Nonlinear optics of semiconductor and molecular nanostructures; a common perspective

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A unified microscopic theoretical framework for the calculation of optical excitations in molecular and semiconductor materials is presented. The hierarchy of many-body density matrices for a pair-conserving many-electron model and the Frenkel exciton model is rigorously truncated to a given order in the radiation field. Closed equations of motion are derived for five generating functions representing the dynamics up to third order in the laser field including phonon degrees of freedom as well as all direct and exchange-type contributions to the Coulomb interaction. By eliminating the phonons perturbatively the authors obtain equations that, in the case of the many-electron system, generalize the semiconductor Bloch equations, are particularly suited for the analysis of the interplay between coherent and incoherent dynamics including many-body correlations, and lead to thermalized exciton (rather than single-particle) distributions at long times. A complete structural equivalence with the Frenkel exciton model of molecular materials is established. [S0034-6861(98)00201-3]

CONTENTS

I. INTRODUCTION

Optical measurements provide a tremendous insight into the electronic structure of various materials (Mukamel and Chemla, 1996). At moderate excitation densities, the basic physics tested by such experiments performed on semiconductors, conjugated polymers, and molecular aggregates is the dynamics of photogenerated carriers forming correlated structures such as excitons or biexcitons in either bound or unbound states. In ideal molecular crystals, intermolecular charge transfer is not possible and each molecule retains its own electrons. The elementary excitations in this case are tightly bound electron-hole pairs known as Frenkel excitons (Davydov, 1971). The loosely bound pairs in semiconductors form hydrogen-atom-like Wannier excitons (Haken,

1963; Stahl and Balslev, 1987; Haug and Koch, 1993). Intermediate charge-transfer excitons exist in mixed donor-acceptor crystals (Merrifield, 1961; Pope and Swenberg, 1982; Haarer and Phillpott, 1983; Petelenz, 1989; Dubovsky and Mukamel, 1992) and in conjugated molecules (Mukamel and Wang, 1992; Hartmann and Mukamel, 1993; Mukamel *et al.*, 1994; Takahashi and Mukamel, 1994; Chernyak and Mukamel, 1995a, 1996a; Hartmann *et al.*, 1995; Bulović *et al.*, 1996; Bulović and Forrest, 1996).

Apart from the Coulomb interaction, which is mainly responsible for correlations, the interaction of the carriers with phonons is also crucial for a detailed understanding of the dynamics of these systems. A variety of theoretical methods has been developed to address these issues, including the conventional sum-over-states approach,[1] multiconfiguration self-consistent field theories,[2] Bogoliubov transformations,[3] the Bethe-Salpeter equation,[4] "dressed"-exciton theories,[5] semi-phenomenological few-level models,[6] nonequilibrium

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[1]For the sum-over-states approach, see Soos and Ramasesha, 1984, 1988; Yaron and Silbey, 1992; Abe *et al.*, 1993; Soos *et al.*, 1993; Soos *et al.*, 1994; Chen and Mukamel, 1995; Chen *et al.*, 1996; and Mukamel and Chemla, 1996.

[2]For multiconfiguration self-consistent field theories, see Olsen and Jørgensen, 1985; Meyer *et al.*, 1990; and Jaszuński *et al.*, 1993.

[3]For the Bogoliubov transformations, see Comte and Mahler, 1986, 1988.

[4]For the Bethe-Salpeter equation, see Schmitt-Rink and Chemla, 1986; Chernyak *et al.*, 1995.

[5]For the dressed-exciton theories, see Combescot and Combescot, 1989; Combescot and Betbeder-Matibet, 1990; Combescot, 1992.

[6]For the semi-phenomenological few-level models, see Dixit *et al.*, 1990; Bar-Ad and Bar-Joseph, 1991, 1992; Lucht *et al.*, 1992; Mazumdar *et al.*, 1992; Wu *et al.*, 1992; Guo *et al.* 1993; Luo *et al.*, 1993; Bott *et al.*, 1993; Finkelstein *et al.*, 1993; Guo, 1994; Mayer *et al.*, 1994).

Green's functions,[7] and density-matrix theory.[8] Density-matrix theory has become the method of choice in the treatment of experiments with ultrashort pulses because dealing with dynamic variables that are directly related to observables and that depend only on a single time argument provides a very intuitive picture of the time-dependent material response.

The simplest level of theory is based on equations of motion for the reduced single-particle (two-point) density matrix. The optical polarization may be calculated using this density matrix, which constitutes the minimal level of necessary information. The semiconductor Bloch equations (Haug and Koch, 1993), which are at the heart of semiconductor optics, are derived within this framework. The treatment of intermediate (charge-transfer) excitons in conjugated polymers using the single-particle density matrix allowed the interpolation between molecular (Frenkel) limits (Mukamel, 1994) and semiconductor (Wannier) limits (Mukamel and Wang, 1992; Hartmann and Mukamel, 1993; Mukamel et al., 1994; Takahashi and Mukamel, 1994; Chernyak and Mukamel, 1995a, 1995b, 1996b; Hartmann et al., 1995; Tretiak et al., 1996a). One of the major obstacles for a microscopic comparison of various materials is that molecular systems are usually discussed using the global (many-electron) eigenstates in real space, whereas semiconductors are analyzed using elementary excitations (quasiparticles) in k space. Treating all systems according to the same basic strategy yields equations of motion whose structural similarities most clearly reflect the common aspects of the underlying physics and thus allows for a systematic comparison of the remaining differences. An improved level of theory is obtained by retaining higher-order (four-point, six-point, etc.) density matrices. This extension is essential in order to treat two-exciton dynamics properly. Using a model Hamiltonian that conserves the number of electron-hole pairs, it has been shown that for both Frenkel excitons (Dubovsky and Mukamel, 1991; Knoester and Mukamel, 1991; Leegwater and Mukamel, 1992; Mukamel, 1994; Chernyak et al., 1995) and Wannier excitons (Axt and Stahl, 1994a, 1994b; Lindberg et al., 1994; Maialle and Sham, 1994; Victor et al., 1995; Axt, Victor, and Stahl, 1996) it is possible to classify higher-order correlation functions according to their leading order in the laser field. This provides a convenient dynamics-controlled truncation, which allows a systematic method for closing the hierarchy rigorously at any desired order in the radiation field.

In the present paper we consider a general model of many-electron systems whose Hamiltonian conserves the number of electron-hole pairs and whose ground state is therefore given by the Hartree-Fock ground state (a single Slater determinant). The system is further linearly coupled to a phonon bath. This model provides a unified treatment of semiconductors, molecules with weakly correlated electronic structure, and molecular aggregates. We introduce a hierarchy of exciton-phonon generating functions, each representing a given exciton density matrix, and constituting a wave packet in phonon coordinates. We shall show that, to third order in the radiation field, the hierarchy can be truncated at the six-point-density-matrix level. We derive closed equations of motion for the relevant generating functions, representing a formally rigorous description of the optical response up to third order in the laser field including phonons. Taking these equations as a starting point, we work out a reduced scheme, based on eliminating the phonon degrees of freedom perturbatively.

Optical excitations of molecular crystals, superlattices, and aggregates are usually formulated taking Frenkel excitons rather than fermions as the basic entities. However, we shall demonstrate that the resulting dynamic equations can be recast in a form structurally equivalent to the dynamics of the many-electron model, thus revealing most clearly the fundamental similarities between the underlying physics of molecular and semiconductor materials. The Frenkel exciton model is simpler, since each exciton is represented by a single degree of freedom related to the center-of-mass motion of the pair. In semiconductors we need an additional coordinate representing the pair's relative motion. The formal equivalence of the underlying dynamics provides a simpler view of semiconductor optics and allows the clear interpretation of many effects and levels of reduction using the Frenkel exciton Hamiltonian, which is considerably simpler. Higher levels of modeling, which are very tedious for semiconductors, are quite workable for molecular systems. Consequently theoretical studies of molecular materials are more advanced than their semiconductor counterparts. Experimental studies of semiconductor nanostructures are, on the other hand, more advanced due to the superior methods of fabrication and characterization. Both fields can benefit from a free flow of information and ideas. Developing a common language and eliminating the terminology barrier between these two disciplines is the main goal of this article. Our formulation further generalizes previous treatments by including all exchange-type contributions to the Coulomb interaction and keeping a general form for the direct-type interaction, which is expected to be important for a description of samples with strong confinement, such as semiconductor nanocrystals (Brus, 1991; Tolbert and Alivisatos, 1994; Alivisatos, 1995, 1996; Norris and Bawendi, 1996; Norris et al., 1996; Yokojima et al., 1997).

It should be noted that in principle it is possible to formulate an exact theory at any level of reduction. The

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[7]For the nonequilibrium Green's functions, see Müller et al., 1987; Haug, 1988; Hartmann et al., 1990; Bechstedt and Glutsch, 1991; Kuznetsov, 1991a; Haug and Jauho, 1996.

[8]For the density-matrix theory, see Huhn and Stahl, 1984; Schmitt-Rink and Chemla, 1986; Stahl and Balslev, 1987; Lindberg and Koch, 1988; Mukamel and Wang, 1992; Hartmann and Mukamel, 1993; Haug and Koch, 1993; Axt and Stahl, 1994a, 1994b; Mukamel et al., 1994; Takahashi and Mukamel, 1994; Hartmann et al., 1995; Victor et al., 1995.

choice is between including certain variables explicitly or incorporating their effects through self-energies in equations of motion where these variables have been eliminated. Thus the effects of four- and six-point density matrices may be incorporated in a reduction level of two-point density matrices. The price to be paid for this reduction is that the equations of motion become non-local in time. When new resonances are associated with higher-order density matrices, we are better off including these variables explicitly. This allows direct control of the approximations and provides a more transparent physical picture.

The paper is organized as follows: In Sec. II we specify the Hamiltonian commonly used in the microscopic modeling of nonrelativistic many-electron systems. The standard starting points for direct-gap semiconductors and many organic materials, both bulk and nanostructures (quantum wells, dots, and superlattices), are obtained as special cases. The discussion in Secs. III–VI concentrates on a model system in which the material part of the Hamiltonian conserves the number of electron-hole pairs. This applies to many weakly correlated organic and semiconductor materials (conjugated polyenes have some noticeable correlation effects and do not fall into this category). We introduce the dynamics-controlled truncation, identify the relevant dynamic variables, and relate them to observables in Sec. III. In Sec. IV we study the coherent limit, i.e., the idealized situation without phonon coupling. In this case the problem is shown to reduce to the combined dynamics of one- and two-pair interband transition densities. When phonon interactions are taken into account, one has to study in addition the dynamics of intraband coherences and occupation densities. For a system of Frenkel excitons it has been shown (Axt and Mukamel, 1997a) that a rigorous formulation of the dynamics can be obtained by looking at the time evolution of a suitable set of generating functions. In Appendix A we extend this method to the many-electron system, deriving closed equations of motion for the relevant generating functions, representing a rigorous description of the optical response up to third order in the laser field including phonons. Taking these equations as a starting point, we work out in Sec. V an approximate reduction scheme, based on eliminating the phonon degrees of freedom perturbatively. The resulting physical implications are discussed. Our final equations are formulated in the exciton representation. This facilitates a comparison with the Frenkel exciton model (see Sec. VII) and allows us to address long-time relaxation properties in a very natural way. In particular, it is shown that our treatment leads to a thermalization into excitonic occupation densities at long times. Our specific implementation of the exciton representation has the distinguishing feature (Schäfer *et al.*, 1996) that the anticommutation properties of the two-pair transition density, required by the Pauli principle, are preserved even for a truncated scheme that keeps only a finite number of excitons. In Sec. VI we establish the connection with the widely used semiconductor Bloch equations and discuss under which circumstances the results of our approach are expected to differ from the predictions of these equations. The Hamiltonian for interacting Frenkel excitons commonly used in modeling molecular materials is introduced in Sec. VII. We demonstrate that the Frenkel exciton model and its many-electron counterpart lead to formally equivalent equations of motion, despite their different microscopic formulation. Section VIII offers some concluding remarks.

II. THE MICROSCOPIC MANY-ELECTRON MODEL

A system of nonrelativistic electrons interacting with nuclear degrees of freedom (phonons) and with a coherent laser field can generally be represented by the Hamiltonian

$$H \equiv H_{\text{mat}} + H_{\text{ph}} + H_{\text{ep}} + H_{\text{opt}}, \tag{1}$$

where H_{mat} and H_{ph} are the Hamiltonians for isolated electronic and phonon degrees of freedom, while H_{ep} and H_{opt} describe the interactions between electrons and phonons and the coupling to the laser field, respectively. The material part H_{mat} can be further decomposed into a hopping (transfer) contribution H_{hop} and the electron-electron Coulomb interaction,

$$H_{\text{mat}} \equiv H_{\text{hop}} + H_{\text{Coul}}, \tag{2}$$

$$H_{\text{hop}} \equiv \sum_{mn} t_{mn} c_m^\dagger c_n, \tag{3}$$

$$H_{\text{Coul}} \equiv \frac{1}{2} \sum_{ijnm} V_{ijnm} c_i^\dagger c_j c_n^\dagger c_m, \tag{4}$$

$$V_{ijnm} \equiv \int d^3x \int d^3y \, \varphi_i^*(x) \varphi_j(x)$$
$$\times V(x-y) \varphi_n^*(y) \varphi_m(y), \tag{5}$$

where $V(x)$ is the Coulomb potential. The fermion operators $c_n^\dagger$ and c_n create and annihilate electrons in orthogonal single-particle atomic orbitals $\varphi_n(x)$. The label n represents in the most general case the sites j_n, where the orbitals are localized, as well as the spins σ_n and the electronic state of the atom ν_n. This general formulation of the material part is the basis for all standard quantum chemistry treatments of molecular structure, including *ab initio* and semiempirical methods (Szabo and Ostlund, 1989; Fulde, 1991). A recent application to the optical response of semiconductor nanocrystals starting with this model has been worked out by Yokojima *et al.* (1997). The semiempirical models commonly used for the π electrons in polyenes are obtained as special cases, when the hopping-matrix element t_{nm} is restricted to nearest-neighbor coupling alternating from site to site, and the atomic orbitals are strongly localized, resulting in the approximation for the Coulomb matrix element $V_{ijnm} \approx \delta_{ij} \delta_{nm} V_{jn}$. Furthermore, at each site usually only one electronic state (with two possible directions for the spin) is considered, making the index ν_n redundant in this case. In the Pariser-Parr-Pople model

the potential V_{jn} is taken to be of the Ohno form $V_{jn} = U/\sqrt{1+(r_{jn}/a_0)^2}$ (Ohno, 1964; Soos, 1994), while in extended Hubbard models only the interaction between next neighbors is retained (Baeriswyl *et al.*, 1992).

The free phonon Hamiltonian reads

$$H_{\text{ph}} = \sum_{\mu} \hbar \omega_{\mu} b_{\mu}^{\dagger} b_{\mu}, \tag{6}$$

where $b_{\mu}^{\dagger}(b_{\mu})$ are Bose operators creating (annihilating) a phonon in mode μ with energy $\hbar \omega_{\mu}$, and satisfying the commutation relations

$$[b_{\mu}, b_{\lambda}^{\dagger}] = \delta_{\mu\lambda}. \tag{7}$$

We assume that the electron-phonon interaction is linear in the phonon operators,

$$H_{\text{ep}} = \sum_{nm\mu} (\gamma_{nm}^{\mu} c_n^{\dagger} c_m b_{\mu}^{\dagger} + \gamma_{nm}^{\mu *} c_m^{\dagger} c_n b_{\mu}). \tag{8}$$

In Eq. (8) we have followed the common practice of retaining only the lowest-order contribution of an expansion of the transfer-coupling-matrix elements [t_{mn} in Eq. (3)] with respect to deviations of the nuclei positions from their equilibrium values. These contributions are expected to be dominant. A more general treatment would take into account higher-order terms of this expansion as well as contributions resulting from the corresponding expansion of the Coulomb matrix elements (Szabo and Ostlund, 1989). The latter would include interactions involving four electronic operators and one or more phonon operators.

Finally, the coupling to the optical field $\mathbf{E}(t)$ is represented by

$$H_{\text{opt}} = -\mathbf{E}(t)\hat{\mathbf{P}}, \tag{9}$$

with the polarization operator

$$\hat{\mathbf{P}} = \sum_{nm} \mathbf{M}_{nm} c_n^{\dagger} c_m \tag{10}$$

and the dipole matrix element

$$\mathbf{M}_{nm} \equiv -e \langle \varphi_n | \mathbf{X} | \varphi_m \rangle. \tag{11}$$

For simplicity, we consider a spatially homogeneous electric field. An extension to include the space dependence of the field is straightforward (Huhn and Stahl, 1984; Axt and Stahl, 1994a, 1994b; Belleguie and Mukamel, 1994, 1995; Chernyak *et al.*, 1995) and is important for an analysis of propagation effects, examples of which have been studied by Stahl and Balslev (1982, 1987), Huhn (1986), Knorr *et al.* (1995), and Stroucken *et al.* (1996).

It will be advantageous for our further analysis to rewrite the Hamiltonian using the Hartree-Fock molecular orbital (HFMO) representation. To this end we introduce the transformed fermion operators

$$\overline{c}_k^{\dagger} \equiv \sum_j \varphi_j^k c_j^{\dagger}, \tag{12}$$

where φ_j^k are the orthonormal solutions of the Hartree-Fock eigenvalue problem

$$\sum_j h_{aj} \varphi_j^k = \epsilon_k \varphi_a^k, \tag{13}$$

with the Fock matrix

$$h_{ab} \equiv t_{ab} + \sum_{ij} (V_{ijab} - V_{ajib}) \rho_{ij}^0, \tag{14}$$

and ρ^0 is the density matrix representing the Hartree-Fock ground-state. Technical details of the transformations are explained by Hartmann and Mukamel (1993) and Takahashi and Mukamel, 1994. The HFMO representation allows for an easy distinction between occupied and unoccupied states with respect to the Hartree-Fock ground state. Hereafter we refer to initially unoccupied states as electrons and initially occupied states as holes. We shall introduce creation and annihilation operators, $\overline{d}^{\dagger}$ and $\overline{d}$, respectively, for holes by setting $\overline{d}_q^{\dagger} \equiv \overline{c}_q$ for all initially occupied states q. The material part of the Hamiltonian in this basis set reads

$$\overline{H}_{\text{mat}} = \overline{H}_{\text{mat}}^{(0)} + \overline{H}_{\text{mat}}^{(1)} + \overline{H}_{\text{mat}}^{(2)} + E_{\text{full}}, \tag{15}$$

$$\begin{aligned}
\overline{H}_{\text{mat}}^{(0)} = &\sum_{q=\text{e}} \epsilon_q^{\text{e}} \overline{c}_q^{\dagger} \overline{c}_q - \sum_{q=\text{h}} \epsilon_q^{\text{h}} \overline{d}_q^{\dagger} \overline{d}_q \\
&+ \sum_{\substack{pq=\text{h} \\ kl=\text{e}}} (\overline{V}_{plkq}^{\text{heeh}} - \overline{V}_{pqkl}^{\text{hhee}}) \overline{c}_k^{\dagger} \overline{d}_q^{\dagger} \overline{d}_p \overline{c}_l \\
&+ \frac{1}{2}\Bigg[\sum_{pqkl=\text{e}} \overline{V}_{pqkl}^{\text{eeee}} \overline{c}_p^{\dagger} \overline{c}_k^{\dagger} \overline{c}_l \overline{c}_q + \sum_{pqkl=\text{h}} \overline{V}_{pqkl}^{\text{hhhh}} \overline{d}_q^{\dagger} \overline{d}_l^{\dagger} \overline{d}_k \overline{d}_p \\
&+ V(0)\Bigg(\sum_{q=\text{e}} \overline{c}_q^{\dagger} \overline{c}_q - \sum_{q=\text{h}} \overline{d}_q^{\dagger} \overline{d}_q \Bigg)\Bigg],
\end{aligned} \tag{16}$$

$$\begin{aligned}
\overline{H}_{\text{mat}}^{(1)} = \frac{1}{2}\Bigg[&\sum_{\substack{qkl=\text{h} \\ p=\text{e}}} (\overline{V}_{kqpl}^{\text{hheh}} - \overline{V}_{pqkl}^{\text{ehhh}}) \overline{c}_p^{\dagger} \overline{d}_q^{\dagger} \overline{d}_l^{\dagger} \overline{d}_k \\
&+ \sum_{\substack{pkl=\text{h} \\ q=\text{e}}} (\overline{V}_{pqkl}^{\text{hehh}} - \overline{V}_{plkq}^{\text{hhhe}}) \overline{d}_l^{\dagger} \overline{d}_p \overline{d}_k \overline{c}_q \\
&+ \sum_{\substack{pql=\text{e} \\ k=\text{h}}} (\overline{V}_{pqkl}^{\text{eehe}} - \overline{V}_{kqpl}^{\text{heee}}) \overline{c}_p^{\dagger} \overline{c}_q \overline{d}_k \overline{c}_l \\
&+ \sum_{\substack{pkl=\text{e} \\ q=\text{h}}} (\overline{V}_{pqkl}^{\text{ehee}} - \overline{V}_{plkq}^{\text{eeeh}}) \overline{c}_p^{\dagger} \overline{d}_q^{\dagger} \overline{c}_k^{\dagger} \overline{c}_l \Bigg],
\end{aligned} \tag{17}$$

$$\overline{H}_{\text{mat}}^{(2)} = \frac{1}{2}\Bigg[\sum_{\substack{pk=\text{e} \\ ql=\text{h}}} \overline{V}_{pqkl}^{\text{eheh}} \overline{c}_p^{\dagger} \overline{d}_q^{\dagger} \overline{c}_k^{\dagger} \overline{d}_l^{\dagger} + \sum_{\substack{pk=\text{h} \\ ql=\text{e}}} \overline{V}_{pqkl}^{\text{hehe}} \overline{d}_p \overline{c}_q \overline{d}_k \overline{c}_l \Bigg], \tag{18}$$

with

$$\overline{V}_{pqkl} \equiv \sum_{ijnm} V_{ijnm} \varphi_i^{p*} \varphi_j^q \varphi_n^{k*} \varphi_m^l. \tag{19}$$

We have used Eq. (13) and the identity

$$\sum_k \overline{V}_{akkb} = V(0) \delta_{ab}, \tag{20}$$

and $V(x-y)$ was defined in Eq. (5). To make it easier to

identify the type of particle (e or h), we have indicated this information as upper indices of the matrix elements. $\bar{H}_{\mathrm{mat}}$ can be naturally decomposed into three contributions $\bar{H}_{\mathrm{mat}}^{(j)}$, $j=0,1,2$, that change the number of electron-hole pairs by j pairs. E_{full} is a constant representing the energy of the filled valence states. In the following sections we shall concentrate on a simpler model system, in which only the pair-conserving part $H_{\mathrm{mat}}^{(0)}$ is retained. Many-electron models that retain only pair-conserving terms form the starting point for most calculations of the optical response of direct-gap semiconductors (Stahl and Balslev, 1987; Haug, 1988; Zimmermann, 1988; Haug and Koch, 1993) and semiconductor nanocrystals (Hill and Wahley, 1993, 1994, 1995). Non-pair-conserving terms of course play a role in the dielectric screening, but otherwise are not usually needed in dealing with excitations in the vicinity of the gap (Haug, 1988). The reason is that typically in direct-gap semiconductors the optical gap ($\sim$eV) is large compared to the exciton binding energy ($\sim$meV), which implies that the Coulomb interaction can be regarded as a small correction to the single-particle energies. At high excitation non-pair-conserving processes associated with impact ionization or Auger recombination may take place (Quade *et al.*, 1992, 1994). Impact ionization is, however, effective only when the excitation is at about twice the optical gap, while Auger recombination requires higher excitation densities.

