

Basis-set convergence in correlated calculations on Ne, N₂, and H₂O

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Abstract

Valence and all-electron correlation energies of Ne, N₂, and H₂O at fixed experimental geometries are computed at the levels of second-order perturbation theory (MP2) and coupled cluster theory with singles and doubles excitations (CCSD), and singles and doubles excitations with a perturbative triples correction (CCSD(T)). Correlation-consistent polarized valence and core-valence basis sets up to sextuple zeta quality are employed. Guided by basis-set limits established by r_{ij} -dependent methods, a number of extrapolation schemes for use with the correlation-consistent basis sets are investigated. Among the schemes considered here, a linear least-squares procedure applied to the quintuple and sextuple zeta results yields the most accurate extrapolations. © 1998 Elsevier Science B.V.

1. Introduction

In solving the electronic Schrödinger equation for molecular systems, two approximations are introduced: (1) the truncation in the one-electron space to a finite basis, and (2) the selection of an incomplete N -electron description in the Fock space of the chosen one-electron basis. A knowledge of the basis-set limits of the N -electron approximations is important, as it gives us information about the intrinsic errors of the different N -electron models [1], enabling us to investigate the accuracy of standard basis sets and correlation models.

The basis-set limit of correlated methods can be explored in different ways. A direct and efficient tool for this purpose is the explicitly correlated R12

method [2–7]. This method yields results close to the basis-set limit, because it includes terms linear in the interelectronic distance r_{ij} in the wave function, as required by the coulomb cusp condition. From the knowledge of the basis-set limits obtained with the R12 method, we are then able to determine the accuracy attainable with standard basis sets and standard wave functions. This makes reliable basis-set error estimation possible, even in cases where highly accurate basis sets are prohibitively large for use. Furthermore, in series of basis sets, the true basis-set convergence towards the basis-set limit can be established, and the reliability of different fits to the results obtained in these series of basis sets can be determined. The use of extrapolations of fits to results obtained in hierarchical sequences of basis

sets represents another way of deducing the basis-set limit that may be applied for cases that are prohibitively large for the R12 method [8–11]. It is therefore important to establish the accuracy of the different extrapolation schemes, since a fit that reproduces the calculated finite basis-set results will not necessarily yield the correct basis-set limit when extrapolated.

The correlation-consistent polarized valence basis sets, cc-pVXZ, and the correlation-consistent polarized core-valence basis sets, cc-pCVXZ, of Dunning and coworkers [12–16]¹ are examples of hierarchical sequences of basis sets developed for valence correlation energies and all-electron correlation energies, respectively. Several numerical examples have demonstrated that, for these basis sets, a systematic improvement is obtained when going from one level to the next in each series (see for example Refs. [17] and [18] and references therein). Therefore, these basis sets are ideally suited for extrapolation.

In this study, we present standard calculations on Ne, N₂, and H₂O at the self-consistent-field Hartree–Fock (HF) level, the second-order Møller–Plesset (MP2) level, the coupled cluster singles and doubles (CCSD) level, and for CCSD augmented with a perturbative correction for triples excitations (CCSD(T)). For all these models, the full series of cc-pVXZ and cc-pCVXZ, X = D, T, Q, 5, 6, basis sets have been employed, correlating only the valence electrons in the former series and all electrons in the latter. We also present results of MP2-R12, CCSD-R12, and CCSD(T)-R12 calculations and utilize these results to establish the basis-set convergence for the standard calculations. Similar studies have previously been reported for the all-electron correlation energy of the H₂O molecule [17] and the valence correlation energies (and spectroscopic constants) of the N₂ and HF molecules [14] at the

coupled cluster level, and for the MP2 correlation energy of the Ne atom and the HF, H₂O, and N₂ molecules [18–20]. However, the present study is somewhat more thorough as both valence and all-electron correlation energies are investigated for the MP2, CCSD, and CCSD(T) models for the three systems Ne, N₂, and H₂O, thereby increasing the amount of data significantly. With the amount of data now available, we search for the most accurate extrapolation method to the basis-set limit in order to improve our understanding of the basis-set convergence and extrapolation techniques in conjunction with the correlation-consistent basis sets.

