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Molecular Quantum Dynamics, often called “Quantum Dynamics,” is the subfield of Theoretical Chemistry where both the electrons and the nuclei of a molecular system are treated with a quantum-mechanical approach. Molecular Quantum Dynamics can be seen as the encounter of Quantum Physics and Chemistry.

In general, the realm of quantum phenomena is not directly connected to chemistry but rather to physics, for instance atomic physics and quantum optics. These are domains that are now well understood and controlled, as recognized by the Nobel Prize in Physics 2012 awarded to Serge Haroche and David Jeffrey Wineland. Quantum mechanics deals with physical phenomena at the microscopic level, precisely where the action is of the order of magnitude of the Planck constant [1–7]. One of the most intriguing features of quantum mechanics is, as indicated by its name, the hypothesis of quantization. This notion implies that, under some particular conditions, physical observables measured experimentally can only take certain discrete values. These happen to be the eigenvalues of the operator associated with the physical observable. Another fundamental principle of quantum mechanics is the superposition principle, which holds that a quantum system can be in several eigenstates simultaneously. Formally, the corresponding wavefunction can be written as a linear superposition of several eigenfunctions of the operator corresponding to a given physical quantity. In particular, if the observable is the energy, such a linear combination will imply that the probability density, given by the square modulus of the normalized wavefunction at each point in space, will depend on time. The wavefunction is then referred to as a wavepacket, i.e., a coherent superposition of several eigenstates. When the physical quantity is measured, the wavepacket collapses. This results in the observation of only one of the possible eigenvalues. If there is no measurement, and if the system is isolated,

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the different components of the quantum superposition can interfere. This yields new properties that can be measured and that have no classical counterpart. This is illustrated by the famous Schrödinger cat that can be alive and dead simultaneously. In other words, the Schrödinger cat can be in a coherent superposition of both a dead state and an alive state. These two states can interfere to create new behaviors that cannot be observed for a cat that is either alive or dead. The Schrödinger cat can be seen as a paradox only because the cat is large-scale system and creating such a coherent superposition for a cat is not realistic. But for much smaller systems (photons, atoms, molecules, etc.) such coherent superpositions can be created. Perhaps the most surprising of the resulting effects is quantum entanglement, as predicted by Albert Einstein, Boris Podolsky, and Nathan Rosen in 1935, but seen at that time also as a paradox that was supposed to prove the inadequacy of quantum mechanics. After two particles have interacted, a measurement made on one of the particles can modify the quantum state of the second particle instantaneously, even if the distance between the two particles is large. However, in general, the system interacts with its environment, and a loss of coherence between the different quantum states occurs. This is what is called quantum decoherence. The quantum interference terms vanish locally, and the system is formally equivalent to a classical statistical mixture of states rather than a single coherent quantum superposition of them.

Such concepts are well known in physics, but chemistry is rarely interpreted within a full quantum-mechanical perspective. For instance, an elementary chemical process is generally not described as the evolution of a wavepacket. However, very early within the advent of quantum mechanics, quantization of the electronic states and the requirement of describing electrons with a delocalized wavefunction happened to be essential for many processes in chemistry, thus leading to the concepts of molecular orbitals, potential energy surfaces, and non-adiabatic couplings [8,9]. The field of quantum chemistry was born, and its importance has been emphasized since then by Nobel prizes in Chemistry awarded to Linus Pauling in 1954, to Robert Mulliken in 1966, and to Walter Kohn and John A. Pople in 1998. Another significant illustration is found in Rudolph A. Marcus' theory, whereby the rates of electron transfer reactions are rationalized within a semi-classical formulation [10–12]. The latter describes the electron transfer process as a reaction where the system must undergo hops between two quantized electronic states. The hopping probability is estimated using an approximate analytical solution to the equations of motion governing the transition dynamics of a two-level quantum mechanical system (a Landau-Zener-type formula).

Consequently, electrons often are treated (at least partly) quantum-mechanically in theoretical chemistry except for very large systems (in the field of “Molecular Mechanics”). However, if the motion of the nuclei is added to the description of the system it is generally achieved through a classical treatment by solving Newton's equations, i.e., classically. This is the field known as “Molecular Dynamics” [13] (the development of models in this field has earned the Nobel prize in Chemistry to Martin Karplus, Michael Levitt, and Arieh Warshel in 2013). There are good reasons to support this strategy. The nuclei have a much larger mass than the electrons, and,

except for Hydrogen, they thus have a small de Broglie wavelength and generally move as mere mass points. In addition, since the nuclei are heavy, the difference of energy between the vibrational levels is much smaller than between the electronic states: quantization of the vibrational states can be neglected in many applications to reactivity. Besides, the coherence between the vibrational states is lost very quickly due to the very large density of states. The latter density is linked to the heavy mass of the nuclei and also to the fact that the system is entangled in a complex environment that destroys the interference effects [14]. Quantum effects for the nuclei are thus often expected to be weak in chemistry or at least negligible with respect to the other parameters that determine the characteristics of a molecular process.

One noticeable exception is molecular spectroscopy, more specifically infrared spectroscopy, where, almost by definition, quantization of the vibrational states cannot be neglected since it concerns the measurement of the transitions between the quantized vibrational states [15]. Due to its importance in chemistry, for instance for the detection of functional groups in organic chemistry, infrared spectroscopy is one of the very few domains where the students in both physics and chemistry experience the application of a full-quantum mechanical treatment for both the electrons and the nuclei in a molecular system. However, there is growing evidence that a significant number of various chemical reactions are impacted by strong quantum-mechanical effects involving nuclei [16].

In particular, chemical reaction rates can be greatly enhanced by quantum tunneling, namely the fact that particles can tunnel through a barrier that they could not surmount classically. This arises especially if the chemical reaction involves light atoms with large de Broglie wavelengths, such as protons, hydrogen atoms, and hydride ions. Tunneling is observed sometimes experimentally for heavy atoms but almost only at low temperature [17]. As stated by Robert J. McMahon in a paper of 2003 on chemical reactions involving quantum tunneling: “far from being mere curiosities or footnotes in the theory of chemical reaction rates, these quantum phenomena manifest themselves in ‘ordinary’ chemical reactions” [18]. In particular, tunneling is important not only at low, “cryogenic,” temperatures but also at room temperature, in biological processes, for instance. Important changes of chemical reaction rates have been observed in chemical catalysis [19, 20] and interstellar chemistry [21]. It has also been suspected that tunneling plays a key role in some enzymatic reactions [22–28].

