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Extrapolating to the One-Electron Basis Set Limit in Polarizability Calculations

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We report calculations of polarizabilities using total energies extrapolated to the complete basis set limit. A dual-level scheme has been employed, with the complete basis set limit of the correlation energy determined by the recently reported uniform singlet- and triplet-pair extrapolation method. The finite field approach has been employed, with tensors and averaged polarizabilities for the ground electronic states of H_2, N_2, CO, and H_2O reported and compared with available experimental data in the literature. Exploratory results are also presented for $C_6H_4NO_2NH_2$.

1. Introduction

The dipole moment (μ), linear polarizability (α), and the first- and second-order hyperpolarizabilities (β and γ) play a significant role mainly in the study of nonlinear optical (NLO) properties.[1,2] NLO studies are based on the interaction of applied electromagnetic fields in molecular systems to generate new fields altered in frequency, phase, or other physical properties.[3] In general, organic molecules with delocalized electronic clouds besides donor and receptor groups in their extremities (push−pull systems) can show excellent NLO responses, which is due to having large molecular dipole moments and hyperpolarizabilities. Both of these properties are important in electro-optic modulation as the second harmonic generation (SHG) of light. Hyperpolarizabilities may be deduced experimentally, for example, from the direct observation of SHG. However, the experiments are usually difficult to carry out, and the range of uncertainty is often large. An important route for atomic and molecular polarizabilities is via quantum mechanical calculations.[1−4] Indeed, the response of molecules to external electric fields is a major source of information on the fundamental properties of matter.

The energy (E) of a molecular system under an external electric field (F) can be written as[5]

$$E(F) = E(0) - \mu F_i - (1/2\,!)\alpha_{ij}F_iF_j - (1/3\,!)\beta_{ijk}F_iF_jF_k - (1/4\,!)\gamma_{ijkl}F_iF_jF_kF_l - ... \quad (1)$$

where $E(0)$ stands for the energy of the system in the absence of an external field and F_i are the components of the applied field. If this is a uniform electric field aligned along one of the axes of the system, for example, $(F_x, 0, 0)$ with the tensorial elements along that axis being μ_x, α_{xx}, β_{xxx}, and γ_{xxxx}, then eq 1 assumes the form

$$E(F) = E(0) - \mu F_i - (1/2)\alpha_{ii}F_i^2 - (1/6)\beta_{iii}F_i^3 - (1/24)\gamma_{iiii}F_i^4 - ... \quad (2)$$

Thus, truncation of eq 2 at the fourth power in F and evaluation of the energy at four values of the field strengths ($\pm F_i$, $\pm 2F_i$) will lead to four equations in four unknowns. Note that the polarizability tensor for a diatomic molecule has only two independent components, $\alpha_{xx} = \alpha_{yy}$ and α_{zz} (the bond is along the internuclear z axis), with the average polarizability $\bar{\alpha}$ being defined as[6]

$$\bar{\alpha} = \frac{1}{3}(2\alpha_{xx} + \alpha_{zz}) \quad (3)$$

Of course, the results of NLO theoretical investigations are very sensitive to the choice of the basis set since it is well-known that the basis sets must have enough flexibility to describe the response of the molecule to the applied electric field.[2] Sadlej[7] used the basis set polarization method to derive first-order polarized basis sets for such atomic and molecular electric properties, which have shown a good performance in calculations of atomic dipole polarizabilities and dipole moments.

There are two well-established theoretical models for obtaining NLO properties. First is the perturbation method, where the sum-over states (SOS) considers all electronic states of the system. The calculations are carried out on molecules independently of the applied field, and the response involves the coupling of excited states. In the second method, the so-called finite field (FF) approach, the electric field is explicitly included in the Hamiltonian.[1,4] The FF model applies finite differencing of the energy values that can be based on the energy expansion or a dipole moment expansion.[8] Naturally, large basis sets will, in principle, be required in both approaches to obtain accurate results.[6,9] It is then essential to define the theoretical methodology as depending on the objectives and computing resources available. In this paper, we will use the FF method, the simplest for obtaining electric properties of molecules. A major advantage of FF over SOS is that it requires only the ground-sate electronic energy (or dipole moment) rather than all eigenstates and transition dipole moments.[10] Unfortunately, the FF method cannot be extended to dynamical (frequency-dependent) polarizabilities, which is perhaps its major limitation.

