Title
A Symposium in Honor of William A. Lester, Jr. on His 70th Birthday

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Lester Jr., William A.

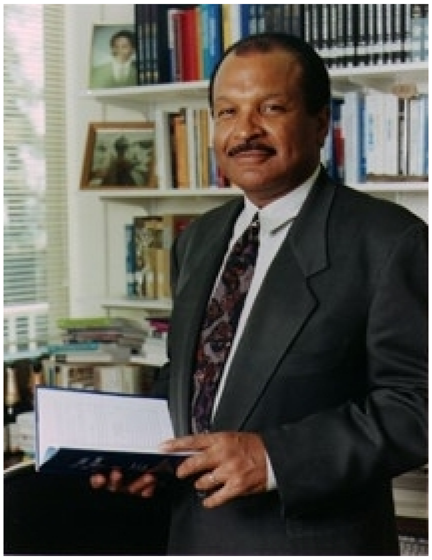
Publication Date
2007-03-19

LBNL-62449

A SYMPOSIUM IN HONOR OF WILLIAM A. LESTER, JR

ON HIS 70TH BIRTHDAY

University of California, Berkeley
March 28-31, 2007



William A. Lester, Jr. was born in 1937 in Chicago, Illinois. He earned B.S. (1958) and M.S. (1959) degrees from the University of Chicago. He was awarded the Ph.D. from the Catholic University of America in 1964 with research carried out at NBS (now NIST) as a regular employee. He went on educational leave from NBS to accept a postdoctoral appointment at the Theoretical Chemistry Institute, University of Wisconsin. During his postdoctoral stint, he accepted an appointment as Assistant Director of the Institute and subsequently resigned his NBS appointment. From 1966 to 1968, Bill also held the position of Lecturer in the UW Chemistry Department.

In 1968 Bill accepted an offer to join the Large Scale Scientific Computations Department at the IBM Research Laboratory in San Jose, CA. In the mid-seventies he spent a year on the Technical Planning at IBM Yorktown Heights research facility, after which he became Manager, Molecular Interactions Group at the San Jose laboratory. In 1977 he was selected to direct the NRCC (National Resource for Computation in Chemistry) housed at Lawrence Berkeley Laboratory. He joined the Berkeley faculty in 1981.

For the period, 1991-95, Bill was Associate Dean for Undergraduate Affairs, College of Chemistry. In 1995, at the request of NSF Director Neal Lane, Bill joined the Foundation as Senior Fellow for Science and Engineering and Assistant to the Director for Human Resource Development to work on HRD matters both internal to NSF and in its national programs.

Bill pioneered high accuracy calculations of cross sections for collisional energy transfer using ab initio interaction potentials - research began at Wisconsin and continued through his years with IBM. Shortly after joining NRCC, he became aware of the quantum Monte Carlo method, and continues research in this area.

He is the recipient of the Amos Alonzo Stagg Medal, University of Chicago, 1957; "Man of the Year," University of Chicago, 1957; IBM Corporation Outstanding Contribution Award, 1974; The Percy L. Julian Award in Pure or Applied Research, National Organization for the Professional Advancement of Black Chemists and Chemical Engineers, 1979; Alumni Achievement Award in Science, The Catholic University of America, 1983; Fellow, American Physical Society, 1984; Outstanding Teacher Award, National Organization for the Professional Advancement of Black Chemists and Chemical Engineers, 1986; Fellow, American Association for the Advancement of Science, 1991; Fellow, California Academy of Sciences, 1994; Outstanding Service Award, National Science Foundation, 1996; Member, President’s Committee on the National Medal of Science, September, 2000-2002 (appointed by President William J. Clinton); selected for Allstate calendar, “From Whence We Came, Pathfinders of the Future” (subject for April 2004); selected ScienceMaker, *The HistoryMakers*, National African American Video Oral History Archive, 2004; inducted into the University of Chicago’s Athletics Hall of Fame, 2004 (captain, basketball team 3 years, 2 scoring records still standing from 1957); UCB Chancellor’s Award for Advancing Institutional Excellence, April 2006; *Who's Who in the World*, 2006.

COLLEGE OF CHEMISTRY COMPLEX
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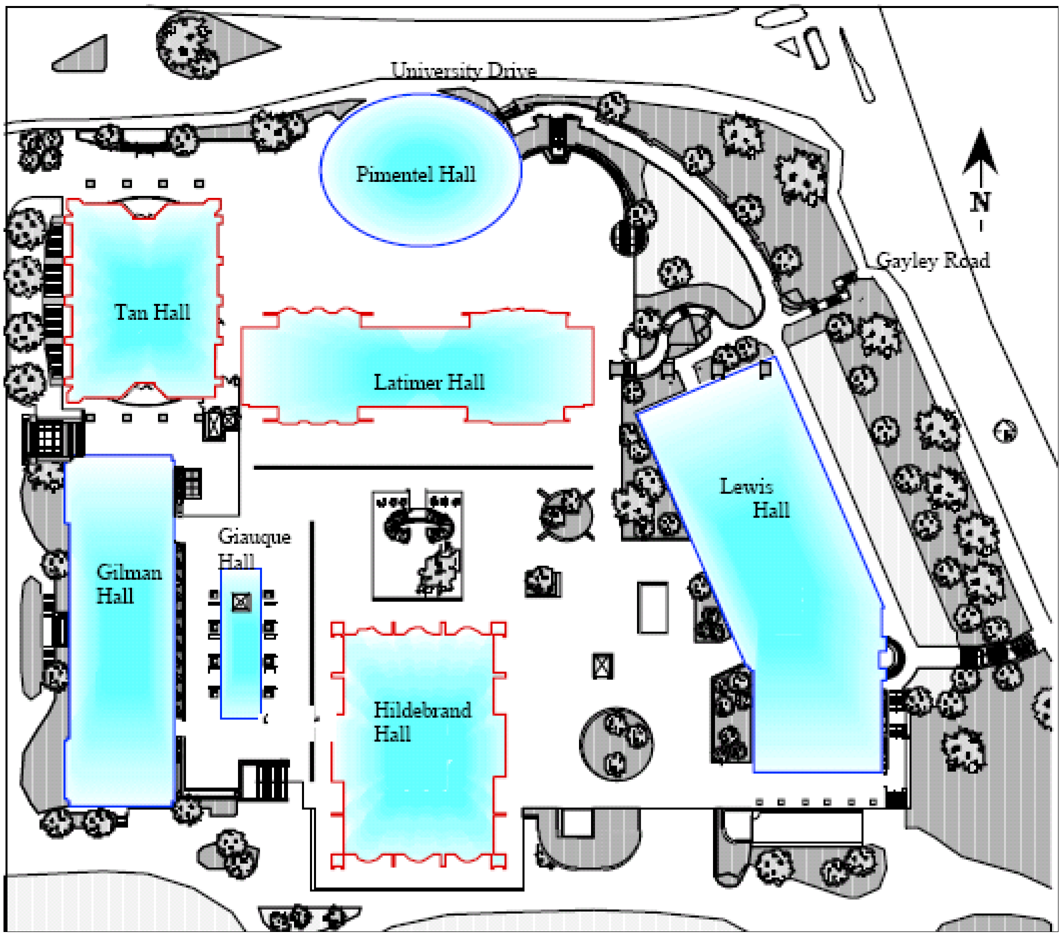


Registration	Tan Hall Lobby
Welcome Gathering	Tan Hall Lobby
Oral Presentations (Speakers and Posters)	120 Latimer Hall (Pitzer Auditorium)
Refreshments	Tan Hall Lobby
Poster Session	Tan Hall Lobby

Symposium Agenda

Wednesday, March 28, 2007		
4:00 pm to 6:00 pm	Registration	Tan Hall Lobby
6:00 pm to 8:00 pm	Welcome Gathering	Tan Hall Lobby
Thursday, March, 29, 2007		
8:00 am to 8:30 am	Continental Breakfast	Tan Hall Lobby
8:30 am to 8:50 am	Opening Ceremonies **Welcome – Alan Aspuru-Guzik**	Pitzer Auditorium
8:50 am to 10:10 am	Session 1A	Pitzer Auditorium
10:10 am to 10:40 am	Refreshments	Tan Hall Lobby
10:40 am to 12:20 pm	Session 1B	Pitzer Auditorium
12:20 pm to 2:00 pm	Lunch	On Your Own
2:00 pm to 3:40 pm	Session 2A	Pitzer Auditorium
3:40 pm to 4:10 pm	Refreshments	Tan Hall Lobby
4:10 pm to 5:30 pm	Session 2B	Pitzer Auditorium
5:30 pm to 8:00 pm	Dinner	On Your Own
8:00 pm to 8:30 pm	Poster Two-Minute Oral Presentations	Pitzer Auditorium
8:30 pm to 10:00 pm	Poster Session	Tan Hall Lobby
Friday, March 30, 2007		
8:00 am to 8:30 am	Continental Breakfast	Tan Hall Lobby
8:30 am to 10:10 am	Session 3A	Pitzer Auditorium
10:10 am to 10:40 am	Refreshments	Tan Hall Lobby
10:40 am to 12:20 pm	Session 3B	Pitzer Auditorium
12:20 pm to 2:00 pm	Lunch	On Your Own
2:00 pm to 3:20 pm	Session 4A	Pitzer Auditorium
3:20 pm to 3:50 pm	Refreshments	Tan Hall Lobby
3:50 pm to 5:10 pm	Session 4B	Pitzer Auditorium
6:15 pm to 7:00 pm	Reception	International House
7:00 pm to 9:00 pm	Symposium Dinner After-dinner talk – Rochelle Lester	International House

