Origin of layer dependence in band structures of two-dimensional materials

Mit H. Naik and Manish Jain

Center for Condensed Matter Theory, Department of Physics,
Indian Institute of Science, Bangalore 560012

(Dated: March 2, 2017)

Abstract

We study the origin of layer dependence in band structures of two-dimensional materials. We find that the layer dependence, at the density functional theory (DFT) level, is a result of quantum confinement and the non-linearity of the exchange-correlation functional. We use this to develop an efficient scheme for performing DFT and GW calculations of multilayer systems. We show that the DFT and quasiparticle band structures of a multilayer system can be derived from a single calculation on a monolayer of the material. We test this scheme on multilayers of MoS$_2$, graphene and phosphorene. This new scheme yields results in excellent agreement with the standard methods at a fraction of the computation cost. This helps overcome the challenge of performing fully converged GW calculations on multilayers of 2D materials, particularly in the case of transition metal dichalcogenides which involve very stringent convergence parameters.
I. INTRODUCTION

Two-dimensional (2D) materials have been extensively studied in the last decade\(^1\)–\(^9\) owing to their applications in electronics and optoelectronics\(^10\)–\(^12\). 2D materials consist of layers that are held together by weak van der Waals forces. A remarkable feature of these layered materials is the difference in properties of a monolayer compared to multilayers of the same material\(^2\)–\(^7\),\(^13\),\(^14\). For instance, monolayer of MoS\(_2\) has a direct band gap, while multilayers of MoS\(_2\) have an indirect gap\(^2\),\(^3\),\(^5\),\(^13\),\(^15\). Most gapped 2D materials, like transition metal dichalcogenides (TMDCs), hexagonal boron nitride and phosphorene, show an unmistakable reduction in band gap with the number of layers\(^2\),\(^3\),\(^6\),\(^7\),\(^13\)–\(^20\).

First principles electronic structure calculations, based on the GW\(^21\),\(^22\) approximation, have resulted in band gaps that are in excellent agreement with experiments\(^6\),\(^8\),\(^16\),\(^23\)–\(^27\) on these materials. Band gaps of these materials calculated using density functional theory (DFT)\(^28\),\(^29\), while underestimated, also show a clear reduction with the number of layers\(^7\),\(^14\),\(^15\),\(^18\)–\(^20\). Most studies have attributed this reduction in the band gap to quantum confinement\(^3\),\(^5\)–\(^7\). However, there are no studies that quantitatively explain this trend.

The idea of quantum confinement comes from the model of an electron in a one-dimensional box. In multilayer stacks of 2D materials, the confining length of the box is directly proportional to the number of layers. In this context, the increase in the confinement length in multilayers as compared to a monolayer, due the summing of constituent layer potentials, is attributed to quantum confinement. On adding the potentials of constituent layers, the inter-layer spacing creates a finite barrier in the interstitial region between adjacent layers. This barrier with a DFT calculated Hartree potential profile has been used to qualitatively explain the trend in the layer dependence of the band gap in phosphorene\(^6\). Recently, perturbation approaches\(^18\),\(^30\), which need input from explicit multilayer calculations, have been used to study layer dependence of band structures.

Furthermore, in the case of TMDCs, it has been shown that the quasiparticle band gap calculated using the GW approximation converges extremely slowly with the number of unoccupied states, k-point sampling and the screened Coulomb cut-off\(^31\),\(^32\). Performing separate GW calculations for a monolayer, bilayer, trilayer or more with parameters that ensure convergence is computationally very challenging. To study the variation of properties as a function of interlayer spacing or stacking of the layers needs one to repeat the calculation.
for different parameters. Moreover, GW calculations on heterostructures of 2D materials are presently intractable due to their lattice incommensurability necessitating the use of large supercells of each material. Identifying the origin of layer dependence opens up the possibility of deriving ground state and excited state properties of multilayer stacks from calculations on a monolayer alone. Doing so would immensely ease the computation cost incurred in performing separate DFT and GW calculations for different configurations of the constituent layers.

We study the physical origin of layer dependence in band structures of 2D materials. We show that while quantum confinement gives qualitatively the right trend, the non-linearity of the $V_{xc}$ functional plays a crucial role in quantitatively determining the layer dependence. We show that within DFT, band structures of multilayer stacks can be derived from a single calculation on a monolayer of the material. We also extend this scheme to obtain quasiparticle energies of multilayer systems from a single GW calculation on a monolayer of the material. We apply this method to understand the layer dependence of band structure in multilayers of a prototypical TMDC, 2H-MoS$_2$, and compare the results to the standard calculations on this material$^{2-4}$. We demonstrate the transferability of this scheme by applying it to graphene and phosphorene.

