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JOHN PETER LUCIA

ENTITLED HIGH LEVEL ELECTRONIC STRUCTURE CALCULATIONS

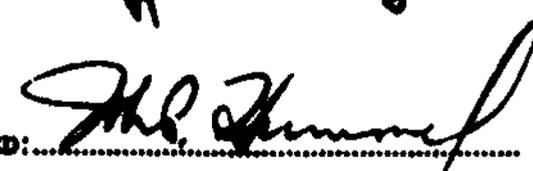
IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF BACHELOR OF SCIENCE IN CHEMISTRY



Instructor in Charge

APPROVED:



HEAD OF DEPARTMENT OF CHEMISTRY

**HIGH LEVEL ELECTRONIC
STRUCTURE CALCULATIONS**

BY

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THESIS

for the

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMISTRY

**College of Liberal Arts and Sciences
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Introduction

The tremendous success of quantum mechanics has laid the foundations for a reliable theory for the predictions of the physical properties of molecules. Solutions to the actual mathematical equations are very involved and have been readily achievable only recently with the great advances in high speed computing. Many different techniques have been suggested for the calculations needed, each having a varied degree of accuracy and efficiency in computing time. Optimizing the accuracy of the calculation and information gained, while making the best use of computing power is a major concern.

One important method of calculation involves the Hartree-Fock, or self consistent field (SCF) theory. Here the electrons are considered to be moving in a field created by the nuclei and the other electrons. It is assumed the electrons are in known orbitals producing an effective field. Using this effective field, new orbitals are found and the process repeated until the orbitals remain constant and are thus self consistent. Since this method ignores any instantaneous electron-electron interactions it is only approximate. Higher level calculations, those that include this type of electron-electron interaction or electron correlation, can be carried out to improve the results.

Many methods have been developed to account for electron correlation. one such method known as the self consistent electron

pair method [24,25] (SCEP) is a variational method which is open ended with respect to the number of configurations. This method uses single and double substitutions of the SCF wavefunction and is equivalent to single and double substitution configuration interaction (CISD) but instead of listing configurations, sets up pair coefficient matrices from dyad products of orbital vectors. An electron pair operator approach for double substitution coupled cluster (CCD) wavefunctions has also been developed [26] which uses an exponential operator on an SCF wavefunction. This operator, even when limited to double substitutions, includes higher order substitutions which enter as unlinked interactions of electron pairs.

An approximation to this (ACCD) has also been developed [3] in which two terms, which at infinite separation cancel, are neglected. These two terms, which are very computationally expensive, present, in many cases, little loss in accuracy when neglected, depending on the specific pair interactions. Both ACCD and CCD are size consistent, invariant to orbital mixing and open ended.

Additional methods for electron correlation calculations include CEPA-0, in which the summation terms of CCD are neglected, and ACCD* which is similar to ACCD in which factors have been changed [5] and is also termed ACPQ. Various configuration interaction approximations, such as with double substitution (CID) have also been used. Determining the value of these methods of electron correlation is important in current research.

Here the application of several ab initio electronic structure methods have been made to simple systems. The restricted

Hartree-Fock self consistent field method has been applied to water, carbon monoxide and diatomic nitrogen. Several forms of electron correlation were employed to the water and effects of geometry studied. The molecular electrical properties of the diatomic molecules were also studied using a derivative Hartree-Fock method.

Single Bond H₂O Stretch

The first series of calculations carried out involved stretching one of the OH bonds in water from the original equilibrium geometry (Fig.1.a), moving one hydrogen atom increasingly farther from the oxygen along the line extending in the equilibrium bond direction, thus maintaining the original value for the hydrogen-oxygen-hydrogen bond angle.

The calculations were carried out at two levels. The first level of treatment consisted of restricted a Hartree-Fock (RHF) self consistent field (SCF) technique employed to the system with a double-zeta contracted gaussian basis set [1,2]. However, since the SCF treatment is a single configurational method, its ability to treat this system, particularly at larger bond distances, is limited. In addition, the restricted wavefunctions used here are also an inaccurate model to describe large bond distances and further limit the method.

A higher level of treatment for this system is required in order to better account for the true properties. Hence the double substitution coupled cluster method (ACCD) [3-5] has been employed to gain correlation energy and better account for the nature of this system.

A potential energy curve was obtained at both the SCF and ACCD levels and it can be seen in figure 2 that the ACCD treatment does in fact offer an appreciable improvement over the SCF method. Also evident is the progressively worse job SCF does at increasing bond length where SCF fails to parallel ACCD and thus ACCD is required to gain increasing amounts of correlation energy.

Bond breaking seems to have occurred at a distance past 2.7 angstroms in the oxygen-hydrogen bond distance. In this region the ACCD curve appears to be leveling off to an essentially constant value for the energy. This offers what appears to be a reasonable picture of bond stretching, but is in no way complete. Further study of effective treatment of electron correlation and bond stretching, by comparison of various methods, is needed.

