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Variational-perturbational treatment for the polarizabilities of conjugated chains. I. Theory and linear-polarizabilities results for polyenes

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We use a perturbative density matrix treatment to investigate the behavior of the static polarizabilities α of linear conjugated chains $C_N H_{N+2}$, with respect to the chain length and to the presence of neutral and charged conjugation defects of soliton and polaron type. The molecules are described by the Pariser-Parr-Pople Hamiltonian; both closed and open shells are treated. It is shown that both the longitudinal component of α and the orientationally averaged linear polarizability scale as different powers of N in each case. It is also shown how the present treatment can be considered as a generalization of standard variation-perturbation methods for the Hartree-Fock case.

I. INTRODUCTION

It has long been recognized¹ that the delocalized character of the π electrons should have a remarkable effect on the optical properties of conjugated organic molecules. Conjugated chain molecules, e.g., are known to exhibit the so-called polarizability exaltation effect, i.e., the longitudinal component of their polarizabilities do not follow a bond additivity scheme, but rather increase nonlinearly with the size of the chain length. In the early 1970's, Hermann and Ducuing performed a series of third harmonic generation studies on members of the polyene family² and have shown that this effect is even more dramatic for the higher order terms of the polarization response; a free-electron model calculation, which reasonably reproduces the experimental data,³ predicts that the longitudinal components of the first and third order optical polarizabilities of these molecules should scale as the third and fifth powers of the chain length, respectively. Subsequent work with good-optical quality samples of solid-state polymerized diacetylenes have shown that the optical nonlinear coefficients for conjugated polymers and crystals can be at least as large as those of traditional inorganic semiconductors.⁴ The discovery of exceptionally large nonlinear optical properties in organic and polymeric solids, plus the inherent flexibility of control of their crystalline structures by appropriate chemical and synthetic methods, has opened the promise of development of a novel class of organic-based optical devices. As a consequence, the experimental and theoretical investigation of the optical properties of organic molecules and crystals as a research area has blossomed in recent years.⁵⁻⁷

As early as in 1952, Coulson has examined the response of conjugated molecules to a strong applied electric field.⁸ When an external uniform electric field of strength F acts upon a molecule of polarizability α , it produces a distortion of the electronic charge distribution. If F is large, i.e., comparable to the internal fields of the system, the induced dipole moment deviates from a simple linear dependence on

the field and can be written as

$$\mu = \alpha \cdot F + 1/2\beta \cdot F^2 + 1/6\gamma \cdot F^3 + \dots$$

Based on qualitative arguments, Coulson suggested that for most molecules the measured total polarizability at high field strengths should be greater than the value at low field strengths. Since then, the term hyperpolarizability has been traditionally associated to the higher-order contributions of the polarization response: the coefficients β and γ are known, respectively, as the first- and second-order hyperpolarizability tensors.

In the present paper, we will be concerned solely with the static polarizability [i.e., $\alpha(0)$]. From the theoretical point of view, studies of the polarizability of large molecules have been hampered by the computational difficulties of carrying out the usual perturbation expansions involving summations over the complete set of virtual states.⁹ For the Hartree-Fock model, for instance, the contribution of the excited states in the continuum to the polarizability cannot be disregarded. For conjugated systems, however, an important simplification can be attained by assuming the separability between σ and π electrons. The polarization contribution of the former is supposed to follow a bond additivity scheme, while the observed nonlinear effects are ascribed to the latter. Early perturbative calculations of the polarizability of organic molecules based on a self-consistent π -electron Hamiltonian have been performed by Amos and Hall,¹⁰ and Diercksen and McWeeny.¹¹ Schweig has used a finite-field method to examine the linear and nonlinear polarizability responses of alternant and nonalternant hydrocarbons.¹² He has considered the π -electrons, described by a Pariser-Parr-Pople Hamiltonian, to be immersed in a medium of dielectric constant equal to 2; for linear polyenes his results indicated that some of the components of the second-order hyperpolarizabilities should have a negative sign, in disagreement with Coulson's suggestion of only positive higher-order polarizabilities.

A systematic study of the electric polarizabilities of linear polyenes $C_N H_{N+2}$ has been carried out by Hameka and collaborators. The first results,¹³ based on a simple Hückel calculation, indicated that for regular polyenes, the longitu-

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dinal components of the linear polarizability α_{xx} and of the second hyperpolarizability γ_{xxxx} should be roughly proportional to the 2.8 and 5.3 powers of N , respectively. However, larger negative values were predicted for the $xyxy$ components and the resulting orientationally averaged hyperpolarizabilities γ^r were increasingly negative. In subsequent papers,^{14,15} transition matrix elements involving singly and doubly excited Hückel molecular states were calculated using a Pariser–Parr–Pople (PPP) Hamiltonian. The main effect of the inclusion of the self-consistent terms was to reduce the values of the different components of γ and, as a consequence, large and positive values for the orientationally averaged hyperpolarizabilities were predicted. An extended Hückel estimate of the contribution of the σ electrons to the polarizability response confirmed that the PPP π contributions should be dominant.¹⁴ However, the required computations for the fourth-order energy corrections were quite laborious and the $N = 12$ was the largest polyene considered. Also, homogeneous bond lengths along the polyenic chain were assumed in the calculation and hence the important consequences of the alternation between single and double bonds were not investigated.

A convenient way to avoid the explicit calculation of transition matrix elements involving individual molecular states had been first advanced by McWeeny in 1962, by suggesting a direct perturbative expansion in terms of the (one-body) Hartree–Fock density matrix.¹⁸ The proposed method is equivalent to a “fully coupled” self-consistent perturbation treatment and formally can be carried out to any desired order to handle different types of perturbations of physical and chemical interest.^{11,16,17} Nicolaides and collaborators have used the technique to compute, within a CNDO approximation, the linear and nonlinear polarizabilities of several organic molecules¹⁸ with very good agreement with available experimental results. However, the inclusion of all valence electrons has to be accompanied by a limitation on the size of the molecules to be examined, and the largest polyene molecules they have investigated were different octetraene ($N = 8$) isomers.

