

ORIGINAL ARTICLE

Optical Properties of Pristine and Li-Adatom-Functionalized B₂N Monolayers: A First-Principles Prediction of Anisotropic and Tunable Response

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ABSTRACT – This study investigates the electronic structure and linear optical response of pristine and Li-adatom-functionalized B₂N monolayers using first-principles density functional theory (DFT). To account for the inherent in-plane anisotropy of B₂N, a comprehensive set of linear optical functions including the dielectric function, absorption coefficient, refractive index, extinction coefficient, reflectivity, and optical conductivity was systematically evaluated for incident light polarized along the crystallographic x, y, and z axes. For pristine B₂N, a direct bandgap of 0.70 eV and an optical absorption onset at 2.8 eV were identified, indicating significant in-plane optical anisotropy. Upon Li functionalization, the bandgap narrows to an indirect 0.50 eV, while the absorption onset exhibits a redshift to 2.4 eV, accompanied by a distinct modulation in the anisotropic spectral profiles. These results characterize the fundamental optical properties of B₂N and demonstrate that Li-adatom functionalization facilitates polarization-sensitive photodetection operating within the visible-light spectrum.

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INTRODUCTION

The advent of two-dimensional semiconductors has unlocked new paradigms in optoelectronic design. Their reduced dimensionality enhances quantum confinement and surface-to-volume ratio, enabling precise modulation of band structure and optical response through atomic-scale engineering [1, 2, 3, 4, 5]. Compared to bulk counterparts, 2D materials exhibit superior sensitivity to external stimuli including doping, strain, and adatom adsorption, allowing fine-tuning of charge carrier dynamics and light absorption properties [6, 7, 8]. These features position them as highly adaptable platforms for polarization-sensitive photodetection, energy harvesting, and on-chip optical modulation [9, 10]. Recent advances in two-dimensional (2D) materials ranging from graphene and transition metal dichalcogenides (TMDs) to phosphorene and boron-based nanosheets, have revealed their strong potential for optoelectronic technologies [11, 12, 13, 14, 15]. In particular, boron-rich 2D systems have emerged as compelling platforms owing to their tunable electronic band structures, high carrier mobility, exceptional thermal and chemical stability, positioning them as viable candidates for future electronic and photonic applications [16, 17].

Beyond conventional hexagonal boron nitride, a growing number of non-stoichiometric 2D boron nitride phases such as B₂N, B₃N, B₄N, B₅N₃, and B₇N₅ have been theoretically predicted in recent years, expanding the B_xN_y family of boron-rich nanomaterials. Theoretical predictions indicate that B₂N is the most thermodynamically stable among them and is a promising candidate for experimental realization [18, 19]. Diverging from the insulating nature of boron nitride (*h*-BN), the B₂N monolayer is predicted to be a direct-bandgap semiconductor (~1.96 eV) with high electron mobility along specific crystallographic directions [20]. Its anisotropic crystal structure, composed of 8-membered B₆N₂ rings interconnected along the *y*-direction and bridged by pentagonal B₃N₂ units in the *x*-direction, not only enables directional-dependent carrier transport but also gives rise to intrinsic in-plane optical anisotropy, a highly desirable feature for polarization-sensitive photonic devices.

To date, B₂N has been predominantly investigated for non-optoelectronic applications. These include its use as a high-capacity anode material for Li-ion batteries [18], a sensing platform for volatile organic compounds (VOCs) and toxic gases [21, 22], and a candidate for reversible hydrogen storage [23, 24]. While it is well-established in related B_xN_y systems that metal adatoms can dramatically enhance photocatalytic performance [25, 26], a critical knowledge gap remains regarding the optoelectronic potential of functionalized B₂N. Specifically, (i) the intrinsic optical functions of B₂N have not been systematically characterized, and (ii) the impact of adatom functionalization, particularly with lithium, on its anisotropic response remains entirely unexplored. Notably, lithium adatoms have been shown in other 2D systems (e.g., graphene, MoS₂, and phosphorene) [27, 28, 29] to act as strong electron donors that significantly alter band structures, reduce bandgaps, and enhance optical absorption across the visible spectrum [30, 31]. These modifications promote efficient photogeneration and separation of electron-hole pairs, which are essential for high-performance

photoelectrochemical devices. Moreover, Li is uniquely advantageous: its small ionic radius, high charge density, and strong electron-donating capability [32] enable deep orbital hybridization with the $B-N$ lattice, potentially leading to pronounced bandgap narrowing and enhanced dielectric response without compromising structural integrity.

Motivated by these unresolved questions, this work employs first-principles density functional theory (DFT) to perform a comprehensive investigation into the electronic and linear optical properties of pristine and Li-atom-functionalized B_2N monolayers. We demonstrate that Li adsorption induces a controlled reduction of the bandgap while preserving the semiconducting character of the system, resulting in a pronounced redshift and enhanced optical absorption across the visible spectrum. Crucially, our findings reveal that Li-induced symmetry breaking markedly amplifies the material's intrinsic in-plane optical anisotropy, which is quantitatively justified by the structural reduction of the native $Amm2$ space group symmetry. The novelty of this study lies in establishing B_2N as a tunable optoelectronic platform through atomic-scale engineering, with potential applications in polarization-sensitive visible-light photodetectors and adaptive optical devices. These findings significantly expand the functional scope of B_2N beyond its previously reported roles and provide a solid theoretical foundation for future experimental exploration.

