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Nonlinear optical properties of one-dimensional semiconductors and conjugated polymers

G. P. Agrawal*
Physics Department, The City College of the City University of New York, Convent Avenue, 138th Street, New York, New York 10031
C. Cojan and C. Flytzanis
Laboratoire d'Optique Quantique,† Ecole Polytechnique, 91128-Palaiseau Cedex, France

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We present a detailed study of the nonlinear optical properties of one-dimensional conjugated polymers and semiconductors. The Bloch wave functions and energies and the dipole transition-matrix elements previously obtained within the tight-binding approximation by linear combination of atomic orbitals (Hückel approximation) were used to calculate the nonlinear optical susceptibilities; the expressions of the lattice were obtained by the Genkin-Mednis approach. The effects of bond alternation and superalternation as well as chain pairing are explicitly considered. It is found, as for the linear optical properties, that the behavior of the nonlinear susceptibilities can be simply expressed in terms of the optical delocalization parameter N_d previously defined; in particular it is shown that the third-order susceptibility $\chi^{(3)}$ in the transparency region of these compounds shows a sixth-power dependence on this parameter. It is further shown that chain pairing has striking effects on the second-order susceptibility and the two-photon absorption spectrum. The case of the polydiacetylene polymer crystals is explicitly discussed.

I. INTRODUCTION

Semiconductors with high nonlinear optical susceptibility values are of general interest. As large single crystals of inorganic materials such as germanium (Ge) or gallium arsenide (GaAs) are readily available, in the past an intense study has been carried out[1] to measure the optical nonlinearities in inorganic semiconductors. There high susceptibility values may be obtained owing to the large number of saturated bonds per unit cell. However, their low absorption threshold, usually in the infrared, prevents one from studying nonlinear optical phenomena in the visible in these materials. Further phase-matching conditions may not be easily satisfied there.

With the recent solid-state polymerization[2] of diacetylene monomers $R{-}C{\equiv}C{-}C{\equiv}C{-}R$, R being an appropriately chosen radical, attention had been focused in organic one-dimensional (1D) semiconductors particularly in view of their high absorption threshold,[3] usually in the visible, and large optical anisotropy.[4] It has been observed[5] that in linear conjugated molecules the third-order superpolarizability γ increases dramatically with the molecular dimension in comparison to the ones corresponding to saturated molecules with the same number of valence electrons, a property attributed to the highly delocalized π electrons along the chain direction.[6] One expects that on polymerization there should be a further enhancement in the values of the nonlinear susceptibilities in the direction along which the different molecules orient to form a long chain. The recent measurements[7] of the third-order susceptibility $\chi^{(3)}$ in polydiacetylene polymer crystals show that under certain conditions $\chi^{(3)}$ may take values which exceed even those generally obtained in inorganic semiconductors.[8] This is particularly striking in view of the much lower valence-electron densities prevailing there and its origin must be sought in the one-dimensionality of the π-electron system.

In the present paper we study the behavior of the second- and third-order susceptibilities in such 1D semiconductors and show how various constraints such as heteroatomicity, bond alternation and superalternation, and chain coupling influence their values. In a previous paper[9] (hereafter referred to as I) we set up the model for the π-electron description and studied the optical properties in systems composed of independent chains of three types (i) atom- and bond-alternated chains, (ii) superalternated chains, and (iii) pairs of coupled chains. We shall be making constant use of these results and all the assumptions made therein should hold here as well.

In Sec. II we give the expressions for $\chi^{(2)}$ and $\chi^{(3)}$ to be used. A derivation of these expressions based on the Genkin-Mednis approach[10] will be deferred until Appendix A. Sections III–V deal with the nonlinear susceptibilities of the three classes of organic 1D semiconductors mentioned above. In Sec. VI we discuss the two-photon absorption spectrum in these systems. The special case of polydiacetylene polymer crystals is considered in some detail in Sec. VII, where a comparison with experiment is also presented. In Sec. VIII the main approximations and simplifications are summarized and reviewed.

II. EXPRESSIONS OF NONLINEAR OPTICAL SUSCEPTIBILITIES FOR 1D SEMICONDUCTORS

The structures of the organic 1D semiconductors were briefly described in I; in the same reference the assumptions and simplifications underlying the description of the π electrons were presented. These materials are assumed to be composed of parallel linear chains extending along the x direction which will be taken to be a crystallographic axis as well. The chains are taken to be independent and infinitely long and we may thus focus our attention to the π-electron band states of a single chain. Let σ be the density of chains per unit cross area of the yz plane. For materials with chains not having a center of inversion, a unit vector can be assigned along each chain; let σ_+ and σ_- be the densities of such chains with their unit vectors pointing in the positive and negative directions, respectively, of the macroscopic x axis (see Fig. 1).

We shall mainly be interested in the optical properties of these materials in their transparency region, the one extending between the main absorption peak due to band-to-band π-electron transition, and the vibrational modes of the chains. In contrast to the case of the linear optical properties considered in I, the contribution of the σ bonds and side groups to the nonlinear susceptibilities may be neglected with respect to that of the π electrons; since the latter are confined along the chains, the only components of interest are $\chi^{(2)}_{xxx}$ and $\chi^{(3)}_{xxxx}$. This is certainly justified in the case of the second-order susceptibility $\chi^{(2)}$ since these bonds are isotropically distributed around the chains. For chains with large π-electron delocalization, the ones in which we are exclusively interested here, it is also justified in the case of the third-order susceptibility $\chi^{(3)}$ as can be inferred by comparing the values of the third-order polarizabilities γ of molecules with saturated bonds, where the additivity hypothesis can be used, with those of conjugated molecules of equal number of π electrons.[5,6]

The expressions of the components $\chi^{(2)}_{xxx}$ and $\chi^{(3)}_{xxxx}$ can be most conveniently obtained using the Genkin-Mednis approach[10] (see Appendix A). The susceptibilities are then expressed in terms of the matrix elements of the position x rather than those of the momentum p as was conventionally done in the past.[11] The advantages of the former representation are particularly transparent when the limiting expressions of the susceptibilities for vanishing frequencies (transparency region) are needed.

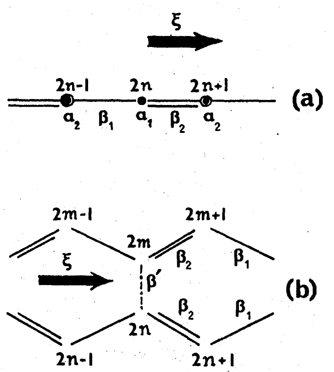


FIG. 1. Axis conventions (director vector ξ) for noncentrosymmetric chains: (a) heteroatomic-bond-alternated chain, (b) pair of coupled chains in the A configuration. These axis conventions must be specified, for instance, when the sign of the second-order susceptibility is stated.

Since the π-electron states in the considered systems can be more or less well approximated with two bands termed in the following valence (v, filled) and conduction (c, empty) bands, the two-band approximation will be adopted. The expressions of $\chi^{(2)}_{xxx}(\omega_1, \omega_2)$ and $\chi^{(3)}_{xxxx}(\omega_1, \omega_2, \omega_3)$ in the two-band approximation are given in Appendix A. In the transparency region of the material we may put $\omega_i \simeq 0$ in these expressions and we obtain the zero-frequency expressions of $\chi^{(2)}_{xxx}$ and $\chi^{(3)}_{xxxx}$ to be denoted $\chi_\pi^{(2)}$ and $\chi_\pi^{(3)}$, respectively. They are

$$\chi^{(2)}_{xxx}(0,0) = \chi_\pi^{(2)} = \frac{6e^3\Delta\sigma}{\hbar^2}\frac{i}{2\pi}\int_{\mathrm{uc}}\left[S_{vc}S_{cv}(\Omega_{vv}-\Omega_{cc}) - \tfrac{1}{2}\left(S_{vc}\frac{\partial S_{cv}}{\partial k} - \frac{\partial S_{vc}}{\partial k}S_{cv}\right)\right]dk \tag{2.1}$$

or

$$\chi_\pi^{(2)} = \chi^{(2)}_{\mathrm{inter}} + \chi^{(2)}_{\mathrm{intra}}$$

where

$$\chi^{(2)}_{\mathrm{intra}} = -\frac{3e^3\Delta\sigma}{\hbar^2}\frac{i}{2\pi}\int_{\mathrm{uc}}\left(S_{vc}\frac{\partial S_{cv}}{\partial k} - \frac{\partial S_{vc}}{\partial k}S_{cv}\right)dk\ , \tag{2.2}$$

$$\chi^{(2)}_{\mathrm{inter}} = \frac{6e^3\Delta\sigma}{\hbar^2}\frac{i}{2\pi}\int_{\mathrm{uc}}S_{vc}(\Omega_{vv}-\Omega_{cc})S_{cv}\,dk\ , \tag{2.3}$$

with $\Delta\sigma = \sigma_+ - \sigma_-$ (see Fig. 1), and

$$\chi_\pi^{(3)} = \frac{8e^4\sigma}{\hbar^3}\frac{1}{2\pi}\int_{\mathrm{uc}}\left[\Omega_{vc}S_{cv}S_{vc}S_{cv} + \frac{1}{\omega_{cv}}\frac{\partial S_{cv}}{\partial k}\frac{\partial S_{vc}}{\partial k} + \frac{(\Omega_{vv}-\Omega_{cc})^2}{\omega_{vc}}S_{vc}S_{cv} + \frac{(\Omega_{vv}-\Omega_{cc})}{\omega_{vc}}\left(\frac{\partial S_{vc}}{\partial k}S_{cv} - S_{vc}\frac{\partial S_{cv}}{\partial k}\right)\right]dk\ , \tag{2.4}$$

or $\chi_\pi^{(3)} = \chi^{(3)}_{\mathrm{inter}} + \chi^{(3)}_{\mathrm{intra}}$

where

$$\chi^{(3)}_{\text{intra}}=\frac{8e^4\sigma}{\hbar^3}\frac{1}{2\pi}\int_{\text{uc}}\left[\frac{1}{\omega_{cv}}\frac{\partial S_{cv}}{\partial k}\frac{\partial S_{vc}}{\partial k}+\frac{(\Omega_{vv}-\Omega_{cc})}{\omega_{vc}}\left(\frac{\partial S_{vc}}{\partial k}S_{cv}-S_{vc}\frac{\partial S_{cv}}{\partial k}\right)\right]dk\,, \tag{2.5}$$

$$\chi^{(3)}_{\text{inter}}=\frac{8e^4\sigma}{\hbar^3}\frac{1}{2\pi}\int_{\text{uc}}\left(\Omega_{vc}S_{vc}S_{vc}S_{cv}+\frac{(\Omega_{vv}-\Omega_{cc})^2}{\omega_{vc}}S_{vc}S_{cv}\right)dk\,. \tag{2.6}$$

Here $\omega_{vc}(k)=[\epsilon_v(k)-\epsilon_c(k)]/\hbar$, $S_{vc}(k)=\Omega_{vc}(k)/\omega_{vc}(k)$, and the dipole transition-matrix elements $\Omega_{nn'}(k)$ are defined by

$$\Omega_{nn'}(k)=\frac{1}{d}\int_{\text{uc}}u^*_{nk}(x)\frac{\partial u_{n'k}(x)}{\partial k}dx\,, \tag{2.7}$$

where $u_{nk}(x)$ is the unit-cell periodic part of the π-electron Bloch function $\psi_{nk}(x)$ and d is the unit-cell (uc) length along the chain direction. In the above expressions use was made of (A14) to replace summations by integrations over the Brillouin zone (BZ) and a factor of 2 has been included to take into account the electron spin states.

