Theoret. chim. Acta (Berl.) 18, 329—340 (1970)
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SCF and Configuration Interaction Calculations of Some Properties of LiH Molecule in Its Ground State*

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Received March 23, 1970

Some ground-state properties of LiH such as multipole moments, electric fields and field gradients at both nuclei are evaluated both by an approximate SCF wave function built up in terms of Slater type orbitals and by configuration interaction wavefunctions obtained through diagonalization of secular matrices involving both singly and doubly-excited configurations. Some possible approximate perturbative solutions of the secular problem are also tested.

Einige Eigenschaften des LiH für den Grundzustand wie z. B. Multipol-Momente, elektrische Felder und Feldgradienten an beiden Kernen werden berechnet: a) mit einer genäherten SCF-Wellenfunktion, die aus Slater-Funktionen aufgebaut ist; b) mit CI-Wellenfunktionen mit einfach und doppelt angeregten Konfigurationen. Einige angenäherte störungstheoretische Lösungen des Säkularproblems werden ebenfalls untersucht.

Evaluation de certaines propriétés de l'état fondamental de LiH (moments multipolaires, champs électriques et gradients du champ aux deux noyaux) à l'aide d'une fonction d'onde SCF approchée construite en termes d'orbitales de Slater et de fonctions d'onde d'interaction de configurations obtenues par diagonalisation de matrices correspondant à des configurations mono- et di-excitées. Une diagonalisation approchée par perturbation est essayée.

1. Introduction

Great attention has been devoted to the LiH molecule by theoretical chemists, the main reason being that it provides the simplest closed-shell system of immediate interest after the hydrogen molecule. In particular, a noticeable bulk of SCF calculations of increasing degrees of complexity has led to results for the energy which have, admittedly, reached the HF limit [1]; at the same time, more sophisticated techniques have enabled a large portion of the correlation energy to be taken into account [2–8]. The molecular energy, a very relevant property in itself, is a sort of obligatory step in molecular calculations, whose importance should perhaps not supersede that of other observables; in fact, we believe that once an energetically satisfying wavefunction has become available in terms of a fairly extended basis set, it should be used as a probe for observables more sensitive than energy.

* Work performed with the financial support of the Consiglio Nazionale delle Ricerche, through its Laboratorio di Chimica Quantistica ed Energetica Molecolare.

In this paper the results for some one-electron observables of LiH in its ground state are presented and discussed; they have been evaluated i) by means of a one-determinant wavefunction, which should be a rather good approximation to the HF one, and ii) by using some CI wavefunctions, where singly and doubly-excited configurations have been included. These results concern the first three electric multipole moments, the electric field, and field gradient at both Li and H nuclei. Moreover, approximate solutions of the secular problem employing the perturbation theory have also been evaluated and the results compared with those of the full diagonalization.

2. SCF Results

The HF equations for the above-stated problem have been, as is usual, approximately solved by Roothaan's method [9], expanding the unknown MO's ϕ_i in terms of a finite basis set of STO's $\{\chi\}$ centered at both nuclei, i.e. $\phi_i = \{\chi\} C_{\cdot i}$. All data needed to characterize the resulting wavefunction are presented in Table 1. The basis set consists of 11 STO's, whose associated orbital exponents ζ have been carefully selected: for example, the ζ's of the Li inner-shell orbitals ($1s_{\mathrm{Li}}$, $1s'_{\mathrm{Li}}$) were fixed by means of a preliminary investigation of the Li^+ ion, while the four STO's centered at the hydrogen atom were determined by optimizing the following basis set with respect to both ζ and ζ': $1s_{\mathrm{Li}}(2.6909)$, $2s_{\mathrm{Li}}(0.7075)$, $2p_{\mathrm{Li}}(0.8449)$, $1s_{\mathrm{H}}(\zeta)$, $2p_{\mathrm{H}}(\zeta)$, $1s'_{\mathrm{H}}(\zeta')$, $2p_{\mathrm{H}}(\zeta')$. (The three STO's centered at Li nucleus are recognized to be the same as those used by Ransil in his BLMO calculation [10] for LiH.) Finally, the outer-shell orbitals at Li were obtained by partial optimization in molecule, keeping unchanged the previously determined orbitals. The energy value $E = -7.98624$ a.u., should be compared with that calculated by Cade and Huo [1], $E = -7.98731$ a.u., which is to be regarded as

