$\chi^{(3)}$ formalism in optically excited semiconductors and its applications in four-wave-mixing spectroscopy

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The truncation of the infinite hierarchy of equations of motion is discussed for optically excited semiconductors. We derive a complete set of equations of motion, which are valid up to third order in the excitation field amplitude. To illustrate the results the induced four-wave-mixing signals for linearly polarized laser fields are computed by numerically integrating the $\chi^{(3)}$ semiconductor Bloch equations. As the dominating nonlinearity a strong excitation-induced dephasing effect is obtained in the $\chi^{(3)}$ regime.

I. INTRODUCTION

As a consequence of the continuum of states and the Coulomb interaction between optically excited charge carriers, the nonlinear optical response of semiconductors exhibits characteristic differences from inhomogeneous two-level systems. In the last few years, both theoretical and experimental work has revealed the importance of many-body Coulomb interaction in semiconductor coherent optics.[1–7] Examples include the single-particle energy renormalization,[7] the approximate doubling of the Rabi oscillation frequency,[8] the exchange interaction enhanced four-wave-mixing or photon-echo signals,[9] excitation induced dephasing effects,[10,11] and polarization scattering effects.[12]

Theoretical descriptions of such coherently excited semiconductors, however, always encounter an inherent difficulty: in a derivation of coupled equations for the relevant expectation values one always arrives at the infinite hierarchy of equations of motion, known as the Bogoliubov-Born-Green-Kirkwood-Yvon hierarchy.[13] The occurrence of this infinite hierarchy is a direct consequence of the Coulomb interaction term in the system Hamiltonian. To solve this problem, several approximation techniques have been developed, such as random-phase-approximation (RPA), Hartree-Fock (HF) approximation, and screened Hartree-Fock (SHF) approximation. In the HF method, the four-operator correlations are factorized into products of "macroscopic" observables like optical polarization and carrier densities, and higher order correlations are neglected. This approximation allows for the truncation of the infinite hierarchy of equations of motion into a closed and finite set of equations. These truncated equations of two-operator correlation functions are often referred to as the semiconductor Bloch equations (SBE) because of their similarity to the optical Bloch equations in atomic systems.[14] They can be written in the form of the atomic optical Bloch equations but with renormalized transition energies and Rabi frequencies. Numerical solutions of the semiconductor Bloch equations have explained successfully various experimental observations in nonlinear spectroscopy of semiconductors and semiconductor laser physics.[7]

The HF truncation of equations of motion plays a central role in the theory of many-body systems. This approach can be justified rigorously only in the limit of infinite plasma density, where the Coulomb interaction becomes negligible with respect to the kinetic energy of the particles.[15] The semiconductor Bloch equations based on the Hartree-Fock factorization are likely to overestimate the optical coherence of the system. At the HF level, they do not contain incoherent effects such as carrier-carrier scattering and polarization dephasing. The theoretical approach to these many-particle correlations are either based on regular perturbative methods or on Feynman diagram techniques. Within the diagrammatic approach, the treatment of the pure plasma case has been most successful, for it can be treated in the so-called SHF approximation (see, for example, Refs. 16 and 1–3). Its simplicity and applicability to the nonequilibrium state allows a straightforward implementation of correlation effects into the semiconductor Bloch equations. This SHF approach, which is based on the Keldysh Green's function technique, contains effects like the screening of the Coulomb potential by a nonequilibrium electron-hole plasma, band gap reduction, and exchange interaction induced renormalization of the effective Rabi frequency. In many applications, the scattering and dephasing rates are computed from the quantum Boltzmann equations and are inserted in the screened SBE.[7] This partially phenomenological

method has been successfully used to describe a variety of semiconductor experiments, such as hole burning in inverted semiconductors[17] and many others.

The extension of the SHF approximation into the low carrier density regime requires a detailed understanding of exciton-exciton scattering, biexciton formation, excitonic screening, or a combination of all such effects. Although the Keldysh diagram technique solves this problem, in general, it is not possible to give a strict estimate for the error one makes summing up certain diagrams and ignoring others. Most of the theoretical calculations of the optical properties of weakly excited semiconductors are based on the semiconductor Bloch equations with various screening models. These calculations provide satisfactory agreement with a large number of experiments. Nevertheless, some recent experiments in the low carrier density regime show the limits of the SHF treatment. A pronounced example of disagreement between the experiments and the theory stems from four-wave-mixing (FWM) measurements in the low density region.[10] These experiments are performed in strained GaAs samples or in quantum wells. The excitation frequency is chosen in the vicinity of the lowest exciton resonance, and, therefore, only the two topmost valence bands are excited. According to the SHF theory, the FWM signal induced by two cross-linearly-polarized pulses would have the same intensity ($I_\perp$) as that induced by two copolarized pulses ($I_\parallel$), i.e., $I_\parallel/I_\perp = 1$ under otherwise same experimental conditions.[18,19] However, experimentally the ratio of $I_\parallel/I_\perp$ is found to be of the order of 10 in some cases and increases even further if the carrier density decreases.

In order to understand the difference between the theory and experiments, we proposed a model based on an extension of the SHF approximation in which the Coulomb hole self-energy is expanded in terms of the carrier density and the exciton screening is modeled using a single plasmon pole approximation.[10,11] This partly phenomenological theory explains the excitation dependence of the polarization selection rules of FWM experiments, showing that the inclusion of incoherent-scattering effects into the SBE significantly affects the predictions for the FWM signals.

A rigorous theoretical treatment of the many-body effects for carrier densities well below the Mott density is not only desirable theoretically, but also necessary for the explanation of experiments. Recently, Axt and Stahl[20,21] pointed out that it is possible to classify the nonlinear optical response of semiconductors according to an expansion in powers of the applied light field. This approach, which is similar to the susceptibility $\chi^{(n)}$ expansion in atomic systems, establishes a systematic truncation scheme up to arbitrary order in the field strength. This method is especially useful when the carrier density is low so that only the lowest nonlinear expansion terms, the $\chi^{(3)}$ terms, are needed in the calculations.

Within our model (i.e., no carrier-phonon or carrier-impurity coupling) the validity of the $\chi^{(3)}$ expansion is restricted to the case of off-resonant excitation where the Rabi frequency is smaller than the normalized detuning, or to the case of small area (= time-integrated E-field amplitude) pulses. Concerning the applicability of the approach in the long-time regime, a $\chi^{(n)}$ expansion with $n > 3$ would extend the range of validity of this approach, because, as we will show in the following, thermalization processes due to carrier-carrier scattering can only be described in such higher order expansions. These processes are crucial for a correct description of the long-time behavior of the system. The absence of these thermalization processes might be of less importance if an extended model would be considered, such as thermalization due to carrier-phonon interaction. Such models are, however, beyond the scope of this paper.

Comparison of the $\chi^{(3)}$ treatment with the widely applied HF truncation approach yields an interesting insight of the validity of the HF factorization in the low density region. As shown by Axt and Stahl, the HF equations (the semiconductor Bloch equations) are similar to the equations of motion in third order in the external electric field.

In this paper, we apply the $\chi^{(3)}$ analysis to compute results for a four-wave-mixing configuration in semiconductors. The paper is organized as follows. In Sec. II, we present the electron-hole Hamiltonian in an arbitrary representation and derive the necessary equations of motion for further discussion. In Sec. III, we analyze the factorization of the expectation values. Using the equations of motion, we establish the minimum order of magnitude of the contribution resulting from particular expectation values of relevant operator products. This discussion shows that for $\chi^{(3)}$ properties only a finite number of operators is necessary, leading to a truncation of the infinite hierarchy of equations into a finite and closed set of equations. In Sec. IV, we discuss the equations of motion up to third order in the external field. The set of equations obtained generalizes the semiconductor Bloch equations. The exciton-carrier scattering introduces excitation induced dephasing which strongly affects the $\chi^{(3)}$ properties of semiconductors. In Sec. V, we give the optical polarization equation in the quasimomentum representation and discuss its application to the two-beam FWM induced by linearly-polarized pulses. For strained GaAs bulk sample, the numerical solutions show that the ratio of $I_\parallel/I_\perp$ could be up to 10^3 when the dephasing time is sufficiently long.

II. HAMILTONIAN AND EQUATIONS OF MOTION

We use the multiband electron-hole Hamiltonian in an arbitrary representation. The Hamiltonian is

$$\begin{aligned} H = & \sum_{\alpha_1,\alpha_2} \varepsilon(\alpha_1,\alpha_2) a^\dagger(\alpha_1) a(\alpha_2) + \frac{1}{2} \sum_{\alpha_1,\alpha_2,\alpha_3,\alpha_4} \\ & \times V(\alpha_1,\alpha_2,\alpha_3,\alpha_4) a^\dagger(\alpha_1) a^\dagger(\alpha_2) a(\alpha_3) a(\alpha_4) \\ & + \frac{1}{2} \sum_{\alpha_1,\alpha_2} \{ (\vec{\mu}_{\alpha_1,\alpha_2} \cdot \vec{E}) a^\dagger(\alpha_1) a^\dagger(\alpha_2) \\ & + (\vec{\mu}_{\alpha_1,\alpha_2} \cdot \vec{E})^* a(\alpha_2) a(\alpha_1) \}. \end{aligned} \tag{1}$$

