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RPPR Final Report

as of 11-Oct-2022

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Final Report for Period Beginning 05-Sep-2017 and Ending 04-Feb-2022

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Begin Performance Period: 05-Sep-2017

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STEM Participants:

Major Goals: We will utilize the unique interplay of geometry, shape and confinement in nanomaterials along with symmetry breaking and precisely tailored fields to produce and probe nontrivial and unprecedented optoelectronic functionalities in topological materials. Our vision is that novel electronic and optoelectronic phenomena are accessible by controllably fabricating nano materials into desired shapes and geometries. This approach will also exploit the strongly confined electrical and optical excitations supported in these systems which are sensitive to boundary effects and thereby enable precisely tunable responses and new device applications. The fundamental tasks that

will be addressed in this project and for which our team is uniquely positioned. - Discovery and probe of new orbitronic topological materials with Berry curvatures arising from orbital degrees of freedom. -Fabrication and manipulation of orbitronic nanomaterials using confinement, shape and morphology. -Developing new optoelectronic probes of topological states of matter

Accomplishments: 1) Discovery of spatially dispersive CPGE in Weyl semimetals (published in Nature Materials, 2019)

2) Orbitronics theory developed for systems lacking strong spin-orbit coupling (published in Physics Rev Letts, 2020)

3) Orbital photogalvanic effect discovered in Weyl semimetals (Science 2020)

4) Quadrupolar photogalvanic effect in strongly correlated excitonic insulators discovered (published in Science Advances, 2022).

5) Formal theory for nonlinear response functions in twisted moire systems developed (m/s under preparation)

Training Opportunities: graduate students and postdocs trained under this grant to design and perform optoelectronic experiments, response function nonlinear theory, data analyses and communications results to the wider scientific community.

Results Dissemination: Exchange coupling-mediated broken symmetries in Ta₂NiSe₅ revealed from quadrupolar circular photogalvanic effect, Science Advances, 2022

<https://doi.org/10.1126/sciadv.abl9020>

RPPR Final Report

as of 11-Oct-2022

Honors and Awards: PI Agarwal received the Heilmeier Award for Research Excellence from the School of Engineering, University of Pennsylvania. This is the highest award of the engineering school at Penn.

PI Agarwal was named the Srinivasa Ramanujan Distinguished Scholar (Endowed Chair) from July 1, 2022.

Zhurun Ji, a female graduate student who worked on the project is a Stanford Fellow, a prestigious fellowship to pursue postdoctoral research at Stanford.

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PARTICIPANTS:

Participant Type: PD/PI

Participant: Ritesh Agarwal

Person Months Worked: 1.00

Project Contribution:

National Academy Member: N

Funding Support:

Participant Type: Co PD/PI

Participant: Eugene Mele

Person Months Worked: 1.00

Project Contribution:

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Participant Type: Graduate Student (research assistant)

Participant: Harshvardhan Jog

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Authors: Harshvardhan Jog, Luminita Harnagea, Eugene J. Mele, Ritesh Agarwal

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Abstract: In low–electron density materials, interactions can lead to highly correlated quantum states of matter. Ta₂NiSe₅, an excitonic insulator (EI) candidate, exists in a novel broken-symmetry phase below 327 K, characterized by robust exchange interaction and electron-lattice coupling. We study this phase of Ta₂NiSe₅ using the quadrupole circular photogalvanic effect (QCPGE). Light-matter interaction in Ta₂NiSe₅ mediated by electric quadrupole/magnetic dipole coupling produces helicity-dependent DC response even with centrosymmetry, making it particularly sensitive to certain other broken symmetries. We show that the exchange interaction in Ta₂NiSe₅ can lead to a triclinic structure with a broken C₂ symmetry. Our results provide an incisive probe of the symmetries of the low-temperature phase of Ta₂NiSe₅ and add new symmetry constraints to the identification of a strongly correlated EI phase. The high sensitivity of QCPGE to subtle symmetry breaking in centrosymmetric systems will enable it

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Signature: Ritesh Agarwal

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Three-dimensional twistrionic photogalvanic effect from spiral lattice-photon momentum interactions

Recent studies of twisted moire systems have elucidated the exquisite effect of quantum geometry of the electronic bands on their measured properties as well as the discovery of new correlated phases determined by the twist angle between 2D layers. While these remarkable discoveries demonstrate the versatility of creating new quantum states arising from the twist degree of freedom, most studies have been limited to only a few layers where the system remains in the quasi 2D limit. The idea of twistrionics generalized to its 3D limit when the twist between the adjacent layers forms a periodic pattern in the third dimension has not been experimentally realized, due to the constraints in manually stacking the 2D layers with precise control. An important question is, if light-matter interactions in 3D helical solid state structures changes fundamentally owing to the lattice lengthscales and sample thickness becoming comparable to optical wavelengths and if the structural helicity influences these interactions. Here we report nonlinear optical Hall effect in self-assembled supertwisted WS₂ system formed by natural screw-dislocation-driven mechanisms with a nonsymmorphic screw symmetry. The polarity of optical Hall current reflects the structural chirality of the supertwisted system, and an unusual photon-momentum dependence of the nonlinear optical response when electrons are modulated by the moire potential is observed. Furthermore, signatures of thickness-dependent exciton-polariton and the associated strong photon momentum-lattice interaction dependent photocurrent response are found, which suggest a fundamentally altered light-matter interaction in this 3D moire system. Our microscopic theory explains the origin of the photon momentum dependent optical response, revealing new observables of the system beyond Berry curvature and other widely explored band geometrical quantities. Our study not only connects 2D and 3D twistrionics, but also provides a seamless bridge connecting the electrons and photons by overriding their significant length scale differences in conventional systems and demonstrates the versatility of 3D moire systems for exploring hidden light-matter interaction phenomena in condensed matter systems, which is of great importance in realizing extreme optical nonlinearities and versatile quantum simulators for future quantum nanophotonic devices.

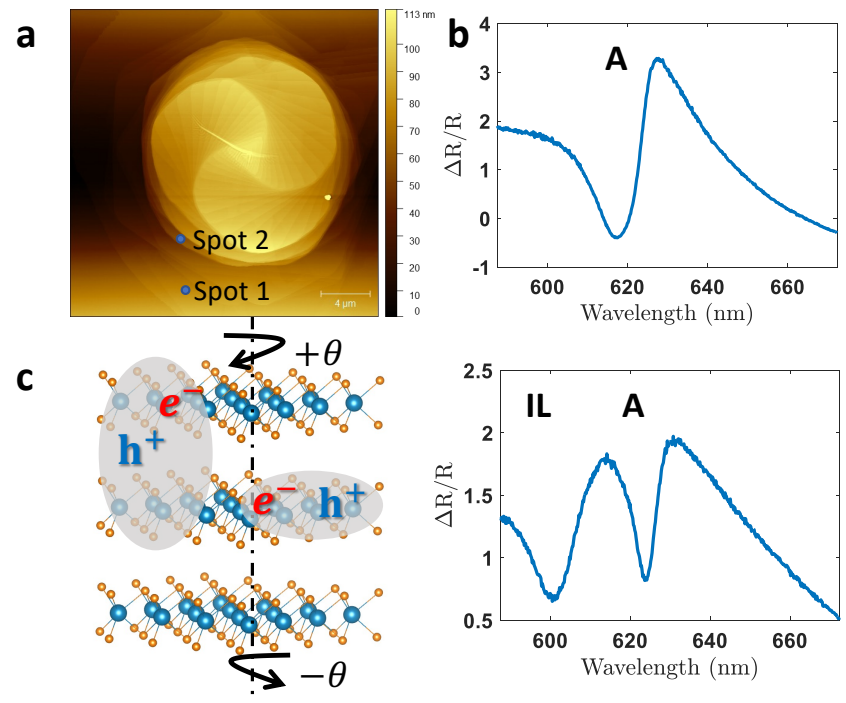


Fig. 1 Supertwisted WSe2 system. a) AFM image of the WSe2 supertwisted flake. Peak thickness is ~ 80 nm. b) Reflectance spectrum at spot 1 (thickness ~ 5 nm, top) showing dominant intralayer A-exciton peak and at spot 2 (thickness ~ 80 nm) bottom) also showing a dominant interlayer exciton. c) Schematic of the supertwisted WSe2 system showing interlayer excitonic correlations.

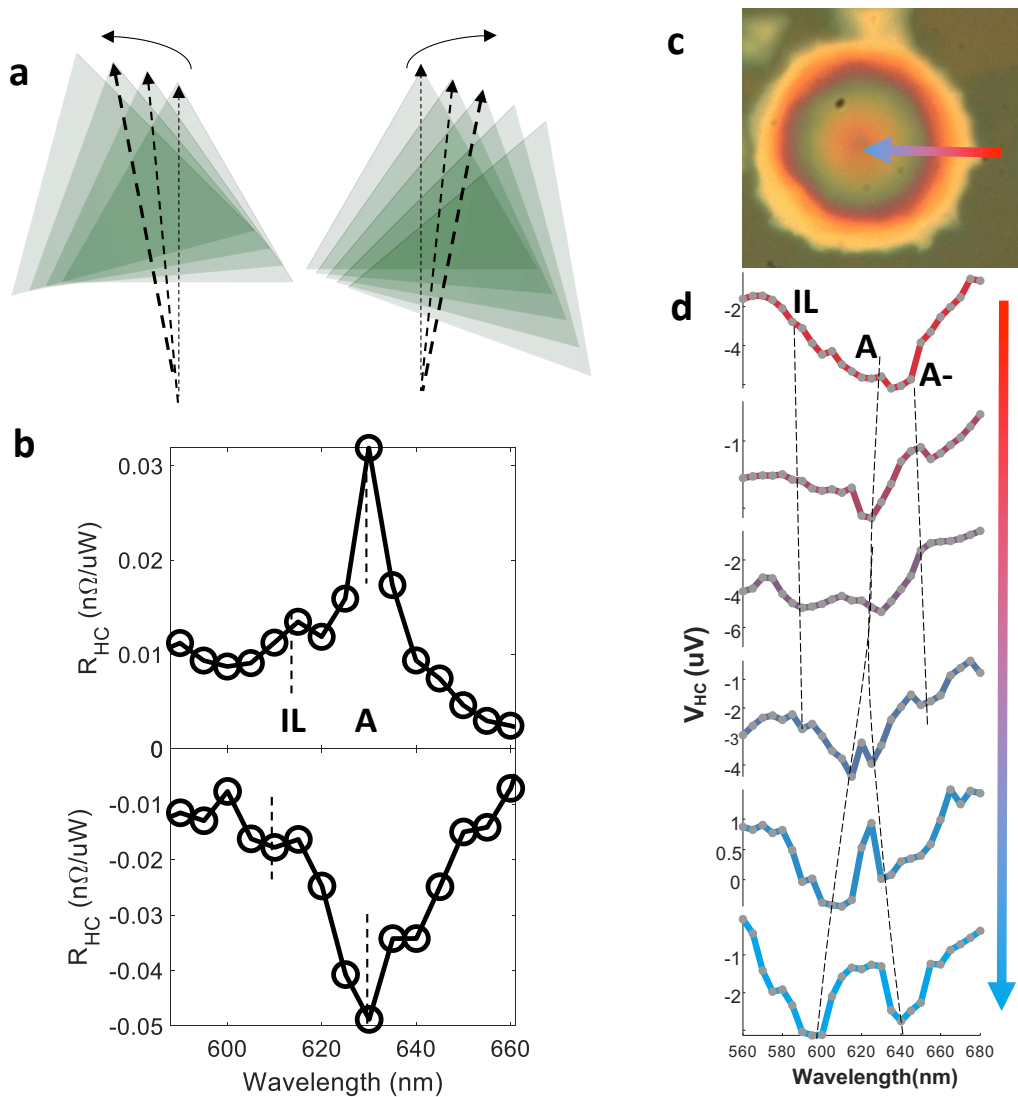


Fig. 3 Chirality and strong light-matter interaction in supertwisted WSe2 system. a) Schematic of the supertwisted system with opposite structural chirality. b) Strong nonlinear Hall coefficient showing opposite magnitude for structurally chiral systems. The origin of optical chirality is due to the pseudomagnetic field due to structural chirality which produces a strong optical Hall effect. c) Optical image of the device. d) Nonlinear Optical hall Voltage as a function of device thickness (arrow shows scan direction in c). Strong polaritonic splitting of the excitonic peaks are observed demonstrating extremely large nonlinearities and strong light-matter coupling in twisted moire systems.

