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Electric and Magnetic Properties of LiH Molecule According to Hartree-Fock Perturbation Theory

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Applying perturbative techniques to Hartree-Fock (HF) equations for the LiH molecule in the presence of external electric and magnetic fields, first order corrections to the molecular orbitals in the fields have been obtained, solving coupled HF equations. The calculated observables, i.e. electric dipole polarizability and hyperpolarizability, magnetic susceptibility, and magnetic shielding constants for the Li and H nuclei, are compared with other calculations and, when possible, with experimental data. The problem of gauge-invariance of the calculated results is examined in some detail for magnetic observables.

Auf die Hartree-Fock (HF)-Gleichung des LiH-Moleküls in Gegenwart von äußeren elektrischen und magnetischen Feldern wurden störungstheoretische Verfahren angewendet und es wurden Korrekturen 1. Ordnung zu den Molekülorbitalen durch die Lösung gekoppelter HF-Gleichungen berechnet. Die berechneten Observablen, nämlich die elektrische Dipol-Polarisierbarkeit und Hyperpolarisierbarkeit, magnetische Susceptibilität und magnetische Abschirmkonstanten für den Li- sowie den H-Kern, werden mit Werten aus anderen Berechnungen sowie, wenn möglich, mit experimentellen Daten verglichen. Das Problem der Invarianz der berechneten Ergebnisse gegenüber der Wahl des Bezugssystems wird für die magnetischen Observablen untersucht.

Par application de techniques de perturbation aux équations de Hartree-Fock pour la molécule LiH en présence de champs électrique et magnétique externes, on obtient les corrections du premier ordre pour les orbitales moléculaires dans ces champs comme solutions d'équations HF couplées. Les observables calculées (polarisabilité et hyperpolarisabilité dipolaires électriques, susceptibilité magnétique, constante d'écran magnétique pour les noyaux Li et H) sont comparées à d'autres valeurs théoriques et si possible aux valeurs expérimentales. Le problème de l'invariance de jauge des résultats calculés est étudié avec détail pour les observables magnétiques.

1. Introduction

Electric and magnetic properties of LiH molecule have been rather extensively evaluated by using more or less approximate wave functions and different methods [1–3], the results being in some cases fairly encouraging. Among the methods employed, Hartree-Fock (HF) perturbation theory, in its coupled form [4], seems to be a conceptually clear and valuable tool to approach the calculation of such subtle quantities as electric polarizabilities (and hyperpolarizabilities), magnetic susceptibilities, etc. Of course, this optimistic statement does not mean that actual problems are completely solved; on the contrary, one need only reflect about computational troubles arising from the large bases necessary in order to obtain meaningful results [1, 5, 6]. Moreover, it remains the hard problem of getting results for magnetic observables, which are as independent as possible of the gauge of the vector potential.

In a separate paper [7], hereafter referred to as (I), a Hartree-Fock-Roothaan (HFR) wave function for LiH molecule has been evaluated, which, from an energetic point of view, is a good approximation to the HF one [8] although its flexibility, when judged with respect to some one-electron operators (multipole moments, electric field gradient at both nuclei, etc.), is not completely satisfying. In the present paper the quality of such wave function is ulteriorly checked evaluating second (and third) order properties, some of which have been mentioned at the beginning of this section.

Sect. 2 is devoted to a review of the HF perturbation scheme (valid references about this subject can be found elsewhere; e.g., see [1, 4]), while Sect. 3 faces the problem of the gauge dependence of magnetic observables, and how to measure it; Sect. 4 reports the results obtained in our actual calculations.

2. Hartree-Fock Perturbation Theory

Let us suppose that our closed-shell system be subjected to the simultaneous action of an electric field $\mathcal{E}$ and a magnetic field $\boldsymbol{H}$, both of which are assumed to be homogeneous and steady. The best single Slater determinant which makes the energy stationary is built up with molecular orbitals (MO) $|\phi_j(\mathcal{E}, \boldsymbol{H})\rangle$, solutions of the HF equations

$$\begin{aligned} \hat{f}(\mathcal{E}, \boldsymbol{H})|\phi_j(\mathcal{E}, \boldsymbol{H})\rangle &= \varepsilon_j(\mathcal{E}, \boldsymbol{H})|\phi_j(\mathcal{E}, \boldsymbol{H})\rangle\,, \\ \langle\phi_j(\mathcal{E}, \boldsymbol{H})|\phi_k(\mathcal{E}, \boldsymbol{H})\rangle &= \delta_{jk}\,, \end{aligned} \tag{1}$$

$\hat{f}$ being the HF Hamiltonian operator. In the Eqs. (1) only the parametric dependence on the fields has been explicitly shown.

If atomic units are used throughout, for any acceptable ket $|u\rangle$:

$$\langle \boldsymbol{r}|\hat{f}|u\rangle = \langle \boldsymbol{r}|\hat{h}|u\rangle + \langle \boldsymbol{r}|\hat{g}|u\rangle\,,$$

$$\langle \boldsymbol{r}|\hat{h}|u\rangle = \left\{\frac{1}{2}\left[-i\nabla + \frac{1}{c}\left(\frac{1}{2}\boldsymbol{H}\times\boldsymbol{r} + \nabla\Lambda + \sum_{N}^{\text{nuclei}} \frac{\boldsymbol{\mu}_N\times(\boldsymbol{r}-\boldsymbol{R}_N)}{|\boldsymbol{r}-\boldsymbol{R}_N|^3}\right)\right]^2 + \mathcal{E}\cdot\boldsymbol{r} + U\right\}\langle \boldsymbol{r}|u\rangle\,,$$

$$\langle \boldsymbol{r}|\hat{g}|u\rangle = \sum_{k}^{\text{occ}}\left\{2\int \mathrm{d}^3\boldsymbol{r}'\,\frac{\langle\phi_k|\boldsymbol{r}'\rangle\langle\boldsymbol{r}'|\phi_k\rangle}{|\boldsymbol{r}-\boldsymbol{r}'|}\langle\boldsymbol{r}|u\rangle - \int \mathrm{d}^3\boldsymbol{r}'\,\frac{\langle\phi_k|\boldsymbol{r}'\rangle\langle\boldsymbol{r}'|u\rangle}{|\boldsymbol{r}-\boldsymbol{r}'|}\langle\boldsymbol{r}|\phi_k\rangle\right\}$$

where Λ is the arbitrary gauge apart from which any vector potential is defined, $\boldsymbol{\mu}_N$ is the magnetic dipole moment of the N-th nucleus located at $\boldsymbol{R}_N$, and U is the potential energy of one electron in the nuclear field.

