Application of the Unified Singlet and Triplet Electron-Pair Extrapolation Scheme With Basis Set Re-Hierarchization to Tensorial Properties.

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Application of the Unified Singlet and Triplet Electron-Pair Extrapolation Scheme with Basis Set Rehierarchization to Tensorial Properties

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S *Supporting Information*

ABSTRACT: A method previously suggested to calculate the correlation energy at the complete one-electron basis set limit by reassigning the basis hierarchical numbers and using the unified singlet- and triplet-pair extrapolation scheme is here utilized to extrapolate tensorial properties, with specific use for the polarizabilities of eight molecules whose raw values are obtained with second-order Møller–Plesset perturbation theory and coupled-cluster singles and doubles excitation methods, both without and with inclusion of the perturbative triples correction. Good agreement is obtained with the best available estimates even when the (d, t) pair of hierarchical numbers is utilized to perform the extrapolations. This conceivably reinforces our previous finding that there is no good reason to exclude double-ζ results in extrapolations, especially if the basis is calibrated to comply with the theoretical model.
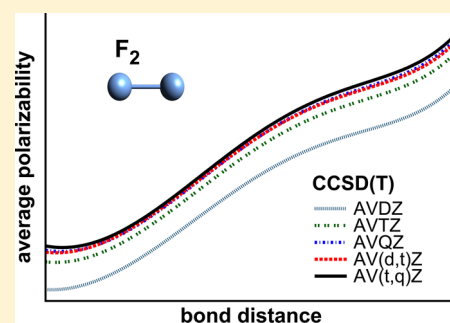
INTRODUCTION

The energy of a molecular system under a small external electric field (**F**) assumes the form

$$E(\mathbf{F}) = E(0) + \sum_{i=1}^{3} \mu_i F_i + \frac{1}{2!} \sum_{i,j=1}^{3} \alpha_{ij} F_i F_j$$
$$+ \frac{1}{3!} \sum_{i,j,k=1}^{3} \beta_{ijk} F_i F_j F_k + \frac{1}{4!} \sum_{i,j,k,l}^{3} \gamma_{ijkl} F_i F_j F_k F_l + \cdots$$

$$(1)$$

where F_i are the components of the applied electric field and $E(0)$ is the total energy in its absence. Thus, if a uniform field is applied along the axes $i = x$, y, or z, it reads

$$E(F_i) = E(0) + \mu_i F_i + \frac{1}{2!} \alpha_{ii} F_i^2 + \frac{1}{3!} \beta_{iii} F_i^3 + \frac{1}{4!} \gamma_{iiii} F_i^4 + \cdots$$

$$(2)$$

where the terms of the dipole moment (μ), dipole polarizability (α), dipole hyperpolarizability (β), and second-order dipole hyperpolarizability (γ) are defined as the negative of the first, second, third, and fourth derivatives of the energy $E(F_i)$ relative to electric field, respectively.[1] They represent some of the most fundamental properties of matter[2] and provide a significant role in the investigation of nonlinear optical properties.[3,4] However, their experimental determination is difficult, and the uncertainty of the measured values is often undesirably large.[2–5] Use of theoretical procedures via *ab initio* electronic

structure calculations remains therefore a most valuable root for the accurate determination of such properties.

In the above process, it proves vitally important the choice of the basis set employed for the calculations, because it must be sufficiently flexible to describe the distortion of the external orbitals when the electric field is applied.[2,5] In this sense, the augmented basis set with extra diffuse and polarization functions of the Dunning correlation consistent family commonly denoted as aug-cc-pVXZ[6–9] (X = D, T, Q, 5, 6, ... is the cardinal number) can offer a good description of the expected trends,[5,7,10–12] mainly for cardinal numbers larger than T. Indeed, alternative basis sets are available[10] (and references therein) but we use the aug-cc-pVXZ basis set in the present work. An advantage of such bases is that they are hierarchically built, such that an improved description of the system is observed when we move upward in the hierarchy. This characteristic enables the construction of extrapolation methods, which allow an estimate of the complete basis set limit (CBS limit) for the correlation[13–18] and Hartree–Fock (HF)[19–21] energies. Such methods can therefore be very useful, mainly for the correlation energy which is well-known to possess a lower convergence rate with X than the HF energy. As a result, calculations of the correlation energy require basis sets with a large number of functions to obtain accurate raw values, which increase dramatically the computational cost

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especially for moderate and large systems. In fact, only for small systems it is possible to use accurate methods such as MP2, CCSD, and CCSD(T) such as to yield results in good agreement with the experimental values, an example being provided by the work of Maroulis[22] (and references therein). Additionally, R12-based methods[23−29] designed to efficiently recover the correlation energy can yield electrical response properties in good agreement with the experimental and best theoretical data[30−33] but, except for small systems, they become unaffordable particularly when associated with large basis sets.[5]

A scheme to obtain the CBS limit of the electrical properties has been proposed by Junqueira and Varandas.[12] The total energy of a system under an electric field is then first separated into HF and correlation contributions:

$$E(F_i) = E^{HF}(F_i) + E^{cor}(F_i) \tag{3}$$

where the abbreviations have an obvious meaning. For the correlation energy, the authors have employed the two-parameter USTE($X − 1, X$) scheme of Varandas,[16] whereas for the HF ones they use the protocol of Karton and Martin.[20] The electrical properties in the CBS limit are then obtained[12] by extrapolating the energies $E(0)$ and $E(F_i)$ for four different values of the electric field ($F_i = \pm 0.005, \pm 0.01$ au) so that, by truncating eq 2 in the fourth term, a linear system of equations can be resolved and the properties calculated. Clearly, the average polarizability will require the procedure to be carried out for the three electric field components: x, y, and z. The values so obtained[12] have been predicted in good agreement with the experimental data. Nevertheless, the method is computationally expensive because four correlated calculations with applied electric fields and one in the absence of the field are required for at least one pair of basis hierarchical numbers. Subsequently, two-parameter (three-parameter for the Hartree−Fock component) extrapolations of correlated polarizabilities for tetravalent actinide ions[34] employing all-electron ANO relativistic core-correlation basis,[35] as well as extrapolations with three-parameter formulas using much larger values of the cardinal number (up to $X = Q, 5, 6$ of the aug-cc-pVXZ basis, and the doubly augmented d-aug-cc-pVXZ one[36]) have been reported.[37] Our major goal in this work is to suggest a more practical scheme for the CBS extrapolation of electrical properties. Besides a lower computational cost than the original scheme of Junqueira and Varandas,[12] the new approach accounts for the different convergence rates of the HF and correlation expansions.