“twistronic” systems in general and could also be utilized for designing efficient SHG crystals over a broad range of wavelengths and their potential applications as novel nonlinear media for device applications.

4.2 The role of photon momentum in nonlinear optical responses

4.2.1 Identifying sources of the photogalvanic effect

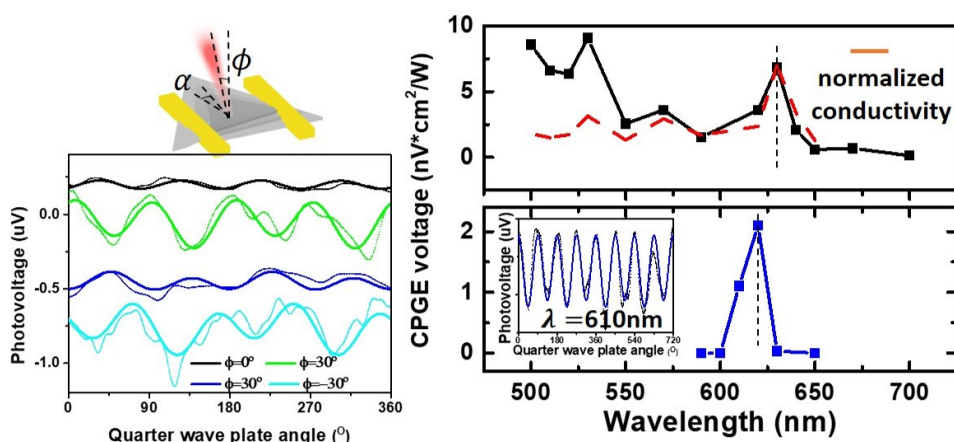


FIGURE 4.4: Left: Photovoltage measured at different angles of incidence; Right: CPGE voltage and normalized conductivity as a function of incident wavelength.

As shown in Fig. 4.4, in our setup, the incident beam can be characterized by a polar angle ϕ , an azimuthal angle α within the 2D plane, and the quarter wave plate angle θ (with respect to its fast axis).

We measured photovoltage response from the quasi-2D, spiral WS₂ samples. Explicitly, on a same sample, we measured at three incidence angles, $\phi = 0^\circ$, $\phi = -30^\circ$, $\phi = 30^\circ$ (left figure). Then, by comparing the photovoltages obtained at quarter wave plate angles $\theta = 45^\circ$ (LCP) and $\theta = 135^\circ$ (RCP), circular photogalvanic effect (CPGE) current was extracted. CPGE current adopted a same sign at $\phi = \pm 30^\circ$, while at $\phi = 0^\circ$, its amplitude was much smaller. On the same device, we

found a peak of CPGE conductivity near the A-exciton frequency of WS₂ (right figure). The trend of CPGE current amplitude changing with incidence angle ϕ appears to contradict the symmetry arguments of CPGE in WS₂. In order to explain this phenomenon, in the following sections, the possible sources of CPGE will be identified, and microscopic models will be discussed.

Let's consider the case of a 2D material illuminated by a monochromatic light source, with electric field defined as the plane wave

$$\mathbf{E}_i(\mathbf{r}, t) = E_i e^{(i\mathbf{q}\cdot\mathbf{r} - \omega t)} + c.c. \quad (4.9)$$

where indices i, j and k represent the Cartesian coordinates, ω is the angular frequency, and \mathbf{q} is the wave vector. Following the definitions in the last section, the incident beam can be characterized by a polar angle ϕ , an azimuthal angle α with the 2D plane, and the quarter wave plate angle θ (with respect to its fast axis). Then, the carried photon momentum can then be written as \mathbf{q} ,

$$\mathbf{q} = -q(\sin \phi \cos \alpha, \sin \phi \sin \alpha, \cos \phi) \quad (4.10)$$

and the electric field would be,

$$\mathbf{E} = \begin{pmatrix} -i \sin \alpha \sin 2\theta + (1 - i \cos 2\theta) \cos \phi \cos \alpha \\ i \cos \alpha \sin 2\theta + (1 - i \cos 2\theta) \cos \phi \sin \alpha \\ -(1 - i \cos 2\theta) \sin \phi \end{pmatrix} E_0 \quad (4.11)$$

For discussion on circularly polarized light, we write the pseudo-vector $\mathbf{E} \times \mathbf{E}^*$ as,

$$\mathbf{E} \times \mathbf{E}^* = \begin{pmatrix} -2i \cos \alpha \sin 2\theta \sin \phi \\ -2i \sin \alpha \sin 2\theta \sin \phi \\ -2i \sin 2\theta \cos \phi \end{pmatrix} E_0^2 \quad (4.12)$$

By doing a Taylor expansion over the wavevector \mathbf{q} , we can write J_l^{DC} as,

$$J_l^{DC} = \sigma_{ljk}^{(2)}(\omega, \mathbf{q}) E_j E_k^* = \kappa_{ljk}(\omega) E_j E_k^* + T_{ljk\mu}(\omega) q_\mu E_j E_k^* \quad (4.13)$$

Here we focus on distinguishing the first, $q^{(0)}$ term (regular photogalvanic effect) from the second, $q^{(1)}$ term.

The photogalvanic current independent of \mathbf{q} can be divided into two parts as follows,

$$J_l^{DC,(0)} = \kappa_{ljk}^{sym}(\omega) E_j E_k^* + \kappa_{ljk}^{antisym}(\omega) E_j E_k^* = J_l^{LPGE,(0)} + J_l^{CPGE,(0)} \quad (4.14)$$

where the Levi-Civita tensor ϵ_{sjk} can be used to contract $\kappa_{ljk}^{antisym}$ to only one pseudo vector index,

$$\sum_{jk} \kappa_{ljk}^{antisym}(\omega) (E_j E_k^* - E_k E_j^*) = i \sum_{sjk} 2\gamma_{ls} \epsilon_{sjk} (E_j E_k^* - E_k E_j^*) = i \sum_s \gamma_{ls} (E \times E^*)_s \quad (4.15)$$

where γ_{ls} is a second order pseudo-tensor and l and s stand for Cartesian coordinates. Then, $J_l^{CPGE,(0)}$ can be expressed as,

$$J_l^{CPGE,(0)} = i \sum_j \gamma_{lj} (E \times E^*)_j \quad (4.16)$$

In a similar fashion, for $J_l^{CPGE,(1)}$ we get,

$$J_l^{CPGE,(1)} = i \sum_{jk} T_{ljk} q_j (E \times E^*)_k \quad (4.17)$$

A free standing 1L-TMDC system (2H phase) has a D_{3h} symmetry. The x-y mirror plane can be sometimes broken by the substrate, reducing its symmetry to C_{3v} . Here we consider the constraints on photocurrent tensors under these two circumstances.

D_{3h} symmetry

The scenario of an ideal crystal has three symmetry operations, a $2\pi/3$ rotation,

$$R = \begin{pmatrix} \cos(2\pi/3) & \sin(2\pi/3) & 0 \\ \cos(2\pi/3) & \sin(2\pi/3) & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (4.18)$$

$(\mathbf{E} \times \mathbf{E}^*)$ becomes $R(\mathbf{E} \times \mathbf{E}^*)$ and \mathbf{j}^{CPGE} becomes $R\mathbf{j}^{CPGE}$, thus we obtain,

$$R\gamma = \gamma R \quad (4.19)$$

On the other hand, imposing that, for a transverse EM wave, $(\mathbf{E} \times \mathbf{E}^*)$ and \mathbf{q} should be parallel with each other, we get $q_j(\mathbf{E} \times \mathbf{E}^*)_k = q_k(\mathbf{E} \times \mathbf{E}^*)_j$. Then, by imposing $\mathbf{j}^{CPGE,(1)} = R\mathbf{j}^{CPGE,(1)}$ under the $2\pi/3$ rotation, we get,

$$T_{\mu ij} R_{ik} q_k R_{jl} (\mathbf{E} \times \mathbf{E}^*)_l = T_{\mu ij} q_i (\mathbf{E} \times \mathbf{E}^*)_j \quad (4.20)$$

From each $q_i(\mathbf{E} \times \mathbf{E}^*)_j$, we have,

$$\begin{aligned} T_{xzz} = 0; T_{xyy} = -T_{xxx}; T_{yxx} &= \frac{\sqrt{3}}{2} T_{xxx}; T_{yxy} + T_{yyx} = -2T_{xxx}; \\ T_{yxz} + T_{yzx} &= -(T_{xyz} + T_{xzy}); T_{yyz} + T_{yzy} = T_{xxz} + T_{xzx}; T_{xyy} = -\frac{1}{2}(T_{xxy} + T_{xyx}); \\ T_{zxx} + T_{zzx} &= T_{yyz} + T_{yzy} = T_{zxy} + T_{zyx} = 0; T_{zyy} = T_{zxx} \end{aligned} \quad (4.21)$$

Another constraint is given by the mirror symmetries,

$$M = \begin{pmatrix} \cos(2\psi) & \sin(2\psi) & 0 \\ \sin(2\psi) & -\cos(2\psi) & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (4.22)$$

where ψ is defined as the angle between its mirror plane and the x axis. As a pseudo-vector, $(E \times E^*)$ becomes $-M(E \times E^*)$. J^{CPGE} becomes MJ^{CPGE} . Therefore, we obtain,

$$M\gamma = -\gamma M \quad (4.23)$$

Combining these two constraints, we find,

$$\gamma = \begin{pmatrix} 0 & \gamma_{xy} & 0 \\ -\gamma_{xy} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (4.24)$$

However, the mirror plane in the xy plane,

$$\sigma_z = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad (4.25)$$

requires $\gamma_{xy} = 0$. As a result, $J^{CPGE,(0)}$ contribution cancels out for the D_{3h} symmetry. For $J^{CPGE,(1)}$, the additional mirror, σ_z does not have further constraints, so it reads,

$$\mathbf{j}^{CPGE,(1)} = i(T_{yxz} + T_{yzx})q_z \begin{pmatrix} -(E \times E^*)_y \\ (E \times E^*)_x \\ 0 \end{pmatrix} \propto \begin{pmatrix} -\sin \alpha \sin 2\theta \sin 2\phi \\ \cos \alpha \sin 2\theta \sin 2\phi \\ 0 \end{pmatrix} \quad (4.26)$$

In conclusion, under D_{3h} , $J^{CPGE,(0)}$ vanishes, and $J^{CPGE,(1)}$ changes sign upon switching the incident angle from ϕ to $-\phi$.

