

**Practical Problems with Dynamical Nuclear Quantum Effects
through Semi-classical Methods**

ABSTRACTS

Ring Polymer Molecular Dynamics

David Manolopoulos

Ring polymer molecular dynamics (RPMD) has emerged as a practical way to include quantum mechanical zero point energy and tunnelling effects in molecular dynamics simulations of condensed phase systems which is especially useful for the calculation of diffusion coefficients and reaction rate coefficients. In this talk, I shall briefly summarise the theory, implementation, applications, and limitations of RPMD, and then end by mentioning some exciting recent developments (including thermostatted RPMD, nonadiabatic RPMD, and ring polymer contraction in ab initio RPMD).

**Semiclassical “Divide-and-Conquer” Method for Spectroscopic Calculations of
High Dimensional Molecular Systems**

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We present a new semiclassical “divide-and-conquer” approach tailored for quantum dynamics simulations of high dimensional molecular systems. We show how the method is tested by calculating the quantum vibrational power spectra of water, methane and benzene, three molecules of increasing dimensionality for which benchmark quantum results are available. Then, we applied it to C60 fullerene, a system characterized by 174 vibrational degrees of freedom. Results show that the approach accurately account for quantum anharmonicities, purely quantum features like overtones, and the method does not suffer from the removal of degeneracy when the molecular symmetry is broken.

Quantum Dynamics with a Smolyak sparse-grid scheme. Applications to Hénon-Heiles potential and H₂ clathrates

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The use of Smolyak sparse grids, $G_{L_c}^{SG}$, in quantum dynamics is an approach that pushes the limits of the current calculations based on a multidimensional grid. The main idea [1] is to substitute a single large direct-product grid by a sum of small direct-product grids (See below). The number of terms in the sum may be large and is controlled through the Smolyak parameter, L_c . In this context, it can be used to perform multidimensional integrals or directly as a multidimensional interpolation scheme.

$$G_{L_c}^{SG} = \sum_{L=[L^1, L^2, \dots, L^n]}^{L_c - n + 1 \leq |L| \leq L_c} (-1)^{L_c - |L|} \cdot C_{n-1}^{L_c - |L|} \cdot G_{L^1}^1 \otimes G_{L^2}^2 \otimes \dots \otimes G_{L^n}^n \quad (1)$$

In quantum dynamics, Avila and Carrington were the pioneers in developing efficient implementations. [2-5] They used a Smolyak grid scheme with 1D-nested grids ($G_{L^i}^i$), which not only reduces the total number of grid points but also avoids the need to perform the calculations on each direct-product grid ($G_{L^1}^1 \otimes G_{L^2}^2 \otimes \dots \otimes G_{L^n}^n$) in the sum (Eq. 1).

Our previous implementations [6,7] avoided the need of 1D-nested grids and was extended to the use of multidimensional grids ($G_{L^i}^i$) in the direct-product grids. [7] However, it required the explicit summation over direct-product so that some identical calculations were performed several times. This had an unfavorable impact on the numerical efficiency, without, however, preventing large calculations from being performed. Recently, we have introduced a new implementation, in which we keep the sums of the direct-product grids but perform the calculations sequentially over the various dimensions. Consequently, the repetition of identical calculations is avoided, which considerably improves the numerical efficiency. Vibrational levels on High dimensional Hénon-Heiles potential will show the efficiency of this approach.

Furthermore, we extend the use of the Smolyak scheme to the grids associated to the spherical harmonic. Therefore, we were able to use this approach to quantum simulations of the H₂ translation/rotation motions in a rigid or partially flexible water clathrate cage.

