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Calculations of Induced Moments in Large Molecules I. Polarizabilities and Second Hyperpolarizabilities in Some Alkanes

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We report the results of coupled Hartree–Fock computations for the average polarizability, α, and hyperpolarizability, γ, of CH_4, C_2H_6, C_3H_6 and C_3H_8. The Hamiltonian matrices are constructed from an extended CNDO model. Small as well as large basis sets were tested. Agreement with available experimental values is within 13% for α and 31% for γ.

Key words: Polarizabilities – Hyperpolarizabilities – CNDO – Coupled Hartree–Fock perturbation theory.

1. Introduction

The increasing need for reasonably accurate theoretical values of polarizabilities (α) and hyperpolarizabilities (β, γ) in large molecules can be related to [1–5]:

(a) The general and fundamental interest in the quantitative understanding of molecular electronic structure and its properties.

(b) Their many important applications to other fields of pure and applied science such as intermolecular forces, non-linear optics, dye chemistry and solid state physics.

(c) Their use as standards for the testing of simple but useful semiquantitative schemes of analysis of linear and nonlinear contributions to induced moments and the testing of the various experimental techniques used in the measurements of these properties.

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Large molecules cannot yet be treated with advanced and accurate methods which have been applied to small atoms and molecules [e.g. 6–12]. In fact, the first electron correlation studies of the hyperpolarizability of three small molecules appeared only recently [9, 10, 12].

Especially for *hyperpolarizabilities*, which are difficult to obtain theoretically as well as experimentally and which constitute our main concern, the theoretical approaches published thus far employ by necessity approximations whose accuracy cannot be considered sufficient for quantitative predictions of the hyperpolarizability tensors [5, 13–17].

Thus, it is timely to develop and apply computational procedures for large molecules which are manageable and reliable to a reasonable degree. The approach which is presented here constitutes an attempt to combine accuracy with efficiency and general applicability. We found that a small basis set, chosen after a series of calculations, can be as successful in calculating α and γ as larger basis sets. The present application concerns the calculation of the polarizability and second hyperpolarizability of some alkanes. Future reports will contain results on other systems [51, 52]. Our results are in good agreement with the available experimental values and allow considerable optimism for our predictions on molecules for which there is no experimental information yet. There are no theoretical results for the second hyperpolarizability.

2. Choice of the Computational Approach

The formal expressions from standard perturbation theory for the polarizability tensors involve sums of matrix elements over excited states or, equivalently, the solution of the corresponding inhomogeneous differential equations for the first and second order perturbed N-electron wave-functions [e.g. 7, 9, 18, 19]. Although for small systems this can be done efficiently [e.g. 7], for large molecules, rigorous approaches which include electron correlation computationally are forbidding while the related effort and cost would probably exceed by far the worth of the resulting information.

Our approach to this problem has been based on the following facts and considerations:

1. A goal of better than 15% error for α and 30% for γ was set. Especially for hyperpolarizabilities, this is a reasonable degree of accuracy given the level of sophistication of other current approaches [e.g. 5, 13–17] and the fact that the derived information from experiment may be uncertain, due to dispersion [38], geometrical averaging or other effects, by more than 20%.
2. π as well as σ electrons should be taken into account [see refs. 5 and 14 and refs. therein].
3. For large molecules, the efficient and accurate representation of excited states is presently impossible. Therefore, approaches which use them explicitly were considered unattractive.