Symmetric Stretch correlation effects

A second series of water calculations have been carried using a new geometry specified first by Saxe, Schaefer, and Handy and Harrison and Handy [6,7] with a bond angle of 110.565° and OH bond distances of R_e , $1.5 R_e$ and $2.0 R_e$ where $R_e = 1.84345$ bohr (fig.1b.) . Several different methods were used to account for the correlation energy, and the results compared.

Full configuration interaction (CI) calculations by Saxe, Schaefer, and Handy [6] established a set of energies using a double-zeta (DZ) basis set that have been used in several other studies of correlation [7,8] and, these energies, and the geometries used, were employed here. Both ACCD and double substitution CI (CID) were compared to CCD at the various geometries and it appears that ACCD more closely parallels over the range from R_e to $2.0 R_e$ than CID. The reason that ACCD parallels CCD over such a range in comparison with CID lies in the size-extensivity of ACCD and CCD [9-12], which was one of the original advantages to ACCD when it was developed [3] . An important correspondence between ACCD and CCD thus comes from the higher order correlation energy, that which is beyond CID or CID with single substitutions (CISD). ACCD accounts for only around 60% of the CCD-CID energy at the R_e geometry, but this is where that energy value is small, and at $2.0R_e$, where this energy value is large, ACCD accounts for more than 95% of the CCD correlation energy beyond that of CID.

In comparing ACCD and CCD to full-CI energies [6,7], the agreement is again quite good. Bartlett and coworkers have already compared CCD, CCSD and CCSD with triple excitations to the full-CI results [13]. In terms of total correlation energy CCD+S, CCD plus single excitations added in linearly, recovers 99%, 97%, and 94% at R_e , $1.5 R_e$, and $2.0 R_e$, respectively, similarly ACCD+S recovers 97%, 95%, and 93%.

Size extensively, however, is not the complete explanation of the correspondence of ACCD to CCD relative to CID, and comparison with other size-extensive techniques also shows good correspondence between ACCD and CCD relative to these. CEPA methods [14-16], which may be considered computationally simple approximations of CCD, were carried out following Saebø and Pulay [17] and results for ACCD to CCD relative to these compared [18]. CEPA-O breaks down and is divergent at $2.0 R_e$ where ACCD was not, and the change in energy in going from R_e to $1.5 R_e$ was almost an order of magnitude greater than the difference for ACCD.

Other methods including self-consistent electron pairs (SCEP) and ACCD*, which is ACCD where a factor in the program was changed to carry out the treatment designated ACPQ as developed by Paldus et al. [5] were carried out and the results found to be less impressive than those for ACCD.

A final calculation involving both ACCD and CCD was carried out employing orbital improvement techniques [19] which manage to incorporate the single substitution contribution to the correlation into the double substitution expansion. For these, the contribution of the

single substitution slowly disappears and the correlation energy increases. The ACCD single contribution parallels that for CCD at R_e and $1.5 R_e$, but at $2.0 R_e$ the ACCD singles contribution exceeds that of CCD by a very significant amount. The contribution of single excitations, at $2.0 R_e$, for ACCD is a factor of 10^5 greater than that for CCD, although the total correlation energies remain parallel. With these calculations however, the correlation energies at $1.5 R_e$ and $2.0 R_e$ are both greater than of full-CI.

The results mentioned above show that ACCD corresponds well to CCD over the increasing bond length of water and can be shown to run parallel to CCD over a potential curve. This property indicates the importance of ACCD as a method for taking into account correlation energy and improving the potential surface since the computing time required is considerably less than for CCD. In addition, the superiority of CCD to many of the other methods further increases the importance of ACCD.

The ability of ACCD to account for a potential surface, as in the bond stretching mentioned previously, therefore depends on and parallels the ability of CCD to do so. This however, appears questionable, as shown by Brown, Shavitt and Shepard [8], since the energy difference between CCSD and full-CI grows in magnitude with bond distance, just as with these new results.

Electrical Properties of Molecules

Interaction of electromagnetic radiation with molecules, as well as interactions of molecules with other molecules is influenced by the electrical properties of those molecules. These properties, the electrical moments such as dipole and quadrupole, as well as polarizabilities and hyperpolarizabilities can be calculated to a relatively high level of agreement with experimental values. A method which has been successful in calculating these properties is derivative Hartree-Fock (DHF) theory [20]. This method provides a route to obtaining properties of all orders. However, electron correlation effects are neglected at this level, and so there is to be some error in properties calculated at the DHF level.

