# Mathematical Methods in Quantum Molecular Dynamics

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ABSTRACT. The workshop on "Mathematical Methods in Quantum Molecular Dynamics" has brought together chemists, mathematicians, and physicists developing new mathematical methods for studying the motion of atoms in molecules and in reacting chemical systems. Thereby, the main focus was on dynamical properties of quantum molecular systems in many dimensions. The development of mathematical methods for quantum molecular systems is an intrinsically interdisciplinary field of research, whose progress can be improved by opening additional channels of communication between the different disciplines. The workshop has contributed to advance the exchange of ideas related to development of new methods as well as the creation of personal links between mathematicians and theorists in chemistry and physics.

## Introduction by the Organizers

The workshop on "Mathematical Methods in Quantum Molecular Dynamics" was devoted to mathematical methods for solving the many-body Schrödinger equation in high dimensions. Such methods are essential in quantum molecular dynamics. 32 talks were presented by an interdisciplinary group of speakers comprised of mathematical physicists, numerical analysts, and chemical physicists.

The many-body Schrödinger equation of quantum molecular dynamics poses several mathematical challenges: The curse of the high dimensionality is accompanied by high frequency oscillations in time and space. When non-adiabatic coupling, which prevents one from solving separate Schrödinger equations for electrons and nuclei, is important, the problem is even harder. Conical intersections of potential

energy surfaces introduce new complexities. Many numerical approaches require solving non-linear equations, even though the original Schrödinger equation is linear. The interdisciplinary mixture of participants, some of whom had met at an earlier Oberwolfach workshop, stimulated the development of new ideas and a common vision. Some of the younger participants presented new provocative ideas.

The mathematical methods considered can be grouped as numerical methods, analytical methods and modelling methods. The main topics and results in these three overlapping groups have been the following:

*Numerical methods:* Many of the numerical methods discussed at the workshop are designed to solve high-dimensional Schrödinger equations for nuclear vibrations and are based on tensor decompositions. At the workshop, participants discussed various aspects and extensions of the multi-configuration time-dependent Hartree method (Hans-Dieter Meyer and Uwe Manthe). Other tensor decompositions (CP and Tensor Train) used with some form of rank reduction were used to solve both the time-dependent and the time-independent Schrödinger equations (Tucker Carrington, Ivan Oseledets, and Victor Batista). Meshless discretization based on variationally determined Gaussian ansatz functions were proposed and applied to non adiabatic systems (Irene Burghardt and Graham Worth) as well as analysed in terms of accuracy and structure preservation (Christian Lubich). Highly successful stochastic approaches were presented for the electronic Schroedinger equation (Ali Alavi). Errors introduced by using Monte Carlo to compute integrals were studied and analysed (Reinhold Schneider). Radial basis function methods were discussed for the interpolation of high-dimensional potential energy surfaces (Elisabeth Larsson) and the solution of the Schroedinger equation (Tucker Carrington). Domain decomposition methods were proposed for studying the effects of coupling between a molecular system and a solvent (Benjamin Stamm). For the time-discretization, geometric numerical integration (Jiri Vanicek) was addressed as well as higher order splitting methods (Vasile Gradinaru). Improved adiabatic surfaces were used with numerical methods to compute highly accurate energy levels of $H_2$ (Edit Matyus).

*Analytical methods:* The analytical methods considered included space adiabatic theory (Stefan Teufel and Ben Goddard). Analytic methods were also applied to the semi-classical analysis of Fourier integral operators based on continuous frame decompositions (Clotilde Fermanian-Kammerer).

*Modelling methods:* Semi classical path integral methods were analysed (Stuart Althorpe) and numerical path integral techniques were applied to highly complex systems (Pierre-Nicholas Roy). Quasi-classical modelling was carried out for nuclear non-adiabatic transitions (Bill Miller). Quantum-classial coupling was addressed from the structural point of view (Ray Kapral). It was shown that by adding approximations similar ideas can be used to model very complex systems (Aaron Kelly).

Most participants made a significant effort to make their presentations comprehensible and as a result there was considerable discussion both during the talks and in the afternoons. The heterogeneous background of the workshop participants and the many open and constructive discussions after the talks and during the breaks made it possible to build important bridges.

## Workshop: Mathematical Methods in Quantum Molecular Dynamics

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# Abstracts

## Two strategies for computing vibrational spectra (molecules with up to 18 atoms): tensor formats and collocation

TUCKER CARRINGTON

In the first part of my talk, I presented the Hierarchical Intertwined Reduced-Rank Block Power Method (HI-RRBPM) for solving the vibrational Schrödinger equation. The memory cost of this method scales linearly with the number of atoms in the molecule. The HI-RRBPM has been used to compute vibrational spectra of uracil and naphthalene, with 12 and 18 atoms, respectively. It uses a tensor product basis but: 1) it is not necessary to store a tensor-product-basis matrix representation of the Hamiltonian matrix; 2) it is not necessary to store vectors whose length is equal to the size of the tensor-product basis. In the HI-RRBPM, a shifted power method is used to build a basis. In the original RRBPM, after each matrix-vector product, the rank of the resulting tensor is reduced. This rank reduction is costly. The cost is reduced by breaking the problem into pieces and using the RRBPM in a hierarchical fashion. It can be further reduced by intertwining the rank reduction and the matrix-vector products. Rakhuba and Oseledets modified two aspects: they use a different tensor format (Tensor Train) and a different eigensolver (inverse iteration). Multiconfiguration time-dependent Hartree also uses a tensor format (Tucker format). Methods that exploit tensor formats and rank reduction can be used only if the potential energy surface (PES) has a simple form, e.g. CP format or Tensor Train format.

In the second part of my talk, I presented new ideas for using collocation to solve the Schrödinger equation when the PES does not have a simple form. When the potential energy surface does not have a special form (e.g. a sum of products), it is common to use quadrature to compute a vibrational spectrum. Direct-product quadrature grids are most popular. The size of a direct-product grid scales exponentially with the number of atoms and it is not not possible to store values of the PES for molecules with more than 5 atoms. I presented collocation methods we are developing. Collocation has advantages: 1) point selection is less important; 2) no integrals, no quadratures, no weights; 3) easy to use with complicated kinetic energy operators; 4) it can be used with any (the best possible) coordinates and basis functions; 5) in many cases fewer collocation than quadrature points are required; 6) the length of the vectors one must store is reduced; 7) it is not necessary to use basis functions that are non-zero wherever wavefunctions have signicant amplitude; 8) collocation points need not cover all regions in which wavefunctions have signicant amplitude.

Collocation can be used with the Multiconfiguration Time-Dependent Hartree (MCTDH) approach. When the basis is good, the accuracy of collocation solutions to the Schrödinger equation is not sensitive to the choice of the collocation points. The original collocation-MCTDH (C-MCTDH) method [J. Chem. Phys. 148, 044115 (2018)] uses, as is also true in standard MCTDH, a tensor product

basis. Because we do not rely on having a sum-of-products potential energy surface, we also have a tensor product grid. By using generalized hierarchical basis functions, that span the same space as the single particle functions we introduced in the first C-MCTDH paper, and a Smolyak grid, we have developed C-MCTDH approach that makes it possible to prune both the basis and the grid. In some cases it is advantageous to use more points than basis functions. In this "rectangular collocation" method, elements of the matrix for the PES have the form of quadrature approximations for integrals, but accurate energies can be obtained even when these quadrature approximations are poor. We have shown that accurate vibrational energy levels of $CH_2O$ can be computed using radial basis functions and collocation points that are localized in a small region of configuration space. Similar ideas are used to solve the electronic Schrödinger equation.

## Multiconfigurational Gaussian wavepacket dynamics: Interpolating between accurate quantum dynamics and the quantum-classical limit

Irene Burghardt
(joint work with David Picconi, Pierre Eisenbrandt, Matteo Bonfanti)

The variational Gaussian-based multiconfiguration time-dependent Hartree (G-MCTDH) approach [1] and its variational multiconfigurational Gaussian (vMCG) [2] variant have proven versatile tools for the explicit representation of system-bath problems [3, 4, 5] as well as *on-the-fly* calculations [6]. However, the Frozen Gaussian (FG) basis sets employed in these methods are far less flexible than the single-particle function (SPF) representation of standard MCTDH, such that a significantly larger number of Gaussian wavepackets (GWPs) are generally required to reach convergence. Against this background, the present contribution addresses several directions that make the variational GWP approach suitable for high-dimensional situations.

First, to remedy the lack of flexibility of the FG basis sets, we recently introduced a hierarchical two-layer approach – denoted 2L-GMCTDH – along with its multi-layer generalization [7]. Here, the first layer is composed of flexible SPFs, while the second layer consists of low-dimensional FGs. We report on the first implementation of the method in an in-house code, along with applications to vibrational energy transport and high-dimensional nonadiabatic dynamics [8, 9].

Second, a hybrid quantum-classical variant of the G-MCTDH approach has been formulated [10], which takes a subset of (potentially many) coordinates to the classical limit. This formulation is shown to yield a multiconfigurational Ehrenfest (MCE) type dynamics [10, 11].

Finally, the combination of the G-MCTDH approach with dissipative dynamics is illustrated, leading to the $\rho$G-MCTDH scheme [12]. Here, we employ a variational *ansatz* which expresses statistical mixtures in terms of population weighted natural states which are in turn expanded in G-MCTDH type configurations. This

approach circumvents undesirable properties of the standard variational formulation for density matrices, based upon the Hilbert-Schmidt norm, which does not generally lead to energy conservation.

In the general context of variational formulations, we further comment on recent developments initiated by Ch. Lubich, related to the formulation the MCTDH equations from the perspective of tangent space projections [13, 14].

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## Quantum Boltzmann-conserving classical dynamics: new developments in path-integral theory and methodology

Stuart C. Althorpe

(joint work with Michael J. Willatt, Timothy J.H. Hele, George Trenins)

The main subject of this talk is a new result in path-integral theory, which we obtained in 2015 [1]. This result still appears strange to us and it may be that a mathematician can help us to understand it better and link it to the bigger picture. It interests us because, first, it solves the conceptual problem of how Newtonian dynamics can conserve the quantum Boltzmann distribution, and second, it has helped us to push path-integral dynamics simulations to lower temperatures (for liquid water and ice) [2].
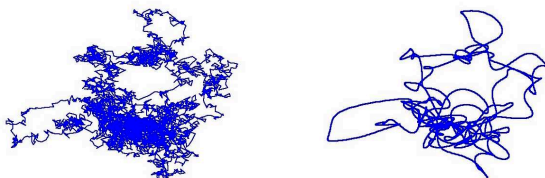


**Fig. 1** Raw and smoothed imaginary-time Feynman paths.

Figure 1 shows two imaginary-time Feynman paths. The path on the left is a "raw" Feynman path, which is jagged and discontinuous; the path on the right has been Fourier-filtered to make it smooth and continuous. It is well known [3] that the smooth paths give equivalent static averages to the jagged paths. The new result [1] is that the real-time dynamics of the smooth paths is classical, whereas real-time dynamics of the raw paths is quantum mechanical. In other words, smoothing the imaginary-time paths makes the real-time dynamics classical.

We do not understand this result, except in a handwaving way, namely that the smooth and continuous space is not big enough to support fluctuations of the real-time Feynman paths (around the classical paths); so the effective $\hbar$ for the dynamics is zero.

The smoothness of the paths makes them imaginary-time-translation invariant. This symmetry ensures that, in addition to conserving energy, the (classical) dynamics of the paths also conserves the non-classical pieces of the quantum Boltzmann distribution.

