Third-order optical response of intermediate excitons with fractional nonlinear statistics

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Received August 28, 1995; revised manuscript received November 28, 1995

The interplay of exciton statistics and Coulomb interactions in the optical response of semiconductors is studied by derivation of an effective Hamiltonian written in terms of exciton operators, starting with a two-band model. Statistical effects are incorporated through the nonboson commutation relations of exciton operators, which contain an exciton-size-dependent parameter q that may vary from $q = 0$ (boson statistics) through $q \ll 1$ (Wannier excitons) to $q = 2$ (Frenkel excitons or Pauli statistics). A unified Green's function expression for $\chi^{(3)}$ that applies to excitons of an arbitrary nature is derived. © 1996 Optical Society of America

1. INTRODUCTION

The nonlinear optical response of confined excitons poses some important fundamental as well as practical problems connected with the synthesis of new materials with large susceptibilities. Excitons of different types have been studied, e.g., Wannier excitons in semiconductors,[1] confined Wannier-type excitons in semiconductor quantum wells and quantum dots,[2–4] Frenkel excitons in molecular crystals and nanostructures,[5–8] and charge-transfer excitons in crystals and conjugated polymers.[9–11] The optical response of large molecules is determined by collective rather than individual properties of the global eigenstates.[12] In such situations the oscillator (quasi-particle) picture of the excitonic optical response[8,12,13] based on the many-body Green's-function approach[14] seems much more attractive than the picture based on the global eigenstates.[15] In the oscillator picture the nonlinear response originates from two sources: exciton–exciton scattering,[16] which is due to the Coulomb interaction (dynamical scattering) between excitons, and the nonboson exciton statistics (kinematic scattering, also known as phase-space filling[2]). The oscillator picture of the optical response permits a clear separation of these two sources of nonlinearity. It has been rigorously established[13,17] within the time-dependent Hartree–Fock approximation[18,19] for a general many-electron system (the widely used semiconductor Bloch–Maxwell equations[1–3] are also based on the time-dependent Hartree–Fock procedure).

The separation of these two sources of nonlinearity can be made without alluding to the time-dependent Hartree–Fock approximation. One way is to use a boson representation for electron–hole operators. A boson representation of the Frenkel exciton Hamiltonian has been developed in Ref. 20. Boson representations for electron–hole operators have been introduced in Refs. 21 and 22 and subsequently have been applied to semiconductor systems by many authors. In this approach, effects of statistics on optical nonlinearities are represented by nonlinear terms in the expansions of the observables (polarization operators) in powers of boson operators. An alternative approach is to use a representation in which the observables are linear combinations of the basic variables (operators). This approach has been applied to Frenkel exciton systems in Ref. 23 and more recently has been applied to semiconductor systems.[24] The off-resonant third-order response in semiconductors has been considered in Ref. 25.

In this paper we use this second approach to develop a unified theory of nonlinear optical response of Frenkel, Wannier, and charge-transfer exciton systems. Our formulation yields equations of motion for the observables, as well as compact expressions for susceptibilities. Effects of statistics are incorporated in commutation relations of the basic operators. This method allows us to pinpoint the effects of statistics in optical nonlinearities of excitonic systems.

In semiconductorlike materials (including bulk, quantum wells, and quantum dots) and in Frenkel exciton systems (e.g., molecular crystals, aggregates, and organic superlattices), the residual Coulomb interaction is typically much smaller than the optical gap; consequently we can neglect processes that do not conserve the number of electron–hole pairs. This provides a justification for the common approximations known as the two-band model in the theory of semiconductors[1,2] and the Heitler–London approximation for Frenkel excitons.[5,19] Within the two-band approximation, the number of electron–hole pairs is conserved, which turns the calculation of the optical response into a finite-body problem; the ground state is the vacuum state with zero electron–hole pairs, the linear response involves states with one electron–hole pair, the third-order nonlinear response involves only states with up to two electron–hole pairs, etc. However, to obtain the third-order susceptibility even within the two-band model, we need to solve a four-body (two-electron, two-hole) problem that cannot be solved exactly, and further approximations are usually made.

In this paper we recast the two-band Hamiltonian in terms of creation and annihilation operators for electron–hole pairs. Because the material Hamiltonian conserves the number of pairs, the resulting physical picture is based on the dynamics of such pairs (rather

0740-3224/96/061302-06$06.00

than on individual electrons and holes). We therefore refer to an electron–hole pair as a particle. We then derive the commutation relations of the particle operators that show their nonboson statistics, and we express the Hamiltonian in terms of them. Applying the equation of motion technique,[8,19] we obtain exact expressions for the third-order optical response in terms of the one-particle Green's function and the two-particle scattering matrix, which in turn is also expressed in terms of the single-particle Green's function. The resulting Green's-function expression (GFE) derived in Section 2 generalizes our earlier result, which was restricted to Frenkel exciton systems.[12,26] The GFE provides a unified description of optical response for all types of excitons: Frenkel, Wannier, and intermediate charge transfer. Moreover, the GPE explicitly reproduces the structure of two-photon resonances on two-exciton states in the third-order optical response, which is completely missed in the Bloch–Maxwell or in local-field approximation schemes. In Section 3 we project all the particle operators into a subspace of exciton operators and derive new commutation relations that contain effects of statistics; we also derive an effective Hamiltonian containing Coulomb interactions by means of anharmonicities. Simplified expressions for the third-order response that allow us to distinguish between the roles of statistical and dynamical interactions of excitons are derived, and limiting cases of various types of excitons are discussed.

