Real-space density-matrix description of dynamic correlations in the optical response of many-electron systems

Vollrath M. Axt and Shaul Mukamel
Department of Chemistry
University of Rochester, NY

A real-space formulation of the Quantum Bogolyubov-Born-Green-Kirkwood-Yvon (QBBGKY)-hierarchy is worked out in a form particularly suitable for applications to the optical response of many-electron systems. Comparison is made to Coupled-Cluster approaches. A new hierarchy of contraction-free correlation functions is presented, that overcomes the problem of violated trace relations inherent in the truncated QBBGKY-hierarchy.

in *Nonlinear optical materials,*
IMA Volumes in Mathematics and Its Applications,
edited by J.V. Maloney, Vol. **101**, pp. 33-47 (Springer,Berlin, 1998).

I. INTRODUCTION

The calculation of the optical response of molecular and semiconductor materials is an open challenge that has attracted great attention in recent years [1–9]. To be specific we shall focus in this article on conjugated polyenes. However, the results we discuss apply as well to other molecular systems and semiconductor nanostructures. Although the conventional sum over states approach [9–13] or multiconfiguration self-consistent field theories with large basis sets [14–16] provide an accurate description of small oligomers, their application to longer chains is not practical due to the rapidly growing number of configurations with system size. Furthermore, the summation over all states leads to delicate cancellations, which have to be performed properly in order to guaranty size-consistency[8, 17–20]. Therefore, for these systems a less demanding reduced description is needed that still contains the essential physics. Simple essential states models [21] often lead to reasonable qualitative fits [22], but it is still an open question, how these states and their effective couplings can be constructed given the microscopic parameters of the many-body Hamiltonian, without having to diagonalize the problem. Configuration-interaction (CI) calculations taking into account all single and/or double configurations can be carried out for quite large systems[23–26], but are, like all truncated CI schemes, not size-consistent[27]. The real-space reduced single-electron density-matrix on the other hand offers a very powerful and intuitive way to deal with this situation. Applications of this approach have already lead to valuable insights into the dynamics of longer polymer chains [28–31]. So far these calculations have been limited to the time dependent Hartree Fock (TDHF) level[32] of description and have thus neglected many-body correlations beyond the mean field treatment. Experiments [33–35] as well as ab initio calculations for small systems strongly suggest that these correlations are responsible for some of the unique features of polymers, like the existence of low lying excited states of A_g symmetry [36–40]. Furthermore, explanation of all biexcitonic features [41–44] certainly requires a treatment beyond the TDHF approach. In the present paper we extend the TDHF treatment to calculate the linear and nonlinear optical response of polyenes, taking into account correlations between pairs of excitons. Our method is based on a cluster decomposition of n-point real space density-matrices and will be described in detail in section III. Coupled-cluster methods have proven to be among the most powerful tools of quantum chemistry for incorporating many-body correlations in calculations of ground state properties[45–47] or excited state energies [48–50]. While these calculations start from an ansatz for the many-body wavefunction, our approach is entirely formulated in terms of reduced density-matrices. Nevertheless, we will show in section IV how these approaches are related.

We proceed as follows: After specifying the model in section II, we present in section III the cluster decomposition of higher order density-matrices in its conventional form. This decomposition results in a hierarchy of equations of motion for higher order correlation functions, also known as the Quantum Bogolyubov-Born-Green-Kirkwood-Yvon (QBBGKY)-hierarchy [51, 52]. In density-matrix theory, the QBBGKY-hierarchy plays the same role as the Martin-Schwinger-hierarchy[53] in the multi-time Green function theory. In section IV we then establish the connection to a coupled-cluster type ansatz for the wavefunction, and discuss the problems commonly encountered when these approaches are implemented as truncated schemes. Both the truncated QBBGKY-hierarchy as well as truncated coupled-cluster schemes are known to be plagued by consistency problems which under certain conditions can lead to unphysical predictions. In order to remedy the main problem of the QBBGKY-hierarchy we reformulate the corresponding equations of motion in section V in terms of a new set of contraction-free correlation functions. We show how this modified hierarchy can be used to derive systematically closed equations of motion for the relevant correlation functions, which do not suffer from these consistency problems.

II. THE MANY-ELECTRON MODEL

The electronic properties of non-relativistic many-electron systems can be described using the following Hamiltonian

$$H = H_{hop} + H_{coul} + H_{opt}\,, \tag{1}$$

where H_{hop} accounts for hopping transport between atomic sites.

$$H_{hop} = \sum_{m,n} t_{mn}\, c_m^\dagger c_n\,. \tag{2}$$

The Fermion operators $c_n^\dagger$, c_n describe the creation (annihilation) of electrons in atomic spin orbitals at sites j_n with spins σ_n. t_{nm} is the hopping matrix element. The Coulomb interaction is given by

$$H_{coul} = \frac{1}{2}\sum_{klmn} V_{klnm}\, c_k^\dagger c_l c_m^\dagger c_n\,. \tag{3}$$

In this article, we assume a simplified form of the Coulomb interaction

$$H_{coul} = \frac{1}{2}\sum_{n,m} V_{nm}\, c_n^\dagger c_n c_m^\dagger c_m\,, \tag{4}$$

which is the form used in semiempirical models for the π electrons in polyenes. For polyenes, V_{nm} is in specific applications mostly taken to be of the Ohno form $V_{nm} = U/\sqrt{1+(r_{nm}/a_0)^2}$ [10, 54]. This is known as the Pariser Parr Pople (PPP) model. Next neighbor interaction of Hubbard type has been used as well[55]. All results derived in this article can be easily generalized to the case of a more general interaction (eq. (3)). However, since all basic concepts can readily be explained using the form

(4), we present explicit formulas only for that case, in order to keep the notation simple.

The last term in (1) represents the coupling to the optical field $E(t)$ polarized along the z-axis, and is given by

$$H_{opt} = -E(t)\,\hat{P}\,, \tag{5}$$

where the molecular polarization operator takes on the form

$$\hat{P} = -e\sum_n z_n\, c_n^\dagger c_n\,. \tag{6}$$

Here, $-e$ is the electron charge and z_n is the z-coordinate of the n-th atom.

