

Short-Range to Long-Range Charge-Transfer Excitations in the Zincbacteriochlorin-Bacteriochlorin Complex: A Bethe-Salpeter Study

I. Duchemin,¹ T. Deutsch,¹ and X. Blase²

¹INAC, SP2M/L_sim, CEA, 38054 Grenoble cedex 09, France

²Institut Néel, CNRS and Université Joseph Fourier, B.P. 166, 38042 Grenoble Cedex 09, France

(Received 10 April 2012; published 15 October 2012)

We study, using the Bethe-Salpeter formalism, the singlet excitation energies of the zincbacteriochlorin-bacteriochlorin dyad, a paradigmatic photosynthetic complex. In great contrast with standard time-dependent density functional theory calculations with (semi)local kernels, charge transfer excitations are correctly located above the intramolecular Q -band transitions found to be in excellent agreement with experiment. Further, the asymptotic Coulomb behavior towards the true quasiparticle gap for charge transfer excitations at long distance is correctly reproduced, showing that the present scheme allows us to study with the same accuracy intramolecular and charge transfer excitations at various spatial ranges and screening environments without any adjustable parameter.

DOI: 10.1103/PhysRevLett.109.167801

PACS numbers: 78.40.Me, 71.15.Qe, 78.67.-n

Photoinduced charge transfer excitations, namely the jump upon photon absorption of an electron from a donor to an acceptor site, is a fundamental process that governs photosynthetic processes in plants and bacteria, [1] or the quantum efficiency in organic or hybrid photovoltaic cells [2]. Such nonlocal excitations are also an important current theoretical issue since it is now well recognized that the time-dependent density functional theory (TDDFT) [3] encounters severe problems describing such excitations when standard (semi)local kernels, or even hybrid kernels mixing some amount of exact exchange, are being used [4]. Besides organic systems, similar problems have been identified in the case of extended Wannier excitons in semiconductors where the large effective excitonic radius leads to a weak average overlap between the hole and the electron [5].

The bacteriochlorin molecule is closely related to the magnesium-containing bacteriochlorophyll system. Due to its importance as a paradigmatic photosynthetic complex, and as one of the earliest charge-transfer system for which the TDDFT difficulties have been unraveled and discussed [4], the zincbacteriochlorin-bacteriochlorin (ZnBC-BC) complex (see Fig. 1) has been studied by a variety of approaches, including TDDFT with local [4,6,7], hybrid [7], Coulomb attenuated hybrid [7] functionals, constrained Δ SCF DFT calculations, [8] and quantum chemistry many-body wave functions techniques such as a combination of Δ SCF DFT and the single excitation configuration interaction (CIS) technique [4], or a more elaborate CIS(D) approach including various scaled perturbative double-excitation correlation corrections [9].

In two recent studies [10,11], charge transfer (CT) excitations in small donor-acceptor complexes, combining tetracyanoethylene with acene derivatives, were studied with the GW approximation and Bethe-Salpeter (BSE) equation within many-body perturbation theory (MBPT)[12]. Excellent agreement with gas phase experiments [13] was

obtained for the lowest CT excitation energy with a mean absolute error of about 0.1 eV [11]. Such an accuracy compared well with recent TDDFT calculations with optimized range-separated functionals [14], while TDDFT calculations with standard PBE or even nonlocal B3LYP kernels [15,16] were shown to lead to discrepancies of several eV with CT states located at much too low energy [14].

In this work, we study the optical absorption spectrum of the ZnBC-BC complex using the GW -BSE many-body perturbation theories. We show that intramolecular excitations are in excellent agreement with experiment, and that the charge-transfer excitations are correctly located above the intramolecular Q -band transitions, in great contrast

