

# Fast and Accurate Electronic Excitations in Cyanines with the Many-Body Bethe–Salpeter Approach

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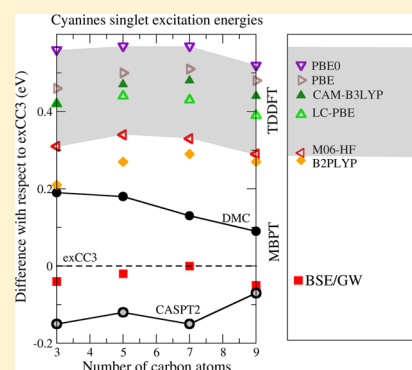
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## Supporting Information

**ABSTRACT:** The accurate prediction of the optical signatures of cyanine derivatives remains an important challenge in theoretical chemistry. Indeed, up to now, only the most expensive quantum chemical methods (CAS-PT2, CC, DMC, etc.) yield consistent and accurate data, impeding the applications on real-life molecules. Here, we investigate the lowest lying singlet excitation energies of increasingly long cyanine dyes within the GW and Bethe–Salpeter Green’s function many-body perturbation theory. Our results are in remarkable agreement with available coupled-cluster (exCC3) data, bringing these two single-reference perturbation techniques within a 0.05 eV maximum discrepancy. By comparison, available TD-DFT calculations with various semilocal, global, or range-separated hybrid functionals, overshoot the transition energies by a typical error of 0.3–0.6 eV. The obtained accuracy is achieved with a parameter-free formalism that offers similar accuracy for metallic or insulating, finite size or extended systems.



## 1. INTRODUCTION

Streptocyanines, the simplest subgroup of the large cyanine family, are charged dyes constituted of a chain containing an odd number of  $sp^2$  carbon atoms, capped at its extremities by (dialkyl)amino groups. These relatively compact molecules present a very sharp and intense absorption band.<sup>1</sup> One of the key features of the cyanine family is the so-called “vinyl shift”: the observed  $\lambda_{\max}$  undergoes an exceptionally large redshift (ca. 100 nm), for each additional  $C_2H_2$  unit cell added in the conjugation path.<sup>1</sup> These specific characteristics have made cyanines and their derivatives (e.g., BODIPY) one of the most experimentally explored classes of colored compounds.<sup>2,3</sup> It is, therefore, unsurprising that theoretical approaches have been applied to model cyanines’ optical spectra. Interestingly, the textbook *electron in the box* approach is able to successfully restore the observed vinyl shift,<sup>4</sup> but it does not allow to model substituents effects in a nonempirical way. To go further, the use of *ab initio* models is welcome, but the *de facto* standard for excited-state simulations in quantum chemistry,<sup>5</sup> namely Time-Dependent Density Functional Theory (TD-DFT), or more precisely the adiabatic approximation to Casida’s linear-response approach of TD-DFT,<sup>6</sup> cannot be considered as satisfying for cyanines. Indeed, while the expected TD-DFT accuracy is 0.2–0.3 eV, if an hybrid exchange–correlation functional is applied,<sup>7,8</sup> comparisons between TD-DFT vertical transition energies and experimental  $\lambda_{\max}$  for cyanines leads to disappointing results, that is, both huge theoretical over-

estimations of the transition energies (up to 1 eV) and concomitant underestimations of the vinyl shift are obtained, a fact recognized since the early 2000s.<sup>9,10</sup>

This is even more intriguing, as early CAS-PT2 calculations did not reveal any significant multideterminantal character for short and medium-sized cyanines.<sup>9</sup> The well-known charge-transfer (CT) problem of conventional TD-DFT<sup>11</sup> is not more suited for explaining the TD-DFT/cyanine difficulty as (i) the first excited-state of cyanines are highly delocalized and do not display significant electron transfer compared to the ground-state (that is the HOMO and LUMO are overlapping); (ii) one would expect predictions of too small rather than too large transition energies if CT was the origin of the problem; (iii) the use of range-separated hybrids does not improve (nor worsen) the quality of TD-DFT predictions.<sup>12</sup> Two main explanations for the large TD-DFT error have been further proposed: an incorrect description of the difference of electronic correlation between the two states,<sup>13,14</sup> and the nonverticality of the process, making the straightforward comparison between computed vertical energies and experimental  $\lambda_{\max}$  particularly poor for streptocyanines.<sup>15,16</sup> For the first aspect, Grimme and Neese have shown that double hybrids which explicitly include contributions from the virtual orbitals indeed provide more accurate estimates than other exchange–correlation functionals,