Table 1. SCF *wave function for* LiH ($1\sigma^2 2\sigma^2, {}^1\Sigma^+$)

Center	STO	Orbital exponent	$C_{1\sigma}$	$C_{2\sigma}$
Li	$1s$	2.4480	0.88989	−0.17850
	$1s'$	4.5800	0.12443	0.01147
	$2s$	0.7198	−0.00867	0.38109
	$2s'$	5.0000	−0.00097	0.01773
	$2s''$	0.6000	0.00101	−0.09951
	$2p$	0.8326	−0.01072	0.18852
	$2p'$	4.0000	−0.00342	0.00480
H	$1s$	1.2000	−0.00807	0.27584
	$1s'$	0.8000	0.02119	0.46590
	$2p$	0.8000	−0.00352	0.03902
	$2p'$	1.2000	−0.00069	−0.04965

$\varepsilon_{1\sigma} = -2.44611$, $\varepsilon_{2\sigma} = -0.30153$ (a.u.).
$E = -7.98624$ a.u.
$T = +7.99304$ a.u.
$2T/V = -1.00042$, $R = 3.015$ a.u.

a true HF limit (for instance, an estimate by Hollister and Sinanoglu [11] locates the above figure as far as 0.0037 a.u. from the HF limit). Thus, at least from an energetic point of view, our more modest SCF wavefunction can be judged as a fairly good approximation to [1]: it remains to be seen how observables more sensitive than energy will respond to it.

All the one-electron properties that we have evaluated are shown in Table 2; they refer, in all cases, to the equilibrium internuclear distance, $R = 3.015$ a.u..

Electric quadrupole and octopole moments are defined as in Ref. [12]; their origin was chosen coincident with the nuclear center of mass (even though, for a polar molecule, i.e. one whose multipole moments higher than dipole are origin-dependent, the nuclear center of mass does not seem to be a natural origin, when possible comparison with experiments are made [13]).

Our dipole moment value ($-6.002\,D$) is identical to that calculated by Cade and Huo [14], and is only 2% larger (in absolute value) than the experimental one ($5.882\,D$). The absence in the basis set of polarization $3d$-type functions does not seem to be too detrimental, although the generally important role of these functions for first-row hydride molecules cannot be ignored [15, 16] as far as the calculation of this property is concerned.

Experimental values for the quadrupole moment θ_{zz} of LiH are not available; the value calculated by Cade and Huo, $\theta_{zz} = -4.58\,B$ [1] [17], should be compared with ours, $-4.435\,B$. It is likely that the difference between these two values may be ascribed to the presence in the Cade and Huo's basis set of higher l atomic orbitals. The reference value $\theta_{zz} = -4.2\,B$, recommended in Ref. [17], is a sort of average value between $\theta_{zz} = -4.58\,B$ and $\theta_{zz} = -4.15\,B$, where the latter is somewhat more weighted. The value $\theta_{zz} = -4.15\,B$ was obtained [18] by means of a good VB–CI wavefunction calculated by Browne and Matsen [4]; however, from our CI calculations (see next section), the correlation effects for one-electron properties appear to be rather small, so that, in our opinion, an admittedly near-HF wavefunction over the whole space, such as that of Cade and Huo, could give a θ_{zz} value to be considered the leading one.

To our knowledge, there is no estimate of the octopole moment of LiH; our computed value, $\Omega_{zzz} = -4.659 \cdot 10^{-34}$ esu. cm^3, is, perhaps, to be considered not too far from the experimental one, even though the possible role of atomic orbitals associated with higher l values might not be completely negligible.

