Analytical solutions to the third-harmonic generation in trans-polyacetylene: Application of dipole-dipole correlation to single-electron models

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The analytical solutions of the third-harmonic generation (THG) for infinite chains under both Su-Shrieffer-Heeger and Takayama-Lin-Liu-Maki model 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_0J_0) correlation or under polarization operator $\hat{P}$ with the same initial distribution functions. Physical backgrounds for those differences are analyzed qualitatively. The van Hove singularity disappears exactly in analytical forms under *DD* correlation, showing that the experimentally observed two-photon absorption peak (TPA) in THG cannot be directly explained by the single-electron models. Our analytical results on TPA are consistent with numerical computations using dipole formulas.

I. INTRODUCTION

The nonlinear optical (NLO) properties of conjugated polymers have received wide attention.[1–4] Experimentally observed nonlinear phenomena in conducting polymers, such as photoinduced absorption, bleaching, photoluminescence, ultrafast optical processes, and exciton behaviors,[5–9] have encouraged theoreticians to look for possible explanations.[10–12]

The large third-order susceptibility ($\chi^{(3)}$) of trans-polyacetylene (PA) was observed experimentally in the early 1990s,[13,14] and theoretical explanations have been suggested.[15–25] The origin of the experimentally observed two-photon absorption peak[13,14] (TPA) has been the subject of persistent theoretical discussions.[15–25] The use of static current-current correlation[15,16,26] (J_0J_0) with Keldysh Green function methods[27] has lead to the interpretation of TPA through analytical forms corresponding to either the Su-Shrieffer-Heeger[28] (SSH) or the Takayama-Lin-Liu-Maki[29] (TLM) models for infinite chains. However, various numerical approaches based on the dipole formalism ($\mathbf{E}\cdot\mathbf{r}$), such as the results of Yu *et al.*[18,19] (who used the Butcher-Cotter-Bloembergen-Shen dipole formula[30–32]), by Wu and Sun[20,21] (who used the Genkins-Mednis approach[33,34]) and by Shuai and Brédas[20] (who used the sum-over-state (SOS) Orr-Ward formalism[35]), have shown that no TPA was found if damping in the energy is considered.[18–25] Therefore, the two-photon cusp under J_0J_0 schemes[15] is considered to be a van Hove singularity[36] caused by the singular density of states (DOS) on the Fermi surface in one-dimensional (1D) systems. This nonresonant property in two-photon cusp was also noticed by Wu in his $\chi^{(3)}$ results.[15]

Besides the difficulty of explaining the TPA under the J_0J_0 current formula, there exists another obvious difficulty in the theory—the zero frequency divergence (ZFD) in the definition of J_0J_0 current formalism.[30] This problem was discussed by Dakhnovskii and Pronin on the basis of computations under the SSH model.[16] Unfortunately, the result for $\chi^{(3)}$ thus obtained under SSH model is the same one under TLM model if the linearization applied to the J_0J_0 scheme.[16]

Because of the ZFD in the J_0J_0 current formula,[30] intensive studies based on the dipole-dipole (DD) correlation have been carried out in order to obtain the physical description of TPA in $\chi^{(3)}$ of trans-polyacetylene. On one hand, weakly correlated and single-electron theories were used in the numerical dipole computations; the finite size effect[21] and the lifetime assumption[22] lead to a peak at the exact position of TPA. On the other hand, strongly correlated electron theories have also been applied to short chains. Soos and Ramesesha obtained the TPA based on the Pariser-Parr-Pople (PPP) model, but the peak was shifted to low frequency and had too low an intensity[17] relative to the experimental peak.[13] Recent works by Guo, Guo, and Mazumdar[24] and by Zhang,[25] based on the extended Hubbard Hamiltonian, show that the TPA could be interpreted as a three-photon resonance from $m(n)B_u$ state to $1A_g$ state. Whether or not the weakly correlated theory or even the single-electron models such as SSH and TLM are suitable in describing TPA still remains an open question.

Etemad and Soos have suggested that attention should be paid to the $\chi^{(3)}$ frequency dependences rather than to the magnitudes,[37] since the experiments are more sensitive to frequency dependences. This leads to the use of typical approximations in the dipole formula. Substitution of the dipole operator $\hat{D}$ by the polarization operator $\hat{P}$ [see Eq. (2.23)], (the zeroth-order dipole approximation[23,38]) has been extensively applied to the nonlinear optical formula. Some theoretical results, like the size dependency of static third-harmonic generation (THG),[23] can be successfully compared to the experiments.[39] However, it has been pointed out that $\hat{P}$ is sensitive to boundary conditions and singular in the thermodynamic limit in $\chi^{(1)}$ computations.[36] For $\chi^{(3)}$, our concern is the following: under what physical situations and to

what extent, can $\hat{P}$ still be considered as good as the dipole operator $\hat{D}$ for practical calculations?