A simple, yet valuable approach to highly accurate energies consists of scaling and extrapolating the calculated energy to the limit of a complete one-electron basis set as this helps elude the slow convergence of correlated electronic structure calculations with increasing basis set size[11−19] (and references therein). If, following the traditional approach, we separate the total energy into its Hartree−Fock (HF) and correlation (cor) contributions, then the latter is expected to assume a major role from the considerations in the previous paragraph. Here, we will employ for the CBS extrapolation of the correlation energy

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TABLE 1: Polarizability Tensor Components (α_{ii}) and Average Polarizabilities ($\bar{\alpha}$) for the Hydrogen Molecule in Atomic Units[a]

		raw				CBS		
method	property	X = D	T	Q	5	(D,T)	(T,Q)	(Q,5)
MP2	$\alpha_{xx} = \alpha_{yy}$	1.15	2.59	3.62	3.85	2.61	3.62	3.85
		4.36	4.58	4.59	4.59	4.57	4.59	4.59
	α_{zz}	6.35	6.51	6.46	6.43	6.49	6.46	6.43
		6.55	6.44	6.43	6.42	6.47	6.43	6.42
	$\bar{\alpha}$	2.88	3.90	4.57	4.71	3.90	4.57	4.71
		5.09	5.20	5.21	5.20	5.20	5.20	5.20
	$\Delta_{\text{calc-exp}}$	−2.43	−1.41	−0.74	−0.60	−1.41	−0.74	−0.60
		−0.22	−0.11	−0.10	−0.11	−0.11	−0.11	−0.11
	CPU time	0.2	0.7	11.6	63.3	0.9	12.3	74.9
		0.3	4.4	72.2	282.1	4.7	76.6	354.3
CCSD	$\alpha_{xx} = \alpha_{yy}$	1.14	2.60	3.63	3.86	2.60	3.63	3.86
		4.35	4.58	4.58	4.59	4.56	4.58	4.58
	α_{zz}	6.33	6.50	6.44	6.41	6.47	6.44	6.41
		6.55	6.41	6.40	6.42	6.45	6.40	6.40
	$\bar{\alpha}$	2.87	3.90	4.57	4.71	3.89	4.57	4.71
		5.08	5.19	5.19	5.20	5.19	5.19	5.19
	$\Delta_{\text{calc-exp}}$	−2.44	−1.41	−0.74	−0.60	−1.42	−0.74	−0.60
		−0.23	−0.12	−0.12	−0.11	−0.12	−0.12	−0.12
	CPU time	0.4	10.3	554.6	9705.0	10.7	564.9	10259.6
		1.9	98.1	10101.4	64040.2	100.0	10199.5	74141.6

[a] The first entry refers to the VXZ results and the second to AVXZ ones. Also given are the differences ($\Delta_{\text{calc-exp}}$) of calculated and experimental values ($\bar{\alpha}$/au = 5.31)[29] as well as extrapolated and not extrapolated CPU times (in s).

TABLE 2: Polarizability Tensor Components (α_{ii}) and Average Polarizabilities ($\bar{\alpha}$) for N_2, CO, and H_2O Molecules in Atomic Units[a]**Also given are the differences (*$\Delta_{calc-exp}$*) of calculated and experimental values**[29]

		raw				CBS		
method	property	X = D	T	Q	5	(D,T)	(T,Q)	(Q,5)
N_2	$\alpha_{xx} = \alpha_{yy}$	5.93	7.91	8.98	9.49	7.91	8.98	9.50
		9.90	10.10	10.11	10.11	10.06	10.12	10.11
	α_{zz}	12.39	13.57	14.03	14.23	13.38	14.02	14.24
		14.36	14.33	14.29	14.28	14.20	14.29	14.28
	$\bar{\alpha}$	8.08	9.80	10.66	11.07	9.73	10.66	11.08
		11.39	11.51	11.50	11.50	11.44	11.51	11.50
	$\Delta_{\text{calc-exp}}$	−3.46	−1.74	−0.88	−0.47	−1.81	−0.88	−0.46
		−0.15	−0.03	−0.04	−0.04	−0.10	−0.03	−0.04
CO	$\alpha_{xx} = \alpha_{yy}$	8.31	10.23	11.19	11.54	10.04	11.18	11.55
		11.68	11.93	11.95	11.95	11.95	11.95	11.95
	α_{zz}	12.81	14.44	15.18	15.46	14.22	15.16	15.47
		15.73	15.61	15.57	15.57	15.52	15.57	15.57
	$\bar{\alpha}$	9.81	11.63	12.52	12.85	11.43	12.51	12.86
		13.03	13.16	13.16	13.16	13.14	13.16	13.16
	$\Delta_{\text{calc-exp}}$	−3.37	−1.55	−0.66	−0.33	−1.75	−0.67	−0.32
		−0.15	−0.02	−0.02	−0.02	−0.04	−0.02	−0.02
H_2O	α_{xx}	7.02	8.36	9.06	9.36	8.17	9.05	9.38
		9.83	9.98	9.96	9.95	9.96	9.96	9.95
	α_{yy}	5.29	7.23	8.32	8.81	7.00	8.29	8.84
		9.11	9.57	9.66	9.68	9.45	9.66	9.68
	α_{zz}	3.20	5.82	7.35	8.32	5.55	7.32	8.38
		8.75	9.34	9.46	9.47	9.21	9.46	9.47
	$\bar{\alpha}$	5.17	7.14	8.24	8.83	6.91	8.22	8.87
		9.23	9.63	9.69	9.70	9.54	9.69	9.70
	$\Delta_{\text{calc-exp}}$	−4.96	−2.99	−1.89	−1.30	−3.22	−1.91	−1.43
		−0.90	−0.50	−0.44	−0.43	−0.59	−0.44	−0.43

[a] The first entry refers to the VXZ results and the second to AVXZ ones. Also given are the differences ($\Delta_{\text{calc-exp}}$) of calculated and experimental values.[29]

the uniform singlet- and triplet-pair extrapolation (USTE) scheme.[16] Since the CBS-extrapolated energies are expected to recover a large fraction of the correlation energy that is missing in the raw calculations, one hopes that they can be successfully utilized to calculate accurate static polarizabilities via the FF method[9] This is a major goal of the current work, with five applications being considered.

