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Hipólito, Fábio; Pedersen, Thomas Garm

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Optical third harmonic generation in black phosphorus

F. Hipolito^{1,*} and T. G. Pedersen^{1,2,†}

¹*Department of Physics and Nanotechnology, Aalborg University, DK-9220 Aalborg Øst, Denmark*

²*Center for Nanostructured Graphene (CNG), DK-9220 Aalborg Øst, Denmark*



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We present a calculation of third harmonic generation (THG) for two-band systems using the length gauge that avoids unphysical divergences otherwise present in the evaluation of the third-order current density response. The calculation is applied to bulk and monolayer black phosphorus (bP) using a nonorthogonal tight-binding model. Results show that the low-energy response is dominated by mixed inter-intraband processes and estimates of the magnitude of THG susceptibility are comparable to recent experimental reports for bulk bP samples.

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I. INTRODUCTION

Nonlinear light-matter interactions provide a vast field of processes with many applications [1,2], particularly at energies comparable to the near-IR and visible radiation. Applications include four-wave mixing [3,4], efficient lasing [5], and harmonic generation, more specifically third harmonic generation (THG) [6,7] and second harmonic generation (SHG) in noncentrosymmetric crystals, such as transition-metal dichalcogenides (TMDs) [8–13] and hexagonal boron nitride (hBN) [8]. Recent advances in atomically thin materials, such as graphene, TMDs, and others have sparked interest in two-dimensional (2D) optoelectronic devices. The isolation of mono- and few-layer crystals of bP provides new 2D materials with remarkable electronic properties, including thickness-dependent gap and strong in-plane anisotropy. On its own, the thickness-dependent gap of bP [14–17] makes it appealing for optoelectronic devices, since its optical gap spans a wide range of the spectrum, from infrared ~ 0.3 eV in bulk samples to visible ~ 1.7 eV in monolayer [17]. Moreover, the low energy dispersion of bP exhibits strong anisotropy, leading to a large discrepancy in the effective masses of the valence and conduction bands along the armchair and zigzag directions.

The low energy dispersion can be accurately captured by anisotropic massive Dirac fermion models [18,19]. In such systems, electrons effectively behave as light massive Dirac fermions along the armchair direction and as heavy fermions along the zigzag direction, consistent with *ab initio* results [14,20–22] and experimental ARPES measurements of the band structure [23]. The manifestations of anisotropy are tightly connected to the lattice symmetry. Both bulk and monolayer bP are orthorhombic crystals with inversion center, with space groups D_{2h}^{18} [24] and D_{2h}^7 [25], respectively. Because of the presence of an inversion center dipole, allowed second-order interactions are blocked [1,2], making the THG the leading order for harmonic generation. Recent reports have demonstrated that the electronic and transport properties of

bP can be used for several applications, including field-effect transistors [16,26–28]. The electronic properties of bP provide fertile ground for opto-electronics devices, such as photodetectors [28,29], dichroic absorption [30] and nonlinear optics, including THG [31–33] and high harmonic generation [19]. In addition, theoretical studies indicate that the anisotropic characteristics of bP can be harnessed and tuned by strain [34–36], opening a door for strain-sensitive or strain-enhanced optoelectronic devices based in bP.

In this work, we evaluate the current density response of two-band systems using the length gauge [19,37] and determine the nonlinear THG conductivity tensor. Moreover, we show that the spurious divergences, present in the straightforward evaluation of the nonlinear conductivity, $\sigma_{\phi\lambda\beta\alpha}$, of the third-order current response [37] vanish by considering the relevant combinations of $\sigma_{\phi\lambda\beta\alpha}$. We then use these results to compute and characterize the low-energy THG in bP.

II. THEORETICAL FRAMEWORK

The aim of the present work is to characterize the THG at the energy scale of the optical gap, $\hbar\omega \sim E_g$. At this energy scale, the electronic and optical properties of bP, and those of many other materials (e.g., biased bilayer graphene [38], hexagonal boron nitride [39], etc.) are dominated by the dynamics of the top valence and bottom conduction bands [14,19–22]. The present work is an extension of Ref. [19], including extensive generalizations to accommodate purely interband and mixed inter-intraband processes involving the valence and conduction band of cold insulators, rather than the purely intraband motion of doped semiconductors or metals that typically manifests itself at a smaller energy scale. The importance of inclusion of mixed inter-intraband processes for an accurate description of nonlinear processes is demonstrated for THG at this energy scale, where the response is clearly dominated by these processes. In addition, we consider a tight-binding (TB) model applicable to both monolayer and bulk bP, rather than an effective model for the conduction band in the vicinity of the Γ point.

We are interested in characterizing the interaction of light with the electronic system of crystals, within the dipole

*fh@nano.aau.dk

†tgp@nano.aau.dk

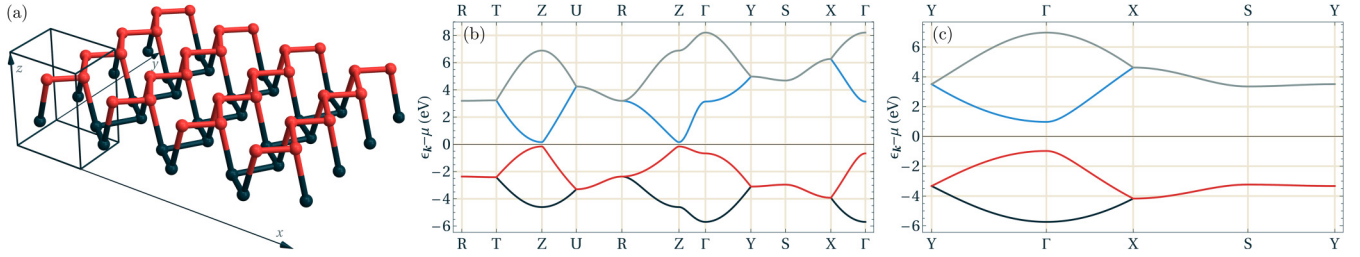


FIG. 1. Monolayer lattice for bP (a) and the energy dispersion along high symmetry paths for bulk (b) and monolayer (c).

approximation, and therefore ignoring the position dependence of the electromagnetic field. In this approximation, the total Hamiltonian reads

$$\hat{H} = \hat{H}_0 + \hat{V}(t), \quad \hat{V}(t) = e \hat{\mathbf{r}} \cdot \mathbf{E}(t), \quad (1)$$

where \hat{H}_0 defines the unperturbed Hamiltonian for the crystal, $\hat{V}(t)$ contains the time-dependent field, and $e > 0$ is the elementary charge. In addition, the electromagnetic field is monochromatic and linearly polarized:

$$\mathbf{E}(t) = \sum_{\alpha=x,y,z} [E_{\omega}^{\alpha} e^{-i\omega t} + E_{-\omega}^{\alpha} e^{i\omega t}] \mathbf{e}_{\alpha}/2, \quad (2)$$

propagating along the z axis, normal to the crystal plane. The polarization plane defined by the angle relative to the x axis, such that $E_{\omega}^{\alpha} \equiv E_{\omega}^0(\cos \theta, \sin \theta, 0)$. The diagonalization of the unperturbed periodic Hamiltonian defines the crystal band dispersions $\epsilon_m(\mathbf{k})$ and respective eigenstates, $|m, \mathbf{k}\rangle$, which serve as the basis for the calculation of the linear and nonlinear response. The calculation of the response is based on the time-dependent density operator, $\hat{\rho}(t) \equiv \sum_{mn} \rho_{mn} |m\rangle \langle n|$, that obeys the quantum Liouville equation $i\hbar \partial \hat{\rho} / \partial t = [\hat{H}, \hat{\rho}]$, which lends itself to a perturbative expansion. In this paper, we do not consider electron-electron interaction, e.g., excitonic effects, and therefore the many-body effects arise from the Fermi-Dirac statistics only.