The static dipole formula[17–25] and the static current formula[15,30] are conventionally considered to be equivalent.[18,30–32] However, as we pointed out in recent works,[40] the static current formula shows a ZFD problem when the gauge phase factor is ignored in the initial wave functions, and it should not lead to the same results as the static dipole formula with the same set of unperturbed wave functions and the same initial distribution functions.[40] In other words, the same initial distribution functions for the different formulas represent different physical situations. Therefore, the results for optical susceptibilities are not necessarily equivalent when these two formulas are used. For $\chi^{(1)}$ under either SSH or TLM models, we have shown the nonequivalence of the two static formulas. Whether this nonequivalence between J_0J_0 and *DD* correlations effects the $\chi^{(3)}$ of trans-polyacetylene theoretical models is another interesting topic. Although the qualitative features of $\chi^{(3)}$ have already been reported in the numerical solutions based on the *DD* correlation,[17–25] the exact analytical solutions have not yet been obtained. The analytical results, if obtained, would be very helpful for a direct check of the above concerns.

Fortunately, both the SSH and TLM models are single-electron models and can be exactly solved for the nonlinear susceptibilities under perturbated schemes, although this no doubt requires cumbersome calculations. After adoption of the conventional long-wavelength approximation,[15–25,41] it would be possible to directly compare the analytical results between the two gauges under either model and thus understand the different physical descriptions.

The paper is organized as follows. In Sec. II A, we discuss the SSH Hamiltonian and compare the physical pictures related to the *DD* and J_0J_0 correlations. The analytical form of $\chi^{(3)}$ associated with the *DD* correlation is obtained and compared with the analytical form associated with J_0J_0 correlation under the SSH model in Sec. II B. In Sec. II C, we present results of $\chi^{(3)}$ using the polarization operator $\hat{P}$, the qualitative and quantitative differences between the results obtained with use of $\hat{D}$ and $\hat{P}$ are outlined, and physical reasons for the difference between $\hat{D}$ and $\hat{P}$ are analyzed. In Sec. III, we obtain the exact analytical forms under *DD* correlation for the TLM model and directly compare them to those under J_0J_0 correlation. The discussion of the possible implications of this work is made in Sec. IV and a brief conclusion is presented in Sec. V.

II. THIRD-ORDER SUSCEPTIBILITIES FOR THE SSH MODEL UNDER DIPOLE CORRELATION

A. SSH Hamiltonian in real and momentum spaces

Based on periodic tight-binding approximations, the SSH Hamiltonian[28] is given by

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

where t_0 is the transfer integral between the nearest-neighbor sites, Δ is the gap parameter, and $\hat{C}^{\dagger}_{l,s}$ ($\hat{C}_{l,s}$) creates (annihilates) an π electron at site l with spin s. Application of the continuum limitation makes the SSH model equivalent to the TLM model.[29] In the SSH model, each site is occupied by one electron.

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

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

with e the electron charge and $\mathbf{E}$ the electric field. Under the J_0J_0 correlation,[26] the interaction Hamiltonian is introduced through a U(1) transformation.[36,41] A detailed derivation for the SSH model with the $\mathbf{p}\cdot\mathbf{A}$ interaction can be found in Ref. 36. As we can clearly see in previous discussions,[41,42] on one hand, the *DD* correlation would be derived by assuming a scalar potential $\mathbf{E}\cdot\mathbf{r}$ for the perturbation, giving rise to the external electric field. On the other hand, the *JJ* correlation[26] could be obtained from the time-dependent uniform vector potential $\mathbf{A}$ as perturbation. As long as one uses periodic boundary conditions, the scalar potential shows saw-shaped behavior and therefore the resulting electric field is not uniform in real space, while $\mathbf{J}_0\cdot\mathbf{A}$ is uniform in real space. From this point of view, the latter treatment will be clearly more appropriate than the former especially for linear optical response.[41,42]

If we want to use the position operator $\hat{\mathbf{r}}$ for a discussion, in order to provide the periodic property and to avoid the ill-posed definition of $\hat{\mathbf{r}}$ in real space we have to express $\hat{\mathbf{r}}$ under the Bloch states $|n,\mathbf{k}\rangle=u_{n,\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}$, where n and $\mathbf{k}$ are the band index and crystal momentum, respectively. $u_{n,\mathbf{k}}(\mathbf{r})$ is the periodic function under the translation of lattice vector.[43] We obtain

$$\mathbf{r}_{n\mathbf{k},n'\mathbf{k}'}=i\,\delta_{n,n'}\nabla_k\delta(\mathbf{k}-\mathbf{k}')+\mathbf{\Omega}_{n,n'}(\mathbf{k})\,\delta(\mathbf{k}-\mathbf{k}'), \tag{2.2}$$

and

$$\mathbf{\Omega}_{n,n'}(\mathbf{k})=\frac{i}{v}\int_v u^{*}_{n,\mathbf{k}}(\mathbf{r})\nabla_{\mathbf{k}}u_{n',\mathbf{k}}(\mathbf{r})d\mathbf{r}, \tag{2.3}$$

where v is the unit cell volume.