C_{3v} symmetry

As discussed above, $J^{CPGE,(0)}$ adopts the form,

$$\mathbf{j}^{CPGE,(0)} = i \begin{pmatrix} 0 & \gamma_{xy} & 0 \\ -\gamma_{xy} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} (\mathbf{E} \times \mathbf{E}^*) \propto \begin{pmatrix} -\sin \alpha \sin 2\theta \sin \phi \\ \cos \alpha \sin 2\theta \sin \phi \\ 0 \end{pmatrix} \quad (4.27)$$

which means it has a $\sin(\phi)$ dependence. $J^{CPGE,(1)}$ has the same form as in the case of D_{3h} symmetry.

Now we consider the geometry of a spiral stack of TMDC layers, with twist angles ~ 0.5 deg between each neighboring layers, and a total twist angle < 20 deg. This system has a chiral point group, C_3 . This is distinct from regular Bernal stacking of TMDC, which has a bulk symmetry of D_{6h} .

 C_3 symmetry

The absence of mirror symmetry M in this case allows more independent parameters in γ_{ij} , and $J^{CPGE,(0)}$ takes the form,

$$\gamma = \begin{pmatrix} \gamma_{xx} & \gamma_{xy} & 0 \\ -\gamma_{xy} & \gamma_{xx} & 0 \\ 0 & 0 & \gamma_{zz} \end{pmatrix} \quad (4.28)$$

$$\mathbf{j}^{CPGE,(0)} = i \begin{pmatrix} \gamma_{xx} & \gamma_{xy} & 0 \\ -\gamma_{xy} & \gamma_{xx} & 0 \\ 0 & 0 & \gamma_{zz} \end{pmatrix} (\mathbf{E} \times \mathbf{E}^*) \propto \begin{pmatrix} \cos \alpha \sin 2\theta \sin \phi \gamma_{xx} + \sin \alpha \sin 2\theta \sin \phi \gamma_{xy} \\ -\cos \alpha \sin 2\theta \sin \phi \gamma_{xy} + \sin \alpha \sin 2\theta \sin \phi \gamma_{xx} \\ \sin 2\theta \cos \phi \gamma_{zz} \end{pmatrix} \quad (4.29)$$

Therefore, upon the reduction of mirror symmetry, $J^{CPGE,(0)}$ still has $\sin(\phi)$ dependence.

On the other hand, more tensor elements in T_{ijkl} are allowed for $J^{CPGE,(1)}$, e.g., T_{yzx} , T_{yxy} . The complete form of the in-plane photocurrent response reads,

$$\begin{aligned}
\mathbf{j}_x^{CPGE,(1)} &\propto \sin(2\theta) \{ (T_{xxx}(\sin 2\alpha + \cos 2\alpha) \sin^2 \phi + [(T_{xyz} + T_{xzy}) \sin \alpha + \\
&\quad (T_{xxz} + T_{zxx}) \cos \alpha] \sin 2\phi) \} \\
\mathbf{j}_y^{CPGE,(1)} &\propto \sin(2\theta) \{ (T_{xxx}(\frac{\sqrt{3}}{2} \cos^2 \alpha - \sin 2\alpha) \sin^2 \phi + [-(T_{xyz} + T_{xzy}) \cos \alpha + \\
&\quad (T_{xxz} + T_{zxx}) \sin \alpha] \sin 2\phi) \}
\end{aligned} \tag{4.30}$$

Here, we find that $J^{CPGE,(1)}$ has a $\sin^2(\phi)$ part, which can be distinguished from the angular dependence (same sign at ϕ and $-\phi$) from all other terms.

Furthermore, this term is only dependent on the in-plane photon momentum, and originates directly from the twisted stacking induced mirror symmetry breaking. A prove is as follows, \mathbf{q} becomes $M\mathbf{q}$, $\mathbf{E} \times \mathbf{E}^*$ becomes $-M(\mathbf{E} \times \mathbf{E}^*)$, \mathbf{j} becomes $M\mathbf{j}$, so tensor element in T with subscripts in the same direction, i.e., T_{iii} would vanish, if there is a mirror perpendicular to it, i.e., M_j with $\epsilon_{ij} = 0$.

C_s symmetry

Consider the case where the rotation symmetry of spiral TMDC stack is extrinsically broken by strain, in-plane fields, all the tensor elements in γ_{ij} describing $J^{CPGE,(0)}$ will be nonzero. Especially, γ_{xz} and γ_{yz} will lead to terms dependent on $\cos \phi$. However, the angular dependence of $\mathbf{E} \times \mathbf{E}^*$, which is proportional to either $\cos \phi$ or $\sin \phi$, determines that the symmetric-of- ϕ part of $J^{CPGE,(0)}$ would reach its maximum at normal incidence. In comparison, $J^{CPGE,(1)} \sim \sin^2(\phi)$ vanishes at normal incidence and increases with ϕ . Consequently, external symmetry breaking induced $J^{CPGE,(0)}$ can be distinguished from $J^{CPGE,(1)}$ by this characteristic.

From the data shown in Fig. 1, where CPGE at $\pm\phi$ are of the same sign, and becomes much smaller at normal incidence, proves the existence of $J^{CPGE,(1)}$, and especially the part of $J^{CPGE,(1)}$ that is not allowed in C_{3v} monolayer WS_2 , nor in D_{3h} WS_2 multilayers, but appears only in the C_3 spiral stack.

There are many phenomena that arise from the breaking of degeneracy between left and right circularly polarized light in media, including rotation of polarization with propagation, e.g., optical activity, Faraday effect, and upon reflection, e.g., Kerr effect. Those phenomena are regarded as the most unambiguous and sensitive tools to probe symmetry breaking in condensed matter.

The optical gyrotropy is described by a first order in \mathbf{q} expansion of an antisymmetric tensor $\Gamma_{ij} = -\Gamma_{ji}$,

$$\Gamma_{ij}(\mathbf{q}) = \Gamma_{ij}(0) + \Gamma_{ijl}q_l + \dots \quad (4.31)$$

The gyrotropic magnetic effect (GME) coefficient can be written as a rank-two linear combination of optical gyrotropy tensor, e.g., $\alpha_{xx} = -\frac{i}{2}\Gamma_{yzx} + \frac{i}{2}\Gamma_{xyz} + \frac{i}{2}\Gamma_{xzy}$. It describes the rotation of polarization plane of light perpendicular to the quasi-2D slab.

Here, $\mathbf{j}^{CPGE,(1)}$ is a nonlinear optical analogue of GME, for its linear dependence on \mathbf{q} . It characterizes a dc current flowing perpendicular to the polarization plane of light, and its geometrical origin (stacking induced symmetry breaking) is reflected in its dependence on the photon momentum (incident angle).

4.2.2 Microscopic interpretation of optical responses in quasi-2D stacks

The tight binding Hamiltonian of a n-layer spiral stack can be written as,

$$H = \sum_{l=1}^n H_l + \sum_{l=1}^n (H_{l+1,l} + H_{l,l+1}) \quad (4.32)$$

where $H_l (l = 1, \dots, n)$ describe the isolated layers, and $H_{l,l'}$ describe the hopping of electrons from layer l' to layer l , which has $H_{l,l'} = H_{l',l}^\dagger$ is the unperturbed Hamiltonian. The assumption here is only closest layers are coupled to each other, because of the exponential suppression of the hopping integrals with distance.

Within each layer l , the Hamiltonian could be written as

$$H_l = \sum_{\mathbf{R}_{l\alpha}, \mathbf{R}'_{l\alpha'}} h_{\alpha\alpha'}^l(\mathbf{R}_l, \mathbf{R}'_{l'}) c_{l, \mathbf{R}_{l\alpha}}^\dagger c_{l, \mathbf{R}'_{l\alpha'}} \quad (4.33)$$

where $h_{\alpha\alpha'}^l$ are hopping parameters, c and c^\dagger are the creation and annihilation operator.

Between layer l and l' , the interlayer Hamiltonian reads

$$H_{l,l'} = \sum_{\mathbf{R}_{l\alpha}, \mathbf{R}'_{l'\beta}} h_{\alpha\beta}^{l,l'}(\mathbf{R}_l, \mathbf{R}'_{l'}) c_{l, \mathbf{R}_{l\alpha}}^\dagger c_{l', \mathbf{R}'_{l'\beta}} \quad (4.34)$$

where $h_{\alpha\beta}^{l,l'}$ are interlayer hopping terms.

The quasi-2D system is periodic and infinite in the (x,y) plane, but has open boundary in \hat{z} direction. Since the tight-binding Hamiltonian of a quasi-2D stack can be expanded under maximally localized Wannier functions $|\mathbf{R}_{l\alpha}\rangle$, where the position $\mathbf{R}_{l\alpha}$ runs over all orbital α in the layer $l(= 1..n)$, N is the number of monolayer unit cells in the whole system. The position operator is diagonalized in the Wannier basis as $\hat{r} |\mathbf{R}_{l\alpha}\rangle = r_{l\alpha} |\mathbf{R}_{l\alpha}\rangle$. The Bloch and Wannier functions are related by [10],

$$|\mathbf{k}_{l\alpha}\rangle = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{r}_{l\alpha}} |\mathbf{R}_{l\alpha}\rangle \quad (4.35)$$

where $\mathbf{k} = (k_x, k_y)$ is the two-dimensional Bloch wave vector. Therefore, the \hat{z} operator is well-defined in the Bloch basis. With cell-periodic wave function $u_{\mathbf{k}n}(\mathbf{r})$, the effective velocity operator \hat{v}_z can be written as,

$$(\hat{v}_z)_{nm} = \langle u_{\mathbf{k}n} | \hat{v}_z | u_{\mathbf{k}m} \rangle = \langle u_{\mathbf{k}n} | \frac{1}{i\hbar} [H, \hat{z}] | u_{\mathbf{k}m} \rangle = \frac{i}{\hbar} (\epsilon_n - \epsilon_m) \langle u_{\mathbf{k}n} | \hat{z} | u_{\mathbf{k}m} \rangle \quad (4.36)$$

It is off-diagonal. Similarly, the 'Berry connection' in the \hat{z} direction reads,

$$i \langle u_n | \nabla_z | u_m \rangle = \langle u_n | \hat{z} | u_m \rangle \quad (4.37)$$

Now, we can consider the vector potential of an electromagnetic wave as, $\mathbf{A}(\mathbf{r}, t) = \mathbf{A}(\mathbf{q}, \omega) e^{i(\mathbf{q}\cdot\mathbf{r}-\omega t)} + \text{c.c.}$.

