Bethe-Salpeter equation insights into the photo-absorption function and exciton structure of chlorophyll *a* and *b* in light-harvesting complex II

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Abstract

The photo-absorption process and the excitation of chlorophyll (Chl) is the primary and essential step of photosynthesis in green plants. By solving the Bethe-Salpeter equation (BSE) on top of the *GW* approximation within *ab initio* many-body perturbation theory, we calculate the photo-absorption function and the excitons structure of Chl *a* and *b* in their *in vivo* conformations as measured by X-ray diffraction in the light-harvesting complex (LHC) II. BSE optical absorption spectra are in good agreement with the experiment and we discuss residual discrepancies. The experimental evidence of multiple Chl*a* forms *in vivo* is explained by BSE. The Chl*a* and Chl*b* BSE exciton wavefunctions present important charge-transfer differences on the Soret band. Q excitons are almost identical, apart from charge (both electron and hole) localization on the Chl*b* C7 aldheide formyl group, absent on the Chl*a* methyl C7, that is exactly the group where the two chlorophylls differ.

Keywords: chlorophyll, photosynthesis, optical photo-absorption, Q Soret excitons, GW, Bethe-Salpeter equation

1. Introduction

Chlorophyll (Chl) is an essential molecule for photosynthesis in green plants, algae and some bacteria [1, 2]. In nature there are at least five [3, 4] chemically different Chl molecules, not including bacteriochlorophylls, but the most abundant are chlorophyll a and b (Chla and Chlb) [1, 2]. While all chlorophylls, together with other pigments like carotenoids, act as important light harvesters, the role of Chla as primary electron donor is central and essential: there is no evidence that oxygenic photosynthesis could occur in absence of Chla [5, 3, 1]. Therefore, the study of the photo-absorption process and the excitations in chlorophyll, focusing in particular on differences between Chlaand Chlb (or other Chls), is an important element to understand photosynthesis.

Recently [6], a structural picture at crystallographic atomic detail of LHC-II, the major light-harvesting complex of PS-II and the principal solar energy collector, has been obtained by high-resolution X-ray diffraction on spinach leaves (*Spinacia oleracea*). The obtained model of the crystallographic structure of LHC-II includes the determination of the identity of the chlorophyll molecules (Chla or Chlb) together with their conformation and the accurate position of their atoms. Within each LHC-II monomer, eight Chla and six Chlb molecules with different conformations were identified. The atomic structure identified by this X-ray study in LHC-II constitutes the basis for our investigation of the photo-absorption process in chlorophyll.

In this work we calculate from first principles the chlorophyll optical absorption, together with the underlying charged and neutral excitations (excitons), by the GW approximation on the self-energy [7, 8, 9, 10] and the resolution of the Bethe-Salpeter equation (BSE) [11] in the framework of ab initio many-body perturbation theory [12]. The BSE describes the bound states of two interacting particles and was originally formulated in nuclear physics to study deuterium, positronium and mesons (proton-neutron, electron-positron and guark-antiguark bound states, respectively). Later [13, 14, 15] it was adapted to solidstate and molecular physics to study electron-hole bound states or excitons, the most fundamental excitations of matter under absorption of photons. Excitonic structure and nature, whether they are charge-transfer, fully localized Frenkel, or delocalized Wannier excitons, is important to understand the photoabsorption process in photovoltaics [16, 17, 18]. The same should hold for photosynthesis, and this is the fundamental motivation of this work.

The BSE is an equation for the two-particle correlation function $L(x_1, x_2; x_3, x_4)$ in terms of the electron/hole propagator or Green function $G(x_1, x_2)$ and of the BSE kernel $\Xi(x_5, x_6; x_7, x_8)$. In a compact form it writes

$$L = GG + GG\Xi L \tag{1}$$



Figure 1: Bethe-Salpeter equation Feynman diagram.

