A complete basis set model chemistry for excited states

George A. Petersson

Hall-Atwater Laboratories of Chemistry,

Wesleyan University,

Middletown, Connecticut 06459-0180

Report Documentation Page

Form Approved
OMB No. 0704-0188

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

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
A Complete Basis Set Model Chemistry for Excited States	**F04611-03-C-0015**
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER
George Petersson	**BMSB**
	5e. TASK NUMBER **R2FT**
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)	8. PERFORMING ORGANIZATION REPORT NUMBER
Spectral Sciences Incorporated,4 Fourth Avenue,Burlington,MA,01803-3304	
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
N/A

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			
unclassified	**unclassified**	**unclassified**		**31**	

Outline

I. Background
   a. John Pople's Model Chemistries
II. Excited state Models
   a. CCSD(T) *vs* FCI
   b. CASSCF and CAS-CISD *vs* FCI
III. CBS Extrapolations
   a. A Systematic Sequence of Basis Sets
   b. The CASSCF CBS Lmit
   c. The CASSCF-CISD CBS Limit
IV. Results
   a. Geometry
   b. Vibrational Frequencies
   c. Excitation energies
   d. Dissociation Energies
V. Acknowledgment

John Pople's Model Chemistries

any

of every

of
we can

eory,
es.

The CBS-Q//B3 Model

Geometry: B3LYP/6-311G(2d,d,p)

ZPE & Thermal: B3LYP/6-311G(2d,d,p)

SCF: UHF/6-311+G(3d2f,2df,2p)

CBS(extrap) - MP2: UHF/6-311+G(3d2f,2df,2p)

MP3, MP4(SDQ): MP4(SDQ)/6-31+G(d(f),d,p)

MP5 - CCSD(T): CCSD(T)/6-31+G(d')

Empirical Corrections:

$-5.79\ mE_h\ |S|^2_{ii}[\Sigma_i C^2_\mu]_{ii}$ (2e⁻)

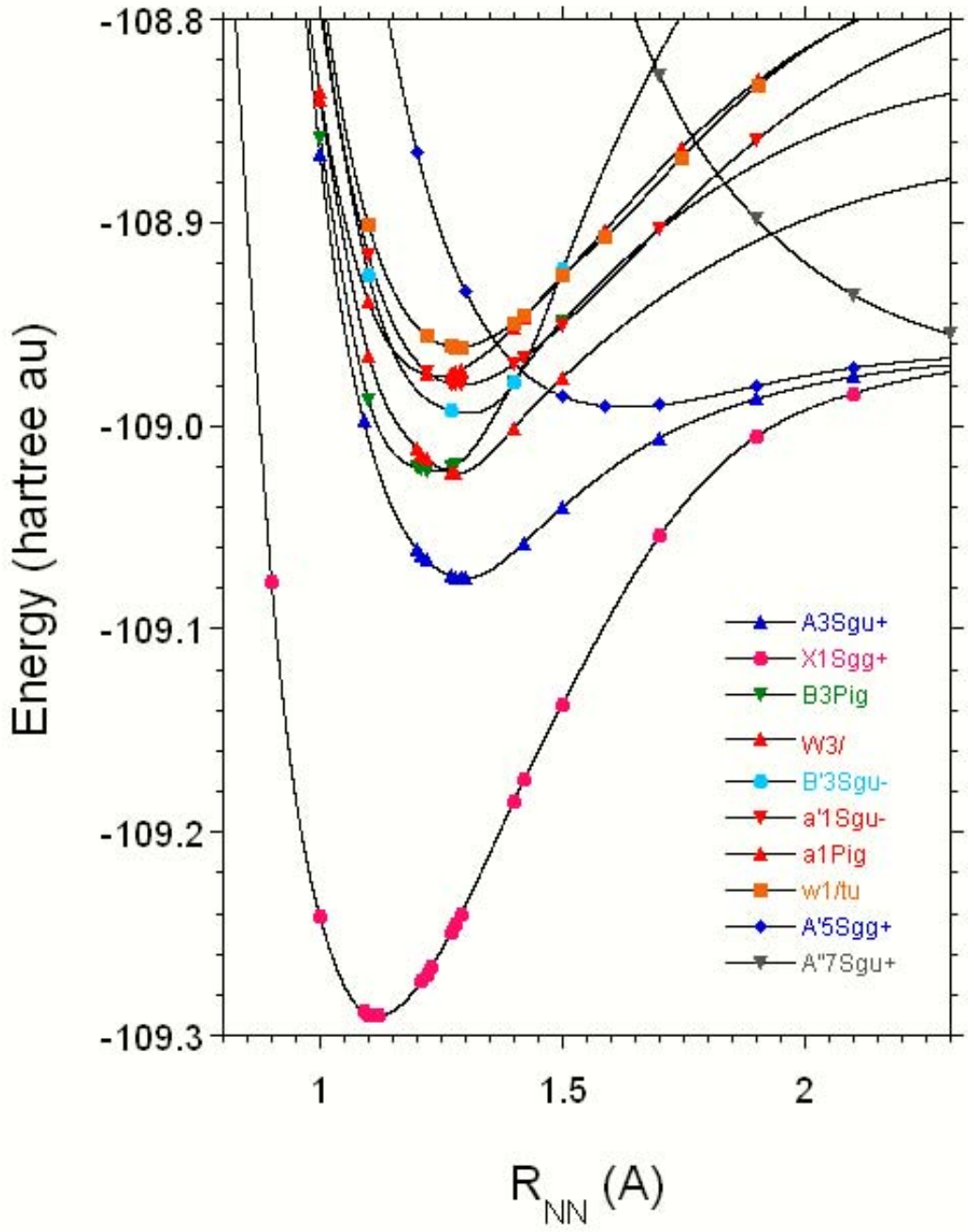
$-9.54\ mE_h\ \Delta(S^2)$ (Spin Contam.)

