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Strong second harmonic generation in SiC, ZnO, GaN two-dimensional hexagonal crystals from first-principles many-body calculations

C. Attaccalite,* A. Nguer,² E. Cannuccia¹ and M. Grüning²

The second harmonic generation (SHG) intensity spectrum of SiC, ZnO, GaN two-dimensional hexagonal crystals is calculated by using a real-time first-principles approach based on Green’s function theory [Attaccalite et al., Phys. Rev. B: Condens. Matter Mater. Phys. 2013 88, 235113]. This approach allows one to go beyond the independent particle description used in standard first-principles nonlinear optics calculations by including quasiparticle corrections (by means of the $GW$ approximation), crystal local field effects and excitonic effects. Our results show that the SHG spectra obtained using the latter approach differ significantly from their independent particle counterparts. In particular they show strong excitonic resonances at which the SHG intensity is about two times stronger than within the independent particle approximation. All the systems studied (whose stabilities have been predicted theoretically) are transparent and at the same time exhibit a remarkable SHG intensity in the range of frequencies at which Ti:sapphire and Nd:YAG lasers operate, thus they can be of interest for nanoscale nonlinear frequency conversion devices. Specifically the SHG intensity at 800 nm ($1.55 \text{ eV}$) ranges from about 40–80 pm $V^2/C_0$ in ZnO and GaN to 0.6 nm $V^2/C_0$ in SiC. The latter value in particular is 1 order of magnitude larger than values in standard nonlinear crystals.

1 Introduction

Following the 2010 Nobel Prize in Physics awarded to Geim and Novoselov for their experiments on graphene,¹ increasing attention has been dedicated to the peculiar electronic and optical properties of two-dimensional (2D) crystals and to their possible technological applications. For example, the photo-luminescence and optical absorption of MoS$_2$ and more in general of transition metal dichalcogenides have been studied extensively. Nonlinear optical properties and specifically second-harmonic generation (SHG) are also the subject of current research. First, SHG is emerging as a spectroscopic tool to non-invasively characterize films of 2D crystals. In fact SHG can probe the number of layers, their orientation and stacking, the edges of the layers, the presence of defects and also the interaction with the substrate.²–⁵ Second, studies on transition metal dichalcogenides indicated that those materials have quite a strong SHG and suggested that they can be integrated in photonic circuits to realize nonlinear optical nanoscale devices.²,⁶,⁷ Finally, besides SHG other nonlinear optical properties are predicted to be particularly strong in 2D crystals, as for example nonlinear optical rectification.⁸

In a previous report⁹ we have studied h-BN and MoS$_2$ 2D crystals using first-principles real-time simulations based on Green’s function theory⁹,¹⁰,¹¹ that includes local-field effects, quasiparticle corrections and excitonic effects. Results from our simulations confirmed the strong SHG of these 2D crystals and highlighted the importance of including many-body effects and going beyond the independent particle (IP) model for those systems. In the IP model [Fig. 1(a)], the optical properties are deduced from the joint-density of states.¹² Spectral features correspond to minima, maxima and saddle points of the joint-density of states. Introducing many-body effects, and specifically electron–hole interaction, may give rise to bound exciton states [Fig. 1(b)] that strongly modify spectral properties. In 2D crystals excitonic effects are expected to be particularly strong due to geometrical confinement and poor screening.⁹ Indeed, we have found strong excitonic one- and two-photon resonances in the SHG of h-BN and MoS$_2$ 2D crystals, affecting the spectral shape and increasing the intensity by a factor 2 when compared with the IP level of theory.

