Supporting Information *for*

# Diabatic Hamiltonian Construction in van der Waals heterostructure complexes

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## Content

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## 1. The frontier VB states of $MoS_2/WS_2$ heterostructure with 6×6 supercell

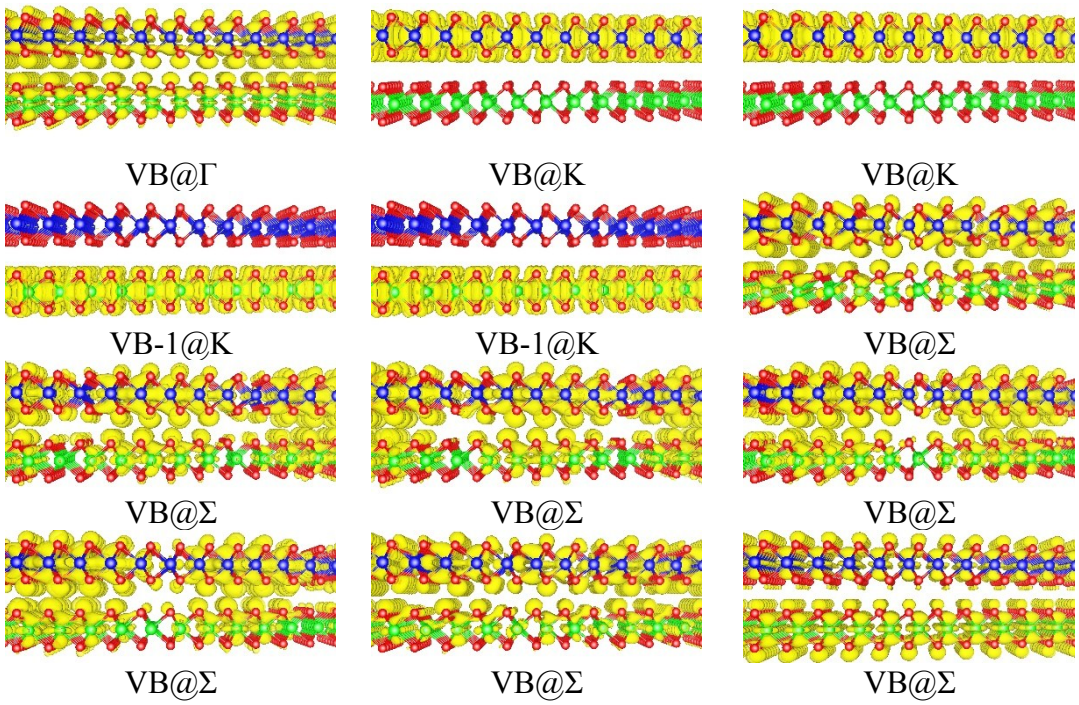


Figure S1. The frontier VB states of $MoS_2/WS_2$ heterostructure with 6×6 supercell. The upper layer is $WS_2$ and the lower layer is $MoS_2$.

