

THEORETICAL CHEMISTRY NEWS

Bulletin of the
Subdivision of Theoretical Chemistry of the
American Chemical Society

Vol. 22, No. 2

Fall 2001

News from the Theoretical Chemistry Subdivision

-- Reported by Susan Tucker, Subdivision Chair

The Executive Committee of the Theoretical Subdivision, which met at the Fall lunch meeting in Chicago on Sunday Aug. 26, 2001, was represented by John Adams (Webmaster), Rod Bartlett, Anne Chaka (Secretary), Mark Gordon, Martin Head-Gordon (Vice-Chair), Ken Jordan, Ned Sibert (Chair-Elect), Rich Strat, Don Truhlar and Greg Voth. These current and past officers focussed their discussion on a delineation of Executive Officer duties, the new Subdivision Website, year to year continuity and future advertisement of the IBM Graduate Student Awards in Computational Chemistry, and, of course, on great ideas for future ACS symposia.

Speaking of Executive Officer duties, it is my pleasure to announce that John Straub (Boston U.) was nominated to be the Subdivision's next Vice-Chair and that he has agreed to take on these duties. Thanks John! I also take this opportunity to pass the Subdivision torch over to the incoming Subdivision Chair, Ned Sibert (U. Wisconsin, sibert@bert.chem.wisc.edu).

But now, on to our most exciting order of business, the new Theoretical Subdivision Website. As was promised in the Spring Newsletter, the Subdivision

Website is now up and running!! Check it out! You can find our site directly at www.ACSTheory.org or by starting from the ACS website and following the links to the Division of Physical Chemistry home page. From there, just click on the Theoretical Subdivision link. The Subdivision site is on its way to becoming an indispensable resource for theoretical/computational chemists. Most importantly, we have started a new post doctoral clearing house — with time-limited postings to ensure their currency. This resource can only be as effective as you, the community, make it. So go post your open positions now! And, as well, it is critically important that we make our students aware of this service.

In addition to the post doctoral clearing house, the Subdivision website also offers a listing of, and links to, upcoming meetings of interest to the theoretical community, links to sites for most popular Chemistry software, information about the IBM Graduate Student Awards in Computational Chemistry, current and past Subdivision newsletters, officer contacts, membership information, and more. So, once again, check it out at www.ACSTheory.org. And, if you have

any suggestions for additional services or site improvements, please send them along to John Adams at AdamsJE@missouri.edu.

such suggestions to Ned Sibert at sibert@bert.chem.wisc.edu.

See everyone in Orlando!

As always, the Executive Committee welcomes your suggestions for future ACS Physical Chemistry Division symposia. Please send any

-Suzi Tucker

Theory Subdivision Webpage

Visit the new, redesigned Theory Subdivision website at www.acstheory.org! There are many new features. We hope that this web site will be a resource for Subdivision members and for those generally interested in the theoretical aspects of chemistry. Please let us know how we can make this site more useful to you by directing your comments to the Subdivision's Webmaster.

NEW: We are compiling a list of useful and interesting links to web sites for theoretical and computational chemists or for individuals wanting to learn more about theoretical/computational chemistry. If you have a recommendation for a site that might be of interest to the larger community, please send the URL and a brief description of the site to the webmaster, John Adams (AdamsJE@missouri.edu).

Theoretical Chemistry Postdoctoral Position Clearinghouse

The Subdivision continues to run a clearinghouse for people looking to hire postdocs and people looking for postdoc positions. Currently there is a list of those looking for a position and one for those looking to hire, both of which are available on the Subdivision web page. If you wish to be on either list, please send John e-mail or drop him a line. The address to contact him is:

Prof. John E. Adams
Department of Chemistry
University of Missouri
Columbia, MO 65211
email: AdamsJE@missouri.edu
voice: (573) 882-3245

Membership

The subdivision now has about 800 members. If you would like to join the Theory Subdivision:

If you are already a dues-paying member of the Division of Physical Chemistry (\$7.00/year, \$2.00 for students), just send a note to the Secretary of the Subdivision (National Institute of Standards and

Technology, 100 Bureau Drive Stop 8380, Gaithersburg, MD 20899-8380, anne.chaka@nist.gov) indicating your wish to join. Please state that you are already a member of the Division.