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- [2] G. Avila and T. Carrington, J. Chem. Phys., 131 (2009) 174103
- [3] G. Avila and T. Carrington, J. Chem. Phys. 134 (2011) 054126
- [4] G. Avila and T. Carrington, J. Chem. Phys. 135 (2011) 064101
- [5] G. Avila and T. Carrington, J. Chem. Phys. 139 (2013) 134114
- [6] D. Lauvergnat and A. Nauts, PCCP 12 (2010) 8405
- [7] D. Lauvergnat and A. Nauts, Spectrochim. Acta Part A 119 (2014) 18

Colored Noise Thermostats for Path Integral Approximations to Dynamical Observables

Mariana Rossi

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Generalized Langevin Equation (GLE) thermostats have been used very effectively as a tool to manipulate and optimize the sampling of thermodynamic ensembles and the associated static properties. Here [1] we show that a similar, exquisite level of control can be achieved for the dynamical properties computed from thermostatted trajectories. In this contribution, we focus on the use of colored noise thermostats in the context of approximate path-integral-based models of quantum nuclear dynamics. We develop quantitative measures of the disturbance induced by the GLE to the dynamics and demonstrate that a custom-tailored GLE can alleviate some of the artifacts associated with these techniques, especially the spurious broadening appearing in vibrational spectra calculated from thermostatted path integral molecular dynamics [2]. We show that this technique improves the quality of results regarding vibrational dynamics of molecules, liquids and solids, albeit still showing different spurious artifacts.

[1] M. Rossi, V. Kapil, M. Ceriotti, J. Chem. Phys. accepted (2017).

[2] M. Rossi, M. Ceriotti, D. Manolopoulos, 140, 234116 (2014).

The stochastic self consistent harmonic approximation: theory and examples

G. Ribeiro, R. Bianco, L. Paulatto, I. Errea, M. Calandra and F. Mauri

The self-consistent harmonic approximation is an effective harmonic theory to calculate the free energy of systems with strongly anharmonic atomic vibrations. Its stochastic implementation has proved to be an efficient method to study, from first-principles, the anharmonic properties of solids [1,2] including proton quantum effects [3,4]. Moreover it allows to access the free energy as a function of average atomic positions (centroids) and it can be used to study quantum or thermal lattice instabilities. Indeed, according to Landau's theory, the knowledge of the second derivative of the free energy (i.e. the curvature) with respect to the centroids in a high-symmetry configuration allows the identification of the phase-transition and of the instability modes.

In this talk I will present the stochastic implementation of the self-consistent harmonic theory [1,2]. I will also show that it is possible to obtain the exact analytic formula for the second derivative of the free energy in the self-consistent harmonic approximation for a generic atomic configuration [5]. The analytic derivative is expressed in terms of the atomic displacements and forces in a form that can be evaluated by a stochastic technique using importance sampling. I will discuss examples showing how the method works in the fields of high-temperature superconductors [3,4], charge density wave materials [6] and thermoelectrics [7].

[1] First-principles theory of anharmonicity and the inverse isotope effect in superconducting palladium-hydride compounds, I Errea, M Calandra, F Mauri, Physical Review Lett. 111 (17), 177002

[2] Anharmonic free energies and phonon dispersions from the stochastic self-consistent harmonic approximation: Application to platinum and palladium hydrides, I Errea, M Calandra, F Mauri, Physical Review B 89 (6), 064302

[3] High-pressure hydrogen sulfide from first principles: a strongly anharmonic phonon-mediated superconductor, I Errea, M Calandra, CJ Pickard, J Nelson, RJ Needs, Y Li, H Liu, Y Zhang, ... Physical review letters 114 (15), 157004

[4] Quantum hydrogen-bond symmetrization in the superconducting hydrogen sulfide system, I Errea, M Calandra, CJ Pickard, JR Nelson, RJ Needs, Y Li, H Liu, ... Nature

[5] Second order structural phase transitions, free energy curvature, and temperature-dependent anharmonic phonons in the self-consistent harmonic approximation: theory and stochastic implementation, R Bianco, I Errea, L Paulatto, M Calandra, F Mauri, arXiv:1703.03212

(Wigner) Sampling of quantum initial conditions and classical trajectories: a match made in purgatory?

