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Communication: A hybrid Bethe–Salpeter/time-dependent density-functional-theory approach for excitation energies

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A hybrid Bethe–Salpeter/time-dependent density-functional-theory method is described that aims at improving the performance of the *GW*/Bethe–Salpeter-equation (*GW*/BSE) method in general and for excited triplet states in particular. The static screened exchange *W* used in the BSE is combined with the correlation kernel of the underlying density functional in a manner that retains a proven feature of the BSE, that is, the correct description of charge–transfer excitations. The performance of the new method, labeled cBSE, is assessed using G_0W_0 or evGW quasiparticle energies, and an improved performance is observed. The cBSE approach shows nearly equal performance for excited singlet and triplet states, rivaling coupled-cluster theory (in the CC2 approximation) in accuracy at a computational cost that is at least one order of magnitude smaller. *Published by AIP Publishing.*
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I. INTRODUCTION

Calculating molecular excitation spectra using the Bethe–Salpeter equation (BSE) has become increasingly popular due to its ability of reliably predicting charge–transfer (CT) states.[1–6] Time-dependent density-functional theory (TD-DFT) lacks this ability although efforts to improve the description of CT states by using long-range-corrected functionals (e.g., ωB97,[7] LC-ωPBE08[8]) or Coulomb-attenuated functionals (e.g., CAM-B3LYP[9]) have been undertaken. Most approaches are based on adding large amounts of Hartree-Fock exchange for longer distances, which shifts the spurious low energy CT states to higher energy, but at the price of decreased performance for other excited states.[10] In contrast to this, the BSE treats CT excitations on the same footing as all other excitations, naturally including them without a loss in accuracy for the rest of the spectrum. Rather than starting from DFT orbital energy differences ($\varepsilon_a^{\text{KS}} - \varepsilon_i^{\text{KS}}$), the BSE starts from quasiparticle energies ($\varepsilon_a^{\text{QP}} - \varepsilon_i^{\text{QP}}$), which are usually obtained from the *GW* method,[11,12] leading to a method known as *GW*/BSE.

Unfortunately, various benchmark studies of the *GW*/BSE method have shown that the description of excited triplet states is insufficient.[3,12–14] Using either a Hartree–Fock reference or the Tamm–Dancoff approximation improves the triplet energies, however at the price of deteriorating the singlet energies. Although one could argue that singlet and triplet excitations could be calculated at separate levels, this may not always be possible. For example, in spin-unrestricted TD-DFT or *GW*/BSE calculations, the $m_s = 0$ component of the triplet state is automatically included. For a generalized Kohn–Sham or Hartree–Fock reference determinant with complex-valued orbitals or spinors, as they occur in two-component quasirelativistic calculations or calculations in strong magnetic fields, spin is no longer conserved and separate calculations of different spin states are no longer possible. The inability of the *GW*/BSE method to reliably treat non-spin-conserving excitations may therefore significantly cripple its applicability in such cases. Although also the TD-DFT method shows deficiencies with respect to triplet states, we will show in the present work that a hybrid BSE/TD-DFT approach can be very successful in treating singlet and triplet excitations simultaneously at the same level of accuracy. We will label the new method cBSE, as it can be viewed as a correlation-kernel-augmented BSE model.

II. cBSE APPROACH

The basic idea of the present work is to combine the advantages of the BSE and TD-DFT methods to construct an exchange–correlation kernel f^{xc}. In computational solid-state physics, where TD-DFT is not as successful as in chemistry due to the inability to describe bound excitonic states, the construction of approximations to f^{xc} from the BSE is a well-known task.[15–17]

The formalism of the BSE for obtaining (optical) properties has been described thoroughly in the literature.[6,18–20] At the BSE level, the excitation energies are obtained as roots of a general Hermitian eigenvalue problem with dimension $2n_{\text{occ}}n_{\text{vir}}$,

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{X}_n \\ \mathbf{Y}_n \end{pmatrix} = \omega_n \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} \begin{pmatrix} \mathbf{X}_n \\ \mathbf{Y}_n \end{pmatrix}, \qquad (1)$$

where the matrices $\mathbf{A}$ and $\mathbf{B}$ are given by

$$\begin{aligned} A_{ia,jb} &= (\varepsilon_a^{\text{QP}} - \varepsilon_i^{\text{QP}})\delta_{ij}\delta_{ab} + v_{ia,jb} - W_{ij,ab}^{\text{QP}}, \\ B_{ia,jb} &= v_{ia,bj} - W_{ib,aj}^{\text{QP}}, \end{aligned} \qquad (2)$$

where $v_{ia,jb} = (ia|bj)$ is a standard Coulomb integral and where matrix elements of $\mathbf{W}^{\text{QP}}$ are defined as

$$W_{pq,rs}^{QP} = \sum_{\kappa\lambda} R_{pq,\kappa}(\epsilon_{QP}^{-1})_{\kappa\lambda}R_{\lambda,rs}^* . \tag{3}$$