The electrical properties, dipole and second moments as well as the polarizabilities and hyperpolarizabilities of diatomic nitrogen and carbon monoxide, were calculated at several bond lengths using a triple-zeta contracted gaussian basis set [1,2] with polarization functions specifically for electrical property calculations designated ELP [22]. The effects of varied bond length on the electrical properties of CO were studied and both the dipole and quadrupole moments exhibit a linear dependence on the bond radius as shown in figures 4 and 5. The dipole polarizability of CO, also plotted in figure 5, exhibits a linear dependence on bond length as well. The corresponding properties of N₂ show similar behavior and can be compared to CO in table 6.

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References

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1. T. H. Dunning, *J. Chem. Phys.* **55**, 716 (1971).
2. S. Huzinaya, *J. Chem. Phys.* **42**, 1293 (1965).
3. R. A. Chiles and C. E. Dykstra, *J. Chem. Phys.* **75**, 2270 (1981).
4. K. Jankowski and J. Paldus, *Int. J. Quantum Chem.* **18**, 1243 (1980).
5. J. Paldus, J. Cizet and M. Takahashi, *Phys. Rev. A* **30**, 2193 (1984).
6. P. Saxe, H. F. Schaefer III and N. C. Handy, *Chem. Phys. Lett.* **79**, 202 (1981).
7. R. J. Harrison and N. C. Handy, *Chem. Phys. Lett.* **95**, 386 (1983).
8. F. B. Brown, I. Shavitt and R. Shepard, *Chem. Phys. Lett.* **105**, 363 (1984).
9. R. J. Bartlett and G. D. Purvis, *Intern. J. Quantum Chem.* **14**, 561 (1978).
10. R. J. Bartlett and G. D. Purvis, *Phys. Scripta* **21**, 255 (1980).
11. R. J. Bartlett, *Ann. Rev. Phys. Chem.* **32**, 359 (1981).
12. R. J. Bartlett and I. Shavitt, *Int. J. Quantum Chem. Symp.* **11**, 165 (1977).
13. R. J. Bartlett, H. Sekino and G. D. Purvis, III, *Chem. Phys. Lett.* **98**, 66 (1983); M. Urban, J. Noga, S. J. Cole and R. J. Bartlett, *J. Chem. Phys.* **83**, 4041 (1985); **85** 5383E (1986).
14. W. Meyer, *Int. J. Quantum Chem. Symp.* **5**, 341 (1971).
15. W. Meyer, *J. Chem. Phys.* **58**, 1017 (1973).

16. R. Ahlrichs, H. Lischka, V. Staemmler and W. Kulzelnigg, *J. Chem. Phys.* **62**, 1225 (1975).
17. S. Saebo and P. Pulay, *Chem. Phys. Lett.* **131**, 384-388 (1986).
18. C. E. Dykstra, S. Y. Liu, M. F. Daskalakis, J. P. Lucia and M. Takahashi, *Chem. Phys. Lett.* , in press.
19. W. Meyer, *J. Chem. Phys.* **64**, 290 (1976).
20. C. E. Dykstra, Ph. D. Thesis (Univ. Calif., Berkeley, (1976).
21. C. E. Dykstra and P. G. Jasien, *Chem. Phys. Lett.* **109**, 388 (1984).
22. S. Y. Liu and C. E. Dykstra, *J. Phys. Chem.*, in press.
23. R. J. Bartlett, H. Sekino and G. D. Purvis III, *Chem. Phys. Lett.* **98**, 66 (1983).
24. W. Meyer, *J. Chem. Phys.* **64** 2901 (1976).
25. C. E. Dykstra, H. F. Scheafer, and W. Meyer, *J. Chem. Phys.* **65** 2740 (1976).
26. R. A. Chiles and C. E. Dykstra, *J. Chem. Phys.* **74** 0000 (1981).

TABLE 1

SINGLE OH BOND STRETCH

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<u>R(A)</u>	<u>E-SCF (a.u.)</u>			<u>E-ACCD (a.u.)</u>		
0.9000	-76.005	507	649	-76.131	690	992
0.9300	-76.008	530	290	-76.136	228	336
0.9572	-76.009	295	049	-76.138	354	948
1.1538	-75.982	311	331	-76.120	118	515
1.3269	-75.939	955	038	-76.088	430	456
1.5000	-75.895	957	388	-76.055	421	309
1.6500	-75.860	150	495	-76.030	747	630
1.8000	-75.827	448	338	-76.010	752	784
1.9500	-75.798	013	816	-75.995	356	397
2.1000	-75.771	775	081	-75.984	125	832
2.2500	-75.748	543	380	-75.976	284	764
2.4000	-75.728	066	952	-75.970	959	593
2.5500	-75.710	063	567	-75.967	437	506
2.7000	-75.694	247	520	-75.965	126	804

BENCHMARK WATER CALCULATIONS

(Double Zeta Basis Set)

