Optical Susceptibilities of Polymers:
Current-Current versus Dipole-Dipole Correlation

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The static current operator leads to definitional zero frequency divergence and unphysical results in studying nonlinear optical susceptibilities of polymers. A well-defined dipole-dipole correlation is superior to the complicated current-current correlation to solve this problem. As illustrative examples, optical susceptibilities under both SSH and TLM models of trans-(CH)₂ are studied. New analytical results are obtained. The reasons of previous improper results are analyzed.

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To study the nonlinear optical (NLO) properties of polymers, periodic approximate models are necessary to simplify the real systems. Some good approximate models of polymers based on the tight-binding approximation (TBA), such as SSH and TLM models in weakly correlated systems, Hubbard and Pariser-Parr-Pople models in strongly correlated and electron-electron (e-e) interaction systems, etc, have yielded physical insights surpassing the complicated non-approximate computations. In considering the optical response of these models, a U(1) transformation has been suggested to provide the gauge invariance of the TBA Hamiltonian.

In linear optical (LO) response theory, the Kubo formula based on current-current (J·J) correlation \( [2] \) is widely used because of simplicity. It is commonly held that in discussing the optical susceptibilities of materials, the J-J correlation (p·A) will play the same role as that of dipole-dipole (D-D) correlation (E·r) \( [3] \) and that the apparent definitional zero frequency divergence (ZFD) in the NLO susceptibilities definition is only a virtual problem, although the proofs only have been shown under certain assumptions. \( [4,10] \) However, there exists some discrepancies from the above conclusion under the models: (i) In the study of conductivity \( \sigma \) under TBA models, the J-J correlation will have ZFD in Im(\( \sigma \)) (related to the real part of J-J) although it can give the correct Re(\( \sigma \)) (related to the imaginary part of J-J). (ii) In third-harmonic generation (THG) trans-(CH)₂, the experimentally observed two-photon absorption peak (TP) \( [5] \) has given rise to the theoretical explanations. Based on J-J correlation, the TP was explained by choosing the TLM model. But it has been criticized by others \( [10,21] \) with simple parity consideration. Also the spectrum is quite different from that under the D-D correlation. \( [21] \) Thus, it casts some doubts in the practical application of J-J correlation.

In this letter, we will show that all above controversies are caused by the improper application of J-J correlation based only on the static current operator \( J_0 \). To recover the correct results, a well-defined D-D correlation is more suitable for studying the optical susceptibilities than the J-J correlation, whose equivalence to the D-D correlation can be satisfied by introducing complicated induced field currents (IFCs). Besides solving the apparent ZFD in the definition of NLO susceptibility, the D-D correlation is to be favored over the J-J correlation due to the lack of the gauge dependence of the vector potential \( A \) \( [3] \) and simplifying the definitional complexity of the contribution by IFCs in the high order expansions. \( [3,4] \) As a deduction, the TP cusp and ZFD \( [3,4] \) will no longer exist in both SSH and TLM models by the well-defined D-D correlation. However, this seemingly trivial conclusion has not been clearly illustrated by the others although the D-D correlation has already been applied in the NLO response of the real systems. \( [3,10,21] \)

The application of J-J correlation is simpler than that of the D-D correlation in LO response because of the convenient search for the static current \( J_0 \) \( [3] \) compared with that for dipole expression \( D \) under the approximate models. As a typical example, the position operator \( \hat{r} \) is ill-defined in periodic systems \( [12,22] \) in real space while \( J_0 \) is not. Further, the static current \( J_0 \) still can give the correct results in the LO absorption \( [3,10,13] \) because the IFCs only contribute to the real part of J-J correlation. Thus the simplicity of the Kubo formula is still satisfied by applying the static current \( J_0 \) and ZFD in the real part of J-J correlation could be solved either by the Kramers-Kronig (KK) relation \( [13] \) or by subtracting \( \langle [j,j] \rangle (\omega = 0) \). \( [13] \) It is not a big surprise to see why the correct results still can be preserved for the LO response through \( J_0 \). However, the advantage of J-J correlation application in LO response is no longer available for the NLO response because of the IFCs, \( [3,13] \) thus the definition of n-th order J-J correlation...
will obtain the IFCs related to all orders of results in NLO response have been recurrently questioned by the others, the direct reason has never been contribute to the optical response. Complexities in handling IFCs (usually related to the intra-band currents) in many approximate models are forbidden and the static current could easily be improperly used. By others. To avoid the ill-definition and to provide the periodicity of the position operator, we express $\hat{\mathbf{r}}$ under $|n, k >$ as:

$$r_{n,k,n',k'} = i \delta_{n,n'} \nabla_k (k - k') + \Omega_{n,n'}(k) \delta(k - k'),$$

where $\Omega_{n,n'}(k) = \frac{i}{v} \int u^*_{n,k}(r) \nabla_k u_{n',k}(r) \, dr$ and $v$ is unit cell volume.

