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Electric moments and polarizabilities for LiH ($X^1\Sigma^+$)

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Near Hartree-Fock values have been obtained for all independent components of electric multipole moment and polarizability tensors up to the fourth rank for the ground state of LiH. The dependence of the electric properties on internuclear separation is inferred from calculations at three different bond lengths. The calculation of the interaction potential LiH. .e^- leads to deductions about the relative importance of the polarizability tensors in intermolecular interaction studies. The independent components of the tensors at $r_e = 3.034286$ a_0 are, in atomic units, $\alpha_{zz} = 22.0884$, $\alpha_{xx} = 25.2846$, $\beta_{zzz} = 224.3$, $\beta_{zxx} = 203.1$, $\gamma_{zzzz} = 76848$, $\gamma_{xxxx} = 21472$, and $\gamma_{xxzz} = 19485$.

Key words: Lithium hydride — Electric moments — Polarizabilities

1. Introduction and theory

The first calculation of an electric hyperpolarizability for LiH was the Uncoupled Hartree-Fock (UCHF) one of the first dipole hyperpolarizability β which appeared in the pioneering work of O'Hare and Hurst [1]. However, the values of β reported did not lead to a reliable prediction for this molecular property as they were found to be strongly basis set dependent. Later studies did not go beyond the study of the first dipole hyperpolarizability nor extend to the calculation of quadrupole polarizabilities. The difficulties everpresent in electric polarizability calculations [2] are expected to be more tantalizing in the case of a "soft" molecule such as LiH.

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Recently, we reported near Hartree–Fock calculations of all electric multipole moment and polarizability tensors up to the fourth rank for FH [2], Ne [3], BH and CH^+ [4], Be, B^+ and C^{2+} [5], OH^-, F^-, NeH^+ and Mg^{2+} [6], Ar [7], Li^+, Li and Li^- [8] and N_2 [9]. The aim of that and the present work is not the calculation of an arbitrary set of properties but a complete theoretical description of the system in question [10], the pertinent description here being the totality of electric multiple moment and polarizability tensors, as they are defined in Buckingham's work [11], up to a sufficiently high rank.

In this work, as regards notation, conventions and the definition of polarizabilities, we follow the spirit if not the letter of Buckingham's work. Following Buckingham [11] and McLean and Yoshimine [12] we write the energy, dipole, quadrupole and octopole moments of a molecule in a general static electric field as

$$\begin{aligned} E = E^0 &- \mu^0_\alpha F - \tfrac{1}{3}\Theta^0_{\alpha\beta} F_{\alpha\beta} - \tfrac{1}{15}\Omega^0_{\alpha\beta\gamma} F_{\alpha\beta\gamma} - \tfrac{1}{105}\Phi^0_{\alpha\beta\gamma\delta} F_{\alpha\beta\gamma\delta} + \cdots \\ &- \tfrac{1}{2}\alpha_{\alpha\beta} F_\alpha F_\beta - \tfrac{1}{3} A_{\alpha,\beta\gamma} F_\alpha F_{\beta\gamma} - \tfrac{1}{6} C_{\alpha\beta,\gamma\delta} F_{\alpha\beta} F_{\gamma\delta} \\ &- \tfrac{1}{15} E_{\alpha,\beta\gamma\delta} F_\alpha F_{\beta\gamma\delta} + \cdots - \tfrac{1}{6}\beta_{\alpha\beta\gamma} F_\alpha F_\beta F_\gamma - \tfrac{1}{6} B_{\alpha\beta,\gamma\delta} F_\alpha F_\beta F_{\gamma\delta} + \cdots \\ &- \tfrac{1}{15}\gamma_{\alpha\beta\gamma\delta} F_\alpha F_\beta F_\gamma F_\delta + \cdots \end{aligned} \tag{1}$$

