Resonant optical nonlinearity of conjugated polymers

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When the energy of a pump wave is in resonance with the exciton creation energy, the electric susceptibility of a conjugated polymer in response to the probe wave is altered by the exciton gas. In this paper we calculate the dependence of this change on the exciton populations by the equation of motion (EOM) method. The magnitude of optical nonlinearity is also influenced by ambient temperature, by the extent of exciton wave functions, and by the strength of electron-electron interaction. All of these factors can be easily incorporated in the EOM approach systematically. Using the material parameters for polydiacetylene, the optical Kerr coefficient \( n_2 \) obtained is about \( 10^{-8} \) cm\(^2\)/W, which is close to experimental value, and is four orders of magnitude larger than the value in nonresonant pump experiments. [S0163-1829(97)02743-4]

I. INTRODUCTION

As a class of materials promising for applications in all-optical devices for communication and data processing, conjugated polymers have been a subject of great research interest. A conjugated polymer such as polydiacetylene (PDA) has long been recognized to exhibit large nonresonant third-order optical nonlinearities. Most of the theoretical works on the nonlinear optics of these materials are based on the perturbative sum-over-state formula that suits a nonresonant pumping well (but is inappropriate for resonant pumping). A fair agreement between experiments and theories has been achieved for a variety of nonresonant spectra, including two-photon absorption, third-harmonic generation, and electroabsorption. In addition, the equation of motion (EOM) approach has also been employed in these studies. The EOM for polarization, which is similar to the semiconductor Bloch equation originally used for inorganic semiconductors, is a general tool whose validity goes beyond the perturbative regime and will be used in this paper.

For conjugated polymers under resonant pumping, most of the optically excited electrons and holes remain bound at room temperature and form an exciton gas, instead of a plasma as in the III-V semiconductors. This is because the magnitude of the exciton binding energy in conjugated polymers (of the order of 1 eV) is much larger than that in inorganic semiconductors (a few meV). This presents a difficult situation for the calculation of resonant nonlinearity. Even though there are numerous experimental works, few theoretical works have been devoted to this subject. A simple and heuristic explanation of this nonlinearity based on phase-space filling (PSF) has been proposed, and the result agrees quantitatively with experiments. The essence of PSF is that when there is a finite concentration of excitons, the phase space for further excitons to form is reduced because of the exclusion principle, and henceforth the probe absorption signal is reduced. The limitation of PSF is that it cannot predict the whole spectral response of the electric susceptibility, nor the effects of temperature, strength of electron-electron interaction, etc.

Motivated by the desire to have a more accurate theoretical tool to understand this phenomenon, we present a detailed analysis of the nonlinear susceptibility based on EOM. We will utilize the technique developed by Haug, Koch, and Schmitt-Rink to make a connection between exciton populations and the electron populations that appear in the EOM. However, since the link is suitable for dilute exciton gas only, we shall concentrate our study in this regime. Furthermore, from the comparison between the lineshapes of time-resolved and cw photoluminescence spectra, the typical intraband scattering time is estimated to be less than a picosecond in polymers. Therefore, it is possible to consider a simpler situation in which the exciton gas is in quasi-equilibrium, and in which the population is determined by the intensity of the pump wave. Because of these approximations, phenomena such as exciton-exciton interaction, excited-state absorption, and off-equilibrium momentum distribution are not considered.

In this paper we have done extensive studies on the optical nonlinearity of PDA. There are several advantages in choosing this material: First, it has the largest nonresonant third-order nonlinearity of all polymers and very large resonant nonlinearity. Second, it is one of a few conjugated polymers that can form high-quality single crystals and is more amenable to theoretical analysis. Third, its chain-to-chain distance is large because of large side groups and, therefore, the interchain interaction is less important. Various aspects of the nonlinear spectra are investigated. By choosing a reasonable value of the Coulomb interaction strength, the resonant optical Kerr coefficient \( n_2 \) being calculated agrees very well with experiments. Furthermore, the effect of electron-electron interaction on the height and position of the exciton absorption peak is studied. We also study the influence of temperature, as well as the relative populations of singlet and triplet excitons, on the probe spectra. This work provides a systematic analysis of the influence of various microscopic parameters on the optical nonlinearity and may serve as a guide for the search for optical materials with larger resonant nonlinearities.

This paper is organized as follows. In Sec. II, the equation...
of motion for polarization in conjugated polymers is derived. In Sec. III, the Coulomb potential matrix elements and electron occupation numbers are calculated. The numerical results are presented in Sec. VI, and Sec. V is the conclusion.

