Excitons in hexagonal boron nitride single-layer: a new platform for polaritonics in the ultraviolet

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The electronic and optical properties of 2D hexagonal boron nitride are studied using first principle calculations. GW and BSE methods are employed in order to predict with better accuracy the excited and excitonic properties of this material. We determine the values of the band gap, optical gap, excitonic binding energies and analyse the excitonic wave functions. We also calculate the exciton energies following an equation of motion formalism and the Elliot formula, and find a very good agreement with the GW+BSE method. The optical properties are studied for both the TM and TE modes, showing that 2D hBN is a good candidate to polaritonics in the UV range. In particular it is shown that a single layer of h-BN can act as an almost perfect mirror for ultraviolet electromagnetic radiation.

I. INTRODUCTION

Two dimensional hexagonal boron nitride (hBN), also called by some white graphene, is an electrical insulator in which the boron (B) and nitrogen (N) atoms are arranged in a honeycomb lattice and are bounded by strong covalent bonds. Like graphene, hBN has good mechanical properties\(^1\) and high thermal conductivity.\(^2\) Specially interesting is the possibility of using hBN as a buffer layer in van der Waals heterostructures, namely ones comprised by layers of h-BN/graphene.\(^3\) Hexagonal boron nitride layer can serve as a dielectric or a substrate material for graphene in order to improve its mobility\(^4\) and open a gap\(^5\). It can also be used to improve the thermoelectric performance of graphene.\(^6\)

Yet, its electronic properties differ significantly from graphene. Graphene \(\pi\) and \(\pi^*\) electronic bands have a linear dispersion at the K point, whereas in hBN there is a lift of the degeneracy at the same point and a wide band gap greater than 7 eV is formed, at least within an independent electron picture. That would, in principle, make it ideal for optoelectronic devices in the deep ultraviolet region\(^7,8\). As we will see, however, excitonic effects play an important role in this material: excitonic peaks are created at the near UV, and this is a much more useful electromagnetic spectral range, when compared to the deep UV.

The optical properties of monolayer hBN at the UV range are characterized by the exciton with a corresponding optical band gap calculated in the range 5.30–6.30 eV (see Sec. II). The presence of the exciton in this range can be used to excite exciton-polaritons, that share some properties with surface plasmon-polaritons\(^9,10\). Therefore, the UV optical properties of hBN can be used as an alternative to the emerging field of UV plasmonics.\(^11–20\) The plasmonics in UV range also attracts interest in biological tissue\(^21\) as consequence of the resonances in nucleotide bases and aromatic amino acids. Plasmonics in this ranges relies in poor metals\(^13,15,16,22\) and Rhodium\(^17,18,20\).

Because of the difficulty of its synthesis, few experimental works have been done for hBN single layer. Also, to study and probe its electronic and optical properties it is necessary to work in UV range. To our best knowledge only one experimental work\(^23\) has been produced that studies the electronic properties of 2D hBN. Those authors observed the band structure of BN monolayer on Ni(111) surface by using angle-resolved ultraviolet-photoelectron spectroscopy and angle-resolved secondary-electron-emission spectroscopy. Because the bond between the interface of h-BN and Ni(111) is weak, the band-structure observed can be regarded as that of the monolayer h-BN. The band gap was determined to be \(\sim 7\) eV and after a comparison with theoretical works, the authors conclude that the band gap is estimated to be within the range of 4.6 to 7.0 eV, too wide when compared with numerical results. These theoretical works were based on first principles calculations using Density Functional Theory (DFT). It is well known that DFT does not predict with good accuracy the electronic and optical properties of semiconductors and insulators. Accurate values require a theory that include many-body effects like the GW approximation.\(^24,25\) To obtain optical properties, a theory that includes the excitonic properties is also needed. Usually, the Bethe-Salpeter equation (BSE)\(^26,27\) is used.

There are several works in the literature that used the GW approximation\(^28–30\) and GW+BSE\(^31–33\) on 2D h-BN. The results from these works vary significantly, as can be seen in Table I. There is no agreement even on whether the gap is direct or indirect. Convergence can be an issue in GW and BSE calculations as can be seen
in References 34 and 35. It is likely that the works summarized in Table I use different criteria for convergence and that may explain the differences.

