

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

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Hyperpolarizabilities for the one-dimensional infinite single-electron periodic systems:

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Abstract

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 $\chi^{(3)}(-\omega; 0, 0, \omega)$, DC-induced second harmonic generation $\chi^{(3)}(-2\omega; 0, \omega, \omega)$, optical Kerr effect $\chi^{(3)}(-\omega; \omega, -\omega, \omega)$ and DC-electric-field-induced optical rectification $\chi^{(3)}(0; \omega, -\omega, 0)$ are derived. By including or excluding $\nabla_{\mathbf{k}}$ terms in the calculations, comparisons show that the intraband contributions dominate the hyperpolarizabilities if they are included. ∇_k term or intraband transition leads to the break of the overall permutation symmetry in $\chi^{(3)}$ even for the low frequency and non-resonant regions. Hence it breaks the Kleinman symmetry that is directly

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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 non-resonant region: $\chi_{non-res}^{(3)}(-3\omega; \omega, \omega, \omega) > \chi_{non-res}^{(3)}(-2\omega; 0, \omega, \omega) > \chi_{non-res}^{(3)}(-\omega; \omega, -\omega, \omega) > \chi_{non-res}^{(3)}(-\omega; 0, 0, \omega) \geq \chi_{non-res}^{(3)}(0; \omega, -\omega, 0)$, and in the resonant region: $\chi_{res}^{(3)}(-\omega; 0, 0, \omega) > \chi_{res}^{(3)}(-\omega; \omega, -\omega, \omega) > \chi_{res}^{(3)}(-2\omega; 0, \omega, \omega) > \chi_{res}^{(3)}(0; \omega; -\omega, 0) > \chi_{res}^{(3)}(-3\omega; \omega, \omega, \omega)$.

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I. INTRODUCTION

The nonlinear optical (NLO) properties of π -conjugated polymers have been extensively studied by both experimentalists [1–11] and theorists [12–29]. Among these polymers, polyacetylene (PA) is the simplest conjugated polymer and has been extensively studied [30]. PA consists of chains of CH units that form a pseudo one-dimensional(1D) lattice. Classical periodic single electron models like Su-Shrieffer-Heeger (SSH) [31] and Takayama-Lin-Liu-Maki (TLM) [32] have been established to interpret the optical properties of polyacetylene. Recent experiments have measured the spectrum of third-order harmonic generations (THG) in polyacetylene [5,6], 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 [33]. 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 [12–26].

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) [12–14,19–23] or from current-current (JJ) correlations [15,16]; (ii). Based on the size of chain, this problem can be treated either as a finite periodic chain [18–20,23–25] or an infinite one [12–15,21]. Furthermore, from the point of view of different techniques to utilize the perturbative method, this problem can be solved either by quantum mechanics [12,17–24] or by the field theory [13–16]. 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 [13–15,19]. On the other hand, in the formulation of DD correlations, there are some controversies about whether or

not the $\nabla_{\mathbf{k}}$ term should be included for an infinite periodic system [28,29,34–36]. 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 [37] in describing the low frequency and non-resonant nonlinear optical properties of many materials and practical systems [38]. But most experiments only measured the $\chi^{(2)}$ in systems without centro- or inversion symmetry. Based on the possible mutual exclusion property between Krammers-Kronig dispersion relations and Kleinman symmetry, Dailey, Burke and Simpson asserted the general failure of Kleinman symmetry. However, physically Kleinman symmetry is only a direct consequence of the overall permutation symmetry [37,39]. 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 non-trivial results for $\chi^{(3)}$ to discuss the validity of both overall permutation and Kleinman symmetries.

In this and the subsequent [40] 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 issues in periodic systems. We will make detailed comparison between our calculation and other theoretical results of hyperpolarizabilities in both papers. The purpose of present paper is to elucidate the physical contribution of each term in the formulation of dipole-dipole correlations. In these models, the important role played by the operator $\nabla_{\mathbf{k}}$ due to its noncommuting feature with ordinary functions of \mathbf{k} is evident. Our calculations show that it is the $\nabla_{\mathbf{k}}$ term, which is physically related to the intraband transition, that leads to the break of the overall permutation symmetry and Kleinman symmetry in the non-resonant region. Based on our calculations, we also suggest some experiments on the measurement of $\chi^{(3)}$ for certain physical systems to test the validity of overall permutation symmetry and our theoretical predictions.

This paper is organized as follows. In Section II, necessary analytical tools and general theoretical framework are introduced. In Section III, analytical results of four-wave-mixing (FWM), DC Kerr effect (DCKerr), DC-induced second harmonic generation(DCSHG), optical Kerr effect or intensity-dependent index of refraction (IDIR), DC-electric-field-induced optical rectification (EFIOR) are derived. The discussions on those results and symmetries, comparisons with other theories and some suggested experiments are then followed in Section IV. A brief conclusion is presented in Section V. Finally, the details of analytical calculations are given in the Appendix.

II. THEORY

A. Models and dipole operator

Both SSH (or dimerized Huckel models) and TLM models have been thoroughly studied in the *trans*-polyacetylene problems [30]. The SSH model is an infinite 1D periodic model, and described by the following Hamiltonian [31]:

$$H_{SSH} = - \sum_{l,s} \left[t_0 + (-1)^l \frac{\Delta}{2} \right] (\hat{C}_{l+1,s}^\dagger \hat{C}_{l,s} + \hat{C}_{l,s}^\dagger \hat{C}_{l+1,s}), \quad (2.1)$$

where t_0 is the transfer integral between the nearest-neighbor sites, Δ is the gap parameter and $\hat{C}_{l,s}^\dagger$ ($\hat{C}_{l,s}$) creates(annihilates) an π 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 [32]:

$$H_{TLM} = \Psi^\dagger(x) (i\sigma_3 v_F \partial_x + \Delta \sigma_1) \Psi^\dagger(x), \quad (2.2)$$

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

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

$$\hat{H}_{\mathbf{E}\cdot\mathbf{r}} = -e\mathbf{E} \cdot \hat{\mathbf{r}} = -\mathbf{D} \cdot \mathbf{E},$$

with e the electron charge and \mathbf{E} the electric field described as follows:

$$\mathbf{E}(\mathbf{r}, t) = \mathbf{E}_0 e^{i\mathbf{k}\cdot\mathbf{r} - i\omega t}, \quad (2.3)$$

where \mathbf{E}_0 is the amplitude, \mathbf{k} and ω are the wave vector and frequency, respectively.

For periodic systems, the position operator \mathbf{r} is often conveniently defined in the momentum space [44]:

$$\mathbf{r}_{n\mathbf{k}, n'\mathbf{k}'} = i\delta_{n, n'} \nabla_{\mathbf{k}} \delta(\mathbf{k} - \mathbf{k}') + \Omega_{n, n'}(\mathbf{k}) \delta(\mathbf{k} - \mathbf{k}'), \quad (2.4)$$

where

$$\Omega_{n, n'}(\mathbf{k}) = \frac{i}{v} \int_v u_{n, \mathbf{k}}^*(\mathbf{r}) \nabla_{\mathbf{k}} u_{n', \mathbf{k}}(\mathbf{r}) d\mathbf{r}, \quad (2.5)$$

with v the unit cell volume, $u_{n, \mathbf{k}}(\mathbf{r})$ the periodic function under the translation of lattice vector [41]. Obviously, $u_{n, \mathbf{k}}(\mathbf{r})$ is related to the wavefunction ψ of Bloch states by the formula:

$$\psi_{n, \mathbf{k}}(\mathbf{r}) = u_{n, \mathbf{k}}(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}}, \quad (2.6)$$

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 non-analytical feature of Bloch wavefunctions for a composite band in higher-dimension periodic models [42].

Following the same procedures described in previous work [13,14,43], we consider the momentum space representation of the Hamiltonian given by Eq.(2.1). With the aid of the spinor description $\hat{\psi}_{k,s}^\dagger(t) = (\hat{a}_{k,s}^{\dagger c}(t), \hat{a}_{k,s}^{\dagger v}(t))$, where $\hat{a}_{k,s}^{\dagger c}(t)$ and $\hat{a}_{k,s}^{\dagger v}(t)$ are excitations of electrons in the conduction band and the valence band with momentum \mathbf{k} and spin s , we obtain the following formula:

$$\hat{H}_{SSH}(k, t) = \hat{H}_0 + \hat{H}_{\mathbf{E}\cdot\mathbf{r}} \quad (2.7)$$

$$= \sum_{-\frac{\pi}{2a} \leq k \leq \frac{\pi}{2a}, s} \varepsilon(k) \hat{\psi}_{k,s}^\dagger(t) \sigma_3 \hat{\psi}_{k,s}(t) - \hat{D} \cdot E_0 e^{i\omega t}, \quad (2.8)$$

where $\vec{\sigma}$ are the Pauli matrices, the operator \hat{D} and the parameter $\varepsilon(k)$ are given by the following formulas, respectively.

$$\hat{D} = e \sum_{-\frac{\pi}{2a} \leq k \leq \frac{\pi}{2a}, s} (\beta(k) \hat{\psi}_{k,s}^\dagger \sigma_2 \hat{\psi}_{k,s} + i \frac{\partial}{\partial k} \hat{\psi}_{k,s}^\dagger \hat{\psi}_{k,s}), \quad (2.9)$$

$$\varepsilon(k) = \sqrt{[2t_0 \cos(ka)]^2 + [\Delta \sin(ka)]^2}, \quad (2.10)$$

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

$$\beta(k) = -\frac{\Delta t_0 a}{\varepsilon^2(k)}. \quad (2.11)$$

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 [13,14].

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

In periodic systems, Bloch functions can not 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 E.I. Blount [44], and later proved by J. Zak [42]. 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 [45] since both valence and conducting bands are simple. Thus, we may avoid the trouble due to the discontinuous or non-analytical feature of Bloch wave functions.

The Berry phase for a 1D crystal with the centro- or inversion symmetric only can only be 0 or $\pi \pmod{2\pi}$ [46], 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 first term in Eq.(2.9) [46,47]. 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 [48], dipole formulas by Shen [49], and Genkin-Mednis approach [50] generalized by Bishop and his coauthors [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 [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, $\mathbf{k}_1 = \mathbf{k}_2 = \mathbf{k}_3 = \mathbf{K} = 0$. The only permutation to be considered in this graph is three different frequencies ω_1, ω_2 and ω_3 .

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

$$\chi^{(3)}(\Omega; \omega_1, \omega_2, \omega_3) = \frac{1}{3!V} \left[\frac{i}{\hbar} \right]^3 \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \int dt_1 dt_2 dt_3 \int d\mathbf{r} dt e^{-i\mathbf{K} \cdot \mathbf{r} + i\Omega t} \langle \hat{T} \hat{\mathbf{D}}(\mathbf{r}, t) \hat{\mathbf{D}}(\mathbf{r}_1, t_1) \hat{\mathbf{D}}(\mathbf{r}_2, t_2) \hat{\mathbf{D}}(\mathbf{r}_3, t_3) \rangle, \quad (2.12)$$

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

For periodic systems, in order to maintain the periodicity of the position operator \mathbf{r} , a "saw-liked" position operator must be introduced [51]. For convenience in studying the nonlinear susceptibilities, we usually express Eqs.(2.12) in the momentum space for further calculations [13,14,43].

III. HYPERPOLARIZABILITIES FOR SSH AND TLM MODELS UNDER DIPOLE FORMULA

The TLM model [32] is simply the continuum limit of the SSH model [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 χ_B^A , the superscript A represents the abbreviation for the different four-wave-mixing (FWM) terms, the subscript B represents the different models such as SSH or TLM models. We also use $\tilde{\chi}$ to represent the hyperpolarizabilities without considering ∇_k term in Eq.(3.1).

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

Under SSH and TLM models, the general four-wave-mixing(FWM) can be expressed as

$$\chi_{SSH}^{FWM}(\omega_1, \omega_2, \omega_3) \equiv \chi_{SSH}^{(3)}(-(\omega_1 + \omega_2 + \omega_3), \omega_1, \omega_2, \omega_3):$$

$$\chi_{SSH}^{FWM}(\omega_1, \omega_2, \omega_3) = \frac{2e^4 n_0}{\hbar^3} \frac{1}{3!L} \sum_{k, \mathcal{P}(\omega_1, \omega_2, \omega_3)} \int \frac{id\omega}{2\pi} Tr \left\{ \begin{aligned} &(\beta(k)\sigma_2 + i\frac{\partial}{\partial k})G(k, \omega) \\ &(\beta(k)\sigma_2 + i\frac{\partial}{\partial k})G(k, \omega - \omega_1) \\ &(\beta(k)\sigma_2 + i\frac{\partial}{\partial k})G(k, \omega - \omega_1 - \omega_2) \\ &(\beta(k)\sigma_2 + i\frac{\partial}{\partial k})G(k, \omega - \omega_1 - \omega_2 - \omega_3) \end{aligned} \right\}, \quad (3.1)$$

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 ω_1, ω_2 and ω_3 (therefore the intrinsic symmetry is maintained [39]). The polymer chains are assumed to be oriented, and Green's function $G(k, \omega)$ is defined as follows [13,14,43]:

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

with $\omega_k \equiv \varepsilon(k)/\hbar$ and $\epsilon \equiv 0^+$.

After tedious derivations in the Appendix B, we obtain the following analytical results

for the SSH model:

$$\begin{aligned}
\chi_{SSH}^{FWM}(\omega_1, \omega_2, \omega_3) = & \chi_0^{(3)} \frac{15}{1024} \int_1^{1/\delta} \frac{xdx}{\sqrt{(1-\delta^2x^2)(x^2-1)}} \\
& \left\{ \frac{(2x-z_1-z_3)}{x^8(x-z_1)(x+z_2)(x-z_3)(x-z_1-z_2-z_3)} \right. \\
& - \frac{(2x+z_1+z_3)}{x^8(x+z_1)(x-z_2)(x+z_3)(x+z_1+z_2+z_3)} \\
& + \frac{4(1-\delta^2x^2)(x^2-1)}{x^8(x-z_1-z_2)} \frac{(3x-2z_1)(3x-2(z_1+z_2+z_3))}{(x-z_1)^2(x-z_1-z_2-z_3)^2} \\
& \left. + \frac{4(1-\delta^2x^2)(x^2-1)}{x^8(x+z_1+z_2)} \frac{(3x+2z_1)(3x+2(z_1+z_2+z_3))}{(x+z_1)^2(x+z_1+z_2+z_3)^2} \right\}, \tag{3.3}
\end{aligned}$$

where

$$\chi_0^{(3)} = \frac{8}{45} \frac{e^4 n_0 (2t_0 a)^3}{\pi \Delta^6} \tag{3.4}$$

and

$$z_i = \frac{\hbar\omega_i}{2\Delta}, \quad \text{for } i = 1, 2, 3. \tag{3.5}$$

By setting $z_1 = z_2 = z_3 = z = \hbar\omega/2\Delta$, 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) [13] or Eq.(9) [14] in our previous works.

