

## MO 10: Posters 1: Cold Molecules, High Resolution Spectroscopy, and Theory

Time: Tuesday 16:30–18:30

Location: S Foyer LLM

MO 10.1 Tue 16:30 S Foyer LLM

**A narrow-line rotational-state-dependent dipole trap for ultracold polar molecules** — ●XING-YAN CHEN<sup>1</sup>, ROMAN BAUSE<sup>1</sup>, MING LI<sup>2</sup>, SCOTT EUSTICE<sup>1</sup>, MARCEL DUDA<sup>1</sup>, FRAUKE SEESSELBERG<sup>1</sup>, SVETLANA KOTOCHIGOVA<sup>2</sup>, IMMANUEL BLOCH<sup>1,3</sup>, and XIN-YU LUO<sup>1</sup> — <sup>1</sup>Max-PlanckInstitut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching, Germany — <sup>2</sup>Department of Physics, Temple University, Philadelphia, PA 19122-6082, USA — <sup>3</sup>Ludwig-Maximilians-Universität, Schellingstraße 4, 80799 München, Germany

Ultracold polar molecules in rotational states with opposite parities offer strong dipole-dipole interaction, thus can be used to encode pseudo-spin and simulate spin models with long-range interactions. We demonstrate a rotational-state-dependent dipole trap for ultracold  $^{23}\text{Na}^{40}\text{K}$  molecules by utilizing a narrow-line rotational transition manifold  $|X^1\Sigma^+, v=0, J=0, 1\rangle \rightarrow |b^3\Pi, v=0, J=0, 1, 2\rangle$ . By selecting an appropriate laser detuning, we are able to make a "magic" trap where the polarizabilities of  $|J=0, 1\rangle$  states are the same, an "anti-magic" trap where the polarizabilities are exactly opposite, or a tune-out trap where the polarizability of one of the rotational states vanishes. Further more, thanks to the narrow natural linewidth of the excited  $|b^3\Pi_0+, v=0\rangle$  state, the photon-scattering of the tune-out trap is negligible. A long-lived universal spin-dependent dipole potential will facilitate novel studies of spin models and many-body localization with ultracold polar molecules.

MO 10.2 Tue 16:30 S Foyer LLM

**Spectroscopic characterization of the  $a^3\Pi \leftarrow X^1\Sigma^+$  and  $A^1\Pi \leftarrow a^3\Pi$  transitions of aluminium monofluoride** — STEFAN TRUPPE<sup>1</sup>, SILVIO MARX<sup>1</sup>, SEBASTIAN KRAY<sup>1</sup>, ●MAXIMILIAN DOPPELBAUER<sup>1</sup>, SIMON HOFSSÄSS<sup>1</sup>, HANNS CHRISTIAN SCHEWE<sup>1</sup>, BORIS SARTAKOV<sup>2</sup>, and GERARD MEIJER<sup>1</sup> — <sup>1</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany — <sup>2</sup>General Physics Institute, Russian Academy of Sciences, Vavilostreet 38, 119991 Moscow, Russia

Aluminium monofluoride is proposed as an excellent candidate molecule for laser cooling and trapping. For this, detailed knowledge of the low-lying rotational levels in the involved  $X^1\Sigma^+$ ,  $A^1\Pi$  and  $a^3\Pi$  states is necessary.

The energy levels in the  $X^1\Sigma^+$ ,  $v=0$  state and within each  $\Omega$ -manifold in the  $a^3\Pi$ ,  $v=0$  state are determined with a relative accuracy of a few kHz, using laser - radio-frequency multiple resonance ionization detection schemes in a jet-cooled, pulsed molecular beam.

The strength of the spin-forbidden  $A^1\Pi$ ,  $v=0 \leftarrow a^3\Pi$ ,  $v=0$  transition is measured to be between six and seven orders of magnitude lower than that of the  $A^1\Pi$ ,  $v=0 \leftarrow X^1\Sigma^+$ ,  $v=0$  transition.

