

Ab initio tight-binding Models for Mono- and Bilayer Hexagonal Boron Nitride (*h*-BN)

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We provide effective tight-binding models of monolayer and bilayer hexagonal boron nitride (*h*-BN) informed by *ab initio* density functional theory calculations within the local density approximation using maximally localized Wannier functions centered at the boron and nitrogen sites. An effective intra-layer tight-binding model with up to four distant hopping neighbors captures the band energies near the *K*-point and *M*-point in the Brillouin zone, including the indirect nature of the band gap for certain stackings. We then propose a two-center interlayer tight-binding model that can be used for any stacking in bilayer *h*-BN based on the relative distance between two atomic sites which can be used to model twisted *h*-BN structures.

I. INTRODUCTION

Using *h*-BN as a two-dimensional substrate for graphene systems is prevalent in emerging electronic devices [1]. When used as a substrate for graphene, the lattice mismatch and relative misorientation between *h*-BN and graphene produce moiré patterns that in turn affect its electronic properties [2–4]. Earlier investigations of single and bilayer *h*-BN systems proposed density functional theory (DFT) fitted minimal tight-binding (TB) model [5], and continuum Hamiltonian model [6] that assumed band edges located at the *K* and *K'*-points. A common shortcoming of the existing TB model parametrizations is the mismatch of the π -bands with respect to the local density approximation (LDA) DFT results away from the *K*-point. In this work, we propose TB models that can reproduce the DFT band edges near the high symmetry points in the first Brillouin zone (FBZ) with a small number of hopping parameters that offer a good balance between simplicity and accuracy.

The manuscript is organized as follows: In Section II, we provide a brief summary of the *ab initio* calculations used in the study. In Section III, we present several TB model approximations to the first-principles-calculated band structures, and we provide the hopping parameters necessary to construct effective models. Section IV discusses the interlayer distance-dependent effective model for *h*-BN bilayers derived from the parametrization method. In Section V, we present the two-center TB model for bilayer *h*-BN, and in Section VI, discuss the conclusions and the advantages of the recommended models. We close the paper with the acknowledgments in Section VII.

II. AB INITIO CALCULATION DETAILS

We carried out our calculations through the first-principles calculation package Quantum ESPRESSO [7][8] that uses a basis of plane waves [9] and then we use WANNIER90 [10] to construct the Wannier functions. The Local-density approximations (LDA) based on the Perdew-Zunger parametrization [11] were used in the DFT calculations. The TB model

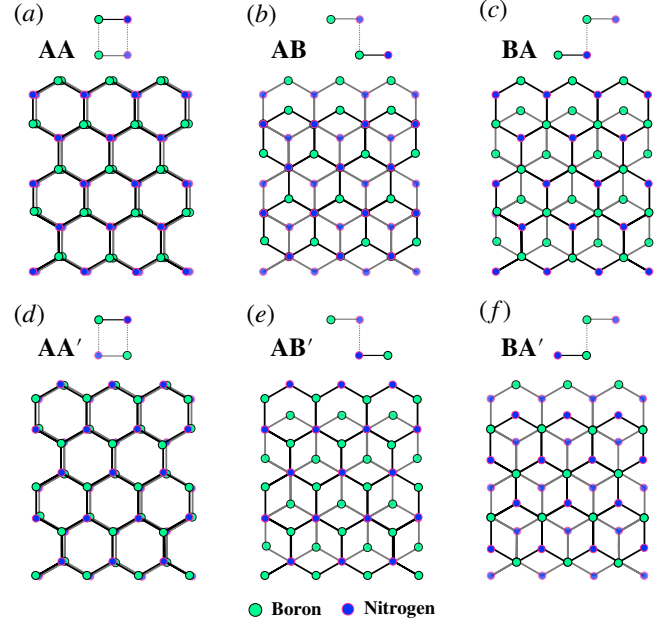


FIG. 1. (Color online) Top views of the hexagonal boron nitride bilayers with standard stackings: a) AA, b) AB, c) BA, d) AA', e) AB' and f) BA'. Here, the green and blue dots represent the boron and nitrogen atoms, respectively. The side view of each stacking is shown at the top of each sub-figure.

parameters were obtained from the DFT calculations, which were performed using a $42 \times 42 \times 1$ *k*-space sampling density.

Six different stackings are considered in *h*-BN bilayers as shown in Fig. 1 which have different interlayer equilibrium distances following from their total energies as shown in Fig. 2. We note that AB- and BA-stackings are energetically degenerate, with their total energies matching to within eight decimal places and are more stable compared to the other stackings [12], followed by the AA'-stacking that benefit from the attractive electrostatic interaction between the vertically alternating boron and nitrogen atoms [13, 14]. In this work, we have built the *h*-BN monolayer and bilayer structures using the LDA-DFT optimized lattice constant $a = 2.48$ Å which is smaller than the experimental value of 2.504 Å [15]. Since the most stable bilayer structure (AB or

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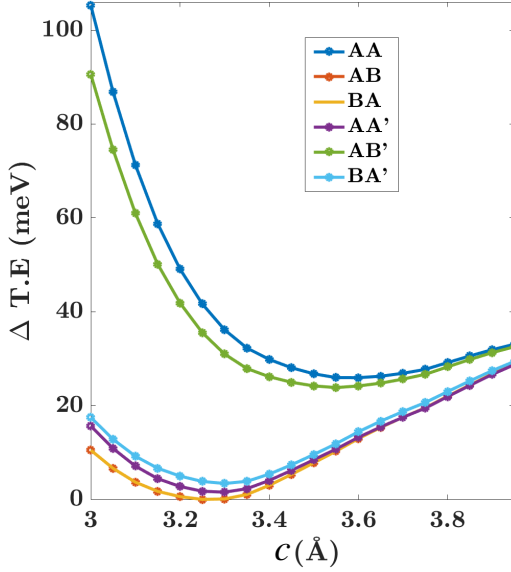


FIG. 2. (Color online) Total energies as a function of interlayer distance in BLBN with different stackings, calculated using DFT within the LDA are shown here. This figure shows the relative stability of the AB(or BA)-stacking at an optimized interlayer distance of 3.261 Å.

BA) is found to have within DFT an equilibrium value of interlayer distance $c = 3.261$ Å (Fig. 2), we have assumed the same c value for all the other stackings when we extract the effective TB-model parameters. Notably, the AA'-stacking, identified as the stable structure after the AB (or BA) stacking, showed a total energy difference of 1.664 meV per unit cell at the equilibrium value of c . In the following sections, we compare the effective TB models proposed in our work against DFT calculations.

III. TIGHT-BINDING MODELS

The π -bands of the monolayer h -BN (MBN) and bilayer h -BN (BLBN) can be studied using a TB model based on the overlap of p_z orbitals between the adjacent boron and nitrogen atoms. The Hamiltonian for the π -bands in BLBN can be represented by a $\mathbf{k}$ -dependent 4×4 size matrix:

$$H_{\text{BLBN}}(\mathbf{k}) = \begin{pmatrix} H_{\text{MBN}_1}(\mathbf{k}) & H_{\text{Coupl}}(\mathbf{k}) \\ H_{\text{Coupl}}^\dagger(\mathbf{k}) & H_{\text{MBN}_2}(\mathbf{k}) \end{pmatrix} \quad (1)$$

where $H_{\text{MBN}_1}(\mathbf{k})$ and $H_{\text{MBN}_2}(\mathbf{k})$ are 2×2 size Hamiltonian matrices that describe the inter- and intra-sublattice hopping processes within the top and bottom layers respectively. They are given by:

$$H_{\text{MBN}_i}(\mathbf{k}) = \begin{pmatrix} H_{\text{B}_i\text{B}_i}(\mathbf{k}) & H_{\text{B}_i\text{N}_i}(\mathbf{k}) \\ H_{\text{N}_i\text{B}_i}(\mathbf{k}) & H_{\text{N}_i\text{N}_i}(\mathbf{k}) \end{pmatrix} \quad (2)$$

where $i = 1, 2$ for the top and bottom layer indices. Here, B_1, N_1 are the atoms of the top layer, while B_2, N_2 are the atoms

Monolayer h -BN					
F_2G_2 model					
G_n	t_{AA}	t_{BB}	F_n	t_{AB}	
G_0	0.1648	-3.8678	F_1	-2.7547	
G_1	0.0542	0.2228	F_2	-0.1329	
G_2	0.0566	0.0429			
F_3G_3 model					
G_0	0.1648	-3.8678	F_1	-2.7547	
G_1	0.0542	0.2228	F_2	-0.2362	
G_2	0.0397	0.0329	F_3	0.2068	
G_3	-0.0337	-0.0200			
F_4G_4 model					
G_0	0.1648	-3.8678	F_1	-2.7547	
G_1	0.0542	0.2228	F_2	-0.2362	
G_2	0.0397	0.0329	F_3	0.0539	
G_3	-0.0361	-0.0250	F_4	-0.0306	
G_4	0.0012	0.0025			

