


# Optical excitations in nanographenes from the Bethe-Salpeter equation and time-dependent density functional theory: Absorption spectra and spatial descriptors

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The *GW* plus Bethe-Salpeter equation (*GW*-BSE) formalism is a well-established approach for calculating excitation energies and optical spectra of molecules, nanostructures, and crystalline materials. We implement *GW*-BSE in the CP2K code and validate the implementation for a standard organic molecular test set, obtaining excellent agreement with reference data, with a mean absolute error in excitation energies below 3 meV. We then study optical spectra of nanographenes of increasing length, showing excellent agreement with experiment. We further compute the size of the excitation of the lowest optically active excitation, which converges to about 7.6 Å with increasing length. Comparison with time-dependent density functional theory using functionals of varying exact-exchange fraction shows that none reproduce both the size of the excitation and optical spectra of *GW*-BSE, underscoring the need for many-body methods for accurate description of electronic excitations in nanostructures.

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## I. INTRODUCTION

When light interacts with a semiconductor, it can promote an electron to the conduction band, leaving behind a hole in the valence band. The electron and hole attract each other through the Coulomb interaction and can form a bound pair known as an exciton [1–10]. A correct description of such a bound state requires including the screened Coulomb interaction between the electron and the hole. Time-dependent density functional theory (TDDFT) with local or semilocal exchange-correlation functionals is widely used to compute excitation energies, but, in these approximations, the long-range electron-hole attraction via Coulomb interaction is absent, and bound excitons are not described [1–3]. Hybrid functionals include a fraction of nonlocal Hartree-Fock exact exchange, which partially restores the bare Coulomb interaction between the electron and hole. For example, a hybrid with 25% exact exchange corresponds, in a simple picture, to an effective static dielectric screening of about four. While hybrids can improve agreement with experiment, their accuracy depends sensitively on the chosen exact-exchange fraction, and they are significantly more computationally expensive than local or semilocal functionals.

An alternative approach is the *GW* plus Bethe-Salpeter equation (*GW*-BSE) [2,3,11–13], which explicitly includes the screened Coulomb attraction between an excited electron and the hole it leaves behind. The *GW*-BSE framework has become a standard in condensed-matter physics for computing optical spectra of semiconductors [2,3,11–25] and is also used in chemistry for accurate calculations of molecular excitation energies [26–43], where a relation to the established

wave function-based approaches has been shown [44–48]. The intermediate regime between small molecules and crystals includes nanometer-sized materials, like nanographenes, which are finite cutouts of a graphene with hydrogen termination that can be synthesized on noble-metal surfaces [49,50]. Applications of them include nanoscale transistors [51,52] and nanoscale optoelectronic devices [53], where *GW*-BSE has been used to characterize the optical absorption spectrum. Another class of nanoscale materials is moiré superlattices built from twisted van der Waals crystals, where *GW*-BSE provides direct access to both the excitation energies and the spatial structure of the electron-hole pair [7]. Here, electron and hole can separate over different layers [4] (“interlayer exciton”), or can be located within a single layer (“intralayer exciton”) [7], where hybrid states [6] as well as the switching between distinct intra- and interlayer character have been observed experimentally [5,8–10]. The spatial structure of the electron-hole pairs determines their excitation energy, and the spatial structure is thus linked to the peak position in optical spectra.

In principle, the spatial properties of an excited state can be obtained directly from its wave function  $\Psi_{\text{exc}}^{(n)}(\mathbf{r}_e, \mathbf{r}_h)$ , which depends on the electron coordinate  $\mathbf{r}_e$  and the hole coordinate  $\mathbf{r}_h$ . A common way to visualize  $\Psi_{\text{exc}}^{(n)}(\mathbf{r}_e, \mathbf{r}_h)$  is to fix one coordinate and plot the probability density of the other, for example,  $|\Psi_{\text{exc}}^{(n)}(\mathbf{r}_e, \mathbf{r}_h^*)|^2$  for a chosen hole position  $\mathbf{r}_h^*$  [7]. The result depends on the choice of  $\mathbf{r}_h^*$ , and important features may be overlooked if the chosen reference position is not representative. As an alternative, following the ideas of Frenkel [54,55] and Wannier [56] in distinguishing between different types of excitons, one can characterize the excited state by expectation values of the electron-hole separation, the electron position, and the hole position. These spatial descriptors have been introduced in quantum chemistry to

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study electronic excitations in molecules and polymer chains [57–68]. The same expectation values can be evaluated as functions of time, providing a direct and compact description of the spatiotemporal evolution of an excited state. Such time-dependent descriptors can be computed using time-dependent  $GW$ -BSE [69–74] or real-time TDDFT [1,75–80]. Beyond the time evolution of electronic states, recent advances in force calculations within  $GW$ -BSE [81–84] enable the description of coupled electronic and nuclear motion, where a simplified frequency treatment in the self-energy appears promising to reduce computational cost and to ensure numerical stability [85–88]. Recent experimental advances enable tracking of such excited-state dynamics with simultaneous femtosecond temporal and subnanometer spatial resolution [8,9,89–93], allowing direct comparison between measured quantities such as the time-dependent exciton radius and their theoretical predictions.

The values of spatial descriptors for excited states, such as the size of the excitation, depend on the method used to compute the excitation, for example, TDDFT or  $GW$ -BSE. The aim of this work is to assess how the choice of the excited-state method influences these descriptors in finite nanostructures. To this end, we implement the  $GW$ -BSE formalism in the CP2K software [94–96], enabling the study of both optical excitations and their spatial extent in nanostructures.

We first present the theory of the  $GW$ -BSE framework in Sec. II.  $GW$ -BSE calculations on nanographenes are presented in Sec. III, where we analyze the convergence of the optical absorption spectrum with increasing size and compare the computed absorption spectrum to experimental data. In Sec. IV, we introduce the theory of spatial descriptors, and we apply these to nanographenes in Sec. V, including a comparison to TDDFT.

## II. OPTICAL ABSORPTION SPECTRUM FROM $GW$ -BSE

The  $GW$ -BSE formalism provides an accurate description of neutral excitations by explicitly accounting for the electron-hole interaction on top of a quasiparticle picture [2,3,11–13]. Starting from Kohn-Sham (KS) density functional theory (DFT), we first obtain the ground-state electronic structure, which provides a convenient single-particle basis  $\{\psi_p(\mathbf{r})\}$  for many-body perturbation theory. The KS energies  $\varepsilon_p^{\text{KS}}$  and orbitals  $\psi_p(\mathbf{r})$  are determined by solving

$$[h_0(\mathbf{r}) + v^{\text{xc}}(\mathbf{r})]\psi_p(\mathbf{r}) = \varepsilon_p^{\text{KS}} \psi_p(\mathbf{r}), \quad (1)$$

where  $h_0(\mathbf{r})$  contains the kinetic energy, the external potential, and the Hartree potential, and  $v^{\text{xc}}(\mathbf{r})$  is the exchange-correlation potential. In our implementation, the KS orbitals are expanded in Gaussian basis functions  $\{\phi_v(\mathbf{r})\}$  as

$$\psi_p(\mathbf{r}) = \sum_v C_{vp} \phi_v(\mathbf{r}), \quad (2)$$

with molecular-orbital indices  $p, q, r, s$ , atomic-orbital indices  $v$ , and we can explicitly separate KS states  $\psi_p$  into  $N_{\text{occ}}$  occupied states  $\psi_i, \psi_j$  and  $N_{\text{empty}}$  unoccupied states  $\psi_a, \psi_b$ .

These KS states serve as the starting point for the  $GW$  calculation (cf. Fig. 1), in which the poles of the single-particle Green's function  $G$  can be interpreted as quasiparticle

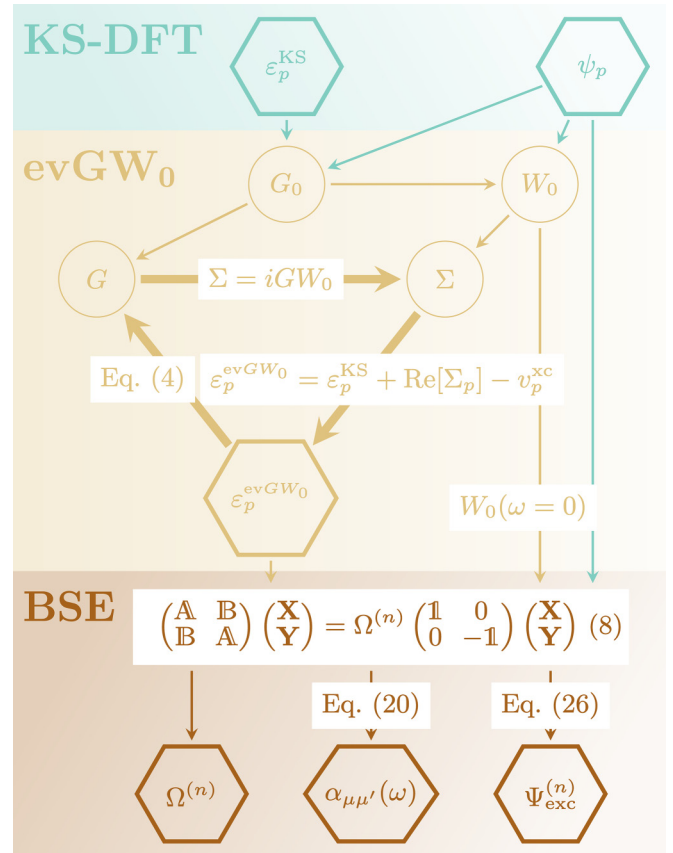


FIG. 1. Workflow of a  $GW$ -BSE calculation within this work, where we employ BSE@evGW<sub>0</sub>@PBE. A KS-DFT calculation provides the KS energies  $\varepsilon_p^{\text{KS}}$  and orbitals  $\psi_p^{\text{KS}}$  as input. In the evGW<sub>0</sub> scheme, the quasiparticle energies are iterated (bold arrows) in a self-consistent loop, starting from  $G = G_0$  and using  $W_0$  from the DFT starting point. This yields the evGW<sub>0</sub> quasiparticle energies  $\varepsilon_p^{\text{evGW}_0}$  [Eq. (6)]. BSE matrices  $A, B$  [Eq. (10)] are constructed from  $\varepsilon_p^{\text{evGW}_0}$ ,  $\psi_p^{\text{KS}}$ , and the statically screened Coulomb interaction  $W_0(\omega = 0)$ . Diagonalizing Eq. (8) gives the excitation energies  $\Omega^{(n)}$ , the absorption spectrum  $\alpha_{\mu\mu'}(\omega)$ , and the excitation wave function  $\Psi_{\text{exc}}^{(n)}(\mathbf{r}_e, \mathbf{r}_h)$ .

energies, effectively improving the KS energies  $\varepsilon_p^{\text{KS}}$ . In practice, we apply a simplification of Hedin's equations [97] by replacing the vertex with a single space-time point (cf. Appendix A), which leads to a self-energy of the form

$$\Sigma^{\text{GW}}(\mathbf{r}_1, \mathbf{r}_2, t) = iG(\mathbf{r}_1, \mathbf{r}_2, t)W(\mathbf{r}_1, \mathbf{r}_2, t). \quad (3)$$

Hence, this simplification is called the  $GW$  approximation, where  $W$  denotes the dynamically screened Coulomb interaction.

In practice, the resulting equations are usually solved non-self-consistently; various flavors are summarized in Appendix A. Here, we use eigenvalue self-consistency in  $G$ , i.e., evGW<sub>0</sub>. In evGW<sub>0</sub>, the KS energies  $\varepsilon_p^{\text{KS}}$  and KS orbitals  $\psi_p(\mathbf{r})$  enter the noninteracting Green's function [98,99]

$$G_0(\mathbf{r}_1, \mathbf{r}_2, i\omega) = \sum_p \frac{\psi_p(\mathbf{r}_1)\psi_p(\mathbf{r}_2)}{i\omega + \varepsilon_F - \varepsilon_p^{\text{KS}}}, \quad (4)$$

with the Fermi energy  $\varepsilon_F$ . Additionally, the screened Coulomb interaction  $W_0$  is computed beforehand as [98]

$$W_0(\mathbf{r}_1, \mathbf{r}_2, i\omega) = \int d^3r' \varepsilon^{-1}(\mathbf{r}_1, \mathbf{r}', i\omega) v(\mathbf{r}', \mathbf{r}_2), \quad (5)$$

where  $v(\mathbf{r}_1, \mathbf{r}_2) = 1/|\mathbf{r}_1 - \mathbf{r}_2|$  is the bare Coulomb interaction and the dynamical dielectric function  $\varepsilon(\mathbf{r}_1, \mathbf{r}', i\omega)$  is computed at the random-phase approximation (RPA) level from the KS energies  $\varepsilon_p^{\text{KS}}$  (cf. Appendix A). Formally, Eq. (5) can be rewritten using a Green's function [100], as depicted for  $G_0$  in Fig. 1.

Combining Eqs. (4) and (5) with Eq. (3), we can compute the quasiparticle energies from

$$\varepsilon_p^{\text{evGW}_0} = \varepsilon_p^{\text{KS}} + \text{Re}[\sum_p^{\text{evGW}_0}(\varepsilon_p^{\text{evGW}_0})] - v_p^{\text{xc}}. \quad (6)$$

With the solution of this nonlinear equation, we recompute the Green's function (4) by replacing  $\varepsilon_p^{\text{KS}}$  with  $\varepsilon_p^{\text{evGW}_0}$  [100]:

$$G_{\text{evGW}_0}(\mathbf{r}_1, \mathbf{r}_2, i\omega) = \sum_p \frac{\psi_p(\mathbf{r}_1)\psi_p(\mathbf{r}_2)}{i\omega + \varepsilon_F - \varepsilon_p^{\text{evGW}_0}}. \quad (7)$$

We repeat this procedure until convergence in  $\varepsilon_p^{\text{evGW}_0}$  is reached, as depicted by the triangle in the  $\text{evGW}_0$ -box in Fig. 1.

While the poles of the single-particle Green's function provide the (formally) correct quasiparticle energies, optical (two-particle) excitations need an extended framework, which includes the two-particle Green's function. This can be done by reintroducing the previously neglected vertex corrections [2] in Hedin's equations [97], which eventually leads to the BSE for the four-point polarizability [2,11,12]. In Appendix B, we derive how the solution of this rather complicated form of the BSE can be transformed to the following generalized eigenvalue problem in the product space of occupied and unoccupied orbitals, which is then typically solved to describe optical excitations [2,12,13,28,29,31,38,39]:

$$\begin{pmatrix} \mathbb{A} & \mathbb{B} \\ \mathbb{B} & \mathbb{A} \end{pmatrix} \begin{pmatrix} \mathbf{X}^{(n)} \\ \mathbf{Y}^{(n)} \end{pmatrix} = \Omega^{(n)} \begin{pmatrix} \mathbb{1} & 0 \\ 0 & -\mathbb{1} \end{pmatrix} \begin{pmatrix} \mathbf{X}^{(n)} \\ \mathbf{Y}^{(n)} \end{pmatrix}, \quad (8)$$

where  $\Omega^{(n)}$  denotes the energy of excitation  $n$  and  $\mathbf{X}^{(n)}$  and  $\mathbf{Y}^{(n)}$  are bi-orthogonal eigenvectors following [1,20,101–106]

$$\sum_{i,a} X_{ia}^{(m)} X_{ia}^{(n)} - Y_{ia}^{(m)} Y_{ia}^{(n)} = \pm \delta_{mn}. \quad (9)$$

The sign corresponds to positive and negative excitation energies  $\Omega^{(n)}$ , respectively, as the solutions of Eq. (8) come in pairs of  $(\Omega^{(n)}, \mathbf{X}^{(n)}, \mathbf{Y}^{(n)})$  and  $(-\Omega^{(n)}, \mathbf{Y}^{(n)}, \mathbf{X}^{(n)})$  [1,101–103,106] with excitation index  $n = 1, \dots, N_{\text{occ}}N_{\text{empty}}$ . We choose  $X_{ia}^{(n)}$  and  $Y_{ia}^{(n)}$  to be real-valued for the finite structures under study.

For a closed-shell ground state, the block matrices in Eq. (8) are defined by (cf. Appendix B) [31,107]

$$\begin{aligned} A_{ia,jb} &= (\varepsilon_a^{\text{evGW}_0} - \varepsilon_i^{\text{evGW}_0}) \delta_{ij} \delta_{ab} + \alpha^{(S/T)} v_{ia,jb} - W_{ij,ab}, \\ B_{ia,jb} &= \alpha^{(S/T)} v_{ia,bj} - W_{ib,aj}, \end{aligned} \quad (10)$$

where the preceding KS-DFT and  $GW$  calculations (cf. Fig. 1) provide quasiparticle energies  $\varepsilon_p^{\text{evGW}_0}$ , and

$$v_{pq,rs} = \int d^3r d^3r' \psi_p(\mathbf{r}) \psi_q(\mathbf{r}) v(\mathbf{r}, \mathbf{r}') \psi_r(\mathbf{r}') \psi_s(\mathbf{r}'), \quad (11)$$

$$W_{pq,rs} = \int d^3r d^3r' \psi_p(\mathbf{r}) \psi_q(\mathbf{r}) W_0(\mathbf{r}, \mathbf{r}', \omega=0) \psi_r(\mathbf{r}') \psi_s(\mathbf{r}') \quad (12)$$

are matrix elements of the bare and the statically RPA-screened Coulomb interaction, respectively. The prefactors  $\alpha^{(S)}$  and  $\alpha^{(T)}$  depend on the spin configuration and are  $\alpha^{(S)} = 2$  for a singlet excited state and  $\alpha^{(T)} = 0$  for a triplet excited state (cf. Appendix B).

In practice, we compute the matrix elements of Eqs. (11) and (12) using the resolution-of-the-identity (RI) technique [34,39], where auxiliary RI basis functions  $\varphi_P$  (indexed by  $P, Q, R$ ) are introduced:

$$v_{pq,rs} \approx \sum_P B_{pq}^P B_{rs}^P, \quad (13)$$

$$W_{pq,rs} \approx \sum_P B_{pq}^P (\varepsilon^{-1})_{PQ} B_{rs}^P. \quad (14)$$

Here, the coefficients  $B_{pq}^P$  are computed from [98]

$$B_{pq}^P = \sum_Q (pq|Q) L_{PQ}^{-1}, \quad (15)$$

where  $(pq|Q)$  denotes three-center Coulomb integrals

$$(pq|Q) = \int d^3r d^3r' \psi_p(\mathbf{r}') \psi_q(\mathbf{r}') v(\mathbf{r}, \mathbf{r}') \varphi_Q(\mathbf{r}), \quad (16)$$

and the  $L_{PQ}$  are obtained from a Cholesky decomposition of the Coulomb matrix

$$(P|Q) = \int d^3r \varphi_P(\mathbf{r}) v(\mathbf{r}, \mathbf{r}') \varphi_Q(\mathbf{r}') = \sum_R L_{PR} L_{RQ}^T. \quad (17)$$

Note that for the Gaussian basis (2) employed in this work, analytical expressions for two- and three-center Coulomb integrals (16), (17) guarantee efficient computations [108–110].

When solving Eq. (8) in practice, we assume that  $\mathbb{A} - \mathbb{B}$  is positive definite, which allows us to recast Eq. (8) into a Hermitian eigenvalue problem with half the size. We skip the details of this procedure and refer instead to the existing literature [1,20,28,103–105,111–114]. By neglecting the coupling blocks  $\mathbb{B}$ , Eq. (8) can be simplified even further, which is called the Tamm-Dancoff approximation (TDA) [14]:

$$\mathbb{A} \mathbf{X}_{\text{TDA}}^{(n)} = \Omega_{\text{TDA}}^{(n)} \mathbf{X}_{\text{TDA}}^{(n)}. \quad (18)$$

Computationally, both approaches are demanding in memory [ $O(N_{\text{occ}}^2 N_{\text{empty}}^2)$ ] and in the number of floating point operations for solving the eigenvalue problem [ $O(N_{\text{occ}}^3 N_{\text{empty}}^3)$ ].

