Two-photon absorption in two-dimensional materials: the case of hexagonal boron nitride

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We calculate the two-photon absorption in bulk and single layer hexagonal boron nitride (h-BN) both by an ab initio real-time Bethe-Salpeter approach and by a the real-space solution of the excitonic problem in tight-binding formalism. The two-photon absorption obeys different selection rules from those governing linear optics and therefore provides complementary information on the electronic excitations of h-BN. Combining the results from the simulations with a symmetry analysis we show that two-photon absorption is able to probe the lowest energy 1s states in the single layer h-BN and the lowest dark degenerate dark states of bulk h-BN. This deviation from the “usual” selection rules based on the continuous hydrogenic model is explained within a simple model that accounts for the crystalline symmetry. The same model can be applied to other two-dimensional materials with the same point-group symmetry, such as the transition metal chalcogenides. We also discuss the selection rules related to the inversion symmetry of the bulk layer stacking.

I. INTRODUCTION

Two-photon absorption (TPA) is a nonlinear optical process in which the absorption of two photons excites a system to a higher energy electronic state. Two-photon transitions obey selection rules distinct from those governing linear excitation processes and thereby provide complementary insights into the electronic structure of excited states, as has been demonstrated in molecular systems and bulk solids. In particular it is frequently argued that one-photon processes are only allowed for excitons of s symmetry whereas p states can be observed in TPA. These rules can be derived within a continuous hydrogenic model for excitons where full rotational symmetry is assumed. They have been invoked to analyze the excitonic effects observed in carbon nanotubes and also recently in bulk h-BN. Actually these rules are not generally valid if the genuine crystalline symmetry is taken into account, but they can at least provide interpretations in terms of high or low oscillator strength.

Nonlinear optical properties of two-dimensional (2D) crystals, and as such the TPA, have been recently the object of several experimental and computational studies. For example, a giant TPA has been reported for transition metal dichalcogenides (TMDs) which has been attributed to the peculiar optical properties of 2D crystals; in another study on TMDs, TPA has been used to probe excited states which are dark in linear optics.

As a consequence, there is a revival of interest about the selections rules for two-photon transitions. In TMDs, the symmetry of the excitonic states is related to the existence of gaps at the K points of the Brillouin zone. Excitonic effects are strong and the exciton wave functions are fairly localized, so that the low threefold symmetry plays an important role. Although it has been first argued that the usual selection rules based on the hydrogenic model are also valid more accurate studies have shown that this is actually not the case, for one-photon as well as for two-photon processes.

Here we analyze the case of the h-BN single layer and bulk, which have the same lattice symmetry as the TMDs and very strongly bound excitons. We combine tight-binding calculations of the two-photon transition probability with sophisticated ab initio real-time Bethe-Salpeter simulations of the two-photon resonance third-order susceptibility. This combination is a unique feature of this work: on the one hand the tight-binding calculations allow us to identify the symmetry properties of the excitons, on the other hand the ab initio real-time Bethe-Salpeter simulations provide the TPA spectra—to our knowledge the first ab initio TPA spectra at this level of theory—which can be compared quantitatively with experiment. These two very different approaches show consistently that the TPA is able to probe the lowest 1s exciton in the bulk and single layer h-BN.

In Sec. II we discuss the choice of h-BN as a case study and describe the tight-binding modeling of its electronic and optical properties. In Sec. III we detail how the two-photon transition probabilities and the two-photon resonance third-order susceptibility are obtained respectively within the tight-binding and the ab initio framework. We then show and compare the results of the ab initio real-time simulations (Sec. IV A) and of the tight-binding calculations (Sec. IV B) for the single layer h-BN. We also contrast the case of the single layer with the bulk, highlighting the role of the inversion symmetry. Finally, we discuss the selection rules for one- and two-photon processes and on the basis of our results we clarify few recent experimental works on nonlinear optical properties of 2D crystals and bulk h-BN (Sec. IV C).
II. ELECTRONIC, OPTICAL PROPERTIES AND TIGHT BINDING MODEL OF h-BN

A. Choice of the system

We have chosen h-BN monolayer as a case study for several reasons. One reason is the abundance of experimental studies (luminescence, X-rays, electron energy loss spectroscopy) on the electronic and optical properties of both the bulk and the single layer. These studies, supported by theoretical investigations, have shown that h-BN is an indirect band gap insulator whose optical absorption spectrum is dominated by strongly bound excitons. Then, the electronic structures of the h-BN monolayer and of the bulk structure are fairly well known—which is convenient for the tight-binding model. A h-BN monolayer is simply the honeycomb lattice where B and N atoms alternate on the hexagons. The bands close to the gap are built from the π states. In the case of the monolayer, there are just a single valence π band and a conduction π∗ band which are nearly parallel along the K-M direction of the Brillouin zone. The gap is direct at K point and about \(7\ eV\). \(\Delta\)

It is of interest as well to compare the TPA in the single layer and in the layered bulk system. The stablisest bulk structure corresponds to a so-called AA′ stacking where B and N atoms alternate along lines parallel to the stacking axis. The periodicity along this axis is twice the inter-planar distance and the lattice parameters used in our simulation are \(a = 2.5\ \text{Å}\) and \(c/a = 2.6\). In the bulk, there are then two π and two π∗ bands and the gap becomes indirect between a point close to \(\pi\) and about \(5\text{ Å}\) and \(\Delta\). The Wannier states associated with the π and π∗ bands are then mainly localized on N and B sublattices with small components ±(π/2Δ) on the other ones. The best fit to \(ab\ initio\) data are obtained with \(t = 2.30\ eV\), \(\Delta = 3.625\ eV\).

Notice than when \(\Delta = 0\) the model is that of graphene where the gap vanishes at K points. This discrete tight-binding model has a continuous counterpart when expanding the equations close to K in reciprocal space. The band structure is then described within a Dirac model for massless 2D electrons. Conversely, in the case of the h-BN monolayer we can use a continuous massive Dirac model. The simplest extension of the 2D TB model to bulk h-BN consists in introducing transfer integrals between nearest neighbours along the stacking axis.

