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Breaking of the overall permutation symmetry in nonlinear optical susceptibilities of one-dimensional periodic dimerized Hückel model

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Abstract

Based on one-dimensional single-electron infinite periodic models of trans-polyacetylene, we show analytically that the overall permutation symmetry of nonlinear optical susceptibilities is, although preserved in bound-state molecular systems, no longer generally held in periodic systems. The overall permutation symmetry breakdown provides a natural explanation of the widely observed large deviations of Kleinman symmetry in off-resonant regions of periodic systems. Finally, physical conditions to experimentally test the overall permutation symmetry breakdown are discussed.

The n th-order optical susceptibility is generally defined as a rank- n tensor $\chi_{\mu\alpha_1\alpha_2\cdots\alpha_n}^{(n)}(-\omega_\sigma; \omega_1, \omega_2, \dots, \omega_n)$, where $\omega_\sigma \equiv \sum_{i=1}^n \omega_i$ is the sum of incoming frequencies and $\mu\alpha_1\cdots\alpha_n$ are the indices of spatial directions. The intrinsic permutation symmetry, as described in Butcher and Cotter's book [1], implies that the n th-order susceptibility is invariant under all $n!$ permutations of pairs $(\alpha_1, \omega_1), (\alpha_2, \omega_2), \dots, (\alpha_n, \omega_n)$. Intrinsic symmetry is a fundamental property of the nonlinear susceptibilities which arises from the principles of time invariance and causality, and applies universally to all physical systems. For the medium that is transparent and lossless for all relevant frequencies, i.e., far away from all transition frequencies, it is generally believed that the optical susceptibilities have a much more interesting property, namely, the overall permutation symmetry (or the full permutation symmetry in Boyd's book [2]), in which the susceptibilities are invariant when the permutation includes the additional pair $(\mu, -\omega_\sigma)$. Therefore, the n th-order susceptibility is invariant under all $(n+1)!$ permutations of the pairs $(\mu, -\omega_\sigma), (\alpha_1, \omega_1), \dots, (\alpha_n, \omega_n)$ [3]. Furthermore, when the optical frequencies are much smaller than any of the transition frequencies, the dispersion of the medium at the relevant frequencies is negligible. It follows that the susceptibility is asymptotically invariant under all

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permutations of the subscripts $\mu, \alpha_1, \dots, \alpha_n$ in the low-frequency limit. This property is known as Kleinman symmetry [1, 2, 4].

However, as observed by Simpson and his coauthors [5], the overwhelming majority of recent optical experiments on organic materials and crystals showed large deviations from Kleinman symmetry, even in the low-frequency off-resonant regions. However, the deviations from Kleinman symmetry in molecular systems are fairly small. In this paper, based on the theoretical framework developed in our previous work [6–10], we prove that the overall permutation symmetry of nonlinear optical susceptibilities is broken in one-dimensional (1D) periodic systems. On the other hand, the overall permutation symmetry remains valid in bound-state molecular systems. Since the overall permutation symmetry is the basis of Kleinman symmetry, this provides a natural explanation of why the deviations from Kleinman symmetry are much larger in periodic systems than in bound-state molecular systems. Indeed, despite the wide acceptance of the overall permutation symmetry in the nonlinear optics [1–3], no direct measurement has tested the validity of the assertion. We will suggest physical conditions to experimentally test the overall permutation symmetry breakdown.

The analytical derivations of the overall permutation symmetry of nonlinear susceptibilities are rigorous and correct in molecular systems [1–3] where the position operator \mathbf{r} is well-defined in real space. However, for periodic systems, the usual definition of \mathbf{r} is no longer valid over all space. Instead a ‘saw-like’ position operator must be introduced to maintain the periodic property of the system [11, 12]. If periodic boundary conditions are applied to a physical system, the average electronic position could be anywhere for delocalized states [11]. This is clearly not the case for most molecular systems with only bound states. For periodic systems, the position operator \mathbf{r} is conveniently defined in momentum space [13]:

$$\mathbf{r}_{n\mathbf{k},n'\mathbf{k}'} = i\nabla_{\mathbf{k}}\zeta_{n,n'}(\mathbf{k},\mathbf{k}') + \Omega_{n,n'}(\mathbf{k})\delta(\mathbf{k}-\mathbf{k}'), \quad (1)$$

