem.*, 3:763, 2012.
- [221] J. Schulze, M. Torbjörnsson, O. Kühn, and T. Pullerits. Exciton coupling induces vibronic hyperchromism in light-harvesting complexes. *New J. Phys.*, 16:04510, 2014.
- [222] M. Sarovar, A. Ishizaki, G. R. Fleming, and K. B. Whaley. Quantum entanglement in photosynthetic light-harvesting complexes. *Nat. Phys.*, 6:462, 2010.
- [223] M. F. Shibl, J. Schulze, M. J. Al-Marri, and O. Kühn. Multilayer-MCTDH approach to the energy transfer dynamics in the LH2 antenna complex. *J. Phys. B*, 50:184001, 2017.
- [224] Moshe Gitterman and Vivian Haim Halpern. *Phase Transitions: A brief account with modern applications*. World Scientific Publishing Company, 2004.
- [225] Michael H Beck and H-D Meyer. An efficient and robust integration scheme for the equations of motion of the multiconfiguration time-dependent hartree (mctdh) method. *Zeitschrift für Physik D Atoms, Molecules and Clusters*, 42(2):113–129, 1997.
- [226] Mikhail Lemeshko, Roman V Krems, John M Doyle, and Sabre Kais. Manipulation of molecules with electromagnetic fields. *Molecular Physics*, 111(12-13):1648–1682, 2013.