

## New theoretical insights into the photoinduced carrier transfer dynamics in WS<sub>2</sub>/WSe<sub>2</sub> van der Waals heterostructure

Huadong Zeng<sup>a</sup>, Xiangyue Liu<sup>b</sup>, Hong Zhang<sup>b</sup> and Xinlu Cheng<sup>\*, a</sup>

<sup>a</sup>Institute of Atomic and Molecular Physics, Sichuan University, Chengdu 610065, China

<sup>b</sup>College of Physics, Sichuan University, Chengdu 610065, China

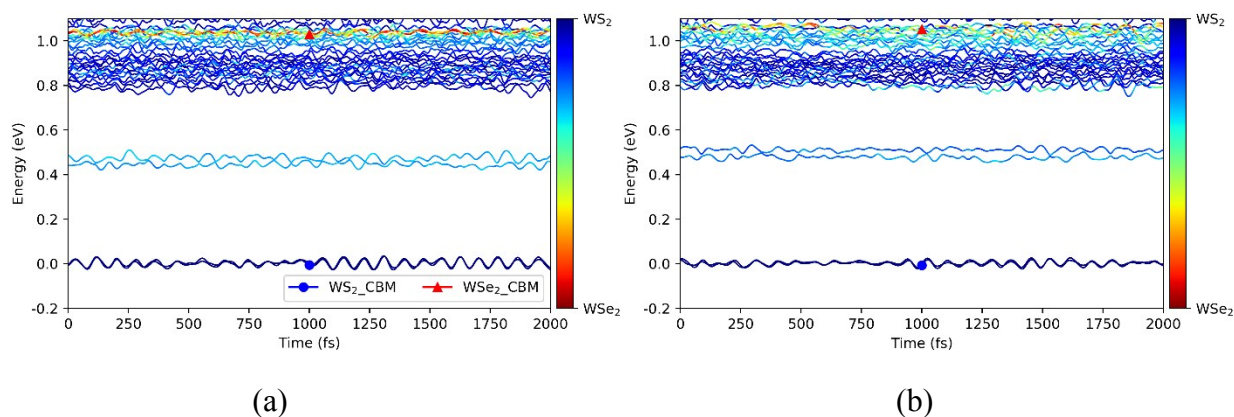


Fig. S1 Time-dependent energy evolutions of the energy states near CBM for the C7 (a) and T (b) stacking configurations at 78 K.

### Momentum assignment using band unfolding method

By using orthogonal 3×3 supercell (108 atoms), we already include most of the effective K-points which may be involved in the interlayer electron/hole transfer. We use the band unfolding method in ref. 1 to determine the momentum of different electronic states. For each structure in the 2 ps molecular dynamics simulation, we calculate the spectral weight define in ref. 1 as:

$P_{Km}(k_i) = \sum_n |\langle Km | k_i n \rangle|^2$ . This quantity represents the contribution of a set of primitive cell states  $|k_i n\rangle$  to the supercell (SC) state  $|Km\rangle$ . Here  $k_i$  represents the high-symmetric k-points in primitive cell. In our case  $k_i$  can be K or 3.  $K$  is the high-symmetric k-points in supercell and in our case it is the  $\Gamma$  point in SC.  $n$  and  $m$  represent the band number of primitive cell and supercell.

## Nonadiabatic Molecular Dynamics with Time-Dependent Density Functional Theory

We utilized *ab initio* nonadiabatic molecular dynamics (NAMD) carried out within time-dependent density functional theory (TDDFT) in the Kohn-Sham (KS) framework to model the photoinduced hole and electron transfer dynamics at the WS<sub>2</sub>/WSe<sub>2</sub> heterostructure. The Runge-Gross theorem asserts that all observables are determined with the knowledge of the one-body electron density. TDDFT in the Kohn-Sham approach maps an interacting many-body system onto a system of noninteracting particles where the electron density of the latter equals to the former. The time-dependent charge density of the interacting system can thus be obtained from the time-dependent KS orbitals,  $\Psi_p(r,t)$  as:

$$\rho(r,t) = \sum_{p=1}^{N_e} |\Psi_p(r,t)|^2 \quad (1)$$

The evolution of the electron density is determined by the TD variational principle, leading to a set of single-electron equations for the evolution of the KS orbitals:

$$i\hbar \frac{\partial \Psi_p(r,t)}{\partial t} = H(r;R) \Psi_p(r,t); \quad p = 1, 2, \dots, N_e \quad (2)$$

By expanding the time-dependent KS orbitals in the adiabatic KS orbital basis,  $\phi(r;R)$ , which is calculated with time-independent DFT from the geometry in the adiabatic MD as shown below,

$$\Psi_p(r,t) = \sum_k C_k(t) \phi(r;R) \quad (3)$$

By inserting Eq. 3 into Eq. 2, one can obtain equations for the expanding coefficients:

$$i\hbar \frac{\partial}{\partial t} C_j(t) = \sum_k C_k(t) (\varepsilon_k \delta_{jk} + d_{jk}) \quad (4)$$

Where  $\varepsilon_k$  is the energy of the adiabatic state  $k$ , and  $d_{jk}$  is the non-adiabatic couplings between the basis  $j$  and  $k$ .

Here, the extent of photogenerated electron transfer between  $\text{WS}_2$  and  $\text{WSe}_2$  is computed by integrating the projected electron density on  $\text{WS}_2$  (it is similar to integrate the projected electron density on  $\text{WSe}_2$ ).

$$\int_{\text{WS}_2} \rho_{PE}(r,t) dr = \int_{\text{WS}_2} |\Psi_{PE}(r,t)|^2 dr = \sum_{i,j} c_i^*(t) c_j(t) \int_{\text{WS}_2} \phi_i^*(r,R(t)) \phi_j(r,R(t)) dr \quad (5)$$

Taking the time-derivative of Eq. 5 gives the expression for adiabatic (AD) and nonadiabatic (NA) contributions to charge transfer:

$$\frac{d \int_{\text{WS}_2} \rho_{PE}(r,t) dr}{dt} = \sum_{i,j} \left\{ \frac{d(c_i^* c_j)}{dt} \int_{\text{WS}_2} \phi_i^* \phi_j dr + c_i^* c_j \frac{d \int_{\text{WS}_2} \phi_i^* \phi_j dr}{dt} \right\} \quad (6)$$

The change in the charge density described by the first term on the right-hand side of Eq. 6 is due to change of state occupations of the adiabatic KS states, which we refer to as nonadiabatic transfer term. On the other hand, the second term causes change of charge density by change of localization of the KS adiabatic states, hence the name adiabatic transfer. The contribution to the total charge transfer was obtained by further integrating the two terms on the right-hand side of Eq. 6.

## References

1. Popescu, V.; Zunger, A. Extracting E versus k effective band structure from supercell calculations on alloys and impurities. *Phys. Rev. B* 2012, 85, 085201.