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Perturbed SCF MO calculations. Electrical Polarizability and Magnetic Susceptibility of HF, H_2O, NH_3 and CH_4

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The perturbation theory is used to evaluate first order SCF corrections upon Roothaan type molecular wave functions due to one-electron perturbations. The method is applied to the one-center SCF MO wave functions of HF, H_2O, NH_3 and CH_4 to calculate the electrical polarizability and the magnetic susceptibility tensors. The results obtained agree reasonably well with the available experimental data. The effects of the limited number of basis functions upon the final results are discussed.

La théorie des perturbations est utilisée pour évaleur les corrections SCF du premier ordre, aux fonctions d'onde moléculaires du type Roothaan, dûes à des perturbations monoélectroniques. La méthode est appliquée aux fonctions d'ondes SCF MO à un centre de HF, H_2O, NH_3 et CH_3, pour le calcul des tenseurs de polarisabilité électronique et de susceptibilité magnétique. Les résultats obtenus sont en accord raisonnable avec les données expérimentales disponibles. L'effet du nombre limité de fonctions de base sur le résultat est discuté.

Es werden Störungen erster Ordnung an SCF-MO-Wellenfunktionen, hervorgerufen durch Einelektronenstöroperatoren, im Rahmen der Störungstheorie behandelt. Insbesondere werden die Tensoren der elektrischen Polarisierbarkeit und der magnetischen Suszeptibilität unter Verwendung von Einzentrumfunktionen für HF, H_2O, NH_3 und CH_4 berechnet. Die Ergebnisse werden mit den verfügbaren experimentellen Daten verglichen. Die Effekte der endlichen Basisgröße auf die Resultate werden diskutiert.

Introduction

The calculation of some observables of interest like electrical and magnetic polarizabilities within the SCF MO scheme can be performed either by the direct calculation of the SCF energy for several values of the applied field [*1*, *2*] or by using the perturbation technique [*3*, *4*, *5*]. Both methods have been used with encouraging results but the second one allows to separate the various orders of perturbation. Thus it offers the possibility of picking out the wanted coefficient of a given power of the perturbation parameter whereas the first procedure needs a subsequent interpolation [*1*, *2*]. Furthermore the perturbation technique offers some computational advantages which are of importance when large basis sets are involved.

In this paper the electrical and magnetic polarizability tensors of HF, H_2O, NH_3 and CH_4 calculated by the perturbation technique using OCE SCF MO [*6*, *7*, *8*] wave functions are reported.

The perturbation theory for SCF wave functions has been given by several authors, and recently an excellent account has been given by McWeeny [*3*, *4*] for the Roothaan type SCF MO [*9*, *10*]. Therefore here only a brief outline of the theory for closed shell cases is given and we refer to McWeeny's paper for the essential literature on the subject.

Theory

Given a certain basis $\{\chi\}$ comprising n real functions, not necessarily orthogonal, m doubly occupied orbital $\varphi_i^0 = \{\chi\}\, \boldsymbol{C}_{\cdot j}^0\,(j = 1, 2, \ldots m)$ are constructed by the Roothaan procedure [*9*]. The resulting HF matrix will determine, besides these m orbitals φ_j, $n - m$ empty, or virtual, orbitals $\varphi_v^0 = \{\chi\}\, \boldsymbol{C}_{\cdot v}^0 (v = m + 1, \ldots n)$. The derivative of the HF energy E with respect to a parameter γ, which appears in the one-electron part of the original hamiltonian is given by

$$\left(\frac{\partial E}{\partial \gamma}\right)_0 = 2 \sum_{j=1}^{m} \langle \varphi_j^0 \,|\, h^\gamma \,|\, \varphi_j^0 \rangle \tag{1}$$

where $\sum\limits_{\mu} h_\mu^\gamma$ with the index μ running over all the electrons, means the derivative of the hamiltonian with respect to γ and the SCF orbitals φ_j^0 are evaluated for the value 0 of γ. Eq. (1) simply indicates the well known fact that the SCF wave functions are stable [*11*] and that the Hellmann-Feynman theorem is valid for SCF wave functions, even of the Roothaan type. Deriving Eq. (1) again with respect to an other possible parameter β still being contained in the one-electron part of the hamiltonian the following expression

