Evaluating Cost and Accuracy in Two-Point Complete Basis Set Extrapolation Schemes Using Efficient Diffuse Basis Sets

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ABSTRACT. A widely used procedure for obtaining the complete-basis set (CBS) limit of an electronic structure method is extrapolating results from a sequence of correlation-consistent basis sets. A recent study by Xi et al. trained two-point extrapolation schemes against a new extensive dataset using aug-cc-pV*X*Z (X = D, T, Q, 5, and 6) basis set pairs. Their results were very promising, providing a significant improvement over previous two-point extrapolation schemes. The present work shows that equally good results can be obtained at lower cost by using the smaller jun-cc- pV*X*Z or jul-cc- pV*X*Z basis sets, which contain fewer diffuse functions. Using the smaller jun and jul basis sets to extrapolate to the CBS limit provides a good compromise between accuracy and computational cost.

1. Introduction

Obtaining accurate electronic energies of molecules is essential for the quantitative analysis of their chemical properties.[1-5] Due to its affordability and accuracy for even moderately sized systems, coupled cluster theory[6] with single and double excitations and a quasiperturbative inclusion of connected triple excitations[7] (CCSD(T)) is sometimes called the gold standard for quantum chemistry calculations, and is often employed for the study of thermochemistry and chemical reactions.[8-11] However, although Gaussian basis sets are in principle complete so that convergence to a solution of the Schrödinger equation is guaranteed if enough Gaussians are used,[12] the convergence of the dynamic correlation energy to the complete basis set (CBS) limit is achingly slow and can be the limiting factor in the accuracy of electronic structure calculations. This is the reason why various schemes that extrapolate the finite basis set results to the CBS limit have been developed and applied in the calculation of molecular properties.[13-22] Extrapolation can greatly reduce the finite-basis-set error with no additional computational cost.

Several two-point and three-point extrapolation schemes have been formulated in past years. The two-point extrapolation schemes are especially convenient.[9,14,23] The best general extrapolation schemes can be obtained by optimizing one or more empirical parameters against a dataset. The accuracy of such an extrapolation scheme depends in part on the quality and appropriateness of the datasets on which the extrapolation schemes are trained.[23-29] A recent paper by Xi et al.[30] revisited the problem of inadequate data sets and trained several two-point extrapolation schemes against a new expansive data set with 183 species that includes several closed-shell, open-shell, ionic, and neutral species extending well-beyond the second period of the periodic table with reference energies calculated at CCSD(T)/aug-cc-pV6Z level. They employed aug-cc-pV{*X,Y*}Z basis sets pairs with {*X,Y*} = {D,T}, {T,Q}, or {Q,5} for the two-point extrapolation schemes. A key aspect of their work is the optimization of separate parameters for each pair of basis sets. The results of the work were very promising, and their results provide a great improvement on the existing extrapolation schemes. The objective of the present paper is to show that using jun-cc-pV*X*Z basis sets or jul-cc-pV*X*Z basis sets instead of aug-cc-pV*X*Z basis sets provides comparable accuracy at greatly reduced costs.

In their paper, Xi et al. used aug-cc-pV*X*Z (where *X* = 2, 3, …) basis sets. However, it has been shown that for many calculations of thermochemistry and thermochemical kinetics, these basis sets contain many diffuse functions that have a relatively small effect on the calculation of several chemical properties. [31-33] For efficient calculations, one wants to eliminate the least useful diffuse functions in a systematic way, and the calendar basis sets

jul-cc-pV*X*Z and jun-cc-pV*X*Z were designed to do this. The jul-cc-pV*X*Z[31-33] basis sets are constructed from their aug counterparts by removing all diffuse functions from hydrogen and helium. The jun-cc-pV*X*Z basis sets[32,33] remove these diffuse functions and also remove the the highest-angular-momentum diffuse function from atoms heavier than He. For example, an aug-pVTZ basis set for a hydrocarbon contains diffuse s, p, and d functions on each H and diffuse s, p, d, and f functions on each C. The jul-pVTZ basis set removes all the diffuse functions on H atoms, and the jun-cc-pVTZ basis set also removes the diffuse f functions on each carbon. The jul and jun basis sets are thus significantly smaller than their aug counterparts, the difference being more pronounced with the increase in system size. However, studies have shown that for practical purposes they perform just as well as the bigger aug-cc-pV*X*Z basis sets. [31-34] This study compares the cost and accuracy of extrapolations with the smaller jul-cc-pVXZ and jun-cc-pVXZ basis sets to those with the aug-cc-pV*X*Z basis.

It has been shown[Error! Bookmark not defined.,35] that extrapolation to the CBS limit of the electronic energy E^{elec} is best performed by separate extrapolation of the Hartree-Fock (HF) energy, E^{HF} and the correlation energy, defined as

$$E^{\mathrm{cor}} = E^{\mathrm{CCSD(T)}} - E^{\mathrm{HF}} \tag{1}$$

and that strategy is adopted in both the Xi et al. study and the present one. One parameter is involved in two-point extrapolation of E^{HF}, and another parameter is involved in two-point extrapolation of E^{corr}; the former is called α, and the latter is called β. Xi et al. examined five formulas for two-point extrapolation of E^{HF}, and five formulas for two-point extrapolation of E^{cor}, they found that, as long as α and β were separately optimized for each formula and each pair of basis sets [D,T or T,Q or Q,5], the results showed similar high accuracy all five formulas for HF extrapolation and similar high accuracy all five formulas for correlation-energy extrapolation. We therefore chose to use only one formula in each case, and we chose the model that they named Truhlar-1998[Error! Bookmark not defined.] for both cases.

Xi et al. reported the mean absolute deviations $\mathrm{MAD}^{\mathrm{HF}}$ and $\mathrm{MAD}^{\mathrm{cor}}$ from the reference values separately for the HF and correlation energies. We combine these into a single figure of demerit Δ by

$$\Delta = \sqrt{(\mathrm{MAD}^{\mathrm{HF}})^2 + (\mathrm{MAD}^{\mathrm{cor}})^2} \tag{2}$$

They found Δ = 1.36, 0.44, and 0.04 kcal/mol, for the *X* pairs (D,T), (T,Q), and (Q,5), respectively. Note that the reference values are supposed to represent CCSD(T)/CBS, not the exact answer (which would be all-electron configuration interaction at the CBS limit). A

previous study of 48 reaction energies and barrier heights gave a mean absolute deviation of CCSD(T)/CBS energies from more accurate benchmarks (with beyond-CCSD(T) contributions) of 0.44 kcal/mol. We conclude that that including beyond-CCSD(T) correlation effects is often more important than improving the CCSD(T) extrapolation from (T,Q) to (Q,5). For this reason and because (Q,5) extrapolation is often unaffordable, the present study is limited to (D,T) and (T,Q).

The original aug-cc-pVXZ paper[36] emphasized electron affinities, but the paper has been cited 13,783 times, and the great majority of these papers are not devoted to electron affinities. It is well known that diffuse functions are useful for accurate calculations of bond energies and barrier heights. For example, a paper[37] on barrier heights showed that the mean unsigned errors in a set of hydrogen-atom transfer reactions involving only neutral species is 1.41 kcal/mol with CCSD(T)/cc-pVTZ and 0.70 kcal/mol with aug-cc-PVTZ. Similarly, the mean unsigned errors in a set of nonhydrogenic-atom transfer reactions involving only neutral species are[37] 1.90 kcal/mol with CCSD(T)/cc-pVTZ and 0.95 kcal/mol with aug-cc-PVTZ. We conclude that augmentation is very useful for neutral species as well as anions. Therefore, the study of quantities other than electron affinities is very relevant. Nevertheless, our test set includes 3 cations and 12 anions along with 106 neutral species, so we made an analysis where we calculated separate errors for cations, neutrals, and anions. Our goal is to see if we can obtain equally as accurate results with jun- and jul- basis sets as with the more expensive aug- basis sets.

Section 2 presents the theory, section 3 gives the computational details and results, and section 4 gives concluding remarks.

2. Theory

For extrapolation to the CBS limit, it is necessary to have a model that describes how the basis set converges. For the two-point models consider by Xi et al., the energy calculated with a finite basis set is related to the CBS limit by

$$E(X) = E_{\mathrm{CBS}} + Af(X) \tag{3}$$

where X is the cardinal number (called X in the introduction) of the basis set used, $E(X)$ is the energy calculated with the basis set of cardinal number X, E_{CBS} is the CBS limit, and $f(X)$ is a function of X with a coefficient, A. The function $f(X)$ approaches zero as X approaches infinity. The coefficient A can be eliminated by substituting two consecutive values of X and Y in eq 3 and subtracting the two equations. This also gives the formula for the linear extrapolation to the CBS limit.

$$E_{\mathrm{CBS}} = \frac{E(Y)f(X) - E(X)f(Y)}{f(X) - f(Y)} \tag{4}$$

For the Truhlar-1998 model, the components of the energy in eq 1 approach the CBS limit by power laws.[Error! Bookmark not defined.] Thus,

$$E^{\mathrm{HF}}(X) = E^{\mathrm{HF}}_{\mathrm{CBS}} + A^{\mathrm{HF}}X^{-\alpha} \tag{5}$$

and

$$E^{\mathrm{cor}}(X) = E^{\mathrm{cor}}_{\mathrm{CBS}} + A^{\mathrm{cor}}X^{-\beta} \tag{6}$$

Substituting these in eq 4 gives

$$E^{\mathrm{HF}}_{\mathrm{CBS}} = \frac{E^{\mathrm{HF}}(Y)X^{-\alpha} - E^{\mathrm{HF}}(X)Y^{-\alpha}}{X^{-\alpha} - Y^{-\alpha}} \tag{7}$$

and[14,23,38]

$$E^{\mathrm{cor}}_{\mathrm{CBS}} = \frac{E^{\mathrm{cor}}(Y)X^{-\beta} - E^{\mathrm{cor}}(X)Y^{-\beta}}{X^{-\beta} - Y^{-\beta}} \tag{8}$$

where α and β are the HF extrapolation parameter and the correlation-energy extrapolation parameter, respectively. The parameters are then optimized by minimizing the root mean square (RMS) deviation:

$$\mathrm{RMSD} = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(x_i - x_i^{\mathrm{ref}})^2} \tag{9}$$

where x_i and x_i^{ref} are the extrapolated and reference values, respectively. The reference values are the single-point HF and correlation energies calculated at the CCSD(T)/aug-cc-pV6Z level, which are obtained from the ref 30.

The CBS limit for the total energy is then given by

$$E^{\mathrm{tot}}_{\mathrm{CBS}} = E^{\mathrm{HF}}_{\mathrm{CBS}} + E^{\mathrm{cor}}_{\mathrm{CBS}} \tag{10}$$

3. Computational Details and Results

The database for this study is taken from the supporting information of ref. 30, which is based on HF and CCSD(T) calculations carried out at B3LYP[39]/cc-pVTZ geometries. Since the optimized geometries are not given in that supporting information, they were recalculated in the present work. In this way, we were able to reproduce the energies for only 158 of the 183 species of the original database. Furthermore, 37 out of the resulting 158 species had their energies reproduced with the default initial guess but had unstable[40] HF wavefunctions making them unfit for inclusion in the database. The instabilities primarily occur for open-shell singlets. By default, *Gaussian* performs singlet calculations by RHF. In

these cases, open-shell singlets with unpaired electrons of opposite spins are poorly described by RHF, which forces pairs of electrons into the same spatial orbitals. As a result, RHF fails to capture the necessary static electron correlation, leading to wave function instabilities in the open-shell singlets within the database. Thus, for the present study we eliminated the data where we did not reproduce the previous work, and we eliminated the data where the stability check failed. Therefore, the present study is based on the remaining 121 species.

Frozen-core single-point energy calculations were carried out for each of the 121 species at the CCSD(T)/jul-cc-pV*X*Z and CCSD(T)/jun-cc-pV*X*Z levels with X = D, T, and Q. All calculations were carried out using the *Gaussian 16* program.[41]

Table 1 gives the mean absolute deviation (MAD), root-mean-square deviation (RMSD), and maximum absolute deviation (MaxAD), of the CCSD(T) energies calculated with jun-, jul-, and aug-cc-pVXZ basis sets. In the present context, we can also label these deviations as "errors." These are the results before extrapolation to the CBS limit. The errors are quite large for the VDZ basis sets, and the numbers get better as one goes from VDZ to VTZ to VQZ. In all cases, the jul basis sets perform just as well as the aug basis sets, and he jun basis sets are slightly worse. However, all the errors are still quite large, and even the more expensive QZ calculations don't reach chemical accuracy making them inadequate for accurate quantitative analysis of chemical properties. Next, we consider how two-point extrapolation to the CBS limit improves the calculated energies.

Table 1. Deviations from reference values of CCSD(T) energies with jun, jul and aug-cc-pVXZ basis sets

Basis	MAD (kcal/mol)	RMSD (kcal/mol)	MaxAD (kcal/mol)
jun-cc-pVDZ	104.16	120.01	305.34
jul-cc-pVDZ	92.62	106.25	267.08
aug-cc-pVDZ	92.04	105.84	267.09
jun-cc-pVTZ	31.12	36.12	94.40
jul-cc-pVTZ	28.25	32.73	86.45
aug-cc-pVTZ	28.01	32.56	86.45
jun-cc-pVQZ	9.87	11.57	33.72
jul-cc-pVQZ	8.79	10.27	30.11
aug-cc-pVQZ	8.71	10.21	30.11

First consider the Hartree-Fock extrapolation. Table 2 shows the errors of the extrapolation to the Hartree-Fock CBS limit. The optimized parameters, MAD, RMSD, MaxAD are compared among extrapolations with aug, jul, and jun basis sets. The naming convention is straightforward; for example, aug{D,T} refers to the two-point extrapolation done with the aug-cc-pVDZ and aug-cc-pVTZ basis sets. Since, as explained above, this study only uses 121 species out of the 183 species in the ref 30, the parameters for the extrapolation with aug basis set and the corresponding MAD, RMSD, and MaxAD were reoptimized for the 121 species considered in this work.

