

Generalized Uniform Singlet- and Triplet-Pair Extrapolation of the Correlation Energy to the One Electron Basis Set Limit

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The relationship between the triplet- and singlet-pair interaction coefficients in the uniform singlet- and triplet-pair extrapolation method recently suggested for extrapolating *ab initio* energies to the one-electron basis set limit is analyzed. Based on the premise that such a ratio is invariant over the configuration space of the molecule, generalizations of the method are investigated and their performance tested on extrapolations with MP2, CCD, CCSD, and MRCI(Q) energies. The best variant requires raw energies calculated using augmented correlated consistent basis sets with cardinal numbers up to $X = 6$ at a single geometry. A scheme is also suggested that performs better than the traditional X^{-3} law and possibly the original uniform singlet- and triplet-pair extrapolation method but requires data only up to $X = Q$.

1. Introduction

It is well-established that the conventional correlated orbital-based methods involve only even powers of r_{ij} while the exact wave function of an atomic or molecular system shows a linear dependence in the interelectronic coordinate r_{ij} as this approaches zero.^{1,2} This is so whatever approach one uses to treat correlation effects [Møller–Plesset perturbation theory (MP), configuration interaction (CI), coupled cluster (CC) method, etc], and explains the slow convergence of such methods with increasing number of Slater determinants used to represent the multi-electron wave function. In fact, this may explain why the highest levels of accuracy in electronic structure calculations have not been achieved via such methods but through unconventional ones such as the quantum Monte Carlo method³ or wave functions that depend explicitly on r_{ij} .^{4–6} Yet, despite the rising success of the latter approaches,⁷ the conventional CI ansatz, the CC family of methods [CCD, CCSD, CCSD(T), CR-CC(2,3), etc; for reviews, see ref 8 and a recent paper⁹ that gives references to such methods as applied to the potential energy surface (PES) of the water molecule] or MP2 perturbation theory⁸ continue to be routine especially when combined with extrapolation techniques. Indeed, the inclusion of r_{ij} coordinates in multireference (MR) approaches has only recently been done using a novel variant of the explicitly correlated multireference averaged coupled-pair functional method and applied to the hydrogen fluoride molecule,¹⁰ with conventional CI methods [usually with the popular degenerate Davidson correction, CI(Q) or MRCI(Q)] proving essential for the calculation of accurate PESs. The same holds for CC methods which are known to treat electron correlation most efficiently, and we will examine here CC results obtained both with the inclusion of double excitations (CCD) and single and double excitations as well as perturbative corrections for connected triple excitations [CCSD and CCSD(T)].

An enormous progress in electronic structure calculations for systems with small and moderate sizes arose with the introduction of correlated-consistent polarized valence basis sets^{11–14} (cc-pVXZ or VXZ), augmented ones (AVXZ) or even more

flexible basis sets now being routinely employed. Built in a systematic manner that is intended to relate the correlation energy to the cardinal number X , such basis sets prompted the search for laws to extrapolate the total energy or its components to the complete basis set (CBS) limit^{8,15–28} (the list is by no means exhaustive), a subject also addressed in the present work.

Extrapolation to the CBS limit finds support on the dependence of the correlation energy on the partial wave quantum number for two-electron atomic systems and second-order pair energies in many-electron atoms.^{29–41} Specifically, the energy has been shown to vary as an inverse power of the cardinal number,

$$E_X^{\text{cor}} = E_\infty^{\text{cor}} + \frac{A_{\text{cor}}}{X^\beta} \quad (1)$$

where E_X^{cor} is the correlation energy for the basis set of cardinal number X , and E_∞^{cor} , A_{cor} , and β are parameters.^{16,17} Asymptotically one expects the value of $\beta = 3$, although Truhlar¹⁷ recommended optimal extrapolation exponents for MP2⁴² ($\beta_{\text{MP2}} = 2.2$), CCSD and CCSD(T) [$\beta_{\text{CCSD}} = \beta_{\text{CCSD(T)}} = 2.4$] calculations by minimizing the root-mean-square deviation (rmsd) in fits to Halkier et al.¹⁶ estimated basis-set limits for Ne, HF, and H₂O. Since his main interests were to develop a rule with potential interest for moderately large systems, such extrapolations focused on small basis sets (D and T) and valence-only limits, as for those systems changes in core correlation energy upon bond formation are usually small compared to other errors.^{43,44} The above numerical values have later been re-evaluated by considering a larger set of reference data.¹⁸ Variable-exponent inverse-power laws have most recently been also utilized by Bakowies,²⁸ who used the adjustable β parameter to quantify deviations from the asymptotic convergence behavior, and analyzed both analytical examples (i.e., other asymptotic expansions^{15,20,22,25,26}) and numerical extrapolations to either large but finite or CBS targets. He observed that deviations from asymptotic convergence are most significant for extrapolations from small basis sets but still noticeable for basis sets as large as V5Z or V6Z. By further defining extrapolation exponents $\beta_{\text{opt}}(X, X + 1, X + N)$ that are optimal for a given set of

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molecules, Bakowies²⁸ suggested to vary β such that the rmsd between extrapolated and explicitly calculated energies E_{X+N} become minimal. Thus, rather than providing a single optimal exponent, he recommends specific exponents for specific extrapolations. His strategy is therefore similar to the one utilized by Schwenke,²⁶ with the only formal difference being that the involved scaling is performed analytically rather than numerically. However, the most popular dual-level CBS law that warrants the correct asymptotic behavior is¹⁵

$$E_X^{\text{cor}} = E_\infty^{\text{cor}} + \frac{A_3}{(X + \alpha)^3} \quad (2)$$

where E_X^{cor} and A_3 are parameters commonly determined from energies for the two highest affordable values of X , and the offset parameter α is fixed from some other condition.²⁷ In fact, the potential benefit of using such rules is well recognized,⁴⁵ justifying that the search for improved extrapolation techniques continues to be an active area of research. The reader is addressed to ref 45 for a detailed analysis of the sources of error in electronic structure calculations and a comparison of the performance of eq 2 with a few other rules on small chemical systems using VXZ basis sets.

Although also utilized for the total energy on the basis of the dominance of the correlation energy lowering (ref 46, and references therein), eq 2 finds its justification in the energy increments of partial-wave expansions of atomic correlation energies^{29–41} or similar expressions derived from the convergence behavior of the principal expansion.^{8,32,47} From a MP2 study on arbitrary excited states of He-like atoms, where the first-order wave function ψ behaves for small r_{12} as $\psi = (1 + \kappa r_{12})\Phi + \mathcal{O}(r_{12}^2)$ with $\kappa = 1/2$ ($1/4$) for singlet (triplet) states^{4,2} and Φ being the HF wave function, Kutzelnigg and Morgan³⁹ established the following: for natural-parity singlet states, the leading contribution at second-order of perturbation theory is proportional to $(\ell + 1/2)^{-4}$, with no contributing odd-terms proportional either to $(\ell + 1/2)^{-5}$ or $(\ell + 1/2)^{-7}$ and the term $(\ell + 1/2)^{-6}$ being universally $-(5/4)$ that of $(\ell + 1/2)^{-4}$; for all triplet states, the leading term is proportional to $(\ell + 1/2)^{-6}$; for unnatural parity singlet states, the coefficient is proportional to $(\ell + 1/2)^{-8}$. Moreover, they have shown³⁹ that the ratio of the $(\ell + 1/2)^{-6}$ and $(\ell + 1/2)^{-4}$ coefficients for natural-parity singlet states is not simply $-(5/4)$ when the unperturbed wave function is a Hartree–Fock one. Such results generalize to the Møller–Plesset energy of atoms with any number of electrons.^{39,41} Note that the single-term extrapolation formula (2) on the cardinal number X (or L , the maximum partial wave number ℓ_{max} in a partial wave expansion of the correlation energy) finds its justification in the fact that the leading contribution at second-order of perturbation theory is proportional to $(\ell + 1/2)^{-4}$. Note further that the use of just one term may be accuracy-limiting as the subset of natural singlet-pairs in a MP2 calculation for the Zn^{2+} ion has been found to contribute only 54.7% of the total correlation energy.⁴¹ Although Klopper²² has utilized distinct one-term expansions for the singlet and triplet pairs (thus accounting for the X^{-3} and X^{-5} behavior, respectively), we have chosen in our uniform singlet- and triplet-pair extrapolation (USTE²⁷) approach not to decompose the total correlation into such contributions. We have done so, first, because it is unnecessary for accurate results;²⁷ second, because such a decomposition scheme cannot be implemented for open-shell CCSD calculations²⁶ (the wave function is not a spin eigenfunction in practical implementations of CCSD theory) nor is it commonly available in most CC codes; and third, because

such a decomposition is extraneous to MRCI calculations as a single excitation out of the reference space can be counted either as a singlet-pair or as a triplet-pair depending on the spin coupling of the $N - 1$ part of the determinant.