TABLE I. The hopping parameters in eV units for MBN, used to construct the F_2G_2 , F_3G_3 , and F_4G_4 models, are listed here. The column labels F_n and G_n emphasize that they consist of the hopping terms related to the f_n and g_n structure factors, respectively, for the n^{th} nearest neighbor.

of the bottom layer. The coupling between these two layers is described by:

$$H_{\text{Coupl}}(\mathbf{k}) = \begin{pmatrix} H_{\text{B}_1\text{B}_2}(\mathbf{k}) & H_{\text{B}_1\text{N}_2}(\mathbf{k}) \\ H_{\text{N}_1\text{B}_2}(\mathbf{k}) & H_{\text{N}_1\text{N}_2}(\mathbf{k}) \end{pmatrix} \quad (3)$$

The elements of this matrix correspond to the possible inter-layer hopping processes between the atoms of the top and bottom layers. Due to the triangular symmetry of h -BN, the hopping energies (t) and structure factors ($f_n(\mathbf{k})$ and $g_n(\mathbf{k})$) for the intra-layer and inter-layer hopping processes can be defined similarly to those in graphene [16]. For both graphene monolayer and bilayer systems, the full tight-binding (FTB) model accurately reproduces the low-energy bands obtained from first-principles LDA calculations [5, 16]. Similarly, for MBN and BLBN systems, the FTB model provides a good fit to the low-energy bands along the high symmetry points in the FBZ, as shown in Fig. 3 and 5. However, since the FTB model considers all the hopping processes up to 15 nearest neighbors, it is desirable to look for simpler models with fewer parameters that can achieve a good compromise between accuracy and simplicity. To this end, we have developed simplified effective models with fewer parameters, such as the single-structure factor (F_1G_0) and double-structure factor (F_2G_2) models, as explained in the references [5, 16]. We have also extended these methods to higher structure factor models, such as F_3G_3 and F_4G_4 , to improve the accuracy of the TB bands near the M -point in the Brillouin zone.

The construction of simplified effective structure factor models is based on the low-energy $\mathbf{k} \cdot \mathbf{p}$ model Hamiltonian obtained by performing a Taylor expansion of the bands near the K -point [5, 16]. In the $\mathbf{k} \cdot \mathbf{p}$ model Hamiltonian where α and β indicate different sublattices, the diagonal elements $\alpha = \beta$ represent the intra-sublattice processes

AA stacked BLBN							
F ₂ G ₂ model							
G _n	t _{AA}	t _{BB}	t _{AA'}	t _{BB'}	F _n	t _{AB}	t _{AB'}
G ₀	1.7666	−2.1843	0.7270	0.2705	F ₁	−2.7001	0.0265
G ₁	0.0053	0.1923	0.0498	−0.0185	F ₂	−0.1105	−0.0077
G ₂	0.0471	0.0370	0.0020	−0.0061			
F ₃ G ₃ model							
G ₀	1.7666	−2.1843	0.7270	0.2705	F ₁	−2.7001	0.0265
G ₁	0.0053	0.1923	0.0498	−0.0185	F ₂	−0.2102	0.0082
G ₂	0.0223	0.0195	0.0089	−0.0025	F ₃	0.1995	−0.0317
G ₃	−0.0497	−0.0351	0.0138	0.0072			
F ₄ G ₄ model							
G ₀	1.7666	−2.1843	0.7270	0.2705	F ₁	−2.7001	0.0265
G ₁	0.0053	0.1923	0.0498	−0.0185	F ₂	−0.2102	0.0082
G ₂	0.0223	0.0195	0.0089	−0.0025	F ₃	0.0797	−0.0176
G ₃	−0.0483	−0.0373	0.0139	0.0070	F ₄	−0.0240	0.0028
G ₄	−0.0007	0.0011	0.0000	0.0001			

TABLE II. For AA-stacked BLBN, the hopping parameters in eV units used to construct the F₂G₂, F₃G₃, and F₄G₄ models are listed here. In the hopping processes of AA-stacking, $t_{A'A'} = t_{AA}$, $t_{B'B'} = t_{BB}$, $t_{A'B'} = t_{AB}$, and $t_{BA'} = t_{AB'}$ by symmetry relations. The column labels F_n and G_n emphasize that they consist of the hopping terms related to the f_n and g_n structure factors, respectively, for the n^{th} nearest neighbor.

$$H_{\alpha\beta}(\mathbf{k}_D + \mathbf{k}) \simeq C'_{\alpha\beta 0} + C'_{\alpha\beta 2} \mathbf{k}^2, \quad (4)$$

while the off-diagonal elements $\alpha \neq \beta$ represent inter-sublattice processes

$$H_{\alpha\beta}(\mathbf{k}_D + \mathbf{k}) \simeq C_{\alpha\beta 1} \mathbf{k} e^{-i\theta_{\mathbf{k}}} + C_{\alpha\beta 2} \mathbf{k}^2 e^{i2\theta_{\mathbf{k}}}. \quad (5)$$

The zeroth and first-order expansion coefficients for intra-sublattice and inter-sublattice processes, respectively, are defined as:

$$C'_{\alpha\beta 0} = t'_0 - 3t'_1 + 6t'_2 - 3t'_3 - 6t'_4 + 6t'_5 + 6t'_6 - 6t'_7 \quad (6)$$

$$C_{\alpha\beta 1} = \frac{\sqrt{3}a}{2} (-t_1 + 2t_2 + t_3 - 5t_4 - 4t_5 + 7t_6 + 5t_7 + 2t_8 - 4t_9 + 11t_{10}) \quad (7)$$

in the same way as graphene [16]. Here, $t_n^{(\prime)} (= t_{\alpha\beta n}^{(\prime)})$ represents the hopping energy of the n^{th} nearest neighbor hopping process from sublattice α to β . The primes that are used both for the expansion coefficients and the hopping terms indicate that they involve expansions of g_n structure factor terms. The double structure factor model F₂G₂ truncates the f_n and g_n functions at $n = 2$. In this model, we use *ab initio* nearest neighbor hopping terms and a corrected hopping term for the most distant ($n = 2$) hopping process [5, 16]

$$t_{\alpha\beta 2} = C_{\alpha\beta 1} / \sqrt{3}a + t_{\alpha\beta 1} / 2, \quad (8)$$

$$t'_{\alpha\beta 2} = \frac{1}{6} (C'_{\alpha\beta 0} - t'_{\alpha\beta 0} + 3t'_{\alpha\beta 1}).$$

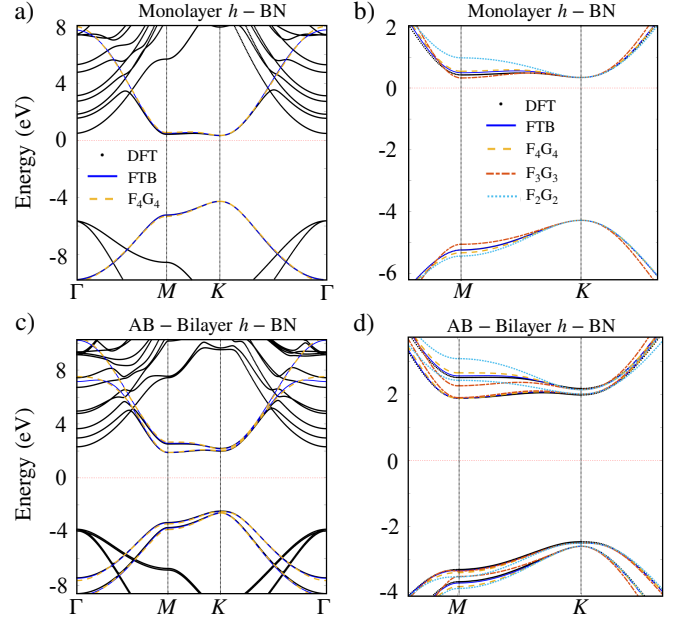


FIG. 3. (Color online) Accuracy of the FTB model and F₄G₄ model in reproducing the *ab initio* π -bands along the given $\mathbf{k}$ -path is shown in a) for MBN and in c) for AB(or BA) stacked BLBN. The merit of the F₄G₄ model when compared to other fewer parameter effective models near K-point and M-point is shown in b) for MBN and in d) for AB(or BA) stacked BLBN.

