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Rapid Communications

Theory of phonon-assisted luminescence in solids: Application to hexagonal boron nitride

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We study the luminescence of hexagonal boron nitride (h-BN) by means of nonequilibrium Green's functions plus finite-difference electron-phonon coupling. We derive a formula for light emission in solids in the limit of a weak excitation that includes perturbatively the contribution of electron-phonon coupling at the first order. This formula is applied to study luminescence in bulk h-BN. This material has attracted interest due to its strong luminescence in the ultraviolet region of the electromagnetic spectrum [K. Watanabe *et al.*, Nat. Mater. **3**, 404 (2004)]. The origin of this intense luminescence signal has been widely discussed, but only recently a clear signature of phonon-mediated light emission started emerging from the experiments [G. Cassabois *et al.*, Nat. Photonics **10**, 262 (2016)]. By means of our theoretical framework, we provide a clear and full explanation of light emission in h-BN.

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Introduction. In standard solid state physics textbooks [1] direct band-gap semiconductors are considered efficient light emitters while indirect ones are regarded as inefficient. Silicon is a typical example: Its indirect nature prohibits applications in optoelectronics. This fact has motivated significant research activity to engineer silicon and transform it into a direct gap semiconductor by means of defects, nanostructuring, etc. A more recent and remarkable example of an indirect-to-direct gap transition is represented by MoS_2 nanostructuring [2]. The luminescence signal increases by four orders of magnitude passing from multilayer to single-layer MoS_2 with an associated indirect-to-direct band gap transition.

Hexagonal boron nitride (h-BN) seems to defy this rule: It has a large indirect band gap of about 7 eV, but it has recently attracted much attention from the scientific community as a very efficient light emitter in the ultraviolet [3]. An internal quantum yield of $\simeq 45\%$ has been reported for h-BN, much closer to the $\simeq 50\%$ one of ZnO (direct band gap) than to the 0.1% one of diamond (indirect band gap) [4].This goes against the common wisdom that indirect band-gap insulators are bad light emitters and in fact the strong luminescence signal was initially attributed to direct exciton recombination [3]. In order to shed some light on this phenomenon, different theories were proposed, including the presence of defects [5] or a dynamical Jahn-Teller effect [6], but only recently, owing to more accurate and precise measurements, it has been shown that luminescence originates from phonon-assisted recombination [7]. This interpretation has also been confirmed by studying the isotopic effect [8] and polarization-resolved photoluminescence measurements [9]. In this Rapid Communication we develop an approach to study phonon-assisted luminescence that treats on the same footing the electron-hole and electron-phonon interactions. We apply our methodology to study h-BN luminescence, a subject that has remained puzzling until recently. Since excitons play a crucial role in the optical response of h-BN, in order to describe luminescence we need a theory that includes both electron-hole interactions and electron-phonon scattering.

In the literature two important approaches have been proposed to study bulk luminescence, one based on nonequilibrium Green‘s functions [10,11] and another on density matrix theory [12]. Both these approaches include the effect of the electron-hole interaction and the formation of excitons at different levels of approximation. In this Rapid Communication we follow Hannewald and co-workers [10] who formulated luminescence in terms of nonequilibrium Green's function theory. The inclusion of exciton-phonon coupling is more involved. Phonon-assisted luminescence has been studied by Kira and Koch using the polaron picture [13]. Their approach has the advantage of being nonperturbative in the electron-phonon coupling while conserving the analytic structure of the zero-phonon response functions. Another possibility would be to include the electron-phonon diagrams directly in the Bethe-Salpeter equation [14,15], but we discarded this option because of its complexity.

In recent years a process has emerged to include the electron-phonon coupling by means of a finite-difference approach [16]. The approach has several advantages, including the ability to combine it with any underlying electronic structure method and to include terms beyond the lowest order in the electron-phonon interaction [16]. Finite-difference methods have been used to study the effects of electron-phonon scattering in multiple contexts, including optical absorption [17,18], topological phase transitions [19], and superconductivity [20]. In all these studies electrons were always considered to be independent particles. Here, in order to include excitonic effects in the response functions, we combine finite-difference electron-phonon coupling calculations with Green's function theory and apply this method to the study of luminescence spectra.

