Revealing exciton masses and dielectric properties of monolayer semiconductors with high magnetic fields

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In semiconductor physics, many of the essential material parameters relevant for optoelectronics can be experimentally revealed via optical spectroscopy in sufficiently large magnetic fields. For the new class of monolayer transition-metal dichalcogenide semiconductors, this field scale can be substantial—many tens of teslas or more—due to the relatively heavy carrier masses and the very large electron-hole (exciton) binding energies. Here we report circularly-polarized absorption spectroscopy of the monolayer semiconductors MoS$_2$, MoSe$_2$, and WS$_2$ in extremely high magnetic fields up to 91 T. By encapsulating exfoliated monolayers in hexagonal boron nitride, we achieve very high optical quality structures that allow to follow the diamagnetic shifts and valley Zeeman splittings of not only the 1s ground state of the neutral exciton but also its excited 2$s$, 3$s$, ..., $n$s Rydberg states. The energies and diamagnetic shifts provide a direct determination of the effective (reduced) exciton masses and the dielectric properties of these monolayer semiconductors—fundamental material parameters that until now were available only from theoretical calculations. Unexpectedly, the measured exciton masses are significantly heavier than predicted for Mo-based monolayers. Moreover, we also measure other important material properties, including exciton binding energies, exciton radii, and free-particle bandgaps. These results provide essential and quantitative parameters for the rational design of opto-electronic van der Waals heterostructures incorporating 2D semiconductor monolayers.

INTRODUCTION

In their bulk form, the transition-metal dichalcogenide (TMD) materials MoS$_2$, MoSe$_2$, WS$_2$, and WSe$_2$ are indirect-gap semiconductors [1, 2]; however they become direct-gap semiconductors when thinned down to a single monolayer [3, 4]. This phenomenon, together with the remarkable valley-specific optical selection rules that emerge in the atomically-thin limit [5], has galvanized tremendous interest in the underlying properties of this new 2D semiconductor family [6–8]. With a view towards future generations of ultrathin devices based on van der Waals assembly [9] of TMD monolayers, a quantitative understanding of their intrinsic material parameters is of obvious and critical importance. For applications in optoelectronics, properties related to the fundamental electron-hole quasiparticle excitations by light—that is, excitons—are particularly relevant: the exciton’s mass, size, binding energy, oscillator strength, and lifetime are key variables, as are the dielectric screening properties and the free-particle bandgap of the monolayer itself. These material parameters constitute necessary inputs for any rational design and engineering of functional van der Waals heterostructures.

To date, however, many of these fundamental parameters are still assumed from density functional theory calculations [10–12] and have not been experimentally measured. This is particularly true for the exciton masses and the effective dielectric screening lengths in the monolayer TMD semiconductors—essential ingredients for realistic optoelectronic device models. In principle, however, these and other crucial material properties can be directly accessed via optical spectroscopy of excitons in large magnetic fields. As myriad studies over the past several decades have amply demonstrated in III-V, in II-VI, and in various layered semiconductors [13–17], the diamagnetic shifts of the exciton transitions in sufficiently high magnetic fields can directly reveal the exciton’s mass, independent of any model. Moreover, quantitative analysis becomes especially straightforward and increasingly accurate when the less-strongly bound excited states of the exciton (i.e., the optically-allowed 2$s$, 3$s$, ..., $n$s Rydberg states) are also observable, in which case the relevant dielectric properties of the material itself can also be determined.

Until quite recently, the optical quality of TMD monolayers was typically not sufficient to achieve very narrow exciton absorption lines or well-resolved Rydberg exciton states. However, by encapsulating TMD monolayers between atomically-smooth hexagonal boron nitride (hBN) slabs, several groups have shown that the optical quality of TMD monolayers can be dramatically improved to the point where exciton spectral lines approach the narrow homogeneously-broadened limit (1–2 meV) and where excited Rydberg exciton states become clearly visible [18–
Recently, the first magneto-optical studies of Rydberg exciton diamagnetic shifts were performed only recently on high-quality hBN-encapsulated WSe$_2$ monolayers [27]: Using pulsed magnetic fields up to 65 T, the diamagnetic shifts of the ground state (1$s$) and the excited 2$s$, 3$s$, and 4$s$ states of the neutral exciton were measured and used to determine the exciton’s mass, size, and binding energy.

However, the exciton masses and dielectric properties have not been experimentally determined for any of the other members of the monolayer TMD semiconductor family, and general trends have not been established. This represents an especially challenging task for the molybdenum-based monolayers, for which electron, hole, and exciton masses are theoretically predicted to be even heavier than those of their tungsten-based counterparts [10–12], potentially requiring even larger magnetic fields. An experimental determination of these basic material parameters is particularly urgent in view of very recent electrical transport measurements in n-type MoS$_2$ and MoSe$_2$ monolayers that reveal an anomalous and surprisingly large electron mass that exceeds theoretical predictions by factor of two [28, 29]. Whether these unexpectedly heavy electron masses result from interactions in the high-density electron gas, or are instead an unanticipated but intrinsic material property, remains an open and crucial question.

