

Calculations of induced moments in large molecules. II. Polarizabilities and second hyperpolarizabilities of some polyenes

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Coupled SCF perturbation theory has been used to calculate the polarizability α and second hyperpolarizability γ of a number of polyenes. An extended basis CNDO wave function has been employed. Our computational approach is based on optimizing the exponents of a small basis set with respect to the experimental values of α and γ of ethylene. We have chosen this scheme having considered in detail several other options. Our results are in reasonable agreement with the limited number of experimental values available for these molecules.

I. INTRODUCTION

The polarizability and hyperpolarizabilities are a measure of the ease with which the electronic charge can be distorted in the presence of a uniform electric field.¹ Thus, these properties are associated with intermolecular forces, electronic interactions within molecules, chemical reactivity, and, of course, they provide information about the electronic structure of molecules, in particular their outer region.²

Besides the above reasons, the strong interest in the second hyperpolarizability γ is due to its magnitude defining, to a large extent the suitability of a material as modulator in optical communication systems.³

The polarizability α and especially the hyperpolarizability γ of large molecules are difficult quantities to compute, particularly if one is aiming at (a) a small error in comparison with the experiment and (b) reasonably small computational effort. For example, perturbation theory methods which include electron correlation involve sums of matrix elements over excited states, but for large molecules their efficient and accurate representation is presently impossible.^{4,5}

In the light of this observation it is not surprising that very little computational work has been carried out on the γ of molecules⁶⁻⁸ apart from Hamerka's pioneering work.⁹⁻¹⁶ Thus, it is timely to develop procedures for calculating hyperpolarizabilities of large molecules.

Our approach is based on the description of a closed shell molecule by a single determinant wave function. A small, properly optimized basis set is used. The integrals are treated according to the CNDO approximations.¹⁷ The effect of the external field is computed by employing McWeeny *et al.*¹⁸⁻²⁰ coupled SCF perturbation theory.

Several options have been considered which could make our approach more flexible, economical, and reliable. Thus, we have carried out extensive "computational experimentation" regarding:

(1) *The semiempirical parameters.* The importance of the parameters entering any semiempirical method is crucial. Thus, we investigated whether or not we

should modify those employed in the standard CNDO theory.

(2) *The virtual molecular orbitals.* The Hartree-Fock virtual MOs are known to be physically wrong,^{21,22} Yet, they are very important in any perturbation theory calculation. Thus, several recipes which produce physically meaningful virtual MOs were studied.

(3) *The dipole moment integrals.* Strictly speaking, even the use of off-diagonal, one-center dipole moment integrals violates the ZDO approximation. Nevertheless, since they are important we considered the option of including two-center dipole moment integrals.

(4) *The use of double-zeta basis sets and their approximation by single-zeta ones.* Double-zeta functions have an extra flexibility, compared to single zetas, which is very useful in polarizability calculations.²³ Thus, we considered the effect of double-zeta sets and their approximation by single zetas.

(5) *The basis set.* The specification of an economical and yet reliable basis set is of vital importance in any calculation. Basis sets including up to *f* orbitals for carbon and up to *d* for hydrogen were studied. A procedure for optimizing a small basis set is proposed. Optimization and standardization of the basis set, for a series of structurally similar compounds, seems to offer a reasonable approach for taking into account, correlation effects of importance for γ .^{6,7}

II. PREVIOUS CALCULATIONS OF α AND γ FOR THE POLYENES

Methods which have been applied to ethylene and which could not be considered applicable to large molecules—at least in terms of computer time and core storage—are beyond the scope of this section.

A. Polarizabilities

Amos and Hall²⁴ calculated the polarizabilities of *trans*-butadiene and *trans*-hexatriene by employing SCF perturbation theory for the π electron contribution, while the σ contribution was estimated from empirical bond polarizabilities. The σ - π interaction was ne-

glected. Hameka's group has applied the VPT-PPP¹⁴ and PT-Hückel¹⁴ methods. Meyer and Schweig²⁵ applied FPT-MNDO/2, while Shinoda and Akutagawa²⁶ used PT-CNDO-CI on C₂H₄ (for explanation of some acronyms see footnotes of Table X).

B. Second hyperpolarizabilities

Hameka *et al.* investigated several polyenes employing: (i) VPT-PPP,¹⁵ (ii) PT-Hückel,³ and (iii) a combination of PPP and extended Hückel.¹⁶ According to this method the π electron contribution is given by a PPP calculation while the σ and σ - π contribution by the extended Hückel.

