Supplemental Material for "Microscopic Theory of Spin Toroidization in Periodic Crystals"

Yang Gao,[1] David Vanderbilt,[2] and Di Xiao[1]

[1]*Department of Physics, Carnegie Mellon University, Pittsburgh, PA 15213, USA*

[2]*Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08854-8019, USA*

I. SPIN TOROIDIZATION IN LINEAR RESPONSE THEORY

In this section we derive the spin toroidization using linear response theory, similar to the calculation of the orbital magnetization in *Phys. Rev. Lett. 99 197202 (2007)*. Without loss of generality, we only calculate the z-th component of the spin toroidization.

As given by Eq. (3) in the main text, the spin toroidization is the response of the free energy density to an external Zeeman field. Consider the perturbation due to the following Zeeman field

$$\boldsymbol{B} = (h/2q)(\sin(qx)\hat{y} - \sin(qy)\hat{x}) \,, \tag{1}$$

where h is small. This Zeeman field has a curl

$$(h/2)(\cos(qx) + \cos(qy))\hat{z} \,, \tag{2}$$

which reduces to h in the limit $q \to 0$. Note that the symmetric part of the derivative of the Zeeman field (1) is $\partial_x B_y + \partial_y B_x = (h/2)(\cos(qx) - \cos(qy))$, which vanishes in the limit $q \to 0$. As a result, the response of the free energy density to this Zeeman field in the limit $q \to 0$ is purely due to its curl.

At zero temperature, the free energy density reads $\hat{F} = \hat{H} - \mu\hat{N}$. With the above Zeeman field, the change in F can be divided into four parts:

$$\delta F(\boldsymbol{r}) = \sum_{n\boldsymbol{k}} (\delta f_{n\boldsymbol{k}})\psi^\star_{n\boldsymbol{k}}\hat{F}_0\psi_{n\boldsymbol{k}} + f_{n\boldsymbol{k}}\psi^\star_{n\boldsymbol{k}}\boldsymbol{B}\cdot\hat{\boldsymbol{s}}\psi_{n\boldsymbol{k}} + f_{n\boldsymbol{k}}(\delta\psi^\star_{n\boldsymbol{k}}\hat{F}_0\psi_{n\boldsymbol{k}} + \psi^\star_{n\boldsymbol{k}}\hat{F}_0\delta\psi_{n\boldsymbol{k}}) \,. \tag{3}$$

Here $\psi_{n\boldsymbol{k}} = e^{i\boldsymbol{k}\cdot\boldsymbol{r}}|u_n(\boldsymbol{k})\rangle$ is the Bloch function of the unperturbed Hamitonian $\hat{H}$ with $\varepsilon_{n\boldsymbol{k}}$ being the corresponding eigenenergy, $f_{n\boldsymbol{k}}$ is the Fermi function, and $\hat{F}_0$ is the unperturbed part of the free energy density.

The spin toroidization can be obtained from the appropriate Fourier component of $\delta F(\boldsymbol{r})$:

$$T_z = -\frac{2}{Vh}\int dx\; \delta F(\boldsymbol{r})(\cos(qx) + \cos(qy)) \,. \tag{4}$$

We first calculate the contribution from the y-th component of the Zeeman field. The perturbation to the wave function can be easily calculated:

$$\delta\psi_{n\boldsymbol{k}} = -\frac{hg\mu_B}{4i\hbar q}\left[\sum_{n'}\frac{e^{i(\boldsymbol{k}+\boldsymbol{q})\cdot\boldsymbol{r}}|n'\boldsymbol{k}+\boldsymbol{q}\rangle\langle n'\boldsymbol{k}+\boldsymbol{q}|\hat{s}_y|n\boldsymbol{k}\rangle}{\varepsilon_{n\boldsymbol{k}} - \varepsilon_{n'\boldsymbol{k}+\boldsymbol{q}}} - (\boldsymbol{q}\to-\boldsymbol{q})\right] \,. \tag{5}$$

Here $\boldsymbol{q} = q\hat{x}$, and $|n\boldsymbol{k}\rangle$ is short for $|u_n(\boldsymbol{k})\rangle$.

