Quasiparticle Self-Consistent $GW$-Bethe-Salpeter Calculations of the Low-Lying Excitations of the Photosystem II Reaction Center

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Abstract

The $GW$-Bethe-Salpeter Equation (BSE) method is promising for calculating the low-lying excited 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 self-consistency in the eigenvalues only leads to an unfaithful description of certain excitonic states for Chlorophyll dimers while the $qsGW$-BSE excitation energies are in excellent agreement with experiment. We use the new implementation to calculate the lowest excitation energies of the six chromophores of the photosystem II (PSII) reaction center (RC) with nearly 2000 correlated electrons in total. Primary charge separation in the PSII RC occurs along the D1 branch via initial formation of Chl$_{D1}^+$ -Pheo$_{D1}^-$ and subsequent hole transfer leading to P$_{D1}^+$ -Pheo$_{D1}^-$. We find the Chl$_{D1}^+$ -P$_{D1}^-$ charge transfer (CT) state to be lowest excited
state, but do not observe the \( \text{Chl}_{D1}^+ - \text{Pheo}_{D1}^- \) CT state at low energy. This is most likely to the neglect of the protein environment. Notwithstanding this discrepancy, our results are in closer agreement to experiment than the ones of previous calculations based on range-separated hybrid kernels which only predicted local excitations among the lowest excited states of the PSII RC.

1 Introduction

The absorption of photons by a molecule or a material upon interaction 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.\(^4\) The RC comprises six chlorin molecules, a "special pair",\(^5,6\) of two Chlorophyll \( a \) (chla) molecules (\( \text{P}_{D1} \) and \( \text{P}_{D2} \)), flanked by two more chla (\( \text{Chl}_{D1} \) and \( \text{Chl}_{D2} \)) and two Pheophytin (\( \text{Pheo}_{D1} \) and \( \text{Pheo}_{D2} \)) 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.

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 range-separated hybrid (RSH) exchange-correlation kernel.\(^7,10–14\) RSHs frequently offer good agreement with experiment for Chla monomers and dimers,\(^13,15,16\) but large deviations with respect to more advanced multi-configurational\(^10,17\) and wave-function based methods have also been ob-
To mitigate such errors, RSHs can be parametrized empirically for each system under investigation (as for example done in references in 19 and 20), but this makes them non-transferable and unreliable for general applications. More systematic parametrization procedures for range-separated functionals have been suggested as well 21–24 but these are labour-intensive and not readily available as ”black-box” procedures.

Turning to wave-function based methods for excited states, we find the second-order algebraic diagrammatic construction scheme (ADC(2)) 25,26 and coupled cluster 27–31 with approximate doubles (CC2) 32 easy to apply and reasonably cost-efficient. CC2 results are typically in good agreement with more involved methods like equation-of-motion (EOM) CC with singles and doubles (EOM-CCSD) or similarity-transformed (ST) EOM-CCSD. 33,34 For these methods we are aware of one study of a tetrameric model by Suomivuori et al. 38 using ADC(2) together with the spin-opposite-scaled 39 and reduced-virtual-space (RVS) 40 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. 14,41,42 This is potentially possible, but we note that most applications of wave-function based methods 16,18,43,44 focus on single chromophores. Utilizing subsystem methods 45–51 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 52–54. 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. 15,40,55 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. This quantity can be obtained from the interacting single-particle Green’s function $G_1$ and the electronic self-energy $\Sigma$, a non-local, non-Hermitian, and frequency dependent one-electron operator, via a Bethe-Salpeter equation (BSE). $G_1$ is obtained from a Dyson equation with $\Sigma$ as its kernel, while $\Sigma$ itself depends implicitly on the 2-particle Green’s function. 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. A popular example is the GW approximation (GWA), with the screened Coulomb interaction $W$ calculated within the random phase approximation (RPA). Typically, the Dyson equation for $G_1$ is solved within the GWA first. Only afterwards, 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. If only a few excitonic states are needed, one may thereby use computationally efficient iterative diagonalization techniques. This procedure is known as the GW-BSE method and is increasingly applied to compute the lowest electronically excited states of molecular systems.

For such applications, the GW part is typically the computational bottleneck of a GW-BSE calculation. 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, often producing results in excellent agreement with conventional GW implementations. 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 ($G_0W_0$). This procedure comes with the notable disadvantage that the outcome of such a calculation will heavily de-
pend on the choice of the underlying exchange-correlation (XC) functional. 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.

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. In QP self-consistent GW (qsGW), then only the low-frequency limit of the self-energy is considered, and the non-interacting $G_1$ closest to the GW $G_1$ is selected. While this approach has been shown to be more accurate than $G_0 W_0$ and evGW for a wide range of molecular systems, qsGW has until now rarely been used in molecular calculations. With only a few exceptions, low-order scaling GW algorithms only target the screened Coulomb interaction, since this requires only evaluation of the diagonal elements of the self-energy. The computational cost for obtaining the full self energy is 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. 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. 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. In section 3, we first contrast the qsGW method to evGW for monomers and then confirm the excellent agreement with experiment and other quantum chemical calculations for both methods. We then use the qsGW-BSE implementation to calculate the low-lying excitation of the hexameric complex. Finally, section 4 summarizes and concludes this work.
2 Theory

2.1 The GW-BSE formalism

The interacting \( n \)-particle Green’s functions corresponding to an \( N \)-electron system with ground state \( \Psi^{(N)}_0 \) are defined by

\[
G_n(1, \ldots 2n) = \left\langle \Psi^{(N)}_0 \right| \mathcal{T} \left[ \hat{\psi}^\dagger(1) \hat{\psi}(2) \ldots \hat{\psi}^\dagger(2n-1) \hat{\psi}(2n) \right] \left| \Psi^{(N)}_0 \right\rangle . \tag{1}
\]

