Geometrical nonlinear phenomena in solids ②

Berry correction

$$a_n(k) = i \langle u_n | \partial_k u_n(k) \rangle$$

Berry curvature

$$F_n(k) = \nabla \times a_n(k)$$

intracell coordinate

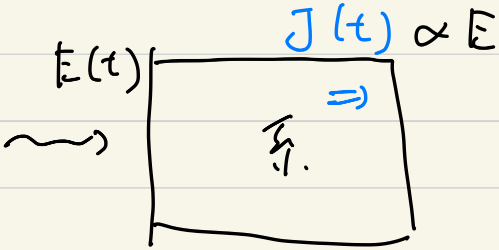
Position operator $r = i\partial_k + \underline{a_n(k)}$

semiclassics

$\Updownarrow$

fully quantum mechanical treatment

3.1 Diagramatic method for EM responses



Electric field $E(t) = E(\omega)\, e^{-i\omega t}$

minimal coupling

$$p \longrightarrow p - q \underbrace{A(t)}_{\text{vector potential}}$$

$(\hbar k) \qquad (\hbar k)$

$$E(t) = -\partial_t A(t)$$

$$\Rightarrow A(t) = \frac{E(\omega)}{i\omega} e^{-i\omega t}$$

unperturbed Hamiltonian: $\hat{H} = \sum_k c_k^\dagger H(k) c_k$

. H in E

$$\tilde{H}(t) = \sum_k c_k^\dagger H\left(k - \frac{q}{\hbar} A(t)\right) c_k$$

$$\tilde{H}(t) = \sum_k c_k^\dagger H\left(k + \frac{iq}{\hbar\omega} \underset{\sim}{E(t)}\right) c_k$$

Taylor expansion in E

$$H\left(k + \frac{iq}{\hbar\omega} E(t)\right) = H(k)$$

$$+ \frac{iq}{\hbar\omega} \partial_k H \, E(t)$$

$$+ \frac{1}{2}\left(\frac{iq}{\hbar\omega}\right)^2 \partial_k^2 H \left(E(t)\right)^2$$

$$+ \cdots$$

- Current operator J

$$J \equiv -\frac{\partial \tilde{H}}{\partial A} = \frac{q}{\hbar}\frac{\partial \tilde{H}}{\partial k}$$

$$= \frac{q}{\hbar}\sum_k c_k^\dagger\, \partial_k H\left(k - \frac{q}{\hbar}A(t)\right) c_k$$

$$= \frac{q}{\hbar}\sum_k c_k^\dagger \Big[\partial_k H(k) + \frac{iq}{\hbar\omega}\partial_k^2 H(k) E(t) + \cdots \Big] c_k$$

paramagnetic current

diamagnetic current

ex. parabolic band

$$H = \frac{(p - qA)^2}{2m} c_k^\dagger c_k$$

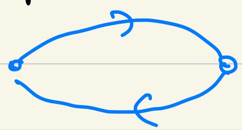
para

dia

$$J = -\frac{\partial H}{\partial A} = \sum_k q\, \frac{p \boxed{- qA}}{m} c_k^\dagger c_k$$

Diagramatic method.

- input vertex (perturbation in $\hat{H}$)
- output vertex (response J)