Such separation of $\chi^{(2)}_\pi$ and $\chi^{(3)}_\pi$ into inter- and intraband contributions is absent in the π-electron contribution to the linear susceptibility (see I); there only interband terms contribute. It shows that the nonlinear susceptibilities strongly depend on the degree of flatness of the bands; *their sign in particular is determined by the relative importance of the two contributions*, as will be shown below.

The third-order susceptibility has a very rich resonance behavior[1,12] and a closely connected effect is the two-photon absorption whose strength is expressed in terms of $\operatorname{Im}\chi^{(3)}(\omega_1,-\omega_1,\omega_2)$ with $\omega_1+\omega_2=\omega_{cv}$. For the degenerate case $\omega_1=\omega_2=\omega$ in general one obtains:

$$\operatorname{Im}\chi^{(3)}(\omega,-\omega,\omega)=-\frac{8e^4\sigma}{\hbar^3}\frac{1}{2\pi}\int\frac{\tau(k)|M_{cv}(k;\omega)|^2}{1+\tau^2(k)(\omega_{cv}-2\omega)^2}dk \tag{2.8}$$

where

$$M_{cv}(k,\omega)=\frac{\Omega_{cv}(\Omega_{cc}-\Omega_{vv})}{\omega_{cv}-\omega+i\tau^{-1}(k)}+\nabla_k\left(\frac{\Omega_{cv}}{\omega_{cv}-\omega+i\tau^{-1}(k)}\right)+\sum_{c'\neq c}\frac{\Omega_{cc'}\Omega_{c'v}}{\omega_{c'v}-\omega+i\tau^{-1}(k)} \tag{2.9}$$

and $\tau(k)$ is a relaxation time; when $\Omega_{cc}=\Omega_{vv}$, this expression reduces to that of Mednis.[13]

III. ATOM- AND BOND-ALTERNATED CHAINS. POLYENES

There are two atoms per unit cell along the chain with Coulomb integrals α_1 and α_2; the hopping integrals alternatively take the values β_1 and β_2 along the chain for long and short bonds, respectively. When $\alpha_1\neq\alpha_2$ and $\beta_1\neq\beta_2$, the chain has no inversion symmetry and we define the director vector as the unit vector pointing from the atom with Coulomb integral α_1 to the atom with Coulomb integral α_2 along the short bond (see Fig. 1).

In the tight-binding approximation the π-electron states are distributed into two bands whose energies and wave functions as well as the dipole transition strengths $\Omega_{nn'}$ were derived in I. Substituting expressions (3.4) and (4.6) of I in (2.1) one obtains

$$\chi^{(2)}_\pi=\frac{3e^3a^2\Delta\sigma}{64\beta_2^2}\frac{\mu(1-\nu^2)}{\pi}\int_0^{\frac{1}{2}\pi}\frac{(1-\nu^2)^2+4\mu\nu^2\sin^2\theta+4\nu(\zeta^2-\mu^2)\cos\theta}{\zeta^5(\zeta^2-\mu^2)^2}d\theta \tag{3.1}$$

where $\theta=ka$, a being the unit-cell length, $\zeta=(\mu^2+1+\nu^2+2\nu\cos\theta)^{1/2}$; the parameters $\mu=(\alpha_1-\alpha_2)/2\beta_2$ and $\nu=\beta_1/\beta_2$ represent the degrees of heteroatomicity and bond alternation, respectively. Using the definitions[14] of the complete elliptic functions of the first and second kind, $E(k)$ and $F(k)$, respectively, one finds

$$\chi^{(2)}_\pi=\frac{\nu(1-\nu^2)}{\pi c^3d^2}\left(\frac{4(\mu^2+\nu^2+1)}{d^2}E(p)-F(p)\right)\frac{3e^3a^2\Delta\sigma}{64\beta_2^2}\,, \tag{3.2}$$

where $c^2=\mu^2+(1+\nu)^2$, $d^2=\mu^2+(1-\nu)^2$, and $p^2=4\nu/c^2$. The constants d and c are related to the smallest band gap, $E_g=2|\beta_2d|$, and the largest one, $E_g'=2|\beta_2c|$, which occur at the edge and the center of the BZ, respectively. We notice from (3.2) that $\chi^{(2)}_\pi=0$ if either $\mu=0$ (homoatomic chain) or $\nu=1$ (no bond alternation, equidistant atoms) as in both cases the chain possesses the inversion symmetry.

For the extreme case of localized (saturated) bonds, namely, $\nu=0$, there is no k dependence (flat bands), and only the interband term contributes to $\chi^{(2)}_\pi$ or

$$\chi^{(2)}_\pi=\frac{3e^3a^3}{(8\beta_2)^2}\frac{\Delta\sigma}{a}\frac{\mu}{(1+\mu^2)^{5/2}}=\frac{3e^3a^3}{(8\beta_2)^2}\frac{\Delta\sigma}{a}f_i^{1/2}(1-f_i)^2\,, \tag{3.3}$$

where $f_i=\mu^2/(1+\mu^2)$ is the degree of ionicity for the dimer; this definition of the ionicity is analo-

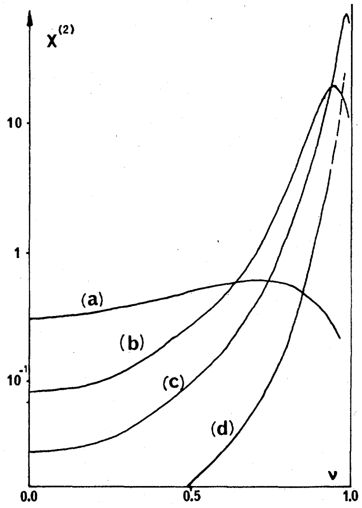


FIG. 2. Second-order susceptibility $\chi^{(2)}$ vs $\nu=\beta_1/\beta_2$ for heteroatomic-bond-alternated chains for four different values of the heteroatomicity parameter $\mu=\Delta\alpha/\beta_2$; (a) $\mu=0.5$, (b) $\mu=0.075$, (c) $\mu=0.025$, and (d) $\mu=0.004$. $\chi^{(2)}$ is expressed in units of $\chi_0^{(2)}=3e^3a^2\Delta\sigma/(8\beta_2)^2$.

gous to the one used by Phillips and van Vechten in their dielectric description[15] of the inorganic semiconductors. Expression (3.3) has a maximum for $f_i=0.2$ which corresponds to $\mu=0.5$. Similar behavior is also obtained for $\chi^{(2)}$ in inorganic semiconductors using the charge transfer model.[16]

Another extreme case is that of the highly delocalized electrons or $\nu\rightarrow 1$. For $\mu<0.5$ one can use the asymptotic expansions for $E(p)$ and $F(p)$ in the limit of $p\simeq 1$ and the leading term in (3.2) is

$$\chi_\pi^{(2)}\simeq\frac{3a^2e^3\Delta\sigma}{\pi(8\beta_2)^2}\,\frac{2(1-\nu^2)\mu}{3[\mu^2+(1-\nu)^2]^2}\,. \tag{3.4}$$

In order to study the variation of $\chi_\pi^{(2)}$ for arbitrary values of μ and ν we computed (3.1) numerically and the results are plotted in Fig. 2. We find that for a given μ, $\chi_\pi^{(2)}$ slowly rises as ν increases. attains a maximum, and then decreases at a faster rate with further increase in ν. With increasing values of μ, the maximum value of $\chi_\pi^{(2)}$ shifts towards lower values of ν. It is evident that given one parameter, the other can be chosen to maximize $\chi_\pi^{(2)}$. This remark is particularly useful when the heteroatomicity is not due to actual atom alternation but is a consequence of the attached side group radicals, as in polyphenylacetylenes (see I); by a proper choice of the side groups it is possible to achieve high values of $\chi_\pi^{(2)}$.

It presently appears difficult to grow such polymer crystals with $\Delta\sigma\neq 0$ and thus one expects $\chi_\pi^{(2)}$ to be small or vanishing. The third-order susceptibility $\chi^{(3)}$ on the other hand does not suffer from such considerations; the contributions of the chains are additive *irrespective of the direction of the director vector with respect to the x-axis direction.* In order to get more insight into the π-electron behavior it is of some interest to use the separation of $\chi_\pi^{(3)}$ into inter- and intraband contributions as shown in (2.4). Substituting the expressions of $\Omega_{nn'}$ and ω_{cv} in (2.5) and (2.6), one obtains

$$\chi_{\text{intra}}^{(3)}=\chi_0^{(3)}\frac{1}{\pi}\int_0^\pi\left(\frac{4\mu^2(1-\nu^2)P}{\zeta_0^6\zeta^9}-\frac{P^2}{\zeta_0^4\zeta^{11}}\right)d\theta\,, \tag{3.5}$$

$$\chi_{\text{inter}}^{(3)}=\chi_0^{(3)}\frac{1}{\pi}\int_0^\pi\left(\frac{2(1-\nu^2)(\nu^2\sin^2\theta+\nu\zeta^2\cos\theta)}{\zeta_0^4\zeta^9}+\frac{\nu^2\sin\theta Q}{\zeta_0^6\zeta^{11}}\right)d\theta\,, \tag{3.6}$$

where $\chi_0^{(3)}=2e^4a^3\sigma/(8\beta_2)^3$, $P=4\mu^2\nu^2\sin^2\theta+\zeta^2(1-\nu^2)$, $Q=2\mu\nu\sin\theta(3\zeta_0^2+\zeta^2)+2\mu\zeta^2\zeta_0^2\cos\theta+\zeta^2(1-\nu^2)^2(2\zeta_0^2+\zeta^2)^2$ and $\zeta_0=(\zeta^2-\mu^2)^{1/2}$.