**Susceptibilities definition by D-D correlation:** Without considering retardation effect, optical susceptibilities are usually defined by expanding the optical polarization in powers of the transverse electric field. Under that approximation, the general $n$th-order susceptibility is a purely material quantity defined as:

$$\chi^{(n)}(\Omega; \omega_1, \ldots, \omega_n) = \frac{1}{n!} \left( \frac{i}{\hbar} \right)^n \int dr_1 \cdots dr_n \int dt_1 \cdots dt_n \int dr dt e^{-i \mathbf{k} \cdot \mathbf{r} + i \Omega t} (\hat{T} \hat{D}(\mathbf{r}, t)) \hat{D}(\mathbf{r}_1, t_1) \cdots \hat{D}(\mathbf{r}_n, t_n),$$

where $\Omega = - \sum_{i=1}^{n} \omega_i$, $\hat{T}$ is the time-ordering operator and $\hat{D}$ is dipole operator.

Based on periodic TBA, SSH Hamiltonian is given:

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

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

In momentum space, the above Hamiltonian with electron-photon ($e\mathbf{A}$) interaction could be found as follows:

$$H(k, t) = \sum_{k,s} \epsilon(k) \tilde{\psi}^\dagger_{k,s}(t) \sigma_3 \tilde{\psi}_{k,s}(t) - \hat{D} \cdot \mathbf{E} e^{i \omega t},$$

where $\epsilon(k) = \sqrt{(2t_0 \cos(ka))^2 + (\Delta \sin(ka))^2}$ and $\tilde{\psi}^\dagger_{k,s}(t) = (\hat{a}^\dagger_{k,s}(t), \hat{a}^\dagger_{k+s}(t))$ is the two-component spinor describing excitations of electrons in the conduction band and valence band. Long wave approximation is applied in electromagnetic field $\mathbf{E}$ with frequency $\omega$. The dipole operator $\hat{D}$ could be obtained by the Eq. (3):

$$\hat{D} = e \sum_{k,s} (\beta(k) \psi^\dagger_{k,s} \sigma_2 \psi_{k,s} + i \frac{\partial}{\partial k} \psi^\dagger_{k,s} \psi_{k,s}),$$
where \( \beta(k) = -\Delta t_0a/\varepsilon^2(k) \), is the coefficient related to the interband transition between the conduction and valence bands in a unit cell 2\( a \) and the second term is related to the intraband transition, \( \varepsilon \) is the electric charge and \( \sigma \) are the Pauli matrices. We neglect the relative distortion \( \eta(\equiv 2u/a) \) in the dipole operator because it is relatively small in the optical contribution. [23]

Due to the fact that \( \pi \) electrons in the SSH model are non-localized, [2] the dipole approximation [20] is no longer valid in the extended states and will lead to wrong results as pointed out by some authors. [4] The Fourier transform of Eq. (4) to coordinate space shows that the transition dipole is related to the electron hopping to all the other sites besides the nearest neighbor sites. Thus the dipole approximation fails for the extended states in periodic systems. Because of the failure of dipole approximation through the polarization operator \( \hat{P} \), computations show a magnitude difference of \( 10^2 \) in \( \chi^{(1)} \) and \( 10^4 \) in \( \chi^{(3)} \) [21] and quite different shape in spectrum compared with the results through the dipole operator \( \hat{D} \) and the experimental values [13,24] in trans-(CH)_x, although the position of some resonant peaks may be correctly obtained.

**LO response by D-D:** The LO susceptibility \( \chi^{(1)}_{SSH}(\omega_1) \) can be obtained from Eq. (2) and Eq. (4):

\[
\chi^{(1)}_{SSH}(-\omega_1, \omega_1) = 2 \frac{i}{\hbar} e^2 \sum_k \int_{-\infty}^{\infty} \text{Tr} \left\{ i \frac{\partial}{\partial k} \left[ G(k, \omega) i \frac{\partial}{\partial k} [G(k, \omega - \omega_1)] \right] + \beta(k) \sigma_2 G(k, \omega) i \frac{\partial}{\partial k} [G(k, \omega - \omega_1)] \right\} \frac{d\omega}{2\pi}, \tag{5}
\]

where the Green function \( G(k, \omega) = \frac{\omega + \omega_k \sigma_3}{\omega^2 - \omega_k^2 + i\epsilon} \) with \( \omega_k \equiv \varepsilon(k) / \hbar \) and \( \epsilon \equiv 0^+ \).

