

Nonlinear optical susceptibilities of conducting polymers

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By use of the Genkin-Mednis approach, a general formalism of the nonlinear optical susceptibilities has been derived for one-dimensional electron-lattice systems. Based on the Su-Schrieffer-Heeger model, we get an analytic expression of the third-harmonic generation $\chi^{(3)}(\omega)$ of conducting polymers. After considering the effects of finite lifetime of the excited states, the cusp at $\hbar\omega = \Delta$ is greatly depressed so that it becomes too small to interpret the observed peak of $\chi^{(3)}(\omega)$ at 0.9 eV. The case of nondegenerate polymers and the effect of electron-electron interaction in the unrestricted Hartree-Fock approximation are also discussed. Our results imply that the electron interaction would play an important role in the nonlinear optical properties of conducting polymers.

I. INTRODUCTION

The nonlinear optical properties of conducting polymers have attracted a great deal of interest both experimentally and theoretically. The experiments^{1,2} have demonstrated that conducting polymers possess a very large third-order optical susceptibility, $\chi^{(3)} \sim 10^{-9}$ esu, and an extremely short response time, ~ 0.1 ps. Such significant properties suggest that the conducting polymers are a promising candidate to be a high-speed nonlinear optical material. There are many interesting phenomena shown in the nonlinear optical susceptibility of polyacetylene. One is that the third-harmonic generation of *trans*-polyacetylene is one order of magnitude larger than of *cis*-polyacetylene. The other is that the spectrum of third-harmonic generation $\chi^{(3)}(\omega)$ of *trans*-polyacetylene has two peaks at $\hbar\omega = 0.6$ and 0.9 eV. Since the energy gap 2Δ of *trans*-polyacetylene is about 1.8 eV, it is obvious that the first peak at 0.6 eV is due to the three-photon resonance enhancement. Meanwhile it seems that the second peak at 0.9 eV comes from the two-photon resonance enhancement. However, because two-photon absorption in a rigid lattice is forbidden by the momentum conservation, how to understand the origin of the second peak becomes a subtle problem.

Recently, Wu³ used the Keldysh Green's function to establish an analytic expression of the third-harmonic generation based on the Takayama-Lin-Liu-Maki (TLM) model;⁴ he found that the theoretical spectrum of $\chi^{(3)}(\omega)$ has a cusp at $\hbar\omega = \Delta$ without any adjustable parameter, and then he attributed the second peak to this cusp. But Su and his co-workers⁵ calculated $\chi^{(3)}(\omega)$ from the Su-Schrieffer-Heeger (SSH) model;⁶ the second peak did not appear in their results. Since the TLM model is a continuum version of the SSH model, these two models should not give qualitatively different results. The above divergence has to be clarified, and it will be helpful to find

the real origin of the observed second peak.

This paper is organized as follows. In Sec. II we derive a general formalism of the nonlinear optical susceptibilities by using the Genkin-Mednis approach.⁷ This general formalism is exact over the full frequency region and it goes beyond the continuum model (TLM model). Then we get an analytic expression of the third-harmonic generation (THG) of conducting polymers based on the discrete lattice model (SSH model) in Sec. III. Through the discussion on the effects of finite lifetime of the excited states, we find that the above divergence can be clarified. In Sec. IV we briefly discuss the effects of electron interaction within the unrestricted Hartree-Fock approximation and the case of nondegenerate polymers.

II. FORMALISM

We use the Genkin-Mednis approach⁷ to search for the solution of the Schrödinger equation in an external electric field

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H} \psi. \quad (1)$$

In the electric dipole approximation, we can write down the Hamiltonian

$$\hat{H} = \frac{1}{2m} \left[\mathbf{p} + \frac{e}{c} \mathbf{A}(t) \right]^2 + V(\mathbf{r}); \quad (2)$$

here, $V(\mathbf{r})$ is a periodic lattice potential. Since the vector potential $\mathbf{A}(t)$ is only dependent on time t and independent of \mathbf{r} , it can be considered as a shift to the wave vector \mathbf{k} . Then, the wave function ψ in Eq. (1) can be expanded on the Bloch wave function with a shifted wave vector, i.e.,

$$\psi = \sum_{\mathbf{n}, \mathbf{k}} \psi_{\mathbf{n}\mathbf{k}}(\mathbf{r}) C_{\mathbf{n}}(\mathbf{k}, t), \quad (3)$$

where the basis function is

$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}), \quad (4)$$

and the shifted wave vector is

$$\boldsymbol{\kappa} \equiv \mathbf{k} + \frac{e}{\hbar c} \mathbf{A}(t). \quad (5)$$