B. Tight-binding model

In tight-binding formalism, we used a simple model that describes top valence and bottom conduction bands close to the gap, and which is stable to catch the most relevant physics of optical excitation in h-BN. It turns out that the valence states close to the gap are almost completely centred on the nitrogen sites whereas the conduction states are centred on the boron sites. For the monolayer this has allowed us to derive a very simple tight-binding model characterized by two parameters: an atomic parameter \(\Delta\) related to the atomic levels, +\(\Delta\) for boron, and −\(\Delta\) for nitrogen, and a transfer integral between first neighbours, \(-t\). In this model the direct gap is exactly equal to \(2\Delta\). Close to the gap the electronic structure can be simplified and the electrons in the conduction band (valence band) can be considered as moving on the B (N) sublattice with an effective transfer integral equal to \(t^2/2\Delta\). The Wannier states associated with the π and π∗ bands are then mainly localized on N and B sublattices with small components ±(π/2Δ) on the other ones. The best fit to \(ab\ initio\) data are obtained with \(t = 2.30\ eV\), \(\Delta = 3.625\ eV\).

To first order (one-photon processes), the coupling with the electromagnetic field is described using the hamiltonian \(H_{11} = -e\mathbf{p} \cdot \mathbf{A}/m\), where \(\mathbf{A}\) is the vector potential varying as \(e^{-i\omega t}\). To this order, \(\mathbf{p}/m = \mathbf{v} = \frac{1}{i\hbar}\left[\mathbf{r}, H\right]\), where \(\mathbf{v}\) is the velocity operator and \(H\) is the hamiltonian of the unperturbed system. Using the tight-binding scheme, where \(|\mathbf{n}\rangle\) denotes a \(\pi\) state at site \(\mathbf{n}\), we have \(\mathbf{v}_{nm} = \langle\mathbf{n}|\mathbf{v}|\mathbf{m}\rangle = (\mathbf{n} - \mathbf{m})/\hbar t_{nm}\), where \(t_{nm}\) is the transfer integral between sites \(\mathbf{n}\) and \(\mathbf{m}\). Using our simple model for the h-BN sheet, we keep only first neighbour integrals \(-t\) and the matrix element couples valence states \(|\mathbf{m}_w\rangle\) to conduction states \(|\mathbf{n}_c\rangle\). Actually, as mentioned above, the atomic states should be replaced by Wannier states:

\[
|m_w\rangle \sim |m_N\rangle + \frac{t}{2\Delta} \sum_\tau |m_N - \tau\rangle
\]

\[
|n_c\rangle \sim |n_B\rangle - \frac{t}{2\Delta} \sum_\tau |n_B - \tau\rangle
\]
where $|m_N\rangle$ and $|n_B\rangle$ denote the genuine atomic states centred on the N and B atoms, and where the three $\tau$ vectors are the first neighbour vectors $n_B - m_N$. The corresponding Bloch functions are given by:

$$|k_c\rangle \simeq |k_N\rangle + \frac{t}{2\Delta} f^*(k)|k_B\rangle$$  \hspace{1cm} (3)

$$|k_s\rangle \simeq |k_B\rangle - \frac{t}{2\Delta} f(k)|k_N\rangle,$$  \hspace{1cm} (4)

where the $|k_{N(B)}\rangle$ are the Bloch functions built from the atomic orbitals, $|k_{N(B)}\rangle = \frac{1}{\sqrt{N}} \sum_{nN(B)} e^{i k n} |n\rangle$, and where $f(k) = \frac{1}{\pi} e^{i k \tau}$, and $N$ is the number of lattice cells. To lowest order in $t/\Delta$, we have therefore:

$$\langle k_s | v | k_c \rangle \simeq \langle k_B | v | k_N \rangle = -\frac{t}{\hbar} \nabla_k f(k) + \epsilon.$$  \hspace{1cm} (5)

At low energy we can expand $k$ close to the $K$ and $K'$ (equivalent to $-K$) points. Up to a phase factor which depends on the choice of the $K$ points, we obtain:

$$\langle k_s | v.e | k_c \rangle \simeq (\pm K_c | v.e | \pm K_s) \simeq v_F (e_x \pm ie_y),$$  \hspace{1cm} (6)

where $v_F = \frac{2}{3} a_{bn} t$ is the slope of $|(f(k + q)|$ for small $q$, $|(f(k + q)| \simeq v_F q$ when $q \to 0$, and $a_{bn}$ is the distance between first neighbor $B$ and $N$ atoms. $v$ is the vector characterizing the light polarization, where $\pm K_c$ are the wave functions at the $\pm K$ points. The matrix elements are therefore maximum for circular polarizations of opposite signs in $K$ and $K'$ valleys. This result is now fairly well known in the case of transition metal dichalcogenides but it is worth insisting on a particular point. The optical coupling between valence and conduction bands is not related here to the symmetry of the $\pi$ states of nitrogen and boron. Indeed, when considering polarization vectors within the sheet plane, they behave as $s$ states. The coupling is due to the fact that the Wannier functions of the $\pi$ and $\pi^*$ bands are centred on different sublattices. Since furthermore there is no symmetry centre connecting these sublattices a finite dipolar moment is allowed, of the circular type here, because of the threefold symmetry.

### D. One-photon absorption for independent single particles

Within a one-particle model and neglecting the photon wave vector, the one-photon absorption is proportional to the transition probability $W$ given by the Fermi golden rule:

$$W = \frac{2\pi}{\hbar} e^2 (E/2)^2 \sum_k |\langle k_c | v.e | k_v \rangle|^2 \delta(E_{k_c} - E_{k_v} - \hbar \omega),$$

where $E$ is the electrical field amplitude. In our model the valence and conduction bands are symmetric, $E_{kv} = -E_{kc}$, so that $E_{kc} - E_{kv} \simeq 2\Delta + \frac{t^2}{\Delta} |f(k)|^2$, where $|f(k)|^2$ is the band energy of a triangular lattice with transfer integrals equal to $t^2/\Delta$ and centred on $2\Delta + 3t^2/\Delta$.

Neglecting the dependence on $k$ of the matrix element, and replacing $E = \hbar \omega$ by $2\Delta$ close to the gap, we recover the usual formula for the absorption, proportional to the joint density of states, which is here also proportional to the densities of states of the valence and conduction bands.

