Supplemental Material for Giant spin-orbit splitting of point defect states in monolayer WS₂

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I. VDW AND SOC

These series of calculations were originally meant to include the bulk WS_2 as well, for which the van der Waals (vdW) force should be considered to address the inter-layer interaction. For this, we compared several vdW correction schemes available in VASP, and found that the vdW density functional¹ optB88-vdW² gave us the most accurate interlayer separation of 12.546 Åcompared to experiment (12.323 Å). Therefore we decided to use the optB88-vdW.

As there is an incompatibility between the optB88-vdW functional and the non-collinear calculations in VASP, we had to include the vdW correction and the SOC effect in different steps. We fist performed the geometry relaxation, and then calculate the total energy with only the vdW correction being included. In the end, we turned off the vdW correction and calculated the electronic properties of the relaxed structure with only the SOC effect included. We used this separation scheme because we tested and found that vdW only affects the geometry but not the electronic properties of the mateiral, while SOC only affects the electronic properties but not the geometry.

II. DERIVATION OF THE BOUNDARIES OF CHEMICAL POTENTIALS μ_S AND μ_W

In this section, the derivation of the boundaries of chemical potentials μ_S and μ_W will be given. However, we would like to lay a foundation by first giving a brief thermodynamic background of formation energy. We know from textbooks that the Gibb's free energy is defined by

$$G = H - TS,\tag{1}$$

where H is the enthalpy of the system, T is temparature in Kelvin, and S is the entropy. The enthalpy is defined as

$$H = E + pV. \tag{2}$$

E is the total energy, p is pressure of the system in atm, V is the system volume. Another definition of G for homogeneous system is

$$G = \sum_{i} n_{i} \mu_{i} \tag{3}$$

By this definition, chemical potentials and the Gibb's free energy are related. What DFT calculates is the electronic total energy of the system without any pressure and temparature (p=0 atm and T = 0K) This energy is the total energy in

Eq. 2. Furthermore, when p = 0 and T = 0K, the Gibb's free energy and enthalpy become simply the total energy of the system, which can be regarded as the summation of the chemical potentials of all the constituent atoms:

$$G = H = E = \sum_{i} n_i \mu_i \tag{4}$$

Viewing Eq. 4 from another angle, we can find that the chemical potential μ_i is in fact very simple: total energy per atom. This also corresponds to the original definition of the chemical potential, which is the partial derivative of the internal energy E with respect to the number of particles n: $\mu = \frac{\partial E}{\partial n}$. Chemical potentials appear when there involves a net change of number of particles in a system, which is our case of defect creation in materials.

Based on the short introduction of the definition of the thermodynamical terms, we can go on to discuss how to define the chemical potentials, thus calculate the defect formation energies by using Eq. 1 in the main text. First, let us consider the formation of the ML WS₂ as a reaction, in which the W atoms and S atoms are taken respectively from their bulk resevoirs to form WS₂:

$$W_{(bulk)} + 2S_{(bulk)} \to WS_{2(ML)} \tag{5}$$

By definition, the formation enthalpy (heat of formation) of a reaction is given by $\sum \mu_{product} - \sum \mu_{reactant}$. Thus here we have

$$\Delta H_{WS_2} = \mu_{WS_2,ML} - \mu_{W,bulk} - 2\mu_{S,bulk} \tag{6}$$

Please note that here $\mu_{W,bulk}$ and $\mu_{S,bulk}$ are the energy per atom of W bulk in the bcc structure, and S in the bulk α -S respectively as we consider these two phases as the atomic resevoir for WS₂. μ_{WS_2} is the energy per forming unit of WS₂.

Furthermore, under the chemical equilibrium, the W and S atoms can "flow" freely between the atomic reservoirs and WS_2 without lossing any energy. This is described by the following reaction:

$$W + 2S \leftrightarrow WS_2.$$
 (7)

The free exchange of atoms are achieved when

$$\mu_W + 2\mu_S = \mu_{WS_2} \tag{8}$$

In realistic experimental conditions, there could be an excess amount of constituent atoms of a product compound in the surroundings depending on different sythesis routes. In order to take into account this factor, in DFT calculations the

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usual practice is to consider the "poor" and "rich" extremes of the amount of the constituent atoms. For instance, we can consider the W-rich (S-poor) and the W-poor (S-rich) conditions for ML WS₂. In the W-rich condition, there are extra W atoms in the surroundings of WS₂. By the help of Eqs. 6 and 8, we can now derive the boundaries for μ_W and μ_S in the two conditions mentioned above.

