

Time-dependent calculations on systems of chemical interest: Dynamical and kinetic approaches

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Abstract

We illustrate the state of the art in time-dependent calculations on systems of chemical interest. In particular, our exposition covers the Gaussian multiconfiguration time-dependent Hartree/variational multiconfiguration Gaussian approach in nuclear dynamics, where the scope is that of explaining dynamical effects in various physicochemical processes. Conversely, the Rice–Ramsperger–Kassel–Marcus/master equation kinetic methods are also examined, used to calculate rate constants of gas phase processes (used in the modeling of combustion, atmospheric, and astrochemical processes).

KEYWORDS

Gaussian multiconfiguration time-dependent Hartree, rate, Rice–Ramsperger–Kassel–Marcus, wavepacket

1 | INTRODUCTION

Systems of chemical interest can be studied from a time-independent or time-dependent viewpoint. Time-independent methodologies tend to deal with characteristic properties of the system under study which are invariant to initial conditions set by the experimenter. The calculation of ground state equilibrium properties of systems, energy level structure, statistical thermodynamical aspects such as densities of states and partition functions, all belong to this class. Even when time is used in such studies, it only serves as an auxiliary parameter without any real time-dependent process being modeled. Examples of this last case include time-dependent scattering wavepacket studies where time is only used as an integrated-over variable to express the time-independent Green function and time-dependent density functional theory (TD-DFT).

Conversely, when one wants to study properties of a system as it is prepared in specific initial conditions, time-dependent calculations are typically the way to proceed. When one is interested in the detailed distribution of energy among degrees of freedom and its consequences in terms of physicochemical effects, one can perform accurate quasiclassical or quantum dynamical calculations. Alternatively, if one is interested in statistically averaged evolution, one enters the realm of kinetics, where master equation calculations with the aim to calculate the rate of production of a specific species under well-defined conditions of temperature and pressure.

In this article, we present some of the current exploits in time-dependent calculations, both in terms of quantum dynamics and kinetics, illustrating them with some of our latest results.

2 | QUANTUM DYNAMICS

Even though quasiclassical dynamics tends to give qualitatively good results, it can never faithfully reproduce quantum effects. Thus, effects such as quantum tunneling, scattering resonances, interference, and so forth can only be quantitatively accounted for by the use of quantum dynamics.

For the case of quantum dynamics it is a wavefunction that is propagated in time, which is a function of the N degrees of freedom comprising the system of interest. When the number of degrees of freedom is limited (typically less than 6) an exact wavepacket calculation can be performed, whereby the basis set consists of discrete variable representation (DVR) functions localized throughout the whole coordinate space.^[1–6] Such an approach has been highly successful in the treatment of elementary (3- and 4-atom) reaction dynamics as it furnishes a detailed picture of the exact process of scattering.

When the number of degrees of freedom exceeds 5–6, an exact wavepacket calculation is, for all practical purposes, no longer feasible and alternative schemes are called for. One of the most

successful ones of recent years is the multiconfiguration time-dependent Hartree (MCTDH) approach.^[7] The main idea of the MCTDH scheme is expressing the wavefunction of the system according to the form

$$\Psi = \sum_J A_J(t) \Phi_J \quad (1)$$

with

$$\Phi_J = \prod_{i=1}^N \phi_{J,i}(r_i, t) \quad (2)$$

where N is the number of DOF and r_i is the coordinate of the i th DOF. Thus, both coefficients and basis functions depend on time and this feature permits a drastic reduction in the basis set. In fact, the MCTDH scheme has been used with considerable success in spectroscopy, photodynamics, and scattering problems. Recently, the MCTDH method has been extended to cover hundreds or thousands of degrees of freedom thanks to the “multilayer MCTDH” (ML-MCTDH) scheme, where the basis functions themselves are expressed in a MCTDH fashion in terms of functions of lower dimensionality.