II. EQUATION OF MOTION FOR POLARIZATION

A conjugated polymer is a macromolecule with many electronic and ionic degrees of freedom. There have been several attempts to include both types of degrees of freedom in calculations on the electronic and optical properties of conjugated polymers. This is a very difficult task. To date, an exact solution for chains longer than 20 sites is still lacking. It is especially challenging to calculate resonant optical nonlinearity by including the effects of electrons (including excitons) and phonons simultaneously. In this paper, we choose a modest approach and focus only on the electronic contribution to the nonlinearity. By doing so, we will not, for example, be able to produce satellite phonon peaks next to the main resonant absorption peak. Our main goal is to calculate the optical nonlinearity due to the exciton gas, which is derived from the dependence of the magnitude of the main absorption peak on the exciton populations. In fact, Greene and co-workers have demonstrated that the PSF which is derived from the dependence of the magnitude of the interaction between polarization and the probe field is easily obtained by integration over all k's. In general, the form of the equation for the EOM is

\[ H = H_0 + H_1 + H_2, \]

where

\[ H_0 = \sum \sigma (\epsilon_{c\sigma} a_{c\sigma}^\dagger a_{c\sigma} + \epsilon_{v\sigma} a_{v\sigma}^\dagger a_{v\sigma}), \]

\[ H_1 = \sum \sum \sum \sum \gamma_{\lambda_1 k_1 k_2 k_3 k_4} a_{\lambda_1 k_1}^\dagger a_{\lambda_2 k_2}^\dagger a_{\lambda_3 k_3} a_{\lambda_4 k_4} + \text{H.c.}, \]

and

\[ H_2 = -E(t) \sum \sum \sum \mu_{\lambda k}(k) a_{\lambda k}^\dagger a_{\lambda k} + \mu_{\lambda k}(k) a_{\lambda k}^\dagger a_{\lambda k}. \]

In these equations, \( \epsilon_{c,v,k} \) are the energies for the dimerization-induced conduction and valence band, \( \gamma_{\lambda_1 k_1 k_2 k_3 k_4} \) are the Coulomb potential matrix elements (\( \lambda = c,v \)), and \( \mu_{\lambda k}(k) \) are the dipole moment elements. \( H_2 \) describes the coupling between polarization and the probe field \( E(t) \) along the chain. The influence of the pump field will be accounted for when calculating the conduction electron populations in the next sections. The potential matrix elements are

\[ \gamma_{\lambda_1 k_1 k_2 k_3 k_4} = \int d^3r d^3r' \Psi_{\lambda_1 k_1}^*(r) \Psi_{\lambda_2 k_2}^* (r') \times V_{ee}(r-r') \Psi_{\lambda_3 k_3}(r') \Psi_{\lambda_4 k_4}(r), \]

where \( V_{ee} \) is the screened Coulomb interaction between the \( \tau \) electrons, and \( \Psi_{\lambda k} \) are the Bloch states solved from \( H_0 \). The usual practice is to neglect, from the very beginning, the terms that do not conserve electron numbers in each band, which include half of the 16 terms that do not have equal indices and phonons simultaneously. In this paper, we choose a modest approach and focus only on the electronic contribution to the nonlinearity. By doing so, we will not, for example, be able to produce satellite phonon peaks next to the main resonant absorption peak. Our main goal is to calculate the optical nonlinearity due to the exciton gas, which is derived from the dependence of the magnitude of the main absorption peak on the exciton populations. In fact, Greene and co-workers have demonstrated that the PSF which is derived from the dependence of the magnitude of the interaction between polarization and the probe field is easily obtained by integration over all k's. In general, the form of the equation for the EOM is

\[ p_{k\sigma} = \langle a_{\lambda k}^\dagger a_{\lambda k}\rangle + E(t) \mu_{\lambda k}(k) (n_{\lambda k} - n_{\lambda k}). \]

After a straightforward but tedious calculation, we have

\[ i\hbar \frac{\partial p_{k\sigma}}{\partial t} = (\epsilon_{v\lambda} - \epsilon_{c\lambda}) p_{k\sigma} + E(t) \mu_{\lambda k}(k) (n_{\lambda k} - n_{\lambda k}), \]

where

\[ \sum k' \left[ \langle \Psi_{l\lambda k}^* \Psi_{l\lambda k} \rangle \right] p_{k\sigma} \]

and

\[ \sum \sigma \left[ \langle \Psi_{l\lambda k}^* \Psi_{l\lambda k} \rangle \right] (n_{\lambda k} - n_{\lambda k}). \]