To address these gaps in our current knowledge of monolayer TMD semiconductors, here we present detailed magneto-absorption studies of WS$_2$, MoS$_2$ and MoSe$_2$ monolayers in extremely high magnetic fields up to 91 T and at low temperatures (4 K). Magneto-optical spectroscopy provides an important and complementary approach to transport techniques, by allowing to study material parameters in the limit of zero doping. The excellent optical quality of our hBN-encapsulated monolayers allows to observe and follow the diamagnetic shifts (and also the valley Zeeman splittings) of not only the 1$s$ ground state of the neutral excitons but also their excited 1$s$ Rydberg states. The energies and diamagnetic shifts of the 1$s$ excitons provide a first experimental measure of the exciton’s mass and also the dielectric screening length in these monolayer semiconductors. Remarkably, the exciton masses are heavier than theoretically predicted, particularly for Mo-based monolayers. Moreover, from the data we also determine other important material properties that are relevant for optoelectronic applications, including exciton binding energies, exciton radii, and free-particle bandgaps. These results, summarized in Table I, provide essential and quantitative material parameters that are necessary for the rational design of van der Waals heterostructures incorporating 2D semiconductor monolayers.

**SAMPLES AND EXPERIMENTAL SETUP**

To prepare high optical quality monolayer samples for magneto-absorption studies in pulsed magnetic fields, exfoliated TMD monolayers were sandwiched between slabs of exfoliated hexagonal boron nitride (hBN) using a dry-stamp method [19]. The thicknesses of the hBN slabs were selected to maximize the absorption of light by the exciton resonances in the TMD monolayer [24]. As shown in Fig. 1(a), each van der Waals structure was assembled directly over the 3-4 μm diameter core of a single-mode optical fiber. Crucially, this ensures a rigid drift- and vibration-free alignment of the optical path through the TMD monolayer during the experiment – conditions which can otherwise be experimentally challenging in high-field optical studies of small samples.

The fiber/sample assembly was then mounted in 4 K exchange gas in the tail of a liquid helium cryostat located in the bore of a pulsed magnet. We used both capacitor-driven 65 T pulsed magnets, as well as a unique generator/capacitor-driven magnet capable of ultrahigh fields up to 100 T [30]. Broadband transmission spectroscopy was performed by coupling unpolarized white light from a Xe lamp into the single-mode fiber. After passing through the sample and a thin-film circular polarizer, the transmitted light was retro-reflected back through a separate multimode collection fiber, and was detected using a spectrometer and high-speed CCD camera. Spectra were continuously acquired every 1 ms throughout the magnet pulse. Access to both $\sigma^+$ and $\sigma^-$ circularly polarized transitions (corresponding to interband optical transitions in the $K$ and $K'$ valley of the TMD monolayer, respectively) was achieved by reversing the direction of the magnetic field. A total of four different MoS$_2$, two MoSe$_2$, and two WS$_2$ monolayer structures were studied.

**MONOLAYER WS$_2$**

We first present and discuss the magneto-optical spectra from the WS$_2$ monolayers, where the exciton absorption signals are very strong and the field-induced diamagnetic shifts are large. Moreover, owing to the very large ($\approx 400$ meV) spin-orbit splitting of the valence bands at the $K/K'$ points in tungsten-based TMD monolayers, the excited 1$s$ Rydberg states of the neutral “A” exciton always remain well below the absorption band of the higher-energy “B” exciton, which simplifies the data analysis (as shown later, this is not the case for the molybdenum-based TMD monolayers). For completeness, in this section we also describe the data analysis and modeling procedure.

Signatures of excited Rydberg excitons in monolayer WS$_2$ were first revealed by optical reflection spectroscopy at zero magnetic field by Chernikov et al. [31]. Subse-
FIG. 1. (a) Image of a sample/fiber assembly: An exfoliated TMD monolayer, sandwiched between hBN slabs, is constructed over the 3-4 μm diameter core of a single-mode optical fiber (white circle). The assembly is mounted in helium exchange gas at 4 K in the bore of a pulsed magnet. The diagram depicts the optical selection rules in the K and K′ valleys. (b) Normalized transmission spectra ($T/T_0$) of monolayer WS$_2$ at selected magnetic fields $B=0$, 20, 40, and 60 T. Blue/red curves indicate $\sigma^+$/\(\sigma^-\) circular polarization (optical transitions in the K/K′ valleys, respectively). (c) Intensity map of all the transmission spectra, from $-65$ to $+65$ T. Excellent sample quality allows observation of the 2s, 3s, 4s, and 5s excited Rydberg states of the neutral “A” exciton. (d) Energies of the 1s−5s excitons for both $\sigma^+$ polarizations. (e) Average energy of the $\sigma^+$ transitions for each ns state, $\frac{1}{2}(E_{\sigma^+} + E_{\sigma^-})$, reveals distinct diamagnetic shifts. Solid lines show calculated energies using the Rytova-Keldysh model described in the text. Parameters: $m_\tau = 0.175 m_0$, $r_0 = 3.4$ nm, $\kappa = 4.35$, and $E_\text{gap} = 2.238$ eV. Inset: Expanded plot of the 1s exciton energy, showing its small quadratic diamagnetic shift. (f) The Zeeman splitting of the 1s, 2s, and 3s exciton states ($E_{\sigma^+} - E_{\sigma^-}$); dashed lines depict linear fits.

quently, the diamagnetic shift and valley Zeeman splitting of the “A” exciton ground state ($A:1s$) were measured via polarized magneto-reflection to 65 T by Stier et al. [32]. More recently, charged excitons and also the excited A:2s exciton in monolayer WS$_2$ were studied up to $\sim$30 T by photoluminescence [33, 34]. Crucially, however, in all these field-dependent studies the sample quality was not sufficient to observe highly-excited Rydberg states, and therefore the exciton’s effective (reduced) mass, $m_\tau = m_e m_h/(m_e + m_h)$, could not be experimentally determined. Rather, it was always assumed that $m_\tau \approx 0.15 - 0.16 m_0$ based on leading density-functional theories [10, 11]. Together with the measured diamagnetic shifts, this allowed estimates of the exciton’s size and binding energy [32-34].

