Note for HopTB.jl

1 Convention

Since HopTB.jl is doing real material calculations, this unit will always be standard units. Especially, it it important to keep in mind that

- e is positive elementary charge. Electrons have charge $-e$.
- $\boldsymbol{v}$ is band velocity, whose unit is $\mathrm{m}\cdot\mathrm{s}^{-1}$. $\nabla_{\boldsymbol{k}}\varepsilon$ is $\hbar\boldsymbol{v}$.
- ω is frequency, whose unit is s^{-1}. $\hbar\omega$ is of energy unit.

2 Gauge choice for NoTB

Although the observables are gauge invariant, their ingredients are not. For example, to calculate the Berry connection $\boldsymbol{A}$, a gauge must be fixed. Our gauge choice is done at each point in the Brillouin zone and is only a local gauge. The gauge choice starts with arbitrary states at $\boldsymbol{k}_0$ point (which is convenient since we won't need to modify the states obtained by direct diagonalization). For a specific band, we collect all the bands that are degenerate everywhere around $\boldsymbol{k}_0$ and call them a band set. Especially, if the band is nondegenerate, the band set contains only one band. For arbitrary band n and band m in a band set, we choose a gauge such that $\boldsymbol{A}_{nm}(\boldsymbol{k}_0)=\boldsymbol{0}$. To show this is possible, we start with a random smooth gauge $|\tilde{u}_{n\boldsymbol{k}}\rangle$

$$\tilde{\boldsymbol{A}}_{nm} = \mathrm{i}\langle\tilde{u}_{n\boldsymbol{k}}|\nabla_{\boldsymbol{k}}\tilde{u}_{m\boldsymbol{k}}\rangle. \tag{2.1}$$

We then do a transformation $|u_{n\boldsymbol{k}}\rangle=\sum_m U_{mn}(\boldsymbol{k})|\tilde{u}_{m\boldsymbol{k}}\rangle$, where $U(\boldsymbol{k})$ is a smooth unitary matrix with $U(\boldsymbol{k}_0)$ being identity matrix. We obtain

$$\boldsymbol{A} = U^\dagger\tilde{\boldsymbol{A}}U+\mathrm{i}U^\dagger\nabla_{\boldsymbol{k}}U, \tag{2.2}$$

and especially at $\boldsymbol{k}_0$,

$$\boldsymbol{A}(\boldsymbol{k}_0) = \tilde{\boldsymbol{A}}(\boldsymbol{k}_0)+\mathrm{i}\nabla_{\boldsymbol{k}}U|_{\boldsymbol{k}=\boldsymbol{k}_0}. \tag{2.3}$$

Since $\tilde{\boldsymbol{A}}$ is Hermitian, we can choose $U(\boldsymbol{k})=\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\tilde{\boldsymbol{A}}(\boldsymbol{k}_0)}$ to make $\boldsymbol{A}(\boldsymbol{k}_0)=0$, arriving at our desired gauge.

3 Derivative of generalized eigenvalues and generalized eigenvectors

The generalized eigenvalue equation is

$$H_{\boldsymbol{k}}v_{n\boldsymbol{k}} = \varepsilon_{n\boldsymbol{k}}S_{\boldsymbol{k}}v_{n\boldsymbol{k}} \tag{3.1}$$

where $\boldsymbol{k}$ is a multidimensional parameter, H is a Hermitian matrix and S is a positive definite matrix. Written as matrices, the generalized eigenvalue equation becomes

$$H_{\boldsymbol{k}}V_{\boldsymbol{k}} = S_{\boldsymbol{k}}V_{\boldsymbol{k}}E_{\boldsymbol{k}}, \tag{3.2}$$

where the columns of $V_{\boldsymbol{k}}$ are $v_{n\boldsymbol{k}}$ and the diagonal elements of $E_{\boldsymbol{k}}$ are $\varepsilon_{n\boldsymbol{k}}$. The eigenvectors are normalized according to $V^\dagger SV=I$, where I is identity matrix. With $\partial_\alpha\coloneqq\partial_{\boldsymbol{k}^\alpha}$ and omitting the $\boldsymbol{k}$ index, we take the derivative of Eq. (3.2) once and then multiply $V^\dagger$ to the left, obtaining

$$\begin{aligned}(\partial_\alpha E)-[E,D^\alpha] &= [\partial_\alpha H]-[\partial_\alpha S]E,\\ D^\alpha &\coloneqq V^\dagger S\partial_\alpha V,\\ [O] &\coloneqq V^\dagger OV.\end{aligned} \tag{3.3}$$

