Lattice dynamics in the conformational environment of bulk hexagonal boron nitride (h-BN) conveys a peculiar optical response

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We report a detailed study of the stability and dynamical lattice properties of five possible differently stacked configurations of bulk hexagonal boron nitride (h-BN). The results are obtained upon comparison among different theoretical methods, namely Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA) Density Functional Theory (DFT) approaches. We devote particular attention to the prominent role played by the pseudopotential approximation in the theoretical framework and differently from previous implementations, we obtain the best performances from GGA rather than LDA. The major complication, nevertheless, consists in the necessity of a complex approach for the non-analytical part of the dynamical matrix. Our conclusions are based on the agreement of the calculated data with a set of infrared spectroscopy measurements, taken from the experimental literature. Besides, we apply the theoretical model to derive, from geometrical considerations, an empirical method for the calculation of the non-analytical part of the dynamical matrix for potential use in discerning techniques.

I. INTRODUCTION

Layered materials are widely studied due to their ability to form stable 2D crystals. Exotic and unexpected properties could arise in some material when reduced to 2D forms, like astounding electronic conductivity or unusual optical response [1]. The ability to tune these features by the actions of material scientists is additionally improved, in 2D conformations, by the large surface area, resulting from the geometrical essence and potentiality of being subjected to chemical modifications [2].

Hexagonal boron nitride (h-BN) is considered a counterpart for graphene as its structure is almost identical, yet is a semiconductor with a relatively large electronic (6.08 eV) [3, 4] and optical (5.69 eV) [4, 5] band gap in bulk. The 2D shaped conformations of h-BN can be efficiently used as dielectric layers in graphene nanostructures, for lubrication or electronics, or directly replace other materials for high temperature applications [6]. The crystalline structure of h-BN has been addressed in previous theoretical studies [4, 7–15], yet the question of stability for different possible stacking orders has not been answered to a satisfactory level [4, 13, 14, 16, 17].

From a geometrical point of view, it is clear that a wide variety of stacking arrangements are possible for the reciprocal orientation and displacement of contiguous planes and a several of them have been reported experimentally [18–23]. Five possible arrangements are shown in Fig.1. The AA’ and AB types of stacking orders have been observed by Atomic Resolution Imaging [18, 23] and are known to be stable. AA’ is considered a generally available form. New experimental routes [21], recently, showed how to produce purely stacked AB material. AA and A’B have been reported by theoretical calculations to be unstable [13], nevertheless found in traces in experimental data [19, 20], while the actual average amount of AB’ stacking in h-BN samples remains unclear [13, 17, 22, 24]. The uncertainty is increased by the wide variability reported in results, e.g. in infrared optical response [25–31], Raman optical activity [25, 32–34], photoluminescence spectroscopy [35–37], due to probable highly poly-crystalline nature of 2B probed specimens. Although many possible stacking combinations, only two [25] or three [38] of them have been considered in different theoretical studies related to the interpretation of experimental results.

An accurate description of the lattice dynamics of bulk h-BN would produce a better explanation of experiments and might contribute to reach deep control over the crystalline aspects of the produced samples, as well as to a better tuning of the final properties of interest, such as the structural orientation in nano-applications [34, 39–41], a precise value of thermal conductivity [42–45] or optical response [46, 47].

Figure 1. Five different stacking orders in hexagonal boron nitride.

The task is particularly challenging for theoretical description. A great anisotropy between the plane parallel and perpendicular dielectric constants has been reported for bulk h-BN in theoretical [11] and experimental studies [25], although a substantial failure of theory in reproducing the measured results [12]. As we thoroughly describe in Section II, the different nature of the physical forces involved (cova lent interactions and weaker van der Waals stacking bonds) makes striving for a uniform theoretical interpretation extremely difficult. Density Functional Theory (DFT) is regarded to be an

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efficient method for the description of the lattice dynamics of solids [48]. Local Density Approximation (LDA) exchange-correlation (xc) functionals are reported to be the best compromise for a consistent description of these physical structures [16, 38, 49, 50].

Janotti et al. [51] performed all electron DFT calculations on bulk h-BN. The comparison of LDA results with the more sophisticated Generalized Gradient Approximation (GGA) did not produce substantial improvement in the interpretation of the stacking interaction. The same conclusion was reported by Mosuang et al. [38] with the use of Norm-conserving (NC) pseudopotential (PP) approximations. LDA theoretical implementations have produced results in a relatively satisfactory agreement with experimental values for the calculations of lattice constants, bulk moduli, cohesive energies of this material employing any Norm-conserving (NC) [11, 38], Ultrasoft (US) [10] or Projector Augmented-Wave (PAW) [52] pseudopotential (PP) approximations.

Kim et al. [53] reported a significant improvement in the calculation of lattice constants using Troullier–Martins [54] NC PP, generated within GGA correction and implemented in an LDA xc functional theory.

As a consequence, the lattice dynamics of 3D h-BN and the issue of relative stability of the different stacking orders has been tackled, until the present work, mainly by LDA approaches to DFT, employing US PP [12, 13, 55, 56] and NC PP [7, 16, 57]. GGA approaches [58] never showed noticeable improvement before.

In this work we present a comprehensive study of the lattice dynamics of bulk h-BN comparing five different possible stacking variants. We compare different levels of theory, LDA and GGA, pseudopotentials approximations (NC, US and PAW) and van der Waals dispersion corrections with reviewed experimental results based on infrared and Raman optical responses. We advance a complex approach based on a separate treatment of the analytical (interatomic force constants) and non-analytical parts (Born effective charges and dielectric tensors) of the dynamical matrix and we propose an empirical method for the precise calculation of the second one.

II. THEORETICAL DESCRIPTION

In a Molecular Orbital (MO) depiction of the inter-planar stacking interaction in h-BN, the $sp^3$ orbitals from nitrogen atoms, bearing the electronic "lone pair”, resonates between two limit forms in the upper and lower sides of the BN plane. Considering the ammonia-like "umbrella" movement, the displacements exactly resemble what is involved in the IR active $A_2$ vibrational mode, which will be described later in the text (see Figure 3 Panel c). Strong instantaneous dipoles are active in producing the van der Waals stacking interaction, in a continuous fluctuation of the charge density between the two sides of the h-BN plane.

Cochran and Cowley [59] elegantly derived the following relation among the lattice dynamics for the fluctuations of the dielectric dispersion and the dielectric constants of a system:

$$\prod_{\nu=4}^{3n} \left( \frac{\omega_{\nu}^2}{\Omega_{\nu}} \right)^2 = \frac{\varepsilon_1^{(0)}}{\varepsilon_1^{(\infty)}}$$  \hspace{1cm} (1)

where $\nu$ is the index denoting different normal vibrational modes, $n$ is the total number of atoms in the unit cell, $\alpha$ is a space direction $<x \vee y \vee z>$, $\varepsilon_1^{(\infty)}$ and $\varepsilon_1^{(0)}$ are respectively the high frequency and static dielectric tensors.

Recall that the high frequency dielectric tensor $\varepsilon_1^{(\infty)}$ depends only on the electronic susceptibility, i.e. just on charge density fluctuations, while the static dielectric tensor $\varepsilon_1^{(0)}$ depends also on the lattice dynamics [59, 60]. $\omega_{\nu}^2$ are the frequency of the vibrational modes, $\Omega_{\nu}$ are the dielectric dispersion frequencies. In a normal mode with zero component of polarization in the $\alpha$ direction: $\Omega_{\nu} = \omega_{\nu}^\alpha$, otherwise the dielectric dispersion frequencies (rigorously defined and explained by the cited authors [59]) are the frequencies of vibration of a fictitious system which reproduces exactly the dielectric dynamics of the studied one. The dielectric dynamics can be described as dependent on an ideal “apparent charge density” $\rho_{Q} (r), r \equiv (x, y, z)$, acting in determining the effective polarization of the crystal.

The total effective polarization is then composed, in addition to the electronic polarization, by an ionic term $QU$, where $U$ is the matrix of the ionic displacements $u_s^\alpha$, $s$ is the index of different nuclei in the system or unit cell [59, 60]:

$$P^\alpha = \sum \chi_{s}^{\alpha\beta} u^{\beta}_{s} + \chi^{\alpha\beta} E^\beta .$$  \hspace{1cm} (2)

The $Q$ matrix (dimension $3n \times 3$, where $n$ is the total number of atoms in the unit cell) is an expression of the "apparent charge density" $\rho_{Q} (r)$. Understanding how this ideal function is related to the $Q$ matrix and $\varepsilon_1^{(\infty)}$ (effectively used in calculations) is one of the purposes of this study. $\chi$ is the electronic susceptibility matrix, $E^\beta$ are the real space components of the macroscopic electric field vector. $\beta$ is a second space direction.

We note that a given geometrical configuration and ground state charge density produce a unique "apparent charge density" $\rho_{Q} (r)$. This means that two systems with different geometrical conformation or two systems with the same geometrical conformation but a different ground state charge density distributions (e.g. calculated with different DFT xc functionals, or different pseudopotential approximations) can be thought as simulating different systems or as simulating different average phases in a charge density fluctuation process, like that involved in a phononic mode vibration.

III. METHODS

A. Lattice dynamics

The vibrational structure of the studied systems has been thoroughly analyzed by means of phonon dynamics within the
theoretical scheme of the harmonic approximation. The vibrational movements, in periodic systems, are defined by a wave vector \( \mathbf{q} \) and a mode number \( \nu \). For each wave vector and mode it is possible to determine an energy (vibrational frequency \( \omega_{\nu}(\mathbf{q}) \)) and displacements vectors \( \mathbf{u}_{\nu,\mathbf{q}}(\mathbf{r}) \) by solving the phononic eigenvalue problem \([61,63] \) deriving the interatomic force constants (IFC) by means of a Finite Displacements (FD) method.

