The convergence of CASSCF energies to the complete basis set limit.

George A. Petersson and David K Malick, *Hall-Atwater Laboratories of Chemistry, Wesleyan University, Middletown, Connecticut 06459-0180*

Michael J. Frisch, *Gaussian, Inc., 340 Quinnipiac St. Bldg. 40, Wallingford, Connecticut 06492-4050*

Matthew Braunstein, *Spectral Sciences, Inc., 4 Fourth Avenue, Burlington, Massachusetts 01803-3304*

(Received

Examination of the convergence of full valence CASSCF energies with expansion of the one-electron basis set reveals a pattern very similar to the convergence of single determinant Hartree-Fock energies. Calculations on twenty-six molecular examples with the sequence of ntuple-ζ augmented polarized (nZaP) basis sets (n = 2, 3, 4, 5, and 6) are used to evaluate complete basis set (CBS) extrapolation schemes. The most effective extrapolation reduces the RMS one- electron basis set truncation errors from 3.03, 0.58, and 0.12 millihartree to 0.23, 0.05, and 0.014 millihartree for the 3ZaP, 4ZaP, and 5ZaP basis sets, respectively.

I. INTRODUCTION

Virtually all *ab initio* electronic structure calculations employ expansions in basis sets of atomic orbitals. Modern treatments of electron correlation such as CCSD(T)[1,2], CASPT2[3], and CAS-CISD[4-7], have reduced the errors from the many-body expansion to the point where truncation of this one-particle basis set is the dominant source of error in these calculations.[8] Over the past twenty years, it has become evident that the slow convergence of molecular energies would require the use of prohibitively large atomic orbital basis sets to achieve "chemical accuracy" of ~1 kcal/mol directly. It is therefore necessary to either employ empirical corrections[9,10], or attempt to extrapolate to the complete basis set (CBS) limit.[11-14] Extrapolation schemes for calculations employing a single reference configuration are now used routinely[11-14]. In this paper we shall begin the development of complete one-electron basis set (CBS) extrapolation schemes for multiconfiguration methods.

We select the full valence complete active space self consistent field (CASSCF) reference.[15-19] These calculations employ a full CI within a variationally optimized set of molecular orbitals that is uniquely determined either by the number of valence-shell

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE **APR 2005**	2. REPORT TYPE	3. DATES COVERED **-**

4. TITLE AND SUBTITLE
The Convergence of CASSCF Energies to the Complete Basis Set Limit PREPRINT

5a. CONTRACT NUMBER
F04611-03-C-0015

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
George Petersson; David Malick; Michael Frisch; Matthew Braunstein

5d. PROJECT NUMBER
BMSB

5e. TASK NUMBER
R2FT

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Air Force Research Laboratory (AFMC),AFRL/PRSA,10 E. Saturn Blvd.,Edwards AFB,CA,93524-7680

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT

Examination of the convergence of full valence CASSCF energies with expansion of the one-electron basis set reveals a pattern very similar to the convergence of single determinant Hartree-Fock energies. Calculations on twenty-six molecular examples with the sequence of ntuple-ζ augmented polarized (nZaP) basis sets (n = 2, 3, 4, 5, and 6) are used to evaluate complete basis set (CBS) extrapolation schemes. The most effective extrapolation reduces the RMS one- electron basis set truncation errors from 3.03, 0.58, and 0.12 millihartree to 0.23, 0.05, and 0.014 millihartree for the 3ZaP, 4ZaP, and 5ZaP basis sets, respectively.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE		**17**	
unclassified	**unclassified**	**unclassified**			

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

orbitals of the constituent atoms or by the number of valence-shell electrons. They are both size consistent MCSCF extensions of single determinant Hartree-Fock theory and require no subjective choices. These CASSCF methods are thus appropriate starting points for a model chemistry.[20-22]

The coupled cluster expansion provides a powerful tool for the study of species with a single dominant configuration.[23,24] However, most excited states and many ground states far from equilibrium geometry require a multi-configuration reference. For example, as the bond is stretched, the $X^1\Sigma_g^+$ ground state of the N_2 molecule shows a 10 kcal/mol error in the UCCSD(T) energy relative to the full CI energy[25] with the same basis set (Figure 1). There are more severe difficulties with the RCCSD(T) energy which diverges to $-\infty$ as the N_2 triple bond dissociates. Both second-order perturbation theory (CASPT2) and CISD (CAS-CISD) corrections to CAS give small absolute errors at all bond lengths. The inclusion of dynamic electron correlation in the full valence CASSCF gives errors that are both small and slowly varying with geometry.

From our experience with Hartree-Fock and CCSD(T) extrapolations, we expect the CASSCF energy to have its own distinct pattern of basis set convergence,[26-30] which will be different from that of the dynamic correlation energy.[11,12] We must therefore extrapolate these energy components separately. Both extrapolations are necessary for accurate potential energy surfaces and excitation energies. We shall examine the basis set convergence of the CASSCF energy in this study and leave the basis set convergence of the PT2 or CISD dynamic correlation for a future publication. We must therefore compare small basis set extrapolations to large basis set CASSCF results, since the CASSCF CBS limit still lacks dynamic correlation and thus will differ from experiment. All numerical results were obtained with a modified version of the Gaussian™ suite of programs.[31]

II. CONVERGENCE OF THE SCF ENERGY TO THE CBS LIMIT

The CASSCF wave function is similar to the SCF wave function in that it consists of a limited number of optimized self-consistent-field orbitals. We shall therefore use our knowledge of the convergence of the single configuration SCF energy as a starting point for a study of the basis set convergence of the multiconfiguration CASSCF energy. We begin with a brief summary of our earlier work on the basis set convergence of SCF energies.[29,30]

Extrapolation requires a well defined sequence of approximations and a model for the convergence of this sequence. The expansion of SCF orbitals in increasing numbers of Gaussian basis functions provides a systematic sequence of approximations. The approximate exponential convergence of SCF energies with the number of such basis functions is well known.[26] As suggested by Kutzelnigg,[27,28] the basis set truncation errors for these SCF calculations are actually better described by a function of the form:

$$\text{Error} \cong A \exp\left[- a \cdot n_p^{1/2}\right] \;, \tag{1}$$

where n_p is the number of primitives and a is a parameter. If we calculate the SCF energy with two different basis sets comprised of n_1 and n_2 sets of optimized Gaussian functions respectively, then Eq.(1) provides the model for a linear extrapolation to the SCF limit:

$$E_{\text{SCF Limit}} \cong E(n_2) + \{\exp[a \cdot n_2^{1/2} - a \cdot n_1^{1/2}] - 1\}^{-1} \{E(n_2) - E(n_1)\} \,. \tag{2}$$

Note that the extrapolation does not explicitly include the coefficient, A in Eq.(1), which varies from one atom or molecule to the next.

