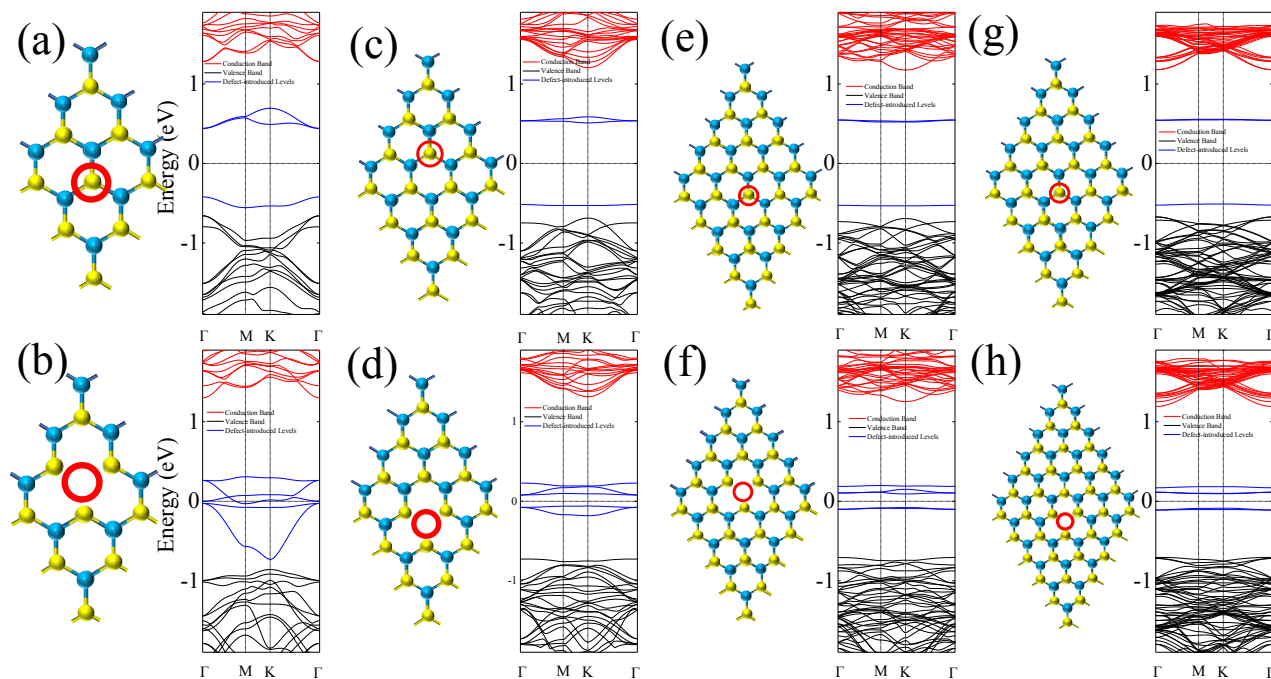


# 1 Piezoelectricity Enhancement and Bandstructure Modification of Atomic Defect-mediated 2 MoS<sub>2</sub> Monolayer

## 3 1. The effect of atomic vacancy

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5 Figure 1s. Bandstructure of MoS<sub>2</sub> with single S vacancy in supercell of (a) 3×3, (c) 4×4, (e)5×5  
6 and (g) 6×6 in size; as well as single Mo vacancy in supercell of (b) 3×3, (d) 4×4, (f)5×5, and  
7 (h) 6×6 in size.

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9 Figure 1s consecutively demonstrates the schematic of our investigated structure with  
10 different defect types and size of supercell: single S vacancy in (a) 3×3, (c) 4×4, (e)5×5 and (g)  
11 6×6; as well as single Mo vacancy in (b) 3×3, (d) 4×4, (f)5×5, and (h) 6×6 repetition of the  
12 smallest unit cell. The red circle highlights the defect position. A hexagonal lattice was  
13 chosen in this study in repetition of the minimum supercell of a MoS<sub>2</sub> monolayer, which  
14 contains 2 Sulfur atoms and 1 Molybdenum atom. The density of the defect is thus 1/18, 1/32,  
15 1/50 and 1/72 for the Sulfur atom and 1/9, 1/16, 1/25 and 1/36 for the Molybdenum atom in  
16 the size of 3×3, 4×4, 5×5 and 6×6 supercell respectively.