The first two terms in Eq. (3) cancel each other. The last two terms read

$$\begin{aligned} T_z &= \frac{g\mu_B}{4i\hbar q}\sum_{nn'\boldsymbol{k}}(\varepsilon_{n\boldsymbol{k}} - \mu)f_{n\boldsymbol{k}}\left(\frac{\langle n\boldsymbol{k}|n'\boldsymbol{k}+\boldsymbol{q}\rangle\langle n'\boldsymbol{k}+\boldsymbol{q}|\hat{s}_y|n\boldsymbol{k}\rangle}{\varepsilon_{n\boldsymbol{k}} - \varepsilon_{n'\boldsymbol{k}+\boldsymbol{q}}} - (\boldsymbol{q}\to-\boldsymbol{q})\right) + c.c. \\ &= \frac{g\mu_B}{4i\hbar q}\sum_{nn'\boldsymbol{k}}[(\varepsilon_{n\boldsymbol{k}} - \mu)f_{n\boldsymbol{k}} - (\varepsilon_{n'\boldsymbol{k}+\boldsymbol{q}} - \mu)f_{n'\boldsymbol{k}+\boldsymbol{q}}]\frac{\langle n\boldsymbol{k}|n'\boldsymbol{k}+\boldsymbol{q}\rangle\langle n'\boldsymbol{k}+\boldsymbol{q}|s_y|n\boldsymbol{k}\rangle - c.c.}{\varepsilon_{n\boldsymbol{k}} - \varepsilon_{n'\boldsymbol{k}+\boldsymbol{q}}} \end{aligned} \tag{6}$$

Now we take the limit $q \to 0$ in the above expression. Terms in Eq. (6) with $n \neq n'$ reads

$$T_{z1} = -\frac{g\mu_B}{4\hbar}\sum_{n\neq n',\boldsymbol{k}}[(\varepsilon_{n\boldsymbol{k}} - \mu)f_{n\boldsymbol{k}} - (\varepsilon_{n'\boldsymbol{k}} - \mu)f_{n'\boldsymbol{k}}]\frac{(A_x)_{nn'}(\hat{s}_y)_{n'n} + c.c.}{\varepsilon_{n\boldsymbol{k}} - \varepsilon_{n'\boldsymbol{k}}} \,, \tag{7}$$

where $\boldsymbol{A}_{nn'} = \langle n\boldsymbol{k}|i\boldsymbol{\partial_k}|n'\boldsymbol{k}\rangle$ is the interband Berry connection and $\boldsymbol{s}_{n'n} = \langle n'\boldsymbol{k}|\hat{\boldsymbol{s}}|n\boldsymbol{k}\rangle$ is the interband element of the spin operator. Terms in Eq. (6) with $n = n'$ reads

$$\begin{aligned} T_{z2} &= \frac{g\mu_B}{4i\hbar}\sum_{n\boldsymbol{k}} f_{n\boldsymbol{k}}(\langle\partial_x n\boldsymbol{k}|s_y|n\boldsymbol{k}\rangle + \langle n\boldsymbol{k}|\partial_x|n\boldsymbol{k}\rangle\langle n\boldsymbol{k}|\hat{s}_y|n\boldsymbol{k}\rangle - c.c.) \\ &- \frac{g\mu_B}{4i\hbar}\sum_{n\boldsymbol{k}}(\varepsilon_{n\boldsymbol{k}} - \mu)f'_{n\boldsymbol{k}}(\langle\partial_x n\boldsymbol{k}|\hat{s}_y|n\boldsymbol{k}\rangle - \langle n\boldsymbol{k}|\partial_x|n\boldsymbol{k}\rangle\langle n\boldsymbol{k}|\hat{s}_y|n\boldsymbol{k}\rangle - c.c.) \\ &= \frac{g\mu_B}{4\hbar}\sum_{n\neq n',\boldsymbol{k}} f_{n\boldsymbol{k}}((A_x)_{nn'}(\hat{s}_y)_{n'n} + c.c.)\ . \end{aligned} \tag{8}$$

Note that to get the last equality in the above equation, we use the fact that at $T = 0$, $f'_{n\boldsymbol{k}} = \delta(\varepsilon_{n\boldsymbol{k}} - \mu)$.

The total contribution from the y-th component of the Zeeman field is

$$T_z = T_{z1} + T_{z2} = -\frac{g\mu_B}{4\hbar}\sum_{n\neq n',\boldsymbol{k}}(\varepsilon_{n'\boldsymbol{k}} - \mu)\frac{f_{n\boldsymbol{k}} - f_{n'k}}{\varepsilon_{n\boldsymbol{k}} - \varepsilon_{n'\boldsymbol{k}}}((A_x)_{nn'}(\hat{s}_y)_{n'n} + \text{c.c.})\ . \tag{9}$$