III. THEORETICAL BACKGROUND

McWeeny *et al.*¹⁸⁻²⁰ have developed a projection operator method to solve the perturbed Hartree-Fock equations. This theory deals directly with the density matrix without involving the intermediate calculation of perturbed orbitals.

The main objective of this section is to review the basic formulas used in our calculation of α and γ and to comment on the rate determining step in the computations.

The energy of a closed shell molecule described by a single determinant and perturbed by a uniform electric field F is given by^{2,18-20}

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

$$= 2 \text{tr} R[f + \frac{1}{2} G(R)] = \text{tr} R(f + h), \quad (2)$$

where $E(F)$ is the perturbed electronic energy, $E^{(0)}$ is the unperturbed electronic energy, μ_{α} is the α component of the permanent dipole moment, $\alpha_{\alpha\beta}$ is the $\alpha\beta$ component of the polarizability, $\beta_{\alpha\beta\gamma}$ is the $\alpha\beta\gamma$ component of the first hyperpolarizability, $\gamma_{\alpha\beta\gamma\delta}$ is the $\alpha\beta\gamma\delta$ component of second hyperpolarizability, R is the density matrix, f is the "framework" Hamiltonian, $G(R)$ is the electron interaction matrix, and h is the Hartree-Fock Hamiltonian. α , β , γ , δ : the Greek suffices denote Cartesian components. For the expansion of f , h , R , and $G(R)$ one uses the relation

$$M = M^{(0)} + (aM^{\alpha} + bM^{\beta} + \dots) + (a^2 M^{\alpha\alpha} + b^2 M^{\beta\beta} + abM^{\alpha\beta} + \dots), \quad (3)$$

where M is a general square matrix and a and b correspond to electric field components.²⁰ The CNDO approximations are used for the definition of the Hartree-Fock Hamiltonian.^{17,26} For the term V_{AB} of the framework Hamiltonian we introduce the approximation

$$(V_{A2sB} + V_{A2pB})/2,$$

when the exponents of $2s$ and $2p$ on atom A are different.

We define $R_1 = R^{(0)}$ and $R_2 = 1 - R^{(0)}$ ¹⁸, where $R^{(0)}$ is the unperturbed density matrix, thus employing the identity

$$M = R_1 M R_1 + R_1 M R_2 + R_2 M R_1 + R_2 M R_2 = M_{11} + M_{12} + M_{21} + M_{22}, \quad (4)$$

we resolve the matrix M into its four projected parts.

We make use of this relation to resolve the first and second order correction to the density matrix into their projections:

$$R^{(1)} = x + x^*, \quad x = R_{12}^{(1)}, \quad (5)$$

$$R^{(2)} = -xx^* + y + y^* + xx^*, \quad y = R_{12}^{(2)}. \quad (6)$$

On the other hand, x and y can be expressed as sums of terms which may be determined independently²⁰:

$$x = ax_{\alpha} + bx_{\beta} + \dots, \quad (7)$$

$$y = a^2 y_{\alpha\alpha} + b^2 y_{\beta\beta} + \dots + aby_{\alpha\beta} + \dots. \quad (8)$$

It has been found that²⁰

$$x_{\alpha} = \sum_{k(\text{occ})} \frac{C_k^* [f^{\alpha} + G(R^{\alpha})] C_l}{\epsilon_k - \epsilon_l} C_k C_l^*, \quad (9)$$

$$y_{\alpha\alpha} = \sum_{k(\text{occ})} \frac{C_k^* [h^{\alpha\alpha} + x_{\alpha} h^{\alpha} - h^{\alpha} x_{\alpha}] C_l}{\epsilon_k - \epsilon_l} C_k C_l^*, \quad (10)$$

$$y_{\alpha\beta} = \sum_{k(\text{occ})} \frac{C_k^* [h^{\alpha\beta} + x_{\alpha} h^{\beta} + x_{\beta} h^{\alpha} - h^{\alpha} x_{\beta}] C_l}{\epsilon_k - \epsilon_l} C_k C_l^*, \quad (11)$$

where C_k is the k th unperturbed eigenvector, ϵ_k is the k th unperturbed eigenvalue, f^{α} is the dipole moment matrix in the α direction, and h^{α} , $h^{\alpha\alpha}$, and $h^{\alpha\beta}$ are terms in the expanded h matrix Eq. (3).²⁰ x_{α} , $y_{\alpha\alpha}$, and $y_{\alpha\beta}$ are calculated iteratively until self-consistency is achieved. The rate-determining step is the calculation of $y_{\alpha\beta}$. On average it needs 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 was performed in single precision on a 32 bit computer.