One can easily compute $\chi_\pi^{(3)}=\chi_{\text{intra}}^{(3)}+\chi_{\text{inter}}^{(3)}$ for arbitrary values of the parameters μ and ν. For $\nu=0$ (saturated bonds, two-level dimer) $\chi_{\text{intra}}^{(3)}=0$ (flat bands) and $\chi_\pi^{(3)}=\chi_{\text{inter}}^{(3)}$ or

$$\chi_\pi^{(3)}=\chi_0^{(3)}(4\mu^2-1)(1+\mu^2)^{-7/2} \tag{3.7}$$

which reverses sign as μ crosses the values $\mu=0.5$, and gives $\chi_\pi^{(3)}=-\chi_0^{(3)}$ for $\mu=0$ indicating that for a chain consisting of homoatomic dimers $\chi_\pi^{(3)}$ is negative. One also finds that except for very low values of ν, nonzero values of μ (heteroatomic chain), at any given value of ν, reduce $\chi_\pi^{(3)}$; it reaches its maximum value for $\mu=0$ (homoatomic chains). This case can be treated exactly and the main results were given elsewhere[17]; here we give some details concerning their derivation.

For $\mu=0, \Omega_{vv}-\Omega_{cc}=0$ in (2.5) and (2.6); one obtains the much simpler expressions

$$\chi_{\text{intra}}^{(3)}=\frac{8e^4\sigma}{\hbar^3}\,\frac{1}{2\pi}\int_{\text{uc}}\frac{1}{\omega_{cv}}\,\frac{\partial S_{cv}}{\partial k}\,\frac{\partial S_{vc}}{\partial k}\,dk\,, \tag{3.8}$$

$$\chi_{\text{inter}}^{(3)}=\frac{8e^4\sigma}{\hbar^3}\,\frac{1}{2\pi}\int_{\text{uc}}\Omega_{vc}S_{cv}S_{vc}S_{cv}\,dk\,, \tag{3.9}$$

and using $\Omega_{cv}=ia(1-\nu^2)/4\zeta_0^2$ (see I), one obtains the expressions for $\chi_{\text{intra}}^{(3)}$ and $\chi_{\text{inter}}^{(3)}$; this can also be obtained by putting $\mu=0$ in (3.5) and (3.6). The integration of the resulting expressions can be performed analytically[17] and expressed in terms[14] of the hypergeometric function $F(a,b,c,z)$. The limit $\nu\rightarrow 1$ is of particular interest since it clearly demonstrates the close relationship between high values of $\chi^{(3)}$ and large π-electron delocalization. To evaluate this limit we express the integrals (3.5) and (3.6) for $\mu=0$ in terms of the elliptic integral of the first kind, $E(m)$ where $m=4\nu/(1+\nu)^2$. Indeed from (3.5) and (3.6), putting $\mu=0$ and using integration by parts and the appropriate recurrence formulas,[14] one has

$$\chi^{(3)}_{\text{intra}} = \chi_0^{(3)} \frac{1}{\pi} \int_0^{\pi} \frac{144\nu^2(1-\nu^2)^2 \sin^2\theta}{(1+2v\cos\theta+\nu^2)^{11/2}} d\theta$$

$$= \frac{128}{35\pi} \chi_0^{(3)} \frac{1}{(1+\nu)^3} \left(\frac{1+\nu}{1-\nu}\right)^6 E(m)$$

and

$$\chi^{(3)}_{\text{inter}} = -\chi_0^{(3)} \frac{1}{\pi} \int_0^{\pi} \frac{(1-\nu^2)^4}{(1+2v\cos\theta+\nu^2)^{11/2}} d\theta$$

$$= -\frac{2}{9} \frac{128}{35\pi} \chi_0^{(3)} \frac{1}{(1+\nu)^3} \left(\frac{1+\nu}{1-\nu}\right)^6 E(m) .$$

Using the notation $N_d = (1+\nu)/(1-\nu)$ introduced in I one obtains for $\chi_\pi^{(3)} = \chi^{(3)}_{\text{intra}} + \chi^{(3)}_{\text{inter}}$

$$\chi_\pi^{(3)} = \frac{128}{45\pi} \frac{E(m)}{(1+\nu)^3} \chi_0^{(3)} N_d^6 , \tag{3.10}$$

which for $\nu \rightarrow 1$, using the series expansion for $E(m)$, finally becomes

$$\chi_\pi^{(3)} = \frac{16}{45\pi} \chi_0^{(3)} N_d^6 . \tag{3.11}$$

This is the result given in Ref. 17 and clearly shows the strong dependence of $\chi^{(3)}$ on the π-electron delocalization as expressed by N_d. This sixth-power dependence of $\chi_\pi^{(3)}$ on N_d and the square dependence of $\chi_\pi^{(1)}$ on N_d derived in I are characteristic of 1D systems. It is a consequence of the rapid variation of the dipole transition strength Ω_{cv} within a very narrow region near the BZ edge where it attains its maximum value $\Omega_{cv}(\pi=\theta) = \frac{1}{4} N_d a$ and where also the joint density of electronic states becomes infinite. Accordingly almost the total contribution to $\chi_\pi^{(3)}$ comes from a very narrow region near the BZ edge and strongly reflects the details of the band structure and Ω_{cv} there. Since N_d measures the π-electron delocalization length, which in many of these organic conjugated chains can attain very high values, the much higher power dependence of $\chi_\pi^{(3)}$ on N_d than the one found for $\chi_\pi^{(1)}$ justifies the neglect of the side-group contribution to $\chi^{(3)}_{xxxx}$ while this was not the case for $\chi^{(1)}_{xx}$; there the contributions of $\chi_\pi^{(1)}$ and the σ bonds to $\chi_\pi^{(1)}$ are of the same order of magnitude. Thus $\chi^{(3)}_{xxxx}$ strongly reflects π-electron delocalization effects.

The above results were derived for the homoatomic bond alternated chain ($\mu = 0$). Since only the details at the BZ edge are of importance as far as the optical transitions are concerned, one may speculate that the sixth-power dependence of $\chi_\pi^{(3)}$ on N_d may persist even in the case of a heteroatomic chain where $\mu \neq 0$ as long as N_d is large. In this case we have (see I)

$$N_d = 4 | \Omega_{cv}(\theta=\pi) | / a = (1+\nu)/[(1-\nu)^2 + \mu^2]^{1/2} , \tag{3.12}$$

and on plotting $\chi_\pi^{(3)}$ vs N_d for arbitrary values of μ and ν we found that indeed to a very good degree of approximation

$$\chi_\pi^{(3)} \sim N_d^6 \tag{3.13}$$

for large N_d, even for a heteroatomic chain.

Using the notations $E_g = 2(\beta_2 - \beta_1)$ and $2E_F = 2(\beta_1 + \beta_2)$, introduced in I, expression (3.10) can also be written

$$\chi_\pi^{(3)} = (16/45\pi) \chi_0^{(3)} (2E_F/E_g)^6 . \tag{3.14}$$

Exactly the same dependence of $\chi^{(3)}$ on the optical energy gap is also obtained within the almost-free-electron model for a one-dimensional semiconductor.[18] It is of interest to consider the extent to which this inverse sixth-power dependence of $\chi^{(3)}$ on E_g obtained in 1D semiconductors even persists in cubic inorganic semiconductors like Ge or Si. Such considerations were discussed in connection with $\chi^{(1)}_{xx}$ in I where it was found that the linear susceptibility of a cubic semiconductor within the spherical band model introduced[19] by Penn shows the same dependence on E_g as the one-dimensional semiconductor. For this purpose we carried out the calculation of $\chi^{(3)}_{xxxx}$ in the Penn band model which with a single band gap E_g is an almost-free-electron (weak-binding) model for an isotropic semiconductor. Because of the spherical symmetry it is sufficient to calculate $\chi^{(3)}$ in only one direction, say the x direction. Since there are only two bands, a valence and a conduction band, expressions (3.8) and (3.9) can be used with only slight modifications to take into account the "three-dimensional" character of the system. Without going into the computational details, which are cursively discussed in Appendix C, we reproduce here the final result

$$\chi^{(3)}_{xxxx} = \tfrac{8}{21} (e^4 / | k_F |^4 E_F^3) (2E_F/E_g)^6 ,$$

where k_F and E_F are the Fermi wave vector and energy, respectively. Van Vechten *et al.*[20] also obtained this same dependence of $\chi^{(3)}$ on E_g in a different way. This remarkably same functional dependence of $\chi^{(3)}$ on the energy gap in the two models strongly indicates that the critical point in Penn's model is of the same type as for a one-dimensional semiconductor, as is also indicated in I from the study of $\chi^{(1)}$.

