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Potential Energy Surfaces and Dynamics For Energetic Ionic Liquids

**Mark S. Gordon**
**Iowa State University, Department of Chemistry**
**201 Spedding Hall, Ames, IA 50011**

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Several ne methods were developed and applied to high energy ionic liquids. The fragment molecular orbital (FMO) method can be applied to very large species while retaining high accuracy. The FMO method has been extended to open shell species and has been interfaced with our effective fragment potential (EFP) solvent method. We are systematically developing the key features of GAMESS for graphical processing unit (GPU) architecture. Electron repulsion integrals and the Hartree-Fock method are now completed. Applciations to triazolium-based and Al13 based ionic lquids have been develoepd and others are under study.

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The main focus of this research is on the design and study of highly energetic species that have the potential to be novel new fuels. Of special importance are energetic ionic liquids. Progress was made in both theory/code development and applications. The **theory/code developments** include advances in *ab initio* quantum chemistry and dynamics and in novel computational approaches.

**Quantum Chemistry and Dynamics[1-4,18,19].** There are several ways that one can expand the sizes of molecular systems that are amenable to accurate quantum mechanics (QM) methods. Two such approaches are to subdivide the system into tractable pieces ("fragments") and the development of highly scalable (parallel) algorithms. Two successful fragmentation methods, the fragment and molecular orbital (FMO) method[1,3,18,19] and the symmetric fragmentation method[1,2,18] (SFM) have been developed and applied to a variety of interesting problems. The FMO approach, which has been implemented for most levels of electronic structure theory, avoids arbitrary procedures like hydrogen atom capping and employs distance cut-offs as criteria for invoking approximations for expensive two-electron integrals. We have extended the method to open shell species[3,19]. The method can include all two-body (FMO2), three-body (FMO3), etc., interactions explicitly, as computer resources allow. Because each fragment can be assigned to a different compute node, the method scales linearly with system size, and it can take advantage of multi-level parallelism. The FMO method has also been interfaced with both implicit and explicit solvent methods. A very important application is to energetic ionic liquids (EIL). The EILs of interest to us are fairly complicated: polynitrogen cyclic cations combined with oxygen-rich anions. To obtain a realistic connection with experiments requires the simulation of at least large clusters, if not the actual condensed phase. The FMO method is proving to be invaluable for this effort[1]. The SFM[1,2], which was designed for the study of large molecule dynamics employs hydrogen capping and is similarly extensible to 2-, 3-, etc., body interactions. SFM is also inherently parallel. The Grow program, which uses a modified Shepard interpolation to construct potential energy surfaces for ground and excited electronic states, has been interfaced with the MCSCF method in GAMESS, in order to enable multi-state dynamics studies. The EFP method, discussed below, has been interfaced with the FMO method[4].

**Solvent Effects and Intermolecular Interactions[4-6].** The EFP method[5] is among the most sophisticated methods for treating intermolecular interactions, including solvent effects. The general (EFP2) method includes all important interaction types, including Coulomb, induction, exchange repulsion, dispersion, and charge transfer. This has been accomplished without the use of any empirically fitted parameters, so an EFP can be generated for any type of system, including charged species. Many-body effects are incorporated via the induction term that is iterated to self-consistency. The ground state EFP2-QM interaction is partially complete, with the energy and analytic gradient implemented for the Coulomb and induction terms, and the energy for the exchange

