Resonant hot charge-transfer excitations in fullerene-porphyrin complexes: a many-body Bethe-Salpeter study

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We study within the many-body Green’s function $GW$ and Bethe-Salpeter approaches the neutral singlet excitations of the zinc-tetraphenylporphyrin and $C_{70}$-fullerene donor-acceptor complex. The lowest transition is a charge-transfer excitation between the donor and the acceptor with an energy in excellent agreement with recent constrained density functional theory calculations. Beyond the lowest charge-transfer state, of which the energy can be determined with simple electrostatic models that we validate, the Bethe-Salpeter approach provides the full excitation spectrum. We evidence the existence of hot electron-hole states which are resonant in energy with the lowest donor intramolecular excitation and show an hybrid intramolecular and charge-transfer character, favouring the transition towards charge separation. These findings support the recently proposed scenario for charge separation at donor-acceptor interfaces through delocalized hot charge-transfer states.

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I. INTRODUCTION

Photo-induced charge-transfer excitations are at the heart of a large variety of physical phenomena and related applications, from photovoltaic cells for renewable energy applications, to light-harvesting biological systems involved e.g. in the photosynthesis processes occurring in plants or bacteria. In the former case of the so-called third generation solar cells such as all-organic devices or dye-sensitized Grätzel cells (DSSCs), the large binding energy of the photoexcited electron-hole pair requires the presence of a donor-acceptor interface in order to dissociate the bound excitons and produce the free carriers at the origin of the photocurrent. Even though the mechanisms explaining such a charge separation are still debated, it is believed that important intermediate states are the so-called charge-transfer excitations, with the hole and electron located respectively on adjacent donor and acceptor units (organic molecules, inorganic surface or cluster, etc.). Understanding the structural and electronic factors that control the transition from the photoinduced intramolecular (Frenkel) excitons, generated by light onto the donor molecules, to a bound charge-transfer (CT) state and subsequently to an unbound electron-hole charge-separated (CS) state, is an important goal on the road of improving the quantum efficiency of solar cells.

From a theoretical point of view, the correct description of non-local excitations, such as charge-transfer excited states with electrons and holes spatially separated, stands as a challenging issue. In particular, it is now well established that “standard” time-dependent density functional theory (TDDFT) approaches based on (semi)local exchange-correlation kernels, fail in providing a correct description of such charge-transfer (CT) excitations. This has been demonstrated in the case of inter- and intra-molecular CT excitations, but also in the case of extended bulk Wannier excitons in semiconductors for which holes and electrons are separated by a large effective bohr radius. Solutions involving non-local kernels based on e.g. range-separated hybrids are being actively developed and tested.

In a recent study, the lowest charge-transfer excitation in the zinc tetraphenylporphyrin (ZnTPP) donor associated with the $C_{70}$ fullerene acceptor was studied using a density functional theory (DFT) approach within an elegant and computationally efficient constrained formalism with a penalty functional forcing the jump of a chosen fraction of an electron from the ZnTPP highest occupied molecular orbital (HOMO) to the $C_{70}$ lowest unoccupied molecular orbital (LUMO). It was shown in particular that the related excitation energy of $\sim 1.8$ eV in case of a full electron transfer was much larger than the $\sim 0.9$ eV energy obtained with TDDFT based on the PBE kernel. Even though the available experiment was performed in a solvent with a different porphyrin, the constrained-DFT result is in much better agreement with the range of experimental values.

Computationally very efficient and accurate, such DFT-based techniques cannot provide however the detailed excitonic (or absorption) spectrum at the donor-acceptor interface. In particular, the energy position of the donor intramolecular (Frenkel) low-lying exciton with respect to the charge-transfer excitonic spectrum, including the higher energy (hot) charge-transfer states, is a crucial information needed to understand the dissociation of the excitons generated on the donor side and that have diffused to the donor-acceptor interface. Mechanisms where intramolecular excitons evolve into charge-separated states through hot (high energy) CT excitations, including the higher energy (hot) charge-transfer states, is a crucial information needed to understand the dissociation of the excitons generated on the donor side and that have diffused to the donor-acceptor interface. The related knowledge of the excitonic wavefunctions is a crucial ingredient governing e.g. the calculation of...
charge-transfer rates. Furthermore, in the case of the constrained DFT study of the $C_{70}$-ZnP complex, the underlying assumption of a full electron transfer may deserve closer inspection.

Recently, charge-transfer excitations in small gas phase donor-acceptor complexes, associating tetracyanoethylene with several acene derivatives, were studied using the many-body perturbation theory framework within the so-called GW and Bethe-Salpeter (BSE) formalisms. It was shown in particular that an excellent agreement with experiment could be obtained for the lowest charge-transfer excitation, with a mean absolute error within 0.1 eV. This accuracy matches that of the latest range-separated functional TDDFT studies with the range parameter adjusted to provide an accurate quasiparticle band gap.

The same formalism was used to study intramolecular charge-transfer excitations in a recent family of molecular dyes for DSSCs, the coumarins, showing a mean absolute error of the order of 0.06 eV as compared to reference quantum chemistry coupled-cluster or tuned range-separated hybrid TDDFT calculations.

