# Semiclassical Theory of Bloch Electrons to Second Order in Electromagnetic Fields

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# Outline

- First Order Theory
  - Anomalous velocity, Anomalous Hall effect
  - Density of States, Other applications
  - Effective Quantum Mechanics
- Second order dynamics
  - Positional shift
  - Magnetoelectric Polarization
  - Nonlinear anomalous Hall effect
- Second order energy
  - Correction to the wave packet state
  - Semiclassical energy and its classification
  - Magnetic susceptibility and model calculations

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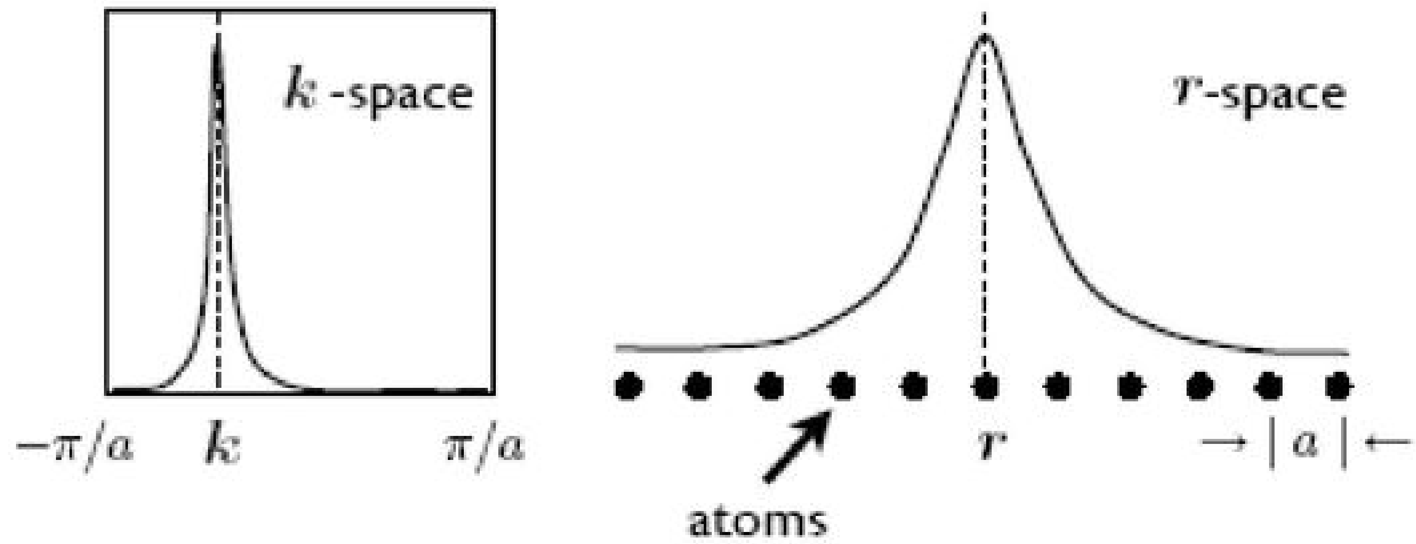
# Semiclassical Equations of Motion

