UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE

OCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

AD-A222 631

1b. RESTRICTIVE MARKINGS

3. DISTRIBUTION/AVAILABILITY OF REPORT
Approved for public release;
Distribution unlimited

...SSIFICATION/DOWNGRADING SCHEDULE

4. PERFORMING ORGANIZATION REPORT NUMBER(S)

5. MONITORING ORGANIZATION REPORT NUMBER(S)
AFOSR-TR- 90-0583

6a. NAME OF PERFORMING ORGANIZATION

6b. OFFICE SYMBOL (If applicable)

7a. NAME OF MONITORING ORGANIZATION
AFOSR/NC

6c. ADDRESS (City, State, and ZIP Code)
Quantum Theory Project
University of Florida
362 Williamson Hall, Gainesville, FL 32611

7b. ADDRESS (City, State, and ZIP Code)
Physics Division
Bldg. 410
Bolling AFB, DC 20332-6448

8a. NAME OF FUNDING/SPONSORING ORGANIZATION
AFOSR

8b. OFFICE SYMBOL (If applicable)
NP

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
AFOSR-88-0041

8c. ADDRESS (City, State, and ZIP Code)
Bldg. 410
Bolling AFB, DC 20332-6448

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.
61102F	2301	A4	

11. TITLE (Include Security Classification)
(U) MOLECULAR INTERACTIONS AND PROPERTIES WITH MANY-BODY METHODS

12. PERSONAL AUTHOR(S)
Rodney J. Bartlett

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
FINAL TECHNICAL	FROM 11/1/87 TO 10/31/89	90/04/17	20

16. SUPPLEMENTARY NOTATION

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	CC/MBPT Theories CC/MBPT Calculations
	20,08		

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

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.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT
☐ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION
Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL
Ralph Kelley

22b. TELEPHONE (Include Area Code)
(202) 767-4908

22c. OFFICE SYMBOL
NP

DD Form 1473, JUN 86 Previous editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE
UNCLASSIFIED

FINAL TECHNICAL REPORT

AFOSR-88-0041 (1987 - 1989)

MOLECULAR INTERACTIONS AND PROPERTIES WITH MANY-BODY METHODS

to

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

Rodney J. Bartlett

Quantum Theory Project

Departments of Physics and Chemistry

University of Florida

Gainesville, FL 32611

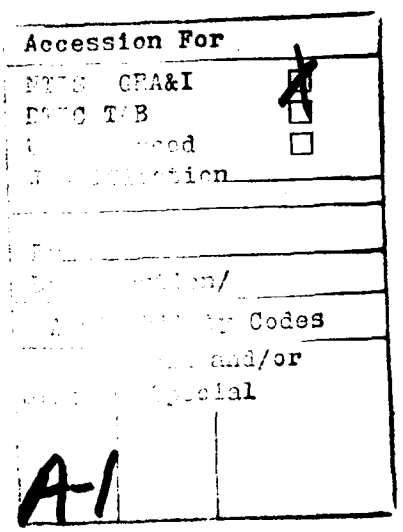

TABLE OF CONTENTS

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 mh (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 mh.

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 mh. 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 $\Delta E = \langle o|(e^{T^\dagger} H e^{T})_C|o\rangle$ 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 CCSDT-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 $\tau=T-T^{\dagger}$, $\Delta E=\langle o|(E^{\tau^{\dagger}}He^{\tau})_C|o\rangle=\langle o|(He^{\tau})_C|o\rangle$. 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 $CH_4 \rightarrow CH_3 + H$, we used color graphics to plot 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 $O(^3P)+Cl \rightarrow OH+Cl$ suggested that 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 <u>all</u> 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 <u>ab initio</u> 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 mh (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 $\alpha=47\pm4$ 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 H_2O surface in 1979, we did an updated and very thorough study of the quartic force field of H_2O 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_2O 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_3CN^-, BH_3NC^-, $HCNBH_3$, 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)

1. E.A. Salter, G.W. Trucks and R.J. Bartlett, "Analytic Energy Derivatives in Many-Body Methods I. First Derivatives," J. Chem. Phys. 90, 1752 (1989).

