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Nonunique fraction of Fock exchange for defects in two-dimensional materials

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By investigating the vacancy and substitutional defects in monolayer WS_2 with hybrid functionals, we find that there is no unique amount of Fock exchange that concurrently satisfies the generalized Koopmans' condition and reproduces the band gap and band-edge positions. Fixing the mixing parameter of Fock exchange based on the band gap can lead to qualitatively incorrect defect physics in two-dimensional materials. Instead, excellent agreement is achieved with both experiment and many-body perturbation theory within the *GW* approximation once the mixing parameters are tuned individually for the defect species and the band edges. We show the departure from a unique optimized mixing parameter is inherent to two-dimensional systems as the band edges experience a reduced screening whilst the localized defects are subject to bulk-like screening.

Two-dimensional (2D) materials are rapidly gaining ground in a range of technologies owing to both their exotic electronic and optical properties due to quantum confinement [1] and the increasing ease of manipulation of their properties on a layer-by-layer basis. Defects have been shown to be viable active sites for enabling electrocatalysis (e.g., hydrogen evolution [2–4]) on otherwise inert basal planes of 2D materials. In quantum information science, 2D materials hold exceptional promise as defect hosts because their associated point defects typically present high spin states and deep defect levels [5–7], and any near-surface defects are easier to manipulate and characterize. The nature of such quantum defects is often elusive from experiment, and reliable theoretical modeling is required to understand their atomistic origins [8, 9]. First-principles defect calculations are now typically carried out with hybrid density functionals, the accuracy of which is closely related to the amount of Fock exchange admixed with semilocal exchange in the framework of generalized Kohn-Sham density-functional theory (DFT) [10]. The mixing parameter of hybrid functionals is commonly determined on the basis of the band gap of host systems from experiment or higher levels of theory. It has been well validated that such band-gap optimized mixing parameters lead to accurate defect levels for localized point defects in bulk materials [11].

The success of hybrid functionals can be attributed to the fulfillment of generalized Koopmans' condition, which for a localized defect, requires that the ionization energy and electron affinity to be equal, hence recovering the exact piecewise linearity of the total energy upon electron occupation [12–15]. Indeed, one can often find a single mixing parameter that describes the host band gap and the defect localization equally well in bulk materials [16]. The uniqueness of optimal mixing parameter promotes the use of a fixed, band-gap targeted mixing parameter in state-of-the-art defect calculations [10]. The same approach has been routinely applied to understand the defect properties in 2D materials [17–20]. In this Letter, we show that, in contrast to bulk 3D materials, there exists no unique amount of Fock exchange that can reproduce the experimental band gap and satisfying Koopmans' conditions for the defect level concurrently. Admixing a single fraction of Fock exchange thus could entail large errors in defect energy levels for 2D materials. We show that imposing appropriate mixing parameters individually for defects and host band edges is needed for an accurate description of defect energy levels, and discuss the failure of the typical hybrid-functional defect computation scheme.

To illustrate this issue, we investigate various point defects in monolayer (ML) WS_2, including the sulfur monovacancy (V_S), the single cobalt atom substituting sulfur (Co_S) or tungsten (Co_W), and the single carbon atom substituting sulfur (C_S). Several of these defects have recently become the subject of increasing theoretical and experimental efforts following the demonstrated quantum light emitters in 2D transition-metal dichalcogenides (TMDs) [21–26], and so are well-motivated for further consideration here [19, 27–29].

Our analysis of Koopmans' condition is primarily carried out using a global hybrid functional in which a single mixing parameter (α) controls the amount of Fock exchange admixed with the semilocal Perdew-Burke-Ernzerhof (PBE) exchange [30]. At $\alpha = 0.25$ this global hybrid functional is essentially the PBE0 functional [31, 32]. Conventionally we refer to this family of one-parameter hybrid functionals as PBE0(α). All hybrid-functional calculations are performed with the projector-augmented-wave method [33] as implemented in VASP [34, 35]. As a higher level of theory, many-body perturbation theory within the *GW* approximation [36, 37] is used to establish an accurate reference for the hybrid functional. Specifically, on top of

