Workshop on Mathematical Methods in Quantum Molecular Dynamics
28 April – 3 May 2013

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
9:00–9:25	Introductory Remarks and Announcements
	Morning Session Chair:　Graham Worth
9:30–9:55	Raymond Kapral
10:00–10:25	Christian Lubich
10:30–10:55	Coffee Break, TCPL
11:00–11:25	Stefan Teufel
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:　Caroline Lasser
14:30–14:55	Todd Martinez
15:00–15:25	Coffee Break, TCPL
15:30–15:55	Michael Griebel
16:00–16:25	Irene Burghardt
16:30–16:55	Brian Jennings
17:30–19:30	Dinner

Tuesday

7:00–9:00	Breakfast
8:30–8:55	Announcements (if needed)

Morning Session Chair: Edward Valeev

9:00–9:25	Uwe Manthe
9:30–9:55	Caroline Lasser
10:00–10:25	Viktor Szalay
10:30–10:55	Coffee Break, TCPL
11:00–11:25	Shi Jin
11:30–11:55	Tucker Carrington
12:00–13:30	Lunch

Afternoon Session Chair: Arnaud Leclerc

14:00–14:25	Anne McCoy
14:30–14:55	Clotilde Fermanian–Kammerer
15:00–15:25	Coffee Break, TCPL
15:30–15:55	David Lauvergnat
16:00–16:25	George Hagedorn
16:30–16:55	Pierre–Nicolas Roy
17:30–19:30	Dinner

Wednesday

7:00–9:00	Breakfast
8:30–8:55	Announcements (if needed)

Morning Session Chair: Ludwig Gauckler

9:00–9:25	Bill Poirier
9:30–9:55	William Miller
10:00–10:25	Reinhold Schneider
10:30–10:55	Coffee Break, TCPL
11:00–11:25	Edward Valeev
11:30–11:55	Gianluca Panati
12:00–13:30	Lunch

Free Afternoon

Tea, coffee, milk, juice and cookies available on a self–serve basis in the 2nd floor lounge of Corbett Hall.

17:30–19:00	Dinner

Evening Session Chair: Alex Brown

19:00–19:25	Dmitry Shalashilin
19:30–19:55	Graham Worth
20:00–20:25	Yimin Wang

Thursday

7:00–9:00   Breakfast

8:30–8:55   Announcements (if needed)

Morning Session Chair: Volker Betz
9:00–9:25   Alain Joye
9:30–9:55   Hans–Dieter Meyer
10:00–10:25   Haobin Wang
10:30–10:55   Coffee Break, TCPL
11:00–11:25   Joel Bowman
11:30–11:55   Jean Christophe Tremblay

12:00–13:30   Lunch

Free Afternoon

Tea, coffee, milk, juice and cookies available on a self–serve basis in the 2nd floor lounge of Corbett Hall.

17:30–19:00   Dinner

Evening Session Chair: Todd Martinez
19:00–19:25   Ove Christiansen
19:30–19:55   Hua Guo
20:00–20:25   Sergei Manzhos
20:30–20:55   Gustavo Avila

Friday

7:00–9:00   Breakfast

8:30–8:55   Announcements (if needed)

Morning Session Chair: George Hagedorn
9:00–9:25   Volker Betz
9:30–9:55   Benjamin Goddard
10:00–10:25   Leland Jefferis
10:30–10:55   Coffee Break, TCPL

12:00–13:30   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. **

Workshop on Mathematical Methods in Quantum Molecular Dynamics
28 April – 3 May 2013

ABSTRACTS
(in alphabetic order by speaker surname)

Speaker: **Gustavo Avila** (Queen's University)
Title: *Solving the Schrodinger equation using Smolyak interpolants*
Abstract: Interpolation on sparse grids using the Smolyak idea has been used to compute the vibrational levels of CH_2O. The complete Watson kinetic energy operator was used. Standard collocation methods require solving a generalized eigenvalue problem, HU=SUE. If the basis is large solving a generalized eigenvalue problem is much more costly than solving HU=UE. The interpolation method we use requires solving HU=UE, but H is not symmetric. Like other sparse grid methods it overcomes the "curse of the dimensionality". The accuracy of the energies depends both on the functions used to interpolate and on the interpolation points. We choose good interpolating functions because, according to the Boys' theorem, this will reduce error in the energies.

Speaker: **Volker Betz** (Technische Universität Darmstadt)
Title: *Effective description of molecular transitions by superadiabatic representations*
Abstract: The behavior of the molecular wave function at avoided crossings in the Born–Oppenheimer approximation is notoriously difficult to predict. In the time–adiabatic approximation, where the nuclear motion is prescribed and only the time evolution of the electronic degrees of freedom is studied, the superadiabatic theory of Michael Berry gives an answer. In joint work with Ben Goddard and Stefan Teufel, we developed a corresponding theory for for the full Born–Oppenheimer theory. The present talk will introduce the basic concepts and ideas. The companion talk by Ben Goddard will then discuss our results in the case of diatomic molecules.

