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## Enhanced Linear and Nonlinear Polarizabilities for the Li<sub>4</sub> 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<sub>4</sub>. 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  $\bar{\gamma}=2394\times10^3~e^4a_0{}^4E_h{}^{-3}$ . 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<sup>1-3</sup> and theoretical<sup>4-10</sup> studies have explored various chemical and physical aspects of these systems. A very recent experimental study<sup>3</sup> of the static dipole polarizability of lithium clusters paved the way to systematic explorations of the electric properties of such systems. Li<sub>4</sub> is one of the more extensively studied lithium clusters. The dipole polarizability of Li<sub>4</sub> 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.<sup>3,11</sup> 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.<sup>13</sup> We note also the interest in intermolecular interactions involving alkali clusters. <sup>14</sup> Our study extends to the hyperpolarizability of Li<sub>4</sub>. 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<sub>4</sub>, has three independent components, and the second dipole hyperpolarizability  $(\gamma_{\alpha\beta\gamma\delta})$  six.<sup>17</sup> The two characteristic Li–Li distances defining the molecular geometry are 2.69 and 3.16 Å.<sup>4</sup> The z axis is defined by the shortest diagonal of the Li<sub>4</sub> 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

$$\bar{\alpha} = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$$
 (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. <sup>18</sup> The various orders of MP used in this work are defined as

$$MP2 = SCF + D2$$

$$MP3 = MP2 + D3$$

$$DQ-MP4 = MP3 + D4 + QR4 = MP3 + DQ4$$

$$SDQ-MP4 = DQ-MP4 + S4$$

$$MP4 = SDQ-MP4 + T4$$

$$\equiv SCF + D2 + D3 + S4 + D4 + T4 + Q4 + R4$$

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. <sup>18</sup> The

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TABLE 1: Basis Set<sup>a</sup> and Electron Correlation Effects<sup>b</sup> for the Electric Properties of Li<sub>4</sub> ( $\alpha_{\alpha\beta}$  and  $10^{-3} \times \gamma_{A\beta\gamma\delta}$ ) at Various Levels of Theory (All Values in Atomic Units<sup>c</sup>)