Table 2. Hartree-Fock extrapolation results

Method	α	MAD (kcal/mol)	RMSD (kcal/mol)	MaxAD (kcal/mol)
jun{D,T}	3.500	0.51	0.67	3.24
jul{D,T}	3.347	0.54	0.78	4.66
aug{D,T}	3.350	0.54	0.78	4.68
jun{T,Q}	4.832	0.35	0.57	4.50
jul{T,Q}	4.817	0.35	0.56	4.37
aug{T,Q}	4.817	0.35	0.56	4.34

Table 2 shows that for the {D,T} extrapolations, the jul basis sets perform just as well as the aug basis sets, and the smallest basis sets, jun, perform the best among the three. As expected, the {T,Q} extrapolation performs better than {D,T} extrapolation for cases. Both jun and jul basis sets perform as well as aug basis sets in the {T,Q} extrapolation (the small differences are not significant). It is also interesting that we obtain similar values of α with jun and jul basis sets as compared to aug basis sets.

Table 3 shows the optimized parameters, MAD, RMSD, and MaxAD for extrapolation of CCSD(T) correlation energy to the CBS limit. The trends for {D,T}are similar to the trends in HF extrapolation; we see that the results get better as one goes from aug to jul to jun basis sets. For the {T,Q} calculations, the jul basis sets match the results of aug basis sets, whereas jun performs slightly worse compared to the other two. The final column of Table 3 shows the overall figure of demerit defined by eq 2. The values are comparable to those mentioned above from Xi et al.

Table 3. CCSD(T) correlation energy extrapolation results and overall figure of demerit.

Method	β	MAD (kcal/mol)	RMSD (kcal/mol)	MaxAD (kcal/mol)	Δ (kcal/mol)

jun{D,T}	2.786	1.25	1.50	4.16	1.35
jul{D,T}	2.750	1.28	1.62	5.27	1.39
aug{D,T}	2.756	1.35	1.71	5.15	1.45
jun{T,Q}	3.738	0.34	0.45	1.52	0.49
jul{T,Q}	3.808	0.27	0.35	0.99	0.44
aug{T,Q}	3.810	0.27	0.35	0.95	0.44

Table 4 gives the most important results, the total energy extrapolation. Since the total energy is the sum of HF and CCSD(T) correlation energies, the trends are the same as the HF and CCSD(T) correlation energy extrapolation. For {T,Q} extrapolation, the jul and aug results are almost the same, and jun is lightly worse. For {D,T} extrapolation, jul is slightly better than aug, and jun is much better.

Table 4. Electronic energy extrapolation results

Method	MAD (kcal/mol)	RMSD (kcal/mol)	MaxAD (kcal/mol)
jun{D,T}	1.23	1.61	7.40
jul{D,T}	1.34	1.88	8.76
aug{D,T}	1.40	1.96	8.99
jun{T,Q}	0.60	0.90	5.99
jul{T,Q}	0.55	0.78	5.09
aug{T,Q}	0.55	0.78	5.10

Comparing the results in Table 1 and 4 shows how much the two-point extrapolation scheme brings down the errors in CCSD(T) energy calculations. . It makes sense to compare the {D,T} extrapolation results with the jun/jul/aug-cc-pVTZ results as the TZ calculations are more accurate as well as more expensive than the DZ calculations. The {D,T} extrapolation brings down the MAD from 31.1 to 1.2 kcal/mol for jun, from 28.3 to 1.3 kcal/mol for jul, and from 28.0 to 1.4 kcal/mol for aug-cc-pVTZ. The RMSD and MaxAD are improved in a similar way. Similarly, we compare the {T,Q} extrapolations to the jun/jul/aug-cc-pVQZ results. The MAD goes down from 9.9, 8.8, and 8.7 kcal/mol for the jun, jul and aug-cc-pVQZ basis sets respectively to 0.60, 0.55, and 0.55 kcal/mol respectively. Moreover, if we define chemical accuracy as 1 kcal/mol, the {D,T} extrapolations are just short of chemical accuracy, but the {T,Q} extrapolation meets the challenge. The {T,Q} extrapolation also comes close to the 0.4 kcal/mol goal mentioned earlier.

It is interesting to also look at the separate results for cations, neutrals, and anions. The test set consists of 3 cations, 106 neutrals, and 12 anions, and Table 5 presents the extrapolated total energies for each charge state separately. In the {D,T} extrapolation, the jul basis set outperforms both jun and aug, while the jun basis set performs slightly worse than both jul and aug for cations and anions. However, in the {T,Q} extrapolation for cations and anions, both jun and jul perform just as well as the aug basis set. The results for neutrals follow the same trends as observed in Table 4, where all three basis sets perform equally well.

Table 5. Electronic energy extrapolation results for cations, neutrals, and anions separately

Species	Method	MAD (kcal/mol)	RMSD (kcal/mol)	MaxAD (kcal/mol)
Cations	jun{D,T}	1.16	1.16	1.32
	jul{D,T}	0.67	0.74	1.10
	aug{D,T}	0.76	0.82	1.19
Cations	jun{T,Q}	0.73	0.82	1.25
	jul{T,Q}	0.63	0.69	1.01
	aug{T,Q}	0.63	0.69	1.01
Neutrals	jun{D,T}	1.25	1.66	7.40
	jul{D,T}	1.42	1.98	8.76
	aug{D,T}	1.48	2.06	8.99
Neutrals	jun{T,Q}	0.63	0.94	5.99
	jul{T,Q}	0.58	0.82	5.09
	aug{T,Q}	0.57	0.82	5.10
Anions	jun{D,T}	1.06	1.24	2.05
	jul{D,T}	0.78	0.92	1.68
	aug{D,T}	0.80	0.97	1.80
Anions	jun{T,Q}	0.35	0.41	0.78
	jul{T,Q}	0.29	0.34	0.62
	aug{T,Q}	0.30	0.35	0.62

Since the above results show that the jun and jul basis sets perform just as well as aug basis sets, the next objective of this study was to compare the computational load associated with the jun, jul, and aug calculations. Table 6 shows the number of contracted basis functions used in the calculations for several molecules with aug, jul, and jun-cc-pVXZ basis sets. The number of contracted basis functions is important because of the scaling of the computational effort of CCSD(T) with the size of the basis. It is often stated that in the limit

of large n, where n is the number of contracted functions, the computational effort of CCSD(T) calculations scales bn^7, where b is a constant. It is more informative to look at the costs of two leading terms, that is the iterative CCSD part and that of the noniterative (T) step. Then the leading terms in the computational effort maybe written as $an_{\mathrm{iter}}n^6 + bn^7$, where n_{iter} is the number of CCSD iterations, and a is a constant. These scalings apply to increasing the size of homonuclear systems, where the number of contracted basis functions is proportional to the number of atoms. When one considers the effect of increasing the basis set size for a given molecule, it is useful to recognize that n is the sum of the number of occupied orbitals n_{o} and the number n_{v} of virtual orbitals, because changing the number of contracted functions changes n_{v} but not n_{o}. Using n_{v} and n_{o} rather than n, the leading terms in the cost are[42] $cn_{\mathrm{iter}}n_{\mathrm{o}}^2n_{\mathrm{v}}^4 + dn_{\mathrm{o}}^3n_{\mathrm{v}}^4$, where c and d are constants. The dependence on the number of contracted functions for a given molecule is thus less steep (asymptotically $n \sim n_{\mathrm{v}}$, so the scaling becomes n^4 rather than n^7); nevertheless, it is still very significant. As the size of the molecule increases, the difference in the number of basis functions between the jun and aug basis sets, as well as between the jul and aug basis sets, becomes more pronounced.

Table 6. Number of contracted basis functions for an illustrative set of molecules larger than the ones included in this study for jun, jul, and aug-cc-pVXZ basis sets.

Molecule	DZ			TZ			QZ		
	jun	jul	aug	jun	jul	aug	jun	jul	aug
H_2O_2	46	56	64	106	120	138	202	220	252
H_2S_2	54	64	72	114	128	146	210	228	260
$Fe(H_2O)_2$	108	125	141	218	241	277	391	420	484
Fe_2O_3	158	187	187	285	324	324	471	520	520
$C_2H_4O_2$	92	112	128	212	240	276	404	440	504
C_2H_6O	84	99	123	201	222	276	393	420	516
$C_2H_5NO_2$	115	140	160	265	300	345	505	550	630
C_6H_6	138	168	192	318	360	414	606	660	756
$C_4H_6O_3$	156	191	215	357	406	460	677	740	836
C_6H_7N	161	196	224	371	420	483	707	770	882
$C_5H_5N_5$	205	255	275	460	530	575	860	950	1030
C_6H_{12}	168	198	246	402	444	552	786	840	1032
$C_4H_7NO_4$	197	242	270	449	512	575	849	930	1042

$C_6H_9N_3O_2$	243	298	334	555	632	713	1051	1150	1294
$C_6H_{12}O_6$	276	336	384	636	720	828	1212	1320	1512
$C_{10}H_{12}N_2O$	294	359	407	675	766	874	1283	1400	1592
$C_{22}H_{14}$	466	576	632	1054	1208	1334	1982	2180	2404

For DZ, Table 6 shows that the number of contracted basis functions in the aug basis set is 18-46% more than in jun and 8-24% more than in jul, where in the comparison to jul we omit molecules that have no hydrogens. For TZ, these numbers change to 14-37% for jun, and they remain 8–24% for jul. For QZ, the increases become 10-31% for jun and 8-23% for jul.

As the number of basis functions increase, so does the computational cost. Table 7 lists the relative CPU time for each CCSD(T) single-point energy calculation for three example molecules. C_4H_4 is one of the most expensive systems in the current study, whereas C_6H_{12} and $C_6H_{12}O_6$ are included as examples of larger, more challenging systems on which to perform a CCSD(T) calculation, and we note that $C_6H_{12}O_6$ was too big for us to perform CCSD(T) calculations with jun/jul/aug-cc-pVQZ basis sets. For DZ, the jun calculations reduce the cost as compared to aug calculations by a factor of 3 to 5. The other comparisons show smaller but still significant ratios. To put things into perspective, it takes two and a half days for a CCSD(T)/jun-cc-pVQZ calculation on C_6H_{12}, and a CCSD(T)/aug-cc-pVQZ calculation would take well over 6 days for completion. A CCSD(T)/aug-cc-pVTZ on $C_6H_{12}O_6$ takes almost 11 days of CPU time, as compared to less than five days for jun-cc-pVTZ. The new science that can be explored with this procedure includes any problem where such cost savings make the calculations more practical.

Table 7. CPU time required for CCSD(T) single-point energy calculations with jun- and jul-cc-pV*X*Z basis sets relative to the corresponding aug-cc-pV*X*Z calculations.

	DZ			TZ			QZ		
Molecule	jun	jul	aug	jun	jul	aug	jun	jul	aug
C_4H_4	0.34	0.68	1.00	0.35	0.62	1.00	0.36	0.57	1.00
C_6H_{12}	0.32	0.53	1.00	0.56	0.64	1.00	0.39	0.42	1.00
$C_6H_{12}O_6$	0.21	0.65	1.00	0.43	0.70	1.00	-	-	-

Table 8 presents the total cost of the CCSD(T) single point energy calculations required for the {D,T} and {T,Q} extrapolations for the jun and jul basis sets relative to that of aug. The combined hours for DZ and TZ calculations closely match the values for TZ

calculations in Table 7. This is because TZ calculations, being more resource-intensive than DZ calculations, dominate the total computation time for both DZ and TZ calculations. Similarly, the combined relative CPU time for TZ and QZ calculations resembles the time taken for QZ calculations in Table 7 due to the higher computational demand of QZ calculations. There is a significant reduction in computational cost with smaller jun and jul basis sets without a loss of accuracy in the calculation of absolute energies.

Table 8. A comparison of total CPU time required for CCSD(T) single-point energy calculations for the {D,T} and {T,Q} extrapolation. Time taken for jun and jul calculations are compared to the corresponding aug calculations.

Molecule	jun-DZ+TZ	jul-DZ+TZ	aug-DZ+TZ	jun-TZ+QZ	jul-TZ+QZ	aug-TZ+QZ
C_4H_4	0.35	0.62	1.00	0.36	0.57	1.00
C_6H_{12}	0.55	0.64	1.00	0.41	0.44	1.00
$C_6H_{12}O_6$	0.42	0.70	1.00	-	-	-

4. Concluding remarks

Our realization that diffuse functions are hardly ever needed on hydrogen atoms dates back a number of years when we noticed that diffuse functions on hydrogen raise the cost but do not usually increase the accuracy. To provide a hard test, we did calculations on a metal hydride, LiH, and found no significant improvement when diffuse functions were added on H. We concluded, "Since metal hydrides are seemingly a "worst case" for omitting diffuse functions on H, it appears to be confirmed that diffuse functions on hydrogen have little importance for most thermochemical calculations."[43] We later reconfirmed this during very extensive studies performed when proposing the calendar basis sets. At that time, we also suggested that the augmented basis sets of Dunning bring in high-angular-momentum diffuse functions at an earlier zeta level than is necessary. For example, for C, N, O, and F, aug-cc-pV*X*Z brings in diffuse f functions already at X = T, whereas jun-cc-pV*X*Z brings them at X = Q; this is particularly important since adding a diffuse f subshell adds seven additional basis functions to the basis set. We have since found that jun-cc-pV*X*Z calculations are usually comparable in accuracy to aug-cc-pV*X*Z calculations but at a lower cost. Here we illustrate this in the context of two-point extrapolations.

The work of Xi et al.[30] shows how two-point extrapolations of the CCSD(T) energy can be much more accurate than previously expected if one optimizes the parameters for each pair of basis sets. Here we build on this outstanding work by showing that this higher accuracy can be obtained at even lower cost by choosing the diffuse basis functions more efficiently. Since jul and jun basis sets have less functions than aug, there is a significant

reduction in the cost of the calculations. Our first finding is that the jul results are almost the same as the aug results. Our second finding is that jun basis set have either a minimal reduction in accuracy or even an improved accuracy as compared to aug basis sets; since there is a huge reduction in computational cost, we recommend using jun basis sets for CBS calculations with the parameters optimized here rather than using aug basis sets.