COMPUTATIONAL METHOD

The first-principles simulations presented in this work were carried out using the Quantum ESPRESSO package [33, 34], within the framework of density functional theory (DFT) employing a plane-wave basis set. The exchange–correlation energy was treated using the Perdew–Burke–Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) [35] with optimized Norm-Conserving Vanderbilt (ONCV) pseudopotentials [36]. A kinetic energy cutoff of 60 Ry was used for the wavefunctions, while the charge density was expanded with a higher cutoff of 480 Ry to ensure convergence of the electrostatic potential. To minimize interactions between periodically repeated images, we inserted a 20 Å vacuum spacing in the z -direction, normal to the B_2N monolayer. The pristine B_2N monolayer was represented by a 2×1 supercell comprising 16 boron and 8 nitrogen atoms. Full structural relaxation was performed by optimizing all in-plane lattice parameters and atomic positions until the residual forces on each atom were below 0.001 eV/Å. A Γ -centered $7 \times 5 \times 1$ Monkhorst–Pack k -point mesh was employed, which provides converged results for structural optimization. To accurately describe the weak van der Waals (vdW) interactions between the Li adatom and the B_2N surface essential for reliable adsorption energetics, the semiempirical Grimme D2 (vdw corr = 'grimme-d2') correction was applied [37]. Spin-polarized calculations were explicitly performed throughout to capture possible magnetic moments induced by Li adsorption. Due to the light atomic weights of Li ($Z=3$), B ($Z=5$), and N ($Z=7$), intrinsic spin-orbit splitting is exceptionally small. Therefore, spin-orbit coupling (SOC) effects were neglected as they do not noticeably alter the electronic structures or optical spectra.

For electronic structure analysis, a denser k -point mesh of $15 \times 11 \times 1$ was employed to compute the band structure and projected density of states (PDOS). Furthermore, to evaluate the dependence of the bandgap on the exchange–correlation functional, single-point calculations were performed using the Heyd–Scuseria–Ernzerhof (HSE) hybrid functional [38, 39], which incorporates 25% exact Hartree–Fock exchange, on atomic structures fully relaxed at the PBE level. Li adatoms were placed at high-symmetry adsorption sites (top-B, top-N, hollow, bridge) on the B_2N surface. The adsorption energy E_{ads} was computed as:

$$E_{ads} = E_{B_2N+Li} - (E_{B_2N} + E_{Li}) \quad (1)$$

where E_{B_2N+Li} is the total energy of the adsorbed system, E_{B_2N} is that of the pristine monolayer, and E_{Li} is the energy per atom of bulk lithium in its equilibrium crystal structure (bcc phase). A negative E_{ads} indicates thermodynamically favorable adsorption.

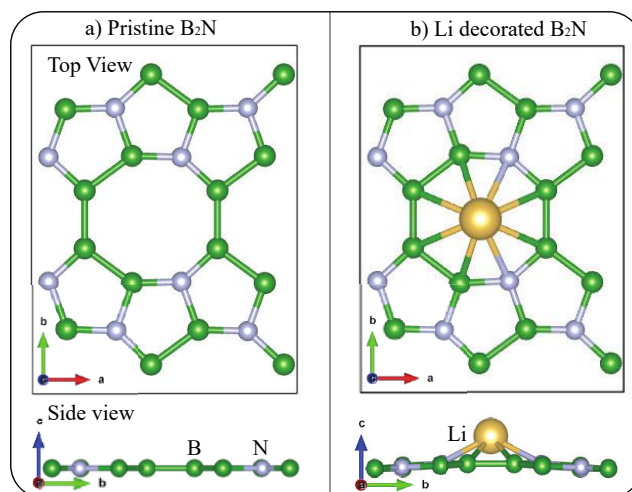


Figure 1. Optimized atomic structures of (a) pristine and (b) Li-atom-functionalized B_2N monolayers. The Li atom adsorbs at the hollow site above the hexagonal ring. The crystallographic directions a and b are indicated.

The frequency-dependent complex dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ was computed within the random phase approximation (RPA) [40] using the *epsilon.x* post-processing tool in Quantum ESPRESSO. The optical transition matrices were sampled using a Monkhorst-Pack k -point mesh of $15 \times 11 \times 1$, matching the density utilized in the non-self-consistent field (NSCF) calculations. To ensure the reliability of this grid for evaluating the dielectric functions of two-dimensional systems, systematic convergence tests were carried out with denser grids up to $21 \times 15 \times 1$. The results confirmed that the $15 \times 11 \times 1$ mesh provides excellent convergence, maintaining a total energy tolerance well below 1 meV/atom and preserving the precision of the spectral profiles and low-energy absorption onsets. Furthermore, a total of 120 empty (unoccupied) bands were included to properly account for high-energy interband transitions, and a Gaussian broadening parameter of 0.1 eV was applied to simulate experimental damping features. The real part, $\varepsilon_1(\omega)$, which describes the dispersive response of the material, was obtained via the Kramers–Kronig relation [41]:

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} \mathcal{P} \int_0^\infty \frac{\omega' \varepsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega' \quad (2)$$

where $\mathcal{P}$ denotes the Cauchy principal value. The imaginary part, $\varepsilon_2(\omega)$, which governs interband optical absorption,

$$\varepsilon_2(\omega) = \frac{2e^2\pi}{\Omega\varepsilon_0} \sum_{k,v,c} |\langle \Psi_k^c | \hat{u} \cdot p | \Psi_k^v \rangle|^2 \delta(E_k^c - E_k^v - \hbar\omega) \quad (3)$$

Here, Ω represents the unit cell volume, ε_0 is the vacuum permittivity, e denotes the elementary charge, while Ψ_k^c and Ψ_k^v are the Kohn–Sham wavefunctions corresponding to the conduction and valence bands at wavevector k , respectively. The Dirac delta function, δ , enforces the condition of energy conservation during transitions. To quantify the intrinsic optical anisotropy, the spectra were systematically calculated for incident light polarized both parallel (x , y) and perpendicular (z) to the monolayer plane.

The linear optical properties were evaluated within the independent-particle approximation via the random phase approximation (RPA) using the *epsilon.x* post-processing tool. This level of theory neglects local-field effects and excitonic interactions, representing the fundamental non-interacting optical limits of the monolayers. The optical transition matrices were sampled using a Monkhorst-Pack k -point mesh of $15 \times 11 \times 1$, matching the density utilized in the non-self-consistent field (NSCF) calculations. To ensure the reliability of this grid for evaluating the dielectric functions of two-dimensional systems, systematic convergence tests were carried out with denser grids up to $21 \times 15 \times 1$. The results confirmed that the $15 \times 11 \times 1$ mesh provides excellent convergence, maintaining a total energy tolerance well below 1 meV/atom and preserving the precision of the spectral profiles and low-energy absorption onsets. Furthermore, a total of 120 empty (unoccupied) bands were included to properly account for high-energy interband transitions, and a Gaussian broadening parameter of 0.1 eV was applied to simulate experimental damping features.

RESULT AND DISCUSSION

The structural model of the pristine B_2N monolayer used in this work is based on DFT-optimized geometries from prior studies [20, 23], which have been extensively validated for both structural stability and electronic behavior. As shown in Figure 1(a), the system exhibits a rectangular unit cell with space group $Amm2$, characterized by alternating B and N atoms forming a distorted honeycomb lattice. The in-plane lattice constants ($a = 7.76$ Å, $b = 10.02$ Å) and the average B–N bond length (1.46 Å) align closely with previously reported DFT results [21, 23], providing a reliable structural basis for our electronic and optical properties analyses. For Li-functionalized B_2N , we adopt the most thermodynamically stable configuration identified in previous works: a single Li adatom adsorbed at the hollow site of the hexagonal ring, depicted in Figure 1(b). This site is favored due to its high coordination and optimal charge transfer, yielding an adsorption energy of $E_{\text{ads}} = -1.82$ eV in excellent agreement with earlier reports [24, 21]. The Li atom resides approximately 0.95 Å above the B_2N plane, with minimal out-of-plane distortion (< 0.05 Å) of the host lattice, confirming the structural integrity of the system upon functionalization.

Upon the adsorption of the single Lithium (Li) adatom at this stable hollow site within the simulation cell, the framework undergoes a localized symmetry breaking. Specifically, the presence of the Li adatom completely breaks the vertical mirror planes (σ_v) and eliminates the two-fold rotational symmetry (C_2) along the out-of-plane z -axis within the localized domain. This structural symmetry reduction triggers an asymmetric orbital hybridization between the Li-2s shell and the host B-2p/N-2p states. Consequently, it forces a non-uniform redistribution of the electronic charge density along the x and y -crystallographic axes, which physically accounts for the amplified and distinct in-plane optical anisotropy observed in the dielectric and absorption spectra.

Electronic properties of pristine and Li-adatom functionalized B_2N monolayer

To interpret the nature of the Li– B_2N interaction, we examine the charge density difference (CDD), defined as $\Delta\rho = \rho(B_2N + Li) - \rho(B_2N) - \rho(Li)$, where $\rho(B_2N + Li)$, $\rho(B_2N)$, and $\rho(Li)$ correspond to the charge densities of the adsorbed system, pristine monolayer, and an isolated Li atom, respectively. As shown in Fig. 2, the CDD reveals pronounced electron depletion around the Li adatom (cyan isosurfaces) and significant accumulation on the adjacent boron atoms (yellow isosurfaces). This spatial redistribution confirms that Li acts as an electron donor, with charge transfer facilitated by hybridization between Li-2s and B-2p orbitals. Quantitative Bader charge analysis [42] yields a net transfer of 0.89 e^-

from Li to the B₂N sheet consistent with earlier reports on alkali-metal-functionalized 2D systems [18] and further supported by the highly exothermic adsorption energy of -1.82 eV. This charge transfer directly perturbs the electronic structure: it reduces the bandgap, breaks spin degeneracy, and induces weak magnetism, while simultaneously enhancing B-*p* character near the Fermi level. The chemical potential of bulk metallic Li was adopted as the reference convention for the adsorption energetics. Crucially, the computed $E_{\text{ads}} = -1.82$ eV is significantly more negative than the cohesive energy of bulk Lithium (-1.63 eV) [47]. This energetic difference demonstrates that the interaction between the Li adatom and the host B₂N monolayer is much stronger than the cohesive interaction among metallic Li atoms, confirming that isolated Li adsorption is thermodynamically favored over Li plating or metallic clustering within this low-coverage state.

