I. NOTES ON THE DERIVATION OF μ^{abcd}, ζ^{abc} AND ξ^{ab}

This notes start the day of August 16, 2016, for $\mu^{\rm abcd}$, and contain the previous notes used for $\zeta^{\rm abc}$ and $\xi^{\rm ab}$.

A. Multiple scale approach

Using the multiple scale approach to solve the equation of motion for the single particle density matrix $\rho_{nm}(\mathbf{k};t)$, one can show that,[?]

$$\begin{aligned}\frac{\partial\rho_{cc'}}{\partial t} &= -i\left(\omega_{cc'}-i\epsilon\right)\rho_{cc'}+\frac{e^2E^a(\omega)E^{b\star}(\omega)}{i\hbar^2}\\ &\times\sum_v r^a_{cv}r^b_{vc'}\left(\frac{1}{\omega-\omega_{c'v}-i\epsilon}-\frac{1}{\omega-\omega_{cv}+i\epsilon}\right).\end{aligned}\tag{1}$$

In order to proceed further, we take $\epsilon\to 0$ in the first term, and then we change the density matrix operator to the so called *interaction* representation, by which $\hat\rho$ is replaced by

$$\tilde{\hat\rho}=e^{iH_0t/\hbar}\hat\rho e^{-iH_0t/\hbar},\tag{2}$$ {rhoi}

with H_0 the ground state Hamiltonian. The matrix elements are now,

$$\begin{aligned}\langle c\mathbf{k}|\tilde{\hat\rho}|c'\mathbf{k}\rangle &= \langle c\mathbf{k}|e^{iH_0t/\hbar}\hat\rho e^{-iH_0t/\hbar}|c'\mathbf{k}\rangle\\ &= e^{i\omega_c t}\langle c\mathbf{k}|\hat\rho|c'\mathbf{k}\rangle e^{-i\omega_{c'}t}\\ \tilde\rho_{cc'}(\mathbf{k}) &= e^{i\omega_{cc'}t}\rho_{cc'}(\mathbf{k}),\end{aligned}\tag{3}$$

where we used $H_0|n\mathbf{k}\rangle=\hbar\omega_n(\mathbf{k})|n\mathbf{k}\rangle$ with $\hbar\omega_n(\mathbf{k})$ the energy of the electronic band n at point $\mathbf{k}$, and $|n\mathbf{k}\rangle$ the Bloch state. The reciprocal lattice vector $\mathbf{k}$ is restricted to the irreducible part of the first Brillouin zone. From Eq. (3) the time derivative of $\tilde\rho_{cc'}(\mathbf{k})$ is given by

$$\begin{aligned}\frac{d\tilde\rho_{cc'}(\mathbf{k})}{dt} &= \Big(i\omega_{cc'}\rho_{cc'}(\mathbf{k})+\frac{\partial\rho_{cc'}(\mathbf{k})}{\partial t}\Big)e^{i\omega_{cc'}t}\\ &= \frac{e^2E^a(\omega)E^{b\star}(\omega)}{i\hbar^2}e^{i\omega_{cc'}t}\\ &\times\sum_v r^a_{cv}r^b_{vc'}\left(\frac{1}{\omega-\omega_{c'v}-i\epsilon}-\frac{1}{\omega-\omega_{cv}+i\epsilon}\right),\end{aligned}\tag{4}$$

where we used Eq. (1), and the $\epsilon\to 0$ still needs to be taken.

The expectation value of an observable $\mathcal{O}$ is given by

$$\mathcal{O}=\mathrm{Tr}(\hat\rho\hat{\mathcal{O}}),\tag{5}$$ {trace}

where Tr denotes the trace, given by the sum over the diagonal matrix elements, and $\hat{\mathcal{O}}$ is the quantum mechanical operator associated to the observable $\mathcal{O}$. Then,

$$\begin{aligned}\mathcal{O} &= \int \frac{d^3k}{8\pi^3} \sum_c \langle c\mathbf{k}|\hat{\rho}\hat{\mathcal{O}})|c\mathbf{k}\rangle \\ &= \int \frac{d^3k}{8\pi^3} \sum_{cc'} \langle c\mathbf{k}|\hat{\rho}|c'\mathbf{k}\rangle\langle c'\mathbf{k}|\hat{\mathcal{O}}|c\mathbf{k}\rangle \\ &= \int \frac{d^3k}{8\pi^3} \sum_{cc'} \rho_{cc'}(\mathbf{k})\mathcal{O}_{c'c}(\mathbf{k}), \end{aligned} \tag{6}$$

where we used the closure relationship $\sum_c |c\mathbf{k}\rangle\langle c\mathbf{k}| = 1$. In the interaction picture, $\tilde{\mathcal{O}}_{c'c} = \langle c'\mathbf{k}|e^{iH_0t/\hbar}\hat{\mathcal{O}}e^{-iH_0t/\hbar}|c\mathbf{k}\rangle = \mathcal{O}_{c'c}e^{-i\omega_{cc'}t}$ and thus we can also write

$$\mathcal{O} = \int \frac{d^3k}{8\pi^3} \sum_{cc'} \tilde{\rho}_{cc'}(\mathbf{k})\tilde{\mathcal{O}}_{c'c}(\mathbf{k}), \tag{7}$$

and so, we can calculate the expectation value using $\hat{\rho}$ and $\hat{\mathcal{O}}$ in either the standard Schrödinger representation or the interaction representation. From the previous equation, the rate of change of $\mathcal{O}$ is given by From Eq. (5) we finally obtain that

$$\frac{d\mathcal{O}}{dt} = \dot{\mathcal{O}} = \mathrm{Tr}(\frac{d\hat{\tilde{\rho}}}{dt}\tilde{\mathcal{O}}), \tag{8}$$ {0.e}

then,

$$\begin{aligned}\dot{\mathcal{O}} &= \int \frac{d^3k}{8\pi^3} \sum_{cc'} \frac{d\tilde{\rho}_{cc'}(\mathbf{k})}{dt}\tilde{\mathcal{O}}_{c'c}(\mathbf{k}) \\ &= \frac{e^2}{i\hbar^2} \int \frac{d^3k}{8\pi^3} \sum_{vcc'} \mathcal{O}_{c'c} r^a_{cv} r^b_{vc'} \left(\frac{1}{\omega - \omega_{c'v} - i\epsilon} - \frac{1}{\omega - \omega_{cv} + i\epsilon}\right) E^a(\omega)E^{b\star}(\omega), \end{aligned} \tag{9}$$

where we used Eq. (4), and we notice that the $e^{i\omega_{cc'}t}$ and $e^{-i\omega_{cc'}t}$ factor cancel ecah other.

B. Spin-current μ^{abcd}

The operator for the spin current is given by

$$\hat{\mathcal{O}} \to \hat{K}^{\mathrm{ab}} \equiv \hat{v}^{\mathrm{a}}\hat{S}^{\mathrm{b}}, \tag{10}$$ {1.e}

from where the matrix elements are

$$\begin{aligned}K^{\mathrm{ab}}_{nm} &= (\hat{v}^{\mathrm{a}}\hat{S}^{\mathrm{b}})_{nm} \\ K^{\mathrm{ab}}_{nm}(\mathbf{k}) &= \sum_l v^{\mathrm{a}}_{nl}(\mathbf{k})S^{\mathrm{b}}_{lm}(\mathbf{k}), \end{aligned} \tag{11}$$ {2.e}

by using $\sum_l |l\mathbf{k}\rangle\langle l\mathbf{k}| = 1$. Using time-reversal invariance, from Sec. III, Eqs. (132) and(134), it follows that, $\mathbf{v}_{nm}(-\mathbf{k}) = -\mathbf{v}_{mn}(\mathbf{k})$ and $\mathbf{S}_{nm}(-\mathbf{k}) = -\mathbf{S}_{mn}(\mathbf{k})$, from where we obtain that

$$\begin{aligned} K^{\mathrm{ab}}_{nm}(-\mathbf{k}) &= \sum_l v^{\mathrm{a}}_{nl}(-\mathbf{k}) S^{\mathrm{b}}_{lm}(-\mathbf{k}) = \sum_l (-v^{\mathrm{a}}_{ln}(\mathbf{k}))(-S^{\mathrm{b}}_{ml}(\mathbf{k})) \\ &= \sum_l v^{\mathrm{a}*}_{nl}(\mathbf{k}) S^{\mathrm{b}*}_{lm}(\mathbf{k}) = \sum_l (v^{\mathrm{a}}_{nl}(\mathbf{k}) S^{\mathrm{b}}_{lm}(\mathbf{k}))^* = K^{\mathrm{ab}*}_{nm}(\mathbf{k}). \end{aligned} \tag{12}$$
{3.e}

From Eq. (9), using $\mathbf{r}_{nm}(-\mathbf{k}) = \mathbf{r}_{mn}(\mathbf{k})$, and taking $\epsilon \to 0$, we obtain,

$$\begin{aligned} \dot{K}^{\mathrm{ab}} &= \frac{e^2}{i\hbar^2} \int \frac{d^3k}{8\pi^3} \sum_{vcc'} K^{\mathrm{ab}}_{c'c} r^{\mathrm{c}}_{cv} r^{\mathrm{d}}_{vc'} \left(\frac{1}{\omega - \omega_{c'v} - i\epsilon} - \frac{1}{\omega - \omega_{cv} + i\epsilon} \right) E^{\mathrm{c}}(\omega) E^{\mathrm{d}\star}(\omega) \\ &= \frac{e^2}{i\hbar^2} \int \frac{d^3k}{8\pi^3} \sum_{vcc'} \left((K^{\mathrm{ab}}_{c'c} r^{\mathrm{c}}_{cv} r^{\mathrm{d}}_{vc'})\big|_{\mathbf{k}>0} + (K^{\mathrm{ab}}_{c'c} r^{\mathrm{c}}_{cv} r^{\mathrm{d}}_{vc'})\big|_{\mathbf{k}<0} \right) \\ &\times \left(\frac{1}{\omega - \omega_{c'v} - i\epsilon} - \frac{1}{\omega - \omega_{cv} + i\epsilon} \right) E^{\mathrm{c}}(\omega) E^{\mathrm{d}\star}(\omega) \\ &= \frac{e^2}{i\hbar^2} \int_{\mathbf{k}>0} \frac{d^3k}{8\pi^3} \sum_{vcc'} \left(K^{\mathrm{ab}}_{c'c} r^{\mathrm{c}}_{cv} r^{\mathrm{d}}_{vc'} + K^{\mathrm{ab}*}_{c'c} r^{\mathrm{c}}_{vc} r^{\mathrm{d}}_{c'v} \right) \\ &\times \left(\frac{1}{\omega - \omega_{c'v} - i\epsilon} - \frac{1}{\omega - \omega_{cv} + i\epsilon} \right) E^{\mathrm{c}}(\omega) E^{\mathrm{d}\star}(\omega) \\ &= \frac{e^2}{i\hbar^2} \int_{\mathbf{k}>0} \frac{d^3k}{8\pi^3} \sum_{vcc'} \left(K^{\mathrm{ab}}_{c'c} r^{\mathrm{c}}_{cv} r^{\mathrm{d}}_{vc'} + (K^{\mathrm{ab}}_{c'c} r^{\mathrm{c}}_{cv} r^{\mathrm{d}}_{vc'})^* \right) \\ &\times \left(\frac{1}{\omega - \omega_{c'v} - i\epsilon} - \frac{1}{\omega - \omega_{cv} + i\epsilon} \right) E^{\mathrm{c}}(\omega) E^{\mathrm{d}\star}(\omega) \\ &= \frac{e^2}{i\hbar^2} \frac{1}{2} \int \frac{d^3k}{8\pi^3} \sum_{vcc'} 2\mathrm{Re}\Big[K^{\mathrm{ab}}_{c'c} r^{\mathrm{c}}_{cv} r^{\mathrm{d}}_{vc'} \Big] \Big\{ \mathcal{P} \left(\frac{\omega_{c'c}}{(\omega - \omega_{c'v})(\omega - \omega_{cv})} \right) \\ &+ i\pi \left(\delta(\omega - \omega_{c'v}) + \delta(\omega - \omega_{cv}) \right) \Big\} E^{\mathrm{c}}(\omega) E^{\mathrm{d}\star}(\omega) \\ &\approx \frac{\pi e^2}{\hbar^2} \int \frac{d^3k}{8\pi^3} \sum_{vcc'} \mathrm{Re}\Big[K^{\mathrm{ab}}_{c'c} r^{\mathrm{c}}_{cv} r^{\mathrm{d}}_{vc'} \Big] \Big(\delta(\omega - \omega_{c'v}) + \delta(\omega - \omega_{cv}) \Big) E^{\mathrm{c}}(\omega) E^{\mathrm{d}\star}(\omega) \\ &= \frac{\pi e^2}{\hbar^2} \int \frac{d^3k}{8\pi^3} \sum_{vcc'} \mathrm{Re}\Big[K^{\mathrm{ab}}_{c'c} r^{\mathrm{c}}_{cv} r^{\mathrm{d}}_{vc'} + K^{\mathrm{ab}}_{cc'} r^{\mathrm{c}}_{c'v} r^{\mathrm{d}}_{vc} \Big] \delta(\omega - \omega_{cv}) E^{\mathrm{c}}(\omega) E^{\mathrm{d}\star}(\omega), \end{aligned} \tag{13}$$
{5.e}

since $\omega_{cc'} \sim 0$ and we exchange $c \leftrightarrow c'$. Now, form Eq. (12) we obtain that