By changing $x \rightarrow x + i\epsilon$ in Eq.(3.3), and by choosing the same parameters used in our previous works for polyacetylene [13,14,21,22], $\Delta = 0.9eV$, $n_0 = 3.2 \times 10^{14} cm^{-2}$, $a = 1.22\text{\AA}$ and $\epsilon \sim 0.03$, we have $\delta = 0.18$ and $\chi_0^{(3)} \approx 1.0 \times 10^{-10}$ esu. The absolute value of FWM is plotted in Fig.1.

From the graph, we find several symmetrical resonant frequencies. The biggest resonant peaks are around $(0, 0, \pm 1)$, $(\pm 1, \pm 1, \mp 1)$ and their permutations, which correspond to DC Kerr effect(DCKerr) and Optical Kerr effect or Intensity-dependent index of refraction(IDIR), respectively. There are some secondary resonant frequencies, the cusps shown in the Fig.1 are around $(\pm 1, \mp 1, 0)$ and their permutations. They correspond to DC-electric-field-induced optical rectification(EFIOR). The resonant peaks for third-harmonic generation (THG) are not obvious in this graph.

As to the magnitudes of resonant peaks, we have $\chi^{(3)}(-\omega; 0, 0, \omega) \gg \chi^{(3)}(-\omega; \omega, \omega, -\omega) \gg \chi^{(3)}(0; \omega, -\omega, 0) \gg \chi^{(3)}(-3\omega; \omega, \omega, \omega)$.

Eq.(3.3) could be further simplified as hyperpolarizabilities under TLM model by letting

$\delta \rightarrow 0$:

$$\begin{aligned}
\chi_{TLM}^{FWM}(\omega_1, \omega_2, \omega_3) = & \frac{45\chi_0^{(3)}}{64} \left\{ \frac{Z^6}{z_1 z_2 z_3 \sigma} L(4, Z) - \frac{Z^6}{z_1^2 z_2^2 z_3^2} M(4, Z) + \sum_{i=1}^3 \frac{z_i^3}{\sigma} L(4, z_i) \right. \\
& + \left. \sum_{P(z_1, z_2, z_3)} \frac{z_1^2(-z_1 + 2(z_2 + z_3))}{2z_2 z_3(z_2 + z_3)} L(4, z_1) \right\} \\
& + \frac{45\chi_0^{(3)}}{64} \left\{ \sum_{P(z_1, z_2, z_3)} \frac{(z_1 + z_2)^5(z_1 + z_2 - 2z_3)}{2z_1^2 z_2^2 z_3^2} M(4, z_1 + z_2) \right. \\
& + \left. \frac{-z_1^2(z_1^2 - 2z_1(z_2 + z_3) + 6z_2 z_3)}{2z_2^2 z_3^2} M(4, z_1) \right\}, \tag{3.6}
\end{aligned}$$

where

$$\sigma := (z_1 + z_2)(z_2 + z_3)(z_3 + z_1), \tag{3.7}$$

$$Z := z_1 + z_2 + z_3, \tag{3.8}$$

$L(n, z)$ and $M(n, z)$ ($n = 0 \dots 4$) are defined by (A2) and (A3) respectively.

B. DC Kerr effect

By setting $z_1 = z_2 = 0$ and $z_3 = z$ ($z = \hbar\omega/(2\Delta)$) in Eq.(B36), we have

$$\begin{aligned}
\chi^{(3)}(0, 0, \omega) = & \chi_0^{(3)} \frac{15}{256} \int_1^{1/\delta} \frac{dx}{x^7 \sqrt{(1 - \delta^2 x^2)(x^2 - 1)}} \\
& \left\{ -\frac{(2x - z)}{x^2(x - z)^2} - \frac{(2x + z)}{x^2(x + z)^2} - \frac{2}{x(x^2 - z^2)} \right. \\
& + 2(1 - \delta^2 x^2)(x^2 - 1) \left\{ \frac{3(3x - 2z)}{x^2(x - z)^2} + \frac{3(3x + 2z)}{x^2(x + z)^2} \right. \\
& + \left. \left. \frac{(3x - 2z)^2}{(x - z)^5} + \frac{(3x + 2z)^2}{(x + z)^5} + \frac{3(3x - 2z)}{x(x - z)^3} + \frac{3(3x + 2z)}{x(x + z)^3} \right\} \right\} \tag{3.9}
\end{aligned}$$

After simplifications, we obtain the DC Kerr effect(DCKerr) coefficient under the SSH

model:

$$\begin{aligned}
\chi_{SSH}^{DCKerr}(0, 0, \omega) &= \chi_0^{(3)} \frac{15}{128} \int_1^{1/\delta} \frac{dx}{\sqrt{(1 - \delta^2 x^2)(x^2 - 1)}} \\
&\left\{ -\frac{2}{x^6(x^2 - z^2)^2} - \frac{1}{x^8(x^2 - z^2)} \right. \\
&+ 2(1 - \delta^2 x^2)(x^2 - 1) \left\{ \frac{16}{(x^2 - z^2)^5} + \frac{12}{x^2(x^2 - z^2)^4} \right. \\
&\left. \left. + \frac{1}{x^4(x^2 - z^2)^3} + \frac{1}{x^6(x^2 - z^2)^2} - \frac{3}{x^8(x^2 - z^2)} \right\} \right\}
\end{aligned} \tag{3.10}$$

As $\delta \rightarrow 0$ in Eq.(3.10), we have the results under TLM model:

$$\begin{aligned}
\chi_{TLM}^{DCKerr}(0, 0, \omega) &= \chi_0^{(3)} \frac{15}{128} (-2L(3, z) - L(4, z) + 32M(0, z) \\
&+ 24M(1, z) + 2M(2, z) + 2M(3, z) - 6M(4, z)),
\end{aligned} \tag{3.11}$$

where $L(n, z)$ and $M(n, z)$ ($n = 0 \dots 4$) are defined by (A2) and (A3) respectively.

Substituting the identities for $L(n, z)$ and $M(n, z)$ into the above equation and simplifying the resulting expression, we obtain

$$\begin{aligned}
\chi_{TLM}^{DCKerr}(0, 0, \omega) &= \chi_0^{(3)} \frac{15}{512z^8(z^2 - 1)^3} \left\{ -(120z^8 - 580z^6 + 1029z^4 - 780z^2 + 216)f(z) \right. \\
&\left. + \frac{1}{105}(384z^{12} - 928z^{10} + 760z^8 - 22182z^6 + 65541z^4 - 66780z^2 + 22680) \right\}
\end{aligned} \tag{3.12}$$

Dropping the terms related to ∇_k or $\frac{\partial}{\partial k}$ in Eq.(3.1), we have

$$\tilde{\chi}_{SSH}^{DCKerr}(0, 0, \omega) = \chi_0^{(3)} \frac{15}{128} \int_1^{1/\delta} \frac{dx}{\sqrt{(1 - \delta^2 x^2)(x^2 - 1)}} \left\{ -\frac{2}{x^6(x^2 - z^2)^2} - \frac{1}{x^8(x^2 - z^2)} \right\} \tag{3.13}$$

As $\delta \rightarrow 0$ in the Eq.(3.13), we have

$$\tilde{\chi}_{TLM}^{DCKerr}(0, 0, \omega) = -\chi_0^{(3)} \frac{15}{128} (2L(3, z) + L(4, z)), \tag{3.14}$$

where $L(n, z)$ is defined by (A2).

Substituting the identities for $L(n, z)$ into the above equation and simplifying the resulting expression, we obtain

$$\begin{aligned}
\tilde{\chi}_{TLM}^{DCKerr}(0, 0, \omega) &= \chi_0^{(3)} \frac{15}{128z^8(z^2 - 1)} \left\{ (7z^2 - 6)f(z) \right. \\
&\left. + \frac{1}{105}(48z^8 - 104z^6 - 154z^4 - 315z^2 + 630) \right\}
\end{aligned} \tag{3.15}$$

C. DC induced second harmonic generation

By setting $z_1 = z_2 = z$ ($z = \hbar\omega/(2\Delta)$) and $z_3 = 0$ in Eq.(B36), we have

$$\begin{aligned}
\chi^{(3)}(0, \omega, \omega) &= \frac{15}{256} \chi_0^{(3)} \int_1^{1/\delta} \frac{dx}{x^7 \sqrt{(1 - \delta^2 x^2)(x^2 - 1)}} \\
&\left\{ -\frac{(2x - z)}{x(x^2 - z^2)(x - 2z)} - \frac{(2x + z)}{x(x^2 - z^2)(x + 2z)} \right. \\
&\quad - \frac{1}{x(x - z)(x - 2z)} - \frac{1}{x(x + z)(x + 2z)} \\
&\quad + 2(1 - \delta^2 x^2)(x^2 - 1) \left\{ \frac{3x(3x - 4z)}{x^2(x - z)(x - 2z)^2} + \frac{3x(3x + 4z)}{x^2(x + z)(x + 2z)^2} \right. \\
&\quad + \frac{(3x - 2z)(3x - 4z)}{(x - z)^3(x - 2z)^2} + \frac{(3x + 2z)(3x + 4z)}{(x + z)^3(x + 2z)^2} \\
&\quad \left. \left. + \frac{(3x - 2z)(3x - 4z)}{(x - z)^2(x - 2z)^3} + \frac{(3x + 2z)(3x + 4z)}{(x + z)^2(x + 2z)^3} \right\} \right\} \quad (3.16)
\end{aligned}$$

After simplifications, we obtain the DC induced second harmonic generation(DCSHG) coefficient under SSH model:

$$\begin{aligned}
\chi_{SSH}^{DCSHG}(0, \omega, \omega) &= \frac{15}{128} \chi_0^{(3)} \int_1^{1/\delta} \frac{dx}{\sqrt{(1 - \delta^2 x^2)(x^2 - 1)}} \\
&\left\{ -\frac{4}{x^8(x^2 - 4z^2)} + \frac{1}{x^8(x^2 - z^2)} \right. \\
&\quad + 2(1 - \delta^2 x^2)(x^2 - 1) \left\{ \frac{6}{x^8(x^2 - z^2)} + \frac{1}{x^6(x^2 - z^2)^2} - \frac{4}{x^4(x^2 - z^2)^3} \right. \\
&\quad \left. \left. - \frac{36}{x^8(x^2 - 4z^2)} + \frac{28}{x^6(x^2 - 4z^2)^2} + \frac{32}{x^4(x^2 - 4z^2)^3} \right\} \right\} \quad (3.17)
\end{aligned}$$

As $\delta \rightarrow 0$ in Eq.(3.17), we have the result under the TLM model:

$$\begin{aligned}
\chi_{TLM}^{DCSHG}(0, \omega, \omega) &= \frac{15}{128} \chi_0^{(3)} (-4L(4, 2z) + L(4, z) + 12M(4, z) + 2M(3, z) \\
&\quad - 8M(2, z) - 72M(4, 2z) + 56M(3, 2z) + 64M(2, 2z)), \quad (3.18)
\end{aligned}$$

where $L(n, z)$ and $M(n, z)$ ($n = 0 \dots 4$) are defined by (A2) and (A3) respectively.

Substituting the identities for $L(n, z)$ and $M(n, z)$ into the above equation and simpli-

fyng the resulting expression, we obtain

$$\begin{aligned}
\chi_{TLM}^{DCSHG}(0, \omega, \omega) &= \chi_0^{(3)} \frac{15}{256z^8(z^2-1)^2} \left\{ (28z^6 - 104z^4 + 118z^2 - 43)f(z) \right. \\
&\quad \left. - \frac{1}{105}(288z^{10} - 184z^8 + 204z^6 - 5068z^4 + 9380z^2 - 4515) \right\} \\
&\quad + \chi_0^{(3)} \frac{15}{2048z^8(4z^2-1)} \left\{ (-48z^4 + 6z^2 + 1)f(2z) \right. \\
&\quad \left. + \frac{1}{105}(12288z^8 + 4992z^6 + 2464z^4 - 910z^2 - 105) \right\}
\end{aligned} \tag{3.19}$$

Dropping the terms related to ∇_k or $\frac{\partial}{\partial k}$ in Eq.(3.1), we have

$$\tilde{\chi}_{SSH}^{DCSHG}(0, \omega, \omega) = \chi_0^{(3)} \frac{15}{128} \int_1^{1/\delta} \frac{dx}{\sqrt{(1-\delta^2x^2)(x^2-1)}} \left\{ -\frac{4}{x^8(x^2-4z^2)} + \frac{1}{x^8(x^2-z^2)} \right\} \tag{3.20}$$

As $\delta \rightarrow 0$ in Eq.(3.20), we have

$$\tilde{\chi}_{TLM}^{DCSHG}(0, \omega, \omega) = \chi_0^{(3)} \frac{15}{128} (-4L(4, 2z) + L(4, z)), \tag{3.21}$$

where $L(n, z)$ is defined by (A2).

