

Exploiting New Advances in Mathematics to Improve Calculations in Quantum Molecular Dynamics

1/24/2016 — 1/29/2016

MEALS

*Breakfast (Buffet): 7:00–9:30 am, Sally Borden Building, Monday–Friday

*Lunch (Buffet): 11:30 am–1:30 pm, Sally Borden Building, Monday–Friday

*Dinner (Buffet): 5:30–7:30 pm, Sally Borden Building, Sunday–Thursday

Coffee Breaks: As per daily schedule, in the foyer of the TransCanada Pipeline Pavilion (TCPL)

***Please remember to scan your meal card at the host/hostess station
in the dining room for each meal.**

MEETING ROOMS

All lectures will be held in the lecture theater in the TransCanada Pipelines Pavilion (TCPL).

An LCD projector, a laptop, a document camera, and blackboards are available for presentations.

SCHEDULE

Sunday

- 16:00** Check-in begins (Front Desk - Professional Development Centre - open 24 hours)
17:30–19:30 Buffet Dinner, Sally Borden Building
20:00 Informal gathering in 2nd floor lounge, Corbett Hall
Beverages and a small assortment of snacks are available on a cash honor system.

Monday

- 7:00–8:45** Breakfast
8:45–9:00 Introduction and Welcome by BIRS Station Manager, TCPL
9:00–9:15 Introductory Comments and Announcements
- Morning Session Chair* George Hagedorn
- 9:15–9:40** Peter Felker
9:45–10:10 Christian Lubich
10:15–10:55 Coffee Break, TCPL
11:00–11:25 Edward Valeev
11:30–13:00 Lunch
13:00–14:00 Guided Tour of The Banff Centre; meet in the 2nd floor lounge, Corbett Hall
14:00 Group Photo; meet in foyer of TCPL (photograph will be taken outdoors so a jacket might be required).
- Afternoon Session Chair* Edward Valeev
- 14:15–14:40** Raymond Kapral
14:45–15:25 Coffee Break, TCPL
15:30–15:55 Vasile Gradinaru
16:00–16:25 Jiří Vaníček
16:30–16:55 Michael Griebel
17:00–17:25 Helmut Harbrecht
17:30–19:30 Dinner

Tuesday

7:00–9:00

Breakfast

9:00–9:15

Announcements (if necessary)

Morning Session Chair Stefan Teufel

9:15–9:40

Gabriel Hanna

9:45–10:10

Tucker Carrington

10:15–10:55

Coffee Break, TCPL

11:00–11:25

Caroline Lasser

11:30–13:30

Lunch

Afternoon Session Chair Tomoki Ohsawa

13:00–13:25

Gustavo Avila

13:30–13:55

George Hagedorn

14:00–14:25

Bill Poirier

14:30–15:10

Coffee Break, TCPL

15:15–15:40

David Tannor

15:45–16:10

Alain Joye

16:15–16:40

Mike Espig

16:45–17:10

Ove Christensen

17:30–19:30

Dinner

Evening Session Chair Volker Betz

19:30–19:55

Johannes Keller

20:00–20:25

Christoph Scheurer

Wednesday

7:00–9:00

Breakfast

Morning Session Chair Arnaud Leclerc

9:00–9:25

David Sattlegger

9:30–9:55

James Brown

10:00–10:40

Coffee Break, TCPL

10:45–11:10

Daniel Peláez–Ruiz

11:30–13:30

Lunch

Free Afternoon

17:30–19:30

Dinner

Thursday

7:00–9:00 Breakfast

Morning Session Chair Tucker Carrington

9:00–9:25 Uwe Manthe

9:30–9:55 Reinhold Schneider

10:00–10:40 Coffee Break, TCPL

10:45–11:10 David Lauvergnat

11:30–13:30 Lunch

Afternoon Session Chair Caroline Lasser

13:30–13:55 Tomoki Ohsawa

14:00–14:25 Stephanie Troppmann

14:30–15:10 Coffee Break, TCPL

15:15–15:40 Arnaud Leclerc

15:45–16:10 Phillip Thomas

16:15–16:40 Attila Császár

16:45–17:10 Volker Betz

17:30–19:30 Dinner

Evening Session Chair Alain Joye

19:30–19:55 Victor Batista

20:00–20:25 Stefan Teufel

Friday

7:00–9:00 Breakfast

Morning Session Chair Victor Batista

9:00–9:25 Robert Wodraszka

9:30–9:55 Pierre-Nicholas Roy

10:00–10:40 Coffee Break, TCPL

10:45–11:10 Ivan Oseledets

11:30–13:30 Lunch

Checkout by 12 noon.

** 5-day workshop participants are welcome to use BIRS facilities (BIRS Coffee Lounge, TCPL and Reading Room) until 3 pm on Friday, although participants are still required to checkout of the guest rooms by 12 noon. **

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ABSTRACTS

(in alphabetic order by speaker surname)

Speaker: **Gustavo Avila** (Chemistry, Queen’s University)
(and **Tucker Carrington, Jr.**)

Title: *Using High-Dimensional Smolyak Interpolation to Solve the Schrödinger Equation and Represent Potentials*

Abstract: Smolyak or sparse-grid interpolation enables one to accurately represent smooth multi-dimensional functions, without using a direct product basis. Instead, the basis is a pruned product basis. Pruning the basis makes it possible to also reduce the number of interpolation points. This attenuates what is referred to as the “curse of dimensionality”, i.e. the exponential increase in the number of basis functions and points with the number of coordinates. In chemical physics Smolyak interpolation can be used to represent potential energy surfaces in sum-of-products form. The number of terms can be minimized by pruning so as to include only the most important product basis functions. Related collocation methods can be used to solve the vibrational Schroedinger equation to study molecules with 6 atoms. The collocation approach enables us to use general potentials (not necessarily of sum-of-products form) and very flexible basis sets. In the collocation approach there is no need to compute the matrix elements and therefore no quadrature.

