How well do static electronic dipole polarizabilities from gas-phase experiments compare with density functional and MP2 computations?

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How well do static electronic dipole polarizabilities from gas-phase experiments compare with density functional and MP2 computations?

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Static electronic dipole polarizabilities for 135 molecules are calculated using second-order Møller-Plesset perturbation theory and six density functionals recently recommended for polarizabilities. Comparison is made with the best gas-phase experimental data. The lowest mean absolute percent deviations from the best experimental values for all 135 molecules are 3.03% and 3.08% for the LC-τHCTH and M11 functionals, respectively. Excluding the eight extreme outliers for which the experimental values are almost certainly in error, the mean absolute percent deviation for the remaining 127 molecules drops to 2.42% and 2.48% for the LC-τHCTH and M11 functionals, respectively. Detailed comparison enables us to identify 32 molecules for which the discrepancy between the calculated and experimental values warrants further investigation. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4932594]

I. INTRODUCTION

The isotropic static electronic dipole polarizability (α) is a fundamental property of a molecule. It is useful in both quantitative and qualitative ways.[1] High accuracy *ab initio* calculations of electric properties of molecules can be challenging but impressive results are possible for small molecules; see, for example, Ref. 2. Systems too large to handle with accurate wave function methods, such as the coupled-cluster approach,[3,4] and large one-particle basis sets have to be handled by computationally simpler methods such as second-order Møller-Plesset perturbation theory (MP2)[5,6] and Kohn-Sham density functional theory (DFT).[7–9]

Since the exact exchange-correlation functional is unknown, a practical difficulty with DFT methods is choosing among the large number of approximate functionals available. This issue is addressed by frequent evaluations of competing functionals; see, for example, Ref. 10. Recently, an assessment[11] of 34 density functionals identified the top performers for reproducing coupled-cluster polarizabilities of 145 representative organic molecules (T145). The T145 set is a subset of the TABS database[12] and of a training set[13] used for constructing additive models.[14] All the molecules contain at least one C atom and possibly one or more atoms from the set H, N, O, F, S, Cl, and Br. A protocol involving at least three DFT calculations was suggested for computing polarizabilities.[11]

It is important to test this protocol against experimental values. The latter should ideally be from gas-phase measurements and be purely electronic values obtained by correcting for vibrational contributions. A recent exhaustive compilation[15] contains such experimental gas-phase electronic dipole polarizabilities. The purpose of this work is to carry out tests of the suggested DFT procedure[11] and of MP2 calculations against experimental electronic polarizability values for 135 of

the molecules listed in Hohm's tables.[15] An important outcome of these tests is that they enable us to identify the molecules for which further investigation, both experimental and computational, is needed. Moreover, they give a clear picture of what standard computations can currently achieve for polarizabilities.

A brief summary of our methods and calculations is given in Sec. II. It is followed by a comparison with experiment and discussion in Sec. III and by some concluding remarks in Sec. IV. Atomic units are used throughout. The 2010 CODATA recommendations for the fundamental physical constants[16] give the SI value of 1 a.u. of the dipole polarizability α as $1.648\,777 \times 10^{-41}$ C^2 m^2 J^{-1}. Multiplication of a value of α in a.u. by $0.148\,184\,7$ yields the polarizability volume in Å^3.

II. COMPUTATIONS

Hohm tabulates polarizabilities for 166 molecules not counting isotopologues as distinct. Of these, we omit the 25 diatomic molecules because high accuracy coupled-cluster calculations are well within reach for diatomics[2,17] and no one would seriously consider DFT calculations for accurate work on diatomics. Further, we omit C_{60} and C_{70} because they are a bit too large for our computational resources, and we omit UF_6, $Nd(C_5H_5)_3$, $Sm(C_5H_5)_3$, and $Er(C_5H_5)_3$ partly because of their size and partly because the specific basis sets[18,19] we use for calculations include neither lanthanides nor elements beyond Rn.

This leaves 135 molecules for consideration. These molecules range in size from triatomics to octane and adamantane each of which contains 26 atoms. Atoms of 23 elements are present in this set of molecules. The structures of these molecules were obtained by energy minimization using the CAM-B3LYP method[20] including the D3 dispersion corrections[21] with Becke-Johnson damping.[22,23] The CAM-B3LYP-D3 method was chosen because of its

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good performance in a benchmark study of rotational constants.[24] We used the triple-zeta valence def2-TZVP basis set[18] coupled, for elements with atomic number $Z > 36$, with energy-consistent Stuttgart effective core potentials (ECPs) with small cores.[25–27] Using ECPs for the heavier elements Rb–Rn reduces the number of basis functions and accounts for scalar relativistic effects. We did not use a larger basis set because a benchmark study[24] demonstrated that the average performance of CAM-B3LYP-D3 for rotational constants is almost the same with the def2-TZVP basis as it is with the larger quadruple-zeta valence def2-QZVP basis set.

Vibrational frequencies were calculated to verify that a local minimum had been found. It is very likely that the structures are global minima as well. Many of these molecules are so simple that the point group of the global minimum is well-known. In less straightforward cases, we examined a few different isomers to ensure that we had found the one with the lowest energy and checked that it agreed with results in the literature. These cases included some of the alkanes,[28–30] perfluorinated hydrocarbons,[31,32] metallocenes,[33–36] and metal halides.[37–40] The only mild surprise was that Al_2I_6 was found to have a puckered central ring and C_{2v} symmetry in agreement with previous MP2 and coupled-cluster calculations but in disagreement with DFT calculations that did not include dispersion.[38,40] All 135 structures are available as supplementary material from the journal's web archive.[41]