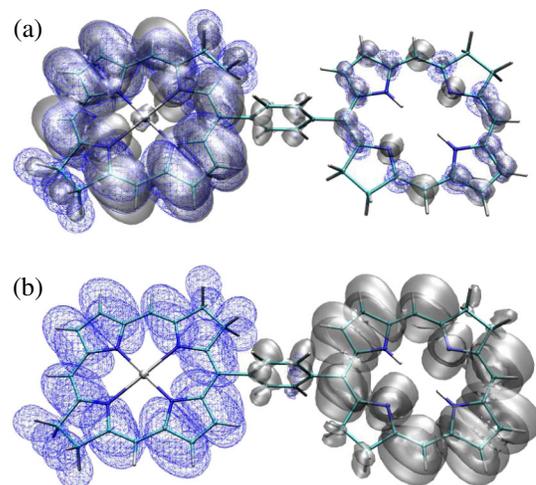


FIG. 1 (color online). Symbolic representation of the (1,4)-phenylene-linked zincbacteriochlorin-bacteriochlorin complex. Isocontour representation of the (transparent grey) hole-averaged electron and (blue wireframe) electron-averaged hole distributions (see text) for the lowest (a) ZnBC Q_x excitation and (b) ZnBC \rightarrow BC charge-transfer excitation.

with time-dependent local density approximation (TDLDA) calculations which locate the charge-transfer excitations about 1.7 eV below the GW -BSE value. It is further shown that the GW -BSE framework correctly reproduces the long-range energy behavior of the charge transfer excitations, a feature shared only with the scaled CIS(D) correlated quantum chemistry approach. The importance of going beyond the Tamm-Dancoff approximation is further discussed.

Our calculations are based on a recently developed auxiliary even-tempered Gaussian-basis [17] implementation of the GW [18–21] and BSE [22–26] formalisms, the FIESTA package, implementing contour deformation techniques for the correlation contribution to the self-energy [11,27]. The needed two-body operators such as the susceptibilities, bare or screened Coulomb potentials, and self-energies, are expressed on an atom-centered Gaussian basis containing six $\exp(-\alpha r^2)$ Gaussian for the radial part of each (s , p , d) channel, with an even tempered distribution of localization coefficient α ranging from 0.1 to 3.2 a.u. Such a basis derives from previous studies [27–29] but with additional diffuse orbitals. Convergence tests can be found in the Supplemental Material [30].

The needed starting single-particle states are taken to be the Kohn-Sham DFT/LDA eigenstates generated by the SIESTA package [31] using a large triple-zeta plus double polarization basis (TZDP). [32] It was shown recently that the combination of a TZDP basis for describing Kohn-Sham occupied and virtual states, with the above described auxiliary bases, was leading to charge-transfer excitation energies in excellent agreement with plane wave GW -BSE calculations [11]. For the isolated ZnBC and BC molecules, for which experimental data are available [33,34], we relax the molecules at the all-electron B3LYP 6-311G (d) level [35]. However, for the ZnBC-BC bridged complex, we adopt the geometry provided in Ref. [4], and used in subsequent studies [7–9], as a means to properly compare to other computational approaches.

In the present many-body framework, one first obtains accurate quasiparticle energies (occupied and virtual electronic energy levels) by using the GW formalism. In the case of gas phase organic molecules such as fullerenes, pentacene, PTCDA or porphyrins, it was shown in several recent studies [27,36–38] that the standard single-shot G_0W_0 calculations based on input Kohn-Sham eigenstates with standard local functionals tends to yield too small HOMO-LUMO gaps, even though already much better than the starting Kohn-Sham values. Better results could be consistently obtained for the quasiparticle spectrum of small molecules either by starting from Hartree-Fock [27,39–41], or hybrid functionals [42] eigenstates, or by performing a full self-consistency on the quasiparticle eigenstates, [40,41] or a limited self-consistency on the eigenvalues only [11,27,29,38,43], allowing us to remove the dependency of the final quasiparticle energies on the

starting point eigenstates. This is such an approach that we adopt in the present study, showing here below as in Ref. [11] that excellent agreement with experiment can be obtained for the excitation energies.