The computed electric field $\mathscr{E}$ at a nucleus (located at $\boldsymbol{R}_N$) is the so-called Hellmann-Feynman field [19], i.e.

$$\mathscr{E}(\boldsymbol{R}_N) = -\int \varrho(\boldsymbol{r}) \frac{(\boldsymbol{r} - \boldsymbol{R}_N)}{|\boldsymbol{r} - \boldsymbol{R}_N|^3}\, \mathrm{d}\tau\,,$$

$$\varrho(\boldsymbol{r}) = \sum_{A \neq N} Z_A \delta(\boldsymbol{r} - \boldsymbol{R}_A) - 2 \sum_{i}^{\mathrm{occ}} |\phi_i(\boldsymbol{r})|^2\,.$$

The values we have calculated are $\mathscr{E}_z(\mathrm{Li}) = -0.0145$ a.u., $\mathscr{E}_z(\mathrm{H}) = -0.0028$ a.u., respectively. The value for $\mathscr{E}_z(\mathrm{H})$ is the same as that found by Cade and Huo's wavefunction [20] ($\mathscr{E}_z(\mathrm{H}) = -0.003$ a.u.), while our computed value for $\mathscr{E}_z(\mathrm{Li})$ is rather bad with respect to [20] ($\mathscr{E}_z(\mathrm{Li}) = -0.0007$ a.u.). The inspection of Table 3, where

[1] B is a shortened notation for Buckingham, just as D is for Debye: 1 Buckingham $= 10^{-26}$ esu. cm^2.

Table 2. *One-electron properties of* LiH *molecule evaluated by the* SCF *wavefunction of this paper*

	μ (Debyes)	r_{el}^2 [a] (a.u.)	θ_{zz} [a] (Buckinghams)	Ω_{zzz} [a] (10^{-34} esu. cm^3)	$\mathscr{E}_z$(Li) (a.u.)	$\mathscr{E}_z$(H) (a.u.)	eq (Li) (a.u.)	eq (H) (a.u.)
Calculated	−6.002	22.596	−4.435	−4.659	−0.0145	−0.0028	−0.0453	0.0586
Exptl.	5.882 [b]	—	—	—	0	0	—	0.050 ± 0.002 [b]

[a] Referred to the nuclear center of mass.
[b] See text.

Table 3. *Orbital contributions to electric field and field gradient at* Li *nucleus*

Orbital		$\mathscr{E}_z$(Li) (a.u.)	eq(Li) (a.u.)
1σ	Cade-Huo	−0.054	+0.00134
	this paper	−0.0671	−0.00176
2σ	Cade-Huo	+0.164	−0.11071
	this paper	+0.1626	−0.11658
Total electronic	Cade-Huo	+0.110	−0.10937
	this paper	+0.0955	−0.11834

$\mathscr{E}_z^{nuc}(\text{Li}) = -0.1100$ a.u.; $eq^{nuc}(\text{Li}) = +0.07297$ a.u.

the individual orbital contributions to $\mathscr{E}_z$(Li) and eq_{Li} (see below) are reported, makes clear that the $\mathscr{E}_z$(Li) value results from a very delicate balance between nuclear and electronic contributions. In particular, it should be noted that the inner-shell MO 1σ in our SCF wavefunction appears to be slightly too polarized away from H atom, with a consequently too large antibonding force on Li nucleus.

The experimentally determined deuteron quadrupole coupling constant e^2qQ_D/h for LiD has been measured as (33 ± 1) KHz [21, 22]; on assuming $eQ_D = +0.2796 \cdot 10^{-26}$ e. cm^2 [23] for the deuteron quadrupole moment, we find $[eq(D)]_{\mathrm{exptl}} = (0.050 \pm 0.002)$ a.u., to be compared with our computed value, $+0.0586$ a.u. (17% too large).

The quadrupole coupling constant has been experimentally determined for ^{7}Li in ^{7}LiH [21, 22] as well; in this case, however no reliable experimental value is known for eQ_{Li}, so that our computed electric field gradient at ^{7}Li nucleus, eq(Li), must be compared with other calculated values. At the present time, at least three reliable values for this quantity are worth mentioning: Browne and Matsen [4], by means of their valence bond-CI wavefunction and after vibrational average, found the value -0.0346 a.u. for eq(Li); the calculations of Bender and Davidson [5], based on natural orbitals, give -0.0364 a.u. for the same quantity; finally, by means of Cade and Huo's near HF-wavefunction, we have computed the value -0.0364 a.u. for eq(Li) (see Table 3), which is identical to the one just mentioned. The calculated value for this observable by our SCF wavefunction is $eq(\mathrm{Li}) = -0.0454$ a.u. (~ 25% off), not especially gratifying.