Considering Eq. (1), we observe that the polarizability and hyperpolarizability components are defined as derivatives of the energy with respect to the field. Thus, they are given in terms of the relevant energy orders for which expressions have been derived²⁰:

$$\alpha_{\alpha\alpha} = -2E^{\alpha\alpha}, \quad (12)$$

$$\gamma_{\alpha\alpha\alpha\alpha} = -24E^{\alpha\alpha\alpha\alpha}, \quad (13)$$

$$\gamma_{\alpha\alpha\beta\beta} = -4E^{\alpha\alpha\beta\beta}. \quad (14)$$

$E^{\alpha\alpha}$, $E^{\alpha\alpha\alpha\alpha}$, and $E^{\alpha\alpha\beta\beta}$ are expressed in terms of x_{α} , $y_{\alpha\alpha}$ and $y_{\alpha\beta}$.

The average values for α and γ are given by²

$$\alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}), \quad (15)$$

$$\gamma = \frac{1}{15}(\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\gamma_{xxyy} + 2\gamma_{xxzz} + 2\gamma_{yyzz}). \quad (16)$$

The number of independent components with which one needs to specify α and γ are related to the symmetry of the molecule.

For the molecules we have studied all three components of α and all six components of γ had to be calculated.

IV. CHOICE OF COMPUTATIONAL APPROACH

The first important choice concerns the selection of the appropriate semiempirical theory by which the wave function is calculated. Our choice was CNDO/2¹⁷ based on the following considerations:

(a) It is an all valence electron theory, known to satisfactorily reproduce dipole moments.²⁷

(b) The program¹⁷ (QCPE 141) can be used for open as well as closed shell molecules, includes d orbitals, is computationally inexpensive and readily extendable as it is not heavily reliant on optimized parameters.

Ethylene was chosen as the test molecule on which the extensive basis set optimization was carried out. Because of its size it is feasible to perform numerous calculations to elucidate the importance of the already defined variants. Also it could be considered as representative of the hydrocarbons which present interesting nonlinearities, being akin to aromatics and serves as a model compound for the polyenes.

A goal of better than 30% error for γ was set. This is a reasonable degree of accuracy since the derived information from experiment may be uncertain due to dispersion,²⁸ geometrical averaging, and other effects by more than 20%. For α , an error up to 15% could be tolerated although the error usually is much smaller.^{29,30}

A. Parameters

The following parametric methods were studied:

(i) Variation of k that premultiplies the bonding parameter¹⁷:

- (a) k for occupied-occupied orbital interaction = 1,
 k for virtual-virtual orbital interaction = 0.2,
 k for occupied-virtual orbital interaction = 0.6.²⁶
- (b) For all p_i -type interactions the value of k proposed

TABLE I. Average ionization potentials I_μ for atomic vacant orbitals (eV).^a

Atom	Orbital	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

^aReference 37.

TABLE II. Effect of the Coulomb integrals, evaluated by various empirical relationships, on α and γ of C_2H_4 . Basis set C: 2s(1.1), 2p(1.1); H: 1s(0.9), 2s(0.37), 2p(0.37).

Method	α (a.u.)	γ (a.u.)
Pople <i>et al.</i> ^a	28.35	9032
Mataga-Nishimoto ^b	38.24	25515
Ohno-Klopman ^b	31.32	12160
Pariser-Parr ^b	29.45	9278

^aThe Coulomb integrals are over s functions evaluated according to formula given in Ref. 17.

^bReference 27.

by Jaffe *et al.*³¹ for the other interactions the values 0.2 (virtual-virtual) and 0.3925 (occupied-virtual) were used.

(c) k as defined in (a) and multiplied by 0.5 and 2.0 (Table III).

(ii) Empirical methods for evaluating the Coulomb integrals, namely, (a) Pariser-Parr,²⁷ (b) Ohno-Klopman,²⁷ and (c) Mataga-Nishimoto²⁷ were tried in addition to the original analytic formulation implemented by Pople *et al.*¹⁷ (Table II).

(iii) Variation of ionization potentials I_μ and electron affinities A_μ by multiplying those defined by Pople *et al.*¹⁷ and their extensions to d and f orbitals by 0.5, 0.75, 1.50, and 2.0 are given in Table IV.

The detailed study indicated that a balanced modification of the parameters would require extensive experimentation, particularly if one wants to describe both α and γ with a unique basis; furthermore, our model would have too many variables (basis set and parameters). Thus, when it became clear, after numerous computations, that a careful specification of the basis set only would be sufficient for a reasonably accurate determination of α and γ we did not proceed further with the optimization of a new set of parameters. So in what follows the standard CNDO/2 parameters¹⁷ with the generalized integral package (QCPE 261) and the extensions proposed in Ref. 26 are employed. The optimization of a new set of parameters was left as an option for future investigation.