The paper is organized as follows. In the next section, we describe the procedure used to obtain tensorial properties at the CBS limit, by illustrating the approach for the polarizability, average polarizability, and anisotropy. The results of some applications are then discussed in a subsequent section, and some remarks gathered in the conclusions.

■ COMPLETE BASIS SET LIMIT

As mentioned above, the elements of the expansion in eq 2 can be written in a general way as follows:

$$\zeta = -\left(\frac{\partial^\sigma E(F_i)}{\partial F_i^\sigma}\right) \tag{4}$$

where $\zeta = \mu_i, \alpha_{i}, \beta_{iii}...$ and the superscript σ stands for first, second, and higher orders derivatives. By using eqs 3 and 4, one then gets

$$\zeta = \zeta^{HF} + \zeta^{cor} \tag{5}$$

where

$$\zeta^{HF} = -\left(\frac{\partial^\sigma E^{HF}(F_i)}{\partial F_i^\sigma}\right) \qquad \zeta^{cor} = -\left(\frac{\partial^\sigma E^{cor}(F_i)}{\partial F_i^\sigma}\right) \tag{6}$$

with ζ^{HF} being the property component obtained at the HF level, and ζ^{cor} the correlation counterpart. If we consider now that the correlation and HF energies under an external electric field, $E^{HF}(F_i)$ and $E^{corr}(F_i)$, converge to the CBS limit at the same rate that the energy in the absence of the field, we can simply use the traditional extrapolation methods to calculate the targeted property.

For the HF component, the same method[20] employed by Junqueira and Varandas[12] has been utilized. The result assumes the form

$$E_\infty^{HF} = E_{X_2}^{HF} + \frac{X_2^{-\kappa}}{X_1^{-\kappa} - X_2^{-\kappa}}(E_{X_2}^{HF} - E_{X_1}^{HF}) \tag{7}$$

where $X_1 = X_2 − 1$ denote the cardinal numbers that have been utilized for the basis, $X_1 = 2, 3, 4, 5, ...,$ and κ depends on the cardinal pair (X_1, X_2) used for the extrapolation, namely $\kappa = 3.54$ for the pair (D, T), 5.34 for (T, Q), 8.74 for ($Q, 5$) and $\kappa = 9.43$ for (5, 6).[20,21] Unfortunately, the values obtained for the pair (D, T) are not as reliable as the others,[21] but the same scheme will be used to get CBS extrapolated values.

To CBS extrapolate the correlation energy $E^{cor}(F_i)$, we will adopt the two-parameter USTE($x − 1, x$) extrapolation scheme,[18,38] and the traditional X3 protocol,[13] whose CBS limit can generally be written as

$$E_\infty^{cor} = E_{X_2}^{cor} + \frac{x_2^{-3}}{x_1^{-3} - x_2^{-3}}(E_{X_2}^{cor} - E_{X_1}^{cor}) \tag{8}$$

where, for USTE($x − 1, x$), $x = d, t, q, p,$ and h are the hierarchical numbers proposed elsewhere:[18] for the MPn theories, they assume the values $x = 2.13, 2.90, 3.78, 4.74,$ and 5.72 whereas, for CC-type methods they read $x = 1.91, 2.71, 3.68, 4.71,$ and 5.70. In turn, for the X3 protocol,[13] they are the traditional cardinal numbers $x = 2, 3, 4, 5,$ and 6. Furthermore, we have utilized the two-parameter extrapolation scheme proposed by Varandas,[16] USTE($X − 1, X$), which for single reference methods assumes the form:[39]

$$E_\infty^{cor} = E_{X_2}^{cor} - A_5^\circ (X_2 + \alpha)^{-5}$$
$$+ \frac{E_{X_1}^{cor} - E_{X_2}^{cor} + A_5^\circ[(X_2 + \alpha)^{-5} - (X_1 + \alpha)^{-5}]}{c[(X_2 + \alpha)^{-5} - (X_1 + \alpha)^{-5}] + (X_2 + \alpha)^{-3} - (X_1 + \alpha)^{-3}}$$
$$\times [(X_2 + \alpha)^{-3} + c(X_2 + \alpha)^{-5}] \tag{9}$$

where A_5° and c are previously determined[16] universal parameters. For MPn energies, one has $A_5^\circ = 0.09606679$ and $c = −1.58200942$, whereas for CC-type[16,38] they read $A_5^\circ = 0.16606993$ and $c = −1.42225121$. In turn, for all single reference methods, $\alpha = −(3/8)$. Note that the USTE($x − 1, x$) scheme has been derived from USTE($X − 1, X$), and shown[18] to perform better than the latter for correlation and atomization energies when tested on a set of 106 molecules formed by atoms of H, C, N, O, and F, and (especially for low pairs of hierarchical numbers) far better than the X3 protocol.[13] Thus, an enhanced accuracy is also expected with USTE($x − 1, x$) when it is applied for the correlation energies under an electric field $E^{cor}(F_i)$.

Table 1. Average Polarizability $\bar{\alpha}$ and Anisotropy $\Delta\alpha$ at the HF/aug-cc-pVXZ Level of Theory, with CBS Extrapolations via Eq 7

molecule	property	AVDZ[a]	AVTZ[a]	AVQZ[a]	(D, T)[b]	(T, Q)[b]
Li$_2$	$\bar{\alpha}$	204.72	203.89	204.20	203.63	204.28
	$\Delta\alpha$	75.84	71.79	70.76	70.52	70.48
	$\delta\bar{\alpha}_{calc-exp}$[c]	−16.28	−17.11	−16.80	−17.37	−16.72
HF	$\bar{\alpha}$	4.39	4.75	4.87	4.86	4.90
	$\Delta\alpha$	1.80	1.44	1.32	1.33	1.29
	$\delta\bar{\alpha}_{calc-exp}$[c]	−1.21	−0.85	−0.73	−0.74	−0.70
CO	$\bar{\alpha}$	12.11	12.31	12.34	12.38	12.35
	$\Delta\alpha$	3.47	3.27	3.21	3.20	3.19
	$\delta\bar{\alpha}_{calc-exp}$[c]	−0.93	−0.73	−0.70	−0.66	−0.69
N$_2$	$\bar{\alpha}$	11.30	11.54	11.56	11.61	11.57
	$\Delta\alpha$	5.36	5.24	5.20	5.20	5.19
	$\delta\bar{\alpha}_{calc-exp}$[c]	−0.44	−0.20	−0.17	−0.13	−0.17
F$_2$	$\bar{\alpha}$	7.94	8.42	8.57	8.57	8.61
	$\Delta\alpha$	9.27	9.09	9.05	9.03	9.04
	$\delta\bar{\alpha}_{calc-exp}$[c]	−0.44	0.04	0.19	0.19	0.23
H$_2$O	$\bar{\alpha}$	8.14	8.43	8.51	8.52	8.53
	$\Delta\alpha$	1.49	1.25	1.16	1.18	1.14
	$\delta\bar{\alpha}_{calc-exp}$[c]	−1.50	−1.21	−1.13	−1.12	−1.11
CO$_2$	$\bar{\alpha}$	15.44	15.80	15.89	15.91	15.92
	$\Delta\alpha$	−2.06	−1.70	−1.61	−1.59	−1.58
	$\delta\bar{\alpha}_{calc-exp}$[c]	12.44	11.91	11.77	11.74	11.73
CH$_4$	$\bar{\alpha}$	15.93	16.00	16.00	16.02	16.00
	$\delta\bar{\alpha}_{calc-exp}$[c]	−0.59	−0.52	−0.52	−0.50	−0.52

