

# Física de Semiconductores

## Lección 16

# Bloch representation expansion

- We wrote earlier the wave functions in the Bloch representation as an integral

$$\Psi(\mathbf{r}) = \int d\mathbf{k} \Psi(\mathbf{k}) \psi_{\mathbf{k}}(\mathbf{r})$$

- We need to be careful with normalization in the continuum.

# Normalization condition I

- In switching from discrete to continuous we note that

$$\sum_{\mathbf{k}} \rightarrow \frac{V}{(2\pi)^3} \int_{BZ} d\mathbf{k}$$

- In the discrete case, we have

$$\int_{\text{crystal}} d\mathbf{r} \psi_{n\mathbf{k}}^* (\mathbf{r}) \psi_{n'\mathbf{k}'} (\mathbf{r}) = \delta_{nn'} \delta_{\mathbf{k}\mathbf{k}'}$$
$$\sum_{\mathbf{k}\mathbf{k}'} \delta_{\mathbf{k}\mathbf{k}'} = N$$

# Normalization condition II

- The normalization condition in the continuum, for consistency with the discrete case is, therefore

$$\int_{\text{crystal}} d\mathbf{r} \psi_{n\mathbf{k}}^* (\mathbf{r}) \psi_{n'\mathbf{k}'} (\mathbf{r}) = \delta_{nn'} C \delta(\mathbf{k} - \mathbf{k}')$$

$$N = \left[ \frac{V}{(2\pi)^3} \right]^2 \int_{\text{BZ}} d\mathbf{k} d\mathbf{k}' C \delta(\mathbf{k} - \mathbf{k}') = \left[ \frac{V}{(2\pi)^3} \right]^2 C \frac{(2\pi)^3}{v_c}$$

- Therefore

$$C = \frac{(2\pi)^3}{V}$$

# Normalization continuum III

- But this implies

$$\begin{aligned} 1 &= \int d\mathbf{r} \Psi^*(\mathbf{r}) \Psi(\mathbf{r}) = \int_{BZ} d\mathbf{k}' \int_{BZ} d\mathbf{k} \Psi^*(\mathbf{k}') \Psi(\mathbf{k}) \int d\mathbf{r} \psi_{n\mathbf{k}'}^*(\mathbf{r}) \psi_{n\mathbf{k}}(\mathbf{r}) \\ &= \frac{(2\pi)^3}{V} \int_{BZ} d\mathbf{k}' \int_{BZ} d\mathbf{k} \Psi^*(\mathbf{k}') \Psi(\mathbf{k}) \delta(\mathbf{k}' - \mathbf{k}) = \frac{(2\pi)^3}{V} \int_{BZ} d\mathbf{k} |\Psi(\mathbf{k})|^2 \end{aligned}$$

- Therefore, the average value of an operator in the Bloch representation is

$$\bar{O} = \frac{(2\pi)^3}{V} \int_{BZ} d\mathbf{k} \Psi^*(\mathbf{k}) O \Psi(\mathbf{k})$$

# Dipole moment

- The dipole moment of a system of charges is defined as

$$\mathbf{p} = \sum_i q_i \mathbf{r}_i$$

- If I shift the origin:

$$\mathbf{p}' = \sum_i q_i (\mathbf{r}_i + \mathbf{r}_0) = \mathbf{p} + \mathbf{r}_0 \sum_i q_i$$

- so that the dipole moment is independent of the origin for a neutral system.