$$\begin{aligned} \mu_\alpha = \mu^0_\alpha &+ \alpha_{\alpha\beta} F_\beta + \tfrac{1}{3} A_{\alpha,\beta\gamma} F_{\beta\gamma} + \tfrac{1}{15} E_{\alpha,\beta\gamma\delta} F_{\beta\gamma\delta} + \tfrac{1}{2}\beta_{\alpha\beta\gamma} F_\beta F_\gamma \\ &+ \tfrac{1}{3} B_{\alpha\beta,\gamma\delta} F_\beta F_{\gamma\delta} + \tfrac{1}{6}\gamma_{\alpha\beta\gamma\delta} F_\beta F_\gamma F_\delta + \cdots \end{aligned} \tag{2}$$

$$\Theta_{\alpha\beta} = \Theta^0_{\alpha\beta} + A_{\gamma,\alpha\beta} F_\gamma + C_{\alpha\beta,\gamma\delta} F_{\gamma\delta} + \tfrac{1}{2} B_{\gamma\delta,\alpha\beta} F_\gamma F_\delta + \cdots \tag{3}$$

$$\Omega_{\alpha\beta\gamma} = \Omega^0_{\alpha\beta\gamma} + E_{\delta,\alpha\beta\gamma} F_\delta + \cdots \tag{4}$$

where E^0, μ^0, Θ^0, Ω^0 and Φ^0 are the energy and permanent multipole moments of the free molecule and α, β, γ, A, C, E and B the static molecular polarizabilities. F_α, $F_{\alpha\beta}$, etc. are the electric field, field gradient etc. at the origin. The greek subscripts denote cartesian tensor components; a repeated subscript denotes a summation over all three cartesian coordinates x, y and z.

For a polar diatomic molecule there is only one independent component for any multipole moment. With z as the molecular axis and the center of mass as the origin we specify the multipole moment tensors by their μ^0_z, Θ^0_{zz}, Ω^0_{zzz} and Φ^0_{zzzz} components; the dipole polarizability by α_{zz} and α_{xx}; the first dipole hyperpolarizability by β_{zzz} and β_{xxx}; the second dipole hyperpolarizability by γ_{zzzz}, γ_{xxxx} and γ_{xxzz}; the dipole-quadrupole polarizability by $A_{z,zz}$ and $A_{x,zx}$; the quadrupole-quadrupole by $C_{zz,zz}$, $C_{xz,xz}$ and $C_{xx,xx}$; the dipole-octopole by $E_{z,zzz}$ and $E_{x,xxx}$; and the dipole-dipole-quadrupole by $B_{zz,zz}$, $B_{xz,xz}$, $B_{xx,zz}$ and $B_{xx,xx}$. Let $E(Q, R, \theta)$, $\mu(Q, R, \theta)$, $\Theta(Q, R, \theta)$ and $\Omega(Q, R, \theta)$ be the energy, dipole, quadrupole and octopole moments of the molecule in the presence of a static electric field due to a charge Q placed at a distance R from the origin, with θ the angle defined by the position vector of the charge and the positive z axis. The relevant algebraic formulae for the computation of the polarizabilities from the induced multipole moments have been given elsewhere [2, 4], however, in this paper we adopt an alternative computational scheme for the β, γ and E tensors.

The independent components of E are obtained from the octopole moment in the presence of a very distant charge which produces a weak almost homogeneous field, $F_z = F_x < -1\times 10^{-4}\ \mathrm{e}^{-1}\mathrm{a}_0^{-1}\mathrm{E_h}$:

$$E_{z,zzz} = \frac{R^2}{Q\cos\frac{\pi}{4}}\left(\Omega^0_{zzz} - \Omega_{zzz}\left(Q, R, \frac{\pi}{4}\right)\right) \tag{5}$$

$$E_{x,xxx} = \frac{R^2}{Q\cos\frac{\pi}{4}}\left(-\Omega_{xxx}\left(Q, R, \frac{\pi}{4}\right)\right) \tag{6}$$