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18 It also demonstrates the calculated electronic band structure of MoS<sub>2</sub> monolayer having  
19 atomic vacancies of different density. A small change in the bandgap is observed for the  
20 continuously expanded lattice with the Sulfur vacancy. As shown in Figure 2, the defect of  
21 atomic vacancy can introduce energy levels within the gap-in the forbidden band. The energy

1 levels induced by Mo vacancy are much closer to Fermi energy level in comparison to those  
 2 arising from S vacancy. Thus, the Mo vacancy introduced structure has much higher  
 3 conductivity compared to S vacancy introduced MoS<sub>2</sub> monolayer. One can notice that the  
 4 position of the direct bandgap transition transfers from K to  $\Gamma$  in the Brillouin Zone in the case of  
 5 6×6 supercell for both S- and Mo-vacancy. Also, the supercell with size of 3x3 unit cells with a  
 6 Mo-vacancy has an indirect bandgap from the  $\Gamma$ -point at conduction band minimum (CBM) to  
 7 K-point at valence band maximum (VBM). The position of CBM and VBM change with the  
 8 larger supercell size due to the reduced defect interaction and the band folding effect.<sup>1</sup>

9

## 10 2. The effect of atomic shift on piezoelectricity along zigzag direction

11 Monolayers of 2H-TMDC belong to the  $D_{3h}(\bar{6}m2)$  point group while MoS<sub>2</sub> bulk belongs  
 12 to  $D_{6h}(6/mmm)$  point group.  $D_{3h}$  symmetry places restrictions on the magnitude and uniqueness  
 13 of the piezoelectric tensor coefficients. In the case of  $D_{3h}$ , only one d and one e-coefficient need  
 14 to be calculated. The atomic shift can also apply effect on other components of the piezoelectric  
 15 coefficient. This is a matrix (3×6 for 3-D models and 2×4 for 2-D models) that relates the  
 16 electric field to stress and strain:

$$17 \quad d_{ijk} = \left( \frac{\partial \varepsilon_{jk}}{\partial E_i} \right)_{\varepsilon, T} = \left( \frac{\partial P_i}{\partial \sigma_{jk}} \right)_{E, T} \quad (1)$$

$$18 \quad e_{ijk} = - \left( \frac{\partial \sigma_{jk}}{\partial E_i} \right)_{\varepsilon, T} = \left( \frac{\partial P_i}{\partial \varepsilon_{jk}} \right)_{E, T} \quad (2)$$

19  $d_{ijk}$  and  $e_{ijk}$  are both piezoelectric coefficients which are correlated with elastic stiffness tensor  
 20  $C_{ijkl}$ . The linear piezoelectric effect in a flat and 2D material can be viewed as a first-order  
 21 coupling between surface polarization ( $P_i$ ) or the macroscopic electric field ( $E_i$ ), and stress  
 22 ( $\sigma_{jk}$ ) or the strain ( $\varepsilon_{jk}$ ) tensors, where  $i, j, k \in \{1, 2, 3\}$  with 1, 2, and 3 corresponding to x, y, and z,  
 23 respectively.

1 The atomic shift along the zigzag direction will break the structural inversion symmetry along  
2 the zigzag direction and the monolayer is outside the range of  $D_{3h}(\bar{6}m2)$  point group. Therefore  
3 the piezoelectric tensor changes in that several components  $e_{ij}$  is no longer 0.

### 4 **3. Calculation of total energy**

5 The total energy is given by the following:

$$6 \quad E(n) = T(n) + E^{xc}(n) + E^H(n) + E^{ext}(n) - k_b TS \quad (3)$$

7  $T(n)$  is the kinetic energy.

8  $E^{xc}(n)$  is the exchange-correlation energy.

9  $E^H(n)$  is the electro-static energy.

10  $E^{ext}(n)$  is the interaction energy with an external field.

11  $-k_b TS$  is the Mermin free energy where  $k_b$  is the Boltzmann constant,  $T$  is the electron  
12 temperature, and  $S$  is the electronic entropy. The electronic entropy is given by:

$$13 \quad S = \sum_i [f_i \ln f_i + (1 - f_i) \ln(1 - f_i)] \quad (4)$$

14 where  $f_i$  denotes the eigenstate occupation factors.

15

### 16 **Reference**

17 1. M. Meyer, S. Glaus and G. Calzaferri, *J. Chem. Educ.*, 2003, **80**, 1221.

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