

**Assistant Scientist,
Assistants in Chemistry,
and
Post Doctoral Associates
Research Interests**

AJITH PERERA
Bartlett Research Group

New Approximation Schemes

My main research interest concerns the development, implementation and application of new approximation schemes in computational and theoretical chemistry. It is often a specific type of experiment that needs theoretical support which triggers my initial motivation to study a problem. Also, as an assistant scientist in Prof. Bartlett's group, my research interests to large extent mirror the interests of the whole research group.

In addition to maintenance of the ACES II program system, most of my recent effort was spent on developing software tools to extend the application of coupled cluster (CC) methods to larger chemical systems. One component of that effort is developing a parallel version of the CC code. A preliminary version of which was developed during last few months in collaboration with Anthony Yau and Piotr Rozyczko. Recently, jointly with Roland Lindh from the University of Lund, I have incorporated new, faster integral and integral derivative packages to ACES II. With the faster integrals and integral derivatives in place, we will soon be able to start to developing codes to do integral direct methods which are essential for large scale applications.

The other on-going projects involve developing general purpose tools to calculate vibrationally averaged spectroscopic parameters (collaboration with Luis Galiano from Spain), computational studies of NMR spin-spin coupling constants of Hydrogen bonded systems (collaboration with Prof. Janet Del Bene), theoretical and computational studies of correlation cusp and correlation energy density (collaboration with Tom Henderson and Igor Schweigert), and computational studies of high energy density materials (collaboration with Stefan Fau).

NORBERT FLOCKE
Bartlett Research Group

Localized coupled cluster (LCC) methods are among the most promising tools to deal with electronic correlation effects in very large molecular systems. LCC methods avoid unphysical delocalization of electron correlation by using spatially well localized one-electron basis functions. All LCC methods presented thus far in the literature are based on either incorporating fully or partially the original AO basis into the LCC equations, leading to more excitation parameters to deal with when compared to the all-MO CC schemes.

An all-MO based LCC can be devised using natural bond orbitals (NBOs), an approach which has been recently implemented. Studies have shown exponential decay and very high transferability between similar molecular systems for the T2 amplitudes at the CCSD level [1]. The NBO T2

transferability property was further used to estimate the correlation energy of diamond from NBO CCSD calculations performed for suitable diamond subunits [2]. While the NBO CC approach is very powerful as far as transferability is concerned, one of the main inconveniences is the mandatory inclusion of the T1 amplitudes to correct for the NBO reference function and the resulting noninvariance of the HF correlation energy. Attention has thus been drawn to the use of natural localized molecular orbitals (NLMOs), which are obtained from the NBOs in one more computational step. The NLMOs retain the locality of the NBOs to a very high degree and at the same time leave the HF density invariant. Calculations performed at NLMO CCSD level show the same nice properties as their NBO CCSD counterparts and are probably the best way to proceed.

A MO-based LCCSD code based on threshold cuts in integrals, intermediates and amplitudes has been implemented into QCPACK using sparse vector addition and matrix multiplication routines. Integrals, intermediates and amplitudes below threshold are never addressed or processed. Preliminary NLMO CCSD runs with this new code have shown it to approach linear scaling in cpu time as the systems get more extended. The most limiting factor at the present stage is the need to perform a full 4-index transformation of the AO integrals into the NLMO basis, which prevents calculations beyond the contemporary 'conventional' limit of approx. 300 basis functions.

In order to achieve a sparse 4-index transformation a necessary ingredient is a direct AO integral code. At present the AO integral code in QCPACK is: 1) not direct and 2) not using the horizontal transfer equations outside the contraction loops. This last point is crucial for efficiency and I have started to recode that part. Eventually, if the new direct AO integral code shows favorable timings, it will be also used for the new parallelized ACES code.

[1] N. Flocke and R.J. Bartlett, Chem. Phys. Lett. 367, 80 (2003).

[2] N. Flocke and R.J. Bartlett, J. Chem. Phys. 118, (2003).

PIOTR ROZYCZKO

Bartlett Research Group

Multiscale Molecular Dynamics Simulations

My current research interests include:

► Improvements to the existing coupled-cluster implementation:

a. Extending the AO-based formalism for the all-virtual terms to gradients. Treating T and Lambda amplitudes as well as two particle density matrix elements (Gamma) in atomic basis lets users apply the CC method to much larger systems, as the most disk demanding terms - those with all four virtual indices are never explicitly stored.

b. Parallelizing the coupled-cluster method. This is an ongoing Common High Performance Computing Software Support Initiative (CHSSI) project undertaken by QTP, AcesQC, Inc., Enscoc, Inc. and University of Delaware.

