LCAO-TDDFT-$k$-$\omega$: Spectroscopy in the Optical Limit

Keenan Lyon,\textsuperscript{1} María Rosa Preciado-Rivas,\textsuperscript{2} Duncan John Mowbray,\textsuperscript{2,1} and Vito Despoja\textsuperscript{3}

\textsuperscript{1}Department of Applied Mathematics, University of Waterloo, Waterloo, Ontario, Canada
\textsuperscript{2}School of Physical Sciences and Nanotechnology, Yachay Tech University, Ucuquil 100119, Ecuador
\textsuperscript{3}Institute of Physics, Bijenička 46, HR-10000 Zagreb, Croatia

Understanding, optimizing, and controlling the optical absorption process, exciton gerniation, and electron-hole separation and conduction in low dimensional systems is a fundamental problem in materials science. However, robust and efficient methods capable of modelling the optical absorbance of low dimensional macro-molecular systems and providing physical insight into the processes involved have remained elusive. We employ a highly efficient linear combination of atomic orbitals (LCAOs) representation of the Kohn–Sham (KS) orbitals within time dependent density functional theory (TDDFT) in the reciprocal space ($k$) and frequency ($\omega$) domains, as implemented within our LCAO-TDDFT-$k$-$\omega$ code, and apply the derivative discontinuity correction of the exchange functional $\Delta$ to the KS eigenergies. In so doing we are able to provide a semi-quantitative description of the optical absorption, conductivity, and polarizability spectra for prototypical 0D, 1D, 2D, and 3D systems within the optical limit ($||\mathbf{q}|| \to 0^+$) as compared to both available measurements and from solving the Bethe–Salpeter equation with quasiparticle $G_0W_0$ eigenvalues ($G_0W_0$-BSE). Specifically, we consider 0D fullerene ($C_{60}$), 1D metallic (10,0) and semiconducting (10,10) single-walled carbon nanotubes (SWCNTs), 2D graphene (Gr) and phosphorene (Pn), and 3D rutile (R-TiO$_2$) and anatase (A-TiO$_2$). For each system, we also employ the spatially resolved electron-hole density to provide direct physical insight into the nature of their optical excitations. These results demonstrate the reliability, applicability, efficiency, and robustness of our LCAO-TDDFT-$k$-$\omega$ code, and open the pathway to the computational design of macromolecular systems for optoelectronic, photovoltaic, and photocatalytic applications in silico.

I. INTRODUCTION

The understanding, optimization, and control of optical absorption processes, exciton generation and recombination, and electron-hole separation and conduction is a basic challenge in nanomaterial design, with a plethora of applications in optoelectronics\textsuperscript{4,5}, photovoltaics\textsuperscript{6,7}, and photocatalysis\textsuperscript{8,9,10}. Functionalizable and tailorable optically active low-dimensional nanomaterials, such as fullerenes ($C_{60}$)\textsuperscript{11–13}, single-walled carbon nanotubes (SWCNTs)\textsuperscript{14,15}, graphene (Gr), phosphorene (Pn)\textsuperscript{16,17}, and rutile (R-TiO$_2$) and anatase (A-TiO$_2$) nanoparticles\textsuperscript{18}, have attracted particular interest as prototypical optoelectronic, photovoltaic, and photocatalytic systems. However, robust and efficient theoretical methods that take into account the peculiarities of modelling optical absorption in low dimensional systems\textsuperscript{18–22} are somewhat scarce.

\textit{Ab initio} time dependent density functional theory (TDDFT) methods\textsuperscript{13,24} are the standard approaches for modelling light–matter interactions. They run the gamut from highly efficient but often qualitatively inaccurate methods based on the Kohn–Sham (KS) density of states\textsuperscript{25} to quantitatively accurate but computationally inefficient methods based on the hybrid exchange and correlation (xc) functional (HSE)\textsuperscript{26} or quasiparticle ($GW$)\textsuperscript{27} electronic structure and the solution to the four-point Bethe–Salpeter equation (BSE)\textsuperscript{28}.

While TDDFT in real space ($r$) and frequency ($\omega$) domains (TDDFT-$r$-$\omega$)\textsuperscript{29,30} often provides the desired balance between accuracy and efficiency, both its restriction to non-periodic (0D) calculations and $O(N^5)$ scaling make it unsuitable for modelling low dimensional (1D or 2D) systems and macromolecules. With a real space (RS) representation of the KS wave functions, one can both perform systematic convergence with respect to the grid spacing $h$ and accurately describe both the local and non-local features which are inherent in low dimensional systems. In this case, TDDFT in real space ($r$) and time ($t$) domains (RS-TDDFT-$r$-$t$)\textsuperscript{31,32} tends to require unnecessarily short time steps to yield stability of the wavefunctions, much shorter than the time steps required to resolve the frequency spectra\textsuperscript{33}, whereas TDDFT in reciprocal space ($k$) and frequency ($\omega$) domains (RS-TDDFT-$k$-$\omega$)\textsuperscript{34,35} has quite high memory costs and its accuracy strongly depends on an appropriate choice of xc functional.

A plane wave (PW) representation of the KS wavefunctions reduces the computational cost and improves stability relative to a RS representation while still allowing a systematic convergence with respect to the PW energy cutoff $E_{\text{cut}}$. However, such a representation is rather unsuitable for non-periodic or mixed boundary condition (0D, 1D, or 2D) systems. Moreover, although PW-TDDFT-$k$-$\omega$ calculations can heavily leverage fast Fourier transforms (FFTs) in their execution, their high memory cost can often make them unfeasible, especially for systems with large unit cells.

The $G_0W_0$-BSE method has proven to be one of the most quantitatively accurate methods for modelling one- and two-particle excitations. Based on a systematic perturbation theory approach around the weaker screened Coulomb interaction, $G_0W_0$ includes the screening of the electronic band structure through the frequency-dependent self energy $\Sigma(\omega)$\textsuperscript{37,38}. The resulting quasiparticle electronic levels\textsuperscript{37} are thus corrected to account for their screening by the media, with unoccupied levels typically upshifted to increase the electronic band gap. To describe the optical band gap, exciton binding, i.e., electron-hole interactions, should also be included through the solution of the four-point Bethe-Salpeter equation\textsuperscript{38} when calculating the macroscopic dielectric function. Computationally, a $G_0W_0$ calculation will scale cubically with the number of plane waves\textsuperscript{38}, whereas constructing and applying the Bethe-
Salpeter Hamiltonian will scale with the k-point sampling of the Brillouin Zone (BZ), resulting in restrictive time and memory costs. Although neither electronic screening nor excitonic binding are included in standard TDDFT calculations, these effects tend to compensate for each other in the calculated G0W0-BSE optical absorbance spectra, often leading to a fortuitous error cancellation with TDDFT. This suggests we should use G0W0-BSE calculations to benchmark less computationally intensive TDDFT methods where both quasiparticle screening and strong excitonic effects are neglected.

In this work, we use linear combinations of atomic orbitals (LCAOs) to represent the KS wavefunctions, and perform TDDFT calculations in reciprocal space (k) and frequency (ω) domains (LCAO-TDDFT-k-ω). In so doing, we provide an efficient and more stable representation of the KS orbitals while obtaining a similar accuracy to PW-TDDFT-k-ω. However, since we cannot efficiently apply an FFT within our LCAO representation of the KS orbitals, we are restricted in our LCAO-TDDFT-k-ω calculations to the head of the dielectric function, and the optical limit ||q|| → 0⁺.

In order for LCAO-TDDFT-k-ω to obtain accurate optical absorption spectra, we require an accurate description of the system’s electronic structure in line with experimentally measured band gaps. To do so, we employ the derivative discontinuity correction to the exchange (x) part of the GLLB-SC functional to perform an ab initio upshift of the unoccupied KS eigenenergies. This approach already successfully described the optical absorbance of both 0D chlorophyll monomers and 1D SWCNTs.

LCAO representations are inherently reliant on the choice of basis set, and unlike PW or RS calculations, systematic convergence cannot be obtained by simply decreasing the grid spacing h or increasing the plane-wave cutoff energy Ecut. The basis set choice is even more important for TDDFT relative to ground state DFT, as the basis set must describe both occupied and unoccupied states equally well. The importance of benchmarking for any LCAO basis set method is thus quite evident.

Herein we compare and contrast for a set of prototypical low-dimensional optically active nanomaterials the response functions and spectra obtained from different LCAO basis sets, PW-TDDFT-k-ω and G0W0-BSE calculations, and experimental measurements. Both p-valence and completeness-optimized basis sets have been put forward as methods for improving the density of states of unoccupied states and resolving the absolute convergence issue. However, since these methods have not been tested on a sufficiently wide range of materials, we shall restrict consideration to the default LCAO basis sets and directly compare to PW representations of the KS wavefunctions here.

As a consequence of having derived quantities independent of spatial dispersion, our LCAO-TDDFT-k-ω calculations have direct access to the transitions involved at a particular energy. This allows the description of the spatially-resolved excited electron and hole densities, providing physical insight into the excitations at different energies. In addition, the oscillator strengths themselves, related to the dipole transition matrix, provide insight into the reciprocal-space distribution of the transitions within the BZ of the material at a given energy.

This paper is organized as follows. In Sec. II we provide theoretical background to LCAO-TDDFT-k-ω, low-dimensional response functions, and real-space electron and hole densities, followed by a complete description of the relevant computational parameters employed herein. To highlight the range of applicability of the LCAO-TDDFT-k-ω method, in Sec. III we apply it to C60 (0D), metallic (10,10) and semiconducting (10,0) SWCNTs (1D), G0W0-BSE, and experimental measurements, and showcasing its spatially-resolved electron-hole density difference. Concluding remarks are given in Sec. IV followed by an Appendix with further details of the derivative discontinuity correction Δx, the LCAO-TDDFT-k-ω method’s treatment of the BZ, the k-point convergence of G0W0-BSE, and the derived model and measurements of Pn’s reflection spectra. Atomic units (ℏ = e = m_e = a_0 = 1) have been employed throughout unless otherwise noted.

