Spin–flip processes and radiative decay of dark intravalley excitons in transition metal dichalcogenide monolayers

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**Transition metal dichalcogenide monolayers**
- Chemical composition: X-M-X, where M = Mo, W and X = S, Se
- D3h point group symmetry, lack of inversion symmetry
- 3 atoms per unit cell, \( d_{\text{xy}} = 3.14 \text{ Å}, |a| = |a'| = 3.15 - 3.3 \text{ Å} \)
- Semiconductors with a direct gap of 1.5 - 2 eV at K/K points of BZ

**Why TMDC?** Emission of light, 2D transistors, valleytronics

**Excitons in TMDC monolayers**
- Exciton - bound state of an electron & a hole
- Exciton binding energy: 0.5 - 0.8 eV
- Exciton mass \( \approx \) free electron mass
- Exciton radius \( \approx 1 \text{ nm} \)
- There are 16 types of excitons in TMDC: in -K/K point: A-bright, B-bright, 2 dark
- 8 intervalley excitons

The lowest energy A-exciton states in WX₂ compounds are dark

**Excitonic eigenstates in TMDCs**
- Equation of self-consistency for \( P \)
- (or poles of reflectivity):
- Exchange interaction lifts the degeneracy of intervalley dark A-excitons; new states are transversal and longitudinal excitons
- Solution gives energy shifts \( \Omega_{\nu}^{T,L} \)
- broadening of the excitation levels \( \Gamma_{\nu}^{T,L} \):

\[
E_{\nu} \rightarrow E_{\nu} + \Omega_{\nu}^{T,L} - \Omega_{\nu}^{L,L} / 2 \equiv E_{\nu} - (\mu_{\nu}^{T,L})^2 \bar{D}_{\alpha \beta}(q, E_{\nu}) \mu_{\nu}^{T,L}
\]

**Conclusions**
- The intrinsic decay mechanism due to interband spin-flip dipole moment perpendicular to the monolayer plane, gives a rate about 100 - 1000 times smaller than that of bright excitons.
- This mechanism also introduces an energy splitting due to a local field effect, and the whole oscillator strength is contained in the higher-energy component, while the lowest-energy state remains dark and needs an extrinsic spin-flip mechanism for the decay.
- Other mechanisms - Rashba interaction due to perpendicular electric field or Zeeman effect - give negligible decay rate in the case not very strong electric field (0.1 V/Å) and magnetic field (B < 30 T)

**Radiative shifts and decay rates**
- **Transversal exciton:**
  - decay due to mixing with bright exciton
  - the effect is very small, the percentage of mixing \( \propto q^2 \propto \omega^2 / c^2 \)

- **Longitudinal exciton:**
  - decay due to dipole moment parameter \( d_{\nu} \)
  - there is a shift in the exciton \( \sim 10 \text{ meV} \)

\[ \Gamma_{\nu} \approx (200 \text{ fs})^{-1} \]

**Spin-flip processes need mirror symmetry breaking**
\[ \langle c | \hat{L}_+ \hat{s}_- + \hat{L}_- \hat{s}_+ | c + 1 \rangle |c + 1| |z| \psi \rangle \neq 0 \]

- Two mechanisms:
  - static electric field (substrate)
  - optical photons electric field

- Spin-orbit coupling

- Intervalley transition

- Bychkov-Rashba interaction:

\[ \mathcal{K}_{\text{BH}}(k) = \frac{\epsilon_{\text{ex}}}{\epsilon_{\text{ex}} - \epsilon_{\text{in}}} \left( k \cdot \sigma \right) \text{Re} d + (|k \times \sigma|) \text{Im} d \]

- Hamiltonian and coupling to light
- 

\[ H(k) = \begin{bmatrix} E_c + \Delta_c & v k_x + i v k_y & 0 & 0 \\ v k_x & E_c - \Delta_c & E_v - \Delta_v & 0 \\ v k_y & E_v - \Delta_v & E_v + \Delta_v & 0 \\ 0 & 0 & 0 & -i \omega \end{bmatrix} \]

\[ \psi = \begin{bmatrix} \psi_{c,T} \\ \psi_{c,L} \\ \psi_{t} \\ \psi_{t} \end{bmatrix} \]

- Peierls substitution + gauge invariant term
  - static electric field generate Bychkov-Rashba term, mixes spin states, and interact via el-activated.
  - optical electric field flips spin by photon emission: \( E \delta d \)

**Band structure, electronic and optical properties**
- Conduction band at -K/K points is made from dσ-orbitals (m=0), valence band - dπ/dπ-orbitals (m=2/2)
- Heavy metal atoms spin splitting: \( \Delta_c \) - tens of meVs; \( \Delta_v \) - hundreds of meVs
- \( \Delta_c > 0 \) for WX₂; \( \Delta_c < 0 \) for MoX₂; \( \Delta_c > 0 \) for all MX₂
- Opposite spin orientation in -K and K points - spin-valley locking
- In -K/K valleys only left/right circularly polarized light is absorbed - valley-dependent optical selection rules