Let us now take a closer look at the various contributions to $\bar{H}_{\mathrm{mat}}^{(0)}$. First we note that the last term, proportional to $V(0)$, does not contribute to the dynamics, since we are dealing with a system with a fixed number of particles, so that the total number of electrons always equals the total number of holes. The remaining terms can be further classified into direct- and exchange-type. When the site arguments in the Coulomb integral can be combined to give electron or hole densities of the respective atomic orbitals, we shall refer to the terms as direct-type contributions. These correspond in our notation to matrix elements of the types $\bar{V}_{\mathrm{hhee}}$, $\bar{V}_{\mathrm{eehh}}$, $\bar{V}_{\mathrm{eeee}}$, and $\bar{V}_{\mathrm{hhhh}}$. Most calculations for direct-gap semiconductors neglect the remaining exchange contributions $\bar{V}_{\mathrm{heeh}}$ and $\bar{V}_{\mathrm{ehhe}}$. Observable effects related to exchange interactions are the splitting between longitudinal and transverse excitons and the details of the energy structure of excitons and biexcitons (Haken, 1963; Bassani and Pastori Parravicini, 1975, Egri, 1985; Ungier, 1989). For direct-gap bulk semiconductors these are usually minor corrections, while noticeable influences have been reported for nanocrystals (Yokojima *et al.*, 1997). A measure of the importance of exchange terms is provided by the ratio between the transverse-longitudinal exciton splitting and the exciton binding energy. The approximation of keeping only the direct Coulomb interaction and neglecting non-pair-conserving as well as exchange-type contributions is viewed in a slightly different perspective when the Coulomb matrix elements are analyzed in a real-space basis set defined, for example, by the Wannier functions for bulk semiconductors (Huhn and Stahl, 1984; Egri, 1985; Stahl, 1988) or more generally by localized molecular orbitals (Foster and Boys, 1960; Edmiston and Ruedenberg, 1963; Fulde, 1991). One can then use the localization properties of the orbitals to perform a multipolar expansion of the Coulomb integrals; the various contributions to the Coulomb interaction can then be interpreted electrodynamically as interactions between multipoles. To leading order the direct interaction equals the monopole-monopole interaction, while the other contributions are, in leading order, either of monopole-dipole or dipole-dipole type (Huhn and Stahl, 1984; Egri, 1985; Stahl, 1988). The monopole-monopole part is the only long-range contribution and is consequently dominant in systems where the electron-hole pairs are only loosely bound (i.e., spatially well separated), as indicated by the large Bohr radii of typical Wannier excitons.

The parts of the Hamiltonian involving phonons in the Hartree-Fock molecular orbital representation read

$$\bar{H}_{\mathrm{ph}}=H_{\mathrm{ph}}=\sum_{\mu}\hbar\omega_{\mu}b_{\mu}^{\dagger}b_{\mu}, \tag{21}$$

$$\bar{H}_{\mathrm{ep}}=\bar{H}_{\mathrm{ep}}^{(0)}+\bar{H}_{\mathrm{ep}}^{(1)}+\bar{H}_{\mathrm{ep}}^{(f)}, \tag{22}$$

$$\bar{H}_{\mathrm{ep}}^{(0)}=\sum_{pq=\mathrm{e},\mu}(\bar{\gamma}_{pq}^{\mu}\bar{c}_{p}^{\dagger}\bar{c}_{q}b_{\mu}^{\dagger}+\bar{\gamma}_{pq}^{\mu*}\bar{c}_{q}^{\dagger}\bar{c}_{p}b_{\mu})$$
$$-\sum_{pq=\mathrm{h},\mu}(\bar{\gamma}_{pq}^{\mu}\bar{d}_{q}^{\dagger}\bar{d}_{p}b_{\mu}^{\dagger}+\bar{\gamma}_{pq}^{\mu*}\bar{d}_{p}^{\dagger}\bar{d}_{q}b_{\mu}), \tag{23}$$

$$\bar{H}_{\mathrm{ep}}^{(1)}=\sum_{\substack{p=\mathrm{h},\mu \\ q=\mathrm{e}}}(\bar{\gamma}_{pq}^{\mu}\bar{d}_{p}\bar{c}_{q}b_{\mu}^{\dagger}+\bar{\gamma}_{pq}^{\mu*}\bar{c}_{q}^{\dagger}\bar{d}_{p}^{\dagger}b_{\mu})$$
$$+\sum_{\substack{p=\mathrm{e},\mu \\ q=\mathrm{h}}}(\bar{\gamma}_{pq}^{\mu}\bar{c}_{p}^{\dagger}\bar{d}_{q}^{\dagger}b_{\mu}^{\dagger}+\bar{\gamma}_{pq}^{\mu*}\bar{d}_{q}\bar{c}_{p}b_{\mu}), \tag{24}$$

$$\bar{H}_{\mathrm{ep}}^{(f)}=\sum_{pq=\mathrm{h},\mu}(\bar{\gamma}_{pq}^{\mu}b_{\mu}^{\dagger}+\bar{\gamma}_{pq}^{\mu*}b_{\mu})\delta_{pq}, \tag{25}$$

$$\bar{\gamma}_{pq}^{\mu}\equiv\sum_{nm}\varphi_{n}^{p*}\varphi_{m}^{q}\gamma_{nm}^{\mu}. \tag{26}$$

First we note that $\bar{H}^{(f)}$, which acts only on the phonon degrees of freedom, represents the interaction energy of the phonons with the filled valence states and does not contribute to the coupling with holes. We shall drop this term. As in the Coulomb interaction case, we obtain contributions $\bar{H}_{\mathrm{ep}}^{(j)}$ that may or may not conserve the number of electron-hole pairs. In contrast to the Coulomb case, however, there is no term that changes the number of pairs by two. $\bar{H}_{\mathrm{ep}}^{(1)}$ changes the number of electron-hole pairs by only one and describes phonon-induced transitions across the gap between occupied and unoccupied states. Such transitions are not energetically favored in many materials and will be neglected as well in the following discussion.

Finally, we obtain for the coupling to the laser field in the HFMO representation

$$\bar{H}_{\mathrm{opt}}=-\mathbf{E}\hat{\bar{\mathbf{P}}}, \tag{27}$$

$$\hat{\bar{\mathbf{P}}} = \sum_{p=h,q=e} \bar{\mathbf{M}}_{pq}^{he} \bar{d}_p \bar{c}_q + \sum_{p=e,q=h} \bar{\mathbf{M}}_{pq}^{eh} \bar{c}_p^\dagger \bar{d}_q^\dagger$$

$$+ \sum_{pq=e} \bar{\mathbf{M}}_{pq}^{ee} \bar{c}_p^\dagger \bar{c}_q - \sum_{pq=h} \bar{\mathbf{M}}_{pq}^{hh} \bar{d}_q^\dagger \bar{d}_p + \bar{\mathbf{P}}_{stat}, \quad (28)$$

$$\bar{\mathbf{M}}_{pq} \equiv \sum_{nm} \varphi_n^{p*} \varphi_m^q \mathbf{M}_{nm}, \quad (29)$$

where $\bar{\mathbf{P}}_{stat}$ is the static polarization of the system.

Although the above model is quite general, relativistic effects are left out completely. The most important of these is the spin-orbit coupling, which leads in many semiconductors to splittings [350 meV in GaAs (Hilsum, 1966)] between the topmost and "split-off" bands. However, as the task of determining the single-particle energies (band structure) can be performed independently from an analysis of the dynamics introduced by the laser field, the main relativistic effects can be accounted for by a simple renormalization of the single-particle energies.

III. GENERATING FUNCTIONS FOR COUPLED EXCITON-PHONON VARIABLES

In this and in the following sections we shall analyze the dynamics of a system described by our many-electron model, when only the electron-hole pair-conserving contributions are taken into account. This will be done on various levels of sophistication. In the present section we explain how the hierarchy of equations of motion can be systematically truncated, resulting in a rigorous scheme for calculating the third-order nonlinear response including phonons. The relevant dynamical variables are introduced, while their coupled equations of motion are given in Appendix A. In Secs. IV and V this formulation will be used as a starting point for the derivation of simplified schemes, better suited for specific calculations.

According to Eqs. (15), (21), (22), and (27), our model is defined by the Hamiltonian

$$\bar{H} \equiv \bar{H}_{mat}^{(0)} + \bar{H}_{ph} + \bar{H}_{ep}^{(0)} + \bar{H}_{opt}. \quad (30)$$

The most interesting dynamical variables for the optical response are the components of the one-particle (two-point) density matrix. Using the definitions

$$Y_{ab} \equiv \langle \bar{d}_a \bar{c}_b \rangle, \quad C_{ab} \equiv \langle \bar{c}_a^\dagger \bar{c}_b \rangle, \quad D_{ab} \equiv \langle \bar{d}_a^\dagger \bar{d}_b \rangle, \quad (31)$$

we can decompose the one-particle density matrix as

$$\bar{\rho}_{ab} = \bar{\rho}_{ab}^0 + \delta_a^e \delta_b^e C_{ab} - \delta_a^h \delta_b^h D_{ba} + \delta_a^e \delta_b^h Y_{ab}$$

$$+ \delta_a^e \delta_b^h Y_{ba}^*, \quad (32)$$

with

$$\delta_a^{e/h} \equiv \begin{cases} 1 & \text{when } a \text{ refers to an electron/hole,} \\ 0 & \text{otherwise,} \end{cases} \quad (33)$$

where $\bar{\rho}_{ab}^0 = \delta_a^h \delta_b^h \delta_{ab}$ is the ground-state Hartree-Fock density matrix. The quantum-mechanical average represented by the brackets $\langle \cdots \rangle$ in Eq. (31) is defined in the usual way as a trace over the respective operators times the density matrix of the many-body system. In the Heisenberg picture the many-body density matrix is independent of time while the operators are time dependent. In the definition (31) a common time argument is assumed.

The electron-hole component Y_{ab} describes transitions across the optical gap, while C_{ab} and D_{ab} represent, respectively, electron and hole densities and coherences. All optical observables can be calculated from the polarization [cf. Eq. (28)], which in terms of these dynamical variables is given by

$$\bar{\mathbf{P}} \equiv \langle \hat{\bar{\mathbf{P}}} \rangle = \sum_{pq} \bar{\mathbf{M}}_{pq} \bar{\rho}_{pq}$$

$$= \sum_{p=h,q=e} \bar{\mathbf{M}}_{pq}^{he} Y_{pq} + \sum_{p=e,q=h} \bar{\mathbf{M}}_{pq}^{eh} Y_{qp}^*$$

$$+ \sum_{p,q=e} \bar{\mathbf{M}}_{pq}^{ee} C_{pq} - \sum_{p,q=h} \bar{\mathbf{M}}_{pq}^{hh} D_{qp} + \bar{\mathbf{P}}_{stat}. \quad (34)$$

Apart from the static part, we obtain two fundamentally different types of contributions: those arising from the creation of electron-hole pairs (interband transitions $\propto Y, Y^*$) and those involving transitions within the electron or hole manifold (intraband transitions $\propto C, D$). For many systems, especially bulk semiconductors, the intraband dipole matrix elements are either forbidden by symmetry or significantly smaller than their interband counterparts and are therefore often neglected. However, for geometrically restricted systems such as quantum wells, superlattices, or nanocrystals, these terms can be important.

Our goal is to calculate the polarization, which is a complicated many-body problem. The equations of motion for the one-particle density matrix are not closed, coupling to higher density matrices in an infinite hierarchy. The functions on each level are coupled to more complicated dynamical objects (higher-order density matrices), forming the next higher level of the hierarchy. Any practical method derived from this hierarchy must provide a recipe for truncation in order to obtain a closed set of equations. The dynamics-controlled truncation relies on the fact that, in a model defined by Eq. (30), all higher-order correlations are ultimately induced by the optical field. As a consequence, there is a close relation between the leading order in the laser field of any given density matrix and the level where this function first enters the hierarchy. For the many-electron system described by the Hamiltonian (30), this relation can be summarized as follows.

Let $\hat{A}_n$ denote the normal-ordered product of $n = n_e + n_h$ Fermi operators $\bar{c}^\dagger$, $\bar{c}$, $\bar{d}^\dagger$, and $\bar{d}$ and an arbitrary number of phonon operators $b^\dagger, b$, where the normal ordering is understood with respect to the electron-hole representation (i.e., all operators $\bar{c}^\dagger, \bar{d}^\dagger$ stand to the left of $\bar{c}, \bar{d}$), n_e is the total number of electron operators $\bar{c}^\dagger, \bar{c}$, and n_h is the total number of hole

operators $\bar{d}^\dagger, \bar{d}$. When the system is initially in the Hartree-Fock ground state, it then follows for the expectation value of $\hat{A}_n$ that

$$\langle \hat{A}_n \rangle = \mathcal{O}(E^m), \quad \text{with} \quad m = \max(n_e, n_h). \tag{35}$$

A formal proof can be found in Axt and Stahl (1994a). It is analogous to a similar relation proven for Frenkel excitons [Spano and Mukamel, 1991a, 1991b; Mukamel, 1994; see also Eq. (102)]. The significance of this observation is that higher-order correlation functions are also of higher order in the laser field, and thus only a finite number of electronic density matrices contributes to the optical response at any prescribed order. In the dynamics-controlled truncation approach this is used to truncate the hierarchy, retaining only those density matrices that contribute to a given order. Applications have been worked out taking the cut at either the third order (Dubovsky and Mukamel, 1991; Knoester and Mukamel, 1991; Leegwater and Mukamel, 1992; Axt and Stahl, 1994b; Axt *et al.*, 1995; Östreich *et al.*, 1995a, 1995b; Axt, Victor, and Stahl, 1996; Schäfer *et al.*, 1996) or the fifth order (Bartels *et al.*, 1995).

The influence of the phonon system on the coupled dynamics of higher-order density matrices is often accounted for by phenomenological damping constants or by simple stochastic approaches such as the Haken-Strobl model (Leegwater and Mukamel, 1992). Perturbative calculations of these effects using phonon-induced self-energies have been made in some cases (Dubovsky and Mukamel, 1991; Chernyak *et al.*, 1995; Axt, Victor, and Stahl, 1996). In this section we develop a rigorous procedure for the derivation of a closed set of equations of motion for a finite number of dynamical variables when phonons are taken into account to third order in the radiation field. This is done by introducing the following five generating functions for phonon-assisted electronic density matrices:

$$Y_{ab}^{\alpha\beta} \equiv \langle \bar{d}_a \bar{c}_b \hat{F}^{\alpha\beta} \rangle, \tag{36}$$

$$B_{abcd}^{\alpha\beta} \equiv \langle \bar{d}_a \bar{c}_b \bar{d}_c \bar{c}_d \hat{F}^{\alpha\beta} \rangle, \tag{37}$$

$$N_{abcd}^{\alpha\beta} \equiv \langle \bar{c}_a^\dagger \bar{d}_b^\dagger \bar{d}_c \bar{c}_d \hat{F}^{\alpha\beta} \rangle, \tag{38}$$

$$Z_{abcdef}^{\alpha\beta} \equiv \langle \bar{c}_a^\dagger \bar{d}_b^\dagger \bar{d}_c \bar{c}_d \bar{d}_e \bar{c}_f \hat{F}^{\alpha\beta} \rangle, \tag{39}$$

$$F^{\alpha\beta} \equiv \langle \hat{F}^{\alpha\beta} \rangle \equiv \langle \hat{F}(\{\alpha_\mu\}, \{\beta_\mu\}) \rangle$$
$$\equiv \left\langle \left(\exp\left(\sum_\mu \alpha_\mu b_\mu^\dagger \right) \right) \left(\exp\left(\sum_\mu \beta_\mu b_\mu \right) \right) \right\rangle. \tag{40}$$

where $\{\alpha_\mu\}$ and $\{\beta_\mu\}$ represent arbitrary sets of real parameters. The shorthand notation α, β in the arguments of these functions denotes the respective sets of parameters. Each of these variables represents a phonon wave packet associated with a given electronic density matrix. The generating-function property implies that all phonon-assisted electronic density matrices can be obtained as derivatives of these functions taken at $\alpha_\mu = \beta_\mu = 0$, e.g.,

$$\frac{\partial^k}{\partial_{\alpha_{\mu_1}} \cdots \partial_{\alpha_{\mu_k}}} \frac{\partial^l}{\partial_{\beta_{\lambda_1}} \cdots \partial_{\beta_{\lambda_l}}} Y_{ab}^{\alpha\beta}|_{\alpha=\beta=0}$$
$$= \langle \bar{d}_a \bar{c}_b b_{\mu_1}^\dagger \cdots b_{\mu_k}^\dagger b_{\lambda_1} \cdots b_{\lambda_l} \rangle. \tag{41}$$

Starting with the Heisenberg equations $i\hbar \dot{A} = [A, H]$, using the Hamiltonian (30), it is straightforward to derive equations of motion for these functions. Neglecting terms that do not contribute to the third-order response, we obtain a closed set of nonlinear partial differential equations coupling the generating functions (36)–(40). The resulting equations [Eqs. (A1)–(A5) given in Appendix A] constitute our most general result and form the basis for the various approximation schemes to be developed in this article. It should be noted that these equations contain the electron-hole variable Y but do not include the intraband variables C and D necessary for computing the intraband part of the polarization (34). However, once solutions to Eqs. (A1)–(A5) are found, the components of the one-particle density matrix are obtained from the corresponding generating functions at the point $\alpha = \beta = 0$,

$$Y_{ab} = Y_{ab}^{\alpha=\beta=0}, \tag{42}$$

$$C_{ab} = C_{ab}^{\alpha=\beta=0} = \sum_{k=\text{h}} N_{akkb}^{\alpha=\beta=0}, \tag{43}$$

$$D_{ab} = D_{ab}^{\alpha=\beta=0} = \sum_{k=\text{e}} N_{kabk}^{\alpha=\beta=0}, \tag{44}$$

where we have used the identities (A21) and (A22).

IV. COHERENT DYNAMICS OF THE PURELY ELECTRONIC SYSTEM

In this section we treat the idealized limiting case of vanishing electron-phonon interaction $\bar{\gamma}^\mu \to 0$. This case is of interest for two reasons. First, the coherent dynamics represented by this limit dominates the early stages of optical experiments, in which the incoherent parts of the signal have not yet built up. In many types of materials, this time regime has become accessible in recent years due to the advent of femtosecond laser systems. Second, it is desirable to establish a clear understanding of this part of the dynamics in order to identify unambiguously signatures of incoherent processes. For vanishing electron-phonon coupling, a closed set of equations involving only the generating functions at $\alpha = \beta = 0$ can be obtained from Eqs. (A1)–(A5). However, instead of having to deal with five density matrices, it turns out that we need only two functions to describe the complete dynamics in this case (Axt and Stahl, 1994a, 1994b; Mukamel, 1994, 1995; Chernyak and Mukamel, 1995b, 1996b; Victor *et al.*, 1995). These are the one- and two-pair transition densities $(Y_{ab}, B_{abcd} \equiv B_{abcd}^{\alpha=\beta=0})$. F is trivially redundant, because at $\alpha = \beta = 0$ this function has the constant value of one. The remaining functions can be eliminated using the relations

$$N_{abcd} \equiv N_{abcd}^{\alpha=\beta=0} = Y_{ba}^* Y_{cd} + \mathcal{O}(E^4), \tag{45}$$

$$Z_{abcdef} \equiv Z_{abcdef}^{\alpha=\beta=0} = Y_{ba}^* B_{cdef} + \mathcal{O}(E^4). \tag{46}$$

These can easily be verified using the equations of motion (A1) and (A2) for Y and B in the limit $\bar{\gamma}^\mu \to 0$ and $\alpha = \beta = 0$, to show that the equations of motion (A3) and (A4) for N and Z are solved by the right-hand sides of Eqs. (45) and (46) in this limit. Equations (45) and (46) are the lowest-order results of a more general theorem (Victor *et al.*, 1995) in which, in the phonon-free case, all density matrices to any order in the laser field can be expressed by suitable combinations of transition amplitudes. For boson fields, like the electromagnetic field, it is common practice to take this fundamental characteristic of coherent dynamics—that variables representing intensities like N_{abcd} can be factorized into transition amplitudes—as a definition of coherence. A measure of the degree of coherence can then be defined using (normalized) deviations from the factorized values (Loudon, 1982; Mandel and Wolf, 1995). Because electron-hole pairs behave like bosons only in the low-intensity limit, there are corrections of higher order in the laser field to the simple factorizations (45) and (46), accounting for the deviations from Bose statistics. Nevertheless, all of these corrections can be expressed by transition amplitudes alone (Victor *et al.*, 1995). Thus this property could be used to generalize the common definition of coherence, used for Bose systems, to systems of electron-hole pairs. These considerations justify the identification of the phonon-free dynamics as the coherent limit.

Using Eqs. (A21)–(A24), (45), (46), (A1), and (A2), we obtain the following equations in the coherent limit:

$$i\hbar \partial_t Y_{ab} = \hbar \Omega_Y(Y)_{ab}$$

$$- \sum_{pq=e,kl=h} (\bar{V}_{pqka}^{eehh} - \bar{V}_{kqpa}^{heeh}) Y_{lp}^* B_{lqkb}$$

$$+ \sum_{pqk=e,l=h} \bar{V}_{bqkp}^{eeee} Y_{lk}^* B_{lpaq}$$

$$+ \sum_{pqk=h,l=e} \bar{V}_{kpqa}^{hhhh} Y_{pl}^* B_{klqb}$$

$$- \sum_{pq=h,kl=e} (\bar{V}_{bkpq}^{eehh} - \bar{V}_{bqpk}^{ehhe}) Y_{ql}^* B_{plak}$$

$$- \mathbf{E}\bigg(\bar{\mathbf{M}}_{ba}^{eh} - \sum_{k=h,l=e} \bar{\mathbf{M}}_{bk}^{eh} Y_{kl}^* Y_{al}$$

$$- \sum_{k=e,l=h} \bar{\mathbf{M}}_{ka}^{eh} Y_{lk}^* Y_{lb} + \sum_{k=e} \bar{\mathbf{M}}_{bk}^{ee} Y_{ak}$$

$$- \sum_{k=h} \bar{\mathbf{M}}_{ka}^{hh} Y_{kb} \bigg), \tag{47}$$

$$i\hbar \partial_t B_{abcd} = \hbar \Omega_B(B)_{abcd}$$

$$- \mathbf{E}(\bar{\mathbf{M}}_{dc}^{eh} Y_{ab} - \bar{\mathbf{M}}_{da}^{eh} Y_{cb} - \bar{\mathbf{M}}_{bc}^{eh} Y_{ad} + \bar{\mathbf{M}}_{ba}^{eh} Y_{cd})$$

$$- \mathbf{E}\bigg[\sum_{k=e} (\bar{\mathbf{M}}_{dk}^{ee} B_{abck} + \bar{\mathbf{M}}_{bk}^{ee} B_{akcd})$$

$$- \sum_{k=h} (\bar{\mathbf{M}}_{kc}^{hh} B_{abkd} + \bar{\mathbf{M}}_{ka}^{hh} B_{kbcd}) \bigg], \tag{48}$$

where the linear operators $\hbar \Omega_Y$ and $\hbar \Omega_B$ are defined in Eqs. (A8) and (A9) and the polarization is given by

$$\bar{\mathbf{P}}^{coh} = \sum_{p=h,q=e} \bar{\mathbf{M}}_{pq}^{he} Y_{pq} + \sum_{p=e,q=h} \bar{\mathbf{M}}_{pq}^{eh} Y_{qp}^*$$

$$+ \sum_{p,q=e,k=h} \bar{\mathbf{M}}_{pq}^{ee} Y_{kp}^* Y_{kq}$$

$$- \sum_{p,q=h,k=e} \bar{\mathbf{M}}_{pq}^{hh} Y_{qk}^* Y_{pk} + \bar{\mathbf{P}}_{stat}. \tag{49}$$

In these equations Y represents transitions involving single electron-hole pairs, while B accounts for two-pair transitions. Analogous equations have been derived for Frenkel excitons (Spano and Mukamel, 1991a, 1991b; Leegwater and Mukamel, 1992; Mukamel, 1994; see also Sec. VII).