$$\frac{\partial^2 E}{\partial \beta\, \partial \gamma} = 2 \sum_j \left[\langle \varphi_j^\beta | \, h^\gamma \,|\, \varphi_j^0 \rangle + \langle \varphi_j^0 \,|\, h^\gamma \,|\, \varphi_j^\beta \rangle + \langle \varphi_j^0 \,|\, h^{\beta\gamma} \,|\, \varphi_j^0 \rangle\right] \tag{2}$$

is obtained. This last expression does not appear symmetric, but it is not difficult to show that it is invariant against an exchange of β and γ.

The derivative φ_j^β of the occupied orbital φ_j appearing in Eq. (2) must be such as to satisfy the following equation obtained by deriving the unperturbed HF equation with respect to β:

$$(f_0 - \varepsilon_j^0)\, \varphi_j^\beta = (\varepsilon_j^\beta - h^\beta - \mathfrak{G}^\beta)\, \varphi_j^0 \tag{3}$$

where f_0 is the unperturbed HF operator, whose eigenfunctions and eigenvalues are φ_j^0 and ε_j^0. $\mathfrak{G}^\beta$ represents the derivative of the HF electron repulsion potential. It can be shown [*3, 4*] that the derivatives of the orbitals can be expressed as

$$\varphi_j^\beta = \sum_{v=m+1}^{n} \frac{\langle \varphi_v^0 | h^\beta + \mathfrak{G}^\beta | \varphi_j^0 \rangle}{\varepsilon_j^0 - \varepsilon_v^0}\, \varphi_v^0 \,. \tag{4}$$

The solution of this last equation can be found by an iterative procedure, starting with $\mathfrak{G}^\beta = 0$ and constructing afterwards the needed matrix elements $G_{vj}^\beta = \langle \varphi_v^0 \,|\, \mathfrak{G}^\beta \,|\, \varphi_j^0 \rangle$ at each iteration, with the φ_j^β obtained from the proceeding iteration by

$$G_{vj}^\beta = \sum_{k=1}^{m} \left[2\langle \varphi_v^0 \varphi_k^\beta \,|\, \varphi_j^0 \varphi_k^0 \rangle + 2\, \langle \varphi_v^0 \varphi_k^0 | \varphi_j^0 \varphi_k^\beta \rangle - \langle \varphi_v^0 \varphi_k^\beta \,|\, \varphi_k^0 \varphi_j^0 \rangle - \langle \varphi_v^0 \varphi_k^0 | \varphi_k^\beta \varphi_j^0 \rangle\right]. \tag{5}$$

In principle this iteration procedure is not needed, in fact from Eq. (5) and (4) we have

$$\begin{aligned} G_{vj}^\beta = \sum_{t=m+1}^{n} \sum_{k=1}^{m} \Bigg\{ &\left(\frac{H_{tk}^{\beta *} + G_{tk}^{\beta *}}{\varepsilon_k^0 - \varepsilon_t^0}\right) \left[2\langle \varphi_v^0 \varphi_t^0 \,|\, \varphi_j^0 \varphi_k^0 \rangle - \langle \varphi_v^0 \varphi_t^0 \,|\, \varphi_k^0 \varphi_j^0 \rangle\right] + \\ &+ \left(\frac{H_{tk}^\beta + G_{tk}^\beta}{\varepsilon_k^0 - \varepsilon_t^0}\right) \left[2\, \langle \varphi_v^0 \varphi_k^0 \,|\, \varphi_j^0 \varphi_t^0 \rangle - \langle \varphi_v^0 \varphi_k^0 \,|\, \varphi_t^0 \varphi_j^0 \rangle\right] \Bigg\} \end{aligned} \tag{6}$$

obtaining an explicit linear relation between the sought matrix elements and the other known quantities. Once the φ_j^β are kwown it is possible to evaluate the energy up to the third order [*3*, *4*].