In the present work, we report the detailed excited state spectrum of the $C_{70}$ fullerene associated with the zinc tetraphenylporphyrin (ZnP). This study is performed within the many-body Green’s function GW and Bethe Salpeter formalisms using the same cofacial geometry as that used in the constrained DFT study of Ref. 11. Our results are in excellent agreement with constrained DFT calculations for the lowest lying $C_{70}$ charge-transfer excitation, but provide further the entire excitation spectrum. It is shown in particular that several hot electron-hole excited states lie in between the lowest intramolecular ZnP* donor excitation and the $C_{70}$ exciplex. Of peculiar importance, several hot states with hybrid intramolecular and charge-transfer character are found to be resonant in energy with the photo-induced ZnP* exciton, a finding important in the perspective of the recently proposed scenarios where charge-separation occurs directly through delocalized hot charge-transfer states.

II. METHODOLOGY

Our calculations are performed with the FIESTA code, a recently developed GW-BSE package based on a Gaussian auxiliary basis expansion of the needed two-body operators such as the dielectric susceptibility, and the bare or screened Coulomb potentials. Dynamical correlations are calculated exactly using contour deformation techniques without any plasmon pole approximation. The needed Kohn-Sham eigenstates are obtained from the SIESTA package with a well-converged triple-zeta plus double polarization basis (TZDP) and standard norm-conserving pseudopotentials combined with the local density approximation (LDA) for the exchange-correlation functional. All empty states are included in the summation over transitions involved in the calculation of the independent-electron susceptibilities. As shown recently in the study of charge-transfer excitations in several $\pi$-conjugated organic donor-acceptor systems, the present scheme provides results in excellent agreement with planewave-based GW-BSE studies performed with the Yambo code exploiting Kohn-Sham eigenstates generated with the Quantum-ESpresso package.

The definition of the auxiliary basis, consisting of six Gaussians per $s,p,d$-channel, together with extensive convergence tests as a function of the auxiliary basis size, can be found in a recent study of a photosynthetic donor-acceptor complex.

We go beyond the standard “single-shot” $G_0W_0$ calculation by performing a partial self-consistent loop onto the quasiparticle eigenvalues, leaving the Kohn-Sham wavefunctions unchanged. Such a scheme has been shown for molecular systems to lead to quasiparticle energy gaps, between the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals, in better agreement with experiment than the standard $G_0W_0$ calculation based on DFT-LDA or DFT-PBE eigenstates at a cost much reduced as compared to full self-consistency. Similarly, GW-BSE CT excitations in reference donor-acceptor complexes were shown to agree much better with experiment if such a partial self-consistency is performed at the initial GW-level. The dependence of the final GW quasiparticle energies on the starting Kohn-Sham eigenstates is significantly reduced, and GW calculations starting from DFT-LDA or Hartree-Fock-like eigenvalues were shown to converge towards the same GW spectrum for several organic molecules.

While the GW calculations provide accurate quasiparticle energies, including not only the correct HOMO-LUMO gap, but also a correct spacing and ordering within the occupied (unoccupied) states, the subsequent resolution of the Bethe-Salpeter equations (BSE) aims at providing the correct neutral excitation energies, accounting in particular for electron-hole interaction. We go beyond the Tamm-Dancoff approximation, including namely the coupling of resonant and non-resonant excitations. As shown in previous work, the Tamm-Dancoff approximation leads in the case of molecular (or nanosized) systems to an overestimation of the transition energies by as much as 0.3 eV.

The BSE Hamiltonian is most commonly expressed in the $|\phi_i^e \phi_j^h>$ product basis, where ($\phi_i^e$) and ($\phi_j^h$) are unoccupied (electron) and occupied (hole) Kohn-Sham states, respectively. In particular, the resonant contribution is composed of a “non-interacting” diagonal part ($H^\text{diag}$), a direct ($H^\text{direct}$) and an exchange contribution ($H^\text{exch}$) term, with:

$$H^\text{diag}_{ij,kl} = \left( \varepsilon_i^{QP} - \varepsilon_j^{QP} \right) \delta_{ik} \delta_{jl}$$

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

where $\varepsilon_i^{QP}$ is the quasiparticle energy of Kohn-Sham state $i$ and $W(\mathbf{r}, \mathbf{r}')$ is the density-density response function.
\[ H_{ij,kl}^{exch} = 2 \int dr dr' \phi_i^*(r) \phi_j^*(r) v(r, r') \phi_k^*(r') \phi_l^*(r'), \]

where the \( \phi_{ij}^{exch} \) are the quasiparticle (GW) energies, while \( W(r, r') \) and \( v(r, r') \) are the (statically) screened and bare Coulomb potential, respectively. It can be noticed in particular that the direct term does not cancel in the limit of spatially non-overlapping electron and hole states, an important remark concerning charge-transfer states.

Due to the fast increase in size with the number of unoccupied states of the electron-hole two-body product \( |\phi_i^e \phi_j^h> \) basis states, we restrict our BSE basis to transitions between the occupied states and 360 unoccupied levels, that is namely empty states up to 20 eV above the HOMO level. Convergency tests can be found again in Ref. 58 for donor-acceptor systems of similar size. We emphasize that the low-lying charge-transfer excitations, with much weight on the lowest occupied and unoccupied Kohn-Sham electron-hole product states, converge extremely quickly with the size of the BSE basis, but this is not necessarily the case for intramolecular excitations or higher (hot) CT excitations.

III. RESULTS

We adopt the same geometry as that used in the constrained-DFT study of the C\(_{70}\)-ZnTPP complex in Ref. 11. Namely, the distance between the Zn atom and the center of the closest electron-rich (6:6) C\(_{70}\) carbon bond is fixed to 2.8 Å using a constrained relaxation scheme. Such a geometry stems in particular from the analysis of the stability of several fullerene-porphyrin complexes in various geometries. However, as shown recently in the case of a fullerene-polythiophenes interface, significant disorder is to be expected at the bulk donor-acceptor interface, so that the present geometry is adopted for sake of comparison with available previous calculations of charge-transfer excitations.

