The analytical solutions for the third-harmonic generation (THG) on infinite chains in both Su-Shrieffer-Heeger (SSH) and Takayama-Lin-Liu-Maki (TLM) models of trans-polyacetylene are obtained through the scheme of dipole-dipole (DD) correlation. They are not equivalent to the results obtained through static current-current ($J_0 J_0$) correlation or under polarization operator $\hat{P}$. The van Hove singularity disappears exactly in the analytical forms, showing that the experimentally observed two-photon absorption peak (TPA) in THG may not be directly explained by the single electron models.

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I. INTRODUCTION

The nonlinear optical (NLO) properties on conjugated polymers have always been received wide interest for study. Experimentally observed nonlinear phenomenon in conducting polymers, such as photoinduced absorption, bleaching, photoluminescence, ultrafast optical process and exciton behaviors, have already encouraged the theorists for the possible explanations. In the early 90s, the large third order susceptibility ($\chi^{(3)}$) of trans-polyacetylene (PA) have been observed experimentally and have been received wide explanations theoretically. For a long time, the origin of the experimentally observed two-photon absorption peak (TPA) receives persistent discussions in theory. However, the various numerical approaches from dipole formalism, such as the results by Yu and Su from Butcher-Bloembergen-Shen dipole formula, the results by Wu and Sun from Genkins-Mednis approach and the results by Shuai and Brédas from sum-over-state(SOS) Orr-Ward formalism, have shown that the TPA is no longer existing if the damping in the energy is considered. Therefore, the two-photon cusp under the current schemes is considered to be a van Hove singularity caused by the singular density of states (DOS) on the Fermi surface in one-dimensional (1d) systems. The fact of the nonresonant property in two-photon cusp is also noticed by Wu in his current formulations. However, besides the difficulty in explaining this TPA under current formulas, there exists another obvious difficulty in theory — apparent zero frequency divergence (ZFD) in the definition of the current formalism. This problem actually was realized by Dakhnovskii and Pronin in their computations based on SSH model. Unfortunately, the results of $\chi^{(3)}$ obtained from SSH model returns TLM model if the process of linearization procedures is made under $J_0 J_0$ scheme.

Because of the apparent divergence difficulties in current formulas, practically, intense studies based on dipole-dipole (DD) correlation have been carried out to obtain the physical pictures of TPA in $\chi^{(3)}$ of trans-polyacetylene. On one hand, the weakly correlated and single electron theories are applied in the numerical dipole computations, thus, the finite size effect and the lifetime assumption are seemingly good in generating a peak at exact position of TPA; On the other hand, the strongly correlated electron theories have also been applied to short chains, Soos and Rameseha obtained the TPA based on Pariser-Parr-Pople (PPP) models, but it is shifted too low in frequency and has too small an intensity relative to the experimental peak. Recent work by Guo and Mazumdar shows that this TPA could be interpreted as a three-photon resonance based on extended Hubbard Hamiltonian. Whether or not the weakly correlated theory or even the single electron models such as SSH and TLM models are still suitable in describing TPA still remains as a question. Meanwhile, in obtaining the qualitatively correct result, it was suggested by Etemad and Soos that the attention should be made to the $\chi^{(3)}$ frequency dependences rather than...
magnitudes. It is certainly reasonable in physical point of view since the experiments are more sensitive to detect frequency dependences. Thus, some typical approximations are made in the dipole formula. Substitution of the dipole operator $\hat{D}$ by the polarization operator $\hat{P}$, namely, the dipole approximation has been extensively applied in the nonlinear optical formula, however, $\chi^{(1)}$ computations have shown both quantitatively and qualitatively different results between $\hat{P}$ and dipole operator $\hat{D}$.\[37\] Whether the problem caused by the dipole approximation still existing in $\chi^{(3)}$ is still under our concern. Furthermore, the static dipole formulas and static current formulas are conventionally considered to be equivalent.\[13,24,30\] However, as we pointed out in a recent work,\[37\] it has ZFD problem in the static current formalism when the gauge phase factor is ignored, the static formalism under two gauges should not return the same results under the exact same basis of unperturbed wave functions.\[37\] Whether this nonequivalence between $J_0J_0$ and $DD$ correlations existing in the specific case of $\chi^{(3)}$ of trans-polyacetylene is another interest topic. Although the qualitative features have already been reported in the numerical solutions based on DD correlation,\[17,24\] the exact analytical solutions from the dipole formulas of $\chi^{(3)}$ have not been obtained previously. The analytical results, if obtained, will be very helpful for us to directly check all above concerns and give more information.

