Supplementary Information

Valley-contrasting optics of interlayer excitons in Mo- and W-based bulk transition metal dichalcogenides

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Experiment. Bulk $MoSe_2$ and WSe_2 crystals are mechanically exfoliated[1] onto 500 μm thick c-cut sapphire substrates. The thickness of the two TMDC crystals as obtained by atomic force microscopy (AFM) is $30 \pm 0.5\, nm$. The samples are mounted on a x-y-z piezo nanopositioner assembly, which is fixed on the front end of an optical fiber-based low-temperature insert (T = $4.2\, K$) installed in the $50\, mm$ diameter bore of a resistive magnet. The magnet creates a magnetic field of up to $29\, T$ at the sample position. Broadband light from a tungsten halogen lamp is routed inside the insert using a $50\, \mu m$ diameter optical fiber, which is focused on the sample using an aspheric lens of $3.1\, mm$ focal length and 0.68 numerical aperture. The full width at half maximum (FWHM) diameter of the focus is $10\, \mu m$. The reflected light from the sample is circularly polarized with a quarter wave plate and a polarizer assembly, before being collected using another $50\, \mu m$ diameter optical fiber. The reflected light is dispersed using a monochromator (focal length of $0.3\, m$) and detected using a liquid nitrogen-cooled Silicon charged coupled device (CCD) detector. The measurements are performed by setting the polarizer and quarter wave plate for a fixed circular polarization of detection, while reversing the magnetic field direction to obtain spectra for both helicities due to time reversal symmetry. The reflectance contrast spectrum $C(\lambda)$ as a function of the wavelength λ is defined as $C(\lambda) = [R(\lambda) - R_0(\lambda)]/[R(\lambda) + R_0(\lambda)]$, where $R(\lambda)$ and $R_0(\lambda)$ are the reflectance spectra of the TMDC crystal on the substrate and the bare substrate, respectively. The $C(\lambda)$ spectral line shapes in Fig. 2 are modeled using a transfer matrix method-based approach, where complex Lorentzians represent the excitonic contribution to the dielectric function as

$$\epsilon(E) = (n_b + ik_b)^2 + \frac{A}{E_0^2 - E^2 - i\gamma E} \quad (1)$$

Here, $n_b + ik_b$ is the background refractive index of the TMDC without excitonic effects. A, E_0, and γ are the excitonic oscillator strength, transition energy, and the FWHM linewidth, respectively.

Theory. We have performed *ab initio* calculations of the four 2H phase TMDC bulk crystals employing a hierarchy of methods (see also Ref. 2). For all calculations, the experimental lattice constants were used[3]. We optimize the internal structure until forces are below $10^{-4} R_y/a_B$ using a $21 \times 21 \times 3$ k-mesh within the local density approximation. A basis of localized Gaussian orbitals (s, p, d, and s*, in total 30 per atom) is used alongside norm-conserving pseudopotentials which include the spin-orbit coupling[4–6]. To improve the description of the electronic properties many-body perturbation theory calculations within the *GdW* approximation[7] are performed with a plane wave cutoff of 2.5 Ry and k-grid of at least $21 \times 21 \times 4$ points. The optical properties are calculated by solving the Bethe-Salpether equation within the Tamm-Dancoff approximation[8,9] employing a grid of $21 \times 21 \times 6$ points. The RMS radius of the excitons $\sqrt{\langle r_X^2 \rangle}$ is evaluated on a $30 \times 30 \times 4$ k-mesh (Ref. 2), using which excitons with radii less than $3\ nm$ can be described fairly reliably.