Despite its successes, the MCTDH scheme is not without disadvantages. One of the major ones is that the potential energy needs to be written as a sum of products of factors, one factor for each degree of freedom. This represents a serious hindrance as fine topological features of surfaces can be masked by such a decomposition.

An alternative is direct dynamics calculations, permitting the use of the potential “on the fly,” evaluating it only as needed at the points relevant to the propagation. Such a possibility is offered by the approach commonly known as Gaussian MCTDH (G-MCTDH). Similar methodologies are known in the literature as “variational multiconfiguration Gaussian” (v-MCG). The central idea goes back to the work of Heller and it comprises the use of moving Gaussian functions as basis sets to describe nuclear wavefunctions. The naturally localized structure of Gaussian wavefunctions offers a natural connection with the classical picture of the dynamics and an idea of the configuration space spanned can be obtained by their trajectories.

Each Gaussian function i , in its most general form (for a single degree of freedom d) can be written as

$$g_i^{(d)}(\phi^{(d)}) = N_i^{(d)} \prod_{i=1}^{n_d} \exp\left(-a_i^{(d)} \phi_i^{(d)2} + b_i^{(d)} \phi_i^{(d)}\right) \quad (3)$$

Here $\phi^{(d)}$ denotes the corresponding coordinate, $N_i^{(d)}$ is the amplitude of the Gaussian, $a^{(d)}$ describes its width and $b^{(d)}$ its position in phase space. $b^{(d)}$ is generally a complex quantity, its real part describing the position and its imaginary part the momentum of the particular Gaussian. Generally, $N^{(d)}$ and $b^{(d)}$ both vary with time. The first evolution is in the spirit of all quantum dynamics calculations, whereas the second one permits a mobility of the basis set which can help reduce drastically its size (much in the same way as in ordinary MCTDH).

Having defined the situation for a single degree of freedom, one proceeds to form configurations (as in the MCTDH case) by multiplying Gaussians from different degrees of freedom, whereby the Gaussians now have the role of the SPFs. The multilayer scheme mentioned previously can also be used here, defining a hierarchy of groups of DOF in the same way as in the MCTDH case.

The method has been used in studying the dynamics of molecules such as pyrazine^[8] and benzene.^[9] Furthermore, a formulation of the method was presented by Shalashilin and Burghardt using trajectories of coupled classical and quantum variables^[10] whereas Mendive-Tapia et al.^[11] applied constant width variationally evolving Gaussian functions to study the nonadiabatic dynamics of fulvene. In general, the use of direct dynamics with coupled Gaussian trajectories is termed the direct-dynamics variational multiconfiguration Gaussian method (DD-vMCG). A review of direct dynamics methods can be found in Ref. [12]. Recently, Römer and coworkers have formulated a two-layer approach of the method (in an analogous fashion to the previously mentioned multilayer MCTDH [ML-MCTDH] scheme).^[13] A trajectory variant of the method (coupled coherent states or CCS) has recently been compared to the standard variational Gaussian method against a number of benchmarks.^[14] Within the context of direct dynamics methods, other methods include the *ab initio* multiple spawn (AIMS)^[15] method as well as the *ab initio* multiconfiguration Ehrenfest (AI-MCE).^[16] An excellent review has been recently written^[17] on the v-MCG method.

3 | KINETICS

Dynamical calculations aside, a chemist is mostly interested in processes whose outcome is statistically averaged over a particular kind of molecular ensemble (typically microcanonical or canonical). In areas such as combustion chemistry, atmospheric chemistry, or astrochemistry it can be assumed that the microprocesses have undergone a statistical averaging, subject to certain constraints peculiar to the system under study (typically a fixed total energy or a fixed temperature). As a result, it would take an enormous number of dynamical calculations to simulate adequately the system and most of the information generated would be of no use due to its highly detailed nature. Such situations constitute the realm of kinetics, where interest lies in rate constants for specific processes as a function of energy or temperature rather than a detailed description of the dynamical paths followed. Even though the adequacy of rate constants to describe chemical processes is not always to be taken for granted, as argued recently,^[18,19] the kinetic approach remains nevertheless the central method of tackling such problems.