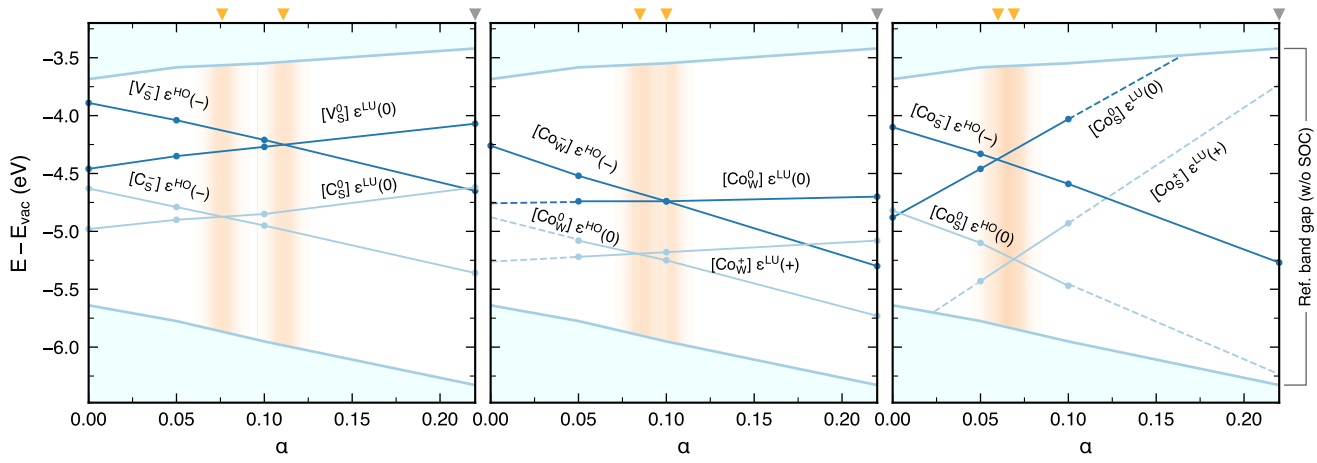

FIG. 1. Single-particle defect levels as a function of mixing parameter α for various defects in the ML WS_2. The eigenvalues are evaluated at the four representative α values shown by the solid dots and interpolated in between (solid lines). Linear extrapolations (indicated by dashed lines) are used when the localized defect state cannot be stabilized within the band gap. The band edges of ML WS_2 are indicated by the blue shades. All energies are referred to the vacuum level. The orange marker indicates the mixing parameter α_K at which the generalized Koopmans' condition $\varepsilon^{HO}(q) = \varepsilon^{LU}(q+1)$ is fulfilled, whereas the grey marker indicates the optimal mixing parameter ($\alpha_G = 0.22$) for reproducing the band gap of ML WS_2. Spin-orbit coupling (SOC) is not taken into account.

a PBE starting point, one-shot G_0W_0 calculations are performed for the ML WS_2 and some selected defects. The truncated Coulomb interaction [38] and the subsampling technique [39] are used to address the slow convergence of quasiparticle (QP) energies specific to 2D systems [40]. The G_0W_0 calculations are performed with BERKELEYGW [41] interfaced to the DFT code from Quantum-ESPRESSO [42]. The details of computational parameters for the hybrid-functional and G_0W_0 calculations are provided in the Supplemental Material (SM) [43].

We first survey the electronic structure of the pristine ML WS_2. Obtained from exfoliating $2H$-WS_2, the ML WS_2 is a direct-gap semiconductor with a K–K transition. As a result of the trigonal prismatic crystal field splitting, the valence band maximum (VBM) is of $d_{x^2-y^2}$ and d_{xy} character whereas the conduction band minimum (CBM) is of d_{z^2} character. The G_0W_0 band gap of the ML WS_2 is 2.9 eV without SOC. To reproduce this reference G_0W_0 band gap, we find that the mixing parameter (dubbed as α_G) needs to be adjusted to 0.22 for the hybrid functional. Once the SOC is included, this PBE0(α_G) functional leads to a band gap of 2.58 eV, in good agreemen with the experimentally reported values ranging from 2.4 to 2.7 eV [27, 44, 45]. We note that the experimental determination of the band gap is subject to the dielectric screening effect arising from the substrate [46, 47].