Speaker: **Joel M. Bowman** *and Stuart Carter* (Emory University)
Title: *MULTIMODE and n–mode strategies for vibrational dynamics in high dimensionality*
Abstract: The bottlenecks to rigorous quantum approaches to the vibrational dynamics of polyatomic molecules and clusters are due to the exponential scaling of setting up and diagonalizing the Hamiltonian matrix. I will describe strategies that effectively deal with these. Illustrations will be given for HOCO and C_2H_4.

Speaker: **Irene Burghardt**, *S. Römer, and M. Ruckenbauer* (Universität Frankfurt am Main)
Title: *Multiconfiguration time–dependent Hartree with variational Gaussian wavepackets: flexible frozen Gaussian–based representations using two (and more) layers*
Abstract: The Gaussian–based multiconfiguration time–dependent Hartree (G–MCTDH) method and its variational multi–configurational Gaussian (vMCG) variant [1] interpolate between the standard MCTDH method and more approximate approaches based upon classically evolving Gaussian basis sets. These methods have been tailored to system-bath problems [2] and on–the–fly applications in conjunction with excited–state electronic structure calculations [3]. Even though good performance and convergence properties have been achieved to date, a significantly larger number of Gaussian wavepacket (GWP) functions may be required as compared with the fully flexible basis sets of the MCTDH method, especially if multi-dimensional "frozen" (FG) GWPs are employed. A remedy is provided by a recently developed two–layer version of the G-MCTDH/vMCG method which effectively re–introduces flexibility into FG basis sets [4]. Since the first layer consists of MCTDH–like, orthogonal single–particle functions, this approach can be straightforwardly combined with existing multi–layer MCTDH schemes. Another avenue that we currently pursue concerns a hybrid quantumclassical variant of G–MCTDH which takes a subset of coordinates to the

classical limit by a suitable scaling procedure, leading to a multiconfigurational Ehrenfest type dynamics [5]. Against this background, the talk will review the current status and prospects of the G–MCTDH/vMCG approach.

[1] I. Burghardt, H.–D. Meyer, and L. S. Cederbaum, *J. Chem. Phys.* **111** 2927 (1999),
G. A. Worth, I. Burghardt, *Chem. Phys. Lett.* **368** 502 (2003).
[2] I. Burghardt, K. Giri and G. A. Worth, *J. Chem. Phys.* **129** 174104 (2008).
[3] G. A. Worth, M. A. Robb, B. Lasorne, *Mol. Phys.* **106** 2077 (2008).
[4] S. Römer, M. Ruckenbauer, I. Burghardt, *J. Chem. Phys.* **138** 064106 (2013).
[5] S. Römer, I. Burghardt, *in preparation.*

Speaker: **Tucker Carrington** (Queen's University)
Title: *Using Smolyak grids and bases pruned to include strongly coupled basis functions to solve the vibrational Schroedinger equation in 12–d*

Abstract: To compute the vibrational spectrum of a molecule without neglecting coupling and anharmonicity one must calculate eigenvalues and eigenvectors of a large matrix representing the Hamiltonian in an appropriate basis. Iterative algorithms (e.g. Lanczos, Davidson, Filter Diagonalisation) enable one to compute eigenvalues and eigenvectors. It is easy to efficiently implement iterative algorithms when a direct product basis is used. However, for a molecule with more than four atoms, a direct product basis set is large and it is better to reduce the number of basis functions required to obtain converged eigenvalues by pruning. This is done without jeopardizing the efficiency of the matrix-vector products required by all iterative algorithms. In this talk, I shall present new basis-size reduction ideas that are compatible with efficient matrix–vector products. The basis is designed to include the product basis functions coupled by the largest terms in the potential and important for computing low–lying vibrational levels. To solve the vibrational Schrdinger equation without approximating the potential, one must use quadrature to compute potential matrix elements. When using iterative methods in conjunction with quadrature, it is important to evaluate matrix-vector products by doing sums sequentially. This is only possible if both the basis and the grid have structure. Although it is designed to include only functions coupled by the largest terms in the potential, the basis we use and also the (Smolyak–type) quadrature for doing integrals with the basis have enough structure to make efficient matrix-vector products possible. Using the quadrature methods of this paper, we evaluate the accuracy of calculations made by making multimode approximations.

Speaker: **Ove Christiansen** (University of Aarhus)
Title: *Tensor decomposition and coupled cluster theory in the context of quantum molecular dynamics*

Abstract: During the last decade we have developed **coupled cluster** based theoretical methods for calculating of vibrational wave functions, spectra and molecular properties.

In this talk I will discuss **tensor decomposition** and it is use in achieving a concise representation of the wave functions for nuclear motion. In particular I will discuss the integration of the tensor decomposition idea in the context of vibrational coupled cluster (VCC) and vibrational configuration interaction (VCI) wave functions.

I will outline the basic aspects of vibrational wave functions focusing and VCC and VCI and the importance of correlation amplitudes: the many small contributions that together make up the total wave function. I will take a tensor decomposition perspective on the relation between VCC and VCI.

A pilot implementation has been made for the CANDECOMP/PARAFAC tensor decomposition within our existing VCC/VCI codes. Numerical studies on models systems, formaldehyde, and thiadiazole will be used to illustrate the theoretical concepts. The significance of size–extensivity in relation to screening away small contributions will also be discussed.