MP4	method	В0	B1	C0	C1	P0	P1	P2
MP4			592.25					576.09
CCSD(T)         643.89         631.82         642.85         631.55         641.11         629.34         6           α <sub>TY</sub> SCF         249.93         252.99         249.04         251.97         248.45         251.47         2           CCSD         237.41         243.63         236.89         243.14         233.59         240.63         2           CCSD(T)         237.81         242.64         236.51         242.34         233.59         241.67         2           CCSD(T)         237.81         242.64         236.51         242.34         233.99         241.67         2           CCSD(T)         238.19         293.11         283.07         29.272         283.56         291.75         2           CCSD(T)         284.55         294.84         284.32         294.36         284.72         293.38         22           CCSD(T)         284.55         294.84         284.32         294.36         284.72         293.38         22           QCSD(T)         387.29         385.75         382.26         383.60         381.11         33           ACS (T)         388.72         385.77         387.89         389.72         385.67         377.37			627.99	639.76	627.90	638.19	625.89	612.80
α <sub>TY</sub> SCF         249.93         252.99         249.04         251.97         248.45         251.47         2           CCSD         237.41         241.60         236.89         243.14         234.60         242.37         2           CCSD         237.81         241.60         236.10         241.31         233.59         240.63         2           CCSD         237.81         242.64         236.51         242.34         233.59         240.63         2           MP4         283.19         293.11         280.07         292.72         283.56         291.75         2           CCSD(T)         284.55         294.84         284.32         292.18         282.96         291.19         2           CCSD(T)         284.55         294.84         284.32         294.36         284.72         293.38         2           CCSD         385.27         385.77         387.93         387.92         385.45         386.61         381.13         3           CCSD(T)         388.75         389.77         387.889         389.42         386.61         388.13         3           Ac         SCF         318.52         316.36         318.52         316.20			623.06	634.46	622.75	632.64	620.37	609.7
MP4	CCSD(T)						629.34	617.4
MP4		249.93	252.99	249.04	251.97	248.45	251.47	249.7
CCSD(T)         237.81         242.64         236.51         242.34         233.99         241.67         22.8           MP4         283.19         293.11         283.07         292.72         283.56         291.19         22           CCSD         282.93         292.66         282.68         292.18         282.96         291.19         22           α         SCF         382.50         383.75         382.26         383.60         381.72         383.11         33           MP4         387.29         388.18         386.57         387.92         385.45         386.67         33           CCSD         385.27         385.77         387.89         389.42         386.61         381.13         33           CCSD(T)         388.75         389.77         387.89         389.42         386.61         381.81         386.57         381.81         386.57         385.41         383.06         381.06         38	MP4	238.12	243.43	236.89	243.14	234.60	242.37	239.13
CCSD(T)         237.81         242.64         236.51         242.34         233.99         241.67         22.8           MP4         283.19         293.11         283.07         292.72         283.56         291.19         22           CCSD         282.93         292.66         282.68         292.18         282.96         291.19         22           ā.         SCF         382.50         383.75         382.26         383.60         381.72         383.11         33           A         MP4         387.29         388.18         386.67         387.92         385.45         386.67         33           CCSD         385.27         385.77         387.89         389.42         386.61         381.13         33           CCSD(T)         388.75         389.77         387.89         389.42         386.61         381.81         386.67         33           Aα         SCF         318.52         316.36         318.52         316.20         318.73         316.28         33         386.73         385.41         383.44         361.37         33         387.15         33         387.15         33         387.15         33         387.15         33         387.15 <t< td=""><td>CCSD</td><td>237.41</td><td>241.60</td><td>236.10</td><td></td><td>233.59</td><td>240.63</td><td>237.6</td></t<>	CCSD	237.41	241.60	236.10		233.59	240.63	237.6
α <sub>CC</sub> SCF         305.13         307.02         305.66         306.82         305.02         306.28         33         93.11         283.07         292.72         2283.56         291.75         22           CCSD         282.93         292.66         282.68         292.18         282.96         291.19         22           ā         SCF         382.50         383.75         382.26         383.60         284.72         293.38         22           CCSD         385.27         385.18         386.57         387.92         385.45         386.67         33           CCSD         385.27         385.77         387.89         389.42         386.61         388.13         33           CCSD(T)         388.75         389.77         387.89         389.42         386.61         388.13         33           MP4         381.91         362.28         381.88         362.52         381.88         362.52         381.48         361.57         33           CCSD         377.37         358.67         377.23         358.71         376.80         357.15         33           MP4         469.8         4783         4648         4774         4632         4822 <t< td=""><td>CCSD(T)</td><td>237.81</td><td>242.64</td><td>236.51</td><td>242.34</td><td>233.99</td><td>241.67</td><td>238.4</td></t<>	CCSD(T)	237.81	242.64	236.51	242.34	233.99	241.67	238.4
MP4		305.13	307.02	305.66	306.82		306.28	304.0
CCSD         282,93         292,66         282,68         292,18         282,96         291,19         22           α         SCF         382,50         383,75         382,26         383,60         381,72         383,11         33           MP4         387,29         388,18         386,57         387,92         385,45         386,67         383,60         384,06         33           CCSD         385,27         385,77         387,89         389,42         386,61         388,13         33           CCSD(T)         388,75         387,89         389,42         386,61         388,13         33           MP4         381,91         362,28         381,88         362,52         381,48         361,37         3           CCSD         377,37         358,67         377,23         358,71         376,80         357,15         3           Versix         SCF         8338         8689         8373         8713         8289         8792         855           MP4         4698         4783         4648         4774         4632         4822         477         477         4674         4632         4822         477         477         3872         387<				283.07			291.75	288.1
