Excited State Properties of Organic Semiconductors: Breakdown of the Tamm-Dancoff Approximation

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The solution of the Bethe-Salpeter equation within the framework of many-body perturbation theory has turned out to be a benchmark for ab-initio calculations of optical properties of semiconductors and insulators. Commonly, however, the coupling between the resonant and anti-resonant excitations is neglected which is referred to as the Tamm-Dancoff approximation (TDA). This is well justified in cases where the exciton binding energy is much smaller than the band gap. Here, we report on the optical properties of a representative series of organic semiconductors where we find the TDA to no longer hold. We observe an increase of the exciton binding energy of up to 44% thereby improving the agreement with experiment.

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Preamble. This work has been conducted already in the years 2006–2007 but was not published at that time [1]. In the meantime several papers have come out which report similar observations regarding the breakdown of the Tamm-Dancoff approximation (TDA), most notably a paper by Grüning and co-workers on the exciton binding energies in organic molecules and carbon nanotubes [2]. The role of the TDA for excited states of biological chromophores has also been assessed in the paper by Ma and coworkers [3]. Nevertheless, the results reported in this manuscript may prove useful for the experts in the field, which motivated us to make them available now. Note that the remaining text of the paper, all figures and tables are kept unaltered from their 2007 version.

Within the framework of many-body perturbation theory the linear response to an optical perturbation is expressed in terms of the equation of motion for the electron-hole (e-h) two-particle Green’s function, the so-called Bethe-Salpeter equation (BSE). The solution of the BSE for the e-h correlation function represents a systematic first-principles approach for the calculation of optical absorption spectra including excitonic effects [4]. Solutions of the BSE in an ab-initio framework have shown that e-h interactions are indeed important in order to correctly account for quantitative (oscillator strengths) as well as qualitative (bound excitons) features of optical spectra of semiconductors and insulators. This is true for inorganic [5–9] as well as for organic semiconductors [10–16]. The exciton binding energy (BE) is a central quantity in the photophysics of these materials since it is intimately related to the probability of radiative emission/absorption and electric-field induced generation of free charge carriers. Indeed, ab-initio BSE results have considerably contributed to the longstanding debate about the nature of the energetically lowest optical excitations in organic semiconductors [10–16]. However, approximations in the state-of-the-art BSE approach, which have been proven to be valid for bulk inorganic semiconductors such as Si or GaAs [4], do not a priori hold for the highly anisotropic organic semiconductors. Transitions at positive (resonant part) and negative (anti-resonant part) frequencies are assumed to be decoupled leading to the Tamm-Dancoff approximation (TDA) [6]. This approximation is well justified, whenever exciton binding energies are much smaller than the band gap and it has been shown to have no influence on the optical absorption spectrum of bulk Si [4,18] while the coupling between the resonant and anti-resonant terms becomes relevant for the electron energy loss spectrum even in this case [18].

In this Letter, we demonstrate that going beyond the TDA, i.e., taking into account the full matrix structure of the BSE, becomes indeed necessary also for the optical absorption when treating organic semiconductors where exciton binding energies amount up to 20% of the band gap. In order to solve the full BSE matrix problem numerically we adapt the time-evolution scheme proposed for the TDA-BSE [19]. This has the advantage that it (i) allows for well-converged spectra with respect to \( k \) grid and number of included bands, (ii) poses no technical problems due to the non-Hermitian character of the full BSE matrix, and (iii) finally enables an efficient parallelization of the numerical computations.

Starting from the BSE in its integral form it can be transformed into a matrix eigenvalue equation by expanding all quantities in terms of single-particle electron and hole states \( \psi_{ek} \) and \( \psi_{ak} \), respectively [20]. From the resulting matrix eigenvalue problem the excitations energies (eigenvalues) as well as the electron-hole coupling coefficients (eigenvectors) can be obtained. The matrix structure of this effective electron-hole Hamiltonian \( H \) is given by the following expression [18]

\[
H = \begin{pmatrix}
R & C \\
-C^* & -R^*
\end{pmatrix}
\]  