### E. Excitons

In the presence of electron-hole interactions, excitonic effects come into play. They are usually treated using a Bethe Salpeter formalism, which, within our TB formalism, can be reduced to an effective Wannier-Schrödinger equation for electron-hole pairs.

#### 1. Formalism

Let then $|\Phi\rangle$ be such an excitonic state. In our model for the monolayer, it can be written as:

$$|\Phi\rangle = \sum_k \Phi_k a_{k_c}^+ a_{k_v} |0\rangle,$$  \hspace{1cm} (7)

where $a_{k_c}^+$ and $a_{k_v}$ are the usual creation and annihilation operators for conduction and valence electrons and $|0\rangle$ is the unperturbed ground state. It is convenient to work in real space, using the Wannier basis for electrons and holes, and to write:

$$|\Phi\rangle = \sum_{nm} \Phi_{nm} a_{n_c}^+ a_{m_v} |0\rangle.$$  \hspace{1cm} (8)

Within this formalism the action of the velocity operator on the ground state can be written:

$$\mathbf{v} |0\rangle = \sum_{nm} \mathbf{v}_{nm} a_{n_c}^+ a_{m_v} |0\rangle = -\sum_{m,\tau} \frac{t}{\hbar} \tau \mathbf{R} a_{(m_c + \tau_c)}^+ a_{m_v} |0\rangle.$$  \hspace{1cm} (9)

Finally we define electron-hole states in reciprocal and real spaces:

$$|k_{vc}\rangle = a_{k_c}^+ a_{k_v} |0\rangle = \frac{1}{\sqrt{N}} \sum_{R} e^{i k R} |R_{vc}\rangle$$  \hspace{1cm} (10)

$$|R_{vc}\rangle = \frac{1}{\sqrt{N}} \sum_{n} a_{n_c}^+ R_{vc} a_{n_v} |0\rangle.$$  \hspace{1cm} (11)

One should be careful in distinguishing the variables associated with the motion of the electron-hole pair as a whole from those describing the relative motion of the electron and of the hole. The latter ones are $k$ and $\mathbf{R}$. The position of the pair is defined here by the position of the hole, whereas its motion as a whole is characterized by $Q = k_c - k_v$ which is a good quantum (conserved) number, taken here equal to 0. Actually $|R_{vc}\rangle$ is nothing...
using diagonalization or Green function techniques. Problem which can be solved with standard techniques, triangle element is:  

\[ (E_{k_e} - E_{k_h}) \Phi_{kec} + \sum_{k'v'c'} \langle kvc|K_{eh}|k'v'c' \rangle \Phi_{k'v'c'} = E \Phi_{kvc}. \]

In this equation, \( E_{k_e} - E_{k_h} \) plays the part of a band (or kinetic) energy, approximated here by \( 2\Delta + t^2/\Delta \). The interaction term \( K_{eh} \) contains a direct Coulomb contribution and an exchange term which will be neglected here. Coming back in real space, we obtain an excitonic hamiltonian \( H_{eh} \):

\[ H_{eh} = H_{eh}^0 + U \]

\[ \langle R|H_{eh}^0|R' \rangle = 2\Delta + 3t^2/\Delta \quad \text{if} \quad R = R' \]

\[ = t^2/\Delta \quad \text{if} \quad R \text{ and } R' \text{ are nearest neighbours} \]

\[ U = \sum_{R} |R|U_{R}(R) . \]

According to our definitions the vectors \( R \) have their origin on a hole (nitrogen) site and their extremities on the electron (boron) triangular sublattice. We then see that the above hamiltonian is similar to a tight-binding hamiltonian for electrons moving on a triangular lattice in the presence of an “impurity” at the origin (at the centre of a triangle). If the potential \( U_{R} \) is known, this is a classical problem which can be solved with standard techniques, using diagonalization or Green function techniques.

In what follows, we detail how we evaluate the TPA

\[ W \propto \sum_{i} \langle \Phi_i|e.v|\Phi_i \rangle \delta(h\omega - E_i)\langle \Phi_i|v.e|\Phi_i \rangle \]

\[ = e.\langle \Phi|v\delta(h\omega - H_{eh})v|\Phi \rangle , \]

where the sum over \( i \) is over all exciton states. Finally, using the Green function \( G(z) = (z - H_{eh})^{-1} \), it is sufficient to calculate \( \langle \Phi|vG(z)v|\Phi \rangle \) [23]

III. TWO-PHOTON ABSORPTION

The TPA is related to the nonlinearity in the attenuation of a laser beam. Considering the intensity \( I \) of a beam propagating along \( \hat{z} \), at the lowest order beyond the linear regime, the attenuation is a nonlinear function of \( I \):

\[ \frac{dI}{dz} = -\alpha I - \beta I^2 , \]

where \( \alpha \) is the linear absorption coefficient, and \( \beta \) is the two-photon absorption coefficient (see e.g. Ref. [44]).

In what follows, we detail how we evaluate the TPA from either the third-order susceptibility extracted from \textit{ab initio} real-time dynamics (Sec. [III A]) and from the transition probability of a two-photon process within a second-order perturbation treatment (Sec. [III B]).
A. Nonlinear susceptibilities from \textit{ab initio} real-time dynamics

The TPA coefficient in Eq. (20) is related to the imaginary part of the third-order response function $\chi^{(3)}$,  
\[
\beta(\omega) = \frac{3\omega}{2n_0^2v_\infty^2(n_0)(\omega)} \text{Im} \left[ \chi^{(3)}(-\omega; \omega, \omega, -\omega) \right]. \tag{21}
\]
where $n_0(\omega)$ is the refractive index. In two-photon measurements, the incoming laser frequency $\omega$ is set around half of the excited state energy $\omega_0$ we want to probe $2\omega \approx \omega_0$.