2. NONLINEAR RESPONSE OF THE TWO-BAND MODEL

We consider a semiconductor described by the two-band Hamiltonian[1–3]

$$\begin{aligned}\widehat{H} = &\sum_{m_1 n_1} t^{(1)}_{m_1 n_1} \hat{a}^+_{m_1} \hat{a}_{n_1} + \sum_{m_2 n_2} t^{(2)}_{m_2 n_2} \hat{b}^+_{m_2} \hat{b}_{n_2} \\ &+ \frac{1}{2} \sum_{m_1 n_1 k_1 l_1} V^{(1)}_{m_1 n_1 k_1 l_1} \hat{a}^+_{m_1} \hat{a}^+_{n_1} \hat{a}_{k_1} \hat{a}_{l_1} \\ &+ \frac{1}{2} \sum_{m_2 n_2 k_2 l_2} V^{(2)}_{m_2 n_2 k_2 l_2} \hat{b}^+_{m_2} \hat{b}^+_{n_2} \hat{b}_{k_2} \hat{b}_{l_2} \\ &+ \frac{1}{2} \sum_{m_1 n_2 k_2 l_1} W_{m_1 n_2 l_1 k_2} \hat{a}^+_{m_1} \hat{b}^+_{n_2} \hat{b}_{k_2} \hat{a}_{l_1}, \end{aligned} \tag{1}$$

where $\hat{a}_{n_1}(\hat{a}^+_{n_1})$ and $\hat{b}_{n_2}(\hat{b}^+_{n_2})$ are the annihilation (creation) Fermi operators of electrons and holes, respectively, that satisfy the commutation relations

$$\hat{a}_{n_1}\hat{a}^+_{m_1} + \hat{a}^+_{m_1}\hat{a}_{n_1} = \delta_{m_1 n_1}, \quad \hat{b}_{n_2}\hat{b}^+_{m_2} + \hat{b}^+_{m_2}\hat{b}_{n_2} = \delta_{m_2 n_2}, \tag{2}$$

and all the other anticommutators are zero. We adopt the following convention for indices: Latin indices with a subscript 1 (2), i.e., m_1 (m_2), stand for electrons (holes). A particle (electron–hole pair) is denoted by a Latin index with no subscript $m = (m_1 m_2)$.

The total Hamiltonian of the system $\widehat{H}_T(\tau)$ driven by an external field $\mathcal{E}(\mathbf{r}, \tau)$ has the form

$$\widehat{H}_T(\tau) = \widehat{H} - \int \mathrm{d}\mathbf{r}\, \mathcal{E}(\mathbf{r}, \tau)\hat{\mu}(\mathbf{r}), \tag{3}$$

with

$$\hat{\mu}(\mathbf{r}) \equiv \sum_{m_1 n_2} \mu_{m_1 n_2}(\mathbf{r})(\hat{a}^+_{m_1}\hat{b}^+_{n_2} + \hat{b}_{n_2}\hat{a}_{m_1}). \tag{4}$$

Let $\mathcal{H}_n$ be the subspace of n-particle states. The complete space of states of our model (denoted $\mathcal{H}$) can then be represented as

$$\mathcal{H} = \bigoplus_{n=0}^{\infty} \mathcal{H}_n, \tag{5}$$

with $\widehat{H}(\mathcal{H}_n) \subset \mathcal{H}_n$, and $\mathcal{H}_0$ is generated by the ground state denoted $|\Omega\rangle$. Defining $\mathcal{W}^{(j)}$, $j = 1, 2$ as the spaces of single-electron and single-hole states, we can treat the parameters of the Hamiltonian given by Eq. (1) as linear operators $t^{(j)}$: $\mathcal{W}^{(j)} \to \mathcal{W}^{(j)}$, $V^{(j)}$: $\mathcal{W}^{(j)} \otimes \mathcal{W}^{(j)} \to \mathcal{W}^{(j)} \otimes \mathcal{W}^{(j)}$, and W: $\mathcal{W}^{(1)} \otimes \mathcal{W}^{(2)} \to \mathcal{W}^{(1)} \otimes \mathcal{W}^{(2)}$; note that $\mathcal{H}_1 = \mathcal{W}^{(1)} \otimes \mathcal{W}^{(2)}$.

Introducing the particle (electron–hole) operators

$$\hat{B}^+_{m_1 m_2} \equiv \hat{a}^+_{m_1}\hat{b}^+_{m_2}, \qquad \hat{B}_{m_1 m_2} \equiv \hat{b}_{m_2}\hat{a}_{m_1}, \tag{6}$$

we can express the commutation relations of particle operators as well as the Hamiltonian in terms of an infinite series of normally ordered operators $\hat{B}^+$ and $\hat{B}$. This can be accomplished in the following way. Expressing the commutation relations of $\hat{B}$ and $\hat{B}^+$ in terms of the electron and the hole operators $\hat{a}$, $\hat{b}$, $\hat{a}^+$, and $\hat{b}^+$ we can project the Hamiltonian and the right-hand side (rhs) of the commutation relations into the subspaces $\mathcal{H}_n \subset \mathcal{H}$. We then make an ansatz and assume that the Hamiltonian and the commutation relations can be expanded in a power series involving normally ordered products of operators. Because the Hamiltonian conserves the number of particles, each term should contain an equal number of creation ($\hat{B}^+$) and annihilation ($\hat{B}$) operators. We can easily determine the expansion coefficients starting with the zero-order terms (in $\hat{B}$ and $\hat{B}^+$), making use of the fact that an operator $\hat{B}^+ \ldots \hat{B}^+ \hat{B} \ldots \hat{B}$ containing n creation and n annihilation operators is zero on all $\mathcal{H}_m$ with $m < n$. This method allows us to determine the coefficients successively, order by order. For calculating the third-order response, we need to expand the Hamiltonian up to the fourth order and the commutation relations up to the second order.[27] The total Hamiltonian is then given by Eq. (3), with

$$\widehat{H} = \sum_{mn} h_{mn} \hat{B}_m{}^+ \hat{B}_n + \frac{1}{2} \sum_{mnkl} \Gamma_{mnkl} \hat{B}_m{}^+ \hat{B}_n{}^+ \hat{B}_k \hat{B}_l, \tag{7}$$

and the dipole operator

$$\hat{\mu}(\mathbf{r}) = \sum_m \mu_m(\mathbf{r})(\hat{B}_m{}^+ + \hat{B}_m). \tag{8}$$