To identify the mixing parameter fulfilling the generalized Koopmans' condition for a given localized defect D, we calculate the single-particle eigenvalue $\varepsilon^{HO}(q)$ associated with the highest occupied (HO) state at charge state q as well as the eigenvalue $\varepsilon^{LU}(q+1)$ of the lowest unoccupied (LU) state at charge state $q+1$. The optimal mixing parameter α_K is determined when the equality $\varepsilon^{HO}(q) = \varepsilon^{LU}(q+1)$ holds. To calculate this we consider candidate defects embedded in an orthorhombic supercell of 90 atoms representing the ML WS_2. In particular, we refer the band edges and single-particle defect eigenvalues to the vacuum level, which is a natural and physical choice for 2D systems [18]. While the alignment is straightforward for neutral defects, the single-particle levels of charged defects are subject to finite-size effect arising from the spurious electrostatic interactions [11, 48–50]. The alignment is further complicated by the fact that the electrostatic potential in the vacuum region experiences an artificial bending due to the dipole moment introduced by the neutralizing charge background. Here we apply the potential correction scheme of Chagas da Silva *et al.* [51], thereby achieving well-defined single-particle eigenvalues with respect to vacuum for charged defects.

Figure 1 depicts the evolution of band edges and single-particle defect eigenvalues with respect to the mixing parameter α. Specifically, the defect eigenvalues are evaluated at four α values (0, 0.05, 0.10, and 0.22). For each of these calculations, the Koopmans' condition is assessed with a fixed structure which is relaxed with PBE0 at the given α value for the charged state. At this stage, we do not take into account SOC for geometric relaxations and hence the determination of α_K due to its computational complexity. For all defects considered, the values of α_K fulfilling the Koopmans' condition are found in a narrow range between 0.06 and 0.11, significantly lower