where

$$\begin{aligned} \zeta_{n,n'}(\mathbf{k},\mathbf{k}') &= \int_V \psi_{n,\mathbf{k}}^*(\mathbf{r})\psi_{n',\mathbf{k}'}(\mathbf{r})\mathbf{r}\mathbf{d}\mathbf{r}, \\ \Omega_{n,n'}(\mathbf{k}) &= \frac{i}{v} \int_v u_{n,\mathbf{k}}^*(\mathbf{r})\nabla_{\mathbf{k}}u_{n',\mathbf{k}}(\mathbf{r})\mathbf{d}\mathbf{r}, \end{aligned} \quad (2)$$

V is the whole system volume, v is the unit cell volume, and $\psi_{n,\mathbf{k}}(\mathbf{r}) = u_{n,\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}$ is the Bloch state with n and \mathbf{k} the band index and crystal momentum, respectively. The two terms in equation (1) correspond to the intra- and inter-band transitions, respectively [13].

On the other hand, the $\mathbf{p}\cdot\mathbf{A}$ (current–current correlation) instead of the $\mathbf{E}\cdot\mathbf{r}$ (dipole–dipole correlation) gauge is often used, where \mathbf{p} is treated as static [1, 11]. Though quite successful in the linear case, the static current–current correlation is actually not equivalent to the dipole–dipole correlation (i.e., the $\mathbf{E}\cdot\mathbf{r}$ gauge) and gives the wrong results for periodic systems [8, 9] in nonlinear optical studies. To restore the equivalence between these two gauges, one needs to incorporate the proper gauge phase factor in the current–current correlation [8]. The importance of the gauge phase factor in gauge equivalence is also verified in a recent work by Rzazewski and Boyd [14]. For simplicity, we have used the $\mathbf{E}\cdot\mathbf{r}$ gauge in this paper.

To demonstrate the symmetry breakdown, we focus on two 1D single-electron periodic models—the Su–Shrieffer–Heeger (SSH) model [15] and its continuum sibling Takayama–Lin–Liu–Maki (TLM) model [16]. These two models are quite successful in explaining the optical properties of trans-polyacetylene (see, for example, [17]). The advantages of 1D single-electron periodic models are twofold. First, since $\zeta_{n,n'}(\mathbf{k},\mathbf{k}') = \delta_{n,n'}\delta(\mathbf{k}-\mathbf{k}')$ can be applied in equation (1), these two models result in 1D simple bands and are analytically solvable [18, 19]. Second, single-electron models also satisfy physical conditions where the overall permutations

symmetry is supposed to be strictly held in existing theories [1–3], since the medium is loss-free at all the relevant optical frequencies under these models. When centro- or inversion symmetry is applied to the system, $\chi^{(2)}$ vanishes and $\chi^{(3)}$ becomes the first non-zero nonlinear susceptibility. Hence, we will concentrate our discussion on $\chi^{(3)}$.

The Hamiltonian of the SSH model with the rigid-lattice approximation (i.e., the dimerized Hückel model) is described as follows [15]:

$$H_{\text{SSH}}^0 = - \sum_{l,s} \left[t_0 + (-1)^l \frac{\Delta}{2} \right] (\hat{C}_{l+1,s}^\dagger \hat{C}_{l,s} + \hat{C}_{l,s}^\dagger \hat{C}_{l+1,s}), \quad (3)$$

where t_0 is the transfer integral between the nearest-neighbour sites, Δ is the gap parameter and $\hat{C}_{l,s}^\dagger$ ($\hat{C}_{l,s}$) creates (annihilates) a π electron at site l with spin s . Following the same procedure described in previous work [6–10], we consider the momentum space representation of the Hamiltonian given by equation (3). With the aid of the spinor description $\hat{\psi}_{k,s}^\dagger(t) = (\hat{a}_{k,s}^{\dagger c}(t), \hat{a}_{k,s}^{\dagger v}(t))$, where $\hat{a}_{k,s}^{\dagger c}(t)$ and $\hat{a}_{k,s}^{\dagger v}(t)$ are the excitations of electrons in the conduction band and the valence band with momentum k and spin s , we obtain the following formula:

$$\begin{aligned} \hat{H}_{\text{SSH}}(k, t) &= \hat{H}_{\text{SSH}}^0 + \hat{H}_{\mathbf{E}\cdot\mathbf{r}} \\ &= \sum_{-\frac{\pi}{2a} \leq k \leq \frac{\pi}{2a}, s} \varepsilon(k) \hat{\psi}_{k,s}^\dagger(t) \sigma_3 \hat{\psi}_{k,s}(t) - \hat{D} \cdot E_0 e^{i\omega t}, \end{aligned} \quad (4)$$

where

$$\hat{D} = e \sum_{-\frac{\pi}{2a} \leq k \leq \frac{\pi}{2a}, s} \left(\beta(k) \hat{\psi}_{k,s}^\dagger \sigma_2 \hat{\psi}_{k,s} + i \frac{\partial}{\partial k} \hat{\psi}_{k,s}^\dagger \hat{\psi}_{k,s} \right), \quad (5)$$

$\varepsilon(k) = \sqrt{[2t_0 \cos(ka)]^2 + [\Delta \sin(ka)]^2}$, σ_i ($i = 1, 2, 3$) are Pauli matrices, and $\beta(k) = -\Delta t_0 a / \varepsilon^2(k)$. $\beta(k)$ 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 equation (5) is related to the intraband transition [6–10].

According to field theory and the Wick theorem [20], the general four-wave mixing (FWM) can be expressed as [6–10]

$$\begin{aligned} \chi_{\text{SSH}}^{(3)}(-\Omega; \omega_1, \omega_2, \omega_3) &= \frac{2e^4 n_0}{\hbar^3} \frac{1}{3!L} \sum_{k, \mathcal{P}(\omega_1, \omega_2, \omega_3)} \int \frac{i d\omega}{2\pi} \text{Tr} \left\{ \left(\beta(k) \sigma_2 + i \frac{\partial}{\partial k} \right) G(k, \omega) \right. \\ &\quad \times \left(\beta(k) \sigma_2 + i \frac{\partial}{\partial k} \right) G(k, \omega - \omega_1) \left(\beta(k) \sigma_2 + i \frac{\partial}{\partial k} \right) G(k, \omega - \omega_1 - \omega_2) \\ &\quad \left. \times \left(\beta(k) \sigma_2 + i \frac{\partial}{\partial k} \right) G(k, \omega - \omega_1 - \omega_2 - \omega_3) \right\}, \end{aligned} \quad (6)$$

where $\Omega = \omega_1 + \omega_2 + \omega_3$, L is the chain length, n_0 is the number of chains per unit cross area, and $\mathcal{P}(\omega_1, \omega_2, \omega_3)$ represents all six permutations over ω_1, ω_2 and ω_3 . The polymer chains are assumed to be oriented. Green's function $G(k, \omega)$ is defined as follows [6–8]:

$$G(k, \omega) = \frac{\omega + \omega_k \sigma_3}{\omega^2 - \omega_k^2 + i\epsilon}, \quad (7)$$

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

The analytical expression for the general four-wave mixing can be found in [10]:

$$\begin{aligned} \chi_{\text{SSH}}^{(3)}(-\Omega; \omega_1, \omega_2, \omega_3) &= \chi_0^{(3)} \frac{15}{1024} \sum_{\mathcal{P}(z_1, z_2, z_3)} \int_1^{1/\delta} \frac{x dx}{\sqrt{(1 - \delta^2 x^2)(x^2 - 1)}} \\ &\quad \times \left\{ \frac{(2x - z_1 - z_3)}{x^8 (x - z_1)(x + z_2)(x - z_3)(x - z_1 - z_2 - z_3)} \right\} \end{aligned}$$