CCSD(T)         284.55         294.84         284.32         294.36         284.72         293.88         22           MP4         387.29         383.75         382.26         383.92         385.45         383.11         3'           MP4         387.29         388.18         386.57         387.99         385.45         386.67         3'           CCSD(T)         388.75         389.77         384.41         385.41         383.06         384.06         3'           CCSD(T)         388.75         389.77         384.41         385.41         383.06         384.06         3'           AC         SCF         318.52         316.36         318.52         316.20         318.73         316.28         3'           CCSD(T)         384.84         365.89         381.88         362.52         381.48         361.37         3'           CCSD(T)         384.84         365.89         384.67         365.98         384.28         364.58         3'           Y.xxxx         SCF         8338         8689         8373         8713         8289         8792         855           MP4         4698         4783         4648         4774         4632         48	CCSD	282.93	292.66	282.68	292.18			287.4
α         SCF         382.50         383.75         382.26         383.60         381.72         383.11         3'           MP4         387.29         388.18         386.57         387.92         385.45         386.67         3'           CCSD         385.27         385.77         384.41         383.06         384.06         3'           CCSD(T)         388.75         389.77         387.89         389.42         386.61         388.13         3'           Δα         SCF         318.52         316.36         318.52         316.36         318.52         316.28         381.88         362.52         381.48         361.37         3'           CCSD         377.37         386.67         377.23         358.71         376.80         357.15         3           CCSD (T)         384.84         365.89         384.37         8713         8289         8792         85           MP4         4698         4783         4648         4774         4632         4822         477           CCSD (T)         4070         4362         4031         4343         4040         4415         43           γ.yyyy         SCF         522         1324         5			294.84	284.32	294.36	284.72	293.38	289.6
MP4		382.50		382.26	383.60	381.72	383.11	376.6
CCSD         385.27         385.77         384.41         385.41         383.06         384.06         3'           Δα         SCF         318.52         316.36         318.52         316.20         318.73         316.28         33           MP4         381.91         362.28         381.88         362.52         381.48         361.37         3'           CCSD         377.37         358.67         377.23         358.71         376.80         357.15         3'           CCSD(T)         384.84         365.89         384.67         365.98         384.28         364.58         3'           MP4         4698         4783         4648         4774         4632         4822         47'           CCSD         3611         3796         3570         3772         3587         3852         37'           Yyyyy         SCF         522         1324         537         1320         729         1311         122'           Yyyyy         SCF         522         1324         537         1320         729         1311         122'           Yyyyy         SCF         522         1324         537         1320         729         1311		387.29	388.18	386.57				380.0
CCSD(T)         388.75         389.77         387.89         389.42         386.61         388.13         33           MP4         381.91         362.28         381.88         362.52         381.48         361.37         33           CCSD         377.37         358.67         377.23         358.71         376.80         357.15         33           CCSD(T)         384.84         365.89         384.67         365.98         384.28         364.58         33           SCF         8338         8689         8373         8713         8289         8792         853           MP4         4698         4783         4648         4774         4632         4822         477           CCSD(T)         4070         4362         4031         4343         4040         4415         433           Yyyyy         SCF         522         1324         537         1320         729         1311         122           CCSD(T)         634         1195         650         1195         861         1185         121           Yzzzz         SCF         976         1568         1027         1556         1176         1570         144		385.27	385.77	384.41	385.41			378.2
Δα         SCF         318.52         316.36         318.52         316.20         318.73         316.28         33           MP4         381.91         362.28         381.88         362.52         381.48         361.37         33           CCSD         377.37         358.67         377.23         358.71         376.80         357.15         33           CCSD(T)         384.84         365.89         384.67         365.98         384.28         364.58         33           MP4         4698         4783         4648         4774         4632         4822         477           CCSD         3611         3796         3570         3772         3587         3852         377           CCSD(T)         4070         4362         4031         4343         4040         4415         433           MP4         638         1283         657         1282         882         1264         122           CCSD (T)         4070         4362         4031         4343         4040         4415         433           Vyyyy         SCF         522         1324         537         1320         729         1311         122	CCSD(T)	388.75	389.77	387.89	389.42	386.61	388.13	381.8
MP4								302.8
CCSD         377.37         358.67         377.23         358.71         376.80         357.15         3           CCSD(T)         384.84         365.89         384.67         365.98         384.28         364.58         33           SCF         8338         8689         8373         8713         8289         8792         855           MP4         4698         4783         4648         4774         4632         4822         473           CCSD(T)         4070         4362         4031         4343         4040         4415         433           Vyyyy         SCF         522         1324         537         1320         729         1311         122           MP4         638         1283         657         1282         882         1264         12.2           CCSD (T)         642         1240         658         1241         875         1229         119           Yexx         SCF         976         1568         1027         1556         1176         1570         144           MP4         1286         1632         1334         1627         1465         1603         154           CCSD(T)		381.91	362.28					351.7
CCSD(T)         384.84         365.89         384.67         365.98         384.28         364.58         33           γxxxx         SCF         8338         8689         8373         8713         8289         8792         85           MP4         4698         4783         4648         4774         4632         4822         477           CCSD         3611         3796         3570         3772         3587         3852         377           CCSD(T)         4070         4362         4031         4343         4040         4415         433           γуууу         SCF         522         1324         537         1320         729         1311         122           MP4         638         1283         657         1282         882         1264         122           CCSD         634         1195         650         1195         861         1185         11:           Yuzz         SCF         976         1568         1027         1556         1176         1570         144           MP4         1286         1632         1334         1627         1465         1603         15-           CCSD	CCSD	377.37	358.67	377.23	358.71	376.80	357.15	349.9