## 2. The frontier VB states of $WS_2$ monolayer with 6×6 supercell

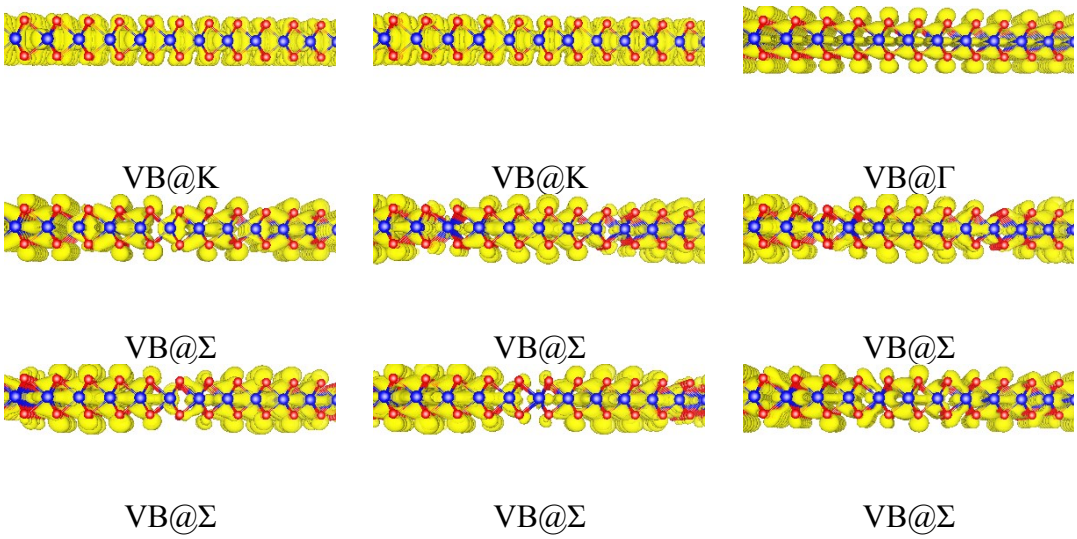


Figure S2. The frontier VB states of WS2 monolayer with 6×6 supercell.

## 3. The frontier VB states of $MoS_2$ monolayer with 6×6 supercell

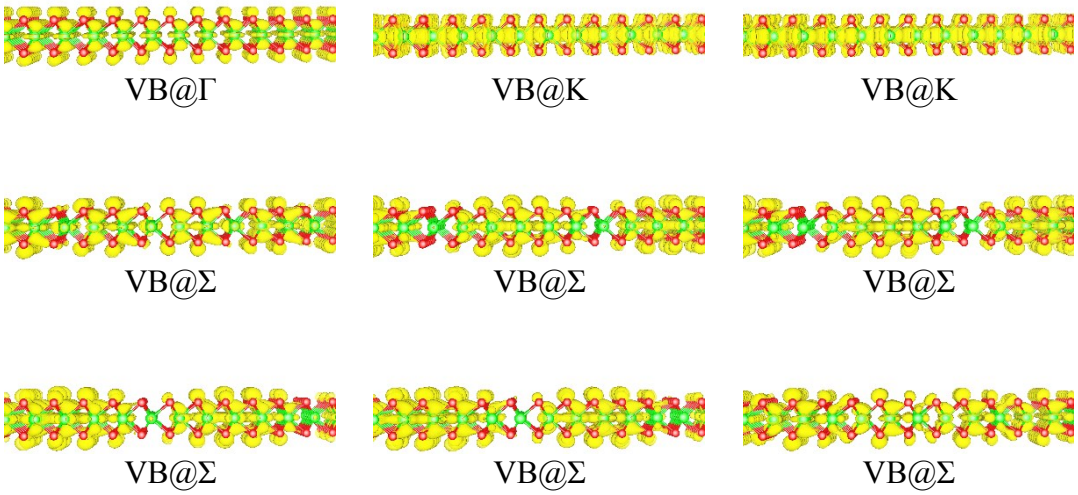


Figure S3. The frontier VB states of $MoS_2$ monolayer with 6×6 supercell.