Expanding these equations in the optical field, we find that the linear response can be derived from

$$i\hbar \partial_t Y_{ab}^{(1)} = \hbar \Omega_Y(Y^{(1)})_{ab} - \mathbf{E}\bar{\mathbf{M}}_{ba}^{eh}. \tag{50}$$

We thus obtain

$$Y_{ab}^{(1)} = \frac{i}{\hbar} \sum_x \int_{-\infty}^t dt' \, e^{-i\bar{\omega}_x(t-t')} \bar{\psi}_{ab}^x \bar{\mathbf{M}}_x \mathbf{E}(t'), \tag{51}$$

where the excitonic eigenfunctions $\bar{\psi}$ and eigenenergies $\bar{E}_x = \hbar \bar{\omega}_x$ are defined by the eigenvalue problem

$$\hbar \Omega_Y(\bar{\psi}^x)_{ab} = (\epsilon_b^e - \epsilon_a^h) \bar{\psi}_{ab}^x + \sum_{p=h,q=e} (\bar{V}_{pqba}^{heeh} - \bar{V}_{pabq}^{hhee}) \bar{\psi}_{pq}^x$$

$$= \bar{E}_x \bar{\psi}_{ab}^x, \tag{52}$$

and the excitonic dipole matrix elements are given by

$$\bar{\mathbf{M}}_x \equiv \sum_{ab} \bar{\psi}_{ab}^{x*} \bar{\mathbf{M}}_{ba}^{eh}. \tag{53}$$

Inserting this solution into Eq. (49) for the polarization and retaining only the linear part results in the classical Elliot formula for the linear susceptibility of exciton systems (Elliot, 1957; Stahl and Balslev, 1987; Haug and Koch, 1993). This simple formula already describes in a unified way many different physical situations. For small aggregates with only a few molecules, Eq. (52) can have only a limited number of eigenvalues, thus leading to a spectrum with only a few discrete lines. Another extreme is marked by bulk semiconductors. In this case Eq. (50) reduces to the Wannier equation, provided the exchange-type contributions $\propto \bar{V}^{heeh}$ to Eq. (52) are neglected and the direct-type Coulomb matrix elements

are treated according to standard approximations (Haken, 1973; Haug and Koch, 1993). We thus expect a spectrum consisting of a series of discrete lines and a continuum resulting from unbound (scattering) solutions. This continuum provides an intrinsic line broadening and will therefore lead to electronic dephasing due to destructive interference. Closed-form Green's-function solutions of the Wannier equation are available, thus avoiding the explicit determination of exciton eigenfunctions (Hostler, 1970; Stahl and Balslev, 1987). Nanocrystals are intermediate cases, in which the linear spectrum comprises a large number of lines, some of which are clustered energetically, eventually forming the continua characteristic of bulk crystals (Yokojima *et al.*, 1997).

We shall now turn to a discussion of two-pair transitions. Under the same conditions, whereby Eq. (50) reduces to an inhomogeneous hydrogenlike, Schrödinger-type equation (the Wannier equation), Eq. (48) transforms into an equation resembling a driven hydrogen molecule (Axt and Stahl, 1994a, 1994b). A typical spectrum of the operator $\hbar\Omega_B$ for bulk semiconductors consists of a very small number of discrete lines representing bound two-electron-hole pair states (biexcitons) and a continuum representing scattering of excitons. Formally it should be possible at this point to introduce eigenstates of $\hbar\Omega_B$ and recast the theory using coupled equations for exciton and biexciton amplitudes. However, this procedure is practical only when the response is dominated by few two-pair states (e.g., bound biexcitons), and provided reasonable approximations for the corresponding wave functions are available. For most systems the explicit determination of biexcitonic wave functions is numerically very demanding. It is therefore more useful to treat the two-pair transitions in terms of interacting excitons. Instead of dealing directly with the density matrix B, it is advantageous to remove uncorrelated (mean-field or unlinked) contributions by defining a new dynamic object $\bar{B}$ that carries the information on genuine many-particle correlations according to the "cluster" decomposition (Wang and Cassing, 1985; Bartels *et al.*, 1995; Axt, Victor, and Stahl, 1996; Schäfer *et al.*, 1996; Axt and Mukamel, 1997b)

$$B_{abcd} = Y_{ab}Y_{cd} - Y_{cb}Y_{ad} + \bar{B}_{abcd}. \tag{54}$$

Using an exciton eigenfunction representation of Y and $\bar{B}$ [and according to Eq. (54) of B] in the form

$$Y_{ab} = \sum_x \bar{\psi}_{ab}^x y_x, \tag{55}$$

$$\bar{B}_{abcd} = \sum_{\bar{x}x} (\bar{\psi}_{ab}^{\bar{x}} \bar{\psi}_{cd}^x - \bar{\psi}_{cb}^{\bar{x}} \bar{\psi}_{ad}^x) b_{\bar{x}x}, \tag{56}$$

$$B_{abcd} = \sum_{\bar{x}x} (\bar{\psi}_{ab}^{\bar{x}} \bar{\psi}_{cd}^x - \bar{\psi}_{cb}^{\bar{x}} \bar{\psi}_{ad}^x)(b_{\bar{x}x} + y_{\bar{x}}y_x), \tag{57}$$

we find that Eqs. (47) and (48) transform into

$$i\hbar\partial_t y_x = \bar{E}_x y_x + \sum_{\bar{x}\bar{x}'x'} \bar{V}_x^{\bar{x}\bar{x}'x'} y_{\bar{x}}^*(y_{\bar{x}'}y_{x'} + b_{\bar{x}'x'})$$
$$- \mathbf{E}\left(\bar{\mathbf{M}}_x - \sum_{\bar{x}'x'} \bar{\mathbf{M}}_x^{\bar{x}'x'} y_{\bar{x}'}^* y_{x'} - \sum_{x'} \bar{\mathbf{M}}_x^{x'} y_{x'} \right), \tag{58}$$

$$i\hbar\partial_t b_{\bar{x}x} = (\bar{E}_{\bar{x}} + \bar{E}_x) b_{\bar{x}x} + \sum_{\bar{x}'x'} \bar{V}_{\bar{x}x}^{\bar{x}'x'} (b_{\bar{x}'x'} + y_{\bar{x}'}y_{x'})$$
$$+ \mathbf{E}\left(\sum_{x'} \bar{\mathbf{M}}_x^{x'} b_{\bar{x}x'} + \sum_{\bar{x}'} \bar{\mathbf{M}}_{\bar{x}}^{\bar{x}'} b_{\bar{x}'x} \right), \tag{59}$$

where the derivation as well as the coefficients $\bar{V}_x^{\bar{x}\bar{x}'x'}$, $\bar{V}_{\bar{x}x}^{\bar{x}'x'}$, $\bar{\mathbf{M}}_x^{\bar{x}'x'}$ and $\bar{\mathbf{M}}_x^{x'}$ are given in Appendix C. It is worth noting that the fundamental anticommutation property

$$\bar{B}_{abcd} = -\bar{B}_{cbad} = -\bar{B}_{adcb} = \bar{B}_{cdab} \tag{60}$$

is satisfied in Eq. (57) by each term of the expansion separately (note, that $b_{\bar{x}x} = b_{x\bar{x}}$ in this representation). This property is particularly important when, instead of using the complete set of exciton eigenfunctions, one truncates the summation in Eq. (57), keeping only a limited set of basis functions. Approximations of this type are necessary for many systems in order to keep the numerics manageable.

The physical origin of the various contributions to Eqs. (58) and (59) is readily understood. The homogeneous parts represent the quasiparticle energies of excitons and two-exciton states (unbound and bound biexcitons). Since we are working in the exciton basis set, the former is diagonal, while the latter also comprises off-diagonal parts [$\propto \bar{V}b$ in Eq. (59)], describing the interaction between excitons. The sources to y proportional to the optical field can be classified as linear and nonlinear. The source $\propto \mathbf{E}y^*y$ is known as "phase-space filling" and describes saturation effects due to Pauli blocking. The term $\propto \mathbf{E}y$ accounts for intraband transitions, including the effects of quasistatic fields on the linear absorption; corresponding terms also appear in the equations for b. The y^*yy term is the coherent limit of the mean-field contribution to the Coulomb interaction (cf. Sec. VI); it has been called a "static exciton-exciton interaction" by Schäfer *et al.* (1996). For bulk semiconductors treated in k-space, this term is usually split into two contributions that can be combined with the linear Coulomb interaction in a form suggesting an interpretation as renormalizations of the band gap and the optical field (Rabi frequency), respectively (Kuhn and Rossi, 1992; Haug and Koch, 1993; Kuhn *et al.*, 1994). A simplified treatment of this term is also known as the "local-field model" (Mukamel *et al.*, 1988; Wegener *et al.*, 1990; Spano *et al.*, 1991; Weiss *et al.*, 1992; Chemla *et al.*, 1994). The contribution $\propto y^*b$ accounts for genuine many-particle correlations arising from the interaction between excitons, including the formation of bound biexcitons. Furthermore, it has been shown by Schäfer

et al. (1996) that the continuum part of *b* can be understood as a microscopic description of processes referred to as ''excitation-induced dephasing,'' a feature discussed by Wang *et al.* (1993, 1994), Hu *et al.* (1994), and Rappen *et al.* (1994). Physical issues that can be addressed on this level of sophistication include the observation of a signal for negative delays in standard four-wave-mixing (FWM) experiments (Leo *et al.*, 1990, 1991; Wegener *et al.*, 1990; Schmitt-Rink *et al.*, 1991) and the deviation of time-resolved FWM signals from the free-induction decay expected from a two-level description (Wegener *et al.*, 1990; Kim *et al.*, 1992; Schäfer *et al.*, 1993). Contributions to these effects arise from the mean-field part as well as from two-pair correlations. The influence of the two-particle correlations *b* is most pronounced in experiments that probe biexcitonic resonances (Miller *et al.*, 1982; Cingolani *et al.*, 1988; Hulin and Joffre, 1990; Feuerbacher *et al.*, 1991; Lovering *et al.*, 1992; Raj *et al.*, 1992; Carmel and Bar-Joseph, 1993; Axt and Stahl, 1994b; Kim *et al.*, 1994; Pantke and Hvam, 1994; Saiki *et al.*, 1994; Vengurlikar *et al.*, 1994; Bartels *et al.*, 1995; Kreller *et al.*, 1995; Häupl *et al.*, 1996; Nickolaus *et al.*, 1996). Apart from that, bound biexcitons as well as two-exciton scattering states (excitation-induced dephasing contributions) are necessary for interpreting the dependence of four-wave-mixing and pump-probe measurements on the polarization of light (Schmitt-Rink *et al.*, 1992; Bennhardt *et al.*, 1993; Wang *et al.*, 1993, 1994; Hu *et al.*, 1994; Rappen *et al.*, 1994; Smith *et al.*, 1994; Axt *et al.*, 1995; Axt, Victor, and Stahl, 1996).

V. PHONON-INDUCED INCOHERENT DYNAMICS

Adding phonons to the system fundamentally alters the exciton dynamics. Two aspects of this alteration are particularly striking: First, phonons introduce relaxation rates of the various dynamic variables. Second, new electronic variables become relevant since the factorizations (45) and (46) no longer hold (Dubovsky and Mukamel, 1991; Knoester and Mukamel, 1991; Axt, Victor, and Stahl, 1996). The generating-function approach presented in Appendices A and B provides a compact rigorous formulation of the coupled electron-phonon dynamics both for the pair-conserving many-electron model and for the Frenkel exciton model. It thus covers in principle the whole range of phonon-related phenomena, including the generation of non-equilibrium (hot) phonon distributions (Hohenester *et al.*, 1993) and coherent phonon effects (Cho *et al.*, 1990; Kütt, 1992; Kuznetsov and Stanton, 1994, 1995). In practice, however, these equations are usually too complicated for a direct numerical integration, except for models of the electron-phonon coupling that are simple enough to allow for analytic solutions (this is illustrated by an example in Axt and Mukamel, 1997a) or provided only a very limited set of phonons is dominantly coupled e.g., when the system contains a few high-frequency Raman-active modes or when the effect of the phonon bath can be represented using a few collective oscillators. A wave-

packet description, particularly suited to deal with the latter case, has been worked out (Chernyak and Mukamel, 1996c). In all other cases, in order to obtain numerically manageable equations, it is necessary to adopt less demanding reduction schemes that focus on selected aspects of the phonon interaction. In this section we shall consider the incoherent aspect of electron-phonon coupling. Our goal is to derive equations for purely electronic-density matrices by eliminating the phonons perturbatively. This level of theory provides a simple microscopic treatment of dephasing and will enable us to study the generation and subsequent thermalization of incoherent exciton occupation densities, i.e., densities that cannot be expressed as products of coherent transition amplitudes.

A systematic procedure for incorporating the phonon contributions is based on expanding Eqs. (A1)–(A5) in a Taylor series around $\alpha_\mu = \beta_\mu = 0$. This results in an infinite hierarchy of equations of motion for all derivatives of the five generating functions with respect to α_μ and β_μ taken at the point $\alpha_\mu = \beta_\mu = 0$. From the generating-function property, it is clear that these derivatives are nothing but the set of all phonon-assisted variables. To lowest order (i.e., $\alpha = \beta = 0$), we obtain equations of motion for the four electronic density matrices Y, B, N, and Z. The combined dynamics of these quantities is our primary target. Besides the transition densities Y, B that govern the coherent limit, we now have to deal with the partially occupationlike density matrices N and Z. In contrast to the procedure for the coherent limit, Eqs. (45) and (46) can no longer be used to eliminate these variables, because of the partial loss of coherence caused by the coupling to the phonon system. As in the case of the two-pair transition density B, it is useful to remove uncorrelated parts from N and Z by defining (Wang and Cassing, 1985; Axt, Victor, and Stahl, 1996; Axt and Mukamel, 1997b)

$$N_{abcd} = Y_{ba}^* Y_{cd} + \bar{N}_{abcd}, \tag{61}$$

$$Z_{abcdef} = Y_{ba}^* \bar{B}_{cdef} + Y_{cd} \bar{N}_{abef} - Y_{cf} \bar{N}_{abed} + Y_{ef} \bar{N}_{abcd}$$
$$- Y_{ed} \bar{N}_{abcf} + Y_{ba}^* (Y_{cd} Y_{ef} - Y_{cf} Y_{ed})$$
$$+ \bar{Z}_{abcdef}. \tag{62}$$

We have written down only those terms of the cluster decomposition for N and Z that belong to the lowest order in the driving field (Axt and Stahl, 1994a; Axt, Victor, and Stahl, 1996) and contribute to $\chi^{(3)}$. The new variables $\bar{N}$ and $\bar{Z}$ are a measure of the partial loss of coherence in the system and vanish in the phonon-free limit. $\bar{Z}$ represents transitions between incoherent phonon-induced exciton densities and two-pair states (scattering states as well as bound biexcitons; Axt, Victor, and Stahl, 1996). These transitions show up, for example, as excited-state absorption. It may be justified to neglect $\bar{Z}$ in situations where either these transitions are off resonance with respect to any of the driving fields or the response is dominated by competing coherent signals arising from the direct two-pair transitions repre-

sented by B (Axt, Victor, and Stahl, 1996). In the following we shall concentrate on this situation, in which $\bar{N}$ is the only new electronic density matrix responsible for incoherent processes. Combining Eq. (61) with the relations (A21) and (A22) leads to a natural decomposition of the carrier densities C and D into coherent and incoherent contributions according to

$$C_{ab} = C_{ab}^{\mathrm{coh}} + C_{ab}^{\mathrm{inc}}, \quad D_{ab} = D_{ab}^{\mathrm{coh}} + D_{ab}^{\mathrm{inc}}, \tag{63}$$

$$C_{ab}^{\mathrm{coh}} \equiv \sum_{k=\mathrm{h}} Y_{ka}^* Y_{kb}, \quad D_{ab}^{\mathrm{coh}} \equiv \sum_{k=\mathrm{e}} Y_{ak}^* Y_{bk}, \tag{64}$$

$$C_{ab}^{\mathrm{inc}} \equiv \sum_{k=\mathrm{h}} \bar{N}_{akkb}, \quad D_{ab}^{\mathrm{inc}} \equiv \sum_{k=\mathrm{e}} \bar{N}_{kabk}. \tag{65}$$

We shall also represent $\bar{N}$, as we did the transitions Y and B, in the exciton basis set using the expansion

$$\bar{N}_{abcd} = \sum_{\bar{x}x} \bar{\psi}_{ba}^{\bar{x}*} \bar{\psi}_{cd}^{x} \bar{n}_{\bar{x}x}. \tag{66}$$

Following standard procedures, we can incorporate the influence of phonons on the dynamics of electronic density matrices approximately through phonon-induced self-energies (Zimmermann, 1990; Kuhn and Rossi, 1992; Kuhn *et al.*, 1994; Schilp *et al.*, 1994, 1995; Axt, Victor, and Stahl, 1996; Axt and Mukamel, 1997a). Details of the specific scheme used here are given in Appendix D. When the definitions (61) and (62) are inserted into the equations of motion (A1)–(A3), taken at $\alpha=\beta=0$, and the results of Appendix D are used for the phonon-induced self-energies, we obtain the following set of equations in the exciton representation:

$$i\hbar\,\partial_t y_x = \bar{E}_x y_x + i\hbar \sum_{x'} \mathrm{Im}(\Omega_Y^{ph})_x^{x'} y_{x'}$$

$$+ \sum_{\bar{x}\bar{x}'x'} \bar{V}_x^{\bar{x}\bar{x}'x'} [y_{\bar{x}}^* (y_{\bar{x}'} y_{x'} + b_{\bar{x}'x'}) + \bar{n}_{\bar{x}x} y_{\bar{x}'}$$

$$+ \bar{n}_{\bar{x}\bar{x}'} y_{x'}] - \mathbf{E}\Bigg[\bar{\mathbf{M}}_x - \sum_{\bar{x}'x'} \bar{\mathbf{M}}_x^{\bar{x}'x'} (y_{\bar{x}'}^* y_{x'} + \bar{n}_{\bar{x}'x'})$$

$$- \sum_{x'} \bar{\mathbf{M}}_x^{x'} y_{x'} \Bigg], \tag{67}$$

$$i\hbar\,\partial_t b_{\bar{x}x} = (\bar{E}_x + \bar{E}_{\bar{x}}) b_{\bar{x}x}$$

$$+ \sum_{\bar{x}'x'} [\bar{V}_{\bar{x}x}^{\bar{x}'x'} + i\hbar\,\mathrm{Im}(\Omega_B^{ph})_{\bar{x}x}^{\bar{x}'x'}](b_{\bar{x}'x'}$$

$$+ y_{\bar{x}'} y_{x'})$$

$$- i\hbar \sum_{x'} [y_{\bar{x}}\,\mathrm{Im}(\Omega_Y^{ph})_x^{x'} y_{x'} + y_x\,\mathrm{Im}(\Omega_Y^{ph})_{\bar{x}}^{x'} y_{x'}]$$

$$+ \mathbf{E}\Bigg(\sum_{x'} \bar{\mathbf{M}}_x^{x'} b_{\bar{x}x'} + \sum_{\bar{x}'} \bar{\mathbf{M}}_{\bar{x}}^{\bar{x}'} b_{\bar{x}'x} \Bigg), \tag{68}$$

$$i\hbar\,\partial_t \bar{n}_{\bar{x}x} = (\bar{E}_x - \bar{E}_{\bar{x}}) \bar{n}_{\bar{x}x}$$

$$+ i\hbar \sum_{\bar{x}'x'} \mathrm{Im}(\Omega_N^{ph})_{\bar{x}x}^{\bar{x}'x'} (\bar{n}_{\bar{x}'x'} + y_{\bar{x}'}^* y_{x'})$$

$$- i\hbar \sum_{x'} [y_{\bar{x}}^*\,\mathrm{Im}(\Omega_Y^{ph})_x^{x'} y_{x'} + y_x\,\mathrm{Im}(\Omega^{ph})_{\bar{x}}^{x'} y_{x'}^*]$$

$$+ \mathbf{E}\Bigg(\sum_{x'} \bar{\mathbf{M}}_x^{x'} \bar{n}_{\bar{x}x'} - \sum_{\bar{x}'} \bar{\mathbf{M}}_{\bar{x}}^{\bar{x}'*} \bar{n}_{\bar{x}'x} \Bigg), \tag{69}$$

where the self-energies $\hbar\Omega^{ph}$ are defined in Eqs. (D7), (D11), and (D28). Expressed in terms of the new variables y_x and $\bar{n}_{\bar{x}x}$, the polarization (34) now reads

$$\bar{\mathbf{P}} = \sum_x (\bar{\mathbf{M}}_x^* y_x + \bar{\mathbf{M}}_x y_x^*) - \sum_{\bar{x}x} \bar{\mathbf{M}}_{\bar{x}}^x (y_{\bar{x}}^* y_x + \bar{n}_{\bar{x}x}) + \bar{\mathbf{P}}_{\mathrm{stat}}. \tag{70}$$

The equation for the one-pair transition density y is modified by the phonon coupling in three ways: (i) the phonon-induced self-energy Ω_Y^{ph}, which is responsible for phonon-induced dephasing of the transition density; (ii) the Pauli blocking now contains an additional term resulting from incoherent exciton densities; and (iii) incoherent exciton densities, which are coupled to y also via the Coulomb potential. The structure of the latter terms may be interpreted as a contribution to density-induced dephasing. The two-pair transition density b has also acquired a self-energy leading to dephasing. In addition, two new phonon-induced source terms ($\propto \Omega_B^{ph} yy$ and $\propto \Omega_Y^{ph} yy$) show up. These contributions are competing with the source $\propto \bar{V} yy$, already present in the coherent limit. This coherent source is expected to be dominant when the perturbative treatment of phonons, used to derive the self-energies, applies. In contrast, the incoherent exciton density $\bar{n}$ has only sources proportional to the phonon coupling, reflecting the fact that $\bar{n}$ has to vanish in the phonon-free limit. The first of the two sources ($\propto \Omega_N^{ph} y^* y$) does not affect the total incoherent exciton occupation density $\bar{n}_{\mathrm{tot}} \equiv \Sigma_x \bar{n}_{xx}$. This can be seen by summing this term over all exciton states x and using the identity $\Sigma_x\,\mathrm{Im}(\Omega_N)_{xx}^{\bar{x}'x'} = 0$, which follows directly from the expression for the self-energy Ω_N given in Appendix D. This term describes the scattering of coherent exciton densities by phonons. The source $\propto \Omega_Y^{ph} y^* y$ is therefore the only term leading to a net generation of incoherent exciton densities. This generation rate equals the loss rate representing the decrease of the corresponding coherent density—in agreement with the property that our model of the electron-phonon interaction conserves separately the total densities of electrons or holes. The density matrix $\bar{n}_{\bar{x}x}$ carries information about incoherent exciton populations ($\bar{x}=x$) as well as intraband coherences ($\bar{x} \neq x$). As the driving source in Eq. (69) is given by the loss rate of the coherent carrier densities, we have to conclude that intraband coherences cannot vanish before the coherent densities have decayed due to the dephasing action of the phonon bath. In fact, they will usually influence the dynamics on a time scale longer than the decay time of coherent den-

sities, because of the finite memory resulting from Eq. (69). This interpretation is supported by recent measurements performed on an $Al_{0.35}GaAs_{0.65}/GaAs$ superlattice (Haring Bolivar *et al.*, 1997), in which oscillations with differences of excitonic energies $(\bar{E}_x - \bar{E}_{\bar{x}})$ had been observed in a THz experiment for times longer than the simultaneously determined interband dephasing time T_2, as predicted by Axt, Bartels, and Stahl (1996). At longer times after the interband transition density Y has vanished, often the intraband coherences start to dephase as well and eventually may vanish. The exciton occupation densities $\bar{n}_x \equiv \bar{n}_{xx}$ are then the only active variables, and we find from Eq. (69) and the definition of the self-energy Ω_N that their dynamics are governed by the master equation

$$\hbar \partial_t \bar{n}_x = \sum_{x'} (R_{xx'} \bar{n}_{x'} - R_{x'x} \bar{n}_x), \tag{71}$$

with

$$R_{xx'} \equiv -2 \operatorname{Im}(\Gamma^N_{x'xxx'}), \tag{72}$$

where Γ^N is defined in Appendix D. Γ^N depends on the relaxation rate γ_N, accounting for the coupling of exciton densities with one phonon assistance to those with double assistance [collisional broadening (Schilp *et al.*, 1994, 1995)]. When this rate approaches zero, it is easy to verify that the rates $R_{xx'}$ obey the detailed balance condition

$$R_{xx'} = \exp\left(\frac{\hbar(\omega_{x'} - \omega_x)}{kT} \right) R_{x'x}, \tag{73}$$

reflecting the conservation of energy in a completed scattering event between excitons and phonons. Finite values of γ_N correspond to an uncertainty in the phonon energies introduced by the coupling with electrons, which in a more complete microscopic treatment would be accounted for by the multiple-phonon-assisted density matrices. The stationary point of the rate equation (71) is, because of Eq. (73), a canonical distribution over the exciton states x. This demonstrates that our model predicts in the long-time regime charge densities corresponding to a thermalized distribution of excitons. Instead of vanishing asymptotically in time, the intraband coherences more generally will eventually reach a steady-state value. In this case, improved expressions for the rates $R_{xx'}$ may be obtained by setting the time derivative of these coherences in Eq. (69) to zero, solving for the coherences, and substituting in the equation for the diagonal elements (Mukamel, 1995).