The Bloch wave function $\psi_{n\mathbf{k}}$ (when $\boldsymbol{\kappa} = \mathbf{k}$) is the eigenfunction of electrons in the periodic potential $V(\mathbf{r})$, and n is an index numbering the electron bands. Substituting Eqs. (3) and (4) into (1) and taking account of the fact that the basis function (4) is orthonormal, we can get

$$i\hbar \frac{\partial C_n(\mathbf{k}t)}{\partial t} = \sum_{n'} [\varepsilon_n(\boldsymbol{\kappa}) \delta_{nn'} + ie \boldsymbol{\Omega}_{nn'}(\boldsymbol{\kappa}) \cdot \mathbf{E}(t)] C_{n'}(\mathbf{k}t), \quad (6)$$

where $\varepsilon_n(\mathbf{k})$ is the eigenvalue corresponding to the Bloch wave function $\psi_{n\mathbf{k}}$,

$$\boldsymbol{\Omega}_{nn'}(\boldsymbol{\kappa}) = \int d\mathbf{r} u_{n\mathbf{k}}^*(\mathbf{r}) \nabla_{\mathbf{k}} u_{n'\mathbf{k}}(\mathbf{r}), \quad (7)$$

the dipole transition strength, and $\mathbf{E}(t)$ the external elec-

tric field. For our purposes, it is convenient to rewrite Eq. (6) in operator form

$$i\hbar \frac{\partial C(\mathbf{k}t)}{\partial t} = [\hat{\mathcal{H}}_0(\boldsymbol{\kappa}) + \hat{\mathcal{H}}_1(\boldsymbol{\kappa}t)] C(\mathbf{k}t). \quad (8)$$

The operators in Eq. (8) correspond to the matrices in (6), respectively. Now, we can get the effective Hamiltonian through carrying out a unitary transformation such that the nondiagonal matrix elements of the Hamiltonian vanish identically, which will self-consistently determine the unitary transformation. For fixed $\boldsymbol{\kappa}$, the matrix of the unitary transformation and then the wave function ψ can be obtained in the form of a power expansion of the electric field $\mathbf{E}(t)$. Once the solution of Schrödinger equation (1) is in hand, the polarization \mathbf{P} can be presented in the form

$$\mathbf{P} = \mathbf{P}_0 + \mathbf{P}_1 + \mathbf{P}_2 + \cdots. \quad (9)$$

Owing to the dependence on $\boldsymbol{\kappa}$, which contains the external fields, the expression is actually expanded to $\boldsymbol{\kappa}$, too. Then, \mathbf{P}_j ($j=0, 1, 2, \dots$) would be the j th response to the external electric field $\mathbf{E}(t)$, i.e.,

$$(P_j)_\alpha = \sum_{\alpha_1, \alpha_2, \dots, \alpha_j} \int d\omega_1 d\omega_2 \cdots d\omega_j \chi_{\alpha\alpha_1\alpha_2 \dots \alpha_j}^{(j)}(\boldsymbol{\Omega}; \omega_1, \omega_2, \dots, \omega_j) E_{\alpha_1}(\omega_1) E_{\alpha_2}(\omega_2) \cdots E_{\alpha_j}(\omega_j) e^{i\boldsymbol{\Omega}t}, \quad (10)$$

where $\chi^{(j)}$ is the j th order nonlinear optical susceptibility, $\omega_1, \omega_2, \dots, \omega_j$ are the frequencies of the incident fields, and $\boldsymbol{\Omega} \equiv -(\omega_1 + \omega_2 + \cdots + \omega_j)$ and $\alpha(\alpha_1, \alpha_2, \dots) (=x, y, z)$ are the space direction.