MO 10.3 Tue 16:30 S Foyer LLM

**State selective laser induced fluorescence detection of cold formaldehyde** — ●MAXIMILIAN LÖW, MARTIN IBRÜGGER, ALEXANDER PREHN, MARTIN ZEPPENFELD, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching

Because of their rich internal structure and long-range dipole-dipole interactions, cold polar molecules have great potential for a wide variety of different applications. In our experiment, we are able to cool formaldehyde ( $\text{H}_2\text{CO}$ ) down to sub-millikelvin temperatures by applying optoelectrical Sisyphus cooling [1]. In the past, the molecules were detected in a robust and reliable way using a quadrupole mass spectrometer. However, the low detection efficiency of  $\sim 10^{-4}$  led to long measurement times thereby severely limiting the experiment.

Here, we present a new detection setup based on laser-induced fluorescence (LIF) of formaldehyde. A quantum yield of up to 30% for radiative decay from the excited state and light collection optics covering a solid angle of  $\sim 70\%$  lead to an increase in detection efficiency of up to a factor of 30. A high signal to noise ratio was achieved by reducing background light by many orders of magnitude. Additionally, we can now detect molecules state selectively, including discrimination of different rotational M-sublevels. This makes LIF detection a powerful tool which will enable us to substantially improve our understanding of our experiment and promises exciting future prospects.

[1] A. Prehn *et al.*, *Phys. Rev. Lett.* **116**, 063005 (2016).

MO 10.4 Tue 16:30 S Foyer LLM

**Building a Zeeman slower for CaF molecules** — ●MARIIA STEPANOVA, PAUL KAEBERT, MAURICE PETZOLD, MIRCO SIERCKE, and SILKE OSPELKAUS — Institut für Quantenoptik, Leibniz Universität Hannover

We will report on our progress towards realizing a large flux source of ultracold Calcium monofluoride (CaF) molecules using molecular Zeeman slowing. We will give details of our test experiment, demonstrating the feasibility of the technique using  $^{39}\text{K}$ . As a first step to implementing our method in molecules we have constructed and characterized a cryogenic buffer gas source, capable of producing molecules with a mean velocity of 150m/s. By comparing our results to simulations using computational fluid dynamics we will discuss several ways to improve on our initial buffer gas cell design, and present data on the molecular flux using our improved cell geometry. Because sufficient laser power is essential for efficient Zeeman slowing of molecules, we will also present data on generating a high power beam of 606nm Laser light through sum frequency generation. By combining all these systems, we hope to finally give current experiments the source they need to produce a quantum degenerate gas of ultracold molecules.

MO 10.5 Tue 16:30 S Foyer LLM

**Sympathetic cooling and quantum state dependant reactions of molecular anions by a localized laser-cooled buffer gas** — ●ERIC ENDRES<sup>1</sup>, JONAS TAUCH<sup>1</sup>, SABA HASSAN<sup>1</sup>, MARKUS NÖTZOLD<sup>2</sup>, BASTIAN HÖLTKEMEIER<sup>1</sup>, HENRY LOPEZ<sup>1</sup>, ROLAND WESTER<sup>2</sup>, and MATTHIAS WEIDEMÜLLER<sup>1</sup> — <sup>1</sup>Physikalisches Institut Heidelberg, INF 226, 69120 Heidelberg — <sup>2</sup>Institut für Ionenphysik und Angewandte Physik, Technikerstrasse 25/3, 6020 Innsbruck

Buffer gas cooling is a versatile technique to cool ions confined in a cryogenic radiofrequency ion traps[1]. However, it is limited to temperature of the coolant, typically being about 4K. By using a laser cold atom cloud, this limitation can be overcome. Furthermore, by localizing the atom cloud and/or a higher order radio frequency trap, theoretical description predicts cooling beyond the critical atom to ion mass ratio [2, 3].