## 4. Energies of diabatic states with 6×6 supercell

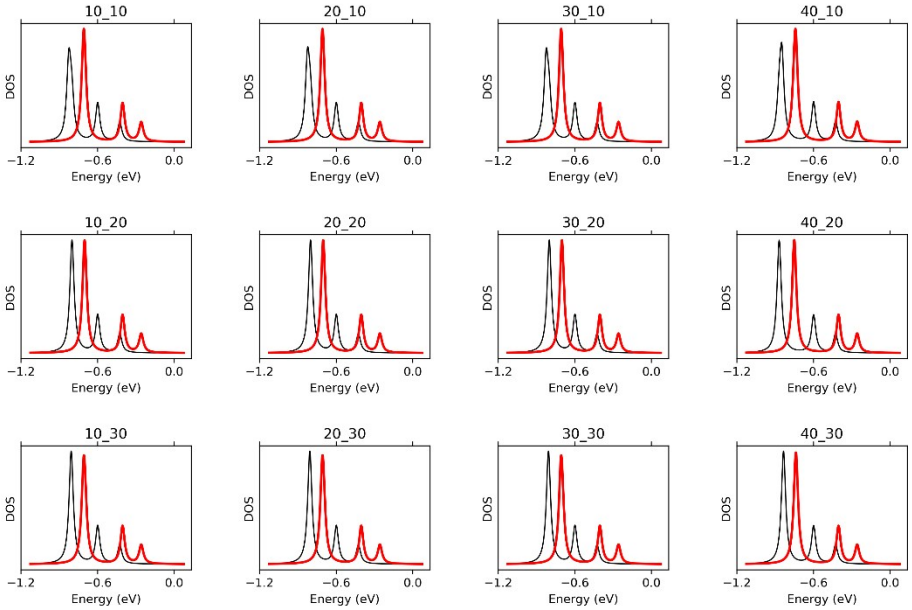


Figure S4. Energies of diabatic states located on located on MoS2 (black line) and WS2 (red line) with 6×6 supercell involving x VB states and y CB states (labeled as x_y).

## 5. Discussion on Model 9×9

The schemes of the state energy levels for the adiabatic states of the MoS2/WS2 complex, the adiabatic states of the single MoS2 monolayer and the single WS2 monolayer, the diabatic states localized either at the MoS2 layer or the WS2 layer of the MoS2/WS2 complex are shown in Figure S5. For the states belonging to the K-point or Γ-point, we get the same physical insight, compared with the results obtained based on the 6×6 supercell model. The only difference is that the VB@Σ states of the $MoS_2/WS_2$ heterostructure shift to higher energy level. As the result, the corresponding diabatic states also display the energy shift. The electronic densities of all relevant state are in Figure S6 ~ S8 in SI. The absolute values of diabatic couplings are given in Figure S10, also consistent with their values in the Model 6×6. For example, the diabatic coupling between the diabatic VB@Γ state of MoS2 and the diabatic state VB@Γ of WS2 is also -0.330 eV, exactly the same as the corresponding value in Model 6×6.

## 6. The band-energy-level schemes with 9×9 supercell

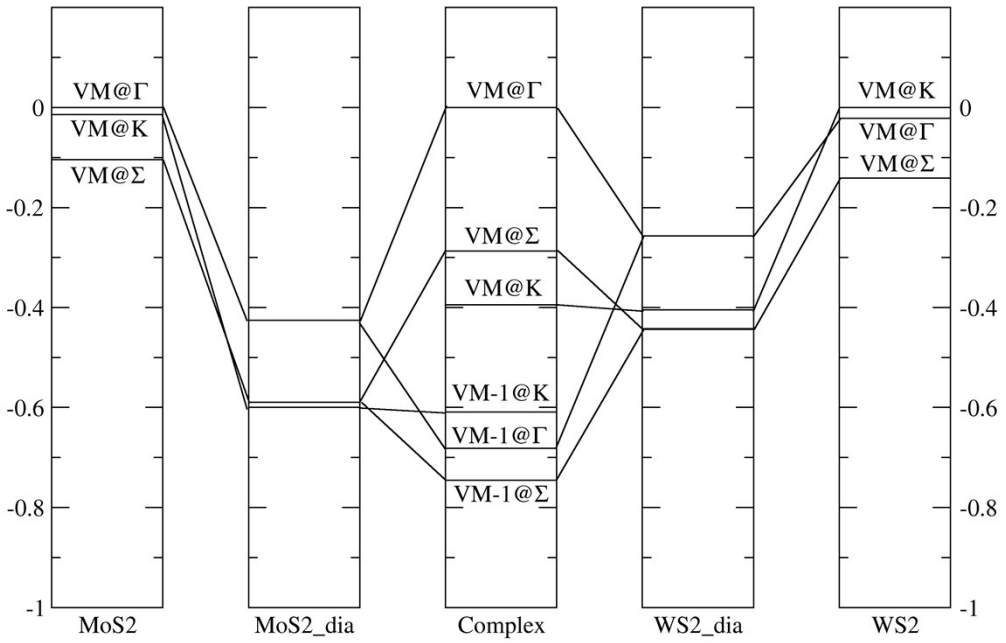


Figure S5. The band-energy-level schemes for adiabatic states in $MoS_2$-monolayer ($MoS_2$), diabatic states located on $MoS_2$ in $MoS_2/WS_2$ heterostructure ($MoS_2$_dia), adiabatic states in $MoS_2/WS_2$ heterostructure (complex), diabatic states located on $WS_2$ in $MoS_2/WS_2$ heterostructure ($WS_2$_dia), and adiabatic states in $WS_2$-monolayer ($WS_2$). 9×9 supercell was employed in these systems. For each individual system (the single $MoS_2$ and $WS_2$ monolayer, and the $MoS_2/WS_2$ complex), their zero energy points are taken as the energy of their Femi level.