Next, polarizability calculations were performed at these energy minima using the MP2 method and six density functionals: M11,[42] M06-2X,[43] ωB97,[44] HISS,[45] LC-ωPBE,[46] and LC-τHCTH which is a range-separated functional obtained[11] by applying a long-range correction scheme[47] to the τHCTH functional.[48] Recent recommendations for DFT polarizability calculations[11] suggest using one functional from each of the three pairs M11 and M06-2X, ωB97 and LC-τHCTH, and HISS and LC-ωPBE but we decided to use all six functionals, partly as a check on the recommended procedure. Since these calculations are to be compared with experimental results, it is important to minimize basis set errors. We use the def2-QZVPD basis set[19] that was optimized for molecular response calculations. This basis set was constructed[19] by augmenting the def2-QZVP set[18] with a small number of diffuse basis functions chosen to maximize atomic Hartree-Fock static polarizabilities. For the sake of computational efficiency, we decided not to use the even larger def2-QZVPPD set because prior tests[19] showed that it is not much more accurate for polarizabilities than def2-QZVPD except for d-block elements.

For 13 of the largest molecules, MP2/def2-QZVPD polarizabilities were approximated by adding a basis set correction δ to a MP2 value in a smaller basis set. Thus,

$$\alpha(\text{MP2/def2-QZVPD}) \approx \alpha(\text{MP2/def2-TZVPD}) + \delta, \quad (1)$$

where def2-TZVPD is a smaller basis set optimized for polarizabilities[19] and δ is calculated at the Hartree-Fock (HF) level from

$$\delta = \alpha(\text{HF/def2-QZVPD}) - \alpha(\text{HF/def2-TZVPD}). \quad (2)$$

III. RESULTS AND DISCUSSION

The polarizability values in Hohm's tabulations[15] are derived from relative dielectric permittivity $\varepsilon(\omega)$ measurements, refractive index $n(\omega)$ measurements, electron-molecule scattering, molecular beam deflection techniques, and matter-wave interferometry. Bonin and Kresin's book[1] is a starting point for learning about these experimental techniques. Hohm[15] also includes polarizabilities derived from constrained dipole oscillator strength distributions (DOSDs) obtained by analysis of mainly photoabsorption cross-section measurements and refractive index data; see, for example, Refs. 49–54 for explanations of this method as it has evolved over the years.

Comparison of theoretical and experimental polarizabilities is fraught with difficulties and pitfalls which must be understood. The theoretically calculated α are static (zero frequency) electronic polarizabilities. On the other hand, experimentally determined polarizabilities depend upon the measuring frequency ω and contain non-electronic contributions. Debye[55] pointed out that

$$\alpha_{\text{exp}}(\omega) = \alpha_{\text{el}}(\omega) + \alpha_{\text{vib}}(\omega) + \alpha_{\text{or}}(\omega) \quad (3)$$

in which $\alpha_{\text{el}}(\omega)$, $\alpha_{\text{vib}}(\omega)$, and $\alpha_{\text{or}}(\omega)$ are the electronic, vibrational, and orientational contributions, respectively. The static electronic polarizabilities $\alpha_{\text{el}}(\omega = 0)$ are referred to as simply α in most of this work.

The GHz frequencies typically used in dielectric permittivity experiments effectively yield static polarizabilities, $\alpha_{\text{exp}}(\omega \approx 0)$, via the Clausius-Mossotti equation. However, both α_{vib}, usually obtained from infrared(IR)-band intensities, and α_{or}, obtained by an extrapolation of temperature(T)-dependent measurements to $T \rightarrow \infty$, must be subtracted from the polarizabilities obtained from the $\varepsilon(\omega \approx 0)$ measurements.

Refractive index measurements are usually carried out at visible and ultraviolet (UV) frequencies and are converted to polarizabilities using the Lorentz-Lorenz equation. Measurements in this frequency range have negligible α_{vib} and α_{or} contributions and the extrapolation of the electronic component to the static limit $\omega \rightarrow 0$ is carried out with Cauchy expansions or Kramers-Heisenberg equations.

Results from electron scattering cross-sections and from molecular beam deflection techniques are less accurate and α_{vib} and α_{or} are either estimated roughly or just neglected. There is no frequency problem associated with these two techniques because the measurements give static polarizabilities. Constrained DOSD reconstructions also directly yield static electronic polarizabilities.

Hohm[15] has made all required adjustments to the published data to obtain the static electronic polarizabilities he tabulates. Moreover, he[15] was very careful to list consistently values of $\alpha_{\text{el}}(0)$ obtained from low density gas-phase and, in a few cases, single-molecule experiments. His selection minimizes the influence of intermolecular interactions on the polarizabilities. Hohm also excluded experimental results of "obscure or questionable quality." Finally, whenever there are several sets of measurements, often non-overlapping, Hohm has indicated a recommended value adding the caveat that, in some cases, the choice is his subjective opinion. Although polarizabilities with a precision of 0.1% are listed[15] for a few
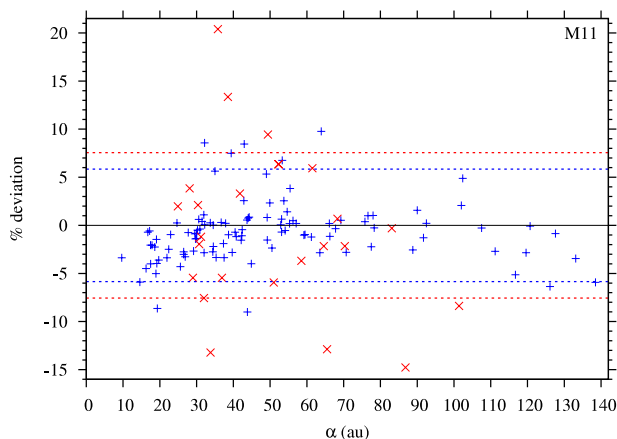
FIG. 1. Percent deviations of the M11 calculated polarizabilities from the recommended experimental values for 135 molecules. The 110 deviations from experimental values that do not depend upon dielectric permittivity measurements are shown by "blue plus" and the remaining 25 deviations are shown by "red multiplication symbol." The deviations for SnI_4, Al_2Br_6, and Al_2I_6 are not shown because their α is off-scale. The dashed lines at ± 7.56 enclose 90% of all the points. The dashed lines at ± 5.85 enclose 90% of all 110 "blue plus" points.