[a]Raw aug-cc-pVXZ (AVXZ) values. [b]CBS/HF extrapolation via eq 7. [c]The differences between the calculated and experimental values are represented by $\delta\bar{\alpha}_{calc-exp}$. All experimental data is from Hohm,[43] except for[44] CH$_4$.

From eqs 6−8, we can write

$$\zeta_{CBS}^{HF} = \zeta_{X_2}^{HF} + \frac{X_2^{-\kappa}}{X_1^{-\kappa} - X_2^{-\kappa}}(\zeta_{X_2}^{HF} - \zeta_{X_1}^{HF}) \tag{10}$$

and

$$\zeta_{CBS}^{cor} = \zeta_{X_2}^{cor} + \frac{x_2^{-3}}{x_1^{-3} - x_2^{-3}}(\zeta_{X_2}^{cor} - \zeta_{X_1}^{cor}) \tag{11}$$

This enables us to obtain from eq 5:

$$\zeta_{CBS} = \zeta_{X_2} + \frac{x_2^{-3}}{x_1^{-3} - x_2^{-3}}(\zeta_{X_2} - \zeta_{X_1}) \\ + \left(\frac{X_2^{-\kappa}}{X_1^{-\kappa} - X_2^{-\kappa}} - \frac{x_2^{-3}}{x_1^{-3} - x_2^{-3}}\right)(\zeta_{X_2}^{HF} - \zeta_{X_1}^{HF}) \tag{12}$$

where ζ_{X_1} and ζ_{X_2} are the properties obtained through the full correlation method [HF+cor; see eq 5] with a basis set of quality X_1 and X_2, and $\zeta_{X_1}^{HF}$ and $\zeta_{X_2}^{HF}$ are the HF properties obtained with the same basis functions. Similarly, for the USTE$(X − 1, X)$[16] scheme in eq 9, the ζ_{CBS} assumes the form

$$\zeta_{CBS} = \zeta_{X_2} + B(X_1,X_2)(\zeta_{X_2} - \zeta_{X_1}) \\ + \left[\frac{X_2^{-\kappa}}{X_1^{-\kappa} - X_2^{-\kappa}} - B(X_1,X_2)\right](\zeta_{X_2}^{HF} - \zeta_{X_1}^{HF}) \tag{13}$$

where

$$B = \\ \frac{-[(X_2 + \alpha)^{-3} + c(X_2 + \alpha)^{-5}]}{c[(X_2 + \alpha)^{-5} - (X_1 + \alpha)^{-5}] + (X_2 + \alpha)^{-3} - (X_1 + \alpha)^{-3}} \tag{14}$$

Note that eq 13 does not depend on the parameter A_5°, unlike eq 9. Thus, eqs 12 and 13 CBS extrapolate both contributions of eq 2, thence containing the intrinsic approximations and errors of the corresponding extrapolation method.

We will hereinafter focus our attention in the polarizability, average polarizability and anisotropy, which are defined as

$$\alpha_{ii} = -\left(\frac{\partial^2 E(F_i)}{\partial F_i^2}\right)_0 \tag{15}$$

$$\bar{\alpha} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \tag{16}$$

and

$$\Delta\alpha = \left(\frac{1}{2}\right)^{1/2} [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2]^{1/2} \tag{17}$$

where, for convenience, all the dipole moments have been oriented along of the positive z axis. The CBS average polarizability in eq 16 assumes then the following form:

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Table 2. Average Polarizability $\bar{\alpha}$ and Anisotropy $\Delta\alpha$ at the MP2/aug-cc-pVXZ Level of Theory (Notation as in Table 1)

molecule	property	$AVDZ^d$	$AVTZ^d$	$AVQZ^d$	$X3^a$		$USTE^b$		$USTE^c$	
					(D, T)	(T, Q)	(D, T)	(T, Q)	(d, t)	(t, q)
Li$_2$	$\bar{\alpha}$	205.37	205.16	204.59	205.16	204.03	205.42	204.00	205.31	203.95
	$\Delta\alpha$	98.22	92.36	90.08	90.33	88.89	89.58	88.84	89.91	88.77
	$\delta\bar{\alpha}_{calc-exp}{}^e$	−15.63	−15.84	−16.41	−15.84	−16.97	−15.58	−17.00	−15.69	−17.05
HF HF	$\bar{\alpha}$	4.95	5.41	5.56	5.56	5.61	5.61	5.62	5.59	5.62
	$\Delta\alpha$	1.88	1.38	1.18	1.21	1.09	1.16	1.09	1.17	1.08
	$\delta\bar{\alpha}_{calc-exp}{}^e$	−0.65	−0.19	−0.04	−0.04	0.01	0.01	0.02	−0.01	0.02
CO	$\bar{\alpha}$	13.16	13.16	13.17	13.14	13.16	13.06	13.16	13.09	13.16
	$\Delta\alpha$	3.71	3.71	3.64	3.73	3.62	3.82	3.62	3.78	3.62
	$\delta\bar{\alpha}_{calc-exp}{}^e$	0.12	0.12	0.13	0.10	0.12	0.02	0.12	0.05	0.12
N$_2$	$\bar{\alpha}$	11.39	11.51	11.51	11.53	11.50	11.48	11.50	11.51	11.50
	$\Delta\alpha$	4.40	4.17	4.14	4.09	4.14	4.04	4.14	4.06	4.14
	$\delta\bar{\alpha}_{calc-exp}{}^e$	−0.35	−0.23	−0.23	−0.21	−0.24	−0.26	−0.24	−0.23	−0.24
F$_2$	$\bar{\alpha}$	7.25	7.87	8.10	8.08	8.20	8.14	8.20	8.11	8.21
	$\Delta\alpha$	5.47	5.14	5.04	5.02	4.99	4.96	4.98	4.99	4.98
	$\delta\bar{\alpha}_{calc-exp}{}^e$	−1.13	−0.51	−0.28	−0.30	−0.18	−0.24	−0.18	−0.27	−0.17
H$_2$O	$\bar{\alpha}$	9.19	9.56	9.66	9.68	9.70	9.72	9.70	9.70	9.70
	$\Delta\alpha$	0.97	0.64	0.50	0.53	0.43	0.50	0.43	0.51	0.43
	$\delta\bar{\alpha}_{calc-exp}{}^e$	−0.45	−0.09	0.02	0.04	0.06	0.08	0.06	0.06	0.06
CO$_2$	$\bar{\alpha}$	17.32	17.71	17.79	17.84	17.81	17.85	17.81	17.84	17.81
	$\Delta\alpha$	15.35	14.67	14.51	14.44	14.46	14.38	14.46	14.41	14.46
	$\delta\bar{\alpha}_{calc-exp}{}^e$	−0.18	0.21	0.29	0.34	0.31	0.35	0.31	0.34	0.31
CH$_4$	$\bar{\alpha}$	16.46	16.53	16.52	16.55	16.51	16.55	16.51	16.55	16.51
	$\delta\bar{\alpha}_{calc-exp}{}^e$	−0.06	0.01	0.00	0.03	−0.01	0.03	−0.01	0.03	−0.01