ASSOCIATED CONTENT

SUPPORTING INFORMATION

Optimized geometries and single point energies calculated with jun, jul and aug-cc-pVXZ basis sets for all the species in the data set.

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References

[1] Winter, B.; Thürmer, S.; Wilkinson, I. Absolute Electronic Energetics and Quantitative Work Functions of Liquids from Photoelectron Spectroscopy. *Acc. Chem. Res.* **2023**, *56*, 77–85.

[2] Andriola, D. M.; Peterson, K. A. Coupled Cluster Study of the Heats of Formation of UF_6 and the Uranium Oxyhalides, UO_2X_2 (X = F, Cl, Br, I, and At). *J. Phys. Chem. A* **2023**, *127*, 7579–7585.

[3] Zhao, S.; Fu, G.; Zhen, W.; Wang, H.; Liu, M.; Yang, L.; Zhang, J. Nucleophile Effects on the E_2/SN_2 Competition for the $X^- + CH_3CH_2Cl$ Reactions: A Theoretical Study. *J. Phys. Chem. A* **2023**, *127*, 3381–3389.

[4] Feng, Z.; Guo, W.; Kong, W. Y.; Chen, D.; Wang, S.; Tantillo, D. J. Analogies Between Photochemical Reactions and Ground-State Post-Transition-State Bifurcations Shed Light on Dynamical Origins of Selectivity. *Nat. Chem.* **2024**, *16*, 615–623.

[5] Wang, B.; Ding, Y.; Tian, X. Benchmarking Model Chemistry Composite Calculations for Vertical Ionization Potential of Molecular Systems. *Chinese Chem. Lett.* **2024**, 109721.

[6] Bartlett, R. J.; Purvis, G. D. Many-body Perturbation Theory, Coupled-Pair Many-electron Theory, and the Importance of Quadruple Excitations for the Correlation Problem. *Int. J. Quantum Chem.* **1978**, *14*, 561–581.

[7] Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-gordon, M. A Fifth-Order Perturbation Comparison of Electron Correlation Theories. *Chem. Phys. Lett.* **1989**, *157*, 479–483.

[8] Feller, D.; Peterson, K. A.; Crawford, T. D. Sources of Error in Electronic Structure Calculations on Small Chemical Systems. *J. Chem. Phys.* **2006**, *124*, no. 054107.

[9] Helgaker, T.; Klopper, W.; Tew, D. P. Quantitative Quantum Chemistry. *Mol. Phys.* **2008**, *106*, 2107–2143.

[10] Peterson, K. A.; Feller, D.; Dixon, D. A. Chemical Accuracy in Ab Initio Thermochemistry and Spectroscopy: Current Strategies and Future Challenges. *Theor. Chem. Acc.* **2012**, *131*, no. 1079.

[11] Yang, D.; Guo, H.; Xie, D. Recent Advances in Quantum Theory on Ro-Vibrationally Inelastic Scattering. *Phys. Chem. Chem. Phys.* **2022**, *25*, 3577–3594.

[12] Klahn, B.; Bingel, W. A., The Convergence of the Rayleigh-Ritz Method in Quantum Chemistry. Theoret. Chim. Acta 1977, 44, 9. 27-43.

[13] Woon, D. E.; Dunning, T. H. Jr. Benchmark Calculations with Correlated Molecular Wave Functions. VI. Second Row A_2 and First Row/Second Row AB Diatomic Molecules. *J. Chem. Phys.* **1994**, *101*, 8877–8893.

[14] Halkier, A.; Helgaker, T.; Jørgensen, P.; Klopper, W.; Olsen, J. Basis-Set Convergence of the Energy in Molecular Hartree–Fock Calculations. *Chem. Phys. Lett.* **1999**, *302*, 437–446.

[15] Butler, P. R.; Ellis, A. M. Application of the Truhlar Basis Set Extrapolation Procedure to Ab Initio Calculations on van der Waals Complexes. *Mol. Phys.* **2001**, *99*, 525–529.

[16] Klopper, W.; Noga, J. Accurate Quantum-Chemical Prediction of Enthalpies of Formation of Small Molecules in the Gas Phase. *ChemPhysChem* **2003**, *4*, 32–48.

[17] Feller, D.; Peterson, K. A.; Hill, G. J. On the Effectiveness of CCSD(T) Complete Basis Set Extrapolations for Atomization Energies. *J. Chem. Phys.* **2011**, *135*, no. 044102.

[18] Schwenke, D. W. On One-Electron Basis Set Extrapolation of Atomic and Molecular Correlation Energies. *Mol. Phys.* **2012**, *110*, 2557–2567.

[19] Varandas, A. J. C. Straightening the Hierarchical Staircase for Basis Set Extrapolations: A Low-Cost Approach to High-Accuracy Computational Chemistry. *Annu. Rev. Phys. Chem.* **2018**, *69*, 177–203.

[20] Varandas, A. J. C.; Pansini, F. N. N. Optimal Basis Sets for CBS Extrapolation of the Correlation Energy: OV*x*Z and oV(x+*d*)Z. *J.* Chem. *Phys.* **2019***, 150*, no. 154106.

[21] Altun, A.; Neese, F.; Bistoni, G. Extrapolation to the Limit of a Complete Pair Natural Orbital Space in Local Coupled-Cluster Calculations. *J. Chem. Theory Comput.* **2020**, *16*, 6142–6149.

[22] Lupi, J.; Alessandrini, S.; Puzzarini, C.; Barone, V. junChS and junChS-F12 Models: Parameter-free Efficient yet Accurate Composite Schemes for Energies and Structures of Noncovalent Complexes. *J. Chem. Theory Comput.* **2021***, 17*, 6974−6992.

[23] Truhlar, D. G. Basis-Set Extrapolation. *Chem. Phys. Lett.* **1998**, *294*, 45–48.

[24] Martin, J. M. L. Ab Initio Total Atomization Energies of Small Molecules - Towards the Basis Set Limit. *Chem. Phys. Lett.* **1996**, *259*, 669–678.

[25] Huh, S. B.; Lee, J. S. Basis Set and Correlation Dependent Extrapolation of Correlation Energy. *J. Chem. Phys.* **2003**, *118*, 3035–3042.

[26] Karton, A.; Martin, J. M. L. Comment on: "Estimating the Hartree-Fock Limit from Finite Basis Set Calculations" [Jensen F (2005) Theor Chem Acc 113:267]. *Theor. Chem. Acc.* **2006**, *115*, 330–333.

[27] Zhong, S.; Barnes, E. C.; Petersson, G. A. Uniformly Convergent *n*-Tuple-ζ Augmented Polarized (nZaP) Basis Sets for Complete Basis Set Extrapolations. I. Self-Consistent Field Energies. *J. Chem. Phys.* **2008**, *129*, no. 184116.

[28] Bakowies, D. Extrapolation of Electron Correlation Energies to Finite and Complete Basis Set Targets. *J. Chem. Phys.* **2007**, *127*, no. 084105.

[29] Varandas, A. J. C.; Pansini, F. N. N. Narrowing the Error in Electron Correlation Calculations by Basis Set Re-Hierarchization and Use of the Unified Singlet and Triplet Electron-Pair Extrapolation Scheme: Application to a Test Set of 106 Systems. *J. Chem. Phys.* **2014**, *141*, no. 224113.

[30] Xi, Z. K.; Ding, Y. H.; Tian, X. Building a New Platform for Significantly Improving Performance of Hartree-Fock and CCSD(T) Correlation Energy Based on Two-Point Complete Basis Set Extrapolation Schemes. *J. Phys. Chem. A* **2024**, *128*, 3742–3749.

[31] Papajak, E.; Truhlar, D. G. Efficient Diffuse Basis Sets for Density Functional Theory. *J. Chem. Theory Comput.* **2010**, *6*, 597–601.

[32] Papajak, E.; Truhlar, D. G. Convergent Partially Augmented Basis Sets for Post-Hartree-Fock Calculations of Molecular Properties and Reaction Barrier Heights. *J. Chem. Theory Comput.* **2011**, *7*, 10–18.

[33] Papajak, E.; Zheng, J.; Xu, X.; Leverentz, H. R.; Truhlar, D. G. Perspectives on Basis Sets Beautiful: Seasonal Plantings of Diffuse Basis Functions. *J. Chem. Theory Comput.* **2011**, *7*, 3027–3034.

[34] Papajak, E.; Truhlar, D. G. What are the Most Efficient Basis Set Strategies for Correlated Wave Function Calculations of Reaction Energies and Barrier Heights? *J. Chem. Phys.* **2012**, *137,* no. 064110.

[35] Martin, J. M. L. Ab Initio Thermochemistry beyond Chemical Accuracy for First-and Second-Row Compounds, in *Energetics of Stable Molecules and Reactive Intermediates*, Dordrecht: Springer Netherlands, **1999**), 373–415.

[36] Kendall, R. A.; Dunning Jr., T. H.; Harrison R. J. Electron affinities of the first-row atoms revisited. Systematic basis sets and wave functions. *J. Chem. Phys.* **1992**, *96*, 6796–6806.

[37] Zheng, J.; Zhao, Z.; Truhlar, D. G. The DBH24/08 Database and Its Use to Assess Electronic Structure Model Chemistries for Chemical Reaction Barrier Heights *J. Chem. Theory Comput.* **2009**, *5,*808-821.

[38] Helgaker, T.; Jørgensen, P.; Olsen, J. *Molecular Electronic-Structure Theory*; Wiley: Chichester, 2000; pp. 322-324.

[39] Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. *J. Phys. Chem.* **1994**, *98*, 11623−11627.

[40] Seeger, R.; Pople, J. A. Self-Consistent Molecular Orbital Theory, XVIII. Constraints and Stability in Hartree-Fock Theory. *J. Chem. Phys.* **1977***, 66*, 3045–3050.

[41] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. a.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. a.; Nakatsuji, H. et al. *Gaussian 16, Revision C.01*, Gaussian, Inc.: Wallingford CT, 2016.

[42] Raghavachari, K.; Anderson, J. B. Electron Correlation Effects in Molecules. *J. Phys. Chem.* **1996***, 100*, 12960-12975.

[43] Lynch, B. J.; Zhao, Y.; Truhlar, D. G. Multilevel Methods for Thermochemistry and Thermochemcial Kinetics. In *Electron Correlation Methodology*; Wilson, A. K., Peterson, K. A., Eds.; ACS Symp. Ser. 958; American Chemical Society: Wasington, DC, 2007; pp. 153-167.

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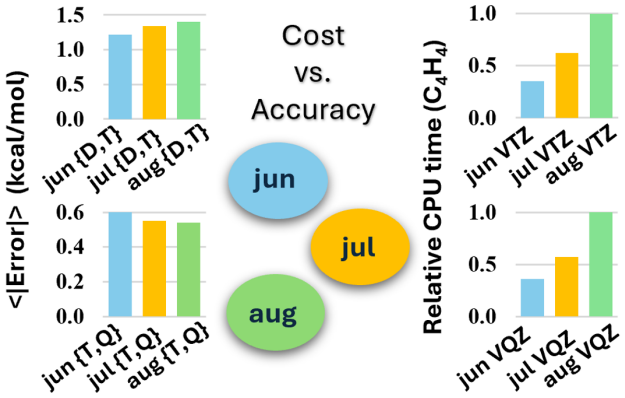

SUPPORTING INFORMATION

Evaluating Cost and Accuracy in Two-Point Complete Basis Set Extrapolation Schemes Using Efficient Diffuse Basis Sets

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1. Hartree-Fock Energies

1.1. HF energies (in hartrees) calculated with aug-cc-pV*X*Z basis sets

Species	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	aug-cc-pV6Z[a]
H	-0.4993343	-0.4998212	-0.4999483	-0.4999993
He	-2.8557047	-2.8611834	-2.8615220	-2.8616731
B	-24.5305738	-24.5321715	-24.5329839	-24.5331532
C	-37.6877633	-37.6918113	-37.6933513	-37.6937323
N	-54.3931834	-54.4011622	-54.4038195	-54.4045376
O	-74.7966008	-74.8129822	-74.8176248	-74.8189614
F	-99.3810918	-99.4068794	-99.4140853	-99.4162785
Ne	-128.4963500	-128.5332728	-128.5437558	-128.5470621
Al	-241.8741580	-241.8791739	-241.8804195	-241.8808051
Si	-288.8509360	-288.8566278	-288.8584325	-288.8589110
P	-340.7099570	-340.7164915	-340.7187412	-340.7192506
S	-397.4987400	-397.5098727	-397.5126914	-397.5133522
Cl	-459.4727810	-459.4859689	-459.4891795	-459.4899117
Ar	-526.8009720	-526.8133520	-526.8168048	-526.8174843
CF^+	-136.8586600	-136.9010979	-136.9111294	-136.9138934
CF^-	-137.1894080	-137.2212715	-137.2300372	-137.2325400
CF	-137.1894670	-137.2268086	-137.2360966	-137.2387592
CH^-	-38.2913356	-38.2975286	-38.2993354	-38.2998003
CN^-	-92.3242067	-92.3425067	-92.3478342	-92.3490098
CN	-92.2171291	-92.2361755	-92.2418107	-92.2430511
CO	-112.7548710	-112.7816852	-112.7893096	-112.7911240
FO	-174.1491530	-174.1953795	-174.2073057	-174.2108489
H_2	-1.1288063	-1.1330054	-1.1334497	-1.1336027
HF	-100.0332170	-100.0608065	-100.0682738	-100.0704821
N_2	-108.9613270	-108.9857967	-108.9927084	-108.9942941
NF	-153.8019420	-153.8395202	-153.8497924	-153.8527303
NH	-54.9719126	-54.9824269	-54.9854370	-54.9862266
NO^+	-128.9349060	-128.9676709	-128.9769936	-128.9791764
NO	-129.2704740	-129.2990625	-129.3076387	-129.3097529
O_2	-149.6427090	-149.6784703	-149.6887618	-149.6914775
OH^-	-75.3955930	-75.4118367	-75.4166024	-75.4179268
OH	-75.4034899	-75.4214479	-75.4264287	-75.4278127
Cl_2^-	-919.0579540	-919.0799340	-919.0860947	-919.0874304
NCl	-513.8825640	-513.9091624	-513.9163754	-513.9189729
NO^-	-129.2593610	-129.2851687	-129.2930140	-129.2950252
SCl^-	-857.0696260	-857.0956355	-857.1020252	-857.1041312
SF^-	-496.9756460	-497.0124688	-497.0232575	-497.0266518