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or by Feynman diagrams as in Fig. 1. The polarizability $\chi(x_1, x_2) = L(x_1, x_1; x_2, x_2)$ is obtained from L by contraction of two indices. Optical absorption and dielectric functions can be calculated from χ . In the GW approximation the BSE kernel Ξ is reduced to the screened Coulomb interaction $W(x_5, x_6)$ which revealed a very good approximation to describe the photo-absorption in atoms, molecules and solids [15, 19, 20, 21, 22, 23, 24, 18]. The BSE approach is more reliable and accurate than time-dependent densityfunctional theory (TDDFT) for which the search for valid approximations of its kernel, beyond the local-density approximation (LDA), is still a problem. On the other hand, the BSE is much more computationally heavy and not applicable to large systems like the whole LHC-II containing over 17000 atoms, as it can be done in hybrid QM/MM approaches [25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37], or with huge effort also in pure TDDFT [38]. For this reason, here our BSE calculations are carried only on the eight Chla and six Chlb as reported in LHC-II by Ref. [6] and neglecting the effect of the LHC-II environment. Or more precisely, neglecting its dielectric/electronic effect on chlorophyll excitation, but taking into account its effect on the conformation/atomic geometry of the chlorophylls which we found important. For the dielectric effect of the LHC-II protein environment on chlorophyll excitation, we refer to the estimation provided by the previous TDDFT study [38] which however was found much smaller than the effect of conformation. The study of full biological complexes as by multi-scale QM/MM approaches [25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37] is important to describe the exciton dynamics, energy transfer and charge separation at time and space scales much larger than the optical absorption step only, and so fundamental to understand the whole photosynthesis process. These studies typically use TDDFT as the molecule QM calculation, but are obliged to correct/shift exciton energies and couplings for the well known systematical errors pertinent to each TDDFT approximation (B3LYP, ω B97XD, TPSS, etc.). To be exempt from such adjustment, they could well use BSE instead of TDDFT with benefits from its higher accuracy, as our results will try to convince. We compare the BSE results to data from all available experiments on chlorophyll in vivo, as well as in vitro (e.g. in ether), and also to some efforts in vacuo [39, 40, 41]: each of them provides complementary information, while, on the other hand, it is unclear which situation our modelling is closer to, as we will discuss.

2. Theoretical and computational methods

The basis and starting point of our calculation is the crystallographic structure at atomic detail of LHC-II obtained by high-resolution X-ray diffraction on spinach leaves (*Spinacia oleracea*) by Ref. [6]. The latter provided the conformation of the eight Chla and six Chl b in LHC-II of all atoms, except hydrogens. We kept on these positions and relaxed only the positions of hydrogen atoms by a density-functional theory (DFT) calculation with the PBE0 functional on the 6-311G** Gaussian basis set. The DFT-PBE0 ground state is then computed on the cc-pVdz and cc-pVtz basis sets. These bases were used also for the following *GW* and BSE excited state calculations applying the resolution of identity technique with Weigend Coulomb fitting basis. The first step of a many-body perturbation-theory calculation is the evaluation of the Green function *G* starting from a zero-order electronic structure, e.g. the DFT Kohn-Sham (KS) energies ϵ_i and wave functions $\phi_i(r)$:

$$G(r_1, r_2, \omega) = \sum_i \frac{\phi_i(r_1)\phi_i^*(r_2)}{\omega - \epsilon_i \mp i\eta},$$
(2)

where η is an infinitesimal and the sign \mp is negative/positive for occupied/empty states. The Green function is then used to calculate the random-phase approximation (RPA) polarizability

$$\Pi^0(r_1,r_2,\omega)=-\frac{i}{2\pi}\int d\omega'\,G(r_1,r_2,\omega+\omega')G(r_1,r_2,\omega'),$$

which provides the RPA dielectric function ε ,

$$\varepsilon(r_1, r_2, \omega) = \delta(r_1, r_2) - \int dr_3 w(r_1, r_3) \Pi^0(r_3, r_2, \omega),$$

and the RPA dynamically screened interaction W,

$$W(r_1, r_2, \omega) = \int dr_3 \,\varepsilon^{-1}(r_1, r_3, \omega) w(r_3, r_2), \tag{3}$$

with $w(r_1, r_2) = 1/|r_2 - r_1|$ being the bare Coulomb interaction. In the *GW* approximation the self-energy Σ is the convolution product of *G*, Eq. (2), and *W*, Eq. (3),

$$\Sigma(r,r',\omega) = \frac{i}{2\pi} \int d\omega' \, e^{i\omega'\eta} G(r,r',\omega+\omega') W(r,r',\omega'),$$

and the integral over ω' is calculated by contour-deformation. The *GW* quasiparticle (QP) energies can be calculated as solutions to the QP equation or, more simply, as first-order corrections to the DFT KS energies

$$\epsilon_i^{GW} = \epsilon_i + \langle \phi_i | \Sigma(\omega = \epsilon_i^{GW}) - V_{xc} | \phi_i \rangle, \tag{4}$$

where V_{xc} is the exchange-correlation potential used in the DFT step. The screened interaction W enters also in the BSE kernel

$$\Xi(r_1, r_2, r_3, r_4) = -i\delta(r_1, r_3)\delta(r_2, r_4)w(r_1, r_2) + + i\delta(r_1, r_4)\delta(r_2, r_3)W(r_1, r_3, \omega = 0)$$
(5)

which is taken static. We have now all the ingredients to solve the BSE Eq. (1) for the correlation function L from which to calculate the optical absorption observables. Or also we can reformulate the BSE as an eigensystem problem

$$\begin{pmatrix} A & B \\ -B^* & -A^* \end{pmatrix} \Psi_{\lambda} = E_{\lambda} \Psi_{\lambda}, \tag{6}$$

with the BSE excitonic Hamiltonian given by a diagonal part plus the BSE kernel Ξ , Eq. (5),

$$A = \left(\epsilon_p^{GW} - \epsilon_h^{GW}\right) \delta_{pp'} \delta_{hh'} + w_{ph'hp'} - W_{ph'p'h}, \tag{7}$$

$$B = +w_{pp'hh'} - W_{pp'h'h}, \qquad (8)$$

with w_{ijkl} and W_{ijkl} matrix elements of the bare and screneed Coulomb interaction between the occupied h, h' and empty p, p'states. The E_{λ} are the BSE exciton energies and Ψ_{λ} the BSE



