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REGULAR ARTICLE

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Novel perspectives in quantum dynamics

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Abstract In the field of theoretical chemistry, we focus on the sub-discipline of quantum dynamics. Special emphasis is placed on novel methods which can provide predictions for medium-sized and large systems and on the difficulties encountered when facing the huge dimension of the primitive basis within a quantum mechanical framework. We try to highlight the possibilities of applications of these methods to atmospheric or astrophysical spectroscopy and organic chemistry and to bring out general perspectives, in particular via comparisons with the electronic structure theory.

1 Introduction

Spectroscopic and dynamic accurate calculations focusing on the motion of the nuclei in molecular systems are a challenging task in environmental science, astrophysics and chemical reactivity including phenomena of biological interest [1,2]. The domain of applications encompasses broad areas: photodissociations or excitations, dissociations of an absorbate on a metal surface, intramolecular vibrational energy redistribution or predissociation, infrared spectroscopy, inelastic surface scattering, molecular reactive scattering, evolution of a molecular system exposed to an ultra-short laser pulse, etc. In general, the corresponding processes involve a limited number of degrees of freedom with large amplitude motions and many with rather small ones. It is significant to dwell upon the fact that the individual steps are often ultrafast, in a time domain ranging from femtoseconds (fs) to picoseconds (ps). On the experimental front, decisive progress, in particular in the field of femto-spectroscopy [3–5] or infra-red/microwave spectroscopy [6–9], allow the scientists to probe chemical phemonema at an atomic level on the real time axis or to obtain fully resolved spectra of highly excited polyatomic systems. These ultra-sophisticated experiments require new theoretical tools to interpret, predict and, in other words, to accompany these experimental works. Moreover, it should be emphasized that these molecular processes generally are significantly impacted by nuclear quantum mechanical effects [10–12] such as tunnelling effects of light atoms through barriers (for instance in the cases of electron or proton transfers), transitions due to strong vibronic couplings such as conical intersections which seem to play a crucial role in many organic or biological systems, interference or zero point energy effects which are essential when dealing with rovibrational spectra of molecules, etc. Rigorously, one should thus solve the time-dependent or the time-independent Schrödinger equations. However, the considerable power of modern computers notwithstanding, the quantum mechanical treatement of molecular dynamics is a formidable task when more than (only !) four degrees of freedom have to be taken into account. Indeed, the numerical effort scales expontentially with the number of degrees of freedom simply because the basis set size also grows expontentially with the dimension of the molecular system. In addition, the approaches and the corresponding programs devised in dynamics were, up to now, almost always confined (and optimized) to very specific physical problems. On the contrary, if we now compare the molecular dynamics with the electronic structure theory, it is very striking that general packages based on a quantum mechanical approach (see for instance [13,14]) have already been routinely utilized for a relatively long time now by researchers interested in the electronic problem. Furthermore, it is remarkable that these latter programs allow one to tackle an extremely large field of applications including relatively large systems. Several reasons can be put forward to explain these differences. First, the resolution of the molecular dynamics problems obviously presupposes the preliminary resolution of the electronic problem. The simulations of the dynamics is thus situated ‘downstream’ and necessitates that ab initio data providing the information regarding the electronic structure, for instance potential energy surfaces or various couplings such as the diabatic couplings between the various electronic states or dipole couplings to laser fields, are already available. Second, whereas in the electronic theory it

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is always the Coulomb potential which appears, in dynamics the interaction potentials of molecular dynamics can present various structures depending on the system, the energy domain, and the electronic state(s) to be considered, leading to myriads of different physical behaviors and often to a strong correlation. Eventually, as the masses of the nuclei are relatively heavy, the nuclear wave function is, even at low energy, characterized by large quantum numbers and shows an oscillatory shape that is awkward to describe numerically. It can therefore be justifiably supposed that the resolution of the Schrödinger equation for the nuclei might turn out to be numerically intractable even when a relatively small number of degrees of freedom are involved and that the development of a unified and general quantum mechanical approach that could routinely treat relatively large systems, remains a very intricate task which has not untill now been achieved.

The crucial points for the future in dynamics can then be summarized as follows: development of a general strategy which is able to take into account the quantum mechanical effects which are ubiquitous in chemical processes and the extension of this approach to ever larger systems. Of course, such problem definitively exceed a the scope of the present paper. However, the goal of this article is to present several novel contributions which have been put forth in the last 15 years and which could open up possibilities to envision the simulation of molecular dynamics in an efficient and more general manner. Here, we confine ourselves to accurate resolutions of the Schrödinger equation in terms of wavefunctions which cover the full multidimensional domain of the systems that can be described by approximated Hamiltonian operators. In particular, we do not discuss semiclassical methods [15–18] which describe the quantum effects in terms of classical trajectories as well as hybrid quantum–classical methods [19,20] (note only that these latter hybrid quantum–classical methods also need a full quantal treatment of several degrees of freedom). The remainder of this paper is as follows. In Sect. 2, several powerful algorithms to solve the Schrödinger equation for relatively large systems are presented. Section 3 is devoted to the Hamiltonian operator in dynamics whose derivation is of upmost importance since it governs all the physical description of the molecular system. In Sect. 4 special emphasis is placed on illlustrations of applications. The paper concludes presenting general perspectives for the future.

2 Resolution of the Schrödinger equation

The usual quantum treatement of dynamics rests on the Born-Oppenheimer separation, in which the full molecular problem is handled in two stages. Within this framework, the electronic energy and the nuclear-nuclear repulsion are first solved for several positions of the nuclei. The resulting electronic energies parametrized by the positions of the nuclei are referred to as the potential energy surfaces (PES). This hierarchic approach is due to the fact that the atomic nuclei are much more massive than the electrons and then almost fixed with respect to the moving electrons. In particular, if the kinetic energy of the nuclei can be really considered as a small perturbation of the electron motion, the adiabatic Born-Oppenheimer approximation which neglects the coupling between the several PESs can be invoked. This approximation represents one of the cornerstones of molecular physics and chemistry since the PESs directly provide the complete description of the molecular vibrational dynamics. If the Born-Oppenheimer approximation is violated, for example when a conical intersection appears, the previous hierarchical treatment is often retained, but the coupling between the PESs must be explicitly taken into account. The bulk of the processes, including a strong vibronic coupling, are treated by introducing suitable diabatic electronic states that may cross as a function of the nuclear distances [21–24].