In this frequency region, well below the band gap, $n_0(\omega)$ is positive, monotonic and slowly varying, therefore the peaks of $\beta(\omega)$ originates only from the imaginary part of $\chi^{(3)}$, that is the quantity we will extract from the real-time simulations\textsuperscript{14}. In the real-time simulations, the electronic system is excited by a time-dependent external field $E$. The time-evolution of the system is given by the following equation of motion for the valence band states,
\[
i\hbar \frac{d}{dt} |v_{mk}\rangle = \left( H_{k}^{\text{MB}} + iE \cdot \tilde{\partial}_k \right) |v_{mk}\rangle, \tag{22}
\]
where $|v_{mk}\rangle$ is the periodic part of the Bloch states. In the r.h.s. of Eq. (22), $H_{k}^{\text{MB}}$ is the effective Hamiltonian derived from many-body theory that includes both the electron–hole interaction and local field effects. The specific form of $H_{k}^{\text{MB}}$ is presented below. The second term in Eq. (22), $E \cdot \tilde{\partial}_k$, describes the coupling with the external field $E$ in the dipole approximation. As we imposed Born-von Kármán periodic boundary conditions, the coupling takes the form of a $k$-derivative operator $\tilde{\partial}_k$. The tilde indicates that the operator is “gauge covariant” and guarantees that the solutions of Eq. (22) are invariant under unitary rotations among occupied states at $k$ (see Ref. 16 for more details).

We notice that we adopt here the length gauge, which presents several advantages for \textit{ab initio} simulations\textsuperscript{17}. Comparing with the velocity gauge approach—that is used in the tight-binding model—the second term of Eq. (22) includes both the $A$ and $A^2$ contributions present in the velocity gauge. The two gauges are equivalent as shown in Appendix I.

From the evolution of $|v_{mk}\rangle$ in Eq. (22) we calculate the time-dependent polarization $P_\parallel$ along the lattice vector $a$ as
\[
P_\parallel = \frac{f|a|}{2\pi \Omega_c} \text{Im} \log \prod_{k}^{N_k-1} \text{det} S(k, k + q), \tag{23}
\]
where $S(k, k + q)$ is the overlap matrix between the valence states $|v_{mk}\rangle$ and $|v_{mk+q}\rangle$, $\Omega_c$ is the unit cell volume, $f$ is the spin degeneracy, $N_k$ is the number of $k$ points along the polarization direction, and $q = 2\pi/(N_k a)$.

The polarization can be expanded in a power series of the incoming field $E_j$ as:
\[
P_i = \chi^{(1)}_{ij} E_j + \chi^{(2)}_{ijkl} E_k E_l + \chi^{(3)}_{ijklm} E_k E_l E_i + O(E^4), \tag{24}
\]
where the coefficients $\chi^{(i)}$ are a function of the frequencies of the perturbing fields and of the outgoing polarization. As explained above, the two-photon absorption is proportional to the imaginary part of the two-photon resonance third-order susceptibility $\chi^{(3)}_{ijkl}(-\omega; \omega, \omega, -\omega)$; i.e. the outgoing polarization has the same frequency $\omega$ of the incoming laser field, as a result of the absorption of two and the emission of one virtual photons.

In order to extract the $\chi^{(3)}$ coefficients we resort to a technique similar to Richardson extrapolation\textsuperscript{17}. In practice, we perform three different simulations with the incoming electric field at frequency $\omega$ and intensities corresponding to the amplitudes $E, E/2$ and $E/4$. The polarization resulting from each simulation can be expanded in the field as:
\[
P(E) = \chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + O(E^4), \tag{25}
\]
\[
P(E/2) = \chi^{(1)} E/2 + \chi^{(2)} E^2/4 + \chi^{(3)} E^3/8 + O(E^4), \tag{26}
\]
\[
P(E/4) = \chi^{(1)} E/4 + \chi^{(2)} E^2/16 + \chi^{(3)} E^3/64 + O(E^4). \tag{27}
\]
Then we combine the three polarizations so to cancel out the linear and quadratic contributions and we obtain:
\[
\chi^{(3)} = \frac{8}{3} \frac{P(E) - 6P(E/2) + 8P(E/4)}{E^3}. \tag{28}
\]

The calculation is repeated for all $\omega$ in the desired range of frequencies.

The level of approximation of the so-calculated susceptibilities depends of the effective Hamiltonian that appears in the r.h.s. of Eq. (22). Here we work in the so-called time-dependent Bethe-Salpeter framework that was introduced in Ref. 18. In this framework the Hamiltonian $H_{k}^{\text{MB}}$ reads:
\[
H_{k}^{MB} = H_{k}^{KS} + \Delta H_{k} + V_h(r)\Delta \rho + \Sigma_{SEX}[\Delta \gamma], \tag{29}
\]
where $H_{k}^{KS}$ is the Hamiltonian of the unperturbed (zero-field) Kohn-Sham system\textsuperscript{19}, $\Delta H_{k}$ is the scissor operator that has been applied to the Kohn-Sham eigenvalues, the term $V_h(r)\Delta \rho$ is the time-dependent Hartree potential\textsuperscript{17} and is responsible for the local-field effects\textsuperscript{20} originating from system inhomogeneities. The term $\Sigma_{SEX}$ is the screened-exchange self-energy that accounts for the electron-hole interaction\textsuperscript{21} and is given by the convolution between the screened interaction $W$ and $\Delta \gamma$. In the same equation:
\[
\Delta \rho \equiv \rho(r; t) - \rho(r; t = 0)
\]
is the variation of the electronic density and:
\[
\Delta \gamma \equiv \gamma(r, r'; t) - \gamma(r, r'; t = 0)
\]
is the variation of the density matrix induced by the external field $\mathcal{E}$.

In the limit of small perturbation Eq. (29) and Eq. (22) reproduce the optical absorption calculated with the standard $GW + $ BSE approach, as shown both analytically and numerically in Ref. [48].

### B. Tight binding model

In tight-binding the second order (two-photon processes) appears in the development of $(p - eA)^2/2m$. In second order perturbation theory with respect to $A$, there are two terms. The first one is related to the linear term $(p - eA)$ treated in a second order perturbation theory, and the second one comes from the $A^2$ term treated to first order. The latter one is frequently considered as non-relevant in the optical regime, which is not the case here as explained below. Let us begin with the first contribution.