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but the errors remain rather large (ca. 0.3 eV for long chains) and the vinyl shift is not yet perfectly reproduced.<sup>13</sup> For the second aspect, Send, Valsson, and Filippi performed a series of wave function calculations for model cyanines, including Diffusion Monte Carlo (DMC) and highly accurate coupled-cluster simulations (exCC3: extrapolated coupled cluster linear response up to third approximate order), providing reliable benchmark data.<sup>15</sup> For the longest chain examined, containing nine carbon atoms in the cyanine skeleton, the DMC, exCC3, and CAS-PT2 (with IEPA shift) vertical energies are 2.62, 2.53, and 2.46 eV, respectively.<sup>15</sup> Taking these values as references, it can be noted that modern exchange-correlation functionals, such as M06-2X,<sup>17</sup> M08-SO,<sup>17</sup> or optimally tuned range-separated hybrids,<sup>14</sup> yield smaller, but far from negligible errors, ca. 0.3–0.5 eV. All these results seriously impede accurate comparisons with experimental values for “real-life” cyanines. On the one hand, highly correlated approaches (e.g., exCC3 or CAS-PT2) do not allow the calculations of the (important) excited-state relaxation but for trivial molecules. On the other hand, TD-DFT transition energies are systematically too large. For instance, for BODIPY derivatives, which are constrained cyanines, a systematic overestimation of the experimental 0–0 energies is noticed, even when geometrical and vibrational relaxation effects are accounted for with a modern exchange-correlation functional.<sup>18</sup>

In a series of recent papers,<sup>19–31</sup> the gas phase optical excitation energies of organic molecules have been studied by a specific family of many-body Green’s functions techniques, the so-called *GW*,<sup>32–38</sup> and Bethe–Salpeter (BSE)<sup>39–45</sup> formalism. The BSE formalism allows to study optical excitations and was initially tested at the *ab initio* level in the late 90s for extended inorganic systems,<sup>43–45</sup> demonstrating a remarkable accuracy in the description of both localized Frenkel and extended Wannier excitons. Such an ability to accurately model extended electron–hole pairs, in which the two particles are on average spatially separated, was also recently demonstrated for CT excitations in a series of donor–acceptor molecules and dimers, such as peptides,<sup>22,31</sup> coumarins,<sup>29</sup> or push–pull complexes of interest for photovoltaic applications.<sup>26,28,46</sup> In these studies, it was shown that BSE provides an equivalent accuracy to TD-DFT relying on optimized range-separated hybrid functionals.<sup>47–51</sup> While the BSE formalism preserves the advantage of being a parameter-free approach valid for both finite and extended, insulating and metallic compounds, there was, up to now, no clear-cut indication that BSE might outperform the best TD-DFT calculations using an adequately selected functional.

In this contribution, we present a many-body *GW* and Bethe–Salpeter perturbation theory study of the model cyanines (see Scheme 1), which have been previously investigated with several variational or perturbative approaches.<sup>12–15,17</sup> We show in particular that the BSE lowest

singlet excitation energies come in excellent agreement with coupled-cluster exCC3 values, with a remarkably small mean absolute error of 0.03 eV and a maximum discrepancy of 0.05 eV. The Bethe–Salpeter and exCC3 techniques, both “single reference” methods, are found to lie in between the results provided by DMC and CAS-PT2 multireference techniques.<sup>15</sup> In particular, the Bethe–Salpeter approach does not suffer from the reported problem associated with TD-DFT calculations. The present results indicate that the Bethe–Salpeter formalism, relying on the use of the microscopic screened Coulomb potential  $W(r,r')$ , allows to capture features of the correlation contribution to the electron-hole matrix elements that are difficult to describe with available global or range-separated hybrids.