This review of evaluated properties seems to indicate that our SCF wavefunction should be, on the average, a good approximation to the near-HF one [1]; when local properties are tested, however, its flexibility does not appear completely satisfying, expecially around Li nucleus, even though a very critical cancellation between electronic and nuclear contributions to electric field and field gradient, acting as an unfavourable element, can be recognized.

3. Configuration Interaction Results

In order to make possible a CI procedure involving π orbitals, the atomic basis set reported in Table 1 was enlarged to include, for any $2p_z$ function already present in the basis set, a pair $(2p_x, 2p_y)$ with the same orbital exponent. The basis set so enlarged leads to 17 virtual orbital (8 of π-type), in terms of which the configurations are to be built up. Taking into account only singly and doubly excited configurations, the total number of these which interact with the HF ground state ($^1\sum$) is 261, 18 of which are singly substituted (SS); the remaining 243 doubly substituted (DS) configurations are subdivided as follows: DC = 34, DO 1 = 96, DO 2 = 17, DD 1 = 48 and DD 2 = 48, where, for the sake of brevity, we have put DC for double-excited, closed-shell configurations, DO 1 for double-excited, open shell in the virtual orbitals, configurations, DO 2 for double-excited, open-shell in the filled orbitals, configurations, DD 1 and DD2 for double-excited, double open-shell, configurations. The last two types of configurations correspond to the following combinations of spin functions $(1) = \alpha\beta\alpha\beta$, $(2) = \beta\alpha\alpha\beta$, $(3) = \beta\beta\alpha\alpha$,

Table 4. *Configuration-interaction results for* LiH *molecule. Characterization of the* CI-*wavefunctions, and energy values*

Wave function	CI 1	CI 2	CI 3	CI 4	CI 5	CI 6
Number of SS type config.s	5	18	0	18	18	18
Number of DC type config.s	13	19	24	24	29	34
Number of DO 1 type config.s	8	39	57	57	71	96
Number of DO 2 type config.s	0	7	9	9	14	17
Number of DD 1 type config.s	0	2	20	20	31	48
Number of DD 2 type config.s	0	11	22	22	37	48
Total number of config.s	27	97	133	151	201	262
Total energy (a.u.)	−8.04382	−8.05476	−8.05511	−8.05528	−8.05542	−8.05545
Energy shift	−0.05758	−0.06852	−0.06887	−0.06904	−0.06918	−0.06921

$(4)=\alpha\beta\beta\alpha$, $(5)=\alpha\alpha\beta\beta$, $(6)=\beta\alpha\beta\alpha$ [2]:

$$\mathrm{DD}\,1=\frac{1}{2}\left[(1)-(2)-(4)+(6)\right],$$

$$\mathrm{DD}\,2=\frac{1}{\sqrt{3}}\left\{(3)-\frac{1}{2}\left[(1)+(2)+(4)+(6)\right]+(5)\right\}.$$

The energy result arising from the diagonalization of the full matrix is reported in Table 4, in correspondence with the wavefunction denoted CI 6; such a value, $E=-8.05545$ a.u., may be compared with those of Ref. [4] (-8.0561 a.u.) and Ref. [5] (-8.0606 a.u.), and with the experimental one (-8.0705 a.u.) (quoted in Ref. [5]). In the same table the energy values corresponding to reduced CI calculations are also presented; in each case the related wavefunctions are characterized through the number of configurations of the various kinds.

The wavefunctions CI 2, CI 4, and CI 5 include all SS configurations and differ in the number of the DS ones, the latter having been selected according to their ability to improve the second-order energy. [Although different second-order energy contributions can be defined, according to either the employed perturbative scheme or to the choice of the unperturbed Hamiltonian (see next section), any one of them leads unambiguously to this selection, at least in this case]. The wavefunction CI 1 corresponds to a still more drastic selection, where the five retained SS configurations have been chosen by inspection of the coefficients in a fuller calculations. The CI 3 wavefunction does not contain SS configurations, but is otherwise the same as CI 4.

[2] The first pair of spin eigenfunctions is associated with electrons in the ground configurations, the second one with two electrons excited in virtual orbitals.