TABLE III. Effect of the bonding parameter, β on α and γ of C_2H_4 . Basis set C: 2s(1.1), 2p(1.1); H: 1s(0.9), 2s(0.37), 2p(0.37).

Method	α (a.u.)	γ (a.u.)
a	28.35	9032
b	23.47	4401
c	34.54	15472
d	26.57	7625

^a k , the premultiplying factor of β , is defined as in Ref. 26.

^b k as defined in (a) and multiplied by 2.0.

^c k as defined in (a) and multiplied by 0.5.

^dJaffé's k is employed, see the text.

TABLE IV. Effect of the variation of I_μ and A_μ on α and γ of C_2H_4 , Basis set C; $2s(1,1)2p(1,1)$; H; $1s(0,9)$, $2s(0.37)$, $2p(0.37)$.

C^a	α (a. u.)	γ (a. u.)
0.5	27.11	7831
0.75	27.72	8401
1.0	28.35	9.032
1.25	29.77	10499
1.5	31.35	12316

^aC multiplies the $\frac{1}{2}(V_\mu + A_\mu)$, see the text and Ref. 17.

B. V^{N-1} and two-center dipole moment integrals

It is well known that an electron in a virtual orbital, produced by a Hartree-Fock calculation, is in a potential of N instead of $N-1$ electrons.^{21,22} There are several methods designed to remedy this deficiency. We have implemented the Fermi-Amaldi potential²² and the Goddard-Hunt²¹ and considered the case whereby the virtual orbitals of the neutral molecule are replaced by those of its positive ion.³² Obviously these virtuals describe excited electrons in an $N-1$ electrons potential.

After several computations the use of these potentials was abandoned because they behaved non-smoothly. That is on adding the potential to the Hartree-Fock operator the value of the second hyperpolarizability can become positive or negative.

For similar reasons we have abandoned the further use of the two-center dipole moment integrals.

C. Approximation of double-zeta basis sets by single-zeta ones

We have approximated double-zeta functions³³ by single-zeta ones using the maximum overlap principle.^{34,35} The required exponent of the single-zeta function was found by minimizing V ,

$$V = \int \left[\psi(\xi) - \sum_i C_i \phi_i \right]^2 d\tau.$$

TABLE V. Effect of (a) the V^{N-1} , (b) the two-center dipole moment integrals, and (c) the application of the maximum overlap principle on α and γ of C_2H_4 .

C		H			α (a. u.)	γ (a. u.)
Exponents of		Exponents of				
2s	2p	1s	2s	2p		
1.625	1.625	1.2	7.66	79
1.625	1.625 ^a	1.2	16.37	-252
1.625	1.625 ^b	1.2	14.67	-127
1.625	1.625 ^c	1.2	9.76	-50
1.55	1.325	1.2	0.877	0.877	32.43	3344
1.55	1.325 ^d	1.2	0.377	0.877	122.4	-5688
Clementi's double zeta		0.7	0.35	0.35	32.64	11754
Clementi's double zeta ^e		0.7	0.35	0.35	33.27	11547

^a V^{N-1} produced by the Fermi-Amaldi potential.

^b V^{N-1} produced by the Goddard-Hunt method.

^c V^{N-1} produced by the positive ion method, see the text.

^dWith one- and two-center dipole moment integrals.

^eClementi's double-zeta basis (Ref. 33) contracted by the maximum overlap principle, see the text.

TABLE VI. Polarizabilities of C_2H_4 .

C			H			α (a. u.)
Exponents of			Exponents of			
2s	2p	3d	1s	2s	2p	
1.1	1.1	...a	0.9	0.37	0.37	28.35
1.325	1.325	...b	0.7	...	0.35	27.35
1.325	1.325	...	0.8	0.4	0.4	28.71
1.5	1.5	1.8	1.2	...	0.877	27.35
1.625	1.625	...	0.76	0.304	0.304	29.04
1.625	1.625	1.08 ^c	1.2	0.6	0.6	28.38
2.0	2.0	...d	0.9	0.45	0.45	28.73
2.0	2.0	1.33	1.0	0.5	0.5	29.23
Experiment						28.48 ^e

^aSlightly modified Kitaura's *et al.* exponents (Ref. 38).

^bOne of Burn's exponents (Ref. 39).

