Many-body simulation of two-dimensional electronic spectroscopy of excitons and trions in monolayer transition metal dichalcogenides

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Indications of coherently interacting excitons and trions in doped transition metal dichalcogenides have been measured as quantum beats in two-dimensional electronic spectroscopy, but the microscopic principles underlying the optical signals of exciton-trion coherence remain to be clarified. Here we present calculations of two-dimensional spectra of such monolayers based on a microscopic many-body formalism. We use a parameterized band structure and a static model dielectric function, although a full ab initio implementation of our formalism is possible in principle. Our simulated spectra are in excellent agreement with experiments, including the quantum beats, while revealing the interplay between excitons and trions in molybdenum- and tungsten-based transition metal dichalcogenides. Quantum beats are confirmed to unambiguously reflect the exciton-trion coherence time in molybdenum compounds, but are shown to provide a lower bound to the coherence time for tungsten analogues due to a destructive interference from coexisting singlet and triplet trions.
tomically thin materials exhibit unique physical phenomena emerging from extreme dimensional constraints, which add to their attractiveness as functional components in ultrathin electronics and optoelectronics. Of particular recent interest are monolayer transition metal dichalcogenides (TMDCs), compounds of type $MX_2$, where $M$ is a transition metal and $X$ represents a chalcogen atom. Monolayer TMDCs are direct bandgap semiconducting analogs of graphene in which charge and spin excitons and associated negatively charged trions (the lower spin $A'$ points, derived from $K$ and $K'$ points of the hexagonal Brillouin zone) are formed. Singlet trions are intervalley in MoX$_2$, bie excitons, and potentially Fermi polarons at large doping.

Excitons are known to follow a non-hydrogenic Rydberg series and form in momentum valleys centered at the (inequivalent) $K$ and $K'$ points of the hexagonal Brillouin zone with wavefunctions primarily composed of transition metal $d$ orbitals. Such states exhibit robust valley and spin coherence due to the sizable spin–orbit coupling. In addition, inversion symmetry breaking results in valley-dependent optical selection rules. In particular, circularly polarized light has been shown to allow for valley-selective excitation.

While the steady-state properties of TMDCs have been studied in detail by linear optical techniques, the recent application of time-resolved nonlinear spectroscopy has enabled the study of excited-state dynamics on femtosecond timescales. In particular, two-dimensional electronic spectroscopy (2DES), which has found extensive use in the study of molecular assemblies, has been applied to TMDCs only quite recently.

2DES is a four-wave mixing technique that improves over two-pulse pump-probe spectroscopy in its ability to map out the full third-order optical susceptibility of a sample by correlating excitation and probe detection frequencies. Through this approach, indications have been applied to TMDCs to focus on the interpretation of experiments that allow for valley-selective excitation.

Despite recent progress, employing first-principles techniques capable of simulating the nonlinear optical susceptibilities of condensed-phase materials has remained challenging, in particular for the full set of four-wave mixing signals contained in 2DES. This is in stark contrast to linear spectroscopy, where time-dependent density functional theory and the Bethe–Salpeter equation both predict accurate spectra, including excitonic effects. Simulating nonlinear spectroscopic signals of trions in atomically thin materials presents further challenges due to the larger trion Hilbert space and the dense Brillouin zone sampling required to resolve the dielectric function.

Here, we present a many-body computational framework for the simulation of 2DES and apply it to the coherent interaction of trions and excitons in monolayer TMDCs. Although the approach can be straightforwardly implemented in a fully first-principles manner, here we use a parameterization of the low-energy band structure and a model dielectric function, both of which could be obtained from a calculation using the GW approximation. The present work builds on an extension of the Bethe–Salpeter equation to simulate linear spectra of three-body excitonic complexes, combined with a Brillouin zone truncation scheme previously applied to excitons. We find our simulations to accurately reproduce experimental 2D spectra, including the quantum beats observed at the cross-peak locations, allowing us to study the underlying coherent phenomena at a microscopic level. For molybdenum-based TMDCs, quantum beats are confirmed to accurately reflect the exciton–trion coherence time. In contrast, they are shown to provide a lower bound to the coherence time for tungsten analogs due to a destructive interference from coexisting singlet and triplet trions.