Extrapolations based on Eq.(2) require using a sequence of basis sets with *systematically* increasing numbers of Gaussian primitives for *each* angular momentum type combined with sets of polarization functions selected to give uniform convergence for each component of the molecular SCF energy. We have constructed such a balanced sequence of ntuple-ζ augmented polarized (nZaP) basis sets (n = 2, 3, 4, 5, and 6) for which the parameter, a, is relatively constant for Hartree-Fock calculations at a fixed geometry.[29,30] We shall now determine the extent to which the parameter, a, is constant for CASSCF calculations with variations of basis set and geometry.

III. CONVERGENCE OF THE CASSCF ENERGY TO THE CBS LIMIT

The convergence of the CASSCF energies of the low-lying states of nitrogen (^4S, ^2D, and ^2P) and oxygen (^3P, ^1D, and ^1S) atoms provide suitable models for the convergence of MCSCF energies with the one-electron basis set. It is clear from Figure 2 that Eq.(1) provides an accurate description of the basis set convergence of these systems.

The extrapolation using Eq.(2) can be simplified to:

$$E_{\text{SCF Limit}} \cong E(n_2) + C(n_1,n_2)\, \{E(n_2) - E(n_1)\} \;, \tag{3}$$

where $C(n_1,n_2)$ will depend on the parameter, a. Alternatively, we can employ our 6ZaP calculations to empirically determine the value of the extrapolation coefficient, $C(n_1,n_2)$:

$$C(n_1,n_2) \cong \{E(6\text{ZaP}) - E(n_2)\} / \{E(n_2) - E(n_1)\}. \tag{4}$$

The CAS($11e^-$,8_{orb}) energies of the $^2\Pi$ NO ground state (which include all valence electrons and orbitals) provide a simple test of the variation of the parameter, $C(n_1,n_2)$. The value of C(2ZaP,3ZaP) in Eq.(4) is not sufficiently constant for this example to permit quantitative extrapolations across the potential energy surface (Figure 3). We must therefore find a way to predict the variation of C(2ZaP,3ZaP). Fortunately, relatively inexpensive UHF SCF calculations provide a good model for this variation (Table I). The CAS($11e^-$,8_{orb}) values for C(2ZaP,3ZaP) vary by over 30% (from 1.40 to

1.83), whereas the ratio of the UHF value of C(2ZaP,3ZaP) to the CAS($11e^-$,8_{orb}) value varies by only 5% (from 0.995 to 1.048). The ROHF values for C(2ZaP,3ZaP) do not follow the CASSCF values as well as the UHF values do. We shall therefore use the UHF convergence as a model for the CASSCF convergence:

$$E_{CAS}(CBS) \cong E_{CAS}(3ZaP) + 1.205\left[E_{UHF}(4ZaP) - E_{UHF}(3ZaP)\right]\left[\frac{E_{CAS}(3ZaP) - E_{CAS}(2ZaP)}{E_{UHF}(3ZaP) - E_{UHF}(2ZaP)}\right], \qquad (5)$$

where the coefficient, 1.205, was obtained from Eq.(2) with a=5, a value obtained from the basis set convergence of atomic UHF calculations.[29,30] The value of the coefficient, 1.205 is uniquely determined by the number of primitives, n_p, in the basis set and the single parameter, a=5. This value for the parameter, a, reduced UHF errors by an order-of-magnitude when used to extrapolate the energies of atoms, molecules, and ions using double-, triple-, quadruple-, and pentuple-ζ basis sets. The use of the UHF energies to measure the basis set convergence makes the extrapolation in Eq.(5) fairly insensitive to our choice for the exponent, a. If we use a = 5.5, the coefficient changes by only 3% (from 1.205 to 1.166). This is because our choice for a affects only the portion of the coefficient above 1 (*i.e.* 0.205).

The form of Eq.(5) also applies to extrapolations using larger basis sets, but the coefficient, 1.205 in Eq.(5), changes. According to Eq.(2) with a=5, this coefficient increases to 1.258 if we extrapolate 3ZaP and 4ZaP energies:

$$E_{CAS}(CBS) \cong E_{CAS}(4ZaP) + 1.258\left[E_{UHF}(5ZaP) - E_{UHF}(4ZaP)\right]\left[\frac{E_{CAS}(4ZaP) - E_{CAS}(3ZaP)}{E_{UHF}(4ZaP) - E_{UHF}(3ZaP)}\right], \qquad (6)$$

and to 1.309 if we extrapolate 4ZaP and 5ZaP energies:

$$E_{CAS}(CBS) \cong E_{CAS}(5ZaP) + 1.309\left[E_{UHF}(6ZaP) - E_{UHF}(5ZaP)\right]\left[\frac{E_{CAS}(5ZaP) - E_{CAS}(4ZaP)}{E_{UHF}(5ZaP) - E_{UHF}(4ZaP)}\right]. \qquad (7)$$

Note that these slowly increasing coefficients multiply rapidly decreasing energy increments as the size of the basis sets increases. The primary justification for our choice of a = 5 is the success of all these extrapolations as described in the next section, where we apply Eqs.(5-7) to extrapolate the CASSCF energy to the complete basis set (CBS) limit for a number of low-lying electronic states of small molecules.

IV. RESULTS

We have assembled a test set of examples to evaluate extrapolation procedures (Table II). These examples include closed- and open-shell species in ground and excited states, cases where the UHF wave function is highly spin contaminated, and both singlet and triplet diradicals. We include the equilibrium geometry for each species as well as with each bond stretched to 3Å, which is a particularly difficult region near the separated atom limit. The UHF energies for all these species have been calculated with the full range of 2ZaP, 3ZaP, 4ZaP, 5ZaP, and 6ZaP basis sets[29,30]. We employ a simple linear extrapolation [Eq.(2) with a=5] of the 5ZaP and 6ZaP energies to estimate the small correction to the 6ZaP energy to give the CBS limit (Table II). We note that here and elsewhere in this paper we are using preliminary versions of these basis sets, which differ insignificantly from the final versions.

The corresponding full valence CASSCF (including all valence electrons and all valence orbitals of the constituent atoms) energies are given in Table III. We again use a simple linear extrapolation [Eq.(2) with a=5] of the 5ZaP and 6ZaP energies to obtain an estimate of the CBS limit (Table III) for use as a benchmark to evaluate extrapolations of the 2ZaP, 3ZaP, 4ZaP, and 5ZaP basis sets (Table IV).

Extrapolations of the 2ZaP and 3ZaP CASSCF energies using Eq.(5) reduce the RMS error from 3.0 mE_h to 0.23 mE_h (Table IV). Extrapolation of the 3ZaP and 4ZaP CASSCF energies using Eq.(6) reduces the RMS error from 0.583 mE_h to 0.048 mE_h and extrapolation of the 4ZaP and 5ZaP CASSCF energies using Eq.(7) reduces the RMS error from 0.118 mE_h to 0.014 mE_h. These extrapolations consistently reduce errors by an order-of-magnitude, which is better than direct calculations with the next larger basis set. For example, (3ZaP,4ZaP) extrapolations are more accurate (RMS error = 0.048 mE_h) than 5ZaP direct calculations (RMS error = 0.118 mE_h). Use of the UHF energies to determine C(nZaP,[n+1]ZaP) is clearly a success.