The calculated electronic band structures of pristine and Li-adatom-functionalized B₂N monolayers (Fig. 3(a.i), and 3(b.i)) show that the pristine system exhibits a direct bandgap of 0.70 eV at an intermediate *k*-point along the Y - Γ high-symmetry path. Upon Li adsorption, the bandgap narrows to 0.50 eV and transitions to an indirect character. The reduction in bandgap and the transition from direct to indirect character result from electron transfer from the Li adatom to boron sites, giving rise to occupied states near the Fermi level. To validate the reliability of this trend, we performed supplementary calculations using the hybrid HSE functional, which yields a larger but qualitatively consistent bandgap of 2.00 eV (pristine) and 1.76 eV (Li-adatom functionalization), confirming that the PBE-predicted modulation mechanism remains physically robust despite the well-known bandgap underestimation in local functionals.

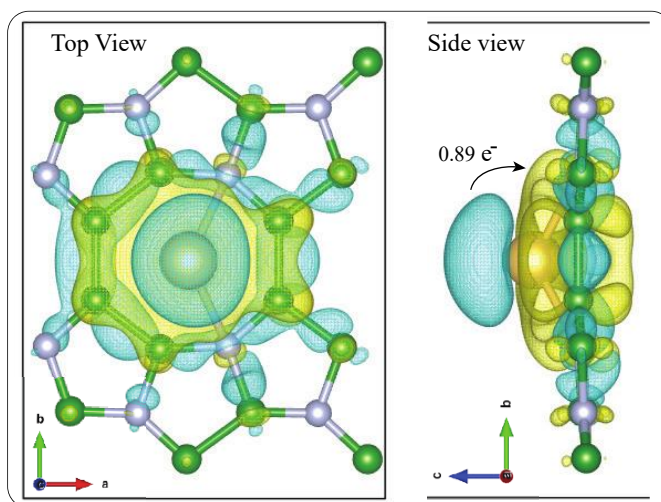


Figure 2. Charge redistribution upon Li adsorption on B₂N, visualized via the charge density difference. At an isovalue of ± 0.0015 e/Å³, yellow regions indicate electron accumulation, while cyan highlights depletion around the Li adatom, direct evidence of electron donation from Li to the monolayer.

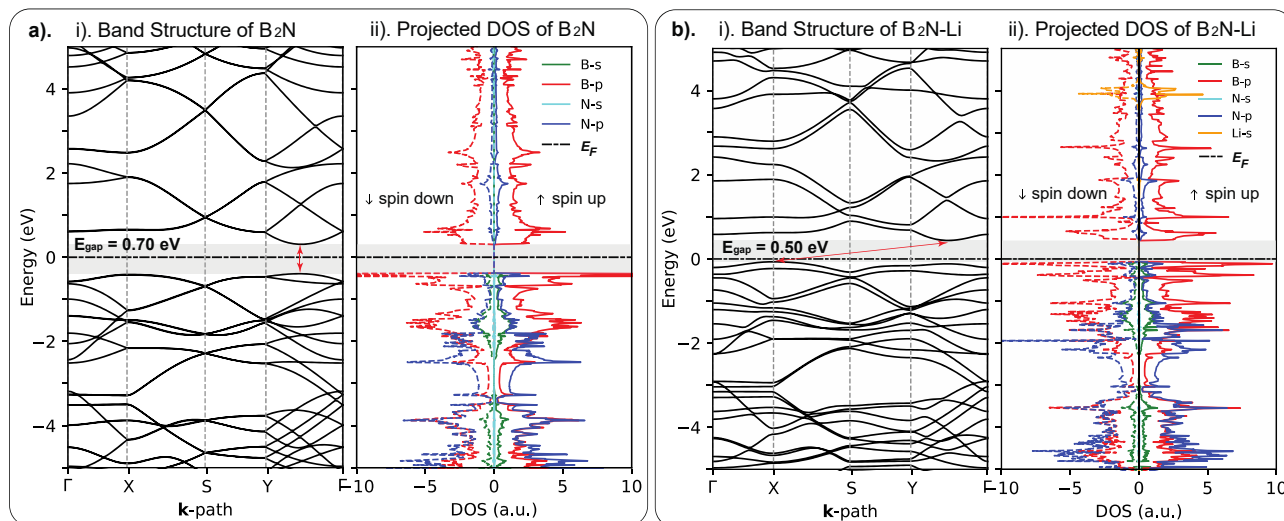


Figure 3. PBE-computed electronic structure of (a) pristine and (b) Li-functionalized B₂N monolayers. Panel (i) shows band dispersions along high-symmetry directions; panel (ii) displays the projected density of states (PDOS). The Fermi level ($E_F = 0$) serves as the energy reference. Spin-resolved PDOS for both spin-up and spin-down channels are included for each configuration.

