# Computational Chemical Dynamics: From Gas–Phase to Condensed–Phase Systems

October 7–9, 2004  
University of Minnesota  
Minneapolis, Minnesota

## Table of Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symposium Sponsor and Organizers</td>
<td>1</td>
</tr>
<tr>
<td>Agenda</td>
<td>3</td>
</tr>
<tr>
<td>Donald G. Truhlar’s Scientific Family Tree</td>
<td>8</td>
</tr>
<tr>
<td>Students and Scientific Collaborators of Donald G. Truhlar</td>
<td>9</td>
</tr>
<tr>
<td>Presentation Abstracts</td>
<td>13</td>
</tr>
<tr>
<td>Participants</td>
<td>40</td>
</tr>
<tr>
<td>Summary of Locations</td>
<td>45</td>
</tr>
<tr>
<td>Administrative Contacts</td>
<td>46</td>
</tr>
</tbody>
</table>
Symposium Sponsor and Organizers

Sponsored by
University of Minnesota
   Supercomputing Institute for Digital Simulation and Advanced Computation
   Digital Technology Center
   Chemistry Department
U.S. Department of Energy
Air Force Office of Scientific Research
IBM
Pacific Northwest National Laboratory
SGI
Unisys

Organizers
Christopher J. Cramer, University of Minnesota
Bruce C. Garrett, Pacific Northwest National Laboratory
Devarajan Thirumalai, University of Maryland
Thanh N. Truong, University of Utah
**Agenda**

**Wednesday, October 6, 2004**

6:00–9:00 p.m. Registration and reception (Radisson Hotel Metrodome)

**Thursday, October 7, 2004**

7:00–8:20 a.m. Registration/Continental breakfast (McNamara Gateway Center)

8:20–8:30 Welcome and introductions (Victor Bloomfield, Interim Dean of the Graduate School, University of Minnesota)

**Session Chair: Bruce C. Garrett**

8:30–9:00 John C. Polanyi, University of Toronto, “Molecular Dynamics of Surface Reaction Followed a Molecule at a Time by STM”

9:00–9:15 Xavier Assfeld, Université Henri Poincaré, “How Well Hydrogen Bonds Are Represented in Hybrid QM/MM Methods”

9:15–9:30 David Giesen, Kodak, “MIDI!—The Little Basis Set That Can”

9:30–9:45 Wesley D. Allen, University of Georgia, “In Pursuit of Subchemical Accuracy in Computational Thermochemistry”

9:45–10:00 Angels González-Lafont, Universitat Autònoma de Barcelona, “Variational Transition State Theory as a Tool to Determine Kinetic Selectivity in Reactions Involving a Valley-Ridge Inflection Point”

10:00–10:20 Break

**Session Chair: J. Ilja Siepmann**

10:20–10:50 Mark S. Gordon, Iowa State University and Ames Laboratory, “An Embedded Cluster Approach to Surface Chemistry”

10:50–11:05 C. Alden Mead, University of Minnesota, “Projection Operator Formalism for Parallel Transport and Distant Parallelism for Two-Dimensional Electronic Subspaces, Including Kramers Doublets”


11:20–11:35 Alejandro Toro-Labbé, Pontificia Universidad Católica de Chile, “The Role of the Reaction Force to Characterize the Hydrogen Transfer Between Sulfur and Oxygen Atoms”

11:35–11:50 Orlando Roberto-Neto, Instituto de Estudos Avançados, Centro Técnico Aeroespacial and Universidade Paulista–UNIP, “Dual-level Direct Dynamics Calculations of the Kinetic Isotope Effects for the CH4 + F → CH3 + HF Abstraction Reaction”

11:50–12:05 p.m. Sean C. Smith, The University of Queensland, “Quantum Lanczos Subspace Methods in Application to Unimolecular and Complex-Forming Bimolecular Reactions”

12:05–1:15 Lunch in Memorial Hall at the McNamara Center
Session Chair: Angela K. Wilson

1:15–1:45 David C. Clary, University of Oxford, “Quantum Dynamics Calculations of Rate Constants for Polyatomic Reactions”


2:00–2:15 Kim K. Baldridge, University of Zürich and San Diego Supercomputer Center, “Electronic Redistribution in Biomolecules, Including Effects of Environment”


2:45–3:00 Yuzuru Kurosaki, Japan Atomic Energy Research Institute, “Potential Energy Surfaces and Thermal Rate Constants for the BrH2 System”

3:00–3:20 Break

Session Chair: Steven M. Bachrach


4:20–4:35 T. N. Truong, University of Utah, “Kinetics of the Hydrogen Abstraction Reaction Class CH3 + H-C(sp3) → CH4 + C(sp3): An Application of the Reaction Class Transition State Theory”

4:35–4:50 Weitao Yang, Duke University, “Reaction Path Potential for Simulation of Chemical Reactions in Enzymes Derived From ab Initio QM/MM Calculations”

4:50–5:20 Aron Kuppermann, California Institute of Technology, “Hyperspherical Harmonics in Quantum Reactive Scattering”

5:20–6:30 Break/unscheduled time

6:30–10:00 Pizza/poster session (Coffman Memorial Union Great Hall)
**Friday, October 8, 2004**

7:45–8:30 a.m.  Registration/Continental breakfast (McNamara Center )

*Session Chair: William B. Gleason*

8:30–9:00  George C. Schatz, Northwestern University, “Reactions of Hyperthermal Atomic Oxygen”

9:00–9:15  Angela K. Wilson, University of North Texas, “High Accuracy Molecular Properties: Successes and Challenges”

9:15–9:30  M. Dupuis, Pacific Northwest National Laboratory, “Direct $ab\text{ Initio}$ Dynamics for Reactivity and Vibrational Spectra”

9:30–9:45  Enrique Sánchez Marcos, Universidad de Sevilla, “Defining the Hydration Structure of Metal Aquaions Exhibiting Anisotropic Solvent Environments: The Pd$^{2+}$ and UO$_2^{2+}$ Cases”

9:45–10:00  V. Moliner, Universitat Jaume I, Castelló, Spain, “A QM/MM Study of the Rate Limiting Step in the Formate Dehydrogenase”

10:00–10:20  Break

*Session Chair: Gillian Lynch*

10:20–10:50  John Tully, Yale University, “Frustrated Hops’ and Detailed Balancing in Mixed Quantum-Classical Dynamics”

10:50–11:05  William C. Stwalley, University of Connecticut, “Opportunities for Chemical Dynamics at Ultracold Temperatures”


11:20–11:35  Darrin M. York, University of Minnesota, “Mechanistic Characterization of the Hydrolysis of Methyl Ethylene Phosphate and the Phosphoryl Transfer Reaction Catalyzed by Phosphoglucomutase”

11:35–12:05 p.m.  Keiji Morokuma, Emory University, “Potential Energy Surfaces and Dynamics of Molecular Systems: Gas Phase Photodissociation, Fullerene Formation and ONIOM Applications”

12:05–1:15  Lunch

*Session Chair: T. N. Truong*

1:15–1:45  Mark A. Ratner, Northwestern University, “Molecular Transport Junctions: Inelastic and Switching Effects”

1:45–2:00  Odd Gropen, University of Tromsø, “Relativistic Quantum Mechanical Methods in Molecular Calculations. Theory and Applications”

2:00–2:15  James R. Rustad, University of California, Davis, “A Molecular Dynamics Investigation of Ferrous-Ferric Electron Transfer in a Hydrolyzing Aqueous Solution: Calculation of the pH Dependence of the Diabatic Transfer Barrier and the Potential of Mean Force”

2:15–2:30  Sachchida N. Rai, North-Eastern Hill University, “Recent Studies on Elastic and Inelastic Processes During Collisions of Protons With Hydrocarbons”

2:30–2:45  Steve Valone, Los Alamos National Laboratory, “Particle-Velocity Dependent Rate Constants From Transition State Theory”

3:00–3:20 Break

Session Chair: Mark Gordon


3:50–4:05 Robert Q. Topper, Monmouth University, “Modeling DNA Damage: Computational Cascade Analyses of N-Acetyl-2-Aminofluorene (AAF) Adducts to Guanine and Deoxyguanosine”

4:05–4:20 Amnon Kohen, University of Iowa, “H-Tunneling, Coupled Motion, and Environmentally Coupled H-Transfer in Enzymatic Reactions”

4:20–4:35 J. Ilja Siepmann, University of Minnesota and Lawrence Livermore National Laboratory, “Simulating Fluid Phase Equilibria From First Principles”


5:20–5:35 Kunizo Onda, Tokyo University of Science, “Full Quantum-Mechanical Study of Collision-Induced Dissociation in Three-Dimensional Non-reactive He + H₂ Collision”

5:35–5:50 Gillian Lynch, University of Houston, “Solvent Structure Studies as a Function of Concentration”

6:00–8:45 Reception and Banquet (Campus Club in Coffman Memorial Union)

8:45–9:30 After-dinner speaker: William A. Goddard, III, California Institute of Technology
Saturday, October 9, 2004

7:45–8:30 a.m. Continental breakfast (McNamara Center)

Session Chair: David Giesen

8:30–9:00 William L. Hase, Texas Tech University, “Role of Computational Chemistry in the Development of Unimolecular Rate Theory”

9:00–9:15 L. Masgrau, University of Leicester, “VTST/MT Kinetic Isotope Effects for the Proton Transfer Catalyzed by AADH”

9:15–9:30 Klaus Ruedenberg, Iowa State University, “Efficient High-Accuracy CI Calculations of Binding Energies Through Controlled Correlation Energy Extrapolation by Intrinsic Scaling”

9:30–9:45 Hyung J. Kim, Carnegie Mellon University, “Menshutkin Reactions in Quadrupolar Solvents”

9:45–10:00 Toshiyuki Takayanagi, Saitama University, “Reduced-dimensionality Quantum Scattering Calculations of the Reaction Between $^3P$ and Acetylene”

10:00–10:20 Break

Session Chair: Darrin M. York


10:50–11:05 Yuan-Ping Pang, Mayo Clinic College of Medicine, “3D Model of a Substrate-Bound SARS Chymotrypsin-Like Cysteine Proteinase Predicted by Multiple Molecular Dynamics Simulations: Catalytic Efficiency Regulated by Substrate Binding”


11:35–11:50 William B. Gleason, University of Minnesota, “From Paper Tape to Mag Tape to Cards… Computing Then (the Seventies) and Now at Minnesota”

11:50–12:05 p.m. Christopher J. Cramer, University of Minnesota, “Mechanism and Dynamics of Methane Metathesis by Group III Metallocenes”

End of conference
Students and Scientific Collaborators of Donald G. Truhlar

Postdoctoral and Visiting Research Associates

Richard Smith, 1971-72
Bruce Garrett, 1977-80
Kunizo Onda, 1978-80
Alan Isaacson, 1980-81
Steven Valone, 1980-82

Najib Abusalbi, 1981-82
Sachchida Rai, 1982-83
Grazyna Staszewska, 1982-83, 2002-2003
Franklin Brown, 1983-85
Jack Lauderdale, 1984-85

David Schwenke, 1985-87
Carmay Lim, 1986
Thomas Georgian, 1986-87
Gene Hancock, 1986-87
Tomi Joseph, 1986-88

Mirjana Mladenovic, 1987-88
Philippe Halvick, 1988-89
Da-hong Lu, 1989-91
Angels Gonzalez-Lafont, 1989-91 (Fulbright Scholarship)
Ronald S. Friedman, 1989-91

Thanh Truong, 1990
Gregory Tawa, 1990-93
Robert Topper, 1990-92
Qi Zhang, 1991-92
Melissa Reeves, 1991-93

Kathleen Kuhler, 1993-94
Ivan Rossi, 1993-95
Candee Chambers, 1994-96
Kiet Nguyen, 1994-96
Xavier Assfeld, 1994-96

Elena Laura Coitiño, 1995-97
Maria Topaler, 1996-98
Jose Corchado, 1996-98 (Fulbright Scholar)
Orlando Robert-Neto, 1996-97
Jordi Villà, 1998

Maria Sanchez, 1998-99
Yongho Kim, 1999-2000
Hisao Nakamura, 2000-2002
Liqiang Wei, 2000-2001
Titus Albu, 2000-2002

Przemek Staszewski, 2002-2003
Chaoyuan Zhu, 2002-present
Hai Lin, 2003-present
Ahren Jasper, 2003-present

Joint Supervision With C. J. Cramer
Joey W. Storer, 1993-94
Tianhai (Tony) Zhu, 1996-98
Jiabo Li, 1997-99
Kevin Silverstein, 1998
James Xidos, 1999-2001
Benjamin Lynch, 2003-present

Joint Supervision With Jiali Gao
Tina Poulsen, 2001-2002
Graduate Thesis Supervision

Joseph Abdallah, Jr., M. S., Chemistry, 1974
Robert W. Numrich, Ph.D., Chemistry, 1974
Maynard A. Brandt, M.S., Chemistry, 1975
James W. Duff, Ph.D., Chemistry, 1975
Nancy Mullaney Harvey, Ph.D., Chemistry, 1979
Devarajan Thirumalai, Ph.D., Chemistry, 1981
Rex T. Skodje, Ph.D., Chemical Physics, 1983
Carmay Siow Chioi Lim, Ph.D., Chemical Physics, 1984
Todd C. Thompson, Ph.D., Chemistry, 1984
 (joint supervision with C. Alden Mead)
David W. Schwenke, Ph.D., Chemistry, 1985
Rozeanne Steckler, Ph.D., Chemistry, 1986
Kenneth Haug, Ph.D., Chemical Physics, 1987
Joni C. Gray, Ph.D., Chemistry, 1989
Susan C. Tucker, Ph.D., Chemistry, 1989
Thanh N. Truong, Ph.D., Chemistry, 1989
Meishan Zhao, Ph.D., Chemical Physics, 1989
Xin Gui Zhao, Ph.D., Chemical Physics, 1990
David Cochrane, M.S., Chemistry, 1990
Haozho Dong, M.S., Chemical Physics, 1990
Paul N. Day, Ph.D., Chemistry, 1991
David C. Chatfield, Ph.D., Chemistry, 1991
Yi-Ping Liu, Ph.D., Chemistry, 1993
Michael Unekis, Ph.D., Chemical Physics, 1993
Vasilios Melissas, Ph.D., Chemistry, 1993
Gillian Lynch, Ph.D., Chemistry, 1993
(joint supervision with Christopher J. Cramer)
Steven Mielke, Ph.D., Chemical Physics, 1995
Wei-Ping Hu, Ph. D., Chemistry, 1995
William Necoechea, Ph. D., Chemistry, 1995
Steven Wonchoba, Ph.D., Chemistry 1997
Thomas Allison, Ph. D., Chemistry, 1997
Gregory Hawkins, Ph. D., Chemistry, 1998
Jianhua Xing, M.S., Chemical Physics, 1998
Eric Schwegler, Ph. D., 1998
 (joint supervision with Jan Almlöf)
Yao-Yuan Chuang, Ph. D., Chemical Physics, 1999
Jay Srinivasan, Ph. D., Chemical Physics, 1999
Sutjano Jusuf, 1999
 (joint supervision with Odd Gropen)
Patton Fast, Ph. D., Chemistry, 2000
Yuri Volobuev, Ph. D., Chemical Physics, 2000
Tiqing Liu, Ph. D., Chemistry, 2000
Michael Hack, Ph. D., Chemistry, 2000
Benjamin Lynch, Ph. D., Chemistry, 2003
Ahren Jasper, Ph. D., Chemistry, 2003
Jingzhi Pu, Ph. D., Chemistry, 2004
Jason Thompson, Chemistry, 2004
 (joint supervision with Christopher J. Cramer)