II. COMPUTATION DETAILS

We performed the DFT calculations using the plane-wave pseudopotential method as implemented in Quantum Espresso$^{33}$ package. Norm-conserving pseudopotentials were used in all calculations. The wave functions were expanded in plane-waves with an energy cut-off of 150 Ry for MoS$_2$. For graphene and phosphorene, we used a wavefunction cut-off of 70 Ry and 40 Ry respectively. The local density approximation to the exchange-correlation functional$^{34}$ was used in MoS$_2$ and graphene calculations. For phosphorene we used the Perdew-Burke-Ernzerhof exchange-correlation functional$^{35}$. The Brillouin zone was sampled with $24 \times 24 \times 1$, $21 \times 21 \times 1$ and $21 \times 15 \times 1$ k-point grids for MoS$_2$, graphene and phosphorene respectively. We kept the in-plane lattice parameter for each material fixed in all the calculations. The bilayer and trilayer were constructed from the monolayer with the appropriate stacking and inter-layer spacing. No atomic relaxations were allowed in the bilayer and trilayer. The supercell dimension in the out-of-plane direction was fixed at 35Å.
The GW calculations were performed using the BerkeleyGW package\textsuperscript{36,37}. For MoS\textsubscript{2}, the dielectric function was evaluated with plane waves up to a cutoff of 35 Ry and was extended to finite frequencies using the generalized plasmon pole (GPP)\textsuperscript{22} model. The self-energy was constructed using the one shot $G_0W_0$ method. The Coulomb interaction was truncated in the out-of-plane direction\textsuperscript{38}. For MoS\textsubscript{2} supercell size of 35 Å in the out-of-plane direction, 24 × 24 × 1 k-point sampling and 8400 valence and conduction states are necessary to ensure convergence\textsuperscript{32}. We perform separate calculations on monolayer, bilayer and trilayer MoS\textsubscript{2} with 12 × 12 × 1 k-point sampling and 6000 valence and conduction states and compare the quasiparticle band structures of bilayer and trilayer with results obtained from the proposed scheme. These parameters, while not fully converged, demonstrate the efficacy of this scheme. We also perform fully converged calculations on a monolayer of MoS\textsubscript{2} and derive the band gap, ionization potential and electron affinity of bilayer and trilayer using our scheme. Our fully converged monolayer band gap is in good agreement with previous calculations\textsuperscript{8,32}. For phosphorene, we perform separate calculations on monolayer, bilayer and trilayer with 21 × 15 × 1 k-point sampling, 800 valence and conduction states, and 15 Ry dielectric cutoff. We compare the band gap, ionization potential and electron affinity obtained using our scheme to those obtained from the full calculation. The static remainder technique was used to speed up convergence with the number of bands\textsuperscript{39} in all calculations.

III. DFT BAND STRUCTURES

In order to understand the layer dependence of the DFT band gap, consider a bilayer of MoS\textsubscript{2} with constituent layers labelled 'a' and 'b' (Fig. 1(a))\textsuperscript{40}. We perform separate DFT calculations on layer 'a', layer 'b' and the bilayer, to obtain the self-consistent charge densities and potentials of each. In Fig. 1(b), we plot the planar averaged charge densities of layer 'a', layer 'b', the bilayer. From the figure one can see that the bilayer charge density, $\rho^{bi}$, lies on top of the sum of the charge densities of the constituent layers, $\rho^a + \rho^b$, which indicates that there is no significant rearrangement of charge in the bilayer compared to the monolayers. Fig. 1(c) shows the planar averaged total DFT potential of the bilayer, $V^{bi}_{tot}$. From this figure, it is clear that the sum of the layer potentials, $V^a_{tot} + V^b_{tot}$, is not equal to the bilayer potential. The sum of the potentials, as described above, is the use of quantum confinement to obtain the potential for the bilayer. The difference, $V^{bi}_{tot} - (V^a_{tot} + V^b_{tot})$, is
FIG. 1. (Color online) (a) Bilayer MoS$_2$ in AB stacking, red spheres represent Mo atoms and yellow spheres S atoms. (b) Planar averaged charge density of bilayer MoS$_2$ (black solid line), planar averaged charge density of layer 'a' (red dash-dot line), layer 'b' (blue dashed line) and sum of layer 'a' and 'b' (magenta line not seen). The shaded regions indicate the position of the MoS$_2$ layers in the simulation cell. (c) Planar averaged DFT potential of the layer 'a', $V_{tot}^{a}$ (red dash-dot line), layer 'b', $V_{tot}^{b}$ (blue dashed line), the sum $V_{tot}^{a} + V_{tot}^{b}$ (solid magenta line) and bilayer, $V_{tot}^{bi}$ (black solid line). (d) Difference $V_{tot}^{bi} - (V_{tot}^{a} + V_{tot}^{b})$ (black solid line) and $V_{xc}[\rho^{a} + \rho^{b}] - (V_{xc}[\rho^{a}] + V_{xc}[\rho^{b}])$ (violet dashed line).