For the one-dimensional lattice system, we are only interested in the chain direction, so that all the vectors above will be taken in this direction. In order to make the calculation more transparent, we restrict it within a two-band system, one a conduction band, the other a valence band. Then, we can get an analytic expression for the third-order nonlinear optical susceptibility after making a complicated calculation,

$$\begin{aligned} & \chi^{(3)}(\boldsymbol{\Omega}; \omega_1, \omega_2, \omega_3) \\ &= \frac{e^4}{6\hbar^3 V} \sum_{k,s} \sum_P \left[\frac{\Omega_{vc}(\Omega_{vv} - \Omega_{cc})^2 \Omega_{cv}}{(\omega_{cv} + \omega_1)(\omega_{cv} + \omega_1 + \omega_2)(\omega_{cv} - \Omega)} \right. \\ & \quad - \frac{1}{2} \left[\frac{\Omega_{vc} \Omega_{cv} \Omega_{vc} \Omega_{cv}}{(\omega_{cv} - \Omega)(\omega_{cv} + \omega_1)(\omega_{cv} - \omega_2)} + \frac{\Omega_{vc} \Omega_{cv} \Omega_{vc} \Omega_{cv}}{(\omega_{cv} + \Omega)(\omega_{cv} + \omega_1)(\omega_{cv} - \omega_2)} \right] \\ & \quad + \frac{(\Omega_{vv} - \Omega_{cc}) \Omega_{cv}}{(\omega_{cv} - \Omega)(\omega_{cv} + \omega_1 + \omega_2)} \frac{\partial}{\partial k} \left[\frac{\Omega_{vc}}{\omega_{cv} + \omega_1} \right] - \frac{(\Omega_{vv} - \Omega_{cc}) \Omega_{vc}}{(\omega_{vc} + \Omega)(\omega_{cv} - \omega_1 - \omega_2)} \frac{\partial}{\partial k} \left[\frac{\Omega_{cv}}{\omega_{cv} - \omega_1} \right] \\ & \quad \left. - \frac{1}{(\omega_{cv} + \omega_1 + \omega_2)} \frac{\partial}{\partial k} \left[\frac{\Omega_{vc}}{\omega_{cv} + \omega_1} \right] \frac{\partial}{\partial k} \left[\frac{\Omega_{cv}}{\omega_{cv} - \Omega} \right] \right], \quad (11) \end{aligned}$$

where $\hbar\omega_{cv} \equiv \varepsilon_c(k) - \varepsilon_v(k)$, the subscripts c, v indicate the conduction and valence bands, respectively, and \sum_P stands for the summation over terms obtained by all permutations of $\omega_1, \omega_2, \omega_3$ and Ω . In principle, the calculation can be performed for any number of bands, but it will be more complicated.

III. THIRD-HARMONIC GENERATION

Since the real chain of polymers has discrete structure, we start our calculation of $\chi^{(3)}(\omega)$ from the Su-

Schrieffer-Heeger model.⁶ The SSH Hamiltonian with a dimerized lattice structure reads

$$H_{\text{SSH}} = - \sum_{l,s} [t_0 + (-1)^{l+1} \frac{1}{2} \Delta] (C_{l+1,s}^\dagger C_{l,s} + C_{l,s}^\dagger C_{l+1,s}), \quad (12)$$

where t_0 is the transfer integral between the nearest-neighbor sites, and Δ the gap order parameter. From this Hamiltonian, we can get the electron-energy spectrum

$$\begin{aligned} \varepsilon_c(k) &= -\varepsilon_v(k) \\ &= \{[2t_0 \cos(ka)]^2 + [\Delta \sin(ka)]^2\}^{1/2}, \end{aligned} \quad (13)$$

the energy gap $E_g = 2\Delta$, and the dipole transition strength

$$\begin{aligned} \Omega_{vv}(k) &= \Omega_{cc}(k) = 0, \\ \Omega_{cv}(k) &= -\Omega_{vc}(k) = [t_0 a \Delta / \varepsilon_c^2(k)] \text{sgn}(k). \end{aligned} \quad (14)$$

$$\chi_{\text{THG}}^{(3)}(\omega) \equiv \chi^{(3)}(-3\omega; \omega, \omega, \omega)$$

$$\begin{aligned} &= \chi_0^{(3) \frac{5}{12}} \int_1^{1/\delta} dx \frac{1}{x^8 [(x^2-1)(1-\delta^2 x^2)]^{1/2}} \left[\frac{5-8x^2(1+\delta^2)+20\delta^2 x^4}{x^2-z^2} + \frac{2048(x^2-1)(1-\delta^2 x^2)}{x^2-(2z)^2} \right. \\ &\quad \left. + \frac{19683-17496x^2(1+\delta^2)+15228\delta^2 x^4}{x^2-(3z)^2} \right], \end{aligned} \quad (15)$$

where

$$\chi_0^{(3)} = \frac{4}{45} \frac{e^4 \sigma}{\pi} \frac{(2t_0 a)^3}{\Delta^6}, \quad (16)$$