[a]Extrapolated via eq 12 with X3($X − 1$, X) scheme. [b]Extrapolated via eq 13. [c]Extrapolated via eq 12 with USTE($x − 1$, x) scheme. [d]Raw aug-cc-pVXZ values. [e]Difference between the calculated and the experimental value, $\delta\bar{\alpha}_{calc-exp}$. All experimental data from Hohm,[43] except for[44] CH$_4$.

Table 3. Average Polarizability $\bar{\alpha}$ and Anisotropy $\Delta\alpha$ at the CCSD/aug-cc-pVXZ Level of Theory (Notation as in Table 1)

molecule	property	$AVDZ^d$	$AVTZ^d$	$AVQZ^d$	$X3^a$		$USTE^b$		$USTE^c$	
					(D, T)	(T, Q)	(D, T)	(T, Q)	(d, t)	(t, q)
Li$_2$	$\bar{\alpha}$	215.38	215.08	214.56	215.04	214.04	215.19	214.03	215.11	214.09
	$\Delta\alpha$	144.62	135.03	132.46	131.43	131.05	129.95	131.03	130.78	131.15
	$\delta\bar{\alpha}_{calc-exp}{}^e$	−5.62	−5.92	−6.44	−5.96	−6.96	−5.81	−6.97	−5.89	−6.91
HF	$\bar{\alpha}$	4.86	5.26	5.38	5.39	5.41	5.40	5.41	5.39	5.41
	$\Delta\alpha$	1.89	1.43	1.25	1.28	1.17	1.25	1.17	1.26	1.18
	$\delta\bar{\alpha}_{calc-exp}{}^e$	−0.74	−0.34	−0.22	−0.21	−0.19	−0.20	−0.19	−0.21	−0.19
CO	$\bar{\alpha}$	12.86	12.95	12.94	12.97	12.92	12.94	12.92	12.95	12.92
	$\Delta\alpha$	4.01	3.72	3.65	3.62	3.62	3.60	3.62	3.61	3.62
	$\delta\bar{\alpha}_{calc-exp}{}^e$	−0.18	−0.09	−0.10	−0.07	−0.12	−0.10	−0.12	−0.09	−0.12
N$_2$	$\bar{\alpha}$	11.54	11.63	11.62	11.64	11.60	11.60	11.60	11.62	11.61
	$\Delta\alpha$	4.75	4.61	4.59	4.56	4.59	4.56	4.59	4.56	4.59
	$\delta\bar{\alpha}_{calc-exp}{}^e$	−0.19	−0.11	−0.12	−0.10	−0.14	−0.14	−0.14	−0.12	−0.13
F$_2$	$\bar{\alpha}$	7.45	8.03	8.22	8.22	8.29	8.25	8.29	8.23	8.29
	$\Delta\alpha$	6.30	6.11	6.07	6.05	6.06	6.05	6.06	6.05	6.06
	$\delta\bar{\alpha}_{calc-exp}{}^e$	−0.93	−0.35	−0.16	−0.16	−0.09	−0.13	−0.09	−0.15	−0.09
H$_2$O	$\bar{\alpha}$	8.98	9.25	9.30	9.33	9.30	9.33	9.30	9.33	9.30
	$\Delta\alpha$	1.09	0.82	0.71	0.74	0.67	0.73	0.67	0.73	0.68
	$\delta\bar{\alpha}_{calc-exp}{}^e$	−0.66	−0.40	−0.34	−0.31	−0.34	−0.31	−0.34	−0.31	−0.34
CO$_2$	$\bar{\alpha}$	16.91	17.17	17.20	17.24	17.18	17.21	17.18	17.23	17.18
	$\Delta\alpha$	14.75	13.98	13.78	13.71	13.70	13.65	13.70	13.69	13.70
	$\delta\bar{\alpha}_{calc-exp}{}^e$	−0.59	−0.33	−0.30	−0.26	−0.32	−0.29	−0.32	−0.27	−0.32
CH$_4$	$\bar{\alpha}$	16.25	16.30	16.27	16.31	16.25	16.31	16.25	16.31	16.25
	$\delta\bar{\alpha}_{calc-exp}{}^e$	−0.27	−0.22	−0.25	−0.21	−0.27	−0.21	−0.27	−0.21	−0.27

[a]Extrapolated via eq 12 with X3($X − 1$, X) scheme. [b]Extrapolated via eq 13. [c]Extrapolated via eq 12 with USTE($x − 1$, x) scheme. [d]Raw aug-cc-pVXZ values. [e]Difference between the calculated and the experimental value, $\delta\bar{\alpha}_{calc-exp}$. All experimental data from Hohm,[43] except for[44] CH$_4$.

