Benchmarks of the \textit{ab initio} Bethe-Salpeter equation approach for the $Q_y$ and $Q_x$ excitations of bacteriochlorophylls and chlorophylls

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Bacteriochlorophyll and chlorophyll molecules are crucial building blocks of the photosynthetic apparatus in bacteria, algae, and plants. Embedded in transmembrane protein complexes, they are responsible for the primary processes of photosynthesis: excitation energy and charge transfer. Here, we use \textit{ab initio} many body perturbation theory within the GW approximation and Bethe-Salpeter equation (BSE) approach to calculate the electronic structure and optical excitations of bacteriochlorophylls $a$, $b$, $c$, $d$ and $e$ and chlorophylls $a$ and $b$. We systematically study the effects of structure, basis set size, partial self-consistency in the GW approach and the underlying exchange-correlation approximation. Furthermore, we compare our calculations with results from time-dependent density functional theory, and find that optical excitations calculated with $GW+BSE$ are in very good agreement with experimental data, on average underestimating the $Q_y$ and $Q_x$ excitations of the entire family of (bacterio)chlorophylls by less than 0.1 eV. Moreover, the $GW+BSE$ approach predicts the energy difference between the two excitations correctly, highlighting the potential of this method for the simulation of larger pigment complexes.

I. INTRODUCTION

Electronic excitations form the foundation of some of the most fundamental natural processes. For example, in photosynthesis, plants, algae and bacteria convert solar energy into chemical energy, utilizing a cascade of coupled energy and charge transfer excitations that are performed by pigment-protein complexes with very high quantum efficiency. Bacteriochlorophyll (BCL) and chlorophyll (CL) molecules are one of the most important building blocks of these pigment-protein complexes.\textsuperscript{[3]} They are responsible for the absorption and transfer of excitation energy, and for the charge separation necessary for establishing a proton gradient that eventually drives the synthesis of chemical energy in plants and bacteria.\textsuperscript{[4]} Accurately calculating the electronic structure and excitations of these molecules, is the prerequisite for understanding their interactions with each other and with the surrounding proteins and, consequently, energy and charge transfer in natural photosynthesis, from first principles.

In the field of finite organic and biological molecular systems, neutral excitations and optical spectra are predominantly calculated using time-dependent density functional theory (TDDFT). TDDFT can be used efficiently and with high accuracy even for large systems. In conjunction with model Hamiltonian approaches, TDDFT can be employed for the simulation of photosynthetic pigment-protein complexes.\textsuperscript{[5,6]} The accuracy of its approximations and implementations has been tested for a variety of biochromophores.\textsuperscript{[7,8]} However, TDDFT's standard approximations are inadequate for describing long-range charge transfer (CT) excitations and high-energy Rydberg states due to their incorrect asymptotic behavior. And while exchange-correlation (xc) functionals that contain long-range exact exchange, such as optimally-tuned range-separated hybrid functionals (OT-RSH) can be employed as a remedy in such cases\textsuperscript{[9]}, no universal \textit{ab initio} TDDFT approximation is yet available.

The \textit{ab initio} Bethe-Salpeter equation (BSE) approach, when rigorously based on many-body Green's function theory, is an alternative method to describe neutral excitations of correlated many-electron systems.\textsuperscript{[10]} It is based on a framework of charged excitation energies that correspond to electron addition and removal energies, and that are most frequently calculated within the GW approximation. The $GW+BSE$ approach has been shown to be successful in predicting the optical spectra of bulk solids and low-dimensional materials.\textsuperscript{[11,12]} In recent years it has also begun to be applied to finite systems, such as small molecules and larger molecular complexes,\textsuperscript{[13,14]} for which its accuracy has been shown to be comparable to single-reference wavefunction methods for both localized and CT excitations\textsuperscript{[15]}, at substantially reduced computational cost.

BCL and CL molecules constitute a family of substituted tetrapyrroles with varying absorption properties depending on conjugation and the number and nature of substitutions. CL $a$ and $b$ are present in plants and green algae, whereas green bacteria mostly rely on BCL $c$, $d$ and $e$ for excitation energy transfer, and BCL $a$ for concentrating excitations close to the reaction center of the photosynthetic unit.\textsuperscript{[16]} BCL $a$ is also the main pigment in purple bacteria, whose light harvesting apparatus and reaction center are among the most thoroughly studied natural light-harvesting systems.\textsuperscript{[23]} The optical excitation spectrum of BCL $a$ possesses two characteristic absorption bands: 1. The $Q_y$ band with excitation $Q_y$ at $\sim$1.6 eV with high oscillator strength and excitation $Q_x$ at $\sim$2.3 eV with lower oscillator strength, 2. The B (or Soret) band in the near ultraviolet.

In this article, we present a benchmark study of the \textit{ab initio} $GW+BSE$ approach for the $Q_y$ and $Q_x$ excitations of several members of the BCL and CL family, and the chemically closely related Bacteriochlorin molecule. We compare two

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different approaches for approximating the electronic self-energy $\Sigma = iG_W$: 1. $G_0W_0$, a one-shot method, in which the zeroth order Green’s function $G_0$ and screened Coulomb interaction $W_0$ are constructed from a DFT eigensystem and directly used to correct DFT eigenvalues perturbatively, 2. partially self-consistent $GW$ (ev$G_sW_s$), in which these eigenvalues are used to re-calculate $G$ and $W$ until self-consistency is reached. We compare our results to TDDFT calculations with the local density approximation (LDA), two global hybrid and an OT-RSH functional, with literature results using perturbation theory to second order in a restricted active space (RASPT2), and with experimental data. In order to elucidate the effect of structure on these excitations, we perform all calculations on two BCL structures from the literature and one geometry-optimized structure.

