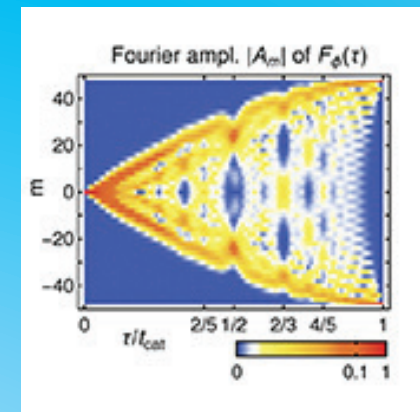


# Developing Flexible and Robust Software in Computational Atomic and Molecular Physics

**MAY 14-16, 2018**

*Organizers:*

**Barry Schneider** ((NIST))  
**Robert Forrey** (Penn State)  
**Naduvath Balakrishnan** (UNLV)



Sponsored by:

Institute for Theoretical Atomic, Molecular and Optical Physics\*

Harvard - Smithsonian Center for Astrophysics  
60 Garden St., Cambridge, MA

<https://www.cfa.harvard.edu/itamp>

Abstracts, Program, Participants, and Guide to ITAMP

\*Funded by the National Science Foundation

Harvard-Smithsonian Center for Astrophysics  
ITAMP  
MS-14, B-326  
60 Garden Street  
Cambridge, MA 02138 USA



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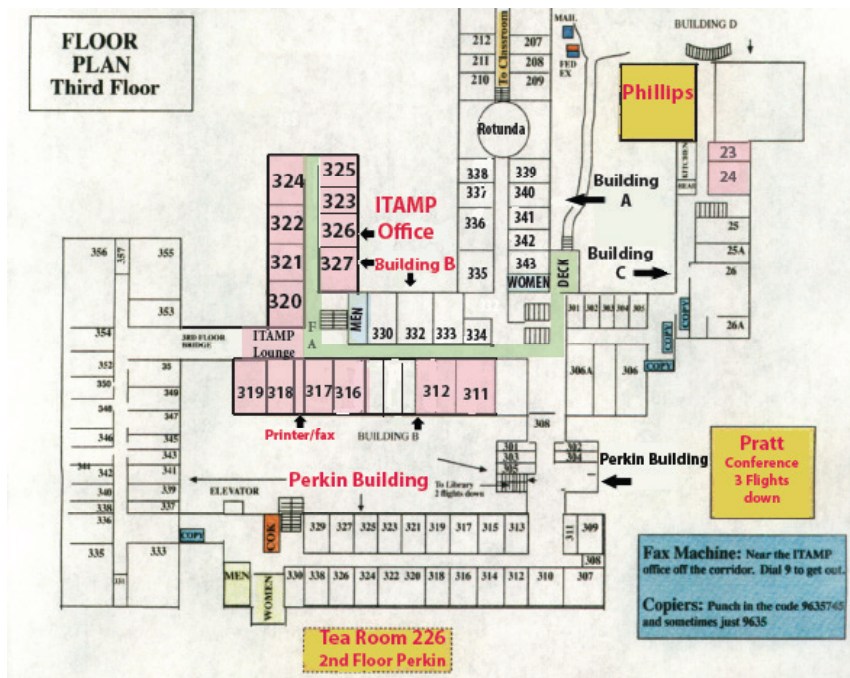
ITAMP began life in 1989 at the Harvard-Smithsonian Center for Astrophysics. It is the only theoretical AMO "user facility" in the United States. It hosts workshops (3-days) and topical group meetings (1-4 weeks), and visitors (short- and long-term), has a flagship speaker series, the Joint Atomic Physics colloquia held in Harvard Physics, and a rigorous postdoctoral program. ITAMP workshops are web-cast, when possible, and beginning in 2010, workshop lectures are available on the ITAMP YouTube channel. There are on average 4-5 workshops each year. A Call for Proposal to organize workshops and a list of workshops & topical groups are available at <http://itamp.harvard.edu>. The postdoctoral program has been a recognized success, placing energetic fellows into junior positions at universities and national labs.

ITAMP thrives in the larger Cambridge-area AMO physics ecosystem, drawing upon the considerable depth and breadth of experimental expertise. The mission of ITAMP continues to be in furthering the cause of theoretical AMO physics by providing resources, centrality of location, and scientific and administrative expertise, to enhance collaborative efforts between theory and experiment, and to be broad in advocating for theoretical AMO.

H. Sadeghpour



## ITAMP Floor Plan



## Developing Flexible and Robust Software in Computational Atomic and Molecular Physics

The workshop participants will be charged with;

1. Identifying and prioritizing the outstanding problems in AMO science which would benefit from a concerted community effort in developing new software tools and algorithms, leading to more rapid progress.
2. Identifying the best approaches to addressing the problems identified in 1.
3. Producing a report and a plan of action on how to accomplish these goals.

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Barry Schneider ((NIST))  
 Robert Forrey (Penn State)  
 Naduvalath Balakrishnan (UNLV)

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- c. Part I section, your SSN
- b. Part II Section, your Signature and Date

Note: Do not e-mail this form that contains your SSN. This confidential data will not be stored and it will be destroyed. If you will be faxing the documents, use +1-617-495-5970, which is a private fax line.

**4) Foreign Individual Vendor Request Form.**

This form is for Foreign Nationals. Please follow the instructions to your individual specifications and fill in the following information:

- 1) Your name
- 2) SSN if applicable (if none, enter N/A)
- 3) Your Mailing address
- 4) Your Email
- 5) Your Visa Type

**5) Federal Awards Travel Reimbursement Exception Form.**

This form is for the traveler who uses non-U.S. Flag air carrier. If applicable, please sign in at the bottom of the form where "Reimburse Signature" and "Date" is.

Thank you for helping us to get your reimbursements back to you quickly as possible. Your check will be sent about a month after we process your paper work. Please contact us with any questions or concerns that you might have.