2. E.A. Salter and R.J. Bartlett, "Analytic Energy Derivatives in Many-Body Methods II. Second Derivatives," J. Chem. Phys. 90, 1767 (1989).

3. C. Sosa, G.W. Trucks, G.D. Purvis, III and R.J. Bartlett, "An Application of the SCF, MBPT and CC Correlated Densities. A Graphical Display Along the Potential Energy Surface of $CH_4 \rightarrow CH_3 + H$," J. Mol. Graphics 7, 28 (1989).

4. G.W. Trucks, J.D. Watts, E.A. Salter and R.J. Bartlett, "Analytical MBPT(4) Gradients," Chem. Phys. Lett. 153, 490 (1988).

5. R.J. Bartlett, "The Coupled-Cluster Approach to Molecular Structure and Spectra: A Step Toward Predictive Quantum Chemistry," J. Phys. Chem. 93, 1697 (1989).

6. R.J. Bartlett, S.A. Kucharski and J. Noga, "Alternative Coupled-Cluster Ansatz II. The Unitary Coupled-Cluster Method," Chem. Phys. Lett. 155, 133 (1989).

7. J. Noga, S.A. Kucharski and R.J. Bartlett, "A Coupled-Cluster Method That Includes Connected Quadruple Excitations," J. Chem. Phys. 90, 3399 (1989).

8. C. Sosa, J. Noga, G.D. Purvis, III and R.J. Bartlett, "An Application of Full CCSDT and Coupled-Cluster Methods to Potential Energy Curves: The $CH_4 \rightarrow CH_3 + H$ Dissociation," Chem. Phys. Lett. 153, 139 (1988).

9. J.D. Watts, G.W. Trucks and R.J. Bartlett, "The Unitary Coupled-Cluster Approach and Molecular Properties. Applications of the UCC(4) Method," Chem. Phys. Lett. 157, 359 (1989).

10. S.A. Kucharski, J. Noga and R.J. Bartlett, "Fifth-Order Many-Body Perturbation Theory for Molecular Correlation Energies," J. Chem. Phys. 90, 7282 (1989).

11. S.A. Kucharski and R.J. Bartlett, "Coupled-Cluster Methods That Include Connected Quadruple Excitations, T_4: CCSDTQ-1 and Q(CCSDT), Chem. Phys. Lett. 158, 550 (1989).

12. M.S. Gordon, K.K. Baldridge, D.E. Bernholdt and R.J. Bartlett, "The Transition State and Barrier Heights for the Reaction $O(^3P)+Cl \rightarrow OH+Cl$," Chem. Phys. Lett. 158, 189 (1989).

13. J.D. Watts, G.W. Trucks and R.J. Bartlett, "Coupled Cluster, Unitary Coupled Cluster and MBPT(4) Open-Shell Analytical Gradient Methods," Chem. Phys. Lett. 164, 502 (1989).

14. J. Geertsen, M. Rittby and R.J. Bartlett, "The Equation-of-Motion Coupled-Cluster Method: Excitation Energies of Be and CO," Chem. Phys. Lett. 164, 57 (1989).

15. R.J. Bartlett, J.D. Watts, S.A. Kucharski and J. Noga, "Non-Iterative Fifth-Order Triple and Quadruple Excitation Energy Corrections in Correlated Methods," Chem. Phys. Lett. 165, 513 (1990).

16. J. Noga, R. J. Bartlett and M. Urban, "Towards a Full CCSDT Model for Electron Correlation II. CCSDT-n Models", Chem. Phys. Lett. 134, 126 (1987).

17. E.A. Salter, H. Sekino and R.J. Bartlett, "Property Evaluation and Orbital Relaxation in Coupled-Cluster Methods," J. Chem. Phys. 87, 502 (1987).

18. J. Noga and R.J. Bartlett, "The Full CCSDT Model for Molecular Electronic Structure," J. Chem. Phys. 86, 7041 (1987).

