Macroscopic Polarization from Berry phase.

Recall, Bloch fn:

$$\left.\begin{aligned} H\psi_{nk} &= E_{nk}\psi_{nk} \\ \psi_{nk} &= \frac{1}{\sqrt{N_k}} e^{ikx} u_{n\vec{k}} \end{aligned}\right] \quad (1)$$

$\frac{1}{\sqrt{N_k}}$ → To preserve normalization of ψ_{nk}

$(1) \Rightarrow \quad \psi_{nk}(x) = \psi_{nk}(x + N_k a)$; $\psi_{nk}(x) = \psi_{n\,\underline{k+G}}(x)$; $E_{nk} = E_{n\,k+G}$

$N_k a \rightarrow$ BVK Cell, $\quad U_{nk}(x) = U_{n\vec{k}}(x+a)$; $a \rightarrow$ Cell.

$N_k \rightarrow$ # of allowed $\vec{k}$ in 1BZ

$$(1) \Rightarrow \int_{\text{BVK cell}} \psi^*_{nk}\psi_{n'k'}\,dx = \delta_{nn'}\delta_{kk'}$$

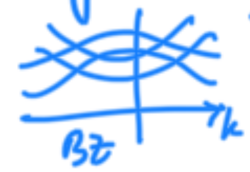
$$(1) \Rightarrow \int_{\text{Cell}} U^*_{nk} U_{n'k}\,dx = \delta_{nn'} \; ; \quad \int_{\text{Cell}} U^*_{nk} U_{nk'}\,dx \neq 0$$

Recall, Wannier fn:

$$W_{nR}(x) = \sqrt{N_k}\,\frac{a}{2\pi}\int_{1BZ} e^{-i\vec{k}\cdot\vec{R}}\,\psi_{n\vec{k}}(x)\,dk$$

; $A \rightarrow$ normalization constant.

$$= \frac{1}{\sqrt{N_k}}\sum_k e^{-ikR}\,\psi_{nk}(x)$$

However, as we discussed in the begining of the tight binding note, when we have crossing bands: "

" we then <u>cannot</u> associate band index "n" <u>unambiguously</u> through out the BZ. In other words, no band will exclusively have a single orbital character.

Therefore in a multiband scenario, which is the actual realistic scenario, we can expect that only a linear combination of Bloch fns at each $\vec{k}$ could be associated exclusively to a single orbital character at best maximally. We can thus define such combinations as:

$$\tilde{\Psi}_{nk} = \sum U_{nm} \Psi_{mk}$$

\# of bands we want to consider for construction of W

Implying:

$$W_{nR} = \sqrt{N_k}\,\frac{a}{2\pi} \int_{1BZ} e^{-i\vec{k}\cdot\vec{R}} \sum_{m}^{N_1} U_{nm}(\vec{k})\, \Psi_{m\vec{k}}\, dk$$

$$\Rightarrow \int_{\text{BVK Cell}} W^{*}_{n}(xR)\, W_{n'}(xR')\, dx = \delta_{nn'}\,\delta_{RR'}$$

Recall, this $\{\underline{\underline{U}}(\vec{k})\}$ is the gauge. The ability to choose it is reffered as "gauge freedom".

Nature of $W_n(x R)$, its localization, depends on $\{\underline{\underline{U}}(\vec{k})\}$.

A derivation of the Berry phase theory of electric polarization.

Since with $N_k \to \infty$, $W_n(x R)$ can be constructed (with effective choice of gauge) to be peaked at the unit cell marked by $\vec{R} = la$, (l some integer) and vanish at $\pm\infty$

We are then allowed to seek to calculate a dipole moment associated with the $W_n(x R)$ as: (Recall that we could not do it with ψ_{nk} since they do not vanish at $\pm\infty$)

$$d_n = \int_{BvK \to \infty} W^{*}_{n R=0}(x) \; x \, W_{n R=0}(x) \, dx$$

Note that we cannot do it with Bloch fns since they are non zero at $\pm\infty$.

