Foldy-Wouthuysen transformation for gapped Dirac fermions in two-dimensional semiconducting materials and valley excitons under external fields

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In this work, we provide a detailed derivation of Foldy-Wouthuysen (FW) transformation for two-dimensional (2D) gapped Dirac fermions under external fields and apply the formalism to study valley excitons in 2D semiconducting materials. Similar to relativistic quantum few-body problem, the gapped Dirac equation can be transformed into a Schrödinger equation with “relativistic” correction terms. In this 2D materials system, the correction terms can be interpreted as the Berry-curvature effect. The Hamiltonian for a valley exciton in external fields can be written based on the FW transformed Dirac Hamiltonian. Various valley-dependent effects on excitons, such as fine-structure splittings of exciton energy levels, valley-selected exciton transitions, and exciton valley Zeeman effect are discussed within this framework.

I. INTRODUCTION

Two-dimensional (2D) semiconducting materials such as transition metal dichalcogenides (TMDCs) are atomic thin semiconductors known for their potential for future applications in electronic and photonic devices. The valley-dependent electronic structure of 2D materials provides a new degree of freedom to manipulate, and the unique topology of band structure introduces strong electron correlations and thus excitonic effect becomes important. A valley exciton is a Wannier-like exciton whose properties are decided by the additional valley degree of freedom and affected by the band-structure geometry. Various physical phenomena related to valley excitons, such as Berry-curvature induced exciton energy-level splitting, valley-selected optical transition, exciton valley Hall effect, and exciton valley Zeeman effect have been observed experimentally and discussed theoretically. While there are a lot of theoretical works using different methods to study different issues of valley excitons, the connection among different theories and interpretations is not manifest.

One of theoretical issues to study valley excitons is to include external-field interactions to the exciton model. For a Wannier exciton, which consists of an electron and a hole bound by the Coulomb interaction, the system is similar to a hydrogen atom in external fields. The electric-field interaction can be included by the dipole-field interaction and the magnetic-field interaction can be included as the vector fields in the kinetic momentums of the electron and hole. For the valley excitons in 2D materials, the exciton Hamiltonian is constructed by the Bloch-electron wavefunctions solved from diagonalizing a Dirac Hamiltonian or a few-band tight-binding Hamiltonian. However, the Dirac Hamiltonian or tight-binding Hamiltonian with including external-field interactions is much more difficult to solve, such that the exciton Hamiltonian under external field also becomes more difficult to derive. To simplify the problem, approximations are necessary. In fact, a similar problem had been intensively studied in the fields of relativistic few-body physics. A relativistic particle which is described by a three-dimensional Dirac fermion under external fields can be reduced to a nonrelativistic particle with relativistic corrections in low-energy limit by the Foldy-Wouthuysen (FW) transformation. A relativistic few-body problem, such as a real hydrogen atom in external fields, can be studied by solving the nonrelativistic Hamiltonian with including the relativistic corrections. The approximation scheme can achieve extreme accuracy in prediction of energy spectra and fine structures. Following the same strategy, the 2D Dirac fermions can also be reduced to nonrelativistic form by the FW transformation, and the valley-exciton Hamiltonian can be approximated as the Wannier-exciton Hamiltonian with band-geometry corrections. The valley excitons in external fields can then be studied by the corrected exciton Hamiltonian.

Semiclassical methods have been used to study the band-structure correction to the properties of excitons. The Berry curvature effect on excitons in 2D materials has been studied theoretically and observed experimentally. The Berry-curvature effect causes energy-level splitting and anomalous selection rule for valley excitons with nonzero angular momentum. It has been shown that the exciton Hamiltonian can be derived from a FW transformation of 2D gapped Dirac fermions. However, the joint effect of the Berry-curvature effect and external fields has yet to be discussed. We intend to fill this gap by extending the derivation of FW transformation to incorporate both effects for 2D gapped Dirac fermions in external fields.

In the present work, the Bloch electron in 2D materials under external fields is described by a 2D gapped Dirac model, and the FW transformation is used to derive the electron-hole representation of the Dirac fermion.
The FW transformed single-particle Hamiltonian, two-particle interaction, and interband transition are derived. Hamiltonians for valley excitons in external fields, including an in-plane electric field, an in-plane electromagnetic field, and an out-of-plane magnetic field can be written. The formalism is applied to the study of physical properties of valley excitons. Within this theoretical framework, several known valley-dependent excitonic effects including exciton energy-level splittings, valley-selected exciton transitions, and exciton valley Zeeman effect are studied and discussed.

The remainder of the article is organized as follows. In Sec. II we review the 2D gapped Dirac fermion model for the band structure of Bloch electrons with a screened Coulomb interaction. The electromagnetic interaction, electron-hole representation, and exciton states based on the Dirac fermion model are also defined here. In Sec. III the FW transformation for the 2D gapped Dirac fermion model is introduced. The FW transformed single-particle Hamiltonian, two-particle interaction, and interband transition are derived. In Sec. IV the formula derived from the FW transformation are applied to valley excitons in 2D materials. The Hamiltonians for valley excitons in an in-plane electric field, an in-plane electromagnetic field, and an out-of-plane magnetic field are derived, and valley-dependent phenomena are studied. Finally, the summary and some perspectives of this theoretical framework are given in Sec. V. In Appendix A the variational method used to solve exciton eigenenergies and exciton wavefunctions is presented in detail.

II. 2D GAPPEP DIRAC FERMION

Before introducing the FW transformation, we first review the 2D gapped Dirac model and derive the exciton model based on the formulation of the Dirac model. In Sec. II A the many-body Dirac Hamiltonian is introduced in the second quantization formalism. In Sec. IIB the electromagnetic-field interaction in the Dirac model and the formula for calculating optical spectra are given. In Sec. II C the electron-hole representation of the many-body Dirac Hamiltonian is introduced and the exciton state is written in this representation.

A. Many-body electronic Hamiltonian

The many-body electronic Hamiltonian for 2D gapped Dirac fermions can be written as

\[ \hat{H} = \sum_{\tau} \int \hat{\psi}_\tau^\dagger(\mathbf{r}) \hat{h}_\tau(\mathbf{r}) \hat{\psi}_\tau(\mathbf{r}) d^2r + \frac{1}{2} \int V(r_{12}) \hat{\rho}(\mathbf{r}_1) \hat{\rho}(\mathbf{r}_2) d^2r \],

(1)

where \( \hat{\psi}_\tau(\mathbf{r}) \), \( \hat{\psi}_\tau^\dagger(\mathbf{r}) \) are the fermion field operators with \( \tau \) being the valley index, \( \hat{\rho}(\mathbf{r}) = \sum_{\tau} \hat{\psi}_\tau^\dagger(\mathbf{r}) \hat{\psi}_\tau(\mathbf{r}) \) is the density operator, \( \hat{h}_\tau(\mathbf{r}) \) is the single-particle Hamiltonian, and \( V(r_{12}) \) is a 2D screened Coulomb potential with \( r_{12} = |\mathbf{r}_1 - \mathbf{r}_2| \). The single-particle Hamiltonian is given by

\[ \hat{h}_\tau(\mathbf{r}) = v_F \mathbf{p} \cdot \mathbf{\alpha}_\tau + m v_F^2 \beta - q \mathbf{F} \cdot \mathbf{r} \]

\[ = \left( m v_F^2 F_z - q \mathbf{F} \cdot \mathbf{r} \right) v_F (\tau \pi^\tau - i \pi^\nu) \]

(2)

with \( \mathbf{\alpha}_\tau = \tau \sigma_\tau \mathbf{e}_z + \sigma_\nu \mathbf{e}_\nu \), and \( \beta = \sigma_3 \), and \( \sigma_\tau \), \( \sigma_\nu \) being Pauli matrices, \( \mathbf{F} \) an in-plane electric field, \( \mathbf{F} \) the kinetic momentum, \( q \) the charge, \( v_F \) the Fermi velocity, and \( m \) the effective mass of the particle. The effective mass can be connected to a band-gap energy by \( \Delta_0 = 2mv_F^2 \). Note that the band gap \( \Delta_0 \) here is not the same with the observed transport band gap, which also contains the contribution from electron correlations. The kinetic momentum of a Dirac particle in an out-of-plane magnetic field is given by

\[ \mathbf{\pi} = \mathbf{p} - \frac{qB}{2} \mathbf{e}_\perp \times \mathbf{r} \],

(3)

where \( \mathbf{p} = -i \nabla \) is the momentum, \( \mathbf{e}_\perp \) is a unit vector perpendicular to the surface of the 2D system, and \( B \) is the amplitude of the out-of-plane magnetic field.