If you are not already a member of the Division of Physical Chemistry but you do belong to the ACS, join the Division by sending a note to Professor Ken Jordan, Department of Chemistry, University of Pittsburgh, 219 Parkman Avenue. Pittsburgh PA, 15260, USA, enclosing a check for \$7.00 (\$2.00 for students) and stating your wish to join the Subdivision at the same time.

IBM Graduate Student Awards in Computational Chemistry

CALL FOR APPLICANTS FOR IBM 2001 AWARDS! (Deadline is October 20, 2001)

There are two Awards in Computational Chemistry that are open to current graduate students. We are grateful to IBM and the Minnesota Supercomputing Institute for their support of these awards. Last year's winners are announced below.

Let me urge you to encourage your graduate students to apply. The competition is open to any graduate student (regardless of citizenship) who began graduate study after August 1, 1998 and who is an ACS member (or whose advisor is an ACS member). These awards are designed to encourage graduate work in computational chemistry, to recognize research accomplishments, and to stimulate interest in the Subdivision of Theoretical Chemistry and the Physical Chemistry Division of the ACS.

An Awards Committee will consider all the applicants. The awards applications should be sent to Professor Ned Sibert at the University of Wisconsin, Madison. Note that the deadline for applications October 20, 2001.

These two awards, supported by IBM, will provide one-time cash stipends of \$2500 and \$1000 as supplements to normal financial aid to doctoral candidates in the research-dissertation

stage in the 2001-2002 academic year. The Minnesota Supercomputing Institute will provide each awardee up to 1000 node-hours on an IBM SP2 cluster for the awardees to actually carry out a portion of the awarded research. The awardees will have access to the consulting services of the Institute normally available to all users. Awardee selection will be made on a competitive basis. Applicants should be working on new and innovative computational chemistry methods or applications in theoretical chemistry **that take advantage of parallel computing resources.**

Applicants should prepare a written description of a computational chemistry research project that requires high performance computing, with an explanation of the scientific importance of the project. Proposals need to include an estimate of the computing resources required in SP2 cpu-hours. Applicants should explain not only how they plan to use the grant funds, but also how their calculations require, or take advantage of, parallel computing. Two letters of recommendation, including one from the student's advisor, along with a vita and transcript, are required. The proposal, including the vita, should not exceed five double-spaced pages. In addition, a faculty person (typically the applicant's research advisor) responsible for the applicant's use of the Minnesota Supercomputing Institute resources must be identified.

Forward applications by October 20, 2001 to
Professor Edwin L. Sibert
Department of Chemistry
University of Wisconsin
1101 University Avenue
Madison WI 53706

(608) 262-0265
sibert@chem.wisc.edu

The awardees will be announced in the Spring
2002 Subdivision newsletter.

THE 2000 IBM AWARDEES:

1st Prize: Nathan A. Baker, Department of Chemistry and Biochemistry, University of California-San Diego. Advisor: Professor J. Andrew McCammon. Proposal: Investigation of Microtubule Assembly by Parallel Solution of the Poisson-Boltzman Equation.

2nd Prize: Sidney P. Elmer, Department of Chemistry, Stanford University. Advisor: Professor Vijay S. Pande. Proposal: Design and Characterization of Self-Folding Polyphenylacetylene-Based Heteropolymers.

NSF Rotator Positions

The National Science Foundation seeks scientists to serve in temporary (rotator) positions in Theoretical and Computational Chemistry. Interested individuals are encouraged to contact the Theoretical Chemistry Subdivision (Suzi Tucker, tucker@chem.ucdavis.edu, 530-752-2203)

The NSF augments its permanent staff of professional employees through the temporary (rotator) appointment of individuals on leave of absence from research and/or educational institutions. This arrangement provides the Foundation with visiting scientists, engineers, and educators who are current in academic, scientific, engineering, or managerial matters. In return, these individuals and their institutions gain knowledge of the philosophy and mechanisms of Federal support for research. The Foundation, the participant, and his/her home institution all benefit from this program.