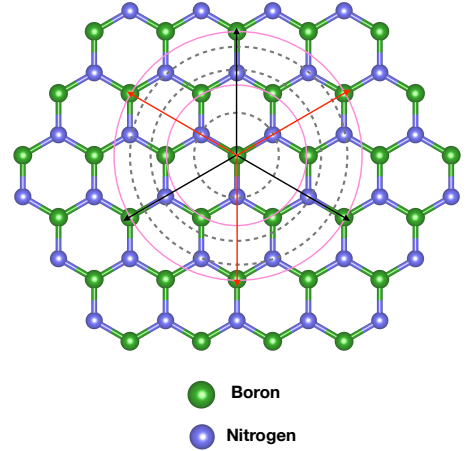


FIG. 4. (Color online) The nearest neighbor representation in the effective TB models is illustrated here. Inter-sublattice nearest neighbors are depicted on the dashed grey circles, while intra-sublattice nearest neighbors are shown on the pink circles, with the boron atom at the origin. The nearest neighbor index n increases with the circle radius.

For single-layer and bilayer graphene, the F₂G₂ model achieves accuracy near the K-point and away from it. This model can capture both the trigonal distortion of the bands near the K-point and the particle-hole symmetry breaking throughout the Brillouin zone [16]. However, for MBN,

AB stacked BLBN											
F ₂ G ₂ model											
G _n	t _{AA}	t _{BB}	t _{A'A'}	t _{B'B'}	t _{BA'}	F _n	t _{AB}	t _{A'B'}	t _{AA'}	t _{BB'}	t _{AB'}
G ₀	1.6636	−2.3393	1.7128	−2.2591	0.3809	F ₁	−2.6971	−2.7190	0.4841	−0.0176	0.1209
G ₁	0.0235	0.1903	0.0108	0.1910	−0.0617	F ₂	−0.1248	−0.1129	0.0457	−0.0545	−0.1437
G ₂	0.0496	0.0388	0.0490	0.0328	−0.0158						
F ₃ G ₃ model											
G ₀	1.6636	−2.3393	1.7128	−2.2591	0.3809	F ₁	−2.6971	−2.7190	0.4841	−0.0176	0.1209
G ₁	0.0235	0.1903	0.0108	0.1910	−0.0617	F ₂	−0.2207	−0.2044	0.0743	−0.0472	−0.1387
G ₂	0.0274	0.0212	0.0257	0.0148	−0.0245	F ₃	0.1917	0.1829	−0.0573	−0.0146	−0.0099
G ₂ [*]	0.0274	0.0212	0.0257	0.0148	−0.0159						
G ₃	−0.0446	−0.0352	−0.0466	−0.0359	−0.0175						
F ₄ G ₄ model											
G ₀	1.6636	−2.3393	1.7128	−2.2591	0.3809	F ₁	−2.6971	−2.7190	0.4841	−0.0176	0.1209
G ₁	0.0235	0.1903	0.0108	0.1910	−0.0617	F ₂	−0.2207	−0.2044	0.0743	−0.0472	−0.1387
G ₂	0.0274	0.0212	0.0257	0.0148	−0.0245	F ₃	0.0779	0.0795	0.0520	0.0207	−0.0215
G ₂ [*]	0.0274	0.0212	0.0257	0.0148	−0.0159	F ₄	−0.0228	−0.0207	0.0219	0.0071	−0.0023
G ₃	−0.0419	−0.0367	−0.0441	−0.0372	−0.0116						
G ₄	−0.0013	0.0007	−0.0012	0.0007	−0.0030						

TABLE III. For AB-stacked BLBN, the hopping parameters in eV units used to construct the F₂G₂, F₃G₃, and F₄G₄ models are listed here. The column labels F_n and G_n emphasize that they consist of the hopping terms related to the f_n and g_n structure factors, respectively, for the n^{th} nearest neighbor.

AA' stacked BLBN									
F ₂ G ₂ model									
G _n	t _{AA}	t _{BB}	t _{A'A'}	t _{B'B'}	t _{AA'}	F _n	t _{AB}	t _{AB'}	t _{BA'}
G ₀	1.6717	-2.3068	-2.3074	1.6716	0.4310	F ₁	-2.7049	0.4239	-0.0613
G ₁	0.0122	0.1900	0.1900	0.0122	-0.0684	F ₂	-0.1176	0.1338	-0.0161
G ₂	0.0520	0.0372	0.0372	0.0520	-0.0344				
F ₃ G ₃ model									
G ₀	1.6717	-2.3068	-2.3074	1.6716	0.4310	F ₁	-2.7049	0.4239	-0.0613
G ₁	0.0122	0.1900	0.1900	0.0122	-0.0684	F ₂	-0.2136	0.1798	0.0031
G ₂	0.0288	0.0186	0.0186	0.0288	-0.0415	F ₃	0.1921	-0.0919	-0.0383
G ₂ [*]	0.0288	0.0186	0.0186	0.0288	-0.0163				
G ₃	-0.0463	-0.0370	-0.0370	-0.0463	-0.0142				
F ₄ G ₄ model									
G ₀	1.6717	-2.3068	-2.3074	1.6716	0.4310	F ₁	-2.7049	0.4239	-0.0613
G ₁	0.0122	0.1900	0.1900	0.0122	-0.0684	F ₂	-0.2136	0.1798	0.0031
G ₂	0.0288	0.0186	0.0186	0.0288	-0.0415	F ₃	0.0803	0.0261	0.0121
G ₂ [*]	0.0288	0.0186	0.0186	0.0288	-0.0163	F ₄	-0.0224	0.0236	0.0101
G ₃	-0.0438	-0.0381	-0.0381	-0.0438	-0.0072				
G ₄	-0.0013	0.0005	0.0005	-0.0013	-0.0035				

TABLE IV. For AA'-stacked BLBN, the hopping parameters in eV units used to construct the F₂G₂, F₃G₃, and F₄G₄ models are listed here. In the hopping processes of AA'-stacking, $t_{BB'} = t_{AA'}$ and $t_{A'B'} = t_{AB}$ by symmetry relations. The column labels F_n and G_n emphasize that they consist of the hopping terms related to the f_n and g_n structure factors, respectively, for the n^{th} nearest neighbor.

the F₂G₂ model achieves accuracy only near the K -point, as shown in the top right panel of Fig. 3. Since the MBN has low-energy band edges near the K -point, the F₂G₂ model could be an alternative to the FTB model. However, for BLBN with different stacking, the lower conduction band edge does not always lie at the K -point. The bands near the M -point for AB(or BA), AA', and AB' stacking, give rise to an indirect bandgap. On the other hand, the AA and BA' stacking give rise to a direct bandgap, as illustrated in Figs. 5 and 8(d). The overall energy variation between the primary conduction band edges located at the K -point and M -point for different stacking is of the order of ± 400 meV, as indicated by the dashed

blue line in Fig. 8(d). Therefore, it is desirable to tailor a simplified TB model that can reproduce the *ab initio* low-energy bands near the K -point as well as at the M -point.

We can improve the accuracy of the effective TB models far from the K -point by taking a larger number of nearest neighbor hopping parameters (n) along with the corresponding structure factors [5]. In this study, we have extended the effective TB models to include $n = 3$ and $n = 4$ truncation in the expansion of the f_n and g_n functions to improve the accuracy of the bands away from the K -point. In these models, we use the *ab initio* near-neighbor hopping terms for the shortest hopping terms, and we correct the most distant

AB' stacked BLBN							
F ₂ G ₂ model							
G _n	t _{AA}	t _{BB}	t _{BA'}	F _n	t _{AB}	t _{AA'}	t _{AB'}
G ₀	1.8176	-2.1740	0.2059	F ₁	-2.6892	0.0687	0.4460
G ₁	0.0183	0.1911	-0.0283	F ₂	-0.1183	-0.0823	-0.0686
G ₂	0.0451	0.0377	0.0129				
F ₃ G ₃ model							
G ₀	1.8176	-2.1740	0.2059	F ₁	-2.6892	0.0687	0.4460
G ₁	0.0183	0.1911	-0.0283	F ₂	-0.2104	-0.0771	-0.0328
G ₂	0.0219	0.0205	0.0170	F ₃	0.1842	-0.0103	-0.0717
G ₂ [*]	0.0219	0.0205	-0.0064				
G ₃	-0.0464	-0.0343	0.0083				
F ₄ G ₄ model							
G ₀	1.8176	-2.1740	0.2059	F ₁	-2.6892	0.0687	0.4460
G ₁	0.0183	0.1911	-0.0283	F ₂	-0.2104	-0.0771	-0.0328
G ₂	0.0219	0.0205	0.0170	F ₃	0.0752	-0.0054	0.0452
G ₂ [*]	0.0219	0.0205	-0.0064	F ₄	-0.0218	0.0010	0.0234
G ₃	-0.0431	-0.0356	0.0063				
G ₄	-0.0016	0.0007	0.0010				