The diagonal elements of the above equation gives the first order derivative of eigenvalues and the off-diagonal elements of the above equation gives the off-diagonal terms of D^α. The diagonal terms of D^α depends on the gauge choice of the eigenvectors. Taking the second order derivative of Eq. (3.2) and then multiply $V^\dagger$ to the left, we obtain

$$\begin{aligned}(\partial_\beta\partial_\alpha E)-[E,F^{\alpha\beta}] &= [\partial_\beta\partial_\alpha H]-[\partial_\beta\partial_\alpha S]E+\{[\partial_\alpha H]D^\beta-[\partial_\alpha S]D^\beta E-[\partial_\alpha S](\partial_\beta E)-D^\alpha(\partial_\beta E)+\alpha\leftrightarrow\beta\},\\ F^{\alpha\beta} &= V^\dagger S\partial_\beta\partial_\alpha V.\end{aligned}$$

Again, the diagonal elements of the above equation are second order derivative of the eigenvalues and the off-diagonal elements gives off diagonal elements of $F^{\alpha\beta}$. The diagonal terms of $F^{\alpha\beta}$ depends on the gauge choice of the eigenvectors. In the above equation, $\{\alpha \leftrightarrow \beta\}$ means switching the α and β of the previous term in the bracket.

4 Berry curvature

Berry curvature is defined as

$$\boldsymbol{\Omega} \;=\; \nabla_{\boldsymbol{k}} \times \boldsymbol{A}, \tag{4.1}$$

where $\boldsymbol{A}$ is Berry connection. Explicitly,

$$\Omega^{\gamma} \;=\; \frac{1}{2}\varepsilon^{\alpha\beta\gamma}\Omega^{\alpha\beta}, \tag{4.2}$$

where $\Omega^{\alpha\beta} = \partial^{\alpha}_{\boldsymbol{k}} A^{\beta} - \partial^{\beta}_{\boldsymbol{k}} A^{\alpha}$. HopTB.jl calculates $\Omega^{\alpha\beta}$.

5 Berry curvature dipole

The Berry curvature dipole contribution to second order photocurrent (charge current, not particle current) is

$$\sigma^{\alpha\beta\gamma}_{\mathrm{BCD}}(-\omega,\omega) \;=\; -\frac{\mathrm{i}e^3}{2\hbar(\hbar\omega+\mathrm{i}\eta)}\sum_n \int_{\mathrm{BZ}} \frac{\mathrm{d}\boldsymbol{k}}{(2\pi)^3}\Omega^{\alpha\beta}_{nn}\partial^{\gamma}_{\boldsymbol{k}} f_n + (\beta \leftrightarrow \gamma, \omega \leftrightarrow -\omega), \tag{5.1}$$

where $\Omega^{\alpha\beta} = \partial^{\alpha}_{\boldsymbol{k}} A^{\beta} - \partial^{\beta}_{\boldsymbol{k}} A^{\alpha}$, $\boldsymbol{A}$ is Berry connection, η accounts for scattering. HopTB.jl calculates the following dimensionless tensor at zero temperature

$$\begin{aligned}
\Lambda^{\alpha\beta\gamma} \;&=\; -\sum_n \int_{\mathrm{BZ}} \frac{\mathrm{d}\boldsymbol{k}}{(2\pi)^3}\Omega^{\alpha\beta}_{nn}\partial^{\gamma}_{\boldsymbol{k}} f_n \\
&=\; \hbar\sum_n \int_{\mathrm{BZ}} \frac{\mathrm{d}\boldsymbol{k}}{(2\pi)^3}\Omega^{\alpha\beta}_{nn} v^{\gamma}_n \delta(\varepsilon_n - \mu),
\end{aligned} \tag{5.2}$$

where μ is the Fermi energy. $\Lambda^{\alpha\beta\gamma}$ can be expressed as a Fermi surface integral

$$\Lambda^{\alpha\beta\gamma} \;=\; \sum_n \int_{\mathrm{FS}_n} \frac{\mathrm{d}\sigma}{(2\pi)^3}\Omega^{\alpha\beta}_{nn}\frac{v^{\gamma}_n}{|\boldsymbol{v}_n|}. \tag{5.3}$$

