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Quantitative determination of interlayer electronic coupling at various critical points in bilayer MoS₂

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Abstract: Tailoring interlayer coupling has emerged as a powerful tool to tune the electronic structure of van der Waals (vdW) bilayers. One example is the usage of the "moiré pattern" to create controllable two-dimensional electronic superlattices through the configurational dependence of interlayer electronic couplings. This approach has led to some remarkable discoveries in twisted graphene bilayers, and transition metal dichalcogenide (TMD) homo-and hetero-bilayers. However, a largely unexplored factor is the interlayer distance, *d*, which can impact the interlayer coupling strength exponentially. In this letter, we quantitatively

determine the coupling strengths as a function of interlayer spacing at various critical points of the Brillouin zone in bilayer MoS₂. The exponential dependence of the coupling parameter on the gap distance is demonstrated. Most significantly, we achieved a 280% enhancement of K-valley coupling strength with an 8% reduction of the vdW gap, pointing to a new strategy for designing a novel electronic system in vdW bilayers.

Main Text

Introduction: In the current topic of van der Waals hetero- and homo-bilayers, the interlayer electronic coupling plays a critical role in determining the electronic structures of the bilayer as a whole [1-7]. Active control of interlayer coupling through moiré superlattices (MSL) has emerged as a powerful tool for tailoring electronic structures in twisted bilayer graphene and TMDs [8-24]. This approach utilizes the formation of periodic modulation of in-plane alignment between the two atomic sheets (either by twisting angle or lattice mismatch) to engineer a periodically modulated moiré potential. Another less explored, but potentially fruitful direction is to control interlayer coupling through interlayer distance. This approach can be used alone or in combination with MSL formation to enhance its functionalities, as demonstrated in twisted bilayer graphene [8-10,21]. For interlayer coupling, although the effect of in-plane stacking configuration is well understood [19,20], the out-of-plane effect due to the change in interlayer spacing is more difficult to capture quantitatively. More significantly, there is evidence that changes in local interlayer spacing can be substantially different from density functional theory (DFT) calculations [6]. Thus, an independent experimental determination of the interlayer coupling as a function of interlayer spacing would play an important role in assessing the theoretical model for predicting the electronic structures.

Such a quantitative determination will enable a new design parameter to tailor the electronic structure of vdW bilayers through interlayer spacing control [21-24].

In this work, by using 2H-stacked bilayer MoS₂ (without MSL effect) as a model system, we report quantitative determination of interlayer coupling strength as a function of the interlayer spacing at different critical points of the Brillouin zone. The usage of 2H-stacked bilayer MoS_2 removes fabrication uncertainties associated with mechanical stacking of bilayers [18,25], making the data interpretation and extraction of coupling energy more straightforward. It also removes the lateral configuration variations in a MSL and allows one to assess the coupling as a function of layer spacing independently. By applying hydrostatic pressure in a diamond anvil cell up to 12.7 GPa, the interlayer spacing is changed from 0.62 nm to 0.57 nm, representing an 8% change. The coupling strength at various critical points is probed using a combination of differential reflectivity (DR) and photoluminescence (PL) spectra from which the exponential decay constants of the interlayer coupling at different critical points are determined. We further compare the results with the *ab-initio* calculations and find that all the results of K, Q and Γ points agree well with the DFT calculations. Importantly, after reducing the interlayer distance by 8%, the K-valley coupling strength is enhanced from 36 meV to 101 meV, representing a 280% enhancement. This result also points to a very promising strategy for designing novel quantum structures based on vdW bilayers.

Results and discussion: Conceptually, the interlayer electronic coupling in vdW bilayers can be described by a 2 × 2 Hamiltonian $H = \begin{bmatrix} \varepsilon_l & -t \\ -t & \varepsilon_u \end{bmatrix}$, where $\varepsilon_l \ (\varepsilon_u)$ is the single-particle energy level of the lower (upper) layer prior to coupling and *t* is the coupling strength (also referred to as interlayer hopping integral). A larger coupling strength *t* and/or a smaller energy difference ($\varepsilon_l - t = \frac{\varepsilon_l}{\varepsilon_l} = \frac{\varepsilon_l}{\varepsilon_l$

 ε_u) can lead to a larger energy splitting of the hybridized states. This model was successfully applied recently to capture the interlayer hybridization in commensurate hetero-bilayers [20]. Crucially, the coupling strength *t* depends on several factors, i.e., the stacking configuration [19,20], the interlayer spacing *d*, and the critical point of the Brillouin zone. Due to the different projected atomic orbitals at different critical points, one expects to observe different coupling strengths at different valleys. Furthermore, when the interlayer spacing *d* decreases, the increased orbital wavefunction overlap enhances the coupling strength *t* and results in a larger energy splitting of the hybridized states, as depicted by the schematic shown in **Fig. 1(a)**.

