The influence of high-energy local orbitals and electron-phonon interactions on the band gaps and optical spectra of hexagonal boron nitride

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We report theoretical results of hexagonal boron nitride (h-BN) using state-of-the-art first-principles methods, focusing on providing well-converged quasiparticle band structures, and upon this unraveling the intricate interplay between the quasiparticle excitations, electron-phonon interactions (EPIs), and excitonic effects. Including high-energy local orbitals (HLOs) is crucial in all-electron linearized augmented plane waves (LAPWs)-based GW calculations, which widens the quasiparticle direct (indirect) band gaps by 0.22 (0.23) eV, and opens the GW0 direct (indirect) band gaps to 6.81 (6.25) eV. EPIs, on the other hand, reduce them to 6.62 (6.03) eV at 0 K and 6.60 (5.98) eV at 300 K. With clamped structure, the first absorption peak is at 6.07 eV, originating from the direct exciton at H in the Brillouin zone (BZ). After including lattice vibrations using the dynamical Heine-Allen-Cardona method, this peak shifts to 5.83 eV at 300 K, lower than the experimental value of 6.00 eV. This accuracy is acceptable to an ab initio description of excited states with no adjustable parameter, and including HLOs plays a determinant role. The shoulder at the lower energy side of the first absorption peak is still absent, which we believe is related to the indirect excitons. This effect is absent in the present treatment, therefore we call for further improved method in future studies.

I. INTRODUCTION

Hexagonal boron nitride (h-BN) is a wide band gap semiconductor with lamellar structure, similar to graphite which is metallic. Its wide band gap nature, low dielectric constant, and high thermal and chemical stability mean that it is a promising candidate material for high-speed electronic and ultraviolet optical and electronic devices.

In spite of the popularity and numerous experimental and theoretical studies of h-BN for several decades, the most basic problem concerning its band structure, i.e., its fundamental band gap being of direct or indirect nature, is still unclear. As one of the most direct methods to study the electronic structure of solids, high-resolution angle-resolved photoemission spectroscopy (ARPES) has determined the valence-band maxima of h-BN. However, the dispersion of the conduction-band states of h-BN has never been reported. In fact, this is a general technical problem of ARPES for wide band gap semiconductors. Therefore, one has to resort to optical experiments to unravel their band structures in an indirect manner. Most optical measurements indicate a direct band gap, but first-principles calculations predict an indirect one. Considering the phenomenological success of first-principles methods in the last more than 30 years, this inconsistency in such a weakly correlated electronic system is fairly uncommon.

Very recently, Cassabois et al. developed a two-photon spectroscopy technique and reported some previously unfound lines, which they assigned them to the indirect band gap excitons of h-BN. Direct simulations of these photoluminescence (PL) spectra, however, is difficult due to the complicated nature of this process and expensive calculation of excited state potential energy surfaces. Hence, most comparisons between theory and ex-
experiment rely on the absorption spectra. State-of-the-art theoretical methods resort to the many-body perturbation theory (MBPT) for single-particle excitations. The exciton effect is then taken into account by using the standard Bethe-Salpeter equation (BSE). In h-BN, relatively strong electron-phonon interactions (EPIs) mean that contributions of the phonon to the final spectra are also important. Along this route, Marini demonstrated that the EPIs deeply modify excitonic states both at zero and at finite temperatures ($T_s$). Nevertheless, a detailed comparison between theory and experiment shows that the theoretical absorption peak has a noticeable redshift compared to the experimental measurement and a shoulder before the first peak as observed in the experiment is absent in theoretical calculations.