$E(core) \sim 3.92\ mE_h\ Q_{Na} + 2.83\ mE_h\ Q^2_{Na}$

Experimental Atomic Spin-Orbit Interaction

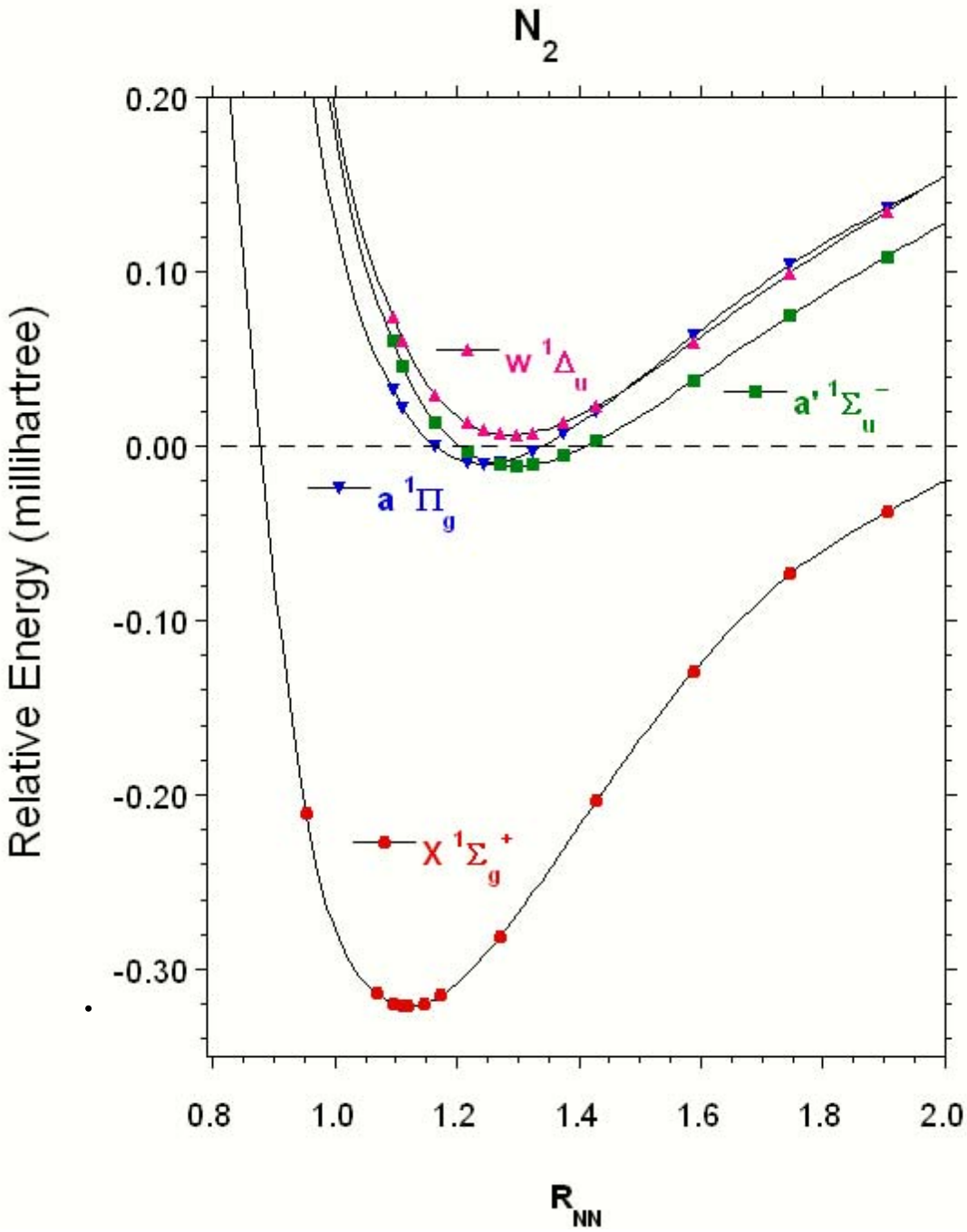
Test Case

The $X\,^1\Sigma_g^+$ ground state, along with the $a\,^3\Sigma_u^+$, $A'\,^5\Sigma_g^+$, and $A''\,^7\Sigma_u^+$ excited states of N_2 dissociates to two $^4S_{3/2}$ ground state N atoms. Other low-lying singlet and triplet states dissociate to N atoms in ^2D and ^2P excited states.



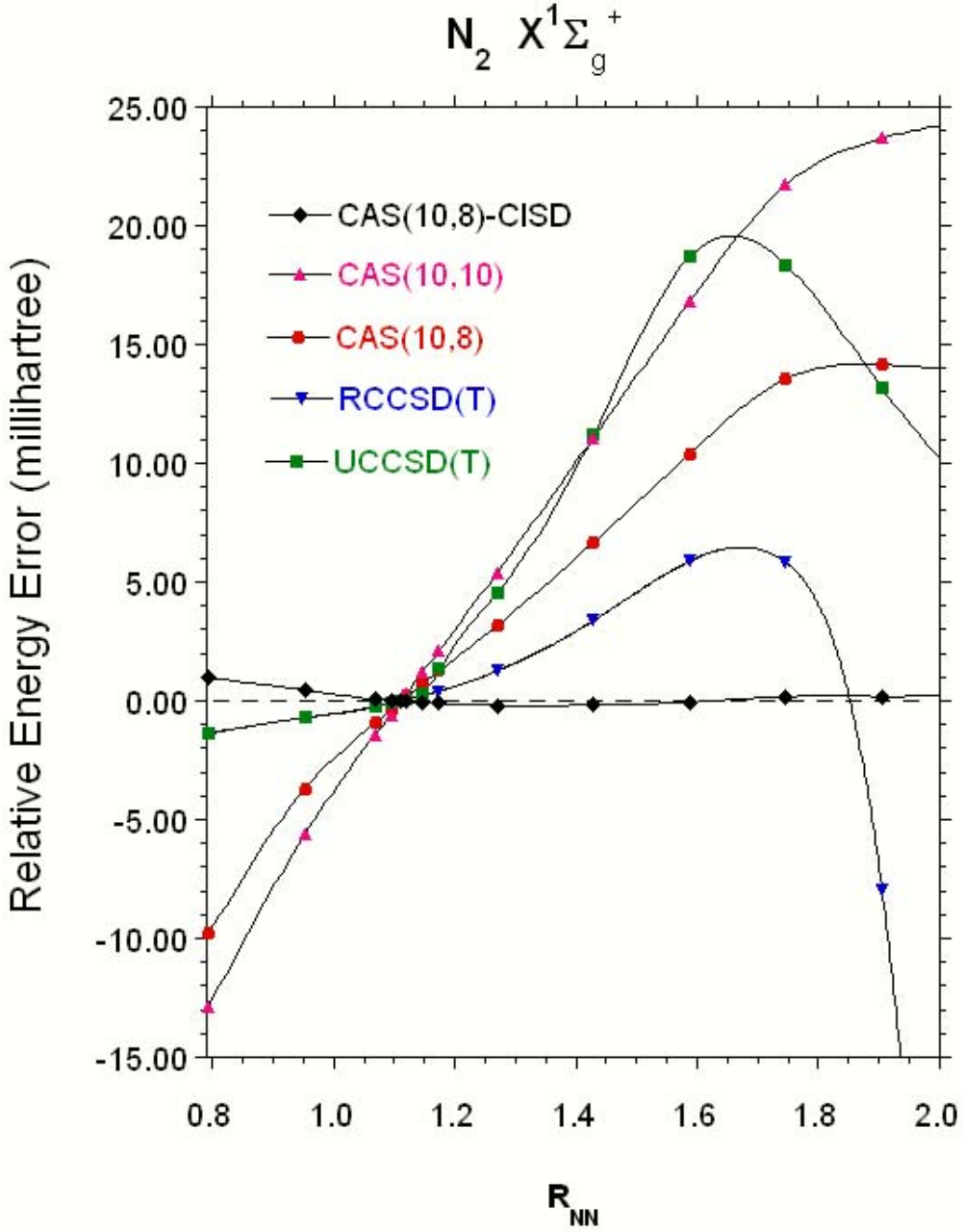
Benchmarks

The **FCI/cc-pVDZ** energies of low-lying states of N_2 [H. Larsen, J. Olsen, P Jørgensen, and O. Christiansen, *J. Chem. Phys.* **113**, 6677 (2000)] provide benchmarks for calibration of model chemistry candidates.