A small number of bands used in the calculation or not using a truncation to avoid interaction with periodic images may also explain some differences. Sometimes there is some ambiguity between the value stated for the gap and the one that can be obtained from the absorption spectrum presented. More difficult to explain are the values obtained in Ref. 33. They differ significantly from our work and others, although they seem to have converged the calculations carefully. One explanation may be that they fixed the lattice constant at the experimental value, instead of relaxing the unit cell. The experimental lattice constant may not match the value that actually optimizes the system and can influence the values of the gaps in the electronic band-structure. An effective-energy technique was adopted in Ref. 31. That technique allowed the calculation of the screened Coulomb interaction $W$ to be converged with only 90 bands and 60 bands for the self-energy $\Sigma$ calculation. The use of such technique certainly will produce some differences in the final results.

In this work we clarify whether the gap in hBN is direct or indirect, as well as their values and the exciton energies. We also calculate the excitonic spectra using an equation of motion formalism and the Elliot formula, fitting it with the GW+BSE calculations thus obtaining a validation of the method. In Section II we describe the details of the $G_0W_0$ calculations and results. In Section III we show the results of the BSE calculations. Both $G_0W_0$ and BSE calculations were performed with the software package BERKELEYGW. Section IV presents the equation of motion formalism and the results for the excitonic properties of monolayer hBN. In Section V we study the properties of exciton-polaritons of hBN and we show that a monolayer of hBN can be used as a UV mirror. We finally draw the conclusions in Section VI.

### Table I. Several band gaps calculated in this work and by other authors using $G_0W_0$, $G_0W_0$ and BSE, in eV. $K\rightarrow K$ indicates the direct gap at the $K$ point, $K\rightarrow \Gamma$ indicates the indirect gap from the $K$ to the $\Gamma$ point, $O$. Gap is the optical gap and EBE the excitonic binding energy.

| Reference | Calculation | $K\rightarrow K$ | $K\rightarrow \Gamma$ | $O$. Gap | EBE |
|-----------|-------------|------------------|----------------------|--------|-----|
| This work | $G_0W_0$ + BSE | 7.77 | 7.32 | 5.58 | 2.19 |
| Ref. 32   | $G_0W_0$ + BSE | 7.80 | - | 6.30 | 2.10 or 1.50 |
| Ref. 31   | $G_0W_0$ + BSE | 7.36 | - | 5.30 | 2.06 |
| Ref. 33   | $G_0W_0$ + BSE | 7.25 | - | - | 1.90 |
| Ref. 30   | $G_0W_0$ | - | 7.40 | - | - |
| Ref. 29   | $GW_0$ | - | 6.86 | - | - |
| Ref. 28   | $G_0W_0$ | - | 6.00 | - | - |

Figure 1. (Color online) Electronic band structure (left) and electronic density of states of h-BN (right) for both DFT and GW calculations.

### II. $G_0W_0$ RESULTS

$G_0W_0$ calculations were done on top of DFT calculations with a scalar-relativistic norm-conserving pseudopotential. The software package QUANTUM ESPRESSO was used for the DFT calculations. The details of the DFT calculations are summarized in Table II. For $G_0W_0$ calculations, a truncation technique is needed due to the non-local nature of this theory.

We found that for DFT calculations a grid of $6 \times 6 \times 1$ $k$-points is enough to reach convergence. For the GW calculations, a grid of $16 \times 16 \times 1$ $k$-points and a cut off energy of 22.6 Ry and 1000 bands were needed for the dielectric matrix calculations. For the $\Sigma$ self-energy calculation we used a cut off energy of 22.6 Ry and 1000 bands. The results obtained for the electronic band gap are summarized in Table III. They show that a monolayer of hBN is a wide band-gap indirect-gap material. Fig. 1 presents the electronic band structure and electronic density of states for both DFT and GW calculations.