The following schematic picture of the dynamics induced by a short laser pulse as predicted by Eqs. (67)–(69) emerges from these considerations: starting with the arrival of the laser pulse, the signals will initially be dominated by the coherent dynamics represented by the variables y and b. At the same time incoherent densities start to build up, driven by the loss rate of coherent carrier densities. This regime is followed by a period in which coherent densities are on the decline, while intraband coherences and incoherent populations take over.

Finally, the incoherent populations are the only active variables left at longer times and their dynamics will eventually result in a thermalized distribution of excitons.

VI. COMPARISON WITH THE SEMICONDUCTOR BLOCH EQUATIONS

In the traditional approach to truncating the hierarchy of equations of motion, which leads to the semiconductor Bloch equations, the electronic part of the dynamics is formulated entirely in terms of the two-point density-matrices Y, C, and D (Haug and Koch, 1993). In contrast, when one institutes the requirement to obtain exact results up to third order, one selects the density matrices Y, B, N, and Z (or, after switching to the cluster representation, Y, $\bar{B}$, $\bar{N}$, and $\bar{Z}$) as the relevant dynamic variables to represent the purely electronic degrees of freedom. These are two-point, four-point, and six-point density matrices, making the third-order dynamics-controlled truncation a six-point density matrix theory. It should be noted, however, that this does not imply that all possible four- and six-point density matrices are taken into account in the third-order dynamics-controlled scheme; e.g., the four-point function $\langle \bar{c}_a^+ \bar{c}_b^+ \bar{c}_c \bar{c}_d \rangle$ is not considered, because it is of $\mathcal{O}(E^4)$, while the six-point function $\langle \bar{d}_a \bar{c}_b \bar{d}_c \bar{c}_d \bar{d}_e \bar{c}_f \rangle$ is of third order, but it is not considered because the lowest order at which it contributes to the polarization is the fifth order (Bartels *et al.*, 1995; Victor *et al.*, 1995). In this section we compare the semiconductor Bloch equations with the third-order dynamics-controlled truncation and explore circumstances whereby the two may lead to different predictions. In order to make the connection, we have to compare the dynamics of the variables Y, C, and D entering the semiconductor Bloch equations. We shall explicitly discuss the transition density Y and the electronic density C. The discussion of the hole density D is analogous to that for C and does not lead to new qualitative insights. When we apply the truncation scheme used to derive the semiconductor Bloch equations (Haug and Koch, 1993) to our model, defined by Eq. (30), we obtain

$$i\hbar \partial_t Y_{ab} = \hbar \Omega_Y(Y)_{ab} + \sum_{pqk=e} \bar{V}^{eeee}_{bqkp}(C_{kp}Y_{aq} - C_{kq}Y_{ap})$$

$$- \sum_{pq=e,k=h} (\bar{V}^{eehh}_{pqka} - \bar{V}^{heeh}_{kqpa})(C_{pq}Y_{kb} - C_{pb}Y_{kq})$$

$$- \sum_{pq=h,k=e} (\bar{V}^{eehh}_{bkpq} - \bar{V}^{ehhe}_{bqpk})(D_{qp}Y_{ak} - D_{qa}Y_{pk})$$

$$+ \sum_{pqk=h} \bar{V}^{hhhh}_{kpqa}(D_{pk}Y_{qb} - D_{pq}Y_{kb})$$

$$- \mathbf{E}\left(\bar{\mathbf{M}}^{eh}_{ba} - \sum_{k=h} \bar{\mathbf{M}}^{eh}_{bk}D_{ka} - \sum_{k=e} \bar{\mathbf{M}}^{eh}_{ka}C_{kb} \right.$$

$$\left. + \sum_{k=e} \bar{\mathbf{M}}^{ee}_{bk}Y_{ak} - \sum_{k=h} \bar{\mathbf{M}}^{hh}_{ka}Y_{kb} \right) + i\hbar \partial_t^{ph}Y_{ab}, \tag{74}$$

$$i\hbar\partial_t C_{ab} = (\epsilon_b^{\mathrm{e}} - \epsilon_a^{\mathrm{e}}) C_{ab} + \sum_{pq=\mathrm{h}, k=\mathrm{e}} [(\bar{V}_{pkbq}^{\mathrm{heeh}} - \bar{V}_{pqbk}^{\mathrm{hhee}})$$

$$\times Y_{qa}^* Y_{pk} - (\bar{V}_{pakq}^{\mathrm{heeh}} - \bar{V}_{pqka}^{\mathrm{hhee}}) Y_{qk}^* Y_{pb}]$$

$$- \mathbf{E}\left[\sum_{k=\mathrm{h}} (\bar{\mathbf{M}}_{bk}^{\mathrm{eh}} Y_{ka}^* - \bar{\mathbf{M}}_{ka}^{\mathrm{he}} Y_{kb}) + \sum_{k=\mathrm{e}} (\bar{\mathbf{M}}_{bk}^{\mathrm{ee}} C_{ak} \right.$$

$$\left. - \bar{\mathbf{M}}_{ka}^{\mathrm{ee}} C_{kb} \right] + i\hbar\partial_t^{ph} C_{ab} + \mathcal{O}(E^4), \qquad (75)$$

where the optical response has to be derived from Eq. (34) for the polarization. The semiconductor Bloch equation for D has a structure similar to that of Eq. (75). Equations (74) and (75) assume the form familiar from the semiconductor Bloch equations for bulk semiconductors (Haug and Koch, 1993),

$$i\hbar\partial_t Y_k = (\epsilon_k^{\mathrm{e}} - \epsilon_k^{\mathrm{h}}) Y_k - \mathbf{E}\mathbf{M}_k^{\mathrm{eh}}(1 - D_k - C_k) - \sum_q \bar{V}_{k-q}$$

$$\times [Y_q(1 - C_k - D_k) + (C_q + D_q) Y_k] + i\hbar\partial_t^{ph} Y_k, \qquad (76)$$

$$i\hbar\partial_t C_k = \sum_q \bar{V}_{q-k}(Y_q^* Y_k - Y_k^* Y_q) - \mathbf{E}(\bar{\mathbf{M}}_k^{\mathrm{eh}} Y_k^*$$

$$- \bar{\mathbf{M}}_k^{\mathrm{eh}*} Y_k) + i\hbar\partial_t^{ph} C_k, \qquad (77)$$

provided the homogeneity of the system in the bulk limit is used to write $Y_{pq} = \delta_{pq} Y_q$, $C_{pq} = \delta_{pq} C_q$, and $D_{pq} = \delta_{pq} D_q$ (the index, here has to be identified with the k-vector of the corresponding bulk Bloch function) and provided that after we neglect exchange-type contributions to the Coulomb interaction, the remaining direct-type matrix elements are approximated as $\bar{V}_{pqkl} \approx \delta(p+k-q-l) \bar{V}_{q-p}$ (Haken, 1973). Furthermore, only the interband dipole matrix element $\mathbf{M}_k^{\mathrm{eh}} = \mathbf{M}_{kk}^{\mathrm{eh}}$ is retained. We shall refer to Eqs. (74) and (75) as the semiconductor Bloch equations although they are slightly more general than the more familiar versions (76) and (77).

Truncation of the electronic part of the hierarchy has been achieved in Eqs. (74) and (75) by factorization of the higher-order electronic density matrices entering the Heisenberg equations of motion for Y and C,

$$S_{abcd} = \langle \bar{c}_a^\dagger \bar{c}_b \bar{d}_c \bar{c}_d \rangle \approx C_{ab} Y_{cd} - C_{ad} Y_{cb}, \qquad (78)$$

$$T_{abcd} = \langle \bar{d}_a^\dagger \bar{d}_b \bar{c}_c \bar{c}_d \rangle \approx D_{ab} Y_{cd} - D_{ac} Y_{bd}, \qquad (79)$$

$$N_{abcd} = \langle \bar{c}_a^\dagger \bar{d}_b^\dagger \bar{d}_c \bar{c}_d \rangle \approx Y_{ba}^* Y_{cd} + C_{ad} D_{bc}$$

$$= Y_{ba}^* Y_{cd} + \mathcal{O}(E^4). \qquad (80)$$

As factorizations like Eqs. (78)–(80) have a long tradition, motivated by many needs, they are known by many names. For example, one can think of Eqs. (78)–(80) as the lowest level of approximation [SUB(2); cf. Axt and Mukamel (1997b)] resulting from the cluster decomposition hierarchy, also known as the quantum Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy. Another way to obtain these factorizations is by

replacing the corresponding contributions to the Coulomb interaction by their mean-field counterparts in Eq. (15). The deviations from these mean-field contributions have been suspected to have rapidly oscillating (random) phases, leading to no macroscopic contributions. That is why the name random phase approximation (RPA) has been used too (Stahl, 1988; Haug and Koch, 1993). The assumption that the wave function can be represented as a single Slater determinant also leads to Eqs. (78)–(80). This approach is known as the time-dependent Hartree-Fock (TDHF) theory (Ring and Schuck, 1976). The TDHF assumption also implies that the one-particle density matrix is a projection operator

$$\rho^2 = \rho. \qquad (81)$$

When Eq. (81) is written in components according to Eq. (32), we obtain

$$C_{ab} = \sum_{k=\mathrm{h}} Y_{ka}^* Y_{kb} + \mathcal{O}(E^4), \qquad (82)$$

$$D_{ab} = \sum_{k=\mathrm{e}} Y_{ak}^* Y_{bk} + \mathcal{O}(E^4), \qquad (83)$$

which coincides with our fundamental equation (63) only in the coherent limit. The assumption that the system may be represented by a single Slater determinant, therefore, no longer holds when phonons are added.

When phonons are taken into account, Eqs. (74) and (75) are not closed; instead these variables are coupled to their phonon-assisted counterparts. This is represented by the terms $i\hbar\partial_t^{ph} Y_{ab}$ and $i\hbar\partial_t^{ph} C_{ab}$. To deal with phonon-assisted variables within the framework of the semiconductor Bloch equations it is common practice to use strategies of the type described in Appendix D. Details of these procedures can be found in Zimmermann (1990), Kuhn and Rossi (1992), Kuhn *et al.* (1994), and Schilp *et al.* (1994, 1995).

The semiconductor Bloch treatment of Y and C resulting from Eqs. (74) and (75) has to be compared with the dynamics of these variables predicted by the third-order dynamics-controlled truncation. Equations (67)–(69) constitute our final result, expressed using the exciton representation. The comparison will, however, be more transparent if we start with Eqs. (A1)–(A5) since, like the semiconductor Bloch equations [Eqs. (74) and (75)], they are written in the single-particle basis. We note, of course, that Eqs. (A1)–(A5) still contain the phonon degrees of freedom that were eliminated in the semiconductor Bloch equations. In the following we shall use Eqs. (A1)–(A5) to derive equations of motion as close as possible to Eqs. (74) and (75) in order to facilitate the comparison. The equation of motion for Y in the third-order dynamics-controlled truncation is obtained as the special case $\alpha = \beta = 0$ of Eq. (A1):

$$i\hbar \partial_t Y_{ab} = \hbar \Omega_Y(Y)_{ab} + \sum_{pqk=e} \bar{V}^{eeee}_{bqkp} S_{kpaq}$$

$$- \sum_{pq=e,k=h} (\bar{V}^{eehh}_{pqka} - \bar{V}^{heeh}_{kqpa}) S_{pqkb}$$

$$+ \sum_{pqk=h} \bar{V}^{hhhh}_{kpqa} T_{pkqb}$$

$$- \sum_{pq=h,k=e} (\bar{V}^{eehh}_{bkpq} - \bar{V}^{ehhe}_{bqpk}) T_{qpak}$$

$$- \mathbf{E}\bigg(\bar{\mathbf{M}}^{eh}_{ba} - \sum_{k=h} \bar{\mathbf{M}}^{eh}_{bk} D_{ka} - \sum_{k=e} \bar{\mathbf{M}}^{eh}_{ka} C_{kb}$$

$$+ \sum_{k=e} \bar{\mathbf{M}}^{ee}_{bk} Y_{ak} - \sum_{k=h} \bar{\mathbf{M}}^{hh}_{ka} Y_{kb} \bigg) + i\hbar \partial^{ph}_t Y_{ab} .$$

$$(84)$$

The variable C is redundant, since in the third-order dynamics-controlled treatment the dynamics of populations and intraband coherences is obtained from a single variable, the pair density N. The particle densities C and D can be eliminated using the identities

$$C_{ab} = \sum_{k=h} N_{akkb} + \mathcal{O}(E^4), \qquad (85)$$

$$D_{ab} = \sum_{k=e} N_{kabk} + \mathcal{O}(E^4). \qquad (86)$$

Nevertheless, it is illustrative to set up the equation of motion for C in order to compare it with the semiconductor Bloch equations. The Heisenberg equation for C reads

$$i\hbar \partial_t C_{ab} = (\epsilon^e_b - \epsilon^e_a) C_{ab} + \sum_{pq=h,k=e} [(\bar{V}^{heeh}_{pkbq} - \bar{V}^{hhee}_{pqbk}) N_{aqpk}$$

$$- (\bar{V}^{heeh}_{pakq} - \bar{V}^{hhee}_{pqka}) N_{kqpb}] - \mathbf{E}\bigg[\sum_{k=h} (\bar{\mathbf{M}}^{eh}_{bk} Y^*_{ka}$$

$$- \bar{\mathbf{M}}^{he}_{ka} Y_{kb}) + \sum_{k=e} (\bar{\mathbf{M}}^{ee}_{bk} C_{ak} - \bar{\mathbf{M}}^{ee}_{ka} C_{kb}) \bigg]$$

$$+ i\hbar \partial^{ph}_t C_{ab} + \mathcal{O}(E^4). \qquad (87)$$

This equation is redundant in the dynamics-controlled approach, because it is solved identically by Eq. (85).

The fundamental difference between the dynamics-controlled truncation and semiconductor Bloch treatment of Y and C is that within the latter the four-point functions S, T, and N, appearing as sources for Y and C, are factorized according to Eqs. (78)–(80). Let us discuss the implications of this approximation for interband dynamics. In order to compare the semiconductor Bloch factorizations (78) and (79) with the corresponding dynamics-controlled results, let us take a closer look at the formulas used in the latter case for the density matrices S and T [see Eqs. (A23) and (A24)].

$$S_{abcd} = \sum_{k=h} Z_{akkbcd} + \mathcal{O}(E^5), \qquad (88)$$

$$T_{abcd} = \sum_{k=e} Z_{kabkcd} + \mathcal{O}(E^5). \qquad (89)$$

These equations can be recast by switching to the cluster representation. Using Eq. (62) we find

$$S_{abcd} = \sum_{k=h} [Y^*_{ka}(\bar{B}_{kbcd} + Y_{kb} Y_{cd} - Y_{kd} Y_{cb})$$

$$+ Y_{kb} \bar{N}_{akcd} - Y_{kd} \bar{N}_{akcb} + Y_{cd} \bar{N}_{akkb}$$

$$- Y_{cb} \bar{N}_{akkb} + \bar{Z}_{akkbcd}]$$

$$= C_{ab} Y_{cd} - C_{ad} Y_{cb} + \sum_{k=h} [Y^*_{ka} \bar{B}_{kbcd}$$

$$+ Y_{kb} \bar{N}_{akcd} - Y_{kd} \bar{N}_{akcb} + \bar{Z}_{akkbcd}], \qquad (90)$$

and analogously

$$T_{abcd} = D_{ab} Y_{cd} - D_{ac} Y_{bd} + \sum_{k=e} [Y^*_{ak} \bar{B}_{bkcd}$$

$$+ Y_{bk} \bar{N}_{kacd} - Y_{ck} \bar{N}_{kabd} + \bar{Z}_{kabkcd}], \qquad (91)$$

where we have used the identities (85) and (86). The first two terms in each equation reproduce the semiconductor Bloch equations. In addition the terms $\propto Y^* \bar{B}$ and $\propto \bar{Z}$ represent genuine many-body correlations. The part $\propto Y^* \bar{B}$ results from two-photon absorption processes to bound biexcitons and exciton-exciton scattering states, while the part $\propto \bar{Z}$ accounts for excited-state absorption from incoherent exciton densities to bound or unbound two-pair states. We therefore expect the dynamics-controlled truncation results to deviate considerably from the semiconductor Bloch equations whenever two-pair correlations are significant. This is always the case when resonances corresponding to bound biexcitons are resolved. But this is not the only situation in which these contributions are important. For example, the dependencies of four-wave mixing (FWM) or pump-probe signals on the polarization of light cannot be accounted for within the semiconductor Bloch equations (Schmitt-Rink *et al.*, 1992; Bennhardt *et al.*, 1993; Wang *et al.*, 1993; Hu *et al.*, 1994; Rappen *et al.*, 1994; Smith *et al.*, 1994; Wang *et al.*, 1994; Axt *et al.*, 1995; Axt, Victor, and Stahl, 1996). Apart from terms related to two-pair transitions, we also obtain two contributions resulting from incoherent exciton densities ($\propto Y\bar{N}$), which cannot be absorbed into the definition of the particle densities C and D. These two terms have a structure similar to the corresponding incoherent parts of the particle densities, suggesting an interpretation as density-induced dephasing. Instead of adding only the phonon part $i\hbar \partial^{ph}_t Y_{ab}$ to the pure mean-field dynamics resulting from the factorizations (78), one often introduces a more general correction through the "collision" term $i\hbar \partial^{col}_t Y_{ab}$. When this term is included, Eq. (74) is in principle a correct equation, as all deviations from the explicitly displayed factorized part can be absorbed in $i\hbar \partial^{col}_t Y_{ab}$. Standard methods used to obtain the Coulomb scattering corrections are the second-order Born approximation (Haug and Koch, 1993; Schäfer *et al.*, 1996) or the Kadanoff-Baym ansatz (Kuznetsov, 1991a).

An overview, together with a systematic derivation of this level of description starting from a correlation expansion based on the quantum BBGKY hierarchy, can be found in Kuhn (1997). The resulting equations represent the traditional starting point for state of the art calculations. In practice, all of these standard procedures lead to scattering kernels of Boltzmann type (Haug and Koch, 1993). It has been shown by Schäfer *et al.* (1996) that the low-density limit of corrections resulting from the second-order Born-approximation can be identified as part of the scattering contributions to $\bar{B}$. To obtain the high-density contributions to the Born approximation within the dynamics-controlled truncation one has to take the cut for truncation at a higher level. The contributions from the Born approximation constitute a significant improvement compared to a theory that retains only the factorized parts of the four-point density matrices S and T. Nevertheless, the treatment of genuine many-body correlations is still incomplete. In particular, transitions involving bound biexcitons are not yet accounted for in the standard treatments of the "collision" term.

We now turn to the discussion of intraband dynamics represented by the electronic density C. The semiconductor Bloch equation (75) can be obtained from the third-order dynamics-controlled truncation equation (87) by invoking the factorization (80) of the pair density N on the right-hand side of Eq. (80). First we note that in the coherent limit the third-order dynamics-controlled result coincides to leading order in the laser field with the semiconductor Bloch factorization (80). This implies that in the coherent limit there is no difference between the third-order dynamics-controlled truncation and the mean-field treatment of particle densities; C and D are given by the coherent densities C^{coh} and D^{coh} defined in Eq. (64). The fundamental difference between the lowest-order dynamics-controlled result and Eq. (75) is that the phonon-induced deviation of N from its factorized value measured by $\bar{N}$ is completely neglected. The dynamic variable N, which in general represents the dynamics of coherent pair densities as well as long-lived intraband coherences and the thermalization of pair occupation densities (three distinct processes each associated with a typical time scale), is therefore reduced to the coherent part only. In addition the semiconductor Bloch treatment is in danger of artificially predicting resonances at frequencies corresponding to the differences $\epsilon_b - \epsilon_a$ of one-particle energies (Binder *et al.*, 1994; Chansungsan *et al.*, 1994; Meier *et al.*, 1994, 1995; Axt, Bartels, and Stahl, 1996). The last point needs further clarification. The fact that Eqs. (85) and (86) are rigorous identities even in the presence of phonons proves that only differences of frequencies associated with interacting electron-hole pairs (with possible phonon renormalizations) can enter the carrier densities. This already follows from the general formulation of the generating function $N^{\alpha\beta}$ given by Eq. (A3) and is preserved by the perturbative treatment of the phonon degrees of freedom established in Eq. (69). To

see this, we note that N describes densities of electron-hole pairs. The propagation of N in configuration space can be related to differences of one-particle energies only in the limiting case when the Coulomb interaction between the electrons and holes forming the pairs is negligible as well as the energetic shifts due to phonon interactions. Furthermore, one-particle frequencies are involved in the sources to N only in this case. In all other situations, the intraband response predicted by dynamics-controlled truncation can consist only of frequencies either imposed by the external field or by the frequencies of electron-hole pairs including interaction-induced renormalizations. This is, however, not so obvious from the equation of motion (75). Indeed it has been pointed out by Axt, Bartels, and Stahl (1996) that each of the sources in this equation alone would lead to components oscillating with differences of one-particle frequencies. In a rigorous treatment, these contributions cancel out completely. Approximations, like the factorization of N in the mean-field equation (75), leave some parts of these components uncompensated, leading to a prediction of oscillations with bare one-particle frequencies even when the renormalizations are significant and the excitation is in resonance with excitonic states (Binder *et al.*, 1994; Chansungsan *et al.*, 1994; Meier *et al.*, 1994, 1995; Axt, Bartels and Stahl, 1996). The measurement of THz signals for times longer than the coherent regime at low excitation densities in the vicinity of the lowest exciton resonance is a critical experimental test of the different predictions (Haring Bolivar *et al.*, 1997). The semiconductor Bloch equations are at variance with this experiment in two respects: (i) The semiconductor Bloch treatment is not able to describe intraband signals oscillating with excitonic frequencies for times longer than $T_2/2$ after the end of the laser pulse, where T_2 is the interband dephasing time, while such oscillations are observed for three times that long by Haring Bolivar *et al.* (1997); (ii) there is no experimental evidence for oscillations with differences of one-particle frequencies for selective excitation at the lowest exciton frequency.

In conclusion, there are two general types of situations in which the predictions of dynamics-controlled truncation and the semiconductor Bloch theory for intraband dynamics coincide: (i) when components with single-particle frequencies entering the semiconductor Bloch approach are small compared to the forced oscillations with the renormalized (excitonic) frequencies. This behavior is typical near the coherent limit and is always realized in the early stages of the dynamics for times when incoherent densities have not yet built up; (ii) measurements dominated by contributions from states in which the interaction-induced renormalizations are negligible. This is realized, for example, when the dominant contribution to the signal comes from scattering states in which the electron and the hole are spatially well separated—a case in which a representation in terms of free carrier densities is adequate and more natural than a description in terms of pair densities, which is still correct but inconvenient in this case. The

tremendous success of the semiconductor Bloch equations indicates that at least one of these conditions is well satisfied for a large number of experimental situations. Finally we note that "collision" terms have been derived for the intraband dynamics as well (Haug and Koch, 1993; Kuhn, 1997). In the standard approaches one obtains Boltzmann-like scattering kernels, which are of fourth order in the external field and thus show up in dynamics-controlled truncation only when truncated at the fourth order. The phonon-induced parts of N discussed above are missing in these standard treatments as in the collision-free semiconductor Bloch equations.

It should be noted that the standard treatment of phonons, performed on the two-point level, leads to a Boltzmann-like scattering kernel for carrier-phonon scattering similar to the results for carrier-carrier scattering (Kuhn and Rossi, 1992; Kuhn et al., 1994; Schilp et al., 1994, 1995; Kuhn, 1997). Both carrier-phonon scattering and carrier-carrier scattering in any Boltzmann-like theory eventually lead to a thermalized distribution of the carriers over the one-particle states with energies ϵ_a. In contrast, the dynamics-controlled truncation predicts a thermalization into excitonic states. This should lead to observable differences between the respective predictions for luminescence measurements. However, it should be stressed that although striking deviations from the semiconductor Bloch equations are expected in certain cases, a great many experimental situations are well reproduced by the simpler treatment of the semiconductor Bloch equations. The results of dynamics-controlled truncation usually reduce smoothly to the semiconductor Bloch limit in these situations.

VII. COMPARISON WITH THE FRENKEL EXCITON MODEL

The optical responses of molecular crystals (Davydov, 1971; Pope and Swenberg, 1982; Silinsh and Cápek, 1994), superlattices (Bulović et al., 1996; Bulović and Forrest, 1996; Forrest, 1997), and aggregates (Knoester and Mukamel, 1991; Knoester, 1993; Mukamel, 1994; Chernyak et al., 1995) are usually analyzed in terms of Frenkel excitons rather than interacting fermions. Developments very similar to those presented for a pair-conserving many-electron system have been made for Frenkel excitons. In this section we shall compare the results obtained for these two-model systems and show that, despite obvious differences in the microscopic formulation, both models lead to dynamic equations having essentially the same structure (Chernyak and Mukamel, 1996a). This should allow the interpretation of many phenomena in semiconductor optics using the simpler Frenkel exciton model.