FIG. 2. Percent deviations of the LC-τHCTH calculated polarizabilities from the recommended experimental values for 135 molecules. The 110 deviations from experimental values that do not depend upon dielectric permittivity measurements are shown by "blue plus" and the remaining 25 deviations are shown by "red multiplication symbol." The deviations for SnI_4, Al_2Br_6, and Al_2I_6 are not shown because their α is off-scale. The dashed lines at ± 7.19 enclose 90% of all the points. The dashed lines at ± 4.91 enclose 90% of all 110 "blue plus" points.

small molecules, Hohm[15] explained that the experimental error is much greater in many cases. Moreover, he warned[15] that "there are also molecules like HI, CH_2Cl_2, or CH_2Br_2 for which the available data do not even overlap within their error bars." The error bars on his recommended values should be treated with caution.

We begin by trying to get an overview of the size of the discrepancies between the calculations and experimental values. The percent differences between the calculations and the recommended experimental polarizabilities of the 135 molecules are shown in Figs. 1 and 2 for the M11 and LC-τHCTH functionals, respectively. Both of these are hybrid functionals with long-range corrections included via range-separation and both include dependence on the kinetic energy density. Although many of the deviations are less than 5% in magnitude, there are several larger differences. The deviations range from -15% to $+20\%$ for the M11 method and from -15% to $+17\%$ for the LC-τHCTH functional.

The errors associated with the experimental polarizabilities are larger for those based on dielectric permittivity measurements because of the uncertainties in both the vibrational and orientational corrections. Figures 1 and 2 show deviations
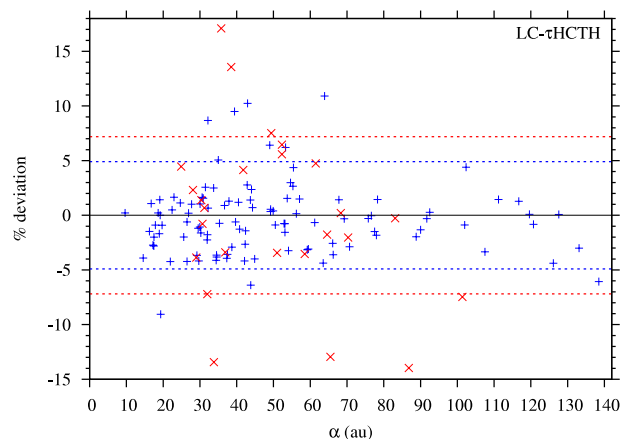
from this group of measurements using a different symbol than is used for the remaining experimental values. It is apparent that the largest deviations from the DFT calculations correspond to experimental values based on dielectric permittivity measurements.

The absolute percent deviations (AD) of the DFT and MP2 polarizabilities from their recommended experimental counterparts can be used in many ways to construct statistical measures of their errors. Two numerical indices constructed from these deviations are the mean (MAD) and 90th percentile (P_{90}). There are no spurious numerical artifacts in the percent deviations because the polarizabilities are not small and range in magnitude from 9.6 a.u. to 268 a.u. for the molecules considered in this work. To provide information about the signs of the deviations, we use a bias measure $B = f_+ - f_-$ in which f_+ and f_- are the fractions of errors that are positive and negative, respectively. The bias ranges from -1 when all the deviations are negative to $B = 1$ when they are all positive. The different deviation measures lead to different rankings of the methods. However, a unique measure is useful. Small values of P_{90}, the upper bound to the absolute percent deviation 90% of the time, are desirable because a general purpose method

TABLE I. The 90 percentile (P_{90}) and mean absolute deviations (MAD) (%) with respect to the recommended experimental values from Ref. 15. B is the bias parameter and $\Delta = P_{90} + |B|$ is an overall error measure. All quantities are unitless. The error measures are listed for all 135 molecules and for the subset of 127 molecules which excludes the eight worst outliers. The bold values in each column indicate the most accurate method as judged by that error measure.

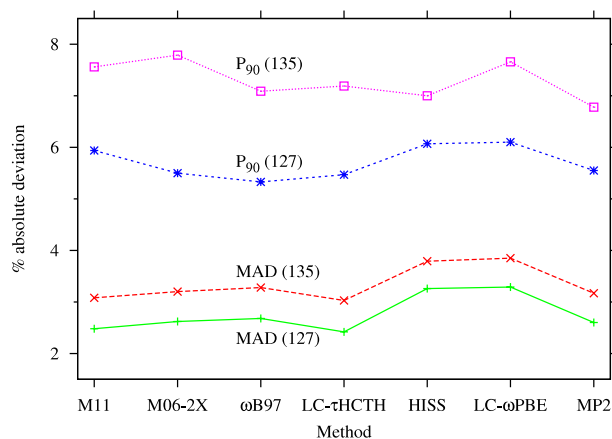| Method	MAD(135)	MAD(127)	P_{90}(135)	P_{90}(127)	B(135)	B(127)	Δ(135)	Δ(127)
M11	3.08	2.48	7.56	5.94	-0.26	-0.28	7.8	6.2
M06-2X	3.20	2.62	7.79	5.50	-0.45	-0.48	8.2	6.0
ωB97	3.28	2.68	7.09	**5.33**	-0.27	-0.29	7.4	**5.6**
LC-τHCTH	**3.03**	**2.42**	7.19	5.47	**-0.13**	**-0.13**	7.3	**5.6**
HISS	3.79	3.26	7.00	6.07	-0.66	-0.70	7.7	6.8
LC-ωPBE	3.85	3.29	7.66	6.10	-0.54	-0.57	8.2	6.7
MP2	3.17	2.60	**6.78**	5.55	-0.32	-0.34	**7.1**	5.9