**Important Note:** In case your expenses are being paid by your institute, you do not need to fill out these forms. Instead we will need an invoice from your institute that contains the information below:

- Invoice number
- Invoice date
- Bill to: Harvard College Observatory  
60 Garden Street, MS 14  
Cambridge, MA 02138
- Make Payment To:  
NAME & ADDRESS of your University
- Description of your visit
- Balance due
- Wire Transfer information (only for international participants with more than 1000 support)



## Instructions for Reimbursement Forms

If you have been promised support to help cover your expenses, the following forms will be required paperwork for your reimbursement. Please, only use the attached forms if you have already received an offer of support. If you feel there has been a mistake or are unsure about your support, please ask and we can assist you.

We will only need receipts that will total up to your promised support in your invitation letter. If your receipts total over that amount, you will simply just be reimbursed up to that promised amount.

Here are the directions for filling out the following forms.

### 1) The Non-Employee Reimbursement Form.

This form is submitted to the University and must be filled out in a specific way. We will fill in the details of your expenses. Please provide the following information:

- a. Your name in the box marked “Reimbursee Name”
- b. Affiliation
- c. Your citizenship and resident information
- d. SIGN the bottom at “Reimbursee Signature” and fill in the check mailing address section below your signature.
- e. Leave the back page blank  
Leave the following sections blank:
  - Business Purpose Section and
  - The box below of “All expenses must be itemized...” Section.

### 2) Missing Receipt Affidavit.

You will only need this document if anything you send does not fit the receipt policy. Harvard’s receipt policy is on the back of this form. If you do not believe there will be a problem, you do not need to submit this form. It is included here, in case of a problem. We would however encourage you to sign this form in any event to quicken the process.

### 3) W-9 Request for Taxpayer Identification

Number and Certification Form. This form should be signed by U.S. citizens or U.S. Residents. Please fill in the following information:

- a. Name
- b. Address, City, State and Zip code

## Participants

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## Developing Flexible and Robust Software in Computational Atomic and Molecular Physics

May 14-16, 2018  
Phillips Auditorium

### Monday, May 14, 2018

8:00 am Coffee, Refreshment  
8:30 am Welcome/Introductory Remarks (Director/Organizers)

### Session I: Many-body Interactions

*Chair: Naduvalath Balakrishnan*

9:00 am **Arghavan Safavi-Naini**  
*“Verification schemes for trapped-ion quantum simulators”*

9:20 am **Johannes Feist**  
*“Manipulating Molecules with Quantized Light Modes: Coupled Electronic, Nuclear and Photonic Dynamics”*

9:40 am **Fernando Martin**  
*“A hybrid-basis close-coupling interface to quantum chemistry packages for ionization problems: the XCHEM code”*

10:00am **Robin Santra**  
*“Atoms and Molecules at High X-ray Intensity: Dedicated Software Development”*

10:20 am **Coffee Break**

11:00 am **Panel Discussion - Lincoln Carr** (*Discussion Leader*)  
Johannes Feist, Robin Santra, Fernando Martin, Roman Krems, Barbara Capogrosso-Sansone, Arghavan Safavi-Naini, Naduvalath Balakrishnan

12:00 -2:00 pm **Lunch at John G. Wolbach Library**

Public Transportation and Taxicabs  
Buses servicing Harvard Square & CfA area are Buses # 72, 74, 75 and 78  
Bus to Harvard Square to MIT is Bus #1  
Buses to Watertown and Belmont are #71, #73  
Harvard Square to Boston: Red Line Train to Park Street Station  
Harvard Square to Airport: Red Line Train to South Station. Take the Silver line to Logan Airport. Silver line stops at all terminals. To see the schedule of buses visit [http://www.mbta.com/schedules\\_and\\_maps/bus/](http://www.mbta.com/schedules_and_maps/bus/)

Taxicabs  
Ambassador: 617 492-1100 Yellow: 617 547-3000

### Dining in and around ITAMP

**At the Observatory** The Cart  
In the Perkin Lobby  
Open from 9:30 to 2:30

**Near the Observatory** Sarah’s Market, 200 Concord Ave.  
The Village Kitchen, 359 Huron Ave.  
Full Moon, 344 Huron Ave.  
House of Chang, 282 Concord Ave.  
Trattoria Pulcinella, 147 Huron Ave.  
Armanado’s Pizza, 163 Huron Ave.  
Hi-Rise Bread CO, 208 Concord Ave.  
Formaggio Kitchen, 244 Huron Ave

**Massachusetts Ave.** Chang-Sho, 1712 Mass. Ave.  
Temple Bar, 1688 Mass. Ave.  
Simons Coffee House, 1736 Mass. Ave.  
Stone Hearth Pizza Co., 1782 Mass. Ave.  
Super Fusion, 1759 Mass. Ave.  
Cambridge Common, 1667 Mass Ave.  
Lizard Lounge, 1667 Mass. Ave.

### Welcome to ITAMP

#### ITAMP Office:

60 Garden St.  
Cambridge, MA 02138 B-326 MS-14

Fax: 617 496-7668

Fax: 617 495-5970 (for confidential material e.g. tax forms, reference letters etc.)

#### Who to Contact:

Naomi Tariri           Tel: 617 495-9524       Office B-326

Alice Kalemkarian   Tel: 617 495-0402     Office B-323

#### Computer Support

The Center for Astrophysics has a large computer network and there are many options for connectivity. In this section, we describe the easiest ways to get on-line. Jim Babb, B-318, can help with questions about how to get connected and related issues. There is also a Computer Help Desk on the second floor, near Room B-215.

#### Internet Access

Most wireless devices will connect to the “Harvard Guest” account. This works fine and there is no paperwork involved in getting internet access. Other connections are available, should this not work for you for some reason. Please see Jim Babb if you run into problems.

#### Copiers/Faxing and Phone Access

Copy Machines are located throughout the building (see map) The access code for copy machines throughout the CfA is 9635.

#### Telephone System

To call outside the University you must dial 9 before the number. The University prefix three digits are 495 and 496. To dial on campus, you simply need to dial the “5” or “6” and the last four digits. For example, ITAMP Admin office’s number is 617-495-9524. You can dial 5-9524 to call internally. The Institute is not permitted to pay for long distance calls.