This analytical approach is, anyway, not sufficient to account for long-range Coulombic forces which originate in real crystal structures and give rise to a longitudinal - transverse optical (LO-TO) modes splitting. It is necessary to introduce a non-analytical (NA) correction term in the computed dynamical matrices. This approach was firstly derived by Cochran and Cowley \([59]\) based on the Born and Huang \([60]\) theoretical framework, successively adapted by Pick et al. in the form which is currently implemented in calculations \([12,44]\). It consists basically in a separation of the dynamical matrix in two different terms. The eigenvalue problem can then be reformulated, in real space, for the \( \alpha \) direction (without noting the explicit dependence over \( \mathbf{q} \) of \( \omega, W \) and \( N \)):

\[
\omega_{\nu}^2 W = \left( N + \frac{4\pi}{\varepsilon_{\alpha\alpha}} Z \delta_{\alpha\beta} Z^T \right) W, \tag{3}
\]

where the \( W \) matrix contains the displacement vectors of the atoms: \( W^\mu = \sqrt{\mu} \cdot \mathbf{u}_{\alpha,\mu}^\alpha \).

The \( N \) matrix contains information about the interatomic force constants (IFC) of the system: \( N_{\alpha\beta}^{st}(\mathbf{q}) \propto \epsilon_{\alpha\beta}^{st}(\mathbf{q}) / (\sqrt{\mu_\alpha \mu_\beta}) \) where \( t \) is a second index for nuclei and \( \mu \) are their mass densities.

\[
\epsilon_{\alpha\beta}^{st}(\mathbf{q}) = \sum_I \epsilon_{\alpha\beta}^{\mathbf{q},I} \epsilon_{\mathbf{q},I}^{\alpha\beta} (R_i) \]

is the analytical part of the dynamical matrix of the system. \( \epsilon_{\alpha\beta}^{\mathbf{q},I} (R_i) \) are the elements of the IFC, defined as:

\[
\epsilon_{\alpha\beta}^{\mathbf{q},I}(l,m) = \frac{\partial^2 E}{\partial \mathbf{u}_{\alpha}^{l}(l) \partial \mathbf{u}_{\beta}^{m}(m)}, \tag{4}
\]

where \( E \) is the total energy of the system, \( R_i \) is the nuclear coordinates matrix in the \( l \) unit cell, \( l \) and \( m \) are indices of different unit cells. The explicit dependency of \( \epsilon^{\mathbf{q},I} \) on couples of unit cell \( (l, m) \) is intended, in Eq. 4, to account for numerical implementations of IFC calculation. In the NA part, the \( Z \) matrix contains elements of the \( Q \) matrix already defined in Equation 2.

Giannozzi et al. \([63]\), Ohba et al. \([12,66]\) and Gonze et al. \([67]\) obtained effective charges and dielectric tensors by Density Functional Perturbation Theory (DFPT) and theoretically related them to the LO-TO splitting of the phononic modes and absorption activities. Conceptually differently, in this work we consider the effective charges \( Q_{\alpha\beta}^{\mathbf{q}} \) and dielectric tensors \( \varepsilon \) calculated by Density Functional Perturbation Theory (DFPT) only as numerical counterparts of the \( Q \) matrix elements and \( \varepsilon^{(\mathbf{q})} \) matrices of a fictitious system fitting the same “apparent charge density” \( \rho_{\mathbf{Q}}(\mathbf{r}) \) of the studied one.

### B. Infrared optical response

Porezag et al. \([68]\) applied the pioneering work of Wilson et al. \([63]\) to derive an expression for the absorption activity of phononic modes. The infrared absorption activity of a mode \( \nu \) is:

\[
I_{\nu}^{IR} = \frac{N \pi}{3c} \left| \frac{\partial \mu}{\partial \mathbf{q}} \right|_{\nu}^2, \tag{5}
\]

where \( N \) is the particle density, \( c \) is the velocity of light and \( \mu \) is the electric dipole moment of the system. The expression is reformulated by defining the Born effective charges \( Q_{\alpha\beta}^{\mathbf{q}} \) \([61]\):

\[
I_{\nu}^{IR} = \sum_{s} \left| \sum_{\alpha,\beta} Q_{\alpha\beta}^{s} \mathbf{u}_{\nu,s}^{\alpha\beta} \right|^2. \tag{6}
\]

As explained in the previous section \([III A]\), here we use DFPT calculated \( Q_{\alpha\beta}^{s} \) in a conceptually different manner with respect to how they were originally conceived, considering them only as a numerical tool to relate charge density functions to absorption spectra.

The \( \Gamma \) point eigenvectors of the IR active modes can be directly compared with the experimental peak frequencies. A natural broadening of the spectral lines, in a Lorentz function shape, occurs due to finite lifetime of the phonon collective excitations as a consequence of scattering processes.

Two vibrational modes are IR active in h-BN (described by the irreducible representations \( A_{2u} \) and \( E_{1u} \)), i.e. have \( I_{\nu}^{IR} \neq 0 \). The ratio between these two intensities can be informative about the microscopical nature of the system \([69]\) and it is interestingly studied here.

Only one vibrational mode is active in Raman spectroscopy (\( E_{2g} \)). The frequency of vibration of this Raman active mode is degenerate with that of the IR active \( E_{1u} \) mode. Therefore, here we do not investigate Raman tensors.

### C. Empirical model for the non-analytical part of the dynamical matrix

The operation of shortening the \( c \) structural parameter along the \( z \) direction, orthogonal to the BN planes, produces systems in which the frequency of vibration of the dielectric dispersion \( \Omega_{\nu}^{\mathbf{q}} \) associated to the \( A_{2u} \) mode, polarized only along the \( z \) direction, approaches progressively more the value \( \Omega_{\nu} \) of the real layout until an optimal shortening value \([59]\).

As defined before, an "apparent charge density" function, statically and effectively modeling the fluctuations, can be introduced in order to define for every system a \( Q \) matrix suitable for Equation 2 \([59]\). By determining an optimal shortening percentage, the DFPT calculated \( Q_{\alpha\beta}^{s} \) and \( \varepsilon \) effectively model the \( Q \) matrix elements and \( \varepsilon^{(\mathbf{q})} \) matrices of real systems (NA parameters of the dynamical matrices).
The presented results are obtained with the Vanderbilt Ultra-soft (US) PP [74], Troullier–Martins FHI Norm-conserving (NC) PP [54, 70–73] methods and the Projector Augmented-Wave (PAW) method of Blöchl [77]. US and PAW PP, in spite of a lower cutoff value in the PW basis set and a sensible reduction of computational time, do not guarantee the conservation of the norm for the resulting wave functions in comparison with all electron calculations, especially outside the core-shell regions of atoms. This drawback could particularly affect properties like phonons, which involve the calculation of interactions at longer than optimal distances with respect to covalent bonds. For this reason, in some of our implementations, we recalculate the charge densities after each diagonalization step, using dramatically higher (8–20 times) values of cutoff for the PW (see values of $E_{\text{cut}} \rho$ with respect to $E_{\text{cut}}$ in Tab. I).

To account for the lack of DFT to properly calculate weak interactions such as the interplanar van der Waals forces we supplemented our DFT with empirical dispersion correction methods: Grimme-D2 [75] and D3 with Becke-Johnson damping (D3BJ) [82] methods, Tkatchenko-Scheffler method (TS) [75] as well as the SCAN+rVV10 [81] functional.

For each different method we performed structural relaxations and phonon dispersion calculations. The calculation parameters and methods are summed up in Table I. We employed different fitting techniques to extrapolate the optimal structural parameters and the resulting values used in subsequent calculations are reported in Supplemental Material [91] (Table TSVI).
tions, by means of a FD approach. For the FD self-consistent field (SCF) calculations we employed VASP in conjunction with the Phonopy code [92] and the PW and FD algorithms included in QE.

We calculated internally defined DFPT Born effective charges and DFPT dielectric tensors [12, 65, 66] (considered here as numerical expressions of $Q$ matrix elements and $e^{(m)}$ matrices, see Sections II and III A) setting a threshold for self-consistency of $1.36 \times 10^{-12}$ eV.

We report IR spectra calculated by applying a Lorentz broadening function to the absorption intensities of the vibrational modes in order to have an half width at half maximum of 10 cm$^{-1}$. We separately applied the broadening functions to the single phonon spectral lines.

The Potential energy surfaces presented in Figures 2 and in the Supplemental Material [91] (Figure S15) have been obtained by QE with single point SCF calculations with the different methods. These diagonalizations have been performed on Monkhorst-Pack $8 \times 8 \times 8$ k-points grids, SCF conv. 1.36$ \times 10^{-7}$, all the other parameters as reported in Table I. The PES are calculated at the resolution of 60$ \times 60$ single point calculations on shifted structures, spanning the x and y directions from -0.5 Å to 0.5 Å.

V. RESULTS AND DISCUSSION

A. Potential energy surfaces

In Figures 2 and in the Supplemental Material [91] (Figure S15) we report potential energy surfaces (PES) calculated within a selection of different methods. The figures are generated keeping fixed the a and c structural parameters, as obtained for the five symmetrical structures (reported in Supplemental Material [91] (Table TSVI)) and by displacing the atoms in the lattices with parallel sliding of contiguous h-BN planes with respect each to the other. The reported results span intervals from -0.5 Å to 0.5 Å in the x and y directions with respect to the symmetrical structures.

Note that we used optimized structural parameters in the different plots (see Supplemental Material [91] (Table TSVI)) and the absolute energies of the symmetrical points are inconsistent. In Table II, we report a comparison of the total energies of the five considered symmetrical structures within different theoretical implementations.