^cSlater's exponents (Ref. 17), $1.08 = Z \text{ eff}/n$, where $Z \text{ eff}$ is the effective nuclear charge and n is the principal quantum number.

^d $2.0 = Z \text{ eff}/n$, where $Z \text{ eff} = 4.0$.

^eReference 48.

The introduced error was 1.8% for α and 1.9% for γ .

This result is particularly encouraging since it implies that single-zeta basis sets contain sufficient flexibility—at this level of approximation—for proper optimization (Table V).

D. Basis sets

The choice of the basis set is the most important element in our approach. Thus, we have carried out a large number of computations in which orbitals of various symmetries and exponents have been used. Detailed analysis of the results indicated that high l AOs like f orbitals for carbon and d orbitals for hydrogen were sufficient (they can lead to reasonable results) but not necessary (Tables VI, VII); although perturbation theory on atomic orbitals suggests that these high l orbitals should be included in the calculation of γ . The redundancy of f orbitals has also been noted by Christiansen and McCullough.⁸

TABLE VII. Hyperpolarizabilities of C₂H₄.

C				H				γ (a. u.)
Exponents of				Exponents of				
2s	2p	3d	4f	1s	2s	2p	3d	
1.0	1.0	0.667	0.5	0.8	0.4	0.4	0.267	10641
1.045	1.045	0.9	0.9	0.9	...	8938
1.06	1.06	0.9	0.45	0.45	...	9182
1.2	1.2	0.8	0.6	0.8	0.4	0.4	0.267	8398
1.325	1.325	0.983	0.662	0.8	0.4	0.4	0.267	7650
1.625	1.625	0.76	0.38	0.38	...	8724
2.0	2.0	0.8	0.4	0.4	...	9041
Zeiss <i>et al.</i> (Ref. 23) expansion ^a								12368
Experiment								9029 ± 202 ^b
								10482 ± 2621 ^c
								-641 ± 4009 ^d

^aZeiss *et al.* (Ref. 23) multi-zeta expansion of polarization functions [using Burn's rules (Ref. 39) for carbon and exponent 1.0 for hydrogen].

^bdc-induced second harmonic generation, 694 nm, gas phase (Ref. 28).

^cThird harmonic generation, 694 nm, gas phase (Ref. 28).

^dKerr effect, 633 nm, gas phase (Ref. 40).

It was very encouraging to find that by judicious choice of the exponents ζ and extensions on H to 2s and 2p alone we can get the required results. Some of these results are given in Table VIII. We also observed the large effect of the 2s in conjunction with the 2p (Table IX).

It has been found that the relationship of α or γ with ζ_{H} or ζ_{C} depends on the basis set and the molecule.⁴⁹ For the molecules we have investigated (which include hydrogen bonded to C or N⁴⁹ CH₄, C₂H₆, C₂H₄, C₈H₈, NH₃) the curve of α or γ vs ζ_{C} has a minimum (Fig. 1), while no minimum has been observed in the above series of compounds, for the variation of α or γ with ζ_{H} (Fig. 2). On the other hand, for molecules which do not include hydrogen [we have studied (CN)₂ and N₂] the shape of the curve of α or γ vs ζ depends on the basis set and does not follow the abovementioned trend.⁴⁹

The figures, besides being useful for the optimization of the basis set as will be seen below, also illustrate some aspects of the model of the molecule which is defined by the wave function we use. Thus, Fig. 1 indicates that as the size of the carbon atoms decrease

with the change in ζ_{C} ,⁵⁰ γ of C₂H₄ decreases. After a certain point which corresponds to the minimum of γ (or α) vs ζ_{C} the further screening of the carbon nuclei allows the hydrogens electrons to polarize more easily since the bond between C and H weakens, ζ_{H} remains constant. However, Fig. 2 indicates that γ (or α) decreases as the size of the hydrogen atoms decreases ζ_{C} remains constant.

To obtain the exponents to be used in calculating α and γ for a series of molecules the approximation that $\zeta_{2s} = \zeta_{2p} = \frac{1}{2} \zeta_{1s}$ for H was initially made. Thus, the variants are ζ_{C} and ζ_{1s} for H. However, the above approximation can be (and has been³⁰) removed if the optimization of the basis set, incorporating this restriction, fails to give good results.

Two suitable model compounds (test cases A and B), representative of the series to be studied and whose experimental α and γ values are known were chosen.

From plots of exponents with properties, values of ζ_{C} and ζ_{H} that adequately reproduce the experimental values of the properties of test case A, are obtained. These are then used to compute α and γ of test case B. Depending on whether these values are too high or too low and consideration of the curves obtained from test case A a new basis may be found that gives α and γ for both models A and B within the prescribed limits.