In this contribution I will present recent results of our hybrid atom-ion trap system [4], consisting of an 8-pole radio frequency wire trap confining  $\text{OH}^-$  and a dark spontaneous-force optical Rubidium trap [5]. By embedding ultra cold atoms in an ion cloud, three kind of collisions can occur. First, elastic collisions leading to cooling of the external degrees of freedom from the hydroxy anion, second inelastic collisions leading to cooling of the internal degrees of freedom. Finally, reactive collisions, namely associative detachment reactions, leading to a loss of the trapped anion.

First sings of sympathetic cooling will be shown, as well as, reactive collisions depending on the quantum state of the Rubidium atoms.

MO 10.6 Tue 16:30 S Foyer LLM

**Spectroscopic characterization of aluminium monofluoride with relevance to laser cooling and trapping** — STEFAN TRUPPE<sup>1</sup>, SILVIO MARX<sup>1</sup>, SEBASTIAN KRAY<sup>1</sup>, MAXIMILIAN DOPPELBAUER<sup>1</sup>, ●SIMON HOFSSÄSS<sup>1</sup>, CHRISTIAN SCHEWE<sup>1</sup>, BORIS SARTAKOV<sup>2</sup>, and GERARD MEIJER<sup>1</sup> — <sup>1</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany — <sup>2</sup>General Physics Institute, Russian Academy of Sciences, Vavilovstreet 38, 119991 Moscow, Russia

The aluminium monofluoride molecule (AlF) is an excellent candidate for laser cooling and trapping. Prior to this, it is necessary to measure the detailed energy level structure in the  $X^1\Sigma^+$  electronic ground state, in the  $A^1\Pi$  state and in the metastable  $a^3\Pi$  state as well as the strength of the transitions between these states. We here report the results of spectroscopic measurements between the  $X^1\Sigma^+$  and the  $A^1\Pi$  state.

MO 10.7 Tue 16:30 S Foyer LLM

**Observation of cold dipolar collisions and electrostatic trapping of centrifuge decelerated molecules** — ●MANUEL KOLLER, THOMAS GANTNER, FLORIAN JUNG, ISABEL RABEY, MARTIN ZEPPENFELD, and GERHARD REMPE — Max-Planck-Institute of Quantum Optics, Garching, Germany

Dense samples of cold polar molecules provide fascinating research pos-

sibilities in physics and chemistry. By combining cryogenic buffer gas cooling and centrifuge deceleration we recently demonstrated a record high flux exceeding  $10^{10}\text{s}^{-1}$  and densities up to  $10^9\text{cm}^{-3}$  of cold polar molecules at kinetic energies corresponding to less than 1K [1]. This allows the observation of cold molecule-molecule collisions for  $\text{CH}_3\text{F}$  and  $\text{ND}_3$ . The low absolute velocity enables the straightforward loading of molecules into an electrostatic trap [2], making much more detailed collision studies possible due to longer interaction times. Beyond the observation of inelastic collisions, the creation of highly nonthermal energy distributions by sharply cutting away hotter molecules with a radio frequency knife should allow the investigation of rethermalization via elastic collisions.

[1] X. Wu et al., Science 2017, 358, 645-648

[2] B. Englert et al., Physical Review Letters 2011, 106, 263003

MO 10.8 Tue 16:30 S Foyer LLM

**Modifications and simulations for a Velocity Map Imaging device aiming for methane activation by transition metal cations** — •LISA-MEDARDA RETTER, JENNIFER MEYER, TIM MICHAELSEN, BJÖRN BASTIAN, FRANZISKA KRAMMER, and ROLAND WESTER — Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, 6020 Innsbruck, Austria

