Hyperpolarizabilities for the one-dimensional infinite single-electron periodic systems: II. Dipole-dipole versus current-current correlations

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Based on Takayama-Lin-Liu-Maki model, analytical expressions for the third-harmonic generation, DC Kerr effect, DC-induced second harmonic optical Kerr effect, optical Kerr effect or intensity-dependent index of refraction and DC-electric-field-induced optical rectification are derived under the static current-current ($J_0J_0$) correlation for one-dimensional infinite chains. The results of hyperpolarizabilities under $J_0J_0$ correlation are then compared with those obtained using the dipole-dipole (DD) correlation. The comparison shows that the conventional $J_0J_0$ correlation, albeit quite successful for the linear case, is incorrect for studying the nonlinear optical properties of periodic systems.

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I. INTRODUCTION

The different gauge approaches ($p \cdot A$ and $E \cdot r$) have been adopted in the theoretical studies of both linear and nonlinear optical (NLO) properties for many materials [1–3]. For the current-current ($JJ$) correlation (i.e., the $p \cdot A$ gauge), most researchers tend to interpret the current operator $J$ as the static current current $J_0$ [2–6]. For the linear transport theory, though the real part of $J_0J_0$ correlation causes the zero frequency divergence (ZFD), the convergent optical properties such as the linear susceptibility, the absorption coefficient, the linear conductivity, etc could be obtained by using the imaginary part of $J_0J_0$ correlation alone, then by applying the Kramers-Kronig (KK) relations on the imaginary part of $J_0J_0$ correlation or including the diamagnetic term [5]. Hence, the static current-current ($J_0J_0$) correlation is widely adopted in the linear transport theory [5–9] and the ZFD is often considered as a harmless technical nuisance and tacitly ignored by most researchers. However, for the nonlinear case, $J_0J_0$ correlation [9] encounters serious difficulties and the analytical results for nonlinear optical properties do not even converge.

Among the polymer studies, theoretical calculations of both linear [6–9] and nonlinear optical properties [4,10–19] have been carried out based on the different gauges for the simplest π-conjugated polymers such as polyacetylene (PA). For polyacetylene, some simple periodic, single electron, and tight-binding approximation models such as Su-Shrieffer-Heeger (SSH) [20] and Takayama-Lin-Liu-Maki (TLM) [21] have been established to interpret the experimental results [22]. But in both linear and nonlinear calculations of the optical properties under the above models, as we pointed out recently [9], there are some discrepancies between the conventional treatments using different gauges. Specifically, if using the same set of wavefunctions but ignoring the phase difference between both gauges and meanwhile applying the static current in $p \cdot A$ gauge, we cannot guarantee the equivalence between the two gauges, even though the final results look quite similar to each other qualitatively. By the example calculation of linear susceptibility under SSH model for one-dimensional infinite chains, we strictly proved the nonequivalence between two gauges and ZFD could be resolved by considering the gauge factor [9]. Since one needs to apply fairly complicated techniques to resolve ZFD in $J_0J_0$ correlation and preserve the equivalence between two gauges, we prefer the dipole-dipole (DD) correlation (i.e., the $E \cdot r$ gauge) for nonlinear optical calculations for the polymers.

On one hand, the DD correlation is derived by assuming a scalar potential $E \cdot r$ as perturbation, giving rise to the external electric field $E$. On the other hand, $J_0J_0$ correlation is obtained by treating the time-dependent uniform vector potential $A$ as perturbation. As long as one uses periodic boundary conditions, the scalar potential shows

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saw-shaped behavior and therefore the resulting electric field is not uniform in the real space, while \( \mathbf{J}_0 \cdot \mathbf{A} \) is uniform in real space. From this point of view, the \( \mathbf{J}_0 \mathbf{J}_0 \) correlation seems more appropriate than the \( DD \) correlation. Thus it is our interest to study some cases which avoid the ZFD difficulties in the \( \mathbf{J}_0 \mathbf{J}_0 \) correlation and reveal the pitfalls of the \( \mathbf{J}_0 \mathbf{J}_0 \) correlation via a detailed comparison between \( DD \) and \( \mathbf{J}_0 \mathbf{J}_0 \) correlations.