In this paper, we studied the electronic structures of h-BN from the theoretical perspective using a combination of ab initio methods, starting from the completeness of the basis set for the expansion of the quasiparticle wave functions. We found that including high-energy local orbitals (HLOs) in the all-electron (linearized) augmented plane waves (LAPW) method increases the direct and indirect band gaps of h-BN by 0.22 and 0.23 eV compared with previous results. The final quasiparticle direct and indirect GW$_0$ band gaps with clamped structure are 6.81 and 6.25 eV. Based on these, the EPIs, the electron-hole interaction, and exciton-phonon interaction were analyzed. The EPIs induce a zero-point renormalization energy of the direct (indirect) band gap of 0.20 (0.22) eV. The renormalized direct (indirect) band gap is 6.62 (6.03) eV at 0 K, and 6.60 (5.98) eV at 300 K. Using the BSE, the excitonic effects are studied first using clamped crystal structure and we found an exciton binding energy of 0.76 eV, associated with the direct band clamped crystal structure and we found an exciton binding energy of 0.76 eV, associated with the direct band gap at $H$ in the BZ. The coupling between EPIs and excitonic effects was then investigated using the dynamical Heine-Allen-Cardona (HAC) theory. The final influence is a redshift of the absorption peak, which results from a competition between the decrease of the quasiparticle band gaps which shifts the absorption peak to lower energy, and the decrease of the exciton binding energy which shifts it to the higher energy. The former factor is dominant. The resulting line shape at finite $T_s$ agrees well with available experiments. But we note that a shoulder before the first absorption peak is absent, which we believe is related to indirect excitons. This effect is still not addressed in the present study, which requires further improved method. This work reemphasizes the importance of basis set completeness in quasiparticle energy calculations. In the mean time, it also highlights role played by the intricate interplay between the electrons, holes, and phonons for descriptions of the electronic structures of this system challenging to routine theory.

This manuscript is organized as follows. In Sec. II we present a short overview on the implementation of the GW in the LAPW basis and a clear account of the methodology for calculating electron-phonon interactions from first-principles. The computational details of the calculations are also provided. In Sec. III, we report the influence of including HLOs in LAPW-based GW calculations. The $T_s$-dependent band renormalization and the zero- and finite-$T_s$ optical absorption incorporating both excitonic effect and EPIs of h-BN were also analyzed. The conclusions are given in Sec. IV.

II. METHODS AND COMPUTATIONAL DETAILS

A. GW in the LAPW basis including HLOs

The LAPW method is among the most accurate methods for performing electronic structure calculations for crystals. It stems from the augmented plane waves (APW) method, where the muffin-tin (MT) approximation originally proposed by John C. Slater is used. The wave functions are atomic-like in the region close to nuclei defined by the MT radius $R_{MT}$, and plane-wave-like in the interstitial region ($I$) between nuclei. Inside the atomic spheres, atomic-like wave function is a linear combination of radial function times spherical harmonics function. Here, $r^α = r - r^{α}_i$, $R_{MT}^α$ is the MT radius of the $i$th atom. $u_{al}(r^α; E_{al})$ is the solution of the radial Schrödinger equation at a fixed reference energy $E_{al}$ in the spherical potential of the respective MT sphere, and $u_{al}(r^α; E_{al})$ is its energy derivative. The expansion coefficients include $A_{al}^{α}(k + G)$ and $B_{al}^{α}(k + G)$, which are determined from the continuity of the basis functions and their first derivative at the boundary of the MT sphere. The LAPW basis can be reduced to an APW basis when $B_{al}^{α}(k + G) = 0$.

In order for the LAPW basis set to be complete for the expansion of the electronic wave functions, local orbitals (LOs) can be supplemented, as in Eq. (2):

$$\phi_*^G(r) = \begin{cases} \sum_{lm} [A_{alm}(k + G)u_{al}(r^α; E_{al}) + B_{alm}(k + G)\tilde{u}_{al}(r^α; E_{al})]Y_{lm}(r^α), & r^α < R_{MT}^α, \\ \frac{1}{\sqrt{4\pi}} e^{i(k+G)\cdot r}, & r \in I. \end{cases}$$

$$\phi_*^{LO}(r) = \begin{cases} A_{alm}^{LO}u_{al}(r^α; E_{al}) + B_{alm}^{LO}\tilde{u}_{al}(r^α; E_{al}) + C_{alm}^{LO}u_{al}(r^α; E_{al}^{(2)})Y_{lm}(r^α), & r^α < R_{MT}^α, \\ 0, & r \in I. \end{cases}$$

