

Quasiparticle Self-Consistent GW-Bethe–Salpeter Equation Calculations for Large Chromophoric Systems

Arno Förster* and Lucas Visscher



Cite This: *J. Chem. Theory Comput.* 2022, 18, 6779–6793



Read Online

ACCESS |



Metrics & More

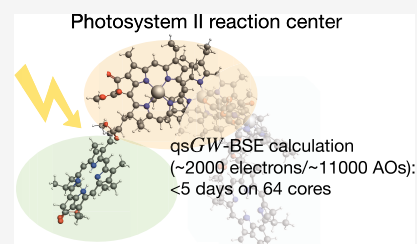


Article Recommendations



Supporting Information

ABSTRACT: The GW-Bethe–Salpeter equation (BSE) method is promising for calculating the low-lying excitonic states of molecular systems. However, so far it has only been applied to rather small molecules and in the commonly implemented diagonal approximations to the electronic self-energy, it depends on a mean-field starting point. We describe here an implementation of the self-consistent and starting-point-independent quasiparticle self-consistent (qsGW)-BSE approach, which is suitable for calculations on large molecules. We herein show that eigenvalue-only self-consistency can lead to an unfaithful description of some excitonic states for chlorophyll dimers while the qsGW-BSE vertical excitation energies (VEEs) are in excellent agreement with spectroscopic experiments for chlorophyll monomers and dimers measured in the gas phase. Furthermore, VEEs from time-dependent density functional theory calculations tend to disagree with experimental values and using different range-separated hybrid (RSH) kernels does change the VEEs by up to 0.5 eV. We use the new qsGW-BSE implementation to calculate the lowest excitation energies of the six chromophores of the photosystem II (PSII) reaction center (RC) with nearly 2000 correlated electrons. Using more than 11,000 (6000) basis functions, the calculation could be completed in less than 5 (2) days on a single modern compute node. In agreement with previous TD-DFT calculations using RSH kernels on models that also do not include environmental effects, our qsGW-BSE calculations only yield states with local characters in the low-energy spectrum of the hexameric complex. Earlier works with RSH kernels have demonstrated that the protein environment facilitates the experimentally observed interchromophoric charge transfer. Therefore, future research will need to combine correlation effects beyond TD-DFT with an explicit treatment of environmental electrostatics.



1. INTRODUCTION

The absorption of photons by a molecule or a material upon interactions with electric radiation is a key process in the conversion of light into chemical or electrical energy. In the photosystem II (PSII) reaction center (RC), photons are captured by chromophoric complexes, which then leads to the generation of free charge carriers.¹ In the first step of this process an electron–hole pair is formed, where electron and hole are bound due to their Coulombic interaction.² Such bound electron–hole states are commonly referred to as excitons and correspond to the energies of the absorbed photons.³ In the current work, we look at the characterization of such low-lying excited states of the RC of PSII, which is at the heart of photosynthetic function.⁴ As shown in Figure 1, the PSII RC contains six chromophores, a “special pair”,^{5,6} of two chlorophyll *a* (chl_a) molecules (P_{D1} and P_{D2}), flanked by two more chl_a (Chl_{D1} and Chl_{D2}), and two pheophytin *a* (Pheo_{D1} and Pheo_{D2}) molecules, with around 2000 electrons in total. By now, it has been firmly established that the primary events of charge separation in PSII are determined by a complex interplay of all these six chromophores.⁷ Therefore, all six chromophores should ideally be treated on a quantum mechanical level and their couplings need to be taken into account.

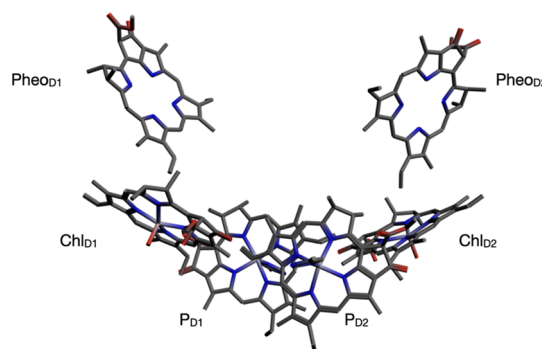
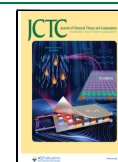


Figure 1. Chromophores of the photosystem II reaction center.

In most current calculations of larger biomolecular complexes, one resorts to Hartree–Fock (HF)^{8,9} or time-dependent (TD) density functional theory (DFT) with a

Received: May 20, 2022

Published: October 6, 2022



range-separated hybrid (RSH) exchange–correlation kernel.^{7,10–16} RSHs frequently offer good agreement with the experiment for Chla monomers and dimers,^{13,17,18} but large deviations with respect to more advanced multi-configurational^{18,19} and wave function-based methods have also been observed.²⁰ To mitigate such errors, RSHs can be parametrized empirically for each system under investigation (as done in refs 21 and 22), but this makes them non-transferable and unreliable for general applications. Systematic tuning procedures for range-separated functionals have been suggested as well.^{23–26} Those however always require to perform exploratory calculations to find the ideal range–separation parameter. Furthermore, heterogeneous systems like multi-chromophoric complexes might require different range separation parameters for different regions of the complex.²⁷

Turning to wave function-based methods for excited states, we find the second-order algebraic diagrammatic construction scheme [ADC(2)]^{28,29} and coupled cluster^{30–34} with approximate doubles (CC2)³⁵ easy to apply and reasonably cost-efficient. CC2 results are typically in good agreement with more involved methods like equation-of-motion (EOM) CC³⁶ with singles and doubles (EOM-CCSD) or similarity-transformed (ST) EOM^{37,38}-CCSD.^{39,40} For these methods, we are aware of one study of a tetrameric model by Suomivuori et al.⁴¹ using ADC(2) together with the spin-opposite-scaled⁴² and reduced-virtual-space (RVS)⁴³ approximations. Unfortunately, they did not include the pheophytin chromophores in their calculations, which are known to play a key role in the initial charge separation immediately after photoexcitation.^{14,44–46} This is potentially possible, but we note that most applications of wave function-based methods^{18,20,47,48} focus on single chromophores. Utilizing subsystem methods,^{49–55} the applicability of these methods can be extended. In this family of methods, one describes the full RC by an effective Hamiltonian with a limited amount of levels for each chromophore. The information needed to build such an effective Hamiltonian are the monomeric excitation energies as well as the inter-monomeric couplings. These parameters can be computed in a first-principles manner with various electronic structure methods.^{56–58} While the subsystem approach can be used with high-level monomer calculations, a drawback is that commonly used approximations to calculate the couplings between the chromophores are often not accurate enough.^{17,43,59} In the current work, we will therefore examine how large a system can be treated directly without having to resort to partitioning and subsystem methods. As the states of interest are the lowest energy ones, we thereby focus on a limited number of states but describe them in a supermolecular fashion that fully accounts for all intermolecular couplings of the chromophores.

Our approach is based on the GW-BSE method that we will briefly summarize in the following. We first note that energy levels of the excitonic states correspond to the poles of the 2-particle generalized susceptibility.^{60–62} This quantity can be obtained from the interacting single-particle Green's function G_1 and the electronic self-energy Σ , a non-local, non-Hermitian, and frequency-dependent one-electron operator, via a Bethe–Salpeter equation (BSE).^{63–65} G_1 is obtained from a Dyson equation with Σ as its kernel, while Σ itself depends implicitly on the 2-particle Green's function.^{65–67} As obtaining the full generalized susceptibility requires N^6 operations, it is advantageous to decouple the BSE from the Dyson equation for G_1 . This is done by using an approximation to the self-

energy, which only depends on the density–density response.^{68,69} A popular example is the GW approximation (GWA), with the screened Coulomb interaction W ^{70,71} calculated within the random phase approximation (RPA).⁷² Typically, the Dyson equation for G_1 is solved within the GWA first. Only afterward, the non-interacting 2-particle Green's function and the corresponding kernel in its zero-frequency limit are constructed and one solves for a few or all roots of the generalized susceptibility.^{73–75} If only a few excitonic states are needed, one may thereby use computationally efficient iterative diagonalization techniques.^{75,76} This procedure is known as the GW-BSE method and is increasingly applied to compute the lowest electronically excited states of molecular systems.^{55,58,77–106}

For such applications, the GW part is typically the computational bottleneck of a GW-BSE calculation.^{90,92,104} The issue has been addressed over the last years: many implementations of G_0W_0 and $evGW$ with reduced asymptotic scaling with system size have been developed^{107–117} often producing results in excellent agreement with conventional GW implementations.^{107,111,112} Another issue is related to the common approximations in solving the GW equations. Typical calculations start from a Kohn–Sham (KS)-DFT or HF Green's function followed by a perturbative update of the QP energies (G_0W_0).^{118,119} This procedure comes with the notable disadvantage that the outcome of such a calculation will heavily depend on the choice of the underlying exchange–correlation (XC) functional.^{84,120–123} Achieving self-consistency in the eigenvalues only ($evGW$) can remove this dependence on the initial density functional approximation to a large extent but not completely.^{90,104,124}

Instead, one can also start from the full GW self-energy and take the Hermitian part only to arrive at a set of effective single-particle equations.^{125,126} In QP self-consistent GW (qsGW), then only the low-frequency limit of the self-energy is considered,^{127–129} and the non-interacting G_1 closest to the GW G_1 is selected.¹³⁰ While this approach has been shown to be more accurate than G_0W_0 and $evGW$ for a wide range of molecular systems,¹³¹ qsGW has until now rarely been used in molecular calculations. With only a few exceptions,^{132,133} low-order scaling GW algorithms only target the screened Coulomb interaction. This is a reasonable choice if one only wishes to calculate the diagonal elements of the self-energy. The computational cost for obtaining the full self-energy is however much larger, and most implementations therefore become inefficient if the full self-energy is required. To address this issue, we have recently presented a low-order scaling implementation of qsGW.¹³³ In the present work, we combine it with an efficient solver for the BSE, resulting in a fast, low-scaling, and starting-point independent implementation of the GW-BSE approach.

The GW-BSE method has recently been shown to reproduce experimental low-lying excitation energies of Chls with high accuracy.^{104,134} So far, it has only been applied to monomeric models of PSII. In this work, we will first give a brief account of the (low-scaling) implementation of the GW-BSE approach in Section 2. After describing some technical details of our calculations in Section 3, in Section 4 we first contrast qsGW-BSE to $evGW$ -BSE for single chromophores and chromophore dimers and confirm the excellent agreement of the former with experimental data. We then use the qsGW-BSE implementation to calculate the low-lying excitation of the hexameric

complex with 2000 correlated electrons in total. Finally, Section 5 summarizes and concludes this work.

2. THEORY

2.1. GW-BSE Formalism. The interacting n -particle Green's functions corresponding to an N -electron system with the ground state $\Psi_0^{(N)}$ are defined by

$$G_n(1, \dots, 2n) = (-i)^n \langle \Psi_0^{(N)} | T [\hat{\psi}^\dagger(1) \hat{\psi}(2) \dots \hat{\psi}^\dagger(2n-1) \hat{\psi}(2n)] | \Psi_0^{(N)} \rangle \quad (1)$$

Here, T is the time-ordering operator, $\hat{\psi}$ is the field operator, and a number $1 = (r_1, \sigma_1, t_1)$ collects space, spin-, and time indices. The relevant cases are $n = 1, 2$. For the $n = 2$ case, we further restrict ourselves to the excitonic part only with $t_3 = t_4$ and $t_1 = t_2$.

The single-particle Green's function can be related to its non-interacting counterpart $G_1^{(0)}$ by a Dyson equation

$$G_1(1,2) = G_1^{(0)}(1,2) + G_1^{(0)}(1,3) \Sigma(3,4) G_1(4,2) \quad (2)$$

in which the self-energy operator Σ appears.¹³⁵ In (2) and in the following, integration over repeated indices is implied. The reduced 2-particle Green's function

$$L(1,2,3,4) = -G_2(1,2,3,4) + G_1(1,2) G_1(3,4) \quad (3)$$

fulfills a BSE,^{62,136}

$$L(1,2,3,4) = L^{(0)}(1,2,3,4) + L^{(0)}(1,6,2,5) \frac{\delta \Sigma(5,7)}{\delta G_1(8,6)} L(8,2,7,4) \quad (4)$$

where¹³⁶

$$L^{(0)}(1,2,3,4) = G_1(1,4) G_1(2,3) \quad (5)$$

The local Hartree kernel is obtained by approximating Σ with the Hartree potential

$$\Sigma_H(1,2) = v_H(1) \delta(1,2) = -i \delta(1,2) \int d^3v_c(1,3) G_1(3, 3^+) \quad (6)$$

where v_c is the Coulomb potential and $1^+ = \lim_{\eta \rightarrow 0^+} (\mathbf{r}_1, \sigma_1, t_1 + \eta)$. Calculating

$$\frac{\delta}{\delta G_1(4,2)} \int d^3v_c(1,3) G_1(3, 3^+) = v_c(1,2) \delta(3,4) \delta(3,2) \quad (7)$$

and inserting the result into (4) one then obtains

$$P(1,2) = P^{(0)}(1,2) + P^{(0)}(1,3) v_c(3,4) P(4,2) \quad (8)$$

with

$$P(1,2) = L(1, 2^+, 1^+, 2) \quad (9)$$

being the v_c -reducible density–density response function in the RPA and

$$P^{(0)}(1,2) = -i G(1,2) G(2, 1^+) \quad (10)$$

P is related to the screened Coulomb interaction W by⁷⁰

$$W(1,2) = v_c(1,2) + v_c(1,3) P(3,4) v_c(4,2) \quad (11)$$

which can be used to define the GW self-energy

$$\Sigma^{(GW)}(1,2) = v_H(1,2) + i G(1,2) W(1^+, 2) \quad (12)$$

Equations 2, 8, and 10–12 constitute a self-consistent set of equations, usually referred to as the GW-approximation.