Symposium Agenda

Saturday, March 31, 2007		
8:00 am to 8:30 am	Continental Breakfast	Tan Hall Lobby
8:30 am to 10:10 am	Session 5A	Pitzer Auditorium
10:10 am to 10:40 am	Refreshments	Tan Hall Lobby
10:40 am to 12:20 pm	Session 5B	Pitzer Auditorium

ORAL PRESENTATIONS

Thursday, March 29, 2007		**Session 1A**
8:50 AM	James B. Anderson	Correlated Sampling in Corrections for Diffusion Quantum Monte Carlo
9:10 AM	Stuart M Rothstein	Critical analysis of reptation quantum Monte Carlo
9:30 AM	John Sabin	Theoretical Investigation of Fragmentation and Energy Deposition Cross Sections for Proton Impact on a Protobiotic Molecule: Formaldehyde
9:50 AM	Paul Bagus	The Origin of Unusual Work Function Changes Induced by Halogens Adsorbed on Metal Surfaces: A Quantum Chemical Analysis
		Session 1B
10:40 AM	A. Z. Msezane	Near-Threshold Electron Elastic Scattering Cross Sections: A Regge Pole Analysis
11:00 AM	Jerzy Leszczynski	New Findings on Proton Transfer in DNA Base Pairs
11:20 AM	Barbara Garrison	Modeling Light Interaction with Materials: Techniques to Successfully Incorporate Chemistry and Physics in Molecular Simulation
11:40 AM	Yngve Ohrn	Fragmentation of polyatomic molecules in collisions with atomic ions
		Session 2A
2:00 PM	Andrew Williamson	Quantum Monte Carlo calculations of weak interactions: The search for hydrogen storage materials
2:20 PM	Arne Luechow	Optimization of nodal hypersurfaces for fixed-node diffusion quantum Monte Carlo
2:40 PM	Henry F. Schaefer	Combustion Chemistry: The Mysterious Ortho Benzyne
3:00 PM	Ursula Roethlisberger	TBA
3:20 PM	Alan Aspuru-Guzik	Quantum Algorithms and Excitonic Energy Transfer
		Session 2B
4:10 PM	Moshe Shapiro	Derivation of the coordinate-momentum commutation relations from Canonical Invariance

ORAL PRESENTATIONS

Thursday, March 29, 2007		**Session 2B (Continue)**
4:30 PM	William H. Miller	Using the Initial Value Representation of Semiclassical Theory to Include Quantum Effects in Classical Molecular Dynamics Simulations
4:50 PM	Joseph S. Francisco	Proton Affinity of Alkyl Nitrites and Alkyl Nitrates: Implications for Measuring Branching Ratios of Nitrates and Nitrites from Atmospheric RO + NO2 and RO2 + NO Reactions
5:10 PM	Barry Dunietz	Exploring conductance switching properties of molecular scale devices - a computational approach
Friday, March 30, 2007		**Session 3A**
8:30 AM	John Shumway	Path Integral Simulations of Atoms and Molecules
8:50 AM	Shigenori Tanaka	Quantum Monte Carlo Calculations of Biomolecules Based on Fragment Molecular Orbital Method
9:10 AM	Krishnan Raghavachari	G3 and G4 models for accurate thermochemistry: Recent advances
9:30 AM	Peter Pulay	Large Coupled Cluster Calculations on Inexpensive Parallel Computers: Applications to Weak Interactions
9:50 AM	Theodore Goodson III	Investigations of Light Harvesting and Enhanced Nonlinear Optical Properties in Organic Dendrimers and Branched Macromolecules
		Session 3B
10:40 AM	Joel M. Bowman	Ab initio-based Potential Energy Surfaces and the “Discovery” of Unusual Dynamics On Them
11:00 AM	George C. Schatz	Theoretical Studies of Metal Cluster Optical Properties
11:20 AM	Frank Rebentrost	Direct Observation of Collisions
11:40 AM	Vladimir Kresin	Pair correlation in metallic nanoclusters: high Tc state and potential for room temperature superconductivity
12:00 PM	Mostafa El-Sayed	Nano-Talk on Nanoscience
		Session 4A
2:00 PM	M. H. Kalos	On Mirror Potentials

ORAL PRESENTATIONS

Friday, March 30, 2007		**Session 4A (Continue)**
2:20 PM	Lubos Mitas	Pfaffian wavefunctions and topology of fermion nodes
2:40 PM	Jeffrey Grossman	Quantum Monte Carlo Calculations for Molecular Systems
3:00 PM	John Harkless	High-Accuracy ab initio studies of S4 energetics
		Session 4B
3:50 PM	Michael R Philpott	Bonding in Transition Metal Sandwich Molecules
4:10 PM	Berni Alder	The History of Quantum Monte Carlo
4:30 PM	Brian Hammond	Wake Me Up Before You QMC: A Retrospective of the Lester Group in the 80's
4:50 PM	William A. Lester, Jr.	My Research Career
Saturday, March 31, 2007		**Session 5A**
8:30 AM	Francesco Pederiva	Shadow Wave Functions for many electron systems
8:50 AM	Frank Hagelberg	The formation of alkanethiol monolayers on the Au(111)
9:10 AM	Michel Dupuis	Electronic Structure in Complex Systems
9:30 AM	Martin Head-Gordon	New electronic structure methods for large radicals
9:50 AM	A. D. Dutoi	Computational Study of Orientation-dependent Molecular High Harmonic Spectra
		Session 5B
10:40 AM	Steven L. Richardson	Diamondoids Are Forever: Novel Molecular Building Blocks for Nanoscience
11:00 AM	Michael Frenklach	Graphene Layer Growth Chemistry
11:20 AM	Glake Hill	The Role of DNA Methylation on Tautomeric Equlibria and Electron Migration
11:40 AM	Carlos Amador-Bedolla	Electron pair localization function: towards a theoretical electrophilicity scale
12:00 PM	Brian Austin	Efficient Optimization of Correlation Functions for Quantum Monte Carlo

Correlated Sampling in Corrections for Diffusion Quantum Monte Carlo

James B. Anderson
Departments of Chemistry and Physics
Pennsylvania State University
University Park, Pennsylvania 16802

We have described previously a scheme for calculating corrections to trial wavefunctions and their energies to obtain fixed-node diffusion QMC results with very high accuracies. The scheme succeeds because the statistical error appears in the small correction terms and not in the complete wavefunctions or the energies. We now report the use of correlated sampling to obtain still higher accuracies in the differences in energies for similar systems and/or similar trial wavefunctions. This extended method succeeds because the differences in weights for correlated walkers are minimized. Results have been obtained for the H_2 and C_{10} systems. We expect it to be especially useful in predicting weak intermolecular interactions.

Critical analysis of reptation quantum Monte Carlo

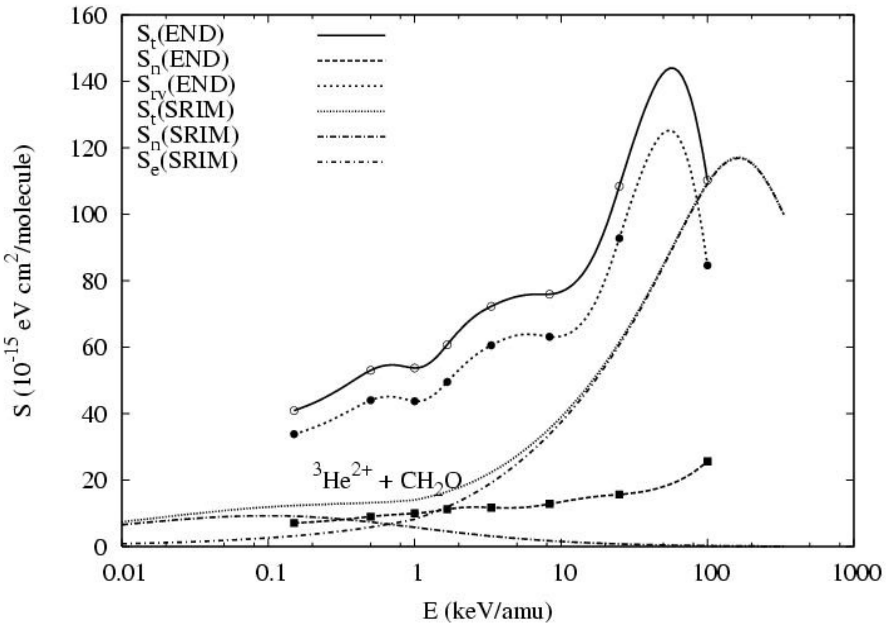
Wai Kong Yuen[1], Thomas J Farrar[1] and Stuart M Rothstein[2]
[1]Department of Mathematics, Brock University, St. Catharines, ON L2S 3A1, Canada.
[2]Departments of Chemistry and Physics, Brock University, St. Catharines, ON L2S 3A1, Canada.