19. S. Kucharski, J. Noga and R.J. Bartlett, "Dipole Moment of IF and Other Interhalogen Molecules," J. Chem. Phys. 88, 1035 (1988).

20. M. Urban and R.J. Bartlett, "MBPT and Coupled Cluster Investigation of Isomerization Reactions: HCN⇌HNC, BH_3CN^-⇌BH_3NC^- and $HCNBH_3$⇌$HNCBH_3$," J. Am. Chem. Soc. 110, 4926 (1988).

21. M. Rittby and R.J. Bartlett, "An Open-Shell Restricted Coupled-Cluster Method: Application to Ionization Potentials in N_2," J. Phys. Chem. 92, 3033 (1988).

22. L. Adamowicz and R.J. Bartlett, "Excited State Electron Affinities of NaF, LiCl and NaCl," J. Chem. Phys. 88, 313 (1988).

23. R.J. Bartlett, S.J. Cole, G. D. Purvis, W.C. Ermler, H.C. Hsieh and I. Shavitt, "The Quartic Force Field of H_2O Determined by Many-Body Methods II. Effects of Triple Excitations," J. Chem. Phys. 87, 6579 (1987).

24. T. Pluta, A.J. Sadlej and R.J. Bartlett, "Polarizability of OH^-," Chem. Phys. Lett. 143, 91 (1988).

25. G.D. Purvis III, H. Sekino and R.J. Bartlett, "Multiplicity of Many-Body Wavefunctions Using Unrestricted Hartree-Fock Reference Functions," Coll. Czech. Chem. Commun. 53, 2203 (1988).

26. C. Sosa, J. Noga and R.J. Bartlett, "A Study of the Be_2 Potential Curve Using the Full (CCSDT) Coupled-Cluster Method: the Importance of T_4 Clusters," J. Chem. Phys. 88, 5974 (1988).

27. G.W. Trucks, J. Noga and R.J. Bartlett, "Convergence of the Coupled-Cluster Singles, Doubles and Triples Method, Chem. Phys. Lett. 145, 548 (1988).

28. G.W. Trucks, E.A. Salter, C. Sosa and R.J. Bartlett, "Theory and Implementation of the Many-Body Perturbation Theory Density Matrix. An Application to One-Electron Properties, Chem. Phys. Lett. 147, 359 (1988).

29. P. Carsky, R.J. Bartlett, G. Fitzgerald, J. Noga and V. Spirko, "Ab Initio Calculations on the Energy of Activation and Tunneling in the Automerization of Cyclobutadiene," J. Chem. Phys. 89, 3008 (1988).

30. G.W. Trucks, E.A. Salter, J. Noga and R.J. Bartlett, "Analytic MBPT(4) Response Properties," Chem. Phys. Lett. 150, 37 (1988).

31. R.J. Bartlett and J. Noga, "The Expectation Value Coupled-Cluster Method and Analytical Energy Derivatives," Chem. Phys. Lett. 150, 29 (1988).

32. S.J. Cole and R.J. Bartlett, "The Electric Dipole Function of CO^+," in: Studies in Physical and Theoretical Chemistry, Vol. 62, ed. R. Carbo, Elsevier, Amsterdam, The Netherlands, pp. 199-211, (1989).

33. R.J. Bartlett, S.A. Kucharski, J. Noga, J.D. Watts and G.W. Trucks, "Some Consideration of Alternative Ansätze in Coupled-Cluster Theory," in: Lectures Notes in Chemistry, Vol. 52, ed. U. Kaldor, Springer-Verlag, Heidelberg, p. 125 (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.
Sept.	1987	National ACS Meeting, Symposium on Bound and Temporary Anions in Chemical Systems, New Orleans, LA.
Feb.	1988	Workshop and Symposium on Aspects of Many-Body Effects in Molecules and Extended Systems, Calcutta, India.
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.	1988	Symposium on Quantum Chemistry, High Tatras, Czechoslovakia.
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

1. L. Wilson, "Report of Workshop on State-to-State Molecular Dynamics," AFOSR Physics 77-111, June, 1976.

2. T.C. Collins and D. Stewart, "Report of Conference on Chemistry and Physics of Plumes," AFOSR Physics 77-062, July, 1976.