6 Drude weight

The optical Drude conductivity is defined as

$$\sigma^{\alpha\beta}_{\mathrm{Drude}}(\omega) \;=\; -e^2\hbar\sum_n \int_{\mathrm{BZ}} \frac{\mathrm{d}\boldsymbol{k}}{(2\pi)^3}\frac{\mathrm{i}v^{\alpha}_{n\boldsymbol{k}}v^{\beta}_{n\boldsymbol{k}}}{\hbar\omega+\mathrm{i}\eta}\frac{\partial f_{n\boldsymbol{k}}}{\partial \varepsilon_{n\boldsymbol{k}}}, \tag{6.1}$$

where η accounts for scattering. The optical Drude conductivity is part of the contribution of the conductivity for metals defined as

$$J^{\alpha}(\omega) \;=\; \sigma^{\alpha\beta}(\omega)E^{\beta}(\omega), \tag{6.2}$$

where $\boldsymbol{J}$ is charge current density (the electron has charge $-e$ and this minus sign has been included) and $\boldsymbol{E}$ is the electric field. At zero frequency,

$$\begin{aligned}
\sigma^{\alpha\beta}_{\mathrm{Drude}}(0) \;&=\; -\frac{e^2\hbar}{\eta}\sum_n \int_{\mathrm{BZ}} \frac{\mathrm{d}\boldsymbol{k}}{(2\pi)^3}\frac{\partial f_{n\boldsymbol{k}}}{\partial \varepsilon_{n\boldsymbol{k}}}v^{\alpha}_{n\boldsymbol{k}}v^{\beta}_{n\boldsymbol{k}}. \\
&=\; \frac{D^{\alpha\beta}}{\eta},
\end{aligned} \tag{6.3}$$

where

$$D^{\alpha\beta} \;=\; -e^2\hbar\sum_n \int_{\mathrm{BZ}} \frac{\mathrm{d}\boldsymbol{k}}{(2\pi)^3}\frac{\partial f_{n\boldsymbol{k}}}{\partial \varepsilon_{n\boldsymbol{k}}}v^{\alpha}_{n\boldsymbol{k}}v^{\beta}_{n\boldsymbol{k}} \tag{6.4}$$

is Drude weight.

7 OpenMX: the ordering of basis

The ordering of basis for OpenMX is

- s orbitals: s;
- p orbitals: p_x, p_y, p_z;
- d orbitals: d_{z^2}, $d_{x^2-y^2}$, d_{xy}, d_{xz}, d_{yz};
- f orbitals: f_{z^3}, f_{xz^2}, f_{yz^2}, $f_{z(x^2-y^2)}$, f_{xyz}, $f_{x(x^2-3y^2)}$, $f_{y(3x^2-y^2)}$.

In `group.jl`, `Us_openmx` contains U_l matrix, defined by

$$[U_l]_{nm} \;=\; \langle Y_l^n | X_l^m \rangle. \tag{7.1}$$

Here, Y_l^n is the complex spherical harmonics in the order of decreasing n; X_l^m is the real spherical harmonics in the order of the OpenMX convention.

8 Wannier90: the ordering of basis

The ordering of basis for Wannier90 is

- s orbitals: s;
- p orbitals: p_z, p_x, p_y;
- d orbitals: d_{z^2}, d_{xz}, d_{yz}, $d_{x^2-y^2}$, d_{xy};
- f orbitals: f_{z^3}, f_{xz^2}, f_{yz^2}, $f_{z(x^2-y^2)}$, f_{xyz}, $f_{x(x^2-3y^2)}$, $f_{y(3x^2-y^2)}$.

In `group.jl`, `Us_wann` contains U_l matrix, defined by

$$[U_l]_{nm} \;=\; \langle Y_l^n | X_l^m \rangle. \tag{8.1}$$

Here, Y_l^n is the complex spherical harmonics in the order of decreasing n; X_l^m is the real spherical harmonics in the order of the Wannier90 convention.