Here, using very high-quality WS$_2$ monolayers encapsulated in hBN, we observe the field-induced shifts of the 1s, 2s, 3s, 4s, and 5s states of the neutral “A” exciton up to 65 T. Crucially, these data provide a quantitative measurement of $m_\tau$ in monolayer WS$_2$. Equally importantly, these results also allow a detailed and quantitative comparison with the popular Rytova-Keldysh model that describes the non-hydrogenic electrostatic potential $V(r)$ between an electron and hole in a 2D material, from which the dielectric screening properties, exciton binding energy and size, and free particle bandgap can also be determined.

Figure 1(b) shows normalized transmission spectra, $T/T_0$, at selected magnetic fields $B$ for both $\sigma^+$ circular polarizations (where $T_0$ is a background reference spectrum). At $B=0$ two narrow absorption lines are visible at 2.058 and 2.199 eV, and with increasing field additional
higher-energy and rapidly-shifting features are observed. To most easily visualize these trends, Fig. 1(e) shows an intensity map of all the $T/T_0$ spectra from $-65$ T to $+65$ T. A systematic series of absorption features are clearly resolved, that correspond (as confirmed below) to the $1s$ ground state and the excited $ns$ Rydberg states of the neutral “A” exciton. Their presence and narrow widths attest to the excellent optical quality of the WS$_2$ monolayer that is achieved by hBN encapsulation. We emphasize that the highly excited Rydberg excitons (4$s$, 5$s$) can only be clearly resolved in large $B$. Primarily this is because large magnetic fields increase the exciton’s absorption oscillator strength by providing an additional effective confining potential which “squeezes” the exciton’s reduced mass $\frac{m_{e}}{m_{r}}$ linearly in high fields. As discussed below, in this regime the exciton’s size – which, in turn, typically depends strongly on the dielectric properties of the material and its immediate surroundings [38–40]. The inset of Fig. 1(e) shows that the shift of the most tightly-bound 1s exciton in monolayer WS$_2$ does indeed increase quadratically over the entire 65 T field range. This is expected, because the 1s exciton in this structure has a large Coulomb binding energy ($>150$ meV, as shown below) and remains firmly in this “weak-field” limit even at 65 T (for comparison, the characteristic cyclotron energy $\hbar \omega_c \approx 40$ meV at 65 T if $m_r = 0.2 m_0$).

Conversely, in the opposite limit where $\hbar \omega_c$ greatly exceeds the Coulomb energy (i.e., for strong $B$ fields and/or weakly-bound excitons), the exciton binding energy is negligible compared to the separation between the electron or hole Landau levels (LLs). To a good approximation, optically-allowed interband transitions therefore occur between the linearly-dispersing free-particle LLs in the valence and conduction bands, and the transition energies of the $ns$ exciton states increase roughly linearly with $B$ as $(N + \frac{1}{2})\hbar \omega_c$, ignoring spin effects. Following convention, $N (= 0, 1, 2, ...)$ labels the transition number starting from the lowest (ground) state, and therefore $n \equiv N + 1$. Note that this behavior holds not only for conventional semiconductors but also for monolayer TMD semiconductors which obey the massive Dirac Hamiltonian and therefore have “$k^\parallel$ free-particle” LLs that are pinned to the bottom of the conduction band and top of the valence band in the $K$ and $K'$ valleys, respectively [41, 42] (for additional details see, for example, Ref. [43] or the Supporting Information in Ref. [27]). In other words, the average transition energy of the $ns$ exciton state, $\frac{1}{2}(E_{\sigma^+} + E_{\sigma^-})$, or equivalently the average of the two corresponding transitions in the $K$ and $K'$ valley, increases with a slope that approaches $(N + \frac{1}{2})\hbar \omega_c = (N + \frac{1}{2})\hbar \omega_c m_r$ in the high-field limit (where, as above, $n \equiv N + 1$).

As discussed previously [27], the slope and the separation of the most weakly-bound excitons therefore provide unambiguous and increasingly stringent upper and lower bounds on $m_r$, respectively, in the limit of large $B$. Crucially, this is independent of any other material parameter or model of the electrostatic potential. For monolayer WS$_2$, the data in Fig. 1(e) reveal a high-field slope of the 5$s$ exciton of 2.65 meV/T, which should asymptotically approach (from below) a value of $\frac{9}{2} \frac{\hbar \omega_c}{m_r}$ in the high-field limit. Conversely, the energy separation be-
TABLE I. Experimentally-determined values of the exciton reduced mass \( m_r \), the 1s exciton binding energy \( E_b \), the free-particle bandgap \( E_{\text{gap}} \), the dielectric screening parameters \( r_0 \) and \( \kappa \), and the root-mean-square radius of the 1s exciton \( r_{1s} \). Typical error bars on experimental values of \( E_b \) and \( E_{\text{gap}} \) are \pm 3 meV. Typical error bars on values of \( r_0 \) and \( r_{1s} \) are \pm 0.1 nm. *Values for hBN-encapsulated WSe\(_2\) taken from [27].