Wave-packet
Dynamics
$(r, k)$




G. Sundaram and Q. Niu, PRB **59**, 14915 (1999)

Nonzero if either time-reversal or inversion symmetry is broken

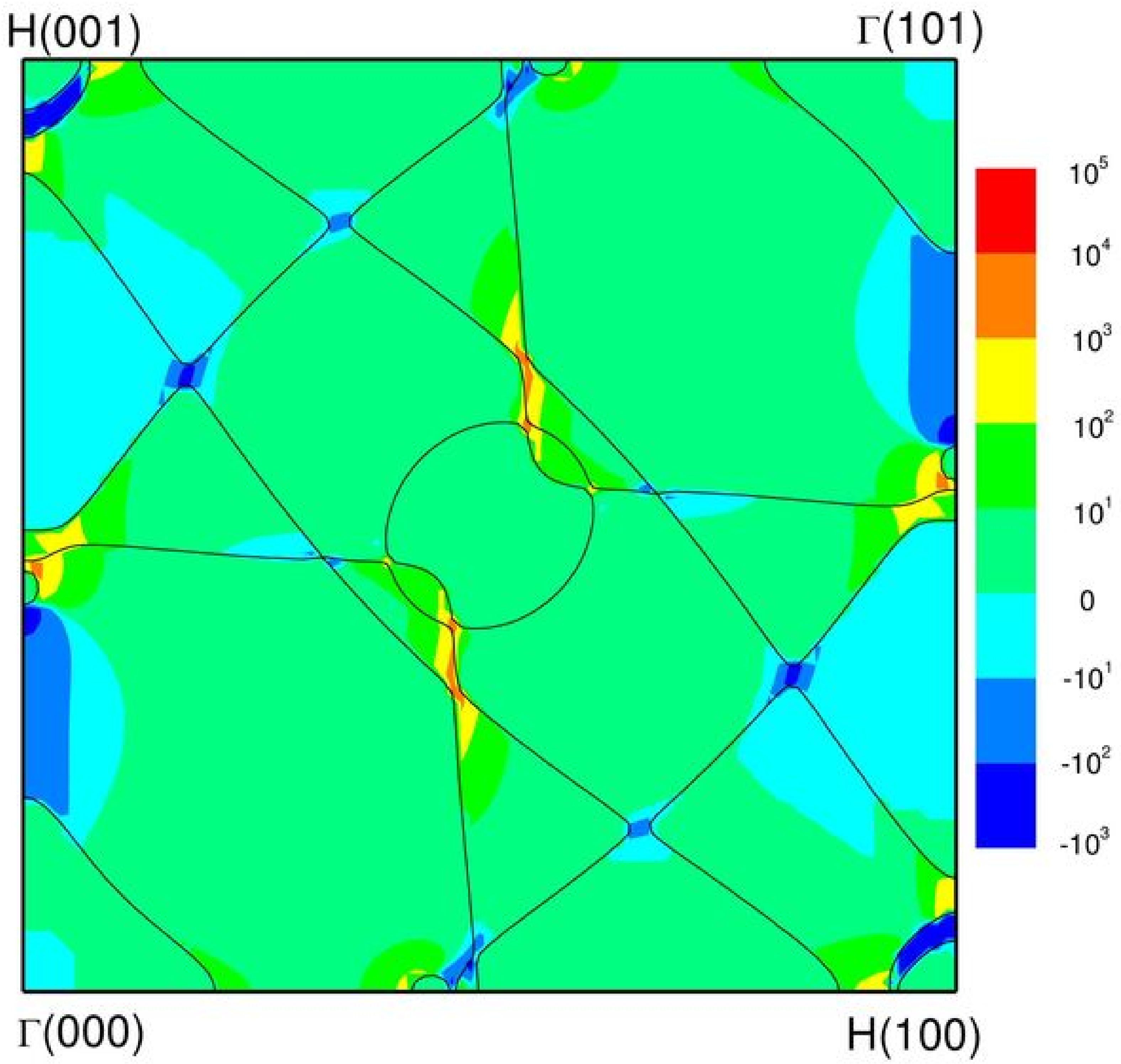
$$\dot{r} = \frac{\partial \varepsilon_n(k)}{\hbar \partial k} - \dot{k} \times \Omega_n(k)$$

$$\hbar \dot{k} = -eE(r) - e\dot{r} \times B(r)$$

Berry Curvature

$$\Omega_n(k) = \mathrm{i}\langle \nabla_{\boldsymbol{k}} u_n(k) | \times | \nabla_{\boldsymbol{k}} u_n(k) \rangle$$

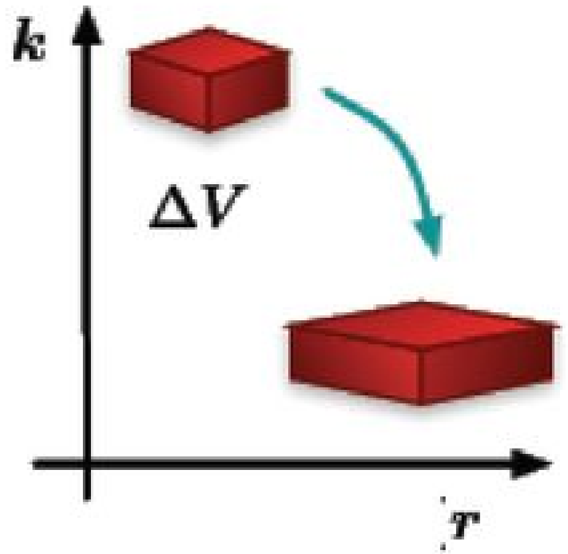
# Berry Curvature in Fe crystal



# Intrinsic AHE in ferromagnets

- Semiconductors, $Mn_xGa_{1-x}As$
  - Jungwirth, Niu, MacDonald , PRL (2002) , J Shi' s group (2008)
- Oxides, $SrRuO_3$
  - Fang et al, Science , (2003).
- Transition metals, Fe
  - Yao et al, PRL (2004),Wang et al, PRB (2006), X.F. Jin' s group (2008)
- Spinel, $CuCr_2Se_{4-x}Br_x$
  - Lee et al, Science, (2004)
- First-Principle Calculations-Review
  - Gradhand et al (2012)