In this series of papers we will use the perturbative expansion for the density matrix (PEDM) suggested by McWeeny¹⁶ to examine the static linear and nonlinear polarizability responses of conjugated chains. In an earlier letter,¹⁹ we have introduced the method and presented preliminary results concerning the second hyperpolarizability of polyenic chains. In the current work, we develop the general theory of the method and calculate the linear polarizabilities of regular polyenic chains as well as those of chains with geometries resembling conformational defects, such as solitons and polarons. In the next paper, we will discuss in more detail the results for the hyperpolarizabilities of polyenic chains and point out that, contrary to the usual assumptions, the first hyperpolarizability β of charged soliton-like chains can be significantly different from zero.²⁰ In a later paper,²¹ we plan to examine the polarization response of polydiacetylenes.

Conformational effects on the optical response of conjugated chains have recently become a point of interest concerning the dramatic change in the color of solutions of poly-

diacetylenes as a result of variations on dilution and temperature.²² Also, conflicting results for the sign of the second hyperpolarizability of polydiacetylenes determined by two different methods (third-harmonic generation techniques applied to PDA solutions²³ and intensity dependent nonlinear coupling experiments on PDA crystals²⁴) could be reconciled if the conformational dependence of the polarizability response of the material is found to be strong. Given the large amount of experimental and theoretical knowledge accumulated in recent years about the effects of conformational changes on the electronic properties of polyacetylenic chains,²⁵ it seems sensible to start this investigation by the analysis of those effects upon the polarizabilities of polyenes. As indicated by a recent *ab initio* calculation of the linear polarizabilities of polyacetylene and polydiacetylene related compounds,²⁶ these properties are extremely sensitive to geometry changes along the chain.

The present paper is divided as follows: in Sec. II, we develop the general theory for the calculation both of polarizabilities and of hyperpolarizabilities and show how the PEDM method can be considered as a generalization of standard variational–perturbational²⁷ procedures; we begin Sec. III with a discussion about how the presence of conformational defects can affect the understanding of the electronic properties of conjugated chains, and present the Hamiltonian and geometries adopted in the calculation; in Sec. IV, we present the calculated values for the linear polarizabilities of polyenes (both with regular structure and presenting defects) and discuss how the results compare to those of previous calculations; finally, in Sec. V, we conclude by making the connection of the present work with subsequent calculations of the hyperpolarizabilities of conjugated chains.

II. THEORY

A. Perturbative expansion of the density matrix

As it is well known, the Hartree–Fock (HF) equations for an isolated N -electron molecular system can be solved directly²⁹ in terms of the single-particle density matrix R_0 . If the unperturbed system is described by the Hamiltonian h_0 , the HF equations can be expressed as

$$h_0 R_0 - R_0 h_0 = 0,$$

where the corresponding density matrix must satisfy the idempotency condition

$$R_0^2 = R_0,$$

with $\text{tr } R_0 = N$, in order to be associated to a single-determinant wave function. In the density matrix approach no treatment of individual one-electron states of the system is required, but rather the whole N -electron distribution is dealt with at once. This is particularly convenient when an external perturbation V is applied upon the original system, for then a standard perturbation treatment would require that each new occupied state be formed as a combination of the originally occupied and unoccupied molecular orbitals. On the other hand, in the density matrix formalism, one is interested in determining the matrix R which satisfies the HF

condition

$$(h_0 + V)R - R(h_0 + V) = 0 \quad (1)$$

and obeys the relations $R^2 = R$ and $\text{tr} R = N$. The fact that the new density matrix R can be constructed without resorting to the determination of the new individual molecular orbitals provides the main computational advantage of the perturbative expansion for the density matrix technique.

The original and the perturbed HF Hamiltonians can be separated in the one- and two-electron parts

$$h_0 = f_0 + G_0(R_0), \\ h = h_0 + V = f + G(R),$$

where their self-consistent character is reflected in the fact that the two-electron terms are functionals of the corresponding density matrices. In the present problem, the perturbation results from the switching of the static external field F . That gives rise to an extra term in the one-electron part of the Hamiltonian

$$f = f_0 + eF \cdot r$$

and, as a consequence, the electronic distribution of the system is distorted. This in turn leads to a correction in the two-electron part of the Hamiltonian and the whole self-consistency process must then be applied to guarantee that condition (1) is satisfied. The electronic energy can then be computed as

$$E = 2 \text{tr} \{ [f + 1/2G(R)]R \},$$

where the factor 1/2 accounts for the double counting of electronic interactions in the HF Hamiltonian.²⁹

After formally introducing the order parameter λ , we can write

$$R = R_0 + \lambda R^{(1)} + \lambda^2 R^{(2)} + \dots$$

and

$$G = G_0 + \lambda G(R^{(1)}) + \lambda^2 G(R^{(2)}) + \dots$$

The HF and idempotency conditions satisfied by the first- and second-order corrections to the density matrices can now be expressed as

$$R_0 R^{(1)} + R^{(1)} R_0 = R^{(1)} \quad (2a)$$

$$h_0 R^{(1)} - R^{(1)} h_0 + \Delta^{(1)} R_0 - R_0 \Delta^{(1)} = 0 \quad (2b)$$

$$R_0 R^{(2)} + R^{(2)} R_0 + R^{(1)} R^{(1)} = R^{(2)} \quad (3a)$$

$$h_0 R^{(2)} - R^{(2)} h_0 + \Delta^{(1)} R^{(1)} \\ - R^{(1)} \Delta^{(1)} + \Delta^{(2)} R_0 - R_0 \Delta^{(2)} = 0, \quad (3b)$$

respectively, where we have defined $\Delta^{(i)} \equiv f^{(i)} + G(R^{(i)})$.