#### 1. Second order perturbation theory

To second order, the transition probability $P_{i \rightarrow f}$ from an initial state $|i\rangle$ towards a final state $|f\rangle$ is given by:

$$ P_{i \rightarrow f} = \frac{2\pi}{\hbar} \left| \frac{1}{4} \sum_{j \neq i,f} W_{fj}W_{ji} \right|^2 \delta(E_f - E_i - 2\hbar\omega), $$

where $W_{ij}$ is the one-photon matrix element towards the intermediate state $j$. A convenient approximation consists here to replace $E_j$ by a mean energy between the initial energy and the exciton levels close to the bottom of the conduction band. The sum in the numerator can then be freely performed, and we are back to a situation similar to the first order calculation, where now the relevant matrix element is equal to $\langle f | W^2 | i \rangle$. Since we are looking at transitions close to the gap, $\hbar\omega \sim \Delta$, and the denominator is also of order $\Delta$. The relevant matrix element is equal to $\langle \Phi | (v.e)(v.e) | \Phi \rangle$. As seen above, the first velocity operator operating on the ground state generates electron-hole states. Therefore, the second one couples different electron-hole states. Since it is related to the kinetic energy part, it operates separately on the electron state and on the hole state, and therefore gives contributions proportional to the velocity of the one-particle states. The corresponding matrix elements in real space are equal to $-\frac{e}{2m} a$, where $a$ is a first neighbour distance on the triangular lattice. The final complete matrix element $\langle \Phi | (v.e)(v.e) | \Phi \rangle / \Delta$ is therefore of order $t^3/\Delta^2$. There is no reason that it vanishes identically for the ground state exciton. Actually the (tensorial) product of velocity operators transform as $E \times E$ which also contains $E$. In the continuous limit however, it can be shown that $\langle \Phi | v \otimes v | \Phi \rangle \sim \nabla \Phi(x)$, which implies that only $p$ states are bright. We are in a typical situation where precise selection rules based on the exact crystalline symmetry allow transitions which become forbidden if an approximate (higher) spherical symmetry is assumed.

#### 2. $A^2$ term

In principle the $A^2$ term is local and its influence is negligible in the optical regime where the wave length is much larger than interatomic distances. At least this is true when using the full Hamiltonian. In band theory we project the Hamiltonian on the subspace defined by the number of bands taken into account, and the correct method to include gauge-invariant coupling with the electromagnetic field is to make the so-called Peierls substitution. This generates non-local coupling at all orders in $A$. More precisely in our case, we make the substitution:

$$ t_{nm} \rightarrow t_{nm} e^{i e (n-m) \cdot A} / \hbar. $$

To first order, we can check that this generates the coupling $H_{11}$ used above, i.e.:

$$ \langle n | H_{11} | m \rangle = i \left( \frac{e}{\hbar} \right) \langle m - n | A | t_{nm} \rangle, $$

and therefore:

$$ \langle 0 | H_{11} | \Phi^\pm \rangle = i \frac{e A}{\hbar} \sum_\tau (\tau, e) \Phi^\pm_\tau, $$

$$ \sum_\tau (\tau, e) \Phi^\pm_\tau = e d_\Phi^\pm = -\frac{3}{2} a_{bn} (e_x \pm i e_y) \Phi^\pm_{e^A}, $$

where $a_{bn} = |\tau|$ and $\Phi^\pm_\tau$ is the amplitude $\langle \tau | \Phi^\pm \rangle$ of the circularly polarized state defined previously. To second order, we obtain:

$$ \langle n | H_{12} | m \rangle = -\frac{1}{2} \left( \frac{eA}{\hbar} \right)^2 \langle (m - n) | A^2 | t_{nm} \rangle, $$

from which we deduce that:

$$ \langle 0 | H_{12} | \Phi^\pm \rangle = -\frac{1}{2} \left( \frac{eA}{\hbar} \right)^2 \sum_\tau (\tau, e)^2 \Phi^\pm_\tau, $$

$$ \sum_\tau (\tau, e)^2 \Phi^\pm_\tau = e \Phi^\pm_\tau = \frac{3}{2} a_{bn} (e_x \pm i e_y)^2 \Phi^\pm_{e^A}, $$

where $\Phi^\pm_{e^A} = \sum_\tau (\tau \otimes \tau) \Phi^\pm_{e^A}$ is a quadrupolar matrix element.

The last result is remarkable. It shows first that the matrix element is similar to that of the first order term and therefore that the corresponding two-photon process should be strongly visible. Then we see that the favored circular polarization for the two-photon process is the opposite of that of the one-photon process. Finally this
direct contribution to first order in $A^2$ is stronger than the contribution discussed above coming from the second order perturbation theory. The latter one is of order $k^2/\Delta^2$ less than the former one. It is interesting also to analyze what happens in reciprocal space. Then the Peierls substitution amounts to replace $k$ by $k-eA/h$ and the non-vanishing $A^2$ contributions appear only if $f(k)$ is expanded up to $k^2$ terms. In the context of studies on graphene, this corresponds to including so-called warping effects. In the context of $k\cdot p$ methods such effects would also appear if coupling with other conduction and valence bands are included.

3. One- and two-photon absorption in bulk h-BN

As mentioned previously and, as far as the band structure is concerned, the extension to three dimensional stackings of BN layers is fairly simple. On the other hand the excitonic formalism should also be extended to the case where there are several atoms per unit cell. In practice, if we continue to define exciton states using the separation between electrons and holes, we must add labels indicating in which type of plane they are.

The general corresponding TB formalism is described elsewhere but if we are principally interested in the ground state excitons, the discussion becomes simpler. Actually the 1s exciton of the monolayer discussed above remains confined within a single plane in bulk h-BN if the hole is fixed in this plane. Along the 0z stacking direction we have therefore to treat a problem similar to that of a Frenkel exciton, where the 2D exciton plays the part of an atomic exciton. We can then build two different excitonic Bloch functions along the 0z stacking direction which we call $|\Phi_A\rangle$ and $|\Phi_{A'}\rangle$. Introducing interplanar transfer integrals in the TB model couples these two states, and since there is an inversion center between any pair of A and A’ planes the final exciton eigenstates should be the usual bonding and antibonding states $|\Phi_A\rangle \pm |\Phi_{A'}\rangle$. The 1s state of the monolayer becomes two split states (Davydov splitting) separated by a small energy (see also Ref. [36 and 56]). Ab initio calculations show that the bonding state is the ground state. Since the threefold symmetry is preserved, the two states are still themselves twofold degenerate.