As test systems, we have chosen three diatomics (H_2, CO, and N_2) and one triatomic (H_2O). The first and simplest diatomic is hydrogen, which has been theoretically much studied for over the past 40 years due to its importance in Raman spectroscopy.[20] As further illustrative diatomics, also simple by today's standards, we have considered nitrogen (N_2) and carbon monoxide (CO). They are special in that N_2 offers the strongest bond in nature, besides being the largest component of Earth's atmosphere. In turn, CO is the second most abundant molecule in interstellar space and the subject of a recent theoretical study.[18] As an application to a triatomic molecule, we have chosen water (H_2O). Besides being the most abundant molecule on Earth's surface, it composes ~70% of the Earth's surface either in liquid or solid states while existing also as a vapor in the atmosphere. Moreover, the dielectric constant of liquid water is higher than that of all other polar liquids made of molecules with a comparable dipole moment, with several theoretical studies on this species being available in literature.[21] Finally, we present exploratory results for a much larger system, *p*-nitroaniline ($C_6H_4NO_2NH_2$ or *p* -NA), a molecule known for

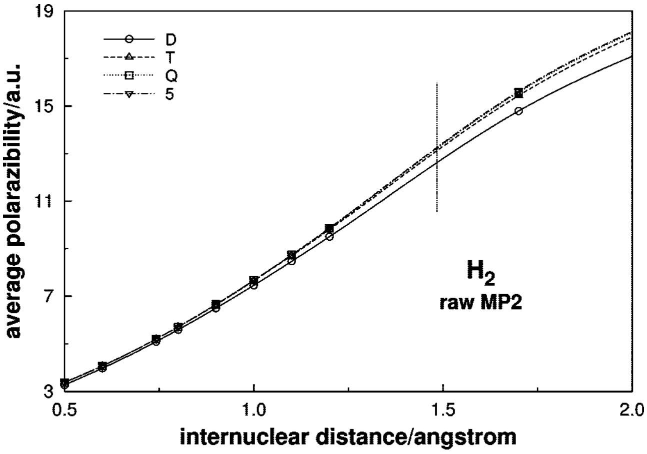

Figure 1. Raw MP2 polarizabilities versus internuclear distance for ground-state molecular hydrogen. The vertical bar in this and the following three figures indicates up to where the curves are likely to be accurate due to the single-reference nature of the underlying theory.

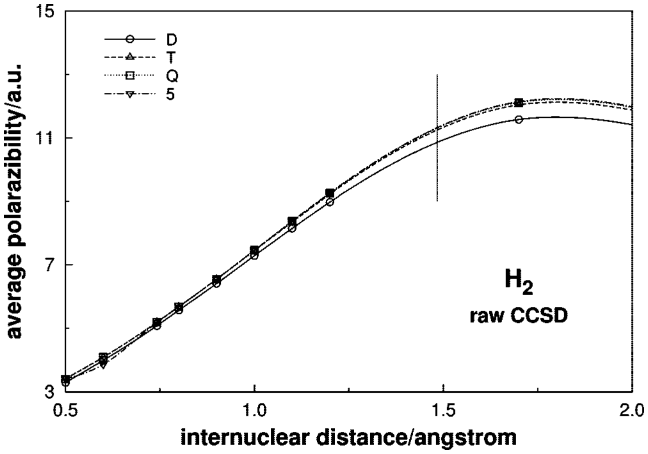

Figure 2. As in Figure 1 but for raw CCSD polarizabilities.

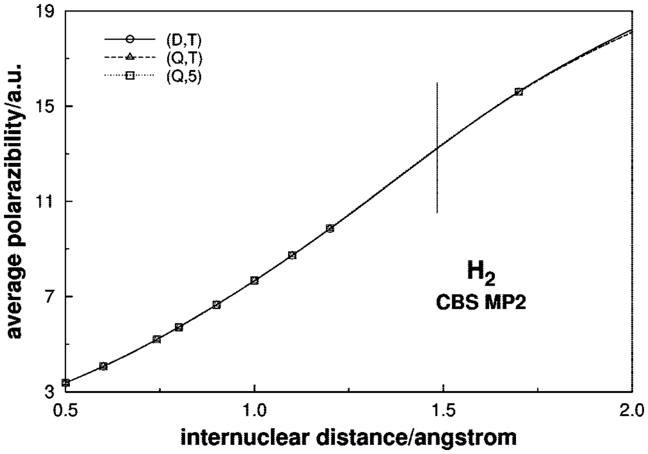

Figure 3. As in Figure 1 but for CBS-extrapolated MP2 polarizabilities.