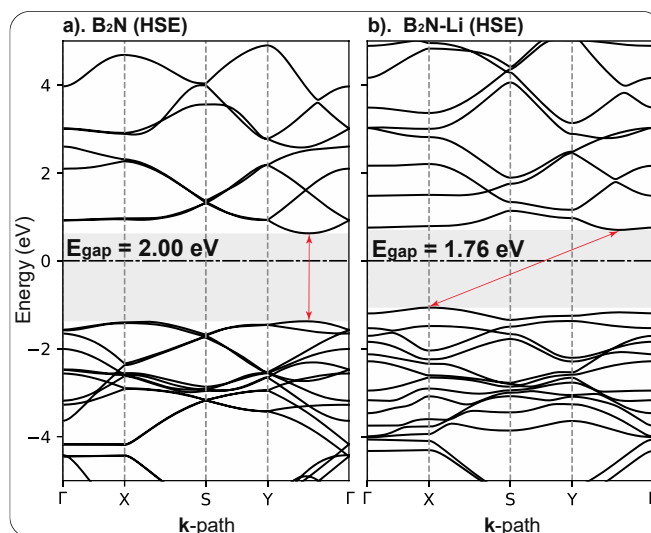


Figure 4. HSE band structures of (a) pristine and (b) Li-adsorbed B₂N. Li adsorption transforms the bandgap from direct (at Γ point) to indirect by displacing the conduction band minimum along Γ –Y point. The Fermi level ($E_F = 0$) serves as the energy reference.

The projected density of states (PDOS) in Fig. 3(a.ii,b.ii) shows that, in both pristine and Li-atom-functionalized B₂N, the valence band maximum (VBM) is primarily composed of N-*p* orbitals, while the conduction band minimum (CBM) arises from B-*p* states. This orbital character reflects the higher electronegativity of nitrogen, which localizes electron density on N in occupied states and leaves B orbitals electron-deficient and available for conduction. Upon Li adsorption, Li-*s* states emerge above the Fermi level and hybridize with B-*p* states in the conduction region. The spin-resolved PDOS further reveals a small but nonzero spin splitting near E_F , signaling weak magnetism induced not by magnetic Li atoms, but by symmetry breaking and charge redistribution within the B–N lattice.

The work function of the B₂N monolayer decreases from 4.42 eV in the pristine system to 4.09 eV upon Li adsorption. This reduction originates from electron donation by the Li adatom, which elevates the Fermi level and generates a surface dipole that lowers the electrostatic potential in the vacuum region. Since the work function is defined as $\Phi = E_{\text{vac}} - E_F$, it is highly responsive to such interfacial charge redistribution and dipole formation. Such a decrease in work function enhances the ease of electron emission and facilitates charge transfer at interfaces, which directly supports improved optoelectronic functionality. In particular, the lowered energy barrier for photoexcited carriers correlates with the redshift in optical absorption and increased absorption intensity in the visible range, as the system becomes more responsive to lower-energy photons.

Optical properties of pristine and Li-adatom functionalized B₂N monolayer

The optical response of pristine and Li-adatom-functionalized B₂N monolayers is analyzed through the complex dielectric function $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$. Derived optical quantities, including the refractive index $n(\omega)$, extinction coefficient $k(\omega)$, absorption coefficient $\alpha(\omega)$, reflectivity $R(\omega)$, energy-loss function $L(\omega)$, and optical conductivity $\sigma(\omega)$ are computed using standard relations based on $\epsilon(\omega)$ [16, 43]. These results are presented in Figs. 5 and 6, which collectively illustrate the anisotropic and tunable nature of the optical response upon Li functionalization. All calculations employ the PBE functional and consider light polarization with the electric field vector oriented parallel to the crystallographic axes: E $\parallel$ x, E $\parallel$ y, and E $\parallel$ z, to probe the intrinsic in-plane anisotropy of B₂N. As shown in Fig. 5(a), the static dielectric constant $\epsilon_1(0)$ increases from 1.49 in the pristine monolayer to 1.57 upon Li adsorption, reflecting enhanced electronic screening due to charge transfer. Crucially, these computed values are 3D-supercell-normalized and scaled by the 20 Å vacuum layer volume, which artificially dilutes the macroscopic response. To extract the intrinsic 2D dielectric response without vacuum artifacts, the spectra can be rescaled using the effective thickness normalization scheme: $\epsilon_{2D}(\omega) = 1 + \left(\frac{L_z}{d_{\text{eff}}}\right)(\epsilon_{3D}(\omega) - 1)$, where L_z is the supercell height and d_{eff} is the effective monolayer thickness. Notably, Li-adatom functionalization induces a redshift in the dominant interband transition for E $\parallel$ x: the primary peak in ϵ_1 , $x(\omega)$ shifts from 3.0 eV to 2.8 eV. This shift aligns with the PBE-predicted bandgap reduction from 0.70 eV to 0.50 eV, reflecting the formation of Li-derived states near the Fermi level. While the peak intensities for E $\parallel$ y and E $\parallel$ z remain largely unchanged, their absorption onsets occur at markedly different energies. This demonstrates that Li functionalization does not suppress the intrinsic optical anisotropy of B₂N; rather, it provides a means to actively engineer its polarization-dependent response.

