

# Supplementary Material: Identification of the Mott insulating CDW state in 1T-TaS<sub>2</sub>

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## SELF-CONSISTENT DETERMINATION OF THE HUBBARD U TERM IN ACBN0 METHOD

In the present work, to determine the Hubbard U term self-consistently, we used the scheme suggested by Agapito, Curtarolo, and Nardelli, hereafter abbreviated by ACBN0 [1–3]. Here, we summarize key components of the ACBN0 formulation, which can be easily extended to our case of multiatomic orbital. For a given ortho-normalized orbital basis set  $\{j^k\}$ , the renormalized occupation number ( $\bar{N}_i^k$ ) and reduced density matrix ( $\bar{P}$ ) [1–3] are defined as follow:

$$\begin{aligned} \bar{N}_i^k &= N_i^k \sum_{j \in \{m\}} c_{j,i}^{k*} c_{j,i}^k; \\ \bar{P} &= \frac{1}{\sqrt{N_k}} \sum_{i,j \in \{m\}} \bar{N}_i^k c_{j,i}^{k*} c_{j,i}^k; \end{aligned} \quad (1)$$

where  $c_{j,i}^{k*} = \langle j^k | i^k \rangle$  is inner product between generalized basis ( $j^k$ ) and Kohn-Sham state ( $i^k$ ). The reduced occupation number, which presents occupation of generalized orbital in subspace, is defined as:

$$N_m = \frac{1}{N_k} \sum_{k,i} f_{k,i} c_{m,i}^{k*} c_{m,i}^k; \quad (2)$$

The unrestricted Hartree-Fock Coulomb and exchange energy in the correlated subspace can be reformulated in terms of reduced density matrix  $\bar{P}$  as follows:

$$\begin{aligned} E_{HF}^{\{j\}} &= \frac{1}{2} \sum_{\{j\}} \sum_{\{j'\}} \sum_{\{j''\}} \sum_{\{j'''\}} \sum_{\{j''''\}} \left( \bar{P}_{jj^o} \bar{P}_{j^o j''''} + \bar{P}_{jj^o} \bar{P}_{j^o j''''} + \bar{P}_{jj^o} \bar{P}_{j^o j''''} + \bar{P}_{jj^o} \bar{P}_{j^o j''''} \right) (jj'jj''j''') \\ &\quad + \frac{1}{2} \sum_{\{j\}} \sum_{\{j'\}} \sum_{\{j''\}} \sum_{\{j'''\}} \sum_{\{j''''\}} \left( \bar{P}_{jj^o} \bar{P}_{j^o j''''} + \bar{P}_{jj^o} \bar{P}_{j^o j''''} \right) (jj''''jj''j'); \end{aligned} \quad (3)$$

where the two-body integral is

$$(jj'jj''j''') = \int \int \psi_j^*(\mathbf{r}_1) \psi_{j^o}(\mathbf{r}_1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \psi_{j^o}^*(\mathbf{r}_2) \psi_{j''''}(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2; \quad (4)$$

From the comparison between the Hubbard U energy (eq. 2 in ref. [1]) and Hartree-Fock energy (eq. 3), the U and J value can be derived as:

$$\begin{aligned}
U &= \frac{\sum_{\vec{r}jg} [\bar{P}_{jj^0} \bar{P}_{j^0j} + \bar{P}_{jj^0} \bar{P}_{j^0j} + \bar{P}_{jj^0} \bar{P}_{j^0j} + \bar{P}_{jj^0} \bar{P}_{j^0j}] (jj^0 | j^0j^0)}{\sum_{j \notin j^0} N_j N_{j^0} + \sum_{\vec{r}jg} N_j N_{j^0} + \sum_{\vec{r}jg} N_j N_{j^0} + \sum_{j \notin j^0} N_j N_{j^0}}; \\
J &= \frac{\sum_{\vec{r}jg} [\bar{P}_{jj^0} \bar{P}_{j^0j} + \bar{P}_{jj^0} \bar{P}_{j^0j}] (jj^0 | j^0j^0)}{\sum_{j \notin j^0} N_j N_{j^0} + \sum_{j \notin j^0} N_j N_{j^0}};
\end{aligned} \tag{5}$$

To evaluate the electron repulsion of isolated localized orbitals under the periodic boundary condition, in addition, we employed truncated Coulomb potential method [4] that is defined as follow:

$$\begin{aligned}
(jj^0 | jj^0) &= \frac{4}{\Omega} \sum_{\mathbf{G}} \frac{1}{2} R_c^2 Y_{jj^0}(\mathbf{G}) Y_{jj^0}^*(\mathbf{G}) + \sum_{\mathbf{G} \neq 0} \frac{Y_{jj^0}(\mathbf{G}) Y_{jj^0}^*(\mathbf{G})}{|\mathbf{G}|^2} (1 - \cos(j\mathbf{G}j R_c)) ; \\
Y_{jj^0}(\mathbf{G}) &= \int_{\Omega} e^{-i\mathbf{G} \cdot \mathbf{r}} j^0(\mathbf{r}) j^0(\mathbf{r}) d\mathbf{r};
\end{aligned} \tag{6}$$

where  $\Omega$  is the cell volume and the  $R_c = \left(\frac{3\Omega}{4}\right)^{1/3}$  is the cut-off radius. This truncated Coulomb potential method uses the modified  $1/r$  potential as follow:

$$V_{modi} = \begin{cases} \frac{8}{r} & \text{for } r \leq R_c \\ 0 & \text{otherwise} \end{cases}; \tag{7}$$

which removes the long-range interaction beyond the cut-off radius and thus avoids the divergence incurred by the infinite sum of the long-range term under the periodic boundary condition.

