Electronic-oscillator analysis of femtosecond four-wave mixing in conjugated polyenes

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Equations of motion which describe the nonlinear optical response of conjugated polyenes using a collective electronic-oscillator representation are derived. Specific signatures of electronic correlations which enter as anharmonicities and scattering between oscillators are predicted in ultrafast resonant four-wave mixing. Only few resonant oscillators need to be considered explicitly; effects of the remaining (off resonant) oscillators are introduced via renormalized anharmonic coupling coefficients. The connection with inorganic semiconductors is established.

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I. INTRODUCTION

Nonlinear optical spectroscopy of organic materials is an intensively developing field. It constitutes both fundamental interest and potential practical applications. Compared to inorganic semiconductors, investigations of organic molecules are more difficult theoretically due to the complicated electronic structure and experimentally due to problems related to sample-quality, controlled synthesis and poor solubility of large molecules [1,2]. Resonant time domain nonlinear spectroscopy provides direct information on the creation of carriers and excitons and their subsequent dynamics [3–7]. Femtosecond time-resolved absorption spectroscopy revealed the strong coupling between electronic and vibrational states in excited state dynamics of the singlet exciton of polydiacetylene [3]. Time-resolved gain and absorption measurements have been performed to study the quantum yield of poly(paraphenylenevinylene) for films, dilute blends and solutions, the defect quenching of luminescence, the formation and decay of excitons [4], and the energy relaxation and field-induced exciton dissociation [5]. Degenerate four-wave mixing measurements have been performed in perylenes [6](b). Recently, the dephasing dynamics of vibronic states in polydiacetylene films has been investigated [7]. These experiments are usually interpreted by simply applying kinetic equations for excited state populations using phenomenological decay rates.

The calculation of electronic excitations in conjugated polyenes constitutes a complex many-body problem due to the strong correlation effects expected for one dimensional electronically delocalized systems. Ab initio quantum chemistry methods are limited to small systems [8–10] and usually look at effects of correlations on positions of energy levels.

In this paper we investigate how ultrafast resonant four-wave mixing (FWM) can be used to provide some alternative, dynamical, signatures of electronic correlations. Our analysis is based on the recently developed coupled electronic oscillator representation of the optical response, obtained by following the dynamics of the reduced single electron density matrix [11]. We expand the equations of motion for the density matrix in terms of amplitudes of the various electron-hole oscillators. With these equations the optical response is mapped onto a set nonlinear equations; optical nonlinearities are attributed to anharmonicities and scattering of oscillators [11–13]. The equations of motion derived here hold for the optical response up to the third order in the incoming field. However, extending the present framework to higher order nonlinearities is straightforward.

We have applied this technique to the calculation of a specific resonant time-domain experiment, namely degenerate FWM in the two-pulse self-diffraction set-up. We consider the signal generated in the $2k_2 - k_1$ direction, where $k_2$ and $k_1$ are the incoming wavevectors. We assume resonant excitation of the lowest $1B_u$ oscillator and identify the oscillators which contribute to this signal. Electronic correlations, which manifest themselves as nonlinear couplings between oscillators, lead to distinct signatures in the FWM signal. Our analysis shows that for the signal considered here, only 2 oscillators have to be considered explicitly, which allows for a very clear and intuitive description of the various nonlinearities [14]. We shall refer to these as the primary oscillators. All other oscillators are excited off-resonance. Their dynamics follows adiabatically the excitation and therefore they can be eliminated from the equations, which results in new anharmonic couplings as well as renormalizations of the existing anharmonicities of the primary oscillators.

To analyze the time-domain signatures of correlations we compare calculations made using the simple Hückel (SSH) model [15], which includes no correlations in the optical response, with the Pariser-Parr-Pople (PPP) model, where Coulomb interactions are included. We find some unique signatures of correlations in the ultrafast signals: First, due to correlations the shape of the FWM amplitude is changed from a free-induction decay, which has a maximum immediately after the excitation, to one which displays a delayed maximum as function of time. The results are compared with inorganic semiconductor nanostructures, where such effects have been predicted [16–18] and observed [19,20]. Second, the correlations also strongly affect the dynamics of the phase of the FWM signal. The relative phase of the FWM signal with respect to the exciting pulses changes from $\pi$ for the Hückel model to about 0 or $\pi$, depending on the signs of the anharmonic coupling coefficients. Third, for the PPP model we find strong signals for negative delays (pulse $k_2$ comes first), which are absent in a simple two-level model. Such signals reflect the contributions of a third level which could either be
a two-photon $A_g$ oscillator or a many body effect of two $B_u$ oscillators [21,22]. Our calculations show, that anharmonicities due to many-particle interactions dominate these signals in conjugated polyenes. This state of affairs is reminiscent of molecular aggregates and was recently analyzed for photosynthetic antenna complexes [23].

II. THE COUPLED ELECTRONIC OSCILLATOR REPRESENTATION

We consider a system of many $\pi$-electrons described by the tight-binding PPP Hamiltonian, which reproduces many important properties of conjugated polyenes [24];

$$
\hat{H} = \sum_{m,n,\sigma} t_{mn} c_{m,\sigma}^+ c_{n,\sigma} + \frac{1}{2} \sum_{m,n,\sigma,\sigma'} V_{nm} c_{m,\sigma}^+ c_{n,\sigma'} c_{n,\sigma'} c_{m,\sigma} - E(t) \sum_{n,\sigma} \mu_{nn} c_{n,\sigma}^+ c_{n,\sigma} 
$$

where $c_{m,\sigma}^+ (c_{m,\sigma})$ is the annihilation (creation) operator of a $\pi$-electron on site $m$ with spin $\sigma$ and $\hat{\rho}_{nm} = c_{m,\sigma}^+ c_{n,\sigma}$ is the reduced single-electron density matrix.

The first term is the Hückel Hamiltonian where the Coulomb interaction is neglected ($m \neq n$) is the nearest-neighbor transfer integral between $n$-th and $m$-th sites: $t_{nm} = \beta_0 - \beta_1 l_{nm}$, and $l_{nm}$ is the deviation of the $n$-th bond length from the mean bond length along the chain. The second term includes electron-electron Coulomb interactions. The repulsion between the $n$-th and $m$-th sites $V_{nm}$ is given by the Ohno formula:

$$
V_{nm} = \frac{U}{\sqrt{1 + (r_{nm}/a_0)^2}}
$$

representing the variation of the repulsion between the $n$-th and $m$-th site with distance; here the one-site Hubbard repulsion between the $n$-th and $m$-th sites $U$ is given by $U = U_0/\epsilon$, and $\epsilon$ is the static dielectric constant. The last term represents the coupling to and external electric field $E(t)$. We assume a localized basis set so that the dipole moment is diagonal $\mu_{nm} = \epsilon z_n \delta_{nm}$. The dipole operator is given by

$$
\mu = \sum_{n,\sigma} \mu_{nn} c_{n,\sigma}^+ c_{n,\sigma}
$$

We further assume that ground state is a singlet, and can be described by the HF single electron density matrix $\hat{\rho}_{nm}$, so that the spin variables may be eliminated [11].

The parameters used were $U_0 = 11.13eV$, $\beta_0 = -2.4eV$, $\beta_1 = -3.5eVÅ^{-1}$, $\epsilon = 1.5$, $a_0 = 1.2935Å$ [12]. For comparison we also performed calculations using the Hückel model where the Coulomb interaction is neglected $U_0 = 0$. In this case we used $\beta_1 = -5eVÅ^{-1}$ in order to reproduce the PPP band edge.

The time-dependent Hartree-Fock (TDHF) technique [25] maps the calculation of the optical response onto the dynamics of coupled electronic oscillators representing the electron-hole pair components of the reduced single electron density matrix [11]. We first find the Hartree-Fock (HF) ground state. The stationary HF density matrix $\hat{\rho}$ satisfies

$$
[h(\hat{\rho}), \hat{\rho}] = 0
$$

where $h(\hat{\rho}) = t + V(\hat{\rho})$

$$
V(\hat{\rho})_{nm} = -V_{nm}\hat{\rho}_{mn} + 2\delta_{nm} \sum_i V_{mi}\hat{\rho}_{il}
$$

$h$ is the Fock operator, $V$ is the Coulomb operator. Eq. (4) can be solved by an iterative diagonalization. We have calculated the geometry optimized HF ground state [26] as described in Ref. [12].

When the polyene is driven by an external field, the density matrix becomes time dependent. We shall represent it as

$$
\rho(t) = \hat{\rho} + \xi(t) + T(\xi(t))
$$

Here $\xi$ represents the particle-hole and $T(\xi)$ is the particle-particle and hole-hole parts of deviation of the reduced single-electron density matrix from the ground state $\hat{\rho}$. All quantities in Eq. (7) are $N \times N$ matrices, where $N$ is the basis set size. In this scheme, which is valid in the absence of pure dephasing, the particle-particle and hole-hole components of the density matrix need not to be considered as independent variables, since they can be expressed in terms of the particle-hole part [11]. Therefore only the particle-hole components of the density matrix, $\xi$, need to be calculated explicitly.