4. For closed shell molecular systems without near-degeneracies, the global zeroth-order wave-function characteristics are described well by a single determinant. The Coupled Hartree–Fock (CHF) perturbation theory [19–21], which introduces into the Fock equations the external perturbations and computes the perturbed wave-functions and energies self-consistently, constitutes a rigorous way of accounting for the distortion of the single determinantal density due to the external one electron perturbing operator.
5. Induced moment calculations are very sensitive to the choice of basis sets-especially for the out of plane components [10–12, 22, 23]. Yet, efficient calculations on large molecules forbid the use of large basis sets. Models which use the more flexible Slater type orbitals (STOs), for the valence as well as for the virtual space, seem to offer the only solution.
6. Since, within the CHF scheme, we are after the polarization of the zeroth order charge distribution and not the total energy, *ab initio*, variationally obtained wave-functions not only are unmanageable from the computational point of view but, perhaps, even unnecessary. The CNDO-like semi-empirical methods, which employ STO bases, bypass the computational bottleneck for large molecules while at the same time yield accurate dipole moments – a ground state property depending on the overall charge distribution [50].
7. The inaccuracy introduced due to the neglect of electron correlation can be made up by optimizing and standardizing, for each similar category of compounds, a small basis set with respect to a few experimental data.

These considerations have led us to the adoption of a computational scheme which uses the CHF method with an extended CNDO type approximation which allows for occupied as well as virtual orbitals, which are expressed in terms of STOs with *s*, *p*, *d* and *f* symmetries. Within this scheme, we have dealt extensively with questions such as: What is the best (universal) basis set? Are high symmetry virtual atomic orbitals necessary? How does orthogonalization change the theory and the results? How should the virtual molecular orbitals be chosen? What is the best integral parametrization? How should the dipole perturbation matrix be approximated? Having made a very large number of runs for organic molecules containing C and H, we were pleasantly surprised to discover that a small basis set with virtual 2s and 2p STOs on H is sufficient. Numerical information on the above questions can also be found in [52].

3. Theory

The energy of a closed shell molecule, described by a single determinant, in the presence of an electric field, *F*, is given by [1, 18–21]

$$E(F) = 2trR(f + \tfrac{1}{2}G(R)) = trR(f + h) \tag{1}$$

$$= E^{(0)} - \mu_\alpha F_\alpha - \tfrac{1}{2}\alpha_{\alpha\beta} F_\alpha F_\beta - \frac{1}{3!}\beta_{\alpha\beta\gamma} F_\alpha F_\beta F_\gamma - \frac{1}{4!}\gamma_{\alpha\beta\gamma\delta} F_\alpha F_\beta F_\gamma F_\sigma \tag{2}$$

where f is the core hamiltonian, $G(R)$ is the electron interaction matrix, R is the density matrix and μ_α, $\alpha_{\alpha\beta}$, $\beta_{\alpha\beta\gamma}$, and $\gamma_{\alpha\beta\gamma\delta}$ are the dipole moment, polarisability, first hyperpolarisability and second hyperpolarisability components respectively.

A matrix M can be expanded as follows [21]

$$M = M^{(0)} + (aM^{a} + bM^{b} + \cdots) + (a^{2}M^{a^{2}} + b^{2}M^{b^{2}} + \cdots + abM^{ab} + \cdots) \tag{3}$$

where a and b are perturbation parameters. This relation is used as a guide in the expansion of f, h and R where a and b correspond to electric field components. The density matrix, R, being a projection operator is idempotent [19]

$$R^{2} = R. \tag{4}$$

Due to this condition

$$\begin{aligned} M &= R_0 M R_0 + R_0 M R'_0 + R'_0 M R_0 + R'_0 M R'_0 \\ &= M_{11} + M_{12} + M_{21} + M_{22} \end{aligned} \tag{5}$$

where R_0 and R'_0 are projectors defined with respect to the occupied and the unoccupied subspaces respectively. By making use of Eq. (5) and the properties of density matrices one finds [21]:

$$R^{(1)} = x + x^{+}, \qquad x = R^{(1)}_{12} \tag{6}$$

$$R^{(2)} = -xx^{+} + y + y^{+} + xx^{+}, \qquad y = R^{(2)}_{12}. \tag{7}$$

It is known that x and y can be expressed as sums of terms which can be found independently [21]:

$$x = ax_a + bx_b + \cdots \tag{8}$$

$$y = a^{2}y_{a^{2}} + b^{2}y_{b^{2}} + \cdots + aby_{ab} + \cdots \tag{9}$$

x_a, y_{a^2}, and y_{ab} are calculated iteratively until self consistency is achieved. The average convergence ratios were found to be

$$R^{(0)}(1) < x_a(4) < y_{a^2}(8) < y_{ab}(12) \tag{10}$$

i.e. the calculation of y_{ab} requires, on average, 12 times more computer time than $R^{(0)}$. The average convergence criterion was six significant figures. The calculation of $R^{(0)}$ was performed in double precision while the computations of the properties in single precision, on a 32 bit computer.

The average values of the polarizability and the second hyperpolarizability are given by [1]:

$$\alpha = \tfrac{1}{2}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \tag{11}$$

$$\gamma = \tfrac{1}{5}(\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\gamma_{xxyy} + 2\gamma_{xxzz} + 2\gamma_{yyzz}) \tag{12}$$

$$\alpha_{\alpha\alpha} = -2E^{\alpha\alpha} \tag{13}$$

$$\gamma_{\alpha\alpha\alpha\alpha} = -24E^{\alpha\alpha\alpha\alpha} \tag{14}$$

$$\gamma_{\alpha\alpha\beta\beta} = -4E^{\alpha\alpha\beta\beta} \tag{15}$$

where $E^{\alpha\alpha}$, $E^{\alpha\alpha\alpha\alpha}$ and $E^{\alpha\alpha\beta\beta}$ are given in terms of the perturbed *f*, *h* and *R* [21]. The number of independent components required to specify α and γ depends on molecular symmetry. Thus, for $CH_4(T_d)$, the following components are required [1]:

$$\alpha_{xx} = \alpha_{yy} = \alpha_{zz}$$

$$\gamma_{xxxx} = \gamma_{yyyy} = \gamma_{zzzz}$$

$$\gamma_{xxyy} = \gamma_{xxzz} = \gamma_{yyzz};$$

for $C_3H_6(D_{3h})$

$$\alpha_{xx} = \alpha_{yy}; \qquad \alpha_{zz}$$

$$\gamma_{xxxx} = \gamma_{yyyy} = 3\gamma_{xxyy}$$

$$\gamma_{xxzz} = \gamma_{yyzz}; \qquad \gamma_{zzzz}$$

for C_2H_6 (fully staggered; D_{3d})

$$\alpha_{xx} = \alpha_{yy}; \qquad \alpha_{zz}$$

$$\gamma_{xxxx} = \gamma_{yyyy} = 3\gamma_{xxyy}$$

$$\gamma_{yyzz} = \gamma_{xxzz}; \qquad \gamma_{zzzz}$$

finally for the other configurations of C_2H_6 and the studied configurations of C_3H_8 all three components of α and all six components of γ were computed.

4. Results and Discussion

In calculating the Hamiltonian matrix elements, we have employed the standard CNDO assumptions and approximations [25]. The expression for $f_{ij}^{(0)}$ given by Shinoda and Akutagawa was used [26]. The average ionization potentials, I_μ, for the virtual orbitals of C and H used in the expression of the core integrals [25] are given in Table 1. The virtual molecular orbitals which enter in the

Table 1. Average Ionization potentials, I_μ, for atomic vacant orbitals (eV) [49]

Atom	Oribital	I_μ
H	2s	3.4
	2p	3.4
	3s	1.511
	3p	1.511
	3d	1.511
C	3s	3.735
	3p	2.509
	3d	1.551
	4s	1.579
	4p	1.247
	4d	0.877
	4f	0.85

Table 2. Extended basis calculations on CH_4 employing our CHF-PT-EB-CNDO method*

α, a.u.		γ, a.u.	
17.31	a	2442	a
18.27	b	2446	c
16.92	d	2065	d

$^+$ The experimental values are given in Table 3.

