**Title:** Molecular Interactions and Properties with Many-Body Methods

**Abstract:** During the course of this research, CC/MBPT theories have been established as being among the most accurate available, and very efficient and generally applicable computer codes have been developed to perform CC/MBPT calculations. These methods have been employed for the first time in large scale ab initio calculations of potential energy surfaces. Two of the papers produced in this research have been identified by authorities as being among the most influential papers in the 50-year history of computational quantum chemistry, and four have been identified by Current Contents as qualifying as science citation classics.
FINAL TECHNICAL REPORT


MOLECULAR INTERACTIONS AND PROPERTIES WITH MANY-BODY METHODS

to

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

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I. INTRODUCTION

In a wide variety of Air Force applications, highly detailed information about atoms, molecules, and their interactions is required [1-3]. This information is necessary in problems ranging from chemical laser development, to the detection and identification of rocket plumes, to clustering and aerosol formations, non-linear optics, electron beam technology, rocket fuels, and even to nuclear weapons effects [1-3].

The crucial component needed to understand molecular reactions is the potential energy surfaces that serve to describe the attractions among the atoms and molecules [1]. However, such information is not easy to obtain. A certain amount of information about the molecular forces near equilibrium in a bound molecule is available from spectroscopy. Some information about the potential energy surface even in the absence of binding can be provided from crossed molecular-beam experiments. But, in general, potential energy surfaces are not amendable to experimental determination. Instead, other types of observations such as kinetics experiments, coupled with very simple theoretical models for a surface, are used to infer pieces of information about the parameters of the model such as what the activation barrier might be. In addition there is an unrelenting need for essential information about other molecular properties like excitation energies, oscillator strengths, moments, polarizabilities, etc.

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 quantum mechanical calculations.

*References are on page 14.*
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 the same old methods, the simultaneous development of new methods can increase computational capability by a further two or three orders of magnitude. In this regard, many-body perturbation theory (MBPT) [4-15] and its infinite-order extensions termed coupled-cluster (CC) methods [11,16-22] offer a number of attractive features that the more traditional configuration interaction approaches lack [21].

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 codes 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 [11,21]. The successes of our original work in this effort have been substantial (see previous AFOSR reports.) Two of our papers [11,22] supported by AFOSR have been identified in a book by Schaefer, *Quantum Chemistry* (Oxford, 1984), as being among the 149 most influential papers in the 50-year history of computational quantum chemistry. Recently four of our papers supported by AFOSR have been identified by Current Contents as qualifying as science citation classics [7,10a,11,21], and one was chosen to be featured [23]. In each case the paper has been cited more than two hundred times and found to be among the ten most cited papers in the respective journals.

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 codes, 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.
III. NOTABLE ACCOMPLISHMENTS (November 1, 1987 - October 31, 1989)

A. For the first time, contributions from "connected" quadruple excitations, $T_4$, have been included into coupled-cluster theory. This allows us to define the CCSDTQ-1 method [24]. Comparisons with reference full CI results demonstrate an average error of only 0.35 mhartree (0.22 kcal/mol). This should be compared with the best prior method, CCSDT, which we presented a few years ago [25], whose error for the same set of examples is 0.93 mhartree.

B. The direct inclusion of $T_4$ into CC theory involves an $n^9$ step, where $n$ is the dimension of the basis set. This is one power of $n$ worse than CCSDT. Deriving from our recently proposed XCC and UCC methods [26-30], we were able to show that the initial contribution of $T_4$ could be introduced with no worse than an $n^7$ step. Exploiting this, we proposed a highly efficient non-iterative inclusion of $T_4$ to be added to any CCSDT-n model. This Q(CCSDT) method [24] was found to very accurately reproduce full CI results to a mean error of only 0.23 mhartree. As this is the most efficient method that includes $T_4$ (no step is worse than $n^7$) it should find wide applicability. It also offers significant improvement for the extreme test case of Be$_2$ [24] (see Figure 2).

C. The first report of results for the new fourth- and fifth-order expectation value XCC methods were made [28,29]. Unlike the usual CC method, for the energy XCC uses the ansatz that $\Delta E = \langle \psi | (e^{-T \cdot H e^T})_e | \psi \rangle$ and approximations are obtained by energy variation to some order in perturbation theory. XCC(4) [29] was shown to provide results falling between MBPT(4), the standard used in most chemical applications today, and our CCSAT-1 method [31]. The fifth-order version XCC(5) along with CCSDTQ-1 and CCSDT+Q(CCSDT)
are the first CC methods correct through fifth-order. Barring convergence difficulties, this method was found to be quite accurate but not as good as the other fifth-order methods. A modified version called XCC(5)M overcame the convergence problems, and had a mean error of 0.84 \( mh \) compared to full CI [28].