Substituting the identities for $L(n, z)$ into the above equation and simplifying the resulting expression, we obtain

$$\tilde{\chi}_{TLM}^{DCSHG}(0, \omega, \omega) = \chi_0^{(3)} \frac{15}{1024z^8} \left\{ 8f(z) - \frac{1}{8}f(2z) - \frac{1}{40}(128z^4 + 200z^2 + 315) \right\} \tag{3.22}$$

D. Optical Kerr effect or intensity-dependent index of refraction

By setting $z_1 = z_3 = z$ ($z = \hbar\omega/(2\Delta)$) and $z_2 = -z$ in Eq.(B36), we have

$$\begin{aligned}
\chi^{(3)}(\omega, -\omega, \omega) &= \chi_0^{(3)} \frac{15}{256} \int_1^{1/\delta} \frac{dx}{x^7 \sqrt{(1-\delta^2x^2)(x^2-1)}} \\
&\quad \left\{ -\frac{4x}{(x^2-z^2)^2} - \frac{1}{(x-z)^3} - \frac{1}{(x+z)^3} \right. \\
&\quad + 2(1-\delta^2x^2)(x^2-1) \left\{ \frac{(3x-2z)^2}{x(x-z)^4} + \frac{(3x+2z)^2}{x(x+z)^4} \right. \\
&\quad \left. \left. + \frac{(3x-2z)^2}{(x-2z)(x-z)^4} + \frac{(3x+2z)^2}{(x+2z)(x+z)^4} + \frac{2(9x^2-4z^2)}{x(x^2-z^2)^2} \right\} \right\}
\end{aligned} \tag{3.23}$$

After simplifications, we obtain the optical Kerr effect or intensity-dependent index of refraction (IDIR) coefficient under the SSH model:

$$\begin{aligned} \chi_{SSH}^{IDIR}(\omega, -\omega, \omega) &= \chi_0^{(3)} \frac{15}{128} \int_1^{1/\delta} \frac{dx}{\sqrt{(1-\delta^2 x^2)(x^2-1)}} \\ &\left\{ \frac{1}{x^6(x^2-z^2)^2} - \frac{4}{x^4(x^2-z^2)^3} \right. \\ &+ 2(1-\delta^2 x^2)(x^2-1) \left\{ -\frac{16}{x^8(x^2-z^2)} - \frac{13}{x^6(x^2-z^2)^2} \right. \\ &\left. \left. - \frac{8}{x^4(x^2-z^2)^3} + \frac{64}{x^8(x^2-4z^2)} \right\} \right\} \end{aligned} \quad (3.24)$$

As $\delta \rightarrow 0$ in Eq. (3.24), we have the result under the TLM model:

$$\begin{aligned} \chi_{TLM}^{IDIR}(\omega, -\omega, \omega) &= \chi_0^{(3)} \frac{15}{128} (L(3, z) - 4L(2, z) - 32M(4, z) \\ &- 26M(3, z) - 16M(2, z) + 128M(4, 2z)), \end{aligned} \quad (3.25)$$

where $L(n, z)$ and $M(n, z)$ ($n = 0 \dots 4$) are defined by (A2) and (A3) respectively.

Substituting the identities for $L(n, z)$ and $M(n, z)$ into the above equation and simplifying the resulting expression, we obtain

$$\begin{aligned} \chi_{TLM}^{IDIR}(\omega, -\omega, \omega) &= \chi_0^{(3)} \frac{15}{256z^8} \left\{ \frac{8z^8 + 44z^6 + 83z^4 - 495z^2 + 315}{15(z^2-1)^2} \right. \\ &\left. - \frac{4z^6 + 22z^4 - 43z^2 + 20}{(z^2-1)^2} f(z) + (4z^2-1)f(2z) \right\} \end{aligned} \quad (3.26)$$

Dropping the terms related to ∇_k or $\frac{\partial}{\partial k}$ in Eq.(3.1), we have

$$\tilde{\chi}_{SSH}^{IDIR}(\omega, -\omega, \omega) = \chi_0^{(3)} \frac{15}{128} \int_1^{1/\delta} \frac{dx}{\sqrt{(1-\delta^2 x^2)(x^2-1)}} \left\{ \frac{1}{x^6(x^2-z^2)^2} - \frac{4}{x^4(x^2-z^2)^3} \right\} \quad (3.27)$$

As $\delta \rightarrow 0$ in the Eq.(3.27), we have

$$\tilde{\chi}_{TLM}^{IDIR}(\omega, -\omega, \omega) = \chi_0^{(3)} \frac{15}{128} (L(3, z) - 4L(2, z)), \quad (3.28)$$

where $L(n, z)$ is defined by (A2).

Substituting the identities for $L(n, z)$ into the above equation and simplifying the resulting expression, we obtain

$$\begin{aligned} \tilde{\chi}_{TLM}^{IDIR}(0, \omega, \omega) &= \chi_0^{(3)} \frac{1}{256z^8(z^2-1)^2} \left\{ -(840z^4 - 1425z^2 + 630)f(z) \right. \\ &\left. + (16z^8 + 88z^6 + 226z^4 - 1005z^2 + 630) \right\} \end{aligned} \quad (3.29)$$

E. DC-electric-field-induced optical rectification

By setting $z_1 = 0$, $z_2 = -z$, $z_3 = z$ ($z = \hbar\omega/(2\Delta)$) in Eq.(B36), we obtain the DC-electric-field-induced optical rectification (EFIOR) under the SSH model:

$$\begin{aligned}
\chi_{SSH}^{EFIOR}(0, -\omega, \omega) &= \chi_0^{(3)} \frac{15}{128} \int_1^{1/\delta} \frac{dx}{x^8 \sqrt{(1 - \delta^2 x^2)(x^2 - 1)}} \\
&\quad \left\{ \frac{-3x^2 + z^2}{(x^2 - z^2)^2} + 6(1 - \delta^2 x^2)(x^2 - 1) \frac{2z^4 + 9x^4 - 7x^2 z^2}{(x^2 - z^2)^3} \right\} \\
&= \chi_0^{(3)} \frac{15}{128} \int_1^{1/\delta} \frac{dx}{\sqrt{(1 - \delta^2 x^2)(x^2 - 1)}} \\
&\quad \left\{ \frac{-2}{x^6(x^2 - z^2)^2} - \frac{1}{x^8(x^2 - z^2)} \right. \\
&\quad \left. + 6(1 - \delta^2 x^2)(x^2 - 1) \left\{ \frac{4}{x^4(x^2 - z^2)^3} + \frac{3}{x^6(x^2 - z^2)^2} + \frac{2}{x^8(x^2 - z^2)} \right\} \right\}
\end{aligned} \tag{3.30}$$

As $\delta \rightarrow 0$, we have the result under the TLM model:

$$\chi_{TLM}^{EFIOR}(0, -\omega, \omega) = \chi_0^{(3)} \frac{15}{128} (-2L(3, z) - L(4, z) + 6(4M(2, z) + 3M(3, z) + 2M(4, z))), \tag{3.31}$$

where $L(n, z)$ and $M(n, z)$ ($n = 0 \dots 4$) are defined by (A2) and (A3) respectively.

Substituting the identities for $L(n, z)$ and $M(n, z)$ into the above equation and simplifying the resulting expression, we obtain

$$\begin{aligned}
\chi_{TLM}^{EFIOR}(0, -\omega, \omega) &= \chi_0^{(3)} \frac{15}{64z^8(z^2 - 1)} \left\{ -\frac{1}{105} (24z^8 - 38z^6 + 119z^4 - 2520z^2 + 2520) \right. \\
&\quad \left. + (15z^4 - 40z^2 + 24)f(z) \right\}
\end{aligned} \tag{3.32}$$

Dropping the terms related to ∇_k or $\frac{\partial}{\partial k}$ in Eq.(3.1), we have

$$\tilde{\chi}_{SSH}^{EFIOR}(0, -\omega, \omega) = \chi_0^{(3)} \frac{15}{128} \int_1^{1/\delta} \frac{dx}{\sqrt{(1 - \delta^2 x^2)(x^2 - 1)}} \left\{ \frac{-2}{x^6(x^2 - z^2)^2} - \frac{1}{x^8(x^2 - z^2)} \right\} \tag{3.33}$$

As $\delta \rightarrow 0$ in the Eq.(3.33), we have

$$\tilde{\chi}_{TLM}^{EFIOR}(0, -\omega, \omega) = \chi_0^{(3)} \frac{15}{128} (-2L(3, z) - L(4, z)), \tag{3.34}$$

where $L(n, z)$ is defined by (A2).

Substituting the identities for $L(n, z)$ and $M(n, z)$ into the above equation and simplifying the resulting expression, we obtain

$$\begin{aligned} \tilde{\chi}_{TLM}^{EFIOR}(0, -\omega, \omega) = \chi_0^{(3)} \frac{15}{128z^8(z^2 - 1)} \left\{ (7z^2 - 6)f(z) \right. \\ \left. + \frac{1}{105}(48z^8 - 104z^6 - 154z^4 - 315z^2 + 630) \right\} \end{aligned} \quad (3.35)$$

F. Third harmonic generation

The results of third harmonic generation (THG) can be computed by setting $z_1 = z_2 = z_3 = z$ in Eq.(B26). They can also be found in our previous works [13,14]. Here we simply state the result:

$$\begin{aligned} \chi_{SSH}^{THG}(\omega) = \chi_0^{(3)} \frac{45}{128} \int_1^{\frac{1}{\delta}} \frac{dx}{\sqrt{(1 - \delta^2 x^2)(x^2 - 1)}} \left\{ -\frac{47 - 48(1 + \delta^2)x^2 + 48\delta^2 x^4}{8x^8(x^2 - z^2)} \right. \\ \left. + \frac{3(1 - \delta^2 x^2)(x^2 - 1)}{x^6(x^2 - z^2)^2} \right. \\ \left. + \frac{9[47 - 48(1 + \delta^2)x^2 + 48\delta^2 x^4]}{8x^8(x^2 - (3z)^2)} \right. \\ \left. + \frac{63(1 - \delta^2 x^2)(x^2 - 1)}{x^6(x^2 - (3z)^2)^2} \right\} \end{aligned} \quad (3.36)$$

and

$$\chi_{TLM}^{THG}(\omega) = \chi_0^{(3)} \frac{45}{128} \left\{ -\frac{14}{3z^8} - \frac{4}{15z^4} + \frac{(37 - 24z^2)}{8z^8} f(z) + \frac{(1 - 8z^2)}{24z^8} f(3z) \right\}. \quad (3.37)$$

Excluding ∇_k terms, we obtain

$$\tilde{\chi}_{SSH}^{THG}(\omega, \omega, \omega) = \chi_0^{(3)} \frac{45}{1024} \int_1^{1/\delta} \frac{dx}{\sqrt{(1 - \delta^2 x^2)(x^2 - 1)}} \left\{ \frac{1}{x^8(x^2 - z^2)} - \frac{9}{x^8(x^2 - (3z)^2)} \right\} \quad (3.38)$$

As $\delta \rightarrow 0$ in the Eq.(3.33), we have

$$\tilde{\chi}_{TLM}^{THG}(\omega, \omega, \omega) = \chi_0^{(3)} \frac{1}{82944z^8} \left\{ 5(729f(z) - f(3z)) - 8(216z^4 + 300z^2 + 455) \right\} \quad (3.39)$$

IV. DISCUSSIONS

A. resonant and non-resonant features

Fig.3 shows the hyperpolarizabilities of DCKerr, DCSHG, IDIR and EFIOR for SSH models. Choosing the same parameters in Section III A, we see the magnitudes of the resonant peaks are in the following order:

$$\begin{aligned} \chi_{res}^{(3)}(-\omega; 0, 0, \omega) &> \chi_{res}^{(3)}(-\omega; \omega, -\omega, \omega) > \chi_{res}^{(3)}(-2\omega; 0, \omega, \omega) \\ &> \chi_{res}^{(3)}(0; \omega, -\omega, 0) > \chi_{res}^{(3)}(-3\omega; \omega, \omega, \omega). \end{aligned} \quad (4.1)$$

Fig.4 shows the comparison of hyperpolarizabilities of DCKerr, DCSHG, IDIR, EFIOR, THG for SSH models for low frequencies. Choosing the same parameters in Section III, we see the non-resonant features are in the following order:

$$\begin{aligned} \chi_{non-res}^{(3)}(-3\omega; \omega, \omega, \omega) &> \chi_{non-res}^{(3)}(-2\omega; 0, \omega, \omega) > \chi_{non-res}^{(3)}(-\omega; \omega, -\omega, \omega) \\ &> \chi_{non-res}^{(3)}(-\omega; 0, 0, \omega) > \chi_{non-res}^{(3)}(0; \omega, -\omega, 0). \end{aligned} \quad (4.2)$$

This non-resonant frequency dependence of nonlinear optical properties is consistent with previous calculations for polyenes [27].

B. ∇_k term, Krammer-Kronig(KK) relation, the overall permutation and Kleinman symmetries

There are some arguments about whether or not one should include the ∇_k terms in the calculations of nonlinear optical properties. The ∇_k terms are usually considered to be related to the intra-band current [12]. Otto suggested not to include this term because of the non-periodic property of ∇_k [28,34,36], and thus the calculations would be purely based on the inter-band transition. In this work, we compute the analytical results with or without ∇_k terms to show the differences of the results under both schemes.