Use of the UHF energies to guide the CASSCF extrapolation gives a significant improvement over extrapolations based purely on CAS energies. A linear extrapolation of the 2ZaP and 3ZaP CASSCF energies using Eq.(3), even with the parameter, $C(n_1,n_2) = 0.155$, adjusted to minimize the RMS error for this test set, nevertheless doubles this error to 0.41 mE_h from 0.23 mE_h obtained using Eq.(5). Furthermore, use of the UHF energies to determine C(3ZaP,4ZaP) and C(4ZaP,5ZaP) is also significantly better than simple linear extrapolations with the optimum fixed values of C(3ZaP,4ZaP)=0.234 and C(4ZaP,5ZaP)=0.251, which result in RMS errors of 0.087 mE_h and 0.017 mE_h respectively. These individually optimized fixed values for C(n1,n2) = 0.155, 0.234, and 0.251 are quite similar to the values predicted with the parameter, a, set to 5 (*i.e.* C = 0.148, 0.205, and .258, respectively), and thus justify this choice for a. Use of the UHF energies reduces the error in (3ZaP,4ZaP) extrapolations by almost a factor of two. The error estimates for (4ZaP,5ZaP) extrapolations are rather uncertain, since our largest direct calculations (*i.e*. 6ZaP) have an estimated RMS error of 0.03 mE_h.

The particular state used to probe the convergence with UHF calculations appears to be of little significance. If we use the UHF O_2 $a^1\Delta_g$ state to extrapolate the CAS O_2

$X^3\Sigma_g^-$ state, the O_2 $X^3\Sigma_g^-$ state to extrapolate the O_2 $a^1\Delta_g$ state, the C_2 $A^1\Pi_u$ state to extrapolate the C_2 $X^1\Sigma_g^+$ state, the C_2 $X^1\Sigma_g^+$ state to extrapolate the C_2 $A^1\Pi_u$ state, the C_2 $b^3\Sigma_g^-$ state to extrapolate the C_2 $a^3\Pi_u$ state, and the C_2 $a^3\Pi_u$ state to extrapolate the C_2 $b^3\Sigma_g^+$ state, then the RMS errors change from 0.233, 0.048, and 0.014 to 0.235 0.049, and 0.016 mE_h, for the (2ZaP,3ZaP) (3ZaP,4ZaP), and (4ZaP,5ZaP) extrapolations respectively. In contrast, switching the UHF calculations at R_e with those at 3Å increases the RMS errors to 0.489 mE_h, 0.117 mE_h, and 0.018 mE_h, which are worse than the errors without using the UHF to probe the basis set convergence. These (nZaP,[n+1]ZaP) extrapolations require UHF calculations at the same geometry, but are not sensitive to which state is employed in the UHF calculations (*i.e.* the basis set convergence is insensitive to the particular state constructed from valence orbitals). This is fortunate, since it is not always possible to associate a single determinant UHF wave function with a multiconfiguration CASSCF state function.

There is considerable current interest in understanding the chemistry of oxygen atoms impacting hydrocarbons at hyperthermal velocities, since this plays a critical role in the surface erosion of spacecraft in low Earth orbit (LEO).[32] This chemistry occurs on triplet potential energy surfaces, and one of the major products of such reactions is the open shell radical OH, for which very good validating experimental data exists. We have therefore chosen to apply and test the extrapolation method for OH as it will be a major product radical fragment in an important class of reactions which inherently involve open shell multi-configuration wave functions.

The application to these extrapolations to the potential energy curves for the $X^2\Pi$ ground state and $A^2\Sigma^+$ and $B^2\Sigma^+$ excited states of the OH radical are given in Figure 4. Note that the rather substantial variation of the basis set error with geometry is very similar for the three states. Extrapolation of the energies using Eq.(5) consistently reduces the basis set errors to very small values for all three states. This graphically demonstrates the importance of using the correct geometry, but not necessarily the same state, when using the UHF energy to probe the effects of larger basis sets.

V. CONCLUSIONS

The convergence of full valence CASSCF energies to the complete basis set limit is very similar to the basis set convergence of UHF energies. This similarity can be exploited with extrapolations based on Eqs.(5-7), which can reduce basis set truncation errors by more than an order-of-magnitude.

ACKNOWLEDGMENTS

We acknowledge support through a Small Business Innovative Research (SBIR) award from the Missile Defense Agency (MDA) Contract No. F04611-03-C-0015, and technical oversight from Dr. Marty Venner of the Air Force Research Laboratory. We are also grateful to Wesleyan University for the support of this research.