Correspondingly, in order to enable the solution of Eq. (8) for large-scale systems, we adopt the standard procedure and reduce the associated prefactors by truncating the considered number of orbitals in Eq. (8) by an energy cutoff [39]. In Appendix C, we discuss the details of this technique and the extent to which it affects the accuracy of the optical absorption spectrum and spatial properties of the excitations.

One focus of this work is to study the optical absorption spectra of finite nanostructures from  $GW$ -BSE. Optical

absorption in the linear-response regime is described by the dynamical dipole polarizability tensor  $\alpha_{\mu\mu'}(\omega)$ , which relates the induced electronic dipole polarization of the nanostructure  $P_{\mu}(\omega)$  to an incident electric field  $E_{\mu'}(\omega)$  of frequency  $\omega$  [1]:

$$P_{\mu}(\omega) = \sum_{\mu'} \alpha_{\mu\mu'}(\omega) E_{\mu'}(\omega), \quad \mu, \mu' \in \{x, y, z\}. \quad (19)$$

In the BSE framework,  $\alpha_{\mu\mu'}(\omega)$  can be computed from the solution  $(\Omega^{(n)}, \mathbf{X}^{(n)}, \mathbf{Y}^{(n)})$  of Eq. (8) for  $\alpha^{(S)} = 2$  [1,29,31,102] (a derivation is also shown in Appendix B):

$$\alpha_{\mu\mu'}(\omega) = - \sum_{n>0} \frac{2\Omega^{(n)} d_{\mu}^{(n)} d_{\mu'}^{(n)}}{(\omega + i\eta)^2 - (\Omega^{(n)})^2}, \quad (20)$$

where the transition dipole moments of the singlet solution are given by [29,31,39,102,107]

$$d_{\mu}^{(n)} = \sqrt{2} \sum_{i,a} \mu_{ia} (X_{ia}^{(n)} + Y_{ia}^{(n)}), \quad (21)$$

with the dipole operator in the KS orbital basis

$$\mu_{ia} = \int d^3r \psi_i(\mathbf{r}) \mathbf{r} \psi_a(\mathbf{r}). \quad (22)$$

For the study of randomly oriented molecules in gases and liquids, the isotropic average  $\bar{\alpha}(\omega)$ , the oscillator strengths  $f^{(n)}$  and the photoabsorption cross section  $\sigma_{\mu\mu'}(\omega)$  are typically used, which we discuss in Appendix D. In periodic crystals, the optical absorption is typically computed from the imaginary part of the (macroscopic) dielectric function  $\epsilon(\omega)$  [2,12,115,116] related to the current-current correlation function [12,117]. In this work, we employ  $\alpha_{\mu\mu'}(\omega)$  for computing optical absorption of finite nanostructures, because of its structural similarity and relation to the dielectric function  $\epsilon(\omega)$  [11,116,118], which is extracted from experimental data (cf. Sec. III). Equivalently, one could include a factor of  $\omega$  in the compared expressions, which would then be the absorption coefficient  $\kappa_{\text{abs}} \propto \omega \epsilon(\omega)$  [11], and the photoabsorption cross section  $\sigma_{\mu\mu'}(\omega) \propto \omega \alpha_{\mu\mu'}(\omega)$ .

To demonstrate the numerical precision of our *GW*-BSE implementation in CP2K, we benchmark the excitation energies  $\Omega^{(n)}$  from Eq. (8) on Thiel's set [119], a standard set of organic molecules. As a reference implementation, we employ the *GW*-BSE implementation in FHI-AIMS [39,120–122]. We do not enforce identical quasiparticle energies as starting points, but both implementations are run from scratch as BSE@evGW<sub>0</sub>@PBE calculation with the aug-cc-pVDZ [123,124] basis set. The computational details are given in Appendix E.

In Fig. 2, we report the absolute error  $|\Omega_{\text{CP2K}}^{(n)} - \Omega_{\text{FHI-AIMS}}^{(n)}|$  for each molecule of Thiel's set and the first ten excitation levels  $n = 1, \dots, N_{\text{exc}}, N_{\text{exc}} = 10$ , between CP2K and FHI-AIMS. The presented mean absolute error (MAE) is computed as

$$\text{MAE} = \frac{1}{28N_{\text{exc}}} \sum_{n=1}^{N_{\text{exc}}} \sum_{M=1}^{28} |\Omega_{\text{CP2K},M}^{(n)} - \Omega_{\text{FHI-AIMS},M}^{(n)}|, \quad (23)$$

where the index  $M$  runs over the 28 molecules in the set and  $\Omega_{\text{CP2K}}^{(n)}$  and  $\Omega_{\text{FHI-AIMS}}^{(n)}$  are the extracted excitation energies from our implementation and the FHI-AIMS implementation

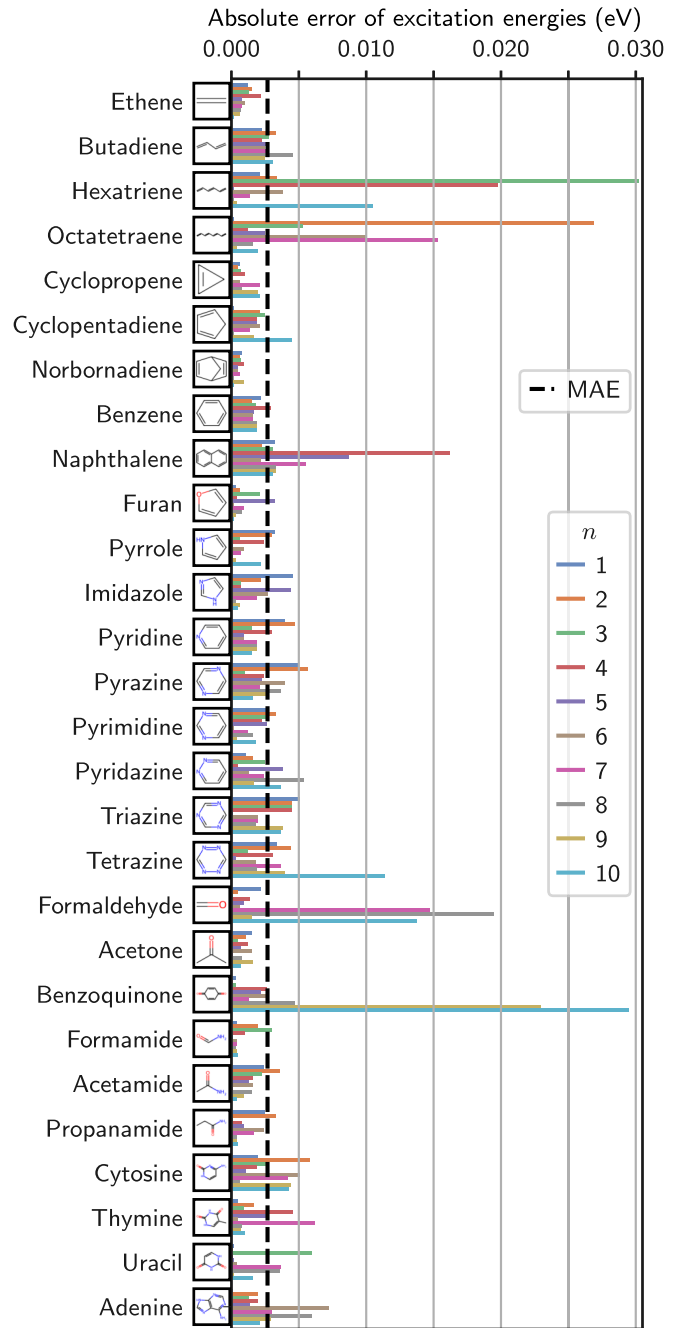


FIG. 2. Absolute error  $|\Omega_{\text{CP2K}}^{(n)} - \Omega_{\text{FHI-AIMS}}^{(n)}|$  of BSE excitation energies  $\Omega^{(n)}$  computed from CP2K and FHI-AIMS by solving Eq. (8) with BSE@evGW<sub>0</sub>@PBE. The mean absolute error (23) over the ten lowest excitation energies across all molecules is only 2.7 meV. For a benchmark on the impact of parameters of *GW* calculations on BSE excitation energies, we refer to Appendix F.

[39], respectively. We observe a small MAE of 2.7 meV in Fig. 2 with single outliers leading to a maximum error of 30 meV. In general, the observed deviations between CP2K and FHI-AIMS can be traced back to the quasiparticle energies  $\epsilon_n^{\text{evGW}_0}$  around the HOMO-LUMO (highest occupied molecular orbital–lowest unoccupied molecular orbital) gap.

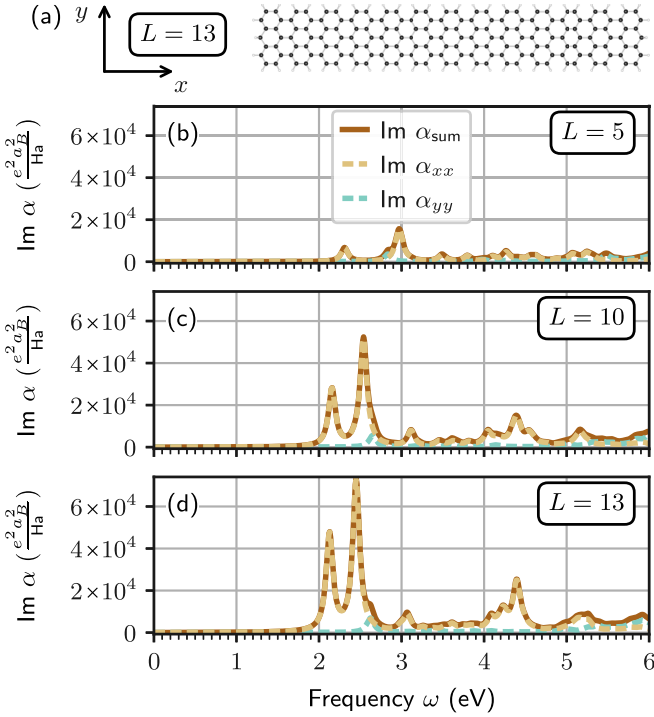


FIG. 3. Optical absorption spectrum from the imaginary part of the dynamical dipole polarizability  $\alpha_{\mu\mu'}(\omega)$  (20) ( $\eta = 0.05$  eV) for finite nanographene flakes with increasing number of repeating units  $L$  from BSE@evGW<sub>0</sub>@PBE. (a) Geometry of a nanographene with  $L = 13$  anthracene units in  $x$  direction, visualized using Ref. [125]. (b)–(d) Components of the dynamical dipole polarizability and the sum,  $\alpha_{\text{sum}} = \alpha_{xx} + \alpha_{yy} + \alpha_{zz}$  as a function of the light frequency. The out-of-plane component  $\alpha_{zz}$  is not shown as its absolute value is below  $\text{Im } \alpha_{zz} = 156 (e^2 a_B^2)/\text{Ha}$ . Computational details are described in Appendix E.

### III. ABSORPTION SPECTRUM OF NANOGRAFENES FROM BSE AND COMPARISON TO EXPERIMENT

We now focus on optical excitations of rectangular nanographenes with seven carbon atoms in zigzag direction and an increasing number of repeating anthracene units,  $L$ , in armchair direction, as displayed in Fig. 3(a).

Since finite nanographenes feature spin-polarized zigzag edge states when passivated by single hydrogen atoms [126], we introduce a second H atom at the outermost central C atoms along the  $x$  direction, suppressing the edge states. We compute optical properties from evGW<sub>0</sub> + BSE employing Eq. (8) when increasing the repeating units in the armchair direction. In Fig. 3, we show the imaginary part of the dynamical dipole polarizability tensor  $\alpha_{\mu\mu'}$  from Eq. (20) for three different numbers of repeating units  $L = 5, 10, 13$ . For all lengths  $L$  in Fig. 3, we observe that the sum  $\alpha_{\text{sum}}(\omega)$  is dominated by the longitudinal  $\alpha_{xx}(\omega)$  component. While the  $\alpha_{xx}(\omega)$  component shows a strong dependence on the system length  $L$ , we can confirm from Figs. 3(b)–3(d) that the optical response in the transverse direction  $\alpha_{yy}(\omega)$  remains largely unaffected by the length  $L$  in  $x$  direction, as it has also been observed in Ref. [127] from semiempirical calculations.

The nanographene studied in Ref. [53] is about 20 nm long, which corresponds to  $L = 46$  and is beyond the

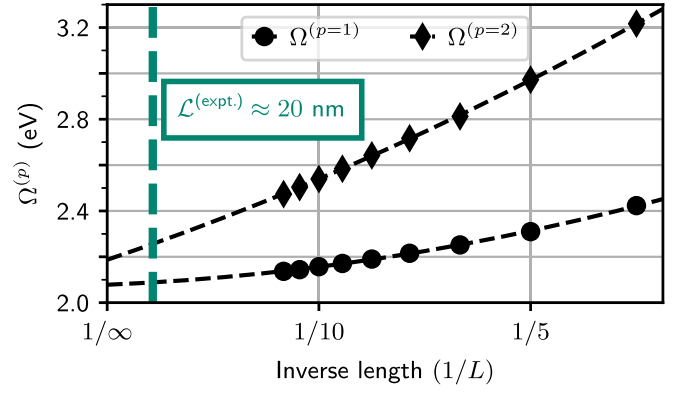


FIG. 4. Excitation frequencies  $\Omega^{(p=1,2)}$  of the first two dominant peaks ( $p = 1, 2$ ) in  $\text{Im}\alpha_{xx}^{(L)}(\omega)$  for  $L \in [4, 13]$  (see example spectra in Fig. 3). We fit the obtained peak frequencies by  $\Omega^{(p)}(L) = a^{(p)} + b^{(p)}/L + c^{(p)}/L^2$  (dashed lines), from which we obtain  $\lim_{L \rightarrow \infty} \Omega^{(p=1)} = 2.08$  eV and  $\lim_{L \rightarrow \infty} \Omega^{(p=2)} = 2.19$  eV. The obtained parameters of the fits for  $p = 1, 2$  are reported in Table I. The vertical dashed line in green indicates the average length of the experimental nanographene  $\mathcal{L}^{(\text{expt.})} \approx 20$  nm [53]. The fit yields  $\Omega^{(p=1)}(\mathcal{L}^{(\text{expt.})}) = 2.09$  eV and  $\Omega^{(p=2)}(\mathcal{L}^{(\text{expt.})}) = 2.26$  eV.

system sizes accessible to our current BSE implementation. To compare with the experimental optical absorption spectrum of Ref. [53], we extract the frequencies of the two lowest longitudinal peaks,  $\Omega^{(p)}$  with  $p = 1, 2$ , from  $\text{Im}\alpha_{xx}^{(L)}(\omega)$  for  $L = 4, \dots, 13$  and extrapolate the resulting  $\Omega^{(p)}(L)$  to the experimental geometry. The data points used for this procedure are shown in Fig. 4. We omit  $L \leq 3$  because the corresponding spectra do not yet exhibit two well-separated low-energy peaks that would yield reliable peak positions. For the extrapolation, we apply a quadratic fit  $\Omega^{(p)}(L) = a^{(p)} + b^{(p)}/L + c^{(p)}/L^2$  motivated by the free-electron model in a one-dimensional box with periodic potential, as it has been already applied to other  $\pi$ -electron systems [128,129]. Taking into account the finite size of the experimental geometries (green vertical line in Fig. 4), which they estimate to be  $\mathcal{L}^{(\text{expt.})} \approx 20$  nm (cf. supporting information of Ref. [53]), we obtain BSE excitation energies of  $\Omega^{(p=1)}(\mathcal{L}^{(\text{expt.})}) = 2.09$  eV and  $\Omega^{(p=2)}(\mathcal{L}^{(\text{expt.})}) = 2.26$  eV from the extrapolation. These values are in excellent agreement with the experimental excitation energies [53]  $\Omega_{\text{expt.}}^{(p=1)} = 2.05$  eV and  $\Omega_{\text{expt.}}^{(p=2)} = 2.31$  eV, yet another demonstration of the success of the BSE formalism.

Beyond the agreement of the peak positions, we compare the peak heights of the GW-BSE and experimental optical absorption spectra. Reference [53] obtains the dielectric function  $\epsilon_x(\omega)$  of the nanographene (20 nm length) experimentally via

TABLE I. Fit parameters of the quadratic fit  $\Omega^{(p)}(L) = a + b/L + c/L^2$  in Fig. 4 and extrapolated excitation energies and experimental measurement (cf. Fig. 5). All quantities are given in eV.

	$a^{(p)}$	$b^{(p)}$	$c^{(p)}$	$\Omega^{(p)}(\mathcal{L}^{(\text{expt.})})$	$\Omega^{(p)}(\text{expt.})$
$p = 1$	2.08	0.39	3.96	2.09	2.05
$p = 2$	2.19	3.13	3.97	2.26	2.31

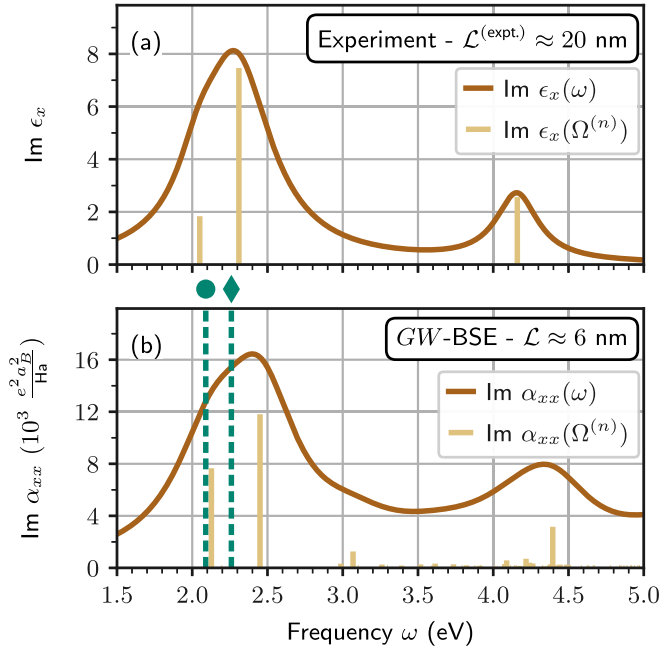


FIG. 5. Optical absorption spectrum (a) reproduced from experimental data [53] via  $\text{Im } \epsilon_x(\omega)$  and (b) calculated using GW-BSE (BSE@evGW<sub>0</sub>) for  $L = 13$  via  $\text{Im } \alpha_{xx}(\omega)$ , which are related by a frequency-independent factor  $C$  [Eq. (24)]. For the GW-BSE calculation, we employ a broadening of  $\eta = 0.3$  eV. The individual peak heights at the resonance energies  $\Omega^{(n)}$ , represented by the beige vertical lines, are computed from Eqs. (G2) and (G3) in Appendix G. Green vertical lines denote the extrapolated peak frequencies  $\Omega^{(p=1)}(\mathcal{L}^{(\text{expt.})}) = 2.09$  eV and  $\Omega^{(p=2)}(\mathcal{L}^{(\text{expt.})}) = 2.26$  eV from Fig. 4.

reflectance difference measurements, whose imaginary part is shown in Fig. 5(a) (see details in Appendix G). In the limit of an infinitely long nanographene, the dielectric function is related to the dynamical dipole polarizability via a frequency-independent factor [118]:

$$\text{Im } \epsilon_x(\omega) = C \text{Im } \alpha_{xx}(\omega), \quad (24)$$

which has the same form as the Clausius-Mossotti relation when neglecting local field effects [116]. Hence, we plot the imaginary part of the dynamical dipole polarizability  $\text{Im } \alpha_{xx}(\omega)$  in Fig. 5(b) for the nanographene with  $L = 13$  (6 nm length).