The smooth-path dynamics cannot be simulated directly (except for toy models) because of a phase problem. But it is proving useful. We have found that two practical simulation methods (centroid molecular dynamics (CMD) and ring-polymer molecular dynamics (RPMD)) which were first obtained heuristically, are in fact approximations to the smooth-path dynamics [4]. This has helped us to develop methods that correct for deficiencies in CMD at low temperatures, giving improved line positions and shapes in the infrared spectrum of liquid water and ice at temperatures down to 150 K [2, 5].

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## Quantum-classical wave functions and densities

RAYMOND KAPRAL

Systems comprising a subsystem S coupled to a bath or environment B are considered. For such systems two routes to the construction of mixed quantum-classical dynamics are described. In the first route one starts with a quantum description of both the subsystem and bath whose evolution is governed by the quantum Liouville equation. Following a partial Wigner transform over the bath, the limit in which the bath is described classically is taken giving the quantum-classical Liouville equation. [1] It is shown that equations of motion for quantum-classical wave functions derived by such methods are not closed but instead depend on the quantum-classical density.

In the second route one starts from a fully classical description of the system described by the classical Liouville equation. From this starting point, an evolution equation for a classical Koopman wave function is derived [2]. This prequantum equation may be quantized, and the Schrödinger equation is obtained after a quantization procedure is carried out [3]. When this procedure is applied to the composite system and only the subsystem S is quantized [4], one obtains a quantum-classical wave function. The equation of motion for the quantum-classical density obtained from this wave function is not closed but depends on the wave function [5]. The quantum-classical wave functions may be expressed in any basis and representation in the adiabatic basis provides a description of nonadiabatic dynamics that differs from that of the quantum-classical Liouville equation.

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# Nonadiabatic transitions through avoided crossings

BENJAMIN GODDARD

(joint work with Volker Betz, Tim Hurst, Uwe Manthe, Stefan Teufel)

For many molecular dynamics applications, the Born-Oppenheimer (infinite nuclear mass) approximation is used; it is assumed that the electronic energy levels are well-separated. However, in many chemical systems this is not valid. Typical examples are ultra-fast chemical reactions, such as the photodissociation of sodium iodide and the reception of light in the retina. We consider the fundamental case of two electronic energy levels with one nuclear degree of freedom $x$, with Schrödinger equation

$$
i\epsilon\partial_t \begin{pmatrix} \psi_1(x,t) \\ \psi_2(x,t) \end{pmatrix} = \left( -\frac{\epsilon^2}{2}\partial_x^2 \boldsymbol{I} + \begin{pmatrix} X(x) & Z(x) \\ Z(x) & -X(x) \end{pmatrix} + d(x)\boldsymbol{I} \right) \begin{pmatrix} \psi_1(x,t) \\ \psi_2(x,t) \end{pmatrix},
$$

where $\boldsymbol{I}$ is the $2 \times 2$ unit matrix, $\epsilon^2$ is the nuclear-electron mass ratio, and $\psi = (\psi_1, \psi_2)^T \in L^2(\mathrm{d}x, \mathbb{C}^2)$.

An interesting physical case is where the two Born-Oppenheimer energy levels become close but do not cross — an avoided crossing. It is natural to change to the adiabatic representation in which the potential matrix becomes diagonal, and the two levels decouple up to errors of order $\epsilon$. Interest lies in starting a wavepacket on the upper level and investigating the (exponentially small) part transmitted, via the avoided crossing, to the lower level, far away from the crossing (in the scattering limit). This exponential smallness, coupled with the highly oscillatory nature of the wavepackets, makes numerical simulations very computationally expensive. However, such transitions are chemically crucial, e.g., in catalysing other reactions.

One typical feature of the adiabatic representation is the non-monotonicity in time of the mass on the lower level. In fact, it can be shown that globally in time this mass is of order $\epsilon$, whereas in the scattering regime, it is exponentially small in both $1/\epsilon$ and the separation of the energy levels. From a numerical perspective, one essentially relies on the cancellation of many large numbers to produce a small value, which is generally an unstable approach. In addition, any absolute errors in the numerical scheme quickly swamp the exponentially small transmitted wavepacket. What is desirable is a methodology which requires only one-level computations (which can be performed to high accuracy) and produces a monotonically-increasing population on the lower level.

By considering generalizations of the adiabatic representation [1], known as superadiabatic representations, we derived a closed form approximation to the transmitted wavepacket, which is in excellent agreement (around 2–3% relative error) with high-precision numerics for a wide range of potentials and wavepackets. The central idea is to find representations in which the off-diagonal elements of the Hamiltonian are of order $\epsilon^n$ for a given $n$. In this way, one moves the complexity of the dynamics into the complexity of the representation. In such cases, direct numerical methods are impractical, but one may take advantage of the fact that all such representations agree (also with the adiabatic one) well away from the avoided crossing. Due to the simplicity of the transition, it may be well-approximated mathematically. This results in an algorithm analogous to surface hopping: The wavepacket is first transported on the upper level (using one's preferred numerical scheme). Once the centre of mass reaches the avoided crossing, a wavepacket is initialised on the lower level, using the formula below. Finally, this wavepacket is evolved on the lower level until it is well away from the avoided crossing.

In contrast to most previous mathematical results, it is highly suited to numerical implementation, with the computation of the lower-level wavepacket requiring only multiplication in momentum space. When the slope of the potential near the crossing, given by $\lambda = \frac{\mathrm{d}d}{\mathrm{d}x}|_{x=0}$, is small the formula is

$$\widehat{\psi_-}^\epsilon(k,t) = \mathrm{e}^{\frac{-\mathrm{i}}{\epsilon}t\hat{H}^-} \chi_{\{k^2 > 4\delta\}} \frac{\eta + k}{2|\eta|} \mathrm{e}^{\frac{\mathrm{i}\tau\delta}{2\delta\epsilon}|k-\eta|}\widehat{\phi}^\epsilon(\eta),$$

where $\hat{H}^-$ is the Born-Oppenheimer propagator on the lower level, $\widehat{\cdot}^\epsilon$ denotes a scaled Fourier transform, $\chi$ is the characteristic function (corresponding to energy conservation), $\eta = \mathrm{sgn}(k)\sqrt{k^2 - 4\delta}$ is the classical incoming momentum for outgoing momentum $k$, $\phi$ is the wavepacket on the upper level at the avoided crossing (at $t = 0$), and $\tau$ and $\delta$ are constants easily derivable from $X$ and $Z$. When $\lambda$ is not small, the formula is analogous but more complicated [2, 3].

Recently, we have applied this approach to the real-world example of sodium iodide, NaI, which has one effective degree of freedom, namely the inter-nuclear distance. The results are given in Figure 1; the relative error is once again around 3% [4]. One crucial advantage of the method is that it preserves the full information of the wavepacket, including phase. Hence it allows the accurate computation of interfering wavepackets, for example during multiple transitions; see Figure 2. This is not the case with standard surface-hopping methodologies.

We have also generalised the approach to arbitrary dimension, essentially by "slicing" the problem into a number of 1D systems near the avoided crossing [5]. In higher dimensions, we are interested in tackling the dynamics near a true crossing, in the case that the centre of the wavepacket travels along a path well away from the crossing, resulting in a type of avoided crossing with a non-zero gap. Along with applying the methodology to real-world systems of higher dimension, we intend to compare to surface-hopping approaches, and to implement the algorithm in one or more quantum molecular dynamics packages.
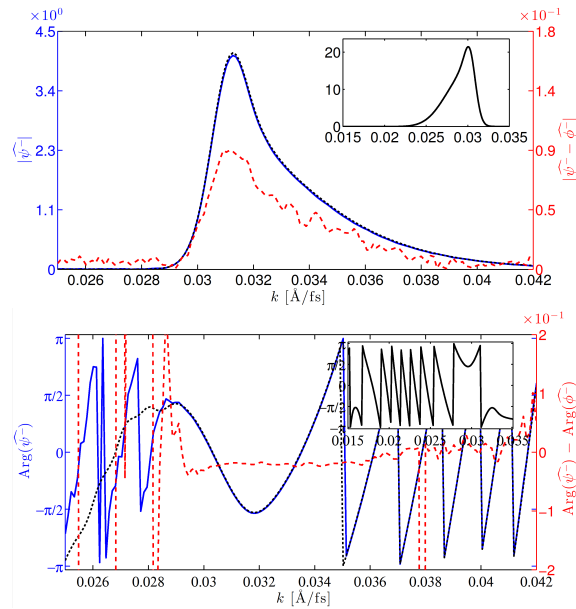
FIGURE 1. (a) The wavepacket on the upper level at the crossing point (subplot), along with the transmitted wavepacket (blue, solid, left axis) and relative error (red, dashed, right axis). (b) Phase of the wavepackets, and error in the phase; axes as in (a).
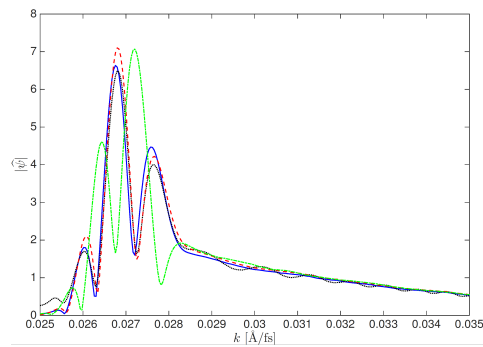


FIGURE 2. Combined transmitted wave packets for second and third transitions. Exact solution (black, dotted), the result of the formula (blue, solid), with the Landau-Zener rate (red, short dashes) and neglecting the prefactor (green,dashed-dotted).

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# An adaptive interpolation scheme for molecular potential energy surfaces

Elisabeth Larsson

(joint work with Markus Kowalewski, Alfa Heryudono)

Evaluating a potential energy surface for quantum dynamics using ab initio calculations is computationally expensive. To reduce the computational cost, different methods of approximation or interpolation have been introduced [10, 9, 8, 6, 3, 7, 11, 2, 1, 4].

The objective of such methods is twofold. In order to save computational effort, the number of function evaluations (ab initio calculations) should be minimized, and for the method to be useful, the representation should be accurate.

The method we propose [5] is an adaptive partition of unity method with local polyharmonic spline approximations. Polyharmonic splines were chosen because they minimize oscillations between data points. Partition of unity methods allows for local interpolants to be computed independently, and are hence suitable for parallelization. The global surface is then computed as a weighted combination of the local interpolants.

The adaptivity is based on a division of the computational domain into cells that can be refined recursively. To determine where to refine, an interpolant of the error is computed that can be used in place of actual potential evaluations.

We show that the adaptive algorithm provides significant savings compared with a full grid calculation, and that the gain increases with the number of dimensions. We also show that the error can be controlled accurately in relation to a user defined tolerance. The methods is tested for problems in two, three and four dimensions. We expect that the method can be used for up to six space dimensions, but for higher dimensions it should be combined with other techniques, as for example a many-body expansion, to reduce the dimensionality.

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# Classical Molecular Dynamics Simulations of Electronically Non-Adiabatic Processes

WILLIAM H. MILLER

A recently described symmetrical quasi-classical (SQC) windowing methodology for classical trajectory simulations has been applied to the Meyer-Miller (MM) model for the electronic degrees of freedom in electronically non-adiabatic dynamics. The approach treats nuclear and electronic degrees of freedom (DOF) equivalently (i.e., by classical mechanics, thereby retaining the simplicity of standard molecular dynamics), providing "quantization" of the electronic states through the symmetrical quasi-classical (SQC) windowing model. The approach is seen to be capable of treating extreme regimes of strong and weak coupling between the electronic states, as well as accurately describing coherence effects in the electronic DOF (including the de-coherence of such effects caused by coupling to the nuclear DOF). It is able to provide the full electronic density matrix from the one ensemble of trajectories, and the SQC windowing methodology correctly describes detailed balance (unlike the traditional Ehrenfest approach). Calculations can be (equivalently) carried out in the adiabatic or a diabatic representation of the electronic states, and most recently it has been shown that a modification of the

canonical equations of motion in the adiabatic representation eliminates (without approximation) the need for second-derivative coupling terms.