$$\begin{aligned} \mathrm{Re}\Big[K^{\mathrm{ab}}_{cc'} r^{\mathrm{c}}_{c'v} r^{\mathrm{d}}_{vc} \Big] &= \frac{1}{2} \Big(K^{\mathrm{ab}}_{cc'} r^{\mathrm{c}}_{c'v} r^{\mathrm{d}}_{vc} + (K^{\mathrm{ab}}_{cc'} r^{\mathrm{c}}_{c'v} r^{\mathrm{d}}_{vc})^* \Big) \\ &= \frac{1}{2} \Big(K^{\mathrm{ab}}_{cc'} r^{\mathrm{c}}_{c'v} r^{\mathrm{d}}_{vc} + K^{\mathrm{ab}}_{cc'} r^{\mathrm{c}}_{vc'} r^{\mathrm{d}}_{cv} \Big) = \mathrm{Re}\Big[K^{\mathrm{ab}}_{cc'} r^{\mathrm{c}}_{vc'} r^{\mathrm{d}}_{cv} \Big], \end{aligned} \tag{14}$$
{6.2}

thus Eq. (13) reduces to

$$\begin{aligned} \dot{K}^{\mathrm{ab}} &= \frac{\pi e^2}{\hbar^2} \int \frac{d^3k}{8\pi^3} \sum_{vcc'} \mathrm{Re}\Big[K^{\mathrm{ab}}_{c'c} r^{\mathrm{c}}_{cv} r^{\mathrm{d}}_{vc'} + K^{\mathrm{ab}}_{cc'} r^{\mathrm{c}}_{vc'} r^{\mathrm{d}}_{cv} \Big] \delta(\omega - \omega_{cv}) E^{\mathrm{c}}(\omega) E^{\mathrm{d}\star}(\omega) \\ &= \frac{\pi e^2}{\hbar^2} \int \frac{d^3k}{8\pi^3} \sum_{vcc'} \mathrm{Re}\Big[K^{\mathrm{ab}}_{c'c} \Big(r^{\mathrm{c}}_{cv} r^{\mathrm{d}}_{vc'} + r^{\mathrm{d}}_{cv} r^{\mathrm{c}}_{vc'} \Big) \Big] \delta(\omega - \omega_{cv}) E^{\mathrm{c}}(\omega) E^{\mathrm{d}\star}(\omega) \end{aligned}$$

$$= \frac{\pi e^2}{\hbar^2}\int\frac{d^3k}{8\pi^3}\sum_{vcc'}\mathrm{Re}\Big[K^{\mathrm{ab}}_{c'c}\Big(r^{\mathrm{c}}_{cv}r^{\mathrm{d}}_{vc'} + (\mathrm{c}\leftrightarrow\mathrm{d})\Big)\Big]\delta(\omega-\omega_{cv})E^{\mathrm{c}}(\omega)E^{\mathrm{d}\star}(\omega)$$

$$= \frac{\pi e^2}{\hbar^2}\int\frac{d^3k}{8\pi^3}\sum_{vcc'}\mathrm{Re}\Big[K^{\mathrm{ab}}_{c'c}\Big(r^{\mathrm{c}}_{vc'}r^{\mathrm{d}}_{cv} + (\mathrm{c}\leftrightarrow\mathrm{d})\Big)\Big]\delta(\omega-\omega_{cv})E^{\mathrm{c}}(\omega)E^{\mathrm{d}\star}(\omega). \qquad (15) \quad \{7.e\}$$

We write

$$\dot{K}^{\mathrm{ab}} = \mu^{\mathrm{abcd}}E^{\mathrm{c}}(\omega)E^{\mathrm{d}\star}(\omega), \qquad (16) \quad \{8.e\}$$

where from Eq. (15) we obtain that

$$\mu^{\mathrm{abcd}} = \frac{\pi e^2}{\hbar^2}\int\frac{d^3k}{8\pi^3}{\sum_{vcc'}}'\mathrm{Re}\Big[K^{\mathrm{ab}}_{c'c}\Big(r^{\mathrm{c}}_{vc'}r^{\mathrm{d}}_{cv} + (\mathrm{c}\leftrightarrow\mathrm{d})\Big)\Big]\delta(\omega-\omega_{cv}), \qquad (17) \quad \{9.e\}$$

where the $'$ in the sum, reminds us that c and c' are quasi degenerate, and thus the sum only covers these states. Above equation is the same as Eq. (3) of? , which was obtained by using the semiconductor optical Bloch equations (SOBEs), solved perturbatively to first order in the field intensity (H. Haug and S. W. Koch, Quantum Theory of the Optical and Electronic Properties of Semiconductors (World Scientific, Singapore, 1993); U. Rössler, Phys. Status Solidi B 234, 385 (2002)).

From **?** , we include the scissors correction to the band gap, and the nonlocal part of the pseudopotentials by taking

$$\mathbf{v} \equiv \dot{\mathbf{r}} = \frac{1}{i\hbar}[\mathbf{r}, H_0], \qquad (18) \quad \{mv\}$$

from where we define

$$\mathbf{v}^{\Sigma} = \mathbf{v} + \mathbf{v}^{\mathrm{nl}} + \mathbf{v}^{S} = \mathbf{v}^{\mathrm{LDA}} + \mathbf{v}^{S}, \qquad (19) \quad \{vop2\}$$

with

$$\begin{aligned}\mathbf{v} &= \frac{\mathbf{p}}{m_e},\\ \mathbf{v}^{\mathrm{nl}} &= \frac{1}{i\hbar}[\mathbf{r}, V^{\mathrm{nl}}], \qquad (20) \quad \{vnl\}\\ \mathbf{v}^{S} &= \frac{1}{i\hbar}[\mathbf{r}, S],\\ \mathbf{v}^{\mathrm{LDA}} &= \mathbf{v} + \mathbf{v}^{\mathrm{nl}}. \qquad (21)\end{aligned}$$

Then,

$$\mu^{\mathrm{abcd}} = \frac{\pi e^2}{\hbar^2}\int\frac{d^3k}{8\pi^3}\sum_{vcc'}\mathrm{Re}\Big[K^{\Sigma,\mathrm{ab}}_{c'c}\Big(r^{\mathrm{c}}_{vc'}r^{\mathrm{d}}_{cv} + (\mathrm{c}\leftrightarrow\mathrm{d})\Big)\Big]\delta(\omega-\omega^{\Sigma}_{cv})$$

$$= \frac{\pi e^2}{2\hbar}\int \frac{d^3k}{8\pi^3}\sum_{vcc'}\sum_{l}\mathrm{Re}\Big[v^{\Sigma,\mathrm{a}}_{c'l}\sigma^{\mathrm{b}}_{lc}\Big(r^{\mathrm{c}}_{vc'}r^{\mathrm{d}}_{cv}+(\mathrm{c}\leftrightarrow\mathrm{d})\Big)\Big]\delta(\omega-\omega^{\Sigma}_{cv}), \tag{22}$$ {10.e}

is the scissor corrected pseudotensor for the spin density injection current that contains the contribution from the nonlocal part of the pseudopotentials, and is valid only for noncentrosymmetric crystals. We used,

$$K^{\Sigma,\mathrm{ab}}_{c'c} = \sum_{l} v^{\Sigma,\mathrm{a}}_{c'l}S^{\mathrm{b}}_{lc} = \frac{\hbar}{2}\sum_{l} v^{\Sigma,\mathrm{a}}_{c'l}\sigma^{\mathrm{b}}_{lc}, \tag{23}$$ {11.e}

and $\omega^{\Sigma}_{cv} = \omega_c + \Delta - \omega_v$ includes the scissor corrected conduction energies, where Δ is the energy correction, and

$$\mathbf{r}_{nm}(\mathbf{k}) = \frac{\mathbf{v}^{\Sigma}_{nm}(\mathbf{k})}{i\omega^{\Sigma}_{nm}(\mathbf{k})} = \frac{\mathbf{v}^{\mathrm{LDA}}_{nm}(\mathbf{k})}{i\omega^{\mathrm{LDA}}_{nm}(\mathbf{k})} \qquad n \notin D_m, \tag{24}$$ {chon.10}

are the position matrix elements, which are the same in the scissored or unscissored LDA case. We mention that $\mathbf{r}_{nm}(\mathbf{k})$ contain the contribution from the nonlocal part of the pseudopotential, $V^{\mathrm{nl}}(\mathbf{k})$. TINIBA® codes $\mathbf{v}^{\Sigma}_{nm}(\mathbf{k})$ under the array `calVsig(3,nMax,nMax)`, where `3` is for the Cartesian directions ($1 \to x, 2 \to y, 3 \to z$) and `nMax` is for the total number of bands. This array works for bulk and surface calculations under the same name; for a surface calculation it contains $\boldsymbol{\mathcal{V}}^{\Sigma}_{nm}(\mathbf{k})$.

1. *Units*

It so happens that in Gaussian (cgs) units (see Eq. (50))

$$\begin{aligned}
[\mu] &= [v][\zeta] \\
[\mu_{\mathrm{S.I.}}] &= [v_{\mathrm{S.I.}}][\zeta_{\mathrm{S.I.}}] \\
\Rightarrow [\mu_{\mathrm{S.I.}}] &= \frac{m}{s}4\pi\frac{\hbar}{2}\frac{\epsilon_0}{\hbar}[\mathrm{Im}[\chi_{\mathrm{cgs}}]],
\end{aligned} \tag{25}$$ {rnn.n20}

where we used Eq. (52), and $\mathrm{Im}[\chi^{\mathrm{ab}}_{\mathrm{cgs}}]$ is dimensionless. Therefore, the units are

$$[\mu_{\mathrm{S.I.}}] = \frac{m}{s}[\hbar]\frac{[\epsilon_0]}{[\hbar]} = \frac{m}{s}Js\frac{F/m}{Js} = \frac{m}{s}Js\frac{C/mV}{CVs} = \frac{m}{s}\frac{J}{mV^2} = \frac{J}{sV^2}, \tag{26}$$ {rnn.n3nn}

in agreement with Ref. **?** , and with the units derived from Eq. (16), i.e.

$$\begin{aligned}
[\dot{K}] &= [\mu][E]^2 \\
\frac{1}{s}\frac{m}{s}\hbar\frac{1}{m^3} = \frac{\hbar}{s^2m^2} &= [\mu]\frac{V^2}{m^2} \\
\Rightarrow [\mu] &= \frac{\hbar}{s^2V^2} = \frac{J}{sV^2}
\end{aligned}$$

$$\Rightarrow [\dot{K}] = \frac{J}{sm^2}, \qquad (27) \quad \{\texttt{zp.1}\}$$

where we recall that $\hat{\mathbf{S}}$ is the spin density. From Eqs. (22) and (50), and using Eq. (53), we get

$$[\mu] = \frac{m}{s}[\zeta] = \frac{m}{s}\frac{J}{mV^2} = \frac{J}{sV^2}, \qquad (28) \quad \{\texttt{um.1}\}$$

which agrees with Eq. (26).

C. Degree of Spin Injection

From Sec. I E, we can take Eq. (58)

$$\dot{n}(\mathbf{r}) = \xi^{ab}(\mathbf{r};\omega)E^a(-\omega)E^b(\omega), \qquad (29) \quad \{\texttt{rnn}\}$$

and define the degree of spin injection as

$$\mathcal{V}^{\mathrm{ab}} \equiv \frac{\dot{K}^{\mathrm{ab}}}{(\hbar/2)\dot{n}}, \qquad (30) \quad \{\texttt{eez.1}\}$$

where as we se from Eqs. (16), (17), (58) and (59), the units are given by

$$\begin{aligned}[\mathcal{V}^{\mathrm{ab}}] &= \frac{[\dot{K}^{\mathrm{ab}}]}{(\hbar/2)[\dot{n}]} \\ &= \frac{2}{\hbar}[v][S] = \frac{m}{s},\end{aligned} \qquad (31) \quad \{\texttt{eez.2}\}$$

i.e. the degree of spin injection, $\mathcal{V}^{\mathrm{ab}}$, gives the speed of an electron along the Cartesian direction "a", with a spin oriented along the Cartesian direction "b", in units of speed, i.e. m/s.

1. Centrosymmetric Crystals

For a centrosymmetric crystals, it follows that $H(\mathbf{r}) = H(-\mathbf{r})$, and that $\psi_n(\mathbf{k},-\mathbf{r}) = \psi_n(-\mathbf{k},\mathbf{r})$ (U.of.Toronto notes, page 42), then

$$\begin{aligned}\mathcal{O}_{nm}(\mathbf{k}) &= \int d^3r\, \psi^*_n(\mathbf{k},\mathbf{r})\, \hat{\mathcal{O}}(\mathbf{r})\, \psi_m(\mathbf{k},\mathbf{r}) \\ \mathcal{O}_{nm}(-\mathbf{k}) &= \int d^3r\, \psi^*_n(-\mathbf{k},\mathbf{r})\, \hat{\mathcal{O}}(\mathbf{r})\, \psi_m(-\mathbf{k},\mathbf{r}) \\ &= \int d^3r\, \psi^*_n(\mathbf{k},-\mathbf{r})\, \hat{\mathcal{O}}(\mathbf{r})\, \psi_m(\mathbf{k},-\mathbf{r}) \\ &= \int d^3r\, \psi^*_n(\mathbf{k},\mathbf{r})\, \hat{\mathcal{O}}(-\mathbf{r})\, \psi_m(\mathbf{k},\mathbf{r}) \quad (\mathbf{r}\to-\mathbf{r}) \\ &= \pm\int d^3r\, \psi^*_n(\mathbf{k},\mathbf{r})\, \hat{\mathcal{O}}(\mathbf{r})\, \psi_m(\mathbf{k},\mathbf{r}) \quad (\mathcal{O}(-\mathbf{r}) = \pm\mathcal{O}(\mathbf{r}))\end{aligned}$$

$$= \pm\mathcal{O}_{nm}(\mathbf{k}). \tag{32}$$ {e.0}

Therefore, we obtain that

$$\mathbf{r}_{nm}(-\mathbf{k}) = -\mathbf{r}_{nm}(\mathbf{k})$$
$$\mathbf{v}_{nm}(-\mathbf{k}) = -\mathbf{v}_{nm}(\mathbf{k})$$
$$\mathbf{S}_{nm}(-\mathbf{k}) = \mathbf{S}_{nm}(\mathbf{k}), \tag{33}$$ {e.1}

since $\hat{\mathbf{r}}(-\mathbf{r}) = -\hat{\mathbf{r}}(\mathbf{r})$, $\hat{\mathbf{v}}(-\mathbf{r}) = -\hat{\mathbf{v}}(\mathbf{r})$ and $\hat{\mathbf{S}}(-\mathbf{r}) = \hat{\mathbf{S}}(\mathbf{r})$, as the spin operator does not depend on position. From Eq. (12)

$$K^{\mathrm{ab}}_{nm}(-\mathbf{k}) = \sum_l v^{\mathrm{a}}_{nl}(-\mathbf{k})S^{\mathrm{b}}_{lm}(-\mathbf{k}) = \sum_l (-v^{\mathrm{a}}_{nl}(\mathbf{k}))S^{\mathrm{b}}_{lm}(\mathbf{k}) = -K^{\mathrm{ab}}_{nm}(\mathbf{k}). \tag{34}$$ {e.2}

Now,

$$(K^{\mathrm{ab}}_{c'c}r^{\mathrm{c}}_{cv}r^{\mathrm{d}}_{vc'})\big|_{\mathbf{k}<0} = -K^{\mathrm{ab}}_{c'c}r^{\mathrm{c}}_{cv}r^{\mathrm{d}}_{vc'}\big|_{\mathbf{k}>0}, \tag{35}$$ {e.3}

that when used in Eq. (13), would leads to

$$\mu^{\mathrm{abcd}} = 0, \tag{36}$$ {e.4}

for centrosymmetric crystals.