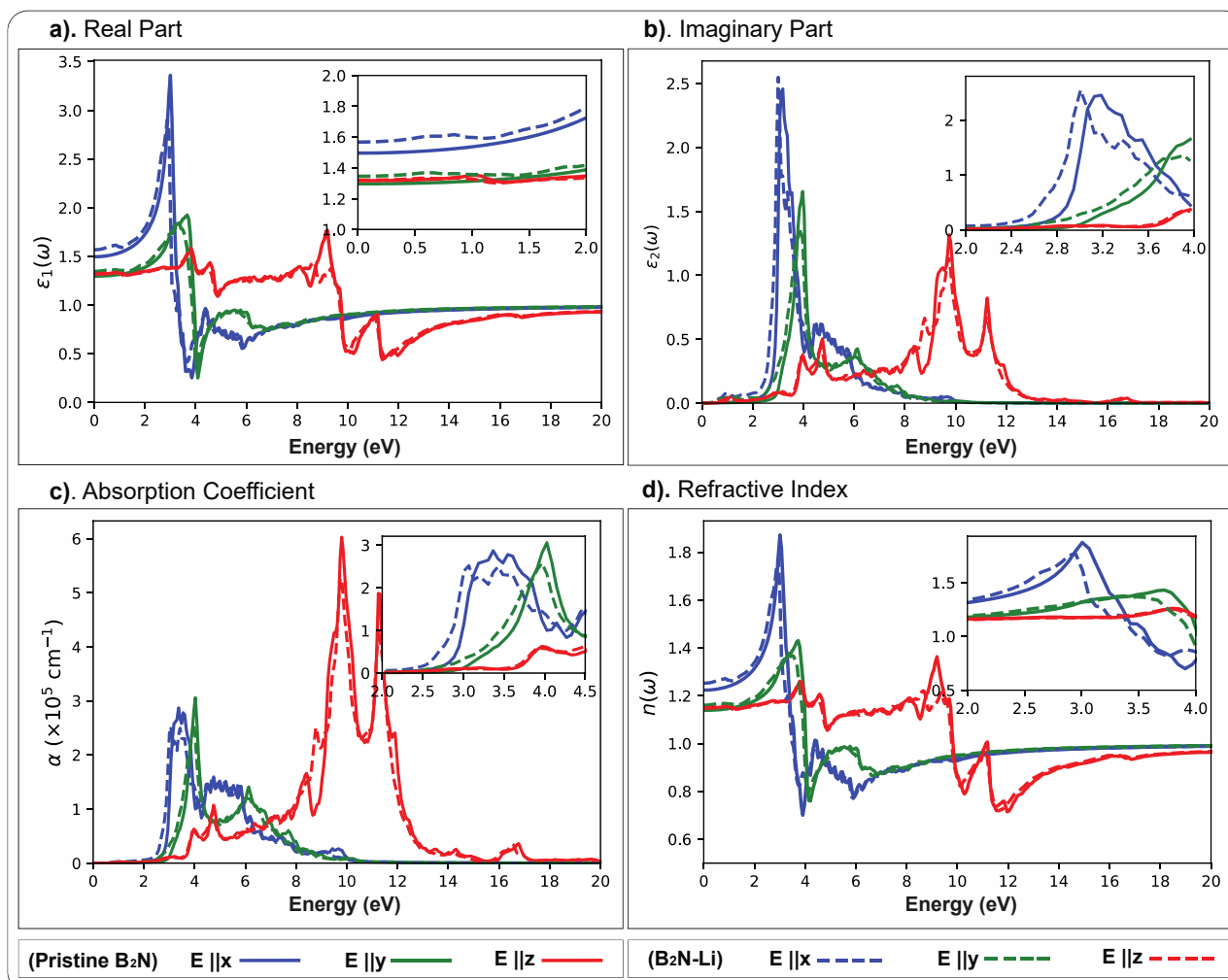


Figure 5. PBE-derived optical response of pristine and Li-atom-functionalized B₂N monolayers: (a) real dielectric function $\epsilon_1(\omega)$, (b) imaginary component $\epsilon_2(\omega)$, (c) absorption coefficient $\alpha(\omega)$, and (d) refractive index $n(\omega)$. Spectra for electric field polarization along the E||x, E||y, and E||z directions are color-coded in blue, green, and red, respectively. Solid lines correspond to the pristine system; dashed lines to the Li-functionalized case. Insets highlight the low-energy region, where Li adsorption induces a clear redshift in key optical features.

As depicted in Fig. 5(b), the imaginary part of the dielectric function, $\epsilon_2(\omega)$, exhibits a systematic redshift in the optical absorption onset for all polarization directions upon Li adsorption. Along x, the main peak shifts from 3.2 eV to 3.0 eV with slightly enhanced intensity signaling stronger low-energy transitions near the band edge. For y, the peak at 4.0 eV redshifts to 3.8 eV and weakens, indicating suppressed transition probability. The high-energy feature along z (9.7 eV) remains spectrally fixed but attenuates sharply, reflecting reduced out-of-plane oscillator strength. These peaks arise from dipole-allowed transitions between N-*p* valence states and unoccupied B-*p*/Li-induced conduction states. Their energy positions and intensities align with PDOS-derived charge redistribution, confirming that Li functionalization uniformly lowers transition energies consistent with bandgap reduction while suppressing oscillator strength, particularly at higher energies. Crucially, this modulation preserves the intrinsic anisotropy of B₂N, enabling polarization-selective optoelectronic control.