where $r^α = r - r^{α}_i$, $R_{MT}^α$ is the MT radius of the $i$th atom. $u_{al}(r^α; E_{al})$ is the solution of the radial Schrödinger equation at a fixed reference energy $E_{al}$ in the spherical potential of the respective MT sphere, and $u_{al}(r^α; E_{al})$ is its energy derivative. The expansion coefficients include $A_{alm}(k + G)$ and $B_{alm}(k + G)$, which are determined from the continuity of the basis functions and their first derivative at the boundary of the MT sphere. The LAPW basis can be reduced to an APW basis when $B_{alm}(k + G) = 0$.
with $E_n^{(2)}$ chosen to be close to the energy of the low-lying or high-lying states of interest and the coefficients $A_{alm}^{LO}$, $B_{alm}^{LO}$, and $C_{alm}^{LO}$ are determined by the requirement that $\phi_{n}^{LO}(\mathbf{r})$ is normalized and is zero in value and slope at the MT sphere boundary. Complement to the conventional understanding that LOs are important for a proper description of quasiparticle energies in system with semi-core states$^{23,24}$, recently, it was realized that the LOs of high-lying unoccupied states are also crucial in getting the quasiparticle band gaps converged$^{22,25}$. The parameter $n_{LO}$ is the additional number of nodes of the high-lying LOs with respect to the corresponding valence orbital and $n_{LO}^{max}$ is the maximal angular quantum number of LOs, which represent the accuracy of the LO-enhanced LAPW basis.

### B. Electron-phonon interaction

The standard form of the Hamiltonian describing a electron-phonon coupled system using second-quantized formalism can be written as$^{26}$

$$
\hat{H} = \hat{H}_e + \hat{H}_p + \hat{H}_{ep}\\
= \sum_{nk} \varepsilon_{nk} \hat{c}_{nk}^\dagger \hat{c}_{nk} + \sum_{q\nu} \hbar \omega_{q\nu} (\hat{a}_{q\nu}^\dagger \hat{a}_{q\nu} + 1/2)\\
+ N_p^{-1/2} \sum_{k_n q n'} g_{nqn'}^{\text{Fan}}(k, q) c_{nk+q}^\dagger \hat{c}_{nk} (\hat{a}_{q\nu} + \hat{a}_{q\nu}^\dagger)\\
+ N_p^{-1} \sum_{k_n q n' \nu} g_{nqn'\nu}^{\text{DW}}(k, q, \nu) c_{nk+q+\nu}^\dagger \hat{c}_{nk+q+\nu} (\hat{a}_{q\nu} + \hat{a}_{q\nu}^\dagger)\\
\times (\hat{a}_{q\nu} + \hat{a}_{q\nu}^\dagger) (\hat{a}_{q'\nu'} + \hat{a}_{q'\nu'}^\dagger).$$(3)

In this expression $\hat{H}_e = \sum_{nk} \varepsilon_{nk} \hat{c}_{nk}^\dagger \hat{c}_{nk}$ is electron Hamiltonian which is obtained from the Kohn-Sham (KS) equation, and $\hat{H}_p = \sum_{q\nu} \hbar \omega_{q\nu} (\hat{a}_{q\nu}^\dagger \hat{a}_{q\nu} + 1/2)$ is the Hamiltonian of the phonons which represents the lattice vibrations in crystals. The electron-phonon coupling Hamiltonian $\hat{H}_{ep}$ can be decoupled to first order $\hat{H}^{(1)}$ and second order $\hat{H}^{(2)}$. The corresponding matrix elements are $g_{nqn'}^{\text{Fan}}$ and $g_{nqn'\nu}^{\text{DW}}$. Here, $\varepsilon_{nk}$ is the single-particle eigenvalue of an electron with crystal momentum $\mathbf{k}$ in the band $n$, $\omega_{q\nu}$ is the phonon frequency with crystal momentum $\mathbf{q}$ in the branch $\nu$, and $\hat{c}_{nk}$ and $\hat{c}_{nk}^\dagger$ ($\hat{a}_{nk}$ and $\hat{a}_{nk}^\dagger$) are the associated fermionic (bosonic) creation and destruction operators. $N_p$ is the number of the unit cells in the Born-von-Kármán (BvK) supercell.