D. Spin polarization ζ^{abc} and Degree of Spin Polarization

Eq. (9) can be used to compute the *spin-injection rate* $\dot{\boldsymbol{S}} \equiv \mathrm{d}\boldsymbol{S}/\mathrm{d}t$ with

$$\hat{\mathcal{O}} \to \hat{S}^a = \frac{\hbar}{2}\hat{\sigma}^a \tag{37}$$

where $\hat{\sigma}^a$ are the Pauli Matrices

$$\hat{\sigma}^x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \hat{\sigma}^y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \text{and} \quad \hat{\sigma}^z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{38}$$

that are operators in spinor space, therefore,

$$\frac{d\mathcal{S}^a}{dt} = \frac{e^2}{i\hbar^2}\int \frac{d^3k}{8\pi^3}\sum_{vcc'} \hat{\mathcal{S}}^a_{c'c}r^b_{cv}r^c_{vc'}\left(\frac{1}{\omega-\omega_{c'v}-i\epsilon} - \frac{1}{\omega-\omega_{cv}+i\epsilon}\right)E^b(\omega)E^{c\star}(\omega). \tag{39}$$

Using the so called,time-reversal invariance by which

$$\omega_m(-\mathbf{k}) = \omega(\mathbf{k}),$$

$$
\begin{aligned}
r^a_{mn}(-\mathbf{k}) &= r^a_{nm}(\mathbf{k}),\\
S^a_{mn}(-\mathbf{k}) &= -S^a_{nm}(\mathbf{k}),
\end{aligned}
\tag{40}
$$

we can add the $\mathbf{k}$ and $-\mathbf{k}$ contributions to the integral in Eq. (39) to obtain

$$
\begin{aligned}
\frac{d\mathcal{S}^a}{dt} &= \frac{e^2}{i\hbar^2}\int_{\mathbf{k}>0}\frac{d^3k}{8\pi^3}\sum_{vcc'}\Big((\mathcal{S}^a_{c'c}r^b_{cv}r^c_{vc'})|_{\mathbf{k}} + (\mathcal{S}^a_{c'c}r^b_{cv}r^c_{vc'})|_{-\mathbf{k}}\Big)\\
&\times\left(\frac{1}{\omega-\omega_{c'v}-i\epsilon}-\frac{1}{\omega-\omega_{cv}+i\epsilon}\right)E^bE^{c\star}\\
&= \frac{e^2}{i\hbar^2}\int_{\mathbf{k}>0}\frac{d^3k}{8\pi^3}\sum_{vcc'}\Big((\mathcal{S}^a_{c'c}r^b_{cv}r^c_{vc'})|_{\mathbf{k}} - (\hat{\mathcal{S}}^a_{cc'}r^b_{vc}r^c_{c'v})|_{\mathbf{k}}\Big)\\
&\times\left(\frac{1}{\omega-\omega_{c'v}-i\epsilon}-\frac{1}{\omega-\omega_{cv}+i\epsilon}\right)E^bE^{c\star}\\
&= \frac{e^2}{i\hbar^2}\frac{1}{2}\int\frac{d^3k}{8\pi^3}\sum_{vcc'}\Big(\mathcal{S}^a_{c'c}r^b_{cv}r^c_{vc'}) - (\hat{\mathcal{S}}^a_{c'c}r^b_{cv}r^c_{vc'})^*\Big)\\
&\times\left(\frac{1}{\omega-\omega_{c'v}-i\epsilon}-\frac{1}{\omega-\omega_{cv}+i\epsilon}\right)E^bE^{c\star}\\
&= \frac{e^2}{\hbar^2}\int\frac{d^3k}{8\pi^3}\sum_{vcc'}\mathrm{Im}\big[\mathcal{S}^a_{c'c}r^b_{cv}r^c_{vc'}\big]\left(\frac{1}{\omega-\omega_{c'v}-i\epsilon}-\frac{1}{\omega-\omega_{cv}+i\epsilon}\right)E^bE^{c\star},
\end{aligned}
\tag{41}
$$

where in going from the second to the third equal sign, we use the fact that for any Hermitian operator $\mathcal{O}_{mn}(\mathbf{k}) = \mathcal{O}^*_{nm}(\mathbf{k})$, and that the one half comes from the unrestricted integration over all values of $\mathbf{k}$ and not only $\mathbf{k} > 0$. Aided by the identity

$$
\lim_{\epsilon\to 0}\frac{1}{x\mp i\epsilon} = \mathcal{P}(\frac{1}{x}) \pm i\pi\,\delta(x),
\tag{42}
$$

where $\mathcal{P}$ means the *principal part*, Eq. (39) can be written as

$$
\begin{aligned}
\frac{d\mathcal{S}^a}{dt} &= \frac{e^2}{\hbar^2}\int\frac{d^3k}{8\pi^3}\sum_{vcc'}\mathrm{Im}\big[\mathcal{S}^a_{c'c}r^b_{cv}r^c_{vc'}\big]\Big\{\mathcal{P}\left(\frac{1}{\omega-\omega_{c'v}}-\frac{1}{\omega-\omega_{cv}}\right)\\
&+ i\pi\left(\delta(\omega-\omega_{c'v})+\delta(\omega-\omega_{cv})\right)\Big\}E^bE^{c\star}\\
&= \frac{e^2}{\hbar^2}\int\frac{d^3k}{8\pi^3}\sum_{vcc'}\mathrm{Im}\big[\mathcal{S}^a_{c'c}r^b_{cv}r^c_{vc'}\big]\Big\{\mathcal{P}\left(\frac{\omega_{c'c}}{(\omega-\omega_{c'v})(\omega-\omega_{cv})}\right)\\
&+ i\pi\left(\delta(\omega-\omega_{c'v})+\delta(\omega-\omega_{cv})\right)\Big\}E^bE^{c\star}\\
&\simeq \frac{i\pi e^2}{\hbar^2}\int\frac{d^3k}{8\pi^3}{\sum_{vcc'}}'\,\mathrm{Im}\big[\mathcal{S}^a_{c'c}r^b_{cv}r^c_{vc'}\big]\left(\delta(\omega-\omega_{c'v})+\delta(\omega-\omega_{cv})\right)E^bE^{c\star},
\end{aligned}
\tag{43}
$$

since the term that goes with the principal part is of the order of $\omega_{cc'}$ which is very small as the states c and c' are quasi degenerate. Indeed, the primed sigma symbol Σ' means that the sum is to be performed on pairs cc' of quasi-degenerate conduction bands. It seems that in 43 there are two resonant frequencies, one at $\omega = \omega_{cv}(\mathbf{k})$ and other at $\omega = \omega_{c'v}(\mathbf{k})$, but actually there is only one. This can be shown if one changes $c \rightleftharpoons c'$ in the second δ function, then

$$\frac{d\mathcal{S}^a}{dt} = \frac{i\pi e^2}{\hbar^2}\int \frac{d^3k}{8\pi^3}\sum_{vcc'}{}' \Big(\mathrm{Im}\big[\mathcal{S}^a_{c'c} r^b_{cv} r^c_{vc'}\big] + \mathrm{Im}\big[\mathcal{S}^a_{cc'} r^b_{c'v} r^c_{vc}\big]\Big)\delta(\omega - \omega_{cv}) E^b E^{c\star}, \tag{44}$$

where it is clear that the only resonant frequency is at $\omega = \omega_{cv}(\mathbf{k})$, and the coherence of the $v \to c$ and $v \to c'$ precesses is given by the addition of the two Im terms that are proportional to the probability of such transitions. Compactly $\dot{S}^a$ is written as,

$$\dot{S}^a = \tilde{\zeta}^{abc} E^b(\omega) E^{c^*}(\omega), \tag{45}$$ {eq:29}

where

$$\tilde{\zeta}^{abc} = \frac{i\pi e^2}{\hbar^2}\int \frac{d^3k}{8\pi^3}\sum_{vcc'}{}' \Big(\mathrm{Im}\big[\mathcal{S}^a_{c'c} r^b_{cv} r^c_{vc'}\big] + \mathrm{Im}\big[\mathcal{S}^a_{cc'} r^b_{c'v} r^c_{vc}\big]\Big)\delta(\omega - \omega_{cv}), \tag{46}$$

is denoted as the *spin-injection 3*$^{\text{th}}$ *rank pseudo-tensor component*. In simple terms, a pseudo-tensor is an object that transforms like a tensor under a proper rotation, but changes sign under an improper rotation. That is, a pseudo-tensor is a transformation that can be expressed as an inversion followed by a proper rotation. ζ^{abc} in the argot of nonlinear optics, plays a similar role than the 2^{th} order susceptibility χ^{abc}. We see that ζ^{abc} is purely imaginary and that $\zeta^{abc} = -\zeta^{acb}$, since

$$\begin{aligned}
2i\Big(\mathrm{Im}\big[\mathcal{S}^a_{c'c} r^b_{cv} r^c_{vc'}\big] + \mathrm{Im}\big[\mathcal{S}^a_{cc'} r^b_{c'v} r^c_{vc}\big]\Big) &= \mathcal{S}^a_{c'c} r^b_{cv} r^c_{vc'} - \Big(\mathcal{S}^a_{c'c} r^b_{cv} r^c_{vc'}\Big)^* \\
&+ \mathcal{S}^a_{cc'} r^b_{c'v} r^c_{vc} - \Big(\mathcal{S}^a_{cc'} r^b_{c'v} r^c_{vc}\Big)^* \\
&= \mathcal{S}^a_{c'c} r^b_{cv} r^c_{vc'} - \mathcal{S}^a_{cc'} r^b_{vc} r^c_{c'v} \\
&+ \mathcal{S}^a_{cc'} r^b_{c'v} r^c_{vc} - \mathcal{S}^a_{c'c} r^b_{vc'} r^c_{cv} \\
&= -\mathcal{S}^a_{cc'} r^b_{vc} r^c_{c'v} + \mathcal{S}^a_{cc'} r^b_{c'v} r^c_{vc} \\
&- \mathcal{S}^a_{c'c} r^b_{vc'} r^c_{cv} + \mathcal{S}^a_{c'c} r^b_{cv} r^c_{vc'} \\
&= -2i\Big(\mathrm{Im}\Big[\mathcal{S}^a_{cc'} r^b_{vc} r^c_{c'v}\Big] + \mathrm{Im}\Big[\mathcal{S}^a_{c'c} r^b_{vc'} r^c_{cv}\Big]\Big) \\
&= -2i\Big(\mathrm{Im}\Big[\mathcal{S}^a_{c'c} r^c_{cv} r^b_{vc'}\Big] + \mathrm{Im}\Big[\mathcal{S}^a_{cc'} r^c_{c'v} r^b_{vc}\Big]\Big).
\end{aligned} \tag{47}$$

Now, from Eq. (45) we have that

$$\begin{aligned}
\dot{S}^a &= \tilde{\zeta}^{abc} E^b E^{c^*} + \tilde{\zeta}^{acb} E^c E^{b^*} \quad \text{no sum over} b \neq c \\
&= \tilde{\zeta}^{abc} E^b E^{c^*} - \tilde{\zeta}^{abc} E^c E^{b^*} \quad \text{no sum over} b \neq c \\
&= \tilde{\zeta}^{abc}\big(E^b E^{c^*} - E^c E^{b^*}\big) \quad \text{no sum over} b \neq c
\end{aligned}$$

$$= \quad -2i\tilde{\zeta}^{abc}\mathrm{Im}[E^{b^*}E^c] \quad \text{no sum over} b \neq c. \tag{48}$$

Writing $\tilde{\zeta}^{abc} = i\zeta^{abc}$, we finally obtain, as we must,

$$\dot{S}^a = 2\zeta^{abc}\mathrm{Im}[E^{b^*}E^c], \tag{49}$$ {sdotnew}

as a real quantity, with

$$\zeta^{abc} \quad = \quad \frac{\pi e^2}{\hbar^2}\int\frac{d^3k}{8\pi^3}\sum_{vcc'}{}' \Big(\mathrm{Im}\big[\mathcal{S}^a_{c'c}r^b_{cv}r^c_{vc'}\big] + \mathrm{Im}\big[\mathcal{S}^a_{cc'}r^b_{c'v}r^c_{vc}\big]\Big)\delta(\omega - \omega_{cv}), \tag{50}$$

For the purposes of this work, bands that are separated from each other by less than 30 meV are considered as quasi-degenerate, which is approximately both the laser pulse energy and the room temperature energy (see 1).

