

REAL-SPACE DENSITY-MATRIX DESCRIPTION OF DYNAMIC CORRELATIONS IN THE OPTICAL RESPONSE OF MANY-ELECTRON SYSTEMS

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Abstract. 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 relation inherent in the truncated QBBGKY-hierarchy.

1. Introduction. The calculation of the optical response of molecular and semiconductor materials is an open challenge that has attracted great attention in recent years [1,2,3,4,5,6,7,8,9]. 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 [9,10,11,12,13] or multiconfiguration self-consistent field theories with large basis sets [14,15,16] 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 [8,17,18,19,20]. 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 [23,24,25,26], 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 [28,29,30,31]. 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 [33,34,35] 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 [36,37,38,39,40]. Furthermore, explanation of all biexcitonic features [41,42,43,44] certainly

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

$$(2.4) \quad H_{coul} = \frac{1}{2} \sum_{n,m} V_{nm} c_n^\dagger c_n c_m^\dagger c_m,$$

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 extended Hubbard type interaction 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. (2.3)). However, since all basic concepts can readily be explained using the form (2.4), we present explicit formulas only for that case, in order to keep the notation simple. The last term in (2.1) represents the coupling to the optical field $E(t)$ polarized along the z -axis, and is given by

$$(2.5) \quad H_{opt} = -E(t) \hat{P},$$

where the molecular polarization operator takes on the form

$$(2.6) \quad \hat{P} = -e \sum_n z_n c_n^\dagger c_n.$$

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

3. 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]: $C_{ab} = \langle c_a^\dagger c_b \rangle$, $C_{abcd} = \langle c_a^\dagger c_b^\dagger c_c c_d \rangle$, $C_{abcdef} = \langle c_a^\dagger c_b^\dagger c_c^\dagger c_d c_e c_f \rangle$, \dots . Equations of motion for these quantities are readily obtained by taking expectation values of the Heisenberg equations of motion:

$$(3.1) \quad i\hbar \dot{X} + [H, X] = 0.$$

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 (2.6).

$$(3.2) \quad \langle \hat{P} \rangle(t) = -e \sum_n z_n C_{nn}(t).$$

Unfortunately, the corresponding equation of motion (3.1) is not closed; instead, it contains C_{abcd} as a source, which in turn is coupled to C_{abcdef} . Equations (3.1) 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

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

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 $A[F_{abcd}] = F_{abcd} - F_{bacd} - F_{abdc} + F_{badc}$. 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 (3.5), 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 [56,63,64,65] and for nuclear many-body problems [51,66]. Successful applications of this scheme have been reported in all three of these fields [61,67,68,69,70,71,72,73,74,75,76]. 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 (3.4) and (3.5) have to be solved with the ground state values of C_{ab} and \bar{C}_{abcd} as initial conditions. These values can

by Wick's theorem. Furthermore, the expectation value of the n -th term in (4.4) 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 (3.3) of the corresponding correlation functions we find after a tedious but straightforward calculation

$$(4.5) \quad \bar{C}_{abcdef} = \mathcal{O}(\beta^2),$$

which means that the ansatz (4.1) 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:

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

This implies for the correlated parts:

$$(4.6) \quad \begin{aligned} \bar{K}_{ab} &\equiv \sum_j \bar{C}_{ajjb} = \sum_j C_{aj} C_{jb} - C_{ab}, \\ \bar{K}_{abcd} &\equiv \sum_j \bar{C}_{abjjcd} \\ &= \sum_j \{C_{aj} \bar{C}_{jbcd} + C_{bj} \bar{C}_{ajcd} + C_{jc} \bar{C}_{abjd} + C_{jd} \bar{C}_{abcj}\} - 2\bar{C}_{abcd}. \end{aligned}$$

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 [62,61,67]. Also the worked out applications in nuclear physics [73,74,75,76] are encouraging. However, in highly correlated systems like the PPP model of