II. METHODOLOGY

A. Theoretical Background

Modelling the optical absorbance, conductivity, or polarizability of low dimensional systems requires an accurate description of their electronic structure, including their electronic band gaps. As a first-order correction, this requires a rigid upshift of their unoccupied KS eigenenergies. This can be obtained at an ab initio level using the derivative discontinuity correction based on the exchange part of the GLLB-SC functional, Δx. This combines the screening and response parts of the PBEsol xc potential with a simple orbital-weighted approximation for the exchange part, and can be used to account for the discontinuity of the potential at integer particle numbers. This may be evaluated at the k-point corresponding to the band gap using the analytic form:

$$\Delta_x = \frac{8 \sqrt{2}}{3 \pi^2} \sum_{n=1}^{N} (\sqrt{\varepsilon_{N+1} - \varepsilon_n} - \sqrt{\varepsilon_N - \varepsilon_n}) \langle \psi_n, \psi_{n+1} \psi_{n+1} \rangle,$$

where N is the number of electrons, ψ_n is the n-th KS wavefunction, and ρ is the electron density.

An LCAO-TDDFT-k-ω calculation of the dielectric response, conductivity, or polarizability begins by determining the non-interacting density-density response function in reciprocal space k and frequency ω domains.

$$\chi^{0}_{GG}(q, \omega) = \frac{1}{\Omega} \sum_{k} \sum_{n,n'} \frac{w_k [f(\varepsilon_{nk}) - f(\varepsilon_{nk+q})]}{\hbar \omega - (\varepsilon_{nk} - \varepsilon_{nk+q} + \Delta_x) + i\eta} \langle \psi_{nk} | e^{-i(q+G) \cdot \mathbf{r}} | \psi_{nk+q} \rangle \langle \psi_{nk} | e^{i(q+G) \cdot \mathbf{r}} | \psi_{nk+q} \rangle$$
where \( \mathbf{q} \) and \( h\omega \) are the momentum and energy of the perturbation, \( \mathbf{G} \) and \( \mathbf{G}' \) are reciprocal lattice vectors, \( \Omega \) is the unit cell volume, \( w_k \) is the weight of \( k \)-point \( \mathbf{k} \), \( f \) is the Fermi-Dirac distribution, \( \varepsilon_{nk} \) and \( \psi_{nk}(r) \) are the eigenenergies and eigenfunctions of the \( n \)-th band at \( k \)-point \( \mathbf{k} \). \( \Delta_i \) is the derivative discontinuity correction to the exchange part of the GLLB-SC functional from (1), and \( \eta \approx 50 \text{ meV} \) is the half width at half maximum of the Lorentzian broadening.

In general, within linear response TDDFT in the random phase approximation (RPA), the dielectric matrix in reciprocal space is given by

\[
\varepsilon_{GG'}(\mathbf{q},\omega) = \delta_{GG'} - v_{GG'}(\mathbf{q}) \chi_{GG'}(0,\omega),
\]

where \( \delta_{GG'} \) is the Kronecker delta and \( v_{GG'}(\mathbf{q}) = \frac{4\pi}{\mathbf{q} \cdot \mathbf{q}'} \delta_{GG'} \) is the Fourier transform of the Coulomb kernel in 3D. The head \((\mathbf{G} = \mathbf{G}' = 0)\) of the dielectric matrix corresponds to the macroscopic dielectric function in the absence of local crystal field effects (LCFs).

In the so-called optical limit \( ||\mathbf{q}|| \to 0^+ \), the matrix elements corresponding to the head of the dielectric function \( \varepsilon_{00} \) in (2) reduce to

\[
\lim_{q \to 0} |\langle \psi_{nk} | e^{-i\mathbf{q} \cdot \mathbf{r}} | \psi_{n'k} + \mathbf{q} \rangle| = -i |\mathbf{q}| \varepsilon_{nk}^{\frac{\mathbf{q}}{2} + \Delta_i},
\]

where \( f_{\mathbf{q}mk} \) is the oscillator strength of the \( n \to n' \) transition at \( k \)-point \( \mathbf{k} \) in the direction of the Bloch vector \( \mathbf{q} \), i.e., \( \mathbf{q} \). It is important to note that, in the optical limit and neglecting LCFs, the radial cutoff and zero-padding methods for describing the Coulomb kernel in lower dimensions (0D, 1D, or 2D) reduce to the 3D Coulomb kernel.

In the optical limit the neglect of LCFs has previously been shown effective for gas phase structures and other low-dimensional materials. This leads to a simplified form for the macroscopic dielectric function in the optical limit

\[
\varepsilon(\mathbf{q},\omega) = 1 - \frac{4\pi}{\Omega} \sum_{\mathbf{k}} \sum_{n,n'} w_k \left[ f(\varepsilon_{nk}) - f(\varepsilon_{n'k}) \right] |f_{\mathbf{q}mk}|^2.
\]

Since the matrix elements \( f_{\mathbf{q}mk} \) must already be calculated to obtain the forces during structural relaxation, calculating the dielectric function using (5) simply involves the multiplication of previously calculated matrices. For this reason, calculations with our LCAO-TDDFT-\( k \)-\( \omega \) code are very efficient, with scaling of \( O(NM^2) \) or better, where \( N \) is the number of KS wavefunctions and \( M \geq N \) is the total number of basis functions used in the LCAO calculation.

In order to properly treat low-dimensional materials, we follow approaches based on mean-field theory laid out in Ref. 19 for non-interacting 1D SWCNTs and in Refs. 20 and 21 for non-interacting 2D sheets to compute the polarizability response functions \( \alpha(\mathbf{q},\omega) \). For a given dimension \( d \), these may be decomposed into the polarizability for light polarized in periodic directions “parallel” to the material, \( \mathbf{q}_\parallel \), and in non-periodic directions “perpendicular” to the material, \( \mathbf{q}_\perp \). These have the general forms

\[
\alpha_d(\mathbf{q}_\parallel,\omega) = \frac{\Omega_d}{4\pi} \left( \frac{\varepsilon(\mathbf{q}_\parallel,\omega) - 1}{\varepsilon(\mathbf{q}_\parallel,\omega)} \right),
\]

\[
\alpha_d(\mathbf{q}_\perp,\omega) = \frac{\Omega_d}{4\pi} \left( 1 - \frac{1}{\varepsilon(\mathbf{q}_\perp,\omega)} \right),
\]

where \( \Omega_d \) represents the “cross-section” of the unit cell for a given dimension \( d \), and \( \varepsilon(\mathbf{q},\omega) \) is the 3D macroscopic dielectric function obtained from (5). In this way the polarization is defined per molecule or per layer rather than per unit volume. \( \Omega_{d3D} \) is the volume of the unit cell, \( \Omega_{d2D} \) is the area of the plane in the unit cell perpendicular to the 1D material, \( \Omega_{d3D} \) is the length of the unit cell perpendicular to the plane of the 2D material, and \( \Omega_{d3D} = 1 \). Using these definitions for the polarizability \( \alpha \), we may express the conductivity \( \sigma \) for any dimension as

\[
\sigma(\mathbf{q},\omega) = -i\omega\alpha(\mathbf{q},\omega).
\]

This allows us to generalize our LCAO-TDDFT-\( k \)-\( \omega \) code to all classes of materials. It is important to note, however, that the neglect of LCFs may have important consequences for excitations polarized perpendicular to a given low-dimensional material with a spatial averaging taking place over the external field. This makes this LCAO-TDDFT-\( k \)-\( \omega \) method most suitable for computing the axial or in-plane conductivities for 1D and 2D materials, respectively.

By working in the optical limit \( ||\mathbf{q}|| \to 0^+ \) and neglecting LCFs, we can define the two-point excitonic density as

\[
\rho_{\text{ex}}(\mathbf{r}_x,\mathbf{r}_h,\mathbf{q},\omega) = \frac{4\pi}{\Omega} \sum_{\mathbf{k}} \sum_{mn} \eta^2 w_k |f_{\mathbf{q}mk}|^2 |\psi_{nk}(\mathbf{r}_x)|^2 |\psi_{nk}(\mathbf{r}_h)|^2 /
\]

\[
(\hbar \omega - (\varepsilon_{nk} - \varepsilon_{n'k} + \Delta_i))^2 + \eta^2, \tag{11}
\]

where \( \mathbf{r}_x \) and \( \mathbf{r}_h \) represent the real space locations of the electron and hole, respectively, and \( f_{\mathbf{q}mk} \) is the matrix element for the \( n \to n' \) transition from (4). Based on (11), we may define expressions for the hole and electron densities by averaging
over the electron and hole coordinates, respectively, as
\[
\rho_{\uparrow}(\mathbf{r}_h, \mathbf{q}, \omega) = \int \rho_{\downarrow}(\mathbf{r}_e, \mathbf{r}_h, \mathbf{q}, \omega) d\mathbf{r}_e
\]
\[
= \frac{4\pi}{\Omega} \sum_k \sum_{m' n'} \frac{\eta^2 w_k|f_{m'k}^\uparrow|^2 |\psi_{nk}(\mathbf{r}_h)|^2}{(\hbar\omega - (E_{nk}^\uparrow - E_{nk}^\downarrow + \Delta_e))^2 + \eta^2},
\]
(12)
\[
\rho_{\downarrow}(\mathbf{r}_e, \mathbf{q}, \omega) = -\int \rho_{\uparrow}(\mathbf{r}_e, \mathbf{r}_h, \mathbf{q}, \omega) d\mathbf{r}_h
\]
\[
= \frac{4\pi}{\Omega} \sum_k \sum_{m' n'} \frac{\eta^2 w_k|f_{n'k}^\downarrow|^2 |\psi_{nk}(\mathbf{r}_e)|^2}{(\hbar\omega - (E_{nk}^\uparrow - E_{nk}^\downarrow + \Delta_e))^2 + \eta^2}.
\]
(13)