In an optical absorption spectrum, the quasiparticle gap is reduced by the electron-hole interaction. In the present MBPT formalism, this excitonic interaction is accounted for by the BSE equations. Namely, the neutral excitation energies can be obtained as the eigenvalues of the BSE H^{e-h} Hamiltonian [22–26] expressed in the $\phi_i^e(r)\phi_j^h(r')$ product basis of the unoccupied ϕ_i^e and occupied ϕ_j^h single-particle states. Of importance for the upcoming discussion, we write the so-called direct term involving the (statically) screened Coulomb potential $W(\mathbf{r}, \mathbf{r}')$, noticing that hole and electron states are not taken at the same space position:

$$H_{ij,kl}^{\text{direct}} = - \int d\mathbf{r}d\mathbf{r}' \phi_i^e(\mathbf{r})\phi_j^h(\mathbf{r}')W(\mathbf{r}, \mathbf{r}')\phi_k^e(\mathbf{r})\phi_l^h(\mathbf{r}').$$

As compiled in Table I, we first verify that our GW -BSE low-lying Q_x and Q_y transition [44] energies for the isolated monomers fall within 0.1 eV of the available experimental values. Consistently with previous observations [28,45], we find that the diagonalization of the full BSE Hamiltonian leads to a red shift which can be as large as 0.35 eV as compared to the GW -BSE results in the Tamm-Dancoff (TDA) approximation, bringing the calculated transitions in excellent agreement with experiment. Such a good agreement with available experimental data can be taken as an indication of the reliability of the present formalism and of the specific implementation aspects.

Concerning the TDLDA calculations, performed with the same Kohn-Sham states and auxiliary basis, we observe that the agreement with experiment is also satisfactory, even though not as good as the BSE values. Our calculated TDLDA results compare very well with former TD-BLYP calculations [4,7]. Again, this allows us to verify that the pseudopotential approximation and the bases we use do not lead to significant errors as compared to all-electron calculations with the standard quantum chemistry basis. For intramolecular transitions with large overlap between hole and electron states, the TDDFT approach with standard kernels is a reliable framework.

We now come to the central point of this study, namely the ZnBC-BC CT excitation energies. The charge-transfer nature of a given transition can be easily identified by analyzing the weight of the two-body BSE eigenstates on the ϕ_{lumo}^e and ϕ_{homo}^h one-body eigenstates localized on either molecule. The expectation value of the electron density operator $\delta(\mathbf{r} - \mathbf{r}_e)$ on a given two-body BSE eigenstate allows us further to build the corresponding hole-averaged electron distribution. An electron-averaged hole spatial distribution can be defined similarly. Such a representation is provided in Fig. 1(b) for the ZnBC \rightarrow BC charge-transfer state obtained at the GW -BSE (full) level. The charge-transfer nature of such an excited state is apparent.

TABLE I. Calculated singlet transition energies (in eV) for the isolated monomers and the (1,4)-phenylene-linked ZnBC-BC complex. The present TD-LDA (TDA), *GW*-BSE (TDA), and *GW*-BSE (full) results are compared to previous TD-DFT calculations with the BLYP and B3LYP functionals. (TDA) means Tamm-Dancoff approximation, while (full) means full diagonalization mixing resonant and antiresonant transitions.

Transitions	BLYP ^{a,b}	LDA	TD-DFT (TDA)		GW-BSE		Exp. ^{c,d}
			B3LYP ^b	CAM-B3LYP ^b	TDA	full	
Isolated BC and ZnBC monomers							
π - π^* Q_x ZnBC	2.07/2.04	2.09	2.05	1.87	1.94	1.59	1.65
π - π^* Q_x BC	2.10/2.10	2.10	2.12	1.92	1.90	1.63	1.6
π - π^* Q_y BC	2.39/2.40	2.45	2.54	2.53	2.38	2.24	2.3
π - π^* Q_y ZnBC	2.44/2.43	2.47	2.60	2.59	2.29	2.27	2.2
ZnBC-BC phenylene-bridged complex							
π - π^* Q_x ZnBC	2.05/2.05	2.08	2.06	1.89	1.99	1.69	
π - π^* Q_x BC	2.09/2.09	2.10	2.11	1.93	2.04	1.73	
π - π^* Q_y BC	2.38/2.37	2.46	2.56	2.49	2.47	2.35	
π - π^* Q_y ZnBC	2.42/2.42	2.44	2.64	2.54	2.49	2.34	
CT ZnBC \rightarrow BC	1.33/1.33	1.25	1.85	2.87	2.95	2.95	
CT BC \rightarrow ZnBC	1.46/1.46	1.39	2.00	3.04	3.13	3.13	

^aRef. [4]. ^bRef. [7]. ^cRefs. [33,34]. ^dRefs. [33,34].