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Several approximate methods for quantum time-correlation functions combine exact sampling of the thermal density matrix with classical propagation of an ensemble of trajectories to compute observables. Results from this family of approaches are often surprisingly accurate, but both steps involve theoretical and practical problems. In this talk, I shall first focus on the sampling of initial conditions, and consider in particular a relatively new method to obtain correlated distributions of positions and momenta from the Wigner density. Some comments on the difficulties of combining exact sampling with classical dynamics, aimed mainly at fostering discussion on the issue of non-conservation of the probability density...et al., will follow.

- [“Computing thermal Wigner densities with the phase integration method”](#), J. Beutier, D. Borgis, R. Vuilleumier, and S. Bonella, *The Journal of Chemical Physics*, 141, 084102 (2014); doi: 10.1063/1.4892597
- [“Quantum dynamical structure factor of liquid neon via a quasiclassical symmetrized method”](#), Michele Monteferrante, Sara Bonella, and Giovanni Ciccotti, *The Journal of Chemical Physics* 138, 054118 (2013)
- [“Gas phase infrared spectra via the phase integration quasi-classical method”](#), J. Beutier, M. Monteferrante, S. Bonella, R. Vuilleumier & G. Ciccotti, *Molecular Simulation*, 40:1-3, 196-207, (2014)
- [“Linearized symmetrized quantum time correlation functions calculation via phase pre-averaging”](#), M. Monteferrante, S. Bonella, and G. Ciccotti, *Molecular Physics*, DOI:10.1080/00268976.2011.619506

Langevin simulations with quantum thermal baths and zero-point energy leakage

Simon Huppert, Fabien Briec, Yael Bronstein, Hichem Dammak, Marc Hayoun,
Philippe Depondt and Fabio Finocchi

The quantum thermal bath (QTB) has been presented as an alternative to path-integral-based methods to introduce nuclear quantum effects in molecular dynamics simulations. The method has proved to be efficient, yielding accurate results for various systems. However, the QTB method is prone to zero-point energy leakage (ZPEL) in highly anharmonic systems. This is a well-known problem in methods based on classical trajectories where part of the energy of the high-frequency modes is transferred to the low-frequency modes leading to a wrong energy distribution. In some cases, the ZPEL can have dramatic consequences on the properties of the system. Thus, in this presentation we investigate the ZPEL by testing the QTB method on selected systems with different degrees of complexity in order to study the parameters that influence the leakage, as well as its influence on the vibrational properties of the system. We will show that the ZPEL can be significantly reduced in many cases by increasing the damping coefficient [1]. A very similar effect is obtained when QTB is used only to sample initial conditions for classical trajectories, in which case ZPEL can be partially avoided by reducing the duration of the trajectories. When using sufficiently high values for the damping coefficient, the expected energy distribution among the vibrational modes is ensured. In particular, the structural properties can be well-reproduced. The dynamical properties should be regarded with caution although valuable information can still be extracted from the vibrational spectrum, even for large values of the damping term.

[1] “Zero-Point Energy Leakage in Quantum Thermal Bath Molecular Dynamics Simulations”, F. Briec, Y. Bronstein, H. Dammak, P. Depondt, M. Hayoun, F. Finocchi, *J. Chem. Th. Comp.* 2016, 12, 5688.

Generalised Langevin Equation : from classical to quantum

Lev Kantorovich

In this talk I will consider a few ideas enabling derivation of stochastic equations describing dynamics of an open system surrounded by a harmonic heat bath.

I will first briefly dwell on the classical case when the equations of motion for atoms of the open system have a form of the Generalised Langevin Equation (GLE) with a memory friction term and multivariable Gaussian random force whose correlation function is proportional to the friction kernel. Our current implementation of these equations is based on introducing fictitious extra degrees of freedom, which emulate the environment and evolve according to white noise memory-less Langevin equations.