When tackling a quantum mechanical subject in dynamics, the study can be performed either in the time-dependent picture by propagation of a wavepacket, or in the time-independent picture by diagonalisation of the Hamiltonian. If the Hamiltonian is itself time-dependent, the time-dependent approach is unavoidable. However, if the Hamiltonian is time-independent both pictures are formally equivalent. Since the time and energy variables are conjugate in the same sense that the position and momentum are, the choice to exploit one of the two pictures mostly depends upon the numerical efficiency. Indeed, the time-dependent or the time-independent Schrödinger equations lead to very different mathematical problems, namely an initial value problem or an eigenvalue problem, respectively. The superiority of one approach over the other depends on the physical system and the physical quantities in question. For instance, it is intuitive to suppose that the quantal motion of the nuclei in a scattering or half-scattering (e.g. photodissociation) is more naturally described by working in the time-dependent frame. Complicated scattering boundary conditions and non L^2-wavefunctions do not appear in the time-dependent picture. In the same manner, it is reasonable to assume that a time-independent approach is more suitable for the extraction of excited state energies with high accuracy since the uncertainty principle implies that a very long propagation is needed to obtain high accuracy. However, this kind of assesments must always be qualified since experience proves that the opposite can be true. For instance, the advent of the filtering method introduced by Neuhauser [25–29] allows one, to some extent, to accuratly compute individual eigen energies with a time-dependent approach using a relatively short propagation. In the same manner, the application of time-independent scattering theory has been very efficient in delivering detailed reaction cross-sections – see for instance the recent works of Chakraborty and Truhlar [30], which show that time-independent quantum mechanics can also be used for accurate polyatomic reaction dynamics.

In this section, we present a sample of significant algorithms which illustrate the present state of the art. Of course, this presentation is not exhaustive, nor does it present a comprehensive survey of the immense amount of existing literature. As aforementioned, the fundamental problem in quantum mechanical studies hampering treatment of large systems, is the huge size of the primitive basis set which is a product basis built from 1D bases for each degree of freedom. In order to attack 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 much smaller and replaces the primitive basis set. If we specifically turn to the time-independent picture, we can mention, as a first example of a contraction scheme, the vibrational self consistent field (VSCF) method used by Gerber and coworkers [31–34] or the configuration interaction (CI)–VCSF approach by Bowman [35]. These methods allow one to calculate rovibrational energy levels of polyatomic molecules beyond the normal modes approximation. The latter powerful tool rests on a preliminary vibrational-SCF step which produces a contracted basis set (similar to the orbitals in the electronic structure theory). This step drastically enhances the convergence of the quantum mechanical problem by reducing the size of the final basis set. Indeed, the SCF functions take into account both the anharmonic behavior of each mode of vibration and part of the intermode couplings through a mean field approximation resulting from a variational principle. In the Multimode code from Bowman and co-workers [36,37], the subsequent CI procedure explicitly brings about the full correlation between the modes yielding accurate results for five- or six-atom molecules and realistic for much larger systems [38]. Nevertheless, in its usual implementation, this method relies on a rectilinear definition of the normal modes, due to their simplicity [39] (the rectilinear coordinates lead to a very simple kinetic energy operator). However, this formulation reduces the efficiency of the method when excited states are of interest, or if overall rotation is explicitly taken into account because motions of large amplitude necessitate a treatment in curvilinear coordinates (see Sect. 3). A genuine multiconfigurational SCF (or MCSCF) vibrational approach similar to the complete active-space SCF (CASSCF) method used in electronic structure theory, has also been developed by Liévin and coworkers [40, 41] based on the use of the generalized Brillouin theorem.

Another example of a contraction scheme is the sequential adiabatic reduction (SAR) method of Bačić and Light [42] which has emerged as an optimal approach to study rovibrational spectra. In this approach, which is reminiscent of the Born-Oppenheimer separation, the variables are ordered by increasing adiabaticity (the hierarchy is chosen according to the frequency molecular vibrations). If the hierarchy in the rapidity of the coordinate motions is very pronounced, this contraction reveals itself as very effective and affords a very compact final basis set in which the time-independent Scrödinger equation can be solved as exemplified by the several studies of tetra-atomic Van der Waals complexes [43].

In our group in Montpellier, we normally use direct methods which are also very powerfull tools to study rovibrational spectra (in general for the electronic ground state) for large systems. By direct method we mean any iterative approach which only applies the Hamiltonian operator to a given vector in order to avoid the bottleneck associated when handling the Hamiltonian matrix. Examples are the Lanczos diagonalization method [44–47] or the Davidson algorithm [48,49]. Essential to applying these direct methods is the use of a pseudospectral approach. Initiated by Feit and Fleck [50], Kosloff and Kosloff [51] and Light et al. [52], two different representations (spectral and grid) associated with the Hamiltonian operator are employed. In its original formulation, the kinetic energy part was evaluated in the spectral representation (plane waves), while a grid was used for the potential. It should be noted that these two representations are equivalent and related by a unitary transformation (for instance a multidimensional FFT). In the adequate spectral representation, the kinetic energy operator can be easily evaluated (often analytically) and allows one to discard the apparent singularities which can occur in the kinetic energy operator (such as for $\theta = 0, \pi$ in the term $\sin^{-2}\theta\partial^2/\partial\varphi^2$) [53–56]. In the grid representation, the potential is diagonal. For molecules with more than three atoms, a contracted basis set has to be defined: an adiabatic one or an optimization of the primitive basis set (grid or spectral) by definition of a zero order Hamiltonian for each mode which partially includes the potential operator and the kinetic energy operator (see for instance [57–59]). We have used such an approach to calculate infrared spectra of tetra-atomic molecules such as NH_3 [60], HFCO [61], H_2CO [49] for instance. Very recently, similar direct methods coupled with contraction schemes have been applied by other groups to study the rovibrational spectra of even larger systems such as CH_4 (9 dimensions) [62,63] or $(H_2)_3$ (12 dimensions) [64].