If the HF energy of the closed-shell system,

$$E = 2\sum_{j}^{\text{occ}} \langle\phi_j|\hat{h} + \tfrac{1}{2}\hat{g}|\phi_j\rangle\,, \tag{2}$$

is expanded in terms of the electric and magnetic field components, it follows that (sum convention over repeated indices),

$$E = E^{(0)} - \mathscr{E}_\lambda \mu_\lambda - \tfrac{1}{2}\mathscr{E}_\lambda \mathscr{E}_{\lambda'} \alpha_{\lambda\lambda'} - \tfrac{1}{6}\mathscr{E}_\lambda \mathscr{E}_{\lambda'} \mathscr{E}_{\lambda''} \beta_{\lambda\lambda'\lambda''} + \cdots$$
$$- \tfrac{1}{2} H_\lambda H_{\lambda'} \chi_{\lambda\lambda'} + \cdots + \sum_N (\mu_N)_\lambda H_{\lambda'} \sigma^{(N)}_{\lambda\lambda''} + \cdots ,$$

where $\alpha_{\lambda\lambda'}$ and $\beta_{\lambda\lambda'\lambda''}$ are the electric dipole polarizability and the first dipole hyperpolarizability [9] tensors, respectively; analogously, $\chi_{\lambda\lambda'}$ and $\sigma^{(N)}_{\lambda\lambda'}$ are the magnetic susceptibility and the magnetic shielding tensors for the N-th nucleus, respectively.

As is well known, the knowledge of the first-order perturbed wave functions allows one to evaluate up to third order correction to $E^{(0)}$; thus, all observables listed above may be evaluated in terms of $|\phi_j^{(\mathscr{E}\lambda)}\rangle$ and $|\phi_j^{(H\lambda)}\rangle$ only, where $\lambda \equiv x, y, z$. The first-order perturbed equation for $|\phi_j^{(B\lambda)}\rangle$, $(B \equiv \mathscr{E}, H)$, is obtained directly from Eq. (1),

$$\hat{f}^{(0)} |\phi_j^{(B\lambda)}\rangle + \hat{f}^{(B\lambda)} |\phi_j^{(0)}\rangle = \varepsilon_j^{(0)} |\phi_j^{(B\lambda)}\rangle + \varepsilon_j^{(B\lambda)} |\phi_j^{(0)}\rangle , \tag{3}$$

the superscript zero denoting a unperturbed quantity.

Our unperturbed MO's $|\phi_j^{(0)}\rangle$ are solutions of the pseudo-eigenvalue problem:

$$\hat{f}^{(0)} |\phi_j^{(0)}\rangle = \varepsilon_j^{(0)} |\phi_j^{(0)}\rangle . \tag{4}$$

The first-order correction $|\phi_j^{(B\lambda)}\rangle$ may be expanded in terms of the unperturbed MO's $|\phi_v^{(0)}\rangle$, so that:

$$|\phi_j^{(B\lambda)}\rangle = \sum_v{}' |\phi_v^{(0)}\rangle \frac{\langle \phi_v^{(0)} | \hat{f}^{(B\lambda)} | \phi_j^{(0)} \rangle}{\varepsilon_j^{(0)} - \varepsilon_v^{(0)}} . \tag{5}$$

Eq. (5) is, of course, only an implicit definition of $|\phi_j^{(B\lambda)}\rangle$; as a matter of fact, the operator $\hat{f}^{(B\lambda)} = \hat{h}^{(B\lambda)} + \hat{g}^{(B\lambda)}$ contains a part $(g^{(B\lambda)})$, corresponding to the first-order change induced into the electronic HF field by the external perturbation, which needs the knowledge of $|\phi_k^{(B\lambda)}\rangle$, for all occupied MO's. In spite of this, Eq. (5) is a useful working formula which allows, for instance, an iterative solution for each $|\phi_j^{(B\lambda)}\rangle$ (one starts usually with $\hat{g}^{(B\lambda)} \equiv 0$).

The electronic polarizability tensor is easily found to be:

$$\alpha_{\lambda\lambda'} = -4 \sum_j^{\text{occ}} \sum_v^{\text{virt}} \frac{\langle \phi_j^{(0)} | \hat{f}^{(\mathscr{E}\lambda)} | \phi_v^{(0)} \rangle \langle \phi_v^{(0)} | r_{\lambda'} | \phi_j^{(0)} \rangle}{\varepsilon_j^{(0)} - \varepsilon_v^{(0)}} ;$$

analogously, the first dipole hyperpolarizability is given by:

$$\beta_{\lambda\lambda'\lambda''} = -4 \sum_j^{\text{occ}} \sum_{v,v'}^{\text{virt}} \left[\frac{\langle \phi_j^{(0)} | \hat{f}^{(\mathscr{E}\lambda)} | \phi_v^{(0)} \rangle \langle \phi_v^{(0)} | \hat{f}^{(\mathscr{E}\lambda')} - \sum_k^{\text{occ}} \varepsilon_{kj}^{(\mathscr{E}\lambda')} | \phi_{v'}^{(0)} \rangle \langle \phi_{v'}^{(0)} | \hat{f}^{(\mathscr{E}\lambda'')} | \phi_j^{(0)} \rangle}{(\varepsilon_j^{(0)} - \varepsilon_v^{(0)})(\varepsilon_j^{(0)} - \varepsilon_{v'}^{(0)})} \right.$$
$$\left. + \text{ cyclic permutations on } (\lambda\lambda'\lambda'') \right] .$$

The appearance of off-diagonal lagrangian multipliers may be noted in the preceding formula.