Our aim is to image the dynamics of transition metal cations with small hydrocarbons, namely the system of tantalum ions with methane [1,2]. In order to study elementary reaction dynamics and energy distributions into different products we operate our experiment under single collision conditions. This is achieved by crossing a neutral molecular beam with an ion beam produced by a laser vaporization source. Detection is managed via velocity map imaging, which allows for the measurement of differential cross sections [3]. We have recently enhanced the experimental setup with alterations in the form of a conductance limiter as well as a supplementary detector for the ion beam. Simulations in SIMION for these modifications as well as currently planned ones are shown for the system of tantalum cations reacting with methane. [1] H. Schwarz. Angew. Chem. Int. Ed. Engl., 1991, 7, 30 [2] L.G. Parke, C.S. Hinton, P. B. Armentrout. J. Phys. Chem. C 2007, 111, 17773-17787. [3] R. Wester, PCCP, 2014, 16, 396

MO 10.9 Tue 16:30 S Foyer LLM

**Monte Carlo simulation of a cryogenic buffer gas cell** — •THOMAS GANTNER, MANUEL KOLLER, MARTIN ZEPPENFELD, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, 85748 Garching, Deutschland

Cryogenic buffer gas cells have been a workhorse for the cooling of molecules for more than 20 years. The straightforward sympathetic cooling principle makes it applicable for a huge variety of different species. Notwithstanding this success, detailed simulations of buffer gas cells are rare, and limited to high buffer gas density regimes, when the mean free path of a molecule is small compared to all dimensions of the cell. Here, we present a new numerical approach based on a molecule trajectory analysis. The implementation following the Monte Carlo method can reproduce the flux of molecules emerging from the buffer gas cell for varying buffer gas densities. Furthermore, it can reproduce the velocity distribution of the resulting molecule beam. This includes the so-called boosting effect, when buffer gas atoms accelerate the molecules after leaving the cell. The simulations provide various insights which could substantially improve buffer-gas cell design.

MO 10.10 Tue 16:30 S Foyer LLM

**Cavity design for spatial resolved detection of cold molecules** — •JANNIS SCHNARS<sup>1,2</sup>, ALESSANDRO ZENESINI<sup>2</sup>, SILKE OSPELKAUS<sup>2</sup>, and KLEMENS HAMMERER<sup>1</sup> — <sup>1</sup>Leibniz Universität Hannover, Institut für Theoretische Physik, 30167 Hannover — <sup>2</sup>Leibniz Universität Hannover, Institut für Quantenoptik, 30167 Hannover

Ultracold polar molecules offer promising research perspectives in particular due to their strong dipole-dipole interactions. Recently there has been tremendous progress in the creation and manipulation of ultracold polar molecules. The highest phase space densities have been achieved by associating molecules from ultracold ensembles of atoms in a controlled way. However, when it comes to imaging, established techniques for the destructive and non-destructive imaging of atoms fail for molecules due to the complex structure of molecules with vibrational and rotational degrees of freedom. Typically, imaging of ultracold molecules is therefore achieved by reversing the creation process of ultracold molecules and subsequently image atoms on an atomic cycling transition. However, it would be desirable to directly image molecules, ideally non-destructively and with high spatial resolution.

Here we present a scheme to detect molecules inside a 2D-optical lattice. The detection relies on an induced phase shift due to off-resonant light matter interaction. The phase shift is enhanced by a small-waist multimode cavity. We identify possible resonator geometries which balance the requirements for a small beam waist and the need to support several frequency degenerate transverse mode facilitating spatial resolution of several lattice sites.

MO 10.11 Tue 16:30 S Foyer LLM

**IR spectroscopy of glycine-water in helium nanodroplets** — •NITISH PAL<sup>1</sup>, DEVENDRA MANI<sup>1</sup>, RAFFAEL SCHWAN<sup>1</sup>, GERHARD SCHWAAB<sup>1</sup>, BRITTA REDLICH<sup>2</sup>, LEX VAN DER MEER<sup>2</sup> und MARTINA HAVENITH<sup>1</sup> — <sup>1</sup>Physikalische Chemie II, Ruhr-Universität Bochum, Germany — <sup>2</sup>Institute for Molecules and Materials (IMM), Radboud University Nijmegen, Nijmegen, Netherlands