We can also calculate the contribution from the x-th component of the Zeeman field. The final result reads

$$T_z = -\frac{g\mu_B}{4\hbar}\sum_{n\neq n',\boldsymbol{k}}(\varepsilon_{n'\boldsymbol{k}} - \mu)\frac{f_{n\boldsymbol{k}} - f_{n'k}}{\varepsilon_{n\boldsymbol{k}} - \varepsilon_{n'\boldsymbol{k}}}((A_x)_{nn'}(\hat{s}_y)_{n'n} - (x \leftrightarrow y) + \text{c.c.}) \tag{10}$$

$$= -\frac{g\mu_B}{2}\text{Im}\sum_{n\neq n',\boldsymbol{k}}(\varepsilon_{n'\boldsymbol{k}} - \mu)\frac{f_{n\boldsymbol{k}} - f_{n'\boldsymbol{k}}}{(\varepsilon_{n\boldsymbol{k}} - \varepsilon_{n'\boldsymbol{k}})^2}(\boldsymbol{v}_{nn'} \times \boldsymbol{s}_{n'n})_z\ , \tag{11}$$

where $v_{nn'} = \langle n\boldsymbol{k}|\hat{\boldsymbol{v}}|n'\boldsymbol{k}\rangle$ is the interband element of the velocity operator. This is the multi-band formula for the spin toroidization. It reduces to Eq. (11) in the main text for a single band.

II. WANNIER REPRESENTATION

In this section we express the spin toroidization in terms of the Wannier functions. Denote by $|w_0(\boldsymbol{R},\boldsymbol{B})\rangle$ the Wannier function located at the lattice site $\boldsymbol{R}$ from band 0, derived from the local Hamiltonian $\hat{H}_c$. The periodic part of the Bloch function $|\tilde{u}_0\rangle$ is given by

$$|\tilde{u}_0\rangle = \frac{1}{\sqrt{N}}\sum_{\boldsymbol{R}} e^{-i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{R})}|w_0(\boldsymbol{R},\boldsymbol{B})\rangle\ , \tag{12}$$

where N is the number of unit cells.

We begin with the spin toroidization formula in Eq. (10), which can be recast as

$$\boldsymbol{T} = -\frac{g\mu_B}{4\hbar}\sum_{n\neq 0}\int\frac{d\boldsymbol{k}}{(2\pi)^3}(\boldsymbol{A}_{0n} \times \boldsymbol{s}_{n0} + c.c.) - \frac{g\mu_B}{2\hbar}\sum_{n\neq 0}\int\frac{d\boldsymbol{k}}{(2\pi)^3}\frac{\varepsilon_n - \mu}{\varepsilon_0 - \varepsilon_n}(\boldsymbol{A}_{0n} \times \boldsymbol{s}_{n0} + \text{c.c.})\ . \tag{13}$$

The first term in Eq. (13) can be expressed in terms of $|\tilde{u}_0\rangle$,

$$\sum_{n\neq 0}\boldsymbol{A}_{0n} \times \boldsymbol{s}_{n0} + c.c. = -i\langle\boldsymbol{\partial_k}\tilde{u}_0| \times \hat{\boldsymbol{s}}|\tilde{u}_0\rangle|_{\boldsymbol{B}\to 0} + i\langle\boldsymbol{\partial_k}\tilde{u}_0|\tilde{u}_0\rangle|_{\boldsymbol{B}\to 0} \times \langle\tilde{u}_0|\hat{\boldsymbol{s}}|\tilde{u}_0\rangle|_{\boldsymbol{B}\to 0} + \text{c.c.}\ , \tag{14}$$

where we have used the identity: $|\tilde{u}_0\rangle\langle\tilde{u}_0| + \sum_{n\neq 0}|\tilde{u}_n\rangle\langle\tilde{u}_n| = I$. Inserting Eq. (12) into the above expression yields

