Deep moiré potentials in twisted transition metal dichalcogenide bilayers

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In twisted bilayers of semiconducting transition metal dichalcogenides, a combination of structural rippling and electronic coupling gives rise to periodic moiré potentials that can confine charged and neutral excitations1–3. Here we show that the moiré potential in these bilayers at small angles is unexpectedly large, reaching values above 300 meV for the valence band and 150 meV for the conduction band—an order of magnitude larger than theoretical estimates based on interlayer coupling alone. We further demonstrate that the moiré potential is a non-monotonic function of moiré wavelength, reaching a maximum at a moiré period of ~13 nm. This non-monotonicity coincides with a change in the structure of the moiré pattern from a continuous variation of stacking order at small moiré wavelengths to a one-dimensional soliton-dominated structure at large moiré wavelengths. We show that the in-plane structure of the moiré pattern is captured by a continuous mechanical relaxation model, and find that the moiré structure and internal strain, rather than the interlayer coupling, are the dominant factors in determining the moiré potential. Our results demonstrate the potential of using precision moiré structures to create deeply trapped carriers or excitations for quantum electronics and opto-electronics.

Many emergent quantum phenomena have recently been observed in transition metal dichalcogenide (TMD) semiconductor homobilayers4 and heterobilayers5–7. In heterobilayers, the low-energy electronic structure can be reasonably approximated by the properties of a single layer on which a spatially dependent potential energy landscape is imposed (termed the moiré potential)8,9. This moiré potential when periodic gives rise to subbands within the valence or conduction bands, which are responsible for the emergent quantum phenomena observed. Theoretical calculations based only on interlayer coupling estimate the size of this moiré potential to be of the order of tens of millielectronvolts (meVs) in TMD bilayers such as MoS2/WSe210, MoSe2/WS2, MoSe2/MoS2 and MoTe2/MoSe211. Recent theoretical work12 that includes lattice relaxation effects indicates a larger moiré potential up to 100 meV in MoTe2/MoS2. However, a theory for the electronic structure that includes lattice relaxation effects at large moiré wavelengths (greater than 5 nm) is not currently available, and experimental measurements of the moiré potential remain an important open problem in these materials.

Scanning tunnelling microscopy (STM), because of its high energy and spatial resolution, is one of the few experimental techniques that can provide direct measurements of the magnitude of the moiré potential. It requires clean surfaces and conducting samples, both of which are substantial challenges for TMD semiconductor layers. A few pioneering STM experiments have been performed on rotationally aligned bilayers grown by chemical vapour deposition13,14 and, more recently, on exfoliated twisted TMD bilayers15–18. All of these previous measurements have been performed for moiré wavelengths near 5 nm at rotational angles close to zero degrees between the two layers. In this work, we study a heterobilayer of MoSe2 on WSe2, at a range of moiré wavelengths from 5 nm to greater than 20 nm. We avoid problems associated with sample conduction by performing our STM measurements at room temperature with a few-layer graphite substrate.

As a consequence of the broken inversion symmetry in TMDs, there are two distinct aligned stacking configurations, which are termed R (0° alignment between the two layers, also termed AA stacking in the literature) and H (180° alignment between the two layers, also termed AB stacking). When a twist angle is present between the layers, the atomic registry between the two layers varies periodically in space19. For nearly R-stacked twisted bilayers, three of the high-symmetry stacking orders that are present in the sample are shown in Fig. 1a, termed RM, RH, and RS, respectively. Here, RM refer to R-type stacking where the metal atoms of the top layer, M, are in vertical registry with the chalcogen atoms, X, from the bottom layer. For nearly H-stacked bilayers, the corresponding high-symmetry stackings are H, HM and HS, as shown in Fig. 1b.

Figure 1c,d presents STM topographs of samples at twist angles of ~3° (near R stacking) and ~61.7° (near H stacking), respectively. We can see that the two stacking orientations present very different structures when visualized in STM. To understand this difference, we calculate the relaxed structure of twisted bilayers based upon a continuous mechanical relaxation model (details are provided in Methods)19–21. The results of these calculations are shown in Fig. 1e,f for the same angles as shown in Fig. 1c,d. For samples near R stacking, the RM stacking is an energetic maximum, while both the RS and RH stackings are minima that are close to each other in energy (in our case, the chemical identity of superscript M = Mo, subscript M = W, X = Se). Consequently, the twisted bilayer shows topographic contrast with the RM region (red dot, Fig. 1c) displaying a larger topographic height, while the RS (green dot, Fig. 1e) and RH (blue dot, Fig. 1c) regions are minima in height. For samples near H stacking, the H stacking is most energetically favourable, while the HS is the global minimum and the HM is a local minimum. As
a result, the H\textsuperscript{H} stacking (red dot, Fig. 1d) region shrinks in size while the H\textsuperscript{M} (blue dot, Fig. 1d) region expands and the H\textsuperscript{H} has an intermediate area (green dot, Fig. 1d). We also see quite clearly for this moiré wavelength (λ ≈ 11 nm) that lattice reconstructions result in sharply triangular domain boundaries between the H\textsuperscript{H} and H\textsuperscript{M} regions. All of these together allow us to clearly identify the various stacking configurations in our STM topograph in Fig. 1d, as indicated in the figure. We see that samples that are near H stacking present a completely different structure to samples near R stacking—this has not been studied previously by STM. For the rest of this work, we focus exclusively on this case.