A. π -electron tight binding

To characterize the low-energy properties of bP, we consider a nonorthogonal TB model with a p_z orbital per atom in the unit cell. The Fourier transforms of the Hamiltonian and the respective overlap matrix read

$$\hat{H}_{ij}(\mathbf{k}) = \sum_{\alpha\beta, \mathbf{R}} t_{ij}^{\alpha\beta}(\mathbf{r}_i - \mathbf{r}_j + \mathbf{R}) e^{i\mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j + \mathbf{R})}, \quad (3a)$$

$$\hat{S}_{ij}(\mathbf{k}) = \sum_{\alpha\beta, \mathbf{R}} s_{ij}^{\alpha\beta}(\mathbf{r}_i - \mathbf{r}_j + \mathbf{R}) e^{i\mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j + \mathbf{R})}, \quad (3b)$$

where \mathbf{r}_i defines the position of the i th atom in the unit cell centered at \mathbf{R} . Furthermore, we consider that the hopping ($t_{ij}^{\alpha\beta}$) and overlap ($s_{ij}^{\alpha\beta}$) integrals between orbitals $\{\alpha, \beta\}$ of atoms $\{i, j\}$ exhibit spatial dependence like that of Slater-Koster two center integrals [40]. The above-mentioned integrals are evaluated with density functional tight binding [19,41,42], using the bulk parameters for bP [24] with a covalent radius of 2.08 Å. The lattice is depicted in Fig. 1(a), where the lattice

parameters read $a_1 = 4.376$, $a_2 = 3.314$ and $a_3 = 5.209$ Å and the respective atom positions read

$$\mathbf{r}_1 = (-d, 0, -h), \quad (4a)$$

$$\mathbf{r}_2 = (d, 0, h), \quad (4b)$$

$$\mathbf{r}_3 = (a_1/2 + d, a_2/2, h), \quad (4c)$$

$$\mathbf{r}_4 = (a_1/2 - d, a_2/2, -h), \quad (4d)$$

with $d = 0.3525$ and $h = 1.065$ Å [24]. This parametrization leads to energy dispersion consistent with *ab initio* results [14,17,34] for monolayer but overestimates the bulk gap. For bulk, the gap [17] can be recovered by rescaling the coupling between different layers with a factor of ~ 0.54 , or conversely by stretching the layer separation by $\sim 9\%$. The latter was used to generate all results computed in this work. Note that we consider normal incidence and as a result, the external field couples solely with the in-plane motion of the electrons via the in-plane components of the position operator which are not affected by the stretching of layer separation. In Figs. 1(b) and 1(c), we show the band structures along the relevant high-symmetry paths for bulk and monolayer bP, respectively. In both systems, the TB dispersions for the top valence and bottom conduction bands are consistent with previous *ab initio* results and experimental data [14,34]. In contrast, the higher conduction and lower valence bands exhibit significant deviations. The poor agreement of the latter does not affect our results, as we restrict our analysis to photon energies comparable with the optical gap, $\hbar\omega \sim E_g$.

Lattice symmetry plays an important role in linear and nonlinear processes as it reduces the number of independent and finite tensors elements. For both bulk and monolayer bP, the optical conductivity is limited to the diagonal components $\sigma_{\alpha\alpha}^{(1)}$ [43]. At third order, symmetry reduces the number of independent tensor components to nine [44], and restricting the external electromagnetic field to normal incidence further reduces the number of effective tensor components to four, namely $\sigma_{11} \equiv \sigma_{xxxx}$, $\sigma_{18} \equiv \sigma_{xxyy} + \sigma_{xyxy} + \sigma_{xyyx}$, $\sigma_{29} \equiv \sigma_{yyxx} + \sigma_{yyxy} + \sigma_{yxyx}$, and $\sigma_{22} \equiv \sigma_{yyyy}$; i.e., “8” denotes xxy and the respective permutations and “9” is xyy and its permutations, according to the convention in Eq. (2) of Ref. [44]. The combinations of the nondiagonal tensor elements, σ_{18} and σ_{29} , will be addressed in detail below, where it is shown that these play a crucial role in the calculation of the THG conductivity and susceptibility, as these combinations ensure that all nonphysical divergences vanish.

B. Perturbative response of two-band systems

Here, we review the current density response to an external electromagnetic field for two-band systems using a perturbative expansion of the time-dependent density matrix, $\hat{\rho}(t)$ in the length gauge [37,45,46] and the single-particle velocity operator $\hat{\mathbf{v}} = \hat{\mathbf{r}} \equiv \hbar^{-1} \nabla_{\mathbf{k}} \hat{H}$. The current density for an electronic system with spin degeneracy $g = 2$ and volume Ω reads $\mathbf{J} = -eg \text{tr}\{\hat{\mathbf{v}}\hat{\rho}\}/\Omega$. Upon explicit evaluation of the trace, the current density becomes

$$\mathbf{J} = -eg \sum_{\mathbf{k}} [(\mathbf{v}_{cc} - \mathbf{v}_{vv})n/2 + \mathbf{v}_{vc}p + \mathbf{v}_{cv}p^*]/\Omega, \quad (5)$$

where we define the population difference $n \equiv \rho_{vv}(t) - \rho_{cc}(t)$ and the coherence $p \equiv \rho_{cv}(t)$. In addition, we made use of the invariance of the trace of the density matrix, i.e., $\rho_{vv}(t) + \rho_{cc}(t) = 1$, together with the fact that the integral of the velocity operator over the Brillouin zone (BZ) vanishes. The quantum Liouville equation reduces to two dynamical equations for p and n , namely,

$$-i \frac{\partial p}{\partial t} + \omega_{cv}p = -i\mathbf{F}(t) \cdot (p)_{;\mathbf{k}} - \mathbf{F}(t) \cdot \mathcal{A}_{cv}n, \quad (6a)$$

$$\frac{\partial n}{\partial t} = \mathbf{F}(t) \cdot \nabla_{\mathbf{k}}n - 2i\mathbf{F}(t) \cdot (\mathcal{A}_{vc}p - p^*\mathcal{A}_{cv}), \quad (6b)$$

with the condensed notation $\mathbf{F} \equiv -ie\mathbf{E}(t)/(2\hbar)$ and $(S_{mn})_{;\mathbf{k}\alpha} = (S_{mn})_{;\alpha} \equiv \partial S_{mn}/\partial k_{\alpha} - iS_{mn}(\mathcal{A}_{mm}^{\alpha} - \mathcal{A}_{nn}^{\alpha})$ defines the “generalized derivative” (GD) as in Ref. [37]. In addition, the matrix elements for the Berry connection read

$$\mathcal{A}_{mn} \equiv \frac{i}{\Omega} \int_{\Omega} d\mathbf{r} u_{m\mathbf{k}}^*(\mathbf{r}) \nabla_{\mathbf{k}} u_{n\mathbf{k}}(\mathbf{r}), \quad (7)$$