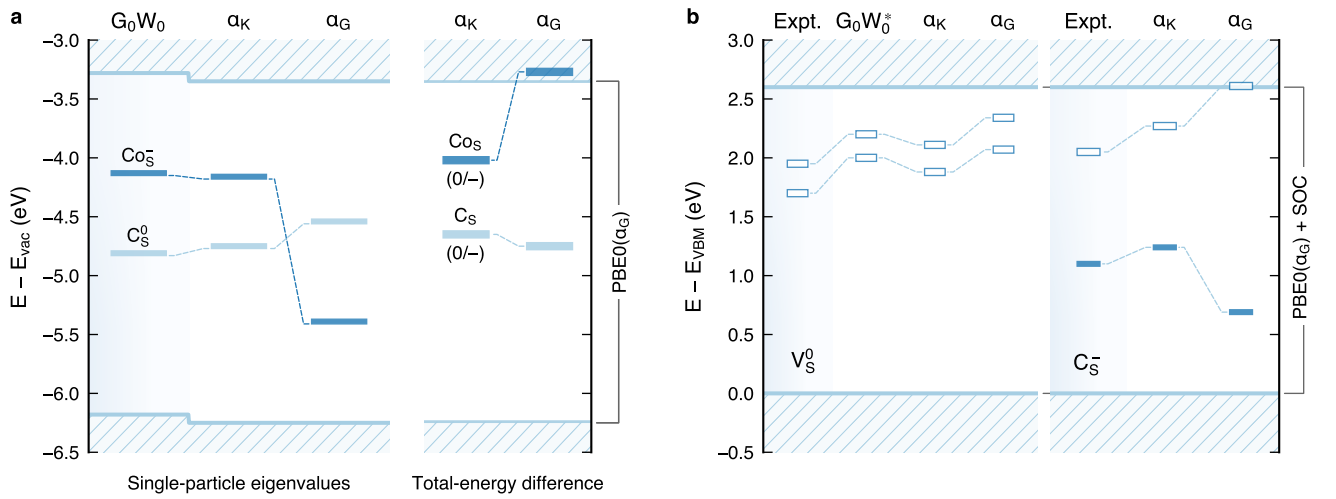

FIG. 2. (a) Defect levels of Co_S^{-1} and C_S^0 obtained with single-particle eigenvalues and total-energy difference with respect to the vacuum level. For each computational scheme, the PBE0(α) defect levels are calculated with α_K and α_G and are benchmarked against the G_0W_0 reference. To exclude the effect of structural relaxation, we use the PBE equilibrium structures throughout. The PBE0 band-edge positions are determined by PBE0(α_G). (b) Calculated single-particle defect levels with PBE0(α_K) and PBE0(α_G) compared to STS measurements for V_S^0 and C_S^-. The structures are relaxed with the corresponding α values for the PBE0 calculations. The defect levels are referred to the VBM and take into account the SOC. The band gap takes the value as obtained with PBE0(α_G)+SOC throughout. The G_0W_0 results (denoted by $G_0W_0^*$) are taken from Ref. 27.

than the band-gap enforced mixing parameter α_G of 0.22. We note that α_K values are largely unaffected by SOC. As we show in Table S1 of the SM, the Koopmans' condition is still fulfilled within 0.1 eV when SOC is included. This is our first key result. Indeed, PBE(α_G) exhibits strong concavity as the ionization energy $-\varepsilon^{HO}(q)$ is consistently larger than the electron affinity $-\varepsilon^{LU}(q+1)$ for any given defect [52]. This is clearly at odds with the existence of a unique mixing parameter for bulk materials which is able to describe the band gap reasonably well without compromising the Koopmans' condition for localized defects [16, 53–55].

Among all defects considered, the effect of mixing parameter is particularly notable for Co_S. The defect levels associated with Co_S is predominately characterized by the strongly localized Co-3d states. Specifically, the (0/−) and (+/0) transitions involve the $d_{x^2-y^2}$ and the d_{z^2} orbitals of the Co atom, respectively. Taking the neutral Co_S^0 for example, we notice that the occupied d_{z^2} and unoccupied $d_{x^2-y^2}$ defect levels move sharply towards the host band edges as α increases and eventually merge into the valence and conduction band when $\alpha = \alpha_G$ (cf. Fig. 1). Consequently, PBE0(α_G) would predict that no localized defect levels exist within the band gap for Co_S, qualitatively at variance with the deep levels obtained with PBE0(α_K).

To settle the conflicting results of Co_S due to the choice of α, we carry out one-shot G_0W_0 calculations for the spin-unpolarized Co_S^- defect (see the SM for computational details). We find excellent agreement between the PBE0(α_K) and G_0W_0 defect levels (mainly of $d_{x^2-y^2}$ and d_{xy} characters of Co) [cf. Fig. 2(a)]. Both methods place the single-particle defect level −4.1 eV below the vacuum level, or equivalently about 2.1 eV above the VBM. By contrast, PBE0(α_G) overestimates the defect ionization energy by nearly 1.3 eV, consistent with the strong concavity noted previously in Fig. 1. The high accuracy of PBE0(α_K) is further demonstrated for C_S^0 [cf. Fig. 2(a)], while PBE0(α_G) still underperforms, albeit to a lesser extent than for Co_S^-.

An arguably more common approach to the determination of defect levels is through the total-energy difference between different defect charge states [10]. When referred to the VBM of the pristine host, the (0/−) charge transition level of defect D can be obtained as $E_{tot}(D^-) - E_{tot}(D^0) - E_{VBM}$. Analogous to the single-particle level, the total energy of charged defects are ill-defined for periodic systems. Here we apply the finite-size correction scheme of Komsa *et al.* [50, 56] as implemented in SLABCC [57] to the total energy of charged defect. The computed (vertical) (0/−) charge transition levels are shown in Fig. 2(a) for Co_S and C_S. In general, defect levels obtained with the total-energy difference scheme are less sensitive to the amount of Fock exchange when aligned to a common reference (e.g., average electrostatic potential or vacuum) [58–61]. While this is the case for the (0/−) level of C_S, for Co_S the agreement with the G_0W_0 QP energy found with PBE0(α_K) is substantially worse if α_G is used instead.