γ xxxx         SCF         8338         8689         8373         8713         8289         8792         853           MP4         4698         4783         4648         4774         4632         4822         473           CCSD         3611         3796         3570         3772         3587         3852         377           CCSD(T)         4070         4362         4031         4343         4040         4415         433           MP4         638         1283         657         1282         882         1264         122           CCSD         634         1195         650         1195         861         1185         111           CCSD(T)         642         1240         658         1241         875         1229         119           MP4         1286         1632         1334         1627         1465         1603         157           CCSD         1263         1537         1306         1536         1147         1594         15           Yxxxx         SCF         1078         1548         1092         1535         1094         1509         14           Yxxxx         SCF         1		384.84	365.89	384 67	365.98			356.1
MP4								8588
CCSD         3611         3796         3570         3772         3587         3852         377           CCSD(T)         4070         4362         4031         4343         4040         4415         43           SCF         522         1324         537         1320         729         1311         122           MP4         638         1283         657         1282         882         1264         122           CCSD         634         1195         650         1195         861         1185         11:           CCSD(T)         642         1240         658         1241         875         1229         119           Yzzzz         SCF         976         1568         1027         1556         1176         1570         144           MP4         1286         1632         1334         1627         1465         1603         155           CCSD         1263         1537         1306         1536         1442         1527         144           CCSD(T)         1288         1604         1332         1603         1477         1594         15           Yzzzz         SCF         1078         154				4648	4774	4632	4822	4783
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$				3570	3772			3721
γ <sub>уууу</sub> SCF         522         1324         537         1320         729         1311         129           MP4         638         1283         657         1282         882         1264         12:           CCSD         634         1195         650         1195         861         1185         11:           CCSD(T)         642         1240         658         1241         875         1229         119           MP4         1286         1632         1334         1627         1465         1603         15-7           CCSD 1263         1537         1306         1536         1442         1527         14           CCSD(T)         1288         1604         1332         1603         1477         1594         15           Yxxxxx         SCF         1078         1548         1092         1535         1094         1509         14           Yxxxx         SCF         1078         1548         1092         1535         1094         1509         14           MP4         489         1043         497         1028         508         993         99         608         508         993         99<					4343			4337
MP4 638 1283 657 1282 882 1264 122 CCSD 634 1195 650 1195 861 1185 111 CCSD(T) 642 1240 658 1241 875 1229 119  SCF 976 1568 1027 1556 1176 1570 144  MP4 1286 1632 1334 1627 1465 1603 155 CCSD 1263 1537 1306 1536 1442 1527 145 CCSD(T) 1288 1604 1332 1603 1477 1594 15  CCSD(T) 1288 1604 1332 1603 1477 1594 15  SCF 1078 1548 1092 1535 1094 1509 144  MP4 489 1043 497 1028 508 993 9  CCSD 489 954 496 936 503 908 88  CCSD(T) 518 1028 525 1012 533 980 88  CCSD(T) 518 1028 525 1012 533 980 88  CCSD(T) 518 1028 525 1012 533 980 88  CCSD(T) 49 164 449 128 451 44  MP4 159 449 164 449 128 451 44  CCSD 147 413 153 418 116 422 33  CCSD(T) 146 428 151 434 113 438 44  γεεκκ SCF 1257 1715 1280 1708 1307 1723 166  MP4 613 1030 622 1019 632 1023 96  CCSD(T) 827 1124 841 1123 840 1131 10  VECSD TYPE 12936 3789 2973 3785 3016 3802 366  MP4 1829 2549 1841 2535 1903 2524 224  CCSD MP4 1829 2549 1841 2535 1903 2524 225	SCF	522	1324	537	1320	729	1311	1298
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	MP4	638	1283		1282	882	1264	1232
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		634	1105		1105			1150
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		642	1240	658	1241	875	1229	1194
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	SCE	976	1568	1027	1556	1176	1570	1488
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		1286	1632	1334	1627	1465	1603	1542
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		1263	1537	1304	1536	1403	1527	1456
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			1604	1300	1602	1442	1504	1518
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	CC3D(1)				1525			
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		1076	1040	1092	1028	509	002	913
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		409	054	497	026	503		834
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		407 518	1028		1012	503		897
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	CCSD(1)	27	420	01	1012	333 41		408
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	MD4	150	440		440	120	450	424
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$								393
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		147	413	155			422	408
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$				131	1709			
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		612	1/13	622	1/00		1/23	923
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		013 771	1030	022 794	1019	052 782	1023	923
$\overline{\gamma}$ SCF 2936 3789 2973 3785 3016 3802 360 MP4 1829 2549 1841 2535 1903 2524 24 CCSD 1664 2265 1678 2254 1739 2259 215			1034	/ 0 <del>4</del> 9 / 1	1030			
MP4 1829 2549 1841 2535 1903 2524 24 CCSD 1664 2265 1678 2254 1739 2259 213			1124 2790	041 2072			1131	1015
CCSD 1664 2265 1678 2254 1739 2259 213	SCF MD4	2930 1920	3/89	29/3 1941	3/83 2525	3010	38UZ 2524	
CCSD 1004 2203 16/8 2254 1/39 2259 21:					2333 2354		2324	
CC(VD/T) = 1706 = 0.472 = 1010 = 0.465 = 1072 = 0.467 = 0.07			2200	10/8	2254	1/39	2239	2129
