REPORT DOCUMENTATION PAGE

AFRL-SR-BL-TR-02-

0053

ources, of this fferson

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	04 Feb 02	Final Report - 01 Dec 98 To 30 Nov 02

4. TITLE AND SUBTITLE
POTENTIAL ENERGY SURFACES AND DYNAMICS FOR HIGH ENERGY MATERIALS

5. FUNDING NUMBERS
F49620-99-1-0063
2303/EV
61102F

6. AUTHOR(S)
Dr Mark S. Gordon

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Iowa State University
Dept of Chemistry
Ames, IA 50011

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AFOSR/NL
801 N. Randolph Street, Room 732
Arlington, VA 22203-1977

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

20020221 068

12a. DISTRIBUTION AVAILABILITY STATEMENT

DISTRIBUTION STATEMENT A
Approved for Public Release
Distribution Unlimited

12b. DISTRIBUTION CODE

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFOSR)
NOTICE OF TRANSMITTAL DTIC. THIS TECHNICAL REPORT
HAS BEEN REVIEWED AND IS APPROVED FOR PUBLIC RELEASE
LAW AFR 190-12. DISTRIBUTION IS UNLIMITED.

13. ABSTRACT (Maximum 200 words)

On the theoretical side, a new highly scalable code for frozen core second order perturbation theory gradients for closed shell molecules has been developed. The development of analogous codes for molecules with unpaired electrons is in progress. A working unrestricted second order perturbation theory code is now in GAMESS, and work on a scalable version of this code will begin shortly. The derivation for the spin-restricted open shell second order perturbation theory gradients has been completed. Other important developments are new convergence methods for MCSCF wavefunctions that facilitate MCSCF calculations on large molecules, the derivation of gradients for multi-reference second order perturbation theory, further developments of our effective fragment potential (EFP) method for studying solvation and liquid behavior, the development of molecular dynamics and Monte Carlo methods to facilitate the study of solvation and liquid behavior, the development and implementation of a new method for producing global potential energy surfaces from sets of ab initio points, the development and implementation of a gridless approach to density functional theory, and the development and implementation of a general, all electron MCSCF approach to spin-orbit coupling. With regard to applications, considerable progress has been made in our understanding of the mechanisms for formation of POSS (polyhedral oligomeric silsesquioxanes) reaction. Careful studies of the potential energy surfaces of B and B2 interacting with H2 have been carried out, and similar studies for Al have been initiated. The reactions leading to Al and B oxides when these species are burned in a rocket engine are underway. Several studies of high energy organic and inorganic compounds are ongoing.

14. SUBJECT TERMS

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT

1. COVER SHEET

FINAL
AFOSR PROGRESS REPORT

POTENTIAL ENERGY SURFACES AND DYNAMICS OF HIGH ENERGY MATERIALS

AFOSR F49620-99-1-0063
12/1/98 – 11/30/02

MARK S. GORDON

IOWA STATE UNIVERSITY

AMES, IA 50011

2. Objectives: **No Change in Objectives**

3. Status of effort: A brief statement of progress towards achieving the research objectives. (Limit to 200 words.)

On the theoretical side, a new highly scalable code for frozen core second order perturbation theory gradients for closed shell molecules has been developed. The development of analogous codes for molecules with unpaired electrons is in progress. A working unrestricted second order perturbation theory code is now in GAMESS, and work on a scalable version of this code will begin shortly. The derivation for the spin-restricted open shell second order perturbation theory gradients has been completed. Other important developments are new convergence methods for MCSCF wavefunctions that facilitate MCSCF calculations on large molecules, the derivation of gradients for multi-reference second order perturbation theory, further developments of our effective fragment potential (EFP) method for studying solvation and liquid behavior, the development of molecular dynamics and Monte Carlo methods to facilitate the study of solvation and liquid behavior, the development and implementation of a new method for producing global potential energy surfaces from sets of *ab initio* points, the development and implementation of a gridless approach to density functional theory, and the development and implementation of a general, all electron MCSCF approach to spin-orbit coupling. With regard to applications, considerable progress has been made in our understanding of the mechanisms for formation of POSS (polyhedral oligomeric silsesquioxanes) reaction. Careful studies of the potential energy surfaces of B and B_2 interacting with H_2 have been carried out, and similar studies for Al have been initiated. The reactions leading to Al and B oxides when these species are burned in a rocket engine are underway. Several studies of high energy organic and inorganic compounds are ongoing.