The Coulomb gauge is adopted here, which is justified by $\nabla \cdot \mathbf{A} = 0$ for plane waves. Furthermore, the longitudinal field represented by the Coulomb potential created by the charges vanishes, $\phi = 0$. Therefore, the minimal coupling Hamiltonian $H = H(\mathbf{p} + e\mathbf{A})$ is valid.

$$H_{int,\omega} = \int d\mathbf{r} \mathbf{j}(\mathbf{r}) \cdot \mathbf{A}(\mathbf{r}, \omega) \quad (4.38)$$

$\mathbf{j}(\mathbf{r})$, the current operator at \mathbf{r} (where \mathbf{r}_j represents position of electron) reads,

$$\mathbf{j}(\mathbf{r}) = \frac{e}{2m} \sum_j [(\mathbf{p} + e\mathbf{A}(\mathbf{r}, t))\delta(\mathbf{r} - \mathbf{r}_j) + \delta(\mathbf{r} - \mathbf{r}_j)(\mathbf{p} + e\mathbf{A}(\mathbf{r}, t))] \quad (4.39)$$

It is a summation over all particles' velocities. The second quantized version of current operator can be rewritten as,

$$\mathbf{j}(\mathbf{r}) = \frac{-i\hbar e}{2m} [\Psi^\dagger(\mathbf{r})\nabla_{\mathbf{r}}\Psi(\mathbf{r}) - \Psi(\mathbf{r})\nabla_{\mathbf{r}}\Psi^\dagger(\mathbf{r})] - \frac{e^2}{m}\mathbf{A}(\mathbf{r}, t)\Psi^\dagger(\mathbf{r})\Psi(\mathbf{r}) \quad (4.40)$$

Since the kinetic momentum operator $\mathbf{P} = -i\hbar\nabla - e\mathbf{A}$ is a gauge invariant quantity, the current is also gauge invariant. The Fourier transform of the current operator has the form,

$$\mathbf{j}(\mathbf{q}) = \sum_{\alpha\beta} c_\alpha^\dagger c_\beta \int d^3r e^{-i\mathbf{q}\cdot\mathbf{r}} \left\{ \frac{-i\hbar e}{2m} [\psi_\alpha^*(\mathbf{r})\nabla_{\mathbf{r}}\psi_\beta(\mathbf{r}) - \psi_\alpha(\mathbf{r})\nabla_{\mathbf{r}}\psi_\beta^*(\mathbf{r})] - \frac{e^2}{m}\mathbf{A}(\mathbf{r}, t)\psi_\alpha^*(\mathbf{r})\psi_\beta(\mathbf{r}) \right\} \quad (4.41)$$

By constructing the creation and annihilation operators out of the Bloch eigenfunctions $\psi_{\mathbf{k}n}$ and field operators $\Psi(\mathbf{r})$,

$$\begin{aligned} c_{\mathbf{k}n} &= \int d^3r \psi_{\mathbf{k}n}^*(\mathbf{r})\Psi(\mathbf{r}) \\ c_{\mathbf{k}n}^\dagger &= \int d^3r \psi_{\mathbf{k}n}(\mathbf{r})\Psi^\dagger(\mathbf{r}) \end{aligned} \quad (4.42)$$

we get,

$$\mathbf{J} = \sum_{\mathbf{k}\mathbf{k}'n\mathbf{m}} \langle \psi_{\mathbf{k}n} | j(\mathbf{q}) | \psi_{\mathbf{k}'m} \rangle c_{\mathbf{k}'n}^\dagger c_{\mathbf{k}m} \quad (4.43)$$

The $j(\mathbf{q})$ operator would be,

$$j(\mathbf{q}) = \frac{e}{2} [\mathbf{v}^A e^{-i\mathbf{q}\cdot\mathbf{r}} + e^{-i\mathbf{q}\cdot\mathbf{r}} \mathbf{v}^A] \quad (4.44)$$

with the diagonal ($\delta_{\mathbf{k}\mathbf{k}'}$) velocity being $\mathbf{v}^A = \frac{\mathbf{p}}{m} + \frac{e\mathbf{A}(\mathbf{r},t)}{m}$.

The density matrix is defined as

$$\rho_{\mathbf{k}\mathbf{k}'nm} = \langle c_{\mathbf{k}'m}^\dagger c_{\mathbf{k}n} \rangle \quad (4.45)$$

In the Heisenberg picture,

$$\frac{\partial \rho_{\mathbf{k}\mathbf{k}'nm}}{\partial t} = \frac{1}{i\hbar} \langle [c_{\mathbf{k}'m}^\dagger c_{\mathbf{k}n}, H] \rangle \quad (4.46)$$

According to H , We proceed to expand the RHS into two parts. The first part is,

$$\begin{aligned} I_1 &= \frac{1}{i\hbar} \left\langle [c_{\mathbf{k}'m}^\dagger c_{\mathbf{k}n}, \sum_{\mathbf{q}\mathbf{r}} \epsilon_{\mathbf{q}\mathbf{r}} c_{\mathbf{q}\mathbf{r}}^\dagger c_{\mathbf{q}\mathbf{r}}] \right\rangle \\ &= \frac{1}{i\hbar} \epsilon_{\mathbf{q}\mathbf{r}} [\delta_{\mathbf{q}\mathbf{k}} \delta_{r\mathbf{n}} \langle c_{\mathbf{k}'m}^\dagger c_{\mathbf{q}\mathbf{r}} \rangle - \delta_{\mathbf{q}\mathbf{k}'} \delta_{m\mathbf{r}} \langle c_{\mathbf{q}\mathbf{r}}^\dagger c_{\mathbf{k}n} \rangle] \\ &= \frac{1}{i\hbar} (\epsilon_{\mathbf{k},n} - \epsilon_{\mathbf{k}'m}) \langle c_{\mathbf{k}'m}^\dagger c_{\mathbf{k}n} \rangle \\ &= \frac{1}{i\hbar} (\epsilon_{\mathbf{k},n} - \epsilon_{\mathbf{k}'m}) \rho_{\mathbf{k}\mathbf{k}'nm} \end{aligned} \quad (4.47)$$

The second part reads,

$$\begin{aligned}
I_2 &= \frac{1}{i\hbar} \left\langle [c_{\mathbf{k}'m}^\dagger c_{\mathbf{k}n}, e\mathbf{A}(\mathbf{r}, t) \cdot \sum_{\mathbf{q}\mathbf{q}'\mathbf{r}\mathbf{r}'} \tilde{\mathbf{v}}_{\mathbf{q}'\mathbf{q}\mathbf{r}'\mathbf{r}} c_{\mathbf{q}'r'}^\dagger c_{\mathbf{q}\mathbf{r}}] \right\rangle \\
&= \frac{e}{i\hbar} \mathbf{A}(\mathbf{r}, t) \cdot \sum_{\mathbf{q}\mathbf{q}'\mathbf{r}\mathbf{r}'} \tilde{\mathbf{v}}_{\mathbf{q}'\mathbf{q}\mathbf{r}'\mathbf{r}} [\delta_{\mathbf{q}'\mathbf{k}} \delta_{\mathbf{r}'n} \langle c_{\mathbf{k}'m}^\dagger c_{\mathbf{q}\mathbf{r}} \rangle - \delta_{\mathbf{q}\mathbf{k}'} \delta_{\mathbf{r}m} \langle c_{\mathbf{q}'r'}^\dagger c_{\mathbf{k}n} \rangle] \\
&= \frac{e}{i\hbar} \mathbf{A}(\mathbf{r}, t) \cdot \sum_{\mathbf{q}\mathbf{q}'\mathbf{r}\mathbf{r}'} \tilde{\mathbf{v}}_{\mathbf{k}\mathbf{q}\mathbf{n}\mathbf{r}} \langle c_{\mathbf{k}'m}^\dagger c_{\mathbf{q}\mathbf{r}} \rangle - \langle c_{\mathbf{q}\mathbf{r}}^\dagger c_{\mathbf{k}n} \rangle \\
&= \frac{e}{i\hbar} \mathbf{A}(\mathbf{r}, t) \cdot (\mathbf{v}\rho - \rho\mathbf{v})_{\mathbf{k}\mathbf{k}'\mathbf{n}\mathbf{m}}
\end{aligned} \tag{4.48}$$

The last term adopts a relaxation time approximation, subtle gauge problem with the relaxation time is not considered here. Therefore, we obtain the equation of motion as,

$$\begin{aligned}
i\hbar \frac{\partial \rho_{\mathbf{k}\mathbf{k}'\mathbf{n}\mathbf{m}}}{\partial t} &= \\
&(\epsilon_{\mathbf{k},n} - \epsilon_{\mathbf{k}'m}) \rho_{\mathbf{k}\mathbf{k}'\mathbf{n}\mathbf{m}} + e\mathbf{A}(\mathbf{r}, t) \cdot \sum_{\mathbf{q}'\mathbf{r}} \tilde{\mathbf{v}}_{\mathbf{k}\mathbf{q}'\mathbf{n}\mathbf{r}} \rho_{\mathbf{q}'\mathbf{k}'\mathbf{r}\mathbf{m}} - \rho_{\mathbf{k}\mathbf{q}'\mathbf{n}\mathbf{r}} \tilde{\mathbf{v}}_{\mathbf{q}'\mathbf{k}'\mathbf{r}\mathbf{m}} - \frac{i\hbar(\rho_{\mathbf{k}\mathbf{k}'\mathbf{n}\mathbf{m}} - \rho_{\mathbf{k}\mathbf{k}'\mathbf{n}\mathbf{m}}^{(0)})}{\tau}
\end{aligned} \tag{4.49}$$

and by expanding into different orders of \mathbf{A} ,

$$\rho_{\mathbf{k}\mathbf{k}'\mathbf{n}\mathbf{m}} = \rho_{\mathbf{k}\mathbf{k}'\mathbf{n}\mathbf{m}}^{(0)} + \rho_{\mathbf{k}\mathbf{k}'\mathbf{n}\mathbf{m}}^{(1)} + \rho_{\mathbf{k}\mathbf{k}'\mathbf{n}\mathbf{m}}^{(2)} + \dots \tag{4.50}$$

the zeroth order density matrix is,

$$\rho_{\mathbf{k}\mathbf{k}'\mathbf{n}\mathbf{m}}^{(0)} = \frac{1}{1 + \exp\left\{\left(\frac{\epsilon_{\mathbf{k},n} - \epsilon_F}{kT}\right)\right\}} \delta_{\mathbf{k}\mathbf{k}'} \delta_{\mathbf{n}\mathbf{m}} \tag{4.51}$$

where ϵ_F is the Fermi energy. The first order $\rho^{(1)} \sim A(\mathbf{q}_1, \omega_1)$ reads,

$$\rho_{\mathbf{k}\mathbf{k}'\mathbf{n}\mathbf{m}}^{(1)} = e \frac{e^{-i\omega_1 t} \mathbf{A} \cdot \tilde{\mathbf{v}}_{\mathbf{k}\mathbf{k}'\mathbf{n}\mathbf{m}}}{\epsilon_{\mathbf{k}'m} - \epsilon_{\mathbf{k}n} + \hbar\omega_1 + i\hbar/\tau} (f_{\mathbf{k}'m} - f_{\mathbf{k}n}) \tag{4.52}$$

$f_{\mathbf{k}n} = \rho^{(0)} \delta_{\mathbf{k}\mathbf{k}'} \delta_{\mathbf{n}\mathbf{m}}$ is the Fermi-Dirac distribution.