Table 5. *Configuration-interaction results for the energy of* LiH *molecule associated with some partitions of the full secular matrix*

Wavefunction	CI $[2\sigma^2, rs]$	CI $[1\sigma^2, tv]$	CI $[1\sigma 2\sigma, rt]$
Energy shift (a.u.)	−0.035876	−0.032970	−0.001538

The reduced calculations may give some ideas about the convergence rate of the procedure; this information is possibly of some value when considering larger electronic systems, where a full diagonalization is out of question.

The convergence rate is very low: faster convergence and somewhat better results were obtained by Bender and Davidson [5], using natural orbitals expanded on elliptic orbitals (incidentally, their energy value, −8.0606 a.u., remains the best available variational approximation to the LiH ground state energy). However, spanning our set of calculated CI wavefunctions, the relative importance of the most significant configurations appears to be practically unchanged when going to larger and larger secular equations; the wavefunction CI 1 includes such configurations.

Some results related to a further partition of the full secular matrix are reported in Table 5. The wavefunction CI $[2\sigma^2, rs]$ includes the configurations arising from promotions of the molecular inner-shell electrons: all possible configurations were considered, i.e. 9 of SS type and 65 of DS type. The resulting energy improvement, −0.035876 a.u. could be interpreted as the correlation energy of the LiH inner-shell.

An analogous remark can be made for the wavefunction CI $[1\sigma^2, tv]$, which includes the configurations arising from excitations of the outer-shell electrons (even in this case the vector consists of 9 SS and 65 DS configurations, respectively). Finally, the wavefunction CI $[1\sigma 2\sigma, rt]$ contains all configurations resulting from simultaneous excitations of the electrons from the 1σ and 2σ orbitals, one from each of them. In this case, only DS configurations result (113 in number), and the corresponding energy improvement could be considered as a part of the intergeminal correlation (higher excitations are lacking).

A slightly different definition of outer-shell (ΔE_0) and inner-shell (ΔE_i) correlation energy was previously introduced by Ebbing [2]. His definition, which relies on perturbative arguments and discards as negligible the simultaneous excitations from inner- and outer-shells, leads to the following expression for the inner-shell correlation energy,

$$\Delta E_i = E_i - E_{\mathrm{SCF}} - \Delta E_0 (1 - c_0'^2)/c_0'^2 ,$$

where E_i is the energy corresponding to our wavefunction CI $[2\sigma^2, tv]$, and c_0' the coefficient of the fundamental configuration in such a wavefunction. The outer-shell correlation energy contribution is analogously

$$\Delta E_0 = E_0 - E_{\mathrm{SCF}} - \Delta E_i (1 - c_0''^2)/c_0''^2 ,$$

E_0 being the energy corresponding to our CI $[1\sigma^2, rs]$ and c_0'' the coefficient of the fundamental configuration in such a wavefunction.

Table 6. *One-electron properties of* LiH *molecule evaluated by* CI *wave functions*

Wave function	μ (Debyes)	r_{el}^2 [a] (a.u.)	θ_{zz} [a] (Buckinghams)	Ω_{zzz} [a] (10^{-34} esu. cm^3)	$\mathscr{E}_z$(Li) (a.u.)	$\mathscr{E}_z$(H) (a.u.)	eq(Li) (a.u.)	eq(H) (a.u.)
CI 1	−5.918	22.653	−4.360	−4.830	−0.0159	+0.0072	−0.0419	+0.0584
CI 2	−5.942	22.707	−4.364	−4.778	−0.0141	+0.0036	−0.0427	+0.0596
CI 3	−5.983	22.658	−4.408	−4.686	−0.0141	+0.0000	−0.0440	+0.0596
CI 4	−5.919	22.625	−4.349	−4.764	−0.0145	+0.0032	−0.0427	+0.0593
CI 5	−5.926	22.678	−4.341	−4.751	−0.0145	+0.0034	−0.0429	+0.0595
CI 6	−5.925	22.678	−4.340	−4.751	−0.0144	+0.0034	−0.0429	+0.0595

[a] Referred to the nuclear center of mass.

The values we obtain by adopting these definitions are: $\Delta E_i = -0.03578$ u.a. and $\Delta E_0 = -0.03192$ a.u. (the best Ebbing results were $\Delta E_i = -0.01969$ and $\Delta E_0 = -0.02104$ a.u.).