Fortunately, both SSH and TLM models are single electron models and can be exactly solvable for the nonlinear susceptibilities under perturbated schemes, although the efforts will be no doubt paid to cumbersome computations. After choosing the long wavelength approximation which are conventionally used previously,\[15–24,37\] we could directly compared those analytical results between two gauges for both models. The paper is organized as follows, we will first discuss the SSH Hamiltonian in Sec.II.A. The analytical form of $\chi$ will be obtained and compared with the analytical form by the polarization operator $\hat{P}$, the qualitative and quantitative difference between the results under $\hat{D}$ and $\hat{P}$ are outlined. In Sec.III, we will obtain the exact analytical forms under $DD$ correlation for SSH models in Sec.II.B. In Sec.II.C, we will obtain the results under the polarization operator $\hat{P}$, the qualitative and quantitative difference between the results under $\hat{D}$ and $\hat{P}$ are outlined. In Sec.III, we will obtain the exact analytical forms under $DD$ correlation for TLM models and directly compared with those under $J_0J_0$ correlation. The discussions on the possible implications of this work are made in Sec.IV and a brief conclusion is made in Sec.V.

II. THIRD ORDER SUSCEPTIBILITIES FOR SSH MODELS UNDER DIPOLE FORMULA

A. SSH Hamiltonian in real and momentum spaces

Based on periodic tight-binding-approximations, The SSH Hamiltonian is given by:

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

(2.1)

where $t_0$ is the transfer integral between the nearest-neighbor sites, $\Delta$ is the gap parameter and $\hat{C}^\dagger_{l,s}(\hat{C}_{l,s})$ creates (annihilates) an $\pi$ electron at site $l$ with spin $s$. In continuum limitation, above SSH model will give the TLM model.\[27\] For the SSH model, each site is occupied by one electron.

Under the $DD$ correlation, the interaction Hamiltonian is expressed by $\hat{H}_{E \cdot r} = -e \mathbf{E} \cdot \mathbf{r} = -\mathbf{D} \cdot \mathbf{E}$, To provide the periodic property and to avoid the ill-definition of position operator $\mathbf{r}$, we should express the position operator $\mathbf{r}$ under the Bloch states: $|n, \mathbf{k} > = u_{n,k}(\mathbf{r}) e^{i \mathbf{k} \cdot \mathbf{r}}$, where $n$ and $\mathbf{k}$ are band index and crystal momentum correspondingly, $u_{n,k}(\mathbf{r})$ is the periodic function under the translation of lattice vector.\[38\] Thus, we obtain:

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

(2.2)

and

$$\Omega_{n,n'}(\mathbf{k}) = \frac{i}{v} \int_{v} u_{n,k}(\mathbf{r}) \nabla_k u_{n',k}(\mathbf{r}) d\mathbf{r},$$

(2.3)

where $v$ is unit cell volume.

We change Hamiltonian Eq.(2.1) into the momentum space by applying the following consecutive transformations:

$$\begin{cases}
\hat{C}_{l,s} = \frac{1}{\sqrt{N}} \sum_{-\frac{\pi}{2} \leq k \leq \frac{\pi}{2}} (\hat{C}^w_{k,s} + \hat{C}^c_{k,s}) e^{i k R_{l,s}}, \\
\hat{C}^\dagger_{l,s} = \frac{1}{\sqrt{N}} \sum_{-\frac{\pi}{2} \leq k \leq \frac{\pi}{2}} (\hat{C}^w_{k,s} - \hat{C}^c_{k,s}) e^{i k R_{l,s}},
\end{cases}$$

(2.4)
and

\[ \begin{align*}
\hat{a}^v_{k,s} &= -i\gamma_k \hat{C}^v_{k,s} + \xi_k \hat{C}^c_{k,s}, \\
\hat{a}^c_{k,s} &= i\xi_k \hat{C}^v_{k,s} + \gamma_k \hat{C}^c_{k,s},
\end{align*} \tag{2.5} \]

with

\[ \begin{align*}
\gamma_k &= \frac{1}{\sqrt{2}} \sqrt{1 + \frac{2t_0 \cos(ka)}{\varepsilon(k)}}, \\
\xi_k &= \frac{\text{sgn}(k)}{\sqrt{2}} \sqrt{1 - \frac{2t_0 \cos(ka)}{\varepsilon(k)}},
\end{align*} \tag{2.6} \]