- connected by electron propagator G

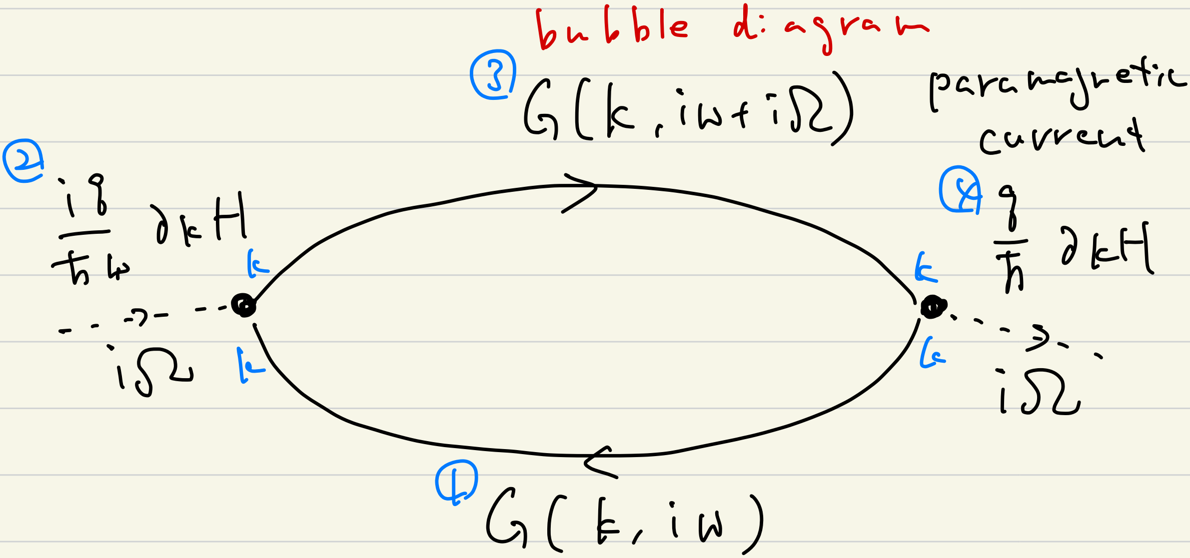
$$G(i\omega) = \frac{1}{i\omega - H} = \sum_a \frac{|u_a\rangle\langle u_a|}{i\omega - \epsilon_a}$$

- k & E conservation at each vertex.

バンドindex 波数

$$H_k\, |u_{a,k}\rangle = \epsilon_{a,k}\, |u_{a,k}\rangle$$

- Linear response (1st order in E)



$$\sigma_p(i\Omega) = \int \frac{d\omega}{2\pi} \int \frac{dk}{(2\pi)^d}$$

$$\mathrm{tr}\left[\frac{q}{\hbar} \partial_k H \; \overset{3}{G(k, i\omega + i\Omega)} \; \overset{2}{\frac{iq}{\hbar\omega}} \partial_k H \; \overset{1}{G(k, i\omega)} \right]$$

$$\sigma_p = \frac{iq^2}{\hbar^2 \omega} \int \frac{d\nu}{2\pi} [dk] \sum_{a,b}$$ ← 固有状態

$$\underbrace{\mathrm{tr}\left[\partial_k H \underset{\uparrow \atop |u_b\rangle\langle u_b|}{} G(i\omega + i\Omega)\, \partial_k H \underset{\uparrow \atop |u_a\rangle\langle u_a|}{} G(i\omega) \right]}$$

$$= \mathrm{tr}\left(\partial_k H |u_b\rangle \frac{\langle u_b | u_b\rangle \langle u_b|}{i\nu + i\Omega - \epsilon_b} \partial_k H \, |u_a\rangle \times \frac{\langle u_a | u_a\rangle \langle u_a|}{i\omega - \epsilon_a} \right)$$

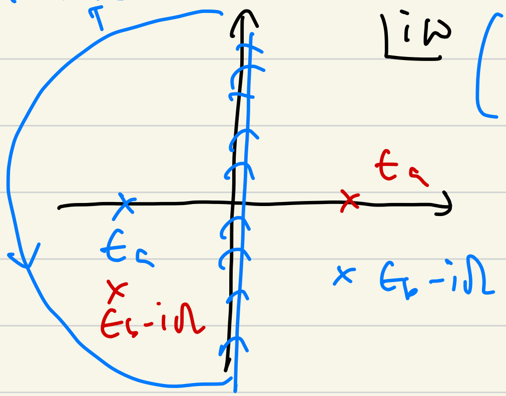
$$v_{ab} \equiv \langle u_a | \partial_k H | u_b \rangle$$

$$= v_{ab} \frac{1}{i\omega + i\Omega - \epsilon_b} v_{ba} \frac{1}{i\omega - \epsilon_a}$$

$$\omega \in (-\infty, +\infty) \quad T = 0.$$

$$= \frac{iq^2}{\hbar^2 \omega} \int \frac{d\omega}{2\pi} \Big(\to \frac{di\omega}{2\pi i} \Big) [dk] \sum_{ab} \underbrace{\frac{v_{ab} v_{ba}}{(i\omega + i\Omega - \epsilon_b)(i\omega - \epsilon_a)}}$$