Current Graduate Students

Jason Thompson, Chemistry
Arindam Chakraborty, Chemistry
Shikha Nangia, Chemistry
Vanessa Audette Lynch, Chemistry
Nathan Schultz, Chemistry
Ben Ellingson, Chemistry
Erin Dahlke, Chemistry
Adam Chamberlin, Chemistry
 (joint supervision with Christopher J. Cramer)
Daniel Theis, Chemistry
Yan Zhao, Chemistry
Undergraduate Research Students

James Sorenson, 1971
Jean Merrick, 1974–75
Radley Olson, 1974
Richard Partridge, 1975
Ruth Poling, 1975
William Tarara, 1975
Laura Clemens, 1976
Charles Horowitz, 1977
Dale Zurawski, 1977
Gerald Fraser, 1978
Nancy Kilpatrick, 1978
Rex Skodje, 1978
Eve Zoebisch, 1979
Roger Grev, 1979–80
Alan Magnuson, 1979
Dmitry Altshuller, 1980
Brian Reid, 1980
Tonny Nam, 1981
Keith Runge, 1982
Susan Tucker, 1983–84
Kenneth Dykema, 1984
Paul Rejto, 1985
Beth Sponholtz, 1988
David Maurice, 1989
Gregory Taylor, 1990
Jason Goeppinger, 1991
Dean Briesemeister, 1992–93
Martine Kalke, 1993
Michael Gu, 1994–present
Michael Hack, 1994

Yuri Volobuev, 1994
Andrew Welch, 1994
Zoran Svetlicic, 1995
Steven Clayton, 1996
Molli Noland, 1996

Jason Lang, 1997-98
Joe Danzer, 1997
Darrell Hurt, 1997
Derek Dolney, 1997-98
Mala Radhakrisnan, 1998

Jocelyn Rodgers, 1998-99
Maegan Harris, 1999
Thomas F. Miller III, 1999
Christine Tratz, 1999
Nathan Schultz, 2000

Timothy Sonbuchner, 2000
Amanda Wensman, 2000
Sam Stechman, 2001
Amber Nolan, 2001-2002
Amos Anderson, 2001-2003

Brian Schmitz, 2002
Jill Leas, 2003

Outside Examiner, Ph.D. Theses

John Scott Carley, University of Waterloo (Canada), 1978
Margot Mandy, University of Toronto (Canada), 1991

Outside Reader, Ph.D. Theses

Stephen Malcolm McPhail, University of Sydney (Australia), 1980
Christofer Tautermann, University of Innsbruck (Austria), 2002
Balkrishna P. Shah, University of Baroda (India), 2003
Visiting Collaborators

Mark S. Gordon, 1985-86 (sabbatical)
John Zhang, 1986
Yaakov Shima, 1986
Yici Zhang, 1987

Yan Sun, 1987
Antonio J. C. Varandas, 1987 (sabbatical)
Omar Sharafeddin, 1987
Don Kouri, 1987-88
Rex Skodje, 1988

Kim Baldridge, 1988
Csilla Duneczky, 1988
Jan Linderberg, 1988
Rozeanne Steckler, 1988
Bruce C. Garrett, 1988, 1992, 1994

Brian Sutcliffe, 1990
Christopher Cramer, 1990-91
Ahmed S. Shalabi, 1991
Charles Jackels, 1993-94 (sabbatical)

Jose Corchado, 1994
Jordi Villa, 1995, 1996-97
Steven Bachrach, 1997 (sabbatical)
Brian Williams, 1997 (sabbatical)
Joaquin Espinosa-Garcia, 1997

Laura Masgrau, 1999
Piotr Paneth, 2000-01 (sabbatical)
Przemek Staszewska, 2002-03 (sabbatical), 2004
Joseph Brom, 2002-03 (sabbatical)

John Keith, 2002
Agnieszka Dybala-Defratyka, 2002
Iva Tatic, 2002
Larry Pratt, 2003, 2004
Keith Kuwata, 2003-04 (sabbatical)

Luis Campos, 2003
Clayton Spencer, 2004-present (sabbatical)
Javier Ruiz Pernia, 2004
Presentation Abstracts

Wesley D. Allen, Michael Schuurman, Steven E. Wheeler, Joseph P. Kenny, and Henry F. Schaefer
University of Georgia

In Pursuit of Subchemical Accuracy in Computational Thermochemistry

Several research projects are highlighted involving our continuing pursuit of purely ab initio methods for thermochemical accuracy to the level of 0.1 kcal/mol. Molecular principal and partial wave expansions of problematic systems have been computed for both conventional and R12 correlation methods, with one-particle basis sets extending to $k$ spherical harmonics, thus probing fundamental accuracy limits and demonstrating the superior convergence behavior of explicitly correlated methods. New cusp-satisfying ansätze for pair correlation functions are investigated by means of analytic work on atomic models. The problem of accurately computing connected quadruple excitation effects on bond dissociation energies is demonstrated and elucidated. Improved formulas are discussed for computing anharmonic zero-point vibrational energies from quartic force fields, with application to species as large as the amino acid proline. Finally, chemical applications are reported ranging from soot formation intermediates to proton affinity scales for biomolecules.

Xavier Assfeld
Université Henri Poincaré

How Well Hydrogen Bonds Are Represented in Hybrid QM/MM Methods

Nowadays, most chemical reactions in organic synthesis involve more and more complex reagents to achieve the desired selectivity or stereoselectivity. It is not possible, from the computational resources point of view, to use quantum mechanics (QM) alone to study these reactions due to the large number of atoms engaged. However, hybrid methods combining QM and molecular mechanics (MM) are particularly well suited for this purpose. The reactive center—generally defined with few atoms—is treated with QM and the remaining of the system—most of the time encumbering groups—with MM. Some years ago, we have developed such a method which used strictly localized bond orbital to connect the QM part to the MM one [1], and which is closely related to an other one published recently by Don Truhlar and co-workers [2]. In addition to the role played by the ancillary groups on the reaction mechanism, the solvent has often a very specific and very important influence on the reaction. We recently propose a three layers model that embeds the solute molecule, described at the QM/MM level, in a polarizable continuum used to simulate the solvent [3]. This type of solvent model is similar to the models developed by Don Truhlar and Chris Cramer [4] some years ago. In this model the solvent molecules are implicit. However, explicit solvent molecules are sometimes needed either because they intervene in the reaction coordinate or because they present specific charge transfer interactions that can hardly be represented with a continuum. One could wonder how well these specific interactions are rendered if the solvent molecules are described by quantum or molecular mechanics. In this lecture, we will present a systematic comparison of hydrogen-bonded solute–solvent complexes (here the solvent is water) where the solvent molecule is depicted either with quantum or with molecular mechanics. In this lecture, we will present a systematic comparison of hybrid QM/MM methods (at the MP2/6-311G(2d, 2p):AMBER level of theory): IMOMM [5] and LSCF/MM [1] the latter differing from the former by the polarization of the wave function. The comparison is mainly focused on geometries, charge distributions, and on energies.

References:
Electronic Redistribution in Biomolecules, Including Effects of Environment

The electronic orbital structure of a molecule determines the nature of its internal charge distribution and fluxion, thereby mediating chemical phenomena (e.g. photon absorption/emission or redox activity). The stability of a given molecular charge distribution is affected by its environment, often the polarity or the medium or solvent. Aromatic or π-conjugated molecules display a special sensitivity toward the redistribution of electron density as a function of nuclear position, photonic excitation and polar solvation. As such, several applications from this class of molecules motivate the development of our methods and validate their utility, including: 1) Characteristics of Biological Redox Centers; 2) Curvature dependant electron affinity; 3) Annellation-induced bond localization; 4) Fluorescence and charge-transfer states, and 5) new pharmaceutical targets. This talk will therefore highlight recent efforts in the methodology and theoretical strategies used in these areas, as well as the science discoveries ascertained in a couple of these key areas.

Dynamic Effects in Enzyme Catalysis. The Catechol O-methyltransferase

In the benchmark of the Transition State Theory (TST), the motions of the protein can promote a more efficient catalysis not only by enhancing the transmission coefficient, but also by lowering the free energy barrier. In this communication we are studying both aspects of the enzyme catalysis in a bimolecular reaction, namely a methyl transfer from S-adenosylmethionine (SAM) to the hydroxylate oxygen of a substituted catechol catalyzed by catechol O-methyltransferase.

From QM/MM internal energy optimizations, we will first analyse the participation of the environment on the transition vector. The study of molecular dynamics trajectories will allow us to estimate the transmission coefficient from previously localized TS as the maximum in the PMF profile. The dynamic contributions to catalysis will be discussed from the comparison of the reactive and non-reactive trajectories in the enzyme environment and in solution. Analysis of geometrical and electronic changes through the trajectories, with special attention to the chemical system movements and the coupling with the environment, will be carried out.

The main result is the approximation of the magnesium cation to the nucleophylic and the hydroxyl group of the catecholate as a result of a general movement of the protein, stabilizing in this way the transition state. In consequence, the free energy barrier of the enzyme reaction is dramatically decreased with respect to the reference reaction in solution.

Dynamics of Polyatomic Radical-Molecule and Radical-Radical Reactions From Crossed Beam Reactive Scattering Experiments Using Soft Electron-Impact Ionization: A Challenge for 21st Century Computational Chemical Dynamics

Computational chemical dynamics has played a central role in the development of gas-phase reaction dynamics in a synergistic fashion with (especially) molecular beam and laser-based dynamics experiments. In particular, toward the end of the 20th century, the calculation of “chemically accurate“ potential energy surfaces (PESs) and exact quantum scattering treatments have become possible for simple 3-atom reactions involving H₂, including non-adiabatic effects, and for the 4-atom reaction OH+H₂; in addition, considerable progress, both experimental
and theoretical, has also been made in the treatment of more complex 3-atom and 4-atom reactions. One of the challenges for 21st century computational chemical dynamics is the extension of similar treatments to polyatomic (i.e., > 4 atoms) reactions, characterized by multiple reaction pathways, and possibly involving more than one PES.

The Crossed Molecular Beam (CMB) scattering technique, based on “universal “ electron-impact (EI) ionization mass spectrometric detection, has been central in the investigation of reaction dynamics over the last 35 years and remains the technique most suitable to tackle the dynamics of polyatomic multichannel reactions.1,2 Unfortunately, the “universality “ of the method has been severely limited by the problem of “dissociative “ ionization, which unavoidably occurs under hard (i.e., 60-200 eV) electron impact, typically used in CMB instruments. In fact, ion fragmentation makes very difficult and often prohibits the detection of many reaction products of polyatomic multi-channel reactions, especially involving hydrocarbon molecules. This recently prompted the introduction of the concept of soft (i.e., nondissociative) photo-ionization (PI) by tunable (5-30 eV) VUV synchrotron radiation.3 A variety of photodissociation studies have shown the power of this approach, but very few applications to reactive scattering have been made to date. A shortcoming of this approach is that absolute PI cross sections are often not known and therefore branching ratios cannot be estimated.

In this contribution, I will illustrate a new, simple route to tackle the problem of dissociative ionization. The method, which is analogous to that of soft VUV photo-ionization by synchrotron radiation, relies on soft EI ionization using tunable (7-100 eV) electrons4 and will be illustrated by reference to recent work on some reactions of O(P) and C(P) with unsaturated hydrocarbons (acetylene and ethylene), which are of significance in areas ranging from combustion to astrochemistry. The presentation will demonstrate how, by tuning the electron energy below threshold for dissociative ionization of interfering species, one can often eliminate background signal that would prohibit experiments using hard EI ionization. In particular, because EI ionization cross sections are known or can be estimated, reaction branching ratios can be determined. In addition, information on the ionization energy of radical products with a well-defined internal energy content can be obtained. All this makes soft EI ionization an attractive alternative to soft PI by synchrotron radiation in many practical cases.

For example, by using 17 eV electrons, angular and velocity distributions of HCCO and CH$_2$ radical products from the O(P)+C$_2$H$_2$ reaction were readily measured, with CH$_2$ detected without contribution from interfering signals.4 Similarly, it was possible to detect, among others, the CH$_2$+C$_2$H$_2$ channel from the C(P)+C$_2$H$_4$ reaction, and H+CH$_3$CHO (vinyl), H+CH$_3$CO (acetyl), H$_2$+CH$_2$CO (ketene), HCO (formyl)+CH$_3$ (methyl), and CH$_2$ (methylene)+HCHO (formaldehyde) products from O(P)+C$_2$H$_4$.5 The dynamics of all energetically allowed pathways were characterized and the branching ratios determined. These studies provide an important link between kinetic and dynamical investigations of polyatomic multi-channel reactions. A call is made for the computational modeling of these polyatomic reactive processes of considerable practical relevance.