We find that, with partial self-consistency, even $GW$+BSE based on LDA results in excitations within 0.2 eV of experiment for BCL $a$, at the same time eliminating spurious CT excitations between Q$_x$ and Q$_y$ that TDDFT with LDA is known to produce. However, the energy and oscillator strengths of these excitations strongly depend on the structure used for these calculations. We explicitly demonstrate that, contrary to TDDFT and RASPT2, $GW$+BSE correctly predicts the energy difference between the two Q-band excitations, a crucial prerequisite for understanding the coupling of excitations in systems consisting of more than one pigment. Self-consistency in the $GW$ eigenvalues is shown to be sufficient to eliminate the dependence on the xc functional in the $GW$+BSE approach, and this is shown to be due to an improved description of charged excitations with the $GW$ method as compared to DFT with LDA or a global hybrid functional. Finally, we report Q$_x$ and Q$_y$ excitation energies for BCL $b$, $c$, $d$ and $e$ and for CL $a$ and $b$, which are in excellent agreement with experimental data and can serve as benchmark and reference for larger scale simulations.

The remainder of this article is structured as follows: In Section III, we will briefly review the $GW$+BSE approach, and report computational details and numerical convergence. In Section III, we will discuss the electronic structure and excitations of Bacteriochlorin and BCL $a$ and compare to experimental and theoretical literature results. Section III contains our results for BCL $b$, $c$, $d$ and $e$, and CL $a$, and $b$.

II. THEORETICAL BACKGROUND AND METHODOLOGY

A. The $GW$+BSE approach

In Green’s function-based many-body perturbation theory (MBPT), the calculation of charged excitations is based on knowledge of the exact interacting single-particle Green’s function $G$, that can in principle be computed from a set of self-consistent equations introduced by Hedin and Lundqvist, linking $G$ to the electronic self energy $\Sigma$, the screened Coulomb interaction $W$, the irreducible polarization $\chi$, and the vertex function $\Gamma$[14]. The zeroth-order expansion of Hedin’s equations, where $\Gamma = 1$, leads to the $GW$ approxima-

tion, in which the electronic self-energy $\Sigma = iG_W$[25]. Quasiparticle (QP) eigenvalues are obtained via approximate solution of the Dyson equation

$$\left[ -\frac{1}{2} \nabla^2 + V_{\text{ion}} + V_{\text{H}} + \Sigma(\epsilon_n^{\text{QP}}) \right] \epsilon_n^{\text{QP}} = \epsilon_n \epsilon_n^{\text{QP}}. \quad (1)$$

Here, $V_{\text{ion}}$ is the ionic (pseudo)potential, $V_{\text{H}}$ is the Hartree potential, and $\epsilon_n^{\text{QP}}$ and $\epsilon_n$ are QP and ground state energies, respectively.

The $GW$ approach is commonly used within a one-shot scenario, in which $G_0$ and $W_0$ are constructed from a generalized Kohn-Sham (gKS) eigensystem obtained from a preceding DFT calculation. We use the notation $G_0W_0@gKS$ to refer to $G_0W_0$ based on the gKS eigensystem ($\phi_{\text{gKS}}^{\text{gKS}}, \epsilon_{\text{gKS}}$) computed with the xc functional $E_{\text{xc}}^{\text{gKS}}$. In this approach, QP corrections are calculated to first order in $\Sigma$ as

$$\epsilon_n^{\text{QP}} = \epsilon_n^{\text{gKS}} + \langle \phi_{\text{gKS}}^{\text{gKS}} | \Sigma(\epsilon_n^{\text{QP}}) - V_{\text{xc}} | \phi_{\text{gKS}}^{\text{gKS}} \rangle, \quad (2)$$

where $V_{\text{xc}}$ is the xc potential, and it is assumed that $\epsilon_n^{\text{QP}} \approx \epsilon_n^{\text{gKS}}$.

The $G_0W_0$ approach has been used with much success, in particular for the calculation of band gaps and band structures of solids, but also increasingly often for molecules and clusters. However, a well-known and well-documented dependence on the gKS eigensystem used to construct $G_0$ and $W_0$, limits its predictive power[26–28]. Partial self-consistency in the QP eigenvalues can mitigate this problem. In eigenvalue self-consistent $GW$, the gKS eigenvalues used to construct $G$ and/or $W$ are replaced with those from the output of a prior GW step; the self-energy corrections are then iterated until the QP eigenvalues converge. This approach, that we call ev$G_sW_s$, has been shown to remove much of the starting point dependence for a range of different systems[29,30].

The BSE is an equation for the two-particle electron-hole Green’s function, and allows for the calculation of the polarizability including electron-hole interactions through the screened Coulomb interaction $W$. In practice, the BSE is usually solved neglecting the frequency dependence of $W$. Within this static approximation, it can be written in a form equivalent to Casida’s equations of TDDFT

$$\begin{pmatrix} A & B \\ -B & -A \end{pmatrix} \begin{pmatrix} X^s \\ Y^s \end{pmatrix} = \Omega_s \begin{pmatrix} X^s \\ Y^s \end{pmatrix}, \quad (3)$$

where $\Omega_s$ are neutral excitations and $(X^s, Y^s)$ are the corresponding eigenvectors[31]. $A$ and $-A$ represent resonant and antiresonant transitions that can be expressed as

$$A_{ia}^{ib} = (\epsilon_a^{\text{QP}} - \epsilon_i^{\text{QP}}) \delta_{ij} \delta_{ab} - 2(ia|jb) + W_{ij}^{ab}(\omega = 0), \quad (4)$$

and that are coupled through $B$ and $-B$, written as

$$B_{ia}^{ib} = -2(ia|bj) + W_{ij}^{ab}(\omega = 0), \quad (5)$$

for singlet excitations. In these expressions $i$ and $j$ are occupied, and $a$ and $b$ are unoccupied states, and $(ia|bj)$ stands for

$$(ia|bj) = \int d^3r d^3r' \phi_{ia}^{\text{QP}}(r) \phi_{ja}^{\text{QP}}(r') \frac{1}{|r-r'|} \phi_{ib}^{\text{QP}}(r') \phi_{bj}^{\text{QP}}(r'). \quad (6)$$
Note that, $\phi_i^{OP} = \phi_i^{KS}$, whenever the $G_0W_0$ or $evG_nW_n$ approaches are used to construct A and B.