Within the Rice–Ramsperger–Kassel–Marcus (RRKM) scheme, it is assumed that the reactants of an elementary reaction are found in the microcanonical ensemble, that is, the available energy is assumed to be uniformly distributed throughout all degrees of freedom of the molecule. Moreover, the usual “transition state” assumption, whereby a specific point along the reaction coordinate serves as a “point of no return” is also made. To carry out a microcanonical rate calculation,

only densities of states of reactants and transition state ($\rho(E)$) are needed as a function of energy. Given a tunneling probability $P(E, \epsilon)$ for a fixed total energy E and a fixed transition state internal energy ϵ (i.e. excluding the energy in the reaction coordinate), the cumulative reaction probability is obtained from the integral

$$N(E) = \int \rho_{TS}(\epsilon) P(E, \epsilon) d\epsilon \quad (4)$$

Thermal equilibrium of the reactants is taken into account by a Boltzmann averaging of many microcanonical rate constants. Care must be taken to include possible energy transfer from or to intermediates. The effect of energy loss of intermediates on a reaction rate can be enormous, as can be testified by cases such as $\text{OH} + \text{CH}_3\text{OH}$ ^[20]: if the initial addition intermediate is not thermalized (and the energy is below the barrier to reaction) then reaction (as opposed to back-dissociation) will only be feasible through tunneling and therefore back-dissociation is expected to prevail. Conversely, at the high pressure limit (and at low temperatures) the initial intermediate will be thermalized and back-dissociation will be energetically impossible, while tunneling to products, albeit improbable, will be the only feasible path.

In realistic cases, the pressure is neither low enough for a microcanonical calculation nor high enough for a fully canonical one. Such is the case, for example, in CRESU experiments,^[21] where some thermalization of intermediates takes place but full thermal equilibrium is not reached. Normally a simple model is assumed to account for such energy transfer such as the “exponential down” model used in the MESMER code.^[22]

Even when one performs calculations in the low or high pressure limit, a master equation needs to be resolved when (as is almost always the case) a reaction scheme is studied which involves many intermediates connected to each other through transition states. Matrix methods can be used to solve the master equation (see e.g., previous works^[23–26]).

4 | RESULTS

We hereby cite recent examples of calculations performed along the schemes previously exposed, that is, G-MCTDH/v-MCG calculations (using one or multiple electronic states) and, conversely, kinetics calculations using RRKM/Master equation methods.

4.1 | Dynamics results

As a preliminary method of validation of our G-MCTDH code, we have used it to obtain harmonic and anharmonic energy levels of the water and glycine molecules through propagation of Gaussians and extraction of the appropriate autocorrelation functions.^[27] In that study, we also proposed a method to calculate the representation error in the wavefunction.

Moreover, as shown in Ref. 28, we have performed a G-MCTDH study on the excited state dynamics of the phenol molecule using a multilayer G-MCTDH code written by us. The study takes into account

all 33 vibrational degrees of freedom of the phenol molecule, as well as the amplitude on three different diabatic electronic states, as calculated by Truhlar and coworkers.^[29,30]

Through these calculations, we were able to identify the three most activated background vibrations in the bound $^1\pi\pi^*$ state (all of them corresponding to C—C—C bending vibrational modes, in agreement with semiclassical calculations performed by Truhlar). Moreover, we were able to calculate the excitation spectrum of phenol using an Ehrenfest-like scheme (through the autocorrelation function) as well as the variation of surface populations after an initial out-of-plane displacement had been effected.

Recently, Richings and Worth have presented a practical diabatisation scheme to be used with the v-MCG and G-MCTDH schemes, through propagation of the diabatic-adiabatic transformation matrix,^[31] testing it on the dynamics of the butatriene cation. This method should permit propagation of Gaussian wavepackets without the necessity of a full diabatisation beforehand.