		SCF MP4 CCSD CCSD(T) SCF	SCF         592.44           MP4         640.56           CCSD         635.47           CCSD(T)         643.89           SCF         249.93           MP4         238.12           CCSD         237.41           CCSD(T)         237.81           SCF         305.13           MP4         283.19           CCSD         282.93           CCSD(T)         284.55           SCF         382.50           MP4         387.29           CCSD         385.27           CCSD(T)         388.75           SCF         318.52           MP4         381.91           CCSD         377.37           CCSD(T)         384.84           SCF         8338           MP4         4698           CCSD         3611           CCSD(T)         4070           SCF         522           MP4         638           CCSD         634           CCSD(T)         642           SCF         976           MP4         1286           CCSD         1263           CCSD(T)         1288<	SCF         592.44         592.25           MP4         640.56         627.99           CCSD         635.47         623.06           CCSD(T)         643.89         631.82           SCF         249.93         252.99           MP4         238.12         243.43           CCSD         237.41         241.60           CCSD(T)         237.81         242.64           SCF         305.13         307.02           MP4         283.19         293.11           CCSD         282.93         292.66           CCSD(T)         284.55         294.84           SCF         382.50         383.75           MP4         387.29         388.18           CCSD         385.27         385.77           CCSD(T)         388.75         389.77           SCF         318.52         316.36           MP4         381.91         362.28           CCSD(T)         384.84         365.89           SCF         8338         8689           MP4         4698         4783           CCSD(T)         4070         4362           SCF         522         1324	SCF         592.44         592.25         592.08           MP4         640.56         627.99         639.76           CCSD         635.47         623.06         634.46           CCSD(T)         643.89         631.82         642.85           SCF         249.93         252.99         249.04           MP4         238.12         243.43         236.89           CCSD         237.41         241.60         236.10           CCSD(T)         237.81         242.64         236.51           SCF         305.13         307.02         305.66           MP4         283.19         293.11         283.07           CCSD         282.93         292.66         282.68           CCSD(T)         284.55         294.84         284.32           SCF         382.50         383.75         382.26           MP4         387.29         388.18         386.57           CCSD         385.27         385.77         384.41           CCSD(T)         388.75         389.77         387.89           SCF         318.52         316.36         318.52           MP4         381.91         362.28         381.88	SCF         592.44         592.25         592.08         592.00           MP4         640.56         627.99         639.76         627.90           CCSD         635.47         623.06         634.46         622.75           CCSD(T)         643.89         631.82         642.85         631.55           SCF         249.93         252.99         249.04         251.97           MP4         238.12         243.43         236.89         243.14           CCSD         237.41         241.60         236.10         241.31           CCSD(T)         237.81         242.64         236.51         242.34           SCF         305.13         307.02         305.66         306.82           MP4         283.19         293.11         283.07         292.72           CCSD         282.93         292.66         282.68         292.18           CCSD(T)         284.55         294.84         284.32         294.36           SCF         382.50         383.75         382.26         383.60           MP4         387.29         388.18         386.57         387.92           CCSD         388.75         389.77         384.41         385.41 <td>SCF         592.44         592.25         592.08         592.00         591.68           MP4         640.56         627.99         639.76         627.90         638.19           CCSD         635.47         623.06         634.46         622.75         632.64           CCSD(T)         643.89         631.82         642.85         631.55         641.11           SCF         249.93         252.99         249.04         251.97         248.45           MP4         238.12         243.43         236.89         243.14         234.60           CCSD         237.41         241.60         236.10         241.31         233.59           CCSD(T)         237.81         242.64         236.51         242.34         233.99           SCF         305.13         307.02         305.66         306.82         305.02           MP4         283.19         293.11         283.07         292.72         283.56           CCSD         282.93         292.66         282.68         292.18         282.96           CCSD(T)         284.55         294.84         284.32         294.36         284.72           SCF         382.50         383.75         382.26</td> <td>SCF         592.44         592.25         592.08         592.00         591.68         591.57           MP4         640.56         627.99         639.76         627.90         638.19         625.89           CCSD         635.47         623.06         634.46         622.75         632.64         620.37           CCSD(T)         643.89         631.82         642.85         631.55         641.11         629.34           SCF         249.93         252.99         249.04         251.97         248.45         221.47           MP4         238.12         243.43         236.89         243.14         234.60         242.37           CCSD         237.41         241.60         236.10         241.31         233.59         240.63           CCSD         237.41         241.60         236.61         241.31         233.59         240.63           SCF         305.13         307.02         305.66         306.82         305.02         306.28           MP4         283.19         293.11         283.07         292.72         282.96         291.75           CCSD (T)         284.55         294.84         284.32         294.36         284.72         293.38</td>	SCF         592.44         592.25         592.08         592.00         591.68           MP4         640.56         627.99         639.76         627.90         638.19           CCSD         635.47         623.06         634.46         622.75         632.64           CCSD(T)         643.89         631.82         642.85         631.55         641.11           SCF         249.93         252.99         249.04         251.97         248.45           MP4         238.12         243.43         236.89         243.14         234.60           CCSD         237.41         241.60         236.10         241.31         233.59           CCSD(T)         237.81         242.64         236.51         242.34         233.99           SCF         305.13         307.02         305.66         306.82         305.02           MP4         283.19         293.11         283.07         292.72         283.56           CCSD         282.93         292.66         282.68         292.18         282.96           CCSD(T)         284.55         294.84         284.32         294.36         284.72           SCF         382.50         383.75         382.26	SCF         592.44         592.25         592.08         592.00         591.68         591.57           MP4         640.56         627.99         639.76         627.90         638.19         625.89           CCSD         635.47         623.06         634.46         622.75         632.64         620.37           CCSD(T)         643.89         631.82         642.85         631.55         641.11         629.34           SCF         249.93         252.99         249.04         251.97         248.45         221.47           MP4         238.12         243.43         236.89         243.14         234.60         242.37           CCSD         237.41         241.60         236.10         241.31         233.59         240.63           CCSD         237.41         241.60         236.61         241.31         233.59         240.63           SCF         305.13         307.02         305.66         306.82         305.02         306.28           MP4         283.19         293.11         283.07         292.72         282.96         291.75           CCSD (T)         284.55         294.84         284.32         294.36         284.72         293.38