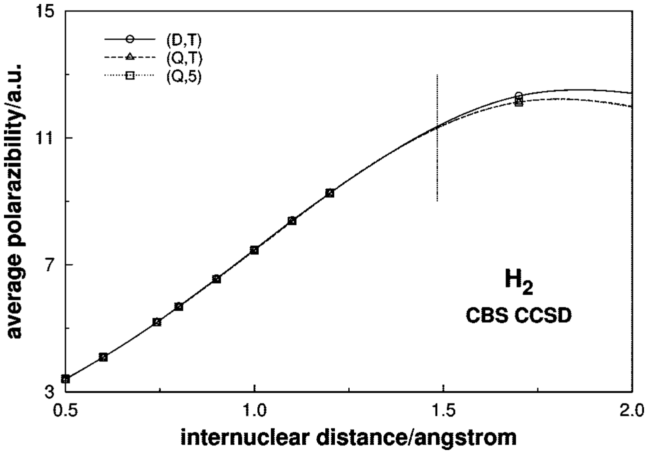

Figure 4. As in Figure 1 but for CBS-extrapolated CCSD polarizabilities.

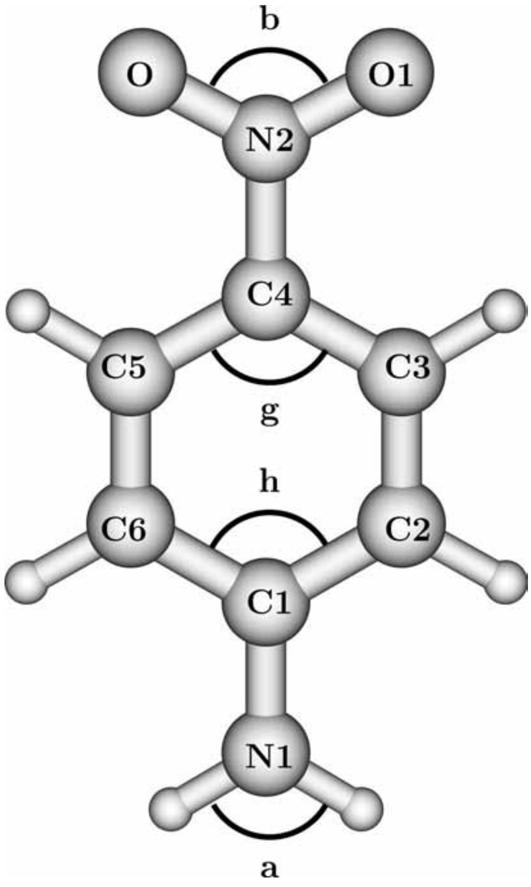

Figure 5. *p*-NA geometry.

its NLO properties and which has been theoretically and experimentally studied (ref 22 and references therein).

As a final introductory remark, note that Christiansen et al.[23] have reported a systematic study of static and frequency-dependent dipole polarizabilities for different diatomic molecules, including CO and N_2, using coupled cluster (CC) methods. Moreover, they have reported eletronic and vibrational contributions to such properties. In turn, Pecul and Coriani[24] have studied the influence of triple excitations in CC calculations when computing Raman scattering cross parameters. They have concluded that "Raman scattering cross sections are more sensitive to the higher-order electron correlation effects than the polarizabilities themselves". In fact, as our results will also show, accounting for higher-order excitations in CC calculations by means of CCSD(T), particularly for N_2 and CO (see Table 3), does not lead to any improvement of the polarizability values. Since we wish to apply the extrapolation scheme suggested here to larger molecular systems, we hope to show that MP2/AV*XZ* ($X = D$, T) calculations will provide an accurate, cost-effective level of theory toward such a goal.

The paper is organized as follows. In section 2, we describe the computational procedure used to obtain total extrapolated energies as well as the polarizability calculations. The results are reported and discussed in section 3, and the concluding remarks are in section 4. As commonly encountered in the literature, bond distances are in angstroms, and polarizabilities are in atomic units (au of dipole polarizability = 1.481847114 × 10^{-7} Å^3).

2. Computational Procedures

All calculations reported here have been performed using the GAMESS suite of programs[25] and basis sets of the correlated-consistent polarized *X*-tuple zeta type[26,27] (cc-pV*XZ*, or simply V*XZ*), augmented (aug-cc-pV*XZ* or AV*XZ*), and double-augmented ones (daug-cc-pV*XZ* or dAV*XZ*), with cardinal numbers X = D: 2; T: 3; Q: 4, 5, 6,... Following common wisdom, the total energy has been partitioned as $E^{\mathrm{tot}} = E^{\mathrm{HF}} + E^{\mathrm{cor}}$, where E^{HF} is the Hartree−Fock energy and E^{cor} is the total correlation energy. Both energy components have then been extrapolated to their basis set limits.