Comparing the experimental and BSE absorption spectra in Figs. 5(a) and 5(b), we observe a nice match of the overall line shape. The observable difference between experiment and BSE spectrum, particularly the resonance frequencies  $\Omega^{(n)}$ , may originate from the different lengths in the experimental and GW-BSE geometries (20 nm versus 6 nm). When extrapolating BSE excitation energies to 20 nm length, the agreement between BSE and experiment is excellent, cf. Table I.

#### IV. SPATIAL DESCRIPTORS OF ELECTRONIC EXCITATIONS WITHIN THE BSE

Beyond the optical response, excited states have an associated spatial structure, which can be of interest to better understand oscillator strengths or transition rates in

excited-state dynamics. To enable a quantitative analysis of these spatial properties, we discuss expectation values (descriptors) associated with particular spatial properties of an excitation in this section, as proposed in Refs. [60–62,66].

The starting point is the wave function of the electronic excitation [66],

$$\Psi_{\text{exc}}^{(n)}(\mathbf{r}_e, \mathbf{r}_h) = \int d^3 r_2 \cdots d^3 r_N \Phi_0(\mathbf{r}_h, \mathbf{r}_2, \dots) \Phi_n(\mathbf{r}_e, \mathbf{r}_2, \dots), \quad (25)$$

where  $\Phi_0$  and  $\Phi_n$  are the ground and an excited-state wave function of the full many-body Hamiltonian. Within GW-BSE, Eq. (25) can be expressed in the product space of occupied and unoccupied KS orbitals as [12,31,62]

$$\Psi_{\text{exc}}^{(n)}(\mathbf{r}_e, \mathbf{r}_h) = \sum_{i,a} X_{ia}^{(n)} \psi_a(\mathbf{r}_e) \psi_i(\mathbf{r}_h) + Y_{ia}^{(n)} \psi_i(\mathbf{r}_e) \psi_a(\mathbf{r}_h). \quad (26)$$

The physics behind Eq. (26) can be understood in terms of electrons and holes: Concerning the first part, an electron is excited to a (formerly) unoccupied orbital  $\psi_a(\mathbf{r}_e)$  and leaves a hole behind at the occupied orbital  $\psi_i(\mathbf{r}_h)$ , where the excitation  $n$  can mix different KS orbitals as described by the transition amplitudes  $X_{ia}^{(n)}$ . Vice versa, the amplitudes  $Y_{ia}^{(n)}$  describe the reverse process, i.e., deexcitations [130].

The expectation value associated with excitation (26) for a generic operator  $\hat{O}$  then reads

$$\langle \hat{O} \rangle_{\text{exc}}^{(n)} = \frac{\langle \Psi_{\text{exc}}^{(n)} | \hat{O} | \Psi_{\text{exc}}^{(n)} \rangle}{\langle \Psi_{\text{exc}}^{(n)} | \Psi_{\text{exc}}^{(n)} \rangle}. \quad (27)$$

From here on, we drop the excitation index  $n$  to simplify the notation of the expectation values. Specifically, we focus on the size of the excitation [66]

$$d_{\text{exc}} = \sqrt{\langle |\mathbf{r}_e - \mathbf{r}_h|^2 \rangle_{\text{exc}}}, \quad (28)$$

which can be divided into the following contributions:

$$d_{\text{exc}} = \sqrt{d_{e \rightarrow h}^2 + \sigma_h^2 + \sigma_e^2 - 2\sigma_h \sigma_e R_{eh}}. \quad (29)$$

The first contribution is the distance between the electron and hole:

$$d_{e \rightarrow h} = |\langle \mathbf{r}_e - \mathbf{r}_h \rangle_{\text{exc}}|, \quad (30)$$

which naturally quantifies the charge-transfer character of an excitation. The electron-hole separation  $d_{e \rightarrow h}$  is large for a so-called charge-transfer excitation [62,66] where the electron at  $\langle \mathbf{r}_e \rangle_{\text{exc}}$  is located on a different part of the molecule [36,57,131–133] or of a van der Waals crystal [7,134,135] than the hole at  $\langle \mathbf{r}_h \rangle_{\text{exc}}$ . Further contributions to Eq. (29) are the size of the electron

$$\sigma_e = \sqrt{\langle (\mathbf{r}_e - \langle \mathbf{r}_e \rangle_{\text{exc}})^2 \rangle_{\text{exc}}}, \quad (31)$$

analogously, the size of the hole,  $\sigma_h$ , and the electron-hole correlation coefficient  $R_{eh}$

$$R_{eh} = \frac{1}{\sigma_e \sigma_h} (\langle \mathbf{r}_h \cdot \mathbf{r}_e \rangle_{\text{exc}} - \langle \mathbf{r}_h \rangle_{\text{exc}} \cdot \langle \mathbf{r}_e \rangle_{\text{exc}}). \quad (32)$$

If  $R_{eh}$  is nonzero, it allows us to distinguish between bound electron-hole-pairs ( $R_{eh} > 0$ ) and pairs, which are avoiding

each other dynamically ( $R_{eh} < 0$ ). Consequently,  $R_{eh} = 0$  indicates uncorrelated electron and holes. By the Cauchy-Schwarz inequality, we find that  $R_{eh} \in [-1, 1]$ , i.e., maximal anticorrelation (correlation) is indicated by  $-1$  ( $+1$ ), respectively.

To describe the strongly anisotropic nanographenes, we additionally define directional exciton descriptors, where the coordinates of electron and hole are projected into the Cartesian directions. This leads, exemplarily for the  $x$  direction, to the size of the electron,

$$\sigma_e^{(x)} = \sqrt{\langle (x_e - \langle x_e \rangle_{exc})^2 \rangle_{exc}}, \quad (33)$$

and by analogy for  $\sigma_h^{(x)}$ , the (directional) electron-hole separation

$$d_{e \rightarrow h}^{(x)} = |\langle x_e - x_h \rangle_{exc}|, \quad (34)$$

as well as the size of the excitation in  $x$  direction

$$d_{exc}^{(x)} = \sqrt{\langle |x_e - x_h|^2 \rangle_{exc}}. \quad (35)$$

We define the correlation coefficient in  $x$  direction as

$$R_{eh}^{(x)} = \frac{1}{\sigma_e^{(x)} \sigma_h^{(x)}} (\langle x_h x_e \rangle_{exc} - \langle x_h \rangle_{exc} \langle x_e \rangle_{exc}). \quad (36)$$

We implement all descriptors based on multipole moments in the KS orbital basis following Refs. [66,136].

### V. SIZE OF EXCITATIONS IN NANOGRAFENES FROM BSE AND TDDFT

In this section, we analyze the spatial characteristics of the electronic excitations in the nanographenes of Sec. III, focusing on the lowest-energy bright state ( $p = 1$ ) for each length  $L$ . The size of the excitation  $d_{exc}^{(x,p=1)}$  is shown in Fig. 6(a) as a function of the nanographene length. For small  $L \in [1,4]$ , we observe a linear increase, which saturates for larger system sizes to  $\approx 7.6$  Å for a length of 4 nm. The plateau indicates that the size of the excitation is controlled by an intrinsic correlation length (exciton radius) that is smaller than the nanographene length, consistent with bound excitons in crystals. In contrast, the individual spreads of electron and hole,  $\sigma_e^{(x,1)}$  and  $\sigma_h^{(x,1)}$ , increase with  $L$  [Fig. 6(b)], as expected for single-particle densities in a one-dimensional box, which extend over the system, whereas the relative separation of electron and hole is bounded via the screened Coulomb interaction. The correlation coefficient in Fig. 6(c) confirms this view: it increases with  $L$  and approaches one, indicating strongly correlated electron-hole motion for large  $L$ .

To assess the extent to which a simpler framework can reproduce these excitonic characteristics, we next turn to TDDFT [1], which offers a computationally cheaper alternative to the  $GW$ -BSE approach. Beyond that, it is available in most electronic-structure codes, making it attractive for systematic studies of large nanographenes. However, results from TDDFT computations depend strongly on the employed exchange-correlation functional, which implicitly determines the electron-hole interaction [64]. In semilocal exchange-correlation kernels in the generalized gradient approximation (GGA), this interaction is absent, while hybrid and range-separated hybrid functionals reintroduce parts of the bare

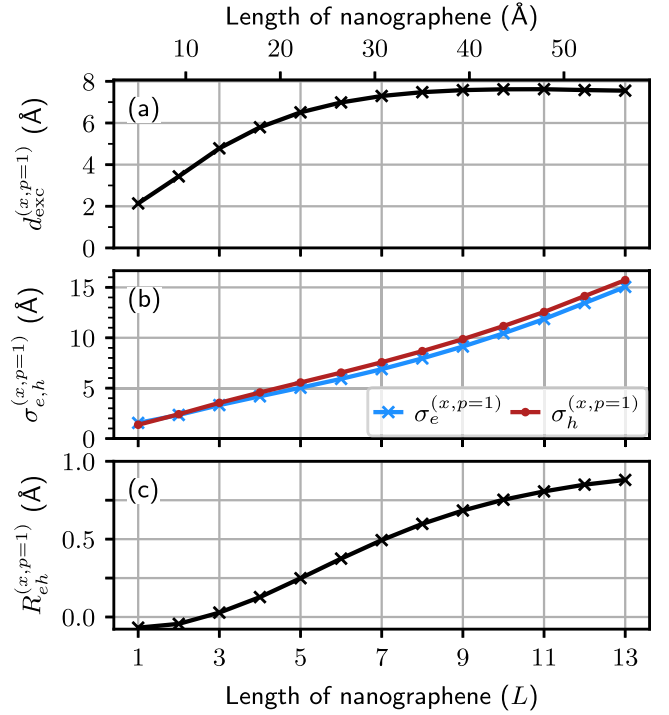


FIG. 6. Spatial properties of the first bright peak  $p = 1$  in the optical absorption spectra along the  $x$  direction computed from  $GW$ -BSE. (a) Longitudinal size of the excitation at the first peak  $d_{exc}^{(x,p=1)}$ , Eq. (35), (b) longitudinal sizes of electron  $\sigma_e^{(x,p=1)}$  (blue) and hole  $\sigma_h^{(x,p=1)}$  (red) from Eq. (33), (c) longitudinal electron-hole correlation coefficient  $R_{eh}^{(x,p=1)}$  (36) associated with the first peak  $p = 1$ .

Coulomb attraction through exact exchange. For example, PBE0 includes 25% of the unscreened interaction, whereas HSE06 restricts it to short range, effectively mimicking a fully screened Coulomb potential in the long range.

For metallic systems, TDDFT with (semi-)local functionals captures the features of plasmonic excitations [1,137,138]. This is commonly attributed to strong metallic screening, which suppresses the interaction of the excited electrons and holes. In gapped materials, however, (semi-)local TDDFT kernels typically miss the required long-range electron-hole attraction and therefore yield inaccurate excitation spectra (e.g., for Si) [2,139]. Within TDDFT, a reliable description then requires a suitably nonlocal exchange-correlation kernel, for instance, based on (range-separated) hybrid functionals or other long-range corrected kernels.

Figure 7 compares excitation energies and sizes of the excitation obtained in nanographenes from TDDFT with those from  $GW$ -BSE. In Fig. 7(a), all methods show the expected redshift of the first bright excitation with increasing nanographene length, but the absolute values differ. GGAs (PBE [140], BLYP [141,142]) substantially underestimate the excitation energies, while hybrids (PBE0, B3LYP [141,143,144], HSE06 [145,146]) yield values closer to  $GW$ -BSE. The exception is CAM-B3LYP [147], overestimating the BSE excitation energy by  $\approx 0.5$  eV, which we attribute to the large long-range exact-exchange fraction of 65%, binding the exciton too strongly. Figure 7(b) shows the corresponding size of the excitation  $d_{exc}^{(x,p=1)}$ : GGAs predict overly

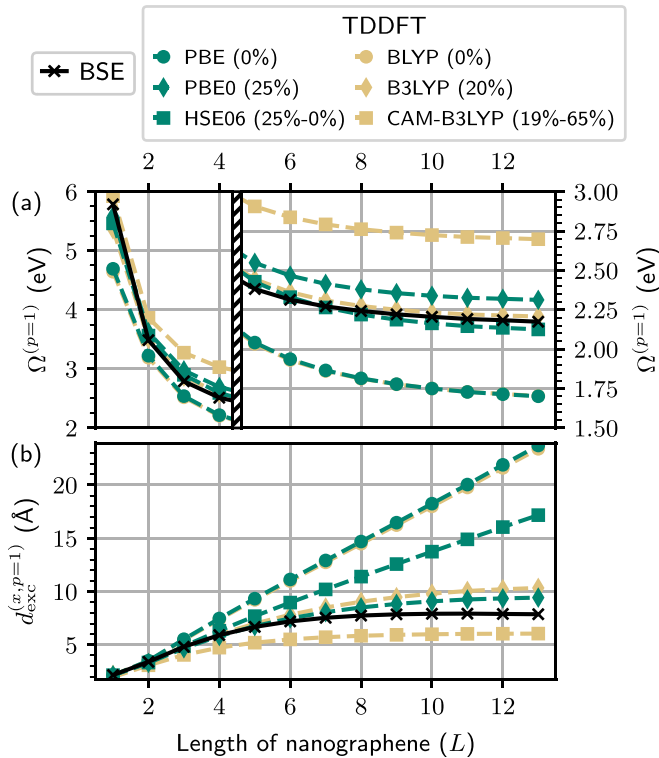


FIG. 7. Excitation energy  $\Omega^{(p=1)}$  and size of the excitation  $d_{\text{exc}}^{(x,p=1)}$  computed from BSE@evGW<sub>0</sub> and TDDFT (both in TDA; effect of TDA investigated in Appendix H) employing different exchange–correlation functionals (exact exchange fraction shown in the legend). (a) Peak frequency of the first prominent peak in the optical absorption spectrum  $\Omega^{(p=1)}$ . (b) Longitudinal size of the excitation for the first bright peak  $d_{\text{exc}}^{(x,p=1)}$ , Eq. (35). We show excitation energies and sizes computed with PBE-based hybrids as a function of the exact-exchange fraction in Appendix I.

delocalized excitations whose size grows linearly with  $L$ , which we attribute to the absent attractive Coulomb interaction between electron and hole. Hybrid functionals confine the excitation more strongly, although HSE06 still shows an increase in the size of the excitation with nanographene length since the Coulomb interaction of electron and hole is only present at short range. Overall, our TDDFT calculations reproduce qualitative trends of the BSE only when the functional contains sufficient long-range electron-hole attraction, but its quantitative accuracy remains limited by the absence or approximate treatment of screening. Accordingly, manual tuning of functional parameters to mimic the screened long-range electron-hole attraction should also enable better quantitative prediction of excitation energies, oscillator strengths, and spatial descriptors. We discuss such a tuning for the exact-exchange fraction in PBE-based hybrid functionals in Appendix I. By analogy, functionals with more parameters might allow us to match several properties simultaneously for a given material. However, the loss of generality caused by this manual tuning for a given material strongly limits its applicability to novel materials.

Figure 7 establishes which hybrid functionals yield a reasonable excitation energy and corresponding size of the lowest bright excitation; however, their ability to reproduce

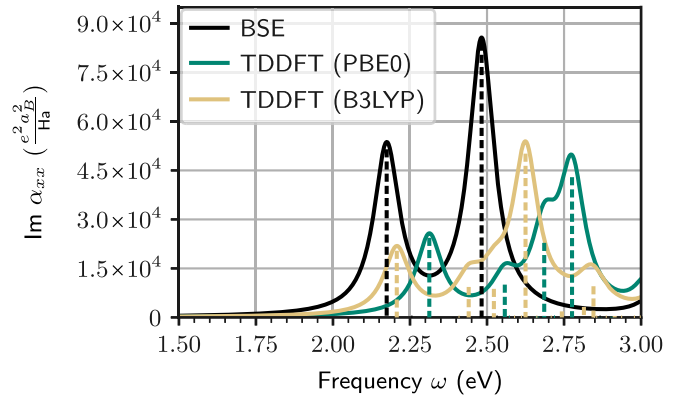


FIG. 8. Optical absorption spectrum for GW-BSE (black) and TDDFT with two different hybrid functionals PBE0 (green) and B3LYP (beige) for the nanographene with  $L = 13$  (all in TDA; effect of TDA investigated in Appendix H), computed from Eq. (20) employing  $\eta = 0.05$  eV. Dashed lines denote the contribution of individual excitations  $n$  to  $\text{Im } \alpha_{xx}(\omega = \Omega^{(n)})$  from Eq. (20) [cf. Eq. (G3)].

the overall spectral shape has not yet been assessed. To assess how well TDDFT reproduces the full optical spectra beyond the lowest excitation, we now compare the absorption spectra from TDDFT and GW-BSE in Fig. 8. For the nanographene with  $L = 13$ , the TDDFT spectra obtained with PBE0 and B3LYP differ significantly from the GW-BSE reference (Fig. 8): the number and relative intensity of peaks are inconsistent, and additional side peaks appear both at lower and higher energies. Assuming GW-BSE as the reference, these discrepancies indicate that the TDDFT excitation spectrum is qualitatively incorrect, which we attribute to the incorrect interaction of electron and hole in our TDDFT calculations. Recently, advances in range-separated hybrid functionals [148–150] might be able to mimic the screened interaction more accurately, but their application is beyond the scope of this work. In any case, the large experimental linewidths (cf. Fig. 5) would likely wash out these differences even for standard functionals, such that the broadened TDDFT spectra could still appear compatible with experiment despite the incorrect underlying peak structure.

## VI. CONCLUSION

We have implemented and applied the GW-BSE formalism in CP2K to rectangular nanographenes with a fixed width of seven carbon atoms along the zigzag direction and variable length along the armchair direction. The BSE@evGW<sub>0</sub>@PBE approach reproduces the measured absorption spectrum, and the two lowest bright excitations agree with experiment within 0.05 eV after finite-size extrapolation. The size of the excitation of the first bright state converges to about 7.6 Å, establishing a bound exciton with a well-defined spatial extent. TDDFT with PBE0 and B3LYP reproduces this size of the excitation and yields reasonable lowest excitation energies, but the spectra around the lowest bright peaks display additional sidebands and altered intensities that are absent in GW-BSE. Thus, while selected descriptors can be matched

within TDDFT, *GW*-BSE provides a consistent description of both spectral and spatial properties for nanographenes.

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### DATA AVAILABILITY

Inputs and outputs of all calculations reported in this work are available in a GitHub [151] and a Zenodo [152] repository, as well as via the University of Regensburg library [153]. The *GW* + BSE algorithm developed in this work is available in the open-source package CP2K [94–96].