D. The other new method we investigated was the unitary, UCC method [27]. Using

\[
\tau = T - T^\dagger, \quad \Delta E = \langle \eta (E^\tau He^\tau)_C | \phi \rangle \approx \langle \eta (E^\tau He^\tau)_C | \phi \rangle.
\]

Energy variation leads to the UCC(n) equations. Unlike other CC methods, UCC is guaranteed to satisfy the generalized Hellmann-Feynman theorem. This makes it far easier to evaluate properties other than the energy. We implemented UCC(4) for analytical gradients which facilitates the search for minima and transition states on energy surfaces and for the determination force constants which leads to the prediction of vibrational spectra. UCC(4) was found to give very good structures and vibrational frequencies for several examples [30].

E. A byproduct of the above was that we were able to report general results for fifth-order MBPT for the first time [32]. MBPT(5) constitutes the reference point for all CC methods correct through fifth-order. We reported results for a number of examples including \( O_3 \) which is known to require a multi-configurational zeroth-order description. Consequently, a single reference method should show large errors in higher-order. We find that \( E_5 \) amounts to 20 \( mh \) and that contributions from connected quadruples is a very large \( -16 \) \( mh \).

F. One of our other primary accomplishments this year has been the continued development of our "relaxed density" correlated method [33-36]. This new density is fundamental to many studies of chemical bonding. In our study of
the bond-breaking reaction \( \text{CH}_4 \rightarrow \text{CH}_3 + \text{H} \), we used color graphics to plot \( r_1 \), correlated relaxed densities to facilitate an understanding of correlation effects on this bond breaking reaction [37].

G. The relaxed density permits the facile evaluation of any one-electron property. This was illustrated by our study of numerous properties like field gradients, dipole and quadrupole moments, and several other properties [35, 36].

H. The relaxed density is also the cornerstone of all our recently developed analytical gradient methods. In the last year, we have generalized such techniques to include the full MBPT(4) method and CCD [36].

I. In another major advance, we presented the theory for full CCSDT analytical gradients [38] and CCSDT-1 analytical second derivatives [39]. The general theory has other methods such as Pople's so-called "quadratic CI" as special cases.

J. In a study demonstrating the beneficial mutual interaction of theory with experiment, an experiment of Zare, et al. [40] for the barrier height of \( \text{O}({}^3\text{P}) + \text{Cl} \rightarrow \text{OH} + \text{Cl} \) suggested that \( \text{OH} \) was produced vibrationally hot. This is easier to understand if the transition state is non-linear. Using high-level correlated methods, we found a non-linear transition state with a CCSDT-1 barrier of 10.2 kcal/mol for the forward reaction and 7.4 for the reverse [41]. Zare's experiment estimates a barrier height of -6 kcal/mol.

K. The theory and implementation of analytical gradients for the full SDTQ-MBPT(4) [36]* method has been accomplished this year for the first time. This will enable us to routinely and efficiently search potential energy
surfaces for minima and transition states at the very attractive and accurate MBPT(4) level of approximation.

L. Similarly, we have defined a "response" density which can be directly obtained for all levels of MBPT [36]. Using the response density we can readily evaluate any one-electron property very efficiently. We have used this technique to calculate moments, field gradients and some second-order properties like polarizabilities [36].

M. Using our recently implemented CCSDT model, the extremely difficult problem of the potential energy curve for Be\(_2\) has finally been resolved [43]. Be\(_2\) has been found to have a minimum near 2.5 Å with a depth of about 2 kcal/mol, in addition to the expected VanderWaal's minimum at about 4 Å (see Fig. 1). CCD, CCSD, and CCSDT-1 do not find this inner minimum despite the latter being within about 1.2% of the exact result (i.e. full CI) because the 1.2% of the correlation energy accounts for the small, inner well. To go beyond CCSDT-1 to the full CCSDT method, it is necessary to fully include all effects of connected triple excitations, \(T_3\). In our recent implementation of the full CCSDT model [25], we once again studied the Be\(_2\) potential curve. The full inclusion of \(T_3\) accounts for the inner minimum as shown in the figure.

