Hyperpolarizabilities for the one-dimensional infinite single-electron periodic systems. I. Analytical solutions under dipole-dipole correlations

Shidong Jiang
Department of Mathematical Sciences, New Jersey Institute of Technology, Newark, New Jersey 07102

Minzhong Xu
Department of Chemistry, New York University, New York, New York 10003

(Received 19 April 2005; accepted 7 June 2005; published online 15 August 2005)

The analytical solutions for the general-four-wave-mixing hyperpolarizabilities $\chi^{(3)}[-(\omega_1+\omega_2+\omega_3)\omega_1,\omega_2,\omega_3]$ on infinite chains under both Su–Shrieffer–Heeger and Takayama–Lin–Liu–Maki models of trans-polyacetylene are obtained through the scheme of dipole-dipole correlation. Analytical expressions of dc Kerr effect $\chi^{(3)}(-\omega_3;0,0,\omega)$, dc-induced second-harmonic generation $\chi^{(3)}(-2\omega_3;0,\omega,\omega)$, optical Kerr effect $\chi^{(3)}(-\omega_3;\omega,-\omega,\omega)$, and dc electric-field-induced optical rectification $\chi^{(3)}(0;\omega,-\omega,0)$ are derived. By including or excluding $V_k$ terms in the calculations, comparisons show that the intraband contributions dominate the hyperpolarizabilities if they are included. $V_k$ term or intraband transition leads to the break of the overall permutation symmetry in $\chi^{(3)}$ even for the low-frequency and nonresonant regions. Hence it breaks the Kleinman [Phys. Rev. 126, 1977 (1962)] symmetry that is directly based on the overall permutation symmetry. Our calculations provide a clear understanding of the Kleinman symmetry breaks that are widely observed in many experiments. We also suggest a feasible experiment on $\chi^{(3)}$ to test the validity of overall permutation symmetry and our theoretical prediction. Finally, our calculations show the following trends for the various third-order nonlinear optical processes in the low-frequency and nonresonant region: $\chi_{\text{nonres}}^{(3)}(-3\omega;\omega,\omega,\omega) > \chi_{\text{res}}^{(3)}(-2\omega;0,\omega,\omega) > \chi_{\text{res}}^{(3)}(-\omega;\omega,-\omega,0) > \chi_{\text{res}}^{(3)}(-\omega;\omega,\omega,-\omega,0) > \chi_{\text{res}}^{(3)}(0;\omega,-\omega,0)$, and in the resonant region: $\chi_{\text{res}}^{(3)}(-\omega;0,0,\omega) > \chi_{\text{res}}^{(3)}(-\omega;\omega,-\omega,0) > \chi_{\text{res}}^{(3)}(-\omega;\omega,\omega,0)$.

I. INTRODUCTION

The nonlinear optical (NLO) properties of $\pi$-conjugated polymers have been extensively studied by both experimentalists and theorists. Among these polymers, polyacetylene (PA) is the simplest conjugated polymer and has been extensively studied. PA consists of chains of CH units that form a pseudo-one-dimensional (1D) lattice. Classical periodic single-electron models such as Su–Shrieffer–Heeger (SSH) and Takayama–Lin–Liu–Maki (TLM) have been established to interpret the optical properties of polyacetylene. Experiments have measured the spectrum of third-order harmonic generation (THG) in polyacetylene which requires theoretical explanations. The contribution from the lattice relaxation to the third-order optical susceptibilities $\chi^{(3)}$ is believed to be small because of the slow process involved in the lattice relaxation. Based on either the periodic single-electron models (SSH and TLM) or the inclusion of electron-electron interactions extended from both models, the frequency dependence of the THG in PA has been extensively studied theoretically.

Even for these simple single-electron models, the theoretical studies on frequency dependence of $\chi^{(3)}$ have been approached in various ways: (i) Based on the different gauges, this problem can be studied either from dipole-dipole (DD) or from current-current (JJ) correlations; (ii) based on the size of chain, this problem can be treated either as a finite periodic chain or an infinite one. Furthermore, from the point of view of different techniques to utilize the perturbative method, this problem can be solved either by quantum mechanics or by the field theory. Obviously, different approaches on the same model should yield the same results if every step is carried out correctly. However, this seemingly simple problem turns out to be nontrivial in the actual computations because different results of $\chi^{(3)}$ for polyacetylene have been obtained from the different approaches. A typical example is the THG calculation. There different gauges yield different results both numerically and analytically. On the other hand, in the formulation of DD correlations, there are some controversies about whether or not the $V_k$ term should be included for an infinite periodic system. It is our interest to illustrate the differences and understand the reasons why the discrepancies exist in the theoretical calculations.

Recently, many experiments showed the general failure of Kleinman symmetry in describing the low-frequency and nonresonant nonlinear optical properties of many materials and practical systems. But most experiments only measured the $\chi^{(2)}$ in systems without centro- or inversion symmetry. Based on the possible mutual exclusion property...
between Kramers-Kronig dispersion relations and Kleinman symmetry, Dailey et al. asserted the general failure of Kleinman symmetry. However, physically Kleinman symmetry is only a direct consequence of the overall permutation symmetry. Thus we would also like to investigate the overall permutation symmetry under SSH and TLM models in this work. For the trans-polyacetylene system where the centro- or inversion symmetry is applied, $\chi^{(2)}$ vanishes. Hence we will use the nontrivial results for $\chi^{(3)}$ to discuss the validity of both overall permutation and Kleinman symmetries.