### APPENDIX A: HEDIN'S EQUATIONS AND COMMONLY APPLIED SIMPLIFICATIONS

In Sec. II, we have introduced the *GW* approximation to the self-energy in Eq. (3), which reads in simplified notation [97,100]

$$\Sigma^{GW}(\mathbf{1}, \mathbf{2}) = iG(\mathbf{1}, \mathbf{2})W(\mathbf{1}^+, \mathbf{2}), \quad (\text{A1})$$

where the numbers denote combined space-spin-time coordinates, e.g.,  $\mathbf{1} = (\mathbf{r}_1, s_1, t_1)$  and  $\mathbf{1}^+$  denotes an infinitely small time-shift on  $t_1$  to a later time. More generally, the full set of Hedin's equations reads [100]

$$\Sigma(\mathbf{1}, \mathbf{2}) = i \int d(\mathbf{34})G(\mathbf{1}, \mathbf{4})W(\mathbf{1}^+, \mathbf{3})\Gamma(\mathbf{4}, \mathbf{2}, \mathbf{3}), \quad (\text{A2})$$

$$G(\mathbf{1}, \mathbf{2}) = G_0(\mathbf{1}, \mathbf{2}) + \int d(\mathbf{34})G_0(\mathbf{1}, \mathbf{3})\Sigma(\mathbf{3}, \mathbf{4})G(\mathbf{4}, \mathbf{2}), \quad (\text{A3})$$

$$W(\mathbf{1}, \mathbf{2}) = v(\mathbf{1}, \mathbf{2}) + \int d(\mathbf{34})\chi_0(\mathbf{3}, \mathbf{4})v(\mathbf{1}, \mathbf{3})W(\mathbf{4}, \mathbf{2}), \quad (\text{A4})$$

$$\chi_0(\mathbf{1}, \mathbf{2}) = -i \int d(\mathbf{34})G(\mathbf{4}, \mathbf{2})G(\mathbf{2}, \mathbf{3})\Gamma(\mathbf{3}, \mathbf{4}, \mathbf{1}), \quad (\text{A5})$$

$$\begin{aligned} \Gamma(\mathbf{1}, \mathbf{2}, \mathbf{3}) &= \delta(\mathbf{1}, \mathbf{2})\delta(\mathbf{1}, \mathbf{3}) + \int d(\mathbf{4567})\frac{\partial \Sigma(\mathbf{1}, \mathbf{2})}{\partial G(\mathbf{4}, \mathbf{5})} \\ &\times G(\mathbf{4}, \mathbf{6})G(\mathbf{7}, \mathbf{5})\Gamma(\mathbf{6}, \mathbf{7}, \mathbf{3}), \end{aligned} \quad (\text{A6})$$

where the *GW* approximation, Eq. (A1), follows from Eq. (A2) when assuming  $\Gamma(\mathbf{1}, \mathbf{2}, \mathbf{3}) = \delta(\mathbf{1}, \mathbf{2})\delta(\mathbf{1}, \mathbf{3})$ . The resulting *GW* equations can be solved fully self-consistently (fully self-consistent *GW*, *scGW*). However, it has been

observed that *scGW* exhibits worse accuracy than other (partially) self-consistent schemes, related to an error cancellation observed for non- or partial self-consistency and missing vertex corrections in *GW* [2,3,110]. As a result, single-shot and partially self-consistent *GW* schemes emerged. The simplest scheme is single-shot  $G_0W_0$ , where both the Green's function  $G_0$  as well as the screened Coulomb interaction  $W_0$  are computed only once from the initial KS states and energies. Due to missing self-consistency,  $G_0W_0$  shows a strong starting point dependence on the exchange-correlation (xc) functional used in the preceding KS-DFT calculation [26,28,35,42,100,157–160]. By partially introducing self-consistency in  $G$  via updates of the eigenvalues, but keeping the screened Coulomb interaction fixed as  $W_0$  (*evGW*), the starting point dependence is reduced, and it has been shown that band gaps of crystals computed from *evGW* are in best agreement with experiments among the *GW* schemes [100,161–163]. For small molecules, *GW* schemes are benchmarked against energies of the highest occupied and lowest unoccupied molecular orbital (HOMO, LUMO) computed from high-level wave function theory. For molecules, it has been found that updating the screened interaction  $W$  (*evGW*) is on average slightly more favorable than keeping it fixed as  $W_0$  [26,35,159]. While nanographenes have a size between the limits of small molecules and extended crystals, their excitations have a spatial extent comparable to those in crystals. Consequently, we use the *evGW* scheme in this work. It has been found that partially self-consistent approaches (*evGW*, *evGW*) still show a starting point dependence, which has been observed to be around 50–250 meV [26,35,40,42] in molecular systems or even more than 500 meV for halide perovskites [164], since KS orbitals depend on the employed xc functional. This remaining starting point dependence can be eliminated by updating the quasiparticle wave functions self-consistently (*qsGW*, *qsGW*). This approach has been successfully employed, e.g., by Ref. [165], but that is beyond the scope of this work.

Table II summarizes the starting-point dependence of the *GW* HOMO-LUMO gaps and BSE@*evGW* excitation energies, using the DFT functionals PBE [140] and PBE0 [166] as starting points for ethene, benzene, and a nanographene consisting of a single unit cell ( $L = 1$ ; 9,10-dihydroanthracene). In general, we confirm the starting point dependency between 50 and 250 meV, as given above. Moreover, the ordering of HOMO-LUMO gaps and excitation energies (ethene > benzene > nanographene) is identical for every starting point. The good agreement of *evGW* band gaps of crystals with experiments can be reasoned with in a simple picture: We consider the effect of an external perturbation potential  $V_{\text{ext}}(\mathbf{r}, t)$  on the electronic system (in linear response), given by the change of the electronic density [1,2]

$$\Delta n(\mathbf{r}, t) = \int d\mathbf{r}' \int dt' \chi(\mathbf{r}, t, \mathbf{r}', t')V_{\text{ext}}(\mathbf{r}', t'), \quad (\text{A7})$$

where the reducible polarizability (or density-density response function)  $\chi$  is exact and includes the poles of the full many-body wave function.  $\chi$  follows from the irreducible

TABLE II. HOMO-LUMO gaps and first excitation energies (all in eV) for the molecules ethene, benzene, and the  $L = 1$  nanographene, employing PBE [140] and PBE0 [166] as starting point. The excited-state methods all employ the Tamm-Dancoff approximation (TDA) for comparability.

	Eq. (A11)		Ethene		Benzene		Nanographene with $L = 1$	
	$\varepsilon_p$	$F_{pq,rs}$	PBE	PBE0	PBE	PBE0	PBE	PBE0
$\Delta\varepsilon^{\text{KS}}$			5.64	7.77	5.11	6.99	4.14	5.92
$\Delta\varepsilon^{\text{evGW}_0}$			11.19	11.14	9.66	9.64	8.65	8.71
$\Delta\varepsilon^{\text{evGW}}$			11.47	11.30	9.98	9.80	9.01	8.88
$\Omega_{\text{BSE@evGW}_0}^{(n=1)}$	evGW <sub>0</sub>	$-W_{pq,rs}$	6.24	6.44	4.84	4.98	4.62	4.74
$\Omega_{\text{TDDFT}}^{(n=1)}$	KS	$f_{pq,rs}^{\text{xc}}$	6.48	6.87	5.24	5.48	4.35	4.97
$\Omega_{\text{RPA@KS}}^{(n=1)}$	KS	0	6.61	8.12	5.41	7.30	4.40	6.19
$\Omega_{\text{RPA@evGW}}^{(n=1)}$	evGW	0	11.59	11.40	10.03	9.84	9.04	8.90

polarizability  $\chi_0$  (A5) in Hedin's equations via

$$\chi(\mathbf{1}, \mathbf{2}) = \chi_0(\mathbf{1}, \mathbf{2}) + \int d(\mathbf{3}\mathbf{4})\chi_0(\mathbf{1}, \mathbf{3})v(\mathbf{3}, \mathbf{4})\chi(\mathbf{4}, \mathbf{2}), \quad (\text{A8})$$

with spectral representation [100,167]

$$\chi(\mathbf{r}, \mathbf{r}', \omega) = \sum_n 2 \frac{\Omega^{(n)}}{\omega^2 - (\Omega^{(n)})^2} \rho^{(n)}(\mathbf{r})\rho^{(n)}(\mathbf{r}'), \quad (\text{A9})$$

where  $\Omega^{(n)}$  are the excitation energies of the system, and  $\rho^{(n)}(\mathbf{r})$  are the transition densities of a given excitation index  $n$ . The crucial aspect to accurately describe the electronic response is the pole structure of  $\chi$  in Eq. (A9), i.e., inserting accurate excitation energies  $\Omega^{(n)}$ . These are typically computed from a Casida-like equation [167,168]

$$\begin{pmatrix} \mathbb{A} & \mathbb{B} \\ \mathbb{B} & \mathbb{A} \end{pmatrix} \begin{pmatrix} \mathbf{X}^{(n)} \\ \mathbf{Y}^{(n)} \end{pmatrix} = \Omega^{(n)} \begin{pmatrix} \mathbb{1} & 0 \\ 0 & -\mathbb{1} \end{pmatrix} \begin{pmatrix} \mathbf{X}^{(n)} \\ \mathbf{Y}^{(n)} \end{pmatrix}, \quad (\text{A10})$$

where the entries of the eigenvectors  $X_{ia}^{(n)}$  and  $Y_{ia}^{(n)}$  enter the transition densities  $\rho^{(n)}(\mathbf{r})$ . The specific entries of the matrices  $\mathbb{A}$  and  $\mathbb{B}$  read for singlet states excited from a closed-shell ground state [1,31,102,104,107,169,170]

$$\begin{aligned} A_{ia,jb} &= (\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab} + 2v_{ia,jb} + F_{ij,ab}, \\ B_{ia,jb} &= 2v_{ia,bj} + F_{ib,aj}. \end{aligned} \quad (\text{A11})$$

Here, the single-particle energies of the electronic system  $\varepsilon_p$  enter, as well as the bare Coulomb interaction

$$v_{pq,rs} = \int d^3r d^3r' \psi_p(\mathbf{r})\psi_q(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{r}'|} \psi_r(\mathbf{r}')\psi_s(\mathbf{r}'), \quad (\text{A12})$$

which comes with a spin factor 2 (cf. Appendix B). Both the energies  $\varepsilon_p$  as well as the matrix elements  $F_{pq,rs}$  depend on the chosen excited-state method: For the reducible polarizability  $\chi$  (A9) in GW, the excitation energies and transition densities are computed via the random-phase approximation (RPA), which uses  $F_{pq,rs} = 0$  in Eq. (A11) [1,167,168]. In contrast, other excited-state methods employ a nonzero  $F_{pq,rs}$ , i.e., TDDFT employs the exchange-correlation kernel  $F_{pq,rs} \rightarrow f_{pq,rs}^{\text{xc}}$  [1,169,170], which is in principle exact, but practical calculations employ approximations like PBE [140] or PBE0 [166] there. For the BSE,  $F_{pq,rs}$  is the screened Coulomb interaction  $-W_{pq,rs}$  [31,107], as we discuss in Sec. II.

In Table II, we further report the excitation energies of these methods (RPA, TDDFT, and BSE) with varying KS starting point (PBE and PBE0) and refinement of the entering eigenenergies (KS, evGW<sub>0</sub>, and evGW). In particular, we observe that RPA tends to strongly overestimate the first excitation energy when starting from PBE0 ( $\Omega_{\text{RPA@KS}}^{(n=1)}$  with PBE0) or evGW ( $\Omega_{\text{RPA@evGW}}^{(n=1)}$  for both PBE and PBE0), whereas  $\Omega_{\text{RPA@KS}}^{(n=1)}$  based on PBE agrees better with the results from the higher-level methods TDDFT or GW-BSE (cf. Ref. [168] for a detailed discussion). Hence, in order to compute  $\chi$  (A9) with physically meaningful excitation energies, we conclude that  $W_0$  instead of  $W$  should result in improved accuracy when choosing one of the earlier discussed GW schemes. For further details on the GW approximation and different (self-consistent) solution schemes, we refer to Refs. [3,100,171].

## APPENDIX B: DERIVATION OF THE DYNAMICAL DIPOLE POLARIZABILITY AND THE DEFINING MATRIX EQUATION

In Eq. (20), we have introduced the tensor elements of the dynamical dipole polarizability [1,29,31]

$$\alpha_{\mu\mu'}(\omega) = - \sum_{n>0} \frac{2\Omega^{(n)}d_{\mu}^{(n)}d_{\mu'}^{(n)}}{(\omega + i\eta)^2 - (\Omega^{(n)})^2}, \quad (\text{B1})$$

with [29,31,39,107]

$$d_{\mu}^{(n)} = \sqrt{2} \sum_{i,a} \mu_{ia} (X_{ia}^{(n)} + Y_{ia}^{(n)}),$$

where  $(\Omega^{(n)}, X_{ia}^{(n)}, Y_{ia}^{(n)})$  are the solutions of Eq. (8).

In the following, we derive the form of  $\alpha_{\mu\mu'}(\omega)$  as well as the defining matrix equation in Eq. (8). We start from the general definition of the dynamical dipole polarizability [1,2,107]

$$\alpha_{\mu\mu'}(\omega) = - \int d^3r d^3r' r_{\mu} \chi(\mathbf{r}, \mathbf{r}', \omega) r'_{\mu'} \quad (\text{B2})$$

where we have introduced the reducible polarizability  $\chi(\mathbf{r}, \mathbf{r}', \omega)$  [cf. Eq. (A9)]. In TDDFT, one can directly use the  $\chi$  to arrive at Eq. (B1) [1]. However, within the BSE framework (and similar frameworks like, e.g., TDHF [102]), the retarded four-point polarizability  $L(\mathbf{1}, \mathbf{2}, \mathbf{3}, \mathbf{4})$  is needed,

which relates to the two-point  $\chi$  in time-domain via  $\chi(\mathbf{1}, \mathbf{2}) = L(\mathbf{1}, \mathbf{1}^+, \mathbf{2}, \mathbf{2})$ . We denote combined space-spin-time coordinates as  $\mathbf{1} = \{\mathbf{r}_1, s_1, t_1\}$  (as in Appendix A) and, in the following, combined space-spin coordinates as  $l = \{\mathbf{r}_l, s_l\}$ . Furthermore, we follow the convention of the main text regarding indexing, such that  $p, q, r, s$  denote a generic KS orbital, whereas  $i, j$  denote occupied, i.e.,  $i, j \in [1, N_{\text{occ}}]$ , and  $a, b$  denote unoccupied orbitals, i.e.,  $a, b \in [N_{\text{occ}} + 1, N_{\text{occ}} + N_{\text{empty}}]$ .

Changing to the frequency domain, we find the Bethe-Salpeter equation for the four-point polarizability [2,3,11–13,107]

$$\begin{aligned} L(1, 2, 3, 4; \omega) &= L^0(1, 2, 3, 4; \omega) \\ &+ \int d(5, 6, 7, 8) L^0(1, 2, 5, 6; \omega) \\ &\times K(5, 6, 7, 8) L(7, 8, 3, 4; \omega), \end{aligned} \quad (\text{B3})$$

with the noninteracting four-point polarizability  $L^0(1, 2, 3, 4; \omega)$  and the BSE kernel  $K(5, 6, 7, 8)$ . In the GW approximation [cf. Eq. (3)] and neglecting dynamical screening, i.e.,  $W(\omega = 0)$ , the kernel reads [36,38,107]

$$K(1, 2, 3, 4) = v(1, 3)\delta(1, 2)\delta(3, 4) - W(1, 2)\delta(1, 3)\delta(2, 4). \quad (\text{B4})$$

For the following derivation, we bring the four-point polarizability into the basis of spin-orbitals  $\psi_p(1) = \psi_p(\mathbf{r}_1)\sigma_p(s_1)$  with quasiparticle orbitals  $\psi_p(\mathbf{r}_1)$  [which we take to be the KS orbitals from Eq. (2)] and spin function  $\sigma_p(s_1)$ , which can be either  $\alpha(s_1)$  or  $\beta(s_1)$ :

$$L(1, 2, 3, 4; \omega) = \sum_{pqrs} \psi_p(1)\psi_q(2)L_{pq,rs}(\omega)\psi_r(3)\psi_s(4), \quad (\text{B5})$$

with matrix elements

$$\begin{aligned} L_{pq,rs}(\omega) &= \int d(1, 2, 3, 4) \psi_p(1)\psi_q(2) \\ &\times L(1, 2, 3, 4; \omega)\psi_r(3)\psi_s(4). \end{aligned} \quad (\text{B6})$$

Note that we skip all complex conjugates since the KS orbitals are real-valued.

By means of the residue theorem, the matrix elements of  $L^0$  can be computed from the interacting Green's function  $G$  [cf. Eq. (7)], which becomes diagonal in the basis of the KS

orbitals [2,107]:

$$L_{pq,rs}^0(\omega) = \delta_{pr}\delta_{qs} \frac{f_p - f_q}{\omega - (\varepsilon_q^{\text{evGW}_0} - \varepsilon_p^{\text{evGW}_0}) + i\eta}, \quad (\text{B7})$$

where  $i\eta$  (with small  $\eta$ ) is included, since we are focusing on the retarded polarizability needed for optical responses [3,107].

We rewrite Eq. (B3) in matrix form

$$\mathbf{L}(\omega) = [\mathbf{1} - \mathbf{L}^0(\omega)\mathbf{K}]^{-1}\mathbf{L}^0(\omega), \quad (\text{B8})$$

where we denote all matrices with generic indices  $p, q, r, s$  in bold. After some matrix algebra, we obtain [2,107]

$$\mathbf{L}(\omega) = \mathbf{M}^{-1}(\omega)\mathbf{F}, \quad (\text{B9})$$

where  $\mathbf{M}$  and  $\mathbf{F}$  have a block structure in the product space of occupied and unoccupied orbitals, i.e., the rows and columns are ordered via electron-hole ( $ia, jb$ ), hole-electron ( $ai, bj$ ), electron-electron ( $ii', jj'$ ) and hole-hole ( $aa', bb'$ ) sector:

$$\mathbf{M}(\omega) = \begin{matrix} & \begin{matrix} jb & bj & jj' & bb' \end{matrix} \\ \begin{matrix} ia \\ ai \\ ii' \\ aa' \end{matrix} & \begin{pmatrix} \tilde{\Omega} - \mathbb{K} & -\mathbb{K} & -\mathbb{K} & -\mathbb{K} \\ \mathbb{K} & \tilde{\Omega} + \mathbb{K} & \mathbb{K} & \mathbb{K} \\ 0 & 0 & \tilde{\Omega} & 0 \\ 0 & 0 & 0 & \tilde{\Omega} \end{pmatrix} \end{matrix}, \quad (\text{B10})$$

and

$$\mathbf{F} = \begin{matrix} & \begin{matrix} jb & bj & jj' & bb' \end{matrix} \\ \begin{matrix} ia \\ ai \\ ii' \\ aa' \end{matrix} & \begin{pmatrix} \mathbb{1} & 0 & 0 & 0 \\ 0 & -\mathbb{1} & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \end{matrix}. \quad (\text{B11})$$

Correspondingly,  $\tilde{\Omega}$  are block matrices of the respective sector with the denominator of Eq. (B7) as matrix elements:

$$\tilde{\Omega}_{pq,rs}(\omega) = (\omega + i\eta + \varepsilon_p^{\text{evGW}_0} - \varepsilon_q^{\text{evGW}_0})\delta_{pr}\delta_{qs}. \quad (\text{B12})$$

The triangular shape of  $\mathbf{M}(\omega)$  and the block form of  $\mathbf{F}$  in Eq. (B9) reduce the number of nonzero entries of  $\mathbf{L}(\omega)$  considerably, i.e., to the upper-left  $2 \times 2$  block  $\mathbb{L}^{ia \oplus ai}(\omega)$  [2].

Until now, all quantities still comprise the spin degree of freedom. However, even for a singlet closed-shell ground state, the single-particle excitation is not diagonal in the spins, which one immediately sees by explicitly writing down the spin indices of the upper left block of  $\mathbf{M}$ . The spin structure of  $-\tilde{\Omega} + \mathbb{K}$ , which follows from the contractions in Eqs. (B4) and (B7), then reads

$$\begin{matrix} & \begin{matrix} \bar{\alpha}\bar{\alpha}' & \bar{\beta}\bar{\beta}' & \bar{\alpha}\bar{\beta} & \bar{\beta}\bar{\alpha} \end{matrix} \\ \begin{matrix} \alpha\alpha' \\ \beta\beta' \\ \alpha\beta \\ \beta\alpha \end{matrix} & \begin{pmatrix} -\tilde{\Omega} + \mathbb{V} - \mathbb{W} & \mathbb{V} & 0 & 0 \\ \mathbb{V} & -\tilde{\Omega} + \mathbb{V} - \mathbb{W} & 0 & 0 \\ 0 & 0 & -\tilde{\Omega} - \mathbb{W} & 0 \\ 0 & 0 & 0 & -\tilde{\Omega} - \mathbb{W} \end{pmatrix} \end{matrix}, \quad (\text{B13})$$

with elements of the block matrices  $\mathbb{V}$  and  $\mathbb{W}$  given by  $v_{pq,rs}$  and  $W_{pq,rs}$  [cf. Eqs. (11) and (12)].