TABLE V. For AB'-stacked BLBN, the hopping parameters in eV units used to construct the F₂G₂, F₃G₃, and F₄G₄ TB models are listed here. In the hopping processes of AB'-stacking, $t_{A'A'} = t_{BB}$, $t_{B'B'} = t_{AA}$, $t_{A'B'} = t_{AB}$, and $t_{BB'} = t_{AA'}$ by symmetry relations. The column labels F_n and G_n emphasize that they consist of the hopping terms related to the f_n and g_n structure factors, respectively, for the n^{th} nearest neighbor.

hopping term using the following relations:

$$n = 3:$$

$$\begin{aligned} t_{\alpha\beta 3} &= 2C_{\alpha\beta 1}/\sqrt{3}a + t_{\alpha\beta 1} - 2t_{\alpha\beta 2}, \\ t'_{\alpha\beta 3} &= \frac{1}{3}(-C'_{\alpha\beta 0} + t'_{\alpha\beta 0} - 3t'_{\alpha\beta 1} + 6t'_{\alpha\beta 2}), \end{aligned} \quad (9)$$

$$n = 4:$$

$$\begin{aligned} t_{\alpha\beta 4} &= \frac{-1}{5}(2C_{\alpha\beta 1}/\sqrt{3}a + t_{\alpha\beta 1} - 2t_{\alpha\beta 2} - t_{\alpha\beta 3}), \\ t'_{\alpha\beta 4} &= \frac{1}{6}(-C'_{\alpha\beta 0} + t'_{\alpha\beta 0} - 3t'_{\alpha\beta 1} + 6t'_{\alpha\beta 2} - 3t'_{\alpha\beta 3}) \end{aligned} \quad (10)$$

The band structures for *h*-BN monolayer and bilayer that are obtained from DFT, the FTB model, and different simplified effective models are compared in Fig. 3 and Fig. 5. The F₄G₄ effective model reproduces the *ab initio* low-energy bands near the *K*-point and at the *M*-point. All the effective TB models with $n = 2, 3, 4$ can capture the low energy bands at the *K*-point including band crossing for AA', AB', BA'-stackings and its absence for AA, AB, and BA-stackings.

As shown in Fig. 4, the pink large circle ($n = 2$) enclosing the boron and nitrogen atoms represents the six intra-sublattice (G₂) nearest neighbors, among which the alternating sublattices are oriented with 60° rotations with respect to the other three, as represented with black and red arrows from the origin. In the G₂ interlayer hopping processes of AB(or BA), AA', AB' & BA'-stacked bilayers, these alternating sublattice hopping energies are expected to be different even if they are at the same distance from the origin because of the

BA' stacked BLBN							
F ₂ G ₂ model							
G _n	t _{AA}	t _{BB}	t _{AB'}	F _n	t _{AB}	t _{AA'}	t _{BA'}
G ₀	1.8325	-2.1688	0.7813	F ₁	-2.6866	0.0763	0.0604
G ₁	0.0096	0.1965	0.0877	F ₂	-0.1202	-0.0569	-0.0735
G ₂	0.0497	0.0379	0.0242				
F ₃ G ₃ model							
G ₀	1.8325	-2.1688	0.7813	F ₁	-2.6866	0.0762	0.0604
G ₁	0.0096	0.1965	0.0877	F ₂	-0.2187	-0.0622	-0.0665
G ₂	0.0244	0.0204	0.0312	F ₃	0.1971	0.0106	-0.0140
G ₂ [*]	0.0244	0.0204	0.0193				
G ₃	-0.0507	-0.0352	0.0140				
F ₄ G ₄ model							
G ₀	1.8325	-2.1688	0.7813	F ₁	-2.6866	0.0763	0.0604
G ₁	0.0096	0.1965	0.0877	F ₂	-0.2187	-0.0622	-0.0665
G ₂	0.0244	0.0204	0.0312	F ₃	0.0794	-0.0141	0.0122
G ₂ [*]	0.0244	0.0204	0.0193	F ₄	-0.0235	-0.0049	0.0052
G ₃	-0.0466	-0.0370	0.0093				
G ₄	-0.0020	0.0009	0.0024				

TABLE VI. For BA'-stacked BLBN, the hopping parameters in eV units used to construct the F₂G₂, F₃G₃, and F₄G₄ TB models are listed here. In the hopping processes of BA'-stacking, $t_{A'A'} = t_{BB}$, $t_{B'B'} = t_{AA}$, $t_{A'B'} = t_{AB}$, and $t_{BB'} = t_{AA'}$ by symmetry relations. The column labels F_n and G_n emphasize that they consist of the hopping terms related to the f_n and g_n structure factors, respectively, for the n^{th} nearest neighbor.

different arrangements of atoms around them. The F₂G₂ effective model's inability to accurately reproduce the *ab initio* bands near the *M*-point can be attributed to the assumption that all six interlayer G₂ hopping energies are equal. This inaccuracy is corrected in higher-order effective models, as demonstrated in Tables. III to VI. In the presented data tables, the four sub-lattices of *h*-BN, namely B₁, N₁, B₂, and N₂, are denoted by the labels A, B, A', and B', respectively. Note that for the BA-stacked BLBN, the data is not explicitly given, as it can be obtained from the AB-stacked bilayer data by swapping the corresponding hopping energies. Specifically, the hopping energies t_{AA} , t_{BB} , $t_{A'A'}$, $t_{B'B'}$, $t_{BA'}$, t_{AB} , $t_{A'B'}$, $t_{AA'}$, $t_{BB'}$, and $t_{AB'}$ of the AB-stacked bilayer correspond to the hopping energies $t_{A'A'}$, $t_{B'B'}$, t_{AA} , t_{BB} , $t_{AB'}$, $t_{A'B'}$, t_{AB} , $t_{AA'}$, $t_{BB'}$, and $t_{BA'}$, respectively, for the BA-stacked bilayer.

Since the precise determination of the band extrema in the Brillouin zone is critical for understanding and optimizing the electronic properties of these materials, additionally, we have presented the surface plots of lower energy bands calculated in the whole Brillouin zone, using the FTB model in Fig. 6. Here, VB₁ and CB₁ refer to the valence and conduction bands, respectively, that are closest to the Fermi level, as indicated in Fig. 5. In the upper panel of Fig. 6, it is shown that for all stackings except AA', the valence band maxima occur at the Brillouin zone corners (*K*-points), while the valence band minima occur at the Γ -point. However, for the AA'-type, the valence bands cross at the *K*-points, as also shown in Fig. 5. The bottom panel of Fig. 6 shows that the conduction band minima occur at the *M*-point for all stackings except for AA and BA'. However, for the AA and BA'-types, the conduction band minima occur at the *K*-point.

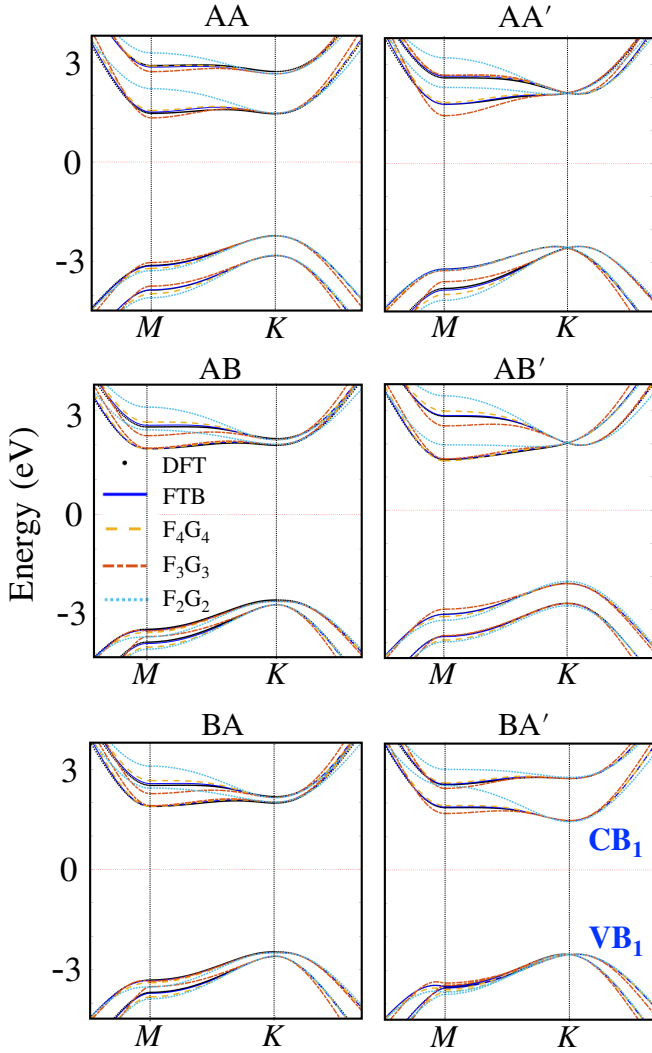


FIG. 5. (Color online) Accuracy of the FTB and F_4G_4 model in reproducing the *ab initio* π -bands along the given k -path compared to other fewer parameter effective models is shown for AA, AB, BA, AA', AB' and BA' stacked BLBN.