As mentioned in the Introduction, the only experimental work we are aware of is the one from Ref. 23, which in fact estimates the band gap based on theoretical works that used mean field calculations to predict the electronic properties of bulk h-BN. Mean field theories such as DFT underestimate the band gap value of semiconductors and insulator materials. They obtain a wide range of possible values, from 4.6 to 7.0 eV. We believe that a value closer to 7.0 eV is more reliable, since the gap value for the

| Reference | Calculation | $K\rightarrow K$ | $K\rightarrow \Gamma$ | $O$. Gap | EBE |
|-----------|-------------|------------------|----------------------|--------|-----|
| Exchange-correlation functional | GGA-PBE$^{41}$ | | | | |
| Plane-wave cut-off | 70 Ry | | | | |
| $K$-point sampling (Monkhorst-Pack) | $6 \times 6 \times 1$ | | | | |
| Interlayer distance | 15.8 Å | | | | |
| Lattice constant | 2.5 Å | | | | |
Table III. $G_0W_0$ gap values for the transitions $K \rightarrow \Gamma$, $K \rightarrow K$ and $\Gamma \rightarrow \Gamma$, and optical gap and exciton binding energy (EBE) obtained from BSE in this work. The results show that hBN is an indirect-gap insulator.

| Transition | $K \rightarrow \Gamma$ | $K \rightarrow K$ | $\Gamma \rightarrow \Gamma$ | Optical | EBE |
|------------|------------------------|-------------------|-----------------------------|---------|-----|
| Energy [eV] | 7.32                   | 7.77              | 9.07                        | 5.58    | 2.19 |

bulk materials are lower when compared to the monolayer counterpart. And is actually closer to the ones obtained by works referred in Table I. Still, more experimental work is needed.

Ref. 23 also calculated the width of the valence bands, and they found no good agreement with theoretical works of the time. Table IV shows the width of the valence bands as calculated with DFT, GW and the experimental determination of Ref. 23. The $\pi$-band is the one that has its highest energy at the K-point, while the $\sigma_1$ and $\sigma_2$ are the bands that have the highest energy at the $\Gamma$ point. Table IV shows that DFT results differ from the experimental ones by values greater than 0.5 eV in all cases. On the other hand, $G_0W_0$ results differ from the experimental results by values equal or smaller than 0.1 eV.

We also calculated the effective masses of the highest valence band and lowest conduction band using both $G_0W_0$ and DFT (Table V). We found no differences between $G_0W_0$ and DFT, except for the effective mass at $K \rightarrow \Gamma$ on the first conduction band (DFT value greater by 0.08$m_e$). Thus we conclude that DFT calculations are reliable to obtain the values of the effective masses in this material.

Ref. 28 also calculated the effective mass at the $\Gamma$ point for the conduction band, and obtained a value of $(0.95 \pm 0.05)m_e$ with only slight variations for different planar directions. In our work we obtained differences of $0.3m_e$ between different directions in reciprocal space at the $\Gamma$ point.

III. BSE RESULTS

After determining the conduction and valence band states, the electron-hole pair states are determined using the Bethe-Salpeter (BSE) equation. The imaginary part of the dielectric function $\epsilon_2(\omega)$ is then

$$\epsilon_2(\omega) = \frac{8\pi^2e^2}{\omega^2} \sum_{S} |\epsilon \cdot (0) \cdot |S|)^2 \delta(\omega - \Omega^S) \quad (1)$$

where $\Omega^S$ is the energy for an excitonic state $S$, $\langle 0 | v | S \rangle$ is the velocity matrix element, and $e$ is the direction of the polarization of incident light with energy $\omega$. $e$ is the electron charge.

If we do not consider excitonic effects, the expression becomes a transition between single particle states

$$\epsilon_2(\omega) = \frac{8\pi^2e^2}{\omega^2} \sum_{v \neq k} |\epsilon \cdot (v k) \cdot |v k|)^2 \delta(\omega - (E_{ck} - E_{ck})) \quad (2)$$

which is a random phase approximation (RPA). The labels $v$ ($c$) denotes valence (conduction) band states, and $k$ denotes the single particle momentum (only vertical transitions are considered).

Fig. 2 shows the imaginary part of the dielectric function calculated by BSE, done on top of a $G_0W_0$ calculation with a grid of $16 \times 16 \times 1$ k-points. The convergence of the $G_0W_0$ band structure with a particular grid of k-points does not imply that BSE will be converged with the same grid. An interpolation with a fine grid of $120 \times 120 \times 1$ k-points was needed to achieve convergence. Fig. 2 also shows the imaginary part of dielectric function without excitonic effects. The first peak has an energy of 5.58 eV and the second peak has an energy of 6.48 eV. In Table III we summarize the gap values of the band structure, the optical gap and the excitonic binding energy. Fig. 3 shows the real part of the dielectric function calculated with and without excitonic effects.

