Calculation of the Polarisability and Second Hyperpolarisability of Ferrocene, $Fe(C_5H_5)_2$, Using the Extended CHF-PT-EB-CNDO Method

J. Waite and M. G. Papadopoulos

National Hellenic Research Foundation, Athens, Greece

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The polarisability and second hyperpolarisability of ferrocene have been calculated using the CHF-PT-EB-CNDO method, which has been extended for the study of compounds containing transition metal elements. The computed polarisability value is in good agreement with experiment.

I. Introduction

Ferrocene, since its discovery [1, 2], has been the subject of many theoretical and experimental studies and was instrumental in the understanding of the electronic structure of organometallic compounds [3–5]. However, a computational study on the hyperpolarisability of ferrocene (or any other organometallic compound which involves transition metal elements) has not yet been reported. The non-linear electric properties of ferrocene are furthermore of interest due to the charge-transfer from iron to the ligands, a process for which the non-linear electric properties have been found to be sensitive [6].

We have computed the polarisability and the second hyperpolarisability of ferrocene by employing CHF-PT-EB-CNDO, which has given reasonably accurate polarisabilities and hyperpolarisabilities for a large number of compounds [7]. This method has been appropriately modified for the treatment of compounds containing transition metal elements.

II. Computational Method

The various aspects of the CHF-PT-EB-CNDO method for molecules involving elements with atomic numbers up to 18 have been given in detail elsewhere (e.g., [7 b, c, e, f]); in the Appendix, however, we give a brief description of this. Extension of the method to the treatment of transition metal compounds involved the separation of the s, p and d orbitals of the transition metals, because this gives more flexible parametrization schemes, and it has been shown that this allows for a correct description of the transition metal compounds [8, 9] (e.g., bonding properties [8] and the analysis of many body effects in PE-spectra [10]). The values for the electronegativity factors, $\frac{1}{2}(I_\mu + A_\mu)$ and the resonance parameters, β_μ° (μ = s, p, d) of Fe are from [9], where a successful application of these has been presented. The computations have been performed by employing the following orbitals for the aromatic ring [11 a]:

C: 2s (1.625), 2p (1.625),
H: 1s (0.9), 2s (0.4223), 2p (0.4223).

These have been optimized with respect to α and γ of benzene [11 a]. The adequacy of these functions has been confirmed for naphthalene [11 b], where there is good agreement between the computed (α = 128 a.u. and γ = 48300 a.u.) and experimental (α = 118 a.u. [11 c] and $\gamma = 61900 \pm 12400$ a.u. [11 d]) values.

For Fe, exponents derived by Burns' rules [11 e] (these have been determined by matching the corresponding wave functions to accurate atomic HF functions [11 f]) have been used:

4s (1.575), 4p (0.975), 3d (3.150),

because our experience indicates that Burns' exponents are, in general, close to the optimal ones for polarisability and hyperpolarisability calculations.

Reprint requests to Dr. J. Waite, National Hellenic Research Foundation, 48 Vas. Constantinou Ave., GR-116 35 Athen, Griechenland.

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A question of major importance is the reliability of the method. The following observations and considerations confirm the adequacy of CHF-PT-EB-CNDO for the present study:

(a) It has been found that the choice of a suitable basis set is of great importance for the accurate determination of molecular polarisabilities and in particular hyperpolarisabilities [7a, 7f, 12a, 12b]. Thus we have performed extensive experimentation with basis sets involving up to f orbitals and many different exponents. Analysis of these data has shown that high l AOs like f orbitals for carbon and d orbitals for hydrogen are sufficient (they can lead to reasonable results), but not necessary within a semiempirical framework, if one takes advantage of the flexibility and freedom allowed within such schemes [7a, 7f]. It has also been established that careful optimization of the exponents of a slightly extended basis set (which usually involves 2s and 2p STOs on H) provides, in general, the right computational apparatus for a physically sound description of the various orders of polarisation, as reasonably accurate results for the polarisabilities and hyperpolarisabilities of a large number of molecules belonging to several families, demonstrate (e.g., alkanes [7a], polyenes [7b], aromatics [7c], amines [7f], amides [7g], etc.). It is also noted that Teixeira-Dias and Murrell [12c] demonstrated that good values for the polarisability of saturated hydrocarbons can be derived by adding contracted hydrogen 2p orbitals to the minimum basis set. These findings are encouraging (since they mean that rather compact basis sets can be used for the semiempirical calculation of α and γ of large molecules) and they are probably due to the multicenter nature of the MOs.