It is convenient to introduce the density matrix U_0 associated with the unperturbed unoccupied states ($U_0 = 1 - R_0$); since the perturbation preserve the total number of electrons, any operator A acting on the N -electron Hilbert space can be resolved as

$$A = R_0 A R_0 + R_0 A U_0 + U_0 A R_0 + U_0 A U_0 \\ \equiv (A)_{11} + (A)_{12} + (A)_{21} + (A)_{22}, \quad (4)$$

where we have used the fact that R_0 and U_0 can be considered as projectors into the unperturbed orthogonal occupied and unoccupied spaces, respectively. If we then project Eq.

(2a) into the two diagonal blocks, we see directly that $R_0 R^{(1)} R_0 = (R^{(1)})_{11} = 0$ and $U_0 R^{(1)} U_0 = (R^{(1)})_{22} = 0$, i.e., the first-order correction for the density matrix acts only to couple originally occupied states to the corresponding unoccupied ones and vice versa. Hence, in first order, the off-diagonal blocks convey all the modification in the electronic distribution brought about by the perturbation. They can be determined after obtaining the corresponding projections of Eq. (2b). It's convenient at this point to work in the basis in which h_0 (and therefore R_0) is diagonal, for then the matrix elements of $R_0^{(1)}$ can be written as

$$(\tilde{R}_0^{(1)})_{ij} = 0, \quad i \in R_0, j \in R_0, \text{ or } i \in U_0, j \in U_0, \quad (5) \\ (\tilde{R}_0^{(1)})_{ij} = \frac{\tilde{\Delta}_{ij}^{(1)}(r_i - r_j)}{(\epsilon_i - \epsilon_j)}, \quad i \in R_0, j \in U_0, \text{ or } i \in U_0, j \in R_0,$$

where the tilde indicates quantities in the new basis and r_i and ϵ_i are the eigenvalues of R_0 (or U_0) and h_0 , respectively. Since Δ depends on R , Eq. (5) has to be solved in a self-consistent way.

Once $R^{(1)}$ is found, the diagonal blocks of $R^{(2)}$ can be directly determined since the projection of Eq. (3a) gives, both for $i, j \in R_0$ and $i, j \in U_0$,

$$(\tilde{R}^{(2)})_{ij} = - \sum_k \frac{(\tilde{R}^{(1)})_{ik} (\tilde{R}^{(1)})_{kj}}{(r_i + r_j - 1)}.$$

To determine the off-diagonal blocks of $R^{(2)}$, one has to solve the new self-consistent equation which results from the projection of the commutation relation (3b)

$$(\tilde{R}^{(2)})_{ij} = \frac{(\tilde{\Delta}^{(2)})_{ij}(r_i - r_j)}{(\epsilon_i - \epsilon_j)} \\ - \sum_k \frac{[(\tilde{\Delta}^{(1)})_{ik} (\tilde{R}^{(1)})_{kj} - (\tilde{R}^{(1)})_{ik} (\tilde{\Delta}^{(1)})_{kj}]}{(\epsilon_i - \epsilon_j)}. \quad (6)$$

If necessary, higher-order corrections of R can be determined in a similar way. In the present case, the knowledge of the second-order correction $R^{(2)}$ will be sufficient for our purposes.

The different corrections in the electronic energy can be separated in successive orders as

$$E^{(1)} = 2 \text{tr} [f^{(1)} R_0], \quad (7a)$$

$$E^{(2)} = 2 \text{tr} (1/2 f^{(1)} R^{(1)}), \quad (7b)$$

$$E^{(3)} = 2 \text{tr} [\Delta^{(1)} \{ (R^{(2)})_{11} + (R^{(2)})_{22} \}], \quad (7c)$$

$$E^{(4)} = 2 \text{tr} \{ h_0 [- (R^{(2)} R^{(2)})_{11} + (R^{(2)} R^{(2)})_{22} \\ + 1/2 \Delta^{(2)} R^{(2)}] + 4 \text{tr} \{ - (\Delta_{11}^{(1)} (R^{(2)})_{12} (R^{(1)})_{21} \\ + (\Delta_{21}^{(1)} (R^{(2)})_{21} (R^{(1)})_{12} \} \}, \quad (7d)$$

where we have used the notation introduced in Eq. (4). As can be easily verified, the successive corrections in energy depend on increasingly higher powers of the external field strength F . On the other hand, we can expand the change in energy as a power series in F :

$$\Delta E(F) = -1/2 \sum_{i,j} \alpha_{ij} F_i F_j - 1/6 \sum_{i,j,k} \beta_{ijk} F_i F_j F_k \\ - 1/24 \sum_{i,j,k,l} \gamma_{ijkl} F_i F_j F_k F_l + \dots \quad (8)$$

Hence, once the first-order correction to the density matrix is known, the polarizability α and the first hyperpolarizability β can be calculated. To obtain the second hyperpolarizability γ , one has to determine the second-order correction $R^{(2)}$. Comparison of expressions (7) and (8) show that in the present method the calculated polarizabilities do not depend on the field strength; in this way the numerical difficulties commonly found in methods based on the direct computation^{12,26} of the derivatives of Eq. (8) are altogether avoided.

To solve for the different components of α , β , and γ , one has to repeat the calculation for different field directions. However, usually symmetry considerations allow the reduction of the number of independent components to be calculated for each specific molecule.

An extension of the PEDM formalism to open-shell systems was carried by McWeeny and Diercksen.³⁰ However, if an unrestricted Hartree-Fock (UHF) approximation is adopted, it is a simple matter to generalize the above formalism to deal with the different spin distributions. We will follow this procedure for the calculation of the polarizabilities of neutral solitons and charged polarons.