For many practical reasons it is quite desiderable to work with matrix elements between the basis functions χ and not with those between the molecular orbitals φ. Thus Eqs. (3) and (4) will became respectively

$$(\boldsymbol{F} - \varepsilon_j^0 \, \boldsymbol{S}) \, \boldsymbol{C}_{.j}^\beta = (\varepsilon_j^\beta \, \boldsymbol{S} - \boldsymbol{F}^\beta) \, \boldsymbol{C}_{.j}^0 \, , \tag{3a}$$

$$\boldsymbol{C}_{.j}^\beta = \sum_v \frac{\boldsymbol{C}_{.v}^{0\dagger} \boldsymbol{F}^\beta \boldsymbol{C}_{.j}^0}{\varepsilon_j^0 - \varepsilon_v^0} \boldsymbol{C}_{.v}^0 \, , \tag{4a}$$

where $\boldsymbol{F}$ is the unperturbed HF matrix in the basis $\{\chi\}$, $\boldsymbol{S}$ is the overlap matrix, and $\boldsymbol{F}_{\lambda\varrho}^\beta = \langle \chi_\lambda \mid h^\beta + \mathfrak{G}^\beta \mid \chi_\varrho \rangle$. It is now possible to write down the expressions for the energy derivatives, up to the third derivative, as functions of the $\boldsymbol{C}^\circ$, $\boldsymbol{C}^\beta$ and of integrals over the basis functions $\{\chi\}$. It happens that the overlap matrix $\boldsymbol{S}$ will appear only in the third derivatives.

If the perturbation is due to an homogeneous electrical or magnetic field $\mathscr{E}$ or $\mathscr{K}$, the derivatives of the hamiltonian are

$$\sum_\mu h_\mu^{\mathscr{E}_g} = - \sum_\mu g_\mu \tag{7}$$

$$\sum_\mu h_\mu^{\mathscr{K}} = - \frac{1}{2C} \sum_\mu (\mathfrak{L}_\mu)_g \, , \tag{8}$$

$$\sum_\mu h^{\mathscr{K}_g \mathscr{K}_g} = \frac{1}{4C^2} \sum_\mu (r_\mu^2 - g_\mu^2) \, , \tag{9a}$$

$$\sum_\mu h^{\mathscr{K}_g \mathscr{K}_g} = \frac{1}{4C^2} \sum_\mu g_\mu g'_\mu , \qquad (g' \neq g) \, , \tag{9b}$$

$$(g, g' = x, y, z)$$

where atomic units are used throughout. $(\mathfrak{L}_\mu)_g$ indicates the g component of the angular momentum operator for the μ^{th} electron, and the origin of the vector potentials have been taken coincident with the origin of the axes [*12*]. The electrical and magnetic polarizability tensors α and χ are related to the second derivative of the energy, as here calculated, by the following relations

$$\left.\begin{aligned} \alpha_{gg'} &= - \frac{\partial^2 E}{\partial \mathscr{E}_g \, \partial \mathscr{E}_{g'}} \\ \chi_{gg'} &= - \frac{\partial^2 E}{\partial \mathscr{K}_g \, \partial \mathscr{K}_{g'}} \end{aligned}\right. \qquad (g, g' = x, y, z) \, . \tag{10}$$

Results

Electrical polarizability

The iteration procedure based upon the use of Eq. (4a) has been employed to calculate the electrical polarizability tensors of HF, H_2O, NH_3 and CH_4. The unperturbed SCF wave functions chosen were the one-center expansion type already published [*6*, *7*, *8*].