Since its publication, the reptation quantum Monte Carlo algorithm of S. Baroni and S. Moroni (1999 Phys. Rev. Lett. **82** 4745) has been applied to several important problems in physics, but its mathematical foundations are not wellunderstood. We will demonstrate the (in principle) beneficial effect of relaxing some of the assumptions that underlie the algorithm. Furthermore, we will compare its facility for exact property estimation to that of more commonly-used algorithms.

Theoretical Investigation of Fragmentation and Energy Deposition Cross Sections for Proton Impact on a Protobiotic Molecule: Formaldehyde

John R. Sabin[1,2]
PO Box 118435, University of Florida, Gainesville, Florida 32611, USA

The subject of the theoretical and computational work presented in this talk is related to damage of cellular matter caused by energetic, charged particle radiation such as electrons, protons, and alpha particles. The direct damage to DNA by swift ions is less important than the damage caused to DNA by intermediate species produced by interaction of the radiation with other components of the cellular medium. These intermediate species include ions, radicals, and electrons, which, by a variety of mechanisms, can be involved in reactive processes which result in serious damage to DNA and other biomolecules. We investigate these processes using a theoretical scheme known as Electron Nuclear Dynamics (END), which is time dependant, direct, and non-adiabatic. As no potential surfaces are required in this approach, the instantaneous coulomb forces among the participating electrons and nuclei steer the dynamics of the process. The coupling among all electrons and electrons is explicit. The major advantage of this method is that all possible product channels are considered together, and all at the same level of approximation, thus increasing the reliability of prediction of product distributions. The studies reported here involve protons colliding with a small biomolecules, namely formaldehyde. In particular we will discuss fragmentation and energy deposition (stopping) cross sections for the $^3He^{2+} \rightarrow H_2CO$ collision.



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[1] In collaboration with Nikolaus Stolterfoht, Remigio Cabrera-Trujillo, Erik Deumens, and Yngve Öhrn

[2] sabin@qtp.ufl.edu

The Origin of Unusual Work Function Changes Induced by Halogens Adsorbed on Metal Surfaces: A Quantum Chemical Analysis

Paul S. Bagus

Department of Chemistry, University of North Texas, Denton, Texas

and

Christof Wöll

Lehrstuhl für Physikalische Chemie I, Ruhr-Universität Bochum, D-44780 Bochum, Germany

The traditional explanation of changes in the work function, ϕ, induced by adsorbates on metal surfaces has been in terms of charge transfer, CT, between the substrate and the adsorbate. This explanation was introduced by Langmuir and Kingdon,[1] who interpreted the lowering of ϕ, $\Delta\phi<0$, when Cs was adsorbed on a W surface as arising from charge transfer from Cs, a cationic adsorbate, to the metal surface. Similarly, anionic adsorbates, as occurs with electron acceptors like halogens, should increase ϕ because charge flows from the surface to the adsorbate. However, there is evidence for Pt[2] and for Ni[3] surfaces that the adsorption of anionic Iodine may actually lower rather than raise ϕ. Our recent work,[4, 5] based on the rigorous determination of the electronic wavefunctions for cluster models of the surfaces, shows that other factors, in addition to CT, contribute to $\Delta\phi$. In this presentation, we compare the $\Delta\phi$ induced by Cs, a cationic adsorbate, and by I, an anionic adsorbate, on Cu(111), representative of transition metal surfaces. We show that adsorption of Cs, as expected, lowers ϕ but that I also leads to a significant decrease in ϕ even though it is adsorbed essentially as a fully anionic species. We use a theoretical method of constrained variations[6] to determine the importance of the different chemical mechanisms that contribute to $\Delta\phi$ and show why an adsorbed anion can actually lower ϕ.

[1] I. Langmuir and K. H. Kingdon, Phys. Rev. **21**, 381 (1921).
[2] S. K. Jo and J. M. White, Surf. Sci. **261**, 111 (1992).
[3] Y. Yang and J. A. Yarmoff, J. Vac. Sci. Technol., A **21**, 1317 (2003).
[4] P. S. Bagus, V. Staemmler, and C. Woll, Phys. Rev. Lett. **89**, 096104 (2002).
[5] P. S. Bagus, K. Hermann, and C. Woll, J. Chem. Phys. **123**, 184109 (2005).
[6] P. S. Bagus and F. Illas, J. Chem. Phys. **96**, 8962 (1992).

Near-Threshold Electron Elastic Scattering Cross Sections: A Regge Pole Analysis

A. Z. Msezane[1], Z. Felfli[1] and D. Sokolovski[2],
[1]Department of Physics and Center for Theoretical Studies of Physical Systems,
Clark Atlanta University, Atlanta, Georgia 30314, USA.
[2] School of Mathematics and Physics, Queen's University of Belfast,
Belfast, BT7 1NN, UK

In quantum scattering, the presence of a sufficiently narrow resonance allows the collision partners to form a long-lived intermediate complex. In order to preserve the total angular momentum this complex must rotate as it decays back into its constituent parts. Rotation of the complex takes scattering into angular regions not readily accessible to a direct scattering mechanism, and alters the appearance of the differential cross section (DCS). In this paper we consider a system trapped in such a resonance state and allow it to decay at zero scattering angle, which through the optical theorem can be related to the total cross section (TCS).

Within the novel and elegant Mulholland description of the total elastic cross sections as implemented within the complex angular momentum (CAM) representation of scattering, wherein resonances are rigorously defined as singularities of the S-matrix, we exploit the recent successful analysis of low-energy oscillations in the elastic total cross sections for proton – hydrogen scattering [1] to study the formation of negative ions as Regge resonances in electron-atom scattering [2, 3]. The Regge trajectories allow us to probe electron attachment at its most fundamental level near threshold, thereby uncovering new manifestations and possibilities. In particular, the near threshold region in electron elastic scattering from atoms, ions and molecules is generally difficult to access experimentally. But the CAM method allows us to probe electron scattering to very near threshold, yielding unprecedented body of knowledge, which is incredibly simple to interpret and the fundamental physics is transparent (*e.g.* the Ramsauer-Townsend minima, positions of resonances and, most recently the DCS's critical minima and the Wigner threshold law).

Our methodology could also be used to extract the scattering length with significant implications for *inter alia* Bose-Einstein Condensation and related phenomena. Preliminary results in e^- -K and e^--Rb attachment exhibit peculiarities, including a d-wave Wigner threshold law and research on e^--Au and e^--Pt as well as e^--Ag and e^--Cu reveals exciting signatures. Partial Regge cross sections, DCS's and TCS's for various electron collisions at near threshold energies will be presented and discussed.

Acknowledgements

This work was supported by U.S. DoE, Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research and AFOSR.

[1] J. H. Macek, P.S. Krstic and S. Yu. Ovchinnikov, Phys. Rev. Lett. **93**, 183203 (2004)
[2] D. Sokolovski, Z. Felfli, S. Yu. Ovchinnikov, J.H. Macek and A.Z. Msezane, Phys. Rev. A, Submitted (2006)
[3] Z. Felfli, A.Z. Msezane and D. Sokolovski, J. Phys. B At. Mol. Opt. Phys. **39,** L353-L359 (2006)

New Findings on Proton Transfer in DNA Base Pairs

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Computational Center for Molecular Structures and Interactions
Jackson State University, Jackson, MS 39217-0510, USA
E-mail: Jerzy@ccmsi.us

The structure, function and dynamics of nucleic acid molecules are influenced by a variety of factors. These phenomena are far too complex to be revealed by any single research method. Among the techniques successfully applied in investigations of features of different species including large biomolecules, computational methods have increasingly gained popularity. Fast development of hardware and constant improvements in computer coding make high-performance computational techniques a promising alternative to experimental studies. This is especially attractive when experimental data are not available and a theoretical approach could supply information of accuracy matching those of reliable experiments.

In order to acquire information concerning complex molecular systems, a number of different techniques have to be applied. DNA components certainly are among the most elaborated biomolecules, and details of their activity are far from being completely understood. Recently computers are routinely applied in such studies, and at least visualization, database, and simple energy minimalization procedures are performed in most experimental laboratories. Nonempirical calculations, which employ a high level of theory, are alternative sources of information for DNA fragments. Ab initio techniques have been in the last few years successfully applied to reveal information concerning their structures and characteristics. In particular ab initio methods predict the nonplanarity of amino groups in nucleic acid bases, the flexibility of the bases and their complexes, and origins of stabilization of the stacked pairs. This type of accurate calculations also provides reference data for verification and parametrization of empirical potentials. Recent predictions have brought details of the influence of polar solvents on the molecular structures and stabilities of isolated and hydrogen-bonded bases and also explain the role of metal cations in metal cation-assisted stabilization of triplexes of the DNA bases. It is important to realize that although the current qualitative estimations could change upon application of more accurate calculations schemes, we do believe that the general conclusions will remain. In the near future one will see an extension of such calculations to bigger fragments of DNA and more complex interactions and also faster and more accurate tools for such predictions.