where

\[ \varepsilon(k) = \sqrt{[2t_0 \cos(ka)]^2 + [\Delta \sin(ka)]^2}, \tag{2.7} \]

and \( \hat{a}^{c,v}_{k,s}(t) \) and \( \hat{a}^{c,v}_{k,s}(t) \) are the excitations of electrons in the conduction band and the valence band with momentum \( k \) and spin \( s \), \( R_l \) and \( R_{l_e} \) are odd and even position defined by

\[ R_l = la + (-1)^l u, \tag{2.8} \]

If we choose the spinor description \( \hat{\psi}^\dagger_{k,s}(t) = (\hat{a}^c_{k,s}(t), \hat{a}^v_{k,s}(t)) \) and apply the long wavelength approximation, \[28\] SSH Hamiltonian including \( \mathbf{E} \cdot \mathbf{r} \) in momentum space is described by:

\[ \hat{H}_{SSH}(k,t) = \hat{H}_0 + \hat{H}_{\mathbf{E} \cdot \mathbf{r}}, \tag{2.9} \]

where

\[ \hat{H}_0 = \sum_{-\pi \leq k \leq \pi, s} \varepsilon(k) \hat{\psi}^\dagger_{k,s}(t) \sigma_3 \hat{\psi}_{k,s}(t) \tag{2.10} \]

and

\[ \hat{H}_{\mathbf{E} \cdot \mathbf{r}} = -\hat{D} \cdot \mathbf{E}_0 e^{i\omega t}. \tag{2.11} \]

By Eq. (2.2), the dipole operator \( \hat{D} \) could be obtained as follows: \[37\]

\[ \hat{D} = e \sum_{-\pi \leq k \leq \pi, s} (\beta(k) \hat{\psi}^\dagger_{k,s} \sigma_2 \hat{\psi}_{k,s} + i \frac{\partial}{\partial k} \hat{\psi}^\dagger_{k,s} \hat{\psi}_{k,s}), \tag{2.12} \]

where

\[ \beta(k) = -\frac{\Delta t_0 a}{\varepsilon^2(k)}, \tag{2.13} \]

is the coefficient related to the interband transition between the conduction and valence bands in a unit cell \( 2a \) and the second term in Eq. (2.12) is related to the intraband transition, \[37\] \( e \) is the electric charge and \( \sigma \) are the Pauli matrices. We have already omitted the relative distortion \( \eta(\equiv 2u/a) \) in this computation since the contribution of \( \eta \) is quite small according to the linear case. \[37\]

**B. Analytical form of \( \chi^{(3)} \) through DD correlation**

Within the semiclassical theory of radiation, \[28 \ 30\] the electrical field is treated classically and the third order susceptibility \( \chi^{(3)} \) is described by: \[28 \ 30\]
\[
\chi^{(3)}(\Omega; \omega_1, \omega_2, \omega_3) = \frac{1}{3!} \left[ \frac{i}{\hbar} \right]^3 \int dr_1 dr_2 dr_3 \int dt_1 dt_2 dt_3 \int dr dt e^{-i k r + i \Omega t} \langle T \hat{D}(r, t) \hat{D}(r_1, t_1) \hat{D}(r_2, t_2) \hat{D}(r_3, t_3) \rangle,
\]

(2.14)

where \( \Omega \equiv - \sum_{i=1}^{3} \omega_i \) and \( T \) is the time-ordering operator with \( \hat{D} \) is a dipole operator.

The third-harmonic generation (THG) is defined by setting \( \omega_1 = \omega_2 = \omega_3 \). Following similar procedures as we have done in the linear computations, \([37]\) by Eq.(2.12) and Eq.(2.14), we obtained the following expression for \( \chi_{SSH}^{THG}(\omega_1) \equiv \chi_{SSH}^{(3)}(-3\omega_1, \omega_1, \omega_1, \omega_1) \):

\[
\chi_{SSH}^{THG}(\omega_1) = \frac{2e^4 n_0}{h^3} \sum_k \int \frac{d\omega}{2\pi} \left\{ (\beta(k)\sigma_2 + i \frac{\partial}{\partial k}) G(k, \omega) \right. \\
(\beta(k)\sigma_2 + i \frac{\partial}{\partial k}) G(k, \omega - \omega_1) \\
(\beta(k)\sigma_2 + i \frac{\partial}{\partial k}) G(k, \omega - 2\omega_1) \\
(\beta(k)\sigma_2 + i \frac{\partial}{\partial k}) G(k, \omega - 3\omega_1) \left\}, \tag{2.15}
\]

where \( \beta(k) \) is defined in Eq.(2.12) and \( n_0 \) is the number of chains in unit cross area and the polymer chains are assumed to be oriented, and Green Function \( G(k, \omega) \) defined as following: \([37]\)