In practical calculations, we consider the EPIs by a dynamical HAC method in the MBPT framework$^{19,20}$. In recent years, Marini et al. included the dynamical effects beyond the adiabatic approximation$^{17,27-29}$. Hence, we label this method as dynamical HAC method with non-adiabatic effects. The EPI is treated as perturbations by considering the first and second-order Taylor expansion in the nuclear displacement, commonly known as the Fan and DW terms, respectively. In quasiparticle approximation (QPA), the $T$-dependent quasiparticle energies are defined as

$$
\varepsilon_{nk}(T) = \varepsilon_{nk} + Z_{nk}(T) \left[ \Sigma_{nk}^{\text{Fan}}(\varepsilon_{nk}, T) + \Sigma_{nk}^{\text{DW}}(T) \right].$$

(4)

where $Z_{nk}(T) = \left[ 1 - \frac{\partial \Re \Sigma_{nk}^{\text{Fan}}(\omega)}{\partial \omega} \bigg|_{\omega=\varepsilon_{nk}} \right]^{-1}$ is the renormalization factor. The $T$-dependent quasiparticle energies $\varepsilon_{nk}(T)$ are complex numbers, where the real part is the quasiparticle energy and the imaginary part corresponds to the inverse of its lifetime due to EPIs. $\Sigma_{nk}^{\text{Fan}}$ represents the KS ground-state eigenenergy for frozen atoms. $\Sigma_{nk}^{\text{DW}}$ is the Fan self-energy correction

$$
\Sigma_{nk}^{\text{Fan}}(i\omega_n, T) = \sum_{n' \nu} \left| g_{n'n\nu}^{\text{Fan}} \right|^2 N \left[ \frac{n_{q\nu}(T) + 1 - f_{n'k-q}}{2} \right] \frac{1}{i\omega_n - \varepsilon_{n'k-q} - \omega_{q\nu}}$$

(5)

$$
+ \frac{n_{q\nu}(T) + f_{n'k-q}}{i\omega_n - \varepsilon_{n'k-q} - \omega_{q\nu}},$$

and $\Sigma_{nk}^{\text{DW}}$ is the Debye-Waller correction

$$
\Sigma_{nk}^{\text{DW}}(T) = -\frac{1}{2} \sum_{n' \nu} \left| g_{n'n\nu}^{\text{DW}} \right|^2 \frac{2n_{q\nu}(T) + 1}{\varepsilon_{nk} - \varepsilon_{n'k}}.$$ 

(6)

Here, $n_{q\nu}$ and $f_{n'k-q}$ correspond to the Bose-Einstein and Fermi-Dirac distribution functions, while $N$ is the number of $\mathbf{q}$ points in the BZ. We include 400 electronic bands and 47 random $\mathbf{q}$-points for the phonon momentum to evaluate Eqs. (5) and (6). $g_{n'n\nu}^{\text{DW}}$ is the electron-phonon coupling matrix elements

$$
g_{n'n\nu}^{\text{DW}} = \langle u_{nk+q}\mid \Delta_{q\nu} v^{\text{KS}} \mid u_{n'k} \rangle_{uc},$$

(7)

which represents the probability amplitude for an electron to be scattered on account of emission or absorption of phonons. $g_{n'n\nu}^{\text{DW}}$ is the second-order electron-phonon matrix elements

$$
g_{n'n\nu}^{\text{DW}} = \frac{1}{2} \langle u_{nk+q}\mid \Delta_{q\nu} \Delta_{q'\nu'} v^{\text{KS}} \mid u_{n'k} \rangle_{uc},$$

(8)

with $u_{nk}$ and $u_{nk+q}$ being the Bloch-periodic components of the KS electron wave functions, $\Delta_{q\nu} v^{\text{KS}}$ is the phonon-induced variation of the self-consistent potential experienced by the electrons, and the integral extends over one unit cell. It is worth noting that the frequency-dependent Fan term is a dynamic correction to the electronic excitation energies and the frequency-independent DW term corresponds to the time-independent correction due to the nuclear charge density around the equilibrium nuclear positions$^{26}$. 