We also calculated the eigenvalues of the two particle states. Figure 4 shows the energies of the 8 lowest energy excitonic states. From now we label each state by the corresponding energy in an ascending order. The pairs of states $(1,2)$, $(3,4)$, and $(7,8)$ are degenerate. States 1 and 2 are the degenerated ground state. We plot the probability density $|\phi(r_1, r_2)|^2$ obtained from the BSE for these eight excitonic states in Fig. 5. These plots show the probability to find an electron at position $r_1$ if the hole is located at $r_2$. We set the hole localized slightly above the nitrogen atom. The results were calculated using a coarse grid of $12 \times 12 \times 1$ k-points and a BSE interpolation of $72 \times 72 \times 1$ k-points. It can be noticed the complementarity of the degenerate states. For instance,
if one adds the probability density of states 3 and 4, the symmetry of the lattice is recovered. And the same can be seen for the other degenerate states. The work of Ref. 33 has also studied the excitonic states. Their results are in good agreement with the ones obtained from this work.

IV. BSE IN THE EQUATION OF MOTION FORMALISM AND THE ELLIOT FORMULA

In this section we will follow the approach of the equation of motion derived in Ref. 43 and detailed in the Appendix A. The formalism is grounded on the calculation of the expected value of the polarization operator $\hat{P}(t)$ after we introduce an external electric field of intensity $E_0$ and frequency $\omega$ that couples with the electron gas in the 2D material. The optical conductivity and other properties can be obtained from the macroscopic relations. The starting point of our model is an effective Dirac hamiltonian,\textsuperscript{44} that can be obtained from a power series expansion of the tight-binding hamiltonian. The electron-electron interaction for a 2D material is given by the Keldysh potential.\textsuperscript{45} This effective model only considers the top valence band and the bottom conductance band.

From the equation of motion we derive the following BSE:

$$\omega - \tilde{\omega}_{\lambda\mathbf{k}} p_{\lambda}(\mathbf{k},\omega) = (\mathcal{E}_0 d_{\lambda}(\mathbf{k}) + B_{\mathbf{k}\lambda}(\omega)) \Delta f_{\mathbf{k}},$$ (3)

where $\lambda = \pm$, $p_{\pm}(\mathbf{k},\omega)$ is the interband transition amplitude, $\tilde{\omega}_{\lambda\mathbf{k}}$ is the transition energy renormalized by the exchange self-energy and $B_{\mathbf{k}\lambda}(\omega)$ is a term that renormalizes the Rabi-Frequency, $d_{\lambda}(\mathbf{k})$ is the dipole matrix element and $\Delta f_{\mathbf{k}}$ is the occupation difference, given by the Fermi-Dirac distribution. See Appendix A for more details.

From the homogeneous part of Eq. (3) we can obtain the exciton energies and the wave functions. Using the procedure explained in Ref. 43, we can obtain the corresponding Elliot formula for the optical conductivity:

$$\frac{\sigma(\omega)}{\sigma_0} = 4i\hbar \omega \sum_n \frac{p_n}{\hbar \omega - E_n + i\gamma},$$ (4)

where $n$ labels the exciton state, $\gamma$ is the exciton linewidth, $E_n$ the exciton energy, $p_n$ the corresponding exciton weight and $\sigma_0 = e^2/4\pi$. Fig. 6 shows that the $G_0W_0$ + BSE described in section III fits well to the Elliot formula, with a very good agreement in the real part and a small shift in the imaginary part. The energies and weights of the fit for the $G_0W_0$ + BSE and the equation of motion method are compared in table VI. We use the parameters from Ref. 44: $a_0 = 2.51$ Å, $t_0 = 2.33$ eV $\hbar v_F = \sqrt{3/2} t_0 a_0$, $m v_F^2 = 3.92$ eV. The Keldysh potential parameter $r_0$ was calculated in Ref. 33 to be $r_0 = 10$ Å. We can see a excellent agreement between the exciton energies of both methods. The difference in the weights $p_n$ series.
Figure 5. (Color online) Probability density $|\phi(r_x, r_h)|^2$ for the exciton states 1 to 8. The hole is localized slightly above the nitrogen atom (light color) at the centre of the lattice.
can be explained by the oversimplification of the Dirac Hamiltonian used for the Elliot formula and consequently the less accurate dipole matrix elements that enter their calculation.