Speaker: **Clotilde Fermanian** (Université de Paris Est)
Title: *Single switch algorithm for molecular dynamics*
Abstract: In this talk, we present the single switch surface hopping for molecular quantum dynamics elaborated in collaboration with Caroline Lasser. This algorithm relies on an Egorov type description of the dynamics. The underlying time dependent Schrdinger equation has a two by two matrix–valued potential whose eigenvalue surfaces have an avoided crossing. We will present numerical simulations for examples taken from Tully's famous 1994 paper on the surface hopping of the fewest switches.

Speaker: **Benjamin Goddard** (Imperial College London)
Title: *Transitions through avoided crossings in diatomic molecules*
Abstract: The photo–dissociation of diatomic molecules is one of the paradigmatic chemical reactions of quantum chemistry. The associated mathematical problem is the study of non–adiabatic transitions at avoided crossings in a two–level system, with one effective spatial degree of freedom. Given a wavepacket that travels through the avoided crossing on the upper electronic energy surface, the challenge is to determine the size and shape of the part of the wavepacket transmitted to the lower level.

Such problems are highly multi–scale; the transmitted wavefunction is typically very small. This leads to great difficulty in performing accurate numerical calculations, and an alternative method is required. The relevant small parameter ϵ is the square root of the the ratio of the electron and nuclear masses. In the standard adiabatic representation the transmitted wavepacket is of order ϵ near the avoided crossing but exponentially small (order $\exp(-1/\epsilon)$) well away from it. This strongly suggests that this representation is not the optimal one in which to study the problem.

Using the more general superadiabatic representations, and an approximation of the dynamics near the crossing region, we obtain an explicit formula for the transmitted wavefunction. Our results agree extremely well with high precision ab–initio calculations.

Speaker: **Michael Griebel** (Universität Bonn)
Title: *On the ANOVA decomposition of high–dimensional functions with applications to chemistry*
Abstract: We discuss the ANOVA decomposition of functions and certain generalizations. We then employ these dimension–wise decompositions to the Schrödinger equation. Here, for the electronic equation, the well-known CI approach results. For the full equation, we obtain our new BOSSANOVA fragmentation approach from of the Born–Oppenheim energy hypersurface with additional knowledge on the bonds of a molecule. We will discuss its properties in detail.

Speaker: **Hua Guo** (University of New Mexico)
Title: *Potential energy surfaces and quantum reactive scattering*
Abstract: We will discuss the role of multidimensional potential energy in quantum reactive scattering calculations in polyatomic systems, focus on the issues related to efficiency and accuracy of potential fitting and numerical solution of the Schrodinger equation. In particular, the combustion reaction $HO + CO \rightarrow H + CO_2$ system will be used as an example.

Speaker: **George A. Hagedorn** (Virginia Tech)
Title: *Molecular Resonance Raman and Rayleigh Scattering Stimulated by a Short Laser Pulse*
Abstract: We study a simple model for a molecule subjected to a short laser pulse. We derive very simple expressions for resonance Raman and resonance Rayleigh scattering amplitudes to leading order in the strength μ of the laser and the Born–Oppenheimer parameter ϵ for the molecule.

Speaker: **Leland Jefferis** (University of Wisconsin – Madison)
Title: *Computing high frequency solutions of symmetric hyperbolic systems with polarized waves*
Abstract: I will introduce methods for computing the high frequency solution for general symmetric hyperbolic systems in both Lagrangian and Eulerian frames. Symmetric hyperbolic systems include many physically relevant systems of partial differential equations such as Maxwells equations, the elastic equations

and the acoustic equations. I will introduce new numerical methods (including a Gaussian beam method) for handling the difficulties of high frequency wave simulation and in particular I will address of issues of eigenvalue degeneracy and polarization. Finally I will discuss how the ideas developed in the symmetric hyperbolic system framework may extend to the Schrödinger equation.

Speaker: **Brian Jennings** (Westfield State University)
Title: *Semiclassical Propagation in Bargmann Space, and the Herman–Kluk Propagator*
Abstract: In this talk I will discuss an approximation to the kernel of the propagator where the Hilbert space of states is Bargmann space. We'll see how this particular approximation is surprisingly closely related to the Herman–Kluk propagator from the theoretical chemistry literature.

Speaker: **Shi Jin** (Shanghai Jiao Tong University and University of Wisconsin – Madison)
Title: *Semi–classical models for the Schrödinger equation with periodic potentials and band–crossings*
Abstract: The Bloch decomposition plays a fundamental role in the study of quantum mechanics and wave propagation in periodic media. Most of the homogenization theory developed for the study of high frequency or semi–classical limit for these problems assumes no crossing of the Bloch bands, resulting in classical Liouville equations in the limit along each Bloch band.

We derive semi–classical models for the Schrödinger equation in periodic media that take into account band crossing, which is important to describe quantum transitions between Bloch bands. Our idea is still based on the Wigner transform (on the Bloch eigenfunctions), but in taking the semi–classical approximation, we retain the off–diagonal entries of the Wigner matrix, which cannot be ignored near the point of band crossing. This results in coupled inhomogeneous Liouville systems that can suitably describe quantum tunneling between bands that are not well-separated. It contains important quantum information such as the Berry connection. We also develop a domain decomposition method that couples these semi–classical models with the classical Liouville equations (valid away from zones of band crossing) for a multiscale computation. Solutions of these models are numerically compared with those of the Schrödinger equation to justify the validity of these new models for band–crossings.