C. Computational details

In this work, the experimental lattice parameters\(^\text{30}\) (a = 2.504 and c = 6.661 Å) are adopted to perform all calculations, in alignment with treatments of others\(^\text{14,17}\). To compare computational results obtained using different implementation, three kinds of codes were chosen including: (i) the all-electron linearized augmented plane waves method based WIEN2k\(^\text{31}\) and GAP2\(^\text{22,32}\), (ii) the projector-augmented-wave (PAW) method based Vienna \textit{Ab initio} Simulation Package\(^\text{33}\) (VASP), and (iii) the pseudopotentials method based QUANTUM ESPRESSO (QE)\(^\text{34}\) and YAMBO\(^\text{35,36}\). In electronic band structure calculations, density-functional theory ground states are performed in the local density approximation (DFT-LDA). In WIEN2k code, LDA results presented in Table I are obtained with a \(12 \times 12 \times 4\) k-mesh, and we choose \(R_{\text{MT}}(\text{B,N}) = (1.23,1.35)\) Bohr and \(R\text{K}_{\text{max}} = 7.0\). In VASP code, PAW potentials were used along with a 800-eV plane wave cutoff energy and the band gaps were converged with a \(6 \times 6 \times 2\) k-point grid. In QE code, the DFT ground state calculations were performed using LDA norm-conserving pseudopotentials with a kinetic energy cut-off at 110 Ry and a \(6 \times 6 \times 2\) k-point grid.

The excited states are performed using the GW approximation (including one-shot \(G_0W_0\) and partially self-consistent \(GW_0\) schemes). In LAPW-based GAP2 code, the results are converged at \(12 \times 12 \times 4\) k-point grid, \(n_{LO} = 2\), and \(n_{\text{Lmax}} = 4\). In VASP code, PAW potential potentials were used along with a 800-eV plane wave cutoff energy and the band gaps were converged with a \(12 \times 12 \times 4\) k-point grid. The optical spectra including excitonic effects were obtained using YAMBO. We used a scissor operator of 2.314 eV to correct the eigenvalue and the 6-10th bands were included for solving BSE. A dense uniform \(18 \times 18 \times 6\) k-point grid is necessary to converge the optical absorption spectra.

Electron-phonon interactions were considered by combining QE and YAMBO. The phonon dispersion was obtained using a uniform \(12 \times 12 \times 8\) sampling for electron BZ and a uniform \(8 \times 8 \times 6\) samping for phonon BZ. Electron-phonon self-energies were obtained using 600-random \(q\) points in phonon BZ, a uniform \(6 \times 6 \times 2\) k-grid for electron BZ and 300 electronic bands. The quasi-particle approximation was used to correct LDA eigenvalues based on electron-phonon self-energies. In doing so, the real parts of quasi-particle energies give T-dependent band gaps and the imaginary parts give the life time due to electron-phonon renormalizations. Finally, these quasi-particle energies were thrown into the T-dependent BSE and exciton-phonon coupling was considered in this way.

\[\text{III. RESULTS AND DISCUSSION}\]

A. Quasiparticle band structure

Since the quasiparticle band structure is the basis upon which the electron-hole interactions and EPIs are analyzed, we start by looking at the accuracy and convergence of the band diagrams, in the theoretical calculations. Using standard LAPW basis set, the LDA and GW band diagram obtained from Wien2k and GAP2 were shown by black and red solid lines in Fig. 1. The smallest direct band gap is at \(H\) \([k = (-1/3,2,1/2)]\) from \(v\) to \(c\). The fundamental gap, however, is an indirect one between \(T_1\) (close to \(K\) \([k = (-3/3,2,3,0)]\)) and \(M\) \([k = (0,1/2,0)]\) (denoted by VBM and CBM). The LDA direct and fundamental band gaps are 4.04 and 4.50 eV. The \(GW_0\) direct and fundamental band gaps are 6.02 and 6.59 eV. These numbers are consistent with previous reports. We note, however, that Jiang \textit{et al.} and Nabok \textit{et al.} have separately reported that the GW band gaps obtained this way in most semiconductors can be changed by including HLOs in the all-electron LAPW-based GW calculations\(^\text{22,25}\). Motivated by this, we applied the LAPW+HLOs method to \(h\)-BN system. The results are shown by blue solid lines in Fig. 1. It is clear that the inclusion of HLOs has a strong influence on the GW corrections, which enlarges the band gaps by ~0.2 eV, for both the direct and the indirect ones.