Here we investigate the SHG in GaN, SiC and ZnO 2D hexagonal crystals by first-principles numerical simulations.
The stability of those crystals has been predicted theoretically. Recently, few layer films of ZnO and SiC have been as well realized experimentally: ultrathin hexagonal SiC nanoflakes (0.5–1.5 nm) have been obtained by exfoliation, and monolayers and bilayers of ZnO have been prepared by reactive deposition of Zn on Au(111). Because of their non-centrosymmetric structure GaN, SiC and ZnO 2D crystals are expected to have non-negligible SHG. In fact, a SHG of the order of pm V$^{-1}$ has been measured for ZnO thin films. Indeed, GaN is of particular interest because its electronic and thermal characteristics are remarkable SHG intensity for GaN, SiC and ZnO 2D crystals in the transparency region. Many-body effects are again found to be key in the quantitative description of SHG: excitonic effects enhance the intensity up to about a factor two and redistribute spectral weight significantly.

2 Computational methods

Ground-state densities are obtained within the Kohn–Sham (KS) density functional theory. Density functional theory also provides the KS band structure that however cannot be used directly to extract band gaps but it can be considered to be a good starting point mean-field Hamiltonian for many-body perturbation theory. We then use the GW approach—briefly described here in Section 2.1—to obtain the quasiparticle band structures perturbatively from the KS one (for a review of methods available to predict electronic energies see e.g. Walsh and Butler). The obtained quasiparticle energies are then input to the calculations for optical properties within the Bethe–Salpeter equation framework (see Section 2.1 for the linear response and Section 2.2 for the real-time approach).

2.1 Quasiparticle band structure and optical absorption

The quasiparticle band structures are obtained within the GW approach. Specifically, we use non-self-consistent GW (denoted as $G_0W_0$) in which the screened Coulomb potential, $W$, and the Green’s function, $G$, are built from the KS eigensolutions $|\psi_{nk}\rangle/nk\rangle$ (with $k$ the crystal wave vector and $n$ the band index) and then the quasiparticle energies are obtained from:

$$\varepsilon_{nk}^{QP} = \varepsilon_{nk} + Z_{nk}\Delta\varepsilon_{nk}(\varepsilon_{nk}).$$

In eqn (1)

$$Z_{nk} = [1 - \partial\Delta\varepsilon_{nk}/\partial\varepsilon_{nk}|_{\varepsilon_{nk}}]^{-1},$$

is the renormalization factor and

$$\Delta\varepsilon_{nk} = \langle nk|\Delta\varepsilon|nk\rangle,$$

where

$$\Delta\varepsilon = \Sigma - V^{\text{xc}},$$

is the difference between $\Sigma = GW$, the GW self-energy, and $V^{\text{xc}}$, the exchange–correlation functional used in the KS calculations.

The optical-spectra are calculated by solving the Bethe–Salpeter equation (BSE):

$$\left(\varepsilon_{nk}^{QP} - \varepsilon_{nk}^{OP}\right) A_{\gamma\epsilon\gamma'}^{\epsilon\gamma'} + \sum_{\gamma\epsilon\gamma'} \langle\gamma\epsilon|K_{\gamma\epsilon}|\gamma\epsilon'\gamma'\rangle A_{\gamma\epsilon\gamma'}^{\epsilon\gamma'} = \Omega^{\gamma\epsilon}\epsilon_{nk}^{\gamma\epsilon'}.$$

Here, the electronic excitations are expressed in a basis of electron–hole pairs $|\gamma\epsilon\rangle$ corresponding to transitions at a given $k$ from a state in the valence band $|\gamma\rangle$ with energy $\varepsilon_{nk}^{OP}$ (hole) to a conduction-band $|\epsilon\rangle$ state with energy $\varepsilon_{nk}^{OP}$ (electron). $A_{\gamma\epsilon\gamma'}^{\epsilon\gamma'}$ are the expansion coefficients of the excitons in the electron–hole basis and the $\Omega^{\gamma\epsilon}$ are the excitation energies of the system.