III. CLUSTER DECOMPOSITION AND EQUATIONS OF MOTION FOR HIGHER ORDER CORRELATION FUNCTIONS

In the density-matrix approach the basic dynamical variables are equal time expectation values of normal ordered fermion operators[57, 58]: $C_{ab} = \langle c_a^\dagger c_b\rangle$, $C_{abcd} = \langle c_a^\dagger c_b^\dagger c_c c_d\rangle$, $C_{abcdef} = \langle c_a^\dagger c_b^\dagger c_c^\dagger c_d c_e c_f\rangle$, $\cdots$. Equations of motion for these quantities are readily obtained by taking expectation values of the Heisenberg equations of motion:

$$i\hbar\dot{X} + [H, X] = 0\,. \tag{7}$$

where X can be any of the above operators. The two-point density-matrix C_{ab} is of particular interest for the calculation of the optical response, as it is directly related to the optical polarization via equation (6).

$$\langle\hat{P}\rangle(t) = -e\sum_n z_n\, C_{nn}(t)\,. \tag{8}$$

Unfortunately, the corresponding equation of motion (7) is not closed; instead, it contains C_{abcd} as a source, which in turn is coupled to C_{abcdef}. Equations (7) therefore form an open hierarchy of equations of motion. The most crucial step in any practical application of the density-matrix is finding a truncation procedure in order to close the hierarchy. In the form (7) ,however, the hierarchy is not well suited for truncation, because correlated and uncorrelated contributions are mixed. In order to separate them it is desirable to reformulate the dynamics in terms of correlation functions $\bar{C}_{ab}$, $\bar{C}_{abcd}$ etc., where the n-th order correlation function can be interpreted as a measure of genuine correlations between n-particles. A systematic way for defining these correlation functions is provided by a cluster decomposition of the n-point density-matrices which gives[51, 52, 56]:

$$\begin{aligned}
C_{abcd} &= C_{bc}\,C_{ad} - C_{ac}\,C_{bd} + \bar{C}_{abcd}\ , \\
C_{abcdef} &= \ \ C_{cd}\,\bar{C}_{abef} - C_{bd}\,\bar{C}_{acef} + C_{ad}\,\bar{C}_{bcef} - C_{ce}\,\bar{C}_{abdf} \\
&\quad + C_{be}\,\bar{C}_{acdf} - C_{ae}\,\bar{C}_{bcdf} + C_{cf}\,\bar{C}_{abde} - C_{bf}\,\bar{C}_{acde} \\
&\quad + C_{af}\,\bar{C}_{bcde} + C_{cd}\,(C_{be}\,C_{af} - C_{bf}\,C_{ae}) \\
&\quad - C_{ce}\,(C_{bd}\,C_{af} - C_{bf}\,C_{ad}) + C_{cf}\,(C_{bd}\,C_{ae} - C_{be}\,C_{ad}) + \bar{C}_{abcdef}\,, \\
&\ \vdots\ .
\end{aligned} \tag{9}$$

The right hand side of (9) is obtained using the following prescription: we factorize the density-matrix on the left hand side in all possible ways into products of correlation functions of lower order, and then add these terms with a sign determined by the permutation needed to rearrange the corresponding indices. The correlated part $\bar{C}$ associated with each density-matrix C is then defined as the difference between C and the sum of all factorizations. Physically, the factorized terms represent contributions to the density-matrices arising from mutually uncorrelated subsystems (clusters). The contributions $\bar{C}$ result only from interaction processes, where all particles corresponding to the indices of these functions are involved. These functions are therefore referred to as the *irreducible part* of the corresponding density-matrix [52]. For non-interacting particles all correlation functions with four or more indices, often denoted higher order correlation functions, vanish identically. The signs in (9) ensure that at any order the correlation functions obey the same symmetry relations with respect to the exchange of identical fermions as the density-matrices themselves. Correlations brought forth by the Pauli statistics rather than the interaction are therefore accounted for at any level of the hierarchy formed by the functions $\bar{C}$. Further general properties of the above decomposition have been derived in 51.

Using the definition (9) and the Heisenberg equations of motion for the density-matrices, it is straightforward to reformulate the dynamics in terms of the correlation functions $\bar{C}$. Keeping terms up to the four-point level, we obtain the following equations of motion

$$\begin{aligned} i\hbar\partial_t C_{ab} &= \sum_j \{t_{bj}\, C_{aj} - t_{ja}\, C_{jb}\} + \sum_j (V_{bj} - V_{aj})\, \{\bar{C}_{ajjb} - C_{aj}\, C_{jb}\} \\ &+\phi_{ba}\, C_{ab} + e\, E\, (z_b - z_a)\, C_{ab}\ , \end{aligned} \tag{10}$$

$$\begin{aligned} i\hbar\partial_t \bar{C}_{abcd} &= \frac{1}{2} A[\sum_j \{t_{dj}\, \bar{C}_{abcj} - t_{ja}\, \bar{C}_{jbcd}\} + (V_{cd} - V_{ab})\, C_{bc}\, C_{ad}] \\ &-\frac{1}{2} A[\sum_j (V_{dj} + V_{cj} - V_{bj} - V_{aj})\, \{C_{aj}\, \bar{C}_{jbcd} + C_{jd}\, \bar{C}_{abcj}\}] \\ &+(V_{cd} - V_{ab} + \phi_{cd} + \phi_{da})\, \bar{C}_{abcd} + A[C_{bc} \sum_j (V_{cj} - V_{bj}) \{\bar{C}_{ajjd} - C_{aj}\, C_{jd}\}] \\ &+e\, E\, (z_d + z_c - z_b - z_a)\, \bar{C}_{abcd} + \sum_j (V_{dj} + V_{cj} - V_{bj} - V_{aj})\, \bar{C}_{abjjcd}\, , \end{aligned} \tag{11}$$

with

$$\phi_{ab} \equiv \sum_j (V_{aj} - V_{bj})\, C_{jj}\ .$$

Here, the action of the anti-symmetrizing operator A on an arbitrary function F_{abcd} is defined as $A[F_{abcd}] = F_{abcd} - F_{bacd} - F_{abdc} + F_{bacd}$.