## REVIVAL OF THE DERIVATIVE DISCONTINUITY ON APPLICATION OF THE HUBBARD U TERM TO THE GENERALIZED BASIS SET

Here, we summarize that the lost derivative discontinuity in DFT and DFT+U for the molecular orbital states can be restored by using the DFT+GOU. We start with the example of O<sub>2</sub> molecule. We varied the electron numbers in the O<sub>2</sub> molecule (see Fig. S1(a)), and we calculated the Hubbard energies with given the U parameter of 7 eV applied onto the molecular orbital, which is denoted by PBE+GOU(7eV), as presented in Fig. S1(b). In exact analogy with the simplified model system shown in Fig. 1(b), the self-consistently obtained Hubbard energy for O<sub>2</sub> molecular orbitals, calculated with the PBE+GOU, clearly produces kink structures in the Hubbard energy at the point of integer electron numbers. In

contrast, the conventional scheme with the atomic orbital projector (PBE+U(7eV)) makes the Hubbard energy decreases almost monotonically, which clearly lose the derivative discontinuity.

The first derivatives of the total energy ( $E_{tot}$ ) with respect to the electron number ( $dE_{tot}=dN$ ) are summarized in Fig. S1(c). The calculation of PBE+GOU provides a sharp discontinuous change of the derivative at integer charge ( $\pm 1$ ). For comparison, we also calculated the same derivative discontinuity with the hybrid functional PBE0, as shown in Fig. S1(c). The same inspection is performed for the charge state of the bulk 1T-TaS<sub>2</sub>. We tested with the two values of the Hubbard energy parameters:  $U = 0.3\text{eV}$  and  $U = 0.6\text{eV}$ . Starting from the integer charge, the first derivative values ( $dE_{tot}=dN$ ) with PBE+GOU(0.3eV) produce rather discontinuous changes, whereas the  $dE_{tot}=dN$  obtained with PBE and PBE+U leads to very smooth variations near the integer number of electrons.

## GENERATION OF THE GENERALIZED ORBITAL BASIS SET

Here we describe the generation scheme for the multiatomic basis orbital to which the Hubbard potential is applied. For the molecular system, such as O<sub>2</sub> described in the main text, the known molecular orbital can be used for this purpose, and the procedure is rather straightforward. To deal with localized states in solid states, a closer inspection of the electronic structure is required. In our example of the double layer supercell of the bulk 1T-TaS<sub>2</sub>, there are four CDW states, one for each spin state in each layer. To obtain the generalized orbital basis for these four CDW states, we first performed the SCF procedure for the monolayer 1T-TaS<sub>2</sub>. In this case, the flat band CDW state ( $\psi^{\text{CDW}}$ ) in the monolayer well isolated and clearly distinguished with the gap region. On each Bloch point, we extract the Kohn-Sham orbital of the flat band, as shown in Fig. S2(a). We performed the calculation of the bulk 1T-TaS<sub>2</sub> with the Hubbard potential applied onto the extracted orbital. For example, in our double layer unit cell for the bulk 1T-TaS<sub>2</sub>, we have four basis orbitals :

$$\psi_{\text{upper}}^{\text{CDW}}(\mathbf{r};\mathbf{k}) = \psi^{\text{CDW}}(\mathbf{r};\mathbf{k}) \text{ and } \psi_{\text{lower}}^{\text{CDW}}(\mathbf{r};\mathbf{k}) = \psi^{\text{CDW}}(\mathbf{r};\mathbf{k}) \text{ for each spin state .}$$

Instead, the Wannier orbital of the flat band can be used in the construction of the generalized basis orbital. In particular, when the flat band is not isolated within the gap region, the wannierization can lead to a straightforward procedure. The Wannier orbital

$w_{\mathbf{R}}(\mathbf{r})$  is defined in terms of Bloch state  $\psi_{\mathbf{k}}(\mathbf{r})$  in the Brillouin zone as follows:

$$w_{\mathbf{R}}(\mathbf{r}) = \frac{1}{N} \sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{R}} \psi_{\mathbf{k}}(\mathbf{r}) \quad (8)$$

when  $\mathbf{R}$ ,  $\mathbf{k}$  and  $N$  are Bravais lattice vector, Bloch vector and number of primitive cells, respectively. Once we prepared the set of Wannier orbitals, we restart the self-consistent field calculation by applying the GOU parameter onto the basis orbital at each Bloch point ( $\psi_{\mathbf{k}}(\mathbf{r})$ ), defined as

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{N} \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} w_{\mathbf{R}}(\mathbf{r}) \quad (9)$$

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