Fortunately, the TLM model is one typical case that avoids the ZFD problem, although its sibling model - the SSH model is not [11]. The static current operator \( \mathbf{J}_0 \) derived from TLM model could give us the convergent results for hyperpolarizabilities when the frequency approaches 0. However, we consider this result as a mere coincidence, since the linear susceptibility calculation based on TLM model diverges in the real part of \( \mathbf{J}_0 \mathbf{J}_0 \) correlation [9]. Nevertheless, we could use TLM model as a common ground to do the comparison between \( DD \) and \( \mathbf{J}_0 \mathbf{J}_0 \) correlations.

In [23], we have computed the analytical forms of hyperpolarizabilities for infinite chains by \( DD \) correlation under both SSH and TLM models. In this paper, we first present a brief description of the static current operator \( \mathbf{J}_0 \) for both models and general formulas for hyperpolarizabilities under \( \mathbf{J}_0 \mathbf{J}_0 \) correlation in Section II. We then proceed to carry out analytical calculations for DC Kerr effect, DC-induced second harmonic generation, optical Kerr effect and DC-electric-field-induced optical rectification by \( \mathbf{J}_0 \mathbf{J}_0 \) correlation under TLM model for infinite chains (Section III). A detailed comparison of the results between \( DD \) and \( \mathbf{J}_0 \mathbf{J}_0 \) correlations is followed subsequently (Section IV). The comparison shows that though there are some similarities for some features such as resonant peaks and general shapes between these two correlations, important and evident differences abound. For instance, while \( DD \) correlation clearly indicates the nonexistence of the two-photon cusp in the third-harmonic generation (THG) spectrum [12,13], such cusp appeared in \( \mathbf{J}_0 \mathbf{J}_0 \) correlation; and while \( DD \) correlation obviously shows the break of overall permutation and Kleinman symmetries [23], \( \mathbf{J}_0 \mathbf{J}_0 \) correlation maintains both the overall permutation [3] and Kleinman symmetries [24] for all frequencies. Finally, we present our conclusions in Section V.

II. THEORY

A. Nonlinear optical susceptibility under current-current correlation

The \( n \)-th-order nonlinear optical susceptibility under current-current (\( JJ \)) correlation is conventionally reduced to the static current-current (\( \mathbf{J}_0 \mathbf{J}_0 \)) correlation and defined as follows [3,4,9,12]:

\[
\chi^{(n)}(\Omega; \omega_1, \ldots, \omega_n) = -\delta_{n,1} \frac{n^{(e)} e^2}{\epsilon_0 m \omega_1^2} \hat{I} + \frac{\chi^{(n)}_{\mathbf{J}_0\mathbf{J}_0}(\Omega; \omega_1, \ldots, \omega_n)}{\epsilon_0 \Omega \omega_1 \ldots \omega_n},
\]

(2.1)

with \( \Omega \equiv -\sum_{i=1}^{n} \omega_i \), \( n^{(e)} \) the electronic density, \( m \) the electron electron mass, \( \epsilon_0 \) the dielectric constant, \( \hat{I} \) the unit dyadic, \( \delta_{n,1} \) the Kronecker symbol, and

\[
\chi^{(n)}_{\mathbf{J}_0\mathbf{J}_0}(\Omega; \omega_1, \ldots, \omega_n) = \frac{1}{n! V} \frac{1}{\hbar} \int d\mathbf{r}_1 \cdots d\mathbf{r}_n \int dt_1 \cdots dt_n \int d\mathbf{r} e^{-i \mathbf{k} \cdot \mathbf{r} + i \mathbf{r} \cdot \hat{T} \mathbf{J}_0(\mathbf{r}, t) \mathbf{J}_0(\mathbf{r}_1, t_1) \cdots \mathbf{J}_0(\mathbf{r}_n, t_n)},
\]

(2.2)

where \( V \) is the total volume, \( \hat{T} \) is the time-ordering operator, and \( \mathbf{J}_0 \) is the static current operator.

The Feynman diagram of \( \chi^{(3)} \) is simply described as one connected circle in the preceding paper (see Fig. 1 in [23]).

B. Static current operator under SSH and TLM models

The static current operator \( \mathbf{J}_0 \) could be found by the commutator between the dipole operator and Hamiltonian. For both SSH and TLM models, the current operators were derived in many previous works [4,6–9], here we only list the final results.