弧の寄与は消える



$$\begin{cases} \epsilon_a < 0 \\ \epsilon_b > 0 \end{cases} \Rightarrow \frac{v_{ab} v_{ba}}{i\Omega - \epsilon_b + \epsilon_a} \qquad f_{ab} = 1$$

$$\begin{cases} \epsilon_b < 0 \\ \epsilon_a > 0 \end{cases} \Rightarrow \frac{1}{-i\Omega + \epsilon_b - \epsilon_a} \qquad f_{ab} = -1$$

これら以外は 0.

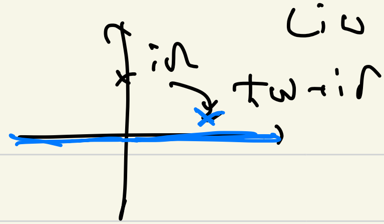
$$\sigma_p(i\Omega) = \frac{iq^2}{\hbar^2 \omega} \int [dk] \sum_{ab} \frac{f_{ab} v_{ab} v_{ba}}{i\Omega - \epsilon_{ba}}$$

$f_{ab} = f_a - f_b$ ： f_a : フェルミ分布

$$= \begin{cases} 1 & \epsilon_a < 0 \\ 0 & \epsilon_a > 0 \end{cases}$$

$$\epsilon_{ba} = \epsilon_b - \epsilon_a$$

- analytic continuation



$$i\Omega \longrightarrow \hbar\omega + \underbrace{i\delta}_{>0} \quad \text{(causality)}$$

Optical conductivity (absorption spectra)

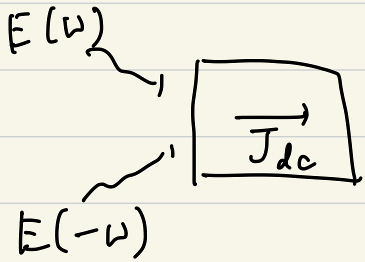
$$\sigma_p(\omega) = \frac{i g^2}{\hbar^2 \omega} \int [dk] \sum_{ab} \frac{f_{ab}\, v_{ab}\, v_{ba}}{\hbar\omega - \epsilon_{ba} + i\delta}$$

$$\rightarrow -i\pi\,\delta(\hbar\omega - \epsilon_{ba})$$

$$\sigma(\omega) = \frac{\pi g^2}{\hbar^2 \omega} \int [dk]\, f_{ab}\, |v_{ab}|^2\, \delta(\hbar\omega - \epsilon_{ba})$$

3.3 Shift current

- 2nd order nonlinear optical effect



$$\cos\omega t = \frac{1}{2}\left(e^{i\omega t} + e^{-i\omega t}\right)$$

$$J_{dc} = \sigma^{(2)}(\omega)\, E(\omega)\, E(-\omega)$$

solar cell action of bulk crystals

cf. pn junctions

- requires broken inversion symmetry I.

If I is present

$$I : J \to -J \qquad (\text{LHS}) : I \text{ odd}$$

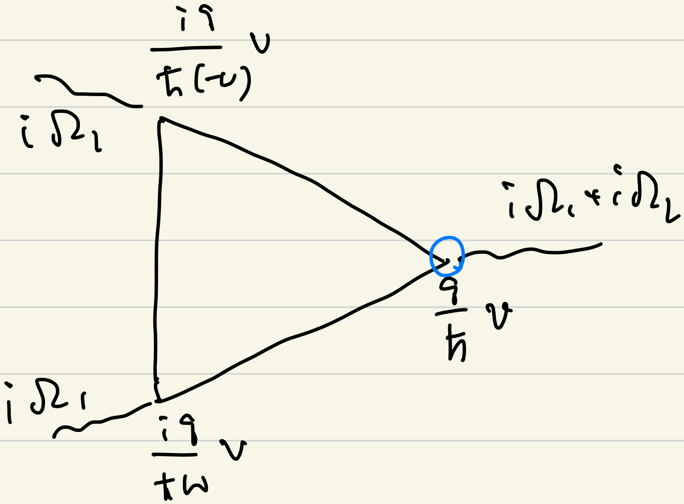
$$E \to -E \qquad (\text{RHS}) : I \text{ even}$$

$$\Rightarrow \sigma^{(2)} = 0$$

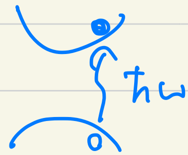
I broken system (e.g. ferroelectrics) is necessary for shift current

Diagrams for E^2 responses.