| Material       | \( m_r \) (\( m_0 \)) | \( E_b \) (meV) | \( E_{\text{gap}} \) (eV) | \( \kappa \) | \( r_0 \) (nm) | \( r_{1s} \) (nm) |
|----------------|------------------------|----------------|------------------|--------|----------------|----------------|
| hBN | MoS\(_2\) | hBN | 0.275 \pm 0.015 | 221 | 2.160 | 4.45 | 3.4 | 1.2 |
| hBN | MoSe\(_2\) | hBN | 0.350 \pm 0.015 | 231 | 1.874 | 4.3 | 3.9 | 1.1 |
| hBN | WS\(_2\) | hBN | 0.175 \pm 0.007 | 180 | 2.238 | 4.35 | 3.4 | 1.8 |
| hBN | WSe\(_2\) | hBN* | 0.20 \pm 0.01 | 167 | 1.890 | 4.5 | 4.5 | 1.7 |

between the 4s and 5s states, which equals 47 meV at 65 T, should asymptotically approach (from above) a value of \( \hbar \omega_c = \hbar B/m_r \) in the limit of very high fields. From these experimental values alone we can conclude that \( m_r \) lies approximately midway between the lower and upper bounds of 0.160 \( m_0 \) and 0.197 \( m_0 \).

Modeling exciton energies with the Rytova-Keldysh potential

More refined estimates of \( m_r \) are achieved by modeling the magnetic field dependence of all the \( ns \) exciton energies. To this end we numerically solve the eigenvalue (Schrödinger) equation \( H\psi_{ns}(r) = E_{ns}\psi_{ns}(r) \) to find the energies and wavefunctions of the \( ns \) exciton states in an applied magnetic field. For radially-symmetric \( s \)-type exciton states in 2D in a perpendicular magnetic field, \( H = -(\hbar^2/2m_r)\nabla^2 + e^2 B^2 r^2/2m_r + V(r) \), where \( r \) is the relative distance between the electron and hole and \( V(r) \) is a realistic functional form of the electrostatic potential between the electron and hole. Very general and broadly-applicable formulations of \( V(r) \) can be derived for 2D materials based on first principles [38, 44, 45]. Here we adopt the popular “Rytova-Keldysh potential” [46–48] that has been shown to accurately describe this potential in a thin semiconductor slab that is confined between dielectrics with \( \varepsilon_{\text{top}} \) and \( \varepsilon_{\text{bottom}} \), and provide good agreement with measured \( ns \) exciton energies [27, 31]. In the limit of an infinitely thin 2D slab and reasonably large dielectric contrast between the 2D material and the surrounding materials, the Rytova-Keldysh potential can be expressed analytically as

\[
V_{\text{RK}}(r) = -\frac{e^2}{8\varepsilon_0 r_0} \left[ H_0 \left( \frac{\kappa r}{r_0} \right) - Y_0 \left( \frac{\kappa r}{r_0} \right) \right],
\]

where \( H_0 \) and \( Y_0 \) are the Struve function and Bessel function of the second kind. The average dielectric constant of the encapsulating materials is given by \( \kappa = \frac{1}{2}(\varepsilon_{\text{top}} + \varepsilon_{\text{bottom}}) \), and the dielectric properties of the 2D layer itself are characterized by its screening length \( r_0 = 2\pi\chi_{2D} \), where \( \chi_{2D} \) is the material’s 2D polarizability. At large electron-hole separations \( r \gg r_0 \), \( V_{\text{RK}}(r) \) scales as \(-1/\kappa r \), similar to a bulk semiconductor. However when \( r \leq r_0 \), \( V_{\text{RK}}(r) \) begins to diverge much more slowly and tends towards \( \log(r/r_0) \). This leads to a spectrum of \( ns \) exciton states with energy separations that deviate markedly from a conventional hydrogen-like Rydberg spectrum, especially for the most tightly-bound 1s and 2s excitons.

Material parameters for monolayer WS\(_2\)

Using \( V_{\text{RK}} \) we model the exciton spectrum shown in Fig. 1(e), where the solid red lines show the calculated energies. As noted above, at large \( B \) the most weakly-bound excitons (4s, 5s) are approaching the “strong-field limit”, where their shifts are determined primarily by \( m_r \) and are virtually independent of the dielectric parameters \( \kappa \) and \( r_0 \). From the fits we determine \( m_r = 0.175 \pm 0.007 m_0 \). Fixing this value of \( m_r \) we then determine the values of \( r_0 \) and \( \kappa \) that best model both the energies and the field-dependent shifts of the more tightly-bound exciton states at lower fields. The influence of these two parameters is not completely independent – both affect the separation between the \( ns \) exciton energy levels. However, while \( \kappa \) affects all the exciton energies (similar to the case of bulk semiconductors), \( r_0 \) influences primarily the lowest (smallest) 1s exciton state and therefore mostly tunes only the calculated 1s-2s energy spacing. This puts significant constraints on the values of these material parameters. For our hBN-encapsulated WS\(_2\) monolayer, we find that \( r_0 = 3.4 \pm 0.1 \) nm and \( \kappa = 4.35 \pm 0.10 \) reproduces the energies and field-dependent shifts of all the experimental data very well, as shown in Fig. 1(e).