B. Relation to usual variation-perturbation methods

The complicated form of perturbation-theory expressions for the polarizabilities and hyperpolarizabilities have precluded realistic calculations of these quantities for systems with a large number of electrons. As a consequence, several schemes which avoid the direct computation of matrix elements involving perturbed states have been proposed. Of these, the so-called F -operator technique originally introduced by Dalgarno and Lewis,²⁷ and later put on a more formal basis by Schwartz,²⁸ deserves special attention. The method is based on the definition of an operator F obeying a special commutation relation with the unperturbed Hamiltonian h_0 . A variational principle can be constructed for F and it can be shown that this operator is uniquely determined by the unperturbed ground-state electronic density of the system. Once F is found (usually by solving an inhomogeneous differential equation),²⁸ the higher-order corrections in the energy can be determined. Flytzanis and Ducuing have used the technique to compute the second-order susceptibilities of inorganic semiconductors.³¹

In this section, we will show that the PEDM method can be considered as the HF generalization of the standard variational perturbation technique, in which the perturbative corrections are computed not for individual electronic states, but instead to the whole electronic distribution. Also, the PEDM treatment offers a simple procedure to obtain corrections in successive orders both for the total electronic energy and electronic distribution, where only matrix manipulations are involved. We will show explicitly that the operator F has a simple relation to the first-order density matrix correction $R^{(1)}$ and that the variational condition for F proposed by Schwartz²⁸ is connected to the stability requirement satisfied by the energy correction in second order.

Let us suppose that a perturbation V acting upon an eigenstate $|\mu^{(0)}\rangle$ of the original Hamiltonian h_0 . We can

write the corresponding first-order energy correction as

$$E_{\mu}^{(1)} = \langle \mu^{(0)} | V | \mu^{(0)} \rangle.$$

In standard perturbation theory, the corrections for the wave function associated with this state as well as all subsequent energy corrections will require the calculation of transition matrix elements involving the excited states of the unperturbed system. On the other hand, in the F -operator technique, the second-order energy correction and the first-order correction for the wave function for a given unperturbed eigenstate are entirely determined by the form of the applied perturbation V . This is accomplished by introducing the operator F which satisfies

$$[F, h_0] |\mu^{(0)}\rangle = (V - E_{\mu}^{(0)}) |\mu^{(0)}\rangle \quad (9)$$

and the adjoint condition, for then it is simple to show that

$$E_{\mu}^{(2)} = \langle \mu^{(0)} | VF | \mu^{(0)} \rangle - E_{\mu}^{(1)} \langle \mu^{(0)} | F | \mu^{(0)} \rangle$$

and

$$|\mu^{(1)}\rangle = F |\mu^{(0)}\rangle - \langle \mu^{(0)} | F | \mu^{(0)} \rangle |\mu^{(0)}\rangle.$$

If F is assumed to be a function of the space coordinates, it can be in principle determined after solution of the differential equation defined by Eq. (9). Schwartz has introduced the variational condition for F as

$$J = \langle \mu^{(0)} | \Phi (V - E_{\mu}^{(1)}) + (V - E_{\mu}^{(1)}) \Phi - 1/2 [\Phi, [\Phi, h_0]] | \mu^{(0)} \rangle, \quad (10)$$

where J will be stationary with respect to variations of Φ , if Φ satisfies condition (9) and its adjoint.

To explore the relationship between this approach and the PEDM method, let us multiply Eq. (9) at the right by $\langle \mu^{(0)} |$ and sum over all occupied states of the Hamiltonian h_0 :

$$\begin{aligned} \sum_{\mu}^{\text{occ}} \{ F h_0 |\mu^{(0)}\rangle \langle \mu^{(0)} | - h_0 F |\mu^{(0)}\rangle \langle \mu^{(0)} | \} \\ = \sum_{\mu}^{\text{occ}} V |\mu^{(0)}\rangle \langle \mu^{(0)} | - \sum_{\mu}^{\text{occ}} E_{\mu}^{(1)} |\mu^{(0)}\rangle \langle \mu^{(0)} |. \end{aligned} \quad (11)$$

If we realize that the unperturbed density operator is defined in terms of the unperturbed states $|\mu^{(0)}\rangle$ as²⁹

$$R_0 = \sum_{\mu}^{\text{occ}} |\mu^{(0)}\rangle \langle \mu^{(0)} |,$$

Eq. (11) can be written as

$$F h_0 R_0 - h_0 F R_0 = V R_0 - \sum_{\mu}^{\text{occ}} E_{\mu}^{(1)} |\mu^{(0)}\rangle \langle \mu^{(0)} |.$$

After subtraction of the above equation from its adjoint, we obtain finally

$$F h_0 R_0 - R_0 h_0 F - h_0 F R_0 + R_0 F h_0 = V R_0 - R_0 V. \quad (12)$$

This equation can be considered as an equivalent definition of the operator F . Note that in the present form F can be determined entirely by matrix manipulation; to find the explicit form of F , we resolve Eq. (12) in its four component blocks and subsequently transform to the basis in which h_0

and R_0 are diagonal. It is easy to verify then that

$$\begin{aligned} \tilde{F}_{ij} &= 0, \quad i, j \in R_0, \text{ or } i, j \in U_0, \\ \tilde{F}_{ij} &= \frac{\tilde{V}_{ij}(r_i - r_j)}{(\epsilon_i - \epsilon_j)}, \quad i \in R_0, j \in U_0, \text{ or } i \in U_0, j \in R_0. \end{aligned} \quad (13)$$

In the Hartree–Fock approximation, the role of the perturbation V is played by the first-order correction $\Delta^{(1)}$ in the Hamiltonian. Thus, a comparison of Eqs. (5) and (13) shows that at the HF level, Dalgarno's operator F can be identified to the first-order correction for the density matrix $R^{(1)}$.