In order to be as specific as possible, we chose the arbitrary gauge Λ to have it correspond to a definite translation, by the amount $\boldsymbol{r}_0$, of the origin of the vector potential $\boldsymbol{A}(\boldsymbol{r}) = \frac{1}{2}\boldsymbol{H} \times \boldsymbol{r}$, i.e., we put $\Lambda = -\frac{1}{2}(\boldsymbol{H} \times \boldsymbol{r}_0) \cdot \boldsymbol{r}$.

Throughout this paper, only this particular gauge transformation has been investigated.

The magnetic susceptibility consists of the sum of a diamagnetic and a paramagnetic contribution,

$$\chi_{\lambda\lambda'} = \chi^d_{\lambda\lambda'}(\boldsymbol{r}_0) + \chi^p_{\lambda\lambda'}(\boldsymbol{r}_0)\,, \tag{6}$$

where,

$$\chi^d_{\lambda\lambda'}(\boldsymbol{r}_0) = -\frac{1}{4c^2} \sum_j^{\text{occ}} \langle \phi_j^{(0)} | (\boldsymbol{r} - \boldsymbol{r}_0)^2 \delta_{\lambda\lambda'} - (\boldsymbol{r} - \boldsymbol{r}_0)_\lambda (\boldsymbol{r} - \boldsymbol{r}_0)_{\lambda'} | \phi_j^{(0)} \rangle$$

$$\chi^p_{\lambda\lambda'}(\boldsymbol{r}_0) = -\frac{1}{c} \sum_j^{\text{occ}} \sum_v^{\text{virt}} \frac{1}{\varepsilon_j^{(0)} - \varepsilon_v^{(0)}} \{ \langle \phi_j^{(0)} | \mathscr{L}_\lambda(\boldsymbol{r}_0) | \phi_v^{(0)} \rangle \langle \phi_v^{(0)} | \hat{f}^{(H_{\lambda'})}(\boldsymbol{r}_0) | \phi_j^{(0)} \rangle + \text{c.c.} \}\,,$$

$\mathscr{L}_\beta(\boldsymbol{r}_0)$ being the λ-component of the angular momentum operator with respect to an origin at $\boldsymbol{r}_0$. It may be noted that $\chi^d_{\lambda\lambda'}$ and $\chi^p_{\lambda\lambda'}$ are separately dependent upon the choice of $\boldsymbol{r}_0$, only their sum, Eq. (6), being independent of it (see next section).

The nuclear magnetic shielding tensor for a given nucleus at $\boldsymbol{R}_N$ is, analogously, the sum of a diamagnetic and a paramagnetic contribution,

$$\sigma_{\lambda\lambda'} = \sigma^d_{\lambda\lambda'}(\boldsymbol{r}_0) + \sigma^p_{\lambda\lambda'}(\boldsymbol{r}_0)\,,$$

where

$$\sigma^d_{\lambda\lambda'}(\boldsymbol{r}_0) = \frac{1}{c^2} \sum_j^{\text{occ}} \langle \phi_j^{(0)} | \frac{(\boldsymbol{r} - \boldsymbol{R}_N) \cdot (\boldsymbol{r} - \boldsymbol{r}_0) \delta_{\lambda\lambda'}}{|\boldsymbol{r} - \boldsymbol{R}_N|^3} - \frac{(\boldsymbol{r} - \boldsymbol{r}_0)_\lambda (\boldsymbol{r} - \boldsymbol{R}_N)_{\lambda'}}{|\boldsymbol{r} - \boldsymbol{R}_N|^3} | \phi_j^{(0)} \rangle\,,$$

$$\sigma^p_{\lambda\lambda'}(\boldsymbol{r}_0) = \frac{2}{c} \sum_j^{\text{occ}} \sum_v^{\text{virt}} \frac{1}{\varepsilon_j^{(0)} - \varepsilon_v^{(0)}} \left\{ \langle \phi_v^{(0)} | \frac{\mathscr{L}_\lambda(\boldsymbol{R}_N)}{|\boldsymbol{r} - \boldsymbol{R}_N|^3} | \phi_v^{(0)} \rangle \langle \phi_v^{(0)} | \hat{f}^{(H_{\lambda'})}(\boldsymbol{r}_0) | \phi_j^{(0)} \rangle + \text{c.c.} \right\}.$$

Also in this case, the separate contributions to $\sigma_{\lambda\lambda'}$ depend upon the particular choice of $\boldsymbol{r}_0$.

3. Gauge Dependence of Magnetic Observables

As is well known, an effective independence of $\chi_{\lambda\lambda'}$ and $\sigma_{\lambda\lambda'}$ of the origin $\boldsymbol{r}_0$ of the vector potential, through which the external magnetic field $\boldsymbol{H}$ is introduced in the Hamiltonian, is to be expected to be verified to the extent that the MO's constitute a complete set.

In actual calculations, one disposes of finite basis sets of expansion and, consequently, of a finite number of virtual MO's, in order to attempt to describe the distortion induced in the filled ones by the magnetic perturbation (this is true for the electric perturbation, too); in this way a rigorous gauge-invariance is out of the question, and one is satisfied if "reasonable invariant" $\chi_{\lambda\lambda'}$ and $\sigma_{\lambda\lambda'}$ values are found.

The perturbation $H_\lambda \hat{f}^{(H_\lambda)}(\boldsymbol{r}_0) = \frac{1}{2c} H_\lambda \mathscr{L}_\lambda(\boldsymbol{r}_0) + H_\lambda \hat{g}^{(H_\lambda)}(\boldsymbol{r}_0)$ may be written as

$$H_\lambda \hat{f}^{(H_\lambda)}(\boldsymbol{r}_0) = H_\lambda \left[\frac{1}{2c} \mathscr{L}_\lambda(0) + \hat{g}^{(H_\lambda)}(0)\right] + (\boldsymbol{H} \times \boldsymbol{r}_0)_\lambda \left[-\frac{1}{2c} p_\lambda + \hat{g}^{(\boldsymbol{H} \times \boldsymbol{r}_0)_\lambda}\right],$$

where $\mathscr{L}_\lambda(0)$ is the λ-component of the angular momentum operator with respect to an arbitrary origin (for instance, the origin of the coordinate system), $\hat{g}^{(H_\lambda)}(0)$ is the change of the HF electronic field induced by the external magnetic field $H_\lambda = (\nabla \times A)_\lambda$, when the corresponding vector potential $A = \frac{1}{2}\boldsymbol{H} \times \boldsymbol{r}$ is referred to the same origin as above; $\hat{g}^{(\boldsymbol{H} \times \boldsymbol{r}_0)_\lambda}$ is proportional to the adjustment to $\hat{g}^{(H_\lambda)}(0)$ brought about when the origin of $\boldsymbol{A}$ is translated by $\boldsymbol{r}_0$, and p_λ is the λ-component of the linear momentum operator (see also Ref. [5]).