4. Accomplishments/New Findings: Describe research highlights, their significance to the field, their relationship to the original goals, their relevance to the AF's mission, and their potential applications to AF and civilian technology challenges.

A. THEORY/MODEL DEVELOPMENT

Parallel Developments. A highly scalable code for frozen core second order perturbation theory gradients for closed shell molecules has been developed and is on-line for general use at several IBM SP2 and Cray T3E systems, including the T3Es at ERDC and NAVO and the SP2 at Maui. This new code uses the Distributed Data Interface (DDI) so that the large arrays do not have to be replicated. This means that much larger molecules can be studied using geometries based on correlated wavefunctions. The code scales very well for as many as 512 nodes and has already been applied to several challenging compounds. The development of analogous codes for molecules with unpaired electrons, using both restricted and unrestricted wavefunctions, is in progress. A paper on the

restricted open-shell derivation has been accepted. New developments will include the use of DDI for both SCF (completed, paper in print) and MCSCF wavefunctions (in progress). In an important related development, parallel GAMESS now runs on clusters of PCs and Macs (running Linux) and high end workstations. This is more challenging than self-contained massively parallel computers, since the overhead due to inter-node communications is more complex. This issue has been solved to some extent by using a Gigabit Ethernet switch with large data packets. It is, however, still a major research area. As for all other GAMESS developments, we will make our experiences in developing scalable PC and Mac clusters available to all users.

Condensed Phase Methods. We have already shown that our effective fragment potential (EFP) method for solvation is excellent for water, in a variety of applications. We are now working on extending the capabilities of the method in several ways. We are exploring several alternative approaches for incorporating dispersion and other higher order terms into the method. Such terms are particularly important for nonpolar solvents. We are also in the process of extending the model so that it is equally applicable and accurate for any solvent. Key to the success will be the derivation of general expressions for charge transfer and dispersion contributions that contain no fitted parameters. A very important new development (by co-worker Jan Jensen) is a new method for using EFPs across covalent bonds. This will facilitate the representation of large substituents, as well as the treatment of large biological molecules. We have also interfaced the EFP method with two continuum methods, the simple Onsager reaction field and the more sophisticated polarizable continuum model (PCM).

As the number of solvent molecules in the system increases, the number of configurations to be considered increases rapidly, and traditional small molecule geometry optimization methods are not effective. We are therefore developing both molecular dynamics and Monte Carlo simulation codes so that the configurational space can be probed more effectively, not only for minima, but for transition states and reaction paths as well. This is also an important first step in the development of methods based on the EFP model for predicting bulk properties and super-critical behavior. We are therefore incorporating Ewald summations into our MD method. Collaborators in this effort are Dr. Paul Day (AFRL) and Professors Teresa Head-Gordon (UC-Berkeley) and Grant Merrill (University of Missouri). Related to these dynamical methods is our development and implementation of a method for converting the large numbers of points generated in *ab initio* trajectories into a global potential energy surface, using a modified Shepard interpolation approach.

Major James Shoemaker's Ph.D dissertation in Engineering Physics at the Air Force Institute of Technology focused on the development and applications of an embedded cluster model for treating surface chemistry. A paper on the theoretical method, called SIMOMM, has been published in the Journal of Physical Chemistry. Several papers applying this method have now been published or submitted, and a manuscript that describes applications to silicon carbide surfaces is in progress. Extensions of this method to transition metal catalysts are planned; however, molecular mechanics is not likely to be a viable approach for the bulk, since electrons in such systems are too

delocalized. To overcome this potential problem, we have begun to explore fast multipole methods (FMM) that scale linearly and are also highly parallel, so that the bulk part of the system can be treated by quantum mechanics. One preliminary paper has been published and the first FMM paper has also been published.