In the Frenkel exciton model the electron-hole pair is tightly bound; consequently, instead of operators for the creation or annihilation of fermions, the basic building blocks are operators $B_n^\dagger$ and B_n for the creation or annihilation of an excitation (electron-hole pair) on site n. Often only one excited state per molecule is taken into account (Dubovsky and Mukamel, 1991; Leegwater and

Mukamel, 1992), although multilevel extensions are possible (Chernyak and Mukamel, 1996c; Kühn et al., 1996; Kühn and Mukamel, 1997). For simplicity we shall focus on the former case. The operators $B_n^\dagger$ and B_n then obey the Pauli commutation rules (Mukamel, 1995)

$$[B_n, B_m] = [B_n^\dagger, B_m^\dagger] = B_n^2 = (B_n^\dagger)^2 = 0, \tag{92}$$

$$[B_n, B_m^\dagger] = \delta_{nm}(1 - 2B_n^\dagger B_n). \tag{93}$$

As in the many-electron model, the Frenkel exciton Hamiltonian comprises the following contributions:

$$\widetilde{H} \equiv \widetilde{H}_{\mathrm{mat}} + \widetilde{H}_{\mathrm{ph}} + \widetilde{H}_{\mathrm{ep}} + \widetilde{H}_{\mathrm{opt}}. \tag{94}$$

For typical molecular assemblies it is justified to consider a material Hamiltonian that conserves the number of excitations. This is known as the Heitler-London approximation and the material part of the Hamiltonian then reads

$$\widetilde{H}_{\mathrm{mat}} \equiv \hbar \sum_n \Omega_n B_n^\dagger B_n + \sum_{m \neq n} J_{nm} B_n^\dagger B_m, \tag{95}$$

where Ω_n is the electronic transition frequency of the nth isolated molecule and J_{nm} accounts for dipole-dipole as well as for short-range exchange exciton couplings. The purely phonon Hamiltonian has the form

$$\widetilde{H}_{\mathrm{ph}} \equiv \sum_\mu \hbar \widetilde{\omega}_\mu \widetilde{b}_\mu^\dagger \widetilde{b}_\mu, \tag{96}$$

and the exciton-phonon interaction is assumed to be linear in phonon coordinates [analogous to Eq. (8)],

$$\widetilde{H}_{\mathrm{ep}} \equiv \sum_{nm\mu} \widetilde{\gamma}_{nm}^\mu B_n^\dagger B_m (\widetilde{b}_\mu^\dagger + \widetilde{b}_\mu). \tag{97}$$

The operators $\widetilde{b}_\mu^\dagger$ and $\widetilde{b}_\mu$ are boson operators for the creation or annihilation of a phonon in mode μ. Finally, the dipole coupling to the optical field $\mathbf{E}(t)$ is given by

$$\widetilde{H}_{\mathrm{opt}} \equiv -\mathbf{E}(t)\widehat{\widetilde{\mathbf{P}}}, \tag{98}$$

where the optical polarization operator, from which all optical properties are derived, is given by

$$\widehat{\widetilde{\mathbf{P}}} = \sum_n [\boldsymbol{\mu}_n (B_n + B_n^\dagger) + \boldsymbol{\mu}_n' B_n^\dagger B_n] + \widetilde{\mathbf{P}}_{\mathrm{stat}}. \tag{99}$$

Here $\boldsymbol{\mu}_n$ represents the transition dipole matrix element at site n, $\boldsymbol{\mu}_n'$ accounts for the change of the permanent dipole moment when site n gets excited, and $\widetilde{\mathbf{P}}_{\mathrm{stat}}$ is the static polarization of the assembly. The polarization is therefore given by

$$\widetilde{\mathbf{P}} \equiv \langle \widehat{\widetilde{\mathbf{P}}} \rangle = \sum_n [\boldsymbol{\mu}_n (\widetilde{Y}_n + \widetilde{Y}_n^*) + \boldsymbol{\mu}_n' \widetilde{N}_{nn}] + \widetilde{\mathbf{P}}_{\mathrm{stat}}, \tag{100}$$

where we have introduced the definitions

$$\widetilde{Y}_n \equiv \langle B_n \rangle, \quad \widetilde{N}_{nm} \equiv \langle B_n^\dagger B_m \rangle. \tag{101}$$

As in Eq. (34) for the many-electron system we have two distinct types of contributions; those proportional to

$\widetilde{Y}$ are analogous to the interband transitions [$\propto Y$ in Eq. (34)], while those proportional to $\widetilde{N}$ correspond to the intraband transitions [$\propto C,D$ in Eq. (34)]. The optical response in this model is thus fully determined once the transition density $\widetilde{Y}$ and the population-like density $\widetilde{N}$ are calculated. As in the many-electron system it is not possible to obtain a closed set of equations of motion for these fundamental dynamic variables, and we have to face the problem of an infinite hierarchy of equations of motion. For the Frenkel system, a classification of the higher-order density matrices according to the leading order in the laser field can be based on the following observation (Dubovsky and Mukamel, 1991; Knoester and Mukamel, 1991; Mukamel, 1994, 1995):

Let $\hat{\bar{A}}_n$ denote the normal-ordered product of n operators $B^\dagger, B$ and an arbitrary number of phonon operators $\widetilde{b}^\dagger, \widetilde{b}$, where the normal ordering means that all $B^\dagger$ operators stand to the left of B. When the system is initially in the ground state, it then follows for the expectation value of $\hat{\bar{A}}_n$ that

$$\langle \hat{\bar{A}}_n \rangle = \mathcal{O}(E^n). \tag{102}$$

This classification makes the application of dynamics-controlled truncation to the Frenkel exciton model possible. Proceeding along the same lines as in the many-electron case, we can set up equations of motion for the generating functions (Axt and Mukamel, 1997a),

$$\widetilde{Y}_j^{\alpha\beta} \equiv \langle B_j \hat{\bar{F}}^{\alpha\beta} \rangle, \tag{103}$$

$$\widetilde{B}_{ij}^{\alpha\beta} \equiv \langle B_i B_j \hat{\bar{F}}^{\alpha\beta} \rangle, \tag{104}$$

$$\widetilde{N}_{ij}^{\alpha\beta} \equiv \langle B_i^\dagger B_j \hat{\bar{F}}^{\alpha\beta} \rangle, \tag{105}$$

$$\widetilde{Z}_{kij}^{\alpha\beta} \equiv \langle B_k^\dagger B_i B_j \hat{\bar{F}}^{\alpha\beta} \rangle, \tag{106}$$

$$\bar{F}^{\alpha\beta} \equiv \langle \hat{\bar{F}}^{\alpha\beta} \rangle$$
$$\equiv \left\langle \left(\exp\left(\sum_\mu \alpha_\mu \widetilde{b}_\mu^\dagger \right) \right) \left(\exp\left(\sum_\mu \beta_\mu \widetilde{b}_\mu \right) \right) \right\rangle. \tag{107}$$

The equations relevant for the third-order response are given by Eqs. (B1)–(B5).

We begin our comparison with the many-electron dynamics by discussing the coherent limit defined by $\widetilde{\gamma}^\mu \to 0$. In this case we again obtain closed equations for electronic variables alone. Factorization rules analogous to Eqs. (45) and (46) hold,

$$\widetilde{N}_{ij} \equiv \widetilde{N}_{ij}^{\alpha=\beta=0} = Y_i^* Y_j + \mathcal{O}(E^4), \tag{108}$$

$$\widetilde{Z}_{kij} \equiv \widetilde{Z}_{kij}^{\alpha=\beta=0} = Y_k^* B_{ij} + \mathcal{O}(E^4), \tag{109}$$

as can be seen from Eqs. (B1)–(B4). The coherent dynamics is therefore determined by the one- and two-pair transition densities $\widetilde{Y}_j$ and $\widetilde{B}_{ij} \equiv \widetilde{B}_{ij}^{\alpha=\beta=0}$. The resulting equations of motion according to Eqs. (B1) and (B2) are given by

$$i\hbar \partial_t \widetilde{Y}_j = \hbar \widetilde{\Omega}_Y(\widetilde{Y})_j - 2\sum_m \widetilde{J}_{jm} \widetilde{Y}_j^* \widetilde{B}_{jm}$$
$$- \mathbf{E}[\boldsymbol{\mu}_j(1 - 2\widetilde{Y}_j^* \widetilde{Y}_j) + \boldsymbol{\mu}_j' \widetilde{Y}_j], \tag{110}$$

$$i\hbar \partial_t \widetilde{B}_{ij} = \hbar \widetilde{\Omega}_B(\widetilde{B})_{ij}$$
$$- \xi_{ij}\mathbf{E}[\boldsymbol{\mu}_j \widetilde{Y}_i + \boldsymbol{\mu}_i \widetilde{Y}_j + (\boldsymbol{\mu}_j' + \boldsymbol{\mu}_i')\widetilde{B}_{ij}], \tag{111}$$

where

$$\xi_{ij} \equiv 1 - \delta_{ij}, \quad \widetilde{J}_{jm} \equiv \delta_{jm}\hbar\Omega_j + J_{jm} \tag{112}$$

and $\hbar\widetilde{\Omega}_Y$ and $\hbar\widetilde{\Omega}_B$ are defined in Eqs. (B6) and (B7). The polarization of the Frenkel model in the coherent limit is given by [cf. Eq. (100)]

$$\widetilde{\mathbf{P}} \equiv \langle \hat{\widetilde{\mathbf{P}}} \rangle = \sum_n [\boldsymbol{\mu}_n(\widetilde{Y}_n + \widetilde{Y}_n^*) + \boldsymbol{\mu}_n' \widetilde{Y}_n^* \widetilde{Y}_n] + \widetilde{\mathbf{P}}_{\text{stat}}. \tag{113}$$

These equations are analogous to Eqs. (47) and (48). They have been used by Spano and Mukamel (1991a, 1991b); Leegwater and Mukamel (1992); and Chernyak and Mukamel (1993) to study the two-exciton problem for the Frenkel system in great detail. Equation (111) is equivalent to a model of bosons interacting via an infinite on-site repulsion, which accounts for Pauli exclusion. From the analogy to this "hard-core" model it is clear that Eq. (111) may not describe bound biexciton states, because the repulsion can only lead to exciton-exciton scattering. By adding attractive interactions, one can easily extend the Frenkel exciton formalism to obtain bound two-exciton states (Dubovsky and Mukamel, 1991; Spano et al., 1991). Equation (111) is considerably easier to solve than its counterpart equation (48) for the many-electron system. In particular it has been shown that the two-exciton Green's function which solves Eq. (111) can be expressed explicitly in terms of the corresponding one-exciton Green's function (Leegwater and Mukamel, 1992; Chernyak and Mukamel, 1993). Our goal in this section is to demonstrate that, despite differences from the many-electron system, Eqs. (110) and (111) can be recast in a form analogous to Eqs. (58) and (59). To this end we first introduce exciton eigenfunctions $\widetilde{\psi}$ and eigenvalues $\widetilde{E}_x = \hbar\widetilde{\omega}_x$ defined as the solution of the eigenvalue problem

$$\hbar\widetilde{\Omega}_Y(\widetilde{\psi}^x)_j = \sum_m \widetilde{J}_{jm} \widetilde{\psi}_m^x = \widetilde{E}_x \widetilde{\psi}_j^x. \tag{114}$$

We then define a function $\bar{\bar{B}}_{ij}$ by

$$\widetilde{B}_{ij} = \xi_{ij}(\bar{\bar{B}}_{ij} + \widetilde{Y}_i \widetilde{Y}_j). \tag{115}$$

The factor ξ_{ij} [cf. Eq. (112)] explicitly enforces the Pauli repulsion. It is clear that Eq. (115) leaves the values of $\bar{\bar{B}}_{ij}$ for $i=j$ undefined. From Eqs. (110) and (111) we obtain

$$\xi_{ij} i\hbar \partial_t \bar{\bar{B}}_{ij} = \xi_{ij}\left[\sum_n (\widetilde{J}_{jn}\bar{\bar{B}}_{in} + \widetilde{J}_{in}\bar{\bar{B}}_{nj}) - \widetilde{J}_{ji}(\bar{\bar{B}}_{ii} + \widetilde{Y}_i \widetilde{Y}_i) \right.$$
$$\left. - \widetilde{J}_{ij}(\bar{\bar{B}}_{jj} + \widetilde{Y}_j \widetilde{Y}_j) - \mathbf{E}(\boldsymbol{\mu}_i' + \boldsymbol{\mu}_j')\bar{\bar{B}}_{ij} \right]. \tag{116}$$

We shall use our freedom to choose $\bar{\bar{B}}_{jj}$ by requiring that Eq. (116) still holds when the common factors ξ_{ij} are dropped on both sides. We then expand $\bar{\bar{B}}$ and $\bar{Y}$ in terms of exciton eigenfunctions

$$\bar{Y}_j = \sum_j \ \tilde{\psi}_j^x \tilde{y}_x, \quad \bar{\bar{B}}_{ij} = \sum_{\bar{x}x} \ \tilde{\psi}_i^{\bar{x}} \tilde{\psi}_j^x \tilde{b}_{\bar{x}x}. \tag{117}$$

The relevant equations for the coherent Frenkel exciton dynamics assume in this representation the form

$$i\hbar \partial_t \tilde{y}_x = \tilde{E}_x \tilde{y}_x + \sum_{\bar{x}x'x'} \tilde{V}_x^{\bar{x}\bar{x}'x'} \tilde{y}_{\bar{x}}^* (\tilde{y}_{\bar{x}'} \tilde{y}_{x'} + \tilde{b}_{\bar{x}'x'})$$
$$- \mathbf{E}\left(\tilde{\mathbf{M}}_x - \sum_{\bar{x}'x'} \tilde{\mathbf{M}}_x^{\bar{x}'x'} \tilde{y}_{\bar{x}'}^* \tilde{y}_{x'} - \sum_{x'} \tilde{\mathbf{M}}_x^{x'} \tilde{y}_{x'} \right), \tag{118}$$

$$i\hbar \partial_t \tilde{b}_{\bar{x}x} = (\tilde{E}_{\bar{x}} + \tilde{E}_x) \tilde{b}_{\bar{x}x} + \sum_{\bar{x}'x'} \tilde{V}_{\bar{x}x}^{\bar{x}'x'} (\tilde{b}_{\bar{x}'x'} + \tilde{y}_{\bar{x}'} \tilde{y}_{x'})$$
$$+ \mathbf{E}\left(\sum_{x'} \tilde{\mathbf{M}}_x^{x'} \tilde{b}_{\bar{x}x'} + \sum_{\bar{x}'} \tilde{\mathbf{M}}_{\bar{x}}^{\bar{x}'} \tilde{b}_{\bar{x}'x} \right), \tag{119}$$

where $\tilde{V}_x^{\bar{x}\bar{x}'x'}$, $\tilde{V}_{\bar{x}x}^{\bar{x}'x'}$, $\tilde{\mathbf{M}}_x$, $\tilde{\mathbf{M}}_x^{x'}$, and $\tilde{\mathbf{M}}_x^{\bar{x}'x'}$ are defined in Eqs. (C13)–(C17).

Equations (118) and (119) are identical in form to Eqs. (58) and (59). From this discussion it is clear that the pair-conserving many-electron model and the Frenkel exciton model essentially describe the same basic dynamics. The great variety of possible optical responses realized for different materials as seen from the point of view of Eqs. (118), (119), (58), and (59) reflect only different sets of parameters in these equations. This formal analogy is not limited to the coherent limit and also holds when phonons are incorporated in the model.

The combined dynamics of coherent transition densities and incoherent populations can be worked out for the Frenkel exciton model in complete analogy to the many-electron model (Axt and Mukamel, 1997a). The new partially populationlike variables in this case are $\bar{N}_{ij} = \langle B_i^\dagger B_j \rangle$ and $\bar{Z}_{kij} = \langle B_k^\dagger B_i B_j \rangle$. Variables measuring the deviation from the coherent limit can, in analogy to Eqs. (61) and (62), be defined as

$$\bar{N}_{ij} = \bar{Y}_i^* \bar{Y}_j + \bar{\bar{N}}_{ij}, \tag{120}$$

$$\bar{Z}_{kij} = \xi_{ij}[\bar{Y}_k^* (\bar{\bar{B}}_{ij} + \bar{Y}_i \bar{Y}_j) + \bar{\bar{N}}_{ki} \bar{Y}_j + \bar{\bar{N}}_{kj} \bar{Y}_i + \bar{\bar{Z}}_{kij}], \tag{121}$$

where the factor ξ_{ij} in Eqs. (121) explicitly enforces the Pauli exclusion. In the following we shall neglect $\bar{\bar{Z}}$, resulting in a factorization of $\bar{Z}$ that coincides apart from the factor ξ_{ij} with the one previously obtained from a maximum-entropy argument (Dubovsky and Mukamel, 1991). When we introduce the exciton representation of $\bar{\bar{N}}$ by

$$\bar{\bar{N}}_{ij} = \sum_{\bar{x}x} \tilde{\psi}_i^{\bar{x}*} \tilde{\psi}_j^x \tilde{n}_{\bar{x}x} \tag{122}$$

and eliminate the phonon degrees of freedom perturbatively, we obtain the following set of equations:

$$i\hbar \partial_t \tilde{y}_x = \tilde{E}_x \tilde{y}_x + i\hbar \sum_{x'} \ \mathrm{Im}(\tilde{\Omega}_Y^{ph})_x^{x'} \tilde{y}_{x'}$$
$$+ \sum_{\bar{x}x'x'} \tilde{V}_x^{\bar{x}\bar{x}'x'} [\tilde{y}_{\bar{x}}^* (\tilde{y}_{\bar{x}'} \tilde{y}_{x'} + \tilde{b}_{\bar{x}'x'})$$
$$+ \tilde{n}_{\bar{x}x'} \tilde{y}_{\bar{x}'} + \tilde{n}_{\bar{x}\bar{x}'} \tilde{y}_{x'}]$$
$$- \mathbf{E}\Bigg[\tilde{\mathbf{M}}_x - \sum_{\bar{x}'x'} \tilde{\mathbf{M}}_x^{\bar{x}'x'} (\tilde{y}_{\bar{x}'}^* \tilde{y}_{x'} + \tilde{n}_{\bar{x}'x'})$$
$$- \sum_{x'} \tilde{\mathbf{M}}_x^{x'} \tilde{y}_{x'} \Bigg], \tag{123}$$

$$i\hbar \partial_t \tilde{b}_{\bar{x}x} = (\tilde{E}_x + \tilde{E}_{\bar{x}}) \tilde{b}_{\bar{x}x}$$
$$+ \sum_{\bar{x}'x'} (\tilde{V}_{\bar{x}x}^{\bar{x}'x'} + i\hbar \ \mathrm{Im}(\tilde{\Omega}_B^{ph})_{\bar{x}x}^{\bar{x}'x'})(\tilde{b}_{\bar{x}'x'}$$
$$+ \tilde{y}_{\bar{x}'} \tilde{y}_{x'}) - i\hbar \sum_{x'} (\tilde{y}_{\bar{x}} \ \mathrm{Im}(\tilde{\Omega}_Y^{ph})_x^{x'} \tilde{y}_{x'}$$
$$+ \tilde{y}_x \ \mathrm{Im}(\tilde{\Omega}_Y^{ph})_{\bar{x}}^{x'} \tilde{y}_{x'})$$
$$+ \mathbf{E}\left(\sum_{x'} \tilde{\mathbf{M}}_x^{x'} \tilde{b}_{\bar{x}x'} + \sum_{\bar{x}'} \tilde{\mathbf{M}}_{\bar{x}}^{\bar{x}'} \tilde{b}_{\bar{x}'x} \right), \tag{124}$$

$$i\hbar \partial_t \tilde{n}_{\bar{x}x} = (\tilde{E}_x - \tilde{E}_{\bar{x}}) \tilde{n}_{\bar{x}x}$$
$$+ i\hbar \sum_{\bar{x}'x'} \ \mathrm{Im}(\tilde{\Omega}_N^{ph})_{\bar{x}x}^{\bar{x}'x'} (\tilde{n}_{\bar{x}'x'} + \tilde{y}_{\bar{x}'}^* \tilde{y}_{x'})$$
$$- i\hbar \sum_{x'} [\tilde{y}_{\bar{x}}^* \ \mathrm{Im}(\Omega_Y^{ph})_x^{x'} \tilde{y}_{x'}$$
$$+ \tilde{y}_x \ \mathrm{Im}(\Omega^{ph})_{\bar{x}}^{x'} \tilde{y}_{x'}^*]$$
$$+ \mathbf{E}\left(\sum_{x'} \tilde{\mathbf{M}}_x^{x'} \tilde{n}_{\bar{x}x'} - \sum_{\bar{x}'} \tilde{\mathbf{M}}_{\bar{x}}^{\bar{x}'*} \tilde{n}_{\bar{x}'x} \right), \tag{125}$$

where the phonon-induced self-energies $\hbar \tilde{\Omega}^{ph}$ are given in Appendix E. In terms of the variables of Eqs. (123)–(125) the polarization (100) now reads

$$\bar{\mathbf{P}} = \sum_x (\tilde{\mathbf{M}}_x^* \tilde{y}_x + \tilde{\mathbf{M}}_x \tilde{y}_x^*) - \sum_{\bar{x}x} \tilde{\mathbf{M}}_x^x (\tilde{y}_{\bar{x}}^* \tilde{y}_x + \tilde{n}_{\bar{x}x}) + \tilde{\mathbf{P}}_{stat}. \tag{126}$$

Equations (123)–(125) demonstrate that the Frenkel model leads to dynamic equations having the same structure as the corresponding ones for the pair-conserving many-electron system [cf. Eqs. (67)–(69)]. As in the coherent case [Eqs. (118), (119), (58), and (59)], the different microscopic definition of the parameters entering the equations is the only difference between these systems in the above representation.

VIII. CONCLUDING REMARKS

The theoretical framework developed in this paper yields a unified description beyond the semiconductor Bloch equations treatment of the optical response of a large class of semiconductor and organic materials. It is particularly suitable for confined systems such as molecular aggregates, quantum wells, heterostructures, and nanocrystals. Starting with a general Hamiltonian that conserves the number of electron-hole pairs and can represent Frenkel, Wannier, and intermediate excitons, we obtained exact generating-function results [Eqs. (A1)–(A5)]. Using these together with Eqs. (42)–(44) and Eq. (34), we then established the structural equivalence of the semiconductor model [Eqs. (58) and (59)] with the Frenkel model [Eqs. (118) and (119)] recast in the exciton representation in the coherent limit. This equivalence is also retained when phonons are included and additional dynamic variables are added [cf. Eqs. (67)–(69) for the semiconductor and Eqs. (123)–(125) for the Frenkel system]. We further compared these results with the semiconductor Bloch equations [Eqs. (74) and (75)]. Issues addressed, using our equations, that cannot be studied on the semiconductor Bloch level include many-body resonances associated with two-pair states (bound or unbound biexcitons), the influence of two-pair transitions on the polarization dependence of various signals such as four-wave-mixing or pump-probe measurements, and excited-state absorption between one-pair and two-pair states. Furthermore, we have shown that under certain conditions the proper modeling of intraband dynamics also requires a treatment beyond the semiconductor Bloch equations. The reduced description derived in Sec. V is particularly suitable for exploring the interplay between coherent and incoherent dynamics. We have demonstrated that our treatment will eventually lead to a thermalized occupation of excitonic states at long times.