In the present work, we follow our previous strategy²⁷ by seeking an analytic scheme that extrapolates accurately the correlation energy irrespectively of the diversity of basis set data used for the extrapolations while preserving the correct asymptotic behavior. For practical reasons, it will be dual-level type in the sense that reference calculations for two basis-sets will suffice for the extrapolation; for a one-parameter rule (to our knowledge, the only one available thus far), see ref 20. Since the method is expected to allow reliable extrapolations from energies calculated with any basis sets including those with small X values, one hopes that it will capture the differences between such bases in a realistic manner. In fact, although the angular momentum is not a good quantum number for many-particle systems, and the subsets of wave functions of different angular momentum are difficult to saturate or even balance, it is also true that extrapolations with fairly low ℓ values have shown excellent results^{22,26,27} for small molecules when using cc-type basis sets.^{11–14} Indeed, this has been a major motivation for carrying out the present work.

A final remark goes to the extrapolation of the uncorrelated Hartree–Fock (HF) and complete-active-space-self-consistent-field (CASSCF or simply CAS; uncorrelated in the sense of lacking dynamical correlation) energies. Since it is a topic that lies outside the scope of the present work, we will address the reader to refs 27, 48, 49 (and references therein) for details. Suffice it to say that both extrapolations are geometry-dependent, and hence performed pointwise. Moreover, the use of HF extrapolated energies plus correlation-scaling/USTE-extrapolated ones^{50,51} has recently shown^{51,52} great promise in obtaining accurate PESs at a low cost, a hybrid approach that will also be of no concern to us here.

The paper is organized as follows. In section 2, we describe the method, while the results are reported and discussed in section 3. The conclusions are in section 4.

2. Method

The asymptotic limit in eqs 1 and 2 can be imposed by expressing the correlation energy as a rational fraction, which we write in the form

$$E_X^{\text{cor}} = \frac{p_0 + p_M X^{-M} + p_{M+1} X^{-(M+1)} \dots}{1 + q_N X^{-N}} \quad (3)$$

where the p 's and q 's are coefficients, and $M \geq N$; for convenience, we may also think of X as $X + \alpha$. The simplest function of this type is obtained with $M = \infty$, which assumes the form of eqs 1 and 2 if one recalls that for large X values a Taylor expansion in X^{-1} yields $\lim_{X \rightarrow \infty} 1/(1 + q_N X^{-N}) \sim 1 - q_N X^{-N}$. Furthermore, if $N = 3$, one has $E_\infty^{\text{cor}} = p_0$, and $A_3 = -p_0 q_3$. Another variant that will be discussed later consists of limiting the numerator to odd powers, and keeping only the term for $M = 5$. In fact, such a continued fraction representation proves to be general and reliable for representing the calculated correlation energies. For example, with $M = \infty$ and the two parameters determined from the results for the two largest cardinal numbers (9 and 10) used in ref 45 for the neon atom, one gets $E_\infty^{\text{cor,S}} = -210.64$ mE_h and $E_\infty^{\text{cor,T}} = -104.88$ mE_h for the singlet-pair and triplet-pair CCSD/VXZ energies, to be compared with -210.61 mE_h and -104.87 mE_h from explicitly

TABLE 1: Ratios τ_{53} from Valence Shell Correlation Energies Obtained with MP2, CCD and CCSD Calculations^a

system	MP2				CCD				CCSD			
	τ_{53}^b	$\tau_{53}^{DTQ\ c}$	$\tau_{53}^{Q56\ d}$	$\bar{\tau}_{53} \pm \Delta\bar{\tau}_{53}^e$	τ_{53}^b	$\tau_{53}^{DTQ\ c}$	$\tau_{53}^{Q56\ d}$	$\bar{\tau}_{53} \pm \Delta\bar{\tau}_{53}^e$	τ_{53}^b	$\tau_{53}^{DTQ\ c}$	$\tau_{53}^{Q56\ d}$	$\bar{\tau}_{53} \pm \Delta\bar{\tau}_{53}^e$
CH ₂	-1.33	-1.228513	-1.319114	-1.27 ± 0.05	-0.72	-0.945620	-0.720395	-0.83 ± 0.11	-0.68	-0.931833	-0.707320	-0.82 ± 0.11
CO	-1.50	-1.374233	-1.512582	-1.44 ± 0.07	-1.24	-1.304091	-1.241865	-1.27 ± 0.03	-1.24	-1.287849	-1.221248	-1.26 ± 0.03
F ₂	-1.54	-1.342934	-1.522513	-1.43 ± 0.09	-1.33	-1.307606	-1.302514	-1.30 ± 0.00	-1.32	-1.304388	-1.303390	-1.30 ± 0.00
H ₂ O	-1.48	-1.308266	-1.426115	-1.37 ± 0.06	-1.18	-1.221478	-1.108013	-1.16 ± 0.06	-1.17	-1.219178	-1.098821	-1.16 ± 0.06
HF	-1.50	-1.347506	-1.483362	-1.37 ± 0.06	-1.23	-1.304170	-1.246653	-1.28 ± 0.03	-1.22	-1.300331	-1.245373	-1.27 ± 0.03
N ₂	-1.50	-1.360448	-1.498338	-1.43 ± 0.07	-1.22	-1.260942	-1.190430	-1.23 ± 0.04	-1.21	-1.248841	-1.179869	-1.21 ± 0.03
Ne	-1.51	-1.358759	-1.564583	-1.46 ± 0.10	-1.28	-1.350284	-1.357015	-1.35 ± 0.00	-1.27	-1.345554	-1.348784	-1.35 ± 0.00

^a Although the ratios τ_{53}^{DTQ} and τ_{53}^{Q56} are reported in this table and Table 2 with six significant figures as actually employed in the calculations, their average values and associated errors at midpoint (defined such as to embrace both estimates) are quoted for convenience up to two significant figures. ^b Determined from eq 5 using the values of A_3 from ref 27. ^c Determined from a fit of eq 6 to $X = D, T, Q$ energies. ^d As in ^c but using up to $X = 6$ energies. ^e Average of τ_{53}^{DTQ} and τ_{53}^{Q56} , and error; see the text.

correlated calculations (CCSD-R12) reported in the same paper. Instead, if one chooses $M = 5$ with the three parameters determined from calculations for $X = 8-10$, one obtains for the singlet-pair energy $E_{\infty}^{\text{cor},S} = -210.63$ mE_h. In fact, the raw nonfitted energies for small- X basis sets consistently show fair to good agreement with the predicted values, thus supporting the reliability of the extrapolation. The rational fraction (3) has indeed been found to be accurate even when unusual asymptotic dependences (M and N must then be appropriately chosen or left as adjustable parameters) are found as with explicitly correlated energies.⁵³ Of course, related forms that preserve the correct asymptotic behavior such as $E_X^{\text{cor}} = A \exp(-bX^{-3})$ may perform similarly, with the data (partly due to the fact that X is not an exact quantum number) being often unable to discriminate the one that performs best.

The USTE²⁷ scheme has its basis on the simplest three-parameter rule of the above general type in eq 3. Including the offset parameter α , it assumes the form

$$E_X^{\text{cor}} = E_{\infty}^{\text{cor}} + \frac{A_3}{(X + \alpha)^3} + \frac{A_5}{(X + \alpha)^5} \quad (4)$$

where E_{∞}^{cor} , A_3 , and A_5 are parameters to be determined from energies calculated with correlation-consistent basis sets of different cardinal numbers. For a fixed value of α , eq 4 is then transformed to the effective two-parameter USTE rule by defining²⁷

$$A_5 = A_5^o + cA_3^m \quad (5)$$

with the parameters $A_5^o = A_5(A_3 = 0)$, c and m determined from *ab initio* energies for a variety of systems. For example, from anew²⁷ MRCI(Q)/AV XZ calculations for 24 systems, as well as MP2/VXZ, CCD/VXZ, and CCSD/VXZ energies available in the literature²² for cardinal numbers ranging from $X = D$ to $X = 6$, the following sets of parameters have been obtained with²⁷ $\alpha = -3/8$: $A_5^o = 0.003769$, $c = -1.1784771$ E_h^{-5/4}, and $m = 5/4$ for MRCI(Q); $A_5^o = 0.1660699$, $c = -1.4222512$ E_h⁻¹, and $m = 1$ for the CC family of methods; $A_5^o = 0.0960668$, $c = -1.582009$ and $m = 1$ for MP2. It has further been shown²⁷ that both the full correlation in systems studied by MP2 and CC [CCD, CCSD, and CCSD(T)] methods and its dynamical part in MRCI(Q) calculations⁵² or even correlation energies obtained by correlation energy extrapolation via intrinsic scaling⁵⁴ could be accurately extrapolated to the CBS limit with the USTE rule. Naturally, the above coefficients are likely to vary with the method and the basis set. However, this dependence should not be significant for methods and basis sets