## 2. METHOD

We briefly introduce the self-energy formalism that provides a rigorous framework for calculating quasi-particle energies, namely occupied and virtual electronic energy levels. In such an approach, the one-body (quasiparticle) eigenvalue equation reads:

$$\left( \frac{-\nabla^2}{2} + V^{\text{ionic}}(\mathbf{r})\phi(\mathbf{r}) + V^{\text{Hartree}}(\mathbf{r})\phi(\mathbf{r}) \right. \\ \left. + \int d\mathbf{r}' \Sigma(\mathbf{r}, \mathbf{r}'; E)\phi(\mathbf{r}') = E\phi(\mathbf{r}) \right) \quad (1)$$

where the self-energy  $\Sigma(\mathbf{r}, \mathbf{r}'; E)$  replaces the well-known exchange-correlation potential of the density functional theory or the exchange operator in the Hartree–Fock (HF) formalism. The self-energy  $\Sigma$  is nonlocal, energy-dependent and non-Hermitian in general. Derived initially within Schwinger’s functional derivative approach to perturbation theory,<sup>52</sup> the *GW* approximation to the self-energy reads:

$$\Sigma^{\text{GW}}(\mathbf{r}, \mathbf{r}'; E) = \frac{i}{2\pi} \int d\omega e^{-i\delta\omega} G(\mathbf{r}, \mathbf{r}'; E + \omega) \\ \times W(\mathbf{r}, \mathbf{r}'; \omega) \quad (2)$$

where  $G$  and  $W$  are the time-ordered one-particle Green’s function and the dynamically screened Coulomb potential, respectively. The small positive infinitesimal  $\delta = 0^+$  indicates that the energy integration can be performed by closing the contour in the upper half-plane.  $G$  and  $W$  can be expressed as follows:

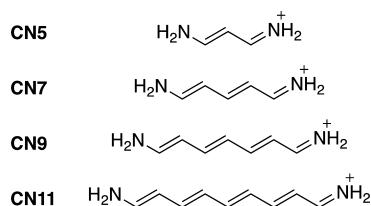
$$G(\mathbf{r}, \mathbf{r}'; E + \omega) = \sum_n \frac{\phi_n(\mathbf{r})\phi_n^*(\mathbf{r}')}{E + \omega - \epsilon_n - i\delta \operatorname{sgn}(\epsilon_n - \mu)} \quad (3)$$

$$\chi_0(\mathbf{r}, \mathbf{r}'; \omega) = \sum_{n,n'} \frac{f_n - f_{n'}}{\epsilon_n - \epsilon_{n'} - \omega} \phi_n^*(\mathbf{r})\phi_n(\mathbf{r}')\phi_{n'}^*(\mathbf{r}')\phi_{n'}(\mathbf{r}) \quad (4)$$

$$W(\mathbf{r}, \mathbf{r}'; \omega) = v(\mathbf{r}, \mathbf{r}') + \iint d\mathbf{r}_1 d\mathbf{r}_2 v(\mathbf{r}, \mathbf{r}_1)\chi_0(\mathbf{r}_1, \mathbf{r}_2|\omega) \\ \times W(\mathbf{r}_2, \mathbf{r}'|\omega) \quad (5)$$

in terms of the one-body ( $\epsilon_n\phi_n$ ) eigenstates, typically DFT Kohn–Sham (KS) or Hartree–Fock solutions. We have also introduced the dynamical independent-electron susceptibility ( $\chi_0$ ) and the occupation numbers ( $f_n$ ). Several groups have shown that excellent quasi-particle energies can be obtained for

**Scheme 1.** Sketch of the Investigated Cyanine Dyes



gas phase organic molecules, in particular when self-consistently “reinjecting” the calculated quasiparticle energies without updating the wave functions.<sup>26,29,31,46,53–57</sup> Such a partially self-consistent approach, computationally very efficient, will be labeled *ev-GW@XX*, where *XX* is the acronym of the ground state method, e.g. *XX* = HF or *XX* = PBE, used to generate the “frozen” input wave functions.

