Quantum dynamics with *ab initio* potentials

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Hua Guo,[1,a] [iD] Graham Worth,[2] [iD] and Wolfgang Domcke[3] [iD]

AFFILIATIONS

[1] Department of Chemistry and Chemical Biology, University of New Mexico, Albuquerque, New Mexico 87131, USA
[2] Department of Chemistry, University College London, London WC1H 0AJ, United Kingdom
[3] Department of Chemistry, Technical University of Munich, D-85747 Garching, Germany

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[a]Author to whom correspondence should be addressed: hguo@unm.edu

I. INTRODUCTION

Ever since the dawn of quantum mechanics, it has been recognized that molecular systems are intrinsically quantum and should be treated as such if a quantitatively accurate characterization of their spectroscopy and dynamics is to be achieved. A key early breakthrough was the separation of electronic and nuclear motion proposed by Born and Oppenheimer (BO),[1] which allows the solution of the total Schrödinger equation in two steps. The first step is the solution of the electronic Schrödinger equation at fixed molecular geometries, which is followed in the second step by a solution of the nuclear Schrödinger equation for the molecular energy levels for the bound states and/or scattering information in continua. The BO approximation naturally led to the concept of the potential energy surface (PES), which is the electronic energy obtained from the first step as a function of nuclear coordinates. Although increasing evidence has suggested that couplings between different electronic states lead to the breakdown of the BO approximation, the construct remains a powerful one even today.[2]

Electronic structure theory, which is often called quantum chemistry,[3] has advanced to a level that the energy of small to medium sized molecules can be determined with chemical (~1 kcal/mol), and sometimes spectroscopic (~1 cm^{-1}), accuracy. It thus allows the accurate determination of the PES over the relevant configurations. This new development essentially eliminates the uncertainty in the Born–Oppenheimer potentials, allowing meaningful comparisons of quantum dynamical calculations with experiment. Indeed, numerous examples have demonstrated that fully quantum mechanical characterizations of chemical dynamics on high quality PESs not only reproduce but also predict experiments. The emergence of these accurate PESs has also stimulated new quantum theory, both exact and approximate. Such quantum mechanical treatments of nuclear dynamics are necessary to understand quantum effects such as zero-point energy, resonances,

non-adiabatic transitions, tunneling, and interference effects, in uni- and bimolecular reactions and molecular spectroscopy.

This Special Topic issue on Quantum Dynamics with *Ab Initio* Potentials contains 53 contributions from the theoretical chemical physics community on new methods and applications of quantum mechanical characterization of dynamical processes using *ab initio* potential energy surfaces. These publications provide a snapshot of this vibrant field. In this Guest Editorial, we provide an overview of the field through these contributions and offer our prospects of future developments.

II. SUMMARY OF THE COLLECTION
A. Collisional dynamics on *ab initio* potentials in small systems

The development of accurate global PESs for collision dynamics represents a major recent advance in this field, which has benefited from the fast improving computational power and accurate electronic structure theory, such as coupled cluster and configurational interaction methods. In addition, machine learning tools, such as neural networks, have become a powerful driving force in representing the PESs from discrete *ab initio* points, as discussed extensively in a recent Special Topic issue in J. Chem. Phys.[4] In the current Special Topic issue, several highly accurate PESs are reported. Qu *et al.*[5] report *ab initio* potentials for several low-lying electronic states of NO, which allow the accurate determination of its rovibrational levels. Three-dimensional atom–diatom PESs include those for CN$^-$ + Rg (Rg = He and Ar) by Mant *et al.*[6] and for Ar + ArH$^+$ by Koner.[7] PESs for systems involving more than three atoms are more challenging. For non-reactive scattering, fortunately, it suffices to construct the interaction potential between rigid monomers, as done by Desrousseaux *et al.*[8] for the PN + H$_2$ system, by Ben Krid *et al.*[9] for the CH$_3$Cl + He system, and by Loreau *et al.* for the H$_2$O + HF complex. However, the involvement of vibrational