Results

Excitons and trions in TMDCs.

Recent interest in TMDCs has mostly focused on compounds based on molybdenum and tungsten as transition metals, and sulfur and selenium as chalcogens. Across these compounds, the quasiparticle band structure is particularly distinct for molybdenum-based (MoX$_2$) and tungsten-based (WX$_2$) TMDCs. This is illustrated in Fig. 1, showing a schematic of the band structures near the $K$ and $K'$ points, highlighting the spin–orbit splitting of the conduction bands. The splitting of the valence bands is an order of magnitude larger than that of the conduction bands, and results in two distinct absorptive transitions observable in the exciton spectrum. We restrict ourselves to the lowest-energy transition (referred to as $A$ exciton) and its associated negatively charged trion complexes to focus on the interpretation of experiments that.

![Fig. 1](https://example.com/fig1.png)
energy selectively excite this transition, although noting that a
generalization to the other transition (B exciton) is straightforward.
We furthermore consider helicity-selective excitation in the K valley; identical results would be obtained for the K’ valley
upon flipping the spins of the involved quasiparticles. As is well
known, the combination of energy and helicity selectivity to
probe A excitons in the K valley effectively corresponds to spin-
selective excitation, since the involved quasiparticles are con-
strained to a well-defined spin (spin-up, following the convention
of Fig. 1).

Negatively charged trions, consisting of two conduction band
electrons interacting with one hole in the valence band, are
commonly characterized based on the spin of the two electrons,
leading to singlet or triplet trions when the spins are opposite or
equal, respectively. In TMDCs, the combination of valley and
spin selectivity implies selection rules for trions at low
temperatures (with the thermal energy smaller than the conduction
band splitting). The behavior is illustrated in Fig. 1, which
considers selective excitation of the A transition in the K valley,
creating an electron–hole pair in addition to an initial one-
electron state. At low temperatures, the initial electron is relaxed
in the conduction band minimum of either the spin-down state in the
K’ valley or the spin-up state in the K valley. As a result, the
controlling interband trions have singlet spin, whereas intravalley trions have triplet spin. It is easily verified that the
opposite relation holds for WS$_2$. We note that the excited
electrons have identical valley and spin states only for the triplet
trion in MoS$_2$, and (repulsive) exchange interactions between
conduction band electrons are therefore expected to be strongest
in this case.

Since the many-body Hamiltonian conserves momentum, the trion
states can be expressed as

$$|\Psi^\alpha(m)| = \sum_{c_1, c_2, v} \sum_{k_1, k_2} C_{c_1, c_2, v}^{\alpha} (k_1, k_2, \mathbf{Q}) a_{c_2, k_1}^\dagger a_{c_1, k_2}^\dagger |0\rangle,$$

(1)

where $c_1$, $c_2$, and $v$ label the conduction and valence bands
(including spin) and with $\mathbf{Q}$ as the momentum of the initial
conduction band electron. In our simulation, details of which can
be found in Supplementary Methods, the band structure is
described by a parameterized two-band model$^{11,37,38}$, motivated
by prior work showing negligible differences in optical properties
compared to a more sophisticated three-band analog$^{11,38}$. The
trion states are calculated by configuration interaction using a
many-body Hamiltonian containing a screened Coulomb cou-
pling term, as done in previous extensions of the Bethe–Salpeter
equation to three-particle complexes$^{37,39,40}$. The screened Coulomb
interaction is approximated as orbital-independent and
isotropic, using a model dielectric function, $W(\mathbf{q}) = 2\pi\varepsilon_0 \varepsilon(q)$ with $\varepsilon(q) = 1 + 2\pi\chi_{2D}q^2$, where $\chi_{2D}$ is the material-dependent two-
dimensional polarizability$^{43,41,42}$. For two-dimensional materi-
als, a very dense sampling of the Brillouin zone is required for
convergence$^{35}$; however, such a dense sampling makes the trion
Hilbert space prohibitively large. To overcome this obstacle, we
use a uniform $N \times N$ Monkhorst–Pack mesh with a cut-off
radius around the K and K’ points, denoted $k_0$. Employed
previously by Qiu et al.$^{35}$ for excitons, this truncation scheme
utilizes the valley confinement of low-energy excited states, and
results in two convergence parameters, $N$ and $k_0$.