These definitions for the excitonic, electron, and hole densities all satisfy
\[
\iint \rho_{\uparrow}(\mathbf{r}_e, \mathbf{r}_h, \mathbf{q}, \omega) d\mathbf{r}_e d\mathbf{r}_h = \text{Im}[\varepsilon(\mathbf{q}, \omega)].
\]
(14)

In this way, (11–13) provide means for spatially and energetically resolving the exciton, hole, and electron densities. We may then define the electron-hole density difference as
\[
\Delta \rho(\mathbf{r}, \mathbf{q}, \omega) = \rho_{\uparrow}(\mathbf{r}, \mathbf{q}, \omega) + \rho_{\downarrow}(\mathbf{r}, \mathbf{q}, \omega)
\]
\[
= \frac{4\pi}{\Omega} \sum_k \sum_{m' n'} \frac{\eta^2 w_k|f_{m'k}^\uparrow|^2 \left(|\psi_{nk}(\mathbf{r}_e)|^2 - |\psi_{nk}(\mathbf{r}_e)|^2\right)}{(\hbar\omega - (E_{nk}^\uparrow - E_{nk}^\downarrow + \Delta_e))^2 + \eta^2}.
\]
(16)

### B. Computational Details

All our DFT calculations employ the PAW method code gpaw within the atomic simulation environment ase. The generalized gradient approximation for solids and surfaces (PBEsol) was employed throughout for the xc functional. This allowed a self-consistent calculation of the GLBB-SC derivative discontinuity correction to the exchange functional \(\Delta_e\) from (1). We employed a grid spacing of \(h \approx 0.2\) Å and electronic temperature of \(k_B T \approx 1\) meV with all energies extrapolated to \(T \to 0\). The KS wavefunctions have been represented with either LCAOs and a double-\(\zeta\)-polarized (DZP) basis set, after performing convergence tests with basis sets of varying quality up to a quadruple-\(\zeta\)-polarized (QZP) basis set, or PWs with an converged energy cutoff of \(E_{\text{cut}} \approx 340\) eV. The radial functions \(\zeta(r)\) can describe spatially distinct bonds involving the same atom, whereas polarization refers to a mixing with orbitals of higher angular momentum number. The reliability of LCAO-TDDFT-\(k\omega\) is inherently basis set dependent, although DZP is an often chosen default for its balance between accuracy and computational efficiency.

For \(C_{60}\) we relaxed the atomic structure until maximum forces below 0.03 eV/Å were obtained, within a 20×20×20 Å³ unit cell. Given the 0D nature of \(C_{60}\), we performed \(\Gamma\)-point calculations employing non-periodic boundary conditions, i.e., both the electron density \(\rho\) and KS wave functions \(\psi_n\) were set to zero at the cell boundaries.

The (10,0) zigzag and (10,10) armchair SWCNTs’ atomic structures were relaxed until maximum forces less than 0.05 eV/Å were obtained, and the unit cells were relaxed parallel to the SWCNT (\(z\)) axis, yielding unit cell parameters of \(L \approx 4,30\) and 2.46 Å, respectively, including 10 Å of vacuum perpendicular to the nanotube axis. Given the 1D nature of SWNTs, \(k\)-point samplings of \(1 \times 1 \times 281\) and \(1 \times 1 \times 489\) were employed for the (10,0) and (10,10) SWCNTs, respectively, with periodic boundary conditions only along the SWCNT axis, and the electron density and KS wave functions set to zero at the unit cell boundaries perpendicular to the SWCNT’s axis.

For all Gr calculations we have employed an in-plane unit-cell constant of \(a = 4.651\) a₀ \(\approx 2.46\) Å, with the Gr layers stacked in a periodic super-lattice along the \(z\)-axis separated by a distance of \(L = 5a \approx 23.255\) a₀ \(\approx 12.3\) Å. To calculate the ground-state electronic density and KS wavefunctions we have employed a dense Monkhorst-Pack 301×301×1 \(k\)-point mesh over the first BZ with 18 bands, corresponding to seven unoccupied bands per atom. This was previously found to be sufficient to converge both the \(\pi\) and \(\sigma + \pi\) peaks in the energy loss of Gr within RS-TDDFT-RPA. Since our chosen \(k\)-point mesh does not include the Dirac (K) point, an electronic temperature of \(k_B T \approx 1\) meV ensures all electronic levels have integer occupations. A total of 18 bands were employed for all LCAO calculations to accommodate the reduced degrees of freedom present in SZP calculations.

All calculations of Pn have employed the crystal structure found in the gpaw Computational 2D Materials Database. The Pn layers are stacked in a periodic super-lattice along the \(z\)-axis separated by a distance of \(L \approx 17.1\) Å. A dense Monkhorst-Pack 603×603×1 \(k\)-point mesh is chosen over the first BZ with 32 bands, which we found to be sufficient to converge the main peaks up to 20 eV.

For A-TiO₂, a Monkhorst-Pack 11×11×5 \(k\)-point mesh was chosen over the first BZ with approximately 9 unoccupied bands per atom, whereas for R-TiO₂ we employed a Monkhorst-Pack 7×7×11 \(k\)-point mesh over the first BZ with a similar number of bands. Due to the fact that the LCAO-TDDFT-\(k\omega\) method is only concerned with the head of the dielectric function, using more bands will only affect the higher energy part of the optical spectra, so using more than the number of bands needed to converge the calculation reasonably is not required.

It is important to note that the effects of excitonic binding on the spectra have been neglected within the LCAO-TDDFT-\(k\omega\) formalism. Such effects may be substantial, especially for low-dimensional systems where electron–hole screening is significantly reduced, e.g., SWCNTs. To determine the impact of excitonic binding on the measured spectra, we have systematic compared our LCAO-TDDFT-\(k\omega\) results with \(G_0W_0\)-BSE calculations for \(C_{60}\), (10,0) SWCNT, and Pn, A-TiO₂, and R-TiO₂.

Our \(G_0W_0\)-BSE calculations for the (10,0) SWCNT and Pn were performed using the PW implementation within gpaw, employing reduced \(1 \times 1 \times 64\) and \(33 \times 47 \times 1\) samplings of the BZ, respectively. We used the Godby-Needs plasmon-pole approximation to describe the screening \(W\) and 1D and 2D truncation schemes for the Coulomb kernel to remove
TABLE I. Measured and calculated energies of the third bright $\pi - \pi^*$ exciton of fullerene ($C_{60}$) $\hbar\omega_x$ in eV.

| Method                        | $\hbar\omega_x$ (eV) |
|-------------------------------|----------------------|
| Measurement in Gas Phase      | 5.97$^a$             |
| Measurement in Hexane         | 5.86$^b$             |
| $G_0W_0$ BSE (VASP)           | 6.04$^c$             |
| $G_0W_0$ BSE (QE)             | 6.50$^d$             |
| LCAO-TDDFT-$k$-$\omega$ ($\varepsilon_n^e - \varepsilon_n$) | 4.79$^e$          |
| LCAO-TDDFT-$k$-$\omega$ ($\varepsilon_n^e - \varepsilon_n + \Delta_x$) | 5.56$^e$          |

$^a$ Ref. 74. $^b$ Ref. 75. $^c$ Ref. 71. $^d$ Ref. 76. $^e$ This work.

spurious interactions with periodic images orthogonal to the SWCNT’s axis and the Pn sheet, respectively.

One method for representing the electron and hole densities is simply, for a given energy, to present a 3D isosurface for producing both types of spatial representations of the electron and hole densities within the unit cell perpendicular to the desired axis. The functionality for producing both types of spatial representations of the electron and hole densities has been incorporated into our LCAO-TDDFT-$k$-$\omega$ code59.

The axes of electron and hole density projections cannot be chosen arbitrarily within our LCAO-TDDFT-$k$-$\omega$ code59, as the summation method for projection requires that the axis passes through voxels in a co-linear way. Beyond this requirement, projection of the spatially-resolved electron and hole densities is not limited to any specific crystal structure so long as it has dimension greater than zero.

III. RESULTS AND DISCUSSION

A. 0D Fullerene

We begin our assessment of the LCAO-TDDFT-$k$-$\omega$ method by considering the non-periodic or 0D carbon-based system of an isolated fullerene ($C_{60}$) molecule. $C_{60}$ provides an excellent system for benchmarking optical absorption spectra due to both its usefulness in OPVs4-7 and the availability of experimental measurements74,75 and theoretical calculations76,77.

In Table I we directly compare the energies obtained for $C_{60}$’s third bright $\pi - \pi^*$ exciton, $\hbar\omega_x$, from experiments in gas phase74 and hexane solution75 with $G_0W_0$-BSE74,76 and our LCAO-TDDFT-$k$-$\omega$ calculations neglecting and including the derivative discontinuity correction $\Delta_x$. While both $G_0W_0$-BSE and LCAO-TDDFT-$k$-$\omega$ including $\Delta_x$ reproduce the measured excitonic energy semi-quantitatively, neglecting the derivative discontinuity correction leads to an underestimation by more than 1 eV. This clearly demonstrates the essential role played by the derivative discontinuity correction $\Delta_x$ in providing a sufficiently accurate description of a system’s electronic structure to reproduce the measured spectra.

In Figure 1(a) and (b) we show the spatial distribution of the electron and hole densities associated with $C_{60}$’s third bright $\pi - \pi^*$ exciton, $\rho_e(\mathbf{r}, \omega_x)$ and $\rho_h(\mathbf{r}, \omega_x)$, respectively, from LCAO-TDDFT-$k$-$\omega$ at $\hbar\omega_x \approx 5.6$ eV and $G_0W_0$-BSE71 at $\hbar\omega_x \approx 6.0$ eV. In both cases, the electron density $\rho_e(\mathbf{r}, \omega_x)$ is predominately on $\pi$ anti-bonding orbitals located on the exterior of the $C_{60}$, whereas the hole density $\rho_h(\mathbf{r}, \omega_x)$ is predominately on $\pi$ bonding orbitals located on the interior of the $C_{60}$, as expected71. Overall, the two methods yield electron and hole densities in semi-quantitative agreement, justifying the use of our LCAO-TDDFT-$k$-$\omega$ code59.