We have studied the microsolvation of glycine with water molecules using helium droplet isolation infrared spectroscopy. Glycine exists in neutral form in gaseous state and in zwitterionic form in aqueous solutions. We address the question: "what is the minimum number of water molecules required to convert a neutral glycine molecule to its zwitterionic form?" The stepwise addition of water molecules to one glycine molecule was achieved using helium droplets isolation technique. The superfluid helium droplets allow a barrier free diffusion of the dopant molecules and enable the formation of large molecular clusters. The infrared spectra were recorded in the range of  $1000\text{-}1850\text{ cm}^{-1}$ , using the free electron lasers (FELs) at FELIX laboratory in Nijmegen.

MO 10.12 Tue 16:30 S Foyer LLM

**Analysis of the coupled  $(2)^2\Sigma^+$  and  $(1)^2\Pi$  of LiSr** — •ERIK SCHWANKE, JULIA GERSCHMANN, HORST KNÖCKEL, SILKE OSPELKAUS, and EBERHARD TIEMANN — QUEST und Inst. f. Quantenoptik, Leibniz Universität Hannover

We present a description of several vibrational states of the  $(1)^2\Pi$  state of LiSr. Although the  $(1)^2\Pi$  state is not directly visible in our recorded infrared spectra due to a weak transition dipole moment to the  $X(1)^2\Sigma^+$  state, we could use observed perturbations in the  $(2)^2\Sigma^+$  state to model the coupling between the spectroscopically observed  $(2)^2\Sigma^+$  state and the  $(1)^2\Pi$  state.

The coupling model leads to a description of the rotational ladders of the coupled  $v' = 0$  and  $v' = 1$  states of  $(2)^2\Sigma^+$  and several vibrational states of both  $(1)^2\Pi_{1/2}$  and  $(1)^2\Pi_{3/2}$ , thus giving local rotational and vibrational constants, as well as the spin-orbit coupling constant for the  $(1)^2\Pi$  states. Relative overlap integrals for the involved vibrational states of  $(1)^2\Pi$  and  $(2)^2\Sigma$  are derived. Furthermore, the perturbation reveals the correct assignment of the  $F_1$  and  $F_2$  levels in the  $(2)^2\Sigma^+ - (1)^2\Sigma^+$  system.

We will report on the status of the investigations.

MO 10.13 Tue 16:30 S Foyer LLM

**Investigation of quadrupole moment effects on the determination of excited state dipole moments in solution** — •MATTHIAS ZAJONZ, TIM OBERKIRCH, MIRKO LINDIC, and MICHAEL SCHMITT — Institute for Physical Chemistry I, Heinrich-Heine-University Düsseldorf

The molecule under investigation, 2,5-cyclohexadiene-1,4-dione (p-benzoquinone), is highly symmetric and by looking at its structure it is obvious that it has a quadrupole moment instead of a dipole moment.

To improve thermochromic methods for determination of excited state dipole moments in solution the effects of quadrupole moments have to be investigated.

For the molecule under investigation we measured thermochromic shifts, in order to assess the influence of quadrupole moments on the dipole moment determination in electronically excited states.

MO 10.14 Tue 16:30 S Foyer LLM

**The influence of vibrational excitation on the reaction of  $\text{F}^-$  with  $\text{CH}_3\text{I}$**  — •TIM MICHAELSEN, BJÖRN BASTIAN, JENNIFER MEYER, and ROLAND WESTER — Institut f. Ionenphysik und Angewandte Physik, Universität Innsbruck

We study ion molecule reaction dynamics in a crossed beam setup using velocity map imaging [1]. One focus of our research are reactions of halide anions with methylhalides, which represent an interesting model system to study bimolecular nucleophilic substitution reactions ( $\text{S}_\text{N}2$ ). In recent years we have extended our investigations of such systems to study microsolvation effects as well as the influence of vibrational

excitation on branching ratios and reaction dynamics [2].