In the standard basis, the index α contains both the

band (includes the spin) and the momentum, $\alpha = (b, \vec{k})$, where the band index b denotes either the conduction band or the valence band of interest, and $\vec{k}$ is the quasi-momentum. However, the notation is completely independent of the choice of the single-particle states, so that any other basis set can be used as well. $\varepsilon(\alpha_1, \alpha_2)$ is the kinetic energy matrix element in the chosen basis. An example of such kinetic matrices is the Luttinger Hamiltonian[22] for the valence bands of a semiconductor with zinc-blende structure. In the dipole approximation the field-semiconductor interaction is expressed through the scalar products, $\vec{\mu}_{\alpha_1,\alpha_2} \cdot \vec{E}$, where $\vec{\mu}_{\alpha_1,\alpha_2}$ is the antisymmetrized dipole moment between the single-particle states $|\alpha_1\rangle$ and $|\alpha_2\rangle$, i.e., $\vec{\mu}_{\alpha_1,\alpha_2} = \langle\alpha_2|e\vec{r}|\alpha_1\rangle$ if α_2 is in the conduction band and α_1 in the valence band and $\vec{\mu}_{\alpha_1,\alpha_2} = -\langle\alpha_2|e\vec{r}|\alpha_1\rangle$ if the opposite is true. The matrix element is zero if both indices refer to the same band. These scalar products determine the polarization selection rules for optical transitions. Because of the hermiticity of the Hamiltonian Eq. (1) and the anticommutation of the field operators, the Coulomb potential matrix elements can be chosen to have the symmetries

$$\begin{aligned} V(\alpha_1,\alpha_2,\alpha_3,\alpha_4) &= V(\alpha_4,\alpha_3,\alpha_2,\alpha_1)^*, \\ V(\alpha_1,\alpha_2,\alpha_3,\alpha_4) &= -V(\alpha_2,\alpha_1,\alpha_3,\alpha_4) \\ &= -V(\alpha_1,\alpha_2,\alpha_4,\alpha_3). \end{aligned}$$

The antisymmetrization of the matrix elements is used to compress the notation in the equations of motion. In the Heisenberg picture, straightforward commutator manipulations yield the basic equations for the field operators ($\hbar \equiv 1$ throughout this paper),

$$\begin{aligned} i\frac{\partial}{\partial t}a(\alpha) &= \sum_{\alpha_1}\varepsilon(\alpha,\alpha_1)a(\alpha_1) \\ &\quad + \sum_{\alpha_1,\alpha_2,\alpha_3} V(\alpha,\alpha_1,\alpha_2,\alpha_3)a^\dagger(\alpha_1)a(\alpha_2)a(\alpha_3) \\ &\quad + \sum_{\alpha_1}(\vec{\mu}_{\alpha,\alpha_1}\cdot\vec{E})a^\dagger(\alpha_1), \\ i\frac{\partial}{\partial t}a^\dagger(\alpha) &= -\sum_{\alpha_1}\varepsilon(\alpha,\alpha_1)^* a^\dagger(\alpha_1) \\ &\quad - \sum_{\alpha_1,\alpha_2,\alpha_3} V(\alpha_1,\alpha_2,\alpha_3,\alpha)a^\dagger(\alpha_1)a^\dagger(\alpha_2)a(\alpha_3) \\ &\quad - \sum_{\alpha_1}(\vec{\mu}_{\alpha,\alpha_1}\cdot\vec{E})^* a(\alpha_1). \end{aligned} \tag{2}$$

The expectation values of the normally ordered operator products

$$\{N,M\} \equiv a^\dagger(\alpha_N)a^\dagger(\alpha_{N-1})\cdots a^\dagger(\alpha_1)a(\beta_1)\cdots a(\beta_M)$$

contain all the dynamical information needed to study the optical polarization and carrier densities. Here, we use the short hand notation $\{N,M\}$ to denote any operator belonging to the complete set of operator products which have N creation operators and M annihilation operators normally ordered. We obtain the equations of motion for these normally ordered operator products by inserting the equation of motion Eq. (2) into the time derivative of the corresponding definitions. In general, an iterative form for the equations of motion can be derived from

$$\begin{aligned} i\frac{\partial}{\partial t}\{N+1,M+1\} &= \left(i\frac{\partial a^\dagger(\alpha_{N+1})}{\partial t}\right)\{N,M\}a(\beta_{M+1}) \\ &\quad + a^\dagger(\alpha_{N+1})\left(i\frac{\partial\{N,M\}}{\partial t}\right) \\ &\quad \times a(\beta_{M+1})a^\dagger(\alpha_{N+1})\{N,M\} \\ &\quad \times \left(i\frac{\partial a(\beta_{M+1})}{\partial t}\right). \end{aligned} \tag{3}$$

After Eq. (2) has been inserted into the right hand side of the equation of motion, it has to be normally ordered in order to obtain a closed set of equations. Similar equations of motion can be derived for the products containing no creation or no annihilation operators. In the Heisenberg picture the state is time independent and the expectation values of operators satisfy the same equations of motion as the operators. As we will see in the next section, the operators for which N-M is odd are not coupled to the operators for which N-M is even. Therefore all expectation values for operator combinations for which N-M is odd are initially zero. Furthermore, they remain zero during the interaction for the case that the initial condition is $\langle\{0,0\}\rangle$ =1 and all other expectation values are zero.

III. DYNAMICAL TRUNCATION OF THE HIERARCHY OF EQUATIONS: FACTORIZATION OF EXPECTATION VALUES

Equation (3), with a normally ordered right hand side, shows that the external field couples the operator $\{N,M\}$ to operators like $\{N-1,M+1\}$, $\{N+1,M-1\}$, $\{N-2,M\}$, and $\{N,M-2\}$. The Coulomb potential, however, couples the operator $\{N,M\}$ only to $\{N,M\}$ and $\{N+1,M+1\}$. This important feature was first noticed by Axt and Stahl.[20] All couplings to smaller moments are at least proportional to the external field amplitude. This coupling scheme makes it possible to classify all operator products according to the powers of the external field amplitude because the lowest order of magnitude of each operator is solely determined by field driven terms in the dynamical equations. The Coulomb interaction only couples higher order terms into the equations for operator products of any given order. Consequently, the lowest order of magnitude of $\{N,M\}$ is determined by the corresponding equations of motion in which the Coulomb potential is neglected.

We study the case when the system is initially completely unexcited. Then the only initially nonzero expectation value is $\langle\{0,0\}\rangle = 1$ and all other expectation values are zero. In the general case with nonzero initial carrier density, the orders of magnitude of the initial conditions must be taken into account. The coupling scheme of the optically excited semiconductor is plotted in Fig. 1. The circled numbers denote the corresponding minimum order of the expectation value $\langle\{N,M\}\rangle$. The solid lines denote the Coulomb coupling and the dashed

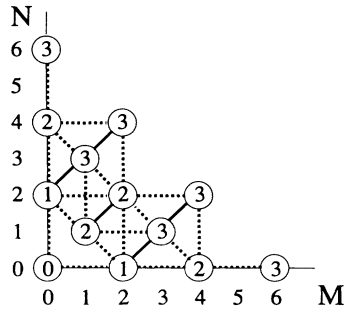

FIG. 1. Sketch of coupling between dynamical variables, $\langle\{N,M\}\rangle$. The numbers in the circles are for the minimum order of the corresponding operator $\langle\{N,M\}\rangle$ in the external field amplitude. The dotted lines denote the coupling due to the dipole interaction between the light field and the semiconductor. The solid lines denote the coupling due to the Coulomb interaction.

lines indicate the coupling by the external field. Well-known examples of the such operators are the interband polarization, $\langle a^\dagger_{e\vec{k}} a^\dagger_{h-\vec{k}}\rangle$ corresponding to {2,0} and carrier densities $\langle a^\dagger_{i\vec{k}} a_{i\vec{k}}\rangle$, $i = e,h$ corresponding to {1,1}, which are of first and second order in terms of the external field, respectively. As noted by Axt and Stahl,[20] the many-body hierarchy equations of motion, Eq. (3), can be truncated into a formally finite set of equations according to the powers of the electric field. It is evident from Fig. 1 that for a given order of magnitude in the amplitude of the external field only a finite number of variables contribute to the semiconductor optical properties. For example, in the $\chi^{(3)}$ regime, which is the most important special case in nonlinear optics, we need the expectation values up to third order in the external field. These are $\langle\{0,0\}\rangle, \langle\{1,1\}\rangle, \langle\{2,2\}\rangle, \langle\{2,0\}\rangle, \langle\{0,2\}\rangle, \langle\{4,0\}\rangle, \langle\{0,4\}\rangle, \langle\{6,0\}\rangle, \langle\{0,6\}\rangle, \langle\{3,1\}\rangle, \langle\{1,3\}\rangle, \langle\{4,2\}\rangle$, and $\langle\{2,4\}\rangle$. The polarization of the semiconductor, which determines the optical properties of the semiconductor, is given by $\langle\{2,0\}\rangle$ or $\langle\{0,2\}\rangle$. They can also be called exciton amplitudes. In this manner, $\langle\{4,0\}\rangle$ and $\langle\{0,4\}\rangle$ can be called biexciton amplitudes and $\langle\{6,0\}\rangle$ and $\langle\{0,6\}\rangle$ triexciton amplitudes. However, the triexciton amplitudes couple back to the optical polarization equation in a higher order than E^3, as shown in Fig. 1, so they can be neglected in a $\chi^{(3)}$ treatment. The equations of motion of other relevant operators can be derived from Eqs. (2) and (3). In Ref. 20, these equations are given in real space coordinates. As is seen from Fig. 1, and more rigorously proven in Appendix A, the minimum order of $\langle\{N,M\}\rangle$ in the field amplitude is $(N+M)/2$ if both N and M are even and $(N+M)/2+1$ if they are both odd, i.e.,

$$\langle a^\dagger(\alpha_{2N})\cdots a^\dagger(\alpha_1)a(\beta_1)\cdots a(\beta_{2M})\rangle = O(E^{N+M}), \quad (4)$$

and

$$\langle a^\dagger(\alpha_{2N+1})\cdots a^\dagger(\alpha_1)a(\beta_1)\cdots a(\beta_{2M+1})\rangle = O(E^{N+M+2}). \quad (5)$$

These orders of magnitude can then be used to consistently truncate the equations of motion in arbitrary order.

If the system is initially excited so that electron and hole states are partially occupied but there is no induced polarization nor other higher order correlations, we can also find the orders of magnitudes for the expectation values. In this case, initially only $\langle\{N,N\}\rangle$ is nonzero and of the order of 1. The coupling scheme shows that in this case the nonzero expectation values have

$$\langle a^\dagger(\alpha_N)\cdots a^\dagger(\alpha_1)a(\beta_1)\cdots a(\beta_M)\rangle = O(E^{|N-M|/2}).$$

This relation is not as restricting as that for the unexcited initial state. In the thermal case the hierarchy of equations cannot be truncated rigorously to a finite set of equations in any order in the field amplitude. It, however, limits the number of correlations needed in a given order.