Finally, recent developments in our laboratory have also made the detailed dynamics of important radical-radical reactions, as those of O, N, and C atoms with alkyl radicals (CH$_3$, C$_2$H$_5$, C$_3$H$_7$, C$_4$H$_9$, etc.) to come within reach of the CMB method. Time permitting, the first direct measurements of product angular and velocity distributions in CMB experiments for a radical-radical reaction will also be discussed.6

References:
Quantum Dynamics Calculations of Rate Constants for Polyatomic Reactions

This lecture will describe a general reduced dimensionality method that combines accurate quantum chemistry calculations of a small number of key points on the potential energy surface with a quantum-dynamical treatment of the bonds being broken and formed in a chemical reaction. Recent applications of the method to the reactions of H atoms with methane, ethane, methanol, and propane will be described. In the latter two cases, branching ratios for different reaction products are also calculated. The results demonstrate significant tunneling in these reactions and the calculated rate constants compare favourably with experiment. These promising results, obtained by Dr. Boutheina Kerkeni in our group, suggest that this will be a general procedure for making accurate predictions on the reaction kinetics and dynamics of larger polyatomic molecules.


New theoretical tools for understanding the angular scattering of chemical reactions are being developed at the University of Manchester. Our research is closely related to, and has been stimulated by, that done by Don Truhlar over many years. The following topics will be discussed:

**Glory analysis of forward angle scattering**

The famous enhanced forward angle scattering in the F + H\(_2\) \rightarrow\) FH(v' = 3) + H reaction has been a puzzle for many years. Recently, I have analysed this scattering and discovered that it is an example of glory scattering.[1] This is also the case for the H + D\(_2\) \rightarrow\) HD(v' = 3) + D reaction. One new approximation derived in Ref. [1] is a uniform semiclassical expression that correctly describes the angular distribution, as the scattering angle changes from zero degrees to larger values.

**LAM-LIP (Local Angular Momentum-Local Impact Parameter) analysis of angular scattering**

This is a technique that uses the exact (or approximate) scattering amplitude to extract a local angular momentum (and a local impact parameter) and their dependence on the scattering angle. A Nearside-Farside (NF) decomposition of the LAM can also be performed. [2] Applications have been made to the F + H\(_2\) and H + D\(_2\) reactions. It is found that a LAM analysis can provide new insights into the reaction dynamics, being more sensitive to interference effects than are the corresponding cross sections. [2]

**Reactive scattering in the time domain.**

The NF LAM theory, combined with a resummation of the partial wave series for the scattering amplitude, has also been used to analyse reactive scattering in the time-domain, which is related to scattering in the energy-domain by a Fourier transform. Application has been made to the H + D\(_2\) reaction in order to understand better the time-direct and time-delayed (by about 25 fs) mechanisms recently discovered for this reaction. Movies illustrating the time-evolution of the reaction will be shown.

References:

---


Christopher J. Cramer and Edward C. Sherer
University of Minnesota

**Mechanism and Dynamics of Methane Metathesis by Group III Metalloccenes**

The dimerization, unimolecular methane ejection, and bimolecular methane metathesis reactions of \(L_2MCH_3\) species where \(L = H, Cl, Cp,\) and \(Cp^*\) and \(M = Sc, Y,\) and Lu have been modeled at the density functional level using a relativistic effective core potential basis set. Results for cases with H or Cl ligands were in poor quantitative agreement with analogous results for cases with \(Cp^*\) ligands; in some instances, \(Cp\) ligands provided results in good agreement with those for \(Cp^*\), but in the case of methane metathesis, activation enthalpies were underestimated by 3 to 4 kcal mol\(^{-1}\) with the unmethylated ligand. Unimolecular methane ejection via formation of a tuck-in complex vs. bimolecular methane metathesis was predicted to be a potentially competitive process for Sc, but to be comparatively too high in energy for Y and Lu to be thermodynamically significant under typical sets of reaction conditions (the difference is ascribable to the shorter metal-ligand distances observed for Sc). For \((Cp^*)_2LuCH_3\), quantum mechanical tunneling was predicted to increase the overall rate of methane metathesis by factors of 4 to 93 over the temperature range 300–400 K. When tunneling was accounted for in the experimentally measured rate constants, a semiclassical activation enthalpy of 19.2 kcal mol\(^{-1}\) was determined for the methane metathesis reaction, in good agreement with a direct prediction from density functional theory of 20.3 kcal mol\(^{-1}\).

M. Dupuis\(^1\) and M. Aida\(^2\)
\(^1\)Pacific Northwest National Laboratory
\(^2\)University of Hiroshima

**Direct ab Initio Dynamics for Reactivity and Vibrational Spectra**

The methodology of direct *ab initio* dynamics using accurate levels of electronic structure theories is a powerful tool for the theoretical characterization of the dynamics of chemical systems. We will highlight two recent studies in which finite temperature simulations point to markedly different chemical reactivity features compared to the mechanisms derived from intrinsic reaction pathway analyses.

The direct dynamics methodology permits also the calculation of vibrational spectra (density of states, IR and Raman intensities) that include the effects of anharmonicities and mode couplings when using quasi-classical initial conditions. Results for spectra calculated for a number of water and water-ion clusters, \((H_2O)_n, (H_2O)_nH^+(n=1,2,3),\) and \((H_2O)X^- (X=F,Cl)\) using the direct dynamics MP2 level of theory will be presented and discussed in the context of experimental spectra recently obtained for these clusters.

MD’s work was supported by the U.S. Department of Energy’s Office of Basic Energy Sciences, Chemical Physics Program. Pacific Northwest National Laboratory is operated by Battelle for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830. MA’s work was supported in part by a Grant-in-Aid for Scientific Research on Priority Areas “Molecular Physical Chemistry “ from the Ministry of Education, Culture, Sports, Science and Technology of Japan, and in part by the Asahi Glass Foundation and by Goho Life Sciences International Fund.
Antonio Fernández-Ramos\textsuperscript{1} and Donald G. Truhlar\textsuperscript{2}
\textsuperscript{1}University of Santiago de Compostela
\textsuperscript{2}University of Minnesota


text_content

B. C. Garrett, S. M. Kathmann, and G. K. Schenter
Pacific Northwest National Laboratory

A Molecular Approach to Homogeneous Gas-to-Particle Nucleation

Nucleation of aerosol particles from gas-phase molecules is an important process in the troposphere because it leads to the formation of new particles, thus increasing aerosol number, and it creates ultrafine (nanoscale) particles. The development of a consistent theoretical framework of nucleation, particularly one that allows treatment of systems composed of multiple gas-phase precursors, has been a persistent challenge. We report on our progress in developing a multicomponent nucleation theory, Dynamical Nucleation Theory, which is based upon a molecular-level approach. In this approach, we use variational transition state theory to evaluate rate constants for cluster evaporation and condensation that are the elementary kinetic steps in the nucleation mechanism.

This work was supported by the Office of Basic Energy Sciences and the Office of Biological and Environmental Research of the U.S. Department of Energy (DOE). Pacific Northwest National Laboratory is operated for the DOE by Battelle.
Dave Giesen  
Kodak  

*MIDI! – The Little Basis Set That Can*  
The MIDI! basis set was developed at the University of Minnesota as a small basis set that would give results comparable to larger basis sets. This basis set has proven quite handy as a tool for every day computation. In contrast to previously existing literature, it will be shown how small basis sets, and particularly MIDI!, can be used for computing accurate 13C NMR shifts. An example will also be given in which the potential energy surface and corresponding 13C NMR shifts computed with MIDI! were used to confirm the crystal structure of a molecule.  

Eric R. A. Johnson and William B. Gleason  
University of Minnesota  

*From Paper Tape to Mag Tape to Cards… Computing Then (the Seventies) and Now at Minnesota*  
(Dedicated to Professor Don Truhlar on the occasion of his 60th birthday.)  
Don Truhlar was a beginning faculty member at Minnesota in the early seventies when WBG was a beginning graduate student. WBG will tell a few stories about Don and give a “worm’s eye view” of computing at Minnesota over the years. It is because of Don that any faculty member, post-doc, or undergraduate, e.g. ERAJ, can get the computing resources they need to initiate new projects.  
Protein/ligand interactions are of continuing interest for drug discovery. A wide variety of docking programs are in use and many pharmaceutical developers have a Linux cluster for in silico screening. But docking programs can also be used for lengthy calculations on single molecules, especially when these have many torsional parameters. We will describe the use of AUTODOCK ((http://www.scripps.edu/pub/olson-web/doc/autodock/) for the docking heparin-like models with biologically relevant targets.  

Systems to be described include fibroblast growth factor (FGF)/sucrose octasulfate (PDB = 1AFC), the antithrombin/heparin complex (PDB = 1AZX), an FGF dimer complexed with a heparin model (PDB = 2AXM), and the 2:2:1 complex of FGF:FGFR:heparin (PDB = 1EO0).  
The Lamarckian genetic algorithm option was used and it seems to be a significant improvement over the alternative simulated annealing procedure. For the antithrombin case an exhaustive run (256 cpu hours) produced excellent results—the top three solutions being within 1.25 Å of the crystal structure. Acceptable solutions can be obtained in four hours on four processors using less exhaustive methods. Acceptable solutions (ca 1 Å) can be obtained for the FGF dimer with heparin in 16 hours on a single cpu. It is possible to get an acceptable solution (ca 1.5 Å rmsd to the crystal structure) for the 1EO0 complex in about a week on four processors.  
The current version of AUTODOCK uses a rigid protein model—in some cases undesirable. Thus, work directed at using AUTODOCK results for input into molecular dynamics simulations will be briefly described as well as general methods for producing pdb coordinates of complex heparin structures.  

William A. Goddard, III  
California Institute of Technology  

*Strategies for de Novo Multi-Scale Simulations and Applications to Materials, Catalysis, Protein Folding, and Nanotechnology*  
Advances in theoretical and computational chemistry are making it practical to consider fully first principles (*de novo*) predictions of important systems and processes in the Chemical, Biological, and Materials Sciences. Quantitative models based on theory and computation are starting to become the basis for design and operations
in industry, but the most important applications require strategies for linking the time scales from electrons to macroscale.

We will highlight some recent advances in methodology and will illustrate them with recent applications to problems involving Materials, Catalysis, Protein Folding, and Nanotechnology selected from

- First principles protein folding for 3D structures of G Protein Coupled Receptors (GPCRs)
- Predictions on drugs for GPCRs (receptors for dopamine, epinepherin, lipids)
- Nanoelectronic switches, self-assembled monolayers and switching performance
- Domain switching in BaTiO$_3$ ferroelectrics
- Nafion and new membranes for PEM-FC, electrocatalysis and proton transport
- Reversible high capacity H$_2$ storage for transportation fuel cells
- *De novo* Force Fields (from QM) to describe reactions and phase transitions (ReaxFF)

**Angels González-Lafont**, Miquel Moreno and José M. Lluch
Universitat Autònoma de Barcelona

**Variational Transition State Theory as a Tool to Determine Kinetic Selectivity in Reactions Involving a Valley-Ridge Inflection Point**

Variational transition state theory has been used to calculate the kinetic isotope effects affecting product ratios in the reaction between $^{16}$O$_2$ and $^{d_6}$-tetramethylethylene. The minimum energy path on the potential energy surface for this process reaches a valley-ridge inflection point and then bifurcates leading to the two final products. Using canonical variational transition state theory, two distinct dynamical bottlenecks were located corresponding to the H- and the D-abstraction, respectively. The calculated KIE at 263 K turns out to be 1.126. Analogously, a H/T KIE of 1.17 at the same temperature has been found for the reaction of $^{16}$O$_2$ with the tritiated derivative of tetramethylethylene.

**Mark S. Gordon**
Iowa State University and Ames Laboratory

**An Embedded Cluster Approach to Surface Chemistry**

The chemistry that occurs on surfaces is central to phenomena such as hetergoeneous catalysis and the preparation of new devices for a variety of applications. The embedded cluster model SIMOMM (surface integrated molecular orbital molecular mechanics) method will be introduced. This will be followed by a discussion of applications of the method to reactions on the Si(100) surface.

**Odd Gropen**
University of Tromsø

**Relativistic Quantum Mechanical Methods in Molecular Calculations. Theory and Applications**

During the last decade elements heavier than the second row transition metals have become readily accessible for theoretical studies due to the development of relativistic methods [1]. At the spin-free level, i.e. when spin-orbit interactions are neglected, calculations using relativistic ECP:s on complexes involving the third row transition elements are common [2]. It is also possible, but less frequent, to make spin-free *ab initio* calculations using the no-pair approximation, one component equations obtained after transformation of the Dirac equation [3].

Concerning the spin-orbit effect, it is fairly well known how to calculate it, and this may be done at the two-component level by the no-pair form of the Hamiltonian or by solving the four-component Dirac equation.
Over the last fifteen years we have emphasized on the development of methods for systems containing heavy elements with the ultimate goal to study catalyses. We have developed methods for doing Relativistic Effective Core Potentials, one component Douglas-Kroll method, two component Douglas-Kroll Spin-Orbit method[4] and relativistic four component methods [5].

Theory and results from several applications are presented [6].

References:

Shuqiang Niu, Lisa Thomson, Shuhua Li, Zexing Cao, Hua-Jun Fan, Yubo Fan, Alejandro Pardo, and
Michael B. Hall
Texas A&M University

**Modeling Metalloenzymes: Nickel-Iron and Iron-Only Hydrogenases**

The catalytic cycles for \( \text{H}_2 \) oxidation in [NiFe] and [Fe-only] hydrogenases have been investigated through density functional theory (DFT) for a wide variety of redox and protonated structures of the active site models, \((\text{CO})(\text{CN})_2\text{Fe}(\mu-\text{SMe})_2\text{Ni(SMe)}_2\) and \((\text{L})(\text{CO})(\text{CN})\text{Fe}(\mu-\text{SCH}_2)_2\text{X}(\mu-\text{CO})\text{Fe(CO)(CN)}(\text{SMe})\), respectively. By combining a calibration curve for the calculated CO bond distances and frequencies and the measured IR stretching frequencies from related complexes with the DFT calculations on the [NiFe] model, the redox states and structures of the active site are predicted. Dihydrogen activation on the Fe(II)-Ni(III) species is more favorable than on the corresponding Ni(II) or Ni(I) species. Our final proposed structures are consistent with IR, EPR, and ENDOR measurements and the correlation coefficient between the measured CO frequency in the enzyme and the CO distance/frequency calculated for the model species is excellent. The unconstrained optimized geometries for high-spin Ni(II) species and for the Ni(III) species involved in the \( \text{H}_2 \)-cleavage reaction, especially the transition state, show remarkable structural resemblance to the active site in the enzyme crystal structure. For the [Fe-only] modeling, full frequency calculations on models for the active site and for well-characterized complexes show that observed and catalytically active redox species in the enzyme must correspond to Fe(II)-Fe(II), Fe(II)-Fe(I), and Fe(I)-Fe(I). Furthermore, when \( X \) is NH rather than CH\(_2\), a single Fe and this N create a very favorable thermodynamic path for the heterolytic cleavage of \( \text{H}_2 \). The \( \text{H}_2 \)-cleaved species shows an unusually short “dihydrogen bond “, \( \text{Fe—H} - - - - \text{H—N} \).