Warning: in the code the factor of $(\hbar/2)$ is NOT included in ζ^{abc}. This factor comes from $\hat{S}^a = (\hbar/2)\hat{\sigma}^a$. Since the spin of the electron is given in $(\hbar/2)$ units we leave it out in the code. Thus, this is the reason why $\mathcal{D}^a$ (see Sec. I F) is defined by canceling this $(\hbar/2)$ factor! As explained in Sec. I F this factor is correctly taken into account in $\mathcal{D}^a$. Therefore the output of the code must be used as it comes out of the cluster in order to compute $\mathcal{D}^a$ without any extra $(\hbar/2)$ factor! To report the value of ζ^{abc} alone, we must multiply by $(\hbar/2)$ and use the appropriate S.I. units!

1. *Units*

From Eq. (45), the units are

$$\begin{aligned}\frac{\hbar}{2}\frac{1}{s} &= [\zeta]\frac{V^2}{m^2}\\ \Rightarrow [\zeta] &= \frac{\hbar}{2}\frac{m^2}{V^2 s},\end{aligned} \tag{51}$$ {n.100}

It so happens that in Gaussian (cgs) units (see Eq. (63))

$$\begin{aligned}[\zeta] &= \frac{\hbar}{2}\frac{1}{\hbar}[\mathrm{Im}[\chi]]\\ \Rightarrow [\zeta_{\text{S.I.}}] &= 4\pi\frac{\hbar}{2}\frac{\epsilon_0}{\hbar}[\mathrm{Im}[\chi_{\text{cgs}}]],\end{aligned} \tag{52}$$ {rnn.n2}

where $\mathrm{Im}[\chi^{\text{ab}}_{\text{cgs}}]$ is dimensionless. Therefore, the units are

$$[\zeta_{\text{S.I.}}] = [\hbar]\frac{[\epsilon_0]}{[\hbar]} = Js\frac{F/m}{Js} = Js\frac{C/mV}{CVs} = \frac{J}{mV^2}, \tag{53}$$ {rnn.n3}

in agreement with Ref. **?** .

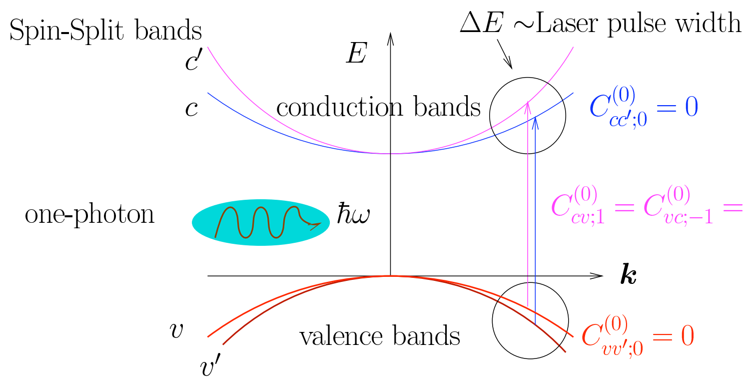

FIG. 1: (color online) Coherence arise from simultaneous excitation of two close conduction bands, c and c', by the nite energy width of the laser beam.

E. Carrier injection rate $\dot{n}$

From Eq. (9) we have that

$$\begin{aligned} \frac{d\mathcal{O}}{dt} &= \frac{e^2}{i\hbar^2}\int\frac{d^3k}{8\pi^3}\sum_{vcc'}\mathcal{O}_{c'c}r^a_{cv}r^b_{vc'}\left(\frac{1}{\omega-\omega_{c'v}-i\epsilon}-\frac{1}{\omega-\omega_{cv}+i\epsilon}\right)E^a(\omega)E^{b\star}(\omega) \\ &= \frac{e^2}{i\hbar^2}\int\frac{d^3k}{8\pi^3}\sum_{vcc'}\mathcal{O}_{c'c}r^a_{vc'}r^b_{cv}\left(\frac{1}{\omega-\omega_{c'v}-i\epsilon}-\frac{1}{\omega-\omega_{cv}+i\epsilon}\right)E^{a\star}(\omega)E^b(\omega), \end{aligned} \tag{54}$$

where we only exchanged $a \leftrightarrow b$. Using Eq. (42)

$$\begin{aligned} \frac{d\mathcal{O}}{dt} &= \frac{e^2}{i\hbar^2}\int\frac{d^3k}{8\pi^3}\sum_{vcc'}\mathcal{O}_{c'c}r^a_{vc'}r^b_{cv}\Big[\mathcal{P}\left(\frac{1}{\omega-\omega_{c'v}}-\frac{1}{\omega-\omega_{cv}}\right) \\ &+\; i\pi\left(\delta(\omega-\omega_{c'v})+\delta(\omega-\omega_{cv})\right)\Big]E^a(-\omega)E^b(\omega) \\ &= \frac{e^2}{i\hbar^2}\int\frac{d^3k}{8\pi^3}\sum_{vcc'}\mathcal{O}_{c'c}r^a_{vc'}r^b_{cv}\Big[\mathcal{P}\left(\frac{\omega_{c'c}}{(\omega-\omega_{c'v})(\omega-\omega_{cv})}\right) \\ &+\; i\pi\left(\delta(\omega-\omega_{c'v})+\delta(\omega-\omega_{cv})\right)\Big]E^a(-\omega)E^b(\omega) \\ &\approx \frac{\pi e^2}{\hbar^2}\int\frac{d^3k}{8\pi^3}\sum_{vcc'}\mathcal{O}_{c'c}r^a_{vc'}r^b_{cv}\Big[\delta(\omega-\omega_{c'v})+\delta(\omega-\omega_{cv})\Big]E^a(-\omega)E^b(\omega) \\ &= \frac{\pi e^2}{\hbar^2}\int\frac{d^3k}{8\pi^3}\sum_{vcc'}\Big[\mathcal{O}_{cc'}r^a_{vc}r^b_{c'v}+\mathcal{O}_{c'c}r^a_{vc'}r^b_{cv}\Big]\delta(\omega-\omega_{cv})E^a(-\omega)E^b(\omega). \end{aligned} \tag{55}$$

We take $\hat{\mathcal{O}} \to |\mathbf{r}\rangle\langle\mathbf{r}|$ for the electron number density, the

$$\hat{\mathcal{O}}_{cc'} = \langle c\mathbf{k}|\mathbf{r}\rangle\langle\mathbf{r}|c'\mathbf{k}\rangle = \psi^*_{c\mathbf{k}}(\mathbf{r})\psi_{c'\mathbf{k}}(\mathbf{r}) \equiv \rho_{cc'}(\mathbf{r};\mathbf{k}), \tag{56}$$ {rho}

the density matrix elements for the electron in the conduction bands cc', since we only want to calculate the DSP for electrons. Using time-invariance $\psi_{c(-\mathbf{k})}(\mathbf{r}) = \psi^\star_{c\mathbf{k}}(\mathbf{r})$ it follows that $\rho_{cc'}(\mathbf{r};-\mathbf{k}) = \rho_{c'c}(\mathbf{r};\mathbf{k}) = \rho^\star_{cc'}(\mathbf{r};\mathbf{k})$. The latter is the hermiticity of the density matrix.

Then, the carrier injection rate is given by

$$\dot{n}(\mathbf{r}) = \frac{\pi e^2}{\hbar^2}\int\frac{d^3k}{8\pi^3}\sum_{vcc'}\left[\rho_{cc'}r^a_{vc}r^b_{c'v}+\rho_{c'c}r^a_{vc'}r^b_{cv}\right]\delta(\omega-\omega_{cv})E^a(-\omega)E^b(\omega), \tag{57}$$

that we write as a response function, i.e.

$$\dot{n}(\mathbf{r}) = \xi^{ab}(\mathbf{r};\omega)E^a(-\omega)E^b(\omega), \tag{58}$$ {rn}

with

$$\xi^{ab}(\mathbf{r};\omega) = \frac{\pi e^2}{\hbar^2}\int\frac{d^3k}{8\pi^3}\sum_{vcc'}\left[\rho_{cc'}(\mathbf{r};\mathbf{k})r^a_{vc}(\mathbf{k})r^b_{c'v}(\mathbf{k})+\rho_{c'c}(\mathbf{r};\mathbf{k})r^a_{vc'}(\mathbf{k})r^b_{cv}(\mathbf{k})\right]\delta(\omega-\omega_{cv}(\mathbf{k})). \tag{59}$$

To obtain the contribution from the ℓ-th layer we simply do the following integration

$$\begin{aligned}\xi^{ab}(\ell;\omega) &= \frac{1}{\Omega}\int d\mathbf{r}\mathcal{F}_\ell(z)\xi^{ab}(\mathbf{r};\omega)\\ &= \frac{\pi e^2}{\hbar^2}\int\frac{d^3k}{8\pi^3}\sum_{vcc'}\left[\rho_{cc'}(\ell;\mathbf{k})r^a_{vc}(\mathbf{k})r^b_{c'v}(\mathbf{k})+\rho_{c'c}(\ell;\mathbf{k})r^a_{vc'}(\mathbf{k})r^b_{cv}(\mathbf{k})\right]\delta(\omega-\omega_{cv}(\mathbf{k}))\end{aligned} \tag{60}$$

with

$$\begin{aligned}\rho_{cc'}(\ell;\mathbf{k}) &= \frac{1}{\Omega}\int d\mathbf{r}\,\mathcal{F}_\ell(z)\rho_{cc'}(\mathbf{r};\mathbf{k})\\ &= \frac{1}{\Omega}\int d\mathbf{r}\,\mathcal{F}_\ell(z)\psi^\star_{c\mathbf{k}}(\mathbf{r})\psi_{c'\mathbf{k}}(\mathbf{r}).\end{aligned} \tag{61}$$

For a bulk system (or the whole slab) we take $\mathcal{F}_\ell(z)=1$ and then $\rho_{cc'}(\ell;\mathbf{k})=\delta_{cc'}$, with which we get

$$\xi^{ab}(\omega) = \frac{2\pi e^2}{\hbar^2}\int\frac{d^3k}{8\pi^3}\sum_{vc}r^a_{vc}(\mathbf{k})r^b_{cv}(\mathbf{k})\delta(\omega_{cv}(\mathbf{k})-\omega), \tag{62}$$

which is the same as Eq. (16) of Nastos et al. (PRB **76**, 205113 (2007)). We write Eq. (6) Mendoza et al. Physical Review B **74**, 075318 (2006).

$$\begin{aligned}\mathrm{Im}[\chi^{ab}(\omega)] &= \frac{\pi e^2}{\hbar}\int\frac{d^3k}{8\pi^3}\sum_{vc}r^a_{vc}(\mathbf{k})r^b_{cv}(\mathbf{k})\delta(\omega_{cv}(\mathbf{k})-\omega)\\ &= \frac{\hbar}{2}\xi^{ab}(\omega).\end{aligned} \tag{63}$$ {imchi}

Expanding the wave functions in plane waves we obtain

$$\begin{aligned}\rho_{cc'}(\ell;\mathbf{k}) &= \frac{1}{\Omega}\int d\mathbf{r}\,\mathcal{F}_\ell(z)\psi^*_{c\mathbf{k}}(\mathbf{r})\psi_{c'\mathbf{k}}(\mathbf{r})\\ &= \sum_{\mathbf{G},\mathbf{G}'}\left(C^{\uparrow *}_{c\mathbf{k}}(\mathbf{G}),C^{\downarrow *}_{c\mathbf{k}}(\mathbf{G})\right)\begin{pmatrix}C^{\uparrow}_{c'\mathbf{k}}(\mathbf{G}')\\ C^{\downarrow}_{c'\mathbf{k}}(\mathbf{G}')\end{pmatrix}\frac{1}{\Omega}\int d\mathbf{r}\,\mathcal{F}_\ell(z)e^{i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{r}}\end{aligned}$$

$$= \sum_{\mathbf{G}\mathbf{G}'} \left(C^{\uparrow *}_{c\mathbf{k}}(\mathbf{G}) C^{\uparrow}_{c'\mathbf{k}}(\mathbf{G}') + C^{\downarrow *}_{c\mathbf{k}}(\mathbf{G}) C^{\downarrow}_{c'\mathbf{k}}(\mathbf{G}') \right) \delta_{\mathbf{G}_\parallel, \mathbf{G}'_\parallel} f_\ell(G_\perp - G'_\perp), \qquad . \tag{64}$$

where the reciprocal lattice vectors $\mathbf{G}$ are decomposed into components parallel to the surface $\mathbf{G}_\parallel$, and perpendicular to the surface $G_\perp \hat{\mathbf{z}}$, so that $\mathbf{G} = \mathbf{G}_\parallel + G_\perp \hat{\mathbf{z}}$, and

$$f_\ell(g) = \frac{1}{L} \int_{z_\ell - \Delta^b_\ell}^{z_\ell + \Delta^f_\ell} e^{igz}\, dz. \tag{65}$$ {four}