By splitting the self-energy into Hermitian and anti-Hermitian part and discarding the latter one, we can restrict the solution of (2) to its QP part only.^{125,126,137,138} We then have an effective single-particle problem and restricting the self-energy further to its static limit and transforming into the molecular orbital basis $\{\phi_n\}_{n=1 \dots N}$ (in which the single-particle Hamiltonian is diagonal), we arrive at

$$\sum_m \left\{ (e_n - e_n^{\text{QP}}) \delta_{nm} + \frac{1}{2} [\Sigma_{nm}^{(GW)}(e_n) + \Sigma_{nm}^{(GW)*}(e_n)] \right\} \phi_n = 0 \quad (13)$$

where the e_n are the single-particle energies. Solving eqs 8 and 10–13 self-consistently is known as the qsGW approximation within the RPA.^{127–129}

After solving the qsGW equations self-consistently, we can then use the zero-frequency limit of the self-energy (12) for the kernel of (4). As it is typically done, we also set $\delta W / \delta G \approx 0$. This is referred to as the qsGW-BSE approach. After Laplace transformation to the complex frequency plane, eq 4 can be transformed into an eigenproblem in a basis of particle-hole states whose solution provides the Lehmann representation of L (see refs 139 or 140 for detailed derivations)

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}_S = \Omega_S \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}_S \quad (14)$$

Ω_S is a neutral excitation energy, $(\mathbf{X}, \mathbf{Y})_S^T$ contains the expansion coefficients of the corresponding eigenvector and for a closed-shell system the matrix elements of \mathbf{A} and \mathbf{B} are, respectively, defined as

$$A_{ia,jb} = 2v_{c_{iab}} - W(\omega = 0)_{ijab} + \delta_{ab} \delta_{ij} (e_i^{\text{QP}} - e_a^{\text{QP}}) \\ B_{ia,jb} = 2v_{c_{ajb}} - W(\omega = 0)_{ajbi} \quad (15)$$

where we have chosen to reserve the labels i, j, \dots for occupied and a, b, \dots for virtual orbitals. The QP energies entering the equations are the ones from (13).

2.2. Implementation. For our implementation of the qsGW methods, we refer to our previous work.^{110,133,141} We expand single-particle Green's functions and the self-energy in a basis of Slater type functions (primary basis) which is related to the MOs by

$$\phi_i(\mathbf{r}) = \sum_{\mu} c_{i\mu} \chi_{\mu}(\mathbf{r}) \quad (16)$$

while all quantities appearing in (11) are expanded in a basis of auxiliary fit functions (auxiliary basis). We then switch to the particle-hole basis to solve (14), whereby the matrix elements in (15) are expanded in the basis of MOs.

Because we do not use the screened interaction at zero frequency in our GW implementation, we calculate the zero-frequency component of P from the imaginary time representation of the polarizability by

$$P(\omega = 0) = \frac{1}{2\pi} \int P(i\tau) d\tau \quad (17)$$

and we then use (11) to obtain $W(\omega = 0)$.

Replacing the matrix elements of the screened Coulomb interaction by the bare ones in (15), and using the HF self-energy in (13), the TD-HF method is obtained. It is clear that any solver which can be used to solve (14) in the TD-HF case

can also be used for *GW*-BSE. We use an extension of the Davidson algorithm¹⁴² originally proposed by Stratmann and Scuseria.⁷⁶ It solves (4) by projecting the generalized problem

$$(\mathbf{A} - \mathbf{B})(\mathbf{A} + \mathbf{B})(\mathbf{X} + \mathbf{Y}) = \Omega_S^2(\mathbf{X} + \mathbf{Y}) \quad (18)$$

on a sequence of orthonormal subspaces

$$\text{span}\{b_1^{(n)}, \dots, b_k^{(n)}\} \quad (19)$$

in which (18) is solved. k denotes the size of the n th subspace and the b_k are linear combinations of particle-hole states. The vectors forming the subspace are then updated until the subspaces are converged. The procedure can be interpreted as an iterative optimization of the basis of particle-hole states, where the part which does not carry useful information (i.e., the particle-hole transitions which do not contribute to the low-lying excitons) is projected out.

The time-determining step in the diagonalization is the projection of the eigenproblem in the full space on the subspaces. The term containing the bare Coulomb potential is easily evaluated following the procedure in ref 143. For the matrix elements of the screened interaction in the $(n + 1)$ th subspace iteration, we define a column in the subspace labeled by $s_{ij}, s_{jp}, \dots, s_{ai}, s_{bi}, \dots$, respectively, as

$$(\mathbf{A} \pm \mathbf{B})_{s_{ij} s_{ai}}^{(n+1)} = \sum_{s_{ij} s_{bi}} \{-W(\omega = 0)_{s_{ij} s_{bi}}^{(n)} \mp W(\omega = 0)_{s_{ai} s_{bi}}^{(n)}\} b_{s_{ai}}^{(n)} \quad (20)$$

In the minus case, this is equivalent to the evaluation of the greater or lesser component of self-energy for a single imaginary time point. In the plus case, a similar algorithm can be used, but the resulting matrix needs to be antisymmetrized. We solve (20) in the basis of Slater functions and then transform to the basis which spans the subspace. For detailed working equations, we refer to Appendix B.

A key element in our approach is to use pair-atomic density fitting (PADF)^{110,144–148} to calculate the transformation from auxiliary basis to primary basis and back. In PADF, all the coefficients in the transformation matrix corresponding to auxiliary functions, which are not centered on the same atoms as the primary basis functions are restricted to zero. While making the resulting basis transformation very efficient this also is an approximation which does not necessarily conserve important properties of the original matrices, like, for example, positive definiteness of the Coulomb potential.¹⁴⁷ These deficiencies can always be traced back to products of diffuse Slater functions, which are difficult to expand in the auxiliary basis. To overcome these issues, we introduce a projection technique to remove problematic linear dependencies from the matrices appearing in eq 20. This projection technique is described in Appendix C.

3. COMPUTATIONAL DETAILS

All calculations have been performed with a locally modified development version of ADF2022.1^{149,150} The *GW* implementation is the same as outlined in refs 110133141, except for the modification outlined in Appendix C.

For the hexameric unit of PSII, we used the structure of ref 16, which has therein been optimized at the PBE level of theory taking into account environmental effects using a QM/MM approach. Dimer structures have been optimized in this work using CAM-B3LYP-D3(BJ), a triple- ζ + polarization (TZP)¹⁵¹ basis set, and *Good* numerical quality. The monomer

structures used in Sections 4.1 and 4.2 are taken from the structure published in ref 12 based on the experimental structure at 1.9 Å resolution by Umena et al.¹⁵² and where the positions of the hydrogen atoms have been optimized using a semi-empirical model with all other coordinates frozen. All structures used in this work can be found in the Supporting Information.

We also benchmarked the basis set dependence of the *GW*-BSE calculations using the larger TZ3P and QZ6P basis sets¹⁴¹ for Chla monomers in Section 4.2. All qs*GW*-BSE results shown there have been obtained with the *veryGood* auxiliary basis. This allows us to reliably compare excitation energies obtained with different primary basis sets. TZ3P and QZ6P contain *f*-functions for second-row atoms and for such basis sets, the *Good* auxiliary fit set is generally insufficient. For monomers, we calculate the lowest 6 eigenstates of (18).

For chromophore dimers, we calculated the lowest 6 eigenstates of (18), using TZP (triple- ζ + polarization)¹⁵¹ as the primary basis set, *Good* numerical quality, and 16 imaginary time and frequency points each. In all calculations for monomers and dimers, we terminate the sequence of subspace iterations if all eigenvalues are converged within 10^{-5} Ha (0.27 meV).

In the *GW*-BSE calculations of the excited states of the hexamer, we used the TZP basis set, *Basic* numerical quality, and 12 imaginary time and frequency points each. We restrict the basis, in which we solve the BSE to the subspace spanned by all particle-hole pairs with transition energies below 1.5 Ha. In agreement with earlier *GW*-BSE studies for such systems,⁸⁰ we found this approximation to change the low-lying excitation energies by only around 10–20 meV compared to calculations including all particle-hole pairs.¹⁵³ This improves numerical stability of our algorithm and accelerates the convergence of the subspace iterations in the Davidson algorithm. We perform 8 subspace iterations in the Davidson algorithm and calculate the 24 lowest eigenstates of (18). This is sufficient to converge the low-lying excited states to within less than 5 meV. We also calculated the low-lying excited states of the same system using TD-DFT with the ω B97-X kernel using the same numerical settings. However, in contrast to our *GW*-BSE calculations, we calculated the 12 lowest states and converged all eigenvalues to within 10^{-6} Ha.

In all calculations, we took into account scalar relativistic effects in the zeroth-order regular approximation.^{154–156} The threshold ϵ_s , described in Appendix C has been set to 5×10^{-3} . Also, in all KS calculations, we set the threshold for the Löwdin orthogonalization to 5×10^{-3} . If not stated otherwise, in all qs*GW* calculations, we first perform a PBE0 calculation with 40% exact exchange (PBEH40), which is a good preconditioner for qs*GW* and leads to fast convergence.¹⁵⁷ Aside from numerical inaccuracies, the final results are independent of this choice, which we have verified in ref 133 and which we will verify also for the case of Chla in the next section. For qs*GW*, we terminate the calculations when the Frobenius norm of the difference between the density matrices of two subsequent iterations falls below 5×10^{-9} .¹³³ We also performed ev*GW*-BSE calculations based on the LDA and PBEH40 functionals (ev*GW*@LDA, ev*GW*@PBEH40). We terminate the ev*GW* calculations if the HOMO QP energy difference between two subsequent iterations falls below 3 meV.

To compare our method to the RSH TD-DFT approach, we also performed calculations using the CAMY-B3LYP and ω B97-X kernels using the TZP basis set and *Good* numerical

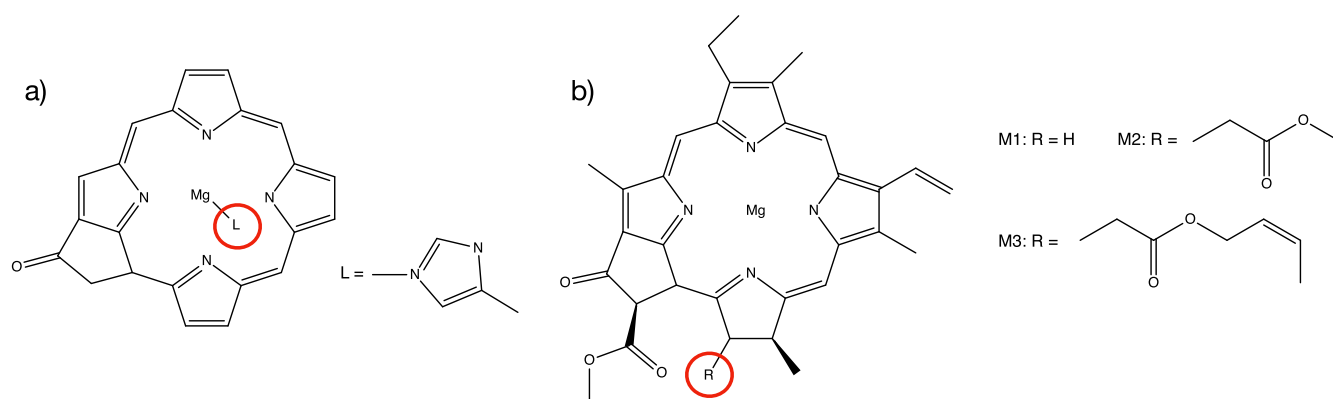


Figure 2. Different models of Chl a used in this work: (a) model used by Suomivuori et al.⁴¹ with ligating histidine residue. (b) Models without histidine residue but containing all ligands at the chlorin core and different models for the phytyl chain (M1, M2, and M3, respectively).

Table 1. HOMO–LUMO Gap, Value of the Q_y Excitation for Different Starting Points, Number of Iterations Until Convergence and Time per GW Iteration, Measured in Core Hours, for qsGW and evGW^a

	evGW				qsGW			
	gap	Q_y [eV]	n_i	t [h]	gap	Q_y [eV]	n_i	t [h]
LDA	4.405	1.764	9	5.67	4.499	1.752	9	5.79
PBE	4.417	1.837	9		4.501	1.745	10	
PBEH40	4.476	1.772	7		4.493	1.760	8	
HF	4.671	1.766	9		4.496	1.753	9	

^aCalculations were performed on a 2.2 GHz intel Xeon (E5-2650 v4) node (broadwell architecture) with 24 cores and 128 GB RAM.