A. Quasiparticle spectrum within GW

We show in Fig. 1 a cartography of the Kohn-Sham (left) and GW (right) eigenvalues together with a representation of a few associated eigenstates. As expected, the quasiparticle HOMO-LUMO gap is significantly opened from the DFT-LDA to the GW calculation. The quasiparticle GW HOMO-LUMO gap is found to be of 3.45 eV, namely 2.6 eV larger than the corresponding DFT-LDA Kohn-Sham result. Our GW HOMO-LUMO gap is in very good agreement with the 3.56 eV value found for the same system in Ref. 54 by taking differences of total energy between the neutral and positively or negatively charged complex at the DFT-PBE level within the standard ∆SCF approach. Similarly, our ionization potential of 6.25 eV is in close agreement with the reported 6.21 eV ∆SCF-PBE value. In the absence of gas phase experimental data, such a close agreement between the two approaches is very satisfactory.

The donor-acceptor, or type-II, character of the complex is evidenced by the relative positions (frontier orbitals energy offsets) of the C\(_{70}\) and ZnTPP eigenstates across the gap. At the GW level, the ZnTPP HOMO (LUMO) is located 0.95 eV (1.05 eV) above the C\(_{70}\) HOMO (LUMO) state. The (HOMO) and (HOMO-1) orbitals are the standard porphyrin Guterman orbitals, the (HOMO-2) being also localized onto ZnTPP, while the (nearly) 3-fold level beneath derives from the HOMO of the C\(_{70}\) fullerene. The three lowest unoccupied levels, (LUMO) to (LUMO+2), derive from the 2-fold e\(_1\) and a\(_1\) unoccupied levels of C\(_{70}\), the two unoccupied Guterman orbitals located on ZnTPP being the (LUMO+6) and (LUMO+7) levels. Such a mapping of orbitals will allow us to analyze the optical excitations in terms of intramolecular (Frenkel) versus charge-transfer transitions.

The intramolecular ZnTPP HOMO-(LUMO+6) gap is found to be 4.5 eV, of comparable size with the intramolecular C\(_{70}\) (HOMO-3)-LUMO gap (4.4 eV), but ~1.1 eV larger than the true charge-transfer HOMO-
LUMO quasiparticle gap. The relative strength of the intramolecular (Frenkel) and charge-transfer electron-hole pairs binding energy will reshuffle the ordering of the photo-induced transition as compared to the GW occupied to unoccupied quasiparticle energy differences. The comparison between the ∼3.5 eV HOMO-LUMO gap and the 1.6-1.8 eV optical absorption threshold found in Refs. 11,12 indicates that in such systems the electron-hole interaction is extremely large, amounting to about half the quasiparticle gap. This is what we now study within the Bethe-Salpeter formalism that aims at accurately describing the electron-hole interaction in the photo-induced excited states.

B. The low-lying charge-transfer state within BSE

Our GW-BSE results for the neutral (singlet) excitation energies are provided in Fig. 2 where we have distinguished the excitations with respect to their intramolecular or charge-transfer character. Such a distinction stems from the analysis of the weight of the Bethe-Salpeter two-body eigenstates onto the Kohn-Sham occupied-unoccupied product state basis. We provide further, in Fig. 2 and Fig. 3 a representation of selected two-body excitonic eigenstates $\psi^{\nu}_{\nu'}(r_e, r_h)$, with $(r_e, r_h)$ the electron and hole positions, respectively, and $\nu$ the excitation index, by plotting in grey the hole-averaged electron-density, that can be obtained by taking the expectation value of the electron $\delta(r - r_e)$ position operator over $\psi^{\nu}_{\nu'}$. Similarly, the electron-averaged hole distribution is represented in blue (wireframe).

The GW-BSE low-lying singlet excitation is a clear charge-transfer state located at 1.65 eV above the ground-state (we will use the notation $CT_0$ in the following). Since the $C_{70}$ LUMO is (nearly) 3-fold degenerate (see Fig. 1), the 3 low-lying CT excitations are linear combinations of transitions between the HOMO and the LUMO, LUMO+1 and LUMO+2 levels, namely:

$$\psi_{\nu=1,2,3}(r_e, r_h) \simeq \sum_{n=0}^{2} c_{n, \nu}^\nu \phi_{\text{homo}}(r_h) \phi_{\text{lumo}+n}(r_e).$$

For the lowest lying transition, we find typically: $(|c_1|^2 = 0.29, |c_2|^2 = 0.27, |c_3|^2 = 0.42)$. As such, these low-lying excitations are very clear charge-transfer states with the jump of nearly one electron from the donor related HOMO level to the manifold of the acceptor LUMO. This reflects in the representation of the two-body wavefunction for the lowest $CT_0$ state (Fig. 3b) showing that the (hole-averaged) electron density is very clearly located onto the $C_{70}$ molecule while the (electron-averaged) hole density resides onto the donor ZnTPP molecule.