In Figure 1(c), we compare experimental photoexcitation data74,75, ab initio models utilizing the quasiparticle $G_0W_0$ eigenenergies within the Bethe–Salpeter equation ($G_0W_0$-BSE) to better describe excitonic effects, and our LCAO-TDDFT-$k$-$\omega$ calculations including the derivative discontinuity correction to the GLLB-SC exchange functional $\Delta_x$. We find that both $G_0W_0$-BSE and our LCAO-TDDFT-$k$-$\omega$ calculations yield well-separated single-transition peaks at energies in semi-quantitative agreement with the experimental mea-
measurements in solution.\textsuperscript{24,75}

To allow a direct comparison of the measured and calculated spectra, in Figure 1(c) we have normalized the peak intensities by $C_{\text{eq}}$'s second $\pi - \pi^*$ excitation at about 5 eV. Whereas $G_0W_0$-BSE yields peaks gradually increasing in intensity in qualitative agreement with the experimental spectra, LCAO-TDDFT-$k$-$\omega$ shows the opposite behavior. This may be related to LCAO-TDDFT-$k$-$\omega$’s neglect of charge-transfer excitations or other excitonic effects which are better described at the $G_0W_0$-BSE level. However, the $G_0W_0$-BSE spectrum’s most intense peak at about 7 eV is almost completely absent in both the LCAO-TDDFT-$k$-$\omega$ and experimental\textsuperscript{74} spectra.

It is also worth noting that the inclusion of the GLLB-SC correction from (1) not only blue-shifts the calculated spectrum, but also reduces the intensities of the lower energy peaks, in better agreement with experiment and $G_0W_0$-BSE calculations. This is clearly seen from the inclusion of $\Delta_k$ in the denominator of the matrix elements $f_{mnk}$ in (4).

Despite these differences, it is apparent that the computationally less intensive LCAO-TDDFT-$k$-$\omega$ method is able to capture both the spatial distribution, peak locations, and peak intensities qualitatively and semi-quantitatively for this prototypical 0D system. We note that the absorption data for $C_{\text{eq}}$ in hexane solution was not adjusted by a Chako factor\textsuperscript{74} since we are mostly interested in the location of the peaks. Having demonstrated the reliability of the LCAO-TDDFT-$k$-$\omega$ method for describing both the optical absorption spectra and electron and hole density distributions for a non-periodic 0D carbon-based molecular system, we shall next consider extended semi-periodic systems.

**B. 1D (10,10) & (10,0) SWCNTs**

To continue our assessment of the LCAO-TDDFT-$k$-$\omega$ method, we next consider a structure that is periodic in only one direction or 1D. Specifically, we consider the prototypical 1D carbon-based system of an isolated single-wall carbon nanotube (SWCNT). SWCNTs provide excellent systems to benchmark optical absorption spectra due to their utility as conducting layers in OPVs since we are mostly interested in the location of the peaks. Having demonstrated the reliability of the LCAO-TDDFT-$k$-$\omega$ method for describing both the optical absorption spectra and electron and hole density distributions for a non-periodic 0D carbon-based molecular system, we shall next consider extended semi-periodic systems.

In fact, for a set of fifteen semiconducting and four metallic SWCNTs, our LCAO-TDDFT-$k$-$\omega$ code\textsuperscript{39} with the $\Delta_k$ correction has already been shown to reproduce these experimental measurements semi-quantitatively.\textsuperscript{44} For this reason we shall focus herein on the axial optical conductivity $\sigma(q||,\omega)$ obtained from the 1D polarizability $\alpha_{1D}(q||,\omega)$ using (8) and (10). Specifically, we consider the conductivity of two prototypical SWCNTs: the metallic armchair (10,10) SWCNT and the semiconducting zigzag (10,0) SWCNT.

In Figure 2 we compare the axial conductivity of the metallic (10,10) SWCNT from PW-TDDFT-$k$-$\omega$ and LCAO-TDDFT-$k$-$\omega$ employing a systematic improvement from single $\zeta$ polarized (SZP) to quadruple $\zeta$ polarized (QZP) LCAO basis sets. While the PW-TDDFT-$k$-$\omega$ conductivity is somewhat greater than that obtained with LCAO-TDDFT-$k$-$\omega$, irrespective of the basis set employed, the two methods are in semi-quantitative agreement. This underestimation of intensities by LCAO-TDDFT-$k$-$\omega$ could be partially attributed to an improved description of unoccupied wave functions when employing a PW representation. Comparing the LCAO-TDDFT-$k$-$\omega$ spectra employing various levels of basis sets, we find a DZP basis set is already sufficient to converge the conductivity spectra.

In each case, the real part of the (10,10) SWCNT’s conductivity $\text{Re}\{\sigma(q||,\omega)\}$ consists of a series of intense peaks at 1.5,
2.7, 3.4, and 3.9 eV, of \( \sim 100 \, h/m_e \) per SWCNT. This intensity is consistent with the ballistic conductance expected for a metallic armchair SWCNT.

Figure 2(c) shows the spatial distribution of the (10,10) SWCNT’s \( \pi - \pi^* \) electron-hole density difference \( \Delta \rho(\mathbf{r}, \mathbf{q}, \omega) \) at \( \hbar \omega_n \approx 4.1 \, \text{eV} \) from (16). This exciton’s hole is located primarily on \( \pi \) orbitals of the C–C bonds wrapping around the (10,10) SWCNT, whereas the excited electron is primarily located above the C–C bond along the (10,10) SWCNT’s axis. We also clearly see the hole has greater weight inside the (10,10) SWCNT whereas the excited electron is predominantly outside the (10,10) SWCNT. Overall, the electron density is arranged in a series of “strips” running along the outside of the nanotube parallel to its axis, whereas the hole is more localized.

It is important to note that, since the (10,10) armchair SWCNT is metallic, the derivative discontinuity correction \( \Delta_x \) may be taken implicitly to be zero. By considering the spectra of the semiconducting (10,0) zigzag SWCNT, we may probe the relevance of the derivative discontinuity correction to the description of 1D systems such as SWCNTs.

In Figure 3 we compare the axial conductivity of the semiconducting (10,0) armchair SWCNT from PW-TDDFT-\( k-\omega \), \( G_0W_0 \)-BSE, and LCAO-TDDFT-\( k-\omega \), again employing a systematic improvement from SZP to QZP LCAO basis sets. As was the case for the metallic (10,10) SWCNT, we find our LCAO-TDDFT-\( k-\omega \) calculations somewhat underestimate the intensities of the PW-TDDFT-\( k-\omega \) calculations, irrespective of the basis set employed, whereas the two methods yield semi-quantitative agreement in both their intensities and peak positions. Our \( G_0W_0 \)-BSE calculations\(^4\) show the effects of excitonic binding on the axial conductivity, which is expected to be quite strong for semiconducting SWCNTs. \( G_0W_0 \) yields a quasiparticle band gap of \( E_{\text{gap}}^{\text{QP}} \approx 1.83 \, \text{eV} \), consistent with \( E_{\text{gap}} \approx 1.72 \, \text{eV} \) from Ref. 80, while BSE yields a strong binding energy for the first bright exciton of \( E_{\text{bind}} = E_{\text{gap}}^{\text{QP}} - \hbar \omega_{\pi} \approx 0.49 \, \text{eV} \). Altogether, we obtain a \( G_0W_0 \)-BSE energy for the first transition of \( E_{11} \approx 1.34 \, \text{eV} \), in semi-qualitative agreement with \( E_{11} \approx 1.55 \, \text{eV} \) from our LCAO-TDDFT-\( k-\omega \) and PW-TDDFT-\( k-\omega \) calculations. Our \( G_0W_0 \)-BSE calculations are in qualitative agreement with our LCAO-TDDFT-\( k-\omega \) results for the axial conductivity intensity, with \( G_0W_0 \)-BSE yielding somewhat greater intensities for the \( E_{11} \) and \( E_{22} \) transitions. This is consistent with the inclusion of excitonic effects at the BSE level.

For the (10,0) zigzag SWCNT, the application of the derivative discontinuity correction \( \Delta_x \) changes the calculated spectra qualitatively, not only in the peak positions, but also the intensities. For the (10,0) SWCNT we obtain a significant derivative discontinuity correction of \( \Delta_x \approx 0.788 \, \text{eV} \), which is half the energy of the first intense peak in the conductivity spectra, at \( \hbar \omega \approx 1.55 \, \text{eV} \). However, since energy shifts are only employed \textit{a posteriori} by the PW-TDDFT-\( k-\omega \) implementation within \textsc{gpaw}, it is necessary to include the renormalization of the matrix elements in (6) in an \textit{ad hoc} manner when calculating the conductivity from the 3D dielectric function \( \varepsilon(\omega) \) obtained from PW-TDDFT-\( k-\omega \) (see Appendix A). Although this approximate renormalization works reasonably well for the real part of the conductivity shown in Figure 3(a), it fails when applied to the imaginary part of the conductivity. For this reason, we do not include PW-TDDFT-\( k-\omega \) results in Figure 3(b).

Overall, the real part of the semiconducting (10,0) SWCNT’s conductivity \( \text{Re}[\sigma(\mathbf{q}_i, \omega)] \) consists of a series of intense peaks at 1.6, 2.8, 3.2, 3.7, and 4.8, of \( \sim 40 \, h/m_e \) per SWCNT, qualitatively half that of the metallic (10,10) SWCNT.

Figure 3(c) shows the spatial distribution of the (10,0) SWCNT’s \( \pi - \pi^* \) electron-hole density difference \( \Delta \rho(\mathbf{r}, \mathbf{q}_i, \omega) \) at \( \hbar \omega \approx 4.1 \, \text{eV} \) from (16). In this case, the exciton’s hole is again located primarily on \( \pi \) orbitals of the C–C bonds wrap-
ping around inside the (10,10) SWCNT, whereas the excited electron is primarily located above the C–C bonds along the (10,0) SWCNT’s axis. We also again see the hole has greater weight inside the (10,0) SWCNT whereas the excited electron is predominantly outside the (10,0) SWCNT. However, unlike the (10,10) SWCNT, it is the hole density which is arranged in a series of “rings” inside the (10,0) SWCNT along its circumference, whereas the excited electron is more localized.

