Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Supplemental Material for "Relativistic and electron-correlation effects in static dipole polarizabilities for group 12 elements"

YingXing Cheng*

Institute of Applied Analysis and Numerical Simulation, University of Stuttgart, Pfaffenwaldring 57, 70569, Stuttgart, Germany

E-mail: yingxing.cheng@mathematik.uni-stuttgart.de

Contents

Static dipole polarizabilities (α) and hyperpolarizabilities (γ) are determined using the finite-field method 1. The energy of an atom placed in an external electric field of magnitude F_z along the z axis is expressed as

$$E(F_z) \approx E_0 - \frac{1}{2}\alpha F_z^2 - \frac{1}{24}\gamma F_z^4, \tag{S1}$$

where E_0 represents the energy of the atom in the absence of the field. By applying least-squares fitting to energies computed at various field strengths, values for α and γ were extracted. If γ yielded unphysical results, only α was retained using the simplified expression

$$E(F_z) \approx E_0 - \frac{1}{2}\alpha F_z^2. \tag{S2}$$

Each calculation is identified using a string representation of the computational setup, such as "2C-SR-CC@s-aug-ANO-RCC@(core 3)[vir 279]". These identifiers consist of components separated by the delimiter "@":

1. The first part specifies the computational method (e.g., NR-CC, SR-CC, or DC-CC), with the prefix "1C" or "2C" indicating the use of one- or two-component relativistic Hamiltonians, respectively.

2. The second part denotes the basis set.

3. The third part describes the correlation level, providing details on the number of active electrons and virtual orbitals as "(core N)[vir M]". Here, "N" is the total number of valence and outer-core electrons, and "M" specifies the virtual orbitals included. The coupled-cluster module 2 supports a variety of correlated methods, including DHF, MP2, CCSD, and CCSD(T), all adhering to this identifier format.

Additional details can be found in the main text.

The percentage error δ_m of a property $X = \alpha$ or γ is computed as

$$\delta_m = \frac{X_m - X_{\mathrm{CCSD(T)}}}{X_{\mathrm{CCSD(T)}}} \times 100\%, \tag{S3}$$

where m refers to the method employed, such as DHF, MP2, or CCSD. For $X = \gamma$, γ_{CCSD} is used as the reference in Eq. (S3) instead of $\gamma_{\mathrm{CCSD(T)}}$.

S1 Hyperpolarizabilities Derived from Fitting Eq. (S1)

Table S1 presents the γ values for group 12 elements obtained by fitting Eq. (S1). For clarity, all negative γ values have been excluded from the table.

Table S1: Dipole hyperpolarizabilities (γ, in 10^4 a.u.) for group 12 elements. Uncertainties due to the numerical fitting procedure ($\Delta P_{\mathrm{fitting}}$) are shown as error bars for values exceeding 500 a.u.

Z	Atom	γ (10^4 a.u.)	δ (%)	Method	Comments
30	Zn	54.16 ± 0.01	33.67	DHF	1C-NR-CC@s-aug-dyall.cv4z@(core 20)[vir 276]
		37.22	-8.14	MP2	
		42.05	3.77	CCSD	
		40.52	−−	CCSD(T)	
		50.83	35.48	DHF	1C-SR-CC@dyall.cv4z@(core 20)[vir 204]
		33.76	-10.01	MP2	
		39.00	3.96	CCSD	
		37.52	−−	CCSD(T)	
		50.93 ± 0.01	33.91	DHF	1C-SR-CC@s-aug-dyall.cv4z@(core 20)[vir 276]
		34.65	-8.90	MP2	
		39.48	3.79	CCSD	
		38.04	−−	CCSD(T)	
		50.95 ± 0.01	33.94	DHF	1C-SR-CC@d-aug-dyall.cv4z@(core 20)[vir 348]
		34.71	-8.77	MP2	
		39.49	3.80	CCSD	
		38.04	−−	CCSD(T)	
		50.92 ± 0.01	33.61	DHF	2C-DC-CC@s-aug-ANO-RCC@(core 20)[vir 314]
		34.72	-8.88	MP2	
		39.60	3.91	CCSD	

(continued)

Table S1. continued.