Closing the hierarchy on the lowest level, i.e. setting $\bar{C}_{abcd} = 0$, leads to the TDHF equations. The next higher level, denoted SUB(2) [59], is obtained retaining the subset of all two-pair correlations described by $\bar{C}_{abcd}$ in (11), while neglecting the higher order correlations $\bar{C}_{abcdef}$ describing three or more pairs. In general, truncating the hierarchy at the SUB(n) level means keeping the subset of all correlation functions with less or equal than $2n$ indices, while neglecting all higher order correlations.

A formal analysis of the level of description obtained by keeping two pair variables has previously been carried out for Frenkel excitons [61, 62], for direct gap semiconductors[56, 63–65] and and for nuclear many-body problems[51, 66]. Successful applications of this scheme have been reported in all three of these fields [61, 67–76].

For the standard band model of direct gap semiconductors [57, 58] it has been shown[63] that the application of the above factorization scheme leads to equations that can in principle be used to calculate the optical response rigorously up to third order in the field. Although polyenes can be regarded as one dimensional semiconductors, there are two essential differences between the PPP Hamiltonian and the band model: (i) the ground state of the band model is uncorrelated, and (ii) the material part of the band model Hamiltonian conserves the number of electron-hole pairs. The above factorization scheme therefore leads to approximate results in the PPP case even in the low excitation regime. In the next section we will further clarify the level of accuracy obtained by this procedure.

When the system is assumed to be unexcited before the action of the laser field, equations (10) and (11) have to be solved with the ground state values of C_{ab} and $\bar{C}_{abcd}$ as initial conditions. These values can in principle be obtained from any method that gives the ground state wave function. A self-consistent scheme to calculate these values as stationary points of the QBBGKY-equations has been proposed in 60; But in the applications worked out so far, it has turned out to be sufficient to start initially from the Hartree-Fock ground state. This is certainly true for the Frenkel-exciton system and the direct gap semiconductors, because there are no ground state correlations in these models. For the PPP model of conjugated polyenes, the Hartree Fock ground state has an overlap with the exact ground state of more than 90% [38]. Taking the Hartree Fock ground state as initial condition may therefore be appropriate even in this case.

IV. CONNECTION TO COUPLED-CLUSTER THEORIES

In this section we show that the above factorization scheme can alternatively be derived using an ansatz of coupled-cluster type for the many-body wavefunction. To be specific we consider the wavefunction

$$|\psi\rangle \;\equiv\; \exp(S)|\psi^{\mathrm{II}}\rangle e^{i\varphi} \equiv \exp(S)\,\exp(S^{\mathrm{II}})|\psi_0\rangle e^{i\varphi}\,, \tag{12}$$

$$\begin{aligned} S \;&\equiv\; \sum_{klmn} \beta^{kl}_{mn}\, c^\dagger_k c^\dagger_l c_m c_n \quad , \quad S^{\mathrm{II}} \equiv \sum_{ij} \alpha^i_j\, c^\dagger_i c_j\,, \\ \text{with} \quad & \alpha^i_j = -\alpha^{j*}_i \quad , \quad \beta^{kl}_{mn} = -\beta^{nm*}_{lk}\,, \end{aligned} \tag{13}$$

where $|\psi_0\rangle$ is the Hartree Fock ground state and α, β, φ are time dependent parameters. The ansatz (12) belongs to the class of unitary coupled-cluster wavefunctions UCC [77]. We have written the part with double excitations (S) and the part with single excitations (S^{II}) as two exponentials like in the Brueckner coupled-cluster ansatz [78, 79]. The single excitation part ensures that orbital rotations are fully taken into account. In the limiting case $\beta = 0$, (12) reproduces therefore the TDHF wavefunction [78]. Starting from (12), the n-point density-matrices can be expressed in terms of the parameters α, β of the wavefunction. To illustrate this we introduce the Liouville space operator (superoperator) counterpart to S by its action on an arbitrary operator A

$$\tilde{S}\,A \equiv [S, A]\,. \tag{14}$$

For C_{ab} we thereby obtain

$$C_{ab} = \sum_{n=0} \frac{(-1)^n}{n!}\,\langle\phi^{\mathrm{II}}|(\tilde{S}^n\, c^\dagger_a c_b)|\phi^{\mathrm{II}}\rangle\,. \tag{15}$$

Similar expressions can be deduced for the higher order correlation functions. As $|\phi^{\mathrm{II}}\rangle$ represents a single slater determinant, the expectation value in (15) reduces to sums of products of the function $C^{\mathrm{II}}_{ij} \equiv \langle \phi^{\mathrm{II}} | c^{\dagger}_i c_j | \phi^{\mathrm{II}} \rangle$ by Wick's theorem. Furthermore, the expectation value of the n-th term in (15) is easily seen to be of order $\mathcal{O}(\beta^n)$. Analogous expressions may be found for the higher order density-matrices. Inserting these expressions into the definition (9) of the corresponding correlation functions we find after a tedious but straightforward calculation

$$\bar{C}_{abcdef} = \mathcal{O}(\beta^2)\,, \tag{16}$$

which means that the ansatz (12) up to linear order in β reproduces the decoupling scheme based on the neglect of the six-point correlation function $\bar{C}_{abcdef}$. The expansion involved in the above derivation is analogous to the procedure invoked in the derivation of the linear coupled-cluster approximation (L-CCA)[27, 80] used for the calculation of ground state energies.

Although we have demonstrated that the coupled-cluster ansatz and the QBBGKY-hierarchy are closely related, in practical applications these two approaches have lead to quite different computational schemes, each encountering its own characteristic problems.