B. Methodological details

Structures: In this article, we report results from $G_0W_0$+BSE, $evG_nW_n$+BSE and TDDFT calculations for three different structures of the BCL a molecule, in order to be able to compare our calculations to computational and experimental literature results: 1. A BCL a unit from the light-harvesting ring LH2 of *Rhodoblastus acidophilus* as reported by Anda et al.\textsuperscript{[31]} This structure was extracted from an experimental X-ray crystallographic structure of the LH2 complex (with structure ID 1NKZ in the RCSB Protein Data Bank)\textsuperscript{[32]} The phytyl tail was truncated and replaced by a hydrogen atom, and no further geometry optimization was carried out. In the following, we will call this structure ‘A’. 2. A BCL a structure reported by Oviedo et al.\textsuperscript{[33]} that was relaxed using a density functional tight binding approach\textsuperscript{[33]} This structure will be called ‘O’. A visual comparison between ‘A’ and ‘R’ is shown in Fig. 1. The large differences that we observe between the experimental crystal structure ‘A’ and our relaxed structure ‘R’ are unsurprising, given that we perform our geometry optimizations without taking into account the protein environment in which BCL a ‘A’ is embedded in *in vivo*.

We also performed calculations for the simpler, but chemically related tetrahydroporphyrin Bacteriochlorin (BC), for which we used the structure reported in Ref.\textsuperscript{[19]} and for other pigments of the BCL and CL family, namely BCL b, c, d, e and CL a, and b from Ref.\textsuperscript{[35]} which we relaxed using the same methodology as above. Atomic coordinates of all relaxed structures can be found in the Supplementary Material.

GW+BSE and TDDFT calculations: Our calculations of charged and neutral excitations were performed using the GW+BSE and TDDFT implementation in the MOLGW software package, which relies on Gaussian basis functions\textsuperscript{[36]}. We used the frozen-core approximation throughout, which changes excitation energies by less than 1 meV. We also employed the resolution-of-the-identity (RI) method, in order to reduce the calculation of 4-center integrals to 2- and 3-center integrals. We find that for BC the effect of using the RI on the $Q_x$ and $Q_y$ excitations is $\sim$10 meV, using a 6-311G basis set and the B3LYP xc functional. For BCL a, we tested that the RI changes the QP HOMO-LUMO gap by less than 50 meV using a 6-31G basis set and BHLYP, but expect the effect of the RI to be even smaller for the larger basis sets used in the remainder of this article.\textsuperscript{[37]}

To further reduce the computational cost of the evaluation of the GW polarizability, we use the Single Pole Approximation (see Supplementary Material). The Tamm-Dancoff approximation, which corresponds to neglecting the B matrix elements in equation 3 is not used, because we find that it consistently increases both GW+BSE and TDDFT results by $\sim$0.3 eV, in agreement with previous findings.\textsuperscript{[40]} We calculate a total of eight excitations and find that both $Q_y$ and $Q_x$ are converged to within 1 meV using this setting.

Basis set convergence: We tested the influence of the Gaussian basis set size on HOMO-LUMO gaps and $Q_x$ and $Q_y$ excitations of ‘A’ using $G_0W_0$@BHLYP+BSE, considering seven different basis sets, namely the Pople basis sets 6-31G, 6-311G, 6-311+G** and 6-311++G(2d,2p), combined with the DeMon auxiliary basis set,\textsuperscript{[43]} the Karlsruhe basis sets def2-SVP, def2-TZVP and def2-TZVPP and their corresponding auxiliary basis sets.\textsuperscript{[43]}

Fig. 2 and Fig. S2 show the convergence of the HOMO-LUMO gap and $Q_x$ and $Q_y$ excitation energies as a function of the inverse number of basis functions, $1/N_{basis}$ (see also Table S1 and Figure S2 and Table S2 for convergence of TDDFT results). We find that the HOMO-LUMO gap depends significantly more on $1/N_{basis}$ than $Q_x$ and $Q_y$, and that TDDFT results are less sensitive to the choice of basis set than GW+BSE. Based on these tests, we use the 6-311++G(2d,2p) basis set for all calculations reported in the following. We estimate the error in the GW(+BSE) HOMO-LUMO gap, $Q_y$ and $Q_x$ by linearly extrapolating to an infinite basis set. We exclude the very small 6-31G and 6-311G basis sets from these fits and obtain extrapolated values of 3.57 eV for the
find, in accordance with prior studies, that most, but not all, of the starting point dependence of the $G_0W_0$+BSE results is inherited from the starting point dependence of the HOMOLUMO gap.\cite{17} Eigenvalue self-consistency in $G$ alone only slightly changes the results. In contrast, full eigenvalue self-consistency largely eliminates the starting point dependence with results for both the HOMO-LUMO gap, and the $Q_y$ and $Q_x$ excitations differing by a maximum of ~0.07 eV. In the following, we are only reporting excitations based on one-shot $G_0W_0$ and fully eigenvalue-self-consistent $G_nW_n$.

As expected, (generalized) Kohn-Sham HOMO-LUMO gaps show a much larger dependence on the xc functional, with LDA, B3LYP and BHLYP leading to significantly lower and $\omega$PBE to a slightly higher HOMO-LUMO gap as compared to $G_0W_0$ and eigenvalue-self-consistent $GW$. In turn, $Q_y$ and $Q_x$ excitation energies from TDDFT are considerably less dependent on the xc functional than HOMO-LUMO gaps, although important qualitative differences exist that we discuss in Section III.B.

| Method          | xc functional | H-L gap (eV) | $Q_y$ | $Q_x$ | $\Gamma_y$ | $\Gamma_x$ |
|-----------------|---------------|-------------|-------|-------|-------------|-------------|
| $G_0W_0$+BSE    | LDA           | 3.17        | 0.59  | 0.06  | 1.25        | 0.10        |
|                 | B3LYP         | 3.46        | 0.95  | 0.14  | 1.59        | 0.09        |
|                 | BHLYP         | 3.69        | 1.18  | 0.22  | 1.87        | 0.10        |
|                 | $\omega$PBE   | 3.64        | 1.14  | 0.21  | 1.88        | 0.11        |
| $evG_0W_0$+BSE  | LDA           | 3.39        | 0.92  | 0.13  | 1.23        | 0.01        |
|                 | B3LYP         | 3.50        | 1.02  | 0.16  | 1.71        | 0.11        |
|                 | BHLYP         | 3.69        | 1.19  | 0.22  | 1.89        | 0.11        |
|                 | $\omega$PBE   | 3.65        | 1.15  | 0.22  | 1.90        | 0.11        |
| $evG_0W_n$+BSE  | LDA           | 3.62        | 1.17  | 0.23  | 1.90        | 0.01        |
|                 | B3LYP         | 3.67        | 1.19  | 0.23  | 1.90        | 0.12        |
|                 | BHLYP         | 3.72        | 1.23  | 0.24  | 1.92        | 0.11        |
|                 | $\omega$PBE   | 3.68        | 1.16  | 0.22  | 1.91        | 0.11        |
| TDDFT           | LDA           | 0.92        | 1.59  | 0.26  | 1.99        | 0.08        |
|                 | B3LYP         | 1.60        | 1.64  | 0.34  | 2.17        | 0.10        |
|                 | BHLYP         | 2.61        | 1.57  | 0.40  | 2.34        | 0.12        |
|                 | $\omega$PBE   | 4.01        | 1.48  | 0.31  | 2.02        | 0.10        |