Our ∼1.65 eV GW-BSE excitation energy for the lowest excitation is in good agreement with the 1.8 eV value extrapolated from constrained-DFT calculations under the assumption that a full electron is transferred between the donor and the acceptor. On general grounds, apart from the performances of the PBE functional in calculating differences of total energies for such systems, a constrained approach within a variational framework necessarily yields an upperbound for the excitation energy. As emphasized further in Ref. 11, the assumption of a slightly reduced electron transfer would bring the constrained-DFT and BSE calculations in even better agreement. An analysis of Fig. 5 of Ref. 11 shows that the largest charge transfer explicitly studied by Ghosh and Gebauer corresponds to a transfer of ∼0.97 electron with a corresponding excitation energy of ∼1.7 eV, in close agreement with our findings, the 1.8 eV value being an extrapolated energy for full electron transfer.

As observed in Refs. 11,55, the direct comparison with experiment is difficult. Existing experimental values by Mukherjee and coworkers report the lowest excitation for the parent octadecyloxyporphyrin-$H_2$TPP (freebase porphyrin) $C_{70}$ at 1.7 eV in toluene solvent and 1.8 eV in chlorophorin. As shown in Refs. 57,60, the replacement of the freebase porphyrin by a central Zn atom leads
to a 0.1-0.2 eV redshift of the CT$_0$ excitation energy. On the contrary, removing the effect of solvent would lead to a compensating 0.2-0.3 eV blueshift (see analysis in Ref. 60), even though the redshift of the CT excitation energy observed by Mukherjee and coworkers upon changing chlorophorme by the less polar toluene solvant indicates potentially more complex trends.

Even though the comparison with experiment is difficult, we observe that the agreement is significantly better than what is obtained within TDDFT and (semi)local kernels, namely ~0.9 eV in the TD-PBE study of Ref. 11. The underestimation of charge-transfer excitations energy within TDDFT and (semi)local kernels is now well documented. Such a discrepancy lies in the lack of electron-hole interaction in the case of non-overlapping HOMO-LUMO states, a situation that can be clearly evidenced e.g. by the absence of dispersion of the CT excitation energy as a function of donor-acceptor distance, contradicting the simple electrostatic limit of a (-1/D) scaling of the interaction between two well separated positive and negative charges, where D is some averaged measure of the electron-hole distance. The lack of electron-hole interaction for CT states indicates that the CT$_0$ excitation energy reduces to the (too small) Kohn-Sham HOMO-LUMO gap, that is indeed the ~0.85 eV HOMO-LUMO gap that we find at the DFT-LDA level.

C. Testing models for charge-transfer excitations

The very clear charge-transfer character of the CT$_0$ low-lying excitation allows further to test approximations of use in the quantum chemistry community by extracting from the BSE Hamiltonien the following matrix elements of the bare and (statically) screened Coulomb operator, namely:

$$E_{eh}^{B,(1)} = \int \int d\mathbf{r} d\mathbf{r}' |\phi_{\text{homo}}(\mathbf{r})|^2 W(\mathbf{r}, \mathbf{r}') |\phi_{\text{lumo}+n}(\mathbf{r}')|^2,$$

$$E_{eh}^{B,(2)} = \int \int d\mathbf{r} d\mathbf{r}' |\phi_{\text{homo}}(\mathbf{r})|^2 v(\mathbf{r}, \mathbf{r}') |\phi_{\text{lumo}+n}(\mathbf{r}')|^2,$$

with (n=0,1,2). Such matrix elements are nearly independent of (n) with: $E_{eh}^{B,(1)}=1.56 \pm 0.02$ eV and $E_{eh}^{B,(2)}=1.72$ eV $\pm 0.06$ eV. The exchange matrix elements, namely:

$$E_{eh}^{X} = \int \int d\mathbf{r} d\mathbf{r}' \phi_{\mathbf{h}}(\mathbf{r}) \phi_{\mathbf{l}}(\mathbf{r}) v(\mathbf{r}, \mathbf{r}') \phi_{\mathbf{h}}(\mathbf{r}') \phi_{\mathbf{l}}(\mathbf{r}')$$

where (h) stands for (homo) and (l) for either (lumo), (lumo+1) or (lumo+2), amount only to less than 1 meV as a result of the charge separation between the (HOMO) and the (LUMO) states. Subtracting now the screened Coulomb electron-hole interaction $E_{eh}^{B,(1)}$ to the GW quasiparticle HOMO-LUMO gap (3.45 eV), one obtains a simple estimation of the CT excitation energy, namely 1.89 eV, in reasonable agreement with the 1.65 eV value obtained with the full GW-BSE treatment. As an even simpler approximation, which does not necessitate the calculation of the full dielectric matrix, subtracting now the bare Coulomb potential related $E_{eh}^{B,(2)}$ energy to the GW HOMO-LUMO gap, one obtains 1.72 eV in (accidentally) even better agreement with the GW-BSE value.

The present results clearly suggest that even in the limit of a separation of ~2.8 Å in a cofacial geometry, namely a distance and a configuration maximizing the wavefunction overlap between the donor and the acceptor for such π-stacking systems, the rather crude “electrostatic” model consisting in replacing the electron-hole binding energy by the bare Coulomb integral $E_{eh}^{B,(2)}$ provides very acceptable results, with an error as compared to the full BSE value of the same order of magnitude than the difference between the GW-BSE treatment and the (extrapolated) constrained-DFT approach. This simple evaluation of the electron-hole binding energy in charge-transfer states was used for example in Ref. 61 to predict the evolution of the electron-hole binding energy for several donor-acceptor complexes and relative geometry. This simple scheme relies however on the assumption that the excited state is a clear charge-transfer state, with no mixing with higher energy ($\phi_{\mathbf{h}}^i \phi_{\mathbf{l}}^j$) single-particle transitions, an approximation of the same nature than the ones used in the constrained-DFT approach with the “guess” that a full electron is transferred.
D. “Hot” excited states: resonant intramolecular and charge-transfer excitations