REFERENCES

1. R. J. Bartlett and G. D. Purvis, *Int. J. Quant. Chem.* **14**, 516 (1978); G. D. Purvis and R. J. Bartlett, *J. Chem. Phys.* **76**, 1910 (1982).
2. J. A. Pople, M. Head-Gordon, and K. Raghavachari, *J. Chem. Phys.* **87**, 5968 (1987); K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, *Chem. Phys. Lett.* **157**, 479 (1989).
3. K. Andersson, P. Malmqvist, and B. Roos, *J. Chem. Phys*. **96**, 1218 (1992).
4. B. Huron, P. Rancurel, and J. P. Malrieu, *J. Chem. Phys*. **75**, 5745 (1973).
5. R. J. Buenker and S. D. Peyerimhoff, *Theoret. Chim. Acta* **35**, 33 &1974).
6. B. J. Moss and W. A. Goddard, *J. Chem. Phys.* **63**, 3523 (1975).
7. J. Olsen, B. O. Roos, P. Jørgensen, and H. J. A. Jensen, *J. Chem. Phys*.**89**, 2185 (1988).
8. G. A. Petersson, pp. 237, In *Computational Thermochemistry. ACS Symposium Series 677*, K. K. Irikura and D. J. Frurip, Eds., American Chemical Society, Washington, D. C., 1998.
9. L. A. Curtiss, K. Raghavachari, G. W. Trucks and J. A. Pople, J. Chem. Phys. 94, 7221 (1991).
10. M. R. Zachariah and C. F. Melius, pp. 162, In *Computational Thermochemistry. ACS Symposium Series 677*, K. K. Irikura and D. J. Frurip, Eds., American Chemical Society, Washington, D. C., 1998.
11. M. R. Nyden and G. A. Petersson, *J. Chem. Phys.* **75**, 1843 (1981).
12. G. A. Petersson, pp. 99, In *Quantum-Mechanical Prediction of Thermochemical Data*, J. Cioslowski, Ed., Kluwer Academic Publishers, Dordrecht, the Netherlands, 2001.
13. T. H. Dunning, Jr., *J. Chem. Phys.* **90**, 1007 (1989).
14. J. M. L. Martin, pp. 212, In *Computational Thermochemistry. ACS Symposium Series 677*, K. K. Irikura and D. J. Frurip, Eds., American Chemical Society, Washington, D. C., 1998.
15. D. Hegarty and M. A. Robb, *Mol. Phys*. **38**, 1795 (1979).
16. R. H. E. Eade and M. A. Robb, *Chem. Phys. Lett*. **83**, 362 (1981).
17. B. O. Roos, P. Linse, P. E. M. Siegbahn, and M. R. A. Blomberg, *Chem. Phys*. **66**, 197 (1981).
18. H. B. Schlegel and M. A. Robb, *Chem. Phys. Lett*. **93**, 43 (1982).
19. M. J. Frisch, I. N. Ragazos, M. A. Robb, and H. B. Schlegel, *Chem. Phys. Lett*. **189**, 524 (1992).
20. J. A. Pople, in *Energy, Structure and Reactivity*, edited by D. W. Smith and W. B. McRae (Wiley, New York, 1973), p. 51.
21. J. A. Pople, J. S. Binkley, and R. Seeger, *Int. J. Quantum Chem. Symp*. **10**, 1 (1976).
22. R. Krishnan and J. A. Pople, *Int. J. Quantum Chem*. **14**, 91 (1978).
23. J. M. L. Martin and S. Parthiban, pp. 31, In *Quantum-Mechanical Prediction of Thermochemical Data*, J. Cioslowski, Ed., Kluwer Academic Publishers, Dordrecht, the Netherlands, 2001.
24. T. Helgaker, W. Klopper, A. Halkier, K. A. Bak, Poul Jørgensen, and Jeppe Olsen, pp. 1, In *Quantum-Mechanical Prediction of Thermochemical Data*, J. Cioslowski, Ed., Kluwer Academic Publishers, Dordrecht, the Netherlands, 2001.
25. H. Larsen, J.Olsen, P.Jørgensen, and O. Christiansen, *J. Chem. Phys*. **113**, 6677 (2000).
26. F. B. van Duijneveldt, IBM Publ. RI 945, Yorktown Hts., New York, 1971.
27. W. Klopper and W. Kutzelnigg, *J. Mol. Struct*. **135**, 339 (1986).
28. W. Kutzelnigg pp79-101 in: Strategies and applications in quantum chemistry, Y. Ellingr and M. Defranceschi Eds., Kluwer, Dordrecht, the Netherlands , 1996.
29. G. A. Petersson, S. Zhong, J. A. Montgomery, Jr., and M. J. Frisch, *J. Chem. Phys*. **118**, 1101 (2003).
30. S. Zhong, D. Ashen-Garry, and G. A. Petersson, “The nZaP Basis Sets, I. Uniformly Convergent Basis Sets for CBS Extrapolations of SCF Energies”, in preparation.
31. Gaussian 03, Revision B.04, M. J. Frisch, G. W. Trucks, H. B. Schlegel, *et al.* Gaussian, Inc., Pittsburgh PA, 2003.
32. D. Troya and G. C. Schatz, *J. Chem. Phys*. **120**, 7696 (2004).

Table I. The variation of C(2ZaP,3ZaP) for the $^2\Pi$ NO ground state.

Method	**R_{NO} (Å)**							
	1.1	**1.2**	**1.3**	**1.4**	**1.5**	**1.6**	**1.7**	**1.8**
ROHF	0.179	0.161	0.150	0.148	0.153	0.163	0.171	0.175
UHF	0.182	0.165	0.151	0.145	0.144	0.147	0.151	0.154
CAS(11,8)	0.183	0.164	0.149	0.141	0.140	0.142	0.145	0.147
UHF/ CAS(11,8)	0.995	1.006	1.013	1.028	1.029	1.035	1.041	1.048

Table II. . Calculated UHF energies (hartree au).

	2ZaP	3ZaP	4ZaP	5ZaP	6ZaP	Limit[a]
C_2 $X^1\Sigma_g^+$(Re)	-75.5053629	-75.5234499	-75.5258460	-75.5263111	-75.5263878	-75.5264151
C_2 $X^1\Sigma_g^+$(3A)	-75.3731809	-75.3857403	-75.3871148	-75.3873315	-75.3873753	-75.3873909
C_2 $a^3\Pi_u$(Re)	-75.5006172	-75.5183372	-75.5205873	-75.5210742	-75.521172	-75.5212068
C_2 $a^3\Pi_u$(3A)	-75.3481802	-75.3622539	-75.3638612	-75.3641309	-75.3641946	-75.3642173
C_2 $b^3\Sigma_g^-$(Re)	-75.4976695	-75.514791	-75.5168839	-75.5173352	-75.5174259	-75.5174582
C_2 $b^3\Sigma_g^-$(3A)	-75.3497501	-75.3641237	-75.3658517	-75.3661562	-75.3662347	-75.3662627
C_2 $A^1\Pi_u$(Re)	-75.4681974	-75.4855129	-75.487837	-75.4883056	-75.4884046	-75.4884399
C_2 $A^1\Pi_u$(3A)	-75.3713171	-75.38391	-75.3852513	-75.3854591	-75.3854998	-75.3855143
CN $X^2\Sigma^+$(Re)	-92.2199607	-92.2392899	-92.2423166	-92.2428140	-92.2428964	-92.2429257
CN $X^2\Sigma^+$(3A)	-92.0243867	-92.0390666	-92.0409403	-92.0412650	-92.0413359	-92.0413611
CO $X^1\Sigma^+$(Re)	-112.7635809	-112.7869434	-112.7903437	-112.7909208	-112.7910338	-112.7910740
CO $X^1\Sigma^+$(3A)	-112.4334152	-112.4525259	-112.4550176	-112.4554385	-112.4555409	-112.4555774
N_2 $X^1\Sigma_g^+$(Re)	-108.9681375	-108.9894216	-108.9926598	-108.9934600	-108.9935797	-108.9936223
N_2 $X^1\Sigma_g^+$(3A)	-108.7969923	-108.8069299	-108.8081889	-108.8083996	-108.8084313	-108.8084426
NO $X^2\Pi_i$(Re)	-129.2814165	-129.3051751	-129.3086155	-129.3092885	-129.3094159	-129.3094613
NO $X^2\Pi_i$(3A)	-129.2061620	-129.2208765	-129.2228208	-129.2231506	-129.2232161	-129.2232394
O_2 $X^3\Sigma_g^-$(Re)	-149.6562449	-149.6867982	-149.6905200	-149.6913116	-149.6914855	-149.6915474
O_2 $X^3\Sigma_g^-$(3A)	-149.5773531	-149.5983395	-149.6012004	-149.6016855	-149.601795	-149.6018340
O_2 $a^1\Delta_g$(Re)	-149.6291445	-149.6600763	-149.6637730	-149.6645547	-149.6647219	-149.6647814
O_2 $a^1\Delta_g$ (3A)	-149.6149872	-149.6344944	-149.6371239	-149.6375694	-149.6376695	-149.6377051
O_3 X^1A_1(Re)	-224.3948331	-224.4426423	-224.4479589	-224.4491128	-224.4493494	-224.4494337
O_3 X^1A_1(3A)	-224.4637792	-224.5038233	-224.5088213	-224.5098202	-224.5100398	-224.5101180
OH $X^2\Pi$(Re)	-75.4126337	-75.4256766	-75.4273923	-75.4276966	-75.4277703	-75.4277965
OH $X^2\Pi$(3A)	-75.3069243	-75.3173162	-75.3186838	-75.3189133	-75.3189636	-75.3189815
OH $A^2\Sigma^+$(Re)	-75.2577850	-75.2716397	-75.2733534	-75.2736456	-75.2737238	-75.2737516
OH $A^2\Sigma^+$(3A)	-75.3061329	-75.3165512	-75.3179223	-75.3181487	-75.3181964	-75.3182134
RMS Error	0.0248530	0.0034117	0.0006873	0.0001502	0.0000394	

a. Equation (2) with a = 5.