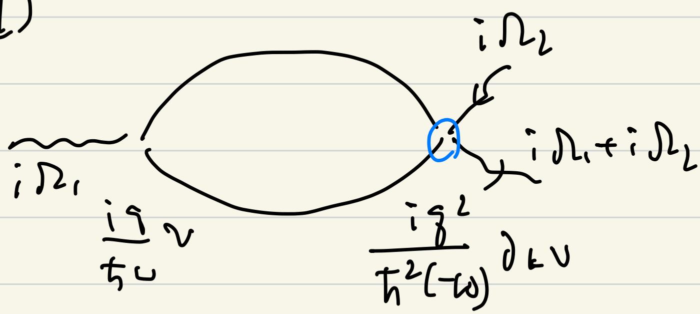
②



$(i\Omega_1 \leftrightarrow i\Omega_2)$



①

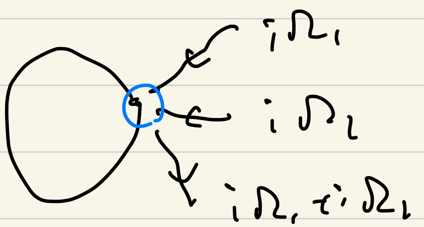


- Analytic continuation

$$\left(\begin{array}{l} i\Omega_1 \to \hbar\omega + i\delta \\ i\Omega_2 \to -\hbar\omega + i\delta \end{array} \right.$$

H : $\frac{(p+eA)^2}{2m}$ へ [illegible]

Shift current : photocurrent upon light absorption



$$\frac{q}{\hbar}\left(\frac{iq}{\hbar\omega}\right)\left(\frac{iq}{\hbar(-\omega)}\right)\partial_k^2 v$$

← off resonant (no δ-function)

$$J_{dc} = \sigma^{(2)}(\underset{\text{output energy}}{0} : \underbrace{\omega, -\omega}_{\text{input energy}})\, E(\omega)\, E(-\omega)$$

① bubble

$$\sigma_1^{(2)} = \frac{q^3}{\hbar^3 \omega^2} \int [dk] \, \frac{f_{ab} (\partial_k v)_{ab} v_{ba}}{\hbar\omega - \epsilon_{ba} + i\delta}$$

② triangle

$$\sigma_2^{(2)} = \frac{q^3}{\hbar^3 \omega^2} \int [dk] \sum_{a,b,c\neq a} \frac{v_{ac} v_{cb} v_{ba}}{\epsilon_{ac}}$$

$$\times \left(\frac{f_{ab}}{\hbar\omega - \epsilon_{ba} + i\delta} - \frac{f_{cb}}{\hbar\omega - \epsilon_{bc} - i\delta} \right)$$