To study the remaining possible dependence on the starting wave functions, a fully self-consistent approach, where both energies and wave functions ( $\epsilon_n, \phi_n$ ) are updated can be performed within the so-called static Coulomb-hole plus screened-exchange (COHSEX) approximation to the *GW* self-energy. Namely, we perform *GW* calculations with partial self-consistency on the eigenvalues, but starting from fully self-consistent COHSEX eigenstates and eigenenergies. This scheme has been shown to yield excellent results for transition metal oxides,<sup>58,59</sup> gold,<sup>60,61</sup> or quaternary semiconductors,<sup>62</sup> in which the topology of the *3d*-orbitals is too strongly affected by self-interaction with standard semilocal functionals. Such a full self-consistent approach, where the final results are independent of the starting input eigenstates, will be simply labeled *GW* in the following. The Coulomb-hole (COH) and screened-exchange (SEX) terms read:

$$\Sigma_{\text{static}}^{\text{SEX}}(E) = - \sum_n^{\text{occ}} W(\mathbf{r}, \mathbf{r}'; \omega = 0) \phi_n(\mathbf{r}) \phi_n^*(\mathbf{r}') \quad (6)$$

$$\Sigma_{\text{static}}^{\text{COH}}(E) = \frac{1}{2} \sum_n \phi_n(\mathbf{r}) \phi_n^*(\mathbf{r}') W(\mathbf{r}, \mathbf{r}'; \omega = 0) \quad (7)$$

$$= \frac{1}{2} \delta(\mathbf{r} - \mathbf{r}') W(\mathbf{r}, \mathbf{r}'; \omega = 0) \quad (8)$$

where the SEX terms, with summation over the occupied states only, resembles the bare exchange Fock operator, replacing the bare Coulomb potential by the (statically) screened one. The COH term corresponds to the adiabatically built interaction of an electron and its correlation hole.

From the knowledge of the quasiparticle energies and wave functions, one can in a second step calculate the optical excitation energies using the Bethe-Salpeter formalism, which accounts for electron-hole interactions. The BSE equation resembles Casida's equation for TD-DFT in the product space of the occupied and virtual single-particle states, that is, the excitation energies are the eigenvalues of an electron-hole Hamiltonian equation:

$$\begin{pmatrix} R & C \\ -C^* & -R^* \end{pmatrix} \begin{pmatrix} [\phi_a(\mathbf{r}_e) \phi_i(\mathbf{r}_h)] \\ [\phi_i(\mathbf{r}_e) \phi_a(\mathbf{r}_h)] \end{pmatrix} = \begin{pmatrix} \lambda_{ai} \\ \mu_{ia} \end{pmatrix} \begin{pmatrix} [\phi_a(\mathbf{r}_e) \phi_i(\mathbf{r}_h)] \\ [\phi_i(\mathbf{r}_e) \phi_a(\mathbf{r}_h)] \end{pmatrix} \quad (9)$$

where the indexes (*ij*) and (*ab*) indicate the occupied and virtual orbitals, and ( $\mathbf{r}_e, \mathbf{r}_h$ ) the electron and hole positions, respectively. In this block notation, the vector  $[\phi_a(\mathbf{r}_e) \phi_i(\mathbf{r}_h)]$  represents all excitations (e.g.,  $\phi_a(\mathbf{r}_e)$  means that an electron is placed into a virtual orbital), while the vector  $[\phi_i(\mathbf{r}_e) \phi_a(\mathbf{r}_h)]$  represents all disexcitations. The so-called resonant *R* part is Hermitian and reads:

$$R_{ai,bj} = \delta_{a,b} \delta_{i,j} (\epsilon_a^{\text{QP}} - \epsilon_i^{\text{QP}}) - \iint \phi_a(\mathbf{r}_e) \phi_i(\mathbf{r}_h) W(\mathbf{r}_e, \mathbf{r}_h) \phi_b(\mathbf{r}_e) \phi_j(\mathbf{r}_h) d\mathbf{r}_e d\mathbf{r}_h + 2\eta \iint \phi_a(\mathbf{r}_e) \phi_i(\mathbf{r}_e) V^C(\mathbf{r}_e, \mathbf{r}_h) \phi_b(\mathbf{r}_h) \phi_j(\mathbf{r}_h) d\mathbf{r}_e d\mathbf{r}_h \quad (10)$$