Z	Atom	γ (10^4 a.u.)	δ	Method	Comments
		38.11	−−	CCSD(T)	
		50.89 ± 0.01	33.92	DHF	2C-DC-CC@s-aug-dyall.cv4z@(core 20)[vir 276]
		34.62	-8.91	MP2	
		39.44	3.79	CCSD	
		38.00	−−	CCSD(T)	
48	Cd	76.25 ± 0.02	40.26	DHF	1C-NR-CC@s-aug-dyall.cv4z@(core 30)[vir 344]
		44.86	-17.48	MP2	
		57.26 ± 0.01	5.32	CCSD	
		54.36 ± 0.01	−−	CCSD(T)	
		63.82 ± 0.01	39.91	DHF	1C-SR-CC@dyall.cv4z@(core 30)[vir 272]
		36.70	-19.55	MP2	
		47.97	5.16	CCSD	
		45.62	−−	CCSD(T)	
		63.95 ± 0.01	39.50	DHF	1C-SR-CC@s-aug-dyall.cv4z@(core 30)[vir 344]
		37.22	-18.79	MP2	
		48.17 ± 0.01	5.09	CCSD	
		45.84 ± 0.01	−−	CCSD(T)	
		63.95 ± 0.01	39.49	DHF	1C-SR-CC@d-aug-dyall.cv4z@(core 30)[vir 416]
		37.24	-18.77	MP2	
		48.18 ± 0.01	5.09	CCSD	
		45.84 ± 0.01	−−	CCSD(T)	
		63.75 ± 0.01	39.70	DHF	2C-DC-CC@s-aug-ANO-RCC@(core 30)[vir 366]
		38.11	-16.48	MP2	
		47.68 ± 0.01	4.48	CCSD	
		45.63 ± 0.01	−−	CCSD(T)	
		63.83 ± 0.01	39.51	DHF	2C-DC-CC@s-aug-dyall.cv4z@(core 30)[vir 344]
		37.16	-18.79	MP2	
		48.09 ± 0.01	5.10	CCSD	
		45.75 ± 0.01	−−	CCSD(T)	
80	Hg	81.65 ± 0.02	43.27	DHF	1C-NR-CC@s-aug-dyall.cv4z@(core 44)[vir 362]
		44.25 ± 0.01	-22.36	MP2	
		60.33 ± 0.01	5.86	CCSD	
		56.99 ± 0.01	−−	CCSD(T)	
		45.12	32.32	DHF	1C-SR-CC@dyall.cv4z@(core 44)[vir 290]
		27.21	-20.19	MP2	
		35.34	3.64	CCSD	
		34.10	−−	CCSD(T)	
		45.20 ± 0.01	31.99	DHF	1C-SR-CC@s-aug-dyall.cv4z@(core 44)[vir 362]

(continued)

Table S1. continued.