$$\begin{aligned}
& - \frac{(2x + z_1 + z_3)}{x^8(x + z_1)(x - z_2)(x + z_3)(x + z_1 + z_2 + z_3)} \\
& + \frac{4(1 - \delta^2 x^2)(x^2 - 1)}{x^8(x - z_1 - z_2)} \frac{(3x - 2z_1)(3x - 2(z_1 + z_2 + z_3))}{(x - z_1)^2(x - z_1 - z_2 - z_3)^2} \\
& + \frac{4(1 - \delta^2 x^2)(x^2 - 1)}{x^8(x + z_1 + z_2)} \frac{(3x + 2z_1)(3x + 2(z_1 + z_2 + z_3))}{(x + z_1)^2(x + z_1 + z_2 + z_3)^2} \Big\}, \quad (8)
\end{aligned}$$

where

$$\chi_0^{(3)} \equiv \frac{8}{45} \frac{e^4 n_0}{\pi} \frac{(2t_0 a)^3}{\Delta^6}, \quad z_i \equiv \frac{\hbar \omega_i}{2\Delta} \quad (i = 1, 2, 3), \quad \delta = \frac{\Delta}{2t_0},$$

and $\mathcal{P}(z_1, z_2, z_3)$ represents all six permutations over z_1, z_2 and z_3 (please note that the summation over all six permutations was missing in the original equation (3.3) in [10] due to a typographical error).

To discuss the breaking of the overall permutation symmetry, we may simply consider the difference

$$\delta\chi^{(3)} = \chi_{\text{SSH}}^{(3)}(-\Omega; \omega_1, \omega_2, \omega_3) - \chi_{\text{SSH}}^{(3)}(\omega_1; -\Omega, \omega_2, \omega_3). \quad (9)$$

Due to the trivial permutation of the spatial indices, the spatial indices $\mu\alpha_1 \cdots \alpha_n$ can be dropped in the expression of $\chi^{(n)}$ in the 1D case. Thus, the Kleinman symmetry is exactly the same as the overall permutation symmetry for the 1D case, though it is generally different from the overall permutation symmetry for higher dimensional cases. Obviously, $\delta\chi^{(3)}$ in equation (9) should be identically zero if the overall permutation symmetry were preserved. However, it is easy to see from (8) that $\chi_{\text{SSH}}^{(3)}(-\Omega; \omega_1, \omega_2, \omega_3)$ is symmetric in ω_1, ω_2 , and ω_3 , while $\chi_{\text{SSH}}^{(3)}(\omega_1; -\Omega, \omega_2, \omega_3)$ is only symmetric in ω_2 and ω_3 . Hence, $\delta\chi^{(3)}$ cannot be zero everywhere. Indeed, replacing ω_1 by $-(\omega_1 + \omega_2 + \omega_3)$ in (8), substituting the resulting expression into (9), and then simplifying the final expression, we obtain

$$\begin{aligned}
\delta\chi^{(3)} & = \chi_{\text{SSH}}^{(3)}(-(\omega_1 + \omega_2 + \omega_3); \omega_1, \omega_2, \omega_3) - \chi_{\text{SSH}}^{(3)}(\omega_1; -(\omega_1 + \omega_2 + \omega_3), \omega_2, \omega_3) \\
& = \chi_0^{(3)} \frac{15}{256} \sum_{\mathcal{P}(z_2, z_3)} \int_1^{1/\delta} \frac{\sqrt{(1 - \delta^2 x^2)(x^2 - 1)} dx}{x^7} \\
& \quad \times \left\{ \frac{(3x + 2z_2)(3x + 2(z_1 + z_2 + z_3))}{(x + z_2)^2(x + z_1 + z_2 + z_3)^2} \left(\frac{1}{x + z_1 + z_2} + \frac{1}{x + z_2 + z_3} \right) \right. \\
& \quad + \frac{(3x - 2z_2)(3x - 2(z_1 + z_2 + z_3))}{(x - z_2)^2(x - z_1 - z_2 - z_3)^2} \left(\frac{1}{x - z_1 - z_2} + \frac{1}{x - z_2 - z_3} \right) \\
& \quad - \frac{(3x + 2z_1)(3x - 2z_2)}{(x + z_1)^2(x - z_2)^2} \left(\frac{1}{x + z_1 + z_3} + \frac{1}{x - z_2 - z_3} \right) \\
& \quad \left. - \frac{(3x - 2z_1)(3x + 2z_2)}{(x - z_1)^2(x + z_2)^2} \left(\frac{1}{x - z_1 - z_3} + \frac{1}{x + z_2 + z_3} \right) \right\}, \quad (10)
\end{aligned}$$

where the summation is over the two permutations of z_2 and z_3 . Equation (10) provides a general expression for the deviation of the overall permutation symmetry under the SSH or 1D dimerized Hückel model.