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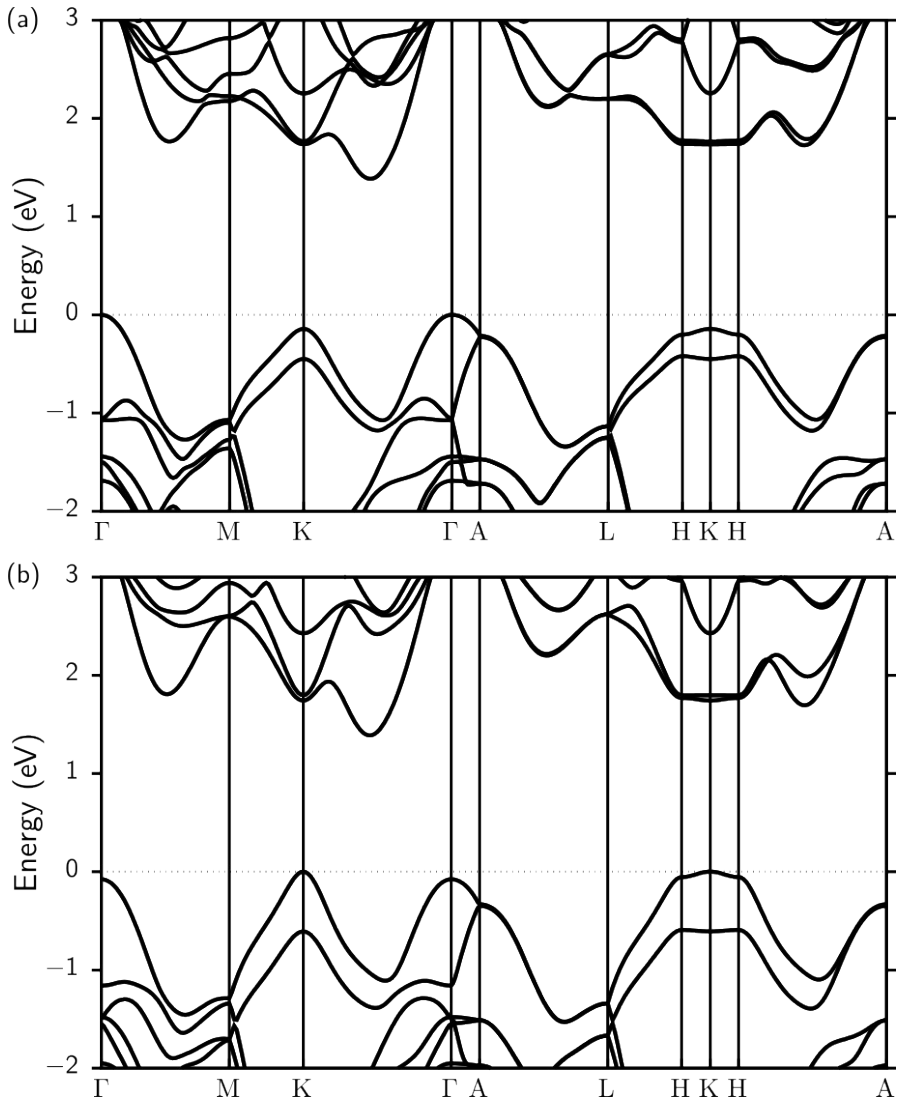

Fig. S1. Band structures of 2H bulk (a) $MoSe_2$ and (b) WSe_2 in the *GdW* approximation. We employ a plane wave cutoff of 2.5 Ry and a k grid of $21 \times 21 \times 4$ points.

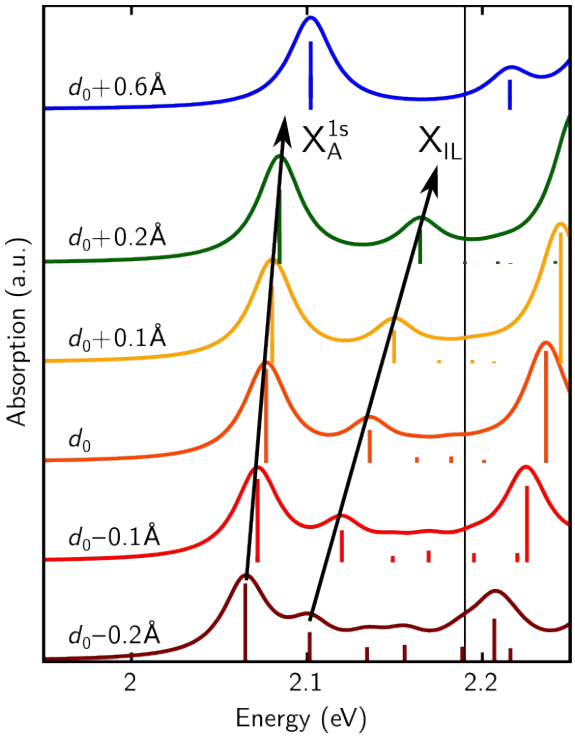

Fig. S2. Calculated absorption spectra of bulk MoS_2 for different interlayer distance d. Six different spectra (vertically shifted for clarity) are shown for distances $d = d_0 - 0.2\text{Å} \ldots d_0 + 0.6\text{Å}$. The first two bright peaks are X_A^{1s} and X_{IL}. Their energetic separation increases almost linearly with increasing the interlayer distance, leading to a tunable intralayer-interlayer splitting.