Here, \( \mathcal{T} \) 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

\[
G_1^{(0)}(1, 2) = G_1^{(0)}(1, 2) + G_1^{(0)}(1, 3) \Sigma(3, 4) G_1(4, 2) , \tag{2}
\]

in which the self-energy operator \( \Sigma \) appears. In the following, integration over repeated indices is implied. The generalized susceptibility is defined as

\[
L(1, 2, 3, 4) = iG_2(1, 2, 3, 4) - iG_1(1, 2) G_1(3, 4) , \tag{3}
\]

and fulfills a BSE,

\[
L(1, 2, 3, 4) = L^{(0)}(1, 2, 3, 4) + L^{(0)}(1, 2, 6, 5) I(5, 7, 6, 8) L(8, 2, 7, 4) , \tag{4}
\]

where

\[
L^{(0)}(1, 2, 3, 4) = -iG_1(1, 4) G_1(2, 3) \tag{5}
\]
and \cite{134}

\[
I(1, 2, 3, 4) = i \frac{\delta \Sigma(1, 3)}{\delta G_1(4, 2)}. \tag{6}
\]

The local Hartree kernel is obtained by approximating \(\Sigma\) with the Hartee potential,

\[
\Sigma_H(1, 2) = v_H(1)\delta(1, 2) = -i\delta(1, 2) \int d3 \ v_c(1, 3)G_1(3, 3^+) , \tag{7}
\]

where \(v_c\) is the Coulomb potential and \(1^+ = \lim_{\eta \to 0^+}(r_1, \sigma_1, t_1 + \eta)\). Applied to (6) this gives

\[
\frac{\delta}{\delta G_1(4, 2)} \int d3 \ v_c(1, 3)G_1(3, 3^+) = v_c(1, 2)\delta(3, 4)\delta(3, 2) , \tag{8}
\]

and inserting (8) into (4), one then obtains

\[
P(1, 2) = P^{(0)}(1, 2) + P^{(0)}(1, 3)v_c(3, 4)P(4, 2) , \tag{9}
\]

with

\[
P(1, 2) = L(1, 2^+, 1^+, 2) \tag{10}
\]

the \(v_c\)-reducible density-density response function in the RPA and

\[
P^{(0)}(1, 2) = -iG(1, 2)G(2, 1) . \tag{11}
\]

\(P\) is related to the screened Coulomb interaction \(W\) by\cite{67}

\[
W(1, 2) = v_c(1, 2) + v_c(1, 3)P(3, 4)v_c(4, 2) , \tag{12}
\]

which can be used to define the \(GW\) self-energy,

\[
\Sigma^{(GW)}(1, 2) = v_H(1, 2) + iG(1, 2)W(1^+, 2) . \tag{13}
\]
Equations (2), (9) and (11)–(13) 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. We then have an effective single-particle problem and restricting the self-energy further to its static limit and transforming to the molecular orbital basis $\{\phi_n\}_{n=1...N}$ (in which the single-particle Hamiltonian is diagonal), we arrive at

$$
\sum_m \left\{ (\epsilon_n - \epsilon_n^{QP}) \delta_{nm} + \frac{1}{2} \left[ \Sigma^{(GW)}_{nm}(\epsilon_n) + \Sigma^{(GW)*}_{mn}(\epsilon_n) \right] \right\} \phi_n = 0 ,
$$

(14)

where the $\epsilon_n$ are the single-particle energies. Solving eqs. (9) and (11)–(14) self-consistently is known as the qs$GW$ approximation within the RPA.

After solving the qs$GW$ equations self-consistently, we can then use the zero-frequency limit of the self-energy (13) in (3) in (4). As it is typically done, we also set $\frac{\delta W}{\delta G} \approx 0$. This is referred to as the qs$GW$-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 for example ref. 137 or ref. 138 for detailed derivations),

$$
\begin{pmatrix}
A & B \\
-B & -A
\end{pmatrix}
\begin{pmatrix}
X \\
Y
\end{pmatrix}_S = \Omega_S
\begin{pmatrix}
X \\
Y
\end{pmatrix}_S .
$$

(15)

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

$$
A_{ia,jb} = 2v_{cia,jb} - W(\omega = 0)_{ijab} + \delta_{ab}\delta_{ij}(\epsilon_i^{QP} - \epsilon_a^{QP}) ,
$$

$$
B_{ia,jb} = 2v_{cia,jb} - W(\omega = 0)_{ajib} ,
$$

(16)
where we have chosen to reserve the labels $i,j,...$ for occupied and $a,b,...$ for virtual orbitals. The QP energies entering the equations are the ones from (14).

### 2.2 Implementation

For our implementation of the qs$GW$ methods we refer to our previous work.\textsuperscript{107,130,139} 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

$$
\phi_i(r) = \sum_{\mu} c_{i\mu} \chi_{\mu}(r),
$$

while all quantities appearing in (12) are expanded in a basis of auxiliary fit functions (auxiliary basis). We then switch to the particle-hole basis to solve (15), whereby the matrix elements in (16) are expanded in the basis of MOs.

Since 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

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

and we then use (12) to obtain $W(\omega = 0)$.

Replacing the matrix elements of the screened Coulomb interaction by the ones of the bare one in (16), and using the HF self-energy in (14), the TD-HF method is obtained. It is clear, that any solver which can be used to solve (15) in the TD-HF case, can also be used for $GW$-BSE. We use an extension of the Davidson algorithm\textsuperscript{140} originally proposed by Stratmann and Scuseria.\textsuperscript{73} It solves (14) by projecting the generalized problem

$$
(A - B)(A + B)(X + Y) = \Omega_S^2 (X + Y),
$$

9
on a sequence of orthonormal subspaces

\[ \text{span} \left\{ b_1^{(n)}, \ldots, b_k^{(n)} \right\}, \]  

(20)
in which (19) 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 141. For the matrix elements of the screened interaction in the \((n+1)\)th subspace iteration, we define a column in the subspace labeled by \( s_i, s_j, \ldots, s_a, s_b, \ldots \), respectively, as

\[ (A \pm B)^{(n+1)}_{s_i s_a} = \sum_{s_j, s_b} \left\{ -W(\omega = 0)_{s_a s_b, s_j s_i} \mp W(\omega = 0)_{s_a s_j, s_b s_i} \right\} b^{(n)}_{s_i s_a}. \]  

(21)

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 (21) in the basis of Slater functions and then transform to the subspace basis functions. For detailed working equations, we refer to appendix B.