Model

The error in the energy of the ground state of N_2, relative to the energy at the equilibrium bond length. Note that the Multi-reference CAS-CISD is far more accurate than CCSD(T).



The error in the energy of the ground state of N_2, relative to the Full CI energy is insensitive to bond length, but a constant size-consistency correction must be made for comparisons with atoms.

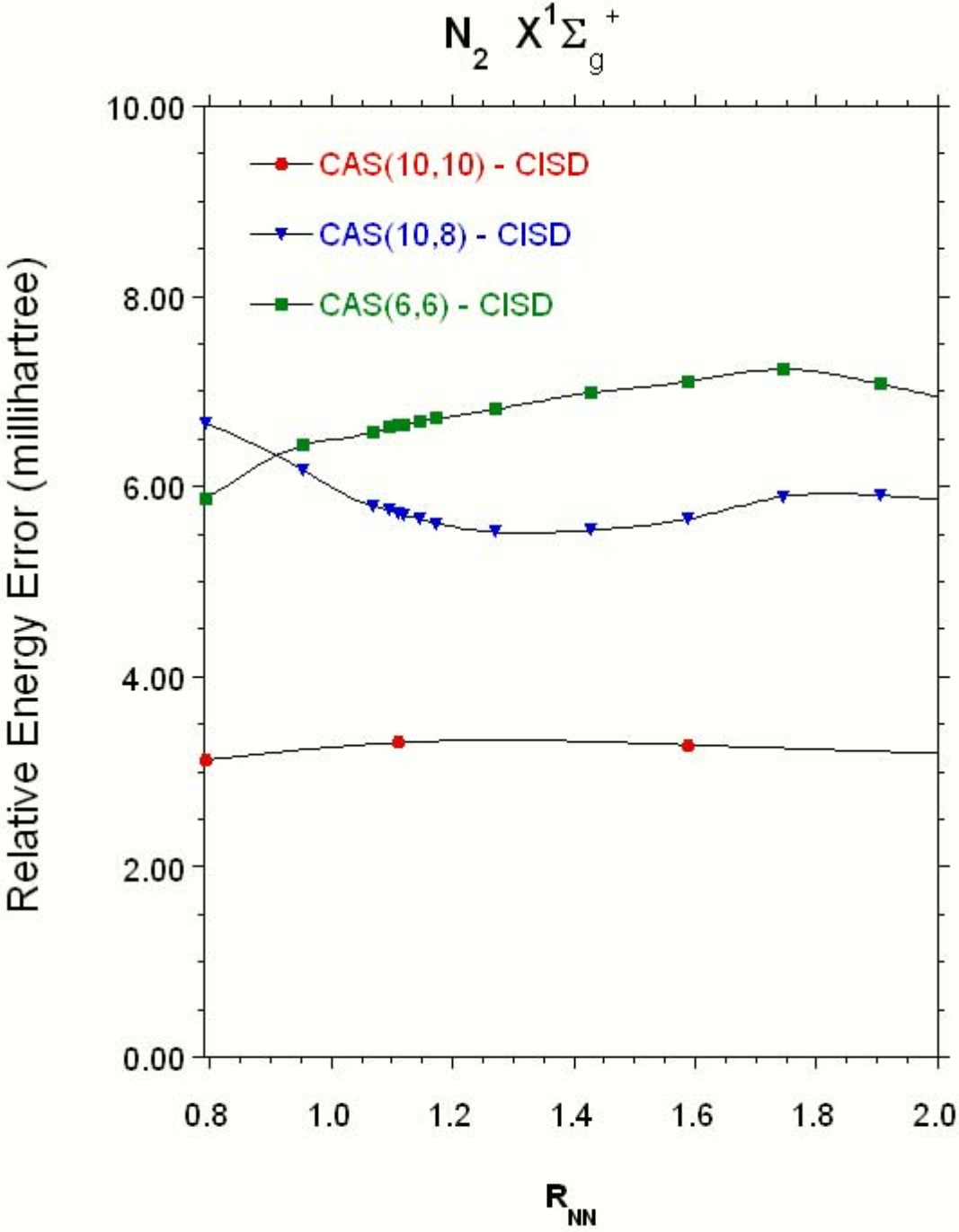


Table I. The effect of **state averaging** on CASCF and CASSCF-CISD

State	R_{NN} (Å)	Basis Set	N_{root}=1 (E_h)	N_{root}=6 (E_h)	ΔE (mE_h)
			CAS(6_{e-},6_{Orb})		
$X^1\Sigma_g^+$	1.10	2ZaP	-109.1045238	-109.0781418	26.3820
		3ZaP	-109.1251169	-109.0979344	27.1825
$A^3\Sigma_u^+$	1.27	2ZaP	-108.8740932	-108.8606554	13.4378
		3ZaP	-108.8898435	-108.8761258	13.7177
			CAS(6_{e-},6_{Orb}) – CISD		
$X^1\Sigma_g^+$	1.10	2ZaP	-109.2896344	-109.2885919	**1.0425**
$A^3\Sigma_u^+$	1.27	2ZaP	-109.0736612	-109.0733565	**0.3047**

Table II. Calculated N_2 cc-pVDZ **excitaton energies** (mE_h).

RNN(Å)	Excitation	CAS(6,6)	CAS(6,6)-CISD	FCI
1.1113	$X\,^1\Sigma_g^+ \rightarrow a\,^1\Pi_g$	**404.8**	**345.6**	**343.2**
	$\rightarrow a'\,^1\Sigma_u^-$	**375.9**	**367.9**	**367.0**
	$\rightarrow w\,^1\Delta_u$	412.1	383.5	381.7
1.2700	$X\,^1\Sigma_g^+ \rightarrow a\,^1\Pi_g$	313.8	274.6	272.2
	$\rightarrow a'\,^1\Sigma_u^-$	280.6	271.6	270.6
	$\rightarrow w\,^1\Delta_u$	336.9	290.3	288.2
1.4288	$X\,^1\Sigma_g^+ \rightarrow a\,^1\Pi_g$	252.8	226.7	223.4
	$\rightarrow a'\,^1\Sigma_u^-$	215.9	207.0	206.2
	RMS Error	**35.3**	**2.0**	