The sum of the energy improvements obtained by CI $[1\sigma^2, tv]$, CI $[2\sigma^2, rs]$ and CI $[1\sigma 2\sigma, rt]$ is too low with respect to the result from CI 6, because the exclusion effects have not been completely accounted for. The values according to Ebbing, on the other hand, are too high since the inter-shell correlation was completely neglected. In a superposition of configurations, the partition of the correlation energy into contributions pertaining to electron pairs seems to be rather ambiguous and not easily performable [24].

The expectation values for the same one-electron operators considered in the previous section (SCF results) are reported in Table 6. Although a manifest correspondence between the dimension of the CI wavefunction and the resulting numerical values does not appear, some general considerations seem to be possible. A limited configuration interaction calculation involving both SS and DS determinants gives the SCF dipole moment value a small but noteworthy improvement toward the experimental value (wavefunction CI 1). More extended calculations show how important the SS configurations are (compare CI 3 with CI 4); such comparison may supplement the conclusions of Grimaldi *et al.* [25] and Bender and Davidson [7] on the same topic. With reference to the latter paper, it may be noted that the difference between our SCF + DS (CI 3) and SCF + DS (CI 4) values of the dipole moment lies between the corresponding differences of their limited and extended basis set calculations (Table 9 of Ref. [7]): actually, also our wavefunction is intermediate in goodness, the energies of the two calculations in Ref. [7] being −8.0430 and −8.05998 a.u., respectively. It seems possible to infer that the effect of single substitutions is overestimated in less complete calculations. The lack of experimental data concerning higher multipole moments together with the scarcity of evaluated values, makes our calculated value for θ_{zz} and Ω_{zzz} not fully appreciable. It may be argued that the trend of θ_{zz} to decrease as well as that of Ω_{zzz} to increase (in absolute value), with respect to the SCF values, are in the right way. A variation of about 2% between SCF and CI 6 results for both θ_{zz} and Ω_{zzz} may be seen from a perusal of the data in Table 6; thus, if such a figure is assumed representative of the correlation role, a value of $\theta_{zz} \simeq -4.50\,B$ could be put forward for the quadrupole moment of LiH.

While no appreciable effects are found for $\mathscr{E}_z$(Li), $\mathscr{E}_z$(H) changes its sign with respect to the SCF result (whereas its absolute value remains almost unchanged). Since the true HF wavefunction (as well as the exact one, of course) should satisfy exactly the Hellmann-Feynman theorem, in which case for any distance $\mathscr{F}$(Li) $= -\mathscr{F}$(H) ($\mathscr{F} = Z\mathscr{E}$, Z being the nuclear charge), these results for the electric fields at the nuclei can be related to the improvement of the employed wavefunction when going from SCF to CI wavefunctions.

The computed electric field gradients at both nuclei display small changes with respect to the SCF results; however, owing to the unsatisfactory quality of the atomic basis as far as these observables are concerned, an appreciation of the correlative effects on them seems out of place.

4. Perturbative Approach to the Secular Problem

Apart from the fact that a great deal of time is required to set up secular matrices of considerable dimensions, their exact diagonalization becomes quite impractical when the involved configurations exceed a few hundred, and as a result perturbative approaches to the problem are, to say the least, in demand. The basic method is simple: after a "unperturbed" Hamiltonian operator has been chosen, higher and higher perturbation orders are considered, until the difference between the results of two consecutive orders becomes smaller than a prefixed value. In practice, the calculations are stopped at a low order, usually the second one, and the difference between the perturbative and exact results are assumed to be negligible; in this approximation, the choice of the "unperturbed" Hamiltonian may become decisive.

A comparison of the diagonalization results of the preceding section with those obtained by using second-order perturbation techniques with different "unperturbed" Hamiltonian, is, therefore, of some interest.

The Hamiltonian H of the system can be partitioned, quite generally, as follows:

$$H = H^0 + V,$$

H^0 being the "unperturbed" Hamiltonian and V the "perturbation". If $|\Psi_0^0\rangle$ is the Slater determinant, eigenstate of H^0 with eigenvalue E^0 corresponding to the ground state, then the energy shift $E_0 - E_0^0$ is given by

$$E_0 - E_0^0 = \langle \Psi_0^0 | V | \Psi_0 \rangle ,$$

where $H|\Psi_0\rangle = E_0|\Psi_0\rangle$, and $\langle \Psi_0^0 | \Psi_0 \rangle = 1$.