### Session II: Scattering (Light particles)

*Chair: Lee Collins*

- 2:00 pm       **Klaus Bartschat**  
*“The B-Spline R-Matrix Method for Electron and Photon Collisions with Atoms and Ions”*
- 2:20 pm       **Robert Lucchese**  
*“Electron-Molecule Scattering Calculations using Grid Based Methods”*
- 2:40 pm       **Igor Bray**  
*“CCC computer codes for calculating atomic and molecular collisions”*
- 3:00 pm       **Ann Orel**  
*“Problems along the way”*
- 3:20 pm       **Coffee Break**
- 4:00 pm       **Panel Discussion - Jonathan Tennyson** (*Discussion Leader*)  
Klaus Bartschat, Ann Orel, Lee Collins, James Colgan, Igor Bray, Robert Lucchese, Janine Shertzer
- 5:00 - 6:00 pm   Open Discussion and adjourn for dinner

### Tuesday, May 15, 2018

### Session III: Electronic Structure

*Chair: Hossein Sadeghpour*

- 9:00 am       **Mark Pederson**  
*“Drivers for Innovation in and Development of Robust Software for Computational Science”*
- 9:20 am       **Jeppe Olsen**  
*“Towards a Flexicurity Model for Electronic Structure Calculations”*

9:40am	<b>Joel Bowman</b> <i>“Model-Free Representations of Full Dimensional Ab initio Potential Energy Surfaces – the “Long-Range Challenge”</i>
10:00 am	<b>Gerrit Groenenboom</b> <i>“Making AMO data and software accessible, inspiration from computational chemistry”</i>
10:20 am	<b>Coffee Break</b>
11:00 am	<b>Panel Discussion -Krzysztof Szalewicz</b> ( <i>discussion leader</i> ), Mark Pederson, Jeppe Olsen, Joel Bowman, Gerrit Groenenboom, Hossein Sadeghpour
12:00 -2:00 pm	<b>Lunch at John G. Wolbach Library</b>
<b>Session IV: Molecular Dynamics</b> <b>Chair: Bob Forrey</b>	
2:00 pm	<b>Oriol Vendrell</b> <i>“Correlated electron dynamics in the presence of nuclear motion”</i>
2:20 pm	<b>Phillip Stancil</b> <i>“Successes and Failures in Code Maintenance and Development for Many-atom Inelastic Scattering Problems”</i>
2:40 pm	<b>Brian Kendrick</b> <i>“The APH3D quantum reactive scattering code”</i>
3:00 pm	<b>Timur Tscherbul</b> <i>“Quantum scattering calculations on molecular collisions in external fields: Recent progress and computational challenges”</i>
3:20 pm	<b>Coffee Break</b>
4:00 pm	<b>Panel Discussion - Millard Alexander</b> ( <i>Discussion Leader</i> ), Timur Tscherbul, Oriol Vendrell, Brian Kendrick, Phillip Stancil, Robert Forrey, Naduvalath Balakrishnan
5:00 - 6:00 pm	Open Discussion and adjourn for dinner

**Machine learning for quantum molecular dynamics****Roman Krems***University of British Columbia*

Over the past few years, we have been engaged in three types of numerical calculations of relevance to AMO physics: (1) time independent scattering calculations of molecular collision properties with a focus on chemically reactive scattering and molecular collisions in fields; (2) time dependent scattering calculations of chemical reaction probabilities; (3) recursive calculations of Green's functions of interacting particles in disordered lattices and lattices with phonons. Following the instructions of the organizers, I will describe the bottlenecks of these calculations and the major problems that limit the predictive power of rigorous quantum scattering calculations. In particular, I will address the problem of the sensitivity of the scattering observables to the molecular interaction potentials. I will argue that some of these problems can be solved with the help of statistical machine learning. Time permitting, I will show how machine learning can be used to construct multi-dimensional chemically reactive potential energy surfaces which yield scattering observables matching the experimental data.

## A new time-dependent ab-initio close-coupling program for atomic ionization

**Luca Argenti**

*<sup>1</sup>Dept. of Physics & CREOL, 4111 Libra Drive, Orlando, FL32816, U.S.A*

Autoionizing states are a pervasive aspect of atomic and molecular ionization and a distinct signature of electronic correlation. Only with the advent of attosecond sources, however, did it become possible to resolve the evolution of autoionizing states in real time, and to study how they are affected, and can be controlled, by light [1-4].

Ab initio time-dependent close coupling (TDCC) has affirmed itself as the leading tool to simulate the ionization of atoms under the influence of ultrashort pulses, beyond the single-active-electron approximation [9-12]. In this seminar I will present a new time-dependent program to compute the photoionization of polyelectronic atoms by arbitrary light pulses.

The program merges the capabilities of the Stock B-spline close-coupling structure code [7] with those of the time-dependent two-active-electron code described in [5]. It builds a close-coupling space in which multi-reference parent ions [3] are augmented with a spherical B-spline basis up to an assigned radius, and it solves the time-dependent Schrödinger equation with a second-order split-exponential propagator.

Channel-specific mask functions periodically extract and analyze the outer part of the state vector, allowing us to simulate the effect of arbitrarily long moderately weak pulses while employing comparatively small quantization boxes. Reflection of the faster components at the box edge is prevented by complex-absorbers. The channel- and energy-resolved photoelectron spectrum is computed by projecting the state function on a complete set of scattering states. The program predictions are benchmarked against test simulations in helium, and applied to selected resonant attosecond pump-probe simulations for the argon and neon atom.

[1] Ott C et al., Nature 516, 374 (2014).

[2] Gruson V et al., Science 354, 734 (2016).

[3] Kotur M et al., Nature Commun. 7, 10566 (2016).

[4] Chew A et al., Phys. Rev. A 97, 031407(R) (2018).

[5] Argenti L et al., Phys. Rev. Lett 105, 053002 (2010).

[6] Argenti L et al., Phys. Rev. A 87, 053405 (2013).

[7] Carette T et al., Phys. Rev. A 87, 023420 (2013).

[8] Cirelli C et al., Nature Commun. 9, 955 (2018).