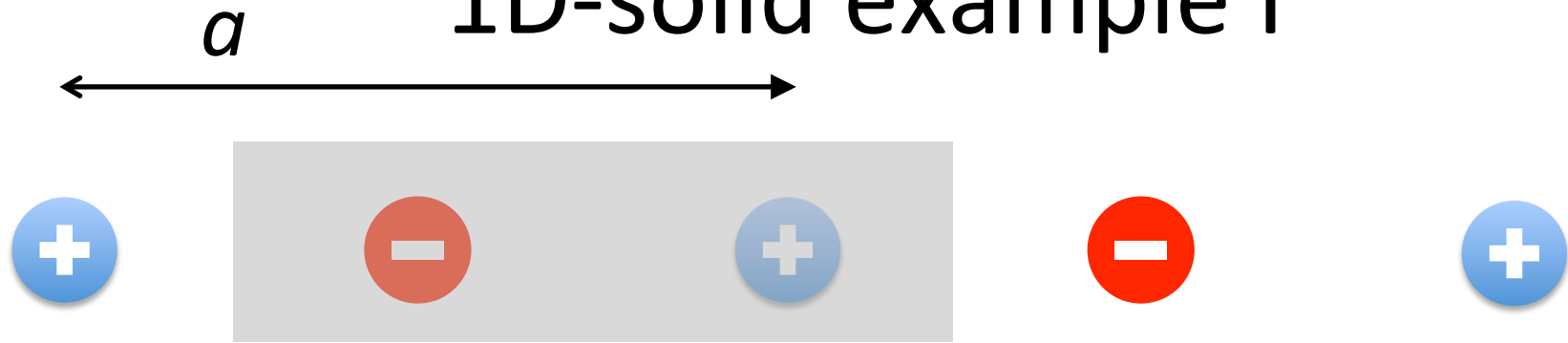
# Infinite solid

- In an infinite periodic solid, the dipole moment definition is meaningless, but I can define a polarization as a dipole moment per unit cell:

$$\mathbf{P} = \frac{1}{v_c} \sum_{\text{unit cell}} q_i \mathbf{r}_i$$

- If the solid is neutral, any of its unit cells will give the same value because of the translation theorem, but the choice of unit cell is not unique, and it matters:

# 1D-solid example I

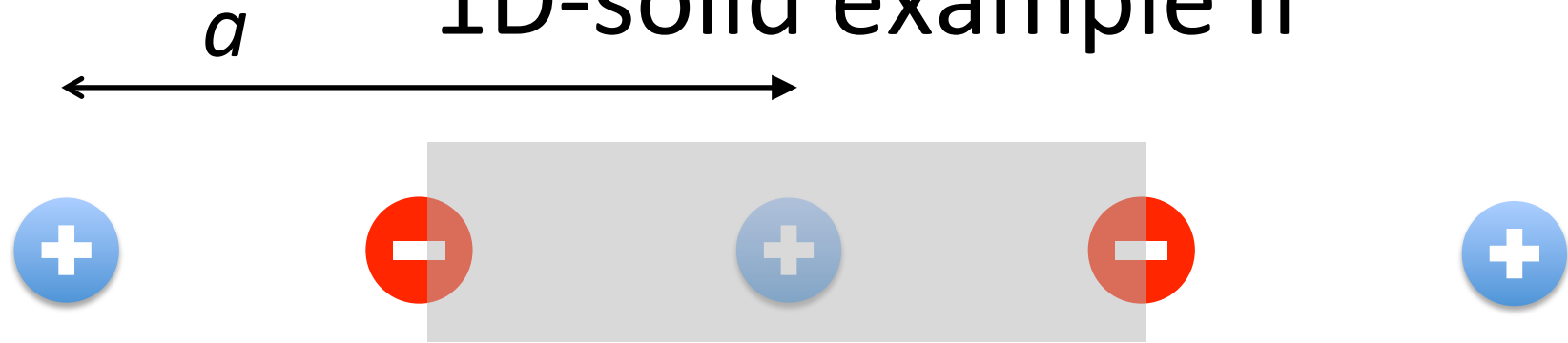


$$P = \frac{e}{a} \left[ -\frac{1}{4}a + \frac{3}{4}a \right] = \frac{e}{2}$$



$$P = \frac{e}{a} \left[ \frac{1}{4}a - \frac{3}{2}a \right] = -\frac{e}{2}$$

# 1D-solid example II



$$P = \frac{e}{a} \left[ -0 + \frac{1}{2}a \right] = \frac{e}{2}$$



$$P = \frac{e}{a} \left[ -\frac{1}{4}a + \frac{7}{4}a \right] = \frac{3}{2}e$$

# Possible values

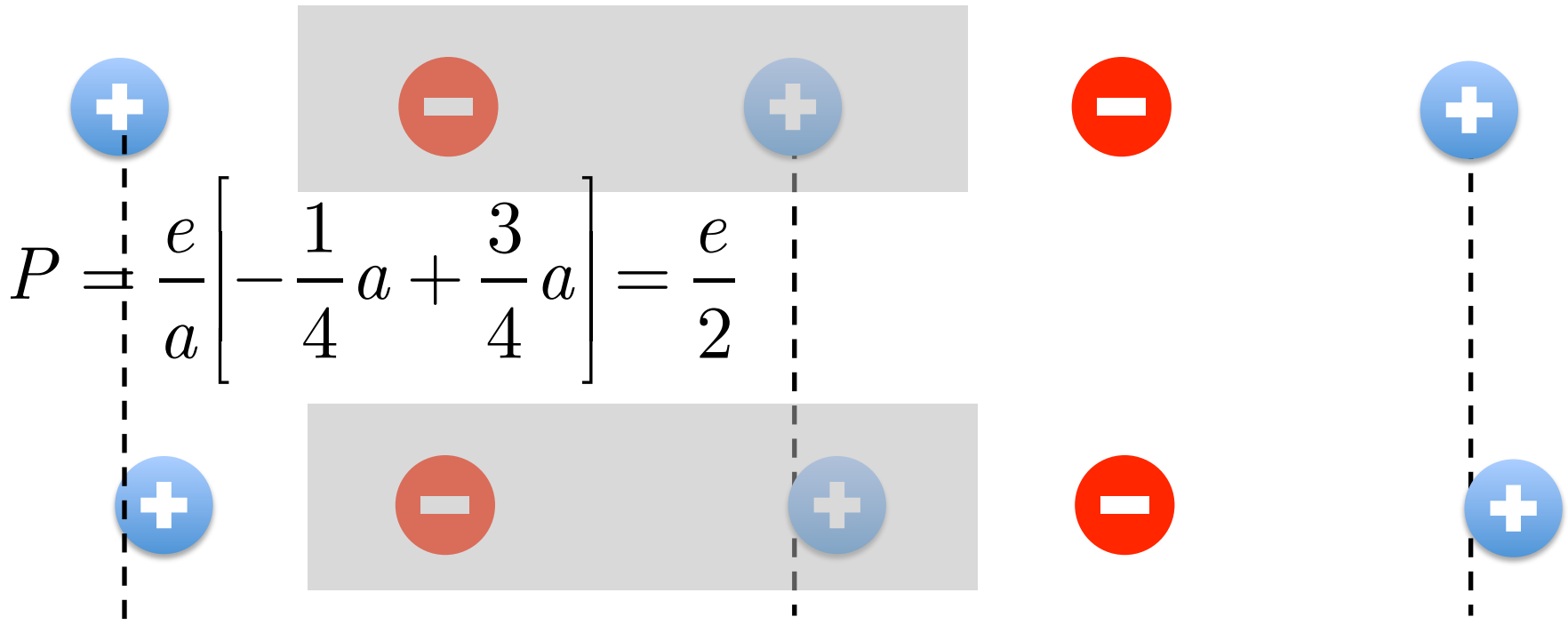
- Depending on my choice of unit cell, I get

$$\dots -\frac{5}{2}e, -\frac{3}{2}e, -\frac{1}{2}e, \frac{1}{2}e, \frac{3}{2}e, \frac{5}{2}e$$

- que difieren entre sí en una unidad  $e$ . Decimos que la polarización está definida módulo un cuanto de polarización, en este caso  $e$ .

# Cambios de P I

- Desplazo un átomo una pequeña cantidad  $\delta$  y calculo el cambio en la polarización.



