Molecular Quantum Dynamics

23–26 May 2023, Lysebu Hotel, Oslo

Supported by:

Centre for Advanced Study (CAS), cas.oslo.no
The Hylleraas Centre for Quantum Molecular Sciences, www.hylleraas.no

Venue:

Lysebu Hotel, www.lysebu.no
Lysebuveien 12,
0790 Oslo
Tel. +47 21511000, email: resepsjon@lysebu.no

Organizers:

Simen Kvaal (simen.kvaal@kjemi.uio.no, tel. +47 90199552, SMS only)
Thomas Bondo Pedersen (t.b.pedersen@kjemi.uio.no, tel. +47 94978990)
Ludwik Adamowicz (ludwik@arizona.edu)
Caroline Lasser (classer@ma.tum.de)

Centre for Advanced Study
at the Norwegian Academy of Science and Letters

Hylleraas

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Program

Tuesday 23 May

12:30	Lunch
13:45	Opening
14:00	Talk: Sølve Selstø
14:45	Talk: Stefanos Carlström
15:30	Break
16:00	Talk: Benjamin Lasorne
16:45	Talk: Pranav Singh
19:00	Dinner

Wednesday 24 May

09:00	Talk: González-Vázquez
09:45	Talk: Wozniak
10:30	Break
11:00	Talk: Appel
11:45	Talk: Vacher
12:30	Lunch
14:00	Talk: Orimo
14:45	Talk: Højlund
15:30	Break
16:00	Talk: Reiher
16:45	Talk: Fasshauer
19:00	Dinner

Thursday 25 May

09:00	Talk: Burghardt
09:45	Talk: Kjønstad
10:30	Break
11:00	Talk: Mátyus
11:45	Talk: Stanke
12:30	Lunch and group photo
14:00	Talk: Schneider
14:45	Talk: Sutterud
15:30	Break
16:00	Talk: Koch
16:45	Talk: Crawford
19:00	Dinner

Friday 26 May

09:00	Talk: Coriani
09:45	Talk: Svensson
10:30	Break
11:00	Talk: Laestadius
11:45	Closing remarks
12:00	Lunch
13:00	Departure

Abstracts

Heiko Appel
Max Planck Institute for the Structure and Dynamics of Matter, Hamburg, Germany
heiko.appel@mpsd.mpg.de

Title: Time-dependent density-functional theory for quantum electrodynamics: a novel tool for strong light-matter coupling in cavities, nanostructures, and for (non)-linear spectroscopies

Abstract: TBA

Irene Burghardt
Goethe University, Frankfurt, Germany
burghardt@chemie.uni-frankfurt.de

Title: Multiconfigurational quantum dynamics with multiplicative neural network potentials

Abstract: The combination of machine learning approaches with efficient wavepacket propagation in many dimensions is a promising route towards accurate excited-state molecular dynamics. Here, we discuss an approach that combines variational multiconfigurational methods of the Multiconfiguration Time-Dependent Hartree (MCTDH) class with multiplicative neural network (MNN) potentials that match the sum-of-products form of the wavefunction ansatz. Applications are shown for vibronic absorption spectra and ultrafast photoinduced isomerization dynamics at conical intersections, where MNN potentials are combined with the multi-layer ML-MCTDH and multi-layer Gaussian-based ML-GMCTDH propagation schemes.

Stefanos Carlström
University of Lund, Sweden
stefanos.carlstrom@gmail.com

Title: Photoionization spectra from small molecules

Abstract: We demonstrate the implementation of the surface flux techniques to compute photoionization spectra from small gas-phase molecules.

This is a continuation of the work described in
https://journals.aps.org/pra/abstract/10.1103/PhysRevA.106.043104
https://journals.aps.org/pra/abstract/10.1103/PhysRevA.106.042806

Sonia Coriani
Danish Technological University, Denmark
soco@kemi.dtu.dk

Title: Correlated methods for local and ultrafast processes, also involving the electronic continuum.