The perturbations considered (7) are such as to cause a mixing of the original basis functions with those excluded by symmetry considerations in the unperturbed problem. Therefore the functions of Tab. 1 identified by the value of their para-

Table 1

	n	l	m	ζ
HF	3	2	2	2.00
	3	2	−2	2.00
	4	3	2	2.40
	4	3	−2	2.40
H_2O	3	2	−2	1.60
	4	3	−2	1.95
NH_3	4	3	3	2.00
CH_4	4	2	2	1.90
	4	2	0	1.90
	7	3	2	2.90

meters n, l. m and ζ [6] where added. These added functions are needed to obtain a presumably equally balanced basis set in the presence of the perturbations.

With these extended basis sets the iteration procedure for the perturbated SCF wave functions was carried on until the variations of the perturbed vectors $C^{\mathscr{E}}_{\cdot j}$ of Eq. (4a) where such as to give no significant variation of the value of the $\alpha_{gg'}$ elements. The convergence was rather nice and its almost geometrical behaviour strongly suggests that a suitable extrapolation procedure should easily be found. The vectors obtained were not checked against those obtainable by solving directly Eq. (6). This is because our basis sets of ∼30 functions are already too large, from a numerical viewpoint, for the direct solution. On the other hand the convergence was such as to not raise doubts about the iteration procedure results.

A different check was obtained by calculating some atomic electrical polarizabilities already evaluated by a direct SCF procedure by COHEN and ROOTHAAN [2]. The results obtained agree to four significant figures with those of COHEN.

Tab. 2 shows the unperturbed orbitals of HF and their derivatives with respect to the electrical field strengths $\mathscr{E}_x$ and $\mathscr{E}_z$, obtained after nine iterations. The reported figures for these derivatives should be those of the asymptotic values. Tab. 3 reports the electrical polarizabilities here obtained together with those given as experimentals.

Only the diagonal elements are included because the orientations of the axes were those of the principal axes. Precisely:

1. the z axis was chosen coincident with the axis of higher simmetry, except for CH_4 where the orientation does not matter,

2. the yz plane was chosen coincident with the molecular plane for H_2O.

The polarizabilities were calculated for the theoretical equilibrium configurations [6, 7, 8], but their value changes negligibly if evaluated for the experimental configurations. As an example in Tab. 3 the polarizabilities of H_2O and NH_3 are also reported at their experimental equilibrium configurations. For these two molecules there was the greatest difference between the calculated and the experimental equilibrium configurations.

Table 2

n	l	m	ζ	Unperturbed Orbitals 1σ	2σ	3σ	$1\pi_x$	Perturbed Orbitals $1\sigma^{\mathscr{E}_x}$	$1\sigma^{\mathscr{E}_z}$	$2\sigma^{\mathscr{E}_x}$	$2\sigma^{\mathscr{E}_z}$	$3\sigma^{\mathscr{E}_x}$	$3\sigma^{\mathscr{E}_z}$	$1\pi_x^{\mathscr{E}_x}$	$1\pi_x^{\mathscr{E}_z}$
1	0	0	12.10	0.10428	0.04024	−0.01023	—	—	0.000	—	−0.007	—	−0.024	−0.023	—
1	0	0	8.30	0.89499	−0.30511	−0.07107	—	—	−0.000	—	0.017	—	−0.050	−0.039	—
2	0	0	2.40	−0.01838	0.65766	0.30942	—	—	−0.002	—	0.079	—	2.051	1.859	—
2	0	0	1.60	0.00693	0.14471	0.19422	—	—	0.000	—	−0.023	—	−1.777	−1.632	—
2	0	0	3.60	0.02239	0.26143	−0.03652	—	—	0.002	—	−0.064	—	−0.467	−0.421	—
2	1	0	1.68	0.00117	0.14927	0.84494	—	—	−0.004	—	−0.337	—	−0.416	−0.148	—
2	1	0	2.45	−0.00232	−0.02036	−0.13931	—	—	0.010	—	0.346	—	0.612	0.180	—
2	1	0	4.00	0.00206	0.02897	0.35487	—	—	−0.008	—	−0.005	—	−0.038	−0.022	—
3	2	0	1.30	−0.00009	−0.02412	−0.01379	—	—	0.000	—	−0.051	—	−0.697	0.258	—
3	2	0	3.10	−0.00041	−0.02884	−0.10930	—	—	0.001	—	0.017	—	0.077	0.046	—
3	2	0	2.00	0.00029	0.10232	0.23400	—	—	−0.000	—	0.013	—	0.029	−0.054	—
3	2	0	4.20	0.00021	0.00351	0.03281	—	—	−0.000	—	−0.007	—	−0.047	−0.009	—
4	3	0	1.60	−0.00003	−0.00215	0.02465	—	—	0.000	—	−0.011	—	−0.162	0.021	—
4	3	0	2.40	0.00007	0.03326	0.05108	—	—	0.000	—	0.002	—	0.010	−0.003	—
2	1	1	1.80	—	—	—	0.66091	0.006	—	0.118	—	0.098	—	—	−0.030
2	1	1	1.20	—	—	—	0.07537	−0.003	—	−0.214	—	−0.087	—	—	0.086
2	1	1	4.10	—	—	—	0.35895	−0.004	—	0.076	—	−0.006	—	—	−0.028
3	2	1	1.40	—	—	—	0.02552	0.000	—	−0.040	—	−0.454	—	—	−0.471
3	2	1	2.30	—	—	—	0.02051	0.000	—	0.012	—	0.053	—	—	0.058
4	3	1	2.40	—	—	—	0.01448	0.000	—	0.000	—	0.018	—	—	0.009
4	3	1	1.60	—	—	—	0.00470	0.000	—	0.000	—	−0.108	—	—	−0.048
3	2	2	2.00	—	—	—	—	—	—	—	—	—	—	−0.269	—
4	3	2	2.40	—	—	—	—	—	—	—	—	—	—	−0.012	—