## 7. The frontier VB states of $MoS_2/WS_2$ heterostructure with 9×9 supercell

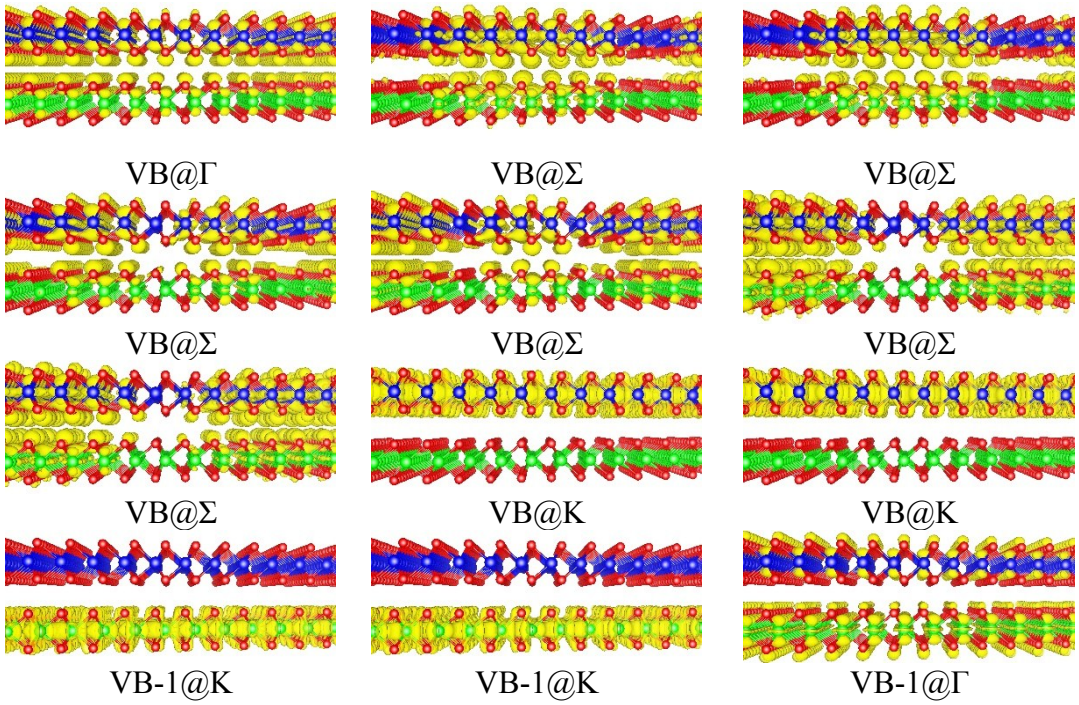


Figure S6. The frontier VB states of $MoS_2/WS_2$ heterostructure with 9×9 supercell. The upper layer is $WS_2$ and the lower layer is $MoS_2$.

