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Enhanced Linear and Nonlinear Polarizabilities for the Li_4 Cluster. How Satisfactory Is the Agreement between Theory and Experiment for the Static Dipole Polarizability?

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Highly accurate ab initio calculations with specially designed basis sets are reported for Li_4. The molecule emerges as a particularly soft system, with a very anisotropic dipole polarizability and a very large second dipole hyperpolarizability. An extensive investigation of basis set and electron correlation effects leads to values of $\bar{\alpha} = 387.01$ and $\Delta\alpha = 354.60\ e^2a_0^2E_h^{-1}$. The mean hyperpolarizability is $\bar{\gamma} = 2394 \times 10^3\ e^4a_0^4E_h^{-3}$. The computational aspects of the present effort are discussed in view of the extension of quantumchemical studies to large lithium clusters. Our values for the mean dipole polarizability are systematically higher than the recently reported experimental static value ($326.6\ e^2a_0^2E_h^{-1}$) of this important quantity [Benichou et al. *Phys. Rev. A* **1999**, *59*, R1].

The structure and properties of lithium clusters have emerged as an intensively active research field in recent years. Experimental[1−3] and theoretical[4−10] studies have explored various chemical and physical aspects of these systems. A very recent experimental study[3] of the static dipole polarizability of lithium clusters paved the way to systematic explorations of the electric properties of such systems. Li_4 is one of the more extensively studied lithium clusters. The dipole polarizability of Li_4 has been studied at the Hartree−Fock level of theory by various groups.[4,9,10] All of these efforts, relying on ab initio calculations with small basis sets, have produced mean dipole polarizabilities systematically higher than the recent experimental results included in an important recent paper by Benichou et al.[3,11] In this Letter we rely on post-Hartree−Fock methods of high predictive capability and carefully designed basis sets to give a definite shape to this apparent discrepancy between theory and experiment. Electric dipole polarizability is a fundamental molecular property, of particular importance in the interpretation of a wide spectrum of phenomena,[12] but also because of its link to significant molecular characteristics such as softness/hardness.[13] We note also the interest in intermolecular interactions involving alkali clusters.[14] Our study extends to the hyperpolarizability of Li_4. To our knowledge, no previous results have been reported for the nonlinear polarizability of metal clusters. The timeliness of our theoretical endeavor is well evidenced by the active interest in the nonlinear optics of small and medium sized molecules.[15,16]

The dipole polarizability ($\alpha_{\alpha\beta}$) of a molecule of D_{2h} symmetry, such as Li_4, has three independent components, and the second dipole hyperpolarizability ($\gamma_{\alpha\beta\gamma\delta}$) six.[17] The two characteristic Li−Li distances defining the molecular geometry are 2.69 and 3.16 Å.[4] The *z* axis is defined by the shortest diagonal of the Li_4 rhombus, with xz as the molecular plane. In addition to the Cartesian components of these tensors, we calculate the mean and the anisotropy of $\alpha_{\alpha\beta}$ and the mean of $\gamma_{\alpha\beta\gamma\delta}$, defined as

$$\bar{\alpha} = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3 \tag{1}$$
$$\Delta\alpha = 2^{-1/2}[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{xx})^2 + (\alpha_{zz} - \alpha_{xx})^2]^{1/2}$$
$$\bar{\gamma} = (\gamma_{zzzz} + \gamma_{yyyy} + \gamma_{zzzz} + 2\gamma_{xxyy} + 2\gamma_{yyzz} + 2\gamma_{zzxx})/5$$

Our approach to the calculation of these molecular properties is a finite field one, relying on fourth-order many-body perturbation theory (MP) and coupled cluster (CC) calculations of the energy of the molecule perturbed by weak, static electric fields.[18] The various orders of MP used in this work are defined as

$$\mathrm{MP2} = \mathrm{SCF} + \mathrm{D2} \tag{2}$$
$$\mathrm{MP3} = \mathrm{MP2} + \mathrm{D3}$$
$$\mathrm{DQ\text{-}MP4} = \mathrm{MP3} + \mathrm{D4} + \mathrm{QR4} = \mathrm{MP3} + \mathrm{DQ4}$$
$$\mathrm{SDQ\text{-}MP4} = \mathrm{DQ\text{-}MP4} + \mathrm{S4}$$
$$\mathrm{MP4} = \mathrm{SDQ\text{-}MP4} + \mathrm{T4}$$
$$\equiv \mathrm{SCF} + \mathrm{D2} + \mathrm{D3} + \mathrm{S4} + \mathrm{D4} + \mathrm{T4} + \mathrm{Q4} + \mathrm{R4}$$

where the fourth-order terms are contributions of single, double, triple, and quadruple excitations from the reference zeroth-order SCF wave function. R4 is the renormalization term.