FIG. 3. The 90 percentile (P_{90}) and mean absolute deviations (MAD) (%) with respect to the recommended experimental values from Ref. 15. The statistical measures are shown for all 135 molecules and the subset of 127 molecules from which the eight extreme outliers are excluded.

should be accurate most of the time. Moreover, as small a bias as possible is desirable. Hence, as in previous work,[11] we define a composite error measure by $\Delta = P_{90} + |B|$ and use the smallness of Δ as an indicator of the overall accuracy of a method. This choice of Δ is subjective but so are other choices. All these measures are listed in Table I.

We begin by considering these statistical measures for the full set of 135 molecules. Table I shows that the MAD ranges from 3.03% for LC-τHCTH to 3.85% for LC-ωPBE and P_{90} ranges from 6.78% for MP2 to 7.79% for M06-2X. All methods have a negative B indicating that they are more likely to underestimate, as opposed to overestimate, the experimental value. A small negative bias is reasonable because the calculated values do not include the effects of zero-point vibrational averaging which would tend to increase α. The least biased method is the long-range corrected LC-τHCTH functional with $B = -0.13$ whereas the non-empirical screened-exchange density functional HISS is the most biased with $B = -0.66$.

TABLE II. Static electronic dipole polarizabilities α (in a.u.) of molecules with 3 and 4 atoms. The M11, M06-2X, ωB97, LC-τHCTH, HISS, LC-ωPBE, and MP2 values were computed with a def2-QZVPD basis set. The experimental values are those recommended by Hohm, see Ref. 15. Multiplication of a value of α in a.u. by 0.148 184 7 yields the polarizability volume in Å^3.

Molecule[a]	M11	M06-2X	ωB97	LC-τHCTH	HISS	LC-ωPBE	MP2	Experiment[b]
H_2O	9.317	9.380	9.744	9.663	9.234	9.546	9.688	9.642 ± 0.096(O)
HCN	16.63	16.70	16.82	16.93	16.43	16.54	16.30	16.75 ± 0.20(R)
H_2S	24.74	24.62	24.26	24.96	24.17	24.04	24.50	24.68 ± 0.08(R)
CO_2	16.80	16.78	17.19	17.15	16.54	16.96	17.55	17.50 ± 0.02(R)
N_2O	18.99	18.97	19.37	19.52	18.76	19.10	19.42	19.70 ± 0.20(O)
O_3	18.42	18.61	18.92	19.18	18.33	18.59	15.94	19.18 ± 0.50(O)
OCS	33.81	33.82	33.90	34.56	33.29	33.59	34.72	33.72 ± 0.60(O)
SO_2	24.51	24.67	25.13	25.10	24.37	24.73	25.59	25.61 ± 0.50(O)
CS_2	55.40	55.40	55.08	56.77	54.42	54.73	56.53	55.3 ± 1.0(O)
H_2Se	30.78	31.03	30.95	31.38	30.60	30.30	30.60	30.90 ± 0.30(R)
$SnCl_2$	68.72	70.37	68.43	68.66	68.54	68.16	69.29	70.7 ± 2.0(R,H)
$SnBr_2$	86.53	88.60	87.31	87.06	86.80	85.82	87.23	88.8 ± 3.0(R,H)
SnI_2	116.2	119.6	120.1	119.7	119.8	117.5	120.3	119.6 ± 5.0(R,H)
$HgCl_2$	60.46	60.60	59.45	60.79	59.61	58.81	61.90	61.2 ± 1.3(R,H)
$HgBr_2$	78.09	78.77	78.18	79.43	77.82	76.38	79.91	78.3 ± 1.5(R,H)
HgI_2	108.2	110.5	111.0	112.8	110.9	108.2	113.4	111.2 ± 2.2(R,H)
†NH_3	13.70	13.86	13.98	13.99	13.54	13.73	14.14	14.56 ± 0.30(O)
C_2H_2	22.74	22.90	22.83	23.34	22.58	22.39	22.29	22.96 ± 0.50(O)
†H_2CO	17.65	17.43	17.64	17.57	17.25	17.38	17.54	19.32 ± 0.25(O)
PH_3	31.04	30.36	30.12	30.82	30.02	29.82	30.10	30.4 ± 1.5(D)
NCCN	32.22	32.20	32.31	32.41	31.94	31.81	31.14	32.2 ± 1.0(R)
BF_3	15.54	15.36	16.31	16.03	15.40	16.09	15.81	16.27 ± 0.20(R)
NF_3	18.00	17.99	18.75	18.63	17.92	18.44	18.23	18.95 ± 0.20(R)
†AsH_3	34.89	35.58	35.22	35.65	35.08	34.84	35.00	36.9 ± 1.2(D)
SO_3	27.42	27.44	28.02	27.88	27.06	27.63	28.60	29.0 ± 1.5(A)
SOF_2	25.77	25.81	26.60	26.34	25.60	26.20	26.72	26.50 ± 0.80(R)
CCl_2O	44.67	44.59	44.22	44.60	43.87	43.89	44.90	44.29 ± 0.50(R)
CCl_2S	63.20	63.38	62.45	63.46	62.50	61.97	62.77	64.6 ± 3.5(D)
BCl_3	55.12	55.10	54.06	54.58	53.99	53.95	54.96	53.75 ± 0.60(R)
P_4	90.51	90.65	89.17	91.42	89.76	88.35	91.88	91.7 ± 1.0(R,H)
PCl_3	68.78	68.89	67.84	68.87	67.85	67.44	69.17	70.3 ± 8.7(D)
†$AsCl_3$	73.97	74.49	73.51	74.68	73.43	73.09	74.91	86.8 ± 6.0(D)
BBr_3	77.37	77.75	76.97	76.57	76.46	75.73	77.02	76.6 ± 1.0(R)
As_4	110.7	115.3	115.8	118.2	115.6	114.3	116.2	116.7 ± 1.1(R,H)