In this and the subsequent papers, we will present the analytical results of hyperpolarizabilities $\chi^{(3)}$ for both the SSH and TLM models based on the field theory. Both SSH and TLM models describe periodic single-electron systems. The analytical form for the nonlinear optical response can be obtained under both models and used to illustrate the subtle differences in periodic systems. We will make detailed comparisons between our calculation and other theoretical results of hyperpolarizabilities in both papers. The purpose of the present paper is to elucidate the physical contribution of each hyperpolarizabilities in both papers. The purpose of the present paper is to elucidate the physical contribution of each term in the formulation of dipole-dipole correlations. The energy bands of 1D SSH model are simple—

\begin{equation}
E_0 = \text{constant} + \sum_{l,s} \Delta t \left( C_{l,s}^\dagger C_{l,s} + C_{l,s}^\dagger C_{l,s} \right),
\end{equation}

where $t_0$ is the transfer integral between the nearest-neighbor sites, $\Delta$ is the gap parameter, and $C_{l,s}^\dagger$ creates an electron at site $l$ with spin $s$. For the SSH model, each site is occupied by one electron. In the continuum limit, the SSH model will tend to the TLM model given by the formula

\begin{equation}
H_{\text{TLM}} = \Psi^\dagger(x) \left( i \sigma_3 v_F \partial_x + \Delta \sigma_j \right) \Psi(x),
\end{equation}

where $\Psi(x) = [\Psi_1^\dagger(x), \Psi_2^\dagger(x)]$ is the two-component spinor describing the left-going and right-going electrons, $v_F$ is the Fermi velocity, $\Delta$ is the gap parameter, and $\sigma_j$ ($j=1,2,3$) are the Pauli matrices.

Under the DD correlation, the interaction Hamiltonian is expressed by the formula

\begin{equation}
\hat{H}_{E \cdot r} = - e E \cdot \hat{r} = - D \cdot E,
\end{equation}

with $\hat{r}$ the electron charge and $E$ the electric field described as follows:

\begin{equation}
E(r,t) = E_0 e^{i(k \cdot r - \omega t)},
\end{equation}

where $E_0$ is the amplitude, and $k$ and $\omega$ are the wave vector and frequency, respectively.

For periodic systems, the position operator $r$ is often conveniently defined in the momentum space:

\begin{equation}
\mathbf{r}_{\mathbf{k},n,n'}^i = i \delta_{\mathbf{n},n'} \nabla_{\mathbf{k}} \delta(\mathbf{k} - \mathbf{k}') + \Omega_{\mathbf{n},n'}(\mathbf{k}) \delta(\mathbf{k} - \mathbf{k}'),
\end{equation}

where

\begin{equation}
\Omega_{n,n'}(\mathbf{k}) = \frac{i}{u} \int \mathbf{r} u_{n,h,k}(\mathbf{r}) \nabla_{\mathbf{k}} u_{n',h,k}(\mathbf{r}) d\mathbf{r},
\end{equation}

with $u$ the unit-cell volume, and $u_{n,h,k}(\mathbf{r})$ the periodic function under the translation of lattice vector. Obviously, $u_{n,h,k}(\mathbf{r})$ is related to the wave function $\psi$ of Bloch states by the formula

\begin{equation}
\psi_{n,h,k}(\mathbf{r}) = u_{n,h,k}(\mathbf{r}) e^{i k \cdot r},
\end{equation}

where $n$ and $\mathbf{k}$ are the band index and crystal momentum, respectively.

The energy bands of 1D SSH model are simple—conduction and valence bands. Thus, this 1D model avoids certain problems due to the discontinuous and nonanalytical feature of Bloch wave functions for a composite band in higher-dimension periodic models.

Following the same procedures described in previous work, we consider the momentum space representation of the Hamiltonian given by Eq. (2.1). With the aid of the spinor description $\hat{D}_{\mathbf{k},s}(t) = [\hat{a}_{\mathbf{k},s}^\dagger(t), \hat{a}_{\mathbf{k},s}^\dagger(t)]$, where $\hat{a}_{\mathbf{k},s}^\dagger(t)$ and $\hat{a}_{\mathbf{k},s}(t)$ are excitations of electrons in the conduction band and the valence band with momentum $\mathbf{k}$ and spin $s$, we obtain the following formula:

\begin{equation}
\hat{H}_{\text{SSH}}(\mathbf{k},t) = \hat{H}_0 + \hat{H}_{E \cdot r},
\end{equation}

where

\begin{equation}
\hat{H}_{\text{SSH}}(\mathbf{k},t) = \hat{H}_0 + \hat{H}_{E \cdot r},
\end{equation}

where $\sigma$ are the Pauli matrices, the operator $\hat{D}$ and the parameter $e(k)$ are given by the following formulas, respectively:
\[ \hat{D} = e \sum_{-\pi/2a \leq k \leq \pi/2a} \left( \beta(k) \hat{\psi}_{k,s}^\dagger \hat{\sigma}_2 \hat{\psi}_{k,s} + i \frac{\partial}{\partial k} \hat{\psi}_{k,s}^\dagger \hat{\psi}_{k,s} \right). \]  

(2.9)

\[ \epsilon(k) = \sqrt{[2t_0 \cos(ka)]^2 + [\Delta \sin(ka)]^2}. \]  

(2.10)

The coefficient \( \beta(k) \) in Eq. (2.9) is given by the formula

\[ \beta(k) = -\frac{\Delta_{k\beta}}{\epsilon'(k)}. \]  

(2.11)

The coefficient \( \beta(k) \) is related to the interband transition between the conduction and valence bands in a unit cell of length \( 2a \), and the second term in Eq. (2.9) is often related to the intraband transition.\(^\text{13,14}\)

**B. Berry phase and analytical format of one-dimensional Bloch functions**

In periodic systems, Bloch functions cannot be analytical and are discontinuous for a composite band in which one band structure contains more than one branch. This fact was firstly pointed out by Blount,\(^\text{42}\) and later proved by Zak.\(^\text{44}\) Generally speaking, Eq. (2.4) is not analytical for composite bands. Fortunately, for the 1D periodic system being discussed here, it has been proved by Kohn that analytical results can be obtained\(^\text{46}\) since both valence and conducting bands are simple. Thus, we may avoid the trouble due to the discontinuous or nonanalytical feature of Bloch wave functions.