 $^{a}B0 \equiv [6s2p], B1 \equiv [6s3p1d], C0 \equiv [6s2p], C1 \equiv [6s3p1d], P0 \equiv [15s2p], P1 \equiv [15s3p1d], P2 \equiv [15s7p1d]. Five-membered d-GTF were used in all cases. \\ ^{b}All electrons correlated. \\ ^{c}Polarizability \alpha, 1 \\ e^{2}a_{0}{}^{2}E_{h}{}^{-1} = 1.648778 \\ \times 10^{-41} \\ C^{2} \\ m^{2} \\ J^{-1}; second dipole hyperpolarizability \\ \gamma, 1 \\ e^{4}a_{0}{}^{4}E_{h}{}^{-3} = 6.235378 \\ \times 10^{-65} \\ C^{4} \\ m^{4} \\ J^{-3}.$ 

basis sets used in this work are  $B0 \equiv [6s2p]$  and  $B1 \equiv [6s3p1d],^{19}$   $C0 \equiv [6s2p]$  and  $C1 \equiv [6s3p1d],^{20}$   $P0 \equiv [15s2p],$   $P1 \equiv [15s3p1d],$   $P2 \equiv [15s7p1d]^{21}$  (see Table 1), and  $A \equiv [7s5p2d].^{22}$  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  $\alpha_{xx}$  component increases while  $\alpha_{yy}$  and  $\alpha_{zz}$  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<sub>4</sub> 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  $A \equiv [7s5p2d]$ ; All Values in Atomic Units)