Remark 1. A closer examination shows that the first two terms in (8) come from the interband transition, and the last two terms in (8) come from the intraband transition. The deviation of the overall permutation symmetry (equation (10)) is due to the intraband transition alone.

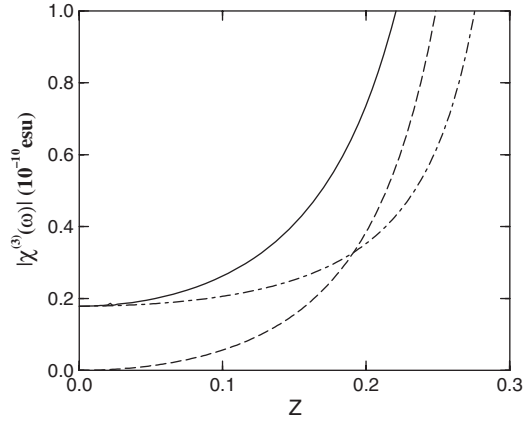


Figure 1. Hyperpolarizabilities under the TLM model in the off-resonant region: $\chi_{\text{TLM}}^{(3)}(-3\omega; \omega, \omega, \omega)$ (solid line), $\chi_{\text{TLM}}^{(3)}(\omega; \omega, \omega, -3\omega)$ (dot-dashed line), and their difference (long dashed line); the horizontal axis is defined by $Z \equiv \hbar\omega/2\Delta$.

To demonstrate the large deviation of the overall permutation symmetry quantitatively, we may consider two special cases under the TLM model (the continuum limit of the SSH model): $\chi_{\text{TLM}}^{(3)}(-3\omega; \omega, \omega, \omega)$ and $\chi_{\text{TLM}}^{(3)}(\omega; \omega, \omega, -3\omega)$. Our analysis shows that

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

and

$$\begin{aligned} \chi_{\text{TLM}}^{(3)}(\omega; \omega, \omega, -3\omega) &= \chi_0^{(3)} \frac{5}{1024z^8} \left\{ \frac{5}{3}(40z^2 - 61)f(z) + \frac{16}{3}(4z^2 - 1)f(2z) \right. \\ &\quad \left. - \frac{1}{243}(1944z^2 - 241)f(3z) + \frac{32}{243}(27z^4 - 30z^2 + 805) \right\} \\ &= \chi_0^{(3)} \left(\frac{5}{28} + \frac{80}{33}z^2 + \frac{28500}{1001}z^4 + O(z^6) \right) \quad (z \rightarrow 0). \end{aligned} \quad (12)$$

where $z = \hbar\omega/2\Delta$, and the function f is defined by the formula

$$f(z) \equiv \begin{cases} \frac{\arcsin(z)}{z\sqrt{1-z^2}}, & (z^2 < 1) \\ -\frac{\cosh^{-1}(z)}{z\sqrt{z^2-1}} + \frac{i\pi}{2z\sqrt{z^2-1}}, & (z^2 > 1). \end{cases} \quad (13)$$

For polyacetylene, using typical parameters of $t_0 = 2.5$ eV, $\Delta = 0.9$ eV, $n_0 = 3.2 \times 10^{14}$ cm⁻² and $a = 1.22$ Å results in $\chi_0^{(3)} \approx 1.0 \times 10^{-10}$ esu [6–10]. In figure 1 we have plotted $\chi_{\text{TLM}}^{(3)}(-3\omega; \omega, \omega, \omega)$, $\chi_{\text{TLM}}^{(3)}(\omega; \omega, \omega, -3\omega)$ and the difference between the above two $\chi^{(3)}$ in the off-resonant region. The graph shows that there is about a 40% difference for $z = 1/6$ (about 0.3 eV or 4.14 μm) between these two quantities. Subtracting the two asymptotic expressions in equations (11) and (12) reveals that the difference between $\chi_{\text{TLM}}^{(3)}(-3\omega; \omega, \omega, \omega)$

and $\chi_{\text{TLM}}^{(3)}(\omega; \omega, \omega, -3\omega)$ in the off-resonant region satisfies the following relationship:

$$\delta\chi^{(3)}(\omega) \propto \frac{e^4 n_0 t_0^3 a^3 \hbar^2 \omega^2}{\Delta^8}. \quad (14)$$