The Berry phase for a 1D crystal with the centro- or inversion symmetric only can only be 0 or \( \pi \) (mod \( 2\pi \)),\(^\text{47}\) therefore one can expect a vanishing Berry phase for closed path in this specific problem. The Berry phase in the crystals is related to the diagonal matrix of the first term in Eq. (2.9).\(^\text{47,48}\) However, in the problem we are discussing, the Berry phase is 0.

**C. Field theory of hyperpolarizabilities**

There are a lot of different formulas to compute the hyperpolarizabilities—Orr-Ward sum-over-state (SOS) method,\(^\text{49}\) dipole formulas by Shen,\(^\text{50}\) and Genkin–Mednis approach\(^\text{51}\) generalized by Kirtman et al.\(^\text{29}\) Different gauge approaches can be applied to this problem. All are based on the perturbation expansion. Recently, the field theory has been used to discuss this nonlinear problem.\(^\text{13,15}\)

For this single-electron problem, the Feynman diagram of \( \chi^{(3)} \) is simply described as one connected cycle in Fig. 1. If the long-wavelength approximation is applied, \( k_1 = k_2 = k_3 = K = 0 \). The only permutation to be considered in this graph is three different frequencies \( \omega_1, \omega_2, \) and \( \omega_3 \).

The general third-order susceptibility under \( \mathbf{D} \cdot \mathbf{E} \) gauge is described by

\[ \chi^{(3)}(\Omega; \omega_1, \omega_2, \omega_3) = \frac{1}{3!V} \int \frac{dt_1 dt_2 dt_3}{h^3} \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \]

\[ \times \int d\mathbf{r} d\mathbf{t} e^{-i K \cdot \mathbf{r} + i \Omega t} \langle \hat{D}(\mathbf{r}, t) \hat{D}(\mathbf{r}_1, t_1) \hat{D}(\mathbf{r}_2, t_2) \hat{D}(\mathbf{r}_3, t_3) \rangle, \]  

(2.12)

where \( V \) is the total volume, \( \Omega = -\sum_{i=1}^{3} \omega_i \), \( T \) is the time-ordering operator, \( \hat{D} \) is the dipole operator, and \( \langle \cdots \rangle \) represents the average over the unperturbed ground state.

For periodic systems, in order to maintain the periodicity of the position operator \( \mathbf{r} \), a “sawliked” position operator must be introduced.\(^\text{52}\) For convenience in studying the nonlinear susceptibilities, we usually express Eq. (2.12) in the momentum space for further calculations.\(^\text{13,14,45}\)

**III. HYPERPOLARIZABILITIES FOR SSH AND TLM MODELS UNDER DIPOLE FORMULA**

The TLM model\(^\text{32}\) is simply the continuum limit of the SSH model,\(^\text{31}\) and analytical results for the TLM model can be easily derived from those under the SSH model. Therefore in the following part, we will first focus on the hyperpolarizabilities under the SSH model. Then we will deduce results under TLM model by simply passing to the continuum limit. As for the notations \( \chi_B^A \), the superscript \( A \) represents the abbreviation for the different FWM terms, and the subscript \( B \) represents the different models such as SSH or TLM models. We also use \( \tilde{\chi} \) to represent the hyperpolarizabilities without considering \( \mathbf{V}_k \) term in Eq. (3.1).

**A. General four-wave-mixing (FWM) results**

Under SSH and TLM models, the general FWM can be expressed as
\[ \chi_{SSH}^{FWM}(\omega_1, \omega_2, \omega_3) = \chi_{SSH}^{(3)}[(- (\omega_1 + \omega_2 + \omega_3), \omega_1, \omega_2, \omega_3)], \]

\[ \chi_{SSH}^{FWM}(\omega_1, \omega_2, \omega_3) = \frac{e^2 n_0}{\pi} \sum \int \frac{id\omega}{2\pi} \text{Tr} \left( \left( \beta(k) \sigma_2 + i \frac{\partial}{\partial k} \right) G(k, \omega) \left( \beta(k) \sigma_2 + i \frac{\partial}{\partial k} \right) G(k, \omega - \omega_1) \times \left( \beta(k) \sigma_2 + i \frac{\partial}{\partial k} \right) G(k, \omega - \omega_1 - \omega_2 - \omega_3) \right) , \quad (3.1) \]

where \( L \) is the chain length, \( n_0 \) is the number of chains per unit cross area, and \( \mathcal{P}(\omega_1, \omega_2, \omega_3) \) represents all permutations for \( \omega_1, \omega_2, \) and \( \omega_3 \) (therefore the intrinsic symmetry is maintained\(^3\)). The polymer chains are assumed to be oriented, and Green’s function \( G(k, \omega) \) is defined as follows:\(^{13,14,45}\)

\[ G(k, \omega) = \frac{\omega + \omega_k \sigma_3}{\omega^2 - \omega_k^2 + i\varepsilon}, \quad (3.2) \]

with \( \omega_k = \varepsilon(k)/\hbar \) and \( \varepsilon = 0^+\).