Once this identification is made, the analogy between the two methods can be carried a step further. If we write the variational condition (10) in the basis where H_0 is diagonal and take into account the fact that the diagonal elements of F are zero in this basis, we obtain

$$\begin{aligned} \sum_i J_i &= \sum_{i,j} [(\tilde{R}^{(1)})_{ij}(\tilde{\Delta}^{(1)})_{ji} + (\tilde{\Delta}^{(1)})_{ij}(\tilde{R}^{(1)})_{ji}] \\ &\quad - \sum_{i,j} (\tilde{R}^{(1)})_{ij}(\epsilon_i - \epsilon_j)(\tilde{R}^{(1)})_{ji} \\ &= \sum_{i,j} (\tilde{R}^{(1)})_{ij}(\tilde{\Delta}^{(1)})_{ji} = \text{Tr}(R^{(1)}\Delta^{(1)}) = E^{(2)}. \end{aligned}$$

We see therefore that in a Hartree–Fock treatment the variational condition for the corresponding F operator leads naturally to the expression of the energy correction in second order satisfied by any perturbed Hamiltonian, which has the appropriate commutation relation with the complete density matrix.

Hence, the PEDM method provides a simple and general method to obtain the successive corrections for the energy and electronic distribution of a system (described by a self-consistent Hamiltonian) submitted to an external perturbation, where only matrix manipulations are involved and that can be carried exactly to any desired order. In the next section, we are going to utilize this technique for the treatment of the polarizability response of conjugated chains described by a PPP Hamiltonian.

III. MODEL CALCULATION

A. Defects in conjugated chains

In spite of its very simple semiempirical nature, the Su–Schrieffer–Heeger³² model was of extreme success in explaining the peculiar electronic and transport properties of polyacetylene (PA) in terms of the presence of conjugation defects along the chain. In this soliton model, the defects (which are assumed to exist in low concentration in pristine PA samples as an unavoidable result of the polymerization process) are associated to conformational changes in the polymer. In the *trans* isomer of PA, one of these defects would connect two isoenergetic chains since the system is degenerate with respect to the order in which single and double bonds alternate. On the other hand, the motional barrier for the displacement of the center of the defect to neighboring sites is estimated to be small. As a consequence, at room temperature the defects (solitons) should be extremely mobile along the chain. By reasons of symmetry, the model

predicts that the energy level of the soliton should lie exactly halfway between the highest occupied and the lowest unoccupied energy level of the regular polymer.

When introduced, the soliton picture was in general agreement to the bulk of known experimental results for the electronic and transport properties of polyacetylene. However, the later discovery that other conjugated polymers with no degenerate ground states have transport properties similar to those of PA²⁵ has required an extension of the soliton model to accommodate the existence of polarons.^{33,34} Briefly, a polaron is a conformational defect of local character (in the sense in which only sites in the neighborhood of the defect are affected by its presence) that can be thought to result from the interaction between a charged and a neutral soliton.³⁵ Contrary to solitons, polarons would introduce two energy levels in the gap and can exist as singly or doubly charged defects (a neutral polaron being unstable with respect to soliton–soliton annihilation).

The exact position of the energy levels localized in the gap became a point of interest in recent years as more precise optical measurements on conjugated polymers became available.³⁶ To account for the exact position of these levels, more sophisticated treatments which include electron–electron repulsion terms in a self-consistent manner are desirable. However, usual self-consistent electronic calculation methods for extended systems cannot handle the presence of translational defects³⁷ and therefore finite chain model calculations appear as a desirable route in the short term. In these treatments, a balance must always be attained between the degree of sophistication of the adopted model and the maximum size of the systems to be studied.

B. Hamiltonian

In the present calculation, we have adopted the PPP Hamiltonian^{38,39} because it represents an excellent compromise between efficiency and realism in the description of the electronic structure of polyenes. We had set the initial goal of analyzing: (i) the changes of the polarizabilities and first and second hyperpolarizabilities of regular (i.e., with no conjugation defects) conjugated chains $C_N H_{N+2}$ with the increase of the number of π electrons up to the limit of $N \sim 20$, (ii) the effects of different conformational defects (solitons and polarons); and (iii) the changes due to the different charge states of these defects. Although some CNDO results for the hyperpolarizabilities of small polyenes are available for some time,¹⁸ and *ab initio* polarizabilities have been calculated for polyenic chains comprising up to 20 carbon atoms,²⁶ to our knowledge no systematic studies of geometric effects on the hyperpolarizabilities of large conjugated chains have been performed.

If no spin polarization effect is considered, for conjugated chains the PPP Hamiltonian can be written in a site representation as

$$\begin{aligned} h_{\mu\mu}^{\text{PPP}} &= U_{\mu\mu} R_{\mu\mu} + \sum_{\nu \neq \mu} (2R_{\nu\nu} - 1) U_{\mu\nu}, \\ h_{\mu\nu}^{\text{PPP}} &= \beta_{\mu\nu} - R_{\mu\nu} U_{\mu\nu}, \end{aligned}$$

where the one-center Coulomb integrals for the carbon atom are taken to be zero. We have adopted the standard parame-

trization suggested in Ref. 39 with Ohno's expression

$$U_{\mu\nu} = 14.397 \text{ eV} (1.635 + r_{\mu\nu}^2)^{-1/2}$$

for the intersite Coulomb interactions, with the distance between sites $r_{\mu\nu}$ given in Å. In the site (or Wannier) basis, the matrix elements of the coupling terms to the external field F can be written as $f_{ij} = eF \cdot r \delta_{ij}$.