Next I'll consider two approaches when both the open system and the bath are treated fully quantum-mechanically. Both methods solve the Liouville equation for the reduced density matrix of the open system; however, this is done in completely different ways. The first method, albeit approximate, results in a GLE for average atomic positions in the open system and is similar to the classical case (although the random force is shown to be non-Gaussian). The second method, based on integration of the degrees of freedom of the bath using influence functional approach, leads to an exact solution and the corresponding stochastic Liouville equation for the reduced density matrix with real time forward-backward and imaginary time propagations (similar to the Konstantinov-Perel's counter in the NEGF formalism), each described by Hamiltonians with different stochastic fields. In this method the quantum bath is effectively "replaced" by classical stochastic Gaussian processes on real and imaginary times. The stochastic fields are related to each other via a set of non-trivial correlation functions. An efficient way of generating these will also be discussed.

Fully Quantum Description of Water Clusters: Combining Variational Quantum Monte Carlo with Path Integral Langevin Dynamics

Michele Casula, F. Mouhat, S. Sorella, R. Vuilleumier, A.M. Saitta

We introduce a novel approach for a fully quantum description of coupled electron-ion systems from first principles[1]. It combines the variational quantum Monte Carlo (QMC) solution of the electronic part with the path integral formalism for the quantum nuclear dynamics. Nuclear quantum fluctuations are included via a set of fictitious classical particles (beads), linked by harmonic interactions, whose dynamics is driven by accurate ionic forces computed at the QMC level. The stochastic noise affecting the QMC forces contributes to thermalize the particles in a path integral Langevin dynamics framework.

Our general algorithm relies on a Trotter breakup between the dynamics driven by ionic forces and the one set by the harmonic inter-bead couplings. The latter is exactly integrated, even in the presence of the Langevin thermostat, thanks to the mapping onto an Ornstein-Uhlenbeck process. This framework turns out to be also very efficient in the case of noiseless (deterministic) ionic forces. The new implementation is first validated on the Zundel ion (H_5O_2^+) by direct comparison with standard path integral Langevin dynamics calculations made with a coupled cluster potential energy surface. We then apply our method to the protonated water hexamer, where its thermal distribution functions are provided for the first time by a framework which explicitly includes electron correlation, together with thermal and quantum nuclear effects.

Observation of quantum effects in liquid water and glasses

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The specific and unusual properties of liquid water have been studied and discussed since long time, but many questions remain opened and puzzling particularly at low temperature and at the vicinity of glass transitions. Theory and simulation are mostly achieved by effective potentials which reproduce relatively well either structure, dynamics or thermodynamic properties but without a real knowledge of the intermolecular potential.

Isotope effects are extremely large, although they are not necessarily due to quantum effects as, most of the time, they can be qualitatively explained by the amplitude of librations of hydrogen atoms, which are thermally activated. For example, important isotope effects on the glass transition water – low density amorphous ice have been interpreted as due to quantum effects but remain questionable.

In other cases, quantum effects play a major role but not fully understood. This is the case of molecular dissociation and electrical conduction by collective hopping processes, such as the Grothuss mechanism. Many experiences tackle the properties of hydrogen bonds and of the extended network that they form. In particular, NMR and neutron scattering perform specific measurements of the dynamics of hydrogen atoms which are essential for comparisons with ab initio simulations.

We will summarise the main problems to be solved from the experimental point of view.

Nuclear quantum effects in atomic clusters through quantum thermal baths and path-integral molecular dynamics: successes and failures

Florent Calvo

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In this contribution we present some applications of quantum thermal baths (QTB) to describe finite atomic systems at low temperature. We first assess the performance of QTB versus more conventional methods based on the path-integral molecular dynamics (PIMD) framework to evaluate vibrational spectra. The QTB approach appears indeed reasonable in producing semiclassical initial conditions that capture the most important delocalization effects, not only at thermal equilibrium but also in out-of-equilibrium situations of an excitation due to an electric field.

The QTB method applied to water clusters turns out to yield a qualitatively erroneous description of its thermodynamical behavior due to strong zero-point energy leakage between intra-molecular and inter-molecular modes. However, the predicted infrared spectrum surprisingly does not suffer too much from this issue.

Finally, we discuss a more qualitative application of the QTB method as an exploration tool of energy landscapes associated to the $T=0$ vibrational ground state wave function, inherent structures being obtained along the way. Fluctuations among the inherent structures are related to the intrinsic stability, and we show in the case of cationic neon clusters how such fluctuations can be used to interpret experimental mass spectra.