Other developments There are many problems that involve species for which one cannot write one simple Lewis structure. Such species must be treated with multi-configurational (MCSCF) wavefunctions. However, the computational demands for MCSCF calculations are very high. So, we have developed a set of methods for converging such wavefunctions that range from very rapid convergence with high CPU and disk requirements to methods that converge more slowly but have very modest computational demands. The advantage of the latter is that much larger molecules than normal can be treated with this method.

For species that must be treated with MCSCF wavefunctions, non-traditional methods are also needed to recover the dynamic correlation. One method that has been implemented into GAMESS is multi-reference second order perturbation theory. The gradient formulas for this method have been derived, and the implementation into GAMESS is in progress. The key collaborator in this effort is Dr. Haruyuki Nakano (University of Tokyo).

There are many problems that involve multiple electronic states on multiple potential energy surfaces. Since such surfaces can cross and therefore induce radiationless transitions, it is important to have the capability to predict non-adiabatic coupling among these surfaces. One origin of non-adiabatic interactions among surfaces is spin-orbit coupling. Spin-orbit coupling matrix elements must be calculated using multi-reference wavefunctions, but until recently, there have been no generally available codes for the computation of these matrix elements using all electrons and any arbitrary MCSCF wavefunction for any arbitrary set of spin states. We have now developed and implemented such a method. It will be particularly valuable for the study of high energy density materials and for the study of any processes involving transition metals, since both types of species involve multiple electronic states. Since such all-electron calculations are very demanding, two alternative approaches to this problem have also been develop and implemented into GAMESS for use with larger molecules. One of these is called the Z_{eff} method, in which the two electron term is ignored and a fitted empirical parameter is introduced into the one-electron part of the Hamiltonian. While this is a very efficient approach, its accuracy is limited. However, there is an intermediate method, in which only those matrix elements connecting orbitals in the active space with each other are neglected. We have shown that in this case excellent agreement with the all electron method is obtained, without any need for fitted parameters.

Density functional theory (DFT) has become extraordinarily popular in recent years, because it has the same computational requirements as Hartree-Fock theory, but often has a level of accuracy that is comparable to second order perturbation theory. One difficulty with DFT is that most implementations involve evaluation of integrals using numerical

grids, and this is inherently unstable. We have developed and implemented a gridless approach to DFT, by using the resolution of the identity to evaluate the complicated integrals. This procedure requires the use of auxiliary basis sets to resolve the identity. After extensive analysis of the convergence of several molecular properties as a function of basis set, we have recommended a series of auxiliary basis sets for use with the first row in the periodic table. The next step will be to extend this basis set development to heavier elements.

Another approach that is very important for large molecules, especially molecules that contain heavier elements, is the effective core potential (ECP) method. This method replaces inner shell electrons by model potentials, making the calculations much more efficient. These potentials include relativistic corrections for the heavier elements. To make these calculations more useful, we have developed much more efficient methods for obtaining the first and second energy derivatives; that is, the gradients and hessians. The increase in speed is a factor of 5-10, and the method has been implemented to take advantage of parallel computers.

As calculations on larger and larger species are made feasible by advances in parallel programs and other innovative algorithms, it becomes increasingly important to develop graphical methods for interpreting the results of complex calculations. This has led to the continuing development of MacMolPlt, a graphical interface for GAMESS. MacMolPlt provides the ability to visualize (and rotate in real time) orbitals, wavefunctions, electron densities and electrostatic potentials in two and three dimensions.

