

Quasiparticle states of hexagonal BN: A van der Waals density functional study

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(Received 19 November 2025; revised 8 March 2026; accepted 16 April 2026; published 18 May 2026)

We compute and track the impact of truly nonlocal-correlation effects on the quasiparticle (QP) band structure of hexagonal boron-nitride (h-BN) systems. To that end, we start with the consistent-exchange vdW-DF-cx version [K. Berland *et al.*, *Phys. Rev. B* **89**, 035412 (2014)] of the van der Waals (vdW) density functional (vdW-DF) method for exchange-correlation (XC) functional design and enforce piecewise linearity in the energy changes with partial charging, using the Koopmans-integer (KI) DFT framework [E. B. Linscott *et al.*, *J. Chem. Theory Comput.* **19**, 7097 (2023)]. Our approach and results, denoted KI-CX(CX) to emphasize the importance of consistency in structure and QP predictions, extends present-standard use of KI DFT, denoted KI-PBE (as it is based on the semilocal PBE XC functional but computed at the experimental structure), to capture, for example, the impact of the interlayer coupling on the QP band structure, including a full account of vdW signatures. We find that KI-CX(CX) predictions generally agree with GW studies and also with recent experimental data for bulk h-BN. We contrast QP predictions obtained in KI-CX(CX) and KI-PBE and well as in KI-PBE(PBE) (that is, KI-PBE studies based the PBE structure) and we correlate these with the core (vdW) nature of differences between the PBE and CX functionals. This analysis permits us to provide a precise discussion of what are direct and indirect vdW signatures in these layered systems and to define a new QP-based method, also denoted KI-CX(CX), for testing quality and consistency in XC functionals.

DOI: [10.1103/bl2s-c8w7](https://doi.org/10.1103/bl2s-c8w7)

I. INTRODUCTION

The goal of improving materials predictions by parameter-free theory prompts us to seek deeper understanding of sudden charged excitations in light-matter interactions and of ground state (GS) properties in concert. For the former, we can summarize the nature of such excitations as quasiparticle (QP) states, whose energies and spatial variation reflect the characteristics of the electronic-structure changes [1–3] upon photon absorption or emission. Formally exact many body perturbation theory (MBPT), for example, in the GW Γ [4–6] or equation-of-motion coupled-cluster [7–10] (EOMCC) approaches, permit us to predict the QPs as solutions to effective dynamics problems. One can also predict QPs by use of orbital-density dependent minimization schemes [11,12] in density functional theory [13] (DFT), including Koopmans-DFT forms [14–19] or using a Wannier-localized optimally tuned range-separated hybrid (RSH) exchange-correlation (XC) functional [20–23]. Meanwhile, the formally exact DFT of the GS [13] permits predictions of the atomic structure and electron-density variations, using either the popular Kohn-Sham (KS) scheme [24–27] with regular XC functionals or the

generalized-KS scheme [28–30] with corresponding hybrid extensions [20,22,29–41]. The same is also true for at least the Koopmans-integer (KI) form [16–18,42,43] of Koopmans DFT, where the solution strategy reduces to the KS scheme at integer electron occupations. Such GS-DFTs rely on an equation-of-motion framework [44,45], analogous by design to the GW formulation [5,44,46,47] but used for fictitious, independent particles in an effective potential that must reflect enough of the QP dynamics to describe the GS electron behavior [27,44,47–50].

In practice, we need MBPT input to define robust so-called exchange-correlation (XC) functional approximations [47–59]. Approximations also enter MBPT-based QP studies (e.g., in GW [6]) and we seek consistency in XC design work [15,30,44,45,47,50,54,60]. Progress in such a concerted approach should and can be tested on both GS and QP properties [3,22,30,42,61,62].

With an accurate XC functional approximation, KS-DFT lets us predict the atomic configurations [27] and materials vibrations; see, e.g., Refs. [63,64]. Such computational characterizations permit theory validation both directly (on thermophysical properties and phases; e.g., Ref. [65]) and indirectly on the QPs, as revealed in electrical transport measurements [66], scanning tunneling microscopy (STM) [67], angle-resolved photoemission (ARPES) [68–71], or inverse photoemission [72]. These properties generally reflect the QP band structure (energy variation with momentum in an extended system). In terms of MBPT and XC quality testing, one key observation is that (sub-)picometer accuracy at atomic structure characterization is typically required to, in turn, accurately predict the light-matter interactions in the more costly MBPT methods. This accuracy-at-structure-and-QPs (and

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exciton) goal is, for example, achieved for oligoacene crystals by combining the consistent-exchange vdW-DF-cx version (here abbreviated CX) [47,73–75] of the van der Waals (vdW) density functional (vdW-DF) method [30,40,47,59,75–79] with GW (and Bethe-Salpeter-equation solutions) [3]. We note that this molecular-crystal study is consistent both among methods and with the nature of the systems: The CX step for structure and the GW step for QPs both directly reflect the vdW interaction in their equation of motion formulations [3,5,47,80,81].

Direct and consistent theory-experiment testing on QPs has a high, if sometimes overlooked, value for developing materials theory. As is further discussed within, value of securing consistency in methods for QP predictions [3] comes because the Hedin QP-equation-of-motion framework [44] is equivalent to the formal adiabatic-connection formula (ACF) specification of the XC functional designs [44,47–49,58]: Relevant QP characterizations *can guide* better XC design [44,47]. Moreover, there exists a rigorous proof [62,82] that GS-DFT simultaneously yield a formally exact determination of the first frequency moment of the occupied part of the fully interacting spectral function (or equivalently, the sum of occupied Dyson-orbital densities weighted by their QP energies) in standard GS-DFT energy components, when supplemented by a coupling-constant analysis of the system-specific XC energy [83] and thereby given a value for the average electron energy [62]. This spectral-function measure is simply a functional of the GS electron density and so the formal result suggests 1) that relevant QP characterizations *may perhaps more often guide* XC developments, and 2) that striving for consistency in GS structure and in QP determinations adds value [3].

Aiming to leverage consistent GS-QP testing for development, we here introduce CX-based KI-DFT studies to track and discuss vdW signatures on QPs of hexagonal boron-nitride (h-BN) systems. We observe that KI-DFT [16,18], using a linear-response (LR) description based on a given input XC functional, stands out by providing relatively fast QP predictions without changing neither total energies nor the forces that set structure when that XC input is used in KS-DFT [43]. The choice of picking the CX version as the basis for our vdW-inclusive KI-DFT approach is motivated within. We note that the QUANTUM ESPRESSO (QE) suite of DFT codes [84,85], with the module for KOOPMANS-DFT extension [19,43], permits KI-CX studies as QE has the LR-kernel for the vdW-DF nonlocal-correlation term [77,86,87].

Accurate tools, linking the structure and QP aspects of materials modeling, are generally valuable for characterizations in their own rights but use of the KI-DFT offers a potential for more synergy in continued method developments. One property of interest is the band structure, that is, the energy variation of occupied and empty QPs with the QP momentum. When using a versatile XC functional, for molecular or layered materials [3,23], we expect to find fingerprints of the vdW interactions. With KI-CX and when using the CX to first the zero-pressure GS structure, we can secure full consistency between in the vdW inclusion for both the structure and QP predictions. Success or failure in comparison with measurements (or with GW studies [3]) is then a double test of CX and, as such, a probe of consistency in the MBPT inputs to this GS (and QP) descriptor [62].

Present-standard KI-DFT studies [16–18,42,43,88–95], rely on either the local-density approximation (LDA) [44,96] or the semilocal Perdew-Burke-Ernzerhof (PBE) [58] XC functional. The latter functional is developed for KS-DFT and gives what we here label as PBE results. Via an extension to density functional perturbation theory (DFPT), PBE also permits efficient QP characterizations in what we call KI-PBE, when a piecewise-linearity (PWL) constraint [14,42,43,97,98] is imposed on the energy variation with partial charging. One of us have helped demonstrate, by comparison with exact descriptions, that PBE does a remarkable job at retaining consistency with the MBPT physics that underpins its design logic [44,48,49,54,56,58] for small, individual molecules [62]. However, KI-DFT still reflects the nature of the underlying XC functional [43] and KI-PBE is not set up to capture vdW attraction [47,76,78,79] that brings cohesion to both molecular crystals and layered materials [3,76,99]. An accurate structure characterization is a prerequisite for a trusted QP prediction [3] but use of KI-PBE for QP studies in weakly interacting complex systems [40] (where a complete characterization is per definition lacking) is expected to fail: Stacking two-dimensional layers alters the band structure [23,68,100,101] and an underbinding corresponds to a (false) expansion that implies further QP changes [102,103]. One may use pressure or apply a PBE correction but that should then be reflected also at the QP step. Ref. [62] implies that KI-PBE for soft matter gives QP predictions under an effective pressure that is not in the experiments and pressure certainly changes the electronic structure [104,105]. One cannot, *a priori*, be sure that KI-PBE suffice to capture the full QP nature as there may be offsetting effects.

The h-BN systems are insulating and have been thoroughly studied both theoretically and experimentally. h-BN has emerged as one of the most prominent two-dimensional materials, owing in part to a graphene-like honeycomb structure in its layers and to its wide band gap [106,107]. Additionally, h-BN exhibits a suite of advantageous properties, such as excellent thermal conductivity [108], unique thickness-dependent behavior [109], chemical stability [110], optical functionality [111], and polymer compatibility [112]. These attributes enable applications in aerospace [110,113], environmental science, and energy technologies—spanning adsorption, photo-catalysis, membrane separation, disinfection, environmental sensing, as well as energy conversion and storage [114]. We focus on QPs in three systems that are experimentally available, and we first set the atomic structure by observations. This means that KI-CX versus KI-PBE differences reflect the direct impacts of truly nonlocal-correlation effects (primarily interlayer coupling) on the QPs. We next track the full impact of including nonlocal-correlations the QP description via our new KI-CX(CX) tool, namely KI-CX at the structure predicted in CX, and contrast with QP predictions obtained with the correspondingly defined KI-PBE(PBE) tool. There are local and global valence-band (conduction-band) extrema, together forming a number of (indirect) QP gaps in h-BN systems. We assess KI-CX(CX), KI-CX, KI-PBE(PBE) and KI-PBE quality on accuracy for those gaps, comparing with experimental observations and with GW band gap predictions [23,68,69,100,103].

The paper is structured as follows. The following two sections summarize the CX functional and use of KI-DFT, including computational parameters, input configurations, and work flows. Our results and discussion section presents and interprets KI-CX versus KI-PBE performance differences. Section V contains our conclusions and outlook. The paper has two appendices.

II. THEORY

In this section, we first summarize the formulation of the nonlocal energy term E_c^{nl} that enters in a vdW-DF like CX. Next, we present rationale for our exchange choice, i.e., why we choose the CX as the functional start of our nonlocal-correlation KI-DFT. Finally, we identify the components responsible for capturing nonlocal interactions in QP states in KI-CX.

A. Truly nonlocal correlation in CX

The design of the vdW-DFs relies on MBPT characterizations [48,49,51,54–57,59] of the density-density response function $\chi_\lambda(\mathbf{r}, \mathbf{r}', \omega)$, i.e., the ratio of the density change $\delta n(\mathbf{r})$ that arise when external potential at frequency ω is applied at position $\mathbf{r}'$. As indicated by the subscript, this response is determined while assuming that the raw inter-electron Coulomb matrix element $V = |\mathbf{r} - \mathbf{r}'|^{-1}$ is scaled by a coupling constant $0 < \lambda < 1$. The adiabatic connection formula (ACF) [47,48,49,53,115],

$$E_{\text{xc}}[n] = - \int_0^1 d\lambda \int_0^\infty \frac{du}{2\pi} \text{Tr}[V \chi_\lambda(iu)] - E_{\text{self}}, \quad (1)$$

is used to convert the formal MBPT input into versions of an XC energy functional of the electron density variation $\rho(\mathbf{r})$. The trace indicate integration with respect the spatial coordinates of $\chi_\lambda(\mathbf{r}, \mathbf{r}', \omega = iu)$ and V .