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

(2.16)

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

After tedious derivation, we obtained the following analytical expressions for the third-harmonic generation for the SSH models \( \chi_{SSH}^{THG}(\omega) \):

\[
\chi_{SSH}^{THG}(\omega) = \frac{2e^4 n_0}{h^3} \sum_k \left\{ \frac{\beta_4(k)}{2\omega(2\omega_k + \omega)(2\omega_k + 3\omega)} \\
\frac{\beta_4(k)}{2\omega(2\omega_k - \omega)(2\omega_k - 3\omega)} \\
- \frac{\beta(k)}{(2\omega_k + 3\omega) \frac{\partial}{\partial k}} \left[ \frac{1}{2\omega_k + 2\omega} \frac{\partial}{\partial k} \left[ \frac{\beta(k)}{2\omega_k + \omega} \right] \right] \\
- \frac{\beta(k)}{(2\omega_k - 3\omega) \frac{\partial}{\partial k}} \left[ \frac{1}{2\omega_k - 2\omega} \frac{\partial}{\partial k} \left[ \frac{\beta(k)}{2\omega_k - \omega} \right] \right] \right\}, \tag{2.17}
\]

The above expression Eq.(2.17) are almost identical to Eq.(A13) in Agrawal et al.’s work \([32]\) except one more term (last term in (A13)), and with the following substitution is applied in Eq.(A13):

\[
\begin{align*}
\Omega_{ev} &= \Omega_{cc} = 0, \\
\Omega_{ce} &= -\Omega_{ec} = \beta(k)
\end{align*}
\]

(2.18)

Eq.(2.17) is also quite similar to Eq.(11) in Wu and Sun’s result \([20]\) based on Genkins-Mednis approach \([31]\) with the above substitution (2.18) made and if the symmetric procedures on the negative frequency term should be applied.

For infinite chains, we could separate two full derivative terms of \( k \) from Eq.(2.17) as follows:

\[
I_T = \frac{2e^4 n_0}{h^3} \sum_k \left\{ - \frac{\partial}{\partial k} \left[ \frac{\beta(k)}{(2\omega_k + 3\omega)(2\omega_k + 2\omega) \frac{\partial}{\partial k} \left[ \frac{\beta(k)}{2\omega_k + \omega} \right]} \right] \\
- \frac{\partial}{\partial k} \left[ \frac{\beta(k)}{(2\omega_k - 3\omega)(2\omega_k - 2\omega) \frac{\partial}{\partial k} \left[ \frac{\beta(k)}{2\omega_k - \omega} \right]} \right] \right\}, \tag{2.19}
\]
If we consider following two facts in actual optical process: (i). The velocity on the Fermi surface $\nabla_k \varepsilon(k)|_{k=\pm \frac{\pi}{a}} = 0$. (ii). The life time of the states, thus, we should include the damping in the process, that is, $\omega_k \to \omega_k + i\epsilon_k$ and $\epsilon_k \neq 0$. The above full derivative term $I_T$ after integral of $k$ then is 0 for the infinite chains. Eq.(2.17) can be simplified as following:

$$
\chi_{SSH}^{THG}(\omega) = \chi_0^{(3)} \frac{45}{128} \int_1^4 \frac{dx}{(1 - \delta x^2)(x^2 - 1)^{\frac{1}{2}}} \left\{ 37 - 24(1 + \delta^2)x^2 + 12\delta^2x^4 \right\} \\
+ \frac{9}{8} \frac{243 - 216(1 + \delta^2)x^2 + 188\delta^2x^4}{x^8(x^2 - (3z)^2)} \\
= \chi_0^{(3)} \frac{5}{1024z^8} \left\{ -336E(\frac{\pi}{2}, \sqrt{1 - \delta^2}) + 120z^2\delta^2F(\frac{\pi}{2}, \sqrt{1 - \delta^2}) \\
+ \frac{8z^2}{5} \left[ (-12 + 7\delta^2 - 12\delta^4)E(\frac{\pi}{2}, \sqrt{1 - \delta^2}) + 6(1 + \delta^2)\delta^2F(\frac{\pi}{2}, \sqrt{1 - \delta^2}) \\
+ 9(37 - 24(1 + \delta^2)z^2 + 12\delta^2z^4)g(z) + (3 - 24(1 + \delta^2)z^2 + 188\delta^2z^4)g(3z) \right] \right\}, \quad (2.20)
$$