$T$ can be expanded in a Taylor series which contains only even powers of $\xi$. For optical signals not higher than $\chi^{(2)}$ it is sufficient to retain only the lowest (second order) term.

$$
T(\xi) = \frac{1}{2} [\xi, \hat{\rho}, \xi]
$$

The equation of motion for the particle-hole part of the density matrix is given by ($h = 1$):

$$
\frac{\partial}{\partial t} (\xi(t)) = L(\xi) - E[\mu, \hat{\rho}, \xi + T(\xi)] + [V(\xi), \xi] + [V(\xi), T(\xi)] + [V(T(\xi)), \xi] + [V(T(\xi)), \hat{\rho}],
$$

where the Liouville space operator (superoperator) $L$ represents the linear part of the equation [12]

$$
L(\xi) = [t + V(\hat{\rho}), \xi] + [V(\xi), \hat{\rho}]
$$

The induced-polarization (neglecting the equilibrium polarization $Tr(\mu \hat{\rho})$, which does not affect in the optical response) is given by the sum of its particle-hole and particle-particle contributions

$$
P(\xi(t)) = Tr(\mu \xi(t)) + Tr(\mu T(\xi(t)))
$$

where $\mu$ is the dipole operator defined in Eq. (3), and $\xi(t)$ is the time-dependent driven electron-hole part of the density matrix.
A. Equations of motion for electron-hole oscillators

As shown in Ref. [11] the particle-hole part of the density matrix can be expanded on terms of modes $\xi_a$

$$\xi(t) = \sum_{\alpha>\beta}(\xi_{\alpha}z_{\alpha}(t) + \xi_{\alpha}^{*}z_{\alpha}^{*}(t)) \quad .$$  

(12)

Each oscillator $\alpha$ is described by two operators $\xi_{\alpha}$ and $\xi_{\alpha}^*$. These oscillator variables are related to the oscillator coordinate $Q_{\alpha} = \frac{1}{\sqrt{2}}(\xi_{\alpha} + \xi_{\alpha}^*)$ and the momentum $P_{\alpha} = \frac{1}{\sqrt{2i}}(\xi_{\alpha} - \xi_{\alpha}^*)$ [11]. As in Ref. [11] we define $\xi_{\alpha} = \xi_{\alpha}^* \cdot z_{\alpha}$ and its complex conjugate $\bar{z}_{\alpha} = z_{\alpha}^{*}$ will be denoted complex oscillator amplitudes. The oscillator variables, are the eigenmodes of the linear part of Eq. (9) and satisfy:

$$L(\xi_{\alpha}) = \Omega_{\alpha}\bar{\xi}_{\alpha}, \quad L(\xi_{\alpha}) = -\Omega_{\alpha}\xi_{\alpha} \quad .$$  

(13)

They are normalized using the condition:

$$Tr(\rho[\xi_{\alpha},\bar{\xi}_{\alpha}]) = 1 \quad .$$  

(14)

Inserting the expansion Eq. (12) into Eq. (9) gives the following equations for the complex amplitude $z_{\alpha}(t)$ of the oscillator variable $\xi_{\alpha}$:

$$\frac{\partial}{\partial t}z_{\alpha} = \Omega_{\alpha}z_{\alpha} - E\mu_{\alpha} - E\sum_{\beta} \mu_{\alpha,\beta}z_{\beta} + E\sum_{\gamma} \mu_{\alpha,\gamma}z_{\gamma}$$

$$+ \sum_{\beta\gamma} V_{\alpha,\beta\gamma}z_{\beta}z_{\gamma} + \sum_{\beta\gamma\delta} V_{\alpha,\beta\gamma\delta}z_{\beta}z_{\gamma}z_{\delta} \quad ,$$  

(15)

with

$$\mu_{\alpha} = Tr([\rho,\xi_{\alpha}][\mu,\bar{\rho}])$$

$$\mu_{\alpha,\beta} = Tr([\rho,\xi_{\alpha}][\mu,\bar{\xi}_{\beta}])$$

$$\mu_{\alpha,\beta\gamma} = Tr([\rho,\xi_{\alpha}][\mu,\frac{1}{2}([\xi_{\beta},\bar{\rho}],\xi_{\gamma}])$$

$$V_{\alpha,\beta\gamma} = Tr([\rho,\xi_{\alpha}][V(\xi_{\beta},\bar{\xi}_{\gamma})]$$

$$+ Tr([\rho,\xi_{\gamma}][V(\frac{1}{2}([\xi_{\beta},\bar{\rho}],\xi_{\gamma}),\bar{\rho}))$$

$$V_{\alpha,\beta\gamma\delta} = Tr([\rho,\xi_{\alpha}][V(\frac{1}{2}([\xi_{\beta},\bar{\rho}],\xi_{\gamma}),\xi_{\delta}])$$

$$+ Tr([\rho,\xi_{\delta}][V(\xi_{\delta},\frac{1}{2}([\xi_{\beta},\bar{\rho}],\xi_{\gamma})]) \quad .$$  

(16)

Eq. (15) constitutes the equations of motion for $z_{\alpha}$ with $\alpha > 0$. The amplitudes for the adjoint (negative frequency) variables are simply the complex conjugates, see Eq. (12). The summation indices $\beta$, $\gamma$, and $\delta$ on the right hand side of Eq. (15) run over all (positive and negative frequency) oscillator variables.

The first two terms in the right hand side of Eq. (15) represent a linearly driven harmonic oscillator. The other terms are anharmonicities describing coupling among electronic oscillators. We label field-induced and purely material anharmonic coefficients by $\mu$ and $V$, respectively. Note that the summations on the right hand side include terms where the summation indices are equal ($\beta = \gamma = \delta$) (diagonal anharmonicities). It is important to note that, as is evident from Eq. (16), all the anharmonic coefficients can be calculated using the ground state density matrix $\rho$ as well as the eigenmodes $\xi_{\alpha}$ of the linearized TDHF equation.

FIG. 1. Frequencies of all $B_u$ and $A_g$ oscillators for the Hückel model of a 30 carbon atom polyacetylene chain. There are 113 $B_u$ and 112 $A_g$ oscillators. The frequencies of the first eight $B_u$ ($A_g$) oscillators are: 2.28, 3.35, 3.46, 3.46, 4.63, 4.66, and 4.79eV (2.82, 2.82, 3.99, 3.99, 4.13, 4.13, 5.30, and 5.30eV).

The optical polarization is given by:

$$P(t) = \sum_{\beta} \tilde{\mu}_{\beta}z_{\beta}(t) + \sum_{\beta\gamma} \tilde{\mu}_{\beta\gamma}z_{\beta}(t)z_{\gamma}(t) \quad ,$$  

(17)

with

$$\tilde{\mu}_{\beta} = Tr(\mu_{\beta})$$

$$\tilde{\mu}_{\beta\gamma} = Tr(\mu_{\frac{1}{2}([\xi_{\beta},\bar{\rho}],\xi_{\gamma})) \quad .$$  

(18)

Like in Eq. (15) also in Eq. (17) the summation indices $\beta$ and $\gamma$ run over all oscillator variables. Eqs. (15) and (17) may be used to compute the optical response of our many-electron system. This task has therefore been mapped onto finding the oscillators and the nonlinear couplings $\mu$ and $V$. $\mu$ describes optical transitions between the oscillators whereas $V$ describes scattering between oscillators, induced by the many-body Coulomb-interaction.

For a polyacetylene chain with $N$ carbon atoms and $N\pi$-electrons there are $\frac{N^2}{2}$ particle-hole oscillators. Eq. (15) therefore represents the equations of motion for the $\frac{N^2}{2}$ complex amplitudes of oscillator variables associated with positive frequencies. In Ref. [11] equivalent equations of motion have been given for the coordinate $Q_{\alpha}$ and the momentum $P_{\alpha}$ of the oscillators. In the analysis of resonant optical nonlinearities it is more convenient to use the complex amplitudes, rather than coordinates and momenta. The expansion of the density matrix in the wave-vectors of the exciting fields, which
corresponds to an expansion with respect to the central excitation frequencies, is simpler in this case. The equations used in Ref. [27] contain also particle-particle and hole-hole oscillator terms, as well as renormalization effects. In Appendix A we assume that the relaxation times for the populations, i.e., particle-particle and hole-hole components of the density matrix, are given by $T_1 = T_2/2$. We thus do not include pure dephasing processes. To investigate pure dephasing one needs to consider additional dynamic variables [28]; This goes beyond the present treatment. In principle the inclusion of dephasing times for the off-resonant oscillators results in imaginary contributions to the renormalization terms $X_i, Y_i$. Since in our case the detuning for the off-resonant terms is very large compared to the dephasing rate, these imaginary parts can be neglected.