TABLE 2: Ratios τ_{53} Extracted from MRCI(Q) Calculations

system	τ_{53}^d	$\tau_{53}^{DTQ\ b}$	$\tau_{53}^{Q56\ c}$	$\bar{\tau}_{53}^d$
H ₂	-0.28	-0.182891	-0.151363	-0.17 ± 0.02
H ₃ ⁺	-0.28	-0.348692	-0.380301	-0.36 ± 0.02
HeH ⁺	-0.46	-0.805712	-0.751268	-0.78 ± 0.03
He ₂ ⁺⁺	-0.44	-0.680290	-0.624268	-0.65 ± 0.03
BH	-0.68	-1.007223	-0.760193	-0.88 ± 0.12
CH	-0.70	-0.796840	-0.636825	-0.72 ± 0.08
NH	-0.82	-0.895582	-0.780484	-0.84 ± 0.06
OH	-0.97	-1.137639	-1.056519	-1.10 ± 0.04
HF	-1.08	-1.305956	-1.243364	-1.28 ± 0.03
SH	-0.91	-0.803153	-0.879484	-0.84 ± 0.04
H ₂ O		-1.651679	-1.655947	-1.65 ± 0.00
B ₂	-0.56	-0.899805	-0.517532	-0.71 ± 0.19
C ₂	-0.89	-1.050512	-0.843869	-0.95 ± 0.10
N ₂	-1.06	-1.135105	-1.041680	-1.09 ± 0.05
O ₂	-1.16	-1.195966	-1.147989	-1.17 ± 0.02
F ₂	-1.28	-1.275911	-1.270502	-1.27 ± 0.00
BN	-0.93	-1.102373	-0.922511	-1.01 ± 0.09
BO	-0.99	-1.265508	-1.136348	-1.20 ± 0.07
CN	-1.05	-1.095757	-0.971588	-1.03 ± 0.07
CO	-1.08	-1.220184	-1.144859	-1.18 ± 0.04

^a Determined from eq 5 using the values of A_3 reported in ref 27. ^b Determined from a fit of eq 6 to $X = D, T, Q$ energies. ^c As in ^a but using up to $X = 6$ ($X = 5$ in the case of H₂O) energies. ^d Average of τ_{53}^{DTQ} and τ_{53}^{Q56} , and error. See footnote ^a of Table 1.

that belong to related families, and we have even explored its extendibility (“universality”) by showing that accurate results could be obtained for systems not belonging to the calibrating set.^{49,52}

The USTE rule may also assume the form

$$E_X^{\text{cor}} = E_{\infty}^{\text{cor}} + \frac{A_3}{(X + \alpha)^3} \left[1 + \frac{\tau_{53}}{(X + \alpha)^2} \right] \quad (6)$$

with the ratio τ_{53} defined by

$$\tau_{53} = \frac{A_5^o}{A_3} + cA_3^{m-1} \quad (7)$$

Having the correct asymptotic behavior, one expects eq 4 or eq 6 to be among the best three-parameter models to accurately fit the data, and hence allow a reliable estimate of the ratio $\tau_{53} = A_5/A_3$ to be extracted from the reported correlation energies. The values of τ_{53} obtained in this way are reported in Table 1 for seven systems calculated by the MP2, CCD, and CCSD methods with VXZ ($X = D, T, Q, 5, 6$) basis sets, while Table 2 gathers the results for twenty systems calculated by the MRCI-

(Q)/AVXZ removed method for the same cardinal numbers. Also shown for comparison are the values obtained from eq 5 using the rounded parameters from Table 1 (second entries) of ref 27. Two observations can be made. First, in the limit $A_3 \rightarrow 0$ [this coefficient vanishes for pure triplet-pair interactions such as in $\text{He}(^3P_u)$ or $\text{H}_3^+(^3\Sigma_u^+)$], numerical problems may arise when determining E_∞^{cor} and A_3 due to the division by A_3 in eq 7. This can be overcome simply by adding a small constant (say $\delta = 10^{-16}$) to the denominator of eq 7. The second observation is of physical nature and concerns the ratio τ_{53} itself, which assumes the value²⁷ of -0.75 for natural-parity singlet states in the $1/Z$ expansion for various states of the He isoelectronic series [using the standard notation, it corresponds to the ratio³⁹ of the $(\ell + 1/2)^{-6}$ and $(\ell + 1/2)^{-4}$ terms, $a_2/a_1 = -5/4$]. Note that such a ratio may vary slightly if instead of the wave function for the bare-nuclear Hamiltonian one uses a HF wave function,³⁹ as it has actually been shown in MP2 studies of symmetry-adapted pairs.⁴¹ Similarly, it may assume distinct values (unknown thus far) for other levels of theory.³⁹

We should observe at this point that the ratio τ_{53} involves not only the $(\ell + 1/2)^{-6}$ term arising from natural parity singlet states but also the leading contribution with the same dependence arising for triplet states. Thus, all electron pairs are essentially involved. Equation 7 with $m = 1$ gives for this ratio $\tau_{53} = A_5^o/A_3 + c$, thus predicting τ_{53} to depend both on the value of the intersection at the origin and slope c in eq 5. For $A_3 = 1$, one gets the values of -1.18 for the MRCI(Q) energies, -1.26 for CCD or CCSD, and -1.49 for MP2, all differing significantly from -0.75 . If one uses instead the optimum values of A_3 determined in ref 27, the results in columns two, six and ten of Table 1 as well as those in column two of Table 2 are obtained. As one could anticipate, except for a few systems with small values of A_3 (notably H_2 , H_3^+ , HeH^+ , and He_2^{++} ; see comment above), the agreement between the USTE values and the ones from the present work is generally good.

In the present work, we conjecture that τ_{53} is invariant over (most) configuration space of the molecule, and hence generalize the USTE model by constraining the extrapolation to reproduce its best estimate as obtained from the fits via eq 6. Such a procedure has the merit of alerting for the fact that systems with similar values of A_3 may somehow have distinct A_5 coefficients, as shown³⁹ for helium-like systems with $A_3 = 0$ where distinct triplet electronic states are found to have different values of A_5 . The simplest approach toward this generalization consists of writing

$$A_5 = \eta A_5^o + c A_3^m \quad (8)$$

where η is a scaling constant that moves the curve in eq 5 up or down parallel to the original law [$A_5(0) = A_5^o$, with $\eta = 1$] such as to fit best the system under analysis. This is illustrated in Figure 1 for the MP2 energies, with similar plots (including He_2) shown elsewhere⁵⁵ for CC [CCD, CCSD, and CCSD(T)] and CI [CI(Q) and MRCI(Q)] energies. Of course, this approach will lead to the original three-parameter rule in eq 3 or eq 4 unless an auxiliary criterion is used to fix the system-dependent η parameter. Note that a three-parameter model would require three points per geometry to extrapolate a PES, which would be hopelessly time-consuming in a multidimensional situation. We envisage therefore an effective two-parameter generalized USTE (GUSTE) rule.

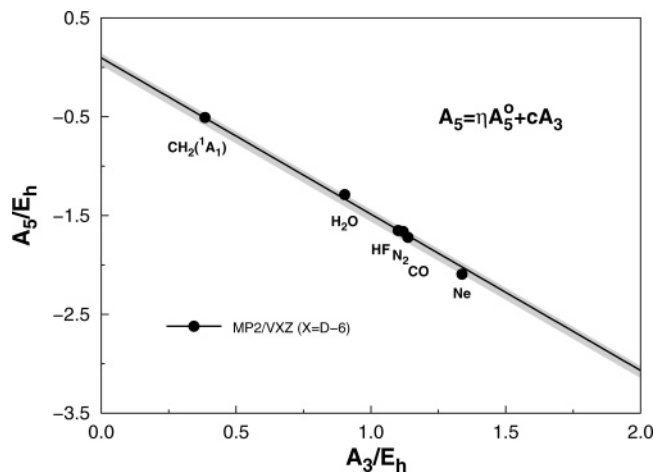


Figure 1. A_5 vs A_3 plot²⁷ for MP2 energies calculated with VXZ correlated consistent orbital basis sets ($X = D, T, Q, 5, 6$). The shadowed area has been obtained by moving the fitted line^{27,52} up and down such as to encompass all calculated points: $0.023 \leq \eta A_5^o \leq 0.141$. Similar plots for CC and CI(Q) energies are shown in ref 55.