In the above equation, the subscript "QP" on ϵ_{QP}^{-1} indicates that the inverse dielectric function is built from quasiparticle energies. A spin-orbital formalism is used and the indices $i, j, \ldots$ refer to occupied, $a, b, \ldots$ refer to virtual, and $p, q, r, s,$ $\ldots$ refer to arbitrary spin orbitals. Greek letters $\kappa, \lambda, \ldots$ refer to the auxiliary basis used.[20]

The general structure of the BSE matrix eigenvalue problem is the same as for TD-DFT. Therefore, it is a simple exercise to combine the two. We have done so by choosing **A** and **B** in the following manner:

$$
\begin{aligned}
A_{ia,jb} &= (\epsilon_a^{QP} - \epsilon_i^{QP})\delta_{ij}\delta_{ab} + v_{ia,jb} + f_{ia,jb}^c - W_{ij,ab}^{KS}, \\
B_{ia,jb} &= v_{ia,bj} + f_{ia,bj}^c - W_{ib,aj}^{KS} .
\end{aligned}
\tag{4}
$$

Note that quasiparticle energies are used for the diagonal of **A**, whereas Kohn–Sham orbital energies are used for the construction of the screened exchange $\mathbf{W}^{KS}$. Our rationale for suggesting Eq. (4) is as follows:

(a) In the asymptotic limit, a charge-transfer excitation corresponds to removing an electron from a hole site and adding it to a particle site, and the excitation energy corresponds to the difference of GW quasiparticle energies when the distance between the hole and the particle tends to infinity.

(b) The improvement of triplet states due to the Tamm–Dancoff approximation hints at missing correlation at the BSE level.[13] For triplets, the Coulomb integrals v do not contribute, leaving the screened exchange W as the only contribution besides the difference of GW quasiparticle energies. Coupling of **A** with **B** leads to overscreening and yields too low excitation energies. The correlation kernel $\mathbf{f}^c$ is considered to be a good approximation to the correction needed to include correlation.

(c) The G_0W_0 model relies on W_0 constructed from a Kohn–Sham reference to be sufficiently close to the true W that would be obtained from a fully self-consistent treatment of Hedin's equations. We therefore take $\mathbf{W}^{KS} = (\mathbf{1} - \mathbf{v}\chi_0^{KS})^{-1}\mathbf{v}$ for the exchange part of the exchange–correlation kernel.

III. RESULTS

The computations were performed with a modified version of the TURBOMOLE program package.[21] Computational details (basis sets, functionals, thresholds, etc.) are identical to those given in Ref. 12 and need not be repeated here.

A. Performance assessment of the cBSE approach with the Thiel test set

To evaluate the performance of the cBSE ansatz in a non-relativistic environment, we have carried out calculations on the Thiel test set.[22–24] The methodology is the same as in Ref. 12 and the GW/BSE energies reported in the present work are the same as in Ref. 12. Only the GW/cBSE values are new.

TABLE I. Deviations of triplet excitation energies (eV) obtained in the def2-TZVP basis with respect to the CC3/aug-cc-pVTZ reference. The PBE0 functional was used.

			G_0W_0		evGW	
	PBE0	CC2	BSE	cBSE	BSE	cBSE
Mean	−0.48	0.17	−1.14	−0.70	−0.56	−0.09
Mean abs.	0.48	0.18	1.14	0.70	0.56	0.14
RMS	0.53	0.22	1.16	0.74	0.60	0.23
Std. dev.	0.23	0.13	0.21	0.24	0.22	0.21
Max. abs.	0.97	0.53	1.66	1.52	1.05	0.87
Median abs.	0.47	0.15	1.12	0.65	0.54	0.07

Table I shows that the triplets are significantly improved by adding the correlation part of the underlying DFT functional. Especially evGW/cBSE now yields very good triplet excitation energies, without the singlet excitation energies being deteriorated significantly (Table II). Careful inspection of the excitation energies in the supplementary material reveals that the $+\mathbf{f}^c$ correction indeed specifically targets the triplets, indicating that the proper terms are included in the scheme. For example, for ethene/E-butadiene/E-hexatriene, the first triplet excitation is shifted by +0.76/+0.72/+0.70 eV while the first singlet excitations are shifted by +0.15/+0.08/+0.08 eV. Also the G_0W_0 starting point sees an overall improvement from the hybrid cBSE scheme. Figure 1 shows the spread of errors of the G_0W_0/cBSE and evGW/cBSE excitation energies with respect to the CC3 reference values. The cBSE approach significantly lowers the gap between the singlet (blue circles) and triplet (red crosses) excitation energies such that the average error of the triplet excitations is much closer to that of the singlet excitations than in the standard BSE method (see Ref. 12).