The shape of the PES confirms the stability of the AA’ and AB symmetrical structures, with comparable total energies. The AB configuration results to be the most stable one with a difference between them from 0.22 meV/atom within NC-PBE-TS, to 2.04 meV/atom within PAW-PBE-TS. Slightly differently, the AB’ structure results to be the most stable one from the PAW-PBE-TS method with a 0.76 meV/atom difference from AB.

Within the other tested methodologies, the total energy of the symmetrical AB’ configuration results to be from 1.81 meV/atom (NC-PBE-TS) to 5.37 meV/atom (PAW-PBE-D2, Set a) above the AB symmetrical minimum. The values calculated with PAW-PBE-D2 (Set a), and in a lesser amount NC-SCAN, are significantly out of the range of the other methods. The shape of the PES in the proximity of the symmetrical AB’ point is located in a prominently flat valley (a soft groove in NC-SCAN and US-LDA). Although the AA’ configuration, located at (-0.33,0.33) Å from the AB’ symmetrical point, is easily reachable upon simple sliding, the AB’ stacking configuration results to be metastable, leading to possible dynamical stability related interpretations of the experimental data [41]. The noisy shape of the PES in the vicinity of the AB’ point results particularly clear from the NC-SCAN outcomes, reported in the Supplemental Material [91] (Figure S15 uppermost panel).

A 60° rotational movement is, instead, necessary to reach the AB (P3m1) configuration from AA’ or AB’ (P63/mmc), due to the different symmetry of the lattice space group.

The AA and A’B configurations are located on local maxima stationary points (Fig. 3), implying instability of the cited stacking variants. The energy drop is significantly dependent on the theoretical methodology: the NC-PBE-TS method calculates significantly lower total energies for these unstable configurations, while the higher energy results are obtained with PAW-PBE-D2 (Set a).

Table II. Relative energies (meV/at), with respect to the most stable configuration, calculated for every adopted method.

| Method      | AA | AB | AB’ | AB’ | AA |
|-------------|----|----|-----|-----|----|
| PBE-D2$^a$ (b) | 0.27 | 0.00 | 2.34 | 15.60 | 18.48 |
| NC-PBE-D2$^b$ | 0.32 | 0.00 | 2.04 | 15.63 | 18.29 |
| NC-SCAN$^a$ | 3.20 | 0.76 | 0.00 | 15.98 | 17.72 |
| NC-SCAN+rV10$^a$ | 0.42 | 0.00 | 2.49 | 17.86 | 21.02 |
| PBE-D2$^a$ (a) | 1.50 | 0.00 | 5.37 | 22.87 | 25.22 |
| LDA$^a$ | 0.61 | 0.00 | 2.19 | 12.09 | 13.18 |
| PBE-TS$^a$ | 0.22 | 0.00 | 1.81 | 9.26 | 9.96 |
| SCAN$^a$ | 1.04 | 0.00 | 4.64 | 24.45 | 26.61 |

1. Projector Augmented-Wave PP
2. Ultrasoft PP
3. Norm-conserving PP.

B. Energy dispersion of the vibrational modes

We calculated the energy dispersion functions of the phononic modes for all the examined stacking variants. The clearest results are shown in Fig. 4 using PBE GGA level of theory, PAW pseudopot., van der Waals dispersion corrections (Grimme-D2) and NA part of the dynamical matrices calculated adopting numerically DFPT results obtained at the same level of theory: PAW-PBE (Set a).

Besides the three acoustic modes, two plane sliding modes are easily recognizable below 100 cm$^{-1}$ ($E_{2g}$ irreducible representation) at the Γ point in all the five dispersion diagrams, becoming imaginary in the unstable ones as was to be expected from the potential energy surfaces.

A symmetrical "plane bumping" mode along the z direction ($B_{1g}$ irreducible representation) is distinguishable from 150 cm$^{-1}$ to 200 cm$^{-1}$.

At about 800 cm$^{-1}$ at the Γ point, two "umbrella movement" modes (symmetrical and asymmetrical) can be de-
Figure 2. Potential Energy Surfaces (PES) cuts originating from the symmetrical points of the AA', AB, AB' stacking structures. The cell parameters are kept constant, the PESs are calculated at the PAW-PBE-D2 (Set a) level of theory, by sliding of contiguous h-BN planes. Zero points in the energy scales correspond to the energies of the symmetrical structures.

The asymmetrical one ($A_{2u}$ irreducible representation) is IR active and we denote it, here, as Peak 1. In Figure 4 lower part, we report a graphical representation of the resulting eigenvectors displacements for the IR active modes at the $\Gamma$ point in the structure of the AA' system. The $A_{2u}$ mode is showed in Panel c, structured by out-of-plane displacements of boron and nitrogen atoms in opposite directions (asymmetric bouncings), interplanar van der Waals interactions are highly involved in it.

Finally, the higher energetic group of phonons is composed by four modes (higher than 1300 cm$^{-1}$ at the $\Gamma$ point) and arises from BN stretching modes which energy comes primarily from the deformation of in-plane covalent interactions. One of these modes is symmetrical, $E_{2g}$ irreducible representation, Raman active. Another one, $E_{1u}$ irreducible representation, basically composed by in-plane asymmetric stretching movements, is IR active and LO-TO split by the macroscopic electric field in two perpendicular branches. These two signals generally overlap each other in experimental spectra and we denote them, here, as a singular Peak 2. The displacement vectors relevant to it are represented in Panels a and b in the lower part of Figure 4.

The stable and unstable structures can also be distinguished by the behaviour of the $B_{1g}$ and $A_{2u}$ modes (at ~ 800 cm$^{-1}$ at the $\Gamma$ point) in the $A - \Gamma$ direction where the unstable structures exhibit a full degeneracy of the two modes, in contrast to the split seen in the stable stackings. The five stackings have otherwise an almost identical phonon structure.

Concerning the IR and Raman active modes, the two most stable stackings (AA’ and AB) exhibit identical phonon frequencies whereas the AB’ presents slightly higher vibrational energies leading to different optical activity.
Figure 3. Potential Energy Surfaces (PES) cuts originating from the symmetrical points of the A'B and AA stacking structures. The cell parameters are kept constant, the PESs are calculated at the PAW-PBE-D2 (Set a) level of theory, by sliding of contiguous h-BN planes.

Table III. Phonon frequencies at the Γ point (in $cm^{-1}$) for the AA’ stacking of h-BN as calculated by different theoretical approaches and software implementations and compared with experimental values taken from literature. The NA part of the dynamical matrix is calculated adopting numerically DFPT effective charges and dielectric tensors, where not differently specified, with the same method of the IFC. The same theoretical data are provided for the AB and AB’ stackings in the Supplemental Material [91] (Tables TSVIII and TSIX).

| Mode     | VASP                     | QE                       | Experiment |
|----------|--------------------------|--------------------------|------------|
|          | PBE1 PBE-D2 1 (b) PBE-D3BJ1 PBE-TS1 SCAN 1 +VV10 | PBE-D2 1 (a) PBE-TS3 PBE-TS3 NA: PAW-PBE3 SCAN1 |           |
| E2g**    | 47 47 46 37 47           | 50 60 48 48 51           | 51 52      |
| B1g      | 126 88 119 138 129        | 113 182 131 131 113      | 767-810    |
| A2u*     | 745 742 744 744 741       | 751 722 756 756 736      |            |
| B1g      | 797 793 797 800 795       | 811 791 810 810 797      |            |
| E2g**    | 1354 1359 1354 1356 1381  | 1384 1350 1345 1345 1367 | 1369-1376  |
| E1u*     | 1354 1359 1354 1356 1381  | 1384 1351 1345 1345 1367 | 1338-1404  |
| E1u*     | 1589 1593 1589 1591 1629  | 1615 1591 1570 1573 1596 | 1616 25   |

1 - Projector Augmented-Wave PP, 2 - Ultrasoft PP, 3 - Norm-conserving PP
* - IR active modes
** - Raman active modes

We have calculated the phonon dispersion schemes with various dispersion correction methods (see Fig. 4, Table III and the Supplemental Material [91] (Tables TSVIII, TSIX, Figures S24, S28, S30, S31, S32). One would assume that due to the nature of the system in study different approaches to the weak binding would have a significant impact on the phononic structure but this is not the case. The effect of the van der Walls correction can be seen only for the $B_{1g}$ mode arising from the planar shifts along the vertical axis $\sim 120$-200 $cm^{-1}$ as well as the $E_{2g}$ sliding of the planes along each other $\sim 40$-60 $cm^{-1}$. Both of these modes do not induce a change in the dipole moment and therefore will not be visible in the IR spectrum. When compared with experimental results, as shown in Tab. III for the AA’ variant and in the Supplemental Material [91] (Tables TSVIII and TSIX) for the AB and AB’, all of the methods agree well on a qualitative level.
Figure 4. Comparison of the phonon energy dispersions along high symmetry directions in the first Brillouin zone for the five considered differently stacked h-BN systems. The IFC matrices are calculated by Finite Displacements method, Set a, Table I, with DFT PBE functionals, PAW pseudopotential approximations and Grimme-D2 dispersion corrections. The NA parts of the dynamical matrices are calculated adopting numerically the resulting DFPT PAW-PBE (Set a) effective charges and dielectric tensors. In the lower boxes (a, b and c), a graphical representation of the displacement eigenvectors for the IR active modes at the Γ point in the AA' stacked system. The displacements are represented as green vectors.