The easiest way to fix η is by performing a calculation with the $X = Q$ basis set to obtain τ_{53}^{DTQ} , a variant denoted as GUSTE/DTQ. Thus,

$$\eta_{DTQ} = A_3(\tau_{53}^{DTQ} - c A_3^{m-1})/A_5^o \quad (9)$$

with the label *DTQ* implying that only calculations with the three smallest cardinal numbers are required. Table 1 gathers the values so obtained. Naturally, A_3 varies with the cardinal numbers used for the extrapolation, and so does η_{DTQ} . Clearly, if additional information is available, one may impose the ratio obtained with the three highest affordable cardinal numbers, τ_{53}^{Q56} . It will then be preferable to avoid the three-point fit to a three-parameter form by using the calculations for the whole set of X values, with larger weights given to increasing X values as in ref 27. The use of the ratios so obtained (still denoted τ_{53}^{Q56}) leads to GUSTE/Q56, while in GUSTE (we reserve the unaltered acronym for this variant of the method) the average ratio $\bar{\tau}_{53} = (\tau_{53}^{DTQ} + \tau_{53}^{Q56})/2$ is imposed instead. Note that both η_{Q56} and η (this refers to GUSTE) vary too with the X values used for the extrapolation.

3. Results and Discussion

Table 3 illustrates how the GUSTE method performs when the CCSD/VXZ ($X \leq 10$) energies of Feller et al.⁴⁵ are utilized for the neon atom. Since the singlet- and triplet-pair energies are treated uniformly by GUSTE, we will consider only their sum for the present analysis. Such raw energies are listed in column two of Table 3, while the extrapolated energies are given in columns six to eight. In turn, columns three to five list the predicted energies for the X_2 basis sets not involved in the fit. Included for comparison are the results obtained from the X^{-3} law in eq 2 and the USTE²⁷ rule. Since they are nearly coincidental with the GUSTE ones, no further reference to them will be needed. Two other remarks are in order. First, the predicted energies from GUSTE show a tendency to slightly overestimate the unsigned raw energies but never by more than 1 mE_h. Conversely, eq 2 tends to underestimate those energies at both X_2 ends, with deviations up to 5 mE_h or so for $X = T$. Regarding the extrapolated energies, the GUSTE method is seen to overestimate the unsigned CCSD-12B⁴⁵ explicitly correlated energy by 0.20 mE_h, while eq 2 underestimates it by 0.06 mE_h.

TABLE 3: Raw versus CBS Extrapolated Valence Shell CCSD Correlation Energies (in Millihartrees) for the Ground Electronic State of the Neon Atom

$(X_1, X_2)^a$	X ₂ energies				CBS extrapolated		
	raw ^b	eq 2 ^c	USTE	GUSTE ^d	eq 2 ^c	USTE	GUSTE ^d
(D,T)	-266.34	-261.11	-267.33	-267.30			
(T,Q)	-294.68	-294.80	-295.35	-295.35	-312.03	-315.24	-315.22
(Q,5)	-305.49	-305.49	-305.49	-305.49	-315.53	-316.36	-316.35
(5,6)	-309.90	-309.90	-309.90	-309.90	-315.42	-315.68	-315.68
(6,7)	-312.15	-312.04	-312.10	-312.10	-315.70	-315.81	-315.81
(7,8)	-313.36	-313.20	-313.32	-313.31	-315.67	-315.72	-315.72
(8,9)	-314.02	-313.89	-314.04	-314.04	-315.50	-315.52	-315.52
(9,10)	-314.43	-314.32	-314.49	-314.49	-315.48	-315.49	-315.49
CCSD-R12B	-315.48						
rmsd ^e		1.85	0.40	0.40	1.31	0.35	0.35

^a (X_1, X_2) denotes the cardinal number pair used for CBS extrapolation. ^b From ref 45. ^c Using the offset parameter $\alpha = -3/8$. ^d Instead of τ_{53}^{DTQ} , the ratio $\tau_{53}^{TQ5} = -1.655690$ has been used since the energy for $X = D$ is unavailable;⁴⁵ $\tau_{53}^{Q56} = -1.260341$. ^e Root mean squared deviation with respect to CCSD-R12B.

TABLE 4: CBS Extrapolated Valence Shell MP2, CCD and CCSD Correlation Energies (in Millihartrees) for the Ground Electronic States of CH₂, CO, F₂, H₂O, N₂, and Ne

system	$(X_1, X_2)^a$	MP2				CCD				CCSD			
		Klopper ^b	eq 2 ^c	USTE ^d	GUSTE ^e	Klopper ^b	eq 2 ^c	USTE ^d	GUSTE ^e	Klopper ^b	eq 2 ^c	USTE ^d	GUSTE ^e
CH ₂	(D,T)		-147.5	-156.8	-155.6 ± 0.7 ^f		-171.4	-173.7	-174.7 ± 0.7 ^g		-172.3	-174.4	-175.6 ± 0.7 ^f
	(T,Q)	-154.5	-153.9	-155.0	-155.0 ± 0.1	-175.3	-174.9	-175.4	-175.4 ± 0.1	-176.2	-175.8	-176.2	-176.3 ± 0.1
	(Q,5)	-155.4	-155.2	-155.2	-155.5 ± 0.0	-174.8	-174.7	-174.8	-174.8 ± 0.0	-175.8	-175.6	-175.7	-175.8 ± 0.0
	(5,6)	-155.6	-155.4	-155.5	-155.5 ± 0.0	-174.7	-174.7	-174.8	-174.8 ± 0.0	-175.7	-175.6	-175.6	-175.7 ± 0.0
CO	(D,T)		-376.6	-406.9	-403.6 ± 3.7 ^f		-373.9	-390.4	-392.0 ± 1.0 ^g		-378.1	-394.4	-395.7 ± 1.1 ^f
	(T,Q)	-397.7	-396.9	-400.5	-400.4 ± 0.2	-391.1	-390.5	-392.9	-393.0 ± 0.1	-394.9	-394.3	-396.7	-396.7 ± 0.1
	(Q,5)	-402.1	-401.7	-402.7	-402.7 ± 0.1	-392.3	-391.9	-392.5	-392.5 ± 0.0	-396.1	-395.8	-396.4	-396.4 ± 0.0
	(5,6)	-402.9	-402.6	-403.0	-402.9 ± 0.0	-392.0	-392.2	-392.2	-392.2 ± 0.0	-395.8	-395.7	-395.9	-395.9 ± 0.0
F ₂	(D,T)		-562.4	-624.4	-612.0 ± 8.9 ^f		-559.1	-597.7	-596.1 ± 0.2 ^g		-564.3	-603.1	-601.6 ± 0.0 ^f
	(T,Q)	-599.1	-598.3	-605.2	-604.6 ± 0.5	-592.0	-591.1	-596.4	-596.2 ± 0.0	-597.2	-596.5	-601.7	-601.6 ± 0.0
	(Q,5)	-608.5	-608.1	-610.0	-609.8 ± 0.1	-596.3	-596.1	-597.5	-597.4 ± 0.0	-601.6	-601.3	-602.7	-602.6 ± 0.0
	(5,6)	-609.9	-609.5	-610.2	-610.1 ± 0.0	-596.0	-595.8	-596.2	-596.2 ± 0.0	-601.2	-601.2	-601.6	-601.6 ± 0.0
H ₂ O	(D,T)		-280.1	-306.0	-300.5 ± 2.3 ^f		-283.7	-297.2	-296.7 ± 1.3 ^g		-284.9	-298.3	-297.9 ± 1.4 ^f
	(T,Q)	-296.4	-295.8	-298.8	-298.5 ± 0.2	-296.7	-296.1	-298.1	-298.0 ± 0.1	-297.9	-297.4	-299.3	-299.3 ± 0.1
	(Q,5)	-299.8	-299.6	-300.4	-300.3 ± 0.0	-297.3	-297.1	-297.8	-297.6 ± 0.0	-298.6	-298.3	-298.8	-298.8 ± 0.0
	(5,6)	-300.0	-299.8	-300.1	-300.1 ± 0.0	-296.8	-296.8	-297.0	-297.0 ± 0.0	-298.1	-298.0	-298.2	-298.2 ± 0.0
HF	(D,T)		-293.5	-324.8	-317.3 ± 2.7 ^g		-293.5	-311.1	-312.6 ± 1.0 ^g		-294.8	-312.3	-313.9 ± 1.0 ^f
	(T,Q)	-313.8	-313.3	-316.9	-316.5 ± 0.2	-311.5	-310.8	-313.5	-313.5 ± 0.1	-312.8	-312.1	-314.7	-314.8 ± 0.1
	(Q,5)	-318.5	-318.1	-319.1	-319.0 ± 0.0	-313.2	-313.0	-313.6	-313.7 ± 0.0	-314.4	-314.4	-315.0	-315.0 ± 0.0
	(5,6)	-318.9	-318.6	-318.9	-318.9 ± 0.0	-312.8	-312.7	-312.8	-312.9 ± 0.0	-314.1	-314.0	-314.1	-314.2 ± 0.0
N ₂	(D,T)		-394.8	-424.6	-420.6 ± 3.5 ^g		-387.6	-403.5	-403.8 ± 1.0 ^g		-391.5	-407.3	-407.5 ± 1.0 ^f
	(T,Q)	-414.9	-414.3	-417.8	-417.6 ± 0.2	-403.0	-402.5	-404.8	-404.8 ± 0.1	-406.8	-406.2	-408.4	-408.4 ± 0.1
	(Q,5)	-419.2	-418.8	-419.7	-419.7 ± 0.1	-404.1	-404.0	-404.5	-404.5 ± 0.0	-407.8	-407.7	-408.2	-408.2 ± 0.0
	(5,6)	-420.9	-419.8	-420.1	-420.1 ± 0.0	-403.9	-403.8	-403.9	-403.9 ± 0.0	-407.6	-407.5	-407.6	-407.6 ± 0.0
Ne	(D,T)		-288.8	-324.6	-321.0 ± 6.8 ^g		-289.5	-310.9	-314.9 ± 0.2 ^f		-290.3	-311.7	-315.6 ± 0.1 ^g
	(T,Q)	-312.1	-311.5	-315.7	-315.6 ± 0.4	-312.0	-311.2	-314.4	-314.7 ± 0.0	-312.8	-312.1	-315.3	-315.6 ± 0.0
	(Q,5)	-318.2	-317.9	-319.1	-319.0 ± 0.1	-314.9	-314.7	-315.6	-315.6 ± 0.0	-315.8	-315.5	-316.4	-316.4 ± 0.0
	(5,6)	-319.0	-318.8	-319.2	-319.2 ± 0.0	-314.8	-314.6	-314.9	-314.9 ± 0.0	-315.6	-315.4	-315.6	-315.7 ± 0.0