where $u_{m\mathbf{k}}$ are cell-periodic functions [46]. A detailed review of the evaluation of topological quantities, including the Berry connection, can be found in Ref. [47]. The numerical implementation of all derivatives relies on central finite-difference approximations [48]. Since this requires multiple numerical diagonalizations of the unperturbed Hamiltonian and the eigenvectors have phase freedom (in the complex plane), all eigenstates are rotated to ensure a phase that varies smoothly in \mathbf{k} space. In all calculations, we rotate the eigenvectors such that the first element is real and positive. The dynamical equations are solved by iteration, generating solutions in the form of power series in the external electric field. The iterative process starts with initial conditions defined by the equilibrium density matrix for a cold insulator, i.e., absence of coherence $p^{(0)}(t) = 0$ and fully occupied valence band $n^{(0)}(t) = 1$. The process is straightforward and has been discussed in detail in Refs. [37,46]; hence we display only results for the first- and third-order iterations. At linear order, the difference in the populations is identically zero, $n^{(\alpha)}(t) = 0$, and the coherence reads $p^{(\alpha)}(t) = p_{\omega}^{(\alpha)} \exp[-i\bar{\omega}t] + p_{-\omega}^{(\alpha)} \exp[i\bar{\omega}^*t]$, with Fourier coefficients

$$p_{\omega}^{(\alpha)} = F_{\omega}^{\alpha} \mathcal{A}_{cv}^{\alpha}/(\bar{\omega} - \omega_{cv}), \quad (8)$$

where we introduce the complex frequency $\bar{\omega} \equiv \omega + i\eta$. The introduction of positive infinitesimal frequency $\eta \equiv 0^+$ in the external field ensures the interaction switches on adiabatically [49]. At third order, the interaction with an external

monochromatic electromagnetic field generates two contributions with different fundamental frequencies $\{3\omega, \omega\}$. The former contributes to the THG and the latter introduces the intensity-dependent correction to refractive index [1,2]. The total third order $p(t)$ and $n(t)$ can be cast as

$$p^{(\lambda\beta\alpha)}(t) = p_{3\omega}^{(\lambda\beta\alpha)} e^{-3i\bar{\omega}t} + p_{-\omega}^{(\lambda\beta\alpha)} e^{3i\bar{\omega}^*t} + p_{\omega}^{(\lambda\beta\alpha)} e^{-i\bar{\omega}t} + p_{-\omega}^{(\lambda\beta\alpha)} e^{i\bar{\omega}^*t}, \quad (9a)$$

$$n^{(\lambda\beta\alpha)}(t) = n_{3\omega}^{(\lambda\beta\alpha)} e^{-3i\bar{\omega}t} + n_{-\omega}^{(\lambda\beta\alpha)} e^{3i\bar{\omega}^*t} + n_{\omega}^{(\lambda\beta\alpha)} e^{-i\bar{\omega}t} + n_{-\omega}^{(\lambda\beta\alpha)} e^{i\bar{\omega}^*t}. \quad (9b)$$

The relevant THG coherence reads

$$p_{3\omega}^{(\lambda\beta\alpha)} = -\frac{\hbar^3 F_{\omega}^{\lambda} F_{\omega}^{\beta} F_{\omega}^{\alpha}}{3\hbar\bar{\omega} - \epsilon} \left\{ \frac{\mathcal{A}_{cv}^{\lambda}}{2\hbar\bar{\omega}} \left(\frac{\mathcal{A}_{vc}^{\beta} \mathcal{A}_{cv}^{\alpha}}{\epsilon - \hbar\bar{\omega}} - \frac{\mathcal{A}_{vc}^{\alpha} \mathcal{A}_{cv}^{\beta}}{\epsilon + \hbar\bar{\omega}} \right) + \left[\frac{1}{2\hbar\bar{\omega} - \epsilon} \left(\frac{\mathcal{A}_{cv}^{\alpha}}{\hbar\bar{\omega} - \epsilon} \right)_{;\beta;\lambda} \right] \right\}, \quad (10a)$$

where we introduce the shorthand notation $\epsilon \equiv \hbar\omega_{cv}$. It is important to highlight the presence of a $1/\omega$ divergence in the purely interband contribution. This divergence is shown to be spurious in two steps, first by isolating the divergent terms by means of partial fraction decomposition and then by considering the physical observable, rather than the individual components of the density matrix. With regards to the first step, the coherence becomes

$$p_{3\omega}^{(\lambda\beta\alpha)} = -\frac{\hbar^3 F_{\omega}^{\lambda} F_{\omega}^{\beta} F_{\omega}^{\alpha}}{3\hbar\bar{\omega} - \epsilon} \left\{ \frac{\mathcal{A}_{cv}^{\lambda}}{2\epsilon} \left[\frac{\mathcal{A}_{vc}^{\beta} \mathcal{A}_{cv}^{\alpha} - \mathcal{A}_{vc}^{\alpha} \mathcal{A}_{cv}^{\beta}}{\hbar\bar{\omega}} + \frac{\mathcal{A}_{vc}^{\beta} \mathcal{A}_{cv}^{\alpha} (\epsilon + \hbar\bar{\omega}) + \mathcal{A}_{vc}^{\alpha} \mathcal{A}_{cv}^{\beta} (\epsilon - \hbar\bar{\omega})}{\epsilon^2 - \hbar^2 \bar{\omega}^2} \right] + \left[\frac{1}{2\hbar\bar{\omega} - \epsilon} \left(\frac{\mathcal{A}_{cv}^{\alpha}}{\hbar\bar{\omega} - \epsilon} \right)_{;\beta;\lambda} \right] \right\}. \quad (10b)$$

In the context of light-matter interaction, the current density, Eq. (5) (or the respective polarization density), represents the physical observable; more specifically the THG Fourier components read

$$j_{\phi}(3\omega) = -\frac{eg}{\Omega} \sum_{\mathbf{k}} \sum_{mn} v_{nm}^{\phi} \sum_{\lambda\beta\alpha} \rho_{mn}^{(\lambda\beta\alpha)} = \sum_{\lambda\beta\alpha} \sigma_{\phi\lambda\beta\alpha}(3\omega) E_{\omega}^{\lambda} E_{\omega}^{\beta} E_{\omega}^{\alpha},$$

which in turn defines the rank-4 tensor. Moreover, the physically relevant elements of a general rank-4 tensor in three dimensions can be grouped into 30 effective tensors according to the dependence on the external field [44]. This can be summarized in three classes according to the combinations of indices 2, 3, and 4:

(1) $\sigma_{\phi\alpha\alpha\alpha}$: 9 individual components, 3 diagonal ($\alpha = \phi$) and 6 with three repeated entries ($\alpha \neq \phi$);

(2) $\sigma_{\phi\beta\alpha\alpha} + \sigma_{\phi\alpha\beta\alpha} + \sigma_{\phi\alpha\alpha\beta}$: $3 \times 6 = 18$ combinations with two repeated entries (α appears twice) in tensor indices 2, 3, and 4;

(3) $\sigma_{\phi\lambda\beta\alpha} + \sigma_{\phi\lambda\alpha\beta} + \sigma_{\phi\alpha\lambda\beta} + \sigma_{\phi\alpha\beta\lambda} + \sigma_{\phi\beta\alpha\lambda} + \sigma_{\phi\beta\lambda\alpha}$: 3 combinations with no repeating entries in tensor indices 2, 3, and 4.

By considering these combinations, it becomes clear that the divergence in the coherence [Eq. (10b)] is spurious, as the $1/\omega$ terms add up to zero. Therefore, the divergent term can be removed from the original definition, and thus define the divergence-free effective density matrix $\langle\rho\rangle$, e.g., in tensors with two repeating entries $\langle\rho^{(\beta\alpha\alpha)}\rangle = \rho^{(\beta\alpha\alpha)} + \rho^{(\alpha\beta\alpha)} + \rho^{(\alpha\alpha\beta)}$.