METHOD	Re	1.5Re	2.0Re
SCF	-76.009 837 696	-75.803 529 490	-75.595 179 524
ACCD	-76.152 836 690 (-0.142 998 994)	-75.999 684 595 (-0.196 155 105)	-75.870 726 372 (-0.275 546 873)
ACCD+S	-76.153 704 088 (-0.143 866 391)	-76.004 171 228 (-0.200 641 738)	-75.883 065 574 (-0.287 886 075)
ACCD _B ^a	-76.153 385 554 (-0.144 564 449)	-76.004 814 548 (-0.207 547 602)	-75 890 305 091 (-0.314 747 768)
ACCD _B +S	-76.153 385 581 (-0.144 564 476)	-76.004 816 926 (-0.207 549 979)	-75.891 898 438 (-0.316 341 116)
CCD	-76.155 272 382 (-0.145 434 685)	-76.003 118 782 (-0.199 589 292)	-75.872 222 967 (-0.277 043 468)
CCD+S	-76.156 181 715 (-0.146 344 019)	-76.007 777 450 (-0.204 247 961)	-75.885 318 524 (-0.290 139 025)
CCD _B	-76.155 862 376 (-0.147 098 754)	-76.008 363 776 (-0.211 341 991)	-75.896 938 318 (-0.324 053 655)
CCD _B +S	-76.155 862 412 (-0.147 098 790)	-76.008 366 188 (-0.211 344 404)	-75.896 938 329 (-0.324 053 666)
MBPT4 ^b	-76.156 876 (-0.147 038)	-76.008 395 (-0.204 866)	-75.888 867 (-0.293 687)
CID ^c	-76.149 178 (-0.139 340)	-75.987 968 (-0.184 439)	-75.833 462 (-0.238 282)
CISD ^c	-76.150 015 (-0.140 177)	-75.992 214 (-0.188 611)	-75.844 817 (-0.249 637)
CISDT ^c	-76.151 156 (-0.141 318)	-75.995 843 (-0.192 314)	-75.855 527 (-0.260 347)
CISDTQ ^c	-76.157 603 (-0.147 765)	-76.013 418 (-0.209 889)	-75.900 896 (-0.305 716)
ACCD ^{*d}	-76.152 988 323 (-0.143 150 627)		-75.870 661 . 65 (-0.275 481 918)
ACCD ^{*d} +S	-76.153 857 823 (-0.144 020 127)		-75.882 971 680 (-0.287 792 234)
SCEP	-76.149 177 706 (-0.139 340 009)		-75.833 461 946 (-0.238 282 499)
SCEP+S	-76.149 992 813 (-0.140 155 116)		-75.843 236 400 (-0.248 056 954)
CEPA-O	-76.155 444 (-0.145 606)	-76.011 635 (-0.208 106)	e)
FULL-CI f)	-76.157 866 (-0.148 028)	-76.014 521 (-0.210 992)	-75.905 247 (-0.310 067)

Table Notes

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- a.) Indicates orbital improvement calculation or Brueckner orbitals
- b.) Ref. [1,2]
- c.) Ref. [6,7]
- d.) ACCD* calculations are those where a factor in the ACCD program was changed to make it carry out the treatment designated ACPQ as developed by paldus et al. [5].
- e.) CEPA-O is divergent at $2.0 R_e$.
- f.) Ref. [6,7]
- g.) All energies are listed in atomic units

TABLE 3 FULL ENERGY DIFFERENCES
(Hartrees)

METHODS	R_e	$1.5 R_e$	$2.0 R_e$
CCD - CID	-0.006 095	-0.015 150	-0.038 761
CCD - ACCD	-0.002 436	-0.003 434	-0.001 497
CCD - ACCD*	-0.002 284		-0.001 562
CCD - CEPA-0	+0.000 172	+0.008 516	
CCD - MBPT4	+0.001 603	+0.001 603	+0.016 644
CCD - SCEP	-0.006 095		-0.038 761
CCD - Full CI	+0.002 539	+0.011 403	+0.033 024
ACCD - Full CI	+0.005 029	+0.014 837	+0.034 520
ACCD - CID	-0.003 659	-0.011 716	-0.037 265
CCD+S - CISD	-0.006 167	-0.015 637	-0.040 502
CCD+S - ACCD+S	-0.002 478	-0.003 606	-0.002 253
CCD+S - ACCD*+S	-0.002 324		-0.002 347
CCD+S - CEPA-0	-0.000 738	-0.003 858	
CCD+S - MBPT4	+0.000 694	+0.000 618	+0.003 548
CCD+S - SCEP+S	-0.006 184		-0.042 082
CCD+S - Full CI	+0.001 421	+0.006 744	+0.019 928
ACCD+S - Full CI	+0.004 162	+0.010 350	+0.022 181
ACCD+S - CISD	-0.003 689	-0.012 031	-0.038 249