$z \equiv \hbar\omega/2\Delta$, $\delta \equiv 2\Delta/4t_0$ is the energy gap in the unit of bandwidth $4t_0$, σ is the number of chains in unit cross area, and the polymer chains are assumed to be oriented. It is easy to see that, in the limit of $\delta=0$, which happens if the bandwidth is considered to be infinite, our formula (15) reduces to Wu's expression of $\chi_{\text{THG}}^{(3)}(\omega)$ [Eq. (11) in Ref. 3]. That is to be expected, since the TLM model is a continuum version of the SSH model.

As we know, due to the residual electron-lattice interaction and/or the imperfection of the lattice, the excited state will be unstable and then the energy of excited states should contain a small imaginary part, i.e., $x \equiv \hbar\omega_{cv}/2\Delta \rightarrow x + i\eta$ in Eq. (15); here the imaginary part η is the damping of excited states in units of 2Δ . In the ideal case, $\eta \rightarrow 0^+$, we found that the shape of $\chi_{\text{THG}}^{(3)}(\omega)$ is insensitive to δ and its magnitude is changed only a few percent for different δ , which is not surprising, since the integrand in Eq. (15) is dependent on x^{-8} . This result shows that the contribution of deep inside states to $\chi^{(3)}(\omega)$ is not important. In this special case without damping, the spectrum of third-harmonic generation from Eq. (15) is almost the same as Wu's result. However, in the real case, the damping η is finite, i.e., the lifetime of excited states is not infinite. For polyacetylene, $t_0 = 2.5$ eV, $\Delta = 0.9$ eV,⁶ $\sigma = 3.2 \times 10^{14}$ cm⁻², and $\eta \sim 0.03$;⁵ next we have $\delta = 0.18$ and $\chi_0^{(3)} \approx 1.0 \times 10^{-10}$ esu; then the numerical spectrum of $\chi^{(3)}(\omega)$ can be obtained from Eq. (15). It is plotted in Fig. 1 (the real part and the imaginary part) and in Fig. 2 (the absolute magnitude). In order to compare with Wu's work, the special case $\eta \rightarrow 0^+$ of Eq. (15) is also calculated and plotted as a dashed line in Fig. 2. From these curves, we can clarify the divergence about the second peak at $\hbar\omega = \Delta$. Wu³ calculated $\chi^{(3)}$ by taking an infinite long lifetime of excited states, while Su and his co-workers⁵ added an imaginary part to the excited-state energies in their calculation for a polymer chain with finite length. Our results show that the cusp at $\hbar\omega = \Delta$ exists distinctly only in the ideal

In principle, we can calculate any third-order nonlinear susceptibilities from Eq. (11). Since the experimental result¹⁻² is about the spectrum of third-harmonic generation, we would focus on that in this section. The third-harmonic generation susceptibility can be obtained by taking $\omega_1 = \omega_2 = \omega_3 = \omega$ and substituting Eqs. (13) and (14) into (11),

case $\eta \rightarrow 0^+$, and that once the finite lifetime of excited states is taken into account, the cusp at $\hbar\omega = \Delta$ is greatly depressed, so that it becomes too small to explain the experimental results² (the circles in Fig. 2). Therefore it is necessary to go beyond the simple electron-lattice interaction model to interpret this nontrivial two-photon resonance enhancement. We think that the effects of electron-electron interaction and various elementary excitations or defects have to be considered.

Concluding this section, it should be noted that a split of the peak at $\hbar\omega = 2\Delta/3$ appears in Fig. 2 after considering the finite lifetime of excited states. This theoretical prediction can be checked by measuring the detailed structure of the three-photon resonant absorption.