Outline

VI. Background

a. John Pople's Model Chemistries

VII. Excited state Models

a. CCSD(T) *vs* FCI
b. CASSCF and CAS-CISD *vs* FCI

VIII. CBS Extrapolations

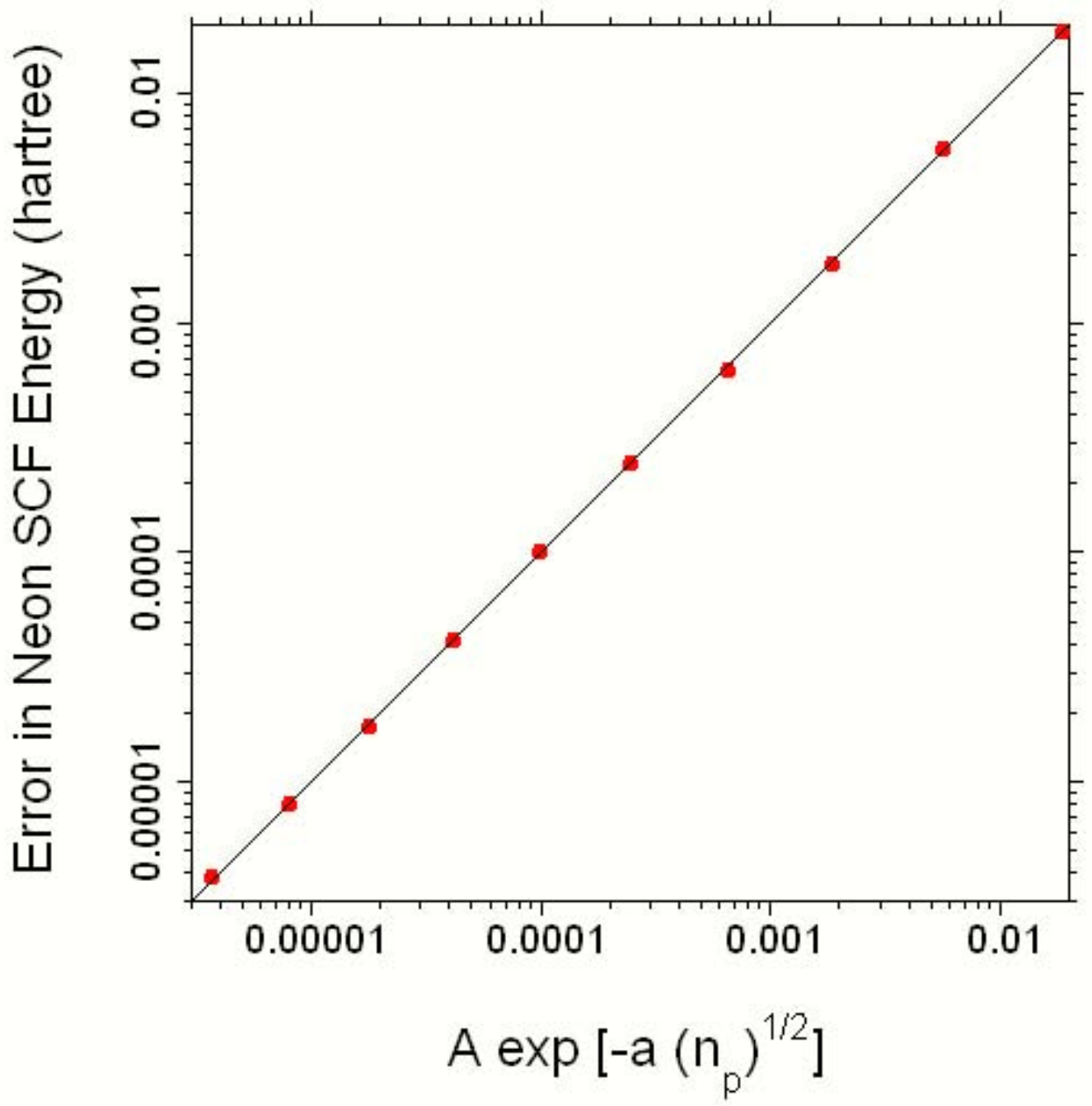
a. A Systematic Sequence of Basis Sets
b. The CASSCF CBS Lmit
c. The CASSCF-CISD CBS Limit

IX. Results

a. Geometry
b. Vibrational Frequencies
c. Excitation energies
d. Dissociation Energies

X. Acknowledgment

The **SCF** energy converges to the **CBS** (complete basis set) limit as the exponential of the square-root of the number of Gaussian basis functions.



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

Table III. Linear SCF extrapolation parameters for the neon atom.

n_1	n_2	$\{\exp[a(n_1)^{1/2} - a(n_2)^{1/2}] - 1\}^{-1}$
5	6	0.426
6	7	0.490
7	8	0.551
8	9	0.609
6	**8**	**0.132**
8	**10**	**0.178**
10	**12**	**0.220**
12	**14**	**0.262**

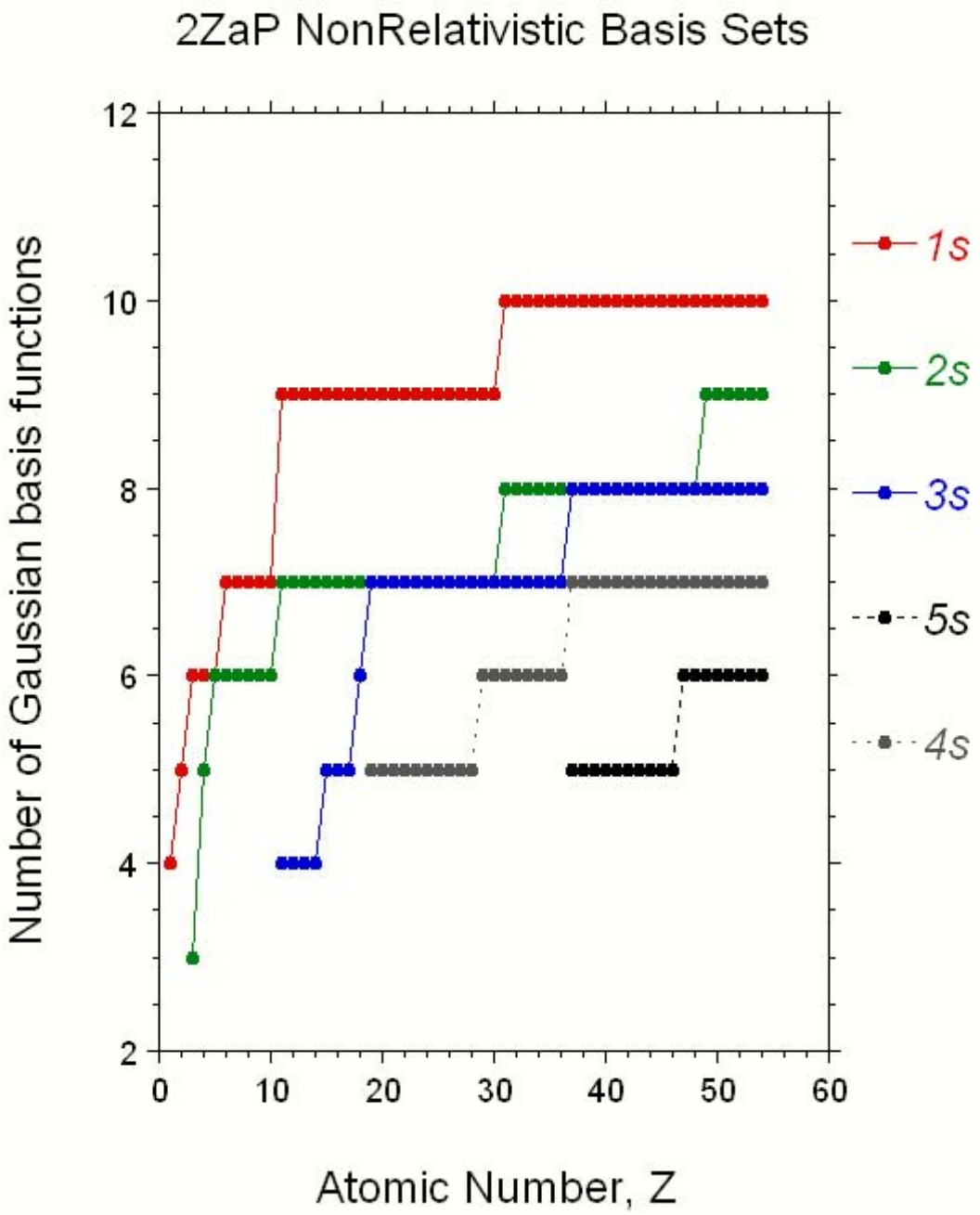
Table IV. The convergence of the N_2 SCF anisotropy energy (hartree) with the number of polarization functions in the basis set.