IV. INTERLAYER DISTANCE-DEPENDENT EFFECTIVE TIGHT-BINDING MODELS

The interlayer distance of BLBN can vary due to external conditions, such as strain or pressure. To provide effective TB models that can account for such variations in the atomic structure, we have presented a fitting parametrization for the c -dependence of each of the standard stackings in BLBN. This allows for simplified and efficient modeling of the electronic properties of bilayer BLBN under different external conditions. We focus on the dependence of the F_4G_4 -TB model on the interlayer distance c as this model accurately predicts the low-energy band structures. To investigate the dependence of hopping energies on c , we have computed the F_4G_4 -TB model hopping data for different stacking at interlayer distances of $c = 3.1, 3.2, 3.3, 3.4$, and 3.5 Å. We have fitted this data with

an exponential function of the form:

$$t_i(c) = a_i e^{b_i c} + c_i e^{d_i c} \quad (11)$$

for each of the intralayer and interlayer hopping processes between intra- and inter-sublattices in all the stackings studied in this work. The corresponding fitting parameters a_i , b_i , c_i , and d_i , which define the hopping term $t_i(c)$ in eV units, are listed in Tables A1 to A5 in the appendix. Here, we have omitted the sublattice indices for brevity and the index i refers to the distant neighbor for each stacking and hopping process corresponding to the G or F structure factors that we have parameterized against DFT values up to $n = 4$. Specifically, for the hopping processes corresponding to the G structure factor, the i index takes the values 0, 1, 2, 3, and 4, while the hopping processes corresponding to the F structure factor, i takes the values 1, 2, 3, and 4. The fitting parameters a_i , b_i , c_i , and d_i for each process are provided in TABLES. A1 to A5 in Appendix. We show in Fig. 7(a) and (b) the quality of this fitting for the B to A' -sublattice interlayer hopping process and the A to B -sublattice intra-layer hopping process for an AB-stacked bilayer. We represent the calculated data with circles that fit an exponentially decaying function. This fitting function is suitable for all the hopping processes including the distant neighbor terms having the energy of the order of 10^{-3} eV. This parametrization can accurately reproduce the F_4G_4 -TB model band structures, at any intermediate interlayer distance. For instance, at the intermediate interlayer distance of $c = 3.261$ Å in the AB-stacking, the fitting function can produce hopping terms as accurate as those listed in Table. III, and the resulting band structures are in close agreement, as compared in Fig. 7(c). The increasing interlayer distance leads to an increase in the energy separation between the primary and secondary bands, as shown in Fig. 7(d) & (e). Specifically, the separation between the primary valence band VB_1 and primary conduction band CB_1 at the K -point is plotted as a function of interlayer distance.

We have also studied the impact of the lattice constant on the effective hopping parameters in these bilayer systems. Our results indicate that the effective hopping parameters at $n = 4$ remain nearly unchanged with variations in the lattice parameters for all the hopping processes in each stacking. The dominant hopping energies in AB-stacked BLBN calculated for three specific lattice constant values of $a \sim 2.42, 2.48, 2.51$ Å are illustrated in Fig. 8(a)&(b) for the hopping processes from B to A' sublattice corresponding to G_n structure factors and from A to B sublattice corresponding to F_n structure factors. It is observed that, for a $\sim 1\%$ variation in a , the magnitude of the nearest neighbor ($n = 1$) hopping energy changes by $\sim 3\%$ in the intra-layer A to B process and by $\sim 2\%$ in the interlayer B to A' process. To understand the effect of bond distortions on the Fermi velocity in BLBN systems, we have calculated the first nearest neighbor hopping energy for the intra-layer process of A -site to B -site as a function of bond length, in the most stable AB-stacked structure. The hopping energy exhibits an exponential dependence on the bond length ($r_{ij} = |\mathbf{r}_{ij}|$), which we fit with the following relation:

$$t_{AB}(r_{ij}) = t_{AB}(r_{0,ij}) \exp\left(-2.45\left(\frac{r_{ij} - r_{0,ij}}{r_{0,ij}}\right)\right) \quad (12)$$

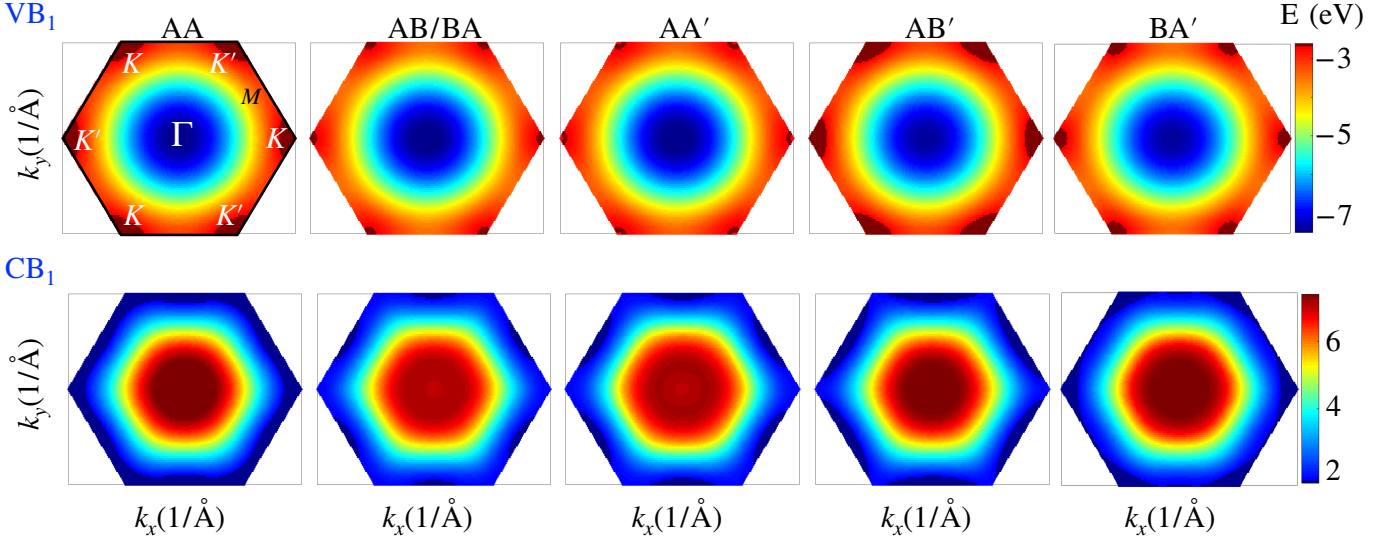


FIG. 6. (Color online) The primary bands VB_1 and CB_1 calculated using the FTB model across the entire FBZ for various BLBN stackings are depicted here. The letters in the top left panel denote the high symmetry points within the FBZ.

