

$\pi$ -ELECTRON HYPERPOLARIZABILITY OF EVEN-NUMBERED POLYENES  
IN THE COMPLETE CONFIGURATION INTERACTION METHOD

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It has been established that the second hyperpolarizability of short polyenes with 2-10 carbon atoms increases in proportion to  $N^{3.95}$  in the complete configuration interaction method, and in proportion to  $N^{5.97}$  in the restricted Hartree-Fock method.

The development of polymeric materials with high, nonlinear optical susceptibility has placed before theoreticians a problem that is not at all trivial: determination of how the higher-order polarizabilities vary with the dimensions of the region of  $\pi$ -conjugation in extended molecular systems. Even though much work has been published in this area (see review in [1]), the extremely complicated situation has not been ultimately resolved, since the studies that have been reported do not give adequate consideration to electron correlation effects. The work reported here was aimed at determining the dependence of the  $\pi$ -component of hyperpolarizability  $\alpha^{(3)}$  on the length of the conjugation chain in even-membered polyenes by the most rigorous  $\pi$ -electron method, i.e., the method of complete configuration interaction (CCI) of all possible  $\pi$ -states in the LCAO approximation. Also entering into our task was a comparison of exact values of  $\alpha^{(3)}$  with values calculated within the framework of the coupled perturbation theory (CPT) of the restricted Hartree-Fock (HRF) method.

The calculations were performed by the finite field method. In the CCI and RHF models, the Gell-Mann-Feynman theorem is observed, and hence the polarizabilities can be calculated as the corresponding derivatives of the energy (E) or the field-induced dipole moment (d) with respect to the field. We will estimate the accuracy of these two approaches, while following the procedure of [2, 3]. To this end, we will represent the energy and the dipole moment in the form of Taylor series expansions with respect to the perturbation h:

$$E(h) = E(0) - d_i h_i - \frac{\alpha_{ij}^{(1)} h_i h_j}{2!} - \frac{\alpha_{ijk}^{(2)} h_i h_j h_k}{3!} - \frac{\alpha_{ijkl}^{(3)} h_i h_j h_k h_l}{4!}, \quad (1)$$

$$d_i(h) = d_i(0) - \alpha_{ij}^{(1)} h_j - \frac{\alpha_{ijk}^{(2)} h_j h_k}{2!} - \frac{\alpha_{ijkl}^{(3)} h_j h_k h_l}{3!}, \quad (2)$$

where the summation pertains to the repeating indexes, with the tensor indexes i, j, ... assuming the values x, y, z. We will denote as  $\Delta$  the relative errors of the calculated values. Then, assuming that the accuracy in calculating the total energy  $\Delta(E)$  is independent of h and that the error in calculating d is equal to the error  $\Delta(P)$  in the elements of the density matrix (P), we obtain an approximate evaluation of the errors of computation in (1) and (2)

$$\delta_E = \Delta(\alpha^{(M)}) \simeq \Delta(E) (M+1)! / h^{M+1}, \quad \delta_P = \Delta(\alpha^{(M)}) \simeq \Delta(P) M! / h^M. \quad (3)$$

For the usual variation calculations,  $\Delta(E) \simeq (\Delta P)^2$ ; and from the relationships (3) the advantage of determining the M-th polarizability by means of the energy becomes obvious. When we apply to (1) and (2) certain numerical differentiation formulas of [4], for example with respect to seven values of the functions, we obtain for the diagonal components of the tensor  $\alpha^{(3)}$  the expression

$$\alpha^{(3)} = \frac{1}{6h^4} [-E(-3h) - E(3h) + 12\{E(2h) + E(-2h)\} - 39\{E(h) + E(-h)\} + 56E(0)] + \frac{7}{240} \alpha^{(7)} h^{(4)} + O(h^6), \quad (4)$$

$$\alpha^{(3)} = \frac{1}{8h^3} [d(-3h) - d(3h) + 8\{d(2h) + d(-2h)\} + 13\{d(-h) - d(h)\}] + \frac{7}{120} \alpha^{(7)} h^{(4)} + O(h^6). \quad (5)$$