[a] A † indicates that we think further theoretical and/or experimental work on α is warranted.
[b] Recommended values from Ref. 15. The first letter in parentheses denotes the type of experiment: O-dipole oscillator strength distribution, R-refractive index, D-dielectric permittivity, A-combined R and D data, E-electron-molecule scattering. An H after the comma denotes high temperature experiments.

TABLE III. Static electronic dipole polarizabilities α (in a.u.) of molecules with 5–7 atoms. The M11, M06-2X, ωB97, LC-τHCTH, HISS, LC-ωPBE, and MP2 values were computed with a def2-QZVPD basis set. The experimental values are those recommended by Hohm, see Ref. 15. Multiplication of a value of α in a.u. by 0.148 184 7 yields the polarizability volume in Å^3.

Molecule[a]	M11	M06-2X	ωB97	LC-τHCTH	HISS	LC-ωPBE	MP2	Experiment[b]
CH_4	17.14	16.69	16.65	16.77	16.40	16.49	16.50	17.240 ± 0.026(R)
SiH_4	32.32	31.39	31.18	31.25	30.89	31.04	30.41	31.97 ± 0.30(O)
†CH_3F	17.10	16.81	17.08	16.97	16.62	16.86	16.79	17.46 ± 0.30(R)
CH_3Cl	29.73	29.52	29.22	29.66	28.99	28.96	29.29	29.98 ± 0.32(R)
CH_2F_2	17.52	17.37	17.95	17.73	17.26	17.68	17.53	17.89 ± 0.18(R)
†SiH_3Cl	43.10	41.99	41.65	41.92	41.35	41.45	41.29	35.8 ± 1.5(D)
CHF_3	18.21	18.10	18.92	18.67	18.04	18.63	18.41	18.63 ± 0.25(R)
†GeH_4	34.95	35.02	34.57	34.98	34.48	34.45	34.15	32.19 ± 0.62(R)
†CH_2Cl_2	43.10	43.04	42.40	43.10	42.26	42.05	42.74	44.89 ± 0.50(R)
$CHClF_2$	30.79	30.71	31.03	31.10	30.33	30.69	30.80	30.6 ± 1.0(R)
CF_4	18.82	18.67	19.64	19.37	18.65	19.34	19.08	19.10 ± 0.20(O)
CH_3Br	36.80	36.63	36.58	37.02	36.06	35.86	36.10	36.69 ± 0.95(R)
†SiH_2Cl_2	54.06	53.25	52.65	53.11	52.41	52.42	52.76	49.4 ± 1.0(D)
†$CHCl_2F$	43.64	43.59	43.29	43.72	42.88	42.90	43.45	38.5 ± 1.4(D)
SiF_4	21.88	21.71	23.04	22.55	21.74	22.72	22.30	22.44 ± 0.22(O)
$CClF_3$	31.13	30.98	31.54	31.47	30.66	31.20	31.20	32.04 ± 0.60(O)
$CHCl_3$	56.49	56.53	55.49	56.30	55.48	55.07	56.14	56.22 ± 0.05(R)
CCl_2F_2	43.95	43.86	43.84	44.04	43.20	43.46	43.85	42.85 ± 0.50(O)
†SO_2Cl_2	56.34	56.28	55.99	56.43	55.31	55.58	57.33	58.5 ± 1.0(D)
†$SiHCl_3$	65.15	64.75	63.85	64.42	63.66	63.58	64.40	61.5 ± 1.0(D)
†CCl_3F	56.90	56.85	56.13	56.61	55.84	55.72	56.60	53.3 ± 1.0(O)
CH_3I	48.49	48.70	49.20	49.51	48.72	48.12	48.41	49.24 ± 0.50(R)
GeF_4	26.04	25.72	27.56	26.97	25.98	27.07	26.86	26.92 ± 0.50(R)
$CBrF_3$	37.97	37.84	38.58	38.38	37.49	37.90	37.83	37.89 ± 0.53(R)
CCl_4	69.59	69.59	68.21	69.01	68.35	67.78	69.23	69.23 ± 0.09(R)
$SiCl_4$	76.09	76.07	74.89	75.58	74.80	74.66	75.92	75.8 ± 1.0(R)
CH_2Br_2	57.54	57.62	57.25	57.84	56.75	56.06	56.62	55.42 ± 0.60(R)
†$TiCl_4$	92.90	92.35	92.46	93.83	91.59	91.87	98.20	101.4 ± 2.0(D,H)
ClF_3	49.31	49.41	50.62	50.05	49.51	49.64	49.65	50.5 ± 1.3(R)
$GeCl_4$	82.85	81.94	81.42	82.87	81.46	81.10	82.82	83.1 ± 4.0(D,H)
†OsO_4	47.97	48.19	49.08	49.25	47.49	48.32	55.40	51.0 ± 1.0(A,H)
$SnCl_4$	92.69	91.44	90.86	92.75	90.82	90.17	92.99	92.5 ± 1.0(R,H)
†$SiBr_4$	107.4	107.9	107.1	106.9	106.5	105.4	106.8	102.4 ± 1.0(R)
$SnBr_4$	126.5	125.4	126.1	127.7	125.4	123.8	126.9	127.6 ± 1.3(R,H)
SnI_4	185.5	185.8	188.7	190.6	188.8	185.1	190.4	187.5 ± 2.0(R,H)
C_2H_4	27.51	27.24	27.32	28.00	27.06	26.81	26.91	27.72 ± 0.08(R)
†CH_3OH	21.20	20.90	21.07	21.01	20.59	20.78	21.01	21.94 ± 0.30(O)
CH_3CN	29.26	29.06	29.08	29.17	28.62	28.68	28.48	29.52 ± 0.30(R)
CH_3SH	36.97	36.69	36.08	36.77	36.00	35.72	36.48	35.0 ± 2.2(E)
†N_2O_4	39.88	40.05	40.72	41.03	39.41	40.14	41.31	43.83 ± 0.50(R)
PF_5	25.39	25.19	26.59	26.01	25.20	26.19	25.82	24.9 ± 3.0(D)
†CH_3NH_2	25.70	25.44	25.33	25.38	24.95	24.99	25.53	26.50 ± 0.30(O)
propadiene	40.19	39.96	40.05	40.96	39.89	39.42	39.54	40.48 ± 0.50(R)
†propyne	36.21	36.01	35.71	36.13	35.51	35.15	35.11	37.47 ± 0.40(R)
acetaldehyde	30.10	29.73	29.78	29.76	29.33	29.35	29.81	30.25 ± 0.30(O)
†oxirane	28.41	28.12	28.10	28.12	27.67	27.71	28.28	29.19 ± 0.30(R)
SF_6	29.63	29.52	30.81	30.35	29.40	30.36	30.11	30.04 ± 0.30(O)
SeF_6	34.12	33.63	35.52	35.04	33.92	35.00	34.89	35.3 ± 0.9(R)
TeF_6	38.58	37.79	40.13	39.46	38.29	39.54	39.70	39.7 ± 1.0(R)