Figure 6. (Color online) Fit of the Elliot formula to the \(G_0W_0+BSE\) result. There is a very good agreement for the real part and a small shift in the imaginary part; the exciton linewidth used was \(\gamma = 0.1\) eV. The parameters of the fitting are shown in table VI.

Finally, we used the equation of motion to predict the behavior of the exciton energy and the \(K \rightarrow K\) transition energy as a function of the environment dielectric constant. The result can be seen in Fig. 7. There is a strong decrease in the \(K \rightarrow K\) transition energy and an almost linear behavior, also decreasing, of the first exciton energy as the external dielectric constant increases. This effect is simple to understand, since a large dielectric constant screens more effectively the electron-electron interaction.

\[\epsilon_1 \kappa_1 + \epsilon_2 \kappa_2 - i \omega \mu_0 \sigma(\omega) = 0,\]  
(5)

and for the TE mode:

\[\kappa_1 + \kappa_2 - i \omega \mu_0 \sigma(\omega) = 0,\]  
(6)

with \(\sigma(\omega)\) the hBN optical conductivity and:

\[\kappa_i = \sqrt{q^2 - \epsilon_i \omega^2 c^2},\]  
(7)

where \(q\) is the exciton-polariton in-plane wavevector and \(c\) is the velocity of light in vacuum. We shall consider the simplest case of \(\epsilon_1 = \epsilon_2 = 1\). A rule of thumb is that when \(\Im \sigma(\omega) > 0\) (\(\Im \sigma(\omega) < 0\)) TM (TE) modes are supported.

**V. EXCITON-POLARITONS**

In this section we discuss the exciton-polariton modes in 2D hBN. Those modes are electromagnetic evanescent waves along the direction perpendicular to the hBN sheet. We assume that the hBN monolayer is cladded between two uniform, isotropic media with dielectric constants \(\epsilon_1\) and \(\epsilon_2\) and that the hBN sheet is in the \(xy\)-plane. So the electromagnetic mode is evanescent in the \(z\) axis and proportional to \(e^{-\kappa_i z}\) \((i = 1, 2)\). The modes can be classified as transverse magnetic or transverse electric (TM/TE).

| Table VI. Comparison of the Elliot formula parameters used in the \(G_0W_0+BSE\) calculation and the equation of motion approach. The spin and valley degeneracy is already included in the weight. |
|-----------------|--------|--------|--------|--------|
|                | \(E_1\) (eV) | \(p_1\) | \(E_2\) (eV) | \(p_2\) |
| \(G_0W_0+BSE\) | 5.48   | 0.088  | 6.41   | 0.027  |
| Eq. of Motion   | 5.52   | 0.354  | 6.53   | 0.045  |

Figure 7. (Color online) Exciton and \(K \rightarrow K\) transition energy as function of the environment dielectric constant. We can see that the dependence of the first exciton energy is almost linear while the \(K \rightarrow K\) transition energy has a greater dependence on the dielectric constant.

The dispersion relation for the TM mode is given by the solution given in Ref. 46:

\[\frac{\epsilon_1}{\kappa_1} + \frac{\epsilon_2}{\kappa_2} + \frac{\sigma(\omega)}{\epsilon_0 \omega} = 0,\]  
(5)

and for the TE mode:

\[\kappa_1 + \kappa_2 - i \omega \mu_0 \sigma(\omega) = 0,\]  
(6)

with \(\sigma(\omega)\) the hBN optical conductivity and:

\[\kappa_i = \sqrt{q^2 - \epsilon_i \omega^2 c^2},\]  
(7)

where \(q\) is the exciton-polariton in-plane wavevector and \(c\) is the velocity of light in vacuum. We shall consider the simplest case of \(\epsilon_1 = \epsilon_2 = 1\). A rule of thumb is that when \(\Im \sigma(\omega) > 0\) (\(\Im \sigma(\omega) < 0\)) TM (TE) modes are supported.