The second order density matrix $\rho^{(2)} \sim A(\mathbf{q}_1, \omega_1)A(\mathbf{q}_2, \omega_2)$ can be written as,

$$\begin{aligned} \rho_{\mathbf{k}\mathbf{k}'nm}^{(2)} = & e^2 \frac{e^{-i(\omega_1+\omega_2)t} A_\gamma}{\epsilon_{\mathbf{k}'m} - \epsilon_{\mathbf{k}n} + \hbar(\omega_1 + \omega_2) + i\hbar/\tau} \\ & \times \sum_{\mathbf{q}'r} \left[\frac{\tilde{v}_{\mathbf{k}\mathbf{q}'nr}^\gamma A_\beta \tilde{v}_{\mathbf{q}'\mathbf{k}'rm}^\beta}{\epsilon_{\mathbf{k}'m} - \epsilon_{\mathbf{q}'r} + \hbar\omega_1 + i\hbar/\tau} (f_{\mathbf{k}'m} - f_{\mathbf{q}'r}) - \frac{A_\beta \tilde{v}_{\mathbf{k}\mathbf{q}'nr}^\beta \tilde{v}_{\mathbf{q}'\mathbf{k}'rm}^\gamma}{\epsilon_{\mathbf{q}'r} - \epsilon_{\mathbf{k}n} + \hbar\omega_1 + i\hbar/\tau} (f_{\mathbf{q}'r} - f_{\mathbf{k}n}) \right] \end{aligned} \quad (4.53)$$

The general velocity operator $\tilde{v}_{\mathbf{k}\mathbf{k}'nm}$ is an anticommutator of velocity matrix $v_{\mathbf{k}nm}$ and $e^{i\mathbf{q}\cdot\mathbf{r}}$.

The matrix elements of the velocity operator v in the Bloch basis reads,

$$\begin{aligned} v_{\mathbf{k}\mathbf{k}'nm} &= \langle n, \mathbf{k} | \frac{\hat{p}}{m} | m, \mathbf{k}' \rangle = \frac{1}{V} \int d^3r \psi_{\mathbf{k}n}^*(\mathbf{r}) \left(\frac{-i\hbar}{m} \nabla \right) \psi_{\mathbf{k}'m}(\mathbf{r}) \\ &= \frac{-i\hbar}{m} \frac{1}{V} \int d^3r e^{-i\mathbf{k}\cdot\mathbf{r}} e^{i\mathbf{k}'\cdot\mathbf{r}} u_{\mathbf{k}n}^*(\mathbf{r}) (i\mathbf{k} + \nabla) u_{\mathbf{k}'m}(\mathbf{r}) \\ &= \frac{-i\hbar}{m} \frac{1}{V} \sum_{\mathbf{R}} e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{R}} \int d^3r u_{\mathbf{k}n}^*(\mathbf{r}) (i\mathbf{k} + \nabla) u_{\mathbf{k}'m}(\mathbf{r}) \quad (4.54) \\ &= \frac{-i\hbar}{m} \delta_{\mathbf{k}'\mathbf{k}} \frac{1}{v_c} \int_{uc} d^3r u_{\mathbf{k}n}^*(\mathbf{r}) (i\mathbf{k} + \nabla) u_{\mathbf{k}'m}(\mathbf{r}) \\ &= \delta_{\mathbf{k}\mathbf{k}'} v_{\mathbf{k}nm} \end{aligned}$$

The above expression can be evaluated as,

$$\begin{aligned} \nabla_{\mathbf{k}} \langle u_{\mathbf{k}n} | H(\mathbf{k}) | u_{\mathbf{k}'m} \rangle &= \langle u_{\mathbf{k}n} | \nabla_{\mathbf{k}} H(\mathbf{k}) | u_{\mathbf{k}'m} \rangle + \langle \nabla_{\mathbf{k}} u_{\mathbf{k}n} | H(\mathbf{k}) | u_{\mathbf{k}'m} \rangle + \langle u_{\mathbf{k}n} | H(\mathbf{k}) | \nabla_{\mathbf{k}} u_{\mathbf{k}'m} \rangle \\ &= \delta_{\mathbf{k}\mathbf{k}'} \epsilon_{\mathbf{k}'m} \langle \nabla_{\mathbf{k}} u_{\mathbf{k}n} | u_{\mathbf{k}'m} \rangle + \delta_{\mathbf{k}\mathbf{k}'} \epsilon_{\mathbf{k}n} \langle u_{\mathbf{k}n} | \nabla_{\mathbf{k}} u_{\mathbf{k}'m} \rangle + \frac{\hbar^2}{m} + \hbar v_{\mathbf{k}\mathbf{k}'nm} \end{aligned} \quad (4.55)$$

recall that $\nabla_{\mathbf{k}} \langle u_{\mathbf{k}n} | H(\mathbf{k}) | u_{\mathbf{k}'m} \rangle = \delta_{nm} \delta_{\mathbf{k}\mathbf{k}'} \nabla_{\mathbf{k}} \epsilon_{\mathbf{k}n}$, and $\langle u_{\mathbf{k}n} | \nabla_{\mathbf{k}} u_{\mathbf{k}'m} \rangle + \langle \nabla_{\mathbf{k}} u_{\mathbf{k}n} | u_{\mathbf{k}'m} \rangle = 0$, we get the velocity operator,

$$\mathbf{v}_{\mathbf{k}nm} = \frac{1}{\hbar} [\nabla_{\mathbf{k}} \epsilon_{\mathbf{k}n} \delta_{nm} + \mathbf{r}_{\mathbf{k}nm}^\alpha (\epsilon_{\mathbf{k}m} - \epsilon_{\mathbf{k}n})] \quad (4.56)$$

with $r_{nm} = i \langle u_n | \nabla_{\mathbf{k}} u_m \rangle$ being the Berry connection. On the other hand, the plane wave operator, $e^{i\mathbf{q}\cdot\mathbf{r}}$ can be simplified,

$$\begin{aligned}
\langle n, \mathbf{k} | e^{i\mathbf{q}\cdot\mathbf{r}} | m, \mathbf{k}' \rangle &= \frac{1}{V} \int d^3\mathbf{r} e^{i(\mathbf{k}'+\mathbf{q}-\mathbf{k})\cdot\mathbf{r}} u_{\mathbf{k}n}^*(\mathbf{r}) u_{\mathbf{k}'m}(\mathbf{r}) \\
&= \frac{1}{V} \int d^3\mathbf{r} u_{\mathbf{k}n}^*(\mathbf{r}) u_{\mathbf{k}'m}(\mathbf{r}) \sum_{\mathbf{R}} e^{i(\mathbf{k}'+\mathbf{q}-\mathbf{k})\cdot\mathbf{R}} \\
&= \frac{1}{v_c} \int_{uc} d^3\mathbf{r} u_{\mathbf{k}n}^*(\mathbf{r}) u_{\mathbf{k}'m}(\mathbf{r}) \delta_{\mathbf{k}',\mathbf{k}-\mathbf{q}} \\
&= \delta_{\mathbf{k}',\mathbf{k}-\mathbf{q}} \langle u_{\mathbf{k}n} | u_{\mathbf{k}-\mathbf{q}m} \rangle
\end{aligned} \tag{4.57}$$

where the lattice sum rule is adopted. Then, the anticommutator of v and $e^{i(\mathbf{q}\cdot\mathbf{r})}$ reads,

$$\begin{aligned}
\tilde{v}_{\mathbf{k}\mathbf{k}'nm} &= \frac{1}{2} \langle n, \mathbf{k} | \{v, e^{i\mathbf{q}\cdot\mathbf{r}}\} | m, \mathbf{k}' \rangle \\
&= \frac{1}{2} \sum_{\mathbf{k}''l} (\langle n, \mathbf{k} | v | l, \mathbf{k}'' \rangle \langle l, \mathbf{k}'' | e^{i\mathbf{q}\cdot\mathbf{r}} | m, \mathbf{k}' \rangle + \langle n, \mathbf{k} | e^{i\mathbf{q}\cdot\mathbf{r}} | l, \mathbf{k}'' \rangle \langle l, \mathbf{k}'' | v | m, \mathbf{k}' \rangle) \\
&= \frac{1}{2} \left[\sum_l v_{\mathbf{k}nl} \langle u_{\mathbf{k}l} | u_{(\mathbf{k}-\mathbf{q})m} \rangle + \langle u_{\mathbf{k}n} | u_{(\mathbf{k}-\mathbf{q})l} \rangle v_{(\mathbf{k}-\mathbf{q})lm} \right] \delta_{\mathbf{k}',\mathbf{k}-\mathbf{q}}
\end{aligned} \tag{4.58}$$

Another way of derivation would be

$$\begin{aligned}
\tilde{v}_{\mathbf{k}\mathbf{k}'nm} &= \langle n, \mathbf{k} | \frac{\hat{p}}{m} | m, \mathbf{k}' \rangle = \frac{1}{V} \int d^3\mathbf{r} \psi_{\mathbf{k}n}^*(\mathbf{r}) \left(\frac{-i\hbar}{2m} (\nabla e^{i\mathbf{q}\cdot\mathbf{r}} + e^{i\mathbf{q}\cdot\mathbf{r}} \nabla) \right) \psi_{\mathbf{k}'m}(\mathbf{r}) \\
&= \frac{-i\hbar}{2m} \frac{1}{V} \int d^3\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} e^{i\mathbf{k}'\cdot\mathbf{r}} u_{\mathbf{k}n}^*(\mathbf{r}) (i\mathbf{k}' + i\mathbf{q} + \nabla + i\mathbf{k}' + \nabla) u_{\mathbf{k}'m}(\mathbf{r}) \\
&= \frac{-i\hbar}{m} \frac{1}{V} \sum_{\mathbf{R}} e^{i(\mathbf{k}'-\mathbf{k}+\mathbf{q})\cdot\mathbf{R}} \int d^3\mathbf{r} u_{\mathbf{k}n}^*(\mathbf{r}) (i(\mathbf{k}' + \frac{\mathbf{q}}{2}) + \nabla) u_{\mathbf{k}'m}(\mathbf{r}) \\
&= \frac{-i\hbar}{m} \delta_{\mathbf{k}',(\mathbf{k}-\mathbf{q})} \frac{1}{v_c} \int_{uc} d^3\mathbf{r} u_{\mathbf{k}n}^*(\mathbf{r}) (i(\mathbf{k}' + \frac{\mathbf{q}}{2}) + \nabla) u_{\mathbf{k}'m}(\mathbf{r}) \\
&= \langle n, \mathbf{k} | v_{\mathbf{k}-\frac{\mathbf{q}}{2}} | m, \mathbf{k} - \mathbf{q} \rangle
\end{aligned} \tag{4.59}$$