The most serious problem connected with the SUB(2) dynamics of the QBBGKY-hierarchy is that the truncation violates fundamental trace relations; Thus, for an N-particle system the density-matrices obviously have to fulfill the relations:

$$(N-1)\,C_{ab} = \sum_j C_{ajjb} \quad , \quad (N-2)\,C_{abcd} = \sum_j C_{abjjcd}, \cdots .$$

This implies for the correlated parts:

$$\bar{K}_{ab} \equiv \sum_j \bar{C}_{ajjb} = \sum_j C_{aj}\,C_{jb} - C_{ab}\,,$$

$$\begin{aligned}
&\bar{K}_{abcd} \equiv \sum_j \bar{C}_{abjjcd} = \\
&\sum_j \{C_{aj}\,\bar{C}_{jbcd} + C_{bj}\,\bar{C}_{ajcd} + C_{jc}\,\bar{C}_{abjd} + C_{jd}\,\bar{C}_{abcj}\} - 2\,\bar{C}_{abcd}\,.
\end{aligned} \tag{17}$$

The truncated QBBGKY equations of motion do however preserve these relations only when the truncation is at the lowest (TDHF) level. For the SUB(n) $n \geq 2$ dynamics it has been shown that this violation can lead to unphysical results in certain cases [59, 81]. Whether or not the principal shortcomings of this scheme pose a severe problem strongly depends on the specific system and application under consideration; e.g. the calculation of the third order response within the band model of direct gap semiconductors is one extreme case, where the above inconsistency has no effect at all, because the contributions violating the trace relations are of higher order in the optical field. The same is true for Frenkel exciton systems[61, 62, 67]. Also the worked out applications in nuclear physics [73–76] are encouraging. However, in highly correlated systems like the PPP model of conjugated polyenes, it has to be expected that taking care of the trace relations is crucial for a successful application of the density-matrix. We will address this problem in section V.

Coupled-cluster theory, on the other hand, is an alternative approach which does not suffer from the trace problem, because trace relations like (17) are automatically fulfilled by any density-matrix calculated from an arbitrary N-particle wavefunction. But the price to be paid for tractability within coupled-cluster calculations of dynamic properties is only deferred. In principle, the time-dependent variational principle underlying the Schrödinger equation could be used to obtain equations of motion for the parameters in the coupled-cluster wavefunction at any SUB(n) level. However, this procedure is usually not applied in practice, because the resulting equations are too complicated to be of practical use especially for large systems[59]. Instead, equations of motion for the parameters of the coupled-cluster wavefunction are commonly obtained by projecting the Schrödinger equation for the exact wavefunction on n-particle, n-hole amplitudes [82–86]. This is equivalent to the variational principle only for an untruncated scheme. These projection techniques are essential in order to derive tractable dynamic equations. That is the main reason why in most applications of the coupled-cluster approach the wavefunction is not parameterized in the unitary form (12); instead the operators S and S^{II} usually contain only excitation operators (i.e. operators $c^\dagger_{\tilde{\mu}} c_\lambda$, or $c^\dagger_{\tilde{\mu}} c^\dagger_{\tilde{\nu}} c_\lambda c_\kappa$, where λ, κ are restricted to occupied orbitals with respect to the Hartree-Fock ground state, while $\tilde{\mu}$,$\tilde{\nu}$ refer to unoccupied orbitals). The evaluation of any physical observable other than the ground state energy then requires not only a parameterization of the ket state $|\psi_K\rangle$ but also of the bra state $\langle\psi_B|$. The most straightforward parameterization, namely to take the bra to be the adjoint of the ket, unfortunately leads to non-terminating, rather involved, expressions for the observables in terms of the wavefunction parameters [82, 83]. Nevertheless,a tractable scheme can be obtained when the bra is parameterized differently from the ket [82–84]. The parameterization suggested in 82, 84 is made in such a way that in the limiting case of an untruncated scheme the conventional definition of an expectation value $\langle A\rangle = \langle\psi|A|\psi\rangle$ is recovered from $\langle\psi_B|A|\psi_K\rangle$. But for any SUB(n) level, the density-matrix calculated according to this scheme will be non-Hermitian. Obviously this can under certain conditions invalidate the results of the coupled-cluster dynamics just as the trace problem does in the case of the QBBGKY-hierarchy. It should be noted that the QBBGKY-hierarchy does not suffer from non-hermiticity, because the dynamic equations (10),(11) manifestly preserve the hermiticity of the density-matrix.

V. CONTRACTION-FREE CORRELATION FUNCTIONS

In the last section we have seen that the standard formulations of the many-body dynamics in terms of coupled-cluster wavefunctions as well as in terms of the QBBGKY-hierarchy face some fundamental difficulties when applied at a truncated level. Truncation, however, is a must for any method that is meant to be useful for a description of large systems. In this section we propose a modified truncation scheme for the QBBGKY-hierarchy which avoids the above problems without significantly increasing the computational cost. To that end we first have to briefly analyze what causes the trace problem. According to (17) we find that contractions of higher order correlation functions can be expressed in terms of lower order functions. Basically this means that higher order functions contain not only additional information on the system not accessible by lower order functions, but also to some extend information already contained in the lower order functions. Neglecting higher order functions becomes inconsistent, because the overlapping part of information is kept in one place and discarded in an other. But as this overlapping part is readily contained in lower order functions, it is in principle available via these functions and thus can be used to define new correlation functions having this information removed.