Bringing the upper block to diagonal form by the unitary transformation

$$\frac{1}{\sqrt{2}} \begin{pmatrix} \mathbb{1} & \mathbb{1} \\ \mathbb{1} & -\mathbb{1} \end{pmatrix}, \quad (\text{B14})$$

i.e., transforming the matrix to the basis of singlet and triplet solutions, we obtain the singlet-triplet factor (with  $\alpha^{(S)} = 2$  and  $\alpha^{(T)} = 0$ ) in Eq. (10) [13,102,107,172]

$$A_{ia,jb} = (\varepsilon_a^{\text{evGW}_0} - \varepsilon_i^{\text{evGW}_0}) \delta_{ij} \delta_{ab} + \alpha^{(S/T)} v_{ia,jb} - W_{ij,ab},$$

$$B_{ia,jb} = \alpha^{(S/T)} v_{ia,bj} - W_{ib,aj}.$$

With this shorthand notation and by further utilizing the symmetry of the kernel  $K_{pq,rs}$  under index-permutation, we can rewrite the upper left  $2 \times 2$  block of  $\mathbf{M}$  as

$$\begin{aligned} \mathbf{M}^{ia \oplus ai}(\omega) &= - \begin{pmatrix} \mathbb{1} & \mathbf{0} \\ \mathbf{0} & -\mathbb{1} \end{pmatrix} \\ &\times \begin{pmatrix} \mathbb{A} - (\omega + i\eta)\mathbb{1} & \mathbb{B} \\ \mathbb{B} & \mathbb{A} + (\omega + i\eta)\mathbb{1} \end{pmatrix}, \end{aligned} \quad (\text{B15})$$

and thus for the corresponding block of  $\mathbf{L}$  [31]

$$\mathbb{L}^{ia \oplus ai}(\omega) = - \left[ \begin{pmatrix} \mathbb{A} & \mathbb{B} \\ \mathbb{B} & \mathbb{A} \end{pmatrix} - (\omega + i\eta) \begin{pmatrix} \mathbb{1} & \mathbf{0} \\ \mathbf{0} & -\mathbb{1} \end{pmatrix} \right]^{-1}. \quad (\text{B16})$$

We do not explicitly denote the spin here, but the  $\alpha^{(S,T)}$  in  $\mathbb{A}$  and  $\mathbb{B}$  implicitly accounts for the spin degrees of freedom.

In the next step, we use the spectral representation of Eq. (B16) (cf. Appendix of Ref. [113]) to rewrite  $\mathbb{L}^{ia \oplus ai}(\omega)$ . Thus, Eq. (B16) also defines the central eigenvalue equation in Eq. (8). With the spectral representation, we obtain four blocks with elements

$$L_{ia,jb}(\omega) = \sum_{n=1}^{N_{\text{occ}} N_{\text{empty}}} \frac{X_{ia}^{(n)} X_{jb}^{(n)}}{\omega + i\eta - \Omega^{(n)}} - \frac{Y_{ia}^{(n)} Y_{jb}^{(n)}}{\omega + i\eta + \Omega^{(n)}}, \quad (\text{B17a})$$

$$L_{ia,bj}(\omega) = \sum_{n=1}^{N_{\text{occ}} N_{\text{empty}}} \frac{X_{ia}^{(n)} Y_{jb}^{(n)}}{\omega + i\eta - \Omega^{(n)}} - \frac{Y_{ia}^{(n)} X_{jb}^{(n)}}{\omega + i\eta + \Omega^{(n)}}, \quad (\text{B17b})$$

$$L_{ai,jb}(\omega) = \sum_{n=1}^{N_{\text{occ}} N_{\text{empty}}} \frac{Y_{ia}^{(n)} X_{jb}^{(n)}}{\omega + i\eta - \Omega^{(n)}} - \frac{X_{ia}^{(n)} Y_{jb}^{(n)}}{\omega + i\eta + \Omega^{(n)}}, \quad (\text{B17c})$$

$$L_{ai,bj}(\omega) = \sum_{n=1}^{N_{\text{occ}} N_{\text{empty}}} \frac{Y_{ia}^{(n)} Y_{jb}^{(n)}}{\omega + i\eta - \Omega^{(n)}} - \frac{X_{ia}^{(n)} X_{jb}^{(n)}}{\omega + i\eta + \Omega^{(n)}}. \quad (\text{B17d})$$

In the case of the TDA, all components comprising an element of  $\mathbf{Y}^{(n)}$  drop out and we recover Eq. (32) from Ref. [107].

Coming back to the dynamical dipole polarizability  $\alpha_{\mu\mu'}(\omega)$ , we write Eq. (B2) including the spin channels as

$$\alpha_{\mu\mu'}(\omega) = - \sum_{s_1 s_2} \int d^3 r_1 d^3 r_2 r_1^{(\mu)} L(1, 1, 2, 2, \omega) r_2^{(\mu)}. \quad (\text{B18})$$

TABLE III. Number of unoccupied states  $N_{\text{empty}}$  for a nanographene with  $L = 4$  resulting from the cutoffs  $E_{\text{cut}}^{\text{empty}}$  in Fig. 9.

$E_{\text{cut}}^{\text{empty}}$	all	80 eV	40 eV	20 eV	10 eV
$N_{\text{empty}}$	1195	1138	709	425	204

With Eq. (B5) and after transforming to the singlet-triplet basis [cf. Eq. (B14)], only the singlet contribution remains with a factor of  $\sqrt{2}$  resulting from the sum over spin indices [13,31,102,107]:

$$\alpha_{\mu\mu'}(\omega) = -(\sqrt{2})^2 \sum_{pqrs} \mu_{pq} \mu'_{rs} L_{pqrs}^{(\text{Singlet})}(\omega). \quad (\text{B19})$$

Combining Eq. (B19) with the block structure of  $L_{pq,rs}(\omega)$  in Eqs. (B17), we arrive at Eq. (B1), where the spin factor is absorbed in the transition dipole moments  $d_{\mu}^{(n)}$  from Eq. (21).

### APPENDIX C: ENERGY CUTOFF FOR THE BSE

In the following, we discuss the truncation of the considered number of orbitals in Eq. (8), motivated by its heavy computational scaling: Since both the number of occupied  $N_{\text{occ}}$  and unoccupied orbitals  $N_{\text{empty}}$  scales linearly with the system size  $N$ , the index structure of Eq. (10) leads to a memory scaling of  $O(N_{\text{occ}}^2 N_{\text{empty}}^2) = O(N^4)$  and a runtime scaling of  $O(N_{\text{occ}}^3 N_{\text{empty}}^3) = O(N^6)$ .

Beyond that, the computational effort associated with the calculation of the  $GW$  quasiparticle energies needed for Eq. (10) scales with the number of included orbitals.

Hence, we adopt the idea of Ref. [39] to impose an energy cutoff on the included states since we do not expect that low-lying optical excitations are strongly affected by the high-lying states, which reduces the number of states and therefore enables calculations with a reasonable amount of computational resources. Specifically, we apply the truncation as follows: (i) We already truncate the number of orbitals based on their KS energies, which are refined in the  $GW$ -module (cf. Fig. 1) to keep the computational effort to the possible minimum. Correspondingly, only these refined states enter the construction of Eq. (10) (cf. Fig. 1). (ii) In addition to the cutoff for unoccupied states, we also specify a separate cutoff for the occupied states targeting core levels.

We test the accuracy of this cutoff procedure for a nanographene with  $L = 4$ . To only exclude the core level states, we choose a cutoff for the occupied states of  $E_{\text{cut}}^{\text{occ}} = 80$  eV, which keeps excitation energies virtually unchanged (within less than 1 meV), but reduces  $N_{\text{occ}}$  by approximately 30% from 180 to 124. Given the negligible influence of  $E_{\text{cut}}^{\text{occ}} = 80$  eV on the accuracy of the calculation, we use it throughout all further cutoff checks.

Since the unoccupied states exhibit a continuous distribution of orbital energies  $\varepsilon_a$ , we check four different cutoff values  $E_{\text{cut}}^{\text{empty}} = 10, 20, 40, 80$  eV and plot the resulting spectra in Fig. 9.

We observe only minor changes in the absorption spectrum, even for the smallest cutoff of  $E_{\text{cut}}^{\text{empty}} = 10$  eV, which reduces unoccupied states from 1195 to 204. In Table III, we

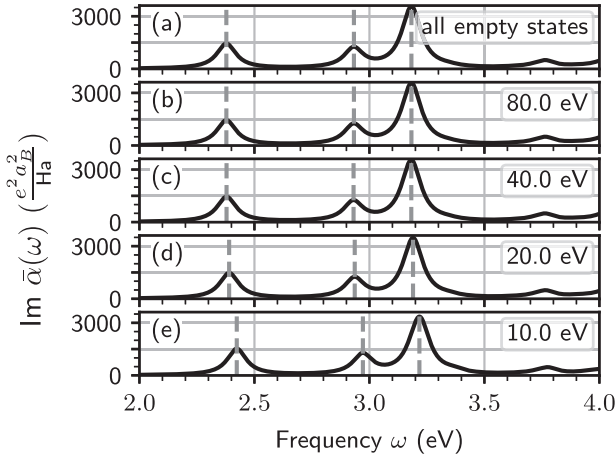


FIG. 9. Optical absorption spectra computed from  $\text{Im } \bar{\alpha}(\omega)$  [Eq. (D1)] for (a) all unoccupied states and (b)–(e) four different cutoffs  $E_{\text{cut}}^{\text{empty}}$  with a broadening of  $\eta = 0.05$  eV for a nanographene with  $L = 4$ . The changes for the first three peaks (gray vertical lines) are reported in Table IV.

additionally report the respective number of unoccupied states for each of the cutoffs  $E_{\text{cut}}^{\text{empty}}$  in Fig. 9.

In Table IV, we report the extracted peak positions  $\Omega^{(p)}$  and heights  $\bar{\alpha}^{(p)}$  from the first three ( $p = 1, 2, 3$ ) peaks in Fig. 9. Even for the smallest cutoff  $E_{\text{cut}}^{\text{empty}} = 10$  eV, we only observe minor changes of less than 50 meV in  $\Omega^{(p)}$  and 10% in the relative peak heights  $\Delta\bar{\alpha}^{(p)}/\bar{\alpha}^{(p)}$ , respectively.

Beyond the absorption spectrum, we report the impact of the cutoffs on the spatial descriptors, specifically on the longitudinal size of the excitation  $d_{\text{exc}}^{(x)}$  in Table V. We determine the corresponding excitation level  $n$  from the largest oscillator

TABLE IV. Peak frequencies  $\Omega^{(p)}$  and heights  $\bar{\alpha}^{(p)}$  as well as the respective deviations  $\Delta\Omega^{(p)}$ ,  $\Delta\Omega^{(p)}/\Omega^{(p)}$ , and  $\Delta\bar{\alpha}^{(p)}/\bar{\alpha}^{(p)}$  of the three highest peaks  $p = 1, 2, 3$  extracted from Fig. 9 for four cutoffs  $E_{\text{cut}}^{\text{empty}}$ . We do not explicitly denote the imaginary parts for the reported peak heights for the sake of readability.

$E_{\text{cut}}^{\text{empty}}$ (eV)	$\Omega^{(p)}$ (eV)	$\bar{\alpha}^{(p)}$ ( $\frac{e^2 a_B^2}{\text{Ha}}$ )	$\Delta\Omega^{(p)}$ (meV)	$\Delta\Omega^{(p)}/\Omega^{(p)}$ (%)	$\Delta\bar{\alpha}^{(p)}/\bar{\alpha}^{(p)}$ (%)
Ref.	2.378	1.954			
	2.933	1.709			
	3.183	4.828			
80.0	2.378	1.954	0	0.0	0.0
	2.933	1.709	0	0.0	0.0
	3.183	4.827	0	0.0	0.0
40.0	2.379	1.963	1	0.0	0.4
	2.931	1.707	-2	-0.1	-0.1
	3.182	4.803	-1	0.0	-0.5
20.0	2.390	1.995	12	0.5	2.1
	2.936	1.701	4	0.1	-0.4
	3.190	4.699	7	0.2	-2.7
10.0	2.423	2.064	45	1.9	5.6
	2.972	1.742	39	1.3	2.0
	3.217	4.534	35	1.1	-6.1

TABLE V. Peak frequencies  $\Omega^{(n)}$  and corresponding size of the excitation in the longitudinal direction  $d_{\text{exc}}^{(x)}$  as well as the respective deviations  $\Delta\Omega^{(p)}$  and  $\Delta d_{\text{exc}}^{(x)}/d_{\text{exc,ref}}^{(x)}$  for the excitation level  $n$  with the largest oscillator strength  $f^{(n)}$  for four explicit cutoffs  $E_{\text{cut}}^{\text{empty}}$ .

$E_{\text{cut}}^{\text{empty}}$	$\Omega^{(n)}$ (eV)	$d_{\text{exc}}^{(x)}$ (Å)	$\Delta\Omega^{(n)}$ (eV)	$\frac{\Delta d_{\text{exc}}^{(x)}}{d_{\text{exc,ref}}^{(x)}} (%)$
Ref.	3.184	5.813		
80.0	3.184	5.811	0.000	0.0
40.0	3.184	5.758	0.000	-0.9
20.0	3.193	5.704	0.009	-1.9
10.0	3.223	5.679	0.038	-2.3

strength  $f^{(n)}$  [corresponding to the highest peak of  $\text{Im } \bar{\alpha}(\omega)$ , cf. Eq. (G3)] for each cutoff value  $E_{\text{cut}}^{\text{empty}}$ . Again, we find only minor deviations around 2%.

Based on these results for  $L = 4$ , we execute the calculations for all  $L$  in the main text employing the cutoffs  $E_{\text{cut}}^{\text{occ}} = 80$  eV and  $E_{\text{cut}}^{\text{empty}} = 10$  eV. Our motivation to rely on the explicit energy cutoffs rather than the number of states (cf. Table III) is based on a rough estimate via first-order perturbation theory, which estimates the contribution of higher-lying unoccupied states based on their respective level energy. This enables simulation of  $GW$ -BSE for large system sizes with up to 242 atoms for  $L = 13$ , which in turn corresponds to  $N_{\text{occ}} = 394$  and  $N_{\text{empty}} = 573$ , i.e., the BSE matrices  $\mathbb{A}$ ,  $\mathbb{B}$  in Eq. (8) have dimension  $N_{\text{occ}}N_{\text{empty}} = 2.3 \times 10^5$ .

#### APPENDIX D: ISOTROPIC POLARIZABILITY AND PHOTOABSORPTION CROSS SECTION

In the main text and in Appendix B, we have derived a form for the dynamical dipole polarizability tensor  $\alpha_{\mu\mu'}(\omega)$ , which enables the computation of optical absorption spectra with  $GW$ -BSE. In the following, we introduce a number of additional quantities, which can be used to describe optical excitations and are computed by our implementation.

In gases and liquids, where molecules are oriented randomly, the complicated tensor structure of  $\alpha_{\mu\mu'}(\omega)$  can be simplified by averaging over the three Cartesian components, leading to the spatial average

$$\bar{\alpha}(\omega) = \frac{1}{3} \sum_{\mu \in \{x, y, z\}} \alpha_{\mu, \mu}(\omega). \quad (\text{D1})$$

We can then rewrite  $\bar{\alpha}(\omega)$ ,

$$\bar{\alpha}(\omega) = -\text{Im} \left[ \sum_{n>0} \frac{f^{(n)}}{(\omega + i\eta)^2 - (\Omega^{(n)})^2} \right], \quad (\text{D2})$$

where the residues are the oscillator strengths  $f^{(n)}$  [31,39]

$$f^{(n)} = \frac{2}{3} \Omega^{(n)} \sum_{\mu \in \{x, y, z\}} |d_{\mu}^{(n)}|^2. \quad (\text{D3})$$

Here, we have used the transition dipole moments from Eq. (21)

$$d_{\mu}^{(n)} = \sqrt{2} \sum_{i,a} \langle \psi_i | \hat{\mu} | \psi_a \rangle (X_{ia}^{(n)} + Y_{ia}^{(n)}).$$

We further compute the photoabsorption cross-section tensor  $\sigma_{\mu\mu'}(\omega)$ , which is defined by [1]

$$\sigma_{\mu\mu'}(\omega) = \frac{4\pi\omega}{c} \text{Im}[\alpha_{\mu\mu'}(\omega)]. \quad (\text{D4})$$

#### APPENDIX E: COMPUTATIONAL DETAILS OF GW-BSE AND TDDFT CALCULATIONS

The majority of the calculations in this paper is done with the CP2K package [94–96]. CP2K uses Gaussian basis sets for representing the KS orbitals in Eq. (2), where we employ the aug-cc-pVDZ basis set [123,124] throughout the paper, provided by the EMSL database [173]. These all-electron calculations are executed within the Gaussian and augmented plane-waves scheme [174]. The GW implementation is based on Ref. [98], where the analytic continuation is applied in the computation of the self-energy (3) using 16 Padé approximants and a frequency grid with 100 points unless stated otherwise. By using  $\text{evGW}_0@PBE$ , we get rid of numerical artifacts caused by the pole structure of the self-energy [168,175], which can occur for the PBE functional [140].

The reference calculations to check the numerical validity of our implementation have been done using the FHI-AIMS code [39,120–122], where we have used the Gaussian-tight settings together with the aug-cc-pVDZ basis set [123,124], applying the same parameters for the  $\text{evGW}_0$  calculations specified before.

The TDDFT module in CP2K is based on the Tamm-Dancoff approximation [176–180], which uses the auxiliary density matrix method to enable efficient calculations with hybrid functionals. There, we have chosen the aug-cc-pVDZ [123,124] and aug-DZVP-MOLOPT-GTH-tier-2 basis sets (basis set generation recipe as in Refs. [181,182]) in combination with the admm-2 [183] auxiliary basis. The exchange-correlation functionals employed in this work (cf. Sec. V and Appendix I) are PBE [140], BLYP [141,142], PBE0 [166], B3LYP [141,143,144], HSE06 [145,146], as well as CAM-B3LYP [147].

#### APPENDIX F: GW-BSE BENCHMARK ON THIEL'S SET

In this Appendix, we provide further details about the parameters of the analytic continuation, which we have used to compute the real-frequency self-energy both in the GW-modules of CP2K [98] and FHI-AIMS [120,121].

In Fig. 2, we have presented a benchmark for Thiel's set [119], where the CP2K calculation employed 128 parameters for the Padé function and 500 points in the frequency grid whereas we have used 16 and 100, respectively, for the calculation with FHI-AIMS, resulting in mean absolute error [MAE; cf. Eq. (23)] of 2.7 meV and a maximum absolute error of 30.2 meV.

In Fig. 10, we show another comparison for 16 Padé parameters and 100 points for the frequency grid in both CP2K and FHI-AIMS. We observe slightly larger deviations between the implementations of 4.7 meV MAE and a maximum absolute error of 42.3 meV over the ten lowest excitation energies across all molecules.