Another approach which can be briefly mentioned is the canonical Van Vleck perturbation theory applied by Sibert and co-workers to calculate highly vibrationally excited states [65]. This approach being based on a perturbative approximation cures the main drawback of the quantum mechanical approach, i.e., the fact that the numerical effort scales expontentially with the number of degrees of freedom. This approach is not a crude perturbative one, for the Hamiltonian has a block diagonal form characterized by one or more polyad quantum numbers. These integers are chosen such that the resonance interactions (the Fermi resonances) are not perturbatively decoupled and treated. When the perturbative approximation and the definition of the polyads are reasonable, the canonical Van Vleck perturbation method yields very accurate results much faster (often by several orders of magnitude) than the quantum mechanical approaches mentioned above as demonstrated for instance in recent applications to rovibrational spectra penta-atomic systems [66] or to CH_3OH including all the 12 (!) degrees of freedom [67]. Note only that this approach is specifically devoted (at least up to now) to rovibrational spectra and that it can be sometimes intricate to find one adequate, or several, polyad(s) to take into account all the couplings which cannot be perturbatively treated.

To our knowledge, there are very few full quantum mechanical methods which are able to achieve the dynamics studies for larger systems. Pioneering work has been carried out in the 1990s and technically based on the determination of an active space in which the dynamics is studied. The active space is extracted from the primitive space by the wave operator method based on the Bloch formalism [68–70]. This approach has been applied by R. Wyatt, C .Iung and co-workers [71–79] to perform full 9- and 30-dimensional (!) studies of the spectroscopy and the intramolecular vibrational energy redistribution (IVR) of HCF_3 and benzene, respectively. In these methods, the primitive basis set can contain billions of states but the active space is limited to 10,000–50,000 states. These pioneering studies were of utmost importance since they have demonstrated that relatively large systems can be tackled within the framework of a full quantal approach. The spectra of such large systems are obtained by using the Lanczos or filtered Lanczos [80] schemes in this active space. The time evolution of the wave packet are obtained by using a Chebychev polynomial expansion of the evolution operator U(t) [81] within the active space.

Another method we personally apply routinely is the Heidelberg package [82] of the multi-configuration time dependent hartree (MCTDH) algorithm devised by H.-D. Meyer and co-workers [83–86] (see also references [87,88] for pioneering works concerning a time-dependent multi-configuration treatment). The MCTDH method also exploits an active space, but this space is built from time–dependent functions $\varphi(q,t)$, the so-called *single-particle functions* (SPFs). The direct product space of the SPFs generates the MCTDH active space. The MCTDH wavefunction reads

$$\Psi(Q_1,\dots,Q_f,t) \equiv \Psi(q_1,\dots,q_p,t) = \sum_{j_1}^{n_1}\cdots\sum_{j_p}^{n_p} A_{j_1,\dots,j_p}\prod_{\kappa=1}^{p}\varphi^{(\kappa)}_{j_\kappa}(q_\kappa,t), \tag{1}$$

where f denotes the number of degrees of freedom and p the number of MCTDH particles, also called *combined modes*. Here, $q_\kappa = (Q_{\kappa_1},\dots,Q_{\kappa_L})$ denotes a multi-dimensional variable accounting for L degrees of freedom ($L = L(\kappa)$ may be one for some κ's and $\sum_\kappa L(\kappa) = f$). There are n_κ SPFs for the κ's particle. The equations of motion of these single-particle functions are obtained by using the Dirac–Frenkel variational principle – all the single-particle functions 'see' mean-fields operators. The variational principle guarantees that the SPFs are optimal, and thus ensure a fast convergence. In a sense, this approach is similar to the MCSCF approach from Liévin [40,41] except that the 'contracted' functions (i.e. the single-particle functions) are now time-dependent.

This time-dependence is of ulmost importance for it introduces a crucial versatility in the basis set – the functions follow the evolving wavepacket and adapt to the shape of the potential. As pointed out in the introduction, it is precisely this large variety of structures of the potential in dynamics which precludes the developement of a general approach. The introduction of this time-depedent basis set is thus a clever way to overcome this impediment.

However, the power of this method lies not only in its flexibility and also in its theoretically solid basis. Indeed, the result converges to the exact results as the spf basis is increased in size. Moreover, the Heidelberg package provides very simple tools to easily control the convergence of the calculation.

The convergence with the number of configurations totally depends upon the correlation. If the coupling between the various modes is equal to zero, the system is described straigt-forwardly by one configuration only, even if the behavior for each degree of freedom is very complicated. If the correlation increases, the number of configurations needed for convergence grows correspondingly. Unfortunately, as mentioned in the Introduction, the correlation is often strong in the problems encountered in dynamics. For this reason adequate coordinates have to be chosen to describe the system. An adequate set of coordinates can reduce the correlation, then greatly enhance the convergence of the MCTDH (see the discussion concerning the choice of the coordinates by Moiseyev et al. [89, 90]).

Moreover, it should be emphasized that the SPFs may be multi-dimensional functions so that it is possible to combine the coordinates which are strongly coupled. The correlation among the combined degrees of freedom is then fully accounted for at single-particle levels. Only the correlation betweeen the MCTDH-particles must be provided by the multi-configuration ansatz.

Multi-configuration time dependent Hartree (MCTDH) is a powerful algorithm designed to solve quantum molecular dynamics of large systems, i.e. systems, for which the primitive product grid ceases to fit into the computer memory. An example which demonstrates the power of MCTDH is the study of the photo-excitation spectrum of pyrazine [91–94]. Here a 24-dimensional wavepacket was propagated on two coupled electronic potential energy surfaces (through a conical intersection).

Multi-configuration time dependent Hartree (MCTDH) was also applied to the spin-boson model [95] or the multi-dimensional Henon–Heiles model, a standart test for semi-classical and other approximate methods which gives rise to a chaotic behavior high in energy, including up to 32 dimensions [96]. This method has been applied successfully to a large number of phenomena such as direct photodissociation [84,97–100], photodissociation on a surface [101,102], photo-absorption [92,93,103], and pre-dissociation [104]. It has been used to calculate photo-electron [105,106] and resonance Raman spectra [107]. It has also been applied to compute cross-sections of both reactive scattering [108–110] and inelastic molecule-surface scattering [111–114] events. Cumulative isomerization probabilities and reactions rates have also been calculated directly using a flux correlation function [115–118]. Other studies include the electron transfer along a conjugated chain [119], and resonant excitation by electron impact [120]. As it is a time-dependent method, including a time-dependent Hamiltonian is a trivial matter. An example of the sort of process that can then be studied is laser-driven proton transfer [121]. Finally, combined with filter diagonalization, it has been even used to calculate bound-state spectra with a high accuracy (however, only for tri-atomic systems was it possible to extract a large part of the spectrum, for larger systems the filter diagonalization was used to extract very specific states only) [122,29]. It is also possible to envision calculating resonances just by adding a complex absorbing potential [123–127] (which are already implemented in the MCTDH package [82]) in conjunction with the filter diagonalization. Recently, we have performed several simulations of the IVR in the molecules HONO, Toluene and HCF_3 [128–131] along with some selective extraction of specific bound states.