For an in-depth understanding of the impact of HLOs on \(GW\) band gap of \(h\)-BN, we show the influence of additional HLOs on the KS single-particle spectrum. Fig. 2 gives the band energies of \(h\)-BN at the \(\Gamma\) point \([k = (0,0,0)]\) obtained with \(n_{LO} = 0\) (the default LAPW basis) and \(n_{LO} = 1\) (including the HLOs in the LAPW basis), respectively. Both of these two sets of data show that the energy of unoccupied states increases smoothly as a function of the band index (nbands) up to the plane-wave cutoff energy \(c_{\text{max}}\) (36.0 Ry in the current case),
and then it increases rapidly to much higher energy with the data of $n_{LO} = 0$ increasing faster than $n_{LO} = 1$, which means adding LOs tends to decrease the energies of these states. Therefore, it is worth noting that adding additional HLOs can improve the description of highly unoccupied states and make additional high-energy states available. The inset of Fig. 2 shows the convergence of the $G_0W_0$ direct band gap as a function of the total number of states (nbands). We can see that both the accuracy of the conduction-band states within the plane-wave cutoff and the availability of the high-energy LO states beyond the plane-wave cutoff are important for the numerically accurate $G_0W_0$ band gap.

In Table I, we compare three different codes by their DFT-LDA and GW@LDA results. The computational details are given in Sec. II.C. The GW results of YAMBO code come from Ref. 4 and 37. Nearly all of the band gap calculations without considering HLOs give consistent results within 20 meV difference, especially between GAP2 and VASP. Therefore, including HLOs in LAPW-based GW results widens the direct (indirect) band gap of $h$-BN by 0.22 (0.23) eV. Considering the fact that the quasiparticle excitation is the basis upon which the absorption spectrum is calculated, a built-in underestimation of the absorption energy should exist at the quasiparticle level when this issue related to the completeness of the basis set is neglected. This might be the case in many previous theoretical calculations of the optical spectra.

**B. Band gap renormalization**

The above calculations have adopted a clamped crystal structure. However, even at 0 K, the nuclei are not fixed and they vibrate around the equilibrium positions. This motion is known as zero-point motion and its influence on the quasiparticle excitation energy is known as zero-point renormalization to the quasiparticle excitation energy. At finite $T$s, the EPIs also influence the quasiparticle excitation energy, with contributions from both classical and quantum motions of the nuclei. At high $T$s, the quantum contribution to the motion of the nuclei is negligible and the electron and phonon interacts through a classical manner. Such $T$-dependent renormalization of the single particle excitation energy due to EPIs can be calculated using Eq. (4), and so can the fundamental and direct band gaps.

In Fig. 3, we show the EPIs-induced correction to the direct band gap of $h$-BN (obtained using clamped crystal structure). The red circles are results obtained using Eq. (4), when both classical and quantum contributions to the nuclear motion are taken into account. It is clear that the EPIs-induced correction to the static direct band gap has a weak $T$-dependence below room $T$ (300 K), and increases almost linearly beyond it. The zero-point renormalization to the direct band gap at 0 K is 0.20 eV, larger than many typically semiconductor, which means that the EPIs are strong in $h$-BN. In Fig. 4 we also show the $T$-dependence of the indirect band gaps, which is similar to that of the direct one. These theoretical results, including the zero-point correction and the $T$-dependence of the band gaps, agree with the experimental results in Ref. 38. The difference between 300 K and 0 K in Fig. 4 is only 0.02 eV, also in alignment with Ref. 38. Besides these, our results are also close to the recent calculation from Mishra[39] who reported a significant zero-point renormalization energy of 0.27 eV to the direct band gap at $K$ in the BZ of monolayer $h$-BN. The residual difference probably comes from the dimensionality effects.