The talk covers the results of recent high level ab initio studies on single and double proton transfer in model complexes and the GC and AT DNA base pairs. The discussion will focus on their molecular structures, stabilities, hydrogen bonding, proton transfer and vibrational characteristics.

Modeling Light Interaction with Materials: Techniques to Successfully Incorporate Chemistry and Physics in Molecular Simulation

Patrick F. Conforti[1], Manish Prasad[1], and **Barbara J. Garrison**[2].
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(2) Department of Chemistry, The Pennsylvania State University Fax: 814-863-8403,
bjg@psu.edu

Irradiation of a substrate by laser light initiates the complex chemical and physical process of ablation where large amounts of material are removed. Ablation has been successfully used in techniques such as MALDI and LASIK surgery, however, a fundamental understanding of the process is necessary in order to further optimize and develop applications. To accurately describe the ablation phenomenon, a model must take into account the multitude of events which occur when a laser irradiates a target including electronic excitation, bond cleavage, desorption of small molecules, on going chemical reactions, propagation of stress waves, and bulk ejection of material. We have developed a coarse-grained molecular dynamics (MD) protocol with an embedded Monte Carlo scheme which effectively addresses each of these events during the simulation. Using the simulation technique, the effects ultraviolet photon absorption and the subsequent dynamics of poly(methyl methacrylate) (PMMA) is detailed.

Fragmentation of polyatomic molecules in collisions with atomic ions

Yngve Öhrn
Quantum Theory Project, University of Florida, Gainesville, FL, 32611

Reactive encounters of atomic ions with polyatomic molecules at energies in the keV range commonly falls outside the scope of adiabatic theory. Such processes involves a large number of stationary electronic states and associated many-dimensional potential energy surfaces making approaches that employ such quantities prohibitively difficult. Electron Nuclear Dynamics[1] (END)[2] offers a time-dependent and nonadiabatic approach to molecular processes that works via instantaneous Coulombic interactions among participating electrons and atomic nuclei. A brief presentation of recent advances in this approach to dynamical processes will be followed by a discussion of results with comparisons to experiment for proton collisions with hydrocarbon molecules. Calculated and experimental cross sections and fragmentation patterns for He^{2+} and He^{+} collisions with water molecules[3] will also be presented.

This work was supported by NSF grant 0513386.

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[1] Y. Öhrn et.al., in *Time-Dependent Quantum Molecular Dynamics*, edited by J. Broeckhove and L. Lathouwers (Plenum, New York, 1992), pp279-292

[2] E. Deumens, A. Diz, R. Longo, and Y. Öhrn, Rev. Mod. Phys. 66, 917 (1994)

[3] N. Stolterfoht, R. Cabrera-Trujillo, R. Hellhammer, Z. Pesic, E. Deumens, Y. Öhrn, and J. R. Sabin, Adv. Quantum Chemistry (in press) (2006)

Quantum Monte Carlo calculations of weak interactions:
The search for hydrogen storage materials

Andrew Williamson
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Hydrogen is a clean energy source with the potential to replace fossil fuels. However, the practical implementation of H fuel has been impeded by the lack of a safe, economical, and efficient means of storing hydrogen at room temperature. Among the various available approaches, carbon-based nanostructures have attracted considerable attention as well as heated debate. In this talk, we investigate the possibility of using a non-dissociative H adsorption mechanism to store H in boron and beryllium doped carbon fullerenes. Our calculations were performed using a combination first-principles, electronic structure methods. Structural searches were carried out using density functional theory calculations within the local density approximation. To enable us to make quantitative predictions of the hydrogen binding energetics we have selectively carried out fixed node, diffusion quantum Monte Carlo calculations using the linear scaling version of the CASINO QMC code.

Optimization of nodal hypersurfaces for fixed-node diffusion quantum Monte Carlo

Arne Lüchow
Institute for Physical Chemistry
Aachen university of technology, 52056 Aachen, Germany

The accuracy of the fixed-node diffusion quantum Monte Carlo method is limited only by the accuracy of the nodal hypersurface of the guide function. First results for the direct optimization of CI coefficients of a multideterminant guide function are presented using a local criterion for the accuracy of the nodal hypersurface.

Combustion Chemistry: The Mysterious Ortho Benzyne

Henry F. Schaefer III
Center for Computational Chemistry
University of Georgia

Ortho benzyne was discovered in 1953 by Professor John D. Roberts (then at MIT, now at Cal Tech). Since then, benzyne has been accepted as one of the most appealing and important reactive intermediates in organic chemistry. The unimolecular decomposition of benzyne to acetylene plus diacetylene provides a mechanism for the loss of benzyne under conditions suitable for combustion.

Quantum algorithms and coherent excitonic energy transfer

Alán Aspuru-Guzik, Masoud Mohseni, Ali Najmaie and Ivan Kassal,
Department of Chemistry and Chemical Biology
Harvard Univesrity
12 Oxford Street M113, Cambridge, MA 02138

Recently, Engel *et al.* [1] have shown experimental evidence of quantum beats in the Fenna-Mathews-Olson [2] chromophore complex of green sulfur bacteria. Engel *et al.* suggest that the complex "effectively acts as a quantum computational device". We explore their suggestion formally and make a connection between excitonic energy transfer in the coherent regime and quantum algorithms.

[1] G S. Engel, T. R. Calhoun, E. L. Read,1 T. K. Ahn, T. Mancal, Y.-C. Cheng, R. E. Blankenship and G. R. Fleming, *Nature*, In press.
[2] R. E. Fenna and B. W. Matthews, *Nature* **258**, 573 (1975).

Derivation of the coordinate-momentum commutation relations from Canonical Invariance

Moshe Shapiro
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The University of British Columbia, Vancouver, Canada
and
Department of Chemical Physics,
The Weizmann Institute, Rehovot, Israel

We discuss our recent derivation [Phys. Rev. A **74**: 042104 (2006)] of the coordinate-momentum commutation relations. The derivation is based on three very basic building blocks: the spectral resolution definition of the momentum operator, the linearity of the correspondence between physical observables and quantum Hermitian operators, and the definition of conjugate coordinates-momenta in classical mechanics. Using these building blocks we show that the $[q,p]$ coordinate-momentum commutator must have the value $i*a$ where a is a real non-zero C-number (which we naturally identify with $\hbar$). The results are then generalized to include all types of canonical coordinates and momenta as well as the Cartesian special-relativistic case. Finally we show how to derive the time-energy commutation relation and the quantum mechanical evolution equations.

Using the Initial Value Representation of Semiclassical Theory to Include Quantum Effects in Classical Molecular Dynamics Simulations

William H. Miller
Department of Chemistry
University of California
Berkeley, CA 94720

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

Proton Affinity of Alkyl Nitrites and Alkyl Nitrates: Implications for Measuring Branching Ratios of Nitrates and Nitrites from Atmospheric RO + NO_2 and RO_2 + NO Reactions

Joseph S. Francisco

Department of Chemistry and Department of Earth and Atmospheric Science

Purdue University

West Lafayette, IN 47907

Alkyl nitrates have been thought to contribute to the missing NO_y fraction, due to their relatively long atmospheric lifetimes, greater than or equal to a week at Earth's surface and several days at high altitudes. NO_y comprised of NO_X(NO + NO_2) leads to tropospheric ozone. Moreover, alkyl nitrate formation is key to the role of volatile organic compounds in global NO_X transport. VOC's also contribute to air pollution and ozone formation. We need to have a better understanding of the abundance, formation and loss mechanism, at a molecular level, for organic nitrites and nitrates; in particular alkyl nitrites and nitrates. Branching ratios are very important because they set the relative importance of chain propagation and termination and its dependence on the identity of the R alkyl group. In order to determine what fraction of RO_2 + NO gives alkyl nitrates and alkyl nitrites, a new experimental method will be discussed based on results from computational studies of alkyl nitrites and alkyl nitrates that should allow the measurement of branching ratios cleanly and unambiguously for alkyl nitrites and alkyl nitrates.

Exploring conductance switching properties of molecular scale devices - a computational approach

Barry D. Dunietz
Department of Chemistry, University of Michigan, Ann Arbor, MI 48109

A computational approach is used and developed to study electron transport through molecular scale devices. The study identifies and provides insight into mechanisms underlying transport switching properties. These systems include: 1. Spin-dependent electronic transport through a Porphyrin ring Ligating an Fe(II) atom, 2. Contact geometry and orientation effects of conjugated molecular transistors and 3. Chemical sensors with focus on metal recognition properties recently exhibited only for certain short peptide chains. The research also involves developing new models and methods to describe electron conductance through single molecular systems.