Qualitatively speaking describing a cubic semiconductor by Penn's model amounts to replacing the actual three-dimensional electronic structure by one of an assembly of hypothetical chains in the four [111] directions in these crystals. The E_2 Van Hove singularity in the joint density of states of the cubic semiconductors probably originates[21] from this one-dimensional character of the valence electrons. We compare the order of magnitude of $\chi^{(3)}_{xxxx}$ in two cases, a hypothetical one-dimensional polymer crystal with polyene-type chains and a hypothetical Ge crystal whose structure is reduced to an assembly of independent chains in the four [111] directions (ξ direction) with the valence electrons not allowed to hop from one chain to the other. For a polyene chain one characteristically has[22] $\beta_2 = 4$ eV, $\beta_1/\beta_2 = 0.75$, $a = 2.5$ Å, and $\sigma = 10^{14}$ cm^{-2} (which corresponds to the chains being 10 Å apart). Hence $E_g = 2$ eV and $N_d \simeq 7.5$; from (3.14), one then has $\chi^{(3)}_{xxxx} = 2.5 \times 10^{-10}$ esu. For the hypothetical Ge crystal $E_g = 5$ eV, corresponding to the position of the E_2 peak in the absorption curve, and the value of the valence electron density $N \simeq 64/a^3$ (a is the lattice constant) one obtains[20] $\chi^{(3)}_{\xi\xi\xi\xi} \simeq 10^{-11}$ esu. This value, however, substantially underestimates the actual value of $\chi^{(3)}$ for Ge as the main contribution to $\chi^{(3)}_{\xi\xi\xi\xi}$ comes from the critical point E_0, characterized as three dimensional[20] and situated at $\simeq 0.5$ eV, the absorption threshold. Including the contribution from the E_0 critical point one finally obtains[20] $\chi^{(3)}_{\xi\xi\xi\xi} \simeq 10^{-10}$ esu which is close to the experimental value. In contrast to $\chi^{(3)}$ it should be noted that $\chi^{(1)}$ for Ge can be well accounted for[21,22] by only considering the E_2-peak contribution (Penn's model); the contribution from the E_0 peak is negligible. This is due to the fact that $\chi^{(1)}$ only contains an interband contribution while $\chi^{(3)}$ has both intra- and interband contributions, the former being the most important.

As can be seen from the above discussion, high susceptibility values can be obtained in one-dimensional conjugated polymer crystals comparable to the one measured in Ge, the highest known value for $\chi^{(3)}$, but with a high absorption threshold, much higher than in Ge. This advantage along with the optical anisotropy and the low refractive index make these materials very appropriate candidates as nonlinear optical components.[18] Polyene-type polymer crystals have not been obtained yet, but the same features can be obtained with superalternated chains like the polydiacetylenes.

IV. SUPERALTERNATED CHAINS. POLYDIACETYLENES

The superalternated chain whose band structure was derived in I is homoatomic and possesses a center of inversion; consequently, $\chi^{(2)} \equiv 0$. However, if there are two different side groups per unit cell, R_1 and R_2, the chain may not possess a center of inversion; this is because the carbon atoms to which the side groups are attached behave differently because of the inductive effect.[23] This introduces an effective heteroatomicity and a nonzero value of $\chi^{(2)}$ is possible. The calculations for such a chain are quite involved and will not be given here. Nonetheless it is possible to treat this case in an approximate way by replacing the actual heteroatomic superalternated chain by "the optically equivalent associated heteroatomic polyene chain" defined as the one having the same smallest and largest band gaps and the same degree of heteroatomicity as the superalternated chain; this allows one then to calculate the hopping energies $\tilde{\beta}_1, \tilde{\beta}_2$ and the difference of Coulomb integrals $\alpha_1 - \alpha_2$ for the polyene chain, and to proceed to the estimation of $\chi^{(2)}$ as previously. Order-of-magnitude calculations of this type show that $\chi^{(2)}$ is not very large even when $\sigma_+ \simeq \sigma$ and therefore the use of these systems for second harmonic is of limited practical interest. As a matter of fact it is more likely that $\sigma_+ = \sigma_-$ in these systems or that the chains polymerize in a centrosymmetric configuration of the side groups along the chain, so that $\chi^{(2)} = 0$ by symmetry.

The case of $\chi^{(3)}$, on the other hand, is of considerable interest in particular in chains with the same radical in both positions in the unit cell, as it corresponds to the whole class of polydiacetylene polymer crystals which are now available as large defect-free samples on which preliminary measurements of $\chi^{(3)}$ have already been performed, and our results can be directly compared.

The band structure of a homoatomic superalternated chain was derived in I. As was found there, there are four bands since all $\Omega_{nn'}$ between two bands do not vanish in general. Strictly speaking Eq. (4.1) cannot be used to calculate $\chi^{(3)}$ as it is valid for a two-band system. For not too high values of ν', however, it turns out that the dipole transition strength for the transitions $2 \rightarrow 4$ and $1 \rightarrow 3$ are much smaller in comparison to those of the transitions $1 \rightarrow 4$ and $2 \rightarrow 3$ and can be neglected. If the bands are depicted in the Jones zone, this amounts to keeping only vertical transitions there and neglecting transitions between different halves of the Jones zone. The four-band system can be treated as a two-band system with a discontinuity in the middle of the Jones zone and hence Eq. (2.4) can still be used with the understanding that the integration must be performed over the Jones zone.

In Ref. 17 we depicted the dependence of $\chi^{(3)}_\pi$ of a superalternated chain as a function of $(1+\nu)/(1-\nu)$ for four different values of $\nu' = \beta_3/\beta_2$. We see that superalternation can substantially reduce $\chi^{(3)}$ for large values of $(1+\nu)/(1-\nu)$ from its value with no superalternation ($\nu' = 1$). The main contribution to $\chi^{(3)}$ comes from the edge of the Jones zone ($\theta = \pi$) where the dipole transition strength Ω_{vc} attains its maximum value, namely, $\Omega_{23}(\pi)$. If one plots the quantity $\chi^{(3)}_\pi$ as a function, of of $N_d = 4|\Omega_{23}(\theta = \pi)|/a$, the optical π-electron delocalization parameter, one finds that, for large values of N_d ($\gg 1$), $\chi^{(3)}_\pi$ is solely a function of this parameter and that

$$\chi^{(3)}_\pi \sim N_d^6 \;;$$

namely, the dependence is the same as for a simple bond-alternated chain. No such simple relation in terms of the band gaps was found as in the case of the polyene chain [compare Eq. (3.11)].

V. TWO COUPLED CHAINS. POLYACENES

As discussed in I, two bond-alternated chains may get coupled either in the centrosymmetric configuration (S configuration) or in the noncentrosymmetric configuration (A configuration). Both configurations have the same four-band structure but markedly different band wave functions and dipole transition elements. A nonzero value of $\chi^{(2)}$ will exist only for the later configuration. Since the selection rules for the dipole transition strengths $\Omega_{nn'}$ in the A configuration are such that the system rigorously behaves as two uncoupled "heteroatomic"-bond-alternated chains with an effective heteroatomicity $\delta' = \beta'/\beta_2$, where $2\beta'$ is the interchain hopping energy for a π electron, the results of Sec. III apply here. In particular $\chi^{(2)}$ has two contributions each of the form (2.1) for each pair of bands, (1, 3) and (2, 4). Since, however, $\Omega_{11} - \Omega_{33} = -(\Omega_{22} - \Omega_{44})$, the interband contributions cancel and the total contribution to $\chi^{(2)}$ comes from the intraband terms only or

$$\chi_{\pi A}^{(2)} = \frac{\delta'(1-\nu^2)A}{\pi} \int_0^{\pi} \frac{\nu^2 \sin^2\theta + \nu\zeta\cos\theta}{\zeta_0^2 \zeta^7}\, d\theta\,, \qquad (5.1)$$

where $A = 3e^3a^2\Delta\sigma/(8\beta_2)^2$, $\zeta^2 = \zeta_0^2 + \delta^2$, and $\zeta_0^2 = 1 + \nu^2 + 2\nu\cos\theta$, and $\Delta\sigma = \sigma_+ - \sigma_-$, where σ_+ (σ_-) is the density of pairs with the director vector parallel (antiparallel) to the positive x axis of the medium (see Fig. 1). The values of $\chi_\pi^{(2)}$ calculated from (5.1), unless $\Delta\sigma = 0$, can be measured (see Fig. 3). This is a quite remarkable result since the isolated chains before they get coupled in pairs possess inversion symmetry and hence $\chi^{(2)} = 0$.

The third-order susceptibility $\chi_\pi^{(3)}$, on the other hand, is nonzero for both configurations. As for $\chi_\pi^{(2)}$, in the A configuration, $\chi_\pi^{(3)}$ has two contributions each of the form (2.4) for each pair of bands, (1, 3) and (2, 4), and the results of Sec. III for bond-alternated chains can be used here, too. In particular

$$\chi_{\pi A}^{(3)} \sim N_{dA}^6$$

for large N_{dA}, where $N_{dA} = 4\,|\,\Omega_{13}(\pi = \theta)\,|\,/a$.

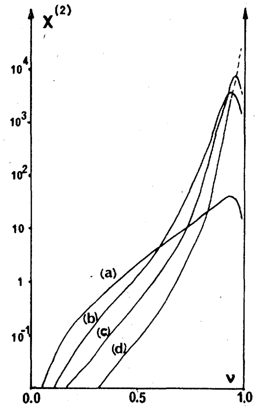


FIG. 3. Second-order susceptibility vs $\nu = \beta_1/\beta_2$ for pairs of coupled chains in the A configuration, for four different values of the coupling parameter $\delta = \beta'/\beta_2$; (a) $\delta = 0.5$, (b) $\delta = 0.075$, (c) $\delta = 0.025$, and (d) $\delta = 0.004$. $\chi^{(2)}$ is expressed in units of $\chi_0^{(2)} = 3e^3a^2\Delta\sigma/(8\beta_2)^2$.

For the S configuration strictly speaking a four-band expression for $\chi_\pi^{(3)}$ must be used. Since, however, $\Omega_{12} = \Omega_{34} = 0$, the total expression of $\chi_\pi^{(3)}$ contains two two-band contributions of the form (2.4) for the pairs of bands (1, 4) and (2, 3) and an additional interband term which for very delocalized π-electron systems may be neglected as long as β'/β_2, the coupling parameter, is small compared to β_1/β_2. Thus the results obtained in Sec. III for the bond-alternated chain, a two-band system, can be used here too. In particular

$$\chi_\pi^{(3)} \sim N_{dS}^6$$

for large N_{dS} where $N_{dS} = 4\,|\,\Omega_{23}(\theta = \pi)\,|\,/a$. It is easy to see that, since $N_{dS} > N_d > N_{dA}$ (or equivalently $D_s > D > D_A$, see I) the following relation will hold for the third-order susceptibilities

$$\chi_{\pi S}^{(3)} > \chi_\pi^{(3)} > \chi_{\pi A}^{(3)}.$$

Thus $\chi^{(3)}$ may decrease or increase depending upon which configuration will be preferred.