The above treatment represents $\hat{\mathbf{r}}$ in momentum $\mathbf{k}$ space, and the calculation of *DD* correlation was restricted to only one single unit cell v. This allows us to avoid the nonuniform property of the scalar potential. Provided that the number (N) of periodic unit cells goes to infinity, $\chi^{(3)}$ obtained from a single unit in momentum space shows the saturation behavior and the second hyperpolarizability is linearly proportional to N.[22,23]

Based on the calculations for $\chi^{(1)}$ under SSH and TLM models, we have noticed the following facts:[40] (i) the real part of the J_0J_0 correlation shows the ZFD problem, although the imaginary part of the J_0J_0 correlation is exactly the same as that of the *DD* correlation; (ii) after the gauge phase factor is properly considered for the initial distribution functions, the results under both correlations are equivalent; (iii) the single unit cell computation using the *DD* correlation was successfully performed, showing that nonuniform scalar potential under periodic boundary conditions may not cause a problem in momentum space. Thus, for $\chi^{(3)}$, we may

assume that the results under a nonuniform saw-shaped scalar potential should not be different from those under a uniform vector potential for infinite chains if the calculations use a single unit cell in momentum space.

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

$$\hat{C}_{l_o,s}=\frac{1}{\sqrt{N}}\sum_{-\pi/2a\leqslant k\leqslant \pi/2a}(\hat{C}^v_{k,s}+\hat{C}^c_{k,s})e^{ikR_{l_o}},$$

$$\hat{C}_{l_e,s}=\frac{1}{\sqrt{N}}\sum_{-\pi/2a\leqslant k\leqslant \pi/2a}(\hat{C}^v_{k,s}-\hat{C}^c_{k,s})e^{ikR_{l_e}}, \quad (2.4)$$

and

$$\hat{a}^v_{k,s}=-i\gamma_k\hat{C}^v_{k,s}+\xi_k\hat{C}^c_{k,s},$$

$$\hat{a}^c_{k,s}=i\xi_k\hat{C}^v_{k,s}+\gamma_k\hat{C}^c_{k,s}, \quad (2.5)$$

with

$$\gamma_k=\frac{1}{\sqrt{2}}\sqrt{1+\frac{2t_0\cos(ka)}{\varepsilon(k)}},$$

$$\xi_k=\frac{\mathrm{sgn}(k)}{\sqrt{2}}\sqrt{1-\frac{2t_0\cos(ka)}{\varepsilon(k)}}, \quad (2.6)$$

where

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

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

$$R_l=la+(-1)^l u. \quad (2.8)$$

We choose the spinor description $\hat{\psi}^\dagger_{k,s}(t)=(\hat{a}^{\dagger c}_{k,s}(t),\hat{a}^{\dagger v}_{k,s}(t))$ and apply the long-wavelength approximation,[30] the SSH Hamiltonian including $\mathbf{E}\cdot\mathbf{r}$ in momentum space is described by

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

where

$$\hat{H}_0=\sum_{-\pi/2a\leqslant k\leqslant \pi/2a,s}\varepsilon(k)\hat{\psi}^\dagger_{k,s}(t)\sigma_3\hat{\psi}_{k,s}(t) \quad (2.10)$$

and

$$\hat{H}_{\mathbf{E}\cdot\mathbf{r}}=-\hat{D}E_0e^{i\omega t}. \quad (2.11)$$

From Eq. (2.2), the dipole operator $\hat{D}$ could be obtained as follows:[40,41]

$$\hat{D}=e\sum_{-\pi/2a\leqslant k\leqslant \pi/2a,s}\left(\beta(k)\,\hat{\psi}^\dagger_{k,s}\sigma_2\hat{\psi}_{k,s}+i\frac{\partial}{\partial k}\hat{\psi}^\dagger_{k,s}\hat{\psi}_{k,s}\right), \quad (2.12)$$

where

$$\beta(k)=-\frac{\Delta t_0 a}{\varepsilon^2(k)} \quad (2.13)$$

is the coefficient related to the interband transition between the conduction and valence bands in a unit cell of length $2a$ and the second term in Eq. (2.12) is related to the intraband transition,[40,41] and $\vec{\sigma}$ are the Pauli matrixes. We have omitted the relative distortion $\eta\ (\equiv 2u/a)$ in this computation because the contribution of η is quite small in the linear case.[40]