(b) It has been recognized that the principal deficiency of Hartree-Fock models is the neglect of correlation between motions of electrons of opposite spin [13]. This effect, which is of considerable importance for the accurate determination of hyperpolarisabilities [14, 15], is taken into account, at least partially, in our CHF-PT-EB-CNDO method (through the optimization of the basis set with respect to some judiciously chosen experimental property values).

Table 1. The polarisability, α, and second hyperpolarisability, γ, of $Fe(C_5H_5)_2$[a]. (The properties are reported in a.u.[b].)

Property[c]	CHF-PT-EB-CNDO (extended)	Experiment
α	146	128 [20, 27]
γ	48800[d]	
	46800[e]	

[a] The structure of $Fe(C_5H_5)_2$ is from [18]. The rings, C_5H_5, are treated in our work as planar.

[b] 1 a.u. of polarisability $\cong 0.148176 \times 10^{-24}$ esu $\cong 0.164867 \times 10^{-40}\,C^2\,m^2\,J^{-1}$; 1 a.u. of second hyperpolarisability $\cong 0.503717 \times 10^{-39}$ esu $\cong 0.623597 \times 10^{-64}\,C^4\,m^4\,J^{-3}$.

[c] The average polarisability, α, and second hyperpolarisability, γ, are given by [26]:

$\alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$,

$\gamma = \frac{1}{5}(\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\gamma_{xxyy} + 2\gamma_{xxzz} + 2\gamma_{yyzz})$,

where x, y and z define Cartesian components. Expressions for the relevant tensor components, in terms of which α and γ are defined, are given in [24].

[d] This value has been calculated by employing the rigorous formula (see footnote c).

[e] This value has been calculated by employing the approximate formula [19] $\gamma \cong \frac{1}{3}(\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz})$.

III. Results and Discussion

It is known that the Hartree-Fock model fails to predict correctly the bonding in ferrocene [5d, 16, 17]. Even very elaborate theoretical models have given a metal-ligand distance which disagrees with the experimental value [5d]. These problems are circumvented in our computations by using the experimental geometry [18].

We observe (Table 1) that the computed polarisability of ferrocene agrees reasonably well with the experimental value. This indicates that the polarised charge distribution is well represented by our wave function and thus renders credibility to the proposed value for the hyperpolarisability.

Recently we have proposed an approximate formula for the average second hyperpolarisability γ (Table 1, footnote e and [19]), with which considerable savings in computer time are achieved without significant loss of accuracy (in comparison to the value determined by the rigorous formula). Comparing the values for γ of ferrocene determined by the rigorous formula (48800 a.u.) with the approximate one (46800 a.u.), we note the remarkable performance of the approximate expression for γ.

Aroney and colleagues [20] have found that ferrocene, from the viewpoint of polarisability and molar Kerr constant, is equivalent to Kr sandwiched be-

tween two $(CH)_5$. We observe that this equivalence holds for the hyperpolarisability as well. Namely:

$$\gamma \cong (24500 \times \tfrac{5}{6} \times 2 + 3180) \text{ a. u.} \cong 44000 \text{ a. u.},$$

where 24500 a.u. [21] and 3180 a.u. [22] are the hyperpolarisabilities of C_6H_6 and Kr, respectively. This value for ferrocene differs by 9% from that computed by CHF-PT-EB-CNDO.

In summary, the extended version of CHF-PT-EB-CNDO developed for the study of the polarisabilities and hyperpolarisabilities of organometallic compounds with transition metal elements, gave a value for the polarisability of ferrocene in reasonably good agreement with experiment and a prediction for its second hyperpolarisability which is considered to be reliable to within 30%. This is an acceptable degree of accuracy since the derived information from experiment may be uncertain due to dispersion [21], geometrical averaging and other effects by more than 20% [7 b].

IV. Appendix

The CHF-PT-EB-CNDO method relies on:

(a) An extended basis (EB) CNDO/2 [23] wave function.

(b) The coupled Hartree-Fock perturbation theory (CHF-PT) developed by McWeeny et al. [24].

(c) The optimization of the basis set with respect to property values (α and/or γ) of some judiciously chosen model compounds [7 b, 7 c, 7 g].

The convergence criteria for the iterative calculation of the zeroth order density matrix $R^{(0)}$, as well as the first and second order corrections to the density matrices, $R^{(1)}$, $R^{(2)}$, have been given elsewhere [25].

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