with  $\eta = 1$  for the singlet states studied here ( $\eta = 0$  for triplets). The quasiparticle energies  $\epsilon_{a,b,i,j}^{\text{QP}}$  are the *GW* quasiparticle energies, while the  $\phi_{a,b,i,j}$  are the “frozen” KS, Hartree-Fock, hybrid or the self-consistent COHSEX eigenfunctions, depending on the selected *GW* approach. One can observe that the matrix elements involving the screened-Coulomb potential *W* replace the matrix elements stemming from the Fock exchange operator in TD-DFT with hybrid functionals. Such matrix elements are responsible, in particular, for the success of the BSE formalism for CT excitations.<sup>47–51,53</sup> Our formalism goes beyond the Tamm-Dancoff approximation (TDA), allowing the coupling between resonant (*R*) and antiresonant (*R*<sup>\*</sup>) transitions. TDA is known to yield significant upward shifts in TD-DFT calculations of cyanines, for example, 0.6 eV with PBE0.<sup>14,17</sup> Consistently, the effect of the TDA on the *GW*@BSE excitation energies was found to yield ca. 0.45 eV upward shifts, the details can be found in the Supporting Information (SI).

A convergence study of the *GW*/BSE excitation energy with respect to correlation-consistent Dunning basis sets,<sup>63</sup> displayed in Table S–III in the SI, showed that *augmentation* (with the addition of diffuse orbitals) is crucial and that a triple- $\zeta$  basis is required to have an error smaller than 10 meV. On the other hand, the oscillator strengths converged rather quickly. Consequently, our calculations are performed with the all-electron *aug-cc-pVTZ* atomic basis set<sup>63</sup> using the *Fiesta* package<sup>26,53</sup> that implements the *GW* and BSE formalisms using resolution of the identity techniques. The input ( $\epsilon_n, \phi_n$ ) eigenstates are provided by the *NWChem* package.<sup>64</sup> The needed Coulomb matrix elements are calculated with an even tempered<sup>65</sup> auxiliary basis and the resolution of the identity technique with the Coulomb metric.<sup>66</sup> This even-tempered basis was found by converging the excitation energies and oscillator strengths upon varying the number of Gaussians and the maximum angular channel (see the SI). The minimum and maximum Gaussian exponents per angular channel were conservatively fixed to the minimum value of the Kohn-Sham basis and the maximum value of the product basis (onsite products of the Kohn-Sham basis). The resulting accuracy is estimated to be ca. 30 meV. The frequency integral involved in the evaluation of the dynamical correlations (see eq 2) are calculated exactly using contour deformation techniques without any plasmon-pole approximation. All the virtual states are included in the summation for the calculation of the susceptibility  $\chi_0$  and for building the  $\phi_i(\mathbf{r}_e) \phi_a(\mathbf{r}_h)$  product space on which the Bethe-Salpeter Hamiltonian is acting. Full convergence tests can be found in the SI. Within the present resolution of the identity technique, the *GW* formalism offers a  $N^4$  scaling, while the cost of the Bethe-Salpeter calculations is identical to that of TD-DFT within Casida's formulation. For the records, the self-consistent *GW*/BSE calculations on the longer *CN11* structure amounts to about three hours of CPU time.<sup>67</sup>

### 3. RESULTS AND DISCUSSION

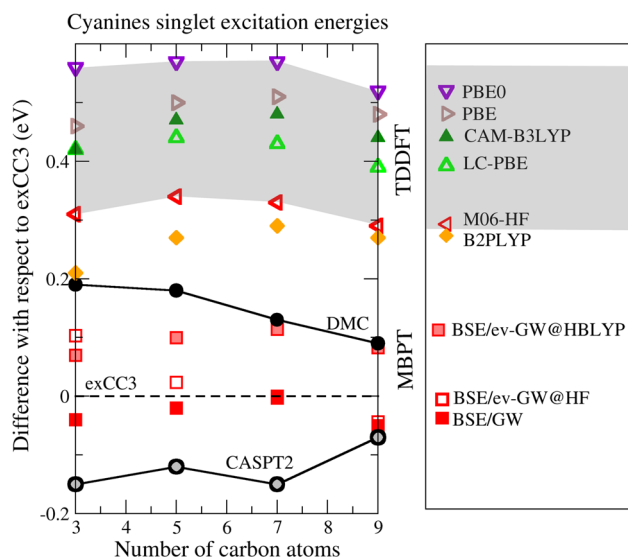
We adopt the PBE0/cc-pVQZ geometry used in the TD-DFT studies of ref 17. Comparisons with the TD-DFT calculations performed by Autschbach's group on the MP2/cc-pVQZ structures show that the influence of the geometry is marginal.<sup>14</sup> The studied structures are represented in Scheme 1 and given in the SI.