VI. TWO-PHOTON ABSORPTION

Two-photon absorption may occur whenever $\omega_1 + \omega_2 = \omega_{cv}(k)$ where $\hbar\omega_1$ and $\hbar\omega_2$ are the incident photon energies. The corresponding absorption cross section is determined by $\mathrm{Im}\chi^{(3)}(\omega_1, -\omega_1, \omega_2)$ whose expression is given by (2.8); we shall only consider the degenerate case $\omega_1 = \omega_2 = \omega$. Further, it is sufficient to limit the discussion to the atom- and bond-alternated chains and the coupled bond-alternated chains in the S configuration; the other cases can be reduced to these two.

The two-photon transition strength M in the degenerate case ($\omega_1 = \omega_2 = \omega$) is given by (2.9); for $\omega_{cv} - \omega \gg 1/\tau(k)$ one has

$$M_{cv}(k) = \frac{\Omega_{cv}(\Omega_{cc}\,\Omega_{vv})}{\omega_{cv} - \omega} + \frac{\partial}{\partial k}\left(\frac{\Omega_{cv}}{\omega_{cv} - \omega}\right) + \sum_{c' \neq c} \frac{\Omega_{cc'}\Omega_{c'v}}{\omega_{c'v} - \omega}\,, \qquad (4.1)$$

which inserted in (2.8) allows one to calculate the two-photon absorption cross section.

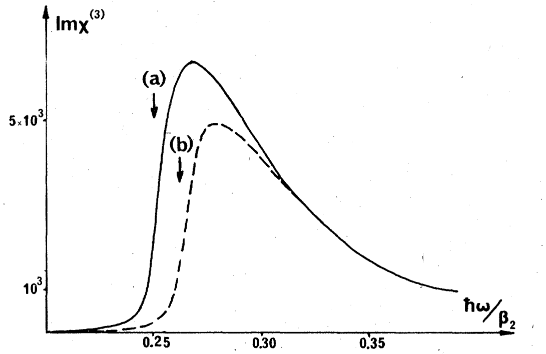


FIG. 4. Two-photon absorption intensity, $\mathrm{Im}\chi^{(3)}(\omega, -\omega, \omega)$, vs frequency for heteroatomic bond-alternated chains for $\nu = 0.75$ and two different values of the heteroatomicity parameter $\mu = \Delta\alpha/\beta_2$: (a) $\mu = 0.0$ and (b) $\mu = 0.5$; $\mathrm{Im}\chi^{(3)}$ is expressed in units of $\chi_0^{(3)} = 2e^4a^3\sigma/(8\beta_2)^3$. The relaxation time (see text) was assumed constant over the Brillouin zone and had the same value for both cases, $\hbar/\tau\beta_2 = 0.005$. *The arrows indicate the positions of the one-photon optical gaps; notice the shift in the peaks.*

The results for the two cases mentioned above are depicted in Figs. 4 and 5; the same value for β_1/β_2 was chosen for all cases. For the case of the atom- and bond-alternated chains the calculation was performed for two different values of the heteroatomicity parameter μ, namely, $\mu = 0$ (homoatomic-bond-alternated chain, e.g., polyene) and $\mu = 0.075$, while for the coupled chains in the S configuration the calculation was done for three different values of the coupling coefficient $\delta = \beta'/\beta_2$, namely, $\delta = 0$ (homoatomic-bond-alternated chain) $\delta = 0.025$, and $\delta = 0.05$. The relaxation time $\tau(k)$ was taken constant over the BZ, $\hbar/\tau\beta_2 \simeq 0.0053$ for all cases.

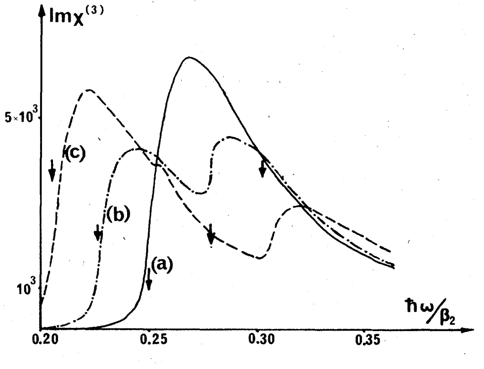


FIG. 5. Two-photon absorption intensity, $\mathrm{Im}\chi^{(3)}(\omega, -\omega, \omega)$, vs frequency for pairs of coupled chains in the S configuration for $\nu = 0.75$ and three different values of the coupling strength $\delta = \beta'/\beta_2$. (a) $\delta = 0.0$, (b) $\delta = 0.025$, and (c) $\delta = 0.05$. $\mathrm{Im}\chi^{(3)}$ is expressed in units of $\chi^{(3)} = 2e^4a^3\sigma/(8\beta_2)^3$. The relaxation time (see text) was taken constant over the Brillouin zone and had the value $\hbar/\tau\beta_2 = 0.005$ for all three cases. The arrows indicate the positions of the one-photon optical gaps.

The general features of the curves can be easily explained by considering (4.1). This quantity contains two "two-band" terms, the first and the second term, and a "three-band term," the third one in (4.1). The three-band term does not contribute in any of the cases considered ($\Omega_{cc'} = 0$ for all k for the coupled chain system). Thus (4.1) reduces to

$$M_{cv}(k) = \frac{\Omega_{cv}(\Omega_{cc} - \Omega_{vv})}{\omega_{cv} - \omega} + \frac{\partial}{\partial k}\left(\frac{\Omega_{cv}}{\omega_{cv} - \omega}\right).$$

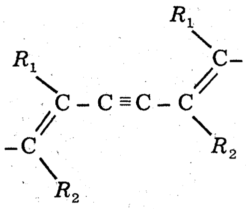
In the case of the homoatomic-bond-alternated chain, the first term is zero throughout the BZ and only the second term contributes. This vanishes at the edge of the BZ ($\theta = \pi$), where the density of states is infinite; thus the two-photon transitions are forbidden there, while the one-photon transitions are allowed. Hence the peak of the two-absorption strength *does not occur at the edge of the BZ* as in one-photon absorption, but is shifted to higher frequencies and is much broader than the latter. This shift is determined by the degree of the flatness of the two bands and the variation of Ω_{cv} as we move away from edge of the BZ.

In the case of the heteroatomic-bond-alternated chains ($\mu \neq 0$) $\Omega_{vv} - \Omega_{cc} \neq 0$ throughout the BZ and at the edge in particular. Hence two-photon transition is allowed in this case at the edge of the BZ, where the one-photon absorption peak also occurs.

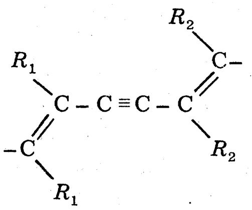
For the coupled chains in the centrosymmetric configuration, the transitions $1 \rightarrow 4, 2 \rightarrow 3$ are forbidden at the edge of the BZ but allowed inside the zone where they overlap to a large extent. On the other hand, the transitions $1 \rightarrow 3$ and $2 \rightarrow 4$ are allowed at the edge of the BZ. However, their strength is proportional to $\delta' = \beta'/\beta_2$ and for weak coupling ($\delta' \ll 1$) this transition is completely masked by the transitions $1 \rightarrow 4$ and $2 \rightarrow 3$. For large values of δ'(>0.1) a narrow peak due to the transitions $1 \rightarrow 3$ and $2 \rightarrow 4$ appears between the two broad peaks due to the $1 \rightarrow 4$ and $2 \rightarrow 3$ two-photon transitions.

VII. POLYDIACETYLENE POLYMER CRYSTALS

This class of polymers can be obtained in the form of large defect-free crystals and is presently the only class of materials where the previous considerations can be applied and compared with experimental results. Their structure is described in I. Polydiacetylene chains with two different side groups can adopt either of the following two configurations



or



The former has inversion symmetry and $\chi^{(2)}=0$, while the latter has not and one may expect $\chi^{(2)} \neq 0$. However, it presently seems difficult to grow large crystals with all chains directed the same way; it is more probable that $\sigma_+ = \sigma_-$ so that $\chi^{(2)}$ again vanishes. If $\sigma_+ \gg \sigma_-$, the order-of-magnitude calculations indicate that, with the prevailing values for the hopping and Coulomb energies in these chains, one expects at best $\chi_\pi^{(2)} \sim 10^{-8}$ esu.

In contrast, the third-order susceptibility in these materials may show high values when the two side groups R_1 and R_2 are identical ($R_1 = R_2 = R$). In Table I we give the values of $\chi^{(3)}$ for the polydiacetylenes whose linear properties were considered in I.

The calculated values of $\chi_\pi^{(3)}$ for the PTS and TDCU diacetylenes are in satisfactory agreement with the measured ones. They are of the same order of magnitude as the values of $\chi_{\xi\xi\xi\xi}^{(3)}$ in Ge and GaAs which are $\simeq 10^{-10}$ and $\simeq 10^{-11}$ esu, respectively, ξ being one of the [111] crystal directions. Further the optical gap in the polydiacetylene occurs around 2 eV compared to only 0.5 and 1.3 eV in Ge and GaAs, respectively, allowing one to study nonlinearities in a dispersion-free region in the visible with favorable phase-matching conditions. The high values of $\chi^{(3)}$ are due to the high delocalization of the π electrons, a consequence of the large conjugation that is established upon polymerization. This is clearly seen when one compares the value of $\chi_\pi^{(3)}$ in the polymer with that of the monomer; in the latter case $\chi_\pi^{(3)}$ has values less than 10^{-13} esu. The same is true for the values of $\chi^{(3)}$ across the chains in the polymer crystal; these are less than 10^{-13} esu. These low values can be well accounted for by using hyperpolarizability additivity arguments similar to the ones used in I for the calculation of the linear susceptibility. This dramatic increase of $\chi_{xxxx}^{(3)}$ over the other components because of the π-electron conjugation is particularly striking when contrasted with the facts that (a) the density of the localized electrons, which are the only ones contributing to the other components, is much higher than that of the π electrons (~1 out of 40 electrons per unit cell is a π electron) and (b) their contribution to $\chi^{(3)}$ across the chain direction is further enhanced by local-field corrections (see I). Because of the much milder dependence of $\chi_\pi^{(1)}$ on N_d, the linear susceptibility does not show such marked anisotropy. The above values of $\chi_\pi^{(3)}$ were measured at room temperature. At lower temperatures, below 160 °K, the optical properties of some of these polymers, like the PTS-diacetylene, undergo some dramatic changes (absorption peak splitting, etc.) and the conjecture[24] was made that the chains get coupled in pairs in an S configuration at low temperature. The mechanism of the pairing is probably a rearrangement of the side groups allowing the π electrons of one chain of the pair to jump over to its partner chain. If this is the case and the equivalent associated polyene is used to replace the actual polydiacetylene, the considerations of Sec. V indicate that $\chi^{(3)}$ may increase by an amount outside the experimental error.