A basic fact sheet about the NSF can be accessed at: <http://www.nsf.gov/cgi-bin/getpub?nsf9763>
while general information regarding rotator positions can be accessed at:
<http://www.nsf.gov/home/chart/rotate.htm>.

Most academic scientists become rotators under the Visiting Scientist program (<http://www.nsf.gov/home/chart/visiting.htm>) although some enter under the Intergovernmental Personnel Act (<http://www.nsf.gov/home/chart/intergov.htm>). Both of these sites contain information about salary, benefits, relocation allowances, and the Independent Research/Development program. This program permits a scientist temporarily performing service at NSF to maintain involvement with his/her research at his/her home institution.

Symposium Reports

The following are reports from the Fall 2001 national ACS meeting in Chicago. We thank the symposium organizers for taking the time to put these wonderful reports together for us.

WHAT CAN WE REALLY LEARN ABOUT CONDENSED PHASES FROM CLUSTERS?

Reported by Bruce C. Garrett and Douglas Ray (Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory), Organizers.

Studies of small ensembles of atoms and molecules affords detailed observation of structures, energetics and dynamical processes that are difficult, if not impossible, in condensed phase systems. One rationale for studying clusters is the hope that they can provide a bridge from the rarefied environment of gas-phase molecular processes to condensed phases and that information about cluster properties can shed light on the properties of condensed phases. Clusters are also of interest in their own right because they display unique characteristics, such as large surface/volume ratio, large cooperative effects particularly in hydrogen-bonded clusters, effects of finite size on electronic structure (e.g., for metal clusters), and high reactivity or catalytic activity. The goals of this symposium were to identify where cluster studies have made an impact on understanding condensed phases and also to identify unique properties of clusters and how they differ from the condensed phase properties. The symposium was comprised of six sessions: Solvation Effects on Molecular and Electronic Structure (Spectroscopy), Solvation Effects on Reactions – Reaction Dynamics, Time-Resolved Solvation, Intermolecular Interactions, Thermodynamic Properties and Phase Transitions, Properties of Solids – Evolution of the Metallic State and Crystal Growth, and Heterogeneous Catalysis.

The speakers took seriously the charge to address the question of the symposium title, and

many successful connections between clusters and condensed phases were identified, as well as unique differences and cases where the results of cluster studies did not reproduce trends seen in condensed phases. The presentations in the session on Solvation Effects on Molecular and Electronic Structure indicated that clusters have and will continue to have an impact on our understanding of solvent structure and energetics. Spectroscopic studies of intermolecular vibrations provide information about intermolecular potentials and solvent-induced shifts in intramolecular vibrations are signatures of binding patterns. A key difference from condensed phases is that cluster energetics dominate over entropy in determining probable solvation structures and binding patterns.

Perhaps the clearest example of where cluster studies have influenced condensed phase research is in the development of interaction potentials that can be used in condensed phase simulations. Cluster studies allow many-body effects on interaction energies to be systematically probed, and many-body decompositions have played a major role in the development of transferable interaction potentials that model intermolecular interactions across a range of environments from clusters to condensed phases.

An area where a direct connection between clusters and condensed phases is more tenuous is in the study of solvation effects on reactions

and dynamics. Theoretical studies of a chemical reaction and proton transport indicate that cluster models do not reproduce trends seen in condensed phase. Effects seen in condensed phases are often enhanced in clusters, and clusters provide a more unique entity rather than a “bridge” to the condensed phase. In these cases it is more profitable to look for new insights from clusters. In this respect, clusters have been very successful at providing insight into understanding the role solvent mediated charge transfer plays in ionic recombination in clusters. It is interesting that in these studies condensed phase concepts (such as the Marcus picture of the effects of solvent reorganization on charge transfer) have play a role in understanding processes in clusters.