William L. Hase
Texas Tech University

**Role of Computational Chemistry in the Development of Unimolecular Rate Theory**

Initiated by the pioneering work of Don Bunker, computational chemistry has had a profound contribution to the development of unimolecular rate theory. Computer simulations have related the intramolecular dynamics and lifetimes of highly vibrationally excited molecules to properties of potential energy surfaces, and have characterized intrinsic and apparent non-RRKM behavior and their relationships to experimental studies. The computations have shown how intrinsic non-RRKM dynamics arises from specific phase space structures and
dynamics, e.g. quasiperiodic trajectories. Most recently, large-scale quantum dynamical calculations of unimolecular resonances by Schinke and co-workers have provided fundamental comparisons with RRKM theory, whose roots are in classical not quantum mechanics. This work, as well as that of others, has provided insight into the ability to observe “steps “ in unimolecular rate constants. Recent direct dynamics simulations have given a direct link between electronic structure theory and unimolecular dynamics, and a deeper understanding has resulted in the relationship between potential energy surface properties and non-RRKM dynamics.

James T. Hynes\textsuperscript{1,2}, Irene Burghardt\textsuperscript{1} and Lenz Cederbaum\textsuperscript{3}
\textsuperscript{1}Ecole Normale Superieure
\textsuperscript{2}University of Colorado
\textsuperscript{3}Universität Heidelberg

Excited Electronic State Charge Transfer at a Conical Intersection: Effects of an Environment

Excited electronic state processes at conical intersections (CIs) have received intense scrutiny in photochemical experiment and theory in recent years. CIs often provide a “funnel “ for passage from a photochemically accessed S1 state to the ground state S0, governing nonadiabatic transition rates; they have been referred to as “transition states “ for photochemical processes.

Recent experiments on, for example, photoactive proteins highlight the pronounced influence of a solvent or protein environment on CI dynamics. S1-S0 population transfer can be substantially modified, suggesting major changes in the underlying CI topology. A central theoretical challenge is to select and describe the relevant features governing the complex chromophore-environment supermolecular systems.

The present contribution focuses on excited electronic state processes at CIs where a charge transfer is involved. We describe the key features of a theoretical formulation recently developed to describe the chromophore-environment interaction and its consequences. This generalizes considerably an early important treatment by Bonacic-Koutecky, Koutecky, and Michl to include important molecular coordinates, e.g. isomerization twisting motions, and the polar/polarizable environment’s influence. The environment’s electrostatic effects are accounted for by a dielectric continuum model. Applications to a model for the S1-S0 CI in protonated Schiff bases provide a free energy surfaces description for the coupled system represented by molecular coordinates (e.g. twisting and bond stretching/contracting) plus a solvent coordinate. The environment’s significant impact on the CI is investigated, as are “reaction paths “ leading to and through the CI. Nonequilibrium “solvation “ effects are shown to be critical.

William L. Jorgensen
Yale University

Computational Studies of Organic and Enzymatic Reactions

Combined quantum mechanics and Monte Carlo statistical mechanics simulations are being used to study reaction mechanisms and the origin of solvent effects on reaction rates. The calculations have been highly automated with the BOSS program; complete free-energy profiles with full sampling of solute and solvent coordinates can be obtained through one job submission. The reacting systems are represented using semiempirical PDDG/PM3 calculations and the environment is described by the OPLS-AA force field and TIP4P water model. Illustrative results will be presented for prototypical organic reactions including S\textsubscript{N}2, S\textsubscript{N}Ar, Menshutkin, and Diels-Alder reactions, and Cope and Kemp eliminations, as well as enzymatic reactions catalyzed by chorismate mutase and macrophomate synthase.

References:
\textit{J. Am. Chem. Soc.} 2003, 125, 6663, 6892
Hyung J. Kim  
Carnegie Mellon University

**Menshutkin Reactions in Quadrupolar Solvents**

A reaction field theory to account for solvent quadrupole moments in solvation is presented. As an illustration of the theory, Menshutkin reactions in benzene are studied. The results for their reaction rates under equilibrium solvation conditions are compared with those in nonpolar cyclohexane and highly dipolar acetonitrile. Also brief comparison is made with experiments.

Lin Wang, Nitish Agrawal, Baoyu Hong, and **Amnon Kohen**  
University of Iowa

**H-Tunneling, Coupled Motion, and Environmentally Coupled H-Transfer in Enzymatic Reactions**

Theoretical studies commonly address only events that are close to the H-transfer transition state, while for most experimental data that step is only one component in a complex kinetic expression. Our studies are directly aimed at exposing that step and comparing the experimental and theoretical results. Dihydrofolate reductase (DHFR) and thymidylate synthase (TS) from *E. coli* were examined using isotopically labeled cofactors (H, D, and T). 1º and 2º Kinetic isotope effects (KIEs) were measured and the intrinsic KIEs and their temperature dependency were examined. The experimental findings with DHFR at 25º C are in excellent agreement with QM/MM calculations by Truhlar and by Hammes-Schiffer. All Arrhenius preexponential factors were above the semiclassical range, which indicates a contribution of quantum mechanical H-tunneling to reactions¹ rate. Initial velocity experiments over the same temperature range enabled calculations of activation parameters. Energies of activation for both enzymes were small, but significant, which indicated probable contribution of ³environmentally coupled tunneling² to reactions¹ rate. The ability to study the nature of the chemical transformation in these kinetically complex enzymatic cascades result in data that are directly comparable to simulation and shaded a new light on the use of the Swain-Schaad relationship and 2º KIEs in determining the location and nature of the transition sate.

Donald J. Kouri  
University of Houston

**Distributed Approximating Functionals, Discretizing Derivatives, and Heisenberg’s Uncertainty Principle: Nature’s Wavelets**

An overview of the distributed approximating functionals and their use in computations of various types will be presented. Their relation to the Heisenberg uncertainty principle will be briefly discussed, along with their properties as “little waves “ (wavelets).

Aron Kuppermann  
California Institute of Technology

**Hyperspherical Harmonics in Quantum Reactive Scattering**

In performing quantum reactive scattering calculations by solving the time-independent Schrödinger equation, row-orthonormal hyperspherical coordinates are used for the strong interaction region of configuration space. A very important property of these coordinates is that they sample configuration space democratically, permitting any pair of reaction products to be described without bias. They include a hyperradius $\rho$ and five (for triatomic systems) or eight (for tetraatomic systems) hyperangles. A difficulty resulting from this choice of coordinates is that the corresponding kinetic energy operator $\hat{T}$ and the associated grand canonical angular momentum operator $\hat{\Lambda}^2$ have poles for configurations of the system for which any two of its three principal moments of inertia are
equal. Hyperspherical harmonics are defined as simultaneous eigenfunctions of $\hat{\Lambda}^2$ (having quantum number $n$) and a set of additional operators, including the square $\hat{j}^2$ of the total angular momentum operator $\hat{j}$ and its space-fixed $z$ axis component. These harmonics behave regularly at those poles. If they could be determined analytically, they would constitute an excellent basis set for performing accurate \textit{ab initio} scattering calculations. For triatomic and tetraatomic reactions, however, hyperspherical harmonics for values of $n$ up to 30, 40 or more are required. For triatomic systems, their number, for $n=40$, is about 2.3 million and for tetraatomic systems and $n=30$, about 43.8 million. In order to cope with these large numbers, computer algebra programs were developed and used to determine all of these harmonics analytically. In addition, for the weak interaction region of configuration space, Delves hyperspherical coordinates are used and the corresponding harmonics have been derived. The methods used to obtain these functions will be described, and their properties discussed, as well as the formalism for using them in scattering calculations.

References

Yuzuru Kurosaki
Japan Atomic Energy Research Institute

\textit{Potential Energy Surfaces and Thermal Rate Constants for the BrH$_2$ System}

Reactions of triatomic systems have been the subjects of great importance in the study of chemical reaction dynamics. In particular, the triatomic H$_3$ and FH$_2$ systems have served as the stringent tests for newly developed theoretical methods since the results of the theoretical calculations using the high-quality potential energy surfaces (PESs) can be compared with plenty of available experimental data for these reactions. However, other triatomic reactions including heavier atoms have not been fully examined theoretically since it is computationally demanding to obtain high-quality PESs for these systems. In the present study we focus on the abstraction reaction of the BrH$_2$ system and calculate its PESs and rate constants.

PESs for the lowest three doublet states ($1^2A'$, $2^2A'$, and $1^2A''$) for the BrH$_2$ system have been calculated using the internally contracted MRCI method with the aug-cc-pVTZ basis set. The spin-orbit coupling effects were considered on the basis of approximate Breit-Pauli Hamiltonian. The calculated energies were fitted to the analytical function of polynomial expansion. Thermal rate constants were calculated for the $\text{H} + \text{HBr} \rightarrow \text{H}_2 + \text{Br}$ abstraction reaction and its isotopic variants on the ground ($12A'$) state PES using the improved canonical variational transition state theory (ICVT) with the least-action adiabatic ground-state (LAG) approximation.

The barrier height of the fitted $12A'$ state potential for the abstraction was 1.17 kcal mol$^{-1}$. The value obtained at the MRCI/aug-cc-pVTZ level was 1.28 kcal mol$^{-1}$; therefore, the fitting was done within the accuracy of ~ 0.1 kcal mol$^{-1}$ in the barrier region. The theoretical and experimental rate constants for the abstraction reaction and its isotopic variants are compared in Table 1. It is seen that the calculated rate constants reported by Lynch et al. are slightly smaller than the experimental values for all the listed reactions, while the present results are a bit larger than them except for the Mu substituted reaction. This suggests that the barrier height of Lynch et al. (1.9 kcal mol$^{-1}$) is still higher than the true value and that of the present work is lower. Note, however, that the present calculations have shown that there is a relatively deep van der Waals well of ~ 0.7 kcal mol$^{-1}$ in the long-range interaction region of H + HBr. It is therefore possible that the measured rate constants are contributed from the trajectories starting from the vibrational levels supported in the van der Waals well. If this is the case, then it is not at all surprising that the present calculated rate constants are slightly larger than experiment because in calculation the potential energy only above the H + HBr asymptotic energy is considered. As for the Mu substituted reaction the present calculated values are still considerably lower than experiment. This implies that
more quantitative comparison between theory and experiment needs more accurate theoretical methods such as those based on three dimensional quantum dynamics calculations.

Table 1. Theoretical (ICVT/LAG) and experimental rate constants for the abstraction reaction

<table>
<thead>
<tr>
<th>$T$(K)</th>
<th>Lynch</th>
<th>This work</th>
<th>Expt.</th>
<th>$T$(K)</th>
<th>Lynch</th>
<th>This work</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>258</td>
<td>3.42</td>
<td>8.51</td>
<td>4.87</td>
<td>250</td>
<td>0.71</td>
<td>3.24</td>
<td>1.9</td>
</tr>
<tr>
<td>300</td>
<td>4.48</td>
<td>10.73</td>
<td>6.00</td>
<td>300</td>
<td>1.18</td>
<td>4.66</td>
<td>2.70</td>
</tr>
<tr>
<td>250</td>
<td>1.12</td>
<td>5.06</td>
<td>3.20</td>
<td>159</td>
<td>13.6</td>
<td>8.81</td>
<td>10.8</td>
</tr>
<tr>
<td>300</td>
<td>1.79</td>
<td>6.99</td>
<td>4.10</td>
<td>240</td>
<td>14.2</td>
<td>12.14</td>
<td>16.5</td>
</tr>
<tr>
<td>250</td>
<td>1.07</td>
<td>4.67</td>
<td>3.20</td>
<td>376</td>
<td>16.0</td>
<td>17.43</td>
<td>23.0</td>
</tr>
<tr>
<td>300</td>
<td>1.67</td>
<td>6.46</td>
<td>4.70</td>
<td>419</td>
<td>16.8</td>
<td>19.01</td>
<td>28.3</td>
</tr>
</tbody>
</table>

References:

Jiabo Li¹, Brian Duke² and Roy McWeeny³
¹SciNet Technologies
²Charles Darwin University
³University of Pisa

A General Implementation of the Group Function Theory in an ab Initio Valence Bond Program and the Application to a $S_{N}2$ Reaction

Group Function Theory (GFT) provides a solid mathematical foundation of quantum mechanical description of chemical building blocks, yet its most general implementation has not been seen until very recently. This paper presents a general algorithm for obtaining the optimized GFT wave functions. According to GFT, a molecule system can be divided into chemically sensible groups, the system wave function can be expressed as a generalized production of all group functions, and each group can be treated at a level of a user’s choice (HF, VBSCF, VBCI or CASVB). The algorithm has been implemented in VB2000, an efficient $ab$ initio Valence Bond (VB) program based on algebrant algorithm. The combination of GFT and a highly efficient VB method provides a unique and versatile tool for high quality correlated wave functions of large systems while keep the simplicity and compactness of VB wave functions. As an example of application of GFT/VB method, the $S_{N}2$ identity reaction $\text{Cl}^- + \text{CH}_3\text{Cl} \rightarrow \text{ClCH}_3 + \text{Cl}^-$ has been studied. The system has been divided into three groups, and two of them are described by CASVB (the MO-based counterpart is CASSCF), and can be denoted as CASVB(8,5)•CASVB(6,6)/6-31G* level. The changes of VB structure weights alone the reaction path is also shown.