As discussed in recent literature [38–40, 44, 45, 49–53], the dielectric environment near a monolayer TMD significantly influences exciton binding energies and the free-particle band gap energy. Such “Coulomb engineering” could be used to tune and laterally modulate the band structure of 2D semiconductors using (patterned) dielectrics, with hBN being an obvious choice of dielectric material. From the data and model shown in Fig. 1(e) we directly determine that for hBN-encapsulated monolayer WS\(_2\) the free-particle bandgap is \( E_{\text{gap}} = 2.238 \pm 0.003 \) eV, and that the binding energy of the 1s exciton ground state is 180 ± 3 meV and its rms radius \( r_{1s} = 1.8 \) nm. These fundamental material parameters, which we antic-
ipate will be of use for the future design of van der Waals heterostructures incorporating hBN and WS$_2$ monolayers, as shown in Table I.

Figure 1(c) also confirms that the 1s:2s:3s ratios of exciton binding energies in hBN-encapsulated WS$_2$ (1:1:25) deviates markedly from the expectations of a purely hydrogenic $-1/r$ potential in 2D (1:5:25) or in 3D (1:5:25), an expected consequence of the non-hydrogenic electrostatic potential that exists in real 2D materials. In fact the measured binding energy ratios correspond more closely to expectations from a 3D hydrogenic potential – a consequence of the relatively large dielectric constant of the encapsulating hBN slabs used here. We note that a suitably modified hydrogenic potential can give analytic solutions and reasonable agreement with the measured exciton energies in hBN-encapsulated WSe$_2$ monolayers [54].

The inferred value of $\kappa$ is in quite reasonable agreement with the reported high-frequency dielectric constant of hBN ($\varepsilon_{\text{hBN}} \approx 4.5$) [55]; however we point out that the use of a fixed $\kappa$ is likely oversimplified, since $\varepsilon_{\text{hBN}}$ is known to vary at energies below $\sim 100$ meV due to optical phonon modes, and therefore the effective $\kappa$ may in fact vary somewhat for different ns exciton states.

Finally, we note that the experimentally-determined exciton mass in monolayer WS$_2$ ($m_e = 0.175 m_0$) is slightly heavier (by $\sim 10\%$) than predicted by recent density functional theory [10–12], and that the monolayer’s screening length $r_0 = 3.4$ nm is about $10\%$ smaller. A discrepancy of similar magnitude was also recently reported for the exciton mass in monolayer WSe$_2$ [27], suggesting that further refinements of existing theories may be warranted. Furthermore, and perhaps more interestingly, as shown below we find that these differences become even more pronounced in the molybdenum-based TMD monolayers MoS$_2$ and MoSe$_2$, where the experimentally-determined exciton masses are significantly heavier than predicted.

**MONOLAYER MoS$_2$**

Following a similar measurement and analysis protocol, we next investigate the high-field magneto-absorption of MoS$_2$ monolayers encapsulated by hBN. MoS$_2$ is arguably the most well-known and archetypal member of the TMD semiconductor family, due to its abundance in the form of the natural mineral molybdenite. Consequently, MoS$_2$ was the first to be thinned to a single monolayer [3, 4, 56], the first to evoince valley-selective optical pumping [57–60], and the first for which the electronic and exciton structure were theoretically calculated [10, 11, 61–67]. Despite these milestones the optical quality of monolayer MoS$_2$ has, until very recently, typically proven to be inferior to its W- and Se-based counterparts, with exciton absorption and PL spectra exhibiting significant inhomogeneous broadening. Nonetheless, magneto-optical studies of the valley Zeeman effect in monolayer MoS$_2$ were first performed via reflectivity to 65 T by Stier et al. [32] and then by Mitioglu et al. [68]; however the much smaller exciton diamagnetic shifts were not measurable due to the limited optical quality of these unprotected and CVD-grown monolayers. Very recently, however, encapsulation of exfoliated MoS$_2$ monolayers by hBN was shown to significantly improve its optical quality [19], to the point where the neutral “A” exciton’s linewidth approached the narrow homogeneously-broadened limit (~2 meV) and – crucially – where excited 2s and 3s exciton Rydberg states were clearly observed in zero-field optical spectra [24]. To our knowledge, however, magneto-optical spectroscopy of the excited exciton states in monolayer MoS$_2$ has not yet been reported, and therefore an experimental determination of the exciton’s mass based on diamagnetic shifts remains unavailable. An important goal of this work is to resolve this issue.

Figure 2(a) shows transmission spectra through an hBN-encapsulated MoS$_2$ monolayer at 0, 25, 50, and 75 T. At zero field, the spectra show the strong absorption resonance of the ground (1s) state of the neutral “A” exciton at 1.939 eV, as well as a broader and weaker absorption $\sim 150$ meV higher in energy that is associated with ground state of the neutral “B” exciton, in line with previous studies and the known spin-orbit splitting of the valence bands at the $K/K'$ points of the MoS$_2$ Brillouin zone [10]. More importantly, just above the “B” exciton an additional narrow absorption feature appears at 2.109 eV, or $\sim 170$ meV above the A:1s state. This new peak was observed recently at zero magnetic field by Robert et al. in reflectivity spectra of hBN-encapsulated MoS$_2$ monolayers [24], where it was tentatively ascribed to the excited A:2s state based on its energy and on its polarization properties in PL excitation measurements. As shown immediately below, using high-magnetic field spectroscopy we confirm the identity of this 2s exciton, and also reveal additional highly excited ns exciton Rydberg states in monolayer MoS$_2$ that can be used to determine several important material parameters, including the exciton mass $m_e$ and dielectric screening length $r_0$.