B. Electromagnetic-field interaction

The electromagnetic-field interaction with the Dirac fermion can be included by extending the kinetic momentum

\[ \mathbf{\pi}^*(t) = \mathbf{\pi} - q \int \hat{A}(\mathbf{k}, t) e^{i \mathbf{k} \cdot \mathbf{r}} \frac{d^2k}{(2\pi)^2} \]

(4)

where \( \hat{A}(\mathbf{k}, t) e^{i \mathbf{k} \cdot \mathbf{r}} \) is the vector potential in an electromagnetic mode with wavevector \( \mathbf{k} \). In the long-wavelength limit, the vector potential can be simplified as

\[ \hat{A}(\mathbf{k}, t) e^{i \mathbf{k} \cdot \mathbf{r}} \approx \hat{A}(\mathbf{k}, t) \left( 1 + i \mathbf{k} \cdot \mathbf{r} + \cdots \right) \approx \hat{A}(\mathbf{k}, t) \]

(5)

Including the electromagnetic-field interaction, the electronic Hamiltonian can be rewritten as

\[ \hat{\mathcal{H}}^*(t) = \hat{\mathcal{H}} - \hat{j} \cdot \hat{\mathcal{A}}(t) \]

(6)

where \( \hat{\mathcal{A}}(t) = \int \hat{A}(\mathbf{k}, t) d^2k/(2\pi)^2 \) is the electromagnetic vector potential and

\[ \hat{j} = q \sum_{\tau} \int \hat{\psi}_\tau^\dagger(\mathbf{r}) \mathbf{u}_\tau \hat{\psi}_\tau(\mathbf{r}) d^2r \]

(7)

is the current operator with \( \mathbf{u}_\tau = v_F \mathbf{\alpha}_\tau \) the velocity matrix. We define \( d\hat{\mathbf{\xi}}(t) = \int_0^t \hat{j}(t') dt' \) as the polarization operator. It can be shown that the polarization operator can be related to the current operator by

\[ \frac{d\hat{\mathbf{\xi}}}{dt} = i \left[ \hat{\mathcal{H}}, \hat{\mathbf{\xi}} \right] = \hat{j} \]

(8)
where the interaction picture is used for the time-dependent fermion field operators. By using a length-gauge transformation, the electromagnetic-field interaction in the electronic Hamiltonian can be rewritten as a dipole-field interaction, and we have

\[
\hat{H}_L(t) = e^{-i\hat{\mathcal{A}}(t)} \left[ \hat{H}_L(t) - i \frac{\partial}{\partial t} \right] e^{i\hat{\mathcal{A}}(t)} + i \frac{\partial}{\partial t} = \hat{\mathcal{H}} - \hat{\boldsymbol{\xi}} \cdot \mathcal{F}(t),
\]

(9)

with \( \mathcal{F} = -\partial \mathcal{A} / \partial t \) being the electromagnetic field. The formula of electromagnetic-field interaction in Eq. (9) is known as the electric-dipole approximation. On the other hand, if the polarization matrix element is difficult to solve, the current matrix element can also be used to calculate the transition probabilities. The current matrix element can be related to the polarization matrix element by using Eq. (8), as

\[
\langle N | \hat{J} | M \rangle = \langle N | \frac{d}{dt} \hat{\xi} | M \rangle = i(E_N - E_M) \langle N | \hat{\xi} | M \rangle,
\]

(10)

with \( |N\rangle \) the \( N \)-th state wavefunction and \( E_N \) the \( N \)-th state eigenenergy. Therefore, the transition probabilities can be related to the current matrix element via the relation \( \xi_{N,M}^\mu = -i j_{N,M}^\mu / (E_N - E_M) \), where \( \xi_{N,M}^\mu = \langle N | \hat{J}^\mu | M \rangle \) is the polarization matrix element and \( j_{N,M}^\mu = \langle N | j^\mu | M \rangle \) is the current matrix element. It is what we will do to solve one-exciton transition probability in Sec. [V] because it is more convenient to find the current matrix element by the FW-transformed formulations.

Based on Fermi’s golden rule, the one-photon transition probability is given by

\[
\Gamma_{1P}(\omega) = 2\pi \sum_{N,M} g_M |\xi_{N,M}^\mu|^2 \delta(\omega - E_N + E_M),
\]

(11)

where \( g_M = \exp(-\beta_0 E_M) / \sum_{M'} \exp(-\beta_0 E_{M'}) \) is the distribution function of the initial state with \( \beta_0 \) the inverse temperature. The two-photon transition probability is given by the Kramers-Heisenberg formula

\[
\Gamma_{2P}(2\omega) = 2\pi \sum_{N,M} g_M |\mathcal{Y}_{N,M}^\mu(\omega)|^2 \delta(2\omega - E_N + E_M),
\]

(12)

where \( \mathcal{Y}_{N,M}^\mu(\omega) = \sum_Q \xi_{N,Q}^\mu \xi_{Q,M}^\mu / (E_Q - E_M - \omega - i\eta) \) is the two-photon transition amplitude with \( \eta \) a line-broadening factor. By using these formulations, the one-photon and two-photon absorption spectra can be studied.

C. Electron-hole representation

The Fourier transformed single-particle Hamiltonian and fermion field operator are defined as \( \hat{h}_r(k) = \int h_r(r) e^{-i\boldsymbol{k} \cdot \boldsymbol{r}} d^3r \), \( \hat{\psi}_r(k) = \int \hat{\psi}_r(r) e^{-i\boldsymbol{k} \cdot \boldsymbol{r}} d^3r \). It can be found that there is an unitary transformation matrix such that

\[
\hat{U}_e(k) \hat{\psi}_r(k) \hat{U}_e^\dagger(k) = \hat{\xi}_r(k) \beta,
\]

(13)

\[
\hat{\psi}_r(k) = \hat{U}_e^\dagger(k) \left( \hat{c}_r(k) \right),
\]

(14)

\[
\hat{\psi}_r^\dagger(k) = \left( \hat{c}_r^\dagger(k) \hat{d}_r(-k) \right) \hat{U}_e(k),
\]

(15)

where \( \hat{\xi}_r(k) \) is the single-particle energy, \( \hat{c}_r^\dagger(k) \), \( \hat{c}_r(k) \) are the electron creation, annihilation operators and \( \hat{d}_r^\dagger(k) \), \( \hat{d}_r(k) \) are the hole creation, annihilation operators. The kinetic part of the many-body Hamiltonian can be transformed as

\[
\hat{\mathcal{H}}_{\text{kinetic}} = \sum_{\tau} \int \hat{\psi}_r^\dagger(k) \hat{h}_r(k) \hat{\psi}_r(k) d^3r
\]

\[
= E_0 + \sum_{\tau} \int \hat{\xi}_r(k) \left[ \hat{c}_r^\dagger(k) \hat{c}_r(k) + \hat{d}_r^\dagger(-k) \hat{d}_r(-k) \right] \frac{d^2k}{(2\pi)^2},
\]

(16)

where \( E_0 \) is the ground-state energy.

The polarization and current operators can be rewritten by integrations in quasi-momentum space as

\[
\hat{\boldsymbol{\xi}} = i q \sum_{\tau} \int \hat{\psi}_r^\dagger(k) \nabla_k \hat{\psi}_r(k) \frac{d^2k}{(2\pi)^2},
\]

(17)

\[
\hat{\boldsymbol{j}} = q \sum_{\tau} \int \hat{\psi}_r^\dagger(k) \boldsymbol{u}_r \hat{\psi}_r(k) \frac{d^2k}{(2\pi)^2}.
\]

(18)

Because the hole can be seen as the electron with negative energy in the present formulation, the electron with charge \( q = -e \) is chosen for the polarization and current operators. The momentum matrix elements are defined by

\[
\left( \hat{\mathcal{P}}_{ee,\tau}(k) \right) \left( \hat{\mathcal{P}}_{eh,\tau}(k) \right) = \hat{U}_e(k) \hat{u}_r \hat{U}_e^\dagger(k),
\]

(19)

and then the current operator can be rewritten as

\[
\hat{\boldsymbol{j}} = -e \sum_{\tau} \int \left[ \hat{c}_r^\dagger(k) \hat{\mathcal{P}}_{ee,\tau}(k) \hat{c}_r(k) + \hat{d}_r^\dagger(-k) \hat{\mathcal{P}}_{eh,\tau}(k) \hat{d}_r(-k) \right] \frac{d^2k}{(2\pi)^2}.
\]

(20)

The dipole-moment matrix elements are defined by

\[
\left( \hat{\mathcal{D}}_{ee,\tau}(k) \right) \left( \hat{\mathcal{D}}_{eh,\tau}(k) \right) = i \nabla_k + \hat{U}_e(k) i \nabla_k \hat{U}_e^\dagger(k).
\]

(21)
and the polarization operator becomes

\[
\hat{\xi} = -e \sum_{\tau} \int \left[ \frac{\mathcal{E}_\tau^\dagger(k) \mathcal{D}_{\text{ee},\tau}(k) \mathcal{E}_\tau(k)}{2\pi^2} + d_{\tau}^\dagger(-k) \mathcal{D}_{\text{ee},\tau}(k) \mathcal{E}_\tau(k) + \frac{d_{\tau}^\dagger(-k) \mathcal{D}_{\text{eh},\tau}(k) \mathcal{E}_\tau(k)}{2\pi^2} \right] d^2k.
\]

By using the electron-hole representation, it is convenient to write the excitonic excited states, and the optical transition amplitudes can also be formulated.

