Twist Angle Dependent Interlayer Exciton Lifetimes in van der Waals Heterostructures

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In van der Waals (vdW) heterostructures formed by stacking two monolayers of transition metal dichalcogenides, multiple exciton resonances with highly tunable properties are formed and subject to both vertical and lateral confinement. We investigate how a unique control knob, the twist angle between the two monolayers, can be used to control the exciton dynamics. We observe that the interlayer exciton lifetimes in MoSe₂/WSe₂ twisted bilayers (TBLs) change by one order of magnitude when the twist angle is varied from 1° to 3.5°. Using a low-energy continuum model, we theoretically separate two leading mechanisms that influence interlayer exciton radiative lifetimes. The shift to indirect transitions in the momentum space with an increasing twist angle and the energy modulation from the moiré potential both have a significant impact on interlayer exciton lifetimes. We further predict distinct temperature dependence of interlayer exciton lifetimes in TBLs with different twist angles, which is partially validated by experiments. While many recent studies have highlighted how the twist angle in a vdW TBL can be used to engineer the ground states and quantum phases due to many-body interaction, our studies explore its role in controlling the dynamics of optically excited states, thus, expanding the conceptual applications of “twistronics”.

Van der Waals (vdW) heterostructures offer a unique material platform with rich electronic and optical properties highly tunable via a wide selection of layer composition, strain, electric gating, and doping [1]. Because the lattice matching restriction is lifted at the interface [2], the twist angle between two monolayers (MLs) has emerged as a unique control knob to engineer the moiré superlattice formed by periodic variations of atomic alignment between the two layers. Following exciting discoveries in graphene twisted bilayers (TBLs) [3, 4], transition metal dichalcogenide (TMD) based TBLs have also been found to exhibit rich correlated electronic phases [5]. These phases can be probed via optical spectroscopy featuring excitonic resonances [6, 7]. In a different context, the lateral confinement introduced by the moiré potential may be used to realize a regular array of quantum emitters, a long-standing goal in the field of solid-state quantum information technology [8, 9].

A type-II band alignment is typically found in a TMD TBL (Fig. 1a), leading to the formation of both intralayer and interlayer excitons [11, 15]. We focus on interlayer excitons (IXs) because they are most likely to experience a deep moiré potential, particularly interesting for realizing quantum emitters. Because of the similar lattice constants of MoSe₂ and WSe₂ MLs, the size of the moiré supercell is determined by the twist angle (Fig. 1b). The twist angle in real space translates into a rotation in the momentum space, causing the relative rotation of Brillouin zones associated with each monolayer (Fig. 1c). Consequently, valleys in each layer are shifted from each other, changing the indirect optical transition near the K-valley to an indirect transition, introducing longer IX lifetimes [12, 16].

We illustrate the exciton center of mass wavefunction in its own reference frame (i.e., the Γ point) in the excitation picture of Fig. 1d. In TBLs with small twist angles (Θ < 5°), the thermally broadened IX distribution is sufficient to satisfy the momentum conservation requirement of an indirect transition, allowing the radiative decay process. A wide range of IX lifetimes in TMD TBLs have been reported in time-resolved photoluminescence (TRPL) measurements previously [12, 13, 17–22]. However, no prior studies have explained the origin of such variations.

We perform TRPL measurements on a series of stacked MoSe₂/WSe₂ TBLs with accurately controlled twist angles and observe that the IX lifetime changes by one order of magnitude when the twist angle is changed from 1° to 3.5°. Theoretically, we examine two mechanisms that influence the IX radiative lifetimes. We find that both the shift to indirect optical transition with an increasing twist angle and the moiré potential have a significant effect on the lifetime. Our theory further predicts that IX lifetimes exhibit different temperature dependence in TBLs with different twist angles. This prediction is partially validated by the experimental observations.
Two samples with $\Theta = 2^\circ$ are shown in Fig. 2b. We present the PL spectra for the other IX resonances in the PL spectrum by Gaussian functions as consistent with previous experiments [12–14]. We fit multiple exciton lifetimes in the SM. Different possible interpretations for these resonances have been proposed, including phonon-mediated states, defect-bound states, and spin triplet states [29,32]. While we cannot rule out these alternative explanations definitively, we find that the interpretation of quantized exciton resonances confined within the moiré potential captures the essential features of our data [13].

The TRPL measurements were performed at $\sim 10$ K unless stated otherwise. The TRPL signals are fitted with a biexponential decay function. Such a biexponential decay indicates that a simple two-level model is not sufficient to explain the dynamics of IXs. This biexponential decay may originate from scattering between a bright and dark exciton [33–35]. In all samples, we observe shorter IX lifetimes as the energy of the resonance increases as shown in the inset to each panel in Fig. 3a–c. This systematic change with energy is consistent with the interpretation that the higher energy excitons are excited states in the moiré potential with additional relaxation channels [13]. The reduced exciton lifetimes associated with the excited states are often found in spatially localized excitons in other materials such as InGaAs quantum dots [36].