We first consider the exciton and trion binding energies predicted by this approach. The results are summarized in
Table 1, while details are presented in Supplementary Figs. 1 and
2. The exciton binding energies are found to rapidly converge
with $k_0$, with near convergence reached already for $k_0 = 0.10$ (in
units of the inverse lattice constant, $2\pi/a$ (The inverse lattice
constants for MoS$_2$, WS$_2$, MoSe$_2$, and WSe$_2$ are 1.97, 1.96, 1.90,
and 1.90 Å$^{-1}$, respectively)). However, convergence with $N$ is
very slow, with $N$ ranging from a few tens to a few hundred.
Extrapolation of our results to $N = \infty$ yields exciton binding
energies in reasonable agreement with those obtained in a
numerically exact diffusion Monte Carlo study of the closely
related real-space exciton problem$^{43}$, with 0.53 eV (vs. 0.55 eV)
for MoS$_2$, 0.50 eV (0.52 eV) for WS$_2$, 0.46 eV (0.51 eV) for MoSe$_2$, and
0.45 eV (0.47 eV) for WSe$_2$. In contrast, the trion binding
energies depend only weakly on $N$, suggesting a cancellation
of sampling errors between the total exciton and trion energies,
while a modest dependence on $k_0$ is found. For MoS$_2$ and MoSe$_2$, our model predicts singlet trion binding energies of 31 and
27 meV, respectively, whereas the triplet trion is found to be
unbound as a result of the repulsive interactions between
conduction band electrons. These interactions are negligible for
tungsten-based TMDCs, where we find bound singlet and triplet
trions with virtually identical binding energies of 40 and 37 meV
for WS$_2$ and WSe$_2$, respectively. We note, however, that modest
energetic splitting between these states$^{44–47}$ is in principle
possible due to exchange interactions involving conduction and
valence band electrons not considered in our model. The
agreement with diffusion Monte Carlo results (singlet trion
binding energies of 34 meV for both for MoS$_2$ and WS$_2$, 28 meV
for MoSe$_2$, and 30 meV for WSe$_2$)$^{43}$ is again reasonable.

### Linear absorption and doping dependence.

Figure 2a presents zero-temperature exciton and trion linear absorption spectra for MoS$_2$, evaluated via

$$S(\omega) = \frac{2\pi}{\hbar} \sum_{\alpha} \left| \langle \Psi^\alpha | \mathbf{V} | \Psi^\alpha \rangle \right|^2 \Gamma(E^\alpha - E^\beta - \hbar \omega).$$

Here, $V = (eA/m_c) \mathbf{\lambda} \cdot \mathbf{p}$ is the light–matter interaction, where $A$ is the vector potential, $e$ and $m$ are the electron charge and mass, $c$ is the speed of light, $\mathbf{p}$ is the momentum operator, and $\mathbf{\lambda}$ is the polarization of the optical field. Here we use circular polarization that selectively excites carriers in the K valley. For the exciton spectrum, the sum is over all eigenstates of the electron–hole Bethe–Salpeter equation, whereas the initial state, labeled “i,” is the Fermi vacuum. For the trion spectrum, the sum is over all eigenstates of the two-electron-one-hole Bethe–Salpeter equation, and the initial state has one excess electron at the minimum of the conduction band, as discussed above. Physically, this implies that the absorption event occurs such that an excess electron (i.e., due to negative doping) resides within the coherence length of the optically created electron–hole pair. For singlet (triplet) trions, this electron has spin down (up) and momentum $\mathbf{Q}$ at the K’ (K) point; see Fig. 1. Note that the optical selection rules involved in exciton and trion absorption are otherwise fully identical (in terms of momenta, spin, and valley degrees of freedom). The function $\Gamma$, containing the excited-state lifetime and other line-
shape broadening effects, is taken to be a Lorentzian with a width
of 4 meV. Shown in Fig. 2a are results for $N = 80$ and $k_0 = 0.10$, while spectra resulting from different convergence parameters are shown in Fig. 2b and in Supplementary Fig. 3.