Based on the electron-hole representation, an one-exciton excited state, also known as an exciton, can be written as

\[
|X_{\tau}\rangle = \int \Psi_{X,\tau}(k) \mathcal{E}_\tau^\dagger(k) d^2k |0\rangle,
\]

where the exciton wavefunction \(\Psi_{X,\tau}(k)\) can be solved from the eigenvalue equation

\[
\int \tilde{H}_{X,\tau}(k,k') \Psi_{X,\tau}(k') \frac{d^2k'}{2\pi^2} = E_{X,\tau} \Psi_{X,\tau}(k),
\]

and the exciton Hamiltonian can be derived from

\[
\tilde{H}_{X,\tau}(k,k') = |0\rangle \langle 0| \tilde{d}_{\tau}(-k) \mathcal{E}_\tau(k') \mathcal{E}_\tau^\dagger(k') \tilde{d}_{\tau}(-k') |0\rangle.
\]

The transition between an one-exciton excited state and the ground state is known as the “intra-exciton transition” and the transition amplitude can be calculated in terms of \(\xi_{\tau N}^\mu\) or \(j_{\tau N}^\mu\), where

\[
\xi_{\tau N}^\mu = -e \int \Psi_{X,\tau,\tau N}^\dagger(k) \mathcal{D}_{\text{ee},\tau,\tau N}^\mu(k) \frac{d^2k}{2\pi^2},
\]

and

\[
j_{\tau N}^\mu = -e \int \Psi_{X,\tau,\tau N}^\dagger(k) \mathcal{D}_{\text{eh},\tau,\tau N}^\mu(k) \frac{d^2k}{2\pi^2}.
\]

The transition between different one-exciton excited states is known as the “intra-exciton transition” and the transition amplitudes can be calculated in terms of \(\xi_{\tau N M}^\mu\) or \(j_{\tau N M}^\mu\), where

\[
\xi_{\tau N M}^\mu = -e \int \Psi_{X,\tau,\tau N}^\dagger(k) \mathcal{D}_{\text{ee},\tau,\tau N}^\mu(k) \Psi_{X,\tau,\tau M}^\dagger(k) \frac{d^2k}{2\pi^2},
\]

and

\[
j_{\tau N M}^\mu = -e \int \Psi_{X,\tau,\tau N}^\dagger(k) \mathcal{D}_{\text{eh},\tau,\tau N}^\mu(k) \Psi_{X,\tau,\tau M}^\dagger(k) \frac{d^2k}{2\pi^2}.
\]

with \(\mathcal{D}_{\text{ee},\tau}(k) = \mathcal{D}_{\text{ee},\tau}^\mu(k) - \mathcal{D}_{\text{eh},\tau}^\mu(k)\) and \(\mathcal{D}_{\text{eh},\tau}(k) = \mathcal{D}_{\text{eh},\tau}^\mu(k) - \mathcal{D}_{\text{eh},\tau}^\mu(k)\). The ground-state energy can be assigned as \(E_0 = 0\) and the excited-state energy for an one-exciton excited state is given by \(E_N = E_{X,\tau,\tau N}\). With the relations given above optical spectra involving one-exciton transitions and intra-exciton transitions can be calculated.

### III. FW Transformation

Based on the derivation in Sec. II C, we find that the key to connect the Dirac equation and the exciton Hamiltonian is the unitary transformation matrix \(U(k)\). We need to solve the diagonalization problem in Eq. (13) first to find the electron and hole energies. However, it will be difficult if external fields are included in the Dirac Hamiltonian matrix. One way to solve this problem is to replace the wavevector \(k\) by \(-i\nabla\) in Eq. (13). Namely, \(\xi_{\tau}(k) = h_\tau(-i\nabla) = \xi_{\tau}(r)\). We get

\[
U(-i\nabla) h_\tau(r) U(-i\nabla) = \xi_{\tau}(r) \beta.
\]

Eq. (30) is the basic idea of FW transformation. By a proper choice of the unitary transformation, the analytic formulation of the single-particle Hamiltonian \(\xi_{\tau}(r)\) can be derived. Since \(\xi_{\tau}(r) \beta\) is still a functional of \(-i\nabla\), \(\xi_{\tau}(r)\) is actually the electron Hamiltonian and \(-\xi_{\tau}(r)\) is the hole Hamiltonian.

#### A. Eriksen method

The FW transformation connecting the initial Hamiltonian \(H\) and the transformed Hamiltonian \(H_{\text{FW}}\) can be written as\[\]

\[
H_{\text{FW}} = U_{\text{FW}} \left( H - \frac{i}{\partial t} \right) U_{\text{FW}}^\dagger + \frac{i}{\partial t},
\]

where \(U_{\text{FW}}\) is an unitary operator named as the FW transformation operator. Based on Eriksen’s method[31–32], we assume that the initial Hamiltonian can be divided into

\[
H = \beta mv^2 + \mathcal{E} + \mathcal{O} + \mathcal{O}',
\]

with \(\beta \mathcal{E} = \beta \mathcal{O} = -\mathcal{O} \beta, \beta \mathcal{O}' = -\mathcal{O}' \beta\), where \(\mathcal{E}\) is an even operator and \(\mathcal{O}\) is an odd operator in the Hamiltonian, \(\mathcal{O}'\) is an odd operator of the external interaction of the Hamiltonian. Accordingly, the FW transformation operator up to the order of \(1/m^2\) has the expression[32, 33]

\[
U_{\text{FW}} = \exp \left( \frac{1}{2} \mathcal{S}, \mathcal{S}' \right) \exp \left( \mathcal{S} \right) \exp \left( \mathcal{S}' \right),
\]

with

\[
\mathcal{S} = -i \beta \mathcal{O}/(2mv^2), \quad \mathcal{S}' = -i [\mathcal{O}, \mathcal{G}]/(4m^2v_F^4),
\]

with

\[
\mathcal{G} = \mathcal{E} + \mathcal{O}' - \mathcal{O}/\partial t.
\]

The FW Hamiltonian up to the order of \(1/m^2\) can be written as

\[
H_{\text{FW}} = \beta mv^2 + \mathcal{E} + \mathcal{O}' + \frac{\beta \mathcal{O}^2}{2mv^2} - \frac{[\mathcal{O}, \mathcal{O}]}{8m^2v_F^4}.
\]

Note that the odd operator \(\mathcal{O}'\) is not discussed by cited literatures[31–33]. As we will show lately in Sec. III D, the operator contributes mainly to the interband transition, which is not considered in atomic systems.
B. Single-particle Hamiltonian

In the present case, the correspondences between the single-particle Hamiltonian and the Eriksen’s Hamiltonian are given by

\[ H = \hbar - qr \cdot \mathbf{F}, \quad \mathcal{E} = -qr \cdot (\mathbf{F} + \mathbf{F}), \quad (36) \]

\[ \mathcal{O} = v_F \pi \cdot \alpha_r, \quad \mathcal{O}' = 0. \quad (37) \]

By using \( \pi \times \pi = \iota B \mathbf{e}_1 \) and \( (\alpha \cdot \alpha_r) (\mathbf{b} \cdot \alpha_r) = a \cdot b + \iota q \mathbf{e}_1 \cdot \mathbf{b} \beta \), we find \( \mathcal{O}' = v_F^2 (|\pi|^2 - \beta q B) \), \( [\mathcal{O}, \mathcal{G}] = \iota q v_F (\mathbf{F} + \mathbf{F}) \cdot \alpha_r \), and \( [\mathcal{O}, [\mathcal{O}, \mathcal{G}]] = 2 \tau q v_F^2 \beta e_+ \cdot (\mathbf{F} + \mathbf{F}) \times \pi \). The FW Hamiltonian is given by

\[ H_{FW} = \beta \left[ m v_F^2 + \frac{|\pi|^2}{2m} - \tau q e_+ \cdot (\mathbf{F} + \mathbf{F}) \times \pi \right] \]
\[ - q (\mathbf{F} + \mathbf{F}) \cdot \mathbf{r} + \tau q B \frac{e_+}{2m}. \quad (38) \]

Based on the FW single-particle Hamiltonian, the effective single-particle energy is given by

\[ \varepsilon_{FW,i} = m v_F^2 + \frac{|\pi|^2}{2m} - \tau q e_+ \cdot (\mathbf{F} + \mathbf{F}) \times \pi \]
\[ - q (\mathbf{F} + \mathbf{F}) \cdot \mathbf{r} + \tau q B \frac{e_+}{2m}, \quad (39) \]

where \( i \in \{ e, h \} \), \( q = -e \) for electrons and \( q = e \) for holes, \( \tau_e \) and \( \tau_h \) are valley indices of the effective electron and hole.