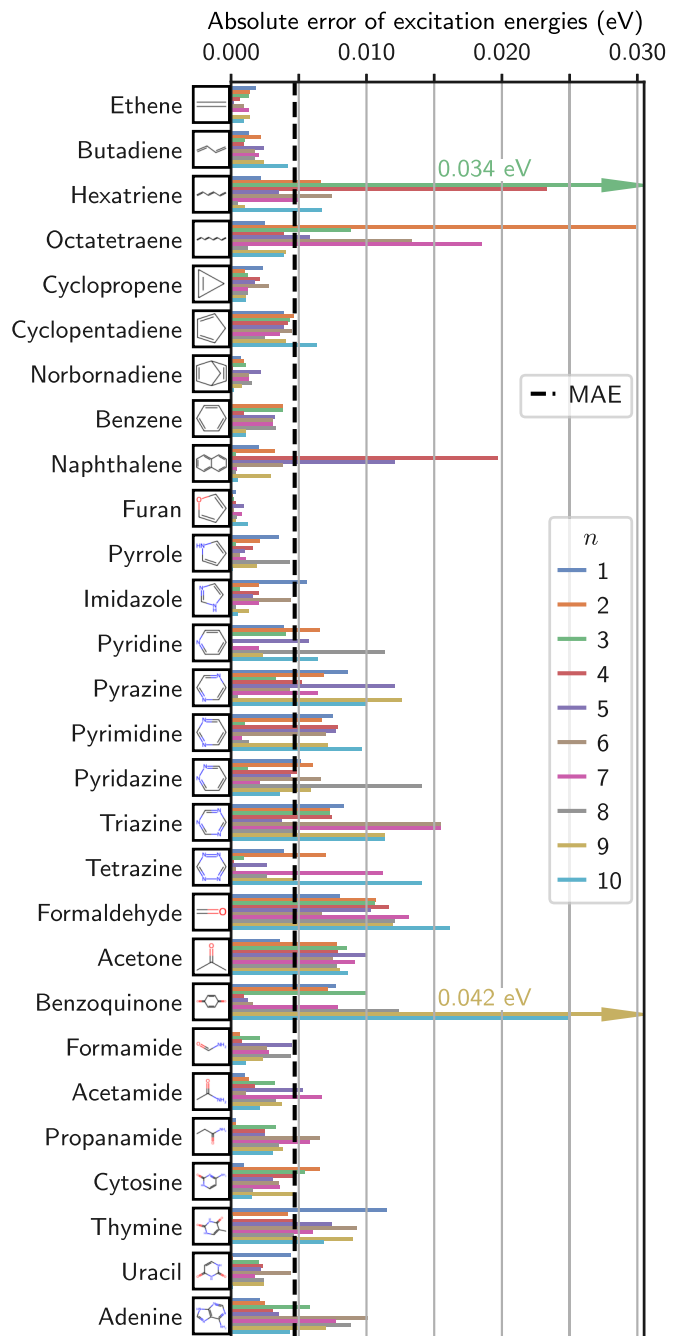


FIG. 10. Absolute error  $|\Omega_{\text{CP2K}}^{(n)} - \Omega_{\text{FHI-AIMS}}^{(n)}|$  of BSE excitation energies  $\Omega^{(n)}$  computed from CP2K and FHI-AIMS by solving Eq. (8) with  $\text{BSE@evGW}_0@PBE$ . The analytical continuation for the GW modules in both codes was applied with 16 parameters of the Padé function and 100 points for the frequency grid, which results in a mean absolute error (MAE) of 4.7 meV and a maximum absolute error of 42.3 meV over the ten lowest excitation energies across all molecules.

#### APPENDIX G: ABSORPTION SPECTRA FROM EXPERIMENT AND THEORY: DIELECTRIC FUNCTION AND POLARIZABILITY

In this Appendix, we connect the optical absorption spectrum of a rectangular nanographene from experiment [53]

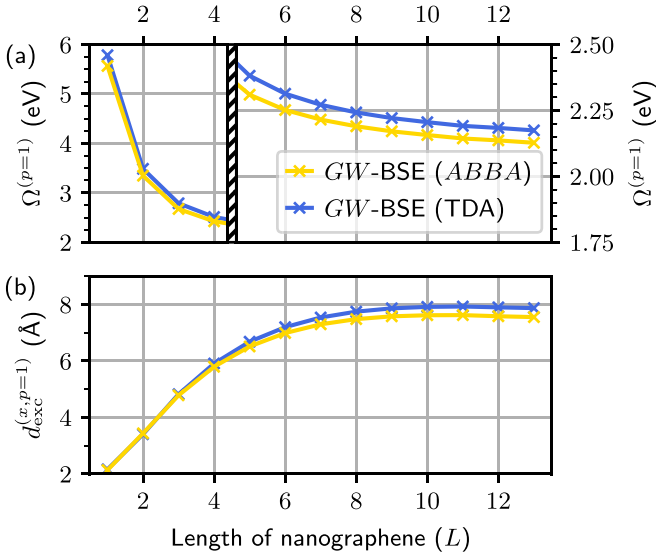


FIG. 11. Excitation energy  $\Omega^{(p=1)}$  and size of the excitation  $d_{\text{exc}}^{(x,p=1)}$  computed from BSE@evGW<sub>0</sub> via Eq. (8) (yellow) and Eq. (18) (blue). (a) Peak frequency of the first prominent peak in the optical absorption spectrum  $\Omega^{(p=1)}$ . (b) Longitudinal size of the excitation for the first bright peak  $d_{\text{exc}}^{(x,p=1)}$ , Eq. (35).

quantified via the dielectric function and from  $GW\text{-BSE}$  computed via the polarizability of a finite nanographene. To that end, we start from the experimental reflectance difference measurements, from which they extract the anisotropic dielectric function  $\Delta\epsilon = \epsilon_x - \epsilon_y$ . We approximate the anisotropic dielectric function  $\Delta\epsilon$  by its longitudinal component  $\epsilon_x$ , i.e.,  $\Delta\epsilon \approx \epsilon_x$ , since the overall optical spectrum is dominated by the longitudinal component (cf. Ref. [53] and also Sec. III).

The dielectric function along the long ribbon axis  $\epsilon_x^{(\text{expt.})}$  is then obtained from the three Lorentzian peaks ( $n = 1, 2, 3$ ) at frequencies  $\Omega_{(\text{expt.})}^{(n)}$  reported in the supporting information of

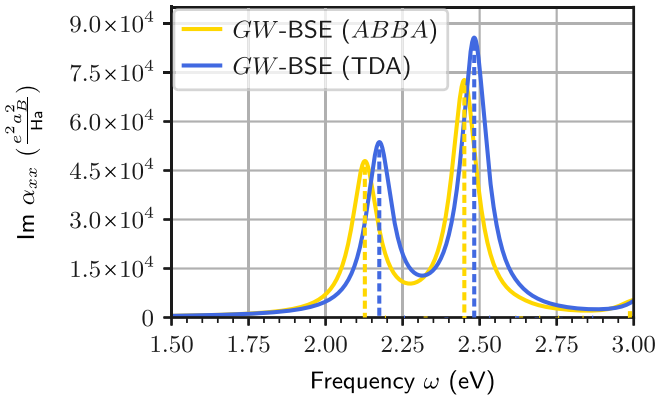


FIG. 12. Optical absorption spectrum for  $GW\text{-BSE}$  via Eq. (8) (yellow) and Eq. (18) (blue) from  $\text{Im } \alpha_{xx}(\omega)$  [Eq. (20)]. Dashed lines denote the contribution of individual excitations  $n$  to  $\text{Im } \alpha_{xx}(\omega = \Omega^{(n)})$ .

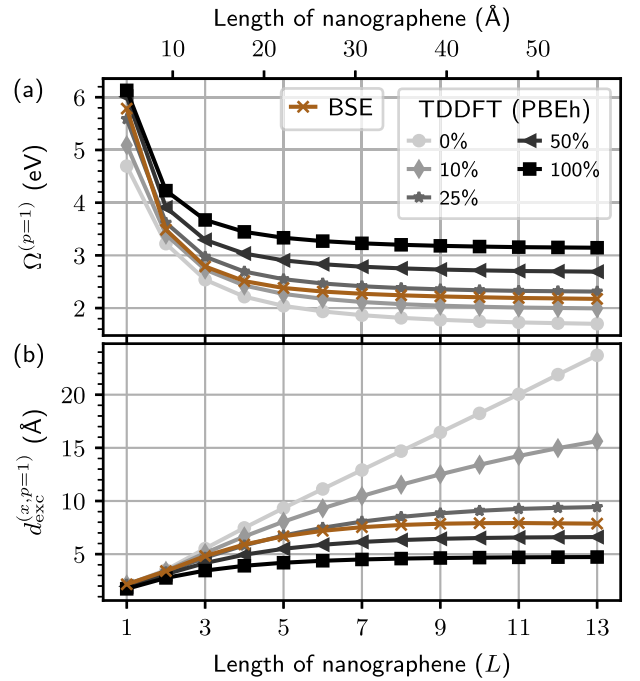


FIG. 13. Excitation energy  $\Omega^{(p=1)}$  and size of the excitation  $d_{\text{exc}}^{(x,p=1)}$  computed from BSE@evGW<sub>0</sub> and TDDFT (both in TDA; effect of TDA investigated in Appendix H) employing the PBEh functional with varying amount of exact exchange (exact exchange fraction shown in the legend). (a) Peak frequency of the first prominent peak in the optical absorption spectrum  $\Omega^{(p=1)}$ . (b) Longitudinal size of the excitation for the first bright peak  $d_{\text{exc}}^{(x,p=1)}$ , Eq. (35).

Ref. [53]:

$$\epsilon_x^{(\text{expt.})}(\omega) = \sum_{n=1}^3 \frac{A_{(\text{expt.})}^{(n)}}{(\Omega_{(\text{expt.})}^{(n)})^2 - \omega^2 - i\omega\Gamma_{(\text{expt.})}^{(n)}}, \quad (\text{G1})$$

where  $A_{(\text{expt.})}^{(n)}$  and  $\Gamma_{(\text{expt.})}^{(n)}$  further denote the amplitude and the width of the respective transition  $n$ , respectively. In our analysis, the amplitudes  $A_{(\text{expt.})}^{(n)}$  are expressed with the dimension  $(\text{eV})^2$ , ensuring that the resulting dielectric function  $\epsilon_x^{(\text{expt.})}$  reproduces the dimensionless line shape  $\Delta\epsilon^{(\text{expt.})} \approx \epsilon_x^{(\text{expt.})}$  from Ref. [53]. In Fig. 5(a), we plot the imaginary part  $\text{Im } \epsilon_x(\omega)$  as well as the height of an individual transition  $n$ :

$$\text{Im } \epsilon_x^{(\text{expt.})}(\omega = \Omega^{(n)}) = \frac{A_{(\text{expt.})}^{(n)}}{\Omega_{(\text{expt.})}^{(n)} \Gamma_{(\text{expt.})}^{(n)}}. \quad (\text{G2})$$

On the side of  $GW\text{-BSE}$ , we utilize Eq. (24) and plot  $\text{Im } \alpha_{xx}^{(L)}(\omega)$  with a broadening of  $\eta = 0.3$  eV in Fig. 5(b), for which we obtain a similar line shape as in the experimental data. Additionally, we show the height of an individual transition  $n$  obtained from the BSE [cf. Eq. (20)]

$$\text{Im } \alpha_{xx}(\omega = \Omega^{(n)}) = f_x^{(n)} \frac{2\eta\Omega^{(n)}}{4\eta^2(\Omega^{(n)})^2 + \eta^4}, \quad (\text{G3})$$

where we abbreviate the oscillator strength in  $x$  direction as  $f_x^{(n)} = 2\Omega^{(n)}|d_x^{(n)}|^2$  [cf. Eq. (D3)].

#### APPENDIX H: EFFECT OF THE TAMM-DANCOFF APPROXIMATION IN $GW$ -BSE

In Fig. 7, we have compared the excitation properties computed from BSE@evGW<sub>0</sub> against TDDFT with different exchange-correlation functionals, where we have employed the TDA [Eq. (18)] for both frameworks. Here, we want to assess the deviations introduced by the TDA and compare the results obtained from the TDA in Eq. (18) against the solution of the full  $ABBA$ -matrix in Eq. (8) within BSE@evGW<sub>0</sub>. In Fig. 11, we plot the excitation energy and the corresponding size of the respective lowest bright state ( $p = 1$ ) for the solutions of Eqs. (8) and (18). We observe only minor deviations of at most 0.22 eV for energies (at small  $L$ ) and of 0.32 Å in sizes of the excitation (at large  $L$ ) for all nanographene lengths  $L$ .

The details of the respective optical absorption spectra computed via Eq. (20) are shown in Fig. 12 for  $L = 13$ . Despite minor changes in peak frequencies and heights, we

conclude that our findings from Sec. V do not change when diagonalizing Eq. (8) instead of Eq. (18).

#### APPENDIX I: TDDFT WITH MANUALLY TUNED PBEH

In Sec. V, we have discussed several popular exchange-correlation functionals and the respective properties of the first bright excitation  $p = 1$ . There, we have observed that the fraction of exact exchange in the exchange-correlation functional in TDDFT strongly influences both the excitation energy and the size of the excitation.

However, the employed functionals do not only feature different fractions of exact exchange, but also different contributions for the underlying exchange and correlation functionals. To unambiguously tie the accuracy for predictions of excitation properties to the exact exchange fraction, we show energies and sizes of the first bright excitation for varying amounts of exact exchange in the PBEh functional in Fig. 13, i.e., PBE0 (25%) with exact exchange varied between 0% (PBE) and 100%. Again, we observe that both excitation energies and sizes critically depend on the chosen exact-exchange fraction.

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- [1] C. A. Ullrich, *Time-Dependent Density-Functional Theory: Concepts and Applications* (Oxford University Press, Oxford, 2011).
- [2] G. Onida, L. Reining, and A. Rubio, Electronic excitations: Density-functional versus many-body Green's-function approaches, *Rev. Mod. Phys.* **74**, 601 (2002).
- [3] R. M. Martin, L. Reining, and D. Ceperley, *Interacting Electrons: Theory and Computational Approaches* (Cambridge University Press, New York, 2016).
- [4] J. Kunstmann, F. Mooshammer, P. Nagler, A. Chaves, F. Stein, N. Paradiso, G. Plechinger, C. Strunk, C. Schüller, G. Seifert, D. R. Reichman, and T. Korn, Momentum-space indirect interlayer excitons in transition-metal dichalcogenide van der Waals heterostructures, *Nat. Phys.* **14**, 801 (2018).
- [5] P. Merkl, F. Mooshammer, P. Steinleitner, A. Girnghuber, K.-Q. Lin, P. Nagler, J. Holler, C. Schüller, J. M. Lupton, T. Korn, S. Ovesen, S. Brem, E. Malic, and R. Huber, Ultrafast transition between exciton phases in van der Waals heterostructures, *Nat. Mater.* **18**, 691 (2019).
- [6] T. Siday, F. Sandner, S. Brem, M. Zizlsperger, R. Perea-Causin, F. Schiegl, S. Nerreter, M. Plankl, P. Merkl, F. Mooshammer, M. A. Huber, E. Malic, and R. Huber, Ultrafast nanoscopy of high-density exciton phases in WSe<sub>2</sub>, *Nano Lett.* **22**, 2561 (2022).
- [7] M. H. Naik, E. C. Regan, Z. Zhang, Y.-H. Chan, Z. Li, D. Wang, Y. Yoon, C. Shen Ong, W. Zhao, S. Zhao, M. Iqbal Bakti Utama, B. Gao, X. Wei, M. Sayyad, K. Yumigeta, K. Watanabe, T. Taniguchi, S. Tongay, F. H. da Jornada, F. Wang, *et al.*, Intralayer charge-transfer moiré excitons in van der Waals superlattices, *Nature (London)* **609**, 52 (2022).
- [8] D. Schmitt, J. P. Bange, W. Bennecke, A. AlMutairi, G. Meneghini, K. Watanabe, T. Taniguchi, D. Steil, D. R. Luke, R. T. Weitz, S. Steil, G. S. M. Jansen, S. Brem, E. Malic, S. Hofmann, M. Reutzel, and S. Mathias, Formation of moiré interlayer excitons in space and time, *Nature (London)* **608**, 499 (2022).
- [9] J. P. Bange, D. Schmitt, W. Bennecke, G. Meneghini, A. AlMutairi, K. Watanabe, T. Taniguchi, D. Steil, S. Steil, R. T. Weitz, G. S. M. Jansen, S. Hofmann, S. Brem, E. Malic, M. Reutzel, and S. Mathias, Probing electron-hole Coulomb correlations in the exciton landscape of a twisted semiconductor heterostructure, *Sci. Adv.* **10**, eadi1323 (2024).
- [10] M. Liebich, M. Florian, N. Nilforoushan, F. Mooshammer, A. D. Koulouklidis, L. Wittmann, K. Mosina, Z. Sofer, F. Dirnberger, M. Kira, and R. Huber, Controlling Coulomb correlations and fine structure of quasi-one-dimensional excitons by magnetic order, *Nat. Mater.* **24**, 384 (2025).
- [11] G. Strinati, Application of the Green's functions method to the study of the optical properties of semiconductors, *Riv. Nuovo Cimento* **11**, 1 (1988).
- [12] M. Rohlfing and S. G. Louie, Electron-hole excitations and optical spectra from first principles, *Phys. Rev. B* **62**, 4927 (2000).
- [13] F. Bechstedt, *Many-Body Approach to Electronic Excitations: Concepts and Applications* (Springer, Berlin Heidelberg, 2015), Vol. 181.
- [14] L. X. Benedict, E. L. Shirley, and R. B. Bohn, Optical absorption of insulators and the electron-hole interaction: An *ab initio* calculation, *Phys. Rev. Lett.* **80**, 4514 (1998).
- [15] S. Albrecht, L. Reining, R. Del Sole, and G. Onida, *Ab initio* calculation of excitonic effects in the optical spectra of semiconductors, *Phys. Rev. Lett.* **80**, 4510 (1998).
- [16] A. Marini, C. Hogan, M. Grüning, and D. Varsano, Yambo: An *ab initio* tool for excited state calculations, *Comput. Phys. Commun.* **180**, 1392 (2009).
- [17] J. Deslippe, G. Samsonidze, D. A. Strubbe, M. Jain, M. L. Cohen, and S. G. Louie, BerkeleyGW: A massively parallel computer package for the calculation of the quasiparticle and