With regards to $n_{3\omega}^{(\lambda\beta\alpha)}$, the dynamical equation leads to a rather lengthy and cumbersome expression that contains $1/\omega$ divergences. As in the case of $p_{3\omega}^{(\lambda\beta\alpha)}$, these divergences are

shown to vanish for the physically relevant combinations of the $\sigma_{\phi\lambda\beta\alpha}$. The process of extricating the spurious terms is made simpler by expanding the numerator in a power series of the photon energy, which naturally isolates the divergent terms

$$n_{3\omega}^{(\lambda\beta\alpha)} = F_{\omega}^{\lambda} F_{\omega}^{\beta} F_{\omega}^{\alpha} \frac{i\hbar^3 \sum_{j=0}^5 (\hbar\bar{\omega})^{j-1} n_j^{\lambda\beta\alpha}}{3\epsilon^2(\hbar^2\bar{\omega}^2 - \epsilon^2)^2(4\hbar^2\bar{\omega}^2 - \epsilon^2)}, \quad (11)$$

where coefficients $n_j^{\lambda\beta\alpha}$ are frequency independent and retain the tensorial nature of $n_{3\omega}^{(\lambda\beta\alpha)}$. The respective elements are expressed in terms of the gauge-invariant GD [37],

$$n_0^{\lambda\beta\alpha} = 2\epsilon^5[(\mathcal{A}_{vc}^{\lambda}\mathcal{A}_{cv}^{\alpha} + \mathcal{A}_{vc}^{\alpha}\mathcal{A}_{cv}^{\lambda})\partial\epsilon/\partial k_{\beta} - (\mathcal{A}_{vc}^{\beta}\mathcal{A}_{cv}^{\alpha} + \mathcal{A}_{vc}^{\alpha}\mathcal{A}_{cv}^{\beta})\partial\epsilon/\partial k_{\lambda}] + \epsilon^6[(\mathcal{A}_{vc}^{\beta}\mathcal{A}_{cv}^{\alpha} + \mathcal{A}_{vc}^{\alpha}\mathcal{A}_{cv}^{\beta})_{;\lambda} - 2\mathcal{A}_{vc}^{\lambda}(\mathcal{A}_{cv}^{\alpha})_{;\beta} - 2(\mathcal{A}_{vc}^{\alpha})_{;\beta}\mathcal{A}_{cv}^{\lambda}], \quad (12a)$$

$$n_1^{\lambda\beta\alpha} = -\epsilon^4[3(\mathcal{A}_{vc}^{\lambda}\mathcal{A}_{cv}^{\beta} - \mathcal{A}_{vc}^{\beta}\mathcal{A}_{cv}^{\lambda})\partial\epsilon/\partial k_{\lambda} + 8(\mathcal{A}_{vc}^{\alpha}\mathcal{A}_{cv}^{\lambda} - \mathcal{A}_{vc}^{\lambda}\mathcal{A}_{cv}^{\alpha})\partial\epsilon/\partial k_{\beta}] + \epsilon^5\{6[(\mathcal{A}_{vc}^{\alpha})_{;\beta}\mathcal{A}_{cv}^{\lambda} - \mathcal{A}_{vc}^{\lambda}(\mathcal{A}_{cv}^{\alpha})_{;\beta}] + (\mathcal{A}_{vc}^{\alpha}\mathcal{A}_{cv}^{\beta} - \mathcal{A}_{vc}^{\beta}\mathcal{A}_{cv}^{\alpha})_{;\lambda}\}, \quad (12b)$$

$$n_2^{\lambda\beta\alpha} = \epsilon^3[10(\mathcal{A}_{vc}^{\lambda}\mathcal{A}_{cv}^{\alpha} + \mathcal{A}_{vc}^{\alpha}\mathcal{A}_{cv}^{\lambda})\partial\epsilon/\partial k_{\beta} + 8(\mathcal{A}_{vc}^{\beta}\mathcal{A}_{cv}^{\alpha} + \mathcal{A}_{vc}^{\alpha}\mathcal{A}_{cv}^{\beta})\partial\epsilon/\partial k_{\lambda}] - \epsilon^4\{2[(\mathcal{A}_{vc}^{\alpha})_{;\beta}\mathcal{A}_{cv}^{\lambda} + \mathcal{A}_{vc}^{\lambda}(\mathcal{A}_{cv}^{\alpha})_{;\beta}] + 5(\mathcal{A}_{vc}^{\beta}\mathcal{A}_{cv}^{\alpha} + \mathcal{A}_{vc}^{\alpha}\mathcal{A}_{cv}^{\beta})_{;\lambda}\}, \quad (12c)$$

$$n_3^{\lambda\beta\alpha} = \epsilon^2[4(\mathcal{A}_{vc}^{\lambda}\mathcal{A}_{cv}^{\alpha} - \mathcal{A}_{vc}^{\alpha}\mathcal{A}_{cv}^{\lambda})\partial\epsilon/\partial k_{\beta} + 13(\mathcal{A}_{vc}^{\alpha}\mathcal{A}_{cv}^{\beta} - \mathcal{A}_{vc}^{\beta}\mathcal{A}_{cv}^{\alpha})\partial\epsilon/\partial k_{\lambda}] + \epsilon^3\{6[(\mathcal{A}_{vc}^{\lambda}(\mathcal{A}_{cv}^{\alpha})_{;\beta} - (\mathcal{A}_{vc}^{\alpha})_{;\beta}\mathcal{A}_{cv}^{\lambda}) + 5(\mathcal{A}_{vc}^{\beta}\mathcal{A}_{cv}^{\alpha} - \mathcal{A}_{vc}^{\alpha}\mathcal{A}_{cv}^{\beta})_{;\lambda}]\}, \quad (12d)$$

$$n_4^{\lambda\beta\alpha} = 4\epsilon^2[(\mathcal{A}_{vc}^{\alpha})_{;\beta}\mathcal{A}_{cv}^{\lambda} + \mathcal{A}_{vc}^{\lambda}(\mathcal{A}_{cv}^{\alpha})_{;\beta} + (\mathcal{A}_{vc}^{\beta}\mathcal{A}_{cv}^{\alpha} + \mathcal{A}_{vc}^{\alpha}\mathcal{A}_{cv}^{\beta})_{;\lambda}], \quad (12e)$$

$$n_5^{\lambda\beta\alpha} = 4\epsilon^0(\mathcal{A}_{vc}^{\beta}\mathcal{A}_{cv}^{\alpha} - \mathcal{A}_{vc}^{\alpha}\mathcal{A}_{cv}^{\beta})\partial\epsilon/\partial k_{\lambda} - 4\epsilon^1(\mathcal{A}_{vc}^{\beta}\mathcal{A}_{cv}^{\alpha} - \mathcal{A}_{vc}^{\alpha}\mathcal{A}_{cv}^{\beta})_{;\lambda}; \quad (12f)$$

however, several terms reduce to regular derivatives, as the Berry connection part of the GD vanishes. Following the procedure outlined above for the coherence, it is straightforward to show that the contributions from the effective coefficients $\langle n_0^{\lambda\beta\alpha} \rangle$ vanish, thus showing that the $1/\omega$ divergence is spurious. Additional spurious contributions are found in the higher order terms of this expansion. Discarding these contributions allows for the simplification of several terms, namely $\langle n_1^{\lambda\beta\alpha} \rangle \equiv -\epsilon^2\langle n_3^{\lambda\beta\alpha} \rangle \equiv 6\epsilon^5[(\mathcal{A}_{vc}^{\alpha})_{;\beta}\mathcal{A}_{cv}^{\lambda} - \mathcal{A}_{vc}^{\lambda}(\mathcal{A}_{cv}^{\alpha})_{;\beta}]$ and $\langle n_5^{\lambda\beta\alpha} \rangle \equiv 0$.

It is worth noting that the approach to the evaluation of the nonlinear density matrix can accommodate additional bands and, also, be used for metals. Thus, the present formulas still hold; however, additional contributions exist for the response of multiband and metallic systems. These terms concern transitions to other bands and, in case of metallic systems, terms involving the gradient of Fermi functions, i.e., $\partial f(\epsilon_n(\mathbf{k}))/\partial k_{\alpha}$. The latter are only relevant for metals, because such gradients are vanishingly small for cold insulators [37].