C. Vibrational spectroscopy

Table IV. Overview of results taken from experimental literature about IR spectroscopy in bulk h-BN samples. In the third column we report the ratio between the two intensities of the IR absorption peaks as extrapolated from graphical representations. In the fourth and fifth column, the frequencies of the two IR active peaks.

| Label | Source | Ratio | Freq. 1 (cm$^{-1}$) | Freq. 2 (cm$^{-1}$) |
|-------|--------|-------|---------------------|---------------------|
| Sample 1 | Ref. [26] | 1.805 | 802 | 1365 |
| Sample 2 | Ref. [27] | 2.636 | 805 | 1381 |
| Sample 3 | Ref. [28] | 1.043 | 767 | 1338 |
| Sample 4 | Ref. [29] | 1.282 | 825 | 1378 |
| Sample 5 | Ref. [30] | 1.236 | 810 | 1390 |
| Sample 6 | Ref. [31] | 1.737 | 777 | 1404 |

In Figure 5 we report the resulting vibrational spectra for the three stable variants. In these results, the IFC matrices are calculated at NC-PBE-TS level, while the NA contributions to the dynamical matrix (to compute the LO-TO splitting of phonon eigenvalues and the absorption intensities, see Sections III A and III B) are implemented with PAW-PBE (Set a) within DFPT (see the sections II and III A for our considerations about the use of DFPT as a numerical tool for this purpose).

The peak frequencies of the AB' spectrum reported in Figure 5 lie on higher values (1396 cm$^{-1}$ and 751 cm$^{-1}$) with respect to the two compared functions (1355 cm$^{-1}$, 724 cm$^{-1}$ in AA' and 1357 cm$^{-1}$, 733 cm$^{-1}$ in AB). The ratio between the intensities of the two active absorptions is 12.129 in the AB' structure. Considerably higher with respect to the other two systems (8.211 in AA' and 9.500 in AB).

In Figure 6 we compare the ratios calculated with three different theoretical implementations. The same trend and peculiar behaviour ($Ratio_{AB'} >> Ratio_{AB} > Ratio_{AA'}$) is noticeable within all the tested physical models. In Appendix A (VI) we show how these numerical results are essentially related to the geometrical structures.

It is possible to compare the resulting absorption functions with experimental infrared spectra. Unfortunately, up
Figure 5. Vibrational spectra calculated for the three stable h-BN configurations using NC-PBE-TS IFCs and NA parts numerically obtained adopting DFPT at PAW-PBE (Set a) level. Red solid vertical lines indicate the average experimental peak values and blue vertical dotted lines indicate the highest and lowest experimental values, considering the six experimental spectra cited in the text (Table IV).

Figure 6. Ratios between the absorption intensities of the two IR active peaks in vibrational spectra calculated for the three stable structures (AA', AB and AB') by means of three different theoretical implementations (for PAW-PBE we use Set a).

to date, it is not present, in literature, a simple way to unravel the stacking composition of samples. For this reason, here we gather a number of different experimental measurements without insights about their conformational compositions. This collection of data is, anyway, useful to give an assessment of the quality of our calculations and, in view of our theoretical results (Section IV, Appendix A [VI]), it works as a testing set for our empirical method (see Section IV, Appendix B [VI]).

In Figure 7 and in Table IV, we report the peak frequencies of the IR experimental set. The range and average values are also reported in Figures 5 and 8 for comparison with theoretical results. It is noticeable a good agreement in the values of the main peak (Peak 2). Concerning the second most intense peak (Peak 1), the frequencies lay, instead, systematically lower with respect to the experimental range.

In general, the experimental frequencies show a wide variability (from 767 to 825 cm\(^{-1}\) for Peak 1 and from 1338 to 1404 cm\(^{-1}\) for Peak 2) and significant trends. Sample number 3, regarding both of the peaks, presents the lowest values. Comparing the two active peaks, among Samples number 1, 2 and 3 the whole spectrum shifts homogeneously while Samples 4 and 6 show a different and opposite order. The anomaly of Samples 4 and 6 can be better noticed comparing the two central insets in Figure 7. The distance between the two peaks in different samples is reported in the lower inset, while the sum of the frequencies of the two peaks is reported in the upper inset. This different behaviour of Samples 4 and 6 could arise from a number of factors involving systematical structural deformations deeply affecting the BN planar meshes, e.g. effects of working temperatures, impurities, nanostructuring processes and so on, nevertheless, the description of these effects goes beyond the purposes of this work.

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In Figure 9 we report the ratios between the intensities of the two peaks in the referred experimental works. The reported data show a considerable variability, spanning from 2.64 of Sample 2 to 1.04 of Sample 3.

Considering the ratios and not just the absolute values permits to obtain direct information within an internal standard mechanism [69]. The variability in this parameter is related to structural differences at the atomistic level. Furtherly enforcing this consideration, we note the complete lackness of correlation between the data reported in Figure 9 and the width of the experimental peaks measured at 1/2 of the peak height (reported in the inset of the same Figure 9), which arises, instead, from macroscopic, or anyway larger than atomistic, features of the specific measured materials (like, e.g., the grain size).

As noticed before, with the exclusion of the anomalous Samples 4 and 6, already discussed, the relation between peak values ratios (Figure 9) and peak frequencies (Figure 7) ap-
Figure 7. Experimental peak frequencies from the infrared absorption spectra of bulk h-BN samples cited in the text (Table IV). Red horizontal lines indicate the average values. Blue dotted lines delimit the reported experimental range. In the central insets we compare the summed values and differences between them.

Figure 8. Vibrational spectra calculated for the AA’ stacking configuration of h-BN with different theoretical approaches, as described in legend (for PAW-PBE we use Set a). In insets, details of Peak 1 and Peak 2 regions are showed. Red solid vertical lines indicate the average experimental peak values and blue vertical dotted lines indicate the range limits of measured high absorptions in the six references cited in text (Table IV).

Figure 9. Experimental ratios between the intensities of the two IR absorption peaks in the six different experimental measures hexagonal boron nitride samples, taken from different works published from different research groups (Table IV).

Figure 8. Vibrational spectra calculated for the AA’ stacking configuration of h-BN with different theoretical approaches, as described in legend (for PAW-PBE we use Set a). In insets, details of Peak 1 and Peak 2 regions are showed. Red solid vertical lines indicate the average experimental peak values and blue vertical dotted lines indicate the range limits of measured high absorptions in the six references cited in text (Table IV).

Figure 9. Experimental ratios between the intensities of the two IR absorption peaks in the six different experimental measures hexagonal boron nitride samples, taken from different works published from different research groups (Table IV).

We reasonably hypothesize that the experimental variability (Figures 7 and 9) is due to different conformational composition, including the stacking variants, of the referred samples. Following this hypothesis, we deduce, comparing with our theoretical results reported in Figure 5, that Sample 2 contains the highest amount of AB’ stacked material in our experimental set, while Sample 3 contains the lowest amount of it.

D. Accuracy of the model

In Figure 8 we report the results of calculated vibrational spectra obtained with different theoretical implementations for the AA’ stacked system. For an easy comparison, the experimental average values and range limit lines are showed in the same graphical scheme. Analogous data, calculated for the other two stable variants are reported in the Supplemental Material [91] (Figures S16 and S18). The agreement between experimental and theoretical values is particularly satisfactory regarding the most intense peak ($E_{1u}$ mode, Peak 2), within all the analyzed theoretical perspectives. The calculated frequencies of vibration of the $A_{2u}$ mode
As clearly visible in Figure 8 changing only the NA part of the dynamical matrix does not produce significant changes in the peak frequencies. The differences among the results obtained in calculated frequency eigenvalues are mainly attributable to the IFC part.

It is possible to assess the suitability of the examined descriptive approaches for the studied physical systems and relevant physical behaviour. The distance of the resulting frequencies of vibration for the $A_{2u}$ mode (corresponding to Peak 1) from the lower edge of the experimental range for the relevant observable can be regarded as a first assessment criterion (See the Peak 1 enlargement, in the lower part of Figure 8). In regard of this, the best performance is achieved by the NC-PBE-TS IFC, while the worst results are produced by the PAW-PBE-D2 IFC.

A second assessment criterion can be introduced considering the computed intensities of the two IR active peaks. The ratio between the two values should be considered with particular interest, as discussed also in Section V C.

The gathered experimental values of ratios (Figure 9, Table VI) span a considerably narrower interval and lower average with respect of the calculated ones. E.g. with PAW-PBE-D2 (Set a) IFC the theoretical range goes from 8.13 (with PAW-PBE [Set a] NA part) to 11.27 (with NC-PBE-TS NA part). In Figure 10 we report a wide collection of calculated ratios, using different theoretical approaches concerning IFC and NA parts. From the comparison, it clearly emerges that the main source of variability is, now, the NA part of the dynamical matrix. Analyzing the two enlargements of Figure 8 we notice that the variability in value of ratio between the two IR active peaks, mainly derives from the intensities of Peak 1.

General considerations following the definition of the two assessment criteria depict a framework of substantial failure of the employed methods (DFT with the inclusion of the generally accepted dispersion corrections for the van der Waals interaction) in the description of the physics related to the $A_{2u}$ vibrational movement (see the lower part of Figure 4 Panel c).

It is known that the GGA methods model the covalent bonds in a superior way with respect to the LDA methods. We confirm, instead, as reported in literature [16, 38, 49, 51], the surprisingly good performances of LDA in the calculation of phonon frequencies and average performances in the reciprocal intensities of absorption peaks. It results to be a theory of intermediate quality in our set (see Peak 1 enlargement in Fig. 8 for the first assessment criterion: frequencies, and Fig. 10 concerning the second assessment criterion: ratios) and we report better results concerning all the aspects and assessment criteria within a complex approach implementing GGA (IFC: NC-PBE-TS, NA: PAW-PBE [Set a]).

