We find that the motion of the valley electrons – electronic states close to the K and K' points of the Brillouin zone – is confined into two dimension when the layers of MoS$_2$ follow the 3R stacking, while in the 2H polytype the bands have dispersion in all the three dimensions. According to our first-principles band structure calculations, the valley states have no interlayer hopping in 3R-MoS$_2$, which is proved to be the consequence of the rotational symmetry of the Bloch functions. By measuring the reflectivity spectra and analyzing an anisotropic hydrogen atomic model, we confirm that the valley excitons in 3R-MoS$_2$ have two-dimensional hydrogen-like spectral series, and the spreads of the wave function are smaller than the interlayer distance. In contrast, the valley excitons in 2H-MoS$_2$ are well described by the three-dimensional model and thus not confined in a single layer. Our results indicate that the dimensionality of the valley degree of freedom can be controlled simply by the stacking geometry, which can be utilized in future valleytronics.

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The monolayer systems of group-VI dichalcogenides, MX$_2$ (M=Mo, W; X=S, Se, Te) [1] have received considerable interest as unique alternatives of graphene for their various intriguing properties [2]: direct band gap of 2 eV [3,12], high photoluminescence yield [3,4], high on/off switching ratio in field effect transistors [13,14], and electric field-induced superconductivity [15,16]. Most notably, their staggered-honeycomb-like lattice structure (the structure and the unit cell are shown in Fig. 1 (a)–(c)) hosts a model system for valley-dependent phenomena [17] originally proposed for graphene [18,20]. The bottom of the conduction band and the top of the valence band are located at the K points of the hexagonal Brillouin zone in MX$_2$. Since the K and K'=−K points are not equivalent, the electronic states in the opposite pockets can carry an additional quantum number, the valley index. Furthermore, the spin-orbit coupling results in sizable valley-dependent spin splitting at the valence top (VT). On the basis of the strong coupling between the spin, orbital and valley degrees of freedom [15,16], which is proved to be the consequence of the rotational symmetry of the Bloch functions. According to our first-principles band structure calculations and group-theoretical analysis, we show that the valley electronic states in the opposite pockets can carry an additional quantum number, the valley index. Furthermore, the spin-orbit coupling results in sizable valley-dependent spin splitting at the valence top (VT). On the basis of the strong coupling between the spin, orbital and valley degrees of freedom, the control of the carrier population of each valley by orbital/spin-sensitive probes has been proposed, which could lead to the novel information processing termed as valleytronics [17,18,21]. Indeed, valley-selective excitation of the electrons and excitons by circularly polarized light has been demonstrated [22,26].

The above progress led to renewed attention to the rich polymorphism of multilayered MX$_2$ [2,27] in view of the valley physics. In inversion-symmetric bilayers with 2H stacking [Fig. 1 (d)], the net valley-dependent spin polarization is absent. This property has been proposed to be utilizable for switching of the polarization with a symmetry-breaking electric field [28,29] or mechanical bending [30]. It has also been stated that a layer degree of freedom (upper/lower layer) couples to the valley degrees of freedom [31,32] and this coupling should cause magnetoelectric effects [31]. On the other hand, very recently, Suzuki et al. [33] observed valley-dependent spin polarization in multilayered MoS$_2$ by utilizing the noncentrosymmetric 3R stacking [Fig. 1 (e)]. This success paves a very different way to the control of the valley carriers: Valleytronics by engineering the stacking geometry. However, knowledge of the valley electronic states in the 3R systems is still scarce, which prevents us from advancing along this way further.

In this Letter, we study the valley electronic states in MoS$_2$ with 3R stacking and compare them with those in the 2H-MoS$_2$. Combining ab initio band structure calculations and group-theoretical analysis, we show that the interlayer hopping amplitude of the valley states is exactly zero in the family of 3R-MX$_2$, i.e. the electrons are confined within the two-dimensional (2D) layers. Furthermore, we study how this confinement affects the exciton spectrum with an anisotropic hydrogen atomic model. Finally, we compare the theoretical results to the reflectivity spectra measured on both 3R-MoS$_2$ and 2H-MoS$_2$ compounds.