C. Two-particle interaction

Now we consider a two-particle Hamiltonian

\[ H = h_1 + h_2 + \mathcal{V}_{12}, \quad (40) \]

where \( \mathcal{V}_{12} \) is a two-particle interaction, and \( h_i = v_F \pi_i \cdot \alpha_r + m v_F^2 \beta_i + q \Phi_i \) is the single-particle Hamiltonian matrix. The Hamiltonian can be divided as

\[ H = \beta_1 m v_F^2 + \beta_2 m v_F^2 + \mathcal{E} + \mathcal{O}_1 + \mathcal{O}_2, \quad (41) \]

\[ \mathcal{E} = q_1 \Phi_1 + q_2 \Phi_2 + \mathcal{V}_{12}, \quad (42) \]

\[ \mathcal{O}_1 = v_F \pi_1 \cdot \alpha_{r_1}, \quad \mathcal{O}_2 = v_F \pi_2 \cdot \alpha_{r_2}. \quad (43) \]

The FW transformed Hamiltonian is then given by

\[ H_{FW} = h_1 + h_2 - \frac{[\mathcal{O}_1, [\mathcal{O}_1, \mathcal{G}]]}{8m^2 v_F^2} - \frac{[\mathcal{O}_2, [\mathcal{O}_2, \mathcal{G}]]}{8m^2 v_F^2} \]
\[ - \frac{[\mathcal{O}_1, [\mathcal{O}_2, \mathcal{G}]] + [\mathcal{O}_2, [\mathcal{O}_1, \mathcal{G}]]}{8m^2 v_F^2}, \quad (44) \]

with \( \mathcal{G} = \mathcal{V}_{12} - \iota \partial / \partial t \). It can be shown \( [\mathcal{O}, \mathcal{G}] = -i v_F \pi \alpha_r \cdot \nabla_i \mathcal{V}_{12}, [\mathcal{O}, [\mathcal{O}, \mathcal{G}]] = -v_F^2 \nabla_i \mathcal{V}_{12} - 2v_F^2 \beta \tau_i \alpha_r \cdot \nabla_i \mathcal{V}_{12} \). and \( [\mathcal{O}_1, [\mathcal{O}_1, \mathcal{G}]] = -v_F^2 (\alpha_{r_1} \cdot \nabla_i \mathcal{V}_{12} (\alpha_{r_1} \cdot \nabla_i) \mathcal{V}_{12}) \) for \( i \neq j \). The FW transformed two-particle interaction is given by

\[ \mathcal{V}_{FW,12} = \mathcal{V}_{12} + \beta_1 \tau_i \frac{e_+ \cdot \nabla_i \mathcal{V}_{12} \times \pi_1}{4m^2 v_F^2} + \frac{\nabla_i^2 \mathcal{V}_{12}}{8m^2 v_F^2} \]
\[ + \frac{\beta_2 \tau_i e_+ \cdot \nabla_i \mathcal{V}_{12} \times \pi_2}{4m^2 v_F^2} + \frac{\nabla_i^2 \mathcal{V}_{12}}{8m^2 v_F^2} \]
\[ + \frac{(\alpha_{r_1} \cdot \nabla_{i_1}) (\alpha_{r_2} \cdot \nabla_{i_2}) \mathcal{V}_{12}}{4m^2 v_F^2}. \quad (45) \]

For 2D materials, the two-particle interaction is assumed to be given by the screened Coulomb interaction

\[ \mathcal{V}_{ij} = q_i q_j \frac{e}{\epsilon^2} V(r_{ij}). \quad (46) \]

The FW transformed screened Coulomb potential is then given by

\[ \mathcal{V}_{FW,ij} = V(r_{ij}) + \tau_i e_+ \cdot \nabla_i V(r_{ij}) \frac{\pi_i}{4m^2 v_F^2} + \frac{\nabla_i^2 V(r_{ij})}{8m^2 v_F^2} \]
\[ + \tau_j e_+ \cdot \nabla_j V(r_{ij}) \frac{\pi_j}{4m^2 v_F^2} + \frac{\nabla_j^2 V(r_{ij})}{8m^2 v_F^2} \quad (47) \]

for \( i, j \in \{ e, h \} \). The FW transformed screened Coulomb potential can be used to describe the electron-electron interaction, the electron-hole interaction, and the hole-hole interaction in 2D materials.

D. Interband transition

Assuming that the contributions from the static electric and magnetic fields to the interband transition can be neglected, the correspondences between electromagnetic-field interaction and Eriksen’s Hamiltonian are given by

\[ H = h^{(0)} - q v_F \pi \cdot \mathcal{A}, \quad \mathcal{E} = 0, \quad \mathcal{O} = v_F p \cdot \alpha_r, \quad (48) \]

\[ \mathcal{O}' = -q v_F \pi \cdot \mathcal{A}. \quad (49) \]

We find \( [\mathcal{O}, [\mathcal{O}, \mathcal{G}]] = 2iq v_F^2 e_+ \cdot \mathcal{A} \times p \beta, \quad [\mathcal{O}, [\mathcal{O}, [\mathcal{O}, \mathcal{G}]]] = -4q v_F^2 (e_+ \cdot \mathcal{A} \times p) (e_+ \cdot \alpha_r \times p) \). The FW transformed Hamiltonian with electromagnetic-field interaction is given by

\[ H_{FW} = h^{(0)}_{FW} - q u_{FW} \cdot \mathcal{A}, \quad (50) \]

where the FW effective velocity matrix is

\[ u_{FW} \cdot \mathcal{A} = v_F \pi \cdot \mathcal{A} - \frac{v_F (e_+ \cdot \mathcal{A} \times p)}{2m^2 v_F^2} \quad (51) \]

By defining the circular-polarized components of variables \( \mathcal{A} = (\mathcal{A}^x \pm i \mathcal{A}^y) / \sqrt{2}, \quad p = (p^x \pm i p^y) / \sqrt{2}, \) and

\[ \alpha^\pm = \frac{1}{\sqrt{2}} (\alpha^x \pm i \alpha^y) = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & \tau \pm 1 \\ \tau \mp 1 & 0 \end{pmatrix}, \quad (52) \]
we can find $\alpha_\perp \cdot \mathbf{A} = \alpha^+ \mathbf{A}^- + \alpha^- \mathbf{A}^+$ and

$$
\left( \mathbf{e}_\perp \cdot \mathbf{p} \right) \left( \mathbf{e}_\perp \cdot \alpha_\perp \times \mathbf{p} \right) = \left[ \alpha^- p^2/2 - \alpha^+ (p^-)^2 \right] \mathbf{A}^+ + \left[ \alpha^+ p^2/2 - \alpha^- (p^+)^2 \right] \mathbf{A}^-.
$$

The FW velocity matrix, $u_{\perp \text{FW}} = (u_{\perp \text{FW}} \pm 1 u_{\perp \text{FW}})/\sqrt{2}$, is given by

$$
u_\perp \text{FW} = \left( 1 - \frac{p^2}{4m^2 v_F^2} \right) v_F \alpha_\perp + \frac{(p^\perp)^2}{2m^2 v_F^2} v_F \alpha_\parallel.
$$

The velocity matrix will be used to derive the selection rule and transition amplitude in Sec. [IV.C]

**IV. APPLICATIONS TO VALLEY EXCITONS**

In this section, we will use the formulation derived from the FW transformation of a gapped Dirac Hamiltonian to study valley excitons in 2D materials. Based on the formulations, the Hamiltonian for a valley exciton in external fields can be written. The valley-exciton Hamiltonian, similar to the Wannier-exciton Hamiltonian, is written as an electron and a hole bound by an attractive Coulomb interaction, except that the band-geometry correction terms are added. The effects of external-field interactions, including electric-field interaction, electromagnetic-field interaction, and magnetic-field interaction, on valley excitons can then be studied.