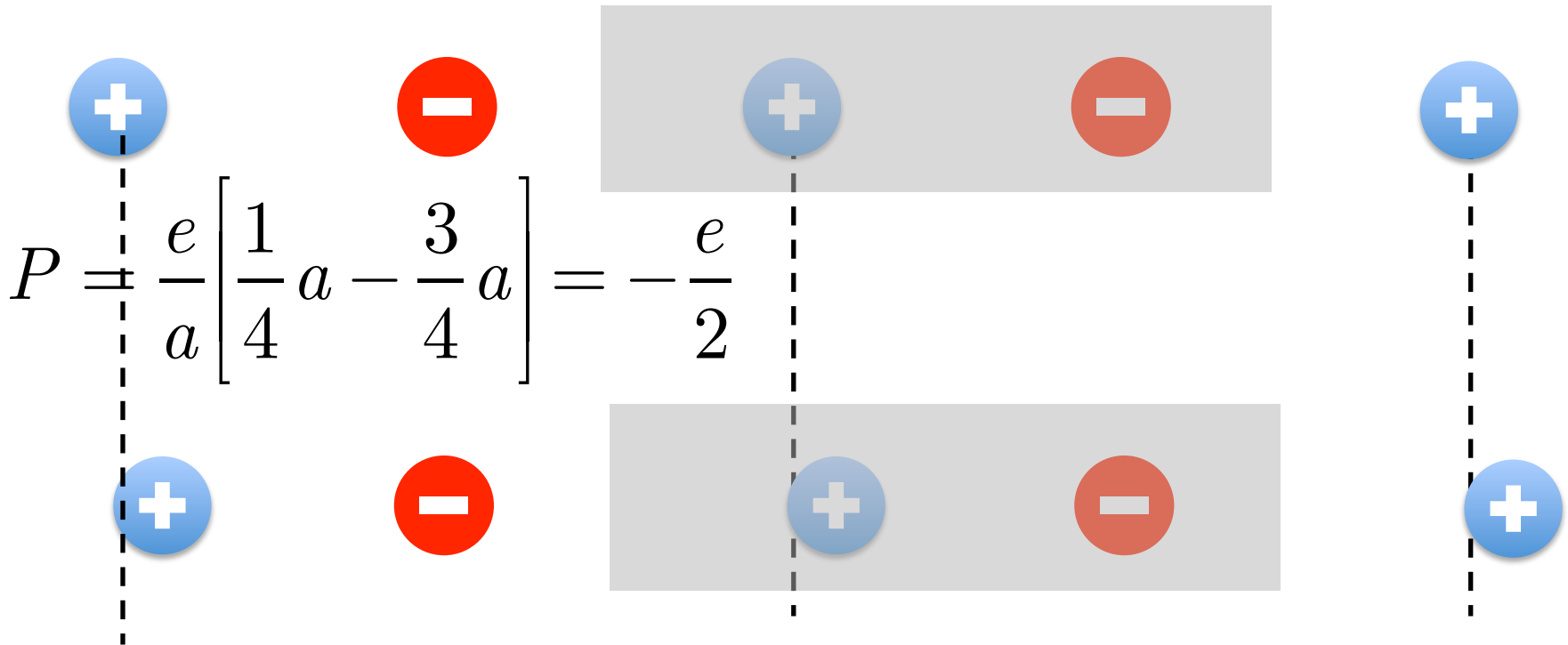
The diagram illustrates a crystal lattice with positive (blue circles with '+') and negative (red circles with '-') ions. A central vertical dashed line represents the initial position of an atom. Two gray rectangular regions highlight the displacement of a negative ion by a distance  $\delta$  to the right. The top region shows the initial state, and the bottom region shows the state after displacement. The displacement is indicated by a dashed line extending from the initial position to the new position of the negative ion.

$$P = \frac{e}{a} \left[ -\frac{1}{4}a + \frac{3}{4}a \right] = \frac{e}{2}$$

$$P' = \frac{e}{a} \left[ -\frac{1}{4}a + \frac{3}{4}a + \delta \right] = -\frac{e}{2} + e \left( \frac{\delta}{a} \right) \Rightarrow \Delta P = e \left( \frac{\delta}{a} \right)$$

# Cambios de P II

- Desplazo un átomo una pequeña cantidad  $\delta$  y calculo el cambio en la polarización.

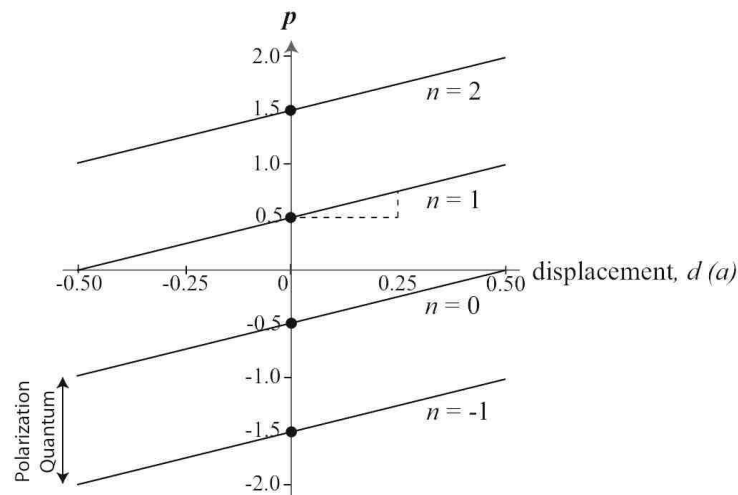


$$P = \frac{e}{a} \left[ \frac{1}{4}a - \frac{3}{4}a \right] = -\frac{e}{2}$$

$$P' = \frac{e}{a} \left[ \frac{1}{4}a + \delta - \frac{3}{4}a \right] = -\frac{e}{2} + e \left( \frac{\delta}{a} \right) \Rightarrow \Delta P = e \left( \frac{\delta}{a} \right)$$