The highest level of theory used in this paper is CCSD(T), single and double excitation coupled cluster theory (CCSD) with an estimate of connected triple excitations obtained via a perturbational treatment, and we write simply CCSD(T) = CCSD + T. We have designed a series of basis sets for our calculations. Very little is known about basis set effects on the calculated electric properties of lithium clusters. We avoid possible systematic errors due to the structure of particular types of basis sets by carefully augmenting variously sized substrates of Gaussian-type functions (GTF). Thus, we aim at obtaining self-consistent field (SCF) values quite close to the Hartree−Fock limit and accurate estimates of the electron correlation correction (ECC) for all properties. This computational philosophy has been presented in detail in previous work.[18] The

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TABLE 1: Basis Set[a] and Electron Correlation Effects[b] for the Electric Properties of Li_4 ($\alpha_{\alpha\beta}$ and $10^{-3} \times \gamma_{A\beta\gamma\delta}$) at Various Levels of Theory (All Values in Atomic Units[c])

property	method	B0	B1	C0	C1	P0	P1	P2
α_{xx}	SCF	592.44	592.25	592.08	592.00	591.68	591.57	576.09
	MP4	640.56	627.99	639.76	627.90	638.19	625.89	612.86
	CCSD	635.47	623.06	634.46	622.75	632.64	620.37	609.77
	CCSD(T)	643.89	631.82	642.85	631.55	641.11	629.34	617.46
α_{yy}	SCF	249.93	252.99	249.04	251.97	248.45	251.47	249.71
	MP4	238.12	243.43	236.89	243.14	234.60	242.37	239.13
	CCSD	237.41	241.60	236.10	241.31	233.59	240.63	237.61
	CCSD(T)	237.81	242.64	236.51	242.34	233.99	241.67	238.45
α_{zz}	SCF	305.13	307.02	305.66	306.82	305.02	306.28	304.07
	MP4	283.19	293.11	283.07	292.72	283.56	291.75	288.17
	CCSD	282.93	292.66	282.68	292.18	282.96	291.19	287.44
	CCSD(T)	284.55	294.84	284.32	294.36	284.72	293.38	289.66
$\bar{\alpha}$	SCF	382.50	383.75	382.26	383.60	381.72	383.11	376.63
	MP4	387.29	388.18	386.57	387.92	385.45	386.67	380.05
	CCSD	385.27	385.77	384.41	385.41	383.06	384.06	378.27
	CCSD(T)	388.75	389.77	387.89	389.42	386.61	388.13	381.86
$\Delta\alpha$	SCF	318.52	316.36	318.52	316.20	318.73	316.28	302.88
	MP4	381.91	362.28	381.88	362.52	381.48	361.37	351.78
	CCSD	377.37	358.67	377.23	358.71	376.80	357.15	349.92
	CCSD(T)	384.84	365.89	384.67	365.98	384.28	364.58	356.17
γ_{xxxx}	SCF	8338	8689	8373	8713	8289	8792	8588
	MP4	4698	4783	4648	4774	4632	4822	4783
	CCSD	3611	3796	3570	3772	3587	3852	3721
	CCSD(T)	4070	4362	4031	4343	4040	4415	4337
γ_{yyyy}	SCF	522	1324	537	1320	729	1311	1298
	MP4	638	1283	657	1282	882	1264	1232
	CCSD	634	1195	650	1195	861	1185	1150
	CCSD(T)	642	1240	658	1241	875	1229	1194
γ_{zzzz}	SCF	976	1568	1027	1556	1176	1570	1488
	MP4	1286	1632	1334	1627	1465	1603	1542
	CCSD	1263	1537	1306	1536	1442	1527	1456
	CCSD(T)	1288	1604	1332	1603	1477	1594	1518
γ_{xxyy}	SCF	1078	1548	1092	1535	1094	1509	1431
	MP4	489	1043	497	1028	508	993	913
	CCSD	489	954	496	936	503	908	834
	CCSD(T)	518	1028	525	1012	533	980	897
γ_{yyzz}	SCF	87	420	91	426	41	436	408
	MP4	159	449	164	449	128	451	424
	CCSD	147	413	153	418	116	422	393
	CCSD(T)	146	428	151	434	113	438	408
γ_{zzxx}	SCF	1257	1715	1280	1708	1307	1723	1621
	MP4	613	1030	622	1019	632	1023	923
	CCSD	771	1032	784	1030	783	1037	933
	CCSD(T)	827	1124	841	1123	840	1131	1015
$\bar{\gamma}$	SCF	2936	3789	2973	3785	3016	3802	3659
	MP4	1829	2549	1841	2535	1903	2524	2415
	CCSD	1664	2265	1678	2254	1739	2259	2129
	CCSD(T)	1796	2473	1812	2465	1873	2467	2337