For both metallic and semiconducting SWCNTs, we find the hole is located predominantly on the inside whereas the excited electron is located predominantly on the outside of the tube. This is consistent with both the LCAO-TDDFT-\(k\)-\(\omega\) and \(G_0W_0\)-BSE spatial distributions for \(C_{60}\)’s third bright exciton (cf. Figure 1(a,b)). Interestingly, we also find in both the (10,10) and (10,0) SWCNTs that the hole’s density is arranged predominantly “around” the nanotube’s circumference, whereas the excited electron’s density is arranged predominantly “along” the nanotube’s axis. It is when these densities are aligned with the zigzag direction on the SWCNT that they become spatially delocalized in rings inside or strips outside the SWCNT, respectively. To probe the generality of these observations, we will next consider carbon’s 2D allotrope, graphene.

C. 2D Graphene & Phosphorene

We will now assess the reliability of the LCAO-TDDFT-\(k\)-\(\omega\) method for describing isolated surface layers that are non-periodic in only one direction, or 2D. We will first consider the prototypical 2D system of an isolated 2D graphene layer (Gr). Gr is an excellent material for benchmarking due to its wide range of technologically relevant optoelectronic properties\(^8\), its place as a “toy” system due to its simplicity from a computational point of view\(^3\), and the great breadth of literature studying this material\(^8\).

In Figure 4 we compare Gr’s in-plane conductivity \(\sigma(\omega)\) from PW-TDDFT-\(k\)-\(\omega\) using Quantum Espresso (QE) or gpaw to LCAO-TDDFT-\(k\)-\(\omega\) calculations employing either SZP, DZP, TZP, or QZP basis sets. Our results in Figure 4 show excellent agreement between the PW-TDDFT-\(k\)-\(\omega\) and LCAO-TDDFT-\(k\)-\(\omega\) spectra up to the \(\pi \to \pi^*\) transition near 4.2 eV, after which LCAO-TDDFT-\(k\)-\(\omega\) predicts a much longer-ranged tail than PW-TDDFT-\(k\)-\(\omega\). The location of the \(\sigma \to \sigma^*\) transition for LCAO-TDDFT-\(k\)-\(\omega\) employing DZP, TZP, or QZP basis sets also agree with that predicted by PW-TDDFT-\(k\)-\(\omega\). Finally, Gr’s conductivity exhibits additional peaks beyond the \(\sigma \to \sigma^*\) transition. A small peak near 16 eV is evident in both PW-TDDFT-\(k\)-\(\omega\) and LCAO-TDDFT-\(k\)-\(\omega\) spectra, whereas LCAO-TDDFT-\(k\)-\(\omega\) calculations with DZP, TZP, or QZP basis sets have a secondary peak near 18 eV. To determine whether this peak has a physical origin or is an artifact of the LCAO basis set, we must consider the spatial distribution of the exciton. Overall, the choice of the DZP basis set appears to be sufficient to capture the main peak locations and intensities for the conductivity of Gr.

So far we have restricted consideration to carbon-based low-dimensional materials. To further test the range of applicability of the LCAO-TDDFT-\(k\)-\(\omega\) method, we will now consider another prototypical 2D material, monolayer phosphorene (Pn). This material has found many potential uses in electronic and photonic applications due to its mid-infrared band gap\(^5\), strong layer dependence, and its ability to sustain hyperbolic plasmons due to the anisotropy present in the dielectric tensor\(^6\).

In Figure 5 we show Pn’s PW-TDDFT-\(k\)-\(\omega\), \(G_0W_0\)-BSE, and LCAO-TDDFT-\(k\)-\(\omega\) in-plane conductivity. Due to Pn’s well-known in-plane anisotropy\(^16,86\), conductivities are shown in both the \(x\) and \(y\) directions in Figure 5. PW-TDDFT-\(k\)-\(\omega\), \(G_0W_0\)-BSE, and LCAO-TDDFT-\(k\)-\(\omega\) all capture the anisotropic peak in the conductivity near 1.8 eV in the \(x\)-direction, and the greater intensity of the main peak in the conductivity near 5 eV in the \(y\)-direction.

Overall, we see that both \(G_0W_0\)-BSE and LCAO-TDDFT-\(k\)-\(\omega\) yield greater conductivities for Pn compared to PW-TDDFT-\(k\)-\(\omega\) for energies beyond 3 eV. While the magnitude of the matrix elements \(\langle \psi_n | \nabla | \psi_n \rangle\) in (4) are generally smaller when employing an LCAO representation of the KS orbitals\(^46\) due to difficulties representing unoccupied wave functions, this is not always the case. For the conductivity at higher ener-
conductivity 

Re[$\sigma(\omega)$] (e$^2$/h) 

Im[$\sigma(\omega)$] (e$^2$/h) 

Energy $\hbar\omega$ (eV) 

Conductivity 

FIG. 5. Phosphorene (Pn) in-plane (a) real and (b) imaginary parts of the conductivity $\sigma(\omega)$ in e$^2$/h versus energy $\hbar\omega$ in eV from $\text{G}_0\text{W}_0$-BSE (black), PW-TDDFT-$k$-$\omega$ (blue) and LCAO-TDDFT-$k$-$\omega$ (red) for $\mathbf{q}_1$ (solid lines) and $\mathbf{q}_c$ (dashed lines) polarized light.

gies LCAO-TDDFT-$k$-$\omega$ yields longer tails in both G\textsc{r} and Pn relative to PW-TDDFT-$k$-$\omega$ and $\text{G}_0\text{W}_0$-BSE, showing another main difference between the three approaches.

Since we restrict consideration to the core of the dielectric function $\varepsilon_{\omega_0}(\omega)$ in (3), thereby neglecting LCFs, the LCAO-TDDFT-$k$-$\omega$ method provides direct access to the individual transitions. In this way, we may visualize the exciton’s distribution within the BZ via the oscillator strengths $f_{m'k}^{\mathbf{q}_c}$ defined in (4), which are directly related to the dipole transition matrix elements. In Figures 6 and 7 we show, for a given k-point and energy $\hbar\omega$, the sum of oscillator strengths $f_{m'k}^{\mathbf{q}_c}$ for transitions $n \rightarrow n'$ within $h\Delta\omega = \pm 0.2$ eV of $\hbar\omega$ weighted by a Lorentzian broadening of 0.1 eV. Despite the choice to sum oscillator strengths $f_{m'k}^{\mathbf{q}_c}$ for excitations polarized in-plane, these diagrams can also be made to visualize the relevant bands for excitations in other directions. Since this can be done for any k-point, a contour map over the entire BZ can be constructed for a given energy and associated range and broadening parameters. This yields more information at a given energy than the band structure by also showing connections within the BZ beyond linear cross-sections between different high-symmetry points.

In Figure 6(a), (b), and (c) we show the weights of G\textsc{r}’s transitions over its hexagonal BZ for its $\pi-\pi^*$, $\sigma-\sigma^*$, and $\pi-\sigma^*$ excitations, respectively. Due to the symmetry of G\textsc{r}’s crystal structure, these transitions must exhibit a six-fold symmetry over the BZ. Figure 6(a) and (b) show that for the conductivity peaks located at 4.1 eV and 14.1 eV, respectively, the bulk of the transitions occur at or near the high symmetry M-point, with the $\pi-\pi^*$ transition distributed along the M$\rightarrow$M’ direction. This may also be seen from the band structure of Figure 6(e), where the $\pi-\pi^*$ and $\sigma-\sigma^*$ transitions at the M-point are marked using arrows. Likewise, the peak at 16.3 eV in Figure 6(c) can be attributed to a $\pi-\sigma^*$ transition occurring predominantly at the $\Gamma$ point (cf. Figure 6(e)). The annulus surrounding the $\Gamma$-point in Figure 6(c) may be related to the choice of energy range being somewhat lower than the $\pi-\sigma^*$ peak, as seen in Figure 6(d).

In Figure 7(a), (b), and (c) we show the weights of Pn’s three main transitions over its orthorhombic BZ. Due to Pn’s orthorhombic symmetry we expect its transitions to exhibit a four-fold symmetry over the BZ. Figure 7(a) shows the distribution of the oscillator strengths $f_{m'k}^{\mathbf{q}_c}$ for an anisotropic excitation sensitive to x-polarized light at $\omega_x \approx 1.9$ eV. This energy is $\sim 0.1$ eV above the peak (cf. Figure 7(d)) to better show the transition’s anisotropy. Not only do we notice the expected centering behaviour around the $\Gamma$ high symmetry point, but also an anisotropy between the $k_x$ and $k_y$ directions, yielding an elliptical annulus in the BZ.

Figure 7(b) and (c) show BZ plots for energies higher in the spectrum corresponding to y dominant $\omega_y \approx 5.1$ eV and a second x-polarized $\omega_x \approx 9.5$ eV transition, respectively. The weak yet scattered density of $f_{m'k}^{\mathbf{q}_c}$ suggests contributions from many bands with clear $k_x$ and $k_y$ dependencies. Ellipse-like shapes also appear, and give some indication of which k-points in the BZ are most relevant for a given transition energy, information that is not clearly evident from the band structure alone (cf. Figure 7(e)).

As given in (11), the oscillator strengths $f_{m'k}^{\mathbf{q}_c}$ derived in the LCAO-TDDFT-$k$-$\omega$ method can also be used to define a two-point excitonic density $\rho_{\mathbf{q}_c}(\mathbf{r}_n, \mathbf{r}_n, \mathbf{q}_c, \omega)$ from which position-resolved hole and excited electron densities, $\rho_\mathbf{h}(\mathbf{r}_n, \mathbf{q}_c, \omega)$ and $\rho_\mathbf{e}(\mathbf{r}_n, \mathbf{q}_c, \omega)$, can be obtained from (12) and (13) by integration over the electron and hole positions, respectively. Figures 8 and 9, show the separate electron and hole densities and their difference.