In Appendix A (VI) we rigorously show how the different results obtained by varying the theoretical approaches give dynamical information about the process of charge density fluctuation related to the $A_{2u}$ vibrational mode. Following this consideration we can assert that the effective charge density obtained from the LDA calculation, in the nitrogen hypothetical polar cones (see Appendix A [VI]), is more similar to the “apparent charge density” $\rho(r)$ of the real system than how it is the effective charge density produced by NC-PBE-TS (but less similar than the one produced by PAW-PBE), commenting that, in this aspect, LDA has effectively to be considered a well-performing theory.

On the other side, the good performances of LDA depend also on its poor description of the covalent bonds: the underestimation of the bond strengths results in an underestimation of the spring recall forces which compensate the inadequacy of the models to account for the van der Waals stacking interaction.
VI. CONCLUSIONS

We compared the phononic structures of five possible stacking configurations of bulk h-BN with experimental outcomes (gathered here from literature review). The comparison is based on two distinct criteria: (1) the agreement between the calculated phononic frequencies (of selected vibrational modes, active in infrared or Raman spectroscopy, at \( q = \Gamma \)) and the experimental peak absorption frequencies and (2) the evaluation of the ratio between the intensities of the two IR active peaks.

We provided results for different DFT theoretical implementations, comparing GGA and LDA functionals, as well as NC, US and PAW pseudopotential approximations and different treatments of the van der Waals dispersion correction.

Differently from what previously reported by other authors, we obtained better results from GGA functionals rather than from LDA, nevertheless contradictory conclusions with respect to the investigated PP approximations, finding that the FHI Troullier-Martins NC PP implementations produce a better agreement of the eigenvalues with respect to the measured vibrational frequencies, while Kresse-Joubert PAW PP deliver a better performance in approaching the experimental order in the ratios between intensities.

LDA is presented as a uniform theoretical description, able to sufficiently describe the vibrational properties of bulk h-BN. Here we found, instead, that a complex theoretical approach, based on GGA, better resolves the heterogeneous physics of the examined systems and produces a closer agreement with respect to the experimental measures. We reported, instead, scarce or no influence on the results from the different formal treatments of the van der Waals dispersion corrections.

The analysis of the PES surfaces produced by parallel shifting of h-BN planes confirms the stability of the AA’ and AB structures. The surrounding area nearby the AB’ symmetry point presents the features of a wide plateau and significant dynamical stability for this configuration can be advanced. An extended analysis of the energy dispersion schemes for the

Figure 11. Ratios between the absorption intensities of the IR active peaks reported as functions of the shortening percentage applied to the c structural parameter. The analytical IFC are calculated by NC-PBE-TS on the relevant relaxed systems. The NA parameters are calculated numerically by DFPT and PAW-PBE (Set a) on fictitious systems constructed by applying the shortening percentage to the fully optimized (PAW-PBE-D2 [Set a]) structural parameter and no further optimization (atomic centers in relative positions). Each circle shaped point results from a numerical DFPT calculation of NA parameters and spectral calculation. The continuous interpolation lines are calculated by second degree polynomials for AA’ and AB and twelfth degree polynomial for AB’. The horizontal blue line is drawn at 1.043 (experimental value Sample 3). A vertical blue line (32.94%) is drawn at the intersection between the 1.043 horizontal line and the AA’ interpolation line.

E. Empirical calculation of the non-analytical part of the dynamical matrix

Considering the description in the Methods section (Section IIIF), we report, in Figure 11, the results of calculations performed on fictitious systems built from the fully optimized structures PAW-PBE-D2 (Set a) (cell parameters in Supplemental Material [91] Table [TIV]) by arbitrary shortening of the \( c \) structural parameter and no further geometrical optimization (the atomic centers are in relative positions with respect to the cell parameters). Figure 11 shows the calculated ratio between the absorption peaks of the IR active modes as a function of the shortening percentage on the \( c \) parameter. The IFC are calculated by NC-PBE-TS in fully NC-PBE-TS geometrically optimized systems and the employed numerical values for NA parameters are obtained adopting the results of DFPT PAW-PBE (Set a) in shortened systems. The Lorentz broadening functions are always applied separately to each phonon spectral line (Peak 2 is composed by four spectral lines, Peak 1 by one spectral line).

We interpolate the AA’ and AB points with parabolic functions and the AB’ points with a twelfth degree polynomial function. The AB’ function lays systematically above of the other two, presenting higher values of ratios. Besides it shows an asymptotic behaviour at about 35% of shortening value, making it unreasonable to consider optimal shortening values above it for the specific stacking structure.

To show an application of the model we propose an optimal shortening of 32.94 % with respect of the \( c \) parameter. We used the same value of percentage for the three stable systems (but starting from the respective optimized geometries, calculated within PAW-PBE-D2 [Set a] and reported in Supplemental Material [91] Table [TSIV]).

The decision comes from the consideration of experimental Sample 3 as purely composed by AA’ stacked material. The chosen optimal value lays at the intersection between the AA’ function in Figure 11 and the Sample 3 horizontal line. It is convenient to use the same optimal shortening percentage for the three structures, nevertheless not theoretically motivated. In Appendix B (VI) we show the results of the calculations.

The real space charge density functions \( \rho^{f_{\text{PBE}}}_{\text{PAW-PBE}}(r) \) (Set a) of these fictitious systems are, in our view, approximation of \( \rho_{\text{PBE}}(r) \) in nitrogen polar cones of real systems. Nitrogen \( xz \) sections of them and the resulting NA parameters, calculated by numerical implementation of DFPT PAW-PBE (Set a), are reported in Supplemental Material [91] (Fig. S20 and Tab. TSVII).
phononic modes confirmed the hints of stability for the AB’ structured configurations.

A dynamical stability of the AB’ conformation, variable upon experimental conditions, produces a systematical presence, in different amounts, of this structured material in real samples. This conclusion theoretically explains the wide range of reported experimental values for ratios between the intensities of IR active absorption peaks. The results can be directly related to purely geometrical considerations, based on the different stacking structures (see Appendix A [VI]), and led us to the formulation of an original empirical method for the calculation of the non-analytical part of the dynamical matrices of the systems (Born $Q$ matrices and dielectric tensors).

Extended experimental data sets and validation methods are necessary to foresee the application of these theoretical findings to technological contexts, nevertheless the perspective could be upcoming (see Appendix B [VI]) and meet our suggested necessity for efforts in providing peculiar experimental data for the specific differently stacked variants.

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APPENDIX A: DERIVATION OF THE DIELECTRIC DISPERSION DYNAMICS FROM GEOMETRY

By the definition of "apparent charge density" given above (Theoretical Description Section II) and in view of the obtained numerical results reported in Figure 10, considering the calculated DFPT $Q^*_\alpha\beta$ and $\epsilon$ as numerical counterparts of the $Q$ matrix elements and $\epsilon^{(\infty)}$ matrices as defined in the current work (Theoretical Description Section II and Methods Section II A), in a conical system of coordinates centered on the nitrogen nuclei:

$$
dx\,dy\,dz = dR \left( \sin\phi \tan\theta \, dR + R \cos\phi \tan\theta \, d\phi + \frac{R \sin\phi \, d\theta}{\cos^2\theta} \right) \left( -R \sin\phi \tan\theta \, d\phi + \cos\phi \tan\theta \, dR + \frac{R \cos\phi \, d\theta}{\cos^2\theta} \right),
$$

(7)

it is possible to state, with respect to the nitrogen nuclei, the existence of polar cones of space $(R_{PC}, \theta_{PC})$, characterized by:

![Equilibrium Structures](image)

![Figure 12](image) (a, b, c) Valence electronic charge density functions (re-calculated with a $40 \times 30 \times 20$ Monkhorst-Pack k-points grid in the first Brillouin zone of an equivalent orthorhombic unit cell), on the nitrogen $xz$ real plane (atomic centres in the middle of the panels) for the optimized AA’ stacked structure, obtained by means of three different theoretical methods: (a) NC-PBE, (b) US-LDA, (c) PAW-PBE (Set a). In insets (d, e): normalized difference functions between charge densities calculated with different methods as reported in the bottom-left of the panels (where a, b and c are the functions depicted in the left panels, NC-LDA: PW cutoff 2041 eV for diagonalization, 8163 eV for the charge density). Light blue lines indicate the projections of polar cones in which it is not possible to identify an angular structure, at the calculated resolution, in the represented functions. In Panels a, b and c, the 0.5718 $e \cdot a.u.^{-3}$ isolines of charge density are highlighted in green. Close-up details in Supplemental Material [91] (Figure S21).
where \( P_{(\phi)}(R_{PC}, \theta_{PC}) \) are integrated charge densities in the fraction of space included in the polar cones. The indices \((x)\) represent the different theoretical methods used to obtain the charge density functions \( \rho_{(x)}(R, \theta, \phi) \). \( \theta_{PC} \) is the conical angle, \( R_{PC} \) is the cone height along the \( z \) axis and \( \phi \) is the \( xy \) planar angle:

\[
P_{(\phi)}(R_{PC}, \theta_{PC}) = \int_{R \leq R_{PC}, \theta \leq \theta_{PC}} dRd\theta \int_{0}^{2\pi} \rho_{(\phi)}(R, \theta, \phi) d\phi.
\]

\( \rho_{(\phi)}(R, \theta, \phi) \) is the "effective charge density" as given above.