Thus, the first-order correction to each filled MO $\phi_j^{(0)}$ may be expressed as a sum of two contributions: $H_\lambda \phi_j^{(H_\lambda,\theta)}$, arising from $H_\lambda \left[\frac{1}{2c} \mathscr{L}_\lambda(0) + \hat{g}^{(H_\lambda)}(0)\right]$, and $(\boldsymbol{H} \times \boldsymbol{r}_0)_\lambda \phi_j^{(\boldsymbol{H} \times \boldsymbol{r}_0)_\lambda}$, arising from $(\boldsymbol{H} \times \boldsymbol{r}_0)_\lambda \left[-\frac{1}{2c} p_\lambda + g^{(\boldsymbol{H} \times \boldsymbol{r}_0)_\lambda}\right]$, and the knowledge of $\phi_j^{(H_\lambda,0)}$ and $\phi_j^{(\boldsymbol{H} \times \boldsymbol{r}_0)_\lambda}$ will allow one to evaluate χ^p and σ^p, for any $\boldsymbol{r}_0$.

For a linear molecule, on assuming the z axis along the nuclear array, the only contribution to $\chi^p(\sigma^p)$ is $\chi^p_{xx} = \chi^p_{yy} = \chi^p_\perp(\sigma^p_{xx} = \sigma^p_{yy} = \sigma^p_\perp)$, since, then, $\chi^p_{zz}(\sigma^p_{zz}) = 0$. In this case, by some manipulations, it is found that:

$$\chi^d_\perp(\boldsymbol{r}_0) = \chi^d_\perp(0) + \left[\frac{1}{4c^2} 2z_0 \langle z \rangle - N_0(y_0^2 + z_0^2)\right], \tag{7a}$$

$$\begin{aligned}\chi^p_\perp(\boldsymbol{r}_0) = \chi^p_\perp(0) + \frac{1}{c}\Bigg[&2z_0 \sum_j^{\text{occ}} \{\langle \phi_j^{(0)} | \mathscr{L}_x(0) | \phi_j^{(\boldsymbol{H} \times \boldsymbol{r}_0)_y} \rangle + \text{c.c.} \\ &+ y_0^2 \sum_j^{\text{occ}} \{\langle \phi_j^{(0)} | p_z | \phi_j^{(\boldsymbol{H} \times \boldsymbol{r}_0)_z} \rangle + \text{c.c.}\} + z_0^2 \sum_j^{\text{occ}} \{\langle \phi_j^{(0)} | p_y | \phi_j^{(\boldsymbol{H} \times \boldsymbol{r}_0)_y} \rangle + \text{c.c.}\}\Bigg],\end{aligned} \tag{7b}$$

where N_0 is the total number of electrons, $\langle z \rangle = 2 \sum_j^{\text{occ}} \langle \phi_j^{(0)} | z | \phi_j^{(0)} \rangle$, and $\chi(0)$ is the value of χ for an arbitrary choice of the origin $\boldsymbol{r}_0$ of $\boldsymbol{A}(\boldsymbol{r})$.

Analogously, for a nucleus located at $(0, 0, Z_N)$, $\sigma_\perp$ is found to be:

$$\sigma^d_\perp(\boldsymbol{r}_0) = \sigma^d_\perp(Z_N) + \frac{1}{2c^2}(Z_N - z_0) \left\langle \frac{z - Z_N}{|\boldsymbol{r} - \boldsymbol{R}_N|^3} \right\rangle, \tag{8a}$$

$$\sigma^p_\perp(\boldsymbol{r}_0) = \sigma^p_\perp(Z_N) - \frac{2}{c}(Z_N - z_0) \sum_j^{\text{occ}} \left\{ \langle \phi_j^{(0)} | \frac{\mathscr{L}_x(\boldsymbol{R}_N)}{|\boldsymbol{r} - \boldsymbol{R}_N|^3} | \phi_j^{(\boldsymbol{H} \times \boldsymbol{R}_{0N})_y} \rangle + \text{c.c.} \right\}, \tag{8b}$$

where $\boldsymbol{R}_{0N} = \boldsymbol{R}_N - \boldsymbol{r}_0$.

Thus, a true invariance of $\chi_\perp$(Eqs. 7) and $\sigma_\perp$ (Eqs. 8), under a translation $\boldsymbol{r}_0$ of the origin of the vector potential $\boldsymbol{A} = \frac{1}{2}\boldsymbol{H} \times \boldsymbol{r}$, implies that

$$4c \sum_j^{\text{occ}} \{\langle \phi_j^{(0)} | \mathscr{L}_x(0) | \phi_j^{(\boldsymbol{H}\times\boldsymbol{r}_0)_y} \rangle + \text{c.c.}\} = \langle z \rangle\,, \tag{9a}$$

$$4c \sum_j^{\text{occ}} \{\langle \phi_j^{(0)} | p_\lambda | \phi_j^{(\boldsymbol{H}\times\boldsymbol{r}_0)_\lambda} \rangle + \text{c.c.}\} = N_0 \qquad (\lambda \equiv y, z)\,, \tag{9b}$$

$$2c \sum_j^{\text{occ}} \left\{\langle \phi_j^{(0)} | \frac{\mathscr{L}_x(\boldsymbol{R}_N)}{|\boldsymbol{r}-\boldsymbol{R}_N|^3} | \phi_j^{(\boldsymbol{H}\times\boldsymbol{r}_0)_y} \rangle + \text{c.c.}\right\} = \left\langle \frac{z - Z_N}{|\boldsymbol{r}-\boldsymbol{R}_N|^3} \right\rangle \tag{9c}$$