**TABLE I.** HOMO-LUMO gaps, $Q_y$ and $Q_x$ excitation energies (in eV) and corresponding oscillator strengths $\Gamma_y$ and $\Gamma_x$ for BCL a structure ‘A’ calculated with the 6-311++G(2d,2p) basis set.

### III. RESULTS AND DISCUSSION

#### A. Bacteriochlorin

Having established our methodological setup, we start by calculating the two lowest energy excitations of BC, using a structure from Ref. 19. Following the notation in that paper, we denote the lowest energy excitations $Q_y$ and $Q_x$, respectively, according to the direction of their transition dipole moments. The results of our TDDFT and $GW$+BSE calculations are summarized in Table I. In agreement with previous studies, we find that TDDFT overestimates the experimental values for $Q_y$ and $Q_x$ by ~0.3 eV.\cite{17} We further find that $G_0W_0$@LDA underestimates $Q_y$ by 0.4 eV and $Q_x$ by 0.6 eV, whereas the use of a BHLYP or $\omega$PBE starting point results

FIG. 2. Convergence as a function of number of basis functions $1/N_{basis}$ for a) the HOMO-LUMO gap and b) the $Q_y$ and $Q_x$ excitation energies, calculated with $G_0W_0$@BHLYP+BSE. Dashed lines represent a linear fit.

HOMO-LUMO gap, 1.11 eV for $Q_y$ and 1.81 eV for $Q_x$, respectively. We conclude that by using the 6-311++G(2d,2p) basis set for all further calculations, we likely overestimate $GW$+BSE HOMO-LUMO gaps and $Q_y$ and $Q_x$ excitation energies by <0.1 meV. Conversely, use of the SPA leads to a slight underestimation of the HOMO-LUMO gap, and the $Q_y$ and $Q_x$ excitations (see Supplemental Material), resulting in a fortuitous error cancellation.

**Exchange-correlation functionals and level of self-consistency in GW:** We test the effect of different xc functionals on our $GW$+BSE and TDDFT results. We use the local density approximation (LDA), two global hybrid functionals (B3LYP and BHLYP), and the range separated hybrid functional $\omega$PBE, where we obtain the range separation parameter $\omega$ through the tuning procedure outlined in Ref. 39. We use the QChem code and a 6-31G(d,p) basis set for the tuning.\cite{20} The tuned range separation parameters for all systems discussed in the following can be found in Table S3.

In order to investigate the effect of eigenvalue self-consistency in the $GW$+BSE approach, we tested for structure ‘A’ the effect of updating the eigenvalues in the construction of $G$ only ($evG_nW_0$), and of both $G$ and $W$ ($evG_nW_n$). Table I lists the HOMO-LUMO gaps, and the $Q_y$ and $Q_x$ excitations, calculated for different DFT starting points and at these different levels of eigenvalue self-consistency. We find, in accordance with prior studies, that most, but not all of the starting point dependence of the $G_0W_0$+BSE results is inherited from the starting point dependence of the HOMO-LUMO gap.\cite{17} Eigenvalue self-consistency in $G$ alone only slightly changes the results. In contrast, full eigenvalue self-consistency largely eliminates the starting point dependence with results for both the HOMO-LUMO gap, and the $Q_y$ and $Q_x$ excitations differing by a maximum of ~0.07 eV. In the following, we are only reporting excitations based on one-shot $G_0W_0$ and fully eigenvalue-self-consistent $G_nW_n$.

As expected, (generalized) Kohn-Sham HOMO-LUMO gaps show a much larger dependence on the xc functional, with LDA, B3LYP and BHLYP leading to significantly lower and $\omega$PBE to a slightly higher HOMO-LUMO gap as compared to $G_0W_0$ and eigenvalue-self-consistent $GW$. In turn, $Q_y$ and $Q_x$ excitation energies from TDDFT are considerably less dependent on the xc functional than HOMO-LUMO gaps, although important qualitative differences exist that we discuss in Section III.B.

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in excitations within 0.1 eV of the experimental results. Self-consistency in the QP eigenvalues eliminates most of the starting point dependence, and leads to excellent agreement with experiment.

| Method         | xc functional | H-L gap | Qx   | Gx   | Qy   | Gy   |
|----------------|---------------|---------|------|------|------|------|
| G0W0+BSE       | LDA           | 4.15    | 1.21 | 0.09 | 1.67 | 0.04 |
|                | BHLYP         | 4.56    | 1.67 | 0.19 | 2.23 | 0.05 |
|                | oPBE          | 4.59    | 1.64 | 0.19 | 2.26 | 0.05 |
| evGnWn+BSE     | LDA           | 4.42    | 1.51 | 0.17 | 2.21 | 0.05 |
|                | BHLYP         | 4.60    | 1.69 | 0.20 | 2.27 | 0.05 |
|                | oPBE          | 4.56    | 1.61 | 0.18 | 2.26 | 0.04 |
| TDDFT          | LDA           | 1.38    | 2.04 | 0.18 | 2.39 | 0.03 |
|                | BHLYP         | 3.27    | 1.93 | 0.28 | 2.55 | 0.04 |
|                | oPBE          | 4.38    | 1.87 | 0.23 | 2.42 | 0.05 |
| Exp$^{[1]}$    |               |         | —    | 1.60 |      | 2.30 |

TABLE II. HOMO-LUMO gaps, Qx, and Qy excitation energies (in eV) and corresponding oscillator strengths $\Gamma_x$ and $\Gamma_y$ for bacteriochlorin calculated with the 6-311++G(2d,2p) basis set.