In Figure 8 we show four real-space contours of either the electron or hole density projected onto either the x-z plane, summing over the xy-plane, or along the C-C bond, summing over the plane normal to the C-C bond. From Figure 8(a) and (b) we can clearly see that both the electron and hole densities at $\hbar\omega_n \approx 4.1$ eV have nodal planes in the G\textsc{r} plane, consistent with $\pi$ and $\pi^*$ orbitals, whereas the electron and hole densities at $\hbar\omega_n \approx 14.1$ eV are localized within the G\textsc{r} plane, consistent with $\sigma^*$ and $\sigma$ orbitals. The peak at 16.3 eV is more difficult to analyze, although the lack of a nodal plane at that energy suggests this transition should have some $\sigma$ character.

The 18 eV peak of Figure 4 in the LCAO-TDDFT-$k$-$\omega$ spectra has an excited electron with a significant spatial extent into the vacuum out of the G\textsc{r} plane (cf. Figure 8(a)). This suggests the excitation could be to a Rydberg state. How-
**Graphene's (Gr)**

(a) $\pi \rightarrow \pi^*$ transition $\hbar \omega_{\pi} = 4.1 \text{ eV}$, (b) $\sigma \rightarrow \sigma^*$ transition $\hbar \omega_{\sigma} = 14.1 \text{ eV}$, and (c) $\pi \rightarrow \sigma^*$ transition $\hbar \omega_{\pi\sigma} = 16.3 \text{ eV}$ weights in reciprocal $k$-space, in-plane (d) real (blue) and imaginary (red) parts of the conductivity $\sigma(\mathbf{q}, \omega)$ in $e^2/\hbar$ versus energy $\hbar \omega$ in eV from LCAO-TDDFT-$k$-$\omega$, and (e) band structure.

**Phosphorene’s (Pn)**

(a) $\hbar \omega_x = 1.8 \text{ eV}$, (b) $\hbar \omega_{yx} = 5.1 \text{ eV}$, and (c) $\hbar \omega_{2x} = 9.5 \text{ eV}$ weights in reciprocal $k$-space, in-plane (d) real (blue) and imaginary (red) parts of the conductivity $\sigma(\mathbf{q}, \omega)$ in $e^2/\hbar$ versus energy $\hbar \omega$ in eV from LCAO-TDDFT-$k$-$\omega$ for $\mathbf{q}_x$ (solid lines) and $\mathbf{q}_y$ (dashed lines) polarized light, and (e) band structure.

However, this peak is absent in both the PW-TDDFT-$k$-$\omega$ and SZP LCAO-TDDFT-$k$-$\omega$ spectra (cf. Figure 4). Moreover, a proper description of diffuse Rydberg states, which sample the long-range area of the Coulomb potential tail, is not viable in standard TDDFT implementations. Altogether, this suggests this peak is an artifact of the basis set choice.

Figure 8(c) and (d) yield spatially-resolved information about an excitation’s electron and hole, respectively, along the C–C bonds within Gr’s unit cell. Again, $\pi^*$ and $\pi$ behavior is clearly seen at the 4.1 eV peak, with the electron density shared between the two C atoms and the hole density centred on the atoms themselves. The opposite behavior is seen for the 14.1 eV $\sigma \rightarrow \sigma^*$ transition, with the spatial extent of the density stretching to the edges of the unit cell.
Since $G_0 W_0$-BSE, PW-TDDFT-$k\-\omega$ and LCAO-TDDFT-$k\-\omega$ calculations of the real and imaginary parts of the dielectric function $\varepsilon(\omega)$. $G_0 W_0$-BSE and PW-TDDFT-$k\-\omega$ calculations are included to determine the role played by many body effects, LCFs, and exciton binding in the description of A-TiO$_2$ and R-TiO$_2$’s optoelectronic response functions. It is also important to see to what extent the more computationally efficient LCAO-TDDFT-$k\-\omega$ method can describe the measured spectra.

As can be seen for both PW-TDDFT-$k\-\omega$ and LCAO-TDDFT-$k\-\omega$ curves in Figures 10 and 11, due to the relatively flat $d$-orbital bands that compose the conduction band minima (CBM) for these polymorphs of TiO$_2$, the dielectric function is characteristically flat.

At the quasiparticle $G_0 W_0$-BSE level, we find the excitonic binding is quite weak ($\sim 0.1$ eV) in both A-TiO$_2$ and R-
TiO$_2$\textsuperscript{69}, so that the positions of the first bright excitons are reasonably consistent with our PW-TDDFT-$k$-$\omega$ and LCAO-TDDFT-$k$-$\omega$ results, as shown in Table II. Moreover, the LCAO-TDDFT-$k$-$\omega$ and PW-TDDFT-$k$-$\omega$ methods do qualitatively peak and trough with the experimental data (cf. Figures 10 and 11).

The inclusion of exchange and correlation effects in the kernel $f_{xc}$, beyond the Coulomb kernel $v$, allow quasiparticle $G_0W_0$-BSE calculations\textsuperscript{68,69} to reproduce the spectral intensities semi-quantitatively. For both A-TiO$_2$ and R-TiO$_2$ the dielectric functions obtained via LCAO-TDDFT-$k$-$\omega$ are generally more intense than their PW-TDDFT-$k$-$\omega$ equivalents. Finally, we expect the flat bands of TiO$_2$ will not exhibit a strong dependence on the choice of LCAO basis set or $k$-point sampling.

The electron-hole density difference $\Delta \rho(\mathbf{r}, \mathbf{q}_e, \omega_{ex})$ for the bright excitonic peak $\hbar \omega_{ex}$ in $\text{Im}[\varepsilon(\mathbf{q}_e, \omega)]$ for LCAO-TDDFT-$k$-$\omega$ are marked and shown in Figures 10 and 11. We note, as in the case of graphene, that the symmetry of the in-plane response functions means that $\Delta \rho(\mathbf{r}, \mathbf{q}_e, \omega_{ex})$ will be isomorphic to $\Delta \rho(\mathbf{r}, \mathbf{q}_e, \omega_{ex})$. In both cases, the exciton electron is

| Method | A-TiO$_2$ (eV) | R-TiO$_2$ (eV) |
|--------|----------------|----------------|
| Reflectometry | 4.31$^a$ | 4.09$^b$ |
| Ellipsometry | — | 4.22$^c$ |
| $G_0W_0$-BSE | 4.63$^d$ | 4.01$^e$ |
| $G_0W_0$-BSE | 4.61$^f$ | 4.12$^g$ |
| PW-TDDFT-$k$-$\omega$ | 4.93$^h$ | 4.55$^i$ |
| PW-TDDFT-$k$-$\omega$ | 4.90$^j$ | 4.56$^k$ |
| LCAO-TDDFT-$k$-$\omega$ | 4.81$^l$ | 3.48$^m$ |

$^a$ Ref. 88
$^b$ Ref. 91
$^c$ Ref. 92
$^d$ Ref. 68
$^e$ Ref. 69
$^f$ Ref. 89
$^g$ This work.
predominantly located on $d$-orbitals of the Ti atoms. For A-TiO$_2$, these orbitals all point in the same direction, whereas for R-TiO$_2$ there are two orientations of the electron orbitals depending on the Ti atom’s site. The hole, by contrast, is centred on the O atoms. It is clearly seen from Figure 11 that the hole has a 2$p$-character for the R-TiO$_2$, whereas for A-TiO$_2$ (cf. Figure 10) the hole has a mixture of $s$ and $p$-orbital character but is still centred on the O atoms. This is consistent with previous $G_0W_0$ results$^{68}$ which found these excitations are predominantly from O 2$p$ occupied to Ti 3$d$ unoccupied orbitals.

**IV. CONCLUSIONS**

In this work, we have performed a thorough benchmarking of our LCAO-TDDFT-$k$-$\omega$ code$^{59}$, which uses a highly efficient linear combination of atomic orbitals (LCAOs)$^{59}$ to represent the KS wavefunctions, and performs TDDFT calculations in reciprocal space ($k$) and frequency ($\omega$) domains, while restricting calculations to the optical limit $||q|| \rightarrow 0^\circ$. Specifically, we consider a large class of low-dimensional materials, namely C$_{60}$ (0D), metallic (10,10) and semiconducting (10,0) SWCNTs (1D), G$_x$ and P$_n$ (2D), and bulk R-TiO$_2$ and A-TiO$_2$ (3D). Our calculations agree qualitatively and semi-quantitatively with PW-TDDFT-$k$-$\omega$, $G_0W_0$-BSE, and experimental measurements, while reducing the computational cost and improving stability relative to similar TDDFT methods. Working in the optical limit also provides direct access to the exciton’s spatial distribution within the LCAO-TDDFT-$k$-$\omega$ method, and we demonstrate in this work how real space electron and hole density distributions, their difference, both in 3D and 2D projections, and the weights of the transitions in the BZ, provide a better understanding of energy-resolved spatial and reciprocal space excitation profiles. The significant reduction in computational cost when using the LCAO-
TABLE III. Derivative discontinuity correction $\Delta_n$ in eV obtained from a linear combination of atomic orbitals (LCAO) or a plane wave (PW) representation of the KS wavefunctions for a fullerene (C$_{60}$), (10,0) SWCNT, phosphorene (Pn), anatase (A-TiO$_2$), and rutile (R-TiO$_2$).

| Material       | LCAO | PW |
|----------------|------|----|
| C$_{60}$       | 0.77 | —  |
| (10,0) SWCNT   | 0.79 | —  |
| Pn             | 0.58 | 0.55|
| A-TiO$_2$      | 0.85 | 0.89|
| R-TiO$_2$      | 0.67 | 0.72|

TDDFT-$k$-$\omega$ method, combined with its accuracy, opens the door to future studies utilizing this method to perform computational screening studies of optoelectronic, photovoltaic, and photocatalytic systems in silico.