We have also been exploring alternatives and extensions to the popular G2 and G3 methods developed by Pople and co-workers for the accurate prediction of such theormodynamic properties as heats of formation, ionization potentials and electron affinities. One limitation of these methods is that they are applicable only to species that are adequately described by single configuration wavefunctions. This eliminates many transition metal compounds, diradicals and most transition states. We have therefore initiated, in collaboration with the Radom group, the development of multi-reference analogs of the G2 and G3 methods. The multi-reference methods are based on CASSCF wavefunctions, instead of Hartree-Fock, followed by multi-reference perturbation theory (instead of MP2) and finally multi-reference CI.

B. APPLICATIONS

POSS Compounds. Polyhedral oligomeric silsesquioxanes (POSS) have a wide variety of important applications, including lubricants and coatings. Consequently, there is considerable interest in these species in industry, universities and Air Force Laboratories. We have therefore initiated a detailed study of POSS compounds, with primary emphasis on the mechanisms by which these species form, in both the gas phase, and in solution and the presence of catalysts. In the first series of calculations, we examined the three stepwise hydrolysis steps of trichlorosilane, followed by the condensation of the product trihydroxysilane. All four reactions are predicted to have large barrier heights in the gas phase, but the addition of just one extra water molecule is sufficient to reduce all barriers

to zero or nearly zero, except for the first hydrolysis step. In the latter, there is still a residual barrier of a few kcal/mol. So, the next step will be to examine the effect of additional water molecules, especially on this first step. Since these are rather large species, the additional water molecules will be treated with the EFP method. The molecular dynamics (MD) and Monte Carlo (MC) codes, now almost completed, will be essential as the number of water molecules is increased. A new paper discussing the effects of waters and subituent effects is in preparation.

For both the hydrolysis and condensation steps in the POSS mechanism, there exist low lying intermediates. Even though the net barriers are nearly all small in the presence of an additional water molecule, the barriers separating these intermediates from products are large. So, it is not entirely clear how easily products will be obtained in solvent. To determine this, *ab initio* dynamics "on-the-fly" will be carried out in the presence of waters, using the MD and MC codes.

Calculations have also been completed on the next steps in the mechanism, in which the initial condensation products, disiloxanes, are further condensed to the ring compounds D3 and D4. These results are consistent with those reported above, in that initially high barriers are reduced to nearly zero by an additional water molecule. The next steps in this process will include further condensation to the three-dimensional cages and analysis of substituent effects on the reaction mechanism and energetics.

Although our main focus is on Si-based POSS, the Ti analogs are also of interest. We have therefore initiated a series of calculations on the Ti-POSS compounds to study their properties.

Fuels with High N-Content. There has been considerable interest in the last several years in the potential for cubic molecules as high energy fuels. Cubane itself has been considered, and so far rejected because of the complexity of its synthesis. The octasila analog of cubane has been prepared. Unlike the carbon system, the cubic structure is the most stable Si_8H_8 isomer. This makes it potentially very interesting, since it is still rather high in energy. However, the heavy mass of Si precludes any viability of such species as high energy fuels.

On the other hand, cubic N_8 is a light, very high energy fuel that has been the subject of considerable attention. Extensive calculations, however, illustrate that the upper limit of the barrier separating this species from four nitrogen molecules is 20 kcal/mol. It is, therefore, not a viable high energy fuel. In the process of studying the cubic N_8 potential energy surface, it was discovered that there are three N_8 isomers that are much lower in energy than the cube, yet still much higher in energy than molecular nitrogen. The potential energy surfaces for these isomers have now been studied in detail. Two of these have barriers on the order of 15-20 kcal/mol (too small), but the third has a barrier of nearly 30 kcal/mol. So, this isomer may be a viable synthetic target.

Related to the foregoing, much attention has been paid recently to N_4 as a potential fuel. Many references are made to a barrier on the order of 50-65 kcal/mol, even though it has

been shown by Yarkony that non-adiabatic interactions reduce this barrier to less than 40 kcal/mol. For the first time, we have mapped out the potential energy surface that leads from tetrahedral N_4, using second order perturbation theory. One also must consider the possibility that two N_4 molecules could interact and form molecular nitrogen. This possibility is being explored in this laboratory.