Basis Set	E_{SCF}	$\Delta E_{SCF}(n)$	E_{SCF} Error	Extrapolation Factor[a]
16s10p	-108.910331			
			0.082734	
16s10p1d	-108.981649	-0.071318	-0.011416	
16s10p2d1f	-108.991667	-0.010018	-0.001398	**0.139**
16s10p3d2f1g	-108.992847	-0.001180	-0.000218	**0.184**
16s10p4d3f2g1h	-108.993025	-0.000178	-0.000040	**0.22**
16s10p5d4f3g2h1i	-108.993057	-0.000032	-0.000008	**0.25**
SCF Limit =	-108.993065			

a. Factor = E_{SCF} Error(n) / $\Delta E_{SCF}(n)$

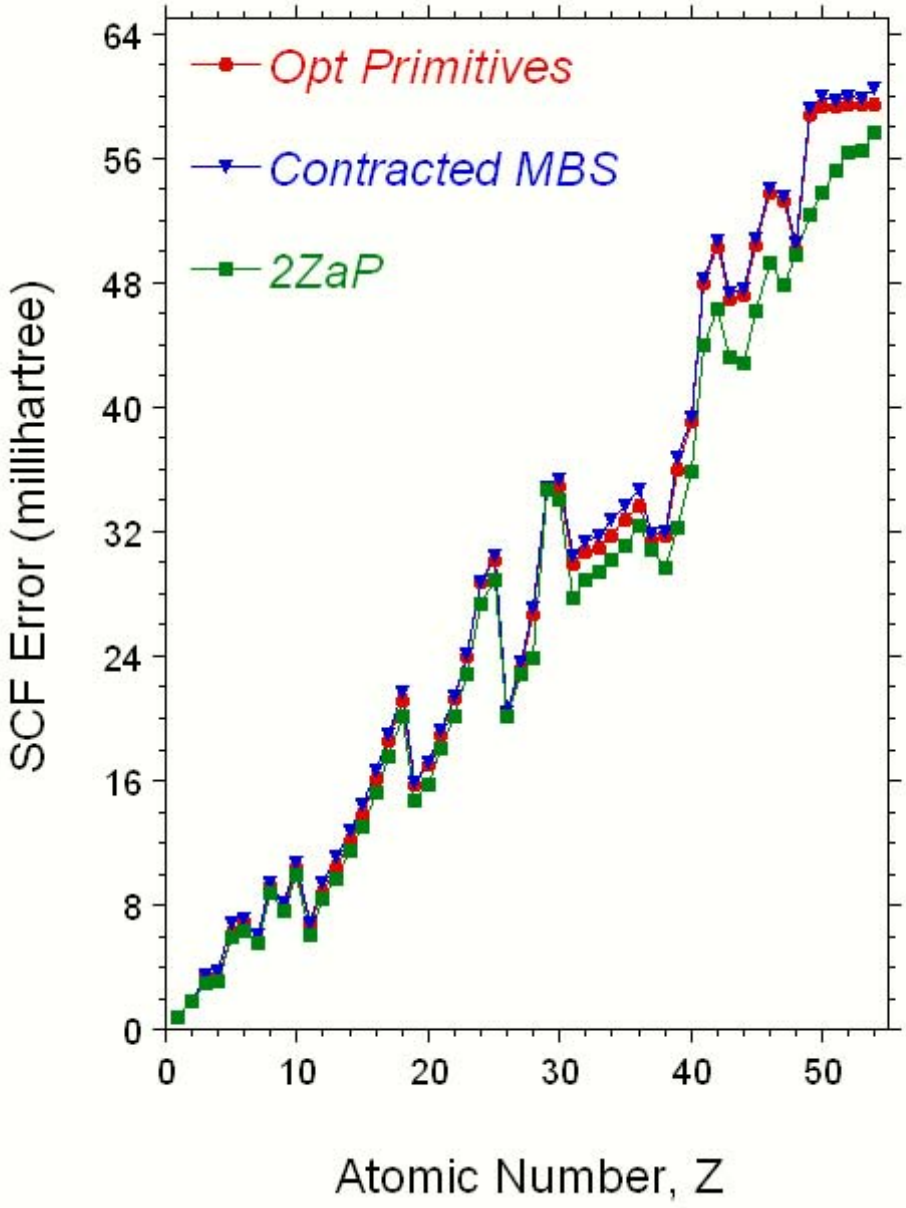
The nZaP BasisSets

The number of Gaussian primitives in the 2ZaP basis sets was selected to give a constant, *1 millihartree, SCF error per electron*. The 3ZaP basis sets each contain two more primitives of each angular momentum. The 4ZaP basis sets include an additional two, etc.



The nZaP BasisSets

The contracted nZaP basis sets are similar in structure to the cc-pVnZ basis sets, but with *diffuse valence functions added*. The number of primitives in each contracted function is sufficient to prevent contraction from significantly raising the SCF energy. All "correlation primitives" (*valence and polarization*) were optimized at the MP2 level.



UHF energies mimic the basis set convergence of **CASSCF** energies, but **ROHF** energies do not.