For the SSH model, under the same notation of the preceding paper [23], the static current operator \( \mathbf{J}_{0,SSH} \) is defined by the formula
\[ J_{0,SSH} = - \sum_{l,s} \frac{e}{\hbar} \left[ t_0 + (-1)^l \frac{\Delta}{2} \right] [a - 2(-1)^l u] \left( \hat{C}_{l+1,s} \hat{C}_{l,s} - \hat{C}_{l,s}^\dagger \hat{C}_{l+1,s}^\dagger \right), \]

where \( t_0 \) is the transfer integral between the nearest-neighbor sites, \( \Delta \) is the gap parameter and \( \hat{C}_{l,s}^\dagger (\hat{C}_{l,s}) \) creates (annihilates) an \( \pi \) electron at site \( l \) with spin \( s \).

For the TLM model (Eq.(2.2) in [23]), by adopting the notation in Maki [6] and Wu [4]'s work, the static current operator \( J_{0,TLM} \) is defined by the formula

\[ \hat{J}_{0,TLM} = v_F \Psi^\dagger(x) \sigma_3 \Psi(x), \]

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 and \( \sigma \) are the Pauli matrices.

As pointed out in our recent work [9], detailed calculations show that the above static current operators lead to the ZFD in the linear response for both models. However, in the subsequent calculation for \( \chi^{(3)} \), we show that the static current operator \( J_0 \) gives the convergent results for the TLM model. This provides us a convenient base to carry out the comparison of the analytical results of \( \chi^{(3)} \) between \( DD \) and \( J_0J_0 \) correlations. Hence, the following calculations are based on the TLM model only.

III. HYPERPOLARIZABILITIES FOR TLM MODEL UNDER STATIC CURRENT-CURRENT CORRELATION

A. General four-wave-mixing results

We apply the general definition Eq.(2.1) and Eq.(2.2) to the TLM model and obtain the following expression for \( \chi^{(3)}_{TLM}(\Omega \equiv -(\omega_1 + \omega_2 + \omega_3); \omega_1, \omega_2, \omega_3) \) (or \( \chi^{(3)}(\omega_1, \omega_2, \omega_3) \) for short):

\[ \chi^{(3)}_{TLM}(\Omega; \omega_1, \omega_2, \omega_3) \equiv \frac{\chi^{(3)}_{J_0J_0}}{i \Omega \omega_1 \omega_2 \omega_3}, \]

where \( \chi^{(3)}_{J_0J_0} \) is defined by the formula

\[ \chi^{(3)}_{J_0J_0} = \frac{-2e^4 n_0 v_F^4}{\hbar^3} \frac{1}{3! L} \sum_{k,p(\omega_1, \omega_2, \omega_3)} \int \frac{d\omega}{2\pi} \text{Tr} \left\{ \sigma_3 G(k, \omega) \sigma_3 G(k, \omega - \omega_1) \sigma_3 G(k, \omega - \omega_1 - \omega_2) \sigma_3 G(k, \omega - \omega_1 - \omega_2 - \omega_3) \right\}, \]

\[ \equiv \frac{-2e^4 n_0 v_F^4}{\hbar^3 L} \sum_k S(\omega_1, \omega_2, \omega_3) \]

with \( L \) the chain length, \( S(\omega_1, \omega_2, \omega_3) \) the summation of the permutations for \( \omega_1, \omega_2, \omega_3 \), and Green’s function \( G \) defined by the formula

\[ G(k, s) = \frac{\omega - s + v_F k \sigma_3 + \Delta \sigma_1 / \hbar}{(\omega - s)^2 - \omega_k^2 + i\epsilon}. \]

In Eq. (3.4), \( \omega_k \) is defined by the formula

\[ \omega_k = [(v_F k)^2 + (\Delta / \hbar)^2]^{1/2}. \]

We now introduce the following three new variables:

\[ c := \Delta / \hbar, \]

3
\[ x = \frac{\omega_k}{c} = \sqrt{1 + \left(\frac{v_F \hbar k}{\Delta}\right)^2}, \quad (3.7) \]

\[ z = \frac{\omega}{2c} = \frac{\hbar \omega}{2\Delta}, \quad (3.8) \]