Based on the regularized expressions for the coherence and population difference, we define the THG conductivity as a combination of three terms $\sigma_{\phi\lambda\beta\alpha}^{(3)} = \sigma_{\phi\lambda\beta\alpha}^{(3,A)} + \sigma_{\phi\lambda\beta\alpha}^{(3,B)} + \sigma_{\phi\lambda\beta\alpha}^{(3,C)}$ separated according to the nature of the transitions involved in each term. Contributions arising from purely interband transitions are captured in the first term, *A*, whereas the remaining terms concern mixed processes, involving *one* or

two intraband transitions, *B* and *C* respectively. The full form of each contribution becomes

$$\frac{\sigma_{\phi\lambda\beta\alpha}^{(3,A)}(3\omega)}{i\sigma_3\mathcal{N}_d} = \hbar^3 \sum_{\mathbf{k}} \frac{v_{vc}^{\phi} v_{cv}^{\lambda}}{3\hbar\bar{\omega} - \epsilon} \frac{v_{vc}^{\beta} v_{cv}^{\alpha} + v_{vc}^{\alpha} v_{cv}^{\beta}}{\epsilon^3(\hbar^2\bar{\omega}^2 - \epsilon^2)} + (c \leftrightarrow v), \quad (13a)$$

$$\frac{\sigma_{\phi\lambda\beta\alpha}^{(3,B)}(3\omega)}{i\sigma_3\mathcal{N}_d} = \sum_{\mathbf{k}} \frac{v_{cc}^{\phi} - v_{vv}^{\phi}}{4\hbar^2\bar{\omega}^2 - \epsilon^2} \frac{\sum_{j=0}^5 (\hbar\bar{\omega})^{j-1} n_j^{\lambda\beta\alpha}}{3(\hbar^2\bar{\omega}^2 - \epsilon^2)^2}, \quad (13b)$$

$$\frac{\sigma_{\phi\lambda\beta\alpha}^{(3,C)}(3\omega)}{i\sigma_3\mathcal{N}_d} = \hbar \sum_{\mathbf{k}} \left(\frac{v_{vc}^{\phi}}{3\hbar\bar{\omega} - \epsilon} \right)_{;\lambda} \frac{1}{2\hbar\bar{\omega} - \epsilon} \left(\frac{v_{cv}^{\alpha}/\epsilon}{\hbar\bar{\omega} - \epsilon} \right)_{;\beta} + (c \leftrightarrow v), \quad (13c)$$

where the interband position matrix elements are expressed as velocity matrix elements via $\mathcal{A}_{mn}^{\alpha} = -i\hbar v_{mn}^{\alpha}/\epsilon_{mn}$ [37,46]. \mathcal{N}_d is a normalization constant and σ_3 sets the scale of the THG conductivity. Given that the dimensionality of the system under consideration defines the dimensions of $\sigma^{(N)}$ and $\chi^{(N)}$, we choose to set the σ_3 and \mathcal{N}_d for 2D systems. In 2D, the THG conductivity scale reads $\sigma_3 = e^4 a_0^2 / (8\gamma_0^2 \hbar) = 3.04 \times 10^{-25} \text{ Sm}^2/\text{V}^2$, with $\gamma_0 = 1 \text{ eV}$, $a_0 = 1 \text{ \AA}$. The respective normalization constant $\mathcal{N}_2 \equiv g\gamma_0^2 \hbar / (a_0^2 A)$, where $A \equiv A_c N_x N_y$ is the total area for $N_x N_y$ unit cells with area A_c . For the 3D system, the normalization constant is defined

as $\mathcal{N}_3 \equiv a_3 g \gamma_0^2 \hbar / (a_0^2 N_x N_y N_z V_C) = \mathcal{N}_2 / N_z$, with unit cell volume $V_C = a_3 A_C$ and N_z unit cells along the z direction. The conversion of 3D to 2D nonlinear conductivity is obtained through the multiplication by the vertical lattice parameter a_3 . Moreover, to improve numerical stability and account for broadening in realistic spectra, we keep the adiabatic coupling finite, $\hbar\eta = 0.05$ eV, throughout all calculations. It is worth mentioning that in case of the diagonal tensor elements, the A and B contributions reduce to compact closed-form expressions

$$\frac{\sigma_{\phi\phi\phi\phi}^{(3,A)}(3\omega)}{i\sigma_3\mathcal{N}_d} = \hbar^3 \sum_{\mathbf{k}} \frac{12\hbar\bar{\omega} |v_{vc}^\phi|^4 / \epsilon^3}{(9\hbar^2\bar{\omega}^2 - \epsilon^2)(\hbar^2\bar{\omega}^2 - \epsilon^2)}, \quad (14a)$$

$$\begin{aligned} \frac{\sigma_{\phi\phi\phi\phi}^{(3,B)}(3\omega)}{i\sigma_3\mathcal{N}_d} &= \hbar^2 \sum_{\mathbf{k}} \frac{2(v_{cc}^\phi - v_{vv}^\phi)\epsilon^2}{(4\hbar^2\bar{\omega}^2 - \epsilon^2)(\hbar^2\bar{\omega}^2 - \epsilon^2)} \\ &\times \left[\frac{6\hbar\bar{\omega} |v_{vc}^\phi|^2 / \epsilon}{\hbar^2\bar{\omega}^2 - \epsilon^2} \frac{\partial \epsilon}{\partial k_\phi} + \left(\frac{v_{vc}^\phi}{\epsilon} \right)_{;\phi} \frac{v_{cv}^\phi (2\hbar\bar{\omega} - \epsilon)}{\epsilon} \right. \\ &\left. + \frac{v_{vc}^\phi (2\hbar\bar{\omega} - \epsilon)}{\epsilon} \left(\frac{v_{cv}^\phi}{\epsilon} \right)_{;\phi} \right], \quad (14b) \end{aligned}$$

that allow for a more clear understanding of the nature of each process.

Under irradiation by an external electromagnetic field, the linear and nonlinear optical conductivities generate currents in the material, which in turn radiate an electromagnetic field, $\mathcal{E}(t)$, that includes among other contributions the n th harmonic field [1,2]. For a thin sheet in the interface of two media, the currents radiate a flux density $I(\omega) = \epsilon_0 c |\mathcal{E}_\omega|^2 / 2 = \mu_0 c |\mathbf{j}(\omega)|^2 / 8$ [50,51], that can be analyzed with a linear polarizer, such that the flux density transmitted through the linear polarizer reads $I_\zeta(\omega) = \mu_0 c |\mathbf{j}(\omega) \cdot (\cos \zeta, \sin \zeta, 0)|^2 / 8$. The latter provides a tool to analyze n th harmonic generation as it allows us to disentangle the contributions from different tensor elements, using exclusively optical techniques. For third order processes in orthorhombic crystals, with the external field linearly polarized at an angle θ with respect to the x axis, the intensity of the filtered signals along x ($\zeta = 0$) and y ($\zeta = \pi/2$) read

$$I_x/I_0 = |\bar{\sigma}_{11}|^2 \cos^6 \theta + 2\Re[\bar{\sigma}_{11}\bar{\sigma}_{18}^*] \cos^4 \theta \sin^2 \theta, \quad (15a)$$

$$I_y/I_0 = |\bar{\sigma}_{22}|^2 \sin^6 \theta + 2\Re[\bar{\sigma}_{22}\bar{\sigma}_{29}^*] \cos^2 \theta \sin^4 \theta, \quad (15b)$$

where $I_0 = \mu_0 c \sigma_3^2 E_0^6 / 8$ sets the intensity scale, with $\bar{\sigma}_{ij} \equiv \sigma_{ij} / \sigma_3$. Equations (15) can be used to probe the magnitudes of effective tensor elements and a couple of relative phases from experimental data. Additional relative phases can be determined by measuring the so-called parallel and perpendicular intensity, i.e., analyzer synchronized with the polarization plane such that $\zeta = \theta$ and $\zeta = \theta + \pi/2$ for parallel and perpendicular intensities.