If the initial state is unexcited, the number of equations can be further reduced because the expectation values $\langle\{N,M\}\rangle$ factorize in their minimum order. We show in Appendix A that

$$\begin{aligned}\langle a^\dagger(\alpha_{2N})\cdots a^\dagger(\alpha_1)a(\beta_1)\cdots a(\beta_{2M})\rangle &\\ = \langle a^\dagger(\alpha_{2N})\cdots a^\dagger(\alpha_1)\rangle\langle a(\beta_1)\cdots a(\beta_{2M})\rangle &\\ + O(E^{N+M+2}), & \quad (6)\end{aligned}$$

and

$$\begin{aligned}\langle a^\dagger(\alpha_{2N+1})\cdots a^\dagger(\alpha_1)a(\beta_1)\cdots a(\beta_{2M+1})\rangle &\\ = \sum_{\delta_1}\langle a^\dagger(\alpha_{2N+1})\cdots a^\dagger(\alpha_1)a^\dagger(\delta_1)\rangle &\\ \times\langle a(\delta_1)a(\beta_1)\cdots a(\beta_{2M+1})\rangle + O(E^{N+M+4}). & \quad (7)\end{aligned}$$

This factorization is not the same as the Hartree-Fock factorization since here the factorization only takes place between the creation and annihilation operators. We can loosely say that in the first approximation, all expectation values can be represented in terms of the exciton amplitudes, biexciton amplitudes, etc., because there are no free carriers in the low excitation regime. In $\chi^{(3)}$, we do not need now the equations of motion for {2,2}, {4,2}, and {2,4} since their expectation values factorize in this order according to Eq. (6). We can also factorize the expectation values of {1,1}, {3,1}, and {1,3} according to Eq. (7). However, here the benefits are not straightforward since a single expectation value is given in terms of a sum of products. This adds one degree of freedom which is not always wanted in numerical evaluations. One sees, however, that in $\chi^{(3)}$ the problem is formally completely solved in terms of the exciton and biexciton amplitudes. To complete our discussion, we provide a finite and closed set of equations, which give the optical polarization in the third order of the external field.

IV. THE SEMICONDUCTOR $\chi^{(3)}$ BLOCH EQUATIONS

The equations of motion for the interband polarization $\langle\{2,0\}\rangle$ and for the carrier density $\langle\{1,1\}\rangle$ are given by

$$\begin{aligned} i\frac{\partial}{\partial t}\langle a^\dagger(\alpha_1)a^\dagger(\alpha_2)\rangle = &-\sum_{\delta_1}\varepsilon^*(\alpha_1,\delta_1)\langle a^\dagger(\delta_1)a^\dagger(\alpha_2)\rangle - \sum_{\delta_1}\varepsilon^*(\alpha_2,\delta_1)\langle a^\dagger(\alpha_1)a^\dagger(\delta_1)\rangle \\ &- \sum_{\delta_1,\delta_2} V(\delta_1,\delta_2,\alpha_2,\alpha_1)\langle a^\dagger(\delta_1)a^\dagger(\delta_2)\rangle + \sum_{\delta_1,\delta_2,\delta_3} V(\delta_1,\delta_2,\delta_3,\alpha_1)\langle a^\dagger(\delta_1)a^\dagger(\delta_2)a^\dagger(\alpha_2)a(\delta_3)\rangle \\ &- \sum_{\delta_1,\delta_2,\delta_3} V(\delta_1,\delta_2,\delta_3,\alpha_2)\langle a^\dagger(\alpha_1)a^\dagger(\delta_1)a^\dagger(\delta_2)a(\delta_3)\rangle \\ &-(\vec{\mu}_{\alpha_1,\alpha_2}\cdot\vec{E})^* + \sum_{\delta_1}(\vec{\mu}_{\alpha_1,\delta_1}\cdot\vec{E})^*\langle a^\dagger(\alpha_2)a(\delta_1)\rangle + \sum_{\delta_1}(\vec{\mu}_{\delta_1,\alpha_2}\cdot\vec{E})^*\langle a^\dagger(\alpha_1)a(\delta_1)\rangle \end{aligned} \tag{8}$$

and

$$\begin{aligned} i\frac{\partial}{\partial t}\langle a^\dagger(\alpha_1)a(\alpha_2)\rangle = &-\sum_{\delta_1}\varepsilon^*(\alpha_1,\delta_1)\langle a^\dagger(\delta_1)a(\alpha_2)\rangle + \sum_{\delta_1}\varepsilon(\alpha_2,\delta_1)\langle a^\dagger(\alpha_1)a(\delta_1)\rangle \\ &- \sum_{\delta_1,\delta_2,\delta_3} V(\delta_1,\delta_2,\delta_3,\alpha_1)\langle a^\dagger(\delta_1)a^\dagger(\delta_2)a(\delta_3)a(\alpha_2)\rangle \\ &+ \sum_{\delta_1,\delta_2,\delta_3} V(\alpha_2,\delta_1,\delta_2,\delta_3)\langle a^\dagger(\alpha_1)a^\dagger(\delta_1)a(\delta_2)a(\delta_3)\rangle \\ &-\sum_{\delta_1}(\vec{\mu}_{\alpha_1,\delta_1}\cdot\vec{E})^*\langle a(\delta_1)a(\alpha_2)\rangle + \sum_{\delta_1}(\vec{\mu}_{\alpha_2,\delta_1}\cdot\vec{E})\langle a^\dagger(\alpha_1)a^\dagger(\delta_1)\rangle. \end{aligned} \tag{9}$$

These equations are still completely general. The many-body effects are embedded in the expectation values $\langle a^\dagger(\alpha_1)a^\dagger(\delta_1)a^\dagger(\delta_2)a(\delta_3)\rangle$and $\langle a^\dagger(\delta_1)a^\dagger(\delta_2)a(\delta_2)a(\alpha_2)\rangle$. The expectation value $\langle a^\dagger(\alpha_1)a^\dagger(\delta_1)a^\dagger(\delta_2)a(\delta_3)\rangle$ describes the momentum transfer between an exciton and an electron or a hole and hence can be called the exciton-carrier scattering amplitude. Similarly, $\langle a^\dagger(\delta_1)a^\dagger(\delta_2)a(\delta_2)a(\alpha_1)\rangle$ is called the exciton-exciton scattering amplitude. The Hartree-Fock factorization of these expectation values of the four-operator products lead to the well-studied semiconductor Bloch equations. According to Eq. (6) the exciton-exciton scattering in Eq. (9) factorizes exactly in the third order, i.e.,

$$\langle a^\dagger(\alpha_1)a^\dagger(\alpha_2)a(\alpha_3)a(\alpha_4)\rangle = \langle a^\dagger(\alpha_1)a^\dagger(\alpha_2)\rangle\langle a(\alpha_3)a(\alpha_4)\rangle + O(E^4).$$

As a consequence, Eq. (9) is reduced to the density equation in the semiconductor Bloch equations if we neglect the carrier density variation of the order of E^4 or higher.

$$\begin{aligned} i\frac{\partial}{\partial t}\langle a^\dagger(\alpha_1)a(\alpha_2)\rangle = &-\sum_{\delta_1}\varepsilon^*(\alpha_1,\delta_1)\langle a^\dagger(\delta_1)a(\alpha_2)\rangle + \sum_{\delta_1}\varepsilon(\alpha_2,\delta_1)\langle a^\dagger(\alpha_1)a(\delta_1)\rangle \\ &-\sum_{\delta_1}\{(\vec{\mu}_{\alpha_1,\delta_1}\cdot\vec{E})^* + \sum_{\delta_2,\delta_3} V(\delta_2,\delta_3,\delta_1,\alpha_1)\langle a^\dagger(\delta_2)a^\dagger(\delta_3)\rangle\}\langle a(\delta_1)a(\alpha_2)\rangle \\ &+\sum_{\delta_1}\{(\vec{\mu}_{\alpha_2,\delta_1}\cdot\vec{E}) + \sum_{\delta_2,\delta_3} V(\alpha_2,\delta_2,\delta_3,\delta_1)\langle a(\delta_3)a(\delta_2)\rangle\}\langle a^\dagger(\alpha_1)a^\dagger(\delta_1)\rangle. \end{aligned} \tag{10}$$

The carrier-carrier scattering, which stems from the expectation value of $\{3,3\}$,[7] is of the order of E^4. Hence, in third order, the carrier-carrier scattering does not give any contribution to the optical properties.

In the polarization equation (8) the exciton-carrier scattering amplitude does not factorize in third order the same way as in the Hartree-Fock factorization. According to Eq. (7) we would have

$$\langle a^\dagger(\alpha_3)a^\dagger(\alpha_2)a^\dagger(\alpha_1)a(\alpha)\rangle = \sum_{\delta_1}\langle a^\dagger(\alpha_3)a^\dagger(\alpha_2)a^\dagger(\alpha_1)a^\dagger(\delta_1)\rangle\langle a(\delta_1)a(\alpha)\rangle + O(E^5).$$

However, in order to derive numerically tractable equations, we will assume that the biexciton binding energy is small compared with the exciton linewidth. Therefore, the bound biexciton states can be neglected. We write the deviation from the Hartree-Fock factorized contribution in the form,

$$\begin{aligned} \langle a^\dagger(\alpha_3)a^\dagger(\alpha_2)a^\dagger(\alpha_1)a(\alpha)\rangle \equiv &\,\delta\langle a^\dagger(\alpha_3)a^\dagger(\alpha_2)a^\dagger(\alpha_1)a(\alpha)\rangle + \langle a^\dagger(\alpha_3)a^\dagger(\alpha_2)\rangle\langle a^\dagger(\alpha_1)a(\alpha)\rangle \\ &-\langle a^\dagger(\alpha_3)a^\dagger(\alpha_1)\rangle\langle a^\dagger(\alpha_2)a(\alpha)\rangle + \langle a^\dagger(\alpha_2)a^\dagger(\alpha_1)\rangle\langle a^\dagger(\alpha_3)a(\alpha)\rangle. \end{aligned} \tag{11}$$