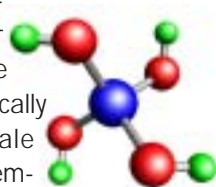
► Continuing work on the dynamics of the CF_3^+ ion and CF_3^+ radical impact on silica surface. We use the transfer hamiltonian combined with sparkle atoms (O^* atoms that have one valence to use to terminate bonds in a quantum mechanical region). The work is done in cooperation with Dr. Susan Sinnott from Materials Science and Engineering Dept at University of Florida.

AFAF AL DERZI
Bartlett Research Group

Quantum Mechanical to Molecular Dynamical Interface

My present research work is part of the NSF-KDI project. specifically the quantum mechanical problem of interionic potentials for simulation of the properties of SiO_2 . These published potentials are a class calibrated to both first principles electronic structure results for a small cluster and experimental crystalline data. We test the underlying realism and reliability of this procedure as part of an exploration of the necessary and sufficient transfer of information across the

quantum mechanical to the molecular dynamical interface
 QM-MD in a chemically realistic, multi-scale simulation with no empirical inputs: Our Model system is



BKS Cluster, H_4SiO_4
CCSD(T)-FC/aug-cc-pVDZ Optimized Geometry
 $R(\text{Si-O}) = 1.6806 \text{ \AA}$, $R(\text{O-H}) = 0.9636 \text{ \AA}$
 $\text{O-Si-O} = 109.47^\circ$, $\text{H-O-Si} = 113.52^\circ$
 $\text{H}_i\text{-O}_i\text{-Si-O}_{i+1} = 0^\circ$

Our Model system is SiO_2 . We focus on the TTAM and BKS

potentials because they share important assumptions about methodology of parameterization. The prospect is a correct encoding of both the local behavior of a SiO_4 cluster (with different terminations) and compatible encoding of the zero-pressure, zero-temperature behavior of the long-range ordered system. If the encoding is successful, both amorphous states and ordered phases will be described equally well in molecular dynamics.

My other research interest is to calculate highly accurate isotropic hyperfine coupling constants (iHFCCs) of organic radicals and develop basis sets for hydrogen to be used in these calculations.

ASHLEY ALFORD
Trickey Research Group

My primary research interests lie in the development of large scale parallel codes to calculate properties of complex materials at the level of chemical accuracy. There are two main thrusts currently under this broad heading.

The first is the implementation of Green's function techniques to calculate band gaps and absorption spectra. An as yet unsolved problem is that of the 'switchable' optical property of some rare-earth hydrides which go from being reflective to transparent in the visible as a function of hydrogen concentration. Unfortunately, standard *ab-initio* techniques predict these materials to have negative band gaps and to never transition to this state.

I have redeveloped existing parallel codes implementing the 'GW' (Greens function, screened potential) method for the purpose of improving these predictions. Results have demonstrated approximations that have been assumed for these materials in the literature are in fact inadequate and invalidate recent explanations of the theory/experiment discrepancy via a dipole

selection rule. Absorption spectra calculations for magnesium hydrides, candidates for hydrogen storage applications, are in excellent agreement with experiment and have been published with the experimental data. A recent calculation of the magnesium dihydride beta phase has confirmed its role in what experimentalists refer to as the 'black' state.

My current work is focused on the construction of an all-electron Gaussian basis set DFT package for extended periodic systems in one, two, and three dimensions. A particularly exciting aspect of this will be the inclusion of effects due to internal currents via current density functional theory and effects due to an external magnetic field.

MARSHALL CORY

Bartlett Research Group

Gas Phase Chemical Reactions

My current research interests are, simply put, concerned with gas phase chemical reactions, these include:

- ▶ Developing/improving methods for the calculation of accurate kinetic barrier heights.
- ▶ Developing low level (rank) methods capable of yielding descriptions of intrinsic reaction paths (swaths) comparable to methods of higher rank.

STEFAN FAU

Bartlett Research Group

Polynitrogen High Energy Density Materials (HEDM) are a current area of research. The N_5^+ cation is promising because of its high heat of formation. Unfortunately, it is also very electronegative with a vertical electron affinity of 6.1 eV. This strongly reduces the number of compatible anions. It also causes high reactivity with Lewis bases in general. We are currently investigating the mechanism for the oxidation of Br_2 by N_5^+ [1].