As shown in Table I, TD-LDA severely underestimates the CT excitation energies which are found to lie significantly below the intramolecular Q bands. Identical conclusions were found with the BLYP functional [4,7]. Such a behavior can be understood from the analysis of the TDDFT electron-hole coupling terms which vanish for transitions between nonoverlapping electron and hole states in the case of the (semi)local exchange-correlation kernel. One is then left with the noninteracting diagonal part, namely the too small Kohn-Sham HOMO-LUMO gap. Such a situation is slightly improved with the B3LYP functional due to its 20% of exact exchange, but with a residual error as large as 1.1 eV. This cancellation of the interacting term for nonlocal charge-transfer excitations does not occur in the BSE formalism since in the $H_{ij,kl}^{\text{direct}}$ interaction term, hole and electron states are not taken at the same position in space and are connected by the nonlocal screened Coulomb potential $W(\mathbf{r}, \mathbf{r}')$.

The *GW*-BSE CT excitation energies lie well above the intramolecular Q bands, consistently with TDDFT calculations with optimized (parametrized) CAM-B3LYP functionals [7] and CIS(D) calculations [9] (see analysis below). Concerning the CAM-B3LYP results, with CT states located less than 0.1 eV below the *GW*-BSE one, compared to the ~ 1.7 eV discrepancy with TDLDA, the agreement is very good considering that the needed scaling parameters [46] have been trained on a very different set of molecules, the so-called G2 set, and on very different properties, namely ionization energies. These results confirm the agreement already found between *GW*-BSE and a TDDFT calculation with another optimized range-separated functional (the BNL functional [47]) in the study of small tetracyanoethylene complexes, both calculations coming in close agreement with experiment for CT states [11,14].

The ability of the BSE approach to describe charge-transfer excitations can be further illustrated by studying the long range limit where the BC and ZnBC units are separated by removing the phenylene bridge. The distance R between the two monomers in the unbridged model dimer is defined in Fig. 2 (Inset). $R \sim 5.84$ Å is the corresponding distance between the two monomers in the phenylene-bridged complex. Our results are represented in Fig. 2. As expected, intramolecular charge transfer excitations are independent of the distance between the molecules. On the contrary, in the large distance limit, the CT exciton binding energies are found to scale like $1/D$, where D is the distance between the \mathbf{R}_1 and \mathbf{R}_2 molecule centres, as indicated in Fig. 2 (thick grey line). In the large D limit, the direct interaction terms converge to: $H_{ij,kl}^{\text{direct}} \simeq -W(\mathbf{R}_1, \mathbf{R}_2)Q_{ik}^e Q_{jl}^h$, where $W(\mathbf{R}_1, \mathbf{R}_2)$ reduces to the bare $1/|\mathbf{R}_1 - \mathbf{R}_2|$ Coulomb potential for the two molecules in the vacuum [48] and $Q_{ik}^e = \langle \phi_i^e | \phi_k^e \rangle$. With $Q_{ik}^e = \delta_{ik}$ and $Q_{jl}^h = \delta_{jl}$, there is no mixing with higher subbands, so that the lowest CT state is primarily composed of the HOMO and LUMO eigenstates in the long distance limit, as verified by analyzing the BSE eigenstates.