degrees of freedom in collisions, including bond breaking and forming processes, requires the inclusion of the relevant coordinates in constructing the PESs. To this end, Mazo-Sevillano et al.[10] demonstrate the construction of a full-dimensional PES for the H_2CO + OH reaction, which possesses multiple product channels, using a neural network approach. An important issue in such systems is the enforcement of permutation symmetry among identical nuclei, which is necessary for a correct description of the reaction dynamics. The permutation symmetry was adapted using permutation invariant polynomials as the input layer of the neural network.[11] Nandi et al.[12] construct PESs suitable for spectroscopic calculations for methane, H_3O^+, and N-methyl acetamide. They enforce permutation symmetry and use machine learning to correct a "cheap" surface at the density functional theory (DFT) level of theory to the accurate Coupled cluster singles and doubles (CCSD) level.

The construction of ab initio based PESs is not restricted to the adiabatic approximation. In the work of Wang et al.,[13] a diabatic potential energy matrix (DPEM) is developed for the lowest two singlet states and the lowest triplet state of NH_3, also using the permutation invariant polynomial-neural network approach. Such a DPEM is vital for studying dissociation dynamics, internal conversion, and intersystem crossing of the photoexcited molecule, beyond the BO approximation.

With these PESs, it is possible to compute quantum mechanically the rovibrational energy levels for a bound molecule or complex, as shown by Koner for the Ar_2H^+ system,[7] by Ben Krid et al.[9] for the CH_3Cl–He complex, and by Loreau et al.[14] for the H_2O–HF hydrogen bonded complex. In addition, these PESs facilitate dynamics investigations of collisions, including both inelastic and reactive scattering. For small systems, quantum mechanical treatments of scattering dynamics are possible and they are well suited for identifying quantum features in collision dynamics, such as resonances. Since resonances are exquisitely sensitive to the details of the PES, comparison with the experiment presents a stringent probe of the accuracy of the PES, as demonstrated by Shuai et al.[15] for the NO + H_2 system. Resonances are typically more pronounced at low collision energies, as averaging over the partial waves (namely, the impact parameter) is often insufficient to wash out the quantum features. Jambrina et al.[16] investigate the non-reactive scattering of $S(^1D)$ + H_2 and examine the impact of shape resonances on the differential cross section. Morita and Balakrishnan[17] explore the stereodynamics in the cold collision between HD and He. Gianturco et al.[18] investigate the rotationally inelastic scattering between HeH^+ and He. Desrousseaux et al.[8] study the rotational excitation of PN by collisions with H_2. In addition, Mant et al.[6] report vibrational quenching cross sections for CN^- by He and Ar.

Quantum reactive scattering calculations are much more challenging because the reactant and product channels cannot be easily described by the same coordinate system. So far, such elaborate studies have mostly been restricted to atom–diatom systems. To this end, Kendrick reports a time-independent quantum scattering calculation for the Li + LiNa → Li_2 + Na reaction under cold and ultracold conditions.[19] On the other hand, Sanz-Sanz et al.[20] investigate the nonadiabatic charge transfer reaction between H + H_2^+ using a wave packet method on an ab initio determined DPEM. Koner[7] studies the Ar + Ar'H^+ → Ar' + ArH^+ proton exchange reaction using both quantum and classical methods so that a comparison between the two can be made. In addition, the H^+ + H_2 reaction is investigated

by González-Lezana et al.[21] using a statistical model in which the energy randomization in the reaction intermediate is considered to be complete. Finally, the lifetime spectrum of the O_3^* species formed by collisions between O and O_2 is reported by Privat et al.[22]

For larger systems that are not amenable to quantum scattering calculations, the ring-polymer molecular dynamics (RPMD) method offers an accurate and efficient approach to rate calculations.[23] In RPMD, the atoms are represented by harmonically connected necklaces (ring polymers), which approximately include quantum features such as tunneling and zero-point energy.[24] Mazo-Sevillano et al.[10] use RPMD to determine the rate coefficient for the H_2CO + OH reaction on the ab initio PES and found good agreement with the experiment.