Speaker: **Victor Batista** (Chemistry, Yale University)

Title: *Time-Sliced Thawed Gaussian Propagation for Simulations of Quantum Dynamics*

Abstract: We introduce a rigorous method for simulations of quantum dynamics by implementing a simple concatenation of semiclassical thawed Gaussian propagation steps. During each finite-time propagation, the time-dependent wavefunction is represented as a linear superposition of overlapping Gaussians which are evolved, according to their characteristic equations of motion, by using 4th-order Runge-Kutta, or Velocity-Verlet integration. After each propagation step, the expansion coefficients of the linear superposition are updated analytically by using the Fast Gaussian Wavepacket Transform in the limit of closely overlapping basis functions. The method is illustrated as applied to simulations of quantum tunneling, showing quantitative agreement with benchmark calculations based on the Split-Operator Fourier Transform method.

Speaker: **Volker Betz** (Technische Universität – Darmstadt)

Title: *Accurate lower band wave function for transitions through avoided crossings*

Abstract: In a series of papers, Ben Goddard, Stefan Teufel and I introduced a method to compute the lower band wave function for transitions through avoided crossings in diatomic molecules. Here we report on the result of applying the method to realistic systems, using the paradigmatic example of NaI. It turns out that after some modifications, which are easy to explain and to implement, the method performs well on these models, leading to relative errors of 2% for the first transition and around 10% for the third one. Since the method computes the whole wave function, it can also resolve interference effects.

Speaker: **James Brown** (Chemistry, Queen’s University)
(and **Tucker Carrington, Jr.**)

Title: *Improving the Efficiency of Phase-Space Localized Basis Functions*

Abstract: For decades scientists have attempted to use ideas of classical mechanics to choose basis functions for calculating spectra. The hope is that a classically-motivated basis set will be small because it

covers only the dynamically important part of phase space. One popular idea is to use phase-space localized (PSL) basis functions. Because the overlap matrix, in the matrix eigenvalue problem obtained by using PSL functions with the variational method, is not an identity, it is costly to use iterative methods to solve the matrix eigenvalue problem. Iterative methods are imperative if one wishes to avoid storing matrices which is important for larger molecules. Previously, we showed that it was possible to circumvent the orthogonality (overlap) problem and use iterative eigensolvers. Here, we present a reformulation that improves the PSL basis functions themselves, and also a new method which more efficiently chooses the PSL functions. These methods are applied to the calculation of vibrational energies of CH_2O and CH_2NH using the iterative Arnoldi algorithm and PSL functions. We show that our PSL basis is competitive with other previously used basis sets for these molecules.

Speaker: **Tucker Carrington, Jr.** (Chemistry, Queen's University)
(and **Xiao-Gang Wang**)

Title: *Using Contracted Basis Functions and the Lanczos Algorithm to Compute Spectra of Flexible Van der Waals Dimers*

Abstract: We have developed a new method to compute numerically exact ro-vibrational levels of Van der Waals dimers with flexible monomers and applied it to water dimer, 12 vibrational coordinates, and Cl^-H_2O , 6 vibrational coordinates. The method uses vibrational basis functions that are products of an inter-monomer function and intra-monomer functions. The inter-monomer function is a product of Wigner functions and an inter-monomer stretch function. The intra-monomer functions are monomer vibrational wavefunctions. When the coupling between inter- and intra-monomer coordinates is weak, this new basis is very efficient and only a few monomer vibrational wavefunctions are necessary. The product structure of the basis makes it efficient to use the Lanczos algorithm to calculate eigenvalues and eigenfunctions of the Hamiltonian matrix. For water dimer, it is necessary to do (12-D) integrals by quadrature, but crucial to obviate the need to keep values of the potential on the full direct product quadrature grid in memory (if there were 10 quadrature points per coordinate, the full grid would have 1012 points (≈ 8000 GB)). This is done by storing an intermediate matrix (X.-G. Wang and T. Carrington Jr., J. Chem. Phys. **119** 101 (2003) and **129** 234102 (2008)). It represents the potential at a set of values of the 6 intermolecular coordinates in the intra-monomer basis. For water dimer, we have obtained numerically exact inter-monomer energy levels on the CCpol-8sf *ab initio* potential energy surface and compare them with results obtained using the 6D + 6D adiabatic approach of C. Leforestier, K. Szalewicz, and A. van der Avoird, J. Chem. Phys. **137** 014305 (2012).

Speaker: **Ove Christiansen** (Chemistry, University of Aarhus)

Title: *Tensor Decomposition in Vibrational Coupled Cluster Response Theory*

Abstract: I will discuss the integration of the tensor decomposition idea in the context of calculation of vibrational coupled cluster (VCC) wave functions and VCC response functions. Traditionally explicit quantum calculations for molecules with more than a few atoms is hampered by the curse of dimensionality leading to an explosion in complexity with system size. This includes both the fast increase in computational cost per quantum state with increasing system size, as well as the problem of the explosion in the number of available quantum states in relevant energy ranges. I will describe how response functions can be used to calculate vibrational spectra (IR or Raman) without the need for calculation of eigenstates, but requiring instead solution of complex linear response equations. On the other hand, a pole and residue search of the response function shows, that if needed, explicit state-by-state information can be obtained through solving response eigenvalue equations. The complex linear equation and real eigenvalue equations can in turn be solved by iterative methods. I will show how one iteratively can build up a subspace consisting of vectors that are stacked decomposed tensors. I will hereunder describe current progress in exploiting the computational advantages of the tensor decomposition in the transformations required for the iterative algorithms.