### Table 1: Exciton and trion binding energies predicted by our model

| Exciton (eV) | Singlet X (meV) | Triplet X (meV) |
|------------|----------------|----------------|
| MoS$_2$    | 0.53 (0.55)    | 31 (34)        | Unbound        |
| WS$_2$     | 0.50 (0.52)    | 40 (34)        | 40             |
| MoSe$_2$   | 0.46 (0.51)    | 27 (28)        | Unbound        |
| WSe$_2$    | 0.45 (0.47)    | 37 (30)        | 37             |

Shown are extrapolations of our calculated data to $N = \infty$. Numbers within parentheses are exact results from ref. 43. Note that the results shown here do not include repulsive interactions between conduction and valence band electrons (see text).
singlet trion state, these wavefunctions confirm that the entire Rydberg series is reproduced by the trion calculations, including the broken degeneracy between 2s and 2p excitons (the finite oscillator strength observed for the latter is the result of limited sampling, and disappears with increasing N). We conclude that the bound trion state and such exciton resonances share a common ground state, corresponding to a single excess electron at the conduction band minimum. This common ground state suggests that a coherent exciton–trion cross-peak should be observable in 2DES, which we turn to next, after briefly discussing the role of electron doping.

While the density of Brillouin zone sampling serves as a convergence parameter, it also provides a proxy to study the doping dependence. Our k-space calculations effectively involve a real-space periodic lattice with $N \times N$ unit cells over which a single excess electron is distributed in the initial state. Hence, with increasing $N$ the electron doping density decreases. This is borne out in Fig. 2b where we show singlet trion absorption for varying $N$, which shows an intensity redistribution from trion-to-exciton with increasing sampling resolution. This behavior is quantified in terms of the effective doping density in Fig. 2c, showing a linear dependence of the trion-to-exciton peak intensity ratio to the electron doping density. We note that the simplified electronic structure used here (two bands and a static, model dielectric function) combined with the Brillouin zone truncation scheme enables us to study convergence behavior and low doping densities beyond that achievable by a fully first-principles approach and full Brillouin zone sampling.

**Exciton–trion coherence and spectral quantum beats.** We next turn our attention to 2DES, through which the coherent and incoherent dynamics of excited states can be monitored. In this technique, details of which can be found elsewhere, a material interacts with four ultrashort laser pulses, which can be grouped into an initial “excitation” pair and a subsequent “detection” pair, and the resulting signal is commonly presented as an excitation–detection correlation spectrum for each time delay between the two pulse pairs. Different combinations of pulse interactions result in different spectral signals. In our aim to interpret recent experiments on TMDCs, we specifically focus on the non-rephasing stimulated emission signal,

$$S(\omega_1, \tau_2, \omega_3) = \sum_{\alpha,\beta} \left| \langle \Psi_\alpha | V | \Psi_\beta \rangle \right|^2 \left| \langle \Psi_\beta | V | \Psi_\alpha \rangle \right|^2 \times e^{-i[(\omega_3 - \omega_3)\tau_2]} \Gamma^* (E^\alpha - E^\alpha - i\omega_3) \Gamma (E^\beta - E^\beta - i\omega_3).$$

(3)

Here, $\omega_1$ and $\omega_3$ are the excitation and detection energies, respectively, and $\tau_2$ is the time delay. The complex lineshape function is given by $\Gamma(\omega) = 1/(\omega - \sigma)$, with $\sigma$ as the linebroadening parameter. The excitation energy difference between excited states $\alpha$ and $\beta$ is given by $\omega_{\alpha\beta} = (E_\alpha - E_\beta)/h$ and $\gamma_{\alpha\beta}$ represents the associated decoherence rate. The most important mechanistic origin of decoherence is believed to be the scattering of quasiparticles with lattice phonons, and a microscopic investigation of this phenomenon is an interesting topic for future research, albeit beyond the scope of the present study. The damped oscillation as a function of the time delay (quantum beat) contained in the exponential is mapped onto the 2DES signal weighted by the product of transition matrix elements between the excited states and a common initial state $\Psi_i$. In particular, excited states that do not share a common initial state, as might arise in inhomogeneous samples, do not show coherent cross-peaks in 2DES.