method	$\alpha_{xx}$	$\alpha_{yy}$	$\alpha_{zz}$	$\bar{\alpha}$	$\Delta \alpha$	$\gamma_{xxxx}$	$\gamma_{yyyy}$	$\gamma_{zzzz}$	$\gamma_{xxyy}$	$\gamma_{yyzz}$	$\gamma_{zzxx}$	$\overline{\gamma}$
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
$\Delta$ CCSD	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<sub>4</sub>

method	$\alpha_{xx}$	$\alpha_{yy}$	$\alpha_{zz}$	$\bar{\alpha}$	Δα
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					
_				$326.6^{f}$	

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

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  $\gamma_{zzzz}$  but not for the  $\gamma_{xxxx}$  or the  $\gamma_{yyyy}$  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<sub>4</sub>. 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.<sup>3</sup> 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 Li4. 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  $\gamma_{\alpha\beta\nu\delta}$ 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  $\alpha$  = 164.111  $e^2a_0{}^2E_h{}^{-1}$  and  $\gamma=2.9\times 10^3~e^4a_0{}^4E_h{}^{-3}$ , see King<sup>25</sup>) we observe impressive magnitudes for  $\bar{\alpha}(Li_4) - 4\bar{\alpha}(Li)$  and  $\bar{\gamma}(\text{Li}_4) - \bar{\gamma}(\text{Li})$ . 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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## References and Notes