Our calculated BSE excitation energies are compared to other calculations in Table 1 and in Figure 1. The present

**Table 1.** GW Ionization Potentials (IP) and Electronic Affinities (AE), Together with the GW/BSE Excitation Energies ( $\Delta E$ ) and Oscillator Strengths ( $f$ )<sup>a</sup>

	CN5	CN7	CN9	CN11
BSE/GW Calculations				
IP	13.39	11.78	10.67	9.91
AE	3.76	4.13	4.23	4.33
$\Delta E$	4.80	3.63	2.96	2.48
$f$	0.48	0.74	1.00	1.24
Reference Calculations				
exCC3 $\Delta E$	4.84	3.65	2.96	2.53
DMC $\Delta E$	5.03	3.83	3.09	2.62
CAS-PT2 $\Delta E$	4.69	3.53	2.81	2.46
TD-DFT Calculations				
PBE0 $\Delta E$	5.33	4.18	3.50	3.03
B2PLYP $\Delta E$	5.05	3.92	3.25	2.80
CAM-B3LYP $\Delta E$	5.26	4.12	3.44	2.97
M06-2X $\Delta E$	5.23	4.09	3.41	2.95

<sup>a</sup>Energies are in eV. The available exCC3, DMC, and CASPT2 values are from ref 15, and the same holds for TD-DFT but for the M06-2X data taken in ref 17.



**Figure 1.** Lowest singlet excitation energies in cyanines as a function of the number of carbon atoms in the chain. Several theoretical frameworks are compared. Excitation energies are provided with respect to the reference exCC3 data. Previous TD-DFT results from ref 17 are provided with triangles. The double hybrid B2PLYP calculations taken in ref 15 are indicated with orange diamonds. Multideterminantal CAS-PT2 and DMC data from ref 15 are indicated by connected hatched and filled black circles, respectively. The shaded area gathers all TD-DFT data.

Bethe–Salpeter formalism, as it stands,<sup>68</sup> is a single-reference approach. Therefore, we have represented our results in Figure 1 as errors with respect to the exCC3 data,<sup>15</sup> since it is the most accurate single-reference technique that has been applied, so far, to these systems. The variational multideterminantal CAS-PT2 and diffusion Monte Carlo (DMC) data of ref 15, are also presented and their variation compared to exCC3 are rather small (ca. 0.15 eV). A discussion of the differences between these three refined methods is beyond our scope here.<sup>15</sup>

As indicated in Table 1 and in Figure 1, our BSE excitations energies based on fully self-consistent GW eigenstates are in almost perfect agreement with the exCC3 values, with a mean-

absolute error (MAE) of 0.03 eV and a maximum discrepancy of 0.05 eV for CN11. These deviations are of the order of the convergence criteria for the auxiliary basis. This is the key result of the present investigation, since it demonstrates, for the first time, that one can accurately restore cyanine transition energies with an *ab initio* method computationally tractable for large compounds. In particular, it appears that the BSE values are significantly different from the TD-DFT results, which are systematically too high (see the Introduction).