A key element in our approach is to use Pair-atomic density fitting (PADF)107,142–146 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. 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 primary basis which is described in appendix C.

3 Computational Details

All calculations have been performed with a locally modified development version of ADF2022.1. The GW implementation is the same as outlined in refs. 107, 130, 139, except for the modification outlined in appendix C. For the hexameric unit of PSII, we used the structure from ref. 12 which is based on the experimental structure at 1.9 Å resolution by Umena et al. and where the positions of the Hydrogen atoms have been optimized using a semi-empirical model with all other coordinates frozen. Structures of the subunits have been then cut out of the larger structures without further optimizations. The structures can be found in the supporting information.

The lowest 12 eigenstates of (19) for the hexameric complex have been calculated using the DZ (double-ζ) basis set and Normal numerical quality with 12 imaginary time and frequency points each. For systems with up to \( n = 4 \) chromophores, we always calculate the lowest 3\( n \) eigenstates of (19), using TZP (triple-ζ + polarization) as primary basis set, Good numerical quality and 16 imaginary time and frequency points each. We also benchmarked the basis set dependence of the GW-BSE calculations using the larger TZ3P and QZ6P basis sets for Chla monomers in section 4.2. All qsGW-BSE calculations reported in table 2 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. In all calculations we terminate the sequence of subspace
iterations if all eigenvalues are converged within $10^{-5}$ Hartree ($0.27$ meV). In order to improve numerical stability and accelerate the convergence of the subspace iterations in the Davidson algorithm, we restrict the basis in which we solve the BSE to the subspace spanned by all particle-hole pairs with transition energies below 2 Hartree (1.5 Hartree for the tetramers). In agreement with earlier $GW$-BSE studies for such systems, 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.

We took into account scalar relativistic effects in the zeroth-order approximation. The threshold $\epsilon_s$ described in appendix C has been set to $5 \times 10^{-3}$. If not stated otherwise, in all $qsGW$ calculations we first perform a PBE0 calculation with 40 % exact exchange (PBEH40), which in our experience is a good preconditioner for $qsGW$ and leads to fast convergence. Aside from numerical inaccuracies, the final results are independent of this choice which we have verified in ref. and which we will verify also for the case of Chla in the next section. We also performed evGW calculations based on the LDA and PBEH40 functionals (evGW@LDA, evGW@PBEH40). We terminate the evGW calculations if the HOMO QP energy difference between two subsequent iterations falls below 3 meV. For $qsGW$, we terminate the calculations when the Frobenius norm of the difference between the density matrices of two subsequent iterations falls below $5 \times 10^{-9}$. In all KS calculations we set the threshold below which we set eigenvalues of the inverse of the overlap matrix to zero during the canonical orthonormalization procedure to $5 \times 10^{-3}$.

To compare our method to the RSH TD-DFT approach, we also performed calculations using the CAMY-B3LYP kernel using the TZP basis set and Good numerical quality. We thereby also investigated the effect of the protein matrix using the conductor like screening model (COSMO) as implemented in ADF. Following ref. we set the dielectric constant of the environment to a value of 4.0 which should approximately account for solvent and protein environment.
4 Results

![Different Chlorophyll a structures used in this work.](image)

4.1 Starting-point dependence

As discussed in the introduction, a major advantage of qsGW over evGW is that the former doesn’t depend on the choice of a DFT functional. To illustrate this, we report here vertical excitation energies (VEE) for qsGW and evGW for the M82 structure in figure 1 with four different starting points, LDA, PBE, HF and PBEH40. 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. 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 $Q_y$ excitations 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. 101. Also, the results are in good agreement with qsGW. However, since 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.

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

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

4.2 Basis Set Errors

Table 2: VEEs for M70 and M82 with different basis sets for qsGW-BSE and evGW@LDA-BSE. The values in the last row denote the differences in VEEs calculated with the TZP$^{150}$ and QZ6P$^{139}$ basis sets. All values are in eV.

| Basis Set | M70 $Q_y$ | M70 $Q_x$ | M82 $Q_y$ | M82 $Q_x$ | M70 $B$ | M82 $B$ | M70 $Q_y$ | M70 $Q_x$ | M82 $B$ | M82 $B$ |
|-----------|-----------|-----------|-----------|-----------|---------|---------|-----------|-----------|---------|---------|
| TZP       | 1.74      | 1.93      | 2.68      | 1.76      | 1.94    | 2.71    | 1.72      | 1.98      | 2.84    | 1.74    | 2.00 |
| TZ3P      | 1.77      | 1.96      | 2.72      | 1.79      | 1.98    | 2.76    | 1.72      | 1.98      | 2.84    | 1.73    | 1.97 |
| QZ6P      | 1.71      | 1.94      | 2.64      | 1.74      | 1.92    | 2.68    | 1.71      | 1.96      | 2.80    | 1.71    | 1.96 |
| $\Delta_{TQ}$ | 0.03 | -0.01 | 0.04 | 0.02 | 0.02 | 0.03 | 0.01 | 0.02 | 0.04 | 0.03 | 0.04 |