Table III. Calculated Full Valence CASSCF[a] energies (hartree au).

	2ZaP	3ZaP	4ZaP	5ZaP	6ZaP	Limit[b]
C_2 $X^1\Sigma_g^+$(Re)	-75.6233832	-75.6412898	-75.6437447	-75.6442121	-75.6442908	-75.6443188
C_2 $X^1\Sigma_g^+$(3A)	-75.4013789	-75.4128440	-75.4140195	-75.4141737	-75.4142010	-75.4142107
C_2 $a^3\Pi_u$(Re)	-75.6073350	-75.6230710	-75.6251470	-75.6255495	-75.6256266	-75.6256541
C_2 $a^3\Pi_u$(3A)	-75.4006072	-75.4121197	-75.4132989	-75.4134563	-75.4134827	-75.4134921
C_2 $b^3\Sigma_g^-$(Re)	-75.5777931	-75.5941905	-75.5962600	-75.5966964	-75.5967840	-75.5968152
C_2 $b^3\Sigma_g^-$(3A)	-75.3993449	-75.4108243	-75.4120302	-75.4121864	-75.4122166	-75.4122274
C_2 $A^1\Pi_u$(Re)	-75.5627890	-75.5788475	-75.5809697	-75.5813798	-75.5814615	-75.5814906
C_2 $A^1\Pi_u$(3A)	-75.4015136	-75.4129861	-75.4141585	-75.4143118	-75.4143390	-75.4143487
CN $X^2\Sigma^+$(Re)	-92.3544025	-92.3730997	-92.3761806	-92.3766716	-92.3767524	-92.3767812
CN $X^2\Sigma^+$(3A)	-92.0970989	-92.1080349	-92.1092814	-92.1094517	-92.1094886	-92.1095017
CO $X^1\Sigma^+$(Re)	-112.8946223	-112.9181416	-112.9218328	-112.9224855	-112.9226137	-112.9226594
CO $X^1\Sigma^+$(3A)	-112.5055048	-112.5201809	-112.5219114	-112.5221589	-112.5222132	-112.5222325
N_2 $X^1\Sigma_g^+$(Re)	-109.1166132	-109.1373292	-109.1406653	-109.1414826	-109.1415931	-109.1416324
N_2 $X^1\Sigma_g^+$(3A)	-109.7910295	-109.8006174	-109.8018265	-109.8020034	-109.8020367	-109.8020486
NO $X^2\Pi_i$(Re)	-129.3892421	-129.4106758	-129.4138042	-129.4143983	-129.4144941	-129.4145282
NO $X^2\Pi_i$(3A)	-129.1968657	-129.2095960	-129.2111468	-129.2113709	-129.2114140	-129.2114293
O_2 $X^3\Sigma_g^-$(Re)	-149.7411441	-149.7681917	-149.7713131	-149.7719475	-149.7720640	-149.7721055
O_2 $X^3\Sigma_g^-$(3A)	-149.6046361	-149.6217927	-149.6241839	-149.6245139	-149.6245849	-149.6246102
O_2 $a^1\Delta_g$(Re)	-149.7059304	-149.7327122	-149.7358092	-149.7364403	-149.7365522	-149.7365920
O_2 $a^1\Delta_g$ (3A)	-149.6036064	-149.6201523	-149.6221939	-149.6224992	-149.6225606	-149.6225825
O_3 X^1A_1(Re)	-224.5478659	-224.5938866	-224.5991383	-224.6002546	-224.6004950	-224.6005806
O_3 X^1A_1(3A)	-224.5419937	-224.5765004	-224.5804565	-224.5811915	-224.5813130	-224.5813563
OH $X^2\Pi$(Re)	-75.4325178	-75.4440618	-75.4456305	-75.4458720	-75.4459251	-75.4459441
OH $X^2\Pi$(3A)	-75.3003228	-75.3086425	-75.3095833	-75.3097133	-75.3097362	-75.3097444
OH $A^2\Sigma^+$(Re)	-75.2670507	-75.2808979	-75.2825953	-75.2828559	-75.2829216	-75.2829450
OH $A^2\Sigma^+$(3A)	-75.2991736	-75.3075077	-75.3084437	-75.3085717	-75.3085938	-75.3086017
RMS Error	0.0224147	0.0030328	0.0005829	0.0001180	0.0000310	

a. (n_{e-},n_{orb}): C_2(8,8), CN(9,8), CO(10,8), N_2(10,8), NO(11,8), O_2(12,8), O_3(18,12), OH(7,5).

b. Equation (2) with a = 5.

Table IV. Extrapolated Full Valence CASSCF energies (hartree au).