All parameters appearing in Eqs. (20) and (21) have been defined in Eqs. (C5-C10). In Appendix C we also present the equations in more detail, including indices denoting the propagation directions. To obtain the FWM signal we solve Eqs. (20) and (21) order by order. In first order one has to solve the equation for $z_1$ keeping just the $\mu_1 E$ terms on the right hand side. This represents a linearly driven harmonic oscillator with frequency $\Omega_1$ and transition dipole $\mu_1$. The solution of this equation yields $z_1$ for the propagation directions $k_1$ and $k_2$. $z_{-1}$ is then the complex conjugate of $z_1$ with the inverse directions $-k_1$ and $-k_2$ (see Appendices). Then we solve the equation for $z_2$ in second order, keeping inhomogeneities representing two-photon resonances, which correspond to the direction $2k_2$. In the equation for $z_2$ the first term represents an oscillator with frequency $\Omega_2$. The other terms are nonlinear sources. $\mu_{12}$ is a transition dipole coupling the two oscillators and $V_{12}$ a many-body induced nonlinear coupling. Finally, the first and second order terms are inserted again into the equation for $z_1$ to calculate the third order $k_3 = 2k_2 - k_1$ component. The induced polarization in this direction is given by:

$$ P_5(t) = e^{-i\omega_{12}t}(\mu_1 z_1 + \sum_\beta \mu_{-1\beta}z_{-1}z_\beta + \sum_\beta \mu_{1\beta}z_1z_\beta). $$

As shown in Appendix C the amplitudes for the virtual $A_g$ oscillators can be evaluated analytically. Inserting these expressions, Eqs. (C1)-(C4), into Eq. (22) simplifies the expression for the polarization.

$$ P_5(t) = e^{-i\omega_{12}t}(\mu_1 z_1 + \mu_{12} z_{-2} + (A_1 + B_1)z_{-1}(z_1)^2 + (A_2 + B_2)E z_{-1}z_1 + A_3 E(z_1^2)) $$

$$ = e^{-i\omega_{12}t}|P_5(t)|e^{-i\varphi(t)}. $$

The anharmonic constants $A_1, A_2, A_3, B_1$, and $B_2$ arise from the elimination of the virtual oscillators, see Eq. (C11). $|P_5(t)|$ is the time-resolved amplitude and $\varphi(t)$ the slowly varying part of the phase. The total phase of the signal is given by $\varphi_S(t) = -i(\omega_{12} + \varphi(t)) = -\varphi_L(t) - \varphi(t)$, where $\varphi_L(t)$ is exactly the phase of the exciting laser pulses, see Eq.

**B. Two-oscillator representation of resonant four-wave mixing**

In Appendices A and B we show how our equations of motion can be applied to compute optical nonlinearities induced by a multiple-pulse excitation. A major advantage of the oscillator representation is that in practical applications it is usually necessary to include only very few oscillators. For off-resonant susceptibilities these are the oscillators that couple most strongly to the ground state density matrix. A tree diagram scheme for identifying the dominant oscillators for the nonresonance response, order by order, has been developed in Ref. [27]. In this article we consider resonant response, and the most natural way to select the relevant oscillators is by including those oscillators whose frequencies are close to various combinations of the incoming field frequencies. The selectivity is expected to be more pronounced in the resonant case, which enables us to discuss the response using very few parameters (frequencies and anharmonic coefficients) connected to the relevant oscillators.

The exciting field is given by:

$$ E(t) = \sum_{j=1,2} \hat{E}_j e^{-i(t-\tau_j)/\tau_j} (e^{i\Omega_j t} + e^{-i\Omega_j t}). $$

Here $\hat{E}_j$ is the real amplitude, $\tau_j$ the time delay and $\omega_j$ the central frequency of pulse $j$. In our numerical calculations we have assumed that the central frequencies of both exciting pulses coincide with that of the $1B_u$ oscillator, which has the largest oscillator strength, i.e. $\omega_1 = \omega_2 = \Omega(1B_u) = \Omega_1$, and we used a duration of $\tau_1 = \tau_2 = 20 fs$ for the Gaussian pulse envelopes. Since the spectral width of these very short laser pulses (about 0.1 eV) is small compared to the frequency spacing between the oscillators, only a few oscillators will be excited resonantly. Our calculations show that the first and third order response is to very good accuracy dominated by the $1B_u$ oscillator. In second order there may be one $A_g$ oscillator which appears as resonantly excited two-photon transition. This will be discussed later using Figs. 1 and 7.

In Appendix C we have developed equations which retain only two resonantly excited primary oscillators, the $1B_u$ and one $A_g$ oscillator, explicitly. The off-resonant contributions from all other virtual $A_g$ oscillators in second order, were adiabatically eliminated from the equations of motion, which results in renormalization of anharmonicities and scattering constants. We thus obtain the following equations of motion for the complex amplitudes of the two primary oscillators.

$$ \frac{\partial}{\partial t} z_1 = (\Omega_1 - \omega_L - i\frac{1}{T_2})z_1 - \mu_1 E $$

$$ - E^2(Y_1 + X_1)z_1 - E^2 X_{-1}z_{-1} - E\mu_{12}z_2 $$

$$ \frac{\partial}{\partial t} z_{-1} = z_{-1}^* \Omega_1 - \omega_L - i\frac{1}{T_2}z_{-1} + \mu_1 E $$

$$ + 2E^2(Y_1 + X_1)z_{-1} - E\mu_{12}z_2. $$

Here we have added phenomenological dephasing times $T_2$ and $T_2'$ for the two-oscillators and $z_{-1}$ denotes the amplitude of the negative frequency variable $\xi_{-1}$ of the $1B_u$ oscillator, see Appendix A. We assume that the relaxation times for the populations, i.e., particle-particle and hole-hole components of the density matrix, are given by $T_1 = T_2/2$. We thus do not include pure dephasing processes. To investigate pure dephasing one needs to consider additional dynamic variables [28]; This goes beyond the present treatment. In principle the inclusion of dephasing times for the off-resonant oscillators results in imaginary contributions to the renormalization terms $X_i, Y_i$. Since in our case the detuning for the off-resonant terms is very large compared to the dephasing rate, those imaginary parts can be neglected.

All parameters appearing in Eqs. (20) and (21) have been defined in Eqs. (C5-C10). In Appendix C we also present the equations in more detail, including indices denoting the propagation directions. To obtain the FWM signal we solve Eqs. (20) and (21) order by order. In first order one has to solve the equation for $z_1$ keeping just the $\mu_1 E$ terms on the right hand side. This represents a linearly driven harmonic oscillator with frequency $\Omega_1$ and transition dipole $\mu_1$. The solution of this equation yields $z_1$ for the propagation directions $k_1$ and $k_2$. $z_{-1}$ is then the complex conjugate of $z_1$ with the inverse directions $-k_1$ and $-k_2$ (see Appendices). Then we solve the equation for $z_2$ in second order, keeping inhomogeneities representing two-photon resonances, which correspond to the direction $2k_2$. In the equation for $z_2$ the first term represents an oscillator with frequency $\Omega_2$. The other terms are nonlinear sources. $\mu_{12}$ is a transition dipole coupling the two oscillators and $V_{12}$ a many-body induced nonlinear coupling. Finally, the first and second order terms are inserted again into the equation for $z_1$ to calculate the third order $k_3 = 2k_2 - k_1$ component. The induced polarization in this direction is given by:

$$ P_5(t) = e^{-i\omega_{12}t}(\mu_1 z_1 + \sum_\beta \mu_{-1\beta}z_{-1}z_\beta + \sum_\beta \mu_{1\beta}z_1z_\beta). $$

As shown in Appendix C the amplitudes for the virtual $A_g$ oscillators can be evaluated analytically. Inserting these expressions, Eqs. (C1)-(C4), into Eq. (22) simplifies the expression for the polarization.

$$ P_5(t) = e^{-i\omega_{12}t}(\mu_1 z_1 + \mu_{12} z_{-2} + (A_1 + B_1)z_{-1}(z_1)^2 $$

$$ + (A_2 + B_2)E z_{-1}z_1 + A_3 E(z_1^2)) $$

$$ = e^{-i\omega_{12}t}|P_5(t)|e^{-i\varphi(t)}. $$

The anharmonic constants $A_1, A_2, A_3, B_1$, and $B_2$ arise from the elimination of the virtual oscillators, see Eq. (C11). $|P_5(t)|$ is the time-resolved amplitude and $\varphi(t)$ the slowly varying part of the phase. The total phase of the signal is given by $\varphi_S(t) = -i(\omega_{12} + \varphi(t)) = -\varphi_L(t) - \varphi(t)$, where $\varphi_L(t)$ is exactly the phase of the exciting laser pulses, see Eq.
(19). We later examine the relative phase of the signal with respect to the exciting pulses [29]
\[ \Delta \varphi(t) = \varphi_L(t) - \varphi_S(t) = \varphi'(t) . \] (24)
This phase can be measured using heterodyne detection. The time-integrated FWM signal is given by
\[ S_{INT}(\tau) = \int |P_S(t)|^2 dt , \] (25)
where \( \tau \) is the time delay between the two-pulses.