Such $(1/D)$ behavior of the CT excitonic binding energy is the correct asymptotic limit of an electrostatic interaction between opposite charges. In this limit, the CT excitation energies correctly converge towards the noninteracting (diagonal) part of the BSE Hamiltonian, namely the true quasiparticle gap between the concerned hole and electron states as given by the *GW* calculation. The ability of the *GW*-BSE approach to correctly describe without adjustable parameter both intramolecular and short to long-range charge transfer excitations energies, both in

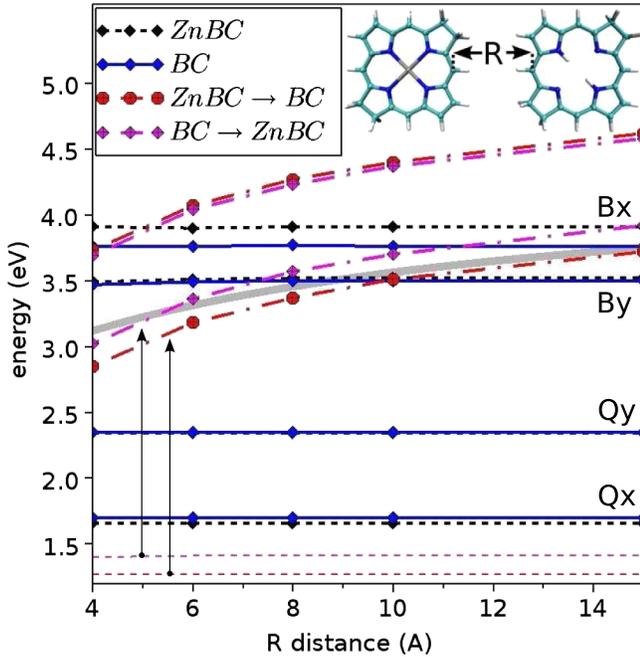


FIG. 2 (color online). GW -BSE excitation energies as a function of the ZnBC to BC distance R in the absence of the phenylene bridge as indicated on the atomic representation. The inset indicates the intramolecular or charge-transfer nature of the represented GW -BSE transitions. The lowest ZnBC \rightarrow BC CT excitation energy is compared to the $(E_{\text{gap}}^{GW} - e^2/D)$ Mulliken limit (thick grey line), with E_{gap}^{GW} the dimer GW quasiparticle band gap in the large D limit, where D is the distance between the two molecule centers. For the sake of comparison, the TDLDA values for the two low lying CT excitons are indicated by the two nondispersive dotted lines below 1.5 eV. The two vertical arrows indicate the difference between the TDLDA and GW -BSE values. For completeness, the higher lying intramolecular Soret B transitions and CT excitations, not detailed in the Table, are also reproduced.

finite (molecular) and extended (infinite solids) systems [49], is an important feature as discussed here below by comparison with previous studies.

As emphasized above, TD-DFT calculations with local kernels cannot reproduce the long-range electron-hole interaction: the CT energies remain constant and equal to the Kohn-Sham band gap. This is now well documented [4,6,7] and we clearly verify that point with our TDLDA data (see dotted lines below 1.5 eV in Fig. 2). As a dramatic improvement over local kernels, the TD-CAM-B3LYP approach [7] provides a much better agreement with GW -BSE calculations in the short-range limit of the bridged dimer (see above). However, as already noticed in Ref. [7], the $0.65/D$ long-range behavior [46] does not reproduce the correct $1/D$ long-range limit. Similarly, the asymptotic limit of the TD-B3LYP approach would reduce to $0.2/D$, thanks to the 20% of exact exchange. This discussion clearly underlines the difficulty of working with fixed parameter functionals performing equally well

at any range and in any screening environment (vacuum, solvent, etc.) [48].

As a final comparison, we now analyze the difference with the hybrid single configuration interaction (CIS) approach proposed in the seminal Ref. [4]. In the TDA approximation, valid for CT states in the long-range limit, CIS is equivalent to the time-dependent Hartree-Fock showing the correct $1/D$ asymptotic limit for charge transfer excitations, but with an incorrect asymptotic limit given by the donor-HOMO to acceptor-LUMO gap calculated in the absence of correlations. The neglect of correlation in TD-HF was corrected by a distance independent term obtained from DFT Δ SCF calculations at large distance. For $R = 5.85$ Å, the R distance in the true bridged configuration, this scheme was shown to lead a low-lying ZnBC \rightarrow BC CT excitation energies of 3.75 eV. This is ~ 0.6 eV larger than our GW -BSE 3.16 eV value found for the model dimer at the same distance.