The resulting vdW-DF functionals are in practice given by treating the XC design work as an electrodynamics problem [76,78,116]. Critical are the focus on collective excitations, compliance with Lindhard screening, and enforcing current conservation and time-reversal symmetry in modeling the local-field response [47,77,78]. We start with a generalized-gradient approximation (GGA) for a so-called internal XC function $E_{\text{xc}}^{\text{in}}[\rho]$, comprising the XC terms of the local-density approximation (LDA) [44,117] and a MBPT-guided choice for the gradient-corrected exchange [77,79,118,119]. This ensures a GGA-type exchange component $E_{\text{x}}^{\text{in}}[\rho]$ in the starting point for the vdW-DF design. We next use an electrodynamics-based recast of the ACF [47,76,116] to extract a corresponding initial-guess dielectric function $\epsilon(\mathbf{r}, \mathbf{r}', \omega = iu)$ [79,118]:

$$E_{\text{xc}}^{\text{in}} = \int \frac{du}{2\pi} \text{Tr}[\ln[\epsilon(iu)]] - E_{\text{self}}. \quad (2)$$

This reformulation of the semilocal functional $E_{\text{xc}}^{\text{in}}$ reflects an exponential resummation, $\epsilon(\omega) \equiv \exp[S_{\text{xc}}(\omega)]$, of a plasmon-propagator $S_{\text{xc}}(\mathbf{r}, \mathbf{r}', \omega)$ that corresponds to the internal GGA [79], so that the initial guess for the collective excitations [found at $\epsilon(\omega) = 0$] are tracked by logarithmic singularities [78,120]. Third, we note that the Coulomb Green

function G is set up to trace also long-ranged electrodynamics couplings of virtual electron dynamics (for example, as reflected by plasmons) [76,78] and that the vdW forces are naturally included when we enforce current conservation, $\epsilon(\omega) \rightarrow \kappa(\omega) \equiv \nabla \epsilon(\omega) \cdot \nabla G$ [76–78,116]. We therefore use the resulting beyond-GGA recast of the ACF for a formal vdW-DF-method specification [47,79,118]

$$E_{\text{xc}}^{\text{vdW-DF}} = \int \frac{du}{2\pi} \text{Tr}[\ln[\kappa(iu)]] - E_{\text{self}}. \quad (3)$$

Finally, we often (but not always [76,116]) expand the truly nonlocal correlation term

$$E_c^{\text{nl}}[\rho] \equiv E_{\text{xc}}^{\text{vdW-DF}} - E_{\text{xc}}^{\text{in}}, \quad (4)$$

in terms of both the Lindhard screening and the exponential resummation to second order in $S_{\text{xc}}(\omega)$ [47,77,79]:

$$E_c^{\text{nl}} = \int \frac{du}{2\pi} \text{Tr}[S_{\text{xc}}^2 - (\nabla S_{\text{xc}} \cdot \nabla G)^2]. \quad (5)$$

The complete specification of the CX energy functional [73,74] is denoted $E_{\text{xc}}^{\text{CX}}$. It has an exchange component that mirrors that of $E_{\text{xc}}^{\text{in}}$ (as far as possible) to ensure XC balance in calculations of energy differences [47,73]. CX yields a local effective potential that defines the equation of motion for the KS-DFT orbitals. The consistent focus on the plasmon behavior means that the specification of the total correlation, $E_c^{\text{LDA}} + E_c^{\text{nl}}$, is explicitly given by the density. Using Eq. (5) we can even cast the nonlocal-correlation energy functional [59,77]

$$E_c^{\text{nl}} = \frac{1}{2} \iint \rho(\mathbf{r}) \Phi_c^{\text{nl}}[\rho](\mathbf{r}, \mathbf{r}') \rho(\mathbf{r}') d\mathbf{r} d\mathbf{r}', \quad (6)$$

with a spline representation [86] for what is a universal nonlocal-correlation kernel $\Phi_c^{\text{nl}}[\rho]$. This keeps computational costs comparable to that of any GGA-based KS-DFT [86], for example, PBE [58].

B. The exchange choice in CX and KI-CX

We see two advantages of focusing on KI-CX(CX), in effect, prioritizing what is a consistent exchange component to balance the nonlocal correlation description [47,73]. First, the CX performs well as a general-purpose vdW-inclusive XC functional for KS-DFT [3,40,47,63,64,73–75,121–123] and we trust it also when addressing complex- and soft-matter problems [65,74,124–128]. For example, CX has a track record of working together with GW in predictions of QPs for the weakly interacting oligoacene crystals [3]. Second, the CX design stands out (among the vdW-DF versions and variants) as being the most direct implementation of the formally exact ACF recast that defines the vdW-DF framework [47,59,77,78]. The current conservation is as important as the screening logic summarized above, because the vdW-DFs tracks integrated shifts in plasmons [47,78,120]. We base our vdW-inclusive KI-DFT studies on the CX because it preserves the screening and current-conservation logic of the overall vdW-DF framework as far as it goes [39,47,73]. Our here-introduced KI-CX(CX) studies not only leads the way at getting vdW interactions consistently represented in KI-DFT QP predictions, CX is also deserving, by its

consistency emphasis, of being cross tested on the QP nature that CX implicitly reflects [47,62].

In a set of recent designs we have sought to design and leverage generalized-KS vdW-DFs [30,36,39,40,129,130]. This is done in part to overcome residual accuracy issues in PBE or CX KS-DFT characterizations and sometimes also in the PBE-based RSH, denoted HSE [20,35,37,131]. Starting, for example, with two robust vdW-DF versions, CX and rev-vdW-DF2 [132], and replacing, for example, part of the short-ranged GGA exchange, we arrive at two RSH vdW-DFs, denoted AHCX [39] and AHBR [40]. They generalize the HSE by providing a consistent inclusion of truly nonlocal-correlation effects and, in particular vdW interactions. The AHCX and AHBR are general-purpose options, noting that they are applicable also to metallic systems [39,40] and for cases where we can expect strong static-correlation effects on molecular structure [128]. Still, we can motivate adjustments of these basic RSH vdW-DF designs when used for example, for molecular systems where we expect an absence of asymptotic screening in the exchange descriptions. This is implemented in our recent AHBR-mRSH [21,30,133] that can be combined with the optimal-tuning argument [21–23,34,133,134]. Excitingly, use of AHBR-mRSH with optimal tuning constitute a generalized KS-DFT that complies with the PWL constraint [14,22,30,34,97] and has high accuracy for both binding energies and QPs of nitrogen-base systems [30,41].

The present work implicitly suggests moving KI-DFT towards a vdW-DF start and thus to supplement our introduction of the optimally tuned AHBR-mRSH as a QP predictor. The same applies also (to some extent) for approaches and when a Hubbard-U term (U) [12,135,136] is added to vdW-DF as the starting XC functional choice [137]. All of these methods restore PWL [61] to varying extents and, for example, RSH vdW-DFs simultaneously improve parameter-free vdW-DF descriptions of total energies and structure [40]. Also, AHBR-mRSH delivers QP predictions that employ the same nonlocal-correlation description [118] that is already in wide KS-DFT usage [30,40,132]. However, by including some Fock exchange in AHBR-mRSH we also simultaneously correct some density-driven errors, e.g. for transition states, that affects the underlying rev-vdW-DF2 functional [30,40]. In contrast, the here-introduced KI-CX approach (further described below) leaves the GS energies and structure unchanged [18,43] and tests CX simultaneously and consistently on GS and QP properties.

C. CX in Koopmans DFT: KI-CX(CX)

The eigenstates of KS-DFT, obtained using a regular XC functional like CX, provide a first approximation for studying charge excitations [13,24]. Still, while KS-DFT serves us to accurately predict GS properties, its eigenvalues ϵ_i^{KS} and orbitals $\phi_i^{\text{KS}}(\mathbf{r})$ do not directly describe charged excitations such as the set of vertical ionization energies, i.e., the QPs. This is true even though we can determine a frequency moment of the fully interacting spectral function directly from the terms of the KS-DFT energy descriptions [62,83,138].

The limitation of using KS-DFT orbitals as a predictor for QPs arises because KS-DFT relies on using (regular,

nonhybrid) XC functionals to define an effective local potential contribution [21,44] that helps set the orbital structure. Plotting the total energy as a function of the number of electrons then yields a convex curvature [21]. Use of regular XC functionals to thus get KS-DFT orbitals implies a lack of the PWL that is, for example, needed for a DFT-type framework to also satisfy a thermodynamics constraints on charge transfers [21,97].

Additional information, concealed as MBPT input to the XC functional designs, is needed to also recover accurate results for QP levels [14,21,22]. Fortunately, the information is still formally retained in the MBPT input and physics logic of good XC designs [62]. By switching to Koopmans-compliant DFT and using the KI-DFT framework with a LR extensions of an underlying XC functional (like PBE or the CX version of the vdW-DF method), we can leverage more of the underlying MBPT contents [44,47,62] of such robust XC designs also for accurate QP predictions [18,22,30,34,98,133].

On a formal level, KI-DFT employs a class of orbital-density-dependent functionals (ODDFs) designed to enforce *generalized PWL*. Specifically, the ODDFs are crafted to enforce that we have a linear energy change with respect to variations in the electron occupation [14,21,97]. The CX-based adjustments for KI-DFT, what can also be called the Koopmans functional, is given:

$$E_{\text{xc}}^{\text{KI-CX}}[\rho, \{\rho_i\}] = E_{\text{xc}}^{\text{CX}}[\rho] + \sum_i \alpha_i \Pi_i^{\text{CX}}[\rho, \rho_i]. \quad (7)$$

Here $\{\alpha_i\}$ are screening parameters that account for electronic relaxation effects and ρ_i are orbital-specific density variations $\rho_i(\mathbf{r}) = f_i |\phi_i(\mathbf{r})|^2$, with $0 < f_i < 1$ [14]. We are using the KI form [16,18,42,43] so that the formal KI-functional specification, $E_{\text{xc}}^{\text{KI-CX}}[\rho, \{\rho_i\}]$, reduces exactly to the underlying CX functional form when there is an integer charge in the unit cell (and hence KI-CX does not change KS-DFT structure predictions obtained by CX). However, for partial orbital occupation, the Koopmans-correction term Π_i^{CX} in Eq. (7) restores PWL: It converts the nonlinear dependence of the CX functional on changes in orbital-specific occupations, $\int \rho_i(\mathbf{r}) d\mathbf{r}$, into a linear form between any two integer occupations. This approach suffices to convert the KS-DFT input (i.e., the choice of the XC) into the KI-DFT tool for making corresponding QP predictions [17,42,43]. Further details are provided in Refs. [14,43].

Conventionally, spectral properties computed via Eq. (7) require minimization of, e.g., the $E_{\text{xc}}^{\text{KI-CX}}[\rho, \{\rho_i\}]$ term, through a two-step nested procedure. The inner loop minimizes the orbital-density-dependent functional contribution, while the outer loop optimizes orbitals in directions orthogonal to the subspace. At convergence one obtain the variational orbitals. These variational orbitals enable computation of $\{\alpha_i\}$ via finite differences. For periodic systems, this parametrization approach requires supercell treatment to eliminate spurious interactions between periodic images.

Although this method rigorously provides both variational orbitals and $\{\alpha_i\}$, its application remains challenging due to the requirement of multiple constrained DFT and Koopmans calculations in supercells for periodic systems. To address this limitation, the KCW formulation, discussed in Refs. [17,18,139], employs a second-order Taylor expansion

of $\Pi_i[\rho, \rho_i]$ and use of DFPT in primitive cells. This approach assumes coincidence between variational orbitals and maximally localized Wannier functions (MLWFs) $\{w_{\mathbf{k}}\}$ [140], that are computed by use of the same underlying functional. These MLWFs simplify the minimization of $E_{\text{xc}}^{\text{KI-CX}}[\rho, \{\rho_i\}]$.

To obtain spectral properties within KCW, the resulting total energy $E_{\text{tot}}^{\text{KI-CX}}[\rho]$ is varied with respect to the orbital densities $\rho_i(\mathbf{r})$. This is done by representing it in the Wannier-function basis set

$$\langle w_{\mathbf{k}i} | (\hat{h}^{\text{CX}} + \alpha_{0i} \mathcal{V}_{0i}^{\text{CX}}) | w_{\mathbf{k}j} \rangle = \mathcal{H}_{ij}(\mathbf{k}), \quad (8)$$

where $\mathcal{V}_{0i}^{\text{KI}}$ is the orbital-density-dependent potential (ODDP) and corresponds to the variation $\delta \sum_j \Pi_j / \delta \rho_i$, and $\hat{h}^{\text{CX}}$ is the effective potential defined by CX functional [27]. The subscript index 0 in $\mathcal{V}_{0i}^{\text{CX}}$ and α_{0i} refers to a decomposition into a set of independent problems, where a supercell calculation with Γ -point sampling corresponds to sampling the folded Brillouin zone (BZ) of the primitive cell [18]. Hamiltonian diagonalization in Eq. (8),

$$\mathcal{H}_{ij}(\mathbf{k}) \rightarrow \varepsilon_{\mathbf{k}i} \delta_{ij}, \quad (9)$$

yields so-called canonical orbitals that corresponds to the eigenvectors $\tilde{w}_{\mathbf{k}i}$. The eigenvalues of Eq. (9), $\varepsilon_{\mathbf{k}i}$ define the KI-CX (or KI-DFT) predictions for the QP energies. We note that the canonical orbitals have a Bloch-wave-function-like character; They are delocalized as they are linear combination of MLWFs $w_{\mathbf{k}i}$. It has been shown that use of an ODDP can provide a QP approximation to the frequency-dependent contraction of the many-body self-energy term [15]. The implication is that ODDFs have the flexibility to accurately describe both total energies and QP excitations.

