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14. ABSTRACT Great progress was made in both theory/code development and in a variety of applications that are important to the Air Force. The theory/code developments include advances in ab initio quantum chemistry and dynamics, in the development of the effective fragment potential method for the study of the complete range of intermolecular interactions, in spectroscopy in both the gas and condensed phases, and in the development of novel computational approaches. The latter include massively parallel algorithms and the introduction of many of the most time-consuming electronic structure methods for graphical processor hardware. More than 30 publications have resulted from this work.					
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Progress was made in both theory/code development and in a variety of applications that are important to the Air Force. The **theory/code developments** include advances in *ab initio* quantum chemistry and dynamics, in the development of the EFP method for the study of the complete range of intermolecular interactions, in spectroscopy in the gas and condensed phases, and in novel computational approaches.

**Quantum Chemistry and Dynamics.** 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 molecular orbital (FMO) method<sup>4,8,10,14,23,28,33</sup> and the symmetric fragmentation method<sup>4,9,14,33</sup> (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. 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. Fully analytic gradients for the FMO/HF method have now been derived and implemented. This is especially important for the FMO molecular dynamics code that is in the testing stage. The SFM<sup>4,9,13</sup>, 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. A recent development has been to design and implement a time-dependent density functional theory (TDDFT) approach to finding conical intersections in photochemistry.<sup>13</sup> Ordinarily, TDDFT fails for conical intersections, but we have implemented a new TDDFT approach that is based on the spin-flip approach developed by Krylov and co-workers. This method has been successful in correctly finding and characterizing the conical intersection in ethylene. We are now moving on to more complex species, such as stilbene. A method that has the same goals as the FMO and SFM approaches, but specifically designed to extend the sizes of active spaces in MCSCF (multi-configuration self-consistent field) calculations, is the ORMAS (Occupation Restricted Multiple Active Space) method. As noted below, ORMAS is a very powerful method for surface science, but its limitation is that it does not include the dynamic correlation that is necessary to predict accurate energies. We have now derived and implemented a second order perturbation theory method (ORMAS-PT) that is built upon ORMAS<sup>32</sup>. This most general method approach for capturing dynamic correlation in a multi-reference approach.

**Solvent Effects and Intermolecular Interactions.** The EFP method<sup>3,4,8,10,22,23,24,30</sup> 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 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 a preliminary code has been implemented, with testing underway. The EFP and FMO methods have been interfaced to provide both energies and gradients<sup>8,23</sup>. 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<sup>2,4,9,22,33</sup>. Interfacing of the EFP method with several excited state methods is in progress. The EFP method has now been interfaced with both the TDDFT method<sup>24</sup> and the multi-reference perturbation theory method<sup>30</sup>. Interfaces with other excited state methods are under way.

**Spectroscopy.** Both electronic and vibrational spectroscopy are important diagnostic tools for the complex systems of interest to the Air Force. In electronic spectroscopy, there is interest in multi-photon excitations, unusual nonlinear optical phenomena, and solvent effects on these properties and processes. We have therefore implemented time-dependent density functional theory in GAMESS, and interfaced this method with the EFP solvent method<sup>24</sup>. Together with a recently developed and implemented QM/EFP molecular dynamics (MD) method, one can now study solvent effects on UV spectra<sup>24</sup>. A major bottleneck in using TDDFT for this purpose is the limitations of common functionals for many excited state problems. We have therefore implemented several new meta GGA and range separated functionals into GAMESS and enabled TDDFT with these functionals. These results will be reported in a forthcoming benchmark paper. We have also worked with the HPCMP (High Performance Computing Modernization Program) HTPi team to greatly improve the efficiency of the DFT and TDDFT codes in GAMESS. Computational chemists commonly correct for the harmonic approximation in the calculation of vibrational spectra and thermodynamic properties by applying a scaling factor to the calculated frequencies. However, the use of one scale factor for the entire range of frequencies is a serious over-simplification, and for some thermodynamic properties (e.g., entropy, free energy), the harmonic approach is fundamentally flawed, since such properties are dominated by the lowest frequency, most anharmonic modes. Also, for these low frequency modes, the most commonly used Cartesian coordinates are inappropriate, since in Cartesian space the torsion, bending and even stretching modes tend to be highly coupled<sup>29</sup>. We showed that in the context of the vibrational self-consistent field (VSCF) approach (which fails for low frequency modes when Cartesians are used), expanding the potential energy surface (PES) using internal (local) coordinates gives rise to a marked improvement in the predicted vibrational spectra and associated thermodynamic properties.<sup>29</sup> This approach represents a major advance in the study of vibrational spectra of polyatomic molecules.

**Novel Computational Methods.** 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. We have therefore demonstrated how to take advantage of novel architectures, such as the IBM BlueGene and the Cray XT<sup>1</sup>. A major new direction is the development and implementation of electronic structure methods that can take advantage of graphical processing unit (GPU) technology. We have developed and implemented new GPU code for the high angular momentum two-electron integrals<sup>17</sup> that are so important for high-level *ab initio* calculations. An important side benefit of this development is that we have also improved the original CPU code. We have also released a new GPU-based Hartree-Fock code in GAMESS. We are now proceeding to develop both MP2 and CCSD(T) capabilities on GPU architecture.

The **applications** that were addressed include studies of catalysis, surface science, spectroscopy and related dynamics, clusters and precursors, and a variety of chemical reaction mechanisms.