We plausibly hypothesize the existence of a second type of nitrogen polar cones, which we define by the hypothetical parameters \( R_{HP} \) and \( \theta_{HP} \), in which:

\[
\left[ \rho_{(NC-PBE)}(R, \theta, \phi) \leq \rho_{(US-LDA)}(R, \theta, \phi) \right]_{R \leq R_{HP}, \theta \leq \theta_{HP}}.
\]

Stated the properties of the radial solutions of the Schrödinger equation, \( R_{HP} \) can be chosen in order to be:

\[
[R > R_{HP}]_{\theta \leq \theta_{HP}} \Rightarrow \left[ \frac{\partial \rho_{(NC-PBE)}(R, \theta, \phi)}{\partial R} = \frac{\partial \rho_{(US-LDA)}(R, \theta, \phi)}{\partial R} = \frac{\partial \rho_{(PAW-PBE)}(R, \theta, \phi)}{\partial R} \right].
\]

In this case \( R_{HP} \) is smaller than the atomic radius of nitrogen atom (0.65 \( \text{Å} \)) and the validity of Eq. 10 depends only on the choice of \( \theta_{HP} \). A right choice of it implies that the different charge densities reported in Figure 12 concerning just the part of space included in hypothetical cones \( (R_{HP}, \theta_{HP}) \), approximate different phases of the fluctuation process of the charge density, relevantly to the \( A_{2u} \) vibrational mode (Peak 1) in purely crystalline, homogeneously stacked real systems.

In Figure 12 we highlight conical regions in the poles of nitrogen atoms, in which no angular structure is detectable in the reported charge density functions.

An important radial structure can be described (truncated spherical crown, marked in red in all of the panels in Fig. 12) extended from 0.2 to 0.4 \( \text{Å} \) from the nitrogen nuclei.

Analyzing the difference functions, Panels \( d \) and \( e \) in Figure 12 it is possible to notice that the same regions are marked in red, presenting high values of difference. Reasonably, the hypothetical cones \( (R_{HP}, \theta_{HP}) \) are contained in the light blue section lines of Figure 12. In this hypothesis, the red truncated spherical crowns from 0.2 to 0.4 \( \text{Å} \) in the polar regions of nitrogen atoms are places of a major charge density variation in the fluctuation movement associated to the \( A_{2u} \) vibrational mode (Peak 1).

In Figure 13 we report, instead, the electronic charge density functions calculated in displaced structures, i.e. structures in which displacement vectors have been applied to atoms as resulting from phonon eigenvectors (\( A_{2u} \) vibrational mode: IR Peak 1, \( \Gamma \) point). It is possible to notice a macroscopic difference among the functions calculated from different stacking geometries. Indeed this difference is well depicted from the 0.5718 \( e \cdot \text{a.u.}^{-3} \) isoline in Figure 13 (marked in green), and is exactly contained in the highly fluctuating region (red truncated spherical crown from 0.2 to 0.4 \( \text{Å} \) from nitrogen nuclei) and noticeable in the polar regions of nitrogen atoms (see the light blue conic lines in Panel \( c \), Figure 13), relating the higher ratio between the IR active absorptions of the \( AB' \) structure (Figure 6) to barely geometric considerations.

![Displaced Structures](image-url)

Figure 13. (\( a, b, c \)) In displaced structures with application of the \( A_{2u} \) phononic eigenvectors: valence electronic charge density functions (PAW-PBE [Set \( a \)], recalculated with a \( 40 \times 30 \times 20 \) Monkhorst-Pack \( k \)-points grid in the first Brillouin zone of an equivalent orthorhombic unit cell), on the \( xz \) real plane sections of 45\(^\circ\) polar cones with vertex in the centres of the nitrogen atoms. Displaced structures obtained starting from the optimized (\( a \)) \( AA' \), (\( b \)) \( AB \), (\( c \)) \( AB' \) geometries and applying displacement vectors on atoms as the resulting eigenvectors of the phononic structures reported in Figure 4 (\( v = 7, q = \Gamma \)). The 0.5718 \( e \cdot \text{a.u.}^{-3} \) isocontours of charge density are highlighted in green, being the most meaningful feature detectable at the depicted level of resolution. In Panel \( c \), light blue lines indicate the projection of a polar cone in which it is not possible to detect an angular structure in the function at the depicted resolution. The same characteristic can not be evidenced in the other two structures, as described in the text. Close-up details in Supplemental Material [91] (Fig. S21).
APPENDIX B: CALCULATION OF THE COMPOSITION OF EXPERIMENTAL SAMPLES

The hypothesis that the remarkably low value of intensity ratio between the two IR peaks in Sample 3 is produced by an high pureness of the specific analyzed material, namely composed only by AA’ stacking variant, as a result of particular experimental conditions, lead to a possible quantitative interpretation of the reported measured variability among the referred six samples. We report these results in appendix because they are necessarily based on reasonable but arbitrary hypothesis. Nevertheless they can be useful to stimulate further analysis.

We recalculated the NA parameters for the three systems with the numerical implementation DFPT PAW-PBE (Set a), optimized a cell parameter obtained with PAW-PBE-D2 (Set a) and c shortened of 32.94% with respect to the optimized PAW-PBE-D2 value and no further geometrical optimization (atomic centers in relative positions). The vibrational spectra calculated with these NA parameter and NC-PBE-TS IFC matrices are reported in Fig. 14. The calculated ratios are reported as inset of the same figure. Note that the Lorentz broadening functions are always applied separately to each phonon spectral line (i.e. Peak 2 is composed by four spectral lines, Peak 1 by only one spectral line).

We interpreted the data considering the same optimal shortening percentage as suitable for all the three stable stacking structures. This assumption, stated the asymptotic behaviour of the AB’ interpolating function showed in Fig. 11 moves us to exclude a purely thermodynamical behaviour, namely a constant ratio, almost unitary, between the amounts of AA’ and AB variants in all the samples. This hypothesis, in fact (e.g. applied to Sample 3: 50% AA’, 50% AB and absence of AB’ ) would produce a shortening percentage above the asymptote for AB’, making it impossible to use the same value for the three variants.

The initial hypothesis (Sample 3 is purely composed by AA’) appears, so, reasonable to us. From this, it is possible to obtain the optimal shortening percentage, which results to be 32.94%, at the intersection between the horizontal line at ratio value 1.043 (Sample 3) and the AA’ interpolation line, reported in Fig. 11.

| Label      | Source | Exp. Ratio AA (%) | AB (%) | AB’ (%) |
|------------|--------|-------------------|--------|---------|
| Sample 1   | Ref. 26| 1.805             | 30.74  | 51.00   | 18.27   |
| Sample 2   | Ref. 27| 2.636             | 9.27   | 51.00   | 39.73   |
| Sample 3   | Ref. 28| 1.043             | 100.00 | 0.00    | 0.00    |
| Sample 4   | Ref. 29| 1.282             | 59.29  | 40.02   | 0.69    |
| Sample 5   | Ref. 30| 1.236             | 66.75  | 32.53   | 0.72    |
| Sample 6   | Ref. 31| 1.737             | 30.39  | 55.04   | 14.56   |

Figure 14. Vibrational spectra calculated by NC-PBE-TS (analytical IFC) and empirically obtained NA part of the dynamical matrices with numerical implementation of DFPT PAW-PBE (Set a) on fictitious systems (32.94% shortened on the c parameter with respect to the PAW-PBE-D2 [Set a] optimal values and no further geometrical optimization [atomic centers in relative positions]).

In Section V E we showed how the construction of fictitious systems, with shortened structural parameter (c) perpendicularly to plane directions, permits to obtain a spatial charge density distribution function more similar to the effective function $\rho_Q(\mathbf{r})$, at least in the nitrogen polar cones $(R_{HP}, \theta_{HP})$, as showed in Appendix A [25]. This leads to the obtainment of empirical NA parameters for the dynamical matrices which produce a better agreement with the experimental values concerning the resulting ratio between IR active peaks, as evident from Fig. 11.

We interpret the data considering the same optimal shortening percentage as suitable for all the three stable stacking structures. This assumption, stated the asymptotic behaviour of the AB’ interpolating function showed in Fig. 11 moves us to exclude a purely thermodynamical behaviour, namely a constant ratio, almost unitary, between the amounts of AA’ and AB variants in all the samples. This hypothesis, in fact (e.g. applied to Sample 3: 50% AA’, 50% AB and absence of AB’ ) would produce a shortening percentage above the asymptote for AB’, making it impossible to use the same value for the three variants.

The initial hypothesis (Sample 3 is purely composed by AA’) appears, so, reasonable to us. From this, it is possible to obtain the optimal shortening percentage, which results to be 32.94%, at the intersection between the horizontal line at ratio value 1.043 (Sample 3) and the AA’ interpolation line, reported in Fig. 11.

Table V. Theoretical compositions of the cited experimental samples, calculated following the premise that Sample 3 is purely composed by AA’ stacked material. The convolution of the spectra reported in Fig. [14] shifted in frequency in order to superimpose the two peak values and multiplied by the reported coefficients (Columns from 4 to 6) exactly reproduces the experimental ratios (Column 3).

We recalculate the NA parameters for the three samples referenced in this work. To obtain these results, the IR spectra of Fig. [14] must be shifted in frequency in order to have correspondence of the peaks. Thermodynamic considerations have also been applied in case of multiple solutions, keeping the fraction of AB’ the lowest possible.

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Supplemental Material

List of provided supplemental data:
TS - Supplemental table.
S - Supplemental figure.