Z	Atom	γ (10^4 a.u.)	δ	Method	Comments
		27.47	-19.79	MP2	
		35.47	3.57	CCSD	
		34.25	−−	CCSD(T)	
		45.20 ± 0.01	32.25	DHF	1C-SR-CC@d-aug-dyall.cv4z@(core 44)[vir 460]
		27.35	-19.97	MP2	
		35.42	3.62	CCSD	
		34.18	−−	CCSD(T)	
		44.88 ± 0.01	30.52	DHF	2C-DC-CC@s-aug-ANO-RCC@(core 44)[vir 282]
		28.05	-18.43	MP2	
		35.52	3.30	CCSD	
		34.39	−−	CCSD(T)	
		44.94	31.90	DHF	2C-DC-CC@s-aug-dyall.cv4z@(core 44)[vir 362]
		27.38	-19.66	MP2	
		35.29	3.56	CCSD	
		34.07	−−	CCSD(T)	
112	Cn	109.43 ± 0.04	47.38	DHF	1C-NR-CC@s-aug-dyall.cv4z@(core 44)[vir 434]
		52.78 ± 0.01	-28.92	MP2	
		79.78 ± 0.02	7.45	CCSD	
		74.25 ± 0.02	−−	CCSD(T)	
		30.25	8.87	DHF	1C-SR-CC@dyall.cv4z@(core 44)[vir 336]
		25.83	-7.06	MP2	
		27.81	0.10	CCSD	
		27.79	−−	CCSD(T)	
		30.26	9.09	DHF	1C-SR-CC@s-aug-dyall.cv4z@(core 44)[vir 434]
		25.79	-7.02	MP2	
		27.77	0.12	CCSD	
		27.73	−−	CCSD(T)	
		30.26	9.12	DHF	1C-SR-CC@d-aug-dyall.cv4z@(core 44)[vir 532]
		25.75	-7.11	MP2	
		27.76	0.13	CCSD	
		27.73	−−	CCSD(T)	
		30.52	8.71	DHF	4C-DC-CC@dyall.cv4z@(core 12)[vir 264]
		26.93	-4.08	MP2	
		27.98	-0.33	CCSD	
		28.07	−−	CCSD(T)	
		30.47	9.11	DHF	2C-DC-CC@s-aug-dyall.cv4z@(core 48)[vir 434]
		25.97	-7.01	MP2	
		27.95	0.08	CCSD	

(continued)

Table S1. continued.

Z	Atom	γ (10^4 a.u.)	δ	Method	Comments
		27.93	−−	CCSD(T)	

A summary of the highlighted γ values for group 12 elements is provided in Table S2, based on data from Table S1.

Table S2: Static hyperpolarizabilities (in 10^4 a.u.) with nonrelativistic, scalar-relativistic, full Dirac-Coulomb relativistic effects of group 12 elements.

$\hat{H}$	Method	Zn	Cd	Hg	Cn
NR	DHF	4.54 ± 0.33	11.58 ± 0.14	11.21 ± 0.17	21.62 ± 0.23
	CCSD	2.63 ± 0.33	6.64 ± 0.14	6.79 ± 0.17	12.86 ± 0.23
	CCSD(T)	2.40 ± 0.43	5.90 ± 0.14	6.06 ± 0.28	11.32 ± 0.34
SR	DHF	4.48	8.07	3.16	0.57
	CCSD	2.61	4.44	1.99	−0.49
	CCSD(T)	2.39 ± 0.19	3.88 ± 0.06	1.81 ± 0.22	-0.71 ± 0.54
DC	DHF	4.49	8.01	3.04	0.51
	CCSD	2.59	4.41	2.00	−0.43
	CCSD(T)	2.38 ± 0.19	3.86	1.81 ± 0.21	-0.65 ± 1.18

S2 Polarizabilities Derived from Fitting Eq. (S2)

Table S3 lists the α values for group 12 elements, obtained using Eq. (S2). The most accurate results for NR-CC, SR-CC, and DC-CC calculations are highlighted.

Table S3: Dipole polarizabilities (α, in a.u.) for group 12 elements. Error bars reflect the uncertainties arising from the numerical fitting procedure ($\Delta P_{\text{fitting}}$) for cases where the errors exceed 0.005 a.u.

Z	Atom	α (a.u.)	δ (%)	Method	Comments
30	Zn	54.07 ± 0.01	33.60	DHF	1C-NR-CC@s-aug-dyall.cv4z@(core 20)[vir 276]
		37.18 ± 0.01	-8.13	MP2	
		41.99 ± 0.01	3.76	CCSD	
		40.47 ± 0.01	−−	CCSD(T)	
		50.79	35.46	DHF	1C-SR-CC@dyall.cv4z@(core 20)[vir 204]

(continued)

Table S3. continued.