In this derivation, \( \Psi_{l\lambda k} \) are the Bloch states solved from \( H_0 \). The usual practice is to neglect, from the very beginning, the terms that do not conserve electron numbers in each band, which include half of the 16 terms that do not have equal indices and phonons simultaneously. In this paper, we choose a modest approach and focus only on the electronic contribution to the nonlinearity. By doing so, we will not, for example, be able to produce satellite phonon peaks next to the main resonant absorption peak. Our main goal is to calculate the optical nonlinearity due to the exciton gas, which is derived from the dependence of the magnitude of the main absorption peak on the exciton populations. In fact, Greene and co-workers have demonstrated that the PSF which is derived from the dependence of the magnitude of the interaction between polarization and the probe field is easily obtained by integration over all k's. In general, the form of the equation for the EOM is

\[ p_{k\sigma} = \langle a_{\lambda k}^\dagger a_{\lambda k}\rangle + E(t) \mu_{\lambda k}(k) (n_{\lambda k} - n_{\lambda k}), \]

where

\[ \sum k' \left[ \langle \Psi_{l\lambda k}^* \Psi_{l\lambda k} \rangle \right] p_{k\sigma} \]

and

\[ \sum \sigma \left[ \langle \Psi_{l\lambda k}^* \Psi_{l\lambda k} \rangle \right] (n_{\lambda k} - n_{\lambda k}). \]
where \( n_{c,k\sigma} = (a_{c,k\sigma}^\dagger a_{c,k\sigma}) \) are the one-electron occupation numbers in the conduction or valence band, \( \gamma_{kk'} \) and \( \tilde{\gamma}_{kk'} \) are abbreviations for \( \gamma_{kk'kk''} \) and \( \tilde{\gamma}_{kk'kk''} \) respectively. The terms that are quadratic in \( p_{k\sigma} \) are neglected in Eq. (2.6), because only the linear response of the probe wave is considered. Also, relations such as \( \gamma_{cc'} = \gamma_{kk'} \) and \( \tilde{\gamma}_{cc'} = \tilde{\gamma}_{kk'} \) have been used, which are based on the symmetry between the conduction band and valence band in the present model. Note that the potential matrix elements with unequal numbers of \( c \) and \( v \) indices result in the last three lines of Eq. (2.6). These matrix elements are multiplied by terms quadratic in electron or hole occupations, which under resonant pumping may be large. Notwithstanding, because of inversion symmetry, it can be shown that for thermalized exciton gas, these terms actually have no effect on the dynamics (see the Appendix). Consequently, Eq. (2.6) becomes

\[
[(\epsilon_{c,k} - \epsilon_{v,k}) - \omega - i \gamma] p_{k\sigma}(\omega) = E(\omega) \mu_{vc}(n_{c,k\sigma} - n_{c,k\sigma}) - \sum_{k'} [\gamma_{kk'vv} - \gamma_{kk'vc}] (n_{c,k'\sigma} - n_{c,k'\sigma}) \\
- \sum_{\sigma'} [\gamma_{kk'vc} - \gamma_{kk'vc}] (n_{v,k'\sigma'} - n_{v,k'\sigma'}) \] \\
+ \sum_{k'} \gamma_{kk'vk} \tilde{p}_{k'\sigma}(\omega) + \sum_{k'} \gamma_{kk'vk} \tilde{p}_{k'\sigma}(\omega) \\
- \sum_{\sigma'} [\gamma_{kk'vc} \tilde{p}_{k'\sigma'}(\omega) + \gamma_{kk'vc} \tilde{p}_{k'\sigma'}(\omega)] \\
\times (-\omega)] (n_{v,k\sigma} - n_{c,k\sigma}),
\]