# Phase Space Density of States




Evolution of a phase space volume

$$\frac{1}{\Delta V}\frac{\mathrm{d}\Delta V}{\mathrm{d}t} = \nabla_{\boldsymbol{r}} \cdot \dot{\boldsymbol{r}} + \nabla_{\boldsymbol{k}} \cdot \dot{\boldsymbol{k}}$$

$$\Delta V = \Delta V_0 / (1 + \frac{e}{\hbar}\boldsymbol{B} \cdot \boldsymbol{\Omega}_n)$$

Liouville's theorem breaks down

Density of States

$$D_n(\boldsymbol{r}, \boldsymbol{k}) = (2\pi)^{-d}(1 + \frac{e}{\hbar}\boldsymbol{B} \cdot \boldsymbol{\Omega}_n)$$

Thermal dynamic quantity

$$\bar{Q} = \sum_n \int \mathrm{d}\boldsymbol{k}\, D_n(\boldsymbol{k}) f_n(\boldsymbol{k}) Q_n(\boldsymbol{k})$$

(homogenous system)

# Applications

- Orbital Magnetization

  Xiao et al, PRL (2005)
  Thonhauser et al, PRL (2005)
  Ceresoli et al PRB (2006)
  Shi et al, PRL (2007)

- Anomalous Nernst Effect

  Xiao et al, PRL (2006), Onoda et al (2008)

  Lee et al, (2004), Miyasato et al (2007) Hanasaki et al (2008), Pu et al (2008).

# Effective Quantum Mechanics

- Wavepacket energy $\mathcal{H}(\boldsymbol{r}_c, \boldsymbol{k}_c) = \varepsilon_0(\boldsymbol{k}_c) - e\phi(\boldsymbol{r}_c) + \frac{e}{2m}\mathcal{L}(\boldsymbol{k}_c) \cdot \boldsymbol{B}$
- Energy in canonical variables

$$E(\boldsymbol{q},\boldsymbol{p}) = \varepsilon_0(\boldsymbol{\pi}) - e\phi(\boldsymbol{q}) + e\boldsymbol{E} \cdot \boldsymbol{R}(\boldsymbol{\pi})$$
$$+ \frac{e}{2m}\boldsymbol{B} \cdot \left[\boldsymbol{L}(\boldsymbol{\pi}) + 2\boldsymbol{R} \times m\frac{\partial \varepsilon_0}{\partial \boldsymbol{\pi}}\right],$$

$\pi = \mathbf{p} + e\mathbf{A}(\mathbf{r})$

Spin-orbit

Spin & orbital moment

Yafet term

- Quantum theory

$$[q, p] = i\hbar$$

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# Why Second Order?

- In many systems, first order response vanishes
- May be interested in magnetic susceptibility, electric polarizebility, magneto-electric coupling
- Magnetoresistivity
- Nonlinear anomalous Hall effects

# Positional Shift

- Use perturbed band: $|\tilde{u}_0\rangle = |u_0\rangle + |\delta u_0\rangle$
- Solve $|\delta u_0\rangle$ from the first order energy correction:

$$\hat{\mathrm{H}}' = \frac{1}{4m}\boldsymbol{B}\cdot\left[(\hat{\boldsymbol{q}} - \boldsymbol{r}_c)\times\hat{\boldsymbol{V}} - \hat{\boldsymbol{V}}\times(\hat{\boldsymbol{q}} - \boldsymbol{r}_c)\right] + \boldsymbol{E}\cdot\boldsymbol{r}_c$$

- Modification of the Berry connection – the positional shift

$$\begin{aligned}\boldsymbol{a}_0' &= \langle u_0|i\boldsymbol{\partial}|\delta u_0\rangle + c.c.\\ &= \sum_{n\neq 0}\mathrm{Re}\frac{\langle u_0|\hat{D}_{\boldsymbol{p}}|u_n\rangle\langle u_n|(\hat{\boldsymbol{v}}\times\hat{D}_{\boldsymbol{p}})\cdot\boldsymbol{B} - (\hat{D}_{\boldsymbol{p}}\times\hat{\boldsymbol{v}})\cdot\boldsymbol{B} + 2\boldsymbol{E}\cdot\hat{D}_{\boldsymbol{p}}|u_0\rangle}{\varepsilon_0 - \varepsilon_n}\end{aligned}$$

$$\hat{D}_{\boldsymbol{p}} = \partial_{\boldsymbol{p}}\mathcal{P}\ ,\ \mathcal{P} = |u_0(\boldsymbol{p})\rangle\langle u_0(\boldsymbol{p})|$$