3. "Rocket-Plume High Altitude Infra-Red Workshop," August 3-4, 1978, Air Force Geophysics Laboratory, sponsored by AFRPL.

4. K.A. Brueckner, Phys. Rev. 97, 1353 (1955); 100, 36 (1955).

5. J. Goldstone, Proc. Royl. Soc. A239, 267 (1957).

6. H.P. Kelly, Advan. Chem. Phys. 14, 129 (1969); Phys. Rev. 131, 684 (1963); 136B, 896 (1964); 144, 39 (1966).

7. R.J. Bartlett, Annual Revs. Phys. Chem. 32, 359 (1981).

8. J. Cizek and J. Paldus, Advan. Quantum Chem. 9, 105 (1975).

9. R.J. Bartlett and D.M. Silver, Intern. J. Quantum Chem. 9S, 183 (1975).

10. R.J. Bartlett and I. Shavitt, Chem. Phys. Lett. 50, 190 (1977); Int. J. Quantum Chem. 11S, 165 (1977).

11. R.J. Bartlett and G.D. Purvis, Proceedings of American Conference on Theoretical Chemistry, Int. J. Quantum Chem. 14, 561 (1978).

12. M.A. Robb, Chem. Phys. Lett. 20, 274 (1973); S. Prime and M.A. Robb, Chem. Phys. Lett. 35, 86 (1975).

13. D.L. Freeman and M. Karplus, J. Chem. Phys. 64, 2641 (1976).

14. L.T. Redmon, G.D. Purvis and R.J. Bartlett, J. Am. Chem. Soc. 101, 2856 (1976).

15. J.A. Pople, J.S. Binkley and R. Seeger, Int. J. Quantum Chem. 10S, 1 (1976).

16. J.A. Pople, J.S. Binkley and R. Krishnan, Int. J. Quantum Chem. 11S, 149 (1977).

17. H. Kümmel, Lectures on the Many-Body Problems, ed. E.R. Cainiello, Academic Press, New York, 1962.

18. J. Cizek, J. Chem. Phys. 45, 4256 (1966); Adv. Chem. Phys. 14, 35 (1969).

19. J. Cizek and J. Paldus, Int. J. Quanatum Chem. 5, 359 (1971).

20. J. Paldus, J. Cizek and I. Shavitt, Phys. Rev. A5, 50 (1972).

21. R.J. Bartlett and G.D. Purvis, Physica Scripta 21, 255 (1980).

22. (a)R.J. Bartlett, I. Shavitt and G.D. Purvis, III, J. Chem. Phys. 71, 281 (1979); (b)R.J. Bartlett, S.J. Cole, G.D. Purvis, III, W.C. Ermler, H.C. Hsieh and I. Shavitt, J. Chem. Phys. 87, 6579 (1987).

23. R.J. Bartlett, Citation Classic, Current Contents 29, 20 (1989).

24. S.A. Kucharski and R.J. Bartlett, Chem. Phys. Lett. 158, 550 (1989).

25. J. Noga and R.J. Bartlett, J. Chem. Phys. 86, 7041 (1987).

26. R.J. Bartlett and J. Noga, Chem. Phys. Lett. 150, 29 (1988).

27. R.J. Bartlett, S.A. Kucharski and J. Noga, Chem. Phys. Lett. 155, 133 (1989).

28. J. Noga, S.A. Kucharski and R.J. Bartlett, J. Chem. Phys. 90, 3399 (1989).

29. R.J. Bartlett, S.A. Kucharski, J. Noga, J.D. Watts and G.W. Trucks, in: Lecture Notes in Chemistry, Vol. 52, ed. U. Kaldor, Springer-Verlag, Heidelberg, p. 125 (1989).

30. J.D. Watts, G.W. Trucks and R.J. Bartlett, Chem. Phys. Lett. 157, 359 (1989).

31. (a)Y.S. Lee, S. Kucharski and R.J. Bartlett, J. Chem. Phys. 81, 5906 (1984); (b)J. Noga and R.J. Bartlett, J. Chem. Phys. 86, 7041 (1987).