It can be seen that the $\tilde{v}_{\mathbf{k}\mathbf{k}'\mathbf{q}}$ operator only correlates \mathbf{k} and $\mathbf{k} - \mathbf{q}$. In the long wavelength limit, $q \ll q_F$, the above equation can be simplified by only considering terms up to first order of \mathbf{q} . In the leading order of \mathbf{q} , we can expand $u_{\mathbf{k}-\mathbf{q}}(\mathbf{r}) \sim u_{\mathbf{k}n}(\mathbf{r}) - \mathbf{q} \cdot (\nabla_{\mathbf{k}} u_{\mathbf{k}n})$. With this expansion,

we can write it in terms of the Berry connection,

$$\langle u_{\mathbf{k}n} | u_{\mathbf{k}-\mathbf{q}m} \rangle = \delta_{nm} + i\mathbf{q} \cdot \mathbf{r}_{\mathbf{k}nm} \quad (4.60)$$

$\mathbf{r}_{\mathbf{k}nm}$ is the Berry connection. The result follows,

$$\tilde{v}^\alpha(q_\beta) = \frac{1}{2} \langle n | \{ \tilde{v}^\alpha, e^{iq^\beta r^\beta} \} | m \rangle = v_{\alpha, nm} + \frac{i}{2} q^\beta \{ v_\alpha, r_\beta \}_{nm} - \frac{1}{2} q^\beta \partial_\beta v_{\alpha, nm} \quad (4.61)$$

where the first term is the conventional velocity, and the latter two terms are akin to the covariant derivative in its form. The diamagnetic part $\mathbf{v} \sim \mathbf{A}$ does not contribute to $(\omega, -\omega)$ response, since $\rho^{(1)}$ is off-diagonal, $\text{Tr}[\rho^{(1)}, A]$ vanishes.

4.2.3 Symmetry analysis and the circular dichorism

With $\mathbf{E}(\omega) = i\omega\mathbf{A}(\omega)$, we can define the conductivity tensor, $\sigma_{\alpha\beta\gamma}(\mathbf{q}_1, \omega_1; \mathbf{q}_2, \omega_2)$, by,

$$j_\alpha^{(2)}(\mathbf{q}_3, \omega_3) = \sum_{\beta\gamma} \sigma_{\alpha\beta\gamma} E_\beta E_\gamma = \sum_{\beta\gamma} \omega_1 \omega_2 \sigma_{\alpha\beta\gamma}(\mathbf{q}_1, \omega_1; \mathbf{q}_2, \omega_2) A_\beta(\mathbf{q}_1, \omega_1) A_\gamma(\mathbf{q}_2, \omega_2) \quad (4.62)$$

Here α, β, γ are Cartesian indices and α indicates the direction of the current, while β and γ are the polarization of the incident optical electric field. With the derived generalized velocity operator and

density matrix, we can write the nonlinear optical response as,

$$\begin{aligned}
j_{\alpha}^{(2)}(\mathbf{q}_3, \omega_3; \mathbf{q}_1, \omega_1, \mathbf{q}_2, \omega_2) &= e \sum_{\mathbf{k}\mathbf{k}'nm} \tilde{v}_{\mathbf{k}\mathbf{k}'nm}^{\alpha} \rho_{\mathbf{k}'kmn}^{(2)} \\
&= e \sum_{\mathbf{k}nmr} \sum_{\pm\beta\pm\gamma} \rho_{\mathbf{k}(\mathbf{k}-\mathbf{q}_1-\mathbf{q}_2)nm}^{(2)} \tilde{v}_{(\mathbf{k}-\mathbf{q}_1-\mathbf{q}_2)kmn}^{\alpha} \\
&= e^3 \sum_{\mathbf{k}nm} \sum_{\pm\beta\pm\gamma} \frac{e^{-i(\omega_1+\omega_2)t} A_{\gamma} A_{\beta} \tilde{v}_{(\mathbf{k}-\mathbf{q}_1-\mathbf{q}_2)kmn}^{\alpha}}{\epsilon_{(\mathbf{k}-\mathbf{q}_1-\mathbf{q}_2)m} - \epsilon_{\mathbf{k}n} + \hbar(\omega_1 + \omega_2) + 2i\hbar/\tau} \\
&\quad \times \left[\frac{\tilde{v}_{\mathbf{k}(\mathbf{k}-\mathbf{q}_2)nr}^{\gamma} \tilde{v}_{(\mathbf{k}-\mathbf{q}_2)(\mathbf{k}-\mathbf{q}_2-\mathbf{q}_1)rm}^{\beta}}{\epsilon_{(\mathbf{k}-\mathbf{q}_2-\mathbf{q}_1)m} - \epsilon_{(\mathbf{k}-\mathbf{q}_2)r} + \hbar\omega_1 + i\hbar/\tau} (f_{(\mathbf{k}-\mathbf{q}_2-\mathbf{q}_1)m} - f_{(\mathbf{k}-\mathbf{q}_2)r}) \right. \\
&\quad \left. - \frac{\tilde{v}_{\mathbf{k}(\mathbf{k}-\mathbf{q}_1)nr}^{\beta} \tilde{v}_{(\mathbf{k}-\mathbf{q}_1)(\mathbf{k}-\mathbf{q}_2-\mathbf{q}_1)rm}^{\gamma}}{\epsilon_{(\mathbf{k}-\mathbf{q}_1)r} - \epsilon_{\mathbf{k}n} + \hbar\omega_1 + i\hbar/\tau} (f_{(\mathbf{k}-\mathbf{q}_1)r} - f_{\mathbf{k}n}) \right]
\end{aligned} \tag{4.63}$$

It includes summation over $\pm\omega_1(\pm\mathbf{q}_1)$, $\pm\omega_2(\pm\mathbf{q}_2)$, and $\gamma \iff \beta$. Specifically, the dc photocurrent response under a monochromatic field $\mathbf{A}(\omega, \mathbf{q})$ would be,

$$\begin{aligned}
j_{\alpha}^{(2,dc)}(\mathbf{q} - \mathbf{q}, \omega - \omega) &= e^3 \delta_{\mathbf{q}'} \sum_{\mathbf{k}nmr} \sum_{\pm s, \gamma \iff \beta} \frac{A_{\gamma} A_{\beta} \tilde{v}_{\mathbf{k}kmn}^{\alpha}}{\epsilon_{\mathbf{k}m} - \epsilon_{\mathbf{k}n} + 2i\hbar/\tau} \\
&\quad \times \left[\frac{\tilde{v}_{\mathbf{k}(\mathbf{k}-s\mathbf{q})nr}^{\gamma} \tilde{v}_{(\mathbf{k}-s\mathbf{q})krm}^{\beta}}{\epsilon_{\mathbf{k}m} - \epsilon_{(\mathbf{k}-s\mathbf{q})r} - s\hbar\omega + i\hbar/\tau} (f_{\mathbf{k}m} - f_{(\mathbf{k}-s\mathbf{q})r}) \right. \\
&\quad \left. - \frac{\tilde{v}_{\mathbf{k}(\mathbf{k}+s\mathbf{q})nr}^{\beta} \tilde{v}_{(\mathbf{k}+s\mathbf{q})krm}^{\gamma}}{\epsilon_{(\mathbf{k}+s\mathbf{q})r} - \epsilon_{\mathbf{k}n} - s\hbar\omega + i\hbar/\tau} (f_{(\mathbf{k}+s\mathbf{q})r} - f_{\mathbf{k}n}) \right]
\end{aligned} \tag{4.64}$$

where the summation $s = \pm 1$ incorporates $(\omega, -\omega)$ and $(-\omega, \omega)$ contributions. $\tilde{v}_{\mathbf{k}kmn}^{\alpha}$ reduces to velocity matrix $v_{\mathbf{k}nm}$. Subsequently, $\sigma_{\alpha\beta\gamma}(\mathbf{q}, \omega, -\mathbf{q}, -\omega)$ would be,

$$\begin{aligned}
\sigma_{\alpha\beta\gamma}(\mathbf{q}, \omega, -\mathbf{q}, -\omega) &= \frac{e^3}{\omega^2} \int_{BZ} d\mathbf{k} \sum_{nmr} \sum_s \frac{v_{\mathbf{k}mn}^{\alpha}}{\epsilon_{\mathbf{k}m} - \epsilon_{\mathbf{k}n} + 2i\hbar/\tau} \\
&\quad \times \left[\frac{\tilde{v}_{\mathbf{k}(\mathbf{k}-s\mathbf{q})nr}^{\gamma} \tilde{v}_{(\mathbf{k}-s\mathbf{q})krm}^{\beta}}{\epsilon_{\mathbf{k}m} - \epsilon_{(\mathbf{k}-s\mathbf{q})r} - s\hbar\omega + i\hbar/\tau} (f_{\mathbf{k}m} - f_{(\mathbf{k}-s\mathbf{q})r}) \right. \\
&\quad \left. - \frac{\tilde{v}_{\mathbf{k}(\mathbf{k}+s\mathbf{q})nr}^{\beta} \tilde{v}_{(\mathbf{k}+s\mathbf{q})krm}^{\gamma}}{\epsilon_{(\mathbf{k}+s\mathbf{q})r} - \epsilon_{\mathbf{k}n} - s\hbar\omega + i\hbar/\tau} (f_{(\mathbf{k}+s\mathbf{q})r} - f_{\mathbf{k}n}) \right]
\end{aligned} \tag{4.65}$$

This is the major result of this section. When $q \sim 0$, the second order dc conductivity recovers the result of quadratic response theory proposed by von Baltz and Kraut.

$$\begin{aligned} \sigma_{\alpha\beta\gamma} = & \frac{e^3}{\omega^2} \int_{BZ} d\mathbf{k} \sum_{nmr} \sum_s \frac{v_{mn}^\alpha}{\epsilon_m - \epsilon_n + 2i\hbar/\tau} \\ & \times \left[\frac{v_{nr}^\gamma v_{rm}^\beta}{\epsilon_m - \epsilon_r - s\hbar\omega + i\hbar/\tau} (f_m - f_r) - \frac{v_{nr}^\beta v_{rm}^\gamma}{\epsilon_r - \epsilon_n - s\hbar\omega + i\hbar/\tau} (f_r - f_n) \right] \end{aligned} \quad (4.66)$$

In the small q limit, we evaluate the first order in q terms in the conductivity tensor, $\sigma_{\alpha\beta\gamma}^{(1)}$.