This host of applications of MCTDH stems from the flexibility of the single-particle-function basis set. Finally, Wang and Thoss [95] recently devised a multilayer formulation of MCTDH (called 'cascading' in [86]). This approach is based on the same idea that makes MCTDH very attractive – a better representation obtained through a variational principle. In the multilayer formulation of MCTDH the single-particle functions of the original MCTDH themselves are further expressed, employing a MCTDH expansion on the single-particle functions:

$$\varphi_{j_\kappa}^{(\kappa)}(q_\kappa, t) = \sum_{i_1}^{m_1} \cdots \sum_{i_q}^{m_L} B_{i_1,\dots,i_L}^{(\kappa)} \prod_{l=1}^{L} v_{i_l}^{(\kappa,l)}(Q_{\kappa_l}, t) \;, \tag{2}$$

so that

$$\begin{aligned}\Psi(Q_1, \dots, Q_f, t) &\equiv \Psi(q_1, \dots, q_p, t) \\ &= \sum_{j_1}^{n_1} \cdots \sum_{j_p}^{n_p} A_{j_1,\dots,j_p} \prod_{\kappa=1}^{p} \varphi_{j_\kappa}^{(\kappa)}(q_\kappa, t)\end{aligned} \tag{3}$$

can rewritten as:

$$\begin{aligned}&\Psi(Q_1, \dots, Q_f, t) \equiv \Psi(q_1, \dots, q_p, t) \\ &\quad = \sum_{j_1}^{n_1} \cdots \sum_{j_p}^{n_p} A_{j_1,\cdots,j_p} \\ &\qquad \times \prod_{\kappa=1}^{p} \left[\sum_{i_1}^{m_1} \cdots \sum_{i_L}^{m_L} B_{i_1,\dots,i_L}^{(\kappa)} \prod_{l=1}^{L} v_{i_l}^{(\kappa,l)}(Q_{\kappa_l}, t) \right]\end{aligned} \tag{4}$$

Equation 4 shows that cascading may be interpreted as a MCTDH expansion in the SPFs $v_{i_l}^{(\kappa,l)}$ when the coefficient vector assumes a product form: $A_{j_1,\dots,j_p} B_{i_1,\dots,i_L}^{(1)} \cdots B_{i_1,\dots,i_L}^{(L)}$. Wang and Thoss [95] have applied this approach to a spin–boson model including up to 1000 (!) degrees of freedom. They have shown that this multilayer formulation of MCTDH can treat a very large number of degrees of freedom with a moderate computational effort. These very recent developements obviously offer very encouraging perspectives for the future.

Finally, it should be mentioned that the Feynman's path integral formulation of time-dependent quantum mechanics [132–134] provides an attractive and equally rigorous alternative to the resolution of the standard Schrödinger equation, in particular for studying condensed matter. The limitation due to the prohibitive storage of the multidimensional wavefunction is then circumvented since quantum mechanical amplitudes are expressed as sums over paths. The two difficulties of this approach come from the fact that first the quantum interferences are reproduced by the amplitude along the path which is a complex-valued phase. As this phase can exhibit rapid oscillations, this approach requires a very fine discretization. Second, the number of paths increases exponentially with the number of degrees of freedom and the total propagation time. However, Makri and coworkers [135–143] and others [144–147] have shown that this approach can be a very efficient tool in certain very important situations, in particular for calculating the dynamics of systems in contact with dissipative baths. Another formulation of the concept of the exact real time dynamics based on the concept of path integral centroid variables of Feynman has also been devised by Voth and coworkers [148]. Within the framework of this centroid molecular dynamics method, several approximations have been applied and they have shown that they could capture the main quantum effects for condensed phase dynamical processes [148–153].

3 Hamiltonian operator

Armed with the previous algorithms, we are in a position to solve the Schrödinger equation for relatively large systems. However, it is a preliminary basic necessity to have at one's disposal a Hamiltonian operator, including the kinetic energy and the potential surface(s), which contains the physics of the molecular system. At this stage, the choice of the set of coordinates for describing the physical systems and for expressing the operators is of great importance. Indeed, as aforementioned, the convergence of the contraction schemes, which are inescapable to tackle large systems, strongly depends upon the correlation between the coordinates. An inadequate set of coordinates entails a strong artificial correlation and thus a very poor convergence. As regards the ro-vibrational spectroscopy low in energy and around a local minimum, the molecule vibrates in a quasi-harmonic way and a description in rectilinear coordinates (usually normal rectilinear coordinates) is satisfactory. An advantage of the rectilinear coordinates comes from these coordinates leading to a very simple formulation of the kinetic energy operator. However, when the vibrations become more anharmonic or in the case of systems with motions of large amplitude such as isomerizations, dissociations, scattering systems, rectilinear coordinates must be abandoned altogether and curvi-linear coordinates employed. Furthermore, the use of curvilinear coordinates allows one to easily split the coordinates into two subsystems: the three Euler angles which define the body-fixed frame and the 3N-6 internal coordinates describing the deformations of the molecules. This separation is easy when rectilinear coordinates are used and only when mall amplitude motions are considered. The Eckart Frame then accomplishes this separation [39]. This separation facilitates the construction of the irreducible representations of the rotation group symmetry and thus the reduction of the size of the calculations. Finally, curvilinear coordinates are generally the most efficient in describing potential energy surfaces since they improve the convergence of the potential energy expression [154]. Unfortunately, the use of curvilinear coordinates generally leads to far more involved expressions [155, 156] of the kinetic energy operator which are generally very specific to each particular system [157–159]. In fact, the problem is not really to derive the kinetic energy operator. Indeed, a program such as MATHEMATICA [160] can now be used to analytically evaluate the operators or a numerical computation of the action of the kinetic operator is also feasible. Several contributions in this way have been put forth (see references [161, 162] for instance). In order to obtain a general quantum mechanical approach in dynamics, the crucial point is rather to have a relatively simple and general form of this operator in curvilinear coordinates which can be applied to a large variety of molecular systems and, above all, which is well suited for the numerical methods used in dynamics (in particular, a large number of terms in the operator can drastically slow down the numerical resolution of the Schrödinger equation). Recently [163–172], a general formulation of the exact kinetic energy operator based on a polyspherical parametrization of the N-atom system has been devised. We have shown that, for a particular family of curvilinear coordinates (the 'polyspherical coordinates'), a relatively simple expression of the kinetic energy operator could be explicitely obtained without resorting to lenghty differentiation calculations. This expression is valid irrespective of the number of atoms and the set of vectors : Jacobi, Radau, Valence (the usual vectors used in chemistry which join one atom to another), satellite, etc or a combination of those. Moreover, it includes rotation and Coriolis coupling. This general operator is always separable; i.e., it can be written as a sum of products of monomode operators. This property can be very profitable for contraction schemes such as MCTDH: see [128, 129] for an application to a tetra-atomic system HONO, [130, 173] for nine-dimensional calculations with MCTDH in valence coordinates, and other applications with orthogonal coordinates to tetra-atomic systems [61, 49, 174] or penta-atomic systems [62, 175, 63]. Finally, within this framework, it is very easy to find the correct spectral basis set which discards all the singularities which can occur in the kinetic energy operator: see references [64, 169, 176–178] for appplications to systems with four and six atoms. To our knowledge, this approach in polyspherical coordinates is the first one leading to a general expression of the kinetic energy operator in curvilinear coordinates if we except the well-known Wilson G matrix formulation [39, 179] which is based on a different familly of coordinates (see [67, 66] for very impressive applications using this Wilson G matrix formulation). Note however that this latter approach leads the generic expression only for the valence vectors and does not explicitly provide the rotation energy and the Coriolis coupling in curvilinear coordinates. Moreover, the terms cannot be generally expressed as the sum of products of monomode operators. This last feature can be a drawback for many numerical methods.