In Eq. (11), we merely define $\delta\langle a^\dagger(\alpha_3)a^\dagger(\alpha_2)a^\dagger(\alpha_1)a(\alpha)\rangle$ as the expected deviation of the factorized form from the real four-operator expectation value. From its definition with the single-operator equation, Eq. (2), it is straightforward, although tedious, to obtain the dynamical equation for $\delta\langle a^\dagger(\alpha_3)a^\dagger(\alpha_2)a^\dagger(\alpha_1)a(\alpha)\rangle$,

$$
\begin{aligned}
i\frac{\partial}{\partial t}\delta\langle a^\dagger(\alpha_3)a^\dagger(\alpha_2)a^\dagger(\alpha_1)a(\alpha)\rangle = &\sum_\delta\{\varepsilon(\alpha,\delta)\delta\langle a^\dagger(\alpha_3)a^\dagger(\alpha_2)a^\dagger(\alpha_1)a(\delta)\rangle - \varepsilon^*(\alpha_3,\delta)\delta\langle a^\dagger(\delta)a^\dagger(\alpha_2)a^\dagger(\alpha_1)a(\alpha)\rangle \\
&-\varepsilon^*(\alpha_2,\delta)\delta\langle a^\dagger(\alpha_3)a^\dagger(\delta)a^\dagger(\alpha_1)a(\alpha)\rangle - \varepsilon^*(\alpha_1,\delta)\delta\langle a^\dagger(\alpha_3)a^\dagger(\alpha_2)a^\dagger(\delta)a(\alpha)\rangle\} \\
&-2\sum_{\delta_1,\delta_2}\{V(\delta_1,\delta_2,\alpha_3,\alpha_2)\langle a^\dagger(\alpha_1)a^\dagger(\delta_2)\rangle - V(\delta_1,\delta_2,\alpha_3,\alpha_1)\langle a^\dagger(\alpha_2)a^\dagger(\delta_2)\rangle\} \\
&\times\langle a^\dagger(\delta_1)a(\alpha)\rangle + 2\sum_{\delta_1,\delta_2,\delta_3}\{V(\delta_1,\delta_2,\delta_3,\alpha_2)\langle a^\dagger(\alpha_1)a^\dagger(\delta_1)\rangle\langle a^\dagger(\alpha_3)a^\dagger(\delta_2)\rangle \\
&-V(\delta_1,\delta_2,\delta_3,\alpha_1)\langle a^\dagger(\alpha_2)a^\dagger(\delta_1)\rangle\langle a^\dagger(\alpha_3)a^\dagger(\delta_2)\rangle \\
&-V(\delta_1,\delta_2,\delta_3,\alpha_3)\langle a^\dagger(\alpha_1)a^\dagger(\delta_1)\rangle\langle a^\dagger(\alpha_2)a^\dagger(\delta_2)\rangle\}\langle a(\delta_3)a(\alpha)\rangle. \qquad (12)
\end{aligned}
$$

In Eq. (12), all contributions of the order of E^5 or higher are neglected. We have also neglected the Coulomb interaction in the homogeneous part of the equation. Moreover, all contributions from biexciton binding, which are of order of E^3, are neglected. The biexciton amplitudes, described by the correlations $\langle a^\dagger(\alpha_1)a^\dagger(\alpha_2)a^\dagger(\alpha_3)a^\dagger(\alpha_4)\rangle$, are created when excitons interact via the Coulomb potential. Here, we assume that the excitons do not form molecules but remain unbound units, i.e., the binding energy of biexciton is neglected. In this case, $\langle a^\dagger(\alpha_1)a^\dagger(\alpha_2)a^\dagger(\alpha_3)a^\dagger(\alpha_4)\rangle$ is factorized. These assumptions are not in agreement with the $\chi^{(3)}$ treatment of semiconductors, in general, but simplify our problem remarkably. This approach should be a reasonable approximation for conditions where the bound biexcitons are not dominating, for example, when the excitation frequency is above the biexciton resonance and close to the exciton resonance. The biexciton contribution to $\chi^{(3)}$ of optically excited semiconductors, especially the optical Stark effects, was studied by Axt and Stahl.[21] The absence of terms proportional to the external field amplitude in Eq. (12) show concretely that the interaction with the light field creates excitons which are described by the factorized contributions of the expectation values. However, one should note that by neglecting the biexciton binding we have also neglected a contribution which in powers of the Coulomb interaction V are of the order of V^3 as can be seen from Eqs. (B3), and (B4). In the theory of plasma screening, however, the terms proportional to V^3 in the equation for the optical polarization are of the order of E^5. Hence, the terms omitted do not describe plasma screening.

In an optical field, $\delta\langle a^\dagger(\alpha_3)a^\dagger(\alpha_2)a^\dagger(\alpha_1)a(\alpha)\rangle$ oscillates with the external field frequency, ω, and has a relatively slowly varying envelope. This time dependence enables us to separate the envelope from the fast varying oscillation part by replacing the time derivative $i\partial/\partial t$ in Eq. (12) with $-\omega$. We further insert the obtained solutions of Eq. (12) into Eq. (8) and find

$$
\begin{aligned}
i\frac{\partial}{\partial t}\langle a^\dagger(\alpha_1)a^\dagger(\alpha_2)\rangle = &-\sum_{\delta_1}\{\varepsilon^*(\alpha_1)\delta_{\alpha_1,\delta_1} - 2\sum_{\delta_2,\delta_3}V(\delta_2,\delta_1,\delta_3,\alpha_1)\langle a^\dagger(\delta_2)a(\delta_3)\rangle\}\langle a^\dagger(\delta_1)a^\dagger(\alpha_2)\rangle \\
&-\sum_{\delta_1}\{\varepsilon^*(\alpha_2)\delta_{\alpha_2,\delta_1} - 2\sum_{\delta_2,\delta_3}V(\delta_2,\delta_1,\delta_3,\alpha_1)\langle a^\dagger(\delta_2)a(\delta_3)\rangle\}\langle a^\dagger(\alpha_1)a^\dagger(\delta_1)\rangle \\
&-\sum_{\delta_1,\delta_2}V(\delta_1,\delta_2,\alpha_2,\alpha_1)\langle a^\dagger(\delta_1)a^\dagger(\delta_2)\rangle - (\vec{\mu}_{\alpha_1,\alpha_2}\cdot\vec{E})^* \\
&-\sum_{\delta_1}\{(\vec{\mu}_{\alpha_1,\delta_1}\cdot\vec{E})^* + \sum_{\delta_2,\delta_3}V(\delta_2,\delta_3,\delta_1,\alpha_1)\langle a^\dagger(\delta_2)a^\dagger(\delta_3)\rangle\}\langle a^\dagger(\alpha_2)a(\delta_1)\rangle \\
&-\sum_{\delta_1}\{(\vec{\mu}_{\delta_1,\alpha_2}\cdot\vec{E})^* + \sum_{\delta_2,\delta_3}V(\delta_2,\delta_3,\alpha_2,\delta_1)\langle a^\dagger(\delta_2)a^\dagger(\delta_3)\rangle\}\langle a^\dagger(\alpha_1)a(\delta_1)\rangle \\
&-\sum_{\delta_1,\delta_2,\delta_3}\frac{2V(\delta_1,\delta_2,\delta_3,\alpha_1)}{\omega-\varepsilon(\delta_3)+\varepsilon(\delta_1)+\varepsilon(\delta_2)+\varepsilon(\alpha_2)}\Bigg(\sum_{\delta_{1'},\delta_{2'}}\{V(\delta_{1'},\delta_{2'},\delta_1,\delta_2)\langle a^\dagger(\alpha_2)a^\dagger(\delta_{2'})\rangle \\
&-V(\delta_{1'},\delta_{2'},\delta_1,\alpha_2)\langle a^\dagger(\delta_2)a^\dagger(\delta_{2'})\rangle + V(\delta_{1'},\delta_{2'},\delta_2,\alpha_2)\langle a^\dagger(\delta_1)a^\dagger(\delta_{2'})\rangle\}\langle a^\dagger(\delta_{1'})a(\delta_3)\rangle \\
&-\sum_{\delta_{1'},\delta_{2'},\delta_{3'}}\{V(\delta_{1'},\delta_{2'},\delta_{3'},\delta_2)\langle a^\dagger(\alpha_2)a^\dagger(\delta_{1'})\rangle\langle a^\dagger(\delta_1)a^\dagger(\delta_{2'})\rangle - V(\delta_{1'},\delta_{2'},\delta_{3'},\alpha_2) \\
&\times\langle a^\dagger(\delta_1)a^\dagger(\delta_{2'})\rangle\langle a^\dagger(\delta_2)a^\dagger(\delta_{1'})\rangle - V(\delta_{1'},\delta_{2'},\delta_{3'},\delta_1)\langle a^\dagger(\alpha_2)a^\dagger(\delta_{1'})\rangle\langle a^\dagger(\delta_2)a^\dagger(\delta_{2'})\rangle\} \\
&\times\langle a(\delta_{3'})a(\delta_3)\rangle\Bigg) - \sum_{\delta_1,\delta_2,\delta_3}\{\alpha_1\longleftrightarrow\alpha_2\}. \qquad (13)
\end{aligned}
$$

$\{\alpha_1 \longleftrightarrow \alpha_2\}$ means the indices α_1 and α_2 are interchanged. In order to simplify the expression, we have chosen the kinetic energy eigenstates as the basis states, i.e., $\varepsilon(\alpha_1,\alpha_2) = \varepsilon(\alpha_1)\delta_{\alpha_1,\alpha_2}$. It is remarkable that the first part of Eq. (13) is identical to the HF equation of the interband polarization although the starting points of both methods are quite different. In addition to these HF-like terms, we have scattering terms which contains both an out- and an in-scattering rate. These scattering terms occur as exciton-electron, exciton-hole, or exciton-exciton scattering instead of carrier-carrier scattering in the quantum Boltzmann equation. The real parts of these exciton-carrier scattering terms contribute to an energy renormalization and the imaginary parts result in an induced polarization dephasing, which has been referred to as the excitation induced dephasing (EID). The exciton-exciton scattering (the triple product of the optical polarization) has recently been studied in Ref. 12. To show more concretely how these non-HF scattering terms contribute, we neglect in the following the exciton-exciton scattering and assume for the rest of this paper that the carrier-exciton scattering dominates the intraband coherences.