D

Table 4. Average Polarizability $\bar{\alpha}$ and Anisotropy $\Delta\alpha$ at the CCSD(T)/aug-cc-pVXZ Level of Theory (Notation as in Table 1)

molecule	property	AVDZ[d]	AVTZ[d]	AVQZ[d]	X3[a] (D, T)	X3[a] (T, Q)	USTE[b] (D, T)	USTE[b] (T, Q)	USTE[c] (d, t)	USTE[c] (t, q)
HF	$\bar{\alpha}$	4.92	5.36	5.49	5.51	5.53	5.53	5.53	5.52	5.53
	$\Delta\alpha$	1.92	1.43	1.24	1.26	1.16	1.23	1.16	1.25	1.16
	$\delta\bar{\alpha}_{calc-exp}$[e]	−0.68	−0.24	−0.11	−0.09	−0.07	−0.07	−0.07	−0.08	−0.07
CO	$\bar{\alpha}$	12.97	13.09	13.08	13.11	13.06	13.09	13.06	13.10	13.06
	$\Delta\alpha$	3.96	3.68	3.61	3.58	3.58	3.56	3.58	3.57	3.58
	$\delta\bar{\alpha}_{calc-exp}$[e]	−0.07	0.05	0.04	0.07	0.02	0.05	0.02	0.06	0.02
N_2	$\bar{\alpha}$	11.66	11.76	11.75	11.78	11.73	11.74	11.73	11.76	11.74
	$\Delta\alpha$	4.81	4.62	4.59	4.55	4.59	4.53	4.59	4.54	4.59
	$\delta\bar{\alpha}_{calc-exp}$[e]	−0.07	0.02	0.01	0.04	−0.01	0.00	−0.01	0.02	0.00
F_2	$\bar{\alpha}$	7.51	8.11	8.31	8.31	8.39	8.34	8.39	8.32	8.38
	$\Delta\alpha$	6.32	6.02	5.95	5.91	5.92	5.88	5.92	5.90	5.92
	$\delta\bar{\alpha}_{calc-exp}$[e]	−0.87	−0.27	−0.07	−0.07	0.01	−0.04	0.01	−0.06	0.00
H_2O	$\bar{\alpha}$	9.13	9.45	9.51	9.55	9.52	9.56	9.52	9.56	9.52
	$\Delta\alpha$	1.06	0.75	0.62	0.65	0.58	0.64	0.58	0.65	0.58
	$\delta\bar{\alpha}_{calc-exp}$[e]	−0.52	−0.20	−0.13	−0.09	−0.12	−0.08	−0.12	−0.08	−0.12
CO_2	$\bar{\alpha}$	17.08	17.40	17.45	17.50	17.45	17.48	17.44	17.49	17.45
	$\Delta\alpha$	14.81	14.11	13.92	13.87	13.85	13.83	13.84	13.85	13.85
	$\delta\bar{\alpha}_{calc-exp}$[e]	−0.42	−0.10	−0.05	0.00	−0.05	−0.02	−0.06	−0.01	−0.05
CH_4	$\bar{\alpha}$	16.37	16.43	16.41	16.45	16.40	16.45	16.40	16.45	16.40
	$\delta\bar{\alpha}_{calc-exp}$[e]	−0.15	−0.09	−0.11	−0.07	−0.12	−0.07	−0.12	−0.07	−0.12

[a]Extrapolated via eq 12 with X3($X − 1$, X) scheme. [b]Extrapolated via eq 13. [c]Extrapolated via eq 12 with USTE($x − 1$, x) scheme. [d]Raw aug-cc-pVXZ values. [e]Difference between the calculated and the experimental value, $\delta\bar{\alpha}_{calc-exp}$. All experimental data from Hohm,[43] except for[44] CH_4.
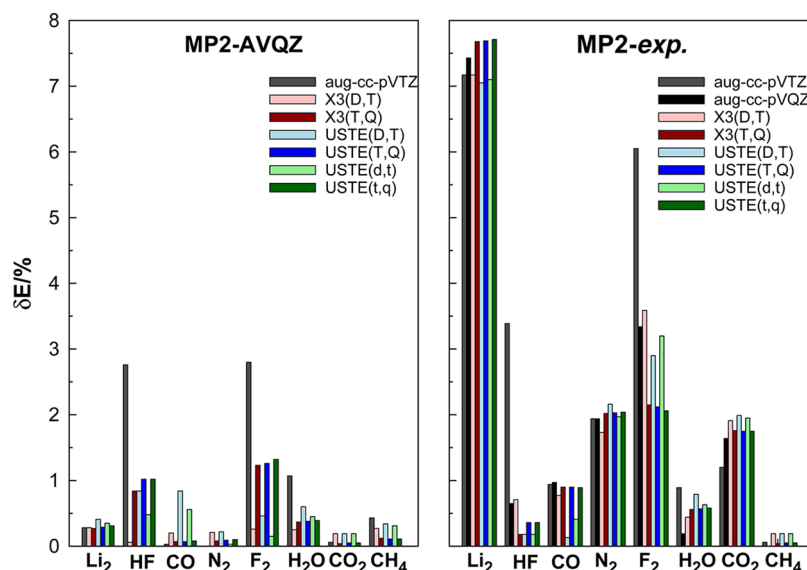

Figure 1. Percent absolute error of the various extrapolation methods with respect to the MP2/aug-cc-pVQZ average polarizability or its experimental value.

$$\bar{\alpha}_{CBS} = \bar{\alpha}_{X_2} + \frac{x_2^{-3}}{x_1^{-3} - x_2^{-3}}(\bar{\alpha}_{X_2} - \bar{\alpha}_{X_1})$$
$$+ \left(\frac{X_2^{-\kappa}}{X_1^{-\kappa} - X_2^{-\kappa}} - \frac{x_2^{-3}}{x_1^{-3} - x_2^{-3}}\right)(\bar{\alpha}_{X_2}^{HF} - \bar{\alpha}_{X_1}^{HF})$$

$$(18)$$

where, for USTE($X − 1$, X), the parameter $x_2^{-3}/(x_1^{-3} - x_2^{-3})$ must be replaced by $B(X)$ as defined in eq 14.

To calculate the values of these electrical properties, we may use finite difference numerical methods. In the present work we choose the three-point midpoint formula, which for the component α_{ii} yields

$$\alpha_{ii} = -\left[\frac{E(F_i^{(1)}) - 2E(F_i^{(2)}) + E(F_i^{(3)})}{h^2}\right]_0$$

$$(19)$$

where $F_i^{(1)} = -h$, $F_i^{(2)} = 0$ and $F_i^{(3)} = h$ are the applied electric fields in the direction $i = x$, y, and z. The field magnitude h must be sufficiently small to yield converged and numerically stable results, while being large enough to facilitate numerical differentiation:[2] in this work, the value $h = 0.005$ au is utilized.