First, we calculated the band structures of bulk 2H- and 3R-MoS$_2$ using the WIEN2K code employing the full-potential linearized augmented plane-wave method [34,35]. The calculated band structures are shown in Fig. 2. The apparent difference seen around the Γ point in va-
lence bands is trivial because they agree well by folding the 3R Brillouin zone with respect to }
\((k_z = \pi/(2c))\) plane. Notably, along the K–H path, the band at the conduction
state is invariant, then the phases for \(A\) and \(A'\) are inverse of those for \(A\) because their valley states are exchanged by spatial inversion and

dispersion, whereas those for 3R is flat. This feature has been first found in Ref. 33 but its origin has remained un-
tested. In order to understand the microscopic origin of the
flat bands along the K–H path, first the symmetries of the electronic states in a monolayer of type \(A\) in Fig. 1 are considered. The little group of K point includes three fold rotation \((C_3)\). Under the rotation around the axis crossing the center of the honeycomb unit \([\alpha\) in Fig. 1(c)], the VT (CB) state, which is formed by Mo 4\(d_{z^2-\sigma^2} + d_{xy}\) (4\(d_{z^2}\)) orbital having orbital angular momentum \(l_z = -2\)
(0), gets phase 1 \((e^{i\pi/3})\) [24].

As a matter of fact, there are two more rotational axes inequivalent to \(\alpha\): \(\beta\) and \(\gamma\) crossing S and Mo sites, respectively [Fig. 1(c)]. In order to calculate the phase
factors for different \(C_3\) axes, let us divide the \(C_3\) rotation into two successive operations: permutation of the atomic sites \(P\) and rotation of the local coordinates at each lattice point \(R\). The \(C_3\) around \(j\) axis is defined as \(C_{3j} \equiv RP_j\) \((j = \alpha, \beta, \gamma)\), where \(P_j\) denotes the corresponding site permutation. The contribution to the total phase from \(R\) is simply \(e^{i\theta_{lm}}\) with \(\theta = 2\pi/3\). The contribution from \(P_j\) can be calculated by examining how the Bloch wave function transforms under the site permutation. In Fig. 1 the phase of the K-point Bloch state is depicted, where three values \((1, e^{i\pi/3}, e^{-i\pi/3})\) are represented by circle, triangle and square, respectively. By operating \(P_j\), e.g., the configuration depicted with solid symbols is transformed to that with shaded symbols [panel (a)]. Comparing these symbols on each site, the phase contribution \(\delta_{ij}\) for \(P_{\alpha}\) can be deduced. Applying similar arguments to \(j = \beta\) and \(\gamma\), and to the monolayer of type \(A'\), we get the results summarized in Table I. Note that the phases for \(A'\) are inverse of those for \(A\) because their valley states are exchanged by spatial inversion and time reversal.

On the basis of the axis-dependent phases derived above [30], interlayer hopping amplitude defined by \(t_{ij} = \langle \Psi^b_{K,1}|H|\Psi^b_{K,2} \rangle\) \((b = \text{VT, CB})\) is considered in the bulk material. \(|\Psi^b_{K,L}\rangle\) denotes the K-point Bloch functions at \(L\)th layer, which are eigenstates in the limit where the layer is isolated from others. \(H\) is the total Hamiltonian of the bulk crystal. Suppose \(C_3\) denotes a certain threefold rotation under which \(H\) is invariant, then

\[
\langle \Psi^b_{K,1}|H|\Psi^b_{K,2}\rangle = \langle \Psi^b_{K,1}|C_{3j}^{-1}C_3C_{3j}^{-1}C_3|\Psi^b_{K,2}\rangle = \langle \Psi^b_{K,1}|C_{3j}^{-1}H(C_{3j}',|\Psi^b_{K,2}\rangle) = \exp[-2\pi i\Delta_{12,j,j'}^b]|\Psi^b_{K,1}|H|\Psi^b_{K,2}\rangle. \tag{1}
\]

Here, \(\Delta_{12,j,j'}^b = \delta_{12,j}^b - \delta_{2,j'}^b\) and \(\delta_{12,j}^b\) denotes the phase summarized in Table I for the \(L\)th layer. Note that \(j\) and \(j'\) in the second and last lines depend on the stacking