Advances in quantum scattering theory are also represented in the collection. For example, Liu et al. present a ten-dimensional quantum scattering model for X + $YCAB_2$ type reactions.[25] Zuo and Guo report a full-dimensional time-independent theory for inelastic scattering between open-shell diatoms and atoms.[26] New approaches within the multi-configurational time-dependent Hartree (MCTDH) framework are also proposed by Panadés-Barrueta and Peláez.[27] Finally, Zhang and Jiang investigate the mode specificity and bond selectivity in the scattering of H_2O and HDO from a rigid Cu(111) surface using a wave packet method.[28] These new developments are important for a more efficient and accurate treatment of quantum scattering in various conditions.

B. Spectroscopy with ab initio potentials in small and medium sized systems

An important use of quantum dynamics calculations is the simulation of light–matter interactions that can be used to assign spectra in terms of quantum states and molecular motions, help interpret time-resolved spectra by providing a description for observed timescales, and predict and describe non-equilibrium phenomena initiated by light. As demonstrated by the contributions to this Special Topic issue, exact solutions to the time-dependent Schrödinger equation using ab initio PESs are presently available to accurately treat small and medium sized molecules (around ten atoms) and using parameterized models up to hundreds of degrees of freedom.

The basic tool for these calculations is the use of suitable coordinates and time-independent basis functions, such as discrete variable representations (DVRs)[29] to represent the Hamiltonian and wavefunction. In six contributions, these are used to solve the time-independent Schrödinger equation to obtain eigenfunctions and energies to analyze and assign vibrational spectra. Ouyang and Xie[30] use a two-dimensional model based on "active modes" to study the propargyl cation ($C_3H_3^+$), important in combustion and astrochemistry. The results are used to assign the lines in the electronic absorption spectrum. Nejad and Sibert[31] study the trans-formic acid Raman spectrum, this time including all degrees of freedom. The key finding is the importance of the anharmonicity of the torsional motion in the eigenenergies. The results allow a detailed assignment of recent spectra, including some new lines and isotopic effects. The eigenstates of CH_4F are studied by Zhao and Manthe,[32] who introduce a new "extended space" DVR to treat the singularities in the standard rovibrational kinetic energy operator. This is shown to be an efficient, stable way to calculate the lowest 13 states.

Wang and Carrington[33] use state-of-the-art time-independent calculations with symmetry adapted functions and a Wigner DVR to remove the kinetic energy singularities in a study on the eigenstates of the methane–water complex. Line strengths and symmetries are obtained and used to assign available spectra. Finally, Šmydke and Császár[34] calculate 600 eigenstates of ammonia, emphasizing the importance of the coordinate choice to provide a good description. With the help of reduced density matrices, these states are compared to data from a line list, which shows that previous assignments were inconsistent.

A second set of papers all solve the time-dependent Schrödinger equation to address the dynamics of a molecular system after photo-excitation. For these, a key feature is the need to go beyond the BO approximation and include what are known as nonadiabatic effects. Ariyageadsakul and Baeck[35] use a set of three coupled three-dimensional *ab initio* DPEM to study the photodetachment of the NH_3Cl^- anion. By solving both the time-independent and the time-dependent Schrödinger equations, they are able to analyze the branching ratios into the two reaction channels as a function of isotopic substitution and initial vibrational excitation.

As exemplified in this Special Topic issue, the use of model Hamiltonians carefully parameterized using *ab initio* data, such as the vibronic coupling model,[36] has become a powerful tool for describing nonadiabatic dynamics, which is an inherently multi-dimensional problem. The multi-configurational time-dependent Hartree (MCTDH) method[37] is used in the majority of these studies, and has become the standard way to extend the grid-based solution of the time-dependent Schrödinger equation to large molecules. A good example of this approach is given by Kanakati and Mahapatra[38] in their study on the pentafluorylbenzene cation. Six states and all degrees of freedom are included in the calculation in which photoelectron spectra and relaxation dynamics are calculated and compared to experiments. Fumanal *et al.*[39] study the photophysics of a manganese complex, the so-called photoCORM, using an 11 state model with 16 degrees of freedom parameterized using Time-dependent density functional theory (TDDFT). These complexes release CO on photo-excitation and are used in medical diagnostics. The simulations provide mechanistic details for the energy transfer leading up to the CO release. Aleotti *et al.*[40] provide a number of different parameterizations of a vibronic model Hamiltonian for pyrene using different levels of electronic structure theory. Using the multi-layer variant of MCTDH (ML-MCTDH), they could treat seven excited states and all 49 vibrational degrees of freedom and assess the accuracy of the different models. Di Maiolo *et al.*[41] again use the ML-MCTDH method and study an even larger system. Using a parameterized vibronic coupling model, the photo-initiated charge transfer in a fullerene–oligothiophene complex with up to 300 vibrational modes is studied. This full quantum treatment provides the population dynamics and gives a detailed picture of the coherent transfer that takes place in these materials.