It should be added that the polyspherical approach presented above can be applied to problems with strong vibronic coupling such as conical intersections [21]. To conclude, the polyspherical approach can be exploited to treat a large familly of problems in dynamics and the use of curvilinear coordinates is no longer an obstacle as far as the kinetic energy operator is concerned at least for the systems accessible with the current numerical methods. For large systems, the number of internal coordinates makes a reduction of dimensionality unavoidable. This is true not only for the dynamics but also, and above all, for the calculation of the potential operator. By a clever choice of internal coordinates, the separation into inactive coordinates and active coordinates is very often possible, so that a reduction of dimensionality can then be achieved [180, 7]. A widely used approach is the rigid-constraint one, which consists in freezing some bond lengths, angles or entire atomic groups. However, if the internal motions of these atomic groups have to be explicitly considered, the rigid model is insufficient and it becomes necessary to invoke at least an adiabatic model. If curvilinear coordinates are used, care must be taken when deriving the correct kinetic energy operator of the system subjected to constraints (rigid or adiabatic). We refer the reader to [181] for a detailed discussion on the importance of 'correction terms' in the constrained models. It is shown that without these corrections the kinetic energy operator can lead to a completely distorded pattern of ro-vibrational levels in infrared spectroscopy for instance. In references [182, 164, 181], the derivation of rigidly and adiabatically constrained kinetic energy operators was presented in a full ab initio and general context (see also [183] for another formulation). The results presented in these foregoing articles were not specific to the polyspherical coordinates. But, armed with the general expression of the kinetic energy operator in polyspherical coordinates, we have shown [172] that it is straigtforward to afford the constrained kinetic operators for a large variety of systems so that the derivation of constrained kinetic energy operators in curvilinear coordinates is now feasible for a large field of applications (see also the works of Lauvergnat and Nauts [162] for a numerical implementation of the same constrained approach). For instance, the adiabatically constrained model was applied to the water dimer in a recent paper [184] in which a determination of the 12D water dimer potential energy surface via direct inversion of spectroscopic data was reported.

Let us now turn to the potential energy surface. All the studies in dynamics obviously depend upon having high quality potential energy surfaces determined by high quality electronic structure calculations which are represented using analytical functions. Besides, the potential energy surfaces and the various couplings must be available in the global domain of physical interest. It is not the goal of this paper to discuss ab initio calculations and global modeling of single- and multi-sheeted potential energy surfaces which constitute an entire field by themselves [185–188]. Nevertheless, it is important to mention two points directly related to our subject. First, the calculation of global potential energy surfaces is restricted to systems with only few degrees of freedom since it requires a prohibitive amount of computing time. It is extremely important for our purpose to stress that this situation can be remedied by focusing on phenomena for which we assume that only a limited number of degrees of freedom with large amplitude motions are involved which carry most of the information. Under these conditions it is reasonable to invoke simplifying approximations for the other degrees of freedom which permit the construction of simple model Hamiltonians. It should be emphasized that the potential of applications for such an approach can then be extremely large. As noticed above for the kinetic energy operator, the reduced dimensionality (rigidly or adiabatically) constraints are very widespread (and essential for large systems) and can lead to accurate results, for instance, in spectroscopy. An improvement of the model can also be envisioned by means of the reaction path Hamiltonian approaches of Miller and Coworkers [189, 190] which makes use of a harmonic approximation locally defined along one or several reaction coordinates (in its simplest version, this approach resorts to one or several reaction coordinates coupled to a frozen bath [190]). Finally, another very fruitful model has been formulated in the group of Heidelberg [21, 23, 24] to tackle multistate-multimode vibronic couplings (see also reference [191, 192] if a motion of large amplitude such as an isomerization is involved). These examples prove that is not inaccessible to circumvent the bottleneck associated by calculating global potential energy surfaces. Second, as aforementioned for the kinetic energy, It is important to insist on the fact that the potential operators must also be given in a form which is well adapted to the numerical methods used in dynamics. For instance, in order to ensure a fast evaluation of the mean-fields which are built at every time step, a full efficiency of the MCTDH algorithm requires the Hamiltonian to be provided as a sum of products of operators, which act on a 'limited' number of degrees of freedom exclusively, or more precisely, which act on an MCTDH particle which may have 1–4 degrees of freedom