III. RESULTS

We start by addressing the key properties of the energy dispersion of the π -electron tight-binding model for bulk and monolayer. Figure 1(b) shows the bulk energy dispersion along a high-symmetry path in the orthorhombic BZ, with chemical potential $\mu = -5.31$ eV. It exhibits a direct gap,

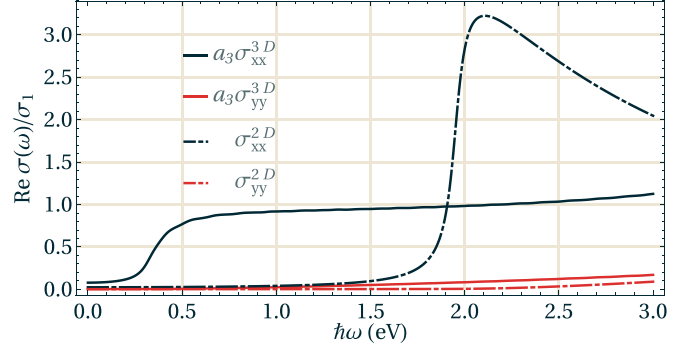


FIG. 2. Linear response of bulk and monolayer bP $\hbar\omega = 0.793$ eV ~ 1560 nm. The conductivity is plotted in units of 2D conductivity $\sigma_1 = e^2/4\hbar$, where the bulk conductivity is converted into 2D conductivity by multiplying by the vertical lattice parameter $a_3 = 5.209$ Å.

$E_g = \epsilon_{cv}(\mathbf{k} = \mathbf{Z}) = 0.316$ eV, at the $\mathbf{Z} = (0, 0, \pi/a_3)$ point, and the second lowest resonant vertical transition is associated with the Γ point and has a much larger energy separation, $\Delta E = 3.80$ eV. Therefore, the low-energy ($\hbar\omega \simeq 1$ eV) optical response, including THG, should depend mostly on transitions associated with the vicinity of the \mathbf{Z} point. With regards to the monolayer, the energy dispersion is shown in Fig. 1(c), with $\mu = -4.75$ eV. It also exhibits a direct gap, $E_g = 1.95$ eV found at the BZ center Γ . Moreover, the relative difference to the next resonant vertical transition, $\Delta E(\mathbf{k} = \mathbf{S}) = 6.58$ eV is significantly smaller than in bulk, where $\mathbf{S} = \pi(a_1^{-1}, a_2^{-1}, 0)$. As discussed below, transitions occurring in the vicinity of \mathbf{S} can play a role in THG at the energy scale of the gap, i.e., $\hbar\omega \sim E_g$.

Regarding the optical properties, we start by considering the optical conductivity, evaluated with Eq. (22) of Ref. [46]. In Fig. 2, we plot the real part of diagonal elements of the conductivity tensor, σ_{xx} (black) and σ_{yy} (red), with solid lines and dot-dashed lines representing the bulk and monolayer responses. The off-diagonal conductivity elements are identically zero, as expected for crystals with inversion symmetry. The lattice anisotropy manifests itself similarly in bulk and monolayer systems, where the $|\sigma_{xx}|/|\sigma_{yy}| \sim 20$ ratios at the respective band gap threshold, $\hbar\omega \sim E_g$, exhibit the dominant nature of σ_{xx} at low energy. In spite of the clearly distinct frequency dependence, results show (upon conversion to a 2D conductivity) that the bulk response has a magnitude comparable to that of the monolayer and to the quantum of conductance $\sim \sigma_1 = e^2/4\hbar$. The presence of the finite broadening energy, $\hbar\eta = 0.05$ eV, smooths the response at the optical gap and is responsible for the apparently finite conductivity at zero frequency in the bulk results [14,17]. The optical conductivity of bulk is in agreement with reports on extinction spectra [52] and with the dielectric function computed from electron energy loss spectroscopy (EELS) data [53]. Results for monolayer are consistent with previous calculations in the single-particle approximation [14,20,21] but show limitations of this approximation by not accounting for excitonic resonances present in monolayer bP [17,52,54].

With respect to THG, Fig. 3(a) shows the magnitude of the four effective nonlinear conductivity tensors, namely σ_{11} , σ_{18} ,

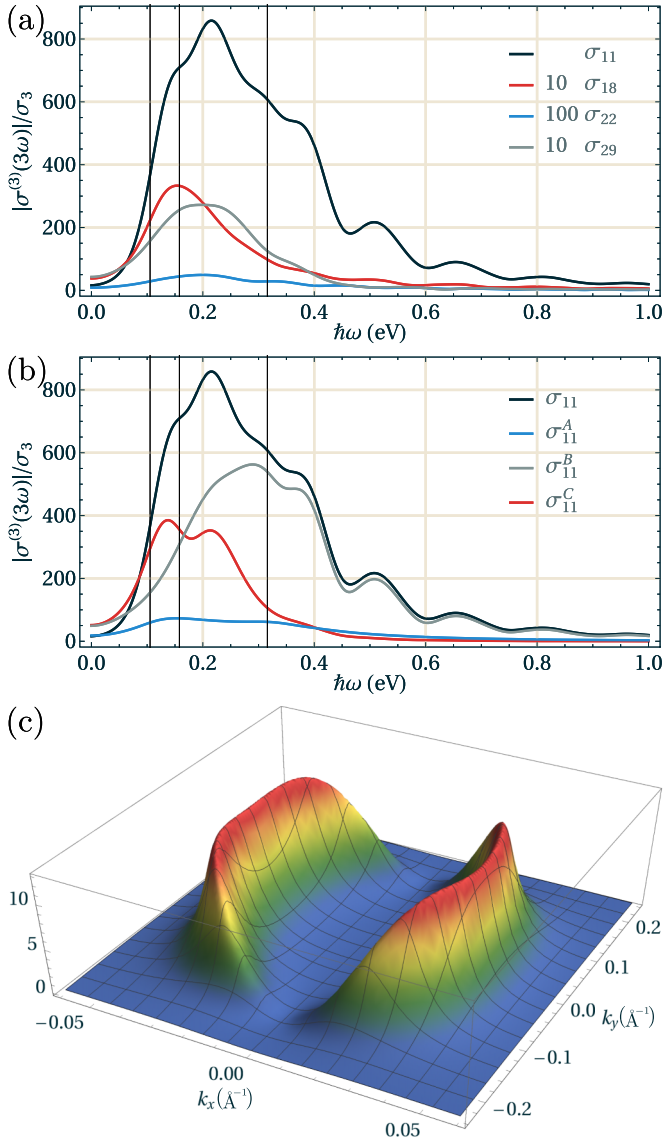


FIG. 3. THG of bulk bP in dimensions of 2D nonlinear conductivity σ_3 . In panel (a), we plot the absolute value of the effective tensor components of $\sigma^{(3)}(3\omega)$. Curves for σ_{18}, σ_{29} are scaled by a factor of 10 and σ_{22} by 100. Black vertical lines indicate THG resonances, $\hbar\omega = E_g/3, E_g/2, E_g$. Panel (b) illustrates the decomposition of the dominant term, σ_{11} , into the components of Eqs. (13). Panel (c) shows the magnitude (in arbitrary units) integrand $(\phi\lambda\beta\alpha) = xxxx$ of Eq. (13b) near \mathbf{Z} with $\hbar\omega = 0.5$ eV and $k_z = \pi/a_3$.