To elucidate the role of the CX functional in the QP states described by Eq. (8), we note the dependence on the XC kernel f_{Hxc} , that is, the double derivative of the XC energy functional with density variations. This kernel includes a contributions from the nonlocal-correlation energy functional defined in Eq. (5), specifically, through its second functional derivative:

$$f_c^{\text{nl}}(\mathbf{r}, \mathbf{r}') = \frac{\delta^2 E_c^{\text{nl}}[\rho]}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')}. \quad (10)$$

This LR kernel f_c^{nl} depends itself on the electronic density $\rho(\mathbf{r})$. This dependence is in turn explicitly incorporated into the screening parameters $\{\alpha_i\}$, thereby influencing the QP energy solutions.

Appendix A provides details on a formal representation of a plane-wave and grid-based determination of Eq. (10) using the Roman-Soler spline formulation [86] for (the functional nature [59,77,78] of) the nonlocal-correlation kernel $\Phi_c^{\text{nl}}[\rho](\mathbf{r}, \mathbf{r}')$ entering Eq. (6). The formal expressions are already coded in the LR module (KCW) of QE thanks to a previous study documenting fingerprints of vdW and nonlocal-correlation interactions on phonon predictions [87].

III. COMPUTATIONAL DETAILS

We compute the QP states by the KOOPMANS-DFT code package [19,43], using the KI-DFT versions, and the above-summarized KCW formulation [18]. All those calculations as well corresponding KS-DFT studies are done using

norm-conserving PBE-type (scalar-relativistic) pseudopotentials from the PseudoDojo library [141]. That is, we employ dual projectors and generalized norm conservation to accurately reproduce all-electron potential binding and scattering properties. Appendix B presents a discussion of numerical stability and fair convergence for the QP-energy predictions with the wave-function energy cutoff $E_{\text{cut}}^{\text{ef}}$ and with the k -point sampling (as well as, for the strictly two-dimensional BN1 system, the height c of the modeling cell). This analysis leads us to use $E_{\text{cut}}^{\text{wf}} = 200$ Ry (400 Ry) for the wave-function grid for bulk (single-sheet) h-BN and a 7×7 in-plane k -point sampling. We double the grid for the density variations. Exceptions are explicitly stated.

The workflow for KI-DFT QP studies can be summarized in the following steps:

- (1) Do a MLWFs ($\{w_{\mathbf{k}i}\}$) for the KS states.
- (2) Convert the $\{w_{\mathbf{k}i}\}$ to Wannier orbital densities $\{w_{\mathbf{k}i}^* w_{\mathbf{k}i}\}$.
- (3) Calculate $\{\alpha_{\mathbf{k}i}\}$ via DFPT.
- (4) Diagonalize the Hamiltonian in Eq. (8) to obtain $\{\tilde{w}_{\mathbf{k}i}\}$ and $\{\varepsilon_{\mathbf{k}i}\}$.

In the initial step, KOOPMANS code executes the QE codes PW.X and PH.X. Subsequently, the MLWF algorithm is carried out through PW2WANNIER90.X and WANNIER90.X [142]. Steps 2 through 4 employ the KCW.X code that also gave the workflow naming [18].

The QP band structure calculations is given by Eqs. (7) and (8); The orbital resulting in KI-CX results are themselves the KI-CX QP predictions. These results are compared to QP states of KI-PBE and the KS states of the corresponding underlying functionals CX and PBE. KI-PBE calculations are standard in the KOOPMANS-DFT code. To do band structure calculations with KI-CX it is necessary to explicitly introduce a selection of the CX functional in the “QE” specification; see the tutorial [19].

We compute QP states in KI-CX/KI-CX(CX), technically, “Koopmans DFPT” [18] with a CX start, for the h-BN monolayer (BN1) and for bulk h-BN in the experimentally observed AB and AA' stacking configurations. The structural characters of these h-BN systems are illustrated in Fig. 1 that also identifies the set of relevant high-symmetry k -points in the BZ).

The BN1 structure (first column) is a monolayer exhibiting the conventional *honeycomb* lattice, where boron (green) and nitrogen (gray) atoms with valence 3 occupy alternating vertices of the hexagonal network. In-plane sp^2 bonding between boron and nitrogen atoms provides structural stability and rigidity for this single-sheet system. The choice of in-plane lattice constants for the BN1 system is set by an early experimental structure characterizations of h-BN [143]: For BN1 we use an hexagonal unit cell with in-plane parameters $a = b = 2.504$ Å and a $7 \times 7 \times 1$ k -point grid sampling. In our periodic modeling used for QE studies we set $c = 20$ Å; This choice gives sufficient distance between repeated images of the BN1 layer that we can, in practice, ignore spurious interlayer forces in characterizations of cohesion as well as of QP energies, as discussed in Appendix B.

Bulk AB stacking (second column of Fig. 1) features a graphite-like staggered arrangement of hexagons where half of the atoms (for example, all of the nitrogens) sit directly on top of a different type of atom in neighboring layers. For our

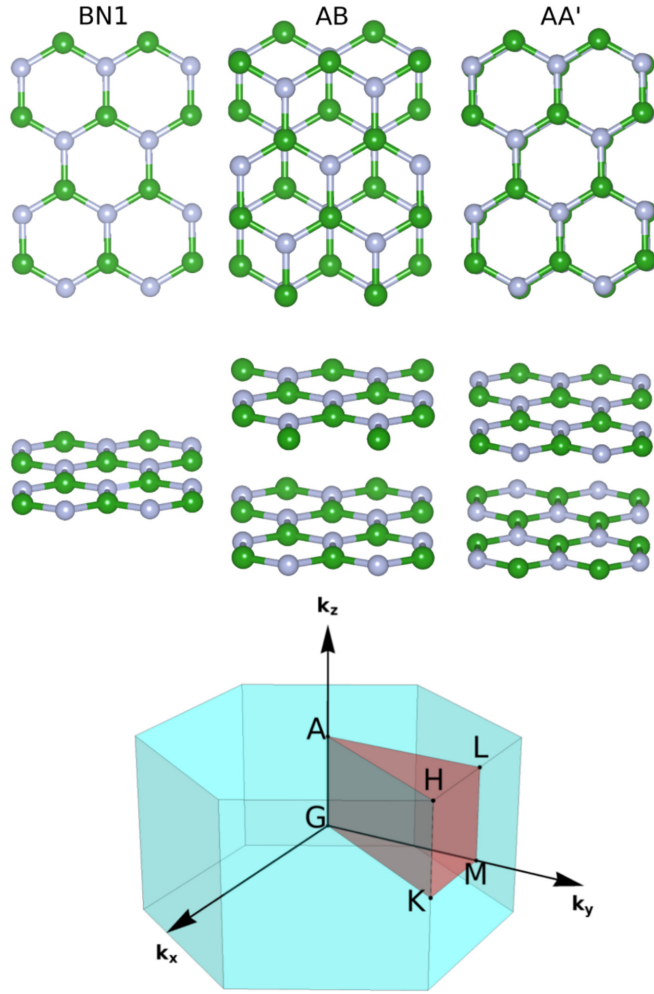


FIG. 1. Atomic as well as BZ structure of h-BN structures in the single-sheet form, denoted BN1, and in the two stable bulk forms, AB and AA'. The panels of the first and second row show the atomic structures as shown from a perspective perpendicular and parallel to the slide plane. The bottom panel shows the BZ of the bulk h-BN forms in blue and the reduced BZ zone in red. This panel also identifies the set of high-symmetry k -points of the reduced BZ for these systems with a hexagonal unit cell. In addition, a k point “T” [68] (not shown here, but lying along the “G” to “K” path, close to “K”) is potentially relevant for the h-BN systems because these may also be represented within an orthorhombic unit cell. The “T” k point emerges as the VBM in bulk-h-BN as seen in both experiment [69] and (theory [68,101,144] and by the presently launched KI-CX QP predictor) because the interlayer vdW and nonlocal-correlation binding in bulk h-BN causes what is termed a trigonal warping [69], splitting two π bands that are otherwise degenerate near the “K” point.

AB calculations, we use a $7 \times 7 \times 3$ k -point grid with lattice constants set at an average over measurements on what are interpret [145] as experimentally characterized AB structures, $a = b = 2.505 \text{ \AA}$ and $c = 6.661 \text{ \AA}$.

The third column of panels in Fig. 1 show schematics of the AA' form that is the ground state of h-BN. Contrary to the AB form, the ground-state configuration stacks the BN layers so that all of boron (nitrogen) atoms in a given layer sit directly above a nitrogen (boron) atom in neighboring layers.

TABLE I. Projections for the iterated MLWF determination.

Site	Angular momentum $\Theta(\theta, \phi)$	Radial functions
Occupied bands		
N	s	$R_2(r)$
N	p_x, p_y, p_z	$R_2(r)$
Virtual bands		
B	p_z	$R_2(r)$

For our AA' studies, we use an hexagonal unit cell with lattice constants, $a = b = 2.504 \text{ \AA}$ and $c = 6.66 \text{ \AA}$, that represent averages of values extracted by experiments [143,145,146]. Also, we again use a $7 \times 7 \times 3$ k -point sampling.

Additionally, we include a study demonstrating the full vdW impact on the QP band structure, contrasting what we call consistent-KI-CX and consistent-KI-PBE descriptions. That is, we track not only the *direct* changes arising when we switch from a PBE to a CX starting point in KI-DFT at the same fixed geometry, but also the *additional indirect signatures* that arise because a GGA PBE is not set up to accurately characterize the bulk h-BN structure [47,99,99,147]. The importance of this is discussed in the following Sec. IV. In practice, we complete KI-PBE and KI-CX QP characterizations, having first relaxed the interlayer distance of the AA' system using KS-DFT with the PBE and the CX functionals, respectively. Specifically, we find that CX-based and PBE-based structure optimizations yield lattice constants $c = 6.448 \text{ \AA}$ and $c = 8.560 \text{ \AA}$, respectively. The former and latter structure is then used in ensuing KI-CX(CX) and KI-PBE(PBE) QP characterizations.

For the three materials forms at experimental structures, and for the demonstration of indirect vdW fingerprints, we presents analysis of the resulting QP band structures, using a shared computational treatment. The Gygi-Baldereschi method [148] is used to address the $\mathbf{q} \rightarrow 0$ divergence of the Coulomb interaction in our periodic systems, both in the initial QE code stages and when setting the screening coefficients α_i for the KI-DFT studies, above. The Gygi-Balderashi approach assumes some level of isotropy and its use is more motivated for the bulk BN cases than for the single-sheet BN1 system.

As highlighted in Eq. (8), Wannier functions serve as the initial basis for our set of KOOPMANS DFPT studies. That is, we use MLWFs to generate localized orbitals $\{|w_{\mathbf{R}_i}\rangle\}$ and we find a set of initial Wannier functions that work for the layered h-BN systems. These initial Wannier functions are selected using an initial projected density of states (PDOS) that we obtain via use of the QE PROJWFC.X code. They take the form of modified spherical harmonics, with details listed in Table I.

The occupied bands are located at the nitrogen atoms in the unit cell, with the angular momentum shapes s and p_x, p_y , and p_z and each of these having a radial function $R_2(r)$. For the virtual states we chose p_z but now located at the boron atoms, with the radial functions $R_2(r)$. This process is verified by the convergence of the MLWF algorithm. We have also tried to use hybrid sp^2 orbitals instead but they did not converge in the MLWF procedure, even though suggested by chemical intuition.

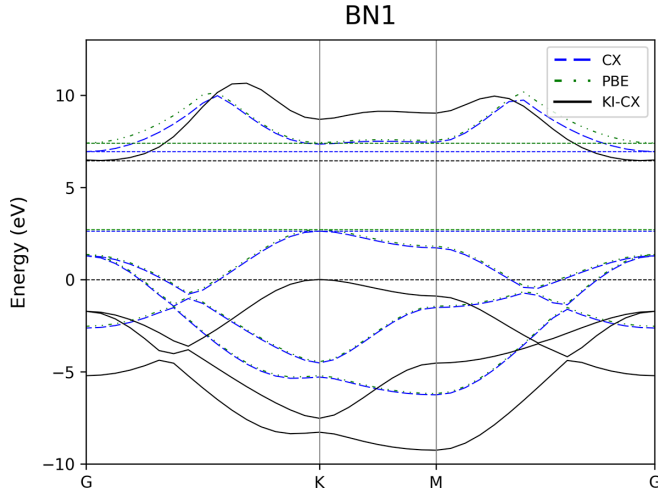


FIG. 2. Comparison of BN1 QP band structure predictions, as evaluated in PBE, CX and in KI-CX in a $c = 20$ Å cell to minimize the impact of spurious couplings between repeated images in our plane-wave-DFT studies. The top of the KI-CX QP-valence band is used as a shared reference energy, as motivated in the text.