Since the errors accumulate in the summation and computation, we can write

$$\delta_E \simeq 26.7\Delta(E) h^{-4} + 0.03\alpha^{(7)} h^4, \quad (6)$$

$$\delta_P \simeq 5.5\Delta(P) h^{-3} + 0.06\alpha^{(7)} h^4. \quad (7)$$

The optimal magnitude of the perturbation is found from (6) and (7) by equating the derivatives with respect to  $h$  to zero:

$$h_{\text{opt}} \simeq 2.34\Delta(E)^{1/8} (\alpha^{(7)})^{-1/8}, \quad (8)$$

$$h_{\text{opt}} \simeq 1.84\Delta(P)^{1/7} (\alpha^{(7)})^{-1/7}. \quad (9)$$

By substituting (8) into (6) and (9) into (7), we obtain the minimum possible error

$$\delta_E \simeq 1.76\Delta(E)^{1/2} (\alpha^{(7)})^{1/2}, \quad (10)$$

$$\delta_P \simeq 1.55\Delta(P)^{4/7} (\alpha^{(7)})^{3/7} \cdot \delta_P. \quad (11)$$

Now we will divide the error with respect to energy (10) by the error with respect to the density matrix (11):

$$\delta_E \simeq 1.14\Delta(E)^{1/2} \Delta(P)^{-4/7} (\alpha^{(7)})^{1/14} \cdot \delta_P.$$

We will take as typical values  $\Delta(E) = 10^{-14}$  and  $\Delta(P) = 5 \cdot 10^{-8}$ , and we will estimate  $\alpha^{(7)}$  from the Hückel approximation for ethylene:

$$\alpha^{(7)} = 1575l^8 \cdot 128\beta^7,$$

where  $\beta$  is the resonance integral of the bond;  $l$  is the bond length. We will set  $l = 1.4 \text{ \AA}$  and  $\beta = -2.274 \text{ eV}$ ; then  $\alpha^{(7)} = 1.04 \cdot 10^{12} \text{ au}$ . After increasing this last result by five orders of magnitude as a safety factor, we find the ratio between errors for the polyenes

$$\delta_E \simeq 0.03\delta_P.$$

It can be seen that even with extremely favorable assumptions, the calculation of hyperpolarizability on the basis of energy leads to an error that is two orders of magnitude smaller than when the calculation is based on the dipole moment, even though in the latter case the formula that is used is for a derivative that is one order lower.

Specific calculations of  $\alpha^{(3)}$  were performed in the same system of semiempirical parameters I from [5], where the dependence of  $\alpha^{(1)}$  on the conjugation chain length was investigated. Solution of the CCI equations was accomplished by the wave operator method [6, 7] in a two-step gradient method, with an accuracy of the norm of the gradient  $5 \cdot 10^{-8}$ . Calculations in the Hartree-Fock approximation were performed by a cyclic procedure for obtaining self-consistency with gradient acceleration [8], also with an accuracy of  $5 \cdot 10^{-8}$  with respect to the density matrix. The excitation parameter, according to Eq. (8), was  $0.000972 \text{ au}$  ( $0.05 \text{ eV/\AA}$ ). The error for the diagonal components of the tensor  $\alpha^{(3)}$  was a few atomic units.

Before we proceed to examine the dependence of  $\alpha^{(3)}$  on the length of the polyene chain, let us dwell on the simplest case of a  $\pi$ -system, namely ethylene. The analytical expression that we found in the CCI method for the longitudinal xxx component of  $\alpha^{(3)}$  has the form (in atomic system of units)

$$\alpha_{xxx}^{(3)}(S_0) = \frac{48\beta^2 l^4 (\Gamma^3 + 4\Gamma\beta^2 - \beta^2 \sqrt{\Gamma^2 + 4\beta^2})}{(\Gamma^2 + \Gamma \sqrt{\Gamma^2 + 4\beta^2} + 4\beta^2)^2}.$$