^a (X_1, X_2) denotes the cardinal number pair used for CBS extrapolation. ^b Reference 22. See this reference for further comparisons. ^c Using the offset parameter $\alpha = -3/8$. ^d Reference 27. ^e This work, with the error defined such as to encompass the results from GUSTE/DQT and GUSTE/Q56. ^f The lower bound for this system is obtained with η_{DTQ} . ^g The lower bound for this system is obtained with η_{Q56} .

Since eq 2 also underestimates the target unsigned energy at $X_2 = 10$, and the CCSD-R12B energy is itself not free from error, it will be impossible to say which estimate is more reliable. However, the rms error in GUSTE is seen to be a factor of 4 smaller than for eq 2.

We now turn to Tables 4–9 which compare the results obtained from the GUSTE method with the USTE²⁷ and traditional X^{-3} laws for MP2, CCD, CCSD, and MRCI(Q) energies. As in the previous paragraph, the GUSTE energies provide a substantial improvement relative to the results from eq 2 or GUSTE/DTQ. However, such improvements are relatively small compared with the USTE results, except for

the (D,T) extrapolated energy that tends to lie closer to the (5,6) result. A similar pattern is observed for GUSTE/Q56, with the improvements over USTE being now expected for extrapolated energies with larger X values. Relatively small, albeit significant, improvements arise though from GUSTE, but (as in GUSTE/Q56) at the expense of knowing τ_{53}^{Q56} which implies calculations with the largest affordable cardinal numbers. For two electron systems, where exact energies are available, the differences between the GUSTE and USTE energies are predicted to be in the micro- or submicrohartree range, amounting at most to $-3 \mu\text{E}_h$ for HeH^+ . A favorable case is He_2^{++} ,

TABLE 5: Extrapolated MRCI(Q) Dynamical Correlation Energies (in Millihartrees) for the Ground Electronic States of Some Two-Electron Systems^a

system	$(X_1, X_2)^b$	eq 2 ^c	USTE ^d	GUSTE ^e
H ₂	(D,T)	-22.249	-22.363	-22.310 ± 0.006 ^f
	(T,Q)	-22.307	-22.321	-22.315 ± 0.001
	(Q,5)	-22.320	-22.324	-22.322 ± 0.000
	(5,6)	-22.307	-22.308	-22.308 ± 0.000
H ₃ ⁺	(D,T)	-13.031	-13.067	-13.165 ± 0.007 ^g
	(T,Q)	-13.140	-13.154	-13.159 ± 0.001
	(Q,5)	-13.194	-13.198	-13.199 ± 0.000
	(5,6)	-13.161	-13.162	-13.163 ± 0.000
HeH ⁺	(D,T)	-23.295	-23.428	-23.889 ± 0.032 ^f
	(T,Q)	-23.836	-23.880	-23.919 ± 0.003
	(Q,5)	-23.890	-23.902	-23.910 ± 0.001
	(5,6)	-23.886	-23.890	-23.893 ± 0.000
He ₂ ⁺⁺	(D,T)	-16.614	-16.853	-17.063 ± 0.027 ^f
	(T,Q)	-17.025	-17.064	-17.088 ± 0.003
	(Q,5)	-17.079	-17.089	-17.094 ± 0.001
	(5,6)	-17.065	-17.068	-17.070 ± 0.000

^a Similar to ref 27, we quote the extrapolated MRCI(Q) energies with microhartree accuracy. The error indicated in the last column of this and the following tables (Table 2 included as well) measures the variation associated with the use of τ_{53}^{DTQ} and τ_{53}^{Q56} which should not be confused with the error relative to the exact nonrelativistic energy (or the true CBS limit for systems with more electrons) that is difficult to obtain for all but few-electron systems (see ref 54). ^b (X_1, X_2) denotes the cardinal number pair used for extrapolation. ^c Using the offset parameter $\alpha = -3/8$. ^d Reference 27. ^e This work. ^f The lower bound for this system is obtained with η_{DTQ} . ^g The lower bound for this system is obtained with η_{Q56} .

where the total energy (the CAS energy has been taken from our best estimate in ref 27) is predicted to be -3681.456 mE_h, in excellent agreement with Wolniewicz's⁵⁶ result. Note that the requirement of knowing τ_{53}^{Q56} should pose no significant limitation for many systems of interest, since our experience suggests that calculations at a single geometry should suffice to calibrate the method. Note especially that the conjecture that τ_{53} is (approximately) invariant over the molecule configuration space finds support in exploratory calculations for diatomic molecules where the extrapolated energies appear to be predicted reliably from the repulsive wing of the potential curve up to dissociation. In fact, although the number of coupled electron pairs is expected to diminish upon bond breaking, such a fluctuation is likely to be small. Moreover, their number should vary smoothly with separation, suggesting that any small change in the scaling factor used for the extrapolation may largely be irrelevant. Unfortunately, we are not aware of any rigorous study of this problem for a polyatomic molecule.

The only piece of data at our disposal to test the above conjecture refers to the MRCI(Q)/AVXZ energies for the ground electronic states of H₂O and OH, as the latter can be a dissociation product of the former (for a recent accurate *ab initio* study on the water molecule that also addresses CBS extrapolation, see ref 57). Although the calculated τ_{53} values seem to bear little relation to each other, we alert for the fact that they have been estimated using different sets of cardinal numbers. In an attempt to assess the performance of the GUSTE method for H₂O, we have therefore examined in some detail the dependence in X of the dynamical correlation energy. The atypical pattern illustrated in panel (a) of Figure 2 may be rationalized as due to the fact that the basis is saturated faster for OH than H₂O. This can be understood by considering the dynamical correlation per electron. For H₂O, we will first divide the total dynamical correlation by 10 electrons (valence plus