As analyzed in Ref. [9], the assumption of a distance independent correlation correction to CIS leads to somehow too large excitation energies. This problem was addressed in a recent study [9] where scaled (parametrized) perturbative CIS(D) double excitation corrections to CIS were introduced to account for correlations [50], reducing the discrepancy with our BSE calculations to about 0.25 eV [51]. While differences in basis size may possibly explain part of the small residual discrepancy [51], we note that the various scaled CIS(D) approaches account for double excitations that are not described by the BSE formalism. The comparison of quantum chemistry post-Hartree-Fock correlated techniques, such as second-order Møller-Plesset (MP2) methods (see Note Ref. [50]), with the present GW -BSE approach, is a current challenge, with MP2 techniques facing scaling and divergency problems for extended systems with large polarizability, [52] while the GW -BSE approach on the contrary still needs further validation for finite size molecules. The present study clearly aims at contributing to that important goal.

In conclusion, we have performed an *ab initio* many-body GW -BSE perturbation theory analysis of the optical transition energies for the ZnBC-BC complex. For the isolated monomers, the calculated GW -BSE Q -band transition energies are found to be in remarkable agreement with experiment, in particular if one goes beyond the Tamm-Dancoff approximation. In the case of the ZnBC-BC complex, the GW -BSE calculations correctly locate the charge-transfer excitations above the monomer Q band transitions. Our CT excitation energies are found to be within less than 0.1 eV from parametrized TDDFT-CAM-B3LYP values for the short range charge transfer in the bridged configuration, but only the GW -BSE formalism can reproduce the correct long distance asymptotic limit. The possibility to study on the same footing, namely without any system-dependent parameter, charge transfer excitation energies at various ranges, both in the vacuum or

in a screening environment (solid, solvent, etc.), opens the way to important developments in the study of charge-transfer excitations and energy transfer processes at stake in photosynthetic processes or in organic photovoltaic cells.

I. D. acknowledges funding from the CEA “Eurotalent” program. The authors are indebted to C. Faber, C. Attaccalite, and V. Olévano, for many discussions and critical readings of our manuscript, and to M. Ernzerhof, M. Casida and M. B. Lepetit for discussions concerning TDDFT and quantum chemistry techniques. Calculations have been performed thanks to the French national super-computing IDRIS center at Orsay under Contract No. i2012096655 and the European research infrastructure PRACE (Program or Project No. 2010PA0880).

Note added in proofs.—After submission of the present manuscript, a Bethe-Salpeter study of charge-transfer excitations in organic systems was also published [53] confirming in particular the results of Ref. [11] where theory and available gas phase experiments are compared.