While our GW-BSE calculations yield results in good agreement with the computationally more efficient constrained-DFT approach for the low-lying CT\textsubscript{0} level, the GW-BSE framework provides the entire excitation spectrum as illustrated in Fig. 2. In particular, the relative position of the lowest intramolecular (Frenkel) donor excitation (labeled ZnTPP\textsuperscript{*} here below), and the charge-transfer excitations at the donor-acceptor interface, is believed to be a crucial factor in understanding the mechanism(s) controlling the transition from a strongly bound electron-hole pair to a charge-separated (CS) state with unbound holes and electrons diffusing to the electrodes. In recent combined experimental and theoretical studies\textsuperscript{44,45}, the role of hot CT\textsubscript{n} charge-transfer excitations in mediating the transition between Frenkel and CS states was advocated on the basis of experimental pump-probe experiments and quantum chemistry calculations. Located at higher an energy than the lowest lying CT\textsubscript{0} level studied here above, the CT\textsubscript{n} hot states are significantly more delocalized due to their extra kinetic energy, a favourable feature for evolving into a charge-separated state\textsuperscript{46,47}.

We can now analyze the present ZnTPP-CT\textsubscript{70} system along these lines and study in particular the position of the ZnTPP\textsuperscript{*} lowest intramolecular excitation with respect to the manifold of CT states. Within the present GW-BSE approach, the ZnTPP\textsuperscript{*} Q-like\textsuperscript{44,45} excited state is located at \(\sim 2.14\) eV (see left “donor” column in Fig. 2) with a corresponding two-]{}body eigenstate provided in Fig. 3(b). Such a state is composed of transitions from the (HOMO-\(n\)) \(n=0,1,2\) ZnTPP-related levels to the (LUMO+6) and (LUMO+7) levels deriving from the lowest unoccupied levels of the isolated ZnTPP molecule (see Fig. 4). The GW-BSE excitation energy (\(\sim 2.14\) eV) is very close to the experimental \(Q_{x,y}\) value of 2.09 eV for gas phase ZnTPP\textsuperscript{45}. Previous GW-BSE calculations of Q-transitions in a parent zincbacteriochlorin molecule\textsuperscript{44} and freebase H\textsubscript{2}ZnTPP\textsuperscript{44} were shown to lead as well to an agreement within 0.1 eV as compared to experiment for such intramolecular low-lying excitations.

As depicted in Fig. 2 the ZnTPP\textsuperscript{*} intramolecular excitation lies near or above several charge-transfer excitations located above the CT\textsubscript{0} state. Among these higher-energy, or hot, excited states, interesting transitions are the excitations \((\nu = 16)\) and \((\nu = 17)\) that lies within 10 meV of the ZnTPP\textsuperscript{*} lowest intramolecular excitation. With the notations defined above, one finds for the corresponding two-body eigenstates:

\[
\psi_{\nu=16,17}(r_e, r_h) \simeq c_{h,l=6}^{\nu} \phi_{\text{homo}}(r_h) \phi_{\text{lumo}+6}(r_e) + c_{h,l=7}^{\nu} \phi_{\text{homo}+1}(r_h) \phi_{\text{lumo}+7}(r_e) + c_{h,l=7}^{\nu} \phi_{\text{homo}+2}(r_h) \phi_{\text{lumo}}(r_e),
\]

with \(\{|c_{h,l=6}^{\nu}|^2, |c_{h,l=7}^{\nu}|^2, |c_{h,l=7}^{\nu}|^2\}\) equal to (0.40, 0.32, 0.15) for \((\nu = 16)\) and (0.10, 0.09, 0.74) for \((\nu = 17)\). Again, the (lumo+6) and (lumo+7) levels are mainly the nearly degenerate lowest unoccupied Gouterman orbitals of the ZnTPP molecule. As such, the two-body wavefunctions present both a charge-transfer character, with the (homo-2) to (lumo) transition component, but also an intramolecular ZnTPP character, with the (homo) to (lumo+6) and (homo-1) to (lumo+7) components. The corresponding excitonic wavefunctions are represented in Fig. 3(c,d), evidencing this hybrid character. The \((\nu = 16)\) excitation is mainly a ZnTPP intramolecular transition showing however a significant probability for the electron (grey contours) to jump onto the C\textsubscript{70} acceptor. The \((\nu = 17)\) excitation is mainly a CT transition with the excited electron sitting mainly onto the C\textsubscript{70} acceptor, but with a strong weight as well onto the ZnTPP donor, in great contrast with the low lying CT\textsubscript{0} state which is a pure charge-transfer state.

While the present system, comprising only one donor-acceptor complex, cannot be used to test the delocalization of the hot excited states over several donor (for the hole) or acceptor (for the electron) molecules, a delocalization expected to favour charge separation\textsuperscript{45} the present finding indicates that the extra kinetic energy of the hot excited states, as compared to the low lying CT\textsubscript{0} state, induces also the delocalisation of the hole and electron over the neighbouring donor and acceptor molecules, generating hybrid intramolecular and charge-transfer states. The present results are consistent with a previous semi-empirical study\textsuperscript{65} of a C\textsubscript{60}-polymer blend evidencing a rapid drop of the “ionicity” of charge-transfer excited states with increasing energy, a reduction of the charge-transfer character characterizing an hybridization with intramolecular transitions. It was shown however that the number, energy and character of the CT states lying below the intramolecular donor (polymer) excitations were strongly dependent on the parametrization of the intersite \((V_{ij})\) Coulomb potential, making the case for accurate parameter-free \textit{ab initio} calculations.