Implementations have been made using the standard canonical tensor decomposition format. (CP: CANDECOMP/PARAFAC). Numerical studies illustrate the theoretical concepts.

Speaker: **Attila G. Császár** (Chemistry, Eötvös University)

Title: *Mathematical Tools Applied to High-Resolution Molecular Spectroscopy*

Abstract: In the fourth age of quantum chemistry [1] there are several areas of first-principles nuclear motion theory which require significant development and these efforts can be helped greatly by various mathematical tools. A couple of related attempts, characterizing our groups research efforts, will be reviewed during the talk.

While analytic derivation of kinetic energy operators expressed in internal coordinates is certainly feasible, especially using techniques of geometric algebra, it seems more practical to rely on numerical handling of the kinetic energy operators [2, 3] during the solution of the time independent nuclear Schrödinger equation. The ensuing fully numerical handling of both the kinetic and potential energy operator parts of the Hamiltonian allows (a) the treatment of both full- and reduced-dimensional models of molecular systems within the same code for arbitrary systems, (b) the inclusion of the Eckart embedding in arbitrary nuclear motion computations, and (c) the efficient consideration of non-adiabatic effects, considerably improving the accuracy of the computation of rovibrational energy levels.

Iterative determination of a large number of eigenstates of huge Hamiltonian matrix representations is a special requirement during the solution of the time-independent nuclear Schrödinger equation. Certain results from our own experience are summarized, related to the iterative Lanczos technique and FEAST.

It is still true that quantum theory is usually unable to match the accuracy of high-resolution spectroscopic experiments. Thus, experimental determination of a large number of rovibrational energy levels is important, especially in view of the many applications which need such data. The theory of spectroscopic networks (SN) has been introduced [4] and developed in our group, providing an interesting chemical application of graph theory. Based on the concept of SNs, experimental-quality rovibrational energy levels can be derived via the Measured Active Rotational-Vibrational Energy Levels (MARVEL) approach [5].

[1] A. G. Császár, C. Fábri, T. Szidarovszky, E. Mtyus, T. Furtenbacher, and G. Czakó, *Phys. Chem. Chem. Phys.* **14** 1085–1106 (2012).

[2] E. Mátyus, G. Czakó, and A. G. Császár, *J. Chem. Phys.* **130** 134112 (2009).

[3] C. Fábri, E. Mátyus, and A. G. Császár, *J. Chem. Phys.* **134** 074105 (2011).

[4] A. G. Császár and T. Furtenbacher, *J. Mol. Spectrosc.* **266** 99 (2011).

[5] T. Furtenbacher and A. G. Császár, *J. Quant. Spectrosc. Rad. Transfer* **113** 929 (2012).

Speaker: **Mike Espig** (RWTH Aachen University)

Title: *The numerical treatment of high dimensional problems by means of tensor format representations*

Abstract: The coming century is surely the century of high dimensional data. With the rapid growth of computational chemistry and distributed parameter systems, high-dimensional data becomes very common. Thus, analyzing high dimensional data is an urgent problem of great practical importance. However, there are some unique challenges for analyzing data of high dimensions, including (1) the curse of dimensionality and (2) the meaningfulness of the similarity measure in the high dimension space. With standard techniques it is impossible to store all entries of the high-dimensional data explicitly. The reason is that the computational complexity and the storage cost are growing exponentially with the number of dimensions. Besides of the storage one should also solve this high-dimensional problems in a reasonable (e.g. linear) time and obtain a solution in some compressed (low-rank/sparse) tensor formats. The complexity of many existing algorithms is exponential with respect to the number of dimensions. With increasing dimensionality, these algorithms soon become computationally intractable and therefore inapplicable in many real applications. During the last years, tensor format representation techniques were successfully applied to high-dimensional problems. In our talk, we show how these low-rank approximations can be computed, stored and manipulated with minimal effort.

Speaker: **Peter M. Felker** (Chemistry and Biochemistry, UCLA)

Title: *Translational/Rotational Dynamics of Multiple Confined Species*

Abstract: We describe computational approaches to the elucidation of the quantal translational/rotational dynamics of entrapped molecular clusters. The particular focus is on dihydrogen clusters entrapped in clathrate hydrate cages. We discuss nuclear-orbital/configuration-interaction methods applied to the dynamics of $(H_2)_3$ and of $(H_2)_4$ entrapped in the large cage of type-II clathrate hydrate. We also discuss an approach in which the correlated translation motion of the two H_2 moieties in clathrate-entrapped $(H_2)_2$ is solved for first, the results of which are then used to build up a translation/rotational basis for the solution of the full dynamics of the entrapped $(H_2)_2$ cluster.

Speaker: **Vasile Gradinaru** (Seminar for Applied Mathematics, ETH – Zürich)

(and **Raoul Bourquin** and **George A. Hagedorn**)

Title: *Semiclassical Dynamics in Several Spaces Dimensions with Wavepackets: New Ideas and Challenges*

Abstract: We present a technique for solving the time-dependent Schrödinger equation for small \hbar in two or more space dimensions. The main idea is to expand the solution as a linear combination of semiclassical wave packets, but we use a new technique to avoid an unstable part of the computations.

Speaker: **Michael Griebel** (University of Bonn)

Title: *An adaptive multiscale bond order dissection ANOVA approach for efficient electronic structure calculations*

Abstract: We present a multi-scale decomposition approach for the efficient approximate calculation of the electronic structure problem for molecules. It is based on a dimension-wise decomposition of the space the underlying Schrödinger equation lives in. This decomposition is similar to the ANOVA-approach (analysis of variance) which is well-known in statistics. It represents the energy as a finite sum of contributions which depend on the positions of single nuclei, of pairs of nuclei, of triples of nuclei, and so on. Under the assumption of locality of electronic wave functions, the higher order terms in this expansion decay rapidly and may therefore be properly truncated. Furthermore, additional terms are eliminated according to the bonding structure of the molecule. This way, only the calculation of the electronic structure of local parts, i.e. small subsystems of size k of the overall system, is necessary to approximate the total ground state energy. This is approximately done by e.g. the HF-approach, DFT, CI, CC or MP2.