Most remarkably, the IX lifetime changes drastically as a function of the twist angle, as shown in Fig. 3d. The fast (slow) decay time is $1.7 (10.9)$ to $8.3 (102.4)$ ns. We focus on understanding this twist angle dependence of IX lifetimes in TBLs. To understand this drastic twist angle dependence, we calculate the radiative recombination rate of IXs in the TBLs. We note that the lifetime measured is in fact the total lifetime, determined by both radiative and non-radiative processes. It is impractical to calculate all non-radiative processes, which may depend on many extrinsic properties. Thus, our calculations can only be compared to ideal emitters with unity quantum yield. Nevertheless, these calculations provide important understanding of IX dynamics controlled by the twist angle in a TBL and guide the search for more efficient emitters in a moiré crystal. Our calculations start with Fermi’s golden rule [37]

$$\tau_{\text{IX}}^{-1} = \frac{2\pi}{\hbar} \sum_{i f} | \langle f | H_{\text{rad}} | i \rangle |^2 \delta(\varepsilon_i - \varepsilon_f) N_i$$

where the optical matrix element describes transitions between the initial IX state $| i \rangle$ and the final photon state $| f \rangle = b^\dagger_{q,\sigma}|0\rangle$. Here, $b^\dagger_{q,\sigma}$ creates a photon with wave vector $q$.
FIG. 3. Twist angle dependent lifetimes of several IX resonances measured from (a) $\Theta = 1.0 \pm 0.3^\circ$, (b) $2.2 \pm 0.3^\circ$, and (c) $3.5 \pm 0.3^\circ$ TBLs, respectively. The solid lines represent fitting with a biexponential decay. The inset shows the energy dependence of the fast and slow decay components of IX lifetimes. (d) Twist angle dependence of IX lifetimes measured near 1345 - 1355 meV in the TBLs. The inset summarizes the extracted fast and slow decay components in the three TBLs.

$q$ and polarization $\sigma$ with respect to the vacuum state $|0\rangle$, and $N_i$ is the occupation of the initial IX states. To describe the moiré exciton states we use a low energy continuum model that we derive along the lines of Ref. [10] [11] [18] [58]. As the basis of describing the hybridized IXs later, we have first written the wave function of IXs in the absence of interlayer coupling as:

$$|Q\rangle = \frac{1}{\sqrt{A}} \sum_k \phi_X(k) a_{K_v + \parallel - k}^{\lambda \sigma} |Q\rangle_{K_v + \parallel - k - m_{\parallel} - m_{\parallel} Q} |0\rangle$$

with eigenenergies $E(Q) = \hbar^2|Q|^2/(2M) + E_{gap} - E_B$ that are characterized by the center-of-mass momentum $Q$. Here, $a_{K_v + \parallel - k}^{\lambda \sigma}$ creates (annihilates) an electron in the $K_v$ ($K_v$)-valley of the conduction (valence) band, $M = m_e + m_h$ is the total exciton mass, and $m_e$ ($m_h$) is the electron (hole) effective mass. $A$ is the crystal area. The electron-hole relative-motion wave function in momentum space $\phi_X(k)$ is determined by the Wannier equation (see the SM for details). Its solution determines the IX energy $E_{gap} - E_B$, where $E_B$ is the IX binding energy and $E_{gap}$ is the band gap.

An interlayer twist in real space generates a relative shift in momentum space ($K_v - K_v$, see Fig. 1c) as well as a spatial modulation of the exciton energy. In all three TBLs, the moiré periodicity can be assumed to be large compared to the IX Bohr radius. Thus, we neglect the variation of the binding energy in the moiré pattern and use a local approximation of the IX moiré potential $V^M(R)$ according to Ref. [11]. In this framework, the IX Hamiltonian reads

$$H = -\frac{\hbar^2}{2M} \Delta_R + V^M(R)$$

and can be diagonalized using a plane-wave expansion with eigenenergies $\varepsilon_{Q,\lambda}$ and eigenstates

$$|Q, \lambda\rangle = \sum_{G_M} c^\lambda_{Q,G_M} |Q - G_M\rangle .$$

The moiré reciprocal lattice vectors $G_M$ are derived as differences of top and bottom layer reciprocal lattice vectors. Therefore, the size of the moiré Brillouin zone (MBZ) scales with the interlayer twist angle. We represent its center and boundary by $\gamma$ and $\kappa$, respectively. We use the above plane-wave expansion, and solve the optical matrix element between the initial moiré exciton state $|Q, \lambda\rangle$ and the final photon state $|q, \sigma\rangle$. Moir excitons can only recombine if the momentum conservation law $Q - q_{\parallel} = K_v - K_v := Q_{1X}$ is fulfilled where $q_{\parallel}$ represents the in-plane component of the photon wavevector. We assume that the twist angle is sufficiently large so that typical photon momenta are still small compared to the MBZ, which in our case is well-justified for twist angles larger than $0.5^\circ$. In this case, we can discard umklapp processes.

