

# **Supporting Information: Rational Design of Monolayer Transition Metal Dichalcogenide@Fullerene van der Waals Photovoltaic Heterojunctions with the Aid of Time-Domain Density Functional Theory Simulations**

*Hong-Jun Zhou<sup>1</sup>, Dong-Hui Xu<sup>1</sup>, Qing-Hong Yang<sup>1</sup>, Xiang-Yang Liu<sup>1\*</sup>, Ganglong Cui<sup>2</sup>, and Laicai Li<sup>1\*</sup>*

<sup>1</sup>College of Chemistry and Material Science, Sichuan Normal University, Chengdu 610068, China  
and <sup>2</sup>Key Laboratory of Theoretical and Computational Photochemistry, Ministry of Education,  
College of Chemistry, Beijing Normal University, Beijing 100875, China

**Email:** xiangyangliu@sicnu.edu.cn; lilcmail@163.com

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# 1. Computational Methods

## 1.1 Nonadiabatic Dynamics Methods

Nonadiabatic dynamics simulations are carried out using the fewest-switches surface-hopping method based on time-domain density functional theory as conducted by Prezhdo and co-workers.[1-4] The time-dependent density functional theory in the Kohn-Sham framework maps an interacting many-body system onto a system of noninteracting particles where electron density of the latter equals to the former; as a result, the time-dependent charge density  $\rho(r, t)$  of the interacting system is obtained from a set of time-dependent Kohn–Sham orbitals  $\psi_p(r, t)$  [5-9]

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

The electron density evolution finally leads to a set of single electron equations for the evolution of Kohn–Sham orbitals  $\psi_p(r, t)$  [8,10-14]

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

If expanding a time-dependent Kohn-Sham orbital in terms of adiabatic Kohn–Sham orbitals  $\phi_p(r, t)$  calculated from time-independent density functional theory calculations along adiabatic molecular dynamics trajectories

$$\psi_p(r, t) = \sum_k c_k(t) \phi_k(r; R)$$

one can obtain a set of equations of motion for the expanding coefficients  $c_j(t)$

$$i\hbar \frac{\partial c_j(t)}{\partial t} = \sum_k c_k(t) (\varepsilon_k \delta_{jk} - i\hbar d_{jk})$$

where  $\varepsilon_k$  is the energy of the  $k$ th adiabatic state and  $d_{jk}$  is the nonadiabatic coupling

between adiabatic states  $j$  and  $k$ . The former is directly obtained from density functional theory calculations and the latter is calculated numerically, through a finite difference method, as overlaps of adiabatic states at times  $t$  and  $t + \Delta t$  :

$$d_{jk} = \left\langle \phi_j(r; R) \left| \frac{\partial \phi_k(r; R)}{\partial t} \right. \right\rangle \approx \frac{\langle \phi_j(t) | \phi_k(t + \Delta t) \rangle - \langle \phi_j(t + \Delta t) | \phi_k(t) \rangle}{2\Delta t}$$

in which  $\phi_j(t)$  and  $\phi_k(t + \Delta t)$  are electronic wave functions of adiabatic states  $j$  and  $k$  at times  $t$  and  $t + \Delta t$ , respectively. It is noteworthy that previous algorithms are primarily implemented with plane wave basis sets; [4, 15, 16] instead, in this work we have implemented this nonadiabatic dynamics method with Gaussian basis sets.

## 1.2 Electron Transfer Analysis

To estimate electron transfer from one fragment to another one in nonadiabatic dynamics simulations, we have developed an efficient density-matrix based method. First, we can define a density matrix  $D$  in terms of atomic orbitals  $\chi_\mu$

$$D_{\mu\nu i}(t) = p_i(t) \chi_{\mu i} \chi_{\nu i}^*$$

in which  $p_i(t)$  is the time-dependent occupation number of the  $i$ th adiabatic state calculated on the basis of the above expanding coefficients  $c_i(t)$  and  $\chi_{\mu i}$  is the  $\mu$ th atomic orbital coefficient of the  $i$ th adiabatic state. Similarly to the Mulliken charge analysis, [17] we have then defined a population matrix  $P$  using the density matrix  $D$  and atomic overlap matrix  $S$

$$P_{\mu\nu i} = D_{\mu\nu i} S_{\mu\nu}$$

Finally, we can obtain the  $a$ th atomic charge through summing all basis functions  $\mu$  belonging to that atom and all involved adiabatic states  $i$

$$P_a = \sum_i \left( \sum_{\mu \in a, \nu \in a} P_{\mu\nu i} + \frac{1}{2} \left( \sum_{\mu \in a, \nu \notin a} P_{\mu\nu i} + \sum_{\mu \notin a, \nu \in a} P_{\mu\nu i} \right) \right)$$