We showed that N_5^- (which was recently detected in mass spectroscopy experiments [2]) has an ionization potential just high enough to form a salt with N_5^+ [3]. However, there are side reactions, *e.g.* the formation of covalently bound N_{10} , that threaten the practical usefulness of this salt as a high energy density material.

A more stable salt requires a less electronegative cation, a more electronegative anion, or both. Therefore, we explore cations derived from N_5^+ by replacing one or more nitrogen atoms with the less electronegative CH group or phosphorus. We also explore N-oxide derivatives of N_5^- .

A new long-term interest is the decomposition of small nitramines R_2N-NO_2 ($R=H, CH_3$) in condensed phases. We investigate reaction paths made possible by the presence of a second nitramine molecule or impurities like water. These data may later be used in dynamics treatments of the decomposition reaction.

[1] A. Vij, W.W. Wilson, V. Vij, F.S. Tham, J.A. Sheehy, K.O. Christe, *J. Am. Chem. Soc.* **2001**, *123*, 6308.

[2] A. Vij, J.G. Pavlovich, W.W. Wilson, V. Vij, K.O. Christe, *Angew. Chem. Int. Ed.* **2002**, *41*, 3051.

[3] S. Fau, K.J. Wilson, R.J. Bartlett, *J. Phys. Chem. A* **2002**, *106*, 4639.

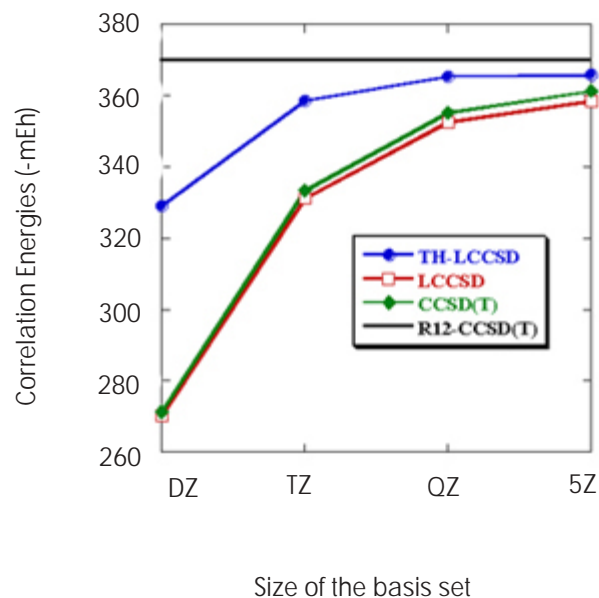
OSAMU HINO
Bartlett Research Group

Transcorrelated Method

The ultimate goal of quantum chemistry is to predict the properties of various atoms and molecules. This is achieved by solving the eigenvalue problem on the many-electron Hamiltonian. There are a number of sophisticated theories of quantum chemistry like the Coupled-Cluster method. However, even with these theories, we have to use a very large basis set to reach "chemical accuracy". This is due to the difficulty in describing the correlation cusp of the eigenfunction as a linear combination of the products of the one-electronic functions. This difficulty is dramatically ameliorated by the use of two-electron functions (geminals), which are more appropriate to describe the correlation cusp. The purpose of our research is to apply various theories of quantum chemistry to the transcorrelated Hamiltonian (TH). TH is defined as a many-electron Hamiltonian similarity transformed by the correlation factor. It is tuned to remove the singularity of the inter-electronic Coulomb potential. By using this TH, we can improve the convergence behavior of the many-electron eigenfunctions and correlation energies against the number of basis functions since the correlation cusp is already taken into account in TH. This enables us to obtain more accurate theoretical results than when we use the usual Hamiltonian.

Application of the singular value decomposition to the coupled cluster method

Modern quantum chemistry is expected to study the electronic structures of (I) relatively small molecules with "chemical accuracy" and (II) large molecules such as polymers or proteins. For both of these purposes, we have to perform correlated calculations with a large basis set. The coupled cluster method is one of the most reliable and feasible theories in the quantum chemistry for such calculations. However, the scaling of the computational requirements of the conventional coupled cluster method is often too steep to carry out these calculations within restricted computational resources. In this study, we try to reduce the computational requirements of the coupled cluster method by using the singular value decomposition (SVD). The singular value decomposition analysis for the coupled cluster amplitudes enables avoiding their redundancy. SVD is also useful to extract the essential part of the electron correlation and to eliminate the unimportant degrees of freedom systematically.