Such an energy alignment and wavefunction overlap between the ZnTPP\textsuperscript{*} intramolecular low-lying excitation and these hot CT\textsubscript{n} states is a strong indication that transitions between these resonating states will be strongly favoured\textsuperscript{65}. The present findings may suggest an additional criteria for designing donor-acceptor complexes with efficient charge separation through transient hot (delocalized and weakly bound) charge-transfer states, namely the existence, at the energy of the lowest ZnTPP\textsuperscript{*} donor intramolecular excitation, of a large density of resonating states with hybrid intramolecular and charge-transfer character. Adopting a simple hydrogenoid model for the electron-hole pair, this can be expected to be achieved by maximizing the energy difference between the low-lying CT\textsubscript{0} charge-transfer state and the intramolecular ZnTPP\textsuperscript{*} donor excitation. Even though equivalent to the standard criteria for energy-
gradient-driven transitions to the CT$_n$ state, we emphasize that the argument here applies to a scenario where electron-hole dissociation occurs through hot charge-transfer states, avoiding as much as possible the adverse recombination in the low lying strongly bound CT$_0$ exciplex. Following Ref. 8, we represent schematically in Fig. 4 a flow of transitions from donor intramolecular to resonant hot CT$_n$ states, and finally to a charge-separated (CS) state.

In a recent GW-BSE study of a C$_{60}$-quaterthiophene system, much emphasis was given to calculating the difference of energy ($\Delta \Omega$) between the lowest donor intramolecular Frenkel (FE) exciton and the charge-transfer CT$_0$ state. $\Delta \Omega$ was found to be sensitive to the relative donor-acceptor orientation, with an average positive value strongly detrimental to the FE $\rightarrow$ CT$_0$ transition. Further, as observed above, the binding energy ($E_{CT0}^B$) of the electron-hole pair in the CT$_0$ state was found to be much larger than room temperature. Even though based on very accurate calculations, such results do not allow to understand the observed efficiency of state-of-the-art fullerene-polythiophene systems. While the difference between isolated gas phase donor-acceptor dimers, on which calculations are usually performed, and more realistic bulk donor-acceptor heterojunctions (BHJ) was invoked, a possible alternative interpretation lies in the scenario where charge separation occurs directly through hot CT$_n$ states, without transition to the highly bound CT$_0$ state, so that variations in $\Delta \Omega$ and $E_{CT0}^B$ become less relevant.

Back to the present ZnTPP-$C_{70}$ system, the further analysis of the CT states lying between the CT$_0$ and ZnTPP$^*$ levels shows several states with hybrid charge-transfer and intramolecular character, but with a clear weight onto intra-fullerene excitations. Since photoexcited pairs are mainly generated in the donor (ZnTPP) part of the heterojunction, such excitations cannot be efficient intermediate states for charge separation, indicating on the contrary a pathway to an adverse relocalization of the electron-hole pair onto the fullerene side.

As a final analysis, we now compare our results to a recent study of the excited states of fullerene-porphyrin complexes based on another computationally efficient DFT-based framework. As described in Ref. 68, this efficient, but approximate, approach relies on a second-order perturbative correction to the “excited” Slater determinant obtained by replacing one occupied single-particle DFT Kohn-Sham orbital by an empty one in the ground-state Kohn-Sham many-body wavefunction. Since the empty and occupied orbitals considered were the (HOMO) to (HOMO-2) and (LUMO) to (LUMO+2) orbitals, only low-lying charge-transfer states could be studied, excluding in particular the intramolecular ZnTPP excitations, involving the (LUMO+6) and (LUMO+7) single-particle empty orbitals, and the hybrid states above-mentioned.

The lowest charge-transfer CT$_0$ excitation within this scheme was found to be located at 1.95 eV above the ground-state. Our GW-BSE value is $\sim 0.3$ eV smaller. Even though slightly less satisfactory than the comparison with the variational constrained DFT calculation, the agreement remains reasonable. Since this approach is perturbative, it is difficult to conclude whether, on general grounds, it should produce an upper- or lower-bound for the exact result. In however excellent agreement with this perturbative technique, the three lowest excitations are CT excitations with a strong weight on the HOMO to LUMO, LUMO+1 and LUMO+2 quasidegenerate levels, the following excitation being mainly a (HOMO-1) to (LUMO+2) transition. Inclusion of intramolecular transitions in the pool of studied excitations may certainly help in favouring the comparison with other techniques and in revealing the excitations with hybrid intramolecular and charge-transfer character.

**IV. CONCLUSION**

We have studied within the many-body Green’s function GW and Bethe-Salpeter formalisms the singlet excitation energies in a fullerene-porphyrin $C_{70}$-ZnTPP complex. The lowest-lying excited state is a charge-transfer (CT$_0$) state with $\sim 1.65$ eV energy, a value in good agreement with recent constrained DFT calculations leading, for the same geometry, to a 1.8 eV upper-bound in the asymptotic limit of a full electron transfer. The energy of the CT$_0$ state can be estimated simply from the knowledge of the correct GW HOMO-LUMO