Table 2. VEEs for M1 and M2 with Different Basis Sets for qsGW-BSE and evGW@LDA-BSE^a

	evGW@LDA-BSE						qsGW-BSE					
	M1			M2			M1			M2		
	Q_y	Q_x	B	Q_y	Q_x	B	Q_y	Q_x	B	Q_y	Q_x	B
TZP	1.74	1.93	2.68	1.76	1.94	2.71	1.72	1.98	2.84	1.74	2.00	2.86
TZ3P	1.77	1.96	2.72	1.79	1.98	2.76	1.72	1.98	2.84	1.73	1.97	2.84
QZ6P	1.71	1.94	2.64	1.74	1.92	2.68	1.71	1.96	2.80	1.71	1.96	2.84
Δ_{TQ}	0.03	-0.01	0.04	0.02	0.02	0.03	0.01	0.02	0.04	0.03	0.04	0.02

^aThe values in the last row denote the differences in VEEs calculated with the TZP¹⁵¹ and QZ6P¹⁴¹ basis sets. All values are in eV.

quality. We also calculated the electrochromatic shifts due to the presence of the protein environment using the conductor-like screening model (COSMO),^{158–160} as implemented in ADF.¹⁶¹ these results are shown in Appendix A. Following ref 41, we set the dielectric constant of the environment to a value of 4.0 in these calculations, which should approximately account for solvent and protein environments.

4. RESULTS

4.1. Starting-Point Dependence of GW-BSE Calculations. As discussed in the introduction, its starting point independence is a major advantage of qsGW over evGW. To verify the starting point independence of our implementation, we report here vertical excitation energies (VEEs) for qsGW and evGW for the M2 model in Figure 2b with 82 atoms in total for the LDA, PBE, PBEH40, and HF starting points. We thereby use a tighter convergence criterion of 1 meV for the HOMO QP energy for evGW than the default value. The results for the Q_y excitation are shown in Table 1. The qsGW calculations converge to the same HOMO–LUMO gap within an accuracy of 10 meV within less than 10 iterations. This also results in Q_y excitation energies, which are converged within 10 meV. The remaining differences are due to numerical noise in

the imaginary frequency and time grids used in the GW calculations, which then translates into uncertainties in the analytical continuation of the self-energy to the complex plane.^{111,141} The differences in the HOMO–LUMO gaps of the evGW calculations are much larger and differ by almost 300 meV between evGW@LDA and evGW@HF, which results in Q_y excitation energies differing by about 80 meV. This is the most extreme case, for starting points other than HF there are only very small differences between the different evGW results. This has already been observed in ref 104. Because the computational overhead of a qsGW calculation is negligible compared to evGW (5.79 vs 5.67 core hours per iteration) and the number of iterations needed for convergence is essentially the same, there is little advantage to be gained by using evGW instead of the more robust qsGW approach.

4.2. Basis Set Errors. Next, we investigate the dependence of the Q_y excitation energy on the basis set size. For GW calculations, it is well known that individual QP energies converge slowly with respect of the size of the single-particle basis. In practice, extrapolation techniques are needed to obtain converged results.^{162–164} For QP energy differences, which are entering the BSE, the situation is much better because the basis set error for the QP energies usually have the

same sign.¹⁶³ In Table 2, we compare the lowest excitation energies calculated with different basis sets for the two different Chla models M1 and M2 shown in Figure 2b). For evGW and qsGW, the QZ6P VEEs are only slightly lower than the TZP ones, indicating that they are almost converged also with the smaller basis set. These errors are certainly smaller than other possible sources of error in our calculations like shortcomings of GW-BSE or uncertainties in structural parameters. Therefore, to a very good approximation, we can ignore the basis set incompleteness error in all of the following TZP calculations.

4.3. Comparison to Experiments and Different Ab-initio Calculations. **4.3.1. Monomers.** Next, we assess the accuracy of qsGW-BSE by comparison to experimental gas-phase data for Chla by Gruber et al.¹⁶⁵ In Table 3, we directly

Table 3. VEEs for Chla Calculated with Different Quantum Chemical Methods for Two Different Gas-Phase-Optimized Structures and Experimental Reference Data^a

	Q_y	Q_x	B	$\Delta_{Q_y-Q_x}$
exp. (VEE)	1.99	2.30	3.12	0.31
exp. (band max)	1.94	2.23	3.08	0.29
CAM-B3LYP-D3(BJ)/def2-TZVP Optimized Structure				
DLPNO-STEOM-CCSD	1.75	2.24	3.17	0.49
qsGW	1.97	2.29	3.15	0.32
evGW@PBEH40	1.98	2.29	3.15	0.31
evGW@LDA	1.94	2.20	3.01	0.26
CAMY-B3LYP	1.94	2.23	3.08	0.29
ω B97-X	2.10	2.71	3.57	0.61
B3LYP/def2-TZVP Optimized Structure				
evGW@LDA-BSE(ADF/TZP)	1.85	2.09	2.91	0.24
evGW@LDA-BSE (MOLGW/6-311++G(2d,2p))	1.85	2.13	2.91	0.28

^aAll values are in eV.

compare VEEs calculated with different computational methods to the experimental VEE, which has recently been extracted from the experimental spectrum by Sirohiwal et al.⁴⁷ The domain based local pair-natural orbital^{166,167} (DLPNO)-STEOM-CCSD^{168–170} results are taken from ref 47, while the evGW@LDA-BSE/6-311++G(2d,2p) results calculated using MOLGW¹⁷¹ are by Hashemi and Leppert.¹⁰⁴ Two different,

gas-phase optimized structures have been used: one has been optimized at the CAM-B3LYP-D3(BJ)/def2-TZVP level of theory by Sirohiwal et al.,⁴⁷ while the other has been optimized by Hashemi and Leppert using B3LYP/def2-TZVP.

We performed evGW@LDA-BSE calculations for both structures. Our results for the CAM-B3LYP-D3(BJ)-optimized structure are consistently around 0.1 eV lower than the ones for the B3LYP optimized structure. This illustrates the large influence of small changes in structural parameters on the final excitation energies. However, CAM-B3LYP has been shown to describe the structural features of chlorophyll monomers very well.^{47,172} For the B3LYP optimized structure, we can compare our herein calculated VEEs to the ones from Hashemi and Leppert calculated on the same level of theory. Except for the Q_x excitation energies, which are slightly different (40 meV), we find a perfect agreement between both implementations.

All evGW results agree very well with qsGW also for Chla. All GW-BSE results for the CAM-B3LYP-D3(BJ) optimized structure are in excellent agreement with the experimental values. For instance, the qsGW-BSE VEEs agree all with the experimental VEEs within 30 meV. On the other hand, DLPNO-STEOM-CCSD not only severely underestimates the Q_y excitation energy, but it also overestimates the gap between both Q-bands, $\Delta_{Q_y-Q_x}$, considerably. Considering this difference, we note that STEOM-CCSD is not necessarily a reliable reference for qsGW. In STEOM-CCSD, a much larger number of diagrams is considered in the single- and two-particle Green's functions compared to GW.¹⁷³ QP approximations to GW approximate the effect of these diagrams instead by neglecting the vertex.¹²⁹ The diagrams contained in GW are not a subset of the ones contained in EOM-CCSD but only of those contained in EOM-CCSDT.¹⁷³ Accounting for excitations to triples (at least to some extent) is known to be of high importance for the reliable description of charged¹⁷⁴ and neutral excitations.^{39,40,175} Consequently, STEOM-CCSD shows mean signed errors compared to EOM-CCSDT calculations of around 0.1 eV for a set of medium organic molecules, but errors can be as large as 0.5 eV in some cases.³⁹ Moreover, apart from the neglect to triple excitations, the DLPNO approximation can also introduce some artifacts. The pairs, which are treated on the CC level, are selected based on

Table 4. Lowest Six Excitation Energies for Two Different Models of the Chla Dimer^a

	Ω_1	Ω_2	Ω_3	Ω_4	Ω_5	Ω_6
exp. (VEE) ¹⁷⁸	1.95	(estimated)				
exp. (band max) ¹⁷⁸	1.90					
B3LYP-D3(BJ)/def2-SVP Optimized Structure ^b						
qsGW	1.89	1.92	2.07	2.10	2.83	2.92
evGW@PBEH40	1.92	1.95	2.09	2.11	2.84	2.93
evGW@LDA	1.87	1.88	1.90	1.90	2.72	2.75
CAMY-B3LYP	2.12	2.15	2.29	2.32	2.63	2.76
RVS-LT-SOS-ADC(2) ^c	2.04	2.06				
CAM-B3LYP-D3(BJ)/TZP Optimized Structure ^d						
qsGW	1.94	1.98	2.25	2.28	2.56	2.68
evGW@PBEH40	1.97	2.02	2.24	2.27	2.58	2.67
evGW@LDA	1.98	1.99	2.16	2.22	2.51	2.64
CAMY-B3LYP	2.12	2.16	2.38	2.43	2.51	2.61
ω B97-X	2.05	2.10	2.63	2.68	3.10	3.27

^aAll values are in eV. ^bThe B3LYP-D3(BJ)/def2-SVP structure has been taken from Suomivuori et al.⁴¹ ^cResults taken from Suomivuori et al.⁴¹

^dThe structure of the M3 dimer has been optimized in this work at CAM-B3LYP-D3(BJ)/TZP.

Table 5. Characterization and Comparison of the Low-Lying Excited States of Chla Dimer (Structure by Suomivuori et al.⁴¹) Calculated with evGW@LDA-BSE and evGW@PBEH40-BSE^a

	evGW@LDA				evGW@PBEH40			
	VEE	character	weight	f	VEE	character	weight	f
Ω_1	1.87	238 \rightarrow 240	0.49	0.08	1.92	238 \rightarrow 240 237 \rightarrow 239	0.28 0.26	0.30
Ω_2	1.88	237 \rightarrow 240 237 \rightarrow 239	0.22 0.17	0.14	1.95	238 \rightarrow 241 237 \rightarrow 239	0.41 0.34	0.03
Ω_3	1.90	236 \rightarrow 239	0.38	0.13	2.09	235 \rightarrow 239	0.53	0.04
Ω_4	1.90	237 \rightarrow 240 235 \rightarrow 239	0.37 0.31	0.00	2.11	236 \rightarrow 240	0.49	0.03
Ω_5	2.72	238 \rightarrow 239	0.51	0.37	2.84	238 \rightarrow 239	0.56	0.24
Ω_6	2.75	237 \rightarrow 239 237 \rightarrow 242	0.27 0.24	0.14	2.93	237 \rightarrow 240	0.31	0.20

^aShown are the excitation energies Ω_s (in eV), the dominant coefficients of the corresponding eigenvector, and the associated particle-hole transitions, as well as the oscillator strengths f .

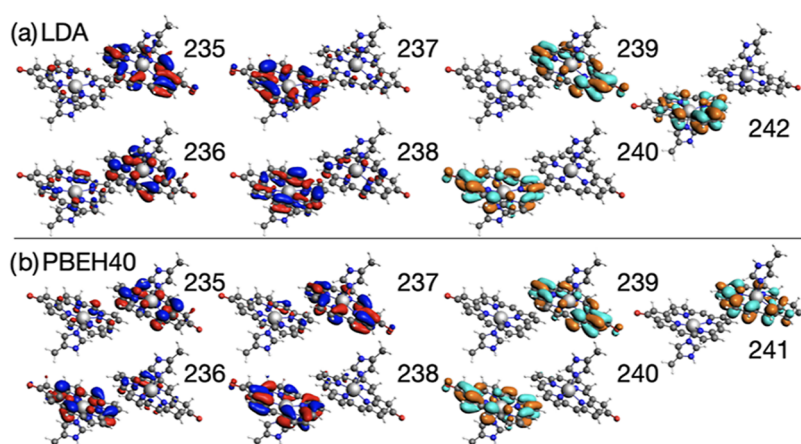


Figure 3. Selected valence single-particle KS orbitals for the Chla dimer (structure by Suomivuori et al.⁴¹) calculated using LDA and PBEH40.

an MP2 calculation,¹⁶⁷ which is not always reliable for systems with strongly screened electron–electron interactions.^{176,177}

Lastly, the RSH kernels CAMY-B3LYP and ω B97-X, which are typically used in computational studies of the PSII RC^{11–13,16} give very different results. CAMY-B3LYP is actually in excellent agreement with the experiment and the GW-BSE calculations, while ω B97-X gives much too high excitation energies and also massively overestimates $\Delta_{Q_y-Q_x}$.

4.3.2. Dimers. In Table 4, we show the low-lying excitations of GW-BSE calculations for different models of P_{D1} – P_{D2} . The first dimer structure has been optimized in the gas phase by Suomivuori et al. at the B3LYP-D3/def2-SVP level of theory and consists of two Chla monomers, whose structure is shown in Figure 2a. This structure lacks most substituents of the Chlorin core present in Chla (see Figure 2b) which complicates comparison of excitation energies to experimental results. However, these calculations give some indication on the performance of GW-BSE in comparison to the RVS-LT-SOS-ADC(2) VEEs by Suomivuori et al. Comparison of experimental band maximum and VEE for a single Chla measured in ref 165 suggests that the VEE of the chlorophyll dimer might be around 1.95 eV (50 meV higher than the band maximum).

As for the monomer, the GW-BSE results are in excellent agreement with these values, while the RVS-LT-SOS-ADC(2) VEEs are much too high. In contrast to the case of the Chla monomer, CAMY-B3LYP overestimates the VEEs by far. The

VEEs, Ω_3 and Ω_4 , of the BSE calculation based on evGW@LDA are almost 0.2 eV lower than the ones based on evGW@PBEH40 and in the former calculation, the four lowest excited states are almost degenerate. The character of these excitations are compared in more detail in Table 5 with the corresponding KS single-particle orbitals shown in Figure 3. Comparison of the most important contributions to the eigenvector $|\mathbf{X}, \mathbf{Y}\rangle_1^T$ already shows that evGW@LDA-BSE predicts the lowest excitation to be localized on the P_{D1} fragment, while in the evGW@PBEH40-BSE calculation it is delocalized over both monomers with almost equal weights. Using evGW@LDA-BSE, the second excited state has a large contribution of a particle-hole transition located on P_{D1} , while it is localized on P_{D2} using evGW@PBEH40-BSE. Also, the oscillator strengths in Table 5 show that the different excitations differ substantially in their brightness. Together with the large difference in some of the VEEs, this shows that different KS starting points can lead to different excitation characters, even when the eigenvalues are updated self-consistently.