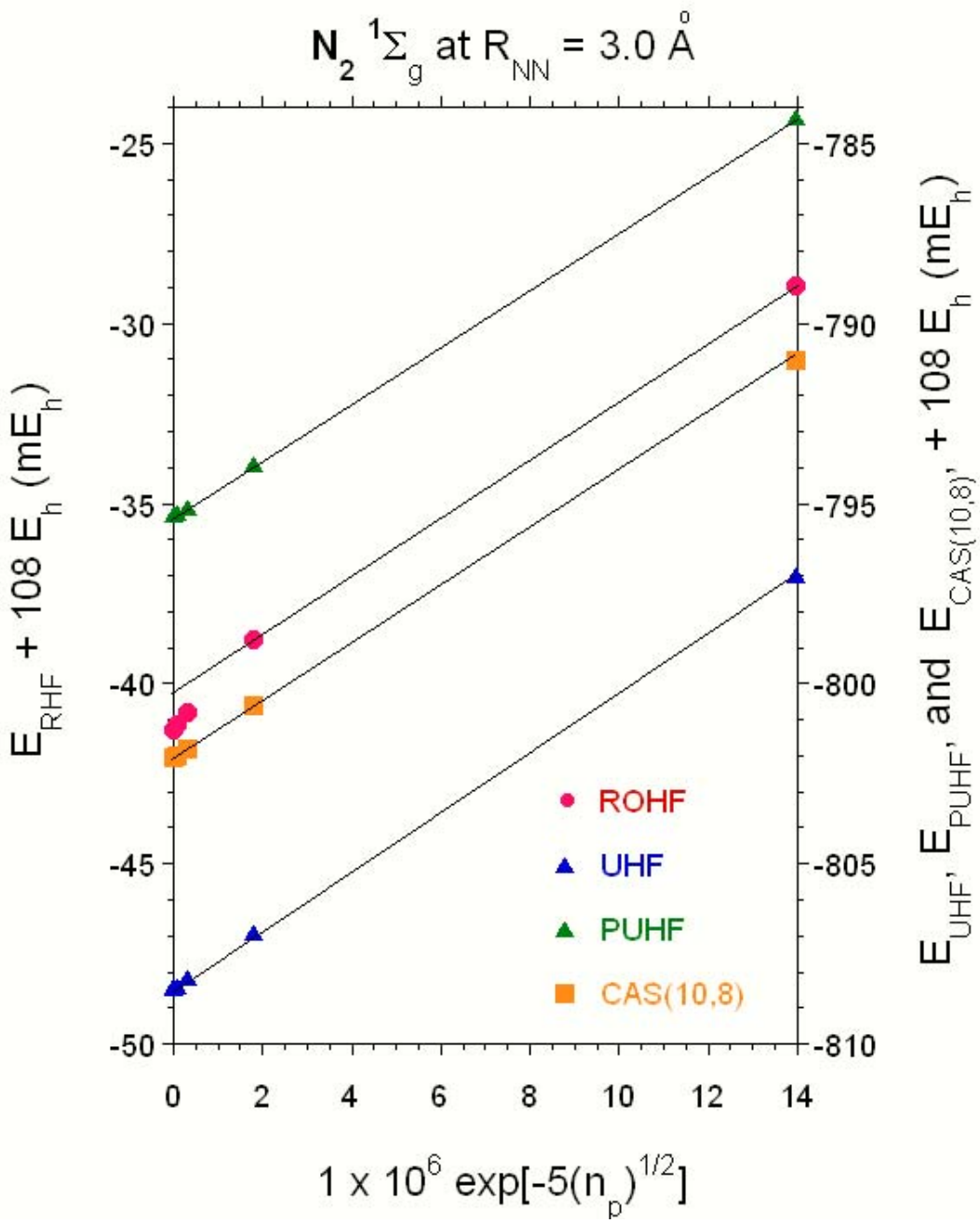


Table V. Basis set convergence of CASSCF and UHFSCF as a function of geometry.

R_{NN} (Å)	Basis Set	CAS(6,6) (E_h)	ΔE (mE_h)	$\Delta(\Delta E)_R$ (mE_h)	UHF (E_h)	ΔE (mE_h)	$\Delta(\Delta E)_R$ (mE_h)
1.09	2ZaP	-109.1035124			-108.9687667		
	3ZaP	-109.1246270	-21.1146	0.5215	-108.9903071	-21.5404	0.4654
	4ZaP	-109.1279935	-3.3665	0.1042	-108.9935983	-3.2912	0.0966
	5ZaP	-109.1288265	-0.8330	0.0213	-108.9944093	-0.8110	0.0198
	6ZaP				-108.9945297	-0.1204	0.0013
1.10	2ZaP	-109.1045238			-108.9674580		
	3ZaP	-109.1251169	**-20.5931**	**0.4819**	-108.9885330	**-21.0750**	**0.4264**
	4ZaP	-109.1283792	**-3.2623**	**0.0978**	-108.9917276	**-3.1946**	**0.0898**
	5ZaP	-109.1291909	**-0.8117**	**0.0204**	-108.9925188	**-0.7912**	**0.0189**
	6ZaP				-108.9926379	-0.1191	0.0011
1.11	2ZaP	-109.1049575			-108.9655455		
	3ZaP	-109.1250687	-20.1112	0.4447	-108.9861941	-20.6486	0.3898
	4ZaP	-109.1282332	-3.1645	0.0917	-108.9892989	-3.1048	0.0833
	5ZaP	-109.1290245	-0.7913	0.0195	-108.9900712	-0.7723	0.0181
	6ZaP				-108.9901892	-0.1180	0.0011

$$E_{CAS}(CBS) \cong E_{CAS}(3ZaP)$$

$$+1.2\times\left[E_{UHF}(4ZaP)-E_{UHF}(3ZaP)\right]$$

$$\times\left[\frac{E_{CAS}(3ZaP)-E_{CAS}(2ZaP)}{E_{UHF}(3ZaP)-E_{UHF}(2ZaP)}\right]$$

Table VI. Calculated Full Valence CASSCF energies (hartree au).