## 8. The frontier VB states of $WS_2$ monolayer with 9×9 supercell

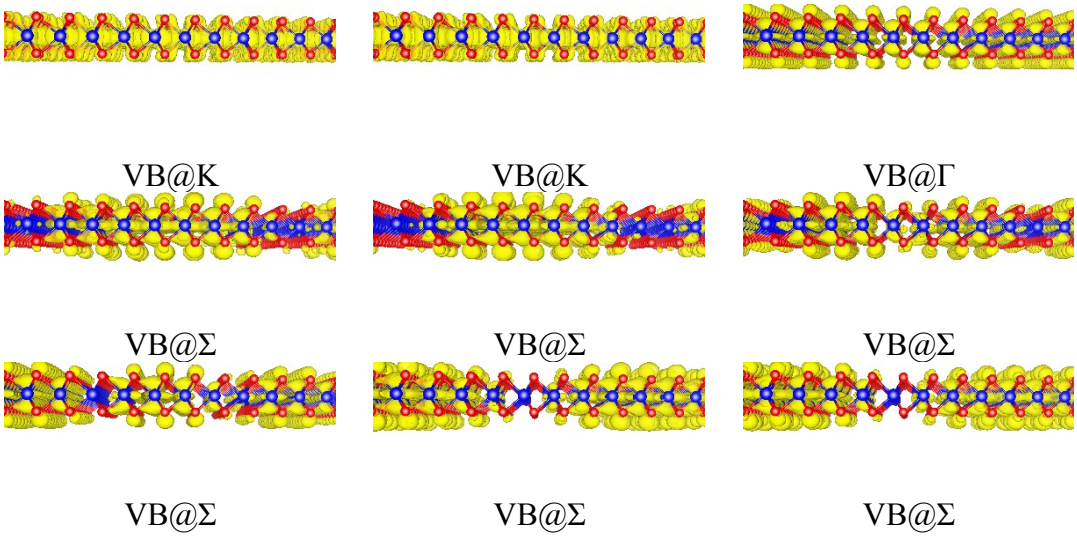


Figure S7. The frontier VB states of $WS_2$ monolayer with 9×9 supercell.

## 9. The frontier VB states of $MoS_2$ monolayer with 9×9 supercell

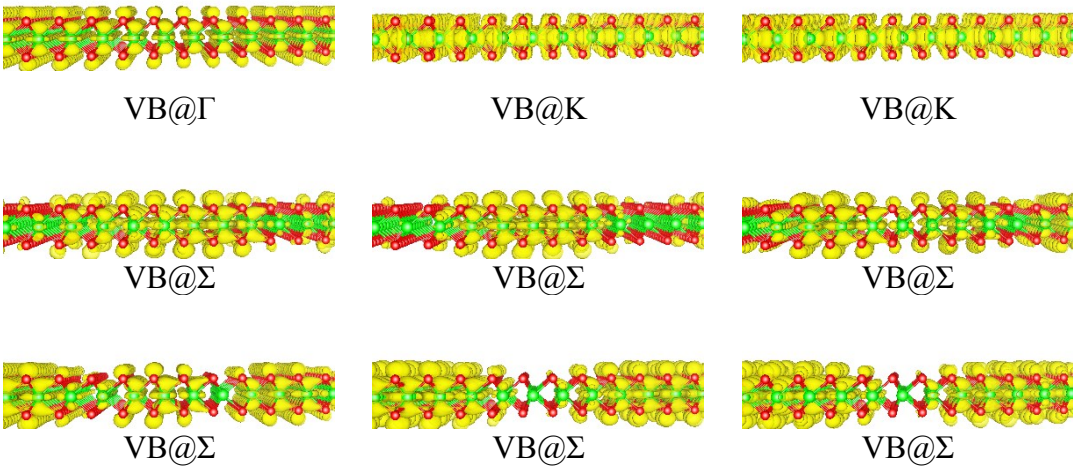


Figure S8. The frontier VB states of $MoS_2$ monolayer with 9×9 supercell.