TABLE 4 ENERGY DIFFERENCES FOR BRUECKNER ORBITALS
(Hartrees)

METHODS	R_e	1.5 R_e	2.0 R_e
CCD - ACCD	-0.002 534	-0.003 794	-0.009 306
CCD+S - ACCD+S	-0.002 534	-0.003 794	-0.007 713
CCD - Full CI	+0.000 929	-0.000 352	-0.013 987
ACCD - Full CI	+0.003 464	+0.003 444	-0.004 681
CCD _B - CCD	-0.001 664	-0.011 753	-0.047 010
ACCD _B - ACCD	-0.001 566	-0.011 393	-0.039 201

TABLE 5 ENERGY DIFFERENCES WITH FULL CI
(Hartrees)

METHODS	R_e	1.5 R_e	2.0 R_e
ACCD	-0.005 029	-0.014 837	-0.034 520
CCD	-0.002 593	-0.011 403	-0.033 024
ACCD+S	-0.004 162	-0.010 350	-0.022 181
CCD+S	-0.001 421	-0.006 744	-0.019 928
CEPA-0	-0.002 422	-0.002 886	
CID	-0.008 688	-0.026 553	-0.071 785
ACCD _B	-0.003 464	-0.003 444	+0.004 681
CCD _B	-0.000 929	+0.000 352	+0.013 987

TABLE 6

ELECTRICAL PROPERTIES

(a.u.)

N₂

PROPERTY	1.03 Å	1.06 Å	1.09 Å
----------	--------	--------	--------

$\mu_{x,y,z}$	0	0	0
α_{xx}	-21.905	-22.810	-23.628
$\alpha_{yy,zz}$	-7.539	-7.641	-7.728
$\alpha_{x,x}$	-13.392	-14.140	-14.827
$\alpha_{y,y;z,z}$	-9.128	-9.405	-9.658

CO

PROPERTY	1.06 Å	1.10 Å	1.13 Å	1.16 Å	1.19 Å
----------	--------	--------	--------	--------	--------

μ_x	0.009	-0.055	-0.113	-0.172	-0.244
$\mu_{y,z}$	0	0	0	0	0
α_{xx}	-22.999	-23.908	-24.728	-25.565	-26.591
$\alpha_{yy,zz}$	-7.484	-7.553	-7.612	-7.670	-7.738
$\alpha_{x,x}$	-13.268	-13.852	-14.390	-14.951	-15.653
$\alpha_{y,y;z,z}$	-10.803	-10.980	-11.143	-11.313	-11.525

Figure 1. H₂O Geometries

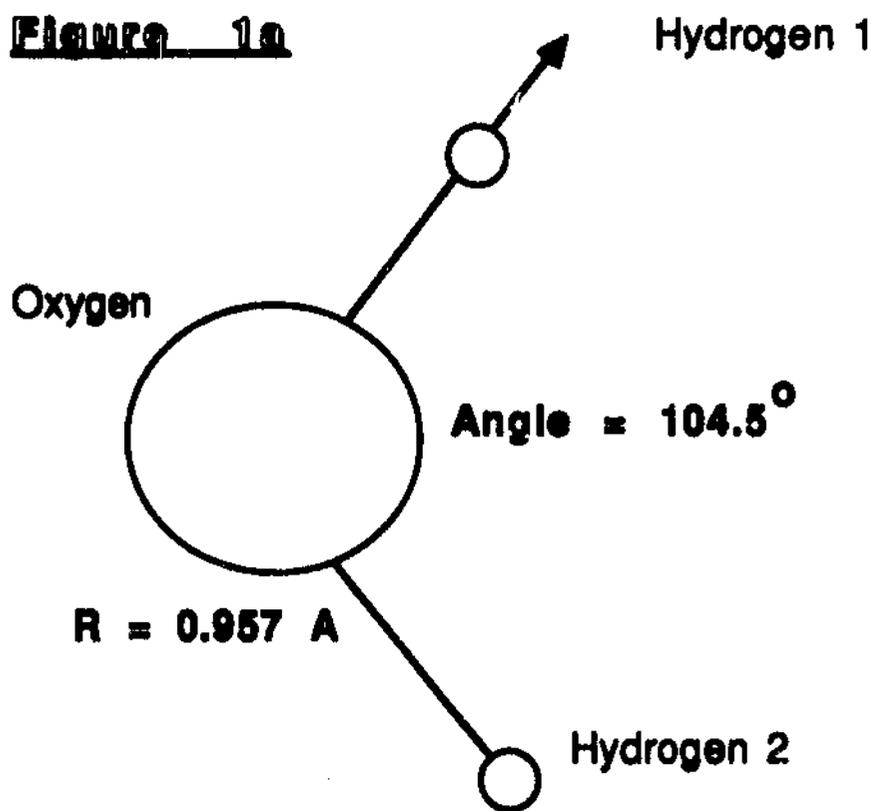
Figure 2. Potential Energy Curve for Single OH Bond Stretch