Anharmonic contribution to the equilibrium isotopic fractionation of dissolved ionic species, as evidenced by Li isotopes

Magali Benoit, R. Dupuis, M.E. Tuckerman and M. Meheut

Equilibrium fractionation of stable isotopes involving dissolved species is a key phenomenon in fields ranging from electrochemistry and medicine to environmental science and geochemistry [1,2,3]. Natural lithium isotopic signatures, for example, provide information about oceanic crust alteration and continental weathering.

Computational approaches to equilibrium isotopic fractionation must consider the pure quantum nature of the phenomenon and employ appropriate methodology. Unfortunately, theoretical predictions of isotope fractionation have lagged behind experiment due, primarily, to a reliance on the harmonic approximation. One might expect this approximation to fail in describing isotope fractionation of ions between solid and liquid phases, yet a recent study showed that it accurately predicts the isotope fractionation of Mg^{2+} between aqueous solution and carbonate materials [3], thus suggesting its general reliability for dissolved ionic species.

Here, we consider the isotope fractionation of Li between aqueous solution and phyllosilicate materials to demonstrate that the harmonic approximation breaks down severely, overestimating the isotope fractionation by 30% in this case [5]. We further show that the use of Feynman path integrals (PIs), which generate exact quantum statistics for a given model, yield results in good agreement with both experimental data and natural observations. Importantly, PI calculations can be carried out at temperatures that are experimentally inaccessible yet relevant for natural phenomena and they provide atomistic insights into the origin of anharmonic effects.

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[4] Pinilla et al., *Geochim. et Cosmochim. Acta* 163, 126 (2015)

[5] R. Dupuis, M. Benoit, M.E. Tuckerman and M. Meheut, submitted to *Acc. Chem. Res.*

Proton-conducting perovskites : quantum effects

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Oxides with perovskite structure (e.g. BaZrO₃, BaCeO₃, BaSnO₃) are potential candidates as electrolytes for protonic ceramic fuel cells (PCFCs) because, after doping on the B site by elements of lower valence (e.g. Y, Gd, In, etc), these materials are able to catch and dissociate water, forming protonic defects. Under this hydration reaction, they become protonic conductors. The diffusion of protons is subject to quantum effects even at high temperature (600-800 K), in the semi-classical regime, where an H/D isotopic effect on the activation energy of the conductivity ($E_D - E_H \sim 0.03-0.06$ eV) is experimentally observed. This effect may be simply explained by the difference in the zero-point energies (ZPE) of H and D. We will show how it can be modeled by density-functional calculations in the case of BaSnO₃ [1]. At lower temperature (below 300 K), quantum effects may be more complex. In the framework of GGA-PBE, we show that proton transfers in BaSnO₃ are probably adiabatic, taking place by the ground state in configurations with a very low transfer barrier, and a protonic ZPE above the barrier (no tunneling). We discuss the possibility of tunneling at very low temperature, by comparing proton transfers in these oxides to hydrogen jumps in some metals such as Nb or Ta. Finally, based on our recent implementation of the Blue-Moon Ensemble Method (coupled to Path-Integral Molecular Dynamics) in the ABINIT code, we illustrate these concepts on an inter-octahedral proton transfer in BaCeO₃ at 200 K.

[1] G. Geneste, A. Ottochian, J. Hermet, G. Dezanneau, Phys. Chem. Chem. Phys. **17**, 19104 (2015)

Diffusion of Oxygen atoms on cold surfaces : Evidence of quantum tunnelling ?

François Dulieu, Marco Minissale, Emanuele Congiu et al

LERMA, (Université de Cergy Pontoise, Sorbonne Universités, UPMC Univ. Paris 6, PSL Research University, Observatoire de Paris, UMR 8112 CNRS)

When the density of interstellar clouds increases the interaction of the gas with the surface of dust grains becomes a major agent of the molecular evolution of the matter. We have performed experiments studying the physical and chemical properties of O atoms, the second reactive species in the interstellar medium, on cold (7 – 100 K) amorphous surfaces.