Clusters also provide unique entities in terms of thermodynamic properties and phase transitions. In clusters compared to condensed phase, fluctuations (which scale like $N^{-1/2}$) are much larger, time scales (which are much faster) do not always separate, traditional rules (such as the Gibbs phase rule) lose relevance, thermodynamically unfavored phases can still exist, and the distinction is lost between phases and components. Even so, concepts from clusters, such as disconnectivity graphs that provide information about the energy landscape and crystal packing have provided insight into phase transitions such as freezing.

Direct connections between clusters and condensed phases have been more evident in studies of structures and structural changes, phases and phase changes, and metal-insulator transitions in solids, particularly metals. This area of study is one in which bulk concepts (e.g., crystal packing) has also played a role in understanding the clusters.

The perspective that clusters are unique was

also evident in the presentations on heterogeneous catalysis. Nanoclusters of metals supported on metal oxide surfaces show unique reactive and catalytic behavior not seen in the bulk metals. Cluster properties are extremely sensitive to size and on the nature of the support. Studies of the properties of isolated clusters are being used to learn about the supported clusters and the role the support plays. Both experimental and theoretical approaches towards characterizing the support and electronic structure of the clusters are important to gaining a detailed understanding of the unique properties of these systems.

In the past, cluster studies have been used to provide answers to the question, “how big is big enough to model bulk behavior?” Several examples were reported on studies of the effects of sequentially increasing cluster size on properties. Studies of the sequential solvation of multiply charged anions provided information about the adiabatic ionization energy of bulk water compared to the solvation anion. Extrapolation of cluster binding energies for water and for anions and cations were used to obtain the lattice energy of ice and solvation energy of the proton, and properties such as binding energies of metals clusters have been used to extrapolate to bulk lattice energies. This symposium made it clear that the unique properties of clusters are just as important. Equally important questions are “what new insights do cluster provide” and “what is the role condensed phase properties and processes play in developing these insights?”

The organizers would like to thank Shawn Kathmann and Gregory Schenter for providing copies of their notes to aid in writing this report. Acknowledgement for partial support of the symposium is made to Pacific Northwest National Laboratory, which is operated for the

Department of Energy by Battelle, the Donors of The Petroleum Research Fund, administered

by the American Chemical Society (ACS), and the Division of Physical Chemistry of the ACS.

THREE-DIMENSIONAL SILICON-OXYGEN CAGES. Reported by Mark Gordon (Ames Laboratory, Iowa State University), Organizer.

Takako Kudo discussed possible mechanisms for the formation of polyhedral oligomeric silsesquioxanes (POSS), using *ab initio* quantum chemistry. The study included analyses of the initial hydrolysis of the starting silanes, subsequent condensation to disiloxanes, and further condensation to cyclic structures. The latter are the direct precursors to the POSS. Professor Kudo also considered substituent effects, the effects of aqueous solvent and the related compounds in which POSS are partially or completely substituted by Ti atoms. The calculations were performed with a range of methods, from Hartree-Fock to coupled cluster. Correlation effects are very large, but MP2 and coupled cluster calculations do not differ greatly. Adding solvent water molecules decreases the barrier heights for nearly all steps to zero. Except for the increase in the initial barrier when H is replaced by t-butyl in the POSS compounds, the substituent effects are small.

Ravi Pandey presented the results of density functional studies on the polymer to SiO₂ conversion process for H-silsesquioxanes (HSQ). Gas-fill and planarization on electronic circuits can be achieved by low-temperature processing of HSQ. Professor Pandey considered HSQ with cage sizes varying from 8 to 16, that while local DFT methods reproduce the structures reasonably well, they over-estimate the binding energies/silicon atom. The basic bonding picture does not change upon going from T₈ to T₁₆, but there is a large change in the HOMO-LUMO gap, and therefore the band structure along this sequence, due mainly

to large changes in the LUMO. T₁₄ and T₁₆ show gaps that arise mainly from SiH contributions to the LUMO.