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repulsion. The modified Fock operator and the gradient have been derived for the exchange repulsion-QM gradient. The EFP2-QM dispersion energy has been derived and the coding is in progress. The EFP and FMO methods have been interfaced[6]. We have demonstrated that the EFP method is able to capture both 2- and 3-body interactions very well. This means EFP can greatly reduce the computational cost of calculating 3-body interactions rather than the correlated methods. In the SFM, for example, one can calculate all inter-fragment interactions with EFP and maintain high accuracy[1,2].
**Novel Computational Methods**[11-16,21]. One way to increase the applicability of *ab initio* electronic structure methods to more complex species is to develop novel algorithms that take advantage of modern computer technology. Our new advances in this direction include a parallel analytic Hatree-Fock Hessian[9], parallel analytic gradients for restricted open shell second order perturbation theory[7], and parallel closed shell coupled cluster CCSD(T) theory[10,11]. Our recent advances in scalable electronic structure have been summarized in a review paper.[8] New advances will include improved scalable coupled cluster algorithms for both open and closed shells, including completely renormalized methods that are capable of breaking single bonds, and our novel, new multi-reference methods. A major new direction is the development and implementation of electronic structure methods that can take advantage of modern computing architectures. One such architecture, embodied in the BlueGene series and the Cray XT series, combines low-cost cores with low heat output to engineer computer systems with tens of thousands of cores. We have demonstrated that the MP2 code in GAMESS can take great advantage of such architectures[12]. Very recently, we have implemented the FMO method on the BG/P system at Argonne National Laboratory, demonstrating that we can efficiently use 20,000 cores. We are also in the process of developing many features of GAMESS on graphical processing unit (GPU) technology. We have developed and implemented new GPU code for the high angular momentum two-electron integrals[13] that are so important for high-level *ab initio* calculations. We have also developed a new Hartree-Fock code with much improved efficiency on both CPU and GPU architecture[21]. Imilar efforts are under way for second order perturbation theory and coupled cluster codes. An important side benefit of these developments is that we have significantly improved the original CPU codes.

The **applications** that were addressed include studies of ionic liquids, novel anionic species, and electrospray processes. An important aspect of studying ionic liquids is that simple models, such as small clusters, cannot realistically model the liquid. Earlier studies in our group showed, for example, that one cation combined with one anion is unstable, with a proton typically jumping spontaneously from the cation to the anion to form a neutral pair. As noted above, studying multiple cation-anion pairs is computationally challenging. However, we performed a high-level calculation of the double pair with 1,2,4-triazolium as the cation and dintiramide as the anion[15]. We showed, using a combination of MP2 and CCSD(T), that this species forms a $\pi$–stacked arrangement, with the two positively charged rings facing each other like a benzene dimmer sandwich compound. This species, at the CCSD(T) level of theory, is fully 6 kcal/mol *lower* in energy than the corresponding neutral formed by a double proton transfer. This suggests that two ion pairs at least begin to show some resemblance to the liquid. We are now using the FMO method to examine larger clusters[18,20]. We have also used the EFP method to systematically study benzene-benzene interactions, in which one

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benzene ring has one substituent[16]. The interaction energies and geometries are in good agreement with experiment. Castleman has proposed that $Al_{13}^-$ behaves as a "superhalide" that might functions as an appealing anion. The only previous studies of this species have employed density functional theory, which is an inappropriate method for such species. We have therefore employed MP2 and CCSD(T) to explore the potential energy surfaces of both $Al_{13}^-$ and $Al_{13}$ neutral. This allows us to calculate the ionization potential with high accuracy and to predict the structures of both anion and neutral, at a much reliable level of theory than heretofore reported[17].

In a joint experiment-theory study[14], we analyzed the clustering of $I^-$ with 1-4 formamide molecules in order to interpret field-ion evaporation of these species.