Having understood the details of the moiré pattern at small length scales, we proceeded to perform STM measurements over large areas of nearly H-stacked samples. One such topograph is shown in Fig. 1g, over an area of 500 × 500 nm\textsuperscript{2}. This topograph shows many interesting features, including a spatially varying moiré period, large (greater than 100 nm) regions of uniform H\textsuperscript{H} stacking, and one-dimensional (1D) solitons. Interesting electronic and optical properties have been reported in these 1D solitons\textsuperscript{22–24}. All this disparate behaviour can be captured with the continuum mechanical relaxation calculation shown in Fig. 1h. The only inputs (beyond those of the periodic case shown in Fig. 1I) that go into this calculation are the locations and stacking registry of selected H\textsuperscript{H} stacking points. Given this information, a detailed spatial account of the relaxed structure is resolved. Because of the existing dislocations, the process was repeated by surrounding dislocations from different sides to generate the integrated map in Fig. 1b (see Methods and Supplementary Information).

We now examine the structure of the moiré pattern at various length scales. Figure 2a–e presents a sequence of topographs obtained in regions with increasing moiré length scales. At the smallest of these length scales (λ ≈ 6 nm, Fig. 2a), the moiré pattern features nearly equal regions of H\textsuperscript{H} and H\textsuperscript{M} stacking. As the size of the moiré wavelength increases (Fig. 2b–d), the area of the H\textsuperscript{M} stacked region decreases at the expense of the area of the H\textsuperscript{H} stacking region. For moiré wavelengths that are larger than 20 nm, the H\textsuperscript{M} region shrinks to a shear soliton of width ~4 nm. Above this wavelength, moiré patterns resemble honeycomb lattices formed by the shear solitons rather than the triangular lattices seen at small wavelengths (see Supplementary Information for a typical image). The large moiré wavelengths are extremely susceptible to small amounts of strain, which can distort the honeycomb structure severely. An example is shown in Fig. 2e, where the individual honeycomb cells have been distorted to form quasi-rectangular strips of H\textsuperscript{H} stacking that are separated by soliton domain walls.

We now consider the spectroscopic properties of samples exhibiting different moiré wavelengths. Figure 2f–j shows measurements of the differential conductance (dI/dV) obtained at the...
three high-symmetry locations of the moiré lattice, namely \( H_{X}^{M} \), \( H_{M}^{M} \) and \( H_{N}^{M} \), for the moiré patterns shown in Fig. 2a–e, respectively (details about spectroscopy on R-stacked samples is provided in Supplementary Information). Clear and systematic differences are seen in the spectroscopic properties of the different sites within the moiré unit cell. It is seen that the edges of both the valence band and the conduction band are closest to the Fermi level for the \( H_{X}^{M} \) site for all moiré wavelengths. The difference in valence band edges between the \( H_{M}^{M} \) and \( H_{N}^{M} \) regions reaches a maximum at a moiré wavelength around 13 nm (Fig. 2c) and decreases for both smaller and larger moiré wavelengths. Similar behaviour is observed for the conduction band edges. The wavelength at which the moiré potential is largest corresponds structurally to the length scale where the \( H_{X}^{M} \) region transitions from a triangular region to a soliton. The valence band edge observed in Fig. 2f–j is derived from the states with primarily MoSe\(_2\) character, while the conduction band edge states are derived from states with primarily WSe\(_2\) character\(^8\). The states with WSe\(_2\) character have a small tunnel matrix element due to the larger physical distance from the STM tip. The conduction band edges, the difference in the band-edge positions inside and outside the well is then simply equal to the well depth, that is, the magnitude of the moiré potential. Our spectroscopic results indicate that the \( H_{M}^{M} \) region of the moiré unit cell is the region with a potential minimum for both the valence and conduction band; that is, the low-energy physics of this system is dominated by electrons or holes trapped within these regions. A cursory inspection of Fig. 2f–j also reveals that this trapping potential is large—around 300 meV at its largest in the valence band and 100 meV for the conduction band. This consideration becomes especially interesting for large moiré wavelengths, where the \( H_{M}^{M} \) regions shrink to soliton lines. Our results indicate that carriers are confined to these 1D lines at low energies in these structures. This quantum well picture, based on a single moiré unit cell, is only slightly modified by the periodic boundary conditions imposed by the moiré pattern—the coupling between neighbouring wells broadens each of the eigenstates within the well to a ‘flat band’ with width determined by interwell coupling\(^6\).