The interpretation of the various terms in Eq. (20), which generate the FWM signal are as follows. First we discuss the terms which only involve the 1Bu oscillator. \( s_1 \) is the only nonlinearity which is also present in a simple two level system [30]. It represents the creation of a transient grating \((k_2 - k_1)\). It has its origin in the fact that electrons are Fermions and is usually referred to as Pauli blocking or phase-space filling nonlinearity [16,17,19]. \( s_2 \) describes a similar process, where now the field is scattered off a term rotating with twice the transition frequency of the 1Bu oscillator \(( -2\omega_2)\), instead of a transient grating term \((\omega_1 - \omega_2)\), which has no optical rotation frequency, since \( \omega_1 = \omega_2 \). \( V_1 \) formally appears as a local-field like nonlinearity [16,28]. It describes self-scattering of the excitation of the 1Bu oscillator induced by the many-particle Coulomb-interaction. Next we discuss the terms resulting from the \( A_9 \) oscillator, which is excited resonantly in second order. \( \mu_{12} \) is the transition dipole which couples the \( A_9 \) and \( 1Bu \) oscillators. It describes the creation of a third order polarization associated with the 1Bu oscillator, created from the excitation of the \( A_9 \) oscillator times a field. \( \mu_{12} \) also appears in the definition of the polarization. This term comes from the particle-particle part of the density matrix. \( V_{12} \) describes the many-particle induced coupling between the \( A_9 \) and the 1Bu oscillator, which gives rise to nonlinear signals. All other terms \((X_i \text{ and } Y_i)\) come from the elimination of off-resonant second order contributions. \( X_1, Y_1, X_{-1} \) describe the creation of a FWM signal by scattering of a linear term by two-fields. In the definition of these coefficients it follows that they are determined only by dipole moments between oscillators. All other terms resulting from the elimination process involve many-particle interactions between oscillators, which means that they are zero for the Hückel model. By inspection of the equations of motion one finds that all these terms lead to renormalizations of already existing nonlinear coupling coefficients \( s_1, s_2, V_1 \). Finally, the particle-particle part of the density matrix leads to the quadratic terms in the polarization, Eq. (22).

Depending on the time delay, the FWM technique considered here yields information about different anharmonic couplings. For positive delay (pulse \( k_1 \) comes first) this technique is known as photon echo, since in an inhomogeneously broadened system the amplitude of the signal will have an echo-like envelope [30,31]. As can be analyzed using Eq. (C7), for a positive delay larger than the pulse duration, when the overlap between the two pulses can be neglected, only few of the inhomogeneities in Eq. (20) contribute to the signal. Like in a two-level system, the phase-space filling \( s_1 \) and its renormalizations \( Y_2 \) and \( X_2 \), only contribute for positive delay [30,31]. Also the small renormalization term \( X_{-1} \) only contributes for positive delay. All of these inhomogeneities explicitly contain pulse \( k_2 \) multiplying a term which is present after both pulses have excited the system, see Eq. (C7). This only leads to a nonvanishing results, if pulse \( k_2 \) comes after pulse \( k_1 \). For positive delays also the many-particle induced terms represented by the nonlinear scattering potentials \( V_{12} \) and \( V_1 \), as well as its renormalizations \( Y_3 \) and \( X_3 \) contribute [16,17]. The sources of these terms do not contain an electric field, but are given by products of complex amplitudes. These amplitudes do not vanish as fast as the exciting pulses, but decay slowly as determined by the dephasing times. Therefore these many-particle terms will contribute to the signal for any time delay [16–18].

For large negative delay the two-photon resonances induce FWM signals even if many-particle interactions are neglected [21,22]. (Note that for a linearly driven harmonic three-level system, i.e. equal energy spacing and dipole moments scaling like \( \sqrt{n} \), all nonlinear terms cancel identically, and the optical response is purely linear.) This is represented by \( \mu_{12} \) and \( s_2 \), as well as its renormalizations \( Y_2 \) and \( X_2 \). These inhomogeneities contain pulse \( k_1 \) multiplying a term which is present after pulse \( k_2 \) has excited the system, see Eq. (C7). Such terms are nonvanishing only if pulse \( k_1 \) comes after \( k_2 \). For a small (positive or negative) delay, when the two pulses temporarily overlap, all of the inhomogeneities in Eq. (20) contribute. In addition to the ones discussed before, also the small source terms \( Y_3 \) and \( X_3 \), may contribute to the signal. Since they contain explicitly both pulse \( k_1 \) and \( k_2 \) they vanish unless both pulses overlap.

III. NUMERICAL RESULTS

In this section we compare the calculated FWM signals for the Hückel and the PPP models for a 30 carbon atom polyacetylene chain. The signal will be analyzed in terms of the anharmonicities and scattering of the oscillators as described in the previous section. We tabulate all relevant coupling constants and show how many virtual oscillators are needed for calculating the renormalized anharmonicities.

A. The Hückel model

We first discuss the properties of the geometry optimized ground state for the Hückel model [12,26]. The ground state is characterized by a uniform charge density \( \rho_{an} = 0.5 \) at each carbon atom. The second quantity, which is closely related to the stabilization mechanism of the ground state, is the bond order defined by
\[ p_n = \tilde{\rho}_{a,n+1} + \tilde{\rho}_{n+1,a} . \] (26)
We further introduce the bond order alternation parameter \( p'_{n} \)
\[ p'_n = <p_n> - (-1)^n p_n \] (27)
where \(<p_n>\) is the average bond order, which is 0.64 in our calculation. The geometry optimized ground state is a bond order wave, where \( p_n \) alternates between every two bonds [12,13]. Except for boundary effects near the chain ends it
has an almost uniform bond order alternation parameter of $\rho'_0 = 0.21$. The average bond length is $1.06 \pm 0.11 \text{\AA}$. Thus the transfer integral can be approximated by $t_{n,n\pm 1} = \beta (1 - (-1)^n \delta)$, with $\beta = -3.9 eV$ and $\delta = 0.13$.

For the Hückel model most of the coupling constants appearing in the equations of motion, Eqs. (20) and (21), are zero, since the Coulomb matrix vanishes, see Table I. The surviving terms $\mu_1, s_1, s_2, \mu_{12}$ do not include the Coulomb interaction. As can be seen in Appendix C, most of the terms arising from the elimination of the off-resonant $A_g$ oscillators involve the Coulomb interaction. Therefore only $X_1, X_{-1}, Y_1$ are finite. Additionally, for the Hückel model we find no $A_g$ oscillator which can be resonantly excited as a two-photon resonance. This can be seen from Fig. 1, which displays the frequencies of all oscillators. The frequency of the lowest $1B_u$ oscillator is $2.28 eV$. The $A_g$ oscillators which are closest in frequency to twice the frequency of the $1B_u$ are the $6A_g$ and $7A_g$ oscillators at $4.13 eV$. The frequency difference $2\Omega(1B_u) - \Omega(6A_g) = 0.43 eV$ is already larger than the spectral width of the exciting $20 fs$ laser pulses, which is about $0.1 eV$. Therefore all contributions from $A_g$ oscillators can be assumed to be off-resonant and the only primary oscillator is the $1B_u$. In the numerical calculations of the FWM signal we have included the phenomenological relaxation times $T_2 = 80 fs$ for the $B_u$ and $T_2' = 40 fs$ for the $A_g$ oscillators.

In Fig. 2 we show the density matrices of the ground-state and of the $1B_u$ oscillator using the $\pi$ orbital (real-space) basis. The diagonals of these plots represent the charge density $\rho_{n,n}$, the off diagonal elements shows the electronic coherences in the system. The ground state is more localized along the diagonal than the oscillator, which shows that the optical excitation creates electronic coherence in the system.

In Table I we give the relevant coupling constants for the Hückel model. It turns out that $\mu_1 = -s_1$; this resembles a simple two-level model, where the inhomogeneity of the optical Bloch equation for the polarization reads $\mu E(1 - n)$ (here $n$ is the population) [30]. We also find that $s_2$ is zero, indicating that no two-photon resonance involving solely the $1B_u$ oscillator contributes to the signal, which again mimics a simple two-level system. Therefore the only nonlinearity, involving just the $1B_u$ oscillator, is given by $s_1$, which represents a scattering of the field off a transient grating.

Looking at the coupling coefficients arising from the elimination of the $A_g$ oscillators, it turns out that $X_{-1}$ vanishes, and $X_1$ and $Y_1$ are finite. Both of these coefficients represent the scattering of two fields of the linear excitation. These terms result in small contributions to the FWM signal and, as can be seen from Eq. (C7), they only contribute when the two pulses overlap in time.

To find out how many virtual oscillators contribute to these two terms, we show in Fig. 3 the convergence of $X_1$ and $Y_1$ with the number of virtual $A_g$ oscillator variables taken into account. The summations over the $A_g$ oscillators, see Eq. (C10), have been made in such a way that we start with the largest term and then one by one include the smaller coupling terms. We see that by taking just 2 (out of 224) $A_g$ oscillator variables into account to obtain a 0.5% accuracy for $X_1$ and 2.5% for $Y_1$. The two oscillators most strongly coupled to the $1B_u$ oscillator are the $2A_g$ and $3A_g$ oscillators; both have a frequency of $2.82 eV$.