Speaker: **Alain Joye** (Institut Fourier, Université de Grenoble I)
Title: *Emergence of exponentially accurate reflected or tunneling semiclassical wave packets*
Abstract: We review the one dimensional time–dependent scattering of a quantum mechanical wave packet at a potential barrier for energies larger, respectively lower, than the barrier height, in the semi–classical regime. Making use of complex WKB methods, we provide a precise space–time description of the reflected, respectively transmitted, exponentially small wave packets. This talk is based on two joint works with V. Betz and S. Teufel and with V. Gradinaru and G. Hagedorn.

Speaker: **Raymond Kapral** (University of Toronto)
Title: *Nonadiabatic Dynamics in Open Quantum–Classical Systems*
Abstract: Nonadiabatic processes, which occur when an open quantum system interacts with its environment giving rise to a breakdown of the Born–Oppenheimer approximation, are prevalent in chemical, physical and biological systems. Examples include the dynamics in the vicinity of conical intersections, energy transfer in light harvesting systems, and proton and electron transfer processes in chemical and biological systems. The talk will focus on the description of such processes from the perspective of quantum–classical dynamics where the environment to which the quantum subsystem of interest is coupled may be treated classically to a good approximation. Methods for simulating the dynamics of such open quantum–classical systems will be described, with emphasis on schemes that based on a mapping representation of the discrete quantum degrees of freedom and a forward–backward solution of the equations of motion.

[1]   C.–Y. Hsieh and R. Kapral, *J. Chem. Phys.*, **137**, 22A507 (2012)
[2]   Hsieh and R. Kapral, *J. Chem. Phys.*, **138**, 134110 (2013).

Speaker: **Caroline Lasser** (Technische Universität – München)
Title: *Semiclassical approximations for quantum molecular dynamics: a computational point of view*

Abstract: The talk aims at the direct computation of expectation values for quantum molecular dynamics with respect to a single potential energy surface. We explain, how the Egorov theorem allows to reformulate the time evolution of expectation values as a numerical quadrature problem combined with the discretization of ordinary differential equations. We discuss the initial sampling via the Wigner or the Husmi function and address the possibilities of variational corrections.

Speaker: **David Lauvergnat** *and André Nauts* (CNRS, Université Paris-Sud, and Université Catholique de Louvain)
Title: *Quantum dynamics with sparse grid: a combination of Smolyak scheme and cubature*

Abstract: Quantum dynamical approaches based on product-grids are limited to the studies of molecular systems with few degrees of freedom, typically less than ten. Recently, Avila and Carrington [1] have introduced the Smolyak scheme, [2] which considerably reduces the size of the grids. This approach has pushed back the present calculation limits on the vibrational spectra of polyatomic molecules. In the present study, we have developed an extension of the standard Smolyak scheme in which this scheme is combined with multidimensional grids, like cubatures, to obtain new sparse grids.

This scheme has been applied to the study of the torsional energy levels of methanol in full dimensionality (12D).

[1] G. Avila and T. Carrington, *J. Chem. Phys.* **131** (2009) 174103.
[2] S. A. Smolyak, *Soviet Mathematics Doklady* **4** (1963) 240.

Speaker: **Christian Lubich** (Universität Tübingen)
Title: *On the MCTDH method*

Abstract: This talk discusses the multiconfiguration time–dependent Hartree (MCTDH) method of quantum dynamics from a mathematician's viewpoint. Topics considered are structural properties, approximation properties and convergence questions, and numerical time–integration methods for solving the MCTDH equations of motion.

Speaker: **Uwe Manthe** (Universität Bielefeld)
Title: *Multi–layered wavefunction representations and quadratures: the multi–configurational time–dependent Hartree approach*

Abstract: The scaling of the numerical effort with dimensionality is a key problem of quantum dynamics calculations. The multi–configurational time–dependent Hartree (MCTDH) approach is one of the most efficient numerically accurate schemes for treating high–dimensional systems.

The original MCTDH approach employs a two layer representation:

$$\Psi(x_1, \cdots, x_f, t) = \sum_{j_1=1}^{n_1} \cdots \sum_{j_f=1}^{n_f} A^{(1)}_{j_1\cdots j_f}(t) \prod_{\kappa=1}^{f} \varphi^{(\kappa)}_{j_\kappa}(x_\kappa, t), \tag{1}$$

$$\varphi^{(\kappa)}_{j_\kappa}(x_\kappa, t) = \sum_{i_\kappa=1}^{N_\kappa} A^{(2)}_{i_\kappa, j_\kappa}(t) \; \chi^{(\kappa)}_{i_\kappa}(x_\kappa). \tag{2}$$

The multi–dimensional wavefunction Ψ is represented in an optimized, contracted basis of single–particle functions (SPFs) φ while the SPFs are represented in a large basis of "primitive" basis functions or grid points χ. Equations of motion for the expansion coefficients can be straightforwardly obtained from the Dirac–Frenkel variational principle. Using propagation in imaginary time, also iterative schemes to compute Hamiltonian eigenstates have been developed.