Another situation where quantum effects are essential occurs in the presence of strong vibronic couplings between several electronic states through the nuclear motion. The extreme case occurs around conical intersections, namely molecular geometries where two potential energy surfaces cross (the corresponding states are degenerate). These nonavoided crossings are called conical intersections because of the local shape of the two potential energy surfaces around the degeneracy point. In the vicinity of a conical intersection, the Born–Oppenheimer approximation breaks down, allowing non-adiabatic processes to take place. Conical intersections were predicted by John von Neumann and Eugene Wigner in 1929 and seem to be ubiquitous in polyatomic molecules [29, 30]. In particular, they are suspected

to play a key role during the first steps of photosynthesis [31] or vision [32, 33], and in the photostability of DNA bases [34, 35]. As already mentioned about Rudolph A. Marcus' theory, the fact that a system can be transferred from one quantized state to another is per se a quantum effect. Besides this effect, the electronic states can remain coherent with respect to each other during a non-negligible period of time, leading to new quantum interference effects that are expected to exist even in living material [36]. For instance, a long-lived quantum superposition of (vibrational or vibronic) states has been observed experimentally in the photosynthetic system at low temperature [37] or at room temperature [38, 39], and in the chromophore of rodhopsin [40]. This does not mean that photosynthesis itself implies the same quantum interference effects since in the experiments this long quantum coherence is induced by pulsed coherent light. In contrast, photoinduced biological processes occur via one-photon absorption in natural light, which is incoherent [41]. As explained by Paul Brumer and Moshe Shapiro, "one-photon molecular excitation with pulsed coherent laser light and with natural incoherent light yield qualitatively different processes" [41]. In any case, the fact that photosynthetic systems can induce a long quantum coherence after excitation with laser pulses is a very important result on its own.

Another quantum effect is the so-called zero-point effect. The latter corresponds to the fact that a quantum molecular system has a zero-point energy greater than the minimum of its potential-energy well. It thus creates an effective uphill "shift" of the potential energy for a quantum particle along the minimum-energy path when compared to a classical particle [42, 43]. In addition, the wave properties of molecules have been revealed by diffraction experiments for systems as large as fullerene [44], perfluoroalkylated molecules, and complex derivatives of the tetraphenylporphyrin molecule with up to 430 atoms [45], and the subfemtosecond entanglement of protons with adjacent particles, such as other protons and electrons, has been highlighted by recent experiments [46]. As stated by Aris Chatzidimitriou-Dreismann and Markus Arndt as conclusions of a workshop on entanglement and decoherence of complex quantum systems: "in contrast to the popular view among chemists, atomic nuclei can not always be considered as classical mass points" [46].

On the experimental front, decisive progress has been achieved with the ability to use time-resolved pump-probe laser methods to study chemical processes on the femtosecond time scale ( $10^{-15}$ s), i.e., the typical period of molecular vibrations [47–49]. This was at the origin of the development of femtochemistry that earned Ahmed Zewail the Nobel Prize in Chemistry 1999. This technique allows experimentalists to follow the motion of the nuclei in real time: when chemical bonds break, form, or geometrically change. More recently, possibilities have emerged to generate sub-femtosecond or attosecond laser pulses [50–52] for observing electrons on their natural time scale. These techniques open the door to even measuring coupled electronic and nuclear dynamics [53–56]. Controlling the behavior of electrons and nuclei has become a key component to understand all sorts of quantum effects in molecular systems, in particular quantum coherence. It is also feasible with a closed-loop laboratory-learning procedure to create optimal ultrafast laser pulses that lead the molecular systems to a desired target outcome [57–60]. Another major

advance has been the possibility to orientate or align molecules, which allows one to excite molecular systems with laser pulses in a much more efficient way [61–64]. Polar molecules can be indeed (partially) oriented in the gas phase with a static field or with an external field that varies smoothly in a way that is concerted with the internal motion [65]. The introduction of crossed molecular beam methods mainly by Dudley Herschbach and Yuan T. Lee, for which they were awarded the Nobel Prize in Chemistry 1986 (along with John C. Polanyi for his work in chemical kinetics), has allowed experimentalists to measure collision cross sections strongly impacted by quantum effects [66,67], even when resonances, i.e., quantized metastable states, play a dominant role [68–70]. If one adds the fact that it is now possible to measure all the vibration-rotation-tunneling spectra even for very floppy systems such as water clusters [71–74], it appears clearly that it is now possible to detect, quantify precisely, and even manipulate most quantum effects in molecules.

In practice, one has to solve the time-dependent or the time-independent Schrödinger equation for the nuclei after having solved the Schrödinger equation for the electronic Hamiltonian that provides the potential energy surfaces and the couplings between the different electronic states. In principle, semiclassical theory is capable of describing all types of quantum effects [75–78] and is very efficient to add some quantum corrections to the description of very large systems [16]. The present book will however focus essentially on full quantum-mechanical methods. The latter not only give definitive comparisons with experimental results and validate more approximate theoretical approaches, but also provide the most complete characterization of a molecular process allowed by the basic laws of nature. In this context, fully-quantum-mechanical or semi-classical approaches can be seen as more complementary than in competition: quantum-mechanical methods offer quantitative benchmarks and, above all, a qualitative understanding of the quantum effects. Then, in a second step, variously elaborate semiclassical methods can be built, calibrated by the quantum methods, and applied to much larger systems.

Despite the considerable power of modern computers, the quantum-mechanical treatment of molecular dynamics is a formidable task when more than (only!) six nuclear degrees of freedom have to be taken into account. Indeed, the numerical effort scales exponentially with the number of degrees of freedom simply because the size of the basis set also grows exponentially with the dimension of the molecular system. Consequently, the development of molecular quantum dynamics has been directly linked to progress in computer power and even more importantly to the development of new algorithms to solve the Schrödinger equation. Joel M. Bowman, Tucker Carrington, and Hans-Dieter Meyer have given a short history of the quantum approaches in a recent review [79], albeit they focus on the computation of vibrational energies only. John Z. H. Zhang has also published a book describing the numerical methods in quantum dynamics and focusing more on reactive scattering [80]. Basically, the work can be divided into three main steps: (1) the numerical resolution of the (time-independent or time-dependent) Schrödinger equation for the nuclei, (2) the calculation of the potential energy surface(s), and (3) the choice of the set of coordinates to describe the system and the derivation of the corresponding kinetic energy operator.

