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Molecular Interactions and Properties with Many-Body Methods

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Please see report for abstract

Molecular Interactions and Properties with Many-Body Methods

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to

Air Force Office of Scientific Research

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I. Introduction

A variety of Air Force applications require highly detailed information about atoms, molecules, and their interactions. This information is necessary in problems ranging from chemical laser development, to the detection and identification of rocket plumes, to non-linear optics, electron beam technology, and high density and energy fuels.

The crucial component needed to understand molecular reactions is the potential energy surfaces (PES) that serve to describe the attractions among the atoms and molecules. However, such information is not easy to obtain. In many cases, the most direct approach to obtaining accurate potential surfaces for molecules, and detailed information about their excited states, vibrational spectra, and a wealth of other quantities, is high level ab initio solutions of the Schrödinger equation.

However, more so than in most other areas, the ability to provide reliable quantum mechanical results for increasingly large molecules depends critically on improved method development. Whereas supercomputers can enable us to make much larger computations with old methods, the simultaneous development of new methods can increase computational capability by further orders of magnitude. In this regard, many-body perturbation theory (MBPT) and its infinite-order extensions termed coupled-cluster (CC) methods offer a number of attractive features that the more traditional configuration interaction approaches lack.

Under AFOSR support, we have established these CC/MBPT theories as being among the most accurate available, and have developed very efficient and generally applicable computer programs to perform CC/MBPT calculations. Also, we have employed these methods for the first time in large-scale ab initio calculations of potential energy surfaces. The successes of our original work in this effort have been substantial (see previous AFOSR reports).

Following a statement of research objectives, we review the recent scientific advances we have made under AFOSR support.

II. Research Objectives

The overall objective of our continuing research program for AFOSR has included the following:

1. The development of new, more accurate and more efficient ab initio quantum mechanical methods based upon coupled-cluster (CC) and many-body perturbation theory (MBPT) for determining molecular properties and potential energy surfaces for molecular interactions.

2. The implementation of these methods into highly efficient, transportable computer programs (ACES II), to enable computations on molecules to be made on an almost routine basis, for a wide variety of different properties.

3. The application of these techniques to a variety of problems that are of interest to AFOSR, and that serve to establish the range of accuracy for CC/MBPT methods.

The underlying goal of our effort is highly accurate first principle quantum mechanical predictions of molecular properties. Such tools are already making possible the determination of dissociation energies, moments, polarizabilities, excitation energies, and vibrational and
rotational spectra for molecules to an accuracy that is predictive and comparable to experiment. Furthermore, for transient molecules as occur in rocket plumes, combustion, flame chemistry, and interstellar space that are generally difficult to study experimentally, theoretical calculations will provide otherwise inaccessible information. In addition, theoretical work provides the underlying framework to understand innumerable important molecular phenomena and to suggest previously unanticipated solutions to defense related problems. All of the new methods which we develop are being incorporated into our Advanced Concepts in Electronic Structure II (ACES II) program system. The program has been established at Air Force installations for use by other Air Force researchers.

III. Notable Accomplishments This Past Year

A. In a major achievement, we presented the first results from the full CCSDT method for open shell molecules.\(^2\)\(^*\) Comparison with full CI demonstrated exceptional agreement. We also employed several different open-shell references, including unrestricted Hartree Fock (UHF), restricted open-shell Hartree Fock (ROHF), and quasi-restricted Hartree Fock (QRHF). This study complements our presentation of CCSDT for closed shells in 1987.

B. Our next major contribution was to present an algorithm for the convenient inclusion of Abelian symmetry into CC calculations.\(^4\) This "Direct Product Decomposition Approach" provides an enormous improvement in computational speed. All steps after the molecular integrals can potentially gain by a factor of \(h^2\) where \(h\) is the order of the symmetry group. For a \(D_{2h}\) molecule, this means a CC calculation can be done up to 64 times faster than without symmetry. By also recognizing that we can represent all the products in the highly non-linear CC equations exclusively in terms of recursively computed intermediates, we are able to perform CC calculations solely in terms of generalized matrix products. These features are incorporated into our entirely rewritten ACES II program with the net result that we can do correlated calculations from about 2 to 100 times faster than other popular program packages like GAUSSIAN 90.

C. The ozone (\(O_3\)) molecule has proven to be a highly demanding test case for the most powerful quantum mechanical methods. Usually reliable methods give a very wrong ordering of the vibrational frequencies, with some even implying that \(O_3\) would not have \(C_{2v}\) symmetry, e.g. Since \(O_3\) is much too large for a full CI result, we provided a benchmark CCSDT result.\(^5\) Unlike all methods that had a less complete inclusion of triple excitations like MBPT(4), CCSDT-1, CCSD+T(CCSD), etc. and multi-reference CI, CCSDT provides the most accurate results for \(O_3\) frequencies compared to experiment. This application is also the largest CCSDT calculation ever reported.