The expansion coefficients are given by

$$h_{mn} \equiv t^{(1)}_{m_1 n_1}\delta_{m_2 n_2} + \delta_{m_1 n_1} t^{(2)}_{m_2 n_2} + W_{m_1 m_2 n_1 n_2}, \tag{9}$$

$$\begin{aligned}\Gamma_{mnkl} \equiv &-\frac{1}{2}[t^{(1)}_{m_1 k_1}\delta_{m_2 k_2}\delta_{n_1 l_1}\delta_{n_2 l_2} + \delta_{m_1 k_1} t^{(2)}_{m_2 k_2}\delta_{n_1 l_1}\delta_{n_2 l_2} \\ &+ \delta_{m_1 k_1}\delta_{m_2 k_2} t^{(1)}_{n_1 l_1}\delta_{n_2 l_2} + \delta_{m_1 k_1}\delta_{m_2 k_2}\delta_{n_1 l_1} t^{(2)}_{n_2 l_2}] \\ &+ \frac{1}{2}[V^{(1)}_{m_1 n_1 k_1 l_1}\delta_{m_2 k_2}\delta_{n_2 l_2} + \delta_{m_1 k_1}\delta_{n_1 l_1} V^{(2)}_{m_2 n_2 k_2 l_2}], \end{aligned} \tag{10}$$

where h stands for one-particle energy and Γ describes the anharmonicity. The commutation relations are

$$[\hat{B}_m, \hat{B}_n^{+}] = \delta_{mn} - 2\sum_{pq} P_{mpnq}\hat{B}_p^{+}\hat{B}_q\,. \tag{11}$$

P represents the deviation from particle boson statistics and is given by

$$P = {}^1\!/_2[P^{(1)} + P^{(2)}]. \tag{12}$$

Here $P^{(1)}$ $[P^{(2)}]$ is the electron (hole) permutation operator:

$$\begin{aligned} P^{(1)}_{mnpq} &\equiv \delta_{m_1q_1}\delta_{p_1n_1}\delta_{m_2p_2}\delta_{n_2q_2}\,,\\ P^{(2)}_{mnpq} &\equiv \delta_{m_2q_2}\delta_{p_2n_2}\delta_{m_1p_1}\delta_{n_1q_1}\,. \end{aligned} \tag{13}$$

Alternatively, Eqs. (9), (10), and (13) can be written in operator notation:

$$\begin{aligned} \Gamma &= -{}^1\!/_2[t^{(1)}\otimes I\otimes I\otimes I + I\otimes t^{(2)}\otimes I\otimes I\\ &\quad + I\otimes I\otimes t^{(1)}\otimes I + I\otimes I\otimes I\otimes t^{(2)}]\\ &\quad + {}^1\!/_2[V^{(1)}\otimes I\otimes I + I\otimes I\otimes V^{(2)}], \end{aligned} \tag{14}$$

$$h = t^{(1)}\otimes I + I\otimes t^{(2)} + W\,, \tag{15}$$

$$\begin{aligned} &P^{(1)}(u_1\otimes u_2\otimes v_1\otimes v_2)\\ &\quad = v_1\otimes u_2\otimes u_1\otimes v_2\,,\\ &P^{(2)}(u_1\otimes u_2\otimes v_1\otimes v_2)\\ &\quad = u_1\otimes v_2\otimes v_1\otimes u_2\,. \end{aligned} \tag{16}$$

With Eqs. (7) and (11), the Heisenberg equation of motion for the particle operators $i\mathrm{d}\hat{B}_n/\mathrm{d}\tau = [\hat{B}_n, \hat{H}]$ reads

$$\begin{aligned} i\frac{\mathrm{d}\hat{B}_n}{\mathrm{d}\tau} &= \sum_m h_{nm}\hat{B}_m - \mathcal{E}_n + \sum_{mpq} U_{nmpq}\hat{B}_m^{+}\hat{B}_p\hat{B}_q\\ &\quad + \sum_{mpq} P_{nmpq}\hat{B}_m^{+}(\hat{B}_p\mathcal{E}_q + \hat{B}_q\mathcal{E}_p), \end{aligned} \tag{17}$$

where we have defined

$$\mathcal{E}_n \equiv \int \mathrm{d}\mathbf{r}\,\mu_n(\mathbf{r})\mathcal{E}(\mathbf{r}) \tag{18}$$

$$U \equiv [(I-P)\Gamma - P(I\otimes h + h\otimes I)]\frac{I-P}{2}\,. \tag{19}$$

After some simple algebra, Eq. (19) may be recast in the form

$$U = V^{(1)}\otimes I\otimes I + I\otimes I\otimes V^{(2)} + P(I\otimes W + W\otimes I)P\,. \tag{20}$$

Equation (17) can be used to obtain the following closed system of equations for $\langle\hat{B}_m\rangle$ and $\langle\hat{B}_m\hat{B}_n\rangle$. In closing these equations we have used the factorization $\langle\hat{B}^{+}\ldots\hat{B}^{+}\hat{B}\ldots\hat{B}\rangle = \langle\hat{B}^{+}\ldots\hat{B}^{+}\rangle\langle\hat{B}\ldots\hat{B}\rangle$, which is justified for calculating the third-order response.[8,27]

$$\begin{aligned} i\frac{\mathrm{d}\langle\hat{B}_n\rangle}{\mathrm{d}\tau} &= \sum_m h_{nm}\langle\hat{B}_m\rangle - \mathcal{E}_n + \sum_{mpq} U_{nmpq}\langle\hat{B}_m^{+}\rangle\langle\hat{B}_p\hat{B}_q\rangle\\ &\quad + \sum_{mpq} P_{nmpq}\langle\hat{B}_m^{+}\rangle(\langle\hat{B}_p\rangle\mathcal{E}_q + \langle\hat{B}_q\rangle\mathcal{E}_p)\,, \end{aligned} \tag{21}$$

$$\begin{aligned} &i\frac{\mathrm{d}\langle\hat{B}_n\hat{B}_{n'}\rangle}{\mathrm{d}\tau} - \sum_{mm'}(h_{nm}\delta_{n'm'} + \delta_{nm}h_{n'm'})\langle\hat{B}_m\hat{B}_{m'}\rangle\\ &\qquad - \sum_{mm'} U_{nn'mm'}\langle\hat{B}_m\hat{B}_{m'}\rangle\\ &\qquad = -(\delta_{nm}\delta_{n'm'} - P_{nn'mm'})(\mathcal{E}_m\langle\hat{B}_{m'}\rangle + \langle\hat{B}_m\rangle\mathcal{E}_{m'})\,. \end{aligned} \tag{22}$$