The very first full quantum-mechanical approaches were undertaken in the early 1970s [81–85]. One major progress has been the definition of appropriate “primitive” basis functions to calculate the matrix elements of the Hamiltonian. The basis set must be complete and orthonormal in the space of its variable (which can be one or several degrees of freedom). In general, two basis sets of functions are employed that are related to one another by a unitary transformation. One basis corresponds to the so-called Finite Basis Representation (FBR) that is made of mathematical functions such as spherical harmonics, Hermite, sine, and exponential functions. The expression of the matrix elements of the kinetic energy operator in the FBR is analytical and simple [86]. The second representation is the so-called Discrete Variable Representation (DVR) in which the potential matrix is diagonal [87, 88]. Another important achievement has been the use of the Lanczos algorithm that allows one to calculate the eigenvalues of a given Hamiltonian without resorting to diagonalizing a full matrix [89, 90]. Perturbative treatments have also been applied to calculate vibrational eigenvalues [91]. As regards the time-dependent Schrödinger equation, after pioneering works by Robert E. Wyatt and co-workers [81, 82, 92], the time-dependent picture has been popularized by several papers of Eric J. Heller [93–95]. After this preliminary stage, the community spent a lot of time in the 1980s on developing integrators to solve the time-dependent Schrödinger equation [96] (Chebyshev, Lanczos, Split Operator, etc.): they are listed in a review by Ronnie Kosloff [97] who played an important role in this domain [98]. Previously, the evolution of wavepackets was hardly studied in academic courses on quantum mechanics. David J. Tannor has recently published a book, “Introduction to Quantum Mechanics, a time-dependent perspective,” that now fills in this lack. The book also presents some applications to molecular quantum dynamics. The development of robust integrators has thus been a great achievement, not only to study molecular systems, but also for any field where quantum mechanics is required.

Generally speaking, the fundamental problem faced in quantum-mechanical studies of large systems is the huge dimension of the primitive basis set, which is a product basis built from 1D bases for each degree of freedom. In order to tackle the exponential scaling of the numerical effort, several strategies have been developed, which are based on a “contraction” of the primitive basis. The contracted basis set is built in the primitive basis set but its size is much smaller. Some examples of contraction schemes are the Sequential Adiabatic Reduction (SAR) method of Z. Bačić and J. C. Light [87] or the contraction schemes developed by Tucker Carrington and co-workers that have emerged as optimal approaches to study rovibrational spectra [99–102]. One decisive step forward has been the systematic use of variational principles to build this intermediate “contracted” basis set. If we specifically turn to the time-independent picture, a systematic comparison between quantum dynamics and quantum chemistry can be made. The “contracted” functions obtained with the variational principle and primitive functions play the same role as the molecular orbitals and the atomic-orbital basis set functions in quantum chemistry, respectively. Several variants have been proposed. For the time-independent picture, one can cite Vibrational Self-Consistent Field (VSCF) methods

combined with perturbation theory [103–108]. Another approach is the VSCF procedure combined with a Configuration-Interaction (CI) method [109–111] that has given rise to the MULTIMODE package to calculate vibrational eigenvalues [112]: the subsequent CI procedure explicitly deals with the full correlation between the modes, yielding accurate results for five- or six-atom molecules and realistic results for much larger systems [113]. Vibrational Multi-Configuration Self-Consistent Field (MCSCF) methods have also been proposed that are similar to the Complete Active-Space SCF (CASSCF) method used in quantum chemistry [114–117]. The variational principle has also been applied to the time-dependent Schrödinger equation leading to the Time-Dependent Hartree (TDH) method [118, 119], and to multi-configuration time-dependent self-consistent field methods [120, 121] and more precisely to the Multi-Configuration Time-Dependent Hartree (MCTDH) method [122–125]. The Heidelberg MCTDH package [126] is probably the first software with a general character in the field of Molecular Quantum Dynamics. Its versatility is well illustrated by the fact that it has been applied to all the domains presented in the chapters of the present book: heterogeneous catalysis, reactive or non-reactive collisions, infrared spectroscopy, ultraviolet spectroscopy involving or not non-Born–Oppenheimer processes, photochemistry, processes guided by laser pulses, optimal control. Finally, it is worth noting that the calculation of metastable quantum states, in particular the calculation of their lifetimes, requires additional numerical techniques [127–132].

Molecular dynamics studies heavily depend on high-quality potential energy surfaces obtained from electronic structure calculations within the framework of quantum chemistry. These calculations and their global representation using analytical functions constitute a field on its own that is not the topic of the present book. Much progress has been achieved in this area in the last decades [133–135]. However, the description of systems by means of global potential energy surfaces is still limited to rather small systems. This limitation can be overcome, to some extent, by assuming that chemical phenomena can be described by a limited number of active coordinates that involve motions of large amplitude and that the other modes, the inactive ones, play a less important role. Under these conditions, it is possible to invoke simplifying approximations. For instance, a “reaction-path Hamiltonian” approach that makes use of a harmonic approximation defined along one or several active or “reactive” coordinates can be considered [136–142]. Another fruitful model has been devised by Cederbaum and co-workers to treat multistate-multimode vibronic couplings that uses a Taylor expansion of the different potential energy surfaces around the Franck–Condon geometry [143].