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.$^{160}$ For orbital energy differences which are entering the BSE, the situation is much better since the basis set error for the QP energies usually have the same sign.$^{161}$ In Table 2 we compare the lowest excitation energies calculated with different basis
sets for the two different Chla monomers shown in figure [1]. For evGW and qsGW the QZ6P excitation energies are only slightly lower than the TZP ones, indicating that also with the smaller basis set the $Q_y$ excitation energies are almost converged. These errors are certainly smaller than other sources of error in our calculations like inaccuracies of the computational methods to calculate the VEEs or error due to the employed structures. 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 Experiment and different ab-initio Calculations

Table 3: VEEs for Chla calculated with different quantum chemical methods for two different gas-phase optimized structures and experimental reference data. All values are in eV.

| Method | $Q_y$ (eV) | $Q_x$ (eV) | $B$ (eV) | $\Delta Q_y - Q_x$ (eV) |
|--------|-----------|-----------|---------|------------------------|
| 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-BSE | 1.97 | 2.29 | 3.15 | 0.32 |
| evGW@PBEH40-BSE | 1.98 | 2.29 | 3.15 | 0.31 |
| evGW@LDA-BSE | 1.94 | 2.20 | 3.01 | 0.26 |
| CAMY-B3LYP-TD-DFT | 1.94 | 2.23 | 3.08 | 0.29 |
| 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 |

We first assess the accuracy of qsGW-BSE by comparison to experimental gas-phase data for Chla by Gruber et al. [163]. For the comparison of the calculated excitation energies to experimental data, the vertical excitation energy (VEE) needs to be distinguished from the band maximum. The latter is directly obtained from experimental spectra, while the former corresponds to the poles of the generalized susceptibilities we are calculating here. To facilitate the comparison between the theoretical and experimental values we also list
the VEEs which have recently been extracted from the experimental spectrum by Sirohiwal et al.\textsuperscript{43} Different calculated values alongside the experimental values for Chla are shown in table 3. The domain based local pair-natural orbital\textsuperscript{164,165} (DLPNO)-STEOM-CCSD\textsuperscript{166–168} results are taken from ref. \textsuperscript{43} while the evGW@LDA-BSE/6-311++G(2d,2p) results calculated using MOLGW\textsuperscript{169} are by Hashemi and Leppert.\textsuperscript{101} 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.\textsuperscript{43} (referred to as St1 in the following), while the other has been optimized by Hashemi and Leppert using B3LYP/def2-TZVP (St2 in the following). For an unbiased comparison, it is important to use exactly the same structures in all calculations.

We performed evGW@LDA-BSE calculations for both structures. Our results for St1 are consistently around 0.1 eV lower than the ones for St2. This illustrates the large influence of small changes in structural parameters on the final excitation energies. We believe St1 to be more accurate, since dispersion interactions often play an important role for the structure of organic molecules and it is known that B3LYP usually does not describe them correctly.\textsuperscript{170} For St2, 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 perfect agreement between both implementations.

All evGW results agree very well with qsGW also for Chla. Interestingly, all GW-BSE and CAMY-B3LYP results for the St1 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 \textit{GW}.\textsuperscript{171} QP approximations to \textit{GW} approximate the effect of these diagrams instead by neglecting the
vertex. The diagrams contained in GW are not a subset of the ones contained in EOM-CCSD but only of the ones contained in EOM-CCSDT. Accounting for triples (at least to some extent) is known to be of high importance for the reliable description of charged and neutral excitations. 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. 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 an MP2 calculation which is not always reliable for systems with strongly screened electron-electron interactions.

Table 4: The two $Q_y$ excitation energies for a Chla dimer. The gas-phase optimized structure and the RVS-LT-SOS-ADC(2) reference values have been taken from Suomivuori et al. All values are in eV.

| kernel                  | $\Omega_1$ | $\Omega_2$ | $\Omega_3$ | $\Omega_4$ | $\Omega_5$ | $\Omega_6$ |
|-------------------------|------------|------------|------------|------------|------------|------------|
| evGW@LDA                | 1.87       | 1.88       | 1.90       | 1.90       | 2.72       | 2.75       |
| evGW@PBEH40             | 1.92       | 1.95       | 2.09       | 2.11       | 2.84       | 2.93       |
| qsGW                    | 1.89       | 1.92       | 2.07       | 2.10       | 2.83       | 2.92       |
| CAMY-B3LYP              | 2.12       | 2.15       | 2.29       | 2.32       | 2.63       | 2.76       |
| RVS-LT-SOS-ADC(2)       | 2.04       | 2.06       |            |            |            |            |
| exp.                    |            |            |            |            | 1.94       |            |

In table 4 we also show GW-BSE results for a model of the Chla dimer. The gas-phase structure, optimized at the B3LYP-D3/def2-SVP level of theory, as well as the RVS-LT-SOS-ADC(2) results have been taken from ref. RVS-LT-SOS-ADC(2) slightly overestimates the excitation energies compared to the experimental band maxima reported in table 3, while the GW-BSE results are again in excellent agreement with these values. In contrast to the case of the Chla monomer, CAMY-B3LYP overestimates the VEEs by far. Also, all methods overestimate the experimental excitonic splitting of 10-20 meV. Most strikingly, the VEEs $\Omega_3$ and $\Omega_4$ 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
Table 5: Characterization and comparison of the low-lying excited states of D108 calculated with $\text{evGW}@$LDA-BSE and $\text{evGW}@$PBEH40-BSE. The excitation energies $\Omega^{(0)}_S$ (in eV), the dominant coefficient of the corresponding eigenvector and the associated particle-hole transition, as well as the oscillator strength $f$.