After tedious derivations, we obtain the following analytical results for the SSH model:\(^{41}\)

\[ \chi_0^{(3)} = \frac{15}{1024} \frac{1}{\pi \Delta^5} \frac{e^2 n_0 (Z_{0G})^3}{h \omega}, \quad (3.5) \]

\[ z_i = \frac{h \omega_i}{2 \Delta}, \quad \text{for } i = 1, 2, 3. \quad (3.6) \]

By setting \( z_1 = z_2 = z_3 = z = h \omega/2 \Delta \), Eq. (3.3) can be simplified as third-harmonic generation \( \chi^{(3)}(-3\omega; \omega, \omega, \omega) \). It is easy to prove that Eq. (3.3) is the same as Eq. (2.20) (Ref. 13) or Eq. (9) (Ref. 14) in our previous works.

By changing \( x \rightarrow x + i\varepsilon \) in Eq. (3.3), and by choosing the same parameters used in our previous works for polyacetylene,\(^{13,14,21,22}\) \( \Delta = 0.9 \text{ eV}, \quad n_0 = 3.2 \times 10^{14} \text{ cm}^{-2}, \quad a = 1.22 \AA, \quad \delta = 0.18, \quad \text{and} \quad e \sim 0.03, \) we have \( \chi_0^{(3)} \approx 1.0 \times 10^{-10} \text{ esu} \). The absolute value of FWM is plotted in Fig. 2.

From the graph, we find several symmetrical resonant frequencies. The biggest resonant peaks are around \( (0, 0, \pm 1), (\pm 1, \pm 1, \pm 1) \) and their permutations correspond to dc Kerr and optical Kerr effect or IDIR, respectively. There are some secondary resonant frequencies: the cusps shown in Fig. 1 are around \( (\pm 1, \pm 1, 0) \) and their permutations. They correspond to dc EFIOR. The resonant peaks for THG are not obvious in this graph.

FIG. 2. (Color) The magnitude of four-wave mixing (FWM) \( \chi^{(3)} \times (-\Omega; \omega_1, \omega_2, \omega_3) \) under SSH model is in \( 10^{-8} \text{ esu} \). \( Z_i \) is defined by Eq. (3.6).
where

\[ \sigma = (z_1 + z_2)(z_2 + z_3)(z_3 + z_1), \]  
\[ \tilde{Z} = z_1 + z_2 + z_3, \]  
\[ L(n, z) \text{ and } M(n, z) \text{ (} n = 0, \ldots, 4 \text{) are defined by (A2) and (A3), respectively.} \]

The parameter \( \delta \) defined in (3.4) is proportional to the optical gap \( \Delta \) of the SSH model. Though the \( \delta = 0 \) limit yields hyperpolarizabilities in the TLM model, the continuum model nevertheless has a finite optical gap (albeit a very small one, negligible compared to the bandwidth in the linearized model, in contrast with conjugated polymers whose optical gap is about 20\% of the bandwidth).

### B. dc Kerr effect

By setting \( z_1 = z_2 = 0 \) and \( z_3 = z [\hbar \omega / (2 \Delta)] \) in Eq. (3.3), we have

\[ \chi^{(3)}(0, 0, \omega) = \chi_0^{(3)} \left\{ \frac{15}{256} \int_{1/\delta}^{11/\delta} \frac{dx}{x^7(1 - \Delta^2 x^2)(x^2 - 1)} \left[ -\frac{(2x - z)}{x^2(x - z)} - \frac{(2x + z)}{x^2(x + z)} - \frac{2}{x(2x^2 - z^2)} + 2(1 - \Delta^2 x^2)(x^2 - 1) \right] \frac{3(3x - 2z)}{x^2(x - z)^2} + \frac{3(3x + 2z)}{x^2(x + z)^2} + \frac{(3x - 2z)^2}{x^2(x + z)^5} + \frac{(3x + 2z)^2}{x^2(x - z)^5} + \frac{3(3x - 2z)}{x^2(x - z)^3} + \frac{3(3x + 2z)}{x^2(x + z)^3} \right] \right\} \]  
\[ \chi_{\text{dc Kerr}}^{(3)}(0, 0, \omega) = \chi_0^{(3)} \left\{ \frac{125}{128} \right\} \left\{ -\frac{2L(3, z) - L(4, z) + 32M(0, z) + 24M(1, z) + 2M(2, z) + 2M(3, z) - 6M(4, z))}{x^2(x^2 - z^2)} \right\} \]  
\[ \chi_{\text{dc TLM}}^{(3)}(0, 0, \omega) = \chi_0^{(3)} \left\{ \frac{512 \varepsilon^8(z^2 - 1)}{x^2(z^2 - 1)} \right\} \left\{ -120 \varepsilon^8 - 580 \varepsilon^6 + 1029 \varepsilon^4 - 780 \varepsilon^2 + 216 \right\} f(z) + \frac{1}{105} \left( 384 \varepsilon^{12} - 928 \varepsilon^{10} + 760 \varepsilon^8 - 22182 \varepsilon^6 + 65541 \varepsilon^4 - 66780 \varepsilon^2 + 22680 \right) \]  
\[ \chi_{\text{dc TLM}}^{(3)}(0, 0, \omega) = \chi_0^{(3)} \left\{ \frac{128 \varepsilon^8(z^2 - 1)}{x^2(z^2 - 1)} \right\} \left\{ -120 \varepsilon^8 - 580 \varepsilon^6 + 1029 \varepsilon^4 - 780 \varepsilon^2 + 216 \right\} f(z) + \frac{1}{105} \left( 48 \varepsilon^8 - 104 \varepsilon^6 - 154 \varepsilon^4 - 315 \varepsilon^2 + 630 \right) \]  