Figure 3. Correlation Energy Curves for Symmetric Stretch

Figure 4. Dipole Moment for CO

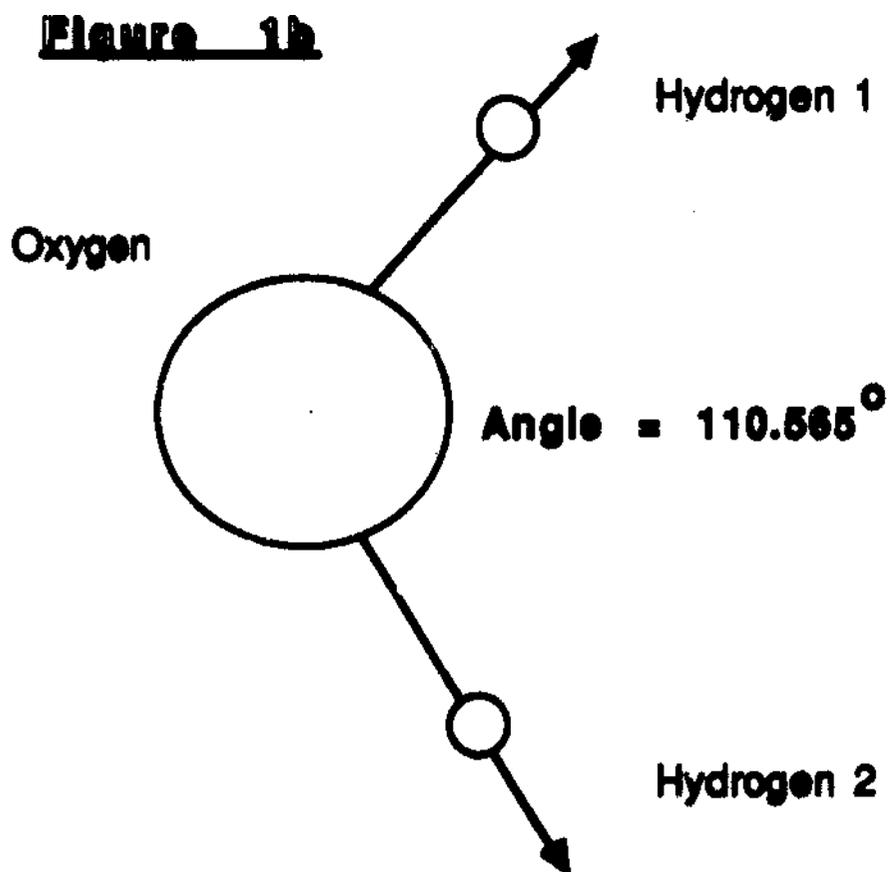
Figure 5. Additional Electrical Properties for CO