(2.7)

where \( \tilde{p}_{k\sigma}(\omega) = (p_{k\sigma} + p_{k\sigma})/2 \), and a damping term \( i \gamma \) has been added. Notice that \( \tilde{p}_{k\sigma}(\omega) \) because \( \tilde{p}_{k\sigma} \) is not Hermitian. Therefore, Eq. (2.7) has to be solved in conjunction with the equation satisfied by \( \tilde{p}_{k\sigma}(\omega) \), which is similar to Eq. (2.7) but with \( \omega \) replaced by \( -\omega \) and \( \tilde{p}_{k\sigma} \) replaced by \( \tilde{p}_{k\sigma}^\ast \). The meaning of the various parts on the right-hand side of the equation is explained below: The first square bracket, after being summed over \( k' \), contributes to the band-gap renormalization. The magnitude of renormalization depends on the strength of interelectron interaction, as well as the electron populations. Inside the second square bracket, the \( \gamma_{kk'vv} \) term is most crucial to the formation of excitons; the \( \gamma_{kk'vc} \) term is related to the singlet-triplet splitting of the exciton levels and leads to an unusual coupling between positive and negative frequency components of the polarization. It will be shown in the next section that \( \tilde{\gamma}_{kk'vv} = \tilde{\gamma}_{kk'vc} \) because of the charge neutrality condition. We can also show that \( \tilde{\gamma}_{kk'vc} \) and \( \tilde{\gamma}_{kk'vc} \) are simply constants and can be treated as corrections to \( \gamma_{kk'vc} \) and \( \gamma_{kk'vc} \). The only unknowns in Eq. (2.7) are \( \{\tilde{p}_{k\sigma}(\omega), \tilde{p}_{k\sigma}(-\omega)\} \). All of the other quantities, including the potential matrix elements and the electron populations, can be obtained given physical conditions such as the strength of electron interaction, the intensity of pump wave, etc. This is derived in the next section.

### III. Potential Matrix Element and Electron Population

#### A. Potential matrix element

A natural choice for the interaction potential between electrons is \( V_0/|\mathbf{r} - \mathbf{r}'| \), where \( V_0 \) is given by \( e^2/\epsilon a_0 \), \( \epsilon \) is the intrachain dielectric constant, and \( a_0 \) is the average distance between neighboring sites. The position \( r \), being dimensionless now, is measured in units of \( a_0 \). To calculate \( \gamma_{kk'} \), the unperturbed eigenstates are expanded by localized Wannier functions,

\[
\Psi_{kk}(\mathbf{r}) = \sum_{j=1,2} u_{k,j}(\mathbf{r}) \left( \frac{1}{\sqrt{M}} \sum_{m=1}^{M} e^{2i\mathbf{k}mM} W_{2(m-1) + j}(\mathbf{r}) \right),
\]

(3.1)

where \( M \) is the number of unit cells. The total chain length is \( 2M \). Defining \( \xi_k = [e^{\epsilon t_0} \cos k - i \delta \sin k/\epsilon _{\mathbf{k}}]^{1/2} \), where \( t_0 = (-1)^j \delta t \) is the hopping amplitude between neighboring sites, then

\[
\begin{pmatrix}
\bar{u}_{c1}(k) \\
\bar{u}_{c2}(k) \\
\bar{u}_{v1}(k) \\
\bar{u}_{v2}(k)
\end{pmatrix} =
\begin{pmatrix}
\xi_k^* \\
\xi_k \\
-\xi_k \\
-\xi_k^*
\end{pmatrix}.
\]

(3.2)

When calculating the matrix elements of \( \tilde{V}_{vc}(\mathbf{r} - \mathbf{r'} \), only the integrals involving Wannier functions at the same site are kept (zero differential overlap approximation). To improve upon this, we need to know the shape of atomic orbitals, which will not be considered here. For the same site, there is a finite on-site energy

\[
U_0 = 1/2 \int d^3 \mathbf{r} d^3 \mathbf{r'} W^*(\mathbf{r}) W^*(\mathbf{r'}) V_{ee}(\mathbf{r} - \mathbf{r'}) W(\mathbf{r}) W(\mathbf{r'}) W(\mathbf{r}).
\]

Since the exact form of the Wannier function is not known, \( U_0 \) is treated as a parameter independent of \( V_0 \). So our choice of the potential is essentially of the Pariser-Parr-Pople form. Defining

\[
V_1(q) = \frac{1}{M} \sum_m V_{ee}(2m + 1) e^{-i2m+1} q,
\]

\[
V_2(q) = \frac{1}{M} \sum_m V_{ee}(2m) e^{-2im} q,
\]