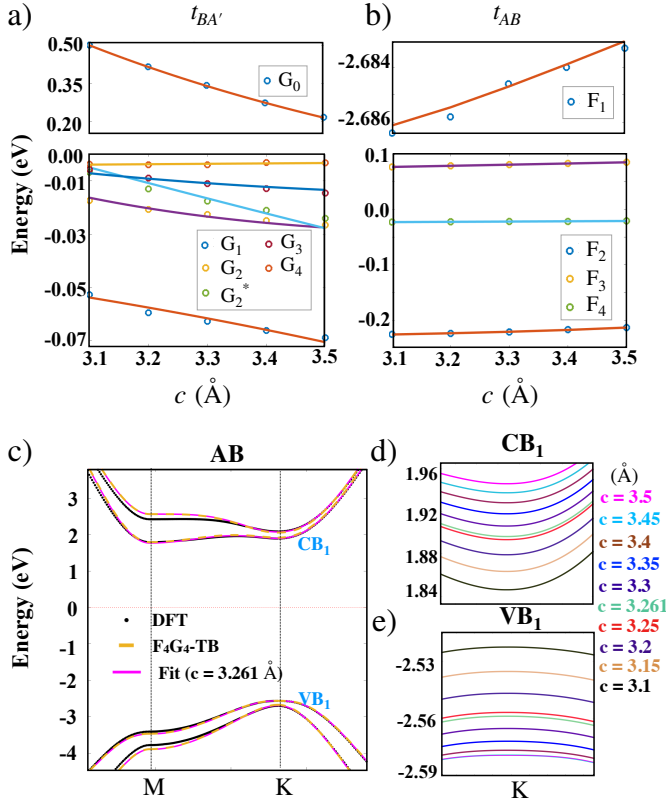


FIG. 7. (Color online) a) Fitting lines for the calculated hopping energies (circles) as a function of c are shown for the interlayer hopping process between sublattice B to A' , and b) for the intra-layer hopping process between sublattice A to B , in AB-stacked BLBN. c) A comparison of the band structures of AB-stacked BLBN at $c = 3.261$ Å, obtained from DFT and the F_4G_4 -TB model, and the fitted F_4G_4 -TB model from Eq. (11). At the K -point, the separation between the primary bands d) CB_1 and e) VB_1 is depicted for different values of c (Å).

This relation can also account for hopping terms that use lattice constants more closely comparable to the experimental values. Here, $t_{AB}(r_{0,ij})$ is the hopping energy calculated at the equilibrium bond length $r_{0,ij} = 1.43$ Å in this work, which is approximately -2.7 eV. The comparison between the hopping data and the fitting function in Eq. (12) is shown in Fig. 8(c).

V. DISTANCE-DEPENDENT TWO-CENTER APPROXIMATION FOR INTERLAYER HOPPING PROCESSES

So far we have discussed the effective TB models that reproduce the LDA band edges for zero-twist standard stackings in BLBN. However, we would like to build a Hamiltonian model that describes the electronic structures of twisted BLBN configurations, covering both large and small twist angles. Such a generalized model for twisted bilayer graphene has been addressed previously through two center (TC) distance-dependent approximations [17–20]. Atomic species dependent interlayer tunneling models were proposed in earlier literature to fit the bands against DFT results [21, 22]. Here, we propose a TC interlayer model for BLBN distinguishing B-B, B-N and N-N interactions whose interlayer tunneling Hamiltonian at the K -point matches the DFT calculations [23].

We note that the TC-approximation is used to compute the interlayer hopping energies as a function of the relative distance r_{ij} between two sublattices positioned at boron or nitrogen atoms from different layers, each located at $\mathbf{r}_i$ and $\mathbf{r}_j$, respectively. Meanwhile, the intra-layer hopping energies are extracted from the FTB model data of AA-stacked BLBN. For calculation convenience, we have truncated both intra- and interlayer hopping processes up to the sixth nearest neighbors. The distance-dependent interlayer hopping energy in this TC-

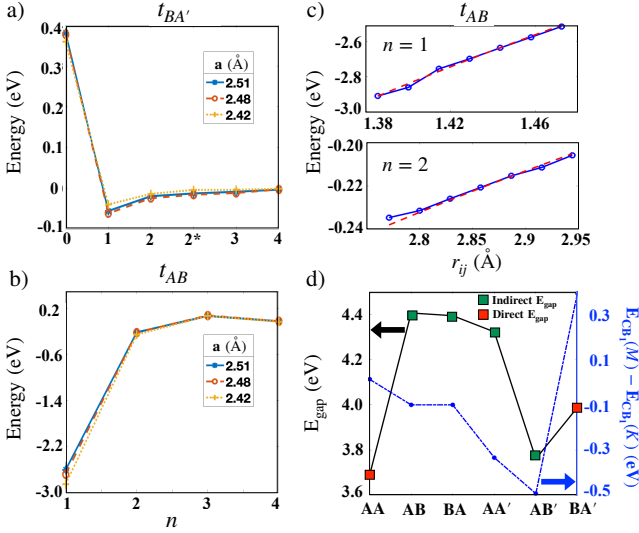


FIG. 8. (Color online) a) A comparison of the hopping parameters of the F_4G_4 -TB model for the processes of a) B to A' and b) A to B in AB-stacked BLBN is provided for different lattice parameters. c) The hopping data t_{AB} (blue) for the nearest neighbors $n = 1, 2$ as a function of bond length (r_{ij}) is illustrated along with the fitting function (red) given in Eq. (12). d) The energy difference between the primary conduction band edges at the M -point and K -point is represented with a dashed blue line, while the primary bandgap (E_{gap}) is depicted by the black line. The direct and indirect band gaps are indicated by red and green rectangles, respectively. The data is obtained using DFT for different stackings of BLBN.

approximation [17–20] is defined as,

$$t(r_{ij}) = n_{ij,z}^2 V_{pp\sigma}(r_{ij}) + (1 - n_{ij,z}^2) V_{pp\pi}(r_{ij}) \quad (13)$$

where $n_{ij,z}$ is the direction cosine of r_{ij} , defined as $n_{ij,z} = z_{ij}/r_{ij}$, where z_{ij} is the coordinate of r_{ij} along the z -axis. We have

$$\begin{aligned} V_{pp\sigma}(r_{ij}) &= \gamma_1 \exp(q\sigma(1 - \frac{r_{ij}}{c})), \\ V_{pp\pi}(r_{ij}) &= \gamma_0 \exp(q\pi(1 - \frac{r_{ij}}{a_{\text{BN}}})) \end{aligned} \quad (14)$$

and

$$\frac{q\sigma}{c} = \frac{q\pi}{a_{\text{BN}}} = \frac{\ln(\gamma'_0/\gamma_0)}{a_{\text{BN}} - a} \quad (15)$$

where we use the same parameters as graphene for the nearest neighbor interaction γ_0 within a plane of -2.7 eV and the second nearest neighbor interaction γ'_0 as $0.1\gamma_0$ [17]. The a_{BN} is the LDA bond length between boron and nitrogen (1.43 Å) and a is the LDA optimized lattice parameter (2.48 Å). The interlayer distance c (3.261 Å) is constant since each h -BN layer in the BLBN is considered to be flat in these calculations. We fit the interlayer hopping parameter prefactors in the TC approximation to be

$$\begin{aligned} \gamma_{\text{BB},1} &= 0.831 \text{ eV}, \\ \gamma_{\text{NN},1} &= 0.3989 \text{ eV}, \\ \gamma_{\text{BN},1} &= 0.6601 \text{ eV} \end{aligned} \quad (16)$$

for boron-boron, nitrogen-nitrogen and boron-nitrogen atoms.

As mentioned already, the γ_1 term is obtained by fitting the TB tunneling Hamiltonian element $H(K : \mathbf{d}_{xy})$ with *ab initio* data near the K -point [23]. Here $\mathbf{d}_{xy}$ indicates all possible sliding vectors in real space within the span of $\mathbf{d}_x = 0$ to a and $\mathbf{d}_y = 0$ to $\sqrt{3}a$ in BLBN. The fitting process aims to minimize the error between the $H(K : \mathbf{d}_{xy})$ data obtained from both the TB model and LDA [18]. By substituting these values in Eqs. (13) to (15), we calculate the TC-approximated interlayer hopping energy for the BLBN system.

In Fig. 9, we compare the band structures obtained from LDA calculations with those from the TC-approximated TB model for various high symmetry stacking configurations of BLBN. The comparison reveals that away from the K -point the band dispersion is not as precise as that obtained from the full- or effective ($n = 4$) TB models but the TC-approximation method effectively captures the presence of both crossing and non-crossing bands at the K -point for all standard stackings. However, it should be noted that the indirect bandgap in the AB (or BA) stacking is not recovered.

In summary, although the interlayer coupling model may not accurately reproduce the band dispersion away from the K -point in zero-twist atomic structures, it remains a viable approach for accurately calculating the low-energy bands near the K -point in twisted BLBN systems containing a large number of atoms in the unit cell.

VI. SUMMARY AND CONCLUSIONS

We have derived the π -band tight-binding (TB) models for h -BN monolayer and bilayer using maximally localized Wannier functions. We presented three effective TB models as simpler alternatives to the 15-parameter full tight-binding (FTB) model to describe the bands near the high symmetry points K and M in the FBZ. It is found that we need up to $n = 4$ distant hopping terms, namely the F_4G_4 model, to capture the indirect nature of the LDA band gaps for AB and BA stackings. The fact that the double structure factor effective model F_2G_2 with $n = 2$ truncation is accurate only near the K -point stems from the limiting approximation that all six interlayer G_2 hopping parameters are equal. To offer effective TB models capable of accommodating external conditions like strain or pressure, we introduced an interlayer distance-dependent F_4G_4 model for each of the standard stacking types of BLBN, covering interlayer distances c ranging from 3.1 to 3.5 Å. The impact of changing lattice parameters on the effective hopping parameters of BLBN is also discussed.