Rob Schmitt at SRI proposed an intriguing series of potential high energy compounds that we have been exploring computationally. The procedure is to use a modified version of G2 to predict the heats of formation and then to use these predictions to assess the specific impulse. For the most promising species, further studies are performed in which the stability of these compounds with respect to unimolecular decomposition, bimolecular interactions and attack by environmental species such as water.

Christe and co-workers at AFRL (Edwards) have isolated the first new all-nitrogen species in nearly a century. With the counter ion, this species is $[AsF_6^-][N_5^+]$. We have now studied the potential energy surface of this species as it forms AsF_5 + FN_5, and subsequently the pathway leading from FN_5 to FN_3 + N_2.

There has been considerable experimental and theoretical interest in metal-doped solid hydrogen. We have an ongoing series of investigations of the low-lying electronic states of BH_2 system, to determine the energetics by which the metal is held as a weakly bound species in the matrix and the ease with which two metal atoms find each other. Similar studies are under way on the B_2-H_2 system and the Al analogs.

The desired reaction product for burning Al-doped H_2 is Al_2O_3, since it is the thermodynamically most stable aluminum oxide. However, it is unknown how or when this species forms in the process. We have therefore initiated an extensive study of the potential energy surface that leads from Al and O_2 to various oxides. The first step, the reaction of Al with O_2 to from AlO_2 is nearly complete. The disproportionation reaction between two AlO_2 molecules is in progress.

5. <u>Personnel Supported</u>: List professional personnel (Faculty, Post-Docs, Graduate Students, etc.) supported by and/or associated with the research effort.

Dr. Michael W. Schmidt, Senior Research Associate
Dr. Brett Bode, graduate student, postdoctoral research associate
Professor Larry Burggraf
Dr. Cheol Ho Choi, postdoctoral research associate
Professor Gyusung Chung
Mr. Dmitri Fedorov, graduate student.
Mr. Mark Freitag, graduate student.
Dr. Kurt Glaesemann, graduate student, postdoctoral research associate
Ms. Vassiliki-Alexandra Glezakou, graduate student.
Professor Takako Kudo, Gunma University.
Dr. Grant Merrill, postdoctoral research associate.

Mr. Michael Pak, graduate student.
Professor Leo Radom, Australian National University.
Major James Shoemaker

6. Publications: List peer-reviewed publications submitted and/or
accepted during the 12-month period starting the previous 1 October (or since
start for new contracts).

1. J.H. Jensen and M.S. Gordon, "An Approximate Formula for the Intermolecular Pauli Repulsion Between Closed Shell Molecules. II. Application to the Effective Fragment Potential Method", J. Chem. Phys., 108, 4772 (1998).

2. G.N. Merrill and M.S. Gordon, "A Study of Small Water Clusters Using the Effective Fragment Potential (EFP) Method, J. Phys. Chem. A, 102, 2650 (1998).

3. M.W. Schmidt and M.S. Gordon, "The Construction and Interpreation of MCSCF Wavefunctions", Ann. Rev. Phys. Chem. (INVITED), 49, 233 (1998).

4. T. Taketsugu, T. Yanai, K. Hirao, and M.S. Gordon, "Dynamic Reaction Path Study of $SiH_4 + F^-$ and the Berry Pseudorotation with Valley-Ridge Inflection", THEOCHEM (Huzinaga Special Issue),), 451, 163 (1998).

5. T. Takata, T. Taketsugu, K. Hirao and M. S. Gordon, "*Ab initio* potential energy surface by modified Shepard interpolation: Application to the $CH_3 + H_2 \rightarrow CH_4 + H$ reaction", J. Chem. Phys., 109, 4281 (1998).

6. T. Kudo and M.S. Gordon, "Theoretical Studies of the Mechanism for the Synthesis of Silsesquioxanes. I. Hydrolysis and Initial Condensation", J. Am. Chem. Soc., 120, 11432 (1998).