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{(a) Trigonal prismatic unit cell of monolayer MoS\(_2\); (b)–(c) side and top views of the monolayer, where the trigonal prisms are depicted as shaded triangles. \(\alpha\), \(\beta\) and \(\gamma\) represent inequivalent three-fold rotational axes and \(a_1\) and \(a_2\) are primitive lattice vectors. (d)–(e) side view (top) and top view (bottom) of 2H and 3R stackings, respectively. Rotational axes for each layer are also indicated.}
\end{figure}
pattern and definition of $C_3$. In 2H stacking, without loss of generality, we can assume the first and second layers to be $A$ and $A'$, respectively. In this case, the possible combinations $(j,j')$ are $(\alpha,\alpha)$, $$(\beta,\gamma)$$ and $(\gamma,\beta)$ [Fig. 1 (d)], all of which yield $\Delta_{12j,j'}^{(A)} = 0$ ($b=VT$) and $2/3$ ($b=CB$), respectively. In 3R stacking, where only layers of $A$ type are stacked, $(j,j') = (\alpha,\beta)$, $$(\beta,\gamma)$$, $(\gamma,\alpha)$ [Fig. 1 (e)], and therefore $\Delta_{12j,j'}^{(3R)} = 1/3$ ($b=VT, CB$). According to Eq. (1), the nonzero $\Delta_{12j,j'}^{(3R)}$ forces $t_b$ to be zero, which consistently explains the dispersionless bands along the K–H direction in the 3R polytype.

The difference in the band structures of 2H- and 3R-MoS$_2$ should cause different optical properties of their valley excitations. To verify this experimentally, we measured the normal incidence reflectivity spectra on the cleaved (001) surfaces of both polytypes at $T=20$ K (see Fig. 4). The details of the crystal growth were reported elsewhere [33]. Since the reflectivity were measured in the limited photon energy range of $E=1.5$–3 eV, the spectra were extended up to 30 eV using the data published for 2H-MoS$_2$ [38] to facilitate proper Kramers-Kronig transformation. The imaginary part of the dielectric function calculated from the reflectivity is shown in Fig. 4. Although the two main features in the $\varepsilon_2$ spectra, the $A$ and $B$ exciton peaks corresponding to the optical excitations from the spin-orbit split VT to the CB, look similar, there are several important differences between the two spectra. First, the energy separation between the $A_1$ and the $B$ peaks is larger for the 2H compound (197 meV) compared with the 3R polytype (148 meV), which agrees with the theoretical prediction for the splitting at the VT (see Fig. 2 and Ref. 33). Beside the main excitonic resonances, smaller peaks were observed on the high energy shoulder of the $A$ exciton, labeled as $A_2$. In a hydrogen-atom-like model of excitons, $A_1$ and $A_2$ are assigned to the 1s and 2s bound states of the electron-hole pair. In the 3R case, $A_1$ and $A_2$ peaks are more separated and their intensity ratio is larger than in the 2H structure.

To understand these differences, we employed an anisotropic hydrogen atomic model [39]:

\[
- \frac{\nabla_x \cdot \nabla_y}{2m^*_\perp} - \frac{\nabla_z \cdot \nabla_z}{2m^*_\parallel} \frac{1}{\sqrt{\varepsilon_\perp \varepsilon_\parallel (k^2 + y^2) + \varepsilon_\perp z^2}} \phi(r) = E \phi(r),
\]

where $\varepsilon_\perp$ and $\varepsilon_\parallel$ are the components of the dielectric constant tensor perpendicular and parallel to the $z$-direction respectively, and $m^*_\perp$ and $m^*_\parallel$ are those of the reduced effective-mass tensor of excitons at the K-point. Note that in a monolayer system, the screened electron-hole interaction is rather different from that in Eq. (2) owing to the surrounding vacuum [40] [41]. Bulk environment allows us to use the present model as in earlier studies [42] [33]. The values of $\varepsilon_\perp$, $\varepsilon_\parallel$, $m^*_\perp$ and $m^*_\parallel$ were extracted from \textit{ab initio} calculations [35]. The reduced effective masses were estimated from a parabolic curve fitting of the band dispersions of electrons and holes around the K-point. Calculated dielectric constants and reduced effective masses are presented in Table II. Since both VT and CB are flat along the K–H line, $m^*_\parallel$ is quite large in the 3R stacking, whereas it is small in the 2H stacking where only CB is flat. Note that the effective masses were determined in the close vicinity of the K point, and the valence and conduction bands in 3R-MoS$_2$ have less than 2 meV dispersion along the K–H line. Since this range is much smaller than the binding energy of 1s or 2s exciton, in the following analyses, we regard the 3R