2.2 Second-harmonic generation

Nonlinear optical properties are obtained within the real-time approach suggested by Souza et al. This approach was recently implemented by the authors within a first-principles framework. In this approach the time-dependent Schrödinger equation

$$ih\frac{d}{dt}|\psi_{nk}\rangle = \left(\hat{H}_0^{\text{KS}} + i\hat{\sigma} \cdot \hat{\partial}_{\varepsilon}\right)|\psi_{nk}\rangle.$$

is integrated to obtain the time-dependent valence states, $|\psi_{nk}\rangle$. The latter is the periodic part of the Bloch states that determines the system polarization. In the r.h.s. of eqn (3), $\hat{H}_0^{\text{KS}}$ is the system Hamiltonian—which in this section; the second term, $\hat{\sigma} \cdot \hat{\partial}_{\varepsilon}$, describes the coupling...
with the external field $\varepsilon$ in the dipole approximation. As we impose the Born–von Kármán periodic boundary conditions, the coupling takes the form of a $k$-derivative operator $\partial_k$. The tilde indicates that the operator is “gauge covariant” and guarantees that the solutions of eqn (3) are invariant under unitary rotations among occupied states at $k$ (see Souza et al.\textsuperscript{30} for a thorough discussion of this point).

From $|v_{nk}|$, the time-dependent polarization of the system $P_t$ along the lattice vector $a$ is calculated as

$$P_t = \frac{ef}{2\pi N_k} \sum_{k} \text{Im} \log \prod_{k_i} \det S(k, k + q_j).$$ \hspace{1cm} (4)

where $S(k, k + q_j)$ is the overlap matrix between $|v_{nk}|$ and $|v_{nk-q_j}|$. Furthermore, $v$ is the unit cell volume, $f$ is the spin degeneracy, $N_k$ and $N_{k_i}$ are respectively the number of $k$ points along and perpendicular to the polarization direction, and $q_j = 2\pi|N_{nk-a}|$. Finally, the second harmonic coefficient is extracted from the power series of the polarization in the laser field $\varepsilon$

$$P = \chi^{(1)} + \chi^{(2)} \varepsilon \varepsilon + \ldots$$ \hspace{1cm} (5)

as detailed in Attaccalite et al.\textsuperscript{11}

In eqn (3), the model Hamiltonian chosen for $H_{\text{sys}}^{\text{KS}}$, determines the level of approximation in the description of correlation effects in the SHG spectra. In this work we use two different models for the system Hamiltonian: (i) the independent-particle (IP) model,

$$H_{\text{IP}}^{\text{KS}} \equiv H_{\text{KS}},$$ \hspace{1cm} (6)

and (ii) the $GW + BSE$ model,

$$H_{\text{GW+BSE}}^{\text{KS}} \equiv H_{\text{KS}} + \Delta H_k + V_0(r)[\Delta \rho] + \Sigma_{\text{SEX}}[\Delta \gamma],$$ \hspace{1cm} (7)

where

$$\Delta \rho = \rho(r; t) - \rho(r; t = 0)$$

is the variation of the electronic density and

$$\Delta \gamma = \gamma(r, r'; t) - \gamma(r, r'; t = 0)$$

is the variation of the density matrix induced by the external field $\varepsilon$.

In eqn (6) and (7), $H_{\text{KS}}^{\text{KS}}$ is the unperturbed KS Hamiltonian. In eqn (7), the second term, $\Delta H_k$ contains the quasiparticle corrections to KS energies as obtained from eqn (1). The next term, $V_0(r)[\Delta \rho]$ is the Hartree\textsuperscript{10} potential and is responsible for the local-field effects\textsuperscript{31} originating from system inhomogeneities. The last term $\Sigma_{\text{SEX}}$, is the screened-exchange self-energy that accounts for the electron–hole interaction,\textsuperscript{29} and is given by the convolution between the screened interaction $W$ and $\Delta \gamma$. In the linear response limit the $GW + BSE$ model reproduces the optical absorption calculated as in eqn (2), as shown both analytically and numerically in Attaccalite et al.\textsuperscript{10}

### 2.3 Numerical details

Density functional calculations of the ground-state density, optimized cell geometry and KS electronic structure are performed using the QUANTUM ESPRESSO code.\textsuperscript{34} The KS wave functions are expanded in plane-waves and the effects of core electrons are simulated by norm-conserving pseudopotentials.\textsuperscript{35} The exchange–correlation functional is treated within the local density approximation (LDA).\textsuperscript{36,37} Table 1 reports the relevant parameters for the specific KS calculations.