Figure 2: Chlorophyll optical absorption spectra. The GW+BSE spectra (lines) are the sum of all Chl *a* (blue) and *b* (red) components found in the LHC II of spinach leaves. The blue and red dots are the experimental spectra measured for Chl*a* and Chl*a* dissolved in ether [47]. The black dots is the Chl*a*+*b* in vivo spectrum measured in *Lactuca sativa* [48].

exciton wavefunctions which are related to the exciton oscillator strength. All BSE calculations include coupling beyond the Tamm-Dancoff approximation. We used NWCHEM [42] for the ground-state and Fiesta [43, 44, 45] for the excited-state calculations.

To calculate the RGB color codes we started from the complex dielectric function ε which can be calculated from the BSE excitonic eigenvalues and eigenvector once fixed the chlorophyll concentration to the value of $2 \cdot 10^{-4}$ mol/L (which we found the standard for chlorophyll in solvents). From ε we calculated the real v and imaginary κ refraction indeces $v + i\kappa = \sqrt{\varepsilon}$ and then the absorption coefficient $\alpha = 2\kappa\omega/c$. The transmission function is $T = e^{\alpha l}$ where l is the width to be crossed, which we fixed to 1 cm, typical test-tube width. The transmission T is then convoluted with the CIE D65 standard illuminant (average sunny midday light) and the RGB code (or preferably the device independent $L^*a^*b^*$ code) is extracted by further convolution with the R G B functions defined by the CIE (Commission Internationale de l'Éclairage). Our procedure is very similar to what has been done in Ref. [46], with the difference that we work in transmission while they worked in reflectance.

3. Results

3.1. Photo-absorption and optical (neutral) excitations

In Fig. 2 we compare GW+BSE theoretical and experimental optical absorption spectra of chlorophyll. The RGB colors which can be calculated from these spectra are used to paint clip-art test-tubes in Fig. 3 which are compared to photographs of real test-tubes of chlorophyll. Finally, in Table 1 we detail the precise position of the two major chlorophyll red and blue



Figure 3: Chlorophyll color: Photographs of test-tubes containing ether solutions of Chla (left) and Chlb (right) shown in reflection (left-side) and transmission (bottom) (courtesy of William Erb, Univ. Rennes 1 [49]). Clip-art test-tubes colored using the RGB codes calculated from experimental optical transmission spectra of chlorophyll in ether [47, 50, 51] (two central test-tubes, to be compared with the real colors in photographs), and the RGB codes issued from theoretical BSE transmission spectra calculated in *in vivo* conformations (two right-most test-tubes).

absorption peaks, the Q and the Soret band respectively, as in the BSE calculation and from various experiments in the literature.

The BSE optical absorption spectra in Fig. (2) are calculated separately for chlorophyll a (blue line) and b (red line) by summing over the contributions from the eight Chla and the six Chlb conformations reported in LHC-II by Ref. [6]. The Q (red) peak is well identified in both chlorophylls, whereas the Soret band appears more articulated, especially in Chla. In the same figure we report also optical absorption spectra measured in vitro (in a diethylether solution [47]) for both Chla (blue dots) and Chlb (red dots). The last curve we report in Fig. (2) is the optical absorption of chlorophyll measured in vivo (Lactuca sativa [48], black dots). The latter represents the merged contribution of the two Chla and Chlb components with the best effort by the authors to exclude contributions from other pigments, though a residual contribution from carotenoids might be present. The BSE spectra appear half-way between in vivo and in vitro experimental spectra. For both Chla and Chlb, the Q band appears more in agreement with in vivo red peaks (within 0.02 eV) and red-shifted wrt ether (by 0.05 eV), whereas the Soret band is more in agreement with Chl in ether (within 0.04 eV) and blue-shifted wrt in vivo (by up to 0.13 eV in Chlb). However, these results can be considered in an unexpected very good agreement with the experiment, no matter the term of comparison. Indeed, the accuracy of the GW+BSE method has been rigorously estimated [23, 52] in comparison to exact results, to never exceed 0.1 eV. As it can be more clearly appreciated from Table 1, here the BSE disagreement