- optical properties of materials and nanostructures, *Comput. Phys. Commun.* **183**, 1269 (2012).
- [18] D. Y. Qiu, F. H. da Jornada, and S. G. Louie, Optical spectrum of MoS<sub>2</sub>: Many-body effects and diversity of exciton states, *Phys. Rev. Lett.* **111**, 216805 (2013).
- [19] A. J. Bradley, M. M. Ugeda, F. H. da Jornada, D. Y. Qiu, W. Ruan, Y. Zhang, S. Wickenburg, A. Riss, J. Lu, S.-K. Mo, Z. Hussain, Z.-X. Shen, S. G. Louie, and M. F. Crommie, Probing the role of interlayer coupling and Coulomb interactions on electronic structure in few-layer MoSe<sub>2</sub> nanostructures, *Nano Lett.* **15**, 2594 (2015).
- [20] T. Sander, E. Maggio, and G. Kresse, Beyond the Tamm-Dancoff approximation for extended systems using exact diagonalization, *Phys. Rev. B* **92**, 045209 (2015).
- [21] C. Vorwerk, B. Aurich, C. Cocchi, and C. Draxl, Bethe-Salpeter equation for absorption and scattering spectroscopy: Implementation in the exciting code, *Electron. Struct.* **1**, 037001 (2019).
- [22] D. Sangalli, A. Ferretti, H. Miranda, C. Attaccalite, I. Marri, E. Cannuccia, P. Melo, M. Marsili, F. Paleari, A. Marrazzo, G. Prandini, P. Bonfà, M. O. Atambo, F. Affinito, M. Palumbo, A. Molina-Sánchez, C. Hogan, M. Grüning, D. Varsano, and A. Marini, Many-body perturbation theory calculations using the yambo code, *J. Phys.: Condens. Matter* **31**, 325902 (2019).
- [23] K. Merkel and F. Ortman, Linear scaling approach for optical excitations using maximally localized Wannier functions, *J. Phys. Mater.* **7**, 015001 (2024).
- [24] K. Merkel, J. Greiner, and F. Ortman, Understanding the electronic pi-system of 2D covalent organic frameworks with Wannier functions, *Sci. Rep.* **13**, 1685 (2023).
- [25] R. Zhou, Y. Yao, V. Blum, X. Ren, and Y. Kanai, All-electron BSE@GW method with numeric atom-centered orbitals for extended periodic systems, *J. Chem. Theory Comput.* **21**, 291 (2025).
- [26] D. Jacquemin, I. Duchemin, and X. Blase, Benchmarking the Bethe-Salpeter formalism on a standard organic molecular set, *J. Chem. Theory Comput.* **11**, 3290 (2015).
- [27] D. Jacquemin, I. Duchemin, and X. Blase, 0-0 Energies using hybrid schemes: Benchmarks of TD-DFT, CIS(D), ADC(2), CC2, and BSE/GW formalisms for 80 real-life compounds, *J. Chem. Theory Comput.* **11**, 5340 (2015).
- [28] F. Bruneval, S. M. Hamed, and J. B. Neaton, A systematic benchmark of the *ab initio* Bethe-Salpeter equation approach for low-lying optical excitations of small organic molecules, *J. Chem. Phys.* **142**, 244101 (2015).
- [29] F. Bruneval, T. Rangel, S. M. Hamed, M. Shao, C. Yang, and J. B. Neaton, MOLGW 1: Many-body perturbation theory software for atoms, molecules, and clusters, *Comput. Phys. Commun.* **208**, 149 (2016).
- [30] X. Blase, P. Boulanger, F. Bruneval, M. Fernandez-Serra, and I. Duchemin, GW and Bethe-Salpeter study of small water clusters, *J. Chem. Phys.* **144**, 034109 (2016).
- [31] D. Jacquemin, I. Duchemin, A. Blondel, and X. Blase, Assessment of the accuracy of the Bethe-Salpeter (BSE/GW) oscillator strengths, *J. Chem. Theory Comput.* **12**, 3969 (2016).
- [32] T. Rangel, S. M. Hamed, F. Bruneval, and J. B. Neaton, An assessment of low-lying excitation energies and triplet instabilities of organic molecules with an *ab initio* Bethe-Salpeter equation approach and the Tamm-Dancoff approximation, *J. Chem. Phys.* **146**, 194108 (2017).
- [33] D. Jacquemin, I. Duchemin, and X. Blase, Is the Bethe-Salpeter formalism accurate for excitation energies? comparisons with TD-DFT, CASPT2, and EOM-CCSD, *J. Phys. Chem. Lett.* **8**, 1524 (2017).
- [34] K. Krause and W. Klopper, Implementation of the Bethe-Salpeter equation in the TURBOMOLE program, *J. Comput. Chem.* **38**, 383 (2017).
- [35] X. Gui, C. Holzer, and W. Klopper, Accuracy assessment of GW starting points for calculating molecular excitation energies using the Bethe-Salpeter formalism, *J. Chem. Theory Comput.* **14**, 2127 (2018).
- [36] X. Blase, I. Duchemin, and D. Jacquemin, The Bethe-Salpeter equation in chemistry: Relations with TD-DFT, applications and challenges, *Chem. Soc. Rev.* **47**, 1022 (2018).
- [37] C. Holzer, X. Gui, M. E. Harding, G. Kresse, T. Helgaker, and W. Klopper, Bethe-Salpeter correlation energies of atoms and molecules, *J. Chem. Phys.* **149**, 144106 (2018).
- [38] X. Blase, I. Duchemin, D. Jacquemin, and P.-F. Loos, The Bethe-Salpeter equation formalism: From physics to chemistry, *J. Phys. Chem. Lett.* **11**, 7371 (2020).
- [39] C. Liu, J. Kloppenburg, Y. Yao, X. Ren, H. Appel, Y. Kanai, and V. Blum, All-electron *ab initio* Bethe-Salpeter equation approach to neutral excitations in molecules with numeric atom-centered orbitals, *J. Chem. Phys.* **152**, 044105 (2020).
- [40] A. Förster and L. Visscher, Quasiparticle self-consistent GW-Bethe-Salpeter equation calculations for large chromophoric systems, *J. Chem. Theory Comput.* **18**, 6779 (2022).
- [41] N. Rauwolf, W. Klopper, and C. Holzer, Non-linear light-matter interactions from the Bethe-Salpeter equation, *J. Chem. Phys.* **160**, 061101 (2024).
- [42] I. Knysh, F. Lipparini, A. Blondel, I. Duchemin, X. Blase, P.-F. Loos, and D. Jacquemin, Reference CC3 excitation energies for organic chromophores: Benchmarking TD-DFT, BSE/GW, and wave function methods, *J. Chem. Theory Comput.* **20**, 8152 (2024).
- [43] C. Holzer and Y. J. Franzke, A guide to molecular properties from the Bethe-Salpeter equation, *J. Phys. Chem. Lett.* **16**, 3980 (2025).
- [44] G. E. Scuseria, T. M. Henderson, and D. C. Sorensen, The ground state correlation energy of the random phase approximation from a ring coupled cluster doubles approach, *J. Chem. Phys.* **129**, 231101 (2008).
- [45] T. C. Berkelbach, Communication: Random-phase approximation excitation energies from approximate equation-of-motion coupled-cluster doubles, *J. Chem. Phys.* **149**, 041103 (2018).
- [46] M. F. Lange and T. C. Berkelbach, On the relation between equation-of-motion coupled-cluster theory and the GW approximation, *J. Chem. Theory Comput.* **14**, 4224 (2018).
- [47] R. Quintero-Monsebaiz, E. Monino, A. Marie, and P.-F. Loos, Connections between many-body perturbation and coupled-cluster theories, *J. Chem. Phys.* **157**, 231102 (2022).
- [48] J. Tölle and G. Kin-Lic Chan, Exact relationships between the GW approximation and equation-of-motion coupled-cluster theories through the quasi-boson formalism, *J. Chem. Phys.* **158**, 124123 (2023).
- [49] J. Cai, P. Ruffieux, R. Jaafar, M. Bieri, T. Braun, S. Blankenburg, M. Muoth, A. P. Seitsonen, M. Saleh, X. Feng,

- K. Müllen, and R. Fasel, Atomically precise bottom-up fabrication of graphene nanoribbons, *Nature (London)* **466**, 470 (2010).
- [50] S. Jiang, T. Neuman, A. Boeglin, F. Scheurer, and G. Schull, Topologically localized excitons in single graphene nanoribbons, *Science* **379**, 1049 (2023).
- [51] G. Borin Barin, Q. Sun, M. Di Giovannantonio, C.-Z. Du, X.-Y. Wang, J. P. Llinas, Z. Mutlu, Y. Lin, J. Wilhelm, J. Overbeck, C. Daniels, M. Lamparski, H. Sahabudeen, M. L. Perrin, J. I. Urgel, S. Mishra, A. Kinikar, R. Widmer, S. Stolz, M. Bommert, *et al.*, Growth optimization and device integration of narrow-bandgap graphene nanoribbons, *Small* **18**, 2202301 (2022).
- [52] J. Zhang, B. Ghawri, D. Dutta, R. Fasel, M. Calame, G. Borin Barin, and M. L. Perrin, Bottom-up-synthesized graphene nanoribbons for nanoelectronics, *Nat. Rev. Mater.* **11**, 194 (2026).
- [53] R. Denk, M. Hohage, P. Zeppenfeld, J. Cai, C. A. Pignedoli, H. Söde, R. Fasel, X. Feng, K. Müllen, S. Wang, D. Prezzi, A. Ferretti, A. Ruini, E. Molinari, and P. Ruffieux, Exciton-dominated optical response of ultra-narrow graphene nanoribbons, *Nat. Commun.* **5**, 4253 (2014).
- [54] J. Frenkel, On the transformation of light into heat in solids. I, *Phys. Rev.* **37**, 17 (1931).
- [55] J. Frenkel, On the transformation of light into heat in solids. II, *Phys. Rev.* **37**, 1276 (1931).
- [56] G. H. Wannier, The structure of electronic excitation levels in insulating crystals, *Phys. Rev.* **52**, 191 (1937).
- [57] F. Plasser and H. Lischka, Analysis of excitonic and charge transfer interactions from quantum chemical calculations, *J. Chem. Theory Comput.* **8**, 2777 (2012).
- [58] F. Plasser, M. Wormit, and A. Dreuw, New tools for the systematic analysis and visualization of electronic excitations. I. Formalism, *J. Chem. Phys.* **141**, 024106 (2014).
- [59] F. Plasser, S. A. Bäßler, M. Wormit, and A. Dreuw, New tools for the systematic analysis and visualization of electronic excitations. II. Applications, *J. Chem. Phys.* **141**, 024107 (2014).
- [60] S. A. Bäßler, F. Plasser, M. Wormit, and A. Dreuw, Exciton analysis of many-body wave functions: Bridging the gap between the quasiparticle and molecular orbital pictures, *Phys. Rev. A* **90**, 052521 (2014).
- [61] F. Plasser, B. Thomitzni, S. A. Bäßler, J. Wenzel, D. R. Rehn, M. Wormit, and A. Dreuw, Statistical analysis of electronic excitation processes: Spatial location, compactness, charge transfer, and electron-hole correlation, *J. Comput. Chem.* **36**, 1609 (2015).
- [62] S. A. Mewes, F. Plasser, and A. Dreuw, Communication: Exciton analysis in time-dependent density functional theory: How functionals shape excited-state characters, *J. Chem. Phys.* **143**, 171101 (2015).
- [63] S. A. Mewes, J.-M. Mewes, A. Dreuw, and F. Plasser, Excitons in poly(para phenylene vinylene): A quantum-chemical perspective based on high-level *ab initio* calculations, *Phys. Chem. Chem. Phys.* **18**, 2548 (2016).
- [64] S. A. Mewes, F. Plasser, and A. Dreuw, Universal exciton size in organic polymers is determined by nonlocal orbital exchange in time-dependent density functional theory, *J. Phys. Chem. Lett.* **8**, 1205 (2017).
- [65] D. Hirose, Y. Noguchi, and O. Sugino, Quantitative characterization of exciton from *GW*+Bethe-Salpeter calculation, *J. Chem. Phys.* **146**, 044303 (2017).
- [66] S. A. Mewes, F. Plasser, A. Krylov, and A. Dreuw, Benchmarking excited-state calculations using exciton properties, *J. Chem. Theory Comput.* **14**, 710 (2018).
- [67] S. A. Mewes and A. Dreuw, Density-based descriptors and exciton analyses for visualizing and understanding the electronic structure of excited states, *Phys. Chem. Chem. Phys.* **21**, 2843 (2019).
- [68] P. Kimber and F. Plasser, Toward an understanding of electronic excitation energies beyond the molecular orbital picture, *Phys. Chem. Chem. Phys.* **22**, 6058 (2020).
- [69] C. Attaccalite, M. Grüning, and A. Marini, Real-time approach to the optical properties of solids and nanostructures: Time-dependent Bethe-Salpeter equation, *Phys. Rev. B* **84**, 245110 (2011).
- [70] X. Jiang, Q. Zheng, Z. Lan, W. A. Saidi, X. Ren, and J. Zhao, Real-time *GW*-BSE investigations on spin-valley exciton dynamics in monolayer transition metal dichalcogenide, *Sci. Adv.* **7**, eabf3759 (2021).
- [71] D. Sangalli, Excitons and carriers in transient absorption and time-resolved ARPES spectroscopy: An *ab initio* approach, *Phys. Rev. Mater.* **5**, 083803 (2021).
- [72] Y.-H. Chan, D. Y. Qiu, F. H. da Jornada, and S. G. Louie, Giant exciton-enhanced shift currents and direct current conduction with subbandgap photo excitations produced by many-electron interactions, *Proc. Natl. Acad. Sci. USA* **118**, e1906938118 (2021).
- [73] E. Perfetto, Y. Pavlyukh, and G. Stefanucci, Real-time *GW*: Toward an *ab initio* description of the ultrafast carrier and exciton dynamics in two-dimensional materials, *Phys. Rev. Lett.* **128**, 016801 (2022).
- [74] Š. Marek and J. Wilhelm, Linear and nonlinear optical properties of molecules from real-time propagation based on the Bethe-Salpeter equation, *J. Chem. Theory Comput.* **21**, 9814 (2025).
- [75] X. Li, N. Govind, C. Isborn, A. Eugene DePrince, III, and K. Lopata, Real-time time-dependent electronic structure theory, *Chem. Rev. (Washington, DC, U. S.)* **120**, 9951 (2020).
- [76] J. Mattiat and S. Luber, Comparison of length, velocity, and symmetric gauges for the calculation of absorption and electric circular dichroism spectra with real-time time-dependent density functional theory, *J. Chem. Theory Comput.* **18**, 5513 (2022).
- [77] M. Kick, E. Alexander, A. Beiersdorfer, and T. Van Voorhis, Super-resolution techniques to simulate electronic spectra of large molecular systems, *Nat. Commun.* **15**, 8001 (2024).
- [78] L. Schreder and S. Luber, Propagated (fragment) Pipek-Mezey Wannier functions in real-time time-dependent density functional theory, *J. Chem. Phys.* **160**, 214117 (2024).
- [79] M. Choi, M. S. Okyay, A. P. Dieguez, M. D. Ben, K. Z. Ibrahim, and B. M. Wong, QRCODE: Massively parallelized real-time time-dependent density functional theory for periodic systems, *Comput. Phys. Commun.* **305**, 109349 (2024).
- [80] K. Hanasaki and S. Luber, Development of real-time TDDFT program with *k*-point sampling and DFT + *U* in a Gaussian and plane waves framework, *J. Chem. Theory Comput.* **21**, 1879 (2025).

- [81] J. Villalobos-Castro, I. Knysh, D. Jacquemin, I. Duchemin, and X. Blase, Lagrangian Z-vector approach to Bethe–Salpeter analytic gradients: Assessing approximations, *J. Chem. Phys.* **159**, 024116 (2023).
- [82] J. Tölle, Fully analytic  $G_0W_0$  nuclear gradients, *J. Phys. Chem. Lett.* **16**, 3672 (2025).
- [83] J. Tölle, M.-P. Kitsaras, and P.-F. Loos, Fully analytic nuclear gradients for the Bethe–Salpeter equation, *J. Phys. Chem. Lett.* **16**, 11134 (2025).
- [84] M.-P. Kitsaras, J. Tölle, and P.-F. Loos, Analytic  $g_0w_0$  gradients based on a double-similarity transformation equation-of-motion coupled-cluster treatment, *J. Chem. Phys.* **164**, 044122 (2026).
- [85] J. A. Berger, P.-F. Loos, and P. Romaniello, Potential energy surfaces without unphysical discontinuities: The Coulomb hole plus screened exchange approach, *J. Chem. Theory Comput.* **17**, 191 (2021).
- [86] R. Tyagi and V. K. Voora, Single-pole polarization models: Rapid evaluation of electron affinities of solvated-electron and superatomic molecular anionic states, *J. Phys. Chem. Lett.* **15**, 1218 (2024).
- [87] R. Tyagi, A. Ghosal, and V. K. Voora, Optical gaps of F-center defects in LiF using many-body methods, *Phys. Chem. Chem. Phys.* **27**, 18567 (2025).
- [88] R. Tyagi and V. K. Voora, Polarization-induced quantum confinement of negative charge carriers by organic nanoporous frameworks, *Angew. Chem. Int. Ed.* **64**, e202422923 (2025).
- [89] C. Roelcke, L. Z. Kastner, M. Graml, A. Biereder, J. Wilhelm, J. Repp, R. Huber, and Y. A. Gerasimenko, Ultrafast atomic-scale scanning tunnelling spectroscopy of a single vacancy in a monolayer crystal, *Nat. Photonics* **18**, 595 (2024).
- [90] T. Siday, J. Hayes, F. Schiegl, F. Sandner, P. Menden, V. Bergbauer, M. Zizlsperger, S. Nerreter, S. Lingl, J. Repp, J. Wilhelm, M. A. Huber, Y. A. Gerasimenko, and R. Huber, All-optical subcycle microscopy on atomic length scales, *Nature (London)* **629**, 329 (2024).
- [91] M. Zizlsperger, S. Nerreter, Q. Yuan, K. B. Lohmann, F. Sandner, F. Schiegl, C. Meineke, Y. A. Gerasimenko, L. M. Herz, T. Siday, M. A. Huber, M. B. Johnston, and R. Huber, In situ nanoscopy of single-grain nanomorphology and ultrafast carrier dynamics in metal halide perovskites, *Nat. Photonics* **18**, 975 (2024).
- [92] S. Anglhuber, M. Zizlsperger, E. A. A. Pogna, Y. A. Gerasimenko, A. D. Koulouklidis, I. Gronwald, S. Nerreter, L. Viti, M. S. Vitiello, R. Huber, and M. A. Huber, Spacetime imaging of group and phase velocities of terahertz surface plasmon polaritons in graphene, *Nano Lett.* **25**, 2125 (2025).
- [93] S. Maier, R. Spachtholz, K. Glöckl, C. M. Bustamante, S. Lingl, M. Maczejka, J. Schön, F. J. Giessibl, F. P. Bonafé, M. A. Huber, A. Rubio, J. Repp, and R. Huber, Attosecond charge transfer in atomic-resolution scanning tunnelling microscopy, [arXiv:2507.10206](https://arxiv.org/abs/2507.10206).
- [94] CP2K, <https://www.cp2k.org>, <https://github.com/cp2k/cp2k>.
- [95] T. D. Kühne, M. Iannuzzi, M. Del Ben, V. V. Rybkin, P. Seewald, F. Stein, T. Laino, R. Z. Khaliullin, O. Schütt, F. Schiffmann, D. Golze, J. Wilhelm, S. Chulkov, M. H. Bani-Hashemian, V. Weber, U. Borštnik, M. TAILLEFUMIER, A. S. Jakobovits, A. Lazzaro, H. Pabst, *et al.*, CP2K: An electronic structure and molecular dynamics software package - Quickstep: Efficient and accurate electronic structure calculations, *J. Chem. Phys.* **152**, 194103 (2020).
- [96] M. Iannuzzi, J. Wilhelm, F. Stein, A. Bussy, H. Elgabarty, D. Golze, A.-S. Hehn, M. Graml, S. Marek, B. S. Gökmen, C. Schran, H. Forbert, R. Z. Khaliullin, A. Kozhevnikov, M. TAILLEFUMIER, R. Meli, V. V. Rybkin, M. Brehm, R. Schade, O. Schütt, *et al.*, The CP2K program package made simple, *J. Phys. Chem. B* **130**, 1237 (2026).
- [97] L. Hedin, New method for calculating the one-particle Green's function with application to the electron-gas problem, *Phys. Rev.* **139**, A796 (1965).
- [98] J. Wilhelm, M. Del Ben, and J. Hutter, GW in the Gaussian and plane waves scheme with application to linear acenes, *J. Chem. Theory Comput.* **12**, 3623 (2016).
- [99] Here, we adapt the typically used nomenclature, although our initial guess from KS-DFT should rather be called “mean-field”  $G_0$  [100].
- [100] D. Golze, M. Dvorak, and P. Rinke, The GW compendium: A practical guide to theoretical photoemission spectroscopy, *Front. Chem. (Lausanne, Switz.)* **7**, 377 (2019).
- [101] D. J. Thouless, Vibrational states of nuclei in the random phase approximation, *Nucl. Phys.* **22**, 78 (1961).
- [102] A. D. McLachlan and M. A. Ball, Time-dependent Hartree-Fock theory for molecules, *Rev. Mod. Phys.* **36**, 844 (1964).
- [103] N. Ullah and D. J. Rowe, Properties of real RPA matrices and a simple diagonalization procedure, *Nucl. Phys. A* **163**, 257 (1971).
- [104] J. Oddershede, P. Jørgensen, and D. L. Yeager, Polarization propagator methods in atomic and molecular calculations, *Comput. Phys. Rep.* **2**, 33 (1984).
- [105] R. E. Stratmann, G. E. Scuseria, and M. J. Frisch, An efficient implementation of time-dependent density-functional theory for the calculation of excitation energies of large molecules, *J. Chem. Phys.* **109**, 8218 (1998).
- [106] F. Plasser, On the meaning of de-excitations in time-dependent functional theory computations, *J. Comput. Chem.* **46**, e70072 (2025).
- [107] M. P. Ljungberg, P. Koval, F. Ferrari, D. Foerster, and D. Sánchez-Portal, Cubic-scaling iterative solution of the Bethe-Salpeter equation for finite systems, *Phys. Rev. B* **92**, 075422 (2015).
- [108] S. Obara and A. Saika, Efficient recursive computation of molecular integrals over Cartesian Gaussian functions, *J. Chem. Phys.* **84**, 3963 (1986).
- [109] E. F. Valeev, Libint: A library for the evaluation of molecular integrals of many-body operators over Gaussian functions (2024), <https://github.com/evaleev/libint>.
- [110] D. Golze, N. Benedikter, M. Iannuzzi, J. Wilhelm, and J. Hutter, Fast evaluation of solid harmonic Gaussian integrals for local resolution-of-the-identity methods and range-separated hybrid functionals, *J. Chem. Phys.* **146**, 034105 (2017).
- [111] C. W. McCurdy and L. C. Cusachs, Simplification of the RPA secular equation, *J. Chem. Phys.* **55**, 1994 (1971).
- [112] P. Jørgensen and J. Simons, *Second Quantization-Based Methods in Quantum Chemistry* (Academic Press, New York, 1981).
- [113] F. Furche, On the density matrix based approach to time-dependent density functional response theory, *J. Chem. Phys.* **114**, 5982 (2001).