For computation reasons, only the ground-state HF electronic distribution was considered and no basis set optimization or reparametrization was attempted. Our results should therefore be considered in what they reveal about trends or patterns for the variation of the polarizability response with increasing chain sizes and different structures. In the case of open shell molecules (as solitons and charged polarons), it is easy to generalize the above Hamiltonian to perform an UHF calculation.

C. Geometries for regular polyenes, solitons, and polarons

Conformational defects such as solitons and polarons are associated to changes in the degree of alternancy between single and double bonds along the conjugated chains and result from the existence of localized spin or charge density on certain carbon atoms. As a good approximation, we can assume all different chains considered here to be planar; we have chosen the molecules to lie in the xy plane, with the chains oriented along the x axis.

For all cases considered, we have taken the bond angles equal to 120° . For regular polyenes, lengths of 1.35 and 1.46 Å were assumed for the double and single bonds, respectively, and no attempt was made of simulating end-chain effects. On the other hand, for the case of defects, geometric relaxation effects are known to be responsible for the pinning of the extra charge or spin density near the center of the molecule.³⁸ In the case of solitons, the alternation between single and double bonds is inverted at the middle of the chain. For polarons, we have assumed that each carbon atom at the center of the soliton-like defects is connected through single bonds to both of its neighbors. The geometry adopted for the different structures is schematized in Fig. 1. For solitons and polarons the positions of the carbon atoms can be indicated by

$$\mathbf{r}_n = (x_0 + nr_0 + u_n) \cos 30^\circ \hat{i} + (-1)^n r_0 / 2 \sin 30^\circ \hat{j},$$

where the parameters r_0 and u_0 have the values of 1.405 and 0.0275 Å, respectively; for solitons $x_0 = 0$, $u_n = (-1)^{n+1} u_0 \tanh(n/\nu)$, and $0 \leq n \leq (N-1)/2$, while for polarons $x_0 = -r_0/2$, $u_n = (-1)^n u_0 [-1 + 2 \operatorname{sech}(0.65848n)]$, and $1 \leq n \leq N/2$. The most stable solitons should occur at odd N chains, since then the terminal bonds will have a double character. We have used this criterion to determine the parameter ν , by requiring that the lengths of the terminal bonds be as close as possible to that of a true double bond (1.35 Å). The optimum values of ν were 1.7080, 1.9756, 2.3096, 2.6425, and 2.9667 for the $N = 5, 9, 13, 17,$ and 21 chains, respectively. For polarons, the minimum meaningful value of N is 4 and subsequent chains will have to increase by that many carbon atoms to preserve the correct symmetry of the defect. The positions of the carbon atoms on the left-

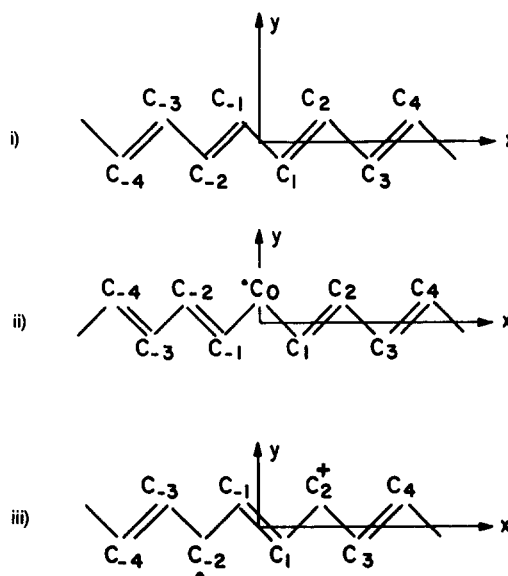


FIG. 1. Schematic geometry adopted for (i) regular polyene; (ii) soliton-; and (iii) polaron-like chains.

hand side of each chain are easily found by symmetry.

With the above choices of geometry, one can easily verify that regular polyenes and polaron chains belong to the same symmetry group (C_{2h}), while the soliton chains belong to the C_{2v} group. As a consequence, while α_{xx} , α_{xy} , and α_{yy} have to be determined in the first case, only the axial components of the linear polarizabilities are different from zero for the soliton chains.

We have assumed the same geometries for the neutral and charged species. As first suggested by Flytzanis,⁴⁰ time intervals of the order of ps should be involved in the chain relaxation of a chain after electronic excitation. Immediately after excitation, the corresponding electron states will find themselves in the "foreign lattice" of the unexcited molecule. Recently,⁴¹ directly photogenerated charged-soliton pairs and neutral- to charged-soliton conversion have been unequivocally identified in polyacetylene. While the former decay on the subpicosecond scale, the lifetime of the charged solitons are estimated to be greater than 20 ps. Although relaxation effects should lead to small geometry differences between neutral and charged solitons, and between single and double charged polarons, we do not expect a drastic change in the pattern of variation of the polarizabilities. Hence, considering that the PPP Hamiltonian is not particularly reliable for the prediction of geometries, we have not tried to mimic the eventual geometry differences between different charge states of a given molecule. For completeness, we have included results for the polarizabilities of neutral polarons even if in this particular charge state these defects are not expected to be stable.