This decomposition approach is combined with rising the number p of approximation functions in the discretization of the k -sized subsystems. Then, it turns out that a sparse grid-like approach in the parameters k and p results in a very fast and parallel solution procedure which allows to treat huge biomolecules in decent run time and results in excellent approximations. Furthermore, our new approach can be used in an adaptive sparse-grid fashion which speeds up things even further.

This is joint work with J. Hamaekers and R. Chinnamsetty.

Speaker: **George A. Hagedorn** (Virginia Tech)

(and **Stephanie Gamble**)

Title: *Stretching Vibrations of the Hydrogen Bond in $HOHOH^-$*

Abstract: Low order Born-Oppenheimer approximations describe most molecular systems very well, but they fail for some molecules or ions, including many with Hydrogen bonds. Alternative approximations for Hydrogen bonded molecules were developed together with Alain Joye several years ago. With an emphasis on simplicity, we have recently attempted to apply the appropriate alternative approximation to $HOHOH^-$, in which the central Hydrogen nucleus feels a double well effective potential. We describe some preliminary results about the symmetric and antisymmetric stretching vibrations of the Hydrogen bond in this ion.

Speaker: **Gabriel Hanna** (Chemistry, University of Alberta)

Title: *Self-Consistent Filtering Scheme for Efficient Calculations of Observables via the Mixed Quantum-Classical Liouville Approach*

Abstract: Over the past two decades, several algorithms have been developed for calculating observables using mixed quantum-classical Liouville dynamics, which differ in how accurately they solve the quantum-classical Liouville equation (QCLE). One of these algorithms, known as sequential short-time propagation (SSTP), is a surface-hopping algorithm that solves the QCLE almost exactly, but obtaining converged values of observables requires very large ensembles of trajectories due to the rapidly growing statistical errors inherent to this algorithm. To reduce the ensemble sizes, two filtering schemes (viz., observable cutting and transition filtering) have been previously developed and effectively applied to both simple and complex models. However, these schemes are either ad hoc in nature or require significant trial and error for them to work as intended. In this study, we present a self-consistent scheme, which in combination with a soundly motivated probability function used for the Monte Carlo sampling of the nonadiabatic transitions, avoids the ad hoc observable cutting and reduces the amount of trial and error required for the transition filtering to work. This scheme is tested on the spin-boson model, in the weak, intermediate, and strong coupling regimes. Our transition filtered results obtained using a newly proposed probability function, which favours the sampling of nonadiabatic transitions with small energy gaps, show a significant improvement in accuracy and efficiency for all coupling regimes over the results obtained using observable cutting and the original implementation of transition filtering, and are comparable to those obtained using the combination of these two techniques. It is therefore expected that this novel scheme will substantially reduce ensemble sizes and simplify the computation of observables in more complex systems.

Speaker: **Helmut Harbrecht** (Universität Basel)

Title: *Wavelet Boundary Element Methods for the Polarizable Continuum Model*

Abstract: The present talk is concerned with the rapid solution of boundary integral equations which arise from solvation continuum models. We apply a fully discrete wavelet Galerkin scheme for the computation of the apparent surface charge on solvent accessible and solvent excluded surfaces. This scheme requires parametric surfaces. We therefore developed a mesh generator which automatically constructs a parametrization of the molecular surface by four-sided patches. Numerical results are presented which demonstrate the feasibility and scope of our approach.

Speaker: **Alain Joye** (Institut Fourier, Université de Grenoble I)

Title: *Representations of canonical commutation relations describing infinite coherent states*

Abstract: We investigate the infinite volume limit of quantized photon fields in multimode coherent states. We show that for states containing a continuum of coherent modes, it is natural to consider their phases to be random and identically distributed. The infinite volume states give rise to Hilbert space representations of the canonical commutation relations which are random as well and can be expressed with the help of Itô stochastic integrals. We analyze the dynamics of the infinite state alone and the open system dynamics of small systems coupled to it. We show that under the free field dynamics, initial phase distributions are driven to the uniform distribution, and we demonstrate that coherences in small quantum systems, interacting with the infinite coherent state, exhibit Gaussian time decay, in contrast with the decay caused by infinite thermal states, which is known to be exponentially rapid only.

Work in collaboration with M. Merkli

Speaker: **Raymond Kapral** (Chemistry, University of Toronto)

Title: *Surface Hopping*

Abstract: Fewest-switches surface hopping is one of the most widely used methods for describing nonadiabatic dynamics. It is simple but does suffer from some shortcomings, mainly due to the way decoherence is treated. The talk will discuss the approximations that must be made to the quantum-classical Liouville description of nonadiabatic dynamics in order to obtain fewest-switches surface hopping.

Speaker: **Johannes Keller** (Technische Universität – München)

Title: *Computing Quantum Expectations with Spectrograms*

Abstract: Many quasiclassical methods for the propagation of molecular quantum expectations, like the LSC–IVR method, build on discretizations of Egorov’s theorem. Hence, they require to sample from the initial state’s Wigner function, which is not a probability density. We present novel phase space densities based on Hermite spectrograms. These densities are better amenable for numerical sampling purposes and allow to approximate expectation values up to any order of accuracy in the high frequency parameter.

Speaker: **Caroline Lasser** (Technische Universität – München)

Title: *Simulating the Dynamics of the Ammonia Cation*

Abstract: The nonadiabatic dynamics of the ammonia cation are interesting both from a chemical and a mathematical perspective. The talk will focus on the mathematical aspects of the recent cooperation with Andrey Belyaev, Wolfgang Domcke, and Giulio Trigila, and present the results of the performed 12-dimensional surface hopping calculations.