localized to the interstitial region between the two layers where the charge densities overlap. It can not arise from the Hartree potential since it is a linear functional of the charge density and here the charge density of the bilayer is a sum of the charge densities of the individual layers. It can not arise from the ionic potential either, due to the absence of atomic relaxations in the bilayer. The difference must arise due to the non-linearity of the exchange-correlation functional. Fig. 1(d) plots this difference which is an additional barrier between the layers. Fig. 1(d) also plots $V_{xc}[\rho^{a} + \rho^{b}] - (V_{xc}[\rho^{a}] + V_{xc}[\rho^{b}]) = \Delta V_{xc}$, showing that this additional barrier indeed comes solely from the exchange-correlation difference. The total bilayer potential can thus be expressed as a sum of the individual layer potentials and $\Delta V_{xc}$. Thus, the layer dependence of properties is an effect of quantum confinement and non-linearity of the $V_{xc}$ functional.

We can construct the DFT Hamiltonian for the bilayer in terms of the potential and
FIG. 2. (Color online) Panels (a), (b) and (c) plot the DFT band structure of monolayer, bilayer and trilayer MoS$_2$ respectively. Panels (d), (e) and (f) plot the DFT band structures of monolayer, bilayer and trilayer graphene. The black solid line indicates the result from separate DFT calculations on these systems. The red dashed line shows the result obtained by a single-shot diagonalisation of the constructed Hamiltonian Eq 1 for these systems in the basis of the wavefunctions of the constituent layers. The blue dashed lines are the eigenvalues obtained by considering only quantum confinement in these systems.

The charge density of the constituent layers as:

\[ H = \hat{T} + V_{tot}^a + V_{tot}^b + \Delta V_{xc} \]  

where $\hat{T}$ is the kinetic energy operator. It should be noted that everything required to construct this Hamiltonian can be obtained from a single monolayer calculation, say on layer ‘a’. Based on the relative configuration of atoms in layer ‘b’ with respect to layer ‘a’, a suitable transformation can be applied on $\rho^a$ and $V_{tot}^a$ to obtain $\rho^b$ and $V_{tot}^b$ respectively. The wavefunctions of layer ‘a’, $\{\psi^a_{nk}\}$, can similarly be transformed to obtain the wavefunctions of layer ‘b’, $\{\psi^b_{nk}\}$. The Hamiltonian can then be constructed in the basis of the wavefunctions.
FIG. 3. (Color online) Modulus squared wavefunctions of monolayer MoS$_2$, integrated out along [010] lattice vector direction. z is the out-of-plane direction and x the [100] direction. Top panel: CBM wavefunctions at K, Λ and Γ points, respectively. Bottom panel: VBM wavefunctions at K, Λ and Γ points, respectively.

of the two layers, \{ψ^a, ψ^b\}, keeping in mind that the wavefunctions of the two layers do not form an orthogonal basis. The generalized eigenvalue problem can be solved to yield eigenvalues and eigenfunctions of the bilayer. This procedure can easily be generalized to N layers: $H = \hat{T} + \sum_{i=1}^{N} V_{tot}^i + \Delta V_{xc}$; where $\Delta V_{xc} = V_{xc} \left[ \sum_{i=1}^{N} \rho^i \right] - \sum_{i=1}^{N} V_{xc} \left[ \rho^i \right]$. It is worth noting that while constructing the Hamiltonian we use $V_{xc}(r)$ and not just the planar averaged quantities.