# Equations of Motion

- Effective Lagrangian:

$$\mathcal{L} = \langle \Psi | i\partial_t | \Psi \rangle - \langle \Psi | \hat{\mathrm{H}}_c + \hat{\mathrm{H}}' + \hat{\mathrm{H}}'' | \Psi \rangle$$
$$= -(\boldsymbol{r}_c - \boldsymbol{a}_0 - \boldsymbol{a}_0') \cdot \dot{\boldsymbol{k}}_c - \frac{1}{2}\boldsymbol{B} \times \boldsymbol{r}_c \cdot \dot{\boldsymbol{r}}_c - \tilde{\varepsilon}$$

- Equations of motion

$$\dot{\boldsymbol{r}}_c = \frac{\partial \tilde{\varepsilon}}{\partial \boldsymbol{k}_c} - \dot{\boldsymbol{k}}_c \times \tilde{\boldsymbol{\Omega}}$$
$$\dot{\boldsymbol{k}}_c = -\boldsymbol{E} - \dot{\boldsymbol{r}}_c \times \boldsymbol{B}$$

$$\tilde{\boldsymbol{\Omega}} = \boldsymbol{\partial} \times \boldsymbol{a}_0 + \boldsymbol{\partial} \times \boldsymbol{a}_0'$$

# Magnetoelectric Polarization

- Polarization in solids:

$$\delta \boldsymbol{P} = \int \frac{d^3k}{(2\pi)^3} \boldsymbol{a}_0$$

- Correction under electromagnetic fields:

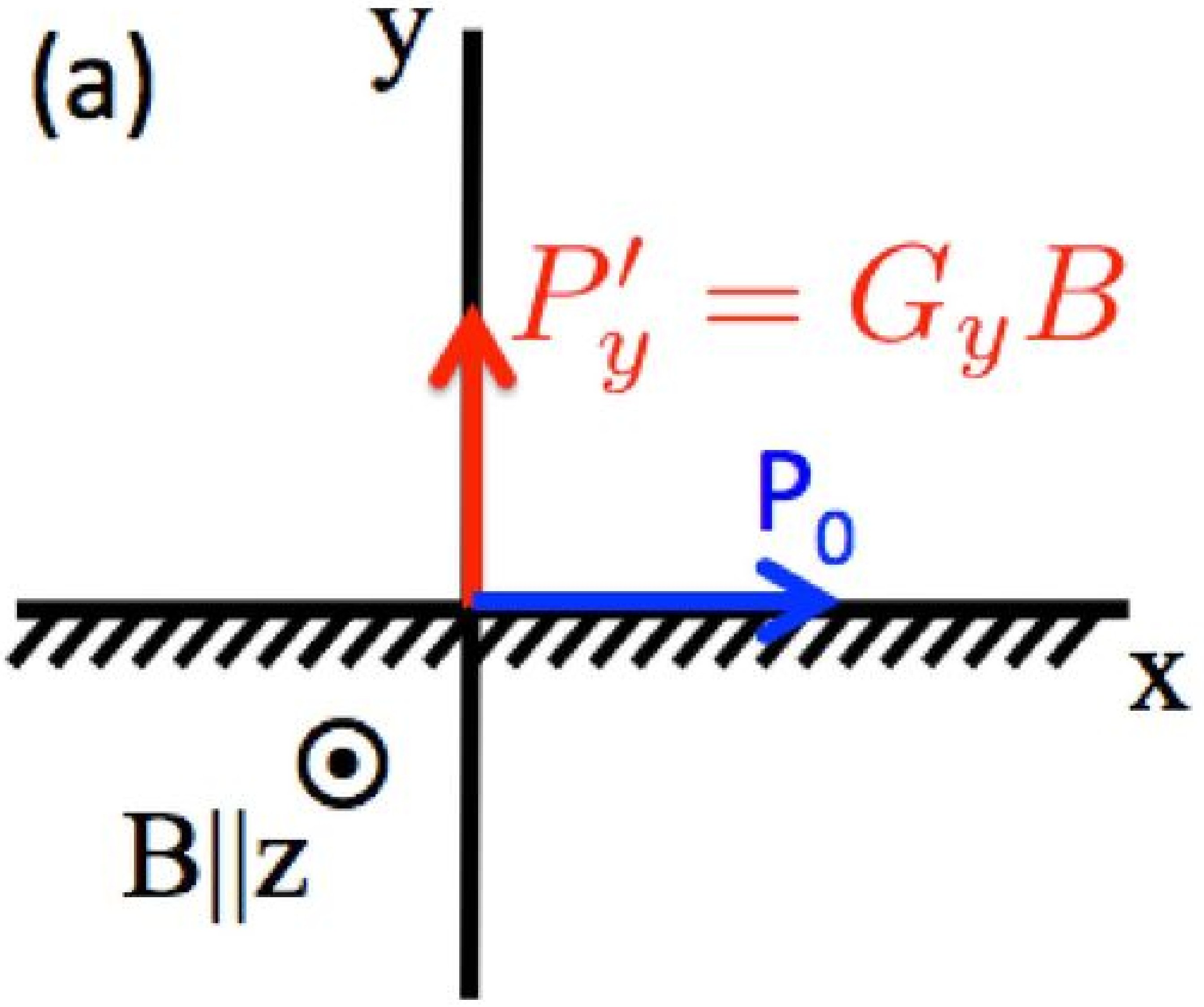
$$\frac{1}{(2\pi)^3} \to \frac{1 + \boldsymbol{B} \cdot \tilde{\boldsymbol{\Omega}}}{(2\pi)^3}$$