### C. dc-induced second-harmonic generation

The dc-induced second-harmonic generation (dc SHG) coefficient under the SSH and TLM models can be obtained in an almost identical manner as the dc Kerr effect except that here we set \( z_1 = z_2 = z \) and \( z_3 = 0 \) in Eq. (3.3). The results are
D. Optical Kerr effect or intensity-dependent index of refraction

The optical Kerr effect or IDIR coefficient under the SSH and TLM models can be computed similarly by setting \( z_1 = z_3 = z \) and \( z_2 = -z \) in Eq. (3.3). We have

\[
\chi^{\text{dc SHG}}_{\text{SSH}}(0, \omega, \omega) = \frac{15}{128} \chi^{(3)}_0 \int_1^{\infty} \frac{dx}{\sqrt{(1 - \delta^2 x^2)(x^2 - 1)}} \left\{ \frac{4}{x^8(x^2 - 4z^2)} + \frac{1}{x^8(x^2 - z^2)} + 2(1 - \delta^2 x^2)(x^2 - 1) \left[ \frac{6}{x^8(x^2 - z^2)} \right. \right. \\
\left. \left. + \frac{1}{x^6(x^2 - z^2)^2} - \frac{4}{x^4(x^2 - z^2)^2} \right] \right\} \right\}
\]

(3.15)

and

\[
\chi^{\text{dc SHG}}_{\text{TLM}}(0, \omega, \omega) = \chi^{(3)}_0 \frac{15}{256z^2(z^2 - 1)} \left( \frac{28z^6 - 104z^4 + 118z^2 - 43f(z)}{105} \right) - \frac{1}{105} \left( 288z^{10} - 184z^8 + 204z^6 - 5068z^4 + 9380z^2 \\ - 4515 \right) + \chi^{(3)}_0 \frac{15}{2048z^8(4z^2 - 1)} \left( \frac{-48z^6 + 6z^2 + 1}{10} f(z) \right) \right\}
\]

(3.16)

Similarly, only the first two terms of Eq. (3.15) survive when the gradient terms are omitted, and Eq. (3.16) is changed as follows:

\[
\chi^{\text{dc SHG}}_{\text{TLM}}(0, \omega, \omega) = \chi^{(3)}_0 \frac{15}{1024z^8} \left\{ 8f(z) - \frac{1}{8} f(2z) - \frac{1}{40} \left( 128z^2 + 200z^2 + 315 \right) \right\}.
\]

(3.17)

E. dc electric-field-induced optical rectification

The dc EFIOR under the SSH and TLM models can be computed by setting \( z_1 = 0, z_2 = -z, \) and \( z_3 = z \) in Eq. (3.3). We have

\[
\chi^{\text{EFIOR}}_{\text{SSH}}(0, -\omega, \omega) = \chi^{(3)}_0 \frac{15}{128} \int_1^{\infty} \frac{dx}{\sqrt{(1 - \delta^2 x^2)(x^2 - 1)}} \left\{ \frac{1}{x^8(x^2 - z^2)^2} - \frac{4}{x^8(x^2 - z^2)} + 2(1 - \delta^2 x^2)(x^2 - 1) \right\}
\]

(3.18)

and

\[
\chi^{\text{EFIOR}}_{\text{TLM}}(0, -\omega, \omega) = \chi^{(3)}_0 \frac{15}{256z^8} \left\{ \frac{8z^6 + 44z^4 + 83z^2 + 495z^2 + 315}{15(z^2 - 1)^2} - \frac{4z^6 + 22z^4 + 43z^2 + 20}{(z^2 - 1)^2} f(z) + (4z^2 - 1) f(2z) \right\}.
\]

(3.19)

When the gradient terms are omitted, only the first two terms of Eq. (3.18) survive, and Eq. (3.19) is changed as follows:

\[
\chi^{\text{EFIOR}}_{\text{TLM}}(0, \omega, \omega) = \chi^{(3)}_0 \frac{1}{256z^8(z^2 - 1)^2} \left\{ (840z^4 - 1425z^2 + 630)f(z) + (16z^6 + 88z^6 + 226z^6 - 1005z^2 + 630) \right\}.
\]

(3.20)
Again, only the first two terms of Eq. (3.21) survive when the gradient terms are omitted, and Eq. (3.22) is changed as follows:

\[
\chi^{\mathrm{EFIOR}}_{\mathrm{TLM}}(0, -\omega, \omega) = \chi_0^{(3)} \frac{15}{128z^8(z^2 - 1)} \left\{ (7z^2 - 6)f(z) + \frac{1}{105} (48z^8 - 104z^6 - 154z^4 - 315z^2 + 630) \right\}.
\]

(3.23)

**F. Third-harmonic generation**

The results of THG can be computed by setting \(z_1 = z_2 = z_3 = z\) in Eq. (3.3). They can also be found in our previous works.\(^{13,14}\) Here we simply state the results,

\[
\chi^{\mathrm{THG}}_{\mathrm{SSH}}(\omega) = \chi_0^{(3)} \frac{45}{128} \int_1^{1/\delta} \frac{dx}{\sqrt{(1 - \delta x^2)(x^2 - 1)}} \left\{ \frac{1}{8x^8(x^2 - z^2)} - \frac{21}{8x^6(x^2 - 9z^2)} - \frac{18}{x^8(x^2 - 9z^2)} \right\}.
\]

(3.24)

and

\[
\chi^{\mathrm{THG}}_{\mathrm{TLM}}(\omega) = \chi_0^{(3)} \frac{45}{128} \left\{ \frac{14}{3z^8} - \frac{4}{15z^4} + \frac{37 - 24z^2}{8z^8} f(z) + \frac{1 - 8z^2}{24z^8} f(3z) \right\}.
\]