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## References

**1**. M.S. Gordon, J.M. Mullin, S.R. Pruitt, L.B. Roskop, L.V. Slipchenko and J.A. Boatz, "Accurate Methods for Large Molecular Systems", J. Phys. Chem. B (Invited Centennial Feature Article), 113, 9646 (2009).
**2**. J.M. Mullin, L.B. Roskop, S.R. Pruitt, M.A. Collins, and M.S. Gordon, "Systematic Fragmentation Method and the Effective Fragment Potential: An Efficient Method for Capturing Molecular Energies", J. Phys. Chem. A113, 9945 (2009).
**3**. S.R. Pruitt, D.G. Fedorov, K. Kitaura, and M.S. Gordon, "Open-Shell Formulation of the Fragment Molecular Orbital Method", J. Comp. Theoret. Chem., 6, 1 (2010).
**4**. T. Nagata, D. Fedorov, K. Kitaura, and M.S. Gordon, "A Combined Effective Fragment Potential - Fragment Molecular Orbital Method. I. The Energy Expression and Initial Applications", J. Chem. Phys., 131, 024101 (2009).
**5**. M.S. Gordon, L. Slipchenko, H. Li, and J.H. Jensen, "The Effective Fragment Potential: A General Method for Predicting Intermolecular Forces", Ann. Rep. Comp. Chem., 3, 177 (2007).
**6**. T. Nagata, D. Fedorov, K. Kitaura, and M.S. Gordon, "A Combined Effective Fragment Potential - Fragment Molecular Orbital Method. I. The Energy Expression and Initial Applications", J. Chem. Phys., 131, 024101 (2009).
**7**. C.M. Aikens, G.D Fletcher, M.W. Schmidt, and M.S. Gordon, "Scalable Implementation Of Analytic Gradients For Second-Order Z-Averaged Perturbation Theory Using The Distributed Data Interface", J. Chem. Phys., 124, 014107 (2006).
**8**. M.S. Gordon, K. Ruedenberg, M.W. Schmidt, L. Bytautas, T.J. Dudley, T. Nagata, R. Olson, and S. Varganov, "Scalable correlated electronic structure theory", J. Phys Conf Series, 46, 229 (2006)
**9**. Y. Alexeev, M.W. Schmidt, T.L. Windus, M.S. Gordon, "A Parallel Distributed Data CPHF Algorithm for Analytic Hessians, J. Comp. Chem., 28, 1685 (2007).
**10**. J.L. Bentz, R.M. Olson, M.S. Gordon, M.W. Schmidt, and R.A. Kendall, "Coupled Cluster Algorithms for Networks of Shared memory Parallel Processors", Comp. Phys. Comm., 176, 589 (2007).
**11.** R. M. Olson, J. L. Bentz, R. A. Kendall, M. W. Schmidt, and M. S. Gordon, "A Novel Approach to Parallel Coupled Cluster Calculations: Combining Distributed and Shared Memory Techniques for Modern Cluster Based Systems", J. Comp. Theoret. Chem., 3, 1312 (2007).
**12**. A. Asadchev, B.M. Bode, and M.S. Gordon, "Performance of Electronic Structure Calculations on Blue Gene and Cray XT4 Computers", J. Comput. Theoret. Nanoscience, 6, 1290 (2009).
**13**. A. Asadchev, V. Allada, J. Felder, B.M. Bode, T.L. Windus, and M.S. Gordon, "Unconracted Rys Quadrature Implementation of up to g Functions on Graphical Processing Units", J. Comp. Theor. Chem., 6, 696 (2010).
**14**. W.D. Luedtke, Uzi. Landman, Y.-H. Chiu, D. J. Levandier, R. A. Dressler, S. Sok and M. S. Gordon, "Nanojets, Electrospray, and Field-Ion Evaporation: Molecular Dynamics Simulations and Laboratory Experiments", J. Phys. Chem. A, 112, 9628 (2008) (Feature Article).

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**15.** T. Smith, L.V. Slipchenko, and M.S. Gordon, "Modeling π-π interactions with the effective fragment potential method: The benzene dimer and substituents", J. Phys. Chem. A, 112, 5286 (2008).
**16**. H. Li, J.A. Boatz, and M.S. Gordon, "Cation-cation P□P stacking in small ionic clusters of 1,2,4-triazolium", J. Am. Chem. Soc., 130, 392 (2008).
**17.** Q.A. Smith and M.S. Gordon, "The Electron Affinity of $Al_{13}$. A Correlated Electronic Structure Study", J. Phys. Chem. A, 115, 899 (2011).
**18**. M.S. Gordon, D.G. Fedorov, S.R Pruitt, and L.V. Slipchenko, "Fragmentation Methods: A Route to Accurate Calculations on Large Systems", Chem. Rev, 112, 632 (2012) (INVITED).
**19.** S.R. Pruitt, D.G. Fedorov, and M.S. Gordon, "Geometry Optimizations of Open Shell Systems with the Fragment Molecular Orbital Method", J. Phys. Chem. A, in press.
**20.** P.J. Carlson, S. Bose, D.W. Armstrong, T. Hawkins, M.S. Gordon and J.W. Petrich, "Structure and Dynamics of the 1-Hydroxyethyl-4-amino-1,2,4-triazolium Nitrate (HEATN) High Energy Ionic Liquid System", J. Phys. Chem. B, 116, 503 (2012)
**21.** A. Asadchev and M.S. Gordon, "New Multithreaded Hybrid CPU/GPU Approach to Hartree-Fock", J. Chem. Theory Comp., submitted.

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