In the W-rich condition, it is required that

$$\mu_W = \mu_{W,bulk}.\tag{9}$$

Otherwise, if μ_W is larger than $\mu_{W,bulk}$, then the W atoms will leave WS₂ and start to precipitate the bulk W metal because of the fact that atoms always move from a place with higher chemical potential to another place with a lower chemical potential. Then by combining Eqs. 6, 8 and 9, we can obtain the lower bound for μ_S

$$\mu_S = \mu_{S,bulk} + \frac{1}{2} \Delta H_{WS_2}.$$
(10)

On the contrary, in the S-rich condition,

$$\mu_S = \mu_{S,bulk}.\tag{11}$$

Thus by Eqs. 6, 8 and 11, we have the lower limit of μ_W :

$$\mu_W = \mu_{W,bulk} + \Delta H_{WS_2} \tag{12}$$

One can then obtain the upper and lower limits for both μ_W and μ_S :

$$\mu_{W,bulk} + \Delta H_{WS_2} \le \mu_W \le \mu_{W,bulk}, \tag{13a}$$

$$\mu_{S,bulk} + \frac{1}{2}\Delta H_{WS_2} \le \mu_S \le \mu_{S,bulk}. \tag{13b}$$

However, in order to use Eq. 13 for DFT calculations, we need to change the thermodynamical terms with energy. For this purpose, we see that $\mu_{WS_2,ML} = E_{WS_2,ML}$, $\mu_{W,bulk} = E_{W,bulk}$ and $\mu_{S,bulk} = E_{S,bulk}$. Eventually, we arrive the final expressions of the boundaries of μ_W and μ_S which is used to calculate the defect formation energies:

$$E_{WS_2} - 2E_S \le \mu_W \le E_W \tag{14a}$$

$$\frac{1}{2}(E_{WS_2} - E_W) \le \mu_S \le E_S.$$
 (14b)

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III. DENSITY OF STATES

Fig. 1 presents the total DOS of all the ML WS_2 slabs in order to show the SO splitting of the defect states.

Fig. 2 compares the DOS of the NSP and SP W_S-WS₂ and W_{S2}-WS₂ as well as the projected DOS (PDOS) of each orbital. The purpose of this Figure is to allow us to trace back the origin of the magnetic moment existing in SP W_S-WS₂ and W_{S2}-WS_{S2}. In each plot, the total density of states (TDOS) is shown on top, followed by the DOS projected onto the S p orbitals and the five W d orbitals. The contribution of the d orbitals of the antisite W atom is also plotted and compared to all other W atoms. Fig. 2 (a) and (c) show that the defect state under the Fermi level is mainly composed of the d_{xy} and $d_{x^2-y^2}$ orbitals of the defect W atom. Fig. 2 (b) and (d) further prove that this defect state is spin-polarized (spin-up) and therefore it bears the magnetic moment.

IV. ORBITAL DECOMPOSED CHARGE DENSITIES OF THE BAND STRUCTURES OF PERFECT BULK AND ML WS₂ UNITCELLS

Fig. 3 and 4 provide the orbital decomposed charge densities of the band structures of perfect bulk and ML WS_2 unitcells. These Figures are to illustrate the crystal field splitting of the bands.

V. ORBITAL DECOMPOSED BAND STRUCTURES OF PERFECT AND DEFECTIVE ML WS₂ SUPERCELLS

This series of figures show that the defect states are composed of either the d_{z^2} orbital or $d_{xy} + d_{x^2-y^2}$.

¹ M. Dion, H. Rydberg, E. Schröder, D. C. Langreth, and B. I. Lundqvist, Phys. Rev. Lett. **92**, 246401 (2004).

² J. Klimeš, D. R. Bowler, and A. Michaelides, J. Phys.: Condens. Matter 22, 022201 (2010).



FIG. 1: Total DOS of all the ML WS₂ slabs considered in this study. Only the W_S and W_{S2} antisite defects are shown to be spin-polarized, thus they have both spin-up (black) and spin-down (red) DOS. Fermi level is indicated as the dashed blue lines.



FIG. 2: TDOS and PDOS plots for both the non-spin-polarized (NSP) and spin-polarized (SP) W_S and W_{S2} antisites. PDOSs are enlarged 10 times to make them visually comparable to TDOSs.

FIG. 3: Orbital decomposed BSs of bulk WS2 unitcell.

FIG. 4: Orbital decomposed BSs of ML WS₂ unitcell. The W d orbitals are split due to the crystal field effect.

FIG. 5: The band structures of all the ML WS₂ slabs considered in this study. The bands are decomposed in terms of the five d orbitals of the W atoms. The brownish color indicates the mixture of the d_{xy} (green) and $d_{x^2-y^2}$ (red) orbitals.