- TSVI - Lattice parameters calculated with a selection of different methods.
- S15 - PESs cuts for rigid sliding of h-BN planes from the AB’ structure calculated with a selection of different methods.
- TSVII - Empirical Born Q matrices and dielectric tensors calculated as explained in Sections III C and V E of the Main Text.
- TSVIII, TSIX - Phonon frequencies at the Γ point for the AB and AB’ structures calculated with a selection of different methods.
- S16, S17, S18, S19 - Vibrational spectra for AB and AB’ structures calculated with a selection of different methods.
- S20 - Sections of the valence charge density functions $\rho_{\text{PW-PBE}}(r)$ of fictitious systems obtained as explained in Sections III C and V E of the Main Text, used to calculate the data reported in Table TSVII.
- S22 - Phonon energy dispersions calculated with the empirical non-analytical corrections of Table TSVII.
- S23 - Ultrasoft PP, LDA energy dispersions of phonons (NA: numerical implementation US-LDA DFPT).
- S24 - NC PP, PBE, Tkatchenko-Scheffler corrected energy dispersions of phonons (NA: numerical implementation PAW-PBE [Set a] DFPT).
- S25 - NC PP, SCAN energy dispersions of phonons (NA: numerical implementation NC-SCAN DFPT).
- S28 - PAW PP, PBE, D2 vdW energy dispersions of phonons (NA: numerical implementation PAW-PBE [Set b] DFPT).
- S29, TSVI, TSVIII, TSIX - Tests for the effects of the formal vdW corrections.
- S26, S27, S29 - Non-standard explorations of the potential energy hypersurfaces.
- S30, S31, S32 - Convergence studies.
## Lattice constants

Table TSVI. Lattice constants (in Å) for the five analyzed conformations, resulting from geometrical optimization with different theoretical approaches. Details about theoretical and computational methods are specified in the relevant sections of the Main Text: Sections III, IV and Table I.

| Method       | AA  | AB  | AB' | AAA |
|--------------|-----|-----|-----|-----|
| PBE-D2       | 2.509 | 2.508 | 2.508 | 2.508 |
| PBE-D3BJ     | 2.507 | 2.507 | 2.506 | 2.506 |
| PBE-TS       | 2.505 | 2.505 | 2.504 | 2.503 |
| SCAN+rVV10   | 2.497 | 2.497 | 2.496 | 2.495 |

**Table TSVII.** Empirically obtained non-analytical parts of the dynamical matrices for the three stable systems, calculated numerically with DFPT and PAW-PBE (Set a) on fictitious 32.94% c shortened systems. The shortening operation has been performed with respect to optimized geometry obtained with PAW-PBE-D2 (Set a, reported in Table TSVI) and no further geometrical optimization (atomic centers in relative positions with respect to the cell parameters). See Sections III C, V E and Appendix B (VI) of the Main Text of this work.

### AA'

| Dielectric tensor $\varepsilon^{(\infty)}$ (e) | Born Q matrix elements $Q^{(s)} (e)$ | Born Q matrix elements $Q^{(c)} (e)$ |
|---------------------------------------------|-----------------------------------|-----------------------------------|
| $x$ 5.410 0.000 0.000  | $x$ 7.010 0.000 0.000           | $x$ 67.994 -26.684 0.000          |
| $y$ 0.000 5.410 0.000  | $y$ 0.000 7.011 0.000           | $y$ -26.684 37.182 0.000          |
| $z$ 0.000 0.000 9.578   | $z$ 0.000 0.000 7.615           | $z$ 0.000 0.000 9.046             |

### AB

| Dielectric tensor $\varepsilon^{(\infty)}$ (e) | Born Q matrix elements $Q^{(s)} (e)$ | Born Q matrix elements $Q^{(c)} (e)$ |
|---------------------------------------------|-----------------------------------|-----------------------------------|
| $x$ 7.010 0.000 0.000  | $x$ 7.010 0.000 0.000           | $x$ 67.994 -26.684 0.000          |
| $y$ 0.000 7.011 0.000  | $y$ 0.000 7.011 0.000           | $y$ -26.684 37.182 0.000          |
| $z$ 0.000 0.000 7.615   | $z$ 0.000 0.000 7.615           | $z$ 0.000 0.000 9.046             |

### AB'

| Dielectric tensor $\varepsilon^{(\infty)}$ (e) | Born Q matrix elements $Q^{(s)} (e)$ | Born Q matrix elements $Q^{(c)} (e)$ |
|---------------------------------------------|-----------------------------------|-----------------------------------|
| $x$ 2.513 2.513 2.510  | $x$ 2.513 2.513 2.510           | $x$ 2.513 2.513 2.510             |
| $y$ 2.490 2.490 2.490  | $y$ 2.490 2.490 2.490           | $y$ 2.490 2.490 2.490             |
| $z$ 2.504 2.504 2.501   | $z$ 2.504 2.504 2.501           | $z$ 2.504 2.504 2.501             |

### AA

| Dielectric tensor $\varepsilon^{(\infty)}$ (e) | Born Q matrix elements $Q^{(s)} (e)$ | Born Q matrix elements $Q^{(c)} (e)$ |
|---------------------------------------------|-----------------------------------|-----------------------------------|
| $x$ 2.509 2.508 2.508  | $x$ 2.509 2.508 2.508           | $x$ 2.509 2.508 2.508             |
| $y$ 2.507 2.507 2.506  | $y$ 2.507 2.507 2.506           | $y$ 2.507 2.507 2.506             |
| $z$ 2.505 2.505 2.504   | $z$ 2.505 2.505 2.504           | $z$ 2.505 2.505 2.504             |

### Notes:

1. Projector Augmented Wave PP
2. Ultrasoft PP
3. Norm-conserving PP

### Empirical Born Q matrices and dielectric tensors

Table TSVII. Empirically obtained non-analytical parts of the dynamical matrices for the three stable systems, calculated numerically with DFPT and PAW-PBE (Set a) on fictitious 32.94% c shortened systems. The shortening operation has been performed with respect to optimized geometry obtained with PAW-PBE-D2 (Set a, reported in Table TSVI) and no further geometrical optimization (atomic centers in relative positions with respect to the cell parameters). See Sections III C, V E and Appendix B (VI) of the Main Text of this work.
**AB' structure**

Potential energy surfaces

Figure S15. Potential energy surfaces (PES) calculated, with different theoretical implementations, upon rigid sliding movements of contiguous h-BN planes, keeping fixed the optimized cell structural parameters obtained for the AB' symmetrical settlement with each different method (reported in Table TSVI). For Computational details see the relevant section IV and Table II in the Main Text.
Table TSVIII. Phonon frequencies at the Γ point (in cm\(^{-1}\)) for the AB stacking as calculated by different theoretical approaches and software implementations and compared with experimental values taken from literature. The NA part of the dynamical matrix is calculated adopting numerically DFPT effective charges and dielectric tensors, where not differently specified, with the same method of the IFC. See Computational details and Methods, Sections III, IV and Table I of the Main Text of this work.

| Mode   | VASP | QE | Experiment |
|--------|------|----|------------|
| E_{1g}** | 45   | 45 | 51 [22]   |
| B_{1g} | 125  | 118 | 767-810 [25,31] |
| A_{2u} | 751  | 755 | 1369-1376 [25,32,33] |
| B_{1g} | 798  | 798 | 1338-1404 [25,32,33] |
| E_{1g}** | 1357 | 1356 | 1616 [25] |
| E_{2g} | 1359 | 1359 | 1616 [25] |
| E_{1u} | 1360 | 1360 | 1616 [25] |

* - IR active modes
** - Raman active modes

Table TSIX. Phonon frequencies at the Γ point (in cm\(^{-1}\)) for the AB’ stacking as calculated by different theoretical approaches and software implementations and compared with experimental values taken from literature. The NA part of the dynamical matrix is calculated adopting numerically DFPT effective charges and dielectric tensors, where not differently specified, with the same method of the IFC. See Computational details and Methods, Sections III, IV and Table I of the Main Text of this work.

| Mode   | VASP | QE | Experiment |
|--------|------|----|------------|
| E_{1g}** | 36   | 35 | 51 [32]   |
| B_{1g} | 128  | 121 | 767-810 [25,31] |
| A_{2u} | 756  | 756 | 1369-1376 [25,32,33] |
| B_{1g} | 796  | 795 | 1338-1404 [25,32,33] |
| E_{1g}** | 1357 | 1357 | 1616 [25] |
| E_{2g} | 1359 | 1359 | 1616 [25] |
| E_{1u} | 1360 | 1360 | 1616 [25] |

* - IR active modes
** - Raman active modes
Figure S16. Vibrational spectra calculated for the AB stacking configuration with different theoretical approaches, as described in legend (for PAW-PBE we use Set a). In insets, details of Peak 1 and Peak 2 regions are showed. Red solid vertical lines indicate the average experimental peak values and blue vertical dotted lines indicate the range limits of measured high absorptions in the six experimental references [26–31]. Computational details and Methods are thoroughly examined in the relevant sections of the Main Text: Sections III, IV and Table I.

Figure S17. Ratios between the intensities of absorption of the two IR active peaks of vibrational spectra calculated for the simulated AB stacking structure with different theoretical implementations (for PAW-PBE we use Set a). Computational details and theoretical information on Methods are provided in the relevant sections of the Main Text: Sections III, IV and Table I.
Figure S18. Vibrational spectra calculated for the AB’ stacking configuration with different theoretical approaches, as described in legend (for PAW-PBE we use Set a). In insets, details of Peak 1 and Peak 2 regions are showed. Red solid vertical lines indicate the average experimental peak values and blue vertical dotted lines indicate the range of the experimental data for the two peak frequencies, as gathered from the six experimental references [26–31]. Computational details and theoretical information are provided in Sections III, IV and Table I in the Main Text.

Figure S19. Ratios between the intensities of absorption of the two IR active peaks of vibrational spectra calculated for the simulated AB’ stacking structure with different theoretical implementations (for PAW-PBE we use Set a). See the Computational details and Methods sections of the Main Text of this work: Sections III, IV and Table I for the relevant explanations.
Charge density functions $\rho_{\text{PAW-PBE}}^{\text{fict.}}(\mathbf{r})$ of the fictitious systems, $\mathbf{r} \equiv (R, \theta, \phi)$.