SH^-	-398.1337280	-398.1452406	-398.1485678	-398.1496774
SiH^-	-289.4587290	-289.4670424	-289.4694567	-289.4702666
SN^-	-451.9710340	-451.9957682	-452.0029341	-452.0056745
AlF	-341.4392530	-341.4729890	-341.4839235	-341.4873484
AlH_3	-243.6325500	-243.6444695	-243.6481086	-243.6496437
BN	-79.0019723	-79.0162404	-79.0207922	-79.0217872
BP	-365.3014970	-365.3150504	-365.3192517	-365.3206853
Cl_2O	-993.7292210	-993.7787982	-993.7917841	-993.7962610
Cl_2	-918.9660270	-918.9994012	-919.0068683	-919.0096561
ClCN	-551.7958750	-551.8325129	-551.8419980	-551.8449706
ClO	-534.2692430	-534.3059620	-534.3153455	-534.3188495
COS	-510.2999120	-510.3410843	-510.3526744	-510.3563575
CS_2	-832.9307650	-832.9673591	-832.9779102	-832.9821809
CS	-435.3340280	-435.3535928	-435.3597382	-435.3621045
FS	-496.9254180	-496.9698133	-496.9816249	-496.9857793
H_2S_2	-796.2301380	-796.2618248	-796.2700766	-796.2738932
H_2S	-398.6980880	-398.7137347	-398.7180196	-398.7199201
HCl	-460.0925960	-460.1074737	-460.1112498	-460.1125922
HS	-398.0921410	-398.1058204	-398.1093862	-398.1106877
PH_2	-341.8741880	-341.8874108	-341.8912949	-341.8929179
PO^+	-415.2764500	-415.3210144	-415.3321219	-415.3371046
PO^-	-415.6122050	-415.6497973	-415.6592694	-415.6630369
PO	-415.5795980	-415.6215833	-415.6319666	-415.6364223
S_2	-795.0669390	-795.0971120	-795.1048876	-795.1083454
SiF	-388.3772180	-388.4179109	-388.4295069	-388.4332752
SiH_4	-291.2432310	-291.2608213	-291.2660603	-291.2683448
SiO	-363.8021970	-363.8406139	-363.8502596	-363.8542598
SiS	-686.4845050	-686.5068168	-686.5130689	-686.5155525
SO_3	-622.0250270	-622.1427441	-622.1736886	-622.1909326
SO	-472.3633740	-472.4045419	-472.4149895	-472.4196112
PO_2	-490.4481220	-490.5241555	-490.5430673	-490.5519476
BH_3	-26.3912059	-26.4003042	-26.4021326	-26.4026079
C_2H	-76.1586520	-76.1780166	-76.1824769	-76.1835158
FCN cyanogen fluoride	-191.7214230	-191.7723342	-191.7850588	-191.7885068
FNC isocyanogen fluoride	-191.6060790	-191.6553717	-191.6680240	-191.6713952
CH_2	-38.9281187	-38.9380038	-38.9401820	-38.9407905
CH_3	-39.5658098	-39.5779853	-39.5804112	-39.5811137
CO_2	-187.6627600	-187.7094239	-187.7221281	-187.7252544
FNO	-228.6547150	-228.7104273	-228.7260225	-228.7301968
H_2O	-76.0411795	-76.0603284	-76.0656957	-76.0671541
HCN	-92.8880397	-92.9100033	-92.9154890	-92.9167832
HCO	-113.2672510	-113.2947633	-113.3022304	-113.3041055
HO_2	-150.2024220	-150.2395310	-150.2495353	-150.2522722

N_2O	-183.7105410	-183.7530387	-183.7649319	-183.7678624
NH_2	-55.5749363	-55.5878344	-55.5911626	-55.5920423
NO_2	-204.0664510	-204.1137363	-204.1275371	-204.1309424
AlH_2	-243.0266760	-243.0366944	-243.0396013	-243.0407655
BF	-124.1149220	-124.1571580	-124.1662401	-124.1686744
BO	-99.5321401	-99.5575447	-99.5645175	-99.5662123
BS	-422.1733660	-422.1896834	-422.1945750	-422.1962996
C_2H_3	-77.4005438	-77.4204862	-77.4250116	-77.4261835
CH_3Cl	-499.1222360	-499.1487632	-499.1547835	-499.1566611
HOCl	-534.8865950	-534.9213205	-534.9303902	-534.9333840
HOF	-174.7616770	-174.8076242	-174.8195894	-174.8231088
NSi	-343.2751590	-343.3027954	-343.3100887	-343.3128702
P_2H_4	-683.7983800	-683.8269038	-683.8353293	-683.8392300
SiH_3Cl	-750.2260260	-750.2589662	-750.2677083	-750.2712300
SiO_2	-438.6522120	-438.7209913	-438.7373654	-438.7445186
CCl	-497.2390190	-497.2601298	-497.2659844	-497.2680196
HN_3	-163.8691100	-163.9062830	-163.9164501	-163.9188649
NF_2	-253.1973250	-253.2633787	-253.2808826	-253.2859389
PF_2	-539.6711350	-539.7519318	-539.7730713	-539.7805663
C_2F_2	-274.4935760	-274.5713827	-274.5900830	-274.5953978
C_3H_4 cyclopropene	-115.8365360	-115.8664311	-115.8732863	-115.8750030
C_4H_4 tetrahedrane	-153.6161880	-153.6535719	-153.6625157	-153.6646974
CH_2F_2	-237.9314290	-237.9987311	-238.0151323	-238.0199806
CH_2N_2 cyanamide	-147.9355890	-147.9698252	-147.9786630	-147.9807953
CH_2O	-113.8855420	-113.9142450	-113.9216910	-113.9236247
CH_3F	-139.0574290	-139.0972054	-139.1066537	-139.1094671
CH_3N	-94.0473879	-94.0697668	-94.0754896	-94.0769300
HOCN cyanic acid	-167.7530280	-167.7931860	-167.8037432	-167.8063664
HCNO fulminic acid	-167.6567330	-167.6979852	-167.7086510	-167.7112779
HNCO isocyanic acid	-167.7912760	-167.8321124	-167.8428880	-167.8455259
HONC isofulminic acid	-167.6570570	-167.6971870	-167.7078011	-167.7104118
C_2H_2	-76.8286946	-76.8507559	-76.8551893	-76.8562906
C_2H_3N	-131.9436280	-131.9753354	-131.9829923	-131.9849068
C_2H_4	-78.0437046	-78.0649477	-78.0696540	-78.0709050
CF_2O	-311.6541030	-311.7402299	-311.7621082	-311.7682481
CH_4O	-115.0615330	-115.0920221	-115.0995167	-115.1015936
CH_4	-40.1996281	-40.2136085	-40.2162338	-40.2170255
CHF_3	-336.8142770	-336.9105449	-336.9340091	-336.9409063
CHFO	-212.7782400	-212.8351348	-212.8497483	-212.8537629
H_2O_2	-150.8015740	-150.8391843	-150.8491165	-150.8518755
N_2H_4	-111.2009730	-111.2275307	-111.2345649	-111.2363617

[a]aug-cc-pV6Z results are obtained from *J. Phys. Chem. A* **2024**, 128, 18, 3742–3749.

1.2. HF energies (in hartrees) calculated with jul-cc-pV*X*Z basis sets

Species	jul-cc-pVDZ	jul-cc-pVTZ	jul-cc-pVQZ
H	-0.4992784	-0.4998098	-0.4999456
He	-2.8551605	-2.8611533	-2.8615142
B	-24.5305738	-24.5321715	-24.5329839
C	-37.6877633	-37.6918113	-37.6933514
N	-54.3931834	-54.4011622	-54.4038195
O	-74.7966007	-74.8129822	-74.8176248
F	-99.3810918	-99.4068794	-99.4140853
Ne	-128.4963497	-128.5332728	-128.5437558
Al	-241.8741580	-241.8791739	-241.8804195
Si	-288.8509362	-288.8566278	-288.8584325
P	-340.7099574	-340.7164915	-340.7187412
S	-397.4987400	-397.5098727	-397.5126914
Cl	-459.4727811	-459.4859689	-459.4891795
Ar	-526.8009722	-526.8133520	-526.8168048
CF^+	-136.8586593	-136.9010975	-136.9111290
CF^-	-137.1894078	-137.2212735	-137.2300393
CF	-137.1894641	-137.2267960	-137.2360827
CH^-	-38.2911600	-38.2974609	-38.2993167
CN^-	-92.3242071	-92.3425074	-92.3478350
CN	-92.2171292	-92.2361758	-92.2418110
CO	-112.7548715	-112.7816854	-112.7893098
FO	-174.1491502	-174.1953757	-174.2073016
H_2	-1.1287277	-1.1329390	-1.1334356
HF	-100.0327347	-100.0606926	-100.0682391
N_2	-108.9613362	-108.9858124	-108.9927249
NF	-153.8019426	-153.8395209	-153.8497933
NH	-54.9717943	-54.9823732	-54.9854208
NO^+	-128.9349121	-128.9676797	-128.9770028
NO	-129.2704742	-129.2990626	-129.3076388
O_2	-149.6426997	-149.6784606	-149.6887517
OH^-	-75.3947775	-75.4115768	-75.4165048
OH	-75.4032536	-75.4213838	-75.4264012
Cl_2^-	-919.0579740	-919.0799619	-919.0861235
NCl	-513.8825534	-513.9091589	-513.9163741
NO^-	-129.2593568	-129.2851633	-129.2930083
SCl^-	-857.0696259	-857.0956331	-857.1020223
SF^-	-496.9756439	-497.0124624	-497.0232505
SH^-	-398.1331486	-398.1451538	-398.1485483
SiH^-	-289.4584378	-289.4670014	-289.4694448

SN^-	-451.9710252	-451.9957683	-452.0029369
AlF	-341.4392653	-341.4730221	-341.4839663
AlH_3	-243.6320054	-243.6443335	-243.6480673
BN	-79.0019837	-79.0162538	-79.0208067
BP	-365.3014987	-365.3150555	-365.3192579
Cl_2O	-993.7291836	-993.7787405	-993.7917227
Cl_2	-918.9660375	-918.9994250	-919.0068955
ClCN	-551.7958743	-551.8325066	-551.8419904
ClO	-534.2692308	-534.3059621	-534.3153482
COS	-510.2999032	-510.3410778	-510.3526687
CS_2	-832.9307630	-832.9673538	-832.9779039
CS	-435.3340312	-435.3535992	-435.3597455
FS	-496.9254202	-496.9698550	-496.9816720
H_2S_2	-796.2294005	-796.2617328	-796.2700481
H_2S	-398.6977270	-398.7136588	-398.7179859
HCl	-460.0923270	-460.1074163	-460.1112332
HS	-398.0919116	-398.1057881	-398.1093855
PH_2	-341.8739658	-341.8873645	-341.8912803
PO^+	-415.2764454	-415.3210049	-415.3321110
PO^-	-415.6122022	-415.6497883	-415.6592590
PO	-415.5795979	-415.6215835	-415.6319669
S_2	-795.0669330	-795.0971010	-795.1048751
SiF	-388.3772123	-388.4179299	-388.4295309
SiH_4	-291.2431024	-291.2606746	-291.2660312
SiO	-363.8021963	-363.8406091	-363.8502540
SiS	-686.4845055	-686.5068170	-686.5130691
SO_3	-622.0250148	-622.1427136	-622.1736530
SO	-472.3633649	-472.4045208	-472.4149655
PO_2	-490.4481273	-490.5241737	-490.5430884
BH_3	-26.3908261	-26.4002017	-26.4021050
C_2H	-76.1582337	-76.1778484	-76.1824563
FCN cyanogen fluoride	-191.7214169	-191.7723255	-191.7850498
FNC isocyanogen fluoride	-191.6060879	-191.6553812	-191.6680338
CH_2	-38.9277827	-38.9379273	-38.9401695
CH_3	-39.5652527	-39.5778980	-39.5803989
CO_2	-187.6627567	-187.7094198	-187.7221238
FNO	-228.6547183	-228.7104295	-228.7260239
H_2O	-76.0406766	-76.0601800	-76.0656236
HCN	-92.8877349	-92.9098900	-92.9154826
HCO	-113.2669844	-113.2946897	-113.3022195
HO_2	-150.2021436	-150.2394643	-150.2495305
N_2O	-183.7105360	-183.7530320	-183.7649247
NH_2	-55.5747332	-55.5877384	-55.5911334