32. S.A. Kucharski, J. Noga and R.J. Bartlett, J. Chem. Phys. 90, 7282 (1989).

33. R.J. Bartlett, in Geometrical Derivatives of Energy Surfaces and Molecular Properties, ed. P. Jørgensen and J. Simons, Reidel, Dordrecht, The Netherlands, p. 35 (1986); L. Adamowicz, W.D. Laidig and R.J. Bartlett, Int. J. Quantum Chem. Symp. 18, 245 (1984); G.B. Fitzgerald, R.J. Harrison and R.J. Bartlett, J. Chem. Phys. 85, 5143 (1986).

34. E.A. Salter, G.W. Trucks, G.B. Fitzgerald and R.J. Bartlett, Chem. Phys. Lett. 141, 61 (1987); G.W. Trucks, E.A. Salter, C. Sosa and R.J. Bartlett, Chem. Phys. Lett., in press.

35. G.W. Trucks, E.A. Salter, C. Sosa and R.J. Bartlett, Chem. Phys. Lett. 147, 359 (1988).

36. G.W. Trucks, E.A. Salter, J. Noga and R.J. Bartlett, Chem. Phys. Lett. 150, 37 (1988); G.W. Trucks, J.D. Watts, E.A. Salter and R.J. Bartlett, Chem. Phys. Lett. 153, 490 (1988).

37. C. Sosa, G.W. Trucks, G.D. Purvis, III and R.J. Bartlett, J. Mol. Graphics 7, 28 (1989); C. Sosa, J. Noga, G.D. Purvis, III and R.J. Bartlett, Chem. Phys. Lett. 153, 139 (1988).