TABLE I. Values of the third-order susceptibility $\chi_{xxxx}^{(3)}$ for different polydiacetylenes; the experimental values of *bis*-poly(toluene sulfonate) (PTS) and *bis*-(phenylurethane) of 5,7-dodecadyine-1,2-diol (TCDU) diacetylenes were taken from Ref. 7.

Poly-R_i-diacetylene	$\chi_{xxxx}^{(3)}$ in units of 10^{-10} esu Calc.	Measured
CH_2–O–CO–C_6H_5	0.84	
CH_2–O–CO–NH–ϕ	0.77	
CH_2O–SO_2–ϕ–CH_3 (PTS)	0.70	1.6 ± 1.0
$(CH_2)_3$–O–CO–NE–ϕ	0.27	
$(CH_2)_4$–O–CO–NH–ϕ (TCDU)	0.25	0.37 ± 0.14
CH_2–O–CO–NH–ϕ–C_2H_5	0.62	
$(CH_2)_3$–O–CO–NH–ϕ–C_2H_5	0.21	
Monomers	$\lesssim 10^{-3}$	$\lesssim 10^{-3}$

The two-photon spectrum has not been measured yet in polydiacetylenes. In principle it should allow one to obtain additional evidence about the applicability of the band picture for the π-electron system. We use the Jones zone to discuss this effect. At room temperature the two-photon absorption is not allowed at the edge of the Jones zone because of symmetry arguments; it is, however, allowed inside the zone and in the band picture adopted here it appears as a broad peak at an energy higher than the band gap E_g (see Fig. 4). Its actual appearance should be much more complicated than this because of vibration-assisted transitions which are altogether neglected here. At a lower temperature, <160 °K, the spectrum should change as shown in Fig. 5, this spectrum consists of two superposed broad peaks corresponding to the 2 → 3 and 1 → 4 band transitions in the coupled chain band scheme. On these broad peaks an additional weaker peak should be present corresponding to the transition 1 → 3 (and 2 → 4) which is weakly allowed at the BZ edge. The strength of this peak being proportional to the square of the chain coupling strength for polydiacetylenes should not be observable. Two-photon absorption experiments in polydiacetylenes will greatly clarify the electronic states in these materials.

In the above discussion of the two-photon absorption a relaxation time is introduced, Eq. (2.9), and assumed to be constant over the Brillouin zone, or $\tau(k)=\tau=\text{constant}$; its value was taken the same as the one used to calculate the one-photon absorption spectrum and the frequency dispersion of the linear susceptibility (see I). This is a drastic simplification, however, and $\tau(k)$ is in general expected to rapidly vary over the Brillouin zone (strong dependence on k). Since the two-photon and one-photon absorption peaks for an homoatomic (centrosymmetric) chain do not occur at the same point of the Brillouin zone, the two-photon absorption peak occurs at higher energies (or $ka<\pi$) than the one-photon absorption peak which is situated at the BZ edge ($ka\simeq\pi$), this can drastically alter the appearance of the two-photon absorption spectrum with respect to the one calculated here using $\tau=\text{const}$. Experimental work is needed to clarify this point and the meaning to be given to the relaxation time.

VIII. DISCUSSION

The different points arised in Ref. 9 concerning the applicability of the one-electron picture prevail even when the nonlinear properties are considered. At present the main argument in favor of our picture is that it allows one to give a unified and quantitative description of all the optical properties in these materials. On the other hand, the exciton picture (essentially the "molecules-in-molecules" picture) is hampered by enormous difficulties.[25] The observed high values of $\chi^{(3)}$ are more compatible with the band picture than the excitonic one; electron correlation in general leads to a reduction of the electron delocalization. A quantitative evaluation of this influence is difficult since it requires, in its simplest aspect, introducing an on-site electron repulsion energy γ and using the Hubbard Hamiltonian. When the Hartree-Fock approximation is used, the solution of the eigenvalue problem leads to states again distributed in bands but different for different spin directions and supplemented with a self-consistency condition; with these bands one can again calculate the dipole transition strengths $\Omega_{nn'}$ and compute the susceptibilities taking into account electron correlation. Preliminary calculations for the linear susceptibility show that as long as $\gamma/2\beta_2\ll 1$ the results are only slightly different from those obtained in the one-electron theory. On the other hand, for $\gamma/2\beta_2\sim 1$ reduction of the linear susceptibility occurs, but at the same time the Hartree-Fock approximation breaks down.

Another question that may arise is to what extent the behavior of the third-order susceptibility discussed in the previous sections persists down to finite chains. Indeed the chains are seldom infinitely long and interruptions by impurities or other defects may occur. The relevant quantity is now the third-order polarizability $\gamma_{xxxx}=\gamma_N$, where N is the number of unit cells in the finite chain; for finite bond-alternated chains (polyenes) with $2N$ atoms as is shown in Ref. 17, as long as $N_d<N$, one has $\gamma_N\sim N_d^6$, namely, the same functional dependence on N_d as for an infinite chain. Similar calculations with superalternated as well as coupled finite chains show that the same conclusions apply even there, namely, $\gamma_N\sim N_d^6$, as long as $N_d\ll N$. This strongly suggests that the dielectric and optical properties of infinite one-dimensional chains are determined by the electron behavior within a region $N_d d$ where d is the unit-cell length and the chain end effects are irrelevant. However, with N_d approaching N these become important and a destructive interference occurs because of the π-electron reflection at the chain ends; for a given N, γ_N attains a maximum around $N_d\sim N$ and starts decreasing afterwards. For the limiting case of complete delocalization (equal hopping energies for all bonds), as is shown in Appendix D, one obtains $\gamma\sim N^5$, the same result previously obtained by Rustagi and Ducuing within the free-electron model.[6]

From the previous sections it can be inferred that the measurement of the nonlinear coefficients constitutes a quite powerful tool to study modifications of the π-electron behavior and π-electron delocalization in particular. This is because of the highly nonlinear dependence of these coefficients on π-electron delocalization which totally suppresses the σ-electron contribution; this is not the case for the linear properties where the latter make a substantial contribution. Further nonlinear optical spectroscopy like two-photon absorption and the Franz-Keldysh effect provide powerful means to ascertain many features of the π-electron states in these materials.

ACKNOWLEDGMENTS

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APPENDIX A: THE GENKIN-MEDNIS APPROACH

In this approach the solution of the Schrödinger equation

$$i\hbar\frac{\partial\psi}{\partial t}=H\psi \tag{A1}$$

with

$$H=(1/2m)[\vec{\mathrm{p}}+(e/c)\vec{\mathrm{A}}(t)]^2+V(\vec{\mathrm{r}})$$

is sought in the form of the expansion

$$\psi=\sum_{n\vec{\mathrm{k}}}\psi_{n\vec{\kappa}}c_n(\vec{\mathrm{k}}t)\,, \tag{A2}$$

where $\vec{\kappa}=\vec{\mathrm{k}}+(e/\hbar c)\vec{\mathrm{A}}(t)$ and $\psi_{n\vec{\kappa}}=e^{i\vec{\mathrm{k}}\cdot\vec{\mathrm{r}}}u_{n\vec{\kappa}}(\vec{\mathrm{r}})$ are the Bloch states of the unperturbed Hamiltonian $H_0=p^2/2m+V(r)$ and $\vec{\mathrm{A}}$ is the vector potential. Substituting (A2) into (A1) and taking into account that the $\psi_{n\vec{\kappa}}$ constitute an orthonormal basis, one has

$$i\hbar\frac{\partial c_n(\vec{\mathrm{k}}t)}{\partial t}=\sum_{n'}\,[\epsilon_n(\vec{\kappa})\delta_{nn'}+ie\vec{\Omega}_{nn'}(\vec{\kappa})\vec{\mathrm{E}}(t)]c_{n'}(\vec{\mathrm{k}}t)\,, \tag{A3}$$

where $E(t)=(1/c)(\partial A(t)/\partial t)$ and $\vec{\Omega}_{nn'}(k)$ is the dipole transition strength

$$\vec{\Omega}_{nn'}(\vec{\mathrm{k}})=\frac{1}{v}\int_{\mathrm{uc}}U^*_{n\vec{\kappa}}(\vec{\mathrm{r}})\vec{\nabla}_{\vec{\kappa}}U_{n\vec{\kappa}}(\vec{\mathrm{r}})\,d\vec{\mathrm{r}}\,. \tag{A4}$$

v is the unit-cell (uc) volume. Equation (A3) can also be written in matrix form

$$i\hbar\frac{\partial c(\vec{\mathrm{k}}t)}{\partial t}=[H_0(\vec{\kappa})+H(\vec{\kappa}t)]c(\vec{\mathrm{k}}t)\,. \tag{A5}$$

The solution of (A5) in powers of $\vec{\mathrm{E}}$ is obtained by carrying out a unitary transformation $S(\vec{\kappa}t)$ on the c's

$$c_n(\vec{\mathrm{k}}t)=\sum_{n'}S_{nn'}(\vec{\kappa}t)\tilde{c}_{n'}(\vec{\mathrm{k}}t)$$

such that

$$H'(\vec{\kappa}t)=S^\dagger(\vec{\kappa}t)[H_0(\vec{\kappa})+H(\vec{\kappa}t)]S(\vec{\kappa}t)+ieS^\dagger(\vec{\kappa}t)\vec{\nabla}_{\vec{\kappa}}S(\vec{\kappa}t)\vec{\mathrm{E}}(t)-i\hbar S^\dagger(\vec{\kappa}t)\frac{\partial S(\vec{\kappa}t)}{\partial t} \tag{A6}$$

has only diagonal terms, or

$$H'_{nn'}(\vec{\kappa}t)=0\quad\text{for } n\neq n'\,;$$

one obtains

$$i\hbar\frac{\partial\tilde{c}_n(\vec{\mathrm{k}}t)}{\partial t}=H'_{nn}(\vec{\kappa}t)\tilde{c}_n(\vec{\mathrm{k}}t)\,. \tag{A7}$$

The perturbation solution of (A7) is obtained by putting

$$S(\vec{\kappa}t)=1+\sum_n S^{(n)}(\vec{\kappa}t) \tag{A8}$$

in (A6) where $S^{(n)}$ is of order n in the field intensity. This only determines the nondiagonal elements of S; the diagonal ones are determined by the additional condition $S_{nn}=S^\dagger_{nn}$.