B. Analytical expression for $\chi^{(3)}$ (*DD* correlation)

Within the semiclassical theory of radiation,[30–32] the electrical field is treated classically and the third-order susceptibility $\chi^{(3)}$ is described by[30–32]

$$\chi^{(3)}(\Omega;\omega_1,\omega_2,\omega_3)=\frac{1}{3!V}\left[\frac{i}{\hbar}\right]^3\int d\mathbf{r}_1d\mathbf{r}_2d\mathbf{r}_3\int dt_1dt_2dt_3\times\int d\mathbf{r}\,dt\,e^{-i\mathbf{k}\cdot\mathbf{r}+i\Omega t}\times\langle\hat{T}\hat{\mathbf{D}}(\mathbf{r},t)\hat{\mathbf{D}}(\mathbf{r}_1,t_1)\hat{\mathbf{D}}(\mathbf{r}_2,t_2)\hat{\mathbf{D}}(\mathbf{r}_3,t_3)\rangle, \quad (2.14)$$

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

If the J_0J_0 correlation is applied, we usually do the following substitutions for $\hat{\mathbf{D}}$ in Eq. (2.14):[30,40]

$$\hat{\mathbf{D}}(\mathbf{r_i})\rightarrow\hat{\mathbf{J}}(\mathbf{r_i})/(i\omega_i)$$

$$\hat{\mathbf{D}}(\mathbf{r})\rightarrow\hat{\mathbf{J}}(\mathbf{r})/(i\Omega).$$

The average $\langle\cdots\rangle$ is still based on the same unperturbed ground state as in the case of *DD* correlation. The physical background in applying either *DD* or J_0J_0 correlations has been discussed in detail in Ref. 40.

The THG is defined by setting $\omega_1=\omega_2=\omega_3$. Following similar procedures to those used in the linear calculations,[40] from Eqs. (2.12) and (2.14), we obtained the following expression for $\chi^{THG}_{SSH}(\omega_1)\equiv\chi^{(3)}_{SSH}(-3\omega_1,\omega_1,\omega_1,\omega_1)$:

$$\chi^{THG}_{SSH}(\omega_1)=\frac{2e^4n_0}{\hbar^3}\frac{1}{L}\sum_k\int\frac{d\omega}{2\pi}\left\{\left(\beta(k)\sigma_2+i\frac{\partial}{\partial k}\right)G(k,\omega)\times\left(\beta(k)\sigma_2+i\frac{\partial}{\partial k}\right)G(k,\omega-\omega_1)\times\left(\beta(k)\sigma_2+i\frac{\partial}{\partial k}\right)G(k,\omega-2\omega_1)\times\left(\beta(k)\sigma_2+i\frac{\partial}{\partial k}\right)G(k,\omega-3\omega_1)\right\}, \quad (2.15)$$

where L is the chain length, $\beta(k)$ is defined by Eq. (2.13) and n_0 is the number of chains per unit cross area. The polymer chains are assumed to be oriented, and the Green function $G(k,\omega)$ defined as follows:[40,41]

$$G(k,\omega)=\frac{\omega+\omega_k\sigma_3}{\omega^2-\omega_k^2+i\epsilon}, \tag{2.16}$$

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

After tedious derivations, we obtained the following analytical expressions for the third-harmonic generation under the SSH model:

$$\begin{aligned}\chi_{SSH}^{THG}(\omega)=&\frac{2e^4n_0}{\hbar^3}\frac{1}{L}\sum_k\left\{+\frac{\beta^4(k)}{2\omega(2\omega_k+\omega)(2\omega_k+3\omega)}\right.\\&-\frac{\beta^4(k)}{2\omega(2\omega_k-\omega)(2\omega_k-3\omega)}-\frac{\beta(k)}{(2\omega_k+3\omega)}\\&\times\frac{\partial}{\partial k}\left[\frac{1}{(2\omega_k+2\omega)}\frac{\partial}{\partial k}\left(\frac{\beta(k)}{(2\omega_k+\omega)}\right)\right]\\&-\frac{\beta(k)}{(2\omega_k-3\omega)}\frac{\partial}{\partial k}\\&\left.\times\left[\frac{1}{(2\omega_k-2\omega)}\frac{\partial}{\partial k}\left(\frac{\beta(k)}{(2\omega_k-\omega)}\right)\right]\right\}.\end{aligned} \tag{2.17}$$

The above expression is almost identical to Eq. (A13) in Ref. 34 except the disappearance of one term [the last term in Eq. (A13)]. In order to compare the two equations, the following substitution should be applied to Eq. (A13):

$$\Omega_{vv}=\Omega_{cc}=0,$$

$$\Omega_{vc}=-\Omega_{cv}=\beta(k). \tag{2.18}$$

Equation (2.17) is also quite similar to Eq. (11) in Ref. 20 which was based on the Genkins-Mednis approach.[33] In order to compare the equations, one has to use Eq. (2.18) and apply the symmetric condition on the negative frequency in the Wu and Sun Eq. (11).