**A. Complex \(q \times \text{Complex } \omega\)**

First, we note that both Eqs. (5) and (6) are complex. Therefore, for a given \(q (\omega)\) real, the solution will be a complex \(\omega (q)\). Each of these approaches (complex \(q\) or complex \(\omega\)) lead to different dispersion relations for the exciton-polaritons as discussed elsewhere.\(^{47-51}\) Both complex \(q\) and complex \(\omega\) approaches give the same results when an active media is used to balance the losses.\(^{51}\) The complex \(q\) approach is suitable when the polariton is excited in a finite region of space with a monochromatic wave, while the complex \(\omega\) approach is valid instead when the entire sample is excited by a pulsed light.\(^{49}\)

The dispersion relation for both the TE and TM modes in the complex \(\omega\) approach was obtained by solving Eqs. (5) and (6) and using the Elliot formula (4) with the parameters of table (VI) for the \(G_0W_0+BSE\) calculation and a damping of \(\gamma = 0.1\) eV. The result is shown in
For a negligible background provent from interband transitions and other excitonic distribution that arises from the background conductivity where $\alpha$ is the fine-structure constant and $b_0$ is the contribution that arises from the background conductivity provenient from interband transitions and other excitonic states. For a negligible background $b_0 \approx 0$, the exciton-polariton lifetime is proportional to the inverse of the exciton linewidth $\gamma$.

Next we shall consider the case of complex $q$. There will be then a simple relation to obtain $q$ for a given frequency (assuming $\varepsilon_i = 1$):

$$c^2 q^2 = \omega^2 + i \gamma^2 (\omega),$$

with $\alpha = TM/TE$ and from Eqs. (5) and (6) we have:

$$\kappa_{TE}(\omega) = 1 - i \varepsilon \omega / 2 \sigma(\omega),$$

$$\kappa_{TM}(\omega) = 1 - i \omega / 4 \pi \varepsilon \sigma(\omega),$$

The condition for the existence of polaritons is $\Re \kappa > 0$. These equations allowed us to calculate the dispersion relation shown in Fig. 9 for several values of the damping constant $\gamma$. The dependence of the $\gamma$ parameter of excitons was studied for WS$_2$ in Ref. 52 as function of temperature, showing that the linewidth decreases as the temperature decreases. From Fig. 9, we can see that the TE mode is strongly supressed except when the damping has the very low value of 4 meV, close to the intrinsic line-width. The opposite happens for the TM mode, for which the dispersion relation is almost insensitive to the damping $\gamma$.

An important figure of merit is the ratio of the propagation length $l = \Re q^{-1}$ to the exciton wavelength $\lambda_q = 2\pi / \Re q$, as it indicates if a polariton can propagate before extinction, that is shown in Fig. 10 for several values of $\gamma$. The TM mode is highly supressed except for the very low $\gamma = 4$ meV, while the TE mode has higher propagation rate and two different qualitative behaviours. For larger $\gamma$, the propagation rate increases with the frequency while the opposite happens for $\gamma = 4$ meV. A better understanding of this behavior can be achieved if we consider the confinement ratio $\lambda_0 / \lambda_q$, with $\lambda_0$ being the wavelength of the free-radiation (see Figure 11). The confinement of the TM modes increases with increasing frequency and have a negligible $\gamma$ dependence. On the other hand, the TE modes are poorly confined, with the confinement going to zero faster with increasing $\gamma$. This explains the large propagation rate in this case: the poorly confined field is essentially attenuated free radiation, i.e., there are no more excitons being excited, but the radiation field is attenuated by the material free charges.

The overall conclusion is that 2D hBN is a good platform for exciton-polaritons when we consider the complex $\omega$ approach for both TM and TE modes. In the complex $q$ approach, the results show that exciton-polariton can be observed only for $\gamma = 4$ meV.