be verified. Sum rules of this kind are well known in elementary quantum mechanics, when only local potentials in the Hamiltonian are involved, and their only foundation are the completeness of the unperturbed basis set of expansion and the commutation relations. Eqs. (9) are exactly satisfied by the true HF solutions $\phi_j^{(\boldsymbol{H}\times\boldsymbol{r}_0)_\lambda}$ of Eq. (3): as a matter of fact, owing to the gauge-invariance of the coupled HF perturbation theory [10], a molecular orbital $\phi_j(\boldsymbol{r}; \boldsymbol{H}, 0)$ which satisfies the Eq. (1) for an arbitrary choice of the origin of the vector potential $\boldsymbol{A}(\boldsymbol{r})$, when a translation $\boldsymbol{r}_0$ of the origin of $\boldsymbol{A}(\boldsymbol{r})$ is carried out must transform according to

$$\phi_j(\boldsymbol{r}; \boldsymbol{H}, 0) \xrightarrow{\boldsymbol{r}_0} \phi'_j(\boldsymbol{r}; \boldsymbol{H}, \boldsymbol{r}_0) = \phi_j(\boldsymbol{r}; \boldsymbol{H}, 0) \exp[(i/2c)(\boldsymbol{r}_0 \times \boldsymbol{r}) \cdot \boldsymbol{H}]\,,$$

i.e., to first-order in $\boldsymbol{H}$:

$$\phi'_j(\boldsymbol{r}; \boldsymbol{H}, \boldsymbol{r}_0) = \phi_j^{(0)}(\boldsymbol{r}) + H_\lambda [\phi_j^{(H_\lambda, 0)}(\boldsymbol{r}) + (i/2c)(\boldsymbol{r}_0 \times \boldsymbol{r})_\lambda \phi_j^{(0)}(\boldsymbol{r})] + \cdots.$$

On the other hand, from the perturbation equations it follows that:

$$\phi'_j(\boldsymbol{r}; \boldsymbol{H}, \boldsymbol{r}_0) = \phi_j^{(0)}(\boldsymbol{r}) + H_\lambda [\phi_j^{(H_\lambda, 0)}(\boldsymbol{r}) - (\boldsymbol{r}_0 \times \phi_j^{(\boldsymbol{H}\times\boldsymbol{r}_0)})_\lambda] + \cdots$$

so that the condition

$$\frac{i}{2c} \boldsymbol{r} \phi_j^{(0)}(\boldsymbol{r}) = -\phi_j^{(\boldsymbol{H}\times\boldsymbol{r}_0)} \tag{10}$$

should be verified at each point in order that gauge-invariance be assured. From this equation, it follows rather directly that Eqs. (9) are satisfied also by the exact solutions to first order HF perturbed equations.

4. Results

Our results are concerned with properties of the ground state of LiH molecule, at the experimental equilibrium distance (3.015 a.u.), within the Born-Oppenheimer approximation. Our unperturbed (approximated) HFR MO's have been obtained in terms of a limited basis set of atomic functions $\{\chi\}$ (19 Slater-type orbitals). After filling the two lowest levels ($1\sigma, 2\sigma$), we have at our disposal 17 virtual MO's ($3\sigma, \cdots, 11\sigma$; $1\pi \cdots 4\pi$; $1\bar{\pi} \cdots 4\bar{\pi}$) by which to expand the perturbed (filled) MO's. In Table 1 the orbital exponents (ζ) of the AO's included in the

Table 1. *Characterization of the unperturbed and first-order perturbed filled* MO's *for* LiH *molecule*

Center	AO	ζ	$C_{\alpha,1\sigma}^{(0)}$	$C_{\alpha,2\sigma}^{(0)}$	$C_{\alpha,1\sigma}^{(\mathscr{E}_y)}$	$C_{\alpha,2\sigma}^{(\mathscr{E}_y)}$	$C_{\alpha,1\sigma}^{(\mathscr{E}_z)}$	$C_{\alpha,2\sigma}^{(\mathscr{E}_z)}$	$-icC_{\alpha,1\sigma}^{(H_y,0)\mathrm{a}}$	$-icC_{\alpha,2\sigma}^{(H_y,0)}$	$-icC_{\alpha,1\sigma}^{(H_yz_0)}$	$-icC_{\alpha,2\sigma}^{(H_yz_0)}$
Li	$1s$	2.4480	0.88989	−0.17850	0.0	0.0	0.0034	1.3101	0.0	0.0	0.0	0.0
	$1s'$	4.5800	0.12443	0.01147	0.0	0.0	−0.0095	0.1438	0.0	0.0	0.0	0.0
	$2s$	0.6000	0.00101	−0.09951	0.0	0.0	0.0666	1.1179	0.0	0.0	0.0	0.0
	$2s'$	0.7198	−0.00867	0.38109	0.0	0.0	−0.1842	1.3401	0.0	0.0	0.0	0.0
	$2s''$	5.0000	−0.00097	0.01773	0.0	0.0	−0.0094	0.1806	0.0	0.0	0.0	0.0
	$2p_x$	0.8326	0.0	0.0	0.0	0.0	0.0	0.0	−0.0160	1.6809	+0.1788	+0.1174
	$2p_y$		0.0	0.0	−0.0412	−1.6840	0.0	0.0	0.0	0.0	0.0	0.0
	$2p_z$		−0.01072	0.18852	0.0	0.0	−0.1512	−0.1145	0.0	0.0	0.0	0.0
	$2p'_x$	4.0000	0.0	0.0	0.0	0.0	0.0	0.0	−0.0024	0.0147	+0.2244	−0.0350
	$2p'_y$		0.0	0.0	−0.0104	−0.0009	0.0	0.0	0.0	0.0	0.0	0.0
	$2p'_z$		−0.00342	0.00480	0.0	0.0	−0.0419	0.0208	0.0	0.0	0.0	0.0
H	$1s$	0.8000	0.02119	0.46590	0.0	0.0	0.3366	−2.8574	0.0	0.0	0.0	0.0
	$1s'$	1.2000	−0.00807	0.27584	0.0	0.0	−0.1803	1.2143	0.0	0.0	0.0	0.0
	$2p_x$	0.8000	0.0	0.0	0.0	0.0	0.0	0.0	0.0096	2.6350	−0.1341	+1.2836
	$2p_y$		0.0	0.0	0.0239	−5.2655	0.0	0.0	0.0	0.0	0.0	0.0
	$2p_z$		−0.00352	0.03902	0.0	0.0	−0.0689	−4.7130	0.0	0.0	0.0	0.0
	$2p'_x$	1.2000	0.0	0.0	0.0	0.0	0.0	0.0	−0.0010	0.2520	+0.0769	−0.0771
	$2p'_y$		0.0	0.0	−0.0196	2.2737	0.0	0.0	0.0	0.0	0.0	0.0
	$2p'_z$		−0.00069	−0.04965	0.0	0.0	0.0168	1.9410	0.0	0.0	0.0	0.0