In bilayer MoS₂ [26-28] and other hetero-bilayer TMDs [29-31], the effect of interlayer electronic coupling is manifested in the band splittings at various critical points [32-34] such as K, Q, and Γ . Figure 1(b) shows the band structures for MoS₂ from 1 monolayer (black curve) to 2Hstacked bilayer (red curve) based on DFT at their natural state with d = 0.62 nm for the bilayer. Figure 1(c) shows the calculated band structure for the bilayer at a reduced interlayer spacing of 0.58 nm (see **fig. S1** in Supplemental Material [35] for other *d*). The critical points of interest are K_V , Q_C , and Γ_V . Note that interlayer coupling at K_C is zero in the 2H stacking due to symmetry [19,20]. An increase in interlayer coupling will lead to an increase in energy splitting at these critical points [32-34]. At K_V, the energy separation between X_A and X_B excitons in the DR spectrum can be used to determine the *d*-dependence of interlayer coupling [20]. The PL transition X_I from the lower Q_C state and the upper Γ_V state (an indirect transition) can be used to determine the d-dependence of interlayer coupling at $Q_{\rm C}$ and $\Gamma_{\rm V}$. Some early studies have reported pressure tuning of the bandgap in bilayer MoS₂ and WSe₂ up to $\sim 2-5$ GPa [48-50], indicating that interlayer coupling indeed depends on interlayer spacing. Here, we quantitatively determine coupling strength at various critical points, in which the magnitude and exponential dependence

of *t* are independently demonstrated. Our results are particularly useful for vdW bilayers consisting of monolayers with different chalcogen atoms such as MoS_2/WSe_2 , where the lattice corrugation and/or structure reconstruction effects can result in a more than 20% modulation of the vdW gap [29].

Experimentally, we exfoliate the MoS₂ sample directly onto the diamond surface (**Figs. 1(d-e**)), where the monolayer, bilayer, and bulk regions can be identified by optical contrast and second harmonic generation measurements. The compressive pressure is uniformly transferred by the inert gas Ne medium. Due to the weak interlayer vdW force, the applied pressure leads to much greater compression along the out-of-plane direction [51], generating a quasi-vertical compressive strain on the 2D sample and resulting in a reduced interlayer spacing *d*. We use the lattice parameters obtained by X-ray diffraction (XRD) of thicker MoS₂ samples under pressure [51] to convert the pressure dependence to the interlayer spacing dependence.

Exciton resonances in MoS₂ monolayers and bilayers occur at the K valley and exhibit large oscillator strength. As shown in **Fig. 2(a)**, for a monolayer MoS₂, the spin splittings of the conduction band $(2\lambda_c)$ and valence band $(2\lambda_V)$ result from the spin-orbital coupling of the transition metal atoms [38,52,53]. The band splitting for bilayer and multilayer systems is further enhanced by the interlayer coupling, which is determined by the stacking configuration, band alignment, and valley spin [19,20]. For a 2H-stacked bilayer (**Fig. 2(b**)), the coupling strength is zero (finite) for the conduction (valence) band edge [19,20]. In this context, the valence band splitting of the bilayer becomes $2\sqrt{\lambda_V^2 + t^2}$, which can be accessed optically. For example, two excitonic absorptions of K valley (known as X_A and X_B excitons) are typically observed in the DR spectra [54-56]. Since $2\lambda_v$ is much larger than $2\lambda_c$ [38,52,53], the energy difference between two

bright excitons $\Delta E \equiv X_B - X_A$ becomes a good measure of the valence band splitting $2\lambda_v$ $(2\sqrt{\lambda_v^2 + t^2})$ for monolayer (bilayer) MoS₂ (also see **Note S1** in Supplemental Material [35]).