Considering sets of coordinates as new (logical) coordinates and representing the SPFs depending on these logical coordinates as MCTDH–type wavefunctions, a multi–layer representation can be generated. This multi–layer MCTDH approach can facilitate rigorous quantum dynamics simulations of

high–dimensional systems which include for favorable examples up to hundreds of degrees of freedom. Furthermore, a multi–layer grid representation and quadrature corresponding to the multi–layer MCTDH wavefunction can be introduced. This multi–layer extension of the correlation discrete variable representation (CDVR) provides an efficient quadrature for the potential matrix elements appearing in the equations of motion.

The talk will introduce the multi–layer MCTDH and CDVR approaches, discuss perspectives and existing problems, and mention some current applications.

Speaker: **Sergei Manzhos** (National University of Singapore), *Tucker Carrington, and Matthew Chan*
Title: *Enabling Quantum dynamics with or without Potential Energy Surfaces by removing extra fitting*
Abstract: One of the bottlenecks preventing routine quantum dynamics calculations on systems with more than about five degrees of freedom is the absence of potential energy surfaces. When PESs are available, they often need to be expressed in a form suitable for quantum dynamics, such as the sum–of–products form frequently used with MCTDH. Conversion to a sum–of–products form in dynamically suitable coordinates from e.g. inverse interatomic distances is itself a source of error and introduces extra human and computational cost.

We present two approaches addressing this problem. One directly obtains a sums–of–products representation of the potential right at the point of fitting to ab initio data. The other eliminates the PES and makes it possible to obtain observables (such as the vibrational spectrum) directly from ab initio data. Both approaches have in common the removal of a step between ab initio calculations and the calculation of observables. They involve the use of parameterized basis functions in the expressions for the PES and the wavefunction, respectively.

Speaker: **Todd Martinez** (Stanford University)
Title: *Tensor Compression in Quantum Chemistry*
Abstract: We review methods to represent two electron integrals in electronic structure theory which accelerate the construction of common contractions. We then introduce the tensor hypercontraction (THC) scheme we have recently developed to (near)–optimally compress the two electron integrals. Within THC, the two-electron integrals are viewed as a fourth order tensor which can be rewritten in compressed form as a product of five second order tensors. We highlight the relationship to quadrature approaches to integration and show that THC may be considered as a direct quadrature of the six dimensional integrals which maintains high accuracy in spite of integration over the Coulomb singularity. We further show that THC is in fact exact within polynomial basis sets, by analogy to Gaussian quadrature. This leads to the development of new grid construction approaches which are tuned for THC, and we discuss a full discrete variable representation (DVR) grid in non–direct product form. These full DVR grids lead to millihartree accuracy in THC applications with fewer than 50 points per atom. Finally, we demonstrate that the THC approximation leads to reductions in scaling behavior of up to two powers of the molecular size, i.e. the THC approximation applied to a variety of electronic structure methods (e.g., Moller–Plesset perturbation theory through third order and coupled cluster with single and double excitations) leads to $O(N^4)$ scaling, where N is the number of basis functions used in the calculation. This should be compared to conventional approaches which scale as $O(N^5)$ or $O(N^6)$. This reduced scaling is achieved while maintaining chemical accuracy.

Speaker: **Anne McCoy**, *Charlotte E. Hinkle, Zhou Lin, Andrew S. Petit and Bethany A. Wellen* (Ohio State University)
Title: *Diffusion Monte Carlo Approaches for studying rotational and vibrational motions of highly anharmonic systems*
Abstract: In this talk we will focus on the diffusion Monte Carlo approach as applied to rotation–vibration problems in quantum mechanics. Diffusion Monte Carlo can be developed from the isomorphism between the Diffusion Equation and the time–dependent Schrödinger Equation, when it is expressed in imaginary time. This allows us to obtain a Monte Carlo Sampling of the lowest-energy state of a particular symmetry

via a Monte Carlo Simulation. Recent work in our group has focused on how we can use such a Monte Carlo sampling of the ground state wave function to obtain spectroscopic properties of the system of interest, and how the approach can be modified to generate rotational and vibrational excited states. The discussion will be put in the context of recent studies of H_3^+, H_5^+, CH_5^+ and their deuterated analogues.

Speaker: **Hans–Dieter Meyer** (Universität Heidelberg)
Title: *Multiconfiguration Time–Dependent Hartree (MCTDH) and Multi–Layer MCTDH (ML–MCTDH) viewed as tensor decomposition methods*

Abstract: The *Multi–Configuration Time–Dependent Hartree* (MCTDH) approach [1–4] and its recent extension *multi-layer* MCTDH (ML–MCTDH) [5–7] are revisited. These methods were originally derived by expanding high–dimensional (wave–) functions into sums of products of low dimensional ones. Representing functions on a grid, however, turns them into vectors or tensors. Then the MCTDH method can be viewed as a time–dependent Tucker expansion of a time–dependent tensor, which, in turn, represents the multi–dimensional wave function. ML–MCTDH can be viewed as a more complicated tensor decomposition, which is best described by a tree structure.