In molecular quantum dynamics, the choice of the set of coordinates to describe the physical system and to express the Hamiltonian operator is very important. As explained above, the main problem we have to face is the very large size of the basis sets, primitive or contracted, and this size is directly linked to the correlation between the coordinates. An inadequate set of coordinates can entail a strong artificial correlation and thus a poor convergence. Consequently, the set of coordinates must be carefully chosen to minimize as much as possible the size of the basis set. First, it is important to split the set of coordinates into two subsets,



one corresponding to the three Euler angles that define the Body-Fixed frame and that describe the overall rotation and one corresponding to the  $3N-6$  internal coordinates,  $N$  being the number of atoms in the molecular system that describe the deformation of the system. The potential energy surfaces depend on the  $3N-6$  internal degrees of freedom only, and if the molecular system is isolated one can take advantage of the fact that the quantum number associated with the total angular momentum is a constant of motion. As regards the choice of the  $3N-6$  internal coordinates, for systems low in energy around a local minimum, the molecular system vibrates in a quasi-harmonic way and a description in terms of rectilinear normal coordinates that are linear combinations of the Cartesian coordinates of the atoms is correct. But higher in energy or for systems with large-amplitude motions such as systems undergoing scattering, dissociations, or isomerizations, a description with rectilinear coordinates is no longer adapted, and a description in curvilinear coordinates, i.e., involving angles, is required. Unfortunately, the use of curvilinear coordinates leads to very complicated expressions of the kinetic energy operator that are very specific to particular systems [144–147]. Recently, more general expressions of the kinetic energy operator have been given and general programs to provide them are now available [148, 149], in particular the formulation in polyspherical coordinates combined with a separation into subsystems [149–151] seems promising to treat large systems with curvilinear coordinates in a systematic way. The possibility to obtain the kinetic energy operators numerically in a systematic way is also an important achievement [148].

Typically, it is now possible in molecular quantum dynamics to treat systems with an *ab initio* potential energy surface and curvilinear coordinates up to 6–7 atoms in full dimensionality such as  $(\text{H}_2)_3$  [152],  $\text{CH}_5^+$  [102], and  $\text{H}_5\text{O}_2^+$  [153, 154]. When a model is used for the potential and/or a description with normal coordinates is adopted, it is possible to deal with systems a little bit larger such as pyrazine, including two electronic states coupled through a conical intersection [155] or malonaldehyde [156]. One can also mention the  $\text{H} + \text{CH}_4$  system that undergoes a reactive process [157]. We will see later that the recent Multi-Layer MCTDH approach will allow one to treat even larger systems. Note also that Feynman’s path integral formulations have been applied to study condensed matter [158], but they will not be addressed in the present book.

The field of applications of molecular quantum dynamics covers broad areas of science not only in chemistry but also in physics and biology. Historically, due to the fact that the full quantum-mechanical simulation of molecular processes is limited to small systems, molecular quantum dynamics has given rise mainly to important applications of astrophysical and atmospheric relevance. In the interstellar medium or the Earth atmosphere, molecules are generally in the gas phase. Since many accurate spectroscopic data are available, these media have provided various prototype systems to study quantum effects in molecules and to calibrate the theoretical methods used to simulate these effects. In this context, it is not surprising that much theoretical effort is still directed toward modeling the full quantum-mechanical treatment of small molecules. Among others, one can cite the studies of the spectroscopy of water [159–161], and of the spectroscopy, photodissociation,



and formation of ozone, in particular the studies of the Hartley and Huggins bands that absorb most of the Sun medium-frequency ultraviolet light [162–164]. Molecular systems that are important for the greenhouse effect, ozone depletion, or for the study of the composition of the atmosphere of the Earth, planets in the solar system, or exoplanets have also been studied with full quantum-mechanical approaches:  $\text{N}_2\text{O}$  [165],  $\text{NH}_3$  [140, 166–168],  $\text{CH}_4$  [100, 169–173], etc.

But the most important goal of molecular quantum dynamics is probably to describe, understand, and control the elementary chemical processes at the most fundamental level, and it is the aim of the present book to provide some illustrations. This can be achieved by transferring all the methodology developed in quantum physics to the realm of molecular problems. In particular, the concepts of eigenstates, wavepackets, or even “dressed states” (dressed by an external field) used in quantum optics to describe atom-field interactions [174, 175] can be used to describe chemical phenomena. Such an approach can lead to new insights into the interpretation of chemical processes not available with a pure static picture or a classical or even a semi-classical picture of the motion of the nuclei (at least not directly in the latter case).

One central question in chemistry is how indeed to control reactivity and selectivity. A chemical reaction is often made of a series of several “elementary reactions” that can be described by using collision theory for bimolecular reactions since they can be seen as encounters between two chemical species [176]. The understanding of the dynamics of a system at the molecular level is the key to the interpretation of macroscopic kinetics, in particular to calculate thermal reaction rates,  $k(T)$ . As aforementioned, the development of crossed molecular beam methods allows the experimentalists to obtain an even more detailed information on the collisions, i.e., the state-to-state cross sections. Understanding all these elementary processes quantum-mechanically remains a very challenging task of tremendous practical importance, in particular for industrial reasons. Let us consider an example, the production of most synthetic compounds with heterogeneous catalysis involving the interaction of gas- or liquid-phase molecules with metal surfaces. In this context, the Nobel Prize in Chemistry 2007 was awarded to G. Ertl for his complete description of elementary molecule-surface reactions by which ammonia is produced for fertilizer [177]. But, for such a process, a detailed description of the mechanism behind each elementary act itself is still unavailable. In other words, if great progress has been achieved to produce new catalysts, the processes to find them remains empirical. It is what G.-J. Kroes and co-workers explain: “in many cases this progress [in the field of catalysis] is dictated by experience, intuition and trial and error” and thus “a full atomic scale picture of reaction dynamics at surfaces is desirable so that existing processes can be optimized and new and better catalysts can be designed” [178]. The ultimate goal is to reach a much higher level of control of the corresponding reactions. G.-J. Kroes mentions the fact that a demand for new catalysts is particularly strong in the automotive industry nowadays [178].

To determine in detail how molecules react on metals, many questions have to be answered [179]: how does the molecule dissipate or store internal vibrational energy during the collision with the surface? How does a bond of the incident

molecule break and how do the fragments bind chemically to the surface? How do the molecules scatter on the surface? What is the role of the phonons and electron-hole pair excitations in the process? etc. At this level of description, quantum effects can be dominant. In Chap. 2, Cristina Díaz et al. give some illustrations using a time-dependent quantum-mechanical approach. For instance, they present calculated reaction probabilities for  $\text{H}_2 + \text{Cu}(111)$  and  $\text{D}_2 + \text{Cu}(111)$  using all six molecular degrees of freedom and in excellent agreement with experiments [180]. They describe other simulations, for instance  $\text{H}_2 + \text{Pd}(100)$ ,  $\text{Pd}(110)$  or  $\text{Pd}(111)$  [181]. The  $\text{H}_2 + \text{Pd}(100)$  system has revealed the importance of the zero-point energy effect in the hydrogen dynamics: the quantum particles cannot propagate along the bottom of the valley of the potential energy surface since they require at least the zero-point energies perpendicular to the propagation direction. As a consequence, the sticking probability of  $\text{H}_2$  on  $\text{Pd}(100)$  is much larger for the quantum particle than for a classical one [42]. In addition, the simulations given in Chap. 2 allow one to analyze the role played by the internal (vibrational or rotational) degrees of freedom for instance for the  $\text{CH}_4/\text{Ni}(100)$  system. They prove that the excitation of specific modes, for instance the C-H symmetric stretching mode for  $\text{CH}_4/\text{Ni}(100)$ , can increase and guide the reactivity. This is the kind of information that cannot be obtained with a pure static description of a chemical process and that can be exploited to manipulate the reactivity by selectively exciting the corresponding modes of vibration using laser pulses. Such mode selectivity in chemistry has been experimentally demonstrated in the context of reactions on surfaces [182, 183].