Recently, Hao et al. recorded time-dependent oscillatory signals in 2DES of electron-doped MoSe$_2$ monolayers at 20 K.
indicating the phenomenological exciton dashed). For WSe₂, results are shown for fully degenerate singlet and triplet trions (solid), and for which the triplet trion is blue-shifted by 7 meV as a result of exchange interactions (dashed). Shown in all cases are the real (absorptive) part of the complex signal

yielding indications of coherent interactions between the bound trion and the 1s exciton, and the observed quantum beat decay suggested an associated dephasing time of \( \gamma^{-1}_{X-X^\pm} = 250 \, \text{fs} \). However, a reliable determination of the exciton–trion coherence time requires detailed knowledge of how such quantum beats are affected by possible interfering oscillatory signals. Our many-body formalism, in its ability to simulate 2DES, allows us to address this in a straightforward manner, while offering the prospect of microscopically investigating the decoherence mechanisms. For now we resort to a phenomenological treatment of the latter, and study the 2DES of TMDCs using MoSe₂ and WSe₂ as representative examples. In Fig. 3a, we show the sum of the singlet and triplet 2D spectrum for MoSe₂ resulting from Eq. (3) at zero time delay and with co-circularly polarized pulses, obtained for the same convergence parameters as in Fig. 2a. The impulsive signal is multiplied by a Gaussian laser spectrum centered at the bound trion state and with a standard deviation of 17 meV, accounting for the limited laser bandwidth affecting the experimental measurements. The agreement with the 2DES measurements by Hao et al is excellent, with the spectrum showing four peaks in a square arrangement, resulting from two optical transitions readily identified with the bound trion and the 1s exciton.

According to Eq. (3), the quantum beats due to the exciton–trion coherence are mapped onto the cross-peaks corresponding to trion excitation and exciton detection, and vice versa. Indeed, these spectral locations were employed in the quantum beat measurements by Hao et al. However, as discussed above, the quantum beats only result from pairs of states (\( \alpha \) and \( \beta \)) that are optically coupled to a common initial state, \( \Psi^i \). In Fig. 2a we observed the 1s exciton in all of the trion and exciton calculations, but only its resonance in the singlet trion configuration contributes to exciton–trion quantum beats observed for MoX₂, since only this resonance optically couples to the same initial state as the bound trion (an excess spin-down electron relaxed in the \( K^\prime \) valley). Hence, it is by virtue of the emergence of an exciton resonance in the trion (two-electron-one-hole) Hilbert space, that coherent interactions between excitons and trions arise.

Figure 3b shows the time-dependent signal of the lower (below-diagonal) cross-peak for MoSe₂ resulting from our model while imposing \( \gamma^{-1}_{X-X^\pm} = 250 \, \text{fs} \) (the other cross-peak, shown in Supplementary Fig. 4, in principle exhibits an identical signal except for incoherent contributions from population transfer that are not considered in our simulation). The signal features a pronounced oscillation, consistent with the measurements, with the oscillation period matching the Fourier inverse of the singlet trion binding energy. Consistent with the above discussion, we find this quantum beat to result from the bound singlet trion state coherently interacting with its exciton resonance. A comparison of the associated quantum beat decay with the reference decay function \( e^{-\gamma t} \) shows the destructive interference with auxiliary states to be negligible, such that the exciton–trion coherence time is indeed accurately reflected in this oscillatory signal. This substantiates that quantum dephasing in MoSe₂ induces a measurable coherence decay time of 250 fs, as inferred from the reported 2DES experiments.