Figures 2(c) and 2(d) show the DR spectra of monolayer and bilayer MoS₂ with applied compressive pressure, respectively. While $\Delta E (= 2\lambda_v)$ of the monolayer is nearly independent of pressure, we find that $\Delta E = 2\sqrt{\lambda_V^2 + t^2}$ of the bilayer increases significantly with the applied pressure, demonstrating that t is increasing. Figure 3(a) summarizes the pressure-dependent ΔE . Under applied pressure, the exciton energy difference ΔE of bilayer MoS₂ exhibits a nonlinear increase, while that of monolayer MoS₂ remains almost unchanged. The significant difference between them demonstrates the pressure-dependent interlayer electronic coupling. For the monolayer sample, we notice that there are rigid X_A and X_B peak blueshifts (~20 meV) between zero and 1.9 GPa, which may be caused by strain-induced changes in bandgap energy [51]. However, since our approach relies on energy difference, the influence of bandgap energy has been largely eliminated. Based on the model, we extracted the coupling strength $t^{(K_V)}$ as a function of pressure, as displayed in Fig. 3(b) (also see Note S2 in Supplemental Material [35]). At the highest applied pressure (12.7 GPa), we determined a coupling strength $t^{(K_V)} = 101$ meV, which is ~280% greater than the value found at zero-pressure ($t^{(K_V)} = 36$ meV). We also observe that $t^{(K_V)}$ exhibits an increasing slope at larger pressures.

Here we use the lattice parameters obtained by XRD of thicker MoS_2 sample under pressure [51] to convert the pressure dependence to the *d*-dependence, as shown in **Fig. 3(c)**. In **Fig. 3(d)**, we compare the experimental results (dots) with the spacing-dependent *t* extracted from the band structure calculations (blue line, DFT-1). In this calculation, we only change the interlayer spacing *d* and keep the in-plane lattice as a constant. It is clear that the coupling strength $t^{(Kv)}$ exhibits an

exponential growth as a function of *d*. The results are fitted by an exponential function $t^{(K_V)} = t_0^{(K_V)} e^{-(d-d_0)/\lambda_0^{(K_V)}}$, with the equilibrium spacing $d_0 = 0.6165$ nm. We determine $t_0^{(K_V)} = 34$ meV (42 meV) and $\lambda_0^{(K_V)} = 0.046$ nm (0.070 nm) for the experimental (DFT-1) data. The discrepancy between the experimental and DFT results cannot be neglected, especially the decay length differs by about 34% (also see **Tables S1-S2** in Supplemental Material [35]).

We realize that this difference arises from the effect of in-plane lattice compression, which occurs simultaneously when hydrostatic pressure is applied [51]. Based on the XRD data, we include both the in-plane and out-of-plane lattice compression in the calculation (red line, DFT-2). Clearly, after considering the effect of in-plane lattice compression, the calculations fit the experimental data much better. We obtain parameters of $t_0^{(K_V)} = 41$ meV and $\lambda_0^{(K_V)} = 0.054$ nm, which are only ~15% different from the experimental data. Therefore, our results demonstrate that both in-plane and out-of-plane lattice compression can enhance the interlayer coupling strength, with the latter playing a major role. The reason can be readily understood from the view of orbital wavefunction overlap: both in-plane and out-of-plane compression can bring the Mo atoms of adjacent layer closer, resulting in higher wavefunction overlap and greater coupling strength.

We further evaluate the coupling strength at other valleys using the pressure-dependent PL spectra of bilayer MoS₂ (**Fig. 4(a)**). The PL spectra feature two peaks, one from the direct K-K exciton and another from the indirect exciton X_I [26,27]. In stark contrary to the nearly unchanged K-K exciton (X_A) energy, the indirect exciton X_I exhibits a significant redshift of ~240 meV from zero to 6.3 GPa. The PL redshift indicates the shrinkage of the indirect gap under pressure. At pressure higher than 6.3 GPa, the X_I indirect exciton emission is no longer detectable. After converting to the interlayer distance dependence, the indirect exciton transition energy as a