Path Integral Simulations of Atoms and Molecules

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By closing random walks after an imaginary time beta, finite temperature properties may be sampled. We are exploring techniques to simulate chemical bonding and atomic motion within ab initio path integral simulations. I will present benchmark calculations on small atoms and molecules, focusing on our recent work to extract equilibrium geometries, polarizabilities, and vibrational frequencies.

Quantum Monte Carlo Calculations of Biomolecules Based on Fragment Molecular Orbital Method

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Fragment molecular orbital (FMO) method has successfully been applied to the calculations of electronic structure of huge biomolecules and their complexes such as proteins and nucleic acids [1]. Exploiting the advantage of FMO methodology regarding high accuracy and much reduced computational cost due to the fragmentation and parallelization, we have attempted the inclusion of quantum Monte Carlo (QMC) method into the highly accurate calculations of biopolymers. This idea is amenable to the hierarchical and layered formulation of FMO method which also enables us to perform costly QMC calculations only for focused regions to be investigated in electron-correlated details. As for benchmark QMC calculations coupled with the FMO concept, we report the results of Hartree-Fock and variational (Slater-Jastrow) Monte Carlo calculations for the ground-state energies of glycine trimer and stacked DNA base pairs, finding that the combined QMC-FMO approach works very well.

[1] *"Modern Methods for Theoretical Physical Chemistry of Biopolymers"*, ed. by E.B. Starikov, J.P. Lewis, and S. Tanaka (Elsevier B.V., Amsterdam, The Netherlands, 2006).

G3 and G4 models for accurate thermochemistry: Recent advances

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Accurate quantum chemical techniques such as Gaussian-3 (G3) theory have been proposed in recent years to evaluate the thermochemistry of small molecules from first principles. We analyze the molecules where there are significant deviations and discuss schemes for extending the range of applicability of such methods. In this work, we discuss the recently developed Gaussian-4 (G4) theory and illustrate its performance for a comprehensive test set of first- and second-row molecules. Extensions to molecules containing heavier elements (main-group as well as transition metals) are also discussed.

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Large Coupled Cluster Calculations on Inexpensive Parallel Computers: Applications to Weak Interactions

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A new parallel Coupled Cluster program (including related electron correlation methods such as Quadratic CI, CEPA-2, MP4) is described. The method uses Array Files [1] for message-passing parallelization, and is intended to be used on PC-based parallel computers. The program allows calculations of unprecedented size (e.g. over 1500 basis functions for QCISD) on inexpensive PC clusters. We have recently implemented triple substitutions. The new program has allowed us to get definitive results, e.g. for the benzene-benzene interaction, and for the attractive force between aromatic molecules and H_2, an important problem in view of the potential use of carbon nanotubes for hydrogen storage.

[1] A. R. Ford, T. Janowski and P. Pulay, J. Comput. Chem. **2007**, in press.

Investigations of Light Harvesting and Enhanced Nonlinear Optical Properties in Organic Dendrimers and Branched Macromolecules

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Organic conjugated macromolecules have received great attention due to their use in optical and electronic applications. Certain molecular aggregate systems have shown enhanced nonlinear optical properties by virtue of excitonic coupling in the multi-chromophore system. Organic dendrimers and other branched multi-chromophore systems (were the chromophores are covalently attached) have also shown characteristic properties of strong intra-molecular interactions which have been utilized in light harvesting processes, light emitting diodes, as well as for enhanced nonlinear optical effects. The mechanism of the strong intramolecular interactions in branched chromophores depends on the nature of the branching center, the geometrical orientation of covalently attached chromophores, and the extent of delocalization in the dendrons. Through steady-state and time-resolved spectroscopy, we have characterized the mechanism of energy transport and the relative strength of intra-molecular interactions. In this presentation, organic dendrimers and other branched chromophores are described by their time-resolved fluorescence and absorption properties. Different dendrimers with varying branching centers, dendrons, and degree of intramolecular interactions will be presented. For particular dendrimer systems the processes of efficient energy transfer, fast energy re-distribution, enhanced two-photon absorption cross-sections, and a delocalized excitation with weaker electronic coupling to the bath (solvent) will be discussed.

Representative Publications

Varnavski, O. P.; Ranasinghe, M.; Yan, X.; Bauer, C. A.; Chung, S.-J.; Perry, J. W.; Marder, S. R.; Goodson, T., III *Ultrafast Energy Migration in Chromophore Shell-Metal Nanoparticle Assemblies J. Am. Chem. Soc.;* **2006**; *128*(34); 10988-10989

Bhaskar, A.; Ramakrishna, G.; Lu, Z.; Twieg, R.; Hales, J. M.; Hagan, D. J.; Van Stryland, E.; Goodson, T., III *Investigation of Two-Photon Absorption Properties in Branched Alkene and Alkyne Chromophores J. Am. Chem. Soc.;* **2006**; *128*(36); 11840-11849.

Bhaskar, A.; Guda, R.; Haley, M. M.; Goodson, T. G., III
Building Symmetric Two-Dimensional Two-Photon Materials
J. Am. Chem. Soc.; **2006**; *128*(43); 13972-13973

Goodson, T "Optical Excitations in Organic Dendrimers Investigated by Time-Resolved and Nonlinear Optical Spectroscopy" Accts. Chem. Res. **2005**; *38*(2); 99-107

Varnavski, O and Goodson, T "Exciton Dynamics in a Branched Molecule Probed with Three Pulse Photon Echo Peak Shift and Transient Grating Spectroscopy", *J. Phys. Chem*., **2004**, *108*(29); 10484-10492.

Wang, Y; Ranasinghe, M.; Goodson, T.; "Mechanistic Studies of Energy Transport in a Phosphorous Cored Branching Structure," *J. Amer. Chem. Soc.* **2003**, 125, 9562-9563.

Ranasinghe, M.I.; Varnavski, O.P.; Pawlas, J.; Hauck, S.I.; Louie, J.; Hartwig, J.F.; Goodson, T., "Femtosecond Energy Transport in Triarylamine Dendrimers," *J. Am. Chem. Soc.* **2002**,*124*, 6520-6521.

ABSRACT FOR THE BILL LESTER SYMPOSIUM

Ab initio-based Potential Energy Surfaces and the "Discovery" of Unusual Dynamics On Them

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I will present an example of unusual molecular motion using an *ab initio*-based global potential energy surface, which has the property of invariance with respect to permutation of like atoms. The example will be one of the following: "roaming- atom" reaction dynamics in H_2CO[1] and possibly CH_3CHO photodissociation, vibrational motion and IR spectroscopy of CH_5^+ and isotopomers,[2] the $OH+NO_2$ association reaction to form HOONO and $HONO_2$.[3]

Acknowledgments: Many thanks to Bas Braams, Anne McCoy, Larry Harding and Stuart Carter for wonderful collaborations and to John Farnum, Ben Shepler, Chao Chen, and Xinchuan Huang for doing the coding, calculations, and other essential research. Also thanks to the Department of Energy, the National Science Foundation and the Office of Naval Research for financial support.

1. (a) D. Townsend, S. A. Lahankar, S. K. Lee, S. D. Chambreau, A. G. Suits, X.-B. Zhang, J. Rheinecker, L. B. Harding, and J. M. Bowman, Science **306**, 1158 (2004); (b) H. M. Yin, S. H. Kable, X. Zhang, and J. M. Bowman, Science **311** (5766), 1443 (2006).
2. (a) X. Huang, A. B. McCoy, J. M. Bowman, L. M. Johnson, C. Savage, F. Dong, and D. J. Nesbitt, Science **311**, 60 (2006); (b) X. Huang, L. M. Johnson, J. M. Bowman, and A. B. McCoy, J. Amer. Chem. Soc. **128** (11), 3478 (2006).
3. "Potential Energy Surface and Reaction Dynamics of the $OH+NO_2$ Reaction", C. Chen, B. C. Shepler, B. J. Braams and J. M. Bowman, J. Amer. Chem. Soc., submitted.

Theoretical Studies of Metal Cluster Optical Properties

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This talk describes the use of electronic structure theory to calculate extinction, Rayleigh and Raman scattering and other optical properties of silver and gold metal clusters, both in the presence and absence of adsorbed molecules. These calculations are designed to provide a “first principles” understanding of electronic excitations in clusters with 2-100 atoms, and the connection of these results to plasmon excitation. We also model surface enhanced Raman spectroscopy (SERS), to determine the importance of the chemical (CHEM) and electromagnetic (EM) enhancement mechanisms.

This work is a followup to extensive work that my group has done with continuum electrodynamics methods to describe the optical properties of larger (>5 nm) nanoparticles. This past work has provided estimates of SERS EM enhancement factors that range up to as high as 10^{11} for very special structures in which two particles form a junction, and the intensities refer to an electromagnetic hot spot that occurs at the junction location. These calculations inevitably predict highest enhancements for particle separations of 1 nm or less, which is too small to enable reliable predictions based on continuum theory.