One now introduces a projection operator $Q = \sum_{k \neq 0} |\Psi_k^0\rangle \langle \Psi_k^0|$ defined into the Hilbert space spanned by the complete set of Slater determinants eigensolutions of H^0. Then, an iterative solution of the considered problem, starting from $|\Psi_0^0\rangle$, is [26]

$$|\Psi_0\rangle - |\Psi_0^0\rangle = |\delta\Psi_0\rangle = \sum_{n=1}^{\infty} \{[\varepsilon - H^0]^{-1} Q[\varepsilon - E_0 + V]\}^n |\Psi_0^0\rangle ,$$

ε being an arbitrary energy parameter. At the first order ($n=1$), one obtains:

$$|\delta\Psi_0^{(1)}\rangle = [\varepsilon - H^0]^{-1} Q[\varepsilon - E_0 + V]|\Psi_0^0\rangle .$$

The Brillouin-Wigner (BW) expansion is obtained by choosing $\varepsilon = E_0$, so that

$$|\delta\Psi_0^{(1)}) = [E_0 - H^0]^{-1} Q V|\Psi_0^0\rangle = \sum_{k\neq 0} (E_0 - E_k^0)^{-1} |\Psi_k^0\rangle \langle\Psi_k^0|H|\Psi_0^0\rangle ;$$

the Rayleigh-Schrödinger (RS) expansion immediately follows with the choice $\varepsilon = E_0^0$:

$$|\delta\Psi_0^{(1)}\rangle = [E_0^0 - H^0]^{-1} Q[E_0^0 - E_0 + V]\,|\Psi_0^0\rangle = \sum_{k\neq 0} (E_0^0 - E_k^0)^{-1} |\Psi_k^0\rangle \langle\Psi_k^0|H|\Psi_0^0\rangle .$$

By introducing $|\Psi_0\rangle = |\Psi_0^0\rangle + |\delta\Psi_0^{(1)}\rangle$ into the expression of the energy shift, one obtains the second-order contribution $E_0^{(2)}$ to it.

Next turn to define H^0. By choosing $H^0 = \Sigma_i f^0(i)$, where $f^0(i)$ is the one-particle HF operator for the i-th electron, $V = H - \sum_i f^0(i)$, the so-called "fluctuation potential" [27], and E_k^0 is the energy associated with the k-th Slater determinant (or proper combination of some of them) and is obviously a sum of the orbital energies of the spinorbitals contained in Ψ_k^0: $E_k^0 = \langle\Psi_k^0|H^0|\Psi_k^0\rangle \equiv H_{kk}^0$.

Another interesting choice for the "unperturbed" Hamiltonian is

$$H^{0'} = H^0 + \sum_{k\neq 0} \langle\Psi_k^0|V|\Psi_k^0\rangle\,|\Psi_k^0\rangle\langle\Psi_k^0|$$

so that in this case the perturbation is:

$$V' = V - \sum_{k\neq 0} \langle\Psi_k^0|V|\Psi_k^0\rangle|\Psi_k^0\rangle\langle\Psi_k^0| ;$$

as is easily seen, the "unperturbed" eigenvalues are now given by:

$$E_k^{0'} = E_k^0 + \langle\Psi_k^0|V|\Psi_k^0\rangle = \langle\Psi_k^0|H|\Psi_k^0\rangle \equiv H_{kk} ,$$

(see also Ref. [28]).

To perform calculations only up to the second-order energy means to work in the subspace of the complete Hilbert space spanned by the doubly-excited Slater determinants, built up in terms of our limited one-particle basis set.