[9] Argenti L et al., Phys. Rev. A 91, 061403 (2015).

[10] Jiménez Galán A et al., Phys. Rev. Lett. 113, 263001 (2014).

[11] Jiménez Galán A et al., Phys. Rev. A 93, 023429 (2016).

[12] Argenti L et al., Phys. Rev. A 95, 043426 (2017).

**Wednesday, May 16, 2018**

## Session V: Interactions with External Fields and Software Engineering

*Chair: Hugo Van der Hart*

- 8:30 am **Amin Scrinzi**  
*“The tRecX code - Easy Strong Field Physics”*
- 8:50 am **Luca Argenti**  
*“A new time-dependent ab-initio close-coupling program for atomic ionization”*
- 9:10 am **Roman Krems**  
*“Machine learning for quantum molecular dynamics”*
- 9:30am **Coffee Break**
- 10:00-11:00 am **Panel Discussion - Barry Schneider** (*Discussion Leader*)  
Luca Argenti, Hugo Van der Hart, Roman Krems, Armin Scrinzi)
- 11:30 -2:00 pm **Lunch at John G. Wolbach Library**
- 2:00pm **Lincoln Carr**
- 2:30 pm **Jonathan Tennyson**
- 3:00 pm **Krzysztof Szalewicz**
- 3:30 pm **Coffee Break**
- 4:00 pm **Millard Alexander**
- 4:30 pm **Barry Schneider**
- 5:00 -6:00pm **Summary (Organizers), Workshop concludes.**

## Verification schemes for trapped-ion quantum simulators

Arghavan Safavi-Naini

*JILA*

One and two-dimensional arrays of trapped ions with variable range interactions mediated by the phonon modes of the Coulomb crystal realize quantum simulators of various spin models. However the presence of spin-motion coupling in the Hamiltonian may also lead to significant spin-motion entanglement. I will show that in this regime, where the phonons and the spins have to be treated together, the simulator realizes the Dicke model. I will present two numerical approaches that allow us to simulate the full spin-phonon dynamics. The first approach is exact and uses the t-DMRG method developed for generic spin-boson models, while the second approach combines the Truncated Wigner Approximation (TWA) and the discrete TWA method. I will show extensive theory-experiment comparisons which have allowed us to fully verify the trapped-ion simulator at NIST-boulder.

[1] The tRecX code - a universal Schrödinger and Maxwell solver  
<https://trex.physik.uni-muenchen.de>

[2] tSurff: fully differential two-electron photo-emission spectra.  
Armin Scrinzi. *New Journal of Physics*, 14(8):085008, 2012.

[3] Infinite-range exterior complex scaling as a perfect absorber in time-dependent problems.  
Armin Scrinzi, *Physical Review A*, 81(5):1-10, May 2010.

[4] Anomalous Fano Profiles in Strong Fields  
A. Zielinski et al., *Phys. Rev. Lett.* 115, 243001 (2015).

[5] Double photo-electron momentum spectra of Helium at infrared wavelength  
Alejandro Zielinski, Vinay Pramod Majety, Armin Scrinzi, *Phys. Rev. A* 93, 023406 (2016).

[6] Photoionization of few electron systems: a hybrid coupled channels approach.  
V. P. Majety, A. Zielinski and A. Scrinzi. *N.J. Physics*, *New J. Phys.* 17:063002, 2015.

[7] Static field ionization rates for multi-electron atoms and small molecules  
Vinay Pramod Majety and Armin Scrinzi, *J. Phys. B* 48:245603 (2015).

[8] Dynamic exchange in the strong field ionization of molecules

Vinay Pramod Majety and Armin Scrinzi. *Phys. Rev. Lett.* 115, 103002, (2015), (arXiv).



## The tRecX code - Easy Strong Field Physics

**Armin Scrinzi**

*Ludwig Maximilians Universität, München*

The development of the tRecX code [1] for applications in strong-field and attosecond physics will be reported. The main goals of the development are

- transparently implement a range of new techniques (tSurff [2], irECS [3], haCC[4])
  - provide a flexible test bed for new models and pilot studies
  - provide parallel and high performance code
  - work in arbitrary dimensions (1d - 6d)
  - allow diverse discretizations, e.g. FE, FE-DVR, FD-grids, Gaussian-based CI functions
  - ensure code extendibility
  - provide an error-robust interface for developers and users
- At present, these goals have been achieved, on a reasonable level, with results for some of the outstanding hard problems of the field [5-8]. Main strategies were
- C++ code, using standard physics and math objects (e.g. "HilbertSpace", "Operator")
  - recursive structures (template class Tree) for all multi-index objects
  - human-readable, string-driven definition of discretization and operators (see below)

Interfacing to standard electronic structure codes is as yet unsatisfactory, with a sole interface to COLUMBUS. A public domain git-repository is available, proper RPM and DEB packaging as well as a GUI are currently under development.

Example input of discretization and operators:

```
Axis: name, nCoefficients, lower end, upper end, functions, order
Phi, 1 # polar coordinates
Eta, 2, -1,1, assocLegendre{Phi} # can be permuted at will
Rn, 40, 0,BOX, polynomial,20 # various discretization functions
Rn, 20, BOX,Infy, polExp[0.5] # piece-wise [0,BOX],[BOX,infy]
```

```
Operator: hamiltonian='1/2<<Laplacian>>-<1><1><trunc[5,10]/Q>'
Operator: interaction='iLaserA0[t]<<D/DZ>>'
Operator: expectationValue='<1><1><chi[0,20]>,<1><2/3 Q*Q><chi[15,20]>'
```

## Manipulating Molecules with Quantized Light Modes: Coupled Electronic, Nuclear and Photonic Dynamics

**Johannes Feist**

*Departamento de Física Teórica de la Materia Condensada and Condensed Matter Physics Center (IFIMAC), Universidad Autónoma de Madrid, E-28049 Madrid, Spain*

Strong coupling is achieved when the coherent energy exchange between a confined electromagnetic field mode and material excitations becomes faster than the decay and decoherence of either constituent. This creates a paradigmatic hybrid quantum system with eigenstates that have mixed light-matter character (polaritons). It has recently been realized that polariton formation in organic molecules also affects their internal nuclear degrees of freedom, raising the possibility to manipulate and control molecular structure and dynamics simply by bringing them into coupling with a quantized light mode in an optical (nano)cavity, leading to the advent what is now known as polaritonic chemistry.