ACKNOWLEDGMENTS

This work was made possible by the facilities of the Shared Hierarchical Academic Research Computing Network (SHARCNET: www.sharcnet.ca) and Compute/Calcul Canada, employed the Imbabura cluster of Yachay Tech University, which was purchased under contract No. 2017-024 (SIE-UITEY-007-2017), and was supported by the QuantXLie Centre of Excellence, a project co-financed by the Croatian Government and European Union through the European Development Fund – the Competitiveness and Cohesion Operational Program (Grant KK.01.1.1.01.0004). K.L. and V.D. are grateful to Yachay Tech University and D.J.M. is grateful to Zoran Mišković and the University of Waterloo for their hospitality during various stages of this research.

Appendix A: Derivative Discontinuity Correction

The derivative discontinuity correction to the exchange part of the GLLB-SC functional $\Delta_n$ provides an ab initio first-order correction to the unoccupied KS eigenenergies using (1). We have employed this correction for all semiconducting materials studied herein.

As shown in Table III, $\Delta_n$ provides a substantial qualitative correction to the conduction bands of these materials, between 0.5 and 0.9 eV. Moreover, as seen from (4), $\Delta_n$ not only shifts the peak positions in the calculated spectra, but also modifies the relative intensities of the peaks. To account for this renormalization of the matrix elements in our PW-TDDFT-$k$-$\omega$ calculations, it has been necessary to rescale the calculated spectra by an ad hoc $\left( \frac{\omega - \Delta_n}{\omega} \right)^2$ factor, which yields semi-quantitative agreement with our LCAO-TDDFT-$k$-$\omega$ spectra (cf. Figures 3, 4, 10, and 11).

TABLE IV. In-plane directional dependence of the dielectric function $\varepsilon(\omega)$ up to 20 eV over irreducible (IBZ) and reducible (RBZ) Brillouin zones for graphene (Gr), phosphorene (Pn), anatase (A-TiO$_2$) and rutile (R-TiO$_2$).

| Material       | IBZ | RBZ | IBZ | RBZ |
|----------------|-----|-----|-----|-----|
| Gr             | 18.505 | 3.037 | 13.817 | 1.824 |
| Pn             | 10.698 | 11.481 | 9.250 | 9.763 |
| A-TiO$_2$      | 13.643 | 0.766 | 12.126 | 0.695 |
| R-TiO$_2$      | 11.889 | 0.494 | 10.776 | 0.367 |

Appendix B: Irreducible Brillouin Zone (IBZ)

From (2) and (4) it is clear that, by their definition, the optical response functions depend explicitly on the vector components of the wavenumber within the BZ. This means that, while it is often computationally convenient to work within the irreducible Brillouin zone (IBZ), such a naive application of the LCAO-TDDFT-$k$-$\omega$ method within the IBZ on a grid of $k$-points with non-trivial symmetries could yield incorrect response functions.

As a measure of the calculated in-plane anisotropy of the dielectric function, in Table IV we provide the real and imaginary parts of the absolute dielectric function difference between $x$ and $y$ components integrated up to 20 eV, i.e., $\int |\varepsilon_{xx} - \varepsilon_{yy}| \, d\omega$, for the 2D and 3D materials studied herein. We neglect the 0D and 1D materials as they employed trivial $k$-meshes. With the exception of Pn, all these materials should exhibit symmetry of the dielectric tensor in the $xy$-plane, i.e., be isotropic.

Overall, numerical and floating point errors and the incompleteness of the LCAO basis set account for the observed differences in the reducible Brillouin zone (RBZ) calculations for planar isotropic materials. However, these results clearly show in their trends the need to account for the vectorial nature of the matrix elements in (4). For this reason, we have averaged over the two directional components, $\varepsilon_q = \frac{1}{2} (\varepsilon_{xx} + \varepsilon_{yy})$, for the in-plane component of the dielectric function for the isotropic materials (Gr, A-TiO$_2$, and R-TiO$_2$), which can be proven geometrically to yield the appropriate response functions.

Appendix C: Spectral Convergence with $k$-Point Spacing

In Figure 12 we plot the convergence of the real part of the in-plane conductivity $\sigma_q(\omega)$ with $k$-point spacing $\Delta k$ for Gr and Pn. These were chosen as they are the two materials considered herein with the greatest band dispersion. For example, a $\Delta k_x = \Delta k_y = 0.05$ nm$^{-1}$ spacing for Gr corresponds to a Monkhorst-Pack 541 $\times$ 541 $\times$ 1 $k$-point mesh.

For Gr, we find that most peaks in the real part of the conductivity are already converged for rather coarse grid spacings of $\Delta k \leq 0.5$ nm$^{-1}$, whereas the peak at 16.3 eV only achieves full convergence with our LCAO-TDDFT-$k$-$\omega$ code for a
very fine grid spacing of $\Delta k \lesssim 0.1$ nm$^{-1}$. This may be due to the fact that the 16.3 eV transition takes place largely at the $\Gamma$ point, as seen in Figure 6, which due to its high symmetry will be more sensitive to minute changes in the $k$-point mesh. For Pn we find its spectra is basically converged for a coarse $\Delta k \lesssim 2$ nm$^{-1}$ grid spacing, with no substantial changes in the conductivity for denser $k$-point meshes.

Appendix D: Implementation of Low-Dimensional Response Functions for Phosphorene

We have used throughout optical response functions appropriate to the dimension of each material to better convey the importance of separating components of these functions depending on their parallel or perpendicular orientation. The use of appropriate response functions becomes apparent especially when dealing with layered materials. In this case, phenomenological models may treat an atomically thin material as either a thin 3D layer, where the 3D dielectric function should be used, or as a 2D boundary condition, where the 2D in-plane conductivity should be used.

In Figure 13, we show experimental reflection spectra $\Delta R/R$ for Pn sandwiched between a sapphire ($\text{Al}_2\text{O}_3$) substrate and insulating hexagonal boron nitride (hBN) flakes of width 15 nm for $x$ and $y$ polarized light$^{85}$. Also shown are two phenomenological models based on the results of our LCAO-TDDFT-$k$-$\omega$ calculations. One is a 3D thin layer model for the air-hBN-Pn-$\text{Al}_2\text{O}_3$ system based on the dielectric function $\varepsilon(\omega)$ computed via the LCAO-TDDFT-$k$-$\omega$ method$^{85}$. The other treats Pn as a boundary condition with the 2D in-plane conductivity $\sigma_r(\omega)$ computed via (10) using Fresnel’s equations through a transfer matrix formalism$^{93}$. The 2D approach yields a smaller tail compared to the 3D model, as well as a sharper peak, more in line with the experimental spectra$^{85}$. However, the 3D model better predicts the behaviour of the reflection spectra after the 1.8 eV peak. It is important to note that the reflection ratio in the 3D model requires an empirical assumption about the thickness of the Pn layer, to which it is directly proportional. We employ a value of 0.5 nm for this thickness, inferred based on the spacing between layers in multilayer phosphorene$^{85}$. The 2D model, by contrast, does not require any such assumption. In this way it is a phenomenological model with fewer free parameters that agrees well with the experimental spectra$^{85}$. Although the use of the optical polarizability is not limited to the LCAO-TDDFT-$k$-$\omega$ method, it is used in our code$^{99}$ to yield results theoretically more suited to lower-dimensional materials.

1. S. Yasutomi, T. Morita, Y. Imanishi, and S. Kimura, “A molecular photodiode system that can switch photocurrent direction,” Science 304, 1944–1947 (2004).
2. M. Galperin and A. Nitzan, “Molecular optoelectronics: The interaction of molecular conduction junctions with light,” Phys. Chem. Chem. Phys. 14, 9421–9438 (2012).
3. L. Xin, M. Lu, S. Both, M. Pfeiffer, M. J. Urban, C. Zhou, H. Yan, T. Weiss, N. Liu, and K. Lindfors, “Watching a single fluorophore molecule walk into a plasmonic hotspot,” ACS Photonics 6, 985–993 (2019).
4. S. M. Falke, C. A. Rozzi, D. Brida, M. Maiuri, M. Amato, E. Sommer, A. D. Sio, A. Rubio, G. Cerullo, E. Molinari, and
and B. F. Milne, “Optical excitations of chlorophyll $a$ and $b$ monomers and dimers,” J. Chem. Phys. 151, 000000 (2019), eprint arXiv:1907.09430.

43. M. R. Preciado-Rivas, V. A. Torres-Sánchez, and D. J. Mowbray, “Optical absorption and energy loss spectroscopy of single-walled carbon nanotubes,” (2019), eprint arXiv:1907.08036.

44. M. Kuisma, A. Sakko, T. P. Rossi, A. H. Larsen, J. Enkovaara, L. Lehtovaara, and T. T. Rantala, “Localized surface plasmon resonance in silver nanoparticles: Atomicistic first-principles time-dependent density-functional theory calculations,” Phys. Rev. B 91, 115431 (2015).

45. T. P. Rossi, S. Lehtola, A. Sakko, M. J. Puska, and R. M. Nieminen, “Nanoplasmonics simulations at the basis set limit through completeness-optimized, local numerical basis sets,” J. Chem. Phys. 142, 094114 (2015).

46. S. L. Adler, “Quantum theory of the dielectric constant in real solids,” Phys. Rev. 126, 413–420 (1962).

47. L. J. Sham and M. Schlüter, “Density-functional theory of the energy gap,” Phys. Rev. Lett. 51, 1888–1891 (1983).

48. O. Gritsenko, R. van Leeuwen, E. van Lenthe, and E. J. Baerends, “Self-consistent approximation to the Kohn-Sham exchange potential,” Phys. Rev. A 51, 1944–1954 (1995).

49. O. V. Gritsenko, R. van Leeuwen, and E. J. Baerends, “Direct approximation of the long- and short-range components of the exchange-correlation Kohn-Sham potential,” Int. J. Quantum Chem. 61, 231–243 (1997).

50. J. P. Perdew, A. Ruzsinszky, G. I. Csöoka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou, and K. Burke, “Restoring the density-gradient expansion for exchange in solids and surfaces,” Phys. Rev. Lett. 100, 136406 (2008).