From eqs 12 and 13, it is clear that the CBS limit of a tensorial property cannot be obtained by ignoring the second term of these equations. This will be theoretically incorrect because we are considering that the HF and correlation
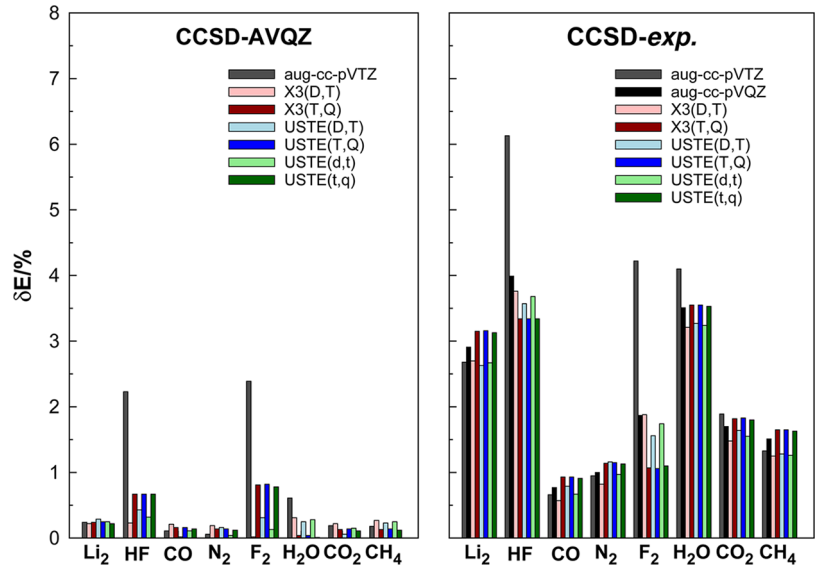
Figure 2. Percent absolute error of the various extrapolation methods with respect to the CCSD/aug-cc-pVQZ average polarizability or its experimental value.
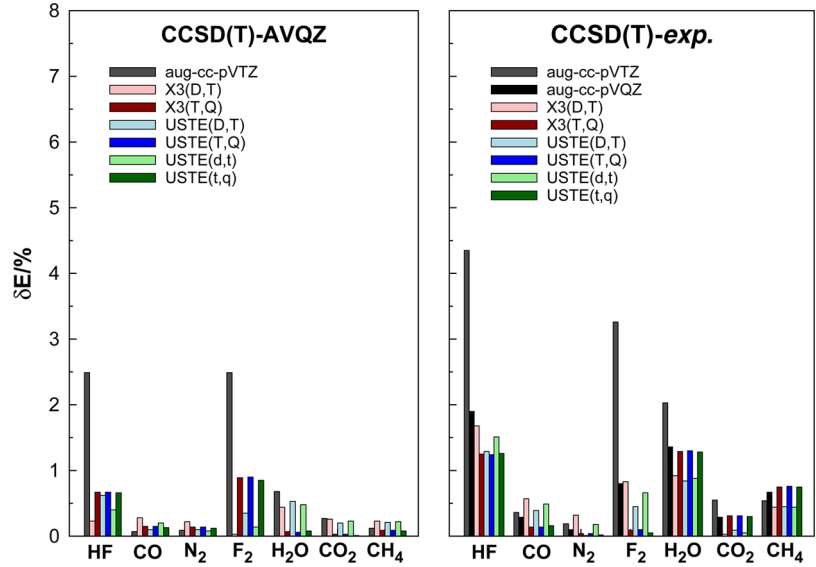

Figure 3. Percent absolute error of the various extrapolation methods with respect to the CCSD(T)/aug-cc-pVQZ average polarizability or its experimental value.

Table 5. Average Polarizability $\bar{\alpha}$ and Anisotropy $\Delta\alpha$ for Li$_2$ at All-Electron MP2, CCSD, and CCSD(T)/aug-cc-pVXZ Levels of Theory

					X3[a]		USTE[b]		USTE[c]	
method	property	AVDZ[d]	AVTZ[d]	AVQZ[d]	(D, T)	(T, Q)	(D, T)	(T, Q)	(d, t)	(t, q)
MP2	$\bar{\alpha}$	205.23	204.40	204.71	204.13	205.65	204.08	205.72	204.10	205.83
	$\Delta\alpha$	76.46	72.45	71.42	71.39	71.62	72.14	71.65	71.81	71.71
	$\delta\bar{\alpha}_{calc-exp}$[e]	−15.77	−16.60	−16.29	−16.87	−15.35	−16.92	−15.28	−16.90	−15.17
CCSD	$\bar{\alpha}$	209.99	209.04	207.51	215.46	214.95	215.51	214.95	215.48	214.98
	$\Delta\alpha$	136.63	125.18	121.80	112.36	106.76	114.35	106.69	113.23	107.04
	$\delta\bar{\alpha}_{calc-exp}$[e]	−11.01	−11.96	−13.49	−5.54	−6.05	−5.49	−6.05	−5.52	−6.02
CCSD(T)	$\bar{\alpha}$	209.73	209.08	207.70	215.44	215.51	214.72	215.51	215.12	215.52
	$\Delta\alpha$	136.46	126.28	123.62	112.67	108.70	112.26	108.65	112.49	108.96
	$\delta\bar{\alpha}_{calc-exp}$[e]	−11.27	−11.92	−13.30	−5.56	−5.49	−6.28	−5.49	−5.88	−5.48