(3.3)

then a straightforward calculation gives

\[
\begin{align*}
\tilde{V}_{\lambda_1,\lambda_2,\lambda_3}(\mathbf{r}) &= V_2(q) \left[ \sum_{j=1}^{2} u_{\lambda_2,j}(k) u_{\lambda_3,j}(k') u_{\lambda_1,j}(k) u_{\lambda_2,j}(k') \right] + V_1(q) \left[ e^{iq} u_{\lambda_1,j}(k) u_{\lambda_2,j}(k') u_{\lambda_1,j}(k) u_{\lambda_2,j}(k') \right] \\
&+ e^{-iq} u_{\lambda_1,j}(k) u_{\lambda_2,j}(k') u_{\lambda_1,j}(k) u_{\lambda_2,j}(k')
\end{align*}
\]

\[
\gamma_{kk'} = \int d^3 \mathbf{r} \int d^3 \mathbf{r}' W^*(\mathbf{r}) W^*(\mathbf{r'}) V_{ee}(\mathbf{r} - \mathbf{r'}) W(\mathbf{r}) W(\mathbf{r'}) W(\mathbf{r}).
\]
where \( q = k - k' \). We require \( V_1(0) + V_2(0) = 0 \) because of the charge neutrality condition. After combining Eq. (3.4) with Eq. (3.2), it can be shown that \( \tilde{V}^{kk'}_{\text{ave}} = \tilde{V}^{kk'}_{\text{vee}} = \frac{[V_2(0) + V_1(0)]/2 = 0, and \( \tilde{V}^{kk'}_{\text{ave}} - \tilde{V}^{kk'}_{\text{vee}} = [V_2(0) - V_1(0)]/2 \). We emphasize that this nonzero correction is crucial to the reduction of the exciton binding energy when \( U_0 \) is tuned to a larger value while keeping \( V_0 \) fixed. The same behavior is observed by Abe, Yu, and Su,\textsuperscript{13} where their concern is the energy spectrum of the excitons.\textsuperscript{17}

### B. Electron population

The electron population can be linked to the exciton population by using the method developed by Haug, Koch, and Schmitt-Rink. Their relation is derived below. First, the connection between exciton operators and an electron creation operator \( e_{njmK}^\dagger \) is\textsuperscript{10}

\[
a_{ck1\sigma}^\dagger a_{ck2\sigma_2} = \frac{1}{\sqrt{2M}} \sum_{njm} \langle jm|\sigma_1\sigma_2\rangle \phi_{njm}(k)e_{njmK}^\dagger, \tag{3.5}
\]

where \( \langle jm|\sigma_1\sigma_2\rangle \) is the Clebsh-Gordon coefficient, \( k = (k_1 + k_2)/2 \), \( K = k_1 - k_2 \), and \( \phi_{njm}(k) \) is the wave function of an exciton at the \( n \)th bound state with angular momentum \( (jm) \). Helped by this relation, we can write \( n_{ck} \) in terms of exciton operators as follows: By using an identity operator

\[
I = \frac{1}{N_c} \left( N - \sum_{k\sigma} a_{ck\sigma}^\dagger a_{ck\sigma} \right) = \frac{1}{N_c} \sum_{k\sigma} a_{ck\sigma}^\dagger a_{ck\sigma}, \tag{3.6}
\]

where \( N \) is the total number of electrons and \( N_c \) is the number of conduction electrons, we have

\[
\hat{n}_{ck} = \sum_{\sigma_1} \hat{n}_{ck1\sigma_1} = \frac{1}{N_c} \sum_{k_2\sigma_2} a_{ck1\sigma_1}^\dagger a_{ck1\sigma_1} a_{ck2\sigma_2}^\dagger a_{ck2\sigma_2}^\dagger
\]

\[
= \frac{1}{2M} \sum_{n'jm} \sum_{k_2} \phi_{njm}(k)\phi_{n'jm}(k)e^\dagger_{njmK}e_{n'jmK}. \tag{3.7}
\]

For a dilute exciton gas, the exciton number \( \langle e_{njmK}^\dagger e_{njmK}^\dagger \rangle = n_{njmK}\delta_{m't} \), where \( g_{njmK} \) is the thermal distribution of excitons.\textsuperscript{10} Therefore,\textsuperscript{10}

\[
n_{ck} = \frac{1}{2M} \sum_{m't} \left[ |\phi_{n}(k)|^2 g_{nk} + 3|\phi_{n}'(k)|^2 g_{nk} \right]. \tag{3.8}
\]

where the subscripts \( s \) and \( t \) stand for ′′singlet′′ (\( j = 0, m = 0 \)) and ′′triplet′′ (\( j = 1, m = \pm 1 \)) respectively; the factor 3 in front of \( g_{nk} \) accounts for the triplet degeneracy.
This identity is used to determine the values of the chemical potentials $\mu_s$ and $\mu_t$, once the total population of, and the relative populations between singlet and triplet excitons are given.