Light emission from nonequilibrium Green's functions. Light absorption and emission can be described by means of the Green's function theory. Both these processes are related to the two-particle polarization functions. The different two-particle correlation functions can be obtained from the solution of the so-called Bethe-Salpeter equation (BSE) at equilibrium or out of equilibrium [21]. In the BSE particle-hole pairs are coupled by correlation effects [22]. In the literature different levels of the approximation for this coupling have been presented, from the T matrix [23] that can account for the effects of finite excitonic populations, to the simpler static ladder approximation [21]. Here, we use the latter. The static ladder approximation has been shown to reproduce well the optical properties of h-BN at equilibrium [24], and since we consider very few excited carriers we expect similar results to hold also in our case. In this approximation the particle-hole coupling is composed of two terms, one derived from the density fluctuations through the Hartree potential, called v, and the other one due to the fluctuations of the screened exchange potential, the so-called electron-hole interactions W. The last term is normally considered in a static approximation, and derived from the Coulomb hole plus screened exchange (COHSEX) self-energy [21].In nonequilibrium conditions, when part of the carriers has been excited to the conduction bands, it is possible to write down an out-of-equilibrium BSE to describe the optical absorption. This approach has been used to investigate excitonic Mott transitions [25] or transient absorption in pump-probe experiments [10].

The out-of-equilibrium BSE then reads

$$[\Delta\varepsilon_K\delta_{K,K'} + \sqrt{f_K}\,\Xi_{K,K'}\sqrt{f_{K'}}]A_\lambda^{K'} = E_\lambda A_\lambda^K, \qquad (1)$$

where K is a general index for $\{vc\mathbf{k}\}$, $f_K = f_{v\mathbf{k}} - f_{c\mathbf{k}}$ are the occupation factors, and E_λ and A_λ^K are the eigenvalues and eigenvectors, namely, the exciton energy and wave functions. Here, $\Delta\varepsilon_K = \varepsilon_{c\mathbf{k}}^{\mathrm{QP}} - \varepsilon_{v\mathbf{k}}^{\mathrm{QP}}$ are the quasiparticle energy differences. The kernel is written as $\Xi = i[W - v]$ [21]. The screened Coulomb potential W that appears in Eq. (1) is calculated by taking into account the nonequilibrium electron and hole distributions. In Eq. (1) we use the symmetrization via $\sqrt{f_K}$, introduced by Schleife and co-workers [25], to ensure that the Bethe-Salpeter Hamiltonian remains pseudo-Hermitian even in the presence of fractional occupations, or Hermitian in the case of the Tamm-Dancoff approximation.

Notice that the reality of the solution of Eq. (1) is no longer guaranteed in stationary excited states. However, if the excitation is weak, namely, the quasiparticle occupations only slightly differ from their equilibrium values, as in the case studied here, then the solutions continue to be real [26]. The solution of Eq. (1) leads to the different response functions that are related to the absorption or emission spectra [10]. Following the derivation of Refs. [10,27], in the limit of low excitations, within the Tamm-Dancoff approximation, the luminescence power spectra can be expressed as

$$I(\omega) \propto \sum_\lambda |\Pi_\lambda|^2 f_\lambda^< \delta(\omega - E_\lambda), \qquad (2)$$

where E_λ are the eigenvalues of the out-of-equilibrium BSE [Eq. (1)], Π_λ are the exciton dipole matrix elements, and $f_\lambda^<$ their occupations. For a definition of Π_λ, $f_\lambda^<$, and the derivation of Eq. (2), see Sec. 2 of the Supplemental Material (SM) [28].

The excitonic occupation $f_\lambda^<$ is often approximated with a Bose-Einstein distribution $f_\lambda^< \simeq n_B(E_\lambda, T)$ in light emission [4,29] while it is equal to one in the absorption process at equilibrium. As one can see from Eq. (2), the luminescence spectra resonate at the same frequencies as the absorption does but excitons are weighted in a different way.

Notice that in the independent particle approximation, light emission is described by an equation equivalent to Eq. (2) where the sum over excitons is replaced by one over independent electron-hole pairs.

Scattering with phonons. In order to include the coupling between electrons and phonons, we consider the electron-phonon interaction at first order in the atomic displacements,

$$\hat{H}_{\text{el-ph}} = \frac{1}{\sqrt{N_p}} \sum_{\substack{\mathbf{k},\mathbf{q}\\ mn\nu}} g_{mn\nu}(\mathbf{k},\mathbf{q})\hat{c}^\dagger_{m\mathbf{k}+\mathbf{q}}\hat{c}_{n\mathbf{k}}(\hat{a}_{\mathbf{q}\nu} + \hat{a}^\dagger_{-\mathbf{q}\nu}), \qquad (3)$$

where $\hat{c}^\dagger_{m\mathbf{k}}/\hat{c}_{n\mathbf{k}}$ ($\hat{a}^\dagger_{-\mathbf{q}\nu}/\hat{a}_{\mathbf{q}\nu}$) are the fermionic (bosonic) creation/annihilation operators with crystal momentum $\mathbf{k}$ ($\mathbf{q}$) and N_p is the number of unit cells in the Born–von Kármán supercell.