An alternative approach for calculating optical susceptibilities and nonlinear response functions is based on expanding them in the global (many-electron) eigenstates. All optical properties can then be recast in the form of summations involving the eigenvalues and the corresponding dipole matrix elements. This is known in the molecular literature as the sum-over-states (SOS) approach. For the present pair-conserving Hamiltonian, the single excitations and the double excitations may be separately diagonalized, thereby giving the relevant eigenstates. With these in hand and the matrix elements of the dipole operator calculated, one can use the SOS approach to find the nonlinear optical responses. Formulating the density-matrix dynamics in terms of the global eigenstates corresponding to excitations with definite numbers of pairs is not the same as our exciton representation of the dynamics; there is no one-to-one correspondence between the respective dynamic variables. Instead they are connected by a linear transformation that mixes variables having different lowest orders in the laser field (Victor *et al.*, 1996). The equations of motion also have very different structures (Mukamel,

1994; Chen *et al.*, 1996; Victor *et al.*, 1996). The dynamics-controlled truncation approach developed here has numerous advantages over the SOS formulation, which is much more computationally intensive. Both calculating the eigenstates and performing the necessary multiple summations become intractable for large systems. In the equation-of-motion dynamics-controlled approach we calculate the necessary Green's functions (and observables) directly, considerably reducing the number of redundant calculations. Another major difficulty with the SOS approach is the issue of size consistency. Optical susceptibilities (like any other bulk property) must scale linearly with system size, once the size is sufficiently large compared with all relevant coherence sizes. In SOS calculations this thermodynamic limit is the result of a cancellation of terms that scale with higher powers of the size. These cancellations limit the accuracy of SOS calculations; simple approximations may become dangerous since they destroy the delicate balance among large cancelling terms, resulting in huge, unphysical consequences and making it hard to develop physical intuition.

In the dynamics-controlled truncation approach, these cancellations are built-in from the very start, and each individual contribution to the response has the proper scaling with size (Spano and Mukamel, 1991a, 1991b; Chernyak and Mukamel 1996b; Victor *et al.*, 1996). The SOS expressions for susceptibilities are universal and apply to all types of materials. However, the approximations made in calculating the global eigenstates of molecules, molecular aggregates, semiconductors, and conjugated polyenes are very different, making it extremely difficult to trace the origin of the different optical response of different materials. In contrast, the equations-of-motion approach provides a unified description of various materials. This can be accomplished by varying simple parameters such as the Coulomb interaction strength or the hopping-matrix elements. A convenient, transparent physical picture then emerges (Chernyak and Mukamel, 1996a). In a sum-over-states approach it is virtually impossible to make contact with the standard semiconductor literature, while our formulation easily allows one to recover most major developments in this field as a limiting case. In addition, the sum-over-states approach is limited to a strict perturbative treatment of the radiation field, while the equations truncated by dynamics-control can be useful in many cases at excitation densities beyond the scope of strict perturbation theory. The dynamics-controlled truncation results in a set of equations for which a perturbative solution yields the optical response rigorously up to the prescribed order chosen by the cut for truncation. When one solves these equations numerically, nonperturbatively in the field, the solution will also contain contributions of higher orders in the laser field than the one used for truncation. This is a partial resummation in the external field. In connection with other truncation schemes such as factorizations leading to the semiconductor Bloch equations (which is exact only for the linear response), similar strategies have been widely used to study the

dependence of optical signals on the excitation density. Recently calculations of this type have been performed within the dynamics-controlled truncation (Mukamel *et al.*, 1996; Victor and Stahl, 1996; Bartels *et al.*, 1997) truncated at the third order. The results reproduce those of corresponding experiments, including signatures of many-body correlations for excitation densities well beyond the strict validity of third-order perturbation theory. Only strategies developed for rather high excitation densities, in particular screening models (Wyld and Fried, 1963; Zimmermann *et al.*, 1978; Haug and Schmitt-Rink, 1984; Yu-Kuang Hu *et al.*, 1989; Hartmann *et al.*, 1990; Bechstedt and Glutsch, 1991; Collet, 1993), have so far not been systematically incorporated within our approach. Parts of these contributions are already covered by the present equations but not systematically classified as a contribution to screening, while some high-density corrections are surely missing.

The primary limitation of the present theory is the restriction to pair-conserving systems. While this is justified for many materials, the situation is fundamentally different for related classes of materials such as conjugated polymers. This can be seen upon examination of typical numbers, characterizing the Coulomb interaction for the Pariser-Parr-Pople (PPP) model, which is a common semiempirical model for conjugated polymers. The one-particle (Peierls) gap given by $E_p = 4|t|\delta$, where δ is the alternation and t is the mean strength of the next-neighbor coupling, is $E_p \sim 0.7$ eV for standard PPP values for polyacetylene [$|t| = 2.4$ eV, $\delta = 0.07$] (McWilliams *et al.*, 1991), while the total optical gap is ~ 2 eV in the long chain limit. Thus, instead of decreasing the one-particle gap by the exciton binding energy, as in the case of direct-gap semiconductors, adding the Coulomb interaction more than doubles the one-particle gap, due to the dominance of the repulsive parts of the interaction in this case. Furthermore, due to the non-pair-conserving terms, components with one and two electron-hole pairs are strongly mixed in the excited states of conjugated polymers. For small oligomers the mixing is typically $\sim 50\%$ for excited states of A_g symmetry (McWilliams *et al.*, 1991). On the other hand, it is known from full configuration interaction calculations that the ground state has an overlap of more than 90% with the Hartree-Fock ground state, even for small oligomers, in which correlation effects are expected to be most pronounced (McWilliams *et al.*, 1991). Furthermore, most of the linear absorption is concentrated in transitions to only one excited state of B_u type, which is well represented by the corresponding Hartree-Fock state too. Consequently many of the modifications brought forth by the non-pair-conserving parts of the Hamiltonian may be well represented by applying a mean-field theory to these terms. This is demonstrated by the success of the time-dependent Hartree-Fock description of conjugated polymers (Meier and Mukamel, 1996; Meier *et al.*, 1996; Tretiak *et al.*, 1996b). The present approach can be extended to the case in which non-pair-conserving parts of the Coulomb interaction are replaced in the Hamiltonian by their mean-field

counterparts. Further work is required to analyze the implications of such an extended scheme.

ACKNOWLEDGMENTS

APPENDIX A: EQUATIONS FOR ELECTRON-HOLE GENERATING FUNCTIONS

In this appendix we present the equations of motion for the generating functions defined by Eqs. (36)–(40) for the many-electron system. Starting with our pair-conserving Hamiltonian (30) and neglecting contributions that do not contribute to the third-order response, we obtain the Heisenberg equations

$$i\hbar\partial_t Y_{ab}^{\alpha\beta} = \hbar\Omega_Y(Y^{\alpha\beta})_{ab} + \hbar\Omega_Y^{ph}(Y)_{ab}^{\alpha\beta} + Q_{Y\,ab}^{ph\,\alpha\beta}$$

$$+ \sum_{pqk=e} \bar{V}_{bqkp}^{eeee} S_{kpaq}^{\alpha\beta}$$

$$- \sum_{pq=e,k=h} (\bar{V}_{pqka}^{eehh} - \bar{V}_{kqpa}^{heeh}) S_{pqkb}^{\alpha\beta}$$

$$+ \sum_{pqk=h} \bar{V}_{kpqa}^{hhhh} T_{pkqb}^{\alpha\beta}$$

$$- \sum_{pq=h,k=e} (\bar{V}_{bkpq}^{eehh} - \bar{V}_{bqpk}^{ehhe}) T_{qpak}^{\alpha\beta}$$

$$- \mathbf{E}\Bigg(\bar{\mathbf{M}}_{ba}^{eh} F^{\alpha\beta} - \sum_{k=h} \bar{\mathbf{M}}_{bk}^{eh} D_{ka}^{\alpha\beta} - \sum_{k=e} \bar{\mathbf{M}}_{ka}^{eh} C_{kb}^{\alpha\beta}$$

$$+ \sum_{k=e} \bar{\mathbf{M}}_{bk}^{ee} Y_{ak}^{\alpha\beta} - \sum_{k=h} \bar{\mathbf{M}}_{ka}^{hh} Y_{kb}^{\alpha\beta} \Bigg), \tag{A1}$$

$$i\hbar\partial_t B_{abcd}^{\alpha\beta} = \hbar\Omega_B(B^{\alpha\beta})_{abcd} + \hbar\Omega_B^{ph}(B)_{abcd}^{\alpha\beta} - \mathbf{E}(\bar{\mathbf{M}}_{dc}^{eh} Y_{ab}^{\alpha\beta}$$

$$- \bar{\mathbf{M}}_{da}^{eh} Y_{cb}^{\alpha\beta} - \bar{\mathbf{M}}_{bc}^{eh} Y_{ad}^{\alpha\beta} + \bar{\mathbf{M}}_{ba}^{eh} Y_{cd}^{\alpha\beta})$$

$$- \mathbf{E}\Bigg[\sum_{k=e} (\bar{\mathbf{M}}_{dk}^{ee} B_{abck}^{\alpha\beta} + \bar{\mathbf{M}}_{bk}^{ee} B_{akcd}^{\alpha\beta})$$

$$- \sum_{k=h} (\bar{\mathbf{M}}_{kc}^{hh} B_{abkd}^{\alpha\beta} + \bar{\mathbf{M}}_{ka}^{hh} B_{kbcd}^{\alpha\beta}) \Bigg] + \mathcal{O}(E^4), \tag{A2}$$

$$i\hbar\partial_t N_{abcd}^{\alpha\beta} = \hbar\Omega_N(N^{\alpha\beta})_{abcd} + \hbar\Omega_N^{ph}(N)_{abcd}^{\alpha\beta}$$

$$- \mathbf{E}(\bar{\mathbf{M}}_{dc}^{eh} Y_{ba}^{\beta\alpha*} - \bar{\mathbf{M}}_{ba}^{he} Y_{cd}^{\alpha\beta})$$

$$- \mathbf{E}\Bigg[\sum_{k=e} (\bar{\mathbf{M}}_{dk}^{ee} N_{abck}^{\alpha\beta} - \bar{\mathbf{M}}_{ka}^{ee} N_{kbcd}^{\alpha\beta})$$

$$- \sum_{k=h} (\bar{\mathbf{M}}_{kc}^{hh} N_{abkd}^{\alpha\beta} - \bar{\mathbf{M}}_{bk}^{hh} N_{akcd}^{\alpha\beta}) \Bigg] + \mathcal{O}(E^4), \tag{A3}$$

$$i\hbar\partial_t Z^{\alpha\beta}_{abcdef}=\hbar\Omega_Z(Z^{\alpha\beta})_{abcdef}+\hbar\Omega_Z^{ph}(Z)^{\alpha\beta}_{abcdef}$$

$$-\mathbf{E}(\overline{\mathbf{M}}^{eh}_{fe}N^{\alpha\beta}_{abcd}-\overline{\mathbf{M}}^{eh}_{fc}N^{\alpha\beta}_{abed}-\overline{\mathbf{M}}^{eh}_{de}N^{\alpha\beta}_{abcf}$$

$$+\overline{\mathbf{M}}^{eh}_{dc}N^{\alpha\beta}_{abef}-\overline{\mathbf{M}}^{he}_{ba}B^{\alpha\beta}_{cdef})+\mathcal{O}(E^4),\qquad(A4)$$

$$i\hbar\partial_t F^{\alpha\beta}=\hbar\Omega_F^{ph}(F)^{\alpha\beta}+\sum_{pq=e,\mu}(\overline{\gamma}^\mu_{pq}\beta_\mu-\overline{\gamma}^{\mu*}_{qp}\alpha_\mu)C^{\alpha\beta}_{pq}$$

$$-\sum_{pq=h,\mu}(\overline{\gamma}^\mu_{pq}\beta_\mu-\overline{\gamma}^{\mu*}_{qp}\alpha_\mu)D^{\alpha\beta}_{qp},\qquad(A5)$$

with

$$C^{\alpha\beta}_{ab}\equiv\langle\overline{c}^\dagger_a\overline{c}_b\hat{F}^{\alpha\beta}\rangle,\quad D^{\alpha\beta}_{ab}\equiv\langle\overline{d}^\dagger_a\overline{d}_b\hat{F}^{\alpha\beta}\rangle,\qquad(A6)$$

$$S^{\alpha\beta}_{abcd}\equiv\langle\overline{c}^\dagger_a\overline{c}_b\overline{d}_c\overline{c}_d\hat{F}^{\alpha\beta}\rangle,\quad T^{\alpha\beta}_{abcd}\equiv\langle\overline{d}^\dagger_a\overline{d}_b\overline{d}_c\overline{c}_d\hat{F}^{\alpha\beta}\rangle.\qquad(A7)$$

The linear operators $\hbar\Omega$ and $\hbar\Omega^{ph}$ form the homogeneous part of the respective equations. The operators $\hbar\Omega$ act only on the electronic indices. The eigenvalues of these operators can be identified with the energies of excitons or biexcitons including bound as well as scattering states. They are defined by

$$\hbar\Omega_Y(Y^{\alpha\beta})_{ab}\equiv(\epsilon^e_b-\epsilon^h_a)Y^{\alpha\beta}_{ab}$$

$$+\sum_{p=h,q=e}(\overline{V}^{heeh}_{pqba}-\overline{V}^{hhee}_{pabq})Y^{\alpha\beta}_{pq},\qquad(A8)$$

$$\hbar\Omega_B(B^{\alpha\beta})_{abcd}\equiv(\epsilon^e_d-\epsilon^h_c+\epsilon^e_b-\epsilon^h_a)B^{\alpha\beta}_{abcd}$$

$$+\sum_{pq=e}\overline{V}^{eeee}_{bpdq}B^{\alpha\beta}_{apcq}+\sum_{pq=h}\overline{V}^{hhhh}_{pcqa}B^{\alpha\beta}_{qbpd}$$

$$+\sum_{\substack{p=h\\q=e}}[(\overline{V}^{heeh}_{pqdc}-\overline{V}^{hhee}_{pcdq})B^{\alpha\beta}_{abpq}$$

$$+(\overline{V}^{heeh}_{pqda}-\overline{V}^{hhee}_{padq})B^{\alpha\beta}_{pbcq}$$

$$+(\overline{V}^{heeh}_{pqbc}-\overline{V}^{hhee}_{pcbq})B^{\alpha\beta}_{aqpd}$$

$$+(\overline{V}^{heeh}_{pqba}-\overline{V}^{hhee}_{pabq})B^{\alpha\beta}_{pqcd}],\qquad(A9)$$

$$\hbar\Omega_N(N^{\alpha\beta})_{abcd}\equiv(\epsilon^e_d-\epsilon^h_c+\epsilon^h_b-\epsilon^e_a)N^{\alpha\beta}_{abcd}$$

$$+\sum_{p=h,q=e}[(\overline{V}^{heeh}_{pqdc}-\overline{V}^{hhee}_{pcdq})N^{\alpha\beta}_{abpq}$$

$$-(\overline{V}^{heeh}_{baqp}-\overline{V}^{hhee}_{bpqa})N^{\alpha\beta}_{qpcd}],\qquad(A10)$$

$$\hbar\Omega_Z(Z^{\alpha\beta})_{abcdef}\equiv(\epsilon^e_f-\epsilon^h_e+\epsilon^e_d-\epsilon^h_c+\epsilon^h_b-\epsilon^e_a)Z^{\alpha\beta}_{abcdef}$$

$$+\sum_{pq=e}\overline{V}^{eeee}_{dpfq}Z^{\alpha\beta}_{abcpeq}$$

$$+\sum_{pq=h}\overline{V}^{hhhh}_{peqc}Z^{\alpha\beta}_{abqdpf}$$

$$+\sum_{\substack{p=h\\q=e}}[(\overline{V}^{heeh}_{pqfe}-\overline{V}^{hhee}_{pefq})Z^{\alpha\beta}_{abcdpq}$$

$$+(\overline{V}^{heeh}_{pqfc}-\overline{V}^{hhee}_{pcfq})Z^{\alpha\beta}_{abpdeq}$$

$$+(\overline{V}^{heeh}_{pqde}-\overline{V}^{hhee}_{pedq})Z^{\alpha\beta}_{abcqpf}$$

$$+(\overline{V}^{heeh}_{pqdc}-\overline{V}^{hhee}_{pcdq})Z^{\alpha\beta}_{abpqef}$$

$$-(\overline{V}^{heeh}_{baqp}-\overline{V}^{hhee}_{bpqa})Z^{\alpha\beta}_{qpcdef}].\qquad(A11)$$

Unlike $\hbar\Omega$, the operators $\hbar\Omega^{ph}$ act on electronic indices as well as on the phonon-related arguments α,β. We shall see later that these terms can be used to define phonon-induced self-energies [cf. Eqs. (D7), (D11), and (D27)]. The definition of these operators is

$$\hbar\Omega_Y^{ph}(Y)^{\alpha\beta}_{ab}\equiv\hbar\hat{\overline{\omega}}Y^{\alpha\beta}_{ab}+\sum_{k=e}\overline{\Lambda}^\beta_{bk}Y^{\alpha\beta}_{ak}-\sum_{k=h}\overline{\Lambda}^\beta_{ka}Y^{\alpha\beta}_{kb},$$
$$(A12)$$

$$\hbar\Omega_B^{ph}(B)^{\alpha\beta}_{abcd}\equiv\hbar\hat{\overline{\omega}}B^{\alpha\beta}_{abcd}+\sum_{k=e}(\overline{\Lambda}^\beta_{dk}B^{\alpha\beta}_{abck}+\overline{\Lambda}^\beta_{bk}B^{\alpha\beta}_{akcd})$$

$$-\sum_{k=h}(\overline{\Lambda}^\beta_{kc}B^{\alpha\beta}_{abkd}+\overline{\Lambda}^\beta_{ka}B^{\alpha\beta}_{kbcd}),\qquad(A13)$$

$$\hbar\Omega_N^{ph}(N)^{\alpha\beta}_{abcd}\equiv\hbar\hat{\overline{\omega}}N^{\alpha\beta}_{abcd}+\sum_{k=e}(\overline{\Lambda}^\beta_{dk}N^{\alpha\beta}_{abck}-\overline{\Lambda}^\alpha_{ka}N^{\alpha\beta}_{kbcd})$$

$$-\sum_{k=h}(\overline{\Lambda}^\beta_{kc}N^{\alpha\beta}_{abkd}-\overline{\Lambda}^\alpha_{bk}N^{\alpha\beta}_{akcd}),\qquad(A14)$$

$$\hbar\Omega_Z^{ph}(Z)^{\alpha\beta}_{abcdef}\equiv\hbar\hat{\overline{\omega}}Z^{\alpha\beta}_{abcdef}+\sum_{k=e}(\overline{\Lambda}^\beta_{fk}Z^{\alpha\beta}_{abcdek}$$

$$+\overline{\Lambda}^\beta_{dk}Z^{\alpha\beta}_{abckef}-\overline{\Lambda}^\alpha_{ka}Z^{\alpha\beta}_{kbcdef})$$

$$-\sum_{k=h}(\overline{\Lambda}^\beta_{ke}Z^{\alpha\beta}_{abcdkf}+\overline{\Lambda}^\beta_{kc}Z^{\alpha\beta}_{abkdef}$$

$$-\overline{\Lambda}^\alpha_{bk}Z^{\alpha\beta}_{akcdef}),\qquad(A15)$$

$$\hbar\Omega_F^{ph}(F)^{\alpha\beta}\equiv\hbar\hat{\overline{\omega}}F^{\alpha\beta},\qquad(A16)$$

with

$$\overline{\Lambda}^\alpha_{ab}\equiv\sum_\mu[\overline{\gamma}^\mu_{ab}\partial_{\alpha_\mu}+\overline{\gamma}^{\mu*}_{ba}(\partial_{\beta_\mu}+\alpha_\mu)],\qquad(A17)$$

$$\overline{\Lambda}^\beta_{ab}\equiv\sum_\mu[\overline{\gamma}^\mu_{ab}(\partial_{\alpha_\mu}+\beta_\mu)+\overline{\gamma}^{\mu*}_{ba}\partial_{\beta_\mu}],\qquad(A18)$$

$$\hat{\overline{\omega}}\equiv\sum_\mu\hbar\omega_\mu(\beta_\mu\partial_{\beta_\mu}-\alpha_\mu\partial_{\alpha_\mu}).\qquad(A19)$$

Finally, the phonon-induced inhomogeneity Q_Y^{ph} is given by

$$Q_{Y\ ab}^{ph\,\alpha\beta}\equiv\sum_{pq=e,\mu}(\overline{\gamma}^\mu_{pq}\beta_\mu-\overline{\gamma}^{\mu*}_{qp}\alpha_\mu)S^{\alpha\beta}_{pqab}$$

$$-\sum_{pq=h,\mu}(\overline{\gamma}^\mu_{pq}\beta_\mu-\overline{\gamma}^{\mu*}_{qp}\alpha_\mu)T^{\alpha\beta}_{qpab}.\qquad(A20)$$

Similar contributions to the other equations of motion are at least order $\mathcal{O}(E^4)$. Q_Y^{ph} is third order in the laser field and it vanishes for $\alpha=\beta=0$. It therefore leads to third-order corrections of the phonon-assisted variables. When the four-point density matrices S and T are factorized in Eq. (A20) according to the mean-field treatment of electronic correlations, these terms lead to density-dependent contributions to the phonon self energies (Bányai *et al.*, 1992; Haug, 1992; Kuhn and Rossi, 1992; Tran Thoai and Haug, 1993; Kuhn *et al.*, 1994; Schilp *et al.*, 1994, 1995). In the low-density regime these contributions can be neglected. We shall not discuss these terms further in this article.

Looking at Eqs. (A1)–(A5) one could get the impression that equations of motion should also be set up for the variables C, D, S, and T defined in Eqs. (A6) and (A7) in order to obtain a closed set of equations. This is, however, deceiving, because these variables can be expressed as

$$C_{ab}^{\alpha\beta}=\sum_{k=\mathrm{h}} N_{akkb}^{\alpha\beta}+\mathcal{O}(E^4), \qquad (A21)$$

$$D_{ab}^{\alpha\beta}=\sum_{k=\mathrm{e}} N_{kabk}^{\alpha\beta}+\mathcal{O}(E^4), \qquad (A22)$$

$$S_{abcd}^{\alpha\beta}=\sum_{k=\mathrm{h}} Z_{akkbcd}^{\alpha\beta}+\mathcal{O}(E^5), \qquad (A23)$$

$$T_{abcd}^{\alpha\beta}=\sum_{k=\mathrm{e}} Z_{kabkcd}^{\alpha\beta}+\mathcal{O}(E^5). \qquad (A24)$$

These relations may be proved using the results of Axt, Victor, and Stahl (1996), who showed that, in a system described by a pair-conserving material Hamiltonian, all density matrices defined as expectation values of operators that can only partially be combined to pair operators $\bar{d}^\dagger \bar{c}^\dagger$ or $\bar{d}\,\bar{c}$ can be eliminated to any order in the driving field by suitable combinations of density matrices defined only through pair operators. This holds even in the presence of a phonon bath. In Appendix F we provide a different derivation of Eqs. (A21)–(A24), which also shows that, unlike the truncated quantum BBGKY hierarchy, dynamics-controlled truncation does not violate fundamental trace relations (Schmitt *et al.*, 1989, 1990; Cassing and Pfitzner, 1992; Reinhard and Toepffer, 1994; Axt and Mukamel, 1997b).

When one uses Eqs. (A21)–(A24), Eqs. (A1)–(A5) form a closed set representing the dynamics of the pair-conserving many-electron model rigorously up to third order in the laser field, including phonon degrees of freedom. A calculation of the third-order polarization based on these equations can be performed iteratively according to the following steps. First, one has to calculate the generating function $F^{\alpha\beta}$ for phonon correlations in thermal equilibrium. Here is the point where the temperature enters the equations. F is the only one of the five functions that has nonzero temperature-dependent values prior to the optical excitation. The linear response is completely determined by $Y_{ab}^{\alpha\beta}$, while the other variables are needed in order to calculate nonlinear optical signals.