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**TABLE I:** Phases $\delta_j^b$ of the eigenvalues $e^{2\pi i \delta_j^b}$ of $C_{3,j} \equiv RP_j$ around different rotational axes ($j = \alpha, \beta$ and $\gamma$) for the K-point states ($b$=VT, CB).

| $b$ | VT | CB | $\Lambda$ | VT | CB |
|-----|----|----|----------|----|----|
| $j$ | $\beta$ | $\gamma$ | $\alpha$ | $\beta$ | $\gamma$ |
| $P_\alpha$ | $\frac{1}{4}$ | $0$ | $\frac{1}{4}$ | $0$ | $\frac{1}{4}$ | $0$ |
| $P_\beta$ | $\frac{1}{4}$ | $0$ | $\frac{1}{4}$ | $0$ | $\frac{1}{4}$ | $0$ |
| $P_\gamma$ | $0$ | $\frac{1}{4}$ | $0$ | $\frac{1}{4}$ | $0$ | $\frac{1}{4}$ | $0$ |

**TABLE II:** Parameters adopted for Eq. (2) extracted from \textit{ab initio} band structure calculations: dielectric constants and reduced effective masses of excitons at the K-point (in units of electron mass $m_0$).

|       | $\varepsilon_\perp$ | $\varepsilon_\parallel$ | $m^*_\perp$ | $m^*_\parallel$ |
|-------|---------------------|------------------------|------------|---------------|
| 2H    | 16.0                | 10.2                   | 0.27       | 1.87          |
| Ref. 33 | 13.5                | 8.5                    | -          | -             |
| Ref. 38 | 16                 | 10                    | -          | -             |
| 3R    | 15.9                | 10.1                   | 0.24       | 28            |
| Ref. 46 | -                 | -                      | -          | 0.22 (K–Γ)    |
|       | -                   | -                      | -          | 0.23 (K–M)    |
|       | -                   | -                      | -          | 1.7           |
all the parameters in the 2H and 3R cases are similar to each other except \(m_\parallel\) we attribute the differences solely to the 2D confinement of the electrons and holes in the 3R compound.

To see another aspect of the 2H and 3R excitons with respect to their dimensionality, we examined the exciton radii by using a simple trial wave function [45] for the 1s eigenstate of Eq. (2),

\[
\varphi_{1s}(r) = \frac{1}{\sqrt{\pi r_\perp^2 r_\parallel}} \exp \left[ -\sqrt{(x^2 + y^2)/r_\perp^2 + z^2/r_\parallel^2} \right],
\]

with the parameters \(r_\perp\) and \(r_\parallel\), which represent exciton in-plane and out-of-plane radii, respectively, optimized in a variational manner. For the 3R exciton, we used a finite \(m_\parallel\) listed in Table II to estimate an upper bound of \(r_\parallel\). The obtained values of \(r_\parallel\) are almost the same values for 2H and 3R structures: 19 and 15 Å, respectively. In contrast, obtained values of \(r_\parallel\) are 8.9 and 2.7 Å for 2H and 3R structures, respectively. Comparing these values with the interlayer distance (6.1 Å for both structures), we can see that the 3R exciton is tightly confined in a single layer while the 2H exciton extends to the neighboring layers.

The present results establish the 2D nature of the valley exciton in bulk MoS\(_2\) with 3R stacking. Note that an apparently similar confinement effect has also been discussed for the 2H stacking against the spin-layer locking effect [31, 32]. Since this effect exploits the fact that the sign of the spin-orbit coupling of the K-point states depends on layer [A and A’ in Fig. 1 (d)] in the 2H bilayers [31], its strength essentially relies on atomic number of \(M\). Distinctively, the layer-confinement effect in the 3R stacking is a quantum interference effects caused by the symmetry of the crystal and therefore is guaranteed to be relevant in general \(MX_2\) systems with the same structure.

To summarize, we showed perfect suppression of the interlayer hopping for the valley electrons in 3R-MoS\(_2\), which was substantiated with group-theoretical arguments. Through the measurement of the reflectivity spectra and analyses with an anisotropic hydrogen atomic model, the suppressed hopping has been shown to make the exciton absorption spectrum 2D hydrogen-like and the exciton wave function confined in a single layer. Our results exemplify the control of spatial dimensionality of the valley excitations in the 2H- and 3R-MX\(_2\), which may help to develop new valleytronics devices.