![FIG. 4: (Color online) Symbolic representation (following Ref. 8) showing the potential flow of transitions from intramolecular (Frenkel) excitations, localized on the donor, to resonant hot charge-transfer (CT$_n$) states (red arrow) and subsequently unbound charge-separated (CS) electron-hole pair (orange arrow). The adverse decay into the low lying CT$_0$ state is also represented with the green arrow.](image-url)
gap and of simple Coulomb integrals between the HOMO and LUMO Kohn-Sham eigenstates density. Beyond the lowest excitation, the GW-BSE framework provides the full excitation spectrum, allowing in particular to assess the relative position of the lowest intramolecular ZnTPP$^*$ donor excitation with respect to the manifold of hot charge-transfer $CT_n$ states. We reveal in particular the existence of several excitons with an hybrid intramolecular and charge-transfer character which are resonant in energy with the ZnTPP$^*$ excitation. Such findings suggest a rapid transition from the photo-generated ZnTPP$^*$ state to hot CT$_n$ states with excess kinetic energy as compared to the lowest CT$_0$ state, favouring thus the transition towards unbound charge-separated states. More direct comparison to experimental results requires to account for environmental effects, namely the renormalisation of the quasiparticle and neutral excitation energies from the gas phase to realistic bulk phases. The combination of the present GW and Bethe-Salpeter formalisms with proper and accurate polarizable models is certainly an important goal for the community in order to properly discriminate between the various scenario proposed for charge separation in a realistic environment.

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1. N.S. Sariciftci, L. Smilowitz, A.J. Heeger, F. Wudl, Science 258, 1474 (1992); S.A. Jenekhe, J.A. Osaheni, Science 265, 765 (1994); J.L. Bredas, D. Beljonne, V. Coropceanu, J. Cornil, Chem. Rev. 104, 4971 (2004).
2. H. van Amerongen, R. van Grondelle, and L. Valkunas, in Photosynthetic Excitons (World Scientific, Singapore, 2000).
3. For a recent discussion, see: A.A. Bakulin, A. Rao, V.G. Pavelyev, PHM van Loosdrecht, MS. Pshenichnikov, D. Niedzialek, J. Cornil, D. Beljonne, RH. Friend, Science 335, 1340-1344 (2012); and references therein.
4. Domenico Caruso and Alessandro Troisi, Proc. Natl. Acad. Sci. USA 109, 13498 (2012); and references therein.
5. E. Runge and E.K.U. Gross, Phys. Rev. Lett. 52, 997 (1984); M.A.L. Marques, C.A. Ulrich, F. Nogueira, A. Rubio, K. Burke, and E.K.U. Gross (eds.), Time-Dependent Density Functional Theory (Springer-Verlag, 2006); Mark E. Casida, J. Mol. Struct. (Theochem) 914, 3 (2009).
6. A. Dreuw, J.L. Weisman, M. Head-Gordon, J. Chem. Phys. 119, 2943 (2003).
7. Andreas Dreuw and Martin Head-Gordon, J. Am. Chem. Soc. 2004, 126, 4007–4016.
8. S. Botti, F. Sottile, N. Vast, et al., Phys. Rev. B 69, 155112 (2004).
9. A. Savin, in Recent Developments and Applications of Modern Density Functional Theory, edited by J. M. Seminario (Elsevier, Amsterdam, 1996), Chap. 9, pp. 327-354; T. Leininger, H. Stoll, H. J. Werner, and A. Savin, Chem. Phys. Lett. 275, 151 (1997); J. Toulouse, F. Colonna, and L.X. Benedict, E. Shirley, R.B. Bohn, Phys. Rev. Lett. 86, 155315 (2001).
10. For a recent review, see e.g.: L. Kronik, T. Stein, S. Refaely-Abramzon, and R. Baer, J. Chem. Theo. Comp. 8, 1515 (2012).
11. Prasenjit Ghosh and Ralph Gebauer, J. Chem. Phys. 132, 104102 (2010).
12. J.P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
13. P. Mukherjee, S. Bhattacharya, S.K. Nayak, S. Chattopadhyay, S. Bhattacharya, Chem. Phys. 360, 116 (2009).
14. For other constrained-DFT approaches to obtain the lowest lyong charge-transfer states, see: Q. Wu, and T. Van Voorhis, J. Chem. Theo. Comp. 2, 765 (2006); Yosuke Kanai and Jeffrey C. Grossman, Nano Lett. 7, 1967-1972 (2007).
15. J. M. Garcia-Lastra and K. S. Thygesen, Phys. Rev. Lett. 106, 187402 (2011).
16. X. Blase, C. Attaccalite, Appl. Phys. Lett. 99, 171909 (2011).
17. B. Baumeier, D. Andrienko, and M. Rohlfing, J. Chem. Theor. Comp. 8, 2790 (2012).
18. L. Hedin, Phys. Rev. 139, A796 (1965).
19. G. Strinati, H.J. Mattausch, W. Hanke, Phys. Rev. Lett. 45, 290 (1980); ibid, Phys. Rev. B 25, 2867 (1982).
20. M.S. Hybertsen and S.G. Louie, Phys. Rev. B 34, 5390 (1986).
21. R.W. Godby, M. Schlüter, and L.J. Sham, Phys. Rev. B 37, 10159 (1988).
22. G. Onida, L. Reining, A. Rubio, Rev. Mod. Phys. 74, 601 (2002).
23. For a compilation of GW results in the crystalline solid phase, see, e.g., W. G. Aulbur, L. Jonsson, J.W. Wilkins, in Solid State Physics, edited by H. Ehrenreich (Academic, Orlando, 1999), Vol. 54, p. 1.
24. L.J. Sham and T.M. Rice, Phys. Rev. 144, 708 (1966); W. Hanke and L.J. Sham, Phys. Rev. Lett. 43, 387 (1979).
25. 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).
26. M. Rohlfing and S.G. Louie, Phys. Rev. Lett. 80, 3320 (1998).
27. L.X. Benedict, E. Shirley, R.B. Bohn, Phys. Rev. Lett. 80, 4514 (1998).
28. S. Albrecht, L. Reining, R. Del Sole, G. Onida, Phys. Rev. Lett. 80, 4510 (1998).
29. I.J. Hanazaki, Phys. Chem. 76, 1982 (1972).
30. T. Stein, L. Kronik, and R. Baer, J. Chem. Phys. 131, A796 (2009).
31. C. Faber, I. Duchemin, T. Deutsch, X. Blase, Phys. Rev. B 86, 155315 (2012).
32. Y. Kurashige, T. Nakajima, S. Kurashige, K. Hirao, and N. Nishikita, J. Phys. Chem. A 111, 5544 (2007).
33. B. M. Wong and J. G. Cordaro, J. Chem. Phys. 129, 214703.
(2008).