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

$$\begin{aligned}I_T=&\frac{2e^4n_0}{\hbar^3}\frac{1}{L}\sum_k\\&\times\left\{-\frac{\partial}{\partial k}\left[\frac{\beta(k)}{(2\omega_k+3\omega)(2\omega_k+2\omega)}\frac{\partial}{\partial k}\left(\frac{\beta(k)}{(2\omega_k+\omega)}\right)\right]\right.\\&\left.-\frac{\partial}{\partial k}\left[\frac{\beta(k)}{(2\omega_k-3\omega)(2\omega_k-2\omega)}\frac{\partial}{\partial k}\left(\frac{\beta(k)}{(2\omega_k-\omega)}\right)\right]\right\}.\end{aligned} \tag{2.19}$$

This term (I_T) vanishes for infinite chains if we consider following two facts in the optical process: (i) the velocity on the Fermi surface $\nabla_k\varepsilon(k)|_{k=\pm\pi/2a}$ is zero, and (ii) the lifetime of the states is not zero. (We should include the damping in the process, that is, $\omega_k\rightarrow\omega_k+i\epsilon_k$ and $\epsilon_k\neq 0$.) Equation (2.17) can be simplified as follows:

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

and

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

where $\chi_0^{(3)}\equiv\frac{8}{45}(e^4n_0/\pi)[(2t_0a)^3/\Delta^6]$, $x\equiv\hbar\omega_k/\Delta$, $z\equiv\hbar\omega/(2\Delta)$, and $\delta\equiv\Delta/(2t_0)$. F,E, and Π are first, second, and third types of complete elliptical integrals.[44]

An alternative analytical form of Eq. (2.20) has been described in Ref. 41. There is no two-photon cusp in Eq. (2.20). This result is consistent with those of Yu and Su[18] and of Shuai and Brèdas.[22] It is quite different from the expression obtained from J_0J_0 correlation, which shows the following form for χ_{SSHjj}^{THG} under the SSH model:[16]

$$\begin{aligned}\chi_{SSHjj}^{THG}=&Bz^{-8}\left\{[5-8z^2(1+\delta^2)+20z^4\delta^2]g(z)-8\right.\\&\times[1-4z^2(1+\delta^2)+16z^4\delta^2]g(2z)\\&+[3-24z^2(1+\delta^2)+188z^4\delta^2]g(3z)\\&\left.-8\delta^2z^4E\left(\frac{\pi}{2},\sqrt{1-\delta^2}\right)\right\},\end{aligned} \tag{2.22}$$

where $B\equiv 5\chi_0^{(3)}/1024$, with $\chi_0^{(3)}$ as defined after Eq. (2.20) and $g(z)$ is given by Eq. (2.21). We should point out that the

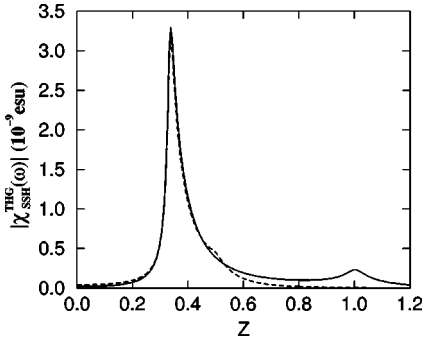

FIG. 1. Computed *DD* values (solid line) vs J_0J_0 values (dashed line) of $|\chi^{THG}_{SSH}(\omega)|$ with $z\equiv\hbar\omega/(2\Delta)$ and $\epsilon=0.03$.