## 10. Energies of diabatic states with 9×9 supercell

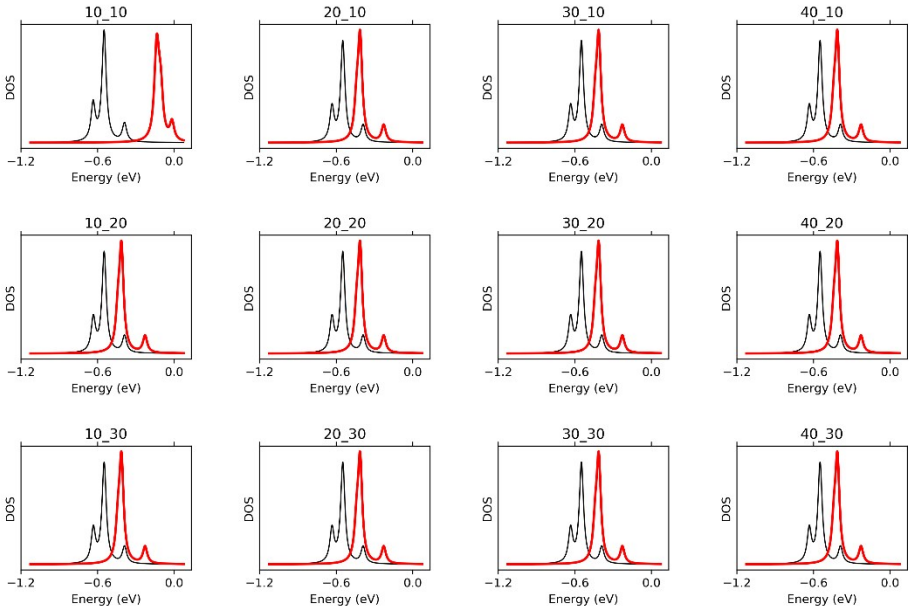


Figure S9. Energies of diabatic states located on located on $MoS_2$ (black line) and $WS_2$ (red line) with 9×9 supercell involving x VB states and y CB states (labeled as x_y).

## 11. The diabatic couplings of $MoS_2/WS_2$ heterostructure with 9×9 supercell

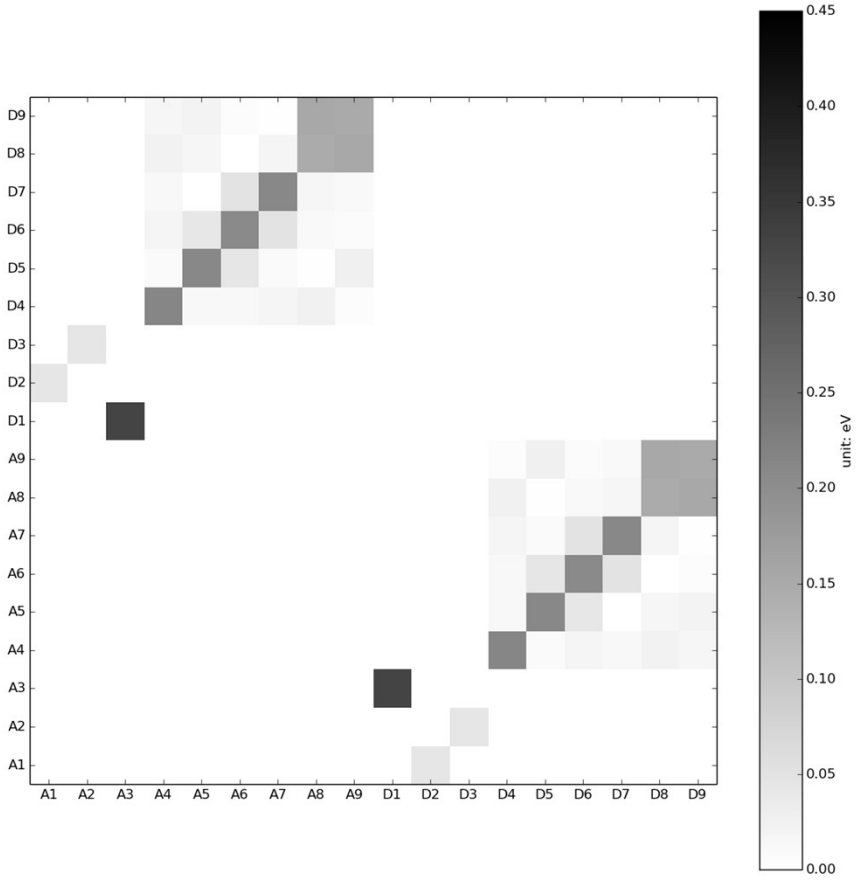


Figure S10. The absolute values of diabatic couplings of $MoS_2/WS_2$ heterostructure with 9×9 supercell. The diagonal elements in the diabatic matrix are set zero here. The donor states are labelled as D1-D5 according to their decent energy order, while the acceptor states are labelled as A1-A5 in the same way. All labels are: D1 (the diabatic VB@Γ state located on $MoS_2$); D2 and D3 (the diabatic VB@K states located on $WS_2$); D4-D9 (VB@Σ states located on $MoS_2$); A1 and A2 (the diabatic VB@K states located on $WS_2$); A3 (the diabatic VB@Γ state located on $WS_2$); A4-A9 (the diabatic VB@Σ states located on $WS_2$).