(1) The perturbation on the energy denominator gives,

$$\frac{1}{\epsilon_{\mathbf{k}+q\mathbf{r}} - \epsilon_{\mathbf{k}n} - \hbar\omega + i\hbar/\tau} \approx \frac{1}{\epsilon_{\mathbf{k}r} - \epsilon_{\mathbf{k}n} - \hbar\omega + i\hbar/\tau} - q_\eta \frac{\partial \epsilon_{\mathbf{k}r}}{\partial k_\eta} \frac{1}{(\epsilon_{\mathbf{k}r} - \epsilon_{\mathbf{k}n} - \hbar\omega + i\hbar/\tau)^2} \quad (4.67)$$

(2) The perturbation on the Fermi-Dirac distribution,

$$f_{\mathbf{k}+q\mathbf{r}} - f_{\mathbf{k}n} \approx f_{\mathbf{k}r} - f_{\mathbf{k}n} + q_\eta \frac{\partial f_{\mathbf{k}r}}{\partial k_\eta} \quad (4.68)$$

We can then combine these two parts, and by defining their product as a function \tilde{D} ,

$$\tilde{D}_{\mathbf{k}'\mathbf{k}r\mathbf{n}}(\omega) = \frac{f_{\mathbf{k}'r} - f_{\mathbf{k}n}}{\epsilon_{\mathbf{k}'r} - \epsilon_{\mathbf{k}n} - \hbar\omega + i\hbar/\tau} \quad (4.69)$$

We get,

$$\tilde{D}_{(\mathbf{k}+q\boldsymbol{\eta})\mathbf{k}r\mathbf{n}}(\omega) \approx D_{\mathbf{k}r\mathbf{n}} + \left(\frac{\partial f_{\mathbf{k}r}}{\partial \epsilon_\eta} - \frac{1}{\epsilon_{\mathbf{k}r} - \epsilon_{\mathbf{k}n} - \hbar\omega + i\hbar/\tau} \right) q_\eta \cdot \frac{\partial \epsilon_{\mathbf{k}r}}{\partial k_\eta} D_{\mathbf{k}r\mathbf{n}} \quad (4.70)$$

With the above, we can substitute back into the equation of conductivity to arrive at,

$$\begin{aligned} \sigma_{\alpha\beta\gamma} = & \frac{e^3}{\omega^2} q_\eta \int_{BZ} d\mathbf{k} \sum_{nmr} \sum_{\pm s} \frac{v_{mn}^\alpha [v_{nr}^\gamma v_{rm}^\beta D_{mr}(\omega) - v_{nr}^\beta v_{rm}^\gamma D_{rn}(\omega)]}{\epsilon_m - \epsilon_n + 2i\hbar/\tau} \\ & \left(\frac{\partial f_r}{\partial \epsilon_\eta} - \frac{1}{\epsilon_{\mathbf{k}r} - \epsilon_{\mathbf{k}n} - \hbar\omega + i\hbar/\tau} \right) \frac{\partial \epsilon_r}{\partial k_\eta} \end{aligned} \quad (4.71)$$

When we set $n = m$, the injection current piece is obtained,

$$\begin{aligned}
\sigma_{\alpha\beta\gamma}^{(1),I} &= \frac{-i\tau e^3}{2\hbar\omega^2} q_\eta \int_{BZ} d\mathbf{k} \sum_{nr} \sum_{\pm s} v_{rr}^\eta v_{nn}^\alpha [v_{nr}^\gamma v_{rn}^\beta D_{nr}(\omega) - v_{nr}^\beta v_{rn}^\gamma D_{rn}(\omega)] \\
&\quad \left(\frac{\partial f_r}{\partial \epsilon_\eta} - \frac{1}{\epsilon_{\mathbf{k}r} - \epsilon_{\mathbf{k}n} - \hbar\omega + i\hbar/\tau} \right) \frac{\partial \epsilon_r}{\partial k_\eta} \\
&= \frac{\pi\tau e^3}{2\hbar^2\omega^2} q_\eta \int_{BZ} d\mathbf{k} \sum_{nr} \{ v_{nn}^\alpha v_{rr}^\eta \left(\frac{\partial f_r}{\partial \epsilon_\eta} - \frac{1}{\epsilon_{\mathbf{k}r} - \epsilon_{\mathbf{k}n} - \hbar\omega + i\hbar/\tau} \right) \right. \\
&\quad \left. - v_{rr}^\eta v_{nn}^\alpha \left(\frac{\partial f_n}{\partial \epsilon_\eta} - \frac{1}{\epsilon_{\mathbf{k}r} - \epsilon_{\mathbf{k}n} - \hbar\omega + i\hbar/\tau} \right) \right\} (v_{nr}^\gamma v_{rn}^\beta + v_{nr}^\beta v_{rn}^\gamma) (f_r - f_n) \delta(\epsilon_n - \epsilon_r - \hbar\omega)
\end{aligned} \tag{4.72}$$

Different from normal injection current which contributes only to CPGE, $\sigma_{\alpha\beta\gamma}^{(1),I}$ is real, and is hence associated with linearly polarized light (LPGE). The quantum metrics tensor $Q_{nm} = r_{nm}^\alpha r_{mn}^\beta + r_{nm}^\beta r_{mn}^\alpha$ has $Q_{nm}(-\mathbf{k}) = Q_{mn}(\mathbf{k})$. The constraint from \mathcal{T} and \mathcal{I} are the same, so the system need not to be inversion-broken. Furthermore, the vanishing dispersion of bands in \hat{z} indicate that q_z would not appear in this term.

(3) The perturbation on the velocity matrix gives,

$$\tilde{v}_{\mathbf{k}(\mathbf{k}+q_\eta)nr}^\alpha \approx v_{nr}^\beta + \frac{i}{2} q_\eta \{v^\alpha, r^\eta\}_{nr} - \frac{1}{2} q_\eta \partial_\eta v_{nr}^\alpha \tag{4.73}$$

Specifically, for light propagating perpendicular to the 2D plane, i.e., $\mathbf{q} = q_z \hat{z}$, the equation becomes:

$$\tilde{v}_{\mathbf{k}(\mathbf{k}+q_z)nr}^\beta \approx v_{nr}^\beta - \frac{i}{2} q_z \sum_m \{v_{nm}^\alpha, \hat{z}_{mr}\} \tag{4.74}$$

For simplicity, we define an operator $j^\alpha = \frac{1}{2} \{v^\alpha, \hat{z}\}$. The injection current piece reads:

$$\sigma_{\alpha\beta\gamma}^{(1),II} = \frac{-\tau e^3}{2\hbar\omega^2} q_z \int_{BZ} d\mathbf{k} \sum_{nr} (v_{nn}^\alpha - v_{rr}^\alpha) [v_{nr}^\gamma j_{rn}^\beta - j_{nr}^\gamma v_{rn}^\beta] (D_{nr}(\omega) - D_{rn}(\omega)) \tag{4.75}$$

Since $\hat{z}_{\mathbf{k}nm} = (\hat{z}_{\mathbf{k}mn})^*$ and $\hat{v}_{\mathbf{k}nm} = (\hat{v}_{\mathbf{k}mn})^*$, we have $\hat{j}_{\mathbf{k}nm} = (\hat{j}_{\mathbf{k}mn})^*$. Also, in the clean limit, we have,

$$D_{nr}(\omega) = P\left(\frac{f_n - f_r}{\epsilon_n - \epsilon_r - \hbar\omega}\right) + i\pi\delta(\epsilon_n - \epsilon_r - \hbar\omega)(f_n - f_r) \quad (4.76)$$

so that $D_{nr}(\omega) = D_{rn}(-\omega)^*$. Therefore, $\sigma_{\alpha\beta\gamma}^{(1),II}$ is real, and this term contributes to LPGE. On the other hand, if the wavevector of light is partially in-plane, i.e., $\mathbf{q} = (q_x, q_y)$, then in the above equation. \hat{z}_{nm} is replaced by \hat{r}_{nm} . The integrand has, $(vj - jv)_{\mathbf{k}} = -(vj - jv)_{-\mathbf{k}}$, it obeys time reversal symmetry \mathcal{T} , and has no requirement on \mathcal{I} .

Having considered the terms with $n = m$ in Eqn. 4.65, or the terms related to the definition of injection current, we find that those terms would not contribute to CPGE, so now we will analyze terms related to "shift current" from the $n \neq m$ terms. First, we consider the covariant derivative of velocity operator,

$$\begin{aligned} (\nabla_{\mathbf{k}}\mathbf{v})_{nm} &= \nabla_{\mathbf{k}}\mathbf{v}_{nm} - i[\mathbf{r}, \mathbf{v}]_{nm} \\ &= i \sum_{r \neq n, r \neq m} \mathbf{v}_{nr}\mathbf{r}_{rm} - \mathbf{r}_{nr}\mathbf{v}_{rm} + \nabla_{\mathbf{k}}\mathbf{v}_{nm} - i\mathbf{v}_{nm}(\mathbf{r}_{nn} - \mathbf{r}_{mm}) \end{aligned} \quad (4.77)$$

On the other hand, $(\nabla_{\mathbf{k}}\mathbf{v})_{nm} = [\mathbf{D}, \mathbf{v}]_{nm} = \frac{\hbar}{m}\delta_{nm}$. Therefore, When $n \neq m$, we have,

$$\begin{aligned} &\sum_{r \neq n, r \neq m} \mathbf{v}_{nr}\mathbf{r}_{rm} - \mathbf{r}_{nr}\mathbf{v}_{rm} \\ &= i\nabla_{\mathbf{k}}\mathbf{v}_{nm} + \mathbf{v}_{nm}(\mathbf{r}_{nn} - \mathbf{r}_{mm}) \\ &= i(\langle n | \mathbf{v} \left(\frac{\partial}{\partial \mathbf{k}} | m \rangle \right) + \left(\frac{\partial}{\partial \mathbf{k}} \langle n | \right) \mathbf{v} | m \rangle) + \mathbf{v}_{nm}(\langle n | \frac{\partial}{\partial \mathbf{k}} | n \rangle - \langle m | \frac{\partial}{\partial \mathbf{k}} | m \rangle) \end{aligned} \quad (4.78)$$

This equation cannot be calculated directly on a finite k-point grid. An appropriate expression must be constructed that retains gauge invariance and accommodates the ambiguity in band identity near

degeneracies. we can reformulate the this term using

$$\begin{aligned}
r_{nn}^a &= i \langle n\mathbf{k} | \frac{\partial}{\partial k_a} | n\mathbf{k} \rangle \\
&= i \langle n\mathbf{k} | n\mathbf{k}' \rangle \frac{\partial}{\partial k'_a} \Big|_{k'_a=k_a} \ln \langle n\mathbf{k} | n\mathbf{k}' \rangle \\
&= i \lim_{\Delta k_a \rightarrow 0} \frac{1}{\Delta k_a} \ln \langle n\mathbf{k} | n(\mathbf{k} + \Delta\mathbf{k}) \rangle - i \ln \langle n\mathbf{k} | n\mathbf{k} \rangle \\
&= i \lim_{\Delta k_a \rightarrow 0} \frac{1}{\Delta k_a} \ln \langle n\mathbf{k} | n(\mathbf{k} + \Delta\mathbf{k}) \rangle
\end{aligned} \tag{4.79}$$

and,

$$\begin{aligned}
\langle n\mathbf{k} | \mathbf{v} \left(\frac{\partial}{\partial k_a} | m\mathbf{k} \right) \rangle &= \langle n\mathbf{k} | \mathbf{v} | m\mathbf{k}' \rangle \frac{\partial}{\partial k'_a} \Big|_{k'_a=k_a} \ln \langle n\mathbf{k} | \mathbf{v} | m\mathbf{k}' \rangle \\
&= \langle n\mathbf{k} | \mathbf{v} | m\mathbf{k} \rangle \lim_{\Delta k_a \rightarrow 0} \frac{1}{\Delta k_a} \ln \langle n\mathbf{k} | \mathbf{v} | m(\mathbf{k} + \Delta\mathbf{k}) \rangle - \ln \langle n\mathbf{k} | \mathbf{v} | m\mathbf{k} \rangle \\
&= \langle n\mathbf{k} | \mathbf{v} | m\mathbf{k} \rangle \lim_{\Delta k_a \rightarrow 0} \frac{1}{\Delta k_a} \ln \frac{\langle n\mathbf{k} | \mathbf{v} | m(\mathbf{k} + \Delta\mathbf{k}) \rangle}{\langle n\mathbf{k} | \mathbf{v} | m\mathbf{k} \rangle}
\end{aligned} \tag{4.80}$$