It seems that certain triplet outliers have not been corrected (Fig. 1). These are mainly high-lying $\pi - \pi^*$ transitions of benzene, naphthalene, pyridine, and s-tetrazine. For these outliers, the evGW/cBSE excitation energies are in between the evGW/BSE and TD-DFT excitation energies (see Tables S1 and S2 of the supplementary material), which is the case for only six out of 63 excitations, all six located in these four molecules covering all errors larger than 0.5 eV. For all other triplet excitation energies, the cBSE results are higher than the TD-DFT and BSE excitation energies. We therefore suspect that the reason for failure of these excitations is

TABLE II. Deviations of singlet excitation energies (eV) obtained in the def2-TZVP basis with respect to the CC3/aug-cc-pVTZ reference. The PBE0 functional was used.

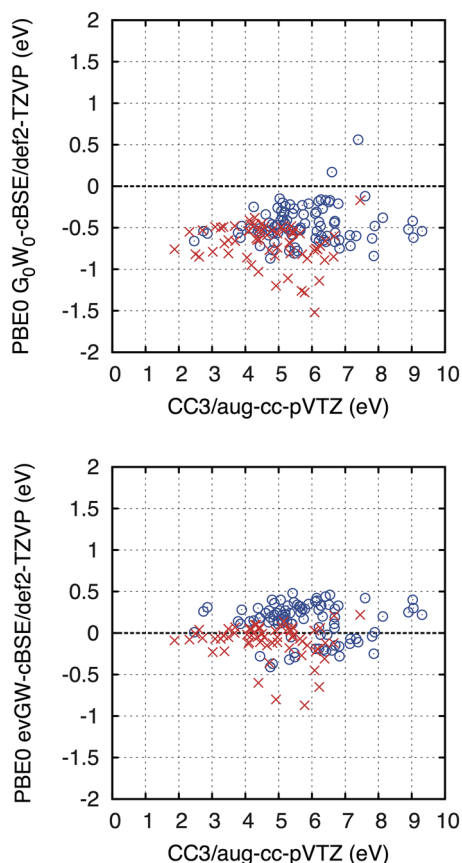|			G_0W_0		evGW	
	PBE0	CC2	BSE	cBSE	BSE	cBSE
Mean	−0.06	0.14	−0.63	−0.46	−0.02	0.14
Mean abs.	0.21	0.17	0.63	0.48	0.16	0.23
RMS	0.27	0.23	0.66	0.51	0.21	0.26
Std. dev.	0.26	0.18	0.21	0.22	0.21	0.22
Max. abs.	0.68	0.92	0.97	0.87	0.48	0.48
Median abs.	0.15	0.14	0.70	0.51	0.12	0.24

FIG. 1. Plot of the computed singlet and triplet excitation energies against the reference CC3/aug-cc-pVTZ values.

different from the general reason for failure of BSE in predicting triplet excitation energies.

The general behavior of singlet excitation energies is not altered by cBSE as seen in Fig. 1. Comparing root-mean-square (RMS) and standard deviations in Table II, cBSE performs very similar to BSE for both *GW* references. Overall the excitation energies are slightly shifted to higher values, but only by a fraction of the shift of triplet excitation energies.

Overall, the performance of ev*GW*/cBSE is en par with CC2, which is quite a respectable result given that cBSE scales at least one order of magnitude better than CC2.

Table III reports the deviations of the $S_1 - T_1$ splittings from the CC3/aug-cc-pVTZ reference values. In comparison with TD-DFT and BSE, the cBSE deviations are reduced by

TABLE III. Deviations of $S_1 - T_1$ splittings (eV) obtained in the def2-TZVP basis with respect to the CC3/aug-cc-pVTZ reference. The PBE0 functional was used.