Note here that the value of d_n will depend on the choice of origin of x axis.

We therefore talk about Δd_n which is the change of d_n due to two different potentials. Δd_n therefore is independent of choice of origin of x axis.

However, let us derive d_n as of now.

We will use $\tilde{u}_{nk} = \sum_m^{N_o} U^{(k)}_{nm} u_{mk}$ and drop the band index n for now.

$N_o \to$ # of occupied bands.

$$d_n = \int_{BvK} \left[\int_{1BZ} N_k \left(\frac{a}{2\pi}\right)^2 \left(\frac{1}{\sqrt{N_k}} e^{-ik'x} \tilde{u}^*_{k'}\right) x \left(\frac{1}{\sqrt{N_k}} \int_{1BZ} \left(e^{ikx} \tilde{u}_k\right)\right) \right] dx$$

$$= -i \left(\frac{a}{2\pi}\right)^2 \iint_{k\,k'} \int_{BvK} e^{-ik'x} \tilde{u}^*_{k'} \left(\frac{\partial}{\partial k} e^{ikx}\right) \tilde{u}_k \, dx \quad dk\,dk'$$

$$= -i \left(\frac{a}{2\pi}\right)^2 \left[\int_k \int_{BvK} \left[e^{-ik'x} \tilde{u}^*_{k'} e^{ikx} \tilde{u}_k \right]_{k=-\pi/a}^{k=+\pi/a} dx\,dk' - \iiint_{k\,k'\,B} e^{-ik'x} \tilde{u}^*_{k'} e^{ikx} \left(\frac{\partial}{\partial k} \tilde{u}_k\right) dx\,dk\,dk' \right]$$

$$= -i \left(\frac{a}{2\pi}\right)^2 \left[\underset{\substack{\downarrow \\ \psi_{\frac{\pi}{a}} = \psi_{-\frac{\pi}{a}}}}{0} - \iint_{k\,k'} \sum_{\substack{l=1 \\ N\to\infty}}^{N_o} \int_{C\to cell} e^{-ik'(x+la)} \tilde{u}_{k'}(x+la) e^{ik(x+la)} \left(\frac{\partial}{\partial k} \tilde{u}_k(x+la)\right) dx\,dk\,dk' \right]$$

$$= i \left(\frac{a}{2\pi}\right)^2 \iint_{k\,k'} \underbrace{\left(\sum_l e^{ial(k-k')}\right)}_{N_k \delta_{kk'}} \left\{ \int_C e^{-ik'x} e^{ikx} \tilde{u}_{k'}(x) \left(\frac{\partial}{\partial k} \tilde{u}_k(x)\right) dx \right\} dk\,dk'$$

$$= i N_k \left(\frac{a}{2\pi}\right)^2 \iint_{k\,k'} \delta_{kk'} \; e^{ix(k-k')} \langle \tilde{v}_{k'} | \frac{\partial}{\partial k} | \tilde{v}_k \rangle \, dk\, dk'$$

$$= i N_k \left(\frac{a}{2\pi}\right)^2 \sum_{k'} \int_k \delta_{kk'} \, e^{ix(k-k')} \langle \tilde{v}_{k'} | \frac{\partial}{\partial k} | \tilde{v}_k \rangle \, dk \; \underbrace{\Delta k'}_{\frac{2\pi}{a N_k}}$$

$$= i \frac{a}{2\pi} \int_k \langle \tilde{v}_k | \frac{\partial}{\partial k} | \tilde{u}_k \rangle \, dk$$

$$\boxed{d_n = i \frac{a}{2\pi} \int_k \langle \tilde{u}_{nk} | \frac{\partial}{\partial k} | \tilde{u}_{nk} \rangle \, dk} \quad 1$$