NO_2	-204.0664377	-204.1137205	-204.1275208
AlH_2	-243.0263716	-243.0365931	-243.0395760
BF	-124.1149218	-124.1571580	-124.1662402
BO	-99.5321261	-99.5575264	-99.5644966
BS	-422.1733663	-422.1896845	-422.1945763
C_2H_3	-77.3998988	-77.4203264	-77.4250017
CH_3Cl	-499.1217309	-499.1486688	-499.1547752
HOCl	-534.8864309	-534.9212875	-534.9304220
HOF	-174.7612895	-174.8074730	-174.8195003
NSi	-343.2751679	-343.3027980	-343.3100892
P_2H_4	-683.7975257	-683.8267626	-683.8352492
SiH_3Cl	-750.2256812	-750.2587952	-750.2676605
SiO_2	-438.6522126	-438.7209945	-438.7373691
CCl	-497.2390186	-497.2601298	-497.2659845
HN_3	-163.8688705	-163.9061627	-163.9164090
NF_2	-253.1973625	-253.2634219	-253.2809272
PF_2	-539.6711191	-539.7519555	-539.7731016
C_2F_2	-274.4935678	-274.5713701	-274.5900700
C_3H_4 cyclopropene	-115.8355837	-115.8662489	-115.8732557
C_4H_4 tetrahedrane	-153.6151402	-153.6533927	-153.6624560
CH_2F_2	-237.9307601	-237.9984257	-238.0150503
CH_2N_2 cyanamide	-147.9352753	-147.9696702	-147.9786301
CH_2O	-113.8849631	-113.9141168	-113.9216470
CH_3F	-139.0568509	-139.0969638	-139.1066061
CH_3N	-94.0467997	-94.0695967	-94.0754412
HOCN cyanic acid	-167.7529344	-167.7930885	-167.8037211
HCNO fulminic acid	-167.6562523	-167.6978833	-167.7086336
HNCO isocyanic acid	-167.7910101	-167.8320266	-167.8428887
HONC isofulminic acid	-167.6567851	-167.6970809	-167.7077713
C_2H_2	-76.8280415	-76.8505468	-76.8551567
C_2H_3N	-131.9433447	-131.9752021	-131.9829675
C_2H_4	-78.0427270	-78.0647651	-78.0696193
CF_2O	-311.6541027	-311.7402293	-311.7621075
CH_4O	-115.0608088	-115.0918233	-115.0994702
CH_4	-40.1991340	-40.2135146	-40.2162139
CHF_3	-336.8137347	-336.9103299	-336.9339395
CHFO	-212.7777773	-212.8349873	-212.8496912
H_2O_2	-150.8009914	-150.8390067	-150.8490410
N_2H_4	-111.2001430	-111.2273195	-111.2345464

1.3. HF energies (in hartree) calculated with jun-cc-pV*X*Z basis sets

Species	jun-cc-pVDZ	jun-cc-pVTZ	jun-cc-pVQZ
H	-0.4992784	-0.4998098	-0.4999456
He	-2.8551605	-2.8611533	-2.8615142
B	-24.5302109	-24.5321672	-24.5329837
C	-37.6874175	-37.6918081	-37.6933512
N	-54.3931834	-54.4011622	-54.4038195
O	-74.7960730	-74.8127782	-74.8176248
F	-99.3805620	-99.4066796	-99.4140853
Ne	-128.4963497	-128.5332728	-128.5437558
Al	-241.8737506	-241.8791661	-241.8804191
Si	-288.8505905	-288.8566212	-288.8584322
P	-340.7099574	-340.7164915	-340.7187412
S	-397.4983254	-397.5095938	-397.5126913
Cl	-459.4724326	-459.4857033	-459.4891795
Ar	-526.8009722	-526.8133520	-526.8168048
CF^+	-136.8537088	-136.9007227	-136.9110847
CF^-	-137.1868000	-137.2209210	-137.2299632
CF	-137.1855708	-137.2264155	-137.2360145
CH^-	-38.2898593	-38.2974164	-38.2993154
CN^-	-92.3233980	-92.3423437	-92.3478143
CN	-92.2160001	-92.2360085	-92.2417889
CO	-112.7531873	-112.7815305	-112.7892819
FO	-174.1424699	-174.1947529	-174.2071518
H_2	-1.1287277	-1.1329390	-1.1334356
HF	-100.0303801	-100.0606616	-100.0682385
N_2	-108.9596284	-108.9857081	-108.9926926
NF	-153.7966230	-153.8391201	-153.8496631
NH	-54.9705759	-54.9823401	-54.9854194
NO^+	-128.9301022	-128.9675178	-128.9769168
NO	-129.2669023	-129.2988665	-129.3075407
O_2	-149.6360328	-149.6781916	-149.6885904
OH^-	-75.3927922	-75.4115345	-75.4165018
OH	-75.4011438	-75.4212160	-75.4263987
Cl_2^-	-919.0567083	-919.0797202	-919.0860881
NCl	-513.8790124	-513.9089800	-513.9162962
NO^-	-129.2567340	-129.2849457	-129.2929025
SCl^-	-857.0684809	-857.0953930	-857.1019538
SF^-	-496.9703736	-497.0117575	-497.0231409
SH^-	-398.1327172	-398.1450620	-398.1485462
SiH^-	-289.4577531	-289.4668560	-289.4694416

SN^-	-451.9677761	-451.9956270	-452.0028791
AlF	-341.4284028	-341.4716037	-341.4838697
AlH_3	-243.6318195	-243.6443254	-243.6480510
BN	-79.0007296	-79.0160759	-79.0207925
BP	-365.3003963	-365.3147881	-365.3192350
Cl_2O	-993.7186846	-993.7780281	-993.7914573
Cl_2	-918.9641633	-918.9990232	-919.0068177
ClCN	-551.7938159	-551.8323240	-551.8419472
ClO	-534.2626323	-534.3055427	-534.3152144
COS	-510.2957326	-510.3408367	-510.3526146
CS_2	-832.9287668	-832.9672244	-832.9778576
CS	-435.3326844	-435.3534955	-435.3597250
FS	-496.9163483	-496.9688632	-496.9815531
H_2S_2	-796.2270153	-796.2615505	-796.2699682
H_2S	-398.6968792	-398.7135717	-398.7179794
HCl	-460.0916421	-460.1073590	-460.1112304
HS	-398.0910271	-398.1055745	-398.1093817
PH_2	-341.8731278	-341.8872777	-341.8912724
PO^+	-415.2699735	-415.3207160	-415.3320682
PO^-	-415.6056848	-415.6493903	-415.6592087
PO	-415.5730836	-415.6212016	-415.6319177
S_2	-795.0632777	-795.0968637	-795.1048341
SiF	-388.3669824	-388.4168398	-388.4294718
SiH_4	-291.2429483	-291.2606123	-291.2660026
SiO	-363.7964444	-363.8402012	-363.8502023
SiS	-686.4829136	-686.5067688	-686.5130466
SO_3	-622.0036800	-622.1417178	-622.1732857
SO	-472.3552356	-472.4041603	-472.4148875
PO_2	-490.4363750	-490.5235352	-490.5429562
BH_3	-26.3906773	-26.4001755	-26.4021007
C_2H	-76.1579382	-76.1777537	-76.1824474
FCN cyanogen fluoride	-191.7169718	-191.7718342	-191.7849721
FNC isocyanogen fluoride	-191.6007174	-191.6549276	-191.6678987
CH_2	-38.9275667	-38.9378738	-38.9401684
CH_3	-39.5648730	-39.5778158	-39.5803973
CO_2	-187.6586910	-187.7090503	-187.7220397
FNO	-228.6454995	-228.7096611	-228.7258181
H_2O	-76.0372767	-76.0601261	-76.0656173
HCN	-92.8866641	-92.9097221	-92.9154637
HCO	-113.2648595	-113.2945066	-113.3021860
HO_2	-150.1954221	-150.2390780	-150.2493914
N_2O	-183.7038466	-183.7528400	-183.7648095
NH_2	-55.5725801	-55.5876621	-55.5911299

NO_2	-204.0586743	-204.1133010	-204.1272995
AlH_2	-243.0259096	-243.0365443	-243.0395634
BF	-124.1113622	-124.1566182	-124.1661800
BO	-99.5312473	-99.5574517	-99.5644772
BS	-422.1726732	-422.1895971	-422.1945599
C_2H_3	-77.3991918	-77.4202163	-77.4249833
CH_3Cl	-499.1207005	-499.1485576	-499.1547170
HOCl	-534.8790900	-534.9208092	-534.9302445
HOF	-174.7538493	-174.8068723	-174.8193818
NSi	-343.2733319	-343.3026210	-343.3100476
P_2H_4	-683.7961957	-683.8266515	-683.8351859
SiH_3Cl	-750.2240538	-750.2586259	-750.2675960
SiO_2	-438.6431295	-438.7205708	-438.7371995
CCl	-497.2373534	-497.2599871	-497.2659263
HN_3	-163.8634284	-163.9060425	-163.9163151
NF_2	-253.1856620	-253.2624445	-253.2806459
PF_2	-539.6529840	-539.7500518	-539.7729478
C_2F_2	-274.4865051	-274.5705007	-274.5899677
C_3H_4 cyclopropene	-115.8343732	-115.8660740	-115.8732069
C_4H_4 tetrahedrane	-153.6135699	-153.6531244	-153.6624018
CH_2F_2	-237.9234115	-237.9976370	-238.0149054
CH_2N_2 cyanamide	-147.9321386	-147.9693857	-147.9785661
CH_2O	-113.8831105	-113.9139092	-113.9216132
CH_3F	-139.0531733	-139.0966021	-139.1065365
CH_3N	-94.0447287	-94.0694743	-94.0754110
HOCN cyanic acid	-167.7483341	-167.7927349	-167.8036432
HCNO fulminic acid	-167.6519233	-167.6976696	-167.7085414
HNCO isocyanic acid	-167.7866069	-167.8317008	-167.8428200
HONC isofulminic acid	-167.6519538	-167.6967827	-167.7076565
C_2H_2	-76.8278474	-76.8504401	-76.8551537
C_2H_3N	-131.9415420	-131.9749648	-131.9829276
C_2H_4	-78.0419831	-78.0646525	-78.0695980
CF_2O	-311.6436661	-311.7391446	-311.7619284
CH_4O	-115.0570004	-115.0916188	-115.0994153
CH_4	-40.1990176	-40.2134796	-40.2162112
CHF_3	-336.8021157	-336.9089992	-336.9337091
CHFO	-212.7718667	-212.8344117	-212.8495882
H_2O_2	-150.7936961	-150.8385905	-150.8489398
N_2H_4	-111.1957926	-111.2271207	-111.2344558

2. CCSD(T) correlation energies

2.1. CCSD(T) correlation energies (in hartree) calculated with aug-cc-pV*X*Z basis sets

Species	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	aug-cc-pV6Z[a]
H	0.0000000	0.0000000	0.0000000	0.0000000
He	-0.0338438	-0.0394145	-0.0410116	-0.0417823
B	-0.0605282	-0.0662792	-0.0679634	-0.0686631
C	-0.0771026	-0.0900142	-0.0935236	-0.0951370
N	-0.0937982	-0.1157617	-0.1216914	-0.1245376
O	-0.1290527	-0.1659701	-0.1776426	-0.1836075
F	-0.1689776	-0.2209476	-0.2388227	-0.2483350
Ne	-0.2129449	-0.2793750	-0.3037036	-0.3169739
Al	-0.0485318	-0.0523281	-0.0533232	-0.0539461
Si	-0.0673689	-0.0772056	-0.0793569	-0.0806323
P	-0.0867397	-0.1057216	-0.1095260	-0.1118601
S	-0.1118165	-0.1462694	-0.1552928	-0.1601878
Cl	-0.1394404	-0.1902468	-0.2055636	-0.2137281
Ar	-0.1687122	-0.2354063	-0.2582505	-0.2703217
CF^+	-0.3134503	-0.3807793	-0.4044170	-0.4163684
CF^-	-0.3323472	-0.4076824	-0.4329973	-0.4458125
CF	-0.3147173	-0.3875776	-0.4123135	-0.4248316
CH^-	-0.1358687	-0.1576445	-0.1632512	-0.1657667
CN^-	-0.3144826	-0.3702002	-0.3873434	-0.3955666
CN	-0.2843159	-0.3344794	-0.3499460	-0.3573574
CO	-0.3182189	-0.3802988	-0.4009911	-0.4112187
FO	-0.3929498	-0.4895449	-0.5219974	-0.5388001
H_2	-0.0358573	-0.0396302	-0.0404172	-0.0407560
HF	-0.2304211	-0.2887681	-0.3090866	-0.3192799
N_2	-0.3316301	-0.3946316	-0.4143171	-0.4239277
NF	-0.3394217	-0.4216940	-0.4489756	-0.4629004
NH	-0.1337657	-0.1626962	-0.1706956	-0.1744198
NO^+	-0.3545538	-0.4211767	-0.4431244	-0.4541702
NO	-0.3538432	-0.4269350	-0.4504341	-0.4621930
O_2	-0.3780786	-0.4624765	-0.4899127	-0.5038251
OH^-	-0.2482970	-0.2975772	-0.3137004	-0.3216329
OH	-0.1805675	-0.2241366	-0.2380520	-0.2448487
Cl_2^-	-0.3357587	-0.4461473	-0.4818469	-0.5002192
NCl	-0.2952859	-0.3771954	-0.4023539	-0.4155385
NO^-	-0.3640145	-0.4406568	-0.4650750	-0.4772483
SCl^-	-0.3261533	-0.4263262	-0.4579640	-0.4744913