The quasiparticle and optical absorption calculations are carried out using the Yambo code.\textsuperscript{38} The screened Coulomb potential $W$ has been evaluated within the random-phase approximation (RPA). In the GW approach we used the Godby–Needs plasmon-pole model to approximate the dynamical behavior of $W$,\textsuperscript{39} while in the BSE framework we use the static approximation.\textsuperscript{29} The number of unoccupied bands used in the expansion of the self-energy and Green’s function for SiC, ZnO and GaN are respectively 100, 150 and 100. We use a cutoff of 3 Ha for the off-diagonal components of the dielectric matrix $\varepsilon_{ij}^{GQ}$. The same parameters are used to calculate the static dielectric constants.

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<th>$E_{\text{cut}}$(Ha)</th>
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<th>$d$(Å)</th>
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<tr>
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<td>16 (SC)</td>
<td>3.069</td>
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<tr>
<td>80</td>
<td>20 (IP)</td>
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<tr>
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<tr>
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<tr>
<td>Type: TM</td>
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</tr>
</tbody>
</table>

Table 1 Parameters used in the KS calculations. PP: pseudopotential components and scheme for each atom. "vBC" and "TM" refer respectively to the von Barth–Car and Troullier–Martins schemes. $E_{\text{cut}}$: energy cutoff for the plane-waves. $k$-grids: number of $k$ points of the Monkhorst–Pack grid in each of the two periodic dimensions for the self-consistent (SC) calculation of the density, and to obtain the KS eigensolutions for the IP and BSE calculations; $a$: lattice parameter obtained from the geometry optimization; $d$: the effective thickness used to evaluate the second harmonic response (see text)

### 2.4 Time-dependent density functional theory

The time-dependent density functional theory (TDDFT) is an extension of the ground-state density functional theory (DFT) to time-dependent systems. It provides a powerful tool to study the electronic dynamics of materials at the molecular scale. TDDFT is based on the Kohn–Sham (KS) equations and the time-dependent Schrödinger equation (TDSE).

The Hamiltonian for the time-dependent DFT is given by

$$H(t) = H_0 + \sum_{\alpha} \int \rho(t, r) \epsilon_{\alpha}(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') \text{d}^3r'$$

where $H_0$ is the ground-state Hamiltonian and $\rho(t, r)$ is the time-dependent density matrix.

The TDDFT approach is based on the following equations:

$$\frac{\partial \rho(t, \mathbf{r})}{\partial t} = -i [H(t), \rho(t, \mathbf{r})] + \text{G} \rho(t, \mathbf{r})$$

$$\text{G} = \frac{1}{2} \int \text{d}^3r' \text{G}(\mathbf{r}, \mathbf{r}') - \frac{1}{2} \int \text{d}^3r'' \text{G}(\mathbf{r}, \mathbf{r}'')$$

where $\text{G}$ is the Green’s function.

The TDDFT approach provides a way to calculate the electronic transitions in a material by computing the transition dipole moments between the occupied and unoccupied states.

### 2.5 BSE calculations

The Bethe–Salpeter equation (BSE) is an important tool for the calculation of optical properties of materials. It describes the interaction between quasiparticles and provides a way to calculate the quasiparticle energies and optical absorption coefficients.

The BSE is given by

$$\text{G}_{\alpha\beta}(\mathbf{r}, \mathbf{r}') = T_{\alpha\beta} \text{G}_{\alpha\beta}(\mathbf{r}, \mathbf{r}') + \sum_{\gamma} \int \frac{\text{d}^3r''}{(2\pi)^3} V_{\alpha\gamma}(\mathbf{r}, \mathbf{r}'') \text{G}_{\gamma\beta}(\mathbf{r}'', \mathbf{r})$$

where $T_{\alpha\beta}$ is the matrix element for the electron–electron interaction and $V_{\alpha\beta}$ is the matrix element for the electron–photon interaction.