Furthermore, we introduced a two-center (TC) approximated TB model parameterized from LDA input. This model is employed to define the interlayer hopping parameters for any stacking or twisted BLBN configuration, based on the relative distance between a pair of atoms, where we distinguished the hopping terms involving the same and different atomic species. The TC-approximation method effectively captures the presence of both crossing and non-crossing bands at the K -point across all standard stackings. While this method may not accurately reproduce the band disper-

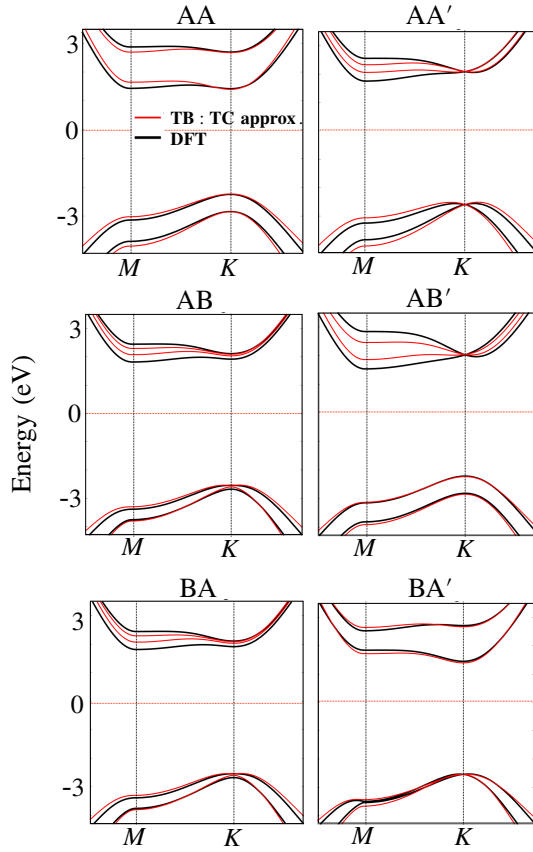


FIG. 9. (Color online) Comparison of band structures obtained using LDA and the TC-approximated TB model for all standard stackings of BLBN. The red lines represent bands from the TC-approximation, while the black lines represent bands from LDA.

sion away from the K -point in zero-twist atomic structures, it remains a viable approach for accurately calculating the low-energy bands at the K -point in twisted BLBN systems.

VII. ACKNOWLEDGEMENTS

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**Appendix: Interlayer distance dependent fitting
parametrization tables for F₄G₄-TB model in BLBN with
stackings**

In this section, we provide the data required for the c -dependent parametrization of the hopping energies in each hopping process within the effective TB model with $n = 4$ for the BLBN system with different stackings. The hopping data obtained from first-principles, as a function of interlayer distance ranging from 3.1 to 3.5 Å for the given stackings, is fitted with a function described in Eq. (11). The fitting parameters for all the hopping processes in AA, AA', AB', BA', and AB stackings are listed in Tables A1, A2, A3, A4, and A5 below, respectively.

	$A-A$	$B-B$	$A-A'$	$B-B'$	$A-B$	$A-B'$
a_0	0.4606	-4.0140	2.2170	1.6800	-	-
b_0	0.3915	-0.1848	-2.7200	-0.1375	-	-
c_0	0.0256	-0.0024	1.4480	-0.2480	-	-
d_0	0.4038	-4.6280	-0.2130	0.3563	-	-
a_1	-0.0093	0.6383	-0.3910	-0.1087	-0.9425	1.9030
b_1	0.6518	0.1833	0.6001	0.1701	-8.8350	-0.9914
c_1	0.0055	-0.4867	0.3238	0.0715	-2.9180	-0.0007
d_1	0.8256	0.2112	0.6629	0.2693	-0.0238	1.2810
a_2	-0.0002	0.0268	0.0202	0.0095	-0.1598	8.8100
b_2	0.6784	0.4281	0.7543	0.3499	0.0820	-2.8300
c_2	0.0040	-0.0191	-0.0403	-0.0157	9.2690	1.3430
d_2	0.5384	0.4734	0.5324	0.2181	-7.2540	-1.5260
a_3	0.5653	0.0108	0.1714	0.4662	0.0015	-0.1925
b_3	-0.2976	0.5824	-0.1436	0.7221	-1.2870	-0.0979
c_3	-0.6604	-0.0367	-0.3223	-0.4688	0.0782	0.4838
d_3	-0.2825	0.3377	-0.3789	0.7200	0.0111	-0.4207
a_4	-0.0077	-0.0005	-0.0725	0.0002	-0.0454	-0.1698
b_4	0.5426	-9.3350	-0.6360	0.8318	-0.1396	0.1638
c_4	0.0072	0.0010	0.0065	-0.0006	0.0214	0.2067
d_4	0.5580	0.0058	0.0999	0.4771	-0.2948	0.1068

TABLE A1. The fitting parameters a_i , b_i , c_i , and d_i for the c -dependent hopping parametrization shown in Eq. (11), for the F_4G_4 model for AA-stacked BLBN are presented. Here, i represents the neighbor index n . The top row of the table illustrates the hopping processes between corresponding sublattices. In AA-stacking, $t_{A'A'} = t_{AA}$, $t_{B'B'} = t_{BB}$, $t_{A'B'} = t_{AB}$, and $t_{BA'} = t_{AB'}$ by symmetry relations. The hopping parameters are given in eV units.

	$A-A$	$B-B$	$A-A'$	$A-B$	$A-B'$	$B-A'$
a_0	0.0164	0.4819	2.8020	-	-	-
b_0	-3.0860	0.2315	-0.3861	-	-	-
c_0	1.5040	-1.7470	-0.0073	-	-	-
d_0	0.0303	0.1979	1.1910	-	-	-
a_1	-0.0931	0.3269	-0.0279	-2.4920	-5.4770	-0.8401
b_1	-0.2723	-0.1689	0.2853	-9.2210	-6.0280	0.2899
c_1	11.750	-1.7430	7.1910	-2.6770	1.8530	0.6791
d_1	-1.6680	-7.4570	-9.0300	0.0038	-0.4450	0.3461
a_2	0.3006	3.9530	0.9573	0.0056	-0.2072	1.0550
b_2	0.3349	-1.0680	0.1134	-0.0310	-0.3630	0.1763
c_2	-0.2654	-4.3010	-0.9907	-0.4010	0.6907	-1.1360
d_2	0.3630	-1.1420	0.1122	-0.1920	-0.3184	0.1531
a_2^*	0.3006	3.9530	0.2170	-	-	-
b_2^*	0.3349	-1.0680	0.4179	-	-	-
c_2^*	-0.2654	-4.3010	-0.2164	-	-	-
d_2^*	0.3630	-1.1420	0.4246	-	-	-
a_3	-0.0187	-0.0178	-0.0703	0.0285	0.1277	0.9009
b_3	0.2587	0.2275	0.3113	0.3129	0.2866	0.5398
c_3	-0.0838	-0.6783	0.0801	0.0061	-0.1503	-0.9120
d_3	-1.8550	-9.6650	0.2584	-10.520	0.2081	0.5353
a_4	0.1765	0.0204	0.1122	0.0183	0.0147	0.0028
b_4	0.3853	-1.1480	-0.1774	-9.8800	0.0422	0.3726
c_4	-0.1565	0.1483	-0.1163	-0.0536	0.0046	-3.7130
d_4	0.4226	-3.4070	-0.1702	-0.2787	0.1945	-4.746

TABLE A2. The fitting parameters a_i , b_i , c_i , and d_i for the c -dependent hopping parametrization shown in Eq. (11), for the F_4G_4 model for AA' -stacked BLBN are presented. Here, i represents the neighbor index n . The top row of the table illustrates the hopping processes between corresponding sublattices. In AA' -stacking, $t_{A'A'} = t_{BB}$, $t_{B'B'} = t_{AA}$, $t_{A'B'} = t_{AB}$, and $t_{BB'} = t_{AA'}$ by symmetry relations. The hopping parameters are given in eV units.