The electron-phonon Hamiltonian [Eq. (3)] can be treated in time-dependent perturbation theory in the independent particle basis [30] or the excitonic one [31]. In the case of indirect semiconductors the main effect of Eq. (3) is to make active the transitions to finite-$\mathbf{q}$ excitons, which are otherwise inactive in the optical absorption/emission processes. The theory of phonon-assisted indirect optical transitions was developed by Hall, Bardeen, and Blatt (HBB) [32], and employed in first-principles calculations in Ref. [18]. In our work we extend their approach to light emission by means of time-dependent perturbation theory in the excitonic basis [31]. We consider the adiabatic limit for the dipole matrix elements, while we retain dynamical effects only in transition energies. Then we express the first-order correction to the dipole matrix elements as a derivative with respect to a phonon mode, as shown in Ref. [17], and we get the final formula for phonon-assisted luminescence as

$$I^{\mathrm{BSE}}(\omega;T) \propto \sum_{\mu\lambda} \frac{\partial^2|\Pi_\lambda|^2}{\partial x_\nu^2} f_\lambda^< \Bigg[\delta(\omega - E_\lambda - \omega_\nu)\frac{n_B(\omega_\nu;T)}{2\omega_\nu} + \delta(\omega - E_\lambda + \omega_\nu)\frac{1 + n_B(\omega_\nu;T)}{2\omega_\nu}\Bigg], \qquad (4)$$

where n_B is the Bose distribution function and x_ν is the atomic displacement associated with the phonon mode with frequency ω_ν. Notice that in Eq. (4) there should also be a term describing light emission without phonons, but in the case of indirect gap insulators this term vanishes. For more details of

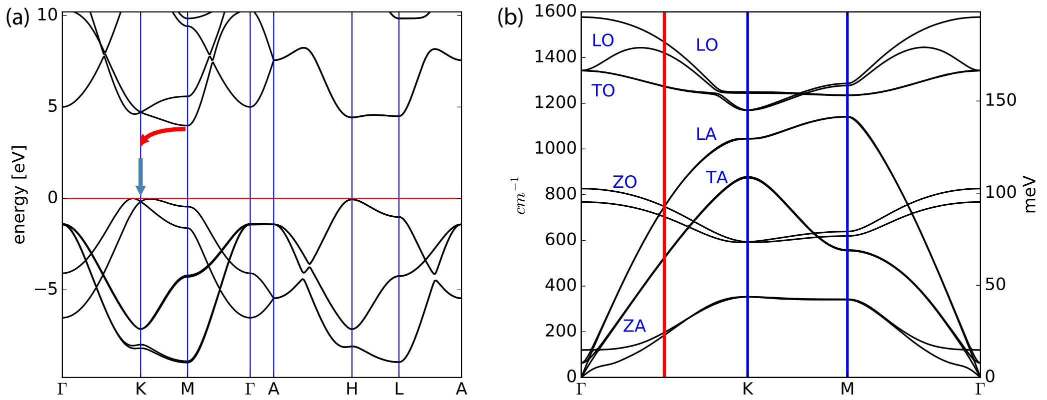

FIG. 1. (a) Electronic band structure of *h*-BN. The red arrow represents the scattering with a phonon between M and K and the blue one the emission of a photon. (b) Phonon band structure of *h*-BN. The red vertical line marks the position of the phonon $\mathbf{q}$ point involved in the luminescence process [see the red arrow in (a)].

the derivation of Eq. (4), see Secs. II and III in SM [28]. The two terms in Eq. (4) describe the absorption and emission of a phonon, respectively. The first process is less important at low temperatures due to the low number of available phonons.

In the adiabatic approximation ($\omega_\nu = 0$ in the delta functions) this formula recovers the standard static approximation, similar to the one derived in Ref. [33] for the dielectric constant. Notice that Eq. (4), and in general the HBB theory, do not capture the smooth increase of the absorption coefficient with temperature, and the concurrent redshift of the absorption onset, but they include dynamical effects that are crucial to reproduce luminescence spectra.