IV. ABSORPTION SPECTRA: NUMERICAL RESULT

Most of this section is devoted to the calculation of the resonant nonlinear optical spectra of PDA for reasons stated in the Introduction. At the end of this section we will comment briefly on the calculation for polyphenylene vinylene (PPV).

PDA has four carbon atoms per unit cell, and consequently four bands in the tight-binding approximation. Since our focus is on the exciton state within the band gap, which is composed of the electron and hole from the middle two bands (conduction and valence band), the outer two bands can be safely neglected. We choose the dimerization-induced band gap, $4\delta_d$, to be the unit of energy. The value of $\delta_d$, which determines the total band width of conduction band and valence band, is chosen to be 1.25. The average bond length of PDA is 1.35 Å. The Coulomb interaction parameter $V_0 = e^2/\epsilon a_0$ can be determined from the intrachain dielectric constant $\epsilon$. According to the Kramers-Kronig analysis of the reflectivity and with permittivity measurements, this value is close to 3. We choose $\epsilon = 3.5$, such that $V_0 = 2.84$ eV, to fit the calculated exciton binding energy with the value observed in experiments. In most of the following calculations the on-site energy $U_0 = 2V_0$. We have also done several calculations using different choices of $U_0$ and $V_0$ values (see Fig. 4). In all of the following calculations the number of sites is 400 and the damping $\gamma$ is 0.02. We have done calculations on a larger system with 800 sites and confirmed that the finite-size effect is unimportant.

Figure 1 displays the electric susceptibility $\chi(\omega)$, in room temperature, for various concentrations of the singlet exciton gas. The percentages of electrons excited from the valence band by the pump wave are indicated in the legend. The absorption peak in $\text{Im} \chi(\omega)$ can be clearly identified at $\hbar \omega = 1.39$ in the absence of pumping (the solid line). The renormalized band gap is determined by the first maximum of $\text{Im} \chi(\omega)$ beyond the exciton peak, which is barely observable at $\hbar \omega = 1.71$. Notice that the band-gap renormalization due to the Coulomb interaction is quite large. With different exciton populations, the magnitude of renormalization also changes [see the discussion after Eq. (2.7)]. The exact value of the conduction-band edge is difficult to measure experimentally because most of the oscillator strength is “concentrated” on the exciton peak. On the other hand, the singlet exciton absorption peak at 1.97 eV is one of the few values that can be determined accurately and is generally agreed upon by researchers. Therefore, it is used to set the overall energy scale and that means $1.39 \times 4\delta_d = 1.97$ eV, or $4\delta_d = 1.42$ eV. Consequently, the position of conduction-band edge is at 2.43 eV in our calculation and the binding energy of the singlet exciton is approximately 0.46 eV. This falls within the range 0.4–0.5 for the values reported.

In Fig. 1, the absorption signal is reduced as exciton concentration increases. The reduction is approximately proportional to the number of excited electrons. This is consistent with the picture of PSF, which gives

$$\delta f/f = -n_{ex}/n_{ex}^\text{sat},$$

where $f$ is the oscillator strength, $n_{ex}$ is the exciton density per unit length, and $n_{ex}^\text{sat}$ is the saturation density, at which exciton wave functions begin to overlap in space. By using Eq. (4.1), we can estimate the exciton radius and the result is about five unit cells, which is again consistent with earlier calculations. Figure 2 shows the absorption coefficient $\alpha$ and the change of refraction index $\delta n$ near the exciton peak. The values of the exciton concentration are the same as in Fig. 1. The chain-to-chain distance for PDA in the crystalline phase is about 10 Å, and the interstite distance is 1.4 Å. Therefore, 1% concentration has $7.1 \times 10^{19}$ cm$^{-3}$ conduction electrons. The pump intensities $I_p$ required for this electron concentration $n_{ex}$ can be obtained from $I_p = n_{ex}h\omega_p/\alpha\tau$ (reflection from the sample is ignored), where $h\omega_p = 1.97$ eV, the peak absorption $\alpha$, (including $\tau$ electrons and the background) is approximately $10^6$ cm$^{-1}$, and the recombination time $\tau$ is 2 ps. Consequently, to excite $7.1 \times 10^{19}$ cm$^{-3}$ electrons requires a pump wave with intensity $I_p = 1.14 \times 10^9$ W/cm$^2$. The optical Kerr coefficient $n_2$, which measures the change

![Image](image-url)
of refraction index due to pumping, is given by
\[ n_2 = \frac{(\delta n) d}{\delta I_p}. \]
For a pulse with \( I_p = 1.14 \times 10^7 \text{ W/cm}^2 \), we have \( (\delta n) d = 0.196 \) at resonance (see Fig. 2(b)) and, therefore,
\[ n_2 = 1.7 \times 10^{-8} \text{ cm}^2/\text{W}. \] This is four orders of magnitude larger than the nonresonant value, and is close to the observation of Greene et al., \( 3.0 \times 10^{-8} \text{ cm}^2/\text{W} \).