## Variational Gaussians revisited

CHRISTIAN LUBICH

(joint work with Caroline Lasser)

The talk reviewed Gaussian wave packets that evolve according to the Dirac–Frenkel time-dependent variational principle for the semi-classically scaled Schrödinger equation. Old and new results on the approximation to the wave function were given, in particular an $L^2$ error bound that goes back to Hagedorn (1980) in a non-variational setting, and a new error bound for averages of observables with a Weyl symbol, which shows the double approximation order in the semiclassical scaling parameter in comparison with the norm estimate.

The variational equations of motion in Hagedorn's parametrization of the Gaussian were presented. They show a perfect quantum–classical correspondence and allow us to read off directly that the Ehrenfest time is determined by the Lyapunov exponent of the classical equations of motion.

A variational splitting integrator was formulated and its remarkable conservation and approximation properties were discussed. A new result shows that the integrator approximates averages of observables with the full order in the time stepsize, with an error constant that is uniform in the semiclassical parameter.

The material presented here for variational Gaussians is part of a review article on computational methods for quantum dynamics in the semiclassical regime, which is currently in preparation [1].

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## Second quantization and the multi-configurational time-dependent Hartree approach

UWE MANTHE

The multi-configurational time-dependent Hartree (MCTDH) approach and its multi-layer extension facilitate accurate high-dimensional quantum dynamics simulations. In the MCTDH approach, the wavefunction is expanded in a direct product of self-adapting time-dependent single-particle functions (SPFs) and the SPFs are represented using a time-independent, "primitive" basis. The equations of motion which govern the time-dependence of all expansion coefficients are obtained via the Dirac-Frenkel variational principle. The approach was originally designed to describe the quantum dynamics of a set of distinguishable particles or coordinates.

Quantum mechanical systems of indistinguishable particles show specific symmetry properties, the total wavefunction is either totally symmetric or totally antisymmetric with respect to the pairwise exchange of two identical particles, and are typically described in *second quantization*. Here operators describing the creation or annihilation of specific single-particle states replace the basis function employed to describe distinguishable particles dynamics. Different strategies have employed by different groups of researchers to utilize the MCTDH approach in this context: the multi-layer MCTDH-second quantization representation (MCTDH-SQR) approach, which relies on the efficiency of the tensor contraction of the multi-layer representation, and the MCTDHB, MCTDHF, and MCTDHX approaches, which focus on an optimized time-dependent linear combination of the creation or annihilation operators. Recently, the (multi-layer) MCTDH approach in optimized second quantization representation (MCTDH-oSQR) has been introduced which combines elements of both groups of methods.

In the present talk, the theory of the MCTDH approach in second quantization will be discussed in detail. Difference to the standard distinguishable particle ("first quantization") MCTDH approach will be outlined and interesting connections between unitary transformations in second quantization and coordinate transformations in first quantization will be highlighted.

## Regularizing the MCTDH and ML-MCTDH equations of motion

Hans-Dieter Meyer

(joint work with Haobin Wang and David Mendive-Tapia)

The Multi-Configuration Time-Dependent Hartree (MCTDH) method [1, 2, 3, 4, 5] is a very efficient algorithm for solving the time-dependent Schrödinger equation in several dimensions. In this approach the wave function is expanded in a direct product of self-adapting time-dependent Single-Particle Functions (SPFs). The equations of motion (EOM) for both the expansion coefficients and the SPFs are derived from a variational principle. In the multi-layer extension of MCTDH (ML-MCTDH) [6, 7, 8] there are several layers of SPFs, the SPFs of one layer are expanded into the SPFs of the layer below. This procedure allows to treat many degrees of freedom.

The EOM of the SPFs can be plagued by singularities. This has led some researches to question the validity of the MCTDH approach. A physical interpretation of the singularities will be presented and it will be argued that the singularities can be removed by regularization. However, it will be shown that the standard approach of EOM-regularization by regularizing the density matrix is not the optimal one. A new regularization scheme, based on a singular value decomposition of the coefficient tensor, will be discussed and it will be shown [9, 10] that this new scheme leads to a faster convergence with respect to the regularization parameter.

The new regularization scheme is tested on a 2D model [11] of coupled oscillators, and on a series of spin-boson models with up to 70 bath oscillators [9, 10].

As an alternative we investigated a spawning approach where SPFs are added when needed. Inspired by an idea of Uwe Manthe [11] we derived equations for optimal unoccupied SPFs and for an optimal form of the corresponding columns of the coefficient tensor. By giving these added optimal columns a small norm $\epsilon_A$ (typically $10^{-7} \cdots 10^{-8}$), the density matrix becomes regular and there is no need to regularize. The price one has to pay is that the norm of the wavefunction is artificially increased by $\epsilon_A$, but this is a negligible quantity. The advantage of this approach is that it simplifies the use of MCTDH. The user no longer needs to specify the numbers of SPFs, he/she only needs to provide a threshold for the lowest natural population (i.e. a measure for the accuracy of the propagation), the algorithm itself will determine the necessary numbers of SPFs. The method is tested by propagating a locally vibrationally excited state of the HONO molecule. This feature will be particularly useful for ML-MCTDH, where otherwise a multitude of numbers of SPFs has to be specified.

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## Gauges-Conditions in Multi-Configuration Time-Dependent Hartree Approaches

THOMAS WEIKE

(joint work with Uwe Manthe)

The multi-configuration time-dependent Hartree (MCTDH) approach is an efficient scheme to solve the time dependent multi-particle Schrödinger equation. In the MCTDH approach the wave function is a time dependent linear combination of direct products of time dependent single particle functions. Due to this ansatz the wave function is invariant under unitary transformations of the single particle functions. This 'gauge' freedom is fixed by choosing a gauge condition.

One extension of the MCTDH approach, which deals with the Schrödinger equation for indistinguishable particles, is the MCTDH approach in optimized second quantisation (MCTDH-oSQR). Any wave function including indistinguishable particles must be symmetric or anti-symmetric with respect to the pairwise exchange of identical particles. This condition is fulfilled if the wave function is represented in second quantisation:

$$|\Psi\rangle = \sum_{i_1..i_f} A_{i_1..i_f}(t)\, \frac{\left(b_1^\dagger\right)^{i_1}}{\sqrt{i_1!}} .. \frac{\left(b_f^\dagger\right)^{i_f}}{\sqrt{i_f!}} \,|0\rangle\,.$$

The operators $b_i^\dagger$ commute in the symmetric (bosonic) case and anti-commute in the anti-symmetric (fermionic) case. In the MCTDH-oSQR approach both the coefficients $A_{i_1..i_f}$ and the operators $b_i^\dagger$ are time dependent. The MCTDH-oSQR ansatz is similar to the usual MCTDH ansatz, but it introduces some new features. The MCTDH-oSQR approach is not invariant under unitary transformations of the operators $b_i^\dagger$ and thus is gauge dependent. Nevertheless the analog of a gauge condition can be introduced. The quality of calculations employing the MCTDH-oSQR method depend on this condition.

In the usual MCTDH approach the ansatz for the wave function is gauge invariant, but the numerical integration depends on the gauge condition. Therefore the choice of the gauge is important in the MCTDH approach. Gauge conditions in MCTDH approaches will be discussed.

## Vibrational quantum graphs and their application to the quantum dynamics of $CH_5^+$

CSABA FÁBRI

The first application of quantum graphs [1] to vibrational quantum dynamics of molecules is reported [2]. The usefulness of the quantum-graph approach is demonstrated for the molecular ion $CH_5^+$, an enigmatic system of high-resolution molecular spectroscopy and molecular physics, challenging our traditional understanding of chemical structure and rovibrational quantum dynamics. The vertices of the quantum graph correspond to the different symmetry-equivalent versions

of the molecule ($5! = 120$ in total for $CH_5^+$), while the differently colored edges represent different collective nuclear motions transforming the distinct versions into one or another (see Figure 1). These definitions allow the mapping of the complex low-energy vibrational quantum dynamics of $CH_5^+$ onto the motion of a one-dimensional particle confined in a quantum graph. The time-independent Schrödinger equation describing free motion on the quantum graph is solved and the energy levels are quantized by imposing an appropriate set of boundary conditions on the eigenstates of the Hamiltonian. The quantum-graph model provides a simple and intuitive qualitative understanding of the intriguing low-energy vibrational dynamics of $CH_5^+$ and is able to reproduce the lowest vibrational energy levels of $CH_5^+$ and $CD_5^+$ [2, 3, 4, 5] with remarkable accuracy.
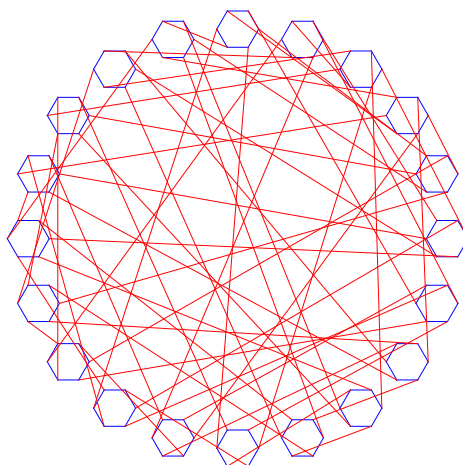


FIGURE 1. Structure of the quantum graph applied to the vibrational quantum dynamics of $CH_5^+$.

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## Tree Tensor Network States for Vibrational Quantum Calculations

### Henrik R. Larsson

One of the main fundamental challenges in computing quantum systems is the exponential scaling of the high-dimensional wavefunction coefficient tensor with dimensionality. A highly successful strategy for reducing or even obviating the exponential scaling is to decompose the coefficient tensor into chunks of lower-dimensional tensors that are connected *via* virtual dimensions. Tensor decompositions are used in different disciplines. In molecular quantum dynamics, the tensor-decomposition based multilayer multiconfiguration time-dependent Hartree method (ML-MCTDH) has been proven to be very efficient [1]. However, highly nonlinear differential equations have to be solved. In condensed matter physics, the ML-MCTDH-based tensor decomposition is called tree tensor network states (TTNS) [2]. In this talk, an application of an algorithm from condensed matter physics [3] to the computation of accurate vibrational spectra is presented. By employing sequential isometrizations of the tensors in the TTNS, the problem of solving nonlinear differential equations is transformed into a sequence of Hermitian eigenvalue problems. This reduces the computational requirements and improves the robustness of the method. Computations for vibrational spectra of a 12-dimensional system are presented.

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## Effective non-adiabatic Hamiltonians for the quantum nuclear motion over coupled electronic states

### Edit Mátyus
#### (joint work with Stefan Teufel)

Recent developments in molecular high-resolution and precision-spectroscopy experiments [1] make it necessary to revise and to go much beyond the usual approximations in quantum chemistry. In particular, relativistic, radiative, and non-adiabatic 'effects' must be explicitly accounted for in the theoretical description [2]. In turn, should similarly precise experimental and theoretical results become available, it may be possible to refine fundamental physical constants, used in the computations, based on molecular spectroscopy experiments.

The proposed talk will focus on the computation of non-adiabatic effects important when we look at molecular transitions under a high energy resolution. The

non-relativistic limit can be approached arbitrarily close through a direct variational solution of the Schrödinger equation. This route, which we call pre-Born–Oppenheimer (pre-BO) theory [3], is currently feasible for selected quantum states of the smallest systems, although we observe a rapid and continuing progress [4] in this important direction, which provides benchmark values for non-relativistic molecular energies.