However, an accurate theoretical description of such systems facing a large amount of challenges: Fundamentally, electronic, nuclear, and (quantized) photonic degrees of freedom in such systems have to be treated on an equal footing, requiring a combination of techniques from historically separate fields such as quantum optics/cavity quantum electrodynamics and quantum chemistry. Additionally, in typical experimental implementations, macroscopic numbers of molecules interact coherently with one or many quantized light modes. The collective nature of this interaction requires the simultaneous treatment of large numbers of molecules and potentially photonic modes. Furthermore, both the molecules and the photonic modes correspond to open quantum systems that are significantly influenced by decoherence due to coupling with solvent molecules and photon leakage/material losses, respectively.

After a short introduction, I will give an overview of currently available computational approaches and discuss their respective capabilities and limitations. I will then discuss future directions and possible extensions to existing methods.

## A hybrid-basis close-coupling interface to quantum chemistry packages for ionization problems: the XCHEM code

Fernando Martín<sup>1,2,3\*</sup>

<sup>1</sup> *Universidad Autónoma de Madrid*

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The theoretical description of observables in attosecond pump-probe experiments requires a good representation of the ionization continuum. For poly-electronic molecules, however, this is still a challenge, due to the complicated short-range structure of correlated electronic wave functions. Whereas quantum chemistry packages designed to compute bound electronic molecular states are well established, comparable tools for the continuum are not widely available yet. To tackle this problem, we have developed a new approach [1,2] that, by means of a hybrid Gaussian-B-spline basis [3] (see Fig. 1), interfaces existing multi-reference quantum chemistry packages with close-coupling scattering methods. In this talk, we will describe the ingredients of the method, already implemented in the XCHEM code, and illustrate its performance for the He and Ne atoms, as well as for the H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O and pyrazine molecules. Our results for the benchmark He, Ne and H<sub>2</sub> systems are in excellent agreement with those obtained from methods especially designed to accurately describe ionization in these systems [1,4]. For N<sub>2</sub>, we have settled down an existing controversy about the role of non-adiabatic effects in the autoionization lifetimes of the Hopfield series of resonances [5] recently investigated by attosecond pump-probe spectroscopic methods. Our findings, together with the versatility of quantum chemistry packages to describe a broad range of chemical systems, indicate that this is a valid approach to study the ionization of poly-electronic systems in which correlation and exchange symmetry play a major role.

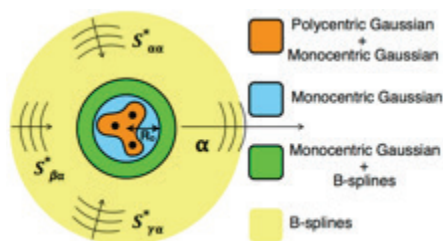


Figure 1: The hybrid Gaussian+B-spline basis set (GABS). Taken from [1].

## Quantum scattering calculations on molecular collisions in external fields: Recent progress and computational challenges

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Recent advances in molecular cooling and trapping have provided direct access to hitherto unexplored regimes of few-body collision physics with ultracold molecules. Rigorous coupled-channel (CC) quantum scattering calculations on molecular collisions in external fields are an indispensable tool to understand and explore the new few-body physics. Such calculations are computationally intensive due to the need to account for a large number of molecular vibrational, rotational, fine, and hyperfine states coupled by strong and anisotropic intermolecular interactions. I will overview the computational tools and methodologies currently available for solving molecular collision problems in the presence of external fields with a focus on the computationally efficient total angular momentum representation [1] applied to ultracold Rb+SrF collisions in a magnetic field [2]. I will outline major computational challenges facing the field of quantum molecular collision dynamics in external fields and identify possible strategies for their resolution, which could benefit theoretical astrochemistry, molecular spectroscopy, and quantum gas-phase and condensed-phase reaction dynamics.

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## The APH3D quantum reactive scattering code

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An overview of the Adiabatically adjusting Principal axis Hyperspherical 3-Dimensional (APH3D) quantum reactive scattering code will be presented. The APH3D code is based on a time-independent coupled-channel approach and has been under development at LANL for over thirty years. It has been extensively validated against both experimental data and other theoretical methods. Total, vibrationally, and rotationally resolved reactive, inelastic, and elastic differential and integral cross sections are computed as function of collision energy for a general  $A + BC$  collision system. Scattering resonance spectra and triatomic bound-state ro-vibrational spectra can also be computed. A numerically exact solution of the quantum 3-body problem for the nuclear motion is performed using one (or more) Born-Oppenheimer electronic potential energy surfaces.

Recent developments have extended the methodology to include excited electronic states enabling the treatment of electronically non-adiabatic dynamics and charge transfer reactions. The methodology is fully parallelized and can be tuned for optimal performance on a variety of architectures from a single workstation to large supercomputers.

The numerical methodology and capabilities of APH3D will be briefly reviewed followed by a discussion of the current code development activities and long term plans. Particular emphasis will be placed on identifying the deficiencies of available software and numerical methods which need to be overcome.