| $\Omega^{(0)}_S$ | VEE | evGW@LDA character | weight | $f$ | VEE | evGW@PBEH40 character | weight | $f$ |
|-----------------|-----|---------------------|--------|-----|-----|-----------------------|--------|-----|
| $\Omega_1^{(0)}$ | 1.87 | 238 $\rightarrow$ 240 | 0.49 | 0.08 | 1.92 | 238 $\rightarrow$ 240 | 0.28 | 0.30 |
|                 |     |                     |        |      |     | 237 $\rightarrow$ 239 |        |      |
| $\Omega_2^{(0)}$ | 1.88 | 237 $\rightarrow$ 240 | 0.22 | 0.14 | 1.95 | 238 $\rightarrow$ 241 | 0.41 | 0.03 |
|                 |     | 237 $\rightarrow$ 239 | 0.17 |      |     | 237 $\rightarrow$ 239 | 0.34 |      |
| $\Omega_3^{(0)}$ | 1.90 | 236 $\rightarrow$ 239 | 0.38 | 0.13 | 2.09 | 235 $\rightarrow$ 239 | 0.53 | 0.04 |
| $\Omega_4^{(0)}$ | 1.90 | 237 $\rightarrow$ 240 | 0.37 | 0.00 | 2.11 | 236 $\rightarrow$ 240 | 0.49 | 0.03 |
|                 |     | 235 $\rightarrow$ 239 | 0.31 |      |     |                       |        |      |
| $\Omega_5^{(0)}$ | 2.72 | 238 $\rightarrow$ 239 | 0.51 | 0.37 | 2.84 | 238 $\rightarrow$ 239 | 0.56 | 0.24 |
| $\Omega_6^{(0)}$ | 2.75 | 237 $\rightarrow$ 239 | 0.27 | 0.14 | 2.93 | 237 $\rightarrow$ 240 | 0.31 | 0.20 |
|                 |     | 237 $\rightarrow$ 242 | 0.24 |      |     |                       |        |      |

Figure 2: Selected valence single-particle KS orbitals for D108 calculated using LDA and PBEH40.

compared in more detail in table 5 with the corresponding KS single-particle orbitals shown in figure 2. Comparison of the most important contributions to the eigenvector $|\mathbf{X}, \mathbf{Y}\rangle^T_1$ already shows that $\text{evGW}@$LDA-BSE predicts the lowest excitation to be localized on the
PD1 fragment, while in the evGW@PBEH40-BSE calculation it is delocalised 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 PD1, while it is localized on PD2 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 excitations, even when the eigenvalues are updated self-consistently.

Table 6: Comparison of the $Q_y$ excitation energies obtained with different methods and experimental values. All values are in eV.

|                | D108 | D140 | D164 |
|----------------|------|------|------|
| evGW@LDA       | 1.68 | 1.71 | 1.78 |
| evGW@PBEH40    | 1.69 | 1.77 | 1.71 |
| qsGW           | 1.69 | 1.71 | 1.71 |
| CAMY-B3LYP     | 1.93 | 1.95 | 1.94 |
| exp.           |      |      | 1.94 |

Comparison to the results for the M78 and M82 models in table 2 shows, that the VEEs for the non-optimized structures are about 0.2 eV lower. Since the VEEs for M70 and M82 are more or less similar, it is also clear that this difference is not due to differences in the structural model. We observe the same for different non-geometry optimized dimers, whose VEEs are shown in table 6. Geometry optimization blueshifts the VEEs for D108 by around 0.2 eV with respect to the crystal structure. Comparison to the VEEs for the M70 and M82 dimers (D140 and D164) again reveal only small changes in the VEEs among adding or cutting off ligands. Taking into account the redshift due to the protein and solvent environment of around 0.12 eV, our calculations based on the crystal structure therefore underestimate the true excitation energies by around 0.2-0.25 eV. This is course not surprising, since it is known, that the direct use of crystal structures can yield substantial errors.

In contrast to the GW-BSE VEEs, the CAMY-B3LYP-TD-DFT results for the crystal
structures are in excellent agreement with the available experimental gas-phase data.\[159,163,170\] In light of the factors just discussed, the excellent agreement of the CAMY-B3LYP-TD-DFT calculations is most likely due to an overestimation of the true VEEs (as shown in tables [4] and [3]) which then cancels with the errors due to inadequate geometries.

Comparing the different \(GW\)-BSE methods, we find that \(\text{evGW@PBEH40}\) and \(\text{qsGW}\) are always in close agreement, while the \(\text{evGW@LDA-BE}\) VEEs are typically a little higher. Overall, the results are in qualitative agreement to each other for D140. For D164, the splitting between both \(Q_y\) VEEs (\(\Delta Q_y - Q_y\)) calculated using the \(\text{evGW@PBEH40}\) and \(\text{qsGW}\) kernels are in good agreement. The value of 30-4m meV aligns better with experimental observations\[177\] and also the calculations of Suomivuori et al.\[38\]. However, as for the calculations based on the geometry optimized structure, there is again a discrepancy between the \(\text{evGW-BSE}\) results obtained for the LDA and PBEH40 starting points. With \(\Delta Q_y - Q_y = 0.08\) eV, \(\text{evGW@LDA}\) considerably overestimates the excitonic splitting and also the VEEs based on the LDA starting point are much higher than with the PBEH40 starting point.

### 4.4 Excited States of the Photosystem II Reaction Center

Table 7: The lowest \(\text{qsGW-BSE}\) excited states of the hexameric chromophore complex in the RC of PSII. The excitation energies \(\Omega^{(0)}\) (in eV), the dominant coefficients of the corresponding eigenvectors, as well as the oscillator strength \(f\) are shown. The corresponding orbitals are shown in figure 4.

| Character      | VEE  | transition | weight | \(f\)  |
|----------------|------|------------|--------|--------|
| \(\Omega_1^{(0)}\) | Pheo\(_{D2}\) → Pheo\(_{D2}\) | 1.89 | 948 → 954 | 0.51 | 0.24 |
| \(\Omega_2^{(0)}\) | \(\text{P}_{D1}\) → Pheo\(_{D1}\) | 1.91 | 946 → 953 | 0.51 | 0.28 |
| \(\Omega_3^{(0)}\) | Pheo\(_{D1}\) → \(\text{P}_{D1}\) | 1.96 | 947 → 952 | 0.46 | 0.17 |
| \(\Omega_4^{(0)}\) | \(\text{P}_{D2}\) → \(\text{P}_{D2}\) | 1.97 | 944 → 951 | 0.48 | 0.03 |