TABLE 3: Polarizability Tensors (α_{ii}) and Average Polarizabilities ($\bar{\alpha}$) for N_2 and CO[a]

	CCSD			CCSD(T)			MP2		
system	*D*	*T*	(*D*,*T*)	*D*	*T*	(*D*,*T*)	*D*	*T*	(*D*,*T*)
N_2	AV*X*Z								
α_{xx}	9.93	10.06	9.99	10.03	10.18	10.12	9.90	10.10	10.06
α_{zz}	14.79	14.71	14.57	14.95	14.85	14.69	14.36	14.33	14.20
$\bar{\alpha}$	11.55	11.61	11.52	11.67	11.74	11.64	11.39	11.51	11.44
$\Delta_{calc-exp}$	0.01	0.07	−0.02	0.13	0.20	0.10	−0.15	−0.03	−0.10
CPU time	503.8	22352.3	22856.1	329.0	11920.8	12249.8	7.2	121.7	128.9
N_2	dAV*X*Z								
α_{xx}	10.16	10.12	10.04	10.28	10.24	10.17	10.14	10.15	10.12
α_{zz}	14.86	14.71	14.58	15.03	14.85	14.69	14.44	14.33	14.21
$\bar{\alpha}$	11.73	11.65	11.55	11.86	11.78	11.68	11.57	11.54	11.48
$\Delta_{calc-exp}$	0.19	0.11	0.01	0.32	0.24	0.14	0.03	0.00	−0.06
CPU time	2448.7	32581.4	35030.1	2157.1	42300.3	44457.4	23.2	238.4	261.6
CO	AV*X*Z								
α_{xx}	11.50	11.70	11.68	11.64	11.85	11.84	11.68	11.93	11.95
α_{zz}	15.62	15.40	15.25	15.70	15.51	15.52	15.73	15.61	15.52
$\bar{\alpha}$	12.87	12.93	12.87	12.99	13.07	13.07	13.03	13.16	13.14
$\Delta_{calc-exp}$	−0.31	−0.25	−0.31	−0.19	−0.11	−0.11	−0.15	−0.02	−0.04
CPU time	502.8	7474.8	7977.6	555.6	17174.9	17730.5	7.0	125.0	132.0
CO	dAV*X*Z								
α_{xx}	11.80	11.75	11.70	11.95	11.90	11.86	11.99	11.98	11.96
α_{zz}	15.62	15.40	15.25	15.74	15.52	15.38	15.73	15.61	15.68
$\bar{\alpha}$	13.08	12.97	12.88	13.21	13.11	13.03	13.25	13.20	13.15
$\Delta_{calc-exp}$	−0.10	−0.21	−0.30	0.03	−0.07	−0.15	0.07	0.02	−0.03
CPU time	2530.7	42684.6	45215.3	1094.9	36955.9	38050.8	14.1	269.0	283.1

[a] Differences ($\Delta_{calc-exp}$) between the calculated and experimental values ($\bar{\alpha}$/au = 11.54 and 13.18, respectively) are also given, as well as the CPU times (in s).

TABLE 4: Structural Parameters[a] Calculated[b,c,d] for the *para*-Nitroaniline Molecule

	B3LYP	MP2					HF				
feature	6-31+G	6-31+G	6-31+G*	6-31+G	6-31G*	6-31+G*	6-31++G	6-31++G**	6-31G**	6-311+G*	exp[d]
C2−C3	1.388	1.407	1.392	1.377	1.376	1.378	1.377	1.378	1.376	1.376	1.377
C3−C4	1.403	1.408	1.395	1.390	1.386	1.387	1.390	1.387	1.386	1.385	1.397
C1−C2	1.418	1.422	1.406	1.404	1.399	1.399	1.404	1.400	1.399	1.398	1.415
C1−N1	1.376	1.402	1.397	1.366	1.376	1.378	1.367	1.375	1.373	1.378	1.355
C4−N2	1.445	1.473	1.464	1.432	1.445	1.448	1.432	1.448	1.445	1.452	1.433
N2−O1	1.273	1.288	1.246	1.233	1.196	1.197	1.233	1.197	1.196	1.190	1.234
g	120.8	121.7	121.6	120.8	120.9	120.9	120.8	120.9	120.9	120.9	121.2
h	118.8	118.8	118.7	118.9	119.0	119.0	118.9	119.0	119.0	118.9	118.8
a	117.5	115.9	111.3	117.5	113.0	112.7	117.5	113.9	114.0	112.9	119.3
b	122.7	123.3	124.4	122.8	124.2	124.3	122.8	124.3	124.2	124.5	122.0

[a] See Figure 5. Bond lengths in angstroms and angles in degrees. [b] B3LYP/6-31+G, MP2/6-31+G, and HF/6-31+G; this work. [c] Ref 22. [d] Experimental values.[35]