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## Atoms and Molecules at High X-ray Intensity: Dedicated Software Development

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One of the key opportunities offered by the development of x-ray free-electron lasers is the determination, at atomic resolution, of the three-dimensional structure of biologically relevant macromolecules. The basic idea underlying molecular imaging using x-ray free- electron lasers is the “diffract-and-destroy” concept: If one uses an x-ray pulse that is sufficiently short (on the order of femtoseconds), then in a single shot an x-ray scattering pattern may be obtained that is practically unaffected by atomic displacements triggered by ionization events during the x-ray pulse. What cannot be eliminated in this way is the impact of the electronic damage on the x-ray scattering patterns. Theory, therefore, plays an important role in the development of this new imaging technique: A quantitative understanding is required of the damage processes occurring during the exposure of a molecule to an ultraintense, ultrafast x-ray pulse. In this talk, I will present progress we have made in order to address this challenge. One tool we have developed, XMDYN [1], is a molecular-dynamics code that utilizes ab-initio atomic electronic-structure information, computed on the fly, within a Monte-Carlo framework. XMDYN has been successfully tested through experiments at LCLS [2] and SACLA [3]. XMDYN is part of a powerful start-to-end simulation framework for single-particle imaging at the European XFEL [4, 5]. Recently, we have taken first steps towards a full ab-initio framework for simulating high-intensity x-ray–matter interactions [6, 7]. Our new XMOLECULE software solves the polyatomic quantum-mechanical electronic-structure problem for every electronic state arising during the exposure of a molecule to a strong x-ray pulse. From this information, electronic transition rates (such as Auger decay rates) are computed on the fly, and the associated rate equations are integrated utilizing a Monte-Carlo method. XMOLECULE played a key role in a recent LCLS experiment on iodomethane, in which hard x-rays focused to a peak intensity exceeding 1019 W/cm<sup>2</sup> produced the highest charge states ever formed using light [8]. Not only did XMOLECULE correctly predict the charge-state distribution observed, but it also helped identify a new molecular ionization enhancement mechanism based on intramolecular charge transfer.

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Figure 1: Status of time-independent (TI) inelastic scattering calculations in terms of the number of atoms  $N_{\text{atom}}$  and PES dimension  $d$ . Regime of TI quantum scattering calculations to date (green). Regime of available PESs which can currently only be treated by quasi-classical dynamical methods (grey).

This work was performed in collaboration with Benhui Yang, N. Balakrishnan, Bob Forrey, Peng Zhang, James Croft, Chen Qu, and Joel Bowman. Work at UGA was partially supported by NASA grants NNX12AF42G and NNX16AF09G.

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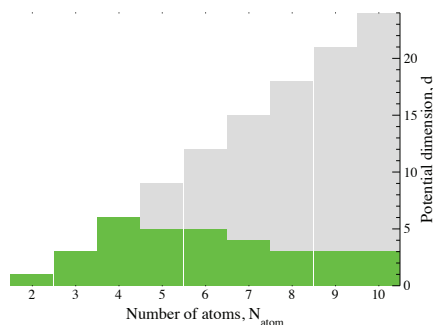
## Successes and Failures in Code Maintenance and Development for Many-atom Inelastic Scattering Problems

**P. C. Stancil**

*Department of Physics and Astronomy and  
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Solutions of the so-called Master equation for molecular level populations require collisional excitation rate coefficients due to the dominant colliders. Master equation studies have applications to a variety of gas-phase environments which are not adequately represented by a Boltzmann distribution. The theory behind inelastic collisional excitation for spherical atom collisions on spin-less diatoms was developed more than 50 years ago [1], becoming the foundation for countless rigidrotor studies and later code development to treat more computationally intensive problems. While a number of inelastic scattering software packages are available for the community, they cannot treat full-dimensional scattering problems larger than atom-diatom systems. Further, as computational resources have grown significantly, most public-domain packages have not been able to take advantage of the resource advances.

In this talk, I will focus on our experience over the last decade in i) speeding up the public domain package MOLSCAT [2] to exploit distributed- and shared-memory architectures (hybrid MPI/OpenMP), ii) generalizing and porting the non-public diatom-diatom code TwoBC [3] to distributed-memory (with MPI) and accelerated architectures (i.e., GPUs) on Titan and SummitDev, and iii) efforts to obtain funding for open-source code development and maintenance. In particular, there is a significant need to extend the full-dimensional scattering available with TwoBC (6D) to the treatment of triatomic and larger molecular targets, currently beyond existing code capabilities (see Fig. 1).



## The B-Spline R-Matrix Method for Electron and Photon Collisions with Atoms and Ions

**Oleg Zatsarinny and Klaus Bartschat**

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Electron collisions with atoms, ions, and molecules represent one of the very early topics of quantummechanics. In spite of the field's maturity, a number of recent developments in detector technology and the rapid increase in computational resources have resulted in significant progress in the measurement, understanding, and theoretical/computational description of few-body Coulomb problems. Close collaborations between experimentalists and theorists worldwide continue to produce high-quality benchmark data, which allow for thoroughly testing and further developing a variety of theoretical approaches. As a result, it has now become possible to reliably calculate the vast amount of atomic data needed for detailed modeling of the physics and chemistry of planetary atmospheres, the interpretation of astrophysical data, optimizing the energy transport in reactive plasmas, and many other topics – including light-driven processes, in which electrons are produced by continuous or shortpulse ultra-intense electromagnetic radiation.

The R-matrix method [1] has been widely employed to solve the close-coupling equations, especially in the low-energy, near-threshold regime, where resonances are very important, as well as in the intermediate-energy regime where coupling to the target continuum via the R-Matrix with Pseudo-States (RMPS) extension [2] has been very successful. The latter extension also allows for the treatment of electron-impact ionization processes.

Implementation of the R-matrix method for electron (and photon) collisions for general atomic and ionic targets (as well as molecules) in the non-relativistic, semi-relativistic (Breit-Pauli), and fullrelativistic (Dirac) frameworks has been pursued in the United Kingdom since the pioneering work of P. G. Burke and his colleagues. The suite of computer programs (non-relativistic with a semirelativistic option) and an extensive write-up were last published in 1995 [3], but the package is being maintained and updates are publicly available [4]. The above package is based on orthogonal sets of one-electron orbitals to construct the many-electron bound and continuum wavefunctions. It has been widely used in the Opacity and Iron Projects [5,6] and continues to be a very important tool for generating high-quality atomic (and molecular) data.