$$\alpha_{xxxx}^{(3)}(S_1) = -\frac{3\Gamma l^4 (\Gamma^4 + 5\Gamma^2\beta^2 + 4\beta^4)}{\beta^6 (4\beta^2 + \Gamma^2)},$$

$$\alpha_{xxxx}^{(3)}(S_2) = \frac{48\beta^2 l^4 (\Gamma^3 + 4\Gamma\beta^2 + \beta^2 \sqrt{\Gamma^2 + 4\beta^2})}{(\Gamma^2 - \Gamma \sqrt{\Gamma^2 + 4\beta^2} + 4\beta^2)^2}, \quad (12)$$

$$E(S_0) = \Gamma - \sqrt{\Gamma^2 + 4\beta^2}, \quad E(S_1) = 2\Gamma, \quad E(S_2) = \Gamma + \sqrt{\Gamma^2 + 4\beta^2},$$

where  $\Gamma = (\gamma_0 - \gamma_1)/2$ ;  $\gamma_0$  and  $\gamma_1$  are the Coulomb integrals of electronic repulsion on the same and different atoms, respectively; the energy of the levels is referred to twice the value of the ionization potential, and it includes the repulsion of nuclei. We will compare  $\alpha^{(3)}(S_0, \text{CCI})$  with CPT in the Hartree-Fock method, and (for completeness of the picture) with the sum over the states (SS):

$$\alpha_{xxxx}^{(3)}(S_0, \text{BPT}) = \frac{3\beta l^4}{8(\Gamma - \beta)^4}, \quad \alpha_{xxxx}^{(3)}(S_0, \text{SS}) = -\frac{3l^4(\Gamma + 2\beta)}{2\beta(\Gamma - 2\beta)^3}. \quad (13)$$

The role of interelectron interaction is manifested in that when the C-C bond is lengthened,  $\alpha^{(3)}$  of the quasihomopolar level  $S_0$  tends toward 0, and the quasi-ionic states  $S_2$  and  $S_3$  tend toward infinity;  $\alpha^{(3)}(S_1, \text{CCI}) \rightarrow -\infty$ ;  $\alpha^{(3)}(S_2, \text{CCI}) \rightarrow +\infty$  [it is considered that  $\gamma \sim 1/l$  and  $\alpha \sim \exp(-l)$ , and that as  $l \rightarrow \infty$ ,  $\Gamma \rightarrow \gamma_0/2$ ]. Here,  $\alpha^{(3)}(S_0, \text{CPT})$  has a regular zero limit, but  $\alpha^{(3)}(S_0, \text{SS}) \rightarrow +\infty$ , since all three configurations (ground, singly excited, and doubly excited) have a quasi-ionic character ( $E_0 = 2\beta + \Gamma$ ,  $E_1 = 2\Gamma$ ,  $E_2 = -2\beta + \Gamma$ ), and the energy denominators tend toward zero as  $l$  increases; see analogous considerations for  $\alpha^{(1)}$  in [5]. This is not the sole defect in the calculation of hyperpolarizability as a sum over the states. Actually, if we substitute into (13) standard values of the semi-empirical parameters, we can see that  $\alpha^{(3)}(S_0, \text{SS})$  is more than twice the value of  $\alpha^{(3)}(S_0, \text{CPT})$ . Moreover, by varying  $\Gamma$  and  $\beta$ , we can change the sign of  $\alpha^{(3)}(S_0, \text{SS})$  or can, in general, cause this value to revert to zero. This example is a good illustration of the general rule of inadequacy of the coupled and so-called uncoupled variants of Hartree-Fock perturbation theory in calculations of  $\alpha^{(3)}$  [1].