$$+ (\omega \leftrightarrow -\omega)$$

$$\sigma^{(2)}(\omega) = \sigma_1^{(2)}(\omega) + \sigma_2^{(2)}(\omega)$$

J_{dc} : real $\Rightarrow$ $\mathrm{Re}[\sigma^{(2)}(\omega)]$

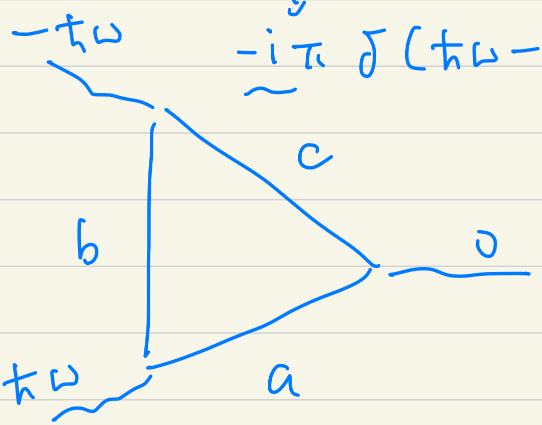
$\Rightarrow$ dc current response

- consider a 2 band system for simplicity

② $\Rightarrow$ $c = b$

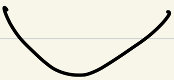
$$\sigma_2^{(2)} = \frac{q^3}{\hbar^3 \omega^2} \int [dk] \sum_{a,b} \underbrace{\frac{v_{ab} v_{bb} v_{ba}}{\epsilon_{ab}}}_{\frac{|v_{ab}|^2 v_{bb}}{\epsilon_{ab}} \text{ real.}}$$

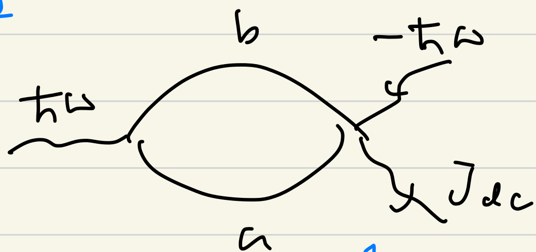
$$\times \left(\underbrace{\frac{f_{ab}}{\hbar\omega - \epsilon_{ba} + i\delta}}_{\to\ -i\pi\,\delta(\hbar\omega - \epsilon_{ba})} - \cancel{\frac{f_{bb}}{\hbar\omega - \epsilon_{bb} - i\delta}} \right) \qquad f_{bb} \to 0$$



$\sigma_2^{(2)}$ is pure imaginary

① bubble diagram gives the shift current

 $b = 2$



 $a = 1$

$$\sigma_1^{(2)} = \frac{q^3}{\hbar^3\omega^2}\int [dk]\,\frac{f_{12}\,(\partial_k v)_{12}\, v_{21}}{\hbar\omega - \epsilon_{21} + i\delta}$$

Rewrite $\langle u_1|\partial_k v|u_2\rangle$:

$$\partial_k\left[\langle u_1|v|u_2\rangle\right]$$

$$= \langle\partial_k u_1|v|u_2\rangle + \langle u_1|\partial_k v|u_2\rangle + \langle u_1|v|\partial_k u_2\rangle$$

$|1\rangle\langle 1| + |2\rangle\langle 2|$

$$\therefore (\partial_k v)_{12} = \partial_k v_{12}$$

$$- \left(\langle\partial_k u_1|u_1\rangle v_{12} + \langle\partial_k u_1|u_2\rangle v_{22}\right.$$

$$\left. + v_{11}\langle u_1|\partial_k u_2\rangle + v_{12}\langle u_2|\partial_k u_2\rangle\right)$$

$$a = i\langle u|\partial_k u\rangle$$

$$\langle u_1|\partial_k u_2\rangle = -\frac{v_{12}}{\epsilon_{12}}$$

$$(\partial_k v)_{12} = \partial_k v_{12}$$

$$- \Big(\underbrace{\langle \partial_k u_1 | u_1 \rangle}_{i a_1} v_{12} + \underbrace{\langle \partial_k u_1 | u_2 \rangle}_{\frac{v_{12}}{\epsilon_{12}}} v_{22}$$

$$+ v_{11} \underbrace{\langle u_1 | \partial_k u_2 \rangle}_{-\frac{v_{12}}{\epsilon_{12}}} + v_{12} \underbrace{\langle u_2 | \partial_k u_2 \rangle}_{-i a_2} \Big)$$

$$= \partial_k v_{12} - v_{12}\left(i a_1 - i a_2 + \frac{v_{22} - v_{11}}{\epsilon_{12}} \right)$$

$$\frac{1}{\hbar\omega - \epsilon_{21} + i\delta} \longrightarrow (-i\pi)\,\delta(\hbar\omega - \epsilon_{21})$$

$$\mathrm{Re}\,\sigma_1^{(2)} = \frac{q^3}{\hbar^3\omega^2}\int [dk]\ \mathrm{Im}\left[(\partial_k v)_{12} v_{21} \right]$$

$$\times\, \delta(\hbar\omega - \epsilon_{21})$$

$$= \frac{\pi q^3}{\hbar^3\omega^2}\int [dk]\ |v_{12}|^2 (\partial_k \varphi - a_1 + a_2)$$

$$\times\, \delta(\hbar\omega - \epsilon_{21})$$

Writing $v_{12} = |v_{12}| e^{i\varphi}$.