In order to visualize the electron phonon coupling strength for a given state $|n\mathbf{k}\rangle$, we compute the gen-

### Table I. Calculated band gaps (in eV) from different theoretical approaches of $h$-BN. The influence of HLOs on the GW band gaps is highlighted.

| Approach | without HLOs | HLOs |
|----------|-------------|------|
| WIEN2k + GAP2 | $G_0W_0$ | $GW_0$ |
| Indirect | 4.04 | 5.71 | 6.02 | 5.90 | 6.25 |
| Direct | 4.50 | 6.26 | 6.59 | 6.45 | 6.81 |
| VASP | $G_0W_0$ | $GW_0$ |
| Indirect | 4.04 | 5.73 | 6.03 |
| Direct | 4.51 | 6.29 | 6.61 |
| QE + YAMBO | $G_0W_0$ | $GW_0$ |
| Indirect | 4.06 | 5.73 | 5.96 |
| Direct | 4.51 | 6.24 | 6.46 |
The band gap Eliashberg function is defined as

\[ F_{g n k}(\omega) = \frac{1}{N} \sum_{n'q} \left[ \frac{|g_{nn'q}^{Fan}|^2}{\epsilon_{nk} - \epsilon_{n'q} - \omega} - \frac{1}{2} \frac{\Delta_{nn'q}^{DW}}{\epsilon_{nk} - \epsilon_{n'q}} \right] \delta(\omega - \omega_{q}), \]  

(9)

The band gap Eliashberg function is defined as \( F_g = F_c - F_v \), where the \( c \) \( v \) refers to a given conduction (valence) state. Eliashberg functions are helpful to analyze contributions from different vibrational modes. Combining Eqs. (4), (5), (6) and (9), it is clear that the \( g^2F \) is directly proportional to band gap renormalization

\[ \Delta E_g(T) \propto \int d\omega g^2 F_g(\omega)[N_{qk}(T) + 1/2]. \]  

(10)

Fig. 5(a) shows the Eliashberg function at \( H \) for \( v \) and \( c \) of the direct band gap in Fig. 1. At high frequencies, \( F_g \) presents the most important peaks spanning from 1400 to 1600 cm\(^{-1}\) owing to scattering events at \( v \). Below the phonon dispersion gap, two dominant peaks exist between 600 and 850 cm\(^{-1}\). Fig. 5(b) shows twelve phonon modes with three acoustic modes \( ZA \), \( TA \) and \( LA \), and nine optical modes \( ZO \), \( TO \) and \( LO \). The notation \( Z \), \( T \), \( L \) represents out-of-plane modes, in-plane transverse modes and in-plane longitudinal modes respectively. In Fig. 5(d) we project \( g^2F \) to each mode. To see more clearly, we separate it into two parts and only the representative modes are shown, below 900 cm\(^{-1}\) in Fig. 5(c) and above that in Fig. 5(f). In the low-frequency part, the electronic states couple mainly with the 3rd branch \( LA \) and the 4th one \( TO_1 \) around 600 cm\(^{-1}\), which reduce the band gap. In the high-frequency part, the electronic states couple mainly with the 12th branch \( LO_3 \) spanning from 1400 to 1600 cm\(^{-1}\), which guarantees the reduction of band gap as \( T \) increases. It is worth pointing out that contributions from the first two modes \( ZA \) and \( TA \) at around 350 cm\(^{-1}\) tend to increase the band gap. However, this is negligible. In Fig. 5(c), we also show results from the Eliashberg function at \( K \) (close to \( T_1 \)) for \( v \) and at \( M \) for \( c \) of indirect band gap, of which the dominant peaks are almost the same as those of the direct band gap.

C. Exciton and phonon coupling

The earlier theoretical simulations proved that both the EPIs and the excitonic effects shift the absorption peaks to much lower energies and change the line shape of the absorption spectrum\(^{14,17,40}\). For a more realistic interpretation of the absorption measured in experiment, we further considered the excitonic effects. The electron-hole amplitudes are calculated using the BSE, and the excitonic effects are included in two steps. With clamped crystal structure, the absorption spectra for \( h-BN \) with and without electron-hole interactions are calculated first and shown in Fig. 6. The excitonic effects substantially decrease the band gap and increase the intensity of absorption. The BSE results with static nuclei give the first oscillator strength at 6.06 eV, leading to an exciton binding energy of 0.76 eV. It is due to the transition of electrons from \( v \) to \( c \) at \( H \).

