Supplemental information: first principles coupled cluster theory of the electronic spectrum of the transition metal dichalcogenides

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COULOMB KERNEL: THE 2D CASE

Given reciprocal lattice vectors G with in-plane G_{xy} and out-of-plane G_z components and vacuum spacing size z the Coulomb kernel from Eq. 2 of the main text reads (formula A6 of Ref. [1]):

$$K(G) = \frac{4\pi}{G^2} \left(1 - \cos \frac{G_z \cdot z}{2} \exp -\frac{G_{xy} \cdot z}{2} \right) . \tag{1}$$

COUPLED CLUSTER SIMULATION DETAILS

Coupled-cluster simulations of 2D MoS_2 were performed in the following steps:

1. The Hartree-Fock determinant $|\Phi\rangle$ and molecular orbitals were computed in the crystalline Gaussian orbital basis. Real-space summation cutoffs and other saturating parameters where chosen to produce sub-μHartree error in the total energy in a 3×3 k-point benchmark model;

2. An "active" single-particle space for the correlated calculations was restricted to the 7 hole and 7 electron bands adjacent to the band gap, see Fig. 1(d) of the main text for the basis set error in the resulting band gap size;

3. The Hamiltonian matrix elements were re-computed within this active space;

4. The ground-state wavefunction $e^T|\Phi\rangle$ was computed at the (spin-restricted) coupled-cluster singles and doubles (CCSD) level[2], where T contains one and two particle-hole excitations;

5. Low-lying equation-of-motion (EOM) spin-restricted CCSD roots were determined in the N_e+1 (electron affinity, EA) and N_e-1 (ionization potential, IP) sectors (N_e is the number of electrons per unit cell multiplied by the number of k points sampled in the Brillouin zone) by diagonalizing the coupled cluster effective Hamiltonian $\bar{H} = e^{-T} H e^T$ in the p, pph (EA) and h, phh (IP) spaces (where p and h denote particle, hole respectively) [2–5]. This was done for a set of uniformly shifted k point grids, where shift vectors sample the Brillouin zone of the supercell uniformly: for example, values

on an 18×18 k point grid were obtained through 6 separate 6×6 ground- and excited-state CCSD calculations (time reversal symmetry was used). The principal roots were interpreted as the band energies.

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