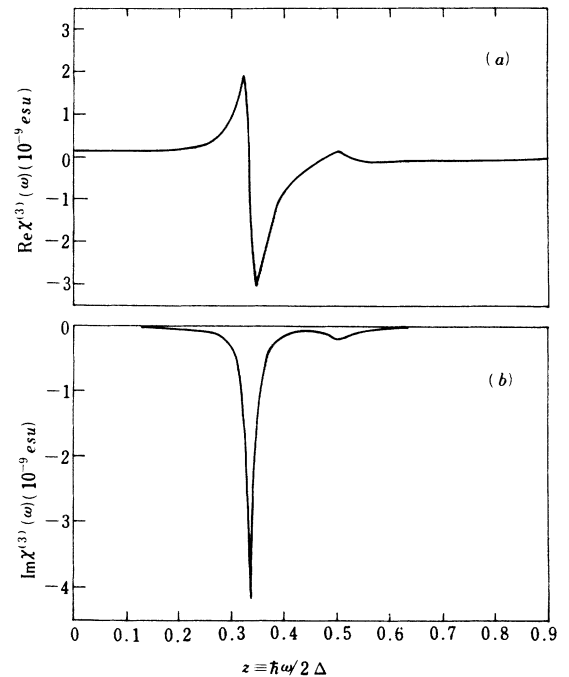


FIG. 1. Third-harmonic generation $\chi_{\text{THG}}^{(3)}(\omega)$ for $\eta=0.03$: (a) the real part and (b) the imaginary part.

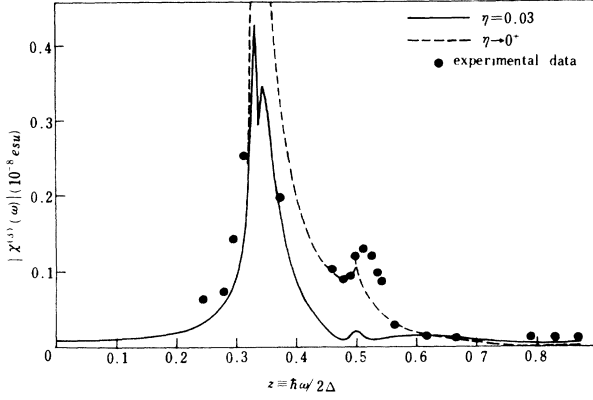


FIG. 2. Absolute magnitude of third-harmonic generation $\chi_{\text{THG}}^{(3)}(\omega)$.

IV. EFFECTS OF ELECTRON INTERACTION AND NONDEGENERATE POLYMERS

In this section, we will briefly discuss the effects of electron-electron interaction and the case of nondegenerate polymers. Before doing that, the third-order zero-frequency susceptibility will be given first, since it is more affected by the electron interaction and degeneracy than the spectrum of third-order nonlinear susceptibility itself.

A. Zero-frequency susceptibility

From the Eq. (15) or Eq. (11), the zero-frequency third-order susceptibility⁸ can be got

$$\chi^{(3)}(0) = \chi_0^{(3)} \frac{45}{64} \int_1^{1/\delta} dx \frac{17 - 12x^2(1 + \delta^2) + 6\delta^2x^4}{x^{10}[(x^2 - 1)(1 - \delta^2x^2)]^{1/2}}, \quad (17)$$

where δ and $\chi_0^{(3)}$ are defined as in Sec. III. The dependence of $\chi^{(3)}(0)$ on the parameter δ is plotted in Fig. 3, from which, we can see that it is insensitive to δ ; the reason is that the contribution of deep inside states to $\chi^{(3)}$ is not important, which has been mentioned in Sec. III. In fact, from the Fig. 2, we can see that in the regions $z(\equiv \hbar\omega/2\Delta) < 0.2$ and $0.53 < z < 0.8$, the susceptibility $\chi_{\text{THG}}^{(3)}(\omega) \sim \chi^{(3)}(0)$, that is, agreement with the experimental data.²

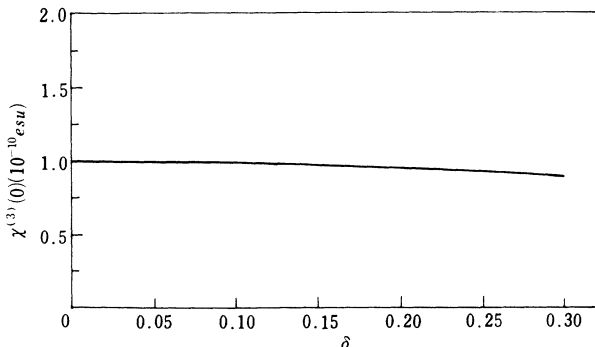


FIG. 3. Dependence of zero-frequency susceptibility $\chi^{(3)}(0)$ on the parameter δ .