Considering the important physical contributions from the intra-band currents [12,29], we are in favor of including the ∇_k terms. Moreover, the restriction of our calculations in

a unit cell implicitly imposes the periodic condition even for $\nabla_{\mathbf{k}}$ operator. For the linear susceptibility $\chi^{(1)}$, our calculations [43] show that the $\nabla_{\mathbf{k}}$ term make 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 $\nabla_{\mathbf{k}}$ term causes the non-commuting 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 $\Omega = -\sum_i \omega_i$) 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 $\chi^{(n)}$ [37,39] 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 $\chi^{DCKerr}(-\omega; 0, 0, \omega)$ and $\chi^{EFIOR}(0; \omega, -\omega, 0)$. 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:

$$\begin{aligned}
\chi_{SSH}^{(3)}(\omega; \omega, \omega, -3\omega) &= \chi_0^{(3)} \frac{15}{1024} \int_1^{1/\delta} \frac{dx}{\sqrt{(1 - \delta^2 x^2)(x^2 - 1)}} \\
&\left\{ \frac{3}{x^8(x^2 - z^2)} - \frac{27}{x^8(x^2 - 9z^2)} \right. \\
&+ 8(1 - \delta^2 x^2)(x^2 - 1) \left\{ -\frac{74}{9} \frac{1}{x^8(x^2 - z^2)} - \frac{11}{3} \frac{1}{x^6(x^2 - z^2)^2} \right. \\
&\left. \left. + \frac{512}{9} \frac{1}{x^8(x^2 - 4z^2)} - 54 \frac{1}{x^8(x^2 - 9z^2)} + 63 \frac{1}{x^6(x^2 - 9z^2)^2} \right\} \right\} \quad (4.3)
\end{aligned}$$

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

$$\begin{aligned}
\chi_{TLM}^{(3)}(\omega; \omega, \omega, -3\omega) &= \chi_0^{(3)} \frac{5}{1024z^8} \left\{ \frac{5}{3}(40z^2 - 61)f(z) + \frac{16}{3}(4z^2 - 1)f(2z) \right. \\
&\left. - \frac{1}{243}(1944z^2 - 241)f(3z) + \frac{32}{243}(27z^4 - 30z^2 + 805) \right\} \quad (4.4) \\
&= \chi_0^{(3)} \left(\frac{5}{28} + \frac{80}{33}z^2 + \frac{28500}{1001}z^4 + O(z^6) \right) \quad (z \rightarrow 0).
\end{aligned}$$

On the other hand, analytical expression for THG under the TLM model is given by the

formula (see, for example, [13,14]):

$$\begin{aligned}\chi_{TLM}^{(3)}(-3\omega; \omega, \omega, \omega) &= \chi_0^{(3)} \frac{45}{128} \left\{ -\frac{14}{3z^8} - \frac{4}{15z^4} + \frac{(37 - 24z^2)}{8z^8} f(z) + \frac{(1 - 8z^2)}{24z^8} f(3z) \right\} \\ &= \chi_0^{(3)} \left(\frac{5}{28} + \frac{80}{11} z^2 + \frac{98580}{1001} z^4 + O(z^6) \right) \quad (z \rightarrow 0).\end{aligned}\tag{4.5}$$

Both $\chi_{TLM}^{(3)}(\omega; \omega, \omega, -3\omega)$ and $\chi_{TLM}^{(3)}(-3\omega; \omega, \omega, \omega)$ in the non-resonant region are plotted in Fig.5. The numerical calculation shows 40% difference between them when $z = 1/6$ (corresponding to $0.3eV$ 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 Eq.(4.4) and Eq.(4.5). Subtracting two asymptotic expressions in Eq.(4.4) and Eq.(4.5), we have the following relationship of the difference in the off-resonant region:

$$\delta\chi^{(3)}(\omega) \propto \frac{e^4 n_0 t_0^3 a^3 \hbar^2 \omega^2}{\Delta^8}.\tag{4.6}$$

By excluding the ∇_k terms, our calculations show both the overall permutation and Kleinman symmetries remain valid. For example, $\chi^{DCKerr} = \chi^{EFIOR}$ and $\chi^{(3)}(-3\omega; \omega, \omega, \omega) = \chi^{(3)}(\omega; \omega, \omega, -3\omega)$ are preserved for all frequencies. Obviously, it is the ∇_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 non-resonant 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 [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. Eq.(4.6) shows that: (i). The break increases with decreasing band gap and is proportional to ω^2 .

These are consistent with the previously reported experiment [52]; (ii). The break increases with t_0 (the hopping of π 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 [53] and some polymers or crystals [54,55], while unfavorable of ($\leq 8\%$) the localized states such as molecular systems such as O_2 , N_2 , etc. [56,57]. 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 [58].

The magnitudes of the hyperpolarizabilities with ∇_k terms are quite close to those without ∇_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 ∇_k terms. Therefore, the intraband current contribution to the hyperpolarizabilities is actually about as twice big as the interband contribution and can not be neglected. The total contribution (without ∇_k terms), interband contribution (with ∇_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 [59], Soos and his coauthors obtained the polarizability of one-dimensional Peierls-Hubbard model based on the static electronic field [60]. 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 Section III under TLM model to study the zero-frequency behaviors, with or without ∇_k terms. The zero-frequency results under SSH models shall be similar.

1. DCKerr

Let $z \rightarrow 0$ in Eq.(3.12), we obtain

$$\chi_{TLM}^{DCKerr}(0, 0, \omega \rightarrow 0) = \chi_0^{(3)} \left(\frac{5}{28} + \frac{10}{11}z^2 + \frac{2160}{1001}z^4 + \frac{1088}{273}z^6 + O(z^8) \right) \quad (4.7)$$

Dropping ∇_k term and let $z \rightarrow 0$ in Eq.(3.15), we obtain

$$\tilde{\chi}_{TLM}^{DCKerr}(0, 0, \omega \rightarrow 0) = \chi_0^{(3)} \left(-\frac{1}{7} - \frac{50}{231}z^2 - \frac{40}{143}z^4 - \frac{48}{143}z^6 + O(z^8) \right) \quad (4.8)$$

2. DCSHG

Let $z \rightarrow 0$ in Eq.(3.19), we obtain

$$\chi_{TLM}^{DCSHG}(0, \omega \rightarrow 0, \omega \rightarrow 0) = \chi_0^{(3)} \left(\frac{5}{28} + \frac{254}{77}z^2 + \frac{68620}{3003}z^4 + \frac{375824}{3003}z^6 + O(z^8) \right) \quad (4.9)$$

Dropping ∇_k term and let $z \rightarrow 0$ in Eq.(3.22), we obtain

$$\tilde{\chi}_{TLM}^{DCSHG}(0, \omega \rightarrow 0, \omega \rightarrow 0) = \chi_0^{(3)} \left(-\frac{1}{7} - \frac{50}{77}z^2 - \frac{360}{143}z^4 - \frac{1360}{143}z^6 + O(z^8) \right). \quad (4.10)$$

3. IDIR

Let $z \rightarrow 0$ in Eq.(3.26), we obtain

$$\chi_{TLM}^{IDIR}(\omega \rightarrow 0, -\omega \rightarrow 0, \omega \rightarrow 0) = \chi_0^{(3)} \left(\frac{5}{28} + \frac{40}{33}z^2 + \frac{5300}{1001}z^4 + \frac{256}{13}z^6 + O(z^8) \right). \quad (4.11)$$

Dropping ∇_k term and let $z \rightarrow 0$ in Eq.(3.29), we obtain

$$\tilde{\chi}_{TLM}^{IDIR}(\omega \rightarrow 0, -\omega \rightarrow 0, \omega \rightarrow 0) = \chi_0^{(3)} \left(-\frac{1}{7} - \frac{100}{231}z^2 - \frac{120}{143}z^4 - \frac{192}{143}z^6 + O(z^8) \right). \quad (4.12)$$

4. EFIOR

Let $z \rightarrow 0$ in Eq.(3.32), we obtain

$$\chi_{TLM}^{EFIOR}(0, -\omega \rightarrow 0, \omega \rightarrow 0) = \chi_0^{(3)} \left(\frac{5}{28} + \frac{10}{33}z^2 + \frac{60}{143}z^4 + \frac{48}{91}z^6 + O(z^8) \right). \quad (4.13)$$

Dropping ∇_k term and let $z \rightarrow 0$ in Eq.(3.35), we obtain

$$\tilde{\chi}_{TLM}^{EFIOR}(0, -\omega, \omega) = \chi_0^{(3)} \left(-\frac{1}{7} - \frac{50}{231}z^2 - \frac{40}{143}z^4 - \frac{48}{143}z^6 + O(z^8) \right). \quad (4.14)$$

5. THG

From Eq.(3.3) in our previous work [13], let $z \rightarrow 0$, we have

$$\chi_{TLM}^{THG}(\omega \rightarrow 0, \omega \rightarrow 0, \omega \rightarrow 0) = \chi_0^{(3)} \left(\frac{5}{28} + \frac{80}{11}z^2 + \frac{98580}{1001}z^4 + \frac{96640}{91}z^6 + O(z^8) \right). \quad (4.15)$$

Dropping ∇_k term and let $z \rightarrow 0$ in Eq.(3.39), we obtain

$$\tilde{\chi}_{TLM}^{THG}(\omega \rightarrow 0, \omega \rightarrow 0, \omega \rightarrow 0) = \chi_0^{(3)} \left(-\frac{1}{7} - \frac{100}{77}z^2 - \frac{120}{11}z^4 - \frac{13120}{143}z^6 + O(z^8) \right). \quad (4.16)$$

From the zero frequency behaviors, we can see the difference of results between having and not having ∇_k terms. Although the magnitude of hyperpolarizabilities at $(0,0,0)$ is quite close, $5\chi_0^{(3)}/28$ vs. $4\chi_0^{(3)}/28$.

D. Comparison with other theoretical results

For the nonlinear properties under single electron periodic models, Genkin-Mednis developed an approach [50] that was later applied to polymer systems by Agrawal, *et al* [12]. In those works, general formulae of nonlinear optical response were developed. BY applying the Genkin-Mednis approach to the SSH model, Wu and Sun obtained the analytical format of third-harmonic generation (THG) [21,22] that yields the same results as those under the static current-current(J_0J_0) correlation [15]. As we discussed previously [13,14], the general results obtained here are quite similar but different from the results obtained before. On the THG problem, our results are qualitatively close to the numerical results obtained by Yu, *et al* [19,20] and Shuai, *et al* [23]'s works. The reason for those difference is caused technically by the treatments of ∇_k operator, but physically by the gauge phase factor [43] that we are going to discuss further in the subsequent paper [40].

Recently Kirtman, Gu and Bishop extended Genkin-Mednis method to the fully coupled perturbed Hartree-Fock theory in discussing the hyperpolarizabilities of infinite chains [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 [29].

Finally, we would like to point out that the results under DD correlation are also different from those under J_0J_0 correlation [15,16]. More details will be discussed in our subsequent paper [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 off-resonant regions [39], the direct measurement of the above assertion does not appear to be present in the literature. In our previous work [61], we suggested experimentalists perform off-resonant $\chi^{(3)}$ measurements on some centro-symmetric 1D periodic systems such as *trans*-polyacetylene, etc to directly test the break of overall permutation symmetry and Eq.(4.6). Though our calculations are based on 1D periodic models, the results may be applied to some delocalized two-dimensional materials such as benzene ring structures where the periodicity is along the circle of ring. Therefore, experimentalists can also perform some off-resonant $\chi^{(3)}$ experiments on some symmetric aromatic molecules to directly test the overall permutation symmetry of hyperpolarizabilities.

Besides the break of overall permutation symmetry, the relationships between different nonlinear optical processes such as Eq.(4.1) and Eq.(4.2) can also be tested experimentally.

V. CONCLUSIONS

Analytical expressions of the general four-wave-mixing (FWM) for infinite chains under the SSH and TLM models are first derived under the DD correlation by the field theory. The hyperpolarizabilities of DCKerr, DCSHG, IDIR and EFIOR are obtained by either including or excluding ∇_k terms. Contrary to the linear response, intraband contributions to

the hyperpolarizabilities dominate the final results if they are included. ∇_k term also breaks the overall permutation and Kleinman symmetry in $\chi^{(3)}$ even for the low frequency and non-resonant regions. The reported deviations 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 centro-symmetry 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 non-resonant region: $\chi_{non-res}^{(3)}(-3\omega; \omega, \omega, \omega) > \chi_{non-res}^{(3)}(-2\omega; 0, \omega, \omega) > \chi_{non-res}^{(3)}(-\omega; \omega, -\omega, \omega) > \chi_{non-res}^{(3)}(-\omega; 0, 0, \omega) \geq \chi_{non-res}^{(3)}(0; \omega, -\omega, 0)$, and in the resonant region: $\chi_{res}^{(3)}(-\omega; 0, 0, \omega) > \chi_{res}^{(3)}(-\omega; \omega, -\omega, \omega) > \chi_{res}^{(3)}(-2\omega; 0, \omega, \omega) > \chi_{res}^{(3)}(0; \omega; -\omega, 0) > \chi_{res}^{(3)}(-3\omega; \omega, \omega, \omega)$. We look forward to the experimental testings on the above theoretical results.

This 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 like Hubbard model [17,24,26], electron-hole pair model [17,25], etc, may be studied by applying similar techniques developed here.