38. E.A. Salter, G.W. Trucks and R.J. Bartlett, J. Chem. Phys. 90, 1752 (1989).

39. E.A. Salter and R.J. Bartlett, J. Chem. Phys. 90, 1767 (1989).

40. D.J. Rakesfraw, K.G. McKendrich, R. Zhang and R.N. Farr, to be published.

41. M.S. Gordon, K.K. Baldridge, D.E. Bernholdt and R.J. Bartlett, Chem. Phys. Lett. 158, 189 (1989).

42. R.J. Bartlett and J. Noga, Chem. Phys. Lett. 150, 29 (1988).

43. C. Sosa, J. Noga and R.J. Bartlett, J. Chem. Phys. 88, 5974 (1988).

44. L. Adamowicz and R.J. Bartlett, J. Chem. Phys. 88, 313 (1988).

45. G.W. Trucks, J. Noga and R.J. Bartlett, Chem. Phys. Lett. 145, 548 (1988).

46. T. Pluta, A.J. Sadlej and R.J. Bartlett, Chem. Phys. Lett. 143, 91 (1988).

47. R.J. Bartlett, S.J. Cole, G.D. Purvis, III, W.C. Ermler, H.C. Hsieh and I. Shavitt, J. Chem. Phys. 87, 6579 (1987).

48. S.A. Kucharski, J. Noga and R.J. Bartlett, J. Chem. Phys. 88, 1035 (1988).

49. M. Urban and R.J. Bartlett, J. Am. Chem. Soc. 110, 4926 (1988).

50. G.D. Purvis, III, H. Sekino and R.J. Bartlett, Coll. Czech. Chem. Commun. 53, 2203 (1988).

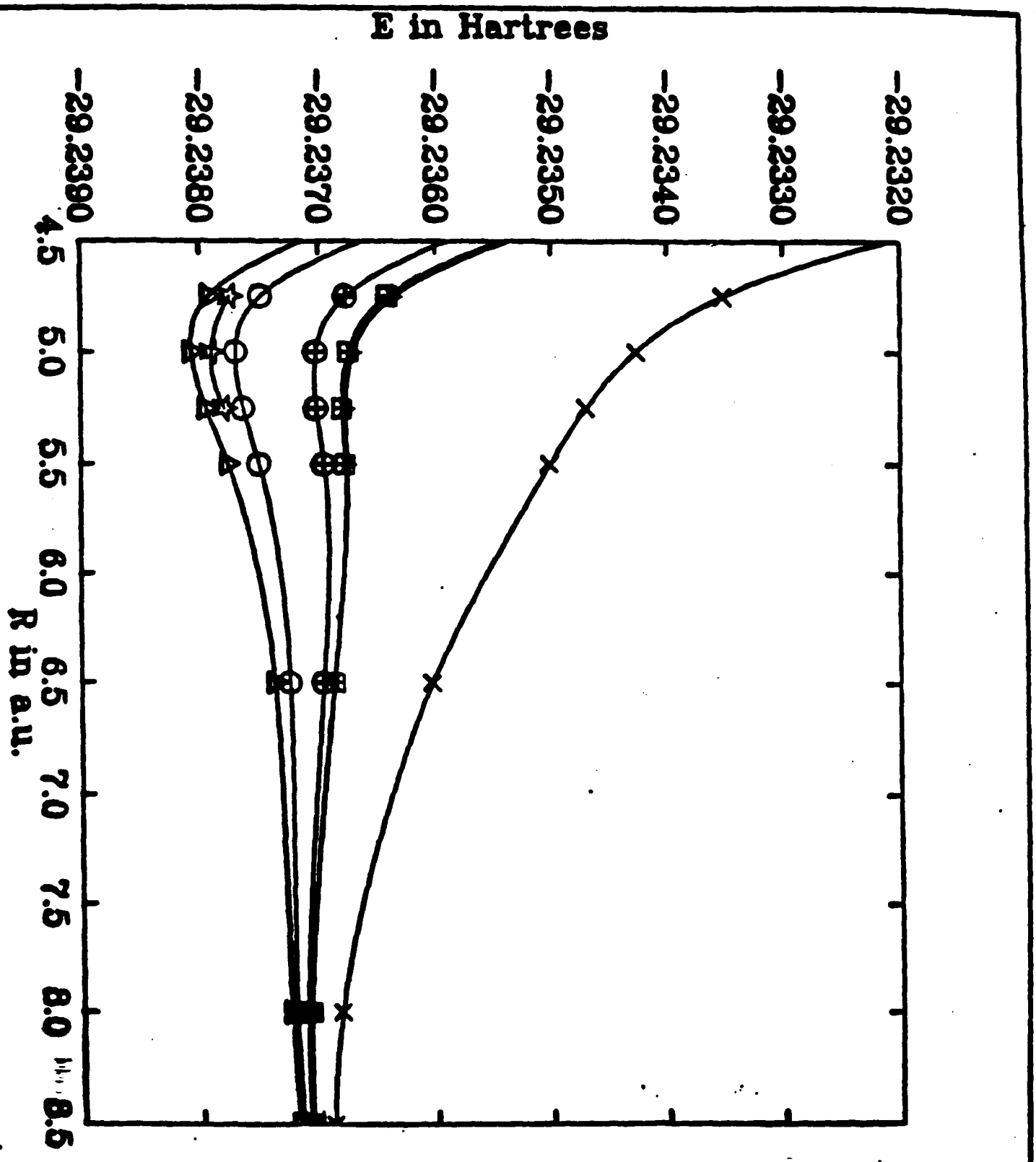

Figure 1 Potential energy curves for the ground state ($^1\Sigma_g^+$) of Be_2. × CCSD, • CCSDT-1a, + CCSDT-1b, ✱ CCSDT-2, □ CCSDT-3, ⊕ CCSD+T(CCSD), ○ CCSDT, ☆ full CI and Δ CCSDT-4.

