COMPUTATIONAL THERMOCHEMISTRY OF JET FUELS AND ROCKET PROPELLANTS

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Introduction and Background

The design of new high-energy density molecules as candidates for jet and rocket fuels is an important goal of modern chemical thermodynamics. The NASA Glenn Research Center is home to a database of thermodynamic data for over 2000 compounds related to this goal, in the form of least-squares fits of heat capacities, enthalpies, and entropies as functions of temperature over the range of 300 - 6000 K. The chemical equilibrium with applications (CEA) program,[1] written and maintained by researchers at NASA Glenn over the last fifty years, makes use of this database for modeling the performance of potential rocket propellants. During its long history, the NASA Glenn database has been developed based on experimental results and data published in the scientific literature such as the standard JANAF tables.

The recent development of efficient computational techniques based on quantum chemical methods provides an alternative source of information for exansion of such databases. For example, it is now possible to model dissociation or combustion reactions of small molecules to high accuracy using techniques such as coupled cluster theory[2] or density functional theory.[3] Composite approaches, in which several such methods are used in concert, such as the Gaussian-n theory (*e.g.*, G2 or G3)[4,5] or complete basis set (CBS) methods (*e.g.*, CBS-Q or CBS-QB3),[6,7] have allowed computations of enthalpies of formation to within so-called "chemical accuracy" — ca. 1-2 kcal/mol.

Unfortunately, the current applicability of reliable computational methods is limited to relatively small molecules containing only around a dozen (non-hydrogen) atoms. High-accuracy methods, such as coupled cluster, scale poorly — upwards of $\mathcal{O}(N^7)$ as the size of the molecule, N, is increased. For example, a single coupled cluster energy computation of one conformation of tetrahydrodicyclopentadiene (THDCPD), $C_{10}H_{16}$, the principal component of the synthetic jet fuel JP10, requires approximately one week on modern high-performance computer hardware. A similar calculation on a THDCPD dimer would require nearly 2.5 years to complete — a factor of $2^7 = 128$ over the monomer. This high-degree polynomial scaling problem clearly limits the usefulness of these methods to a small range of chemical problems.

We propose to extend the applicability of coupled cluster theory — often referred to as the "gold standard" of quantum chemical methods — to molecules containing 30-50 non-hydrogen atoms. The centerpiece of this work is the concept of **local correlation**, in which the description of electron interactions — known as electron correlation effects — are reduced to only their most important localized components. Such an advance has the potential to greatly expand the current reach of computational thermochemistry and thus to have a significant impact on the theoretical study of jet and rocket propellants.

Local Correlation and Coupled Cluster Theory

The source of the polynomial scaling wall described above is the use of molecular orbitals (MO's), simple mathematical functions that describe the motions of individual electrons. The most convenient (and common) choice of these functions are the so-called "canonical" MO's, for which the resulting mathematical equations assume a particularly simple form. Unfortunately, the canonical MO's are also highly delocalized over the entire molecular framework and, as a result, often lead to overestimation of the importance of the interactions of electrons on spatially distant atoms.

Fortunately, as first described by Pulay and Saebø,[8,9] this problem may be overcome by instead choosing a more localized orbital form. As a result, vast numbers of electronic wave function parameters become negligible and may thus be ignored. This approach is tantamount to correlating only the motions of electrons on parts of the molecule that are in close proximity. The local correlation concept was originally applied to many-body perturbation theory (MBPT) and the coupled electron pair approximation (CEPA),[9–14] and has been found to be advantageous not only in the improvement of computational scaling, but also in the reduction of basis-set superposition error (BSSE).[15]

Our research group at Virginia Tech has begun implementation of the local correlation approach within coupled cluster theory. The development platform for this work is PSI3 suite of quantum chemical programs we have been constructing over the last five years in collaboration with researchers at Georgia Tech, the University of Georgia, and Sandia National Laboratories in Livermore, California. We have recently completed a set of "pilot" local correlation programs based on our canonical-MO coupled cluster codes. We have used these pilot programs to simluate the efficacy of orbital localization in reducing the size of the coupled cluster wave function. Our initial tests agree with earlier work by Hampel and Werner,[16] who found that the scaling factor is reduced by approximately *three orders of magnitude*. Hence, the motivation for further effort in this area is strong.

The next stage of this research, which would be partially funded by NASA, is the development of a "production-level" program — one that takes full advantage of the efficiency possible in the local coupled cluster approach. The primary challenge in this component of the research is speed — not only of the final programs but their construction as well. Because this work will involve the from-scratch design of new computer code, our extensive experience with canonical-MO coupled cluster programs will be invaluable. In addition, our planned research will include the design and implementation of a parallel version of our coupled cluster programs. Although our ultimate goal is to make these high-level quantum chemical techniques practical on common computer hardware, simultaneous development of the programs for networked clusters of workstations will allow us to carry out the largest coupled cluster calculations ever attempted, but on relatively modest computer hardware. In addition, we will make our code available to NASA Glenn researchers as soon as it reaches a beta-test stage of development.

The funds requested in this proposal ($20,000) will be used in conjunction with support from the Department of Energy ($10,000), the Jeffress Memorial Trust ($29,000), and Virginia Tech ($35,000) to build a cluster of high-performance computers (including high-speed networking hardware) on which the new parallel local coupled cluster methods will be developed and applied. A "critical mass" of 16 workstations will provide the nucleus for a much larger cluster to be built over the next several years. This level of computational power is necessary because of the extremely large data sets required by quantum chemistry programs. Funding for two graduate students will be provided by the PI's CAREER award from the National Science Foundation ($435,000). A budget for this request is included with this proposal.

Summary

The construction of accurate and reliable quantum chemical methods for large molecules presents many challenges. Although the expected obstacles to developing a parallel local coupled cluster approach are far from trivial, the course of research proposed here promises to significantly advance the applicability of high-accuracy quantum chemistry to molecules long considered to be out of reach. Once the computational challenges described here are met, a new theoretical model chemistry based on coupled cluster theory — the gold standard of quantum chemistry — will undoubtedly have a substantial impact on computational thermochemistry and its ability to predict the thermodynamic properties of rocket and jet propellants.

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