Beyond initial Wannier-function selection, we must disentangle virtual bands from occupied states to construct well-localized Wannier functions. The disentanglement window spans from the Kohn-Sham highest occupied molecular orbital (HOMO) to `dis_win_max`, which defines the upper energy bound for disentanglement. Simultaneously, `dis_froz_max` sets the upper limit of the frozen energy window. The layered bulk systems AA' and AB we employ parameter values of `dis_froz_max` = 0.6 eV and `dis_win_max` = 16.0 eV. For the monolayer BN1 system, we adjust these parameters to `dis_froz_max` = 0.5 eV and `dis_win_max` = 14.0 eV.

In contrasting predictions of the KI-DFT predictions and KS-DFT approximations for the QP band structures we face, in principle, a problem of how to pick a reference energy. Band structure characterizations are often reported with QP energies listed relative to the valence band maximum (VBM) but such values are generally affected by both the atom configurations and choice of methodology. Ideally, as the QPs reflect vertical excitations, we would like to list the variation with QP energies defined relative to the true vacuum. However, in a plane-wave code like QE, we can only get orbital-energy values relative to what is the average electrostatic potential in a given cell, with a given atomic configuration (and choice of pseudopotentials) and for the electron-density variation that is produced in the given DFT method and given choice of XC functional [149].

Nevertheless, in predictions and discussions of the QP band structure differences *at fixed experimental structures*, it is possible and motivated to define a common reference. Specifically, in Figs. 2 and 3 we have shifted all the bands using

$$\sum_{\mathbf{k},i} \varepsilon_{\mathbf{k}i}^M = \sum_{\mathbf{k},i} \varepsilon_{\mathbf{k}i}^M - \varepsilon_{\text{VBM}}^{\text{KI-CX}}, \quad (11)$$

where $\varepsilon_{\text{VBM}}^{\text{KI-CX}}$ the VBM of KI-CX and where M corresponds to difference choices of the methodologies: PBE, CX, KI-PBE, and KI-CX. The point is that since the atomic and cell geometry are shared (and we use the same pseudopotentials in all studies) the average electrostatic potential can only vary because of differences in the electron-density variation. However, PBE and CX are both widely tested and both documented to provide highly accurate accounts of the electron-density variations (at fixed structure) that must therefore be almost identical in the case of PBE and CX studies. Furthermore, by design of the KI-DFT method, it is also so that the KI-CX and CX yields exactly the same electron density variations (at shared geometries), and the same applies for KI-PBE and PBE [43]. By the explicit procedure that the QE code uses to set the average electrostatic potentials [149,150], no differences can therefore arise for the electrostatic reference energy in KI-CX and CX. The *same offset* brings the here-reported band structures in alignment with a QP band structure mapping that reflects the true vacuum level.

IV. RESULTS AND DISCUSSION

Unlike graphite, h-BN experimentally demonstrates five distinct stacking arrangements, with only two being thermodynamically stable and the remaining three metastable [151,152]. A key factor driving interest in h-BN is its wide band gap, which is systematically underestimated in KS-DFT [152]. In contrast, GW approximations align more closely with experimental observations [5]. Here we seek to compute and contrast QP band structure results of the stable h-BN forms AA'-stacked, AB-stacked, and monolayer h-BN (BN1) (Fig. 1).

Our study and analysis highlight changes arising as we move from KS-DFT to KI-DFT and as we include (in KI-CX) nonlocal-correlation effects. In particular, we track differences (i) between use of semilocal and truly nonlocal-correlations in KS-DFT (PBE vs CX results); (ii) between use of a semi-local functional for KS-DFT and for its KI-DFT counterpart (PBE vs KI-PBE); (iii) between use of a vdW-DF for KS-DFT and for the corresponding KI-DFT (CX vs KI-CX); and finally, (iv) arising when we include truly nonlocal correlations in KI-DFT (comparing KI-CX and KI-PBE results).

A. Band structure results and analysis

In Figs. 2 and 3 we show comparisons of the band structure predictions obtained at experimental structures by our set of methodologies.

Figure 2 summarizes our results for the single-sheet BN1 case (at an experimentally relevant atomic in-plane geometry). We trace out the QP dispersion along a k -point path defined by the string “GKMG” of high-symmetry points that are relevant for a two-dimensional hexagonal system; see bottom panel of Fig. 1.

Figure 3 presents our band structure predictions obtained for the two h-BN bulk systems (AB and AA'). We now trace out the QP-energy variation along a richer path, “GKM-GAHLA,” of the high-symmetry k -points that are relevant for such bulk hexagonal systems; see again the bottom panel of

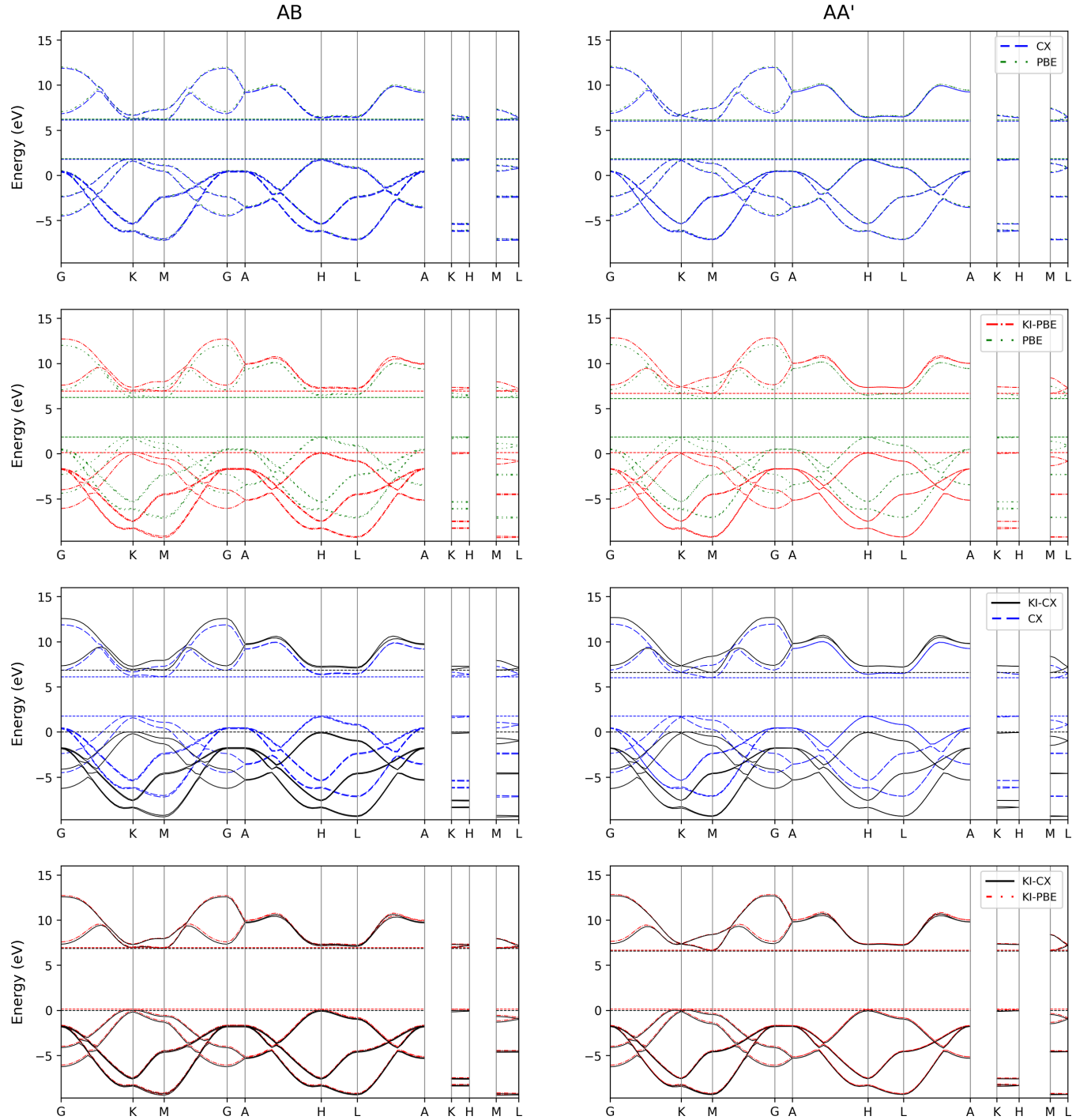


FIG. 3. Band structure comparison for h-BN structures AB and AA', with KI-PBE and KI-CX results provided in KI-DFT and PBE and CX results in KS-DFT, i.e., using the same underlying CX functionals.

Fig. 1. The panels in the first (second) column of Fig. 3, report our results for bulk h-BN in the AB (AA') form. The first row of panels presents comparisons of the QP band structure approximations defined by KS orbitals and obtained in PBE and CX, for the two bulk structures. The third (second) row of panels contrasts QP predictions as provided by CX and KI-CX (by PBE and KI-PBE) studies. The last row of panels reports comparisons of KI-PBE and KI-CX QP predictions, again for the two bulk h-BN forms.

We note in passing, that we are not showing the internal (2s) first bands in any of our band structure mappings. This is done to present a clearer view of what is happening near the valence and conduction band edges.

In the following discussion of the band structures, we will use subscripts at symmetry points to denote the valence and conduction bands that define various (generally indirect) gaps of potential key interband transitions. For example, K_c indicates the conduction band at the K point, while K_v denotes

TABLE II. QP-gap energies (in eV) by PBE, CX, and KI-CX for valence-to-conduction-band transitions at different symmetry points for the single-sheet h-BN structure BN1, with comparison to literature GW_0 and to “GW@WOT,” that is, G_0W_0 that is initialized by the electronic structure predicted via a Wannier-localized optimally tuned RSH study [23].

Method	$G_v \rightarrow G_c$	$M_v \rightarrow M_c$	$K_v \rightarrow G_c$	$K_v \rightarrow K_c$	$M_v \rightarrow G_c$	$K_v \rightarrow M_c$	Fundamental gap
PBE	6.04	5.74	4.69	4.71	5.59	4.83	4.69 ^a
CX	5.65	5.74	4.31	4.72	5.22	4.83	4.31
KI-CX ^b	8.21	9.92	6.48	8.69	7.38	9.02	6.48
KI-CX ^c	8.20	9.99	6.47	8.72	7.37	9.09	6.47
GW_0 ^d			7.43	7.90		8.00	7.43
GW@WOT ^e				8.70			

^aNearly degenerate.

^bComputed at $c = 20 \text{ \AA}$, at $E_{\text{cut}}^{\text{wf}} = 400 \text{ [Ry]}$.

^cComputed at $c = 30 \text{ \AA}$, at $E_{\text{cut}}^{\text{wf}} = 400 \text{ [Ry]}$.

^dRef. [103].

^eRef. [23].

the valence band at the same symmetry point. The set of key (potential) interband transitions are identified by the start and end points, e.g., $K_v \rightarrow K_c$, when we summarize and discuss our set of QP predictions across the structures.

1. BN1

In Fig. 2 we compare PBE, CX and KI-CX results for the QP band structure in the monolayer BN1 system, here in the standard set up using a $c = 20 \text{ \AA}$ cell height for the computational modeling. Table II provides a compilation of our quantitative results for gaps defined by valence-to-conduction-band transitions among the set of high-symmetry k -points. We note that we could not complete a corresponding KI-PBE study because the KI-DFT computational scheme fails to converge the screening parameters that enter in the KI-PBE functional for conduction-band QPs.

Contrasting the KS-DFT descriptions by PBE and CX, we observe a small (a fraction of an eV) rigid downward shift for the valence bands in CX relative to PBE. In the conduction band, CX shifts states downwards occurring at G_c , resulting in a slightly reduced band gap. In both cases, the VBM resides at the K_v symmetry point. The crucial difference lies in the conduction band minima (CBM): PBE finds the CBM as essentially degenerate between K_c and G_c , predicting a minimum direct QP band gap $K_v \rightarrow K_c$ of 4.71 eV and minimum indirect gap $K_v \rightarrow G_c$ of 4.69 eV. In contrast, CX clearly indicates the indirect transition $K_v \rightarrow G_c$ as the fundamental gap at 4.31 eV (compared to 4.72 eV for $K_v \rightarrow K_c$), in qualitatively agreement with GW_0 results; see Table II.