### 2.6 SHG calculations

The second harmonic generation (SHG) is a nonlinear optical effect in which an electric field at frequency $\omega$ produces an electric field at frequency $2\omega$. SHG is calculated as

$$S^{(2)}(2\omega) = \int \text{d}^3r \text{d}^3r' \text{d}^3r'' \rho(t, \mathbf{r}) \rho(t, \mathbf{r}') \rho(t, \mathbf{r}'') \text{G}(\mathbf{r}, \mathbf{r}'') \text{G}(\mathbf{r}'', \mathbf{r})$$

where $\rho(t, \mathbf{r})$ is the electronic density and $\text{G}$ is the Green’s function.

### 2.7 Electronic structure calculations

The electronic structure of a material is calculated using density functional theory (DFT). DFT is a quantum mechanical formalism that allows for the calculation of electronic properties of materials.

The Kohn–Sham equations are given by

$$\text{H}(\mathbf{r}) \phi_i(\mathbf{r}) = E_i \phi_i(\mathbf{r})$$

where $\text{H}$ is the Hamiltonian, $\phi_i$ is the Kohn–Sham orbital, and $E_i$ is the orbital energy.

The electronic structure calculations are performed using the QUANTUM ESPRESSO code. The calculations are done for the ground-state density and to obtain the KS eigensolutions for the IP and BSE calculations.

### 2.8 Optical properties

The optical properties are calculated using the self-energy approach. The self-energy is given by

$$\Sigma(\mathbf{r}, \mathbf{r}') = \sum_{\gamma} \int \frac{\text{d}^3r''}{(2\pi)^3} V_{\gamma\gamma}(\mathbf{r}, \mathbf{r}'') \text{G}_{\gamma\gamma}(\mathbf{r}'', \mathbf{r})$$

The optical properties are calculated using the GW and BSE approaches.

### 2.9 Tables

<table>
<thead>
<tr>
<th>Material</th>
<th>$E_{\text{cut}}$(Ha)</th>
<th>$a$(Å)</th>
<th>$d$(Å)</th>
</tr>
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<tbody>
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<td>40</td>
<td>16 (SC)</td>
<td>3.208</td>
</tr>
<tr>
<td>GaN</td>
<td>40</td>
<td>16 (SC)</td>
<td>3.169</td>
</tr>
</tbody>
</table>

Table 2 Parameters extracted from the GW calculations by a linear fit and used to account for the quasiparticle corrections in the GW + BSE real-time simulations. See text
from the $GW$ calculations by assuming a linear relation between the quasiparticles and KS energies.

As we are working with a plane-wave basis set and thus with periodic boundary conditions, we simulate isolated monolayers by a slab supercell approach with a 30 a.u. inter-sheet distance along the $z$-direction. In the calculations of the screened Coulomb potential $W$, we cutoff the long-range interaction between the periodic images by using the scheme of Rozzi et al.\textsuperscript{40}

Eqn (3) is integrated numerically for a time-interval of 55 fs using the same numerical approach of Souza et al.\textsuperscript{39} (originally taken from Koonin et al.\textsuperscript{41}) with a time-step of $\Delta t = 0.005$ fs that guarantees accuracy and stable results. We use sinusoidal monochromatic laser fields polarized along $y$, with an intensity of $I = 500$ kW cm$^{-2}$. In eqn (3) we add a dephasing term with $\tau = 6$ fs to simulate a finite broadening of about 0.2 eV.\textsuperscript{11} To evaluate the static dielectric constant and the SHG of the two-dimensional layers we used an effective thickness equal to the interlayer distance in the corresponding bulk material for ZnO\textsuperscript{12} and GaN\textsuperscript{43} and equal to the one used by Wu et al.\textsuperscript{22} for the SiC, as reported in Table 1.

### 3 Results

In this section for hexagonal SiC, ZnO and GaN monolayers we discuss the electronic band structure, obtained from the $G_0W_0$ calculations [eqn (1)], the optical absorption spectra obtained within the IP and $GW + BSE$ approaches [eqn (2)] and finally the SHG obtained from real-time simulations again within both the IP and $GW + BSE$ approaches [eqn (3)-(7)].