For β_{zzz} and β_{zxx}, from Eq. (2),

$$\begin{aligned} M_0(Q, R) &\equiv \mu_z(-Q, R, 0) + \mu_z(-Q, R, \pi) + \mu_z(Q, R, 0) + \mu_z(Q, R, \pi) \\ &= 2\beta_{zzz}\frac{Q^2}{R^4} + 4\mu^0_z \end{aligned} \tag{7}$$

$$M_{\pi/2}(Q, R) \equiv \mu_z\left(-Q, R, \frac{\pi}{2}\right) + \mu_z\left(Q, R, \frac{\pi}{2}\right) = \beta_{zxx}\frac{Q^2}{R^4} + 2\mu^0_z \tag{8}$$

so that

$$\beta_{zzz} = \frac{1}{4}\left.\frac{\mathrm{d}^2 M_0(Q, R)}{\mathrm{d}(Q/R^2)^2}\right|_0 \tag{9}$$

$$\beta_{zxx} = \frac{1}{2}\left.\frac{\mathrm{d}^2 M_{\pi/2}(Q, R)}{\mathrm{d}(Q/R^2)^2}\right|_0 \tag{10}$$

The magnitude of the second dipole hyperpolarizability is calculated from the perturbed energy. Let S_0, $S_{\pi/4}$, $S_{\pi/2}$ be:

$$S_0 \equiv S_0(Q, R) \equiv E(-Q, R, 0) + E(-Q, R, \pi) + E(Q, R, 0) + E(Q, R, \pi) \tag{11}$$

$$S_{\pi/4} \equiv E\left(-Q, R, \frac{\pi}{4}\right) + E\left(-Q, R, \frac{3\pi}{4}\right) + E\left(Q, R, \frac{\pi}{4}\right) + E\left(Q, R, \frac{3\pi}{4}\right) \tag{12}$$

$$S_{\pi/2} \equiv E\left(-Q, R, \frac{\pi}{2}\right) + E\left(Q, R, \frac{\pi}{2}\right) \tag{13}$$

Then, the components of the second dipole hyperpolarizability can be computed as follows

$$\gamma_{zzzz} = \frac{R^8}{2Q^4}(4S_0(Q, R) - S_0(2Q, R) - 12E^0) \tag{14}$$

$$\gamma_{xxxx} = \frac{R^8}{Q^4}(4S_{\pi/2}(Q, R) - S_{\pi/2}(2Q, R) - 6E^0) \tag{15}$$

$$\gamma_{zzzz} + \gamma_{xxxx} + 6\gamma_{xxzz} = \frac{2R^8}{Q^4}(4S_{\pi/4}(Q, R) - S_{\pi/4}(2Q, R) - 12E^0) \tag{16}$$

Our approach has three distinct advantages. First, all tensor components are obtained from a few calculations on the molecule-charge system which may be performed with any currently available SCF programme. Second, by using linear sums of energies and/or moments we take into account the symmetry of the applied static field in order to eliminate the contributions of the other tensors or those of immediately higher rank which might otherwise lead to systematic errors. Third, we obtain a complete theoretical molecular description, in the aforementioned sense, which is in fact a true reference description.

Unless otherwise specified, atomic units are used throughout this paper; 1 $a_0 \cong 0.52917706 \times 10^{-10}$ m; 1 a.u. of energy $\cong 4.3598 \times 10^{-18}$ J; of $\mu \cong 8.4784 \times 10^{-30}$ Cm; of $\Theta \cong 4.4866 \times 10^{-40}$ Cm^2; of $\Omega \cong 2.3742 \times 10^{-50}$ Cm^3; of $\Phi \cong 1.2564 \times 10^{-60}$ Cm^4; of $\alpha \cong 0.16488 \times 10^{-40}$ C^{2}m^{2}J^{-1}; of $\beta \cong 0.32063 \times 10^{-52}$ C^{3}m^{3}J^{-2}; of $\gamma \cong 0.62360 \times 10^{-64}$ C^{4}m^{4}J^{-3}; of $A \cong 8.7250 \times 10^{-52}$ C^{2}m^{3}J^{-1}; of C or $E \cong 4.6171 \times 10^{-62}$ C^{2}m^{4}J^{-1}; of $B \cong 1.6967 \times 10^{-63}$ C^{3}m^{4}J^{-2}.