D. We also addressed the fascinating question of whether NO\(_3\) is \(D_{3h}\) (i.e. has all N-O bond lengths equal) as all textbooks would assume, or is a distorted \(C_{2v}\) structure (with one N-O bond different than the others). This problem poses great difficulties for quantum mechanical calculations, because a slight displacement of the molecule from the point where

\(^*\) References in this section refer to the publications listed under: Publications Supported by AFOSR (1990 — 1991), pg. 6.
the molecule is $D_{3h}$ to $C_{2v}$ gives a discontinuity in the energy for most applicable methods.\(^5\)

The reason is that the open-shell UHF or ROHF solution at $D_{3h}$ symmetry does not have $D_{3h}$ symmetry (i.e. "symmetry breaks"). This kind of symmetry breaking permeates many molecular and solid state applications, and even though the exact solution shows no such symmetry breaking, any correlation method short of full CI cannot resolve the difficulty. Our solution to the problem is only made possible in CC theory. The CCSD wavefunction is $\exp(T_2)\exp(T_1)\Phi_0$, and the $\exp(T_1)$ operator has great ability to rotate the orbitals forming the single determinant reference function $\Phi_0$ to be whatever they need to be to describe the relevant physics. This enables us to take orbitals from NO$_3^-$, which is a closed shell, and whose wavefunction, unlike that for NO$_3$, smoothly connects as the $D_{3h}$ anion is distorted to the $C_{2v}$ form. By simply deleting an electron from the highest orbital occupied in NO$_3^-$, we obtain what we have called a quasi-restricted Hartree Fock (QRHF) reference. Like an ROHF, the QRHF reference is an eigenfunction of spin, but unlike the ROHF, it does not suffer from symmetry breaking. At the CCSD level, the $C_{2v}$ form is very slightly lower in energy than is the $D_{3h}$, although the inclusion of triple excitation reverses the slight difference to be in favor of the $D_{3h}$ form. Excitation energies for the lowest lying states are in excellent agreement with recent experimental data, although the experiments remain inconclusive on the definitive structure.

E. As shown above for O$_3$, of great practical importance are the effective inclusion of higher excitations like $T_3$ excitations on top of CCSD methods. For sufficiently difficult examples, even $T_4$ will become important. The computational dependence of such terms can be up to $n^{10}$ ($n$ is the size of basis set) times the number of iterations for CCSDTQ and $n^8$ for CCSDT. Furthermore, compared to $n^6$ for CCSD, their proliferation is such that often the only viable techniques for their inclusion lies in non-iterative methods. We introduced a method called CCSD+TQ*(CCSD) that puts in the initial $T_3$ and $T_4$ contributions as a single evaluation of an $n^8$ quantity. All $T_4$ terms are included with only a single $n^7$ iteration, while the contribution of $T_3$ requires a single $n^8$ procedure. We have presented the first such methods that are correct through fifth order that include the $T_4$ and $T_3$ term.\(^4\) Comparisons with full CI demonstrate their high accuracy. This is also demonstrated for the quasidegenerate $H_4$ system\(^7\) which poses a particular challenge for single reference CC methods. However, CCSD+TQ*(CCSD) performs exceedingly well even for this demanding case.

F. In a notable advance\(^8\) involving open-shell gradients, we report such analytical derivative methods for the QRHF-CCSD method as described above for NO$_3$. The method is illustrated by application to the methyl radical, CH$_3$ and the $^2B_2$ state of the NO$_2$ radical. This implementation is incorporated into ACES II showing the same exceptional speed as in the energy calculations themselves. All such methods are built upon the "relaxed density" concept we introduced some years back.

G. In another paper on this subject\(^9\), we have further generalized our CCSD analytical derivative methods to include restricted open-shell Hartree-Fock (ROHF) references. This permits the treatment of open-shell molecules when spin contamination of an unrestricted Hartree-Fock (UHF) is a problem. Unlike the QRHF method where orbitals are taken from a different molecular state (NO$_2^-$ for NO$_2$, e.g.), the ROHF solution is the energetically
optimum choice, that is still an eigenfunction of spin. This, too, has its range of applications.

H. Finally, symmetry breaking for the potential curve where \( F_2^+ \to F+F^+ \) was considered.\(^{11}\) This is a classic example where at \( R_e, D_{\infty h} \) symmetry applies, but at \( R \to \infty, C_{\infty v} \) applies. At the CC level with triples, we found that several different reference functions, symmetry broken or not, could be used with equal facility.

All of the above are important, timely developments in the field that provide solutions to molecular problems that in many cases, could not be previously addressed.
IV. Publications Supported by AFOSR (1990–1991)


V. Invited Presentations (1990–1991)

June 1990  AFOSR Non-Linear Optical Polymers Contractors Meeting, Washington, DC
June 1990  W.N. Lipscomb 70th Birthday Symposium, Cambridge, MA
July 1990 Seventh American Conference on Theoretical Chemistry, San Diego, CA
July 1990 Seventy-Third Canadian Chemical Conference, Halifax, NS
May 1991 American Chemical Society Joint Central-Great Lakes Regional Meeting, Indianapolis, IN

VI. Students Supported (and Graduated)
    Capt. Walt Lauderdale, Ph.D., December, 1991
    David Bernholdt
    Renee Mattie
    Sullivan Beck

VII. Honors
    Elected a fellow of the International Academy of Quantum Molecular Sciences, Menton, France, 1991. Only 30 members younger than 65 are allowed, and 65 members total.