### B. Bacteriochlorophyll a

Next, we compare $G_0W_0$+BSE, evGW+BSE and TDDFT results for structures 'A', 'O' and 'R' of BCL a based on the LDA. Fig.3 shows the first four excitations calculated at these levels of theory. TDDFT based on the LDA is known to underestimate CT excitations and has been shown to predict spurious excitations with CT character at energies between Qx and Qy for BCL a. Our comparison of structures 'A', 'O' and 'R' shows that while the energy of Qx and Qy is changing only slightly when TD-LDA is used, the relative position of these spurious low-oscillator strength excitations depends strongly on the structure. $G_0W_0$@LDA+BSE results in an even less reassuring picture. For all three structures, the first excitation already appears at energies below or around 1 eV and its oscillator strength is considerably lower than with TD-LDA; for structure 'A' the oscillator strength of Qy is even lower than that of Qx. For structure 'R', excitations 2, 3 and 4 have similar, very low, oscillator strength. All in all, $G_0W_0$@LDA+BSE neither quantitatively nor qualitatively predicts the optical excitation spectrum of BCL a. Eigenvalue self-consistency cures this problem. For all three structures it pushes the dark excitations to energies above Qx and results in a qualitatively correct description of Qx and Qy.

For a more quantitative analysis, we now turn to a comparison of GW+BSE and TDDFT excitation energies based on different xc functional approximations with RASP2 results reported by Anda et al.$^{[12]}$ and with experimental results. We extracted experimental reference values for Qx and Qy excitations from a study by Limantara et al., in which electronic absorption spectroscopy was used to obtain Qy and Qx for a large number of polar and nonpolar solvents.$^{[13]}$, at room temperature. This study demonstrates that both Qx and Qy increase linearly with decreasing dielectric constant $\varepsilon$ for nonpolar solvents. We therefore obtained our reference values by using the regression parameters reported in that article, and extrapolating to $\varepsilon=1$, yielding 1.71 eV and 2.26 eV for Qx and Qy, respectively. Note however, that exact agreement of our calculated results with experimental data should not be expected since we neglect other potentially relevant effects such as those of temperature.

Fig.4 shows the difference between our calculated Qx and Qy excitation energies and the experimental reference values in vacuum for BCL a structures 'A' (blue), 'O' (red), and 'R' (green). We emphasize again that 'A' and 'O' are unrelaxed structures for which agreement with the experimental reference data is not expected. Nonetheless, we report results for these structures in Fig.4 in order to allow for easy comparison of our results with each other and with the RASP2 results by Anda et al. (only for structure 'A'). All calculated excitation energies and corresponding oscillator strengths can also be found in Tables I, S4 and S5. $G_0W_0$@LDA+BSE results are not shown in Fig.4 as they underestimate the experimental results by up to 1.2 eV for structure 'A' and result in unphysically low oscillator strengths.

Our first main observation is, that GW+BSE consistently underestimates the experimental excitations energies independent of the xc functional starting point and whether eigenvalue self-consistency is used, whereas TDDFT is closer to the experimental reference values, albeit more scattered, depending on xc functional and structure. RASP2 underestimates the experimental Qx excitation by ~0.1 eV, but overestimates the Qy excitation by almost 0.2 eV. Note that RASP2 results depend on the choice of active space, as discussed in Ref.42.

Table III lists the mean absolute error (MAE) of $G_0W_0$+BSE, evGW+BSE and TDDFT. Based on these numbers, several additional observations can be made. First, consistent with expectations, the MAEs of the $G_0W_0$+BSE and evGW+BSE approach are smallest for the relaxed structure and largest for the experimental structure. This is expected due to our comparison to experimental results for BCL a in solution and in vivo. Second, eigenvalue self-consistency leads to significantly smaller MAEs as compared to $G_0W_0$, with an MAE of ~0.2 eV for both the Qx and the Qy excitation of 'R'. Third, TDDFT results are within ~0.15 eV of experiment, regardless of the structure.

Furthermore, we find that Qx excitation energies are less sensitive to the choice of structure than Qy excitation energies for all methods. BCL a molecules inside the light-harvesting apparatus of purple bacteria are known to be responsible for excitation energy transfer through coupled Qy excitations. By comparing our results for structures 'A', 'O' and 'R', we can infer that the Qx excitation energy can change by several hundred meV through subtle variations in geometry. This is in line with the well-known paradigm that BCL pigments in natural light-harvesting complexes absorb at different wavelengths depending on the local protein environment, partly due to structural effects mediated by the protein matrix.$^{[13]}$

The remainder of this discussion will focus on structure 'R'. TDDFT with the OT-RSH oPBE is in good agreement with experiment for this structure. The Qx excitation is found at 1.75 eV and the Qy excitation at 2.18 eV. When oPBE is used
FIG. 3. First four excitations for structures 'A' (left), 'O' (middle) and 'R' (right) as calculated with TD-LDA (top), $G_0W_0@LDA+BSE$ (center) and ev$G_nW_n@LDA+BSE$ (bottom). Arrows indicate excitations with very low oscillator strength.

| Structure | $G_0W_0+BSE$ | $G_nW_n+BSE$ | TDDFT |
|-----------|--------------|--------------|-------|
| 'A'       | 0.62 0.48    | 0.52 0.35    | 0.15 0.14 |
| 'O'       | 0.42 0.39    | 0.31 0.26    | 0.06 0.12 |
| 'R'       | 0.29 0.30    | 0.19 0.18    | 0.11 0.10 |

TABLE III. MAEs (in eV) for different BCL a structures for $G_0W_0+BSE$, $G_nW_n+BSE$ and TDDFT, respectively.

as a starting point for ev$G_nW_n$-BSE, $Q_y$ is at 1.49 eV and $Q_x$ at 2.09 eV. However, a computationally much cheaper LDA calculation, used as a starting point for ev$G_nW_n$-BSE leads to very similar results of 1.50 eV for $Q_y$ and 2.07 eV for $Q_x$, underscoring the ability of eigenvalue self-consistency to largely overcome the starting point dependence of the $G_0W_0$ method.