2. Results and discussion

For our calculations we employed a $(14s10p4d/9s4p)$ primitive GTO basis set contracted to $[8s6p4d/6s4p]$. The basis set was built upon the $(13s8p2d/8s2p)$ $[7s4p2d/5s2p]$ one of Van Duijneveldt [13] and Lie and Clement [14]. The exponents of the additional s- and p-GTOs on Li and H are (in a_0^{-2} units): for Li: $s = 0.00985$, $p = 3.486$ and 0.0514, for H: $s = 0.029254$, $p = 7.84$ and 0.044643. The set of d-GTOs added to Li was carefully chosen in order to assure a near-Hartree-Fock quality for both the free and the perturbed molecule. To this end the correct "spread" of the d-GTOs, where $\alpha_d = 0.6K^{2n-3} n = 0, 1, 2, 3$, was achieved by optimizing the energy of the molecule in the presence of a distant charge. The optimal value for K was found to be $K \cong 1.6$ which is also the optimal value in the absence of any perturbation. It was also found that for $1.6 < K < 3$, α_{zz} remains practically stable at 21.8 $e^2a_0^2E_h^{-1}$ while α_{xx} varies only slightly, less than 0.5%. The presence of tight p- and d-GTOs on Li is essential to the accurate description of, at least, the dipole hyperpolarizabilities as in their absence the polarity of the perturbed molecule would be exaggerated. The same trend has been observed in other polar diatomics [2].

Our value for r_e is 3.034286 a_0 and can be compared with the 3.034 a_0 for the quasi-Hartree-Fock potential curve of Cade and Huo [15]. Our energy at r_e is -7.98727064 E_h, only 0.000044 E_h higher than theirs. The electric moments and polarizabilities calculated at three different internuclear separations, including the theoretical one, are given in Tables 1 and 2 along with the first derivative with respect to the displacement parameter $\xi = (r - r_e)/r_e$. Isotropic and anisotropic components for α, β, γ, C and B were also computed and are also given in Tables 1 and 2. Their definition may be found elsewhere [2, 4, 11]. Various experimental values for the internuclear separation are found in the literature, 3.01393 a_0 (1.59490 ± 0.00002 Å) [16] or 3.0154 a_0 (1.5957 Å) [17] but it seems that most theoretical calculations have been performed at 3.015 a_0. To allow a comparison with results reported for the latter we show in Table 3 values

Table 1. Electric moments and dipole polarizabilities for the ground state of LiH and their dependence on the bond length (all entries in atomic units)

P^a	$P(r)$ $r = 3.01347\ a_0$	 $r = 3.034286\ a_0$	 $r = 3.055102\ a_0$	$D_\xi P^b$
μ_z	−2.36159	−2.37171	−2.38190	−1.4803
Θ_{zz}	−3.37020	−3.40476	−3.43979	−5.0720
Ω_{zzz}	−6.36421	−6.48699	−6.61206	−18.0642
Φ_{zzzz}	−11.7622	−12.0833	−12.4133	−47.4545
α_{zz}	21.8091	22.0884	22.3703	40.901
α_{xx}	25.1330	25.2846	25.4285	21.537
$\bar{\alpha}$	24.0250	24.2192	24.4091	27.992
$\Delta\alpha$	−3.3239	−3.1962	−3.0582	19.364
β_{zzz}	215.3	224.3	232.1	1224
β_{zxx}	200.0	203.1	206.1	445
$\bar{\beta}$	369.2	378.3	386.6	1268
$\Delta\beta$	−384.7	−385.0	−386.2	−109
γ_{zzzz}	75 072	76 848	78 824	273.5×10^3
γ_{xxxx}	21 360	21 472	21 680	23.3×10^3
γ_{xxzz}	19 245	19 485	19 799	40.4×10^3
$\bar{\gamma}$	41 802	42 409	43 167	99.4×10^3
$\Delta_1\gamma$	197 511	203 111	209 149	888.6×10^3
$\Delta_2\gamma$	−19 038	−18 590	−18 290	54.5×10^3