With increasing magnetic field, all the exciton resonances split and shift as shown in Fig. 2(a), and additional absorption features appear at even higher energies as $|B| \rightarrow 91$ T. Again, these field-dependent trends can be identified on the intensity map shown in Fig. 2(b). Besides the 1s and 2s excitons, the 3s exciton state is also clearly revealed, and a faint 4s exciton state can also be observed. The polarization-resolved $\sigma^\pm$ energies of these exciton states are plotted in Fig. 2(c), while their polarization-averaged energies are shown in Fig. 2(d). As expected for a series of ns excitons, each state exhibits a very distinct diamagnetic shift.

As we did for the previous case of monolayer WS$_2$,
we model and fit the ns exciton energies by numerically solving Schrödinger’s equation using the Rytova-Keldysh potential \( V_{RK}(r) \). Best results (red lines) are obtained using \( m_r = 0.27 \pm 0.01 \) \( m_0 \), \( r_0 = 3.4 \pm 0.1 \) nm, and \( \kappa = 4.4 \pm 0.1 \); these values most closely reproduce the high- and low-field diamagnetic shifts of the ns exciton states, as well as their energy separations. These fits also reveal a free-particle bandgap of hBN-encapsulated MoS\(_2\) monolayers (\( E_{\text{gap}} = 2.161 \pm 0.003 \) eV), as well as the A:1s exciton’s binding energy (222 ± 3 meV).

To demonstrate the reproducibility of the samples and the reliability of our approach, Figures 2(e-h) show data from a different hBN/MoS\(_2\)/hBN structure that was studied to ±65 T. This sample exhibits a less pronounced B:1s exciton absorption and also a slightly stronger A:4s peak, making it easier to track the diamagnetic shifts of the ns exciton Rydberg states. Best fits to the data yield nearly identical values for the material parameters: \( m_r = 0.28 \pm 0.01 \) \( m_0 \), \( r_0 = 3.4 \pm 0.1 \) nm, and \( \kappa = 4.5 \pm 0.1 \), and \( E_{\text{gap}} = 2.158 \pm 0.003 \) eV.

Interestingly, the experimentally-determined value of the exciton’s reduced mass in monolayer MoS\(_2\) (\( m_r/m_0 \approx 0.275 \)) is noticeably heavier than anticipated by density functional theory, where \( m_r/m_0 \approx 0.24 - 0.25 \) was predicted [10, 11]. Although knowledge of \( m_r \) does not allow to determine the electron and hole masses \( m_e \) and \( m_h \) separately, it is noteworthy that our result is consistent with the unexpectedly large electron mass (\( m_e \approx 0.7 \) \( m_0 \)) that was very recently inferred from the temperature dependence of Shubnikov-de Haas oscillations in transport studies of n-type MoS\(_2\) monolayers by Pisoni et al. [28] For example, assuming (from theory [10]) that \( m_h = 0.54 \) \( m_0 \), our measured value of \( m_r \) suggests that \( m_e \approx 0.6 \) \( m_0 \), in reasonable correspondence with these recent transport results, and well in excess of the calculated electron mass [10]. This suggests that a surprisingly heavy electron mass may be an intrinsic material property, and not the result of electron-electron interactions in...
and are known to lie far (∼40 meV) below the optically-allowed exciton states due mainly to the large spin-orbit splitting of the conduction bands, in monolayer MoS$_2$ the conduction band spin-orbit splitting is thought to be much smaller and of opposite sign, such that dark/grey states may actually lie slightly above the bright states [69]. In this case, large magnetic fields could force a crossing between the blue-shifting ($\sigma^-$) branch of the 1s bright exciton and the dark excitons. If these states mix in large $B$, an apparent asymmetric broadening of the $\sigma^-$ polarized bright state may be expected.

Due to this asymmetric broadening and field-dependent lineshape, a very precise and reproducible fitting of the 1s exciton energy is difficult and susceptible to small but systematic deviations that depend on the exact form of the fitting function used. Consequently, we can report only that the measured diamagnetic shift of the 1s exciton is very small, of order 0.1 $\mu$eV/T$^2$. This is consistent with the exciton’s large mass, small radius, and small diamagnetic shift that we determine by modeling the ns exciton states as described above – using $V_{RKK}$ and the material parameters determined above, we calculate that $\sigma_{1s} = 0.12 \mu$eV/T$^2$, which can be in turn used to estimate the A:1s exciton’s rms radius in encapsulated MoS$_2$ monolayers ($r_{1s} = 1.2$ nm).

Fortunately, however, the broadening and asymmetry of the 1s exciton does not preclude a robust determination of the much larger Zeeman splitting, which highlights the second anomalous behavior revealed by the high-field magneto-optical data: The valley Zeeman splitting of the A:1s ground state exciton in hBN-encapsulated MoS$_2$ monolayers is unexpectedly small. As shown in Fig. 3(e) the 1s exciton splits linearly with field, but with a small effective g-factor of only $g_{1s} \approx -3.0$. In contrast, the excited 2s, 3s, and 4s Rydberg excitons all exhibit larger g-factors from −4.4 to −4.9. Note that an anomalously small value of $g$ for only the 1s exciton state is at odds with results from monolayer WS$_2$ (Fig. 1(e)) and from monolayer WSe$_2$ [27], for which all the ns exciton states exhibited very similar Zeeman splittings with $g \approx -4$.