B. Effects of electron interaction

In order to include the effect of electron-electron interaction, we consider the extended-Hubbard model combined with the SSH Hamiltonian

$$H = H_{\text{SSH}} + U \sum_{l,s} C_{l,s}^\dagger C_{l,s} C_{l,-s}^\dagger C_{l,-s} + V \sum_{l,s,s'} C_{l,s}^\dagger C_{l,s} C_{l+1,s'}^\dagger C_{l+1,s'}, \quad (18)$$

where U, V are the on-site and nearest-neighbor site Coulomb repulsion, respectively. For the dimerized ground state within the unrestricted Hartree-Fock (UHF) approximation, we have

$$\langle C_{l,s}^\dagger C_{l,s} \rangle = \frac{1}{2}, \quad (19)$$

$$\langle C_{l,s}^\dagger C_{l+1,s} \rangle = \bar{m} + (-1)^l \delta m; \quad (20)$$

then, the effective single-electron Hamiltonian is

$$H_{\text{eff}} = - \sum_{l,s} [\tilde{t}_0 + (-1)^{l+1} \frac{1}{2} \tilde{\Delta}] (C_{l+1,s}^\dagger C_{l,s} + C_{l,s}^\dagger C_{l+1,s}), \quad (21)$$

where

$$\tilde{t}_0 = t_0 + V\bar{m}. \quad (22)$$

$$\tilde{\Delta} = \Delta + 2V\delta m.$$

In the UHF approximation, the on-site Coulomb repulsion U cannot affect the structure of the electron energy band and then affect the nonlinear susceptibility. The self-consistent equations for these parameters in Eq. (22) can be obtained by minimizing the total energy,⁹

$$\bar{m} = \frac{1}{\pi} \int_0^{\pi/2} dk \frac{\cos^2(k)}{[\cos^2(k) + \delta^2 \sin^2(k)]^{1/2}}, \quad (23)$$

$$\delta m = \frac{1}{\pi} \int_0^{\pi/2} dk \frac{\delta \sin^2(k)}{[\cos^2(k) + \delta^2 \sin^2(k)]^{1/2}}, \quad (24)$$

$$\Delta = 4t_0\pi\lambda\delta m, \quad (25)$$

where $\bar{\delta} = \tilde{\Delta}/2\tilde{t}_0$ and λ is the electron-lattice coupling constant. For polyacetylene, $\lambda = 0.233$, $t_0 = 2.5$ eV, and $\Delta = 0.9$ eV; then, we can get the dependence of $\tilde{\Delta}$ and $\bar{\delta}$ on the Coulomb repulsion V from Eqs. (22)–(25). The numerical results are shown in Fig. 4.

For this system, Eq. (15) with $\chi_{\text{THG}}^{(3)}(\omega)$ is also valid, but the parameters Δ and δ there should be replaced by $\tilde{\Delta}$ and $\bar{\delta}$. From the discussion of Sec. III, we know that the spectrum structure of $\chi_{\text{THG}}^{(3)}(\omega)$ is insensitive to the parameter δ , and insensitive to the Coulomb repulsion V . Therefore, within the UHF approximation, the shapes of the spectrum $\chi_{\text{THG}}^{(3)}(\omega)$ are almost the same before and after turning on the electron interaction. But the $\chi_0^{(3)}$ is well affected by the electron interaction; the result is shown in Fig. 5. Since $\chi_0^{(3)}$ is a scale factor for the $\chi^{(3)}(\omega)$, the zero-frequency susceptibility $\chi^{(3)}(0)$ [as well as the overall magnitude of $\chi^{(3)}(\omega)$] is quickly decreased with the increase of the Coulomb repulsion V . This fact implies that the electron interaction would play an im-