Our electronic structures calculations are based on a modified version of the ADF code in which we use time dependent density functional theory (TDDFT) to calculate resonant frequency dependent polarizabilities and polarizability derivatives, including for the excited state dephasing with empirical damping factors. We have tested this code with applications to small alkali metal, silver and gold clusters (1-20 atoms) where experimental spectra are known from photodepletion, photodetachment and matrix isolation measurements, and we have also used the code to study the resonance Raman spectra of molecules like uracil, pyrene and rhodamine 6G. For 20 atom Na, Li and Ag clusters, the electronic spectra are dominated by a single strong absorption at a wavelength that is close to the plasmon wavelength, however Au_{20} shows a broad absorption maximum as a result of relativistic effects, and the extinction peak is blue shifted from the plasmon maximum.

Our SERS calculations for pyridine/Ag_{20} show an enhancement factor of about 10^6 with factor of 10 variation of enhancement with adsorption geometry. When the enhancement factor is broken down into CHEM and EM contributions, we find a CHEM enhancement factor of about 10, and EM of 10^5, thus providing a result that is consistent with past estimates from continuum electrodynamics, but for a non-plasmonic excited state. We have also studied junction structures which consist of pyrazine between two Ag_{20} clusters, and we find greatly enhanced CHEM contributions, but suppressed EM contributions such that the total enhancement is about the same. For pyridine/Au_{20} clusters, we find greater CHEM enhancements and smaller EM enhancements than for pyridine/Ag_{20}. We also discuss several issues of importance in extinction spectroscopy, including the coverage dependence of the enhancement factors and influence of particle interactions on the plasmon resonance wavelength.

Direct observation of collision complexes

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Laser excitation of collisional systems is observed in optical collisions

$$A + X + h\nu \rightarrow A^* + X$$

where the active atom A is an alkaline or earth-alkaline atom and X is an atom (typically a rare gas) or a molecule. The laser is detuned from a resonance transition in A. According to the Franck-Condon principle the optical transition occurs localized at geometrical configurations of the transient collision complex where the laser is resonant to the difference of the lower and upper molecular potentials involved (Condon point). The fine-structure interaction in alkaline atoms is the source of nonadiabatic transitions that are observable by the branching ratios of the final A^* states.

With the successful implementation of the crossed-beam technique a new experimental level in the study of optical collisions was reached [1]. The angular resolution obtained by the differential detection of the final A^* state and the well-defined collision energy allows a very selective choice from the ensemble of collision events. This is seen in pronounced oscillatory structures in the differential cross sections that are highly sensitive to the underlying potentials [2]. The well-defined geometry in a crossed-beam experiment allows to localize the internuclear axis at the instant of the excitation of the collision complex (Condon vector) and thus provides a direct image of its geometry. For the case where X is a molecule (N_2, CO, CO_2, C_2H_2) average geometries are seen [3].

The relative population of the fine-structure levels of the product atom A^* reflects nonadiabatic interactions in the exit channel of the optical collision. For molecular colliders, conical intersections in the upper potential surfaces are of significant importance for the nonadiabatic dynamics of optical collisions.

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[2] F. Rebentrost, S. Klose, J. Grosser, Eur. Phys. J. D **1**, 277 (1998).

[3] A. Grimpe, C. Figl, J. Grosser, O. Hoffmann, F. Rebentrost, J. Phys. B **38**, 135 (2005).

Pair correlation in metallic nanoclusters: high T_c state and potential for room temperature superconductivity

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and
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The pair correlation leads to a peculiar state of matter which is manifested in such diverse fields as solid state physics (superconductivity), nuclear physics, astrophysics, biology, etc. The existence of shell structure and accompanying high degeneracy of electronic levels leads to the possibility of strong superconducting pairing in small metallic nanoclusters ($N \approx 10^2$-10^3 delocalized electrons). We focus on small metallic nanoclusters ($N \approx 10^2$-10^3 ; N is a number of free carriers) which contain delocalized electrons. These electrons form shells similar to those in atoms or nuclei. The most favorable cases correspond to some specific “magic”clusters as well as to slightly deformed particles with small Jahn-Teller splitting.One can show that under special, but perfectly realistic conditions the superconducting pairing is very strong and this leads to high values of T_c as well as to a strong alteration of the energy spectrum. This feature is promising for the creation of high T_c tunneling networks. In principle, it is possible to raise T_c up to room temperature .

Nano-Talk on Nanoscience

Mostafa El-Sayed
Chemistry & Biochemistry, Georgia Institute of Technology
901 Atlantic Drive, Atlanta, GA 30332-0400

We will show some slides on: the origin of the Megahype of the Nanofield, Some interesting results on Nano-Catalysis, Nano-Motors and Nano-Medicine.

On Mirror Potentials

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Francesco Pederiva
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Monte Carlo calculations on many-fermion systems can be carried out in principle by using a pair of external many-body potentials that we have called "mirror potentials." They serve to stabilize the populations against the exponential decay of signal-to-noise in a computation without a fixed node. Unfortunately, determining the exact form of the mirror potential is a challenging computation in itself. We have been studying the nature of the mirror potential and experimenting with the idea that adding a small amount of an approximate potential can make our Fermion Monte Carlo more robust. Results of such experiments will be presented.

Pfaffian Wavefunctions and Topology of Fermion Nodes

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Recent developments in quantum Monte Carlo open new avenues to attack the only approximation involved (the fixed-node approximation) by understanding the topology of fermion nodes. In particular, we explicitly prove that for d>1 fermion ground states have the minimal number of two nodal cells for arbitrary system size under very general conditions. We show that pairing wavefunctions, such as the Bardeen-Cooper-Schrieffer and pfaffian wavefunctions, have this important property and enable to decrease the fixed-node errors in a very compact manner. We illustrate the performance of these wavefunctions on the first-row systems.

* in collaboration with L.K. Wagner, M. Bajdich, G. Drobny, K.E Schmidt
(Arizona State U.).

Ref: PRL 96, 130201; 96, 240402; 94, 056403; cond-mat/0610088, /0605550.

Quantum Monte Carlo Calculations for Molecular Systems

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The application of the diffusion Monte Carlo method to compute binding energies, optical properties, and reaction pathway energetics for a variety of molecular systems and properties will be presented, including comparisons with other ab initio methods. In addition, an approach is presented to provide accurate dynamical total energies by coupling stochastic, imaginary-time quantum Monte Carlo steps with real-time atomic quantum molecular dynamics motion.

High-Accuracy ab initio studies of S_4 energetics

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We apply the quantum Monte Carlo method to the problem of energetics of S_4 conformers and dissociation. The results presented here estimate the energy gap between the C_{2V} and D_{4h} conformers of S_4, an important species in interstellar chemistry using variational Monte Carlo (VMC) and diffusion Monte Carlo (DMC). In addition to the energy gap of the conformers, we also provide VMC and DMC estimates of atomization and bond energies of S_4, as well as selected excited states. The overall effectiveness and accuracy of the method is compared against other available theory and experiment.

Bonding in Transition Metal Sandwich Molecules

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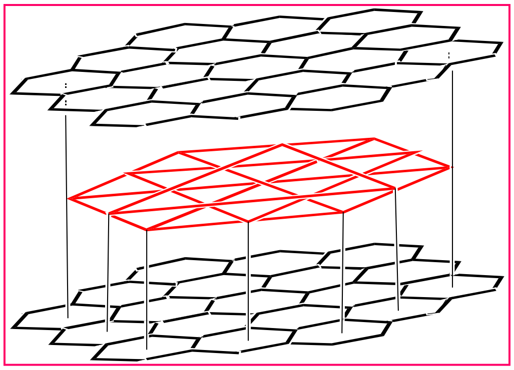
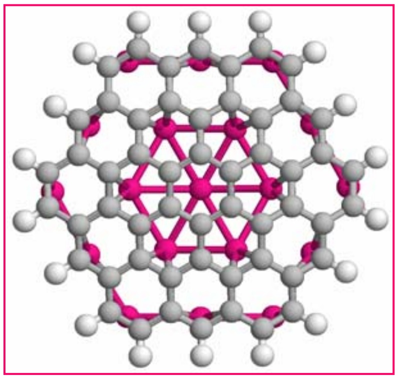
Sandwich molecules M_nR_2 consisting of a layer of transition metal atoms M (Cr, Fe, Pd) between polyacene aromatic hydrocarbon molecules (R) are studied using *ab initio* density functional theory. The polyacenes R range from pyrene $C_{16}H_{10}$ (four rings) to circumcoronene $C_{54}H_{18}$ (nineteen rings). Geometry optimization shows that starting from arrangements where one metal is assigned to each ring (left figure, schematic) there is a preference for metal atoms to coordinate to carbon atoms on the circumference of the sandwich (right figure, top view). This can result in metal-metal distances greater than in bulk metal and so the establishment of metal clusters with metal-metal bonds is frustrated. This effect is studied by changing the number of metal atoms and relaxing symmetry constraints. A neutral C_{2v} symmetry molecule $Pd_5(C_{18}H_{12})_2$ with tetracene and a lopsided arrangement of metal atoms is shown to be consistent with experimental work on dications by Murahashi et al [Science 313 (2006) 1104-1107]. In tetracene sandwiches with n = 5 - 9 the Pd atoms have η^2- and η^3-coordination to edge carbons. In addition to edge bonding, motifs for interior metal atoms are identified from a series of sandwiches with increasing size in the series: pyrene ($C_{16}H_{10}$), tetracene ($C_{18}H_{12}$), coronene ($C_{24}H_{12}$), ovalene ($C_{32}H_{14}$), circumanthracene ($C_{40}H_{16}$), circumpyrene ($C_{42}H_{16}$), hexabenzocoronene ($C_{42}H_{18}$) and circumcoronene ($C_{54}H_{18}$).