[a] i represents the imaginary unit and $c = 137.0373$ a.u.

basis set are shown in column 2, the other columns containing the coefficients of the AO's in both unperturbed and perturbed MO's:

$$\phi_j^{(0)} = \{\chi\} C_{\cdot j}^{(0)}, \quad \phi_j^{(\mathscr{E}\lambda)} = \{\chi\} C_{\cdot j}^{(\mathscr{E}\lambda)}, \quad \phi_j^{(\mathrm{H}\lambda,0)} = \{\chi\} C_{\cdot j}^{(\mathrm{H}\lambda,0)} \quad \text{and} \quad \phi_j^{(\boldsymbol{H}\times \boldsymbol{r}_0)\lambda} = \{\chi\} C_{\cdot j}^{(\boldsymbol{H}\times \boldsymbol{r}_0)\lambda}$$

($j = 1\sigma, 2\sigma$). At the bottom of the same table, the unperturbed energy $E^{(0)}$ is reported together with the location of the electronic centroid $\langle z \rangle = 2 \sum_j^{\mathrm{occ}} \langle \phi_j^{(0)} | z | \phi_j^{(0)} \rangle$ (with respect to Li nucleus as an origin). It may be remarked that the calculated value $\langle z \rangle = 5.3766$ a.u. is in good agreement with the corresponding "experimental" value 5.3293 a.u., obtained from the experimental dipole moment and geometric data. In order to appreciate more fully the degree of accuracy of our unperturbed HFR wave function, one is referred to (I).

In Table 2 the various quantities we have evaluated are given in the second column, and values for comparison are in the others.

The computed values for the electric polarizability components $\alpha_\perp$ and $\alpha_\parallel$ should be compared directly with those of the fifth column, since the same method (coupled HF perturbed theory) has been applied in both calculations. It is very likely that the value of the transversal polarizability $\alpha_\perp$, 4.063 Å^3, is a reliable figure for such quantity, while for $\alpha_\parallel$ an estimate seems to be more doubtful. As a matter of fact, for a molecule such as LiH, whose filled MO's all belong to the same symmetry species (σ), a variational principle can be exploited for second-order properties such as transversal electric polarizability or paramagnetic susceptibility, since the approximate unperturbed HF operator $\tilde{f}^{(0)}$ remains unchanged owing to the addition of π-symmetry functions to the atomic basis; the searched property corresponds, therefore, to an extremum of the functional involved [12]. This is no longer true for the longitudinal polarizability $\alpha_\parallel$, because the first-order perturbed MO's now belong to the same symmetry of the unperturbed ones, so that, in this case, a strictly valid variational principle could be invoked only if the true HF operator $\tilde{f}^{(0)}$ were attained. The value $\alpha_\perp = 4.063$ Å^3 has been obtained by Stevens *et al.* through a careful adjustment of the π basis, enlarging a unperturbed σ basis previously calculated by Kahalas and Nesbet [11], while the value $\alpha_\parallel = 3.35$ Å^3 is reported between parentheses since is judged to be a lower limit to the final value. Our calculated values are both too low with respect to the previous ones; taking, however, into account that our choice of the overall atomic basis was exclusively dictated with a view to obtaining a presumably good SCF wave function, as well as a subsequent configuration interaction procedure for the ground state [see (I)], we think our results are not too bad. Inspection of Table 1 shows that the 1σ MO (essentially a spherically symmetric inner-shell around Li nucleus) is only very slightly polarizable, so that practically the whole effect is associated with the distortion of the 2σ MO, as should be expected. Furthermore, the main contributions to the polarizability appear to arise from the inclusion in the basis set of $2p$ functions associated with relatively low orbital exponents: it seems reasonable to suppose that further enlargement of the atomic basis along this direction should be a profitable way of proceeding. For very high electric field strengths, departures of the induced electric dipole moment $\mu^{(i)}$ from the linearity are to be expected [9]: for a polar