TABLE VIII. Polarizabilities and hyperpolarizabilities of C₂H₄.^a

C		H			α (a. u.)	γ (a. u.)
Exponents of		Exponents of				
2s	2p	1s	2s	2p		
1.045	1.045	0.9	0.45	0.45	32.53	9578
1.06	1.06	0.9	0.45	0.45	32.0	9182
1.1	1.1	0.9	0.37	0.37	28.35	9032
1.325	1.325	0.8	0.4	0.4	29.71	8263
1.625	1.625	0.76	0.38	0.38	30.71	8724
2.0	2.0	0.8	0.4	0.4	32.02	9041
2.0	2.0	0.91	0.405	0.405	31.51	8687

^aThe experimental results are given in Tables VI and VII.

TABLE IX. Effect of 2s and 2p of H on α and γ of C₂H₄.

C		H			α (a. u.)	γ (a. u.)
Exponents of		Exponents of				
2s	2p	1s	2s	2p		
1.625	1.625	0.76	9.10	206
1.625	1.625	0.76	0.38	...	14.21	650
1.625	1.625	0.76	...	0.38	23.23	928
1.625	1.625	0.76	0.38	0.38	30.71	8724

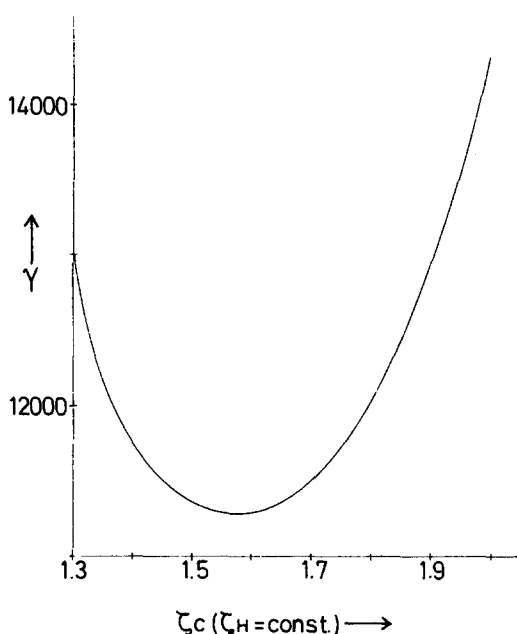


FIG. 1. Plot of γ against ζ_c of C_2H_4 (H: $1s(0.7)$, $2s(0.35)$, $2p(0.35)$).

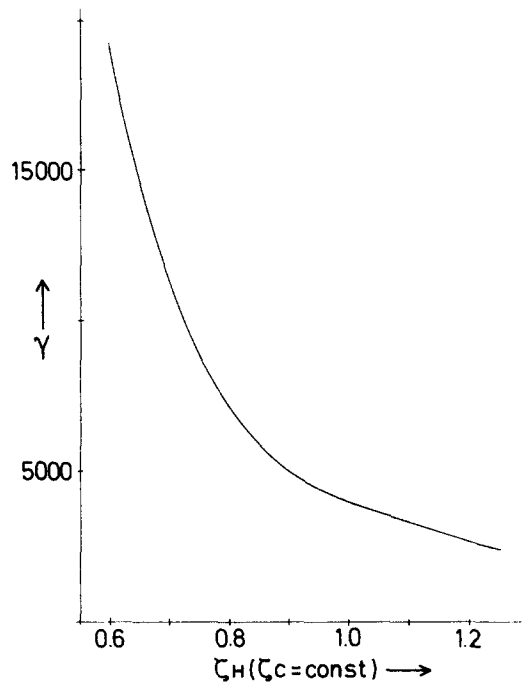


FIG. 2. Plot of γ against ζ_H of C_2H_4 (C: $2s(1.625)$, $2p(1.625)$).

TABLE X. Polarizabilities of some polyenes, in a. u.