IV. LINEAR POLARIZABILITIES

A. Results

While one can expect the largest contribution for the polarizability response of oriented films and crystals to come from the component along the chain axis (α_{xx} in our case) in

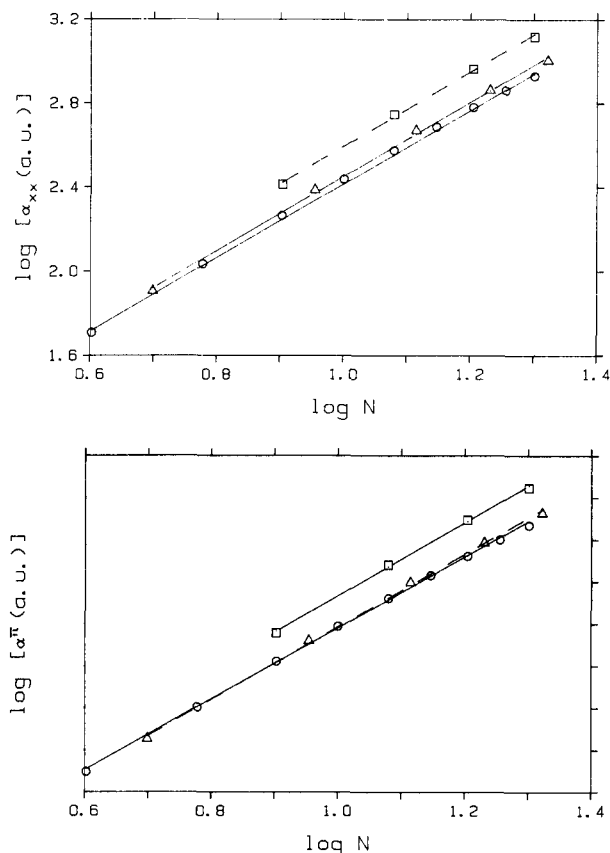


FIG. 2. Linear polarizabilities for neutral conjugated chains: (a) longitudinal component α_{xx} for (i) regular polyenes (O), (ii) solitons (Δ), and (iii) polarons (\square); (b) orientationally averaged polarizability α^π for (i) regular polyenes (O), (ii) solitons (Δ), and (iii) polarons (\square).

principle all individual components of the polarizability matrix can be experimentally determined. For molecules in solution or in the gas phase, on the other hand, the measured polarizability α is a rotational average^{18,42} of the xx , zz , and yy components

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

Hence, in general for a nonoriented medium, the second-order energy correction term has to be calculated for three different field directions [cf. Eq. (8)]. For the C_{2v} group, however, the xy component of the polarizability vanishes by symmetry and therefore for the soliton chains only two independent calculations are required.

To obtain the second-order energy correction given by Eq. (7b), the self-consistent condition (6) has to be satisfied. Even for the largest chains, we have imposed the idempotency of the complete density matrix and its commutation relation to the Hamiltonian to be satisfied to at least 10^{-5} . The results for longitudinal component α_{xx} for neutral chains with geometries corresponding to regular polyenes and soliton and polaron defects are presented in Fig. 2(a), while the corresponding values for the averaged linear polarizability α^π are shown in Fig. 2(b). For all of these molecules, the components of α are positive. As a general rule, the relative contribution of the xx component increases with the length of the chain considered. Considering the $N = 20$ neu-

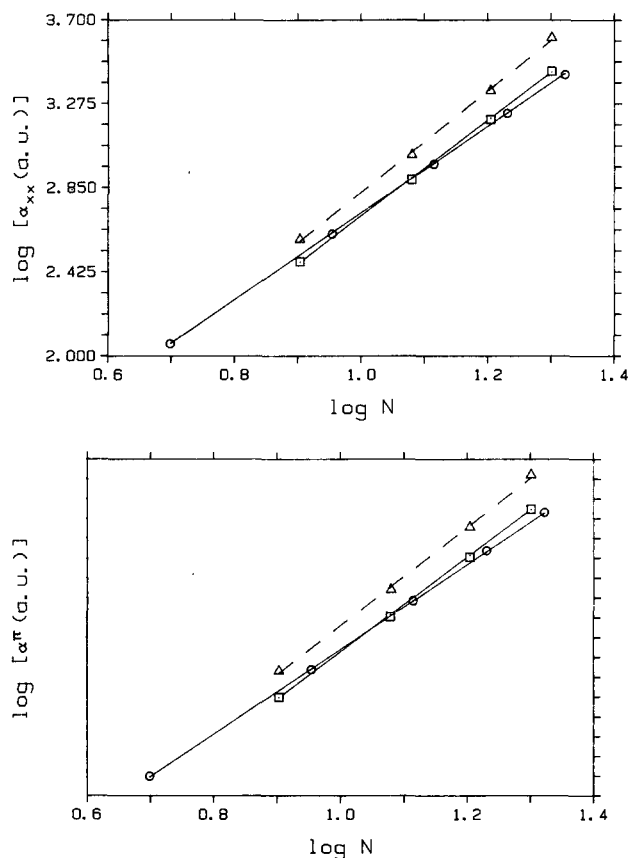


FIG. 3. Linear polarizabilities for charged defects: (a) longitudinal component α_{xx} for (i) charged solitons (O), (ii) single charged polarons (Δ), and (iii) bipolarons (\square); (b) orientationally averaged polarizability α^π for (i) charged solitons (O), (ii) single charged polarons (Δ), and (iii) bipolarons (\square).

tral molecules, the ratio α_{xx}/α_{yy} is of the order of 2 for the C_{2h} chains (regular polyenes and polarons), while α_{xx} is one order of magnitude larger than α_{yy} .

The corresponding results for α_{xx} and α^π for charged solitons, charged polarons, and doubly charged polarons (bipolarons) are presented in Fig. 3. Here, the relative contribution of the xx component to the average polarizability increases with the size of the chain in an even more remarkable manner. Surprisingly, we have found that α_{xy} has negative values for bipolaron chains.