Speaker: **David Lauvergnat** (Physical Chemistry, CNRS and Université de Paris–Sud)
(and **André Nauts**)

Title: *Efficient Implementation of a Smolyak Sparse-grid Scheme with Non-nested Grids*

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

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

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

Our previous implementation[6] avoided the need of 1D-nested grids and was extended to nD-Grids (the $G_{L^i}^i$ could be multidimensional grids). However, it required the explicit summation over direct-product grids (see Eq. 1) so that some identical calculations were performed several times. This had an unfavorable impact on the numerical efficiency, without, however, preventing large calculations from being performed.

Recently, we have introduced a new implementation, in which we keep the sums of the direct-product grids but perform the calculations sequentially over the various dimensions. Consequently, the repetition of identical calculations is avoided, which considerably improves the numerical efficiency.

- [1] S. A. Smolyak, *Soviet Mathematics Doklady* **4** 240 (1963).
- [2] G. Avila and T. Carrington, *J. Chem. Phys.* **131** 174103 (2009).
- [3] G. Avila and T. Carrington, *J. Chem. Phys.* **134** 054126 (2011).
- [4] G. Avila and T. Carrington, *J. Chem. Phys.* **135** 064101 (2011).
- [5] G. Avila and T. Carrington, *J. Chem. Phys.* **139** 134114 (2013).
- [6] D. Lauvergnat and A. Nauts, *Spectrochim. Acta Part A* **119** 18 (2014).

Speaker: **Arnaud Leclerc** (Chemistry, Université de Lorraine) (and **Tucker Carrington**)

Title: *Calculating Vibrational Spectra with Symmetrized Sum-of-Product Basis Functions*

Abstract: The memory cost of representing vibrational wavefunctions of polyatomic molecules with more than 6 atoms is huge if direct product basis sets are used. However the n^D numbers which represent a wavefunction (n being the number of 1-D basis functions for each of the D coordinates) can often be

deduced from a much smaller set of coefficients by using approximate, low-rank tensor decompositions. One possible choice is the CP format [1], i.e. a sum-of-products of 1-D functions whose memory cost scales as $\mathcal{O}(nD)$. In the reduced-rank block power method (RRBPM) introduced in [2], the rank of the SOP basis functions is reduced by iteratively optimizing the 1-D functions from which they are made. The optimized SOP basis functions span a subspace close to that of the desired eigenfunctions. Reduction is done with alternating least square algorithm of ref. [3]. Only 1-D operations are required and there is no need to store multidimensional vectors in memory. With this method one can compute vibrational eigenstates of systems up to $D = 30$ using a few GB of memory. The RRBPM can be improved in several ways, one of which is the use of molecular symmetry [4]. Symmetry properties can be exploited in the RRBPM by using symmetry-constrained sum-of-products without jeopardizing the memory advantage of the algorithm. Since the Hamiltonian is totally symmetric, it is possible to compute states of a particular symmetry by using start vectors each of which has the same symmetry. This makes symmetry assignments easier and improves the accuracy in comparison with symmetry-free calculations. The ideas are illustrated by applying them to the acetonitrile molecule CH_3CN (a 12D problem).

- [1] T. G. Kolda and B. W. Bader, *SIAM Review* **51**455 (2009).
- [2] A. Leclerc and T. Carrington, *J. Chem. Phys.* **140** 174111 (2014).
- [3] G. Beylkin and M. J. Mohlenkamp, *SIAM J. Sci. Comput.* **26**2133 (2005).
- [4] A. Leclerc and T. Carrington, submitted to *Chem. Phys. Lett.*

Speaker: **Christian Lubich** (Universität Tübingen)

Title: *Time integration of MCTDH and matrix product states*

Abstract: A numerical integrator is proposed for solving the multiconfiguration time-dependent Hartree (MCTDH) equations of motion, which are widely used in computations of molecular quantum dynamics. In contrast to existing integrators, the proposed algorithm does not require inverses of ill-conditioned density matrices and obviates the need for their regularization, allowing for large stepsizes also in the case of near-singular density matrices. The nonlinear MCTDH equations are split into a chain of linear differential equations that can all be efficiently solved by Lanczos approximations to the action of Hermitian-matrix exponentials, alternating with orthogonal matrix decompositions. The integrator is an extension to the Tucker tensor format of recently proposed projector-splitting integrators for the dynamical low-rank approximation by matrices and tensor trains (or matrix product states). The integrator is time-reversible and preserves both the norm and the total energy.

Speaker: **Uwe Manthe** (Chemistry, Universität Bielefeld)

Title: *Symmetry and the Entangled Ro-Vibrational Quantum States of a Fluxional Molecule*

Abstract: Separation of rotational and vibrational motion is a key concept in the analysis of the dynamics of isolated molecules. Approximate separability does not only hold for rigid or semi-rigid molecules but often works quite well even in the presence of large amplitude motion. While the precise analysis of spectroscopic experiments often requires to account for rotation-vibration couplings, a separable ansatz typically provides a valid zero order description on which further refinements can be based. A fundamentally different situation is encountered if fluxional molecules like AB_n or B_n with $n > 4$ are considered. Then fundamental symmetry arguments require the complete breakdown of the separability of rotational and internal motion. Rotational and internal motion must always be entangled. The talk will discuss fundamental issues related with the separation of rotational and vibrational motion in fluxional molecules. Challenges regarding the application of group and representation theory to the problem will be highlighted. In addition, numerical results for a prototypical example, the CH_5^+ molecular cation, will be shown.