Combining Eq. (3.3), Eq. (3.6)-Eq. (3.8) and replacing the summation over \( k \) by its continuous limit, we obtain

\[ \chi^{(3)}(\omega_1, \omega_2, \omega_3) = \frac{e^4 n_0 v_F^4}{\pi \hbar^3} \int_{-\infty}^{\infty} S(\omega_1, \omega_2, \omega_3) dk \]

\[ = \frac{2 e^4 n_0 v_F^4}{\pi \hbar \Delta^2} \int_{1}^{\infty} \frac{xdx}{\sqrt{x^2 - 1}}(e^3 S(\omega_1, \omega_2, \omega_3)). \quad (3.9) \]

Substituting Eq. (3.9) into Eq. (3.1), we have

\[ \chi^{(3)}(\omega_1, \omega_2, \omega_3) = \frac{e^4 n_0 (\hbar v_F)^3}{2^3 \pi \Delta^6} \frac{1}{i(z_1 + z_2 + z_3)z_1z_2z_3} \int_{1}^{\infty} \frac{xdx}{\sqrt{x^2 - 1}}(e^3 S(\omega_1, \omega_2, \omega_3)), \quad (3.10) \]

where

\[ z_i = \frac{\hbar \omega_i}{2\Delta}, \quad i = 1 \ldots 3. \quad (3.11) \]

Eq. (3.10) is the general formula for four-wave-mixing under \( J_0 J_0 \) correlation. This is the same as defined in Wu's work [4]. As for nonlinear optical susceptibilities, there is no non-equilibrium situation involved, the usage of Keldish Green function in Wu's work is not necessary.

Now Eq. (3.10) is simplified to compute \( S(\omega_1, \omega_2, \omega_3) \) term. In this work, for the purpose of comparing nonlinear response between different gauges, we only obtain the analytical formats for third harmonic generation (THG), DC Kerr effect (DCKerr), DC-induced second harmonic generation (DCSHG), optical Kerr effect (i.e., intensity-dependent index of refraction (IDIR)), and DC-electric-field-induced optical rectification (EFIOR). The results under \( DD \) correlation with or without \( \nabla_k \) contribution in the corresponding figures are obtained from the preceding paper [23].

**B. Third Harmonic Generation \( \chi^{(3)}(-3\omega; \omega, \omega, \omega) \)**

Applying the Residue theorem and then using Maple to simplify \( S(\omega, \omega, \omega) \) in the Eq. (3.10), we obtain:

\[ S(\omega, \omega, \omega) = \frac{e^2}{\omega^4 \omega_k} \left\{ \frac{4(5e^2 - 2\omega^2)}{3(4\omega_k^2 - \omega^2)} - \frac{8(e^2 - \omega^2)}{3(\omega_k^2 - \omega^2)} + \frac{4(c^2 - 2\omega^2)}{(4\omega_k^2 - 9\omega^2)} \right\} \]

\[ = \frac{1}{2^4 e^4 \Delta^6} \frac{3(1 - 8 z^2)}{3(1 - 4 z^2)} \left\{ \frac{(5 - 8 z^2)}{3(1 - 4 z^2)} - \frac{8(1 - 4 z^2)}{3(1 - 4 z^2)} + \frac{(1 - 8 z^2)}{(x^2 - 9 z^2)} \right\} \]

Combining Eq. (3.10) and Eq. (3.12), we obtain

\[ \chi^{(3)}(\omega, \omega, \omega) = \frac{e^4 n_0 (\hbar v_F)^3}{1152 \pi \Delta^6} \frac{1}{z^8} \left\{ 3(1 - 8 z^2)f(3z) - 8(1 - 4 z^2)f(2z) + (5 - 8 z^2)f(z) \right\}, \quad (3.13) \]

where the function \( f(z) \) is defined by the formula

\[ f(z) = \int_{1}^{\infty} \frac{dx}{(x^2 - z^2)\sqrt{x^2 - 1}} = \begin{cases} \arcsin(z) & (z^2 < 1), \\ \frac{\cosh^{-1}(z)}{z \sqrt{z^2 - 1}} & (z^2 > 1). \end{cases} \quad (3.14) \]
As \( z \to 0 \), we have

\[
\chi^{(3)}(\omega, \omega, \omega) = \frac{e^4 n_0 (\hbar v_F)^3}{\pi \Delta^6} \left( \frac{4}{45} + \frac{32}{21} z^2 + \frac{128}{7} z^4 + \frac{18944}{99} z^6 + O(z^8) \right)
\]  

