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 \( r_e = 3.034286 \text{ a}_0 \) 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 \( \gamma_{xxxx} = 19485. \)

**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 \( \beta \) which appeared in the pioneering work of O'Hare and Hurst [1]. However, the values of \( \beta \) 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.
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

$$E = E^0 - \mu^0 \cdot F - \frac{1}{2} \Theta^0 \cdot F \cdot F - \frac{1}{2} \Omega^0 \cdot F \cdot \gamma \cdot F - \frac{1}{10} \Phi^0 \cdot F \cdot \gamma \cdot \gamma \cdot F + \cdots$$

$$= \frac{1}{2} \alpha_{x, \gamma} F_x F_{x, \gamma} + \frac{1}{2} \beta_{x, \gamma} F_x F_{x, \gamma} + \frac{1}{2} \gamma_{x, \gamma} F_x F_{x, \gamma} + \cdots$$

$$\mu_{x, \gamma} = \mu^0_{x, \gamma} + \alpha_{x, \gamma} F_x + \beta_{x, \gamma} F_{x, \gamma} + \cdots$$

$$\Theta_{x, \gamma} = \Theta^0_{x, \gamma} + A_{x, \gamma} F_x + C_{x, \gamma} F_{x, \gamma} + \cdots$$

$$\Omega_{x, \gamma} = \Omega^0_{x, \gamma} + E_{x, \gamma} F_{x, \gamma} + \cdots$$

where $E^0$, $\mu^0$, $\Theta^0$, $\Omega^0$ and $\Phi^0$ are the energy and permanent multipole moments of the free molecule and $\mu$, $\beta$, $\gamma$, $A$, $C$, $E$ and $B$ the static molecular polarizabilities. $F_x$, $F_{x, \gamma}$, 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 $\mu^0_{x, z}$, $\Theta^0_{x, z}$, $\Omega^0_{x, z}$ and $\Phi^0_{x, z}$ components; the dipole polarizability by $\alpha_{x, z}$ and $\alpha_{x, x}$; the first dipole hyperpolarizability by $\beta_{x, z}$ and $\beta_{x, x}$; the second dipole hyperpolarizability by $\gamma_{x, z}$ and $\gamma_{x, x}$; the dipole-quadrupole polarizability by $A_{x, z}$ and $A_{x, x}$; the quadrupole-quadrupole polarizability by $C_{x, z}$ and $C_{x, x}$, the dipole-octopole polarizability by $E_{x, z}$ and $E_{x, x}$; and the dipole-dipole-quadrupole by $B_{x, z z}$, $B_{x, z x}$, $B_{x, x z}$ and $B_{x, x x}$. 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 $\theta$ 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 $\beta$, $\gamma$ and $E$ tensors.