A complete description of bimolecular reactions involving a moderate number of atoms is also very important for practical reasons, among others in atmospheric and combustion chemistry. U. Manthe and co-workers have, for instance, calculated the thermal rate constant,  $k(T)$ , for the  $\text{H} + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3$  reaction [157, 184]. This H-atom abstraction reaction plays a central role in methane ( $\text{CH}_4/\text{O}_2$ ) combustion [185]. U. Manthe and co-workers have performed a full-dimensional dynamics simulation using the MCTDH approach. By comparison with the classical transition-state theory, they have showed that quantum tunneling drastically fastens the reaction below 400 K. This simulation has been used as a benchmark to calibrate semi-classical methods, more precisely the transition state theory including corrections by Truhlar and co-workers, that could be used for much larger systems [186, 187]. An accurate determination of rates of combustion reactions requires to include quantum effects especially in the low-temperature regime [188]. This accurate determination is very important to point ways toward better fuel systems [189].

In Chap. 3, Hua Guo et al. stress the importance of tunneling in both unimolecular and bimolecular reactions. They have calculated the thermal rate constant,  $k(T)$ , for the exothermic  $\text{HO} + \text{CO} \rightarrow \text{H} + \text{CO}_2$  reaction [190]. In combustion, this reaction is the main source of heat as the last step of hydrocarbon oxidation. They explain that it proceeds via the HOCO intermediate. In the last step of the reaction, the system has to surmount a transition state. There the reaction coordinate is essentially the H-O stretch and tunneling can dominate. This gives rise to a strong non-Arrhenius

kinetics: the rate constant is essentially flat up to 500 K and increases drastically higher. As shown by their calculations the presence of this plateau up to 500 K is due to tunneling.

Another intriguing quantum effect that has attracted great attention in the field of molecular quantum dynamics is the involvement of “quantum resonances.” The resonant states are metastable states: the nuclei can be temporarily trapped during a reactive collision. Their lifetimes can be measured. They last typically for  $10^{-13}$  to  $10^{-12}$  s before they decay into reactants and products [191]. Scattering resonances can be classified in several types such as shape or Feshbach resonances [80]. In a shape resonance, the system is trapped in a one-dimensional well through which it can escape by tunneling. This well can be created by the centrifugal barrier of the system. The Feshbach resonance refers to an even more complex process with more than one dimension: during the collision, the energy associated with the scattering coordinate is partly transferred to other degrees of freedom. The system is temporarily stabilized and forms a metastable state. For instance, the calculated state-to-state probabilities show the existence of shape resonances and Feshbach resonances in  $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$  [192] and  $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$  [193,194] respectively. However, these short-lived states are extremely difficult to observe. Indeed, what is measured experimentally is a reaction cross section, which is a summation over all the probabilities corresponding to all values of the total angular momentum. This summation averages out the resonant contributions and masks their effect [76]. In Chap. 4, Zhigang Sun et al. present several reactive scattering systems involving Feshbach resonances. One of the most interesting results is the fact that they have been able to observe individual resonances in reactions such as  $\text{F} + \text{H}_2$  [195] and  $\text{F} + \text{HD}$  [70]. They have carried out wavepacket propagations in full dimensionality. For  $\text{F} + \text{H}_2$ , the usual way used in chemistry to explain the reaction rates of elementary chemical reactions (mainly based on transition state theory) must be abandoned: the system tunnels below the transition state energy and for certain energies remains temporarily trapped, although the potential is strongly repulsive along the reaction path! The results for  $\text{F} + \text{HD}$  are even more interesting since each of the three peaks observed experimentally in the differential cross sections have been assigned to one Feshbach resonance only. At “normal” temperatures, the effect of these metastable states is masked. But detecting individual resonances is not only an exotic result since “ultracold” chemistry is precisely emerging as a very important field of research [196–201]. Measuring and controlling the reactivity of “cold” ( $1 \text{ mK} < T < 1 \text{ K}$ ) and “ultracold” ( $T < 1 \text{ mK}$ ) molecules are now possible. At these temperatures, wavelike properties of molecules start dominating reaction dynamics and the quantum effects are strongly amplified. Tunneling through potential barriers becomes the dominant reaction mechanism: for instance, two atoms with a large mass such as Cesium can be combined through tunneling to form  $\text{Cs}_2$  at around  $300 \mu\text{K}$  [202–204]. As a consequence, chemical reactions at hyperthermal energies can occur along pathways that deviate far from the minimum-energy path [205]. The resulting chemistry is very rich and could give rise to many applications that are not possible otherwise. In particular, thermochemistry at cold temperature can no longer be described by the

paradigms of reaction path and transition states. In this context, it is conceivable to target the resonant states [191] and to guide the chemical reactions in a way that is completely different from chemistry at higher temperature.