2. Theory

It is well-known that the convergence of the correlation energy with respect to the size of the atomic basis set is very slow. Following earlier work by Schwartz [21], Carroll et al. [22] and Hill [23] established the following relationship between the maximum angular momentum quantum number ℓ of the basis set and the correlation energy of the He atom in configuration interaction calculations:

$$E_{\ell}^{\text{corr}} - E_{\ell-1}^{\text{corr}} = a\left(\ell + \frac{1}{2}\right)^{-4} + b\left(\ell + \frac{1}{2}\right)^{-5} + \dots, \quad (1)$$

assuming that the orbital space is saturated for each angular momentum individually. Similar expressions have been derived for many-electron atoms treated at the MP2 level [24]. For a near-complete basis, the first term in (1) dominates. Retaining only this term and identifying X with $\ell + 1$, straightforward algebra yields (cf. Helgaker et al. [17]):

$$E_X^{\text{corr}} = E_{\infty}^{\text{corr}} + A X^{-3}, \quad (2)$$

where the cardinal number X of the basis set (D: 2, T: 3, Q: 4, ...) has been introduced. E_X^{corr} is the correlation energy obtained with the basis set with cardinal number X , and E_{∞}^{corr} is the basis-set limit of the correlation energy.

Although Eq. (1) was originally obtained for basis sets where the orbital space is saturated for each angular momentum quantum number individually, Helgaker et al. [17] found that Eq. (2) gives accurate

¹ The basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 1.0, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, WA 99352, USA, and funded by the U.S. Department of Energy. The Pacific Northwest Laboratory is a multi-program laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC06-76RLO 1830.

estimates of the basis-set limit when applied to the series of correlation-consistent basis sets. Their estimates were based on triple through sextuple zeta results, but it was not investigated, however, how the accuracy of the estimates varied with the number of results included in the fits producing the estimates – an investigation we will perform in the present study.

For the correlation-consistent basis sets for first-row atoms, which are considered here, the following simple formula relates the number of basis functions to the cardinal number:

$$N_{\text{cc-pVXZ}} = \frac{1}{3}(X+1)(X+\frac{3}{2})(X+2), \quad (3)$$

$$N_{\text{cc-pCVXZ}} = N_{\text{cc-pVXZ}} + N_{\text{cc-pV}(X-1)\text{Z}} - 1. \quad (4)$$

The number of basis functions in the correlation-consistent basis sets thus grows as X^3 . As the leading term in the correlation energy scales as X^{-3} , we

expect to have an approximate inverse linear dependence of the correlation energy on the number of basis functions for the larger correlation-consistent basis sets [25] – that is, for those that are closest to the region where the truncation of Eq. (1) is valid.

3. Results and discussion

3.1. Computational details

All the calculations in this study were carried out at the experimental equilibrium geometries: $R_{\text{N-N}} = 109.77$ pm, $R_{\text{O-H}} = 95.72$ pm, and $\angle_{\text{H-O-H}} = 104.52^\circ$.

The explicitly correlated MP2-R12, CCSD-R12, and CCSD(T)-R12 calculations were carried out using the DIRCCR12-95 program [26]. These calcula-

Table 1

Ground-state energies for the Ne atom in atomic units. For HF the total energy is given. For the correlation models, the correlation energy is given