and

$$
g(mz) = \frac{n_m \delta}{\delta^2 - 1} \Pi(\frac{\pi}{2}, n_m, \sqrt{1 - \delta^2}), \quad n_m = \frac{1 - \delta^2}{(\delta mz)^2 - 1}, \quad (2.21)
$$

where $\chi_0^{(3)} = \frac{8}{45} \frac{e^4n_0(2t_0a)^3}{\Delta^6}$, $x = \hbar \omega_k/\Delta$, $z = \hbar \omega/(2\Delta)$ and $\delta = \Delta/(2t_0)$. $F, E, \Pi$ are first, second and third kind of complete elliptical integrals. There is exactly no two photon cusp in Eq.(2.20). This result is consistent with Yu and Su, Shuai and Brédas’ results. And it is quite different from the expression obtained from $J_0J_0$ correlation, which shows the following form for $\chi_{SSHjj}^{THG}$ of SSH models:

$$
\chi_{SSHjj}^{THG} = B \chi^3 \left\{ (5 - 8z^2(1 + \delta^2) + 20z^4\delta^2)g(z) - 8[1 - 4z^2(1 + \delta^2) + 16z^4\delta^2]g(2z) \\
+ [3 - 24z^2(1 + \delta^2) + 188z^4\delta^2]g(3z) - 8\delta^2z^4E(\frac{\pi}{2}, \sqrt{1 - \delta^2}) \right\}, \quad (2.22)
$$

where $B = 5\chi_0^{(3)}/(1024z^8)$, same as the constant as defined in Eq.(2.20) and $g(z)$ is defined by Eq.(2.21). We should point out that the elliptical form of Eq.(2.22) is the exact the same as the integral form of Eq.(11) in Wu and Sun’s result, which was derived from the incomplete Genkins-Mednis approach. The disappearance of ZFD under static current schemes is somewhat puzzling or simply should be understood as coincidence for the specific SSH model. As we pointed out in a recent work, the ignorance of gauge phase factor in the static current formula will cause ZFD in the susceptibilities and non-equivalent result from the dipole formula. The derivation in the previous current work does not consider the gauge phase factor’s effect, it will cause ZFD even for linear case if following a straightforward computations.

Obviously, we observe the qualitatively difference for results under DD (Eq.(2.20)) and $J_0J_0$ (Eq.(2.22)) correlation especially for $z = 1/2$ and $z = 1$. The inequivalence could be understood by the ignore of the gauge phase factor in optical response theory.

Let $x \to x + i\epsilon$ in the integral of Eq.(2.20), the comparison graph of absolute values between Eq.(2.20) and Eq.(2.22) for the SSH models are plotted in Fig.1 with the following parameters chosen for trans-polyacetylene: $t_0 = 2.5eV$, $\Delta = 0.9eV$, $n_0 = 3.2 \times 10^{14} cm^{-2}$, $a = 1.22Å$ and $\epsilon \sim 0.03$, we have $\delta = 0.18$ and $\chi_0^{(3)} \approx 1.0 \times 10^{-10}$ esu.
Fig. 1. Computed DD values (solid line) vs. $J_0 J_0$ values (dashed line) of $|\chi^{THG}_{SSH}(\omega)|$ with $z \equiv \hbar \omega/(2\Delta)$ and $\epsilon = 0.03$.

From the graph, we find another very obvious peak at $z = 1$ at a ratio of 1/10 of the peak at $z = 1/3$, which is also different comparing with the previous theoretical computations. However, this peak has not been reported by the experiments because it is out of the scanning range of photon energy.

C. Results under polarization operator $\hat{P}$

In a recent work, we discussed the different results caused by polarization operator $\hat{P}$ in linear response. The polarization operator $\hat{P}$ is extensively applied in the NLO theory. Based on SSH model, we can do a comparison of $\chi^{THG}_{SSH}$ between $\hat{D}$ and $\hat{P}$.