Many of the small molecular paradigms are dominated by a single electronic state in the traditional BO picture, and it has been known for a long time that with some 'appropriate' corrections to the mass of the nuclei, most of the small non-adiabatic effects important for high-resolution spectroscopy can be efficiently modeled, thereby giving access to accurate rovibrational energies over a broad dynamical range. The 'mass correction' has been a somewhat obscure concept and was discovered and re-discovered many times. In the meanwhile, everyone working on the numerical solution of the rovibrational Schrödinger equation, have been using atomic masses (instead the nuclear masses which would be dictated by the BO approximation) with the simple argument that the 'extra mass' of the electrons approximately accounts for the small non-adiabatic effects.

First, I will review part of the earlier literature and present the numerical computation of the rigorous mass-correction functions. I will demonstrate for the case of the $^4\mathrm{He}_2^+$ molecular ion that it is important to use these functions [5] instead of some average mass correction value (a naïve choice would be 1.5 times the electron's mass in this case) to arrive at an agreement with the most recent experimental observations [6].

Then, I will speak about the rigorous derivation of the mass-correction terms starting from the full electron-nucleus Hamiltonian [7]. The initial idea for our derivation is a general system which may be dominated by not only a single- but a multi-dimensional electronic subspace, which is separated by a gap from the rest of the electronic spectrum. We have block-diagonalized the electron-nucleus Hamiltonian up to $\mathcal{O}(\epsilon^{n+1})$ – where $\epsilon$ is the square root of the ratio of the electron to nuclear mass –, through a unitary transformation of the electronic subspace to obtain the corresponding $n$th-order effective Hamiltonian for the quantum nuclear motion. As a special case, the second-order Hamiltonian corresponding to an isolated electronic state is recovered from the general expressions. For a multi-dimensional, explicitly coupled electronic band, the second-order Hamiltonian contains the usual Born–Oppenheimer terms and non-adiabatic corrections but generalized mass-correction terms appear as well. These, earlier neglected, corrections perturbatively account for the outlying (discrete and continuous) electronic states not included inthe explicitly coupled electronic subspace. By adapting the numerical implementation of the single-state expression [5] to this multi-state Hamiltonian molecular applications should follow in the near future.

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## Nonadiabatic Charge and Energy Transfer
### Aaron Kelly

Recently developed approximate approaches for simulating nonequilibrium quantum dynamics in nanoscale systems will be discussed. The feature unifying these methods is the statistical ensemble of trajectories that is employed in order to construct observables and transport properties for real-time nonadiabatic quantum processes, such as charge and energy transfer. We will explore the performance of selected techniques of this type in a variety of scenarios, including exciton transport, polaron formation, charge separation at donor-acceptor interfaces, and heat transport through molecular junctions.

## Non-unitary Quantum Chemistry

ALI ALAVI

(joint work with Aron Cohen, Hongjun Luo, Kai Guther, Werner Dobrautz, David Tew)

We investigate the use of non-unitary similarity transformations of the electronic Schrodinger Hamiltonian, based on Jastrow and Gutzwiller factorisation of the electronic wavefunction. This is done as a means to incorporate explicitly-correlated information from the wavefunction into an effective Hamiltonian. It helps in simplifying the problem of obtaining accurate energies in two significant ways. First, by removing Coulomb singularities from the potential terms, basis set convergence is greatly accelerated. Second, the presence of non-Hermitian terms in the effective leads to right eigenvectors which are numerically *sparser* compared to the ground-state eigenvector of the original Hamiltonian [1].

In more specific terms, we write the wavefunction in the form:

$$(1) \qquad \Psi = e^\tau \Phi$$

where $\tau = \sum_{i<j} u(\mathbf{r}_i, \mathbf{r}_j)$ with $u(\mathbf{r}_i, \mathbf{r}_j) = u(\mathbf{r}_j, \mathbf{r}_i)$ is a symmetric correlation function over electron pairs, and $\Phi$ is the associated many-body function which is a solution to the $\tilde{H}\Phi = E\Phi$, with

$$(2) \qquad \tilde{H} = e^{-\tau}\hat{H}e^\tau = \hat{H} + [\hat{H}, \tau] + \frac{1}{2}[[\hat{H}, \tau], \tau]$$

With the Jastrow form of correlators, the commutator expansion terminates at second order, and results in additional (non-hermitian) two-body and (hermitian) three-body terms, which are numerically computable.

The resulting eigenvalue problem can be treated in the full configuration interaction quantum Monte Carlo formalism, adapted to the non-hermitian setting [2]. This is a projective diagonalisation method based on a stochastic realisation of the Power method, and is well suited to the similarity transformed Hamiltonian, since the three-body terms, though numerous in number, are mostly small in magnitude individually, and need only be sampled infrequently.

We show that very flexible correlation factors of the Boys-Handy form:

$$(3) \qquad u(\mathbf{r}_i, \mathbf{r}_j) = \sum_{mno}^{m+n+o\leq 6} c_{mno}(\bar{r}_i^m \bar{r}_j^n + \bar{r}_j^m \bar{r}_i^n)\bar{r}_{ij}^o, \quad \bar{r} = \frac{r}{1+r}$$

can be employed in this formalism, with the parameters of the correlation factor obtained through independent variational Monte Carlo calculations. Use of such correlation factors, in conjunction with standard quantum chemical basis sets (of the form cc-pV$X$Z), lead to extremely accurate atomic total energies, for the first row atoms.

This formalism is now being extended to molecular systems.

The main bottleneck of the methodology is the storage of the 6-index 3-body integrals, and tensor decomposition methods are being investigated to alleviate this.

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## Suitable sparse grid scheme for the calculation of the vibration-translation-rotation eigenstates of confined molecular system

YOHANN SCRIBANO
(joint work with D. Lauvergnat)

The quantum dynamics studies of molecular bound states are actually limited by the well known dimensionality problem. Indeed even for molecules of medium size, usual quadrature techniques have already reached their limit since a multi-dimensional direct-product grid can be very large. An alternative to avoid the direct-product grid is to use the Smolyak sparse-grid techniques, recently investigated by Avila and Carrington [1] for the calculation of vibrational bound states of semi-rigid molecules. Lauvergnat and Nauts [2] have proposed a new implementation of such sparse grid for the study of the torsional levels of methanol in full dimensionality in order to treat one large amplitude motion. The efficiency of this kind of grid is related to the substitution of a single large direct-product grid by a sum of small direct-product grids. We will present a recent adaptation of this kind of sparse grid scheme for the calculation of six-dimensional (6D) vibration-translation-rotation bound states of confined molecule such as $H_2$ (and its isotopologues) in water clathrate [3]. In particular, we are able to use a combination of 2D-grids associated to spherical harmonic basis functions and the usual 1D-gaussian quadrature grids to form the Smolyak sparse-grid [4]. We will discuss the efficiency of this approach for the calculation the intramolecular vibrational shift of $H_2$ as well as the effect of the condensed phase environment.

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## Modelling quantum systems on classical computers: approximation and high-performance computing

Ivan Oseledets

(joint work with Roman Schutsky, Danil Lykov, Maxim Rakhuba, Alexander Novikov)

This talk consists of two main parts. In the first part, we consider the problem of modelling quantum circuits on classical high-performance computers. This topic has attracted a lot of attention in the recent years, due to the challenge of *quantum supremacy*: the size of the problem, which can be solved by a quantum computer, but can not be solved by the existing HPC machines. Mathematically, this boils down to the the contraction of a tensor-network. A natural formalism of for these contraction is the formalism of graphical models, where the edges correspond to contracted indices, and tensors correspond to the cliques of the graph. For the computation of the full tensor, the complexity of the contraction depend on the order, in which the variables are used, and the optimal order is determined by the treewidth of the graph. We have proposed a new heuristics for the partial computation of the amplitudes, which outperform state-of-the art approaches. In short, current simulators are more efficient, than current quantum computers.

The second part covers the results of the paper [1] and is devoted to the efficient modelling of high-dimensional Hamiltonians using tensor-train approximation. The proposed eigensolver combines the best of both worlds: methods for low-rank tensor approximation, and iterative methods for solving eigenproblems. The idea is to use an apriori assumption that eigenvectors can be well approximated by low-rank tensors as a preconditioner for the classical iterative methods. This information is incorporated by the projection of all involved vectors onto the tangent plane to the manifold of low-rank tensors at some point. This projection effectively "flattens" the manifold, and the computation of all the quantities involved becomes very cheap even if many eigenvectors are involved. This projection, whoever makes the variational property of the method invalid, thus we proposed a simple correction term, that always adds the current iterate to the basis. As the result, we need to solve an auxiliary problem for the coefficients, which is no longer a generalized eigenvalue problem, but it is very small.

All the algorithms were implemented in Tensor Train for Tensorflow (t3f) toolbox, which makes possible efficient execution of this code on GPU. The total speed-up of a GPU running time compared to the CPU running time is more than 100 times for the large number of eigenvalues and eigenvectors to be computed.

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## Propagation of Wave Packets and Application to Herman-Kluk Propagator

CLOTILDE FERMANIAN KAMMERER

(joint work with Caroline Lasser and Didier Robert)

Wave packets, also called coherent states, provide with initial data which are highly concentrated in the phase space. The main example of such families consists in the frame of Gaussian states with varying cores and width, such as those used in several methods of quantum chemistry. In this talk, we describe how wave packets propagate through systems of Schrödinger equations, including situations with smooth eigenvalue crossings, and we emphasize the specific case of Gaussians states. We then explain how this can be used to deduce Herman-Kluk's type representations of the propagators associated with these systems of equations, combining the Herman-Kluk approach with ideas issued from Surface Hopping Semi-Groups, and we describe the mathematical results available in terms of convergence and convergence rate.

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## Higher order time-dependent Born-Oppenheimer approximation

STEFAN TEUFEL

(joint work with Edit Matyus)

In a recent work [1] with Edit Matyus we develop a systematic perturbation scheme that allows to compute higher order corrections to effective nuclear Hamiltonians for groups of electronic bands in molecules that take into account the coupling to all other electronic states to any desired order in $\varepsilon := \sqrt{m/M}$. Here $m$ is the electron mass and $M$ the mass of the lightest nuclei in the molecule. The key idea is to approximately block diagonalise the molecular Hamiltonian $\widehat{H} = -\varepsilon^2 \Delta_R + H_{\mathrm{el}}(R)$ with respect to superadiabatic subspaces and to then evaluate

the relevant block using a suitably constructed unitary transformation. While this is a well known procedure, earlier works (e.g. [2, 3, 4, 5, 6]) heavily relied on the use of pseudodifferential calculus with operator-valued symbols. As a consequence, these works were rather technical and did not spread to the physical chemistry community. Moreover, computing higher order terms in the expansion explicitly was a formidable task. Our new approach is rather elementary as it uses merely expansions of exponential series and we are able to explicitly compute, for the first time, the second and third order corrections to the effective nuclear Hamiltonian even in the case of groups of electronic bands.

Let me briefly describe the general form of the second order effective non-adiabatic Hamiltonian $\boldsymbol{H}^{(2)}$ for a group of $d$ electronic levels $E_1(R), \ldots, E_d(R)$ that are separated by a gap from the rest of the spectrum. Our analysis implies for example that its eigenvalues approximate the eigenvalues of the full molecular Hamiltonian up to order $\varepsilon^3$. It thus captures *all* second order contributions.