In Fig. 4 we display the amplitude and the relative phase of the time-resolved FWM signal for time-delay $\tau = 0 fs$ for

<table>
<thead>
<tr>
<th>$\Omega(1B_u)$</th>
<th>$2.28 eV$</th>
<th>$2.28 eV$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Omega(5B_u)$</td>
<td>$3.99 eV$</td>
<td>$4.52 eV$</td>
</tr>
<tr>
<td>$\mu_1$</td>
<td>$3.86 \text{\AA}$</td>
<td>$4.80 \text{\AA}$</td>
</tr>
<tr>
<td>$s_1$</td>
<td>$-3.86 \text{\AA}$</td>
<td>$-2.81 \text{\AA}$</td>
</tr>
<tr>
<td>$s_2$</td>
<td>$0.0 eV$</td>
<td>$0.017 \text{\AA}$</td>
</tr>
<tr>
<td>$V_1$</td>
<td>$0.0 eV$</td>
<td>$0.063 eV$</td>
</tr>
<tr>
<td>$V_{12}$</td>
<td>$0.0 eV$</td>
<td>$0.66 \text{\AA}$</td>
</tr>
<tr>
<td>$X_1$</td>
<td>$21.99 eV^2/V^{-1}$</td>
<td>$5.36 eV^2/V^{-1}$</td>
</tr>
<tr>
<td>$X_{-1}$</td>
<td>$0.0 eV^2/V^{-1}$</td>
<td>$0.078 eV^2/V^{-1}$</td>
</tr>
<tr>
<td>$X_2$</td>
<td>$0.0 e\text{\AA}$</td>
<td>$0.26 \text{\AA}$</td>
</tr>
<tr>
<td>$X_3$</td>
<td>$0.0 e\text{\AA}$</td>
<td>$0.13 \text{\AA}$</td>
</tr>
<tr>
<td>$X_4$</td>
<td>$0.0 eV$</td>
<td>$-0.082 eV$</td>
</tr>
<tr>
<td>$Y_1$</td>
<td>$-36.16 e\text{\AA}^2/V^{-1}$</td>
<td>$-23.0 e\text{\AA}^2/V^{-1}$</td>
</tr>
<tr>
<td>$Y_2$</td>
<td>$0.0 e\text{\AA}$</td>
<td>$-1.33 \text{\AA}$</td>
</tr>
<tr>
<td>$Y_3$</td>
<td>$0.0 e\text{\AA}$</td>
<td>$-0.67 \text{\AA}$</td>
</tr>
<tr>
<td>$Y_4$</td>
<td>$0.0 eV$</td>
<td>$0.035 eV$</td>
</tr>
</tbody>
</table>

FIG. 3. Convergence of anharmonicities for the Hückel model as function of number of virtual $A_g$ oscillator variables. Shown is the relative percent difference of the quantity to its converged value.
FIG. 2. (a) Ground state density matrix and (b) absolute value of density matrix representing the $1B_u$ oscillator for the Hückel model. (c) Ground state density matrix and absolute value of density matrix representing the $1B_u$ (d), $3A_g$ (e), and $5A_g$ (f) oscillators for the PPP model. (Large=blue, green, yellow, red=small)
FIG. 4. (a) Time-resolved amplitude and (b) phase of the FWM signal for time-delay $\tau = 0$ fs for the Hückel model. Solid line: model IH, dashed: model IIH, dotted: model IIIH, and dashed-dotted: laser pulse envelope.

We should however point out, that the absence of the second primary oscillator, appearing as a two-photon resonance is not an intrinsic property of the Hückel model. For other sizes or bond alternation parameters there may be $A_g$ oscillators with frequencies in the vicinity of twice the frequency of the $1B_u$ oscillator, which may then also contribute to the nonlinear response. For the same parameters used here, we find that for a chain containing 22 carbon atoms the $6A_g$ and $7A_u$ oscillators can be resonantly excited as two-photon resonances ($\Omega(1B_u) = 2.56eV$, $\Omega(6A_g) = \Omega(7A_u) = 5.11eV$). Our calculations show, that compared to the $1B_u$ oscillators, even for this case, the $A_g$ oscillators contribute only weakly for the signal. For zero delay they are responsible for only 0.8% of the signal (for the 30 carbon atom chain this value is 0.2%). However, for large negative delays, when the contributions from the $1B_u$ oscillator vanish, the two-photon resonances induce a finite FWM signal. For the chain of 22 carbon atoms these signals for negative delays are very weak. The time-integrated FWM signal for $\tau = 100$ fs is five orders of magnitude smaller than the one for zero delay. We therefore believe that our conclusions drawn for the resonant response of Hückel model, regarding the weak coupling of the $1B_u$ to the $A_g$ oscillators, are of general nature.

B. The PPP model

We shall now explore the role of electronic correlations by repeating the previous calculations for the PPP model. Similar to the Hückel model, the geometry optimized HF ground state is characterized by a bond order wave with a uniform charge density [12,26]. This structure is stabilized
FIG. 5. Absolute value of second-order density matrix $\rho^{(2)}(t)$ at $t = 20$ fs representing transient-grating $(k_2 - k_1)$ for (a) model IH, Eq. (27), (b) model IP, Eq. (28), (c) model IIP, Eq. (27), and (d) two-photon resonances ($2k_2$) for model IIIH, Eq. (29).

by the electron-phonon and the Coulomb exchange interactions. The calculated ground state has an average bond order $<p_n> = 0.63$ and alternation parameter $p'_n = 0.24$. The average bond order alternation is a little larger than in the Hückel model. The average bond length is 1.31 ± 0.05 Å, where the alternation is due to the larger force constant smaller than in the Hückel model [26]. The average transfer integral can be approximated by $t_{n,n'±1} = \beta (1 - (-1)^n \delta)$, with $\beta = -2.7 eV$ and $\delta = 0.07$.

All of the coupling constants in Eqs. (20) and (21) can contribute once the Coulomb interaction is incorporated, see Table I. The frequency of the lowest 1$B_u$ oscillator is again 2.28 eV. The 1$A_g$ oscillator which is closest in frequency to twice the frequency of the 1$B_u$ is the 5$A_g$, at 4.52 eV, see Fig. 7. The frequency difference $2\Omega(1B_u) - \Omega(5A_g) = 0.049$ eV is smaller than the spectral width of the exciting 20 fs laser pulses. All other contributions from 1$A_g$ oscillators can be assumed to be off-resonant. So the two primary oscillators, which are considered explicitly, are 1$B_u$ and 5$A_g$.

In Fig. 2(c) and 2(d) we show the density matrices of the HF ground-state and of the 1$B_u$ oscillator. Compared to the 1$B_u$ oscillator, see Fig. 2, calculated for the Hückel model, which is strongly delocalized in the off-diagonal direction, the many-particle Coulomb-interaction leads to localization of the oscillator towards the diagonal. Still the ground state is again more localized along the diagonal than the oscillator, which shows that the optical excitation creates electronic coherence in the system. Also shown in Fig. 2 are the most strongly contributing $A_g$ oscillators, (e) the 3$A_g$, which gives the strongest off resonant contribution, and (f) the 5$A_g$, which appears as a two-photon resonance.

In Table I we give the relevant coupling constants for the PPP model. To simplify the analysis of these numerous term, we split the discussion into three parts. In model IP, like in model IIIH for the Hückel model, we neglect all contributions except for the ones involving only the 1$B_u$ oscillator. In addition to these contributions we include in model IP the renormalization originating from the elimination of the $A_g$ oscillators appearing as transient-gratings ($X_t$). Finally, in model IIIH we also add the explicitly considered 5$A_g$ oscillator, as well as all renormalizations induced by $A_g$ oscillators appearing as two-photon resonances ($Y_t$).

In model IP only the following terms contribute: $\mu_1, s_1, s_2, V_1$. $s_1$ describes the phase space filling, unlike the Hückel model, due to correlations its magnitude is not equal to the magnitude of the dipole $\mu_1$ but is somewhat smaller. $s_2$ describes a similar process, where now the field is scattered off a term rotating with twice the transition frequency of the 1$B_u$ oscillator, instead of a transient grating term like in $s_1$, which basically has no rotation. In the absence of correlation (the Hückel model) $s_2$ was zero, here $s_2$ is finite, but still very small, only 0.6% of $s_1$, and can therefore be neglected. $V_1$ represents a many-particle induced scattering potential, which formally appears like a local field correction [16–18]. Actually it includes all many-particle contributions involving only the 1$B_u$ oscillator. Neglecting the small $s_2$ contribution, the equation is equivalent to a nonlinear wave-equation, which has been extensively used for the description of nonlinear optical properties of inorganic semiconductors [16,17,19,29]. In this sense the nonlinear wave-equation appears as a special case of the present oscillator equations, obtained when some terms are neglected. This nonlinear wave equations can be derived by expanding the semiconductor Bloch equation [32,33] in an excitonic basis, keeping only the 1s excitation. In the language of the semiconductor Bloch equations the nonlinear scattering potential includes energy and field renormalization terms, which are induced by the many-particle Coulomb interaction [18,29].

The FWM signal for model IP is given by the solid lines in Fig. 8, where both the amplitude of the FWM signal and its relative phase are plotted. Compared to the Hückel model calculations, the amplitude changes its shape. It is no longer a free-induction decay, but has a maximum at later times, which are determined by the dephasing times. This is the same signature that has been observed in time-resolved FWM experiments on inorganic semiconductor nanostructures [19,20,34]. In semiconductors these signal shapes have been interpreted by a nonlinear Ginzburg-Landau like wave equation for the 1s exciton amplitude [16,17,19,29]. If we only consider the 1$B_u$ oscillator and further neglect the small $s_2$ term, we obtain an identical wave equation as a special case of the oscillator equations. Besides the phase-space filling ($s_1$) induced by the many particle Coulomb interaction it has an additional nonlinearity ($V_1$), which formally appears like a local field correction. This nonlinear scattering potential describes scattering of the induced polarizations, resulting in a FWM signal. According to analytical solutions of optical
FIG. 8. (a) Time-resolved amplitude and (b) phase of the FWM signal for time-delay $\tau = 0$ fs for the PPP model: Solid line: model IP, dashed: model IIP, dotted: model IIIP, and dashed-dotted: laser pulse envelope.