The double-summation over the $\mathbf{G}$-vectors can be efficiently done by creating a pointer array to identify all the plane-wave coefficients associated with the same $\mathbf{G}_\parallel$. We take z_ℓ at the center of an atom that belongs to layer ℓ, and thus Eq. (64) give the ℓ-th atomic layer contribution to the carrier injection rate Note that if we take the cut function $\mathcal{F}_\ell(z)$ to be unity through the whole slab, then $f_\ell(g) = \delta_{g,0}$ and from Eq. (64) one would recover the results for the whole slab. Then we need to code Eq. (64) as matrix elements and

$$\xi^{ab}(\ell;\omega) = \frac{2\pi e^2}{\hbar^2} \int \frac{d^3k}{8\pi^3} \sum_{vcc'} \frac{1}{2} \Big[\rho_{cc'}(\ell;\mathbf{k}) r^a_{vc}(\mathbf{k}) r^b_{c'v}(\mathbf{k}) + \rho_{c'c}(\ell;\mathbf{k}) r^a_{vc'}(\mathbf{k}) r^b_{cv}(\mathbf{k}) \Big] \delta(\omega - \omega_{cv}(\mathbf{k})) \tag{66}$$

as a response. We have put a factor of 2 in the prefactor so that $(\hbar/2)\dot{n}$ is $(\hbar/2)\times(2\pi e^2)/\hbar^2 = \pi e^2/\hbar$ which is the same prefactor as that of $\mathrm{Im}[\chi^{ab}]$. Therefore it is more convenient to redefine $\xi^{ab} \to (\hbar/2)\xi^{ab} \to \tilde{\xi}^{ab}$,

$$\tilde{\xi}^{ab}(\ell;\omega) = \frac{\pi e^2}{\hbar} \int \frac{d^3k}{8\pi^3} \sum_{vcc'} \frac{1}{2} \Big[\rho_{cc'}(\ell;\mathbf{k}) r^a_{vc}(\mathbf{k}) r^b_{c'v}(\mathbf{k}) + \rho_{c'c}(\ell;\mathbf{k}) r^a_{vc'}(\mathbf{k}) r^b_{cv}(\mathbf{k}) \Big] \delta(\omega - \omega_{cv}(\mathbf{k})) \tag{67}$$

We notice that $(\hbar/2)\xi^{ab}(\omega) = \mathrm{Im}[\chi^{ab}(\omega)]$, with $\epsilon^{ab}(\omega) = 1 + 4\pi\chi^{ab}(\omega)$, however $(\hbar/2)\xi^{ab}(\ell;\omega) \neq \mathrm{Im}[\chi^{ab}(\ell;\omega)]$

We split the integral in Eq. (67) into $\mathbf{k} > 0$ and $\mathbf{k} < 0$, and take the term in parenthesis,

$$\begin{aligned}
\Big[\rho_{cc'}(\ell;\mathbf{k}) r^a_{vc}(\mathbf{k}) r^b_{c'v}(\mathbf{k}) + \rho_{c'c}(\ell;\mathbf{k}) r^a_{vc'}(\mathbf{k}) r^b_{cv}(\mathbf{k}) \Big]_{\mathbf{k}>0} &+ \Big[\rho_{cc'}(\ell;\mathbf{k}) r^a_{vc}(\mathbf{k}) r^b_{c'v}(\mathbf{k}) + \rho_{c'c}(\ell;\mathbf{k}) r^a_{vc'}(\mathbf{k}) r^b_{cv}(\mathbf{k}) \Big]_{\mathbf{k}<0} \\
\rho_{cc'}(\ell;\mathbf{k}) r^a_{vc}(\mathbf{k}) r^b_{c'v}(\mathbf{k}) + \rho_{c'c}(\ell;\mathbf{k}) r^a_{vc'}(\mathbf{k}) r^b_{cv}(\mathbf{k}) &+ \rho_{c'c}(\ell;\mathbf{k}) r^a_{cv}(\mathbf{k}) r^b_{vc'}(\mathbf{k}) + \rho_{cc'}(\ell;\mathbf{k}) r^a_{c'v}(\mathbf{k}) r^b_{vc}(\mathbf{k}) \\
2\mathrm{Re}\Big[\rho_{cc'}(\ell;\mathbf{k}) r^a_{vc}(\mathbf{k}) r^b_{c'v}(\mathbf{k}) \Big] &+ 2\mathrm{Re}\Big[\rho_{c'c}(\ell;\mathbf{k}) r^a_{vc'}(\mathbf{k}) r^b_{cv}(\mathbf{k}) \Big] \\
2\mathrm{Re}\big[\rho_{cc'}(\ell;\mathbf{k}) r^a_{vc}(\mathbf{k}) r^b_{c'v}(\mathbf{k}) &+ \rho_{c'c}(\ell;\mathbf{k}) r^a_{vc'}(\mathbf{k}) r^b_{cv}(\mathbf{k}) \big]
\end{aligned}$$

Then,

$$\begin{aligned}
\tilde{\xi}^{ab}(\ell;\omega) &= \frac{\pi e^2}{\hbar} \int_{\mathbf{k}>0} \frac{d^3k}{8\pi^3} \sum_{vcc'} \mathrm{Re}\Big[\rho_{cc'}(\ell;\mathbf{k}) r^a_{vc}(\mathbf{k}) r^b_{c'v}(\mathbf{k}) + \rho_{c'c}(\ell;\mathbf{k}) r^a_{vc'}(\mathbf{k}) r^b_{cv}(\mathbf{k}) \Big] \delta(\omega - \omega_{cv}(\mathbf{k})) \\
&= \frac{\pi e^2}{\hbar} \int \frac{d^3k}{8\pi^3} \sum_{vcc'} \frac{1}{2}\mathrm{Re}\Big[\rho_{cc'}(\ell;\mathbf{k}) r^a_{vc}(\mathbf{k}) r^b_{c'v}(\mathbf{k}) + \rho_{c'c}(\ell;\mathbf{k}) r^a_{vc'}(\mathbf{k}) r^b_{cv}(\mathbf{k}) \Big] \delta(\omega - \omega_{cv}(\mathbf{k}))
\end{aligned}$$

$$= \frac{\pi e^2}{\hbar}\int \frac{d^3k}{8\pi^3}\sum_{vcc'}\frac{1}{2}\mathrm{Re}\Big[\rho_{cc'}(\ell)r^a_{vc}r^b_{c'v} + \rho_{c'c}(\ell)r^a_{vc'}r^b_{cv}\Big]\delta(\omega-\omega_{cv}). \tag{68}$$

where the 1/2 comes from the unrestricted values of $\mathbf{k}$ in the integration, and the argument of $\mathbf{k}$ is omitted. Above shows that $\tilde{\xi}^{ab}(\ell;\omega)$ is a real quantity, as it must!

1. Units

We obtain that in the S.I. system of units Eq. (58), leads to

$$\begin{aligned}[\dot{n}] &= [\xi][E]^2 \\ \frac{1}{sm^3} &= [\xi]\frac{V^2}{m^2} \\ \Rightarrow [\xi] &= \frac{1}{msV^2}.\end{aligned} \tag{69}$$ {rn.n1}

It so happens that in Gaussian (cgs) units (see Eq. (63))

$$\begin{aligned}\xi^{\mathrm{ab}} &= \frac{2}{\hbar}\mathrm{Im}[\chi^{\mathrm{ab}}] \\ \Rightarrow \xi^{\mathrm{ab}}_{\mathrm{S.I.}} &= 2\frac{\epsilon_0}{\hbar}\mathrm{Im}[\chi^{\mathrm{ab}}_{\mathrm{cgs}}],\end{aligned} \tag{70}$$ {rn.n2}

where $\mathrm{Im}[\chi^{\mathrm{ab}}_{\mathrm{cgs}}]$ is dimensionless. Therefore, the units are

$$[\xi^{\mathrm{ab}}_{\mathrm{S.I.}}] = \frac{[\epsilon_0]}{[\hbar]} = \frac{F/m}{Js} = \frac{C/mV}{CVs} = \frac{1}{msV^2}, \tag{71}$$ {rn.n3}

which agree with Eq. (69).

F. Degree of Spin Polarization: DSP

The degree of spin polarization is defined as

$$\mathcal{D}^a = \frac{\dot{S}^a}{(\hbar/2)\dot{n}}. \tag{72}$$ {dsp1}

The prefactor of $(\hbar/2)\dot{n}$ is $(\hbar/2)\times(2\pi e^2)/\hbar^2 = \pi e^2/\hbar$ which is the same as that of $\mathrm{Im}[\chi^{ab}]$. Therefore it is more convenient to redefine $\dot{\tilde{n}} = (\hbar/2)\dot{n} = \tilde{\xi}^{ab}E^a(-\omega)E^b(\omega)$, and

$$\mathcal{D}^a = \frac{\dot{S}^a}{\dot{\tilde{n}}}. \tag{73}$$ {dsp2}

The prefactor of $\dot{S}^2$ is $(\pi e^2/\hbar^2)\times(\hbar/2) \propto \pi e^2/\hbar$ where $\hbar/2$ comes from the units of the spin matrix elements that are given through $\hat{S}^a = (\hbar/2)\hat{\sigma}^a$. Therefore we see that $\mathcal{D}^a$ is a dimensionless quantity.

In the code subroutine `inparams.f90` we use the prefactor of $\mathrm{Im}[\chi^{ab}]$ (`Chi1_factor`) as the prefactor of $\tilde{\xi}^{ab}$, although we don't call it "tilde", indeed we call it `ndotccp` for the conduction.

In general, for a circularly polarized beam of light propagating along z (which is normal to the surface), the DSP is equal to

$$\mathcal{D}^z = \frac{2\zeta^{zxy}}{\tilde{\xi}^{xx} + \tilde{\xi}^{yy}}, \tag{74}$$ {dsp3}

where ζ^{zxy} is taken as it comes from the code! (see Eq. (49) and recall that $\tilde{\zeta}^{abc} = i\zeta^{abc}$)

II. ELECTRICAL CURRENT

The operator of the electrical current is given by,

$$\hat{\mathbf{J}} = \frac{1}{\Omega} e\hat{\mathbf{v}}. \tag{75}$$ {ec.1}

From Eq. (55)

$$\begin{aligned}
\dot{\jmath}^{\mathrm{a}} &= \frac{\pi e^3}{\hbar^2} \int \frac{d^3k}{8\pi^3} \sum_{vcc'} \left[v^{\mathrm{a}}_{cc'} r^{\mathrm{b}}_{vc} r^{\mathrm{c}}_{c'v} + v^{\mathrm{a}}_{c'c} r^{\mathrm{b}}_{vc'} r^{\mathrm{c}}_{cv} \right] \delta(\omega - \omega_{cv}) E^{\mathrm{b}}(-\omega) E^{\mathrm{c}}(\omega) \\
&= \eta^{\mathrm{abc}} E^{\mathrm{b}}(-\omega) E^{\mathrm{c}}(\omega),
\end{aligned} \tag{76}$$ {ec.2}

where the volume factor, Ω, is included implicitly, and

$$\begin{aligned}
\eta^{\mathrm{abc}} &= \frac{\pi e^3}{\hbar^2} \int \frac{d^3k}{8\pi^3} \sum_{vcc'} \left[v^{\mathrm{a}}_{cc'}(\mathbf{k}) r^{\mathrm{b}}_{vc}(\mathbf{k}) r^{\mathrm{c}}_{c'v}(\mathbf{k}) + v^{\mathrm{a}}_{c'c}(\mathbf{k}) r^{\mathrm{b}}_{vc'}(\mathbf{k}) r^{\mathrm{c}}_{cv}(\mathbf{k}) \right] \delta(\omega - \omega_{cv}(\mathbf{k})) \\
&= \frac{\pi e^3}{\hbar^2} \int \frac{d^3k}{8\pi^3} \sum_{vcc'} \left[\left(v^{\mathrm{a}}_{cc'}(\mathbf{k}) r^{\mathrm{b}}_{vc}(\mathbf{k}) r^{\mathrm{c}}_{c'v}(\mathbf{k}) \right)\Big|_{\mathbf{k}>0} + \left(v^{\mathrm{a}}_{cc'}(\mathbf{k}) r^{\mathrm{b}}_{vc}(\mathbf{k}) r^{\mathrm{c}}_{c'v}(\mathbf{k}) \right)\Big|_{\mathbf{k}<0} \right. \\
&+ \left. \left(v^{\mathrm{a}}_{c'c}(\mathbf{k}) r^{\mathrm{b}}_{vc'}(\mathbf{k}) r^{\mathrm{c}}_{cv}(\mathbf{k}) \right)\Big|_{\mathbf{k}>0} + \left(v^{\mathrm{a}}_{c'c}(\mathbf{k}) r^{\mathrm{b}}_{vc'}(\mathbf{k}) r^{\mathrm{c}}_{cv}(\mathbf{k}) \right)\Big|_{\mathbf{k}<0} \right] \delta(\omega - \omega_{cv}(\mathbf{k})) \\
&= \frac{\pi e^3}{\hbar^2} \int_{\mathbf{k}>0} \frac{d^3k}{8\pi^3} \sum_{vcc'} \left[v^{\mathrm{a}}_{cc'}(\mathbf{k}) r^{\mathrm{b}}_{vc}(\mathbf{k}) r^{\mathrm{c}}_{c'v}(\mathbf{k}) - v^{\mathrm{a}}_{c'c}(\mathbf{k}) r^{\mathrm{b}}_{cv}(\mathbf{k}) r^{\mathrm{c}}_{vc'}(\mathbf{k}) \right. \\
&+ \left. v^{\mathrm{a}}_{c'c}(\mathbf{k}) r^{\mathrm{b}}_{vc'}(\mathbf{k}) r^{\mathrm{c}}_{cv}(\mathbf{k}) - v^{\mathrm{a}}_{cc'}(\mathbf{k}) r^{\mathrm{b}}_{c'v}(\mathbf{k}) r^{\mathrm{c}}_{vc}(\mathbf{k}) \right] \delta(\omega - \omega_{cv}(\mathbf{k})) \\
&= \frac{\pi e^3}{\hbar^2} \frac{1}{2} \int \frac{d^3k}{8\pi^3} \sum_{vcc'} \left[v^{\mathrm{a}}_{cc'}(\mathbf{k}) r^{\mathrm{b}}_{vc}(\mathbf{k}) r^{\mathrm{c}}_{c'v}(\mathbf{k}) - (v^{\mathrm{a}}_{cc'}(\mathbf{k}) r^{\mathrm{b}}_{vc}(\mathbf{k}) r^{\mathrm{c}}_{c'v}(\mathbf{k}))^* \right. \\
&+ \left. v^{\mathrm{a}}_{c'c}(\mathbf{k}) r^{\mathrm{b}}_{vc'}(\mathbf{k}) r^{\mathrm{c}}_{cv}(\mathbf{k}) - (v^{\mathrm{a}}_{c'c}(\mathbf{k}) r^{\mathrm{b}}_{vc'}(\mathbf{k}) r^{\mathrm{c}}_{cv}(\mathbf{k}))^* \right] \delta(\omega - \omega_{cv}(\mathbf{k})) \\
&= \frac{i\pi e^3}{\hbar^2} \int \frac{d^3k}{8\pi^3} \sum_{vcc'} \mathrm{Im}\left[v^{\mathrm{a}}_{cc'}(\mathbf{k}) r^{\mathrm{b}}_{vc}(\mathbf{k}) r^{\mathrm{c}}_{c'v}(\mathbf{k}) + v^{\mathrm{a}}_{c'c}(\mathbf{k}) r^{\mathrm{b}}_{vc'}(\mathbf{k}) r^{\mathrm{c}}_{cv}(\mathbf{k}) \right] \delta(\omega - \omega_{cv}(\mathbf{k})),
\end{aligned} \tag{77}$$ {ec.3}

since $\mathbf{v}_{nm}(-\mathbf{k}) = -\mathbf{v}_{mn}(\mathbf{k})$ and $\mathbf{r}_{nm}(-\mathbf{k}) = \mathbf{r}_{mn}(\mathbf{k})$.