When elementary reactions are not bimolecular, they are generally unimolecular. Among the latter, many are induced by the absorption of light. But before describing the photochemistry of molecules, it is necessary to understand how they interact with light. Photoabsorption spectra lead to information about the actual values of the eigenvalues of the Hamiltonian of the system and indirectly to the nature of the corresponding quantum eigenstates. In infrared or microwave spectroscopy, the fact that the rotational and vibrational states are quantized must be taken into account since transitions are resonant only if the energy of the photon corresponds to the energy difference between two rovibrational eigenvalues. The accurate knowledge of infrared or microwave spectra of small molecules is important not only for the spectroscopy of the atmosphere or in astrophysics, but it also provides invaluable information to identify molecular properties that can be exploited in different domains of chemistry [206]. Let us consider an example: the water dimer is the archetype for aqueous hydrogen bonding and the dimer interaction constitutes the leading and most important term in a many-body expansion for water clusters and condensed phases of water [73]. Most simulations of water use empirical pair potentials fitted to reproduce some properties obtained with approximate methods (molecular dynamics or Monte Carlo). It is suspected that many simulations suffer from an inadequate representation of the force field since these effective potentials describe very poorly the experimental data of small water clusters [207]. The vibrations and rotations of the monomers in the water dimer have large amplitudes and are highly anharmonic. In addition, the rovibrational levels are all split by quantum tunneling so that nearly exact quantum dynamics is necessary to describe quantitatively the rovibrational spectrum. C. Leforestier and co-workers have developed a code that solves the time-independent Schrödinger equation to calculate the latter [208, 209]. Since very accurate experimental data are available for this system [73], the code has allowed one to provide a test for the different potentials, the two most recent ones [209, 210] giving a very good agreement with experiments [209, 211]. It will allow a much more accurate description of interactions between molecules of water and will result in better models of the liquid or solid phase, which can be used, for instance, to study solvation and reactions in aqueous environments. More generally, it will help for a better understanding of hydrogen bonds that play an important role in many chemical processes [212].

In Chap. 5, Oriol Vendrell et al. give a similar example: the infrared spectrum of the protonated dimer or Zundel cation,  $\text{H}_5\text{O}_2^+$ . Using a time-dependent description with the MCTDH approach including all 15 internal degrees of freedom, they have been able to completely characterize the infrared spectra in the gas phase for this system as well as all its analogues where the hydrogen atoms have been replaced by deuterium atoms [153, 154]. They have also performed time-dependent simulations of the dynamics of a proton between the two water molecules [213]. As explained by S. S. Xantheas, the scope of this work exceeds the simple description of this small cluster alone since hydrogen cations are ubiquitous in nature [214]. The

protonated dimers are important for environmental reasons since, for instance, “they take part in acid-base reactions that determine the formation, fate and transport of the main environmental pollutants that cause acid rain”; they are important also for biological processes since “they are pumped across cell membranes by dedicated proteins, creating gradients in pH and charge that act as energy reservoirs for the cell,” etc. [214]. Describing correctly the potential interaction of this system and the underlying vibrational quantum dynamics has thus a general character. In particular, the time-dependent evolution of the proton obtained with MCTDH can serve as a reference to calibrate more approximate methods [215, 216], which can, in turn, be used to treat much larger clusters. This work can be seen as a first step in a so-called bottom-up approach in nanotechnologies for instance, where a precise description of chemical properties of small components can help to understand much more complex structures created by the self-organization of these components, in this particular case the collective physical phenomena involved when hydrogen ions move through water. In the same vein, Vendrell et al. present simulations concerning the infrared spectrum of malonaldehyde, a prototype for the description of the intramolecular hydrogen bond and the corresponding proton transfer [212, 217–220]. The field of infrared spectroscopy is also linked to the studies of Intramolecular Vibrational Redistribution (IVR). The knowledge of the couplings between the vibrational modes and the time scales of the vibrational energy redistribution in molecules is important to understand the rates and the efficiency of chemical reactions [221–223]. As stated by A. Zewail during his Nobel lecture, knowing and controlling the time scales of IVR are a prerequisite of mode-selective chemistry with lasers [224]. It may happen that the vibrational energy given to a chemical bond for instance is redistributed within the molecule in a statistical way, but IVR can also proceed via very specific pathways. In the latter case and if these specific channels lead to important processes, this opens the way to the induction of isomerizations (or dissociations) by laser pulses in the electronic ground state: the lasers can excite one mode of vibration creating a coherent superposition of several vibrational eigenstates, and the resulting wavepacket moves, in a second step, into the direction of the other isomer [225–227].

If the energy of the photons is higher, in the ultraviolet-visible region, the molecule can also be excited electronically. From the electronic excited state, the molecule can release its excess energy and return to the electronic ground state through light emission: fluorescence from a singlet state or phosphorescence from a triplet state. However, in many cases, the light emission is quenched by a much faster radiationless process that is often due to the presence of a non-adiabatic coupling between the excited electronic state and the electronic ground state. In addition, a photochemical reaction (photo-isomerization or photodissociation) may occur during the deactivation time leading to new photoproducts. In polyatomic molecules, this non-Born–Oppenheimer process is generally due to the presence of a conical intersection [29, 30]. Understanding the physics around these conical intersections is very important for at least two reasons: (1) a transfer through a conical intersection corresponds to a fast change in the electronic wavefunction so that the system can rapidly jump from one chemical state to a very different

one. A conical intersection can be seen as a funnel through which a new chemical reaction can occur. Conical intersections are a central paradigm for understanding reaction mechanisms in photochemistry, as important as transition states in thermal chemistry [228]. (2) As explained above, the presence of conical intersections can be at the origin of strong quantum-mechanical effects since the two nuclear wavefunctions associated with the two electronic states can interfere. Thus, the determination of the corresponding ultraviolet spectra in the gas phase is not only important for astrophysical applications, but it is also an essential test for the description of the quantum effects in molecules, which paves the way to photochemistry induced by strong vibronic couplings. The illustrations given in Chap. 6 by Horst Köppel prove that quantum physics around conical intersections is now perfectly mastered. Time-dependent methods allow one to perfectly reproduce the envelopes of the experimental absorption spectra. The calculation of the eigenstates with a time-independent approach allows the assignment of the main peaks of the spectra. In particular it allows the assignment of those corresponding to “vibronic” states, i.e., vibrational eigenstates with components extending over more than one electronic states such as those corresponding to the “mystery band” in the photoelectron spectrum of the butatriene molecule. The simulations can also capture the most subtle interference effects that characterize the physics around a conical intersection, among others the “geometric phase phenomenon.” The spectroscopy of molecules can also be complicated by the presence of spin–orbit couplings, which is a special class of non-adiabatic coupling, especially for open-shell systems, since the latter have unpaired electrons and an electronic spin that is different from zero [229, 230]. The inclusion of the spin–orbit coupling is performed by adding relativistic coupling terms in the molecular Hamiltonian operator.