Bloch equations including a local field, this contribution has a real positive prefactor [16,29]. Since $V_1$ itself is positive and since the many-particle induced FWM signal is like in inorganic semiconductors larger than the phase-space filling, the relative phase of the FWM signal, solid line in Fig. 8, is about 0, i.e. the induced polarization is in phase with the exciting pulse.

Fig. 5(b) shows the second-order density matrix in real space, representing a transient-grating ($k_2 - k_1$) formed by the $1B_u$ oscillator

$$
\rho^{(-11)}(t) = e^{i(\omega_1 - \omega_2)t} \frac{1}{2} \left[ [\xi_1, \bar{\rho}], \xi_{-1} \right] \\
+ [\xi_{-1}, \bar{\rho}], \xi_1 \right] z_{-1}^{(-10)}(t) z_1^{(01)}(t).
$$

Due to the symmetry of this expression, like in the Hückel model, the density matrix $\rho_{ij}$ representing this term is zero if $i + j$ is even (this is indicated by the red squares). The odd index combinations show a profile similar to the $1B_u$ oscillator shown in Fig. 2(d). Accordingly, like the $1B_u$ oscillator, also the corresponding transient-grating is more localized in the PPP than in the Hückel model.

In model IIP the off resonant transient grating contributions $X_1$-$X_4$ are included. The convergence of these parameters with the number of oscillator variables is shown in Fig. 9. The value for $X_1$, which is a small contribution, since it describes scattering of a linear term off two-fields, is to 2.7% accuracy given by the coupling to the $3A_g$ oscillator. For $X_1$, we have to keep five $A_g$ oscillator variables to get 5% accuracy. For $X_2$, which acts as renormalizations of $s_1$ is to within 5% given by the coupling to the $3A_g$ oscillator alone. For $X_3$, which acts as renormalizations of $s_2$ we have to keep contributions from three $A_g$ oscillators variables to get it to 3% accuracy. To get $X_4$, the renormalization of the nonlinear scattering potential $V_1$ also within 5%, we have to keep 16 oscillators variables. The expression for $X_4$ is entirely determined by the Coulomb-interaction between different oscillators. Its slow convergence as function of the number of oscillators variables compared to the other quantities indicates, that the Coulomb-interaction couples the oscillators much less selectively than the dipole coupling, which is present in the expressions for the other terms.

The FWM signal for model IIP is given in Fig. 8 (dashed lines), where the absolute value as well as the relative phase of the FWM signal are plotted. The most notable changes
between the signal involving only the $1B_u$ oscillator and the present one are the decrease in amplitude and the change in phase. These features can be simply explained by considering the values of $V_1$ and its renormalization $X_4$. While $V_1$ is positive $+0.063$ eV, $X_4$ is calculated to be negative and larger in absolute value $-0.082$ eV. Therefore the effective nonlinear scattering potential $V_1 + X_4 = -0.019$ eV is negative and about a factor 3 smaller than $V_1$. This reduces the amplitude of the interaction-induced contribution to the signal and changes its phase, which in turn explains the observed differences. This change of phase has strong influence on the spectrally resolved FWM signal. While the Fourier transform (FT) of the signal originating from the $1B_u$ oscillator is, like in inorganic semiconductors [29,35], slightly asymmetric with respect to detuning with a tail towards lower frequencies, the FT of the signal for model IIP, is asymmetric with tails towards higher frequencies. These spectral features can also be nicely analyzed using a Wigner spectrogram [36,37] as discussed in Ref. [14].

Fig. 5(c) shows the transient-grating ($k_2 - k_1$) part of the second order density matrix in real space. It is formed by the $1B_u$ oscillator and some $A_g$ oscillators and given by Eq. (28). The density matrix contains contributions from the $1B_u$ and about eight $A_g$ oscillators, which contribute most strongly to $X_4$. $\rho_{ij}$ is again zero if $i + j$ is even (this is indicated by the red squares). Due to the contributing $A_g$ oscillators, the resulting density matrix extends further to the off-diagonal than the one originating from the $1B_u$ oscillator alone.

So far, our analysis demonstrated that the off-resonant terms involving transient gratings contribute significantly. In addition to the previous terms we include in model IIP all renormalizations arising from terms representing two-photon resonances $Y_1-Y_4$. Their convergence with the number of virtual oscillators variables is shown in Fig. 10. The value for $Y_1$ (which is a small contribution, since it describes scattering of a linear term off two-fields) is to 0.7% given by the coupling to the $3A_g$ oscillator. The value for $Y_2, Y_3$), which act as renormalizations of $s_1$ ($s_2$) is to 0.1% (0.2%) given by the coupling to the $3A_g$ oscillator. The reason that we essentially only need the $3A_g$ oscillator to determine $Y_1-Y_4$ is that in addition to its strong dipole coupling to the $1B_u$ oscillator, it is not too much off resonant compared to most other oscillators. To get $Y_4$, the renormalization of the nonlinear scattering potential $V_1$ also within 5%, we have to keep two oscillators the $3A_g$ and the $5A_g$. As a two-photon resonance we also keep the $5A_g$ explicitly. It is dipole and Coulomb coupled to the $1B_u$ oscillator by $\mu_{12}$ and $V_{12}$.

The FWM signal for model IIP is given in Fig. 8 (dotted line). Compared to the model IIP, the amplitude increases again and the phase is close to 0. In order to explain these changes we have to consider two effects. First, like before, the renormalization of $V_1$. The effective nonlinear scattering potential is now given by $V_1 + X_4 + Y_4$ which is 0.016 eV, a positive but quite small value. Second, the increase in amplitude is caused by the contribution from the two-photon resonance represented by $V_{12}$, which describes the Coulomb coupling between the $1B_u$ and the $5A_g$ oscillator.

This change of phase will again influence the spectrally resolved FWM signal, which is now again be asymmetric with respect to the detuning with tails towards negative detuning.

![FIG. 11. (a) Time-resolved amplitude and (b) phase of the FWM signal for time-delay $\tau = 0$ fs for the PPP model. Solid line: model VP, dashed: model IVP, and dashed-dotted: laser pulse envelope.](image)

This is the same signature which appears when we keep only the $1B_u$ oscillator, and is also the typical signature in the FT FWM signal of inorganic semiconductors [29,35].

Fig. 5(d) shows the two-photon resonance ($2k_2$) part of the density matrix in real space, which is formed by the $1B_u$ oscillator and some $A_g$ oscillators, and given by

$$\rho^{(2)}(t) = e^{-2i\omega_2 t} \left( \frac{1}{2} \left( \left[ \xi_1, \overline{\xi} \right] + \left[ \xi_1, \overline{\xi} \right] \right) \left( \rho^{(1)}_{11}(t) \right)^2 + \sum_{\beta} \xi_{3\beta}^{(2)}(t) \right).$$

(30)

The density matrix consists of small contribution from the $1B_u$ and about mainly two $A_g$ oscillators, namely $3A_g$ and $5A_g$. Its shape is essentially a superposition of the density matrices representing the $3A_g$ and the $5A_g$ oscillators, shown in Fig. 2.

Having analyzed the different contributions to the nonlinear optical response within the PPP model, we propose a simplified two-oscillator model [14], which to a good accuracy reproduces the signal. Compared to the model resulting from the elimination of off-resonant contributions, we further neglect small contributions like $X_1$, $X_{-1}$ and $Y_1$, and also $s_2$ and its renormalization $X_3$, and $Y_3$. We further neglect the anharmonic constants $A_1$, $A_2$, $A_3$, $B_1$, and $B_2$ that appear...
in the definition of the polarization. So now the off-resonant oscillators only enter in renormalizations of $s_1$ and $V_1$. The equations considered within this reduced model are [14]

$$\begin{align*}
\frac{\partial}{\partial t} z_1 &= (\Omega_1 - \omega_L - \frac{i}{T_2})z_1 - \mu_1 E \\
&- E\mu_{12} z_2 - E(s_1 + Y_2 + X_2)z_1 z_{-1} \\
&+ 2V_{12} z_2 z_{-1} + (V_1 + Y_4 + X_4)z_{-1} z_1 z_1 \\
&z_{-1} = z_1^* \\
\frac{\partial}{\partial t} z_2 &= (\Omega_2 - 2\omega_L - \frac{i}{T_2})z_2 - E\mu_{12} z_1 + V_{12} z_1 z_1
\end{align*}$$

(31)

(32)

The induced polarization is given by:

$$P_S(t) = e^{-i\omega L} (\mu_1 z_1 + \mu_{12} z_2 z_{-1})$$

(33)

We compare the results obtained for this model (IVP) with results obtained by a full calculation (VP), where we have kept all oscillators explicitly (in practice these results were obtained by a real-space calculation), see Appendix B. The good agreement between the two calculations shown in Fig. 11, confirms the validity of this simplified description. There are only slight differences in the amplitude and the phase of the FWM signal mainly during the initial excitation process.

Another important effect is the existence of strong FWM signals for negative delays, which may be induced by either two-photon $A_g$ oscillator variables, or by many-body anharmonicities of the $B_u$ oscillators. Our calculations show that, as for positive delay, the many-body anharmonicities contribute most strongly to the signal for negative delays. The time-integrated signals in Fig. 12 decay for positive delays with $T_2/2$, and for negative delays with about $T_2/4$ [16,17]. The very weak modulations, which can be seen for negative delays, are due to quantum beats with a frequency determined by $2\Omega(1B_u) - \Omega(5A_g)$. The results for the full model VP (solid line) and the reduced model IVP (dashed line) are again in very good agreement.