SF^-	-0.3805289	-0.4800773	-0.5129163	-0.5299062
SH^-	-0.1820976	-0.2282721	-0.2418298	-0.2484957
SiH^-	-0.1088349	-0.1263910	-0.1305239	-0.1325150
SN^-	-0.3123887	-0.3857936	-0.4081081	-0.4195716
AlF	-0.2755883	-0.3380773	-0.3601241	-0.3715793
AlH_3	-0.1072983	-0.1206612	-0.1240928	-0.1254122
BN	-0.2147632	-0.2549749	-0.2675484	-0.2733684
BP	-0.1841523	-0.2193050	-0.2289656	-0.2338067
Cl_2O	-0.5486454	-0.7001836	-0.7477459	-0.7727367
Cl_2	-0.3288235	-0.4383323	-0.4727465	-0.4912249
ClCN	-0.4682045	-0.5759695	-0.6093711	-0.6262135
ClO	-0.3465517	-0.4423106	-0.4727607	-0.4888766
COS	-0.4839355	-0.5890094	-0.6221162	-0.6388721
CS_2	-0.4479349	-0.5495251	-0.5797376	-0.5955717
CS	-0.2867011	-0.3449459	-0.3623546	-0.3714129
FS	-0.3477882	-0.4403273	-0.4704738	-0.4863895
H_2S_2	-0.3330818	-0.4197736	-0.4448613	-0.4578739
H_2S	-0.1826339	-0.2270901	-0.2392699	-0.2453664
HCl	-0.1796586	-0.2357560	-0.2528984	-0.2617608
HS	-0.1458088	-0.1855156	-0.1963233	-0.2018745
PH_2	-0.1438776	-0.1724888	-0.1795958	-0.1830382
PO^+	-0.3257266	-0.3849028	-0.4046450	-0.4148922
PO^-	-0.3311221	-0.4024850	-0.4250401	-0.4366375
PO	-0.3246879	-0.3907628	-0.4119819	-0.4229801
S_2	-0.2873630	-0.3656824	-0.3891188	-0.4017493
SiF	-0.2923536	-0.3609203	-0.3843616	-0.3966288
SiH_4	-0.1564039	-0.1792471	-0.1855079	-0.1880142
SiO	-0.3069761	-0.3635361	-0.3824914	-0.3921231
SiS	-0.2488753	-0.3036906	-0.3211727	-0.3303384
SO_3	-0.7754729	-0.9456176	-1.0044647	-1.0352039
SO	-0.3377050	-0.4168946	-0.4418406	-0.4549337
PO_2	-0.5372451	-0.6481420	-0.6859147	-0.7052430
BH_3	-0.1210948	-0.1387608	-0.1433294	-0.1451116
C_2H	-0.2480006	-0.2930199	-0.3062328	-0.3120748
FCN cyanogen fluoride	-0.5123092	-0.6220135	-0.6583097	-0.6762699
FNC isocyanogen fluoride	-0.5189336	-0.6270591	-0.6626173	-0.6802016
CH_2	-0.1198378	-0.1420726	-0.1478675	-0.1502959
CH_3	-0.1584410	-0.1856718	-0.1929298	-0.1959621
CO_2	-0.5221573	-0.6310005	-0.6674378	-0.6853883
FNO	-0.6108401	-0.7400425	-0.7835018	-0.8055421
H_2O	-0.2326673	-0.2819942	-0.2978808	-0.3053887
HCN	-0.3145983	-0.3707478	-0.3877275	-0.3956655

HCO	-0.3319779	-0.3975791	-0.4187518	-0.4290034
HO_2	-0.3982527	-0.4870862	-0.5158494	-0.5300994
N_2O	-0.5580766	-0.6670613	-0.7017554	-0.7186350
NH_2	-0.1768923	-0.2120152	-0.2219139	-0.2264020
NO_2	-0.5853113	-0.7032888	-0.7418086	-0.7610051
AlH_2	-0.0798560	-0.0896352	-0.0921752	-0.0931892
BF	-0.2878877	-0.3525372	-0.3754116	-0.3869299
BO	-0.2644276	-0.3182265	-0.3370250	-0.3460174
BS	-0.2179539	-0.2679846	-0.2831962	-0.2909640
C_2H_3	-0.2862536	-0.3364174	-0.3505338	-0.3566016
CH_3Cl	-0.3421755	-0.4266575	-0.4515947	-0.4638945
HOCl	-0.3871329	-0.4877484	-0.5196170	-0.5359034
HOF	-0.4413519	-0.5436142	-0.5777534	-0.5950632
NSi	-0.2611998	-0.3037682	-0.3171180	-0.3236993
P_2H_4	-0.3209999	-0.3850191	-0.4021097	-0.4103877
SiH_3Cl	-0.2992715	-0.3761783	-0.4009298	-0.4131504
SiO_2	-0.5155426	-0.6191272	-0.6545115	-0.6722716
CCl	-0.2722340	-0.3444718	-0.3668170	-0.3785133
HN_3	-0.5436337	-0.6447204	-0.6756594	-0.6901130
NF_2	-0.5890078	-0.7295533	-0.7774361	-0.8020259
PF_2	-0.5377653	-0.6727872	-0.7194884	-0.7440034
C_2F_2	-0.6822299	-0.8403311	-0.8937993	-0.9201577
C_3H_4 cyclopropene	-0.4592979	-0.5385974	-0.5607428	-0.5704411
C_4H_4 tetrahedrane	-0.5976799	-0.7023026	-0.7317017	-0.7449494
CH_2F_2	-0.5838287	-0.7222911	-0.7694731	-0.7930451
CH_2N_2 cyanamide	-0.4989585	-0.5921505	-0.6202610	-0.6332283
CH_2O	-0.3587073	-0.4284472	-0.4505598	-0.4611280
CH_3F	-0.3890406	-0.4740722	-0.5017109	-0.5152124
CH_3N	-0.3487128	-0.4104726	-0.4285247	-0.4366483
HOCN cyanic acid	-0.5124272	-0.6139889	-0.6461539	-0.6615137
HCNO fulminic acid	-0.5343195	-0.6365786	-0.6686128	-0.6839249
HNCO isocyanic acid	-0.5120005	-0.6135322	-0.6459975	-0.6615000
HONC isofulminic acid	-0.5161198	-0.6160818	-0.6476578	-0.6627075
C_2H_2	-0.2900248	-0.3410420	-0.3555717	-0.3619371
C_2H_3N	-0.4765222	-0.5611760	-0.5857404	-0.5969140
C_2H_4	-0.3243428	-0.3785957	-0.3938077	-0.4003050
CF_2O	-0.7492052	-0.9263749	-0.9876212	-1.0184490
CH_4O	-0.3938629	-0.4703275	-0.4936411	-0.5044433
CH_4	-0.1956470	-0.2273128	-0.2354943	-0.2389515
CHF_3	-0.7787322	-0.9706101	-1.0373721	-1.0710334
CHFO	-0.5557991	-0.6792813	-0.7210036	-0.7417140
H_2O_2	-0.4413783	-0.5350618	-0.5651780	-0.5798000
N_2H_4	-0.4072369	-0.4837571	-0.5061333	-0.5161767

[a]aug-cc-pV6Z results are obtained from *J. Phys. Chem. A* **2024**, 128, 18, 3742–3749.

2.2. CCSD(T) correlation energies (in hartree) calculated with jul-cc-pV*X*Z basis sets

Species	jul-cc-pVDZ	jul-cc-pVTZ	jul-cc-pVQZ
H	0.0000000	0.0000000	0.0000000
He	-0.0324347	-0.0390788	-0.0408967
B	-0.0605282	-0.0662791	-0.0679635
C	-0.0771025	-0.0900142	-0.0935235
N	-0.0937982	-0.1157617	-0.1216914
O	-0.1290528	-0.1659701	-0.1776426
F	-0.1689775	-0.2209474	-0.2388227
Ne	-0.2129449	-0.2793750	-0.3037036
Al	-0.0485317	-0.0523281	-0.0533232
Si	-0.0673689	-0.0772056	-0.0793569
P	-0.0867397	-0.1057216	-0.1095259
S	-0.1118165	-0.1462694	-0.1552928
Cl	-0.1394403	-0.1902468	-0.2055635
Ar	-0.1687122	-0.2354063	-0.2582505
CF^+	-0.3134509	-0.3807798	-0.4044174
CF^-	-0.3323455	-0.4076813	-0.4329967
CF	-0.3147363	-0.3875930	-0.4123275
CH^-	-0.1349396	-0.1570852	-0.1630368
CN^-	-0.3144811	-0.3701990	-0.3873422
CN	-0.2843151	-0.3344788	-0.3499453
CO	-0.3182185	-0.3802985	-0.4009908
FO	-0.3929554	-0.4895495	-0.5220017
H_2	-0.0347255	-0.0393976	-0.0403601
HF	-0.2296650	-0.2883794	-0.3088826
N_2	-0.3316048	-0.3946092	-0.4142957
NF	-0.3394201	-0.4216927	-0.4489743
NH	-0.1333122	-0.1623672	-0.1705811
NO^+	-0.3545413	-0.4211652	-0.4431133
NO	-0.3538429	-0.4269346	-0.4504336
O_2	-0.3780903	-0.4624874	-0.4899231
OH^-	-0.2466220	-0.2967069	-0.3133432
OH	-0.1798773	-0.2237413	-0.2378869
Cl_2^-	-0.3357600	-0.4461594	-0.4818636
NCl	-0.2952837	-0.3771984	-0.4023584
NO^-	-0.3640214	-0.4406625	-0.4650802
SCl^-	-0.3261558	-0.4263271	-0.4579644
SF^-	-0.3805345	-0.4800827	-0.5129212
SH^-	-0.1805291	-0.2273224	-0.2414846

SiH^-	-0.1063326	-0.1255202	-0.1302095
SN^-	-0.3123873	-0.3857959	-0.4081121
AlF	-0.2755552	-0.3380472	-0.3600959
AlH_3	-0.1025935	-0.1193355	-0.1237351
BN	-0.2147408	-0.2549553	-0.2675299
BP	-0.1841384	-0.2192959	-0.2289579
Cl_2O	-0.5487058	-0.7002361	-0.7477946
Cl_2	-0.3287942	-0.4383105	-0.4727296
ClCN	-0.4682195	-0.5759803	-0.6093807
ClO	-0.3465466	-0.4423105	-0.4727627
COS	-0.4839386	-0.5890143	-0.6221217
CS_2	-0.4479451	-0.5495329	-0.5797447
CS	-0.2866899	-0.3449364	-0.3623458
FS	-0.3477422	-0.4402863	-0.4704365
H_2S_2	-0.3307057	-0.4183779	-0.4442974
H_2S	-0.1808388	-0.2259118	-0.2388580
HCl	-0.1788931	-0.2351223	-0.2526539
HS	-0.1449831	-0.1849296	-0.1960987
PH_2	-0.1418186	-0.1715164	-0.1792122
PO^+	-0.3257390	-0.3849149	-0.4046566
PO^-	-0.3311304	-0.4024935	-0.4250475
PO	-0.3246875	-0.3907623	-0.4119816
S_2	-0.2873763	-0.3656938	-0.3891287
SiF	-0.2923343	-0.3609033	-0.3843460
SiH_4	-0.1517193	-0.1776799	-0.1850187
SiO	-0.3069822	-0.3635422	-0.3824973
SiS	-0.2488750	-0.3036904	-0.3211725
SO_3	-0.7755064	-0.9456487	-1.0044942
SO	-0.3377277	-0.4169165	-0.4418614
PO_2	-0.5372216	-0.6481193	-0.6858931
BH_3	-0.1182517	-0.1379852	-0.1431175
C_2H	-0.2474245	-0.2926900	-0.3061196
FCN cyanogen fluoride	-0.5123225	-0.6220258	-0.6583214
FNC isocyanogen fluoride	-0.5189231	-0.6270503	-0.6626089
CH_2	-0.1190173	-0.1416188	-0.1477021
CH_3	-0.1571333	-0.1850306	-0.1927032
CO_2	-0.5221627	-0.6310054	-0.6674425
FNO	-0.6108419	-0.7400435	-0.7835023
H_2O	-0.2310353	-0.2812078	-0.2976123
HCN	-0.3138988	-0.3703114	-0.3875998
HCO	-0.3313722	-0.3972604	-0.4186204
HO_2	-0.3973804	-0.4866011	-0.5156307
N_2O	-0.5580877	-0.6670708	-0.7017642

NH_2	-0.1757624	-0.2113484	-0.2216891
NO_2	-0.5853315	-0.7033071	-0.7418261
AlH_2	-0.0765023	-0.0886673	-0.0918996
BF	-0.2878872	-0.3525368	-0.3754112
BO	-0.2644581	-0.3182542	-0.3370505
BS	-0.2179513	-0.2679826	-0.2831946
C_2H_3	-0.2846118	-0.3355721	-0.3502361
CH_3Cl	-0.3402198	-0.4254528	-0.4511846
HOCl	-0.3861723	-0.4871683	-0.5193471
HOF	-0.4405792	-0.5432041	-0.5776123
NSi	-0.2612013	-0.3037687	-0.3171177
P_2H_4	-0.3163518	-0.3828771	-0.4012109
SiH_3Cl	-0.2959090	-0.3748769	-0.4004660
SiO_2	-0.5155378	-0.6191230	-0.6545079
CCl	-0.2722338	-0.3444715	-0.3668166
HN_3	-0.5428783	-0.6443055	-0.6755265
NF_2	-0.5889603	-0.7295131	-0.7773984
PF_2	-0.5377370	-0.6727625	-0.7194643
C_2F_2	-0.6822474	-0.8403455	-0.8938127
C_3H_4 cyclopropene	-0.4566549	-0.5373505	-0.5603342
C_4H_4 tetrahedrane	-0.5941603	-0.7011453	-0.7313468
CH_2F_2	-0.5825506	-0.7215245	-0.7692128
CH_2N_2 cyanamide	-0.4977632	-0.5914159	-0.6200118
CH_2O	-0.3575368	-0.4279067	-0.4503519
CH_3F	-0.3875024	-0.4731727	-0.5014047
CH_3N	-0.3470037	-0.4096281	-0.4282373
HOCN cyanic acid	-0.5117773	-0.6136061	-0.6460038
HCNO fulminic acid	-0.5336728	-0.6362028	-0.6684975
HNCO isocyanic acid	-0.5113713	-0.6131414	-0.6458359
HONC isofulminic acid	-0.5154031	-0.6156941	-0.6475244
C_2H_2	-0.2889872	-0.3404589	-0.3554087
C_2H_3N	-0.4751348	-0.5603071	-0.5854533
C_2H_4	-0.3222739	-0.3775714	-0.3934563
CF_2O	-0.7492063	-0.9263757	-0.9876221
CH_4O	-0.3914931	-0.4690785	-0.4932002
CH_4	-0.1940527	-0.2264581	-0.2352073
CHF_3	-0.7779585	-0.9701484	-1.0372080
CHFO	-0.5551503	-0.6789274	-0.7208766
H_2O_2	-0.4395070	-0.5341550	-0.5648271
N_2H_4	-0.4041894	-0.4820991	-0.5055601