(3.15)

Eq.(3.13) is exactly the same as Wu’s result [4]. By applying the following conversion between SSH and TLM model:

\[ \hbar v_F = 2t_0 a, \]

then defining

\[ \chi^{(3)}_0 = \frac{8 e^4 n_0 (2t_0 a)^3}{45 \pi \Delta^6}, \]

(3.17)

and choosing the same parameters as in the previous works [12,13,23], i.e. \( \Delta = 0.9 eV, n_0 = 3.2 \times 10^{14} cm^{-2} \) and \( a = 1.22 \AA \), we obtain \( \chi^{(3)}_0 \approx 1.0 \times 10^{-10} \) esu.

The magnitude of third-harmonic generation under \( J_0 J_0 \) correlation, and that under \( DD \) correlation with or without intraband contribution are plotted in Fig.1. The theoretical discrepancies of THG under different gauges have been noticed by many others’ works [12–19]. It has been addressed in all works that the two-photon absorption peak observed in the experiments cannot be explained by the single-electron models like SSH and TLM models. Meanwhile, it was also pointed out that both gauges should reach the exact same results if the calculations have been performed correctly. The reason why the discrepancy exists in the different gauges has not been pinpointed in all previous calculations. Recently based on the same models for the linear response [9], we strictly proved that the gauge phase factor, which was ignored in the previous studies of optical properties, is the cause for the difference. When the gauge phase factor is considered, the difference between different gauges could be resolved [9].

C. Optical Kerr effect or intensity-dependent index of refraction \( \chi^{(3)}(-\omega, -\omega, \omega) \)

Following an almost identical procedure of obtaining \( S(\omega, \omega, \omega) \), we have:

\[
S(\omega, -\omega, \omega) = \frac{8 e^2}{3} \frac{(-48 \omega_k^6 + 60 \omega_k^4 \omega^2 + 24 \omega_k^2 \omega^4 - 35 \omega_k^4 \omega^2 - 3 \omega_k^2 \omega^4 + 2 \omega^2 \omega^4)}{(2 \omega_k^2 - \omega)(4 \omega_k^2 - \omega^2)^3} \]

\[
= \frac{1}{6e^2} \left( -12x^6 + 15x^4 + 24x^2 z^2 - 35x^2 z^4 - 12x^2 z^4 + 8z^4 \right) \]

(3.18)

Following a similar procedure of evaluating \( \chi^{(3)}(0, 0, \omega) \), we obtain the optical Kerr effect \( \chi^{(3)}(-\omega, -\omega, \omega) \) (or \( \chi^{(3)}(\omega, \omega, \omega) \) for short) as follows:

\[
\chi^{(3)}(\omega, -\omega, \omega) = \frac{e^4 n_0 (\hbar v_F)^3}{48 \pi \Delta^6} \frac{1}{z^8} \left\{ (4z^2 - 1) f(2z) - \frac{z^2(4z^2 - 1)}{2(1 - z^2)^2} - \frac{8z^6 - 12z^4 + 9z^2 - 2}{2(1 - z^2)^2} f(z) \right\}.
\]

(3.19)

As \( z \to 0 \), we have

\[
\chi^{(3)}(\omega, -\omega, \omega) = \frac{e^4 n_0 (\hbar v_F)^3}{\pi \Delta^6} \left( \frac{4}{45} + \frac{32}{63} z^2 + \frac{128}{63} z^4 + \frac{3584}{495} z^6 + O(z^8) \right)
\]  

(3.20)

The magnitude of optical Kerr effect (i.e., intensity-dependent index of refraction(IDIR)) under \( J_0 J_0 \) correlation, and that under \( DD \) correlation with or without intraband contribution are plotted in Fig.2.