In Table IV we show the energy difference $\Delta Q_x - Q_x$ for our different methods and in comparison with experiment. A correct prediction of $\Delta Q_x - Q_x$ is essential for a correct description of the coupling of excitations of several pigments. We find that $\Delta Q_x - Q_x$ from LDA-based $G_0W_0+BSE$ and TDDFT significantly underestimates this energy difference. Again, eigenvalue self-consistency cures this problem, leading to excellent agreement with experiment, almost independent of the underlying xc functional. $\Delta Q_x - Q_x$ with TDDFT linearly depends on the amount of exact exchange in the underlying xc functional, an observation most straightforwardly made by comparing LDA (0% of exact exchange), B3LYP (~ 23%) and BHLYP (50%). This is primarily due to the shifting of the $Q_x$ excitation to higher energies with increasing amounts of exact exchange.

In order to shed some light on the origin of the differences between TDDFT and $GW+BSE$, we turn to calculating the density of states (DOS) of structure 'R'. Fig. 4 shows the DOS as calculated with $G_0W_0@X$ (X= LDA, BHLYP and $\omega$PBE) and DFT (with the same xc functionals). The $Q_x$ excitation

| Method   | xc functional | $\Delta Q_x - Q_x$ |
|----------|---------------|-------------------|
| $G_0W_0+BSE$ | LDA          | 0.41              |
|           | B3LYP         | 0.47              |
|           | BHLYP         | 0.54              |
|           | $\omega$PBE   | 0.60              |
| ev$G_nW_n+BSE$ | LDA          | 0.57              |
|           | B3LYP         | 0.54              |
|           | BHLYP         | 0.54              |
|           | $\omega$PBE   | 0.59              |
| TDDFT    | LDA           | 0.25              |
|           | B3LYP         | 0.40              |
|           | BHLYP         | 0.64              |
|           | $\omega$PBE   | 0.43              |
| Exp[23]  |               | 0.55              |

TABLE IV. Difference between $Q_x$ and $Q_y$ excitation energies (in eV) using TDDFT, $G_0W_0+BSE$ and ev$G_nW_n+BSE$ for structure 'R'.
is primarily a HOMO → LUMO transition, while $Q_a$ arises from a HOMO-1 → LUMO transition. Given that the tuning procedure underlying oPBE is designed to reproduce the fundamental band gap, it comes as no surprise that the HOMO-LUMO gaps with DFT and $G_0W_0$ based on oPBE are very similar. The HOMO-1 is also at a similar energy, whereas for lower-energy states the differences between the DOS are larger. We further find that the $G_0W_0@BHLYP$ DOS is very similar to the $G_0W_0@oPBE$ DOS, whereas the generalized Kohn-Sham DOS with BHLYP exhibits a lower HOMO-LUMO gap, and larger HOMO to HOMO-1 energy difference. The LDA-based DOS is markedly different. As expected, the DFT-LDA DOS severely underestimates the HOMO-LUMO gap. However, in addition, HOMO-1, HOMO-2 and HOMO-3 are much closer in energy as compared to the predictions of DFT-oPBE and $G_0W_0@oPBE$. This observation explains the presence of spurious dark states between $Q_b$ and $Q_c$, and in the vicinity of $Q_x$ (Fig. 3) with TD-LDA and $G_0W_0@LDA+BSE$, which have significant contributions from transitions involving these lower occupied states. $G_0W_0@LDA$ opens the HOMO-LUMO gap by almost 1 eV as compared to DFT-LDA, but also underestimates the energy difference between the HOMO and HOMO-1 eigenvalue.

C. Excitations of other BCL and CL pigments

In the final part of this paper, we report optical excitation energies of other members of the BCL and CL family, that are prevalent in purple (BCL a and b) and green bacteria (BCL c, d, e), plants and algae (CL a and b). All structures were taken from Ref. 33 and geometry-optimized as described in Section II. In Table V, we report excitation energies as calculated with ev$G_nW_n$+BSE and TDDFT, where we used the oPBE xc functional with an optimally tuned range-separation parameter $\omega$ as before (all range separation parameters used for these calculations are listed in Table S3). Unlike the $Q_x$ excitation of BCL a and b which have significant oscillator strength, the $Q_x$ excitation of BCL c – e is dark, as can be seen in Tables S6 and S7, where we report the excitation energies and oscillator strengths of the first six excitations of BCL a – e, and CL a and b. Following Ref. 7, we therefore also compare our calculations with experimental results for the higher-energy B band in Table V. In these calculations, we included a total of 20 excitations, in order to ensure that the higher lying excitations
are well-converged.

| Molecule | $eG_n W_n + BSE$ | TDDFT | Exp |
|----------|-----------------|-------|-----|
|          | $Q_y$ | $Q_x$ | $B$ | $Q_y$ | $Q_x$ | $B$ | $Q_y$ | $Q_x$ | $B$ |
| BCL $a$ | 1.50 2.10 3.16 | 1.75 2.16 3.33 | 1.60 2.15 3.46 |
| BCL $b$ | 1.45 2.09 3.05 | 1.69 2.15 3.19 | 1.56 2.14 3.37 |
| BCL $c$ | 1.84 2.11 3.02 | 2.05 2.21 3.21 | 1.88 — 2.89 |
| BCL $d$ | 1.89 2.21 3.04 | 2.08 2.29 3.19 | 1.90 — 2.93 |
| BCL $e$ | 1.95 2.13 2.88 | 2.10 2.23 3.02 | 1.92 — 2.72 |
| CL $a$  | 1.86 2.19 3.02 | 2.06 2.29 3.16 | 1.87 2.14 2.88 |
| CL $b$  | 1.93 2.20 2.85 | 2.10 2.29 2.97 | 1.92 2.26 2.72 |

MAE | 0.04 | 0.05 | 0.17 | 0.17 | 0.05 | 0.25 |

TABLE V. $Q_y$, and $Q_x$ excitation energies of relaxed structures of different BCLs and CLs using 6-311++G(2d,2p) basis set and $G_n W_n @ \omega$PBE+$BSE$ approach.