$$\boldsymbol{a}_0 \to \boldsymbol{a}_0 + \frac{1}{2}(\boldsymbol{B} \times \boldsymbol{a}_0 \cdot \boldsymbol{\partial}_{\boldsymbol{p}})\boldsymbol{a}_0 + \frac{1}{2}\boldsymbol{\Omega}_0 \times (\boldsymbol{B} \times \boldsymbol{a}_0) + \boldsymbol{a}_0'$$

- Magnetoelectric polarization:

$$\delta \boldsymbol{P} = -\int_{BZ} \frac{d^3k}{(2\pi)^3} \left( \frac{1}{2}(\Omega_0 \cdot \boldsymbol{a}_0)\, \boldsymbol{B} + \boldsymbol{a}_0' \right)$$

# Magnetoelectric Polarization




Restrictions: No symmetries of time reversal, spatial inversion, and rotation about B.

# Nonlinear Anomalous Hall Current

- Intrinsic current:

$$\boldsymbol{j} = -\int \mathcal{D}\dot{\boldsymbol{r}}_c f(\boldsymbol{k}) \frac{d^3k}{(2\pi)^3}$$

- Results – only anomalous Hall current:

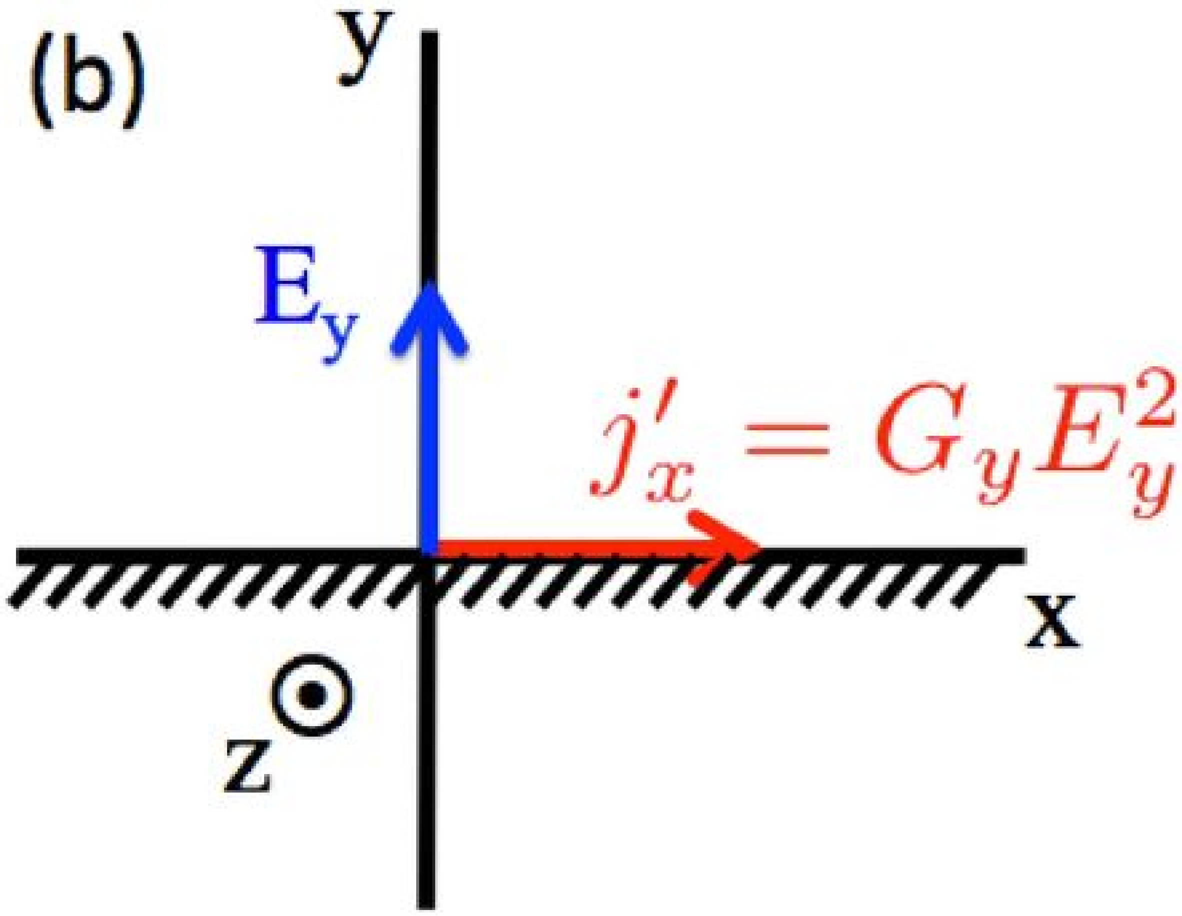
$$\boldsymbol{j}' = -\boldsymbol{E} \times \int (\boldsymbol{\Omega}_0' f(\epsilon_0) - \boldsymbol{\Omega}_0(\boldsymbol{B}\cdot\boldsymbol{m})\partial f/\partial\epsilon_0) \frac{d^3k}{(2\pi)^3}$$