function of interlayer distance, $X_{\rm I}$ vs. d, is plotted in **Fig. 4(b)**. Also shown are DFT calculations for the $Q_{\rm C}$ - $\Gamma_{\rm V}$ transition (red curve) and $K_{\rm C}$ - $\Gamma_{\rm V}$ transition (blue curve) as a function of interlayer distance. Interestingly, the energy redshift of $X_{\rm I}$ vs. d shows an excellent agreement with the $Q_{\rm C}$ - $\Gamma_{\rm V}$ transition except for an apparent offset of ~0.25 eV. This offset is not surprising since DFT calculations often under-estimate the band gap [57]. Due to the close energy of $K_{\rm C}$ and $Q_{\rm C}$ points in the conduction band, the PL emission of the indirect gap in bilayer MoS₂ has been under debate [26,27]. Our results show that indirect PL emission is mainly from $Q_{\rm C}$ - $\Gamma_{\rm V}$ excitons [48]. Under applying compressive pressure, the lifting-up of $\Gamma_{\rm V}$ point and the pushing-down of $Q_{\rm C}$ point both contribute to the shrinkage of the indirect gap (**Figs. 1(b)-(c)**).

Our optical spectroscopy measurements do not independently determine the interlayer coupling at $Q_{\rm C}$ and $\Gamma_{\rm V}$. Rather, it is a combined effect of $Q_{\rm C}$ and $\Gamma_{\rm V}$ as a function of d. However, given the fact the experimental result of $X_{\rm I}$ vs. d shows excellent agreement with the calculated result for the $Q_{\rm C}$ - $\Gamma_{\rm V}$ transition, we can conclude that the calculated results for the interlayer coupling at $Q_{\rm C}$ and $\Gamma_{\rm V}$ individually are accurate (also see **Tables S1-S2** in Supplemental Material [35]). In this context, we are able to extract the coupling strength of $Q_{\rm C}$ and $\Gamma_{\rm V}$ points from the DFT calculations using the 2 × 2 Hamiltonian. As shown in **fig. S4** in Supplemental Material [35], the obtained results also exhibit an exponential dependence on d and can be fitted by an exponential function, with extracted $\lambda_0^{(\Gamma_{\rm V})} = 0.067$ nm ($\lambda_0^{(Q_{\rm C})} = 0.108$ nm) for $t^{(\Gamma_{\rm V})}$ ($t^{(Q_{\rm C})}$). When the pressure changes from zero to 6.3 GPa, we determine that $t^{(\Gamma_{\rm V})}$ changes from 335 meV to 522 meV and $t^{(Q_{\rm C})}$ from 192 meV to 253 meV.

In **Tables S1-S2** in Supplemental Material [35], we summarize and compare the experimental results with DFT calculations. We conclude that the coupling strength (decay length) of $\Gamma_{\rm V}$ and $Q_{\rm C}$

are larger (longer) than that of K_V . This valley-dependent coupling strength is due to the fact that the interlayer hopping integral is affected by the p_z orbitals of the chalcogen atoms. Since the atomic distance between the inner chalcogen atoms of adjacent layers are the shortest, the large orbital wavefunction overlap leads to significant $p_z - p_z$ hybridization [58]. Our results show that the coupling strength is indeed correlated to the p_z -orbital component of the critical point, i.e., p_z orbital components of Γ_V , Q_C and K_V points are $28\%(\Gamma_V) > 11\%(Q_C) > 0\%(K_V)$, which leads to $t_0^{(\Gamma_V)} > t_0^{(Q_C)} > t_0^{(K_V)}$. In addition, the decay length exhibits a trend of $\lambda_0^{(\Gamma_V)}$, $\lambda_0^{(Q_C)} > \lambda_0^{(K_V)}$, which can also be understood by $p_z - p_z$ hybridization. Since the wavefunction of p_z orbitals elongates in the *z*-direction, it can be expected a less sensitive *d*-dependence, which leads to longer decay lengths at Γ_V and Q_C than that at K_V . On the contrary, the states at K_V comprise of transition metal $d_{x^2-y^2}$, d_{xy} as the majority orbital and chalcogen p_x , p_y as the minority orbital (see **Table S3** in Supplemental Material [35]), leading to a rapidly decaying wavefunction along the *z*-direction and a shorter decay length.