All of the above calculations are for singlet excitons at room temperature. Using the same formalism it is quite easy to investigate the influence of exciton species and temperature on the resonant nonlinearity. We consider a two-level model where only the singlet \((^1B_g)\) and triplet \((^3B_u)\) excitons are considered. The exciton radii are chosen to be \( 6a \) \( (r_s) \) and \( 4.5a \) \( (r_t) \). In Fig. 3, we show the extreme cases where the populations are either all singlet or all triplet. This difference traces back to the different distributions of the relative part of the electron-hole pair wave functions \( \phi_{s,t}^i(k) \).

It can be seen that the difference between singlet and triplet curves is more significant at low temperature \(~10 \text{ K}~\). Such a temperature effect has not been studied experimentally, however.

In Fig. 4, we show how different choices of the strength of the electron-electron interaction may affect the absorption spectra. It can be seen that the magnitude of \( V_0 \), the long-range interaction, has significant effect on the band-gap renormalization and the binding energy. For example, the band edges for \( U_0=4 \) and \( V_0=1.5, 2, 2.5 \) are at 1.54, 1.71, and 1.89, respectively (see arrows in the figure). The widths of the band gap vary roughly linearly with \( V_0 \). On the other hand, the short-ranged on-site energy \( U_0 \) has little influence on the band gap. Furthermore, contrary to the effect of \( V_0 \), a larger \( U_0 \) leads to a smaller binding energy. This adverse effect can be traced back to the exchange terms \( \hat{\gamma}_{\mu,\nu,\lambda,\chi} \) in Eq. (3.4).

The dependence of the position of the exciton level on \( U_0 \) and \( V_0 \) resembles closely the calculations by Abe, Yu, and Su. \(^{15}\)

This work is based on the simplified model of an infinite and rigid chain and seems to be applicable to other conjugated polymers with exciton levels as well, such as PPV and polysilane. \(^{23,24}\) At the end of this section, we present a cal-

FIG. 2. The effect of different exciton concentrations on (a) absorption coefficient \( \alpha \) and (b) the change of refraction index \( \delta n \). \( \alpha \) is in units of \( 2.0 \times 10^4 \text{ cm}^{-1} \). The energy is in units of \( 4 \delta \).
calculation for PPV. Its optical nonlinearity (for a perfect crystalline sample) is found to be of the same order as PDA’s. The following parameters obtained from the spin-density profile of nonlinear excitation are used: $t_0 = 2.02$ eV, $U_0 = 2.5t_0$, $V_0 = 1.3t_0$. The displacement of ions due to the double-bond alternation is about $\pm 0.055$ Å. This gives $4\delta t = 1.15$ eV because the lattice stiffness for PPV is $5.23$ eV/Å. From the absorption spectrum being calculated, we estimate the exciton binding energy to be $0.6$ eV, while earlier calculations range from $0.4$ eV (Ref. 23) to $0.8$ eV. The exciton radius in PPV is about $50$ Å, which spans eight unit cells. The interchain distance for PPV is about $4$ Å, while in actual experiments it is finite and may be flexible. The phonon degrees of freedom will contribute to extra features in the absorption curve such as the phonon side bands. We have also used the quasiequilibrium condition for the exciton gas. In future research, the dynamical evolution of exciton density can be included by coupling the equation of motion to the rate equation of the electron population. Finally, the present theory has to be modified at high exciton density when exciton-exciton interaction plays a more important role and the RPA is no longer valid. This may lead to the resonant exciton annihilation, formation of biexcitons, and even the existence of a gain threshold beyond which lasing can happen.