7. H. Nakano, K. Hirao and M.S. Gordon, "Analytic Energy Gradients for Multiconfigurational Self-Consistent Field Second-Order Quasidegenerate Perturbation Theory (MC-QDPT)", J. Chem. Phys., 108, 5660 (1998).

8. K.R. Glaesemann and M.S. Gordon, "Investigation of a Grid-Free Density Functional Theory (DFT) Approach", J. Chem. Phys., 108, 9959(1998).

9. M.S. Gordon, V.-A. Glezakou, and D.R. Yarkony, "Systematic Location of Intersecting Seams of Conical Intersection in Triatomic Molecules: The $1^2A'-2^2A'$ Intersection in BH_2", J. Chem. Phys., 108, 5657 (1998).

10. S. Koseki, M.W. Schmidt and M.S. Gordon, "Effective Nuclear Charges for the First-Through Third-Row Transition Metal Elements in Spin-Orbit Calculations, J. Phys. Chem., 102, 10431 (1998).

11. K.R. Glaesemann and M.S. Gordon, "Evaluation of Gradient Corrections in Grid-

Free Density Functional Theory", J. Chem. Phys., 110, 6580 (1999).

12. J. Shoemaker, L.W. Burggraf and M.S. Gordon, "SIMOMM: An Integrated Molecular Orbital/Molecular Mechanics Optimization Scheme for Surfaces", J. Phys. Chem. A, 103, 3245 (1999).

13. . B.M. Bode and M.S. Gordon, "MacMolPlt: A Graphical User Interface for GAMESS", J Molec. Graphics., 16, 133(1999).

14. G.D. Fletcher, M.W. Schmidt, and M.S. Gordon, "Developments in Parallel Electronic Structure Theory", Adv. Chem. Physics (invited), 110, 267 (1999).

15. C.H. Choi, J. Ivanic, M.S. Gordon, and K. Ruedenberg, "Direct Recurrence Relations for the Rapid and Stable Determination of Rotation Matrices between Spherical Harmonics", J. Chem. Phys., 111, 8825 (1999).

16. M.W. Schmidt, M.S. Gordon, and J.A. Boatz, "Cubic Fuels?", Int. J. Quantum Chemistry, 76, 434 (2000).

17. D.G. Fedorov and M.S. Gordon, "A Study of the Relative Importance of One and Two Electron Contributions to Spin-Orbit Coupling", J. Chem. Phys., 112, 5611 (2000).

18. M.W. Schmidt, G.D. Fletcher, B.M. Bode and M.S. Gordon, "The Distributed Data Interface in GAMESS", Computer Physics Communications, 128, 190 (2000).

19. P.N. Day, R. Pachter, M.S. Gordon and G.N. Merrill, "A Study of Water Clusters Using the Effective Fragment Potential and Monte Carlo Simulated Annealing", J. Chem. Phys., 112, 2063 (2000)

20. M.A. Freitag, M.S. Gordon, J.H. Jensen and W.J. Stevens, "Evaluation of charge penetration between distributed multipolar expansions", J. Chem. Phys., 112, 7300 (2000).

21. Bandyopadhyay and M.S. Gordon, "A Combined Discrete/Continuum Solvation Model: Application to Glycine", J. Chem. Phys., 113, 1104 (2000).

22. G. Chung, M.W. Schmidt and M.S. Gordon, "An Ab Initio Study of Potential Energy Surfaces for N_8 Isomers", J. Phys. Chem. A, 104, 5647 (2000)

23. K.R Glaesemann and M.S. Gordon, "Auxiliary basis sets for grid-free density functional theory", J. Chem. Phys., 112, 10738 (2000).

24. T. Kudo and M.S. Gordon, "Theoretical Studies of the Mechanism for the Synthesis of Silsesquioxanes. 2. Cyclosiloxanes (D_3 and D_4)", J. Phys. Chem., A104, 4058 (2000).