Strikingly, we find that for the entire family of BCL and CL molecules, $eG_n W_n + BSE$ is in excellent agreement with experiment with MAEs of $\sim 0.1$ eV for all three excitations. Similar to Bacteriochlorin and BCL $a$, we observe that $eG_n W_n + BSE$ slightly underestimates the $Q_y$, excitations of these molecules, whereas TDDFT overestimates them, with an MAE of 0.17 eV. Our $eG_n W_n + BSE$ results also accurately reflect the spectral shifts of the $Q_y$ excitation when going from one BCL to the other. For example, the BCL $b$ molecule differs from BCL $a$ through an ethyliden side group, which shifts the $Q_y$ excitation by 40 meV to the red. This redshift is perfectly reproduced in our $GW + BSE$ calculations.

This analysis leads us to conclude that the performance advantage of TDDFT over $GW + BSE$ seen in Fig. 4 is somewhat specific to the case of BCL $a$. When evaluated for the entire family of pigments, TDDFT with an optimally tuned RSH tends to overestimate the optical excitations, by different degrees depending on the nature of the excitation. $GW + BSE$ is in very good agreement with experimental data, on average underestimating all three excitations studied here by $\sim 0.1$ eV.

It should be noted that the $GW$ approach, despite its implementation using Gaussian basis functions and the use of the RI approximation in MOLGW and other codes, remains a major bottleneck of these calculations. Furthermore, our results highlight that $GW$, more so than DFT, requires careful convergence with respect to the basis set size. This limits its applicability to systems with a few (B)CL pigments at most, until algorithms with better scaling become more widely available. However, our results challenge the notion that a multireference treatment is necessary to describe the low-energy optical excitations of this family of systems. Our study joins a growing number of results demonstrating that the $GW + BSE$ approach can accurately predict neutral excitations of complex molecules without empirical parameterization. With new approaches for combining $GW + BSE$ with large scale molecular mechanics simulations and polarizable continuum embedding, emerging, an accurate prediction of excitation energy and charge transfer in complex molecular environments is within reach.

**SUPPLEMENTARY MATERIAL**

The Supplementary Material contains additional figures and data, and the atomic coordinates of all geometry-optimized structures.

**DATA AVAILABILITY**

The data that supports the findings of this study are available within the article, its Supplementary Material, and from the corresponding author upon reasonable request.

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1. R. E. Blankenship, *Molecular Mechanisms of Photosynthesis*, 2nd ed. (Wiley Blackwell, Oxford, 2014).
2. X. Hu, T. Ritz, A. Damjanić, F. Autenrieth, and K. Schulten, “Photosynthetic apparatus of purple bacteria,” *Rev. Biophys.* 35, 1–62 (2002).
3. S. J. Jang and B. Mennucci, “Delocalized excitons in natural light-harvesting complexes,” *Rev. Mod. Phys.* 90, 35003 (2018).
4. Y. Shao, Y. Mei, D. Sundholm, and V. R. Kaila, “Benchmarking the Performance of Time-Dependent Density Functional Theory Methods on Biochromophores,” *J. Chem. Theory Comput.* 16, 587–600 (2020).
5. I. Schelter, J. M. Foerster, A. W. Koszuk, A. T. Gardiner, R. J. Cogdell, M. Ullmann, B. D. Queiroz, and S. Kúmmel, “Assessing Density Functional Theory in real-time and real-space as a tool for studying bacteriochlorophylls and the light-harvesting complex 2,” J. Chem. Phys. 151, 134114 (2019).
6. D. Sundholm, “A density-functional-theory study of bacteriochlorophyll b,” *Phys. Chem. Chem. Phys.* 5, 4265–4271 (2003).
7. Z. Vokácová and J. V. Burda, “Computational study on spectral properties of the selected pigments from various photosystems: Structure-transition energy relationship,” *J. Phys. Chem. A* 111, 5864–5878 (2007).
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5. A. Drew and M. Head-Gordon, “Failure of Time-Dependent Density Functional Theory for Long-Range Charge-Transfer Excited States: The Zinbacteriochlorin-Bacteriochlorin and Bacteriochlorophyll-Spheroide Complexes,” J. Am. Chem. Soc. 126, 4007–4016 (2004).

6. D. J. Tozer and N. C. Handy, “Improving virtual Kohn-Sham orbitals and eigenvalues. Application to excitation energies and static polarizabilities,” J. Chem. Phys. 109, 10180–10189 (1998).

7. N. Kurizki, T. Stein, R. Baer, and L. Kronik, “Charge-Transfer-Like π–π* Excitations in Time-Dependent Density Functional Theory: A Conundrum and Its Solution,” J. Chem. Theory Comput. 7, 2408–2415 (2011).

8. G. Onida, L. Reining, and A. Rubio, “Electronic excitations: density-functional versus many-body Green’s-function approaches,” Rev. Mod. Phys. 74, 601 (2002).

9. S. Albrecht, L. Reining, R. Del Sole, and G. Onida, “Ab initio calculation of excitonic effects in the optical spectra of semiconductors,” Phys. Rev. Lett. 80, 4510 (1998).

10. M. Rolhoff and S. G. Louie, “Electron-hole excitations and optical spectra from first principles,” Phys. Rev. B 62, 4927 (2000).

11. D. Y. Qiu, F. H. Da Jornada, and S. G. Louie, “Optical spectrum of MoS2: Many-body effects and diversity of exciton states,” Phys. Rev. Lett. 111, 216805 (2013).

12. J. C. Grossman, M. Rolhoff, L. Mitas, S. G. Louie, and M. L. Cohen, “High accuracy many-body calculational approaches for excitations in molecules,” Phys. Rev. Lett. 86, 472–475 (2001).

13. M. L. Tiago, P. R. Kent, R. Q. Hood, and F. A. Reboiro, “Neutral and charged excitations in carbon fullerenes from first-principles many-body theories,” J. Chem. Phys. 129, 084311 (2008).

14. F. Bruneval, S. M. Hamed, and J. B. Neaton, “A systematic benchmark of the ab initio Bethe-Salpeter equation approach for low-lying optical excitations of small organic molecules,” J. Chem. Phys. 142, 244101 (2015).