Solving these equations perturbatively in the external field and switching to the frequency domain, we obtain the GFE for the optical response functions. For the linear response we have

$$\begin{aligned} R^{(1)} &= (-\omega_s\mathbf{r}_s;\,\omega\mathbf{r})\\ &= \sum_{mn}\mu_n(\mathbf{r}_s)\mu_m(\mathbf{r})[G_{nm}(\omega) + G_{mn}{}^{*}(-\omega)], \end{aligned} \tag{23}$$

with the single-particle Green's function

$$G(\omega) = [(\omega + i\eta)I - h]^{-1}. \tag{24}$$

For the third-order response we obtain

$$\begin{aligned} &R^{(3)}(-\omega_s\mathbf{r}_s;\,\omega_1\mathbf{r}_1,\,\omega_2\mathbf{r}_2,\,\omega_3\mathbf{r}_3)\\ &\quad = \sum_{nm_1m_2m_3}\mu_n(\mathbf{r}_s)\mu_{m_1}(\mathbf{r}_1)\mu_{m_2}(\mathbf{r}_2)\mu_{m_3}(\mathbf{r}_3)\\ &\qquad \times R_{nm_1m_2m_3}(-\omega_s;\,\omega_1,\,\omega_2,\,\omega_3)\,, \end{aligned} \tag{25}$$

with

$$\begin{aligned} &R_{nm_1m_2m_3}(-\omega_s;\omega_1,\,\omega_2,\,\omega_3)\\ &\equiv \frac{1}{6}\sum_{\substack{\mathrm{perm}\\(\omega_j m_j)}}\sum_{n'm_1'm_2'm_3'}(\omega_2)\\ &\quad \times G_{m_1'm_1}(\omega_1)G_{m_2'm_2}G_{m_3'm_3}{}^{*}(-\omega_3)G_{nn'}(\omega_s)\\ &\quad \times \overline{\Gamma}_{n'm_3'm_1'm_2'}(\omega_1+\omega_2)\,. \end{aligned} \tag{26}$$

Here $\sum_{(\omega_j,m_j)}^{\mathrm{perm}}$ means the sum over six permutations of three pairs (ω_1,m_1), (ω_2,m_2), and (ω_3,m_3), and the two-particle scattering matrix is given by

$$\begin{aligned} \overline{\Gamma}(\omega) &= -2P[\overline{F}(\omega)]^{-1} + 2U[I - \overline{F}(\omega)U]^{-1}\\ &\quad \times \overline{F}(\omega)(I-P)[\overline{F}(\omega)]^{-1}, \end{aligned} \tag{27}$$

with

$$\overline{F}(\omega) \equiv [(\omega + 2i\eta) - (I\otimes h + h\otimes I)]^{-1}, \tag{28}$$

and η is the phenomenological exciton damping rate.

Equations (25) and (26), which generalize the GFE for Frenkel excitons,[12] express the third-order response of the two-band model in terms of the single-particle Green's function $G(\omega)$, and the two-particle scattering matrix $\overline{\Gamma}(\omega)$. $\overline{\Gamma}$ [Eq. (27)] contains both the effects of anharmonicities represented by U and the nonboson statistics represented by P.

3. APPLICATION TO INTERMEDIATE EXCITONS

The GFE for the optical response contains the contributions of all types of particle states, including free electron–hole pairs, weakly interacting pairs, or bound pairs known as excitons. In this section we project these equations into the exciton subspace. To that end, we introduce a basis set in $\mathcal{H}_1 = \mathcal{W}^{(1)} \otimes \mathcal{W}^{(2)}$ generated by the eigenstates denoted $|\alpha\rangle$ with eigenvalues ϵ_α:

$$|\alpha\rangle = \sum_m \Psi_{\alpha m} \hat{\alpha}^+_{m_1} \hat{b}^+_{m_2} |\Omega\rangle , \tag{29}$$

where the wave functions $\Psi_{\alpha m}$ are obtained by solution of a two-body (one-electron, one-hole) problem:

$$\sum_n t^{(1)}_{m_1 n_1} \delta_{m_2 n_2} + \delta_{m_1 n_1} t^{(2)}_{m_2 n_2} + W_{m_1 m_2 n_1 n_2} \Psi_{\alpha n} = \epsilon_\alpha \Psi_{\alpha m} . \tag{30}$$

To calculate the exciton contribution we consider a subset of one-particle exciton eigenstates $|\alpha\rangle$ and define the exciton creation operators $\hat{B}_\alpha{}^+$ as follows:

$$\hat{B}_\alpha{}^+ \equiv \sum_m \Psi_{\alpha m_1 m_2} \hat{\alpha}^+_{m_1} \hat{b}^+_{m_2} . \tag{31}$$

Next we introduce the exciton subspace of states $\mathcal{V} \subset \mathcal{H}$:

$$\mathcal{V} \equiv \bigoplus_{n=0}^{\infty} \mathcal{V}_n , \tag{32}$$

where the n-exciton subspace $\mathcal{V}_n \subset \mathcal{H}_n$ is defined as the subspace generated by the states $\hat{B}^+_{\alpha_1} \ldots \hat{B}^+_{\alpha_n} |\Omega\rangle$. The operators $\hat{B}^+_\alpha$ therefore act in $\mathcal{V}$, and we define the exciton annihilation operators $\hat{B}_\alpha$ as the Hermitian conjugates to $\hat{B}^+_\alpha$ in $\mathcal{V}$. The projection technique is based on choosing a subset $\mathcal{B} \subset \mathcal{A}$ in the basis set $\mathcal{A}$ of one-particle eigenstates $|\alpha\rangle$ defined by Eqs. (6) and (29). In our case $\mathcal{B}$ describes the exciton (bound) particle–hole states. If we take all the states into account, i.e., $\mathcal{B} = \mathcal{A}$, then $\mathcal{V}_n = \mathcal{H}_n$, and we simply formulate the exact theory in terms of our chosen basis set. Projecting the Hamiltonian $\widehat{H_T}$ onto the basis $\mathcal{V}$, we can obtain the commutation relations of exciton operators and the effective Hamiltonian expanded in powers of normally ordered exciton operators, which have the form of Eqs. (7) and (11) written with the basis set of eigenstates $|\alpha\rangle$ confined to $\mathcal{B} \subset \mathcal{A}$ (i.e., $\alpha \in \mathcal{B}$). This yields