(3.25)
When the \( \nabla_k \) terms are omitted, only the first two terms of Eq. (3.24) survive and Eq. (3.25) becomes

\[
\chi^{THG}_{\text{TLM}}(\omega, \omega, \omega) = \chi^{(3)}_{\text{res}}(\omega) - \frac{1}{82944\delta} \{5(729f(z) - f(3z)) - 8(216\delta^4 + 300\delta^2 + 455)\}. \tag{3.26}
\]

### IV. DISCUSSIONS

#### A. Resonant and nonresonant features

Figure 3 shows the hyperpolarizabilities of dc Kerr, dc SHG, IDIR, and EFIG for SSH models. Choosing the same parameters in Sec. III A, we see that the magnitudes of the resonant peaks are in the following order:

\[
\chi^{(3)}_{\text{res}}(-\omega; \omega, \omega, \omega) > \chi^{(3)}_{\text{res}}(-2\omega; 0, \omega, \omega) \\
> \chi^{(3)}_{\text{res}}(0; \omega, -\omega, 0) > \chi^{(3)}_{\text{res}}(3\omega; \omega, \omega, \omega).
\]

(4.1)

Figure 4 shows the comparison of hyperpolarizabilities of dc Kerr, dc SHG, IDIR, EFIG, and THG for SSH models for low frequencies. Choosing the same parameters in Sec. III, we see that the nonresonant features are in the following order:

\[
\chi^{(3)}_{\text{nonres}}(-3\omega; \omega, \omega, \omega) > \chi^{(3)}_{\text{nonres}}(-2\omega; 0, \omega, \omega) \\
> \chi^{(3)}_{\text{nonres}}(-2\omega; \omega, -\omega, \omega) \\
> \chi^{(3)}_{\text{nonres}}(-\omega; 0, 0, 0) \\
\geq \chi^{(3)}_{\text{nonres}}(0; \omega, -\omega, 0).
\]

(4.2)

This nonresonant frequency dependence of nonlinear optical properties is consistent with previous calculations for polyenes.

#### B. \( \nabla_k \) term, Kramers-Kronig (KK) relation, the overall permutation, and Kleinman symmetries

There are some arguments about whether or not one should include the \( \nabla_k \) terms in the calculations of nonlinear optical properties. The \( \nabla_k \) terms are usually considered to be related to the intraband current.\(^{12}\) Otto and co-workers suggested not to include this term because of the nonperiodic property of \( \nabla_k \)\(^{28,34,36}\) and thus the calculations would be purely based on the interband transition. In this work, we compute the analytical results with or without \( \nabla_k \) terms to show the differences of the results under both schemes.

Considering the important physical contributions from the intraband currents,\(^{12,29}\) we are in favor of including the \( \nabla_k \) terms. Moreover, the restriction of our calculations in a unit cell implicitly imposes the periodic condition even for \( \nabla_k \) operator. For the linear susceptibility \( \chi^{(1)} \), our calculations\(^{45}\) show that the \( \nabla_k \) term makes no actual contributions. Due to the centro- or inversion symmetry for both SSH and TLM models, the second-order susceptibility \( \chi^{(2)} \) vanishes; the first nonzero susceptibility is the third-order susceptibility \( \chi^{(3)} \). From the formula, the \( \nabla_k \) term causes the noncommuting problem between operators in the third-order susceptibility \( \chi^{(3)} \) calculations. Therefore, it breaks the overall permutation symmetry [between \( (\omega_1, \omega_2, \omega_3) \) and \( \Omega = -\Sigma_3 \omega_3 \)] that is preserved in molecular systems\(^{39}\) where only bound states exist. Kleinman symmetry, which is defined as the interchangeability of all \( n \) indices in the rank \( n \) tensor \( \chi^{(n)} \) (Refs. 37 and 39) and derived from the overall permutation symmetry, is also broken even for low optical frequencies. Our calculations clearly show the nonequivalent off-resonant behavior between \( \chi^{dc \ Kerr}(\omega; 0, 0, \omega) \) and \( \chi^{EFIG}(0; \omega, -\omega, 0) \). To provide a theoretical result that can be measured by experiments, we also perform the calculation of \( \chi^{(3)}(\omega; \omega, \omega, -3\omega) \), which is the overall permutation of the THG \( \chi^{(3)}(-3\omega; \omega, \omega, \omega) \). We obtain

\[
\chi^{(3)}_{\text{SSH}}(\omega; \omega, \omega, -3\omega) = \chi^{(3)}_{\text{res}}(\omega) \frac{15}{1024\delta} \int_{1/\delta}^{1} \frac{dx}{\sqrt{1 - \delta^2(x^2 - 1)}} \left\{ \frac{3}{x^2(x^2 - 2z^2)} - \frac{27}{28} + 8(1 - \delta^2)(x^2 - 1) \right\}
\]

\[
\times \left\{ -\frac{74}{9} x^6(x^2 - z^2) - \frac{11}{3} x^6(x^2 - z^2)^2 + \frac{512}{9} x^8(x^2 - 4z^2) - \frac{54}{1} x^8(x^2 - 9z^2) + \frac{63}{1} x^8(x^2 - 9z^2)^2 \right\}. \tag{4.3}
\]