With physically justified values of the parameters, as can be seen directly from a comparison of (12) and (13), electron correlation even changes the sign of  $\alpha^{(3)}$ :  $\alpha^{(3)}(S_0, \text{CCI}) > 0$ ;  $\alpha^{(3)}(S_0, \text{CPT}) < 0$ ;  $\alpha^{(3)}(S_0, \text{SS}) < 0$ . Let us note that the sum  $\alpha^{(3)}(S_0, \text{CCI}) + \alpha^{(3)}(S_1, \text{CCI}) + \alpha^{(3)}(S_2, \text{CCI})$ , the same as the analogous sum  $\alpha^{(1)}$  [5], is equal to zero with any internuclear distance  $l$ . This fact is a reflection of a general, readily proved rule: The sum of overall states of the K-th corrections of perturbation theory is equal to zero when  $K \geq 2$ .

Let us pass on now to an analysis of numerical results for longer polyenes. In Table 1 we have listed the individual components of  $\alpha^{(3)}$  and the invariant  $\overline{\alpha^{(3)}} = (\alpha_{xxxx}^{(3)} + \alpha_{yyyy}^{(3)} + 2\alpha_{xxyy}^{(3)})/5$ . The planar polyenes in the trans configuration are positioned in the xy plane, with the x axis passing through the odd atoms. It can be seen from the data of Table 1 that interelectron interaction in the polyenes, with an increase in the number of carbon atoms  $N > 2$ , changes the sign of  $\alpha^{(3)}$ . In the Hartree-Fock model, the change in sign of  $\alpha^{(3)}$  when the change is made from ethylene to butadiene is apparently general in character, since it is also observed in ab initio calculations [1]. In the RHF,  $\alpha^{(3)}$  increases sharply in comparison with the value calculated by the Hückel method, and CCI reduces the hyperpolarizability relative to RHF. For  $\alpha^{(1)}$ , the opposite trend is observed [5]. The dependence of  $\alpha^{(3)}$  on the dimension of the conjugated system is expressed as follows:

$$\overline{\alpha^{(3)}}(\text{Hückel}) \sim N^{3,07}, \quad \overline{\alpha^{(3)}}(\text{RHF}) \sim N^{5,97}, \quad \overline{\alpha^{(3)}}(\text{CCI}) \sim N^{3,95}. \quad (14)$$

Let us note that on plots of  $\log N$  as a function of  $\log \overline{\alpha^{(3)}}$  in these three cases, all points of  $\log \overline{\alpha^{(3)}}$  lie essentially on straight lines in the interval of  $N$  from 2 to 10. It is evident that the CCI leads to an increase in  $\overline{\alpha^{(3)}}$  with increasing  $N$  that is intermediate between the Hückel approximation and the RHF. For comparison, we have listed below the proportionalities found from literature sources [1, 8]:

TABLE 1. Hyperpolarizabilities (au) of Even-Membered Polyenes in Different Methods

N	$\alpha_{xxxx}^{(3)}$			$\alpha_{yyyy}^{(3)}$			$\overline{\alpha^{(3)}}$		
	Hückel	RHF	CCI	Hückel	RHF	CCI	Hückel	RHF	CCI
2	-17704	-1746	2122	-1967	-193	236	-6295	-619	756
4	-53838	16722	43269	-8797	-589	890	-46167	1750	10971
6	161033	158772	238245	-23667	-1417	2064	-159780	26196	56121
8	1356216	705069	797050	-49770	-3316	3742	-406557	126234	180685
10	4893892	2229930	2010898	-90304	-5828	5893	-875066	414109	446001

$$\overline{\alpha} \text{ (MINDO)} \sim N^{4.00}, \quad \overline{\alpha^{(3)}} \text{ (ab initio)} \sim N^{4.35}, \quad \overline{\alpha^{(3)}} \text{ (ab initio)} \sim N^{5.32}.$$

Thus, the relationships (14) obtained in this work point out, on the one hand, the basic role of electron correlation in calculations of hyperpolarizability of extended  $\pi$ -electron systems; and on the other hand, they offer a means for estimating the increase in  $\overline{\alpha^{(3)}}$  as the conjugated system is extended in the relatively short polyene chains that are of practical importance.

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