The transcorrelated LCCSD correlation energies for H_2O are plotted with those of the conventional LCCSD and CCSD(T) methods. TH-LCCSD indicates the transcorrelated LCCSD correlation energies.

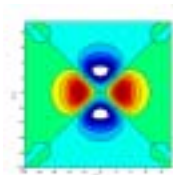
The horizontal solid line indicates the R12-CCSD(T) energies with 301 basis functions, which is almost the exact correlation energy for H_2O . XZ means the basis set composed of the primitive basis functions obtained from the cc-pVXZ basis of Dunning.

ANDREW KOLCHIN

Cheng and Trickey Research Groups

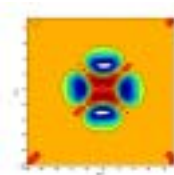
Silica Surfaces and Metallic Clusters

My research investigates the nature of water weakening in amorphous silica surfaces. Bulk amorphous silica is created by heating and cooling of a β -cristobalite crystal via classical molecular dynamics. A surface is obtained from the bulk sample and its topology analyzed. Likely sites of reaction at the surface are identified, and small slabs are taken about them for First-Principles (density functional theory (DFT)) calculations to determine the energetics of their interactions with water molecules. This work supports an ongoing project to determine the mechanisms of hydrolytic weakening in silica materials using multiscale methods in which classical and quantum methods are merged at larger and smaller scale lengths.



*d-orbital in
 Be_6 quintet*

*Excess charge
distribution
in Be_6^+ cation*



Another branch of my research involves DFT studies of neutral and charged metallic clusters. Here, we are interested in the extent to which a shell structure exists in such systems, how resulting Kohn-Sham(KS) orbitals might be envisioned to have arisen from hybridization of atomic orbitals, the roles played by the KS orbitals in bonding, and in the case of charged clusters; how the excess charge distributes itself.

VICTOR LOTRICH

Bartlett Research Group

Ab-initio density functional theory

Ab-initio density functional theory provides a bridge between traditional quantum chemistry and conventional DFT. In particular the optimized effective potential OEP approach is formally an exact theory, however, accurate and efficient approximations must be made for practical implementations. Currently efficient implementations of the second-order theory are being programmed and applied to small molecules. One of the major failings of conventional DFT is the inability to properly account for dispersion forces. Application of the theory to weakly bound systems such as rare gas dimers etc., is showing very favorable comparison when compared to coupled-cluster calculations, much better than Hartree-Fock based MBPT(2). Such success greatly extends the applicability of DFT.

CO-CO dimer potential energy surface

The CO-CO dimer potential energy surface is the subject of some controversy. State of the art techniques generate IP's which differ significantly. We wish to apply OEP-MBPT(2) to this system with the hope of validating the theory and perhaps generating the best potential to date. Computations of the IP at the CCSD(TQf) level may also help resolve this issue and work in this direction is slowly evolving.

MONIKA MUSIAL
Bartlett Research Group

Ionization Energies

I report the first implementation of connected triple excitations in the equation-of-motion (EOM) coupled-cluster (CC) method for ionization energies. This elegant, very general, time independent method exploits the left- and right-hand eigenfunctions of the non-Hermitian operator. The EOM method is a useful tool since it provides, directly, the sought quantity: excitation energies (EE), ionization potentials (IP), or electron affinities (EA).

Using proper factorization of the three- and four-body parts of the effective Hamiltonian an efficient computational procedure has been proposed for IP-EOM-CCSDT (CC Singles, Doubles and Triples) which at the EOM level requires no-higher-than $n_{\text{occ}}^3 n_{\text{vir}}^4$ scaling. I stress that this procedure does not introduce any approximation. The factorization strategy plus the real abelian symmetry implementation, makes it possible to apply the method to larger (> 150) basis sets, offering near benchmark quality for full triples.

The developed program, part of ACES II, has been subsequently applied to the calculations of the low-lying ionization potentials for the series of small molecules. The bottle-neck of the calculations occurs when solving the CCSDT equations for the neutral state which is an $n_{\text{occ}}^3 n_{\text{vir}}^5$ procedure. By exploiting spatial symmetry it has been possible to implement the calculations for quite sizable basis sets (aug-cc-pVQZ).

The proposed method provides the most accurate and rigorous evaluation of valence ionization potentials in the literature, and offers a high level correlation treatment applicable for relatively large basis sets. Detailed IP-EOM-CCSDT working equations are given in a recently published paper [1].