Based on our measurements of multiple hBN/MoS$_2$/hBN structures, we also note that the anomalous Zeeman splitting of the 1s exciton does appear to depend systematically on the overall optical quality of the sample, with our highest-quality structures (samples 1 and 2) showing $g_{1s} \approx -3.0$, while lesser-quality structures that exhibit broader absorption lines and fewer ns states show $g_{1s} = -3.6$ and $-3.8$ (samples 3 and 4, respectively). These trends, though not yet understood, are nonetheless very consistent with previously reported studies: Lower quality unprotected MoS$_2$ monolayers with broad 1s absorption lines exhibited $g_{1s} \sim -4$ [32, 68], while extremely high quality hBN-encapsulated MoS$_2$ monolayers with very narrow exciton linewidths [19] exhibited a very small
$g_{1s} = -1.7$. We tentatively suggest that the small valley splitting of the A:1s exciton in hBN/MoS$_2$/hBN may also arise from the close proximity to and interaction with nearby states, possibly spin- and valley-forbidden dark excitons.

**MONOLAYER MoSe$_2$**

Finally, we perform high-field magneto-absorption of hBN-encapsulated MoSe$_2$ monolayers. Together with WSe$_2$, MoSe$_2$ was the first monolayer TMD semiconductor to be measured in a magnetic field where, in modest fields ($< 10$ T), the Zeeman splitting of the A:1s exciton ground state was observed by polarized PL [73–75]. Similar valley Zeeman splittings were subsequently reported to 65 T on CVD-grown MoSe$_2$ monolayers [68]. However, in all these magneto-optical studies the much smaller exciton diamagnetic shift was not detected, likely due to the limited optical quality of the samples and the (theoretically-predicted) heavier exciton mass [10, 11]. In fact, only very recently was the optical quality of monolayer MoSe$_2$ improved—again by hBN encapsulation—to the point where excited A:2s excitons were observed at zero field, for example by Han et al. [22] and by Horng et al. [23] However, high-field magneto-optical spectroscopy of excited ns excitons has not been reported to date, and consequently an experimental determination of the exciton mass in monolayer MoSe$_2$ is still lacking, along with other fundamental parameters.

Figure 4(a) shows normalized magneto-transmission spectra from a MoSe$_2$ monolayer encapsulated by hBN, at 0, 20, 40, and 60 T. The zero-field spectrum shows a very sharp A:1s exciton ground state at 1.643 eV, indicating excellent optical quality. A broader absorption located ~200 meV higher in energy corresponds to the B:1s exciton, in line with past work [22] and the expected spin-orbit splitting of the valence bands at the $K'/K$ points of the Brillouin zone [10]. A weak absorption feature located at 1.811 eV, just below the B:1s exciton, corresponds closely to a similar weak feature that was reported recently by Han et al. [22], which was tentatively ascribed to the excited A:2s exciton based on reflectivity and upconversion measurements. This means that even-higher A:3s and A:4s Rydberg states in monolayer MoSe$_2$ directly overlap with the broad absorption of the B:1s exciton, making their presence difficult to detect, at least at zero applied field.

With increasing field to 65 T, the A:1s exciton shows a very obvious Zeeman splitting [Figs. 4(a,b)]. The weaker state tentatively ascribed to the A:2s exciton at ~1.811 eV is difficult to follow as it shifts and merges with the B:1s exciton. Interestingly, however, at very large fields above 40 T the spectra show two new resonances emerging rapidly from the high-energy side of the broad B:1s absorption. These features can also be readily identified in the detailed fits shown in Fig. 4(c). As before, these field-dependent trends can be seen in the intensity plot of Fig. 4(b). The energies of all the observed absorption features are plotted in Fig. 4(d), and the polarization-averaged energy of each of these states are plotted in Fig. 4(e).

Fitting these data to the numerically-computed ns exciton energies (again using the Rytova-Keldysh potential for a 2D material) strongly suggests that the two highest-energy absorption features are the A:3s and A:4s excited Rydberg excitons. Using a large reduced mass of $m_r = 0.350 \pm 0.015 \ m_0$ and material parameters $r_0 = 3.9 \pm 0.1$ nm and $\kappa = 4.4 \pm 0.1$, we find that the calculated energies and field-dependent shifts of the 1s–4s exciton states (red lines) very accurately match the measured energy separations and field-dependent diamagnetic shifts of the experimental data. In particular the very small quadratic diamagnetic shift of the A:1s exciton ($\sigma_{1s} = 0.07 \ \mu$eV/T$^2$) is captured very well, from which we also determine its small rms radius, $r_{1s} = 1.1$ nm. In addition, the model also directly reveals the binding energy of the A:1s exciton (231 ± 3 meV), and the free-particle bandgap in hBN-encapsulated MoSe$_2$ monolayers ($E_{gap} = 1.874 \pm 0.003$ eV).