Table 3. *Results of the electrical polarizability calculations*

		HF	H_2O[a]	H_2O[b]	NH_3[a]	NH_3[c]	CH_4
$\alpha_{xx}(\text{cm}^3\,10^{-25})$	Calc.	5.25	9.18	9.20	17.42 (14.50)[e]	17.72	18.89
	Exp.[d]	(7.2)	—		21.8		26.0
$\alpha_{yy}(\text{cm}^3\,10^{-25})$	Calc.	5.25	11.91	12.02	17.42 (14.50)[e]	17.72	18.89
	Exp.[d]	(7.2)	—		21.8		26.0
$\alpha_{zz}(\text{cm}^3\,10^{-25})$	Calc.	7.79	10.73	10.67	16.24 (13.0)[e]	16.27	18.89
	Exp.[d]	(9.06)	—		24.2		26.0
$\alpha(\text{cm}^3\,10^{-25})$	Calc.	6.10	10.61	10.63	17.03 (14.0)[e]	17.24	18.89
	Exp.[d]	24.6	14.56[f]		22.6		26.0

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[a] Calculated at the experimental equilibrium configuration.

[b] Calculated at the theoretical equilibrium configuration of $R_{\text{OH}} = 1.814$ au, $\vartheta_{\text{HOH}} = 106°32'$ Ref. [*8*].

[c] Calculated at the theoretical equilibrium configuration of $R_{\text{NH}} = 1.928$ au, $\vartheta_{\text{HNH}} = 108°54'$ Ref. [*7*].

[d] Taken from LANDOLT-BÖRNSTEIN: Zahlenwerte und Funktionen, Vol. I, Part 3^2, p. 511. Berlin-Göttingen-Heidelberg: Springer 1951.

[e] Calculated with the extended monocentric basis set.

[f] Ref. [*22*].

The calculated polarizabilities seem to agree reasonably well with the experimental ones. Although they are consistently lower than the experimental ones it is rather difficult to say if this is due to the basis employed, limited and monocentric, or to the HF approximations.