By Eq. (2), we have \( \chi^{(1)}_{SSH}(\omega) \equiv \chi^{(1)}_{SSH}(-\omega, \omega) :\)

\[
\chi^{(1)}_{SSH}(\omega) = \frac{e^2 (2t_0a)}{2\pi \Delta^2} \int_1^z \frac{dx}{[(1 - \delta^2x^2)(x^2 - 1)]^{1/2} x^2(x^2 - z^2)},
\]

where \( x \equiv \hbar \omega_k / \Delta, z \equiv \hbar \omega / (2\Delta) \) and \( \delta \equiv \Delta / (2t_0) \).

If the continuum limitation is applied, that is, \( \delta \to 0 \) and \( 2t_0a \to \hbar v_F \), the above integral gives the LO susceptibility \( \chi^{(1)}_{TLM}(\omega) \) under the TLM model [2] as follows:

\[
\chi^{(1)}_{TLM}(\omega) = \frac{e^2 \hbar v_F}{2\pi \Delta^2 z^2} (1 - f(z)), \tag{6}
\]

where

\[
f(z) = \begin{cases} 
\arcsin(z) & (z^2 < 1), \\
\frac{\cosh^{-1}(z)}{z\sqrt{z^2 - 1}} + \frac{i\pi}{2z\sqrt{z^2 - 1}} & (z^2 > 1). 
\end{cases} \tag{7}
\]

The conductivity \( \sigma(\omega) \) given by \( -i\omega \cdot \chi^{(1)}(z) \), is exactly the same as based on \( J-J \) correlation. [14] However, we should point out that the direct computation based on the static current from \( J-J \) correlation under TLM model [2] shows no first term in Eq. (6). [21] ZFD in real part of \( J-J \) correlation is obvious although the correct imaginary part still can be given. These difficulties have never been clearly addressed previously, provided the reason that the static current \( J_0(k) \) is still valid for obtaining the correct imaginary part in the LO absorption. To include the IFCs by changing \( k \to k - eA / \hbar \) in the static current operator \( J_0(k) \), ZFD could be solved to give the same result as that under \( D-D \) correlation. [3] But the complicated way to include the IFCs compared with simple \( D-D \) correlation already makes \( J-J \) correlation impractical even for the LO response. Fortunately, the IFCs only contribute for the real part of \( J-J \) correlation and have no influence on the absorption. Attempts to obtain IFCs directly from TLM Hamiltonian fail because it is forbidden to include \( A^2 \) term by the model. [2] In the discrete SSH Hamiltonian, we have the chance to include the IFCs through Peierls substitution. [4] But a straightforward computation easily shows that they are not correct IFCs to cancel the ZFD. [2] It gives us an impression of the difficulty to obtain the correct IFCs besides the complexity of handling their contributions to the optical response even in well-defined 1-d periodic models. From the above examples, the feasibility of \( J-J \) correlation in more general models will be questioned and the application of \( D-D \) correlation is more reasonable under approximate models to obtain the correct results.
NLO susceptibilities of trans-(CH)\textsubscript{\textit{x}} chain: There are many elegant works in discussing NLO susceptibilities of polymer chains.\cite{11,15–20} The TP\cite{11} obtained from J-J correlation was doubted in the literature\cite{15–20} since it is forbidden by momentum conservation and parity consideration in both TLM and SSH models. Based on the D-D correlation, our analytical results of THG show explicitly that TP no longer exists in both the SSH and the TLM models. This unphysical TP is caused by the same reason – the improper use of the static current \(\hat{J}_0\) and omission of the IFCs in periodic chain. Although the reason for J-J correlation is very clear, we only give the computational results based on D-D correlation. It is expected that if the correct IFCs are considered, J-J correlation will give the same results as D-D correlation although much more complicated computations are inevitable. After a similar definition as Eq. (3) and tedious derivations, the new result of THG per unit length under SSH model for infinite chains is recovered as:

\[
\chi_{\text{SSH}}^{\text{THG}}(\omega) = \chi_0^{(3)} \frac{45}{128} \int_1^\infty \frac{dx}{[(1 - \delta^2x^2)(x^2 - 1)]^{3/2}} \left\{ - \frac{47 - 48(1 + \delta^2)x^2 + 48\delta^2x^4}{8x^8(x^2 - z^2)} + \frac{3(1 - \delta^2x^2)(x^2 - 1)}{x^6(x^2 - z^2)^2} \right.
\]