Here we report on recent results investigating the influence of C-H stretch excitation on the reaction of  $F^-$  with  $CH_3I$  at various collision energies. The  $CH_3I$  is excited by a broadband OPO/OPA laser prior to collision and the excited fraction is probed using a photodissociation and state selective REMPI scheme. The experimental results are compared with recently published quasiclassical trajectory calculations for the same system [3].

[1] R. Wester, Phys. Chem. Chem. Phys. 16, 396 (2014)

[2] M. Stei, et al., Sci. Adv. 4, 7, eaas9544 (2018)

[3] B. Olsasz and G. Czako, J. Phys. Chem. A, 122, 41, 8143-8151 (2018)

MO 10.15 Tue 16:30 S Foyer LLM

**Intramolecular scattering: Simulation of coupled electron-nuclear motion upon photoionization** — FRIEDRICH GEORG FRÖBEL, ●ALEXANDER SCHUBERT, and STEFANIE GRÄFE — Friedrich-Schiller-Universität Jena, Jena, Germany.

We theoretically investigate intramolecular scattering and energy redistribution during photoionization of molecular systems in intense few-cycle XUV laser fields. The molecular model system is described by the extended Shin-Metiu model consisting of two position-fixed nuclei with one movable nucleus in between and two electrons in a single dimension. Dynamics simulations are performed by integrating the time-dependent Schrödinger equation numerically using grid-based methods. Spectral signatures in the photoelectron spectra are shown to contain sensitive information about different ionization pathways revealing the ionization-induced electron and nuclear dynamics and subsequent non-adiabatic effects.

MO 10.16 Tue 16:30 S Foyer LLM

**A modified approach for simulating nonadiabatic dynamics via the generalized quantum master equation** — ELLEN MULVIHILL<sup>1</sup>, ●ALEXANDER SCHUBERT<sup>1,2,3</sup>, XIANG SUN<sup>1,4</sup>, BARRY D. DUNIETZ<sup>2</sup>, and EITAN GEVA<sup>1</sup> — <sup>1</sup>University of Michigan, Ann Arbor, MI, United States — <sup>2</sup>Kent State University, Kent, OH, United States — <sup>3</sup>Friedrich-Schiller Universität Jena, Jena, Germany — <sup>4</sup>New York University Shanghai, Shanghai, China

A modified approach for simulating nonadiabatic dynamics based on the Nakajima-Zwanzig generalized quantum master equation (GQME) is presented. Unlike the most common GQME-based approaches, the modified approach (M-GQME) does not require casting the overall Hamiltonian in a (not uniquely defined) system-bath form, which is neither natural nor convenient in the case of the molecular Hamiltonian that governs the nonadiabatic dynamics. Within the M-GQME framework, the effect of the degrees of freedom of the environment on the time evolution of the reduced density operator is fully captured by a memory kernel superoperator. In the presented numerical implementation, the memory kernel is calculated employing the Ehrenfest mean-field method. The modified approach is demonstrated on a benchmark spin-boson model and shown to lead to significantly more accurate results than a direct application of the Ehrenfest method while being computationally more robust than other GQME-based approaches.

MO 10.17 Tue 16:30 S Foyer LLM

**A classical ride through a conical intersection** — ●THOMAS SCHAUPP and VOLKER ENGEL — Institut für Physikalische und Theoretische Chemie, Emil-Fischer-Str. 42, 97074 Würzburg, Germany

Regarding the correlated electron-nuclear motion in a model system, we investigate the dynamics in the vicinity of a conical intersection (CoIn) between two excited state potential surfaces. It is documented that an ensemble of classical trajectories which move in the complete electronic-nuclear phase space tracks the quantum wave-packet motion through the CoIn which is accompanied by a strong non-adiabatic population transfer. On the contrary, for an adiabatic circular motion around the position of the CoIn, the quantum mechanical and classical densities deviate substantially. In the latter case, the Born-Oppenheimer classical nuclear motion on a single potential surface is able to track the quantum dynamics.