Table 2. *Quantities evaluated in this paper and values for comparison*

I Observable	II This paper	III Karplus-Kolker	IV O'Hare-Hurst	V Stevens *et al.*	VI Experiments
$\alpha_{\perp}{}^{a}$	3.501	5.01^{e}	5.084^{h}	4.063^{i}	
$\alpha_{\|\|}$	2.964	3.76^{e}	3.367^{h}	$(3.35)^{i}$	
$\bar{\alpha}$	3.322	4.59^{e}	4.512^{h}	$(3.83)^{i}$	
$\Delta\alpha = \alpha_{\|\|} - \alpha_{\perp}$	− 0.537	-1.25^{e}	-1.717^{h}	$(-0.65)^{i}$	0.25 ± 0.6^{m}
$\beta_{xxz}{}^{b}$	−113.32		-240.52^{h}		
β_{zzz}	−173.36		-192.40^{h}		
$\chi_{\perp}^{a}(\mathrm{Li})^{c}$	− 26.27				
$\chi_{\perp}^{p}(\mathrm{Li})$	19.35	22.00^{f}		19.25^{l}	19.065 ± 0.060^{n}
$\chi_{\perp}(\mathrm{Li})$	− 6.92				
$\chi_{\|\|}^{d}(\mathrm{Li})$	− 9.41				
$\bar{\chi}(\mathrm{Li})$	− 7.75	-9.15^{f}		-7.63^{l}	
$(\sigma_{\perp}^{d})_{\mathrm{Li}}(\mathrm{Li})^{d}$	111.09				
$(\sigma_{\perp}^{p})_{\mathrm{Li}}(\mathrm{Li})$	− 27.18	-12.03^{g}		-26.53^{l}	-28.05 ± 1.8^{n}
$(\sigma_{\perp})_{\mathrm{Li}}(\mathrm{Li})$	83.91	99.05^{g}			
$(\sigma_{\|\|\mathrm{Li}}^{d}(\mathrm{Li})$	101.48	101.5^{g}			
$\bar{\sigma}_{Li}(\mathrm{Li})$	89.77	99.86^{g}		90.21^{l}	
$(\sigma_{\perp}^{d})_{\mathrm{H}}(\mathrm{H})$	44.80				
$(\sigma_{\perp}^{p})_{\mathrm{H}}(\mathrm{H})$	− 14.70	-18.45^{g}		-19.44^{l}	-20.7 ± 0.75^{n}
$(\sigma_{\perp})_{\mathrm{H}}(\mathrm{H})$	30.09	27.05^{g}			
$(\sigma_{\|\|}^{d})_{\mathrm{H}}(\mathrm{H})$	28.20	28.12^{g}			
$\bar{\sigma}_{H}(\mathrm{H})$	29.46	27.39^{g}		26.53^{l}	

[a] Electric dipole polarizabilities in 10^{-24} cm^3 units.

[b] Electric dipole hyperpolarizabilities in 10^{-32} cm^5/esu.

[c] Magnetic susceptibilities in ppm-cgs/mole. The notation $\chi(A)$ means that the gauge is chosen at A.

[d] Nuclear magnetic shielding constants in ppm. The notation $(\sigma)_B(A)$ indicates the magnetic shielding of the nucleus B, when the gauge is chosen at A.

[e] Ref. [2c]. — [f] Ref. [2b]. — [g] Ref. [2d]. — [h] Ref. [3]. — [i] Ref. [1b]. — [l] Ref. [1a].

[m] Value quoted in Ref. [1b].

[n] Values quoted in Ref. [1a].

diatomic molecule, the lowest nonlinear contribution to $\mu_k^{(i)}$ is $(2!)^{-1}\,\beta_{klm}\mathscr{E}_l\mathscr{E}_m$ (sum convention). The value we have evaluated for $\beta_{xxz}=\beta_{yyz}$ and β_{zzz} may be compared with those calculated by O'Hare and Hurst (column 4): the disagreement is very large for β_{xxz}, while for β_{zzz} a moderate agreement can be recognized. In our opinion, it is hopeless to dispute about which of two calculations is the more reliable; the perturbed MO's we have evaluated are probably rather modest approximations to the true ones (it is not unlikely that $\{\chi\}\,C_{\cdot i}^{(\mathscr{E}_z)}$ is a poorer approximation to $\phi_i^{(\mathscr{E}_z)}$ than $\{\chi\}\,C_{\cdot i}^{(\mathscr{E}_y)}$ to $\phi_i^{(\mathscr{E}_y)}$), so that our computed values are presumably not completely reliable; on the other hand, some approximations inherent in the calculation scheme of O'Hare and Hurst make their results not easily interpretable. We feel that the main justification for calculating such subtle quantities as hyperpolarizabilities from approximate MO's is one of completeness; moreover, the values so obtained seem, in spite of everything, more credible than those arising, for instance, from electrostatic simplified models.

The magnetic susceptibility of a molecule is evaluated as a sum of two contributions (Eq. 6), which present very different difficulties of computation. The so-called diamagnetic contribution needs only the knowledge of the unperturbed electronic ground state wave function, and, admittedly, its HF approximation is a reliable estimate for such quantity, inasmuch as the role of correlative corrections as well as the effect of nuclear vibrational motions should be a minor one [5b]. The evaluation of the paramagnetic contribution faces one with troubling problems, similar to those occurring in the computation of the electric polarizability, because of the approximate nature of our first-order perturbed MO's by a magnetic field. As a consequence, even the parallel problem of obtaining gauge-invariant calculated properties will be solved only approximatively. The value $\chi_\perp^p(\mathrm{Li})=19.35$ ppm-cgs/mole (i.e., the paramagnetic susceptibility, when the origin of the vector potential is chosen at Li nucleus) is quite good, and compares very well with the experiment (19.065 ± 0.06) (value deduced from rotational magnetic moment measurements [13]) and a previous result of Stevens *et al.* (19.25). Since, as stated above, the evaluated diamagnetic contribution is expected to be a reliable estimate for such quantity, a value $\bar{\chi}=-7.5\div7.7$ ppm-cgs/mole could be anticipated for the magnetic susceptibility of LiH, a quantity not yet experimentally determined.

In order to measure the "degree of gauge-invariance" of our results, from Eqs. (7a)–(7b) it follows that:

$$\chi_\perp=\chi_\perp^d(\boldsymbol{r}_0)+\chi_\perp^p(\boldsymbol{r}_0)=-6.922+1.1881\,[2\,(5.377-5.246)\,z_0$$
$$+-(4.-3.561)\,y_0^2-(4.-3.499)\,z_0^2]\ \text{ppm-cgs/mole}$$

where the factor $1.1881\cdot10^{-6}\,\mathrm{cm}^3/\mathrm{mole}=N_0a_0^3/4c^2$, N_0 being the Avogadro number, $a_0=0.529172\cdot10^{-8}$ cm, $c=137.0373$ a.u. and x_0, y_0, z_0 are expressed in a.u. It is immediately seen that the main departure from a good invariance is caused by the quadratic terms in y_0^2, z_0^2; as a matter of fact, while Eq. (9a) is reasonably well satisfied, so that the linear term in z_0 gives rise to a "noninvariance" contribution of $0.309\,z_0$ ppm-cgs/mole (which for a displacement from Li to H nucleus (3.015 a.u.) amounts to 0.93 ppm-cgs/mole), the quadratic terms make the "degree of invariance" definitely bad (for a displacement along z, it amounts to

$0.595\, z_0^2$ ppm-cgs/mole, which, for $z_0 = 3.015$ a.u., corresponds to 5.411 ppm-cgs/mole). Thus, a displacement of the gauge from Li to H nucleus results in a value $\bar{\chi} = -10.74$ ppm-cgs/mole, really not too gratifying. It should be observed, however, that a mostly critical role in this change is played by the rather high value of the displacement involved (3.015 a.u.), inasmuch as the equalities (9a)–(9b), which, whether verified, would assure an exact gauge-invariance, are satisfied within 3% and 12%, respectively, while the value of $\bar{\chi}$ decreases of about 30%.