V. EXCITATION-INDUCED DEPHASING EFFECTS IN FWM MEASUREMENTS

In our previous studies of four-wave-mixing spectroscopy of semiconductors,[10,11] we utilized the excitation-induced dephasing in order to explain the observed polarization and excitation dependence of FWM signals. Equation (13) shows that in the low excitation regime the EID scattering terms might play an equally important role in determining the optical response function as the exchange interaction. As an example for the applications of the general theory discussed in the previous sections, we compute the FWM signal from a strained GaAs sample, in which the hh-lh degeneracy is lifted due to the external strain. This simplification drastically reduces the numerical efforts and keeps most of the physical insight.

We replace the general index α by the momentum and band index, e.g., $\alpha = (b,\vec{k})$, where b refers to $s = \pm 1/2$ for the conduction bands or to $j = \pm 3/2$ for the heavy-hole valence bands. The antisymmetric interaction potential is given by

$$V(b_1\vec{k}_1, b_2\vec{k}_2, b_3\vec{k}_3, b_4\vec{k}_4) = \pm\frac{1}{2}\{v_{|\vec{k}_1-\vec{k}_4|}\delta_{b_1,b_4}\delta_{b_2,b_3} - v_{|\vec{k}_1-\vec{k}_3|}\delta_{b_1,b_3}\delta_{b_2,b_4}\}\delta_{\vec{k}_1+\vec{k}_2,\vec{k}_3+\vec{k}_4}, \tag{14}$$

where the plus sign is used if all four band indices denote either electron or hole bands, and the minus sign indicates the electron-hole interaction, i.e., two band indices are electron indices and two are hole indices. The Coulomb potential v_q has the usual form. In 3D we have

$$v_q = \frac{4\pi e^2}{\varepsilon_0 L^3}\frac{1}{q^2},$$

and in 2D

$$v_q = \frac{2\pi e^2}{\varepsilon_0 L^2}\frac{1}{q}.$$

ε_0 is the background dielectric constant which does not include the contribution from the excited carriers. As usual, we define the optical polarization and carrier densities as

$$\begin{aligned} p^*_{\vec{k}sj} &= \langle a^\dagger_{cs\vec{k}} a^\dagger_{vj-\vec{k}}\rangle, \\ n^e_{\vec{k},s} &= \langle a^\dagger_{cs\vec{k}} a_{cs\vec{k}}\rangle, \\ n^h_{\vec{k},j} &= \langle a^\dagger_{vj-\vec{k}} a_{vs-\vec{k}}\rangle. \end{aligned} \tag{15}$$

Inserting Eqs. (14) and (15) into Eq. (13) and neglecting the exciton-exciton scattering contributions, we obtain the polarization equation in a more familiar form:

$$\begin{aligned} i\frac{d}{dt}p^*_{\vec{k}sj} = &-i\gamma p^*_{\vec{k}sj} - (\varepsilon^e_k + \varepsilon^h_k)p^*_{\vec{k}sj} + \sum_{\vec{k}'} v_{|\vec{k}-\vec{k}'|}p^*_{\vec{k}'sj} + \sum_{\vec{k}'} v_{|\vec{k}-\vec{k}'|}\{(n^e_{\vec{k}'s} + n^h_{\vec{k}'j})p^*_{\vec{k}sj} \\ &-(n^e_{\vec{k},s} + n^h_{\vec{k},j})p^*_{\vec{k}'sj}\} + (\vec{\mu}_{\vec{k}sj}\cdot\vec{E})^* - \sum_{s'}(\vec{\mu}_{\vec{k}s'j}\cdot\vec{E})^* n^e_{\vec{k},s'} - \sum_{j'}(\vec{\mu}_{\vec{k}sj'}\cdot\vec{E})^* n^h_{\vec{k},j'} \\ &- \left(\sum_{s'} N^e_{s'}\right)\sum_{\vec{k}'} W^e(\vec{k},\vec{k}')(p^*_{\vec{k}sj} - p^*_{\vec{k}'sj}) - \left(\sum_{j'} N^h_{j'}\right)\sum_{\vec{k}'} W^h(\vec{k},\vec{k}')(p^*_{\vec{k}sj} - p^*_{\vec{k}'sj}) \\ &+ \sum_{\vec{k}'\vec{k}''}\{U^e_1(\vec{k},\vec{k}',\vec{k}'')n^e_{\vec{k}''s} - U^h_1(\vec{k},\vec{k}',\vec{k}'')n^h_{\vec{k}''j}\}(p^*_{\vec{k}sj} - p^*_{\vec{k}''-\vec{k}'+\vec{k},sj}) \\ &- \sum_{\vec{k}'\vec{k}''}\{U^e_2(\vec{k},\vec{k}',\vec{k}'')n^e_{\vec{k}''s} - U^h_2(\vec{k},\vec{k}',\vec{k}'')n^h_{\vec{k}''j}\}(p^*_{\vec{k}'sj} - p^*_{\vec{k}''+\vec{k}'-\vec{k},sj}), \end{aligned} \tag{16}$$

where $N_i = \sum_{\vec{k}} n_{\vec{k},i}$, is the total carrier density in the band i. Here we have introduced a phenomenological dephasing rate γ to stabilize the following numerical calculations. We have reduced the triple summations in the W terms to double summations by approximating $n_{\vec{k}} \simeq N|\phi_k^{1s}|^2$, where ϕ_k^{1s} is the $1s$-exciton (hydrogenlike) wave function in the momentum representation. This approximation stems from the assumption that if the excitation is in resonance with the ground state exciton, the carrier density follows the square of the ground state exciton wave function when the excitation intensity is sufficiently low. The exciton-carrier scattering matrix elements are

$$W^e(\vec{k},\vec{k}') = v^2_{|\vec{k}-\vec{k}'|} \sum_{\vec{k}_1} \left\{ \frac{1}{\omega - \varepsilon^e_{\vec{k}} - \varepsilon^e_{|\vec{k}_1+\vec{k}'-\vec{k}|} - \varepsilon^h_{\vec{k}'} + \varepsilon^e_{\vec{k}_1} - i\gamma} + \frac{1}{\omega - \varepsilon^e_{\vec{k}'} - \varepsilon^e_{|\vec{k}_1-\vec{k}'+\vec{k}|} - \varepsilon^h_{\vec{k}} + \varepsilon^e_{\vec{k}_1} - i\gamma} \right\} |\phi^{1s}_{k_1}|^2,$$

$$W^h(\vec{k},\vec{k}') = W^e(\vec{k},\vec{k}')|_{e\longleftrightarrow h},$$

$$U^e_1(\vec{k},\vec{k}',\vec{k}'') = \frac{v_{|\vec{k}-\vec{k}'|} v_{|\vec{k}'-\vec{k}''|}}{\omega - \varepsilon^e_{\vec{k}'} - \varepsilon^e_{|\vec{k}''+\vec{k}-\vec{k}'|} - \varepsilon^h_{\vec{k}} + \varepsilon^e_{\vec{k}''} - i\gamma},$$

$$U^e_2(\vec{k},\vec{k}',\vec{k}'') = \frac{v_{|\vec{k}-\vec{k}'|} v_{|\vec{k}-\vec{k}''|}}{\omega - \varepsilon^e_{\vec{k}} - \varepsilon^e_{|\vec{k}''-\vec{k}+\vec{k}'|} - \varepsilon^h_{\vec{k}'} + \varepsilon^e_{\vec{k}''} - i\gamma},$$

$$U^h_1(\vec{k},\vec{k}',\vec{k}'') = U^e_1(\vec{k},\vec{k}',\vec{k}'')|_{e\longleftrightarrow h}, \qquad U^h_2(\vec{k},\vec{k}',\vec{k}'') = U^e_2(\vec{k},\vec{k}',\vec{k}'')|_{e\longleftrightarrow h}. \tag{17}$$

As in the quantum Boltzmann equation, the exciton-carrier scattering terms in Eq. (16) are proportional to v_q^2. However, it should be emphasized here that v_q is the unscreened Coulomb potential. The divergence of the square of the three-dimensional Coulomb potential ($\propto 1/q^4$) is removed by the factor $p_{\vec{k}} - p_{\vec{k}+\vec{q}}$, the angular integral of which approaches zero as q^2. These cancellations may indicate the validity of the susceptibility expansion in this many-body Coulomb system.

Eq. (16) also shows that the exciton-carrier scattering effectively couples the σ_+ and σ_- transitions, which would be completely independent within the HF factorization. In the coherent excitation regime, where $N_{\sigma_+} = N_{h,3/2} = N_{e,-1/2}$ and $N_{\sigma_-} = N_{h,-3/2} = N_{e,1/2}$, the terms proportional to W in Eq. (16) can approximately be expressed in a form of $\delta[N_{\sigma_+} + N_{\sigma_-}]p_{\sigma_+,\vec{k}}$, where δ is the complex excitation induced dephasing coefficient.[11] Hence σ_- excitations significantly influence σ_+ transitions and vice versa. This kind of effective band coupling induced by many-body interactions remarkably modifies the polarization selection rules of four-wave-mixing spectroscopy in semiconductors, resulting in carrier density dependent polarization selection rules.[10,11] A detailed discussion of the carrier density dependence of polarization selection rules formally requires a $\chi^{(5)}$ treatment which is beyond the scope of this paper. The exchange exciton-carrier-scattering terms (U-scattering terms) are less important in determining the $\chi^{(3)}$ properties of semiconductors because the matrix elements contain the product of $v_q v_{q'}$ which are small in the case of small momentum transfer q. Furthermore, these off-diagonal scattering matrix elements do not couple the different optical transitions (here, the σ_+ and σ_- transitions) and, therefore, contribute to the polarization selection rules in a similar manner as the HF exchange terms. In the following calculations, these terms are neglected for numerical simplicity.