Z	Atom	α (a.u.)	δ	Method	Comments
		33.74	-10.02	MP2	
		38.98	3.96	CCSD	
		37.49	−−	CCSD(T)	
		50.84	33.84	DHF	1C-SR-CC@s-aug-dyall.cv4z@(core 20)[vir 276]
		34.61	-8.89	MP2	
		39.43	3.79	CCSD	
		37.99	−−	CCSD(T)	
		50.84	33.84	DHF	1C-SR-CC@d-aug-dyall.cv4z@(core 20)[vir 348]
		34.67	-8.73	MP2	
		39.43	3.79	CCSD	
		37.99	−−	CCSD(T)	
		50.81	33.51	DHF	2C-DC-CC@s-aug-ANO-RCC@(core 20)[vir 314]
		34.69	-8.85	MP2	
		39.54	3.90	CCSD	
		38.06	−−	CCSD(T)	
		50.80	33.85	DHF	2C-DC-CC@s-aug-dyall.cv4z@(core 20)[vir 276]
		34.57	-8.90	MP2	
		39.39	3.79	CCSD	
		37.95	−−	CCSD(T)	
48	Cd	76.02	40.14	DHF	1C-NR-CC@s-aug-dyall.cv4z@(core 30)[vir 344]
		44.80	-17.41	MP2	
		57.12	5.31	CCSD	
		54.24	−−	CCSD(T)	
		63.76	39.90	DHF	1C-SR-CC@dyall.cv4z@(core 30)[vir 272]
		36.65	-19.58	MP2	
		47.92	5.16	CCSD	
		45.57	−−	CCSD(T)	
		63.78	39.38	DHF	1C-SR-CC@s-aug-dyall.cv4z@(core 30)[vir 344]
		37.19	-18.72	MP2	
		48.08	5.08	CCSD	
		45.76	−−	CCSD(T)	
		63.78	39.37	DHF	1C-SR-CC@d-aug-dyall.cv4z@(core 30)[vir 416]
		37.21	-18.69	MP2	
		48.09	5.08	CCSD	
		45.76	−−	CCSD(T)	
		63.59	39.59	DHF	2C-DC-CC@s-aug-ANO-RCC@(core 30)[vir 366]
		38.08	-16.40	MP2	
		47.59	4.47	CCSD	

(continued)

Table S3. continued.

Z	Atom	α (a.u.)	δ	Method	Comments
		45.55	−−	CCSD(T)	
		63.67	39.39	DHF	2C-DC-CC@s-aug-dyall.cv4z@(core 30)[vir 344]
		37.12	-18.72	MP2	
		48.00	5.08	CCSD	
		45.68	−−	CCSD(T)	
80	Hg	81.43	43.18	DHF	1C-NR-CC@s-aug-dyall.cv4z@(core 44)[vir 362]
		44.17	-22.33	MP2	
		60.19 ± 0.01	5.84	CCSD	
		56.87 ± 0.01	−−	CCSD(T)	
		45.08	32.30	DHF	1C-SR-CC@dyall.cv4z@(core 44)[vir 290]
		27.20	-20.18	MP2	
		35.32	3.64	CCSD	
		34.08	−−	CCSD(T)	
		45.14	31.94	DHF	1C-SR-CC@s-aug-dyall.cv4z@(core 44)[vir 362]
		27.46	-19.72	MP2	
		35.43	3.56	CCSD	
		34.21	−−	CCSD(T)	
		45.14	32.21	DHF	1C-SR-CC@d-aug-dyall.cv4z@(core 44)[vir 460]
		27.35	-19.88	MP2	
		35.37 ± 0.01	3.61	CCSD	
		34.14 ± 0.01	−−	CCSD(T)	
		44.82	30.50	DHF	2C-DC-CC@s-aug-ANO-RCC@(core 44)[vir 282]
		28.04	-18.34	MP2	
		35.47 ± 0.01	3.29	CCSD	
		34.34 ± 0.01	−−	CCSD(T)	
		44.88	31.86	DHF	2C-DC-CC@s-aug-dyall.cv4z@(core 44)[vir 362]
		27.37	-19.59	MP2	
		35.25	3.56	CCSD	
		34.04	−−	CCSD(T)	
112	Cn	108.99	47.24	DHF	1C-NR-CC@s-aug-dyall.cv4z@(core 44)[vir 434]
		52.65	-28.87	MP2	
		79.52 ± 0.01	7.43	CCSD	
		74.02 ± 0.01	−−	CCSD(T)	
		30.24	8.78	DHF	1C-SR-CC@dyall.cv4z@(core 44)[vir 336]
		25.82	-7.13	MP2	
		27.83 ± 0.01	0.09	CCSD	
		27.80 ± 0.01	−−	CCSD(T)	
		30.24	8.99	DHF	1C-SR-CC@s-aug-dyall.cv4z@(core 44)[vir 434]