	Soret		Q	
	Chla	Chlb	Chlb	Chla
GW+BSE	431	448	661	679
In vivo (Lactuca sativa) [48]	436	470	653	675
In vivo (Scenedesmus) [53]	439	469	649	677
In vitro (diethylether) [56]	429	454	643	661
In vitro (acetone) [57]	436	452	642	666
In vitro (pyridine) [39, 54, 55]	444	472	655	671
In vacuo (spinach jet) ¹ [58]				647
In vacuo (tag extrap.) ² [40, 41]	405	413	626	642
<i>In vacuo</i> (solvent extrap.) ³ [39]	413			639

Table 1: Q and Soret band peak position (nm), comparison with experiments on chlorophyll in various conditions.

with the most unfavourable case, the in vacuo tag extrapolation of Refs. [40, 41] can be quantified to 35 nm, that is 0.1 eV on the Q and 0.23 eV on the Soret band. In the same table, we report the precise determination of the Q and Soret bands from several other experiments. For in vivo we report the measure of Ref. [53] in *Scenedesmus*, which is very close (< 4 nm) to the already cited experiment in Lactuca sativa of Ref. [48]. Soret and Q peak position differences are larger among in vitro measures. We report in the table the two extreme cases of pyridine [39, 54, 55] and ether [47, 56]. It can be seen that all other solvents in literature, like acetone [57] also reported in the table, lie in between the two extreme cases. We finally compare also with some in vacuo measures, that is a pump&probe laser experiment on a chlorophyll jet evaporated from frozen spinach leaves [58], an experiment on gas-phase chlorophyll tagged with ammonium ions and extrapolated to tag-absence by the help of theoretical models [40, 41], and a gas-phase limit extrapolation from measures in various solvents [39]. The table shows that experimental results are scattered, depending on the different environments or experimental conditions. The fact that the calculated results are not at all completely outside the range of variation among the various experiments, is an evidence of the GW+BSE validity. An important question is which experimental situation our theoretical modelling is closer to and supposed to reproduce, whether the in vivo, the in vitro or the in vacuo. And related to this question, what are the residual discrepancies due to. We postpone our attempt to answer these questions to the last Discussion section.

We close this section by providing further evidence of the validity of the BSE photo-absorption spectra. We have integrated the latter to estimate the CIE $L^*a^*b^*$ and RGB color perceived *in transmission* through a solution of chlorophyll at a given concentration in a test-tube of a given width (see Methods). We have obtained $L^*a^*b^* = 63$ -27 80 for Chla and $L^*a^*b^* = 62$ -13 98 for Chlb. These $L^*a^*b^*$ colors have been transformed into RGB codes which are then used to paint the clip-art testtubes shown in Fig. 3, the right-most ones. To check the validity of this procedure, we have also taken from literature [47] the experimental photo-absorption spectra measured in ether, calculated the transmission function at the same parameters of concentration and width, and using exactly the same procedure for BSE, we have calculated the $L^*a^*b^*$ values associated to the experiment in ether ($L^*a^*b^* = 48$ -49 -14 for Chla and $L^*a^*b^*$ = 35 - 62 23 for Chlb). With the RGB codes associated to these values we have painted two other (left-most ones) clip-art testtubes, which can be directly compared to photographs of real test-tubes containing chlorophyll. On the left side, we report a photograph showing the color of Chla and b by reflection, while the photograph on the bottom shows the color of Chla and bby transmission, that is the geometry which is more comparable to our calculated RGB codes. Indeed, the ether calculated and photographed colors look very close, almost the same. The BSE colors appear close but not the same. However, BSE has provided a clear green color for both chlorophylls, more greenish for Chlb and more blueish for Chla. This is not the case for the TDDFT spectra of Ref. [38] (for Chlb we have obtained $L^*a^*b^* = 35\ 27\ 53$ with a positive a^* providing a brown chlorophyll). Furthermore, we remind that our BSE calculation has been carried out using the in vivo conformation of chlorophyll in LHC-II, different from the conformation of chlorophyll in ether. Different tonalities of green can be expected due to this important difference. We postpone again this question to the Discussion section.

3.2. Multiple spectral forms of chlorophyll found in vivo and Q_x - Q_y split

Our ab initio approach allows to offer also some insights into a long-standing question [59, 60]: the fact that different forms of Chl a (but also b) have been observed in vivo. The most important evidence of this fact is from spectroscopy: while in vitro absorption spectra have shown only one well defined Gaussian Q (red) peak for each chlorophyll a or b, in vivo spectra show more than one peak, or at the lowest resolutions, a peak with several shoulders. Analysis at the lowest temperatures and highest resolutions and looking at the spectral derivatives have provided up to six features for Chla and two for Chlb [61]. In the beginning, these different forms were believed new chemical forms of chlorophyll, beyond Chld or the recently discovered Chlf. But it was impossible to extract and isolate these forms in solvents. Later other explanations were provided, among them the hypothesis that modifications to the chlorophylls induced by the protein in vivo environment, for example, a dielectric effect, could explain the fact. More recently the hypothesis was raised that the different conformation, and in particular the loss of planarity of the tetrapyrrolic ring [62], can lead to a different Q peak position.