In order to allow for some comparisons, the calculations were carried out by using both RS and BW expansions, and for both H^0 and $H^{0'}$. Thus, the following four expressions for $|\delta\Psi_0^{(1)}\rangle$ were employed:

$$|\delta\Psi_0^{(1)}\rangle = \sum_{k\neq 0} (H_{00}^0 - H_{kk}^0)^{-1} |\Psi_k^0\rangle \langle\Psi_k^0|H|\Psi_0^0\rangle \tag{1}$$

$$|\delta\Psi_0^{(1)}\rangle = \sum_{k\neq 0} (E_0 - H_{kk}^0)^{-1} |\Psi_k^0\rangle \langle\Psi_k^0|H|\Psi_0^0\rangle , \tag{2}$$

$$|\delta\Psi_0^{(1)}\rangle = \sum_{k\neq 0} (H_{00} - H_{kk})^{-1} |\Psi_k^0\rangle \langle\Psi_k^0|H|\Psi_0^0\rangle , \tag{3}$$

$$|\delta\Psi_0^{(1)}\rangle = \sum_{k\neq 0} (E_0 - H_{kk})^{-1} |\Psi_k^0\rangle \langle\Psi_k^0|H|\Psi_0^0\rangle . \tag{4}$$

(The four approximations above have been numbered in the same order as the formulae for $E_0^{(2)}$ in a recent paper by one of us (J.T.) *et al.* [29], to which reference will be made later.)

Table 7. *Energy and some one-electron property values calculated by means of the approximate solutions* (1), (2), (3) *and* (4)

	E(a.u.)	$\mu(D)$	eq(Li) (a.u.)	eq(H) (a.u.)
Approx. (1)	−8.04240	−5.993	−0.0448	+0.0590
Approx. (2)	−8.04155	−5.995	−0.0449	+0.0590
Approx. (3)	−8.05659	−5.984	−0.0439	+0.0597
Approx. (4)	−8.05465	−5.989	−0.0442	+0.0596

The energies and values of some observable calculated by means of the approximate wavefunctions listed above are given in Table 7, all doubly-substituted determinants having been employed. The total energy value within approx. 3 may be compared with that of Kahalas and Nesbet [30], whose best result, −8.0171 a.u., is rather significantly improved when going to out basis set. It may be of interest to compare the second-order shifts so calculated with the exact one reported in Table 4 (wavefunction CI 6). The energy deviations found by means of the four approximations are −19%, −20.1%, +1.6%, and −1.2%, respectively. However, a clear relationship between second-order values and the shift associated with a full diagonalization does not come out. For instance, from Grimaldi's calculations on N_2 [31], the second-order energy shifts from RS (our Approx. 1) and BW expansion (Approx. 4) are +6.5% and +23.5% in error, respectively; in addition, results corresponding to our Approx. 3 are in error of +44%. On the other hand, calculations on OF_2, NO_2^- and CN^- [29] show that for the two choices of the "unperturbed" Hamiltonian a bracketing of the exact energy shift takes place. The deviations resulting within the four approximations are, respectively: OF_2: −3.1%, −5.1%, +30.2%, +23.7%; NO_2^-: −7.2%, −9.7%, +27.7%, +19.4%; CN^-: −21.9%, −23.2%, +6.3%, +1.9%. The trend in this cases is decidedly different from that found by Grimaldi for N_2, while our results for LiH compare very well with those for CN^-. We think, however, that the comparison cannot be extended further, since the systems examined are too different in symmetry, number of electrons and configurations considered (the calculations in both Refs. [29], [31] include only DS determinants). The values of other observables than energy, reported in Table 7, do not display very noticeable variations with respect to each other; comparison of these with the results of Table 6 (particularly with wavefunction CI 3 which includes only DS configurations) shows that first-order corrections to the SCF Slater determinant are able to reproduce results obtained from a wavefunction which in turn was determined from the full diagonalization of a secular problem, but which involves only DS substituted configurations.

5. Conclusions

Our approximate HF wavefunction, built up in terms of a finite set of STO's, although quite satisfying from an energetic point of view is not uniformly accurate over the whole space: this appears clearly when its goodness is tested by some observable more sensitive than energy. In particular, the electric field gradient at both Li and H nuclei are found to be not too well predicted, with consequent

overestimation of the deuteron quadrupole coupling constant and poor prevision of the nuclear quadrupole of ^{7}Li nucleus.

A subsequent CI calculation where all singly and doubly excited Slater determinants were taken into account, gives rise to a noticeable energy improvement and not negligible shifts from the SCF values for some one-electron properties. The choice of the atomic basis, however, proves insufficient for other observables like electric field gradients, so that the correlation role found for these latter properties appears to be of little reliability.

Acknowledgements. The authors thank Prof. E. Scrocco and Dr. C. Petrongolo for their continued interest and help during the calculations.

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