$$\widehat{H} = \sum_\alpha \epsilon_\alpha \hat{B}_\alpha{}^+ \hat{B}_\alpha + \frac{1}{2} \sum_{\alpha\beta\mu\nu} \Gamma_{\alpha\beta\mu\nu} \hat{B}_\alpha{}^+ \hat{B}_\beta{}^+ \hat{B}_\mu \hat{B}_\nu , \tag{33}$$

where polarization adopts the form

$$\hat{\mu}(\mathbf{r}) = \sum_\alpha \mu_\alpha(\mathbf{r}) (\hat{B}_\alpha + \hat{B}_\alpha{}^+) , \tag{34}$$

with the commutation relations

$$[\hat{B}_\alpha, \hat{B}_\beta{}^+] = \delta_{\alpha\beta} - 2 \sum_{\mu\nu} P_{\alpha\mu\beta\nu} \hat{B}_\mu{}^+ B_\nu , \tag{35}$$

where the Greek indices run over the values belonging to $\mathcal{B}$.

We can obtain the parameters in Eqs. (33), (34), and (35) from Eqs. (14), (8), and (13) respectively, by transforming to the new basis set. In Eqs. (34) and (38) we have assumed that the wave functions $\Psi_{\alpha m}$ are real:

$$\Gamma_{\alpha\beta\mu\nu} \equiv \sum_{mnkl} \Psi_{\alpha m}{}^* \Psi_{\beta n}{}^* \Psi_{\mu k} \Psi_{\nu l} \Gamma_{mnkl} , \tag{36}$$

$$\begin{aligned} P_{\alpha\beta\mu\nu} &\equiv \sum_{mnpq} \Psi_{\alpha m}{}^* \Psi_{\beta n}{}^* \Psi_{\mu p} \Psi_{\nu q} P_{mnpq} \\ &= \frac{1}{2} \sum_{m_1 m_2 n_1 n_2} (\Psi_{\alpha m_1 m_2}{}^* \Psi_{\nu m_1 n_2} \Psi_{\beta n_1 n_2}{}^* \Psi_{\mu n_1 m_2} \\ &\quad + \Psi_{\alpha m_1 m_2}{}^* \Psi_{\mu m_1 n_2} \Psi_{\beta n_1 n_2}{}^* \Psi_{\nu n_1 m_2}) , \end{aligned} \tag{37}$$

$$\mu_\alpha(\mathbf{r}) \equiv \sum_m \mu_m(\mathbf{r}) \Psi_{\alpha m} . \tag{38}$$

Equation (37) can also be written by the operator notation. Here $\Psi_{\alpha m_1 m_2}$ and $\Psi_{\alpha m_1 m_2}{}^*$ are considered as matrix elements of an operator Ψ_α: $\mathcal{W}_2 \to \mathcal{W}_1$ and its Hermitian conjugate $\Psi_\alpha{}^+$: $\mathcal{W}_1 \to \mathcal{W}_2$, respectively:

$$P_{\alpha\beta\mu\nu} = \tfrac{1}{2} \operatorname{Tr}(\Psi_\alpha{}^+ \Psi_\nu \Psi_\beta{}^+ \Psi_\mu + \Psi_\alpha{}^+ \Psi_\mu \Psi_\beta{}^+ \Psi_\nu) . \tag{39}$$

The Hamiltonian and the commutation relations are formally identical to Eqs. (7) and (11). The only difference is that they use Greek (instead of Latin) indices, which implies that all the parameters should be taken in the eigenstate basis set [Eqs. (36)–(38)]. Therefore the equations of motion and the expressions for the response have the form of Eqs. (17), (21), (22), and (25)–(28), with all the parameters being written with the eigenstate basis set. The one-particle Green's function has a simpler diagonal form:

$$G_{\alpha\beta}(\omega) = \frac{\delta_{\alpha\beta}}{\omega + i\eta - \epsilon_\alpha} . \tag{40}$$

Next we consider a two-band model defined on a d-dimensional infinite lattice, and for each value of momentum $\mathbf{k}$ we retain only the lowest-energy s-type exciton ($\alpha = \mathbf{k}$). The higher-energy excitons and the electron–hole states representing the continuum are neglected. This provides the simplest model that illustrates the effects of statistics on the nonlinear response. The Hamiltonian written in momentum space is

$$\begin{aligned} \widehat{H} = &\int \mathrm{d}\mathbf{k} \epsilon_{\mathbf{k}} \hat{B}_{\mathbf{k}}{}^+ \hat{B}_{\mathbf{k}} + \frac{1}{2} \int \mathrm{d}\mathbf{k}_1 \mathrm{d}\mathbf{k}_2 \mathrm{d}\mathbf{k}_3 \mathrm{d}\mathbf{k}_4 \\ &\times \delta(\mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}_3 - \mathbf{k}_4) \\ &\times \Gamma(\mathbf{k}_1, \mathbf{k}_2; \mathbf{k}_3, \mathbf{k}_4) \hat{B}_{\mathbf{k}_1}{}^+ \hat{B}_{\mathbf{k}_2}{}^+ \hat{B}_{\mathbf{k}_3} \hat{B}_{\mathbf{k}_4} , \end{aligned} \tag{41}$$

where we adopt the following convention $\mathrm{d}\mathbf{k} \equiv (a/2\pi)^d \mathrm{d}^d k$ and $\delta(\mathbf{k}) \equiv (2\pi/a)^d \delta^{(d)}(\mathbf{k})$. The commutation relations for exciton operators are

$$\begin{aligned} [\hat{B}_{\mathbf{k}_1}, \hat{B}_{\mathbf{k}_2}{}^+] = &\delta(\mathbf{k}_1 - \mathbf{k}_2) - 2 \int \mathrm{d}\mathbf{k}_3 \mathrm{d}\mathbf{k}_4 \\ &\times \delta(\mathbf{k}_1 + \mathbf{k}_3 - \mathbf{k}_2 - \mathbf{k}_4) P(\mathbf{k}_1, \mathbf{k}_3; \mathbf{k}_2, \mathbf{k}_4) \hat{B}_{\mathbf{k}_3}{}^+ \hat{B}_{\mathbf{k}_4} , \end{aligned} \tag{42}$$