(bringing back band index)

$$= i \frac{a}{2\pi} \int_k \sum_m U^*_{nm}(k) \langle u_{mk} | \frac{\partial}{\partial k} \sum_l U_{nl}(k) | u_{lk} \rangle \, dk$$

$$= i \frac{a}{2\pi} \int_k \sum_m \sum_l \left[U^*_{nm}(k) \left(\frac{\partial U_{nl}(k)}{\partial k} \right) \langle u_{mk} | u_{lk} \rangle + U^*_{nm} U_{nl} \langle u_{mk} | \frac{\partial}{\partial k} | u_{lk} \rangle \right] dk$$

$$= i \frac{a}{2\pi} \int_k \sum_m \sum_l \left[\left\{ U^\dagger_{mn}(k) \frac{\partial U_{nl}(k)}{\partial k} \delta_{ml} \right\} + U^\dagger_{mn} U_{nl} \langle u_{mk} | \frac{\partial}{\partial k} | u_{lk} \rangle \right] dk$$

$$= i \frac{a}{2\pi} \int_k \sum_m \left[\left\{ U^\dagger_{mn} \frac{\partial U_{nm}(k)}{\partial k} \right\} + \sum_l U^\dagger_{mn} U_{nl} \langle u_{mk} | \frac{\partial}{\partial k} | u_{lk} \rangle \right] dk$$

Sum over all N_o occupied bands.

$$\sum_n^{N_o} d_n = i\frac{a}{2\pi}\int_k \left[\sum_n^{N_o}\sum_m^{N_o}\left\{ U^{\dagger}_{mn}(k)\frac{\partial}{\partial k}U_{nm}(k)\right\} + \sum_m\sum_l \underbrace{\left(\sum_n U^{\dagger}_{mn}U_{nl}\right)}_{\delta_{ml}}\langle u_{mk}|\frac{\partial}{\partial k}|u_{lk}(k)\rangle\right]dk$$

$$= i\frac{a}{2\pi}\int_k\left[\sum_n\sum_m\left\{U^{*}_{nm}\frac{\partial}{\partial k}U_{nm}\right\} + \sum_m\langle u_{mk}|\frac{\partial}{\partial k}|u_{mk}\rangle\right]dk$$

We note at this point that $\underline{\underline{U}}(\vec{k})$ must be periodic in k like Ψ_{nk} across 1BZ

$\sum_{mn}\sum\int_k U^{*}_{nm}\frac{\partial}{\partial k}U_{nm}\,dk$ can be shown as $\int_k \frac{\partial}{\partial k}\ln(\det(U))\,dk$

__Ex__: for a 2×2 matrix: $U^{*}_{nm}\frac{\partial}{\partial k}U_{nm} = U^{-1}_{mn}\frac{\partial}{\partial k}U_{nm}$

for $\begin{bmatrix} U_{11} & U_{12} \\ U_{21} & U_{22}\end{bmatrix}$: $\sum_m\sum_n U^{-1}_{mn}\frac{\partial}{\partial k}U_{nm} = \frac{1}{\det(U)}\left[U_{22}\frac{\partial}{\partial k}U_{11} + U_{11}\frac{\partial}{\partial k}U_{22} - U_{21}\frac{\partial}{\partial k}U_{12} - U_{12}\frac{\partial}{\partial k}U_{21}\right]$

$U^{-1} = \frac{1}{\det(U)}\begin{bmatrix} U_{22} & -U_{12} \\ -U_{21} & U_{11}\end{bmatrix}$ $\quad = \frac{1}{\det(U)}\frac{\partial}{\partial k}\det(U) = \frac{\partial}{\partial k}\ln(\det(U))$

Now $\int_k \frac{\partial}{\partial k}\left[\ln(\det(U(k)))\right]dk = \left[\quad\right]_0^{2\pi/a} = 0$ due to periodicity of $U(k)$ across 1BZ

$$\boxed{\therefore \sum_{n}^{N_0} d_n = i \sum_{m}^{N_0} \frac{a}{2\pi} \int_k \langle u_{mk} | \frac{\partial}{\partial k} | u_{mk} \rangle dk} \quad (3)$$

Independent of choice of $\{u(k)\}$
Gauge independent (has to be)
Since $\sum d_n \rightarrow$ physical observable

$\frac{\partial}{\partial k}|u_{nk}\rangle$ can be calculated using perturbative approach.
However a approximate yet quite accurate approach is often adopted.