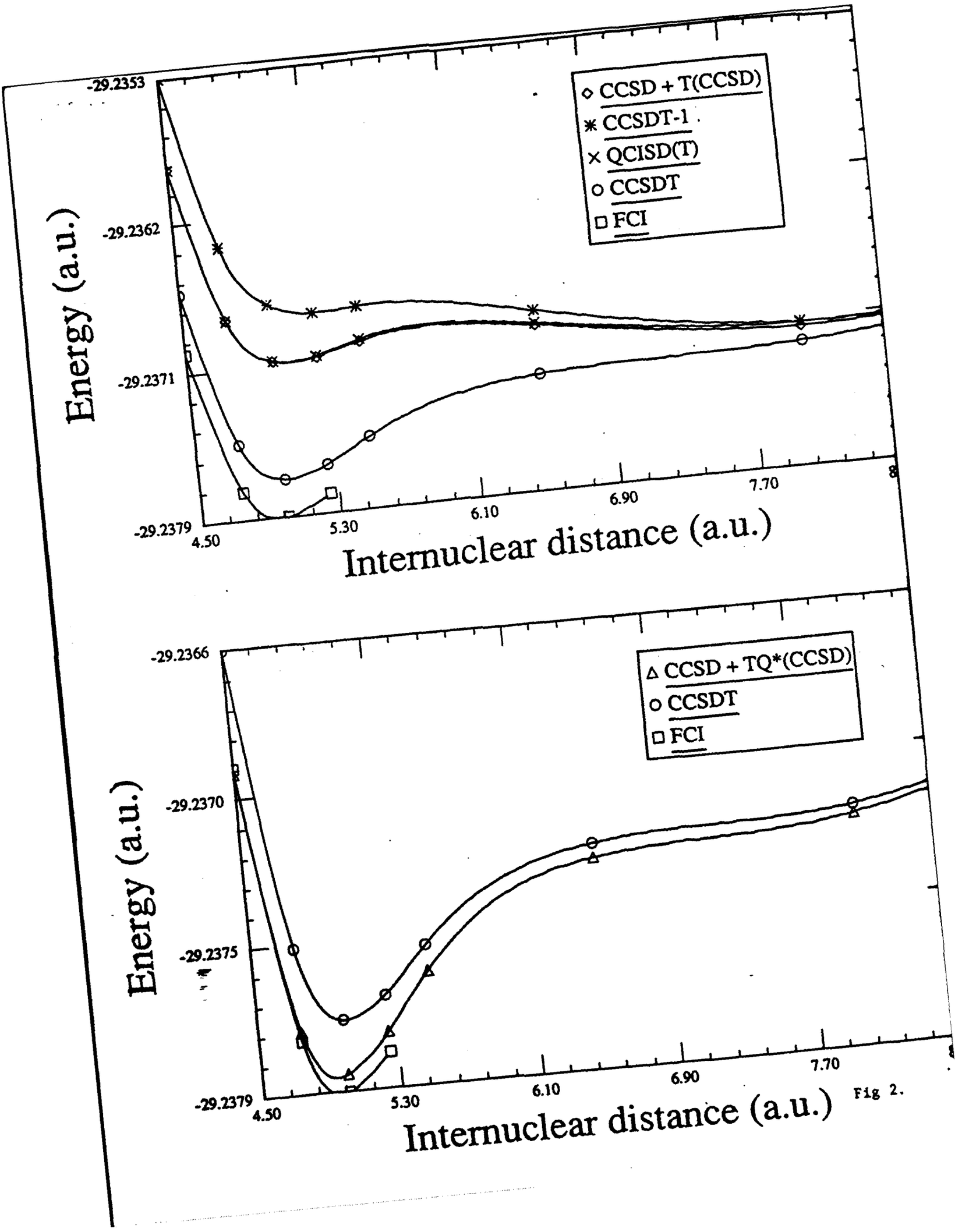
◇ CCSD + T(CCSD)
✱ CCSDT-1
× QCISD(T)
○ CCSDT
□ FCI
Energy (a.u.)
-29.2353
-29.2362
-29.2371
-29.2379
4.50
5.30
6.10
6.90
7.70
Internuclear distance (a.u.)
△ CCSD + TQ*(CCSD)
○ CCSDT
□ FCI
Energy (a.u.)
-29.2366
-29.2370
-29.2375
-29.2379
4.50
5.30
6.10
6.90
7.70
Internuclear distance (a.u.)

Fig 2.