In order to gain some insight in this problem more extended monocentric bases were tried for H_2O and NH_3. The results were disappointing because they showed neither any clear trend toward an asymptotic value nor their agreement with the experimental data improved. For instance for NH_3 a basis of 80 functions including values of l up to 7, which gives for the experimental geometry a molecular energy of -56.122885 au, yields the following polarizabilities in $\text{cm}^3 \cdot 10^{-25}$

$$\alpha_{xx} = 14.495; \quad \alpha_{yy} = 14.495; \quad \alpha_{zz} = 12.986; \quad \alpha = 13.992$$

which differ from the experimental data more than the results obtained with an inferior basis set.

To understand how this could happen it can be observed that Eq. (3), which determines the first order correction to the molecular orbital, represents the condition for which the functional

$$I = 2 \sum_{i=1}^{m} \{\langle\varphi_j^0 \mid h^\beta + \tfrac{1}{2}\,\mathfrak{G}^\beta \mid \varphi_i^\beta\rangle + \langle\varphi_i^\beta \mid h^\beta + \tfrac{1}{2}\,\mathfrak{G}^\beta \mid \varphi_i^0\rangle + \langle\varphi_i^\beta \mid f_0 - \varepsilon_i^0 \mid \varphi_i^\beta\rangle\} \qquad (12)$$

is an extremum for arbitrary variations $\delta\varphi_i^\beta$. When Eq. (3) is satisfied for all values of $j (j = 1, 2 \ldots m)$, I assumes the value of $\frac{\partial^2 E}{\partial \beta^2}$ as given by Eq. (2).

The foregoing is valid also when the φ's are expressed in terms of a limited basis set. All the cases which were examined here exibited, as said, a nice convergence reaching the asymptotic values without oscillations. This gives an indication that for the cases tried the extremum values of I probably were maxima. It must be expected then that by adding some more basis functions which leave the operator f_0 unchanged, or changes it only negligibly, a greater value of I should be obtained. This is the case for instance for the basis functions which, because of symmetry reasons, are not needed in the unperturbed HF problem. It is more difficult to judge the effect upon I of adding basis functions which could became strongly involved in the unperturbed f_0.

By these considerations it would be easy to add some particular functions to the original basis with the aim of improving the calculated polarizabilities. Naturally this would be rather meaningless, therefore no such attempt has been undertaken. The preceeding consideration seem to apply also to the calculations of STEVENS et al. [5] of the paramagnetic susceptivity of LiH.

In fact from the results reported in their Tab. 2 it is clear that the addition of π functions, which obviously leave the unperturbed f_0 unchanged, increase the value of the paramagnetic contribution; whereas going from a limited σ basis (column III) to a much more extended one (column II) with the same π basis, the paramagnetic contribution to the susceptibility decreases.

Owing to the above mentioned difficulties about predicting the effect of the addition of basis functions upon quantities like the electrical polarizabilities, we are forced to rely solely upon the numerical results obtained in order to make some considerations.

It seems highly improbable that a further extension of a monocentric basis for NH_3 could modify noticeably the results here reported. Considering that the energy obtained is already close to the estimated HF energy [7] and that a monocentric wave function is probably poor only in the regions quite close to the protons (which should not contribute a great deal to the polarizabilities) it seems reasonable to think that the discrepancy may be connected with the single detor approximation.

Magnetic susceptibility

As for the electrical polarizabilities the iteration procedure described has been employed to evaluate the modifications caused by the perturbations (8) upon the unperturbed monocentric wave functions of Ref. [6, 7, 8]. The calculations were performed with the extended basis set (Tab. 1). The orientation of the axes, whose origin was always located on the heavy nucleus, was the same as before in order to have both the diamagnetic susceptibility tensor χ^d and the paramagnetic one χ^p in a diagonal form. Even in these cases the convergence was analogous to that found for the electrical polarizabilities, i.e. it was without oscillation and rather fast.