The polarization is then determined by

$$\vec{\mathrm{P}}=e\sum_{\mathrm{el}}\langle\vec{\mathrm{r}}\rangle=-\frac{ie}{V}\sum_{n,n',n''}\sum_{\vec{\mathrm{k}}}f_n(\vec{\mathrm{k}})S^\dagger_{nn'}(\vec{\kappa}t)[\vec{\Omega}_{n'n''}(\vec{\kappa})+\delta_{n'n''}\vec{\nabla}_{\vec{\kappa}}]S_{n''n}(\vec{\kappa}\,t)\,, \tag{A9}$$

where $f_n(\vec{\mathrm{k}})$ is the distribution function over the band states. By inserting (A8) in (A9) one obtains the polarization in powers of the electric field.

$$\vec{\mathrm{P}}=\vec{\mathrm{P}}^{(0)}+\sum_{n=1}^{\infty}\vec{\mathrm{P}}^{(n)} \tag{A10}$$

and hence the expressions of the susceptibilities.

For the one-dimensional systems we are interested in the text one has for the linear and second-order susceptibilities in the chain direction (x direction)

$$\chi^{(1)}_{xx}(\omega)=-\frac{2e^2}{\hbar V}\sum_{n,n'\neq n}\sum_{\vec{\mathrm{k}}}f_n(\vec{\mathrm{k}})\left(\frac{\Omega_{nn'}\Omega_{n'n}}{\omega_{n'n}+\omega}+\frac{\Omega_{nn'}\Omega_{n'n}}{\omega_{n'n}-\omega}\right) \tag{A11}$$

$$\chi^{(2)}_{xxx}(\omega_1,\omega_2)=\frac{2ie^3}{\hbar^2V}\sum_{n,n',n''\neq n}\sum_{\vec{\mathrm{k}}}f_n(k)\times\sum_{\mathcal{P}}\left\{\frac{\Omega_{nn'}(\Omega_{n'n''}-\Omega_{nn}\delta_{n'n''})\Omega_{n''n}}{(\omega_{n'n}+\omega_1)(\omega_{n''n}+\omega_1+\omega_2)}+\frac{1}{2}\left[\frac{\Omega_{nn'}}{(\omega_{n'n}+\omega_1)}\frac{\partial}{\partial k}\left(\frac{\Omega_{n'n}}{(\omega_{n'n}+\omega_1+\omega_2)}\right)-\frac{\partial}{\partial k}\left(\frac{\Omega_{nn'}}{\omega_{n'n}+\omega_1}\right)\frac{\Omega_{n'n}}{(\omega_{n'n}+\omega_1+\omega_2)}\right]\right\}\,, \tag{A12}$$

where $\sum_{\mathcal{P}}$ stands for summation over terms obtained by all permutations of ω_1,ω_2 and $-\omega_1-\omega_2$; V is the crystal volume which for one-dimensional system is $V=Nd/\sigma$ with d being the unit-cell length, N the number of unit cells along a chain, and σ the density of chains per unit cross area. This expression for $\chi^{(2)}_{xxx}$ is equal to $ie^3(\phi^3+\phi^4+\phi^5)/\hbar^2V(\omega_1+\omega_2)$, where ϕ^3, ϕ^4, and ϕ^5 are the quantities defined in Ref. 25.

The expression of the third-order susceptibility is quite involved for a system with an arbitrary number of bands and different frequencies. In the present work we are mainly interested in the nonlinear optical properties of one-dimensional semiconductors with an effectively two-band structure. For such a system the *xxxx*-component of the third-order susceptibility, $\chi^{(3)}(\omega_1, \omega_2, \omega_2)$, has the following expression

$$\begin{aligned}\chi^{(3)}_{xxxx}(\omega_1, \omega_2, \omega_3) = \frac{e^4}{\hbar^3 V} \sum_k \sum_{\mathcal{P}} \Bigg[& \frac{\Omega_{vc}[(\Omega_{vv} - \Omega_{cc})^2 - \Omega_{cv}\Omega_{vc}]\Omega_{cv}}{(\omega_{cv} + \omega_1 + \omega_2 + \omega_3)(\omega_{cv} + \omega_2 + \omega_3)(\omega_{cv} + \omega_3)} + \frac{1}{(\omega_{cv} + \omega_1 + \omega_2 + \omega_3)} \\ & \times \frac{\partial}{\partial k}\left(\frac{\Omega_{vc}}{(\omega_{cv} + \omega_2 + \omega_3)}\right) \frac{\partial}{\partial k} \left(\frac{\Omega_{cv}}{(\omega_{cv} + \omega_3)}\right) \\ & + \frac{\Omega_{vv} - \Omega_{cc}}{(\omega_{cv} + \omega_1 + \omega_2 + \omega_3)} \frac{\partial}{\partial k}\left(\frac{\Omega_{vc}}{\omega_{cv} + \omega_2 + \omega_3}\right) \frac{\Omega_{cv}}{(\omega_{cv} + \omega_3)} - \frac{\Omega_{vc}}{(\omega_{cv} + \omega_2 + \omega_3)} \frac{\partial}{\partial k}\left(\frac{\Omega_{cv}}{(\omega_{cv} + \omega_3)}\right)\Bigg] ,\end{aligned} \tag{A13}$$

where $\sum_{\mathcal{P}}$ stands for summation over terms obtained by all *different* permutations of $\omega_1, \omega_2, \omega_3$ and $-\omega_1 - \omega_2 - \omega_3$. From (1.13) one can easily derive the expressions of $\chi_{xxxx}(\omega_1, \omega, \omega)$ required for third harmonic generation and $\chi_{xxxx}(\omega_1, -\omega_1, \omega_2)$; the imaginary part of the latter, when $\omega_1 + \omega_2 \simeq \omega_{cv}$, describes the two-photon absorption; its expression for the degenerate case, $\omega_1 = \omega_2 = \omega$, is given in the text [Eq. (2.9)], where a relaxation time has been introduced phenomenologically.

If in the above expressions we introduce $V = Nd/\sigma$, we may replace

$$\frac{2\pi}{Nd} \sum_k \to \int dk \tag{A14}$$

for an infinite chain; this will always be the case in the following.

APPENDIX B: PENN'S MODEL

In Penn's spherical band model[19] for a cubic inorganic semiconductor, i.e., Ge or Si, the Bloch energies and wave functions are given by

$$E^{\pm}_k = \tfrac{1}{2}\{E^0_k + E^0_{k'} \pm [(E^0_k - E^0_{k'})^2 + E^2_g]^{1/2}\} ,$$

$$\psi^{\pm}_k = e^{i\vec{k}\cdot\vec{r}} u^{\pm}_k$$

$$= e^{i\vec{k}\cdot\vec{r}}(1 + \alpha^{\pm}_k e^{i(\vec{k}-\vec{k}')\cdot\vec{r}})/[1 + (\alpha^{\pm}_k)^2]^{1/2} ,$$

where

$$\vec{k}' = \vec{k} - 2k_F\hat{k}, \quad \alpha^{\pm}_k = E_g/2(E^{\pm}_k - E^0_{k'}) ,$$

$$E^0_k = \hbar^2 k^2/2m , \quad E^0_{k'} = \hbar^2 k'^2/2m ,$$

k_F is the Fermi-level momentum and E_g is the band gap there; (+) and ($\mp$) refer to valence (v) and conduction (c) band. One can write

$$\alpha^{\pm}_k = c/[K \pm (K^2 + c^2)^{1/2}] ,$$

where $K = (k - k_F)/k_F$ and $c = mE_g/2\hbar^2 k^2_F = E_g/4E_F$.

The expressions of the dipole transition-matrix elements $\Omega_{nn'}(k) = (1/v) \int_{\text{uc}} u^{\pm *}_k \vec{\nabla}_{\vec{k}} u^{\pm}_{\vec{k}}\, d\vec{r}$, where v is the unit-cell (uc) volume and $n = \pm, n' = \pm$, are as follows

$$\Omega_{++} = \Omega_{--} = 0 ,$$

and

$$\Omega_{+-} = -\Omega_{-+} = \frac{1}{2k_F} \frac{c}{K^2 + c^2} \hat{k} \equiv \Omega_{vc} .$$

One can calculate the mean-square spread of the electron position coordinate D^2 defined by $D^2 = \langle \Delta r^2 \rangle$ (see I).

Similarly one can calculate the linear and third-order susceptibility components $\chi^{(1)}_{xx}$ and $\chi^{(3)}_{xxxx}$ for frequencies in the transparency region ($\omega \ll E_g/\hbar$); because of the spherical symmetry, it is sufficient to only consider the components in only one direction. Using the two-band expressions for $\chi^{(1)}_{xx}$ and $\chi^{(3)}_{xxxx}$ one has

$$\chi^{(1)}_{xx} = \frac{2e^2}{\hbar V} \int \frac{\Omega^x_{vc}\Omega^x_{cv}}{\omega_{cv}} d\vec{k} = \frac{Ne^2}{2E_F} \frac{1}{k^2_F} \frac{1}{c^2} [(1 + c)^{1/2} - c]$$

which for $c \ll 1$ becomes

$$\chi^{(1)} = (Ne^2/2E_F k^2_F)(4E_F/E_g)^2 .$$

N is the number of electrons per unit volume.