Figure 1a



STRETCH of HYDROGEN 1 BOND

Figure 1b



SYMMETRIC STRETCH

FIGURE 2

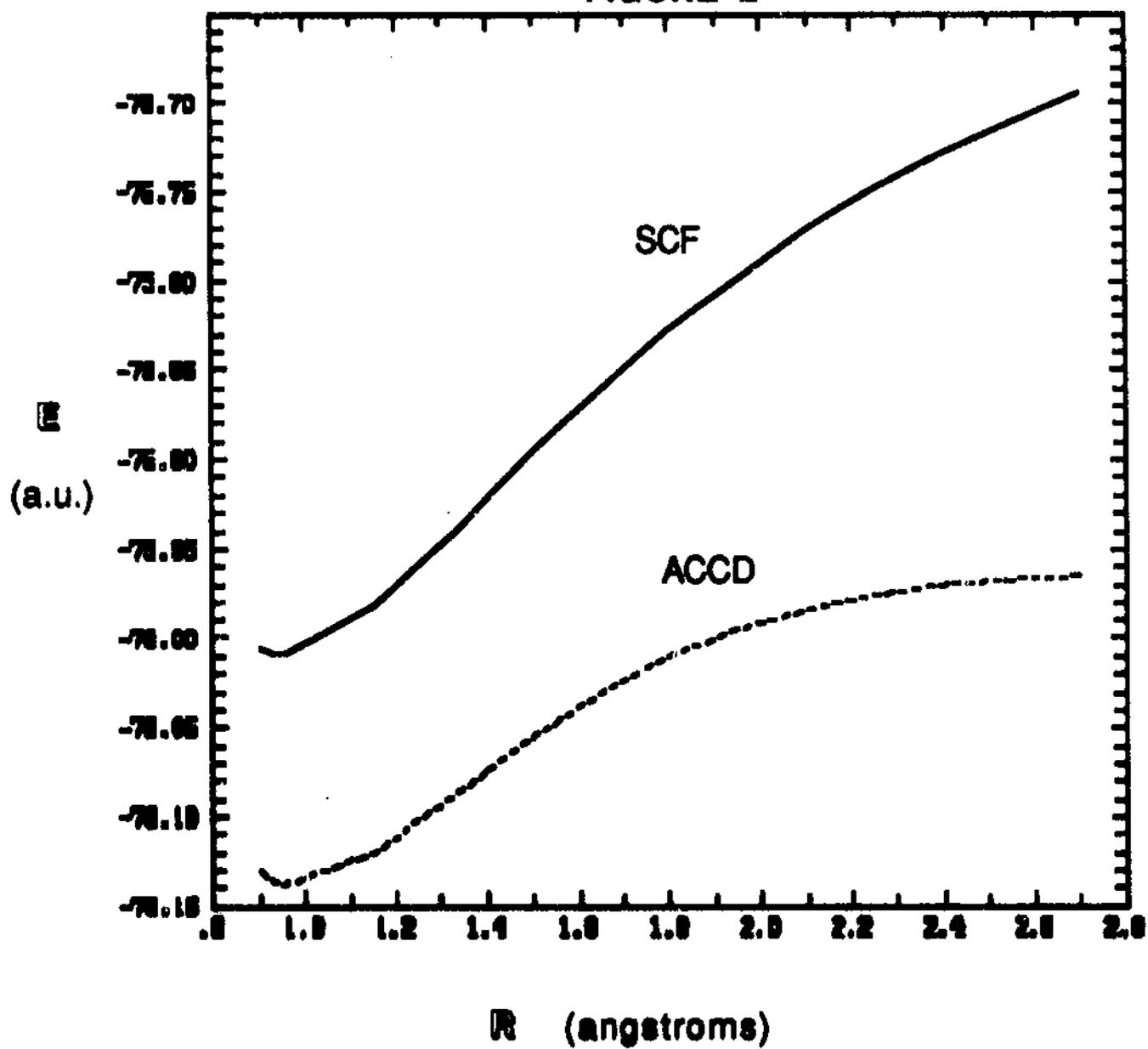