In a standard two pulse FWM setup, two pulses propagate at a small angle in the directions $\vec{K}_1$ and $\vec{K}_2$, respectively. The $\chi^{(3)}$ nonlinearities give rise to an induced optical signal in the direction of $2\vec{K}_1 - \vec{K}_2$. Many-body exchange effects in FWM of semiconductors have been studied using the semiconductor Bloch equation.[9,18] We follow the same numerical technique of Ref. 9. In order to compute the measured far field signal, we first perform the spatial Fourier transform of the polarization equation, Eq. (16), and the density equation, Eq. (9). Second, we use a fourth order Runge-Kutta method to integrate these differential equations. The Coulomb potential matrix elements are computed using a Gaussian quadrature method. In Fig. 2, we show the computed time-

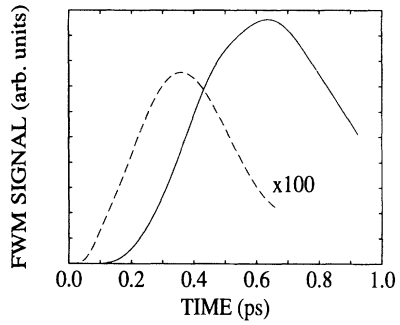

FIG. 2. Computed four-wave-mixing signal, $I_{\|}$ (solid) and $I_{\perp}$ (dashed) from the heavy-hole exciton in a strained GaAs sample. $m_e/m_0 = 0.067$, where m_0 is the free electron mass. The Luttinger parameters are $\gamma_1 = 6.9, \gamma_2 = 2.1, \gamma_3 = 2.9$, the background dielectric constant $\varepsilon_0 = 12.5$. The probe and pump field strengths are, $\mu_{cv}E = 0.01, 0.001E_R$, respectively ($\mu_{cv}$ is the dipole matrix elements). The time delay is 100 fs. The dephasing time is $1/\gamma = 300$ fs. The dashed line is multiplied by a factor of 100.

resolved FWM signals induced by cross-polarized pulses and copolarized pulses. The material parameters are chosen for the heavy-hole band in a strained GaAs sample, i.e., $m_e/m_0 = 0.067$, where m_0 is the free electron mass, the Luttinger parameters are $\gamma_1 = 6.9, \gamma_2 = 2.1, \gamma_3 = 2.9$, the background dielectric constant $\varepsilon_0 = 12.5$. Both pump and probe pulses have a temporal width of 100 fs (full width at half maximum in amplitude) and field amplitudes of $\mu_{cv}E = 0.01, 0.001E_R$, respectively. E_R is the exciton binding energy. The excitation frequency is chosen to be in resonance with the lowest hh exciton state. The time delay is 300 fs (the probe precedes the pump by 300 fs). The dephasing time is chosen as $1/\gamma = 300$ fs. $I_{\|}$ is plotted as solid curves and $I_{\perp}$ is as dashed curves. For comparison, the dashed curve is multiplied by a factor of 10^2.

The numerical solutions of the $\chi^{(3)}$ semiconductor Bloch equations show that the ratio of FWM signals $I_{\|}/I_{\perp}$ drastically increases as the dephasing rate decreases. In the case where the laser fields are extremely low, $I_{\|}/I_{\perp}$ is of an order of 10^2 or higher. Our $\chi^{(3)}$ treatment cannot be applied to study the excitation intensity dependence of the ratio $I_{\|}/I_{\perp}$. However, qualitatively we can predict that, as the pump intensity increases, the increasing carrier density effectively reduces the Coulomb interaction. Screening of Coulomb interaction has a more significant influence on EID terms than on the direct and exchange Coulomb interaction matrix elements since the EID terms are proportional to $|v_q|^2$ while the direct and exchange Coulomb interaction matrix elements are proportional to $|v_q|$. Consequently, as the carrier density increases the exciton-carrier scattering induced effective band coupling decreases more quickly than the renormalization of the Rabi frequency and of the band gap. Theoretically these effects can be studied by solving the equations corresponding to the order of E^5. When the system is doped or optically preexcited, we need to modify our equations according to the discussion in Sec. III.

VI. SUMMARY

In this paper, we present a $\chi^{(3)}$ analysis of coherently excited semiconductors. A theoretical approach to solve the many-body problem in coherently driven semiconductors is discussed in detail and applied to four-wave-mixing spectroscopy of semiconductors. This expansion approach avoids the difficult problem of modeling screening and carrier-carrier scattering in the cases when the carrier densities are far below the Mott density. When the interband polarization and the densities are solely created by the external field, the infinite hierarchy of equations of motion can be truncated according to the powers of the external field. This decoupling scheme stems from the fact that the Coulomb interaction only couples a given correlation function to higher order correlations, not to lower order correlations. Therefore, a finite set of equations can be obtained, which, if solved, provide accurate information about the $\chi^{(3)}$ response in semiconductors. Neglecting the biexciton contribution enables us to generalize the well-studied semiconductor Bloch equations into the low density region. Comparison of the $\chi^{(3)}$ semiconductor Bloch equations with the HF equations yields information about the validity of the HF factorization below the Mott density. The HF factorization gives the leading contribution to the four-operator correlations in terms of the external field in most of the cases. However, in the low excitation regime the exciton-carrier scattering, which is neglected in the HF approach, may be as important to the $\chi^{(3)}$ as the exchange and direct Coulomb interaction. The excitation-induced dephasing effects are derived from first principles as a consequence of the exciton-carrier scattering in the low density regime where the $\chi^{(3)}$ analysis is valid. We also integrate numerically the generalized semiconductor Bloch equations to study the FWM spectroscopy. The excitation induced dephasing effects show remarkable signatures in the nonlinear spectroscopy. In this paper, we limit ourselves to the $\chi^{(3)}$ regime, however, the principle discussed in this paper can be extented into higher order expansions, which may provide new insight into the dynamics of exciton screening, carrier-carrier scattering, and other collective properties of optically excited semiconductors.

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APPENDIX A: DYNAMICAL ORDER OF $\langle\{N, M\}\rangle$ AND ITS FACTORIZATION

A central point of the truncation scheme of the infinite hierarchy of equations discussed in this paper is the well-defined minimum order, in powers of the external field, of each set of operators denoted by $\{N, M\}$. In this Appendix, we show that the order of magnitude of the expectation values, is a direct consequence of the dipole interaction between the field and the semiconductor in an initial state in which no carriers are preexcited or doped. The Coulomb interaction does not change the total number of the carriers and, hence, does not play an active role in determining the order of each operator product. To see this, we write the Hamiltonian in three parts,

$$H = H_0 + V_+ + V_-,$$

where

$$H_0 = \sum_{\alpha_1,\alpha_2} \varepsilon(\alpha_1,\alpha_2) a^\dagger(\alpha_1) a(\alpha_2) + \frac{1}{2} \sum_{\alpha_1,\alpha_2,\alpha_3,\alpha_4} V(\alpha_1,\alpha_2,\alpha_3,\alpha_4) \times a^\dagger(\alpha_1) a^\dagger(\alpha_2) a(\alpha_3) a(\alpha_4),$$

$$V_+ = \frac{1}{2}\sum_{\alpha_1,\alpha_2}(\vec{\mu}_{\alpha_1,\alpha_2}\cdot\vec{E})a^\dagger(\alpha_1)a^\dagger(\alpha_2), \quad V_- = V_+^*.$$

The total carrier number operator N_c commutes with H_0 and its commutators with $V_\pm$ are given by

$$[N_c, V_\pm] = \pm 2V_\pm.$$

These commutators reflect the fact that V_+ creates two carriers when operating on a given state and V_- annihilates two carriers. The commutator of N_c with the operator product $\{N,M\}$ $[N_c,\{N,M\}] = (N-M)\{N,M\}$, meaning that the operator $\{N,M\}$ always creates or annihilates $|N-M|$ carriers.

In the interaction picture, a time dependent operator A_I is defined as

$$A_I(t) = e^{iH_0t}Ae^{-iH_0t},$$

where A is the Schrödinger picture operator. In this appendix, the operators are in the Schrödinger picture unless explicitly denoted by a subscript "I" or "H" for the interaction or Heisenberg picture, respectively. The wave functions have the correspondence

$$|\Psi_I(t)\rangle = U_I(t)|\Psi_H\rangle,$$

where $U_I(t)$ is the solution of the differential equation

$$i\frac{\partial}{\partial t}U_I(t) = H_I(t)U_I(t), \qquad U_I(0) = 1.$$

H_I is the operator $V_+ + V_-$ in the interaction picture similarly to $A_I(t)$. The equation for $U_I(t)$ has a formal solution of the form

$$U_I(t) = \sum_{k=0}^{\infty}U_{Ik}(t) = 1 + \sum_{k=1}^{\infty}\left\{-i\int_0^t dt' H_I(t')U_{I(k-1)}(t')\right\},$$

with an additional condition $U_{I0}(t) = 1$. Because H_I is of the order of E, we have $U_{Ik} = O(E^k)$. Now any expectation value of the operator $\{N,M\}$ is given in the form

$$\langle\{N,M\}\rangle = \sum_{k=0}^{\infty}\sum_{m=0}^{k}\langle\Psi|U^\dagger_{I(k-m)}(t)\{N,M\}_I U_{Ik}(t)|\Psi\rangle \equiv \sum_{k=0}^{\infty}\{N,M\}_k(t).$$

Obviously the order of magnitude of the operator $\{N,M\}_k$ is E^k. The remaining question is, therefore, to determine the smallest value of k for which the expectation value of $\{N,M\}_k$ is not zero.