Gillian Lynch
University of Houston

Solvent Structure Studies as a Function of Concentration

The structure of liquid water at the surface interface continues to be a heavily debated issue in liquid state modeling. For biological systems the solvent structure inside and around the macromolecule is considered important in both structure and binding. This work provides a methodical study of solvent structure as a function of concentration for three systems that mimic both hydrophobic and hydrophilic surfaces. Molecular dynamics simulations will be performed for the three systems with the same all-atom force field, in the same size box, and
with the same number of sodium/chloride ion pairs. Results of the solvent structure around these three model systems as a function of the various concentrations will be presented.

Francisco Torrico, José M. Martínez, Rafael R. Pappalardo and Enrique Sánchez Marcos
Universidad de Sevilla

**Defining the Hydration Structure of Metal Aquaions Exhibiting Anisotropic Solvent Environments: The Pd$^{2+}$ and UO$_2^{2+}$ Cases**

Ion solvation of metal cations has usually been rationalized on the basis of concentric shell models, roughly assuming that the spherical shape of the metal cation determines an interaction field where successive shells of water molecules, called first-, second-hydration shell, and so on were only a function of the distance to the central cation. This work examines the salvation structure when hydrates formed by a cation and a set of water molecules define a very stable planar aquaion. The study addresses the question of how is the structure adopted by water solvent in the regions above and below the molecular plane.

The statistical simulation of highly charged metal cations involves the development of nonempirical intermolecular potentials which are strongly affected by the presence of large manybody contributions. Our group proposed a strategy to deal with this problem, based on the use of the hydrated ion concept. The model is based on the assumption that the charged species interacting in solution is the hydrate, so that the ion-water potential to be built corresponds to the interaction between [M(H$_2$O)$_n$]$^{m+}$ and a water molecule (HIW potential).[1] Improvements related to the flexibility of the hydrate were added to account for the internal dynamics of the first hydration shell (IW1, Ion-Water 1st-shell).[2] Properties of a significant number of ionic solutions derived from classical computer simulations (Montecarlo and Molecular Dynamics) have shown a posteriori the validity of this strategy.[3]

The first application is centered on the case of Pd$^{2+}$ in water.[3] This metal cation forms a square-planar complexes ([Pd(H$_2$O)$_4$]$^{2+}$) in aqueous solution. Structural, dynamic and spectroscopic properties of the ionic solutions are evaluated by means of classical Molecular Dynamics simulations. Water molecules occupying axial regions with respect to the square molecular plane are characterized by a set of structural and dynamic properties which can not be identified neither with those of the first shell nor the second shell. The main conclusion derived from this study is the unambiguous definition of an intermediate solvation region that we propose to be called meso-shell. This could help in the understanding of the peculiar characteristics of square planar complexes of transition metal cations (Pt$^{2+}$, Cu$^{2+}$) such as their particular facility to be incorporated in complex biomolecules or inter-layered solid structures.

The second application presents the extension of this approach to the case of the molecular cation of the uranium, the uranyl. This cation forms an stable pentahydrate in aqueous solutions, thus we have built the interaction potential of [UO$_5$(H$_2$O)$_5$]$^{2+}$-H$_2$O for the HIW. In order to describe the flexible nature of the uranyl cation itself, an Intra Molecular Cation (IMC) potential has been developed. The hydration structure of the axial regions, i.e. the close environment of the oxygen atoms of the UO$_2^{2+}$ cation, shows noticeable difference with the previously defined meso-shell for the square-planar Pd$^{2+}$ aquaion, as well as with the most common hydration structure of octahedral hydrated ions, such as Cr$^{3+}$, Al$^{3+}$ or Mg$^{2+}$. Generalization of this combination of intermolecular potentials to other actinyls such as NpO$_2^{2+}$, PuO$_2^{2+}$, AmO$_2^{2+}$ is proposed.

References:
L. Masgrau¹, K. Ranaghan², L.O. Johannissen¹, N.S. Scrutton¹, A.J. Mulholland² and M.J. Sutcliffe¹
¹University of Leicester
²University of Bristol

VTST/MT Kinetic Isotope Effects for the Proton Transfer Catalyzed by AADH

Variational transition state theory with multidimensional tunneling corrections (VTST/MT) has proved to be a very useful tool for the calculation of rate constants, both in the gas-phase and condensed-phase.[1] In the last years, VTST/MT has also been applied to the study of enzyme-substrate reactions.[2] Within them, especial attention have received the reactions involving hydrogen/proton/hydride transfer due to the potential role of H-tunneling and thus, the importance of calculating tunneling transmission coefficients.

It has been shown that among the different factors affecting the proton transfer reaction in some enzyme active sites there is hydrogen tunneling. The inclusion of this quantum mechanical effect in the calculation of kinetic magnitudes, such as kinetic isotope effects (KIEs), has been necessary to reproduce the experimental data for some systems. This is the case for methylamine dehydrogenase (MADH), which catalyzes a reaction involving a rate-limiting proton transfer (C-H bond breakage) with an experimental KIE of 16.8±0.5 (for its substrate methylamine), that has been shown to be associated with proton tunneling.[3-5]

In this poster we focus on aromatic amine dehydrogenase (AADH) with its substrate tryptamine, for which an even larger KIE (54.7±1.0) has been measured. The presented results give a first insight into this proton transfer at the molecular level. Both quantum mechanical/molecular mechanical umbrella sampling molecular dynamics and VTST/MT calculations have been carried out. Our best estimation for the KIE (52.3) is in good agreement with the experimental value and only obtained when tunneling is taken into account.

References:

C. Alden Mead
University of Minnesota

Projection Operator Formalism for Parallel Transport and Distant Parallelism for Two-Dimensional Electronic Subspaces, Including Kramers Doublets

The Ryb-Baer formalism for calculating geometric phases is recast in terms of projection operators, and used to generate geometric phases for transport of two-dimensional subspaces in general, and Kramers doublets in particular, around closed paths. A similar projection formalism is used to define distant parallelism in a way equivalent to the block diagonalization technique of Cederbaum, Shirmer, and Meyer. With the aid of this formalism, geometric vector potentials and nonsingular nonadiabatic coupling terms can be calculated. There is some discussion from a theoretical point of view of the applicability of a modified Born-Oppenheimer approximation, in which the singular part of the nonadiabatic coupling is transformed away, and the nonsingular part ignored.
A QM/MM Study of the Rate Limiting Step in the Formate Dehydrogenase

A comparative theoretical study of the hydride transfer reaction between formate anion and nicotinamide adenine dinucleotide (NAD+) in aqueous solution and catalyzed by the enzyme in formate dehydrogenase (FDH) has been carried out by a combination of two hybrid QM/MM techniques: statistical simulation methods and internal energy minimizations. We have located and characterized transition structures for the reaction in the enzyme active site, in water and in vacuum, and our potential of mean force calculations are based upon reaction coordinates obtained from features of the potential energy surfaces in the condensed media. The enzyme compresses the substrate and the cofactor into a conformation close to the transition structure, thus facilitating the hydride transfer.

Analysis of the electric field along the reaction coordinate demonstrates that in water the TS is destabilized with respect to the MC-like species because the polarity of the solute diminishes and consequently the reaction field, which is created as a response to the change in the solute polarity, is also decreased. In the enzyme the electric field is mainly a permanent field and consequently there is only a small reorganization of the environment. Therefore stabilization of the TS is greater in the enzyme than in solution thus diminishing the activation barrier.

Finally, a good agreement between experimental and QM/MM primary kinetic isotope effects is found.

Kazuhiro Sakimoto¹ and Kunizo Onda²
¹Institute of Space and Astronautical Science, Yoshinodai, Japan
²Tokyo University of Science

Full Quantum-Mechanical Study of Collision-Induced Dissociation in Three-Dimensional Non-Reactive He + H₂ Collision

A full quantum-mechanical wave-packet method[1] is applied to study dissociation processes in three-dimensional non-reactive He + H₂ collision.

We describe the collision system in Jacobi coordinates R and r, which denote the position vector of He from the center-of-mass of H₂ and the internuclear relative position vector of H₂, respectively. We employ a body-fixed (BF) frame in which the z axis is chosen along R. The rotation from a space-fixed (SF) frame to the BF frame is specified by the three Euler angles (α, β, γ), where R = (α, β), and γ is the azimuthal angle of r in the SF frame. The frame transformation is represented by the parity-adapted Wigner’s rotation matrix element $D^J_M_{\lambda}(\alpha,\beta,\gamma)$, where J, M, and λ are the total angular momentum quantum number, its magnetic component in the SF frame, and the one in the BF frame, respectively, and p is the parity (=±) of the total system. Since the potential energy surface of He + H₂, $V(R, r, \theta)$, depends only on three coordinates $R = |R|$, $r = |r|$, and $\theta$, the collision dynamics is completely described by these three variables. Here $\theta$ is the polar angle of r in the BF frame.
The time-dependent Schrödinger equation is rigorously solved by employing a wavepacket and a discrete variable representation (DVR\(^3\), methods. We choose a set of grid-based functions \(\phi_K(R), u_\mu(r),\) and \(v_\nu(\theta),\) which are constructed from orthogonal polynomials\(^4,5\) associated with grid (quadrature) points, \(R_K (K = 0, 1, \ldots, N_R), r_\mu(\mu = 0, 1, \ldots, N_r),\) and \(\theta_\nu (\nu = 1, 2, \ldots, N_\theta),\) respectively. A set of coupled linear equations with respect to the wave packet given on the DVR grid points \((R_K, r_\mu, \theta_\nu)\) is the one of initial value problems, and is efficiently solved by using the fourth-order Runge-Kutta algorithm.

Calculations are carried out for the initial state \((\nu, j) = (0, 0)\) of \(\text{H}_2\) at the total energy \(1 \leq E_{\text{tot}} \leq 10\) eV. Here, the energy is measured from the bottom of the \(\text{H}_2\) potential energy curve. Numerical results are compared with the one obtained by the semiclassical study, \([6]\), and the details will be presented at the meeting.

References:

Yuan-Ping Pang
Mayo Clinic College of Medicine

3D Model of a Substrate-Bound SARS Chymotrypsin-Like Cysteine Proteinase Predicted by Multiple Molecular Dynamics Simulations: Catalytic Efficiency Regulated by Substrate Binding

Severe acute respiratory syndrome (SARS) is a contagious and deadly disease caused by a new coronavirus. The protein sequence of the chymotrypsin-like cysteine proteinase (CCP) responsible for SARS viral replication has been identified as a target for developing anti-SARS drugs. Here, I report the ATVRLQ\(^{pl}\)A\(^{pl1}\)-bound CCP 3D model predicted by 420 different molecular dynamics simulations (2.0 ns for each simulation with a 1.0-fs time step). This theoretical model was released at the Protein Data Bank (PDB; code: 1P76) before the release of the first X-ray structure of CCP (PDB code: 1Q2W). In contrast to the catalytic dyad observed in X-ray structures of CCP and other coronavirus cysteine proteinases, a catalytic triad comprising Asp187, His41, and Cys145 is found in the theoretical model of the substrate-bound CCP. The simulations of the CCP complex suggest that substrate binding leads to the displacement of a water molecule entrapped by Asp187 and His41, thus converting the dyad to a more efficient catalytic triad. The CCP complex structure has an expanded active-site pocket that is useful for anti-SARS drug design. In addition, this work demonstrates that the SWISSMODEL-based homology modeling followed by a refinement with multiple molecular dynamics simulations is able to generate the 3D structure of the substrate-bound CCP from its amino acid sequence with a root-mean-square deviation of 1.89 Å for all heavy atoms of the protein relative to the corresponding X-ray structure. This work was supported by DARPA, ARO, USAMRAA, NIH/NIAID, HPCMO, SDSC, MSI, and Compaq.

John C. Polanyi
University of Toronto

Molecular Dynamics of Surface Reaction, Followed a Molecule at a Time by STM

Experiments will be described in which light, low-energy electrons or heat have been used to induce reactions between sub-monolayers of adsorbed halides and silicon substrates. The molecular reaction dynamics were inferred in some detail from the STM images. Reagents were halobenzenes and both short and long-chain halides.
The molecules were observed to self-assemble and to undergo localized reaction with the substrate. These findings have been modeled by quantum mechanics; the results will be described.

The experiments were performed by Duncan Rogers, Harikumar Rajamma, Sergey Dobrin, Xuekun Lu, Jody Yang, Rhys Jones, Zafar Waqar and Iain McNab, and the theory by Fedor Y. Naumkin, Chérif Matta, Ioannis Petsalakis and Giannoula Theodorakopoulos, all at the University of Toronto.

Sachchida N. Rai1, Heinz-Peter Liebermann2, Robert J. Buenker2, Mineo Kimura3, H. Suno4, R. K. Janev5, Reiko Suzuki6, and Lukaš Pichl7
1North-Eastern Hill University, India
2Bergische-Universitaet-Gesamthochschule, Germany
3Kyushu University, Japan
4Yamaguchi University and National Institute of Fusion Science, Japan
5National Institute of Fusion Science, Japan, and Macedonian Academy of Sciences and Arts, Macedonia
6Hitotsubashi University, Japan
7Aizu University, Japan

Recent Studies on Elastic and Inelastic Processes During Collisions of Protons With Hydrocarbons

A brief review of our recent theoretical studies on electron capture and direct elastic scattering in collisions of protons with key hydrocarbons are presented. A molecular representation is adopted within a fully quantum-mechanical approach. Different approaches of the proton toward the target molecule are considered. The results of our calculations of the differential cross sections for elastic scattering and electron capture during H+ + C2H4 collisions below 10-keV and H+ + CH2 collisions at 0.5 keV and 1.5 keV are presented and analyzed.

Alessandro Troisi, Abraham Nitzan, Michael Galperin, and Mark A. Ratner
Northwestern University

Molecular Transport Junctions: Inelastic and Switching Effects

Electrical conduction through molecular wires, both in single-molecule junctions and in adlayers, can include broad mechanistic variation. In this presentation, we will focus on the effects of vibrational coupling, inelasticity, hysteresis, intramolecular isomerization and stochastic switching.

The calculations will be based on a non-equilibrium Green’s function approach, combined with appropriate modeling for the electronic Hamiltonian. In particular, to get an appropriately correct answer it is required to deal with full self-consistency in the electron and vibrational Green’s functions — such consistency can be straightforwardly obtained within the Keldysh approach.