#### 3.1 SiC monolayer

We found (Table 3) that within the $GW$ approximation the SiC monolayer has a direct minimum gap at $K$ of 3.96 eV (LDA gives 2.59 eV). For the $K$-$M$ indirect gap our $GW$ calculations gives 4.00 eV (LDA gives 2.54 eV). The values we found agree within one-tenth of eV with previous reports of Lu et al.\textsuperscript{44} and of Bekaroglu et al.\textsuperscript{45} though $GW$ predicts an indirect band gap material there. On the other hand, Hsueh et al.\textsuperscript{46} found by $GW$ calculations that the minimum band gap is direct at $K$ (though again really close to the indirect at $K$-$M$), but reported $G_0W_0$ corrections that are 0.5 eV larger than ours. This quite large disagreement may be the effect of the different plasmon-pole model used to approximate the frequency behaviour of the screened Coulomb potential. In fact it has been recently shown\textsuperscript{47} that the Hybertsen–Louie plasmon-pole model (used by Hsueh et al.\textsuperscript{46}) tends to overestimate the band gap when compared with “full frequency” calculations (that means without any plasmon-pole approximation) or with the Godby–Needs plasmon-pole model, used in this work. The static dielectric constant calculated within the RPA is 8.25, smaller than 9.66 found (experimentally) for the bulk.\textsuperscript{48}

At the IP level the absorption spectrum [Fig. 2(b)] presents two main features in the 0–6 eV laser-frequency range: a shoulder at 2.59 eV and a peak at 3.24 eV. They correspond to transitions from the top-valence to the bottom conduction band predominantly along the $K$-$M$ direction. In the SHG intensity [Fig. 2(a)] one recognizes the corresponding two-photon and one-photon resonances respectively at about 1.3 eV, 1.6 eV and 2.6 eV. The shoulder at 3.2 eV results from the interference of one-photon resonance at 3.24 eV and two-photon resonances with higher energy transitions. Near 4 eV is also visible a two-photon resonance with transitions involving higher lying conduction bands. The shape and the magnitude of the SHG intensity spectrum agree well with the calculations (at the same level of theory) by Wu et al.\textsuperscript{22}

Fig. 2(d) shows the absorption spectrum at the $GW + BSE$ level. Clearly, correlation effects, more specifically electron-hole interaction, dramatically change the monolayer absorption. The van Hove singularities are now replaced by sharply bound excitons peaks at about 2.7 eV, 3.2 eV, 3.4 eV and 3.6 eV. The binding energies of the lowest bright exciton is thus 1.2 eV. The relative height and position of the peaks, and the binding

![Fig. 2](image-url)

**Table 3** Band gap $E_g$ within the KS-density functional theory and the $G_0W_0$ approximation. Static dielectric constant $\varepsilon_0$ within the RPA. SHG intensity (in pm V$^{-1}$) at zero frequency within the IP approximation $|\chi^{(2)}(0)|$ and within the $GW + BSE$ framework $|\chi^{(2)}(0)|$