The band structure of monolayer, bilayer and trilayer MoS$_2$ from separate DFT calculations is plotted in Fig. 2 (a), (b) and (c) respectively. The points Σ and Λ are marked halfway between Γ-M and K-Γ respectively. Fig. 2 (d), (e) and (f) similarly show the band structure of monolayer, bilayer and trilayer graphene respectively. Fig. 2 also shows the band structure obtained by neglecting $\Delta V_{xc}$ from Eqn. (1). This describes the effect of quantum confinement alone on the layer dependence of the band structures. While it captures the qualitative trends like the transition from direct to indirect band gap in MoS$_2$, it fails to give an accurate layer dependence of the value of the band gap, ionization potentials and level splittings in the band structure. In MoS$_2$, the splittings are overestimated at the
conduction band minimum (CBM) of the Λ point and underestimated at the Γ point valence band maximum (VBM). The relative positions of the conduction band edges at the Λ, K and Σ points are also very different from the full DFT calculation. Similarly, in graphene, excluding $\Delta V_{xc}$ overestimates the ionization potential and the band splittings. The band structure obtained from the eigenvalues obtained by diagonalizing the constructed Hamiltonian described previously is also plotted in Fig. 2. As can be seen, these band structures are in excellent agreement with the full calculation for MoS$_2$ and graphene. A slight difference up to 5-10 meV is found due to a small rearrangement of charge in the bilayer or trilayer as compared to the sum of the constituent layer charge densities. Hence to obtain the quantitative layer dependence, both the effects of quantum confinement and non-linearity of the exchange-correlation functional need to be accounted for.

The band structures of MoS$_2$ in Fig. 2 show a transition from a direct band gap at K in the monolayer to an indirect band gap from Γ to Λ in the bilayer. The transition is driven by the large splitting of the VBM at the Γ point and CBM at the Λ point. The K point VBM and CBM on the other hand split only slightly. The amount by which a band splits depends on the off-diagonal elements of the multilayer Hamiltonian represented in the basis of the constituent layer wavefunctions and the overlap between the wavefunctions of the constituent layers. The VBM and CBM of the monolayer at K are localised in space, have a large Mo d orbital character [see Fig 3]. The CBM at Λ and VBM at Γ on the other hand have a strong S p$_z$ character [see Fig 3]. They are hence more delocalized in the out-of-plane direction and hybridize more with the wavefunctions of other layers than the wavefunctions at K. This leads to the large splittings in the band structure at these points for the bilayer and trilayer [see Fig 2 (b) and (c)]. The VBM and CBM at K, VBM at Λ and CBM at Γ show little to no splitting in the band structures owing to their localized nature [see Fig 3].

IV. QUASIPARTICLE BAND STRUCTURES

We can extend this method to calculate the quasiparticle energies and band structures. The DFT eigenvalues can be corrected by using the GW approximation to the electron self-energy, $\Sigma^{22}$. For the bilayer, quasiparticle eigenvalues are given by:

$$\epsilon_i^{QP} = \epsilon_i^{DFT} + \langle \psi_i^{bi} | \Sigma^{bi} (\epsilon_i^{QP}) - V_{xc}^{bi} | \psi_i^{bi} \rangle$$
where $|\psi_i^{bi}\rangle$ is the DFT wavefunction corresponding to the eigenvalue $\epsilon_i^{DFT}$ and $\epsilon_i^{QP}$ is the corresponding quasiparticle energy. Evaluating $\Sigma^{bi}$ with the one-shot $G_0W_0$ method within the GPP approximation requires the bilayer charge density, the bilayer irreducible polarizability, $\chi_0^{bi}$, and wave functions of the bilayer, $\psi^{bi}$.

We now show that all the required quantities can be approximated from the quantities obtained from a monolayer calculation, say on layer 'a'. The procedure to obtain $\psi^{bi}$ and $\rho^{bi}$ is as described before. The bilayer self-energy can be written as a sum over the individual self-energies of the layers and a correction term:

$$\langle \psi^{bi}|\Sigma^{bi}|\psi^{bi}\rangle = \langle \psi^{bi}|\Sigma_{GW}^a + \Sigma_{GW}^b|\psi^{bi}\rangle + \langle \psi^{bi}|\Delta \Sigma|\psi^{bi}\rangle$$ (2)