Abstract: TBA

T. Daniel Crawford
Virginia Tech, US
crawdad@vt.edu

Title: TBA

Abstract: TBA

Elke Fasshauer
University of Tübingen, Germany
elke.fasshauer@uni-tuebingen.de

Title: Fano meets Nuclei: How nuclear degrees of freedom influence time-resolved spectroscopy of electronic decay processes

Abstract: TBA

Jesús González-Vázquez
Autonomous University of Madrid, Spain
jesus.gonzalezv@uam.es

Title: TBA

Abstract: TBA

Mads Greisen Højlund
University of Aarhus, Denmark
madsgh@chem.au.dk

Title: Adaptive basis sets for time-dependent bivariational wave functions: Linear, polar and exponential parametrization of single-particle functions

Mads G. Højlund, Andreas B. Jensen, Alberto Zoccante, Ove Christiansen

Abstract: We present recent developments regarding the parametrization of adaptive basis sets for time-dependent bivariational wave functions. The theory is general with respect to particle type and wave function Ansatz, but our main target is the *time-dependent modals vibrational coupled cluster* (TDMVCC) model [1] for describing nuclear dynamics. This and similar models use a biorthogonal basis set, meaning that the active bra and ket basis functions are allowed to span different spaces. This feature can, in our experience, cause numerical challenges that we address by a new basis set parametrization based on polar decomposition [2]. Single and double exponential basis set parametrizations are also discussed [3].The highly non-linear equations are simplified using Lie algebraic techniques and the resulting working equations can easily be implemented on top of existing code. In contrast to most existing work on exponential basis set transformations, our approach is applicable for any value of the basis set parameters. Finally, we present an efficient, polynomial-scaling implementation of the TDMVCC model with double excitations and two-mode coupled Hamiltonians (TDMVCC[2]/H2).

[1] N. K. Madsen, M. B. Hansen, O. Christiansen, A. Zoccante, *J. Chem. Phys.* 153, 174108 (2020).
[2] M. G. Højlund, A.B. Jensen, A. Zoccante, O. Christiansen, *J. Chem. Phys.* 157, 234104 (2022).
[3] M. G. Højlund, A. Zoccante, O. Christiansen, *J. Chem. Phys.* (accepted for publication).

Eirik Kjønstad
Norwegian University of Science and Technology, Trondheim, Norway
eirik.kjonstad@ntnu.no

Title: Nonadiabatic dynamics at the CCSD level of theory

Abstract: Coupled cluster theory can be an accurate electronic structure method, but it has well-known shortcomings for nonadiabatic dynamics. Here we present two recent developments. First, we demonstrate that the geometric phase effect around conical intersections is correctly reproduced with coupled cluster methods. Second, we present preliminary nonadiabatic

dynamics simulations using the ab initio multiple spawning method and coupled cluster singles and doubles theory.

Henrik Koch
Norwegian University of Science and Technology, Trondheim, Norway
henrik.koch@ntnu.no

Title: Recent advances in time-dependent coupled cluster methods

Abstract: TBA

Andre Laestadius
Oslo Metropolitan University, Norway
andre.laestadius@oslomet.no

Title: Homotopies and Coupled-Cluster Theory

Abstract: Different kind of homotopy approaches have played an important role in the fundamental understanding of coupled-cluster theory. In particular, the role of the multitude of solutions that the coupled-cluster polynomial equations provide. This has been pioneered by quantum chemists that have undertaken both elaborate numerical- as well as mathematical investigations. Recently, from the perspective of applied mathematics, new interest of these approaches have emerged using both topological degree theory and algebraically oriented tools. This article aims at describing the latter development.

Benjamin Lasorne
University of Montpellier, France
benjamin.lasorne@umontpellier.fr

Title: Quantum dynamics beyond the Born-Oppenheimer approximation

Abstract: In this talk, we shall focus on the Born-Oppenheimer approximation and beyond as regards quantum dynamics. The usual nuclear-electronic partition will be addressed, as well as composite systems consisting of rigid and soft vibrational modes. Some general discussion will be provided regarding the concept of diabatisation.

Edit Matyus
Eötvös Loránd University, Budapest, Hungary
edit.matyus@ttk.elte.hu

Title: TBA

Abstract: TBA

Yuki Orimo
University of Tokyo, Japan
ykormhk@atto.t.u-tokyo.ac.jp

Title: Quantum simulation of multielectron dynamics in intense laser fields

Abstract: We present a quantum/classical hybrid simulation to investigate multielectron dynamics in intense laser fields. The hybrid simulation enables solving the time-dependent Schrödinger equation for multielectron systems with polynomial computational cost. By employing a sufficiently simple ansatz, it can be executed on current noisy quantum computers. Here, we combine a simple quantum circuit ansatz designed for implementation on current quantum devices with orbital optimization to enhance the flexibility of the ansatz, which has successfully reproduced full-CI simulations. This work showcases the promising potential of accurate and scalable simulations using quantum computers for multielectron dynamics.