A. Units

We obtain that in the S.I. system of units Eq. (76), leads to ($J = CV$)

$$
\begin{aligned}
[\dot{J}] &= [\eta][E]^2 \\
\frac{1}{s}\frac{1}{m^3}C\frac{m}{s} &= [\eta]\frac{V^2}{m^2} \\
\Rightarrow [\eta] &= \frac{C}{s^2V^2} = \frac{C^3}{J^2s^2},
\end{aligned}
\tag{78}
$$ {ec.4}

which are the same units as those of the injection current.?

B. Swarm Velocity

We define the swarm velocity as

$$
\begin{aligned}
v_s^{\mathrm{a}} &= \frac{\dot{J}^{\mathrm{a}}}{e\dot{n}} \\
&= \frac{\eta^{\mathrm{abc}}E^{\mathrm{b}}(-\omega)E^{\mathrm{c}}(\omega)}{e\xi^{\mathrm{bc}}E^{\mathrm{b}}(-\omega)E^{\mathrm{c}}(\omega)} \\
\Rightarrow [v_s] &= \frac{[\eta]}{C[\xi]} = \frac{\frac{C^3}{J^2s^2}}{\frac{C}{msV^2}} = \frac{mC^2V^2}{sJ^2} = \frac{m}{s},
\end{aligned}
\tag{79}
$$ {sv.1}

where we used Eq. (78) and (71). Now, since $\eta^{\mathrm{abc}} = -\eta^{\mathrm{acb}}$, $\eta^{\mathrm{abb}} = 0$, and then

$$
\begin{aligned}
\dot{J}^{\mathrm{a}} &= \eta^{\mathrm{abc}}E^{\mathrm{b}}(-\omega)E^{\mathrm{c}}(\omega) \\
&= \eta^{\mathrm{abc}}E^{\mathrm{b}}(-\omega)E^{\mathrm{c}}(\omega) + \eta^{\mathrm{acb}}E^{\mathrm{c}}(-\omega)E^{\mathrm{b}}(\omega) \qquad (\mathrm{b} \neq \mathrm{c}) \\
&= \eta^{\mathrm{abc}}\Big(E^{\mathrm{b}*}(\omega)E^{\mathrm{c}}(\omega) - E^{\mathrm{c}*}(\omega)E^{\mathrm{b}}(\omega)\Big) = \eta^{\mathrm{abc}}\Big(E^{\mathrm{b}*}(\omega)E^{\mathrm{c}}(\omega) - (E^{\mathrm{b}*}(\omega)E^{\mathrm{c}}(\omega))^*\Big) \quad (\mathrm{b} \neq \mathrm{c}) \\
&= -2i\eta^{\mathrm{abc}}\mathrm{Im}\Big[E^{\mathrm{b}}(\omega)E^{\mathrm{c}*}(\omega)\Big] \quad (\mathrm{b} \neq \mathrm{c}),
\end{aligned}
\tag{80}
$$ {sv.2}

and since η^{abc} has an i, above is a real quantity, as it should. Now, from above the electric field must have a component along b and c, then

$$
\begin{aligned}
\dot{n} &= \xi^{ij}E^i(-\omega)E^j(\omega) \\
&= \xi^{\mathrm{bb}}|E^{\mathrm{b}}(\omega)|^2 + \xi^{\mathrm{cc}}|E^{\mathrm{c}}(\omega)|^2 + 2\xi^{\mathrm{ab}}E^{\mathrm{b}}(-\omega)E^{\mathrm{c}}(\omega) \quad (\mathrm{b} \neq \mathrm{c}),
\end{aligned}
\tag{81}
$$ {sv.3}

since $\xi^{ij} = \xi^{ji}$, and in going to principal axis $\xi^{ij} = 0$ for $i \neq j$. Finally,

$$
v_s^{\mathrm{a}} = \frac{-2i\eta^{\mathrm{abc}}\sin(\phi_{\mathrm{b}} - \phi_{\mathrm{c}})}{\xi^{\mathrm{bb}} + \xi^{\mathrm{cc}}},
\tag{82}
$$ {sv.4}

where $E^{\mathrm{a}}(\omega) = \mathbf{E}_0 e^{i\phi_{\mathrm{a}}}$, and the maximum swarm velocity is

$$
v_{s,max}^{\mathrm{a}} = \frac{2\tilde{\eta}^{\mathrm{abc}}}{\xi^{\mathrm{bb}} + \xi^{\mathrm{cc}}},
\tag{83}
$$ {sv.5}

with $\tilde{\eta}^{\mathrm{abc}} = i\eta^{\mathrm{abc}}$.

III. TIME REVERSAL

In classical mechanics,

$$\mathbf{p} = m\frac{d\mathbf{r}}{dt}\bigg|_{t\to -t} \to -\mathbf{p}, \tag{84} \quad \{\texttt{e.6}\}$$

and $\mathbf{r}(t) = \mathbf{r}(-t)$, therefore if $\mathbf{r}(t), \mathbf{p}(t)$ is a solution of Newton's equations of motion, so is $\mathbf{r}(-t), -\mathbf{p}(-t)$, therefore the Hamiltonian satisfies

$$H(\mathbf{r}, \mathbf{p}) = H(\mathbf{r}, -\mathbf{p}), \tag{85} \quad \{\texttt{e.7}\}$$

from which H is an even function of $\mathbf{p}$.

In quantum mechanics,

$$\begin{aligned} \hat{\mathbf{p}} &= -i\hbar\boldsymbol{\nabla} \\ \Rightarrow \hat{\mathbf{p}}^* &= -\hat{\mathbf{p}}, \end{aligned} \tag{86} \quad \{\texttt{e.8}\}$$

where we se that the complex conjugation is equivalent to time-reversal, therefore we define the operator of complex conjugation, $\hat{K}_0$, as

$$\hat{K}_0\Big(-i\hbar\boldsymbol{\nabla}\Big)K_0^{-1} = i\hbar\boldsymbol{\nabla}, \tag{87} \quad \{\texttt{e.9}\}$$

in the space representation. $\hat{K}_0$ is the Wigner's time-reversal operator, that satisfies

$$\hat{K}_0^2 = 1, \tag{88} \quad \{\texttt{e.12}\}$$

since applying complex conjugation twice give back the original result, and then

$$\hat{K}_0^{-1} = \hat{K}_0, \tag{89} \quad \{\texttt{e.13}\}$$

is the inverse operator, with which Eq. (88) is satisfied. Eq. (85) becomes

$$\hat{H}_0(\mathbf{r}, -i\hbar\boldsymbol{\nabla}) = \hat{H}_0(\mathbf{r}, i\hbar\boldsymbol{\nabla}), \tag{90} \quad \{\texttt{e.10}\}$$

which, in space representation, $\hat{H}_0$ is a real function. We rewrite Eq. (95) as,

$$\begin{aligned} \hat{K}_0\hat{\mathbf{p}}\hat{K}_0^{-1} &= -\hat{\mathbf{p}} \\ \hat{K}_0\hat{\mathbf{p}} &= -\hat{\mathbf{p}}\hat{K}_0, \end{aligned} \tag{91} \quad \{\texttt{e.11}\}$$

whit which we obtain that

$$\hat{K}_0\hat{\mathbf{p}}^2 = \hat{K}_0\hat{\mathbf{p}}\cdot\hat{\mathbf{p}} = -\hat{\mathbf{p}}\cdot\hat{K}_0\hat{\mathbf{p}} = \hat{\mathbf{p}}\cdot\hat{\mathbf{p}}\hat{K}_0 = \hat{p}^2\hat{K}_0. \tag{92} \quad \{\texttt{e.11n}\}$$

The following Hamiltonian gives that

$$
\begin{aligned}
\hat{H}_0 &= \frac{\hat{p}^2}{2m} + V(\mathbf{r}) \\
\hat{K}_0\hat{H}_0 &= \hat{K}_0\frac{\hat{p}^2}{2m} + \hat{K}_0 V(\mathbf{r}) \\
&= \Big(\frac{\hat{p}^2}{2m} + V(\mathbf{r})\Big)\hat{K}_0 = \hat{H}_0\hat{K}_0, \\
&\Rightarrow [\hat{H}_0, \hat{K}_0] = 0, \\
&\Rightarrow \hat{K}_0\hat{H}_0\hat{K}_0^{-1} = \hat{H}_0,
\end{aligned} \tag{93}
$$ {e.20}

assuming that $V(\mathbf{r})$ is real. Therefore we obtain that

$$
\begin{aligned}
\hat{K}_0\Big(\hat{H}_0\psi = E\psi\Big) \\
\hat{H}_0\Big(\hat{K}_0\psi\Big) = E\Big(\hat{K}_0\psi\Big),
\end{aligned} \tag{94}
$$ {e.13n}

from where we see that ψ and $\hat{K}_0\psi$ are degenerate, as the have the same energy E. Also,

$$
\begin{aligned}
\Big(\hat{H}_0\psi = E\psi\Big)^* \\
\hat{H}_0\psi^* = E\psi^*,
\end{aligned} \tag{95}
$$ {e.14}

from where we have that

$$
\hat{K}_0\psi(\mathbf{r}) = \psi^*(\mathbf{r}). \tag{96}
$$ {e.11nn}

In the presence of spin, the hamiltonian is given by

$$
\begin{aligned}
\hat{H} &= \frac{\hat{p}^2}{2m} + V(\mathbf{r}) + \frac{\hbar^2}{4m^2c^2}\hat{\boldsymbol{\sigma}}\cdot(\boldsymbol{\nabla}V(\mathbf{r})\times\hat{\mathbf{p}}) \\
&= \hat{H}_0 + \hat{\boldsymbol{\sigma}}\cdot(\boldsymbol{\mathcal{V}}(\mathbf{r})\times\hat{\mathbf{p}}),
\end{aligned} \tag{97}
$$ {e.30}

where $\hat{H}_0 = \frac{\hat{p}^2}{2m} + V(\mathbf{r})$ is already treated above, and $\boldsymbol{\mathcal{V}}(\mathbf{r}) = \frac{\hbar^2}{4m^2c^2}\boldsymbol{\nabla}V(\mathbf{r})$. Now, we define a time-reversal operator $\hat{K}$ that leaves above hamiltonian invariant, then

$$
\begin{aligned}
\hat{H} = \hat{K}\hat{H}\hat{K}^{-1} &= \hat{K}\hat{H}_0\hat{K}^{-1} + \hat{K}\hat{\boldsymbol{\sigma}}\cdot(\boldsymbol{\mathcal{V}}(\mathbf{r})\times\hat{\mathbf{p}})\hat{K}^{-1} \\
&= \hat{K}\hat{H}_0\hat{K}^{-1} + \hat{K}\hat{\boldsymbol{\sigma}}\hat{K}^{-1}\cdot(\hat{K}\boldsymbol{\mathcal{V}}(\mathbf{r})\hat{K}^{-1}\times\hat{K}\hat{\mathbf{p}}\hat{K}^{-1}).
\end{aligned} \tag{98}
$$ {e.31}

From Eq. (91) and the fact that functions of $\mathbf{r}$ are invariant under time-reversal, we propose that

$$
\begin{aligned}
\hat{K}\hat{\mathbf{p}}\hat{K}^{-1} &= -\hat{\mathbf{p}}, \\
\hat{K}\hat{H}_0\hat{K}^{-1} &= H_0
\end{aligned}
$$

$$\hat{K}\boldsymbol{\mathcal{V}}(\mathbf{r})\hat{K}^{-1} = \boldsymbol{\mathcal{V}}(\mathbf{r}) \tag{99}$$ {e.32}

and thus,

$$\hat{K}\hat{\boldsymbol{\sigma}}\hat{K}^{-1} = -\hat{\boldsymbol{\sigma}}, \tag{100}$$ {e.33}

to keep $\hat{H}$ invariant. Again, $[\hat{H}, \hat{K}] = 0$, and ψ is degenerate with $\hat{K}\psi$.