	$A-A$	$B-B$	$B-A'$	$A-B$	$A-A'$	$A-B'$
a_0	0.9895	-0.1395	0.8377	-	-	-
b_0	0.2307	-4.9030	-0.0721	-	-	-
c_0	-0.0034	-2.2510	-0.0643	-	-	-
d_0	1.3550	-0.0105	0.5943	-	-	-
a_1	4.1740	1.2190	-0.2888	1.8790	3.9740	-0.0145
b_1	-1.6680	-6.9440	-5.5960	-9.1540	-0.7872	0.6848
c_1	0.1304	0.2440	-10.570	-2.7100	-0.4307	1.0160
d_1	-4.5090	-0.0753	-1.8350	-0.0023	-0.1839	-0.1714
a_2	-0.0037	-0.0112	0.0840	-0.3066	-0.0613	0.0646
b_2	0.7808	0.7136	-9.7680	-0.1052	0.0712	0.1191
c_2	0.0104	0.0235	0.0011	8.1740	-2.8940	-14.240
d_2	0.5810	0.5375	0.8206	-2.1490	-7.2330	-1.4450
a_2^*	-0.0037	-0.0112	-0.5739	-	-	-
b_2^*	0.7808	0.7136	0.3430	-	-	-
c_2^*	0.0104	0.0235	0.5383	-	-	-
d_2^*	0.5810	0.5375	0.3615	-	-	-
a_3	0.0469	7.2940	-0.0343	0.0312	5.2910	-1.3750
b_3	-4.1440	-9.0010	0.6859	0.2687	-1.7530	0.5064
c_3	-0.0225	-0.0157	0.0310	0.0000	-0.0022	1.3750
d_3	0.1979	0.2507	0.7234	-10.900	0.7159	0.5083
a_4	0.2959	0.0045	0.0065	-0.0324	0.4313	-0.0016
b_4	-1.0540	-0.2546	-0.2343	-0.1242	0.2359	0.6225
c_4	-0.1077	-0.0004	-2.2330	2.5360	-0.3990	0.0171
d_4	-0.6937	0.3998	-2.1300	-12.150	0.2594	0.2214

TABLE A3. The fitting parameters a_i , b_i , c_i , and d_i for the c -dependent hopping parametrization shown in Eq. (11), for the F_4G_4 model for AB' -stacked BLBN are presented. Here, i represents the neighbor index n . The top row of the table illustrates the hopping processes between corresponding sublattices. In AB' -stacking, $t_{A'A'} = t_{BB}$, $t_{B'B'} = t_{AA}$, $t_{A'B'} = t_{AB}$, and $t_{BB'} = t_{AA'}$ by symmetry relations. The hopping parameters are given in eV units.

	$A-A$	$B-B$	$A-B'$	$A-B$	$A-A'$	$B-A'$
a_0	1.7450	-0.4610	-1.0390	-	-	-
b_0	0.4394	0.4089	0.7784	-	-	-
c_0	-0.8599	-60.580	1.3910	-	-	-
d_0	0.5683	-1.5240	0.7067	-	-	-
a_1	0.2493	0.0759	-0.0556	-2.6490	3.6570	8.0410
b_1	0.4731	0.1196	1.1320	0.0043	-0.7636	-0.1605
c_1	-0.2362	0.2223	0.0465	0.3333	-0.1874	-7.0360
d_1	0.4874	-0.3001	1.1980	-2.4060	0.05863	-0.1236
a_2	0.0634	0.3877	0.0002	-0.2814	0.1185	5.5470
b_2	0.3311	-0.1194	1.4740	-0.0789	-9.8480	-2.3650
c_2	-0.0482	-0.3550	0.0000	0.0000	-0.0280	-3.0960
d_2	0.3728	-0.1166	-9.9250	-15.660	0.2427	-1.1660
a_2^*	0.0634	0.3877	-0.0779	-	-	-
b_2^*	0.3311	-0.1194	0.4572	-	-	-
c_2^*	-0.0482	-0.3550	0.0682	-	-	-
d_2^*	0.3728	-0.1166	0.5146	-	-	-
a_3	-0.1957	0.0062	-0.3733	-1.7680	0.4363	0.0000
b_3	-0.6550	0.1607	-0.4989	-7.6770	-0.4018	-14.260
c_3	-0.0027	-0.0306	0.1213	0.0595	-0.1385	0.0002
d_3	0.6550	0.1345	-0.1180	0.0894	-0.0170	1.2130
a_4	-0.0725	0.1227	0.0550	2.2160	-0.0660	0.4512
b_4	-1.1070	-1.5420	0.4468	-10.750	0.4113	-0.0064
c_4	0.9846	0.0000	-0.0619	-0.0282	0.0908	-0.4692
d_4	-4.0320	-13.8600	0.4074	-0.0593	0.3079	-0.0221

TABLE A4. The fitting parameters a_i , b_i , c_i , and d_i for the c -dependent hopping parametrization shown in Eq. (11), for the F_4G_4 model for BA' -stacked BLBN are presented. Here, i represents the neighbor index n . The top row of the table illustrates the hopping processes between corresponding sublattices. In BA' -stacking, $t_{A'A'} = t_{BB}$, $t_{B'B'} = t_{AA}$, $t_{A'B'} = t_{AB}$, and $t_{BB'} = t_{AA'}$ by symmetry relations. The hopping parameters are given in eV units.

	$A-A$	$B-B$	$A'-A'$	$B'-B'$	$B-A'$	$A-B$	$A'-B'$	$A-A'$	$B-B'$	$A-B'$
a_0	1.4020	0.0108	2.5140	0.0783	-0.0400	-	-	-	-	-
b_0	0.0526	0.6491	-6.3220	0.9919	0.3796	-	-	-	-	-
c_0	-0.0988	-2.5820	3.6710	-0.7260	42.640	-	-	-	-	-
d_0	-9.7670	-0.0221	-0.2225	0.5373	-1.359	-	-	-	-	-
a_1	1.4180	-0.0553	-0.1604	0.3536	-0.0059	-2.8050	-0.0222	-0.5973	-0.1576	-0.0386
b_1	-0.0319	0.1875	0.0707	-0.1884	0.7141	-0.0033	-4.3200	0.9163	-0.3161	0.3746
c_1	-1.2310	0.3135	0.2551	0.8459	4.2250	0.0924	-2.6880	0.7005	1.3570	9.9740
d_1	0.0069	-0.0232	-0.0568	-4.8530	-8.9810	-0.0101	0.0012	0.8792	-1.0680	-1.1130
a_2	0.5976	0.1805	-0.1176	-0.0004	-0.5243	-2.8900	0.7870	-0.6613	0.0008	-0.2680
b_2	-0.8391	-0.6548	0.3172	1.4970	-0.5917	-7.4550	-0.2730	0.8112	0.8209	-0.2156
c_2	-54.380	-0.0378	0.1424	0.0025	5.0960	-0.3349	-0.9677	0.6552	-0.1054	-0.9209
d_2	-2.5620	-1.4540	0.2810	1.0030	-1.3950	-0.1262	-0.1840	0.8161	-0.1697	-6.4990
a_2^*	0.5976	0.1805	-0.1176	-0.0004	0.4423	-	-	-	-	
b_2^*	-0.8391	-0.6548	0.3172	1.4970	-0.2127	-	-	-	-	
c_2^*	-54.3800	-0.0378	0.1424	0.0025	-0.2044	-	-	-	-	
d_2^*	-2.5620	-1.4540	0.2810	1.0030	0.0444	-	-	-	-	
a_3	0.0000	-0.0798	0.0000	-0.2003	-0.7780	0.0381	0.0364	-0.0089	0.1372	-0.5453
b_3	-18.650	-0.8135	-13.680	-0.9921	-0.6396	0.2253	0.2405	0.6663	0.2613	-0.2354
c_3	-0.0207	-0.0073	-0.0273	-0.0036	1.6600	-1.9910	-4.233	0.0128	-0.1557	1.4150
d_3	0.2181	0.4485	0.1478	0.6417	-0.9052	-7.3900	-5.304	0.7016	0.2034	-0.5496
a_4	-4.3320	0.2453	-4.0280	0.0421	0.0155	0.2825	-0.5826	0.0097	0.0026	-0.6390
b_4	-7.4290	-1.4510	-3.7300	0.1121	-10.720	0.0066	0.4629	0.2387	0.3089	-2.7570
c_4	-0.0005	-0.0968	-0.0003	-0.0377	-0.0132	-0.3180	0.5664	0.7201	-1.8140	4.0990
e_4	0.3698	-1.2520	0.4917	0.1420	-0.4014	-0.0066	0.4690	-3.8410	-5.5240	-3.9340

TABLE A5. The fitting parameters a_i , b_i , c_i , and d_i for the c -dependent hopping parametrization shown in Eq. (11), for the F_4G_4 model for AB-stacked BLBN are presented. Here, i represents the neighbor index n . The top row of the table illustrates the hopping processes between corresponding sublattices. The hopping parameters are given in eV units.