In Chap. 7, Benjamin Lasorne et al. present studies of photochemistry around conical intersections. Of course, the spectral position, shape, and width of the absorption (or emission) spectra depend on all the competing events that dominate the short-timescale dynamics of the system. In other words, there is a link between the spectroscopy and the photochemistry of the molecule. But photochemistry has to go one step further than spectroscopy since the conical intersection can be far from the Franck–Condon region, the latter playing the dominant role for the photoabsorption spectrum. As explained by M. Robb and co-workers, taking into account explicitly the motion of the nuclei is essential for photochemical reactions, in contrast with thermal reactions [228]. The latter are much better described by the concept of minimum energy path and intrinsic reaction coordinate since the system has time to equilibrate and redistribute the nuclear kinetic energy to the surrounding environment. On the other hand, most photochemical reactions are ultrafast, and the most straightforward path leading to the conical intersection can be very different from the minimum energy path. To simulate explicitly the time evolution, Lasorne et al. have adopted several approaches including a Gaussian wavepacket version of the MCTDH algorithm: instead of using a contracted basis set that is fully optimized variationally as in the MCTDH approach, the contracted bases are constrained to keep a Gaussian shape. This allows one to associate, to the propagation of each Gaussian function, a trajectory as in classical mechanics. Along

the trajectory, the electronic potential can be calculated “on-the-fly,” i.e., for each geometry, thus avoiding an explicit calculation of the potential energy surface. In its most elaborate version [231], this Gaussian approach is “variational” in the sense that all the quantum effects can be captured provided that the number of Gaussian functions is very large. In practice, the number of Gaussian functions is limited for numerical reasons, and this approach can be seen as an intermediate stage between a full quantum-mechanical approach (i.e., using *ab initio* potential energy surfaces and an algorithm such as MCTDH) and an approximate semi-classical method. This approach allows one to see the quantum effects appearing step-by-step by adding more Gaussian functions in the propagation. It is illustrated by the nonlocal transfer from one electronic state to another in the case of the photoisomerization of a cyanine model. In the latter case, a nonlocal transfer appears: as for tunneling, the wavefunction disappears in one electronic state and instantaneously reappears in the other electronic state with no indication of physically transiting the intermediate geometries [232]. This effect is due to the presence of a conical intersection and not to tunneling. In the same manner, when the wavepacket goes through the conical intersection, it can split into several components. The latter can then meet again and create strong interferences that can change the dynamics of the system [233]. These effects can be rendered by the Gaussian propagation methods [233]. One of the most important results brought to the fore by these quantum studies has been the impact of the topology of the conical intersection. As stated by M. Robb and co-workers “sloped conical intersections tend to favor regeneration of the starting material (photostability) because both excited-state and ground-state gradients point toward the reactant side of the potential energy surfaces, whereas peaked conical intersections are more likely to lead to photoproducts as one of the two gradients leads to a new reactive channel on the ground-state surface” [228]. It is a sloped topology that probably explains the photostability of DNA bases [34, 35, 234, 235] and a peaked topology the isomerization of retinal in the first step of vision [236] and the electron transfer in the linked porphyrin-quinone molecule that is responsible for the first step of photosynthesis [31]. Conical intersections are perhaps the tools used in nature to transform the energy of light into chemical energy because of the efficiency and the rapidity of the effect they induce.

Explaining the cross sections of collisions and the photoabsorption spectra of molecules is fundamental to understand the properties of materials, but it is even more important to be able to manipulate and control these properties. In traditional chemistry, this is achieved by adjusting external parameters such as temperature, pressure, concentration, solvent, or by adding catalysts. A higher selectivity and precision could be obtained by a systematic use of lasers. In addition, the latter can offer the possibility to control quantum effects such as quantum coherence. In traditional chemistry, the quantum states involved in the chemical process are, in general, populated in an incoherent way described as a “mixed state” in quantum statistical mechanics. The systematic use of laser pulses to induce chemical process opens the possibility to create coherent superpositions of the same quantum states, what is called a “pure state” in quantum statistical mechanics. Such coherent superpositions might drastically increase the efficiency and the control of



the corresponding chemical processes and at a much lower energetical cost. The exploitation of this quantum coherence in molecular processes is seen as one of the main challenges in basic energy sciences [237]. This leads to the concept of coherent control that is presented in Chap. 8 by Sebastian Thallmair et al. The studies presented in Chap. 7 are a first step in the direction of coherent control. For instance, it is observed that a sloped or a peaked topology at the conical intersection leads preferentially to photostability or photoreactivity, respectively. But since a conical intersection is not an isolated point but a subspace of  $3N-8$  dimensions,  $N$  being the number of atoms of the molecule, the topology can be sloped in some regions, while peaked elsewhere [238,239]. By selecting the initial vibrations that are excited by a laser pulse, the system can be guided in a specific direction and access the conical intersection in different regions leading to different processes, photostable or photoreactive for instance [238,239]. Consequently, if it is important to understand the intramolecular vibrational energy redistribution in molecules and the quantum physics around conical intersections, it is even more important to understand the two at the same time since, in polyatomic molecules, excitations result in a rapid mixing of vibrational and electronic motions, which induces both charge redistribution and energy flow in the molecule [240]. The fact that the electronic and nuclear motions can be coupled in the most subtle way is observed even in physiological processes. For instance, as aforementioned, a quantum coherence between two electronic states has been evidenced in photosynthetic systems. In such biological systems, the number of modes of vibration is huge and these vibrations should destroy the quantum interferences very fast [36]. In other words, a quantum decoherence between the two electronic states should be almost instantaneous due to the presence of the “environment” of the numerous vibrations. But since a much longer coherence is observed experimentally, it probably means that a subset of modes of vibrations must themselves be in coherence with the electronic motion and enhance the interferences instead of destroying them, while the other modes of vibration are less coupled to the electronic motion and will play the role of an environment that dissipates the coherence only in a second stage [36,241]. In this context, understanding the coupled quantum behavior between electrons and nuclei is particularly important in molecular quantum dynamics especially with the advent of “attosecond spectroscopy” that allows scientists to measure all the corresponding quantum effects [237]. Understanding how light is converted into chemical energy and the corresponding quantum effects can have many applications [242]. In particular, as stated by C. A. Rozzi et al: “One of the key challenges for the future will be to learn how to construct artificial devices enabling to the harvesting of sunlight and their use either for direct electric power generation (photovoltaic approach) or to drive fuel-producing photochemical reactions (photosynthetic approach)” [243]. In this context, “a fascinating, but so far unexplored, perspective would be to exploit such quantum coherence effects in artificial photosynthetic/photovoltaic systems to improve their performance,” although the quantum effects induced by sunlight or by laser pulses in experiments must be clearly distinguished [41].