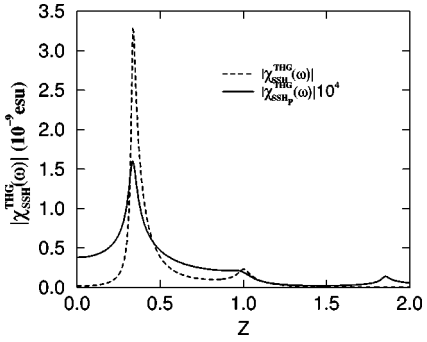

FIG. 2. Computed $|\chi^{THG}_{SSH_P}(\omega)|$ under polarization operator $\hat{P}$ (solid line) vs computed $|\chi^{THG}_{SSH}(\omega)|$ (dashed line) under dipole operator $\hat{D}$ with $z\equiv\hbar\omega/(2\Delta)$, $\epsilon=0.03$, and a magnification of 10^4 in $|\chi^{THG}_{SSH_P}(\omega)|$.

elliptical form[16] of Eq. (2.22) is exactly the same as the integral form of Eq. (11) in the Wu-Sun result,[20] which was derived from the incomplete Genkins-Mednis approach.[33,41] The disappearance of ZFD under static current schemes is somewhat puzzling or simply should be understood as fortuitous coincidence for the SSH model. As we pointed out in a recent paper,[40] the neglect of the gauge phase factor in the static current formula will cause ZFD in the susceptibilities and different results from the dipole formula. The derivation under the J_0J_0 correlation[16] does not consider the gauge phase factor's effect, which causes ZFD even for the linear case if following straightforward calculations.[40]

We observe the qualitative 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 nonequivalence can be understood by the influence of gauge phase factor in optical response theory.[40] We will discuss the difference in Sec. IV.

Setting $x\rightarrow x+i\epsilon$ in the integral of Eq. (2.20), the absolute values obtained numerically with Eq. (2.20) or Eq. (2.22) for the SSH model are those plotted in Fig. 1. The following parameters were chosen for trans-polyacetylene:[18–21] $t_0=2.5$ eV, $\Delta=0.9$ eV, $n_0=3.2\times10^{14}$ cm^{-2}, $a=1.22$ Å, and $\epsilon\sim0.03$. We obtain $\delta=0.18$ and $\chi_0^{(3)}\approx1.0\times10^{-10}$ esu.

Figure 1 shows another peak at $z=1$ at a ratio of 1/10 of the peak at $z=1/3$, which differs from the previous theoretical computations.[15–25] This peak has not been reported by the experiments because it is out of the scanning range of photon energy.[13,14]

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

The polarization operator $\hat{P}$ is extensively applied in NLO theory.[23,38] Under the tight-binding approximation (TBA), $\hat{P}$ is defined in real space as

$$\hat{P}=\sum_l R_l\hat{C}_l^\dagger\hat{C}_l. \tag{2.23}$$

Based on the SSH model, we can do a comparison of χ^{THG}_{SSH} between $\hat{D}$ and $\hat{P}$. If the chain region l is going from 1 to N, we obtain the unit polarization $\hat{P}^{unit}(k)$ from the total polarization $\hat{P}^{total}(k)$ in the momentum space:

$$\hat{P}^{unit}(k)=\lim_{N\rightarrow\infty}\frac{\hat{P}^{total}(k)}{N}=\frac{ea}{2}\sum_{k,s}\psi^\dagger_{k,s}\sigma_2\psi_{k,s}. \tag{2.24}$$

Substituting $\hat{D}$ by $\hat{P}$ in Eq. (2.14), we obtain the $\chi^{THG}_{SSH_P}$ for SSH model for infinite chains:

$$\chi^{THG}_{SSH_P}=\chi_0^{(3)}\frac{45\delta^4}{128}\int_1^{1/\delta}\frac{dx}{[(1-\delta^2x^2)(x^2-1)]^{1/2}}\left\{\frac{1}{x^2-z^2}-\frac{9}{x^2-(3z)^2}\right\}. \tag{2.25}$$

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 $z=1/(3\delta)\approx1.85$ shows up through **P·E**. This peak corresponds 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 ''umklapp enhancement'' in solid states.[36] In *DD* calculations, this peak at $z=1/(3\delta)$ is not obvious. The comparison of the absolute values between $\chi^{THG}_{SSH_P}$ and χ^{THG}_{SSH} is shown in Fig. 2. The different shapes of curves are obvious.

As we can see from Eq. (2.23), $\hat{P}$ only contains on-site information. There are no off-site terms like $\hat{C}_l^\dagger\hat{C}_{l'}$, where $l\neq l'$. However, the off-site terms will appear in the Fourier transformation of $\hat{D}$ [Eq. (2.12)] in real space. Conventionally, $\hat{P}$ is understood as the zeroth-order approximation of $\hat{D}$,[23,38] and some results like size dependency[23] are consistent with experimental observations.[39] However, since delocalized electronic states should be obtained in periodic systems,[43] it suggests that the contributions to the optical susceptibilities from off-site terms cannot be negligible. Under certain cases, if the contributions to optical susceptibilities from off-site terms are relatively small compared to those from on-site terms, for example, if all electronic states are localized or electronic hopping to nearest-neighbor sites is relatively small, it is expected that $\hat{P}$ can serve as a good approximation of $\hat{D}$. Under that situation, computations can be drastically simplified through $\hat{P}$. For the SSH model, the

electron hops from one site to the other nearest-neighbor sites, indicating that electronic states of the system are delocalized. Thus, $\hat{P}$ may not be sufficient to determine the nonlinear susceptibility.