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SUPPLEMENTAL MATERIALS

COMPUTATIONAL DETAILS

For \textit{ab initio} band structure calculations of the bulk 2H- and 3R-MoS\textsubscript{2}, we used the Perdew-Burke-Ernzerhof exchange-correlation functional \cite{S1} and the full-potential linearized augmented plane-wave method including the scalar-relativistic effects \cite{S2} and spin-orbit coupling \cite{S3} as implemented in \textsc{wien2k} code \cite{S34}. Experimental lattice parameters and atomic configurations were taken from Refs. \textit{S4} and \textit{S5}. In the calculation of the band structures and the dielectric matrix the muffin-tin radii for Mo and S atoms, \(r_{\text{Mo}}\) and \(r_{\text{S}}\), were set to 2.44 and 2.10 a.u., respectively. The maximum modulus for the reciprocal lattice vectors \(K_{\text{max}}\) was chosen so that \(r_{\text{S}} \times K_{\text{max}} = 7.00\). To obtain the effective masses, \(r_{\text{Mo}}\), \(r_{\text{S}}\), and \(r_{\text{S}} \times K_{\text{max}}\) were set to 2.20 a.u., 1.89 a.u., and 9.00, respectively.

Dielectric constants \(\varepsilon\) were calculated using the random-phase approximation formula \cite{S6, S7, S8},

\[
\varepsilon_\alpha = 1 + \frac{8\pi}{V} \lim_{q \to 0} \frac{1}{q^2} \sum_{K\sigma} \sum_{i} \sum_{j} \frac{|\langle \phi_{jk+q}\alpha | e^{i q r_{ij}} | \phi_{ik}\sigma \rangle|^2}{\varepsilon_{j\alpha} \varepsilon_{i\alpha} - \varepsilon_{ik\sigma}},
\]

where \(V\) denotes the volume of the simulation cell, \(i\) and \(j\) indices of the occupied and unoccupied bands respectively, \(k\) the wave vector, \(e_\alpha\) (\(\alpha = x, y, z\)) the unit vectors, \(\phi_{ij\alpha}\) the Kohn-Sham wave functions, and \(\varepsilon_{ik\sigma}\) their orbital energies. The effective masses \(m^*\) were estimated from a parabolic curve fitting of the band dispersions of electrons and holes around the K-point. Such fitting was performed at the vicinity of the K point \(\sim 0.02\ \AA^{-1}\) (\(\sim 0.03\ \AA^{-1}\) for \(m^*_\parallel\) of the 3R polytype).

FITTING OF THE IMAGINARY PART OF THE DIELECTRIC CONSTANT

The imaginary part of the dielectric function deduced from the measured reflectivity is fitted by a sum of Lorentzian peaks. The fits (shown in Fig. S1) describe the experimental spectra well. The contributions from the higher energy transitions are also included.

![Fig. S1](image-url) Fig. S1: (a)-(b) Fit of the imaginary part of the dielectric function in 2H- and 3R-MoS\textsubscript{2}, respectively. The dielectric function deduced from the reflectivity (black lines) can be fitted by a sum of Lorentzian peaks (red lines). The green lines show the contribution of the respective peaks.
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[S1] J. P. Perdew, K. Burke, and J. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
[S2] D. D. Koelling and B. N. Harmon, J. Phys. C 10, 3107 (1977).
[S3] J. Kuneší, P. Novák, R. Schmid, P. Blaha, and K. Schwarz, Phys. Rev. B 64, 153102 (2001).
[S4] K. D. Bronsema, J. L. de Boer, and F. Jellinek, Z. anorg. allg. Chem. 540, 15 (1986).
[S5] A. A. Golubichanaya, A. G. Duksina, and V. L. Kalikhman, Inorg. Mater., 15, 1156 (1979).
[S6] H. Ehrenreich and M. H. Cohen, Phys. Rev. 115, 786 (1959).
[S7] S. L. Adler, Phys. Rev. 126, 413 (1962).
[S8] N. Wiser, Phys. Rev. 129, 69 (1963).