We have also computed nonlinear susceptibilities without the ∇_k or ∂_k terms (corresponding to the intraband transitions) in equation (5) [10]. The results preserve the overall permutation symmetry. Excluding the gradient terms is a crude approximation for molecular systems where the polarization current is not present [21]. Therefore in periodic systems, it is the gradient term that breaks the overall permutation symmetry which remains valid in molecular systems [1–3]. Obviously, this is closely related to the fact that the position operator for periodic systems is entirely different from that for molecular systems.

Remark 2. Recently, deviations from Kleinman symmetry in the low-frequency off-resonant regions have been observed in many nonlinear optical experiments [22–31]. Upon a careful examination of these experiments, we observed that: (i) the deviation of the Kleinman symmetry increases with decreasing band gap and is proportional to ω^2 for crystals [22]; (ii) the deviation of the Kleinman symmetry in delocalized states such as aromatic molecules [28, 29] and some polymers [25–27] or crystals [22–24] is usually much larger than that in localized states such as molecular systems such as O₂ and N₂ [30, 31] (20–50% versus $\leq 8\%$). Equation (14) captures the dependence of ω^2 and the band gap observed in (i). Furthermore, since the overall permutation symmetry is the basis of the Kleinman symmetry, our computation also provides a natural explanation about (ii), as we have shown that the overall permutation symmetry is broken in periodic systems. Finally, the vanishing $\chi^{(2)}$ under the SSH or TLM model shows that some symmetries such as centro-symmetry can suppress the deviation from Kleinman symmetry even for periodic systems. This may explain why Kleinman symmetry is still preserved in some $\chi^{(2)}$ experiments of crystals [32].

Kleinman symmetry (or Kleinman conjecture) is considered valid only when $\omega = 0$ [1, 2]. Previous theoretical calculations [33–35] have explicitly shown the Kleinman symmetry breakdown when $\omega \neq 0$ for higher dimensional cases. Nevertheless, it is still generally treated as a valid approximate symmetry for all physical systems in low-frequency off-resonant regions. However, many experiments show that the range of Kleinman symmetry is substantially more restrictive than what is widely assumed in theory, especially for periodic systems [5]. To explain the large Kleinman symmetry deviation in periodic systems [22–31], various models have been presented. For example: Levine’s model, that predicts the second order polarizability tensor $d^{\text{F}}/d^{\text{A}} \propto \omega^2$, where superscripts F and A mean forbidden and allowed respectively [36], dipole contributions from two perpendicular directions [28], harmonic frequency 2ω strongly resonant with the Q band [29], mutual exclusion properties between Kramers–Kronig dispersion relations and Kleinman symmetry [5], etc. Without so many input parameters, the overall permutation symmetry breakdown in periodic systems provides a much more straightforward and general explanation of the above experiments.

In conclusion, the overall permutation symmetry for nonlinear susceptibilities is, although preserved in bound-state molecular systems, no longer generally held in periodic systems with delocalized states. Therefore, it leads to large deviations of Kleinman symmetry. The deviation $\delta\chi^{(3)}$ is proportional to $(e^4 n_0 t_0^3 a^3 \hbar^2 \omega^2)/\Delta^8$ in the off-resonant regions. Theoretically, non-interacting centro-symmetric 1D periodic structures such as single crystals of conjugated molecules are ideal materials for performing off-resonant $\chi^{(3)}$ experiments to directly test the overall permutation symmetry breakdown. Practically, electron–electron correlation and other interactions are very important in 1D conjugated systems [17]. These interactions will certainly change the magnitude of the deviation. However, as long as those interactions are not strong

enough to destroy the band structures where the intraband transitions remain valid, the overall permutation symmetry breakdown can still be observed.

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