(1)

where the diagonal blocks \( R \) and the coupling blocks \( C \),
respectively, have been defined according to
\[ R = (E_{c_1 k_1} - E_{v_1 k_1})\delta_{v_1 v_2}\delta_{c_1 c_2}\delta_{k_1 k_2} + i \Xi_{v_1 v_2 c_1 c_2 k_1 k_2} \]
\[ C = +i \Xi_{v_1 v_2 c_1 c_2 k_1 k_2}. \]
Here, \( E_{c_1 k_1} \) and \( E_{v_1 k_1} \), respectively, denote the electron and hole quasi-particle energies, while \( \Xi_{v_1 v_2 c_1 c_2 k_1 k_2} \) represents the electron-hole interaction kernel given by the sum of the bare exchange and the screened direct interaction \[ \{4\}. \] Note that the diagonal blocks contain the difference in the quasi-particle energy and are therefore greater than the single-particle band gap \( E_g \). Hence, the coupling matrices \( C \) can be neglected when electron-hole interactions are small compared to \( E_g \), which results in the TDA. Employing the TDA reduces the size of the eigenvalue problem of the full BSE matrix \( H \) by a factor of 2 and leaves an eigenvalue problem for the Hermitian matrix \( R \).

In order to go beyond the TDA we start with a general expression for the frequency dependent macroscopic polarizability tensor \( \alpha_{ij}^M \) \[ \{4, 19\} \] where \( i \) and \( j \) stand for the Cartesian coordinates \( x, y, z \)
\[
\alpha_{ij}^M (\omega) = \frac{8\pi}{\Omega} \sum_{\lambda\lambda'} (\mu_i^j | A^\lambda | S_{\lambda\lambda'}^{-1} | A^{\lambda'} \rangle \langle \mu^j |)
\times \left[ \frac{1}{E^\lambda - \omega - i\delta} + \frac{1}{E^\lambda + \omega + i\delta} \right].
\]
\[ (3) \]
\( E^\lambda \) and \( | A^\lambda \rangle \) denote the eigenvalues and eigenvectors of the full Hamiltonian, \( S_{\lambda\lambda'}^{-1} \) is the inverse of the overlap matrix \( S_{\lambda\lambda'} = \langle A^{\lambda'} | A^\lambda \rangle \), \( \delta \) is a broadening parameter, and \( | \mu^j \rangle \) is given by the optical matrix elements normalized by the quasi-particle energy differences
\[
\mu^j_{vck} = \frac{\langle v k | \nabla_j | c k \rangle}{E_{ck} - E_{vk}}.
\]
\[ (4) \]
The scalar products \( \langle . | . \rangle \) in Eq. \[ (3) \] involve summations over all valence, conduction bands, and \( k \) points \( (vck) \) of the full matrix structure. A direct evaluation of Eq. \[ (3) \] by diagonalizing \( H \) is complicated by the fact that \( H \) is non-Hermitian which makes the numerical solution of the eigenvalue problem non-trivial. Moreover, Eq. \[ (3) \] also involves the inverse of the overlap matrix, hence another computationally demanding task would be required. Instead we follow a route proposed by Schmidt et al. for the TDA-BSE \[ \{19\} \] in which the macroscopic polarizability is obtained without requiring the eigenvalues of \( H \) explicitly. It can be shown that the polarizability can be equivalently expressed as
\[
\alpha_{ij}^M (\omega) = \frac{8\pi}{\Omega} \int_0^\infty dt e^{i(\omega+i\delta)t} \left[ \langle \mu^j | \xi^i (t) \rangle - \langle \mu^j | \xi^i (t) \rangle^{*} \right].
\]
\[ (5) \]
Here, we have introduced the time dependent vectors \( | \xi^j (t) \rangle \) whose time evolution is governed by the unitary transformation
\[
| \xi^j (t) \rangle = e^{-iHt} | \mu^j \rangle.
\]
\[ (6) \]
The exponential of the Hamiltonian is defined via the spectral theorem as
\[
e^{-iHt} = \sum_{\lambda\lambda'} e^{-iE^\lambda t} S_{\lambda\lambda'}^{-1} | A^\lambda \rangle \langle A^{\lambda'} |.
\]
\[ (7) \]
Inserting Eqs. \[ (6) \] and \[ (7) \] into \[ (5) \] it is straightforward to demonstrate that both equations for the polarizability, i.e. Eqs. \[ (3) \] and \[ (5) \], are mathematically equivalent. Inspection of Eq. \[ (5) \] reveals that \( \alpha_{ij}^M (\omega) \) is obtained from the Fourier transform of the time-dependent quantity in square brackets evolving in time according to the Schrödinger equation
\[
i \frac{d}{dt} | \xi^j (t) \rangle = \hat{H} | \xi^j (t) \rangle.
\]
\[ (8) \]
Setting the initial value \( | \xi^j (0) \rangle = \mu^j \) this is equivalent to the definition \[ (6) \]. Eq. \[ (8) \] can be integrated numerically, e.g. using an explicit scheme where the time step \( \delta t \) for the numerical integration is given by the usual stability criterion \[ \{14\} \].