Comparison of KI-CX with CX results reveals an essentially rigid downward shift of about 2.5 eV in the KI-CX valence bands. For the conduction band we see that KI-CX lowers the G_c QP energy, while M_c and K_c QP energies are shifted upwards. As a consequence, we find that use of KI-CX as a QP predictor does adjust the underestimated PBE and CX gaps.

The left panel of Fig. 4 shows a plot of the QP wavefunction as obtained by KI-CX for the conduction-band at the high-symmetry Γ point “G.” This variation is shown for reference. It allows us to illustrate and discuss some of the impacts that the interlayer vdW attraction has on the details of bulk-AB and bulk-AA’ QPs, next.

2. AB

In the first column of Fig. 3 (identified by an “AB” header), we show comparisons of the QP dispersion relations for bulk h-BN in the AB structure. The top section of Table III shows a numerical comparison of the gap predictions that we extract for the set of valence-to-conduction QP band gaps.

In the first row of the AB column of Fig. 3, contrasting PBE and CX results, we observe that the valence bands are nearly identical by either of these KS-DFT descriptions. There is merely a small shift of $\approx 0.01 \text{ eV}$ downward in CX near G_c . The VBM is located at H_v . The indirect QP gap reflects a transition $H_v \rightarrow M_c$ at 4.39 eV and 4.36 eV for PBE and CX, correspondingly.

The second-row panel of AB results shows the comparison of PBE and KI-PBE. The occupied bands of KI-PBE are down-shifted relative to PBE, while the unoccupied bands are shifted higher in energy in KI-PBE. In KI-PBE, the fundamental band gap is indirect and corresponds to the transition $T_v \rightarrow M_c$ at 6.83 eV. Here T_v is a k point that lies on the path from G_v to K_v , being close to K_v , and can be seen as a symmetry point corresponding to an orthorhombic-cell representation of the h-BN system. This AB-system VBM corresponds (as a shifted K_v point) to the k point that is also identified as the VBM for the AA’ system in GW [68], HSE + D3 [101,131,153] and even LDA [144] studies. The shift $K_v \rightarrow T_v$ of the VBM reflects a lifting of degeneracy (with interlayer binding) of the two (frontier) π bands, around K_v [69]. We find this lifting of the degeneracy at K_v sets the VBM in KI-PBE and KI-CX as well as (to a lesser extent) in PBE and CX studies for both the AB and AA’ forms of bulk h-BN, and we discuss the nature of the VBM shift further in Sec. IV C. Within the present focus on characterizing the QP band structure for the AB form we furthermore observe that degeneracy of the unoccupied bands breaks between $A_c - H_c$ and $L_c - A_c$ in the KI-PBE description.

In the third-row panel, comparing KI-CX and CX results, we find that use of KI-CX again produces an overall down-shifting of the valence-type QP bands while in the conduction bands we observe some differences. Like for KI-PBE, in the upper part of the BZ hexagon (spanned by high-symmetry points A-H-L-A, Fig. 1), we observe a breaking of the degeneracy between $A_c - H_c$ and $L_c - A_c$. The results of the

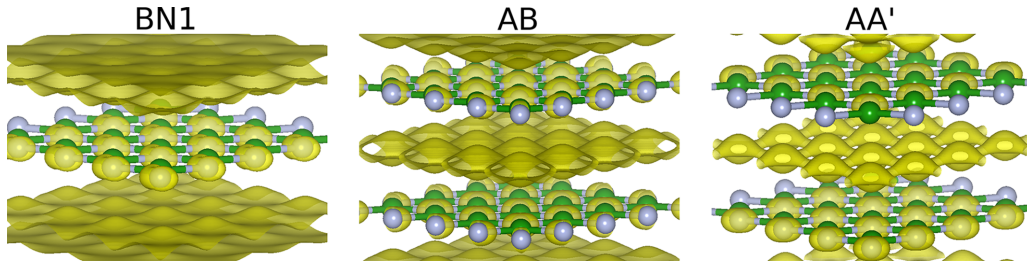


FIG. 4. Real-space canonical orbital densities $|\langle \mathbf{r} | \tilde{w}_{\mathbf{R}_i} \rangle|^2$ at the CBM for h-BN structures BN1, AB, and AA', computed using Koopmans-DFT as KI-CX. The iso-surface constant for BN1 is 5 meV and for AB and AA' corresponds to 7 meV.

second- and third-row panels, taken together, suggest that the use of KI-DFT and the enforcement of PWL (rather than the choice of underlying functional) is responsible for breaking this conduction-band degeneracy. KI-CX predicts the $T_v \rightarrow M_c$ transition as the fundamental gap, at 6.87 eV.

In the last-row panel of AB results, we compare the Koopmans methods directly and find that use of KI-CX gives predictions for valence and conduction bands that primarily causes a small downward shift, largest around G_c . For the conduction bands, between $A_c - H_c$ and $L_c - A_c$, we also observe a slightly smaller separation between the bands in KI-CX near A_c .

The second panel of Fig. 4 shows the canonical orbital density predicted by KI-CX at the CBM. Contrasting with the corresponding BN1 panel, we find that there is now a different p_z -orbital character reflecting orbital overlaps mid-way between the layers. For the small σ -orbital signature of the VBMs, centered on the nitrogen atoms, there are also

differences. These VBM changes arise because the vdW forces provide interlayer attraction to shorten the interlayer separation from essentially decoupled to the experimental value that characterizes our AB study [40,76,79,99]. As such, the QP CBM changes represent vdW signatures but they should be seen as indirect [147], set exclusively by the structural change. In fact, use of the KI-CX and KI-PBE (not shown in Fig. 4) at the experimental structure yields almost identical details in QP CBM orbital densities.

3. AA'

The last column of panels of Fig. 3 reports our predictions for the QP band structure of the AA' system, as described in our set of functionals and DFT frameworks. The bottom section of Table III provides a comparison of our numerical results for the set of high-symmetry band gaps among the methods and with literature GW characterizations and experiment.

TABLE III. QP gap predictions (in eV) for valence-to-conduction-band transitions in h-BN bulk structures AB and AA'. Our results computed in the Koopmans-corrected functionals KI-PBE and KI-CX, as well as in the underlying KS-DFT functionals PBE and CX, are compared to literature GW values and experiment, where available.

Method	$G_v \rightarrow G_c$	$M_v \rightarrow M_c$	$K_v \rightarrow G_c$	$K_v \rightarrow K_c$	$M_v \rightarrow G_c$	$K_v \rightarrow M_c$	Fundamental gap
AB							
PBE	6.53	5.10	5.22	4.51	5.91	4.41	4.39 ^a
CX	6.36	5.07	5.07	4.49	5.76	4.38	4.36 ^a
KI-PBE	9.23	7.52	7.48	6.92	8.14	6.86	6.83 ^b
KI-CX	9.06	7.56	7.36	6.96	8.01	6.90	6.87 ^b
HSE + D3 ^c				6.23			6.02 ^b
AA'							
PBE	6.58	4.75	5.35	4.95	5.71	4.39	4.28 ^b
CX	6.41	4.71	5.20	4.96	5.55	4.36	4.24 ^b
KI-PBE	9.30	7.02	7.62	7.39	7.97	6.67	6.54 ^b
KI-CX	9.14	7.06	7.50	7.46	7.85	6.71	6.58 ^b
KI-CX(CX)	8.65	6.88	7.06	7.49	7.30	6.64	6.47 ^b
GW ^d	8.40	6.50	6.90	6.90	7.30		5.95 ^b
GW@WOT ^e				7.77			
Exper. ^f							6.08

^aCorresponds to $H_v \rightarrow M_c$.

^bCorresponds to $T_v \rightarrow M_c$.

^cRef. [101].

^dRef. [103].

^eRef. [23].

^fRefs. [68,100].

In the first-row panel of AA' results in Fig. 3, we find a similar behavior as in the AB system. The PBE and CX results show no significant differences beyond a small displacement of valence bands, but some changes emerge for the virtual bands. The fundamental gaps emerging in PBE and CX studies reflect an indirect $T_v \rightarrow M_c$ transition at 4.28 and 4.24 eV, respectively. For both PBE and CX, we find that the VBM is at the same k point T_v for the AA' system as for the AB system, and we note that the T_v is consistently thus identified as the VBM for AA' in experiment [69] and in theory, including GW [68], HSE + D3 [101], LDA [144], as well as PBE and CX. The same applies also for KI-PBE and KI-CX, next.

In the second-row panel of AA' results, contrasting PBE and KI-PBE, we observe characteristics similar to those arising for the AB structure. The main difference from the AB case is that here KI-PBE reduces the gap by lowering the energy at the symmetry point M_c . KI-PBE predicts the fundamental-gap QP transition as $T_v \rightarrow M_c$, at 6.54 eV.

In the third-row panel, we contrast CX and KI-CX predictions for the QP band structure. As a Koopmans functional, KI-CX predicts what mostly amounts to an overall lowering of the occupied (valence-type) QP energies, relative to the CX description. However, we find that along the path from M_v to G_v , the band crossing occurs closer to G_v in KI-CX than for CX. A similar shift of band crossing is also evident between L_v and A_v .

Meanwhile, for the conduction-type QP states (unoccupied orbitals), we find that along the full path from G_c to A_c , the use of KI-CX produces a general shift (as does KI-PBE), resembling what is documented above for the AB system. The switch from CX to KI-CX causes an enhanced lowering of the conduction-type QP energies close to M_c . The KI-CX predicts (like KI-PBE) the transition $T_v \rightarrow M_c$ [101] as the fundamental gap, now at 6.58 eV.

Finally, we compare the two KI-DFT descriptions of the QP band structure in the last-row panel of AA' results. We find for the occupied orbitals that use of KI-CX slightly shifts the bands downward while otherwise maintaining a close similarity to KI-PBE results. Both functionals locate the VBM at T_v , again as in experiments and theory, e.g., Refs. [68,69]. Again, both methods predict that the fundamental gap corresponds to a QP transition $T_v \rightarrow M_c$ (Table III).

Nevertheless that are some differences. In the upper BZ region (tracing the set of "A-H-L-A" high-symmetry k points of the BZ) and around the Γ point "G," we observe that KI-CX predicts a small but systematic and visible lowering of valence-band QP energies compared with KI-PBE. There is also a very small uniform lowering of QP energies, which is expected since the reference value of the potential (by which we measure QP energy positions) is affected by the actual electron-density variation $\rho(\mathbf{r})$. While the CX and PBE densities are indeed so close that CX and PBE provide nearly identical work-function predictions for transition metals [47], there are small differences in the $\rho(\mathbf{r})$ profiles that we compute in CX (and hence in KI-CX) and in PBE (in KI-PBE).

The third panel of Fig. 4 identifies again signatures of the vdW interlayer attraction on the variation of the QP-CBM density evaluated at the M_c point. As for the AB structure, the KI-CX predictions for the CMB is a QP orbital which

exhibits lobes with p_z and π -bond characters that resemble those found for the AB structure. However, our KI-CX QP characterization for AA' shows that the corresponding CBM orbital density exhibits a modulation, it has periodically voids in the regions between the h-BN layers. These voids are found at positions that correspond to the centers of the h-BN-atom rings. In effect, we find that the CBM QP is trapped along bonds between the hexagonal network of boron and nitrogen atoms. Accordingly, there are also differences at the in-layer σ -bond positions.

Again we interpret these vdW-binding signatures as indirect QP effects because we find essentially no difference in behavior in the KI-PBE characterization of the AA' system (not shown). We repeat that the PBE lacks an account of vdW and other truly nonlocal correlation effects [47] and that KI-PBE cannot provide a full characterization of the QP signatures in bulk h-BN. The alignment of KI-CX and KI-PBE characterizations of QPs discussed so far only results because we consider bulk systems with the layer separations fixed at experimentally observed values. We shall return to more detailed arguments for seeing changes in the QP CBM spatial variation relative to the BN1 case, Fig. 4, as indirect vdW signatures.

B. Comparison with MBPT

Accuracy for BN1 QPs. Table II presents an overview of the quantitative results we find in the KI-CX characterization for BN1. We observe that both PBE and CX give gaps that are consistently smaller than those found in GW_0 [103]. While minimal differences exist between these functionals, PBE does yield a better agreement for the BN1 fundamental gap, at the $K_v \rightarrow G_c$ transition, while CX is in closer qualitative agreement with GW_0 in that it lifts the PBE near-degeneracy with the gap for the $K_v \rightarrow K_c$ transition. The descriptions of the QP energies can be seen as clearly improved in KI-CX.