The operator U_{Ik} can be expressed as a linear combination of operators annihilating or creating different numbers of carriers. However, the maximum number of carriers created or annihilated is $2k$. Hence, we can write

$$U_{Ik}(t) \equiv \sum_{m=-k}^{k}U^k_{2m}(t),$$

where the operator U^k_{2m} creates $2m$ carriers into a certain state if $m > 0$ and annihilates $2|m|$ carriers if $m < 0$. Note that the all operators U^k_{2m} are of the order of E^k. When U^k_{2m} operates on the ground state, in which there are no carriers, all the annihilation terms vanish and we have

$$U_{Ik}(t)|0\rangle = \sum_{m=0}^{k}U^k_{2m}(t)|0\rangle. \tag{A1}$$

Since the operator $\{N,M\}$ is normally ordered, we can use its annihilation operators to obtain

$$\{N,M\}(t)U_{Ik}(t)|0\rangle = 0$$

if $M > 2k$. Similarly, we can also find that the expectation value

$$\langle 0|U^\dagger_{I(k-m)}(t)\{N,M\}_I(t)U_{Im}(t)|0\rangle = 0$$

if $M > 2m$ or $N > 2k - 2m$. It is also obvious that $N - M$ must be even. With these considerations, we conclude that the smallest possible value of k must satisfy

$$2m \geq M, \qquad 2k - 2m \geq N.$$

Therefore the smallest k, which is also the order of magnitude of the expectation value $\langle\{N,M\}\rangle$, satisfies $k \geq (N+M)/2$, which is the desired result.

We choose the Heisenberg picture to study factorization of the expectation values in the minimum order. Hence, we can write

$$\langle a^\dagger(\alpha_N)a^\dagger(\alpha_{N-1})\cdots a^\dagger(\alpha_1)a(\beta_1)\cdots a(\beta_M)\rangle = \langle 0|a^\dagger_H(\alpha_N,t)a^\dagger_H(\alpha_{N-1},t)\cdots a^\dagger_H(\alpha_1,t)a_H(\beta_1,t)\cdots a_H(\beta_M,t)|0\rangle, \tag{A2}$$

where $|0\rangle$ is the vacuum state and $a^\dagger_H$ are the creation operator in the Heisenberg picture. Inserting the identity operator in the interaction picture into the expectation value (A2), we obtain

$$\langle 0|a_H^\dagger(\alpha_N,t)a_H^\dagger(\alpha_{N-1},t)\cdots a_H^\dagger(\alpha_1,t)a_H(\beta_1,t)\cdots a_H(\beta_M,t)|0\rangle$$

$$\begin{aligned}
&= \langle 0|a_H^\dagger(\alpha_N,t)a_H^\dagger(\alpha_{N-1},t)\cdots a_H^\dagger(\alpha_1,t)|0\rangle\langle 0|a_H(\beta_1,t)\cdots a_H(\beta_M,t)|0\rangle \\
&\quad + \sum_{\delta_1}\langle 0|a_H^\dagger(\alpha_N,t)a_H^\dagger(\alpha_{N-1},t)\cdots a_H^\dagger(\alpha_1,t)a_I^\dagger(\delta_1,t)|0\rangle\langle 0|a_I(\delta_1,t)a_H(\beta_1,t)\cdots a_H(\beta_M,t)|0\rangle \\
&\quad + \frac{1}{2}\sum_{\delta_1,\delta_2}\langle 0|a_H^\dagger(\alpha_N,t)a_H^\dagger(\alpha_{N-1},t)\cdots a_H^\dagger(\alpha_1,t)a_I^\dagger(\delta_2,t)a_I^\dagger(\delta_1,t)|0\rangle \\
&\quad \times\langle 0|a_I(\delta_1,t)a_I(\delta_2,t)a_H(\beta_1,t)\cdots a_H(\beta_M,t)|0\rangle + \cdots . \qquad \text{(A3)}
\end{aligned}$$

The interaction picture is used for the identity operator because the vacuum state is an eigenstate of the interaction picture operators but not of the Heisenberg operators. Consequently the unity cannot be written in the same form in terms of the Heisenberg operators. In the following we show that if both N and M are even the first term in Eq. (A3) is the factorized contribution and the rest of the expansion is of higher order in E. If N and M are both odd the first term is zero and the second term is the factorized contribution and has the lowest order in terms of E. This conclusion follows from the fact that H_0 conserves the total number of particles. It can be expressed as

$$[N_c, a_I(\alpha,t)] = -a_I(\alpha,t).$$

However, the same relation is not valid if $a_I(\alpha,t)$ is replaced by the Heisenberg operator, α_H. The connection between the Heisenberg operators and the interaction operators is

$$a_H(\alpha,t) = U_I^\dagger(t)a_I(\alpha,t)U_I(t).$$

Using the expansion of $U_I(t)$ in Eq. (A1), we see immediately that

$$a_H(\alpha,t) = \sum_{n=-\infty}^{\infty} A_{H,2n-1}(\alpha,t),$$

where $A_{H,2n-1}(\alpha,t)$ creates $2n-1$ carriers if $2n-1 \geq 0$ or annihilates $|2n-1|$ carriers if $2n-1 \leq 0$ and it is of the order $O(E^{|n|})$ or higher. This fact immediately gives that

$$\langle 0|a_I(\delta_1)\cdots a_I(\delta_{2p})a_H(\beta_1)\cdots a_H(\beta_{2M})|0\rangle = O(E^{M+p}), \qquad \text{(A4)}$$

and

$$\langle 0|a_I(\delta_1,t_1')\cdots a_I(\delta_{2p-1},t_{2p-1}')a_H(\beta_1,t_1)\cdots a_H(\beta_{2M+1},t_{2M+1})|0\rangle = O(E^{M+p}). \qquad \text{(A5)}$$

When we insert Eq. (A4) into Eq. (A3), we immediately obtain that

$$\begin{aligned}
&\langle 0|a_H^\dagger(\alpha_{2N},t)\cdots a_H^\dagger(\alpha_1,t)a_H(\beta_1,t)\cdots a_H(\beta_{2M},t)|0\rangle \\
&\qquad = \langle 0|a_H^\dagger(\alpha_{2N},t)\cdots a_H^\dagger(\alpha_1,t)|0\rangle\langle 0|a_H(\beta_1,t)\cdots a_H(\beta_{2M},t)|0\rangle + O(E^{N+M+2}) \qquad \text{(A6)}
\end{aligned}$$

as given in Eq. (6). In the case with an odd number of creation and annihilation operators the first term in Eq. (A3) vanishes and the second term contains interaction picture operators. Hence, the first nonzero term is not directly an expectation value. However, we have that

$$\langle 0|a_H(\delta_1,t_1')a_H(\beta_1,t_1)\cdots a_H(\beta_{2M+1},t_{2M+1})|0\rangle = \langle 0|a_I(\delta_1,t_1')a_H(\beta_1,t_1)\cdots a_H(\beta_{2M+1},t_{2M+1})|0\rangle + O(E^{M+3}),$$

because $A_{H,-1}(\alpha,t) = a_I(\alpha,t) + O(E^2)$. So we obtain the second factorization result

$$\begin{aligned}
&\langle 0|a_H^\dagger(\alpha_{2N+1},t)\cdots a_H^\dagger(\alpha_1,t)a_H(\beta_1,t)\cdots a_H(\beta_{2M+1},t)|0\rangle \\
&\qquad = \sum_{\delta_1}\langle 0|a_H^\dagger(\alpha_{2N+1},t)\cdots a_H^\dagger(\alpha_1,t)a_H^\dagger(\delta_1,t)|0\rangle\langle 0|a_H(\delta_1,t)a_H(\beta_1,t)\cdots a_H(\beta_{2M+1},t)|0\rangle + O(E^{N+M+4}), \qquad \text{(A7)}
\end{aligned}$$

as stated in Eqs. (6,7). We have simultaneously again shown that

$$\begin{aligned}
&\langle a^\dagger(\alpha_{2N})\cdots a^\dagger(\alpha_1)a(\beta_1)\cdots a(\beta_{2M})\rangle = O(E^{N+M}), \\
&\langle a^\dagger(\alpha_{2N+1})\cdots a^\dagger(\alpha_1)a(\beta_1)\cdots a(\beta_{2M+1})\rangle = O(E^{N+M+2}).
\end{aligned}$$

APPENDIX B: COMPLETE AND CLOSED $\chi^{(3)}$ EQUATIONS IN A MULTIBAND SEMICONDUCTOR

As shown in Sec. III, it is possible to truncate the infinite hierarchy of equations of motion into a formally finite and closed set according to the powers of the external field. In this appendix, we write down the missing equations for a multiband semiconductor. Equations (8) and (10) give the general equations for $\langle a^\dagger(\alpha_1)a^\dagger(\alpha_2)\rangle$ and $\langle a^\dagger(\alpha_1)a(\alpha_2)\rangle$ in $\chi^{(3)}$. In a two band semiconductor, the equations are simplified slightly because we can explicitly use conservation laws. In the Hamiltonian (1) we denote the index $\alpha = (b, \vec{k})$, where the band index takes the values ± 1, $+1$ denoting the electrons and -1 the holes. $\vec{k}$ is the momentum vector. Therefore, we have $\vec{\mu}_{+1,-1} = \vec{\mu}_{cv}$, $\vec{\mu}_{-1,+1} = -\vec{\mu}_{cv}$, and $\vec{\mu}_{\alpha_1,\alpha_2} = 0$ else. Also, we have $V(\alpha_1,\alpha_2,\alpha_3,\alpha_4) \neq 0$ only if $\alpha_1 + \alpha_2 = \alpha_3 + \alpha_4$. For the two band model, we obtain

$$\begin{aligned} i\frac{\partial}{\partial t}\langle a^\dagger(\alpha)a^\dagger(-\alpha)\rangle = &-\varepsilon_x(\alpha)\langle a^\dagger(\alpha)a^\dagger(-\alpha)\rangle - \sum_\delta V(\delta,-\delta,-\alpha,\alpha)\langle a^\dagger(\delta)a^\dagger(-\delta)\rangle \\ &+ \sum_{\delta_1,\delta_2,\delta_3}\{V(\delta_1,\delta_2,\delta_3,\alpha)\langle a^\dagger(\delta_1)a^\dagger(\delta_2)a^\dagger(-\alpha)a(\delta_3)\rangle \\ &-V(\delta_1,\delta_2,\delta_3,-\alpha)\langle a^\dagger(\alpha)a^\dagger(\delta_1)a^\dagger(\delta_2)a(\delta_3)\rangle\} \\ &-(\vec{\mu}_{\alpha,-\alpha}\cdot\vec{E})(1-\langle a^\dagger(\alpha)a(\alpha)\rangle - \langle a^\dagger(-\alpha)a(-\alpha)\rangle), \end{aligned} \tag{B1}$$

where $\varepsilon_x(\alpha) = \varepsilon(\alpha) + \varepsilon(-\alpha)$ is the kinetic energy of the exciton, and

$$\begin{aligned} i\frac{\partial}{\partial t}\langle a^\dagger(\alpha)a(\alpha)\rangle = &-\left\{(\vec{\mu}_{\alpha,-\alpha}\cdot\vec{E})^* + \sum_\delta V(\delta,-\delta,-\alpha,\alpha)\langle a^\dagger(\delta)a^\dagger(-\delta)\rangle\right\}\langle a(-\alpha)a(\alpha)\rangle \\ &+\left\{(\vec{\mu}_{\alpha,-\alpha}\cdot\vec{E}) + \sum_\delta V(\alpha,-\alpha,-\delta,\delta)\langle a(-\delta)a(\delta)\rangle\right\}\langle a^\dagger(\alpha)a^\dagger(-\alpha)\rangle + O(E^4). \end{aligned} \tag{B2}$$