[a]Extrapolated via eq 12 with X3($X − 1$, X) scheme. [b]Extrapolated via eq 13. [c]Extrapolated via eq 12 with USTE($x − 1$, x) scheme. [d]Raw aug-cc-pVXZ values. [e]Difference between the calculated and the experimental value, $\delta\bar{\alpha}_{calc-exp}$. Experimental data.[43]
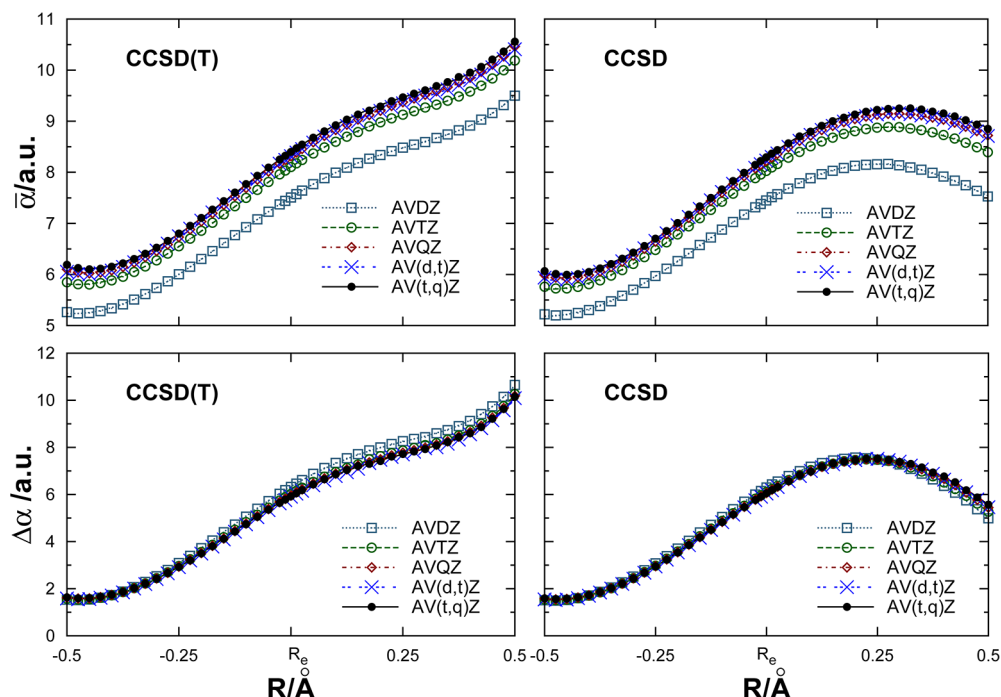
Figure 4. Average polarizability and anisotropy versus internuclear distance for the ground-state of the F_2 molecule. R_e = 1.412 Å is the experimental equilibrium distance.[41]

energies converge to the CBS limit with the same rate. Of course, for large hierarchical numbers, the difference between $\zeta_{ii(X_2)}^{HF}$ and $\zeta_{ii(X_1)}^{HF}$ gets small, and hence such an approach should not introduce any significant error. In turn, as noted above, the present scheme will be significantly less costly than the approach of Junqueira and Varandas.[12] In addition, it is simpler because the extrapolation to the CBS limit is made directly for the property via eqs 12 and 13 and hence avoids any error compensations on the extrapolated energies.

■ RESULTS AND DISCUSSION

The method here developed will be applied to a test set of eight molecules involving first-row atoms which, taken mostly from other data sets,[12,37] are relatively simple to afford calculations of the polarizability up to the frozen-core CCSD(T)/aug-cc-pVQZ level of theory. Although calculations have been reported at higher levels of theory,[37] the targeted level allows more

Table 6. Gradients of Average Polarizability and Anisotropy of F_2 at Equilibrium (Notation as in Table 1)

	CCSD		CCSD(T)	
basis/method	$(d\bar{\alpha}/dR)_{R_e}$	$(d\Delta\alpha/dR)_{R_e}$	$(d\bar{\alpha}/dR)_{R_e}$	$(d\Delta\alpha/dR)_{R_e}$
AVDZ	2.82	6.12	2.77	5.89
AVTZ	2.92	5.85	2.96	5.78
AVQZ	3.03	5.89	3.07	5.74
X3(D,T)	2.96	5.71	3.04	5.76
X3(T,Q)	3.10	5.95	3.15	5.76
USTE(D,T)	2.99	5.68	3.09	5.76
USTE(T,Q)	3.11	5.95	3.15	5.76
USTE(d,t)	2.92	5.73	3.04	5.75
USTE(t,q)	3.07	5.93	3.09	5.71
[9s6p4d1f]^a	2.94	5.31	3.11	5.57

^{a}From Maroulis.[46]

efficiency while being accurate enough for comparisons with the available experimental data. Moreover, the present scheme aims above all to be applicable to moderate and large sized molecules, which are not amenable to basis sets larger than QZ type and most of the time TZ. All results have been obtained with the MOLPRO[40] package of *ab initio* programs for electronic structure calculations and performed at the experimental equilibrium geometry of the various systems as compiled in the NIST standard reference database.[41]

Tables 1−4 give the average polarizabilities and anisotropies obtained from calculations at the HF, MP2, CCSD, and CCSD(T)/aug-cc-pVXZ levels of theory. For convenience, all tabulated values in this and the following tables are given with two decimal places. Also given are CBS extrapolated values obtained via eqs 12, 13, and 18 (or eq 7 at the HF level) for the three CBS extrapolation schemes that are here discussed, and the relative deviations with respect to the experimental values; the reader is referred to the Supporting Information[42] for more complete tables that include the results of the polarizability components, the best estimate, and the estimated maximum uncertainty of a given calculated property. An interesting observation from Table 1 is that the CBS(D,T) extrapolated scheme for the HF energy (eq 7) gives in most cases a value that comes close to the raw HF/aug-cc-pVQZ energies.
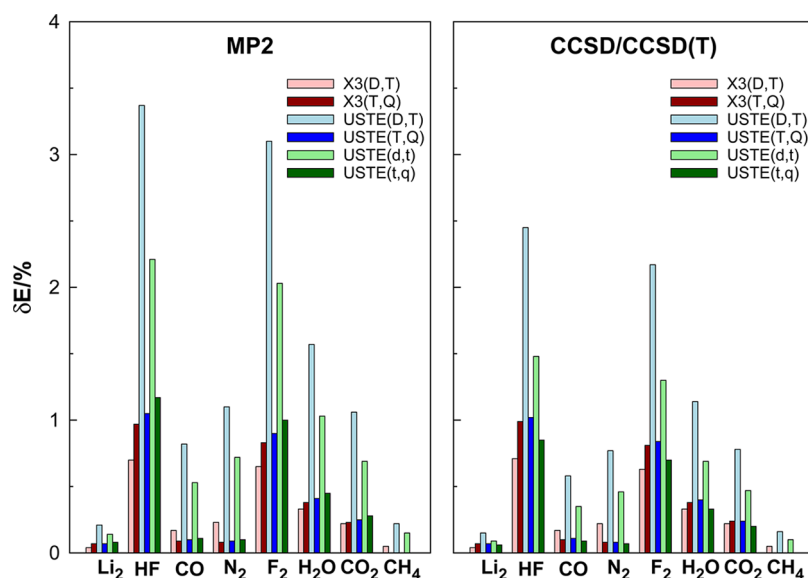
Figures 1−3 show the percentage absolute error for the various extrapolation schemes, with respect to MP2, CCSD, and CCSD(T) levels of theory with the aug-cc-pVQZ basis, and to experimental data.[43,44] Clearly, the improvement obtained with all (D, T) extrapolation schemes here utilized is remarkable, with errors less than ∼1% with respect to the corresponding aug-cc-pVQZ values. For the CCSD(T) method, such errors become also less than ∼1.5% relative to the experimental data. Note that the CCSD(T)/aug-cc-pVTZ errors can themselves be larger than 4%. Note further that a comparison for the HF, CO, N$_2$, F$_2$, and H$_2$O molecules at the CCSD(T)/X = ∞ level[37] (this implies a three-point