In Fig. 4, we show a zoom at the lower broadening of the BSE chlorophyll optical absorption in the Q band range. We report the contributions from all the different Chla and b conformers in LHC-II. It is surprising to remark how conformation can be responsible for large differences in Q peak position, spanning a band of 14 nm for Chla and 10 nm for Chlb. Our BSE results indicate that the different Q features observed in *in vivo* spectra can be explained as due to the different chlorophyll conformers imposed by the LHC-II protein environment. Most of the *in vivo* experiments [59] agree on two peaks for Chla, at 673 and 683 nm (blue vertical lines in Fig. 4), and one for Chlb at 653 nm (red vertical line). Most recent experiments [63, 64] measured optical absorption on LHC-II of



Figure 4: Q band chlorophyll optical absorption. Black dots: LHC-II experiment [63, 64]. Vertical dotted lines: most agreed [59] experimental positions of the Chlb Q peak (653 nm, red) and Chla double feature (673 and 683 nm, blue). Thin lines: BSE contributions from different LHC-II conformations of Chla from the stromal (solid) and lumenal (dashed) sides, and of Chlb from stroma (dot-dashed) and lumen (dotted). Thick lines: BSE sum of all Chla (blue) and Chlb (red) stromal conformers; BSE sum of all Chl contributions (green). A Gaussian broadening of FWHM ≈ 5 nm ($\sigma = 0.006$ eV) has been superimposed.

Spinacia oleracea at 4.2 K (black dots in Fig. 4). They evidenced 4 features: two strong peaks at 676.3 and 650.5 nm and two shoulders at 671.9 and 662.0 [64]. It is surprising to see how it is possible to identify in the BSE spectrum (green line) all 4 features with the correct amplitude. The two lowest energy features are due to Chla molecules, mainly of the stromal side, while the two highest energy features to Chlb, with the 662.0 features due to Chlb605 and Chlb607 of the lumenal side which present practically undistinguishable energy (1.859 eV) and oscillator strength (0.143): this coincidence was already found by the model calculation of Ref. [62]. Most importantly, the BSE spectral shape is in very good agreement with the experiment, pointing to a correct reproduction of exciton oscillator strengths. With respect to the experiment, we observe a red-shift of 2 to 9 nm, depending on the feature, but this corresponds to a max of only 0.025 eV, well beyond the accuracy that in general can be expected from *ab initio* BSE and the GW approximation.

Finally, it could be interesting to compare our *ab initio* BSE results with the predictions of the Gouterman model [65], a simplification with only four π - π * levels in a non-interacting picture (e.g. LCAO) and for ideal cases. In reality, the involved levels are much more and couple each other via many-body interactions. This is exactly the physics taken into account by our microscopic BSE Hamiltonian Eqs. (6), (7) and (8): the diagonal elements represent precisely the coupling between the independent-particle transitions of the LCAO scheme. BSE spectra present a low-energy intense exciton which can be identified with the Q_y peak of the Gouterman model. The latter predicts the split of a Q_x peak at the highest energy and with orthogonal polarization. In BSE we found two and in some

cases three, peaks at energies 0.2 eV above Q_y and with much reduced oscillator strength (at least one order of magnitude, see Appendix A.2 and Fig. 7). As Ref. [66] discusses, we also observe polarization mixing due to the many-body coupling between transitions. However, BSE is unable to reproduce, for instance, the four peaks Q-band structure of Chla in ether experimental spectra (see Fig. 7). As we discuss in Appendix A.2 only the first and third peaks have electronic origin, whereas the second and forth have vibrational origin and cannot be described without introducing vibrational degrees of freedom, as done e.g. in Ref.s [67, 68]. In any case, it can be seen how ab initio BSE theory can provide important contributions to finally settle long-standing questions.

3.3. Chla vs Chlb Q and Soret band excitons

After having hopefully provided convincing evidence about the validity of the GW+BSE approach to describe the photoabsorption function of chlorophyll, we now pass to analyze the photo-excitation process itself of chlorophyll, a study difficult for the experiment and over which theory can provide important and complementary information. The solution of the Bethe-Salpeter equation Eq. (6) directly provides the exciton wavefunctions $\Psi_{\lambda}(r_h, r_e)$ that we now analyze, separating the electron $(\rho(r_e) = \int dr_h |\Psi_\lambda(r_h, r_e)|^2)$ and the hole $(\rho(r_h) =$ $\int dr_e |\Psi_{\lambda}(r_h, r_e)|^2$) probability densities, for both the Q and the Soret band (Fig. 5) for the first two LHC-II conformations, Chl b601 and Chl a602, as representative of both chlorophylls. Although conformation translates into large differences in spectra, differences in the wavefunctions due to conformation are much smaller and difficult to appreciate. However, here our effort and focus will be on evidencing differences between Chla and Chlb allowing to explain the different behaviour and functionality of the two chlorophylls.