$\langle \psi^{bi}|\Sigma_{GW}^a|\psi^{bi}\rangle$ can be computed directly from monolayer irreducible polarizability, $\chi_0^a$, $\rho^a$ and $\psi^a$. To compute $\langle \psi^{bi}|\Sigma_{GW}^b|\psi^{bi}\rangle$, we obtain $\chi_0^b$, $\rho^b$ and $\psi^b$ by applying transformations similar to the ones described above to $\chi_0^a$, $\rho^a$ and $\psi^a$ respectively. The correction term, $\langle \psi^{bi}|\Delta \Sigma|\psi^{bi}\rangle$ contains information on the interaction between the layers. Due to the weak coupling between the layers, we expect $\langle \psi^{bi}|\Delta \Sigma|\psi^{bi}\rangle$ to be a small correction (compared to $\langle \psi^{bi}|\Sigma^a + \Sigma^b|\psi^{bi}\rangle$). We can evaluate $\Delta \Sigma$ at various levels of approximation. It can be evaluated at the DFT level by $\Delta \Sigma = \Delta V_{xc}$; or assuming just exchange interaction between the layers $\Delta \Sigma_x = \Sigma_x^{bi} - \Sigma_x^a - \Sigma_x^b$; or within the static limit of GW (COHSEX) $\Delta \Sigma_{COHSEX} = \Sigma_{COHSEX}^{bi} - \Sigma_{COHSEX}^a - \Sigma_{COHSEX}^b$; or within full GW. The only additional quantity needed in some of these approximations is, $\chi_0^{bi}$, which can be approximated as a sum of the irreducible polarizability of constituent layers: $\chi_0^{bi} = \chi_0^a + \chi_0^b$.

This method can easily be extended to calculate band structures of $n$ layers by computing

$$\langle \psi^n|\Sigma^n|\psi^n\rangle = \langle \psi^n|\sum_{i=1}^N \Sigma_{GW}^i|\psi^n\rangle + \langle \psi^n|\Delta \Sigma|\psi^n\rangle.$$ $\Delta \Sigma = \Sigma^n - \sum_{i=1}^N \Sigma^i$ can then be evaluated at an appropriate level of approximation.

Table 1 shows the ionization potential, electron affinity and band gap for bilayer and trilayer MoS$_2$ for different approximations to $\Delta \Sigma$. We compare them to the full GW calculation on these systems. $\Delta \Sigma = \Delta V_{xc}$ and $\Delta \Sigma = \Delta \Sigma_{COHSEX}$ show good agreement with the converged gap for the bilayer but fail to give the right ionization potential (IP) and electron affinity (EA). The COHSEX approximation to $\Delta \Sigma$ works well for the band gap in trilayer too, but again falls short in the ionization potential and electron affinity. The difference in band gap obtained using $\Delta \Sigma = \Delta \Sigma_{COHSEX}$ and $\Delta \Sigma = \Delta \Sigma_x$ shows that correlation plays an important role in the interaction between the layers. As the next level of approximation,
we compute \( \Delta \Sigma \) using GW with a few number, \( N_c \), of conduction states. We find that a small \( N_c = 800 \) is sufficient to converge the bilayer and trilayer MoS\(_2\) self-energies. Fig 4 (a) and 4 (b) show this convergence. It should be noted that the small number of states are used here only to compute the \( \Delta \Sigma \). We do not calculate \( \chi_{0i}^{bi} \) with a few unoccupied states. The bilayer irreducible polarizability is constructed with the converged monolayer irreducible polarizabilities. With this approximation, we obtain the IP, EA and band gap in good agreement with the full calculation [see Table 1]. A major computational bottleneck in performing separate GW calculations for the monolayer, bilayer and trilayer is the generation of the large number of unoccupied bands on a fine k-point grid and using these to compute the irreducible polarizability. This scheme completely does away with the need to regenerate the unoccupied bands and the polarizability for the bilayer and trilayer once we have the same for a monolayer. Fig 4 (d) and (e) compare the bilayer and trilayer MoS\(_2\) quasiparticle band structures obtained using this scheme with those obtained from full calculations on these. The eigenvalues are in good agreement with the full GW calculation,
FIG. 4. (Color online) (a) and (b) Convergence of the constructed $\langle \psi_{CBM} | \Sigma^{bi} | \psi_{CBM} \rangle$ and $\langle \psi_{CBM} | \Sigma^{tri} | \psi_{CBM} \rangle$ with the number of bands for the CBM at $\Lambda$ (green crosses). The horizontal line is the converged result from full calculations. The blue circles show the slow convergence of the full calculation with the usual procedure. (c), (d) and (e) plot the quasiparticle band structure of monolayer, bilayer and trilayer MoS$_2$ respectively. The black solid line indicates the result from separate GW calculations. The red dashed line shows the result obtained using the scheme described in the text.