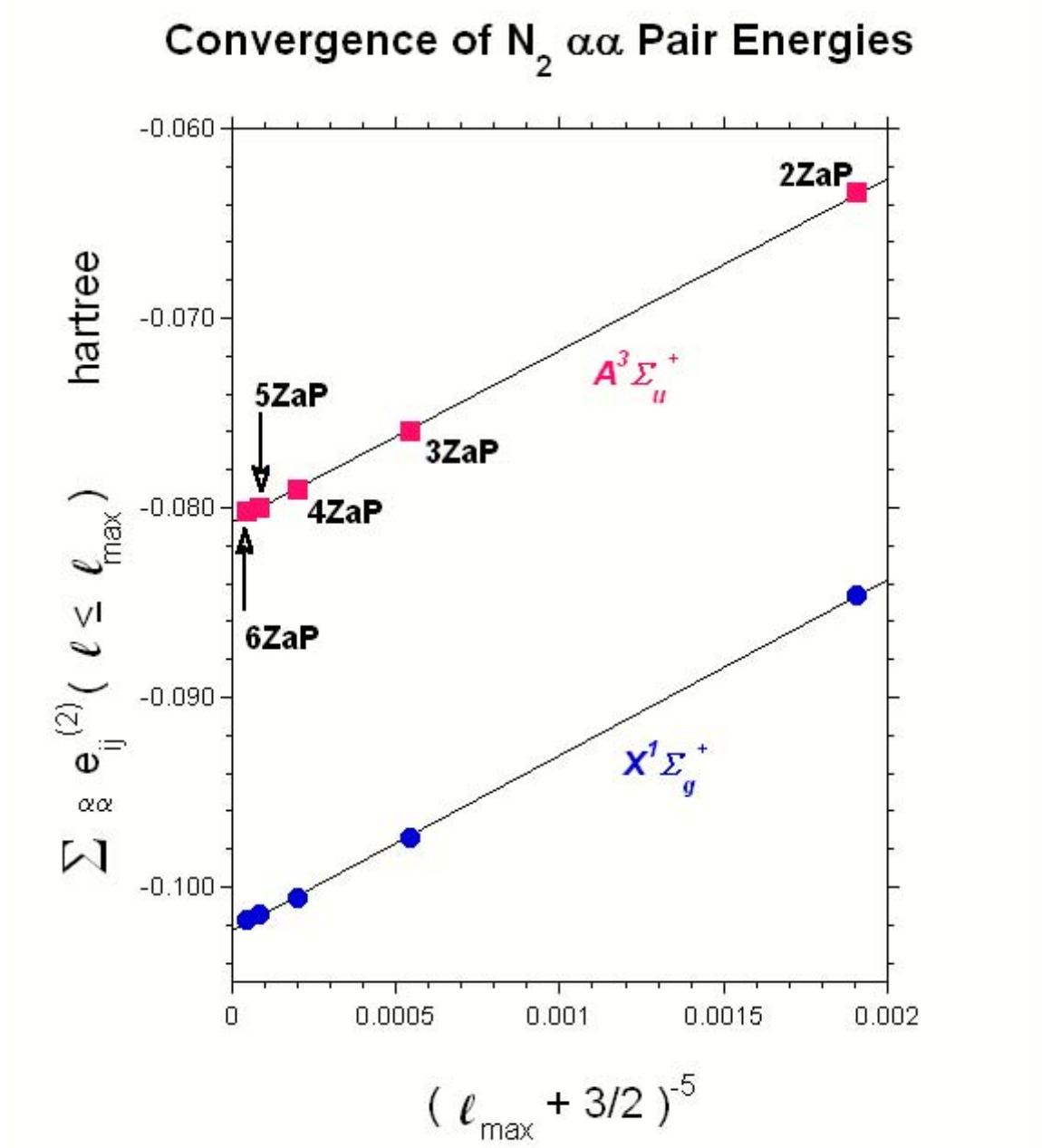
	2ZaP	3ZaP	4ZaP	5ZaP	6ZaP	Limit
$C_2\ X^1\Sigma_g^+$	-75.6233832	-75.6412898	-75.6437447	-75.6442121	-75.6442908	-75.6443188
$C_2\ a^3\Pi_u$	-75.6073350	-75.6230710	-75.6251470	-75.6255495	-75.6256266	-75.6256541
$C_2\ b^3\Sigma_g^-$	-75.5777931	-75.5941905	-75.5962600	-75.5966964	-75.5967840	-75.5968152
$C_2\ A^1\Pi_u$	-75.5627890	-75.5788475	-75.5809697	-75.5813798	-75.5814615	-75.5814906
$CN\ X^2\Sigma^+$	-92.3544025	-92.3730997	-92.3761806	-92.3766716	-92.3767524	-92.3767812
$CO\ X^1\Sigma^+$	-112.8946223	-112.9181416	-112.9218328	-112.9224855	-112.9226137	-112.9226594
$N_2\ X^1\Sigma_g^+$	-109.1166132	-109.1373292	-109.1406653	-109.1414826	-109.1415931	-109.1416324
$NO\ X^2\Pi_i$	-129.3892421	-129.4106758	-129.4138042	-129.4143983	-129.4144941	-129.4145282
$O_2\ X^3\Sigma_g^-$	-149.7411441	-149.7681917	-149.7713131	-149.7719475	-149.7720640	-149.7721055
$O_2\ a^1\Delta_g$	-149.7059304	-149.7327122	-149.7358092	-149.7364403	-149.7365522	-149.7365920
$O_3\ X^1A_1$	-224.5478659	-224.5938866	-224.5991383	-224.6002546	-224.6004950	-224.6005806
$OH\ X^2\Pi$	-75.4325178	-75.4440618	-75.4456305	-75.4458720	-75.4459251	-75.4459441
$OH\ A^2\Sigma^+$	-75.2670507	-75.2808979	-75.2825953	-75.2828559	-75.2829216	-75.2829450
RMS Error	0.0224147	0.0030328	0.0005829	0.0001180	0.0000310	

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

	Error		
	3ZaP	**4ZaP**	**5ZaP**
C_2 $X^1\Sigma_g^+$(Re)	-0.0001705	0.0000255	-0.0000059
C_2 $a^3\Pi_u$(Re)	-0.0001753	0.0000582	0.0000012
C_2 $b^3\Sigma_g^-$(Re)	-0.0002094	0.0000064	-0.0000040
C_2 $A^1\Pi_u$(Re)	-0.0000459	0.0000176	0.0000026
CN $X^2\Sigma^+$(Re)	-0.0001536	0.0000366	-0.0000031
N_2 $X^1\Sigma_g^+$(Re)	-0.0005054	-0.0001428	-0.0000276
NO $X^2\Pi_i$(Re)	-0.0001124	-0.0001120	-0.0000175
O_2 $X^3\Sigma_g^-$(Re)	0.0000564	-0.0001285	-0.0000186
O_2 $a^1\Delta_g$(Re)	-0.0000230	-0.0001280	-0.0000168
OH $X^2\Pi$(Re)	-0.0000524	-0.0000353	-0.0000136
OH $A^2\Sigma^+$(Re)	0.0000168	-0.0000603	-0.0000194
RMS Error	**0.0002327**	**0.0000956**	**0.0000245**
Before Extrap	**0.0030328**	**0.0005829**	**0.0001180**

MP2 CBS Limit

The αα second-order Møller-Plessett electron pair correlation energies converge to the CBS limit as the inverse fifth power of the maximum angular momentum included in the basis set.



MP2 CBS Limit

The αβ second-order Møller-Plesset electron pair correlation energies converge to the CBS limit as the inverse third power of the maximum angular momentum included in the basis set.