# Cambio vs valor absoluto

- Aún cuando la polarización está definida módulo un cuanto, los cambios de polarización son independientes de la “rama” de polarización donde esté:



arXiv: 1202.1831v1

# Realistic infinite solid

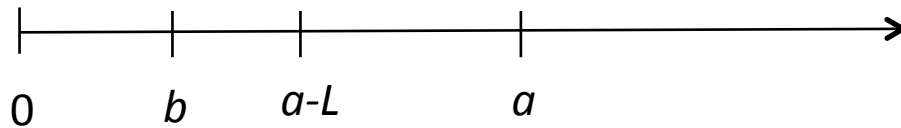
- In a realistic infinite solid, I can approximate the ions as point charges, but the electrons form a cloud. An apparently natural way to address this is to define

$$\mathbf{P} = \frac{e}{v_c} \left[ \sum_i^{\text{unit cell}} Z_i \mathbf{r} - \int_{\text{unit cell}} \mathbf{r} n(\mathbf{r}) d\mathbf{r} \right]$$

- However, this doesn't work in a periodic solid, as shown by the following toy model.

# Polarization in toy model I

- Consider the following model

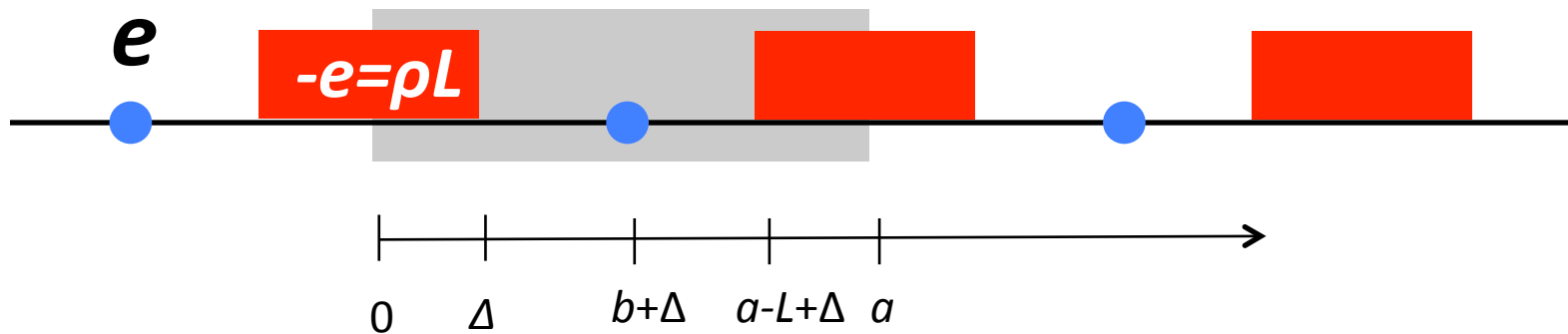


$$P = \frac{1}{a} \left[ eb + \rho \int_{a-L}^a x dx \right] = \frac{eb}{a} + \frac{1}{2} \frac{\rho}{a} \left[ a^2 - (a-L)^2 \right]$$

$$= \frac{eb}{a} + \frac{1}{2} \frac{\rho}{a} L [2a - L] = \frac{e}{a} \left\{ b - \frac{1}{2} [2a - L] \right\}$$

# Polarization in toy model II

- Consider the following model



$$\begin{aligned}
 P &= \frac{1}{a} \left[ \rho \int_0^{\Delta} x dx + e(b + \Delta) + \rho \int_{a-L+\Delta}^a x dx \right] \\
 &= \frac{1}{a} \left\{ \frac{1}{2} \rho \Delta^2 + e(b + \Delta) + \frac{1}{2} \rho \left[ a^2 - (a - L + \Delta)^2 \right] \right\} \\
 &= \frac{1}{a} \left\{ \frac{1}{2} \rho \Delta^2 + e(b + \Delta) + \frac{1}{2} \rho \left[ a^2 - (a - L)^2 - 2(a - L)\Delta - \Delta^2 \right] \right\}
 \end{aligned}$$