$$= \boldsymbol{E} \times \int (\boldsymbol{v}_0 \times \boldsymbol{a}_0' + \boldsymbol{\Omega}_0(\boldsymbol{B}\cdot\boldsymbol{m}))\frac{\partial f}{\partial\epsilon_0} \frac{d^3k}{(2\pi)^3}$$

# Electric-field-induced Hall Effect

- Electric field induced Hall conductivity (2-band model):

$$\sigma'_{xy} = -\int \frac{d^3k}{8\pi^3} \frac{\partial f}{\partial \epsilon_0} \boldsymbol{G} \cdot \boldsymbol{E}$$



# Magnetic-field Induced Anomalous Hall

- Model Hamiltonian:

$$\hat{\mathrm{H}} = v(k_x\sigma_x + k_y\sigma_y) + \Delta\sigma_z$$

- Magnetic field induced Hall conductivity:

$$\sigma'_{xy} = -e^3 \frac{v^2(v^2p_f^2 + 2\Delta^2)}{16\pi(v^2p_f^2 + \Delta^2)^2} B$$

- Compare to ordinary Hall effect

$$\frac{\rho'_{xy}}{\rho_{xy}^{ord}} = \left(\rho_{xx}\frac{e^2}{4h}\right)^2 \left[1 - \left(\frac{\Delta}{\varepsilon_f}\right)^4\right]$$

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# Field Correction to Wave Packet State

- The wave packet state:

$$|\psi\rangle = \int d\boldsymbol{p} e^{i\boldsymbol{p}\cdot\boldsymbol{q}} (C_0 |u_0\rangle + \sum_{n\neq 0} C_n |u_n\rangle) \, .$$

- The interband mixing

$$C_n = \frac{G_{n0}}{\varepsilon_0 - \varepsilon_n} C_0 - \frac{1}{2} i\boldsymbol{B} \cdot (\hat{\boldsymbol{D}} - \boldsymbol{r}_c) C_0 \times \boldsymbol{A}_{n0}$$

# Nature of Field Correction

- The vertical mixing correction (local correction):

$$G_{n0} = -\boldsymbol{B} \cdot \mathcal{M}_{n0} + \boldsymbol{E} \cdot \boldsymbol{A}_{n0}$$

$$\mathcal{M}_{n0} = \boldsymbol{M}_{n0} + \frac{1}{2}(\boldsymbol{v}_0 + \boldsymbol{v}_n) \times \boldsymbol{A}_{n0} + \frac{(\varepsilon_n - \varepsilon_0)}{4}(\partial_{\boldsymbol{p}} + i(\boldsymbol{a}_0 - \boldsymbol{a}_n)) \times \boldsymbol{A}_{n0}$$

$$\boldsymbol{M}_{n0} = \frac{1}{4}(\boldsymbol{V} \times \boldsymbol{A} - \boldsymbol{A} \times \boldsymbol{V})_{n0} \,.$$

- The horizontal mixing (non-local correction):

$$i\boldsymbol{\partial}_{\boldsymbol{p}} \leftrightarrow \boldsymbol{q}$$

- Vertical mixing influenced by gaps; horizontal mixing influenced by geometries.