One way to remove the information contained in contractions is to construct contraction-free correlation (CFC) functions. To be more specific, our goal is to express the correlation functions $\bar{C}_{abcd}$, $\bar{C}_{abcdef}$, $\cdots$ in the QBBGKY-hierarchy in terms of new functions K_{abcd},K_{abcdef},$\cdots$ having the following properties:

$$\sum_j K_{ajjb} = 0 \quad , \quad \sum_j K_{abjjcd} = 0\,, \cdots ; \tag{18}$$

$$\begin{aligned} &K_{abcd} = -K_{bacd} = -K_{abdc} = K_{badc}\,, \\ &K_{abcdef} = \mathrm{sign}(P)\,K_{P(abc)def} = \mathrm{sign}(P)\,K_{abcP(def)}\,, \cdots ; \end{aligned} \tag{19}$$

$$K_{abcd} = K^*_{dcba} \quad , \quad K_{abcdef} = K^*_{fedcba} \quad , \cdots ; \tag{20}$$

where P may be any permutation of the indices. One possibility to construct these CFC functions is to subtract suitably anti-symmetrized diagonal functions from the original correlation functions $\bar{C}$. Using (17) it is easy to verify that for a system with N electrons and $2N$ spin orbitals, the requirements (18)-(20) are fulfilled by the choice:

$$\begin{aligned} &K_{abcd} \equiv \bar{C}_{abcd} - \frac{1}{(2N-2)}\,A[\delta_{bc}\,\bar{K}_{ad}] + \frac{\bar{K}\,\bar{\delta}_{abcd}}{(2N-2)(2N-1)}\,, \\ &K_{abcdef} \equiv \bar{C}_{abcdef} - \frac{(1-P_{bc}-P_{ac})(1-P_{de}-P_{df})}{(2N-4)} \times \\ &\times\{\delta_{cd}\,\bar{K}_{abef} - \frac{\tilde{K}_{cd}\,\bar{\delta}_{abef}}{(2N-3)}\} - \frac{\bar{K}(1-P_{de}-P_{df})\{\delta_{cd}\,\bar{\delta}_{abef}\}}{(2N-4)(2N-3)(2N-2)}\,, \\ &\vdots\,, \end{aligned} \tag{21}$$

where

$$\bar{K} \equiv \sum_j \bar{K}_{jj} \quad , \quad \tilde{K}_{ab} \equiv \sum_j \bar{K}_{ajjb} \quad , \quad \bar{\delta}_{abcd} \equiv \delta_{bc}\,\delta_{ad} - \delta_{ac}\,\delta_{bd}\,. \tag{22}$$

Here P_{ab} is the operator interchanging the indices a and b. Inserting these definitions into (10) and (11) we can reformulate the dynamics as a hierarchy of equations of motion for the density-matrix C_{ab} and the CFC functions K_{abcd},K_{abcdef},$\cdots$. A similar scheme that aims at retaining the part of the six-point correlation function $\bar{C}_{abcdef}$ that enters the trace relation (17) has been proposed by Cassing and Pfitzner 81. Similar to (21), also their scheme leads to corrections scaling like $1/N$. But unlike our proposal the ansatz presented in 81 violates (19). The respective truncated scheme is consequently in conflict with the Pauli principle.

Using the definitions (21) and (22) we obtain

$$\begin{aligned} i\hbar\partial_t C_{ab} &= \sum_j \{t_{bj}\,C_{aj} - t_{ja}\,C_{jb}\} - \sum_j (V_{bj} - V_{aj})\,C_{aj}\,C_{jb} + \phi_{ba}\,C_{ab} \\ &+W_{ab} + \bar{V}_{ab}\,\bar{K}_{ab} + e\,E\,(z_b - z_a)\,C_{ab}\ , \end{aligned} \tag{23}$$

$$\begin{aligned} &i\hbar\partial_t K_{abcd} = \frac{1}{2}A[\sum_j \{t_{dj}\,K_{abcj} - t_{ja}\,K_{jbcd}\} + (V_{cd} - V_{ab})\,C_{bc}\,C_{ad}] \\ &-\frac{1}{2}A[\sum_j (V_{dj} + V_{cj} - V_{bj} - V_{aj})\,\{C_{aj}\,K_{jbcd} + C_{jd}\,K_{abcj}\}] \\ &+A[C_{bc}\,\{W_{abcd} - \sum_j (V_{cj} - V_{bj}) C_{aj}\,C_{jd} + \\ &+\bar{K}_{ad}\,(\frac{\bar{V}_{cb} + \bar{V}_{da} + V_{ab} - V_{cd}}{N-2} + \bar{V}_{cb})\} + \delta_{bc}\,\{F_{ad} + (V_{cd} - V_{ab})\,G_{ad}\}] \end{aligned}$$

$$
\begin{aligned}
&+\{(N-1)(\bar{V}_{cb}+\bar{V}_{da})+V_{ab}-V_{cd}\}\,\frac{(L_{abcd}-2K_{abcd})}{N-2} \\
&+(V_{cd}-V_{ab}+\phi_{cd}+\phi_{da}+e\,E\,(z_d+z_c-z_b-z_a))\,K_{abcd} \\
&+\sum_j (V_{dj}+V_{cj}-V_{bj}-V_{aj})\,K_{abjjcd}\,, \qquad (24)
\end{aligned}
$$

with the abbreviations

$$
\begin{aligned}
&L_{abcd} \equiv \frac{1}{2} A[\sum_j \{C_{aj}\,K_{jbcd}+C_{jd}\,K_{abcj}\}] \quad , \quad L_{ad} \equiv \sum_j L_{ajjd}\,, \\
&W_{abcd} \equiv \sum_j (V_{cj}-V_{bj})\,K_{ajjd} \quad , \quad W_{ad} \equiv W_{aadd}\,, \\
&\bar{W}_{ad} \equiv \sum_j \{C_{aj}\,(W_{jd}+\bar{V}_{dj}\,\bar{K}_{jd})+C_{jd}\,(W_{aj}+\bar{V}_{ja}\,\bar{K}_{aj})\}\,, \\
&\bar{W} \equiv \sum_j \bar{W}_{jj} \quad , \quad \bar{C}_{ad} \equiv \sum_j C_{aj}\,\bar{K}_{jd}\,, \\
&\bar{V}_{da} \equiv \frac{1}{N-1}\sum_j (V_{dj}-V_{aj}) \quad , \quad \bar{\phi}_{ad} \equiv \sum_j (V_{aj}-V_{dj})\,\bar{K}_{jj}\,, \\
&F_{ad} \equiv C_{ad}\{\frac{\bar{\phi}_{da}}{2N-4}-\frac{\bar{K}\bar{V}_{da}(N-1)}{(2N-3)(N-2)}\}+\bar{C}_{ad}\frac{2\bar{V}_{da}(N-1)}{(2N-3)(N-2)} \\
&+\bar{K}_{ad}\{\frac{\phi_{da}}{2(N-1)(N-2)}-\bar{V}_{da}(\frac{N-1}{(N-2)(2N-3)}+\frac{N}{2(N-1)(N-2)})\} \\
&+\frac{1}{2(N-1)}\{\sum_j (V_{aj}-\frac{V_{dj}-V_{aj}}{N-2})\bar{K}_{aj}\,C_{jd}-\sum_j (V_{dj}+\frac{V_{dj}-V_{aj}}{N-2})C_{aj}\,\bar{K}_{jd}\} \\
&+\frac{1}{2(N-1)}\{\frac{\bar{W}\,\delta_{ad}}{(4N-2)}-\bar{W}_{ad}-\frac{N\,W_{ad}}{N-2}\}+\sum_j \frac{(V_{dj}-V_{aj})}{2(N-2)}\,L_{ajjd} \\
&-L_{ad}\,\frac{\bar{V}_{da}(N-1)}{(2N-3)(N-2)}\,,
\end{aligned}
$$