25. M.S. Gordon, M.A. Freitag, P.Bandyopadhyay, V. Kairys, J.H. Jensen, and W.J.

Stevens, "The Effective Fragment Potential Method: A QM-Based MM Approach to Modelling Environmental Effects in Chemistry", J. Phys. Chem. (Feature Article), A105, 293 (2001).

26. C.H. Choi, L. Ruedenberg and M.S. Gordon, "A new parallel optimal-parameter fast multipole method", J. Comp. Chem., 22, 1484 (2001).

27. M.V. Pak and M.S. Gordon, "The Potential Energy Surfaces for AlO_2 using Multi-reference Wave Functions", Chem. Phys. Lett., 344, 236(2001).

28. "Gradient of the ZAPT2 Energy", G.D. Fletcher, M.S. Gordon and R.S. Bell, Theor. Chem. Accts., in press.

29. T. Kudo and M.S. Gordon, "Structures and Stabilities of Titanium Silsesquioxanes", J. Phys. Chem., in press.

30. Y. Alexeev, R.A. Kendall and M.S. Gordon, "The Distributed Data SCF", Computer Physics Commun., 143, 69 (2002)

7. Interactions/Transitions:

a. Participation/presentations at meetings, conferences, seminars, etc.

TALKS AT PROFESSIONAL MEETINGS

1. "Gridless Density Functional Theory", presented by K. Glaesemann, ", National American Chemical Society Meeting, Dallas, TX, April 1998.

2. "Theoretical Studies of Explosive Molecules", presented by V. Glezakou, ", National American Chemical Society Meeting, Dallas, TX, April 1998.

3. "Chemical Reaction Dynamics", AFOSR Molecular Dynamics Contractors' Meeting, Monterey, CA, May 1998.

4. "Effect of Solvents on Chemical Processes", Canadian Symposium on Theoretical Chemistry (INVITED), Vancouver, BC, August 1998.

5. "The Mechanism of Formation of POSS Species", Symposium on High Temperature Materials (INVITED), Maui, HI, January 1999

6. "Effect of the Medium on Chemical Reactions", Morokuma Symposium, Atlanta, GA, May 1999 (INVITED)

7. "Enabling Calculations on Large Molecules Using Parallel Computers", AFOSR High Energy Density Materials Meeting, Cocoa Beach, FL, June 1999 (INVITED)

8. "Medium Effects on Chemical Reactions",, American Conference on Theoretical Chemistry, Boulder, CO, June 1999

9. "Restricted High-Spin Open Shell Theory: The Z Avreaged Perturbation Theory (ZAPT) Gradient", presented by Robert Bell, , American Conference on Theoretical Chemistry, Boulder, CO, June 1999

10. "Improved Implementation of the Fast Multipole Method (FMM)", presented by Cheol Ho Choi, , American Conference on Theoretical Chemistry, Boulder, CO, June 1999

11. "Distributed Dtat MP2 on PC Clusters", presented by Mike Schmidt, , American Conference on Theoretical Chemistry, Boulder, CO, June 1999

12. "Investigation of the First Potential Surfaces of the Systems $B + H_2$ and $B_2 + H_2$ with Large Scale Ab Initio Calculations, presented by Vassiliki-Alexandra Glezakou, , American Conference on Theoretical Chemistry, Boulder, CO, June 1999

13. "QM/MM Methods for solvation and Surface Chemistry", National ACS Meeting, New Orleans, LA, August 1999. (INVITED)

14. "Direct recurrence relations for the rapid and stable determination of rotation matrices between complex spherical harmonics", presented by Cheol Ho Choi, National ACS Meeting, New Orleans, LA, August 1999

15. "The Effect of the Medium on Chemical Reactions", Royal Australian Chemistry Institute Conference, Canberra, Australia, February 2000 (INVITED).