In Table 4, we also show results for a more realistic model of the Chla dimer. Our model consists of two M3 monomers, which includes the first four segments of the phytol chain in stacked conformation. In Table S1 of the Supporting Information, we show that the final excitation energies are however very insensitive to the particular structural model.

The band maximum of ref 178, which we used as the reference has been measured for a charge tagged dimer.

However, as shown in ref 179 for Chl_a monomers, the final excitation energies are insensitive to the type of charge tag and omitting the charge tag entirely only results in a lowering of the excitation energies of around 30–40 meV.

The excitation energies we report here have been calculated for a geometry optimized at the CAM-B3LYP/TZP level of theory. Excitation energies for geometries optimized with different methods can be found in Table S2 of the Supporting Information. In accordance with ref 47 and our results shown in Table 3, we found the VEEs to be very sensitive to the choice of the functional chosen for geometry optimization. For instance, using PBE-D4/TZP lowers the lowest 2 excitation energies by around 0.1 eV with respect to the CAM-B3LYP-D3(BJ) optimized structure. The data shown in Table S3 in the Supporting Information furthermore demonstrates that VEEs for crystal structures considerably underestimate the experimental values.

The lowest qsGW-BSE excitation energy of 1.94 meV is again in an excellent agreement with the VEE of 1.95 eV estimated from the band maximum. As explicitly shown in the Supporting Information and as for the monomers in Table 2, the excitation energies are again rather insensitive to the basis set. Also notice that the remaining small basis set errors will largely cancel with the small error from omitting the charge tag. Again, the lowest two evGW-BSE VEEs are in excellent agreement with the qsGW-BSE one and each other, while there are larger differences in higher-lying VEEs. As for the monomer, CAMY-B3LYP massively overestimates the VEEs compared to the experiment.

4.4. Six-Chromophore Model of the PSII RC. The most complete model of the PSII RC we consider in this work comprises all six chromophores shown in Figure 1 with 476 atoms in total. Time-resolved spectroscopic experiments^{44–46} show that the primary electron transfer in the RC occurs from an exciton localized on Chl_{D1} to Pheo_{D1}, followed by a transfer of the hole to P_{D1}. This would point to the presence and possible mixing in of low-lying CT states with pronounced Chl_{D1}⁺–Pheo_{D1}[−] and P_{D1}⁺–Pheo_{D1}[−] characters in calculations of excitation energies. In previous TD-DFT calculations using RSH kernels for similar multi-chromophoric models, no low-lying CT state, which could be related to this charge separation pathway have been observed.^{11,16} In recent computational studies, both Sirohiwal et al.^{7,16} and Tamura et al.¹⁴ demonstrated that the protein environment is crucial for observing the Chl_{D1}⁺–Pheo_{D1}[−] CT state at low energies.

The low-lying excitations of the hexameric complex at the qsGW-BSE/TZP level of theory are characterized in Table 6. In the Supporting Information, we characterize these excitations in more detail by visualizing the involved single-particle qsGW orbitals. We also present results of our own TD-DFT calculations using the ωB97-X kernel as well as for evGW@PBEH40-BSE/TZP. The excitation energies and the oscillator strengths of the six lowest excited states using these different methods are compared in Table 7.

In agreement with past^{11,16} and our own TD-DFT calculations using the ωB97-X kernel, only states with local characters can be found among the six lowest excitations of the hexamer using both qsGW-BSE and evGW@PBEH40-BSE. As shown in Table 7, also the VEEs using the different methods agree within 50 meV. In all methods, the low-lying states are linear combinations of excitonic states involving the frontier orbitals on each chromophore.

Table 6. Lowest qsGW@-BSE/TZP Excited States of the Hexameric Chromophore Complex in the RC of PSII^a

	VEE	<i>f</i>	character	weight
Ω ₁	1.89	0.22	P _{D2} [*]	0.39
			Chl _{D2} [*]	0.22
Ω ₃	1.90	0.77	P _{D2} [*]	0.24
			P _{D1} [*]	0.14
			Pheo _{D2} [*]	0.09
			P _{D1} ⁺ –P _{D2} [−]	0.09
Ω ₃	1.91	0.04	Chl _{D1} [*]	0.30
			P _{D1} [*]	0.24
			Chl _{D1} ⁺ –Pheo _{D2} [−]	0.08
			Pheo _{D2} [*]	0.39
Ω ₄	1.92	0.22	Chl _{D2} [*]	0.16
			Pheo _{D2} [*]	0.12
			Chl _{D1} [*]	0.09
			Chl _{D2} [*]	0.23
			Chl _{D2} [*]	0.18
			P _{D1} [*]	0.16
Ω ₆	1.97	0.20	P _{D2} [*]	0.15
			Pheo _{D1} [*]	0.54
			Pheo _{D1} [−] –Chl _{D1} ⁺	0.21
Ω ₁₃	2.71	0.00	P _{D2} ⁺ –Chl _{D2} [−]	0.81
			P _{D1} ⁺ –Chl _{D2} [−]	0.13
Ω ₁₄	2.73	0.00	P _{D1} ⁺ –Chl _{D1} [−]	0.70
			P _{D1} ⁺ –Pheo _{D1} [−]	0.20

^aShown are the excitation energies Ω_S (in eV), the dominant coefficients of the corresponding eigenvector, and the associated particle-hole transitions, as well as the oscillator strengths *f*.

Table 7. VEEs and Oscillator Strengths of the Six Lowest Excited States of the Hexameric Complex at Different Levels of Theory^a

	qsGW-BSE		qsGW@PBEH40-BSE		TD-DFT@ωB97-X	
	VEE	<i>f</i>	VEE	<i>f</i>	VEE	<i>f</i>
Ω ₁	1.89	0.22	1.94	0.81	1.92	0.33
Ω ₂	1.90	0.77	1.94	0.32	1.93	0.64
Ω ₃	1.91	0.04	1.96	0.05	1.94	0.14
Ω ₄	1.92	0.22	1.97	0.24	1.96	0.18
Ω ₅	1.94	0.01	1.99	0.15	1.97	0.09
Ω ₆	1.97	0.20	2.00	0.11	1.98	0.07

^aAll values are in eV.

At the qsGW-BSE level, the two lowest states with pronounced CT characters can be found at 2.7 eV and these cannot directly be linked to charge separation pathways in PSII, which have been observed experimentally.^{44–46} Only the third excited state at the qsGW-BSE level of theory at 1.91 eV contains a contribution from a Chl_{D1}⁺–Pheo_{D1}[−] particle-hole transition with a small weight, which is entirely absent in our TD-DFT and evGW-BSE calculations. Future studies at the GW-BSE level with the inclusion of the environmental electrostatics are needed to rationalize how the Chl_{D1}⁺–Pheo_{D1}[−] CT state is influenced by the protein environment at the qsGW-BSE level.

4.5. Timings. Finally, we briefly comment on the computational effort for different basis sets and methods to calculate the lowest *N*_Ω roots of the full hexamer with 476 atoms and 1872 correlated electrons. The computational timings in core hours are given in Table 8. The calculation for

Table 8. CPU Times (in Core Hours) to Calculate the N_{Ω} Lowest Roots of the Full Hexamer with 476 Atoms and 1872 Correlated Electrons with Different Basis Sets and Methods^a

method	basis	N_{bas}	N_{Ω}	iterations		CPU time		
				qsGW	BSE	GW	BSE	total
qsGW-BSE	TZ3P	11116	12	6	10	3401	3447	7283
	TZP	6256	24	6	8	1074	1729	2924
evGW-BSE	TZP	6256	24	5	8	826	1969	2917
ω B97-X	TZP	6256	12		21		2675	2846

^a39,884 auxiliary basis functions have been used in all calculations. All calculations have been performed on an 2.6 GHz AMD Rome 7H12 node with 64 cores and 16 GB RAM per node.

the hexamer can be performed in less than 3000 core hours, that is, in less than 2 days on a node with 64 cores. The qsGW part of the calculation is slightly cheaper than the BSE part. Notice, that the BSE part of the calculation is roughly as expensive as the TD-DFT calculation with the WB97-X kernel if the timings are normalized by the number of states and number of subspace iterations in the Davidson algorithm.

Low-order scaling implementations like ours which rely on sparsity in the primary basis usually do not scale well with the size of the single particle basis, as can be seen by comparing the timings of the qsGW-BSE calculations with different basis sets. We also performed a qsGW calculation for the full hexamer with more than 11,000 basis functions using the TZ3P basis set. Here, a single qsGW iteration already takes around 540 core hours, which is more than three times longer than one iteration using the TZP basis set. While in this work, the TZP basis set was already sufficient to obtain converged results, typically larger basis sets will be required. Finite basis set correction techniques for many-body perturbation theory might be a promising solution to circumvent this problem.^{164,180–182}

For larger calculations, the bottleneck of the computation is the number of auxiliary fit functions N_{fit} (almost 40,000 for the hexamer). When large basis sets are used, also large auxiliary fit sets are necessary to guarantee numerical stability in the PADF approach. The same holds true for related techniques relying on sparse transformation between matrices in primary and auxiliary bases.^{111,112} For each imaginary time and frequency point, a matrix of size $N_{\text{fit}} \times N_{\text{fit}} \approx 14$ GB needs to be stored for the hexamer. This amounts to storage requirements of almost 500 GB and if we were to double the system size, 2 TB of distributed memory would be needed. In our current implementation, we store these matrices on disk and transfer them to the CPU and back, which becomes very time-consuming.

5. CONCLUSIONS

So far, applications of the GW-BSE method have been limited to rather small molecules.^{90,97,104} We presented here a new implementation of the method, which enables its routine application to much larger systems. As opposed to a recently developed simplified GW-BSE scheme,¹⁸³ our implementation does not introduce any empirical approximations to the matrix elements of the BSE Hamiltonian. Our implementation allowed us to calculate the 12 lowest excited states of the complete complex of 6 chromophores in the PSII RC with almost 2000 correlated electrons on the qsGW-BSE/TZP level. The calculation with around 6000 primary basis functions could be performed in a little more than 2 days on a single compute node. The corresponding calculation using qsGW-

BSE/TZ3P with around 11,000 primary basis functions could be performed in around 5 days using the same hardware.

Because the single-particle states are optimized self-consistently, making the results independent of a mean-field reference calculation, qsGW-BSE is a theoretically more rigorous approach than evGW-BSE. qsGW-BSE calculations for optimized geometries are in excellent agreement with experimental VEEs in the gas phase for Chla monomers and dimers. We have shown here explicitly for Chla dimers that evGW-BSE might lead to different excitations for different starting points. This is in contrast to the generally good agreement for different starting points for monomers¹⁰⁴ and can be seen as a major shortcoming of evGW-BSE. We therefore conclude that self-consistency in the single-particle states is decisive for a reliable description of the low-lying excitonic states of large chromophoric complexes.

In agreement with previous results and our own calculations on the TD-DFT/RSH level for the full hexameric complex¹¹ also evGW-BSE and qsGW-BSE only predict states with predominantly local characters in the absence of the protein environment. These states can therefore not be linked to the experimentally observed CT processes.^{44–46} Recent computational studies have established that the environmental electrostatics are responsible for this type of CT.^{7,14,16} Along the lines of previous GW-BSE implementations,^{91,96,184} future research needs to focus on ways to explicitly account for the environmental electrostatics in large-scale GW-BSE calculations.

APPENDIX A

Electrochromatic Shifts

In this appendix, we quantify the electrochromatic shift of the excitation energies of two monomeric and dimeric as well as one tetrameric model of the PSII RC due to solvent effects and protein environments using a polarizable continuum model. The Q_x excitation energies calculated using CAMY-B3LYP-TD-DFT/TZP with and without implicit solvation are shown in Table 9. Our calculated electrochromatic shifts agree well with experimental values of about 0.12 eV,²⁰ which is somewhat surprising and possibly fortuitous because the asymmetry of the protein matrix is not accounted for in this continuum model. For the low-lying VEEs, the shifts are more or less independent of the employed model system and they are transferable to the other multichromophoric complexes as well.

APPENDIX B

Calculating the BSE Hamiltonian

The most time-consuming step in the solution of the BSE is to build the matrix elements of the 2-particle Hamiltonian, eq 20.

Table 9. Q_{ν} Excitation for Different Chla Monomers and Dimers Calculated Using TD-DFT@CAMY-B3LYP/TZP with and without Implicit Solvation^a

	exp.	M1	M2	$P_{D1}-P_{D2}$			
				M1 monomers		M2 monomers	
solv.	1.82	1.81	1.84	1.78	1.81	1.80	1.84
no solv.	1.94	1.98	1.99	1.93	1.95	1.94	1.96
diff.	0.12	0.17	0.15	0.15	0.14	0.14	0.12
	Chl _{D1} -P _{D1} -P _{D2} -Chl _{D2} (M1 Monomers)						
solv.		1.76	1.78	1.81	1.84		
no solv.		1.90	1.92	1.95	2.00		
diff.		0.14	0.14	0.14	0.16		

^aAll values are in eV.