	HF	Δ MP2	Δ CCSD	Δ CCSD(T)
A. Valence only				
cc-pVDZ	–128.488776	–0.185523	–0.189016	–0.190060
cc-pVTZ	–128.531862	–0.264322	–0.266347	–0.270592
cc-pVQZ	–128.543470	–0.293572	–0.294682	–0.300220
cc-pV5Z	–128.546770	–0.306166	–0.305489	–0.311589
cc-pV6Z	–128.547061	–0.311791	–0.309906	–0.316201
R12 basis ^a	–128.547094	–0.312814	–	–
R12/A	–	–0.320311	–	–
R12/B	–	–0.319945	–0.315523	–0.321882
Estimated limit	–	–0.320(1)	–0.316(1)	–0.322(1)
56 Extrapolation ^b	–	–0.3195	–0.3160	–0.3225
FEM ^b	–128.547098	–0.320192	–	–
B. All electrons				
cc-pCVDZ	–128.488926	–0.228302	–0.232224	–0.233426
cc-pCVTZ	–128.531955	–0.329100	–0.331413	–0.336201
cc-pCVQZ	–128.543570	–0.361515	–0.362715	–0.368733
cc-pCV5Z	–128.546771	–0.374140	–0.373676	–0.380165
cc-pCV6Z	–128.547061	–0.379768	–0.378155	–0.384812
R12 basis ^a	–128.547094	–0.379022	–	–
R12/A	–	–0.388295	–	–
R12/B	–	–0.387807	–0.383813	–0.390497
Estimated limit	–	–0.388(1)	–0.384(1)	–0.391(1)
56 Extrapolation ^b	–	–0.3875	–0.3843	–0.3912
FEM ^c	–128.547098	–0.388102	–	–

^a 18s13p11d9f7g5h basis (293 functions).

^b Linear fit of the form (2) to $X = 5$ and $X = 6$ data.

^c Finite-element method result obtained by Flores [32].

Table 2

Ground-state energies for the N_2 molecule in atomic units $R_{N-N} = 109.77$ pm. For HF the total energy is given. For the correlation models, the correlation energy is given

	HF	Δ MP2	Δ CCSD	Δ CCSD(T)
A. Valence only				
cc-pVDZ	–108.954127	–0.306300	–0.309266	–0.321127
cc-pVTZ	–108.983468	–0.373686	–0.371890	–0.390372
cc-pVQZ	–108.991081	–0.398752	–0.393126	–0.413292
cc-pV5Z	–108.992762	–0.409118	–0.400625	–0.421425
cc-pV6Z	–108.993084	–0.413825	–0.403656	–0.424688
R12 basis ^a	–108.992951	–0.398773	–	–
R12/A	–	–0.422785	–	–
R12/B	–	–0.419775	–0.407032	–0.427197
Estimate limit	–	–0.421(2)	–0.408(2)	–0.429(2)
56 Extrapolation ^b	–	–0.4203	–0.4078	–0.4292
Numerical ^c	–108.993188	–	–	–
B. All electrons				
cc-pCVDZ	–108.954917	–0.382709	–0.387846	–0.400366
cc-pCVTZ	–108.984400	–0.477766	–0.478248	–0.498004
cc-pCVQZ	–108.991312	–0.510688	–0.507112	–0.528525
cc-pCV5Z	–108.992828	–0.523145	–0.516697	–0.538680
cc-pCV6Z	–108.993100	–0.528712	–0.520555	–0.542753
R12 basis ^a	–108.992951	–0.511747	–	–
R12/A	–	–0.538888	–	–
R12/B	–	–0.535511	–0.524875	n.a. ^d
Estimated limit	–	–0.537(2)	–0.526(2)	–0.548(2)
56 Extrapolation ^b	–	–0.5364	–0.5259	–0.5483
Numerical ^c	–108.993188	–	–	–

^a 20s15p12d10f basis (390 functions).

^b Linear fit of the form (2) to $X = 5$ and $X = 6$ data.

^c Numerical Hartree–Fock.

^d Not available.

tions require large, non-standard basis sets to satisfy completeness conditions concerning the approximate evaluation of many-electron integrals. For Ne and H_2O , the 18s13p11d9f7g5h and cc-pV6Z(uc) + S basis sets, respectively, were taken from earlier work [5–7,17]. The 20s15p12d10f basis set for N_2 was obtained by augmenting the 18s13p uncontracted basis set of Partridge [27] ² with two diffuse s functions (with exponents 0.032299 and 0.01563), with two diffuse p functions (0.093443 and 0.0452186), with a 12d set with exponents obtained by applying the recipe $\zeta_d = 7\zeta_p/5$ to the exponents 0.032299 through 121.9628 of the p set, and with a 10f set obtained by applying $\zeta_f = 9\zeta_p/5$ to the p-exponents 0.066745 through 46.96009.