At low temperatures, the interaction of adsorbates with passive amorphous surfaces is dominated by Van der Waals interactions. O can react with many others adsorbates (H, CO, H₂CO ...) and firstly among them, with itself. Therefore it is not straightforward to disentangle the diffusion from the reactivity of O. We have exposed different doses (from 5% of a layer to full coverage) of O(³P) atoms to various surfaces held at different temperatures. We observed the formation of O₃ and O₂ in variable amounts via IR spectroscopy or via Temperature Programmed Desorption.

We performed a first set of experiments in the 6 – 25 K regime [1]. Assuming that the reactive system of O is diffusion-limited, we found that diffusion does not exhibit an Arrhenius dependency with the temperature, which would indicate a diffusion mediated by thermal hopping. On the contrary, the diffusion behaviour is very well fitted by a crude model (square barrier) of quantum tunneling diffusion, although our model derived a rather high diffusion barrier (>500 K) and a low barrier width (0.7 Å). The quantum tunneling diffusion is certainly an active process, and the critical temperature below which it's dominant with respect to thermal diffusion is actually as high as 20 K [2].

Therefore we have performed a new set of experiments focused on the 40 – 70 K temperature range [3], in order to check if the all the indications found previously of high diffusion (and desorption) barriers were solid findings. We then proposed a new experimental method to directly derive the correlation between diffusion and desorption of reactive species. In this study we used a simple model based upon thermal diffusion. We find a very constrained set of couples of binding and diffusion energies. These “high temperature” couples of barriers, however, cannot explain the apparent diffusion and reactivity found at very low temperature.

Finally, we studied the diffusion and reactivity of O on amorphous surfaces between 7 and 70 K. This is an observation over one order of magnitude in temperature. The scenario of the quantum tunneling of O atoms at low temperatures still stands, and would deserve advanced theoretical studies to be pursued.

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[3] Minissale, M., E. Congiu, and F. Dulieu. 2016. “Direct Measurement of Desorption and Diffusion Energies of O and N Atoms Physisorbed on Amorphous Surfaces.” *Astronomy & Astrophysics* 585 (January): A146. doi:10.1051/0004-6361/201526702..

Practical quantum reaction-rate methods: instanton theory and ring-polymer molecular dynamics

Stuart C. Althorpe

The rates of hydrogen-tunnelling reactions can be enhanced by orders of magnitude by quantum tunnelling, and zero-point energy effects can also play a crucial role. Here we describe two non-heuristic, practical, methods for including such quantum effects in calculations of thermal reaction rates. Instanton theory goes back a very long way [1], but has had a new lease of life recently, thanks to its connection with discrete path-integral or 'ring-polymer' methods. [2,3] It provides a steepest-descent approximation to the exact quantum rate, which is practical to apply to many gas-phase (or surface) reactions involving hydrogen-transfer. However, instanton theory cannot be used for reactions in solution, where the rate is no longer dominated by a single instanton path. For such systems, a practical alternative approach is ring-polymer molecular dynamics (RPMD) rate-theory, [4] which involves running a classical MD simulation in the extended space of the ring-polymers. One can show that the RPMD rate is a good approximation to a quantum generalization of classical transition-state theory, [5] which obtains an approximation to the exact quantum rate from the instantaneous flux out of a delocalised distribution located near the barrier top.

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Semiclassical Propagation: Hilbert Space versus Wigner Representation

Sergei D. Ivanov

Two topics will be covered. First, a unified viewpoint on the van Vleck and Herman-Kluk propagators in Hilbert space and their recently developed counterparts in Wigner representation would be presented. Based on this viewpoint, the Herman-Kluk propagator in the Wigner representation is conceptually the most general one. Nonetheless, the working expressions that define its numerical protocol are mathematically proven here to coincide with those for its well-established Hilbert-space counterpart up to a mere technical flexibility in choosing the Gaussians' width for the underlying coherent states beyond minimal uncertainty. This flexibility is investigated numerically on prototypical potentials and it turns out to provide neither qualitative nor quantitative improvements. Thus, utilizing the Wigner representation for semiclassical propagation leads to the same performance as employing the respective most-developed Hilbert-space methods [1].