Orlando Roberto-Neto1, Fernando R. Ornellas2, and Francisco B. C. Machado3
1Instituto de Estudos Avançados, Centro Técnico Aeroespacial
2Universidade de São Paulo
3Instituto Tecnológico de Aeronáutica, Centro Técnico Aeroespacial

Dual-Level Direct Dynamics Calculations of the Kinetic Isotope Effects for the CH4 + F → CH3 + HF Abstraction Reaction

Kinetic isotope effects (KIEs) for hydrogen abstraction from the isotopomers CH4, 13CH4, and CD4 by fluorine atoms have been studied by the variational transition state theory with multidimensional tunneling contributions (VTST/MT). Low-level calculations of the potential surface were carried out within the AM1-SRP approach. High-level structural and energetic properties of the reactants, transition state, and products were obtained with
the MP2 and CCSD(T) theories and the cc-pVQZ basis set, and were used to interpolate corrections to the low-
level calculations. The values of the classical barrier height (ΔV*) and the energy of reaction (ΔE), which are
employed as high-level energetic parameters, are set equal to 1.8 kcal/mol and 28.5 kcal/mol, respectively. The
chemical dynamics results show that large-curvature tunneling (LCT) paths provide the dominant contribution,
with significant participation of excited vibrational states. At the CVT/μOMT level, the calculated value of H/D
KIE is equal to 1.74 at 298 K, which is in very close agreement with experiment (1.4—1.7). The 12C/13C KIE is
calculated to have a very small variation in the temperature range of 200 to 2000 K. CVT/μOMT activation
energies at the temperature ranges of 200—300 K and 200—400 K are equal to 0.59 and 0.73 kcal/mol,
respectively, which are comparable to the experimental values of 0.43 and 0.53 kcal/mol.

Laimutis Bytautas and Klaus Ruedenberg
Iowa State University

Efficient High-Accuracy CI Calculations of Binding Energies Through Controlled Correlation Energy
Extrapolation by Intrinsic Scaling

Remarkably accurate scaling relations have been shown to exist between the correlation energy contributions
from various excitation levels of the variational configuration interaction approach, considered as functions of the
size of the correlating orbital space. These relationships have been used to develop a new method for
extrapolating sequences of smaller CI calculations to the full CI energy. Applications to the ground states of the
systems Ne, F₂, O₂, N₂, C₂, H₂O with cc-pVTZ and cc-pVQZ basis sets have demonstrated the ability of this
approach method to yield benchmark quality results with comparatively moderate computational efforts. The
method is called “Controlled Extrapolation by Intrinsic Scaling “. Further extrapolations to the complete basis set
limits have recovered the binding energies of F₂, O₂, N₂, C₂ with an accuracy of 0.3 kcal/mole or better. The
information gained in the context of this extrapolation process has moreover been used to truncate full
configurational expansions without compromising their chemical accuracy. This deletion of configurational
deadwood is accomplished by judiciously limiting the participation of the ranges of predetermined approximate
sets of natural orbitals in the various excitation categories.

James R. Rustad¹, Kevin M. Rosso², and Andrew R. Felmy²
¹University of California, Davis
²Pacific Northwest National Laboratory

A Molecular Dynamics Investigation of Ferrous-Ferric Electron Transfer in a Hydrolyzing Aqueous Solution:
Calculation of the pH Dependence of the Diabatic Transfer Barrier and the Potential of Mean Force

We present a molecular model for ferrous-ferric electron transfer in an aqueous solution that accounts for
electronic polarizability and exhibits spontaneous cation hydrolysis. An extended Lagrangian technique is
introduced for carrying out calculations of electron transfer barriers in polarizable systems. The model predicts
that the diabatic barrier to electron transfer increases with increasing pH, due to stabilization of the Fe⁵⁺ by
fluctuations in the number of hydroxide ions in its first coordination sphere, in much the same way as the barrier
would increase with increasing dielectric constant in the Marcus theory. We have also, for the first time,
calculated the effect of pH on the potential of mean force between two hydrolyzing ions in aqueous solution. As
expected, increasing pH reduces the potential of mean force between the ferrous and ferric ions in the model
system. The magnitudes of the predicted increase in diabatic transfer barrier and the predicted decrease in the
potential of mean force nearly cancel each other at the canonical transfer distance of 0.55 nm. Even though
hydrolysis is allowed in our calculations, the distribution of reorganization energies has only one maximum and is
Gaussian to an excellent approximation, giving a harmonic free energy surface in the reorganization energy F(ΔE)
with a single minimum. There is thus a surprising amount of overlap in electron transfer reorganization energies
for Fe²⁺-Fe(H₂O)₆³⁺, Fe²⁺-Fe(OH)(H₂O)₅²⁺, and Fe²⁺-Fe(OH)(H₂O)₄⁺ couples, indicating that fluctuations in
hydrolysis state can be viewed on a continuum with other solvent contributions to the reorganization energy.
There appears to be little justification for thinking of the transfer rate as arising from the contributions of different hydrolysis states. Electronic structure calculations indicate that Fe(H\textsubscript{2}O)\textsubscript{6}\textsuperscript{2+} - Fe(OH)\textsubscript{n}(H\textsubscript{2}O)\textsubscript{6-n}\textsuperscript{(3-n)+} complexes interacting through H\textsubscript{3}O\textsubscript{2}- bridges do not have large electronic couplings.

George C. Schatz  
Northwestern University

Reactions of Hyperthermal Atomic Oxygen

Recent advances in experimental techniques, primarily by Tim Minton at Montana State, have made it possible to study the dynamics of reactions of O(\textsuperscript{3}P) with small molecules at hyperthermal energies in the 1-5 eV range. In this talk I will show that the use of direct dynamics classical trajectory simulations make it possible to provide a detailed understanding of the hyperthermal reaction dynamics, leading to the discovery of many new features of atomic oxygen chemistry that are largely unknown at lower energies. These include the presence of new reaction mechanisms in which the O atom adds to saturated hydrocarbons to form oxy radicals, the possibility of triplet/singlet crossing effects in the reaction of O with H\textsubscript{2}, and observation of the squeezed atom effect (leading to anomalously large collisional energy transfer) in collisions of O, O\textsubscript{2} and Ar with ethane. I will also describe studies of O atom reactions with fluorinated hydrocarbons, and QM/MM studies of O atom reactions with alkane thiol self-assembled monolayers on gold surfaces. This work has been done in collaboration with Biswajit Maiti and Diego Troya.

Gregory K. Schenter, Daniel T. Chang, and Bruce C. Garrett  
Pacific Northwest National Laboratory

Self-Consistent Polarization NDDO: Application to Water Clusters

Semiempirical SCF methods such as MNDO, AM1, and PM3 have the ability to treat the formation and breaking of chemical bonds but have been found to poorly describe hydrogen bonding and weak electrostatic complexes. In contrast, most empirical potentials are not able to describe bond-breaking and formation, but have the ability to add missing elements of hydrogen bonding using classical electrostatic interactions. We present a new method that combines aspects of both NDDO-based SCF techniques and classical descriptions of polarization to describe the diffuse nature of the electronic wavefunction in a self-consistent manner. We develop the “self-consistent polarization neglect of differential diatomic overlap” (SCP-NDDO) theory with the additional description of molecular dispersion developed as a second-order perturbation theory expression. We will present recent results where we parametrize the water-water interaction. This work follows the philosophy of the pioneering work of A. Gonzalez-Lafont, T. N. Truong, and D. G. Truhlar [J. Phys. Chem. 95, 4618 (1991)] where NDDO semiempirical methods were reparameterized to high level ab initio calculations and experimental measurement to provide a tractable representation of the potential energy surface.

Matthew J. McGrath\textsuperscript{1,2}, J. Ilja Siepmann\textsuperscript{1,2}, I-Feng W. Kuo\textsuperscript{2}, Christopher J. Mundy\textsuperscript{2}, Joost VandeVondele\textsuperscript{3}, Michiel Sprik\textsuperscript{3}, Jürg Hutter\textsuperscript{4}, Fawzi Mohamed\textsuperscript{5}, Matthias Krack\textsuperscript{5}, and Michele Parrinello\textsuperscript{5}

\textsuperscript{1}University of Minnesota  
\textsuperscript{2}Lawrence Livermore National Laboratory  
\textsuperscript{3}University of Cambridge  
\textsuperscript{4}University of Zürich  
\textsuperscript{5}ETH Zürich

Simulating Fluid Phase Equilibria From First Principles

Efficient Monte Carlo algorithms are combined with the Quickstep routines of CP2K to develop a program that allows for direct Gibbs ensemble Monte Carlo (GEMC) simulations of fluid phase equilibria using a first-
principles description of the physical system. Configurational-bias and aggregation-volume-bias Monte Carlo
techniques and pre-biasing using an inexpensive approximate potential are employed to increase the sampling
efficiency and to reduce the frequency of expensive \textit{ab initio} energy evaluations. Results of GEMC simulations
for the vapor-liquid coexistence curve of water are presented that were carried out using the Becke-Lee-Yang-Parr
exchange and correlation energy functionals, norm-conserving Goedecker-Teter-Hutter (GTH) pseudopotentials,
and a triple-zeta valence basis set augmented with two sets of $d$-type or $p$-type polarization functions (TZV2P)
optimized for the use with the GTH pseudopotentials.

Rex T. Skodje
Academia Sinica and University of Colorado

\textbf{State-to-State-to-State Dynamics of Chemical Reactions: The Control of Detailed Collision Dynamics by
Quantized Bottleneck States *}

It has long been realized that the characteristics of the transition state of a chemical reaction control the reaction
rate constant. More recently, Truhlar and coworkers have established that quantized bottleneck states (QBS),
which lie at the maxima of adiabatic potential curves, provide a basis to understand the energy dependence of the
cumulative reaction probability. In this presentation, we discuss new work that reveals that the control exerted by
the QBS extends even to highly detailed state-to-state differential cross sections of elementary reactions. Using
various isotopes of the $H+H_2$ prototype reaction, we show how the angular dependence and product distribution
of the reactions can be rationalized in terms of the properties of the QBS. The understanding of the (initial) state-
to (transition) state-to (final) state reaction dynamics not only provides a basis to observe the QBS, but also adds
predictive power to the study of reaction dynamics.

*This work was done in collaboration with SD Chao, M. Gustafsson, and the experimental group of XM Yang.


Hong Zhang and Sean C. Smith
The University of Queensland

\textbf{Quantum Lanczos Subspace Methods in Application to Unimolecular and Complex-Forming Bimolecular
Reactions}

Recent developments in quantum Lanczos subspace methods are presented. The basic idea of the Lanczos
subspace methods is to transform the primary representation of the fundamental scattering equations (e.g., the
time-independent Schrödinger equation or Kouri’s wavepacket-Lippmann-Schwinger equation) into the
tridiagonal Lanczos representation, inside which an eigen-problem or a linear system is solved to obtain the
related quantities such as resonance energies, widths, and product state distributions in unimolecular dissociation
as well as the S matrix elements in reactive scattering. The recent developments include (i) calculation of
unimolecular resonance energies and widths with all coriolis coupling included for total angular momentum
values up to 20 for the challenging HO$_2$ system and (ii) synthesis of the Lanczos approach with Light’s Artificial
Boundary Inhomogeneity (ABI) method to achieve reactive scattering with a real Lanczos algorithm requiring
neither damping operators nor complex absorbing potentials. This has subsequently enabled the successful
development of a single-subspace version of the Lanczos ABI algorithm, in which the full-S-matrix is computed
with unprecedented efficiency from a single real-symmetric Lanczos recursion. We have also implemented
calculations based on the real, damped Chebychev recursion in all cases to cross validate and compare
performance characteristics of our approaches.
William C. Stwalley  
University of Connecticut

Opportunities for Chemical Dynamics at Ultracold Temperatures

Collision dynamics of atoms and molecules at ultracold temperatures ($T \leq 1\text{mK}$) are not readily predictable from knowledge of collision dynamics above 100 K. Elastic collision cross sections approach a constant as $T \rightarrow 0\text{K}$ while inelastic and reactive cross sections are proportional to $T^{-1/2}$ as $T \rightarrow 0\text{K}$. Extrapolations of high temperature inelastic and reactive cross sections typically underestimate ultracold cross sections by many orders of magnitude. In addition, with at most a few incoming partial waves contributing, the effects of mass, symmetry, resonances and tunneling on ultracold collision dynamics are quite dramatic.

Recently, the techniques for cooling and trapping ultracold atoms (1997 and 2001 Nobel Prizes) have begun to be extended to ultracold diatomic molecules, e.g. using the photoassociation of ultracold atoms [1,2] or the direct formation (and even Bose-Einstein condensation) of very weakly bound molecules via Feshbach resonances using a tunable magnetic field [2,3]. The state-selective conversion of such very weakly bound heteronuclear molecules into molecules in a specific low rovibrational level of the $X 1\Sigma^+$ ground electronic state (e.g. $v=0, J=0$) will be described. This will permit studies of ultracold state-selected collision dynamics involving KRb [4] and K or Rb atoms (various selected isotopes). Such studies will be possible in our new K/Rb magneto-optical trap [4] at $T \sim 200\ \mu\text{K}$.

References:

Toshiyuki Takayanagi  
Saitama University

Reduced-dimensionality Quantum Scattering Calculations of the Reaction Between $C(3P)$ and Acetylene

The reaction of the ground-state atomic carbon $C(3P)$ with acetylene has recently attracted considerable interest due to its fundamental importance in the chemistry of dense interstellar clouds. It is known that the rate constant is quite large even at low temperatures since the potential energy surface is barrierless [1]. Crossed molecular beam experiments have also been performed and it has been found that the reaction cross section is nearly proportional to $E^\alpha$ ($\alpha \sim 0.7-0.8$), where $E$ is the translational energy [1].

Although several *ab initio* electronic structure studies for understanding the reaction mechanism for $C(3P) + \text{C}_2\text{H}_2$ have been carried out so far, there exists only one dynamics study, where Buonomo and Clary report two-dimensional time-dependent quantum wave packet calculations [2]. They have considered two variables describing the position of the carbon atom with respect to acetylene. Here, we extend their calculations to include one more active degree of freedom, C-C stretching coordinate. Therefore, the problem to be solved can be reduced to a usual atom-diatom reaction system. Our three-dimensional model is rather realistic in the sense of the Born-Oppenheimer-like approximation where fast hydrogen atom motions were assumed to be adiabatic. The potential energy values in the entrance region were calculated using the hybrid density functional B3LYP method with the 6-31G(d,p) basis set using the GAUSSIAN package and a total of about 2600 points were calculated. An analytical potential energy function was then developed by a standard fitting technique.
Reactive cross sections were calculated as a function of the collision energy using the time-independent quantum reactive scattering method. The generalized $R$-matrix propagation method with an appropriate imaginary flux-absorbing potential was used. We have also employed the standard centrifugal sudden approximation neglecting Coriolis coupling terms. Details about the computational results as well as comparison to experiment will be presented at the meeting.