[a] The center of mass is at the origin (0, 0, 0) and the H nucleus along the positive z axis. The quadrupole, octopole and hexadecapole moments are relative to the center of mass

[b] $D_\xi P = \left(\frac{dP}{d\xi}\right)_0$, $\xi = \frac{r - r_e}{r_e}$

for all moments and polarizabilities at 3.015 a_0, obtained from Tables 1 and 2 via an interpolation, along with other theoretical results. Only calculations that go beyond the mere determination of the dipole polarizability α are included in Table 3.

The numerical Hartree-Fock values for the dipole quadrupole, octopole and hexadecapole moments of Laaksonen et al. [18] are $-2.36181\ ea_0$, $3.37007\ ea_0^2$, $-6.32633\ ea_0^3$ and $-11.7578\ ea_0^4$ respectively, in excellent agreement with our $-2.3623\ ea_0$, $3.3727\ ea_0^2$, $-6.3732\ ea_0^3$ and $-11.7578\ ea_0^4$ at $3.015\ a_0$. Using the spectroscopic constants of Cade and Huo [15] we obtain the dependence of the electric moments on the vibration-rotation state v, J[19],

$$\mu_{v,J} = -2.37171 - 0.05006(v + \tfrac{1}{2}) - 0.00016(J^2 + J) \tag{17}$$

$$\Theta_{v,J} = -3.40476 - 0.19704(v + \tfrac{1}{2}) - 0.00056(J^2 + J) \tag{18}$$

$$\Omega_{v,J} = -6.48699 - 0.76940(v + \tfrac{1}{2}) - 0.00199(J^2 + J) \tag{19}$$

$$\Phi_{v,J} = -12.0833 - 2.33909(v + \tfrac{1}{2}) - 0.00522(J^2 + J) \tag{20}$$

The only experimental results available so far are the dipole moments $\mu_{0,1} = -2.314 \pm 0.001$, $\mu_{1,1} = -2.357 \pm 0.001$ and $\mu_{2,1} = -2.399 \pm 0.001\ ea_0$ of Wharton et

Table 2. Quadrupole polarizabilities for the ground state of LiH and their dependence on the bond length (all entries in atomic units)

P	$P(r)$ $r = 3.01347\ a_0$	 $r = 3.034286\ a_0$	 $r = 3.055102\ a_0$	$D_\xi P$[b]
$A_{z,zz}$	103.534	105.149	106.790	237.31
$A_{x,zx}$	66.640	67.287	67.941	94.82
$C_{zz,zz}$	203.49	207.12	210.81	533.5
$C_{xz,xz}$	110.28	111.86	113.46	231.8
$C_{xx,xx}$	61.13	61.96	62.80	121.7
$\bar{C}$	157.48	159.77	162.09	336.4
$\Delta_1 C$	969.56	987.35	1 005.49	2 618.6
$\Delta_2 C$	26.98	28.75	30.56	260.9
$B_{zz,zz}$	−1141	−1156	−1172	−2260
$B_{xz,xz}$	−1331	−1352	−1373	−3060
$B_{xx,zz}$	1544	1564	1583	2840
$B_{xx,xx}$	−1634	−1650	−1668	−2480
$\bar{B}$	−1528	−1547	−1567	−2840
$\Delta_1 B$	−1899	−1952	−1995	−7000
$\Delta_2 B$	21225	21612	21938	51970
$\Delta_3 B$	869	920	966	7 070
$E_{z,zzz}$	287.1	292.8	299.0	867
$E_{x,xxx}$	−134.1	−135.4	−137.9	−275