Bibliography

[1] M. Musial, S. A. Kucharski, R. J. Bartlett, J. Chem. Phys. 118, 1128 (2003).



Sam Trickey, Afaf Al Derzi, & Keith Runge during Afaf's going away party

RAFAL PODESZWA

Bartlett Research Group

My research involves developing and improving methods for extended systems. There are two basic approaches to this problem: extrapolation of finite systems and the crystalline orbital (CO) method. The latter method is preferred for the most accurate results due to the lack of end-effects. The main goal is to make the CO method more robust and therefore applicable to systems with larger elementary units. For the SCF and DFT methods, we improved the integral evaluation routine which is the bottleneck of these methods. For the methods that include electronic correlation, it is important to take advantage of the local character of the correlation effects. It can be exploited with the use of the atomic orbitals (AO) based methods. The AO based methods were shown to work well for the large molecules. Our ongoing project is to implement AO-based methods for polymers. With the use of AO based implementation of the CO method, we can take advantage of robustness of the CO method and locality of the AO method.

KEITH RUNGE

Bartlett Research Group

Fracture of Silica

My work, under Dr. Bartlett, involves the application of molecular dynamics to the problem of fracture, particularly the fracture of silica. Molecular dynamics simulations are driven by the forces that act on the atoms whose movements are calculated. For silica, these forces are typically calculated using classical pair potentials which can be found in the literature. However, for the accurate simulation of fracture, it is necessary to be able to describe the interaction of atoms in configurations far from equilibrium. The available pair potentials are not capable of providing accurate forces for these configurations and hence quantum mechanical calculation of the forces involved are needed. We employ a semi-empirical hamiltonian technique, neglect of diatomic differential overlap (NDDO), reparameterized to reproduce forces from higher order coupled cluster singles and doubles (CCSD) calculation which are known to give predictive accuracy for molecular properties.

The calculation of reaction constants for gas phase chemical reactions has led us to a semi-classical implementation of the flux-flux autocorrelation function (SCFFAF), a quantum mechanical technique which owes much of its development to Dr. William H. Miller. While the quantum mechanical technique is limited to systems involving few atoms, we have calculated rate constants for systems including tens of atoms over temperature ranging from below room temperature to as much as 800 K. To date, the results of these calculations have been in excellent agreement with experiment. This work is supported by the National Science Foundation.



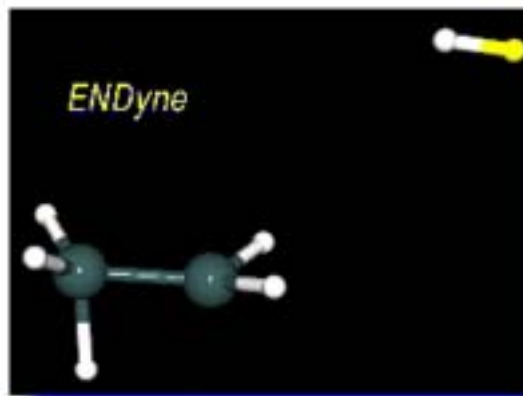
*Stefan Fau & Selman Hershfield
at the Xena reception*

REMIGIO TRUJILLO
Sabin Research Group

Energy Deposition of Charged Particles

My research deals with the problem of energy deposition of charged particles as they pass through material media. In particular, our goal is to develop a single consistent scheme which can treat all dynamical processes that take place over the full range of projectile energies. To that end, we have implemented a time-dependent approach to molecular dynamics, so called Electron-Nuclear Dynamics (END). The END model allows the study of atomic and molecular targets taking into account the nuclear and electronic degrees of freedom and their interactions.

From the END model, we obtain differential cross sections as a function of the scattering angle, the charge exchange cross section as a function of the projectile energy, and the electronic stopping cross section. These quantities are of fundamental interest for many applications in astrophysics, nuclear physics, design of reactors, and the ion-beam surface-layer analysis of materials among other applications. Thus, for example, we have studied collisions for H^+ and H colliding with H , H_2 , D_2 , He , N , N_2 , O , O_2 , Ne , CH_4 , C_2H_2 , and C_2H_6 . In particular, the results for H^+ colliding with N_2 were in collaboration with the experimental group at Rice University (Professor Bernard Lindsay), proving the prediction strength of END.



*Jack Sabin, Remigio Trujillo, & Yngve Öhrn
relaxing during a break during Sanibel 2003*