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 (4.6) 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 extent 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 $\bar{C}_{abcd}, \bar{C}_{abcdef}, \dots$ in the QBBGKY-hierarchy in terms of new functions $K_{abcd}, K_{abcdef}, \dots$ having the following properties:

$$(5.1) \quad \sum_j K_{ajjb} = 0 \quad , \quad \sum_j K_{abjjcd} = 0, \dots;$$

$$(5.2) \quad \begin{aligned} K_{abcd} &= -K_{bacd} = -K_{abdc} = K_{badc} , \\ K_{abcdef} &= \text{sign}(P) K_{P(abc)def} = \text{sign}(P) K_{abcP(def)}, \dots; \end{aligned}$$

$$(5.3) \quad K_{abcd} = K_{dcba}^* \quad , \quad K_{abcdef} = K_{fedcba}^* \quad , \quad \dots;$$

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 (4.6) it is easy to verify that for a system with N electrons and $2N$ spin orbitals, the requirements (5.1)–(5.3) are fulfilled by the choice:

$$(5.4) \quad \begin{aligned} K_{abcd} &\equiv \bar{C}_{abcd} - \frac{1}{(2N-2)} A[\delta_{bc} \bar{K}_{ad}] + \frac{\bar{K} \bar{\delta}_{abcd}}{(2N-2)(2N-1)} , \\ K_{abcdef} &\equiv \bar{C}_{abcdef} - \frac{(1-P_{bc}-P_{ac})(1-P_{de}-P_{df})}{(2N-4)} \\ &\quad \times \left\{ \delta_{cd} \bar{K}_{abef} - \frac{\bar{K}_{cd} \bar{\delta}_{abef}}{(2N-3)} \right\} - \frac{\bar{K}(1-P_{de}-P_{df})\{\delta_{cd} \bar{\delta}_{abef}\}}{(2N-4)(2N-3)(2N-2)} , \\ &\quad \vdots , \end{aligned}$$

$$\begin{aligned}
 \bar{W} &\equiv \sum_j \bar{W}_{jj} \quad , \quad \bar{C}_{ad} \equiv \sum_j C_{aj} \bar{K}_{jd} , \\
 \bar{V}_{da} &\equiv \frac{1}{N-1} \sum_j (V_{dj} - V_{aj}) \quad , \quad \bar{\phi}_{ad} \equiv \sum_j (V_{aj} - V_{dj}) \bar{K}_{jj} , \\
 F_{ad} &\equiv C_{ad} \left\{ \frac{\bar{\phi}_{da}}{2N-4} - \frac{\bar{K} \bar{V}_{da} (N-1)}{(2N-3)(N-2)} \right\} + \bar{C}_{ad} \frac{2\bar{V}_{da}(N-1)}{(2N-3)(N-2)} \\
 &+ \bar{K}_{ad} \left\{ \frac{\phi_{da}}{2(N-1)(N-2)} - \bar{V}_{da} \left(\frac{N-1}{(N-2)(2N-3)} + \frac{N}{2(N-1)(N-2)} \right) \right\} \\
 &+ \frac{1}{2(N-1)} \left\{ \sum_j (V_{aj} - \frac{V_{dj} - V_{aj}}{N-2}) \bar{K}_{aj} C_{jd} - \sum_j (V_{dj} + \frac{V_{dj} - V_{aj}}{N-2}) C_{aj} \bar{K}_{jd} \right\} \\
 &+ \frac{1}{2(N-1)} \left\{ \frac{\bar{W} \delta_{ad}}{(4N-2)} - \bar{W}_{ad} - \frac{N W_{ad}}{N-2} \right\} + \sum_j \frac{(V_{dj} - V_{aj})}{2(N-2)} L_{ajjd} \\
 &\quad - L_{ad} \frac{\bar{V}_{da}(N-1)}{(2N-3)(N-2)} , \\
 G_{ab} &\equiv \frac{C_{ad} \bar{K} - 2\bar{C}_{ad} + (2N-2)\bar{K}_{ad} + L_{ad}}{(2N-4)(2N-3)} .
 \end{aligned}$$

Truncation of the hierarchy of CFC functions at the SUB(2) level (i.e. setting $K_{abcdef} = 0$ in (5.7)) leads to a closed set of equations of motion for the density-matrix C_{ab} and the correlation function K_{abcd} , given by (5.6) and (5.7). Using these equations it can be directly verified that the properties (5.1)-(5.3) are preserved also by the truncated dynamics. As noted earlier, we can see from the definition (5.4) 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 (5.6) and (5.7). 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.

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