To extrapolate the correlation energy, we have used the USTE scheme[13,16]

$$E_X^{\text{cor}} = E_\infty^{\text{cor}} + \frac{A_3}{(X+a)^3} + \frac{A_n}{(X+a)^n} \qquad n \geq 4 \qquad (4)$$

Specifically, we have fixed the offset parameter at $a = -3/8$ [or $-17/64$ for the pair (T,Q)], with A_n (for $n = 5$) depending on A_3. Following recent work,[16] eq 4 has then been transformed into an effective two-parameter rule by using the auxiliary relation $A_5 = A_5(0) + cA_3^m$ where the parameters $A_5(0)$, c, and m are taken as universal-like for a given level of theory and contain no information alien to it; see Table 1 of ref 16 for the numerical values. Such a protocol has been shown to predict the CBS-extrapolated correlation energy with a root mean squares deviation (rmsd) of a few (often a fraction of) millihartree for a large set of molecules studied by Møller−Plesset perturbation theory (MP2) and coupled cluster methods.[12] Moreover, a suitably modified version of the theory revealed itself to work equally well for multireference configuration interaction (MRCI) energies[16] (see also ref 19 for a generalization of the USTE method).

To extrapolate the HF energy, we have employed the two-point extrapolation protocol proposed by Karton and Martin[28] (KM)

$$E_X^{\text{HF}} = E_\infty^{\text{HF}} + B/X^{5.34} \qquad (5)$$

which is expected to work best for extrapolations from the (T, Q) pair of energies. For lower cardinal numbers, no reliable extrapolation formula for the HF energy is known. Thus, the (X_1, X_2) total energies for cardinal numbers smaller than Q will be obtained by combining CBS/HF energies extrapolated from HF/V*X*Z or HF/AV*X*Z energies for $X = T,\ Q$ with the

TABLE 5: Polarizability Calculations (au) for the *para*-Nitroaniline Molecule

method	α_{xx}	α_{yy}	α_{zz}	$\bar{\alpha}$	$\Delta_{\text{calc}-\text{exp}}$[a]
OP[b]	90.7	37.0	121.3	83.0	−31.72
KPD[b]	91.1	48.7	137.7	92.5	−22.22
1P[b]	94.6	46.3	130.3	90.4	−24.32
2P[b]	98.7	53.6	141.3	97.9	−16.82
HF/aug-cc-pVDZ[c]	95.49	52.97	132.81	93.75	−20.97
RPA[d]	97.4	48.5	138.4	94.7	−20.02
CAS[d]	103.4	48.3	130.3	94.0	−20.72
MP2/D95V(p,d)//MP2/6-31G*[e]				100.28	−14.19
MP2/D95V(p,d)//B3LYP/6311G**[e]				100.45	−14.27
MP2/D95V(p,d)//MP2/cc-pV*DZ*[e]				100.50	−14.22
MP2/D95V(p,d)//MP2/cc-pV*DZ*+aug-cc-pV*DZ*(N)[e]				100.77	−13.95
MP2/D95V(p,d)//MP2/aug-cc-pV*DZ*[e]				101.54	−13.18
MP2/D95V(p,d)//B3LYP/cc-pV*TZ*[e]				99.97	−14.75
MP2/D95V(p,d)//MP2/cc-pV*TZ*[e]				99.04	−15.68
MP2/D95V(p,d)//MP2/cc-pV*TZ*+aug-cc-pV*TZ*(N)[e]				99.25	−15.47
MP2/D95V(p,d)//MP2/Pol[e]	152.06	105.19	56.86	104.70	−10.02
CC polarization propagator/CCSD[f]				108.30	−6.42
aug-cc-pV*DZ*//B3LYP/6-31+G[g]	166.00	107.00	56.90	109.97	−4.75
aug-cc-pV*TZ*//B3LYP/6-31+G[g]	166.78	107.68	56.79	110.42	−4.30
aug-cc-pV*DZ*, aug-cc-pV*TZ*//B3LYP/6-31+G[g]	166.65	107.92	57.06	110.54	−4.18

[a] The experimental value is 114.72 au; see ref 43. [b] Ref 36. [c] Ref 40. [d] Ref 41. [e] Ref 39. [f] Ref 42. [g] This work.

appropriate (X_1, X_2) USTE correlation energies. This is a fair approximation, as the HF energies are commonly more economically calculated than correlated ones. By substituting eqs 4 and 5 into eq 2, we have obtained the CBS-extrapolated energies at the MP2 and CCSD levels of theory with V*XZ* and AV*XZ* basis sets, in the absence (0) and in the presence (±0.005, ±0.01 au) of external fields for the electronic ground states of H_2, N_2, CO, and H_2O molecules. Exploratory calculations have also been performed for *p*-nitroaniline, $C_6H_4NO_2NH_2$ (*p*-PNA). Except for this species, where the geometry has been optimized, all molecular geometries have been fixed at the experimental equilibrium values, H_2 ($R_{\text{HH}} = 0.742$ Å), N_2 ($R_{\text{NN}} = 1.098$ Å), CO ($R_{\text{CO}} = 1.128$ Å), and H_2O ($R_{\text{OH}} = 0.9578$ Å and $\angle\text{HOH} = 104.50°$).[29]