σ_{29} , and σ_{22} as discussed in Sec. II A. The THG is similar to the linear response: highly anisotropic and dominated by response along the x axis, i.e., σ_{11} . To make the remaining effective conductivities visible in Fig. 3(a), we amplify σ_{18}, σ_{29} by a factor of 10 and σ_{22} by 100. Figure 3(b) is dedicated to the analysis of the dominant term, σ_{11} , where we compare the magnitude with the individual contributions, as defined in Eq. (13). Results show that the response in the low-energy range is dominated by the mixed inter-intraband processes. The prominence of the mixed processes arises from the fact that, for two-band systems, these contain terms with quadratic resonances, i.e., $\propto 1/\eta^2$, rather than the simple resonances, i.e.,

$\propto 1/\eta$, observed in the purely interband process. The higher order resonances stem from the expansion of the generalized derivatives such as

$$\left(\frac{v_{vc}^\phi}{3\hbar\omega - \epsilon} \right)_{;\lambda} = \frac{(v_{vc}^\phi)_{;\lambda}}{3\hbar\omega - \epsilon} + \frac{v_{vc}^\phi}{(3\hbar\omega - \epsilon)^2} \frac{\partial \epsilon}{\partial k_\lambda}.$$

Considering the first resonance condition, $3\hbar\omega \sim \epsilon$, the leading-order contribution to the C term reads

$$\frac{\sigma_{\phi\lambda\beta\alpha}^{(3,C)}(3\omega)}{i\sigma_3\mathcal{N}_d} \sim -\frac{9/2}{\hbar\eta^2} \sum_{\mathbf{k}} v_{vc}^\phi \frac{\partial \epsilon}{\partial k_\lambda} \left[\frac{(v_{vc}^\alpha)_{;\beta}}{\epsilon^3} + \frac{5}{3} \frac{v_{vc}^\alpha}{\epsilon^4} \frac{\partial \epsilon}{\partial k_\beta} \right],$$

whereas the equivalent resonance in the purely interband term reads

$$\frac{\sigma_{\phi\lambda\beta\alpha}^{(3,A)}(3\omega)}{i\sigma_3\mathcal{N}_d} \sim -\frac{9}{8} \frac{\hbar^2}{i\eta} \sum_{\mathbf{k}} \frac{v_{vc}^\phi v_{cv}^\lambda}{\epsilon^2} \frac{v_{vc}^\beta v_{cv}^\alpha}{\epsilon^3} + \frac{v_{vc}^\alpha v_{cv}^\beta}{\epsilon^3}.$$

By the same token, it is possible to show that the B term contains the highest order resonances for $2\hbar\omega \sim \epsilon$ and $\hbar\omega \sim \epsilon$. Hence, the double intraband process, Eq. (13c), plays an important role at very low energies and decays rapidly for higher energies. Conversely, the single intraband process, Eq. (13b), generates the overall largest contribution and contains multiple resonances including some above the band-gap energy. Moreover, this effect is present even with a broadening parameter, $\hbar\eta = 50$ meV, larger than the energy scale of room temperature fluctuations, $k_B T \approx 25$ meV, thus showing that it is robust, rather than an exclusive feature of ultraclean samples. It is worth noticing that all resonances are blue shifted with respect to the band-gap resonances, i.e., $\hbar\omega = E_g/3, E_g/2, E_g$. In Fig. 3(c), we plot a map of the absolute value of the integrand present in Eq. (13b) in the vicinity of the high symmetry point \mathbf{Z} at $\hbar\omega = 0.5$ eV. This behavior is common for all integrands independently of the photon energy and leads to the blocking of the lowest energy transitions, which in turn causes the blue shift of the resonances. Additionally, it identifies the contributions that generate various features in the THG response, such as the peak at $\hbar\omega \sim 0.5$ eV. The vanishing nature of the integrands of Eqs. (13) at the \mathbf{Z} point stems from three different sources that individually exhibit this behavior. First, products of the velocity matrix elements, such as $v_{vc}^\beta v_{cv}^\alpha$. Second, difference between diagonal velocity matrix, e.g., $v_{cc}^\alpha - v_{vv}^\alpha$. Third, all gradients and GDs present in Eqs. (13).

Turning our attention to the monolayer, Fig. 4(a) shows the magnitude of the four effective THG conductivities. The monolayer THG response exhibits several differences with respect to the bulk response. First, all features appear at resonances associated with a large joint density of states, including the small resonance slightly above the band-gap energy, $\hbar\omega = \epsilon_{cv}(\mathbf{k} = \mathbf{S})/3 \sim 2.19$ eV. The presence of the latter shows that the entire BZ contributes to the THG at the energy scale of the fundamental resonance $\hbar\omega \sim E_g$. Second, Fig. 4(b) shows that the THG conductivity is dominated by the mixed processes but, unlike in the bulk, each term dominates in distinct parts of the spectrum with minimal overlap near the resonance $2\hbar\omega \sim E_g$. The lowest energy response is dominated by the doubly intraband process, whereas the response in the vicinity of the gap threshold is controlled by the single intraband process. Moreover, the largest magnitude of the nonlinear conductivity

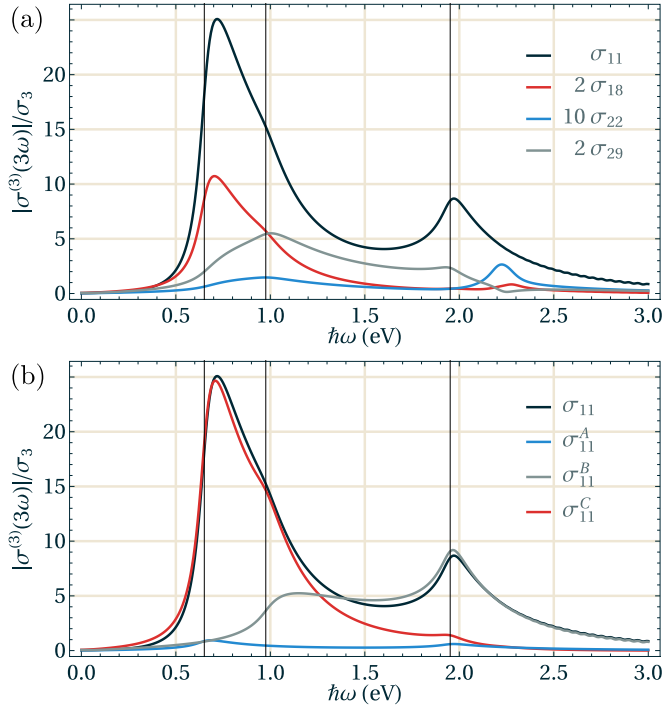


FIG. 4. THG of monolayer bP. In panel (a), we plot the absolute value of the effective tensor components of $\sigma^{(3)}(3\omega)$. Curves for σ_{18}, σ_{29} are scaled by a factor of 2 and σ_{22} by 10. Black vertical lines indicate THG resonances, $\hbar\omega = E_g/3, E_g/2, E_g$. Panel (b) shows the decomposition of the dominant term into the components Eqs. (13).

is found at the lowest resonance, $3\hbar\omega \sim E_g$. Last, but not least, the overall scale of the THG conductivity is significantly smaller than that of the bulk crystal; e.g., the ratio between the maximum THG conductivities is ~ 35 . This can be understood as a consequence of the decay of the nonlinear conductivity with the increase of the gap, as in the case of the second-order response [46]. Yet, due to the intricate nature of Eqs. (13), it was not possible to determine an accurate estimate for the gap dependence of the THG conductivity in bP.