APPENDIX B: GENERATING FUNCTIONS FOR FRENKEL EXCITONS

A generating-function description of Frenkel excitons analogous to Appendix A has been formulated by Axt and Mukamel (1997a). Using the notation (103)–(107), the equations relevant for a third-order calculation within the Frenkel exciton model read

$$i\hbar\partial_t \tilde{Y}_j^{\alpha\beta}=\hbar\tilde{\Omega}_Y(\tilde{Y}^{\alpha\beta})_j+\hbar\tilde{\Omega}_Y^{ph}(\tilde{Y})_j^{\alpha\beta}-2\sum_m \tilde{J}_{jm}\tilde{Z}_{jjm}^{\alpha\beta}$$
$$+\tilde{Q}_{Y\,j}^{ph\,\alpha\beta}-\mathbf{E}[\boldsymbol{\mu}_j(\tilde{F}^{\alpha\beta}-2\bar{N}_{jj}^{\alpha\beta})+\boldsymbol{\mu}_j'\,\tilde{Y}_j^{\alpha\beta}], \tag{B1}$$

$$i\hbar\partial_t \tilde{B}_{ij}^{\alpha\beta}=\hbar\tilde{\Omega}_B(\tilde{B}^{\alpha\beta})_{ij}+\hbar\tilde{\Omega}_B^{ph}(\tilde{B})_{ij}^{\alpha\beta}-\xi_{ij}\mathbf{E}[\boldsymbol{\mu}_j\tilde{Y}_i^{\alpha\beta}$$
$$+\boldsymbol{\mu}_i\tilde{Y}_j^{\alpha\beta}+(\boldsymbol{\mu}_j'+\boldsymbol{\mu}_i')\tilde{B}_{ij}^{\alpha\beta}]+\mathcal{O}(E^4), \tag{B2}$$

$$i\hbar\partial_t \bar{N}_{ij}^{\alpha\beta}=\hbar\tilde{\Omega}_N(\bar{N}^{\alpha\beta})_{ij}+\hbar\tilde{\Omega}_N^{ph}(\bar{N})_{ij}^{\alpha\beta}-\mathbf{E}[\boldsymbol{\mu}_j\tilde{Y}_i^{\beta\alpha*}$$
$$-\boldsymbol{\mu}_i\tilde{Y}_j^{\alpha\beta}+(\boldsymbol{\mu}_j'-\boldsymbol{\mu}_i')\bar{N}_{ij}^{\alpha\beta}]+\mathcal{O}(E^4), \tag{B3}$$

$$i\hbar\partial_t \tilde{Z}_{kij}^{\alpha\beta}=\hbar\tilde{\Omega}_Z(\tilde{Z}^{\alpha\beta})_{kij}+\hbar\tilde{\Omega}_Z^{ph}(\tilde{Z}^{\alpha\beta})_{kij}+\mathbf{E}\boldsymbol{\mu}_k\tilde{B}_{ij}^{\alpha\beta}$$
$$-\xi_{ij}\mathbf{E}(\boldsymbol{\mu}_j\bar{N}_{ki}^{\alpha\beta}+\boldsymbol{\mu}_i\bar{N}_{kj}^{\alpha\beta})+\mathcal{O}(E^4), \tag{B4}$$

$$i\hbar\partial_t \tilde{F}^{\alpha\beta}=\hbar\tilde{\Omega}_F^{ph}(\tilde{F})^{\alpha\beta}+\sum_{nm\mu}\tilde{\gamma}_{nm}^\mu(\beta_\mu-\alpha_\mu)\bar{N}_{nm}^{\alpha\beta}, \tag{B5}$$

with $\xi_{ij}\equiv 1-\delta_{ij}$ and $\tilde{J}_{jm}\equiv\delta_{jm}\hbar\Omega_j+J_{jm}$. The phonon-independent linear operators appearing in the homogeneous parts of the equations are given by

$$\hbar\tilde{\Omega}_Y(\tilde{Y}^{\alpha\beta})_j\equiv\sum_m \tilde{J}_{jm}\tilde{Y}_m^{\alpha\beta}, \tag{B6}$$

$$\hbar\tilde{\Omega}_B(\tilde{B}^{\alpha\beta})_{ij}\equiv\xi_{ij}\sum_m (\tilde{J}_{jm}\tilde{B}_{im}^{\alpha\beta}+\tilde{J}_{im}\tilde{B}_{mj}^{\alpha\beta}), \tag{B7}$$

$$\hbar\tilde{\Omega}_N(\bar{N}^{\alpha\beta})_{ij}\equiv\sum_m (\tilde{J}_{jm}\bar{N}_{im}^{\alpha\beta}-\tilde{J}_{mi}\bar{N}_{mj}^{\alpha\beta}), \tag{B8}$$

$$\hbar\tilde{\Omega}_Z(\tilde{Z}^{\alpha\beta})_{kij}\equiv\sum_m [\xi_{ij}(\tilde{J}_{jm}\tilde{Z}_{kim}^{\alpha\beta}+\tilde{J}_{im}\tilde{Z}_{kmj}^{\alpha\beta})$$
$$-\tilde{J}_{mk}\tilde{Z}_{mij}^{\alpha\beta}], \tag{B9}$$

while the corresponding phonon-dependent linear operators read

$$\hbar\tilde{\Omega}_Y^{ph}(\tilde{Y})_j^{\alpha\beta}\equiv\hbar\hat{\tilde{\omega}}\tilde{Y}_j^{\alpha\beta}+\sum_m \tilde{\Lambda}_{jm}^\beta\tilde{Y}_m^{\alpha\beta}, \tag{B10}$$

$$\hbar\tilde{\Omega}_B^{ph}(\tilde{B})_{ij}^{\alpha\beta}\equiv\hbar\hat{\tilde{\omega}}\tilde{B}_{ij}^{\alpha\beta}+\xi_{ij}\sum_m (\tilde{\Lambda}_{jm}^\beta\tilde{B}_{im}^{\alpha\beta}+\tilde{\Lambda}_{im}^\beta\tilde{B}_{mj}^{\alpha\beta}), \tag{B11}$$

$$\hbar\Omega_N^{ph}(\bar{N})_{ij}^{\alpha\beta}\equiv\hbar\hat{\tilde{\omega}}\bar{N}_{ij}^{\alpha\beta}+\sum_m\,(\bar{\Lambda}_{jm}^\beta\bar{N}_{im}^{\alpha\beta}-\bar{\Lambda}_{mi}^\alpha\bar{N}_{mj}^{\alpha\beta}),\tag{B12}$$

$$\hbar\bar{\Omega}_Z^{ph}(\bar{Z}^{\alpha\beta})_{kij}\equiv\hbar\hat{\tilde{\omega}}\bar{Z}_{kij}^{\alpha\beta}+\sum_m\,[\,\xi_{ij}(\bar{\Lambda}_{jm}^\beta\bar{Z}_{kim}^{\alpha\beta}$$
$$+\bar{\Lambda}_{im}^\beta\bar{Z}_{kmj}^{\alpha\beta})-\bar{\Lambda}_{mk}^\alpha\bar{Z}_{mij}^{\alpha\beta}],\tag{B13}$$

$$\hbar\bar{\Omega}_F^{ph}(\bar{F})^{\alpha\beta}\equiv\hbar\hat{\tilde{\omega}}\bar{F}_{\alpha\beta},\tag{B14}$$

with

$$\bar{\Lambda}_{jm}^\alpha=\sum_\mu\,\tilde{\gamma}_{jm}^\mu(\alpha_\mu+\partial_{\alpha_\mu}+\partial_{\beta_\mu}),\tag{B15}$$

$$\bar{\Lambda}_{jm}^\beta=\sum_\mu\,\tilde{\gamma}_{jm}^\mu(\beta_\mu+\partial_{\alpha_\mu}+\partial_{\beta_\mu}),\tag{B16}$$

$$\hat{\tilde{\omega}}\equiv\sum_\mu\,\tilde{\omega}_\mu(\beta_\mu\partial_{\beta_\mu}-\alpha_\mu\partial_{\alpha_\mu}).\tag{B17}$$

As in the many-electron case, we obtain a phonon-induced inhomogeneity of order lower than $\mathcal{O}(E^4)$ only for the transition amplitude $\bar{Y}$,

$$\bar{Q}_{Y\ j}^{ph\,\alpha\beta}\equiv-2\sum_m\,\bar{\Lambda}_{jm}^\beta\bar{Z}_{jjm}^{\alpha\beta}+\sum_{nm\mu}\,\tilde{\gamma}_{nm}^\mu(\beta_\mu-\alpha_\mu)\bar{Z}_{nmj}^{\alpha\beta}.\tag{B18}$$

Unlike Eq. (A20), $\bar{Q}_{Y\ j}^{ph\,\alpha\beta}$ does not vanish for $\alpha=\beta=0$. Apart from this detail, this contribution has the same physical meaning as the corresponding term (A20). Using Eq. (100) we find that the polarization in the generating-function representation is determined by the values of $\bar{Y}_j^{\alpha\beta}$ and $\bar{N}_{jj}^{\alpha\beta}$ at $\alpha=\beta=0$ due to the identities $\bar{Y}_j=\bar{Y}_j^{\alpha=\beta=0}$ and $\bar{N}_{jj}=\bar{N}_{jj}^{\alpha=\beta=0}$.

Written in the form (A1)–(A5), the equations for the many-electron system look much more complicated than their Frenkel counterparts (B1)–(B5). But inserting the relations (A21)–(A24) in Eqs. (A1)–(A5) reveals that, for both sets of equations, the right-hand sides consist of contributions of analogous types, although the coupling is obviously simpler in the Frenkel case.

APPENDIX C: EXCITON REPRESENTATION OF TWO-EXCITON VARIABLES AND COUPLING CONSTANTS

In this appendix we derive the exciton representation (59) of the equation of motion for the correlated part $\bar{B}$ of the two-pair transition density in the coherent limit. Using the cluster decomposition (54) together with Eqs. (47) and (48) we obtain in the coherent limit

$$i\hbar\partial_t\bar{B}_{abcd}=\hbar\Omega_B(\bar{B})_{abcd}+Q_{abcd}^{\bar{B}}-Q_{cbad}^{\bar{B}}$$
$$-\mathbf{E}\Big[\sum_{k=\mathrm{e}}\,(\bar{\mathbf{M}}_{dk}^{\mathrm{ee}}\bar{B}_{abck}+\bar{\mathbf{M}}_{bk}^{\mathrm{ee}}\bar{B}_{akcd})$$
$$-\sum_{k=\mathrm{h}}\,(\bar{\mathbf{M}}_{kc}^{\mathrm{hh}}\bar{B}_{abkd}+\bar{\mathbf{M}}_{ka}^{\mathrm{hh}}\bar{B}_{kbcd})\Big],\tag{C1}$$

with

$$Q_{abcd}^{\bar{B}}\equiv\sum_{pq=\mathrm{e}}\,\bar{V}_{bpdq}^{\mathrm{eeee}}Y_{ap}Y_{cq}+\sum_{pq=\mathrm{h}}\,\bar{V}_{pcqa}^{\mathrm{hhhh}}Y_{qb}Y_{pd}$$
$$+\sum_{\substack{p=\mathrm{h}\\q=\mathrm{e}}}\,[\,(\bar{V}_{pqda}^{\mathrm{heeh}}-\bar{V}_{padq}^{\mathrm{hhee}})Y_{pb}Y_{cq}$$
$$+(\bar{V}_{pqbc}^{\mathrm{heeh}}-\bar{V}_{pcbq}^{\mathrm{hhee}})Y_{aq}Y_{pd}].\tag{C2}$$

We then introduce an auxiliary function $\bar{B}^A$ defined as the solution of

$$i\hbar\partial_t\bar{B}_{abcd}^A=\hbar\Omega_B(\bar{B}^A)_{abcd}+Q_{abcd}^{\bar{B}}$$
$$-\mathbf{E}\Big[\sum_{k=\mathrm{e}}\,(\bar{\mathbf{M}}_{dk}^{\mathrm{ee}}\bar{B}_{abck}^A+\bar{\mathbf{M}}_{bk}^{\mathrm{ee}}\bar{B}_{akcd}^A)$$
$$-\sum_{k=\mathrm{h}}\,(\bar{\mathbf{M}}_{kc}^{\mathrm{hh}}\bar{B}_{abkd}^A+\bar{\mathbf{M}}_{ka}^{\mathrm{hh}}\bar{B}_{kbcd}^A)\Big].\tag{C3}$$

Because $\hbar\Omega_B$ commutes with the operation of exchanging the indices a and c, we obtain

$$\bar{B}_{abcd}=\bar{B}_{abcd}^A-\bar{B}_{cbad}^A.\tag{C4}$$

We next expand $\bar{B}^A$ in exciton eigenfunctions in the form

$$\bar{B}_{abcd}^A=\sum_{\bar{x}x}\,\bar{\psi}_{ab}^{\bar{x}}\bar{\psi}_{cd}^x b_{\bar{x}x},\tag{C5}$$

which yields

$$\bar{B}_{abcd}=\sum_{\bar{x}x}\,(\bar{\psi}_{ab}^{\bar{x}}\bar{\psi}_{cd}^x-\bar{\psi}_{cb}^{\bar{x}}\bar{\psi}_{ad}^x)b_{\bar{x}x}.\tag{C6}$$

Here we note that each of the sets of functions, $\bar{\psi}_{ab}^{\bar{x}}\bar{\psi}_{cd}^x$ as well as $\bar{\psi}_{cb}^{\bar{x}}\bar{\psi}_{ad}^x$, forms a complete basis set for the space of functions with two-electron and two-hole arguments, reflecting the two distinct ways to select two electron-hole pairs out of the four particles. Instead of expanding $\bar{B}^A$ in the form (C5) we could as well have expanded $\bar{B}$ directly in either of these sets. Compared to these alternatives, the representation (C6) has the advantage that the fundamental anticommutation relation,

$$\bar{B}_{abcd}=-\bar{B}_{cbad}=-\bar{B}_{adcb}=\bar{B}_{cdab},\tag{C7}$$

is satisfied by each term of the expansion separately, which makes a truncation of the expansion (C6) possible, consistent with the Pauli principle. Equation (59) is then obtained by projecting (C3) onto $\bar{\psi}_{ab}^{\bar{x}}\bar{\psi}_{cd}^x$ and inserting the expansions (55) and (C5), where the following auxiliary quantities have been introduced:

$$\bar{V}_{x}^{\bar{x}\bar{x}'x'} \equiv \sum_{\substack{a=\text{h}\\b=\text{e}}} \bar{\psi}_{ab}^{x*} \Bigg[\sum_{\substack{pqk=\text{e}\\l=\text{h}}} \bar{V}_{bqkp}^{\text{eeee}} \bar{\psi}_{lk}^{\bar{x}*} (\bar{\psi}_{lp}^{\bar{x}'} \bar{\psi}_{aq}^{x'}$$

$$- \bar{\psi}_{ap}^{\bar{x}'} \bar{\psi}_{lq}^{x'}) + \sum_{\substack{pqk=\text{h}\\l=\text{e}}} \bar{V}_{kpqa}^{\text{hhhh}} \bar{\psi}_{pl}^{\bar{x}*} (\bar{\psi}_{kl}^{\bar{x}'} \bar{\psi}_{qb}^{x'}$$

$$- \bar{\psi}_{ql}^{\bar{x}'} \bar{\psi}_{kb}^{x'}) - \sum_{\substack{pq=\text{e}\\kl=\text{h}}} (\bar{V}_{pqka}^{\text{eehh}} - \bar{V}_{kqpa}^{\text{heeh}}) \bar{\psi}_{lp}^{\bar{x}*}$$

$$\times (\bar{\psi}_{lq}^{\bar{x}'} \bar{\psi}_{kb}^{x'} - \bar{\psi}_{kq}^{\bar{x}'} \bar{\psi}_{lb}^{x'})$$

$$- \sum_{\substack{pq=\text{h}\\kl=\text{e}}} (\bar{V}_{bkpq}^{\text{eehh}} - \bar{V}_{bqpk}^{\text{ehhe}}) \bar{\psi}_{ql}^{\bar{x}*}$$

$$\times (\bar{\psi}_{pl}^{\bar{x}'} \bar{\psi}_{ak}^{x'} - \bar{\psi}_{al}^{\bar{x}'} \bar{\psi}_{pk}^{x'}) \Bigg], \tag{C8}$$

$$\bar{V}_{\bar{x}x}^{\bar{x}'x'} \equiv \sum_{\substack{ac=\text{h}\\bd=\text{e}}} \bar{\psi}_{ab}^{\bar{x}*} \bar{\psi}_{cd}^{x*} \Bigg\{ \sum_{pq=\text{e}} \bar{V}_{bpdq}^{\text{eeee}} \bar{\psi}_{ap}^{\bar{x}'} \bar{\psi}_{cq}^{x'}$$

$$+ \sum_{\substack{p=\text{h}\\q=\text{e}}} [(\bar{V}_{pqda}^{\text{heeh}} - \bar{V}_{padq}^{\text{hhee}}) \bar{\psi}_{qb}^{\bar{x}'} \bar{\psi}_{cd}^{x'} + (\bar{V}_{pqbc}^{\text{heeh}}$$

$$- \bar{V}_{pcbq}^{\text{hhee}}) \bar{\psi}_{aq}^{\bar{x}'} \bar{\psi}_{pd}^{x'}] + \sum_{pq=\text{h}} \bar{V}_{pcqa}^{\text{hhhh}} \bar{\psi}_{qb}^{\bar{x}'} \bar{\psi}_{pd}^{x'} \Bigg\}, \tag{C9}$$

$$\bar{\mathbf{M}}_x \equiv \sum_{ab} \bar{\psi}_{ab}^{x*} \bar{\mathbf{M}}_{ba}^{\text{eh}}, \tag{C10}$$

$$\bar{\mathbf{M}}_x^{x'} \equiv \sum_{\substack{a=\text{h}\\b=\text{e}}} \bar{\psi}_{ab}^{x*} \Bigg(\sum_{k=\text{h}} \mathbf{M}_{ka}^{\text{hh}} \bar{\psi}_{kb}^{x'} - \sum_{k=\text{e}} \mathbf{M}_{bk}^{\text{ee}} \bar{\psi}_{ak}^{x'} \Bigg), \tag{C11}$$

$$\bar{\mathbf{M}}_x^{\bar{x}'x'} \equiv \sum_{\substack{ka=\text{h}\\qb=\text{e}}} \bar{\psi}_{ab}^{x*} \bar{\psi}_{kq}^{\bar{x}'*} (\mathbf{M}_{bk}^{\text{eh}} \bar{\psi}_{aq}^{x'} + \mathbf{M}_{qa}^{\text{eh}} \bar{\psi}_{kb}^{x'}). \tag{C12}$$

Note that projecting Eq. (C1) for $\bar{B}$ (instead of $\bar{B}^A$) onto the function space spanned by $\bar{\psi}_{abcd}^{xx} \equiv \bar{\psi}_{ab}^{x} \bar{\psi}_{cd}^{x} - \bar{\psi}_{cb}^{x} \bar{\psi}_{ad}^{x}$ does not lead to explicit equations for $b_{\bar{x}x}$ when the representation (C6) is inserted, because the functions $\bar{\psi}_{abcd}^{xx}$ are not orthonormal.

In the Frenkel case the exciton representation of the analogous coupling constants needed in Eqs. (118) and (119) as well as in Eqs. (123)–(125) reads

$$\tilde{V}_x^{\bar{x}\bar{x}'x'} \equiv 2 \sum_j \tilde{\psi}_j^{x*} \tilde{\psi}_j^{\bar{x}*} \tilde{\psi}_j^{\bar{x}'} \tilde{\psi}_j^{x'} (\hbar\Omega_j - \tilde{E}_{x'}), \tag{C13}$$

$$\tilde{V}_{\bar{x}x}^{\bar{x}'x'} \equiv -(\tilde{E}_{\bar{x}} + \tilde{E}_x) \sum_j \tilde{\psi}_j^{x*} \tilde{\psi}_j^{\bar{x}*} \tilde{\psi}_j^{\bar{x}'} \tilde{\psi}_j^{x'}, \tag{C14}$$

$$\tilde{\mathbf{M}}_x \equiv \sum_j \tilde{\psi}_j^{x*} \boldsymbol{\mu}_j, \tag{C15}$$

$$\tilde{\mathbf{M}}_x^{x'} \equiv -\sum_j \tilde{\psi}_j^{x*} \boldsymbol{\mu}_j' \tilde{\psi}_j^{x'}, \tag{C16}$$

$$\tilde{\mathbf{M}}_x^{\bar{x}'x'} \equiv 2 \sum_j \tilde{\psi}_j^{x*} \tilde{\psi}_j^{\bar{x}'*} \tilde{\psi}_j^{x'} \boldsymbol{\mu}_j. \tag{C17}$$

APPENDIX D: PHONON-INDUCED SELF-ENERGIES FOR THE MANY-ELECTRON SYSTEM

In this appendix we calculate the phonon-induced self-energies that appear in Sec. V. In addition to the parts already present in the coherent limit, the equation for each electronic density matrix contains one phonon-induced source term, namely, the term $\propto \Omega^{ph}$ taken at $\alpha = \beta = 0$; e.g., the additional phonon-induced source for the transition density Y reads explicitly

$$\hbar\Omega_Y^{ph}(Y)_{ab}^{\alpha=\beta=0} = \sum_{\mu} \Bigg[\sum_{k=\text{e}} (\bar{\gamma}_{bk}^{\mu} Y_{\mu ak}^{(+)} + \bar{\gamma}_{kb}^{\mu*} Y_{\mu ak}^{(-)})$$

$$- \sum_{k=\text{h}} (\bar{\gamma}_{ka}^{\mu} Y_{\mu kb}^{(+)} + \bar{\gamma}_{ak}^{\mu*} Y_{\mu kb}^{(-)}) \Bigg], \tag{D1}$$

where we have introduced the following phonon-assisted variables:

$$Y_{\mu ab}^{(+)} \equiv \partial_{\alpha_\mu} Y_{ab}^{\alpha\beta}|_{\alpha=\beta=0} = \langle b_\mu^\dagger \bar{d}_a \bar{c}_b \rangle, \tag{D2}$$

$$Y_{\mu ab}^{(-)} \equiv \partial_{\beta_\mu} Y_{ab}^{\alpha\beta}|_{\alpha=\beta=0} = \langle b_\mu \bar{d}_a \bar{c}_b \rangle. \tag{D3}$$

The phonon-induced sources for B, N, and Z couple these quantities in a similar way to their phonon-assisted counterparts (Axt, Victor, and Stahl 1996), which in turn are coupled by their equations of motion to second derivatives of the generating functions (density matrices with two assisting phonon operators). The scheme most often used to obtain a closed set of equations is to keep only those density matrices with zero- or one-phonon assistance (Zimmermann, 1990; Kuhn and Rossi, 1992; Kuhn *et al.*, 1994; Schilp *et al.*, 1994, 1995; Axt, Victor, and Stahl, 1996); double-assisted variables are then factorized according to the recipe $\langle A b_\mu^\dagger b_\nu \rangle \approx \langle A \rangle n_\mu \delta_{\mu\nu}$, where A can be any electronic operator and $n_\mu = 1/[\exp(\hbar\omega_\mu/kT) - 1]$ is the Bose distribution. The contributions neglected by the factorization of electronic and phonon variables result in self-energies for the phonon-assisted variables [collisional broadening (Bányai *et al.*, 1992; Haug, 1992; Tran Thoai and Haug, 1993; Schilp *et al.*, 1994, 1995)]. In many cases it is sufficient to account for these contributions by constant damping rates. For longitudinal optical phonons in a direct-gap semiconductor, a self-consistent estimate of these constants has been given (Bányai *et al.*, 1992; Haug, 1992; Tran Thoai and Haug, 1993). Inverting the equations for the phonon-assisted density matrices in order to eliminate the phonon degrees of freedom leads to two types of contributions to the equations for the electronic density matrices: (i) retarded homogeneous parts (self-energies) and (ii) additional phonon-induced sources arising from the combined action of the phonon coupling and other interactions such as the coupling to the electric field, which is responsible for the intracollisional field effect (Bertoncini *et al.*, 1990; Rossi and Jacoboni, 1992). These additional terms are referred to in the literature as "cross terms" and are often neglected (Schilp *et al.*, 1994, 1995). Here, we shall keep only the density-

independent parts of self-energy type. Finally, to obtain the time-local self-energies in Sec. V, we apply a scheme known as the "Markov approximation" (Brunetti *et al.*, 1989; Zimmermann, 1990; Kuznetsov, 1991b; Kuhn and Rossi, 1992; Kuhn *et al.*, 1994). As an example, the equation of motion for the phonon-assisted transition density $Y_{\mu ab}^{(-)}$ resulting from the decoupling scheme described above reads in the exciton representation ($Y_{\mu ab}^{(\pm)} = \Sigma_x \bar{\psi}_{ab}^x y_{\mu x}^{(\pm)}$)

$$i\hbar \partial_t y_{\mu x}^{(-)} = (\bar{E}_x + \hbar\omega_\mu - i\hbar\gamma_Y)y_{\mu x}^{(-)}$$

$$+ (n_\mu + 1)\sum_{x'} \Gamma_{xx'}^\mu y_{x'}, \qquad (D4)$$

with

$$\Gamma_{xx'}^\mu \equiv \sum_{a=\mathrm{h},b=\mathrm{e}} \bar{\psi}_{ab}^{x*}\left(\sum_{k=\mathrm{e}} \bar{\gamma}_{bk}^\mu \bar{\psi}_{ak}^{x'} - \sum_{k=\mathrm{h}} \bar{\gamma}_{ka}^\mu \bar{\psi}_{kb}^{x'}\right). \tag{D5}$$

Here γ_Y is the damping rate constant accounting for the imaginary parts of the self-energies induced by higher-order phonon-assisted variables. Inversion of Eq. (D4) leads to

$$y_{\mu x}^{(-)}(t) = \frac{n_\mu + 1}{i\hbar}\sum_{x'} \Gamma_{xx'}^\mu \int_{-\infty}^t dt'$$

$$\times e^{-[i(\bar{\omega}_x + \omega_\mu) + \gamma_Y](t-t')} y_{x'}(t')$$

$$\approx \frac{n_\mu + 1}{\hbar}\sum_{x'} \frac{\Gamma_{xx'}^\mu y_{x'}(t)}{\bar{\omega}_{x'x} - \omega_\mu + i\gamma_Y}, \qquad (D6)$$

with $\bar{\omega}_{x'x} \equiv \bar{\omega}_{x'} - \bar{\omega}_x$. In the last step we have invoked the Markov approximation, assuming that y_x can be separated as $y_x = e^{-i\omega_x t}\bar{y}_x$ into a free rotation $e^{-i\omega_x t}$ and a factor $\bar{y}_x$ assumed to be slowly varying on a time scale defined by the memory-loss time of the phonon memory kernel, so that $\bar{y}_x$ can be taken in front of the time integral (Kuhn and Rossi, 1992; Kuhn *et al.*, 1994). Inserting Eq. (D6) and the analogous solution for $y_{\mu x}^{(+)}$ into Eq. (D1), we obtain for the phonon-induced self-energy in the exciton representation

$$\hbar\Omega_{Y\,x}^{phx'} = \sum_{\bar{x}} \Gamma_{x\bar{x}\bar{x}x'}^Y, \quad \Gamma_{xx'\bar{x}\bar{x}'}^Y \equiv \Gamma(\gamma_Y)_{xx'\bar{x}\bar{x}'}, \quad (D7)$$

$$\Gamma(\gamma)_{xx'\bar{x}\bar{x}'} \equiv \sum_\mu \left[\Gamma_{xx'}^\mu \Gamma_{\bar{x}'\bar{x}}^{\mu*} f^{(+)}(\bar{\omega}_{\bar{x}'\bar{x}}, \omega_\mu, \gamma)\right.$$

$$\left. + \Gamma_{x'x}^{\mu*}\Gamma_{\bar{x}\bar{x}'}^\mu f^{(-)}(\bar{\omega}_{\bar{x}'\bar{x}}, \omega_\mu, \gamma)\right], \qquad (D8)$$

$$f^{(\pm)}(\omega, \omega_\mu, \gamma) \equiv \frac{n_\mu + \frac{1}{2} \mp \frac{1}{2}}{\hbar(\omega \pm \omega_\mu + i\gamma)}, \qquad (D9)$$

$$n_\mu = n(\omega_\mu) = \frac{1}{\exp(\hbar\omega_\mu/kT) - 1}. \qquad (D10)$$

We have used the standard procedure and kept only the imaginary part of the self-energy in Eq. (67).