All calculations presented in this Letter have been obtained by utilizing the full-potential linearized augmented plane wave plus local orbitals method (FP-LAPW) as realized in the WIEN2K code \[ \{21\} \]. The implementation of the TDA-BSE scheme within the FP-LAPW method has been described elsewhere \[ \{9, 22\} \]. Convergence with respect to the \( k \) grid and number of valence and conduction bands has been checked. For all spectra we have chosen a broadening of 0.2 eV which typically requires time steps of \( \Delta t \approx 0.01 \) fs and around 3000 time steps within the time evolution scheme. Fig. \[ 1 \] compares the CPU time of the present time evolution method with a traditional matrix diagonalization scheme as a function of the matrix size \( N = 2N_vN_cN_e \), where \( N_k \) denotes the number of \( k \) points, and \( N_v \) and \( N_c \) are the number of valence and conduction states, respectively. The factor of 2 arises from the doubling of the matrix size due to the inclusion of the coupling blocks \( C \).
TABLE I: Exciton binding energies obtained with the TDA, $E_{b}^{\text{TDA}}$, and by including the coupling terms in the BSE, $E_{b}^{\text{BSE}}$. For comparison the static dielectric constants $\varepsilon$ in $x$, $y$ and $z$ directions are also given.

| material | $\varepsilon_x$ | $\varepsilon_y$ | $\varepsilon_z$ | $E_{b}^{\text{TDA}}$ [eV] | $E_{b}^{\text{BSE}}$ [eV] | $\Delta E_{b}$ [eV] |
|----------|----------------|----------------|----------------|-----------------|-----------------|----------------|
| 1D-PA    | 1.9            | 1.5            | 33.0           | 0.50            | 0.60            | 0.10           |
| 3D-PA    | 3.0            | 2.6            | 33.0           | 0.13            | 0.15            | 0.02           |
| 2A       | 2.8            | 3.8            | 4.9            | 0.90            | 1.30            | 0.40           |
| 3A       | 3.1            | 4.1            | 6.3            | 0.70            | 1.00            | 0.30           |
| 2P       | 3.1            | 3.5            | 4.6            | 0.74            | 1.02            | 0.28           |

Clearly, one observes an $N^2$ scaling for the time evolution scheme where the cross-over with the $N^3$ behavior of the diagonalization scheme already takes place at a moderate matrix size of around 2000. We note that the time evolution scheme allows for well-converged spectra at reasonable computational effort and the matrix multiplications necessary for the integration of Eq. (8) makes efficient parallelization of the code possible.

We have benchmarked our approach with bulk Si using a $8 \times 8 \times 8$ $k$ mesh, 4 valence and 15 conduction states. Thus a matrix size of $\approx 60000$ was sufficient in order to obtain converged spectra for the loss function. As has already been noted earlier [18] the inclusion of the resonant-antiresonant coupling terms $C$ has negligible effects on the optical spectra. We note that going beyond the TDA reduces the static dielectric constant of Si by only 3.5%. On the other hand, taking into account the full matrix structure of the BSE has sizable effects on the electron loss function thereby improving the experimental agreement [18].