Robert Q. Topper¹, Nikhil Jain², and Nihal P. Dayal³
Monmouth University

**Modeling DNA Damage: Computational Cascade Analyses of N-Acetyl-2-Aminofluorene (AAF) Adducts to Guanine and Deoxyguanosine**

Aromatic amines are an important class of environmental carcinogens and mutagens. Early studies of N-acetyl-2-aminofluorene (AAF) were so fruitful that AAF has been the subject of more than 70 years of research activity. After hepatic activation, (AAF) forms a major or a minor adduct with DNA both *in vivo* and *in vitro*. The structure of the minor adduct has not been experimentally determined but is believed to be of importance due to its persistence *in vivo*. In the present study, four varieties of modified AAF have been studied: AAF bonded to C8 of guanine or deoxyguanosine (major adduct), and AAF bonded to N² of guanine or deoxyguanosine (minor adduct). Each was subjected to a series of systematic and/or simulated annealing Monte Carlo conformer searches using the MMFF94s force field. After convergence with respect to the search parameters was obtained, the lowest-energy conformers for the major and minor guanine and deoxyguanosine adducts were then geometry optimized via cascades such as (MMFF94s $\rightarrow$ AM1 $\rightarrow$ B3LYP/6-31G* $\rightarrow$ B3LYP/6-31G**) and (MMFF94s $\rightarrow$ B3LYP/6-31G* $\rightarrow$ B3LYP/6-31G**). A finite number of conformers was obtained for the guanine adducts, but the deoxyguanosine adducts displayed a continuous series of minima at the MMFF94s level, making completion of the cascade for all structures considerably more challenging. The structures predicted of the guanine major adduct compare favorably with NMR and x-ray crystallographic data. The major adducts exhibit an energetic preference for adoption of one of two orientations, with guanine or deoxyguanosine oriented either perpendicular to the fluorenyl ring moiety or approximately 45° with respect to the fluorenyl structure. Repulsion between the ribose sugar and acetyl group in deoxyguanosine disrupts the “ideal” dihedral angles observed in the guanine adduct and destroys the symmetry. Results for the N² structures similarly point toward two general conformer classes, one of which is characterized by hydrogen bonding between the acetyl O and the H bonded to N² of guanine, and the other by minimization of repulsion between the guanine structure and the acetyl group. The orientations of -OH groups in the ribose ring contribute substantially to the energy landscape. These results should prove useful in the improvement of force fields for molecular dynamics studies of damaged DNA.

¹To whom correspondence should be addressed. E-mail: rtopper@monmouth.edu
²2004 Merck-SURF Fellow
³2004 U.S. Army REAP Intern.

![Fig.1. Lowest-energy conformer of the major guanine adduct computed at the a) MMFF94s level and at the b) B3LYP/6-31G** level.](image)
Soledad Gutiérrez-Oliva, Bárbara Herrera, and Alejandro Toro-Labbé
Pontificia Universidad Católica de Chile.

The Role of the Reaction Force to Characterize the Hydrogen Transfer Between Sulfur and Oxygen Atoms

The role of the reaction force to characterize the mechanisms of intramolecular hydrogen transfer is analyzed stressing the fact that the force profile gives the elements to define different regions along the reaction coordinate where different steps of the reaction mechanism operates. These steps are characterized by amounts of work that are calculated by integrating the force profile within the region where the specific process takes place. In this way a partition of the potential energy barriers is obtained and used to characterize the energetic cost of the different local processes.

In this work the 1,3-intramolecular hydrogen transfer reactions HSNO ↔ SNOH and HSCH(O) ↔ (S)CHOH are studied with the aim of comparing the hydrogen donor and/or acceptor capability of oxygen and sulfur. DFT/B3LYP/6-311G** calculations indicate that even though the barrier for hydrogen transfer from sulfur to oxygen are higher than those from oxygen to sulfur, the oxygen is still a better hydrogen acceptor than sulfur. This becomes evident from the analysis of the regions that involves only the hydrogenic motion.

Acknowledgments: This work was supported by FONDECYT through Project Nos.1020534.

N. Kungwan, T. N. Truong
University of Utah

Kinetics of the Hydrogen Abstraction Reaction Class·CH₃ + H-C(sp³) → CH₄ + ·C(sp³): An Application of the Reaction Class Transition State Theory

Kinetics of the hydrogen abstraction reaction ·CH₃ + CH₄ → CH₄ + ·CH₃ is studied by a direct dynamics method. Thermal rate constants in the temperature range of 300—2500 K are evaluated by the canonical variational transitional transition state theory (CVT) incorporating corrections from tunneling using the small-curvature tunneling (SCT) method and from the hindered rotations. These results are used in conjunction with the Reaction Class Transition State Theory /Linear Energy Relationship (RC-TST/LER) to predict thermal rate constants of any reaction in the hydrogen abstraction class of ·CH₃ + H-C(sp³) where C(sp³) is a saturated carbon atom. Error analyses are performed and presented.

Priya Parandekar and John Tully
Yale University

“Frustrated Hops” and Detailed Balancing in Mixed Quantum-Classical Dynamics

Mixed quantum-classical procedures have been developed to simulate molecular motions when a classical mechanical description alone is not adequate. A crucial property of such theories is feedback between the classical and quantum motions. Quantum transitions are driven by the time-dependent classical motion and, in turn, the forces governing the classical paths are altered by quantum transitions. Two general approaches have evolved for incorporating quantum-classical feedback, the self-consistent-field (SCF) and surface-hopping methods. We present a rigorous analysis of detailed balancing in these methods, supplemented by simulations. We show that with the SCF method the quantum state populations deviate greatly from the desired equilibrium values at long times. By contrast, surface hopping with the “fewest switches” algorithm satisfies detailed balance exactly, at least in principle. This is only true, however, when transitions to energy forbidden quantum states are disallowed. Thus “frustrated hops, “ often considered a failing of surface hopping, are actually essential to achieve proper equilibrium.
I. Tuñón, J. J. Ruiz-Pernía, E. Silla, S. Martí, V. Moliner
1Universitat de València
2Universitat Jaume I

Improving the QM/MM Treatment of Enzymatic Processes. Dual Level Methods

The study of enzymatic reactions implies the consideration of systems with thousands of atoms. An effective way to treat these systems is the use of hybrid QM/MM methods, where only a small part of the system, where the bond braking and forming processes are taking place, is described at a quantum mechanical level while for the rest of the system a molecular mechanics potential is chosen. Once the potential energy function is defined, the study of these chemical processes usually requires two steps: i) the exploration of the potential energy surface and the localization of the relevant stationary structures and ii) molecular simulations to obtain free energy profiles and averaged properties of the thermodynamic states. The use of the QM/MM approach drastically reduces the number of electrons to be considered but the number of degrees of freedom is usually too large, both for PES explorations and molecular simulations. Then, except in cases where a large fraction of the system is kept frozen, the QM level selected must be computationally inexpensive, i.e. semiempirical Hamiltonians. This can be an important drawback to study some systems and here we present some possible strategies to overcome such limitations.

For the localization of stationary structures we propose a dual level description of the QM subsystem (based on the combination of a High Level (HL) and a Low Level (LL)) that takes advantage of the employment of micro/macro iteration optimization algorithms [1]. The potential energy function of the QM subsystem is described as the sum of gas phase, polarization and interaction energy terms calculated at different levels:

\[ E_{QM} + E_{QM/MM} = E_{HL} + E_{LL}^{pol} + E_{LL}^{int} \]

To obtain more accurate Potentials of Mean Force (PMF) we followed the ideas of Prof. Truhlar [2], implementing a correction energy term obtained as a function of the distinguished reaction coordinate biased during the sampling (\( \zeta \)). This correction term is interpolated using splines under tension [3]:

\[ E(r_1, ..., r_{N-1}, \zeta) = E_{LL}(r_1, ..., r_{N-1}, \zeta) + \text{spline}\{\Delta E(\zeta)\} \]

where \( N \) is the total number of degrees of freedom and \( \Delta E(\zeta) = E_{HL}(\zeta) - E_{LL}(\zeta) \) is obtained along the minimum energy path. This strategy allows obtaining much better free energies at a negligible additional computational cost.

References:
[1] Martí, S.; Moliner, V.; Tuñón, I.; Williams, I. H. Submitted

Steve Valone
Los Alamos National Laboratory

Particle-Velocity Dependent Rate Constants From Transition State Theory

Shock loading sets off complex kinetic processes, including detonations, deformations, fracture, spall, and phase transformations. While many practical models have succeeded in fitting much data, they are unable to predict rate-dependent behavior outside of the fitting range and to account for differences in shock and thermal experiments. It is possible to revise contemporary theories of activated rate processes to be explicitly particle-velocity, \( u_p \), dependent by altering a basic assumption in conventional transition state theory (TST). Analytical, \( u_p \)-dependent rate constants are derived rigorously from TST [1]. Some advantages of this model include the following. The model is able to fit both thermal- and shock-activated PETN and nitromethane (NM) data in a physically sensible way. The model behaves qualitatively correctly to account for the difference in two NM shock
experiments. The focus of the model on the alignment of the shock loading direction with the slip systems in a single crystal is supported by the conclusions of several molecular dynamics simulations [2] and single-crystal shock experiments [3]. The model is hypersensitive to dispersion in the particle velocity, which may contribute to hot-spot behavior around voids.

References:

A. J. C. Varandas
Universidade de Coimbra

Global Potential Energy Surfaces With Near Spectroscopic Accuracy

After a brief survey of the theory, we focus on two case studies. The first refers to H$_3^+$ ($^3A'$) whose potential energy surface has two adiabatic sheets that show a conical intersection for nuclear arrangements with $D_{3h}$ symmetry. Using highly accurate ab initio calculations, a global double-sheeted double many-body expansion (DMBE) potential energy surface has been modeled that should be reliable within a few cm$^{-1}$ over most regions of practical interest. The following results of ro-vibrational calculations both with and without the inclusion of the geometrical phase (GP) effect will then be summarized: (a) rotational term values of the lowest 19 states for a total angular momentum $J \leq 10$, which may hopefully stimulate experiments aiming at their observation; (b) cone states which underline the key role of the GP effect in the upper-sheet calculations. The second case study is ground-state HCN. Using an automated multiproperty least-squares fitting procedure, a global single-sheeted DMBE form has been obtained that fits accurately the best available ab initio energies while reproducing with near spectroscopic accuracy all vibrational levels up to the saddle point for the isomerization reaction HCN $\leftrightarrow$ HNC. The problem of assigning ro-vibrational levels whose wave functions are delocalized over the minima of the linear HCN and HNC isomers is then also addressed. We conclude with some remarks on continuing challenges and planned work.

Scott Yockel, Benjamin Mintz, Xuelin (Nick) Wang, Pankaj Sinha, and Angela K. Wilson
University of North Texas

High Accuracy Molecular Properties: Successes and Challenges

The description of molecular properties to chemical accuracy has been a long-standing, but yet quite challenging, goal of computational chemistry. We examine difficulties and our recent strides toward achieving this goal, particularly from a basis set perspective. Our focus in this presentation is upon energetic, structural, and spectroscopic properties of a number of species ranging from first-row through transition metal species.

Weitao Yang
Duke University

Reaction Path Potential for Simulation of Chemical Reactions in Enzymes Derived From ab Initio QM/MM Calculations

The reaction path potential (RPP) follows the ideas from the reaction path Hamiltonian of Miller, Handy and Adams for gas phase reactions but is designed specifically for large systems described with QM/MM methods. RPP is an analytical energy expression of the combined QM/MM potential energy along the minimum energy path. An expansion around the minimum energy path is made in both the nuclear and the electronic degrees of
freedom for the QM subsystem, while the interaction between the QM and MM subsystems is described as the interaction of the MM charges with polarizable QM charges. The input data for constructing the reaction path potential are energies, frequencies and electron density response properties of the QM subsystem. RPP provides a potential energy surface for rigorous statistical mechanics and mixed quantum/classical reaction dynamics calculations of complex systems, as will be shown for several enzymes.

References:

Olalla Nieto Faza¹, Carlos Silva López¹, Ángel R. de Lera¹ and Darrin M. York²*
¹Universidade de Vigo (Spain)
²University of Minnesota
*Correspondence: york@chem.umn.edu

Mechanistic Characterization of the Hydrolysis of Methyl Ethylene Phosphate and the Phosphoryl Transfer Reaction Catalyzed by Phosphoglucomutase

Phosphate hydrolysis reactions are ubiquitous in biology. In order to understand the mechanisms whereby biological macromolecules such as enzymes and ribozymes can catalyze the hydrolysis of phosphates, it is important to understand the non-enzymatic mechanisms. Detailed study of non-enzymatic phosphate hydrolysis serves to help elucidate the key factors that govern phosphate reactivity, and also aids in benchmarking the accuracy of theoretical methods. Toward this end, solvated density functional calculations have been performed on the complete mechanistic profile for the hydrolysis of methyl ethylene phosphate (MEP) in order to test the overall reliability of the DFT and solvation models and provide benchmark data for design of improved semiempirical quantum models for phosphate hydrolysis reactions. The mechanistic profile includes dianionic, monoanionic and neutral reacting species, and considers both endo-cyclic and exo-cyclic cleavage reactions connected by a pseudorotation reaction pathway. This is the first density-functional characterization of the complete mechanistic profile for a prototype phosphate hydrolysis reaction to be reported.