As a first glance common evidence in all cases (Fig. 5), the electron and hole clouds are both placed all around the tetrapyrrolic ring, with the phytyl tail not involved in the excitation and as a spectator. The delocalization pattern around the ring confirms that both the Q and Soret excitons have mostly π - π^* transitions character, but this was already well known from previous model calculations and some experimental indirect evidence. We now focus on the details. The Chla and Chlb Soret excitons look very different. This should be expected because they are placed at higher energy where a larger many-body mixing of transitions occurs, and all small differences sum up. Then in Chla the electron is delocalized all around the tetra-pyrrolic ring, whereas in Chlb there are some discontinuities evidenced by green lines. Viceversa for the hole which is much more delocalized in Chlb. Perhaps the major difference is on the C7 group: on this group we observe small or no probability density in Chla for both the electron and the hole, whereas we observe an important electron density and a small though non-negligible hole in Chlb, so to configure a charge (electron) transfer excitation. We observe also large Chla-b differences in the hole density on the C3 and C2 groups, and a nitrogen atom in Chlb which presents emptied electron probability.

However, the most important excitation for photosynthesis and with regard to the different functionality of Chla and Chlb,



Figure 5: Chla (a602, top) and Chlb (b601, bottom) Q (left) and Soret (right) exciton wavefunction electron (cyan, $\rho(r_e)$) and hole (violet, $\rho(r_h)$) probability densities (0.0005 iso-surface). Chla vs Chlb differences are evidenced with red arrows (Q) and green lines (Soret).

is the Q band where at the end all the harvested optical energy is transferred by decays. On this exciton, the Chla and Chlb wavefunctions look almost identical. However we were able to evidence (red arrows) a tiny but significant difference precisely on the C7 group where Chla and Chlb present the only chemical difference (an aldheide formyl group COH in Chlb, instead of a metyl CH₃ group in Chla). We observe that on this group the Chla Q exciton wavefunctions present almost no or small probability for both the electron and the hole, whereas in Chlb we found an evident finite probability, in particular on the O atom (in red) of the aldheide, for both the electron and the hole, so to not configure a charge transfer character. *This difference might be the basis to understand the different behaviour and explain the functional difference of Chla with respect to Chlb* in the photosynthesis process.

3.4. Charged excitations

Table 2 presents GW quasiparticle results, that is the ionization potential (IP), the electron affinity (EA) and the HOMO-LUMO gap. These are also important parameters to describe

the charged excitation status (electron addition/removal) of chlorophyll. All the values are determined by averaging over the eight Chla and the six Chlb conformations in LHC-II (the RMSD is 0.05 eV). Our GW IP of 6.46 eV is in good agreement with the value of 6.42 eV measured on a supersonic beam of neutral Chla evaporated from frozen spinach leaves and measured by a single photon photoemission experiment [58]. These can be considered the closest conditions to an in vacuo experiment, but with chlorophyll probably still at the in vivo conformations of LHC-II which we have taken for our calculation. The same work provides also a 2-photons pump&probe indirect measure for the IP of 6.10 eV which the authors indicate more in agreement with the previous value of Ref. [69] obtained by extrapolation to vacuum from TMS. We believe that both the 2-photon and the TMS-in vacuo extrapolation are less accurate than the direct 1-photon measure of the IP, which corresponds to the definition itself of IP. We report also the values for both the IP and the EA measured in ethyl chlorophyllide in the form of a solid die [70]. Ethyl chlorophyllide can be

	IP		EA		HL gap	
	Chla	Chlb	Chla	Chlb	Chla	Chlb
<i>GW</i> (this work)	6.46	6.71	2.11	2.25	4.34	4.46
Spinach jet 1-photon [58]	6.42					
Spinach jet 2-photon [58]	6.10					
Extrap. from TMS [69]	6.1					
In vitro (in TMS) [69]	4.5					
In vitro (in water) [73]	4.28					
Ethyl chlorophyllide [70]	4.93	5.16	2.98	3.13		
DFT B3LYP ASCF [72]	6.23					
GW (PW PBC) [71]	4.96	5.22	3.09	3.32	1.86	1.90

Table 2: The ionization potential (IP), electron affinity (EA) and HOMO-LUMO gap [eV] in Chla and Chlb.

obtained from chlorophyll by replacing the phytyl tail with an ethyl group. This is an important modification that however allows crystallization. We report also the results of Ref. [71] by a *GW* calculation on a periodic boundary conditions planewaves code (BerkeleyGW), which is different with respect to our gaussian isolated molecule calculation. This can explain the agreement of Ref. [71] results with solid dye ethyl chlorophyllide and the disagreement with our results and other experiments. We remark also on the agreement of our *GW* IP with the one of Ref. [72] by Δ SCF. The latter should be considered an in principle exact approach, exactly like many-body theory, to calculate the IP of isolated systems within DFT. Although both DFT and our many-body approach are obliged to resort to approximations, *GW* in our case and B3LYP in theirs.