[a]A † indicates that we think further theoretical and/or experimental work on α is warranted.

[b]Recommended values from Ref. 15. The first letter in parentheses denotes the type of experiment: O-dipole oscillator strength distribution, R-refractive index, D-dielectric permittivity, A-combined R and D data, E-electron-molecule scattering. An H after the comma denotes high temperature experiments.

Consider the extreme outliers. The largest differences occur for $CHCl_2F$, $CClF_2CClF_2$, CH_3CHF_2, $AsCl_3$, and SiH_3Cl for which the measured values are based on dielectric permittivity measurements. It seems highly likely that the experimental values are suspect because the MP2 and all

the DFT results differ from the experimental values by amounts ranging from 11% to 20% whereas the theoretical values differ from each other by much smaller amounts ranging between 0.4% and 3.4%. Similarly, the MP2 and all the DFT results differ from the experimental values by

TABLE IV. Static electronic dipole polarizabilities α (in a.u.) of molecules with 8 or more atoms. The M11, M06-2X, ωB97, LC-τHCTH, HISS, LC-ωPBE, and MP2 values were computed with a def2-QZVPD basis set. The experimental values are those recommended by Hohm, see Ref. [15]. Multiplication of a value of α in a.u. by 0.148 184 7 yields the polarizability volume in Å^3.