[a] The center of mass is at the origin (0, 0, 0) and the H nucleus along the positive z axis. All properties are relative to the center of mass

[b] $D_\xi P = \left(\frac{\mathrm{d}P}{\mathrm{d}\xi}\right)_0, \quad \xi = \frac{r - r_e}{r_e}$

al. [20]. Our respective values are in all cases less than 5% higher (in absolute values); rather good agreement for such a polar molecule. The dipole differences agree equally well; $\mu_{1,1} - \mu_{0,1} \simeq \mu_{2,1} - \mu_{1,1}$ are, from our calculations and [20], 0.501 and 0.042 ea_0, respectively.

The only experimental datum available for any polarizability of LiH is the anisotropy $\Delta\alpha = 1.7 \pm 4.0\ e^2 a_0^2 E_h^{-1}$ by Klemperer et al. [21], a result that does not seem to be in agreement with either SCF or MCSF predictions for this property [22]. The early work of O'Hare and Hurst [1] or Arrighini et al. [23] does not display any pattern of agreement with our results as regards the dipole polarizability and first dipole hyperpolarizability. The first CHF study of α and β reported by Lazzeretti et al. [24] relied on a minimal basis set and consequently a comparison with near Hartree-Fock results would be groundless. A later study by the same authors [25] is in reasonable agreement with our values except for the parallel component of β. Their value for α_{zz} is higher than ours or even that of Bishop and Lam [26], a fact which might be attributed to their perturbed energies being closer to the respective Hartree-Fock limit than that of the free molecule. Our results for α, A and C are in reasonable agreement with those of Bishop and Lam [26]. The disagreement observed in the case of β and B may be attributed to different criteria followed in the construction of the basis sets.

Table 3. Comparision of theoretical estimates of electric moments and polarizabilities for the ground state of LiH and at the experimental internuclear separation of 3.015 a_0 (all entries in atomic units)

	Method					
Property	SCF[a]	UCHF[b]	VPT[c]	CHF[d]	CHF[e]	SCF[f]
μ_z	−2.3623	−2.317	−2.361	−2.3567	−2.3620	−2.3611
Θ_{zz}	−3.3727					−3.3637
Ω_{zzz}	−6.3732					−6.3301
Φ_{zzzz}	−11.786					
α_{zz}	21.829	22.61	20.00	20.94	21.936	21.85
α_{xx}	25.144	34.28	23.63	22.77	25.299	25.29
$\bar{\alpha}$	24.039	30.39	22.42	22.16	24.178	24.14
$\Delta\alpha$	−3.315	−11.67	−3.63	−1.83	−3.363	−3.44
β_{zzz}	216	222.71	200.67	616.30	310.562	309
β_{zxx}	200	278.41	131.17	239.50	188.058	187
$\bar{\beta}$	370	467.71	277.81	657.18	412.007	410
$\Delta\beta$	−385	−612.52	−192.84	−102.20	−253.612	−252
γ_{zzzz}	75.2×10^3					
γ_{xxzz}	19.3×10^3					
γ_{xxxx}	21.4×10^3					
$\bar{\gamma}$	41.8×10^3					
$\Delta_1\gamma$	197.9×10^3					
$\Delta_2\gamma$	-19.0×10^3					
$A_{z,zz}$	103.65					97.35
$A_{x,zx}$	66.69					69.11
$C_{zz,zz}$	203.8					201.6
$C_{xz,xz}$	110.4					111.0
$C_{xx,xx}$	61.2					82.8
$\bar{C}$	157.6					175.2
$\Delta_1 C$	970.9					789.6
$\Delta_2 C$	27.1					42.0
$B_{zz,zz}$	−1140					−570
$B_{xz,xz}$	−1330					−1110
$B_{xx,zz}$	1550					1590
$B_{xx,xx}$	−1630					−2200
$\bar{B}$	−1530					−1630
$\Delta_1 B$	−1900					1240
$\Delta_2 B$	21 260					13 310
$\Delta_3 B$	870					−410
$E_{z,zzz}$	287.5					
$E_{x,xxx}$	−134.2					