**B. UV radiation mirror**

It was pointed out recently that excitons in MoSe$_2$ can lead to very high reflection of electromagnetic radiation$^{53,54}$. In this section we show that the same

![Figure 8](image-url)
Figure 9. (Color online) Exciton-polariton dispersion relation in the complex wavenumber approach. Panel A (B) shows the TM (TE) mode. The TM mode has a dispersion almost insensitive to the relaxation rate while the TE mode changes significantly: the wavenumber is close to the free-light one and only for $\gamma = 4\text{ meV}$ there is a different behavior.

occurs with hBN, but in a different spectral range. We consider a free-standing hBN monolayer. In this case the reflection is given by:

$$R = \left| \frac{\pi \alpha f(\omega)}{2 + \pi \alpha f(\omega)} \right|^2,$$

(11)

where $f(\omega) = \sigma(\omega)/\sigma_0$, $\alpha \approx 137^{-1}$ is the fine structure constant and $\sigma_0 = e^2/4\hbar$. Fig. 12 shows that the reflection can reach almost 100% for the value $\gamma = 4\text{ meV}$ at the $A$ exciton energy. This is a consequence of the very high weights for hBN that appears in the Elliot formula (see table VI). We emphasize that those results are for a free-standing hBN sheet. The $\gamma$ value can be controlled by the temperature as discussed in the sections before. As shown in Fig. 7, the exciton energy and therefore the reflection peak can be controlled by varying the external dielectric constant.

VI. CONCLUSION

We calculated the band structure of 2D hexagonal boron nitride using DFT and the $G_0W_0$ approximation.

Then the Bethe-Salpeter equation was used to determine the excitonic energies of hBN. We determined the values of the band gap, optical gap, excitonic binding energies using a first principles approach. The results are in very good agreement with the ones obtained using a very different approach, namely the equation of motion formalism and the Elliot formula, which are also presented in this paper. This latter formalism allowed us to study the optical properties for both the TM and TE modes. Our results show that 2D hBN is a good candidate to polaritonics in the UV range. We also show that a single layer h-BN can act as an almost perfect mirror for ultraviolet electromagnetic radiation.

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Figure 11. (Color online) Exciton-polariton confinement ratio. Panel A (B) shows the TM (TE) mode. The confinement of the TM mode increases with the frequency and has a small dependence with the relaxation rate $\gamma$. The TE modes for the higher values of $\gamma$ are poorly confined. For the value $\gamma = 4$ meV we have a peak in the confinement below the exciton energy.

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Figure 12. (Color online) Reflection coefficient for monolayer hBN and different values of $\hbar \omega$ with the parameters from table VI. Panel (a) and (c) shows the A and B excitons, respectively, with the $G_0W_0$ parameters, while the panels (b) and (d) shows the result from the equation of motion formalism. As the equation of motion formalism predicts higher excitonic weights, in this case we have broader reflectance peaks around the excitons energies in comparison with the $G_0W_0$ result.

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Appendix A: Equation of motion formalism

The total hamiltonian that we consider in the equation of motion approach is $H = H_0 + H_I + H_{ee}$ where we have the Dirac hamiltonian:

$$H_0(k) = \hbar v_F \left( \mathbf{\sigma} \cdot \mathbf{k} + \sigma_3 m v_F^2 \right), \quad (A1)$$

dealing with the dipole interaction hamiltonian:

$$\hat{H}_I(t) = -e \mathcal{E}(t) \hat{x}, \quad (A2)$$

and the electron-electron interaction:

$$\hat{H}_{ee} = -\frac{e^2}{2} \int d \mathbf{r}_1 d \mathbf{r}_2 \hat{\psi}^\dagger(\mathbf{r}_1) \hat{\psi}(\mathbf{r}_2) \mathbf{V}(\mathbf{r}_1 - \mathbf{r}_2) \hat{\psi}(\mathbf{r}_2) \hat{\psi}(\mathbf{r}_1), \quad (A3)$$

where we used the field operator:

$$\hat{\psi}(\mathbf{r}, t) = \frac{1}{\sqrt{L}} \sum_{k, \lambda} \phi_{\lambda}(k) \hat{a}_{k\lambda}(t) e^{-i \mathbf{k} \cdot \mathbf{r}}, \quad (A4)$$

with the eigenvector of $H_0$:

$$\phi_{\lambda}(k) = \sqrt{E_k/m} \left( \begin{array}{c} 1 \\ i k_y - i 1 \\ \lambda E_k + m \end{array} \right), \quad (A5)$$

and eigenvalues:

$$E_k = \sqrt{k^2 + m^2}. \quad (A6)$$

We note that the electron-electron interaction for charges confined in a 2D material is given by the Keldysh potential:

$$V(q) = -\frac{e^2}{2 \varepsilon_0 \varepsilon |q_0 q + \varepsilon_m|}, \quad (A7)$$