The most complete model of the PSII RC we consider in this work comprises six chromophores with 476 atoms in total. Its structure is shown in figure 3 together with the PBEH40/DZ frontier single-particle orbitals and the low-lying excitations are characterized.
Figure 3: Frontier single-particle KS orbitals (PBEH40/TZP) of the hexameric chromophore complex of the PSII RC.

in table 7. In our current implementation, using larger basis sets is complicated by the requirement to use large auxiliary fit sets which then leads to very large matrix representations of the RPA polarizability and the screened Coulomb interaction. As will be discussed in see section 4.5, storing them on disk and transferring them to the CPU is currently the bottleneck of our implementation. This complicates the calculation of the hexamer using the TZP basis set. Below, we will therefore also discuss results for tetramers for which the use of the TZP basis set was feasible.

The lowest two excited states are almost degenerate. The lowest one is a local $Q_y$ excitation on Pheo$_{D2}$. This is expected, since the lowest VEE of the isolated Pheophytin chromophore has been predicted to be lower than the one of Chla. The following state has pronounced CT character and corresponds to the transfer of an electron from P$_{D1}$ to Pheo$_{D1}$. The third and fourth excited state are nearly degenerate as well, but their is a considerable gap of 50 meV between the second and the third excited state. These states correspond to CT from Pheo$_{D1}$ to P$_{D1}$ and again to a local excitation on P$_{D2}$.

This is interesting for many reasons: First, Frankcombe et al calculated the low-lying
excited states of the same hexameric complex without explicit consideration of the protein matrix as in our study, but they used TD-DFT with a RSH kernel. They did not find any low-lying CT state which could be related to charge separation, which is in clear disagreement with time-resolved spectroscopic experiments\cite{41,42} showing 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 mixing in of low-lying CT states with pronounced Chl_{D1}^+ -Pheo_{D1}^- and Chl_{D1}^+ -P_{D1}^- character in calculations of excitation energies. In our model calculations, we only find the second type of CT. Both Sirohiwal et al.\cite{7} and Tamura et al.\cite{14} identified also the first CT state in recent computational studies and both studies explicitly included the protein environment on a molecular mechanical level. In ref.\cite{7} it was found that the protein environment is exclusively responsible for the unidirectional CT along the D1 branch and the occurrence of the Chl_{D1}^+ -Pheo_{D1}^- state. Therefore, the absence of the explicit protein environment in our work is most likely the reason why we do not observe this particular CT state.

Table 8: The four lowest qsGW-BSE excited states of the T329 (Pheo_{D1}-Chl_{D1}-P_{D1}-P_{D2}) and T328 (Chl_{D1}-P_{D1}-P_{D2}-Chl_{D2}) models: The excitation energies $\Omega^{(0)}$ (in eV), the dominant coefficients of the corresponding eigenvectors, as well as the oscillator strength $f$ are shown. The corresponding orbitals are shown in figure\cite{4}.

|         | T329            | T328            |
|---------|-----------------|-----------------|
|         | VEE transition  | weight          | VEE transition  | weight          |
| $\Omega_1^{(0)}$ | 1.70 658 $\rightarrow$ 663 | 0.67 0.33       | 1.73 664 $\rightarrow$ 666 | 0.48 0.33       |
| $\Omega_2^{(0)}$ | 1.75 659 $\rightarrow$ 662 | 0.80 0.33       | 1.77 662 $\rightarrow$ 665 | 0.36 0.36       |
| $\Omega_3^{(0)}$ | 1.76 657 $\rightarrow$ 661 | 0.53 0.02       | 1.81 663 $\rightarrow$ 668 | 0.69 0.34       |
| $\Omega_4^{(0)}$ | 1.79 656 $\rightarrow$ 660 | 0.49 0.24       | 1.93 661 $\rightarrow$ 667 | 0.79 0.23       |

Besides the neglect of the protein environment, the use of the DZ basis set is another weak point in the six-chromophore model. It is not unlikely that the lack of polarization functions favours local excitations and one might therefore expect that using a larger basis set the character of the excitations might be different. To check this, we report here the
results of calculations on tetrameric complexes using the much larger TZP basis set which we have already seen to give VEEs close to the complete basis set limit. The structures of these tetramers are shown in fig. 4 alongside with the relevant frontier single-particle orbitals. The model T328 abbreviates the complex Pheo$_{D1}$-Chl$_{D1}$-P$_{D1}$-P$_{D2}$ (since it contains 328 atoms) and T329 denotes the complex Pheo$_{D1}$-Chl$_{D1}$-P$_{D1}$-P$_{D2}$. The lowest four excitations for both systems are shown in table 8.

Similarly to the hexamer, the lowest excited state of T329 is a CT state from P$^{+}_{D2}$-Pheo$_{D1}^-$. Note, that the distinction between D1 and D2 is not necessarily meaningful in the absence of the explicit protein environment. Also, it was found in ref. 14 that an exciton can also form initially in the D2 branch which is then subsequently transferred to the D1 branch. Two aspects are of importance here: First, there is no indication of CT from Chl$_{D2}$ to Pheo$_{D1}$ among the first four excited states of T329, which also validates our results for the hexamer. We also repeated the calculations for T329 with the DZ basis set. With the much smaller basis set, the P$^{+}_{D2}$-Pheo$_{D1}^+$ CT is the energetically lowest state, followed by P$_{D2}^+$-Pheo$_{D1}^-$. Second, the P$_{D2}^+$-Pheo$_{D1}^-$ state is 30 meV lower in energy than the lowest excited state of
T328. The lowest two excited states of T328 are dominated by particle-hole transitions, with the hole located on the outer monomers (P$_{D1}$ and P$_{D1}$) and the particle located on the inner ones (Chl$_{D1}$ and Chl$_{D2}$), and the other way round for the next pair. This result is different from the one by Suomivuori et al. who found two of these excitations to be delocalized over the P$_{D1}$/P$_{D1}$ pair and the other two to be localized on Chl$_{D1}$ and Chl$_{D2}$, respectively. In conclusion, in the absence of the protein environment, the P$_{D1}$+/P$_{D2}$+-Pheo$_{D1}$ CT is the lowest excited state in the PSII RC, independent of the basis set.