APPENDIX A: SOME INTEGRALS

Define

$$f(z) := \int_1^\infty \frac{dx}{(x^2 - z^2)\sqrt{x^2 - 1}} \equiv \begin{cases} \frac{\arcsin(z)}{z\sqrt{1 - z^2}} & (z^2 < 1), \\ -\frac{\cosh^{-1}(z)}{z\sqrt{z^2 - 1}} + \frac{i\pi}{2z\sqrt{z^2 - 1}} & (z^2 > 1). \end{cases} \quad (\text{A1})$$

$$L(n, z) := \int_1^\infty \frac{dx}{x^{2n}(x^2 - z^2)^{5-n}\sqrt{x^2 - 1}}, \quad (\text{A2})$$

$$M(n, z) := \int_1^\infty \frac{\sqrt{x^2 - 1}dx}{x^{2n}(x^2 - z^2)^{5-n}}. \quad (\text{A3})$$

Using Maple, we obtain

$$L(4, z) = \frac{1}{105z^8} (105f(z) - (48z^6 + 56z^4 + 70z^2 + 105)), \quad (\text{A4})$$

$$L(3, z) = \frac{1}{30z^8(z^2 - 1)} ((-120z^2 + 105)f(z) + (16z^6 + 24z^4 + 50z^2 - 105)), \quad (\text{A5})$$

$$L(2, z) = \frac{1}{24z^8(z^2 - 1)^2} ((144z^4 - 240z^2 + 105)f(z) - (16z^6 + 40z^4 - 170z^2 + 105)), \quad (\text{A6})$$

$$M(4, z) = \frac{1}{105z^8} ((105z^2 - 105)f(z) - (8z^6 + 14z^4 + 35z^2 - 105)) \quad (\text{A7})$$

$$M(3, z) = \frac{1}{30z^8} ((-90z^2 + 105)f(z) + (4z^4 + 20z^2 - 105)) \quad (\text{A8})$$

$$M(2, z) = \frac{1}{24z^8(z^2 - 1)} ((72z^4 - 180z^2 + 105)f(z) + (-8z^4 + 110z^2 - 105)) \quad (\text{A9})$$

$$M(1, z) = \frac{1}{48z^8(z^2 - 1)^2} ((-48z^6 + 216z^4 - 270z^2 + 105)f(z) + (-92z^4 + 200z^2 - 105)) \quad (\text{A10})$$

$$M(0, z) = \frac{1}{384z^8(z^2 - 1)^3} ((-192z^6 + 432z^4 - 360z^2 + 105)f(z) + (48z^6 - 248z^4 + 290z^2 - 105)) \quad (\text{A11})$$

APPENDIX B: THE DERIVATION OF FWM UNDER SSH MODEL

We're trying to calculate the following integral:

$$\mathcal{I}(\omega_1, \omega_2, \omega_3) = - \int \frac{d\omega}{2\pi i} Tr(\hat{D}_k G(0) \hat{D}_k G(\omega_1) \hat{D}_k G(\omega_1 + \omega_2) \hat{D}_k G(\omega_1 + \omega_2 + \omega_3)), \quad (\text{B1})$$

where

$$\hat{D}_k := \beta(k)\sigma_2 + i\frac{\partial}{\partial k}$$

and

$$G(s) := \frac{\omega - s + \omega_k\sigma_3}{(\omega - s)^2 - \omega_k^2 + i\epsilon}.$$

Let's define

$$p_{\pm} := \frac{1}{2}(1 \pm \sigma_3),$$

$$\hat{A}_k := \beta(k)\sigma_2,$$

$$\hat{B}_k := i\frac{\partial}{\partial k},$$

$$g_+(s) := \frac{1}{\omega - s - \omega_k + i\epsilon},$$

$$g_-(s) := \frac{1}{\omega - s + \omega_k - i\epsilon}.$$

Then it's easy to prove that

$$G(s) = g_+(s)p_+ + g_-(s)p_-,$$

$$\hat{A}_k p_{\pm} = p_{\mp} \hat{A}_k,$$

$$\hat{B}_k p_{\pm} = p_{\pm} \hat{B}_k.$$

$$\begin{aligned}
\mathcal{I}(\omega_1, \omega_2, \omega_3) &= I_1 + I_2 + I_3 + I_4 + I_5 + I_6 + I_7 + I_8 \\
&:= - \int \frac{d\omega}{2\pi i} \text{Tr}(\hat{A}_k G(0) \hat{A}_k G(\omega_1) \hat{A}_k G(\omega_1 + \omega_2) \hat{A}_k G(\omega_1 + \omega_2 + \omega_3)) \\
&\quad - \int \frac{d\omega}{2\pi i} \text{Tr}(\hat{A}_k G(0) \hat{A}_k G(\omega_1) \hat{B}_k G(\omega_1 + \omega_2) \hat{B}_k G(\omega_1 + \omega_2 + \omega_3)) \\
&\quad - \int \frac{d\omega}{2\pi i} \text{Tr}(\hat{A}_k G(0) \hat{B}_k G(\omega_1) \hat{A}_k G(\omega_1 + \omega_2) \hat{B}_k G(\omega_1 + \omega_2 + \omega_3)) \\
&\quad - \int \frac{d\omega}{2\pi i} \text{Tr}(\hat{A}_k G(0) \hat{B}_k G(\omega_1) \hat{B}_k G(\omega_1 + \omega_2) \hat{A}_k G(\omega_1 + \omega_2 + \omega_3)) \\
&\quad - \int \frac{d\omega}{2\pi i} \text{Tr}(\hat{B}_k G(0) \hat{A}_k G(\omega_1) \hat{A}_k G(\omega_1 + \omega_2) \hat{B}_k G(\omega_1 + \omega_2 + \omega_3)) \\
&\quad - \int \frac{d\omega}{2\pi i} \text{Tr}(\hat{B}_k G(0) \hat{A}_k G(\omega_1) \hat{B}_k G(\omega_1 + \omega_2) \hat{A}_k G(\omega_1 + \omega_2 + \omega_3)) \\
&\quad - \int \frac{d\omega}{2\pi i} \text{Tr}(\hat{B}_k G(0) \hat{B}_k G(\omega_1) \hat{A}_k G(\omega_1 + \omega_2) \hat{A}_k G(\omega_1 + \omega_2 + \omega_3)) \\
&\quad - \int \frac{d\omega}{2\pi i} \text{Tr}(\hat{B}_k G(0) \hat{B}_k G(\omega_1) \hat{B}_k G(\omega_1 + \omega_2) \hat{B}_k G(\omega_1 + \omega_2 + \omega_3))
\end{aligned} \tag{B2}$$

1.

$$\begin{aligned}
I_1 &= - \int \frac{d\omega}{2\pi i} \text{Tr}(\hat{A}_k G(0) \hat{A}_k G(\omega_1) \hat{A}_k G(\omega_1 + \omega_2) \hat{A}_k G(\omega_1 + \omega_2 + \omega_3)) \\
&= -\beta^4(k) \int \frac{d\omega}{2\pi i} g_+(0) g_-(\omega_1) g_+(\omega_1 + \omega_2) g_-(\omega_1 + \omega_2 + \omega_3) \\
&\quad - \beta^4(k) \int \frac{d\omega}{2\pi i} g_-(0) g_+(\omega_1) g_-(\omega_1 + \omega_2) g_+(\omega_1 + \omega_2 + \omega_3) \\
&= I_1(\omega_k) - I_1(-\omega_k),
\end{aligned} \tag{B3}$$

where

$$I_1(\omega_k) = - \frac{\beta^4(k)(4\omega_k - \omega_1 - \omega_3)}{(2\omega_k - \omega_1)(2\omega_k + \omega_2)(2\omega_k - \omega_3)(2\omega_k - \omega_1 - \omega_2 - \omega_3)}. \tag{B4}$$

2.

$$\begin{aligned}
I_2 &= - \int \frac{d\omega}{2\pi i} \text{Tr}(\hat{A}_k G(0) \hat{A}_k G(\omega_1) \hat{B}_k G(\omega_1 + \omega_2) \hat{B}_k G(\omega_1 + \omega_2 + \omega_3)) \\
&= \int \frac{d\omega}{2\pi i} \beta(k) g_+(0) \beta(k) g_-(\omega_1) \frac{\partial}{\partial k} g_-(\omega_1 + \omega_2) \frac{\partial}{\partial k} g_-(\omega_1 + \omega_2 + \omega_3) \\
&\quad + \int \frac{d\omega}{2\pi i} \beta(k) g_-(0) \beta(k) g_+(\omega_1) \frac{\partial}{\partial k} g_+(\omega_1 + \omega_2) \frac{\partial}{\partial k} g_+(\omega_1 + \omega_2 + \omega_3) \\
&= I_2(\omega_k) - I_2(-\omega_k),
\end{aligned} \tag{B5}$$

where

$$I_2(\omega_k) = -\frac{\beta^2(k)}{2\omega_k - \omega_1} \left(\frac{\partial}{\partial k} \frac{1}{\omega - \omega_1 - \omega_2 + \omega_k} \frac{\partial}{\partial k} \frac{1}{\omega - \omega_1 - \omega_2 - \omega_3 + \omega_k} \right) \Big|_{\omega=\omega_k}. \quad (\text{B6})$$

3.

$$\begin{aligned} I_3 &= - \int \frac{d\omega}{2\pi i} \text{Tr}(\hat{A}_k G(0) \hat{B}_k G(\omega_1) \hat{A}_k G(\omega_1 + \omega_2) \hat{B}_k G(\omega_1 + \omega_2 + \omega_3)) \\ &= \int \frac{d\omega}{2\pi i} \beta(k) g_+(0) \frac{\partial}{\partial k} g_+(\omega_1) \beta(k) g_-(\omega_1 + \omega_2) \frac{\partial}{\partial k} g_-(\omega_1 + \omega_2 + \omega_3) \\ &\quad + \int \frac{d\omega}{2\pi i} \beta(k) g_-(0) \frac{\partial}{\partial k} g_-(\omega_1) \beta(k) g_+(\omega_1 + \omega_2) \frac{\partial}{\partial k} g_+(\omega_1 + \omega_2 + \omega_3) \\ &= I_3(\omega_k) - I_3(-\omega_k), \end{aligned} \quad (\text{B7})$$

where

$$\begin{aligned} I_3(\omega_k) &= \beta(k) \frac{\partial}{\partial k} \frac{\beta(k)}{(\omega - \omega_2 + \omega_k)(\omega - \omega_1 - \omega_2 + \omega_k)} \frac{\partial}{\partial k} \frac{1}{\omega - \omega_1 - \omega_2 - \omega_3 + \omega_k} \Big|_{\omega=\omega_k} \\ &\quad + \beta(k) \frac{\partial}{\partial k} \frac{\beta(k)}{\omega - \omega_2 + \omega_k} \frac{\partial}{\partial k} \frac{1}{(\omega - \omega_2 - \omega_3 + \omega_k)(\omega - \omega_1 - \omega_2 - \omega_3 + \omega_k)} \Big|_{\omega=\omega_k} \\ &\quad - \frac{\partial \omega_k}{\partial k} \frac{\beta^2(k)}{2(2\omega_k - \omega_2)} \frac{1}{2\omega_k - \omega_2} \frac{\partial}{\partial k} \frac{1}{(2\omega_k - \omega_2 - \omega_3)(2\omega_k - \omega_1 - \omega_2 - \omega_3)} \\ &\quad - \frac{\partial \omega_k}{\partial k} \frac{\beta^2(k)}{2(2\omega_k - \omega_2)} \frac{1}{(2\omega_k - \omega_2)(2\omega_k - \omega_1 - \omega_2)} \frac{\partial}{\partial k} \frac{1}{2\omega_k - \omega_1 - \omega_2 - \omega_3} \\ &\quad - \frac{\partial \omega_k}{\partial k} \frac{\beta^2(k)}{2(2\omega_k - \omega_2)} \frac{1}{2\omega_k - \omega_2 - \omega_3} \frac{\partial}{\partial k} \frac{1}{(2\omega_k - \omega_2 - \omega_3)(2\omega_k - \omega_1 - \omega_2 - \omega_3)} \\ &\quad - \frac{\partial \omega_k}{\partial k} \frac{\beta^2(k)}{2(2\omega_k - \omega_2)} \frac{1}{(2\omega_k - \omega_2 - \omega_3)(2\omega_k - \omega_1 - \omega_2 - \omega_3)} \frac{\partial}{\partial k} \frac{1}{2\omega_k - \omega_2 - \omega_3}. \end{aligned} \quad (\text{B8})$$

4.

$$\begin{aligned} I_4 &= - \int \frac{d\omega}{2\pi i} \text{Tr}(\hat{A}_k G(0) \hat{B}_k G(\omega_1) \hat{B}_k G(\omega_1 + \omega_2) \hat{A}_k G(\omega_1 + \omega_2 + \omega_3)) \\ &= \int \frac{d\omega}{2\pi i} \beta(k) g_+(0) \frac{\partial}{\partial k} g_+(\omega_1) \frac{\partial}{\partial k} g_+(\omega_1 + \omega_2) \beta(k) g_-(\omega_1 + \omega_2 + \omega_3) \\ &\quad + \int \frac{d\omega}{2\pi i} \beta(k) g_-(0) \frac{\partial}{\partial k} g_-(\omega_1) \frac{\partial}{\partial k} g_-(\omega_1 + \omega_2) \beta(k) g_+(\omega_1 + \omega_2 + \omega_3) \\ &= I_4(\omega_k) - I_4(-\omega_k), \end{aligned} \quad (\text{B9})$$

where

$$\begin{aligned}
I_4(\omega_k) &= -\beta(k) \frac{\partial^2}{\partial k^2} \frac{\beta(k)}{(2\omega_k - \omega_1 - \omega_2 - \omega_3)(2\omega_k - \omega_2 - \omega_3)(2\omega_k - \omega_3)} \\
&+ \frac{\beta(k)}{2} \frac{\partial}{\partial k} \frac{\beta(k)}{2\omega_k - \omega_3} \frac{\partial}{\partial k} \frac{1}{(2\omega_k - \omega_1 - \omega_2 - \omega_3)(2\omega_k - \omega_2 - \omega_3)} \\
&+ \frac{\beta(k)}{2} \frac{\partial}{\partial k} \frac{\beta(k)}{(2\omega_k - \omega_3)(2\omega_k - \omega_2 - \omega_3)} \frac{\partial}{\partial k} \frac{1}{2\omega_k - \omega_1 - \omega_2 - \omega_3} \\
&- \frac{\beta^2(k)}{2\omega_k - \omega_3} \left(\frac{\partial}{\partial k} \frac{1}{\omega - \omega_2 - \omega_3 + \omega_k} \frac{\partial}{\partial k} \frac{1}{\omega - \omega_1 - \omega_2 - \omega_3 + \omega_k} \right) \Big|_{\omega=\omega_k}.
\end{aligned} \tag{B10}$$

5.

$$\begin{aligned}
I_5 &= - \int \frac{d\omega}{2\pi i} \text{Tr}(\hat{B}_k G(0) \hat{A}_k G(\omega_1) \hat{A}_k G(\omega_1 + \omega_2) \hat{B}_k G(\omega_1 + \omega_2 + \omega_3)) \\
&= \int \frac{d\omega}{2\pi i} \frac{\partial}{\partial k} g_-(0) \beta(k) g_+(\omega_1) \beta(k) g_-(\omega_1 + \omega_2) \frac{\partial}{\partial k} g_-(\omega_1 + \omega_2 + \omega_3) \\
&+ \int \frac{d\omega}{2\pi i} \frac{\partial}{\partial k} g_+(0) \beta(k) g_-(\omega_1) \beta(k) g_+(\omega_1 + \omega_2) \frac{\partial}{\partial k} g_+(\omega_1 + \omega_2 + \omega_3) \\
&= I_5(\omega_k) - I_5(-\omega_k),
\end{aligned} \tag{B11}$$

where

$$I_5(\omega_k) = - \frac{\partial}{\partial k} \frac{\beta^2(k)}{2(2\omega_k + \omega_1)(2\omega_k - \omega_2)} \frac{\partial}{\partial k} \frac{1}{2\omega_k - \omega_2 - \omega_3}. \tag{B12}$$