| Sys. | $E_g^{KS}$ (eV) | $E_g^{G_0W_0}$ (eV) | $\varepsilon_0$ | $|\chi^{(2)}(0)|$ | $|\chi^{(2)}(0)|$ |
|------|----------------|------------------|-------------|----------------|----------------|
| SiC  | 2.54           | 3.96             | 8.25        | 122(1)         | 141(1)         |
| ZnO  | 1.70           | 3.01             | 5.83        | 10.0(1)        | 14.7(7)        |
| GaN  | 2.36           | 4.27             | 7.33        | 18.07(4)       | 33.6(3)        |
The energy for the first exciton are in quite good agreement with calculation of Hsueh et al.\textsuperscript{46} The absolute position of the peaks differs instead by about 0.4 eV because of the difference in the $GW$ quasiparticle corrections discussed previously. Note that there is a nearly perfect cancellation between the quasiparticle correction (shift towards higher energies) and the effect of the electron–hole attraction (shift towards lower energies) so that the exciton position almost coincides with the corresponding KS minimum gap at $K$. A similar cancellation is observed as well for the MoS\textsubscript{2} monolayer as shown before.\textsuperscript{49} As a consequence the position of the main features in the SHG at the $GW + BSE$ level [Fig. 2(c)] is very similar to the IP one. However, when observed at the same scale, excitonic resonances at two ($\approx 1.4$ eV and $1.7$ eV) and one-photon ($\approx 2.7$ eV) are clearly dominating the spectrum enhancing the intensity by a factor of about 1.5. Fig. 3(a) shows the separate contributions of the SHG real and imaginary components. By comparing the $GW + BSE$ and IP results the effect of excitonic resonances is clearly recognizable from the pronounced features at 1.35 eV in the imaginary part and 1.65 eV in the real part. By extrapolating the low energy part of the SHG spectra we obtain an estimate for the zero-frequency SHG (Table 3). Also in the static limit, out of resonance, excitonic effects enhance the SHG by a factor of almost 1.3 with respect to the IP approximation. The IP value is in good agreement with Wu et al.,\textsuperscript{22} once accounting for the different convention used by the authors.\textsuperscript{50}

### 3.2 ZnO monolayer

For the ZnO monolayer the $GW$ approximation gives a direct minimum gap at $\Gamma$ of $3.01$ eV [LDA gives $1.70$ eV] in agreement with the results of Wei et al.\textsuperscript{51} For the static dielectric constant we found a value of 5.83 (within the RPA) much larger than the experimental value for the bulk of 3.74, but close to the value calculated for the bulk within RPA by Shishkin and Kresse.\textsuperscript{52}

In the bulk the large difference between the calculated and experimental dielectric constant was attributed to the large self-interaction error for the d bands in the KS calculations. In that case overestimating the screening resulted in an underestimation of the $GW$ band gap.

Again the optical absorption spectrum at the IP level [Fig. 4(b)] presents typical van Hove singularities expected in the 2D case: a shoulder at about 1.70 eV, corresponding to the minimum in the joint-density of states at $\Gamma$, and a peak at about 7.2 eV corresponding to transitions between the two lowest conduction and two higher valence bands for points close to $M$ and $K$ (saddle points). The SHG intensity at this level of theory [Fig. 4(a)] presents similar features: a broad shoulder between 0.8 and 2 eV corresponds to two- and one-photon resonances with the minimum gap transition at $\Gamma$; the peak at 3.5 eV is a two-photon resonance with the transition at points close to $K$ and $M$. Remarkably, at this level of theory the ZnO monolayer presents a very weak SHG intensity when compared with the other 2D hexagonal monolayer studied in this or our previous work.\textsuperscript{9}

Similarly to SiC, when we include correlation effects within the $GW + BSE$ approximation, we observe the formation of (bound) exciton states. The optical absorption spectrum [Fig. 4(d)] presents...
two main exciton peaks at about 1.6 eV and 6.2 eV. Good agreement is found with the spectrum in the work of Wei et al. The first exciton peak is mainly associated with the transitions between the first two valence bands and the last conduction bands around $\Gamma$. Its exciton binding energy of 1.5 eV cancels almost completely the quasi-particle blue-shift, so that the spectrum onset is close to the IP one, as observed for SiC and MoS$_2$. Finally, the SHG intensity [Fig. 4(c)] is enhanced by correlation effects, with three strong features at low energy (at about 0.8 eV, 1.5 eV and 1.7 eV) corresponding to the two-and one-photon resonances with the exciton at 1.6 eV. Fig. 3(b) shows the contribution from the real and imaginary part of SHG to those features. Note that at resonances the intensity is enhanced by about 2 times compared with the IP case. A smaller enhancement factor (about 1.5) is observed instead for the SHG in static limit in Table 3.