[a] C: 2s(1.625), 2p(1.625).
H: 1s(1.0), 2s(0.5), 2p(0.5).

[b] C: 2s(1.625), 2p(1.625), 3d(1.08).
H: 1s(1.2), 2s(0.6), 2p(0.6).

[c] C: 2s(1.625), 2p(1.625), 3d(1.08), 4f(0.8125).
H: 1s(1.2), 2s(0.6), 2p(0.6), 3d(0.4).

[c] C: Clementi's et al, double zeta function;
H: 1s(1.0), 2s(0.5), 2p(0.5).

Table 3. Compilation of results for CH_4

Method*	α, a.u.	γ, a.u.
FPT-*ab initio* SCF	12.68 [32]	
FPT-*ab initio* SCF	1541 [32]	
FPT-*ab initio* SCF	16.00 [6]	
FPT-*ab initio* PNO-CI	16.39 [6]	
FPT-*ab initio* CEPA	16.53 [6]	
Frost model	16.47 [33]	
FPT-*ab initio* SCF	15.83 [36]	
FPT-*ab initio* SCF-CI (7383 confs)	16.25 [35]	
FPT-*ab initio* SCF-CI (9455 confs)	16.32 [35]	
CHF-PT-*ab initio*[a]	16.08 [28]	
CHF-PT-*ab initio*[b]	15.12 [28]	
PT-EB-CNDO-CI(*EB/SP*)	20.77 [26]	
FPT-EB-CNDO	15.52±0.07 [23]	
FPT-MNDO/1	11.07 [37]	
FPT-MNDO/2	7.09 [37]	
CHF-PT-CNDO[c]	17.31, this work	2442, this work
Experiment	17.55 [26]	2886±144 [38] 3097[d] [39] 3395[e] [39] 2263[f] [40] 3133 [36]

* FPT: Finite Perturbation Theory, CHF-PT: Coupled Hartree–Fock Perturbation Theory, PT: Perturbation Theory, EB: extended Basis.

[a] Basis set containing up to *d* for C and up to *p* for H.

[b] Basis set containing up to *f* for C and up to *d* for H.

[c] The center of mass is at the center of the coordinate system-Coordinates from Ref. [42].

[d] $\bar{X}_{yyyy}(-2\omega; 0, \omega, \omega)$ as reported in Ref. [41].

[e] $\bar{X}_{yyyy}(-2\omega+\omega s; -\omega s, \omega, \omega)$ as reported in Ref [41].

[f] as reported in Ref. [34].

calculation of Eq. 4 were obtained from the V_N potential [29]. The dipole moment matrix included only the one center integrals.

It is known that a small extension of the basis set of H only can produce good values for α in saturated hydrocarbons [23]. Therefore, as a starting point, we used the basis C: $2s$, $2p$; H: $1s$, $2s$, $2p$. We varied the Slater exponents trying to find a basis set that would optimize (with respect to known experimental values) both α and γ. The best agreement was obtained for C: $2s(1.625)$, $2p(1.625)$; H(1.0), $2s(0.5)$, $2p(0.5)$. The C exponent is the standard Slater exponent while the H exponent has been used before [30]. CH_4 is a molecule for which one can afford to do relatively elaborate calculations with large basis sets. Thus, for the polarizabilities of CH_4 we have used polarization functions up to d for Carbon and up to p for Hydrogen while for the second hyperpolarizability, up to f for Carbon and up to d for Hydrogen. The results are very good (Table 2). To the best of our knowledge this is the first semiempirical study of molecules containing second row elements which uses basis sets involving f orbitals. Clementi's et al. double zeta basis set [24] (without polarization functions) has also been tried giving results very near to the experimental ones.