As far as nuclear magnetic shielding constants are concerned, while for Li nucleus the calculated results compare very well with a previous calculation of Stevens *et al.* and the experience (only the paramagnetic contribution to σ has been determined, from spin-rotational constant measurements [13–15]), for the proton the results are not as good.

In order to appreciate the role of the gauge of the external vector potential in actual calculations, the following results obtained from Eqs. (8a)–(8b) seem rather explicative (they refer to a simple translation of the origin of A along the internuclear axis):

$$\text{Li nucleus: } \sigma_\perp(z_0) = 83.905 - 26.6252 \;\; (0.0955 - 0.0912)\, z_0 \text{ ppm},$$

$$\text{H nucleus: } \sigma_\perp(z_0) = 30.102 + 26.6252 \;\; (3.015 - z_0)\,(-0.3328 + 0.2701) \text{ ppm},$$

where $26.6252 \cdot 10^{-6} = 1/2c^2$, $c = 137.0373$ a.u., and z_0 is the displacement (in a.u.) from the concerned nucleus.

Thus, for Li nucleus, the result for σ changes from 83.905 to 83.559 ppm, when $z_0 = 3.015$ a.u. (gauge at hydrogen nucleus), and a good "degree of invariance" can be recognized; for H nucleus, however, the change for a displacement of the same amount (from H to Li nucleus) is quite noticeable, from 30.102 to 25.072 ppm.

In the latter case, the "degree of invariance" is definitely bad; it is to be noted that the value $\sigma = 25.072$ implies a paramagnetic contribution of $+6.990$ ppm, which is rather close to $+5.91$ ppm evaluated by Stevens *et al.*

This markedly different lack of gauge-invariance in the computed values of the magnetic shielding constants of Li and H nuclei is mainly due to the inhability of our atomic basis to represent the magnetic distortion in the 1σ MO, when the gauge of the vector potential is at the hydrogen nucleus. As a matter of fact, in a rigorous SCF calculation, the contribution to an observable from each occupied orbital would be separately gauge-invariant, since each perturbed MO then transforms (at first order) according to Eq. (10), which warrants the invariance of calculated results. How much this invariance is verified may be appreciated from Table 3, where diamagnetic and paramagnetic orbital contributions to the susceptibility have been collected for two different gauges (Li and H nuclei). It is manifest that the outer MO 2σ gives a contribution to $\chi_\perp$ which does not change sensibly for a translation from Li to H nucleus, while in the case of the inner shell 1σ MO the contribution is anything but invariant. The (almost) spherically symmetric charge distribution associated with the 1σ MO in the presence of a magnetic field precesses nearly free around Li nucleus, when the gauge is chosen at this point, giving rise to a weak diamagnetic contribution.

Table 3. *Contributions from the occupied* MO's *to magnetic susceptibility (ppm. cgs/mole)*

	$\chi_\perp^d(\mathrm{Li})$	$\chi_\perp^p(\mathrm{Li})$	$\chi_\perp(\mathrm{Li})$	$\chi_\perp^d(\mathrm{H})$	$\chi_\perp^p(\mathrm{H})$	$\chi_\perp(\mathrm{H})$
1σ	-0.71	$+0.00$	-0.71	-22.37	$+17.52$	-4.85
2σ	-22.56	$+19.35$	-6.21	-8.58	$+2.17$	-6.41

However, when the gauge is displaced at the hydrogen nucleus, a large diamagnetic circulation is forced around this point, so that an (opposite) paramagnetic circulation should arise in order to cancell the former almost entirely: since the basis is not sufficiently complete, this effect is only partially brought about, with, consequently, too large a circulation associated with the inner orbital 1σ.

The noticeably different values obtained for the proton magnetic shielding constant, when the gauge is displaced from H nucleus to Li one, are explained by the preceding remarks: when the gauge is at Li nucleus, only a very weak diamagnetic contribution, correctly estimated by our atomic basis, is expected from the 1σ MO, due to its near-spherical symmetry about this center; going to H nucleus, the reduction of the paramagnetic circulation takes place no longer and the corresponding contribution is badly taken into account due to the incompleteness of the basis set. For the magnetic shielding of Li nucleus, when the gauge is chosen at Li nucleus itself the annihilation of the paramagnetic contribution from 1σ is brought about as above. When the gauge is transferred on the proton, the paramagnetic magnetization distribution associated with 1σ, which now arises and is only approximatively realized, should, in principle, lead to a worse estimate of the Li magnetic shielding, just as for the proton. In this case, however, the matrix element in Eq. (8b) corresponding to the 1σ MO is practically zero, the annihilation being due to the operator $\mathscr{L}_x(\mathrm{Li})/r_{\mathrm{Li}}^3$ operating on the near-spherically symmetric 1σ MO. Thus, a remarkable gauge-invariant result is obtained for Li nucleus although the correction $(1\sigma)^{(\boldsymbol{H}\times\boldsymbol{R}_{ON})_y}$ is not too well represented by the basis. A way for improving the gauge-invariance of the results requires an enlargement of our basis set, taking into account Eq. (10). Since the 1σ MO (essentially a linear combination of two $1s$ atomic orbitals at Li nucleus, as easily seen from Table 1) is mainly responsible for the lack of invariance, the basis should include some $2p\pi$'s at Li nucleus, with orbital exponents close to those of the $1s$ functions at the same center: it is seen that the inclusion of $2p\pi$ AO's with $\zeta \simeq 2.45$ should be very profitable.

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