### 3.3 GaN monolayer

By $G_0W_0$ calculations we found the GaN monolayer has a direct band gap of 4.27 eV (at $\Gamma$) whereas the LDA the gap is indirect ($K\Gamma$) and gives 2.36 eV. (Table 3). Results for the gap are close to those reported by Chen et al., but smaller than those reported by Ismail–Beigi. As previously discussed for the SiC the difference can be ascribed to the plasmon-pole model used to approximate the frequency dependence of the screening. The static dielectric constant from RPA is 7.33, smaller than the value of 8.9 measured in the bulk. In Fig. 4 the IP optical absorption spectrum [panel (b)] shows a shoulder at 2.6 eV (from $\Gamma$) and a peak at about 5.1 eV (from $M$ and $K$). The SHG [(a) panel] then has a weak two-photon resonance peak around 1.3 eV, a strong peak at 2.55 eV (that corresponds to the interference of one-photon and two-photon resonances with the transitions at about 2.4 eV and at 5.0 eV) and a one-photon resonance with the transitions at about 2.4 eV. At the $GW+BSE$ level the optical absorption spectrum [panel (d)] is again strongly modified. The onset for the absorption is shifted towards higher energies due to the quasiparticle corrections and the spectrum shows two exciton strong peaks at 3.1 eV and 4.8 eV. The position and relative intensity of the peaks are in fair agreement with the calculations of Ismail–Beigi. For the SHG spectrum [Fig. 5(c) and 3(c)], excitonic effects enhance the intensity at the two-photon resonances (1.55 eV and 2.1 eV), by a factor of about 2 and 1.5 respectively. In the static limit the intensity is as well increased by a factor 2. To note that the onset of the absorption spectrum is blue shifted by 0.5 eV with respect to the IP spectrum as quasiparticle shifts are larger than the energy red-shift from the electron–hole interaction for the first exciton. On the other hand in the SHG the strongest feature corresponding to the two-photon resonance with the exciton at 4.8 eV (at the $GW+BSE$ level) is red-shifted with respect to the strongest feature in the IP spectrum. As a consequence, within the $GW+BSE$ approach the strongest SHG is in the transparency region. Conversely at the IP level the strongest SHG is in a region in which the system absorbs.

### 4 Conclusions

We have performed first-principles calculations of SHG of 2D hexagonal crystals with broken inversion symmetry both at the IP level and $GW+BSE$ level of approximation. At the IP level, the SHG intensity spectra reflect closely the electronic structure of the particular material showing two- and one-photon resonances in correspondence of singular points of the joint density of states. On the other hand, the comparison with the more accurate $GW+BSE$ approach clearly shows the importance of including correlation effects. In fact we observed an enhancement of up to 2 times of the SHG intensity at excitonic resonances at the $GW+BSE$ level. Furthermore the example of GaN is emblematic: the IP approach predicts that the light-absorption is significant at the frequencies for which the SHG is the strongest; the $GW+BSE$ approach instead predicts that the most intense SHG is in the transparency region of the material.

Remarkably (also considering the subnanometric effective thickness), for the studied 2D hexagonal crystals we obtain a SHG intensity of the order of tens of nm V$^{-1}$ for SiC and 40–80 pm V$^{-1}$ for ZnO and GaN, smaller than what we predicted for 2D MoS$_2$ and what has been observed experimentally for MoS$_2$ and WS$_2$, but still large. For comparison conventional nonlinear crystal used in frequency doubling of Nd:YAG and Ti:sapphire lasers are of the order of 10 pm V$^{-1}$. Furthermore all the systems under study are transparent below...
1.5 eV (above 825 nm) and the SHG has peaks at 0.93–1.16 eV (1068–1333 nm) for ZnO—thus in the region of Nd:YAG laser emission lines—1.55 eV (800 nm) for GaN and 1.36 eV–1.60 eV (775–911 nm) for SiC—in the emission range of the Tisapphire laser.

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References

35. Pseudopotentials are taken from the libraries at http://www.quantum-espresso.org/pseudopotentials.