16. "Effect of the Medium on Chemical Reactions", Central Regional ACS Meeting, Cincinnati, May 2000 (INVITED)

17. "A Cluster Approach to Solvation and Surface Chemistry", AFOSR Dynamics Contractors' meeeting, Boston, May 2000.

18. "Effect of the Medium on Chemical Reactions", Midwest Theoretical Chemistry Conference, Iowa City, May 2000 (INVITED)

19. "Hydrogen Transfer in Materials and Biomolecules", National ACS Meeting, Washington, DC, August 2000 (INVITED)

INVITED LECTURES

1. "Ubiquitous Water", Advanced Supercomputer Center, Wright-Patterson AFB, October 1997

2. "Ubiquitous Water", Coulson Lecture, University of Georgia, October 1997

3. "Ubiquitous Water", University of Utah, November 1997

4. "Ubiquitous Water", Australian National University, January 1998

5. "Ubiquitous Water", Melbourne University, February 1998

6. "Ubiquitous Water", Sydney University, February 1998

7. "Potential Energy Surfaces for Mechanisms in Organometallic Chemistry", University of Iowa, February 1998

8. "Ubiquitous Water", Roseman Lecture, Johns Hopkins University, April 1998

9. "Ubiquitous Water", University of Nebraska, September 1998

10. "The Role of Water in Chemical Processes", Grinnell University, February 1999

11. "Ubiquitous Water", Marquette University, February 1999

12. "The Effective Fragment Method", Pople Symposium, Amelia Island, FL, March 1999

13. "Ubiquitous Water", Long Island University, Brooklyn, NY, March 1999

14. "Water as a Catalyst", Union Carbide Corp., May 1999

15. "The Effect of the Medium on Chemical Reactions", Boston University, October 1999

16. "The Effect of the Medium on Chemical Reactions", University of Arizona, October 1999

17. "The Effect of the Medium on Chemical Reactions", University of Michigan, October 1999

18. "Quantum Chemistry at Iowa State University", University of Sydney, March 2000

19. "Effect of the Medium on Chemical Reactions", Kansas State University, April 2000

20. "Effect of the Medium on Chemical Reactions", Princton University, May 2000

  b. Consultative and advisory functions to other laboratories and agencies, especially Air Force and other DoD laboratories. Provide factual information about the subject matter, institutions, locations, dates, and name(s) of principal individuals involved.

• Served as co-advisor to Major James Shoemaker, who received his Ph.D. from the Department of Engineering Physics, Air Force Institute of Technology, October 1997. Several papers from this work; are already in print.

• Collaborating with Dr. Robert Schmitt (SRI) and Dr. Jerry Boatz (AFRL) to develop new HEDM compounds.

• Collaborating with Dr. Joe Lichtenhan (AFRL) to determine the mechanisms for the formation of POSS.

• Collaborating with Drs. Paul Day and Ruth Pachter (AFRL) to study the behavior of clusters of water and other solvents.

• Collaborating with Dr. Ruth Pachter to develop density-functional-based effective fragment potentials.

  c. Transitions. Describe cases where knowledge resulting from your effort is used, or will be used, in a technology application. Transitions can be to entities in the DOD, other federal agencies, or industry. Briefly list the enabling research, the laboratory or company, and an individual in that organization who made use of your research.

Both GAMESS and MacMolPlt have an increasing number of users in universities, industry, and government laboratories. The latest version of parallel GAMESS is on-line at all DoD Major Shared Resource Centers.

8. New discoveries, inventions, or patent disclosures. (If none, report None.) **None**

9. Honors/Awards: List honors and awards received during the grant/contract period. List lifetime achievement honors such as Nobel prize, honorary doctorates, and society fellowships prior to this effort.

¶ Coulson Lecturer, University of Georgia, October, 1997

¶ Roseman Lecturer, Johns Hopkins University, April, 1998

¶ Named Distinguished Professor of Chemistry, May, 1998

10. <u>Markings</u>: In order to ensure prompt receipt and acceptance,
mark the outside of the package clearly to indicate that it is a progress report.