No.	Molecule ^a	This work	Other calculations	Method ^b	Experiment
1	Ethylene	29.71	22.94 ^{25c} 30.31 ^d	FPT-MNDO/1 PT-CNDO/1	28.48 ^e
2	Cyclopropene	35.85			
3	Allene	48.16			
4	1,3- <i>cis</i> -butadiene	61.68			
5	1,3- <i>trans</i> -butadiene	69.73	61.91 ^g 32.08 ^f 59.06 ^f	SCF-PT VPT-PPP PT-Hückel	
6	Butatriene	63.19			
7	Cyclobutadiene	50.65			
8	Cyclopentadiene	80.62			
9	1,3,5- <i>cis</i> -hexatriene	120.21			
10	1,3,5- <i>trans</i> -hexatriene	128.19	105.91 ^f 72.99 ^f 165.93	SCF-PT VPT-PPP PT-Hückel	
11	1- <i>cis</i> -octatetraene	188.77			
12	3- <i>cis</i> -octatetraene	189.28			
13	<i>cis</i> -transoid-octatetraene	181.29			
14	<i>Trans</i> -cisoid-octatetraene	167.09			
15	<i>Trans</i> -octatetraene	203.81	131.92 ^f 355.66 ^f	VPT-PPP PT-Hückel	
16	Cyclo-octatetraene	129.67			

^aThe geometries are defined in 1: Ref. 41, 2: Ref. 42, 3: Ref. 43, 4: Ref. 44, 5: Ref. 44, 6: Ref. 43, 7: Ref. 45, 8: Ref. 46, 9: Ref. 44, 10: Ref. 44, 11: Ref. 44, 12: Ref. 44, 13: Ref. 44, 14: Ref. 44, 15: Ref. 44, 16: Ref. 47.

^bPPT: perturbation theory; FPT: finite perturbation theory; VPT: variation perturbation theory.

^cReference 25.

^dReference 26.

^eReference 24.

^fReference 14.

^gReference 48.

TABLE XI. Second hyperpolarizabilities of some polyenes (in a. u.).

No.	Molecule ^b	This work	Other calculations	Method	Experiment
1	Ethylene	8 263	- 336 ^o 5956	PPP-ext. Hückel a	9 029 ± 202 ^b
2	Cyclopropene	11 168			
3	Allene	15 300			
4	1,3- <i>cis</i> -butadiene	26 121			
5	1,3- <i>trans</i> -butadiene	33 447	- 3 752 ^f 16 021 ^g 11 912	PT-Hückel PPP-ext. Hückel a	27 397 ± 1549 ^c
6	Butatriene	27 250			
7	Cyclobutadiene	41 149			
8	Cyclopentadiene	60 675			
9	1,3,5- <i>cis</i> -hexatriene	65 749			
10	1,3,5- <i>trans</i> -hexatriene	72 137	- 12 024 ^f 118 166 ^g 19 059	PT-Hückel PPP-ext. Hückel a	89 696 ± 8 338 ^d
11	1- <i>cis</i> -octatetraene	117 299			
12	3- <i>cis</i> -octatetraene	114 123			
13	<i>Cis</i> -trensoid-cotatetraene	106 142			
14	<i>Trans</i> - <i>cis</i> oid-octatetraene	99 988			
15	<i>Trans</i> -octatetraene	124 313	- 24 973 ^f 817 272 ^g	PT-Hückel VPT-PPP	
16	Cyclooctatetraene	101 494			

^o σ -electron contribution based on bond additivity (Ref. 28).

^bFor more experimental results see Table VII (Ref. 28).

^cGas in which the *cis*-isomer is less than 1% and the *trans* more than 99% (Ref. 28).

^dGas in which the *cis*-isomer is 10%–40% and the *trans* 90%–60% (Ref. 28).

^eReference 15.

^fReference 11.

^gReference 16.

^hFor the geometries of the molecules see footnotes of Table X.

Although certain well known sets of exponents (Tables VI–VIII) have been tried, like Slater's¹⁷ and Burns',³⁹ in general, we vary the orbital exponent on C and H until the experimental values of the reference compounds are properly described. Automatic ways of optimizing the exponents⁵¹ have not been used because they were found to be computationally time consuming.

Our calculations up to now indicate that it is possible to use one basis for α and γ . Sometimes, though, it seems preferable, e.g., in terms of computational cost, to use different basis for α and γ instead of optimizing a single basis set for both.³⁰ The final decision, whether the same basis will be used to describe α and γ or not for a series of molecules is made only when various aspects of the problem, like the rate of change of α and γ throughout the series of molecule, are considered.

As has been stated, we need two molecules in order to calibrate the wave function from which the polarizability and hyperpolarizabilities of a series will be predicted. However, due to scarcity of experimental values of hyperpolarizabilities, data for two molecules may not

have been published, so we consider other relevant information like the dipole moments.

It is further noted that if a study of the change in α and/or γ with rotation, vibration, etc. for a given molecule is of interest, a basis set optimized to this compound alone, within more stringent limits may be obtained, e.g., for ethylene the basis H: 1s(0.9), 2s(0.37), 2p(0.37); C: 2s(1.1), 2p(1.1) is proposed.