Let us denote with the matrix $\mathbf{K}^{(\pm)}$, a column of $\mathbf{A} \pm \mathbf{B}$ as defined in (20), in the primary basis.

Within the density fitting method, we expand products of atomic orbitals in a basis of auxiliary functions. To introduce the PADF variant of this technique, we label atomic orbitals as μ, ν, κ , and λ , auxiliary functions as α, β, γ , and δ , and atomic centers as A, B, C, \dots . We also define the convention that $\mu, \alpha \in A, \nu, \beta \in B, \kappa, \gamma \in C$, and $\lambda, \delta \in D$, that is, μ and α are only labeling functions centered on atom A , and so on. The PADF expansion of the products of AOs can then be written as

$$\chi_{\mu}(\mathbf{r})\chi_{\nu}(\mathbf{r}) = \begin{cases} \sum_{\beta \in B} c_{\mu\nu,\beta} f_{\beta}(\mathbf{r}) + \sum_{\alpha \in A} c_{\nu\mu,\alpha} f_{\alpha}(\mathbf{r}) & A \neq B \\ \sum_{\alpha \in A} \frac{1}{2}(c_{\nu\mu,\alpha} + c_{\mu\nu,\alpha}) f_{\alpha}(\mathbf{r}) & A = B \end{cases} \quad (21)$$

where the factor of 1/2 in the case $A = B$ is introduced to facilitate evaluation with the same algorithm while avoiding double counting. Let us write (20), in the primary basis as

$$\mathbf{K}_{\mu\nu}^{(\pm)} = -\sum_{\kappa\lambda} b_{\kappa\lambda} W(\omega = 0)_{\mu\kappa\nu\lambda} \pm W(\omega = 0)_{\nu\kappa\mu\lambda} \quad (22)$$

where the $b_{\kappa\lambda}$ are elements of the transition density matrix and the $\mathbf{K}_{\mu\nu}^{(\pm)}$ denote the matrix elements of a column of $(\mathbf{A} \pm \mathbf{B})^{(n+1)}$. Inserting (21), the contribution to $\mathbf{K}^{(\pm)}$ for all atom pairs (A, B) is

$$\mathbf{K}^{(\pm)AB} = \mathbf{K}^{(\pm)AB,I} + \mathbf{K}^{(\pm)AB,II} + \mathbf{K}^{(\pm)AB,III} + \mathbf{K}^{(\pm)AB,IV} \quad (23)$$

where

$$\begin{aligned} \mathbf{K}^{(+)AB,III} &= [\mathbf{K}^{(+)AB,II}]^T \\ \mathbf{K}^{(-)AB,III} &= -[\mathbf{K}^{(-)AB,II}]^T \end{aligned} \quad (24)$$

In these and in the following quantities, the matrices are restricted to the primary basis functions centered on the atoms denoted by the indices in the superscripts. We define the intermediates

$$I_{\mu\nu\gamma}^{ABC} = c_{\mu\nu\gamma}^{ABB} W(\omega = 0)_{\beta\gamma}^{BC} \quad (25)$$

and

$$F_{\nu\mu\alpha}^{BAA} = \sum_{\lambda} b_{\lambda\nu}^{DB} c_{\lambda\mu\alpha}^{DAA} \quad (26)$$

Here, $W(\omega = 0)_{\beta\gamma}$ are the matrix elements of the statically screened interaction in the basis of the auxiliary functions $\{f_{\alpha}\}_{\alpha=1,\dots,N_{aux}}$

$$W(\omega = 0)_{\alpha\beta} = \int d\mathbf{r} \int d\mathbf{r}' f_{\alpha}(\mathbf{r}) W(\mathbf{r}, \mathbf{r}', \omega = 0) f_{\beta}(\mathbf{r}') \quad (27)$$

We can then write

$$\begin{aligned} K_{\mu\kappa}^{\pm,AC,I} &= \sum_{\nu\lambda} \sum_{\alpha\gamma} b_{\lambda\nu}^{DB} c_{\lambda\mu\alpha}^{DAA} W(\omega = 0)_{\alpha\gamma}^{AC} c_{\nu\kappa\gamma}^{BCC} \\ &= \sum_{\nu\alpha} F_{\nu\mu\alpha}^{BAA} I_{\nu\kappa\alpha,\tau}^{BCA} \\ K_{\mu\kappa}^{\pm,AC,II} &= \sum_{\nu\lambda} \sum_{\alpha\beta} b_{\lambda\nu}^{DB} c_{\lambda\mu\alpha}^{DAA} W(\omega = 0)_{\alpha\beta}^{AB} c_{\nu\kappa\beta}^{CBB} \\ &= \sum_{\nu\alpha} F_{\nu\mu\alpha}^{BAA} I_{\kappa\nu\alpha}^{CBA} \end{aligned} \quad (28)$$

$$\begin{aligned} K_{\mu\kappa}^{\pm,AC,IV} &= \sum_{\nu\lambda} \sum_{\delta\beta} b_{\lambda\nu}^{DB} c_{\mu\lambda\delta}^{ADD} W(\omega = 0)_{\delta\beta}^{DB} c_{\nu\kappa\beta}^{CBB} \\ &= \sum_{\lambda\delta} \sum_{\nu} b_{\lambda\nu}^{DB} I_{\kappa\nu\delta}^{CBD} b_{\mu\lambda\delta}^{ADD} \end{aligned}$$

where in the + case b is symmetric and antisymmetric otherwise. These are the working equations with which (20) is implemented. They are similar to the ones for the self-energy, outlined in ref 148.

APPENDIX C

Elimination of Diffuse Functions from the Primary Basis
In addition to the usual canonical orthonormalization¹⁸⁵ during the SCF prior to the qsGW calculations we herein introduce an additional step in order to improve the numerical stability of our algorithm. To project out too diffuse functions from the primary basis, we first diagonalize the overlap matrix of primary basis functions \mathbf{S}

$$\mathbf{S} = \mathbf{U}^T \mathbf{\Lambda} \mathbf{U} \quad (29)$$

We then remove a column u_i from the transformation matrix if the corresponding eigenvalue λ_i is smaller than some predefined threshold ϵ_s . We then define

$$\mathbf{V} = \mathbf{U}\mathbf{U}^T \quad (30)$$

and use this projector to transform all matrices in the primary basis, the Green's functions, the self-energy contributions, as well as the matrices defined in (20) according to

$$\mathbf{K} = \mathbf{V}^T \mathbf{K}' \mathbf{V} \quad (31)$$

where \mathbf{K}' would be the original exchange-like matrix in the primary basis including the diffuse part. This transformation is not necessary if a very large auxiliary basis set is used and is switched off in that case.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jctc.2c00531>.

All structures used in this work (ZIP)

VEEs of chlorophyll dimers for different optimized geometries and crystal structures; evGW single-particle energies of the hexameric complex; and dominant

particle-hole contributions; lowest TD-DFT/ ω B97-X/TZP, evGW@PBEH40-BSE/TZP, and qsGW@BSE/TZP excited states (PDF)

AUTHOR INFORMATION

Corresponding Author

Arno Förster – Theoretical Chemistry, Vrije Universiteit, NL-1081 HV Amsterdam, The Netherlands; orcid.org/0000-0002-0957-4081; Email: a.t.l.foerster@vu.nl

Author

Lucas Visscher – Theoretical Chemistry, Vrije Universiteit, NL-1081 HV Amsterdam, The Netherlands; orcid.org/0000-0002-7748-6243

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acs.jctc.2c00531>

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Insightful discussions and comments by Leeor Kronik and Souloke Sen are gratefully acknowledged. This research received funding (project no 731.017.417) from the Netherlands Organization for Scientific Research (NWO) in the framework of the Innovation Fund for Chemistry and from the Ministry of Economic Affairs in the framework of the “TKI/PPS-Toeslagregeling”.

REFERENCES

- (1) Mirkovic, T.; Ostroumov, E. E.; Anna, J. M.; van Grondelle, R.; Govindjee; Scholes, G. D. Light absorption and energy transfer in the antenna complexes of photosynthetic organisms. *Chem. Rev.* **2017**, *117*, 249–293.
- (2) Croce, R.; van Amerongen, H. Light harvesting in oxygenic photosynthesis: Structural biology meets spectroscopy. *Science* **2020**, *369*, No. eaay2058.
- (3) Kasha, M.; Rawls, H. R.; Ashraf El-Bayoumi, M. A. The Exciton Model In Molecular Spectroscopy. *Pure Appl. Chem.* **1965**, *11*, 371–392.
- (4) Reimers, J. R.; Biczysko, M.; Bruce, D.; Coker, D. F.; Frankcombe, T. J.; Hashimoto, H.; Hauer, J.; Jankowiak, R.; Kramer, T.; Linnanto, J.; Mamedov, F.; Müh, F.; Rätsep, M.; Renger, T.; Styring, S.; Wan, J.; Wang, Z.; Wang-Otomo, Z. Y.; Weng, Y. X.; Yang, C.; Zhang, J. P.; Freiberg, A.; Krausz, E. Challenges facing an understanding of the nature of low-energy excited states in photosynthesis. *Biochim. Biophys. Acta, Bioenerg.* **2016**, *1857*, 1627–1640.
- (5) Yin, S.; Dahlbom, M. G.; Canfield, P. J.; Hush, N. S.; Kobayashi, R.; Reimers, J. R. Assignment of the Q_y absorption spectrum of photosystem-i from thermosynechococcus elongatus based on CAM-B3LYP calculations at the PW91-optimized protein structure. *J. Phys. Chem. B* **2007**, *111*, 9923–9930.
- (6) Renger, T.; Schlodder, E. Primary photophysical processes in photosystem II: Bridging the gap between crystal structure and optical spectra. *ChemPhysChem* **2010**, *11*, 1141–1153.
- (7) Sirohiwal, A.; Neese, F.; Pantazis, D. A. Protein Matrix Control of Reaction Center Excitation in Photosystem II. *J. Am. Chem. Soc.* **2020**, *142*, 18174–18190.
- (8) Kitagawa, Y.; Matsuda, K.; Hasegawa, J. Y. Theoretical study of the excited states of the photosynthetic reaction center in photosystem II: Electronic structure, interactions, and their origin. *Biophys. Chem.* **2011**, *159*, 227–236.
- (9) Polyakov, I. V.; Khrenova, M. G.; Moskovsky, A. A.; Shabanov, B. M.; Nemukhin, A. V. Towards first-principles calculation of electronic excitations in the ring of the protein-bound bacteriochlorophylls. *Chem. Phys.* **2018**, *505*, 34–39.
- (10) Reimers, J. R.; Cai, Z. L.; Kobayashi, R.; Rätsep, M.; Freiberg, A.; Krausz, E. Assignment of the Q-Bands of the Chlorophylls: Coherence Loss via Q_x-Q_y Mixing. *Sci. Rep.* **2013**, *3*, 2761.
- (11) Frankcombe, T. J. Explicit calculation of the excited electronic states of the photosystem II reaction centre. *Phys. Chem. Chem. Phys.* **2015**, *17*, 3295–3302.
- (12) Kavanagh, M. A.; Karlsson, J. K.; Colburn, J. D.; Barter, L. M.; Gould, I. R. A TDDFT investigation of the photosystem II reaction center: Insights into the precursors to charge separation. *Proc. Natl. Acad. Sci. U.S.A.* **2020**, *117*, 19705–19712.
- (13) Sen, S.; Mascoli, V.; Liguori, N.; Croce, R.; Visscher, L. Understanding the Relation between Structural and Spectral Properties of Light-Harvesting Complex II. *J. Phys. Chem. A* **2021**, *125*, 4313–4322.
- (14) Tamura, H.; Saito, K.; Ishikita, H. The origin of unidirectional charge separation in photosynthetic reaction centers: nonadiabatic quantum dynamics of exciton and charge in pigment-protein complexes. *Chem. Sci.* **2021**, *12*, 8131–8140.
- (15) Sen, S.; Visscher, L. Towards the description of charge transfer states in solubilised LHCII using subsystem DFT. *Photosynth. Res.* **2022**, DOI: 10.1007/s11120-022-00950-7.
- (16) Sirohiwal, A.; Pantazis, D. A. The Electronic Origin of Far-Red-Light-Driven Oxygenic Photosynthesis. *Angew. Chem.* **2022**, *134*, No. e202200356.
- (17) López-Tarifa, P.; Liguori, N.; van den Heuvel, N.; Croce, R.; Visscher, L. Coulomb couplings in solubilised light harvesting complex II (LHCII): Challenging the ideal dipole approximation from TDDFT calculations. *Phys. Chem. Chem. Phys.* **2017**, *19*, 18311–18320.
- (18) Anda, A.; Hansen, T.; De Vico, L. Q_y and Q_x Absorption Bands for Bacteriochlorophyll a Molecules from LH2 and LH3. *J. Phys. Chem. A* **2019**, *123*, 5283–5292.
- (19) Cai, Z. L.; Crossley, M. J.; Reimers, J. R.; Kobayashi, R.; Amos, R. D. Density functional theory for charge transfer: The nature of the N-bands of porphyrins and chlorophylls revealed through CAM-B3LYP, CASPT2, and SAC-CI calculations. *J. Phys. Chem. B* **2006**, *110*, 15624–15632.
- (20) Sirohiwal, A.; Neese, F.; Pantazis, D. A. How Can We Predict Accurate Electrochromic Shifts for Biochromophores? A Case Study on the Photosynthetic Reaction Center. *J. Chem. Theory Comput.* **2021**, *17*, 1858–1873.
- (21) Saito, K.; Suzuki, T.; Ishikita, H. Absorption-energy calculations of chlorophyll a and b with an explicit solvent model. *J. Photochem. Photobiol. A* **2018**, *358*, 422–431.
- (22) Shao, Y.; Mei, Y.; Sundholm, D.; Kaila, V. R. Benchmarking the Performance of Time-Dependent Density Functional Theory Methods on Biochromophores. *J. Chem. Theory Comput.* **2020**, *16*, 587–600.
- (23) Stein, T.; Eisenberg, H.; Kronik, L.; Baer, R. Fundamental gaps in finite systems from eigenvalues of a generalized Kohn-Sham method. *Phys. Rev. Lett.* **2010**, *105*, 266802.
- (24) Refaely-Abramson, S.; Baer, R.; Kronik, L. Fundamental and excitation gaps in molecules of relevance for organic photovoltaics from an optimally tuned range-separated hybrid functional. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2011**, *84*, 075144.
- (25) Refaely-Abramson, S.; Sharifzadeh, S.; Govind, N.; Autschbach, J.; Neaton, J. B.; Baer, R.; Kronik, L. Quasiparticle spectra from a nonempirical optimally tuned range-separated hybrid density functional. *Phys. Rev. Lett.* **2012**, *109*, 226405.
- (26) Kronik, L.; Stein, T.; Refaely-Abramson, S.; Baer, R. Excitation gaps of finite-sized systems from optimally tuned range-separated hybrid functionals. *J. Chem. Theory Comput.* **2012**, *8*, 1515–1531.
- (27) Karolewski, A.; Kronik, L.; Kümmel, S. Using optimally tuned range separated hybrid functionals in ground-state calculations: Consequences and caveats. *J. Chem. Phys.* **2013**, *138*, 204115.