Our results so far suggest that fixing the α value, which is typically chosen based on the host band gap for studying defects in bulk materials, can be problematic and

even qualitatively change the defect physics in 2D materials. The discernible discrepancy between α_G and α_K suggests that defect levels need to be treated individually from band edges, the alignment of which can be easily achieved through the common vacuum level. To illustrate the validity the proposed scheme, we refer to to the scanning tunneling spectroscopy (STS) measurements of the neutral V_S^0 [27] and the negatively charged C_S^- [29] in Fig. 2(b). To facilitate the comparison, we include SOC in the hybrid-functional calculations and focus on the single-particle eigenvalues with the equilibrium defect structure at the charge state pertinent to experiment. The STS spectra revealed two prominent peaks at 1.8 eV and 2.0 eV above the VBM for V_S^0 [27]. The peaks correspond to the unoccupied d_{xy} and $d_{x^2-y^2}$ orbitals of the W atoms near the vacancy, whose degeneracy is lifted by spin-orbit splitting [17]. The positions of the two defect levels are well reproduced by the single-particle defect energies of our PBE0(α_K) calculations in reference to the band edges obtained with PBE0(α_G), and the accuracy is comparable to that of the G_0W_0 calculation of Ref. [27]. The C_S^- is also characterized by two defect levels deep within the band gap [29]. The two levels are mainly of the C-p_z character, with one occupied at 1.1 eV and the other unoccupied at 2.0 eV above the VBM. The importance of enforcing the Koopmans' condition is again evidenced for C_S^- as the splitting of the two defect levels would be too large if the mixing parameter is fixed at α_G.

To rationalize the departure from the existence of a unique α value as for bulk materials, we turn to the bulk WS_2 and examine the defect levels therein. The bulk 2H-WS_2 comprises repeated layers of ML WS_2, and has an indirect (Γ–K) band gap of 1.3 eV [62, 63]. The markedly smaller band gap leads to a strongly reduced mixing parameter $\alpha_G^{\rm bulk}$ of 0.07. Defects are introduced to an orthorhombic supercell containing 72 atoms, which is based on the 36-atom supercell of the ML WS_2 comprising two alternating MLs stacked along the out-of-plane direction. Figure 3(a) shows the single-particle defect levels at the respective values of α_K for defects in both bulk and ML WS_2. Some defects such as Co_W no longer exhibit deep levels in the bulk WS_2. Interestingly, irrespective of the dimensionality of the host material, the various α_K values fall closely in the vicinity of $\alpha_G^{\rm bulk}$. The consistency in the α_K values implies that the localization of defect in the ML WS_2 is comparable to that of the bulk. This is clearly demonstrated in Fig. 3(b) where the defect charge density $\rho(D^q)-\rho(D^0)$ is plotted for the ML and the bulk host. Particularly for Co_S^- and C_S^-, the charge density along the in-plane direction is nearly intact when going from the bulk to the ML WS_2. The charge density analysis additionally provides an avenue to understand the screening effect. In the presence of a strictly localized defect, the average charge density approaches the delocalized screening charge density $(1-1/\epsilon)q/\Omega$ far away