and the polarization operator becomes

$$\hat{\mu}(\mathbf{r}) = \int \mathrm{d}\mathbf{k} \mathrm{d}\mathbf{p} (\hat{B}_{\mathbf{k}}{}^+ + \hat{B}_{-\mathbf{k}}) \exp(i\mathbf{k} \cdot \mathbf{r}) \mu_{\mathbf{k}}(\mathbf{p}) \Psi_{\mathbf{k}}(\mathbf{p}) , \tag{43}$$

where $\Psi_{\mathbf{k}}(\mathbf{p})$ is determined from the exciton wave function $\Psi_{\mathbf{k}m}$:

$$\Psi_{\mathbf{k}m} = \int d\mathbf{p}\, \exp[i\mathbf{k}\cdot(\mathbf{R}_{m_1} + \mathbf{R}_{m_2}) + i\mathbf{p}\cdot(\mathbf{R}_{m_1} - \mathbf{R}_{m_2})]\Psi_{\mathbf{k}}(\mathbf{p}). \quad (44)$$

The GFE gives the optical response in terms of the Coulomb interaction parameters and the $\mathbf{k}$-dependent wave functions of the relative motion of electrons and holes in the excitons. To obtain a simple physical picture we consider long-wave excitons and neglect the dependence of the relative motion wave function on the center-of-mass momentum. Such factorization of the relative motion holds in the effective-mass approximation (i.e., when the dependence of electron and hole energy on the momentum is quadratic). It breaks down for short wavelengths $k \sim a^{-1}$. This means that $\Psi_{\mathbf{k}}(\mathbf{p})$ from Eq. (44) does not depend on $\mathbf{k}$ and may be denoted $\Psi(\mathbf{p})$. We further neglect the $\mathbf{k}$ dependence of $\mu_{\mathbf{k}}(\mathbf{p})$ on the same scale and denote it simply $\mu(\mathbf{p})$. Furthermore, because $\mu(\mathbf{p})$ changes on the $p \sim a^{-1}$ scale and $\Psi(\mathbf{p})$ is nonzero for $\mathbf{p} \leq r_B{}^{-1} \ll a^{-1}$, where r_B is the exciton Bohr radius [i.e., the size of the region $\mathbf{R}_{m_1} - \mathbf{R}_{m_2}$, where $\Psi_{\mathbf{k}m}$ from Eq. (44) is nonzero], we can replace $\mu_{\mathbf{k}}(\mathbf{p})$ in Eq. (43) with $\mu(0)$ and finally obtain

$$\mu(\mathbf{r}) = q^{1/2}\mu \int d\mathbf{k}\, \exp(i\mathbf{k}\cdot\mathbf{r})(\hat{B}_{\mathbf{k}}{}^{+} + \hat{B}_{-\mathbf{k}}), \quad (45)$$

where

$$\mu \equiv \mu(0), \qquad q^{1/2} \equiv \int d\mathbf{p}\Psi(\mathbf{p}). \quad (46)$$

Equation (45) implies that $\mu_{\mathbf{k}} = q^{1/2}\mu$, and it follows from Eqs. (46) that $q \sim (a/r_B)^d$.

Substituting Eq. (44) into our general expression for P [Eq. (37)], we obtain

$$P(\mathbf{k}_1, \mathbf{k}_2; \mathbf{k}_3, \mathbf{k}_4) = \frac{1}{2}\int d\mathbf{p}[\Psi(\mathbf{p})\Psi(\mathbf{p} + \mathbf{k}_3 - \mathbf{k}_1) \times \Psi(\mathbf{p} + 2\mathbf{k}_3 - \mathbf{k}_1 - \mathbf{k}_2)\Psi(\mathbf{p} + \mathbf{k}_1 - \mathbf{k}_4) + \Psi(\mathbf{p})\Psi(\mathbf{p} + \mathbf{k}_3 - \mathbf{k}_1)\Psi(\mathbf{p} + 2\mathbf{k}_3 - \mathbf{k}_1 - \mathbf{k}_4) \times \Psi(\mathbf{p} + \mathbf{k}_1 - \mathbf{k}_2)]. \quad (47)$$

We now discuss two limiting expressions for P. When $k_j \gg r_B{}^{-1}$, we note that the rhs of Eq. (47) is zero when $|\mathbf{k}_{j1} - \mathbf{k}_{j2}| > r_B{}^{-1}$, and, because we are interested in the scale $k \gg r_B{}^{-1}$, we can write the rhs of Eq. (47) in the form $A\delta(\mathbf{k}_1 - \mathbf{k}_3)\delta(\mathbf{k}_2 - \mathbf{k}_4)\delta(\mathbf{k}_2 - \mathbf{k}_3)$. By integrating Eq. (47) over k_j to determine the coefficient A, we obtain

$$P(\mathbf{k}_1, \mathbf{k}_2; \mathbf{k}_3, \mathbf{k}_4) = q^2\delta(\mathbf{k}_1 - \mathbf{k}_3)\delta(\mathbf{k}_2 - \mathbf{k}_4)\delta(\mathbf{k}_2 - \mathbf{k}_3). \quad (48)$$

Equation (48) yields the following commutation relations in the momentum domain:

$$[\hat{B}_{\mathbf{k}_1}, \hat{B}_{\mathbf{k}_2}{}^{+}] = \delta(\mathbf{k}_1 - \mathbf{k}_2)(1 - 2q^2\hat{B}_{\mathbf{k}_1}{}^{+}\hat{B}_{\mathbf{k}_1}). \quad (49)$$

Because the nonlinear response is determined by two-exciton states with momenta $k \gg r_B{}^{-1}$, we should use the commutation relations of Eq. (49) for large-size excitons. This is the Wannier-exciton limit.