The B-Spline R-Matrix (BSR) implementation developed in our group over the past 15 years is an alternative formulation, where the one-

electron orbitals are constructed from B-splines as the primitive basis. These B-splines are not orthogonal (with the non-vanishing overlaps being limited to a number of neighboring splines), and hence it seemed advantageous to give up the orthogonality requirement also for the one electron orbitals built from them. As a result, the BSR code allows for the use of independently optimized, term-dependent one-electron orbitals. The use of these functions increases the flexibility and accuracy of the target description and has some numerical benefits associated with the B-spline basis, but it also increases the complexity of setting up and ultimately diagonalizing the Hamiltonian, which is needed to solve the problem in the inner region of the R-matrix sphere.

A semi-relativistic version of the code was published [7], and a full-relativistic version has also been presented [8]. The latter, however, is not yet publicly available. Work to produce a version with sufficient documentation and test cases is currently in progress. The general structure of the package will be presented, together with a few sample results. Much more can be found in [9] and the many publications since then. Furthermore, some major challenges will be outlined. These concern future applications as well as plans for making the package usable by the large community of plasma modelers, who are interested in the final output data but are not necessarily experts in the physics of atomic collisions.

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## Correlated electron dynamics in the presence of nuclear motion

**Oriol Vendrell**

*Aarhus University*

Energy and charge transfer in molecules, aggregates and in the condensed phase are determined by correlated electron dynamics, where the role of nuclear motion can vary from a simple bath to an active enabler of the corresponding process through specific atomic displacements. As the density of participating electronic states becomes high, a picture based on pre-calculation of those states (i.e., potential energy surfaces) and their couplings becomes intractable. This realization calls for computational tools able to describe both electrons and nuclei (not necessarily on the same footing!) as dynamically evolving from well defined initial states. Possible courses of action towards these goals based on multi-configuration time-dependent approaches will be discussed.

## Making AMO data and software accessible, inspiration from computational chemistry

**Gerrit C. Groenenboom**

*Theoretical Chemistry, Institute for Molecules and Materials  
Radboud University, Nijmegen, The Netherlands*

The AMO community provides the data and the software to compute the data that is relied upon by many research fields. Growing demand results from, e.g., rapid developments in astronomy - with huge investments in telescopes and the observations of exoplanetary atmospheres - and from the rapid progress in ultracold gases research. In the Netherlands, the Dutch Astrochemistry Networks I (finished in 2016) and II (just started) are funding opportunities for laboratory astrochemistry projects to provide the AMO data needed for astro-chemical modeling. One of the themes concerns the gas phase, and we contribute by calculating ab initio potential energy surfaces and performing quantum scattering calculations.

The computational chemistry community has a long history of developing and sharing software in a well organized manner. Software for quantum chemistry, molecular mechanics, or molecular modeling/design can be easily found from overviews on Wikipedia that summarize main features and license types and provide links. Not only the software, but also chemical data is readily available. For example: `curl https://cactus.nci.nih.gov/chemical/structure/aspirin/sdf` will return the chemical structure and geometry of the aspirin molecule.

In my talk, I propose that big gains for the AMO community and its users are possible by making our data and software more accessible. I believe that many of the tools necessary to modernize our codes and data sharing are already available as free software. I will share some of the things I learned when putting together a web-interface for quantum chemistry calculations for educational purposes, <http://quantum.science.ru.nl>. Such an interface could be extended to make AMO software more easily accessible and user friendly.

## Electron-Molecule Scattering Calculations using Grid Based Methods

**Robert R. Lucchese**

*Chemical Sciences Division, Lawrence Berkeley National Laboratory*

The development of several codes for electron-molecule collisions will be discussed, where the continuum electron is represented on a numerical grid rather than an atomic centered basis set. The first code is for linear molecules using close-coupling expansions for the multi-electron wave function and single-center expansions for the one-electron wave functions and is known as the Multichannel Swinger Configuration Interaction code (MCCSCI).<sup>1,2</sup> A second code, ePolyScat, was developed to treat electron scattering from general polyatomic molecules but only with single configuration wave functions.<sup>3,4</sup> A third code is now in development that uses overset grids, combining small spherical grids around each nuclear center and one central spherical grid which extends out to the asymptotic region.<sup>5</sup> This new code uses the complex Kohn variational expression to compute matrix elements.

The spectral representations of the angular grids are constructed from symmetry adapted real harmonics in the full point group symmetry of the molecule for both abelian and non-abelian point groups. The numerical computations make extensive use of transformations between spectral and coordinate representations, which are easily parallelized. The codes for non-linear molecules use MPI for parallelization with a spatial decomposition over processors. All codes are Fortran95/03 and use libint 6 for standard integrals over atomic centered basis sets.

Work at LBNL was performed under the auspices of the U.S. Department of Energy (DOE) Office of Basic Energy Sciences, Division of Chemical Sciences under Contract No. DE-AC02-05CH11231.

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## CCC computer codes for calculating atomic and molecular collisions

I. B. Abdurakhmanov<sup>1</sup>, C. J. Bostock<sup>1</sup>, A. W. Bray<sup>2</sup>, I. Bray<sup>1</sup>, D. V. Fursa<sup>1</sup>, A. S. Kadyrov<sup>1</sup>, A. S. Kheifets<sup>2</sup>, J. S. Savage<sup>1</sup>, R. Utamuratov<sup>1</sup> and M. C. Zammit<sup>3</sup>

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We briefly review some of the capabilities of several separate convergent close-coupling (CCC) theory implementations to calculating collisions in atomic and molecular physics. All of the computer codes are designed to treat projectiles at any energy and the target space to convergence utilising  $L^2$  expansions, yet with applicability to ionizing processes. The computational implementation utilises both OpenMP and MPI parallelization on any number of loosely connected fat nodes. Multiple GPU utilization is currently under way.

The computer codes are constantly under development, and are not designed for non-expert users. The parallelism is sufficiently challenging requiring careful implementation on the available computational infrastructure. The most practical approach to utilising the CCC codes is via collaboration.

### Electron/positron/photon collisions with quasi one- and two-electron atoms: non-relativistic CCC

Authors: I. Bray, D. V. Fursa, A. S. Kadyrov, A. S. Kheifets, R. Utamuratov, A. W. Bray

This code began with the e-H collision system, then extended to quasi one-electron atoms, helium and quasi two-electron atoms. Application to photon scattering and positron scattering, with positronium formation, have also been incorporated [1, 2]. Application to ionization processes was shown to be relatively straightforward [3]. A simplified version of this code has been published [4].