[a] B0 ≡ [6s2p], B1 ≡ [6s3p1d], C0 ≡ [6s2p], C1 ≡ [6s3p1d], P0 ≡ [15s2p], P1 ≡ [15s3p1d], P2 ≡ [15s7p1d]. Five-membered d-GTF were used in all cases. [b] All electrons correlated. [c] Polarizability α, 1 $e^2a_0^2E_h^{-1} = 1.648778 \times 10^{-41}$ $C^2\ m^2\ J^{-1}$; second dipole hyperpolarizability γ, 1 $e^4a_0^4E_h^{-3} = 6.235378 \times 10^{-65}$ $C^4\ m^4\ J^{-3}$.

basis sets used in this work are B0 ≡ [6s2p] and B1 ≡ [6s3p1d],[19] C0 ≡ [6s2p] and C1 ≡ [6s3p1d],[20] P0 ≡ [15s2p], P1 ≡ [15s3p1d], P2 ≡ [15s7p1d][21] (see Table 1), and A ≡ [7s5p2d].[22] A full analysis of electron correlation effects obtained with basis A is given in Table 2. All electrons were correlated in the post-Hartree–Fock calculations. All calculations were performed with GAUSSIAN 92[23] and 94.[23]

Our SCF values for $\alpha_{\alpha\beta}/e^2a_0^2E_h^{-1}$ converge smoothly to the presumably more accurate P2 and A results. P2 gives $\bar{\alpha} = 376.63$ and $\Delta\alpha = 302.88$, both values quite close to the 379.52 and 306.87 obtained with A. The difference is of the order of 1%. We expect these values to be of near-Hartree–Fock quality. Electron correlation has a non uniform effect on the Cartesian components of $\alpha_{\alpha\beta}$, as the α_{xx} component increases while α_{yy} and α_{zz} decrease. The CCSD(T) values, with the total electron correlation correction ECC = CCSD(T) − SCF for all properties in parentheses, obtained with basis set A are $\alpha_{xx} = 621.41$ (39.73), $\alpha_{yy} = 243.25$ (−8.01), $\alpha_{zz} = 296.36$ (−9.26), and $\bar{\alpha} = 387.01$ (7.49). Thus the SCF values change by 6.8, −3.2, −3.0, and 2.0%, respectively. The dipole polarizability is significantly more anisotropic at the CCSD(T) level as the value of 354.60 represents an increase of 15.6% of the SCF result of 306.87.

The second dipole hyperpolarizability of Li_4 is quite large. The addition of d-GTF on the B0, C0, and P0 basis sets modifies drastically the calculated values of $\gamma_{\alpha\beta\gamma\delta}$. Again, the SCF values converge smoothly to stable results. With P3 we obtain for $10^{-3} \times \gamma_{\alpha\beta\gamma\delta}/e^4a_0^4E_h^{-3}$ $\gamma_{xxxx} = 8588$, $\gamma_{yyyy} = 1298$, $\gamma_{zzzz} = 1488$, $\gamma_{xxyy} = 1431$, $\gamma_{yyzz} = 408$, $\gamma_{zzxx} = 1621$, and $\bar{\gamma} = 3659$. Basis set A yields 8634, 1286, 1531, 1484, 462, 1268, and 3720, respectively. Observe that the $\bar{\gamma}$ value obtained with A is a mere 1.7% above the P3 value, a very satisfactory agreement for a high order molecular property. The electron correlation effects obtained with all basis sets are extremely large and basis set dependent. What is more, while for the dipole polarizability all