Markus Reiher
ETH Zürich, Switzerland
markus.reiher@phys.chem.ethz.ch

Title: Tensor Train Methods for Stationary and Dynamical General Many-Particle Problems

Abstract: TBA

Reinhold Schneider
Technical University of Berlin, Germany
schneidr@math.tu-berlin.de

Title: A Multi-Reference Coupled Cluster Method for the Computation of Excited States

Abstract: Joint work with F. Faulstich (Berkeley), A. Laestadius (OlsoMet) and S. Kvaal (Dept. Chemistry U Oslo)

We aim to compute degenerate and nearly degenerate states as well by a multi-reference CC ansatz. By the bivariational principle we want to derive a suitable approximate multi-state *(state-universal) coupled cluster method*. The idea is that for a Hamiltonian with *n* quasi-degenerate ground states, i.e. the *n* lowest eigenstates, we seek an oblique projection *P* onto this set of eigenstates, that is

$$P = \sum_{i=1}^{n} |\psi_n\rangle\langle\tilde{\psi}_n| \ .$$

We will define our oblique projector *P* via a generalization of the bivariational principle which goes as follows: Consider the function *S*(*P*) = Trace (*HP*). Requiring *S* to be stationary upon arbitrary variations in the projector *P* (i.e., variations that preserve P^2=*P* and Trace (*P*) = *n*) leads to the *two-sided Bloch equation*

$$(I - P)HP = 0, \quad PH(I - P) = 0.$$

In the spirit of the standard CC formulation, we use the ansatz $\psi_k := e^{T_k}|\phi_k\rangle$ with a reference ϕ_k in a CAS space, T_k consists of external excitations, together with the dual functions $\langle\tilde{\psi}_k| = \langle(\tilde{\phi}_k + \Lambda_k)|e^{-T_k}$. We derive a system of equations for these unknowns, which could be solved by a self-consistent iteration.

A computable version of our approach becomes extremely closed to state specific CAS-CC and avoids the usual difficulties like over parametrization of other state universal CC methods. The cost of the solution of the individual CC calculations in each iteration remains similar to that for standard singles doubles CC calculations. The computational bottle neck of the present approach is the full CI solutions on the CAS space. For this purpose, we recommend recent highly efficient full CI solvers, e.g., by tensor approximation (DMRG) or Monte Carlo FCI.

Sølve Selstø
Oslo Metropolitan University, Norway
solvese@oslomet.no

Title: Photo electron spectra directly from absoprtion

Abstract: Describing photo ionization of atoms computationally may be hard for a number of reasons. One of them is that exposure to a long interaction requires a large numerical grid - especially for laser frequencies in the optical or the infra red regime. To this end, imposing absorbing boundary conditions may provide some relief. While this would remove a lot of information about the system, much can still be retained by comparatively simple means. Also, as it turns out, an absorber may, under certain conditions, act as a detector.

Pranav Singh
University of Bath, UK
ps2106@bath.ac.uk

Title: Splitting methods for quantum dynamics and control

Abstract: Advancements in quantum technologies are heavily dependent on the use of computational methods for the prediction of the dynamics of quantum systems, as well as automated techniques for their control and design. Of particular interest in this talk are quantum systems such as spins and electrons under the influence of external time-dependent controls such as lasers and magnetic fields.

The various ingredients required are: (i) numerical solvers for computing quantum dynamics (ii) procedures for computations of gradients and (iii) optimal control routines that are fast, accurate and conserve physical properties of the systems. The problem becomes particularly challenging in the presence of highly oscillatory external fields, unbounded potentials, long temporal windows of simulation, small quantum effects, need for high accuracy, and highly dimensionality.

In this talk I will present some recently developed Magnus expansion based exponential splitting methods for computing quantum dynamics under highly-oscillatory controls, efficient techniques for computing their exact derivatives, and an adaptive procedure for their optimal control called QOALA.

Monika Stanke
Nicolaus Copernicus University of Torun, Poland
ms@umk.pl

Title: The calculations for atoms and molecules in the model without assuming the Born-Oppenheimer approximation.

Abstract: Not assuming the Born-Oppenheimer approximation means
that the theoretical model does not neglect the motion of the heavy particles - the nuclei - and thus all particles
(nuclei and electrons) are treated on equal footing.

Halvard Sutterud
Imperial College London, UK
h.sutterud21@imperial.ac.uk

Title: TBA

Abstract: TBA

Pontus Svensson
University of Oxford, UK
pontus.svensson@worc.ox.ac.uk

Title: A non-adiabatic treatment of warm dense matter via wave packet molecular dynamics

Abstract: TBD

Morgane Vacher
University of Nantes, France
morgane.vacher@univ-nantes.fr

Title: TBA

Abstract: TBA

Aleksander Woźniak
University of Warsaw, Poland
ap.wozniak@uw.edu.pl

Title: TBA

Abstract: TBA