$$
G_{ab} \equiv \frac{C_{ad}\,\bar{K}-2\bar{C}_{ad}+(2N-2)\bar{K}_{ad}+L_{ad}}{(2N-4)(2N-3)}\,.
$$

Truncation of the hierarchy of CFC functions at the SUB(2) level (i.e. setting $K_{abcdef}=0$ in (24)) leads to a closed set of equations of motion for the density-matrix C_{ab} and the correlation function K_{abcd}, given by (23) and (24). Using these equations it can be directly verified that the properties (18)-(20) are preserved also by the truncated dynamics. As noted earlier, we can see from the definition (21) of the CFC functions that the corrections needed to satisfy the trace relations scale at least as $1/N$ with system size. These terms can therefore be expected to gradually become less important with growing system size.

In conclusion, we have shown how a modified version of the QBBGKY-hierarchy can be applied to the optical response of many-electron systems. Our main formal result is the set of equations (23) and (24). It allows a size-consistent calculation of the optical response, taking into account two-exciton contributions. Furthermore, the truncation is performed in a self-consistent way, avoiding the problem of violated trace-relations exhibited by the naive QBBGKY-truncation scheme.

Acknowledgments

This work has been kindly supported in part by the Deutsche Forschungs Gemeinschaft DFG, the National Science Foundation and the US Air Force office of scientific research.

[1] *Nonlinear Optical Effects in Organic Polymers,* NATO Advanced Study Institute, Series E, edited by J. Mrssier, F. Kajzar, P.N. Prasad, D.R. Ulrich (Kluwer Academic, Dordrecht, 1989), Vol. 162.

[2] S. Etemad, Z.G. Soos, in *Spectroscopy of Advanced Materials,* edited by R.J.H. Clark, R.E. Hester (Wiley, New York,1991), pp.87, and references therein.

[3] *Nonlinear Optical Properties of Organic Molecules and Crystals,* Vol. **1,2** eds. J. Zyss, D.S. Chemla (Academic Press, Florida, 1987).

[4] D. Mukhopadhyay, G.W. Hayden, Z.G. Soos, Phys. Rev. B **51**, 9476 (1995).

[5] Z.G. Soos, S. Ramasesha, D.S. Galvão, Phys. Rev. Lett. **71**, 1609 (1993).

[6] S. Abe, M. Schreiber, W.P. Su, J. Yu,J. Lumin. **53**, 519 (1992); S. Abe, M. Schreiber,W.P. Su, J. Yu,Phys. Rev. B **45**, 9432 (1992); S. Abe, J. Yu, W.P. Su, Phys. Rev. B **45**, 8264 (1992); S. Abe, M. Schreiber, W.P. Su, Chem. Phys. Lett. **192**, 425 (1992).

[7] D. Beljonne, Z. Shuai, J.L. Brédas, J. Chem. Phys. **98**, 8819 (1993).

[8] Z. Shuai, J.L. Brédas, Phys. Rev. B **44**, 5962 (1991).

[9] D. Yaron, R. Silbey, Phys. Rev. B **45**, 11655 (1992).

[10] Z.G. Soos, Mol. Cryst. liq. Cryst. **256**, 35 (1994).

[11] Z.G. Soos,D.S. Galvão, S. Etemad, Adv. Mater. **6**, 280 (1994); Z.G. Soos, S. Ramasesha, D.S. Gãlvao, S. Etemad Phys. Rev. B **47**, 1742 (1993); Z.G. Soos, S. Ramasesha, D.S. Gãlvao, R.G. Kepler, S. Etemad, Synth. Metals **54**, 35 (1993); Z.G. Soos, S. Ramasesha, J. Chem. Phys. **90**, 1067 (1988); Z.G. Soos, S. Ramasesha, Phys. Rev. B **29**, 5410 (1984).

[12] S. Abe, M. Schreiber, W.P. Su, J. Yu, Synth. Metals, **57**, 4004 (1993).

[13] G. Chen, S. Mukamel, D. Beljonne,J.L. Brédas, J. Chem. Phys. **104**, 5406 (1996).

[14] M. Jaszuński, P. Jørgensen, H. Koch, H. Ågren, T. Helgaker, J. Chem. Phys. **98**, 7229 (1993).

[15] J. Olsen, P. Jørgensen, J. Chem. Phys. **82**, 3225 (1985).

[16] H.-D. Meyer, U. Manthe, L.S. Cederbaum, Chem. Phys. Lett. **165**, 73 (1990).

[17] H. Ishihara, K. Cho, Phys. Rev. B **42**,1724 (1990).

[18] Z. Soos,G. Hayden,P. McWilliams, *Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics and Molecular Electronics* (Kluver, Dordrecht, 1990), pp. 495-508.