**A. Valley excitons in electric fields**

An exciton in an electric field ($|\mathbf{F}| \neq 0$) and an electromagnetic field ($|\mathbf{A}| \neq 0$) without magnetic field ($B = 0$) is considered in this section. The effective exciton Hamiltonian derived from the FW transformed Dirac Hamiltonian is given by

$$
\mathcal{H}_X = \delta \Delta + (\varepsilon_{\text{FW},e} + \delta \varepsilon_e) + (\varepsilon_{\text{FW},h} + \delta \varepsilon_h) - V_{\text{FW,eh}}
= \Delta + \frac{|p_e|^2}{2m_e} + \frac{|p_h|^2}{2m_h} - V(r_{eh})
+ \tau_e \mathbf{e}_\perp \cdot \left[ e (\mathbf{F} + \mathbf{F}) - \nabla_e V(r_{eh}) \right] \times \mathbf{p}_e
- \tau_h \mathbf{e}_\perp \cdot \left[ e (\mathbf{F} + \mathbf{F}) - \nabla_h V(r_{eh}) \right] \times \mathbf{p}_h
+ e (r_{e} - r_{h}) \cdot \left( \mathbf{F} + \mathbf{F} \right) - \frac{\nabla_e^2 V(r_{eh})}{8m^2 v_F^2} - \frac{\nabla_h^2 V(r_{eh})}{8m^2 v_F^2},
$$

where $\delta \Delta$ is the electron-correlation modification to the band-gap energy, $\Delta = \delta \Delta + 2m_e v_F^2$ is the band-gap energy, $\delta \varepsilon_e$ and $\delta \varepsilon_h$ are band-asymmetry modifications to the electron and hole energies, $m_e$ and $m_h$ are effective electron mass and effective hole mass, which are defined by

$$
\frac{|p_e|^2}{2m_e} = \frac{|p|^2}{2m} + \delta \varepsilon_e, \quad \frac{|p_h|^2}{2m_h} = \frac{|p|^2}{2m} + \delta \varepsilon_h.
$$

Assuming $\delta \varepsilon_e = -\delta \varepsilon_h$, we can find $m = 2\mu$, with $\mu = m_e m_h/(m_e + m_h)$ the reduced mass. A coordinate transformation to the relative coordinate system is applied

$$
\mathbf{R} = \frac{m_e \mathbf{r}_e + m_h \mathbf{r}_h}{m_X}, \quad \mathbf{r} = \mathbf{r}_e - \mathbf{r}_h, \quad \mathbf{pe} = \frac{m_e}{m_X} \mathbf{P} + \mathbf{p}_e, \quad \mathbf{ph} = \frac{m_h}{m_X} \mathbf{P} - \mathbf{p}_h.
$$

where $m_X = m_e + m_h$ is the exciton mass, $\mathbf{R}$ and $\mathbf{P} = -i \nabla_{\mathbf{R}}$ are the center-of-mass position and momentum, $\mathbf{r}$ and $\mathbf{p}$ are internal-coordinate position and momentum. The exciton Hamiltonian becomes

$$
\mathcal{H}_X = \mathcal{H}_X' + \mathcal{H}_X'' + \mathcal{J}_X,
$$

where

$$
\mathcal{H}_X' = \frac{p^2}{2m_X} + \frac{e\Omega(m_e \mathbf{r}_e - m_h \mathbf{r}_h)}{4m_X} \mathbf{e}_\perp \cdot (\mathbf{F} + \mathbf{F}) \times \mathbf{R}
$$

is the exciton translational Hamiltonian,

$$
\mathcal{H}_X'' = \Delta + \frac{p^2}{2\mu} - V(r) + e \mathbf{r} \cdot (\mathbf{F} + \mathbf{F}) - \frac{\Omega}{4} \nabla^2 V(r)
+ \frac{\Omega(r_e + r_h)}{4} \mathbf{e}_\perp \cdot (e (\mathbf{F} + \mathbf{F}) - \nabla V(r)) \times \mathbf{P}
$$

is the exciton internal Hamiltonian with

$$
\Omega = \frac{1}{m^2 v_F^2} = \frac{1}{4\mu^2 v_F^2}
$$

the Berry curvature, and

$$
\mathcal{J}_X = -\frac{e\Omega(m_e \mathbf{r}_e - m_h \mathbf{r}_h)}{4m_X} \mathbf{e}_\perp \cdot \nabla V(r) \times \mathbf{P}
$$

is the exciton translational-internal coupling. For the exciton internal Hamiltonian, the first four terms describe a Wannier exciton in an electric field, the fifth term is the Darwin interaction, and the last term is the exciton valley-orbit coupling, which resembles 2D version of spin-orbit coupling for atomistic systems. Both the exciton valley-orbit coupling and the Darwin interaction can be considered as the contributions from the Berry-curvature effect to the exciton energy levels of intravalley excitons ($r_e = r_h$).

Based on the translational Hamiltonian in Eq. (60), it is also shown that the Berry-curvature effect contributes to the valley-dependent exciton transport and the exciton translational-internal coupling in the electric field for intervalley excitons ($r_e = -r_h$). By using the Heisenberg equation of motion and omitting the translational-internal coupling, the exciton mobility in an electric field can be obtained by

$$
\left\langle \frac{d\mathbf{R}}{dt} \right\rangle = -i\{[\mathbf{R}, \mathcal{H}_X']\}
= \langle \mathbf{P} \rangle + \frac{e\Omega(m_e \mathbf{r}_e - m_h \mathbf{r}_h)}{4m_X} \mathbf{e}_\perp \times \mathbf{F}.
$$

(64)
where \( (P) \equiv 0 \) for the ensemble of excitons. The second term in Eq. \((64)\) can be seen as a contribution to the exciton valley Hall effect, which has been observed experimentally\(^{[21]}\). This effect is believed to be driven by the side-jump together with the skew-scattering mechanism\(^{[22]}\). While the contribution in Eq. \((64)\) to the exciton valley Hall effect is infinitesimal for intravalley excitons, it may be measurable if intervalley excitons also contribute to the exciton mobility. Due to the simplicity of the present model, the contribution of intervalley excitons to the exciton Hall conductivity will be studied by an improved model in future research.

**B. Exciton energy-level splitting**

In this section, exciton internal Hamiltonians without external fields are considered, and the eigenspectrum are used to study the Berry-curvature effect on exciton energy levels. By assuming that \( \tau_e = \tau_h = \tau \), the exciton internal Hamiltonian for the intravalley exciton can be written as

\[
\hat{H}^{\text{I}}_{\text{intra-valley},\tau}(r) = \Delta + \frac{p^2}{2\mu} - V(r) - \frac{\Omega}{4} \vec{n} \cdot \nabla V(r) - \frac{\tau \Omega}{2} \vec{e}_\perp \cdot \nabla V(r) \times \vec{p}. \tag{65}
\]

On the other hand, by assuming that \( \tau_e = -\tau_h = \tau \), the exciton internal Hamiltonian for the intervalley exciton can be written as

\[
\hat{H}^{\text{I}}_{\text{inter-valley},\tau}(r) = \Delta + \frac{p^2}{2\mu} - V(r) - \frac{\Omega}{4} \nabla^2 V(r). \tag{66}
\]

The Darwin interaction is found in both Hamiltonians, but only the intravalley-exciton Hamiltonian contains the exciton valley-orbit coupling. The exciton eigenenergy and wavefunction can be calculated by the eigenvalue equation

\[
\hat{H}^{\text{I}}_{\text{X},\tau}(r) \Psi_{\text{X},I\tau}(r) = E_{\text{X},I\tau} \Psi_{\text{X},I\tau}(r), \tag{67}
\]

for both intravalley excitons and intervalley excitons. Since the exciton internal Hamiltonian and the angular momentum operator commutes, \([\hat{H}^{\text{I}}_{\text{X},\tau}(r), \mathcal{L}(r)] = 0\), with the angular momentum operator being given by

\[
\mathcal{L}(r) = -i \vec{e}_\perp \cdot \vec{r} \times \nabla = -i \frac{\partial}{\partial \phi}, \tag{68}
\]

the exciton wavefunction is also an eigenfunction of the angular momentum operator, \(\mathcal{L}(r) \Psi_{\text{X},I\tau}(r) = l \Psi_{\text{X},I\tau}(r)\), with \(l\) the angular momentum of the exciton. The exciton wavefunction can be written as \(\Psi_{\text{X},I\tau}(r) = \Psi_{\text{X},I\tau}(r) e^{i \vec{R}_n(r)}\), where \(\mathcal{R}_n(r)\) is the radial wavefunction of the exciton, with \(n\) the principal quantum number. By using \(\vec{p} = -i \nabla\) and

\[
e_{\perp} \cdot \nabla V(r) \times \nabla = \frac{1}{r} \frac{\partial V(r)}{\partial r} \vec{e}_\perp \cdot \vec{r} \times \nabla, \tag{69}
\]

it can be shown that the exciton valley-orbit coupling \((\mathcal{V}_{\text{X,VOCC}})\), the fifth term in Eq. \((65)\) and Eq. \((66)\) is proportional to the angular momentum operator

\[
\mathcal{V}_{\text{X,VOCC}}(r) \propto -\frac{\Omega}{2} \frac{1}{r} \frac{\partial V(r)}{\partial r} \mathcal{L}(r), \tag{70}
\]

such that \(\langle \mathcal{V}_{\text{X,VOCC}} \rangle_{I\tau} \propto l\) with

\[
\langle \mathcal{O} \rangle_{I\tau} \equiv \int \Psi_{\text{X},I\tau}(r)^* \mathcal{O}(r) \Psi_{\text{X},I\tau}(r) d^2r \tag{71}
\]

being the expectation value. It is shown that the exciton valley-orbit coupling only causes energy shifts of degenerate exciton states with angular momentums other than zero. Since the only difference between the intravalley and intervalley excitons is the exciton valley-orbit couplings, the binding energies and the wavefunctions of intravalley and intervalley excitons with zero angular momentum \((1s)\) excitons are the same.