The expected value of the polarization operator for the 2D Dirac equation can be written as:

$$P(\omega) = -\frac{i g_{e} e}{2} \sum_{k \lambda} d_{-\lambda}(k) p_{\lambda}(k, \omega), \quad (A8)$$

where $g_{e} = 4$ takes into account the spin and valley degeneracy, $\lambda = \pm$ labels the valence ($-$) or the conduction ($+$) band. The dipole matrix element $d_{-\lambda}(k)$ is:

$$d_{-\lambda}(k) = \frac{1}{2 E_k} \left( \sin \theta + im \frac{E_k}{E_k} \cos \theta \right). \quad (A9)$$

The interband transition amplitude is defined as:

$$p_{\lambda}(k, \omega) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{-i \omega t} \langle \hat{a}^\dagger_{k\lambda}(t) \hat{a}_{k, -\lambda}(t) \rangle. \quad (A10)$$

As explained in Ref. 43, from the equation of motion for the transition amplitude we can derive the following Bethe-Salpeter Equation:

$$(\omega - \tilde{\omega}_{k\lambda}) p_{\lambda}(k, \omega) = (\mathcal{E}_0 d_{\lambda}(k) + B_{k\lambda}(\omega)) \Delta f_k, \quad (A11)$$

where $\tilde{\omega}_{k\lambda}$ is the renormalized transition energy:

$$\tilde{\omega}_{k\lambda} = 2 \lambda E_k + \lambda \Sigma_{x, k\lambda}^{xc}, \quad (A12)$$

where the exchange self-energy is included as

$$\Sigma_{x, k\lambda}^{xc} = \int \frac{d\mathbf{r}}{(2\pi)^2} V(q) \Delta f_{k - \mathbf{q}} \left[ F_{\lambda' \lambda' \lambda}(k, \mathbf{k} - \mathbf{q}) + \frac{1}{2} p_{\lambda'}(\mathbf{q}, \omega) F_{\lambda' \lambda' \lambda}(k, \mathbf{q}) \right]. \quad (A13)$$

The homogeneous part of equation A11, obtained by setting $\mathcal{E}_0 = 0$, can be used to calculate the excitons wavefunctions and energies. From the inhomogeneous solution of A11, $p_{\lambda}(k, \omega)$ the macroscopic polarization $P(\omega)$ can be calculated using Eq. A8 and from there it follows the optical conductivity, permittivity and absorbance.

The overlap of four wavefunctions is given by the $F_{\lambda_1, \lambda_2, \lambda_3, \lambda_4}(k_1, k_2)$ function:

$$F_{\lambda_1, \lambda_2, \lambda_3, \lambda_4}(k_1, k_2) = \phi_{\lambda_1}^\dagger(k_1) \phi_{\lambda_2}(k_2) \phi_{\lambda_3}(k_2) \phi_{\lambda_4}(k_1). \quad (A15)$$

Appendix B: Exciton in the polariton electrostatic limit

In the electrostatic limit the TM exciton-polariton equation read as:

$$\frac{\varepsilon_1 + \varepsilon_2}{q} + \frac{\sigma(\omega)}{\varepsilon_0 \omega} = 0, \quad (B1)$$

with the solution:

$$\hbar \omega(q) = E_n + \frac{M_n}{(\varepsilon_1 + \varepsilon_2) b_n} - ib \gamma, \quad (B2)$$

where $b_n$ can be a complex quantity, the polariton lifetime is given by $-1/|\gamma|$, and:

$$\Im |\omega| = -\gamma - \frac{1}{\hbar} \frac{M_n \Im |b_n|}{(\varepsilon_1 + \varepsilon_2) b_n + 1} \quad (B3)$$
from (B2) we can see that excitons-polaritons always exist in TMD’s systems. For the parameters considered,
\[ \Re \left[ \frac{M_n}{\varepsilon_1 + \varepsilon_2 + 1} + b_n \right] > 0, \]
so the exciton-polariton will always exist for energies higher than the exciton energy. This term also defines the exciton-polariton bandwidth, for \( q \to \infty \):
\[ \Re [\hbar \omega(q \to \infty)] = E_n + M_n \Re [b_n]. \quad (B4) \]