Then we get,

$$\begin{aligned}
\sum_{r \neq n, r \neq m} \mathbf{v}_{nr} r_{rm}^a - r_{nr}^a \mathbf{v}_{rm} &= \lim_{\Delta k_a \rightarrow 0} \frac{1}{\Delta k_a} i \left[\ln \frac{\langle n\mathbf{k} | \mathbf{v} | m(\mathbf{k} + \Delta\mathbf{k}) \rangle \langle n | n(\mathbf{k} + \Delta\mathbf{k}) \rangle}{\langle n\mathbf{k} | \mathbf{v} | m\mathbf{k} \rangle} \right. \\
&\quad \left. + \ln \frac{\langle n(\mathbf{k} + \Delta\mathbf{k}) | \mathbf{v} | m\mathbf{k} \rangle}{\langle n\mathbf{k} | \mathbf{v} | m\mathbf{k} \rangle \langle m | m(\mathbf{k} + \Delta\mathbf{k}) \rangle} \right] \mathbf{v}_{nm}
\end{aligned} \tag{4.81}$$

The coefficient is the so-called shift vector, $\mathbf{R}_{nm}^{ab}(\mathbf{k})$. (1) Perturbation on $\tilde{D}_{\mathbf{k}'\mathbf{k}rn}(\omega)$

First, starting with Eqn. 4.65,

$$\begin{aligned}
& \sigma_{\alpha\beta\gamma}^{(1),III} \\
&= \frac{e^3}{\omega^2} q_\eta \int_{BZ} d\mathbf{k} \sum_{nmr} \sum_{\pm\omega} \frac{v_{mn}^\alpha [v_{nr}^\gamma v_{rm}^\beta D_{mr}(\omega) - v_{nr}^\beta v_{rm}^\gamma D_{rn}(\omega)]}{\epsilon_m - \epsilon_n + 2i\hbar/\tau} \left(\frac{\partial f_r}{\partial \epsilon_\eta} - \frac{1}{\epsilon_{\mathbf{k}r} - \epsilon_{\mathbf{k}n} - \hbar\omega + i\hbar\tau} \right) \frac{\partial \epsilon_r}{\partial k_\eta} \\
&= \frac{e^3}{\omega^2} q_\eta \int_{BZ} d\mathbf{k} \sum_{nmr} \sum_{\pm\omega} r_{mn}^\alpha [v_{nr}^\gamma v_{rm}^\beta D_{mr}(\omega) - v_{nr}^\beta v_{rm}^\gamma D_{rn}(\omega)] \left(\frac{\partial f_r}{\partial \epsilon_\eta} - \frac{1}{\epsilon_{\mathbf{k}r} - \epsilon_{\mathbf{k}n} - \hbar\omega + i\hbar\tau} \right) \frac{\partial \epsilon_r}{\partial k_\eta} \\
&= \frac{e^3}{\omega^2} q_\eta \int_{BZ} d\mathbf{k} \sum_{nmr} \sum_{\pm\omega} [-v_{mn}^\gamma r_{nr}^\alpha v_{mm} (\frac{\partial f_m}{\partial \epsilon_\eta} - \frac{1}{\epsilon_{\mathbf{k}r} - \epsilon_{\mathbf{k}n} - \hbar\omega + i\hbar\tau}) \\
&+ r_{mn}^\alpha v_{nr}^\gamma v_{rr}^\eta (\frac{\partial f_r}{\partial \epsilon_\eta} - \frac{1}{\epsilon_{\mathbf{k}r} - \epsilon_{\mathbf{k}n} - \hbar\omega + i\hbar\tau})] v_{rm}^\beta D_{mr}(\omega)
\end{aligned} \tag{4.82}$$

$\sigma_{\alpha\beta\gamma}^{(1),III}$ is purely imaginary. Here, only when $E^\beta(\omega)E^\gamma(-\omega)$ is imaginary, i.e., light has a circularly polarized component, would induce a nonzero current. When $q = 0$, the expression corresponds to the shift current.

(2) Perturbation on $\tilde{v}_{\mathbf{k}'k\eta n}$

We define an operator G to describe the "derivative" of the velocity matrix induced by \mathbf{q} ,

$$G_{nr}^{\alpha\eta} = \frac{i}{2} \{v^\alpha, r^\eta\}_{nr} - \frac{1}{2} \partial_\eta v_{nr}^\alpha \tag{4.83}$$

Then,

$$\begin{aligned}
\sigma_{\alpha\beta\gamma}^{(1),IV} &= \frac{e^3}{2\hbar\omega^2} q_\eta \int_{BZ} d\mathbf{k} \sum_{nmr} \sum_{\pm\omega} r_{mn}^\alpha \{ [G_{nr}^{\gamma\eta} v_{rm}^\beta - v_{nr}^\gamma G_{rm}^{\beta\eta}] D_{mr}(\omega) + [G_{nr}^{\beta\eta} v_{rm}^\gamma - v_{nr}^\beta G_{rm}^{\gamma\eta}] D_{rn}(\omega) \} \\
&= \frac{e^3}{2\hbar\omega^2} q_\eta \int_{BZ} d\mathbf{k} \sum_{mr} \sum_{\pm\omega} R^\alpha(v^\gamma)_{mr} G_{rm}^{\beta\eta} D_{mr}(\omega) + S^\alpha(G^{\gamma\eta})_{mr} v_{rm}^\beta D_{mr}(\omega)
\end{aligned} \tag{4.84}$$

When $\mathbf{q} = q_z \hat{z}$, Eqn. 4.84 changes to,

$$\begin{aligned}\sigma_{\alpha\beta\gamma}^{(1),IV} &= -\frac{e^3}{2\hbar^2\omega^2}q_z \int_{BZ} d\mathbf{k} \sum_{rm} (D_{rm}(\omega) - D_{mr}(-\omega))(R_{mr}^{\alpha\gamma}v_{mr}^{\gamma}j_{rm}^{\beta} - R_{mr}^{\alpha\gamma}j_{mr}^{\gamma}v_{rm}^{\beta}) \\ &= -\frac{i\pi e^3}{2\hbar^2\omega^2}q_z \int_{BZ} d\mathbf{k} \sum_{rm} \delta(\epsilon_m - \epsilon_r - \hbar\omega)(f_m - f_r)(R_{mr}^{\alpha\gamma}v_{mr}^{\gamma}j_{rm}^{\beta} - R_{mr}^{\alpha\gamma}j_{mr}^{\gamma}v_{rm}^{\beta})\end{aligned}\quad (4.85)$$

Since $(\frac{Dv}{Dk})_{rm} = -(\frac{Dv}{Dk})_{mr}^*$, $D_{rm}(\omega) = D_{mr}(-\omega)^*$ and $j_{mr} = j_{rm}^*$, the response function is imaginary. As a result, it corresponds to the circular dichroism. According to the analysis in the previous section, we arrive at a general response function of the photocurrent,

$$\begin{aligned}\sigma_{\alpha\beta\gamma}(\omega, -\omega) &= \frac{e^3}{2\omega^2}\theta_{\beta\gamma} \int_{BZ} d\mathbf{k} \sum_{nmr} \frac{iq_{\eta}v_{mn}^{\alpha}}{\epsilon_m - \epsilon_n + i\hbar/\tau} \left[\frac{j_{nr}^{\gamma}v_{rm}^{\beta} - v_{nr}^{\gamma}j_{rm}^{\beta}}{\epsilon_m - \epsilon_r - \hbar\omega + i\hbar/\tau} (f_m - f_r) \right. \\ &\quad \left. + \frac{j_{nr}^{\beta}v_{rm}^{\gamma} - v_{nr}^{\beta}j_{rm}^{\gamma}}{\epsilon_r - \epsilon_n - \hbar\omega + i\hbar/\tau} (f_r - f_n) \right]\end{aligned}\quad (4.86)$$

Here the explicit \mathbf{k} dependence of the quantities are omitted. The carrier lifetime and is set to 0.2 ps in the following. $j^{\alpha} = \frac{1}{2}\{v^{\alpha}, \hat{z}\}$ is the differential current operator. $\theta_{\beta\gamma}$ is the coefficient corresponding to the phase between E_{β} and E_{γ} , i.e., $\theta_{xy} = 1$ for LPL, and $\theta_{xy} = \pm i$ for CPL. We consider that the numerator is composed of $N = v^{\alpha}v^{\beta}j^{\gamma}$, and the denominator $M = \frac{1}{(\epsilon_m - \epsilon_n + i\hbar/\tau)(\epsilon_m - \epsilon_r - \hbar\omega + i\hbar/\tau)}$ can be divided into a real part $Re(M) \sim \frac{1}{(\epsilon_m - \epsilon_n)(\epsilon_m - \epsilon_r - \hbar\omega)}$, and an imaginary part $Im(M) \sim \pi \frac{P}{(\epsilon_m - \epsilon_n)} \delta(\epsilon_m - \epsilon_r - \hbar\omega)$.

The symmetry arguments can be summarized as,

	$v^a(\mathbf{k})$	$j^a(\mathbf{k})$	$N^{abc}(\mathbf{k})$
\mathcal{P}	$-v^a(-\mathbf{k})$	$j^a(\mathbf{k})$	$N^{abc}(-\mathbf{k})$
\mathcal{T}	$-v^{a*}(-\mathbf{k})$	$-j^{a*}(-\mathbf{k})$	$-N^{abc*}(-\mathbf{k})$

Therefore, only the imaginary part of N^{abc} would contribute to PGE due to time reversal constraint, while inversion need not to be broken to have this response. The shift current part can be written as $iqN^{abc} \text{Im}(D)$, and the injection current would be $iqN^{abc} \text{Re}(D)(n = m)$. Consequently, shift current gives CPGE response, while injection current gives LPGE response. Especially for Moire

cells, when \mathbf{q} exceeds the Brillouin zone size \mathbf{G} , this equation can be calculated on multiple unit cells, i.e., $v_{\mathbf{k}(\mathbf{k}-\mathbf{q})} = v_{\mathbf{k}(\mathbf{k}-\mathbf{q}+n\mathbf{G})}$.

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