In the opposite limit when $k_j \ll r_B{}^{-1}(j = 1, \ldots, 4)$ we can set $\mathbf{k}_j = 0$ in the rhs of Eq. (47), which yields

$$P(\mathbf{k}_1, \mathbf{k}_2; \mathbf{k}_3, \mathbf{k}_4) = q_0{}^{-1}, \qquad q_0{}^{-1} \equiv \int d\mathbf{p}|\Psi(\mathbf{p})|^4. \quad (50)$$

Equations (46) and (50) imply that $q^{1/2}$ is equal to the exciton wave function $\Psi_{\mathbf{k}m}$ [Eq. (44)] at $m_1 = m_2$ (i.e, when the electron and the hole occupy the same site), whereas q_0 is the participation ratio of the exciton wave function. It follows from Eq. (50) that $q_0 \sim (a/r_B)^d \sim q$, and qualitatively both q and q_0 provide a measure of the exciton size. We can obtain the asymptotic expression of Eq. (50) from Eq. (48) by setting $\mathbf{k}_j = 0$. Because the δ functions have the width of a/r_B, we obtain $\delta(0) \sim q^{-1}$, which leads to $P \sim q^{-1}$.

Equation (50) leads to the following commutation relations in real space (we use Latin indices with overbars to denote sites):

$$[\hat{B}_{\bar{n}}, \hat{B}_{\bar{m}}{}^{+}] = \delta_{\bar{n}\bar{m}}(1 - 2q_0{}^{-1}\hat{B}_{\bar{n}}{}^{+}\hat{B}_{\bar{n}}). \quad (51)$$

Equation (51) with $q_0 = 1$ is identical to the commutation relations for Frenkel excitons. This can be rationalized as follows. For Frenkel excitons $r_B = 0$ and $k \ll r_B{}^{-1}$ for all values of $\mathbf{k}$, and one should use Eq. (50) for P, which leads to Eq. (51).

Equations (49) and (51) resemble commutation relations for nonideal bosons written in real space and in the momentum domain, respectively. The commutation relation [Eq. (49)] was used by Birman[28] in the study of Bose condensation. The deviation from boson statistics decreases as q decreases [see Eq. (49)]. Because $q \sim (a/r_B)^d$ it decreases with the increase of r_B and d, which illustrates that effects of phase-space filling are stronger in low-dimensional systems and for small-radius excitons.[2]

We can obtain the nonlinear optical response by applying the equation-of-motion technique to the Hamiltonian [Eq. (41)] with the commutation relations, Eq. (49). Alternatively, we can use the general GFE [Eqs. (25) and (26)], and, upon switching to the momentum domain, we obtain

$$R^{(3)}(-\omega_s - \mathbf{k}_s; \omega_1\mathbf{k}_1, \omega_2\mathbf{k}_2, \omega_3\mathbf{k}_3) = \mu^4 q^2 \frac{1}{6}\sum_{\substack{\text{perm}\\(\omega_j\mathbf{k}_j)}} G(\omega_1, \mathbf{k}_1)G(\omega_2\mathbf{k}_2)G^*(-\omega_3, -\mathbf{k}_3)G(\omega_s\mathbf{k}_s) \times \overline{\Gamma}(\omega_1 + \omega_2; \mathbf{k}_s, -\mathbf{k}_3; \mathbf{k}_1, \mathbf{k}_2), \quad (52)$$

with

$$G(\omega, \mathbf{k}) = \frac{1}{\omega - \epsilon_{\mathbf{k}} + i\eta}. \quad (53)$$

$\overline{\Gamma}$ is obtained from Eq. (27) by switching to the momentum domain. Using P in the form of Eq. (48), we obtain $\overline{\Gamma} \propto q^{-1}$, which leads to $R^{(3)} \propto q$, which gives $R^{(3)} \propto (a/r_B)^d$.

The approach developed in this paper should be of particular interest in the study of magnitoexcitons in semiconductor quantum wells,[29] where the exciton size and therefore the parameter q describing exciton statistics can easily be controlled by variation of the magnetic-field strength. The Bloch equations for magnetoexcitons have been derived.[30] However, because the Bloch equations

are based on the time-dependent Hartree–Fock scheme, they completely miss the two-photon resonances that are explicitly taken into account in the GFE. In the case of strong magnetic field when the magnetic length is much smaller than the size of an exciton without the field (which corresponds to the strong Landau quantization of electron and hole levels), only the bound exciton states contribute to the response. By application of the GFE it should be possible to analyze the third-order response in the two-photon resonance regime.

ACKNOWLEDGMENTS

We gratefully acknowledge the support of the U.S. Air Force Office of Scientific Research and the National Science Foundation.