The standard HF, MP2, CCSD, and CCSD(T) calculations with the cc-pVXZ and cc-pCVXZ basis sets were carried out using the integral-direct coupled cluster program [28–31] and the MOLPRO program ³. The results are collected in Tables 1–3 for Ne, N_2 , and H_2O , respectively.

3.2. Convergence in Hartree–Fock calculations

For the HF calculations, the convergence towards the basis-set limit is monotonic, smooth, and fast. For N_2 , the numerical HF limit has been determined.

³ MOLPRO is a package of ab initio programs written by H.-J. Werner, P.J. Knowles, with contributions from J. Almlöf, R.D. Amos, M.J.O. Deegan, S.T. Elbert, C. Hampel, W. Meyer, K.A. Peterson, R. Pitzer, A.J. Stone, P.R. Taylor, R. Lindh.

² See footnote 1.

Table 3

Ground-state energies for the H₂O molecule in atomic units ($R_{\text{O-H}} = 1.80885 \text{ a}_0$ and $\angle_{\text{H-O-H}} = 104.52^\circ$). For HF the total energy is given. For the correlation models, the correlation energy is given

	HF	ΔMP2	ΔCCSD	$\Delta\text{CCSD(T)}$
A. Valence only				
cc-pVDZ	−76.026799	−0.201621	−0.211188	−0.214221
cc-pVTZ	−76.057168	−0.261462	−0.267378	−0.275021
cc-pVQZ	−76.064835	−0.282798	−0.285969	−0.294958
cc-pV5Z	−76.067091	−0.291507	−0.292432	−0.301950
cc-pV6Z	−76.067400	−0.295249	−0.294948	−0.304644
R12 basis ^a	−76.067419	−0.295700	—	—
R12/A	—	−0.299955	—	—
R12/B	—	−0.299265	−0.297527	−0.307211
Ref. [5]	—	−0.2993	−0.2972	−0.3067
Estimated limit	—	−0.300(1)	−0.298(1)	−0.308(1)
56 Extrapolation ^b	—	−0.3004	−0.2984	−0.3083
B. All electrons				
cc-pCVDZ	−76.027204	−0.241326	−0.251750	−0.255039
cc-pCVTZ	−76.057358	−0.317497	−0.324185	−0.332420
cc-pCVQZ	−76.064948	−0.342631	−0.346497	−0.356018
cc-pCV5Z	−76.067105	−0.352283	−0.353947	−0.363945
cc-pCV6Z	−76.067404	−0.356407	−0.356852	−0.367013
R12 basis ^a	−76.067419	−0.354286	—	—
R12/A	—	−0.361486	—	—
R12/B	—	−0.360595	−0.359775	−0.369891
Ref. [5]	—	−0.3615	−0.3599	−0.3699
Estimated limit	—	−0.361(1)	−0.361(1)	−0.371(1)
56 Extrapolation ^b	—	−0.3621	−0.3608	−0.3712

^a cc-pV6Z(uc) + S basis (374 functions) [17].

^b Linear fit of the form (2) to $X = 5$ and $X = 6$ data.

The error in the energy is reduced approximately by a factor of four each time X is incremented (i.e., linear convergence). At the sextuple level, we are only about $0.1 \text{ m} E_h$ away from the basis-set limit. The convergence for H₂O is very similar to that observed for N₂. Even though the numerical limit for H₂O is unknown, we expect, by analogy with N₂, that the basis-set error at the cc-p(C)V6Z level is approximately $0.1 \text{ m} E_h$ for H₂O also. The basis-set convergence in the molecular HF calculations is thus approximately linear. For the neon atom, the convergence is somewhat faster than in the molecular cases, as there is no charge polarization. We end up being only $0.04 \text{ m} E_h$ away from the basis-set limit and the error in the energy is reduced by about a factor of ten when the cardinal number is increased from 4 to 5 and from 5 to 6. As expected, at the HF level, there is little difference between the results obtained with the cc-pVXZ and cc-pCVXZ basis sets.