FIGURE 3

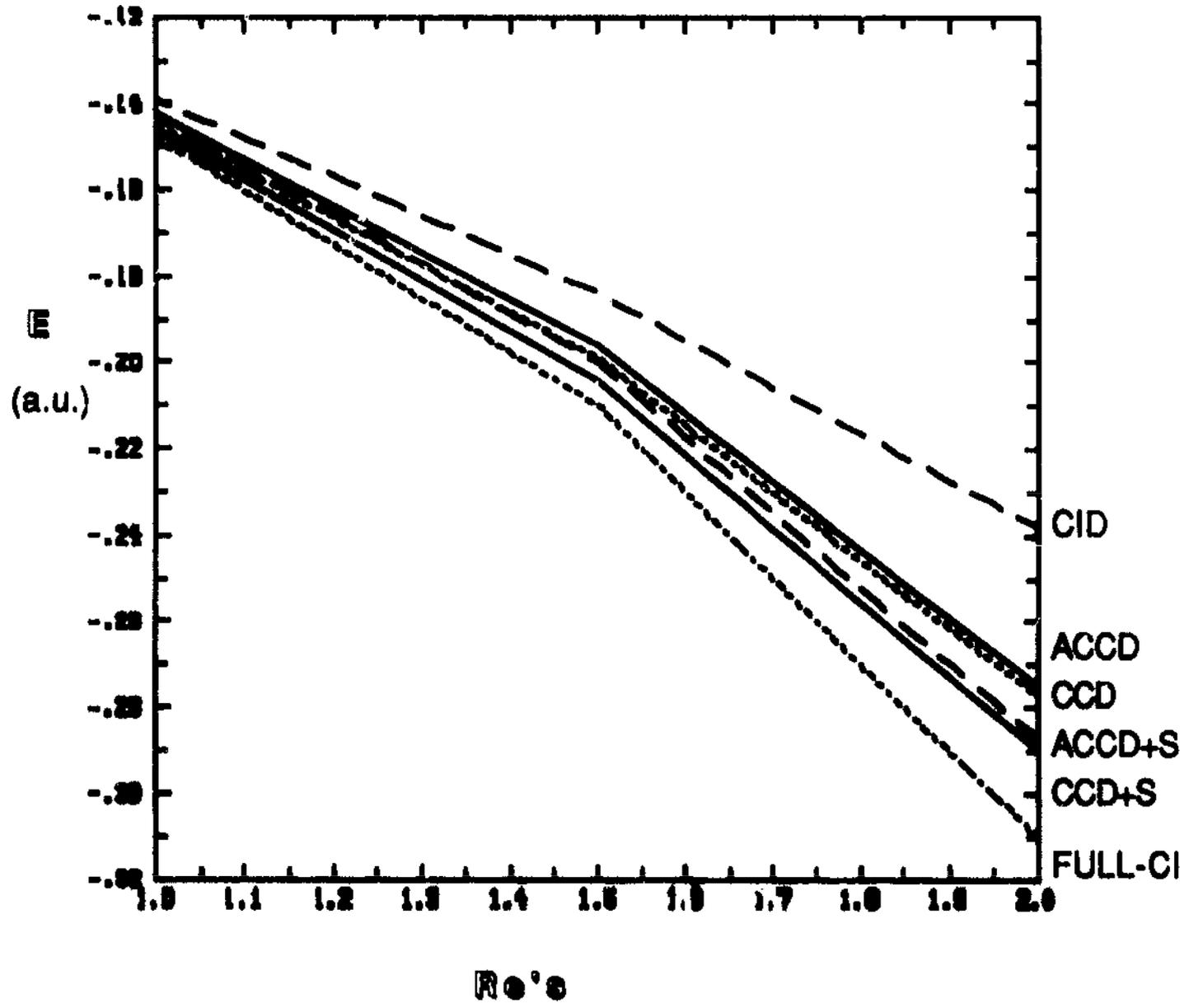


FIGURE 4

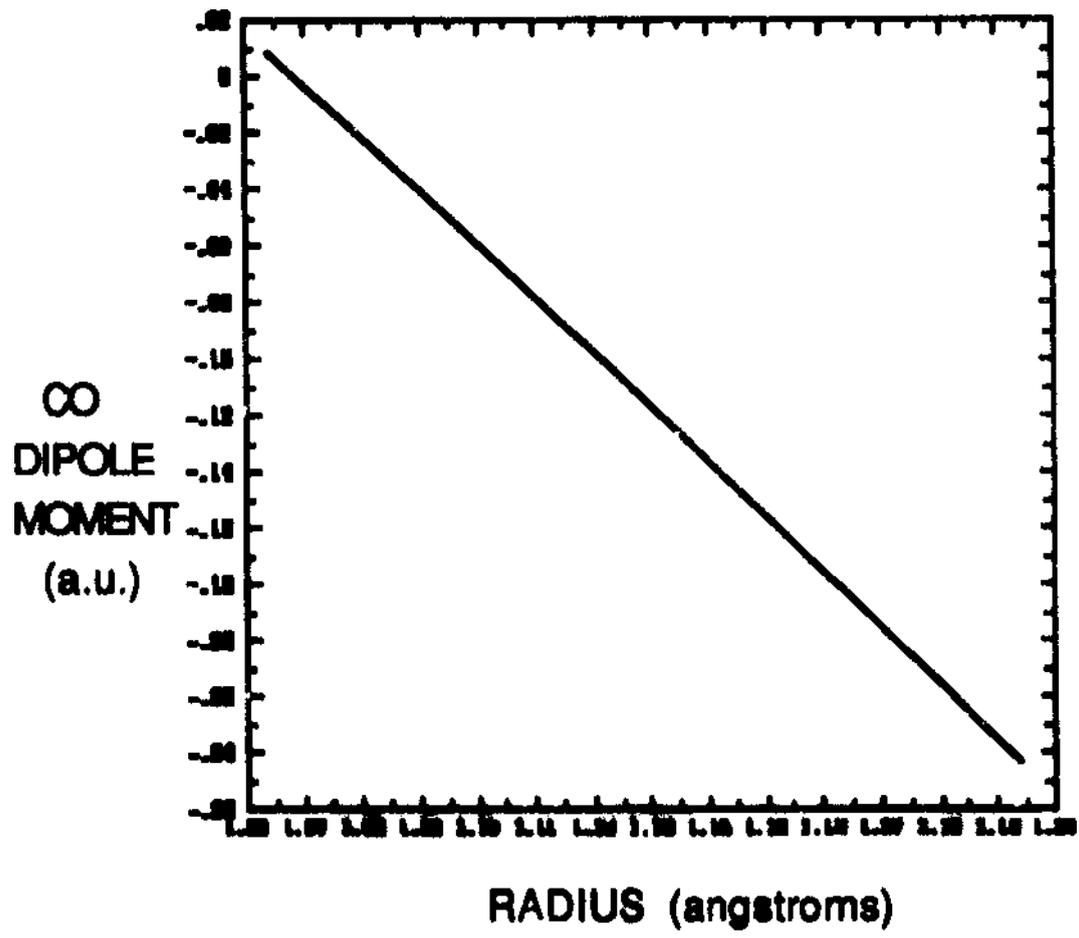


FIGURE 5