[1] H.–D. Meyer, U. Manthe, and L. S. Cederbaum: The multi–configurational time–dependent Hartree approach. *Chem. Phys. Lett.* **165** (1990), 73.

[2] U. Manthe, H.–D. Meyer, and L. S. Cederbaum: Wave–packet dynamics within the multiconfiguration Hartree framework: General aspects and application to NOCl. *J. Chem. Phys.* **97** (1992), 3199.

[3] M. H. Beck, A. Jäckle, G. A. Worth, and H.–D. Meyer: The multiconfiguration time–dependent Hartree method: A highly efficient algorithm for propagating wavepackets. *Phys. Rep.* **324** (2000), 1.

[4] H.–D. Meyer, F. Gatti, and G. A. Worth, editors: *Multidimensional Quantum Dynamics: MCTDH Theory and Applications.* Wiley–VCH, (2009), Weinheim, ISBN: 978-3-527-32018-9.

[5] H. Wang and M. Thoss: Multilayer formulation of the multiconfiguration time–dependent Hartree theory. *J. Chem. Phys.* **119** (2003), 1289.

[6] U. Manthe: A multilayer multiconfigurational time–dependent Hartree approach for quantum dynamics on general potential energy surfaces. *J. Chem. Phys.* **128** (2008), 164116.

[7] O. Vendrell and H.–D. Meyer: Multilayer multiconfiguration time–dependent Hartree method: Implementation and applications to a Henon–Heiles Hamiltonian and to pyrazine. *J. Chem. Phys.* **134** (2011), 044135.

Speaker: **William H. Miller** (University of California, Berkeley)
Title: *Using the Initial Value Representation of Semiclassical Theory to Add Quantum Effects to Classical Molecular Dynamics Simulations*

Abstract: Semiclassical (SC) theory provides a good description of essentially all quantum effects (interference/coherence, tunneling and other classically forbidden processes, symmetry effects of identical particles, quantization of bounded motion, etc.) in molecular dynamics; this has long been appreciated and validated by many applications to small molecular systems [*cf. Adv. Chem. Phys.* **25**, 69–177 (1974)]. Since SC theory is built on the classical trajectories of the dynamical system, it should in principle be possible to use it also to add quantum effects to classical molecular dynamics simulations of complex molecular systems (i.e., those with many degrees of freedom), *e.g.*, chemical reactions in solution, in clusters, in bio–molecular or any complex environment. The practical implementation of SC theory for systems with many degrees of freedom is based on various initial value representations (IVRs), which have recently undergone a re–birth of interest in this regard. This talk reviews the basic idea of the SC–IVR approach and describes a variety of recent applications that have been carried out using it. For some recent more detailed overviews, see *J. Phys. Chem. A* **105**, 2942–2955 (2001); *Proc. Nat. Acad. Sci.* **102**, 6660–6664 (2005); *J. Chem. Phys.* **125**, 132305.1–8 (2006), *J. Phys. Chem. A* **113**, 1405 (2009).

Speaker: **Gianluca Panati** ("Sapienza" University of Rome)
Title: *Topological invariants of eigenvalue intersections and decrease of Wannier functions*

Abstract: We investigate the asymptotic decrease of the Wannier functions for the valence and conduction band of graphene, both in the monolayer and the multilayer case. Since the decrease of the Wannier functions is characterised by the structure of the Bloch eigenspaces around the Dirac points, we introduce a topological invariant of the family of eigenspaces, baptised eigenspace vorticity. We compare it with the pseudospin winding number. For every value n in Z of the eigenspace vorticity, we exhibit a canonical model for the local topology of the eigenspaces. The set of the canonical models is proved to be universal, in a suitable sense. With the help of this universality theorem, we show that the single band Wannier function w satisfies $w(x) \asymp |x|^{-3/2}$. In particular, the expectation value of the modulus of the position operator is infinite.

Speaker: **Bill Poirier** *and Thomas Halverson* (Texas Tech University)
Title: *Exact Quantum Dynamics Calculations using Phase Space Wavelets*

Abstract: In a series of earlier papers, the authors introduced the first exact quantum dynamics method that defeats the exponential scaling of CPU effort with system dimensionality. The method uses a "weylet" basis set (orthogonalized Weyl–Heisenberg wavelets), combined with a phase space truncation scheme first proposed by M. Davis and E. Heller. Here, we use a related, but much simpler, wavelet basis consisting of momentum–symmetrized phase space Gaussians. Despite being non–orthogonal, symmetrized Gaussians exhibit collective locality, allowing for effective phase space truncation and the defeat of exponential scaling. A "universal" and remarkably simple code has been written, which is dimensionally independent, and which also exploits massively parallel algorithms. The codes have been used to calculate the vibrational spectra of several molecules of varying dimensionality.

Speaker: **Pierre–Nicolas Roy** (University of Waterloo)
Title: *Dynamics of quantum rotors in complex environments*

Abstract: We will present approaches for the study molecular rotors embedded in superfluid environments. We will mostly focus on path integral simulation techniques and will consider both atomic and molecular bosons as the constituent of the superfluid. We will show that the superfluid response to the rotation of a molecule can be used to explain microwave and infrared spectroscopic experiments. We will discuss the challenges associated with different types of rigid tops. The question of angular momentum projection axis for the calculation of superfluid fraction will be addressed. Results will be presented for the case of asymmetric top molecules trapped in parahydrogen clusters and the idea of a genuine probe of superfluid response will be introduced. A perspective on future challenges will finally be presented.