The inter- and intraband contributions to $\chi^{(3)}_{xxxx}$ are

$$\chi^{(3)}_{\text{inter}} = -\frac{4e^4}{\hbar^3 V} \int \Omega^x_{vc} S^x_{cv} S^x_{vc} S^x_{cv}\, d\vec{k}$$

$$= -\chi^{(3)}_0 \int_{-1}^{0} \frac{c^2(1 + x)^2}{(x^2 + c^2)^{11/2}} dx ,$$

and

$$\chi^{(3)}_{\text{intra}} = \frac{4e^4}{\hbar^3 V} \int \frac{1}{\omega_{cv}} \frac{\partial S^x}{\partial k_x} \frac{\partial S^x}{\partial k_x} d\vec{k}$$

$$= \chi^{(3)}_0 \int_{-1}^{0} \frac{36x^2(1 + x)^2\, dx}{(x^2 + c^2)^{11/2}} ,$$

respectively and $\chi^{(3)}_0 = Ne^4/(4E^3_F)k^4_F$; for $c \ll 1$ one obtains

$$\chi^{(3)}_{\text{intra}} = -\tfrac{9}{4}\chi^{(3)}_{\text{inter}} = \tfrac{24}{35}[Ne^4/k^4_F(4E^3_F)](4E_F/E_g)^6$$

or

$$\chi^{(3)}_{xxxxx}=\chi^{(3)}_{\mathbf{intra}}+\chi^{(3)}_{\mathbf{inter}}=\tfrac{8}{21}[Ne^4/k_F^4(4E_F^3)](4E_F/E_g)^6 \;.$$

This same dependence was obtained in Ref. 18 in the case of the strictly one-dimensional Penn's model.

APPENDIX C: TRANSITION-MATRIX ELEMENTS FOR A PAIR OF COUPLED CHAINS IN THE *S* CONFIGURATION

When we use the Genkin-Mednis approach to derive the susceptibility expressions in terms of the dipole transition strengths $\Omega_{nn'}(k)$ in the case of a pair of coupled chains in the S configuration, care must be taken so that the corresponding expressions for single chains are recovered when the coupling vanishes. This was only indicated in I; here we give a more detailed derivation.

As is shown in I, the Bloch functions for this system in the absence of an electric field are written in the form

$$\psi_{nk}=(1/\sqrt{2})(\psi^{(1)}_{nk}+e^{ika}\psi^{(2)}_{nk})=e^{ikx}u_{nk}\,,$$

where $\psi^{(1)}_{nk}$ and $\psi^{(2)}_{nk}$ are linear combinations of atomic orbitals centered on atoms of chain 1 and 2, respectively. We write

$$\psi^{(i)}_{nk}=e^{ikx}u^{(i)}_{nk}\quad(i=1,2)\,,$$

where x_i is the coordinate along chain $i(i=1,2)$. Further we define

$$\Omega^{(i)}_{nm}(k)=\frac{1}{a}\int_{\mathrm{uc}}u^{(i)*}_{nk}\frac{\partial u^{(i)}_{mk}}{\partial k}\,dx_i\,.$$

In the presence of an electric field $E=(1/c)(\partial A/\partial t)$ following Genkin and Mednis[10] (see Appendix A) we write that the perturbed wave function ψ can be written

$$\psi=\sum_{n,j}c_n(kt)\tilde{\psi}_{n\kappa}\,,$$

where $\kappa=k-(e/c\hbar)$ and we *impose* that

$$\tilde{\psi}_{n\kappa}=(1/\sqrt{2})(\psi^{(1)}_{n\kappa}+e^{ika}\psi^{(2)}_{n\kappa})\,.$$

Note that in the exponential e^{ika} expressing the relative phase of the two-chain wave functions, k has not been replaced by κ. With this condition the dipole transition strengths for the pair are

$$\Omega^{(k)}_{nm}=\tfrac{1}{2}[\Omega^{(1)}_{nm}(k)+\Omega^{(2)}_{nm}(k)]\,.$$

The analytical expressions of $\Omega_{nm}(k)$ were given in I. It is easy to see that for vanishing coupling between the chains (no π-electron hopping between the two chains) these expressions for Ω_{nm} reduce to those of a bond-alternated chain.

APPENDIX D: HYPERPOLARIZABILITIES FOR A FINITE CONJUGATED CHAIN WITHOUT BOND ALTERNATION

For a finite conjugated chain of $2N$ identical atoms without bond alternation, $\beta_1=\beta_2=\beta$, in the presence of a static electric field E_0, the coefficients c_n of the wave function $\psi=\sum^{2N}c_n\phi_n$ are determined through

$$c_n(-\epsilon+nw)+\beta(c_{n+1}+c_{n-1})=0 \tag{D1}$$

and the boundary conditions $c_0=c_{2N+1}=0$, where $\epsilon=E-\boldsymbol{\alpha}, w=eE_0a$, a is the interatomic distance, and α the Coulomb integral; in (D1) the approximations $\langle\phi_n|x|\phi_n\rangle=na, \langle\phi_n|\phi_m\rangle=\delta_{nm}$ were used. The solution of (D1) is[26]

$$c_n=AJ_{n-\epsilon/w}(-2w/\beta)+BY_{n-\epsilon/w}(-2w/\beta)\,, \tag{D2}$$

where J_ν and Y_ν are the Bessel and Von Neuman functions related by $Y_\nu(x)\sin\nu\pi=J_\nu(x)\cos\nu\pi-J_{-\nu}(x)$. The boundary conditions give

$$J_{-\gamma\xi}(2\gamma)Y_{\gamma(1/\gamma-\xi)}(2\gamma)-J_{\gamma(1/\bar{\gamma}-\xi)}(2\gamma)Y_{-\gamma\xi}(2\gamma)=0\,, \tag{D3}$$

where $\gamma=-\beta/w$, $\xi=-\epsilon/\beta$, and $\bar{\gamma}=(N+1)/\gamma$. The roots of this equation give the eigenvalues ϵ_n. In the case of zero field, $E_0=0$, there are $2\,N$ roots. $\epsilon^0_n=2\beta\cos\theta^0_n$, where $\theta^0_n=n\pi/(N+1)$. We wish to find the changes in these roots in powers of the perturbation strength eaE_0 in the limit where the perturbation theory applies, namely, $-w/\beta\ll1$ (or $\gamma\ll1$) and $Nw/\beta\ll1$ (or $\bar{\gamma}\gg1$). The polarizabilities $\alpha^{(k)}$ of the chain are then obtained from

$$w=\sum_{\mathrm{occ}}\epsilon_n=\omega_0-\sum_{n=1}^{\infty}\frac{1}{2n}\alpha^{(2n-1)}E_0^{2n}\,, \tag{D4}$$

where for symmetry reasons only the odd-order polarizabilities appear.

For this purpose we use the double asymptotic development[26] of $Y_{\gamma u}$ and $J_{\gamma u}$ for large $\gamma>0$

$$J_{2\gamma u}(2\gamma)\xrightarrow{\gamma\to\infty}A_u(L_u\cos\psi_u+M_u\sin\psi_u)\,, \tag{D5}$$

$$Y_{2\gamma u}(2\gamma)\xrightarrow{\gamma\to\infty}A_u(L_u\sin\psi_u-M_u\cos\psi_u)\,, \tag{D6}$$

where with $\gamma u=\nu$, $2\cos\theta=u$, one has[27]

$$A_u=(2/\pi\nu tg\,\theta)^{1/2}\,,$$

$$\psi_u=2\gamma(\sin\theta-\theta\cos\theta)-\tfrac{1}{4}\pi\,,$$

$$M_u=\tfrac{1}{24}(3\,\mathrm{cotg}\,\theta+5\,\mathrm{cotg}^3\theta)(1/\nu)+\dots\,,$$

$$L_u=1-\tfrac{1}{1152}(81\,\mathrm{cotg}^2\theta+462\,\mathrm{cotg}^4\theta+385\,\mathrm{cotg}^6\theta)(1/\nu^2)+\dots\,.$$

Inserting (D5) and (D6) in (D3) and developing in powers of $1/\bar{\gamma}\ll1$ one obtains

$$\sum_{k=1}^{2N}\frac{1}{k!\,\gamma^k}[J(-\xi)Y^{(k)}(-\xi)-J^{(k)}(-\xi)Y(-\xi)]=0\,, \tag{D7}$$

where

$$J(-\xi)=L_{-\xi}\cos\psi_\xi+M_{-\xi}\sin\psi_\xi \xrightarrow{\gamma\to\infty} \sin\psi\,,$$

$$Y(-\xi)=L_{-\xi}\sin\psi_\xi-M_\xi\cos\psi_\xi \xrightarrow{\gamma\to\infty} \cos\psi\,,$$

$\psi=2\gamma(\sin\theta-\theta\cos\theta)-\frac{1}{4}\pi$. After straightforward calculation of the derivatives $Y^{(k)}$ and $J^{(k)}$, then expansion in powers of $1/\overline{\gamma}$ and substitution in (D7) one obtains

$$\sin(N+1)\theta=-\sum_{p=1}^{\infty}\frac{1}{\overline{\gamma}^{p}}\frac{m^{(p+1)}}{(p+1)!}\,, \tag{D8}$$

where $m^{(p)}=[(1/\gamma)(d^p\psi/\partial u^p)]_{u=-\xi}$. In (D8) we suppose that N is very large. Assuming that $|\theta_n-n\pi/N|\ll 1/N$ one obtains from (D8) the normalized energies

$$\xi_n=\frac{\epsilon_n}{\beta}=\sum_{k=0}^{\infty}\frac{\lambda_n^{(k)}}{\overline{\gamma}^{2k}}\,. \tag{D9}$$

For a given k the values of $\lambda_n^{(k)}$ do not differ markedly and one may put $\lambda_n^{(k)}\simeq\lambda^{(k)}$. Then substituting (D9) in (D4) one obtains

$$W=W_0-N\beta\sum_{k=0}^{\infty}\frac{\lambda^{(k)}}{\overline{\gamma}^{2k}}\,, \tag{D10}$$

and by identifying terms of the same power in E_0 in (D10) and (D4) one obtains the expression of the polarizabilities

$$\alpha^{(2n-1)}\sim N^{2n+1}e^{2n}a^{2n}/\beta^{2n-1}\,.$$

In particular the linear and third-order polarizabilities are

$$\alpha^{(1)}\sim N^3e^2a^2/\beta\,,\quad \alpha^{(3)}\sim N^5e^4a^4/\beta^3\,.$$

They show the same behavior as the corresponding expressions derived in the free-electron model.[6]

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