	Energy			**Error**		
	(2ZaP,3ZaP)[a]	**(3ZaP,4ZaP)[b]**	**(4ZaP,5ZaP)[c]**	**(2Z,3Z)[d]**	**(3Z,4Z)[e]**	**(4Z,5Z)[f]**
C_2 $X^1\Sigma_g^+$(Re)	-75.6441483	-75.6443443	-75.6443130	-0.0001705	0.0000255	-0.0000059
C_2 $X^1\Sigma_g^+$(3A)	-75.4143560	-75.4142527	-75.4142145	0.0001452	0.0000420	0.0000038
C_2 $a^3\Pi_u$(Re)	-75.6254788	-75.6257123	-75.6256553	-0.0001753	0.0000582	0.0000012
C_2 $a^3\Pi_u$(3A)	-75.4137040	-75.4135479	-75.4135049	0.0002119	0.0000558	0.0000128
C_2 $b^3\Sigma_g^-$(Re)	-75.5966058	-75.5968216	-75.5968112	-0.0002094	0.0000064	-0.0000040
C_2 $b^3\Sigma_g^-$(3A)	-75.4124873	-75.4122976	-75.4122391	0.0002599	0.0000703	0.0000117
C_2 $A^1\Pi_u$(Re)	-75.5814447	-75.5815082	-75.5814932	-0.0000459	0.0000176	0.0000026
C_2 $A^1\Pi_u$(3A)	-75.4144586	-75.4143871	-75.4143511	0.0001099	0.0000384	0.0000024
CN $X^2\Sigma^+$(Re)	-92.3766276	-92.3768177	-92.3767780	-0.0001536	0.0000366	-0.0000031
CN $X^2\Sigma^+$(3A)	-92.1097169	-92.1095532	-92.1095004	0.0002151	0.0000515	-0.0000014
CO $X^1\Sigma^+$(Re)	-112.9222664	-112.9226211	-112.9226527	-0.0003929	-0.0000382	-0.0000066
CO $X^1\Sigma^+$(3A)	-112.5224867	-112.5222792	-112.5222377	0.0002541	0.0000467	0.0000052
N_2 $X^1\Sigma_g^+$(Re)	-109.1411271	-109.1417027	-109.1416426	-0.0005054	0.0000703	0.0000101
N_2 $X^1\Sigma_g^+$(3A)	-109.8020811	-109.8020811	-109.8020382	0.0000325	0.0000326	-0.0000103
NO $X^2\Pi_i$(Re)	-129.4144158	-129.4145743	-129.4145455	-0.0001124	0.0000461	0.0000173
NO $X^2\Pi_i$(3A)	-129.2116229	-129.2114778	-129.2114291	0.0001936	0.0000485	-0.0000002
O_2 $X^3\Sigma_g^-$(Re)	-149.7721619	-149.7721485	-149.7721299	0.0000564	0.0000431	0.0000244
O_2 $X^3\Sigma_g^-$(3A)	-149.6246110	-149.6246941	-149.6246114	0.0000008	0.0000839	0.0000012
O_2 $a^1\Delta_g$(Re)	-149.7365691	-149.7366333	-149.7366169	-0.0000230	0.0000413	0.0000249
O_2 $a^1\Delta_g$ (3A)	-149.6228398	-149.6226292	-149.6225890	0.0002574	0.0000467	0.0000065
O_3 X^1A_1(Re)	-224.6000534	-224.6005726	-224.6005541	-0.0005272	-0.0000080	-0.0000265
O_3 X^1A_1(3A)	-224.5816902	-224.5814515	-224.5814030	0.0003339	0.0000952	0.0000467
OH $X^2\Pi$(Re)	-75.4458916	-75.4459806	-75.4459485	-0.0000524	0.0000366	0.0000045
OH $X^2\Pi$(3A)	-75.3099618	-75.3097820	-75.3097506	0.0002175	0.0000376	0.0000062
OH $A^2\Sigma^+$(Re)	-75.2829618	-75.2829595	-75.2829472	0.0000168	0.0000145	0.0000022
OH $A^2\Sigma^+$(3A)	-75.3088293	-75.3086382	-75.3086070	0.0002277	0.0000365	0.0000053
RMS Error	0.0002327	0.0000480	0.0000141	0.0002327	0.0000480	0.0000141

a. Equation (5).
b. Equation (6).
c. Equation (7).
d. Limit from Table III minus Equation (5).
e. Limit from Table III minus Equation (6).
f. Limit from Table III minus Equation (7).

Figure Captions

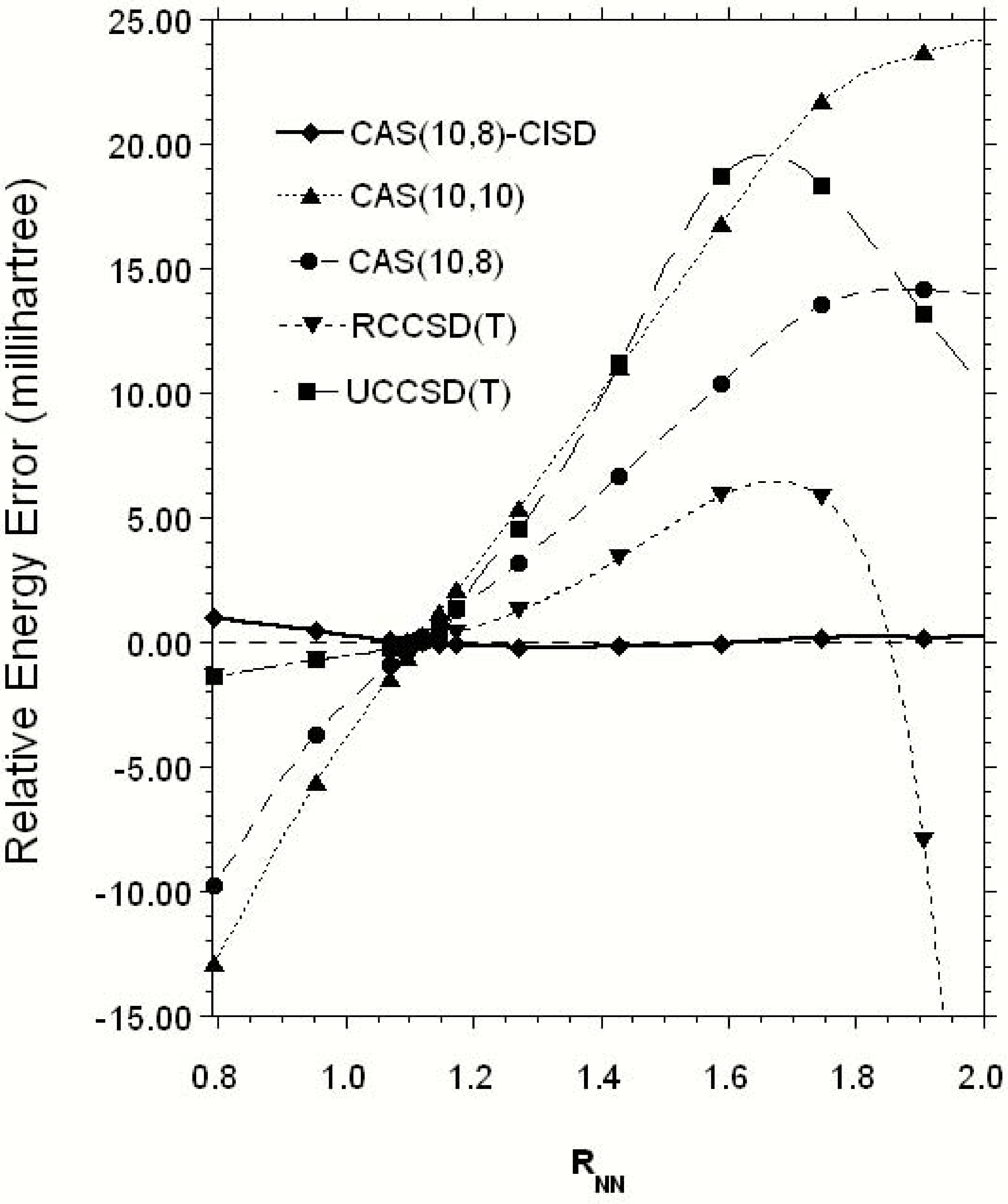
Figure 1. The error in the calculated energy of the N_2 X $^1\Sigma_g^+$ ground state with respect to the 10 electron full CI energy with the same cc-pVDZ basis set relative to this error at R_e. The error is shown as a function of the N-N internuclear distance in Angstrom.