2.3. CCSD(T) correlation energies (in hartree) calculated with jun-cc-pV*X*Z basis sets

Species	jun-cc-pVDZ	jun-cc-pVTZ	jun-cc-pVQZ
H	0.0000000	0.0000000	0.0000000
He	-0.0324347	-0.0390788	-0.0408967
B	-0.0596561	-0.0661256	-0.0679097
C	-0.0745013	-0.0895594	-0.0933774
N	-0.0887730	-0.1148793	-0.1214207
O	-0.1208234	-0.1640578	-0.1769898
F	-0.1566330	-0.2178126	-0.2377223
Ne	-0.1955857	-0.2748436	-0.3020859
Al	-0.0478286	-0.0522208	-0.0532820
Si	-0.0651901	-0.0768924	-0.0792454
P	-0.0826369	-0.1050622	-0.1093150
S	-0.1046213	-0.1447529	-0.1547698
Cl	-0.1288007	-0.1876627	-0.2046527
Ar	-0.1542168	-0.2316240	-0.2568301
CF^+	-0.3035501	-0.3774403	-0.4030414
CF^-	-0.3093056	-0.4018426	-0.4307427
CF	-0.2990753	-0.3831700	-0.4105328
CH^-	-0.1267412	-0.1553189	-0.1625878
CN^-	-0.3023707	-0.3661949	-0.3859564
CN	-0.2768015	-0.3318152	-0.3489317
CO	-0.3078088	-0.3769840	-0.3997046
FO	-0.3700574	-0.4831603	-0.5195321
H_2	-0.0347255	-0.0393976	-0.0403601
HF	-0.2156530	-0.2849166	-0.3075926
N_2	-0.3233599	-0.3913723	-0.4130220
NF	-0.3204941	-0.4164682	-0.4469096
NH	-0.1274870	-0.1610635	-0.1701832
NO^+	-0.3473574	-0.4183723	-0.4420035
NO	-0.3412794	-0.4227774	-0.4488613
O_2	-0.3624645	-0.4574459	-0.4879810
OH^-	-0.2295792	-0.2929711	-0.3119666
OH	-0.1702902	-0.2214571	-0.2370899
Cl_2^-	-0.3022278	-0.4377846	-0.4786038
NCl	-0.2783720	-0.3721478	-0.4004281
NO^-	-0.3436296	-0.4347830	-0.4629043
SCl^-	-0.2969076	-0.4190285	-0.4552019
SF^-	-0.3481891	-0.4717254	-0.5096877

SH^-	-0.1634743	-0.2236840	-0.2401089
SiH^-	-0.0997989	-0.1240725	-0.1297779
SN^-	-0.2908800	-0.3798773	-0.4058558
AlF	-0.2574382	-0.3331000	-0.3579983
AlH_3	-0.1022751	-0.1191030	-0.1236531
BN	-0.2089094	-0.2529109	-0.2667443
BP	-0.1791061	-0.2175446	-0.2282199
Cl_2O	-0.5121731	-0.6899990	-0.7437956
Cl_2	-0.3055249	-0.4318444	-0.4703990
ClCN	-0.4494143	-0.5697830	-0.6071603
ClO	-0.3236370	-0.4360721	-0.4702761
COS	-0.4642979	-0.5828527	-0.6198121
CS_2	-0.4300958	-0.5436490	-0.5775499
CS	-0.2773629	-0.3418121	-0.3611246
FS	-0.3237876	-0.4337722	-0.4678432
H_2S_2	-0.3134015	-0.4135246	-0.4426540
H_2S	-0.1717309	-0.2237242	-0.2381593
HCl	-0.1665184	-0.2321974	-0.2516164
HS	-0.1368066	-0.1830664	-0.1954654
PH_2	-0.1371218	-0.1702864	-0.1787837
PO^+	-0.3159882	-0.3816363	-0.4030709
PO^-	-0.3096700	-0.3965550	-0.4226057
PO	-0.3100221	-0.3864134	-0.4100385
S_2	-0.2729667	-0.3614157	-0.3874985
SiF	-0.2740425	-0.3557724	-0.3821913
SiH_4	-0.1500405	-0.1770325	-0.1848010
SiO	-0.2940406	-0.3595420	-0.3806478
SiS	-0.2382521	-0.3006977	-0.3198760
SO_3	-0.7358722	-0.9339845	-0.9991094
SO	-0.3201362	-0.4119236	-0.4397331
PO_2	-0.5115953	-0.6405355	-0.6823976
BH_3	-0.1177280	-0.1376661	-0.1430176
C_2H	-0.2420983	-0.2905598	-0.3053170
FCN cyanogen fluoride	-0.4910347	-0.6155100	-0.6558320
FNC isocyanogen fluoride	-0.4972687	-0.6204326	-0.6599933
CH_2	-0.1156095	-0.1408248	-0.1474893
CH_3	-0.1529578	-0.1841862	-0.1924617
CO_2	-0.5011009	-0.6246675	-0.6650185
FNO	-0.5821240	-0.7314764	-0.7801066
H_2O	-0.2201650	-0.2787611	-0.2967577
HCN	-0.3055344	-0.3673931	-0.3865511
HCO	-0.3198674	-0.3937143	-0.4172704
HO_2	-0.3785346	-0.4812411	-0.5135654

N_2O	-0.5402633	-0.6606444	-0.6992942
NH_2	-0.1687237	-0.2097673	-0.2211969
NO_2	-0.5633133	-0.6961322	-0.7390191
AlH_2	-0.0762698	-0.0884579	-0.0918252
BF	-0.2748132	-0.3486762	-0.3738502
BO	-0.2552953	-0.3154206	-0.3358134
BS	-0.2096482	-0.2654443	-0.2821976
C_2H_3	-0.2777841	-0.3334394	-0.3495051
CH_3Cl	-0.3241302	-0.4207252	-0.4495118
HOCl	-0.3625203	-0.4809212	-0.5169638
HOF	-0.4158823	-0.5364915	-0.5750370
NSi	-0.2524146	-0.3008767	-0.3158159
P_2H_4	-0.3053470	-0.3795717	-0.4000176
SiH_3Cl	-0.2816522	-0.3710276	-0.3989455
SiO_2	-0.4915918	-0.6117310	-0.6511002
CCl	-0.2591670	-0.3403181	-0.3652915
HN_3	-0.5283981	-0.6387299	-0.6733613
NF_2	-0.5552450	-0.7200301	-0.7735722
PF_2	-0.5008781	-0.6623307	-0.7151145
C_2F_2	-0.6500029	-0.8308311	-0.8899707
C_3H_4 cyclopropene	-0.4474682	-0.5336252	-0.5590894
C_4H_4 tetrahedrane	-0.5803718	-0.6949651	-0.7294925
CH_2F_2	-0.5494959	-0.7128305	-0.7655756
CH_2N_2 cyanamide	-0.4819860	-0.5863456	-0.6182074
CH_2O	-0.3451767	-0.4242693	-0.4489910
CH_3F	-0.3682829	-0.4682335	-0.4994184
CH_3N	-0.3375918	-0.4067893	-0.4272390
HOCN cyanic acid	-0.4936755	-0.6079384	-0.6439088
HCNO fulminic acid	-0.5156133	-0.6301853	-0.6662572
HNCO isocyanic acid	-0.4925457	-0.6072583	-0.6436695
HONC isofulminic acid	-0.4976409	-0.6101566	-0.6453819
C_2H_2	-0.2830304	-0.3381043	-0.3546050
C_2H_3N	-0.4623438	-0.5559887	-0.5839841
C_2H_4	-0.3150513	-0.3755041	-0.3927365
CF_2O	-0.7095882	-0.9151165	-0.9829220
CH_4O	-0.3765895	-0.4653213	-0.4917831
CH_4	-0.1889640	-0.2253092	-0.2349112
CHF_3	-0.7314996	-0.9576365	-1.0319234
CHFO	-0.5285910	-0.6714396	-0.7178299
H_2O_2	-0.4189959	-0.5286407	-0.5627168
N_2H_4	-0.3898208	-0.4782233	-0.5041562

3. B3LYP/cc-pVTZ optimized geometries (Å)

The line below the formula gives the charge and spin multiplicity.

CF^+
1, 1

C	0.57840076	0.00000000	0.00000000
F	-0.57840076	0.00000000	0.00000000

CF^-
-1, 3

C	0.72869744	0.00000000	0.00000000
F	-0.72869744	0.00000000	0.00000000

CF
0, 2

C	0.63790069	0.00000000	0.00000000
F	-0.63790069	0.00000000	0.00000000

CH^-
-1, 3

C	0.57560822	0.00000000	0.00000000
H	-0.57560822	0.00000000	0.00000000

CN^-
-1, 1

C	0.58528138	0.00000000	0.00000000
N	-0.58528138	0.00000000	0.00000000

CN
0, 2

C	0.58140125	0.00000000	0.00000000
N	-0.58140125	0.00000000	0.00000000

CO
0, 1

C	0.56307647	0.00000000	0.00000000
O	-0.56307647	0.00000000	0.00000000

FO
0, 2

F	0.67519692	0.00000000	0.00000000
O	-0.67519692	0.00000000	0.00000000

H_2
0, 1
H 0.37145574 0.00000000 0.00000000
H -0.37145574 0.00000000 0.00000000

HF
0, 1
F 0.46115116 0.00000000 0.00000000
H -0.46115116 0.00000000 0.00000000

N_2
0, 1
N 0.54568651 0.00000000 0.00000000
N -0.54568651 0.00000000 0.00000000

NF
0, 3
N 0.65910573 0.00000000 0.00000000
F -0.65910573 0.00000000 0.00000000

NH
0, 3
N 0.52051547 0.00000000 0.00000000
H -0.52051547 0.00000000 0.00000000

NO^+
1, 1
N 0.52864029 0.00000000 0.00000000
O -0.52864029 0.00000000 0.00000000

NO
0, 2
N 0.57298044 0.00000000 0.00000000
O -0.57298044 0.00000000 0.00000000

O_2
0, 3
O 0.60296471 0.00000000 0.00000000
O -0.60296471 0.00000000 0.00000000

OH^-			
-1, 1			
O	0.48565496	0.00000000	0.00000000
H	-0.48565496	0.00000000	0.00000000
OH			
0, 2			
O	0.48731076	0.00000000	0.00000000
H	-0.48731076	0.00000000	0.00000000
Cl_2^-			
-1, 2			
Cl	1.36052987	0.00000000	0.00000000
Cl	-1.36052987	0.00000000	0.00000000
NCl			
0, 3			
N	0.81702149	0.00000000	0.00000000
Cl	-0.81702149	0.00000000	0.00000000
NO^-			
-1, 3			
N	0.63451525	0.00000000	0.00000000
O	-0.63451525	0.00000000	0.00000000
SCl^-			
-1, 1			
S	0.00000000	0.00000000	0.00000000
Cl	0.00000000	0.00000000	2.15700000
SF^-			
-1, 1			
S	0.87445869	0.00000000	0.00000000
F	-0.87445869	0.00000000	0.00000000
SH^-			
-1, 1			
S	0.00000000	0.00000000	0.00000000
H	0.00000000	0.00000000	1.35200000

SiH^-			
-1, 3			
Si	0.00000000	0.00000000	0.00000000
H	0.00000000	0.00000000	1.56600000
SN^-			
-1, 3			
S	0.00000000	0.00000000	0.00000000
N	0.00000000	0.00000000	1.61300000
AlF			
0, 1			
Al	0.84108500	0.00000000	0.00000000
F	-0.84108500	0.00000000	0.00000000
AlH_3			
0, 1			
Al	0.00014569	0.00027490	-0.00054326
H	1.57864080	-0.11377141	0.00011260
H	-0.88725812	-1.31016829	0.00025014
H	-0.69152836	1.42366481	0.00018052
BN			
0, 3			
B	0.00000000	0.00000000	-0.00015104
N	0.00000000	0.00000000	1.31915104
BP			
0, 3			
B	0.00000000	0.00000000	0.00000000
P	0.00000000	0.00000000	1.74400000
Cl_2O			
0, 1			
O	-0.00072939	0.63517071	0.00000000
Cl	1.42749707	-0.31594634	0.00000000
Cl	-1.42676868	-0.31922337	0.00000000
Cl_2			
0, 1			
Cl	1.01157154	0.00000000	0.00000000
Cl	-1.01157154	0.00000000	0.00000000

ClCN
0, 1

Cl	1.47417353	-0.06258807	0.00000000
C	-0.16100771	0.00747421	0.00000000
N	-1.31316583	0.05511387	0.00000000

ClO
0, 2

Cl	0.79647703	0.00000000	0.00000000
O	-0.79647703	0.00000000	0.00000000

COS
0, 1

C	-0.52740000	0.00000000	0.00000000
O	-1.68340000	0.00000000	0.00000000
S	1.03950000	0.00000000	0.00000000

CS_2
0, 1

S	1.55761326	0.00000000	0.00000000
C	0.00000000	0.00000000	0.00000000
S	-1.55761326	0.00000000	0.00000000

CS
0, 1

C	0.00000000	0.00000000	0.00000000
S	0.00000000	0.00000000	1.53700000

FS
0, 2

F	0.80838773	0.00000000	0.00000000
S	-0.80838773	0.00000000	0.00000000

H_2S_2
0, 1

S	-0.05531720	1.04295798	0.00005921
S	-0.05531720	-1.04295798	-0.00005921
H	0.88391720	1.23861633	0.94928613
H	0.88391720	-1.23861633	-0.94928613

H_2S
0, 1

S	0.00000000	0.00000000	0.10362245
H	0.00000000	0.97156361	-0.82591123
H	0.00000000	-0.97156361	-0.82591123

HCl
0, 1

Cl	0.00000000	0.00000000	0.00027318
H	0.00000000	0.00000000	1.28372682

HS
0, 2

S	0.67446749	0.00000000	0.00000000
H	-0.67446749	0.00000000	0.00000000

PH_2
0, 2

P	-0.00326534	0.66143506	0.00000000
H	-1.02171641	-0.33557791	0.00000000
H	1.02498075	-0.32585716	0.00000000

PO^+
1, 1

P	0.71535094	0.00000000	0.00000000
O	-0.71535094	0.00000000	0.00000000

PO^-
-1, 3

P	0.78027174	0.00000000	0.00000000
O	-0.78027174	0.00000000	0.00000000

PO
0, 2

P	0.74352411	0.00000000	0.00000000
O	-0.74352411	0.00000000	0.00000000

S_2
0, 3

S	0.95690033	0.00000000	0.00000000
S	-0.95690033	0.00000000	0.00000000

SiF
0, 2
Si 0.81399751 0.00000000 0.00000000
F -0.81399751 0.00000000 0.00000000

SiH_4
0, 1
Si -0.00000313 -0.00005059 0.00010636
H -0.25117933 -1.05652093 -1.00923224
H -0.71655175 1.23766594 -0.39061014
H 1.45488654 0.27478118 0.07571282
H -0.48715233 -0.45587560 1.32402319