3.3. Convergence in correlated calculations

The R12/B results are given in Tables 1–3 – note that the all-electron CCSD(T) number for N₂ is not available as, with the present basis set, the computation of the triples correction was not manageable when all electrons are correlated. The R12/A variant of MP2-R12 – differing from R12/B in the approximate computation of some of the required many-electron integrals – has occasionally been found to overestimate the correlation energy, while R12/B usually converges to the basis-set limit from above. We have therefore chosen the average of the R12/A and R12/B results as our best estimates of the basis-set limit at the MP2 level, and a value slightly lower than the R12/B result at the CCSD and CCSD(T) levels. As the difference between the R12/A and R12/B results is smaller for Ne and H₂O than for N₂, the accuracy is expected to be

higher for Ne and H₂O than for N₂, and we believe that our estimates are accurate to within 1 mE_h for Ne and H₂O and to within 2 mE_h for N₂ (i.e., 1 mE_h for each non-hydrogen atom).

With the correlation-consistent basis sets, the convergence of the correlation energy is much slower than the convergence of the HF energy. This is a direct consequence of the problems associated with obtaining a correct description of the coulomb cusp. The error in the correlation energies is reduced only by a factor of 2 to 3 with each increment in the cardinal number, and when the cardinal number increases, this factor decreases. We thus observe that the convergence of the correlation energy is significantly poorer than linear. Furthermore, the convergence for the neon atom is similar to the convergence for the two molecules. Evidently, the correlation-consistent basis sets provide a description of the polarization effects upon bond formation that is at least as good as their description of the atomic correlation effects.

Although the absolute numbers of the valence and all-electron correlation energies differ (the valence correlation energy amounts to about 80% of the all-electron correlation energy for all three systems), their basis-set convergence is very similar.

Finally, we note that there is a difference between

the convergence of the MP2 and CCSD correlation energies. For the smaller basis sets, the CCSD correlation energy is larger in magnitude than the MP2 energy. As the cardinal number increases, the situation is reversed, and the MP2 correlation energy becomes larger in magnitude than the CCSD energy.

In Fig. 1, we have plotted the error in the all-electron correlation energy, that is $E_X^{\text{corr}} - E_\infty^{\text{corr}}$, as a function of the inverse number of basis functions in the cc-pCVXZ basis sets. Similarly, in Fig. 2, we have plotted the error in the valence correlation energy as a function of the inverse number of basis functions in the cc-pVXZ basis sets. The points for the larger basis sets fall almost on straight lines going through the origin, demonstrating that, for the larger correlation-consistent basis sets, the error in the correlation energy is roughly proportional to $1/N$, where N is the number of basis functions.

3.4. Extrapolations to the basis set limit

In the present section, we shall explore the application of the formula (2) for the extrapolation of correlation-consistent energies to the basis-set limit. Clearly, for the application of this formula, a least-squares fitting approach should be taken. Important questions are then what points to use in the least-

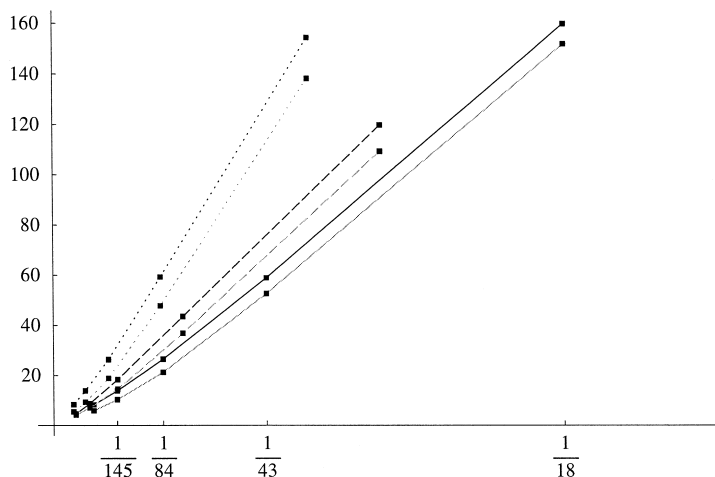


Fig. 1. Error in the all-electron MP2 (black lines) and CCSD (gray lines) correlation energies of Ne (full lines), H₂O (dashed lines), and N₂ (dotted lines), as a function of $1/N$, where N is the number of basis functions.