15. M. Pulcovo, C. Hogan, F. Sottile, P. Bagalà, and A. Rubio, “Ab initio electronic and optical spectra of free-base porphyrins: The role of electronic correlation,” J. Chem. Phys. 131, 084102 (2009).

16. I. Duchemin, T. Deutsch, and X. Blase, “Short-range to long-range charge-transfer excitations in the zinbacteriochlorin-bacteriochlorin complex: A bethe-salpeter study,” Phys. Rev. Lett. 109, 167801 (2012).

17. W. W. M. J. Wehner, L. Brombacher, J. Brown, C. Junghans, O. Caylak, Y. Khalak, P. Madhikar, G. Tirimbò, and B. Baumeier, “Electronic Excitations in Complex Molecular Environments: Many-Body Green’s Functions Theory in VOTCA-XT,” J. Chem. Theory Comput. 14, 6253–6268 (2018).

18. X. Blase, I. Duchemin, and D. Jacquemin, “The Bethe-Salpeter equation in chemistry: Relations with TD-DFT, applications and challenges,” Chem. Soc. Rev. 47, 1022–1043 (2018).

19. R. Croce and H. v. Ambergen, “Natural strategies for photosynthetic light harvesting,” Nature Chem. Bio. 10, 492–501 (2014).

20. R. J. Cogdell, A. Gall, and J. Köhler, “The architecture and function of the light-harvesting apparatus of purple bacteria: from single molecules to in functionally relevant motions,” J. Mol. Biol. 427, 149–161 (2016).

21. J. Zheng, X. Xu, and D. G. Truhlar, “Minimally augmented Karlsruhe basis sets,” Theor. Chem. Acc. 128, 29–35 (2011).

22. J. P. Dow, S. H. A. Qin, D. D. Scalise, and D. R. Baer, “Fundamental Gaps in Finite Systems from Eigenvalues of a Generalized Kohn-Sham Method,” Phys. Rev. Lett. 105, 266802 (2010).

23. Y. Shao, Z. Gan, E. Epifanovsky, A. T. Gilbert, M. Wormit, J. Kussmann, A. W. Lange, A. Behn, J. Deng, X. Feng, D. Ghosh, M. Goldey, P. R. Horn, L. D. Jacobson, I. Kaliman, R. Z. Kahlitullin, T. Kus, A. Landau, J. Liu, E. I. Preonyov, Y. M. Rhee, R. M. Richard, M. A. Rohrdanz, R. P. Steele, E. J. Sundstrom, H. L. Woodcock, P. M. Zimmerman, D. Zuev, B. Albrecht, E. Algüire, B. Austin, G. J. Beran, Y. A. Bernard, E. Berquist, D. Briand, K. B. Brovay, J. B. Brown, D. Casanova, C. M. Chang, Y. Chen, S. H. Chien, K. D. Closser, D. L. Crittenden, M. Diederichsen, R. A. Distasio, H. Do, A. D. Dutoi, R. G. Edgar, S. Fatehi, L. Fusti–Molnár, A. Ghysels, A. Golubeva-Zadorozhnaya, J. Gomes, M. W. Hanson-Heine, P. H. Harbach, A. W. Hauser, E. G. Hohenstein, Z. C. Holden, T. C. Jaga, H. J. Bi, K. Kaduk, K. Khistyae, J. Kim, J. Kim, R. A. King, P. Kluźinger, D. Kosenkov, T. Kowalczyk, C. M. Krauter, K. U. Lao, A. D. Laurer, K. V. Lawler, S. V. Levchenko, C. Y. Lin, F. Liu, E. Livshits, R. C. Lochan, A. Luenser, P. Manohar, S. F. Manzer, S. P. Mao, N. Mardissian, A. V. Marenich, S. A. Maurer, N. J. Mayhall, E. Neuscamman, C. M. Oana, R. Olivares-Amaya, D. P. Onciul, J. A. Parkhill, T. M. Perrine, R. Peverati, A. Prociuk, D. R. Rehn, E. Rosta, N. J. Russ, S. M. Sharada, S. Sharma, D. W. Small, A. Sodt, T. Stein, D. Stück, Y. C. Su, A. J. Thom, T. Tsumochi, V. Vanoschli, V. Vogt, O. Vydroy, T. Wang, M. A. Watson, J. Wenzel, A. White, C. F. Williams, J. Yang, S. Yegneuh, S. R. Yost, C. Z. You, I. Y. Zang, Zhong, Z. Zhao, B. R. Brooks, G. K. Chan, D. M. Chipman, C. J. Cramer, W. A. Goddard, M. S. Gordon, W. J. Helle, A. Klant, H. E. Schaefer, M. W. Schreiibl, D. D. Truhlar, A. Warshel, X. Xu, A. Aspuru-Guzik, R. Baer, A. T. Bell, N. A. Besley, J. D. Chai, A. Drew, B. D. Dunietz, T. R. Furnali, S. R. Gwaltney, C. P. Hsu, Y. Jung, J. Kong, D. S. Lambrecht, W. Liang, C. Oechslen, V. A. Rassolov, L. V. Slipchenko, J. E. Subotnik, T. Van Voorhis, J. M. Herbert, A. P. Krylov, P. M. Gill, and M. Head-Gordon, “Advances in molecular quantum chemistry contained in the Q-Chem 4 program package,” Molec. Phys. 113, R1499 (1999).

24. H. Jiang, R. I. Gomez-Abal, P. Rinke, and M. Scheffler, “First-principles modeling of localized d states with the GW/LEDA+U approach,” Phys. Rev. B 82, 045108 (2010).

25. P. Liao and E. A. Carter, “Testing variations of the GW approximation on strongly correlated transition metal oxides: Hematite (α-Fe2O3) as a benchmark,” Phys. Chem. Chem. Phys. 13, 15189–15199 (2011).
V. Vlček, E. Rabani, D. Neuhauser, and R. Baer, “Stochastic GW Calculations for Molecules,” J. Chem. Theor. Comput. 13, 4997–5003 (2017).

I. Duchemin, C. A. Guido, D. Jacquemin, and X. Blase, “The Bethe-Salpeter formalism with polarisable continuum embedding: Reconciling linear-response and state-specific features,” Chem. Sci. 9, 4430–4443 (2018).