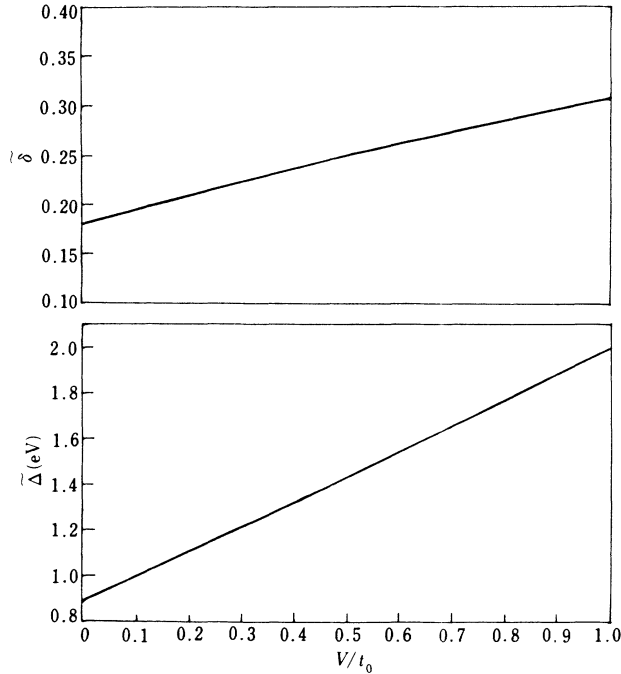


FIG. 4. Dependence of $\tilde{\delta}$ and $\tilde{\Delta}$ on the Coulomb repulsion V .

portant role in the nonlinear optical susceptibilities of conducting polymers.

C. Nondegenerate polymers

For the case of nondegenerate polymers, such as, *cis*-polyacetylene, polythiophene, and poly(3-hexylthienylene) (P3HT), etc, the Hamiltonian should add the following term:¹⁰

$$\Delta H = t_e \sum_{l,s} (-1)^l (C_{l+1,s}^\dagger C_{l,s} + C_{l,s}^\dagger C_{l+1,s}), \quad (26)$$

which lifts the ground-state degeneracy. Then, the total Hamiltonian is

$$\begin{aligned} H &= H_{SSH} + \Delta H \\ &= - \sum_{l,s} [t_0 + (-1)^{l+1} \frac{1}{2} \Delta'] (C_{l+1,s}^\dagger C_{l,s} + C_{l,s}^\dagger C_{l+1,s}), \end{aligned} \quad (27)$$

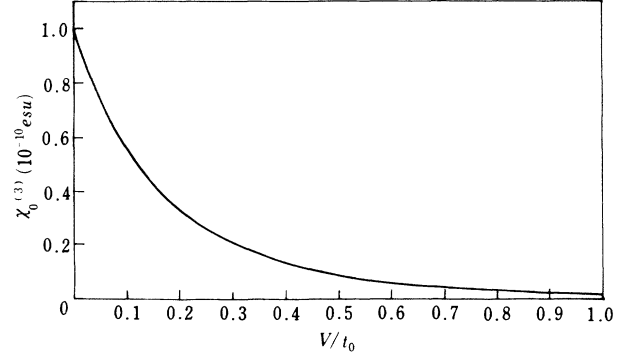


FIG. 5. Dependence of $\chi_0^{(3)}$ on the Coulomb repulsion V .

where, the energy gap order parameter is

$$\Delta' = \Delta + 2t_e. \quad (28)$$

Then from the discussion in Secs. III and IV, we can find that the nondegenerate and degenerate polymers almost have the same shapes of the spectrum $\chi^{(3)}(\omega)$, but the overall absolute magnitude of the third-order susceptibilities $\chi^{(3)}$ is different, since it has the dependence of Δ^{-6} [see Eq. (16)].⁸ For *cis*-polyacetylene, the energy gap $2\Delta' = 2.25$ eV; then, we have

$$\chi_{\text{trans}}^{(3)} / \chi_{\text{cis}}^{(3)} \approx 3.81.$$

Comparing with the experimental results, this ratio between *trans*- and *cis*-polyacetylene is too small. This fact again calls for a new mechanism to the nonlinear optical susceptibilities of conducting polymers.

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