Letting \( \delta \rightarrow 0 \) in Eq. (4.3), we obtain the result under the TLM model

\[
\chi^{(3)}_{\text{TLM}}(\omega; \omega, \omega, -3\omega) = \chi^{(3)}_{\text{res}}(\omega) \frac{5}{1024\delta^3} \left\{ \frac{5}{3} (40z^2 - 61)f(z) + \frac{16}{3} (4z^2 - 1)f(2z) - \frac{1}{243} (1944z^2 - 241)f(3z) + \frac{32}{243} (27z^4 - 30z^2 + 805) \right\}
\]

\[
= \chi^{(3)}_{\text{res}}(\omega) \left\{ \frac{5}{28} 8z^2 + \frac{28500}{1001} z^4 + O(z^6) \right\} (z \rightarrow 0). \tag{4.4}
\]
On the other hand, analytical expression for THG under the TLM model is given by the formula [see, for example, (Refs. 13 and 14)]:

\[
\chi_{\text{TLM}}^{(3)}(-3\omega; \omega, \omega, \omega) = \chi_{0}^{(3)} \left( \frac{45}{128} - \frac{14}{15} + \frac{8}{24} f(z) \right) + \frac{1}{1 - 8z} f(3z)
\]

Both \(\chi_{\text{TLM}}^{(3)}(\omega, \omega, -3\omega)\) and \(\chi_{\text{TLM}}^{(3)}(-3\omega; \omega, \omega, \omega)\) in the nonresonant region are plotted in Fig. 5. The numerical calculation shows 40% difference between them when \(z=1/6\) (corresponding to 0.3 eV or wavelength 4.14 \(\mu\)m) in this model. Thus it clearly shows the break of overall permutation symmetry, while the Kramers-Kronig relation is satisfied in Eqs. (4.4) and (4.5). Subtracting two asymptotic expressions in Eqs. (4.4) and (4.5), we have the following relationship of the difference in the off-resonant region:

\[
\delta \chi^{(3)}(\omega) \propto \frac{e^4 n_0^3 g_0^2}{\hbar^2 \omega^2} \Delta^2.
\]

By excluding the \(\nabla_k\) terms, our calculations show that both the overall permutation and Kleinman symmetries remain valid. For example, \(\chi_{\text{Kerr}}^{(3)} = \chi_{\text{EFIOR}}^{(3)}\) and \(\chi^{(3)}(-3\omega; \omega, \omega, \omega) = \chi^{(3)}(\omega, \omega, -3\omega)\) are preserved for all frequencies. Obviously, it is the \(\nabla_k\) term that breaks the overall permutation in periodic systems. Though the experimental-stimulated Raman scattering does not exhibit the overall permutation symmetry for the resonant region,\(^{38,39}\) it seems that no experiment has been reported to test the validity of the overall permutation symmetry for low-frequency and nonresonant region. Therefore, we suggest a new \(\chi^{(3)}\) experiment on infinite trans-polyacetylene chains to test the break of overall permutation symmetry.

Recent experimental studies have already pointed out the deviation from the Kleinman symmetry for low optical frequencies in numerous investigations of various optical systems.\(^{38}\) The assertion of the general failure in Kleinman symmetry has been made in Ref. 38. Due to the similarity between the overall permutation and Kleinman symmetry, Eq. (4.6) can also be used to explain the break of Kleinman symmetry in experiments qualitatively. Equation (4.6) shows that (i) the break increases with decreasing band gap and is proportional to \(\omega^2\). These are consistent with the previously reported experiment;\(^{53}\) (ii) the break increases with \(t_0\) (the hopping of \(\pi\) electrons between the nearest-neighbor atoms). This explains the experimental results that the deviation of Kleinman symmetry is favorable of (20%–50%) the delocalized states such as aromatic molecules\(^{54}\) and some polymers or crystals,\(^{55,56}\) while unfavorable of (\(\approx 8\%)\) the localized states such as molecular systems such as O\(_2\), N\(_2\), etc.\(^{57,58}\) On the other hand, the vanishing \(\chi^{(2)}\) under the SSH or TLM model shows that some symmetries such as centro-symmetry, etc., can suppress the deviation from Kleinman symmetry even for periodic systems. This may explain why Kleinman symmetry is still preserved in some \(\chi^{(2)}\) experiments of crystals.\(^{59}\)

The magnitudes of the hyperpolarizabilities with \(\nabla_k\) terms are quite close to those without \(\nabla_k\) terms in our results. In this sense, both results can give the correct position of the resonant peaks qualitatively. However, we should notice that there is actually a sign difference between the results of including and excluding \(\nabla_k\) terms. Therefore, the intraband current contribution to the hyperpolarizabilities is actually about as twice big as the interband contribution and cannot be neglected. The total contribution (with \(\nabla_k\) terms), interband contribution (without \(\nabla_k\)), and intraband contribution (the difference of previous two) under TLM model are plotted in Fig. 6.

**C. Zero-frequency behaviors for hyperpolarizabilities**

Hyperpolarizabilities under zero frequency are also called static hyperpolarizabilities. To obtain the static hyperpolarizabilities, there are several different approaches. One way is to obtain the static polarizability by directly applying the static electronic field. For example, by applying Resta’s definition of dipole moment for periodic systems,\(^{60}\) Soos et al. obtained the polarizability of one-dimensional Peierls-Hubbard model based on the static electronic field.\(^{61}\) The other way is to obtain the optical hyperpolarizabilities first,
then let all frequencies approach 0. Obviously, both ways should yield the exactly same results of static hyperpolarizabilities. Here we applies the latter method to do our calculations.

We may use the results in Sec. III under TLM model to study the zero-frequency behaviors (which are the same for all coefficients, and where permutation symmetry does not enter). When the gradient terms are included, we have

\[
\chi_{\text{TLM}}^{\text{THG}}(0,0,0) = \frac{\varepsilon}{28} \chi_0^{(3)}.
\]

When the gradient terms are omitted, we have instead

\[
\chi_{\text{TLM}}^{\text{THG}}(0,0,0) = -\frac{1}{7} \chi_0^{(3)}.
\]

Obviously, the result differs by 1/28 in magnitude on a fractional basis.