3. Results and Discussion

We begin by reporting the polarizabilities calculated for H_2 in its ground electronic state. They are based on HF and MP2 energies calculated with V*XZ* and AV*XZ* basis sets, which are reported in Tables 1−8 of the Supporting Information. According to eq 2, the values of the polarizabilities α_{ii}, β_{iii}, and γ_{iiii} of the H_2 molecule were then calculated along the *x*, *y*, and *z* axes using both raw MP2 and CCSD energies as well as CBS-extrapolated ones from the (*D*, *T*), (*T*, *Q*), and (*Q*,5) pairs of cardinal numbers. The results are collected in Table 1. Also reported in this table are the values of $\bar{\alpha}$ at MP2 and CCSD levels of theory, as well as the differences ($\Delta_{\text{calc}-\text{exp}}$) from the experimental result $\bar{\alpha} = 5.31$ au.[29] As seen, the deviation is predicted to be $\Delta_{\text{calc}-\text{exp}} = -0.60$ au when one considers the pair (*Q*,5) of V*XZ* basis sets at both MP2 and CCSD levels of theory. However, when using AV*XZ* ($X = D, T, Q, 5$) basis sets, our best $\Delta_{\text{calc}-\text{exp}}$ lies close to −0.11 au for both extrapolated and not extrapolated (raw) MP2 and CCSD results. Stated more generally, the results obtained from extrapolated and raw energies with both V*XZ* and AV*XZ* basis sets (Table 1) suggest that the level of theory (MP2 or CCSD) does not significantly affect the calculated polarizabilities. However, as might be expected (due to lack of enough diffuse functions in the V*XZ* basis set), they turn out to be very sensitive to the basis set quality. Indeed, all AV*XZ* calculations have shown similar small deviations ($\Delta_{\text{calc}-\text{exp}}$) at both levels of theory (between −0.11 and −0.12 au), except for the raw *DZ* calculations where the values are close to −0.22 au.

We have also computed polarizabilities for values of the internuclear distance in the range of $0.5 \leq R_{\text{HH}}/\text{Å} \leq 2.2$ using both extrapolated and raw energies. The raw polarizabilities versus internuclear distances calculated at MP2 and CCSD with AV*XZ* basis sets are shown in Figures 1 and 2, while the corresponding CBS polarizabilities versus internuclear distances are in Figures 3 and 4. With the exception of the raw AV*DZ* ones, all extrapolated and raw results are nearly identical at both levels of theory until 1.5 Å or so. Not surprisingly, both the MP2 and CCSD calculations behave poorly afterwords due to being based on single-reference theories. Indeed, it is well-known that such ab initio methods can have severe difficulties because the single Slater determinant upon which they are based is unable to describe the whole range of bond distances up to dissociation. We emphasize that the MP2 calculations for H_2 yield similar values to the CCSD ones. Due to its lower computational cost, we will then adopt only MP2 theory for the studies of the largest polyatomic molecules (H_2O and *p*-nitroaniline in their electronic ground states) considered here.

Following the procedure employed for the hydrogen molecule, energies have been calculated at the HF and MP2 levels of theory with V*XZ* and AV*XZ* basis sets, both in the absence (0) and presence (±0.005, ±0.01 au) of external fields. The calculated energies are also given in the Supporting Information. Table 2 reports the values of $\bar{\alpha}$ calculated both with raw and CBS-extrapolated energies for N_2, CO, and H_2O. Moreover, differences ($\Delta_{\text{calc}-\text{exp}}$) between the calculated and experimental data ($\bar{\alpha} = 11.54$, 13.18, and 10.13 au for N_2, CO, and H_2O,[29] respectively) have been included in Table 2. Except for a few cases where the discrepancy is likely to be within the experimental error, the general trend of the extrapolated values is a systematic decrease of $\Delta_{\text{calc}-\text{exp}}$ with an increasing pair of cardinal numbers used for the CBS extrapolation [from (*D*,*T*) to (*Q*,5)]. In addition $\Delta_{\text{calc}-\text{exp}}$ is, as expected, seen to decrease significantly with the inclusion of diffuse functions on the augmented basis set. For the N_2 molecule, our best result for $\Delta_{\text{calc}-\text{exp}}$ lies close to −0.04 au considering both the extrapolated (*Q*,5) and raw AV5Z energies. Not unexpectedly, the difference $\Delta_{\text{calc}-\text{exp}}$ increases when the modest *DZ* basis sets are employed.

Similar observations apply to the CO molecule, with the differences $\Delta_{\mathrm{calc-exp}}$ lying now (except for the raw AV*D*Z result) close to -0.02 au. For H_2O, $\Delta_{\mathrm{calc-exp}}$ lies, in all cases (both for raw and CBS-extrapolated results), close to -0.3 au when using the AV*X*Z basis set, with the exception being the raw *D*Z value of -0.9 au. In summary, our MP2-extrapolated calculations on H_2, N_2, CO, and H_2O molecules[29] indicate that the use of diffuse functions significantly improves the results when compared to the ones obtained with V*X*Z basis sets, even for the cheapest AV*D*Z basis set. This corroborates early findings[30] that basis sets containing diffuse functions are required to describe higher-order electrical molecular properties such as those studied in the present work.