Appendix B summarizes some challenges that we face in numerically converging these KI-CX results with respect to modeling parameters for BN1, for example, forcing us to use a higher $E_{\text{cut}}^{\text{wf}}$ for the conduction-band QP energies than what is required to converge the KS-DFT/KI-DFT total-energy description (or valence-band QP energies). We expect this numerical challenge arises, in part, because the screening assumption [148] that we presently need to use is not naturally set up to handle strictly two-dimensional problems. That is, future KI-CX (or KI-PBE) studies, using a better screening handling for two-dimensional systems [154], may permit computationally cheaper QP descriptions.

Accuracy for AA' QPs. Table III presents an overview of the accuracy that exists in PBE, CX, KI-PBE, and KI-CX predictions for the QP energies of bulk h-BN, our main focus. The assessments are made in terms of band gaps, that is, energy differences between QP transitions at the set of k points that correspond to local extrema in the QP band structure. Specifically, we make quantitative comparisons of QP predictions for these band gaps by comparing with literature GW results that exist for the bulk AA' structure [103]. We note in passing that the GW value for the AA'-system fundamental gap is in turn in agreement with experimental observations [68,100]; see Table III. We also note that our screening approximation

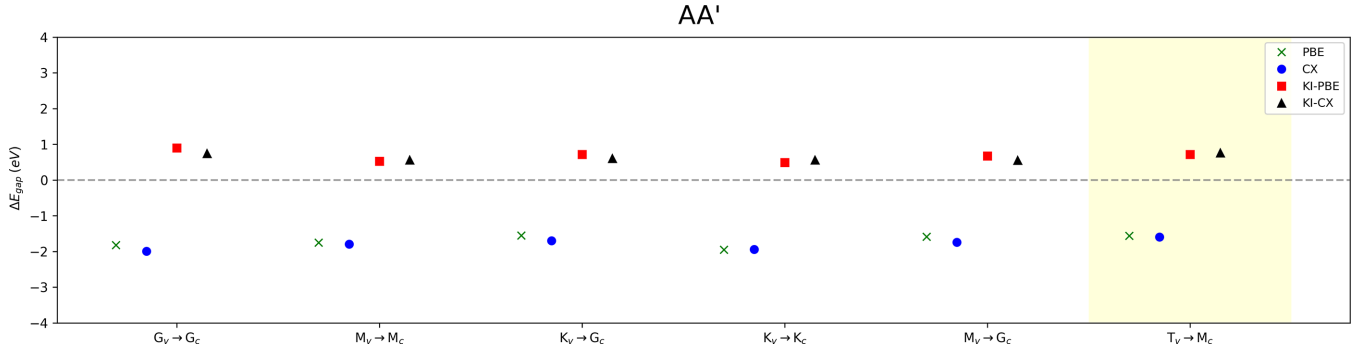


FIG. 5. Deviations with respect to GW of our set of predictions for QP transitions between the indicated set of high-symmetry k -points for AA' . We highlight the performance comparison at the fundamental gap, that is, for the QP transition that corresponds to having the smallest valence-conduction-band QP energy separation.

[148] is motivated for bulk systems and that we found these calculations robust already when picking the same $E_{\text{cut}}^w = 200$ Ry value that suffices for the total-energy description, as discussed in Appendix B.

Figure 5 presents an overview of method performance, as revealed by accuracy on the description compared with GW results that we take as references. The figure focus on the gaps of the AA' system and we mirror the result organization used in Fig. 1. That is, we use identical color coding for the respective KS-DFT and KI-DFT results, summarizing the method performance in terms of the deviation:

$$\Delta E_{\text{gap}}^{\alpha,\beta} = \delta \varepsilon^{\alpha} - \delta \varepsilon^{\beta}, \quad (12)$$

$$\delta \varepsilon^{\alpha/\beta} = \varepsilon_{\text{DFT}}^{\alpha/\beta} - \varepsilon_{\text{GW}}^{\alpha/\beta}. \quad (13)$$

Here $\varepsilon_{\text{DFT}}^{\alpha,\beta}$ ($\varepsilon_{\text{DFT}}^{\beta}$) identifies the QP-energy prediction at a given high-symmetry point of the conduction band (valence band) as described in PBE, CX, KI-PBE, or KI-CX, while $\varepsilon_{\text{GW}}^{\alpha/\beta}$ represents the corresponding reference value. The gray horizontal dashed line (at zero deviation) permits an easy comparison among different types of QP gaps. Color shading highlights the deviation that corresponds to the fundamental QP gap, as consistently determined in KI-DFT and GW for the AA' system.

Figure 5 shows that use of a KS-DFT approach (in CX and PBE) persistently leads to an underestimation of the gaps for QP transitions. Use of the corresponding KI-DFT forms leads instead to small overestimation of gaps and significant reductions in the absolute deviation values. That is, PBE and CX are both good starting points for a KI-DFT characterization of QPs overall, when investigating structures fixed at their experimental geometry.

We observe that, for the transitions $G_v \rightarrow G_c$, $K_v \rightarrow G_c$, and $M_v \rightarrow G_c$, the KI-CX predictions are closer to GW , while for the rest of the transitions, KI-PBE are slightly closer to GW . Both methods for KI-DFT give predictions for band gaps (originating at the set of relevant conduction- and valence-band extrema) that remain within 1 eV from corresponding GW results, taking the form of a near-constant offset. The latter observation suggests that both KI-PBE and KI-CX give an accurate treatment of transitions involving the conduction band G_c symmetry point for bulk systems.

C. Fingerprints of vdW: QP band structures at CX- and PBE-predicted atomic structures

We finally provide analysis that substantiates our interpretation of all so-far discussed major QP changes as indirect vdW-type (or nonlocal-correlation) signatures. Our discussion leads us to identify additional such signatures on the here-predicted QP nature for bulk h-BN.

We first define general vdW fingerprints on the QP band structure and recall the logic of sorting these into what we call direct and indirect features, for example, as discussed in Ref. [147]. We note that proximity of interacting fragments (in our case h-BN layers) impacts the nature [47,83] as well as the scaling and strength of vdW forces [155,156]. We expect stronger vdW signatures to appear also in the QPs band structure [147] as the interlayer separation shortens, something that the inclusions of the vdW-DF E_c^{nl} term itself drives. Use of CX in KI-DFT as well as in a KS-DFT structure optimization means that we (1) include vdW attraction between the layers and thus correct for the large (interlayer) underbinding that exists in a GGA like PBE [40,76,99] and, in turn, that we (2) provide a *consistent-KI-CX* QP characterization, covering vdW impacts to the extent that they are included in CX. The correspondingly defined “KI-PBE(PBE)” approach should only be used as a reference for discussions when vdW forces are important.

By contrasting results for AA' by KI-CX(CX) and KI-PBE(PBE), below, with those of the fixed-structure KI-CX and KI-PBE method, above, we arrive at a precise definition of direct and indirect vdW fingerprints in QP predictions. KI-CX(CX) versus KI-PBE(PBE) differences are nominally a full description of vdW and other truly nonlocal-correlation fingerprints on the QP nature. The same holds in practice for differences between KI-CX(CX) results for AA' and KI-CX characterizations of BN1 (because a switch from PBE to CX has little effect on the description of intralayer bonding). Meanwhile, KI-CX versus KI-PBE differences are denoted as “direct” vdW band structure impacts because they reflect the same atom configuration and track the impact of introducing the truly nonlocal correlation term E_c for what is, in practice, nearly identical electron-density variations $\rho(\mathbf{r})$; The similarity of CX and PBE predictions for $\rho(\mathbf{r})$ at a fixed structure has been validated by comparing work-function shifts and vibrations across many types of systems [47,64,127]. We

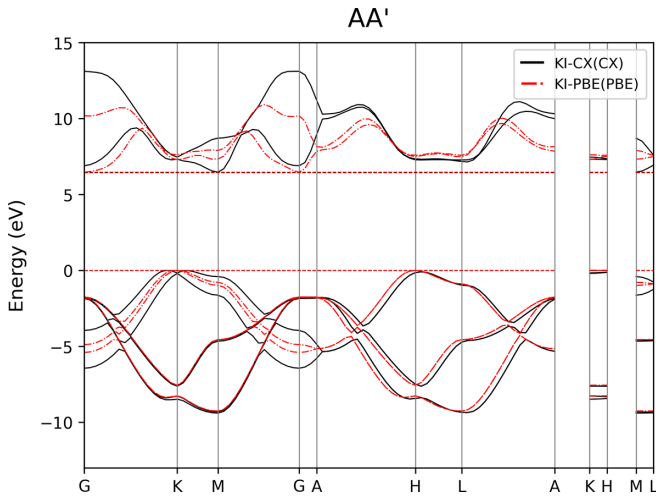


FIG. 6. Comparison of QP predicted for AA' by KI-CX(CX) and KI-PBE(PBE). Here the KI-CX(CX) QP predictor results when we use KI-CX at the atomic configuration predicted by a CX-based KS-DFT structure optimization; KI-PBE(PBE) results instead when we systematically stick to PBE in the modeling procedure. As the atomic structures differs, we shift the pair of resulting KI-DFT band structures differently, i.e., by their respective (functional-specific) predictions for the VBM-energy values.

identify “indirect vdW signatures” on our QP predictions, when KI-CX(CX) versus KI-PBE(PBE) differences cannot be identified as a direct vdW fingerprint.

Before turning to specific interpretations, we express a general expectation that indirect vdW effects on QPs [147] will often be dominant for layered systems. One can test the status for a given system (as presently done for h-BN) by checking a PBE-based prediction of the QPs against GW [23] or by simply supplementing by a KI-CX(CX) study. This follows because PBE and hence KI-PBE(PBE) cannot drive a layered bulk system to any meaningful interlayer proximity as discussed both previously [76,99] and as computed here: It is alone our CX prediction of structure that is close to the experimental characterizations of h-BN; see Sec. III. In any case, having the capability, via KI-CX(CX) studies, to predict both indirect and full vdW effects, is essential when we seek to predict QPs either independently from an existing experimental structure characterization [3], or in the absence of sufficient structure data [127,128,147,157], or even ahead of actual material synthesis [147,158].

Figure 6 reports our comparison of the QP band structure predicted in KI-CX(CX) (solid black line) and in KI-PBE(PBE) (red dashed-dotted line). As stated in the previous sections, for these QP predictions we now employ what we can call native interlayer distances. That is, we set c lattice constant for the AA' system by a CX-based structure optimization (giving $c = 6.448 \text{ \AA}$) for the ensuing KI-CX stage and a PBE-based optimization (giving $c = 8.560 \text{ \AA}$) in the KI-PBE(PBE) study.

We first observe that the variation in the occupied part of the QP band structure as predicted in KI-CX(CX) for the “GKM” part of the BZ is in near-perfect qualitative agreement with experimental observations; compare Fig. 3 of Ref. [69] with Fig. 6. Having confirmed the π -bonding

nature for the valence state, we proceed directly to discuss the theory-experiment alignment using the assignments provided in Ref. [69]. The measurements shows two σ band sitting, with an avoided crossing at “K,” well below two nearly degenerate π bands. The avoided crossing, the lifting of degeneracy for the formation of an offset VBM, as well as shape of the QP band band structure variation in this photoemission data [69] are all well reflected in the here-presented KI-CX(CX) predictions. There is also a very good quantitative alignment even though the experiment probes bands that do not obviously all qualify as frontier orbitals, i.e., the main focus of the KI-DFT method. For example, the experimental observation for the σ -to- π separation at K is measured at $\approx 9 \text{ eV}$ whereas KI-CX(CX) predicts it at 8 eV .

Contrasting the KI-CX(CX) and KI-PBE(PBE) QP results, we first focus on the valence bands along the symmetry path $G_v \rightarrow K_v \rightarrow M_v \rightarrow G_v$. At a general level, we find that use of KI-CX(CX) as our QP predictor lifts the near degeneracy found in KI-PBE(PBE) for the two top-most valence bands around the “K,” placing the VBM at the k -point T_v . We observe that this KI-CX(CX) VBM shift, $K_v \rightarrow T_v$, is in qualitative agreement with both KI-CX and the KI-PBE predictions obtained at the experimental value for the c lattice constant (Fig. 3, lower-right panel). That is expected because a CX structure characterization (unlike for PBE) is in good agreement with experiments, noting that vibration effects will account for some expansion off of raw the CX [and hence KI-CX(CX)] prediction for the c lattice constant; The net residual impact on QPs of CX versus experimental structure differences is small, as may be directly asserted comparing the KI-CX and KI-CX(CX) entries in Table III. Our observations of significant differences in KI-CX(CX) versus KI-PBE(PBE) QP predictions and general alignment of KI-CX and KI-PBE QP characterizations mean that we can identify most of the single sheets to bulk h-BN QP changes as indirect vdW effects and QP signatures [147]. This holds, for example, for the VBM change to T_v [69] that follows as vdW forces and other nonlocal-correlation effects drive an assembly of bulk h-BN from individual sheets [40,76,99].