4. Discussion

4.1. Is our theoretical modelling closer to the in vivo, in vitro or in vacuo experimental situation?

Our calculations are carried out on isolated chlorophylls without the solvent or protein environment, so they should be in principle compared with *in vacuo* experimental extrapolations.⁴ However, our calculations evidenced a large dependence of peaks position, and even spectra shape, on the Chl conformation (see Fig. 4 and Fig. 6 in Appendix Appendix A.1). The effect of the different chlorophyll conformation appears much larger than the effect of the different environments, e.g. of the different solvent into which the chlorophyll is dissolved [39]. Therefore, a more faithful comparison of theoretical with *in*

vitro or *in vacuo* experimental spectra would require the knowledge of the precise conformation of chlorophyll in solvents or in cation tagged gas-phases which, to the best of our knowledge, are not yet reported in the literature.

For this reason, we believe that our theoretical spectra, calculated at the conformations reported for the LHC-II, should be rather compared and are closer to *in vivo* measures. In our calculation, the effect of the protein environment is taken into account only for its indirect effect on the chlorophyll conformation, but neglected for its dielectric effect on chlorophyll excitation. The validity of this assumption relies on both experiments and previous calculations: optical absorption spectra measured [39] for chlorophyll in the most different solvent environments, from polar to aromatic, do not show large differences; the effect of the LHC-II protein environment on chlorophyll has been already estimated in the TDDFT calculation of Ref. [38] and shown to reduce mostly to a simple almost rigid spectral redshift of $0.1 \sim 0.2$ eV, especially for all Chl *a*, but also in Chl *b* with the only exception of Chl b606 (see Fig. S4 in Suppl. Mat. of Ref. [38]). The same TDDFT calculation also found, like our GW+BSE calculation, that the effect of chlorophyll conformation is very important and in any case much larger than the dielectric effect of the protein environment. All these arguments bring us to the conclusion that our GW+BSE results should be considered as the optical response of in vivo LHC-II chlorophyll, artificially separating the Chla and Chlb contributions, as well as contributions from other pigments in LHC-II, taking into account the effect of the protein environment on the chlorophyll conformations, but neglecting its dielectric/electronic effect.

4.2. Residual theory-experiment discrepancies

Hence the residual differences of BSE with respect to in vivo spectra in Fig. 2, could then be attributed to the effect of the protein environment. The same could be said for the differences with in vitro spectra, but here the chlorophyll conformation is unknown and can be in principle very different from the in vivo conformations we relied on. Ref. [38] found that the LHC-II protein environment is responsible for a red shift of peaks which is small on the Q band, and larger ($\sim 0.1 \text{ eV}$) on the Soret band, especially on the Chlb of the lumenal side, achiving almost 0.3 eV on b606 (which is also the Chl whose Soret band was found by our BSE calculation at the highest energies, see Fig. 6 in Appendix Appendix A.1). These shifts are compatible with the residual error of the GW+BSE with respect to the in vivo on the Soret band position, although they do not help on the Q band. On the Q peak, our BSE spectra are already in good agreement with the in vivo positions. In any case, we cannot straightforwardly transfer these shifts from TDDFT to our BSE calculation. Indeed, the effect of the environment enters in TDDFT differently from GW and BSE. In TDDFT screening enters indirectly, via the exchange-correlation kernel, which in the simplest approximations is taken local or almost local. In GW and BSE, on the other hand, the screening is taken into account explicitly via the screened Coulomb interaction W directly entering into the GW self-energy, $\Sigma = iGW$, or into the

⁴The limits of the extrapolation from solvents have been already discussed in Ref. [39], showing that the extrapolation can get rid of all dielectric effects but will tend to a solvated chlorophyll. While tagging with cations, such as tetrabutylammonium, has been discussed in Ref. [1] pag. 87-90: "Spectra of the phase test intermediates of chlorophyll a, chlorophyll b, pheophytin a, and pheophytin b, prepared by adding tetrabutylammonium hydroxide (1 M in methanol) to a solution of pigment in pyridine, are shown in Figs. 1-4. The profound alteration in the spectrum on making the phase test intermediate suggests that its negative charge is not confined to the oxygen of the enolate ion but is distributed over the entire conjugated system (143). As the pyrrolenine rings in porphyrin systems tend to attract electrons (50), it is possible that the resonance structure (XXXII) makes an important contribution to the state of the ion. In this structure, the conjugated system no longer makes a closed loop, and so an altered spectrum might be expected." Nevertheless, since these different extrapolations achieve not so far gas-phase values, we considered it appropriate to compare also with them.



Figure 6: Photo-absorption spectra of selected LHC-II Chla (left) and Chlb (right) conformations from both the stromal (a602, a610, b601) and lumenal (a604, b606) sides.