It should be noted that if only an atomic orbital belongs to the  $a$ th atom, just half of  $P_{\mu\nu i}$  is used, as done by the Mulliken charge analysis method. [17] Accordingly, the total electron on a fragment A is the sum of all atomic charges belonging to that fragment

$$P_A = \sum_i p_i(t) P_{Ai}$$

in which

$$P_{Ai} = \sum_{a \in A} \left( \sum_{\mu \in a, \nu \in a} \chi_{\mu i} \chi_{\nu i}^* S_{\mu\nu} + \frac{1}{2} \left( \sum_{\mu \in a, \nu \notin a} \chi_{\mu i} \chi_{\nu i}^* S_{\mu\nu} + \sum_{\mu \notin a, \nu \in a} \chi_{\mu i} \chi_{\nu i}^* S_{\mu\nu} \right) \right)$$

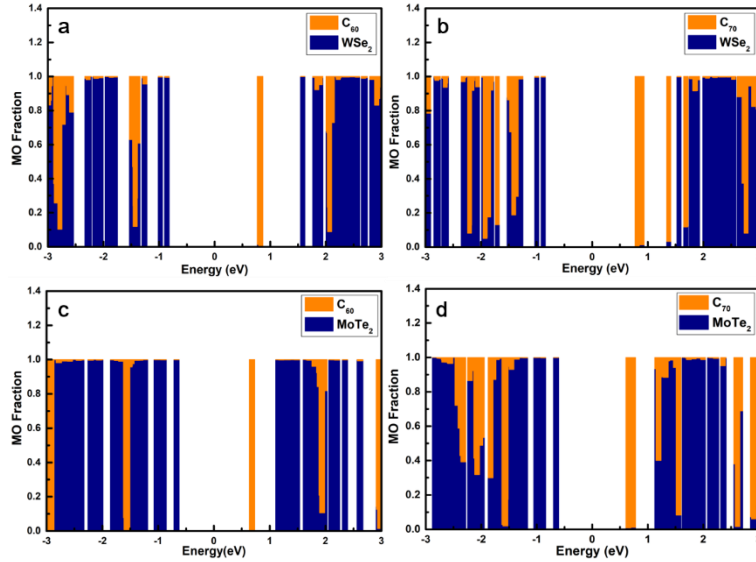
In such a case, the differentiation of  $P_A$  is then derived as

$$dP_A = d \left( \sum_i c_i^* c_i P_{Ai} \right) = \sum_i (d(c_i^* c_i) P_A + c_i^* c_i dP_{Ai})$$

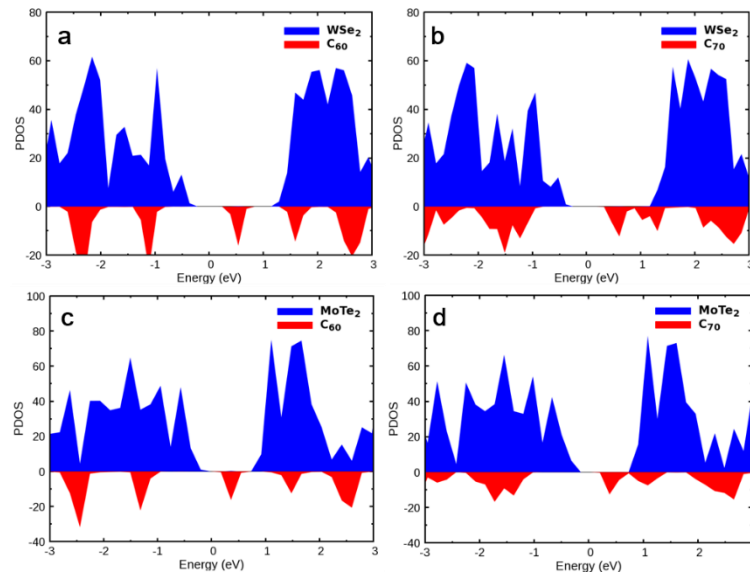
in which the first term has variational occupations for adiabatic states  $i$  and the second term has constant adiabatic state occupations but changeable electron population. These two contributions actually correspond to nonadiabatic and adiabatic electron transfers, respectively. The former is mainly caused by state hoppings between different adiabatic states and the latter is primarily originated from changes of adiabatic states induced by atomic motions. Finally, it should be noted that Gaussian basis sets are used in our simulations, so molecular coefficients  $\chi_{\mu i}$  are real numbers. Adiabatic states' expanding coefficients  $c_i(t)$  are complex numbers, but they are not directly used; instead, their  $c_i(t)c_i^*(t)$  products are used for calculating the time-dependent

occupation number  $p_i(t)$  of the  $i$ th adiabatic state, which is a real number.

## 2. Additional Figures



**Figure S1:** HSE06+D3 calculated molecular fractions of constructed TMD@Fullerene heterostructures. (a) WSe2@C60; (b) WSe2@C70; (c) MoTe2@C60; (d) MoTe2@C70.



**Figure S2:** PBE+D3 calculated projected density of states (PDOS) of constructed TMD@Fullerene heterostructures. (a) WSe2@C60; (b) WSe2@C70; (c) MoTe2@C60; (d) MoTe2@C70.

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