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[a] Present investigation, basis set (14*s*6*p*4*d*/9*s*4*p*) [8*s*6*p*4*d*/6*s*4*p*]. The center of mass is at the origin (0, 0, 0) and the H nucleus along the positive *z* axis. All origin-dependent properties are relative to the center of mass

[b] Ref. [1]. Uncoupled Hartree-Fock results. Basis set from: Kahalus SL, Nesbet RK (1963) J Chem Phys 39:529

[c] Ref. [23]. Variational-perturbation results

[d] Ref. [24]. Coupled Hartree-Fock results. Basis set (14*s*12*p*4*d*/10*s*6*p*)[2*s*2*p*1*d*/1*s*1*p*]

[e] Ref. [25]. Basis set (14*s*7*p*3*d*/10*s*6*p*) [9*s*7*p*3*d*/8*s*6*p*]

[f] Ref. [26]. Basis set (13*s*5*p*2*d*/7*s*4*p*) [7*s*5*p*2*d*/4*s*4*p*]

Table 4. Contribution of the electric multipole moments and polarizabilities to the LiH..e$^-$ interaction energy, collinear[a] approach (all entries in E_h units)

	R/a_0				
	4	6	10	15	20
μ_z	0.1482	0.0659	0.0237	0.0105	0.0059
Θ_{zz}	0.0532	0.0157	0.0034	0.0010	0.0004
Ω_{zzz}	0.0253	0.0050	0.0006	0.0001	0.0000
Φ_{zzzz}	0.0118	0.0016	0.0001	0.0000	0.0000
α_{zz}	−0.0431	−0.0085	−0.0011	−0.0002	−0.0001
β_{zzz}	−0.0091	−0.0008	−0.0000	−0.0000	−0.0000
$A_{z,zz}$	−0.1027	−0.0135	−0.0011	−0.0001	−0.0000
$C_{zz,zz}$	−0.0758	−0.0067	−0.0003	−0.0000	−0.0000
$E_{z,zzz}$	−0.0715	−0.0063	−0.0003	−0.0000	−0.0000
$B_{zz,zz}$	0.0353	0.0021	0.0001	0.0000	0.0000
γ_{zzzz}	−0.0489	−0.0019	−0.0000	−0.0000	−0.0000
E_{el}^{b}	0.2385	0.0882	0.0278	0.0116	0.0063
E_{ind}^{c}	−0.3158	−0.0356	−0.0027	−0.0003	−0.0001
E_{int}^{d}	−0.0773	0.0526	0.0251	0.0113	0.0062

[a] The center of mass is at the origin (0, 0, 0) with H along the positive z axis and e$^-$ at (0, 0, R). The bond length for LiH is 3.034286 a_0

[b] The sum of the contributions of the multipole moments

[c] The sum of the contributions of the polarizabilities

[d] $E_{int} = E_{el} + E_{ind}$

Table 5. Contribution of the electric multipole moments and polarizabilities to the LiH..e$^-$ interaction energy, perpendicular[a] approach (all entries in E_h units)

	R/a_0					
	2	4	6	10	15	20
Θ_{zz}	−0.2128	−0.0266	−0.0079	−0.0017	−0.0005	−0.0002
Φ_{zzzz}	0.1416	0.0044	0.0006	0.0000	0.0000	0.0000
α_{xx}	−0.7901	−0.0494	−0.0098	−0.0013	−0.0003	−0.0001
$C_{xx,xx}$	−1.4522	−0.0227	−0.0020	−0.0001	−0.0000	−0.0000
$E_{x,xxx}$	2.1156	0.0331	0.0029	0.0001	0.0000	0.0000
$B_{xx,xx}$	6.4453	0.0504	0.0029	0.0001	0.0000	0.0000
γ_{xxxx}	−3.4948	−0.0137	−0.0005	−0.0000	−0.0000	−0.0000
E_{el}^{b}	−0.0712	−0.0222	−0.0073	−0.0017	−0.0005	−0.0002
E_{ind}^{c}	2·8228	−0.0023	−0.0065	−0.0012	−0.0003	−0.0001
E_{int}^{d}	2.7516	−0.0247	−0.0138	−0.0029	−0.0008	−0.0003