TABLE I. a and b parameters derived from linear least-square fitting aN^b for calculated values (in a.u.) of the longitudinal component (α_{xx}) and orientational average (α^π) of the linear polarizability of finite chains of regular polyenes (rp), neutral solitons (ns), neutral polarons (np), charged solitons (cs), singly charged polarons (cp), and bipolarons (bp).

		rp	ns	np	cs	cp	bp
α_{xx}	a	4.63	4.81	6.53	3.41	1.85	1.94
	b	1.75	1.77	1.78	2.19	2.56	2.42
α^π	a	2.07	1.91	2.62	1.33	0.80	0.73
	b	1.69	1.73	1.74	2.14	2.48	2.39

With the possible exception of regular polyenes (for which the onset of a "saturation" behavior can be considered to occur for $N \sim 16$), the plots of Figs. 2 and 3 do not indicate saturation of the calculated polarizabilities with the increase of the length of the chains. A linear least-square fitting of these values to the general form aN^b expresses the higher sensitivity of the charged defects to the increasing of the chain length, as revealed in Table I. It should be noted, the effect of different geometries on the evolution of the linear polarizability with chain length; both free-electron³ and Hückel¹³ models predict $\alpha = 2.0$ for regular polyenes.

B. Discussion

As discussed before, a convenient way of calculating the polarizability response of large conjugated chains is to resort to simple semiempirical methods. However, the scarcity of the experimental data available makes difficult the testing and development of new parametrization schemes specific to the molecules considered. For instance, in his PPP calculation,¹² Schweig has assumed the π electrons to be immersed in a medium of dielectric constant equal to 2; in our case, preliminary exploration of sets of parameters have shown us that for a given molecule, the resulting values of α , and specially γ , are quite sensitive to the form adopted for the intersite Coulomb interactions U . In the lack of sufficient experimental information for optimizing the choice of parameters, we felt that a better option was to adopt the standard PPP parametrization in our treatment and to look for trends of qualitative nature on the behavior of the polarizabilities of conjugated chains of different conformations. We decided in favor of Ohno's form for the Coulomb integrals instead of the alternative Mataga-Nishimoto expression,³⁹ due to the fact that the latter usually led to higher energies for the closed-shell ground state and to unrealistic spin densities for the open-shell molecules.

Unfortunately, to our knowledge there are no experimental data available for the linear polarizability of the molecules considered. Previous theoretical results for the rotational averaged polarizability α were available for the $N = 4, 6,$ and 8 regular polyenes (see Table II). Our calculated values of α are slightly smaller than the corresponding results of the perturbation treatment of the PPP Hamiltonian performed by Zamani-Khamiri and Hameka¹⁴ (although it should be noticed that the latter values include the σ electron contribution estimated by the extended Hückel method)

TABLE II. Orientationally averaged linear polarizabilities of some regular *trans* polyenes C_NH_{N+2} , in a.u.

N	This work	VPT-PPP ^a	PT-Huckel ^a	SCF-PT ^b	CNDO-PEDM ^c
4	20.9	32.08	59.06	61.91	69.73
6	42.5	72.99	165.93	105.91	128.19
8	70.2	131.92	355.66	...	203.81

^a Reference 14.

^b Reference 10.

^c Reference 18.

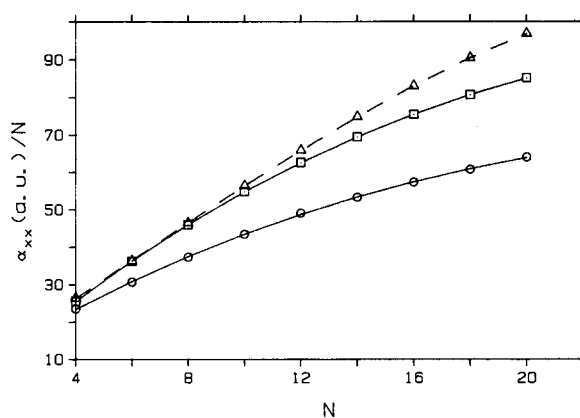


FIG. 4. Evolution of the longitudinal unit-cell polarizability α_{xx}/n with respect to chain length for different values of the alternation parameter as calculated in our method: (\square ; $\Delta r = 0.11 \text{ \AA}$), and in Ref. 26 (\circ ; $\Delta r = 0.10 \text{ \AA}$) and (\triangle ; $\Delta r = 0.05 \text{ \AA}$).

and are of the order of half the corresponding CNDO results.¹⁸ On the other hand, the calculated values for the longitudinal component of the linear polarizability α_{xx} of regular polyenes agree remarkably well with the *ab initio* results of Bodart *et al.*²⁶ In Fig. 4, we compare our results for the linear polarizability per unit cell α_{xx}/n (where $n = N/2$) with those of Ref. 26 computed for different values of the alternation parameter Δr (defined as the difference between the lengths of single and double bonds). For conjugated polymers, even in solution or gas phase, the linear polarizability response should be dominated by the longitudinal contribution. It can then be argued from the results of Fig. 4 that, for the same values of Δr as those we have used, an *ab initio* calculation should lead to even smaller values of α^{π} . From Fig. 4, it can also be seen that both calculations predict the onset of the saturation behavior of the unit-cell polarizability for the alternant conjugated chain to occur at $N \sim 16$. However, our results reveal that for the molecules with soliton or polaron structures saturation should occur only for larger chains. For these conjugated chains, calculated values are very well fitted through exponential relations as those of Table I.

V. CONCLUSION

The results of the present calculation indicate that the static linear polarizabilities of conjugated chains are extremely sensitive to both conformational changes and the charge state of the molecule. As revealed by Table I, the presence of conjugational defects of soliton or polaron nature could dominate the polarization response of longer conjugated chains.

Our preliminary exploration of the nonlinear response of conjugated chains have suggested that the sensitivity of the hyperpolarizabilities to charge and conformational changes are at least as noticeable as that of α . If the present suggestion turns out to be confirmed by further investigation, this effect will be of particular importance for the designing of new materials suitable for the construction of optical devices. For instance, it can be expected that if the lateral

hydrogen atom connected to a given carbon atom is substituted by a highly electrophilic side group, strong charge fluctuations could be induced along the conjugated chain; thus, by appropriate choice of substituent groups, one could in principle "fine tune" the polarization response of the original molecule.

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