The shift to T_v of the QP VBM for the AA' structure, the bottom section of Table III and Ref. [69], can be seen as a so-called trigonal warping that lifts the degeneracy of two π bands at K_v . At the MBPT and XC level that constitutes the main focus of our method goal and discussion, it can be interpret as an example of a general nonlocal-correlation effect that we call incipient covalency in the vdW-DF-method program [79,159]. It makes for a strong effect in bulk h-BN because the VBM orbitals have a pronounced p_z character, Fig. 4, so that occupied orbitals extend further into the interlayer regions, and because screening is a natural and integral part of the description of nonlocal-correlation effects in the vdW-DF method and hence in CX [47,76,78]. Specifically, the strength of binding by vdW and other nonlocal-correlation effects (captured in CX) do not have a simple variation with the atom-to-atom separation [76,156]. Rather the binding enhances when two nonvanishing electron concentration are brought in fair proximity to one another [47,76]. The consequence is, in turn, that the CX nonlocal-correlation term (at times, incorrectly seen as being just a vdW term) can drive a binding (in bulk h-BN) that may in turn cause a small

hybridization of slightly overlapping p_z orbitals. The net effect is that vdW-type fingerprints appear in the electronic structure.

In the upper hexagon of high-symmetry k -points in the BZ (corresponding to the A-H-L-A path), we note that use of KI-CX(CX) as our QP predictor generally causes only small shifts of KI-PBE(PBE) predictions for the occupied-state energies; These shifts are upwards in some and downwards in other parts of this region of the BZ. However, in the paths of k points that connects the upper and lower parts of the irreducible BZ, we find that use of KI-CX(CX) causes QP-dispersion changes in the $G_v - A_v$ and $M_v - L_v$ variations.

The major differences between KI-CX(CX) and KI-PBE(PBE) predictions arise for the QP conduction bands, Fig. 6. For example, KI-CX(CX) predicts a ~ 3 eV larger dispersion in the BZ region near G (for the lowest-lying conduction bands). We find that KI-CX(CX) predicts a CBM at the M_c symmetry point, while the KI-PBE(PBE) predictor places it near G. The difference arises because KI-CX(CX) can be seen as raising the conduction-band QP values at the G_c point, making KI-CX(CX) consistent with GW on the CBM [103]. We can interpret these effects as again being mostly indirect vdW signatures. Nevertheless, even when we compared the KI-CX and KI-PBE at the same (experimental) structure, we did find some differences for the energy variation in QP conduction-band predictions.

Finally, we can interpret the accuracy of the KI-CX(CX) predictor in terms of vdW interactions producing a lowering of the $T_v \rightarrow M_c$ QP energy gap (6.47 eV). This is consistent with the observation that a closer (vdW-induced) proximity of the layers causes an overlap of the p_z orbitals, something that KI-PBE(PBE) entirely misses. Again, the absence of a consistent vdW and general nonlocal-correlation inclusion in KI-PBE(PBE) causes it to predict a $K_v \rightarrow G_c$ transition as the fundamental gap, at 7.32 eV.

D. Broader relevance of KI-CX usage

We observe that moving towards a full and consistent inclusion of vdW interactions in the descriptions of both QPs and GS structure and energies (the traditional role of DFT) is no easy task. Traditional MBPT methods, like GW, and wave-function methods, like EOMCC, are today practical computational tools that can be used to characterize excited-state properties. However, these are costly compared to KI-DFT (that has the cost of DFPT) or gKS methods (that have the cost of hybrids). Also, a full capture of vdW-interaction effects requires self-consistent GW with vertex corrections (GW Γ) [81,160]. Similarly, wave-function methods can predict charge-excited states with high accuracy, for example, EOMCC for ionized states [7,9,10] or EOMCC for electron-attached states [8]. However, in such a framework, it is expected that the use of symmetry-adapted perturbation theory is necessary for incorporation of vdW effects [161,162].

We consider KI-CX (which reduces to use of CX in KS-DFT when used for structure optimizations) as a faster alternative to GW and EOMCC studies when seeking to predict QPs and identify fingerprints of vdW interactions [3]. The CX functional is, as a conserving vdW-DF [47,73,77,78], designed to capture the vdW interactions

directly within the MBPT framework, as far as possible. The CX captures vdW forces [47,59,76–78] but it may not capture all nonlocal-correlation effects, in spite of employing exponential resummation in an equivalent Green function representation of its underlying XC functional design [47]. Continued testing, e.g., via KI-CX(CX) predictions and analysis, is important.

We repeat our observation that KI-CX(CX) stands out by proceeding with the atomic-structure and QP characterizations in concert. As stated in the introduction, the CX (in KS-DFT) and KI-CX (in KI-DFT) use exactly the same MBPT input to define the nonempirical XC functional, *per se*. We think that a possible success of the CX design as a dual-use (KS-DFT and KI-DFT) functional, is helped by its inherent emphasis on current conservation and thus, the implied reflection of the plasmon nature. On the one hand, the plasmon-energy shifts by electro-dynamical coupling [47,79] is a natural framework to count the integrated effects of nonlocal-correlation effects [78,120]. On the other hand, a consistent modeling of virtual currents (as in plasmons) are essential when moving electrons (as in the excitations that QPs characterize).

Our interest in KI-CX goes well beyond the present focus on testing. By use of KI-CX we may be able to provide fast predictions of atomic and electronic (QP) structure in concert, for example, tracking fingerprints of vdW and, in general, noncovalent interactions in DNA systems while comparing with, e.g., optimally-tuned RSH vdW-DFs [30].

V. CONCLUSIONS AND OUTLOOK

A comparative analysis of results reveals systematic trends across h-BN systems. The data are obtained by PBE and CX functions in KS-DFT functionals (denoted PBE, CX results) and with the corresponding use in KI-DFT (giving corresponding KI-PBE, KI-CX results). The performance is compared against GW results, where available. For both PBE and CX, we find that their use in KI-DFT consistently leads to better performance on QP descriptions than what their traditional (and originally intended) usage gives via KS-DFT.

Overall, we find that the KI-CX and KI-CX(CX) results for the QP band structure validate CX as a robust and GS + QP-consistent XC functional, performing at least as well as PBE (as used in KI-PBE) for predicting the nature of QPs in h-BN, a standard example of layered materials and of other cases where cohesion is provided by vdW and noncovalent binding. By the “GS + QP-consistent” identifier on functional quality, we highlight a formal MBPT criterion: The first frequency moment of the fully interacting spectral function is formally given by GS DFT components, and can therefore also be evaluated in a given density-explicit XC approximation, CX or PBE [62,82]. We find that KI-CX(CX), or almost equivalently the frozen-coordinate KI-CX, holds advantages over the traditional (also frozen-coordinate) KI-PBE approach to QP predictions for bulk h-BN, and likely also more broadly.

We have considered both direct and indirect effects of the nonlocal-correlation effects on the QP. The former type of nonlocal-correlation or vdW-attraction effects are revealed when considering the QP band structure predictions by KI-CX and KI-PBE at the same structure. The latter, indirect effects

contribute to and are therefore revealed by contrasting what we call KI-CX(CX) and KI-PBE(PBE) studies, that is, QP predictions by KI-CX at the atomic structure defined by CX (and correspondingly so for the PBE-based approach).

We observe that KI-CX adjusts KI-PBE predictions and delivers accuracy for QPs as asserted by comparison with GW studies, an approach that also captures vdW interactions. Our finding of good KI-CX performance as a QP predictor holds true also when asserted at the experimentally observed structure, i.e., when focusing on just the direct effects of including vdW interactions via the E_c^{nl} term in CX. That is, there are differences for bulk h-BN QP gaps even when we compare KI-CX and KI-PBE at this fixed structure, specifically changes in the conduction-band QP energies at and near the G_c , A_c , and even K_c high-symmetry points of the BZ. There is therefore also impact on the valence-to-conduction gaps. Even if such direct vdW signatures are relatively small ($\sim 0.15\text{eV}$ as gauged at “G”) for h-BN, one cannot *a priori* assume lack of relevance in experimental comparisons for general layered and soft matter.

We extract two observations relevant for our interest in the link between MPBT and functionals [44,47,62]. First, PBE has (as a semilocal functional with a GGA-type correlation) the same MPBT source on correlation that CX has (as the nonhybrid vdW-DF version that is designed to reflect the core vdW-DF design logic as far as it goes [47,56,59,73,78]). Also, GGAs emphasize a direct implementation of hole conservation whereas consistent vdW-DFs get this charge-conservation criterion via current conservation [47,77,78]. However, when Langreth and Vosko provided the core argument for the logic of GGA correlation [56], namely, a need to exclude small-wave-vector contributions from the relevant MBPT input to ensure hole conservation, they identified the nature of this GGA exclusion as vdW attractions [56,59]. This finding provided key impetus for starting Rutgers-Chalmers work on the vdW-DF method that bypass this problem, as discussed further in Refs. [47,59,79]. Nevertheless, in spite of having an explicit vdW exclusion [56], we find here that a PBE-based QP predictions sometimes succeed at getting indirect vdW effects on QPs.

Second, we can interpret the shared KI-PBE and KI-CX ability to represent indirect-vdW signatures on QP in bulk h-BN (when sticking to the experimental structure) to the value of basing XC functional design off of MBPT input and conservation laws; We are thus motivated to continue such approaches to XC functional designs. A key point is that KI-PBE [but not KI-PBE(PBE)] manages to capture the indirect vdW signatures in spite of the fact that it have had (as a GGA) the leading part of the vdW effects deliberately excluded from it underlying MBPT input [51,56,59]. By the logic of Refs. [47,62], and given that PBE cannot accurately describe structure in layered materials (or molecular systems), the KI-PBE characterizations are working under an implicit pressure, as discussed in the introduction. The partial success of KI-PBE on indirect vdW signatures (when structure is frozen as in the experiment) reflects the strong transferability of PBE, again as touched upon in the introduction. Still, we suggest trying the vdW-DF tools, including CX/KI-CX(CX), for consistent structure-and-QP predictions [30,41], because the vdW-DFs are set up to reflect more of the MBPT input

as well as constraints [40,47,59,73,75,77,78] and because the CX in particular seeks to reflect current conservation [47].

We find that KI-CX(CX) (in effect, CX) is significantly better as a GS + QP-consistent functional [62] than KI-PBE (that reflects PBE) for bulk h-BN. GW results at the experimental (or CX) geometry is a good measure of QP quality because GW also reflects the vdW interactions that provide cohesion in soft matter [3,40]. However, our assessment of relative functional quality is not primarily made upon comparison of the QP predictions to GW, although we find that KI-CX(CX) does very well. Rather, we make this statement because the relevant comparison of functional capability, according to MBPT logic [62], should be made at the KI-CX(CX) versus KI-PBE(PBE) level and thus reflect GS + QP consistency. KI-DFT studies require attention also to hidden assumptions and use of KI-PBE implicitly means getting QP that differs from those defined [via KI-PBE(PBE)] by the zero-stress PBE GS structure [62].

We add that we often face (soft- and) complex-matter problems [40,64,128,163], where advantages of KI-CX(CX) will likely also manifest themselves, although illustrations are beyond the present scope. Still, for material discovery, there is broad interest in such cases where the system is not yet fully characterized (or even synthesized) but where we would still like to predict optoelectronic properties and potential function. Of course, we presently picked the h-BN material focus because its bulk structure is after all known (so that we can make comparison with QP observations and other vdW-inclusive theory descriptions, like GW). Nevertheless, working under assumed conditions reflecting a (soft- and) complex-matter challenge is the fair and relevant test of functional capabilities. Under such conditions, corresponding also, for example, to a new layered system or new so-called vdW heterostructure before structure characterization, use of KI-CX(CX) for QP predictions appears the safer route: First, CX is generally significantly better at layered-matter structure than PBE [40,47,76,99]; second, we can then argue that the interacting spectral function reflects the electron-density variation computed at relevant conditions [62].

Finally, returning the goal of maximizing value for continued XC functional developments, we see the KI-CX(CX) approach as versatile and promising because it maintains GS and QP consistency. The CX is strong at general structure characterizations so when we find alignment of the KI-CX(CX) predictions and GW results, as for h-BN bulk, we can draw conclusions for the GS electronic structure, knowing that we have both direct and indirect vdW signatures also for QPs. Going forward we plan to apply KI-CX(CX) to wider types of layered and other (soft) materials and correlate success or failure with the nature of classes of (soft) systems. We may thus identify and understand residual XC issues to help us further improve accuracy in MBPT-based functionals.