[a] The center of mass of LiH is at the origin (0, 0, 0) with H along the positive z axis and e$^-$ on the xz plane at distance R from the origin, (R, 0, 0). The bond length for LiH is 3.034286 a_0

[b] The sum of the contributions of the multipole moments

[c] The sum of the contributions of the polarizabilities

[d] $E_{int} = E_{el} + E_{ind}$

The basis set used in this work is closer to the Hartree-Fock limit in the case of both the free and the perturbed molecule, due to the optimization of the d-GTOs in the presence of an electric perturbation. The saturation of the basis set with respect to the higher polarizabilities is not always obvious [5, 8]. The values for γ and E reported here are, to our knowledge, the first to appear in the literature. The magnitude of the second dipole hyperpolarizability is very large, in fact the isotropic component $\bar{\gamma}$ is near to that for the isoelectronic Be [5]. It is fairly obvious that the neglect of this tensor in calculations of tensors of lower rank from either the energy or the induced dipole moment might lead to important systematic errors. For instance, a finite-field calculation of α from $\mu(F)$ would necessitate a polynomial of at least degree four in the field in order to eliminate contamination from γ.

All polarizabilities for LiH were found to be strongly dependent on the internuclear separation. Although our values for the respective derivatives do not compare, in a strict sense, with the results of other authors computed at different bond lengths, our r_e is close enough to that of Lazzeretti et al. [25]. The agreement between their values for the first derivatives and ours is in some cases, surprisingly enough, better than that observed between the respective tensor components. The fourth rank tensors are particularly sensitive to the molecular geometry along the symmetry axis and $|D_\xi C_{zz,zz}| < |D_\xi E_{z,zzz}| < |D_\xi B_{zz,zz}| < |D_\xi \gamma_{zzzz}|$. Strong rovibrational corrections are anticipated for these properties. The correction scheme followed in the case of the electric moments is not rigorous for second and higher order properties. This problem will be examined in detail elsewhere [27].

In order to assess the relative importance of all tensors involved in the present work in intermolecular interaction studies, we have computed their contribution to the interaction energy of LiH..e$^-$ for both the collinear and perpendicular approaches. The respective quantities are given in Tables 4 and 5. It is seen that while for $R > 15\ a_0$ the interaction is essentially electrostatic, the inductive part of the interaction energy is the more important one for $R < 5\ a_0$. However, one should note that the energy expansion in Eq. (1) becomes less valid as the perturbing e$^-$ gets closer to the molecule. A pertinent remark concerning the importance of higher order tensors in strong interactions is to be found in an early work by Buckingham [28]. He estimated that for the interaction $Al^{3+}\cdots OH_2$ the contribution of μ is less important than that of either α, β or γ and the ratio of the contributions of the latter three is 9.7:8:7. Last, we observe that the contribution of either $B_{zz,zz}$ or $B_{xx,xx}$ is positive. This tensor represents the electrophobic character in electron-atom or electron-molecule interactions [5, 7, 8] and is expected to be of some importance in the relevant scattering problems but should be also involved in other phenomena [28].

3. Conclusions

We have computed electric moments and polarizabilities for the ground state of LiH. Our results should be close to the Hartree-Fock limit. All electric properties depend strongly on the molecular geometry. Large rovibrational corrections are anticipated for the higher tensors. Fourth order properties make substantial contributions to the LiH...e$^-$ interaction energy. As the electron distribution of LiH appears to be quite "soft", electric moments and polarizabilities of still higher rank, fifth and sixth, should be included in further studies. This work did not examine the effect of electron correlation on the calculated electric properties.

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