# Semiclassical Energy

- Definition:

$$\tilde{\varepsilon} = \langle\psi|\hat{\mathrm{H}}|\psi\rangle - (\langle\psi|i\partial_t|\psi\rangle)_{\text{correction to the norm of } \mathrm{C}_0}$$

- Results:

$$\tilde{\varepsilon} = \varepsilon_0 - \boldsymbol{B}\cdot\boldsymbol{m} + \boldsymbol{E}\cdot\boldsymbol{r}_c + \frac{1}{4}(\boldsymbol{B}\cdot\boldsymbol{\Omega})(\boldsymbol{B}\cdot\boldsymbol{m}) - \frac{1}{8}\varepsilon_{\theta i\alpha}\varepsilon_{\phi j\beta}B_\theta B_\phi \alpha_{ij} g_{\alpha\beta}$$
$$+ (-\boldsymbol{E} - \boldsymbol{v}_0\times\boldsymbol{B})\cdot\boldsymbol{a}_0' + \sum_{n\neq 0}\frac{G_{0n}G_{n0}}{\varepsilon_0-\varepsilon_n} + \sum_{n\neq 0}\frac{1}{4}\partial_i[(\boldsymbol{B}\times\boldsymbol{A}_{0n})_i G_{n0} + c.c.]$$
$$+ \frac{1}{8}\sum_{(m,n)\neq 0}(\boldsymbol{B}\times\boldsymbol{A}_{0m})_i(\Gamma_{ij})_{mn}(\boldsymbol{B}\times\boldsymbol{A}_{n0})_j - \frac{1}{16}(\boldsymbol{B}\times\boldsymbol{\partial})_i(\boldsymbol{B}\times\boldsymbol{\partial})_j\langle 0|\Gamma_{ij}|0\rangle$$

- Hessian matrix: $\Gamma_{ij} = \partial_{ij}\hat{\mathrm{H}}$

# Classification of Second Order Semiclassical Energy

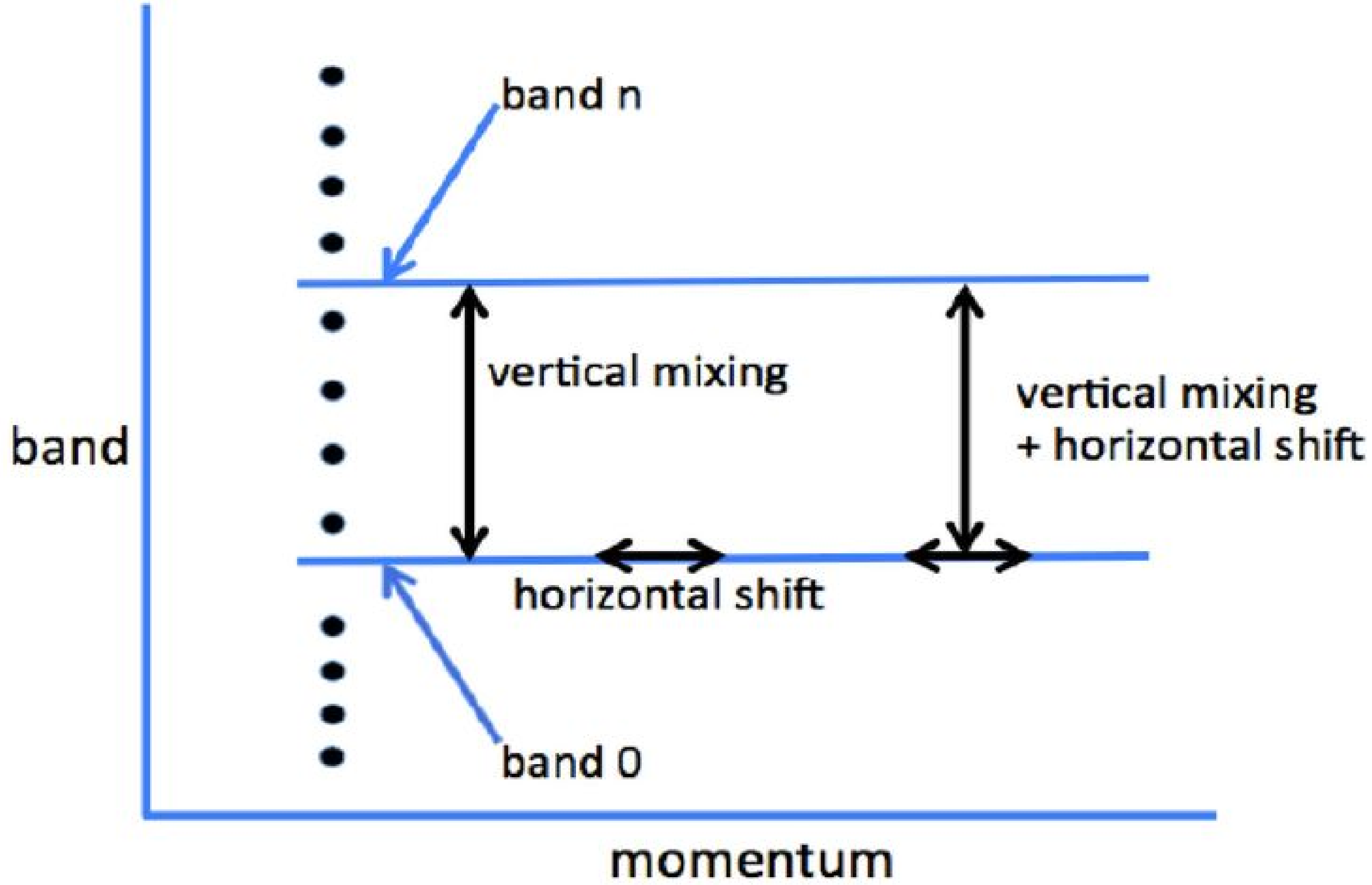


Figure 1: The scheme of the second order perturbation.