Jahn–Teller and similar symmetry-determined vibronic coupling problems can also be treated in this way. Vasilyev *et al.*[42] set up and study a five state, nine mode model of Niobium tetrafluoride to look at the importance of Jahn–Teller and pseudo-Jahn–Teller coupling in its photo-excited dynamics. Viel *et al.*[43] study the Jahn–Teller effect in the photodetachment of the nitrate anion (NO_3^-), extending the standard vibronic coupling model to higher orders, and building in the full symmetry of the problem,

resulting in a full spectral assignment for this atmospherically relevant molecule. Mukerjee *et al.*[44] study the Jahn–Teller coupling in a five-state model of the benzene cation. They use a model Hamiltonian formed from the quantum chemistry data with a sophisticated diabatization scheme, and in place of the MCTDH algorithm used by the other authors to solve the time-dependent Schrödinger equation using a set of propagated Hermite polynomials to form a time-dependent DVR (TDDVR) grid. The results provide a thorough analysis of the vibronic coupling in this molecule and its effect on the observed spectrum.

Two contributions use what are termed "direct dynamics" methods to study photo-excited processes. In these, the PESs are not calculated before the dynamics simulations are performed, as must be done for grid-based methods. Instead, the surfaces are obtained "on-the-fly" using quantum chemistry calculations as the nuclear wavepacket evolves in time. Such techniques provide a great efficiency for multi-dimensional problems as the surfaces are only calculated where required. They also allow the full range of motions to occur, which usually is not possible with parameterized models. Makhov and Shalashilin[45] use the multiple-cloning algorithm to study the photodissociation of pyrrole, looking at the importance of vibrational pre-excitation of the N–H bond. Multiple-cloning uses Gaussian wavepacket basis functions that follow trajectories to solve the time-dependent Schrödinger equation, as does the variational Multi-Configurational Gaussian (vMCG) method used by Christopoulou *et al.*[46] This latter contribution studies the nonadiabatic dynamics in the allene cation, but focuses more on the formal aspects of the method, presenting details of the algorithm used to provide the DPEM which is stored as a database of points.

The frontier of chemical dynamics at present is being driven by the new light sources in Europe, Japan, and the USA. These provide light pulses down into the attosecond range, allowing the tracking of not only the nuclear dynamics but also the electronic motion itself. This new field is exemplified in the collection by the contribution of Schnappinger and de Vivie-Riedle.[47] They include the electron dynamics in a study on NO_2 by using a basis set of electronic eigenfunctions to couple the electron density to grid-based nuclear dynamics. In this way, the possibility of controlling the nuclear dynamics by directly controlling the electronic wavepacket with an IR pulse can be studied.

In addition to the applications described above, several contributions introduce new methodologies that demonstrate the lively progress presently taking place in the field. The development of a new DVR by Zhao and Manthe,[32] the extension of the ML-MCTDH algorithm to use a Gaussian wavepacket basis by Di Maiolo *et al.*,[41] and the improvements to direct dynamics calculations using the vMCG method by Christopoulou *et al.*[46] have already been mentioned. Two further contributions are purely methodological. The first, by Wodraszka and Carrington,[48] reformulates the MCTDH algorithm based on a multi-dimensional collocation that allows the easy evaluation of complicated multi-dimensional potentials. Its ability is demonstrated by calculating accurate vibrational eigenfunctions for CH_3 and CH_4. The second describes a new method for coupled electron-nuclear dynamics. Sasmal and Vendrell[49] present a new formulation, again of the MCTDH algorithm, using a second quantization representation to provide a basis for the electrons. The method is representation-free for the electronic motion (neither diabatic nor adiabatic) and has the potential for the

accurate and efficient description of the full molecular motion in a strong laser pulse. A demonstration is made using HeH^+ as a test case.