4.5 Timings

Table 9: CPU times (in core hours) for the different steps of the qsGW-BSE calculations for D164 and T328. All calculations have been performed on an AMD Zen3 node with 64 CPUs and 256GB of memory. The GW and BSE timings are per iteration.

| N$_{atoms}$ | N$_{elec}$ | N$_{bas}$ | N$_{fit}$ | N$_{roots}$ | Iterations | CPU time |
|------------|-----------|----------|----------|-------------|------------|----------|
|            |           |          |          |             | qsGW       | BSE      | GW       | BSE       | total     |
| 329        | 1318      | 4242     | 41835    | 12          | 10         | 15       | 445      | 425       | 9232      |
| 476        | 1896      | 3084     | 44646    | 12          | 8          | 15       | 148      | 117       | 3030      |

Finally, we briefly comment on the computational time needed to perform these calculations. The CPU times for the GW-BSE calculations for one of the tetramers and the hexamer are given in table 9. The calculation for the tetramer can be performed in around 7200 core hours, i.e. around 4-5 days on 64 cores. The qsGW part of the calculation is approximately as expensive as the BSE part per iteration. Even though the hexamer has around 50 % more electrons than the tetramer, the calculation is three times faster. This is mostly due to the fact that most basis functions decay very fast with the distance from the atomic centers, so that the overlap of most pairs of basis functions can be neglected. For larger calculations, the bottleneck of the computation is the number of auxiliary fit functions N$_{fit}$ (more than 40,000 for the tetramer). The large auxiliary fit sets are necessary to guarantee numerical stability in the PADF approach and also in related techniques which rely on sparse transformation between matrices in primary and auxiliary basis.
each imaginary time and frequency point, a matrix of size $N_{fit} \times N_{fit} \approx 14$GB needs to be stored. In case of T329, this amounts to 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 transferring them to the CPU and back becomes very time-consuming.

5 Conclusions

We have calculated the low-lying excited states of the RC in PSII using $\text{qsGW}$-BSE. So far, $\text{GW}$-BSE calculations have been limited to rather small systems.\textsuperscript{87,94,101} 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 $\text{GW}$-BSE scheme,\textsuperscript{180} our implementation does not introduce any empirical approximations to the matrix elements of the BSE Hamiltonian. Provided a low-order scaling implementation of the $\text{GW}$ method and iterative solver for large eigenproblems is available, the proposed algorithm is easy to implement.

We calculated the 12 lowest excited states of the complete complex of six chromophores in the PSII RC with almost 2000 correlated electrons on the DZ level. Owing to the small basis set, the calculation could be performed in less than 2 days on a single compute node. We have also calculated the 12 lowest excited states of a tetrameric complex with around 1300 correlated electrons with a TZ + polarization basis set. With around 6 days of wall time, the latter calculation is far more expensive, even though the system is 50 % smaller. Low-order scaling implementations like ours which rely on sparsity in the primary basis usually do not scale well with the size of the basis set. Finite basis set correction techniques for many-body perturbation theory might therefore be a promising solution to circumvent this problem.\textsuperscript{162,181–183} Applications to larger systems with polarized basis sets are currently complicated by the requirement to store large matrices on disk. This problem could be
overcome by using a very large number of nodes which would enable us to keep them in
direct memory.

qsGW-BSE is a theoretically more rigorous variant of the GW-BSE method than evGW-
BSE, since it is independent of a mean-field reference calculation. 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 monomers\cite{100} and can
be seen as a major shortcoming of evGW-BSE. We therefore conclude, that self-consistency
in the eigenfunctions is decisive for a reliable description of the low-lying excitonic states of
large chromophoric complexes. qsGW-BSE results are in good agreement with experimental
VEEs in the gas phase, provided an optimized geometry is employed. When crystal structures
are used, qsGW-BSE underestimates the true VEEs by about 0.2 eV.

In contrast to previous results on the RSH level for the full hexameric complex\cite{11}, qsGW-
BSE predicts many low-lying CT states even in the absence of the protein environment,
which is in line with experimental observations\cite{111,112,113}. However, our current calculations
do not fully agree with experiment and previous calculations. It is known,\cite{7,14,41,42} that the
primary charge separation in the PSII RC occurs along the D1 branch via the Chl\textsubscript{D1}\textsuperscript{+} -
Pheo\textsubscript{D1}\textsuperscript{-} and Chl\textsubscript{D1}\textsuperscript{+} -P\textsubscript{D1}\textsuperscript{-} CT states. In our calculations, the Chl\textsubscript{D1}\textsuperscript{+} -P\textsubscript{D1}\textsuperscript{-} state is the
lowest one, but we could not identify the Chl\textsubscript{D1}\textsuperscript{+} -Pheo\textsubscript{D1}\textsuperscript{-} state. This is most likely due
to the neglect of the protein environment which plays a crucial role in the functionality of
the PSII RC.\cite{7} To take the explicit protein environment into account, it would be highly
desirable to interface our code with a molecular mechanics code, along the lines of previous
GW-BSE implementations\cite{88,93,95,96}.