For another study of intramolecular charge-transfer excitations using the Bethe-Salpeter approach, see: D. Rocca, D.Y. Lu, and G. Galli, J. Chem. Phys. 133, 164109 (2010).

34 X. Blase, C. Attaccalite, V. Olevano, Phys. Rev. B 83, 115103 (2011).

35 Carina Faber, Claudio Attaccalite, V. Olevano, E. Runge, X. Blase, Phys. Rev. B 83, 115123 (2011).

36 C. Faber, J. Lafmann Janssen, M. Côté, E. Runge, X. Blase, Phys. Rev. B 84, 155104 (2011).

37 I. Duchemin, T. Deutsch, X. Blase, Phys. Rev. Lett. 109, 167801 (2012). See convergency tests in the Supplemental Material.

38 José M. Soler et al., J. Phys.: Condens. Matter 14, 2745-2779 (2002).

39 N. Troullier and J.-L. Martins, Phys. Rev. B 43, 1993 (1991). For Zn, we include the 3s and 3p semicore states in the valence to account in particular for (semi)core-valence exchange.

40 D.M. Ceperley and B.J. Alder, Phys. Rev. Lett. 45, 566 (1980).

41 A. Marini, C. Hogan, M. Grüning, and D. Varsano, Comput. Phys. Commun. 180, 1392 (2009).

42 P. Giannozzi, S. Bonini, N. Bonini, M. Calandra, R. Car, C. Faber, J. Lafmann Janssen, M. Côté, E. Runge, X. Blase, Phys. Rev. B 84, 155104 (2011).

43 For a recent study of the $G_0W_0$ approximation performed on small molecules with several starting points see e.g. F. Bruneval and M.A.L. Marques, J. Chem. Theory Comput. 9, 324 (2013); and references therein.

44 M. Grüning, A. Marini, and X. Gonze, Nano Lett. 9, 2820 (2009).

45 Y. Ma, M. Rohlfing, and C. Molteni, Phys. Rev. B 80, 241405 (2009); J. Chem. Theory Comput. 6, 257 (2010), and references therein.

46 Yi-Bo Wang and Zhenyang Lin, J. Al. Chem. Soc. 126, 6072 (2003).

47 David P. McMahon, David L. Cheung, and Alessandro Troisi, J. Phys. Chem. Lett. 2, 2737-2741 (2011).

48 R.R. Zope, M. Olguin, T. Baruah, J. Chem. Phys. 137, 084317 (2012).

49 Even though partial hybridization between ZnTPP and C$_{70}$ molecular orbitals takes place, the resulting molecular states preserve a clear ZnTPP or C$_{70}$ character for states around the energy gap.

50 The low-lying Q-lines and Soret B-lines in the absorption spectra of porphyrins, and the related selection rules and intensities, can be interpreted in terms of $\pi-\pi^*$ transitions between the (HOMO-1,HOMO) and the (LUMO,LUMO+1) levels. See: M. Gouterman, J. Mol. Spectrosc. 6, 138 (1961).

51 Gustavo E. Scuseria, Chem. Phys. Lett. 180, 451 (1991).

52 Susumu Saito and Atsushi Oshiyama, Phys. Rev. B 44, 11532 (1991).

53 V. Chukharev, N.V. Tkachenko, A. Efimov, H. Lemmetyinen, Chem. Phys. Lett. 411, 501 (2005).

54 E.B. Isaacs, S. Sharifzadeh, B. Ma, et al., Jo. Phys. Chem. Lett. 2, 2531 (2011).

55 M. Muntwiller, Q. Yang, W.A. Tisdale, X.-Y. Zhu, Phys. Rev. Lett. 101, 196403 (2008).

56 L. Edwards, D.H. Dolphin, and M. Gouterman, J. Mol. Spec. 38, 16-32 (1971).

57 M. Palummo, C. Hogan, F. Sottile, P. Bagalà, and A. Rubio, J. Chem. Phys. 131, 084102 (2009).

58 K. Aryanpour, D. Psiachos, S. Mazumdar, Phys. Rev. B 81, 085407 (2010).

59 See e.g. for transition rate calculations: T. Kawatsu, V. Coropceanu, A. Ye, and J.-L. Brédas, J. Phys. Chem. C 112, 3429 (2008).

60 Y. Yi, V. Coropceanu, and J. L. Brédas, J. Am. Chem. Soc. 131, 15777 (2009).

61 T. Baruah and M.R. Pederson, J. Chem. Theory Comput. 5, 834 (2009).