Michael Bowers discussed the application of the MALDI (matrix-assisted laser desorption ionization) and ESI (electrospray ionization) techniques to the study of POSS compounds. The Bowers group combines these experimental methods with molecular mechanics computations to study ion mobilities and collision cross sections of R_nT_n cages, where R is either cyclohexyl (Cy) or vinyl (Vi). Agreement between experiment and theory for the cross sections is excellent. According to MALDI, the least compact structure is the most abundant. The calculations predict that the more compact structures have smaller cross sections.

Sharon Hammes-Schiffer discussed nuclear quantum effects in hydrogen transfer reactions in POSS formation. Instead of using the more standard approaches, in which the moving H atom is first treated classically, with subsequent corrections for tunneling to account for "corner cutting", the Hammes-Schiffer group directly calculate the nuclear quantum effects. To avoid computationally demanding grid-based calculations, they have developed an analytical approach that uses nuclear electronic orbitals (NEO). The method uses multi-configurational treatments of both the nuclear and electronic motions. This method was applied to the initial condensation reaction, for which it was discovered that a proper quantal treatment of

nuclear motion can lower barrier heights by as much as 9 kcal/mol.

Ian Carmichael discussed a study on atomic H in silsesquioxane cages, using density functional theory calculations to predict hyperfine splittings. This is of interest, since H inside T_8 was reported in 1994. The predicted temperature dependence of the hyperfine coupling agrees with experiment, but it is too weak, probably because a rigid cage potential was used.

Jack Tossell the behavior of Ti atoms in aluminosilicate minerals and zeolite catalysts. The particular questions addressed were: What are the spectral signatures for different local Ti geometries? How are Si and O signatures altered the proximity of Ti? How are the reactivity and properties of Ti-O-Ti affected by the proximity of Si-O? The calculations were done by using both Hartree-Fock and density functional theory to predict the NMR shielding. It is predicted that the presence of Ti has little effect on the ^{29}Si shielding but a very large effect on the O shielding.

Mark Banaszak-Holl presented results on his group's study of adsorption of POSS compounds on the Si(100) surface using STM techniques. It is found that the POSS prefer to adsorb at one Si, rather than on an edge, with the cluster remaining largely intact. They have also studied adsorption onto gold surfaces. In this case they find that the clusters react rapidly with the gold surface, including H exchange with the surface. A novel SiH activation is also observed at ambient temperatures.

Hai-Lung Dai discussed the photo-chemistry of silsesquioxane thin films. They are studying spin-on glass materials using new low-temperature deposition methods and 193 nm light. They then study the surface morphology using atomic force microscopy (AFM). It is believed that the RSiO group absorbs the photon, giving rise to R and SiO radicals. An oxygen source is required for the photochemistry to go to completion. Stochastic simulations were used to study the kinetics. Diffusion of the photofragments through the solid matrix is observed, followed by secondary reactions.

Barry Farmer used molecular dynamics (MD) simulations based on molecular mechanics to study the glass transition temperature of POSS-containing polymers. The glass transition temperature is predicted to increase with the weight percent of POSS, from 0 to 60%. His group also studied the diffusion of gaseous oxygen molecules in the presence of POSS with sizes varying from T_8 to T_{14} . It is predicted that even the largest cage is too small to permit diffusion of small molecules through the POSS cages.

Baudilio Tejerina studied the energetics of both N_2 and O_2 molecules passing through the faces of POSS cages, ranging in size from T_8 to T_{12} , using both Hartree-Fock and second order perturbation theory (MP2) methods. Inserting these molecules into the cages is endothermic in all cases, but the endothermicity and barrier height are smaller for O_2 than for N_2 , and both the endothermicity and the barrier decrease substantially as the size of the cage is increased. Preliminary MP2 results suggest that insertion of O_2 into the T_{12} cage may be feasible.

COMPUTATIONAL CHEMISTRY IN THE UNDERGRADUATE CURRICULUM.

Reported by Hannes Jonsson (University of Washington, Seattle). F. Rioux and H. Jonsson, Organizers.