To understand the systematic evolution of the moiré potential as a function of moiré wavelength, we can utilize strain-induced inhomogeneity in the sample to our advantage. Shown in Fig. 3a is a region of the sample where the moiré wavelength interpolates...
continuously between a minimum of 5 nm to greater than 20 nm. We took \(dI/dV\) spectroscopic measurements at every point on a 256\(\times\)256-pixel grid in the area bounded by the dashed box in Fig. 3a. For each spectrum, we determined the edge of the valence band and the edge of the conduction band and plotted their values in Fig. 3b,c, respectively. We used this information, together with the areas of the individual moiré unit cells, to plot the conduction and valence band edges as a function of moiré wavelength in Fig. 3d (details of the analysis are provided in the Supplementary Information). The scatter in this figure primarily arises from the fact that different moiré triangles in Fig. 3a have differing shapes and thus display slightly different properties when represented by a single length scale (see Supplementary Information for a discussion of the effect of external strain on the moiré potential). The trends shown in Fig. 3d confirm the selected point spectra shown in Fig. 2—the non-monotonicity of the band edges as a function of moiré wavelength from Fig. 2 is clearly confirmed in Fig. 3d in a much more extensive dataset.

Having obtained, separately, the conduction and valence band edges for the \(H_{M}^{M}\) and \(H_{X}^{M}\) sites in Fig. 3, we can utilize this information to extract the moiré potential as a function of wavelength, which is simply the energy difference in band positions between an \(H_{M}^{M}\) region and its \(H_{X}^{M}\) neighbours (details of the analysis are provided in the Supplementary Information). This is plotted in Fig. 4a for both the conduction and valence bands. We can see clearly that the moiré potential is large and non-monotonic for both the conduction and valence band edges. For \(WSe_{2}/MoSe_{2}\), the hybridization differences between bilayers with uniform \(H_{M}^{M}\) and \(H_{X}^{M}\) stacking order are small (of order 10 meV), and thus there has been an expectation that the moiré potential is also similarly small in magnitude. Previous STM and photoemission experiments on moiré patterns in varied TMD bilayers\(^{13,14,16,25}\) along with our current results indicate that the observed moiré potential is substantially larger than the expectation based on stacking order alone. The common feature of all of the works (including ours) is that real moiré patterns feature structural distortions in both the lateral and vertical dimensions and these distortions must, therefore, be dominating the moiré potential.

Distortions within the moiré unit cell give rise to substantial lateral and vertical strain. Because of the large unit cell sizes we consider in our work, accurate ab initio calculations of the electronic properties of the moiré are not feasible. We expect substantial vertical strain to be present in the structure. For uniformly stacked bilayers, the \(H_{M}^{M}\) stacking configuration displays a larger interlayer spacing compared to \(H_{X}^{M}\) (6.7 Å instead of 6.5 Å). We thus expect that, within the moiré structure, the \(H_{M}^{M}\) regions are being compressed by the \(H_{X}^{M}\) regions, while the \(H_{X}^{M}\) regions are under tensile strain along the \(c\) axis. These strains can give rise to substantial changes in electronic structure. Figure 4b shows a density functional theory (DFT)
calculation of the electronic structure of a uniform $H^M$ stacked region at interlayer distances $d$ of 6.7 Å (equilibrium) and 6.5 Å (compressed). This compression gives rise to a shift of $\sim 0.2$ eV in the valence band position at the $\Gamma$ point in a direction that is consistent with the experimental finding (Supplementary Information provides further discussions of orbital mixing). We also expect substantial lateral strains to be present within the unit cell, which we estimate using our mechanical relaxation model within the moiré unit cell. We write the strain tensor as $\epsilon = \epsilon(C, I) + \epsilon(S, \phi)\sigma_x + \sin(2\phi)\sigma_z$, where $\epsilon(C)$ is an isotropic compression and $\epsilon(S)$ is a volume-preserving shear. $I$ is the identity matrix and $\sigma_x, \sigma_z$ are the Pauli matrices in standard notation. The magnitude $\epsilon(I)$ is plotted within the moiré unit cell in Fig. 4c for a moiré wavelength of $\sim 10$ nm ($\epsilon(C)$ is small at this wavelength). The total variation in strain across the unit cell is seen to be greater than 3%, as can be seen in the line cut of strain tensor elements shown in Fig. 4d. For comparison, a uniform tensile strain of 1% changes the bandgap of TMDs by $\sim 0.2$ eV (ref. 22). It is thus no surprise that these large values of strain in the moiré unit cell dominate the electronic properties. Figure 4e shows the maximal shear strains for electrons and excitons in heterobilayers of transition-metal dichalcogenides. It is seen that the experimentally measured moiré potentials are much larger than this theoretical expectation. Open problems include the finding that the largest moiré potentials are realized for a narrow range of angles, and engineering high-quality structures with uniform moiré lattices with these wavelengths remains an open problem.