Figure 2. The basis set truncation error for the low lying states of nitrogen and oxygen atoms. The solid line shows the behavior for Eq.(1) with $A=9x10^7$ and $a=5.5$.

Figure 3. The variation of C(2ZaP,3ZaP) in Eq.(4) for a CAS(11e-,8orb) calculation of the $^2\Pi$ NO ground state.

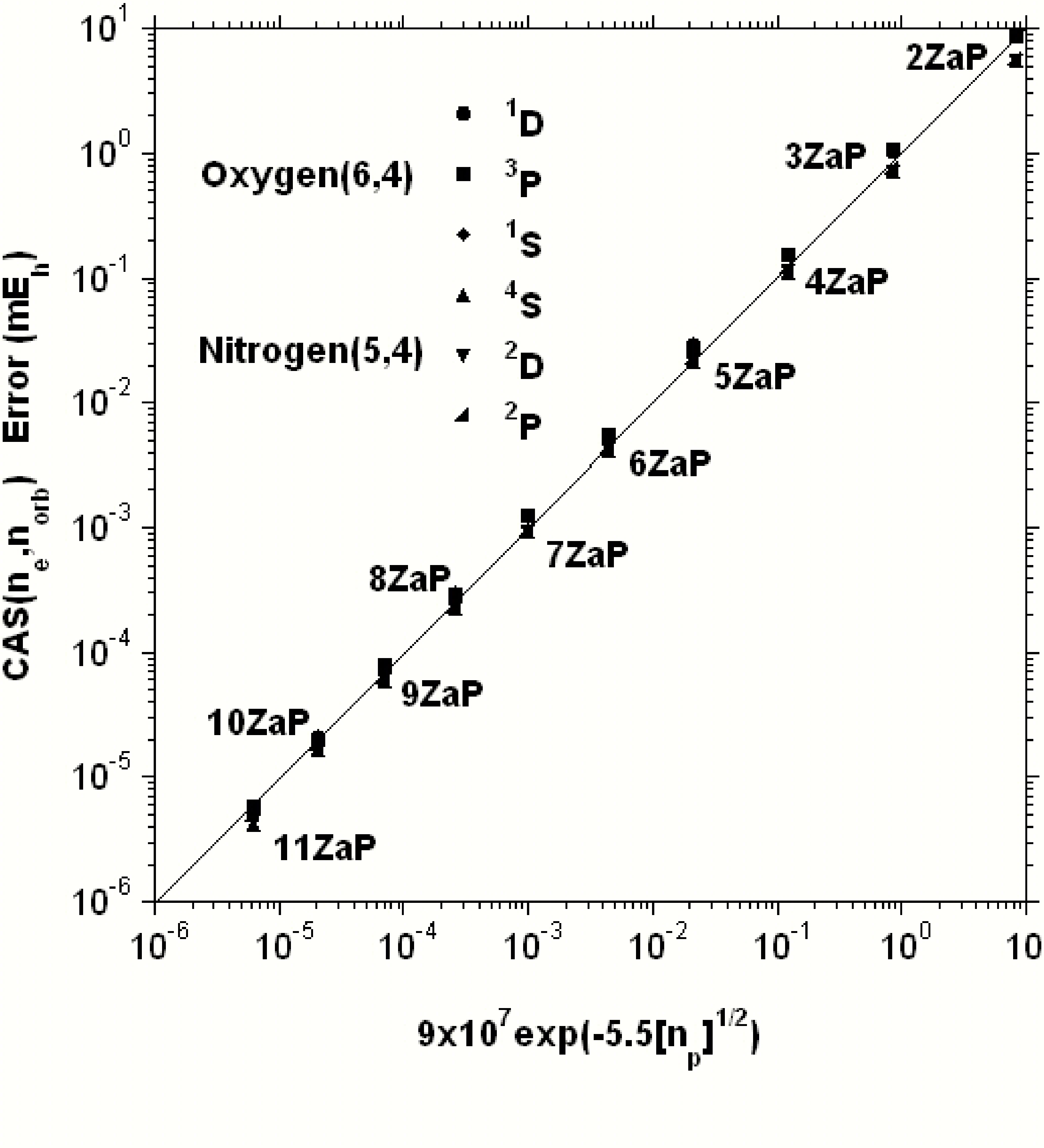
Figure 4. The basis set errors in the CASSCF potential energy curves for the $X^2\Pi$ ground state and $A^2\Sigma^+$ and $B^2\Sigma^+$ excited states of the OH radical, before and after extrapolation using Eq.(5).

Figure 1



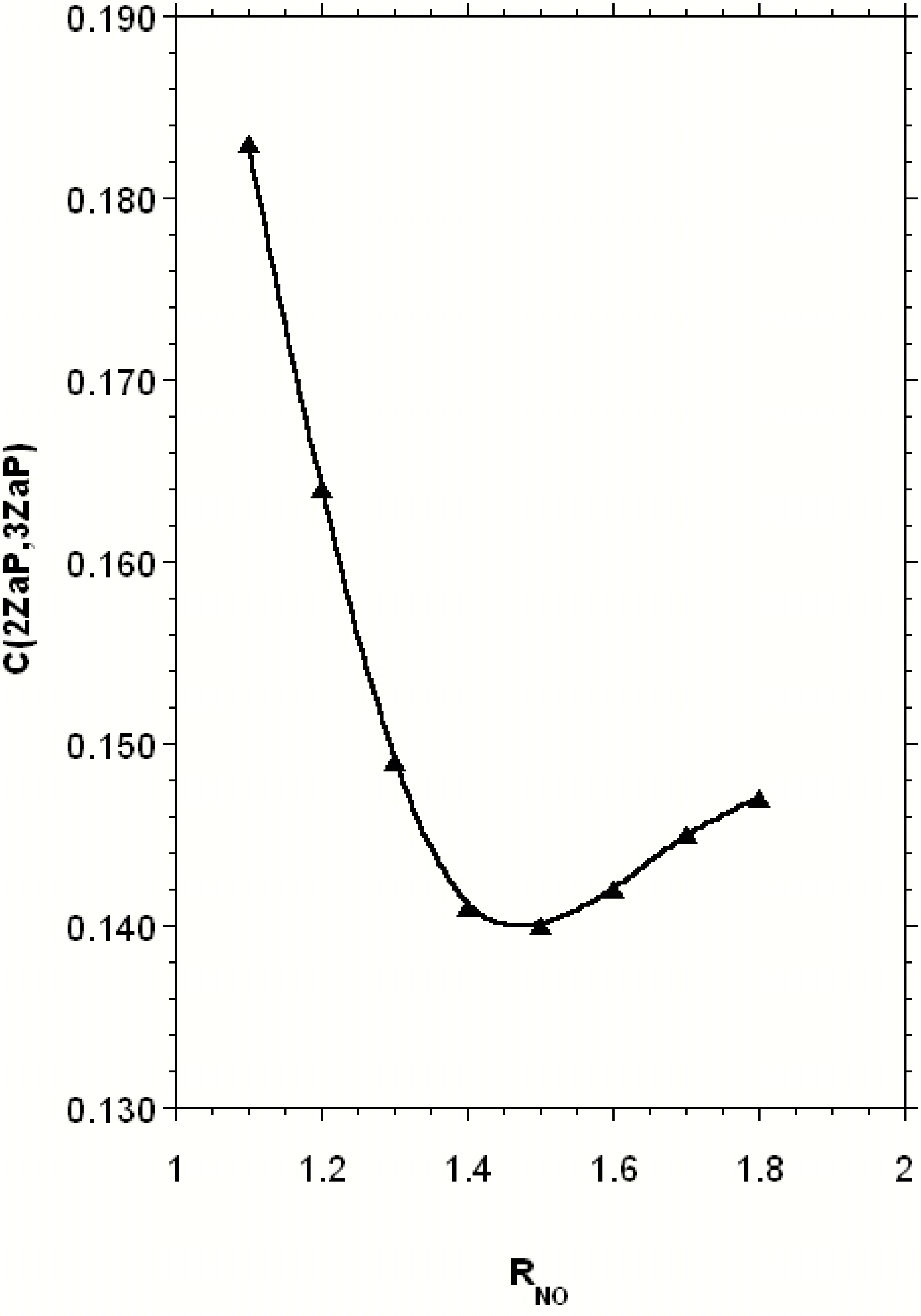
CAS(10,8)-CISD
CAS(10,10)
CAS(10,8)
RCCSD(T)
UCCSD(T)
Relative Energy Error (millihartree)
25.00
20.00
15.00
10.00
5.00
0.00
-5.00
-10.00
-15.00
0.8
1.0
1.2
1.4
1.6
1.8
2.0
R_{NN}