Used to obtain the empirical Born $Q$ matrices and dielectric tensors reported in Table TSVII.

$[R < R_{\text{HP}}] \land [\theta \leq \theta_{\text{HP}}] \implies \rho_{\text{PAW-PBE}}^{\text{fict.}}(\mathbf{r}) \approx \rho_{Q}(\mathbf{r})$.

see Sections II, III C, V E and Appendix A of the Main Text.

Figure S20. Nitrogen $xz$ sections of the valence charge density functions $\rho_{\text{PAW-PBE}}^{\text{fict.}}(\mathbf{r})$ (Set $a$, recalculated with a $40 \times 30 \times 20$ Monkhorst-Pack $k$-points grid in the first Brillouin zone of an equivalent orthorhombic unit cell, see Computational details section IV and Table I in the Main Text) calculated in fictitious systems obtained as explained in Sections III C and V E of the Main Text, by applying the 32.94% shortening percentage to the $c$ parameter in the $z$ direction from fully optimized (PAW-PBE-D2 $[\text{Set } a]$) structures (AA’, AB and AB’) and no further geometrical optimization (nuclei in relative positions). Nitrogen nuclei in the centres of the panels. The 0.5718 $e \cdot a.u.^{-3}$ isolines of charge density are highlighted in green. In insets, details of polar cones sections. Close-up details are reported in Figure S21.
Figure S21. Nitrogen xz sections, detailed maps for selected real space valence charge density functions. Nitrogen nuclei are in the centre of the concentric zones, approximately in the middle of the panels. The $0.5718 \text{ e} \cdot \text{a.u.}^{-3}$ isolines of charge density are highlighted in green. The legends attached to Panel a inform about the four panels.
Phonon energy dispersions with empirical non-analytical corrections
Empirical NA parameters reported in Table TSVII

Figure S22. Comparison of the phonon energy dispersions along high symmetry directions in the first Brillouin zone for the three stable systems. The IFC matrices are calculated by Finite Displacements method with DFT PBE functional, NC pseudopotential approximations and TS dispersion corrections (see Computational details section IV and Table I of Main Text). The NA parts (reported in Table TSVII) are empirically obtained by DFPT PAW-PBE (Set a, see Computational details section IV and Table I in Main Text) on fictitious systems shortened on the c parameter of 32.94% with respect to the optimized PAW-PBE-D2 (Set a) geometry and no further geometrical optimization from PAW-PBE-D2 (Set a) optimal (atomic centers in relative positions with respect to the cell parameters). See Sections III C, V E and Appendix B VI of the Main Text of this work.

Ultrasoft PP, LDA energy dispersions of phonons

Figure S23. Comparison of the phonon energy dispersions along high symmetry directions in the first Brillouin zone for four differently stacked systems. The IFC matrices are calculated by Finite Displacements method with DFT LDA functional, US pseudopotential approximations. The NA parts of the dynamical matrices are calculated adopting numerically US-LDA DFPT effective charges and dielectric tensors. Computational details and theoretical information are provided in the relevant sections of the Main Text: Sections III IV and Table I.
Figure S24. Comparison of the phonon energy dispersions along high symmetry directions in the first Brillouin zone of four differently stacked systems. The IFC matrices are calculated by Finite Displacements method with DFT PBE functional, NC pseudopotential approximations and TS dispersion corrections. The NA parts of the dynamical matrices are calculated adopting numerically the resulting PAW-PBE (Set a) DFPT effective charges and dielectric tensors. See further Computational details and theoretical information on Methods in the relevant sections of the Main Text: Sections III, IV and Table I.

Figure S25. Comparison of the phonon energy dispersions along high symmetry directions in the first Brillouin zone of three differently stacked systems. The IFC matrices are calculated by Finite Displacements method with DFT SCAN functional and NC pseudopotential approximations. The NA parts of the dynamical matrices are calculated adopting numerically the results of NC-SCAN DFPT effective charges and dielectric tensors. See further Computational details and theoretical information on Methods in the relevant sections of the Main Text: Sections III, IV and Table I.
AA structure
Non-standard explorations of the potential energy hypersurface

Figure S26. Non-standard explorations of the potential energy hypersurface of the AA structure. Phonon eigenvalues obtained from the diagonalization of a dynamical matrix in which the IFC results from long-range finite displacements. Supercell $6 \times 6 \times 1$. Finite displacements (1) 0.10 Å, (2) 0.11 Å. Cell parameters obtained from PAW-PBE-D2 (Set a, Table TSVI). **No van der Waals dispersion correction in the FD SCF calculations.** The NA part of the dynamical matrix is calculated adopting numerically PAW-PBE (Set a) DFPT effective charges and dielectric tensors. All the other parameters as reported in Main Text, Table I, Set a. Interesting hints come from the comparison of these unstable structures with the AB’ scheme reported in Fig. 4, Panel 3 of the Main Text, obtained with the same theoretical implementation (Set a, Table I of the Main Text) and long-range displacement of 0.15 Å.

A'B structure
Non-standard explorations of the potential energy hypersurface

Figure S27. Non-standard explorations of the potential energy hypersurface of the A'B structure. Phonon eigenvalues obtained from the diagonalization of a dynamical matrix in which the IFC results from long-range finite displacements. Supercell $6 \times 6 \times 1$. Finite displacements (1) 0.14 Å, (2) 0.15 Å. Cell parameters obtained from PAW-PBE-D2 (Set a, Table TSVI). **No van der Waals dispersion correction in the FD SCF calculations.** The NA part of the dynamical matrix is calculated adopting numerically PAW-PBE (Set a) DFPT effective charges and dielectric tensors. All the other parameters as reported in Main Text, Table I, Set a. Interesting hints come from the comparison of these unstable structures with the AB’ scheme reported in Fig. 4, Panel 3 of the Main Text, obtained with the same theoretical implementation (Set a, Table I of the Main Text) and long-range displacement of 0.15 Å.
PAW PP, PBE, D2 vdW energy dispersions of phonons

Figure S28. Comparison of the phonon energy dispersions along high symmetry directions in the first Brillouin zone for the five considered differently stacked systems. The IFC matrices are calculated by Finite Displacements method with FD of 0.01 Å, DFT PBE functionals, PAW pseudopotential approximations, Grimme-D2 dispersion corrections (VASP code. Set b Table I, Main Text). Cell parameters obtained with the same implementation PAW-PBE-D2 (Set b, Table ITSVI). The NA parts of the dynamical matrices are calculated adopting numerically the resulting PAW-PBE (Set b) DFPT effective charges and dielectric tensors. See further Computational details and theoretical information on Methods in the relevant sections of the Main Text: Sections III, IV and Table I. Interesting hints come from the comparison, in view of the different computational implementations, of these schemes with the ones reported in Fig. 4 of the Main Text. Consider the different FD lengths used for the AB’ structure (and the AA and A’B non-standard explorations reported here).

A’B structure optimized without vdW corrections
Phonon energy dispersions with a non-standard exploration of the potential energy hypersurface

Figure S29. Phonon energy dispersions along high symmetry directions in the first Brillouin zone for the A’B structure. Cell parameters obtained from PAW-PBE (Set a) calculations (without vdW dispersion corrections): a=2.51 Å, c=8.20 Å. No van der Waals dispersion correction in the FD SCF calculations. Supercell 6×6×1. Finite displacements: (1) 0.03 Å, (2) 0.15 Å. The results reported in panel 2 represent a non-standard way to explore the potential energy hypersurface of the structure. In fact, the eigenvalues are obtained from the diagonalization of a dynamical matrix resulting from untypical long-range finite displacements (0.15 Å). The NA part of the dynamical matrix is calculated adopting numerically PAW-PBE (Set a) DFPT effective charges and dielectric tensors. All the other parameters as reported in Main Text, Table I Set a.
Convergence study for the finite displacement value in FD SCF calculations

**AA' structure**

Figure S30. Evolution of the phonon frequencies (a) along high symmetry directions in the first Brillouin zone and (b) in the Γ point, for the AA' structure (cell parameters obtained with PAW-PBE-D3BJ, reported in Table I of the Main Text, supercell size of \(2 \times 2 \times 1\) unit cells), obtained with a set of different finite displacement values. Calculations performed with PAW-PBE and D3BJ van der Waals dispersion correction, see Computational details (Section IV) and Table I of the Main Text.

*Other tested values: 0.005 Å, 0.01 Å, 0.015 Å, 0.02 Å, 0.04 Å, 0.1 Å, 0.14 Å, 0.15 Å, 0.2 Å, 0.5 Å (the results are superimposable in Panel a, showed as light blue lines).*

Convergence study for the \(xy\) planar supercell size in FD SCF calculations

**AA' Structure**

Figure S31. Phonon energy dispersions for the AA' structure with varying supercell size in the in-plane \(xy\) directions (a) along high symmetry directions in the first Brillouin zone and (b) in the Γ point. Calculations performed with PAW-PBE and D3BJ van der Waals dispersion correction, FD value of 0.015 Å, see further information in Computational details (Section IV) and Table I of the Main Text (cell parameters obtained with PAW-PBE-D3BJ, reported in Table I of the Main Text).
Convergence study for the z planar supercell size in FD SCF calculations

AA' Structure

Figure S32. Phonon energy dispersions for the AA' structure with varying supercell size in the z direction, perpendicular to the h-BN sheet, (a) along the A – Γ high symmetry direction in the first Brillouin zone, (b) in the Γ point and (c) in the A point. Calculations performed with PAW-PBE and D3BJ van der Waals dispersion correction, FD value of 0.015 Å, see further information in Computational details (Section IV and Table 1 of the Main Text (cell parameters obtained with PAW-PBE-D3BJ, reported in Table TSV1).