Speaker: **Tomoki Ohsawa** (University of Texas at Dallas)

Title: *The Hagedorn-Hermite correspondence*

Abstract: I will explain the correspondence between the semiclassical wave packets of Hagedorn and the Hermite functions by looking into the relationship between their ladder operators. The correspondence

provides simple derivations of some fundamental properties of the Hagedorn wave packets—such as its completeness, transformation properties, and their generating functions—by linking them to the corresponding properties of the Hermite functions.

Speaker: **Ivan Oseledets** (Skolkovo Institute of Science and Technology)

Title: *Tensor Train Methods for Quantum Molecular Dynamics*

Abstract: In this talk I will describe our recent result for using TT (tensor train) machinery for solving basic problem for nuclear Schrödinger equations, including potential energy surface approximation using cross approximation and active subspaces, efficient integration of equation of motion using projector-splitting integrator and computation of vibrational states using block TT-format.

Speaker: **Daniel Peláez–Ruiz** (Physics, Université de Lille)

(and **Hans–Dieter Meyer**)

Title: *The Singular–Value Decomposition Multigrid POTFIT (SVD–MGPF) Algorithm* Abstract: We present the new Singular–Value Decomposition Multigrid POTFIT (SVD–MGPF), a grid–based tensor decomposition algorithm for large dimensional systems with particular focus on Quantum Dynamical problems. SVD–MGPF constitutes a generalisation of our previous (eigenvalue–decomposition based) EVD–MGPF method [1].

Both MGPF methods provide the Tucker decomposition of a target tensor (e.g. a potential energy surface). For such, a fine grid, the one needed to accurately represent the system, and a coarse one, a subset of the former, are defined. Tucker factor matrices are obtained from a series of POTFIT [2] decompositions carried out on grids which are fine for some degrees of freedom and coarse for the rest. The core tensor is obtained by overlapping these factor matrices with the values of the original tensor on the coarse grid.

The difference between SVD–MGPF and EVD–MGPF (or POTFIT) lies in the fact that the Tucker factor matrices are obtained through singular value decompositions of one-particle potential density matrices instead of eigenvalue ones. This is shown to remove the numerical instabilities present in MGPF. Additionally, a black–box method for the choice of the coarse grid choice is proposed. The novelty of the latter is that it leads to a fully-relaxed non- product coarse grid.

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[2] A. Jäckle, H.–D. Meyer, *J. Chem. Phys.* **104** 7974 (1996).

Speaker: **Bill Poirier** (Chemistry, Texas Tech University)

Title: *Quantum Mechanics Without Wavefunctions*

Abstract: Five years ago, the first paper was published [1] that describes what has come to be known as the “Many Interacting Worlds” (MIW) interpretation of quantum mechanics (QM) [2]. MIW is based on a new mathematical formulation of QM [1, 3], in which the wavefunction $\Psi(t, x)$ is discarded. Instead, the quantum state is uniquely represented as an ensemble, $x(t, C)$, of quantum trajectories or “worlds,” each of which has well–defined real–valued particle positions and momenta at all times. Unlike the Everett many–worlds interpretation (MWI), no world–branching occurs, and nearby trajectories/worlds influence one another dynamically. Indeed, it is through this very interworld interaction that all quantum behavior manifests. The quantum trajectory ensemble $x(t, C)$ satisfies an action principle, leading to a dynamical partial differential equation (via the Euler–Lagrange procedure), as well as to conservation laws (via Noether’s theorem).

The MIW approach offers a direct “realist” description of nature that is beneficial in interpreting quantum phenomena such as entanglement, measurement, spontaneous decay, etc. It is also amenable to a straightforward relativistic generalization [4], which provides a notion of global simultaneity even for accelerating observers. Moreover, whereas the original MIW theory is fully consistent with Schrödinger wave mechanics, the more recently developed flavors offer the promise of new experimental predictions. These and other developments, e.g. for many dimensions, multiple particles, and spin, will be discussed.

- [1] B. Poirier, *Chem. Phys.* **370** 4 (2010).
- [2] B. Poirier, *Phys. Rev. X* **4** 040002 (2014).
- [3] J. Schiff and B. Poirier, *J. Chem. Phys.* **136** 031102 (2012).
- [4] B. Poirier, arXiv:1208.6260 [quant-ph], (2012).

Speaker: **Pierre–Nicholas Roy** (Chemistry, University of Waterloo)

Title: *Path Integrals and Quantum Dynamics*

Abstract: We will discuss the use of path integral methods for the study of the low temperature properties of confined molecular systems. Both Path Integral Monte Carlo and Path Integral Molecular dynamics approaches will be considered. Issues such as the determination of entanglement measures and estimators will be discussed, along with an analysis of many-body correlations and superfluid measures. Applications to molecules confined in bosonic droplets and nano–cavities will be presented.

Speaker: **David Sattlegger** (Technische Universität – München)

Title: *Efficient Algorithms for Semiclassical Quantum Dynamics*

Abstract: We study the well–known Herman–Kluk propagator in order to calculate approximate solutions to the time–dependent semiclassical Schrödinger equation in high dimensions. We derive a discretisation scheme and provide its approximation properties. This scheme, as well as other semiclassical methods, are of an intrinsically parallel nature. This allows for the design of highly efficient algorithms employing state of the art parallelization and vectorization techniques.

Speaker: **Christoph Scheurer** (Chemistry, Technische Universität – München)

Title: *Sparse Grids and the Hierarchical Expansion of the Kinetic Energy Operator for the Anharmonic Vibrational Problem*

Abstract: The determination of the fully anharmonic vibrational spectrum and the corresponding eigenstates is one of the prototypical quantum dynamical problems. Even though many approximate methods have been developed in the past and normal modes are computed routinely nowadays, the solution of the full problem still poses computational challenges for medium (i.e. dozens of degrees of freedom) to large sized systems. A powerful and systematically improvable approach employs the vibrational self-consistent field (VSCF) method and its correlated extensions, like the vibrational configuration interaction (VCI) or the vibrational coupled cluster (VCC) expansions.