6.

$$\begin{aligned}
I_6 &= - \int \frac{d\omega}{2\pi i} \text{Tr}(\hat{B}_k G(0) \hat{A}_k G(\omega_1) \hat{B}_k G(\omega_1 + \omega_2) \hat{A}_k G(\omega_1 + \omega_2 + \omega_3)) \\
&= \int \frac{d\omega}{2\pi i} \frac{\partial}{\partial k} g_-(0) \beta(k) g_+(\omega_1) \frac{\partial}{\partial k} g_+(\omega_1 + \omega_2) \beta(k) g_-(\omega_1 + \omega_2 + \omega_3) \\
&+ \int \frac{d\omega}{2\pi i} \frac{\partial}{\partial k} g_+(0) \beta(k) g_-(\omega_1) \frac{\partial}{\partial k} g_-(\omega_1 + \omega_2) \beta(k) g_+(\omega_1 + \omega_2 + \omega_3) \\
&= I_6(\omega_k) - I_6(-\omega_k),
\end{aligned} \tag{B13}$$

where

$$\begin{aligned}
I_6(\omega_k) &= \frac{\partial}{\partial k} \frac{\beta(k)}{(2\omega_k + \omega_1)(2\omega_k + \omega_1 + \omega_2)} \frac{\partial}{\partial k} \frac{\beta(k)}{2\omega_k - \omega_3} \\
&+ \frac{\partial}{\partial k} \frac{\beta(k)}{2\omega_k + \omega_1} \frac{\partial}{\partial k} \frac{\beta(k)}{(2\omega_k - \omega_2 - \omega_3)(2\omega_k - \omega_3)} \\
&- \frac{\partial}{\partial k} \frac{\beta^2(k)}{2(2\omega_k + \omega_1)(2\omega_k - \omega_3)} \frac{\partial}{\partial k} \frac{1}{2\omega_k - \omega_2 - \omega_3} \\
&+ \frac{\partial}{\partial k} \frac{\beta^2(k)}{2(2\omega_k + \omega_1)(2\omega_k - \omega_3)} \frac{\partial}{\partial k} \frac{1}{2\omega_k + \omega_1 + \omega_2}.
\end{aligned} \tag{B14}$$

7.

$$\begin{aligned}
I_7 &= - \int \frac{d\omega}{2\pi i} \text{Tr}(\hat{B}_k G(0) \hat{B}_k G(\omega_1) \hat{A}_k G(\omega_1 + \omega_2) \hat{A}_k G(\omega_1 + \omega_2 + \omega_3)) \\
&= \int \frac{d\omega}{2\pi i} \frac{\partial}{\partial k} g_-(0) \frac{\partial}{\partial k} g_-(\omega_1) \beta(k) g_+(\omega_1 + \omega_2) \beta(k) g_-(\omega_1 + \omega_2 + \omega_3) \\
&\quad + \int \frac{d\omega}{2\pi i} \frac{\partial}{\partial k} g_+(0) \frac{\partial}{\partial k} g_+(\omega_1) \beta(k) g_-(\omega_1 + \omega_2) \beta(k) g_+(\omega_1 + \omega_2 + \omega_3) \\
&= I_7(\omega_k) - I_7(-\omega_k),
\end{aligned} \tag{B15}$$

where

$$\begin{aligned}
I_7(\omega_k) &= - \frac{\partial}{\partial k} \frac{\beta^2(k)}{2(2\omega_k + \omega_2)(2\omega_k - \omega_3)} \frac{\partial}{\partial k} \frac{1}{2\omega_k + \omega_1 + \omega_2} \\
&\quad - \frac{\partial}{\partial k} \frac{1}{2\omega_k + \omega_1 + \omega_2} \frac{\partial}{\partial k} \frac{\beta^2(k)}{(2\omega_k + \omega_2)(2\omega_k - \omega_3)}.
\end{aligned} \tag{B16}$$

8.

$$\begin{aligned}
I_8 &= - \int \frac{d\omega}{2\pi i} \text{Tr}(\hat{B}_k G(0) \hat{B}_k G(\omega_1) \hat{B}_k G(\omega_1 + \omega_2) \hat{B}_k G(\omega_1 + \omega_2 + \omega_3)) \\
&= - \int \frac{d\omega}{2\pi i} \hat{B}_k g_+(0) \hat{B}_k g_+(\omega_1) \hat{B}_k g_+(\omega_1 + \omega_2) \hat{B}_k g_+(\omega_1 + \omega_2 + \omega_3) \\
&\quad - \int \frac{d\omega}{2\pi i} \hat{B}_k g_-(0) \hat{B}_k g_-(\omega_1) \hat{B}_k g_-(\omega_1 + \omega_2) \hat{B}_k g_-(\omega_1 + \omega_2 + \omega_3) \\
&= 0
\end{aligned} \tag{B17}$$

The expression for $\mathcal{I}(\omega_1, \omega_2, \omega_3)$ is extremely messy. However, the quantity which we're really interested in is the sum of its six permutations

$$\begin{aligned}
\mathcal{S} &= \frac{1}{6} (\mathcal{I}(\omega_1, \omega_2, \omega_3) + \mathcal{I}(\omega_1, \omega_3, \omega_2) + \mathcal{I}(\omega_2, \omega_1, \omega_3) \\
&\quad + \mathcal{I}(\omega_2, \omega_3, \omega_1) + \mathcal{I}(\omega_3, \omega_1, \omega_2) + \mathcal{I}(\omega_3, \omega_2, \omega_1))
\end{aligned} \tag{B18}$$

Due to its highly symmetric character, we expect a great simplification would occur. This is indeed the case as shown below. The key technique used is that we can permute ω_1 , ω_2 and ω_3 freely when computing the summation. We present some details of the simplification procedure in the following.

1.

$$\begin{aligned}
I_5(\omega_k) + I_6(\omega_k) + I_7(\omega_k) &= -\frac{\partial}{\partial k} \frac{\beta^2(k)}{2(2\omega_k + \omega_1)(2\omega_k - \omega_2)} \frac{\partial}{\partial k} \frac{1}{2\omega_k - \omega_2 - \omega_3} \\
&+ \frac{\partial}{\partial k} \frac{\beta(k)}{(2\omega_k + \omega_1)(2\omega_k + \omega_1 + \omega_2)} \frac{\partial}{\partial k} \frac{\beta(k)}{2\omega_k - \omega_3} \\
&+ \frac{\partial}{\partial k} \frac{\beta(k)}{2\omega_k + \omega_1} \frac{\partial}{\partial k} \frac{\beta(k)}{(2\omega_k - \omega_2 - \omega_3)(2\omega_k - \omega_3)} \\
&- \frac{\partial}{\partial k} \frac{\beta^2(k)}{2(2\omega_k + \omega_1)(2\omega_k - \omega_3)} \frac{\partial}{\partial k} \frac{1}{2\omega_k - \omega_2 - \omega_3} \\
&+ \frac{\partial}{\partial k} \frac{\beta^2(k)}{2(2\omega_k + \omega_1)(2\omega_k - \omega_3)} \frac{\partial}{\partial k} \frac{1}{2\omega_k + \omega_1 + \omega_2} \\
&- \frac{\partial}{\partial k} \frac{\beta^2(k)}{2(2\omega_k + \omega_2)(2\omega_k - \omega_3)} \frac{\partial}{\partial k} \frac{1}{2\omega_k + \omega_1 + \omega_2} \\
&- \frac{\partial}{\partial k} \frac{1}{2\omega_k + \omega_1 + \omega_2} \frac{\partial}{\partial k} \frac{\beta^2(k)}{(2\omega_k + \omega_2)(2\omega_k - \omega_3)} \\
&= -\frac{\partial}{\partial k} \frac{\beta^2(k)}{(2\omega_k + \omega_1)(2\omega_k - \omega_2)} \frac{\partial}{\partial k} \frac{1}{2\omega_k - \omega_2 - \omega_3} \\
&+ \frac{\partial}{\partial k} \frac{\beta(k)}{(2\omega_k + \omega_1)(2\omega_k + \omega_1 + \omega_2)} \frac{\partial}{\partial k} \frac{\beta(k)}{2\omega_k - \omega_3} \\
&+ \frac{\partial}{\partial k} \frac{\beta(k)}{2\omega_k + \omega_1} \frac{\partial}{\partial k} \frac{\beta(k)}{(2\omega_k - \omega_2 - \omega_3)(2\omega_k - \omega_3)} \\
&- \frac{\partial}{\partial k} \frac{1}{2\omega_k + \omega_1 + \omega_2} \frac{\partial}{\partial k} \frac{\beta^2(k)}{(2\omega_k + \omega_2)(2\omega_k - \omega_3)} \\
&= +\frac{\partial}{\partial k} \frac{\beta(k)}{(2\omega_k + \omega_1)(2\omega_k - \omega_2 - \omega_3)} \frac{\partial}{\partial k} \frac{\beta(k)}{2\omega_k - \omega_2} \\
&- \frac{\partial}{\partial k} \frac{\beta(k)}{(2\omega_k - \omega_3)(2\omega_k + \omega_1 + \omega_2)} \frac{\partial}{\partial k} \frac{\beta(k)}{2\omega_k + \omega_1} \\
&= +\frac{\partial}{\partial k} \frac{\beta(k)}{(2\omega_k + \omega_3)(2\omega_k - \omega_1 - \omega_2)} \frac{\partial}{\partial k} \frac{\beta(k)}{2\omega_k - \omega_1} \\
&- \frac{\partial}{\partial k} \frac{\beta(k)}{(2\omega_k - \omega_3)(2\omega_k + \omega_1 + \omega_2)} \frac{\partial}{\partial k} \frac{\beta(k)}{2\omega_k + \omega_1}.
\end{aligned} \tag{B19}$$

Since the above expression is an even function of ω_k , we obtain

$$I_5 + I_6 + I_7 = 0. \tag{B20}$$

2.

$$\begin{aligned}
I_4(\omega_k) = & -\frac{\beta(k)}{2} \frac{\partial}{\partial k} \frac{1}{(2\omega_k - \omega_1 - \omega_2)(2\omega_k - \omega_1 - \omega_2 - \omega_3)} \frac{\partial}{\partial k} \frac{\beta(k)}{2\omega_k - \omega_1} \\
& - \frac{\beta(k)}{2} \frac{\partial}{\partial k} \frac{1}{2\omega_k - \omega_1 - \omega_2 - \omega_3} \frac{\partial}{\partial k} \frac{\beta(k)}{(2\omega_k - \omega_1)(2\omega_k - \omega_1 - \omega_2)} \\
& - \frac{\beta^2(k)}{2\omega_k - \omega_1} \left(\frac{\partial}{\partial k} \frac{1}{\omega - \omega_1 - \omega_2 + \omega_k} \frac{\partial}{\partial k} \frac{1}{\omega - \omega_1 - \omega_2 - \omega_3 + \omega_k} \right) \Big|_{\omega=\omega_k}.
\end{aligned} \tag{B21}$$

3. Let

$$T(\omega_k) = I_2(\omega_k) + I_3(\omega_k) + I_4(\omega_k). \tag{B22}$$

Then

$$\begin{aligned}
T(\omega_k) = & -\frac{\beta(k)}{2} \frac{\partial}{\partial k} \frac{1}{(2\omega_k - \omega_1 - \omega_2)(2\omega_k - \omega_1 - \omega_2 - \omega_3)} \frac{\partial}{\partial k} \frac{\beta(k)}{2\omega_k - \omega_1} \\
& - \frac{\beta(k)}{2} \frac{\partial}{\partial k} \frac{1}{2\omega_k - \omega_1 - \omega_2 - \omega_3} \frac{\partial}{\partial k} \frac{\beta(k)}{(2\omega_k - \omega_1)(2\omega_k - \omega_1 - \omega_2)} \\
& - \frac{2\beta^2(k)}{2\omega_k - \omega_1} \left(\frac{\partial}{\partial k} \frac{1}{\omega - \omega_1 - \omega_2 + \omega_k} \frac{\partial}{\partial k} \frac{1}{\omega - \omega_1 - \omega_2 - \omega_3 + \omega_k} \right) \Big|_{\omega=\omega_k} \\
& + \beta(k) \frac{\partial}{\partial k} \frac{\beta(k)}{(\omega - \omega_1 + \omega_k)(\omega - \omega_1 - \omega_2 + \omega_k)} \frac{\partial}{\partial k} \frac{1}{\omega - \omega_1 - \omega_2 - \omega_3 + \omega_k} \Big|_{\omega=\omega_k} \\
& + \beta(k) \frac{\partial}{\partial k} \frac{\beta(k)}{\omega - \omega_1 + \omega_k} \frac{\partial}{\partial k} \frac{1}{(\omega - \omega_1 - \omega_2 + \omega_k)(\omega - \omega_1 - \omega_2 - \omega_3 + \omega_k)} \Big|_{\omega=\omega_k} \\
& - \frac{\partial \omega_k}{\partial k} \frac{\beta^2(k)}{2(2\omega_k - \omega_1)^2} \frac{\partial}{\partial k} \frac{1}{(2\omega_k - \omega_1 - \omega_2)(2\omega_k - \omega_1 - \omega_2 - \omega_3)} \\
& - \frac{\partial \omega_k}{\partial k} \frac{\beta^2(k)}{2(2\omega_k - \omega_1)^2} \frac{1}{(2\omega_k - \omega_1 - \omega_2)} \frac{\partial}{\partial k} \frac{1}{2\omega_k - \omega_1 - \omega_2 - \omega_3} \\
& - \frac{\partial \omega_k}{\partial k} \frac{\beta^2(k)}{2(2\omega_k - \omega_1)} \frac{1}{(2\omega_k - \omega_1 - \omega_2)^2} \frac{\partial}{\partial k} \frac{1}{(2\omega_k - \omega_1 - \omega_2 - \omega_3)} \\
& - \frac{\partial \omega_k}{\partial k} \frac{\beta^2(k)}{(2\omega_k - \omega_1)} \frac{1}{(2\omega_k - \omega_1 - \omega_2)(2\omega_k - \omega_1 - \omega_2 - \omega_3)} \frac{\partial}{\partial k} \frac{1}{2\omega_k - \omega_1 - \omega_2} \\
& := T_1 + T_2 + T_3 + T_4 + T_5 + T_6 + T_7 + T_8 + T_9,
\end{aligned} \tag{B23}$$