- [114] J. M. Herbert, Chapter 3 - Density-functional theory for electronic excited states, in *Theoretical and Computational Photochemistry*, edited by C. García-Iriepa and M. Marazzi (Elsevier, Amsterdam, 2023), pp. 69–118.
- [115] S. L. Adler, Quantum theory of the dielectric constant in real solids, *Phys. Rev.* **126**, 413 (1962).
- [116] N. Wisser, Dielectric constant with local field effects included, *Phys. Rev.* **129**, 62 (1963).
- [117] G. D. Mahan, *Many-Particle Physics* (Springer US, Boston, 2000).
- [118] J. A. Berger, P. L. de Boeij, and R. van Leeuwen, A physical model for the longitudinal polarizabilities of polymer chains, *J. Chem. Phys.* **123**, 174910 (2005).
- [119] M. Schreiber, M. R. Silva-Junior, S. P. A. Sauer, and W. Thiel, Benchmarks for electronically excited states: CASPT2, CC2, CCSD, and CC3, *J. Chem. Phys.* **128**, 134110 (2008).
- [120] V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter, and M. Scheffler, *Ab initio* molecular simulations with numeric atom-centered orbitals, *Comput. Phys. Commun.* **180**, 2175 (2009).
- [121] X. Ren, P. Rinke, V. Blum, J. Wieferink, A. Tkatchenko, A. Sanfilippo, K. Reuter, and M. Scheffler, Resolution-of-identity approach to Hartree–Fock, hybrid density functionals, RPA, MP2 and GW with numeric atom-centered orbital basis functions, *New J. Phys.* **14**, 053020 (2012).
- [122] J. W. Abbott, C. M. Acosta, A. Akkoush, A. Ambrosetti, V. Atalla, A. Bagrets, J. Behler, D. Berger, B. Bieniek, J. Björk, V. Blum, S. Bohloul, C. L. Box, N. Boyer, D. S. Brambila, G. A. Bramley, K. R. Bryenton, M. Camarasa-Gómez, C. Carbogno, F. Caruso, *et al.*, Roadmap on advancements of the FHI-AIMS software package, [arXiv:2505.00125](https://arxiv.org/abs/2505.00125).
- [123] T. H. Dunning, Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen, *J. Chem. Phys.* **90**, 1007 (1989).
- [124] R. A. Kendall, T. H. Dunning, and R. J. Harrison, Electron affinities of the first-row atoms revisited. Systematic basis sets and wave functions, *J. Chem. Phys.* **96**, 6796 (1992).
- [125] K. Momma and F. Izumi, *VESTA 3* for three-dimensional visualization of crystal, volumetric and morphology data, *J. Appl. Crystallogr.* **44**, 1272 (2011).
- [126] J. Wilhelm, D. Golze, L. Talirz, J. Hutter, and C. A. Pignedoli, Toward GW calculations on thousands of atoms, *J. Phys. Chem. Lett.* **9**, 306 (2018).
- [127] C. Cocchi, D. Prezzi, A. Ruini, E. Benassi, M. J. Caldas, S. Corni, and E. Molinari, Optical excitations and field enhancement in short graphene nanoribbons, *J. Phys. Chem. Lett.* **3**, 924 (2012).
- [128] J. S. de Melo, L. M. Silva, L. G. Arnaut, and R. S. Becker, Singlet and triplet energies of  $\alpha$ -oligothiophenes: A spectroscopic, theoretical, and photoacoustic study: Extrapolation to polythiophene, *J. Chem. Phys.* **111**, 5427 (1999).
- [129] J. Torras, J. Casanovas, and C. Alemán, Reviewing extrapolation procedures of the electronic properties on the  $\pi$ -conjugated polymer limit, *J. Phys. Chem. A* **116**, 7571 (2012).
- [130] A. Dreuw and M. Head-Gordon, Single-reference *ab initio* methods for the calculation of excited states of large molecules, *Chem. Rev. (Washington, DC, U. S.)* **105**, 4009 (2005).
- [131] X. Blase and C. Attaccalite, Charge-transfer excitations in molecular donor-acceptor complexes within the many-body Bethe-Salpeter approach, *Appl. Phys. Lett.* **99**, 171909 (2011).
- [132] P.-F. Loos, M. Comin, X. Blase, and D. Jacquemin, Reference energies for intramolecular charge-transfer excitations, *J. Chem. Theory Comput.* **17**, 3666 (2021).
- [133] I. Knysh, J. D. J. Villalobos-Castro, I. Duchemin, X. Blase, and D. Jacquemin, Exploring Bethe–Salpeter excited-state dipoles: The challenging case of increasingly long push–pull oligomers, *J. Phys. Chem. Lett.* **14**, 3727 (2023).
- [134] T. Deilmann and K. S. Thygesen, Interlayer excitons with large optical amplitudes in layered van der Waals materials, *Nano Lett.* **18**, 2984 (2018).
- [135] Y.-h. Chan, M. H. Naik, J. B. Haber, J. B. Neaton, S. G. Louie, D. Y. Qiu, and F. H. da Jornada, Exciton–phonon coupling induces a new pathway for ultrafast intralayer-to-interlayer exciton transition and interlayer charge transfer in  $WS_2$ – $MoS_2$  heterostructure: A first-principles study, *Nano Lett.* **24**, 7972 (2024).
- [136] Exemplarily, the individual expectation values for the average position of hole  $\mathbf{r}_h$  and electron  $\mathbf{r}_e$  in an excited state  $n$  are computed from their cartesian components ( $\mu \in \{x, y, z\}$ )
- $$\langle r_e^{(\mu)} \rangle_{exc} = \frac{1}{C_n} \left( \sum_{a,i,j} X_{ia}^{(n)} X_{ja}^{(n)} \mu_{ij} + \sum_{a,b,i} Y_{ia}^{(n)} Y_{ib}^{(n)} \mu_{ab} \right)$$
- $$\langle r_h^{(\mu)} \rangle_{exc} = \frac{1}{C_n} \left( \sum_{a,b,i} X_{ia}^{(n)} X_{ib}^{(n)} \mu_{ab} + \sum_{a,i,j} Y_{ia}^{(n)} Y_{ja}^{(n)} \mu_{ij} \right).$$
- Here, we have introduced the dipole moments  $\mu_{pq} = \langle \psi_p | \hat{\mu} | \psi_q \rangle$  in the KS orbitals  $\psi_p(\mathbf{r})$ , which are computed in the length gauge [cf. Eq. (21)], as well as the normalization factor
- $$C_n = \langle \Psi_{exc}^{(n)} | \Psi_{exc}^{(n)} \rangle = \sum_{i,a} (X_{ia}^{(n)})^2 + (Y_{ia}^{(n)})^2$$
- $$= 1 + 2 \sum_{i,a} (Y_{ia}^{(n)})^2 \geq 1,$$
- where we have used Eq. (9) [106]. Hence,  $C_n = 1$  for all  $n$  in the case of TDA.
- [137] A. A. Quong and A. G. Eguiluz, First-principles evaluation of dynamical response and plasmon dispersion in metals, *Phys. Rev. Lett.* **70**, 3955 (1993).
- [138] I. G. Gurtubay, J. M. Pitarke, W. Ku, A. G. Eguiluz, B. C. Larson, J. Tischler, P. Zschack, and K. D. Finkelstein, Electron-hole and plasmon excitations in  $3d$  transition metals: *Ab initio* calculations and inelastic x-ray scattering measurements, *Phys. Rev. B* **72**, 125117 (2005).
- [139] S. Botti, F. Sottile, N. Vast, V. Olevano, L. Reining, H.-C. Weissker, A. Rubio, G. Onida, R. Del Sole, and R. W. Godby, Long-range contribution to the exchange-correlation kernel of time-dependent density functional theory, *Phys. Rev. B* **69**, 155112 (2004).
- [140] J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [141] C. Lee, W. Yang, and R. G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, *Phys. Rev. B* **37**, 785 (1988).

- [142] A. D. Becke, Density-functional exchange-energy approximation with correct asymptotic behavior, *Phys. Rev. A* **38**, 3098 (1988).
- [143] A. D. Becke, Density-functional thermochemistry. III. The role of exact exchange, *J. Chem. Phys.* **98**, 5648 (1993).
- [144] P. J. Stephens, F. J. Devlin, C. F. Chabalowski, and M. J. Frisch, *Ab initio* calculation of vibrational absorption and circular dichroism spectra using density functional force fields, *J. Phys. Chem.* **98**, 11623 (1994).
- [145] J. Heyd, G. E. Scuseria, and M. Ernzerhof, Hybrid functionals based on a screened Coulomb potential, *J. Chem. Phys.* **118**, 8207 (2003).
- [146] A. V. Krukau, O. A. Vydrov, A. F. Izmaylov, and G. E. Scuseria, Influence of the exchange screening parameter on the performance of screened hybrid functionals, *J. Chem. Phys.* **125**, 224106 (2006).
- [147] T. Yanai, D. P. Tew, and N. C. Handy, A new hybrid exchange–correlation functional using the Coulomb-attenuating method (CAM-B3LYP), *Chem. Phys. Lett.* **393**, 51 (2004).
- [148] M. Camarasa-Gómez, A. Ramasubramaniam, J. B. Neaton, and L. Kronik, Transferable screened range-separated hybrid functionals for electronic and optical properties of van der Waals materials, *Phys. Rev. Mater.* **7**, 104001 (2023).
- [149] G. Ohad, S. E. Gant, D. Wing, J. B. Haber, M. Camarasa-Gómez, F. Sagredo, M. R. Filip, J. B. Neaton, and L. Kronik, Optical absorption spectra of metal oxides from time-dependent density functional theory and many-body perturbation theory based on optimally-tuned hybrid functionals, *Phys. Rev. Mater.* **7**, 123803 (2023).
- [150] M. Camarasa-Gómez, S. E. Gant, G. Ohad, J. B. Neaton, A. Ramasubramaniam, and L. Kronik, Excitations in layered materials from a non-empirical Wannier-localized optimally-tuned screened range-separated hybrid functional, *npj Comput. Mater.* **10**, 288 (2024).
- [151] M. Graml, Data archive - Optical excitations in nanographenes, GitHub (2026), <https://github.com/MGraml/DataArchive-OpticalExcitationsInNanographenes>.
- [152] M. Graml and J. Wilhelm, Optical excitations in nanographenes from the BSE and TDDFT [Data set], Zenodo (2026), <https://doi.org/10.5281/zenodo.17476368>.
- [153] M. Graml and J. Wilhelm, Data archive of “Optical excitations in nanographenes from the Bethe-Salpeter equation and time-dependent density functional theory: Absorption spectra and spatial descriptors” [dataset], University of Regensburg Library (2026), <https://doi.org/10.5283/epub.79375>.
- [154] C. Bauer, T. Kenter, M. Lass, L. Mazur, M. Meyer, H. Nitsche, H. Riebler, R. Schade, M. Schwarz, N. Winnwa, A. Wiens, X. Wu, C. Plessl, and J. Simon, Noctua 2 supercomputer, *JLSRF* **9**, A187 (2024).
- [155] S. Ehtesabi, M. Hossain, T. Kenter, A. Krawinkel, H. Nitsche, L. Ostermann, C. Plessl, H. Riebler, S. Rohde, R. Schade, M. Schwarz, J. Simon, N. Winnwa, A. Wiens, and X. Wu, Otus supercomputer, [arXiv:2512.07401](https://arxiv.org/abs/2512.07401).
- [156] [www.nhr-verein.de/en/our-partners](http://www.nhr-verein.de/en/our-partners).
- [157] X. Blase, C. Attaccalite, and V. Olevano, First-principles GW calculations for fullerenes, porphyrins, phthalocyanine, and other molecules of interest for organic photovoltaic applications, *Phys. Rev. B* **83**, 115103 (2011).
- [158] F. Caruso, M. Dauth, M. J. van Setten, and P. Rinke, Benchmark of GW approaches for the GW100 test set, *J. Chem. Theory Comput.* **12**, 5076 (2016).
- [159] F. Kaplan, M. E. Harding, C. Seiler, F. Weigend, F. Evers, and M. J. van Setten, Quasi-particle self-consistent GW for molecules, *J. Chem. Theory Comput.* **12**, 2528 (2016).
- [160] D. Jacquemin, I. Duchemin, A. Blondel, and X. Blase, Benchmark of Bethe-Salpeter for triplet excited-states, *J. Chem. Theory Comput.* **13**, 767 (2017).
- [161] M. Shishkin and G. Kresse, Self-consistent GW calculations for semiconductors and insulators, *Phys. Rev. B* **75**, 235102 (2007).
- [162] H. Jiang and P. Blaha, GW with linearized augmented plane waves extended by high-energy local orbitals, *Phys. Rev. B* **93**, 115203 (2016).
- [163] M. Grumet, P. Liu, M. Kaltak, J. Klimeš, and G. Kresse, Beyond the quasiparticle approximation: Fully self-consistent GW calculations, *Phys. Rev. B* **98**, 155143 (2018).
- [164] L. Leppert, T. Rangel, and J. B. Neaton, Towards predictive band gaps for halide perovskites: Lessons from one-shot and eigenvalue self-consistent GW, *Phys. Rev. Mater.* **3**, 103803 (2019).
- [165] W. Chen and A. Pasquarello, Band-edge positions in GW: Effects of starting point and self-consistency, *Phys. Rev. B* **90**, 165133 (2014).
- [166] C. Adamo and V. Barone, Toward reliable density functional methods without adjustable parameters: The PBE0 model, *J. Chem. Phys.* **110**, 6158 (1999).
- [167] M. J. van Setten, F. Weigend, and F. Evers, The GW-method for quantum chemistry applications: Theory and implementation, *J. Chem. Theory Comput.* **9**, 232 (2013).
- [168] M. Schambeck, D. Golze, and J. Wilhelm, Solving multipole challenges in the GW100 benchmark enables precise low-scaling GW calculations, *Phys. Rev. B* **110**, 125146 (2024).
- [169] R. Bauernschmitt and R. Ahlrichs, Treatment of electronic excitations within the adiabatic approximation of time dependent density functional theory, *Chem. Phys. Lett.* **256**, 454 (1996).
- [170] F. Furche, R. Ahlrichs, C. Wachsmann, E. Weber, A. Sobanski, F. Vögtle, and S. Grimme, Circular dichroism of helicenes investigated by time-dependent density functional theory, *J. Am. Chem. Soc.* **122**, 1717 (2000).
- [171] L. Reining, The GW approximation: Content, successes and limitations, *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **8**, e1344 (2018).
- [172] Since Ref. [102] has derived these matrix elements for TDHF, the  $W_{pq,rs}$  are replaced by  $v_{pq,rs}$  there.
- [173] B. P. Pritchard, D. Altarawy, B. Didier, T. D. Gibson, and T. L. Windus, New basis set exchange: An open, up-to-date resource for the molecular sciences community, *J. Chem. Inf. Model.* **59**, 4814 (2019).
- [174] G. Lippert, J. Hutter, and M. Parrinello, The Gaussian and augmented-plane-wave density functional method for *ab initio* molecular dynamics simulations, *Theor. Chem. Acta* **103**, 124 (1999).
- [175] M. VÉril, P. Romaniello, J. A. Berger, and P.-F. Loos, Unphysical discontinuities in GW methods, *J. Chem. Theory Comput.* **14**, 5220 (2018).
- [176] J. Strand, S. K. Chulkov, M. B. Watkins, and A. L. Shluger, First principles calculations of optical properties for oxygen

- vacancies in binary metal oxides, *J. Chem. Phys.* **150**, 044702 (2019).
- [177] A.-S. Hehn, B. Sertcan, F. Belleflamme, S. K. Chulkov, M. B. Watkins, and J. Hutter, Excited-state properties for extended systems: Efficient hybrid density functional methods, *J. Chem. Theory Comput.* **18**, 4186 (2022).
- [178] B. S. Gökmen, J. Hutter, and A.-S. Hehn, Excited-state forces with the Gaussian and augmented plane wave method for the Tamm–Dancoff approximation of time-dependent density functional theory, *J. Chem. Theory Comput.* **20**, 8494 (2024).
- [179] J.-R. Vogt, J. Wilhelm, and A.-S. Hehn, Perturbative spin–orbit couplings for the simulation of extended framework materials, *J. Chem. Phys.* **162**, 082502 (2025).
- [180] J.-R. Vogt, M. Schulz, R. Souza Mattos, M. Barbatti, M. Persico, G. Granucci, J. Hutter, and A. Hehn, A density functional theory and semiempirical framework for trajectory surface hopping on extended systems, *J. Chem. Theory Comput.* **21**, 10474 (2025).
- [181] R. Pasquier, M. Camarasa-Gómez, A.-S. Hehn, D. Hernangómez-Pérez, and J. Wilhelm, Efficient *GW* band structure calculations using Gaussian basis functions and application to atomically thin transition-metal dichalcogenides, *Phys. Rev. B* **112**, 205130 (2025).
- [182] R. Pasquier, M. Graml, and J. Wilhelm, Gaussian basis sets for all-electron excited-state calculations of large molecules, *J. Chem. Theory Comput.* **22**, 540 (2026).
- [183] C. Kumar, H. Fliegl, F. Jensen, A. M. Teale, S. Reine, and T. Kjærgaard, Accelerating Kohn-Sham response theory using density fitting and the auxiliary-density-matrix method, *Int. J. Quantum Chem.* **118**, e25639 (2018).