It has long been known that the rate of convergence of these expansions depends critically on the choice of basis states and their correlations which may be reduced by a skilled choice of the underlying coordinate system. For molecular systems the topology of the Born–Oppenheimer potential energy surface (PES) in the vicinity of the minima is frequently best described in terms of a set of curvilinear internal coordinates, which has been shown by Wilson and coworkers more than 60 years ago.

We have recently developed a hierarchical expansion of the resulting curvilinear kinetic energy operator which allows for systematic approximations that are well suited for the VSCF and VCI methods [1]. The combination with sparse grid approximations for the many–body sub- operators yields a method which is adaptive on two levels [2]. Based on some heuristic criteria derived from perturbation theory an efficient fully self–adaptive method has been devised which generates an approximate vibrational Hamiltonian for a given system (PES and underlying coordinate system) and a prescribed tolerance for some part of the vibrational spectrum without further input.

- [1] Daniel Strobusch and Christoph Scheurer, A General Nuclear Motion Hamiltonian and Non–Internal Curvilinear Coordinates. *J. Chem. Phys.* **138(9)** 094107 (2013).
- [2] Daniel Strobusch and Christoph Scheurer, Adaptive Sparse Grid Expansions of the Vibrational Hamiltonian. *J. Chem. Phys.* **140(7)** 074111 (2014).

Speaker: **Reinhold Schneider** (Technische Universität – Berlin)

Title: *Alternating Directional Gradient Algorithms and Tensor Completion in Hierarchical Tensor Formats*

Abstract: Hierarchical tensor representation, e.g. Tucker tensor format (Hackbusch), Multi-layer TDMCH (Meyer et al.), or tree tensor network states (G. Chan et al.) and Tensor Trains (TT) (Oseledets) or Matrix product states (MPS) offer stable and robust approximation by a low order cost.

We will discuss tensor recovery, in particular tensor completion for hierarchical tensors (resp. tree tensor networks) in analogy to matrix completion. The goal is to recover or to approximate a low rank tensor from few samples or measurements. A typical application can be the approximation of the potential energy surface. For this purpose, we will discuss ALS (one site DMRG) approach and a new ADF and an alternating directional gradient method which has a better scaling than ALS. However the ADF approach can also be used for eigenvalue computation (e.g. ground state) and time evaluation. We will investigate the intimate relationship to Riemannian gradient optimization techniques and Dirac Frenkel principle.

Speaker: **David Tannor** (Chemical Physics, Weizmann Institute of Science)

Title: *Phase Space Approach to Solving the Schrodinger Equation: Thinking Inside the Box*

Abstract: For many decades quantum dynamicists have been seeking accurate methods to solve the vibrational Schrodinger equation for medium-sized polyatomic molecules. A promising approach is to use a basis of localized Gaussians that can be tailored to the classical phase space of the fully coupled, multidimensional system. Unfortunately, most previous attempts to use Gaussians to solve the vibrational Schrodinger equation have suffered from numerical difficulties due to the nonorthogonality of the Gaussians. We have recently discovered a one-to-one mapping between the von Neumann basis (Gaussians located on an evenly spaced lattice in phase space) and the discrete Fourier basis, provided a simple but crucial modification is made: that the von Neumann basis is taken to be periodic in both position and momentum; the periodic von Neumann (pvN) basis leads to Fourier accuracy with Gaussian flexibility. Preliminary results show 1) orders of magnitude improvement in accuracy over the standard von Neumann basis; 2) a significant reduction in basis set size relative to the Fourier Grid Hamiltonian/sinc DVR method; 3) attainment, as $\hbar \rightarrow 0$, of the theoretically optimal efficiency of one basis function per eigenstate; 4) compatibility of the method with a wavelet scaling transformation suitable for multiple length scale problems. An error analysis of the method shows that the method formally defeats exponential scaling with dimensionality. This talk will summarize the current status of the method and some of the key remaining obstacles.

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Speaker: **Stefan Teufel** (Universität Tübingen)

Title: *Constraints and Dimensional Reduction in Quantum Mechanics*

Abstract: We review a number of mathematical results concerning the derivation and justification of effective equations for quantum systems constrained to small neighbourhoods of submanifolds of configuration space. For example, in some chemical reactions the nuclei move along a lower dimensional reaction path in configuration space and an effective description involving only the coordinates on the path can be justified. This effective description takes into account effects from the geometry of the path resp. submanifold.

Speaker: **Phillip Thomas** (Chemistry, Queen’s University)

Title: *Hierarchical Tensor Decompositions: A Tool for Computing Energy Levels of Molecules with More than 6 Atoms*

Abstract: Whenever coupling is important, numerical methods must be used to compute ro–vibrational spectra and model the dynamics of molecules and reacting systems. However, they become expensive as the number of atoms increases due to the explosion of data needed to represent the wavefunction. This phenomenon, known as the “curse of dimensionality”, makes it impossible to store wavefunctions computed in direct-product basis, for molecules having more than 4–5 atoms, effectively limiting quantum dynamics to small molecules.

Tensor decomposition methods show promise for alleviating the curse, enabling quantum dynamics on larger molecules. We recently computed energy levels for some 6– and 7–atom molecules using a sum-of-products tensor format, known as canonical polyadic (CP), to store the wavefunction. By arranging the coordinates of the molecule into a tree and computing energy levels for a series of Hamiltonians involving subsets of the coordinates, it is possible to compute energy levels for even larger molecules.