where

$$\begin{aligned}
T_3 + T_4 + T_5 &= +\beta(k) \left(\frac{\partial}{\partial k} \frac{\beta(k)}{\omega - \omega_1 + \omega_k} \right) \left(\frac{1}{\omega - \omega_1 - \omega_2 + \omega_k} \frac{\partial}{\partial k} \frac{1}{\omega - \omega_1 - \omega_2 - \omega_3 + \omega_k} \right) \Big|_{\omega=\omega_k} \\
&+ \beta(k) \left(\frac{\partial}{\partial k} \frac{\beta(k)}{\omega - \omega_1 + \omega_k} \right) \left(\frac{\partial}{\partial k} \frac{1}{(\omega - \omega_1 - \omega_2 + \omega_k)(\omega - \omega_1 - \omega_2 - \omega_3 + \omega_k)} \right) \Big|_{\omega=\omega_k} \\
&+ \frac{\beta^2(k)}{2\omega_k - \omega_1} \frac{\partial}{\partial k} \frac{1}{\omega - \omega_1 - \omega_2 - \omega_3 + \omega_k} \frac{\partial}{\partial k} \frac{1}{\omega - \omega_1 - \omega_2 + \omega_k} \Big|_{\omega=\omega_k} \\
&= + \frac{\partial \beta(k)}{\partial k} \frac{\beta(k)}{2(2\omega_k - \omega_1)(2\omega_k - \omega_1 - \omega_2)} \frac{\partial}{\partial k} \frac{1}{2\omega_k - \omega_1 - \omega_2 - \omega_3} \\
&+ \frac{\partial \beta(k)}{\partial k} \frac{\beta(k)}{2(2\omega_k - \omega_1)} \frac{\partial}{\partial k} \frac{1}{(2\omega_k - \omega_1 - \omega_2)(2\omega_k - \omega_1 - \omega_2 - \omega_3)} \\
&- \frac{\partial \omega_k}{\partial k} \frac{\beta^2(k)}{2(2\omega_k - \omega_1)^2} \frac{1}{(2\omega_k - \omega_1 - \omega_2)} \frac{\partial}{\partial k} \frac{1}{2\omega_k - \omega_1 - \omega_2 - \omega_3} \\
&- \frac{\partial \omega_k}{\partial k} \frac{\beta^2(k)}{2(2\omega_k - \omega_1)^2} \frac{\partial}{\partial k} \frac{1}{(2\omega_k - \omega_1 - \omega_2)(2\omega_k - \omega_1 - \omega_2 - \omega_3)} \\
&+ \frac{\beta^2(k)}{4(2\omega_k - \omega_1)} \left(\frac{\partial}{\partial k} \frac{1}{2\omega_k - \omega_1 - \omega_2} \right) \left(\frac{\partial}{\partial k} \frac{1}{2\omega_k - \omega_1 - \omega_2 - \omega_3} \right) \\
&+ \frac{\beta^2(k)}{2(2\omega_k - \omega_1)} \frac{1}{(2\omega_k - \omega_1 - \omega_2 - \omega_3)} \frac{\partial^2}{\partial k^2} \frac{1}{2\omega_k - \omega_1 - \omega_2} \\
&+ \frac{\partial \omega_k}{\partial k} \frac{\beta^2(k)}{(2\omega_k - \omega_1)(2\omega_k - \omega_1 - \omega_2)(2\omega_k - \omega_1 - \omega_2 - \omega_3)} \frac{\partial}{\partial k} \frac{1}{2\omega_k - \omega_1 - \omega_2}.
\end{aligned}$$

Then

$$\begin{aligned}
T' &= T_3 + T_4 + T_5 + T_6 + T_7 + T_8 + T_9 \\
&= + \frac{\partial \beta(k)}{\partial k} \frac{\beta(k)}{2(2\omega_k - \omega_1)(2\omega_k - \omega_1 - \omega_2)} \frac{\partial}{\partial k} \frac{1}{2\omega_k - \omega_1 - \omega_2 - \omega_3} \\
&\quad + \frac{\partial \beta(k)}{\partial k} \frac{\beta(k)}{2(2\omega_k - \omega_1)} \frac{\partial}{\partial k} \frac{1}{(2\omega_k - \omega_1 - \omega_2)(2\omega_k - \omega_1 - \omega_2 - \omega_3)} \\
&\quad + \frac{\beta^2(k)}{2} \left(\frac{\partial}{\partial k} \frac{1}{2\omega_k - \omega_1} \right) \left(\frac{1}{2\omega_k - \omega_1 - \omega_2} \frac{\partial}{\partial k} \frac{1}{2\omega_k - \omega_1 - \omega_2 - \omega_3} \right) \\
&\quad + \frac{\beta^2(k)}{2} \left(\frac{\partial}{\partial k} \frac{1}{2\omega_k - \omega_1} \right) \left(\frac{\partial}{\partial k} \frac{1}{(2\omega_k - \omega_1 - \omega_2)(2\omega_k - \omega_1 - \omega_2 - \omega_3)} \right) \\
&\quad + \frac{\beta^2(k)}{2(2\omega_k - \omega_1)} \left(\frac{\partial}{\partial k} \frac{1}{2\omega_k - \omega_1 - \omega_2} \right) \left(\frac{\partial}{\partial k} \frac{1}{2\omega_k - \omega_1 - \omega_2 - \omega_3} \right) \\
&\quad + \frac{\beta^2(k)}{2(2\omega_k - \omega_1)} \frac{1}{(2\omega_k - \omega_1 - \omega_2 - \omega_3)} \frac{\partial^2}{\partial k^2} \frac{1}{2\omega_k - \omega_1 - \omega_2} \\
&= + \frac{\beta(k)}{2} \left(\frac{\partial}{\partial k} \frac{\beta(k)}{2\omega_k - \omega_1} \right) \left(\frac{1}{2\omega_k - \omega_1 - \omega_2} \frac{\partial}{\partial k} \frac{1}{2\omega_k - \omega_1 - \omega_2 - \omega_3} \right) \\
&\quad + \frac{\beta(k)}{2} \left(\frac{\partial}{\partial k} \frac{\beta(k)}{2\omega_k - \omega_1} \right) \left(\frac{\partial}{\partial k} \frac{1}{(2\omega_k - \omega_1 - \omega_2)(2\omega_k - \omega_1 - \omega_2 - \omega_3)} \right) \\
&\quad + \frac{\beta^2(k)}{2(2\omega_k - \omega_1)} \frac{\partial}{\partial k} \frac{1}{2\omega_k - \omega_1 - \omega_2 - \omega_3} \frac{\partial}{\partial k} \frac{1}{2\omega_k - \omega_1 - \omega_2}.
\end{aligned}$$

Therefore

$$\begin{aligned}
T(\omega_k) &= T_1 + T_2 + T' \\
&= - \frac{\beta(k)}{2} \frac{1}{(2\omega_k - \omega_1 - \omega_2)(2\omega_k - \omega_1 - \omega_2 - \omega_3)} \frac{\partial^2}{\partial k^2} \frac{\beta(k)}{2\omega_k - \omega_1} \\
&\quad - \frac{\beta(k)}{2} \frac{1}{2\omega_k - \omega_1 - \omega_2 - \omega_3} \frac{\partial^2}{\partial k^2} \frac{\beta(k)}{(2\omega_k - \omega_1)(2\omega_k - \omega_1 - \omega_2)} \\
&\quad + \frac{\beta^2(k)}{2(2\omega_k - \omega_1)(2\omega_k - \omega_1 - \omega_2 - \omega_3)} \frac{\partial^2}{\partial k^2} \frac{1}{2\omega_k - \omega_1 - \omega_2} \\
&= - \frac{\beta(k)}{(2\omega_k - \omega_1 - \omega_2)(2\omega_k - \omega_1 - \omega_2 - \omega_3)} \frac{\partial^2}{\partial k^2} \frac{\beta(k)}{2\omega_k - \omega_1} \\
&\quad - \frac{\beta(k)}{2\omega_k - \omega_1 - \omega_2 - \omega_3} \left(\frac{\partial}{\partial k} \frac{\beta(k)}{2\omega_k - \omega_1} \right) \left(\frac{\partial}{\partial k} \frac{1}{2\omega_k - \omega_1 - \omega_2} \right) \\
&= - \frac{\beta(k)}{2\omega_k - \omega_1 - \omega_2 - \omega_3} \frac{\partial}{\partial k} \frac{1}{2\omega_k - \omega_1 - \omega_2} \frac{\partial}{\partial k} \frac{\beta(k)}{2\omega_k - \omega_1}.
\end{aligned}$$

Combining the above results, we obtain

$$\begin{aligned}
\mathcal{I}'(\omega_1, \omega_2, \omega_3) &= I_1(\omega_k) + T(\omega_k) - I_1(-\omega_k) - T(-\omega_k) \\
&= \frac{\beta^4(k)(4\omega_k - \omega_1 - \omega_3)}{(2\omega_k - \omega_1)(2\omega_k + \omega_2)(2\omega_k - \omega_3)(2\omega_k - \omega_1 - \omega_2 - \omega_3)} \\
&\quad - \frac{\beta^4(k)(4\omega_k + \omega_1 + \omega_3)}{(2\omega_k + \omega_1)(2\omega_k - \omega_2)(2\omega_k + \omega_3)(2\omega_k + \omega_1 + \omega_2 + \omega_3)} \\
&\quad - \frac{\beta(k)}{2\omega_k - \omega_1 - \omega_2 - \omega_3} \frac{\partial}{\partial k} \frac{1}{2\omega_k - \omega_1 - \omega_2} \frac{\partial}{\partial k} \frac{\beta(k)}{2\omega_k - \omega_1} \\
&\quad - \frac{\beta(k)}{2\omega_k + \omega_1 + \omega_2 + \omega_3} \frac{\partial}{\partial k} \frac{1}{2\omega_k + \omega_1 + \omega_2} \frac{\partial}{\partial k} \frac{\beta(k)}{2\omega_k + \omega_1},
\end{aligned}$$

and

$$\mathcal{S} = \frac{1}{6} \sum_{\mathcal{P}(\omega_1, \omega_2, \omega_3)} \mathcal{I}'(\omega_1, \omega_2, \omega_3) \quad (\text{B24})$$

We now proceed to compute the general four-wave-mixing third order susceptibility $\chi^{(3)}(\omega_1, \omega_2, \omega_3)$ which is defined by:

$$\chi^{(3)}(\omega_1, \omega_2, \omega_3) = \frac{2e^4 n_0}{\hbar^3} \frac{1}{L} \sum_k \mathcal{S}. \quad (\text{B25})$$

For infinite chains, the summation is replaced by the integral:

$$\begin{aligned}
\chi^{(3)}(\omega_1, \omega_2, \omega_3) &= \frac{2e^4 n_0}{\hbar^3} \int_{-\frac{\pi}{2a}}^{\frac{\pi}{2a}} \mathcal{S} \frac{dk}{2\pi} = \frac{2e^4 n_0}{\pi \hbar^3} \int_0^{\frac{\pi}{2a}} \mathcal{S} dk \\
&= \frac{1}{6} \sum_{\mathcal{P}(\omega_1, \omega_2, \omega_3)} \frac{2e^4 n_0}{\pi \hbar^3} \int_0^{\frac{\pi}{2a}} \mathcal{I}'(\omega_1, \omega_2, \omega_3) dk \\
&:= \sum_{\mathcal{P}(\omega_1, \omega_2, \omega_3)} \chi(\omega_1, \omega_2, \omega_3).
\end{aligned} \quad (\text{B26})$$

We first recall:

$$\omega_k = \frac{\epsilon(k)}{\hbar}, \quad (\text{B27})$$

$$\epsilon(k) = \sqrt{[2t_0 \cos(ka)]^2 + [\Delta \sin(ka)]^2}, \quad (\text{B28})$$

$$\beta(k) = -\frac{\Delta t_0 a}{\epsilon^2(k)}. \quad (\text{B29})$$

Furthermore, we define the following quantities:

$$\delta = \frac{\Delta}{2t_0}. \quad (\text{B30})$$

$$\chi_0^{(3)} = \frac{8 e^4 n_0 a^3}{45 \pi \Delta^3 \delta^3}, \quad (\text{B31})$$

$$z_i = \frac{\hbar \omega_i}{2\Delta}, \quad \text{for } i = 1, 2, 3, \quad (\text{B32})$$