Another possible reason to cause those differences is the ill-posed definition of $\hat{P}$ for 1D chains,[36] because periodic boundary conditions imply that the electron on site $N+1$ is the same as that on site 1. To avoid this difficulty, the 2D ring structure could be considered as physically meaningful boundary condition.[23] Under a 2D structure, this unphysical feature can be eliminated from $\hat{P}$.

III. THIRD-ORDER SUSCEPTIBILITY FOR THE TLM MODEL UNDER THE DIPOLE FORMULA

The result under TLM model with the *DD* correlation can be obtained by setting $\delta \to 0$ and $(2t_0 a) \to \hbar v_F$ in Eq. (2.20).[20,21,40,41] We have the following properties for the complete elliptical integrals:[44]

$$\lim_{\delta\to 0} E\left(\frac{\pi}{2}, \sqrt{1-\delta^2}\right) = 1,$$

$$\lim_{\delta\to 0} \delta^2 F\left(\frac{\pi}{2}, \sqrt{1-\delta^2}\right) = 0, \tag{3.1}$$

$$\lim_{\delta\to 0} \Pi\left(\frac{\pi}{2}, n_m, \sqrt{1-\delta^2}\right) = f(mz),$$

where

$$f(z) \equiv \begin{cases} \dfrac{\arcsin(z)}{z\sqrt{1-z^2}} & (z^2<1), \\ -\dfrac{\cosh^{-1}(z)}{z\sqrt{z^2-1}} + \dfrac{i\pi}{2z\sqrt{z^2-1}} & (z^2>1). \end{cases} \tag{3.2}$$

We obtain the following expression for THG under TLM model for *DD* correlation:

$$\chi^{THG}_{TLM}(\omega) = \chi^{(3)}_0 \frac{5}{1024 z^8}\left\{ -336 - \frac{96 z^4}{5} + 9(37-24z^2) f(z) + 3(1-8z^2) f(3z)\right\}, \tag{3.3}$$

where $\chi^{(3)}_0$ defined as in Eq. (2.20). A plot of χ^{THG}_{TLM} is shown in Fig. 3. No singular behavior at $z=1/2$ (such as van Hove singularity) shows in χ^{THG}_{TLM} under *DD* correlation.

In $J_0 J_0$ correlation, the result of χ^{THG}_{TLMjj} obtained by Wu is as follows:[15]

$$\chi^{THG}_{TLMjj}(\omega) = \chi^{(3)}_0 \frac{5}{1024 z^8}\{(5-8z^2) f(z) - 8(1-4z^2) f(2z) + 3(1-8z^2) f(3z)\}. \tag{3.4}$$

The comparison between our result (*DD*) and Wu's result[15] ($J_0 J_0$) for the absolute value of χ^{THG}_{TLM} is shown in Fig. 4. If the zero-frequency limitation is made, letting $z \to 0$, we obtain different values for the zero-frequency limit (static limit) for both *DD* and $J_0 J_0$ correlations:

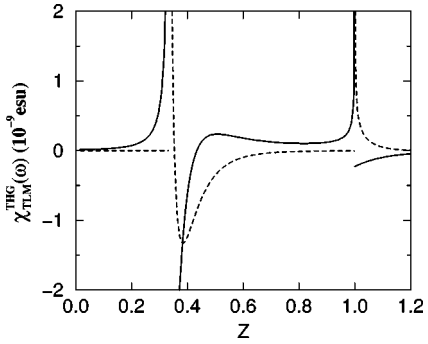

FIG. 3. The real part (solid line) and the imaginary part (dashed line) of $\chi^{THG}_{TLM}(\omega)$ with $z \equiv \hbar\omega/(2\Delta)$.

$$\chi^{THG}_{TLM}(0) = \frac{5}{28}\chi^{(3)}_0 \approx 1.8\times 10^{-11} \text{ esu}, \quad DD \text{ correlation}$$

$$\chi^{THG}_{TLMjj}(0) = \frac{1}{2}\chi^{(3)}_0 \approx 5.0\times 10^{-11} \text{ esu}, \quad J_0 J_0 \text{ correlation}. \tag{3.5}$$

Nonequivalent results between the *DD* and $J_0 J_0$ correlation are obvious even for the static limit. The disappearance of ZFD could be understood as coincidence.[40]