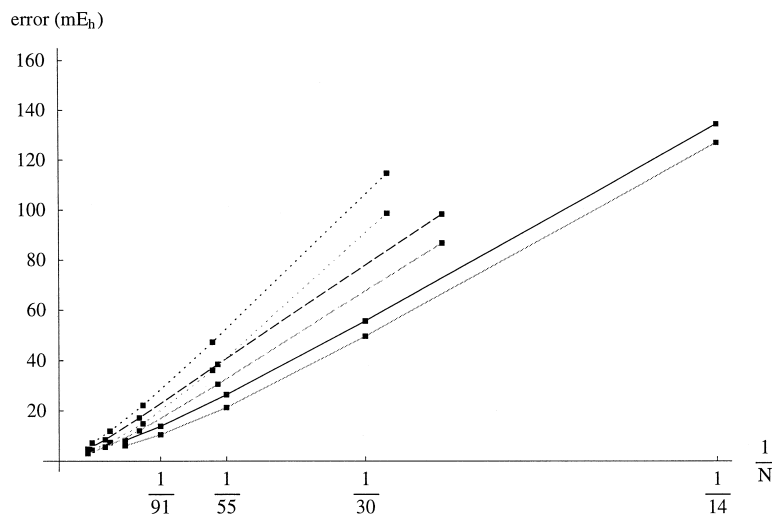


Fig. 2. Error in the valence MP2 (black lines) and CCSD (gray lines) correlation energies of Ne (full lines), H₂O (dashed lines), and N₂ (dotted lines), as a function of $1/N$, where N is the number of basis functions.

squares fitting and what are the accuracies that may be obtained with the different fits. To answer these questions, we have in Table 4 listed statistical information about all possible fits of the form (2) that include a range of correlation-consistent energies with cardinal numbers $X_{\min} \leq X \leq X_{\max}$. The table includes the mean errors, the standard deviations, the mean absolute errors, and the maximum errors compared with the R12 results. In Fig. 3, we have made plots of the normal distributions of the same extrapolations.

Table 4

Mean error, standard deviation, mean absolute error, and maximum absolute error of the extrapolated basis-set limits obtained from fits of the form (2) using data with $X = X_{\min}, \dots, X_{\max}$. All errors in mE_h

X_{\min}	X_{\max}	Mean error	Standard deviation	Mean abs. error	Max. abs. error
2	3	13.54	5.22	13.54	22.50
2	4	8.23	4.00	8.23	15.27
2	5	5.66	3.12	5.66	11.12
2	6	4.27	2.52	4.27	8.66
3	4	0.73	2.42	2.01	5.08
3	5	0.27	1.70	1.41	3.17
3	6	0.16	1.30	1.08	2.31
4	5	-0.35	0.86	0.86	1.41
4	6	-0.17	0.69	0.63	1.26
5	6	0.06	0.52	0.42	1.07

From Fig. 3, we conclude that the best extrapolations are obtained using two-point fits with the two highest cardinal numbers. In other words, if cc-pCV6Z calculations can be carried out with the software and hardware available, then the most reliable extrapolation to the basis-set limit is obtained by combining the cc-pCV6Z energy with the cc-pCV5Z energy in a two-point fit. Although easily generated, the energies of cardinal numbers $X < 5$ should be omitted from the fit as they contain less information about the asymptotic limit than the points $X \geq 5$ and will thus introduce more noise than information in the extrapolation. In particular, we note

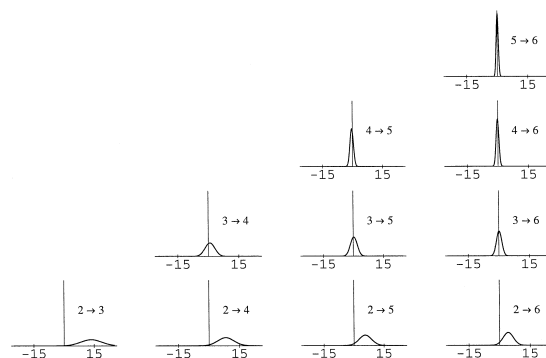


Fig. 3. Normal distributions of the two-parameter fits $E_X^{\text{corr}} = E_Z^{\text{corr}} + AX^{-3}$ as a function of the data fitted (from X_{\min} to X_{\max}).

that the inclusion of double-zeta basis sets in the fits lowers the accuracy significantly, so even in cases where quintuple or sextuple basis sets cannot be employed, one should omit the double-zeta results in the fitting procedure.