$$V = \sum_{r=1}^{s} c_r \prod_{\kappa=1}^{p} v_r^{(\kappa)} , \tag{5}$$

where $v_r^{(\kappa)}$ operates on the κ-th particle (combined mode) and where the c_r are numbers. Note, however, that the correlated discrete variable representation by Manthe [193] allows one, to a certain extent, to eliminate this problem for MCTDH, see also [194] for the disadvantages of this latter approach. The product form, Eq. 5, is not only useful for MCTDH. Indeed, in order to avoid the calculation of high-dimensional integrals and to substantially alleviate the requirement of core memory, it is necessary (and even essential for large systems) to deal with operators in which the coordinates are partially decoupled as in each term of Eq. 5. For instance, in the the canonical Van Vleck perturbation theory applied by Sibert and coworkers to CH_3OH [67], the Hamiltonian operator is also rewritten in a direct product form. For a direct method such as the Lanczos algorithm, the 'limited' number of degrees of freedom in the operators can be of course larger since the direct method only requests the results of acting the Hamiltonian operator on a given vector (not the evaluation of a matrix) but the difficulty also appears for large systems since the vector itself becomes very large (see [64] for a discussion about this point and how to reduce the core memory requirement for a large system with the Lanczos algorithm). To circumvent this difficulty in a systematic way, Jäckle and Meyer [195, 196] devised a scheme called *potfit*, to recast any function into the required product form. The potential is fitted through an expansion in natural potentials which show a great similarity to the SPFs in the expansion of the MCTDH wavefunction. The original *potfit* procedure was restricted to the transformation to products of operators, which act on one degree of freedom only. Recently [130], we have generalized *potfit* to enable us to expand the potential into multi-dimensional functions and applied it to nine-dimensional problems [130, 173]. In the future, we envisage sharpening this theroretical tool in order to exploit the *potfit* procedure to directly fit ab initio points in a systematic manner within the MCTDH package from Heidelberg. It is already feasible to interpolate with *potfit* the values of the potential energy surfaces even if they are given on a coarse product grid. The low-dimensional natural potential terms are then interpolated with either cubic (bicubic) spline or Fourier-series interpolations.

4 Examples of applications

In the two previous sections, a sample of algorithms have been presented which allow accurate resolutions of the Schrödinger equation in terms of wavefunctions, the systems being described by approximated Hamiltonian operators. To partially conclude one can say that, on one hand, it is extremely difficult to conceive that a unique approach could treat all the phenomena encountered in dynamics. It is clear that multidimensional quantum reactions dynamics is still in its beginnings. In particular, if a very high precision for the calculations is necessary, very specific programs will still (and probably always) be inescapable. On the other hand, the existence of a package such as the MCTDH from Heidelberg [82], which has been applied to almost all the domains in quantum dynamics, demonstrates that general tools are not out of reach. MCTDH can indeed optimally tackle a wide area of problems which are strongly impacted by quantum effects and do not require an extremely high accuracy (such as calculations of reaction rate constant involving a proton transfer or the simulation of spectra strongly affected by a conical intersection). But it is also versatile enough to treat problems with a higher precision. In this latter case, this approach cannot however replace a specific program if the problem demands an extremeley high precision. However, one can consider that the developement of general tools along with particular codes specific to particular systems is more complementary than contradictory. In a general way, all these methods require that the Hamiltonian should be available and they all have an exponential type of scaling depending on the dimensionality. It is then reasonable to anticipate that these methods will be restricted in the near future (say the next 15 years) to systems including a few degrees of freedom with large amplitude motion plus possibly a few dozens of degrees of freedom with near harmonic amplitude motions (note, however, that the multilayer formulation of MCTDH by Wang and Thoss [95] can treat 1000 degrees of freedom with a model Hamiltonian). However, it should again be emphasized that the number of applications within such a general framework could be extremely large. It is precisely the aim of this section to illustrate this assessment by presenting a selection of possible applications of very high chemical interest.

4.1 Intramolecular vibrational-energy redistribution

The first example is the IVR, which is a fundamental energy transfer mechanism that occurs in all polyatomic molecules [197,70]. The IVR process can have a decisive influence on the overall dynamics and reactivity of a molecular system. The specificity and efficiency of IVR pathways are extremely diverse depending on the molecular structure of each system. At energies just above the threshold for a given bond dissociation, vibrational energy is required to flow between vibrational modes into the reaction coordinate. This energy flow can be the limitating factor in determining the rate of unimolecular dissociation. It is crucial to determine the timescale corresponding to the energy flow through the system. It is also decisive to modelize this energy flow and to find some general rules that governs this phenomenon. IVR study aims at answering questions such as: Starting from a well-defined initial excitation in the CH stretch, where does the energy go? How long does it take to get there? To what extend is this flow state or mode specific? What is the detailed mechanism leading to this flow? What is the nature of the dynamics that is induced in the bath modes when they acquire energy from the hot spot? It is intuitive to think that the energy located at time $t = 0$ in a given vibrational mode will be redistributed in a statistical way through all the vibrational modes of the system. It is also natural to postulate that the IVR timescale is directly linked to the state density according to the Fermi Golden Law. However, different experimental proofs demonstrate that IVR does not necessary increase with the state density. It is now established that the IVR mechanism is more subtle and difficult to analyze [8,9]. Morevover the scope of applications is far larger since the knowledge of the IVR is an essential prerequisite [198] for the induction of chemical reactions by means of vibrational mode-selection with lasers. Indeed, one dream of the chemists [198] is to employ ultrashort laser pulses to control reactions in a way that only the desired products occur. Experimentally, it is now feasible to create optimal ultrafast light pulses which prepare the targets leading the molecular systems on to a desired reaction path [199,200]. Much theoretical effort must therefore be directed toward modeling these systems and to further develop general methods of molecular quantum dynamics which, coupled with quantum chemistry calculations, could predict the vibrational states leading to a desired reaction path. Recently, it was demonstrated that MCTDH is a very efficient tool to investigate the IVR in relatively large systems such as HONO (six degrees of freedom) [128,129], Toluene [130] and Fluoroform (nine degrees of freedom) [131]. For such systems quantum mechanical effects are very strong and a quantal approach is crucial to correctly describe the dynamics. The HONO molecule is characterized by a reversible Cis/Trans isomerization which complicates the dynamics in the molecule [201–203]. We have confirmed that the Cis/Trans process proceeds faster than the opposite direction and that there are very large differences between the energy redistributions after different initial excitations stressing the strong mode selectivity of HONO. In the Fluoroform and Toluene systems, the energy flow from CH stretching to the various other modes occurs in very different time-scales and therefore multiple IVR pathways. For the molecule of Fluoroform, we have reinvestigated the dominant feature in the CH overtone spectra, i.e., the strong Fermi resonance between the CH stretch and the two FCH bends. New simulations very high in energy have been performed establishing the crucial role played by the FCH bends, which constitute an energy reservoir. Note that the IVR of the CH chromophore is of high interest since it can be probed in myriads of molecular environments and has pronounced absorption signals [204–207]. For Toluene, the situation is even more complicated since it is not yet clear if the complex structure of the experimental CH spectra can be ascribed to the CH stretch-bend Fermi resonance (like for Fluoroforme) or to a coupling with the almost free internal rotation of the methyl group [208,209]. Interestingly enough, for HONO and Toluene (and more recently for HCF_3 [173]), we have implemented the corresponding kinetic energy operators in polyspherical coordinates. This proves that curvilinear coordinates can be routinely implemented in the MCTDH package without any technical difficulty. As aformentioned, in order to simulate the experimental processes, it is mandatory to combine the dynamics with quantum chemistry calculations [128,129]. Even more important, we are now in a position to implement the corresponding dipole momenta which are available [210] as well as the overall rotation of the molecules and then to truly simulate the dynamics during the interaction with the laser pulses for systems such as HONO, H_2CO, HFCO, HCF_3. We have already started such a simulation including the implementation of the potential and dipole operators, the kinetic energy in polyspherical coordinates for the H_2CS molecule [211] in the MCTDH package. These works are encouraging since they could show that it is feasible to develop a systematic study of the IVR and laser control for numerous molecular sytems and could offer a precious framework for a synergy between experimenters and theoreticians in this field. Such joint experimental/theoretical studies are essential to establish unambiguously the connection between the experimental signals that are measured and the molecular dynamics that is to be observed. Note finally that we have also recently implemented the calculation of cumulative reaction probabilities [118] in the Heidelberg MCTDH package. The calculation of these quantities which allows direct computing of thermal reaction constants [116], could complete these studies in IVR by highlighting the selectivity of the processes (for instance the Cis/Trans isomerization in the HONO molecule).