Then the absorption spectrum was calculated at different \( T \)'s to include exciton-phonon coupling. This is done by using the \( T \)-dependent Bethe-Salpeter equation, with excitonic Hamiltonian given by

\[ H_{ee'hh'}^{FA} = [E_e + \Delta E_e(T) - E_h - \Delta E_h(T)] \delta_{ee',hh'} + (f_e - f_h) \Omega_{ee'hh'}. \]  

(11)

Here, \( E_{e(h)} \) and \( f_{e(h)} \) are the quasiparticle energy of the electron (hole) and their occupation number. \( \Delta E_{e(h)}(T) \) stands for the renormalization of electron and hole...
The quasiparticle energies after EPIs are included using the method discussed in Sec. III B. Ξ is the Bethe-Salpeter (BS) kernel, which are calculated using KS orbitals and energies with no adjustable parameters. The dielectric function depends explicitly on $T^2$, through

$$
\epsilon(\omega, T) \propto \sum_X |S_X(T)|^2 \text{Im} \left[ \frac{1}{\omega - E_X(T)} \right],
$$

where $S_X(T)$ is the oscillator strength of each exciton and $E_X(T)$ is the eigenvalues of Hamiltonian in Eq.(11). Fig. 6 shows that the absorption peak position slowly shifts to lower energies with increasing $T$, and the linewidth broadens. The 0 K dominant peak position is at 5.86 eV, which shifts to 5.83 eV at 300 K. Comparing with the results obtained using clamped crystal structure, this means that the exciton-phonon interactions shift the absorption peak to lower energies by 0.21 eV at 0 K and by 0.24 eV at 300 K. The intensity of absorption also decreases. With the help of Eliashberg function in Sec III B, we have shown that the LO phonon branch around 180 cm$^{-1}$ is responsible for the exciton-phonon coupling. It is obvious that the calculated optical spectrum exhibits good agreement with experiment without any adjustable parameter.

One deficiency of the present theoretical spectrum is that a shoulder on the lower energy side of the absorption peak, as observed in experiment, is still absent. Considering the facts that direct excitons are included in the present treatment, while lattice vibration induced indirect excitons are still absent, and the indirect excitons lie on the lower energy side of the direct one, we believe that this shoulder should be originate from the indirect excitons. The method used in this study can not address this issue. Therefore, we call for further improved method to be developed.

### IV. CONCLUSIONS

Using a combination of state-of-the-art theoretical method, we have demonstrated that h-BN is an indirect band gap semiconductor with 5.98 eV fundamental, 6.60 eV direct, and 5.83 eV optical gaps at 300 K. Among these three quantities, the optical gap is the only experimentally accessible observable, and the experimental result is $\sim 6.00$ eV. Considering the ab initio feature of this study, this agreement is quantitatively very good. The HLOs play a crucial role on widening the quasiparticle band gaps by $\sim 0.2$ eV, without which the agreement between theory and experiment for the optical band gap will be much worse. Besides HLOs, other issues challenging to routine theory in h-BN include EPIs and exciton effects, and both of them are much larger by magnitude than...
in other semiconductors. Taking the zero-point renormalization of the band gaps as an example, this value is \(\sim 0.2\) eV in \(h\)-BN, in comparison with the values of a few tens of meV in other semiconductors. The exciton binding energy is 0.76 eV with clamped crystal structure and 0.77 eV when lattice vibration at 300 K is taken into account. These values are also much larger than other bulk semiconductors. Overall this study emphasizes the intricate interplay between the electrons, the holes, and the nuclei, and highlights a fully quantum treatment of these degrees of freedom in alike systems. The remaining discrepancy with experiment also calls for further improved method in future studies, especially concerning the phonon-induced indirect excitons.

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