Speaker: **Reinhold Schneider** (Technische Universität Berlin)
Title: *Approximation of the electronic Schrödinger equation by low rank approximation in novel tensor formats*

Abstract: Hierarchical Tucker tensor format (Hackbusch) and Tensor Trains (TT) (Tyrtyshnikov) have been introduced recently offering stable and robust approximation by a low order cost. Considering an occupation number labeling of Slater determinants, the discrete Fock space becomes isometric to $\mathcal{V} = \bigotimes_{i=1}^{d} \mathbb{C}^2$. Therein these formats are equivalent to tree tensor networks states and matrix product states (MPS) originally introduced for the treatment of quantum spin systems.

We demonstrate the behavior of these ranks, namely the entanglement depending on bilinear approximation rates and corresponding trace class norms.

For numerical computations, we cast the computation of an approximate ground solution into an optimization problems constraint by the restriction to tensors of prescribed ranks **r**. For approximation by elements from this highly nonlinear manifold, we apply a non–linear Galerkin framework, the extension for the dynamical problems correspond to the Dirac Frenkel variational principle developed in a similar fashion as for Multi–Configurational Hartree (–Fock) by observing the differential geometric structure of the novel tensor formats. This provides a variational formulation of the QC (Quantum Chemistry) DMRG (Density

Renormalization Group) algorithm. We analyse the (open) manifold of such tensors and its projection onto the tangent space. We further investigate the derived differential equations. We discuss its advantage for the treatment of some strongly correlated problems in quantum chemistry.

[1] O. Legeza, T. Rohwedder and R. Schneider: *Tensor methods in quantum chemistry*, to appear in *Encyclopedia of Applied and Computational Mathematics*.
[2] C. Lubich, T. Rohwedder, R. Schneider and B. Vandereycken: *Dynamical approximation of hierarchical Tucker and tensor train tensors*. SPP1324 Preprint (126/2012)
[3] B. Khoromskij, I. Oseledets and R. Schneider: *Efficient time–stepping scheme for dynamics on TT– manifolds*, MIS Preprint 80/2011

Speaker: **Dmitry Shalashilin** (University of Leeds)
Title: *Basis sets of trajectory guided Gaussians for efficient and accurate multidimensional quantum dynamics*
Abstract: The approaches to quantum dynamics, based on trajectory guided basis sets of Gaussian Coherent States will be presented. The methods of Coupled Coherent States [1] and Multiconfigurational Ehrenfest method [2, 3] are capable of treating short time multidimensional dynamics on a fully quantum level. Well converged and accurate results have been obtained for a number of systems comprised of tens and in some cases hundreds of degrees of freedom. The applications range from "*ab initio* on the fly" wavepacket dynamics of vibrationally and electronically excited polyatomic molecules [4] to electron dynamics in strong laser field [5]. The methods can be derived from quantum variational principle [6] and rely heavily on efficient basis set samplings [7].

[1] Shalashilin D V, Child M S, *Chem. Phys.* **304** (2004) 103;
[2] Shalashilin D V, *J. Chem. Phys.* **130** (2009) 244101;
[3] Shalashilin D V, *J. Chem. Phys.* **132** (2010) 244111;
[4] Saita K., Shalashilin D V, *J. Chem. Phys.* **137** (2012) 22A506;
[5] Shalashilin D V, Child M S, Kirrander A, *Chem. Phys.* **347** (2008) 257;
[6] Shalashilin D V, Burghardt I, *J. Chem. Phys.* **129** (2008) 084104;
[7] Shalashilin D V, Child M S, *J. Chem. Phys.* **128** (2008) 054102.

Speaker: **Viktor Szalay** (Hungarian Academy of Sciences)
Title: *Variational discrete variable representation*
Abstract: Variational properties of the discrete variable representation (DVR) method are discussed. DVRs which are variational with repect to selection of the grid points and truncation of the basis set are introduced.

Speaker: **Stefan Teufel** (Universität Tübingen)
Title: *Spontaneous decay of resonant energy levels for molecules with moving nuclei*
Abstract: I present, on a nontechnical level, some mathematical results and problems concerning the justification of the time–dependent Born–Oppenheimer approximation starting from the full Schödinger equation for electrons and nuclei coupled to the quantized radiation field. In particular, I will discuss spontaneous emission of photons. This is based on joint work with Jakob Wachsmuth.

Speaker: **Jean Christophe Tremblay** (Univerität Potsdam)
Title: *Computing vibrational states of CO on metal substrates*
Abstract: In this contribution I present numerical calculations of vibrational eigenstates of carbon monoxide (CO) adsorbed on two distinct metallic substrates for which physically sound potential energy surfaces are available: a cubic copper surface [1], and a hexagonal ruthenium surface [2]. Combinations of methods based on the Lanczos algorithm, symmetry–adapation, and approximate spectral transform are used to extract eigenvalues of the molecular Hamiltonian. These combinations allow to circumvent the convergence problems due to the wide range of transition frequencies spanned by the vibrational and librational

motions. Full–dimensional (6D) eigenfunctions and eigenenergies of the systems, represented in system–specific hybrid grid–pseudospectral bases, are compared and discussed. Reduced–dimension models are also presented to reveal the couplings between the different degrees of freedom.