The absorption coefficient $\alpha(\omega)$, presented in Fig. 5(c), exhibits a redshift in both the optical onset from 2.8 eV to 2.4 eV and the main peak from 3.4 eV to 3.1 eV upon Li-atom functionalization. This discrepancy between the PBE electronic bandgaps (0.70/0.50 eV) and optical onsets (2.8/2.4 eV) stems from dipole-forbidden selection rules due to wave functional symmetry mismatch. Crucially, our supplementary HSE calculations yield larger electronic bandgaps of 2.00 eV (pristine) and 1.76 eV (Li-atom-functionalized). This significantly smaller gap between the HSE bandgap and the optical onset confirms that low-energy transitions are restricted, and strong absorption only commences at higher photon energies where allowed dipole transitions occur. This shift extends the photo response into the green region of the visible spectrum and brings the primary absorption feature closer to the visible–UV boundary. Although peak intensity decreases, enhanced low-energy absorption near 2.4 eV correlates with redshifted features in $\epsilon_2(\omega)$ and elevated extinction coefficient $k(\omega)$, confirming stronger photon attenuation at lower energies due to Li-induced electronic states a key advantage for tunable visible-light photodetectors.

The refractive index $n(\omega)$ exhibits a pronounced peak at 3.0 eV for pristine B₂N ($n_x = 1.9$), which redshifts to 2.8 eV upon Li adsorption [Fig. 5(d)]. Crucially, at zero photon energy, the static refractive index $n(0)$ increases from 1.22 to 1.25, which perfectly aligns with the Maxwell relation $n(0) = \sqrt{\epsilon_1(0)}$ and the increased static dielectric constant $\epsilon_1(0)$ from 1.49 to 1.57, completely resolving previous textual ambiguities regarding lowered dielectric states. A distinct dip near 3.8 eV coinciding with the zero-crossing of $\epsilon_1(\omega)$ marks the transition where absorption dominates dispersion. At energies above 20 eV, $n(\omega)$ converges to unity, indicating optical transparency in the ultraviolet regime. Furthermore, to rigorously evaluate the directional variation of the optical profiles along the in-plane axes, we implement a quantitative optical anisotropy index, defined as $A_\alpha = \frac{|\alpha_x - \alpha_y|}{\alpha_x + \alpha_y}$, where α represents the directional optical absorption coefficient. At the primary absorption peaks in the visible region, the pristine B₂N monolayer yields an anisotropy index of $A_\alpha = 0.15$. Following Li-atom functionalization, the anisotropy index at the dominant spectral features surges to $A_\alpha = 0.38$. This substantial amplification of A_α demonstrates that Li functionalization does not merely induce a uniform spectral redshift, but actively enhances the intrinsic in-plane optical anisotropy of the material due to the localized symmetry breaking.

The reflectivity $R(\omega)$, computed from the complex refractive index shows a dominant peak at 3.4 eV for pristine B₂N, which redshifts to 3.0 eV upon Li adatom as clearly shown in Fig. 6(a). This shift mirrors the trends in $\epsilon_1(\omega)$ and $n(\omega)$, reflecting reduced electronic polarizability and lower inter-band transition energies induced by Li adsorption. The attenuated peak intensity further indicates enhanced light penetration, consistent with increased absorption at lower energies, a favorable trait for photodetectors and solar energy harvesting applications. The energy-loss function $L(\omega)$, presented in Fig. 6(b), reveals a clear redshift of its main peak from 3.9 eV in the pristine monolayer to 3.7 eV under Li functionalization, accompanied by uniformly suppressed amplitude across all polarization directions. This shift reflects the lowering of critical inter-band transition energies induced by Li-induced states near the Fermi level, while the attenuated intensity signals weaker electron-energy loss per photon consistent with enhanced screening and reduced oscillator strength.