We write $\hat{K} = \hat{U}\hat{K}_0$ and look for $\hat{U}$. From Eq. (38)

$$\hat{\sigma}_x^* = \hat{\sigma}_x \quad \hat{\sigma}_y^* = -\hat{\sigma}_y \quad \hat{\sigma}_z^* = \hat{\sigma}_z, \tag{101}$$ {e.34}

and using $\hat{\sigma}_i\hat{\sigma}_j = i\epsilon_{ijk}\hat{\sigma}_k$ and $\{\hat{\sigma}_i, \hat{\sigma}_j\} = 0$, we can show that

$$\begin{aligned}
\hat{\sigma}_y\boldsymbol{\sigma}^* = (\hat{\sigma}_y\hat{\sigma}_x, -\hat{\sigma}_y\hat{\sigma}_y, \hat{\sigma}_y\hat{\sigma}_z) = -(\hat{\sigma}_x, \hat{\sigma}_x, \hat{\sigma}_x)\sigma_y = -\hat{\boldsymbol{\sigma}}\hat{\sigma}_y \\
\Rightarrow \hat{\sigma}_y\boldsymbol{\sigma}^*\hat{\sigma}_y^{-1} = -\hat{\boldsymbol{\sigma}} \\
\Rightarrow \hat{\sigma}_y\hat{K}_0\boldsymbol{\sigma}\hat{K}_0^{-1}\hat{\sigma}_y^{-1} = -\hat{\boldsymbol{\sigma}} \\
\Rightarrow \hat{K} = \hat{\sigma}_y\hat{K}_0.
\end{aligned} \tag{102}$$ {e.34n}

since $\hat{K}_0\hat{\boldsymbol{\sigma}}\hat{K}_0^{-1} = \hat{\boldsymbol{\sigma}}^*$ Now, we confirm that $\hat{K} = \hat{\sigma}_y\hat{K}_0$ really works, then we take

$$\hat{H}_{so} = \frac{\hbar^2}{4m^2c^2}\hat{\boldsymbol{\sigma}} \cdot (\boldsymbol{\nabla}V(\mathbf{r}) \times \hat{\mathbf{p}}) \neq \hat{H}_{so}^*, \tag{103}$$ {e.35}

since $\hat{\mathbf{p}}^* = -\hat{\mathbf{p}}$ but $\boldsymbol{\sigma}^* \neq \boldsymbol{\sigma}$, and write $\hat{H}_{so} = \hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{A}}$ with $\hat{\mathbf{A}} = \frac{\hbar^2}{4m^2c^2}(\boldsymbol{\nabla}V(\mathbf{r}) \times \hat{\mathbf{p}})$, and obtain that

$$\begin{aligned}
\hat{H}_{so} &= \hat{A}_x\hat{\sigma}_x + \hat{A}_y\hat{\sigma}_y + \hat{A}_z\hat{\sigma}_z \\
\hat{H}_{so}^* &= -\hat{A}_x\hat{\sigma}_x + \hat{A}_y\hat{\sigma}_y - \hat{A}_z\hat{\sigma}_z \\
\hat{\sigma}_x\hat{H}_{so}^* &= \Big(- \hat{A}_x\hat{\sigma}_x - \hat{A}_y\hat{\sigma}_y + \hat{A}_z\hat{\sigma}_z\Big)\hat{\sigma}_x \\
\hat{\sigma}_z\hat{H}_{so}^* &= \Big(\hat{A}_x\hat{\sigma}_x - \hat{A}_y\hat{\sigma}_y - \hat{A}_z\hat{\sigma}_z\Big)\hat{\sigma}_z \\
\hat{\sigma}_y\hat{H}_{so}^* &= \hat{H}_{so}\hat{\sigma}_y \\
\Rightarrow \hat{\sigma}_y\hat{H}_{so}^*\hat{\sigma}_y^{-1} &= \hat{H}_{so} \\
\Rightarrow \hat{\sigma}_y\hat{K}_0\hat{H}_{so}\hat{K}_0^{-1}\hat{\sigma}_y^{-1} &= \hat{H}_{so} \\
\Rightarrow \hat{K}\hat{H}_{so}\hat{K}^{-1} &= \hat{H}_{so},
\end{aligned} \tag{104}$$ {e.36}

where we see that $\hat{U} = \hat{\sigma}_y$ works and that $\hat{U} = i\hat{\sigma}_y$ will work as well.

A. Bloch's theorem

We define $T_{\mathbf{R}_\ell}$ as the translation operator, such that,

$$T_{\mathbf{R}_\ell} f(\mathbf{r}) = f(\mathbf{r} + \mathbf{R}_\ell), \tag{105}$$ {ee.1}

for a crystal,

$$T_{\mathbf{R}_\ell} H(\mathbf{r}) = H(\mathbf{r} + \mathbf{R}_\ell) = H(\mathbf{r}), \tag{106}$$ {ee.2}

then

$$\begin{aligned} T_{\mathbf{R}_\ell}\Big(H\psi(\mathbf{r}) &= E\psi(\mathbf{r})\Big) \\ H\Big(T_{\mathbf{R}_\ell}\psi(\mathbf{r})\Big) &= E\Big(T_{\mathbf{R}_\ell}\psi(\mathbf{r})\Big) \\ \Rightarrow \psi(\mathbf{r}) &= e^{i\phi} T_{\mathbf{R}_\ell}\psi(\mathbf{r}), \end{aligned} \tag{107}$$ {ee.2n}

from

$$|\psi(\mathbf{r})|^2 = |T_{\mathbf{R}_\ell}\psi(\mathbf{r})|^2$$

$$\Rightarrow T_{\mathbf{R}_\ell}\psi(\mathbf{r}) = e^{i\alpha_\ell}\psi(\mathbf{r}), \tag{108}$$ {ee.3}

where $\mathbf{R}_\ell$ are the crystal lattice vectors, that satisfy $\mathbf{R}_\ell + \mathbf{R}_m = \mathbf{R}_p$ or $T_{\mathbf{R}_\ell} T_{\mathbf{R}_m} = T_{\mathbf{R}_p}$. This last requirement is easily satisfied by $\mathrm{Exp}[i(\alpha_\ell + \alpha_m)] = \mathrm{Exp}[i\alpha_p]$, where we take $\alpha_\ell = \mathbf{k} \cdot \mathbf{R}_\ell$, and finally get that

$$T_{\mathbf{R}_\ell}\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{R}_\ell}\psi(\mathbf{r}), \tag{109}$$ {ee.4}

where $\mathbf{k}$ is used to classify the states (then, its the crystal momentum), so Bloch's Theorem reads,

$$T_{\mathbf{R}_\ell}\psi_n(\mathbf{k}, \mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{R}_\ell}\psi_n(\mathbf{k}, \mathbf{r}), \tag{110}$$ {ee.5}

where n is the energy band. The Bloch's wave function is written as

$$\begin{aligned} \psi_n(\mathbf{k}, \mathbf{r}) &= e^{i\mathbf{k}\cdot\mathbf{r}} u_n(\mathbf{k}, \mathbf{r}) \\ \Rightarrow T_{\mathbf{R}_\ell}\psi_n(\mathbf{k}, \mathbf{r}) &= \psi_n(\mathbf{k}, \mathbf{r} + \mathbf{R}_\ell) = e^{i\mathbf{k}\cdot(\mathbf{r}+\mathbf{R}_\ell)} u_n(\mathbf{k}, \mathbf{r} + \mathbf{R}_\ell) = e^{i\mathbf{k}\cdot\mathbf{R}_\ell} e^{i\mathbf{k}\cdot\mathbf{r}} u_n(\mathbf{k}, \mathbf{r}) \\ &= e^{i\mathbf{k}\cdot\mathbf{R}_\ell}\psi_n(\mathbf{k}, \mathbf{r}), \end{aligned} \tag{111}$$ {ee.6}

since $u_n(\mathbf{k},\mathbf{r}+\mathbf{R}_\ell) = u_n(\mathbf{k},\mathbf{r})$ is periodic, thus fulfilling Bloch's theorem. The reciprocal lattice vectors, $\mathbf{G}$ are defined, by (we drop the labels in $\mathbf{G}$ and $\mathbf{R}$, for ease of notation)

$$e^{i\mathbf{G}\cdot\mathbf{R}} = 1, \tag{112} \quad \{\texttt{ee.7}\}$$

thus we have that

$$\Rightarrow T_{\mathbf{R}}\psi_n(\mathbf{k}+\mathbf{G},\mathbf{r}) = e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{R}}\psi_n(\mathbf{k}+\mathbf{G},\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{R}}\psi_n(\mathbf{k}+\mathbf{G},\mathbf{r}), \tag{113} \quad \{\texttt{ee.8}\}$$

which has the same eigenvalue as Eq. (110), then

$$\psi_n(\mathbf{k}+\mathbf{G},\mathbf{r}) = \psi_n(\mathbf{k},\mathbf{r}), \tag{114} \quad \{\texttt{ee.9}\}$$

is periodic in reciprocal space as well. From Eq. (110), it also follows that

$$\begin{aligned}
T_{\mathbf{R}}\psi_n^*(\mathbf{k},\mathbf{r}) &= e^{-i\mathbf{k}\cdot\mathbf{R}}\psi_n^*(\mathbf{k},\mathbf{r}) \\
T_{\mathbf{R}}\psi_n(-\mathbf{k},\mathbf{r}) &= e^{-i\mathbf{k}\cdot\mathbf{R}}\psi_n(-\mathbf{k},\mathbf{r}) \\
\Rightarrow \psi_n(-\mathbf{k},\mathbf{r}) &= \psi_n^*(\mathbf{k},\mathbf{r}) \\
\Rightarrow e^{i(-\mathbf{k})\cdot\mathbf{r}}u_n(-\mathbf{k},\mathbf{r}) &= e^{-i\mathbf{k}\cdot\mathbf{r}}u_n^*(\mathbf{k},\mathbf{r}) \\
\Rightarrow u_n(-\mathbf{k},\mathbf{r}) &= u_n^*(\mathbf{k},\mathbf{r}),
\end{aligned} \tag{115} \quad \{\texttt{ee.10}\}$$

thus complex-conjugation is equivalente to taking $\mathbf{k} \to -\mathbf{k}$. Then,

$$\begin{aligned}
\Big(H\psi_n(\mathbf{k},\mathbf{r}) &= E_n(\mathbf{k})\psi_n(\mathbf{k},\mathbf{r})\Big)^* \\
H\psi_n^*(\mathbf{k},\mathbf{r}) &= E_n(\mathbf{k})\psi_n^*(\mathbf{k},\mathbf{r}) \\
H\psi_n(-\mathbf{k},\mathbf{r}) &= E_n(\mathbf{k})\psi_n(-\mathbf{k},\mathbf{r}) \\
\mathbf{k} &\to -\mathbf{k} \\
H\psi_n(\mathbf{k},\mathbf{r}) &= E_n(-\mathbf{k})\psi_n(\mathbf{k},\mathbf{r}) \\
\Rightarrow E_n(\mathbf{k}) &= E_n(-\mathbf{k}),
\end{aligned} \tag{116} \quad \{\texttt{e.n11}\}$$

B. Spin-Orbit coupling

Schrödinger equation with the spin-orbit coupling reads

$$\Big[\frac{\hat{p}^2}{2m} + V(\mathbf{r}) + \frac{\hbar^2}{4m^2c^2}\hat{\boldsymbol{\sigma}}\cdot(\boldsymbol{\nabla}V(\mathbf{r})\times\hat{\mathbf{p}})\Big]\psi(\mathbf{r},s) = E\psi(\mathbf{r},s), \tag{117} \quad \{\texttt{e.5}\}$$

which is invariant upon time reversal, $t \to -t$. The Bloch states when the H_{so} is present, are spinors of the form

$$\psi = \begin{pmatrix} u \\ v \end{pmatrix} \tag{118}$$

and Eq. (142) reduces to

$$\begin{pmatrix} H_0 + A_z & A_x - iA_y \\ A_x + iA_y & H_0 - A_z \end{pmatrix} \begin{pmatrix} u \\ v \end{pmatrix} = E \begin{pmatrix} u \\ v \end{pmatrix} \tag{119}$$

where in general $u \neq v \neq 0$, and $|u|^2$ is the probability of spin up, while $|v|^2$ is the probability of spin down. Then, we can write

$$\langle \mathbf{r}|ns\mathbf{k}\rangle = \psi_{ns}(\mathbf{k};\mathbf{r}) = \begin{pmatrix} u_{ns}(\mathbf{k};\mathbf{r}) \\ v_{ns}(\mathbf{k};\mathbf{r}) \end{pmatrix} e^{i\mathbf{k}\cdot\mathbf{r}} = \begin{pmatrix} u_{ns}(\mathbf{k};\mathbf{r};\uparrow) \\ v_{ns}(\mathbf{k};\mathbf{r};\downarrow) \end{pmatrix} e^{i\mathbf{k}\cdot\mathbf{r}} \tag{120}$$

where n denotes the band and s the spin.