upto 100 meV, and obtained at a small fraction of the computation cost. Note that the results in Fig 4 and Table 1 were obtained with slightly softened convergence parameters (see Computation details section). We also perform a monolayer calculation with the fully converged parameters and use this scheme to derive the band gap, IP and EA for bilayer and trilayer [see Table 1]. The converged IP, EA and band gap for the monolayer are found to be 6.76, 4.02 and 2.74 eV respectively. The band gap for the monolayer is found to be in good agreement with previous calculations.$^{8,32}$

Table 2 compares the IP, EA and band gap for bilayer and trilayer phosphorene obtained using this scheme to those obtained from the full calculation on these. Here we find that $N_c = 300$ is sufficient to converge the bilayer and trilayer self-energies. The COHSEX approximation to $\Delta \Sigma$ again shows good agreement with the full calculation for the band gap (upto 100 meV), but fails to give the right IP and EA. Evaluating $\Delta \Sigma$ at the COHSEX level thus seems to be a consistent approximation to obtain the converged quasiparticle band gap.
TABLE II. Ionization potential (IP), electron affinity (EA) and band gap (in eV) of bilayer and trilayer phosphorene evaluated using the constructed Σ for various approximations of ΔΣ described in the text. ΔΣ\textsuperscript{300} GW denotes ΔΣ evaluated at the GPP level with 300 bands.

| ΔΣ     | Bilayer | Trilayer |
| ------- | ------- | -------- |
|        | IP     | EA      | Gap    | IP     | EA      | Gap    |
| ΔV\textsubscript{xc} | 5.47   | 3.71    | 1.76   | 5.12   | 3.74    | 1.38   |
| ΔΣ\textsubscript{x}   | 6.45   | 4.62    | 1.83   | 6.66   | 4.86    | 1.80   |
| ΔΣ\textsubscript{COHSEX} | 5.27   | 3.69    | 1.58   | 4.69   | 3.60    | 1.09   |
| ΔΣ\textsubscript{GW}\textsuperscript{300} | 5.73   | 4.17    | 1.56   | 5.50   | 4.25    | 1.25   |
| Full   | 5.73   | 4.20    | 1.53   | 5.49   | 4.29    | 1.20   |

V. INTERLAYER SPACING DEPENDENCE IN BILAYER

The transition in bilayer MoS\textsubscript{2}, from interacting monolayers to non-interacting ones can be studied by gradually increasing the interlayer spacing. Fig. 5 shows the evolution of the DFT band structure, charge density and potential of bilayer MoS\textsubscript{2} as a function of increasing interlayer spacing, d. The equilibrium spacing is d\textsubscript{eq} = 6 Å. As the spacing between the layers increase, the interaction between them weakens and the splitting of the valence bands at Γ and the conduction bands at Λ reduces. This leads to a band gap transition from Γ − Λ to Γ − K to K − K. At d = 7.5 Å, the charge densities of the two layers stop overlapping, but the potential barrier between the layers is not zero. At this point the layers are weakly interacting and the nature of interaction within DFT is purely due to quantum confinement; ΔV\textsubscript{xc} is zero. At d = 9 Å and above, the two layers are completely non-interacting at the DFT level and the gap is that of monolayer MoS\textsubscript{2}.

We construct the bilayer self energy at different interlayer spacings using the various approximations to ΔΣ. The gap thus computed is shown in Fig. 6 (a). In the approximation of ΔΣ = ΔΣ\textsubscript{x} and ΔΣ = ΔV\textsubscript{xc}, the layers become non interacting once the charge densities of the two layers stop overlapping. Thus the gap in this approximation goes to the monolayer gap for spacing larger than d = 7.5 Å. The approximations of ΔΣ = ΔΣ\textsubscript{COHSEX} and ΔΣ = ΔΣ\textsubscript{GW}\textsuperscript{300} include the long range correlation interaction between the layers. The band gap computed in these approximations thus show a slower convergence to the mono-
FIG. 5. (Color online) (a), (b) and (c) DFT charge density, potential and band structure of bilayer MoS$_2$ at the equilibrium interlayer spacing of 6.0 Å, respectively. (d), (e) and (f) For interlayer spacing of 7.5 Å. (g), (h) and (i) For interlayer spacing of 9.0 Å.