In view of the superiority of the two-point fits, we note that these may be cast in a particularly simple analytical form. Assume that we have carried out two calculations with cardinal numbers X and Y and obtained the energies E_X^{corr} and E_Y^{corr} . Writing these energies in the form

$$E_X^{\text{corr}} = E_{XY}^{\infty} + A X^{-3}, \quad (5)$$

$$E_Y^{\text{corr}} = E_{XY}^{\infty} + A Y^{-3}, \quad (6)$$

and eliminating the linear parameter A , we obtain

$$E_{XY}^{\infty} = \frac{E_X^{\text{corr}} X^3 - E_Y^{\text{corr}} Y^3}{X^3 - Y^3}. \quad (7)$$

It is remarkable that, using this simple formula, the R12 correlation energies have been extrapolated with maximum errors of 1.1 mE_h from the cc-pCV5Z and cc-pCV6Z sets, 1.4 mE_h from the cc-pCVQZ and cc-pCV5Z sets, and 5.1 mE_h from the cc-pCVTZ and cc-pCVQZ energies. The corresponding mean absolute errors are 0.4, 0.9, and 2.0 mE_h , respectively. Again we note that the extrapolations including the double-zeta basis sets are considerably less accurate, with mean absolute and maximum errors of 13.5 and 22.5 mE_h , respectively, at the 23-fit level.

In the literature, extrapolations have been carried out using expressions of the more general form

$$E_X^{\text{corr}} = E^{\infty} + A (X + a)^{-\alpha}, \quad (8)$$

where the two nonlinear parameters a and α have been introduced [10,11]. Clearly, since new parameters have been introduced, a better fit to the calculated numbers is possible. On the other hand, the nonlinearity of the new fitting parameters makes the fits more complicated since (a) more points are needed and (b) multiple solutions may exist. The need for more points in the fits is particularly worrying since our experience with the linear fits based on (2) indicates that the inclusion of energies of lower cardinal numbers may spoil the quality of the fits, although – with more parameters available in the

fitting function (8) – this particular disadvantage may not be so serious.

To explore the usefulness of the more elaborate fitting function (8), we have carried out extrapolations with the full set of energies of cardinal numbers $3 \leq X \leq 6$ in which the parameters a and α are systematically varied. In Fig. 4, the mean absolute errors of these fits are plotted as functions of a and α . The most striking feature of this plot is the strong linear coupling that is revealed between the optimal values of a and α . Indeed, for a wide range of values of the parameter a , the optimization of α yields an extrapolation virtually identical to that of the simpler expression (2). In Fig. 5, we have, as a function of a , plotted the optimal value α_{opt} of α (to the left) and the mean absolute error (to the right). For $a = 0$ (which corresponds to the linear fit (2)), the optimal value of α is $\alpha_{\text{opt}} = 3.01$, indicating that the linear fit (2) is very nearly optimal. In short, any nonlinear optimization of a and α may improve the fit, but not necessarily the quality of the extrapolation.

In a recent paper by Martin and Taylor, a was fixed at $a = 1/2$, as a compromise between $a = 0$ for hydrogen and $a = 1$ for first-row atoms. This a yields an optimal value of $\alpha_{\text{opt}} = 3.40$ in the fits employing $3 \leq X \leq 6$, slightly smaller than the range of values of $\alpha_{\text{fit}} = 3.52\text{--}4.66$ found by these authors