Applying the same strategies to the exciton density N, we obtain

$$\hbar\Omega_{N\,xx}^{ph\bar{x}'x'} = \delta_{\bar{x}\bar{x}'}\sum_{\tilde{x}} \Gamma_{xx\tilde{x}x'}^N - \delta_{xx'}\sum_{\tilde{x}} \Gamma_{\bar{x}\tilde{x}\tilde{x}\bar{x}'}^{N*}$$

$$+ \Gamma_{x'\bar{x}x\bar{x}'}^{N*} - \Gamma_{\bar{x}'\bar{x}xx'}^N, \qquad (D11)$$

$$\Gamma_{xx'\bar{x}\bar{x}'}^N \equiv \Gamma(\gamma_N)_{xx'\bar{x}\bar{x}'}. \qquad (D12)$$

The derivation of the self-energy for B is complicated by the fact that the homogeneous parts of the equation for the assisted variables are not diagonal in the exciton representation and also by the desire to obtain a representation that obeys the Pauli principle at all levels of truncation. To address the latter problem, we introduce auxiliary functions B^A and $B^{(\pm)A}$ in order to decompose B and $B^{(\pm)}$ in analogy to Eq. (C4),

$$B_{abcd} = B_{abcd}^A - B_{cbad}^A, \qquad (D13)$$

$$B_{\mu abcd}^{(\pm)} = B_{\mu abcd}^{(\pm)A} - B_{\mu cbad}^{(\pm)A}, \qquad (D14)$$

where the phonon-assisted density matrices $B^{(\pm)}$ are defined by

$$B_{\mu abcd}^{(+)} \equiv \partial_{\alpha_\mu} B_{abcd}^{\alpha\beta}\big|_{\alpha=\beta=0} = \langle b_\mu^\dagger \bar{d}_a \bar{c}_b \bar{d}_c \bar{c}_d\rangle, \qquad (D15)$$

$$B_{\mu abcd}^{(-)} \equiv \partial_{\beta_\mu} B_{abcd}^{\alpha\beta}\big|_{\alpha=\beta=0} = \langle b_\mu \bar{d}_a \bar{c}_b \bar{d}_c \bar{c}_d\rangle. \qquad (D16)$$

Obviously, the decompositions (D13) and (D14) are not unique, as one can add to B^A and/or $B^{(\pm)A}$ any function that is symmetric with respect to the exchange of the indices a and c, without changing B or $B^{(\pm)}$. For any of these decompositions we obtain a corresponding separation of the phonon-induced sources

$$\hbar\Omega^{ph}(B)_{abcd}^{\alpha=\beta=0} = Q_{abcd}^{Bph} - Q_{cbad}^{Bph}, \qquad (D17)$$

$$\hbar\Omega^{ph}(B_\mu^{(\pm)})_{abcd}^{\alpha=\beta=0} = Q_{\mu abcd}^{Bph(\pm)} - Q_{\mu cbad}^{Bph(\pm)}, \qquad (D18)$$

with

$$Q_{abcd}^{Bph} \equiv \sum_\mu \left[\sum_{k=\mathrm{e}} (\bar{\gamma}_{dk}^\mu B_{\mu abck}^{(+)A} + \bar{\gamma}_{kd}^{\mu*} B_{\mu abck}^{(-)A}\right.$$

$$+ \bar{\gamma}_{bk}^\mu B_{\mu akcd}^{(+)A} + \bar{\gamma}_{kb}^{\mu*} B_{\mu akcd}^{(-)A})$$

$$- \sum_{k=\mathrm{h}} (\bar{\gamma}_{kc}^\mu B_{\mu abkd}^{(+)A} + \bar{\gamma}_{ck}^{\mu*} B_{\mu abkd}^{(-)A} + \bar{\gamma}_{ka}^\mu B_{\mu kbcd}^{(+)A}$$

$$\left. + \bar{\gamma}_{ak}^{\mu*} B_{\mu kbcd}^{(-)A})\right], \qquad (D19)$$

$$Q_{\mu abcd}^{Bph(+)} \equiv n_\mu\left[\sum_{k=\mathrm{e}} (\bar{\gamma}_{kd}^{\mu*} B_{abck}^A + \bar{\gamma}_{kb}^{\mu*} B_{akcd}^A)\right.$$

$$\left. - \sum_{k=\mathrm{h}} (\bar{\gamma}_{ck}^{\mu*} B_{abkd}^A + \bar{\gamma}_{ak}^{\mu*} B_{kbcd}^A)\right], \qquad (D20)$$

$$Q_{\mu abcd}^{Bph(-)} \equiv (n_\mu + 1)\left[\sum_{k=\mathrm{e}} (\bar{\gamma}_{dk}^\mu B_{abck}^A + \bar{\gamma}_{bk}^\mu B_{akcd}^A)\right.$$

$$\left. - \sum_{k=\mathrm{h}} (\bar{\gamma}_{kc}^\mu B_{abkd}^A + \bar{\gamma}_{ka}^\mu B_{kbcd}^A)\right]. \qquad (D21)$$

We remove the ambiguity in the choice of B^A and $B^{(\pm)A}$ by requiring that sources of the respective equations of motion be given by Q^{Bph}_{abcd} and $Q^{Bph(\pm)}_{\mu abcd}$. Using the expansions

$$B^A_{abcd} = \sum_{\bar{x}x} \bar{\psi}^{\bar{x}}_{ab} \bar{\psi}^x_{cd} (y_{\bar{x}} y_x + b_{\bar{x}x}), \tag{D22}$$

$$B^{(\pm)A}_{abcd} = \sum_{\bar{x}x} \bar{\psi}^{\bar{x}}_{ab} \bar{\psi}^x_{cd} b^{(\pm)}_{\mu\bar{x}x}, \tag{D23}$$

we obtain

$$i\hbar \partial_t b^{(+)}_{\mu\bar{x}x} = (\bar{E}_{\bar{x}} + \bar{E}_x - \hbar\omega_\mu - i\hbar\gamma_B) b^{(+)}_{\mu\bar{x}x}$$
$$+ n_\mu \sum_{\bar{x}'x'} g^{\mu\bar{x}x*}_{\bar{x}'x'} (y_{\bar{x}'} y_{x'} + b_{\bar{x}'x'})$$
$$+ \sum_{\bar{x}'x'} \bar{V}^{\bar{x}'x'}_{\bar{x}x} b^{(+)}_{\mu\bar{x}'x'}, \tag{D24}$$

$$i\hbar \partial_t b^{(-)}_{\mu\bar{x}x} = (\bar{E}_{\bar{x}} + \bar{E}_x + \hbar\omega_\mu - i\hbar\gamma_B) b^{(-)}_{\mu\bar{x}x}$$
$$+ (n_\mu + 1) \sum_{\bar{x}'x'} g^{\mu\bar{x}'x'}_{\bar{x}x} (y_{\bar{x}'} y_{x'} + b_{\bar{x}'x'})$$
$$+ \sum_{\bar{x}'x'} \bar{V}^{\bar{x}'x'}_{\bar{x}x} b^{(-)}_{\mu\bar{x}'x'}, \tag{D25}$$

with

$$g^{\mu\bar{x}'x'}_{\bar{x}x} \equiv \delta_{\bar{x}\bar{x}'} \Gamma^\mu_{xx'} + \delta_{xx'} \Gamma^\mu_{\bar{x}\bar{x}'}. \tag{D26}$$

The last term in Eq. (D24) as well as that in Eq. (D25) describes the interaction between phonon-assisted excitons. This term is responsible for the appearance of the two-pair Green's function in a complete calculation of the phonon-induced self-energy for the two-pair transition density B (Axt, Victor, and Stahl, 1996; Axt and Mukamel, 1997a), reflecting the combined action of phonon-coupling and Coulomb interaction. We shall neglect this cooperative effect in the following. In this way we eventually obtain, after inverting Eqs. (D24) and (D25) and invoking the Markov approximation,

$$\hbar\Omega^{ph\bar{x}'x'}_{\bar{x}x} = \delta_{\bar{x}\bar{x}'} \sum_{\tilde{x}} \Gamma^B_{x\tilde{x}\tilde{x}x'} + \delta_{xx'} \sum_{\tilde{x}} \Gamma^B_{\bar{x}\tilde{x}\tilde{x}\bar{x}'}$$
$$+ \Gamma^B_{xx'\bar{x}\bar{x}'} + \Gamma^B_{\bar{x}\bar{x}'xx'}, \tag{D27}$$

$$\Gamma^B_{\bar{x}\bar{x}'xx'} = \Gamma(\gamma_B)_{\bar{x}\bar{x}'xx'}. \tag{D28}$$

APPENDIX E: PHONON-INDUCED SELF-ENERGIES FOR FRENKEL EXCITONS

The phonon-induced self-energies for the Frenkel system can be derived along the same lines used in Appendix D, resulting in

$$\hbar\tilde{\Omega}^{phx'}_{Y\,x} = \sum_{\bar{x}} \Gamma^Y_{x\bar{x}\bar{x}x'}, \tag{E1}$$

$$\hbar\tilde{\Omega}^{ph\bar{x}'x'}_{N\,\bar{x}x} = \delta_{\bar{x}\bar{x}'} \sum_{\tilde{x}} \Gamma^N_{x\tilde{x}\tilde{x}x'} - \delta_{xx'} \sum_{\tilde{x}} \Gamma^{N*}_{\tilde{x}\bar{x}\tilde{x}\bar{x}'}$$
$$+ \Gamma^{N*}_{x'x\bar{x}\bar{x}'} - \Gamma^N_{\bar{x}'\bar{x}xx'}, \tag{E2}$$

$$\hbar\tilde{\Omega}^{ph\bar{x}'x'}_{B\,\bar{x}x} = \sum_{\mu\tilde{x}\tilde{x}'} \tilde{g}^{\mu\tilde{x}\tilde{x}'}_{\bar{x}x} \tilde{g}^{\mu\bar{x}'x'}_{\tilde{x}\tilde{x}'} f(\tilde{\omega}_{\bar{x}'\tilde{x}}$$
$$+ \tilde{\omega}_{x'\tilde{x}'}, \tilde{\omega}_\mu, \tilde{\gamma}_B), \tag{E3}$$

$$\Gamma^Y_{xx'\bar{x}\bar{x}'} \equiv \Gamma(\tilde{\gamma}_Y)_{xx'\bar{x}\bar{x}'}, \tag{E4}$$

$$\Gamma^N_{xx'\bar{x}\bar{x}'} \equiv \Gamma(\tilde{\gamma}_N)_{xx'\bar{x}\bar{x}'}, \tag{E5}$$

$$\Gamma(\gamma)_{xx'\bar{x}\bar{x}'} \equiv \sum_\mu \Gamma^\mu_{xx'} \Gamma^\mu_{\bar{x}\bar{x}'} f(\tilde{\omega}_{x'\bar{x}}, \tilde{\omega}_\mu, \gamma), \tag{E6}$$

$$\Gamma^\mu_{xx'} \equiv \sum_{nm} \tilde{\psi}^{x*}_n \tilde{\gamma}^\mu_{nm} \tilde{\psi}^{x'}_m, \tag{E7}$$

$$\tilde{g}^{\mu\bar{x}'x'}_{\bar{x}x} \equiv \sum_{ijn} \tilde{\psi}^{\bar{x}*}_i \tilde{\psi}^{x*}_j (\tilde{\gamma}^\mu_{jn} \xi_{in} \tilde{\psi}^{\bar{x}'}_i \tilde{\psi}^{x'}_n + \tilde{\gamma}^\mu_{in} \xi_{nj} \tilde{\psi}^{\bar{x}'}_n \tilde{\psi}^{x'}_j), \tag{E8}$$

$$f(\omega, \omega_\mu, \gamma) \equiv f^{(+)}(\omega, \omega_\mu, \gamma) + f^{(-)}(\omega, \omega_\mu, \gamma), \tag{E9}$$

where the functions $f^{(\pm)}(\omega, \omega_\mu, \gamma)$ have been defined in Eq. (D9). To derive the self-energy for $\tilde{B}$ we introduce the auxiliary functions $\tilde{B}^A$ and $\tilde{B}^{(\pm)A}$ by

$$\tilde{B}_{ij} = \xi_{ij} \tilde{B}^A_{ij}, \quad \tilde{B}^{(\pm)}_{ij} = \xi_{ij} \tilde{B}^{(\pm)A}_{ij} \tag{E10}$$

and remove the ambiguity of the values at $i = j$ in the same way as in Eq. (116). Expanding these functions in exciton eigenfunctions and neglecting the exciton-exciton interaction in the phonon-assisted equations, leads to Eq. (E3), which reduces to the simpler form (D28) when the factor ξ_{ij} in Eq. (E8) is replaced by one. This factor explicitly enforces the Pauli exclusion for the phonon-assisted two-pair transitions, which was taken care of by the proper antisymmetrization in the many-electron case.

APPENDIX F: CONTRACTION RELATIONS

In this appendix we prove the fundamental relations (A21)–(A24) and show that the dynamics-controlled truncation, unlike schemes such as the truncated quantum BBGKY hierarchy (Axt and Mukamel, 1997b), does not violate fundamental trace relations. From the fact that the density matrix of a system with fixed number of particles N_p can always be written as a superposition of matrices for pure states, in which each state is an eigenvector of the total-particle operator with eigenvalue N_p, it follows that

$$(N_p-1)C_{ab}^{\alpha\beta}=\sum_{k=e,h}\langle\,\vec{c}_a^{\dagger}\vec{c}_k^{\dagger}\bar{c}_k\bar{c}_b\hat{F}^{\alpha\beta}\rangle$$

$$=\sum_{k=h}\langle\,\vec{c}_a^{\dagger}\vec{d}_k\vec{d}_k^{\dagger}\bar{c}_b\hat{F}^{\alpha\beta}\rangle$$

$$+\sum_{k=e}\langle\,\vec{c}_a^{\dagger}\vec{c}_k^{\dagger}\bar{c}_k\bar{c}_b\hat{F}^{\alpha\beta}\rangle$$

$$=\sum_{k=h}\langle\,\vec{c}_a^{\dagger}(1-\vec{d}_k^{\dagger}\vec{d}_k)\bar{c}_b\hat{F}^{\alpha\beta}\rangle$$

$$+\sum_{k=e}\langle\,\vec{c}_a^{\dagger}\vec{c}_k^{\dagger}\bar{c}_k\bar{c}_b\hat{F}^{\alpha\beta}\rangle$$

$$=N_p C_{ab}^{\alpha\beta}-\sum_{k=h}\langle\,\vec{c}_a^{\dagger}\vec{d}_k^{\dagger}\bar{d}_k\bar{c}_b\hat{F}^{\alpha\beta}\rangle$$

$$+\sum_{k=e}\langle\,\vec{c}_a^{\dagger}\vec{c}_k^{\dagger}\bar{c}_k\bar{c}_b\hat{F}^{\alpha\beta}\rangle,\qquad\text{(F1)}$$

or equivalently

$$C_{ab}^{\alpha\beta}=\sum_{k=h}N_{akkb}^{\alpha\beta}-\sum_{k=e}\langle\,\vec{c}_a^{\dagger}\vec{c}_k^{\dagger}\bar{c}_k\bar{c}_b\hat{F}^{\alpha\beta}\rangle$$

$$=\sum_{k=h}N_{akkb}^{\alpha\beta}+\mathcal{O}(E^4).\qquad\text{(F2)}$$

In the last step, we have used the result that the expectation value of four electron operators is at least of fourth order in the laser field. Along the same lines we obtain the relations

$$D_{ab}^{\alpha\beta}=\sum_{k=e}N_{kabk}^{\alpha\beta}+\mathcal{O}(E^4),\qquad\text{(F3)}$$

$$S_{abcd}^{\alpha\beta}=\sum_{k=h}Z_{akkbcd}^{\alpha\beta}+\mathcal{O}(E^5),\qquad\text{(F4)}$$

$$T_{abcd}^{\alpha\beta}=\sum_{k=e}Z_{kabkcd}^{\alpha\beta}+\mathcal{O}(E^5),\qquad\text{(F5)}$$

from the identities

$$(N_p+1)D_{ab}^{\alpha\beta}=\sum_{k=e,h}\langle\,\vec{d}_k^{\dagger}\vec{c}_k^{\dagger}\bar{c}_k\bar{d}_b\hat{F}^{\alpha\beta}\rangle,\qquad\text{(F6)}$$

$$(N_p-1)S_{abcd}^{\alpha\beta}=\sum_{k=e,h}\langle\,\vec{c}_a^{\dagger}\vec{c}_k^{\dagger}\bar{c}_k\bar{c}_b\bar{d}_c\bar{c}_d\hat{F}^{\alpha\beta}\rangle,\qquad\text{(F7)}$$

$$(N_p+1)T_{abcd}^{\alpha\beta}=\sum_{k=e,h}\langle\,\vec{d}_a^{\dagger}\vec{c}_k^{\dagger}\bar{c}_k\bar{d}_b\bar{d}_c\bar{c}_d\hat{F}^{\alpha\beta}\rangle.\qquad\text{(F8)}$$

These are special cases of general relations connecting n-point to $(n+2)$-point density matrices in every system with a fixed number N_p of particles. For $n=2$ and $n=4$ we obtain (the indices a,b,c,d in the following formulas may refer to either an electron or a hole)

$$(N_p-1)\langle\,\vec{c}_a^{\dagger}\bar{c}_b\hat{F}^{\alpha\beta}\rangle=\sum_{k=e,h}\langle\,\vec{c}_a^{\dagger}\vec{c}_k^{\dagger}\bar{c}_k\bar{c}_b\hat{F}^{\alpha\beta}\rangle,\qquad\text{(F9)}$$

$$(N_p-2)\langle\,\vec{c}_a^{\dagger}\vec{c}_b^{\dagger}\bar{c}_c\bar{c}_d\hat{F}^{\alpha\beta}\rangle=\sum_{k=e,h}\langle\,\vec{c}_a^{\dagger}\vec{c}_b^{\dagger}\vec{c}_k^{\dagger}\bar{c}_k\bar{c}_c\bar{c}_d\hat{F}^{\alpha\beta}\rangle.\qquad\text{(F10)}$$

It has been pointed out (Schmitt *et al.*, 1989, 1990; Cassing and Pfitzner, 1992; Reinhard and Toepffer, 1994) that the truncation scheme suggested by the quantum BBGKY hierarchy violates Eqs. (F9) and (F10). This violation is believed to be a major cause of chaotic behavior exhibited by truncated quantum BBGKY dynamics in certain cases (Schmitt *et al.*, 1989, 1990; Cassing and Pfitzner, 1992; Reinhard and Toepffer, 1994). We shall demonstrate, that a dynamics-controlled truncation preserves these relations. For the particle-particle components C_{ab},D_{ab} of the one-particle density matrix this is trivial, since, instead of solving separate equations for C and D, these functions are constructed from these relations. In order to prove that Eq. (F9) is preserved, it remains only to discuss the electron-hole components. When a refers to a hole and b represents an electron, Eq. (F9) reads

$$(N_p-1)\langle\,\bar{d}_a\bar{c}_b\hat{F}^{\alpha\beta}\rangle$$

$$=(N_p-1)Y_{ab}^{\alpha\beta}$$

$$=\sum_{k=e}\langle\,\bar{d}_a\vec{c}_k^{\dagger}\bar{c}_k\bar{c}_b\hat{F}^{\alpha\beta}\rangle$$

$$+\sum_{k=h}\langle\,\bar{d}_a(1-\vec{d}_k^{\dagger}\bar{d}_k)\bar{c}_b\hat{F}^{\alpha\beta}\rangle$$

$$=\sum_{k=e}S_{kkab}^{\alpha\beta}+N_p Y_{ab}^{\alpha\beta}-\sum_{k=h}\langle\,(\delta_{ak}-\vec{d}_k^{\dagger}\bar{d}_a)\bar{d}_k\bar{c}_b\hat{F}^{\alpha\beta}\rangle$$

$$=(N_p-1)Y_{ab}^{\alpha\beta}+\sum_{k=e}S_{kkab}^{\alpha\beta}-\sum_{k=h}T_{kkab}^{\alpha\beta}.\qquad\text{(F11)}$$

Thus satisfying Eq. (F9) is equivalent to

$$\sum_{k=e}S_{kkab}^{\alpha\beta}=\sum_{k=h}T_{kkab}^{\alpha\beta}.\qquad\text{(F12)}$$

Relation (F12) is guaranteed within the dynamics-controlled truncation approach by the representations (F4) and (F5) for S and T, irrespective of the values of Z. Similar arguments prove the consistency of the dynamics-controlled scheme with Eq. (F9) when a is an electron and b a hole. In order to check Eq. (F10) one has to discuss 16 cases corresponding to the possible assignments of a, b, c, and d as either an electron or a hole. The general strategy is as follows: First, both sides of Eq. (F10) are expressed completely in terms of expectation values of normally ordered operators with respect to the electron-hole representation, because these are the variables we have chosen to formulate the dynamics. Second, the truncation has to be applied to both sides, i.e., for a cut at the $\mathcal{O}(E^3)$ level, one has to neglect normal-ordered expectation values containing more

than three Fermi operators of one type (electron or hole). Finally one has to compare both sides. In this way it is easy to show that for all 16 combinations Eq. (F10) either reduces to one of the cases (F2)–(F5) or leads to trivial identities like Eq. (F11). We have therefore demonstrated that using Eqs. (F2)–(F5) in conjunction with the dynamics-controlled truncation prescription guarantees that the fundamental trace relations (F9) and (F10) are fulfilled. It is worthwhile to note that this holds regardless of whether further approximations are invoked in the calculation of the remaining density matrices.

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