$$\begin{aligned} \boldsymbol{t}_1 =& -\frac{g\mu_B}{4N\hbar}\sum_{\boldsymbol{R},\boldsymbol{R}_1}\int\frac{d\boldsymbol{k}}{(2\pi)^3}e^{i\boldsymbol{k}\cdot(\boldsymbol{R}_1-\boldsymbol{R})}\langle w_0(\boldsymbol{R},\boldsymbol{B})|(\boldsymbol{r}-\boldsymbol{R}) \times \hat{\boldsymbol{s}}|w_0(\boldsymbol{R}_1,\boldsymbol{B})\rangle|_{\boldsymbol{B}\to 0} + \text{c.c.} \\ &+ \frac{g\mu_B}{4N^2\hbar}\sum_{\boldsymbol{R},\boldsymbol{R}_1,\boldsymbol{R}_2,\boldsymbol{R}_3}\int\frac{d\boldsymbol{k}}{(2\pi)^3}e^{i\boldsymbol{k}\cdot(\boldsymbol{R}_1-\boldsymbol{R}+\boldsymbol{R}_3-\boldsymbol{R}_2)}\langle w_0(\boldsymbol{R},\boldsymbol{B})|\boldsymbol{r}-\boldsymbol{R}|w_0(\boldsymbol{R}_1,\boldsymbol{B})\rangle|_{\boldsymbol{B}\to 0} \\ =& -\frac{g\mu_B}{2\hbar V_{\text{cell}}}\langle w_0(\boldsymbol{B})|\boldsymbol{r} \times \hat{\boldsymbol{s}}|w_0(\boldsymbol{B})\rangle|_{\boldsymbol{B}\to 0} \\ &+ \frac{g\mu_B}{2\hbar V_{\text{cell}}}\sum_{\boldsymbol{R}_1}\langle w_0(\boldsymbol{B})|\boldsymbol{r}|w_0(\boldsymbol{R}_1,\boldsymbol{B})\rangle|_{\boldsymbol{B}\to 0} \times \langle w_0(\boldsymbol{R}_1,\boldsymbol{B})|\hat{\boldsymbol{s}}|w_0(\boldsymbol{B})\rangle|_{\boldsymbol{B}\to 0}\ . \end{aligned} \tag{15}$$

Here $|w_0(\boldsymbol{B})\rangle = |w_0(\boldsymbol{R},\boldsymbol{B})\rangle$ with $\boldsymbol{R}=0$.

Next we focus on the second term of Eq. (13). Using $-g\mu_B\hat{\boldsymbol{s}}/\hbar = \boldsymbol{\partial_B}\hat{H}_c$, we have,

$$-g\mu_B \boldsymbol{s}_{n0}/\hbar = \langle\tilde{u}_n|\boldsymbol{\partial_B}\hat{H}_c|\tilde{u}_0\rangle|_{\boldsymbol{B}\to 0} = (\tilde{\varepsilon}_0-\tilde{\varepsilon}_n)|_{\boldsymbol{B}\to 0}\langle\tilde{u}_n|\boldsymbol{\partial_B}\tilde{u}_0\rangle|_{\boldsymbol{B}\to 0}\ , \tag{16}$$

and

$$-\sum_{n\neq 0}\frac{g\mu_B}{\hbar}\frac{\varepsilon_n-\mu}{\varepsilon_0-\varepsilon_n}(\boldsymbol{A}_{0n}\times\boldsymbol{s}_{n0}+c.c.) = -i\langle\boldsymbol{\partial_k}\tilde{u}_0|\times(\hat{H}_c-\mu)\boldsymbol{\partial_B}|\tilde{u}_0\rangle|_{\boldsymbol{B}\to 0}+\text{c.c.}\ . \tag{17}$$

The second term in Eq. (13) then becomes

$$\begin{aligned}\boldsymbol{t}_2 &= \frac{1}{2}\int\frac{d\boldsymbol{k}}{(2\pi)^3}(-i\langle\boldsymbol{\partial_k}\tilde{u}_0|\times(\hat{H}_c-\mu)\boldsymbol{\partial_B}|\tilde{u}_0\rangle+c.c.)|_{\boldsymbol{B}\to 0}\\ &= \frac{1}{V_{\text{cell}}}\text{Re}\langle w_0(\boldsymbol{B})|\boldsymbol{r}\times(\hat{H}_c-\mu)\boldsymbol{\partial_B}|w_0(\boldsymbol{B})\rangle|_{\boldsymbol{B}\to 0}\ .\end{aligned} \tag{18}$$

Combining Eq. (15) and Eq. (18), we obtain the final expression [Eq. (17) in the main text] of the spin toroidization in the Wannier representation,

$$\begin{aligned}\boldsymbol{T} = &-\frac{g\mu_B}{2\hbar V_{\text{cell}}}\langle w_0(\boldsymbol{B})|\boldsymbol{r}\times\hat{\boldsymbol{s}}|w_0(\boldsymbol{B})\rangle|_{\boldsymbol{B}=0}\\ &+\frac{g\mu_B}{2\hbar V_{\text{cell}}}\sum_{\boldsymbol{R}}\langle w_0(\boldsymbol{B})|\boldsymbol{r}|w_0(\boldsymbol{R},\boldsymbol{B})\rangle|_{\boldsymbol{B}\to 0}\times\langle w_0(\boldsymbol{R},\boldsymbol{B})|\hat{\boldsymbol{s}}|w_0(\boldsymbol{B})\rangle|_{\boldsymbol{B}=0}\\ &+\frac{1}{V_{\text{cell}}}\text{Re}\langle w_0(\boldsymbol{B})|\boldsymbol{r}(\hat{H}_c-\mu)\times\boldsymbol{\partial_B}|w_0(\boldsymbol{B})\rangle|_{\boldsymbol{B}=0}\ .\end{aligned} \tag{19}$$