Shadow Wave Functions for many electron systems

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Integral Shadow Wave Functions (SWF) have been employed in the past for describing inhomogeneous bosonic quantum systems such as Helium or molecular Hydrogen. The main features of these wave functions, usually employed in connections with Variational Monte Carlo techniques, are the capability of describing a variety of states (quantum crystals either perfect or defective, phase coexistence, excited states such as vortices and phonons) including in an effective way correlations at all orders, and therefore giving results of a quality which is usually higher than that obtained starting from standard Feenberg wave functions. In this talk the non-trivial extensions of this formalism to the case of many fermions, and in particular of electrons, will be discussed, and some preliminary results will be presented.

The formation of alkanethiol monolayers on the Au(111) surface

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Self-assembled monolayers (SAMs) are molecular films that form spontaneously on solid surfaces. These systems have been the subject of intense research in recent years, both experimental and computational. This level of interest is related to their importance in wetting phenomena, tribology, chemical and biological sensing, optics and nanotechnology. Among the many varieties of SAMs, alkanethiol molecules on the Au(111) surface have been given special attention because of the relative simplicity of their structure, their highly stable and ordered SAM patterns, and the ease of preparing the Au(111) surface. Despite the elementary nature of this system, its observation in various experiments has led to controversial results. Among the much-debated key issues are two related questions:

1. Does S-H bond dissociation occur upon deposition of an alkanethiol molecule on the gold surface?
2. Do the alkanethiol adsorbates dimerize on the Au(111) surface?

Recent density functional computations [1] have addressed these problems and arrived at a new unified model of alkanethiol SAM formation on gold surfaces that is consistent with all experimental observations. Specifically, it was found for the first time that the S-H bond of the adsorbate remains intact when the methanethiol molecules are adsorbed on the regular Au(111) surface, as confirmed by experiment [2]. It breaks, however, when admission is made for surface defects. This finding leads to the expectation of different dimerization patterns of thiols on gold substrates, depending on whether or not they have undergone S-H bond scission, turning into thiolates. It is further demonstrated that methanethiol adsorbates on the Au(111) surface form Van der Waals dimers. For methylthiolate, it is shown that dimerization exists below a certain coverage threshold and is absent at high coverage levels, in full agreement with experimental data.

[1] J.-G. Zhou, F.Hagelberg, Phys.Rev.Lett. 97, 45505 (2006).
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Electronic Structure in Complex Systems

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In this presentation, we will highlight the application of electronic structure theories and simulation methods to the characterization of the reactivity and charge transport in complex systems. Those might include radical reactions in aqueous phase relevant to radiation chemistry, proton transport dynamics in electrolyte membranes, and electron/hole transport in photocatalytic metal oxides. This research was supported by the Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division of the U.S. Department of Energy (DOE). The research was performed in part using the Molecular Science Computing Facility in the William R. Wiley Environmental Molecular Sciences Laboratory (EMSL) at the Pacific Northwest National Laboratory (PNNL). The EMSL is funded by DOE’s Office of Biological and Environmental Research. PNNL is operated by Battelle for DOE.

New electronic structure methods for large radicals

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Electronic structure methods form the basis for first principles characterizations of the potential energy surfaces that underlie molecular properties, chemical reaction mechanisms, and nuclear dynamics. Despite tremendous progress, the most ubiquitous electronic structure methods, based on density functional theory (DFT), that can be applied to molecules ranging well over 100 atoms, exhibit failures for molecules with strong correlations, some types of radicals, and systems where dispersion interactions are important. At the same time, the most accurate electronic structure methods, based on coupled cluster theory, remain too computationally demanding to enable the routine treatment of molecules containing more than about 20 atoms. This means there is a continuing need for new electronic structure methods that can address on the one hand, the physical deficiencies of present-day density functionals, and on the other hand, the excessive computational cost of state-of-the-art wavefunction-based methods.

In this talk, I will discuss electronic structure methods under development in my group that offer the prospect of bridging this gap. The central goal is to mimic coupled cluster methods at greatly reduced cost. Building upon Brueckner orbital methods, is a new approach that correctly and inexpensively recovers dispersion interactions, without either excessive spin-contamination for radicals (as plagues traditional unrestricted Hartree-Fock-based methods), or the difficulties of self-interaction that can affect DFT calculations of radicals. The performance of this optimized second order (O2) approach for relative energies, structures, and frequencies will be assessed, both for closed shell molecules, radicals, as well as some cases which exhibit pathological failures at both the DFT and MP2 levels of theory.

Computational Study of Orientation-dependent Molecular High Harmonic Spectra

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Abstract

Recently, there has been much interest in high harmonic generation (HHG) by aligned molecules [*Phys. Rev. A* **67** 023819, *Nature* **432** 867, *Nature* **435** 470]. During HHG, an electron is ionized and driven back to the cation by a strong, low-frequency field, and radiation is emitted at harmonics of this driving pulse. Because this process is sensitive to the orientation of a molecule, rotational dynamics can be probed on very short time scales. We are working to predict the time-dependent HHG spectra for aligned rotational wavepackets. In conjunction with experiment, these simulations should be valuable for studying the loss of rotational coherence in media such as dense gases. Within the presented formalism, Born-Oppenheimer rotational dynamics are handled exactly, while HHG at any given orientation is estimated by numerical time integration of a one-electron Schrödinger equation. Propagation outside of the integration grid can be handled using an analytical Volkov propagator at the expense of ignoring the cation field at this distance.

DIAMONDOIDS ARE FOREVER: NOVEL MOLECULAR BUILDING BLOCKS FOR NANOSCIENCE

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Diamondoids are cage-like saturated hydrocarbon molecules that possess a rigid carbon framework which is superimposable upon crystalline diamond. While lower-order diamondoids (e.g. adamantane ($C_{10}H_{16}$), diamantane ($C_{14}H_{20}$), triamantane ($C_{18}H_{24}$), and *anti*-tetramantane ($C_{22}H_{28}$)) have been synthesized in the lab, attempts to make even larger diamondoids have not been successful to date.

Recently this field has been rejuvenated with the fascinating report by Dahl *et al.* of the Molecular Diamond Technologies Group of the Chevron Company (J. E. Dahl, S. G. Liu, and R. M. K. Carlson, *Science* **299,** 96 (2003)) of the isolation of new diamondoids from petroleum oil. Given the rigid structures and unique shapes of diamondoids they might be potential building blocks for various applications in nanotechnology and biochemistry.

In this talk we will demonstrate that density-functional theory (DFT) can accurately compute the electronic, structural, and vibrational properties of a variety of existing lower and medium-order diamondoids. We believe that DFT is an important tool that will assist experimentalists in identifying more complicated diamondoids that can either be isolated from natural products or made by rational synthesis.

Steven L. Richardson, Tunna Baruah, Michael J. Mehl, and Mark R. Pederson, *Chem. Phys. Lett.* **403,** 83 (2005).
Steven L. Richardson, Tunna Baruah, Michael J. Mehl, and Mark R. Pederson, *Diamond Relat. Mater.* **15,** 707 (2006).

Graphene Layer Growth Chemistry

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University of California at Berkeley

There are a variety of carbonaceous materials whose growth is envisioned through the extension of aromatic edges; familiar examples may include pyrolytic graphite, carbon black, combustion soot, interstellar “dust”, fullerenes, nanotubes, and recently graphene sheets. In combustion, it is estimated that nearly 80 % of soot mass comes from surface growth. Our goal is to gain fundamental understanding of evolution of soot particles, including their atomistic structures and surfaces. In pursuit of this goal, we discovered a new phenomenon—migration of five-membered ring along the zigzag edge of the evolving graphene layer. This phenomenon of migration alters significantly the framework for surface chemistry of graphene layer, and introduces a large number of possible elementary reaction steps that could take place on an evolving surface. Recent examples are the “collision” of migrating rings and “flipping” of the product examined by us recently in collaboration with William Lester’s group.