After choosing $d$ electronic states $\psi_1(R), \ldots, \psi_d(R)$ that are smooth functions of $R$ and pointwise form an orthonormal basis of the selected electronic subspace (i.e. an adiabatic or weakly diabatic basis set for the selected electronic subspace), the effective non-adiabatic Hamiltonian $\boldsymbol{H}^{(2)}$ takes the form of an operator acting on wave functions on the nuclear configuration space $\mathbb{R}^{3N}$ that take values in $\mathbb{C}^d$, and thus can be written as a $d \times d$-matrix of operators $(\boldsymbol{H}^{(2)})_{\alpha\beta}$ acting on functions on $\mathbb{R}^{3N}$:

$$(\boldsymbol{H}^{(2)})_{\alpha\beta} = \sum_{i,j=1}^{3N} \left[ \tfrac{1}{2} \left( -\mathrm{i}\varepsilon\partial_i \mathbf{1} + \varepsilon\mathbf{A}_i \right) \left( \delta_{ij}\mathbf{1} + \varepsilon^2 \mathbf{M}_{ij} \right) \left( -\mathrm{i}\varepsilon\partial_i \mathbf{1} + \varepsilon\mathbf{A}_i \right) \right]_{\alpha\beta}$$

$$+ (\mathbf{E} + \varepsilon^2 \boldsymbol{\Phi})_{\alpha\beta}.$$

Here the boldface objects are $d \times d$-matrix valued functions on the nuclear configuration space, with $(\mathbf{1})_{\alpha\beta} := \delta_{\alpha\beta}$ denoting the identity matrix, and the others given as follows in terms of the electronic states $\psi_1(R), \ldots, \psi_d(R)$.

The coefficients of the non-abelien Berry connection, are as expected, $\mathbf{A}_{\alpha\beta,i}(R) = -\mathrm{i}\langle \psi_\alpha(R) | \partial_i \psi_\beta(R) \rangle$. The "diabatic" electronic level matrix becomes $\mathbf{E}_{\alpha\beta}(R) = \langle \psi_\alpha(R) | H_{\mathrm{el}}(R) | \psi_\beta(R) \rangle$, where $H_{\mathrm{el}}(R)$ is the electron Hamiltonian for fixed nuclear configuration $R$. The second order diagonal correction is

$$\boldsymbol{\Phi}_{\alpha\beta}(R) = \tfrac{1}{2} \sum_{i=1}^{3N} \langle \partial_i \psi_\alpha(R) | P^\perp(R) | \partial_i \psi_\beta(R) \rangle,$$

where $P^\perp(R) = 1 - P(R)$ projects onto the orthogonal complement of the selected electronic subspace, i.e. onto the orthogonal complement of the span of $\psi_1(R), \ldots, \psi_d(R)$.

While the matrix versions of the terms discussed up to now could have been easily guessed from the single band ($d = 1$) case, the determination of the second order mass correction matrix requires the systematic perturbation approach

developed by us. The resulting expression is

$$\mathbf{M}_{\alpha\beta,ij} = \sum_{a,b=1}^{d} \langle \psi_\alpha | P_a (\partial_j P)(\mathcal{R}_a + \mathcal{R}_b)(\partial_i P) P_b | \psi_\beta \rangle ,$$

where for better readability we dropped the argument $R$ in all the functions. Here $\mathcal{R}_a(R) := (H_{\mathrm{el}}(R) - E_a(R))^{-1} P^\perp(R)$ is the reduced resolvent of the level $E_a(R)$ acting as a bounded operator on the range of $P^\perp(R)$, and $P_a(R)$ is the projection onto the eigenspace of $H_{\mathrm{el}}(R)$ corresponding to the eigenvalue $E_a(R)$. In the special case that $\psi_1(R), \ldots, \psi_d(R)$ form an adiabatic basis set, i.e. $H_{\mathrm{el}}(R)\psi_\alpha(R) = E_\alpha(R)\psi_\alpha(R)$ for $\alpha = 1, \ldots, d$, the expression for the mass correction term simplifies to $\mathbf{M}_{ab,ij}(R) = \langle \partial_j \psi_a(R) | \mathcal{R}_a(R) + \mathcal{R}_b(R) | \partial_i \psi_b(R) \rangle$.

While Edit Matyus implemented the second order terms and obtained extremely accurate theoretical predictions for spectra of small molecules (see her talk for references), in my talk I discussed, how our approximation scheme can be used to obtain highly accurate approximations over very long times also in the case of time-dependent problems. Finally I also present numerical tests on a simple toy problem performed by Daniel Weber in his master's thesis [7]. His results show that the theoretical error bounds obtained by our method describe the asymptotic behaviour of the true approximation error in this toy model very well.

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## Obtaining Potentials for Molecular Excited States: The Vibronic Coupling Model and Beyond

### Graham Worth

The non-equilibrium time evolution of a molecular system can be described by the solving the time-dependent Schrödinger equation (TDSE). Efficient algorithms exist for the general solution of this equation, but a significant bottleneck in these studies is that potential energy functions are required that are non-trivial to obtain.

After photo-excitation, a molecular wavepacket evolves in a manifold of electronic states. Potential energy functions for these states can be described by a set of coupled potential energy surfaces. These surfaces and couplings, however,

are difficult to obtain for molecules beyond three atoms due to the size of the space to be covered. In addition, the *non-adiabatic* coupling between the surfaces is singular at nuclear configurations where the potential surfaces are degenerate, points known as conical intersections. Two approaches were presented to provide realistic potential functions. In each case the approximations being made were discussed along with the advantages and disadvantages of each.

The first approach is to use the *Vibronic Coupling Model*. This used diabatization by ansatz to provide a simple Hamiltonian. It is useful for an accurate description of the short-time dynamics and photophysics of a system, but fails to correctly describe the long-time dynamics required to describe photochemistry. This is because the model functions are short polynomial expansions around the Franck-Condon point, and thus are not accurate once the system is far from this geometry, which happens on the order of a few picoseconds. It can, however, be used with grid based methods, such as the multi-configurational time-dependent Hartree (MCTDH algorithm), to solve the TDSE for polyatomic molecules and has had much success in describing absorption spectra and short-time non-adiabatic dynamics [1].

The second approach is to use the *direct dynamics variational multi-configurational Gaussian* (DD-vMCG) method [2]. This uses a localised Gaussian function basis set to describe the evolving wavepacket and the potential functions are calculated on-the-fly in the vicinity of the Gaussian functions as the nuclei evolve. Standard quantum chemistry programs can be used to calculate the potential energies and gradients required, making the method flexible and alleviating the problem of calculating the global surfaces a priori. It does, however require an on-the-fly diabatisation procedure that is not rigourously defined [3]. The method shows promise but requires further testing.

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## Confined Molecules

Pierre-Nicholas Roy

We introduce numerical methods to compute the Quantum molecular dynamics of systems under confinement. Both path integrals and basis set approaches are considered. We introduce a symbolic representation of different path integral topologies for applications to finite temperature, ground state, bosonic exchange, rotations, and entanglement estimation. We illustrate the Langevin Equation Path

Integral Ground state method for the harmonic oscillator and present an application of the approach for the prediction of Raman vibrational shifts of parahydrogen clusters. [1] The concept of Rényi Entanglement entropies is introduced in the context of the path integral ground state method [2, 3]. Results for the spatial Entanglement in liquid helium are shown [4]. Following this example of atomic entanglement, the quantum of entanglement between molecules is addressed. Confined rotors are chosen to explore molecular entanglement. A model Hamiltonian is introduced for chains od confined rotors with dipole interactions. The effects of basis truncation on ground state energies and entanglement entropies are discussed [5]. A new approach based on path integral Monte Carlo and the replica trick for interacting rotors is presented. The method is amenable to calculations in two and three spatial dimensions. We show that for one dimension, the Density Matrix Renormalization Group (DMRG) can be used to obtain accurate ground state properties of chains of dipolar rotors over a broad range of interaction strengths [6]. The DMRG results can in turn be used to train Restricted Boltzmann machines and allow machine learning tools to be used in the description of confined molecules.

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## Calculation of global, high-dimensional Potential Energy Surface fits in CANDECOMP form using Monte-Carlo Methods

Markus Schröder

(joint work with Hans-Dieter Meyer, Oriol Vendrell)

We propose a novel method for obtaining global representations of high-dimensional potential energy surfaces evaluated on discrete grid points in a sum-of-products form, more precisely in canonical polyadic decomposition form. To this end we modify a standard method for obtaining canonical polyadic decompositions of arbitrary tensors. The standard method employs an alternating least squares method to iteratively optimize single degrees of freedom. Our modification replaces

numerically exact integrals with Monte-Carlo integrals. This allows integration of correlated weights straight forwardly. We demonstrate the power of the method by transforming the 15D potential [1] of the protonated water dimer (Zundel cation) in a sum-of-products form while preserving all symmetries of the original potential.

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## Time Dependent Schrödinger Equation: Semiclassical Type Propagation of Order 6 at the Price of Order 2

### Vasile Gradinaru

(joint work with Sergio Blanes)

The talk gave a short overview on the recently improved algorithms for the time integration of the semiclassical Schrödinger equation.

The time–dependent Schrödinger equation in its semiclassical formulation is

$$i\,\varepsilon^2\,\partial_t\psi \;=\; H(\varepsilon)\,\psi\,.$$

Here, $\psi = \psi(x,t)$ is the wave function that depends on the spatial variables $x = (x_1,\ldots,x_d) \in \mathbb{R}^d$ and the time variable $t \in \mathbb{R}$. The Hamiltonian

$$H(\varepsilon) \;=\; -\,\frac{\varepsilon^4}{2}\,\Delta_x \,+\, V(x)$$

involves the Laplace operator $\Delta_x$ and a smooth real potential $V$. The standard techniques for the numerical solution of this equation were known to be able to give only convergence of order $h^k/\varepsilon^2$, see [3, 2, 4]. Hence, in order to have physically relevant solutions, we are forced to use very small time-steps $h$ and also a very fine grid in space. However, significant progress has been made recently in improving the pessimistic behavior in $\varepsilon$, see [1] and [6]. Instead of a Fourier basis, we use Hagedorn wavepackets, which provide a spectral, meshless and time dependent basis of $L^2$. If the exact solution stays localized in space or in frequency domain, good approximations in terms of $\varepsilon$ are possible: concrete assumptions and results are in [7]. Starting from these ideas, [5] made the foundations of the algorithms based on Hagedorn wavepackets. The advantages of the spectral approximation were used in order to attack higher dimensional problems; [6] defines the semiclassical splitting, which is rigorously proven to be of order $\varepsilon\,h^2$. The order of convergence was improved in the same work to $\varepsilon\,h^4$ via a combination of the semiclassical splitting with a Magnus integration step, which roughly triples the computational time. We recently found a way to systematically improve the convergence order, even to order 6 in time only at the expense of the computational effort of the semiclassical splitting. A paper on these new algorithms is in preparation.

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## Automatic Computation of Global Potential Energy Surfaces in Sum-of-Products Form using Specific Reaction Hamiltonians

Daniel Peláez

(joint work with Ramón L. Panadés-Barrueta, Emilio Martínez-Núñez)

Quantum phenomena are ubiquitous and cannot be neglected if a physically correct molecular simulation is aimed for [1, 2]. However, despite the current boost in the development of dynamical methods, semiclassical or fully quantal, the availability of a Potential Energy Surface (PES) is still a major bottleneck. For grid-based ones, the PES is represented *globally*, formally as a multidimensional tensor. In the case of on-the-fly approaches, the PES is expressed in a *local* representation at *every* time-step. In the first category, the limitation lies on the possibility of fitting the PES to an appropriate functional form for a large number of degrees of freedom. Powerful and accurate as the existing methods are, a high degree of expertise is still required to master and apply these techniques, particularly when considering medium-large systems ($\geq$6D), thus preventing a wider-spread use. In the second case, the limiting factor is the number of *electronic structure calls* (energies, gradients, Hessians, properties, etc.) needed to perform the propagation. Consequently, on-the-fly approaches are constrained to modest levels of theory.