**D. Comparison with other theoretical results**

For the nonlinear properties under single-electron periodic models, Genkin-Mednis developed an approach\textsuperscript{51} that was later applied to polymer systems by Agrawal \textit{et al.}\textsuperscript{12} In those works, general formulas of nonlinear optical response were developed. By applying the Genkin-Mednis approach to the SSH model, Wu and Sun obtained the analytical format of THG (Refs. 21 and 22) that yields the same results as those under the static current-current \((J_0J_0)\) correlation.\textsuperscript{15} As we discussed previously,\textsuperscript{13,14} the general results obtained here are quite similar but different from the results obtained

![Graph showing the total contribution, intraband contribution, and interband contribution of hyperpolarizabilities under TLM models.](image-url)
Before. On the THG problem, our results are qualitatively close to the numerical results obtained by Yu and co-workers\textsuperscript{39,26} and Shuai and Brédas\textsuperscript{23} works. The reason for those difference is caused technically by the treatments of $\nabla_k$ operator, but physically by the gauge phase factor\textsuperscript{28} that we are going to discuss further in the subsequent paper.\textsuperscript{40}

Recently Kirtman et al. extended Genkin-Mednis method to the fully coupled perturbed Hartree-Fock theory in discussing the hyperpolarizabilities of infinite chains.\textsuperscript{29} In our results, it is still an uncoupled treatment because the fully filled valence- and empty conduction-band structures in both SSH and TLM models lead no difference in the final results.\textsuperscript{29}

Finally, we would like to point out that the results under DD correlation are also different from those under $J_pJ_0$ correlation.\textsuperscript{15,16} More details will be discussed in our subsequent paper.\textsuperscript{40}

E. Some suggested experiments

Our calculations predict the break of overall permutation symmetry of hyperpolarizabilities for periodic systems in off-resonant regions. Despite of the wide acceptance of overall permutation symmetry in experiments are explained from Kleinman symmetry in experiments are explained qualitatively in this work. A new feasible off-resonant $\chi^{(3)}$ experiment is suggested to test the break of overall permutation symmetry in infinite 1D periodic polymer chains with centrosymmetry such as trans-polyacetylene, etc. For the infinite single-electron periodic systems, our calculations show the following trends for the various third-order nonlinear optical processes in the nonresonant region: $\chi_{\text{nonres}}^{(3)} \times (-3\omega; \omega; \omega, \omega) > \chi_{\text{nonres}}^{(3)} (-2\omega; 0; \omega, \omega) > \chi_{\text{nonres}}^{(3)} (-\omega; \omega, -\omega, \omega) > \chi_{\text{nonres}}^{(3)} (0; \omega; 0, \omega, 0)$, and in the resonant region: $\chi_{\text{res}}^{(3)} (-\omega; 0; 0, \omega) > \chi_{\text{res}}^{(3)} (-\omega; \omega, -\omega, \omega) > \chi_{\text{res}}^{(3)} (-2\omega; 0, 0, \omega) > \chi_{\text{res}}^{(3)} (0; \omega; -\omega, 0) > \chi_{\text{res}}^{(3)} (-3\omega; \omega, \omega, \omega)$. We look forward to the experimental testings on the above theoretical results.

These analytical calculations of hyperpolarizabilities are tedious, but helpful to illustrate both single-electron models and theoretical methodologies in nonlinear calculations. Based on single-electronic models, more sophisticated models such as Hubbard model,\textsuperscript{17,24,26} electron-hole pair model,\textsuperscript{17,25} etc., may be studied by applying similar techniques developed here.

APPENDIX A: SOME INTEGRALS

Let us define $f(z)$, $L(n, z)$, and $M(n, z)$ via the formulas

$$f(z) := \int_{1}^{\infty} \frac{dx}{(x^2 - z^2)^{\frac{3}{2}}},$$

$$L(n, z) := \int_{1}^{\infty} \frac{dx}{x^{2n}(x^2 - z^2)^{\frac{3}{2}}},$$

$$M(n, z) := \int_{1}^{\infty} \frac{\sqrt{x^2 - 1} dx}{x^{2n}(x^2 - z^2)^{\frac{3}{2}}}.$$

Obviously, $L(n, z)$ and $M(n, z)$ can either be found in Ref. 63 or Ref. 64 or converted to the standard integrals in them. For readers’ convenience, we list several relevant results below.

$$L(4, z) = \frac{1}{105z^8}(105f(z) - (48z^6 + 56z^4 + 70z^2 + 105)),$$

$$L(3, z) = \frac{1}{30z^8}(z^2 - 1)((-120z^2 + 105)f(z) + (16z^6 + 24z^4 + 50z^2 - 105)),$$

$$L(2, z) = \frac{1}{24z^8}(z^2 - 1)((144z^4 - 240z^2 + 105)f(z) - (16z^6 + 40z^4 - 170z^2 + 105)),$$

$$M(4, z) = \frac{1}{105z^8}((105z^2 - 105)f(z) - (8z^6 + 14z^4 + 35z^2 - 105)).$$
\[ M(3,z) = \frac{1}{30z^8}((-90z^2 + 105)f(z) + (4z^4 + 20z^2 - 105)), \]  
\[ M(2,z) = \frac{1}{24z^8}(72z^4 - 180z^2 + 105)f(z) + (-8z^4 + 110z^2 - 105)), \]  
\[ M(1,z) = \frac{1}{48z^8}(198z^6 + 216z^4 - 270z^2 + 105)f(z) + (-92z^4 + 200z^2 - 105)), \]  
\[ M(0,z) = \frac{1}{384z^8}(192z^6 + 432z^4 - 360z^2 + 105)f(z) + (48z^6 - 248z^4 + 290z^2 - 105)). \]