Eq.(3.19) is exactly the same as Eq.(13) in Wu’s work [4]. From Fig.2, the results from \( DD \) and \( J_0 J_0 \) correlations all show the cusp \( z = 1/2 \). We would like to point out this is merely the van Hove singularity [8] by the singular state density in one-dimensional polymer structure [22], not the real resonant peak. Furthermore, the calculation through \( DD \) correlations by dropping \( \nabla_k \) terms does not exhibit the \( z = 1/2 \) cusp, showing that the cusp is related to the process of intraband-transition.
D. DC Kerr effect $\chi^{(3)}(-\omega; 0, 0, \omega)$

To evaluate the DC Kerr effect $\chi^{(3)}(-\omega; 0, 0, \omega)$ (or $\chi^{(3)}(0, 0, \omega)$ for short), we first evaluate $S(\omega_1, \omega_2, \omega_3) = S(z_1, z_2, z_3)$ for general $z_i$ ($i = 1, 2, 3$), then substitute it into Eq. (3.10) and take the limit $z_1 \to 0$, $z_2 \to 0$, and $z_3 \to z$. We obtain

$$\chi^{(3)}(0, 0, \omega) = \frac{e^4 n_0 (\hbar v_F)^3}{576 \pi \Delta^6} \frac{1}{z^4 (z^2 - 1)^3} \left\{3(3 - 8z^2)f(z) + (16z^6 - 40z^4 + 18z^2 - 9)\right\}$$

(3.21)

As $z \to 0$, we have

$$\chi^{(3)}(0, 0, \omega) = \frac{e^4 n_0 (\hbar v_F)^3}{\pi \Delta^6} \left(\frac{4}{45} + \frac{16}{63} z^2 + \frac{32}{63} z^4 + \frac{256}{297} z^6 + O(z^8)\right)$$

(3.22)

The magnitude of DC Kerr effect (DCKerr) under $J_0, J_0$ correlation, and that under $DD$ correlation with or without intraband contribution are plotted in Fig. 3. The figure only shows one resonant peak at $z = 1$ for all 3 cases.

E. DC induced second harmonic generation $\chi^{(3)}(-2\omega; 0, \omega, \omega)$

Following a similar procedure of evaluating $\chi^{(3)}(0, 0, \omega)$, we obtain the DC induced second harmonic generation $\chi^{(3)}(-2\omega; 0, \omega, \omega)$ (or $\chi^{(3)}(0, \omega, \omega)$ for short) as follows:

$$\chi^{(3)}(0, \omega, \omega) = \frac{e^4 n_0 (\hbar v_F)^3}{384 \pi \Delta^6} \frac{1}{z^8} \left\{2 - 9z^2 f(2z) + z^2 (1 + z^2 - 8z^4) \left(\frac{z}{2^2 - 1}\right) - \frac{2}{z^2 - 1} f(z)\right\}$$

(3.23)

As $z \to 0$, we have

$$\chi^{(3)}(0, \omega, \omega) = \frac{e^4 n_0 (\hbar v_F)^3}{\pi \Delta^6} \left(\frac{4}{45} + \frac{16}{21} z^2 + \frac{32}{21} z^4 + \frac{11776}{495} z^6 + O(z^8)\right)$$

(3.24)

The magnitude of DC induced second harmonic generation (DCSHG) under $J_0, J_0$ correlation, and that under $DD$ correlation with or without intraband contribution are plotted in Fig. 4. The figure clearly shows two resonant peaks at $z = 1/2$ and $z = 1$. The width of $z = 1$ peak suggests that the peak will not be so huge under $J_0, J_0$ correlation than $DD$ correlation if the damping is included.

F. DC-electric-field-induced optical rectification $\chi^{(3)}(0; \omega, -\omega, 0)$

After the calculations, we obtain the same results as in DC Kerr effect. Kleinman symmetry [24] is preserved in this calculation for all regions. This result is different from $DD$ correlation since $J_0, J_0$ correlation maintains the commuting feature for all operators. Due to the nonequivalence between EFIOR and DC Kerr under $DD$ correlation, we still plot the magnitude of EFIOR under $J_0, J_0$ correlation, and that under $DD$ correlation with or without intraband contribution in Fig. 5.

IV. DISCUSSIONS

A. Nonequivalence between $DD$ and $J_0, J_0$ correlations

From the above calculations in Sec. III, the nonequivalence of hyperpolarizabilities between $DD$ and $J_0, J_0$ correlations can be found in all results, though there are some similarities in the resonant peak, the shape of the curve, etc. To understand the difference between the gauges in the models, we present a possible explanation in our previous work [9]. To maintain the self-completeness of this work, we also briefly address the explanation here.