ACKNOWLEDGMENTS

We thank Nicola Colonna and Edward Linscott for valuable discussions. The present work is supported by the Swedish Research Council (VR) through Grant No. 2022-03277, and by the Chalmers Area of Advance (AoA) Nano and Chalmers AoA Production. The computations were

performed using computational and storage resources at Chalmers Centre for Computational Science and Engineering (C3SE), and with computer and storage allocations from the National Academic Infrastructure for Supercomputing in Sweden (NAISS), under Contracts No. NAISS2023/3-22, No. NAISS2023/6-306, No. NAISS2024/3-16, and No. NAISS2024/6-432.

DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

APPENDIX A: LINEAR RESPONSE FOR NONLOCAL CORRELATIONS

As mentioned in Sec. II C, the DFPT response of the nonlocal potential $v^{\text{nl}}(\mathbf{r})$ is implemented in the KCW module of QE. The necessary LR steps are derived in Ref. [87] with respect to a general perturbation $\Delta^\lambda v^{\text{nl}}(\mathbf{r})$ and with the purpose (there) of computing vdW signatures on phonons and their interactions. Here we summarize how this DFPT formulation for $\Delta^\lambda v^{\text{nl}}(\mathbf{r})$ appears when considered with respect to the removal or addition of a fractional electron, i.e., for KI-DFT use.

As a starting point, consider the definition of the nonlocal energy in Eq. (6), approximating the spatial integrals by sums over a uniform grid of points (at fixed positions ρ_i and $\mathbf{r}_i$) and the gradients by finite differences on the same grid. This allows the use of partial derivatives of the density variation on the grid to be used in place of formal functional derivatives [86]. Applying these finite differences and simplifying, we obtain

$$E_c^{\text{nl}} = \sum_\alpha \sum_i u_{\alpha i}(\mathbf{r}_i) \Theta_{\alpha i}(\mathbf{r}_i), \quad (\text{A1})$$

where the first factor corresponds to the auxiliary function

$$u_{\alpha i} = \sum_\beta \sum_j \phi_{\alpha\beta}(\mathbf{r}_{ij}) \Theta_{\beta j}(\mathbf{r}_j).$$

Here $\Theta_{\alpha i} = \rho_i P_\alpha[q(\rho_i, |\nabla \rho_i|)]$, the values q_α are chosen to ensure accurate interpolation of the function ϕ , and P_α is the function resulting from the interpolation.

From Eq. (A1), one can obtain the nonlocal potential $(\partial E_c^{\text{nl}}/\partial \rho)$ in a more compact notation:

$$\begin{aligned} v_i^{\text{nl}} &= \sum_\alpha \left[\left(u_{\alpha i} \frac{\partial \Theta_{\alpha i}}{\partial \rho_i} \right) + \sum_j u_{\alpha j} \left(\frac{\partial \Theta_{\alpha j}}{\partial |\nabla \rho_j|} \frac{\partial |\nabla \rho_j|}{\partial \rho_i} \right) \right] \\ &\equiv b_i + \sum_j h_j, \end{aligned} \quad (\text{A2})$$

where b_i corresponds a term defined exclusively by differentiating direct by density (at the specific grid site i). The second term, defined by a set of h_j contributions, reflects instead derivations with respect to the density gradients. The evaluation of a gradient in QE makes use of specific stencil

so that the gradient at site i can be expressed in terms of the density values at neighboring grid sites j [86].

To obtain the nonlocal response kernel for E_c^{nl} , Eq. (10), it is necessary to apply DFPT to Eq. (6). To do this, consider an infinitesimal fraction of an electron $\delta 0n$ added or removed to the n th MLWF at $\mathbf{0}$. This generates a perturbation in the effective KS potential $\Delta^{\delta 0n} v_{\text{KS}}$, leading, in turn to a new variation of the density, with relative changes denoted $\Delta^{\delta 0n} \rho(\mathbf{r})$. The first-order change in this nonlocal potential is

$$\Delta^{\delta 0n} v_i^{\text{nl}} = \sum_j \frac{\partial v_i^{\text{nl}}}{\partial \rho_j} \Delta^{\delta 0n} \rho_j. \quad (\text{A3})$$

Expressing also the v_i^{nl} in Eq. (A3) reveals the second derivatives present in Eq. (10). To get a numerical evaluation, we adapt the grid-specific implementation [85–87] of the formal determination

$$\sum_{ij} \frac{\partial^2 E_c^{\text{nl}}[\rho_i]}{\partial \rho_i \partial \rho_j} \Delta^{\delta 0n} \rho_j \approx \iint d\mathbf{r} d\mathbf{r}' \frac{\delta^2 E_c^{\text{nl}}}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} \Delta^{\delta 0n} \rho(\mathbf{r}'). \quad (\text{A4})$$

Finally, to get the DFPT, we can simply linearize the two components of Eq. (A3):

$$\Delta^{\delta 0n} v^{\text{nl}} = \sum_i \left(\frac{\partial b_j}{\partial \rho_i} + \sum_k \frac{\partial b_k}{\partial \rho_i} \right) \Delta^{\delta 0n} \rho_i. \quad (\text{A5})$$

The details of these two components are explicitly derived, for the stencil used in QE, in Ref. [87].

In summary, KI-DFT in QE is in fact already set up to move to a KI-CX(CX) form and general-purpose starting point for QP characterizations, as here illustrated.

APPENDIX B: PRECISION IN KI-CX

For KS-DFT studies using norm-conserving pseudopotentials, past experience suggest that a choice $E_{\text{cut}}^{\text{wf}} = 200$ Ry for wave function kinetic-energy cutoff is sufficient to converge predictions of total-energy differences and structure [30,40].

We find that the same choice also consistently leads to robust predictions for the valence-type QP energies. This is expected and can be understood from the following observations. First, the KS-DFT studies can only converge the total energy and the density variation when the spatial variation in the occupied KS-DFT orbitals are all themselves converged. Second, we find vanishing differences, besides an overall energy shifts, between the valence band structure as described in, for example, CX and KI-CX. Our experience is that the process of making the MLWF representations, and hence the completion of the KI-CX functional specification, is inherently robust for descriptions of the set of occupied QPs states.

For descriptions of conduction-band QP states we see a need to seek numerical stability with regard to changes in choices for implicit modeling parameters; This observation has practical implications for our KI-CX study of the single-sheet BN1 system. The description of unoccupied QPs is generally a challenge for KS-DFT, for example, documented for electron attachment in nitrogen-base systems [30,90]. This problem emerges, in part, because the spatial variation of unoccupied KS-orbitals does not naturally enter in the

TABLE IV. Search for precision (numerical stability with respect to choice of modeling parameters) in KI-CX predictions of BN1 QP-gap energies (in eV) as defined by transitions between indicated valence- and conduction-band symmetry points. Italicized table entries identify the set of model parameters (along with corresponding gap results) that we use, in the main text, to report and discuss the QP behavior for the strictly two-dimensional BN1 system.

c [Å]	$E_{\text{cut}}^{\text{wf}}$ [Ry]	$G_v \rightarrow G_c$	$M_v \rightarrow M_c$	$K_v \rightarrow G_c$	$K_v \rightarrow K_c$	$M_v \rightarrow G_c$	$K_v \rightarrow M_c$
20	100	7.62	8.98	5.90	7.94	6.79	8.08
20	200	8.14	9.90	6.42	8.61	7.31	9.00
20	300	8.18	9.86	6.46	8.62	7.36	8.96
20	<i>400</i>	<i>8.21</i>	<i>9.92</i>	<i>6.48</i>	<i>8.69</i>	<i>7.38</i>	<i>9.02</i>
30	100	8.36	10.01	6.63	8.81	7.53	9.11
30	200	8.28	9.95	6.55	8.65	7.45	9.05
30	300	8.28	10.17	6.56	8.89	7.45	9.27
30	400	8.20	9.99	6.47	8.72	7.37	9.09

iterative optimization of the actual ground-state electron density $\rho(\mathbf{r})$. In contrast, with a hybrid like AHBR-mRSH and with the KI-DFT framework, we can overcome also this KS-DFT problem to accurately describe the empty QPs [30,90] because we make the iterative computational scheme dependent on the nature of these empty orbitals. However, the requirements on the $E_{\text{cut}}^{\text{wf}}$ choice for stability in the description of conduction-band states might well be higher. Also, given our screening handling [148], we must validate that the chosen height c of the modeling cell for the strictly two-dimensional BN1 system is sufficient to electrically decouple the sheets.

Table IV presents an overview of the numerical work we completed to assert the level of precision we presently have for a KI-DFT description of (empty-state) QP energies in BN1. We see that the step of crafting the MLWF representation can sometimes cause abrupt changes in the resulting predictions of conduction-band QP energies. A complication is that the $E_{\text{cut}}^{\text{wf}}$ variation also depends on the choice of c . Our criterion for using these BN1 QP predictions is that we reach a fair numerical stability with regards to changes in both these modeling parameters. Tables II and IV report our finding that we have a fair cross-checked stability for the conduction-band QPs of BN1 when using $c = 20$ Å and $E_{\text{cut}}^{\text{wf}} = 400$ Ry, as also stated in the main text.

We also performed a study of numerical stability for the bulk AA' system in KI-CX but found no variation in predictions for QP gap results as we increased $E_{\text{cut}}^{\text{wf}}$ from 150 Ry to 300 Ry. Accordingly we choose to complete all KI-DFT characterizations for bulk h-BN at the value $E_{\text{cut}}^{\text{wf}} = 200$ Ry that is adequate for total-energy and structure characterizations in KS-DFT.

We finally turn to a discussion of the choice of k point sampling. We seek to introduce KI-CX(CX) as a test in the dual GS and QP predictor role and we do focus the discussion on qualitative signatures. We note that seeking k convergence is not as straightforward with KI-DFT as it is in GS-DFT studies. At least for this paper, introducing a new vdW-inclusive QP tool and XC-testing method, we have a need to reliably compare QP determinations across different types of systems/structures and functionals while also checking for potential instabilities, above. Again, we expect occasional Wannier impacts are consequences of the fact that the KI-DFT implementation in QE is presently relying on an isotropic screening model for handling the electrostatics, an issue for KI-CX(CX) that we expect will disappear longer term. Still, this paper relies on a present-day Koopmans-DFT implementation and we must navigate under finite computer resources. We use a general choice of a 7×7 in-plane k point sampling because we developed trust in thus minimizing impact of numerical effects for the set of descriptions that illustrate our method use.

Table V summarizes the data that allow us to extract a plausible limit on the residual impact of using this good if moderate k point sampling and possible numerical sensitivities. Our analysis is based on finding a variation that does not have a systematic behavior with the k choices but scatter that can be interpret as uncertainty in the process. We observe that in the column termed “Mesh,” it is the set of third numbers that identify the extent that we sample this AA' bulk system in the out-of-plane or c axis direction. Also, at the CX structure prediction, there is a ratio of about 2.5 between the c axis and in the in-plane lattice constant a , and so we find that the most balanced k point samplings are the

TABLE V. Quasiparticle gaps for AA' for different k -point meshes, for KI-CX(CX) studies.

Mesh	$G_v \rightarrow G_c$	$M_v \rightarrow M_c$	$K_v \rightarrow G_c$	$K_v \rightarrow K_c$	$M_v \rightarrow G_c$	$K_v \rightarrow M_c$
663	9.275	7.147	7.675	7.640	7.914	6.908
664	9.323	7.186	7.723	7.664	7.961	6.947
773	9.314	6.927	7.719	7.541	7.963	6.684
775	9.374	6.983	7.778	7.587	8.021	6.740
883	9.078	7.091	7.474	7.617	7.721	6.844
884	9.279	7.095	7.674	7.704	7.921	6.848

$7 \times 7 \times 3$ (773) and $8 \times 8 \times 3$ (883) cases, namely where the ratio of the first and last number in the “Mesh” label approximate that ratio. We proceed with an estimate as follows: First, we find only a moderate variation in the band gap predictions as we increase the ratio of out-of-plane and in-plane k point samplings at a fixed in-plane k choice: At most 0.2 eV and exclusively arising for the transitions corresponding to the largest band gaps. We take this observation as a reflection of having a fair numerical stability at the Wannier-function

steps. Second, tracking the variation in band-gap predictions with the in-plane sampling at k -point ratios that are closest to the ratio in cell dimensions, there is a variation (about 0.2 eV) even when considering the two smallest QP gaps. However, we also note that these gaps are consistently (at all samplings) identified as $K_v \rightarrow M_c$ and $M_v \rightarrow M_c$ transitions. We note that the 0.2 eV value is small on the energy scale that characterizes KI-CX(CX) versus KI-PBE(PBE) differences (Fig. 6).

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