(continued)

Table S3. continued.

Z	Atom	α (a.u.)	δ	Method	Comments
		25.78	-7.09	MP2	
		27.78 ± 0.01	0.11	CCSD	
		27.75 ± 0.01	$--$	CCSD(T)	
		30.25	9.04	DHF	1C-SR-CC@d-aug-dyall.cv4z@(core 44)[vir 532]
		25.75	-7.17	MP2	
		27.77 ± 0.01	0.12	CCSD	
		27.74 ± 0.01	$--$	CCSD(T)	
		30.51	8.71	DHF	4C-DC-CC@dyall.cv4z@(core 12)[vir 264]
		26.92	-4.07	MP2	
		27.97	-0.33	CCSD	
		28.07	$--$	CCSD(T)	
		30.46	9.01	DHF	2C-DC-CC@s-aug-dyall.cv4z@(core 48)[vir 434]
		25.97	-7.08	MP2	
		27.96 ± 0.02	0.06	CCSD	
		27.94 ± 0.02	$--$	CCSD(T)	

Table S4 summarizes the most accurate α results for group 12 elements, as derived from Table S3.

Table S4: Static dipole polarizabilities (in a.u.) are presented with nonrelativistic, scalar-relativistic, and fully relativistic Dirac-Coulomb contributions for the elements of group 12, compared with the values reported in Ref. 3.The uncertainty due to the numerical fitting procedure ($\Delta P_{\text{fitting}}$) is accounted for as the error bar. Only uncertainties where $\Delta P_{\text{fitting}} > 0.005$ a.u. are shown.

$\hat{H}$	Method	Zn	Cd	Hg	Cn
NR	DHF	54.16 ± 0.01	76.25 ± 0.02	81.65 ± 0.02	109.43 ± 0.04
	CCSD	42.05 ± 0.01	57.26 ± 0.02	60.33 ± 0.02	79.78 ± 0.04
	CCSD(T)	40.52	54.36 ± 0.01	56.99 ± 0.01	74.25 ± 0.02
SR	DHF	50.93 ± 0.01	63.95 ± 0.01	45.20 ± 0.01	30.26
	CCSD	39.48 ± 0.01	48.17 ± 0.01	35.47 ± 0.01	27.77
	CCSD(T)	38.04	45.84 ± 0.01	34.25	27.73
DC	DHF	50.89 ± 0.01	63.83 ± 0.01	44.94	30.47
	CCSD	39.44 ± 0.01	48.09 ± 0.01	35.29	27.95
	CCSD(T)	38.00	45.75 ± 0.01	34.07	27.93
Ref. 3	$--$	38.67 ± 0.3	46 ± 2	33.91 ± 0.34	28 ± 2

References

(1) Das, A. K.; Thakkar, A. J. Static Response Properties of Second-Period Atoms: Coupled Cluster Calculations. *J. Phys. B At. Mol. Opt. Phys.* **1998**, *31*, 2215.

(2) DIRAC18. `https://doi.org/10.5281/zenodo.2253986`, Accessed on Jun 7, 2021.

(3) Schwerdtfeger, P.; Nagle, J. K. 2018 Table of Static Dipole Polarizabilities of the Neutral Elements in the Periodic Table. *Mol. Phys.* **2019**, *117*, 1200–1225.