4.2 | Kinetic results

RRKM/Master equation calculations were recently performed in the modeling of the pyrolysis and combustion of *n*-butanol.^[32] A complicated reaction scheme, starting from the butanol molecule to all possible products of its pyrolysis was calculated and rate constants were calculated for each channel as a function of both temperature and pressure (as intermediates can exchange energy before further reaction). In all, 121 species and 658 reactions were treated.

A more recent example involves the reaction between the CN radical and the CH_3CN molecule^[33] at low temperatures. RRKM/ME calculations were essential for this system as they highlighted the competition between chemical reaction and collisional stabilization of the initial $\text{CN} \cdots \text{CH}_3\text{CN}$ van der Waals complex formed.

In addition, we have performed^[34–36] RRKM and master equation calculations on the formation of the cyanomethanimine, a molecule of considerable astrochemical interest as well as of prebiotic potential (as a probable precursor of adenine). The reaction we considered was the addition of the CN radical to the methanimine (CH_2NH) molecule. The reaction scheme is considerably complicated, as the CN radical has the possibility of adding to the C or to the N atom of the methanimine double bond. Moreover, when the CN radical adds to the C atom it has the possibility of forming either of two isomers, *E*- or *Z*-cyanomethanimine. As it turned out, *N*-cyanomethanimine was only formed in very small amounts whereas between the other two isomers *E*-cyanomethanimine is the one predominantly formed. The reason for this is the smaller potential barriers involved in the relevant unimolecular reactions.

5 | CONCLUSIONS AND PERSPECTIVE

Nowadays there is a multitude of ways in which the physical and chemical properties of matter can be studied theoretically. Time-

dependent methodologies, both for dynamics and kinetics, constitute an important part of this endeavor. Monitoring the temporal evolution of the system, apart from the purely calculational scope, aids visualization of the relevant properties in a unique way. As the degrees of freedom of the chemical systems of interest increases, without a corresponding increase in computational capabilities, the ingenuity of the researcher is challenged to devise valid approximations to tackle the problems that come up. Such methods can include a simple treatment in statistical averages (as done in the case of kinetics) or a suitable representation of a wavepacket and the corresponding time-dependent Schrödinger equation (as done in the G-MCTDH) scheme. It is in any case clear that, in the future, such calculations are expected to play a major role in the understanding of chemistry.

The dimensionality problem has always been a major bottleneck in dynamical calculations and detailed dynamical calculations have only been possible for systems comprising up to four or five atoms. This is not likely to change much in the future—there is no way of escaping the “exponential curse” plaguing exact calculations. Thus, quantities such as state-to-state differential cross sections, or angular momentum polarization vector distributions will only be able to generate (without drastic approximations) for small systems.

Conversely, dynamics is much more than these highly detailed quantities and includes insights such as the excitation of particular vibrational modes during a photoinduced process or the relative populations on different electronic surfaces (possibly connected through conical intersections). When the number of degrees of freedom is of an order higher than the hundreds, modeling using classical mechanics reigns supreme because of the undisputed computational advantage. However, quantum mechanical modeling is rapidly gaining ground. The MCTDH method, with the possibility of a hierarchical separation of the degrees of freedom, is already capable of treating tens of DOF. Its multilayer extension has already been shown capable of treating systems with DOF well into the hundreds. It is expected that the scope of these methods will be further broadened in the future and quantum mechanical modeling will continuously gain in popularity.

Conversely, even though MCTDH (as well as dynamics calculations) have been used to generate rate constants successfully, it is expected that the TST/RRKM scheme will remain the method of choice in the cases where detailed state information is not essential but only rates of formation/destruction of chemical species are concerned (as in atmospheric, combustion, or astrochemical modeling). It is now routine to include pressure-dependent processes of energy dissipation in complex schemes of chemical reactions using packages such as MESMER or Multiwell and thus solving the master equation for systems including tens of atoms is now a well-established practice.

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