IV. DISCUSSIONS

The analytical forms, Eqs. (2.20) and (3.3), show that there will be exactly no TPA or even no van Hove singularity under *DD* correlation. They are qualitatively different from Eqs. (2.22) and (3.4), which were derived from $J_0 J_0$ correlation. The results with no TPA peak under single-electron models are certainly reasonable from a physical perspective, which also agrees with previous arguments and numerical computations on this problem.[17–25]

The nonequivalence between the two gauges for periodic systems in a linear problem has already been noticed by others, and there are several explanations.[42,45,46] In a recent work of $\chi^{(1)}$ computations based on the SSH and TLM models, we gave another possible reason.[40] The gauge transformation between $\mathbf{E}\cdot\mathbf{r}$ and $\mathbf{p}\cdot\mathbf{A}$ contains two parts: (i) the transformation involving the scalar potential ϕ and vector

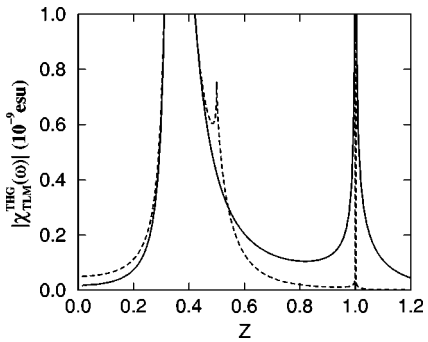

FIG. 4. Computed *DD* values (solid line) vs $J_0 J_0$ values (dashed line) of $|\chi^{THG}_{TLM}(\omega)|$ with $z \equiv \hbar\omega/(2\Delta)$.

potential **A**; (ii) the transformation involving the phase factor between the wave functions under the two gauges. Conventionally the static current formula ignores part (ii) and it uses the same ground state average $\langle \cdots \rangle$ [see Eq. (2.14)] as that in the dipole formula, without considering the influence of the phase factor. Thus, it causes a problem even for the linear case in periodic models. Equivalent results can be obtained when the phase factor is properly considered in the ground state for the *JJ* correlation.[15,16,26,30] In other words, both dipole formula and the *JJ* current formula represent different physical situations for the same unperturbed ground state, and therefore yield different results. Introduction of the gauge phase factor in the *JJ* correlation will complicate the computation, especially for nonlinear optical studies. In this sense, we draw the conclusion that *DD* is more appropriate than the *JJ* correlation. Computational details and discussions of different physical backgrounds for both formulas have been presented in Ref. 40.

Results in this paper demonstrate that the simplest single-electron models (like either the SSH or the TLM model) may not be suitable in describing this nontrivial TPA in $\chi^{(3)}$ of trans-polyacetylene. Thus, more sophisticated models (like the Hubbard model,[17,24,25] electron-hole pair model,[17,23,38] etc.) should be used. Previous computations have already shown that the information inadequately conveyed in the single-electron models, thus the size effect,[21] lifetime considerations,[17–25] exciton effects,[4,17,24,25] quantum fluctuations, or disorders should be included in order to explain this nontrivial TPA. Both SSH and TLM models still can serve as a basis for the inclusion of all those interactions.

Our computations have shown another new peak at $z=1$ which was missed by both experimental[13] and theoretical studies.[15–22] It would be interesting if the experimental $\chi^{(3)}$ behavior around $z=1$ could be measured in the future.

V. CONCLUSIONS

Analytical solutions of the THG for infinite chains under the SSH and TLM models are obtained with the *DD* correlation. They do not show the existence of TPA. We have provided a possible qualitative explanation based on the influence of the gauge phase factor[40] for nonequivalent results between *DD* and J_0J_0 correlations.[26] The complexity introduced by the gauge phase factor for *JJ* correlation suggests that *DD* correlation may be much more suitable for obtaining reasonable NLO results than *JJ* correlation. The polarization operator $\hat{P}$ (the zeroth-order approximation of $\hat{D}$) leads to different results for delocalized systems such as 1D periodic systems, although it may provide some good qualitative features for localized systems or under 2D structure. We shall emphasize that we only provide one possible reason to understand the difference between the two gauges for periodic systems, and there are some other possible reasons for the difference.[45,46] The question about the difference still remains open, and further investigation is needed.

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[26] J_0 represents the static current, which can be directly derived from the commutator of position operator **r** and nonperturbed Hamiltonian $\hat{H}_0$. However, the total current J should also in-

clude the field currents coming from the **p·A** interaction Hamiltonian with the gauge phase factor. Thus, conventional equivalence between J_0J_0 and *DD* correlations should be understood as *JJ* and *DD* correlations. Detailed explanations can be found in Ref. 40.

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