Based on the Hamiltonian given in Eq. \((64)\), we can solve the exciton energy levels by the variational method\(^{[42–45]}\) (see Appendix A). In Table. I, the calculated exciton binding energies of different intravalley excitons, and the calculation method are given in Appendix A. It is found that the energy-level splittings for \(2p_+ / 2p_-\) excitons are about 10.6 meV for MoS\(_2\) with \(\kappa = 1\) and 10.1 meV for MoSe\(_2\) with \(\kappa = 1\). The former value is consistent with the calculated result in Ref. 14. However, the latter value is lower than the experimentally observed value 14 meV in Ref. \(18\). It suggests that the Berry curvature calculated by the present model might be underestimated in comparison to the full band-structure model.

**C. Exciton transitions**

In this section, the one-exciton and intra-exciton transitions for intravalley excitons are studied, and their transition amplitudes are derived. The exciton wavefunction in momentum space is given by the Fourier transform

\[
\tilde{\Psi}_{\text{X},I\tau}(k) = \int e^{-i \vec{k} \cdot \vec{r}} \Psi_{\text{X},I\tau}(r) d^2r = e^{i \vec{k} \cdot \vec{R}_n(k)}, \tag{72}
\]

where \(\mathcal{R}_n(k)\) is the radial part of the exciton wavefunction in momentum space, with \(n\) the principal quantum number and \(l\) the angular momentum. By using Eq. \((69)\) and the FW transformed velocity matrix in Eq. \((54)\), the momentum matrix element is given by

\[
\tilde{p}_{\text{e},\tau}(k) = \begin{pmatrix}
\tilde{p}_{\text{e},\tau}(k) \\
\tilde{p}_{\text{e},\tau}(k) \\
\end{pmatrix}^* = \begin{pmatrix}
\tilde{p}_x(k) \\
\tilde{p}_y(k) \\
\end{pmatrix} = \begin{pmatrix}
\delta_{\tau,\tau,\pi} \frac{\Omega k^2}{4} + \delta_{\tau,\tau,\pi} \frac{\Omega k^2}{4} e^{i 2 \phi} \\
\delta_{\tau,\tau,\pi} \frac{\Omega k^2}{4} + \delta_{\tau,\tau,\pi} \frac{\Omega k^2}{4} e^{i 2 \phi} \\
\end{pmatrix}.
\] \tag{73}

The same result has been derived in Ref. \(19\). By inserting the exciton wavefunction in Eq. \((72)\) and the momentum
Fermi velocity is given by \( v_F \).

**TABLE I.** Parameters of TMDCs (\( \Delta \) the band-gap energy; \( a \) the lattice constant; \( t \) the hopping coupling; \( r_0 \) the screening length; \( \kappa \) the dielectric constant) and calculated exciton binding energies (in meV) of intravalley excitons with \( \tau = 1 \). The Fermi velocity is given by \( v_F = at \). The parameters are obtained from Ref. [43] except the last row. The parameters \( (m_e/m_h, m_h/m_0, r_0(\text{Å}), \kappa) \) in the last row are chosen to fit the experimentally observed photoluminescence spectra reported in Ref. [46].

The electron-hole exchange effect has been included in the last row according to Ref. [44].

| Materials | \( \Delta \) (eV) | \( a \) (Å) | \( t \) (eV) | \( m_e/m_0 \) | \( m_h/m_0 \) | \( r_0 \) (Å) | \( \kappa \) | \( 2s \) | \( 3s \) | \( 2p_+ / 2p_- \) | \( 3p_+ / 3p_- \) | \( 3d_+ / 3d_- \) |
|-----------|-----------------|-------------|-------------|-------------|-------------|-----------|---------|---------|---------|-----------------|-----------------|-----------------|
| MoS\(_2\)  | 1.918           | 3.193       | 1.0799      | 0.47        | 0.54        | 44.68     | 1.0     | 506.2   | 243.3 | 151.3      | 292.4/303.0      | 174.6/178.8      | 197.7/202.5     |
|           |                 |             |             |            |             |           | 2.0     | 333.6   | 124.4 | 66.1       | 156.7/163.4      | 78.6/80.8        | 89.8/92.0       |
| MoSe\(_2\)| 1.516           | 3.313       | 0.8984      | 0.55        | 0.59        | 53.16     | 1.0     | 458.7   | 230.5 | 147.6      | 274.0/284.1      | 169.0/173.2      | 190.5/195.3     |
|           |                 |             |             |            |             |           | 2.0     | 309.2   | 122.8 | 67.6       | 152.9/159.7      | 79.9/82.2        | 91.4/93.8       |
| WS\(_2\)  | 2.042           | 3.197       | 1.3315      | 0.32        | 0.35        | 40.17     | 1.0     | 488.2   | 215.8 | 127.0      | 263.8/274.2      | 148.3/152.3      | 169.0/173.4     |
|           |                 |             |             |            |             |           | 2.0     | 308.2   | 102.4 | 51.1       | 130.8/136.6      | 61.1/62.9        | 69.4/71.1       |
| WSe\(_2\)| 1.761           | 3.310       | 1.1395      | 0.34        | 0.36        | 47.57     | 1.0     | 437.2   | 200.6 | 120.9      | 242.9/254.2      | 140.5/144.3      | 159.5/164.0     |
|           |                 |             |             |            |             |           | 2.0     | 281.2   | 98.3  | 50.4       | 124.5/130.6      | 60.0/61.9        | 68.4/70.2       |

\( \Delta l = 0, \pm 2 \) and \( \tau = \pm 1 \). While the valley index \( \tau \) stands for the angular momentum difference between the ground state and the one-exciton state, the selection rule can be seen as the consequence of angular momentum conservation in the photoabsorption process.

To derive the intra-exciton transition, which is defined as the transition between exciton states, we consider the exciton internal Hamiltonian with an in-plane electromagnetic-field interaction. The internal Hamiltonian for intravalley excitons is written as

\[
H_{\text{X},\tau}^\mu(r) = \Delta + \frac{p^2}{2\mu} - V(r) - \frac{\Omega}{4} \nabla^2 V(r) + eD_{\text{X},\tau}(r) \cdot \mathcal{F} - \frac{\tau\Omega}{2} e_{\perp} \cdot \nabla V(r) \times \mathbf{p},
\]

where the exciton dipole-moment operator is defined as

\[
D_{\text{X},\tau}(r) = \mathbf{r} - \frac{\tau\Omega}{2} e_{\perp} \times \mathbf{p}.
\]

The electromagnetic-field interaction can be rewritten as

\[
\mathcal{D}_{\text{X},\tau}(r) \cdot \mathcal{F} = \mathcal{D}_{\text{X},\tau}^+(r)\mathcal{F}^- + \mathcal{D}_{\text{X},\tau}^-(r)\mathcal{F}^+,
\]

where \( \mathcal{F}^\pm = (F^x \pm iF^y) / \sqrt{2} \) and

\[
\mathcal{D}_{\text{X},\tau}^\pm(r) = \frac{1}{\sqrt{2}} [\mathcal{D}_{\text{X},\tau}^+(r) \pm i\mathcal{D}_{\text{X},\tau}^-(r)] = r^\pm + i\frac{\tau\Omega}{2} p^\pm,
\]

with \( p^\pm = (x \pm iy) / \sqrt{2} = re^{\pm i\varphi} / \sqrt{2} \) and

\[
p^\pm = -\frac{i}{\sqrt{2}} \left( \frac{\partial}{\partial x} \pm i \frac{\partial}{\partial y} \right) = -\frac{1}{\sqrt{2}} e^{\pm i\varphi} (\frac{\partial}{\partial r} \pm i \frac{\partial}{\partial \varphi}).
\]