Starting with: $\langle u_{mk} | u_{m\,k+\Delta k}\rangle = \langle u_{mk} | \left(|u_{mk}\rangle + \frac{\partial |u_{mk}\rangle}{\partial k} \Delta k \right)$

$$= 1 - (i)^2 \langle u_{mk} | \frac{\partial |u_{mk}\rangle}{\partial k} \Delta k \approx e^{-i \gamma_{mk} \Delta k}; \quad \gamma_{mk} = i \langle u_{mk} | \frac{\partial}{\partial k} | u_{mk} \rangle$$

$$\therefore \gamma_{mk} = \frac{1}{\Delta k} i \ln \left[\langle u_{mk} | u_{m\,k+\Delta k} \rangle \right]$$

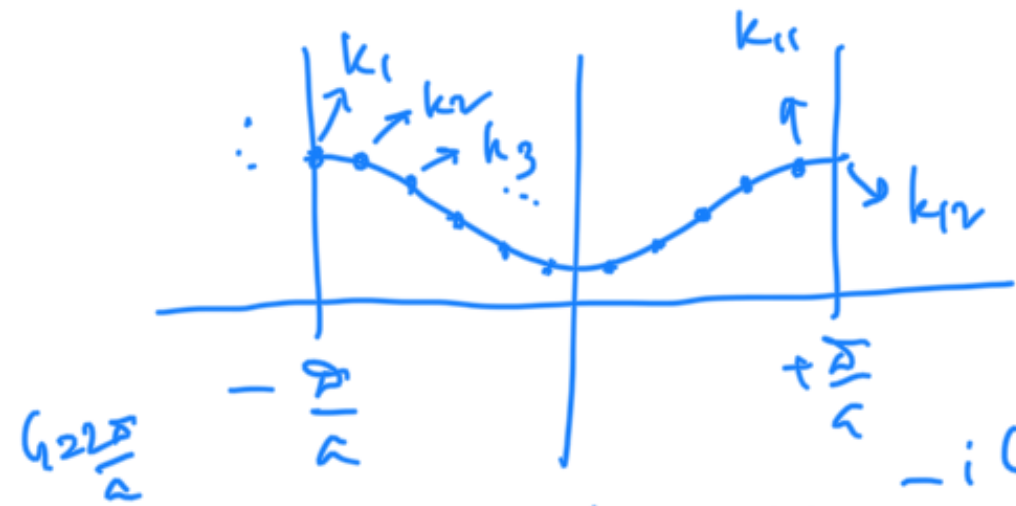
$$d_m = i \frac{a}{2\pi} \int_k \langle u_{mk} | \frac{\partial}{\partial k} | u_{mk} \rangle dk = i \frac{a}{2\pi} \frac{1}{\Delta k} \int_k \ln \langle u_{mk} | u_{m\,k+\Delta k} \rangle dk$$

$$= i \frac{a}{2\pi} \frac{1}{\Delta k} \sum_k \ln \langle u_{mk} | u_{m,k+\Delta k} \rangle \Delta k$$

$$\boxed{d_m = i \frac{a}{2\pi} \ln \prod_{k}^{N_k} \langle u_{mk} | u_{m\,k+\Delta k} \rangle}$$