			G_0W_0		ev*GW*	
	PBE0	CC2	BSE	cBSE	BSE	cBSE
Mean	0.46	0.04	0.48	0.09	0.48	0.12
Mean abs.	0.46	0.10	0.48	0.20	0.48	0.22
RMS	0.50	0.13	0.51	0.24	0.51	0.25
Std. dev.	0.21	0.13	0.17	0.23	0.19	0.22
Max. abs.	0.98	0.33	0.85	0.37	0.82	0.39
Median abs.	0.37	0.05	0.43	0.08	0.41	0.22

TABLE IV. Deviations of singlet and triplet excitation energies (eV) obtained at the cBSE/aug-cc-pVTZ level with respect to the CC3/aug-cc-pVTZ reference values. The PBE0 functional was used.

	G_0W_0		ev*GW*	
	Singlet	Triplet	Singlet	Triplet
Mean	−0.59	−0.81	−0.09	−0.35
Mean abs.	0.62	0.82	0.20	0.35
RMS	0.66	0.86	0.26	0.46
Std. dev.	0.29	0.29	0.24	0.30
Max. abs.	1.41	1.39	0.76	1.48
Median abs.	0.61	0.79	0.19	0.27

a factor of roughly two. Furthermore, the influence of the underlying *GW* model is small.

B. Diffuse basis sets within *GW*/cBSE

With the aug-cc-pVTZ basis set, the test results in Table IV are also promising. As expected,[6,12] the use of diffuse functions leads to slightly lower excitation energies in comparison with the def2-TZVP results in Tables I and II. The singlet excitation energies of ev*GW*/cBSE are in very good agreement with the CC3 reference results, and also the triplet excitation energies improve vastly compared to ev*GW*/BSE.[12]

One can, however, see a spike in the maximal absolute deviation in Table IV. Especially for acetamide and propanamide, too low excitation energies are obtained when the aug-cc-pVTZ basis set is used, in agreement with the findings of Bruneval *et al.*[6] In their work, they showed that this ill-behavior is caused by the presence of diffuse functions and not by the cc-pVTZ basis. This is an insufficiency of the underlying *GW* quasiparticle-energy calculation, which predicts the lowest unoccupied molecular orbital (LUMO) to be too low. This carries over to cBSE. cBSE and BSE rely on good quasiparticle energies and a failure of obtaining them will automatically be carried over to the excitation energies. The $S_1 - T_1$ splittings appear to be rather robust with respect to the basis set (Table S3).

C. Charge-transfer excitations within *GW*/cBSE

To validate the cBSE scheme for charge-transfer excitations, the ev*GW*/BSE values of Ref. 12 are compared to the new ev*GW*/cBSE values in Table V for the same systems as studied in Ref. 12. A trend following Λ, which is

TABLE V. Charge-transfer excitation energies (eV) and diagnostics Λ obtained in the def2-TZVP basis for ev*GW*/BSE and ev*GW*/cBSE. The PBE0 functional was used.

Molecule	State	BSE	cBSE	Λ
*p*NA	2^1A_1	4.47	4.50	0.61
DMABN (C_{2v})	2^1A_1	4.86	4.98	0.74
DMABN (C_s)	2^1A_1	4.80	4.92	0.75
B-TCNE	2^1A_1	3.45	3.44	0.20
PP	2^1B_2	5.18	5.27	0.63
	3^1A_1	5.92	5.89	0.24
HCl	$1^1\Pi$	7.66	7.82	0.51

an overlap criterion[25] of hole and particle natural transition orbitals, is observed. Especially for small values of Λ seen for the benzene$\cdots$tetracyanoethylene complex (B-TCNE) and for phenylpyrrole (PP), the BSE and cBSE results are virtually identical due to both converging to the same asymptotic limit. For larger values of Λ, cBSE exhibits the same trend as for standard singlet excitations in comparison with BSE. We therefore conclude that both BSE and cBSE treat CT excitations correctly and on the same footing.

IV. CONCLUSIONS

A hybrid BSE/TD-DFT approach labeled cBSE was proposed and its performance was tested on the Thiel set of small molecules. *GW*/cBSE removes most of the triplet weakness of the *GW*/BSE method without deteriorating the performance for singlet excitation energies. Compared to existing schemes such as range separation or Coulomb attenuation, the cBSE approach neither needs parameters to be fitted nor damping functions.

SUPPLEMENTARY MATERIAL

See supplementary material for the computed excitation energies (Tables S1 and S2) and for the statistics of the $S_1 - T_1$ splittings in the aug-cc-pVTZ basis set (Table S3).

ACKNOWLEDGMENTS

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