C. Semiclassical and quasiclassical approximations to quantum dynamics and laser-driven systems

A substantial fraction of the contributions to this Special Topic issue is devoted to the development and application of semiclassical or quasiclassical approximation methods. Since the computational cost of numerically exact time-independent quantum scattering calculations or time-dependent quantum wave-packet calculations inevitably scales exponentially with the number of nuclear degrees of freedom, it is essential that alternative computational strategies are developed, which exhibit a more favorable scaling with system size. The assessment of the quantitative accuracy of computationally efficient semiclassical or quasiclassical approximations for chemically relevant molecular systems has been an outstanding challenge in theoretical chemistry for decades. The recent development of chemically accurate multi-dimensional PESs together with the possibility of accurate quantum dynamics calculations on these surfaces provides unprecedented possibilities for the scrutinizing of the quantitative accuracy of established as well as novel semiclassical or quasiclassical approximation methods.

Five articles of this Special Topic issue are concerned with the calculation of vibrational spectra with semiclassical methods. Conte *et al.* report the construction of a full-dimensional (24 vibrational degrees of freedom) permutationally invariant ground-state PES of glycine at the DFT/B3LYP level, which covers all eight conformers.[50] Using the semiclassical initial value representation method[51] and diffusion Monte Carlo simulations,[52] Conte *et al.* compute accurate zero-point energies of the eight conformers of glycine. Aieta *et al.* implement the semiclassical initial value representation on-the-fly at the DFT/B3LYP level to compute anharmonic eigenfunctions and vibrational spectra of protonated glycine.[53] Gandolfi *et al.* study the vibrational spectroscopy of N-methylacetamide using an available full-dimensional PES and a machine learning algorithm, which identifies approximately separable subspaces of vibrational modes.[54] Liu *et al.* present a novel machine learning algorithm for the construction of the effective force and the effective mass matrix from path-integral calculations prior to the integration of the semiclassical Liouville dynamics.[55] Rognoni *et al.* use semiclassical and quasiclassical approximations to explore the effects of aqueous solvation on the vibrational spectra of various hydrogen-bonded water clusters up to $(H_2O)_{21}$ using an accurate dedicated water PES.[56] They use these data to assess the accuracy of a typical system-bath model in which the central water molecule is solvated by the surrounding water molecules. The work of Petersen *et al.*, applying optical control theory to a tunneling problem, completes this survey of semiclassical phase-space dynamics.[57]

Nonadiabatic transitions on multiple coupled PESs add an additional non-classical feature in photochemical dynamics. A rigorous and accurate treatment of quantum dynamics on multi-dimensional nonadiabatically coupled PESs is particularly challenging because of the large excess energy that becomes available in radiationless electronic transitions. Therefore, approximate quasi-classical trajectory-based methods that can be implemented on-the-fly with *ab initio* electronic-structure calculations are

potentially powerful tools for the exploration of photochemical reaction mechanisms.

Six articles in this Special Topic issue are concerned with quasiclassical simulations of nonadiabatic photochemistry. The stochastic trajectory surface hopping model first introduced by Tully and Preston[58] is by far the most widely used quasiclassical approximation to nonadiabatic dynamics due to its robustness and ease of implementation. Several variants of the trajectory surface-hopping algorithm are employed in the six studies in this issue. Zhang *et al.* study intersystem crossing dynamics using the "coherent switching with decay of mixing" variant of trajectory surface hopping for a small system, thioformaldehyde. The results are illuminating in so far as they reveal the emergence of Fermi's Golden Rule rate formula from a first-principles atomistic simulation in the limiting case of weak coupling (in this case, spin–orbit coupling).[59] Kanno *et al.* employ the Zhu-Nakamura flavor of trajectory surface hopping to the nonadiabatic photodissociation of the carbon dioxide dimer cation with on-the-fly complete active space self-consistent field (CASSCF) electronic-structure calculations.[60] Fortino *et al.* explore the photophysics of a large system, chlorophyll-a, with fewest switching surface hopping[61] at the TDDFT/CAM-B3LYP level.[62] Ibele *et al.* demonstrate the possibility of performing essentially exact (within the CASSCF electronic-structure model) on-the-fly *ab initio* multiple spawning simulations[63] for three representative medium-size exemplars of photochemistry dominated by conical intersections.[64] By providing a tool for the fully quantitative assessment of the accuracy of trajectory surface hopping approximations in on-the-fly *ab initio* settings, this work is paradigmatic for the present Special Topic. Two articles address the inclusion of the interaction with strong external laser fields in trajectory surface hopping simulations. Heindl and Gonzalez validate the treatment of the dynamics driven by short laser pulses with fewest-switching surface hopping for linear vibronic coupling models of sulfur dioxide and thiocytosine by comparing with quantum MCTDH calculations.[65] Schiro *et al.* study trajectory-based dynamics in the exact factorization formalism for a two-state one-mode model system in a continuous wave (CW) laser field.[66]