If the electromagnetic field is applied, the Schrödinger equation is given by:

$$i\hbar \frac{\partial}{\partial t} \psi(\mathbf{r}, t) = \left[\frac{1}{2m}(\mathbf{p} - q\mathbf{A})^2 + V(\mathbf{r}) + q\phi\right] \psi(\mathbf{r}, t),$$

(4.1)
where $\psi(r, t)$ is the exact wave function at space position $r$ and time $t$, $m$ is the particle mass, $q$ is the electrical charge, $V(r)$ is the potential, and $A$ and $\phi$ are vector and scalar potential, respectively. Suppose now $A$ and $\phi$ undergo the following transformation:

$$\begin{align*}
A & \rightarrow A' = A + \nabla f(r, t) \\
\phi & \rightarrow \phi' = \phi - \frac{\partial}{\partial t} f(r, t),
\end{align*}$$

(4.2)

where $f(r, t)$ is arbitrary, and $A'$ and $\phi'$ are new vector and new scalar potentials after the transformation Eq.(4.2). Then it can be shown [25] that the form of the Schrödinger equation will be exactly the same if the old wave function $\psi$ makes the following change into the new exact wave function $\psi'$:

$$\psi \rightarrow \psi' = e^{iF_g(r, t)} \psi = \hat{T}_G(r, t) \psi,$$

(4.3)

where gauge phase factor $F_g(r, t)$ is defined as:

$$F_g(r, t) = \frac{q}{\hbar} f(r, t).$$

(4.4)

The above Eq.(4.2) and Eq.(4.3) are called gauge transformation (or $U(1)$ transformation [26]).

By utilizing the long-wavelength approximation [3,5], the electric field $E$ is described as $E = E_0 e^{-i\omega t}$.

If we consider the following initial scalar and vector potentials under $E \cdot r$ gauge:

$$A = 0, \phi = -E \cdot r.$$

(4.5)

After choosing the gauge phase factor $F_g$ as

$$F_g = \frac{qE \cdot r}{i\hbar \omega} = \frac{q}{\hbar} A' \cdot r,$$

(4.6)

by Eq.(4.2), we obtain the new vector and new scalar potential under $p \cdot A$ gauge as:

$$A' = \frac{E}{i\omega}, \phi' = 0.$$

(4.7)

The connection between the old and new wave function is determined by Eq.(4.3).

Under perturbative schemes to study the optical response, conventionally people use the exact same set of unperturbed wave functions $\psi_0^n(r, t)$ of Hamiltonian $H_0$ (when $A = 0$ and $\phi = 0$ in Eq.(4.1)) to serve as our expansion basis for both $E \cdot r$ and $p \cdot A$ gauges [2,3]. However, we should point out that the wave functions for both $E \cdot r$ and $p \cdot A$ gauges (before and after gauge transformation) should also be restricted by the gauge phase factor $F_g$ from Eq.(4.3), therefore two basis sets for both gauges are not the exact same unperturbed wave functions $\psi_0^n(r, t)$, but are different by the gauge phase factor $F_g$. And the Hamiltonian under two gauges ($E \cdot r$ and $p \cdot A$) are not necessary equivalent if they are treated independently and are isolated from the connection between the wave functions under the two gauges. Unfortunately, this crucial point has not been clearly illustrated and obviously missed by previous works using perturbation schemes [1–3].

Especially under current-current correlation scheme, the gauge phase factor’s contribution is obviously ignored and $A^2(t)$ term is considered of no physical meanings [3]. Thus the current-current correlation is conveniently reduced into the $J_0J_0$ formula such as Eq.(2.1), and the equivalence between current-current and dipole-dipole correlations is usually considered as $J_0J_0$ and $DD$ correlations under the exact same basis of unperturbed wave functions [2–4].

Langhoff, Epstein and Karplus covered the topics of time-dependent perturbative theory [27] and sharply pointed out that the time-dependent phase in wave functions is very essential, the improper treatment of time-dependent phase will cause secular divergence in time-dependent perturbations. In field theory, it is also well-understood that the improper treatment of the phase factor will cause divergence [5]. Since the gauge phase factor Eq.(4.6) is obviously time-dependent, neglecting this phase factor will cause the ZFD in the susceptibility computations.