BSE kernel $\Xi = \delta \delta W$. This has the effect to temper and counteract the effect of the screening itself.

5. Conclusions

The BSE optical absorption (Fig. 2) is somehow half-way with respect to experimental spectra of chlorophyll in solvent (ether) and in vivo. The agreement with the in vivo experiment is fairly good, especially on the Q band (Fig 4) where BSE provides an explanation to the long-standing question of the multiple forms of chlorophylls found in vivo. It can be improved on the Soret band where the protein environment could have a larger effect. Here our spectra agree better, in particular on the peaks position, with the experiments in ether. A plot of BSE exciton wavefunctions (Fig 5) shows localization of both the hole and the electron on the tetra-pyrrolic ring tipical of π orbitals, for both the Q and the Soret band and without noticeable differences between Chla and Chlb. However, on the Soret band there are important charge-transfer differences between Chla and Chlb on the C3, C7 and C2 groups. Instead, Q excitons are almost identical, apart from charge (both electron and hole) localization on the Chlb C7 aldheide formyl group, absent on the Chla methyl C7, that is exactly the group where the two chlorophylls differ. This feature might be at the basis to explain the functional difference of Chla from Chlb.

6. Abbreviations

BSE	Bethe-Salpeter equation
Chl	chlorophyll
Chla	chlorophyll <i>a</i>
Chlb	chlorophyll <i>b</i>
CIE	Commission Internationale de l'Éclairage
DFT	density-functional theory

EA	electron annity
FWHM	full width at half maximum
HL gap	HOMO-LUMO gap
HOMO	highest occupied molecular orbital
IP	ionization potential
LDA	local-density approximation
LHC	light-harvesting complex
LHC-II	light-harvesting complex II
LUMO	lowest unoccupied molecular orbital
PBC	periodic boundary conditions
PS	photosystem
PS-II	photosystem II
PW	plane-waves
QM/MM	Quantum mechanics / Molecular mechanics
RMSD	root mean-square deviation
TDDFT	time-dependent density-functional theory
TMS	tetramethylsilane

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Appendix A.

Appendix A.1. Effect of LHC-II environment on Chl conformation and spectra

We report in Fig. 6 the BSE photo-absorption spectra of some Chla and Chlb LHC-II conformations, chosen from both the stromal (a602, a610, b601) and the lumenal side (a604, b606), and selected to represent the farthest away spectra. It is evident the important role played by chlorophyll conformation which is



Figure 7: Chla Q band optical absorption analysis. Blue dots: Chla in ether experiment. Colored lines: BSE calculation for Chla in the various LHC-II conformations. All theoretical BSE spectra have been shifted by +0.05 eV to align the Q_y peak with the experiment. A Gaussian broadening of FWHM \approx 5 nm ($\sigma = 0.006$ eV) has been superimposed in the left panel, and of ~ 20 nm ($\sigma = 0.022$ eV) in the right panel which has been also rescaled to the experiment.

enforced by the LHC-II protein environment, and so an indirect effect of the protein environment itself. The effect of conformation is much larger than the direct dielectric/electronic effect of the protein environment which was mostly found responsible for just only a red-shift of $0.1 \sim 0.2$ eV (see main text and Ref. [38]).

Appendix A.2. Q band analysis

In Fig. 7 we report the optical absorption spectra for Chla in the Q band region (500-700 nm). In the left panel we compare the BSE calculation for all the LHC-II conformations to the experimental spectrum mesured in ether. Theoretical spectra have been shifted by +0.05 eV to align the main peak with the experiment. It is evident that BSE can reproduce the first Q_{ν} most intense peak, but cannot reproduce the second peak. However, it seems able to reproduce at least the third peak. Indeed we observe excitons at ~ 0.25 eV larger energy with an order of magnitude reduced oscillator strength. At even larger energy we also observe further, almost dark, excitons (less than two orders of magnitude oscillator strength, see inset). In the right panel we show only the BSE spectrum of the LHC-II Chl a604 which seems the closer to the Chla in ether conformation (provided a rigid shift of +0.05 eV). The picture that emerges is that BSE can describe the first Q_y most intense peak, and also the third, which therefore has electronic nature and can be intepreted as the Q_x peak of the Gouterman model. Its oscillator strength could be raised by electron-vibrational coupling effects. The same could happen to the further dark exciton, which therefore can give rise to a further Q_x -like peak. This is in agreement with a recent analysis [66] which tried to solve the long-standing question of the "traditional" vs "modern" attribution of the Q_x to one of the two visible experimental peaks beyond the Q_{y} . On the other hand, it is evident that BSE is unable to describe the second and the forth peaks which, therefore,

have vibrational origin. They can be described by taking into account the electron coupling to vibrational degrees of freedom (vibrational frequencies v_r and Franck-Condon S_r factors), as done for example in Ref. [67] (see also Ref. [68]).

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