**IV. SUMMARY**

In summary, we have modeled resonant two-pulse four-wave mixing experiments in conjugated polyenes using the electronic-oscillator representation. We found that it is only required to consider two electronic oscillators explicitly. The role of electronic correlations has been clarified by comparing calculations done in the absence of electronic correlations (Hückel model) and with strong electronic correlations (PPP model). While both models have similar linear optical properties, i.e. a strong lowest transition at the same spectral position, their nonlinear optical properties are very different. For the PPP model we predict signatures of electronic correlations, which should be observable in ultrafast optical spectroscopy, in both the phase and the amplitude of the signal. We expect analogous effects to be observable using frequency-domain resonant four-wave mixing techniques [38]. The coupling coefficients leading to the nonlinear optical response as well as the calculated signals have been compared to theoretical and experimental treatments for inorganic semiconductors. The present approach provides a unified theoretical analysis of resonant nonlinear experiments in organic and inorganic materials.

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APPENDIX A: EQUATIONS OF MOTION FOR TWO-PULSE NONLINEAR OPTICAL RESPONSE

In this appendix, we show how the oscillator equations of motion can be used to describe multiple-pulse optical experiments. We consider a two-pulse nonlinear optical experiment, where the exciting field is given by

\[ E(t) = E_1(t)e^{i(k_1 + r + i\omega_1)t} + E_2(t)e^{i(k_2 + r + i\omega_2)t} \]

where the exciting field is given by Eq. (15) and transforming to the rotating frame variables associated with positive frequency (\( \omega_1 \)). We label these different directional components by \( n, m \), where \( n, m \) can be any integers [18,39]. We label these different directional components by \( (n|m) \), which refers to the excitation associated with the direction \( nk_1 + mk_2 \). Inserting this decomposition into the equations of motion Eq. (15) and transforming to the rotating frame, leads to

\[
\frac{\partial}{\partial t} z_{\alpha}^{(n|m)} = (\Omega_\alpha - m\omega_1 - n\omega_2) z_{\alpha}^{(n|m)} - \mu_\alpha (\delta_{\alpha,1}\delta_{n,0}E_1^+ + \delta_{\alpha,-1}\delta_{n,0}E_1^- + \delta_{\alpha,0}\delta_{n,1}E_2^+ + \delta_{\alpha,0}\delta_{n,-1}E_2^- )
- E_1^+ \sum_{\beta} \mu_{\alpha,\beta} z_{\beta}^{(n-1|m-1)} - E_1^- \sum_{\beta} \mu_{\alpha,\beta} z_{\beta}^{(n+1|m)} - E_2^+ \sum_{\beta} \mu_{\alpha,\beta} z_{\beta}^{(n|m-1)} - E_2^- \sum_{\beta} \mu_{\alpha,\beta} z_{\beta}^{(n|m+1)}
- E_1^+ \sum_{n'|m'\beta'\gamma} \mu_{\alpha,\beta'} z_{\beta'}^{(n-1|m-m'-1)} z_{\gamma}^{(n'|m')} - E_1^- \sum_{n'|m'\beta'\gamma} \mu_{\alpha,\beta'} z_{\beta'}^{(n+1|m-m'+1)} z_{\gamma}^{(n'|m')}
- E_2^+ \sum_{n'|m'\beta'\gamma} \mu_{\alpha,\beta'} z_{\beta'}^{(n-1|m-m'-1)} z_{\gamma}^{(n'|m')} + E_2^- \sum_{n'|m'\beta'\gamma} \mu_{\alpha,\beta'} z_{\beta'}^{(n+1|m-m'+1)} z_{\gamma}^{(n'|m')}
+ \sum_{n'|m'\beta'\gamma} V_{\alpha,\beta'} z_{\beta'}^{(n-1|m-m'-1)} z_{\gamma}^{(n'|m')} + \sum_{n'|m'\beta'\gamma} \bar{V}_{\alpha,\beta'} z_{\beta'}^{(n+1|m-m'+1)} z_{\gamma}^{(n'|m')} \tag{A2}
\]

The polarization is given by:

\[
P^{(n|m)}(t) = e^{i(nk_1 + mk_2 + i(n\omega_1 + m\omega_2)t)} \left( \sum_{\beta} \bar{\mu}_{\beta} z_{\beta}^{(n|m)} + \sum_{n',m',\beta'\gamma} \bar{\mu}_{\beta'} z_{\beta'}^{(n-1|m-m'-1)} z_{\gamma}^{(n'|m')} \right) \tag{A3}
\]

These equations can be used to describe two pulse experiments; the generalization to experiments with more than two exciting pulses is straightforward. In Eq. (A2) we have only to solve explicitly for the complex amplitudes of the oscillator variables associated with positive frequency (\( \alpha > 0 \)). The amplitudes for the corresponding modes with negative frequencies are determined by:

\[
z_{-\alpha}^{(n|m)} = (z_{\alpha}^{(n|m)})^* \tag{B1}
\]

APPENDIX B: ITERATIVE CALCULATION OF THE FOUR-WAVE MIXING SIGNAL

In the following we perform a detailed analysis of FWM in self-diffraction geometry, where the third-order signal is monitored in the direction \( 2k_2 - k_1 \). Only \( B_{\alpha} \) oscillators can be excited in the linear response.

\[
i \frac{\partial}{\partial t} z_{\alpha}^{(10)} = (\Omega_\alpha - \omega_1) z_{\alpha}^{(10)} - \mu_\alpha E_1^+ \
i \frac{\partial}{\partial t} z_{\alpha}^{(-10)} = (\Omega_\alpha + \omega_1) z_{\alpha}^{(-10)} - \mu_\alpha E_1^- \
i \frac{\partial}{\partial t} z_{\alpha}^{(01)} = (\Omega_\alpha - \omega_2) z_{\alpha}^{(01)} - \mu_\alpha E_2^+ \
i \frac{\partial}{\partial t} z_{\alpha}^{(0-1)} = (\Omega_\alpha + \omega_2) z_{\alpha}^{(0-1)} - \mu_\alpha E_2^- \tag{B1}
\]

The second order response consists of different contributions. The particle-particle part is given by \( T(\xi) \) and has not to be calculated separately, but is completely determined by the linear response [11]. Additionally \( A_{\gamma} \) oscillators can be excited in second order, representing the particle-hole part of
the response. To calculate the FWM signal in the direction $2\mathbf{k}_2 - \mathbf{k}_1$ in third order, we have to consider a transient-grating ($\mathbf{k}_2 - \mathbf{k}_1; \omega_1 - \omega_2$) and a two-photon ($2\mathbf{k}_2; -2\omega_2$) response.

\[
\frac{\partial}{\partial t} z_{\alpha}^{(-1)[1]} = (\Omega_{\alpha} + \omega_1 - \omega_2) z_{\alpha}^{(-1)[1]} - E_1 \sum_{\beta} \mu_{\alpha, \beta} z_{\beta}^{(0)[1]} - E_2 \sum_{\beta} \mu_{\alpha, \beta} z_{\beta}^{(-1)[1]} + (V_{\alpha, \beta} + V_{\alpha, \gamma}) z_{\beta}^{(-1)[0]} z_{\gamma}^{(0)[1]}
\]

\[
\frac{\partial}{\partial t} z_{\alpha}^{(1)[1]} = (\Omega_{\alpha} + \omega_1 + \omega_2) z_{\alpha}^{(1)[1]} - E_1 \sum_{\beta} \mu_{\alpha, \beta} z_{\beta}^{(0)[1]} - E_2 \sum_{\beta} \mu_{\alpha, \beta} z_{\beta}^{(1)[0]} + (V_{\alpha, \beta} + V_{\alpha, \gamma}) z_{\beta}^{(1)[0]} z_{\gamma}^{(0)[1]}
\]

\[
\frac{\partial}{\partial t} z_{\alpha}^{(0)[2]} = (\Omega_{\alpha} - 2\omega_2) z_{\alpha}^{(0)[2]} - E_2 \sum_{\beta} \mu_{\alpha, \beta} z_{\beta}^{(0)[1]} + \sum_{\beta, \gamma} V_{\alpha, \beta} z_{\beta}^{(0)[1]} z_{\gamma}^{(0)[1]}
\]

\[
\frac{\partial}{\partial t} z_{\alpha}^{(-1)[1]} = (\Omega_{\alpha} + \omega_1 - 2\omega_2) z_{\alpha}^{(-1)[1]} - E_1 \sum_{\beta} \mu_{\alpha, \beta} z_{\beta}^{(0)[1]} - E_2 \sum_{\beta} \mu_{\alpha, \beta} z_{\beta}^{(-1)[1]}
\]

\[
\frac{\partial}{\partial t} z_{\alpha}^{(1)[1]} = (\Omega_{\alpha} + \omega_1 + 2\omega_2) z_{\alpha}^{(1)[1]} - E_1 \sum_{\beta} \mu_{\alpha, \beta} z_{\beta}^{(0)[1]} - E_2 \sum_{\beta} \mu_{\alpha, \beta} z_{\beta}^{(1)[1]}
\]

\[
\frac{\partial}{\partial t} z_{\alpha}^{(0)[2]} = (\Omega_{\alpha} + 2\omega_2) z_{\alpha}^{(0)[2]} - E_2 \sum_{\beta} \mu_{\alpha, \beta} z_{\beta}^{(0)[1]} + \sum_{\beta, \gamma} V_{\alpha, \beta} z_{\beta}^{(0)[1]} z_{\gamma}^{(0)[1]}
\]