TABLE 6: Extrapolated MRCI(Q) Valence Dynamical Correlation Energies (in Millihartrees) for the Ground Electronic States of Some Hydrides (For the Water Molecule, the Core-Correlation Energy Has Also Been Included)

system	$(X_1, X_2)^a$	eq 2 ^b	USTE ^c	GUSTE ^d
BH	(D,T)	-49.398	-49.696	-50.527 ± 0.265 ^e
	(T,Q)	-50.621	-50.721	-50.788 ± 0.028
	(Q,5)	-50.585	-50.607	-50.621 ± 0.006
	(5,6)	-50.547	-50.554	-50.558 ± 0.002
CH	(D,T)	-100.353	-102.160	-102.189 ± 0.304 ^e
	(T,Q)	-102.212	-102.475	-102.475 ± 0.034
	(Q,5)	-102.265	-102.325	-102.326 ± 0.007
	(5,6)	-102.191	-102.209	-102.210 ± 0.002
NH	(D,T)	-153.701	-157.232	-157.345 ± 0.403 ^e
	(T,Q)	-157.205	-157.717	-157.723 ± 0.042
	(Q,5)	-157.484	-157.606	-157.608 ± 0.009
	(5,6)	-157.338	-157.374	-157.375 ± 0.003
OH	(D,T)	-217.260	-223.989	-226.198 ± 0.655 ^e
	(T,Q)	-225.550	-226.643	-226.817 ± 0.059
	(Q,5)	-226.361	-226.629	-226.667 ± 0.013
	(5,6)	-226.208	-226.289	-226.302 ± 0.004
FH	(D,T)	-276.841	-286.828	-292.672 ± 0.916 ^e
	(T,Q)	-291.304	-293.116	-293.546 ± 0.072
	(Q,5)	-292.706	-293.152	-293.244 ± 0.015
	(5,6)	-292.704	-292.844	-292.874 ± 0.005
SH	(D,T)	-186.417	-192.449	-191.662 ± 0.384 ^e
	(T,Q)	-190.617	-191.387	-191.327 ± 0.038
	(Q,5)	-191.453	-191.651	-191.635 ± 0.009
	(5,6)	-191.568	-191.633	-191.628 ± 0.003
H ₂ O	(D,T)	-261.355	-272.809	-298.786 ± 0.190 ^f
	(T,Q)	-293.458	-296.888	-298.606 ± 0.010
	(Q,5)	-297.486	-298.399	-298.755 ± 0.002

^a (X_1, X_2) denotes the cardinal number pair used for extrapolation. ^b Using the offset parameter $\alpha = -3/8$. ^c Reference 27. ^d This work. ^e The lower bound for this system is obtained with η_{DTQ} . ^f The lower bound for this system is obtained with η_{Q56} .

core) as the calculations on this molecule included core-correlation effects: the lowest-energy molecular orbital ($\sim 1s$ orbital of oxygen) was optimized in the CASSCF calculations, but unlike active orbitals that change occupations it remained doubly occupied in all reference determinants defining the CASSCF and MRCI wave functions. The calculated dynamical correlation energy per electron so obtained varies from -18.24 mE_h for $X = D$ to -24.26 mE_h for $X = T$ and -28.62 mE_h for $X = 5$. However, not all the core-valence correlation has been recovered due to having kept closed the $1s$ orbitals in the CASSCF and MRCI calculations. Thus, one may consider that the calculated dynamical correlation is essentially of the valence type, yielding for the dynamical correlation energy per valence electron the values of -22.79 , -30.33 , and -35.78 mE_h in the above order. For OH (and all other systems listed in Tables 6–8), core correlation has been ignored, with the valence dynamical correlation per electron varying from -22.95 mE_h for $X = D$ to -29.11 mE_h for $X = T$ and -31.71 mE_h for $X = 5$. As could be expected,⁸ this is generally smaller for the open-shell hydroxyl radical than for the closed-shell water molecule, where all electrons are paired. Another indicator that the basis is saturated faster for OH than H₂O is the corresponding fraction of recovered correlation energy for $X = D, T$, and 5 : 71, 90, and 98% of the (5,6) valence dynamical correlation energy for OH; 61, 81, and 96% of the (Q,5) extrapolated (mostly valence) dynamical correlation for H₂O. This may even be inferred from the slightly distinct slopes displayed for $X \geq 4$ by the curves in Figures 2 and 3 for the CBS extrapolations in H₂O and OH,

TABLE 7: Extrapolated MRCI(Q) Valence Dynamical Correlation Energies (in Millihartrees) for the Ground Electronic States of First-Row Homonuclear Diatomics

system	$(X_1, X_2)^a$	eq 2 ^b	USTE ^c	GUSTE ^d
B ₂	(D,T)	-88.242	-89.971	-89.995 ± 0.707 ^e
	(T,Q)	-90.440	-90.712	-90.705 ± 0.083
	(Q,5)	-90.212	-90.266	-90.268 ± 0.016
	(5,6)	-90.092	-90.108	-90.109 ± 0.005
C ₂	(D,T)	-160.492	-165.857	-166.374 ± 1.128 ^e
	(T,Q)	-166.614	-167.447	-167.476 ± 0.114
	(Q,5)	-166.718	-166.904	-166.914 ± 0.024
	(5,6)	-166.554	-166.610	-166.614 ± 0.007
N ₂	(D,T)	-266.477	-278.039	-278.824 ± 1.043 ^e
	(T,Q)	-278.057	-279.774	-279.815 ± 0.095
	(Q,5)	-279.149	-279.561	-279.572 ± 0.020
	(5,6)	-278.914	-279.038	-279.044 ± 0.006
O ₂	(D,T)	-404.121	-423.215	-423.456 ± 0.841 ^e
	(T,Q)	-421.529	-424.245	-424.244 ± 0.071
	(Q,5)	-423.502	-424.163	-424.164 ± 0.015
	(5,6)	-423.397	-423.601	-423.605 ± 0.005
F ₂	(D,T)	-506.577	-537.208	-536.722 ± 0.151 ^e
	(T,Q)	-532.692	-536.891	-536.861 ± 0.012
	(Q,5)	-536.420	-537.478	-537.464 ± 0.003
	(5,6)	-536.431	-536.761	-536.762 ± 0.001

^a (X_1, X_2) denotes the cardinal number pair used for extrapolation.

^b Using the offset parameter $\alpha = -3/8$. ^c Reference 27. ^d This work.

^e The lower bound for this system is obtained with η_{DTQ} .

TABLE 8: Extrapolated MRCI(Q) Valence Dynamical Correlation Energies (in Millihartrees) for the Ground Electronic States of BN, BO, CN and CO

system	$(X_1, X_2)^a$	eq 2 ^b	USTE ^c	GUSTE ^d
BN	(D,T)	-178.383	-184.495	-185.592 ± 1.186 ^e
	(T,Q)	-185.696	-186.671	-186.749 ± 0.115
	(Q,5)	-186.021	-186.244	-186.264 ± 0.024
	(5,6)	-185.775	-185.840	-185.848 ± 0.007
BO	(D,T)	-215.559	-224.710	-228.659 ± 1.544 ^e
	(T,Q)	-228.267	-229.878	-230.167 ± 0.132
	(Q,5)	-229.087	-229.465	-229.529 ± 0.027
	(5,6)	-228.967	-229.083	-229.104 ± 0.008
CN	(D,T)	-219.324	-227.470	-228.322 ± 1.016 ^e
	(T,Q)	-228.002	-229.240	-229.294 ± 0.096
	(Q,5)	-228.639	-228.930	-228.945 ± 0.021
	(5,6)	-228.426	-228.513	-228.519 ± 0.006
CO	(D,T)	-266.510	-277.805	-280.941 ± 0.987 ^e
	(T,Q)	-279.831	-281.660	-281.879 ± 0.084
	(Q,5)	-281.147	-281.593	-281.641 ± 0.018
	(5,6)	-281.015	-281.152	-281.169 ± 0.005

^a (X_1, X_2) denotes the cardinal number pair used for extrapolation.

^b Using the offset parameter $\alpha = -3/8$. ^c Reference 27. ^d This work.

^e The lower bound for this system is obtained with η_{DTQ} .

respectively. Thus, a balanced level of description is obtained faster for OH than H₂O, which may explain the small plateau in plot (a) of Figure 2. We should note that removing the $X = D$ or T energies from the fit will not change the above pattern. A more typical trend may, however, be obtained if the AVDZ energy is replaced by -147 mE_h or so rather than the actually calculated value of -182.34 mE_h; see panel (b) of Figure 2. Using the former, the following extrapolated correlation energies are obtained for the water molecule (format as in Table 6): -298.782 ± 2.123 (D,T), -296.988 ± 0.155 (T,Q), and -298.405 ± 0.035 (Q,5). They correspond to $\tau_{53}^{DTQ} = 1.21$ and $\tau_{53}^{Q56} = 1.30$, in somewhat closer agreement with $\tau_{53}^{Q56}(\text{OH})$. The improvement is striking for the (D,T) extrapolation, while remaining good for (Q,5) when comparing with USTE. Fur-