Bulk Si exhibits a high dielectric constant and therefore an efficient screening of electron-hole interactions. Hence, the coupling matrices $C$ are small compared to the diagonal terms, which are in the order of $E_g$, and the effect on the optical absorption spectra remains marginal. On the contrary, one can expect the resonant-antiresonant coupling to play a significant role in the excited state properties of organic semiconductors since exciton binding energies are in the range of 10–20% of the band gap [23]. We have chosen five prototypical organic semiconductors that cover the range from a three-dimensional arrangement of polymer chains with efficient electron-hole screening to molecular crystals consisting of short oligomers where the electron-hole wave function is spatially well-confined. While for the former the exciton binding energies are comparably small and hence effects of resonant-antiresonant coupling, the latter exhibits large excitonic effects and enhancements of excitonic effects by going beyond the TDA are expected to be strongest. Fig. 2 displays the imaginary part of the dielectric function for these five prototypical organic semiconductors using (i) the RPA, (ii) the TDA-BSE and (iii) the full BSE. Panel (a) and (b), respectively, display spectra for an isolated chain of trans-polyacetylene (1D-PA) and a three-dimensional arrangement of PA chains (3D-PA) while panels (c)–(e) show the results for molecular crystals consisting of small organic molecules, namely naphthalene (2A), anthracene (3A) as well as biphenyl (2P). The exciton BEs calculated within the TDA of the above mentioned organic semiconductors are in the range between 0.13 and 0.9 eV [23] as summarized in Table I.

Due to the structure of the full BSE matrix given in Eq. (1) we can expect the coupling matrices to enhance excitonic effects, i.e. shift oscillator strengths towards lower energy or increase the exciton binding energies. This trend is indeed confirmed by our results. For the polymer, both the 1D as well as the 3D case, the effect of the TDA is moderate. Inclusion of the coupling matrices increases the BE from 0.5 to 0.6 eV for the 1D
case while it is only 0.02 eV for the 3D arrangement of polymer chains. For the molecular crystals, on the other hand, we find a substantial enhancement of the exciton BE when going beyond the TDA. In naphthalene (2A), the shortest oligomer under study, the BE increases by 0.4 eV. We emphasize that the resulting BE of 1.3 eV is in much better agreement with experimental values than the previous TDA result \[17\]. When increasing the length of the molecule, that is going from 2A to 3A, the exciton BE decreases due to an enhanced screening of the electron-hole interaction. This results in a TDA value of 0.7 eV while the full BSE calculation gives 1.0 eV. Note that in the case of 3A both theoretical results are within the large experimental error bars. A compilation of the present results for the oligoacene series together with previous TDA results \[17\] as well as corresponding experimental data is given in in Fig. 3. The decrease of the exciton BE with increasing chain length reduces the resonant-antiresonant coupling effect. Hence, we expect an improvement of the experimental agreement also for tetracene (4A) and pentacene (5A), molecular crystals which are intermediate cases between the strongly localized situation of short molecules and the polymers.

In summary, we have found that the TDA does no longer hold in cases where the exciton BE is large compared to the band gap and screening of the electron-hole interaction is inefficient. Hence, the impact of resonant-antiresonant coupling on the exciton binding energy is most pronounced for molecular crystals consisting of short molecules for which we find an increase of up to 0.4 eV (44 %) in the exciton binding energy. We have utilized the numerically efficient time-evolution scheme for solving the full BSE matrix including the coupling between positive and negative frequencies. This approach avoids problems due to the non-Hermiticity of the full BSE matrix and at the same time allows for well converged spectra and efficient parallelization of the code, where we have found a \(N^2\) scaling of the CPU time with matrix size \(N\). The present results should also prove valuable in the search for kernels to be used within time-dependent density functional theory (TDDFT) that are capable of accounting for excitonic effects. In the past, only TDA-BSE results have been used to derive \(ab\)-\(initio\) linear response exchange-correlation kernels for TDDFT \[24, 26\]. By demonstrating that the TDA substantially underestimates excitonic effects in organic semiconductors we also expect implications of our findings on the novel developments in the field of TDDFT.

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