- (1) Broyer, M.; Chavaleyre, J.; Dugourd, Ph.; Wolf, J. P.; Wöste, L. *Phys. Rev. A* **1990**, 42, 6954.
- (2) Blanc, J.; Bonacic-Koutecky, V.; Broyer, M.; Chevaleyre, J.; Dugourd, Ph.; Koutecky, J.; Scheuch, C.; Wolf, J. P.; Wöste, L. *J. Chem. Phys.* **1992**, *96*, 1793.
- (3) Benichou, E.; Antoine, R.; Rayane, D.; Vezin, B.; Dalby, F. W.; Dugourd, Ph.; Broyer, M.; Ristori, C.; Chandezon, F.; Huber, B. A.; Rocco, J. C.; Blundell, S. A.; Guet, C. *Phys. Rev. A* **1999**, *59*, R1.
- (4) Bustani, I.; Pewestorf, W.; Fantucci, P.; Bonacic-Koutecky, V.; Koutecky, J. *Phys. Rev. B* **1987**, *35*, 9437.
- (5) Dahlseid, T. A.; Kappes, M. A.; Pople, J. A.; Ratner, M. A. J. Chem. Phys. 1992, 96, 4924.
- (6) Gardet, G.; Rogemond, F.; Chermette, H. J. Chem. Phys. 1996, 105, 9933.
  - (7) Pacheco, J. M.; Martins, J. L. J. Chem. Phys. 1997, 106, 6039.
  - (8) Rousseau, R.; Marx, D. Phys. Rev. A 1997, 56, 617.
  - (9) Fuentealba, P.; Reyes, O. J. Phys. Chem. A 1999, 103, 1376.
- (10) Rayane, D.; Allouche, A. R.; Benichou, E.; Antoine, R.; Aubert-Frecon, M.; Dugourd, Ph.; Broyer, M. *European Phys. J. D*, in press.
- (11) A quite similar situation has recently emerged in the case of Na<sub>3</sub> where theoretical values predict a dipole polarizability substantially higher than the experimental value. See Lefebre, S.; Carrington, T. *Chem. Phys. Lett.* **1998**, 287, 307.
- (12) Bonin, K. D.; Kresin, V. V. Electric-dipole polarizabilities of atoms, molecules and clusters, World Scientific: London, 1997.
- (13) Simon-Manso, Y.; Fuentealba, P. J. Phys. Chem. A 1998, 102, 2029 and references therein.
- (14) Kresin, V. V.; Tikhonov, G.; Kasperovich, V.; Wong, K.; Brockhaus, P. J. Chem. Phys. 1998, 108, 6660.
  - (15) Shelton, D. P.; Rice, J. E. Chem. Rev. **1994**, 94, 3.
- (16) Kaatz, P.; Donley, E. A.; Shelton, D. P. J. Chem. Phys. 1998, 108, 849.
  - (17) Buckingham, A. D. Adv. Chem. Phys. 1967, 12, 107.
- (18) Maroulis, G. J. Chem. Phys. 1998, 108, 5432 and references therein on the theoretical techniques used in this work.
- (19) Poirier, R.; Kari, R.; Csizmadia, I. G. Handbook of Gaussian basis sets; Elsevier: Amsterdam, 1984; Table 3.23.1. The initial [4s] basis set is augmented to [6s] by diffuse s-GTF. On [6s] p-GTF are added, with tight (chosen to minimize the energy of the free molecule) and diffuse (chosen to maximize  $\bar{\alpha}$ ) exponents. The symmetry of the molecule is also taken into account, in that we have optimized separately the exponents on the two pairs of equivalent Li centers. B1 is obtained from B0  $\equiv$  [6s2p] by the addition of another p-GTF and one d-GTF with exponent equal to that of the most diffuse p-GTF in A0. The same procedure is followed with all basis sets.
  - (20) Substrate [4s] from Table 3.24.1 in ref 19.
- (21) Substrate (13s) from Partridge, H. Near Hartree—Fock quality Gaussian type orbital basis sets for the first- and third-row atoms; NASA technical memorandum 101044, Jan. 1989.
- (22) Schäfer, A.; Huber, C.; Ahlrichs, R. *J. Chem. Phys.* **1994**, *100*, 5829. The substrate is a basis set of TZV quality consisting of (11s) primitive GTF contracted to [5s]. The d-GTF have exponents equal to the two most diffuse p-GTF on the corresponding center.

(23) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; and Pople, J. A. *Gaussian 92 (Revision C)*; Carnegie-Mellon Quantum Chemistry Publishing Unit. 1992.

Mellon Quantum Chemistry Publishing Unit, 1992.
(24) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G.

A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94 (Revision E.1)*; Carnegie-Mellon Quantum Chemistry Publishing Unit, 1994. (25) King, F. W. *J. Mol. Struct.* 1997, 400, 7.