The equation of motion for carrier density equals that of the Bloch equations. In the same way, one can derive the equation of motion for the exciton-carrier scattering amplitudes, $\langle a^\dagger(\alpha_1)a^\dagger(\delta_1)a^\dagger(\delta_2)a(\delta_3)\rangle$. In the equation of motion for $\langle a^\dagger(\alpha_1)a^\dagger(\delta_1)a^\dagger(\delta_2)a(\delta_3)\rangle$, the only relevant six operator expectation values factorize again exactly in third order, i.e.,

$$\langle a^\dagger(\alpha_4)a^\dagger(\alpha_3)a^\dagger(\alpha_2)a^\dagger(\alpha_1)a(\beta_1)a(\beta_2)\rangle = \langle a^\dagger(\alpha_4)a^\dagger(\alpha_3)a^\dagger(\alpha_2)a^\dagger(\alpha_1)\rangle\langle a(\beta_1)a(\beta_2)\rangle + O(E^5).$$

Consequently, for a full $\chi^{(3)}$ description, we need the equations for the biexciton amplitude, $\langle a^\dagger(\alpha_4)a^\dagger(\delta_3)a^\dagger(\delta_2)a^\dagger(\delta_1)\rangle$ and for the exciton-carrier scattering amplitude, $\langle a^\dagger(\alpha_1)a^\dagger(\alpha_2)a^\dagger(\alpha_3)a(\beta)\rangle$. These equations are given by

$$\begin{aligned} i\frac{\partial}{\partial t}\langle a^\dagger(\alpha_4)a^\dagger(\alpha_3)a^\dagger(\alpha_2)a^\dagger(\alpha_1)\rangle = &-[\varepsilon(\alpha_1)+\varepsilon(\alpha_2)+\varepsilon(\alpha_3)+\varepsilon(\alpha_4)]\langle a^\dagger(\alpha_4)a^\dagger(\alpha_3)a^\dagger(\alpha_2)a^\dagger(\alpha_1)\rangle \\ &+\sum_{\delta_1,\delta_2}\{V(\delta_1,\delta_2,\alpha_4,\alpha_3)\langle a^\dagger(\delta_1)a^\dagger(\delta_2)a^\dagger(\alpha_2)a^\dagger(\alpha_1)\rangle \\ &-V(\delta_1,\delta_2,\alpha_4,\alpha_2)\langle a^\dagger(\delta_1)a^\dagger(\delta_2)a^\dagger(\alpha_3)a^\dagger(\alpha_1)\rangle + V(\delta_1,\delta_2,\alpha_4,\alpha_1) \\ &\times\langle a^\dagger(\delta_1)a^\dagger(\delta_2)a^\dagger(\alpha_3)a^\dagger(\alpha_2)\rangle - V(\delta_1,\delta_2,\alpha_3,\alpha_2)\langle a^\dagger(\delta_1)a^\dagger(\delta_2)a^\dagger(\alpha_4)a^\dagger(\alpha_1)\rangle \\ &-V(\delta_1,\delta_2,\alpha_3,\alpha_1)\langle a^\dagger(\delta_1)a^\dagger(\delta_2)a^\dagger(\alpha_4)a^\dagger(\alpha_2)\rangle \\ &+V(\delta_1,\delta_2,\alpha_2,\alpha_1)\langle a^\dagger(\delta_1)a^\dagger(\delta_2)a^\dagger(\alpha_4)a^\dagger(\alpha_3)\rangle\} \\ &-(\vec{\mu}_{\alpha_4,\alpha_3}\cdot\vec{E})^*\langle a^\dagger(\alpha_2)a^\dagger(\alpha_1)\rangle - (\vec{\mu}_{\alpha_2,\alpha_1}\cdot\vec{E})^*\langle a^\dagger(\alpha_4)a^\dagger(\alpha_3)\rangle \\ &+(\vec{\mu}_{\alpha_4,\alpha_2}\cdot\vec{E})^*\langle a^\dagger(\alpha_3)a^\dagger(\alpha_1)\rangle + (\vec{\mu}_{\alpha_3,\alpha_1}\cdot\vec{E})^*\langle a^\dagger(\alpha_4)a^\dagger(\alpha_2)\rangle \\ &-(\vec{\mu}_{\alpha_4,\alpha_1}\cdot\vec{E})^*\langle a^\dagger(\alpha_3)a^\dagger(\alpha_2)\rangle - \vec{E})^*\langle a^\dagger(\alpha_4)a^\dagger(\alpha_1)\rangle + O(E^4), \end{aligned} \tag{B3}$$

and

$$
\begin{aligned}
i\frac{\partial}{\partial t}\langle a^\dagger(\alpha_3)a^\dagger(\alpha_2)a^\dagger(\alpha_1)a(\beta)\rangle = & -[\varepsilon(\alpha_1)+\varepsilon(\alpha_2)+\varepsilon(\alpha_3)-\varepsilon(\beta)]\langle a^\dagger(\alpha_3)a^\dagger(\alpha_2)a(\alpha_1)a(\beta)\rangle \\
& + \sum_{\delta_1,\delta_2}\{V(\delta_1\delta_2\alpha_3\alpha_2)\langle a^\dagger(\delta_1)a^\dagger(\delta_2)a^\dagger(\alpha_1)a(\beta)\rangle \\
& -V(\delta_1\delta_2\alpha_3\alpha_1)\langle a^\dagger(\delta_1)a^\dagger(\delta_2)a^\dagger(\alpha_2)a(\beta)\rangle + V(\delta_1\delta_2\alpha_2\alpha_1)\langle a^\dagger(\delta_1)a^\dagger(\delta_2)a^\dagger(\alpha_3)a(\beta)\rangle\} \\
& + \sum_{\delta_1,\delta_2,\delta_3}\{V(\delta_1\delta_2\delta_3\alpha_2)\langle a^\dagger(\delta_1)a^\dagger(\delta_2)a^\dagger(\alpha_3)a^\dagger(\alpha_1)\rangle \\
& -V(\delta_1\delta_2\delta_3\alpha_1)\langle a^\dagger(\delta_1)a^\dagger(\delta_2)a^\dagger(\alpha_3)a^\dagger(\alpha_2)\rangle \\
& -V(\delta_1\delta_2\delta_3\alpha_3)\langle a^\dagger(\delta_1)a^\dagger(\delta_2)a^\dagger(\alpha_2)a^\dagger(\alpha_1)\rangle\}\langle a(\delta_3)a(\beta)\rangle\} \\
& - \sum_{\delta_1}\{\vec{\mu}_{\beta,\delta_1}\cdot\vec{E}+\sum_{\delta_2,\delta_3}V(\beta\delta_1\delta_2\delta_3)\langle a(\delta_2)a(\delta_3)\rangle\}\langle a^\dagger(\delta_1)a^\dagger(\alpha_3)a^\dagger(\alpha_2)a^\dagger(\alpha_1)\rangle \\
& - \sum_{\delta_1}\{(\vec{\mu}_{\alpha_3,\delta_1}\cdot\vec{E})^*\langle a^\dagger(\alpha_2)a^\dagger(\alpha_1)\rangle - (\vec{\mu}_{\alpha_2,\delta_1}\cdot\vec{E})^*\langle a^\dagger(\alpha_3)a^\dagger(\alpha_1)\rangle \\
& +(\vec{\mu}_{\alpha_1,\delta_1}\cdot\vec{E})^*\langle a^\dagger(\alpha_3)a^\dagger(\alpha_2)\rangle\}\langle a(\delta_1)a(\beta)\rangle \\
& -(\vec{\mu}_{\alpha_3,\alpha_2}\cdot\vec{E})^*\langle a^\dagger(\alpha_1)a(\beta)\rangle + (\vec{\mu}_{\alpha_3,\alpha_1}\cdot\vec{E})^*\langle a^\dagger(\alpha_2)a(\beta)\rangle \\
& +(\vec{\mu}_{\alpha_2,\alpha_1}\cdot\vec{E})^*\langle a^\dagger(\alpha_3)a(\beta)\rangle + O(E^5). \qquad \text{(B4)}
\end{aligned}
$$

In these equations we have assumed the kinetic energy to be diagonal in the chosen basis just to get shorter equations. If the kinetic energy is not diagonal, we need only to do substitutions like

$$
\varepsilon(\alpha_1)\langle a^\dagger(\alpha_3)a^\dagger(\alpha_2)a(\alpha_1)a(\beta)\rangle \rightarrow \sum_{\delta_1}\varepsilon(\alpha_1,\delta_1)\langle a^\dagger(\alpha_3)a^\dagger(\alpha_2)a(\delta_1)a(\beta)\rangle .
$$

Equations (8), (10), (B3), and (B4) form a finite and closed set of equations which when solved give the polarization in third order in the external field. However, solving these equations is a numerically formidable problem since one has to solve the full quantum mechanical three-body and four-body problems which give the homogeneous parts of the equations of motion.

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