In this talk, we present Specific Reaction Parameter Multigrid POTFIT (SRP-MGPF), a method which constitutes a well-balanced solution to the aforementioned issues. SRP-MGPF allows in a *single* fitting process the generation of a *potentially* chemically-accurate (<1 kcal/mol) global (molecular or intermolecular) PES and same-level-of-theory molecular properties surfaces at the cost of semiempirical potentials. SRP-MGPF relies on three steps: (i) a fully automated topographical characterisation of the PES in terms of *all* minima and transition states [3, 4]; (ii) a global reparametrization of a semiempirical Hamiltonian (SRP) using reference geometries derived from the set of stationary points; and (iii) direct

tensor-decomposition of the SRP PES into sum-of-products form with the MGPF algorithm [8]. It should be noted that a SRP PES can be directly interfaced to any on-the-fly method. As preliminary results, we compare Multiconfiguration Time-Dependent Hartree (MCTDH) [5] vibrational eigenstate calculations on a SRP-MGPF PES for the benchmark HONO (6D) system [6, 7]. Finally, we discuss the interface of SRP PES with the Direct-Dynamics Variational Multiconfigurational Gaussian (DD-vMCG) method as well as with the Second Quantization extension of the Multilayer MCTDH (ML-MCTDH-SQR) algorithm [10].

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# A pruned collocation-based multi-configuration time-dependent Hartree approach using a Smolyak grid for solving the Schrödinger equation with a general potential energy surface

Robert Wodraszka

(joint work with Tucker Carrington Jr.)

The multi-configuration time-dependent Hartree (MCTDH) method is one of the most prominent and efficient approaches for rigorous quantum dynamics studies. [1] The key idea behind MCTDH is to use variationally optimised bases (single particle functions, SPFs) to represent quantum mechanical wave functions and operators. The standard MCTDH wavefunction is given as

$$(1) \quad \Psi\left(x_1, \ldots, x_D, t\right) = \sum_{i_1=1}^{n_1} \ldots \sum_{i_D=1}^{n_D} A_{i_1,\ldots,i_D}\left(t\right) \varphi_{i_1}^{(1)}\left(x_1, t\right) \ldots \varphi_{i_D}^{(D)}\left(x_D, t\right),$$

where the SPFs are,

$$(2) \quad \varphi_{i_k}^{(k)}\left(x_k, t\right) = \sum_{j_k=1}^{N_k} c_{j_k,i_k}^{(k)}\left(t\right) \chi_{j_k}^{(k)}\left(x_k\right) \quad \forall\, k = 1 \ldots D.$$

Due to the optimisation, the SPF basis set sizes required for exact computations can often be significantly smaller than the number of fixed (non-optimised) basis functions typically employed in standard calculations. Working equations for the

$A$-tensor and the SPFs can be derived employing the Dirac-Frenkel variational principle, [2]

$$(3) \qquad\qquad 0 = \langle \delta\Psi | \mathrm{i}\partial_t - \hat{H} | \Psi \rangle .$$

The original MCTDH approach uses a direct product SPF basis and relies on the potential energy surface (PES) being in sum of products (SOP) form, i.e,

$$(4) \qquad\qquad V = \sum_s \prod_{k=1}^{D} v_s^{(k)}(x_k) .$$

This set-up has two critical shortcomings. First, the basis size scales exponentially with the number of dimensions of the system and second, using accurate PESs, which are often not given in SOP form, requires introducing approximations.

We present an MCTDH approach that mitigates both deficiencies. [3] We use an optimised non-direct product basis, which includes only a fraction of the direct product basis functions, and we solve MCTDH differential equations with a collocation technique, which obviates the need for any integrals or quadratures; only the evaluation of the potential (given in any form) at the collocation grid points is required. To derive the corresponding working equations, we use a Petrov-Galerkin scheme, which, in the standard MCTDH case, yields the same equations as those obtained with the more common Dirac-Frenkel variational principle. The pruned collocation-based MCTDH A-tensor equation is (for brevity, we do not present here the equation for the SPFs)

$$\sum_{g(i_1,\ldots,i_D)\leq H} \mathrm{i}\,\dot{A}_{i_1,\ldots,i_D}(t) \prod_{k=1}^{D} \varphi_{i_k}^{(k)}\left(r_{a_k}^{(k)}(t),t\right)$$

$$(5) \qquad = \sum_{g(i_1,\ldots,i_D)\leq H} \langle r_{a_1}^{(1)}(t)| \ldots \langle r_{a_D}^{(D)}(t)| \hat{H} | \varphi_{i_1}^{(1)}(t)\rangle \ldots | \varphi_{i_D}^{(D)}(t)\rangle A_{i_1,\ldots,i_D}(t) .$$

The collocation point set $\left(r_{a_1}^{(1)}(t),\ldots,r_{a_D}^{(D)}(t)\right)$ is chosen to be a Smolyak grid [4] built from nested sets of 1-D grid points. The potential function matrix elements can now simply be evaluated as

$$(6)$$
$$\langle r_{a_1}^{(1)}(t)| \ldots \langle r_{a_D}^{(D)}(t)| V | \varphi_{i_1}^{(1)}(t)\rangle \ldots | \varphi_{i_D}^{(D)}(t)\rangle = V\left(r_{a_1}^{(1)}(t),\ldots,r_{a_D}^{(D)}(t)\right) \prod_k B_{a_k,i_k}^{(k)},$$

where

$$(7) \qquad\qquad B_{a_k,i_k}^{(k)} = \varphi_{i_k}^{(k)}\left(r_{a_k}^{(k)}(t),t\right) .$$

Hence, only values of the potential function at the sparse grid points are required. The only approximations are the finite basis and point set. A simple choice for the function restricting the multi-indices of the basis is

$$(8) \qquad\qquad g(i_1,\ldots,i_D) = \sum_{k=1}^{D} (i_k - 1) .$$

The SPF bases are converted into so-called hierarchical bases. They simplify computing the matrix-vector product with the inverse of the (large) matrix whose elements are basis functions evaluated at points,

$$
(9) \qquad B_{\substack{a_1,\ldots,a_D \\ i_1,\ldots,i_D}} = \prod_{k=1}^{D} B^{(k)}_{a_k,i_k}
$$

$$
(10) \qquad g\left(a_1,\ldots,a_D\right) \leq H \ \wedge \ g\left(i_1,\ldots,i_D\right) \leq H,
$$

which is required to transform from the grid to the basis representation in Eq. (5).

Very importantly, it is possible to evaluate all matrix-vector products by doing sums *sequentially*. In particular, one can show that, when using hierarchical 1-D basis functions, the $\mathbf{B}^{(k)}$ matrices become lower-triangular and that

(11)

$$
\sum_{g(a_1,\ldots,a_D)\leq H} \left[\mathbf{B}^{-1}\right]_{\substack{i_1,\ldots,i_D \\ a_1,\ldots,a_D}} z_{a_1,\ldots,a_D}
$$

$$
= \sum_{a_D=1}^{i_D} \left[\left(\mathbf{B}^{(D)}\right)^{-1}\right]_{i_D,a_D} \cdots \sum_{a_2=1}^{i_2} \left[\left(\mathbf{B}^{(2)}\right)^{-1}\right]_{i_2,a_2} \sum_{a_1=1}^{i_1} \left[\left(\mathbf{B}^{(1)}\right)^{-1}\right]_{i_1,a_1} z_{a_1,\ldots,a_D}
$$

(note that the upper limits on the sums correspond to the case where the restriction function is given by Eq. (8), though a generalisation is straightforward). The right hand side of this equation can be efficiently evaluated by doing the sums sequentially, i.e, by first summing over $a_1$ to obtain an intermediate vector $z^{(1)}_{i_1,a_2,\ldots,a_D}$, then over $a_2$ to obtain $z^{(2)}_{i_1,i_2,a_3,\ldots,a_D}$, and so on. The cost (assuming Eq. (8) is used to restrict the indices) then scales as

$$
(12) \qquad \mathcal{O}\left(D\left[\frac{H}{D+1}+1\right]N_{\text{prune}}\right),
$$

where $N_{\text{prune}} = \binom{D+H}{D}$. The numerical cost thus scales almost linearly with the number of sparse grid points $N_{\text{prune}}$ (or, equivalently, non-direct product basis functions). This technique could also be useful outside the field of chemical physics. [5] The validity of the new pruned, collocation-based (PC-)MCTDH approach is confirmed by calculating the first 50 vibrational eigenenergies of $CH_2NH$.

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## Local singularities and Lie algebra within a nonadiabatic context

BENJAMIN LASORNE

(joint work with Benjamin Gonon, Aurelie Perveaux, Fabien Gatti, David Lauvergnat)

Conical intersections and nonadiabatic couplings are essential concepts in quantum molecular dynamics when photoinduced processes involve a manifold of electronic states (eigenvectors) with crossings, *i.e.*, local degeneracies, among their energies (eigenvalues) along continuous variations of the molecular geometry.

However, they essentially correspond to singularities with ill-defined local derivatives. In principle, the adiabatic representation can be unitarily transformed into a regular one, called diabatic, which is more convenient from a practical point of view but suffers from the lack of a global definition.

The primal definition of nonadiabatic couplings among electronic states relies on the knowledge of how electronic wavefunctions vary to first order with nuclear coordinates. However, such derivatives cannot always be computed from first principles, according to the method used in quantum-chemistry calculations. We discuss here how nonadiabatic couplings can be obtained in the vicinity of a conical intersection from energies only, even in cases where wavefunctions are not available explicitly. This approach is based on the diagonalisation of the Hessian of the squared energy half-difference at a conical intersection. Two eigenvalues are outstanding; the corresponding eigenvectors can be identified to the branching-space vectors that span the plane along which degeneracy is lifted to first order [1].

We also show how to extend the seminal two-state model to more general situations with a formulation based on Lie group homomorphisms [2]. In particular, three-state Hamiltonians can be expressed in terms of Gell-Mann basic matrices, which generalise the well-known Pauli matrices of two-state systems. This approach essentially consists in a matrix vectorisation that turns unitary similarity transformations into rotations, thus allowing for less intricate relationships between rotation angles and matrix entries.

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## Excited-State Molecular Dynamics with the exact factorization of the electron-nuclear wavefunction

FEDERICA AGOSTINI

(joint work with E. K. U. Gross, Ali Abedi, Neepa T. Maitra, Seung Kyu Min, Ivano Tavernelli, Giovanni Ciccotti, Rodolphe Vuilleumier)

Excited-state dynamics is at the heart of Photophysics and Photochemistry. Nonadiabatic transitions are induced by the strong coupling between electronic dynamics and the ultrafast motion of the nuclei, and are observed in phenomena such as photosynthesis, photovoltaics, and exciton transport in $\pi$-conjugated complexes. An essential part of the research efforts in these fields is directed towards developing theoretical and computational approaches to describe conformational changes, energy dissipation, or quantum decoherence, i.e., the signature aspects of excited-state processes. In this context, among the most successful frameworks for molecular dynamics simulations of excited-state processes stand trajectory-based quantum-classical methods, as they give access to the study of complex molecular systems. Trajectory-based approaches combine a classical description of nuclear dynamics with a quantum-mechanical description of electronic dynamics. However, the approximations underlying quantum-classical methods are sometimes severe, and are at the origin of controversies as well as of continuous developments.