The polarization operator $\hat{P}$ is defined in real space as:

$$\hat{P} = \sum_{l} R_i \hat{C}_l^\dagger \hat{C}_l.$$  \hspace{1cm} (2.23)

If the chain region $l$ is going from 1 to $N$, we obtain the unit polarization $\hat{P}_{\text{unit}}(k)$ from the total polarization $\hat{P}_{\text{total}}(k)$ in the momentum space:

$$\hat{P}_{\text{unit}}(k) = \lim_{N \to \infty} \frac{\hat{P}_{\text{total}}(k)}{N} = \frac{e a}{2} \sum_{k,s} \psi_{k,s}^\dagger \sigma_2 \psi_{k,s}$$  \hspace{1cm} (2.24)

Substituting $\hat{D}$ with $\hat{P}$ in Eq.(2.14), we obtain the $\chi^{THG}_{SSH_{P}}$ for SSH models as following for infinite chains:

$$\chi^{THG}_{SSH_{P}} = \chi^{(3)}_{0} \frac{45 \delta^4}{128} \int_{1}^{\frac{1}{1}} \frac{dx}{[(1 - \delta^2 x^2)(x^2 - 1)^2]} \left\{ \frac{1}{x^2 - z^2} - \frac{9}{x^2 - (3z)^2} \right\}$$  \hspace{1cm} (2.25)

The above expression lacks TPA. However, the magnitude is too small compared with results under $\hat{D}$. ($\chi^{THG}_{SSH_{P}}$ from $\hat{P}$ is about $10^{-4}$ of $\chi^{THG}_{SSH}$ from $\hat{D}$ if $\delta = 0.18$ for trans-polyacetylene.) Another peak at $z = 1/(3\delta) \approx 1.85$ will shown up through $\mathbf{P} \cdot \mathbf{E}$, this peak corresponding to the transition from the bottom of valence band to the top of conduction band. This peak in infinite chains seems not to agree with ‘unklapp enhancement’ in the solid states.

While in DD computations, this peak at $z = 1/(3\delta)$ will not be very obvious. The comparison on the absolute value between $\chi^{THG}_{SSH_{P}}$ and $\chi^{THG}_{SSH}$ will be shown in Fig.2. From the graph, the different shapes of curves are quite obvious. Besides the possible ill-definition of polarization operator $\hat{P}$, both the qualitative and quantitative features obtained from the $\hat{P}$ are quite different even for nonlinear optical response theory. Thus it will not be quite suitable in using $\hat{P}$ to obtain the equivalent results as $\hat{D}$. 

From the graph, we find another very obvious peak at $z = 1$ at a ratio of 1/10 of the peak at $z = 1/3$, which is also different comparing with the previous theoretical computations. However, this peak has not been reported by the experiments because it is out of the scanning range of photon energy. 

[10–24]
FIG. 2. Computed $|\chi_{THG}^{SSH}(\omega)|$ under polarization operator $\hat{P}$ (solid line) vs. computed $|\chi_{THG}^{SSH}(\omega)|$ (dashed line) under dipole operator $\hat{D}$ with $z \equiv h\omega/(2\Delta)$, $\epsilon = 0.03$ and a magnification of $10^4$ in $|\chi_{THG}^{SSH}(\omega)|$.

III. THIRD ORDER SUSCEPTIBILITY FOR TLM MODEL UNDER DIPOLE FORMULA

The results under TLM model for the $DD$ correlation can be obtained by setting $\delta \to 0$ and $(2\omega a) \to \hbar \nu_F$ in Eq.(2.20). \[37\] Since we have the following properties for the complete elliptical integrals: \[39\]

\[
\begin{align*}
\lim_{\delta \to 0} E\left(\frac{\pi}{2}, \sqrt{1-\delta^2}\right) &= 1, \\
\lim_{\delta \to 0} \delta^2 F\left(\frac{\pi}{2}, \sqrt{1-\delta^2}\right) &= 0, \\
\lim_{\delta \to 0} \Pi\left(\frac{\pi}{2}, n_m, \sqrt{1-\delta^2}\right) &= f(mz),
\end{align*}
\]

where

\[
f(z) = \begin{cases} 
\arcsin(z) / \sqrt{1-z^2} & (z^2 < 1), \\
-\cosh^{-1}(z) / \sqrt{z^2-1} + i\pi / z\sqrt{z^2-1} & (z^2 > 1).
\end{cases}
\]

We will obtain the following expressions for THG under TLM models for $DD$ correlation,

\[
\chi_{THG}^{TLM}(\omega) = \chi_0^{(3)} \frac{5}{1024z^8} \left\{ -336 - \frac{96z^4}{5} + 9(37 - 24z^2)f(z) + 3(1 - 8z^2)f(3z) \right\}
\]

where $\chi_0^{(3)}$ defined in Eq.(2.20). The $\chi_{THG}^{TLM}$ is plotted in Fig.3. And no singular property such as van Hove singular shows in $\chi_{THG}^{TLM}$ under $DD$ correlation.