Similar to the case of monolayer MoS$_2$ discussed above, the exciton mass that we measure in monolayer MoSe$_2$ ($m_e = 0.35 m_0$) is substantially larger than anticipated by available density-functional theories, which predict $m_e \approx 0.29 m_0$ [10, 11]. Again we note that the large measured value of $m_r$ is in fact qualitatively consistent with the unexpectedly large electron mass, $m_e \approx 0.8 m_0$, that was recently suggested by transport studies of n-type MoSe$_2$ monolayers by Larentis et al. [29] Assuming $m_0 = 0.6 m_0$ from theory [10], we note that our value of $m_e$ also suggests a surprisingly heavy $m_e \approx 0.84 m_0$ in monolayer MoSe$_2$. Similar to the case of monolayer MoS$_2$, this suggests that the unexpectedly large $m_e$ may result not from interactions with other electrons, but may be an intrinsic material property of MoSe$_2$ monolayers.

The spectra also reveal approximately similar Zeeman splittings for all the measurable exciton states in monolayer MoSe$_2$ (see Fig. 4(f)). For the 1s ground state, we find $g_{1s} = -4.3$, consistent with previous reports [68, 73–75], while for the 3s and 4s excited states, we find somewhat larger values of about −4.9.

Owing to the excellent optical quality of the hBN/MoSe$_2$/hBN structures it was also possible to observe and track the excited 2s Rydberg state of the higher-energy “B” exciton. Figure 5 shows that the B:2s absorption line is visible about 167 meV above the B:1s exciton, and therefore the 1s–2s energy separation is very similar to that observed for the “A” exciton. In magnetic field the B:2s exciton evinces a strong valley Zeeman splitting with effective g-factor $g \approx -4.9$, as well as a clearly discernable quadratic diamagnetic shift of 1.3 $\mu$eV/T$^2$ that is comparable to the value calculated for
the A:2s state (see Fig. 4). This suggests similar effective masses for the “A” and “B” excitons, which contradicts general expectations that “B” excitons have larger mass [10]; however as discussed in detail above the actual mass of the “A” exciton significantly exceeds predicted values. Clearly the effective mass analysis deserves further work in both experiment and theory in the future in the high quality and tunable samples now available.

SUMMARY

Magneto-absorption spectroscopy of high quality hBN-encapsulated WS₂, MoS₂, and MoSe₂ monolayers allows to resolve and follow the field-dependent shifts and splittings of not only the 1s (ground state) excitons, but also the excited ns Rydberg excitons. Crucially, this permits a detailed analysis and fitting of the data to experimentally determine, for the first time, a number of essential material parameters for monolayer TMD semiconductors including the exciton’s reduced mass $m_r$, the binding energies and rms radii of the various ns exciton states, the free-particle bandgap $E_{gap}$, and the monolayer’s dielectric screening length $r_0$. These fundamental parameters are listed in Table I. It is anticipated that these experimentally-determined material parameters will prove useful for the rational design and engineering of future optoelectronic van der Waals heterostruc-

FIG. 4. (a) Normalized transmission spectra through an hBN-encapsulated MoSe₂ monolayer at selected magnetic fields, for both $\sigma^+$ polarizations. The inset shows a 5x magnified spectrum of the higher energy features at 0 T. (b) Intensity map showing all the spectra from −65 to +65 T. Excited ns Rydberg states of the neutral “A” exciton overlap with and emerge from the broader absorption at 1.85 eV that is due to the “B” exciton ground state. (c) Examples of two-Gaussian fits to the broad feature near 1.85 eV in $\sigma^-$ (upper panel) and $\sigma^+$ (lower panel) polarization at 65 T. In each panel, the two overlapping absorption peaks correspond to the B:1s exciton (wide blue curve) and the A:3s exciton (narrow green curve). The A:4s state is also visible at ~1.9 eV. (d) Measured exciton energies for both $\sigma^\pm$ polarizations. (e) The average energies of the $\sigma^\pm$ transitions. Red lines show the modeled exciton energies (see text). Parameters: $m_1 = 0.35$, $r_0 = 3.9$ nm, $\kappa = 4.4$, and $E_{gap} = 1.874$ eV. The states that emerge at high magnetic fields from the B:1s exciton absorption correspond very well to the A:3s and A:4s Rydberg states. Inset: Expanded plot of the 1s exciton energy, showing its very small quadratic diamagnetic shift. (f) The Zeeman splitting of the A:1s, A:3s, and A:4s exciton states; dashed lines show linear fits.
FIG. 5. (a) Normalized intensity map of the field-dependent transmission spectra through monolayer MoSe2 in the energy range around the excited B:2s exciton. (b) Energies of the $\sigma^+$ polarized B:2s exciton, and their averaged value (black symbols). The black line is a quadratic fit, indicating a diamagnetic shift coefficient $1.3\ \mu$eV/T² for the B:2s exciton. (c) The valley Zeeman splitting of the B:1s and B:2s exciton states; dashed lines show linear fits.

structures that incorporate TMD monolayers and hBN.

It is noteworthy that the measured masses are consistently larger than anticipated by density-functional theories, with the discrepancy being only moderate in tungsten-based TMD monolayers (∼10% difference), but larger for the case of MoS2 and MoSe2 (∼15% and ∼20% difference, respectively). In this context it is also noteworthy that two very recent transport studies [28, 29] have also revealed unexpectedly heavy electron masses in n-type MoS2 and MoSe2 monolayers. This suggests that a key ingredient is missing in current DFT calculations. The mass increase revealed by our accurate measurements could for instance be explained by an efficient electron-phonon polaron coupling [76–78]. The possible role of interface polarons in TMD/hBN structures should also be investigated [79].

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