- (28) Schirmer, J. Beyond the random-phase approximation: A new approximation scheme for the polarization propagator. *Phys. Rev. A: At, Mol., Opt. Phys.* **1982**, *26*, 2395–2416.
- (29) Schirmer, J.; Cederbaum, L. S.; Walter, O. New approach to the one-particle Green's function for finite Fermi systems. *Phys. Rev. A: At, Mol., Opt. Phys.* **1983**, *28*, 1237–1259.
- (30) Coester, F. Bound states of a many-particle system. *Nucl. Phys.* **1958**, *7*, 421–424.
- (31) Coester, F.; Kümmel, H. Short-range correlations in nuclear wave functions. *Nucl. Phys.* **1960**, *17*, 477–485.
- (32) Čížek, J. On the Correlation Problem in Atomic and Molecular Systems. Calculation of Wavefunction Components in Ursell-Type Expansion Using Quantum-Field Theoretical Methods. *J. Chem. Phys.* **1966**, *45*, 4256–4266.
- (33) Čížek, J. On the Use of the Cluster Expansion and the Technique of Diagrams in Calculations of Correlation Effects in Atoms and Molecules. *Adv. Chem. Phys.* **1969**, *14*, 35–89.
- (34) Paldus, J.; Čížek, J.; Shavitt, I. Correlation Problems in Atomic and Molecular Systems. IV. Extended Coupled-Pair Many-Electron Theory and Its Application to the BH₃ Molecule. *Phys. Rev. A: At, Mol., Opt. Phys.* **1972**, *5*, 50–67.
- (35) Christiansen, O.; Koch, H.; Jørgensen, P. The second-order approximate coupled cluster singles and doubles model CC2. *Chem. Phys. Lett.* **1995**, *243*, 409–418.
- (36) Stanton, J. F.; Bartlett, R. J. The equation of motion coupled-cluster method. A systematic biorthogonal approach to molecular excitation energies, transition probabilities, and excited state properties. *J. Chem. Phys.* **1993**, *98*, 7029–7039.
- (37) Nooijen, M.; Bartlett, R. J. A new method for excited states: Similarity transformed equation-of-motion coupled-cluster theory. *J. Chem. Phys.* **1997**, *106*, 6441–6448.
- (38) Nooijen, M.; Bartlett, R. J. Similarity transformed equation-of-motion coupled-cluster theory: Details, examples, and comparisons. *J. Chem. Phys.* **1997**, *107*, 6812–6830.
- (39) Loos, P. F.; Lipparini, F.; Boggio-Pasqua, M.; Scemama, A.; Jacquemin, D. A Mountaineering Strategy to Excited States: Highly Accurate Energies and Benchmarks for Medium Sized Molecules. *J. Chem. Theory Comput.* **2020**, *16*, 1711–1741.
- (40) Monino, E.; Loos, P. F. Spin-Conserved and Spin-Flip Optical Excitations from the Bethe-Salpeter Equation Formalism. *J. Chem. Theory Comput.* **2021**, *17*, 2852–2867.
- (41) Suomivuori, C. M.; Winter, N. O.; Hättig, C.; Sundholm, D.; Kaila, V. R. Exploring the Light-Capturing Properties of Photosynthetic Chlorophyll Clusters Using Large-Scale Correlated Calculations. *J. Chem. Theory Comput.* **2016**, *12*, 2644–2651.
- (42) Winter, N. O.; Hättig, C. Scaled opposite-spin CC2 for ground and excited states with fourth order scaling computational costs. *J. Chem. Phys.* **2011**, *134*, 184101.
- (43) Send, R.; Kaila, V. R.; Sundholm, D. Reduction of the virtual space for coupled-cluster excitation energies of large molecules and embedded systems. *J. Chem. Phys.* **2011**, *134*, 214114.
- (44) Groot, M. L.; Pawłowicz, N. P.; van Wilderen, L. J.; Breton, J.; van Stokkum, I. H.; van Grondelle, R. Initial electron donor and acceptor in isolated Photosystem II reaction centers identified with femtosecond mid-IR spectroscopy. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 13087–13092.
- (45) Romero, E.; Diner, B. A.; Nixon, P. J.; Coleman, W. J.; Dekker, J. P.; van Grondelle, R. Mixed exciton-charge-transfer states in photosystem II: Stark spectroscopy on site-directed mutants. *Biophys. J.* **2012**, *103*, 185–194.
- (46) Yoneda, Y.; Arsenault, E. A.; Yang, S.-J.; Orcutt, K.; Iwai, I.; Fleming, G. R. The initial charge separation step in oxygenic photosynthesis. *Nat. Commun.* **2022**, *13*, 2275.
- (47) Sirohiwal, A.; Berraud-Pache, R.; Neese, F.; Izsák, R.; Pantazis, D. A. Accurate Computation of the Absorption Spectrum of Chlorophyll a with Pair Natural Orbital Coupled Cluster Methods. *J. Phys. Chem. B* **2020**, *124*, 8761–8771.
- (48) Sirohiwal, A.; Neese, F.; Pantazis, D. A. Chlorophyll excitation energies and structural stability of the CP47 antenna of photosystem II: a case study in the first-principles simulation of light-harvesting complexes. *Chem. Sci.* **2021**, *12*, 4463–4476.
- (49) Wesolowski, T. A.; Warshel, A. Frozen density functional approach for ab initio calculations of solvated molecules. *J. Phys. Chem.* **1993**, *97*, 8050–8053.
- (50) Neugebauer, J.; Louwerse, M. J.; Baerends, E. J.; Wesolowski, T. A. The merits of the frozen-density embedding scheme to model solvatochromic shifts. *J. Chem. Phys.* **2005**, *122*, 094115.
- (51) Gomes, A. S. P.; Jacob, C. R. Quantum-chemical embedding methods for treating local electronic excitations in complex chemical systems. *Annu. Rep. Prog. Chem., Sect. C: Phys. Chem.* **2012**, *108*, 222–277.
- (52) Manby, F. R.; Stella, M.; Goodpaster, J. D.; Miller, T. F. A simple, exact density-functional-theory embedding scheme. *J. Chem. Theory Comput.* **2012**, *8*, 2564–2568.
- (53) Höfener, S.; Visscher, L. Calculation of electronic excitations using density embedding frozen-density embedding. *J. Chem. Phys.* **2012**, *137*, 204120.
- (54) Raghavachari, K.; Saha, A. Accurate Composite and Fragment-Based Quantum Chemical Models for Large Molecules. *Chem. Rev.* **2015**, *115*, 5643–5677.
- (55) Tölle, J.; Deilmann, T.; Rohlfing, M.; Neugebauer, J. Subsystem-Based GW / Bethe - Salpeter Equation. *J. Chem. Theory Comput.* **2021**, *17*, 2186–2199.
- (56) Neugebauer, J. Couplings between electronic transitions in a subsystem formulation of time-dependent density functional theory. *J. Chem. Phys.* **2007**, *126*, 134116.
- (57) Höfener, S.; Visscher, L. Wave Function Frozen-Density Embedding: Coupled Excitations. *J. Chem. Theory Comput.* **2016**, *12*, 549–557.
- (58) Leng, X.; Jin, F.; Wei, M.; Ma, H.; Feng, J.; Ma, Y. Electronic energy transfer studied by many-body Green's function theory. *J. Chem. Phys.* **2019**, *150*, 164107.
- (59) Frähmcke, J. S.; Walla, P. J. Coulombic couplings between pigments in the major light-harvesting complex LHC II calculated by the transition density cube method. *Chem. Phys. Lett.* **2006**, *430*, 397–403.
- (60) Sham, L. J.; Rice, T. M. Many-particle derivation of the effective-mass equation for the wannier exciton. *Phys. Rev.* **1966**, *144*, 708–714.
- (61) Hanke, W.; Sham, L. J. Many-particle effects in the optical spectrum of a semiconductor. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1980**, *21*, 4656–4673.
- (62) Strinati, G. Application of the Green's functions method to the study of the optical properties of semiconductors. *Riv. del Nuovo Cim.* **1988**, *11*, 1–86.
- (63) Salpeter, E. E.; Bethe, H. A. A relativistic equation for bound-state problems. *Phys. Rev.* **1951**, *84*, 1232–1242.
- (64) Gell-Mann, M.; Low, F. Bound states in quantum field theory. *Phys. Rev.* **1951**, *84*, 350–354.
- (65) Kugler, F. B. Renormalization Group Approaches to strongly correlated electron systems. Ph.D. Thesis, Ludwig-Maximilians-Universität München, 2018.
- (66) Martin, R. M.; Reining, L.; Ceperley, D. M. *Interacting Electrons*; Cambridge University Press, 2016.
- (67) Rohringer, G.; Hafermann, H.; Toschi, A.; Katanin, A. A.; Antipov, A. E.; Katsnelson, M. I.; Lichtenstein, A. I.; Rubtsov, A. N.; Held, K. Diagrammatic routes to nonlocal correlations beyond dynamical mean field theory. *Rev. Mod. Phys.* **2018**, *90*, 25003.
- (68) Petersilka, M.; Gossmann, U. J.; Gross, E. K. Excitation energies from time-dependent density-functional theory. *Phys. Rev. Lett.* **1996**, *76*, 1212–1215.
- (69) Onida, G.; Reining, L.; Rubio, A. Electronic excitations: density-functional versus many-body Green's-function approaches. *Rev. Mod. Phys.* **2002**, *74*, 601.
- (70) Hubbard, J. The description of collective motions in terms of many-body perturbation theory. *Proc. R. Soc. London, Ser. A* **1957**, *240*, 539–560.