Molecule[a]	M11	M06-2X	ωB97	LC-τHCTH	HISS	LC-ωPBE	MP2[b]	Experiment[c]
B_2H_6	34.53	33.30	33.32	33.26	32.86	33.06	32.73	34.52 ± 0.20(R)
C_2H_6	29.27	28.49	28.27	28.45	28.00	27.96	28.23	29.69 ± 0.06(R)
C_2H_5F	29.18	28.66	28.80	28.75	28.26	28.42	28.57	28.1 ± 2.0(D)
†Si_2H_6	61.72	61.85	60.60	60.75	60.66	60.33	60.00	63.53 ± 0.70(R)
CH_3CH_2Cl	42.21	41.81	41.29	41.80	41.06	40.86	41.50	42.40 ± 0.95(R)
†CH_3CHF_2	29.33	28.97	29.45	29.26	28.65	29.03	29.06	33.8 ± 1.8(D)
CH_3CF_3	29.58	29.23	29.96	29.69	28.98	29.54	29.47	32.0 ± 2.4(D)
CH_2FCF_3	30.10	29.85	30.84	30.46	29.68	30.38	30.22	30.7 ± 2.2(D)
C_2H_5Br	49.60	49.22	48.91	49.37	48.44	48.03	48.58	49.2 ± 1.1(R)
CHF_2CF_3	30.83	30.63	31.86	31.41	30.52	31.38	31.13	31.2 ± 1.2(D)
$CHClFCF_3$	43.18	42.99	43.70	43.53	42.58	43.19	43.28	41.8 ± 1.9(D)
CH_3CCl_2F	55.62	55.36	54.86	55.22	54.44	54.35	55.18	52.3 ± 3.5(D)
C_2F_6	31.63	31.39	32.80	32.31	31.33	32.32	32.02	31.5 ± 0.5(R)
$CHCl_2CF_3$	55.62	55.49	55.55	55.68	54.74	55.02	55.53	52.3 ± 2.7(D)
C_2ClF_5	43.94	43.69	44.63	44.31	43.34	44.12	44.12	43.7 ± 1.0(R)
†$CClF_2CClF_2$	57.06	56.89	57.13	57.02	56.19	56.62	57.03	65.5 ± 1.2(D)
CCl_3CF_3	68.77	68.63	68.29	68.44	67.68	67.75	68.64	68.3 ± 2.9(D)
Al_2Cl_6	120.6	121.0	118.7	119.7	118.7	118.5	120.1	120.7 ± 2.5(R,H)
Al_2Br_6	167.7	168.9	167.8	166.7	166.7	164.9	(167.5)	168.0 ± 3.4(R,H)
†Al_2I_6	249.9	254.8	257.0	253.6	256.9	251.4	(256.3)	268.4 ± 6.0(R,H)
cyclopropane	36.61	36.10	35.59	35.85	35.40	35.14	36.00	37.32 ± 0.20(R)
propene	40.31	39.77	39.62	40.27	39.38	38.99	39.22	40.79 ± 0.50(O)
†ethanol	33.48	32.97	32.97	33.01	32.44	32.50	33.00	34.43 ± 0.60(O)
†dimethylether	33.78	33.19	33.19	33.22	32.72	32.75	33.20	34.54 ± 0.70(O)
perfluoro-1-propene	42.35	42.03	43.61	43.14	42.02	43.00	42.40	39.4 ± 4.0(E)
propane	41.47	40.51	40.09	40.36	39.81	39.60	40.17	42.12 ± 0.40(R)
dimethylamine	38.32	37.77	37.40	37.57	37.11	36.90	37.74	38.70 ± 0.40(O)
1,3-butadiene	55.41	55.04	54.93	56.27	55.10	53.89	53.73	54.64 ± 0.30(R)
E-2-butene	53.47	52.63	52.20	52.72	52.04	51.47	51.75	53.13 ± 0.50(R)
1-butene	52.91	52.19	51.77	52.48	51.60	50.96	51.56	52.88 ± 0.60(O)
2-methyl-1-propene	52.76	52.03	51.65	52.30	51.44	50.87	51.40	53.13 ± 0.60(R)
acetone	41.84	41.36	41.23	41.18	40.73	40.65	41.37	42.30 ± 0.50(O)
n-butane	53.81	52.68	52.04	52.35	51.75	51.37	52.24	54.1 ± 1.0(O)
trimethylamine	51.06	50.39	49.71	50.10	49.54	49.02	50.48	49.9 ± 1.0(O)
n-pentane	66.23	64.94	64.07	64.40	63.77	63.22	64.39	66.1 ± 1.0(O)
neopentane	65.47	64.37	63.44	63.84	63.23	62.62	64.16	66.23 ± 0.40(R)
ethoxyethane	58.93	57.93	57.55	57.66	57.01	56.76	57.80	59.5 ± 1.2(O)
methyl-propyl-ether	58.60	57.61	57.21	57.33	56.69	56.44	57.43	59.2 ± 5.0(O)
benzene	67.56	67.48	67.25	68.75	66.96	66.14	67.99	67.79 ± 0.70(O)
n-hexane	78.80	77.34	76.20	76.58	75.92	75.20	(76.67)	78.0 ± 2.4(O)
n-heptane	91.41	89.82	88.44	88.81	88.14	87.25	(89.01)	90.0 ± 2.7(O)
n-octane	104.1	102.4	100.7	101.1	100.4	99.37	(101.4)	102.0 ± 3.0(O)
adamantane	107.2	105.5	103.6	103.9	103.7	102.4	(105.5)	107.5 ± 2.0(R,H)
†E-$C_2F_6N_2$	46.60	46.41	47.90	47.37	46.20	47.20	46.45	42.97 ± 0.50(R)
†ferrocene	118.1	116.4	119.4	120.6	118.1	118.0	(123.0)	126.13 ± 0.66(R,H)
C_3F_8	44.36	44.01	45.80	45.07	43.89	45.14	44.78	44.03 ± 0.70(R)
†cyclo-C_4F_8	51.61	51.19	52.96	52.14	50.98	52.22	(52.11)	49.0 ± 1.5(R)
†ruthenocene	128.5	129.7	127.6	129.1	128.1	126.1	(137.0)	133.1 ± 1.2(R,H)
C_4F_{10}	57.19	56.78	58.89	57.93	56.58	58.06	(57.76)	57.08 ± 0.80(R)
†C_5F_{12}	70.14	69.66	72.05	70.87	69.38	71.08	(70.76)	63.9 ± 2.0(R)
C_3F_7I	75.77	76.08	77.61	76.35	75.91	76.35	(76.51)	77.5 ± 2.1(R)
osmocene	130.3	131.1	128.8	130.1	129.7	127.4	(138.1)	138.5 ± 4.8(R,H)

[a]A † indicates that we think further theoretical and/or experimental work on α is warranted.

[b]Values in parenthesis are obtained by correcting MP2/def2-TZVPD values for basis set effects using Eqs. (1) and (2).

[c]Recommended values from Ref. [15]. The first letter in parentheses denotes the type of experiment: O-dipole oscillator strength distribution, R-refractive index, D-dielectric permittivity, A-combined R and D data, E-electron-molecule scattering. An H after the comma denotes high temperature experiments.

amounts ranging from 7.5% to 12.8% for C_5F_{12}, H_2CO, and $C_2F_6N_2$ whereas the theoretical values differ from each other by much smaller amounts. It is unclear why the refractive index measurements for C_5F_{12} are in greater error than the calculations. The DOSD value[56] for H_2CO is too high partly because of the refractivity constraints used by Kumar and Meath.[56] They estimated the experimental refractive index measurements to be too low and scaled them up by 3%. However, even if we scale their α back down by 3%, the resulting value of 18.8 a.u. is still 6% higher than the largest calculated value (M11). Moreover, the CCSD(T)/def2-QZVPD value[57] of α is 17.44 a.u. The experimental α for $C_2F_6N_2$ obtained from refractive index measurements is lower than the calculations by amounts ranging between 7.5% and 11.5%. The calculations are for the non-polar E isomer whereas the experiment[58] was performed on a polar molecule, perhaps the Z isomer or a mixture of the two isomers. LC-τHCTH predicts the Z isomer to lie 12.7 kcal/mol higher in energy and have an α smaller by 0.53 a.u., providing another violation[13,59] of the minimum polarizability principle.