TABLE 9: A Comparison of the Calculated GUSTE/DTQ and GUSTE/DD₊T Extrapolated CCSD Correlation Energies (in Millihartrees) and Other Parameters for the Ground Electronic States of CH₂, CO, F₂, H₂O, HF, N₂, and Ne

system	$(X_1, X_2)^a$	GUSTE/DTQ	η_{DTQ}^b	GUSTE/DD ₊ T	$\tau_{53}^{DD+T}{}^c$
CH ₂	(D,T)	-176.4	0.751	-175.9	-0.864
	(T,Q)	-176.4	0.751	-176.3	-0.886
	(Q,5)	-175.8	0.660	-175.7	-0.811
	(5,6)	-175.7	0.631	-175.7	-0.784
CO	(D,T)	-396.8	0.694	-386.7	-0.864
	(T,Q)	-396.8	0.694	-396.2	-1.013
	(Q,5)	-396.5	0.678	-396.3	-1.017
	(5,6)	-395.9	0.630	-395.8	-0.991
F ₂	(D,T)	-601.6	1.197	-581.0	-0.864
	(T,Q)	-601.6	1.197	-600.2	-1.019
	(Q,5)	-602.6	1.236	-602.3	-1.046
	(5,6)	-601.6	1.158	-601.5	-1.025
H ₂ O	(D,T)	-299.4	0.860	-292.5	-0.864
	(T,Q)	-299.4	0.860	-298.9	-0.987
	(Q,5)	-298.8	0.823	-298.7	-0.980
	(5,6)	-298.2	0.740	-298.1	-0.934
HF	(D,T)	-314.9	0.671	-303.8	-0.864
	(T,Q)	-314.9	0.671	-314.1	-1.018
	(Q,5)	-315.1	0.678	-314.9	-1.036
	(5,6)	-314.2	0.608	-314.1	-0.996
N ₂	(D,T)	-408.5	0.843	-399.9	-0.864
	(T,Q)	-408.5	0.843	-408.0	-0.998
	(Q,5)	-408.2	0.826	-408.1	-1.003
	(5,6)	-407.6	0.760	-407.6	-0.971
Ne	(D,T)	-315.6	0.511	-300.8	-0.864
	(T,Q)	-315.6	0.511	-314.6	-1.035
	(Q,5)	-316.4	0.532	-316.2	-1.065
	(5,6)	-315.7	0.497	-315.6	-1.044

^a (X_1, X_2) denotes the cardinal number pair used for extrapolation.

^b Results obtained with the following constrained values of τ_{53}^{DTQ} : -0.932 for CH₂; -1.288 for CO; -1.304 for F₂; -1.219 for H₂O; -1.300 for HF; -1.249 for N₂; -1.346 for Ne. ^c Ratios obtained when the following η_{DD+T} values are fixed (by fitting the $X = D, D_+, T$ energies): 0.813 for CH₂; 1.979 for CO; 3.824 for F₂; 1.743 for H₂O; 2.081 for HF; 1.942 for N₂; 2.397 for Ne; see the text.

thermore, if these ratios are used for the extrapolations in OH, one gets using the same units -229.220 ± 0.919 (D,T), -227.058 ± 0.066 (T,Q), and -226.317 ± 0.004 (5,6), in slightly better agreement with the best estimate than USTE but slightly worse than GUSTE. Finally, one wonders about the error obtained if $\tau_{53}^{Q56}(\text{OH})$ were used for the extrapolations in H₂O. The results (in mE_h) are -273.8 (D,T), -296.4 (T,Q), and -298.3 (Q,5), in good agreement with the USTE values. Keeping in mind the slightly different level of correlation description used for H₂O and OH, two observations are in order from the above results. First, H₂O is the only system where the GUSTE (Q,5) and USTE (Q,5) predictions differ by more than 0.1 mE_h. This reinforces our belief that the (Q,5) extrapolated MRCI(Q) energy from eq 2 may be 1 mE_h or so in error due to a poor balanced level of description: a higher accuracy may require improvements on the basis or in the correlation description or both. Second, and perhaps most interesting, it suggests that in chemical reactions where the chemical bonds are broken (like H₂O splitting into OH and H), it is advantageous to choose τ_{53} somewhere in the middle between the reactant and the product values for the most balanced description of the PES using the GUSTE approach. Finding the optimal balance for the A_5/A_3 ratio in both systems (in this case, H₂O and OH + H) simultaneously may then be an important step for accurately describing a PES with GUSTE.

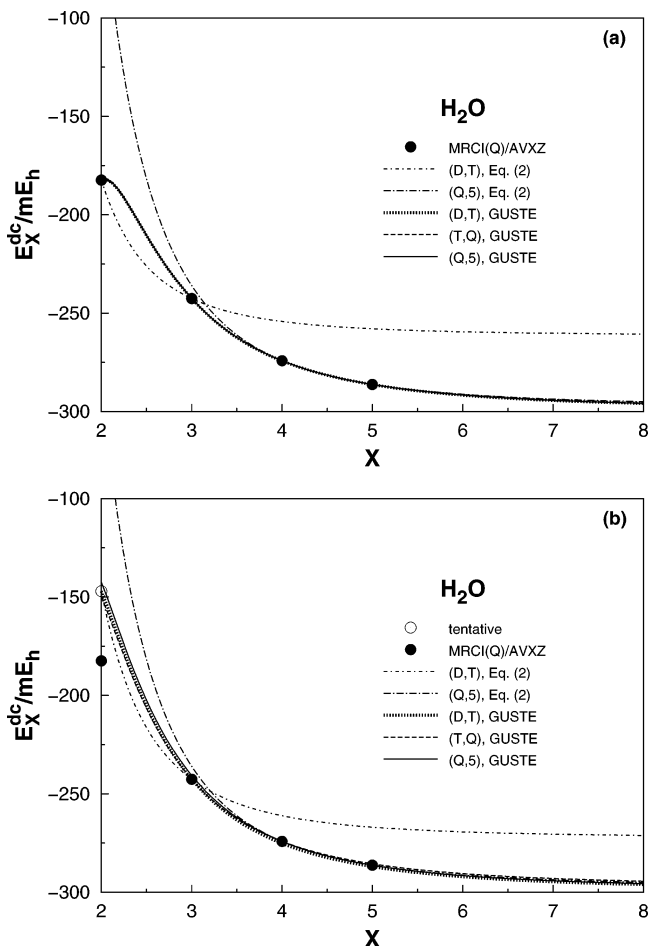


Figure 2. Extrapolations of the dynamical correlation energy for H₂O: (a) using the calculated MRCI(Q)/AVXZ ($X = D, T, Q, 5$) energies; (b) as in (a) but using a tentative MRCI(Q)/AVDZ energy. For clarity, the curves referring to USTE will not be shown as they lie close to the GUSTE ones. See the text.

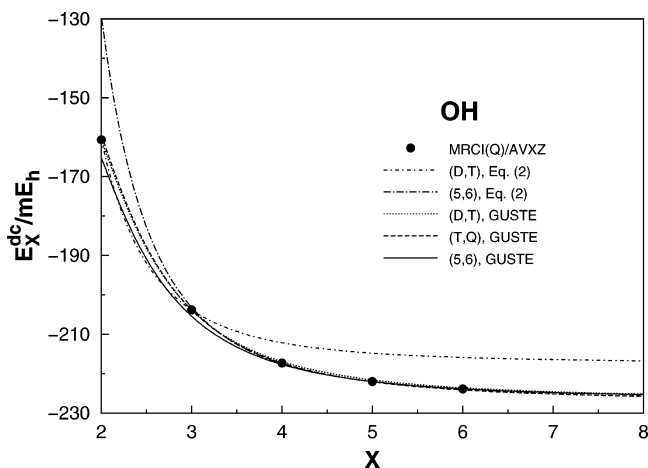


Figure 3. Extrapolations of the dynamical correlation energy for OH using the calculated MRCI(Q)/AVXZ ($X = D, T, Q, 5, 6$) energies. For clarity, the curves referring to USTE will not be shown as they lie close to the GUSTE ones. See the text.

A further remark is in order concerning GUSTE/DTQ. Although this requires only an extra calculation with $X = Q$, one wonders whether this third energy could be for the range $D - T$ or $2 \leq X \leq 3$. Since an *ab initio* approach poses difficulties in specifying the basis set for a non-integer- X calculation, the alternative is to predict the required energy from the results for $X = D$ and T with an independent rule. For

example, Truhlar¹⁷ has proposed the law $E_X = E_\infty + b/X^{2.4}$ optimized for (D, T) extrapolations from CCSD and CCSD(T) energies. The extra point (denoted as D_+) may then be generated from such a rule, with $\tau_{53}^{DD_+T}$ and hence η_{DD_+T} determined (jointly with E_∞ and A_3) by fitting the $X = D, D_+, T$ energies to eqs 4 and 5. Two approaches may then be followed. The first consists of keeping fixed the scaling factor η_{DD_+T} for all extrapolations. Such an approach has been found⁵⁵ to perform well for He₂ using raw energies calculated with both the CC [CCSD and CCSD(T)] and CI(Q) methods. Indeed, it finds support in Figure 4, which shows that the values of η_{DTQ} actually obtained by imposing τ_{53}^{DTQ} assume similar values for all extrapolations (note that the plotted scaling factors have been divided by their averaged value for all extrapolations in a given system). Except in one or two cases that justify the rule, the results obtained from the raw MP2, CCD, and CCSD energies deviate typically by 10 to 20%, a fluctuation that may likely be absorbed by the E_∞ and A_3 fitting parameters. Note that no extrapolation rule has been reported¹⁷ for MRCI(Q) energies. Given that a $X^{-2.4}$ dependence seems to yield acceptable results for He₂ when using CC energies, this suggests that a similar power-law may, once the exponent is optimized, be also valid for MRCI(Q) energies. Indeed, if β_{CI} is defined from $X = D - 6$ fits for the subset of systems studied²⁷ by MRCI(Q) that overlaps with Klopper's²² one, namely H₂O, HF, N₂, CO and F₂, the result will be $\beta_{CI} = 2.2$ (this value decreases to 1.9 if the fit covers only the $D - Q$ range of cardinal numbers).