In this talk I will present a recently-developed trajectory-based approach to nonadiabatic dynamics [1, 2]. The actual numerical scheme has been derived from the exact factorization of the electron-nuclear wavefunction [3, 4], a new framework proposed to investigate, interpret and approximate the coupled dynamics of electrons and nuclei beyond the Born-Oppenheimer approximation. The exact factorization provides a new perspective to analyze nonadiabatic processes: (i) it proposes an alternative [5] to the standard Born-Oppenheimer framework, that pictures excited-state processes in terms of wavepackets moving on and transferring between static potential energy surfaces; (ii) it suggests new interpretations [6] of molecular geometric-phase effects, related to conical intersections; (iii) it provides guidelines for developing simulation algorithms in different [7] nonadiabatic regimes. These points will be discussed during the talk and briefly illustrated on low-dimensional models and molecular systems.

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## Efficient geometric integrators for nonadiabatic quantum dynamics
### Jiří Vaníček
(joint work with Seonghoon Choi, Julien Roulet)

Geometric integrators of the Schrödinger equation conserve exactly many invariants of the exact solution. Among these integrators, the split-operator algorithm is explicit and easy to implement, but, unfortunately, is restricted to systems whose Hamiltonian is separable into a kinetic and potential terms. Here [1], we describe several implicit geometric integrators applicable to both separable and non-separable Hamiltonians, and, in particular, to the nonadiabatic molecular Hamiltonian in the adiabatic representation. These integrators combine the dynamic Fourier method with recursive symmetric composition of the trapezoidal rule or implicit midpoint method, which results in an arbitrary order of accuracy in the time step. Moreover, these integrators are exactly unitary, symplectic, symmetric, time-reversible, and stable, and, in contrast to the split-operator algorithm, conserve energy exactly, regardless of the accuracy of the solution. The order of convergence and conservation of geometric properties are proven analytically and demonstrated numerically on a two-surface NaI model in the adiabatic representation. Although each step of the higher order integrators is more costly, these algorithms become the most efficient ones if higher accuracy is desired; a thousand-fold speedup compared to the second-order trapezoidal rule (the Crank-Nicolson method) was observed for wavefunction convergence error of $10^{-10}$. I will also discuss analogous, arbitrary-order compositions of the split-operator algorithm and show the application of both types of geometric integrators to a higher-dimensional system, i.e., a three-state three-dimensional model of pyrazine in the diabatic representation [2].

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## Tensor train algorithms for quantum dynamics simulations of excited state nonadiabatic processes and quantum control

Victor S. Batista

(joint work with Samuel Greene and Alex Gorodetsky)

We introduce tensor train algorithms for quantum dynamics simulations of excited state nonadiabatic processes and quantum control, including the "tensor-train split-operator Fourier transform" (TT-SOFT) method for simulations of multidimensional nonadiabatic quantum dynamics [1], and a continuous analogue tensor-train implementation of the Chebyshev propagation method.

The TT-SOFT method integrates the time-dependent Schrödinger equation,

$$i\hbar\frac{\partial \psi}{\partial t} = \hat{H}\psi,$$

for the $d$-dimensional wavefunction $\psi(x_1, x_2, \cdots, x_d)$ evolving according to the Hamiltonian $\hat{H} = \hat{T} + \hat{V}$, with $\hat{T} = \sum_{j=1}^{d} \frac{\hat{p}_j^2}{2m_j}$ the kinetic energy operator defined by momenta $p_j = -i\hbar\frac{\partial}{\partial x_j}$ and masses $m_j$, where $\hbar = h/(2\pi)$, with Planck's constant $h$. The potential energy $\hat{V}(x_1, x_2, \cdots, x_d)$ defines the interactions between the physical variables.

We represent the time-dependent wavefunction $\psi$ as a tensor-train [2],

$$\psi(x_1, x_2, \ldots, x_d) = \sum_{\alpha_1=1}^{r_1} \sum_{\alpha_2=1}^{r_2} \cdots \sum_{\alpha_{d-1}=1}^{r_{d-1}} \psi_1(x_1, \alpha_1)\psi_2(\alpha_1, x_2, \alpha_2)\cdots\psi_d(\alpha_{d-1}, x_d),$$

and we evolve it by applying the short-time approximation of the time-evolution operator, as given by the second order Strang splitting (Trotter) expansion:

$$e^{-\frac{i}{\hbar}\hat{H}\tau} = e^{-\frac{i}{\hbar}\hat{T}\frac{\tau}{2}}e^{-\frac{i}{\hbar}\hat{V}\tau}e^{-\frac{i}{\hbar}\hat{T}\frac{\tau}{2}} + \mathcal{O}(\tau^3),$$

with $\hat{V}$ and $\hat{T}$ in tensor-train format in coordinate and momentum representations, respectively.

Substituting the Trotter expansion into the integrated form of the Schrödinger equation, we obtain the time-evolved wavepacket in tensor train format, as follows:

$$\Psi(t+\tau) = \text{IFT}\left[e^{-i\hat{T}\tau/2}\ \text{FT}\left[e^{-i\hat{V}\tau/\hbar}\ \text{IFT}\left[e^{-i\hat{T}\tau/2}\ \text{FT}\left[\Psi(t)\right]\right]\right]\right].$$

FT and IFT denote the Fourier transform and inverse Fourier transform of the tensor trains corresponding to the arguments of the brackets, which are efficiently computed by-passing the "curse of dimensionality" in terms of the corresponding 1-dimensional FT and IFT of the core arrays of individual physical variables. Multiplications and additions of tensor trains are implemented as usual by element wise multiplications and additions, followed by rounding with rank adaptation. The rank is therefore adapted along the propagation to compress the representation and minimize the memory requirements and number of floating-point operations along the propagation.

The resulting TT-SOFT method is essentially the grid-based split-operator Fourier transform method implemented in dynamically adaptive tensor-train representations. In the same spirit of all matrix product states, the tensor-train format enables the representation, propagation, and computation of observables of multidimensional wave functions in terms of grid-based wavepacket tensor components, bypassing the need of actually computing the wave function in its full-rank tensor product grid space. We demonstrate the accuracy and efficiency of the TT-SOFT method as applied to propagation of 24-dimensional wave packets, describing the $S_1/S_2$ interconversion dynamics of pyrazine after UV photoexcitation to the $S_2$ state. Our results show that the TT-SOFT method is a powerful computational approach for simulations of quantum dynamics of polyatomic systems since it avoids the exponential scaling problem of full-rank grid-based representations.

The tensor train Chebyshev (TTC) method is introduced and demonstrated as applied to both real and imaginary time propagation of high-dimensional model systems in terms of both the discrete tensor-train representation [2], and the continuous analogue tensor-train implementation [4]. The time evolution operator is applied, as follows [3]:

$$\psi(t + \tau) = e^{-i\hat{H}\tau}\psi(t) = \sum_{k=0}^{N}(2 - \delta_{k,0})J_k(\tau)(-i)^k TT_k(t),$$

with $J_k$ the Bessel functions of the first kind, and $TT_k(t) = T_k(\hat{H})\psi(t)$ the tensor trains corresponding to the Chebyshev polynomials of the Hamiltonian $T_k(\hat{H})$, applied to $\psi(t)$. In the continuous version, the tensor-product structure is imposed only upon the data structure of core matrix valued *functions* rather than upon the parameters of the constituent univariate functions stored by the discrete tensor train format as two- and three-way core arrays. The continuous version is particularly suitable for efficient differentiation and optimization as necessary by algorithms for quantum or classical control [5, 6].

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## Recent progress on continuum solvation models

BENJAMIN STAMM

In this talk, we have given an introduction to numerical methods based on a domain decomposition strategy to solve problems arising in Continuum Solvation models (CSMs) [1, 2, 3, 4, 5] which are nowadays part of the standard toolbox of computational chemists. Historically, in the quantum chemistry community, polarizable CSMs such as the Polarizable Continuum Model (PCM) [1] or the Conductor-like Screening Model (COSMO) [6] have been developed as a cheap, but physically sound way, to include solvation effects in the quantum mechanical (QM) description of a molecule and its properties.

As the computational cost is usually dominated by the solution of the QM equations, the computational performance of CSM have not been historically taken into much consideration, as the setup and solution of the CSM equations, which are equivalent in some way to solving Poisson's equation in a heterogeneous dielectric medium (see below), has always been assumed to be a negligible additional computational cost. Due to advances in hardware, more efficient implementations and the spread of linear scaling techniques within quantum chemistry, such an assumption started to be less and less true in the last decade. Further, the diffusion of multiscale methods such as quantum mechanics/molecular mechanics (QM/MM) has made large to very large systems accessible to computational chemists. For such systems, the computational cost associated with continuum solvation, which scales as the second or even third power of the size of the system, can easily become the real bottleneck of the calculation [9].

From a modeling viewpoint, there are two main-ingredients for an implicit solvation model. First, the shape of the solute's cavity $\Omega$, or equivalently its surface $\partial\Omega$, is introduced and determines the region where the implicit solvent is present. The second ingredient is the macroscopic description of the solvent that is used to model the (electrostatic) interaction between the solute and the continuum solvent region. More precisely, the electrostatic potential $V$ generated by the solute's charge $\rho$ is then the solution of

$$(1) \qquad -\mathrm{div}(\varepsilon\nabla V) + \kappa^2 V = 4\pi\rho, \qquad \text{in } \mathbb{R}^3,$$

and the electrostatic interaction energy is given by

$$E^s = \frac{1}{2}\int_{\mathbb{R}^3} \rho\, V.$$

Here, the dielectric and Debye-Hückel constants of the solvent are given by $\varepsilon_\mathsf{s}$ and $\kappa_\mathsf{s}$ so that

$$(2) \qquad \varepsilon = \begin{cases} 0 & \text{in } \Omega, \\ \varepsilon_\mathsf{s} & \text{in } \Omega^\mathsf{c}, \end{cases} \qquad \kappa = \begin{cases} 0 & \text{in } \Omega, \\ \kappa_\mathsf{s} & \text{in } \Omega^\mathsf{c}. \end{cases}$$

In this talk, we have given the derivation of the domain decomposition method for COSMO [7, 8, 9, 10], i.e. with $\varepsilon_\mathsf{s} = \infty$ and $\kappa_\mathsf{s} = 0$ in (1). Indeed, in this particular case, the problem is reduced to the bounded domain $\Omega$ (the solute's cavity) which is then split into the union of overlapping and possibly scaled Van der Waals

balls $\Omega_i$ and equation (1) is solved inside each ball and coupled through appropriate boundary conditions. Numerical illustrations were underlying the efficiency of the present method compared to the state-of-the-art.

We also discussed in detail the extension [16] of the domain decomposition method to the linearized Poisson-Boltzmann equation (1) and discussed numerical results. In this case, the problem is reformulated as an integral equation based on Dirichlet-to-Neumann maps which, in turn, can be computed very efficiently using the domain decomposition techniques introduced for the COSMO equation.

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### Variational Monte Carlo Methods for Eigenvalue Problems

Reinhold Schneider

(joint work with K. Fackeldey, F. Nüske and F. Noé)

In a variational framework, we are searching for a function $\Psi \in \mathcal{V}$ as a minimizer of the *target functional*

$$\mathcal{J}(\Phi) : \mathcal{V} \to \mathbb{R} ,$$

that is we aim to find

$$\Psi = \mathrm{argmin}_{\Phi \in \mathcal{V}} \mathcal{J}(\Phi) .$$

In typical applications the space $\mathcal{V}$ is infinite- dimensional Hilbert space, or at least an infeasibly large space. Since we cannot solve this problem, we are instead interested in an approximate solution. This approximate minimizer is sought by restricting the minimization problem to a compact *model class* (or *hypothesis space*) $\mathcal{M} \subseteq \mathcal{V}$. The optimization problem though becomes

$$\Psi_h := \ \mathrm{argmin} \ \{\mathcal{J}(\Phi) : \Phi \in \mathcal{M} \subset \mathcal{V}\} .$$

The choice of the model classes (and the regularization) plays an essential role and certainly depends on the concrete applications. The compactness assumption is essential for the present analysis. For example, if $\mathcal{V}_h$ is a finite-dimensional subspace of $\mathcal{V}$. Since this is not a compact set we have to restrict further to a ball centered e.g. at 0 of sufficiently large radius $R$ choosing $\mathcal{M} := \mathcal{V}_h \cap B_R$. This yields the classical Ritz-Galerkin treatment of variational problems. What we have in mind are tensor product parametrizations, see e.g. [2] which are no longer linear. However one might think about other methods used in statistical learning e.g. kernel methods and/or (deep) neural networks.