Let us now look at the one-photon absorption process. We still consider a polarization e parallel to the planes. The total $d_\Phi$ and $d_{\Phi'}$ dipole for the AA’ stacking is therefore equal to $d_{\Phi_A} = \pm d_{\Phi_{A'}}$. On the other hand the inversion symmetry $d_{\Phi_{A'}} = -d_{\Phi_A}$ and finally the dipole vanishes for the bonding state whereas the upper anti-bonding state is bright. In the case of the two-photon process, we can use a similar argument, but since now $q_{\Phi_{A'}} = q_{\Phi_A}$, the situation is reversed: the bright exciton is the lower bonding one.

![FIG. 1. Two-photon absorption and imaginary part of the dielectric constant in single layer (panel a) and bulk h-BN (panel b). The two curves have been rescaled in such a way to have the same intensity at the maximum position. Vertical lines in panel (b) indicates the position of the maximum.](image)

IV. RESULTS AND DISCUSSION

A. ab initio calculations

All operators in Eq. (22) and Eq. (29) are expanded in the basis set of the Kohn-Sham band states which can be obtained from a standard DFT code. Specifically, we used the QUANTUM ESPRESSO code where the wavefunctions are expanded in plane waves with a cutoff of 60 Ry and the effect of core electrons is simulated by norm-conserving pseudopotentials. A $12 \times 12 \times 4$ ($12 \times 12 \times 1$ for the single layer) k-point shifted grid has been used to converge the electronic density. The band states are obtained from the diagonalization of the Kohn-Sham eigensystem. In order to simulate an isolated h-BN layer we used a supercell approach with a layer-layer distance of 20 a.u. in the perpendicular direction. The scissor operator entering Eq. (29) is chosen so as to reproduce the position of the first bright excitons in the absorption spectra of bulk and monolayer h-BN from Ref. [33]. We expanded $|\psi_{mk}\rangle$ in terms of Kohn-Sham eigenstates and we evolved the coefficients of the bands between 2 and 7 in the monolayer (7 and 12 in the bulk) in Eq. (22). We used a $15 \times 15 \times 15$ ($12 \times 12 \times 1$ in the single layer) k-points $\Gamma$-centered sampling in the real-time simulations which guarantee the convergence of the first peak in the spectra.
Equation (22) is solved numerically for a time interval of 120 fs using the numerical approach described in Ref. [49] (originally taken from Ref. [50]) with a time step of $\Delta t = 0.01$ fs, which guarantees for numerically stable and sufficiently accurate simulations. A dephasing term corresponding to a finite broadening of about 0.05 eV is introduce in order to simulate the experimental broadening.

In Figure 1, panel (a), the two-photon resonant third-order susceptibility at $\chi^{(3)}_{\mu
u
\rho\gamma \delta}(\omega,\omega,\omega,\omega)$ proportional to the TPA— is compared with the imaginary part of the dielectric constant $\varepsilon_2(\omega)$ for the monolayer $h$-BN. To facilitate the comparison there is a factor 2 between the energy scale of the spectra. The first peak of the TPA is found exactly at half the photon energy of the first peak of the imaginary part of the dielectric constant. That means that the two- and one-photon absorption are resonant with the same exciton. In panel (b) the same comparison is shown for bulk $h$-BN. In this case the first peak of the TPA is found 0.076 eV below half the photon energy of the first peak of $\varepsilon_2$. That means that the two-photon absorption is resonant with an exciton at lower energy than the one of one-photon absorption. We also obtained $\varepsilon_2(\omega)$ by solving the standard GW+Bethe-Salpeter equation and diagonalized the excitonic two-particle Hamiltonian. We found—in agreement with previous studies—that the lowest exciton in the linear optical response of bulk $h$-BN is indeed dark. The position of this dark exciton is consistent with the splitting deduced from the TPA calculations. The ab initio results are then fully consistent with the discussion in Sec. III B 3. In the monolayer the ground state exciton is visible in both one-photon and two photon absorption. Instead, in bulk $AA'$ BN, the lowest exciton (pair) is dark in linear optics but becomes visible in two photon absorption. In fact, as explained in Sec. III B 3, the two lowest exciton pairs in the bulk are due to the bonding and anti-bonding combination of excitons in each layer and thus obey different selection rules.

Finally, broader features at higher energies are visible in the spectra. Those features are known to originate from both in-plane excitons with different symmetries and from interplanar excitations. Notice that those peaks may not be fully converged.

B. Tight-binding calculations

1. Monolayer

In the case of the monolayer we have used the TB hamiltonian with the parameters determined in Ref. [12] and have calculated the one-photon absorption spectrum from the Green function $\langle I | G(z) | I \rangle = \sum_{\tau} \langle \tau | G | \tau \rangle$, which is actually independent of the choice for $\mathbf{e}$. This is conveniently done using the recursion method. A cluster of $4 \times 10^4$ atoms is used and 100 recursion levels are calculated. The spectrum, proportional to the imaginary part of the optical dielectric constant is also proportional to the imaginary part of the Green function. We have first calculated the spectrum in the absence of excitonic effects ($U = 0$ in the hamiltonian). It is actually quite similar to the density of states of the triangular lattice. In the presence of excitonic effects the excitons appear as bound states below the continuum. We have checked that they appear at the same positions as those determined from a full diagonalization of the hamiltonian. Furthermore by comparing the optical spectrum to that obtained from a Green function matrix element without any particular symmetry (here $\langle \tau | G | \tau \rangle$) so that all excitons have a finite weight, we can check the selection rules: the non degenerate exciton of symmetry $A_1$ is actually dark in the optical response (Fig. 2).

In the case of two-photon absorption, the calculation of the main contribution due to $J_{12}$, the quadratic term in $A$, can be calculated in a similar way; it suffices to modify the matrix element of the Green function, by taking as initial vector $|I'\rangle = \sum_{\tau} (\tau | e \rangle ^2 | \tau \rangle$. The ground state exciton is then found to be bright as expected.