MO 10.18 Tue 16:30 S Foyer LLM

**First principles calculation of molecular partial autoion-**

**ization rates** — ●GILBERT GRELL, OLIVER KÜHN, and SERGEY BOKAREV — Universität Rostock, Rostock, Deutschland

Autoionization processes such as Auger and interatomic coulombic decay play a key role in the radiation matter interaction on atomic and molecular scales. For instance, the lifetime of a core excited state is primarily defined by its autoionization rate. Further, autoionization cascades after initial ionization or excitation determine the resulting ion and electron yields. First principles calculations of partial autoionization rates are demanding due to the necessary description of continuum states. Standard quantum chemistry (QC) codes usually employ Gaussian basis sets, which describe bound states and orbitals very well. Continuum orbitals, however, are poorly described by these basis sets, prohibiting a simple extension of standard QC methods to include continuum states. We present a protocol that aims at estimating autoionization energies and partial rates, based on standard QC calculations for the bound states that are supplemented with continuum orbitals. A single center model is used to reduce the continuum orbital problem to the solution of a radial Schrödinger equation in the potential of the remaining ion. In this framework we assess the impact of different approximations to the radial potential on the continuum orbitals and resulting partial autoionization rates. Finally, the general applicability of the single center model for the calculation of molecular autoionization rates is analyzed.

MO 10.19 Tue 16:30 S Foyer LLM

**Optimized Sampling of Mixed-State Observables** — ●MAREC W. HEGER, CHRISTIANE P. KOCH, and DANIEL M. REICH — Theoretische Physik, Universität Kassel, Heinrich Plett-Straße 40, 34132 Kassel, Germany

Quantum dynamical simulations of statistical ensembles pose a significant computational challenge due to the fact that mixed states need to be represented by a density matrix instead of a wave function. If the underlying dynamics are fully unitary, for example in coherent control at finite temperatures, one approach to approximate time-dependent observables in this context is to sample the density matrix by solving the Schrödinger equation for a set of wave functions with randomized phases.

We present an in-depth analysis of the average performance for the random-phase wave functions and compare them to deterministic sampling of the energetically lowest-lying eigenstates. In particular, the performance crossing point between these two approaches allows an estimation of the more efficient sampling scheme for an average observable. Moreover, we prove that minimization of the worst-case error among arbitrary observables is uniquely attained by eigenstate-based sampling. Finally, we point out how the structure of low-rank observables can be exploited to further improve eigenstate-based sampling schemes.

MO 10.20 Tue 16:30 S Foyer LLM

**Comparison of two different ways to calculate expectation values** — ●KLAUS RENZIEHAUSEN and INGO BARTH — Max Planck Institute of Microstructure Physics, Weinberg 2, D-06120 Halle (Saale), Germany

We analyze two different ways to calculate quantum mechanical expectation values for several observables. The first ansatz is just the direct calculation of the quantum mechanical expectation value, the second ansatz is to calculate this expectation value using the Ehrenfest theorem. We have performed those calculations for the temporal mass change, the momentum, the force, the torque, and the angular velocity of a particle in three dimensions. As a result, we found for each of these observables an integral equation. On one side of this equation an integrand depending on the mass density appears, while we find on the other side an integrand depending on the mass current density. So, we can calculate these expectation values either using the mass density or the mass current density (as an exception the analysis for the expectation value of the azimuth angular velocity is more complicated). This has application possibilities for molecular systems where electronic current densities cannot be calculated within the Born-Oppenheimer approximation. The papers [I. Barth et al., Chem. Phys. Lett. **481**, 118-123 (2009)] and [T. Schaupp, J. Albert, V. Engel, Eur. Phys. J. B **91**, 97 (2018)] can be interpreted as examples for such applications.