In many applications, and that the case in the applications we have in mind, the exact functional $\mathcal{J}$ is not (explicitly) known or at least unfeasible or expensive to compute. Even more for PDEs in high spatial dimensions the required integrals cannot cannot computed exactly.

Instead, we consider the *empirical optimization problem* only on the model class

$$\Psi_{N,h} := \ \mathrm{argmin} \ \{\mathcal{J}_N(\Phi) : \Phi \in \mathcal{M} \subset \mathcal{V}\} .$$

If the function $\ell : \Omega \to \mathbb{R}$ is continuous and $\mathcal{M}$ is compact there exists at least one minimizer. At the moment, we will defer from the problem of finding such a minimizer, although this problem can be extremely hard in practice. Let us only remark, that local optimization by gradients methods requires the computability of the gradient $\nabla(\ell(\Phi)(x))$, w.r.t. the unknown parameter in $\Phi$, and $\ell(\Phi)(x)$, at $x = x^i$, and not more. With this knowledge a local optimization scheme can be set up easily.

For example, if the target functional has the form

$$\mathcal{J}(\Phi) = \int_\Omega \ell(\Phi(x))\rho(x) \ \mathrm{d}x , \ \Phi \in \mathcal{M} ,$$

we replace the exact integral by its approximation using Monte Carlo integration. For the latter part, we suppose that samples, sampled i.i.d. from a probability

distribution $x^i \sim \rho$ can be calculated relatively inexpensive, or are provided by other means. That is, we are using Monte Carlo integration to built the *surrogate functional* $\mathcal{J}_N : \mathcal{M} \to \mathbb{R}$. The eigenvalue problem cannot be cast directly in the form of a simple integral, but its variational formulation according to the Rayleigh Ritz principle is a quotient of two integrals of the form above.

For a variational framework computing the invariant subspace of the first $m$ *eigenfunctions* $\psi_j$, $j \leq m$, of a symmetric operator $T : \mathcal{V} \to \mathcal{V}'$ eigenfunctions, simultanously, we consider $\Psi = (\psi_j)_{j=0}^m \in \mathcal{V}^m$ subordinated to the *orthogonality constraints*

$$\langle\langle \Psi, \Psi \rangle\rangle := (\langle \psi_j, \psi_k \rangle_\rho w)_{j,k=1}^m = \delta_{i,k}$$

optimization problem

$$\Psi = \operatorname{argmin} \{ \mathcal{J}(\Phi) : \Phi \in \mathcal{V}^m \text{ subject to } \langle\langle \Phi, \Phi \rangle\rangle_\rho = \mathbf{I} \}$$

$$\mathcal{J}(\Phi) \quad := \quad -\langle\langle T_\tau \otimes I\Phi, \Phi \rangle\rangle := -\sum_{j=0}^m \langle \phi_j, T_\tau \phi_j \rangle_{\phi_0}$$

The minimum is attained at $\min \mathcal{J}(\Phi) = \mathcal{J}(\Psi) = -\sum_{j=0}^m \lambda_j$, the sum of the $m$ lowest eigenvalues. We rewrite this constraint minimization problem by an unconstraint optimization problem in Rayleigh quotient form.

We are searching for a function $\Psi \in \mathcal{V}^m$ as a minimizer of the *target functional*

$$
\begin{aligned}
\mathcal{J}(\Phi) &= \sum_{j=0}^{m-1} \sum_{k=1}^{m-1} \big( \int_\Omega t_{j,k}(\Phi(x))\rho(x)\mathrm{d}x \big)_{j,k} \big( \int_\Omega m_{j,k}(\Phi)\rho(x)\mathrm{d}x \big)_{k,j}^{-1} \\
&= \sum_{j=0}^{m-1} \sum_{k=1}^{m-1} \mathbf{T}_{j,k}(\mathbf{M}^{-1})_{k,j}
\end{aligned}
$$

where

$$t_{j,k}(\Psi(x))(x) := \psi_j(x)(T\psi_k)(x)w(x) \ , \ m_{j,k}(\Psi)(x) := \psi_j(x)\psi_k(x)w(x)$$

that is we seek to find

$$\Psi = \operatorname{argmin}_{\Phi \in \mathcal{V}^m} \mathcal{J}(\Phi) \ .$$

On our model class $\mathcal{M}^m$ we can define an *empirical target functional* or *surrogate functional* by replacing the exact expectation by the mean, i.e. an empirical expectation, for given samples $x^\ell$, $\ell = 1, \ldots, N$, distributed according to a given density $\rho$, this is given by

$$\mathcal{J}_N(\Phi) = \sum_{j=0}^{m-1} \sum_{k=1}^{m-1} \big( \frac{1}{N} \sum_{\ell=1}^N t_{j,k}(\Phi(x^\ell)) \big) \big( \frac{1}{N} \sum_{\ell=1}^N m_{j,k}(\Phi(x^\ell)) \big)_{k,j}^{-1} \ .$$

### Error Analysis

We are finally interested to estimate the error of the corresponding minimizers, i.e. $\|\Psi - \Psi_N\|_\mathcal{V}$. Assuming local strong convexity of the functional this can be achieved (at least locally) indirectly by estimating the error in the functional values $\mathcal{J}(\Psi_N) - \mathcal{J}(\Psi)$.

A principal disadvantage of the sampling or Monte Carlo approach is that, in general, we cannot obtain worst case error estimates. However we can try to prove error estimates which hold with high probability, i.e. with a certain confidence which can be improved exponentially fast by increasing the number of samples. Therefore we pursue the concept of *convergence in probability* see e.g. [1]. This theory has been developed in statistical for the purpose of regression and classification, and be carried out with only slight modifications in [4].

In statistics, e.g. for regression and classification, the present approach is already established. We pursue to apply this approach to (deterministic) problems in numerics, and Monte Carlo sampling is only used as a numerical tool. It enables the treatment of high-dimensional problems which have not been feasible by purely deterministic approaches, or at least simplifies the numerical treatment drastically. In particular, it allows the treatment of non-linear problems and simplifies the handling of complex PDE's enormously. On the other hand, this comes at a price that we have accept convergence results in terms of probability. For problems concerning Fokker Planck equation, or quantum mechanics this seems to be a legal perspective. Indeed this approach is systematic reformulation of *Variational Monte Carlo Methods* already used in quantum physics since decades.

The error $|\mathcal{J}(\Psi_N) - \mathcal{J}(\Psi)|$ can be decomposed into three parts,

$$\mathcal{J}(\Psi_N) - \mathcal{J}(\Psi) \leq \mathcal{E}_{\text{appr}} + \mathcal{E}_{\text{gen}} + \mathcal{E}_{\text{opt}}$$
$$\leq \underbrace{|\mathcal{J}(\Psi) - \mathcal{J}(\Psi_h)|}_{\mathcal{E}_{\text{appr}}} + \underbrace{|\mathcal{J}(\Psi_h) - \mathcal{J}(\Psi_N)|}_{\mathcal{E}_{\text{gen}}} .$$

The first term is called the *approximation error* - a pure deterministic quantity due to our modeling. The second is called the *generalization error* and is a result of the use of the empirical surrogate functional. Let us highlight that for given $\Phi \in \mathcal{M}_h$ we cannot compute $\mathcal{J}(\Phi)$ but only its empirical surrogate $\mathcal{J}_N(\Phi)$.

LEMMA: The generalization error $\mathcal{E}_{gen} := |\mathcal{J}(\Psi_h) - \mathcal{J}(\Psi_N)|$ can be estimated by

$$\mathcal{E}_{\text{gen}} \leq 2 \sup_{\Phi \in \mathcal{M}} |\mathcal{J}(\Phi) - \mathcal{J}_N(\Phi)|$$

The approximation error is the error of the exact or deterministic numerical scheme. For strongly convex problems it governed locally by the error a quasi-best approximation of $\Psi$ by functions from the model class $\Phi_h \in \mathcal{M}_h$

$$\mathcal{E}_{\text{approx}} = \mathcal{J}(\Psi_h) - \mathcal{J}(\Psi) = \inf_{\Phi \in \mathcal{M}} |\mathcal{J}(\Phi) - \mathcal{J}(\Psi)| \leq C \inf_{\Phi \in \mathcal{M}} \|\Phi - \Psi\|_{\mathcal{V}}^2$$

For a wide range of functionals and linear subspaces a rigorous analysis is available at text-book level. Estimating the approximation error will not be considered here in more details. It is the central issue in approximation theory and a precise mathematical formulation for the *power of expressivity* of the model class in connection. with the present applications. In principle, the *generalization error* cannot be estimated deterministically. Therefore we are going to estimate the probability for this bound with a given confidence.

We will assume that the following basic assumptions hold:

(1) **Boundedness**: For all $\Phi \in \mathcal{M}$

$$|\ell(\Phi)(x)| \leq C_1 \text{ for almost all } x \in \Omega$$

(2) **Lipschitz continuity**: For all $\Phi_1, \Phi_2 \in \mathcal{M}$

$$|\mathcal{J}(\Phi_1(x)) - \mathcal{J}(\Phi_2(x))| \leq C_2 \|\Phi_1 - \Phi_2\|_{\mathcal{V}}$$

For example both estimates hold for many functionals if $\mathcal{M} \subset L_\infty$. Otherwise this can be considered as an additional restriction to $\mathcal{M}$. For a further analysis we need the definition of the Covering Numbers of $\mathcal{M}$.

DEFINITION: The *covering number* $\nu(\mathcal{M}, \delta)$, is the minimal number of balls of radius $\delta$ covering $\mathcal{M}$, w.r.t. to $\|.-.\|_{\mathcal{V}}$.

Roughly speaking, the covering numbers quantifies the degree of compactness of the embedding $\mathcal{M} \subset \mathcal{V}$. It is also a measure of the (intrinsic) complexity of the model classes $\mathcal{M}$. Covering numbers of *hierarchical tensors* (HT/TT) were considered in [3]. Our main result in [5] is an error estimate holding with a certain confidence of the following form.

THEOREM: For all $\epsilon > 0$ and $\Psi_N$ sufficiently closed to $\Psi$,

- the generalization error $\mathcal{E}_{\text{gen}} = |\mathcal{J}(\Psi_h) - \mathcal{J}(\Psi_N)|$ can be estimated by

$$\mathbb{P}\big[\mathcal{E}_{\text{gen}} > \epsilon\big] \leq 2\nu_\rho(\mathcal{M}, \frac{1}{4C_2}\epsilon)e^{-\mathfrak{c}\epsilon^2 N} \quad \text{where} \quad \mathfrak{c} = (32C_1^2)^{-1}.$$

- the bound for the function

$$\mathbb{P}\big[\|\Psi - \Psi_N\|_{\mathcal{V}}^2 > \epsilon\big] \leq 2\nu_\rho(\mathcal{M}, \frac{1}{4C}\epsilon)e^{-\mathfrak{c}C\epsilon^2 N}$$

provided that $\inf_{\Psi_h \in \mathcal{M}}\|\Psi - \Psi_h\|_{\mathcal{V}}^2 \leq \frac{\epsilon}{2}$

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