2. Bulk $AA'$

We have generalized the TB formalism to the 3D $AA'$ stacking. Once the appropriate hamiltonian is defined the recursion method can again be used. Here, the cluster considered contains $8.10^4$ atoms and 100 recursion levels are calculated. According to our previous discussion, to study the two split ground state excitons we have now to use starting states $|I\rangle$ which are bonding and antibonding combinations of excitons in $A$ and $A'$ planes. The results are shown in Figs. 3. As predicted in the previous section we do find that the lower bonding state is dark for one-photon absorption and bright for two-photon absorption, and conversely for the upper antibonding state.

C. Selection rules

Let us summarize the selection rules which apply to $h$-BN as well as to TMD.

1. One-photon selection rules

We consider first the case of the monolayer, and recall the usual rules for Wannier-Mott excitons within the continuous hydrogenic model. The exciton wave function is written in the form $\Phi(r_h, r_e) = \phi_{k_g}(r_e) \phi_{k_v}(r_h) g(r_e - r_h)$, where the $\phi_{k_g}$ are the single particle Bloch functions at point $k_0$, corresponding to the considered direct gap, and $g(\mathbf{r})$, the envelope function, is the solution of the hydrogenic-like excitonic equation for the relative coordinate $\mathbf{r} = r_e - r_h$. In our case $k_0$ is a $K$ or $K'$ point. Then the optical matrix element is the standard one-particle
matrix element at this point weighted by \( g(r = 0) \). The full excitonic symmetry is the symmetry of the above product, but notations generally use the symmetry of \( g(r) \). Optical one-photon transitions are then only allowed for \( s \) states. On the other hand the direct optical transition is allowed since the standard matrix element varies as \( \nu F(e_x \pm ie_y) \) (see Eq. (1)), corresponding to polarisations \( \sigma_{\pm} \), depending on the valley \( K \) or \( K' \). Hence the rule for the exciton one-photon transitions: only \( s \) states are allowed and the optical transitions involve \( \sigma_{\pm} \) polarisations. These rules are weakened if the dependence on \( k \) of the matrix elements is taken into account. At higher values of \( k \), deviations from an isotropic hamiltonian appear, with so-called warping effects, and the usual orbital selection rules are modified. Furthermore, when the exciton size decreases, its size in reciprocal space increases and intervalley coupling is no longer negligible. Although \( k.p \) method can be used, it is then much more convenient to work in real space so as to take the triangular symmetry fully in account.

The excitonic states characterized by the wave function \( \Phi_K = \langle R | \Phi^0 \rangle \) for the monolayer can then be classified according to the representations of the \( C_{3v} \) point group. Among the three representations \( A_1, A_2 \) and \( E \), only the two-dimensional representation \( E \) is optically active, as discussed in Section II E 3. Let us precise the correspondence between the continuous description in terms of \( s, p, \ldots \) states characterizing the symmetry of the envelope function and the present description using the discrete crystal symmetry. For that, we have to include the symmetry of the product of \( \phi_{k_0\sigma}(r_x)\phi_{k_0\sigma}(r_y) \) at \( K \) point. The relevant group of vector \( K \) is the \( C_3 \) point group so that in our case this product is multiplied by \( e^{\pm 2i\pi/3} \) under a rotation of \( \pm 2\pi/3 \). In other words it transforms as \( e^{i\varphi} \) if \( \varphi \) is the azimuthal angle. For a level of symmetry characterized by an angular momentum \( m \), the envelope function of the corresponding exciton states varies as \( e^{\pm im\varphi} \).

When \( m \neq 0 \) the level is twofold degenerate and the full wave function varies as \( e^{i(1\pm m)\varphi} \). The same is true for \( K' \) point provided \( \varphi \) is changed into \( -\varphi \). So finally the level shows a fourfold degeneracy. This is not consistent with representation group theory which says that the degeneracy is at most equal to two in general. The crystal symmetry is lower than the continuous symmetry and the degeneracy is lifted. Consider the \( p \) states for example \((m = \pm 1)\). It has been shown in Ref. [14] that the four \( p \) levels decompose according to the \( E + A_1 + A_2 \) representations. This can be analysed in a first step as an intravalley splitting into distinct \( 1 \pm 1 \) states. Within the continuous model this can be attributed to Berry phase effects.

Another effect of the lower crystalline symmetry is that \( m_{tot} = 1 \pm m \) should be counted modulo three, since only rotations of order three are involved. Thus only states \( m_{tot} = 0, \pm 1 \) are relevant in each valley. Here the allowed values in valley \( K \) are 0 and 2, i.e. 0 and -1, modulo 3. In valley \( K' \) the allowed values are 0 and +1. These rules are fairly well-know but have been recently re-discovered and discussed in detail.

Then, if intervalley coupling is accounted for, the \( \pm 1 \) states combine to produce a global \( E \) symmetry, whereas the \( m_{tot} = 0 \) states combine to form \( A_1 \) and \( A_2 \) states. Now, only \( E \) states are one-photon bright, since the velocity also transforms as \( E \). More precisely, its compo-

FIG. 2. a) One photon spectrum of the 2D BN monolayer with excitonic effects, but without taking into account the exact selection rules (see the main text); b) zoom in the exciton region; top: general spectrum; middle: one-photon optical spectrum; bottom: two-photon optical spectrum. For convenience a broadening of \( 10^{-2} \) eV has been applied, via the imaginary part of Green functions. The \( A_1 \) exciton is only dark in the one-photon spectrum. The origin of energy is taken at the position of the lowest exciton, which can also be labelled as a 1s exciton whereas the other ones derive from 2s and 2p states. Full ab initio calculations including exchange effects predict the \( A_1 \) level to be at a higher energy.

FIG. 3. One- (green) and two-photon (blue) absorption spectrum of AA'-h-BN. Compare with Fig. [4].
nents \( \mathbf{v}(\mathbf{x} \pm i\mathbf{y}) \) transform as \( e^{\pm i\varphi} \). The ground state 1s exciton is obviously bright and form an \( E \) state with a very strong oscillator strength, but we see that the 2p states give rise also to a bright exciton. This is really a "modulo 3" effect which transforms a forbidden \( m_{\text{tot}} = 2 \) state into an allowed \( m_{\text{tot}} = -1 \) state. Notice also that for a given valley the circular polarizations for the \( s \) and \( p \) states are opposite.