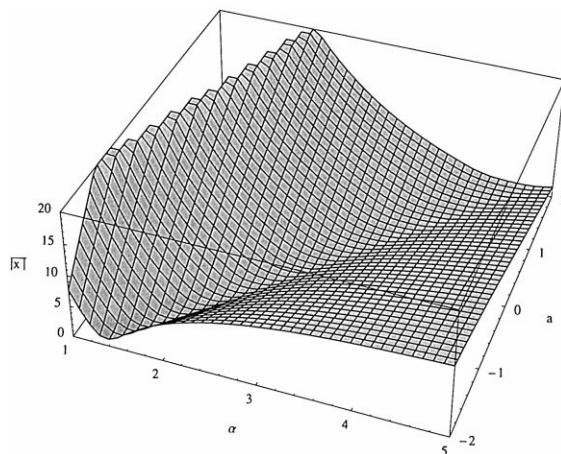


Fig. 4. Mean absolute error of linear two-parameter fits of the type $E_X^{\text{corr}} = E_{\infty}^{\text{corr}} + A(X + a)^{-\alpha}$ as a function of the nonlinear parameters a and α .

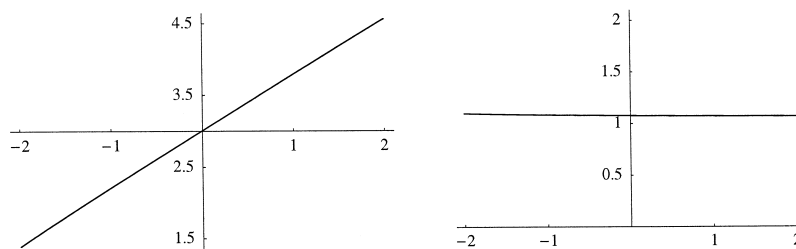


Fig. 5. Optimal value of α (to the left) and mean absolute error (to the right) as a function of the nonlinear parameter a in fits of the form (8).

for H_2O and N_2 [11]. This discrepancy, however, may be explained by the difference in which the exponent α has been determined: The value obtained by Martin and Taylor is determined exclusively as the one that gives the best fit to the calculated values of the correlation contribution to the total atomization energy of the molecules in the correlation-consistent basis sets. Our value α_{opt} , on the other hand, is determined as the α that (for given a) gives the lowest mean absolute error of the extrapolated basis-set limit compared with R12, and thus includes reference to both the calculated molecular correlation energies in the correlation-consistent basis sets and the basis-set limit value as determined by the R12 method. It appears to be a general tendency that $\alpha_{\text{fit}} > \alpha_{\text{opt}}$, suggesting that a nonlinear fitting of α is to be avoided since it will usually produce a fit that underestimates the magnitude of the correlation energy.

For N_2 , the basis-set limit for the total CCSD(T) energy is established to $-109.541(2) E_h$, which is $4 m E_h$ below the complete-basis-set (CBS) limit reported by Peterson et al. [15]. Their CBS value is significantly higher, because in Ref. [15], an exponential form was fitted to the cc-pCVXZ energies. Unfortunately, as we have seen, correlation energies do not converge as rapidly as suggested by an exponential fit. On the other hand, a 56-extrapolation to the cc-pCV5Z and cc-pCV6Z energies reported by Peterson et al. [15] yields the extrapolated total CCSD(T) energy of $-109.5418 E_h$, which is consistent with our results.

4. Concluding remarks

Standard and R12 calculations of the correlation energy at the MP2, CCSD and CCSD(T) levels have

been carried out for Ne, N_2 , and H_2O . We have found that a two-parameter linear Schwartz extrapolation of the correlation energy of the form (2) gives excellent fits with R12 energies, which may be obtained by the simple formula (7). Using this expression, the error in the correlation energy obtained with the highest cardinal number X is reduced by about an order of magnitude, provided the cardinal number Y is one less than X . For extrapolations to within $1 m E_h$, calculations must be carried out at the cc-pCV6Z level, whereas extrapolations to within $5 m E_h$ are possible at the cc-pCVQZ level. The linear Schwartz fits work as well as (or better than) the nonlinear fits and have the advantage of requiring only two calculated energies, thereby avoiding the use of low-order energies, which contain little or no information about the asymptotic convergence of the dynamical correlation energy. Also, with only one solution, the linear fits are more well-defined than the nonlinear ones, making them well suited for automatic incorporation in a broader computational scheme aimed at high-accuracy prediction of energies and molecular properties.

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