For WX₂, both singlet and triplet trions form bound states, and as such both contribute to exciton–trion quantum beats resulting from coherent interactions with their respective exciton resonance. Previous reports have suggested that repulsive exchange interactions between conduction and valence band electrons breaks the degeneracy of the singlet and triplet trions by about 7 meV. Inclusion of such interactions in the interaction kernel of the Bethe–Salpeter equation requires access to the real-space structure of the underlying orbitals, which our level of formalism does not provide. However, such interactions are known to be very local in real space and thus well approximated by a \( k \)-independent contribution to the Bethe–Salpeter equation solution. In our simulation, we are flexible in including or excluding this contribution, thereby modulating the degeneracy of the singlet and triplet trions. If we exclude the interaction, the beating pattern shown in Fig. 3b is very similar to the MoSe₂ quantum beat, apart from a somewhat higher oscillation frequency (consistent with a higher binding energy). Again, the quantum beat decay is found to form a reliable probe of the underlying exciton–trion dephasing time. However, if we include an exchange interaction leading to an energy splitting of 7 meV, the beating signal changes appreciably, as shown in Fig. 3b. The nondegenerate trion states lead to an apparent destructive interference in the total (singlet plus triplet) quantum beat, as a result of which the beat decay occurs considerably faster than the actual dephasing time. Altogether, these results demonstrate that the quantum beats observed at the exciton–trion cross-peak locations in 2DES provide a lower bound to the actual exciton–trion coherence time, and that WX₂ in particular warrants caution because of the presence of two (nearly degenerate) trion species.

**Discussion**

We have presented a many-body formalism for the simulation of time-resolved nonlinear spectroscopy including three-particle excitonic complexes. Although the formalism can be straightforwardly implemented in a first-principles manner, we have here
employed a parameterized two-band model and an isotropic, static dielectric function. Combined with a careful truncation of the Brillouin zone, these choices allowed us to provide highly converged results despite the otherwise high computational cost. In applying this formalism to excitons and trions, we uncover various fundamental properties of these charge carrier complexes that relate to the optoelectronic functionality of TMDCs and provide excellent agreement with recently measured 2DES. As noted before, helicity- and frequency-selective excitation of the A transition in the K valley allows control of the spin state of the optically created electron–hole pair. Consistent with our results, an even more comprehensive spin control can be achieved for bound trion states in MoX₂: helicity-selective excitation at the bound trion transition generates three-body complexes consisting of a spin-up hole, and spin-differing electrons (following the convention from Fig. 1). The resulting state coherently interacts with exciton resonances that optically couple to a shared ground state consisting of an excess spin-down electron relaxed in the K’ valley. In case of WX₂, where both singlet and triplet trions form bound states within near-degenerate transition energies, such selective excitation generates both well-defined spin configurations with ratios dictated by the spins of the doping charges, and each trion state coherently interacts with the exciton resonance with which it shares a one-electron ground state. In real space, such a sharing of a ground state can be thought of as the phot oxected electron–hole pair and the single electron residing within each others coherent domain. This is automatically fulfilled in theoretical models based on Bloch states, representative of pristine, extended crystals with translational symmetry, such as employed here. Nevertheless, actual materials are characterized by a certain degree of impurities and scattering with phonons, which break this symmetry and limits the size of coherent domains. The level of theory employed here in principle allows sufficient flexibility to include electron–phonon couplings parameterized against first-principles calculated electron–phonon coupling strengths, for example, by means of a semiconductor Bloch equation approach or Heine–Allen–Cardona approach, or perturbatively at the level of the Boltzmann transport equation. This would allow to unravel the microscopic origin of electronic decoherence and relaxation.

Methods
Many-body spectral calculations. The theoretical methodology and parameterization employed in this work are described in detail in Supplementary Methods. Our many-body formalism can in principle be combined with an ab initio treatment of the full band structure of TMDCs. For the results presented here, we instead used the two-band model introduced by Xiao et al., which through parametrizations against first-principles calculations allows to realistically account for the band structure in the K and K’ valleys at arbitrary sampling resolution. The Brillouin zone was discretized using a Monkhorst–Pack grid, while a truncation radius was imposed around the Fermi surface. Excitons and trions are described using the Bethe–Salpeter equation and its generalization to three-body systems. The dielectric screening appearing in the Coulomb interaction term was taken to be of analytical form, \( \epsilon(q) = 1 + 2\pi\alpha q^2 \), with the two-dimensional polarizability parameterized against first-principles calculations. Linear spectra were calculated using Fermi’s Golden Rule, while 2D spectra were obtained through its extension to higher dimensions.

Data availability
Figures 2 and 3 and S1–S4 have associated raw data. All relevant data is available by written request to the authors.

Code availability
The code used for simulations is available by written request to the authors.

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Author contributions
R.T. and T.C.B. conceived the project. R.T. developed the simulation code and performed the calculations. R.T. and T.C.B. interpreted the results and wrote the paper.

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