To illustrate how the η -fixed method works, we have considered the seven systems studied in ref 22 with the CCSD/VXZ method. However, rather than using the scaling values that mimic τ_{53}^{DTQ} , we have utilized those that reproduce $\tau_{53}^{DD_+T}$, with the energy for $X = D_+$ obtained by fitting Truhlar's¹⁷ $X^{-2.4}$ law to Klopper's CCSD data for $X = D, T$. The results are collected in Table 9. For comparison, we give also in the third column of this table the extrapolated energies predicted from GUSTE/DTQ, where the ratio A_5/A_3 is constrained to be τ_{53}^{DTQ} . Moreover, we list in column four the corresponding scaling factors η_{DTQ} , while column six reports the $\tau_{53}^{DD_+T}$ ratios predicted when η_{DD_+T} is fixed at its optimum value in the fit to the $X = D, D_+, T$ energies. Although the extrapolated energies from GUSTE/DD₊T (in column five) show an improved accuracy when compared with those obtained from the traditional rule (2) (cf. Table 1), they are poorer than the GUSTE/DTQ or GUSTE/Q56 or GUSTE ones. In fact, the only exception is CH₂, which is due to the fact that $\eta_{DD_+T} \sim \eta_{DTQ}$ for this system. Note that similar results are obtained if the value of $\tau_{53}^{DD_+T}$ associated with the $X = D, D_+, T$ energies ($\tau_{53}^{DD_+T} = -0.864$) is imposed, rather than η_{DD_+T} . This is not surprising since η_{DD_+T} and $\tau_{53}^{DD_+T} = -0.864$ are equivalent attributes of Truhlar's¹⁷ law. Despite the somewhat modest results, it is interesting to note that the GUSTE/DD₊T rule employs raw energies only up to $X = T$ but shows a performance better than the traditional law (2) when using the same cardinal numbers for the extrapolation.

4. Concluding Remarks

We summarize a few properties that the GUSTE rule here developed satisfies:

1. It extrapolates reliably the (full or dynamical) correlation energy to the CBS limit, irrespectively of the cardinal numbers used for the extrapolation.
2. Once calibrated the scheme is dual-level as it requires only two *ab initio* calculations with distinct basis sets for extrapolating the correlation energy.

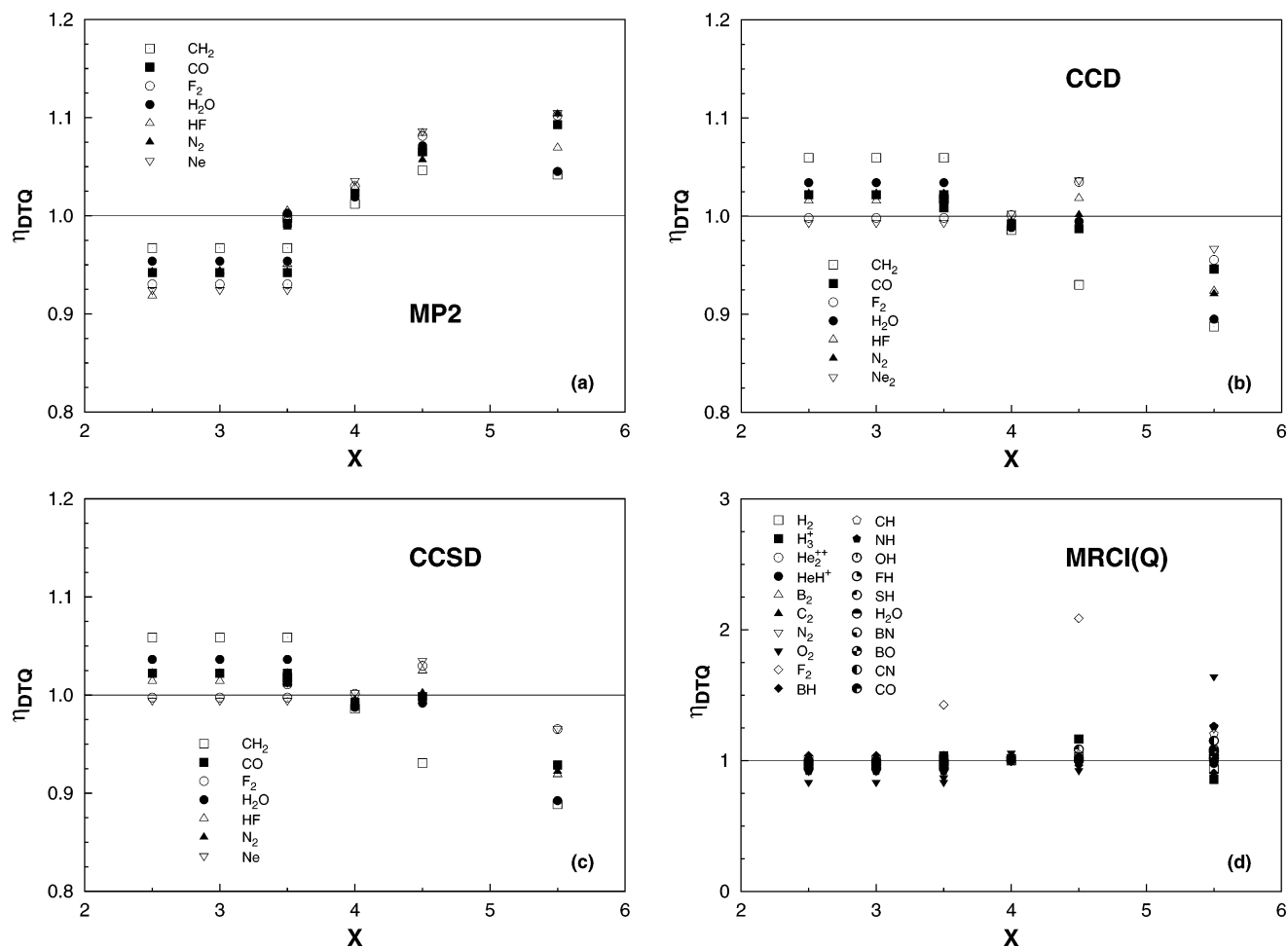


Figure 4. Values of η_{DTQ} obtained by dividing the actually calculated results by the average value obtained in the (D,T) , $(D-Q)$, (T,Q) , $(D-5)$, $(Q,5)$, $(D-6)$, and $(5,6)$ extrapolations: (a) MP2; (b) CCD; (c) CCSD; (d) MRCI(Q).

3. The calibration requires the least possible amount of calculations with high cardinal numbers at a single geometry (without exceeding $X = Q$ in GUSTE/ DTQ), although the accuracy of the method is enhanced when such data is available.

4. The calibration does not utilize data alien to the raw *ab initio* energies (information from other laws may, however, be utilized as discussed in section 3).

5. The method reduces to the original USTE scheme when $\eta = 1$ in eq 8.

In summary, we have analyzed generalizations of the USTE rule that can improve even further the accuracy of the extrapolated energies, especially when using $X = D$ and T basis sets. Such generalizations are based on the premise that the ratio of the triplet-pair (see section 2) to singlet-pair contributions does not vary significantly over the configuration space of the molecule. Work to test this assertion would be valuable though conceptually difficult at regions where more than one electronic configuration plays a role. Finally, the new scheme affords enough flexibility to treat different singlet/triplet-pair situations, and hence is expected to be valid for both ground and excited electronic states. This may help to enhance the development of methods^{50–52} that allow the calculation of accurate potential energy surfaces at an unprecedented low computational cost. Parallel to this, it may open the way for calculating molecular properties that may be sensitive to small energy differences and therefore to quality of the treatment of electron correlation. In particular, its use for studying static electric response properties of molecules or groups or molecules, which are formally

developed via energy derivatives and hence are intrinsic to features of electronic structure,⁵⁸ may be worth pursuing in future work.

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