-
- [1] H. van Amerongen, R. van Grondelle, and L. Valkunas, in *Photosynthetic Excitons* (World Scientific, Singapore, 2000).
- [2] N. S. Sariciftci, L. Smilowitz, A. J. Heeger, and F. Wudl, *Science* **258**, 1474 (1992); S. A. Jenekhe and J. A. Osaheni, *Science* **265**, 765 (1994); J. L. Bredas, D. Beljonne, V. Coropceanu, and J. Cornil, *Chem. Rev.* **104**, 4971 (2004); Y. Kanai and J. C. Grossman, *Nano Lett.* **7**, 1967 (2007).
- [3] E. Runge and E. K. U. Gross, *Phys. Rev. Lett.* **52**, 997 (1984); *Time-Dependent Density Functional Theory*, edited by M. A. L. Marques, C. A. Ullrich, F. Nogueira, A. Rubio, K. Burke, and E. K. U. Gross (Springer-Verlag, Berlin, 2006); M. E. Casida, *J. Mol. Struct. (Theochem)* **914**, 3 (2009).
- [4] A. Dreuw and M. Head-Gordon, *J. Am. Chem. Soc.* **126**, 4007 (2004).
- [5] S. Botti, F. Sottile, N. Vast, V. Olevano, L. Reining, H.-C. Weissker, A. Rubio, G. Onida, R. Del Sole, and R. W. Godby, *Phys. Rev. B* **69**, 166112 (2004).
- [6] Y. Yamaguchi, S. Yokoyama, and S. Mashiko, *J. Chem. Phys.* **116**, 6541 (2002).
- [7] R. Kobayashi and R. D. Amos, *Chem. Phys. Lett.* **420**, 106 (2006); **424**, 225(E) (2006).
- [8] Q. Wu and T. van Voorhis, *Phys. Rev. A* **72**, 024502 (2005).
- [9] Y. M. Rhee and M. Head-Gordon, *J. Phys. Chem. A* **111**, 5314 (2007).
- [10] J. M. Garcia-Lastra and K. S. Thygesen, *Phys. Rev. Lett.* **106**, 187402 (2011).
- [11] X. Blase and C. Attaccalite, *Appl. Phys. Lett.* **99**, 171909 (2011).
- [12] In the case of intramolecular charge transfer excitations, see: D. Rocca, D. Y. Lu, and G. Galli, *J. Chem. Phys.* **133**, 164109 (2010).
- [13] I. Hanazaki, *J. Phys. Chem.* **76**, 1982 (1972).
- [14] T. Stein, L. Kronik, and R. Baer, *J. Am. Chem. Soc.* **131**, 2818 (2009).
- [15] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [16] J. P. Perdew, M. Ernzerhof, and K. Burke, *J. Chem. Phys.* **105**, 9982 (1996).
- [17] I. Cherkes, S. Klaiman, and N. Misseyev, *Int. J. Quantum Chem.* **109**, 2996 (2009) and references therein.
- [18] L. Hedin, *Phys. Rev.* **139**, A796 (1965).
- [19] M. S. Hybertsen and S. G. Louie, *Phys. Rev. B* **34**, 5390 (1986).
- [20] R. W. Godby, M. Schlüter, and L. J. Sham, *Phys. Rev. B* **37**, 10159 (1988).
- [21] G. Onida, L. Reining, and A. Rubio, *Rev. Mod. Phys.* **74**, 601 (2002).
- [22] L. J. Sham and T. M. Rice, *Phys. Rev.* **144**, 708 (1966); W. Hanke and L. J. Sham, *Phys. Rev. Lett.* **43**, 387 (1979).
- [23] G. Strinati, *Phys. Rev. Lett.* **49**, 1519 (1982); H. J. Mattausch, W. Hanke, and G. Strinati, *Phys. Rev. B* **27**, 3735 (1983); *Phys. Rev. B* **29**, 5718 (1984).
- [24] M. Rohlfing and S. G. Louie, *Phys. Rev. Lett.* **80**, 3320 (1998).
- [25] L. X. Benedict, E. L. Shirley, and R. B. Bohn, *Phys. Rev. Lett.* **80**, 4514 (1998).
- [26] S. Albrecht, L. Reining, R. Del Sole, and G. Onida, *Phys. Rev. Lett.* **80**, 4510 (1998).
- [27] X. Blase, C. Attaccalite, and V. Olevano, *Phys. Rev. B* **83**, 115103 (2011).
- [28] Y. Ma, M. Rohlfing, and C. Molteni, *Phys. Rev. B* **80**, 241405 (2009); *J. Chem. Theory Comput.* **6**, 257 (2010).
- [29] C. Faber, C. Attaccalite, V. Olevano, E. Runge, and X. Blase, *Phys. Rev. B* **83**, 115123 (2011).
- [30] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevLett.109.167801> for convergence tests on the bases size, the number of empty states used in the present calculations, and the atomic coordinates for the isolated bacteriochlorins.
- [31] J. M. Soler, E. Artacho, J. D. Gale, A. Garcia, J. Junquera, P. Ordejón, and D. Sánchez-Portal, *J. Phys. Condens. Matter* **14**, 2745 (2002).
- [32] We use standard norm-conserving pseudopotentials. See: N. Troullier and J.-L. Martins, *Phys. Rev. B* **43**, 1993 (1991). For Zn, we include the 3(*s*, *p*) semicore states in the valence to account for the core-valence exchange. However, very small differences are observed as compared to a calculation with frozen semicore states.
- [33] J. Vasudevan, R. T. Stibrany, J. Bumby, S. Knapp, J. A. Potenza, T. J. Emge, and H. J. Schugar, *J. Am. Chem. Soc.* **118**, 11676 (1996).
- [34] H. Scheer and H. H. Inhoffen, in *The Porphyrins* edited by D. Dolphin (Academic, New York, 1978), Vol. 2, p. 45.
- [35] M. J. Frisch *et al.*, *GAUSSIAN 03, Revision C.02* (Gaussian, Inc., Wallingford, CT, 2004). Coordinates are given in the Supplemental Materials.
- [36] L. Tiago, P. R. C. Kent, R. Q. Hood, and F. A. Reboredo, *J. Chem. Phys.* **129**, 084311 (2008).
- [37] M. Palumbo, C. Hogan, F. Sottile, P. Bagala, and A. Rubio, *J. Chem. Phys.* **131**, 084102 (2009).
- [38] S. Sharifzadeh, A. Biller, L. Kronik, and J. B. Neaton, *Phys. Rev. B* **85**, 125307 (2012).