# Magnetic Susceptibility

- The free energy G:

$$G = \int_{BZ} \mathcal{D}(g(\tilde{\varepsilon}) + g_{Landau}) \frac{d^3k}{8\pi^3}$$

$$g(\tilde{\varepsilon}) = -(1/\beta) \ln\{1 + \exp[\beta(\mu - \tilde{\varepsilon})]\}$$

- Correction to density of states up to second order

 + correction to energy = free energy at second order

- Peierls-Landau diamagnetism due to taking the semiclassical limit of the quantum mechanical free energy

$$g_{Landau} = -\frac{1}{48} B_\lambda B_\nu \epsilon_{\lambda \ell k} \epsilon_{\mu\nu\rho} \frac{\partial f(\varepsilon_0)}{\partial \varepsilon_0} \alpha_{\ell\nu} \alpha_{k\rho}$$

# Other contributions to Susceptibility

- Pauli paramagnetism:

$$g_{PL} = \int_{BZ} \frac{d^3k}{8\pi^3} f' \frac{1}{2} (\boldsymbol{B} \cdot \boldsymbol{m})^2$$

- Curvature-moment coupling magnetism:

$$g_{CP} = - \int_{BZ} \frac{d^3k}{8\pi^3} (\boldsymbol{B} \cdot \boldsymbol{\Omega})(\boldsymbol{B} \cdot \boldsymbol{m}) f$$

- Remaining contributions

$$g_r = \int_{BZ} \frac{d^3k}{8\pi^3} (f \varepsilon'' + \boldsymbol{B} \cdot \boldsymbol{\Omega}_0' g)$$

# Model Calculation I: Massless Dirac Model

- Model Hamiltonian:

$$\hat{\mathrm{H}} = v_0(k_1\sigma_1 + k_2\sigma_2) + \Delta\sigma_3$$

- Pauli paramagnetism:

$$\chi_{PL} = \frac{\Delta^2 v_0^2}{8\pi|\mu|^3}$$

- Landau diamagnetism:

$$\chi_{LD} = -\frac{\Delta^2 v_0^2}{24\pi|\mu|^3}$$

- Curvature-moment coupling magnetism:
- $$\chi_{CP} = -\frac{\Delta^2 v_0^2}{12\pi|\mu|^3}$$

# Model Calculation I: Massless Dirac Model

- Other contributions vanish
- Fermi level in the band: susceptibility vanishes
- Fermi level in the gap: susceptibility finite and constant
- Gap goes to zero: susceptibility goes as 1/Gap.
- This divergence is due to the coupling between curvature and magnetic moment.

# Model Calculation II: Massive Dirac Model

- Model Hamiltonian:

$$\hat{H} = \begin{pmatrix} \Delta & -\frac{(k_1 - ik_2)^2}{2m} \\ -\frac{(k_1 + ik_2)^2}{2m} & -\Delta \end{pmatrix}$$

- Susceptibility:

$$\chi = -\frac{1}{16\pi m} \ln \frac{1+\sin\theta_\Lambda}{1-\sin\theta_\Lambda} + \frac{1}{16\pi m} \ln \frac{1+\sin\theta_0}{1-\sin\theta_0} - \frac{1}{24\pi m}$$

$$\cos\theta_\Lambda = \Delta/\varepsilon_{cut}, \ \cos\theta_0 = \Delta/|\mu|$$

- Logarithmic dependence due to the two Hessian susceptibilities; the last constant term from Landau diamagnetic susceptibility
- Can be used to detect trigonal warping.

# Model Calculation III: spin-orbital Model

- Model Hamiltonian:

$$\hat{H} = \frac{k^2}{2m} + \lambda \hat{z} \cdot (\boldsymbol{k} \times \boldsymbol{\sigma})$$

- The partical-hole symmetry is broken due to the kinetic term.

- The pure vertical mixing and horizontal-vertical mixing energy will contribute to a term depends on 1/m (the strength of the particle-hole symmetry breaking).

- Other contribution resembles the first model, except that there are one more Fermi surfaces.

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