Equation (4) is the central formula of this Rapid Communication, and it will be used in the following to evaluate phonon-assisted luminescence from first principles.

Computational details. We studied *h*-BN by means of density functional theory with the QUANTUM ESPRESSO code [34], and many-body perturbation theory with the YAMBO code [35]. The lattice parameters in our simulations are $a = 2.5$ Å and $c/a = 2.6$ [36]. For the calculation of the density we used a $12 \times 12 \times 4$ k-point grid, a cutoff of 80 Ry for the wave functions, and the local density approximation (LDA) approximation to the exchange correlation functional. The same parameters have been used for the phonon dispersion calculation.

In bulk *h*-BN the optical response originates from the two π and two π^* bands and the gap is indirect between a point very close to K (valence bands) and M (conduction bands) [37]. Therefore in the Bethe-Salpeter equation [Eq. (1)] we include only two valence and two conduction bands and the corresponding number of bands in the supercells. A scissor operator of 2.328 eV has been applied to the Kohn-Sham band structure to reproduce the correct position of the lowest exciton with momentum $\mathbf{q} = M - K$ [38], also called an iX exciton in the literature. The dielectric constant that enters the electron-hole interaction of Eq. (1) has been calculated using 40 bands and a 4 Hartree cutoff.

In order to study phonon-assisted emission we build a nondiagonal supercell [39] such that the K and M points are mapped to Γ (for more details, see Sec. I in SM [28]). In this way the phonon modes with momentum $\mathbf{q} = K - M$ are folded to the Γ point in the supercell. Then the derivatives with respect to the phonon modes that appear in Eq. (4) can be calculated by finite differences [16]. A three-point formula is used to evaluate the second derivative, and only the phonon modes compatible with the $\mathbf{q} = K - M$ vector have been included in the calculations. We introduce a broadening of 0.0045 eV in the luminescence spectra in order to simulate the experimental one. Finally, we take a density of excited carriers of $n = 10^{15}$ cm^{-3} between K and M [40] to evaluate the luminescence spectra and consider the emission wave vector parallel to the c axis.

Results. In Fig. 1(a), we report the electronic band structure of *h*-BN calculated at the DFT level, and in Fig. 1(b) the phonon band structure. The maximum of the valence band is located close to the K point while the minimum of the conduction bands is at M. This situation is typical of other layered materials and it is due to the interlayer interaction that induces a transition from a direct to indirect band gap going from the monolayer to bulk. The inclusion of correlation effects does not change this picture, as verified by numerical simulations [37] and experimental measurements [41]. Direct light emission is forbidden in *h*-BN due to the indirect band gap, and only phonon-assisted luminescence is allowed. In the full excitonic dispersion there are two minima (at two $\mathbf{q}$ points which fall very close to the $\mathbf{q} = M - K$ point) and both can contribute to the luminescence [37]. We here consider the iX exciton for the reasons highlighted below. Since the top of the valence band falls very close to the K point of the Brillouin zone, we approximate this point as the K one. In this way the supercell containing both K and M is large but still computationally treatable, and the evaluation of electron-phonon coupling requires a feasible computational cost. The phonons involved in the luminescence process are those with a momentum compatible with the $\mathbf{q} = K - M$ vector, being the ones to contribute to the momentum balance between the bottom of the conduction band and the top of the valence band. Therefore they fall in the middle of the Brillouin zone between Γ and K, and are reported in Fig. 1(b) with a red line.

In order to study luminescence, we first diagonalize the Bether-Salpeter Hamiltonian in the supercell without including electron-phonon coupling, so as to find the position of the iX exciton. We found that the iX is formed by two dark excitons, separated by about 0.01 eV (dashed lines in

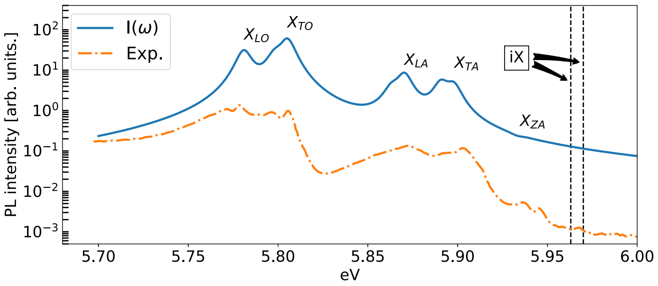

FIG. 2. Blue continuous line: Luminescence spectra calculated using Eq. (4) for bulk h-BN. The vertical lines represent the position of the iX doublet that has zero dipole matrix elements. Orange dashed-dotted line: Experimental results taken Ref. [7]. We choose the normalization of both spectra in such a way as to have an optimal visualization in a single figure.