In conclusion, our experiments firmly establish the exponential dependence of the electronic coupling on the interlayer spacing at various critical points of bilayer MoS₂. In particular, we quantitatively determine the coupling strengths of Γ_V , Q_C and K_V points, as well as their interlayer spacing dependence. We experimentally demonstrate that, due to the increased overlap of atomic orbital wavefunctions, interlayer coupling strength can be enhanced by both in-plane and out-of-plane lattice compression, with the latter playing a major role. By measuring the absorption of X_A and X_B excitons, $t^{(Kv)}$ and its *d*-dependence are independently determined, which are believed to be free from other factors such as band gap and exciton binding energy. In addition, we demonstrate that by applying a moderate pressure of 12.7 GPa, the interlayer K-valley coupling can achieve a 280% enhancement over that in natural bilayers. Through the PL measurement of

indirect excitons, we also determine the *d*-dependence of $t^{(\Gamma_V)}$ and $t^{(Q_C)}$. These results have important implications for vdW heterostructures. Tuning the magic-angle in twisted bilayer graphene through hydrostatic pressure has recently been demonstrated [21]. One therefore expects similar tunability can be achieved in twisted bilayer WSe₂ [11,12]. Most importantly, in the current topic of moiré designing of vdW hetero- and homo-bilayers, in which the shallow moiré potential depth has limited the observation of novel physics at low temperatures. A factor of three enhancement in modulation amplitude will liberate this limitation, thus profoundly impacting the applications of vdW bilayer system [59] in quantum information (e.g. quantum simulator) and other quantum phenomena.

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FIGURES



Fig. 1. Control of interlayer electronic coupling using high-pressure diamond anvil cell. (a) Schematic showing the interlayer hybridization of $|\psi_u\rangle$ and $|\psi_l\rangle$. When the interlayer spacing *d* decreases, the orbital wavefunction overlap increases, which enhances the coupling strength and leads to larger energy splitting of the hybridized state. (b, c) DFT band structure of monolayer MoS₂ (black) and bilayer MoS₂ with interlayer spacing d = 0.62 nm (red) and 0.58 nm (blue). At Γ_V , Q_C and K_V points, band splitting becomes larger for bilayer with a smaller *d*. (d) Schematic showing a diamond anvil cell that can be accessed by optical spectroscopy. (e) An optical image showing the monolayer (1L), bilayer (2L), and bulk MoS₂ loaded in the high-pressure chamber. A ruby sphere is used as a pressure calibrant with the Ne medium loaded in the chamber (see Supplemental Material [35]).



Fig. 2. Pressure-tuning of interlayer hopping integral at K valley. (a) Schematic showing the spin-allowed optical transitions (X_A and X_B) at K⁺ valley of monolayer MoS₂. The spin splitting of the conduction band ($2\lambda_c$) is much smaller than that of the valence band ($2\lambda_v$). (b) Schematic showing the interlayer hybridization of a 2H-stacked bilayer, in which the valence band splitting is enhanced ($2\Delta_v > 2\lambda_v$). Note that the interlayer hopping is allowed (forbidden) at the valence (conduction) band edge. (c, d) DR spectra of the monolayer (c) and bilayer (d) MoS₂ under applied pressure. The spectra have been shifted vertically for clarity.



Fig. 3. Determination of the spacing-dependent coupling strength. (a) Pressure-dependent ΔE of monolayer and bilayer MoS₂. The dots are experimental data, and the solid lines are guide to the eye. (b) Coupling strength *t* as a function of applied pressure, showing a 280% enhancement at 12.7 GPa than that at zero GPa. (c) Pressure-dependent interlayer spacing *d* determined by XRD. (d) Comparison of experimentally-determined (black dots) and DFT-calculated (blue/red curve) coupling strength as a function of *d*. In the calculation of DFT-1 (DFT-2), the compression of the in-plane lattice has not (has) been taken into account (see **figs. S1** and **S2** in Supplemental Material [35] for band structures).



Fig. 4. Pressure-tuning of the indirect gap. (a) PL spectra of bilayer MoS₂ under applied compressive pressure. The indirect gap $X_{\rm I}$ shows a significant redshift at high pressure. (b) A comparison of indirect gap measured by PL (dots) with the predicted evolution of E_{QΓ} and E_{KΓ} gap, showing excellent agreement with the energy evolution of E_{QΓ} gap (red curve). The spacing dependence of $t^{(\Gamma v)}$ and $t^{(Qc)}$ extracted from DFT calculation can be found in **fig. S4** in Supplemental Material [35].