SiO
0, 1
Si 0.75929000 0.00000000 0.00000000
O -0.75929000 0.00000000 0.00000000

SiS
0, 1
Si 0.97241850 0.00000000 0.00000000
S -0.97241850 0.00000000 0.00000000

SO_3
0, 1
O -0.76794098 -1.21669262 0.00131982
S -0.00012989 -0.00012445 -0.00003836
O -0.66985258 1.27360852 0.00146343
O 1.43792446 -0.05679145 -0.00274489

SO
0, 3
S 0.00000000 0.00000000 0.00000000
O 0.00000000 0.00000000 1.50000000

PO_2
0, 2
O -1.35420098 -0.22944875 0.00000000
P -0.00979037 0.39211049 0.00000000
O 1.36399135 -0.16266174 0.00000000

BH_3

0, 1

B	0.00000441	-0.00000813	-0.00005582
H	-0.86119920	-0.81840000	0.00001512
H	-0.27814467	1.15501216	0.00006273
H	1.13933846	-0.33660303	-0.00002203

C_2H

0, 2

C	-0.47180000	0.00000000	0.00000000
C	0.72760000	0.00000000	0.00000000
H	-1.53480000	0.00000000	0.00000000

FCN cyanogen fluoride

0, 1

F	1.11410000	0.00000000	0.00000000
C	-0.15160000	0.00000000	0.00000000
N	-1.30250000	0.00000000	0.00000000

FNC isocyanogen fluoride

0, 1

C	-1.38710000	0.00000000	0.00000000
N	-0.21460000	0.00000000	0.00000000
F	1.09170000	0.00000000	0.00000000

CH_2

0, 3

C	-0.00074798	0.27539281	0.00000000
H	-0.99508313	-0.14011483	0.00000000
H	0.99583111	-0.13527898	0.00000000

CH_3

0, 2

C	0.00001832	-0.00005577	-0.00046233
H	1.05234433	-0.23379677	-0.00184687
H	-0.72873549	-0.79437397	0.00147308
H	-0.32362717	1.02822651	0.00083712

CO_2

0, 1

O	-1.15420435	0.24998321	0.00000000
C	-0.00003589	0.12985655	0.00000000
O	1.15424124	0.01083724	0.00000000

FNO
0, 1

F	1.16961167	-0.25383769	0.00000000
N	-0.15343389	0.49116962	0.00000000
O	-1.01617778	-0.23733193	0.00000000

H_2O
0, 1

O	-0.00034962	0.39235909	0.00000000
H	0.76040112	-0.19551113	0.00000000
H	-0.76005050	-0.19684796	0.00000000

HCN
0, 1

C	0.00000000	0.00000000	-0.49700000
H	0.00000000	0.00000000	-1.56240000
N	0.00000000	0.00000000	0.64920000

HCO
0, 2

C	-0.02707079	0.35653432	0.00000000
O	1.02904209	-0.15390514	0.00000000
H	-1.00197130	-0.20263019	0.00000000

HO_2
0, 2

O	-0.17057496	0.44391353	0.00000000
O	1.00546189	-0.17410690	0.00000000
H	-0.83488593	-0.26980663	0.00000000

N_2O
0, 1

N	0.00000000	0.00000000	-1.19510000
N	0.00000000	0.00000000	-0.07340000
O	0.00000000	0.00000000	1.11000000

NH_2
0, 2

N	-0.00138207	0.42784398	0.00000000
H	-0.80216172	-0.21651483	0.00000000
H	0.80354479	-0.21132915	0.00000000

NO_2
0, 2

N	-0.00594385	0.30795209	0.00000000
O	-1.09554720	-0.17514621	0.00000000
O	1.10149104	-0.13280588	0.00000000

AlH_2
0, 2

Al	-0.00009697	0.54926464	0.00000000
H	1.37340795	-0.27432112	0.00000000
H	-1.37331099	-0.27494352	0.00000000

BF
0, 1

B	0.63213141	0.00000000	0.00000000
F	-0.63213141	0.00000000	0.00000000

BO
0, 2

B	0.60157768	0.00000000	0.00000000
O	-0.60157768	0.00000000	0.00000000

BS
0, 2

B	0.80647843	0.00000000	0.00000000
S	-0.80647843	0.00000000	0.00000000

C_2H_3
0, 2

C	-0.45280457	0.09179040	-0.09688755
C	0.77973952	0.22538269	0.29760068
H	-1.16774536	0.90794731	-0.05611644
H	-0.83245052	-0.85272907	-0.49092924
H	1.67325993	-0.37239133	0.37402655

CH_3Cl
0, 1

C	-0.15573330	-0.00604465	0.00194728
Cl	1.64229476	0.06313730	-0.01398137
H	-0.48120970	-0.16206345	1.02444304
H	-0.47026953	-0.82949614	-0.63004945
H	-0.53508223	0.93446695	-0.38235950

HOCl
0, 1

O	-0.34678619	0.47639615	0.00000000
Cl	1.24173126	-0.15630841	0.00000000
H	-0.89494607	-0.32008775	0.00000000

HOF
0, 1

O	-0.21888459	0.48894550	0.00000000
F	1.02926780	-0.20878537	0.00000000
H	-0.81038320	-0.28016013	0.00000000

NSi
0, 2

N	0.78674499	0.00000000	0.00000000
Si	-0.78674499	0.00000000	0.00000000

P_2H_4
0, 1

P	-1.02445682	-0.56520544	-0.36191222
P	1.07509417	-0.40735865	0.42072721
H	-1.25631190	0.79274886	-0.70729701
H	-1.63159652	-0.44246405	0.91574943
H	1.67552330	-0.37672471	-0.86559732
H	1.16174777	0.99900399	0.59832991

SiH_3Cl
0, 1

Si	-0.13528499	0.00382767	0.00387728
Cl	1.93989373	-0.05395382	-0.05439506
H	-0.65654597	-0.79557103	-1.12516151
H	-0.56655882	1.41267911	-0.11679738
H	-0.58150395	-0.56698193	1.29247666

SiO_2
0, 1

O	-1.51634449	-0.00025872	0.00000000
Si	-0.00000035	0.00028611	0.00000000
O	1.51634484	-0.00002839	0.00000000

CCl
0, 2

C	0.83306581	0.00000000	0.00000000
Cl	-0.83306581	0.00000000	0.00000000

HN_3
0, 1

N	1.57641415	-0.14964774	-0.00106103
N	0.46853437	0.05298021	0.00148001
N	-0.70287367	0.44430202	0.00648435
H	-1.34207384	-0.34763548	-0.00690333

NF_2
0, 2

N	-0.00115298	0.55888695	0.00000000
F	1.06443188	-0.27815433	0.00000000
F	-1.06327890	-0.28073263	0.00000000

PF_2
0, 2

P	-0.00046056	0.69546061	0.00000000
F	1.21624701	-0.34692720	0.00000000
F	-1.21578646	-0.34853341	0.00000000

C_2F_2
0, 1

F	-1.85722671	0.18589723	-0.48938935
C	-0.58546059	0.05699905	-0.35408345
C	0.58552593	-0.05980671	-0.22734777
F	1.85716237	-0.18308957	-0.08570143

C_3H_4 cyclopropene
0, 1

C	0.75844994	-0.08020868	0.00119261
C	-0.52753786	0.70272039	-0.01597835
C	-0.66370428	-0.57629819	0.01401289
H	1.34943290	-0.16495962	-0.90849081
H	1.35130272	-0.12201798	0.91265155
H	-0.96797429	1.68221620	-0.03926921
H	-1.29996813	-1.44145211	0.03588031

C_4H_4 tetrahedrane
0, 1

C	-0.46095635	-0.44745210	-0.63441218
C	-0.52463247	0.11985265	0.72494332
C	0.25453132	0.80359864	-0.32345399
C	0.73100774	-0.47594671	0.23284506

H	-1.00611793	-0.97671174	-1.38467657
H	-1.14503419	0.26152108	1.58240843
H	0.55562736	1.75399004	-0.70596092
H	1.59557353	-1.03885186	0.50830486

CH_2F_2

0, 1

C	-0.00197219	-0.07697796	0.00188014
F	1.12208641	0.68943666	0.02018174
F	-1.08677510	0.74175718	-0.05751183
H	-0.04798488	-0.65231811	0.92726182
H	0.01464575	-0.70189878	-0.89181187

CH_2N_2 cyanamide

0, 1

N	0.76400305	0.87183542	-2.04928230
C	0.28237008	0.30341352	-1.16694599
N	-0.29720727	-0.40122066	-0.18461409
H	-1.08896301	0.04482396	0.25398718
H	0.33979715	-0.81885223	0.47724420

CH_2O

0, 1

C	-0.00532528	0.00049577	-0.00079070
O	1.17534914	-0.11765186	0.17228534
H	-0.51364971	0.98176953	0.05830123
H	-0.65637415	-0.86461345	-0.22979687

CH_3F

0, 1

C	-0.06277083	0.00609723	0.00605028
F	1.31066899	-0.12845322	-0.12578425
H	-0.32552905	-0.04094556	1.06322320
H	-0.36850580	0.96690808	-0.40915939
H	-0.55386331	-0.80360754	-0.53433083

CH_3N

0, 1

C	-0.39045179	-0.02633424	0.00392525
N	0.76890072	-0.52724251	-0.03510036
H	-0.60929492	1.04416927	0.05742540
H	-1.25278996	-0.69219801	-0.01614497
H	1.48363595	0.20160549	-0.01010532

HOCN cyanic acid

0, 1			
O	-0.74724314	-0.26553453	-0.10074117
C	0.48112801	-0.10632134	0.28512924
N	1.59100699	-0.01744495	0.58643973
H	-1.32489086	0.38930082	0.31544520

HCNO fulminic acid

0, 1			
O	1.70951010	-0.30766270	0.12801614
N	0.53312353	-0.09595965	0.03993634
C	-0.60180112	0.10816321	-0.04460780
H	-1.64083250	0.29545815	-0.12334567

HNCO isocyanic acid

0, 1			
O	1.64353400	-0.10518986	0.00224564
C	0.48903860	0.04640674	-0.00076542
N	-0.68177790	0.35241470	-0.00943174
H	-1.45079469	-0.29363158	0.00795152

HONC isofulminic acid

0, 1			
C	1.60866953	-0.12730860	0.00129777
N	0.46558222	0.04548339	-0.18162825
O	-0.79833786	0.43228551	-0.32710037
H	-1.27591389	-0.35046030	-0.64279815

C_2H_2

0, 1			
C	0.56228025	-0.06234818	-0.03601928
C	-0.56231304	0.33833442	0.03615268
H	1.56051330	-0.41785775	-0.10022119
H	-1.56048051	0.69409751	0.10008878

C_2H_3N

0, 1			
C	-0.48845175	-0.00073634	0.00208419
C	0.96638263	0.00056510	-0.00462962
N	2.11608644	0.00326838	-0.00919701
H	-0.86804491	-0.63943299	-0.79478099
H	-0.86000079	-0.37363783	0.95601421
H	-0.86597063	1.00997369	-0.14949179

C_2H_4

0, 1

C	0.60183501	0.06096972	-0.26943890
C	-0.60151421	-0.06091000	0.26928632
H	1.16307981	-0.80043220	-0.60866730
H	1.07501036	1.02656453	-0.39334504
H	-1.07519816	-1.02633612	0.39345860
H	-1.16321282	0.80014507	0.60870532

CF_2O

0, 1

F	-0.82917537	-0.95374719	-0.03601659
C	-0.02692878	0.09217903	-0.00121233
F	1.21230187	-0.35447912	0.05326426
O	-0.35619773	1.21604729	-0.01603523

CH_4O

0, 1

C	-0.35866221	-0.03029044	-0.01916419
O	0.99891087	-0.40948166	-0.19204594
H	-0.62489730	0.09824988	1.03534937
H	-0.96643225	-0.83634978	-0.42669653
H	-0.60663237	0.89019117	-0.55826082
H	1.55771326	0.28768083	0.16081911

CH_4

0, 1

C	0.00080403	-0.00061612	-0.00045168
H	-0.52918824	-0.45235153	-0.83651924
H	-0.10356420	1.08166300	-0.04763505
H	-0.42260132	-0.36288884	0.93436942
H	1.05455073	-0.26580651	-0.04976344

CHF_3

0, 1

C	-0.00269854	-0.00046065	0.06239118
F	-0.08856779	1.25272721	-0.40452881
F	1.15508363	-0.53062933	-0.35252528
F	-1.00912840	-0.71726246	-0.45587459
H	-0.05468889	-0.00437577	1.15053750

CHFO

0, 1

C	-0.08808972	0.00189004	0.00578861
O	-0.87363892	-0.87343545	-0.02432743
F	1.23967338	-0.20200107	-0.09805348
H	-0.27794575	1.07354649	0.11659230

H_2O_2

0, 1

O	-0.62916127	-0.25771350	-0.36304843
O	0.62386399	-0.25945913	0.37073927
H	-1.17702480	0.27403723	0.22863986
H	1.18232209	0.24313541	-0.23633070

N_2H_4

0, 1

N	-0.67922133	-0.25309764	-0.20356341
N	0.69613689	-0.20100235	0.20452571
H	-1.01223911	0.64711273	-0.53418619
H	-1.22674247	-0.50299283	0.60908657
H	1.26085277	-0.41289561	-0.60715298
H	0.96121325	0.72287570	0.53129031