layer gap with increasing interlayer spacing. Note that these calculations are performed using a coarser 12×12×1 k-point sampling and 6000 bands, leading to an overestimate of the monolayer gap in Fig. 6. Fig. 6 (b) shows the VBM and CBM levels computed using $\Delta \Sigma = \Delta \Sigma_{GW}^{800}$, as a function of increasing interlayer spacing. The bilayer CBM shows a weak dependence on the interlayer spacing and is already aligned with the monolayer CBM, while the bilayer VBM shows a slow convergence towards the monolayer VBM as the spacing is increased. This is similar to the effect of a metallic substrate on a molecule, where DFT shows no renormalization of the band gap but accounting for correlation effects in GW shows a significant renormalization\textsuperscript{41–43}. The renormalization of the molecular levels is due to screening from image charge effects, arising from the metal substrate. In the bilayer MoS$_2$ system, similarly, one monolayer feels the screening from the other.
VI. CONCLUSION

We studied the origin of layer dependence in band structures of 2D layered materials and developed a scheme to derive multilayer properties from calculations on a monolayer alone. We showed that the observed trend in layer dependence within DFT is a combined effect of quantum confinement and non-linearity of the DFT exchange-correlation functional. We also constructed the electron self energy for multilayers in terms of monolayer irreducible polarizability, charge density and wavefunctions. The DFT and quasiparticle band structures obtained using this scheme are in excellent agreement with those from the full calculation. The advantage of this scheme is that it can provide accurate results operating at a small fraction of the computation cost of a full calculation on multilayer systems. We show that using this scheme, one is able to capture the long range correlation effects within GW which leads to a significant renormalization of the gap even when DFT finds the layers to be non-interacting at larger interlayer spacings. This scheme can also be useful to study the variation in band structure as a function of stacking between the layers. Furthermore, it can be extended to study the nature of interaction between layers in heterostructures of these materials. It paves a way to derive properties of a heterostructure from just unit cell calculations on the constituent materials. This scheme is a promising tool to study
multilayers and layer dependence of properties in the growing family of 2D layered materials.