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**Appendix A**

Based on the symmetry of inversion, we can show that the terms that are quadratic in $n_{c,oka}$ in Eqs. (2.6) do not affect the dynamics of the total polarization. First, the inversion properties of the Bloch states are

$$\Psi_{ek}(-r) = -\Psi_{e-k}(r),$$

$$\Psi_{ok}(-r) = \Psi_{o-k}(r). \quad (A1)$$

This leads to the following identities:

$$\mu_{uc}(-k) = \mu_{uc}(k), \quad (A2)$$

and

$$\Psi_{-k-k'} \equiv \Psi_{h_{1}h_{2}h_{3}h_{4}}(1) \Pi_{l_{1}} \Pi_{l_{2}} \Pi_{l_{3}} \Pi_{l_{4}},$$

$$\Psi_{-k-k'} \equiv \Psi_{h_{1}h_{2}h_{3}h_{4}}(1) \Pi_{l_{1}} \Pi_{l_{2}} \Pi_{l_{3}} \Pi_{l_{4}}, \quad (A3)$$

where $\Pi_{c} = -1$, $\Pi_{o} = 1$. It is clear that $\Psi_{h_{1}h_{2}h_{3}h_{4}}$ changes sign when the number of $c$ indices does not equal the number of $o$ indices.

**V. Conclusion**

Resonant optical nonlinearity for conjugated polymers can be understood using the simple picture of PSF, in which the probe signal is reduced because the phase space for final states has been occupied by the excitons. This model provides only an order of magnitude estimate and fails to produce more details such as the probe response over the whole spectral range (e.g., the band-edge absorption), the position of the exciton peak, the effect of temperature and Coulomb interaction, etc. The present study is able to access the effects of various microscopic parameters by using the EOM method. We produced the electric susceptibility $\chi(\omega)$ that contains the information about the positions and oscillator strength of exciton level and conduction-band edge. By varying the exciton populations, we can observe the change of the resonant oscillator strength and the trend is consistent with the PSF model [Eq. (4.1)]. We also calculated the optical Kerr coefficient $n_2$ and the value obtained, $1.7 \times 10^{-8}$ cm/2W, agrees well with observations.
Second, combining the exciton wave function, 
\[ \phi_0^e(k) = (2r_0^e/\pi)^{1/2}[1 + ((k \pm \pi/2)r_0^e)^2], \]
and the Bose-Einstein distribution function, 
\[ g_{\epsilon_k} = (\exp[\epsilon_k/(kT)] - 1)^{-1} \]
(see Sec. III B), and using the fact that 
\[ \Psi_k(r) = \Psi_{k \pm \pi}(r), \]
it is not difficult to see from Eq. (3.8) that
\[ n_{c,v-k\sigma} = n_{c,v\sigma}. \]  
(A4) Because of the symmetries in Eqs. (A2), (A3), and (A4), the

equation for \( p_{-k} \) has the same form as the equation for \( p_k \)
[see Eq. (2.6), with \( k \) and \( k' \) being replaced by \( -k \) and \( -k' \)]
ecept that the signs of the terms quadratic in \( n_{c,v\sigma} \) are
changed. Consequently, they do not contribute to the total polarization \( \langle P \rangle \), in which \( p_k \) and \( p_{-k} \) appear through the
combination of \( \mu_{\epsilon_k}(p_k + p_{-k}) \) only. Notice that the conclusion
may not be valid if the electron population is not in
thermal equilibrium.

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13 See, for example, N. Paras and D. Williams, Introduction to Nonlinear Optical Effects in Molecules and Polymers (Wiley, New York, 1991).
18 See, for example, Optical Nonlinearities and Instabilities in Semiconductors, edited by H. Haug (Academic Press, San Diego, 1988).
27 Actually, the expressions of \( V_{k\lambda\chi\lambda_4}^{\epsilon'k\lambda\lambda_4} \) and \( V_{k\lambda\lambda_4\lambda_4}^{\epsilon'k\lambda\lambda_4} \) in Eq. (3.4) are the same as those in Eqs. (8) and (9) of Abe, Yu, and Su (Ref. 15) for optically active excitons that have zero total momenta.
31 This choice is the same as in Ref. 15. The susceptibility being calculated is not sensitive to this parameter. For example, if \( t_0 \) is increased by 50%, the height of an absorption peak is changed by less than 10% and the shift of peak position is insignificant. This is reasonable since dominant contribution to the exciton formation comes from states near the inner band edges.
32 H. Schultes, P. Strohreigel, and E. Dornmann, Z. Naturforsch. Teil A 42, 413 (1986); Also see G. Weiser (Ref. 13).
39 A recent attempt to include both excitons and phonons in the field-theoretic approach for the nonresonant case is done by F. X. Bronold and A. R. Bishop, Phys. Rev. B 53, 13 456 (1996).