4.2 Towards larger organic and biological systems

This section is dedicated more to our hopes for the future. In particular, we are convinced that it is now very important to explicitly show to the community of chemists our ability to treat the quantum dynamics of processes of high chemical interest including motions of large amplitude and a relatively large number of degrees of freedom. Let us consider two possibilities. First, the homogeneous metal-assited or -catalyzed reactions [212,213]. The homogeneous metal-assited or -catalyzed reactions have an oustanding importance both industrially and synthetically: they yield products of special interest in large-scale manufacturing or owing to their properties as powerful drugs, antibiotics, or anticancer reagents [214]. For instance, olefin insertion into M–H bond and the reverse process, the β-hydrogen elimination, represent elementary reaction steps which are of fundamental importance to many transition-metal-catalyzed processes such as hydrogenation, hydroformylation, and olefin polymerization [213]. In order to delve into this domain of phenomena several dynamics treatments are necessary. For instance, it is indeed of high interest to make simulations which amount to the dynamics after a coherent excitation of the system to a transition-state structure by a fast optical transition from hypothetical neutral species and then to calculate the corresponding spectrum and the speed of the isomerization. However, up to now, most of these were based within a classical mechanical framework although quantal effects can play a very important role (coherence and tunneling effects). Recently, Bittner and Köppel [215] have performed the very first one-dimensional quantal calculation on the system $[CpRh(PH_3)H(C_2H_4)]^+$. However, realistic dynamical calculations must incorporate more than one degree of freedom (let say from three to ten degrees of freedom) to simulate the insertion of the ethylene into the Rh–H bond and its inverse, the hydrogen elimination process. To start simulations which include more degrees of freedom one should derive the constrained kinetic energy operator in polyspherical coordinates [182,164,181]. Most of the degrees of freedom will be frozen, i.e., subjected to rigid constraints, and curvilinear coordinates (here polyspherical coordinates) are to be utilized to describe the motions of large amplitude. Of course, an exact quantum calculation of the the full potential energy surface treating all the internal degrees of freedom is not possible for the time being, due to the computational demands. However, here, one bond is broken and another one is formed, whereas others exhibit rather modest changes. According to the reaction-path profile [215], the chemical reaction involves few degrees of freedom with very large amplitude motions and several with rather small ones. Therefore, a locally harmonic expansion of the energy surface around the minimum energy surface will be possible for the potential operator as in the approaches of Miller and coworkers [189,190]. Such studies are good examples of applications of quantum mechanical dynamics to systems which could truly interest chemists. Second, another class of greatly important and fascinating phenomena are the conversion of light into mechanical motion at the atomic scale in organic systems. Even more important, they can be involved in biological phenomena such as the retinal in rhodopsin which is isomerized during the first step in vision [216–218,192] or the pair porphyrin-quinone, which forms the basis for photosynthesis [219]. Another example is the green fluorescent protein [220] from a jellyfish which allows one to look directly into the inner workings of cells. Indeed, this protein can be attached to an object that you are interested in watching (for instance a virus) and you can then follow the behavior of this object by shining ultraviolet light since the green fluorescent protein will then glow bright green. Note that these phenomena can include photo-initiated ultrafast electron and proton transfers. Until the early 1990s, the systematic computation of photochemical reaction paths was unpractical if not impossible. Focusing on a systematic investigation of the basic organic chromophores, alkenes, isolated and conjugated dienes, polyenes, and others, it was possible to compute the entire excited-state reaction path starting at the Franck-Condon structure and often ending at low-lying conical interections [221–223,219,224,225]. Note that these conical intersections are known to provide extremely efficient pathways for fast dynamical molecular processes. It should be emphasized that the study of these systems is only in its early stage [192,225,220]. In particular, the calculations are performed taking into account a 'chromophore' in the gas phase and thus neglecting the protein and solvent environments. However, such studies constitute the necessary and very important preliminary basis in order to undertake more complete simulations including the solvent and the protein for instance. Since a limited number of degrees of freedom are involved in these ultrafast photodynamics and since the quantum yields as well as the direct comparison with time-resolved spectroscopic measurements can only be realized out when direct-dynamics results become available, explicit simulations of the processes are nowadays possible and very highly desirable and could be performed in a systematic way in the near future with the Heidelberg MCTDH package [82] for instance.