However, the most encouraging result was that equally good values could be obtained from a much smaller basis set. Thus the present work indicates that

Table 4. Compilation of results for C_2H_6, C_3H_6, C_3H_8

Molecule	Method*	α, a.u.	γ, a.u.
C_2H_6	Frost-model	28.41 [33]	
	PT-EB-CNDO-CI	35.90 [43]	
	CHF-PT-EB-CNDO	25.46 [22]	
	FPT-EB-CNDO	32.06 [23]	
	CHF-PT-EB-CNDO[a,b]	30.20, This work	5055, this work
	CHF-PT-EB-CNDO[c]	33.25, this work	6008, this work
	CHF-PT-EB-CNDO[d]	32.61 this work	5828, this work
	CHF-PT-CNDO[e]	33.38 this work	6047, this work
	Experiment	30.17 [23]	3849 ± 802 [44]
C_3H_6	Frost Model	38.8 [33]	
	CHF-PT-CNDO[f]	35.78, this work	6212, this work
	Experiment	38.06 [45]	8018 ± 1604 [44]
C_3H_8	FPT-EB-CNDO	48.66 ± 0.34 [23]	
	CHF-PT-CNDO[b,g]	47.78, this work	10 012, this work
	CHF-PT-EB-CNDO[h]	47.35, this work	9812, this work
	Experiment	42.45 [46]	

* The Definition of acronyms is given in Table 1.

Note: In our calculations the center of mass is located at the center of the coordinate system.

[a] Geometry from Ref [47].

[b] Fullystaggered.

[c,d] The angle between the methyl hydrogens equals to 15° and 45° respectively.

[e] fully eclipsed.

[f] Coordinates from Ref. [48].

[g] Coordinates from Ref. [31].

[h] The one methyl group is staggered and the other eclipsed.

Table 5. Conversion of a.u. to electrostatic and SI units

Property	1 a.u. equals (approx.)
α	0.148176×10^{-24} cm$^3 \simeq 0164867 \times 10^{-40}$ C^2 m^2 J^{-1}
γ	0.503717×10^{39} esu $\simeq 0.623597 \times 10^{-64}$ C^4 m^4 J^{-3}

large basis sets, such as those defined above, are certainly sufficient but not necessary. A similar conclusion (regarding the necessity of f functions in the first and second hyperpolarizability computations) has recently been reached by Christiansen and McCullough [27] and by Lazzereti and Zanasi [28].

The best small basis set for CH_4 was used in the calculations on C_2H_6, C_3H_6 and C_3H_8. Our results are presented in Tables 3 and 4 and are compared to previous theoretical and experimental numbers. No-vibrational averaging was done. We also report results which show the effect of molecular geometry on the electric properties. Both for α and γ the agreement with experiment is within the set error. It should be noted that the model was designed for the calculation of average values of polarizabilities and especially hyperpolarizabilities which can be used for the prediction of molecules with large nonlinearities. No attempt has been made to optimize the basis sets with respect to individual components of polarisabilities.

Future publications will deal with aromatics, polyenes and compounds containing a number of different atoms [51, 52]. For example, the accuracy of the present work is repeated in results on 1,3-trans-butadiene, naphthalene etc. [51]. Our γ for the butadience is 33 447 a.u. (experiment [54]: 27397 ± 1549 a.u.) and for naphthalene 60 313 a.u. (experiment [53]: 61942 ± 12 388 a.u.).

5. Synopsis

In this paper we have presented theoretical results of polarizabilities (4% average error) and second hyperpolarizabilities (28% average error) in a few alkanes. The method used is the coupled Hartree–Fock perturbation theory with Hamiltonian matrices built semiempirically at an extended CNDO level. As Tables 3 and 4 show, for α the agreement with most of the other methods is good. For γ there are no other theoretical values and our results constitute the first predictions of these properties.

An important conclusion is that a small basis set, optimized (using CH_4) with respect to the experimental values can be equally successful as larger ones which contain up to f orbitals. This finding allows the systematic study and predictions of induced moments of large molecules containing C and H without prohibitive computational requirements, as our results on polyenes and aromatics have already shown [51, 52].

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