Fig. 2). Then we include electron-phonon coupling by means of Eq. (4). The two iX excitons are replicated by the different phonon modes and acquire a finite optical weight as shown in the final spectra in Fig. 2.

Comparison with experiments. In Fig. 2 we report both the luminescence spectra calculated with our method and the experimental results from Cassabois and co-workers [7]. The two spectra compare very well. We correctly reproduce the position and intensity of the main peaks. The doublets measured in the luminescence spectra are generated by the longitudinal optic–transverse optical (LO-TO) [longitudinal acoustic–transverse acoustic (LA-TA)] splitting along the Γ-K line. We also report the position of the iX exciton that is not visible in luminescence, even if in the experiments there is a small peak probably due to the presence of impurities. The overtones, visible as lower-intensity redshifted sidebands in experimental luminescence spectra [42], are not reproducible in our calculations [43]. The splitting of the X_{TO}, X_{TA}, and X_{LA} peaks originates from the choice of supercell and it is related to the intrinsic exciton structure in our calculations.

In order to estimate the relative intensity of phonon-assisted luminescence in h-BN, we calculate the ratio between a hypothetical direct emission in h-BN and the phonon-mediated one (more details are given in Sec. IV of SM) [28]. We find the ratio between direct and indirect emission to be $I^{\mathrm{DIR}}/I^{\mathrm{IND}} \simeq 10^2$, implying that in going from bulk to monolayer h-BN the luminescence will increase, but not as much as in the MoS_2 case [2]. Our result is also in agreement with the finding of Schué and co-workers [40] that measured an increase of the ratio between direct and indirect peaks as the number of h-BN layers decreases.

Summary and conclusions. In this Rapid Communication we study phonon-assisted luminescence by means of a nonequilibrium Green's function-based formula plus time-dependent perturbation theory in the exciton space, and then the electron-phonon coupling matrix elements are evaluated by a finite-difference method. We find that luminescence in h-BN is dominated by phonon-assisted transitions and that its intensity is unexpectedly large when compared with direct transitions.

Note added. Recently, we have become aware of a paper, Ref. [44], which also studied the phononassisted luminescence in hBN.

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[1] C. Kittel, P. McEuen, and P. McEuen, *Introduction to Solid State Physics*, Vol. 8 (Wiley, New York, 1996).

[2] A. Splendiani, L. Sun, Y. Zhang, T. Li, J. Kim, C.-Y. Chim, G. Galli, and F. Wang, Nano Lett. **10**, 1271 (2010).

[3] K. Watanabe, T. Taniguchi, and H. Kanda, Nat. Mater. **3**, 404 (2004).

[4] L. Schue, L. Sponza, A. Plaud, H. Bensalah, K. Watanabe, T. Taniguchi, F. Ducastelle, A. Loiseau, and J. Barjon [Phys. Rev. Lett. (to be published)], arXiv:1803.03766.

[5] C. Attaccalite, M. Bockstedte, A. Marini, A. Rubio, and L. Wirtz, Phys. Rev. B **83**, 144115 (2011).

[6] K. Watanabe and T. Taniguchi, Phys. Rev. B **79**, 193104 (2009).

[7] G. Cassabois, P. Valvin, and B. Gil, Nat. Photonics **10**, 262 (2016).

[8] T. Vuong, S. Liu, A. Van der Lee, R. Cuscó, L. Artús, T. Michel, P. Valvin, J. Edgar, G. Cassabois, and B. Gil, Nat. Mater. **17**, 152 (2018).

[9] T. Vuong, G. Cassabois, P. Valvin, V. Jacques, A. Van Der Lee, A. Zobelli, K. Watanabe, T. Taniguchi, and B. Gil, 2D Mater. **4**, 011004 (2016).

[10] K. Hannewald, S. Glutsch, and F. Bechstedt, Phys. Rev. B **62**, 4519 (2000).

[11] Pedro Miguel M. C. de Melo and A. Marini, Phys. Rev. B **93**, 155102 (2016).

[12] M. Kira and S. W. Koch, *Semiconductor Quantum Optics* (Cambridge University Press, Cambridge, U.K., 2011).

[13] A. Chernikov, V. Bornwasser, M. Koch, S. Chatterjee, C. Böttge, T. Feldtmann, M. Kira, S. Koch, T. Wassner, S. Lautenschläger *et al.*, Phys. Rev. B **85**, 035201 (2012).