III. MOLECULAR INSULATOR LIMIT

Under this limit the first two terms in Eq. (19) becomes:

$$\boldsymbol{t}_1 = -\frac{g\mu_B}{2\hbar V_{\text{cell}}}\langle w_0(\boldsymbol{B})|(\boldsymbol{r}-\bar{\boldsymbol{r}})\times(\hat{\boldsymbol{s}}-\bar{\boldsymbol{s}})|w_0(\boldsymbol{B})\rangle|_{\boldsymbol{B}\to 0}\ , \tag{20}$$

where $\bar{\boldsymbol{r}} = \langle w_0(\boldsymbol{B})|\boldsymbol{r}|w_0(\boldsymbol{B})\rangle$ is the expectation of the position, and $\bar{\boldsymbol{s}} = \langle w_0(\boldsymbol{B})|\hat{\boldsymbol{s}}|w_0(\boldsymbol{B})\rangle$ is the expectation of spin Pauli matrix. Since the combined time reversal and space inversion symmetry is respected, we must have $\bar{\boldsymbol{s}}=0$. Therefore,

$$\boldsymbol{t}_1 = -\frac{g\mu_B}{2\hbar V_{\text{cell}}}\langle w_0(\boldsymbol{B})|\boldsymbol{r}\times\hat{\boldsymbol{s}}|w_0(\boldsymbol{B})\rangle|_{\boldsymbol{B}\to 0}\ . \tag{21}$$

Now we consider the remaining term in Eq. (19). In the molecular insulator limit, its form does not change. Note that $|w_0(\boldsymbol{B})\rangle$ and $|w_n(\boldsymbol{B})\rangle$ becomes the molecular eigenfunctions and ε_0 and ε_n become the molecular eigenenergy. We further manipulate this term as follows:

$$\begin{aligned}\boldsymbol{t}_2 &= \frac{1}{V_{\text{cell}}}\text{Re}\langle w_0(\boldsymbol{B})|\boldsymbol{r}(\hat{H}_c-\mu)\times\boldsymbol{\partial_B}|w_0(\boldsymbol{B})\rangle|_{\boldsymbol{B}\to 0}\\ &= \frac{g\mu_B}{\hbar V_{\text{cell}}}\sum_{n\neq 0}[\langle w_0(\boldsymbol{B})|\boldsymbol{r}|w_n(\boldsymbol{B})\rangle\times\langle w_n(\boldsymbol{B})|\hat{\boldsymbol{s}}|w_0(\boldsymbol{B})\rangle]\big|_{\boldsymbol{B}\to 0}-\frac{1}{2V_{\text{cell}}}(\varepsilon_0-\mu)(\partial_{\boldsymbol{B}}\times\bar{\boldsymbol{r}})\big|_{\boldsymbol{B}\to 0}\\ &= \frac{g\mu_B}{\hbar V_{\text{cell}}}\langle w_0(\boldsymbol{B})|\boldsymbol{r}\times\hat{\boldsymbol{s}}|w_0(\boldsymbol{B})\rangle\big|_{\boldsymbol{B}\to 0}-\frac{1}{2V_{\text{cell}}}(\varepsilon_0-\mu)(\partial_{\boldsymbol{B}}\times\bar{\boldsymbol{r}})\big|_{\boldsymbol{B}\to 0}\ .\end{aligned} \tag{22}$$

where $\bar{\boldsymbol{r}}$ has been defined before, and stands for the position of electron under external magnetic field. Here $\varepsilon_0-\mu$ is the free energy for state 0.

Therefore, the total toroidization under the molecular insulator limit reads:

$$\begin{aligned}\boldsymbol{T} &= \boldsymbol{t}_1+\boldsymbol{t}_2\\ &= \frac{g\mu_B}{2\hbar V_{\text{cell}}}\langle w_0(\boldsymbol{B})|\boldsymbol{r}\times\hat{\boldsymbol{s}}|w_0(\boldsymbol{B})\rangle\big|_{\boldsymbol{B}\to 0}-\frac{1}{2V_{\text{cell}}}(\varepsilon_0-\mu)(\partial_{\boldsymbol{B}}\times\bar{\boldsymbol{r}})\big|_{\boldsymbol{B}\to 0}\ .\end{aligned} \tag{23}$$