A full quantum description of molecules in interaction with laser pulses is a difficult task. In practice, in molecular quantum dynamics, the light is not described

quantum-mechanically with quantum electrodynamics but classically. But even with this approximation, all the information gained on the isolated systems (i.e., without any external field) about the topology of the potential energy surfaces or the eigen or metastable states cannot be directly transposed to the study of the system in interaction with pulses. Indeed, the presence of the external fields modifies the molecular systems themselves. When the pulse is periodic or when the envelope of the pulse changes smoothly, i.e., “adiabatically” according to precise criteria, it is the Floquet states that play an analogous role to that of the energy eigenstates in time-dependent systems [244, 245]. Since the calculation of the Floquet states is even more complicated than the calculation of the eigenstates, some approximations are often invoked to rationalize the interaction of the system with light. Two extreme cases can be distinguished. If  $\omega$ , the carrier frequency of the laser pulse, is quasis resonant with respect to the transition of interest, the problem can be reformulated in terms of “dressed” states, i.e., eigenstates dressed by the external field. The dressed energies are simply the eigenvalues of the time-independent problem,  $\pm\hbar\omega$ . If the frequency is completely non-resonant, the interaction with the pulse can be reduced to a dynamic Stark effect, i.e., the effective potential seen by the system is simply the electronic potential plus the contributions of the dipole moment and the polarizability that depend on time only through the envelope of the pulse. The eigenstates must be replaced by the eigensolutions for each time  $t$  of the effective Hamiltonian with the effective potential. In this context, joining clearly the targeted chemical properties of systems and the parameters of the laser pulses is still challenging.

As explained by Sebastian Thallmair et al. in Chap. 8, the coherent control of quantum systems, two complementary approaches can be distinguished: the “rational” control (or “single-parameter” control) and the “optimal” control (or “multi-parameter” control). In the first approach, a single parameter (pulse duration, intensity, wavelength, pulse delay, chirp) is used to control the chemical process [246–250]. The second approach is more systematic: several parameters are optimized at the same time using an appropriate control scheme to find an “optimal” laser field in order to reach a predefined target [251, 252]. It is indeed possible experimentally to tailor the driving laser pulse with a pulse-shaping device using a closed-loop laboratory-learning procedure. These two approaches are complementary: the second one is more efficient but is somewhat “blind” since the intrinsic information about the physics of the system is concealed in the optimal pulse [253, 254]. It is precisely the role of rational control to make the link between the physical properties of the system and the parameters used in the field to control the process and to bring out general rules that govern the dynamics. For this, one can split the processes into several categories. First, one focuses on the control of the nuclear motion only, i.e., on chemical processes in one electronic state, typically the electronic ground state, and one uses the Born–Oppenheimer approximation. The understanding and the control of tunneling and of IVR are then the main issues. Second, one adds the possibility to switch from one electronic state to another through a non-adiabatic process induced by the presence of a conical intersection for instance. In this context, the topology of the

potential surfaces around the conical intersection plays a crucial role in the physical process as explained in Chap. 7. Control of the reactivity can then be obtained by changing this topology, for instance, by using a non-resonant laser that creates a Stark effect and shifts the energy of one electronic state with respect to the other one. However, IVR can interfere in the dynamics and the full control of the reactivity can only be achieved by controlling the coupled nuclear and electron dynamics. In Chap. 8, Sebastian Thallmair et al. present several strategies they have employed to control chemical processes with laser pulses, special emphasis being placed on subfemtosecond coherent control of coupled electronic and nuclear dynamics. They present an example of possible optimal control for a molecular switch made of an electrocyclic reaction of fulgides [254]. Molecular switches can be used as versatile devices in nanotechnology and for logic gates in molecular computation. But the most important results they present are probably those concerning the control of the electron localization in the diatomics  $D_2$ , CO,  $K_2$ . Their simulations explain the recent experiments realized for these systems using laser pulses at the sub-femtosecond time scale [53, 255, 256]. These works prove that it is now possible not only to control the motion of the nuclei with laser pulses as in femto-chemistry but, even more importantly, to also control and to “shape” the electronic density by creating an electronic wave packet that is a coherent superposition of several molecular electronic states.

Finally, Alex Brown et al. present in Chap. 9 some applications in the context of quantum computing. The possibilities offered through quantum computation have been well known for many years now [257, 258]. A quantum computer is a computation device that makes direct use of quantum-mechanical phenomena, mainly the fact that the system can be in a coherent superposition of different eigenstates due to the superposition principle. This has no classical counterpart as illustrated by the famous Schrödinger cat as explained above. In classical computers, the basic unit of information is a “bit” that can have only two values often denoted 0 and 1. As explained by Brown et al, in quantum computers, the unit of information is a “qubit” that is a coherent superposition of two quantum states denoted 0 and 1. More precisely, it is a two-state quantum-mechanical system that can be written as:  $\alpha|0\rangle + \beta|1\rangle$ . The advantage of a quantum computer can be understood straightforwardly: whereas a bit must be either 0 or 1, a qubit can be in any superposition of both (due to the superposition principle), and the number of possible combinations is much larger. This possibility to superpose several states offers new possibilities of combinatorial calculations that do not exist with computers based on classical laws. In particular, it is expected that quantum computers could solve certain problems much faster than any classical computer. One of the main challenges in quantum computing is controlling quantum decoherence since the latter destroys the properties that are exploited in quantum computing. In addition to the superposition principle, quantum computers could exploit other quantum properties such as entanglement (for quantum teleportation, i.e., to transmit quantum information from one location to another) or wave function collapse (for cryptography [259]). In the context of molecular quantum dynamics, it has been proposed that electronic vibrational or rotational states of molecules

could be used for quantum computation processes [260–263]. Vibrationally excited molecules in the gas phase could be possible candidates to encode qubits since decoherence could be controlled easily [260, 264]. The final chapter on quantum computing highlights that one key issue in molecular quantum dynamics is the creation of a coherent superposition of quantum states and its conservation over time since quantum decoherence can occur very fast upon interaction with the environment.

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