### Electron collisions with quasi one- and two electron atoms and ions: Relativistic CCC

Authors: D. V. Fursa, C. J. Bostock

The RCCC code solves the Dirac rather than the Schrödinger equation [5, 6]. The Breit and Møller interactions have also been included [7]

### CCC method for heavy projectiles

Authors: A. S. Kadyrov, I. B. Abdurakhmanov

The CCC code for heavy bare projectiles such as protons and antiprotons relies on a transformation to impact-parameter representation. There are two independent computer codes

## Model-Free Representations of Full Dimensional Ab initio Potential Energy Surfaces – the “Long-Range Challenge”

**Joel M. Bowman**

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Several approaches are being actively used to obtain model-free potential energy surfaces from tens of thousands of high-level electronic energies. These include permutationally invariant polynomials (PIP), neural networks (NN), and Gaussian process (GP) representations. These approaches, while general and powerful, are challenged to precisely represent long range interactions, which are of the order of  $10 \text{ cm}^{-1}$  or less (1 meV or less) and to rigorously separate to non-interacting fragments. I will review the issues, especially using the PIP approach, (and thus NN and GP approaches that also using PIPs as inputs) and also some recent progress using a “2-component” approach. This progress will be illustrated for a recent potential energy surface for  $\text{SiO}+\text{H}_2$  [Full-Dimensional Quantum Dynamics of SiO in Collision with H<sub>2</sub>, B. Yang, P. Zhang, C. Qu, X. H. Wang, P. C. Stancil, J. M. Bowman, N. Balakrishnan, B. M. McLaughlin, and R. C. Forrey, *J. Phys. Chem. A* 122, 1511-1520 (2018)] and, most recently, a full-dimensional, non-reactive, potential energy surface for  $\text{H}+\text{H}_2\text{O}$ , done in collaboration with the “SiO+H<sub>2</sub> group”.

## Towards a Flexicurity Model for Electronic Structure Calculations

**Jeppe Olsen**

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There is a growing recognition that it is not possible to design a universal wave function model, which combines efficiency and accuracy for arbitrary types of molecules and molecular states. Instead, it is necessary to develop algorithms and programs that dynamically update the form and content of the wave function, so that only the important parts are included in the expansion.

In this talk, I will give several examples of such developments, including the development of configuration interaction and coupled cluster methods with arbitrary excitation levels. I will in particular discuss recent developments, where single reference coupled cluster states are used as reference and target states for perturbation expansions. By choosing the excitation levels of the parent and target states, a large number of models with various degrees of accuracy and complexity are generated.

The programs and algorithms that allow the calculation of coupled cluster states with arbitrary excitation levels may be twisted to enable the calculation of density matrices of arbitrary rank for general CI expansions. It is therefore possible to calculate 3- and 4- body density matrices for large CI-expansions, which opens for the development of scattering and ionization methods with fewer approximations than the current methods.

1. Fully QuantumMechanical: QM-CCC is based on solving the full Schrödinger equation [8].
2. Semi-Classical: SC-CCC relies on the separation of nuclear and electronic dynamics using a semi-classical approximation. The code contains two treatments of the continuum: Laguerre [9] and wave-packet [10, 11].

### Electron/positron-molecule scattering

Authors: D. V. Fursa, M. C. Zammit, J. S. Savage, R. Utamuratov

The MCCC computer code is a stand-alone code that has been recently developed for molecular targets [12, 13, 14]. It has both a spherical and a prolate spheroidal coordinate system implemented within. It relies on the Born-Oppenheimer approximation, which can be combined adiabatically for different nuclei separation whenever necessary.

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## Problems along the way

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In the spirit of the workshop, we will present two aspects where our current computational capabilities hinder our progress towards the understanding of collision physics systems. In the first case, we will discuss our research into mutual neutralization. In mutual neutralization, oppositely charged ions collide and driven by non-adiabatic couplings, an electron is transferred resulting in formation of neutral fragments. An ab initio description of the reaction is challenging since dynamics on highly excited electronic states has to be considered and the reaction is induced by non-adiabatic couplings between ionic and covalent states, often occurring at large internuclear distances. In addition, the curves involved may be autoionizing at smaller internuclear separation.

In the second case, we will discuss the problem of prediction of the final state distributions of fragment states arising from the dissociative recombination of water ion. We have calculated the total dissociation recombination cross section from the direct process by combining electronic structure and scattering calculations to obtain the quasidiabatic potential energy surfaces of both bound, Rydberg and electronic resonant states of the water molecule and then carrying out wave packet calculations on those surfaces. In order to estimate the cross section arising from the indirect mechanism of dissociative recombination, the scattering matrix calculated at low collision energy was used to obtain explicitly all couplings elements responsible for the electronic capture to bound Rydberg states. However, the calculation of the branching ratios requires the diabaticization of these surfaces and the coupling between

## Drivers for Innovation in and Development of Robust Software for Computational Science

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Through consideration of case studies and community reports, beginning in the late 1980's and extending to today, I will attempt to analyze which drivers are most likely to spur new scientific innovations, including refined theories, in concert with software development and try to identify why such drivers necessarily change depending on the state of legacy codes, new computational architectures, new experimental insights, and availability of community resources. From the standpoint of architecture-driven software initiatives I will discuss whether there are lessons to be learned from past initiatives that have been motivated to move previous-generation codes onto next generation machines as was necessitated by the serial-to-vector, the serial/vector to parallel, and then parallel to massively parallel transitions in the past. Based on experience as a DOE program manager I will describe several modalities that have been used in the past to encourage researchers to be ready for efficient use of next generation machines and discuss why an "all-of-the-above" strategy is necessary to ensure that the community can continue to address near-term scientific challenges while preparing for the future. Based on decades of collaboration on the development of density-functional codes, I will discuss how new mathematical, theoretical, and experimental insights spurred innovation and impacted the trajectory of software development.