Second, a general question of mapping a realistic system onto a Caldeira-Leggett (CL) model (and thus onto a generalized Langevin equation) would be discussed [2-5]. The CL model is the cornerstone for a plethora of methods ranging from fully quantum to purely classical ones. Thus, if such a mapping was established then it would provide a unified framework for reduced dynamics of realistic systems. Furthermore new (semiclassical) methods can be tested against the aforementioned ones on equal footing, resulting in establishing the 'platform for investigating methods'.

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2. F. Gottwald, S. D. Ivanov, O. Kühn, "Applicability of the Caldeira-Leggett Model to Vibrational Spectroscopy in Solution", *J. Phys. Chem. Lett.* **6**, 2722 (2015) [[LINK](#)]
3. F. Gottwald, S. Karsten, S. D. Ivanov, O. Kühn, "Parametrizing linear generalized Langevin dynamics from explicit molecular dynamics simulations", *J. Chem. Phys.* **142**, 244110 (2015) [[LINK](#)]
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5. F. Gottwald, M. Bonfanti, R. Martinazzo, S. D. Ivanov, O. Kühn, "Note: Caldeira-Leggett model describes dynamics of hydrogen atoms on graphene", *J. Chem. Phys.* **145**, 1126101 (2016) [[LINK](#)]

Accelerating quantum dynamics simulations using machine-learning

Scott Habershon

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I will describe recent research which has employed machine-learning methods, principally Gaussian Process Regression (GPR), in order to develop approximations of potential energy surfaces in quantum dynamics simulations. I will highlight three examples of recent work which have shown how GPR can be used to accelerate quantum simulations, focussing on (i) Gaussian wavepacket-based methods for wavefunction propagation [1], (ii) the multiconfigurational time-dependent Hartree (MCTDH) method [2,3], and (iii) path-integral methods [4]. I will conclude by describing ongoing work and associated challenges in developing “on the fly” quantum simulation methods for studying complex systems ranging from molecular photodynamics to reactions at interfaces.

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[2] Direct grid-based quantum dynamics on propagated diabatic potential energy surfaces, G. W. Richings and S. Habershon, *Chem. Phys. Letters*, in press (2017; doi: 10.1016/j.cplett.2017.01.063)

[3] Direct quantum dynamics using grid-based wavefunction propagation and machine-learned potential energy surfaces, G. W. Richings and S. Habershon, submitted to *J. Chem. Theory Comput.* (May 2017)

[4] Accelerated path-integral simulations using ring-polymer interpolation, S. J. Buxton and S. Habershon, in preparation (June 2017)

Bohmian quantum dynamics: from model systems to molecular simulations

Ivano Tavernelli

The non-relativistic quantum dynamics of nuclei and electrons is solved within the framework of quantum Bohmian Dynamics (QBD) using the adiabatic representation of the electronic states. In the first part of this talk, I will derive an on-the-fly trajectory-based QBD molecular dynamics algorithm [1,2], which is able to capture all nuclear quantum effects that are missing in the traditional approaches based on classical trajectories (mixed quantum-classical and semiclassical approximations). The use of correlated trajectories produces a quantum dynamics, which is in principle exact and computationally efficient [2]. In the second part of the talk, I will present an extension of a method that allows to perform QBD in the full, unconstrained, phase space of molecular systems [3]. The problem of solving quantum hydrodynamic equations using trajectories in high dimensions is addressed using an expansion of the nuclear amplitude in atom centered Gaussians that are propagated along the quantum trajectories. In particular, I will investigate the adiabatic limit of this theory, even though the full nonadiabatic case is also accessible [3]. The method is first tested on the H₂ molecule and then applied to the study of the proton transfer dynamics in the phase space of the molecular complex (H₃N-H-NH₃)⁺.

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