[14] G. Antonius and S. G. Louie, arXiv:1705.04245.

[15] T. Östreich, N. Donlagic, C. Wöhler, and K. Schönhammer, Phys. Status Solidi B **206**, 205 (1998).

[16] B. Monserrat, J. Phys.: Condens. Matter **30**, 083001 (2018).

[17] M. Zacharias, C. E. Patrick, and F. Giustino, Phys. Rev. Lett. **115**, 177401 (2015).

[18] J. Noffsinger, E. Kioupakis, C. G. Van de Walle, S. G. Louie, and M. L. Cohen, Phys. Rev. Lett. **108**, 167402 (2012).

[19] B. Monserrat and D. Vanderbilt, Phys. Rev. Lett. **117**, 226801 (2016).

[20] Z. P. Yin, A. Kutepov, and G. Kotliar, Phys. Rev. X **3**, 021011 (2013).

[21] R. M. Martin, L. Reining, and D. M. Ceperley, *Interacting Electrons* (Cambridge University Press, Cambridge, U.K., 2016).

[22] G. Strinati, Riv. Nuovo Cimento **11**, 1 (1988).

[23] N. H. Kwong, G. Rupper, and R. Binder, Phys. Rev. B **79**, 155205 (2009).

[24] L. Wirtz, A. Marini, and A. Rubio, Phys. Rev. Lett. **96**, 126104 (2006).

[25] A. Schleife, C. Rödl, F. Fuchs, K. Hannewald, and F. Bechstedt, Phys. Rev. Lett. **107**, 236405 (2011).

[26] E. Perfetto, D. Sangalli, A. Marini, and G. Stefanucci, Phys. Rev. B **94**, 245303 (2016).

[27] P. M. M. C. de Melo, *Ab initio* approach to photoluminescence based on Green's function theory, Ph.D. thesis, Universidade de Coimbra, 2017.

[28] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.99.081109 for an analytic derivation of the main formula of this Rapid Communication and the construction of the nondiagonal supercell.

[29] E. Torun, H. P. C. Miranda, A. Molina-Sánchez, and L. Wirtz, Phys. Rev. B **97**, 245427 (2018).

[30] F. Bassani and G. P. Parravicini, *Electronic States and Optical Transitions in Solids* (Pergamon, New York, 1975).

[31] V. Perebeinos, J. Tersoff, and P. Avouris, Phys. Rev. Lett. **94**, 027402 (2005).

[32] L. Hall, J. Bardeen, and F. Blatt, Phys. Rev. **95**, 559 (1954).

[33] M. Zacharias and F. Giustino, Phys. Rev. B **94**, 075125 (2016).

[34] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. D. Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos *et al.*, J. Phys.: Condens. Matter **21**, 395502 (2009).

[35] A. Marini, C. Hogan, M. Grüning, and D. Varsano, Comput. Phys. Commun. **180**, 1392 (2009).

[36] V. L. Solozhenko, G. Will, and F. Elf, Solid State Commun. **96**, 1 (1995).

[37] L. Sponza, H. Amara, F. Ducastelle, A. Loiseau, and C. Attaccalite, Phys. Rev. B **97**, 075121 (2018).

[38] We could have applied the *GW* method to correct the Kohn-Sham band structure of *h*-BN, but this approach, at least in the G_0W_0 approximation, is known to underestimate the *h*-BN gap by about 0.5 eV [37] .

[39] J. H. Lloyd-Williams and B. Monserrat, Phys. Rev. B **92**, 184301 (2015).

[40] L. Schue, B. Berini, A. C. Betz, B. Placais, F. Ducastelle, J. Barjon, and A. Loiseau, Nanoscale **8**, 6986 (2016).

[41] R. Schuster, C. Habenicht, M. Ahmad, M. Knupfer, and B. Büchner, Phys. Rev. B **97**, 041201 (2018).

[42] T. Q. P. Vuong, G. Cassabois, P. Valvin, V. Jacques, R. Cuscó, L. Artús, and B. Gil, Phys. Rev. B **95**, 045207 (2017).

[43] Notice that in our computational approach the electron-phonon scattering is limited to one phonon at a time and so we cannot reproduce the overtones involving interlayer shear modes and the asymmetric tails of the emission peaks [42].

[44] F. Paleari, H. P. C. Miranda, A. Molina-Sánchez, and L. Wirtz, arXiv:1810.08976.