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
Table 10: \(Q_y\) excitation for different Chla monomers and dimers calculated using TD-DFT@CAMY-B3LYP/TZP with and without implicit solvation. All values are in eV.

|       | exp. | M70 | M82 | D140 | D164 |
|-------|------|-----|-----|------|------|
| 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 |

|       | 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 |

effects and protein environment using a polarizable continuum model. The \(Q_y\) excitation energies calculated using CAMY-B3LYP-TD-DFT/TZP with and without implicit solvation are shown in table \([10]\). With in between 0.1 and 0.2 eV, the influence of the environment is not negligible. However, For the systems where we consider more than one excitation energy, all values are shifted by more or less the same amount, even though the results suggest that the environment reduces the excitonic splitting with respect to the vacuum. Our calculated electrochromatic shifts agree well with experimental values of about 0.12 eV.\([13]\) 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.

### 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. (21). Let us denote with the matrix \(K^{(\pm)}\), a column of \(A \pm B\) as defined in (21), 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 \(\mu, \nu, \kappa, \lambda\), auxiliary functions as \(\alpha, \beta, \gamma, \delta\) and atomic centers as \(A, B, C\ldots\). We also define the convention that \(\mu, \alpha \in A\), \(\nu, \beta \in B\), \(\kappa, \gamma \in C\) and \(\lambda, \delta \in D\), i.e. \(\mu\) and \(\alpha\)
are only labelling functions centered on atom $A$, and so on. The PADF expansion of the products of AOs can then be written as

\[
\chi_\mu(\mathbf{r})\chi_\nu(\mathbf{r}) = \begin{cases} 
\sum_{\beta \in B} b_{\mu\nu,\beta} f_\beta(\mathbf{r}) + \sum_{\alpha \in A} b_{\nu\mu,\alpha} f_\alpha(\mathbf{r}) & A \neq B \\
\frac{1}{2} \left( b_{\nu\mu,\alpha} + b_{\mu\nu,\alpha} \right) f_\alpha(\mathbf{r}) & A = B ,
\end{cases}
\]

where the factor of $1/2$ in case $A = B$ is introduced to facilitate evaluation with the same algorithm while avoiding double counting. Let us write (21) in the primary basis as

\[
K^{(\pm)}_{\mu\nu} = -\sum_{\kappa\lambda} b_{\kappa\lambda} W(\omega = 0)_{\mu\kappa\nu\lambda} \pm W(\omega = 0)_{\nu\kappa\mu\lambda} .
\]

Inserting (22), the contribution to $K^{(\pm)}$ for all atom pairs $(A,B)$ is

\[
K^{(\pm)AB} = K^{(\pm)AB, I} + K^{(\pm)AB, II} + K^{(\pm)AB, III} + K^{(\pm)AB, IV} ,
\]

where

\[
K^{(+)AB, III} = \left[ K^{(+)AB, II} \right]^T \\
K^{(-)AB, III} = -\left[ K^{(-)AB, II} \right]^T .
\]

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. Defining the intermediates

\[
I^{ABC}_{\mu\nu\gamma} = c_{\mu\nu\beta}^{AB} W(\omega = 0)_{\beta\gamma}^{BC} ,
\]

and

\[
F^{BAA}_{\nu\mu\alpha} = \sum_{\lambda} b_{\lambda\nu}^{DB} c_{\lambda\mu\alpha}^{DAA} .
\]
We can then write

\[ K^{\pm,AC,I}_{\mu k} = \sum_{\nu \lambda} \sum_{\alpha \gamma} b^{DB}_{\lambda \nu} c^{DAA}_{\lambda \mu \alpha} W(\omega = 0)_{\alpha \gamma} c^{BCC}_{\nu \kappa \gamma} \]

\[ = \sum_{\nu \alpha} F^{BAA}_{\nu \mu \alpha} I^{BCA}_{\nu \kappa \alpha} \]

\[ K^{\pm,AC,II}_{\mu k} = \sum_{\nu \lambda} \sum_{\alpha \beta} b^{DB}_{\lambda \nu} c^{DAA}_{\lambda \mu \alpha} W(\omega = 0)_{\alpha \beta} c^{CBB}_{\kappa \nu \beta} \]

\[ = \sum_{\nu \alpha} F^{BAA}_{\nu \mu \alpha} I^{CBA}_{\nu \kappa \alpha} \] (28)

\[ K^{\pm,AC,IV}_{\mu k} = \sum_{\nu \lambda} \sum_{\delta \beta} b^{DB}_{\lambda \nu} c^{ADD}_{\mu \lambda \delta} W(\omega = 0)_{\delta \beta} c^{CBB}_{\kappa \nu \beta} \]

\[ = \sum_{\lambda \delta} \sum_{\nu} b^{DB}_{\lambda \nu} I^{CBD}_{\nu \kappa \delta} b^{ADD}_{\mu \lambda \delta}, \]

where in the + case \( b \) is symmetric, and antisymmetric otherwise. These are the working equations with which (21) is implemented. They are similar to the ones for the self-energy, outlined in ref. [146].

C Elimination of diffuse functions from the primary basis

In addition to the usual canonical orthonormalization [156] during the SCF prior to the qsGW calculation 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 \( \mathbf{S} \),

\[ \mathbf{S} = \mathbf{U}^T \mathbf{\Lambda} \mathbf{U}. \] (29)
We then remove a column $u_i$ from the transformation matrix if the corresponding eigenvalue $\lambda_i$ is smaller than some predefined threshold $\epsilon_s$. We then define

$$V = UU^T,$$  \hspace{1cm} (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 (21) according to

$$K = V^TK'V,$$  \hspace{1cm} (31)

where $K'$ 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.

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**Supporting Information Available**

All structures used in this work.

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Graphical TOC Entry

Photosystem II reaction center

\[ P_D^1 \rightarrow P_{D1}^+ \]

qsGW-BSE calculation
(~2000 electrons):
First CT state

\[ \text{Pheo}_D \rightarrow \text{Pheo}_{D1} \]