for a "isolated" single band

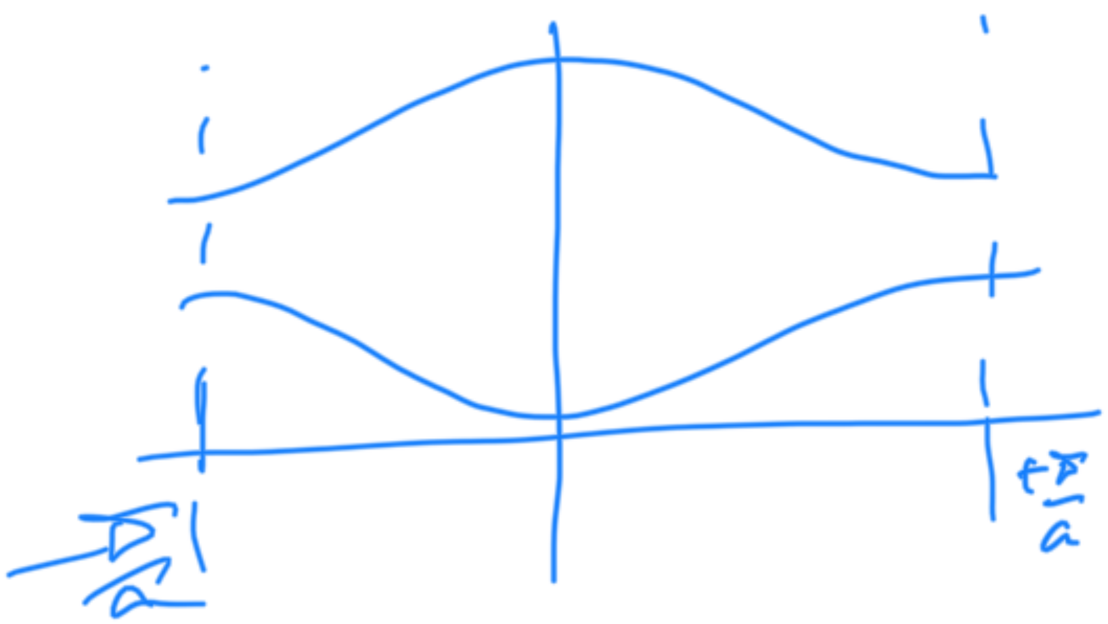
let $N_k = 11$



Note $k_{12} = k_1 + G$; $u_{k_{12}} = u_{k_1} e^{-iGx}$

$$d_m = i\frac{a}{2\pi} \ln\left[\langle u_{mk_1} | u_{mk_2}\rangle \langle u_{mk_2} | u_{mk_3}\rangle \cdots \langle u_{mk_{11}} | u_{mk_{12}}\rangle\right]$$

for multiple bands:



Recall, $X_{mn} = \langle W_{mR=0} | \hat{x} | W_{nR=0}\rangle$

$$= i\frac{a}{2\pi}\int_{BZ} \langle u_{mk} | \frac{\partial}{\partial k} | u_{nk}\rangle dk$$

$$d = \sum_n d_n = \mathrm{Tr}\left[\underline{\underline{X}}\right] = \mathrm{Tr}\left[\frac{ia}{2\pi}\ln \underline{\underline{\Gamma}}\right]$$

$$\underline{\underline{\Gamma}} = \prod_k \underline{\underline{M}}(k) \; ; \; M_{mn}(k) = \langle u_{mk} | u_{n\,k+\Delta k}\rangle$$

$$d = \mathrm{Tr}\left[\frac{ia}{2\pi}\ln\Gamma\right] = \frac{ia}{2\pi}\mathrm{Tr}\left[\ln V \Gamma^D V^{-1}\right] \; ; \; V \to \text{eigenvector matrix}$$

$$= i\frac{a}{2\pi}\mathrm{Tr}\left[V \ln\Gamma^D V^{-1}\right] = i\frac{a}{2\pi}\mathrm{Tr}\left[\ln\Gamma^D\right] = \frac{ia}{2\pi}\sum_i \ln\gamma_i \; ; \; \gamma_i \to \text{eigenvalue of } \Gamma$$