The analysis of the radiated THG signal, Eqs. (15), provides a tool to probe the nonlinear conductivity tensor. In Figs. 5(a) and 5(b), we plot the normalized intensity patterns for bulk and monolayer bP. Solid black (red) curves represent I_x (I_y) intensities at incident photon energy $\hbar\omega = 0.793$ eV, using results obtained from the evaluation of Eqs. (13). The anisotropy of the system manifests itself clearly for both the bulk and monolayer bP, with the patterns dominated by the contribution of $I_x/I_0 \simeq |\bar{\sigma}_{11}|^2 \cos^6 \theta$. To the best of our knowledge, experimental data on THG in bP is limited to bulk or several layer [31–33] and results for the intensity dependence on the polarization angle appear to be inconsistent, e.g., pattern of total intensity presented by Ref. [32] exhibits maxima along the crystal x direction, whereas Refs. [31,33] shows maxima align with directions other than the primitive lattice directions, namely $\theta \sim \{\pm\pi/6, \pm 5\pi/6\}$. Additionally, the pattern for I_y in Ref. [32] is not symmetric with respect to the y direction, i.e., $\theta = \pm\pi/2$, hence not compatible with the THG radiated field by orthorhombic crystals, Eqs. (15). Notwithstanding these differences between the experimental results, all indicate a

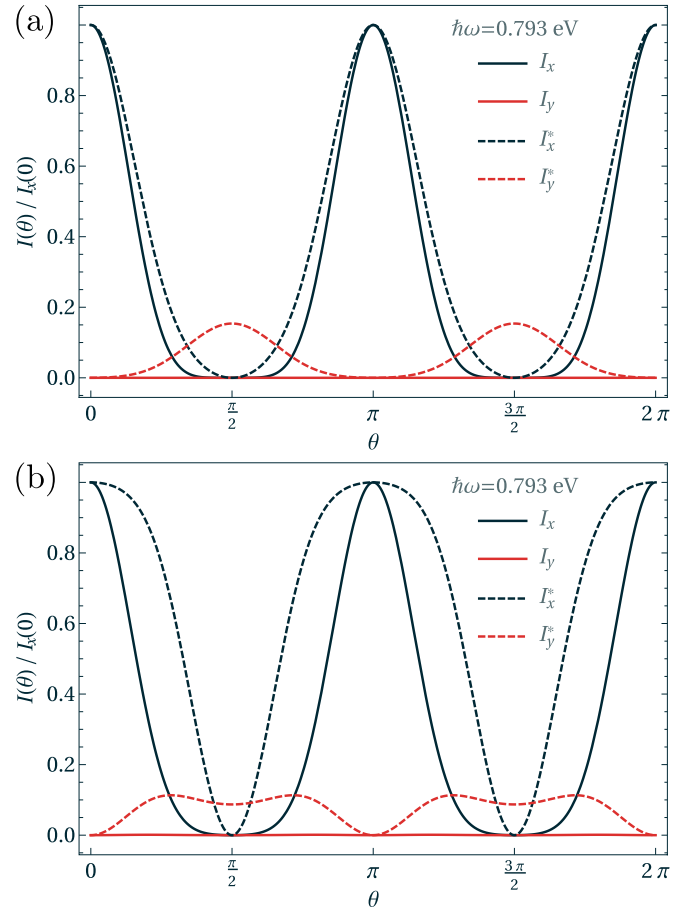


FIG. 5. Normalized THG intensities for bulk (a) and monolayer (b) bP at $\hbar\omega = 0.793$ eV ~ 1560 nm. Solid lines depict the THG intensity pattern using the nonlinear conductivities computed with Eq. (13). Dashed lines depict the THG intensity pattern with increased response along y axis as described in the main text. Black and red lines represent the THG pattern along crystal directions, $\zeta = \{0, \pi/2\}$.

much larger response along the y direction ($\zeta = \pi/2$) than that predicted by our results. Following the spirit of Ref. [14], we consider the effect of artificially increasing the matrix elements along the y direction by a constant factor. Such increase can make I_y visible in the scale of Figs. 5(a) and 5(b) at $\zeta = \pi/2$ as depicted by dashed lines, where the y -direction matrix elements are increased by factors of 4.5 and 3.25, respectively. Nonetheless, these patterns remain inconsistent with reported experimental data, indicating that this discrepancy should stem from additional mechanisms. It is worth noting that recent results of photoluminescence in high-quality samples [17] have shown that the linear response along the y direction is vanishingly small, indicating that the apparently higher response along the y direction can be attributed to mechanisms other than the intrinsic response of the system, such as disorder. In addition, the estimate of the magnitude of $\chi_{\text{eff}}^{(3)}$ and its ratio with regards to graphene's $\chi_{\text{eff}}^{(3)}$ remains an open question, as experimental reports indicate different results that span several orders of magnitude [31–33]. Our results indicate that both bulk and monolayer THG conductivities at $\hbar\omega = 0.793$ eV ($\lambda \sim 1560$ nm) have magnitudes $\sim 20\sigma_3$, which corresponds to

a nonlinear susceptibility $\chi_{\text{eff}}^{(3)} \sim 10 \times 10^{-19} \text{ nm}^2/\text{V}^2$, similar to recent reported results for bulk bP [32,33].

IV. CONCLUDING REMARKS

We studied THG in bP based on derivation of the nonlinear current density response, without the divergences that plague the direct evaluation of $j^{(3)}$ even when computed in the length gauge [37]. We show that these divergences are spurious and can be removed by considering the effective tensor components, i.e., physically relevant combinations of tensor elements, rather than the individual elements $\sigma_{\phi\lambda\beta\alpha}$. The resulting nonlinear conductivities, Eqs. (13), are free of divergences and can be applied directly to two-band systems in the independent particle approximation. Using a nonorthogonal TB model to compute the energy dispersion and eigenstates of bP, we evaluate the low-energy THG conductivity. Results for bulk bP agree, at least qualitatively, with the experimental reports of THG in bulk or many-layer samples bP [31–33]. Furthermore, the results show the importance of the mixed inter-intraband processes for the nonlinear response at energy scales comparable with the optical gap, particularly for systems whose electronic properties are accurately captured by two bands at this energy scale.

The present calculations ignore electron-electron interactions, which can play an important role in the optical response of a material, particularly for insulators with a large gap such as the hexagonal boron nitride (hBN), monolayers of TMDs, as well as mono- and few-layer bP. It has been shown that, due to the large gap in hBN, excitonic binding plays a crucial role in SHG [45] and nonlinear photocurrents [46]. In both cases, the response onset is reduced significantly and most of

spectral weight is transferred to the features associated with the fundamental exciton. First principles studies indicate that the linear responses of single- and few-layer bP exhibit similar behavior [20,21]. Therefore, our results for monolayer bP, computed within the framework of single-particle approximation, should be considered as a qualitative description of the response, rather than quantitatively. With respect to bulk bP, we expect excitonic effects to play a small role, since the exciton binding energy decreases with increasing number of layers [21,55]. Experimental reports on photoluminescence [56] and extinction spectra [52] support the results of theoretical studies on the effects of electron-electron interactions by showing that the excitonic resonances soften with increased number of layers. Furthermore, the small gap of bulk bP facilitates doping with charge carriers, which in turn will suppress the electron-electron interactions even further. This is supported by the smooth and steplike extinction spectra for bulk bP reported in Ref. [52] and also by the dielectric function of bulk bP computed from EELS data in Ref. [53]. Based on these experimental reports and the above-mentioned arguments, we expect that the nonlinear response of bulk bP can be accurately characterized within the framework of the single-particle approximation.

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