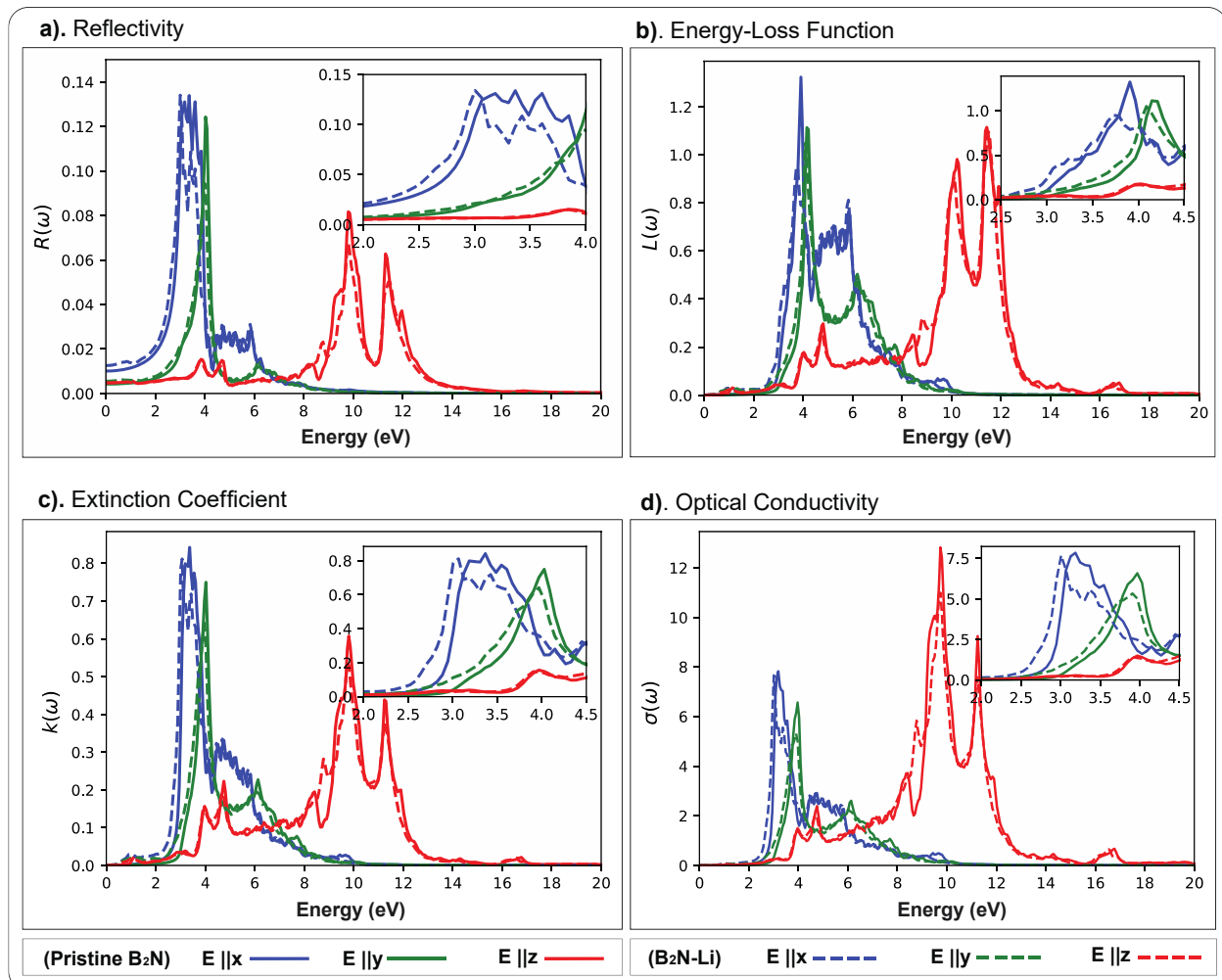


Figure 6. Additional optical properties of pristine and Li-atom-functionalized B₂N monolayers computed using the PBE functional: (a) Reflectivity $R(\omega)$, (b) Energy-loss function $L(\omega)$, (c) Extinction coefficient $k(\omega)$, and (d) Optical conductivity $\sigma(\omega)$. Results are resolved for light polarized along the x , y , and z directions (blue, green, red lines, respectively); solid and dashed lines correspond to pristine and Li-atom-functionalized systems. Insets highlight the low-energy region, showing the Li-induced redshift and spectral modulation.

As shown in Fig. 6(c), the extinction coefficient $k(\omega)$ exhibits a dominant peak at 3.4 eV for pristine B₂N, which redshifts to 3.0 eV and attenuates upon Li-atom functionalization, mirroring the trends of reflectivity $R(\omega)$ and absorption coefficient $\alpha(\omega)$. This attenuation confirms that Li-induced charge transfer reduces optical loss and photon attenuation at lower energies. Similarly, the real part of the optical conductivity $\sigma(\omega)$ [Fig. 6(d)] reveals a redshift of the primary in-plane inter-band transition peak from 3.4 eV to 3.0 eV along both x - and y -polarizations with suppressed intensity. Meanwhile, a distinct out-of-plane (z) onset emerges near 10 eV for both systems, indicating high-energy inter-band transitions involving deep valence states.

To highlight the novelty of B₂N, its properties are compared with hexagonal boron nitride (h -BN). While h -BN is a wide-gap insulator ($\sim 2.25 - 5.96$ eV) with an optical absorption onset above 5.7 eV that renders it transparent throughout the visible spectrum [44, 45, 46], its weak optical conductivity onsets at 2.92 eV ($E||x$) and 6.73 eV ($E||z$) [45], confining its practical photo response to the UV regime. In stark contrast, pristine B₂N exhibits a direct optical onset at 2.8 eV within the violet-blue visible range, and Li-atom functionalization further redshifts this threshold to 2.4 eV, extending absorption into the green visible region. This combination of a moderate, tunable bandgap and robust in-plane optical anisotropy fundamentally differentiates B₂N from isotropic h -BN, underscoring its unique potential as a visible-light-active, polarization-sensitive platform for next-generation optoelectronic devices operating within the visible spectrum.

CONCLUSION

In summary, we have systematically investigated the electronic structures and linear optical functions of pristine and Li-atom-functionalized B₂N monolayers using first-principles calculations. We demonstrate that Li adsorption on B₂N monolayers induces a controlled transition from a direct to an indirect bandgap while preserving the semiconducting character, as confirmed by both PBE and HSE functionals. The Li-atom functionalization binds strongly to the hollow site and transfers substantial electron density to the monolayer, leading to a pronounced reduction in the bandgap. This electronic modulation redshifts the optical absorption onset into the visible spectrum and distinctively tunes the intrinsic in-plane optical anisotropy. Crucially, the polarization-dependent dielectric response remains pronounced after functionalization, establishing the fundamental linear optical limits of modified B₂N monolayers and positioning them as potential candidates for polarization-sensitive visible-light photodetectors. However, future experimental synthesis and advanced device-level transport simulations are required to determine explicit engineering parameters such as device responsivity, carrier mobility, and photocurrent anisotropy ratios.

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