REFERENCES

1. H. Haug and S. W. Koch, *Quantum Theory of the Optical and Electronic Properties of Semiconductors* (World Scientific, Singapore, 1990).
2. S. Schmitt-Rink, D. S. Chemla, and D. B. Miller, "Linear and nonlinear optical properties of semiconductor quantum wells," Adv. Phys. **38,** 89 (1989); S. Schmitt-Rink, D. B. Miller, and D. S. Chemla, "Theory of the linear and nonlinear optical properties of semiconductor microcrystallites," Phys. Rev. B **35,** 8113 (1987).
3. L. Banyai and S. W. Koch, *Semiconductor Quantum Dots* (World Scientific, Singapore, 1993).
4. M. L. Steigerwald and L. Brus, "Semiconductor crystallites: a class of large molecules," Acc. Chem. Res. **23,** 183 (1990); M. Bawendi, M. L. Steigerwald, and L. Brus, "The quantum mechanics of larger semiconductor clusters (quantum dots)," Annu. Rev. Phys. Chem. **41,** 477 (1990).
5. M. Pope and C. Swenberg, *Electronic Processes in Organic Crystals* (Oxford U. Press, Oxford, 1982); A. S. Davydov, *Theory of Molecular Excitons* (Plenum, New York, 1971).
6. E. I. Haskal, Z. Shen, P. E. Burrows, and S. R. Forrest, "Excitons and exciton confinement in crystalline organic thin films grown by organic molecular-beam deposition," Phys. Rev. B **51,** 4449 (1995); F. F. So, S. R. Forrest, Y. Q. Shi, and W. H. Steier, "Quasi-epitaxial growth of organic multiple quantum well structures by organic molecular beam deposition," Appl. Phys. Lett. **56,** 674 (1990); F. F. So and S. R. Forrest, "Evidence for exciton confinement in crystalline organic multiple quantum wells," Phys. Rev. Lett. **66,** 2649 (1991).
7. D. S. Chemla and J. Zyss, eds., *Nonlinear Optical Properties of Organic Molecules and Crystals* (Academic, New York, 1986).
8. S. Mukamel, *Principles of Nonlinear Optical Spectroscopy* (Oxford U. Press, New York, 1995).
9. E. I. Rashba, *Excitons,* E. I. Rashba and M. D. Sturge, eds. (North-Holland, Amsterdam, 1982).
10. V. M. Agranovich and M. D. Galanin, *Electronic Excitation Energy Transfer in Condensed Matter,* V. M. Agranovich and A. A. Maradudin, eds. (North-Holland, Amsterdam, 1982).
11. J. L. Bredas, C. Adant, P. Tackx, A. Persoons, and B. M. Pierce, "Third-order nonlinear optical response in organic materials: theoretical and experimental aspects," Chem. Rev. **94,** 243 (1994).
12. V. Chernyak and S. Mukamel, "Level correlations and dephasing-induced resonances in molecular aggregates," Phys. Status Solidi B **189,** 67 (1995); V. Chernyak, N. Wang, and S. Mukamel, "Four-wave mixing and fluorescence of confined excitons in molecular nanostructures," Phys. Rep. **263,** 213 (1995).
13. A. Takahashi and S. Mukamel, "Anharmonic oscillator modeling of nonlinear susceptibilities and its application to conjugated polymers," J. Chem. Phys. **100,** 2366 (1994); M. Hartmann, V. Chernyak, and S. Mukamel, "Real space coupled oscillator approach to the radiative decay of conjugated polymers," Phys. Rev. B **52,** 2528 (1995).
14. A. A. Abrikosov, L. P. Gorkov, and I. Ye. Dzyaloshinsky, *Quantum Field Theoretical Methods in Statistical Physics* (Oxford U. Press, New York, 1965); L. P. Kadanoff and F. Baym, *Quantum Statistical Mechanics* (Benjamin, New York, 1962); G. D. Mahan, *Many-Particle Physics* (Plenum, New York, 1990).
15. N. Bloembergen, *Nonlinear Optics* (Benjamin, New York, 1965); B. J. Orr and J. F. Ward, "Perturbation theory of the non-linear optical polarization of an isolated system," Mol. Phys. **20,** 513 (1971).
16. N. Chernyak and S. Mukamel, "Time-dependent density matrix functional in Liouville space and optical response of many-electron systems," Phys. Rev. A **52,** 3601 (1995).
17. V. Chernyak and S. Mukamel, "Size-consistent quasiparticle representation of nonlinear optical response in many-electron systems," J. Chem. Phys. **104,** 444 (1996).
18. P. Ring and P. Schuck, *The Nuclear Many-Body Problem* (Springer-Verlag, New York, 1980).
19. H. Sekino and R. J. Bartlett, "Frequency dependent nonlinear optical properties of molecules," J. Chem. Phys. **85,** 976 (1986).
20. V. M. Agranovich and B. S. Toshich, "Collective properties of Frenkel excitons," Sov. Phys. JETP **26,** 104 (1968).
21. G. Wentzel, "Diamagnetism of a dense electron gas," Phys. Rev. **108,** 1593 (1957).
22. T. Usui, "Excitations in a high density electron gas," Prog. Theor. Phys. **23,** 787 (1960).
23. F. C. Spano and S. Mukamel, "Nonlinear susceptibilities of molecular aggregates: enhancement of $\chi^{(3)}$ by size," Phys. Rev. A **40,** 5783 (1989); F. C. Spano and S. Mukamel, "Cooperative nonlinear optical response of molecular aggregates: crossover to bulk behavior," Phys. Rev. Lett. **66,** 1197 (1991); F. C. Spano and S. Mukamel, "Excitons in confined geometries: size scaling of nonlinear susceptibilities," J. Chem. Phys. **95,** 7526 (1991).
24. K. Victor, V. M. Axt, and A. Stahl, "The hierarchy of density matrices in coherent semiconductor optics," Phys. Rev. B **51,** 14164 (1995); V. M. Axt and A. Stahl, "A dynamics-controlled truncation scheme for the hierarchy of density matrices in semiconductor optics," Z. Phys. B **93,** 4195 (1994).
25. F. B. Galagher and F. C. Spano, "Second hyperpolarizability of one-dimensional semiconductors," Phys. Rev. B **50,** 5370 (1994).
26. V. Chernyak and S. Mukamel, "Path integral formulation of retardation effects in nonlinear optics," J. Chem. Phys. **100,** 2593 (1994).
27. J. Knoester and S. Mukamel, "Transient gratings, four-wave mixing and polariton effects in nonlinear optics," Phys. Rep. **205,** 1 (1991).
28. J. L. Birman, "Many-body Green functions of q-deformed oscillators," Phys. Lett. A **167,** 363 (1992); J. L. Birman, "Collective excitations are q-deformed bosons," Solid State Commun. **84,** 259 (1992).
29. C. Stafford, S. Schmitt-Rink, and W. Schäfer, "Nonlinear optical response of two-dimensional magnetoexcitons," Phys. Rev. B **41,** 10000 (1990); S. Glutsch, U. Siegner, M.-A. Mycek, and D. S. Chemla, "Fano resonances due to coupled magnetoexciton and continuum states in bulk semiconductors," Phys. Rev. B **50,** 17009 (1994); U. Siegner, M.-A. Mycek, S. Glutsch, and D. S. Chemla, "Ultrafast coherence dynamics of Fano resonances in semiconductors," Phys. Rev. Lett. **74,** 470 (1995); "Quantum interferences in the system of Lorentzian and Fano magnetoexciton resonances in GaAs," Phys. Rev. B **51,** 4953 (1995); J. B. Stark, W. H. Knox, D. S. Chemla, W. Schäfer, S. Schmitt-Rink, and C. Stafford, "Femtosecond dynamics of excitons under extreme magnetic confinement," Phys. Rev. Lett. **65,** 3033 (1990).
30. S. Glutsch and D. S. Chemla, "Semiconductor Bloch equations in a homogeneous magnetic field," Phys. Rev. B **52,** 8317 (1995).