A symposium jointly sponsored by the physical division and educational division focused on the many new possibilities that have emerged for using computers to help teach chemistry. The symposium served, in part, to bring research active teachers from the larger Universities and college teachers who concentrate on education to share their experience and educational material.

Some of the highlights included a presentation by **Horia Metiu** of a new P-Chem textbook he is writing where computational exercises with a high level mathematics program (such as Mathematica) are integrated into the curriculum, enabling the students to do homework on realistic problems rather than remaining confined to the highly simplified and idealized problems that typically are assigned as homework in P-Chem courses.

Kosloff and Ashkenazi demonstrated a powerful program for visualization of quantum

mechanics and illustrated how the topic can be taught from the point of view of time-dependent systems rather than just time-independent systems.

A web based tool for carrying out *ab initio* calculations was introduced by **Polik and Schmidt**. The software, called WebMO, functions as a "point-and-click" interface for setting up and running calculations with a variety of *ab initio* codes as well as visualization of the output.

Many other interesting approaches to the use of computers in chemical education were presented. Clearly much development has occurred in this area in the last few years. The symposium was well attended.

Conference Announcements

Future ACS Meetings

Orlando, FL, April 7-11, 2002

Program Chair: Professor John C. Hemminger, Department of Chemistry, University of California, Irvine, CA 92697, jchemmin@uci.edu

- Biophysical Chemistry of Protein Binding Events
- Chemistry and the Environment in the 21st Century: Environmental Chemistry at Interfaces
- Dynamics and Friction at Submicron Confining Systems
- Forces in Biology
- Frontiers in Chemical Dynamics
- Modern Aspects of Structure Function Correlations of Biomolecules: Electrostatic Aspects

- Modern Aspects of Structure Function Correlations of Biomolecules: Enzyme Action
- Modern Aspects of Structure Function Correlations of Biomolecules: Phosphoryl and Nucleotidyl Transfer Reactions
- Molecular Modeling and Simulation of Reaction Mechanisms, Kinetics and Catalysis
- Organic and Molecular Electronics
- Structural and Mechanistic Aspects of Amyloid Fibril Formation

Boston, MA, September 8-12, 2002

Program Chair: Professor John C. Hemminger, Department of Chemistry, University of California, Irvine, CA 92697, jchemmin@uci.edu

New Orleans LA March 23-27, 2003

Program Chair: Professor James L. Skinner, Department of Chemistry, University of Wisconsin, Madison, WI 53706, skinner@chem.wisc.edu

New York City NY September 7-11, 2003

Program Chair: Professor James L. Skinner, Department of Chemistry, University of Wisconsin, Madison, WI 53706, skinner@chem.wisc.edu

2002 ACTC: American Conference on Theoretical Chemistry

Organizer: Kenneth D. Jordan
 Seven Springs Mountain Resort, Champion, PA 15622
 July 13 - 18, 2002 <http://www.pitt.edu/~jordan/actc/>

2002 EURESCO: Biophysics from First Principles: From the Electronic to the Mesoscale

Organizers: Anne Chaka, Flavio Seno
 San Feliu du Guixols, Spain
 September 7-12, 2002

2002 Sanibel Symposium: Dedicated to the Memory of Per-Olov Löwdin

Organizers: Quantum Theory Project, University of Florida
 Ponce de Leon Resort, St. Augustine, Florida
 February 23- March 1, 2002 <http://www.qtp.ufl.edu/~sanibel/>

Subdivision Officers

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 Department of Chemistry
 University of California, Davis

Chair-Elect

(Program Chair for 2000,
Subdivision Chair for 2001)

Vice Chair

(Program Chair for 2001,
Subdivision Chair for 2002)

Secretary

Davis, CA 95616

Professor Edwin L. Sibert

Department of Chemistry

University of Wisconsin

Madison, WI

Professor Martin Head-Gordon

Department of Chemistry

University of California, Berkeley

Berkeley CA 94720

Dr. Anne Chaka

National Institute of Standards and Technology

100 Bureau Drive, Stop 8380

Gaithersburg, MD 20899-8380

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