4.3 The water clusters

Finally, we would like to discuss a very important but also very difficult problem: the study of water clusters in order to highlight the importance of developing quantum mechanical codes dedicated to very particular systems. The study of water in all phases remains a central activity nowadays since there is no potential energy surface yet which could perfectly reproduce the properties of the liquid, solid, and aquous solutions. The difficulty comes from these properties depending on the hydrogen bonding interactions and their dynamics. Far-infrared vibration-rotation-tunneling experimental spectroscopy has generated a wealth of highly detailed data for small water clusters [6,7]. The two- and three-body interactions are essential for modeling these condensed phases since they are the major components of the force field. The accurate determination of the water pair potential has given rise to a close collaboration between Leforestier in our group and R. J. Saykally and coworkers from Berkeley [7, 226]. The determination of the dimer water potential energy surfaces are obtained via direct inversion of experimental spectroscopic data. The method developed by Leforestier for the dynamics, i.e., the calculation of the rovibrational spectrum associated with the inter-molecular motions, is based on a time-independent direct approach (a 'pseudospectral split Hamiltonian' method as described in Sect. 2) using the Lanczos algorithm. It is important to dwell on the fact that quantum effects on the nuclear positions, zero-point energy effects or tunneling barriers to hydrogen bond rearrangement, can have a significant influence on the calculated properties [7]. This work is of particular interest for our subject for two reasons. First, it illustrates the relevance of a constrained approach in a particular case. Indeed, most of the calculations have been performed with a rigid monomer description due to the great difference in the frequencies of vibration between the intramolecular and intermolecular modes. This rigid constrained approach has already provided very important results. In addition, we have recently introduced an adiabatic model to explicitely consider the internal motions of each monomer (stretches and bends) [181, 184]. The aim is to fit a 'flexible' dimer potential in order to better describe the difference of the OH length in the different condensed phases. Moreover, the flexibility can be extremely important to study processes such as vibrational predissociation, or dimerization in the gas phase. The numerical calculations have already shown that the adiabatic flexible approach leads to a much better agreement with experiment than does the rigid version, as exemplified by the standard deviation on all observed frequencies being reduced by a factor 3 [184]. It was then shown that monomer flexibility is essential in order to reproduce the experimental transitions. Second, the far-infrared spectroscopy of the water dimer is probably a representative example of a molecular problem which cannot be treated with a general program. The water monomers rearrange their hydrogen bonding orientations through quantum tunneling among eight minima. This effects a splitting of each dimer rovibrational level into a manifold of tunneling states, these splittings can be very small ($<1.0\,\mathrm{cm}^{-1}$) and are measured precisely by high-resolution spectroscopy [7]. The experimental data are then extremely precise and the fitting of the potential necessitates a very large number of calculations of the full spectrum with such an accuracy (all the levels must, in addition, be present in each calculation). That is why a very specific program optimized for this particular problem was here inescapable.

5 Conclusions and outlook

To conclude, we would like to return to the comparison with the electronic structure theory. It is noteworthy to point out that, like in the electronic problem, numerous approaches based on a variational principle such the (time-dependent or time-independent) SCF, CI-SCF or CASSCF and even coulped cluster [227] methods have been developed in dynamics. Morever, likewise as in the electronic structure theory the widely known density theory provides an alternative to the methods based on a variational principle, the dynamics of the systems can be handled also by other approaches. These are based on very different approximations such as the adiabatic reduction method, the wave operator method using the Bloch formalism or the Feynman's path integral formulation of time-dependent quantum mechanics described in Sect. 2. Again, as for the eletronic problem, these quantum mechanical approches are obviously limited to a restricted number of degrees of freedom. Note, however, that the number of applications, within such a framework, could be extremely large and we here refer the reader to our 'partial' conclusion at the beginning of Sect. 4. For larger systems, it is thus possible to anticipate the necessity to envision mixed algorithms as it was necessary to devise methods such as the quantum mechanics molecular mechanics approach for the electrons. The remainder of this conclusion is dedicated to this long-term perspective.

Indeed, as mentioned in the introduction, this paper did not aim at discussing semiclassical approaches [15, 16, 19, 17, 20] in spite of their great importance in modern dynamics. It can, however, be remarked that the semiclassical are often based on a description of the quantum effects in terms of classical trajectories which offer a better insight into the physical phenomena. On the one hand, the use of classical trajectories offers the advantage of better scalings with the dimensionality of the systems and could open the possibility of evaluating the potential 'on the fly' like in the ab initio molecular dynamics methods (Car-Parinello molecular dynamics). On the other hand, the rigorous quantum mechanical methods presented in this paper lead to exact results and it is then possible to perfectly estimate and control the convergence. One can indeed never be certain of the accuracy of an approximate method except by comparison with the true quantum mechanical approach (see the work by Jasper and Truhlar [228] for a very recent systematic comparison between semiclassical and quantum methods). We may conclude with a question regarding the developement of a general approach in quantum dynamics dedicated to carrying out large systems: is it not the solution for such a general approach to exploit these two methodologies together? Indeed, the concept of a 'quantum-*semiclassical*' methodology has emerged in articles by Burghardt and co-workers [229–231] in which the molecular systems are partitioned into a reactive core composed of a limited number of degrees of freedom which are treated with an accurate quantum mechanical approach as in the methods presented in this paper (such as MCTDH or the the multilayer or cascading formulation of MCTDH) and a subset of environmental modes which are handled more approximately (for instance with time-dependent Gaussian functions [231] or sinc functions [232]). It should be emphasized that we are not talking about mixed quantum–classical approaches which are much older. Such a global approach has two important underlying properties: it can fully account for quantum mechanical phase coherence (in contrast with the previous mixed quantum–classical approches) and it can be systematically improved to achieve numerically exact results by variational optimization of the system-environment partitioning. Pioneering works recently have demonstrated that it is possible to study, with such an hybrid quantum-semiclassical method, a spin–boson model including up to 100 degrees of freedom [233, 234]. Note also that the path integral methods by Makri and coworkers [135, 141] mentioned in Sect. 2 could also provide an excellent starting point for the prospect for rigorous quantum-semiclassical treatments. Generalizing such methods is obviously still an enormous task. However, we are convinced that such an approach is a very good way of thinking for the future in quantum dynamics.

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