Speaker: **Stephanie Troppmann** (Technische Universität – München)

Title: *Lindblad Dynamics in Phase Space*

Abstract: The Lindblad equation describes the evolution of open quantum systems by evolving density matrices or trace class operators. In a special but interesting case, we can rewrite the equation as a Schrödinger equation with complex Hamiltonian. This allows us to transfer previous results for semiclassical wave packets to the Lindblad equation and to explicitly describe decoherence effects.

The talk presents joint work with C. Lasser (TU München) and Roman Schubert (U Bristol).

Speaker: **Edward F. Valeev** (Chemistry, Virginia Tech)

Title: *Block-Sparse Tensor Algebra for Electronic Structure of Large Molecules*

Abstract: Exploitable structure of operators and functions of interest to electronic structure can be roughly classified into two classes: factorizability into components of lower rank and/or order (rank sparsity) and small magnitude when expressed in an appropriate basis (element sparsity). Recent evidence suggests that in addition to useful global rank–sparsity (e.g. coupled–cluster style factorization) the local rank–sparsity plays a key role in eliminating the gap between the dense (small molecule) and element–sparse (very large molecule) regimes. We introduce a simple tensor format (Clustered Low Rank, CLR) that can exploit both types of sparsity effectively. The format is a novel combination of several simple ideas: basis clustering, tensor–product tiling, and low-rank approximation to tensor tiles. The format is not specific to electronic structure, but it can be constrained to a surprising number of seemingly unrelated numerical approximations in electronic structure that recently appeared in the literature. To demonstrate practical computation in this format we present a competitive implementation of Hartree–Fock method with density-fitting-style factorization of Coulomb two–electron integrals that is free of ad hoc models of sparsity (e.g., domains) and avoids numerical artifacts of atomic density fitting. Use of the CLR format for the order–2 and order–3 tensors that appear in the context of density fitting (DF) evaluation of the Hartree–Fock (HF) exchange operator significantly reduced the storage and computational complexities below their standard $O(N^3)$ and $O(N^4)$ figures. Even for relatively small systems and realistic basis sets CLR–based DF HF becomes more efficient than the standard DF approach, and significantly more efficient than the conventional non–DF HF, while negligibly affecting molecular energies and properties.

Speaker: **Jiří Vaníček** (Theoretical Physical Chemistry, Ecole Polytechnique Fédéral de Lausanne)
(and Aurélien Patoz)

Title: *Geometric Integrators of Arbitrary Order of Accuracy for Molecular Quantum Dynamics in Electromagnetic Fields*

Abstract: Exact quantum dynamics preserves certain geometric structures, but many currently used numerical algorithms preserve these structures only approximately. We have therefore implemented several geometric integrators for the nonadiabatic quantum dynamics of a molecule interacting with a time-dependent electromagnetic field. These integrators, which are based on a combination of the split-operator algorithm and Magnus factorization, preserve the geometric invariants exactly, and besides exponential convergence in the grid spacing, can also achieve an arbitrary prescribed order of accuracy in the time step. After implementing such an integrator for the exact nonadiabatic quantum dynamics, we also derived and implemented these geometric integrators for several approximations for the molecule-field interaction: the time-dependent perturbation theory, Condon, rotating-wave, and ultrashort pulse approximations, as well as every possible combination of these basic approximations.

In several numerical tests, we first verify that the algorithms have the prescribed order of accuracy and preserve the unitary and symplectic structures of the quantum dynamics. Next, we demonstrate that despite the increased cost of a single numerical step, for finite times the higher-order integrators can provide speedups of several order of magnitudes over the standard second-order split operator method.

Because of the high numerical accuracy, the high-order algorithms allowed us to test the validity of each physical approximation in several model systems with different potential energy surfaces and laser pulse properties. Finally, we describe how the widely used and surprisingly accurate δ -pulse approximation fits into our framework and show an example, using the three-state three-dimensional vibronic coupling model of pyrazine, in which it is essential to go beyond the δ -pulse limit.

Speaker: **Robert Wodraszka** (Chemistry, Queen's University)
(and Tucker Carrington)

Title: *Using a Non-direct Product Single Particle Function Basis within the Multi-Configurational Time-Dependent Hartree (MCTDH) Approach*

Abstract: The theoretical investigation of the vibrational quantum dynamics of molecular systems has been a central task in molecular physics and physical chemistry since the foundation of quantum mechanics.

However, solving the corresponding Schrödinger equation (both time-dependent and time-independent) still nowadays is in general a formidable task for molecules with more than five or six atoms.

Exact numerical methods like the multi-configurational time-dependent Hartree (MCTDH) approach have been developed to cope with the problem of efficiently solving the time-dependent Schrödinger equation. The key idea, in contrast to standard variational approaches, is to use a time-dependent basis set (single-particle functions) which optimally represents the wave function at each instant of time. This significantly reduces the basis set size and hence the numerical cost. However, the (original) MCTDH approach, like standard methods, suffers from what mathematicians call “the curse of dimensionality, that is, an exponential scaling of the numerical effort with the number of degrees of freedom of the molecular system under study. This scaling is due to the fact that although the 1-D basis functions are optimized, a direct product (or tensor product) basis set is used. Significantly better numerical scaling is achieved by employing a non-direct product base. In this case, only a fraction of the full direct product space is used by choosing product basis functions according to some physically reasonable criterion.

Here, we show that it is possible to combine the idea of using a non-direct basis set with the MCTDH method in an efficient way. Assuming a sum-of-products Hamiltonian, the crucial step in the algorithm is the evaluation of matrix-vector products by doing restricted sums sequentially. We illustrate the performance of this approach by calculating the first 69 vibrational eigenstates of acetonitrile, a 12-dimensional problem. Yielding accurate results, the numerical effort is decreased by about one order of magnitude compared to MCTDH calculations employing direct product bases.