Results of density-functional and hybrid QM/MM calculations of a related phosphoryl transfer reaction in phosphoglucomutase are also presented. The phosphoglucomutase is the first enzymatic structure for which an unmodified catalytic intermediate has been trapped by X-ray crystallography, although there is considerable controversy over the interpretation of the crystallographic data. The calculations of the active site of this system provide insight into the reaction free energy profile and stability of the intermediate.
<table>
<thead>
<tr>
<th>Participants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carlo Adamo</td>
</tr>
<tr>
<td>Enscp</td>
</tr>
<tr>
<td><a href="mailto:adamo@ext.jussieu.fr">adamo@ext.jussieu.fr</a></td>
</tr>
<tr>
<td>Robert Binning</td>
</tr>
<tr>
<td>Universidad Metropolitana</td>
</tr>
<tr>
<td><a href="mailto:binningrc@yahoo.com">binningrc@yahoo.com</a></td>
</tr>
<tr>
<td>David C. Clary</td>
</tr>
<tr>
<td>University of Oxford</td>
</tr>
<tr>
<td><a href="mailto:david.clary@mps.ox.ac.uk">david.clary@mps.ox.ac.uk</a></td>
</tr>
<tr>
<td>Titus Albu</td>
</tr>
<tr>
<td>Tennessee Tech University</td>
</tr>
<tr>
<td><a href="mailto:albu@tntech.edu">albu@tntech.edu</a></td>
</tr>
<tr>
<td>Victor Bloomfield</td>
</tr>
<tr>
<td>University of Minnesota</td>
</tr>
<tr>
<td><a href="mailto:victor@umn.edu">victor@umn.edu</a></td>
</tr>
<tr>
<td>J. N. L. Connor</td>
</tr>
<tr>
<td>University of Manchester</td>
</tr>
<tr>
<td><a href="mailto:j.n.l.connor@man.ac.uk">j.n.l.connor@man.ac.uk</a></td>
</tr>
<tr>
<td>Wesley D. Allen</td>
</tr>
<tr>
<td>University of Georgia</td>
</tr>
<tr>
<td><a href="mailto:wdallen@ccqc.uga.edu">wdallen@ccqc.uga.edu</a></td>
</tr>
<tr>
<td>Edward A. Boudreaux</td>
</tr>
<tr>
<td>University of New Orleans</td>
</tr>
<tr>
<td><a href="mailto:eaboudre@uno.edu">eaboudre@uno.edu</a></td>
</tr>
<tr>
<td>Steven Corcelli</td>
</tr>
<tr>
<td>University of Wisconsin</td>
</tr>
<tr>
<td><a href="mailto:corcelli@chem.wisc.edu">corcelli@chem.wisc.edu</a></td>
</tr>
<tr>
<td>Thomas C. Allison</td>
</tr>
<tr>
<td>National Institute of Standards and Technology</td>
</tr>
<tr>
<td>Joao Brandao</td>
</tr>
<tr>
<td>Universidade do Algarve</td>
</tr>
<tr>
<td><a href="mailto:jbrandao@ualg.pt">jbrandao@ualg.pt</a></td>
</tr>
<tr>
<td>Christopher J. Cramer</td>
</tr>
<tr>
<td>University of Minnesota</td>
</tr>
<tr>
<td><a href="mailto:cramer@pollux.chem.umn.edu">cramer@pollux.chem.umn.edu</a></td>
</tr>
<tr>
<td>Amos Anderson</td>
</tr>
<tr>
<td>Caltech</td>
</tr>
<tr>
<td><a href="mailto:amosa@caltech.edu">amosa@caltech.edu</a></td>
</tr>
<tr>
<td>Gregg Caldwell</td>
</tr>
<tr>
<td>3M Company</td>
</tr>
<tr>
<td><a href="mailto:gcaldwell@mmm.com">gcaldwell@mmm.com</a></td>
</tr>
<tr>
<td>Norge Cruz Hernández</td>
</tr>
<tr>
<td>University of Seville</td>
</tr>
<tr>
<td><a href="mailto:norge@us.es">norge@us.es</a></td>
</tr>
<tr>
<td>Kelly Anderson</td>
</tr>
<tr>
<td>University of Minnesota</td>
</tr>
<tr>
<td><a href="mailto:kanderson@chem.umn.edu">kanderson@chem.umn.edu</a></td>
</tr>
<tr>
<td>Piergiorgio Casavecchia</td>
</tr>
<tr>
<td>Università di Perugia</td>
</tr>
<tr>
<td><a href="mailto:piero@dyn.unipg.it">piero@dyn.unipg.it</a></td>
</tr>
<tr>
<td>John Cullen</td>
</tr>
<tr>
<td>University of Manitoba</td>
</tr>
<tr>
<td><a href="mailto:cullen@cc.umanitoba.ca">cullen@cc.umanitoba.ca</a></td>
</tr>
<tr>
<td>Xavier Assfeld</td>
</tr>
<tr>
<td>Universite Henri Poincare</td>
</tr>
<tr>
<td><a href="mailto:xavier.assfeld@lctn.ulhp.nancy.fr">xavier.assfeld@lctn.ulhp.nancy.fr</a></td>
</tr>
<tr>
<td>Alessandro Cembran</td>
</tr>
<tr>
<td>University of Minnesota</td>
</tr>
<tr>
<td><a href="mailto:cembran@chem.umn.edu">cembran@chem.umn.edu</a></td>
</tr>
<tr>
<td>Yuhua Duan</td>
</tr>
<tr>
<td>University of Minnesota</td>
</tr>
<tr>
<td><a href="mailto:duany@dtc.umn.edu">duany@dtc.umn.edu</a></td>
</tr>
<tr>
<td>Steven Bachrach</td>
</tr>
<tr>
<td>Trinity University</td>
</tr>
<tr>
<td><a href="mailto:sbachrach@trinity.edu">sbachrach@trinity.edu</a></td>
</tr>
<tr>
<td>Arindam Chakraborty</td>
</tr>
<tr>
<td>University of Minnesota</td>
</tr>
<tr>
<td><a href="mailto:chakra@comp.chem.umn.edu">chakra@comp.chem.umn.edu</a></td>
</tr>
<tr>
<td>Timothy Dudley</td>
</tr>
<tr>
<td>Iowa State University</td>
</tr>
<tr>
<td><a href="mailto:tim@si.fi.ameslab.gov">tim@si.fi.ameslab.gov</a></td>
</tr>
<tr>
<td>Kim K. Baldridge</td>
</tr>
<tr>
<td>University of Zurich – Irchel</td>
</tr>
<tr>
<td><a href="mailto:kimb@ci.unizh.ch">kimb@ci.unizh.ch</a></td>
</tr>
<tr>
<td>Adam Chamberlin</td>
</tr>
<tr>
<td>University of Minnesota</td>
</tr>
<tr>
<td><a href="mailto:chamberlin@chem.umn.edu">chamberlin@chem.umn.edu</a></td>
</tr>
<tr>
<td>Michel Dupuis</td>
</tr>
<tr>
<td>Pacific Northwest National Lab</td>
</tr>
<tr>
<td><a href="mailto:michel.dupuis@pnl.gov">michel.dupuis@pnl.gov</a></td>
</tr>
<tr>
<td>Juan Bertrán</td>
</tr>
<tr>
<td>Universitat Autonoma de Barcelona</td>
</tr>
<tr>
<td><a href="mailto:bertran@klingon.uab.es">bertran@klingon.uab.es</a></td>
</tr>
<tr>
<td>Shih-Hung Chou</td>
</tr>
<tr>
<td>3M</td>
</tr>
<tr>
<td><a href="mailto:shchou@mmm.com">shchou@mmm.com</a></td>
</tr>
<tr>
<td>Benjamin Ellingson</td>
</tr>
<tr>
<td>University of Minnesota</td>
</tr>
<tr>
<td><a href="mailto:elliingson@chem.umn.edu">elliingson@chem.umn.edu</a></td>
</tr>
<tr>
<td>Divesh Bhatt</td>
</tr>
<tr>
<td>University of Minnesota</td>
</tr>
<tr>
<td><a href="mailto:bhatt@chem.umn.edu">bhatt@chem.umn.edu</a></td>
</tr>
<tr>
<td>Yao-Yuan Chuang</td>
</tr>
<tr>
<td>National University of Kaoshin</td>
</tr>
<tr>
<td><a href="mailto:ychuang@nuk.edu.tw">ychuang@nuk.edu.tw</a></td>
</tr>
<tr>
<td>Joaquin Espinosa-Garcia</td>
</tr>
<tr>
<td>Universidad de Extremadura</td>
</tr>
<tr>
<td><a href="mailto:joaquin@unex.es">joaquin@unex.es</a></td>
</tr>
<tr>
<td>Sudeep Bhattacharyay</td>
</tr>
<tr>
<td>University of Minnesota</td>
</tr>
<tr>
<td><a href="mailto:sudeep@umn.edu">sudeep@umn.edu</a></td>
</tr>
<tr>
<td>Ilaria Ciofini</td>
</tr>
<tr>
<td>ENSCP</td>
</tr>
<tr>
<td><a href="mailto:ciofini@ext.jussieu.fr">ciofini@ext.jussieu.fr</a></td>
</tr>
<tr>
<td>Patton Fast</td>
</tr>
<tr>
<td>University of Minnesota</td>
</tr>
<tr>
<td><a href="mailto:pfast@msi.umn.edu">pfast@msi.umn.edu</a></td>
</tr>
<tr>
<td>Name</td>
</tr>
<tr>
<td>--------------------------</td>
</tr>
<tr>
<td>Doreen Leopold</td>
</tr>
<tr>
<td>John Lewin</td>
</tr>
<tr>
<td>Jane Li</td>
</tr>
<tr>
<td>Jiabo Li</td>
</tr>
<tr>
<td>Jim Licari</td>
</tr>
<tr>
<td>Hai Lin</td>
</tr>
<tr>
<td>Yun Liu</td>
</tr>
<tr>
<td>Tiqing Liu</td>
</tr>
<tr>
<td>Benjamin Lynch</td>
</tr>
<tr>
<td>Gillian Lynch</td>
</tr>
<tr>
<td>Vanessa Lynch</td>
</tr>
<tr>
<td>Dan Major</td>
</tr>
<tr>
<td>Sergio Marti</td>
</tr>
<tr>
<td>Laura Masgrau</td>
</tr>
<tr>
<td>C. Alden Mead</td>
</tr>
<tr>
<td>Steven Mielke</td>
</tr>
<tr>
<td>Sean Mikel</td>
</tr>
<tr>
<td>Thomas Miller</td>
</tr>
<tr>
<td>Denise Mills</td>
</tr>
<tr>
<td>Sanat Mohanty</td>
</tr>
<tr>
<td>Vicent Moliner</td>
</tr>
<tr>
<td>Keiji Morokuma</td>
</tr>
<tr>
<td>Hisao Nakamura</td>
</tr>
<tr>
<td>Kwangho Nam</td>
</tr>
<tr>
<td>Shikha Nangia</td>
</tr>
<tr>
<td>Olalla Nieto Faza</td>
</tr>
<tr>
<td>Kunizo Onda</td>
</tr>
<tr>
<td>Modesto Orozco</td>
</tr>
<tr>
<td>Kim Palmo</td>
</tr>
<tr>
<td>Robert Peterkin</td>
</tr>
<tr>
<td>James Phillips</td>
</tr>
<tr>
<td>John C. Polanyi</td>
</tr>
<tr>
<td>Jingzhi Pu</td>
</tr>
<tr>
<td>Neeraj Rai</td>
</tr>
<tr>
<td>Sachchida N. Rai</td>
</tr>
<tr>
<td>Bala Ramachandran</td>
</tr>
<tr>
<td>Kevin Range</td>
</tr>
</tbody>
</table>
Keith Wiitala  
University of Minnesota  
wiita002@umn.edu

Angela K. Wilson  
University of North Texas  
akwilson@unt.edu

Nathaniel Woodrum  
University of Minnesota  
woodrum@pollu@chem.umn.edu

Hong Wu  
University of Missouri, Columbia  
hwc8a@mizzou.edu

Darrin M. York  
University of Minnesota  
york@chem.umn.edu

Ling Zhang  
University of Minnesota  
lzhang@chem.umn.edu

Xin Zhao  
University of Minnesota  
xzhao@chem.umn.edu

Yan Zhao  
University of Minnesota  
yzhao@chem.umn.edu

Chaoyuan Zhu Zhu  
University of Minnesota  
zhuc@comp.chem.umn.edu
Summary of Locations

Event Overview
There will be a welcome/reception Wednesday night, October 6, at the Radisson Hotel Metrodome. The plenary sessions, breaks, and lunches will be held at the McNamara Gateway Center. The pizza/poster session will be held the evening of October 7 in the Great Hall of Coffman Memorial Union. The reception and banquet, including remarks from William Goddard, will be held on October 8 at the Campus Club, which is located in Coffman Memorial Union. The conference fees include the Wednesday night reception, break and lunches at the McNamara Center, the pizza/poster sessions, and the conference banquet.

Event locations
Radisson Hotel Metrodome (October 6 welcome/registration)
615 Washington Avenue S.E.
Minneapolis, MN 55414
(612) 379-8888

McNamara Gateway Center (plenary sessions)
200 Oak Street S.E.
Minneapolis, MN 55415
612-624-7583
general information: http://www.alumnicenter.umn.edu
parking/directions: http://www.alumnicenter.umn.edu/Dir&Parking.htm

Great Hall (October 7 pizza/poster session)
Ground Floor
Coffman Memorial Union
300 Washington Ave. S.E.
Minneapolis, MN 55455
612-624-9954
http://www.coffman.umn.edu/directions.php

Campus Club (October 8 reception and banquet)
4th Floor
Coffman Memorial Union
300 Washington Ave. S.E.
Minneapolis, MN 55455
612-625-9696
http://www1.umn.edu/cclub/
Administrative Contacts

**Symposium Administrators**
Ann Johns  
Digital Technology Center  
University of Minnesota  
612-624-1556  
johns@dtc.umn.edu

Michael Olesen  
Digital Technology Center  
University of Minnesota  
612-625-6414  
olesen@dtc.umn.edu

**Symposium Support**
Alison Baerwald  
Digital Technology Center  
University of Minnesota  
612-624-0811  
baerwald@dtc.umn.edu

Tracey Bartlett  
Supercomputing Institute  
University of Minnesota  
612-624-2330  
bartlett@msi.umn.edu

Barbara Opal  
Supercomputing Institute  
University of Minnesota  
612-624-7404  
opal@msi.umn.edu

Debbie Schutta  
Supercomputing Institute  
University of Minnesota  
612-624-0528  
dschutta@msi.umn.edu