- (71) Phillips, J. C. Generalized Koopmans' theorem. *Phys. Rev.* **1961**, *123*, 420–424.
- (72) Hedin, L. New method for calculating the one-particle Green's function with application to the electron-gas problem. *Phys. Rev.* **1965**, *139*, A796.
- (73) Onida, G.; Reining, L.; Godby, R. W.; Del Sole, R.; Andreoni, W. Ab initio calculations of the quasiparticle and absorption spectra of clusters: The sodium tetramer. *Phys. Rev. Lett.* **1995**, *75*, 818–821.
- (74) Rohlfling, M.; Louie, S. G. Excitonic effects and the optical absorption spectrum of hydrogenated Si clusters. *Phys. Rev. Lett.* **1998**, *80*, 3320–3323.
- (75) Rohlfling, M.; Louie, S. G. Electron-hole excitations and optical spectra from first principles. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2000**, *62*, 4927–4944.
- (76) Stratmann, R. E.; Scuseria, G. E.; Frisch, M. J. An efficient implementation of time-dependent density-functional theory for the calculation of excitation energies of large molecules. *J. Chem. Phys.* **1998**, *109*, 8218–8224.
- (77) Blase, X.; Attaccalite, C. Charge-transfer excitations in molecular donor-acceptor complexes within the many-body Bethe-Salpeter approach. *Appl. Phys. Lett.* **2011**, *99*, 171909.
- (78) Baumeier, B.; Andrienko, D.; Rohlfling, M. Frenkel and charge-transfer excitations in donor-acceptor complexes from many-body Green's functions theory. *J. Chem. Theory Comput.* **2012**, *8*, 2790–2795.
- (79) Duchemin, I.; Deutsch, T.; Blase, X. Short-range to long-range charge-transfer excitations in the zincbacteriochlorin-bacteriochlorin complex: A bethe-salpeter study. *Phys. Rev. Lett.* **2012**, *109*, 167801.
- (80) Faber, C.; Boulanger, P.; Duchemin, I.; Attaccalite, C.; Blase, X. Many-body Green's function GW and Bethe-Salpeter study of the optical excitations in a paradigmatic model dipeptide. *J. Chem. Phys.* **2013**, *139*, 194308.
- (81) Baumeier, B.; Rohlfling, M.; Andrienko, D. Electronic excitations in push-pull oligomers and their complexes with fullerene from many-body Green's functions theory with polarizable embedding. *J. Chem. Theory Comput.* **2014**, *10*, 3104–3110.
- (82) Körbel, S.; Boulanger, P.; Duchemin, I.; Blase, X.; Marques, M.; Botti, S. Benchmark many-body GW and Bethe-Salpeter calculations for small transition metal molecules. *J. Chem. Theory Comput.* **2014**, *10*, 3934–3943.
- (83) Boulanger, P.; Jacquemin, D.; Duchemin, I.; Blase, X. Fast and accurate electronic excitations in cyanines with the many-body bethe-salpeter approach. *J. Chem. Theory Comput.* **2014**, *10*, 1212–1218.
- (84) Jacquemin, D.; Duchemin, I.; Blase, X. Benchmarking the Bethe-Salpeter Formalism on a Standard Organic Molecular Set. *J. Chem. Theory Comput.* **2015**, *11*, 3290–3304.
- (85) Blase, X.; Boulanger, P.; Bruneval, F.; Fernandez-Serra, M.; Duchemin, I. GW and Bethe-Salpeter study of small water clusters. *J. Chem. Phys.* **2016**, *144*, 034109.
- (86) Ziaei, V.; Bredow, T. GW-BSE approach on S1 vertical transition energy of large charge transfer compounds: A performance assessment. *J. Chem. Phys.* **2016**, *145*, 174305.
- (87) Hung, L.; Bruneval, F.; Baishya, K.; Ögüt, S. Benchmarking the GW Approximation and Bethe-Salpeter Equation for Groups IB and IIB Atoms and Monoxides. *J. Chem. Theory Comput.* **2017**, *13*, 2135–2146.
- (88) Krause, K.; Klopper, W. Implementation of the Bethe-Salpeter equation in the TURBOMOLE program. *J. Comput. Chem.* **2017**, *38*, 383–388.
- (89) Rangel, T.; Hamed, S. M.; Bruneval, F.; Neaton, J. B. An assessment of low-lying excitation energies and triplet instabilities of organic molecules with an ab initio Bethe-Salpeter equation approach and the Tamm-Dancoff approximation. *J. Chem. Phys.* **2017**, *146*, 194108.
- (90) Gui, X.; Holzer, C.; Klopper, W. Accuracy Assessment of GW Starting Points for Calculating Molecular Excitation Energies Using the Bethe-Salpeter Formalism. *J. Chem. Theory Comput.* **2018**, *14*, 2127–2136.
- (91) Duchemin, I.; Guido, C. A.; Jacquemin, D.; Blase, X. The Bethe-Salpeter formalism with polarisable continuum embedding: Reconciling linear-response and state-specific features. *Chem. Sci.* **2018**, *9*, 4430–4443.
- (92) Blase, X.; Duchemin, I.; Jacquemin, D. The Bethe-Salpeter equation in chemistry: Relations with TD-DFT, applications and challenges. **2018**, *47*, 1022. DOI: 10.1039/c7cs00049a
- (93) Holzer, C.; Klopper, W. Communication: A hybrid Bethe-Salpeter/time-dependent density-functional-theory approach for excitation energies. *J. Chem. Phys.* **2018**, *149*, 101101.
- (94) Sharifzadeh, S. Many-body perturbation theory for understanding optical excitations in organic molecules and solids. *J. Phys. Condens. Matter* **2018**, *30*, 153002.
- (95) Holzer, C.; Klopper, W. Ionized, electron-attached, and excited states of molecular systems with spin-orbit coupling: Two-component GW and Bethe-Salpeter implementations. *J. Chem. Phys.* **2019**, *150*, 204116.
- (96) Tirimbò, G.; Sundaram, V.; Çaylak, O.; Scharpach, W.; Sijen, J.; Junghans, C.; Brown, J.; Ruiz, F. Z.; Renaud, N.; Wehner, J.; Baumeier, B. Excited-state electronic structure of molecules using many-body Green's functions: Quasiparticles and electron-hole excitations with VOTCA-XTP. *J. Chem. Phys.* **2020**, *152*, 114103.
- (97) Liu, C.; Kloppenburg, J.; Yao, Y.; Ren, X.; Appel, H.; Kanai, Y.; Blum, V. All-electron ab initio Bethe-Salpeter equation approach to neutral excitations in molecules with numeric atom-centered orbitals. *J. Chem. Phys.* **2020**, *152*, 044105.
- (98) Loos, P.-F.; Scemama, A.; Duchemin, I.; Jacquemin, D.; Blase, X. Pros and Cons of the Bethe-Salpeter Formalism for Ground-State Energies. *J. Phys. Chem. Lett.* **2020**, *11*, 3536–3545.
- (99) Wang, X.; Tom, R.; Liu, X.; Congreve, D. N.; Marom, N. An energetics perspective on why there are so few triplet-triplet annihilation emitters. *J. Mater. Chem. C* **2020**, *8*, 10816–10824.
- (100) Kehry, M.; Franzke, Y. J.; Holzer, C.; Klopper, W. Quasirelativistic two-component core excitations and polarisabilities from a damped-response formulation of the Bethe-Salpeter equation. *Mol. Phys.* **2020**, *118*, No. e1755064.
- (101) Patterson, C. H. Excited states of molecular and crystalline acetylene: application of TDHF and BSE via density fitting methods. *Mol. Phys.* **2021**, *119*, No. e1792568.
- (102) Grupe, M.; Boden, P.; Di Martino-Fumo, P.; Gui, X.; Bruschi, C.; Israil, R.; Schmitt, M.; Nieger, M.; Gerhards, M.; Klopper, W.; Riehn, C.; Bizzarri, C.; Diller, R. Time-Resolved Spectroscopy and Electronic Structure of Mono- and Dinuclear Pyridyl-Triazole/DPEPhos-Based Cu(I) Complexes. *Chem.—Eur. J.* **2021**, *27*, 15252–15271.
- (103) Holzer, C.; Pausch, A.; Klopper, W. The GW/BSE Method in Magnetic Fields. *Front. Chem.* **2021**, *9*, 746162.
- (104) Hashemi, Z.; Leppert, L. Assessment of the Ab Initio Bethe-Salpeter Equation Approach for the Low-Lying Excitation Energies of Bacteriochlorophylls and Chlorophylls. *J. Phys. Chem. A* **2021**, *125*, 2163–2172.
- (105) de Queiroz, T. B.; de Figueroa, E. R.; Coutinho-Neto, M. D.; Maciel, C. D.; Tapavicza, E.; Hashemi, Z.; Leppert, L. First principles theoretical spectroscopy of methylene blue: Between limitations of time-dependent density functional theory approximations and its realistic description in the solvent. *J. Chem. Phys.* **2021**, *154*, 044106.
- (106) Yao, Y.; Golze, D.; Rinke, P.; Blum, V.; Kanai, Y. All-Electron BSE@GW Method for K-Edge Core Electron Excitation Energies. *J. Chem. Theory Comput.* **2022**, *18*, 1569–1583.
- (107) Wilhelm, J.; Golze, D.; Talirz, L.; Hutter, J.; Pignedoli, C. A. Toward GW Calculations on Thousands of Atoms. *J. Phys. Chem. Lett.* **2018**, *9*, 306–312.
- (108) Fujita, T.; Noguchi, Y.; Hoshi, T. Charge-transfer excited states in the donor/acceptor interface from large-scale GW calculations. *J. Chem. Phys.* **2019**, *151*, 114109.
- (109) Kim, M.; Martyna, G. J.; Ismail-Beigi, S. Complex-time shredded propagator method for large-scale GW calculations. *Phys. Rev. B* **2020**, *101*, 035139.

- (110) Förster, A.; Visscher, L. Low-Order Scaling G0W0 by Pair Atomic Density Fitting. *J. Chem. Theory Comput.* **2020**, *16*, 7381–7399.
- (111) Wilhelm, J.; Seewald, P.; Golze, D. Low-scaling GW with benchmark accuracy and application to phosphorene nanosheets. *J. Chem. Theory Comput.* **2021**, *17*, 1662–1677.
- (112) Duchemin, I.; Blase, X. Cubic-Scaling All-Electron GW Calculations with a Separable Density-Fitting Space-Time Approach. *J. Chem. Theory Comput.* **2021**, *17*, 2383–2393.
- (113) Fujita, T.; Noguchi, Y. Fragment-Based Excited-State Calculations Using the GW Approximation and the Bethe–Salpeter Equation. *J. Phys. Chem. A* **2021**, *125*, 10580–10592.
- (114) Neuhauser, D.; Gao, Y.; Arntsen, C.; Karshenas, C.; Rabani, E.; Baer, R. Breaking the theoretical scaling limit for predicting quasiparticle energies: The stochastic GW approach. *Phys. Rev. Lett.* **2014**, *113*, 076402.
- (115) Vlček, V.; Rabani, E.; Neuhauser, D.; Baer, R. Stochastic GW Calculations for Molecules. *J. Chem. Theory Comput.* **2017**, *13*, 4997–5003.
- (116) Vlček, V.; Li, W.; Baer, R.; Rabani, E.; Neuhauser, D. Swift GW beyond 10,000 electrons using sparse stochastic compression. *Phys. Rev. B* **2018**, *98*, 075107.
- (117) Weng, G.; Vlček, V. Efficient treatment of molecular excitations in the liquid phase environment via stochastic many-body theory. *J. Chem. Phys.* **2021**, *155*, 054104.
- (118) Hybertsen, M. S.; Louie, S. G. First-principles theory of quasiparticles: Calculation of band gaps in semiconductors and insulators. *Phys. Rev. Lett.* **1985**, *55*, 1418–1421.
- (119) Hybertsen, M. S.; Louie, S. G. Electron correlation in semiconductors and insulators: Band gaps and quasiparticle energies. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1986**, *34*, 5390.
- (120) Bruneval, F.; Marques, M. Benchmarking the starting points of the GW approximation for molecules. *J. Chem. Theory Comput.* **2013**, *9*, 324–329.
- (121) Bruneval, F.; Hamed, S. M.; Neaton, J. B. A systematic benchmark of the ab initio Bethe–Salpeter equation approach for low-lying optical excitations of small organic molecules. *J. Chem. Phys.* **2015**, *142*, 244101.
- (122) Knight, J. W.; Wang, X.; Gallandi, L.; Dolgounitcheva, O.; Ren, X.; Ortiz, J. V.; Rinke, P.; Körzdörfer, T.; Marom, N. Accurate Ionization Potentials and Electron Affinities of Acceptor Molecules III: A Benchmark of GW Methods. *J. Chem. Theory Comput.* **2016**, *12*, 615–626.
- (123) Caruso, F.; Dauth, M.; van Setten, M. J.; Rinke, P. Benchmark of GW Approaches for the GW100 Test Set. *J. Chem. Theory Comput.* **2016**, *12*, 5076–5087.
- (124) Loos, P. F.; Comin, M.; Blase, X.; Jacquemin, D. Reference Energies for Intramolecular Charge-Transfer Excitations. *J. Chem. Theory Comput.* **2021**, *17*, 3666–3686.
- (125) Hüser, F.; Olsen, T.; Thygesen, K. S. Quasiparticle GW calculations for solids, molecules, and two-dimensional materials. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2013**, *87*, 235132.
- (126) Nakashima, T.; Raebiger, H.; Ohno, K. Normalization of exact quasiparticle wave functions in the Green's function method guaranteed by the Ward identity. *Phys. Rev. B* **2021**, *104*, L201116.
- (127) Faleev, S. V.; van Schilfgaarde, M.; Kotani, T. All-electron self-consistent GW approximation: Application to Si, MnO, and NiO. *Phys. Rev. Lett.* **2004**, *93*, 126406.
- (128) van Schilfgaarde, M.; Kotani, T.; Faleev, S. Quasiparticle self-consistent GW theory. *Phys. Rev. Lett.* **2006**, *96*, 226402.
- (129) Kotani, T.; van Schilfgaarde, M.; Faleev, S. V. Quasiparticle self-consistent GW method: A basis for the independent-particle approximation. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2007**, *76*, 165106.
- (130) Ismail-Beigi, S. Justifying quasiparticle self-consistent schemes via gradient optimization in Baym-Kadanoff theory. *J. Phys. Condens. Matter* **2017**, *29*, 385501.
- (131) Förster, A.; Visscher, L. Exploring the statically screened G3W2 correction to the GW self-energy: Charged excitations and total energies of finite systems. *Phys. Rev. B* **2022**, *105*, 125121.
- (132) Kutepov, A. L. Self-consistent GW method: O(N) algorithm for polarizability and self energy. *Comput. Phys. Commun.* **2020**, *257*, 107502.
- (133) Förster, A.; Visscher, L. Low-Order Scaling Quasiparticle Self-Consistent GW for Molecules. *Front. Chem.* **2021**, *9*, 736591.
- (134) Li, J.; Olevano, V. Bethe–Salpeter equation insights into the photo-absorption function and exciton structure of chlorophyll a and b in light-harvesting complex II. *J. Photochem. Photobiol., B* **2022**, *232*, 112475.
- (135) Luttinger, J. M.; Ward, J. C. Ground-state energy of a many-fermion system. II. *Phys. Rev.* **1960**, *118*, 1417–1427.
- (136) Romaniello, P.; Sangalli, D.; Berger, J. A.; Sottile, F.; Molinari, L. G.; Reining, L.; Onida, G. Double excitations in finite systems. *J. Chem. Phys.* **2009**, *130*, 044108.
- (137) Layzer, A. J. Properties of the one-particle green's function for nonuniform many-fermion systems. *Phys. Rev.* **1963**, *129*, 897–907.
- (138) Sham, L. J.; Kohn, W. One-particle properties of an inhomogeneous interacting electron gas. *Phys. Rev.* **1966**, *145*, 561–567.
- (139) Maggio, E.; Kresse, G. Correlation energy for the homogeneous electron gas: Exact Bethe–Salpeter solution and an approximate evaluation. *Phys. Rev. B* **2016**, *93*, 235113.
- (140) Sander, T.; Maggio, E.; Kresse, G. Beyond the Tamm–Dancoff approximation for extended systems using exact diagonalization. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2015**, *92*, 045209.
- (141) Förster, A.; Visscher, L. GW100: A Slater-Type Orbital Perspective. *J. Chem. Theory Comput.* **2021**, *17*, 5080–5097.
- (142) Davidson, E. R. The iterative calculation of a few of the lowest eigenvalues and corresponding eigenvectors of large real-symmetric matrices. *J. Comput. Phys.* **1975**, *17*, 87–94.
- (143) van Gisbergen, S. J.; Snijders, J. G.; Baerends, E. J. Implementation of time-dependent density functional response equations. *Comput. Phys. Commun.* **1999**, *118*, 119–138.
- (144) Krykunov, M.; Ziegler, T.; Lenthe, E. Hybrid density functional calculations of nuclear magnetic shieldings using slater-type orbitals and the zeroth-order regular approximation. *Int. J. Quantum Chem.* **2009**, *109*, 1676–1683.
- (145) Merlot, P.; Kjaergaard, T.; Helgaker, T.; Lindh, R.; Aquilante, F.; Reine, S.; Pedersen, T. B. Attractive electron–electron interactions within robust local fitting approximations. *J. Comput. Chem.* **2013**, *34*, 1486–1496.
- (146) Ihrig, A. C.; Wieferink, J.; Zhang, I. Y.; Ropo, M.; Ren, X.; Rinke, P.; Scheffler, M.; Blum, V. Accurate localized resolution of identity approach for linear-scaling hybrid density functionals and for many-body perturbation theory. *New J. Phys.* **2015**, *17*, 093020.
- (147) Wirz, L. N.; Reine, S. S.; Pedersen, T. B. On Resolution-of-the-Identity Electron Repulsion Integral Approximations and Variational Stability. *J. Chem. Theory Comput.* **2017**, *13*, 4897–4906.
- (148) Förster, A.; Franchini, M.; van Lenthe, E.; Visscher, L. A Quadratic Pair Atomic Resolution of the Identity Based SOS-AO-MP2 Algorithm Using Slater Type Orbitals. *J. Chem. Theory Comput.* **2020**, *16*, 875–891.
- (149) te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca Guerra, C.; van Gisbergen, S.; Snijders, J. G.; Ziegler, T. Chemistry with ADF. *J. Comput. Chem.* **2001**, *22*, 931–967.
- (150) Baerends, E.; Ziegler, T.; Atkins, A.; Autschbach, J.; Basergio, O.; Bashford, D.; Bérces, A.; Bickelhaupt, F.; Bo, C.; Boerrigter, P.; Cavallo, L.; Daul, C.; Chong, D.; Chulhai, D.; Deng, L.; Dickson, R.; Dieterich, J.; Ellis, D.; van Faassen, M.; Fan, L.; Fischer, T.; Förster, A.; Guerra, C. F.; Franchini, M.; Ghysels, A.; Giammona, A.; van Gisbergen, S.; Goetz, A.; Götz, A.; Groeneveld, J.; Gritsenko, O.; Grüning, M.; Gusarov, S.; Harris, F.; van den Hoek, P.; Hu, Z.; Jacob, C.; Jacobsen, H.; Jensen, L.; Joubert, L.; Kaminski, J.; van Kessel, G.; König, C.; Kootstra, F.; Kovalenko, A.; Krykunov, M.; van Lenthe, E.; McCormack, D.; Michalak, A.; Mitoraj, M.; Morton, S.; Neugebauer, J.; Nicu, V.; Noodleman, L.; Osinga, V.; Patchkovskii, S.; Pavanello,