[1] R. Marquardt, F. Cuvelier, R. A. Olsen, E. J. Baerends, J. C. Tremblay, and P. Saalfrank, *J. Chem. Phys.*, **132**, 074108 (2010)
[2] G. Füchsel, J. C. Tremblay, and P. Saalfrank, *in preparation*

Speaker: **Edward Valeev** (Virginia Tech)
Title: *Multiresolution spectral–element representations of electronic wave functions*

Abstract: One of the grand challenges of quantum chemistry is computing observables (energies, scattering cross–sections, response properties) and their confidence intervals with high precision. This requires fast methods, characterized by a low–order scaling of the computational cost with the system size and error. Despite significant advances in the area, we are still very far from this goal. This talk will address some of our recent work on fast methods, with the word *fast* referring to the scaling with precision (i.e. the discretization error) and with the system size. Specifically, I will discuss our efforts to compute two–particle wave functions in hierarchical (multiresolution) discontinuous spectral–element representations. [1, 2] Each volume element of the six–dimensional wave function is supported by an orthonormal basis set of tensor products of polynomials. To alleviate the severe (exponential) cost of finite–element representation in many dimensions, which makes precise representation and computation of correlated wave functions intractable, we use low–rank tensor approximations, namely the singular value decomposition SVD, and reformulate all operations necessary to solve the Schrödinger equation in low–rank form. [3] The low-rank approximations alone are not sufficient; hence we use explicitly–correlated terms in the wave function to regularize the electron–electron Coulomb singularities of the Hamiltonian. Our approach does not assume any geometric symmetry, hence the method is tractable for molecules. [2] The method was used to compute the first–order Møller-Plesset wave function and the second-order energy of the helium atom with precision guaranteed by construction (our most precise value for the MP2 energy is -37.379 mE_h). We will further highlight the strengths and weaknesses of the adaptive discretization strategy.

[1] F. A. Bischoff, R. J. Harrison, and E. F. Valeev, *J. Chem. Phys.* **137**, 104103 (2012).
[2] F. A. Bischoff and E. F. Valeev, in preparation.
[3] F. A. Bischoff and E. F. Valeev, *J. Chem. Phys.* **134**, 104104 (2011).

Speaker: **Haobin Wang** (New Mexico State University)
Title: *Multilayer Multiconfiguration Time–Dependent Hartree Theory*

Abstract: The multilayer multiconfiguration time–dependent Hartree (ML–MCTDH) theory is a rigorous and powerful method to simulate quantum dynamics in complex many–body problems. This approach extends the regular MCTDH theory of Meyer, Manthe, and Cederbaum to include several dynamically contracted layers whose equations of motion are determined from variational principle. In this talk I will discuss the general derivation of the theory, the scaling of the method, and the application of the theory to simulate dynamics of electron transfer reactions in the condensed phase. Furthermore, a new generalization of the theory, the ML–MCTDH theory within second quantization representation will be presented to treat many–body identical particle (fermion or boson) systems.

Speaker: **Yimin Wang** (Emory University)
Title: *Exact 6d quantum vibrational calculation of three isomers of H_2CO using a new accurate* ab initio *potential energy surface*

Abstract: We report a new full–dimensional semi-global *ab initio* potential energy surface of H_2CO that accurately describes the isomerization of the formaldehyde to hydroxycarbene isomers as well as the isomerization of *trans*– and *cis*–HOCH. We present the exact 6d quantum calculation that obtains vibrational eigenstates of all three isomers of H_2CO.

Speaker: **Graham Worth** (University of Birmingham)

Title: *Using time–dependent Gaussian basis sets in quantum dynamics simulations*

Abstract: Propagating a multi–dimensional wavepacket using the time–dependent Schrödinger Equation is a computationally hard problem that scales exponentially with the number of degrees of freedom in the system. In contrast to the traditional grid–based approach, one way to ease the scaling is to describe the evolving wavepacket by a superposition of Gaussian functions, often referred to as Gaussian Wavepackets (GWPs). There are a variety of algorithms for the propagation of the GWPs that provide the time–dependent basis set. All have advantages and disadvantages, but most use classical trajectories which leads to good scaling, but poor convergence and problems in dealing with quantum phenomena such as tunneling. There is also the problem in selecting the initial functions. All suffer from numerical problems due to the non–orthonormality of the basis set, which can lead to linear dependence and singularities in the equations of motion.

One method that promises to overcome the convergence and initial selection problem is based on the MCTDH wavepacket propagation method [1,2]. This method will be presented to show its potential. It variationally couples the evolving basis functions as well as the expansion coefficients, and as the result the functions follow "quantum trajectories". In addition, it is straightforward to combine the GWP basis with grid–based methods for better convergence when some modes are strongly quantum mechanical [3].

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[2] Worth, Robb and Burghardt. *Farad. Discuss.* **127**, 307 (2004)
[3] Burghardt, Giri and Worth. *J. Chem. Phys.* **129**, 174104 (2008)