The Role of DNA Methylation on Tautomeric Equlibria and Electron Migration

Glake Hill
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Minor tautomers of nucleic acid bases can result by intramolecular proton transfer. These rare tautomers could be stabilized through the addition of methyl groups to DNA bases. A comprehensive theoretical study of tautomers of methylated derivatives of guanine, adenine, cytosine, thymine, and uracil was performed. Molecular geometries of all tautomers were obtained at the DFT and MP2 levels with the 6-31G(d,p) basis set, and single point calculations were performed at the CCSD(T)/6-311G(d,p) level. Tautomers obtained by protonation at the preferred protonation site for methylated isolated bases were compared to their nonmethylated counterparts. The effects of methylation on the relative stabilities of nucleic acid base tautomers are also studied and discussed in this work. The results suggest that some sites on the bases may not be mutagenic and may even stabilize the canonical Watson-Crick form. The results also indicate that a number of methylation sites can stabilize the tautomers, suggesting possible mechanisms for mutagenic changes. The energetic and structural properties of DNA have also been investigated by examining the electron affinities (EA) and ionization potentials (IP) of guanine and several related compounds using the B3LYP density functional hybrid. Using the 6-311++G(df,pd) basis set, the vertical and adiabatic ionization potentials for the keto form of N9H guanine are found to be 8.00 and 7.68 eV, respectively, and are in nice accord with experimental data. At this level, all non-methylated guanine structures show slightly negative adiabatic electron affinities whereas the methylated guanine compounds are relatively stable with respect to dissociation. In addition, structural and electronic distribution changes upon electron removal and attachment lead to decreased and increased dipole moments, respectively.

Electron pair localization function: towards a theoretical electrophilicity scale

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Recently, a modification of the Electron Pair Localization Function (EPLF) [1] has been proposed and an application to the quantification of the electrophilicity of the electron lone pair in possible electrophilic amination reagents has been suggested [2]. In the present report, this method is applied to several amines that have been found experimentally [3] to show electrophilic behaviour in order to validate our theoretical method. Demanding DMC calculations have been carried out for these molecules (containing more than one hundred electrons) and the parameters for assesing their electrophilicity have been calculated. Correlations with experimental results are presented.

[1] Scemama, *et al*., Journal of Chemical Physics **121**, 1725 (2004)
[2] Amador-Bedolla, *et al*., Journal of Chemical Physics, submitted 11.01.06
[3] Berman and Johnson, Journal of Organic Chemistry **71**, 219 (2006)

Efficient Optimization of Correlation Functions for Quantum Monte Carlo

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High quality trial functions are essential for obtaining accurate results from quantum Monte Carlo. We describe a simple implementation of the Drummond and Needs' unreweighted variance minimization scheme that is more amenable to parallel computing.

POSTER PRESENTATIONS

1.	Nandini Ananth	Semiclassical Initial Value Representation – An application to Nonadiabatic Dynamics
2.	Robert A. DiStasio Jr.	An Efficient Resolution-Of-The-Identity Implementation of Local Scaled Opposite Spin Second-Order Møller-Plesset Perturbation Theory: A Correlated Look at Mutual Orientation in the Fullerene Dimer.
3.	Ainsley A. Gibson	Quantum Monte Carlo Studies on the First Row Transition Metals
4.	Thomas Miller	Sampling diffusive transition paths
5.	Zhengji Zhao	The Linear Scaling 3-Dimensional Fragment Method for Petascale Nanoscience Simulations

Semiclassical Initial Value Representation – An application to Nonadiabatic Dynamics

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MD simulations of systems that involve nonadiabatic transitions has always been a challenge because of the coupling between the nuclear and electronic degrees of freedom. The behavior of such systems can best be modeled by making sure that the method used not only provides a way to incorporate quantum effects, but also ensures the equivalent treatment of the electronic and nuclear degrees of freedom. We use the classical electron model (Meyer-Miller)[1] to do the latter; while time evolution using the semiclassical initial value representation (SC-IVR) [2. 3] ensures the inclusion of quantum effects. In order to obtain information on both the relative populations of the various electronic states as well as the transitions between them, we calculate the nuclear momentum distribution. For the propagator, we use the Forward Backward IVR (FB-IVR)[4], a variation of the SC-IVR that presents a simplified formulation for correlation functions with a double propagator, and the Linearized IVR (LSC-IVR)[5] which results in a more `classical' formulation of the problem. Calculations have been done for two simple model systems and the results so far have been extremely encouraging.

A Few Relevant References :

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2. W.H.Miller, J.Phys.Chem. 105, 2942, (2001)
3. X.Sun, W.H.Miller, J.Chem.Phys 106(15), 6346, (1997).
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An Efficient Resolution-Of-The-Identity Implementation of Local Scaled Opposite Spin Second-Order Møller-Plesset Perturbation Theory: A Correlated Look at Mutual Orientation in the Fullerene Dimer.

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In this work, scaled opposite spin second-order Møller-Plesset perturbation theory (SOS-MP2) is recast within the framework of the local triatomics-in-molecules (TRIM) model. The resultant model, SOS-TRIM MP2, emerges as a robust, fourth-order methodology with the ability to treat electron correlation at the MP2 level for hundreds of atoms on a single processor. An efficient algorithm for performing SOS-TRIM MP2 single-point energy evaluations is presented along with computational timings for extended β-pleated glycine strands and compact α-helical DNA sequences within the TATA box using double- and triple-ζ atomic orbital basis sets. A chemical application of SOS-TRIM MP2 theory follows in which the potential energy surface describing intermonomer separation among two competing mutual orientations of the fullerene dimer is explored at the extrapolated SOS-TRIM MP2/cc-pV(DT)Z level.

Quantum Monte Carlo Studies on the First Row Transition Metals

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Abstract

Quantum Monte Carlo methods are used to calculate electronic structure properties of the first row transition metals Sc-Cu. Variational Monte Carlo (VMC) and fixed-node diffusion Monte Carlo (FNDMC) methods are used in this investigation to calculate the electronic energies of the ions, hydrides, and neutral species of Sc-Cu. An effective core potential is used to reduce the computational effort of this study. From this investigation we have been able to calculate properties such as the ionization potentials, electron affinities and proton affinities for each metal. The results of the Monte Carlo calculations as well as results obtained from other *ab initio* [HF, CCSD, CCSD (T), CISD, MP2, and MP4] and DFT-B3LYP calculations are presented. It is found that incorporation of explicit electron-electron correlation as in Monte Carlo calculations allows achievement of high levels of accuracy. Simultaneously, the ability to systematically improve the results is retained. Theoretical results are compared with experimental data where available.

Sampling diffusive transition paths

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We address the problem of sampling double-ended diffusive paths. The ensemble of paths is expressed using a symmetric version of the Onsager-Machlup formula, which only requires evaluation of the force field and which, upon direct time discretization, gives rise to a symmetric integrator that is accurate to second order. Efficiently sampling this ensemble requires avoiding the well-known stiffness problem associated with sampling infinitesimal Brownian increments of the path, as well as a different type of stiffness associated with sampling the coarse features of long paths. The fine-feature sampling stiffness is eliminated with the use of the fast sampling algorithm (FSA), and the coarse-feature sampling stiffness is avoided by introducing the sliding and sampling (S&S) algorithm. A key feature of the S&S algorithm is that it enables massively parallel computers to sample diffusive trajectories that are long in time. We use the algorithm to sample the transition path ensemble for the structural interconversion of the 38-atom Lennard-Jones cluster at low temperature.

The Linear Scaling 3-Dimensional Fragment Method for Petascale Nanoscience Simulations

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Petascale materials simulation requires *a*b initio methods and codes that scale linearly both to the system size and to the number of computer nodes (processors). Unfortunately, Density functional theory (DFT), which is the most widely used *a*b initio method in material simulations, scales as $O(N^3)$ to the size N of the system. Furthermore, the existing codes (various implementations of DFT) don't scale well to the processors used due to the large amount of communication required between processors.

We have developed a linear scaling 3 dimensional fragment (LS3DF) method to overcome this $O(N^3)$ scaling, and also the computer parallelization issue. This method divides a large system into small fragments, and solves the electronic wavefunctions of each fragment independently, then patches the results together. The novel patching scheme assures that the artificial boundary effects of the spatial division will be canceled out. As a result, the LS3DF results are numerically the same as the original full system DFT results (with the difference smaller than other numerical uncertainties, e.g, due to numerical grids), while with a required floating point operation is reduced from $O(N^3)$ to $O(N)$. Meanwhile, in this method, each fragment is solved by a small amount of processors independently, without communication with other group of processors, the code scales almost linear to the number of processors used.

We have tested the scalability of our code using upto 2000 processors on the NERSC machine, with system size upto 15,000 atoms (Silicon quantum dots). And we have also tested the accuracy of the LS3DF method against the original full system LDA result. We will present our results in the poster.

Thank you for joining in the 70th birthday celebration to honor ***William A. Lester, Jr.*** *for his contributions to Theoretical Chemistry, his commitment to Science Education and assisting minority students to become interested in pursuing a career in Science.*

Organizers: Professor Alan Aspuru-Guzik and Professor John Harkless both former grad students in the Lester Group

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