In $J_0 J_0$ correlation, the result of $\chi_{THG}^{TLM_{jj}}$ obtained by Wu as follows: \[15\]

\[
\chi_{THG}^{TLM_{jj}}(\omega) = \chi_0^{(3)} \frac{5}{1024z^8} \left\{ (5 - 8z^2)f(z) - 8(1 - 4z^2)f(2z) + 3(1 - 8z^2)f(3z) \right\}
\]

The comparison between our result($DD$) and Wu’s result ($J_0 J_0$) \[15\] on absolute value of $\chi_{THG}^{TLM}$ is plotted in Fig.4. If the zero frequency limitation is made, let $z \to 0$, we obtain the different values for the zero frequency limit for both $DD$ and $J_0 J_0$ correlations:

\[
\begin{align*}
\chi_{THG}^{TLM}(0) &= \frac{5}{28} \chi_0^{(3)} \approx 1.8 \times 10^{-11} \text{esu.} \quad DD \text{ correlation} \\
\chi_{THG}^{TLM_{jj}}(0) &= \frac{1}{2} \chi_0^{(3)} \approx 5.0 \times 10^{-11} \text{esu.} \quad J_0 J_0 \text{ correlation}
\end{align*}
\]
The nonequivalent results between $DD$ and $J_0 J_0$ correlation are quite obvious even for the static limit. The disappearance of ZFD could be understood as coincidence. [37]

![Figure 3](image_url)

**FIG. 3.** The real part (solid line) and the imaginary part (dashed line) of $\chi_{THG}^{TLM}(\omega)$ with $z \equiv \hbar \omega/(2\Delta)$.

![Figure 4](image_url)

**FIG. 4.** Computed $DD$ values (solid line) vs. $J_0 J_0$ values (dashed line) of $|\chi_{THG}^{TLM}(\omega)|$ with $z \equiv \hbar \omega/(2\Delta)$.

### IV. DISCUSSIONS

The analytical forms Eq.(2.20) and Eq.(3.3) show that there will be exactly no two-photon peak or even no van Hove singularity under $DD$ correlation. They are qualitatively different from the expressions Eq.(2.22) and Eq.(3.4) derived from $J_0 J_0$ correlation. The results with no TPA peak under single electron models are certainly reasonable in physical pictures, which is also agrees with the previous arguments on this problem. [17–24] The nonequivalence between two gauges also provided some evidence that the gauge phase factor in the optical response theory can not be ignored, and the static current expressions [15,16,28] can not be directly used and return the exact same results as $DD$ correlation. On one hand, $DD$ correlation should be much more suitable to study the nonlinear susceptibilities than $JJ$ correlation. [37] On the other hand, based on the exact expression of dipole operator $\hat{D}$, we find that polarization operator $\hat{P}$ can not be directly applied in periodic systems where the electrons are certainly not bounded. And $\hat{P}$ will returns the qualitatively different curves from the rigorous results. From the results we obtained in this paper, it seems that the direct application of single electron models may not be suitable in explaining for TPA. It also implies that the size effect [21], lifetime considerations [17–24], exciton effects [4,17,24], quantum fluctuations or disorders should be included to explain this non-trivial TPA. Both SSH and TLM models still can be served as the good basis to include all those interactions.
V. CONCLUSIONS

The analytical solutions to the THG for both SSH and TLM models obtained under the $DD$ correlation computations, showing nonexistence of the two-photon peak exactly. The nonequivalent results between $DD$ and $J_0 J_0$ correlations provide an evidence for the possible explanations through gauge phase factor.  In actual practical computations, $DD$ will be much more suitable for obtaining reasonable results than $J_0 J_0$ correlation, however, the replacement of $\hat{D}$ by the polarization operator $\hat{P}$ will result in qualitatively different results especially in periodic systems.

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