Tab. 4 shows the results obtained. The comparison with the experimental data is here complicated by the fact that the experimental data of the paramagnetic part of the susceptibility refer to the center of mass taken as origin since they are derived from the rotational magnetic moment. Thus they cannot be compared directly to the present calculated values which refer to an origin centered on the heavy nucleus. Fortunately the experimental diamagnetic part can easily be

Table 4. *Calculated value of magnetic susceptibility. The origin is upon the heavy atom*

χ in [ppm]	HF	H_2O[a]	H_2O[b]	NH_3[a]	NH_3[c]	CH_4
χ^d_{xx}	−11.25	−16.55	−16.56	−21.29	−21.61	−29.22
χ^d_{yy}	−11.25	−14.66	−14.60	−21.29	−21.61	−29.22
χ^d_{zz}	−10.09	−15.19	−15.27	−22.74	−23.33	−29.22
χ^d	−10.87	−15.47	−15.48	−21.77	−22.18	−29.22
χ^p_{xx}	0.520	1.891	1.909	1.961	1.853	6.679
χ^p_{yy}	0.520	0.665	0.641	1.961	1.853	6.679
χ^p_{zz}	0.523	0.862	0.867	3.744	4.032	6.679
χ^p	0.521	1.139	1.139	2.55	2.579	6.679
χ	−10.35	−14.33	−14.33	−19.48	−19.60	−22.54

[a] Calculated at the experimental equilibrium geometry.
[b] Calculated at the theoretical equilibrium geometry Ref. [*8*].
[c] Calculated at the theoretical equilibrium geometry Ref. [*7*].

evaluated for the latter origin once the coordinates of the centroid of the electronic charge are known. These are obtained from the experimental dipole moments considering the positive end of the dipole lying toward the proton(s). Since the experimental susceptibility is obviously gauge invariant, the paramagnetic part for the origin located upon the heavy nucleus is readily derived.

Tab. 5 reports the calculated values together with the experimental ones. The total susceptibilities were taken from LANDOLT-BÖRNSTEIN [*13*] whereas the paramagnetic parts were derived [*14*] from the most recent determination of the rotational magnetic *g* tensors of HF [*15*], H_2O [*16*], NH_3 [*14*], and CH_4 [*17*]. All the diagonal *g* elements were taken to be positive. The columns *A* of Tab. 5 refer to the origin located upon the heavy nucleus while the *B* columns report the values for the center of mass taken as origin. The comparison between calculated and

Table 5. *Comparison of the calculated and experimental magnetic susceptibilities*

		χ^d (ppm)		χ^p (ppm)		χ (ppm)
		A	*B*	*A*	*B*	*A*
HF	Calc.	−10.87	−10.78	0.521	—	−10.35
	Exp.	− 9.30	− 9.13	0.7	0.53[b]	− 8.6[a]
H_2O	Calc.	−15.47	−15.30	1.139	—	−14.33
	Exp.	−14.82	−14.46	1.82	1.46[c]	−13.0[a]
NH_3	Calc.	−21.77	−21.57	2.555	—	−19.48
	Exp.	−23.38	−23.0	4.68	4.3[c]	−18.7[a]
CH_4	Calc.	−29.22	−29.22	6.679	—	−22.54
	Exp.	−21.44	−21.44	9.24	9.24[d]	−12.2[a]

A The origin is upon the heavy nucleus.
B The origin is upon the center of mass.
[a] Ref. [*13*].
[a] Ref. [*15*].
[c] Ref. [*14*].
[d] Ref. [*17*].