1. K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov, and A. K. Geim, Proceedings of the National Academy of Sciences of the United States of America 102, 10451 (2005).
2. K. F. Mak, C. Lee, J. Hone, J. Shan, and T. F. Heinz, Phys. Rev. Lett. 105, 136805 (2010).
3. A. Splendiani, L. Sun, Y. Zhang, T. Li, J. Kim, C.-Y. Chim, G. Galli, and F. Wang, Nano Letters 10, 1271 (2010).
4. Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, and M. S. Strano, Nat Nano 7, 699 (2012).
5. W. Jin, P.-C. Yeh, N. Zaki, D. Zhang, J. T. Sadowski, A. Al-Mahboob, A. M. van der Zande, D. A. Chenet, J. I. Dadap, I. P. Herman, P. Sutter, J. Hone, and R. M. Osgood, Phys. Rev. Lett. 111, 106801 (2013).
6. V. Tran, R. Soklaski, Y. Liang, and L. Yang, Phys. Rev. B 89, 235319 (2014).
7. A. Kuc, N. Zibouche, and T. Heine, Phys. Rev. B 83, 245213 (2011).
8. D. Y. Qiu, F. H. da Jornada, and S. G. Louie, Phys. Rev. Lett. 111, 216805 (2013).
9. H. Liu, A. T. Neal, Z. Zhu, Z. Luo, X. Xu, D. Tománek, and P. D. Ye, ACS Nano 8, 4033 (2014).
10. B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, and A. Kis, Nat Nano 6, 147 (2011).
11. L. Li, Y. Yu, G. J. Ye, Q. Ge, X. Ou, H. Wu, D. Feng, X. H. Chen, and Y. Zhang, Nat Nano 9, 372 (2014).
12. K. Roy, M. Padmanabhan, S. Goswami, T. P. Sai, G. Ramalingam, S. Raghavan, and A. Ghosh, Nat Nano 8, 826 (2013).
13. J. K. Ellis, M. J. Lucero, and G. E. Scuseria, Applied Physics Letters 99, 261908 (2011).
14. J. Hong, K. Li, C. Jin, X. Zhang, Z. Zhang, and J. Yuan, Phys. Rev. B 93, 075440 (2016).
15. J. E. Padilha, H. Peelaers, A. Janotti, and C. G. Van de Walle, Phys. Rev. B 90, 205420 (2014).
16. V. Tran, R. Fei, and L. Yang, 2D Materials 2, 044014 (2015).
17. H.-P. Komsa and A. V. Krasheninnikov, Phys. Rev. B 86, 241201 (2012).
18. J. Kang, L. Zhang, and S.-H. Wei, The Journal of Physical Chemistry Letters 7, 597 (2016).
19. X. Fan, D. J. Singh, and W. Zheng, The Journal of Physical Chemistry Letters 7, 2175 (2016).
20 G. Constantinescu, A. Kuc, and T. Heine, Phys. Rev. Lett. 111, 036104 (2013).
21 L. Hedin, Phys. Rev. 139, A796 (1965); L. Hedin and S. Lundqvist, in Advances in Research and Applications, Solid State Physics, Vol. 23, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic Press, 1970) pp. 1 – 181.
22 M. S. Hybertsen and S. G. Louie, Phys. Rev. B 34, 5390 (1986); Phys. Rev. Lett. 55, 1418 (1985).
23 A. J. Bradley, M. M. Ugeda, F. H. da Jornada, D. Y. Qiu, W. Ruan, Y. Zhang, S. Wickenburg, A. Riss, J. Lu, S.-K. Mo, Z. Hussain, Z.-X. Shen, S. G. Louie, and M. F. Crommie, Nano Letters 15, 2594 (2015).
24 M. M. Ugeda, A. J. Bradley, S.-F. Shi, F. H. da Jornada, Y. Zhang, D. Y. Qiu, W. Ruan, S.-K. Mo, Z. Hussain, Z.-X. Shen, F. Wang, S. G. Louie, and M. F. Crommie, Nat Mater 13, 1091 (2014).
25 J. Lischner, D. Vigil-Fowler, and S. G. Louie, Phys. Rev. Lett. 110, 146801 (2013).
26 Z. Ye, T. Cao, K. O’Brien, H. Zhu, X. Yin, Y. Wang, S. G. Louie, and X. Zhang, Nature 513, 214 (2014).
27 T. Cao, Z. Li, D. Y. Qiu, and S. G. Louie, Nano Letters 16, 5542 (2016).
28 P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).
29 W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).
30 G. A. Tritsaris, S. N. Shirodkar, E. Kaxiras, P. Cazeaux, M. Luskin, P. Plechá, and E. Cancès, Journal of Materials Research 31, 959 (2016).
31 D. Y. Qiu, F. H. da Jornada, and S. G. Louie, Phys. Rev. Lett. 115, 119901 (2015).
32 D. Y. Qiu, F. H. da Jornada, and S. G. Louie, Phys. Rev. B 93, 235435 (2016).
33 P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. D. Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, Journal of Physics: Condensed Matter 21, 395502 (2009).
34 J. P. Perdew and A. Zunger, Phys. Rev. B 23, 5048 (1981).
35 J. P. Perdew, M. Ernzerhof, and K. Burke, The Journal of Chemical Physics 105, 9982 (1996).
36 J. Deslippe, G. Samsonidze, D. A. Strubbe, M. Jain, M. L. Cohen, and S. G. Louie, Computer Physics Communications 183, 1269 (2012).

37 G. Samsonidze, M. Jain, J. Deslippe, M. L. Cohen, and S. G. Louie, Phys. Rev. Lett. 107, 186404 (2011).

38 S. Ismail-Beigi, Phys. Rev. B 73, 233103 (2006).

39 J. Deslippe, G. Samsonidze, M. Jain, M. L. Cohen, and S. G. Louie, Phys. Rev. B 87, 165124 (2013).

40 J. He, K. Hummer, and C. Franchini, Phys. Rev. B 89, 075409 (2014).

41 K. S. Thygesen and A. Rubio, Phys. Rev. Lett. 102, 046802 (2009).

42 J. B. Neaton, M. S. Hybertsen, and S. G. Louie, Phys. Rev. Lett. 97, 216405 (2006).

43 M. Rohlfing, Phys. Rev. Lett. 108, 087402 (2012).