In the present work, we have also calculated polarizabilities for N_2 and CO employing MP2, CCSD, and CCSD(T) with augmented (AV*X*Z) and double-augmented (dAV*X*Z) basis sets. For better comparison with the dAV*X*Z results, the MP2/AV*X*Z ones are duplicated in this table. Values of $\bar{\alpha}$ calculated both with raw and CBS-extrapolated energies, differences between the calculated and experimental values ($\Delta_{\mathrm{calc-exp}}$), and CPU times are also reported. According to the CBS results for N_2, the errors are ~0 (CCSD) and ~0.1 [CCSD(T)], with CPU times being in the same order, 22856.1 (AV*X*Z) and 35030.1 s (dAV*X*Z) and 12249.8 s (AV*X*Z) and 44457.4 (dAV*X*Z). However, considering the MP2 values, the errors are ~0 employing both AV*X*Z (128.9 s) and dAV*X*Z (261.6 s) basis sets. Similarly, the CBS errors for CO are ~0.3 (CCSD) and ~0.1 [CCSD(T)]. Yet, the best CBS result ($\Delta_{\mathrm{calc-exp}} \sim 0$) is obtained with MP2/AV*X*Z at the lowest cost (132 s). One concludes from Table 3 that, although there are not significant differences between the MP2 and CCSD results, the MP2 ones are much cheaper than the former.

To test further the methodology on a larger system, we have considered the organic chromophore *p*-nitroaniline, $C_6H_4NO_2$-NH_2 (*p*-NA). The B3LYP/6-31+G-optimized geometry shown in Figure 5 has been utilized for all of the polarizability calculations reported here. Rashid[22] has recently performed a systematic study of the geometries and energies of *p*-NA in the ground and first excited states using different M-NPG basis sets,[31−34] having concluded that the ring structure of *p*-NA is distorted from that of benzene due to the amine (NH_2) substituent. Moreover, he has found the 6-31+G* basis set to be the most adequate for describing its structure. In the present work, we have utilized instead the 6-31+G basis set since the predicted geometry is closest to the experimental data,[35] especially for the *a* angle (see Figure 5); for a comparison with other structural data available in the literature,[22,35] see Table 4. However, all energy calculations reported here have been done with the AV*X*Z basis set. The electric properties of *p*-NA and its derivatives, such as the dipole moment, polarizabilities, and first and second hyperpolarizabilities, have also been recently studied both theoretically[36−42] and experimentally.[43,44] Feyereisen et al.[36] formulated and implemented a method for the calculation of frequency-dependent response properties at the self-consistent field (SCF) level for studying *p*-NA monomer and its dimer. They noted that accurate polarizability calculations require the use of large, flexible basis sets with diffuse and polarization functions. In turn, Jonsson et al.[41] reported polarizabilities for *p*-NA in the gas phase using both the uncorrelated random phase approximation (RPA) and complete active space (CAS) wave functions, while Reis et al.[39] employed the FF approach to calculate the electric properties of *p*-NA in the gas phase and solution at several levels of theory. Korona et al.[42] have recently proposed a time-independent CC theory of the polarization propagator and implemented it at the CCSD level. Using their computationally less demanding propagator method at the CCSD level, the authors presented static and frequency-dependent dipole polarizabilities for various molecules, including *p*-NA. In the present work, we also report polarizabilities for *p*-NA in the gas phase using the FF approach with CBS-extrapolated and raw energies calculated with AV*D*Z and AV*T*Z basis sets. Table 5 compares our results with those available in the literature. As shown, the deviations between the extrapolated and experimental values vary between -31.72 and -10.02 au, with our results being among the best reported thus far, $\Delta_{\mathrm{calc-exp}} = -4.18$ au for CBS (aug-cc-pVDZ,aug-cc-pVTZ//B3LYP/6-31+G).

4. Conclusions

We have calculated tensorial properties of some molecular systems by using the finite field method and correlation energies extrapolated by the USTE model. The calculated raw and CBS-extrapolated properties have been compared with each other and available experimental data. For H_2, the CCSD calculations have been found to yield polarizabilities similar to those based on the more cost effective MP2 theory, and hence, we have adopted the latter approach for the studies on the other systems. The results have shown that CBS extrapolation of the energy plays an important role in such calculations, in particular for the correlation energy which has been CBS extrapolated by the USTE scheme. Since such tensorial properties require high levels of theory, the possibility of obtaining accurate results from only two points calculated with low-cost basis sets is very relevant. Work is in progress to investigate hyperpolarizabilities as well as even larger molecules.

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Supporting Information Available: HF, MP2, and CCSD energies. This material is available free of charge via the Internet at http://pubs.acs.org.

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