Since the exciton dipole-moment operator is related to the dipole-momentum matrix element by \( \mathcal{D}_{\text{X},\tau}^\pm(r) = \int \mathcal{D}_{\text{X},\tau}^\pm(k) e^{ik \cdot r} d^2k / (2\pi)^2 \), and the intra-exciton transition amplitude can be calculated from Eq. (28), we find

\[
\xi_{NM}^\mu = -e \int \Psi_{\text{X},l_n\tau_n}(r) \mathcal{D}_{\text{X},\tau_n}^\mu(r) \Psi_{\text{X},l_m\tau_m}(r) d^2r.
\]

\[
\text{FIG. 1.} \text{ Calculated one-photon (up) and two-photon (down) absorption spectra of MoS}_2 \text{ with the parameters given in Table I, the valley index } \tau = 1, \text{ and the screening constant } \kappa = 2. \text{ The line-broadening factor for the two-photon absorption is } \eta = 0.1 \text{ eV.}
\]
and $|ξ_{NM}^\pm| \propto δ_{JN} ξ_{M+\pm1}$. The selection rule for the intra-exciton transition can be found as

$$\begin{align*}
\Delta l = 1 & \text{ for } \mathbf{e}^+ \text{ polarized photon} \\
\Delta l = -1 & \text{ for } \mathbf{e}^- \text{ polarized photon}
\end{align*} \quad (81)$$

Therefore, given that an 1s exciton is generated by the one-exciton transition, an intra-exciton transition from the 1s exciton to $2p_\pm$ excitons can be induced by a two-photon process.

In Fig. 1 the calculated one-photon (up) and two-photon (down) absorption spectra of MoS$_2$ based on the one-exciton transition amplitude and the intra-exciton transition amplitude are shown. The formula for the one-photon absorption spectrum is given by Eq. (11) and the formula for the two-photon absorption spectrum is given by Eq. (12). The resonance peaks in the one-photon absorption spectrum can be assigned as the transitions of ns excitons, and the peaks in the one-photon absorption spectrum can be assigned as the transitions of np$\pm$ excitons. It is found that the Berry-curvature corrections to the transition amplitudes are about two order-of-magnitude smaller than the uncorrected transition amplitudes. Therefore, the contributions of Berry-curvature corrections to the one-exciton transition probability and the intra-exciton transition probability are not shown in the optical spectra of TMDCs. The finding is consistent with the calculations in Ref. 19.

D. Exciton valley Zeeman effect

In this section, the case of an exciton in a out-of-plane magnetic field ($B \neq 0$, $|F| = |\mathcal{F}| = 0$) is considered and the exciton valley Zeeman effect is studied. Based on the FW transformed single-particle Hamiltonian and the two-particle potential, the exciton Hamiltonian can be written as

$$\mathcal{H}_X = \Delta + \frac{|\pi_e|^2}{2m_e} + \frac{|\pi_h|^2}{2m_h} - V(\mathbf{r}_{eh}) + \frac{\tau_e eB}{2m_e} - \frac{\tau_h eB}{2m_h} - \frac{\tau_e eB}{2m_e} \cdot \mathbf{V}(\mathbf{r}_{eh}) \times \mathbf{e}_\perp - \frac{\nabla^2 V(\mathbf{r}_{eh})}{8m^2 v_F^2} - \frac{\nabla^2 V(\mathbf{r}_{eh})}{8m^2 v_F^2} \quad (82)$$

Again, we use the coordinate transformation in Eq. (57) and Eq. (68) to rewrite the Hamiltonian by the relative coordinate system. Additionally, we apply the unitary transformation to the exciton Hamiltonian, $\mathcal{H}_X = \mathcal{U}_X \mathcal{H}_X \mathcal{U}^{-1}_X$, with the unitary transformation operator

$$\mathcal{U}_X = \exp \left[ -i eB \mathbf{e}_\perp \cdot (\mathbf{R} \times \mathbf{r}) \right] \quad (83)$$

which causes the momentum operators (note that $\mathbf{p} = -i \nabla$ and $\mathbf{P} = -i \nabla \mathbf{R}$) being transformed as $\mathcal{U}_X \mathbf{p} \mathcal{U}^{-1}_X = \mathbf{p} - (eB/2) \mathbf{e}_\perp \times \mathbf{R}$.

The exciton Hamiltonian is rewritten as

$$\mathcal{H}_X = \mathcal{H}_X' + \mathcal{H}_X'' + \mathcal{J}_X \quad (84)$$

where $\mathcal{H}_X' = \mathcal{H}_X''(2m_X)$ is the exciton translational Hamiltonian,

$$\mathcal{H}_X'' = \Delta + \frac{p^2}{2\mu} - V(\mathbf{r}) - \frac{\Omega(\tau_e + \tau_h)}{4} \mathbf{e}_\perp \cdot \nabla V(\mathbf{r}) \times \mathbf{p} - \frac{eB}{2} \left( \frac{1}{m_e} - \frac{1}{m_h} \right) \mathbf{L}(\mathbf{r}) + \frac{\tau_e - \tau_h}{2\mu} \mathbf{r} \cdot \nabla V(\mathbf{r}) \right] + \frac{e^2 B^2}{8\mu} \mathbf{p} r^2 \quad (85)$$

is the exciton internal Hamiltonian, and

$$\mathcal{J}_X = \mathbf{e}_\perp \cdot \left[ \frac{eB}{m_X} \mathbf{r} - \frac{\Omega(m_e \tau_e - m_h \tau_h)}{4m_X} \nabla V(\mathbf{r}) \right] \times \mathbf{p} \quad (86)$$

is the exciton translational-internal coupling. Note that we have used the identity $\mathbf{e}_\perp \cdot \left[ \nabla V(\mathbf{r}) \times (\mathbf{e}_\perp \times \mathbf{r}) \right] = \mathbf{r} \cdot \nabla V(\mathbf{r})$ in Eq. (85). The first three terms of the exciton internal Hamiltonian are the Wannier exciton Hamiltonian, the forth term is the Darwin interaction, the fifth term is the exciton valley-orbit coupling, the sixth term is the valley Zeeman interaction and the last term is the diamagnetic interaction.

To study the valley Zeeman effect of excitons, it is important to note that the Zeeman splittings are also contributed from the spin and the atomic orbital of the electron or hole. The contributions from the Zeeman splittings of spins and atomic orbitals to the electron energy and the hole energy are given by

$$\xi_e = \xi_{0\text{FW,e}} + \frac{s_e g_{\text{spin}} + \tau_e g_e}{2} \mu_B B, \quad (87)$$

$$\xi_h = \xi_{0\text{FW,h}} - \frac{s_h g_{\text{spin}} + \tau_h g_h}{2} \mu_B B, \quad (88)$$

where $s_e$ and $s_h$ are electron-spin and hole-spin indices, $g_{\text{spin}}$ is the spin Lande g-factor, $g_e$ and $g_h$ are the atomic orbital Lande g-factors for electrons and holes, and $\mu_B = e/(2m_0)$ is the Bohr magneton with $m_0$ the free electron mass. The band-gap energy is given by

$$\tilde{\Delta} = \Delta + \frac{1}{2} \left[ |s_e - s_h| g_{\text{spin}} + \tau_e g_e - \tau_h g_h \right] \mu_B B \quad (89)$$

We assume that the spin and valley indices of the hole are given by $s_e = s_h = \tau_h = \tau$ for both intravalley and intervalley excitons, and the valley index of the electron is given by $\tau_e = \tau$ for intravalley bright excitons and $\tau_e = -\tau$ for intervalley excitons. The exciton valley Zeeman shift is defined by

$$E_{X,I} = E_{X,I}^{(0)} + \frac{1}{2} g_{X,I} \mu_B B + \cdots \quad (90)$$
where $E_{X,i}^{(0)}$ is the exciton energy level without magnetic-field interaction. $g_{X,i}$ is the exciton valley g-factor for the $i$-th exciton state. We can find

$$g_{X,i} = (s_e - s_h) g_{\text{spin}} + \tau_e g_e - \tau_h g_h + e \left( \frac{1}{\mu_B} \left( \frac{1}{m_e} - \frac{1}{m_h} \right) + \frac{e(\tau_e - \tau_h)}{\mu_B(2\mu)} \right) - \frac{e\Omega(\tau_e - \tau_h)}{4\mu_B} (\mathbf{r} \cdot \nabla V(r)) I,$$  \quad (91)

where the last term in Eq. (91) is an interaction-induced Zeeman splitting. Assuming $g_{\text{spin}} = 2$, $g_e = 0$, $g_h = 4$ and using the parameters in the last line of Table. (m_e = m_h = 0.44m_0, r_0 = 50.00, \kappa = 4.0), the g-factors with the exciton state $I$ assigned as the 1s state are given by $|g_{X,1s}| = 4$ for the intravalley exciton and $|g_{X,1s}| = 14.5$ for the intervalley exciton, while the interaction-induced Zeeman splitting contributes about 1.4 for the g-factor of the intervalley exciton. These values are consistent with experimental measurements of excitonic states of WSe_2[21, 44], where the measured g-factors are $|g_{X,1s}| \approx 4$ for the intravalley exciton and $|g_{X,1s}| \approx 13$ for the intervalley exciton.