In the numerical calculation shown in Fig. 4, we assume the exciton population is thermalized obeying a Boltzmann distribution. To clarify the twist angle dependence, we disentangle the influence of the valley shift in reciprocal space from the energy modulation of moiré potential. First of all, a drastic change in IX lifetimes with the twist angle is expected even in the absence of a moiré potential by just considering the shifted valleys illustrated in Fig. 1c and d. Only excitons within the light cone can decay radiatively. For a TBL with a small twist angle, low-temperatures are favorable to thermally keep as many excitons as possible within a narrow region around the $\Gamma$ point in the excitation picture. On the other hand, in a TBL with a large twist angle, light-matter coupling benefits from long tails in the high-temperature exciton distribution to overcome the large momentum shift $Q_{1X}$. As a result, the temperature dependence of IX lifetimes exhibits opposite behavior in TBLs with small and large twist angles. We therefore predict a crossover between these two regimes around an intermediate twist angle of $\theta = 2^\circ$ as shown in Fig. 4b.
FIG. 4. Temperature and twist angle dependence of calculated IX radiative lifetimes in the absence/presence of a moiré potential and measured temperature dependent IX recombination dynamics. Calculated twist angle dependence of the IX lifetimes shown for various temperatures in the (a) absence and (b) presence of a moiré potential. Panels (c) and (d) show the IX band structure in the absence of a moiré potential at twist angles of $\Theta = 1^\circ$ and $\Theta = 3^\circ$, respectively. Moiré exciton states are classified by momenta from the first MBZ shown in inset of (f). The light cone (orange shaded area) occupies a larger fraction of the MBZ for a TBL with a smaller twist angle. Panels (e)-(f) show the moiré exciton band structure, thermal distribution, and density-of-states contribution for different twist angles at low-temperature. The scale of the symbol size is the same for panel (c,d) and (e,f). Note that at small twist angle the IX bands become flat due to the moiré potential. (g, h) Temperature dependent fast and slow decay components of lifetimes measured near 1350 meV in the TBLs with $\Theta = 1.0 \pm 0.3^\circ$ (2.2 $\pm$ 0.3$^\circ$) from 5 to 50 K (10 to 50 K).

To examine the predicted temperature dependence of IX radiative lifetimes, we compare measurements performed on two TBLs with the caveat that the total lifetime is measured. Figure 4g and h show the temperature dependent two decay times extracted by fitting with a bi-exponential function for the two TBLs with $\Theta = 1^\circ$ and 2.2$^\circ$, respectively. Indeed, we experimentally observed opposite trends in the temperature dependent IX lifetimes in two TBLs. The IX lifetime increased (decreased) at higher temperature in the small (large) twist angle sample. This trend is consistent with the calculation (Fig. 4b) although a much weaker temperature dependence was observed.

We discuss the scope and limitations of our studies. First, we focus on MoSe$_2$/WSe$_2$ TBLs with a relatively small twist angle while previous experiments have investigated the change of exciton resonances over a broader range of twist angle [39–42]. In TBLs with a small twist angle, the thermal distribution of the IX may be sufficient to satisfying the momentum conservation requirements of an indirect optical transition. In practice, phonon-assisted transitions do exist. Such transitions play an increasingly important roles in TBLs with larger twist angle ($\Theta > 5^\circ$). Second, the biexponential decay dynamics are not fully explained. We provide a rate equation analysis for a three-level system involving a dark exciton state in the SM. Such a dark state may originate from an indirect transition involving free carriers in a different valley. Third, our calculations only address the radiative decay rate and our experiments measure the total decay rate. The calculation models an ideal situation where the IX dynamics is determined by the radiative process with unity quantum yield. It addresses the question of how radiative decay can be controlled by the twist angle with and without the presence of an moiré superlattice. The qualitative agreement between the experiments and calculations is noteworthy. We speculate that the non-radiative decay processes either do not depend on the twist angle strongly or depend on the twist angle in a similar way.

In conclusion, our studies represent a first step toward understanding how the twist angle of a vdW heterostruc-
ture can be used to control exciton dynamics. These results provide critical guidance to efforts on searching for exciton condensates where a long IX lifetime is preferred to reach an equilibrium temperature with the lattice. On the other hand, light-emitting devices should be built with TMD TBLs with a small twist angle. A faster radiative lifetime can compete favorably with other non-radiative processes and lead to higher quantum efficiency.

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