In third order again only $B_{u}$ oscillators can be excited:

\[
\frac{\partial}{\partial t} z_{\alpha}^{(-1)[2]} = (\Omega_{\alpha} + \omega_1 - 2\omega_2) z_{\alpha}^{(-1)[2]} - E_1 \sum_{\beta} \mu_{\alpha, \beta} z_{\beta}^{(0)[2]} - E_2 \sum_{\beta} \mu_{\alpha, \beta} z_{\beta}^{(-1)[1]}
\]

\[
\frac{\partial}{\partial t} z_{\alpha}^{(1)[2]} = (\Omega_{\alpha} + \omega_1 + 2\omega_2) z_{\alpha}^{(1)[2]} - E_1 \sum_{\beta} \mu_{\alpha, \beta} z_{\beta}^{(0)[2]} - E_2 \sum_{\beta} \mu_{\alpha, \beta} z_{\beta}^{(1)[1]}
\]

The polarization in the $2\mathbf{k}_2 - \mathbf{k}_1$ direction is finally given by:

\[
P^{(-1)[2]}(t) = e^{i(-\mathbf{k}_1 + 2\mathbf{k}_2) \cdot \mathbf{r} - i(\omega_1 + 2\omega_2)t} \left( \sum_{\beta} \mu_{\beta, \gamma} z_{\beta}^{(-1)[2]} + \sum_{\beta, \gamma} (\tilde{\mu}_{\beta, \gamma} + \tilde{\mu}_{\gamma, \beta}) (z_{\beta}^{(-1)[0]} z_{\gamma}^{(0)[2]} + z_{\beta}^{(0)[1]} z_{\gamma}^{(-1)[1]}) \right).
\]

Eqs. (B3) and (B4) include all resonant and nonresonant pathways that can contribute to the two-pulse FWM experiment considered here.
\[ \omega_2 = \Omega (1_B \omega_L) \]. The pulse envelopes are assumed to be Gaussian, \( E(t) \propto e^{-(t-t_0)/\tau^2} \), with a width of \( \tau = 20fs \). Since the spectral width of even these very short laser pulses (about 0.1eV) is small compared to the frequency spacing between the dominant oscillators, only a few oscillators will be excited resonantly. Our calculations show that the first and third order response is to very good accuracy dominated by only the \( 1_B \omega_L \) oscillator. In second order there may be one \( A_g \) oscillator which appears as resonantly excited two-photon transition. We now develop equations which only retain two zero frequency.

The polarization in the direction is given by:

\[ P_{\parallel}(t) = e^{-i(\mathbf{k}_1 + 2\mathbf{k}_2) \cdot \mathbf{r} - i(\omega_1 + 2\omega_2)t}(\mu_1 z_1^{(-1)}(t) + \sum_\beta \mu_\beta z_\beta^{(-1)} + \sum_\beta \mu_{-1\beta} z_\beta^{(1)}). \]

In these equations we have used some abbreviations:

\( \mu_1 = \bar{\mu}_1 \)

\( \mu_n = \mu_{n,1} = \mu_{n,-1} + \bar{\mu}_n \)

\( s_1 = \mu_{-1,1} + \mu_{1,-1} \)

\( s_2 = \mu_{1,1} \)

\( V_i = V_{i,11} + V_{i,1,-1} + V_{i,-11} \)

\( V_{12} = V_{2,11} - V_{1,2,1} \)

The contributions of \( A_g \) oscillator variables associated with negative frequency are given by:

\[ z_{-1,1}(t) = \frac{1}{\Omega_{\beta}}(E_1^{+} \mu_{\beta,1} z_{\beta}^{(1)} + E_2^{+} \mu_{-\beta,1} z_{-\beta}^{(-1)} - (V_{\beta,1,1} + V_{\beta,-1,1}) z_{-\beta}^{(-1)} z_{\beta}^{(1)} - (V_{\beta,-1,-1} + V_{\beta,1,-1}) z_{-\beta}^{(-1)} z_{\beta}^{(1)}). \]

And in third order:

\[ i \frac{\partial}{\partial t} z_1^{(-1)}(0) = (\Omega_1 - \omega_1) z_1^{(0)}(0) - \mu_1 E_1^{+} + \sum_\beta (\mu_{-1,\beta} z_\beta^{(1)} + \mu_{1,-\beta} z_{-\beta}^{(-1)}). \]

In second order:

\[ i \frac{\partial}{\partial t} z_1^{(1)}(0) = (\Omega_2 - \omega_2) z_1^{(0)}(0) - \mu_1 E_2^{+} + \sum_\beta (\mu_{-1,\beta} z_\beta^{(1)} + \mu_{1,-\beta} z_{-\beta}^{(-1)}). \]

And in third order:

\[ i \frac{\partial}{\partial t} z_1^{(-2)}(0) = (\Omega_1 - \omega_1) z_1^{(-2)}(0) - E_1^{+} E_1^{+} (Y_1 + X_1) z_1^{(0)}(0) - (E_1^{+})^2 (X_1) z_1^{(-1)}(0) - E_1^{+} \mu_{1,1} z_1^{(-2)}(0) - E_1^{+} (s_1 + Y_2 + X_3) z_1^{(0)}(0) - E_2^{+} (s_1 + Y_2 + X_2) z_1^{(-1)}(0) + 2\mu_{1,2} z_2^{(0)} z_1^{(-1)}(0) + (V_1 + Y_4 + X_5) z_1^{(-1)}(0) z_1^{(1)}(0) + \sum_\beta \mu_{1,\beta} z_\beta^{(-2)}(0) + \sum_\beta \mu_{-1,\beta} z_\beta^{(0)} z_{-\beta}^{(1)}(0). \]

The expressions for the off-resonant second order quantities can be inserted into the equation for the third order amplitude, which leads to the renormalization of some nonlinear coupling constants and a few additional terms. After this elimination, keeping just two oscillators explicitly (1 refers to the \( 1_B \omega_L \) oscillator and 2 the \( A_g \) considered as a two-photon resonance), the FWM signal is determined by the following set of equations. In first order:

\[ i \frac{\partial}{\partial t} z_1^{(0)}(t) = (\Omega_1 - \omega_1) z_1^{(0)}(t) - \mu_1 E_1^{+} z_1^{(-1)}(t) = (z_1^{(0)}(t)) \]

\[ i \frac{\partial}{\partial t} z_1^{(-1)}(t) = (\Omega_2 - \omega_2) z_1^{(0)}(0) - \mu_2 E_2^{+} + \sum_\beta (\mu_{-1,\beta} z_\beta^{(1)} + \mu_{1,-\beta} z_{-\beta}^{(-1)}). \]
\[ Y_3 = \sum_{\beta} -\frac{1}{\Omega_{\beta} + 2\omega_L} \mu_{\beta,-1} V_{\beta,11} \]

\[ Y_4 = \sum_{\beta} -\frac{1}{\Omega_{\beta} + 2\omega_L} (V_{1,\beta - 1} + V_{1,-\beta}) V_{\beta,11} \]

\[ + \sum_{\beta} -\frac{1}{\Omega_{\beta} + 2\omega_L} (V_{1,\beta - 1} + V_{1,-\beta}) V_{\beta,-1-1} \]

The primes over the sum symbols for \( Y_i \) indicate that the summations exclude the low frequency variable of the one \( \Lambda \) oscillator, which is explicitly considered as a two-photon resonance. In Section III we show, that to a very good accuracy the approximate equations derived in this Appendix reproduce the full results calculated using Eqs. (B1-B4).

Inserting the expressions for the amplitudes of the virtual oscillators Eqs. (C1)-(C4) into Eq. (C9) allows to perform the summations over \( \beta \) and simplifies the expression for the polarization. Like in the equations of motion this procedure results in some new anharmonic couplings.

\[ P^{(-1|2)}(t) = e^{i(-k_1+2k_2) \tau} e^{-i(-\omega_1 + 2\omega_2) \tau} \left[ \mu_1 z_1^{(-1|2)} + \mu_2 z_2^{(-1|2)} + (A_1 + B_1) z_1^{(-1|2)} \right] + \left[ A_2 + B_2 \right] e^{i(-1|0) z_1^{(0|1)}} + A_3 e^{i(0|1)^2}. \]

Here \( A_1, A_2, \) and \( A_3 \) are obtained via elimination of the transient-grating terms involving virtual oscillators, and \( B_1 \), as well as \( B_2 \) from the corresponding two-photon terms.
[26] The geometry optimization enters into the Hamiltonian by a term \( \frac{1}{2} \sum_n K (x_n - \bar{x})^2 \), where \( x_n \) is the \( n \)-th bond length, we have used a force constant of \( K = 21 \text{eV} \text{Å} \) (\( K = 38 \text{eV} \text{Å} \)) for the Hückel (PPP) model and an equilibrium bond length of \( \bar{x} = 1.41 \text{Å} \) for both models, see Ref. [12].