[19] H. Koch, R. Kobayashi,A. Sanchez de Merás, P. Jørgensen, J.Chem. Phys. **100**, 4393 (1994).

[20] V. Chernyak, S. Mukamel, J. Chem. Phys. **104**, 444 (1996).

[21] D. Guo, Mol. Cryst. Liq. Cryst. **256**, 105 (1994); D. Guo, S. Mazumdar, S.N. Dixit, Synth. Metals **49**, 1 (1993); S. Mazumdar, D. Guo, S.N. Dixit, J. Chem. Phys. **96**, 6962 (1992); S. Mazumdar, D. Guo, S.N. Dixit, SPIE Proc. 1436, 136 (1991); S.N. Dixit, D. Guo, S. Mazumdar, Phys. Rev. B **43**, 6781 (1990).

[22] D. Guo, S. Mazumdar, S.N. Dixit, F. Kajzar, F. Jarka, Y. Kawabe, N. Peyghambrarian, Phys. Rev. B **48**, 1433, (1993); S. Mazumdar, D. Guo, S.N. Dixit, Synth. Metals **55-57**, 3881 (1993); Y. Kawabe, F. Jarka, N. Peyghambrarian, D. Guo, S. Mazumdar, S.N. Dixit, F. Kajzar, Phys. Rev. B **44**, 6530 (1991); D. Guo, S. Mazumdar, G.I. Stegeman, M. Cha, D. Neher, S. Aramaki, W. Torruellas, R. Zanoni, *Electrical,Optical, and Magnetic Properties of Organic Solid State Materials,* eds. L.Y. Chiang, A.F. Garito, D.J. Sandman, 151 (1992); S. Mazumdar, F. Guo, J. Chem. Phys. **100**, 1665 (1994).

[23] S. Abe, Y. Shimoi, V.A. Shakin, K. Harigaya, Mol. Cryst. liq. Cryst. **256**, 97 (1994).

[24] V.A. Shakin, S. Abe, Phys. Rev. B **50**, 4306 (1994).

[25] Y. Shimoi, S. Abe, Phys. Rev. B **49**, (1994).

[26] S. Abe, Prog. Theor. Phys. Supp. **113**, 83 (1993).

[27] A. Szabo, N.S. Ostlund,*Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory* (McGraw-Hill, New York, 1989).

[28] S.Mukamel, A. Takahashi, H.X. Wang, G. Chen, Science **266**, 250 (1994).

[29] M. Hartmann, V. Chernyak, S. Mukamel, Phys. Rev. B **52**, 2528 (1995); M. Hartmann, S. Mukamel, J. Chem. Phys. **99**, 1597 (1993);

[30] A. Takahashi, S. Mukamel, J. Chem. Phys. **100**, 2366 (1994).

[31] S. Mukamel, H. X. Wang, Phys. Rev . Lett. **69**, 65 (1992); H. X. Wang,S. Mukamel, J. Chem. Phys. **97**, 8019 (1992).

[32] P. Ring, P. Schuck, *The Nuclear Many-Body Problem* (Springer-Verlag, New York, 1976).

[33] B.E. Kohler,C. Sprangler, C. Westerfield, J. Chem. PHys. **89**, 5422 (1988).

[34] L.A. Heimbrook, B.E. Kohler, I.J. Levy, J. Chem. Phys. **81**,1592 (1984); L.A. Heimbrook, J.E. Kenny, B.E. Kohler, G.W. Scott, J. Chem. Phys. **75**, 4338 (1981).

[35] M.F. Granville, G.R. Holtom, B.E. Kohler, J. Chem. Phys. **72**, 4671 (1980).

[36] J.M. Leng, S. Jeglinski, X. Wei, R.E. Brenner, Z.V. Vardeney, F. Guo, S. Mazumdar, Phys. Rev. Lett. **72**, 156 (1994).

[37] P.D. Townsend, W.S. Fann, S. Etemad, G.L. Baker, Z.G. Soos, P.C.M. McWilliams, Chem. Phys. Lett. **180**, 485 (1991).

[38] P.C.M. McWilliams, G.W. Hayden, Z.G. Soos, Phys. Rev. B **43**, 9777 (1991).

[39] F. Guo,D. Guo, S. Mazumdar, Phys. Rev. B **49**, 10102 (1994).

[40] I. Ohmine, M. Karplus, K. Schulten, J. Chem. Phys. **68**, 2298 (1978).

[41] M. Chandross, F. Guo, S. Mazumdar, Synth. Metals, **69**, 625 (1995); F. Guo, M. Chandross, S. Mazumdar, Phys. Rev. Lett. **74**, 2086 (1995).

[42] K. Ishida, H. Aoki, T. Ogawa, Phys. Rev. B **52**, 8980 (1995).

[43] V.A. Shakin, S. Abe, *IEEE Nonlinear Optics: Materials, Fundamentals, and Applications (Cat.No. 94CH3370-4)* p. 114 (1994).

[44] F. Guo, M. Chandross, S. Mazumdar, Mol. Cryst. liq. Cryst. **256**, 53 (1994).

[45] S.A. Kucharski, R.J. Bartlett, J. Chem. Phys. **97**,4282 (1992); J. Chem. Phys. **95**,8227 (1991).

[46] J.F. Stanton, J. Gauss, J.D. Watts, R.J. Bartlett, J. Chem. Phys. **94**, 4334 (1991).

[47] J.D. Watts, R.J. Bartlett, Chem. Phys. Lett. **190**, 19 (1992); J. Chem. Phys. **97**, 3445 (1992).

[48] S.R. Gwaltney, M. Nooijen, R.J. Bartlett, Chem. Phys. Lett. **248**, 189 (1996); S.R. Gwaltney, R.J. Bartlett, Chem. Phys. Lett. **241**, 26 (1995).

[49] H. Koch, H. Jørgen,A. Jensen, P. Jørgensen,T. Helgaker, J.Chem. Phys. **93**, 3345 (1990).

[50] M. Nooijen,J.G. Snijders, J. Chem. Phys. **102**,1681 (1995).