51. I. E. Castelli, T. Olsen, S. Datta, D. D. Landis, S. Dahl, K. S. Thygesen, and K. W. Jacobsen, “Computational screening of perovskite metal oxides for optimal solar light capture,” Energy Environ. Sci. 5, 5814–5819 (2012).

52. N. Wiser, “Dielectric constant with local field effects included,” Phys. Rev. 129, 62–69 (1963).

53. M. S. Hybertsen and S. G. Louie, “Ab initio static dielectric matrices from the density-functional approach. i. formulation and application to semiconductors and insulators,” Phys. Rev. B 35, 5585–5601 (1987).

54. L. N. Glanzmann, D. J. Mowbray, D. G. F. del Valle, F. Scотовgella, G. Lanzani, and A. Rubio, “Photoinduced absorption within single-walled carbon nanotube systems,” J. Phys. Chem. C 120, 1926–1935 (2015).

55. P. E. Blöchl, “Projector augmented-wave method,” Phys. Rev. B 50, 17953–17979 (1994).

56. P. E. Blöchl, C. J. Först, and J. Schimml, “Projector augmented wave method: Ab initio molecular dynamics with full wave functions,” Bull. Mater. Sci. 26, 33–41 (2003).

57. C. Rostgaard, Exact Exchange in Density Functional Calculations: An Implementation in the Projector Augmented Wave Method, Master’s thesis, Technical University of Denmark, Kongens Lyngby, Denmark (2006).

58. See gitlab.com/lcao-tddft-k-omega/lcao-tddft-k-omega where the LCAO-TDDFT-k-w code is available free of charge.

59. L. S. Blackford, J. Choi, A. Cleary, E. D’Azvedo, J. Demmel, I. Dhillon, J. Dongarra, S. Hammarling, G. Henry, A. Petitet, K. Stanley, D. Walker, and R. C. Whaley, ScalAPACK Users’ Guide (Society for Industrial and Applied Mathematics, Philadelphia, PA, 1997).

60. D. Novko, M. Šunić, and V. Despoja, “Optical absorption and conductivity in quasi-two-dimensional crystals from first principles: Application to graphene,” Phys. Rev. B 93, 125413 (2016).

61. J. J. Mortensen, L. B. Hansen, and K. W. Jacobsen, “Real-space grid implementation of the projector augmented wave method,” Phys. Rev. B 71, 035109 (2005).

62. J. Enkovaara, C. Rostgaard, J. J. Mortensen, J. Chen, M. Dulak, L. Ferrighi, J. Gavnholt, C. Glinsvad, V. Haikola, H. A. Hansen, H. H. Kristoffersen, M. Kuisma, A. H. Larsen, L. Lehtovaara, M. Ljungberg, O. Lopez-Acevedo, P. G. Moses, J. Ojaen, T. Olsen, V. Petzold, N. A. Romero, J. Stausholm-Moller, M. Strange, G. A. Tritisari, M. Vanin, M. Walter, B. Hammer, H. Häkkinen, G. K. H. Madsen, R. M. Nieminen, J. K. Nørskov, M. Puska, T. T. Rantala, J. Schiøtz, S. K. Thygesen, and K. W. Jacobsen, “Electronic structure calculations with GPAW: A real-space implementation of the projector augmented-wave method,” J. Phys.: Condens. Matter 22, 253202 (2010).

63. S. R. Bahn and K. W. Jacobsen, “An object-oriented scripting interface to a legacy electronic structure code,” Comput. Sci. Eng. 4, 56 (2002).

64. A. P.慵ans, J. J. Mortensen, J. Blomqvist, I. E. Castelli, R. Christensen, M. Dulak, J. Friis, M. N. Groves, B. Hammer, C. Hargus, E. D. Hermes, P. C. Jennings, P. B. Jensen, J. Kermode, J. R. Kitchin, E. L. Kolsbjerg, K. Kubal, K. Kaasbjerg, S. Lysgaard, J. B. Maronsson, T. Maxson, T. Olsen, L. Pastewka, A. Petersen, C. Rostgaard, J. Schiøtz, O. Schütt, M. Strange, K. S. Thygesen, T. Vegge, L. Vilhelmsen, M. Walter, Z. Zeng, and K. W. Jacobsen, “The atomic simulation environment—a python library for working with atoms,” J. Phys.: Condens. Matter 29, 273002 (2017).

65. M. Strange, I. S. Kristensen, K. S. Thygesen, and K. W. Jacobsen, “Benchmark density functional theory calculations for nanoscale conductance,” J. Chem. Phys. 128, 114714 (2008).

66. H. J. Monkhorst and J. D. Pack, “Special points for brillouin-zone integrations,” Phys. Rev. B 13, 5188 (1976).

67. H. Sun, D. J. Mowbray, A. Migani, J. Zhao, H. Petek, and A. Rubio, “Comparing quasiparticle H2O level alignment on anatase and rutile TiO2,” ACS Catal. 5, 4242–4254 (2015).

68. A. Migani, D. J. Mowbray, J. Zhao, H. Petek, and A. Rubio, “Quasiparticle level alignment for photocatalytic interfaces,” J. Chem. Theory Comput. 10, 2103–2114 (2014).

69. C. D. Spataru, S. Ismail-Beigi, L. X. Benedict, and S. G. Louie, “Excitonic effects and optical spectra of single-walled carbon nanotubes,” Phys. Rev. Lett. 92, 077402 (2004).

70. D. J. Mowbray and V. Despoja, “Tailoring a molecule’s optical activity using surface plasmonics,” J. Phys. Chem. C (2019), 10.1021/acs.jpcc.9b05770, in press.

71. R. W. Godby and R. J. Needs, “Metal-insulator transition in kohn-sham theory and quasiparticle theory,” Phys. Rev. Lett. 62, 1169–1172 (1989).

72. P. Larson, M. Dvorak, and Z. Wu, “Role of the plasmon-pole model in the gw approximation,” Phys. Rev. B 88, 125205 (2013).

73. J. Berkowitz, “Sum rules and the photoabsorption cross sections of C60,” J. Chem. Phys. 111, 1446–1453 (1999).

74. J. P. Hare, H. W. Kroto, and R. Taylor, “Reprint of: Preparation and uv/visible spectra of fullerene C60 and C70,” Chem. Phys. Lett. 589, 57 – 60 (2013).

75. V. Despoja and D. J. Mowbray, “Using surface plasmonics to turn on fullerene’s dark excitons,” Phys. Rev. B 89, 195433 (2014).

76. R. H. Baughman, A. A. Zakhidov, and W. A. de Heer, “Carbon nanotubes—the route toward applications,” Science 297, 787–792 (2002).

77. X. Wei, T. Tanaka, Y. Yomogida, N. Sato, R. Saito, and H. Katsura, “Experimental determination of excitonic band structures of single-walled carbon nanotubes using circular dichroism spectra,” Nat. Comm. 7, 12899 (2016).

78. R. Senga, T. Pichler, and K. Suenaga, “Electron spectroscopy of single quantum objects to directly correlate the local structure to their electronic transport and optical properties,” Nano Letters 16,
3661–3667 (2016).

P. Umari, O. Petrenko, S. Taioli, and M. M. De Souza, “Communication: Electronic band gaps of semiconducting zig-zag carbon nanotubes from many-body perturbation theory calculations,” The Journal of Chemical Physics 136, 181101 (2012), https://doi.org/10.1063/1.4716178.

A. Vakil and N. Engheta, “Transformation optics using graphene,” Science 332, 1291–1294 (2011).

C. Pai-Yen, A. Christos, F. Mohamed, and G.-D. J. Sebastian, “Flatland plasmonics and nanophotonics based on graphene and beyond,” Nanophotonics 6, 1239 (2017), 6.

T. Susi, D. J. Mowbray, M. P. Ljungberg, and P. Ayala, “Calculation of the graphene C 1s core level binding energy,” Physical Review B 91, 081401(R) (2015).

A. K. Geim and K. S. Novoselov, “The rise of graphene,” Nat. Mater. 6, 183 (2007).

L. Li, J. Kim, C. Jin, G. J. Ye, D. Y. Qiu, F. H. da Jornada, Z. Shi, L. Chen, Z. Zhang, F. Yang, K. Watanabe, T. Taniguchi, W. Ren, S. G. Louie, X. H. Chen, Y. Zhang, and F. Wang, “Direct observation of the layer-dependent electronic structure in phosphorene,” Nat. Nanotechnol. 12, 21 (2016).

Z. Torbatian and R. Asgari, “Plasmonic physics of 2d crystalline materials,” Applied Sciences 8, 238 (2018).

P. M. Echenique and J. B. Pendry, “The existence and detection of rydberg states at surfaces,” J. Phys. C 11, 2065–2075 (1978).

N. Hosaka, T. Sekiya, C. Satoko, and S. Kurita, “Optical properties of single-crystal anatase TiO$_2$,” J. Phys. Soc. Jpn. 66, 877–880 (1997).

M. Landmann, E. Rauls, and W. G. Schmidt, “The electronic structure and optical response of rutile, anatase and brookite TiO$_2$,“ J. Phys.: Condens. Matter 24, 195503 (2012).

L. Chiodo, J. M. García-Lastra, A. Iacomino, S. Ossicini, J. Zhao, H. Petek, and A. Rubio, “Self-energy and excitonic effects in the electronic and optical properties of TiO$_2$ crystalline phases,” Phys. Rev. B 82, 045207 (2010).

M. Cardona and G. Harbecke, “Optical properties and band structure of wurtzite-type crystals and rutile,” Phys. Rev. 137, A1467–A1476 (1965).

M. S. Thomas E. Tiwald, “Measurement of rutile TiO$_2$ dielectric tensor from 0.148 to 33 micrometres using generalized ellipsometry,” Proc. SPIE 4103 (2000), 10.1117/12.403587.

K. Lyon, Analysis of Plasmons Sustained on the Surface of Graphene, Master’s thesis, University of Waterloo, Waterloo, Canada (2014).