$$\partial_k v_{12} = (\partial_k |v_{12}|) e^{i\varphi} + |v_{12}| i(\partial_k \varphi) e^{i\varphi}$$

$$(\partial_k v_{12}) v_{21} = (\partial_k |v_{12}|) |v_{12}| + |v_{12}|^2 \cdot i \partial_k \varphi$$

$\Rightarrow$

$\mathrm{Re}\, \sigma^{(2)}(\omega)$

$$= \frac{\pi q^2}{\hbar^2 \omega^2} \int [dk] \, |v_{12}|^2 R \, \delta(\hbar\omega - \varepsilon_{21})$$

$R = a_2 - a_1 + \partial_k \varphi$: shift vector

gauge invariant

$u_1 \to e^{i\chi} u_1 \qquad a_1 \to a_1 - \partial_k \chi$

$v_{12} = \langle u_2 | v | u_1 \rangle \qquad \varphi \to \varphi + \chi$ cancel

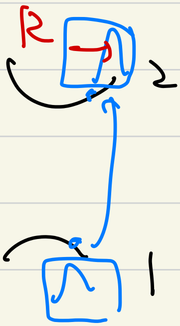
$\to v_{12} e^{i\chi} \qquad \partial_k \varphi \to \partial_k \varphi + \partial_k \chi$

(The same for u_2)

$|V_{12}|^2$: optical transition rate

R : $a_2 - a_1$: difference of intracell coordinates for band 2 & 1.

$\Rightarrow$ shift of Bloch wave packet upon optical transition



including Δ diagrams with sum rule

Also for general multiband systems :

$$\mathrm{Re}\,\sigma^{(2)} = \frac{\pi g^3}{\hbar^3 \omega^2} \int [dk] \sum_{\substack{a \in occ. \\ b \in unocc.}} |V_{ab}|^2 R_{ab} \times \delta(\hbar\omega - \varepsilon_{ba})$$

$$R_{ab} = a_b - a_a + \partial_k \varphi_{ab}$$

Sipe PRB (2000)

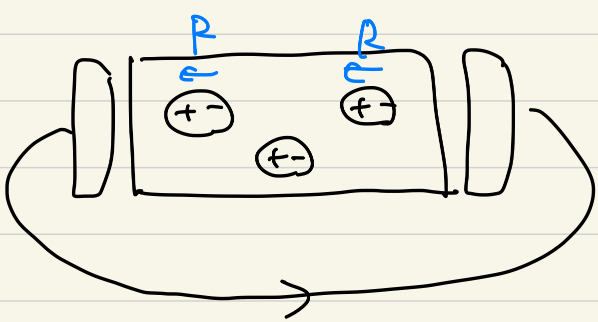
Electric polarization of photoexcited electron-hole pairs : $P_0 \sim qR$

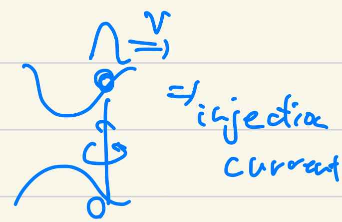
Under cw (laser) light : continuous creation of el-hl pairs

$\Rightarrow$ continuous increase of P

$$\dot{P} \propto |V_{12}|^2 q R$$

$$J = \dot{P} \Rightarrow J_{dc} \propto q\, |V_{12}|^2 R$$





In steady states, 3 processes are balanced:

i) increase of P by photoexcitation

ii) Cancellation of P by local recombination

iii) Release of P by electric current generation through electrodes.

$$\text{(i)} = \text{(ii)} + \underbrace{\text{(iii)}}_{\text{real photocurrent}}$$

extrinsic

shift current formula