Finally, the proposed optimized basis set corresponds to a given set of parameters.^{17,26} If the parameters are modified the basis set has to be reoptimized.

E. Improvement of the rate of convergence

The extrapolation scheme of Dewar³⁶ was implemented

TABLE XII. Conversion of a. u. to electrostatic and SI units.

Property	1 a. u. equals (approx.)
α	$0.148\,176 \times 10^{-24} \text{ cm}^3 \approx 0.164\,867 \times 10^{-40} \text{ C}^2 \text{ m}^2 \text{ J}^{-1}$
γ	$0.503\,717 \times 10^{-39} \text{ esu} \approx 0.623\,597 \times 10^{-64} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$

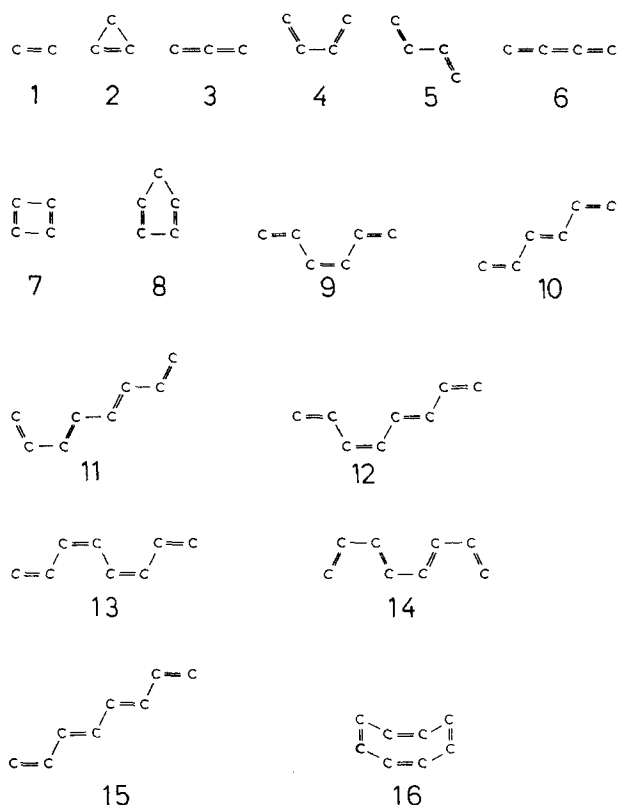


FIG. 3. Structure of the molecules that were considered.

in both the SCF and CHF perturbation theory procedures to improve the rate of convergence.

V. APPLICATIONS

Polyenes were chosen as a family of molecules with interesting nonlinearities^{3,15} where our approach could be illustrated. Ethylene was chosen as model A and 1,3,5-*trans*-hexatriene as model B. The best basis for C₂H₄, i. e., H: 1s(0.9), 2s(0.37), 2p(0.37); C: 2s(1.1), 2p(1.1) failed to give γ for hexatriene within the defined limits of accuracy.

So the second best i. e., H: 1s(0.8), 2s(0.4), 2p(0.4); C: 2s(1.325), 2p(1.325) was tried. The results are very good (Table XI). The idea of using two models i. e., case A as a reference compound where the basis set is optimized and case B for checking it, helps to eliminate any unbalanced basis sets which might be successful for one molecule but may fail for others.

Ward *et al.*²⁸ have measured γ of ethylene, butadiene, and hexatriene, in the gas phase, using dc-induced second harmonic generation. Their sample for butadiene and hexatriene was a mixture of *cis* and *trans*. We have calculated the γ of *cis* and *trans* forms in order to find out which isomer contributes more. Our results show that the *trans* form contributes more (Table XII). For an extension and verification of this finding we carried out computations for the various isomers of octatetraene.

Here as well the all-*trans* form has the highest electric properties.

Since our results agree well with the available experimental data, we think that it is useful to predict α and γ for a few other polyenes (Tables X and XI).

VI. CONCLUSION

Our approach is based on optimizing the exponents of a small set of STOs with respect to the experimental values of α and γ of a suitably chosen compound.

This basis set is then used to calculate α and γ for a series of structurally similar compounds. Our results for γ of ethylene, butadiene, and hexatriene have on average an error of 20%; since no other experimental values are available it is hard to estimate the overall error. Nevertheless, considering our approach has given good results for α and γ of some alkanes and aromatics, we hope the reported polarizabilities and second hyperpolarizabilities, for which no experimental values are available, are reasonable.

Our method relies on CNDO parameters and optimized basis functions so it is semiempirical in nature. However given that this procedure produces good results for a whole series of molecules we believe that it has general validity.

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