We would like to express the matrix elements of an operator upon applying time-reversal symmetry, and relate them to those before applying time-reversal. To this end, we first prove the following identity of the scalar product between to spinor wavefunctions with and without time-reversal,

$$(\hat{K}\phi, \hat{K}\psi) = (\psi, \phi). \tag{121}$$ {z.1}

On one hand,

$$\begin{aligned}(\psi, \phi) &= \int dx\, \psi^\dagger \phi \\ &= \int dx\, (\psi_1^*, \psi_2^*) \begin{pmatrix} \phi_1 \\ \phi_2 \end{pmatrix} = \int dx\, (\psi_1^* \phi_1 + \psi_2^* \phi_2).\end{aligned} \tag{122}$$ {z.2}

On the other hand, we first realize that

$$\begin{aligned}\hat{K}\phi &= i\hat{\sigma}_y \hat{K}_0 \phi = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \begin{pmatrix} \phi_1^* \\ \phi_2^* \end{pmatrix} \\ &= \begin{pmatrix} \phi_2^* \\ -\phi_1^* \end{pmatrix},\end{aligned} \tag{123}$$

where we used Eq. (38). Then,

$$(\hat{K}\phi, \hat{K}\psi) = \int dx\, (\hat{K}\phi)^\dagger \hat{K}\psi$$

$$= \int dx\, (\phi_2, -\phi_1) \begin{pmatrix} \psi_2^* \\ -\psi_1^* \end{pmatrix} = \int dx\, (\phi_2 \psi_2^* + \phi_1 \psi_1^*) \quad \text{Q.E.D.} \tag{124}$$ {z.4}

Now, we denote $\hat{K}\psi = \tilde{\psi}$, so Eq. (121) can be written as,

$$(\hat{K}\phi, \hat{K}\psi) = (\tilde{\phi}, \tilde{\psi}) = (\psi, \phi), \tag{125}$$ {z.5}

but since the dot product also satisfies $(\psi, \phi) = (\phi, \psi)^*$, in braket notation we obtain this useful relationship,

$$\langle \tilde{\phi} | \tilde{\psi} \rangle = \langle \psi | \phi \rangle = \langle \phi | \psi \rangle^*. \tag{126}$$ {z.6a}

For an operator $\hat{\mathcal{O}}$ for which, $\hat{\mathcal{O}}|\phi\rangle = |\varphi\rangle$, ww obtain the following identity,

$$\begin{aligned} \langle \psi | \hat{\mathcal{O}} | \phi \rangle &= \langle \psi | \varphi \rangle = \langle \tilde{\varphi} | \tilde{\psi} \rangle = \langle \tilde{\psi} | \tilde{\varphi} \rangle^* \\ &= \langle \tilde{\psi} | \hat{K} | \varphi \rangle^* = \langle \tilde{\psi} | \hat{K} \hat{\mathcal{O}} | \phi \rangle^* = \langle \tilde{\psi} | \hat{K} \hat{\mathcal{O}} \hat{K}^{-1} \hat{K} | \phi \rangle^* \\ &= \langle \tilde{\psi} | \hat{K} \hat{\mathcal{O}} \hat{K}^{-1} | \tilde{\phi} \rangle^* = \langle \tilde{\phi} | \hat{K} \hat{\mathcal{O}} \hat{K}^{-1} | \tilde{\psi} \rangle \\ \text{or} \quad \langle \tilde{\psi} | \hat{K} \hat{\mathcal{O}} \hat{K}^{-1} | \tilde{\phi} \rangle^* &= \langle \psi | \hat{\mathcal{O}} | \phi \rangle \\ \pm \langle \tilde{\psi} | \hat{\mathcal{O}} | \tilde{\phi} \rangle^* &= \langle \psi | \hat{\mathcal{O}} | \phi \rangle \\ \langle \tilde{\psi} | \hat{\mathcal{O}} | \tilde{\phi} \rangle^* &= \pm \langle \psi | \hat{\mathcal{O}} | \phi \rangle. \end{aligned} \tag{127}$$ {z.6}

Now, from Eqs. (38), (115) and (120)

$$i\hat{\sigma}_y \hat{K}_0 | ns; \mathbf{k} \rangle = i\hat{\sigma}_y | ns; -\mathbf{k} \rangle, \tag{128}$$ {e.40}

and

$$\begin{aligned} i\hat{\sigma}_y | ns; -\mathbf{k} \rangle \quad &\to \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \begin{pmatrix} u_{ns}(-\mathbf{k}; \mathbf{r}) \\ v_{ns}(-\mathbf{k}; \mathbf{r}) \end{pmatrix} e^{-i\mathbf{k}\cdot\mathbf{r}} \\ &= \begin{pmatrix} v_{ns}(-\mathbf{k}; \mathbf{r}) \\ -u_{ns}(-\mathbf{k}; \mathbf{r}) \end{pmatrix} e^{-i\mathbf{k}\cdot\mathbf{r}} \equiv \langle \mathbf{r} | n\bar{s}; -\mathbf{k} \rangle. \end{aligned} \tag{129}$$

We see that if $|u_{ns}(\mathbf{k}; \mathbf{r})|^2 > |v_{ns}(\mathbf{k}; \mathbf{r})|^2$ is true for $\langle \mathbf{r} | ns; \mathbf{k} \rangle$, meaning "spin-up" like, then the fact that in $\langle \mathbf{r} | n\bar{s}; -\mathbf{k} \rangle$ $|u_{ns}(\mathbf{k}; \mathbf{r})|^2$ and $|v_{ns}(\mathbf{k}; \mathbf{r})|^2$ are reversed in the entries of the spinor, would mean that $\langle \mathbf{r} | n\bar{s}; -\mathbf{k} \rangle$ is "spin-down" like. Therefore, $\bar{s}$ is used to denote this fact, and in summary,

$$\hat{K} | ns; \mathbf{k} \rangle = = e^{i\phi_n} | n\bar{s}; -\mathbf{k} \rangle, \tag{130}$$ {e.40nnnn}

in words, time-reversal in the presence of spin, take a spinor with spin s and crystal momentum $\mathbf{k}$ to a spinor of opposite spin, denoted by $\bar{s}$, and crystal momentum $-\mathbf{k}$, and we have added a phase ϕ_m to be more general. Finally, from Eq. (127) we have,

$$\begin{aligned}\langle\tilde{\psi}|\hat{\mathcal{O}}|\tilde{\phi}\rangle^* &= \pm\langle\psi|\hat{\mathcal{O}}|\phi\rangle \\ \langle n\bar{s};-\mathbf{k}|\hat{\mathcal{O}}|m\bar{p};-\mathbf{k}\rangle^* &= \pm e^{-\lambda_{nm}}\langle ns;\mathbf{k}|\hat{\mathcal{O}}|mp;\mathbf{k}\rangle \\ \mathcal{O}^*_{n\bar{s};m\bar{p}}(-\mathbf{k}) &= \pm e^{-\lambda_{nm}}\mathcal{O}_{ns;mp}(\mathbf{k}),\end{aligned} \qquad (131) \quad \{\texttt{z.7}\}$$

with λ_{nm} and arbitrary phase, like in Eq. (130). From above equation and Eqs. (99) and (100)

$$\begin{aligned}v^{\mathrm{a}*}_{n\bar{s};m\bar{p}}(-\mathbf{k}) &= -e^{i\lambda_{nm}}v^{\mathrm{a}}_{ns;mp}(\mathbf{k}), \\ \sigma^{\mathrm{a}*}_{n\bar{s};m\bar{p}}(-\mathbf{k}) &= -e^{i\lambda'_{nm}}\sigma^{\mathrm{a}}_{ns;mp}(\mathbf{k}), \\ K^{\mathrm{ab}*}_{n\bar{s};m\bar{p}}(-\mathbf{k}) &= e^{i\lambda''_{nm}}K^{\mathrm{ab}}_{ns;mp}(\mathbf{k}),\end{aligned} \qquad (132) \quad \{\texttt{en.41}\}$$

that are the same as Eqs, in left column of page 4 of A. Najmaie, R.D.R. Bhat, and J.E. Sipe, PRB **68**,165348 (2003). We recall that for any hermitian operator, the following relationship always holds,

$$\mathcal{O}^*_{nm}(\mathbf{k}) = \mathcal{O}_{mn}(\mathbf{k}), \qquad (133) \quad \{\texttt{e.42}\}$$

and then

$$\mathcal{O}^*_{n\bar{s};m\bar{p}}(-\mathbf{k}) = \mathcal{O}_{m\bar{p};n\bar{s}}(-\mathbf{k}) = \pm e^{i\lambda_{nm}}\mathcal{O}_{ns;mp}(\mathbf{k}), \qquad (134) \quad \{\texttt{en.43}\}$$

where the $\pm$ is decided by $\hat{K}\hat{\mathcal{O}}\hat{K}^{-1} = \pm\hat{\mathcal{O}}$.

IV. UNITS

The units for the spin current density, could be obtained as follows. We use

$$\tilde{\chi}^{(j)}_{\mathrm{S.I.}} = \frac{1}{9\times10^9}\frac{1}{(3\times10^4)^{j-1}}\tilde{\chi}^{(j)}_{\mathrm{cgs}} \times \frac{\mathrm{m}^{j-2}\mathrm{C}}{\mathrm{V}^j}, \qquad (135) \quad \{\texttt{si}\}$$

which is the conversion factor (including the S.I. units) in going from cgs to S.I., where we follow `/Users/bms/research/tiniba/tiniba-manual/tiniba-manual.tex`; then,

$$[\tilde{\chi}^{(j)}_{\mathrm{S.I.}}] = \frac{\mathrm{m}^{j-2}\mathrm{C}}{\mathrm{V}^j}, \qquad (136) \quad \{\texttt{u.691}\}$$

The rate of spin current density is given by

$$\dot{K}^{\mathrm{ab}} = \mu^{\mathrm{abcd}}E^{\mathrm{c}*}(\omega)E^{\mathrm{d}}(\omega), \qquad (137) \quad \{\texttt{e.0}\}$$

with $\hat{K}^{\rm ab} = \hat{v}^{\rm a}\hat{S}^{\rm b}$, where $\hat{\mathbf{v}}$ is the velocity operator, and $\hat{S}^{\rm a} = (\hbar/2)\hat{\sigma}^{\rm a}/\Omega$, with Ω the volume, is the spin operator. We work out the units of $[\dot{K}^{\rm ab}]$ as follows:

$$[\dot{K}^{\rm ab}_{\rm S.I.}] = \frac{1}{s}\frac{m}{s}\frac{\hbar}{2}\frac{1}{m^3} = \frac{\hbar}{2}\frac{1}{m^2 s^2}, \tag{138} \quad \texttt{\{e.1\}}$$

where $1/s$ comes from the time derivative (denoted by the $\cdot$), m/s from the velocity and $(\hbar/2)/m^3$ from the spin density. Then, using Eq. (136)

$$\begin{aligned}[\dot{K}^{\rm ab}_{\rm S.I.}] &= \frac{\hbar}{2}\frac{C}{m^2}\frac{1}{Cs^2} = \frac{\hbar}{2}[\tilde{P}_{\rm S.I.}]\frac{1}{Cs^2} = \frac{\hbar}{2}\frac{1}{Cs^2}[\tilde{\chi}^{(2)}_{\rm S.I.}][\tilde{E}^2_{\rm S.I.}] \\ \Rightarrow [\mu^{\rm abcd}_{\rm S.I.}] &= \frac{\hbar}{2}\frac{1}{Cs^2}[\tilde{\chi}^{(2)}_{\rm S.I.}], = \frac{\hbar}{2}\frac{1}{Cs^2}\frac{C}{V^2} = \frac{\hbar}{2}\frac{1}{V^2 s^2}.\end{aligned} \tag{139} \quad \texttt{\{e.2\}}$$

where we used Eq. (136). From Eq. (135), we further obtain that

$$\mu^{\rm abcd}_{\rm S.I.} = \frac{1}{27\times 10^{13}}\mu^{\rm abcd}_{\rm cgs}\frac{\hbar}{2}\frac{1}{V^2 s^2}. \tag{140} \quad \texttt{\{e.3\}}$$

From Eq. (17), we obtain the prefactor γ of $\mu^{\rm abcd}_{\rm cgs}$ in cgs units is worked out as follows,

$$\begin{aligned}\gamma &= \frac{\pi e^2}{\hbar}\times\frac{1}{[\Omega]}\times[v]\times[S]\times[r^2]\times\frac{1}{[\omega]} \\ &= \frac{\hbar}{2}\frac{\pi e^2}{\hbar}\times\frac{1}{a_0^3}\times\frac{v^3}{\omega^3} = \frac{\hbar}{2}\frac{\pi e^2}{\hbar a_0^3}\times\frac{1}{a_0^3}\times\frac{\hbar^3}{\hbar\omega^3}\times\frac{p^3}{m^3} \\ &= \frac{\hbar}{2}\frac{\pi e^2\hbar^2}{(ma_0)^3}\frac{\hbar^3}{a_0^3}\frac{1}{(eV)^3} = \frac{\hbar}{2}\frac{\pi e^2\hbar^5}{(ma_0)^3 a_0^3}\frac{(27.21\,eV)^3}{H^3}\frac{1}{(eV)^3} \\ &= \frac{\hbar}{2}\frac{\pi e^2\hbar^5}{(ma_0)^3 a_0^3}\frac{(27.21)^3}{e^6/a_0^3} = \frac{\hbar}{2}\frac{\pi e^2\hbar^5}{(\hbar^2/e^2)^3}\frac{(27.21)^3}{e^6} \\ &= \frac{\hbar}{2}\frac{\pi e^2}{\hbar}(27.21)^3,\end{aligned} \tag{141} \quad \texttt{\{e.4\}}$$

where we used that unitwise $[r] = [v]/[\omega]$, $[p] = \hbar/a_0$, and $v = p/m$. Also, $H = e^2/a_0 = 27.2\,eV$, $a_0 = \hbar^2/me^2$. We remind that Abinit®'s units of distance are given in Bohrs a_0 and those of energy en eV. Since $\hbar/2$ is explicitly given in Eq. (140), we remove it from above, and finally write that the overall prefactor used in TINIBA®,

$$\begin{aligned}\gamma &\to \frac{1}{27\times 10^{13}}\frac{\pi e^2}{\hbar}(27.21)^3 \\ &= \pi\times 1.6346410\times 10^{-2}\end{aligned} \tag{142} \quad \texttt{\{e.5\}}$$

where in cgs $e = -4.8066\times 10^{-10}$ statcoulomb and $\hbar = 1.05457\times 10^{-27}$ erg·s. Therefore, from Eq. (139), the units of the output form TINIBA®, are

$$[\mu^{\rm abcd}_{\rm S.I.}] = \frac{\hbar}{2}\frac{1}{V^2 s^2}. \tag{143} \quad \texttt{\{e.6\}}$$