- [39] P. H. Hahn, W. G. Schmidt, and F. Bechstedt, *Phys. Rev. B* **72**, 245425 (2005).
- [40] C. Rostgaard, K. W. Jacobsen, and K. S. Thygesen, *Phys. Rev. B* **81**, 085103 (2010).
- [41] S.-H. Ke, *Phys. Rev. B* **84**, 205415 (2011).
- [42] N. Marom, X. Ren, J. E. Moussa, J. R. Chelikowsky, and L. Kronik, *Phys. Rev. B* **84**, 195143 (2011).
- [43] C. Faber, J. L. Janssen, M. Côté, E. Runge, and X. Blase, *Phys. Rev. B* **84**, 155104 (2011).
- [44] The “*Q*” transitions are the lowest π - π^* transitions, below the strongest Soret “*B*” lines. The *x* and *y* labels indicate the polarization of the light that activates the transition. See: M. Gouterman, *J. Mol. Spectrosc.* **6**, 138 (1961).
- [45] M. Grüning, A. Marini, and X. Gonze, *Nano Lett.* **9**, 2820 (2009).
- [46] T. Yanai, D. P. Tew, and N. C. Handy, *Chem. Phys. Lett.* **393**, 51 (2004).
- [47] E. Livshits and R. Baer, *Phys. Chem. Chem. Phys.* **9**, 2932 (2007).
- [48] The BSE approach with static screening is formally equivalent to time-dependent Hartree plus screened exchange. As such, the screening automatically sets the range and strength of the effective Coulomb interaction. In particular, the correct $1/(\epsilon_M D)$ long-range limit would be correctly described within *GW*-BSE in a medium with macroscopic dielectric constant ϵ_M (e.g., in solvent conditions).
- [49] The *GW*-BSE approach was originally designed for extended semiconductors. See Ref. [23].
- [50] This approach is described in Ref. [9] as an “excited state analogues of ground state scaled second-order Møller-Plesset (MP2) methods.” The word “scaled” indicates that the implementation relies on scaling parameters educated on various molecules, excluding the ZnBC-BC complex.
- [51] Value estimated from Fig. 9 of Ref. [9]. Calculations in Ref. [9] were performed with a 6-31G* basis, namely a DZP basis smaller than the TZDP basis used here.
- [52] For a recent analysis, see: A. Grüneis, M. Marsman, and G. Kresse, *J. Chem. Phys.* **133**, 074107 (2010) and references therein.
- [53] B. Baumeier, D. Andrienko, and M. Rohlfing, *J. Chem. Theory Comput.* **8**, 2790 (2012).