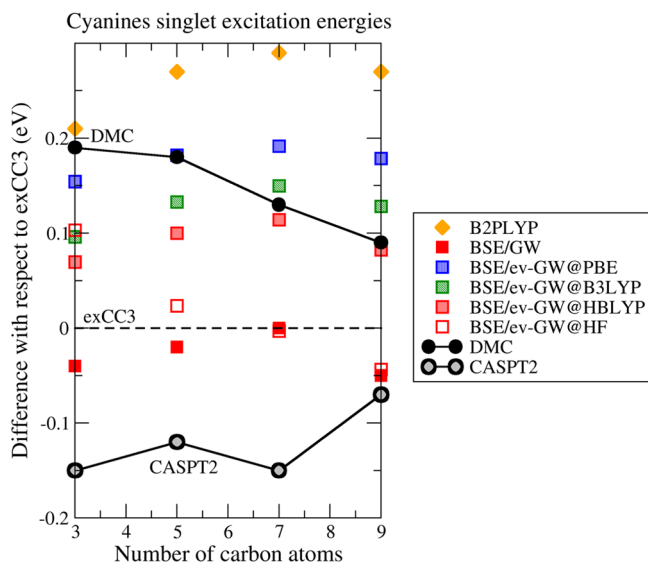
In order to directly compare with exCC3 calculations, which are based on the HF wave function,<sup>69</sup> BSE calculations based on a partially self-consistent GW approach starting from the HF wave function have been performed, updating (correcting) only the quasi-particle energies. This scheme shares with the exCC3 approach the idea that one attempts to correct the excitation energies without modifying the single-determinant wave function on which the cluster operator,  $T$  for exCC3 or the GW self-energy or BSE Hamiltonians, are acting. In Figure 1, the resulting excitation energies (empty red squares) are shown to agree extremely well with both the fully self-consistent GW/BSE calculations and exCC3 data for the longest structures, CN9 and CN11. The agreement remains excellent for CN7, with a ca. 0.04 eV discrepancy. The largest difference occurs for the compact CN5, where a ca. 0.10 eV difference can be observed with respect to exCC3. It was previously noted that the sensitivity of the excitation energies to correlation and other wave function parameters is higher in small molecules.<sup>15</sup> Besides this moderate difference for the CN5 molecule, the present results, with a MAE of ca. 0.04 eV for the entire series, confirm the excellent agreement between BSE and exCC3 approaches.

We now turn to the comparison with the double hybrid B2PLYP approach by Grimme and Neese.<sup>13</sup> This method mixes standard generalized gradient approximations (GGA) for exchange and correlation, with Hartree–Fock exchange (53%) and a perturbative second-order correlation part (PT2) through explicit summation over the occupied to virtual KS eigenstates. For the excited-state calculations, B2PLYP includes on top of the standard TD-DFT results, a CIS(D)-like correction that allows a more accurate description of doubly excited-states, as well as the differential correlation between the ground and excited states. Clearly, the B2PLYP results (orange diamonds in Figure 1) yield a significant improvement compared to conventional TD-DFT calculations relying on global or range-separated hybrids, at least, for the smaller cyanines. Together with the exCC3 and BSE/GW results, the B2PLYP results point out to the importance of nonlocal correlations in cyanines.

Nevertheless, we notice that the B2PLYP transition energies are located ca. 0.2–0.3 eV above the exCC3 and BSE data. While several explanations are certainly plausible, including an incomplete account of the double excitation contributions, we note that the correlation contributions in B2PLYP were built out of transitions from occupied to virtual Kohn–Sham eigenstates, and not from HF or self-consistent GW ones. Building on the observed differences between our BSE/GW and BSE/ev-GW@HF results for the smallest CN5 cyanine, we now start from the same HBLYP hybrid functional (containing 53% of exact-exchange and 73% of LYP correlation) used by Grimme and Neese to build the nonlocal correlation contribution to the excitation energies. Namely, we self-consistently correct the HBLYP single-particle energies while keeping the HBLYP wave functions frozen. The related BSE/

ev-GW@HBLYP data, represented in Figure 1, display a degradation with respect to both exCC3 and BSE calculations based on fully self-consistent *GW* eigenstates, while improving the agreement with the B2PLYP data. This hints that the B2PLYP data, with nonlocal correlations built from scaled second-order perturbation theory, could, in principle, come in even better agreement with exCC3 and BSE/*GW* calculations with a “better” choice of the single-particle states used to build the occupied to virtual transitions.