- M.; Peeples, C.; Philipsen, P.; Post, D.; Pye, C.; Ramanantoanina, H.; Ramos, P.; Ravenek, W.; Reimann, M.; Rodríguez, J.; Ros, P.; Rüger, R.; Schipper, P.; Schlüns, D.; van Schoot, H.; Schreckenbach, G.; Seldenthuis, J.; Seth, M.; Snijders, J.; Solà, M.; Stener, M.; Swart, M.; Swerhone, D.; Tognetti, V.; te Velde, G.; Vernooijs, P.; Versluis, L.; Visscher, L.; Visser, O.; Wang, F.; Wesolowski, T.; van Wezenbeek, E.; Wiesenekker, G.; Wolff, S.; Woo, T.; Yakovlev, A. *ADF2022.1, Locally Modified Development Version*, 2022.
- (151) Van Lenthe, E.; Baerends, J. E. Optimized Slater-type basis sets for the elements 1–118. *J. Comput. Chem.* **2003**, *24*, 1142–1156.
- (152) Umena, Y.; Kawakami, K.; Shen, J. R.; Kamiya, N. Crystal structure of oxygen-evolving photosystem II at a resolution of 1.9 Å. *Nature* **2011**, *473*, 55–60.
- (153) For instance, changing the cut-off for the inclusion of the particle-hole states from 1.5 to 2.0 Ha changes each of the lowest three excitation energies of monomers by less than 10 meV.
- (154) Lenthe, E.; Baerends, E. J.; Snijders, J. G. Relativistic regular two-component hamiltonians. *J. Chem. Phys.* **1993**, *99*, 4597.
- (155) van Lenthe, E.; Baerends, E. J.; Snijders, J. G. Relativistic total energy using regular approximations. *J. Chem. Phys.* **1994**, *101*, 9783–9792.
- (156) van Lenthe, E.; Snijders, J. G.; Baerends, E. J. The zero-order regular approximation for relativistic effects: The effect of spin-orbit coupling in closed shell molecules. *J. Chem. Phys.* **1996**, *105*, 6505–6516.
- (157) Belić, J.; Förster, A.; Menzel, J. P.; Buda, F.; Visscher, L. Automated assessment of redox potentials for dyes in dye-sensitized photoelectrochemical cells. *Phys. Chem. Chem. Phys.* **2022**, *24*, 197–210.
- (158) Klamt, A.; Schüürmann, G. COSMO: A new approach to dielectric screening in solvents with explicit expressions for the screening energy and its gradient. *J. Chem. Soc. Perkin Trans.* **1993**, *2*, 799–805.
- (159) Klamt, A. Conductor-like screening model for real solvents: A new approach to the quantitative calculation of solvation phenomena. *J. Phys. Chem.* **1995**, *99*, 2224–2235.
- (160) Klamt, A.; Jonas, V. Treatment of the outlying charge in continuum solvation models. *J. Chem. Phys.* **1996**, *105*, 9972–9981.
- (161) Pye, C. C.; Ziegler, T. An implementation of the conductor-like screening model of solvation within the Amsterdam density functional package. *Theor. Chem. Acc.* **1999**, *101*, 396–408.
- (162) van Setten, M. J.; Caruso, F.; Sharifzadeh, S.; Ren, X.; Scheffler, M.; Liu, F.; Lischner, J.; Lin, L.; Deslippe, J. R.; Louie, S. G.; Yang, C.; Weigend, F.; Neaton, J. B.; Evers, F.; Rinke, P. GW100: Benchmarking G0W0 for Molecular Systems. *J. Chem. Theory Comput.* **2015**, *11*, 5665–5687.
- (163) Stuke, A.; Kunkel, C.; Golze, D.; Todorović, M.; Margraf, J. T.; Reuter, K.; Rinke, P.; Oberhofer, H. Atomic structures and orbital energies of 61,489 crystal-forming organic molecules. *Sci. Data* **2020**, *7*, 58.
- (164) Bruneval, F.; Maliyov, I.; Lapointe, C.; Marinica, M.-C. Extrapolating unconverted GW energies up to the complete basis set limit with linear regression. *J. Chem. Theory Comput.* **2020**, *16*, 4399–4407.
- (165) Gruber, E.; Kjær, C.; Nielsen, S. B.; Andersen, L. H. Intrinsic Photophysics of Light-harvesting Charge-tagged Chlorophyll a and b Pigments. *Chem.—Eur. J.* **2019**, *25*, 9153–9158.
- (166) Riplinger, C.; Sandhoefer, B.; Hansen, A.; Neese, F. Natural triple excitations in local coupled cluster calculations with pair natural orbitals. *J. Chem. Phys.* **2013**, *139*, 134101.
- (167) Riplinger, C.; Neese, F. An efficient and near linear scaling pair natural orbital based local coupled cluster method. *J. Chem. Phys.* **2013**, *138*, 034106.
- (168) Dutta, A. K.; Neese, F.; Izsák, R. Towards a pair natural orbital coupled cluster method for excited states. *J. Chem. Phys.* **2016**, *145*, 034102.
- (169) Dutta, A. K.; Nooijen, M.; Neese, F.; Izsák, R. Automatic active space selection for the similarity transformed equations of motion coupled cluster method. *J. Chem. Phys.* **2017**, *146*, 074103.
- (170) Dutta, A. K.; Saitow, M.; Demoulin, B.; Neese, F.; Izsák, R. A domain-based local pair natural orbital implementation of the equation of motion coupled cluster method for electron attached states. *J. Chem. Phys.* **2019**, *150*, 164123.
- (171) Bruneval, F.; Rangel, T.; Hamed, S. M.; Shao, M.; Yang, C.; Neaton, J. B. MOLGW 1: Many-body perturbation theory software for atoms, molecules, and clusters. *Comput. Phys. Commun.* **2016**, *208*, 149–161.
- (172) Zamzam, N.; van Thor, J. J. Excited State Frequencies of Chlorophyll f and Chlorophyll a and Evaluation of Displacement through Franck-Condon Progression Calculations. *Molecules* **2019**, *24*, 1–15.
- (173) Lange, M. F.; Berkelbach, T. C. On the Relation between Equation-of-Motion Coupled-Cluster Theory and the GW Approximation. *J. Chem. Theory Comput.* **2018**, *14*, 4224–4236.
- (174) Ranasinghe, D. S.; Margraf, J. T.; Perera, A.; Bartlett, R. J. Vertical valence ionization potential benchmarks from equation-of-motion coupled cluster theory and QTP functionals. *J. Chem. Phys.* **2019**, *150*, 074108.
- (175) Loos, P. F.; Scemama, A.; Blondel, A.; Garniron, Y.; Caffarel, M.; Jacquemin, D. A Mountaineering Strategy to Excited States: Highly Accurate Reference Energies and Benchmarks. *J. Chem. Theory Comput.* **2018**, *14*, 4360–4379.
- (176) Mattuck, R. D. *A Guide to Feynman Diagrams in the Many-Body Problem*, 2nd ed.; Dover Publications Inc.: New York, 1992.
- (177) Nguyen, B. D.; Chen, G. P.; Agee, M. M.; Burrow, A. M.; Tang, M. P.; Furche, F. Divergence of Many-Body Perturbation Theory for Noncovalent Interactions of Large Molecules. *J. Chem. Theory Comput.* **2020**, *16*, 2258–2273.
- (178) Milne, B. F.; Kjaer, C.; Houmøller, J.; Stockett, M. H.; Toker, Y.; Rubio, A.; Nielsen, S. B. On the exciton coupling between two chlorophyll pigments in the absence of a protein environment: Intrinsic effects revealed by theory and experiment. *Angew. Chem., Int. Ed.* **2016**, *55*, 6248–6251.
- (179) Milne, B. F.; Toker, Y.; Rubio, A.; Nielsen, S. B. Unraveling the intrinsic color of chlorophyll. *Angew. Chem., Int. Ed.* **2015**, *54*, 2170–2173.
- (180) Bruneval, F. Optimized virtual orbital subspace for faster GW calculations in localized basis. *J. Chem. Phys.* **2016**, *145*, 234110.
- (181) Riemelmoser, S.; Kaltak, M.; Kresse, G. Plane wave basis set correction methods for RPA correlation energies. *J. Chem. Phys.* **2020**, *152*, 134103.
- (182) Loos, P. F.; Pradines, B.; Scemama, A.; Giner, E.; Toulouse, J. Density-Based Basis-Set Incompleteness Correction for GW Methods. *J. Chem. Theory Comput.* **2020**, *16*, 1018–1028.
- (183) Cho, Y.; Bintrim, S. J.; Berkelbach, T. C. Simplified GW/BSE Approach for Charged and Neutral Excitation Energies of Large Molecules and Nanomaterials. *J. Chem. Theory Comput.* **2022**, *18*, 3438–3446.
- (184) Tirimbò, G.; De Vries, X.; Weijtens, C. H.; Bobbert, P. A.; Neumann, T.; Coehoorn, R.; Baumeier, B. Quantitative predictions of photoelectron spectra in amorphous molecular solids from multiscale quasiparticle embedding. *Phys. Rev. B* **2020**, *101*, 035402.
- (185) Löwdin, P. O. Group algebra, convolution algebra, and applications to quantum mechanics. *Rev. Mod. Phys.* **1967**, *39*, 259–287.