TABLE 2: Analysis of Electron Correlation Effects for the Polarizability and Hyperpolarizability of Li_4 (Basis Set A ≡ [7s5p2d]; All Values in Atomic Units)

method	α_{xx}	α_{yy}	α_{zz}	$\bar{\alpha}$	$\Delta\alpha$	γ_{xxxx}	γ_{yyyy}	γ_{zzzz}	γ_{xxyy}	γ_{yyzz}	γ_{zzxx}	$\bar{\gamma}$
SCF	581.68	251.26	305.62	379.52	306.87	8634	1286	1531	1484	462	1628	3720
D2	14.52	−4.18	−4.32	2.01		−916	54	115	−155	34	−238	−293
D3	10.44	−2.76	−5.08	0.86		−1828	−102	−78	−266	−32	−329	−653
S4	0.62	−0.34	0.36	0.21		76	2	−3	10	−0	10	23
D4	12.02	−0.69	−2.73	2.87		−1036	−58	−27	−150	−15	−198	−369
T4	3.19	0.86	1.43	1.82		352	48	64	48	19	52	141
Q4	−5.30	−0.52	−0.70	−2.17		−146	−39	−54	−30	−16	−24	−76
ΔCCSD	31.16	−9.04	−11.63	3.50		−4576	−191	−76	−629	−45	−743	−1535
T	8.57	1.02	2.37	3.99		613	44	65	63	18	81	209
MP2	596.20	247.08	301.30	381.53	325.42	7719	1340	1646	1328	495	1390	3427
MP3	606.64	244.32	296.22	382.39	339.36	5890	1238	1568	1062	463	1062	2774
DQ-MP4	613.37	243.12	292.79	383.09	348.08	4708	1141	1487	882	432	840	2329
SDQ-MP4	613.99	242.77	293.15	383.30	348.76	4784	1143	1485	892	432	850	2352
MP4	617.18	243.63	294.58	385.13	350.86	5137	1190	1549	941	451	902	2493
CCSD	612.84	242.23	294.00	383.02	347.63	4058	1095	1455	855	416	886	2184
CCSD(T)	621.41	243.25	296.36	387.01	354.60	4672	1139	1521	918	434	966	2394

TABLE 3: Comparison of Theoretical and Experimental Results for the Dipole Polarizability of Li_4

method	α_{xx}	α_{yy}	α_{zz}	$\bar{\alpha}$	$\Delta\alpha$
Theory					
SCF[a]	549.11	219.86	287.48	352.15	301.19
SCF[b]	639.74	242.94	302.33	395.00	370.69
SCF[c]	623.55	218.65	280.73	374.31	377.70
SCF[d]				333	379
SCF[e]	581.68	251.26	305.62	379.52	306.87
CCSD(T)[e]	621.41	243.25	296.36	387.01	354.60
Experiment					
				326.6[f]	

[a] 6-31G* basis set calculation by Dahlseid et al.[5] [b] Sadlej and Urban basis set calculation by Rayane et al.[10] [c] 6-31G basis set calculation by Rayane et al.[10] [d] 6-311G** basis set calculation by Fuentealba and Reyes.[9] [e] Present work, basis set [7s5p2d]. [f] Static value, Benichou et al.[3]

MP methods produce reasonable results, methods of very high predictive capability are needed to obtain reliable values for the hyperpolarizability. The MP series displays fast convergence for the γ_{zzzz} but not for the γ_{xxxx} or the γ_{yyyy} components. The mean hyperpolarizability calculated with P3 and A is 2337 and 2394 $10^3 \times e^4a_0^4E_h^{-3}$, a very close agreement.

In Table 3 we have collected the available dipole polarizability data for Li_4. All previous theoretical efforts relied on SCF calculations with small basis sets. The mean $\bar{\alpha}$ is consistently higher than the static value of 326.6 $e^2a_0^2E_h^{-1}$ reported by Benichou et al.[3] in their pioneering paper on the dipole polarizability of lithium clusters.

In conclusion, we have calculated accurate values for the dipole polarizability and hyperpolarizability of Li_4. To our knowledge, this is the first study of $\alpha_{\alpha\beta}$ for this molecule that includes the effects of electron correlation. The values of $\gamma_{\alpha\beta\gamma\delta}$ appear for the first time in the literature. Our results suggest that there is a discrepancy between theory and experiment for the dipole polarizability. The experimental measurement of the anisotropy $\Delta\alpha$ would be an important step toward the resolution of this situation. Comparing the present values of $\bar{\alpha}$ and $\bar{\gamma}$ to that of four lithium atoms (the atomic properties are α = 164.111 $e^2a_0^2E_h^{-1}$ and $\gamma = 2.9 \times 10^3$ $e^4a_0^4E_h^{-3}$, see King[25]) we observe impressive magnitudes for $\bar{\alpha}(Li_4) - 4\bar{\alpha}(Li)$ and $\bar{\gamma}(Li_4) - \bar{\gamma}(Li)$. Work is in progress in our laboratory for the development of efficient computational strategies for the extension of theoretical studies of electric properties to large and very large lithium clusters. The determination of accurate polarizabilities and hyperpolarizabilities for large lithium clusters appears as a formidable task.

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