\[
+ \frac{9}{8x^8(x^2 - (3z)^2)} \left[ -47 - 48(1 + \delta^2)x^2 + 48\delta^2x^4 \right] + \frac{63(1 - \delta^2x^2)(x^2 - 1)}{x^6(x^2 - (3z)^2)^2} \left\}
\]

where \(\chi_0^{(3)} = \frac{8}{45} \frac{e^4n_0(2t_0a)^3}{\pi \Delta^6}\), \(n_0\) is the number of chains in unit cross area, the polymer chains are assumed to be oriented. \(x\), \(z\) and \(\delta\) are defined the same as in \(\chi_{\text{SSH}}^{(1)}(\omega)\).

Eq. (8) is an elliptical integration and can be numerically integrated if one change \(x \to x + i\epsilon\) in considering the life-time of the state.\cite{16,17} For polyacetylene, by choosing \(t_0 = 2.5eV\), \(\Delta = 0.9eV\), \(n_0 = 3.2 \times 10^{14} cm^{-2}\), \(a = 1.22\) Å and \(\epsilon \sim 0.03\),\cite{17} we have \(\delta = 0.18\) and \(\chi_0^{(3)} \approx 1.0 \times 10^{-11} \text{ esu}\). The absolute value of \(\chi_{\text{SSH}}^{\text{THG}}(\omega)\) is plotted in Fig. 1. It shows the good agreement with the experimental value\cite{13} around \(z = 1/3\).

![Fig. 1. \(|\chi_{\text{SSH}}^{\text{THG}}(\omega)|\) for \(\epsilon=0.03\) with \(z \equiv \hbar\omega/(2\Delta)\).](image1.png)

![Fig. 2. Computed D-D value (solid line) vs. \(J_0-J_0\) value (dashed line) of \(|\chi_{\text{SSH}}^{\text{THG}}(\omega)|\) with \(z \equiv \hbar\omega/(2\Delta)\).](image2.png)
Let $\delta \to 0^+$ and $\epsilon \to 0^+$ in Eq. (8), we obtain the analytical result of THG under TLM model as follows:

$$\chi_{TLM}^{THG}(\omega) = \chi_0^{(3)} \left( \frac{24}{8\pi^6} \left\{ -\frac{14}{3z^8} + \frac{4}{15z^4} + \frac{37 - 24z^2}{8z^8} f(z) + \frac{1 - 8z^2}{24z^8} f(3z) \right\} \right)$$ (9)

where $f(z)$ and $\chi_0^{(3)}$ defined in Eq. (7) and Eq. (8). The comparison between our result ($D$-$D$) and Wu's result ($J_0$-$J_0$) [10] on absolute value of $\chi_{TLM}^{THG}$ is plotted in Fig.2.

The TP disappears in our analytical results, which is more reasonable for the physical situation and consistent with the previous numerical computations. [19-20] It also implies that the $e$-$e$ interactions, [19,20] disorders, quantum fluctuations or finite chain size effects [17] should be taken into account to explain this experimentally observed TP. [13]

Fig.1 shows another new resonant peak $z = 1$ at ratio of 1/10 of $z = 1/3$. This new peak hasn't been reported by the experiments [13] because of the experimental scanning range. The cancellation of ZFD by $J_0$-$J_0$ correlation [11] is actually a coincidence under TLM model, because in the SSH model, we find ZFD in $\chi_{SSH}^{(3)}$ through $J_0$-$J_0$ correlation. [21]

Keldysh formalism [11] is not necessary to apply in this equilibrium system. [10] From THG of trans-(CH)$_x$, $D$-$D$ correlation is superior to $J$-$J$ correlation to obtain NLO susceptibilities.

As a conclusion, the principle about the equivalence of $D$-$D$ vs. $J$-$J$ correlation is still correct under the approximate models while practicality favors $D$-$D$ over $J$-$J$ correlation. Although our discussion is chiefly based on 1-d polymer chains, the main results in this letter can be generalized for 2-d or 3-d periodic systems.

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$-(ev_F \Delta)^2 / \varepsilon^3(k)$. The computation of $J_A$ gives the first term in Eq. (6). But $J_A$ cannot be directly obtained from the field currents in the previous works, thus it shows the difficulty to obtain IFCs in general models.