9 Second order instrinsic nonlinear conductivity

The intrinsic nonlinear conductivity is defined as

$$\sigma^{\alpha\beta\gamma} \;=\; 2e^3 \sum_{n,m}^{\varepsilon_m \neq \varepsilon_n} \int \frac{\mathrm{d}\boldsymbol{k}}{(2\pi)^3} \mathrm{Re}\left[\frac{v_n^\alpha A_{nm}^\beta A_{mn}^\gamma - v_n^\beta A_{nm}^\alpha A_{mn}^\gamma}{\varepsilon_n - \varepsilon_m} \right] f'(\varepsilon_n)$$

where

$$f(E) \;=\; \frac{1}{\mathrm{e}^{\beta(E-\mu)}+1} \tag{9.1}$$

is Fermi-Dirac distribution, $\boldsymbol{A}$ is Berry connection, ε is band energy. At zero temperature, $f'(E) = -\delta(E-\mu)$, and therefore (FS_n is the Fermi surface of band n)

$$\begin{aligned} \sigma^{\alpha\beta\gamma} \;&=\; -2e^3 \sum_{n,m}^{\varepsilon_m \neq \varepsilon_n} \int \frac{\mathrm{d}\boldsymbol{k}}{(2\pi)^3} \mathrm{Re}\left[\frac{v_n^\alpha A_{nm}^\beta A_{mn}^\gamma - v_n^\beta A_{nm}^\alpha A_{mn}^\gamma}{\varepsilon_n - \varepsilon_m} \right] \delta(\varepsilon_n - \mu) \\ &=\; -\frac{2e^3}{\hbar} \sum_n \int_{\mathrm{FS}_n} \frac{\mathrm{d}\sigma}{(2\pi)^3} \sum_m^{\varepsilon_m \neq \varepsilon_n} \mathrm{Re}\left[\frac{v_n^\alpha A_{nm}^\beta A_{mn}^\gamma - v_n^\beta A_{nm}^\alpha A_{mn}^\gamma}{\varepsilon_n - \varepsilon_m} \right] \frac{1}{|\boldsymbol{v}_n|}. \end{aligned} \tag{9.2}$$

10 Second order Drude weight

Second order Drude conductivity is defined by

$$\begin{aligned}\sigma^{\alpha\beta\gamma} &= -\frac{e^3\tau^2}{\hbar^3}\sum_n \int \frac{\mathrm{d}^3\boldsymbol{k}}{(2\pi)^3}(\partial_\alpha\partial_\beta\partial_\gamma\varepsilon_n)f(\varepsilon_n) \\ &= \frac{e^3\tau^2}{\hbar^3}\sum_n \int \frac{\mathrm{d}^3\boldsymbol{k}}{(2\pi)^3}(\partial_\alpha\varepsilon_n)(\partial_\beta\partial_\gamma\varepsilon_n)f'(\varepsilon_n) \end{aligned} \tag{10.1}$$

where ε_n is the band energy, f is the Fermi-Dirac distribution, τ is the scattering lifetime. At zero temperature

$$\begin{aligned}\sigma^{\alpha\beta\gamma} &= -\frac{e^3\tau^2}{\hbar^3}\sum_n \int \frac{\mathrm{d}^3\boldsymbol{k}}{(2\pi)^3}(\partial_\alpha\varepsilon_n)(\partial_\beta\partial_\gamma\varepsilon_n)\delta(\varepsilon_n-\mu), \\ &= -\frac{e^3\tau^2}{\hbar^3}\sum_n \int_{\mathrm{FS}_n} \frac{\mathrm{d}\sigma}{(2\pi)^3}(\partial_\alpha\varepsilon_n)(\partial_\beta\partial_\gamma\varepsilon_n)\frac{1}{|\nabla\varepsilon_n|}. \end{aligned} \tag{10.2}$$

HopTB.jl calculates the following quantity

$$\Lambda^{\alpha\beta\gamma} = -\frac{e^3}{\hbar}\sum_n \int_{\mathrm{FS}_n} \frac{\mathrm{d}\sigma}{(2\pi)^3}(\partial_\alpha\varepsilon_n)(\partial_\beta\partial_\gamma\varepsilon_n)\frac{1}{|\nabla\varepsilon_n|}. \tag{10.3}$$