Figure 2



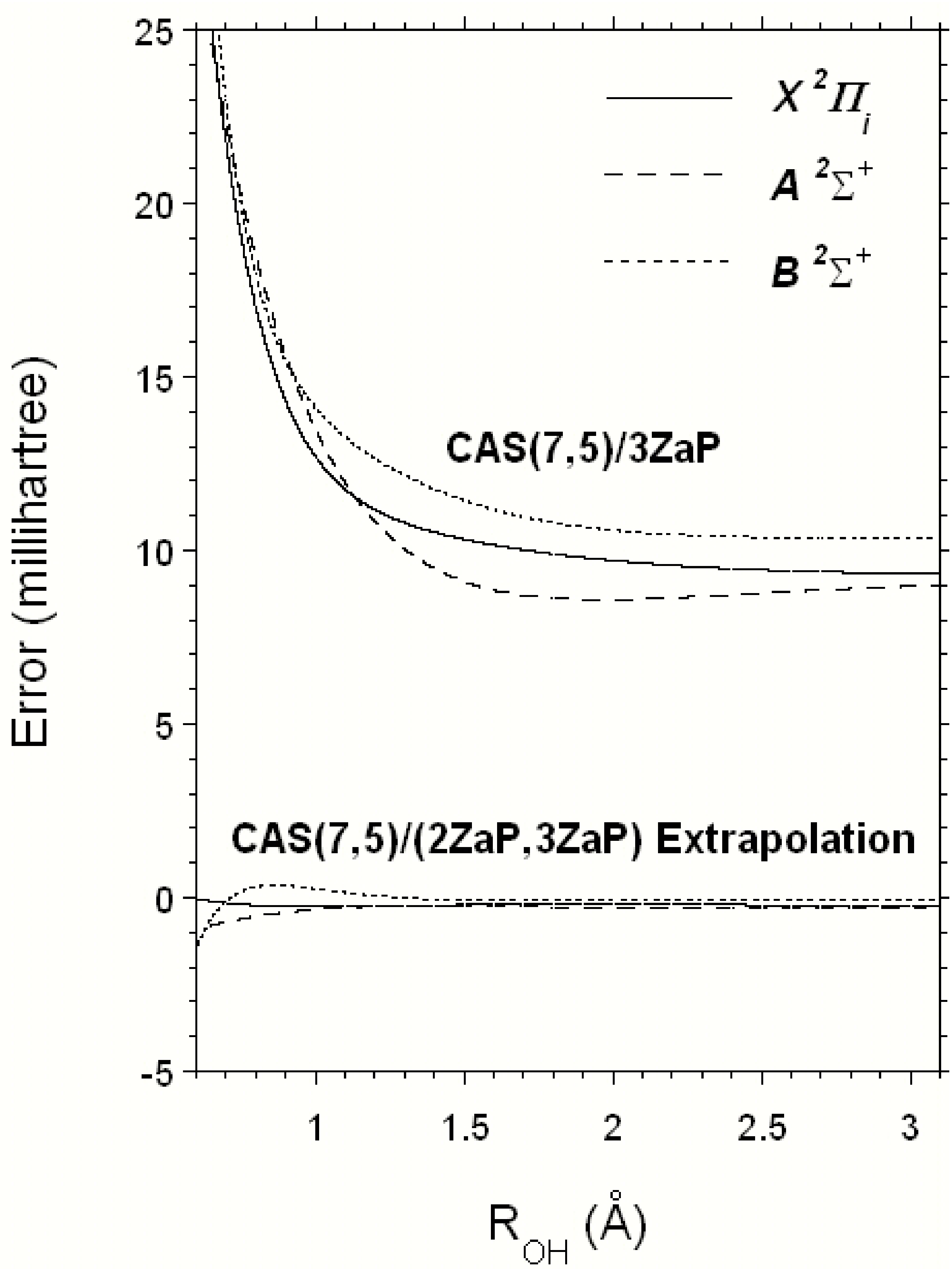
Oxygen(6,4)
● ^{1}D
■ ^{3}P
◆ ^{1}S
▲ ^{4}S
Nitrogen(5,4)
▼ ^{2}D
◢ ^{2}P
2ZaP
3ZaP
4ZaP
5ZaP
6ZaP
7ZaP
8ZaP
9ZaP
10ZaP
11ZaP
10^{1}
10^{0}
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-6}
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
10^{0}
10^{1}
CAS(n_e,n_{orb}) Error (mE_h)
$9\times10^7 \exp(-5.5[n_p]^{1/2})$

Figure 3



0.190
0.180
0.170
0.160
0.150
0.140
0.130
C(2ZaP,3ZaP)
1
1.2
1.4
1.6
1.8
2
R_{NO}

Figure 4



25
20
15
10
5
0
-5
Error (millihartree)
$X\ ^2\Pi_i$
$A\ ^2\Sigma^+$
$B\ ^2\Sigma^+$
CAS(7,5)/3ZaP
CAS(7,5)/(2ZaP,3ZaP) Extrapolation
1
1.5
2
2.5
3
R_{OH} (Å)