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Methods

Device fabrication. Monolayers of WSe₂ and MoSe₂ were obtained by mechanical exfoliation from self-flux-grown bulk crystals. The relative orientation between these TMDC monolayers was determined by second harmonic generation (SHG). We used polypropylene carbonate to pick up a hexagonal boron nitride flake, few-layer graphite and WS₂, and MoSe₂ monolayers, respectively, using a high-precision rotation stage. In the final stage, the sample was flipped on a Si/SiO₂ substrate at an elevated temperature of 120°C.

STM measurements. STM and tunnelling spectroscopy data were acquired at room temperature in ultrahigh-vacuum conditions. A lock-in amplifier with modulation of 25 meV and 917 Hz was used for dI/dV spectroscopy measurements.

SHG measurement. SHG measurements were used to determine the crystal orientations of the WSe₂ and MoSe₂ monolayers. Linearly polarized femtosecond laser light (Spectrum Physics Tsunami, 80 MHz, 800 nm, 80 fs) was focused onto a monolayer with a ×100 objective (Olympus LMPFLN100X). The reflected SHG signal at 400 nm was collected using the same objective and detected by a photomultiplier tube (Hamamatsu R1422P) and recorded with a photon counter (BK Precision 1823A 2.4 GHz universal frequency counter). Triangular monolayer MoS₂ (2D layer) grown by chemical vapour deposition was used to calibrate the SHG set-up.

DFT calculations. We used a slab structure to model the WSe₂/MoSe₂ heterostructure. To avoid artificial interactions between the polar slabs, we placed two oppositely oriented WSe₂/MoSe₂ units with mirror symmetry in the slab. Each slab was separated from its periodic images by vacuum regions (15 Å). The DFT calculations were performed using the Vienna Ab-initio Simulation Package (VASP)39. We used the projector augmented wave (PAW) method to construct pseudopotentials40. The plane-wave energy cutoff was 400 eV. The exchange correlation functional was approximated by the generalized gradient approximation as parameterized by Perdew, Burke and Ernzerhof (PBE)29. The electronic structure was calculated with a plane-wave cutoff of 500 eV, the VASP 5.4.4 software was used. All geometries were optimized using the CASTEP code. The Brillouin zone was sampled using a 2 × 2 × 1 k-point mesh. Van der Waals dispersion forces between the two constituents were taken into account using the optB86b-vdW functional within the vdw-DF method developed by Klimeš and others41.

Atomic relaxation simulation. Modelling of the atomic relaxation of twisted MoSe₂/WSe₂ was performed within a continuum model following the method presented in ref. 39 but solved in real space. In this model, the total energy of the system is taken as the sum of elastic energy and a stacking energy term. The total energy was minimized in search of the interlayer real-space displacement field corresponding to the relaxed structure. The stacking configuration at selected H₂₀ stacking points was imposed as a boundary condition to account for the specific case under study. In the periodic case (Figs. 1c and 4a), such boundary conditions were used to impose a fixed external strain condition. In the case of a non-uniform strain field as in Figs. 1f, such points were needed wherever the moiré superlattice deviates from a uniformly periodic structure. Special care was needed to describe the 11 dislocations in the image. For each dislocation the structure was relaxed using two registry maps for the H₂₀ stacking sites to describe both sides of the dislocation. The stacking energy maps were later stitched together to form the relaxed structure. The stacking energy maps were minimized in search for the interlayer real-space displacement field parameters for the MoSe₂/WSe₂ heterostructures were calculated using DFT as of the relaxation. The stacking energy maps were later stitched to form Fig. 1h.

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Author contributions

S.S. performed STM experiments, assisted by S.L. D.H. performed relaxation calculations. WC. performed SHG experiments. M.C. performed DFT calculations. J.H., W.Y., D.N.B., X.Z. and A.N.P. provided advice. Data analysis and manuscript preparation were performed by S.S. and A.N.P. with input from all coauthors.

Competing interests

The authors declare no competing interests.

Additional information

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