Consider the subset of 127 molecules obtained by removing the above eight outliers. The marked reductions of MAD(127) and $P_{90}(127)$ relative to their counterparts for all 135 molecules are seen clearly in Fig. 3 and Table I for all methods. Table I indicates that MAD(127) ranges from 2.42% for LC-τHCTH to 3.29% for LC-ωPBE and $P_{90}(127)$ ranges from 5.33% for ωB97 to 6.10% for LC-ωPBE. The least biased method is LC-τHCTH and HISS is the most biased one. The overall error measure Δ is smaller by amounts ranging from 12% to 27% for the 127-molecule subset. For both the full set and the subset, LC-τHCTH and ωB97 have the lowest Δ values among the DFT methods. The MP2 method gives the lowest Δ for the complete set of molecules as in earlier work.[11]

The experimental values recommended by Hohm[15] are compared with our DFT and MP2 polarizabilities for 34 tri- and tetra-atomic molecules, for 49 penta-, hexa-, and hepta-atomic molecules, and for 52 molecules with 8 or more atoms in Tables II, III, and IV, respectively.

In all the tables, the molecules are grouped by the number of atoms they contain and, for a given number of atoms, they are ordered by increasing molecular mass. Thus, the molecules are listed in the same order as in Hohm's tables.[15] Bear in mind that other experimental values of the polarizabilities can be found for many molecules in Hohm's compilation.[15]

Next, we try to identify those molecules for which further polarizability studies, theoretical and/or experimental, are warranted. We focus on those molecules for which the calculated α closest to the recommended experimental value differs from the latter by more than 2% and is outside the error bars. There are 32 such molecules and they are indicated in Tables II, III and IV by a †. Eight of these molecules are the extreme outliers already discussed earlier. Of the remaining 24, the deviations of the experimental values from the calculations for ferrocene, ruthenocene, $TiCl_4$, OsO_4, and Al_2I_6 are partly due to the increased contamination from excited vibrational and rotational states that occurs at the high temperatures at which the measurements were made. Moreover, the difficulties with handling compounds containing iodine add to the errors for Al_2I_6.

It is unclear why the MP2 and all the DFT results differ from the experimental values by amounts ranging from 4.0% to 10.1% for CH_2Cl_2, cyclo-C_4F_8, CCl_3F, N_2O_4, GeH_4, and SiH_2Cl_2. The experimental values for the last three molecules in this set are based on dielectric permittivity measurements. Note that four of these molecules have two or more halogen substituents. Both computational and experimental work is needed to settle the smaller discrepancies, ranging from 2.0% to 7.0%, between the computed results and the experimental values for the other 13 identified molecules: SO_2Cl_2, CH_3F, dimethylether, Si_2H_6, oxirane, ethanol, NH_3, $SiBr_4$, CH_3NH_2, propyne, CH_3OH, $SiHCl_3$, and AsH_3.

The spread between the polarizabilities predicted by the four empirical functionals, M11, M06-2X, ωB97, and LC-τHCTH, is of some interest. Define a percent spread σ for each molecule by

$$\sigma = 100(\alpha_{\max} - \alpha_{\min})/\alpha_{\mathrm{mid}}, \qquad (4)$$

in which

$$\alpha_{\mathrm{mid}} = (\alpha_{\max} + \alpha_{\min})/2 \qquad (5)$$

and $\alpha_{\min}$ and $\alpha_{\max}$, respectively, are the smallest and largest α values predicted by the four functionals. The spread is relatively small, $\sigma < 3\%$, for 94 molecules and moderate, $3.0\% \leq \sigma \leq 4.5\%$, for 33 molecules. The largest spreads, $4.5\% < \sigma \leq 6.9\%$, are found for CF_4, PF_5, SeF_6, SiF_4, BF_3, TeF_6, As_4, and GeF_4. Perhaps this reflects inadequate parametrization of the functionals for perfluorinated molecules.

IV. CONCLUDING REMARKS

An important outcome of this work is the identification of 32 molecules for which further experimental and theoretical work on polarizabilities is warranted. Coupled-cluster computations are currently being carried out in our laboratory for the smaller ones.

In our opinion, the comparisons between DFT predictions and experiment in this work are complementary to those made earlier between DFT and CCSD(T) predictions[11] because the number of different elements represented in the test set is greater in this work (23) than in the earlier work (8). However, there are greater errors and scatter in some of the experimental values[15] than in the CCSD(T) reference values used in the previous study[11] and hence all the deviation measures are somewhat larger in this study. We think that this work confirms that the computational protocol suggested by us earlier[11] is a good one. To reiterate, we suggest that computations with a single method are unwise. We recommend using one of the Minnesota functionals M11 and M06-2X, one of the closely related pair ωB97 and LC-τHCTH, and one of the almost[60] non-empirical LC-ωPBE and HISS. The usual choice in each of the first two pairs would be the first one named. M11 would be preferred most of the time because it was designed[10,42] to replace M06-2X. There is very little to choose between ωB97 and the closely related LC-τHCTH except that the use of the kinetic energy density in LC-τHCTH may make it more reliable in some cases. Of the two almost non-empirical functionals,

LC-ωPBE is more suitable for molecules and HISS for solids. A MP2 calculation is always useful if it is computationally feasible. If there are significant differences among the polarizabilities obtained with these methods, then a sequence of calculations with coupled-cluster methods is required if at all possible with the computational resources at hand.

It is impossible to predict which of the functionals will give the most accurate α for a single molecule of interest. However, this unsatisfactory situation is not much worse than with *ab initio* wave function methods[6] where one can say which method is expected to provide the more complete description of electron correlation but, because the convergence of most properties is not monotonic, one cannot say which method gives the best answer for a single molecule of interest. An element of scientific intuition or "art" persists in computational electronic structure theory.

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