V. SUMMARY AND PERSPECTIVES

In the present work, the FW transformation is applied to 2D gapped Dirac fermions under external fields. The single-particle Hamiltonian, two-particle interaction, and interband transition obtained from the FW transformation are used to study the valley-dependent physical properties of 2D materials. Exciton Hamiltonians for intravalley and intervalley excitons in an in-plane electromagnetic field and in an out-of-plane magnetic field are derived. Exciton energy-level splittings, valley-selected exciton transitions, and exciton valley Zeeman effect are formulated analytically and studied. The variational method is used to solve the exciton energy levels and optical spectra. The calculated results are quantitatively coincident with literatures. Even though these effects have been discussed by different theoretical methods in literatures, we believe that the present theoretical framework still provides a new viewpoint on these topics and a straightforward derivation procedure to study related problems.

While the Berry-curvature effects on valley excitons have been studied in literatures, many related topics still demand investigation. One topics of particular importance is the Berry-curvature effect on valley trions and other valley-dependent exciton complexes. For problems involving more than two particles, a semiclassical derivation of Berry-curvature effect becomes much more difficult. Therefore, the present FW transformation method becomes quite useful for deriving effective Hamiltonians for valley-dependent exciton complexes. For trions, some theoretical studies addressing the Berry-curvature effect have been published[47, 48], but joint effects of valley degree of freedom and external fields on trions have yet to be studied. Another possible extension of the present framework is to apply the FW transformation to 2D gapped Dirac fermions with additional interactions or band-structure modifications. For example, the trigonal warping in the band structures of 2D materials can be included by the FW transformation as a non-local kinetic correction to the exciton Hamiltonian and interband transition. Such extensibility shows the potential and versatility of the present theoretical framework. These topics will be considered in future studies.

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Appendix A: Variational method

In the appendix, the variational method to solve the exciton wavefunction and eigenenergy is introduced. By a rescaling of the length unit to the effective Bohr radius $a_B = (m_0/m_e)a_0$ and the energy unit to the effective Hartree $\varepsilon_0 = (m_e/m_0)(2Ry)$, with $m_0$ the free electron mass, $a_0 \approx 0.5291772$ Å the Bohr radius and Ry $\approx 13.60569$ eV the Rydberg constant, the exciton Hamiltonian can be rewritten as

$$\mathcal{H}_X^\prime(r) = -\frac{\sigma + 1}{2} \nabla^2 - V(r) - \frac{\Omega}{4} \nabla^2 V(r) \quad (A1)$$

where $\sigma = m_e/m_h$ is the mass ratio, $V(r)$ is a screened Coulomb potential, $L_X(r)$ is the angular momentum operator,

$$\Omega = \frac{(\sigma + 1)^2 a_0^2 e^2}{4a^2l^2} \quad (A2)$$

is the Berry curvature with $a$ the lattice constant and $t$ the hopping coupling. The 2D screened Coulomb potential is assumed to be given by the Rytova-Keldysh potential[49, 50]

$$V(r) = \frac{\pi}{\kappa \rho_0} \left[ H_0 \left( \frac{r}{\rho_0} \right) - Y_0 \left( \frac{r}{\rho_0} \right) \right]$$

$$= \int e^{i k \cdot r} \frac{2\pi}{k|k|} \frac{d^2 k}{(2\pi)^2}, \quad (A3)$$

where $\rho_0 = r_0/(\kappa a_0)$ with $r_0$ the screening length in unit of Å, $\kappa$ is the dielectric constant, $H_0(r)$ and $Y_0(r)$ are the Struve function and the Bessel function of the second kind.
We use 2D Slater-type (STO) as the basis function to expand the exciton wavefunction \[42\]. The exciton wavefunction can be written as

\[ \Psi_{X,I} = \sum_a c_{a,I} \phi_a(r), \]

where \( c_{a,I} \) is the linear variational parameter and

\[ \phi_a(r) = \frac{e^{i\mu_a \phi}}{\sqrt{2\pi}} r^{n_a-1} e^{-\zeta_a r} \]  

is the STO with \( \zeta_a \) the screening constant and also a variational parameter, \( n_a \) the principal quantum number and \( \mu_a \) angular momentum. By using linear variational method, the exciton coefficient can be solved by the eigenvalue equation

\[ \sum_b h_{ab} c_{b,I} = \epsilon_{X,I} \sum_b o_{ab} c_{b,I}, \]

where \( h_{ab} \) is exciton Hamiltonian matrix, \( o_{ab} \) is overlap matrix, and the eigenvalue of the equation \( \epsilon_{X,I} \) is the exciton energy. The exciton Hamiltonian matrix is given by \( h_{ab} = t_{ab} + v_{ab} + d_{ab} \), with \( t_{ab} \) the kinetic integral, \( v_{ab} \) the potential integral, and \( d_{ab} \) the band-geometry integral. The formulations of the integrals \( t_{ab}, v_{ab}, o_{ab} \) can be found in Ref. \[44\]. The band-geometry integral is given by

\[ d_{ab} = -\frac{\Omega(\tau_a + \tau_b)}{4} \int \phi_a^*(r) \frac{1}{r} \frac{\partial V(r)}{\partial r} \phi_b(r) d^2 r \]

To calculate these orbital integrals containing the screened Coulomb potential, we use the following formula

\[ \frac{\partial}{\partial r} = \cos \varphi \frac{\partial}{\partial x} + \sin \varphi \frac{\partial}{\partial y} = e^{i\varphi} \frac{\partial}{\partial z} + e^{-i\varphi} \frac{\partial}{\partial z^*}, \]

with \( z = x + iy \) and \( z^* = x - iy \), and

\[ k \cdot r = k_x x + k_y y = \frac{k_x}{2} e^{-i\varphi} + \frac{k_z}{2} e^{i\varphi}, \]

\[ \frac{\partial V}{\partial z} = \int e^{-i\kappa r} \left[ -\frac{i\kappa}{2} e^{-i\varphi} \hat{V}(k) \right] \frac{d^2 k}{(2\pi)^2}, \]

\[ \nabla^2 V = \int e^{-i\kappa r} \left[ -k^2 \hat{V}(k) \right] \frac{d^2 k}{(2\pi)^2}, \]

In order to derive the orbital integrals, we can take advantage of the analytic formula for the Fourier transform of the 2D STO

\[ \hat{\phi}_a(k) = \int \phi_a(r) e^{-i\kappa r} d^2 r = \frac{e^{i\mu_a \phi}}{\sqrt{2\pi}} R_{\tau_a,\tau_a}(\zeta_a, k), \]

where the radial function is generated by \[44\]

\[ R_{\tau_a,\tau_a}(\zeta_a, k) = \frac{2\pi(-i)^n}{k^{n+1}} \left[ \frac{d^n}{dz^n} \left( z - i\eta \right)^{1/2} \right] \frac{1}{\sqrt{1 - z^2}} \]

\[ \zeta = \frac{\xi}{k}, \]

with \( \eta = \frac{l}{|l|} \) being the sign of \( l \). The band-geometry integral is given by

\[ d_{ab} = \delta_{\tau_a,\tau_b} \frac{1}{\Omega(\tau_a + \tau_b)} \int \left[ R_{\tau_a,\tau_a + 2,0}(\zeta_a + \zeta_b, k) + R_{\tau_a + 2,\tau_a}(\zeta_a + \zeta_b, k) \right] \frac{k^2 dk}{(2\pi)^2} - \delta_{\tau_a,0} \frac{4}{\Omega \rho_0} \int k \hat{V}(k) R_{\tau_a,\tau_a - 1,0}(\zeta_a + \zeta_b, k) \frac{k dk}{(2\pi)^2} + \delta_{\tau_a,0} \delta_{\tau_b,1} \delta_{\tau_b,1} \frac{\Omega}{4\sqrt{k}}. \]