[51] Wang Shun-Jin, W. Cassing, Annals of Physics **159**, 328 (1985).

[52] R. Balescu, *Equilibrium and nonequilibrium statistical mechanics* New York London Sydney Toronto: Wiley (1975), pp. 100.

[53] P.C. Martin, J. Schwinger, Phys. Rev. **115**, 1342 (1959).

[54] K. Ohno, Theor. Chim. Acta **2**, 219 (1964).

[55] D. Baeryswyl, D.K. Campbell, S. Mazumdar, in *Conducting Polymers*, ed. H. Kiess, Topics in Current Physics (Springer-Verlag, Heidelberg, 1992) p.7.

[56] T. Kuhn, *Ladungsträgerdynamik in Halbleitersystemen fern vom Gleichgewicht: Elektronisches Rauschen und kohärente Prozesse* (Verlag Shaker, Aachen, 1994). In this book, the cluster decomposition is used to truncate the hierarchy of equations of motion for a direct semiconductor. In practical application to these systems, the decoupling procedure is usually followed by a series of further simplifying steps finally leading to the so called scattering contributions to the semiconductor Bloch equations (see also [58]).

[57] A. Stahl, I. Balslev, *Electrodynamic at the semiconductor band edge* Springer Tracts in Modern Physics Vol. 110 (Springer-Verlag, Berlin Heidelberg New York, 1987).

[58] H. Haug, S.W. Koch, *Quantum theory of optical and electronic properties of semiconductors.* Secoond edition, Singapore, New Jersey, London, Hong Kong: World Scientific.

[59] K.-J. Schmitt, P.-G. Reinhard, C. Toepffer, Z. Phys. A, **336**, 123 (1990); Phys. Rev. A **40**, 474 (1989).

[60] M. Tohyama, P. Schuck, S.J. Wang, Z. Phys. A, **339**, 341 (1991).

[61] S. Mukamel, in *Nonlinear Optical Properties of Organic Molecules and Crystals*, Vol. 3, Editor J. Zyss, Academic Press, 1993.

[62] S. Mukamel,*Principles of Nonlinear Optical Spectroscopy* (Oxford,New York) (1995).

[63] V.M. Axt, A. Stahl, Z. Phys. B **93**, 195 (1994).

[64] K. Victor, V.M. Axt, A. Stahl, Phys. Rev. B **51** 14164 (1995); V.M. Axt, K. Victor, A. Stahl, Phys. Rev. B **53**,7244 (1996).

[65] M.Z. Maialle,L.J. Sham, Phys. Rev. Lett. **73**, 3310 (1994).

[66] P.-G. Reinhard, C. Toepffer, Int. J. Mod. Phys. E, Vol.3 Supp., 435 (1994).

[67] J. A. Leegwater S. Mukamel, Phys. Rev. A **46**, 452 (1992).

[68] V. M. Axt, A. Stahl,Z. Phys. B **93**, 205 (1994); V.M. Axt, A. Stahl, E.J. Mayer, P. Haring Bolivar, S. Nüsse, K. Ploog, K. Köhler, Phys. Stat. Sol. (b) **188**, 447 (1995).

[69] M. Lindberg, Y.Z. Hu, R. Binder, S.W. Koch, Phys. Rev. B **50**, 18060 (1994).

[70] T. Östreich, K. Schönhammer,L.J. Sham, Phys. Rev. Lett. **75**, 2554 (1995); Phys. Rev. Lett. **74**, 4698 (1995).

[71] V.M. Axt, G. Bartels, and A. Stahl, Phys. Rev. Lett. **76**, 2543, (1996); G. Bartels, V.M. Axt, K. Victor, A. Stahl, P. Leisching, K. Köhler, Phys. Rev. B, **51** 11217 (1995).

[72] D.S. Kim, W. Schäfer, J. Shah, T.C. Damen, J.E. Cunningham, K.W. Goossen, L.N Pfeiffer, K. Köhler, to be published.

[73] J.M. Häuser, W. Cassing, A. Peter, Nucl. Phys. A **A585**, 727 (1995).

[74] F.V. DeBlasio, W. Cassing, M. Tohyama, P.F. Bortington, R.A. Broglia, Phys. Rev. Lett. **88**, 1663 (1992).

[75] M. Gong, M. Tohyama, Z. Phys. A **335**,153 (1990); M. Gong, M. Tohyama, J. Randrup Z. Phys. A **335**,331 (1990); M. Tohyama,M. Gong, Z. Phys. A **332**, (1989).

[76] W. Cassing, S.J. Wang, Z. Phys. A **328**423, (1987).

[77] P.G. Szalay, M. Nooijen, R.J. Bartlett, J. chem. Phys. **103**, 281 (1995).

[78] H. Koch, R. Kobayashi, P. Jørgensen, Int. J. Quantum Chemestry, **49**, 835 (1994).

[79] R. Kobayashi, H. Koch, P. Jørgensen, T.J. Lee, Chem. Phys. Lett. **211**, 94 (1993).

[80] P. Fulde, *Electron correlations in molecules and solids* (Springer-Verlag, Berlin, New York, 2nd edition 1993).

[81] W. Cassing A. Pfitzner, Z. Phys. A **342**,161 (1992).

[82] J.S. Arponen, R.F. Bishop, E. Pajanne, Phys. Rev. A, **36**, 2519;2539 (1987).

[83] R.F. Bishop, J.S. Arponen, Int. J. Quant. Chem.: *Quantum Chemistry Symposium* **24**, 197 (1990); R.F. Bishop, J.S. Arponen, Int. J. Quantum Chemistry: Quantum Chemistry Symposium 24, 197 (1990).

[84] H. Koch, P. Jørgensen, J.Chem. Phys. **93**, 3333 (1990).

[85] R. Kobayashi, H. Koch, P. Jørgensen, Chem. Phys. Lett. **219**, 30 (1994).

[86] E. Dalgaard, H. J. Monkhorst, Phys. Rev. A **28**,1217 (1983).