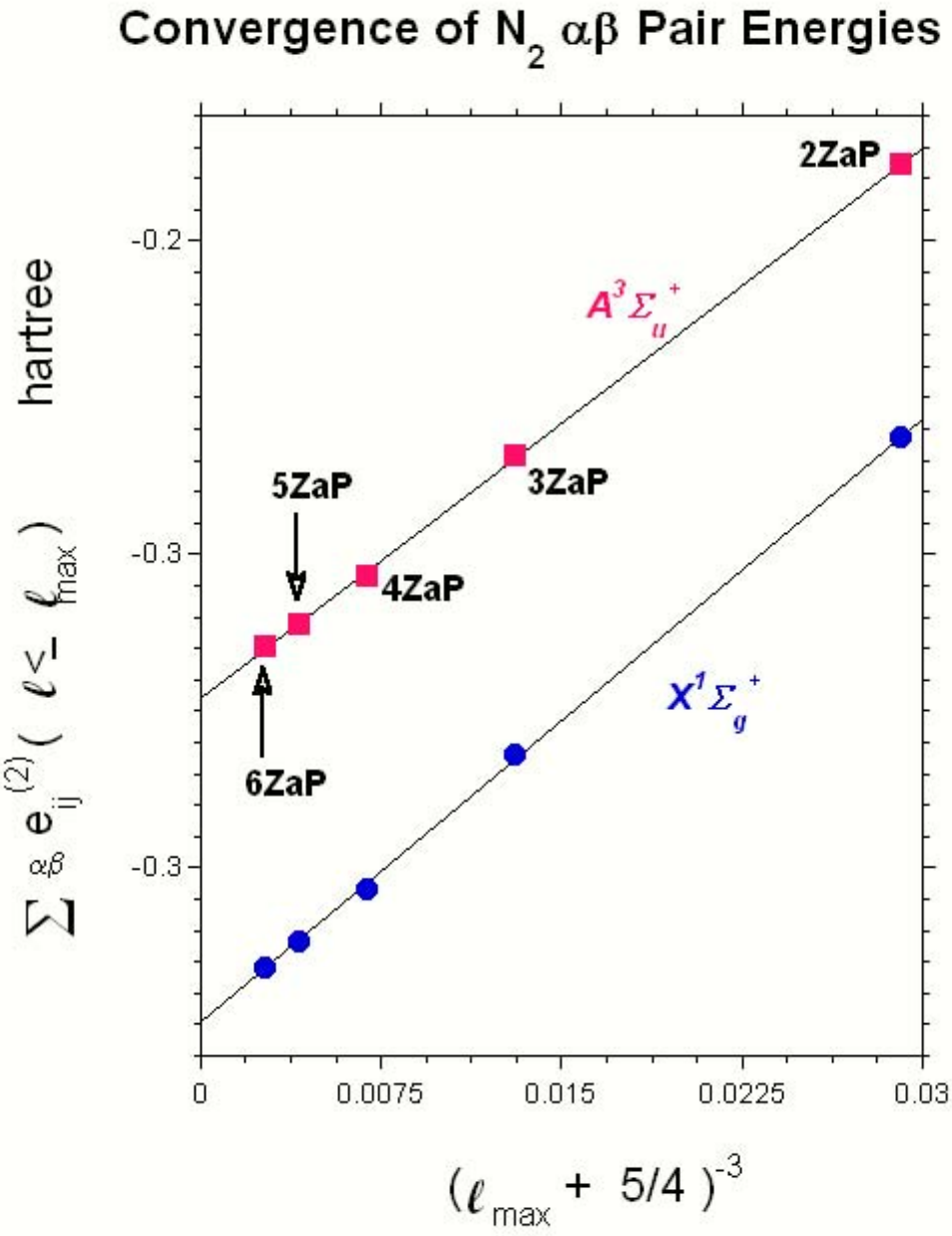


Table VIII. The basis set convergence of dynamic correlaton energy.

State	Basis Set	$E^{(2)}$ (mE_h)	$\Delta E^{(2)}$ (mE_h)	$E_{CAS\text{-}CISD} - E_{CAS}$ (mE_h)	$\Delta(E_{CAS\text{-}CISD} - E_{CAS})$ (mE_h)
$X^1\Sigma_g^+$	2ZaP	-316.0189		-181.9089	
1.10Å	3ZaP	-379.3504	**-63.3315**	-244.4998	**-62.5909**
	4ZaP	-403.7559			
	5ZaP	-413.3317			
	6ZaP	-417.4648			
	CBS Limit	-426.90			
$A^3\Sigma_u^+$	2ZaP	-250.9989		-195.6356	
1.27Å	3ZaP	-310.1058	**-59.1069**	-255.0882	**-59.4526**
	4ZaP	-332.4087			
	5ZaP	-341.1121			
	6ZaP	-344.7652			
	CBS Limit	-353.59			

$$E_{CAS-CISD}(CBS) \cong E_{CAS-CISD}(3ZaP)$$

$$+\left[E^{(2)}(CBS) - E^{(2)}(3ZaP)\right]$$

$$\times\left[\frac{E_{CAS-CISD}(3ZaP) - E_{CAS-CISD}(2ZaP)}{E^{(2)}(3ZaP) - E^{(2)}(2ZaP)}\right]$$

Outline

XI. Background

a. John Pople's Model Chemistries

XII. Excited state Models

a. CCSD(T) *vs* FCI
b. CASSCF and CAS-CISD *vs* FCI

XIII. CBS Extrapolations

a. A Systematic Sequence of Basis Sets
b. The CASSCF CBS Lmit
c. The CASSCF-CISD CBS Limit

XIV. Results

a. Geometry
b. Vibrational Frequencies
c. Excitation energies
d. Dissociation Energies

XV. Acknowledgment

Table IX. Calculated CAS-CISD **geometries** (R_e in Å) for low-lying excited states of N_2.

State	2ZaP	3ZaP	CBS limit	Exp.
$X\,^1\Sigma_g^+$	1.1175	1.1039	1.0991	1.0977
$A\,^3\Sigma_u^+$	1.3066	1.2951	1.2905	1.2866
$B\,^3\Pi_g$	1.2314	1.2201	1.2152	1.2126
$W\,^3\Delta_u$	1.2972	1.2859	1.2815	
$B'\,^3\Sigma_u^-$	1.2955	1.2845	1.2800	1.2784
$a'\,^1\Sigma_u^-$	1.2914	1.2805	1.2759	1.2755
$a\,^1\Pi_g$	1.2390	1.2271	1.2213	1.2203
$w\,^1\Delta_u$	1.2837	1.2728	1.2684	1.268
RMS Error	**0.0181**	**0.0066**	**0.0020**	

Table X. Calculated CAS-CISD harmonic **vibrational frequencies** (ω_e in cm^{-1}) for low-lying excited states of N_2.

State	2ZaP	3ZaP	CBS limit	Exp.
$X\,^1\Sigma_g^+$	2319.1	2345.2	2358.1	2358.57
$A\,^3\Sigma_u^+$	1418.5	1439.7	1450.8	1460.64
$B\,^3\Pi_g$	1707.4	1715.3	1727.4	1733.39
$W\,^3\Delta_u$	1482.0	1499.1	1508.9	$1501._4$
$B'\,^3\Sigma_u^-$	1494.5	1509.9	1518.9	1516.88
$a'\,^1\Sigma_u^-$	1508.6	1528.4	1538.8	1530.25
$a\,^1\Pi_g$	1648.2	1686.1	1696.4	1694.21
$w\,^1\Delta_u$	1543.5	1561.3	1571.3	1559.26
RMS Error	**31.1**	**12.1**	**7.3**	

Table XI. Calculated CAS-CISD **excitation energies** (Ev) of N_2.

State	2ZaP	3ZaP	CBS limit	Exp.
$X\,^1\Sigma_g^+ \rightarrow$				
$A\,^3\Sigma_u^+$	5.843	6.093	6.192	6.224
$B\,^3\Pi_g$	7.275	7.397	7.447	7.392
$W\,^3\Delta_u$	7.233	7.364	7.432	7.415
$B'\,^3\Sigma_u^-$	8.067	8.230	8.265	8.217
$a'\,^1\Sigma_u^-$	8.427	8.471	8.407	8.450
$a\,^1\Pi_g$	8.547	8.653	8.562	8.590
$w\,^1\Delta_u$	8.932	9.008	8.927	8.939
RMS Error	**0.176**	**0.065**	**0.037**	

Table XII. Calculated CAS-CISD dissociation energies (Ev) of N_2.

State	2ZaP	3ZaP	CBS limit	Exp.
$X\,^1\Sigma_g^+ \rightarrow$				
$A\,^3\Sigma_u^+$	5.857	6.093	6.192	6.224
$B\,^3\Pi_g$	7.256	7.397	7.447	7.392
$W\,^3\Delta_u$	7.301	7.364	7.432	7.415
$B'\,^3\Sigma_u^-$	8.063	8.230	8.265	8.217
$a'\,^1\Sigma_u^-$	8.417	8.471	8.407	8.450
$a\,^1\Pi_g$	8.537	8.653	8.562	8.590
$w\,^1\Delta_u$	8.914	9.008	8.927	8.939
RMS Error	**0.167**	**0.065**	**0.037**	

Acknowledgments

Dr. Michael J. Frisch

Dr. Matthew Braunstein

Dr. David K. Malick

$upport

Gaussian Inc.™

Wesleyan University

Department of Defense