**Catalysis.** There has been considerable interest in the catalytic activity of small Au<sub>n</sub> (n up to 20) clusters on metal oxide supports. An analysis of the binding of ethylene clusters to Ag<sup>+</sup> and Au<sup>+</sup> reveals<sup>5</sup> that these clusters bind more strongly to Au<sup>+</sup> than to Ag<sup>+</sup>. The binding energies per ethylene decreases as the number of ethylenes increases, suggesting that the metal-ethylene interaction is not entirely electrostatic. The binding energies to Ag<sup>+</sup>, obtained with CCSD(T) and extrapolated to the complete basis set limit are in excellent agreement with experiments.

**Surface Science**<sup>21,22</sup>. The Si<sub>9</sub>H<sub>12</sub> cluster is commonly used to represent the Si(100) surface. Most previous calculations were based on DFT which tends to predict buckled structures for both this cluster and for the surface itself. In a landmark calculation, we used both coupled cluster theory, CCSD(T), and multi-reference perturbation theory geometry optimizations to demonstrate unequivocally that Si<sub>9</sub>H<sub>12</sub> is planar and symmetric. This does not necessarily mean that the extended surface is planar, but it does suggest that the previous DFT calculations must be called into question. To extend this analysis to larger clusters, we have employed the ORMAS (Occupation Restricted Multiple Active Space) method to study much larger clusters with multiple dimers<sup>19</sup>. These calculations illustrate the accuracy of ORMAS relative to a full CASSCF calculation and also support the notion that the Si(100) surface is not buckled.

**Solvent Effects.** The EFP method has been employed to study several important problems. The process of solvation of biomolecules is inherently important, and such species form the backbones of many important new materials that exhibit novel optical properties. We have systematically studied aqueous solvation of the nonionic – zwitterionic equilibrium for alanine<sup>7,11</sup>. Water molecules tend to localize around the carboxyl group, and only when this region of the amino acid is fully solvated do the waters start to interact strongly with other regions. For alanine, for example, it appears that a first solvent shell is only completed at about 45 water molecules. This number will increase with the size of the amino acid or more complex biomaterial. We have also examined solvent effects on species that have atmospheric importance, such as NaCl<sup>16</sup>, ClNO<sup>18</sup>, and nitrate<sup>12</sup>. We have also used the EFP method to study the interactions of various species with aromatic species<sup>2,31</sup>. This is a problem in which DFT fails and even

MP2 is not very good. The EFP method approaches CCSD(T) in accuracy for these species.

**Spectroscopy & Dynamics.** The new spectroscopic methods have been applied to several interesting problems. In collaboration with experimental colleagues, the VSCF method has been employed to study clusters of H<sub>2</sub> with alkali metal and alkaline metal cations<sup>29</sup>. Agreement with the experimental spectra is excellent. Theory reproduces the unusual trends in the H-H vibrational frequency when H<sub>2</sub> is bound to M<sup>+</sup>. Even though B<sup>+</sup> is not very strongly bound to H<sub>2</sub>, the modification of the H-H frequency upon complexation is dramatic. Since this trend only appears when electron correlation is included in the calculations, simple orbital arguments cannot provide a credible explanation. However, an analysis based on the symmetry adapted perturbation theory reveals that the B<sup>+</sup> interaction with H<sub>2</sub> is much more repulsive than it is for the other cations. Several studies of excited state solvent dynamics using the interface of the EFP method with MCSCF and TDDFT have been completed and others are under way or planned. Most recently, we have used the combined EFP-MRMP2 method to study the solvent-induced shifts in both the n-π\* and π-π\* states of uracil<sup>30</sup>. These calculations constitute the most accurate calculations on this system to date. A novel method has been developed to guide spectroscopists with regard to when it is acceptable (i.e., correct) to interpret spectral shifts along homologous series in terms of orbital behaviors, especially when using TDDFT<sup>21</sup>.

**Clusters & Precursors.** Polyhedral oligomeric silsesquioxanes (POSS) are three-dimensional Si-O cage compounds that have many uses, because of their resistance to extreme conditions of temperature and pressure. Given their three-dimensional nature, they also have potential as hydrogen storage devices. We have now completed a study of the dynamics of multiple H<sub>2</sub> molecules entering POSS cages of various sizes<sup>27</sup>. The direct dynamics trajectories allow us to explore the behaviors of H<sub>2</sub> molecules as they are formed with the cages. Most POSS cages are too small to accommodate more than one hydrogen molecule. Once the cage is big enough (e.g., T<sub>12</sub>), it is too easy for one H<sub>2</sub> to escape from the cage. Atrane molecules are small analogs of POSS compounds that have many important applications. It has been noted previously that the atranes are very difficult to hydrolyze. We have shown, in good agreement with experiment, that if one first protonates one of the equatorial oxygen atoms, the barrier to hydrolysis decreases to nearly zero. The various mechanisms for the process have been mapped out. This work will be reported in a paper to be submitted shortly.

**Other Applications.** The SFM has been used to develop an understanding of intramolecular amide stacking<sup>14</sup>. The MCSCF method has been used to guide experiments in an interpretation of the Raff reaction<sup>20</sup>. Castleman has proposed that novel species can behave as super bases and may therefore be important in the construction of novel ionic liquids. We have performed very high level CCSD(T) calculations on one such species, Al<sub>13</sub><sup>-</sup> to predict its ionization potential in nearly perfect agreement with experiment<sup>25</sup>.

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