Figure 5. Percent absolute error relative to the CBS extrapolated average polarizability when the last term in eq 12 or eq 13 is neglected

extrapolation to the CBS limit with $X = Q, 5, 6$) shows typical average errors at the (d, t) and (t, q) levels to be <0.8% and <0.5%, respectively. Comparing the CCSD extrapolated results with the values obtained from CCSD(F12) and CCSD-(R12)[30−33] for the N_2, CO, and HF molecules, typical average errors (considering all data) are found to be <0.4% and 0.3% for the (d, t) and (t, q) extrapolation pairs, respectively. Additionally, for N_2, the error with respect to CCSD(R12)/A6Z[31] is <0.4%, and ~0.2% for CCSD(R12)/AQZ,[31] when these energies are compared on the basis of the d-aug-cc-pVXZ basis set family with both $(x − 1, x)$ extrapolation pairs. Thus, the USTE$(x − 1, x)$ scheme yields results competitive with the more expensive explicit correlation energies here analyzed, with a similar performance being expected in other cases. An additional remark to observe that the (T, Q) and (t, q) extrapolation schemes show errors relative to the experimental data that in some cases exceed the (D, T) and (d, t) ones. Nevertheless, extrapolating to CBS limit does not necessarily mean approaching the experimental values, because the level of theory employed can play a key role. In fact, we must not only take into account the intrinsic error (due to other contributing factors) of the *ab initio* theory but also recall the uncertainties inherent to the experimental results themselves. Thus, it may not be surprising that a similarity between the two sets of errors only appears at high levels of CCSD(T) theory. Of course, any aim to go into further details may require optimization of the equilibrium geometry at all specific levels of theory under analysis. It also goes without saying that performing valence-only correlation calculations should be seen with care, particularly for systems like Li_2. However, this is not expected to invalidate the major conclusions obtained in a comparative analysis like the one here presented. In an attempt to clarify such issues, we have conducted (all-electron) ae-aug-cc-pVXZ calculations for the floppiest molecule here considered, namely Li_2. The results obtained at the optimized geometries for each method are given in Table 5. As seen (see also Supporting Information[42]), they follow the pattern discussed above at fc level, particularly having in mind the quite significant uncertainties in the experimental values.[43]

Figure 4 shows the average polarizability and anisotropy versus internuclear distance for the ground-state F_2. Notably,

the trend observed in the CBS extrapolation for the equilibrium distance is essentially maintained at all internuclear distances here studied with a given method. In fact, a similarly good agreement is observed with both the USTE$(X − 1, X)$ and X3$(X − 1, X)$ schemes (see also the next paragraph).

The bond-length dependence of the polarizability around the equilibrium internuclear separation is known to play a key role in Raman spectroscopy[45] (and references therein), and so we compile in Table 6 the predicted values of $(d\bar{\alpha}/dR)_{R_e}$ and $(d\Delta\alpha/dR)_{R_e}$. Note that even CBS(d,t) yields results close to the aug-cc-pVQZ raw values, with all CBS extrapolations generally lying significantly closer than the ones recently calculated by Maroulis[46] with a flexible, purpose oriented, molecule specific [9s6p4d1f] Gaussian type basis. As might be anticipated from the curves shown in Figure 4, all CBS extrapolation schemes here considered perform quite well when compared with the best raw values.

In this work, we have calculated the dipole polarizability using the finite field approximation, thus requiring numerical differentiation of the energy with respect to the external perturbation. Such a methodology is computationally costly and may lead to accuracy loss when high-order derivatives are necessary.[47−49] An alternative procedure is coupled-cluster linear response (CC-LR)[47−50] (and references therein). This method requires only a single calculation of the correlation energy and cluster amplitudes in the absence of the external perturbation, followed by solution of a recursive set of linear equations for the first- and higher-order corrections to the cluster amplitudes describing the response of the system to the external perturbation.[47] Thus, the problem with instabilities related to numerical differentiations disappears, and the computational effort diminishes.[47−49] In fact, the CC-LR method is recommended as particularly useful when higher-order properties for highly stretched geometries are evaluated.[48] Because CBS extrapolation via eqs 12 and 13 is done directly for the property, the CC-LR results can be extrapolated with the same equations.

A final remark to emphasize that tensorial properties are often extrapolated[51] with the laws appropriate for energies. In the case of the polarizability, we have shown above that this

H

could only be correct if the CBS extrapolation rule for the Hartree−Fock and correlation contributions followed the same inverse power law. In this case, the second term in eq 12 would cancel, and the polarizability could be CBS extrapolated as it is a mere correlation energy. Because this is not the case, an error emerges due to such an approximation, which can be up to a few percent of the CBS extrapolated property as illustrated in Figure 5. Although such errors look small in magnitude, they are somewhat larger for USTE than X3, which may be attributed to the closer HF and correlation values of the power extrapolation laws in the latter protocol. Note that despite their apparently small value, such errors are larger than the targeted ones for agreement between the calculated and experimental results.

CONCLUSIONS

We have applied the USTE scheme with basis set rehierarchization as developed[18] for the calculation of tensorial properties by focusing on the polarizability of eight (diatomic plus triatomic) molecules. A comparison with the values obtained from other CBS extrapolations has also been presented. The calculated raw and CBS-extrapolated properties have been compared with each other and available experimental data. Even at the lowest level of extrapolation, (d, t), the USTE scheme has been found to yield polarizabilities similar (errors within <1%) to the most accurate raw values calculated at the MP2 and CC levels of theory. The results have also shown that extrapolation of the polarizability based on direct use of the CBS extrapolation law for the energy is generally incorrect, despite the fact that the error is small, yet non-negligible. Because such tensorial properties generally require high levels of theory with large basis sets, the possibility of obtaining accurate results from only two points calculated with low-cost basis sets is therefore a very relevant issue.

ASSOCIATED CONTENT

ⓢ Supporting Information

Tables of polarizability component, average polarizability, and anisotropy. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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