Consider now the bulk \( AA' \) stacking. We still assume the light polarization to be within the planes. Then according to the discussion given in Section 3B of [13,14] we have just to consider a linear superposition of monolayer \( E \) states. For this stacking this gives rise to Davydov pairs of bonding and antibonding states, and only antibonding states are bright. Interlayer excitons where the hole and the electron are in different planes can be discussed as well and are relevant if the light polarization is along the stacking axis.

There are therefore two types of selection rules for such lamellar structures for a polarization in the planes. The first one ensures the existence of a dipole within the planes (exciton of \( E \) symmetry). The second depends on the constructive or destructive arrangement of the dipoles in the stacking.

2. Two photon selection rules

Within the continuous model, the general statement concerning selection rules is that only \( p \) states are visible, corresponding to \( \nabla g(\mathbf{r}) \neq 0 \). What is changing here is the symmetry of the coupling with light which has now a tensorial character and varies therefore as \( e^{\pm i\varphi} \). The ground state 1s exciton is obviously bright and form an \( E \) state with a very strong oscillator strength, but we see that the 2p states give rise also to a bright exciton. This is really a "modulo 3" effect which transforms a forbidden \( m_{\text{tot}} = 2 \) state into an allowed \( m_{\text{tot}} = -1 \) state. Notice also that for a given valley the circular polarizations for the \( s \) and \( p \) states are opposite.

Consider now the bulk \( AA' \) stacking. We still assume the light polarization to be within the planes. Then according to the discussion given in Section 3B of [13,14] we have just to consider a linear superposition of monolayer \( E \) states. For this stacking this gives rise to Davydov pairs of bonding and antibonding states, and only antibonding states are bright. Interlayer excitons where the hole and the electron are in different planes can be discussed as well and are relevant if the light polarization is along the stacking axis.

There are therefore two types of selection rules for such lamellar structures for a polarization in the planes. The first one ensures the existence of a dipole within the planes (exciton of \( E \) symmetry). The second depends on the constructive or destructive arrangement of the dipoles in the stacking.

3. Experimental results

One of our main result is the prediction that the ground state 1s exciton which is bright in one-photon absorption should be bright also in two-photon processes, with opposite circular polarizations. The best experimental evidence is certainly the observation in TMD of resonant second harmonic generation (SHG) [15]. In the absence of symmetry center, SHG is allowed for a dichalcogenide layer and it is actually found to be strongly resonant when the 1s level is excited in a two-photon process. Furthermore the circular polarization of the \( 2\omega \) emission is actually opposite to that of the excitation [13,15]. In the case of \( h \)-BN only two-photon photoluminescence excitation (PLE) spectra are available for the bulk phase [16]. They do show a peak slightly above the one-photon main peak whereas we predict a peak below it. The situation is complicated by the fact that the gap is indirect. This is important for the interpretation of luminescence spectra but it is suspected that absorption spectra are governed by direct transitions [17]. The difference between one-photon and two-photon spectra has been interpreted as the signature of \( s \) and \( p \) states respectively. The present analysis show that this is probably not true because of the non conventional selection rules. Another argument is that the 2p and 2s are predicted to be well above the 1s states (about 1 eV for the monolayer, 0.5 eV for the bulk) and cannot therefore be involved in the observed splitting. But the precise interpretation of the observed splitting remains to be correlated with the calculated Davydov splitting.

To summarize we have performed tight-binding and \( ab \)
initio calculations of two-photon absorption in monolayer and bulk boron nitride and found that at low energy it is driven by excitonic effects. The ground state 1s exciton is predominant as for one-photon absorption, indicating strong deviations from the usual selection rules which are explained within a simple TB model taking into account the crystalline symmetry.

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Appendix: On the equivalence of length and velocity gauge in tight-binding

Optical properties are usually treated using the so-called main velocity gauge: \( \mathbf{p} \) is replaced by \( \mathbf{p} - e \mathbf{A} \). As discussed in the main text this implies that to calculate the response to second order in \( \mathbf{A} \) we have to calculate a first order perturbation term in \( A^2 \) and a second order perturbation term with respect to \( \mathbf{A} \). In the length gauge where the interaction term in the Hamiltonian is equal to \( e \mathbf{r} \mathbf{E} \), there is no quadratic term. Since approximations are made, it is useful to check gauge invariance. If we refer to the discussion made in the velocity gauge in Section III B 1 we have therefore just to calculate the second order perturbation term proportional to \( \Delta \langle \Phi | r \mathbf{e} | r \mathbf{e} \rangle | \Phi \rangle \). We have used the fact that \( \mathbf{E} = i \omega \mathbf{A} \) and that \( \omega \approx \Delta \). The first \( r \) generates electron-hole pairs \( r_{nm} a_n^\dagger a_m \rangle \). To lowest order in \( t/\Delta, r_{nm} \) vanishes, and we must use the improved Wannier basis defined in Eqs (12), and then \( r_{nm} \approx -\langle t/2\Delta \rangle (n - m) \), where \( (n - m) \) is a first neighbour vector \( \tau \), so that:

\[
\langle \Phi | r \mathbf{e} | r \mathbf{e} \rangle | \Phi \rangle \approx -\frac{t}{2\Delta} \sum_\tau \tau | \tau \rangle
\]

The second \( r \) operator connects intraband conduction and valence states, and to lowest order in \( t/\Delta \) it can be checked that \( r | \tau \rangle \approx \tau | \tau \rangle \), so that, finally:

\[
\Delta \langle \Phi | r \mathbf{e} | r \mathbf{e} \rangle | \Phi \rangle \approx -\frac{t}{2} \sum_\tau (\tau \cdot e)^2 \Phi^\pm_\tau
\]

which is exactly the result derived in Eq. (35). Thus to lowest order, the second order perturbation theory in the length gauge reproduces the first order term as a function of \( (\mathbf{A} \cdot \mathbf{e})^2 \) in the velocity gauge. The general equivalence of both gauges for non-linear responses of higher order has also been discussed recently in Ref. 69.

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