Two somewhat solitary applications of nonadiabatic quantum dynamics complete this Special Topic issue. Jasik *et al.* investigate the nonadiabatic two-channel decay dynamics (electron detachment and dissociation) of the silver dimer anion by a fully *ab initio* implementation of the Fermi Golden Rule formula.[67] Sun *et al.* demonstrate the computation of several nonlinear femtosecond time-resolved signals reflecting nonadiabatic dynamics at multiple conical intersections using the Davydov ansatz for an *ab initio* based three-state nine-mode model of the pyrazine molecule.[68]

III. CONCLUSION AND PROSPECTS

Although quantum dynamics has been in existence for some time, it remains a vibrant research field in chemical physics, as amply demonstrated by this Special Topic issue. For small benchmark systems, the improvement of electronic structure theory and machine learning techniques have, in recent years revolutionized the way global PESs are constructed, which have in many cases demonstrated chemical or near spectroscopic accuracy. Coupled with novel quantum scattering algorithms, we have reached a stage

at which molecular spectra and scattering cross sections of small systems can be accurately predicted with high confidence. These advances allowed the exploration of new regimes, such as cold and ultracold collisions, where quantum effects are pronounced. For these small benchmark systems, the future focus is likely to be placed in several directions, including nonadiabatic effects, resonances, and tunneling. These new challenges require novel ways to treat quantum dynamics, with various levels of approximations, in order to defeat the exponential scaling law of quantum mechanics.

In photo-excited systems, huge progress has been made in the last few years and methods are available to treat nuclear motion in large molecules including all quantum effects. These simulations are key in the understanding of state-of-the-art time-resolved laser experiments, even moving down into the attosecond regime where the interplay between electronic and nuclear motion can be observed. In contrast to the electronic ground-state, however, quantum chemistry methods are not as well developed for excited states. One major focus at present is thus the benchmarking and improvement of these calculations. Another area of development is in the representation of the coupled PESs, where machine learning techniques are also starting to play a significant role. While MCTDH and ML-MCTDH are currently dominating the field of rigorous time-dependent quantum wave-packet calculations for multidimensional systems, related as well as novel computational methods, which aim at the efficient pruning of the relevant Hilbert space, such as the density matrix renormalization group (DMRG), matrix product state (MPS), or tensor train (TT) techniques, may reduce or even eliminate the exponential scaling of the cost of accurate quantum dynamics calculations.

Despite the progress made in exact quantum dynamics simulations, approximate methods will have a growing role to play in the simulation of reaction dynamics. They are able to access larger systems at significantly reduced cost and allow the flexibility and simplicity required for a molecular interpretation of quantum phenomena. In the field of *ab initio* trajectory based dynamics calculations, we can expect a competition between the currently popular on-the-fly strategy and the prior construction of computationally inexpensive high-dimensional PES via the interpolation of large sets of *ab initio* data, for example, with a neural network. When high accuracy or long time propagation are desired, the bottleneck in terms of computing time and memory requirements likely will be in the electronic structure calculations, which may give strategies based on accurate precomputed PES an advantage.

As demonstrated by the papers in this Special Topic issue, quantum dynamics simulations using *ab initio* PESs have become a general tool that is able to treat a wide variety of physical problems. They provide support for experimental work probing the fundamental behavior of molecules, and no doubt will continue to grow in power and application in the near future.

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