Let us introduce change of variable:

$$x = \frac{\hbar \omega_k}{\Delta}. \quad (\text{B33})$$

Then for $0 < k < \frac{\pi}{2a}$, we have:

$$\frac{dx}{dk} = -\frac{a \sqrt{(1 - \delta^2 x^2)(x^2 - 1)}}{\delta x}, \quad (\text{B34})$$

and hence

$$\begin{aligned} \chi(\omega_1, \omega_2, \omega_3) &= -\chi_0^{(3)} \frac{15}{1024} \int_1^{1/\delta} \frac{x dx}{\sqrt{(1 - \delta^2 x^2)(x^2 - 1)}} \\ &\quad \left\{ \frac{(2x - z_1 - z_3)}{x^8(x - z_1)(x + z_2)(x - z_3)(x - z_1 - z_2 - z_3)} \right. \\ &\quad + \frac{(2x + z_1 + z_3)}{x^8(x + z_1)(x - z_2)(x + z_3)(x + z_1 + z_2 + z_3)} \\ &\quad + \left(\frac{2\delta}{a} \right)^2 \frac{1}{x^2(x - z_1 - z_2 - z_3)} \frac{\partial}{\partial k} \frac{1}{x - z_1 - z_2} \frac{\partial}{\partial k} \frac{1}{x^2(x - z_1)} \\ &\quad \left. + \left(\frac{2\delta}{a} \right)^2 \frac{1}{x^2(x + z_1 + z_2 + z_3)} \frac{\partial}{\partial k} \frac{1}{x + z_1 + z_2} \frac{\partial}{\partial k} \frac{1}{x^2(x + z_1)} \right\} \\ &= \chi_0^{(3)} \frac{15}{1024} \int_1^{1/\delta} \frac{x dx}{\sqrt{(1 - \delta^2 x^2)(x^2 - 1)}} \\ &\quad \left\{ -\frac{(2x - z_1 - z_3)}{x^8(x - z_1)(x + z_2)(x - z_3)(x - z_1 - z_2 - z_3)} \right. \\ &\quad - \frac{(2x + z_1 + z_3)}{x^8(x + z_1)(x - z_2)(x + z_3)(x + z_1 + z_2 + z_3)} \\ &\quad + \left(\frac{2\delta}{a} \right)^2 \frac{1}{x - z_1 - z_2} \left(\frac{\partial}{\partial k} \frac{1}{x^2(x - z_1)} \right) \left(\frac{\partial}{\partial k} \frac{1}{x^2(x - z_1 - z_2 - z_3)} \right) \\ &\quad \left. + \left(\frac{2\delta}{a} \right)^2 \frac{1}{x + z_1 + z_2} \left(\frac{\partial}{\partial k} \frac{1}{x^2(x + z_1)} \right) \left(\frac{\partial}{\partial k} \frac{1}{x^2(x + z_1 + z_2 + z_3)} \right) \right\} \end{aligned} \quad (\text{B35})$$

By (B34), we have

$$\begin{aligned}
\chi(\omega_1, \omega_2, \omega_3) &= \chi_0^{(3)} \frac{15}{1024} \int_1^{1/\delta} \frac{xdx}{\sqrt{(1-\delta^2x^2)(x^2-1)}} \\
&\quad \left\{ \frac{(2x-z_1-z_3)}{x^8(x-z_1)(x+z_2)(x-z_3)(x-z_1-z_2-z_3)} \right. \\
&\quad - \frac{(2x+z_1+z_3)}{x^8(x+z_1)(x-z_2)(x+z_3)(x+z_1+z_2+z_3)} \\
&\quad + \frac{4(1-\delta^2x^2)(x^2-1)}{x^2(x-z_1-z_2)} \left(\frac{\partial}{\partial x} \frac{1}{x^2(x-z_1)} \right) \left(\frac{\partial}{\partial x} \frac{1}{x^2(x-z_1-z_2-z_3)} \right) \\
&\quad \left. + \frac{4(1-\delta^2x^2)(x^2-1)}{x^2(x+z_1+z_2)} \left(\frac{\partial}{\partial x} \frac{1}{x^2(x+z_1)} \right) \left(\frac{\partial}{\partial x} \frac{1}{x^2(x+z_1+z_2+z_3)} \right) \right\} \\
&= \chi_0^{(3)} \frac{15}{1024} \int_1^{1/\delta} \frac{xdx}{\sqrt{(1-\delta^2x^2)(x^2-1)}} \\
&\quad \left\{ \frac{(2x-z_1-z_3)}{x^8(x-z_1)(x+z_2)(x-z_3)(x-z_1-z_2-z_3)} \right. \\
&\quad - \frac{(2x+z_1+z_3)}{x^8(x+z_1)(x-z_2)(x+z_3)(x+z_1+z_2+z_3)} \\
&\quad + \frac{4(1-\delta^2x^2)(x^2-1)}{x^8(x-z_1-z_2)} \frac{(3x-2z_1)(3x-2(z_1+z_2+z_3))}{(x-z_1)^2(x-z_1-z_2-z_3)^2} \\
&\quad \left. + \frac{4(1-\delta^2x^2)(x^2-1)}{x^8(x+z_1+z_2)} \frac{(3x+2z_1)(3x+2(z_1+z_2+z_3))}{(x+z_1)^2(x+z_1+z_2+z_3)^2} \right\} \\
&:= I_1(\omega_1, \omega_2, \omega_3) + I_2(\omega_1, \omega_2, \omega_3) + I_3(\omega_1, \omega_2, \omega_3) + I_4(\omega_1, \omega_2, \omega_3),
\end{aligned} \tag{B36}$$

With the aid of Mathematica, we find that

$$\begin{aligned}
J &= \sum_{\mathcal{P}(\omega_1, \omega_2, \omega_3)} (I_1(\omega_1, \omega_2, \omega_3) + I_2(\omega_1, \omega_2, \omega_3)) \\
&= \frac{15\chi_0^{(3)}}{128(z_1+z_2)(z_2+z_3)(z_3+z_1)} \int_1^{1/\delta} \frac{dx}{\sqrt{(1-\delta^2x^2)(x^2-1)}} \\
&\quad \frac{1}{x^8} \left(\sum_{i=1}^3 \frac{z_i^3}{x^2-z_i^2} - \frac{(z_1+z_2+z_3)^3}{x^2-(z_1+z_2+z_3)^2} \right)
\end{aligned} \tag{B37}$$

and

$$\begin{aligned}
K &= \sum_{\mathcal{P}(\omega_1, \omega_2, \omega_3)} (I_3(\omega_1, \omega_2, \omega_3) + I_4(\omega_1, \omega_2, \omega_3)) \\
&= \frac{15\chi_0^{(3)}}{128} \int_1^{1/\delta} \frac{\sqrt{(1-\delta^2 x^2)(x^2-1)} dx}{x^8} \\
&\quad \sum_{i=1}^3 \frac{(z_1+z_2)^5(z_1+z_2-2z_3)}{z_1^2 z_2^2 z_3^2 (x^2 - (z_1+z_2)^2)} \\
&\quad + \frac{-(z_1+z_2+z_3)^3((z_1+z_2+z_3)^4(z_1 z_2 + z_2 z_3 + z_3 z_1) - z_1 z_2 z_3(8(z_1+z_2+z_3)^3 + 7z_1 z_2 z_3))}{z_1^2 z_2^2 z_3^2 (z_1+z_2)(z_2+z_3)(z_3+z_1)(x^2 - (z_1+z_2+z_3)^2)} \\
&\quad + \frac{(z_1+z_2+z_3)^3((z_1+z_2+z_3)^3 + z_1 z_2 z_3)(x^2 + (z_1+z_2+z_3)^2)}{z_1 z_2 z_3 (z_1+z_2)(z_2+z_3)(z_3+z_1)(x^2 - (z_1+z_2+z_3)^2)^2} \\
&\quad + \sum_{i=1}^3 \frac{-z_1^2(z_1 - 2(z_2+z_3))(x^2 + z_1^2)}{z_2 z_3 (z_2+z_3)(x^2 - z_1^2)^2} \\
&\quad + \sum_{i=1}^3 \frac{-z_1^2(z_1^2(z_2+z_3) - 8z_2 z_3(z_2+z_3) - 2z_1(z_2+z_3)^2 + 7z_1 z_2 z_3)}{z_2^2 z_3^2 (z_2+z_3)(x^2 - z_1^2)}
\end{aligned} \tag{B38}$$

Using integration by parts, we obtain

$$\begin{aligned}
L &= \int_1^{1/\delta} \frac{\sqrt{(1-\delta^2 x^2)(x^2-1)} dx}{x^8} \frac{x^2+z^2}{(x^2-z^2)^2} \\
&= \int_1^{1/\delta} \frac{\sqrt{(1-\delta^2 x^2)(x^2-1)} dx}{x^8} \frac{1}{x^2-z^2} \left(-8 + \frac{x^2(1+\delta^2-2\delta^2 x^2)}{(1-\delta^2 x^2)(x^2-1)} \right) \\
&= \int_1^{1/\delta} \frac{\sqrt{(1-\delta^2 x^2)(x^2-1)} dx}{x^8} \frac{1}{x^2-z^2} \left(-7 + \frac{1-\delta^2 x^4}{(1-\delta^2 x^2)(x^2-1)} \right)
\end{aligned} \tag{B39}$$

Therefore,

$$\begin{aligned}
K &= \frac{15\chi_0^{(3)}}{128} \int_1^{1/\delta} \frac{\sqrt{(1-\delta^2x^2)(x^2-1)}dx}{x^8} \\
&\quad \sum_{i=1}^3 \frac{(z_1+z_2)^5(z_1+z_2-2z_3)}{z_1^2z_2^2z_3^2(x^2-(z_1+z_2)^2)} \\
&\quad + \frac{-(z_1+z_2+z_3)^6}{z_1^2z_2^2z_3^2(x^2-(z_1+z_2+z_3)^2)} \\
&\quad + \frac{(z_1+z_2+z_3)^3((z_1+z_2+z_3)^3+z_1z_2z_3)}{z_1z_2z_3(z_1+z_2)(z_2+z_3)(z_3+z_1)} \frac{1-\delta^2x^4}{(x^2-(z_1+z_2+z_3)^2)(1-\delta^2x^2)(x^2-1)} \\
&\quad + \sum_{i=1}^3 \frac{-z_1^2(z_1-2(z_2+z_3))}{z_2z_3(z_2+z_3)(x^2-z_1^2)} \frac{1-\delta^2x^4}{(1-\delta^2x^2)(x^2-1)} \\
&\quad + \sum_{i=1}^3 \frac{-z_1^2(z_1^2-2z_1(z_2+z_3)+6z_2z_3)}{z_2^2z_3^2(x^2-z_1^2)}
\end{aligned} \tag{B40}$$

Finally,

$$\begin{aligned}
\chi^{(3)} &= J + K \\
&= \frac{15\chi_0^{(3)}}{128} \int_1^{1/\delta} \frac{dx}{x^8 \sqrt{(1-\delta^2x^2)(x^2-1)}} \\
&\quad \left\{ \frac{Z^3}{z_1z_2z_3\sigma} \frac{Z^3 - (Z^3 + z_1z_2z_3)\delta^2x^4}{x^2 - Z^2} + \sum_{i=1}^3 \frac{z_i^3}{\sigma(x^2 - z_i^2)} + \sum_{P(z_1, z_2, z_3)} \frac{z_1^2(-z_1 + 2(z_2 + z_3))(1 - \delta^2x^4)}{2z_2z_3(z_2 + z_3)(x^2 - z_1^2)} \right\} \\
&\quad + \frac{15\chi_0^{(3)}}{128} \int_1^{1/\delta} \frac{\sqrt{(1-\delta^2x^2)(x^2-1)}dx}{x^8} \\
&\quad \left\{ \sum_{P(z_1, z_2, z_3)} \left(\frac{(z_1+z_2)^5(z_1+z_2-2z_3)}{2z_1^2z_2^2z_3^2(x^2-(z_1+z_2)^2)} + \frac{-z_1^2(z_1^2-2z_1(z_2+z_3)+6z_2z_3)}{2z_2^2z_3^2(x^2-z_1^2)} \right) - \frac{Z^6}{z_1^2z_2^2z_3^2(x^2-Z^2)} \right\}
\end{aligned} \tag{B41}$$

where

$$\sigma := (z_1+z_2)(z_2+z_3)(z_3+z_1), \tag{B42}$$

and

$$Z := z_1 + z_2 + z_3. \tag{B43}$$

We now consider the case $\delta \rightarrow 0$.

Using the results in Appendix A, we obtain

$$\begin{aligned}
\chi^{(3)} = & \frac{15\chi_0^{(3)}}{128} \left\{ \frac{Z^6}{z_1 z_2 z_3 \sigma} L(4, Z) - \frac{Z^6}{z_1^2 z_2^2 z_3^2} M(4, Z) + \sum_{i=1}^3 \frac{z_i^3}{\sigma} L(4, z_i) \right. \\
& + \left. \sum_{P(z_1, z_2, z_3)} \frac{z_1^2 (-z_1 + 2(z_2 + z_3))}{2z_2 z_3 (z_2 + z_3)} L(4, z_1) \right\} \\
& + \frac{15\chi_0^{(3)}}{128} \left\{ \sum_{P(z_1, z_2, z_3)} \frac{(z_1 + z_2)^5 (z_1 + z_2 - 2z_3)}{2z_1^2 z_2^2 z_3^2} M(4, z_1 + z_2) \right. \\
& + \left. \frac{-z_1^2 (z_1^2 - 2z_1 (z_2 + z_3) + 6z_2 z_3)}{2z_2^2 z_3^2} M(4, z_1) \right\}
\end{aligned} \tag{B44}$$

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FIGURES

FIG. 1. The Feynman diagram for $\chi^{(3)}(-\Omega, -\mathbf{K}; \omega_1, \mathbf{k}_1, \omega_2, \mathbf{k}_2, \omega_3, \mathbf{k}_3)$, where $\Omega = \omega_1 + \omega_2 + \omega_3$, $\mathbf{K} = \mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3$.

FIG. 2. (Color) The magnitude of four-wave-mixing(FMW) $\chi^{(3)}(-\Omega; \omega_1, \omega_2, \omega_3)$ under SSH model is in unit of 10^{-8} esu. Z_i is defined by Eq.(3.5).

FIG. 3. The hyperpolarizabilities under the SSH model for frequency region $0 < z < 2.0$, where $z \equiv \hbar\omega/(2\Delta)$: DCKerr (top left), DCSHG (top right), IDIR (bottom left) and EFIOR (bottom right).

FIG. 4. The hyperpolarizabilities under the SSH model for non-resonant region: EFIOR (real line), DCKerr (dotted line), IDIR (long dashed line), DCSHG (dashed line) and THG (dot-dashed line).

FIG. 5. The hyperpolarizabilities under the TLM model for non-resonant region: $\chi_{TLM}^{(3)}(-3\omega; \omega, \omega, \omega)$ (real line) versus $\chi_{TLM}^{(3)}(\omega; \omega, \omega, -3\omega)$ (long dashed line), where $Z \equiv \hbar\omega/2\Delta$.

FIG. 6. The total(real line), intraband contribution(dot dashed line) and interband contribution (long dashed line) of hyperpolarizabilities under TLM models - χ_{TLM}^{DCKerr} (top left), χ_{TLM}^{DCSHG} (top right), χ_{TLM}^{EFIOR} (middle left), χ_{TLM}^{IDIR} (middle right) and χ_{TLM}^{THG} (bottom left).