Another important consequence of this study is that it offers the first ab initio measure of the effect of "connected" quadruple excitations, \(T_4\) (although now our XCC(5) and CCSDTQ-1 have \(T_4\) included). Since Be\(_2\) is studied as a four electron system (the 1s electrons are not correlated) the difference in energy between the full CI result and CCSDT is the effect of \(T_4\). This amounts to about 0.3 me (i.e. 0.18 kcal/mol) for this example.
N. Continuing our work using purely numerical orbitals in CC theory to attempt to get the most accurate solutions of the Schrödinger equation for molecules that have been obtained, we studied excited states of the dipole bound anions of NaF, LiCl and NaCl [44]. We predict the existence of such bound states at 0.012 eV, 0.009 eV and 0.021 eV respectively. We hope our study will inspire their experimental observation.

O. Other work included a study of ways to accelerate the convergence of CC equations. Results were presented for a series of small molecules at several levels, CCD, CCSD, CCSDT-1 and the full CCSDT method [45]. Our reduced linear equation procedure was shown to offer the best convergence of the various methods that have been used.

P. We also studied the polarizability and electron affinity of OH⁻ [46]. Anions have a very large polarizability placing extreme demands on both basis set and the inclusion of electron correlation. To study the basis set effect we investigated electric field variant (EFV) orbitals, which are orbitals that are explicitly field dependent and that are floated off the atomic centers to some optimum location. The polarizability α=47±4 a.u. was almost twice as large as the SCF value attesting to the importance of correlation. The EFV basis, though good, did not give much better results than those from the conventionally chosen basis sets.

Q. Continuing our earlier study of the H₂O surface in 1979, we did an updated and very thorough study of the quartic force field of H₂O obtained by CCSDT-1 and other CC/MBPT methods [47]. We predicted the principal vibrational frequencies and those for twenty overtones. The former were extremely accurate 2-3 cm⁻¹ for the stretch modes, while the full set of frequencies including the overtones had an average error of less than about 30 cm⁻¹. We
also computed the anharmonic constants, all of which were within 2 cm$^{-1}$ of experiment, and the rotational parameters which were also exceptionally accurate. Such a calculation could be done for any small molecule today and the results would be expected to be competitive with experiment as in our H$_2$O study.

R. The IF molecule is potentially very important as the basis for a laser. Its dipole moment and infra-red intensity, as a function of bond length is not known. Hence we used MBPT to study the moments of IF and other interhalogen molecules [48].

This paper also demonstrates the near satisfaction of the Hellman-Feynman theorem for high-order MBPT wavefunctions, which is an important result contributing toward our development of the new class of UCC methods discussed above.

S. Additional applications of our CC/MBPT method focused on the activation barrier and transition state for the autoisomerization of cyclobutadiene [16] and the isomerization energies and related properties of the cyanoborane complexes, BH$_3$CN$^-$, BH$_3$NC$^-$, HCNBH$_3$, and HNCBH$_3$ [49].

T. Formulae to evaluate the spin multiplicity in unrestricted Hartree-Fock (UHF) based CC/MBPT methods were derived and applied to demonstrate how CC theory eliminates most of the spin contamination in such a calculation, enabling UHF/CC theory to provide good potential energy surfaces near atomic dissociation limits [50].
IV. PUBLICATIONS SUPPORTED BY AFOSR (November, 1987 - October, 1989)


V. INVITED PRESENTATIONS (June, 1987 - October, 1989)

June 1987 Ninth Annual West Coast Theoretical Chemistry Conference, Berkeley, CA.

July 1987 American Conference on Theoretical Chemistry, Gull Lake, MN.


June 1988 Workshop on Quantum Chemistry, Basic Aspects, Actual Trends, Girona, Spain.

Aug. 1988 Sixth International Congress on Quantum Chemistry, Jerusalem, Israel.

Aug. 1988 Satellite Symposium to the Sixth International Congress on Quantum Chemistry, Tel Aviv, Israel.


Oct. 1989 Meeting on Forty Years of Quantum Chemistry, Athens, GA.

DEPARTMENTAL COLLOQUIA

March 1987 Florida State University

May 1987 Stanford University

April 1988 University of New Mexico

May 1988 Carnegie-Mellon University

June 1988 Odense University, Denmark
Nov. 1988       University of Washington
Nov. 1988       Battelle, Pacific Northwest Laboratory
Oct. 1989       Bloomsburg University, Bloomsburg, PA; Wilks College, Wilks-Barre, PA
VI. REFERENCES


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Figure 2.