experimental values seems reasonably good except for CH_4 where the calculated value of the diamagnetic part seems to be much too large and the paramagnetic part much too small. The comments made about the calculations of the electrical polarizabilities hold for the paramagnetic part of the susceptibility as well and indicate that no definite statement can be done at the moment. On the other hand the discrepancy between calculated and experimental diamagnetic part seems too large. In order to see if this discrepancy could be ascribed to the limited onecenter basis, some more sophisticated wave functions, always of the SCF MO type, were tried. The first one employed a monocentric basis comprised of 76 functions with values of l up to 7. The energy obtained at the experimental geometry is -40.110321 au [*18*]. The second one employed one $1s$ one $2s$ and one $2p_{x,y,z}$ orbital upon the C atom and one $1s$ centered at each of the H atoms. The resulting energy was -40.11526 au at the experimental equilibrium geometry [*19*]. Finally the third one included two $1s$, two $2s$, two $2p_{x,y,z}$ upon the carbon and two $1s$ orbitals upon each hydrogen. The resulting energy of -40.18455 au is for the experimental geometry [*19*]. These three wave functions give the diamagnetic susceptibility as -28.44, -27.62 and -28.69 ppm respectively. Tab. 6 gives a summary of these calculations. It seems that great changes of this observable should be ruled out if it is evaluated within the one detor approximation. Remembering that the diamagnetic part of the susceptibility is the expectation value of a one-electron operator evaluated with an unperturbed closed shell SCF MO wave function, which satisfy the Brillouin theorem, the discrepancies found do not seem justifiable and cast some doubt on the experimental magnetic susceptibility.

As said before the present calculation were performed only with the origin of the vector potential $\boldsymbol{A}$ located upon the heavy nucleus and their dependence upon different gauges therefore was not investigated.

It is proper however to point out that the choice of the gauge coincident with the center of expansion is the best possible for the paramagnetic contribution. For this gauge in fact the basis would be more nearly close to a complete set than for any other choice. On the other hand the use of gauge invariant basis functions [*20*] would not have brought any advantages. Let us suppose to have used instead of the actual basis a gauge invariant basis [*20*] obtainable from the actual one simply by multiplying each function times $exp\,[(i/c)\,(\mathscr{H} \times \vec{r}_0) \cdot \vec{r}]$. Being all the basis functions centered upon the origin, the vector $\vec{r}_0$, which gives the location of the origin of the vector potential $\boldsymbol{A} = \frac{1}{2}\mathscr{H} \times (\vec{r} - \vec{r}_0)$, is the same for all functions. The matrix elements of the Hartree-Fock matrix $\boldsymbol{F}$, as well as those of the overlap matrix $\boldsymbol{S}$,

Table 6. *Calculated Diamagnetic susceptibility of* CH_4

	Type of basis			
	Monocentric STO l up to 3	Monocentric STO l up to 7	Minimal LCAO STO	Double zeta LCAO STO
Number of basis functions	26	76	9	18
Molecular energy [au]	-39.86597	-40.11032	-40.11526	-40.18455
χ^d [ppm]	-29.22	-28.44	-27.62	-28.69

in this basis would be independent from the particular gauge $\vec{r}_0$. The elements of $\boldsymbol{F}$ will depend only upon the field $\mathscr{H}$. Thus the resulting SCF energy, calculated with this limited basis, will be independent from any particular gauge $\vec{r}_0$, and if expanded as a power series in $\mathscr{H}$, will have the coefficients independent from the gauge. These coefficients will then be coincident with those obtained for $r_0 = 0$, to which the present calculation corresponds. Naturally this gauge invariance is obtained artificially while true gauge invariant results can be obtained only using a complete basis set. Whith limited basis sets, which are the only ones employable, it is probable that a true gauge invariance can be approximated more easily with multicenter basis sets than with monocentric ones. For this latter type in fact, the best results are to be expected when the gauge is coincident with the origin of the axes, while this effect is surely smoothed out for multicenter bases. Obviously the gauge variations meant in this context are restricted within the molecular volume, because for gauges far away from the molecule the same criticism can be applied to the multicenter bases.

Conclusion

The results here reported for limited monocentric bases, although they cannot claim to be a definite answer to the question whether or not the one center expansion is capable of giving reliable values for the electrical and magnetic polarizabilities, are such as to give some indications. First of all, for the cases tested, it appears that the reported results are close to the limits of the one center expansion. These results, on the other hand, do not compare unfavorably with those obtained with the best of multicenter SCF MOs [*21*]. This would mean indeed that the existing discrepancies between experimental and calculated values are ascribable to the single determinant approximation. This point needs more careful investigations which are being undertaken in this laboratory using more sofisticated wave functions. What seems rather clear is that even some experimental data might need further consideration.

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