Generally speaking, the widely-adopted conventional formula under $J_0J_0$ is incorrect. It ignores both the gauge phase factor’s influence and diamagnetic term’s contribution [9]. For the linear case, we strictly proved that after taking the consideration of the diamagnetic term and the gauge phase factor, both $DD$ and $J_0J_0$ correlations yield the exact same result for both SSH and TLM models. The details could be found in [9] and will not be repeated here. But for the nonlinear case as we mentioned in the THG calculations [12,13], the complexity to include the gauge phase factor in $JJ$ correlation suggested $DD$ correlation may be more suitable for further studies.
B. Zero frequency divergence (ZFD)

In general, $J_0J_0$ correlation leads to the zero frequency divergence in the nonlinear optical studies. The static current operator in the TLM model coincidentally avoids ZFD problem in the nonlinear calculations shown above, which does not mean that it is flawless. For example, linear calculation based on $J_0$ in TLM model leads a ZFD problem [9]. By splitting the $J_0$ term into inter- and intra-band currents in the TLM model and performing the nonlinear calculations to determine the contributions from two different currents, we find that the hyperpolarizabilities for both cases have ZFD. For the SSH model, the static current operator $J_0$ [8] leads to the ZFD in nonlinear calculations [11]. If the gauge phase factor [9] is properly considered in our calculations, the ZFD problem could be resolved. Therefore, the ZFD problem for nonlinear calculations under the conventional schema of Eq.(2.1) and Eq.(2.2) is not just a technical nuisance which can be tacitly ignored.

C. The overall permutation and Kleinman symmetries

Based on the $p \cdot A$ gauge, the general formulas of $J_0J_0$ correlations [3,4] preserve both the overall permutation [3] and Kleinman symmetry [24] of hyperpolarizabilities in any systems. Without surprise, our calculations of hyperpolarizabilities under $J_0J_0$ correlation preserve both the overall permutation and Kleinman symmetries. However, the overwhelming majority of recent experiments on various physical systems generally refute Kleinman symmetry [28]. Based on $E \cdot r$ gauge and 1D periodic models, we analytically showed the break of overall permutation and Kleinman symmetry [23,29]. Therefore, the experimental testing on the overall permutation symmetry in periodic systems can also be used as a valid test for the conventional $J_0J_0$ correlation and $p \cdot A$ gauge. Detailed discussions of the symmetry break and some suggested experiments could be found in [23,29].

V. CONCLUSIONS

For the infinite chains under TLM model, the analytical solutions of THG, DCKerr, DCISHG, IDIR and EFIOR are obtained through $J_0J_0$ correlation. The results are not equivalent to those under $DD$ correlations [23]. It shows that the conventional $J_0J_0$ correlation formula is incorrect for studying the nonlinear optical properties. Considering the complexity of including the gauge phase factor and other terms for the current-current correlation, $DD$ correlation may be much more suitable in the nonlinear studies.

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FIG. 1. The magnitude of third-harmonic generation(THG) under $J_0J_0$ correlation(dashed-line), under $DD$ correlation with(real line) or without(dot-dashed) intraband contribution is in unit of $10^{-9}$esu. $z \equiv \hbar \omega/2\Delta$.

FIG. 2. The magnitude of optical Kerr effect or intensity-dependent index of refraction(IDIR) under $J_0J_0$ correlation(dashed-line), under $DD$ correlation with(real line) or without(dot-dashed) intraband contribution is in unit of $10^{-9}$esu. $z \equiv \hbar \omega/2\Delta$. 9
FIG. 3. The magnitude of DC Kerr effect (DCKerr) under $J_0 J_0$ correlation (dashed-line), under $DD$ correlation with (real line) or without (dot-dashed) intraband contribution is in unit of $10^{-9}$ esu. $z \equiv \hbar \omega / 2 \Delta$.

FIG. 4. The magnitude of DC induced second harmonic generation (DCSHG) under $J_0 J_0$ correlation (dashed-line), under $DD$ correlation with (real line) or without (dot-dashed) intraband contribution is in unit of $10^{-9}$ esu. $z \equiv \hbar \omega / 2 \Delta$. 
FIG. 5. The magnitude of DC-electric-field-induced optical rectification (EFIOR) under $J_0J_0$ correlation (dashed-line), under $DD$ correlation with (real line) or without (dot-dashed) intraband contribution is in unit of $10^{-9}$esu. $z \equiv \hbar\omega/2\Delta$. 