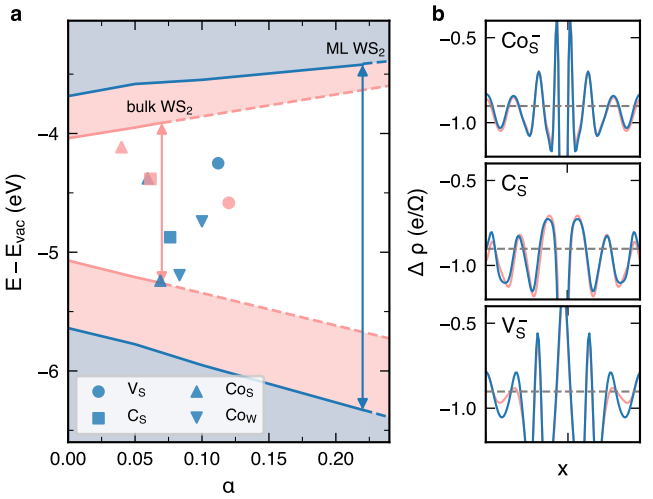

FIG. 3. (a) Single-particle defect levels at the Koopmans-fulfilled α_K in the monolayer (blue) and the bulk (red) WS_2. The band-edge positions of the monolayer and the bulk WS_2 are shown accordingly by the same color scheme. (b) Defect charge density $\rho(D^q)-\rho(D^0)$ of Co_S^-, C_S^-, and V_S^- as obtained with PBE along the in-plane direction in the monolayer (blue) and the bulk (red) WS_2. The horizontal line refers to the delocalized screening charge density $(1-1/\bar{\epsilon})q/\Omega$ given a localized defect at charge state q where $\bar{\epsilon}$ stands for the averaged dielectric constant of the bulk WS_2. The defects are situated near the center.

from the defect [49], where ϵ is the dielectric constant and Ω the volume of the supercell. Using the (geometrically) averaged dielectric constant ($\bar{\epsilon}=10.2$) of the bulk WS_2, we find that the delocalized screening charge is recovered for Co_S^- and C_S^- [cf. Fig. 3(b)]. While this is expected for localized defects in the bulk WS_2, the agreement found in the ML WS_2 is a compelling evidence that the localized defects therein are still subject to the bulk-like screening and can be adequately described by $\alpha_G^{\rm bulk}$. The deviation from the ideal screening charge is more visible for V_S, in accord with its more delocalized nature and hence the larger deviation of α_K from $\alpha_G^{\rm bulk}$ compared to the substitutional defects.

In contrast to α_K, the large α_G for the ML WS_2 is inherent to the strong opening of band gaps for 2D materials. We note in passing that the long-range part of Fock exchange is critical in opening the band gap of 2D materials given the asymptotic $1/r$ decay in vacuum. In fact, the short-ranged Heyd–Scuseria–Ernzerhof (HSE) functional [64] struggles to open up the band gap of the ML WS_2 unless an excessively large mixing parameter is used (0.45 with the PBE structure or 0.55 if the structure is relaxed self-consistently). However, such a large mixing parameter results in a highly distorted band structure (e.g., valence bandwidth) and, more importantly, shifts the whole band edges by -0.3 eV compared to G_0W_0 and PBE0(α_G) (see the SM). Nonetheless, for localized

defects, the HSE defect levels are reasonably aligned to the vacuum level as the short-range bulk-like screening dominates.

In addition to the TMDs, we find that the distinct two-set values (α_K and α_G) also apply to the ML hexagonal boron nitride (h-BN) involving only simple sp elements (see the SM). While systems characterized by localized d electrons are less amenable to treatment for fulfilling the Koopmans' condition [54, 65], we emphasize that the non-uniqueness of α is a general attribute for hybrid-functional defect calculations in 2D materials.

Before closing, we note that our study focuses on defect energy levels. It remains an open question how the nonuniqueness of α affects other defect properties, such as the defect formation energies, the optical transitions, and the phonons. Our findings motivate further investigations of the possible implications for general defect physics in 2D materials.

In conclusion, we have shown that using a fixed amount of Fock exchange in hybrid functionals could lead to qualitatively incorrect description of defects in 2D materials, in contrast with the established practice common to defect calculations in bulk materials. The absence of a unique mixing parameter stems from the reduced screening for the delocalized band-edge states whereas the screening is bulk-like for localized defects. The distinct screening behaviors hence require the band edges and the defect states to be treated separately through their own optimal mixing parameters. We expect these effects to be present in all 2D materials and they should be carefully taken into account to ensure accurate hybrid-functional defect computations.

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