This points out again to the sensitivity of the various perturbative (non self-consistent) correlation contributions to the starting (zeroth-order) eigenstates. For the sake of completeness, we provide in Figure 2a comparison between



**Figure 2.** Lowest singlet excitation energies in cyanines as a function of the number of carbon atoms in the chain. The sensitivity to the starting “frozen” wave function (see text) is demonstrated with different choices of functionals: PBE, B3LYP, HBLYP from ref 13, and HF. The double hybrid B2PLYP calculations, taken in ref 15, are indicated with orange diamonds.

various partially self-consistent BSE/ev-GW calculations starting from selected semilocal (PBE) and global hybrid (B3LYP) eigenstates, keeping the wave functions frozen. For CN7 and larger cyanines, the discrepancy decreases with the amount of exact exchange included in the functional used to generate the zeroth-order eigenstates, while for CN5 the error seems dominated by the correlation term. We emphasize however that this “sensitivity” to the starting eigenstates, if one does not perform fully self-consistent *GW* calculations, leads to errors that are ca. 0.2 eV, that is, smaller than the typical TD-DFT errors. Indeed, all BSE excitation energies lie below the B2PLYP double hybrid data and are in better agreement with CAS-PT2, DMC or exCC3 benchmarks.

#### 4. CONCLUSIONS AND OUTLOOK

Using the *GW* and Bethe–Salpeter Green’s function many-body perturbation theories, we have studied the lowest lying singlet excitation energies of increasingly long cyanine dyes. This family of molecules is one of the few series remaining particularly challenging for TD-DFT. Indeed, semilocal, global, or range-separated hybrids, have been shown to lead to anomalous discrepancies with both experiments<sup>70</sup> and accurate wave function reference methods, such as DMC, CAS-PT2, and

EOM-CC.<sup>15</sup> TD-DFT calculations constantly locate transition energies of cyanines at too large energies, with discrepancies as large as 0.3–0.6 eV when compared with the above-mentioned methods. Our self-consistent *GW* and Bethe–Salpeter calculations lead to results in remarkable agreement with exCC3, with a maximum discrepancy of 0.05 eV, landing 0.1–0.15 eV above (below) the multiconfigurational CAS-PT2 (DMC) values.

Several extra conclusions may be drawn from the present study. First, since the *GW* and Bethe–Salpeter formalisms, as they stand, cannot deal with multiple excitations, it is unlikely that the relative failure of TD-DFT lies in the lack of multiple excitations associated with the use of adiabatic kernels. Further, one can emphasize that the *GW* and BSE approaches explicitly construct a nonlocal correlation contribution to the electron–hole interaction thanks to an explicit summation of occupied to virtual transitions between *GW* quasiparticle orbitals. This may corroborate the idea pushed forward by Grimme and Neese<sup>13</sup> that double-hybrid functionals, namely an hybrid TD-DFT calculation corrected by second-order perturbation theory for adding the effect of nonlocal correlations, may improve TD-DFT estimates for such compounds. Partially self-consistent *GW* and BSE calculations based on the “frozen” KS HBLYP eigenstates used by Grimme and Neese to build their correlation contribution, leads to excitation energies in much better agreement with both the DMC and the double-hybrid TD-DFT calculations, and hence, worsening slightly the agreement with the exCC3 values. Both the near perfect agreement with the exCC3 values, and the lack of initial state dependence, leads us to favor the fully self-consistent *GW* approach. We observe, however, that this sensitivity to the starting point mean-field eigenstates remains rather limited, leaving all the perturbation techniques in close agreement (within 0.2 eV), as compared to the discrepancy related to the TD-DFT values.

As such, BSE stands as a very promising *ab initio* scheme that is both accurate and practically applicable for predicting the transition energies of cyanine derivatives, and applications to industrially relevant molecules is under way in our teams.

#### ■ ASSOCIATED CONTENT

##### Supporting Information

Complete BSE/*GW* data used to generate Figures 1 and 2 along with the *GW* ionization potentials and electron affinities. Discussion of the convergence with respect to the Gaussian basis, the auxiliary basis, and the number of unoccupied orbitals included in the BSE treatment. Impact of the TDA approximation on *GW*/BSE values. Cartesian coordinates for the systems. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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##### Notes

The authors declare no competing financial interest.

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