# Polarization in toy model III

$$\begin{aligned} &= \frac{1}{a} \left\{ \frac{1}{2} \rho \Delta^2 + e(b + \Delta) + \frac{1}{2} \rho \left[ a^2 - (a^2 - 2aL + L^2) - 2a\Delta + 2L\Delta + \Delta^2 \right] \right\} \\ &= \frac{1}{a} \left\{ e(b + \Delta) + \frac{1}{2} \rho \left[ 2aL - L^2 - 2a\Delta + 2L\Delta \right] \right\} \\ &= \frac{1}{a} \left\{ e(b + \Delta) + \frac{1}{2} \rho L \left[ 2a - L - 2a\Delta/L + 2\Delta \right] \right\} \\ &= \frac{1}{a} \left\{ e(b + \Delta) - e \left[ \frac{2a - L}{2} + \Delta \right] + e(\Delta/L)a \right\} \\ &= \frac{1}{a} \left\{ eb - \frac{1}{2} e(2a - L) + e(\Delta/L)a \right\} \\ &= \frac{e}{a} \left\{ b - \frac{1}{2} (2a - L) + (\Delta/L)a \right\} \end{aligned}$$

# Polarization in toy model III

- Now the polarization can be shown to change continuously depending on parameter  $\Delta$ . This makes it impossible to compute changes in polarization due for example to the application of strain.
- It is as if polarization were a surface property

# Change in polarization

- From Maxwell's equations

$$\nabla \cdot \mathbf{P} = -\rho_b$$

$$\mathbf{j}_b = \frac{\partial \mathbf{P}}{\partial t} + \nabla \times \mathbf{M}$$

- Then in a non-magnetic material one can calculate the change in polarization

$$\Delta \mathbf{P} = \int_0^{t_f} \mathbf{j}_b dt$$

# Velocity operator I

- The velocity operator is

$$\frac{d\hat{\mathbf{r}}}{dt} = \frac{i}{\hbar} [H, \hat{\mathbf{r}}] + \frac{\partial \hat{\mathbf{r}}}{\partial t} = \frac{i}{\hbar} \left[ H, i \frac{\partial}{\partial \mathbf{k}} + \mathcal{A}_n(\mathbf{k}) \right] + \frac{\partial \mathcal{A}_n(\mathbf{k})}{\partial t}$$

- Let  $H = -\frac{\hbar^2 \nabla^2}{2m} + V(\mathbf{r}, t)$ , where the time dependence does not change the periodicity, and

$$H \psi_{n\mathbf{k}}(\mathbf{r}, t) = E_{n\mathbf{k}}(t) \psi_{n\mathbf{k}}(\mathbf{r}, t)$$

- the adiabatic solutions.

# Velocity operator I

- Therefore, in the Bloch representation, the hamiltonian is

$$H = E_{n\mathbf{k}}(t)$$

- Then

$$\hat{v}_{n\mathbf{k}}(t) = \frac{i}{\hbar} \left[ E_{n\mathbf{k}}(t), i \frac{\partial}{\partial \mathbf{k}} + \mathcal{A}_n(\mathbf{k}) \right] + \frac{\partial \mathcal{A}_n(\mathbf{k})}{\partial t}$$

$$\hat{v}_{n\mathbf{k}}(t) = \frac{1}{\hbar} \frac{\partial E_{n\mathbf{k}}(t)}{\partial \mathbf{k}} + \frac{\partial \mathcal{A}_n(\mathbf{k})}{\partial t}$$

# Current

- The current density operator is then

$$\hat{\mathbf{j}}_{n\mathbf{k}}(t) = \frac{-e}{V} \left[ \frac{1}{\hbar} \frac{\partial E_{n\mathbf{k}}(t)}{\partial \mathbf{k}} + \frac{\partial \mathcal{A}_n(\mathbf{k})}{\partial t} \right]$$

- So that

$$\mathbf{j}_n = \frac{(2\pi)^3}{V} \sum_{\text{electrons } \rho} \int_{BZ} d\mathbf{k} \Psi_{n\rho}^*(\mathbf{k}) \hat{\mathbf{j}}_{n\mathbf{k}}(t) \Psi_{n\rho}(\mathbf{k})$$

# Wannier functions

- Because the Bloch function is periodic in  $k$  we can write 
$$\psi_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} w_n(\mathbf{R}, \mathbf{r}) e^{i\mathbf{R} \cdot \mathbf{k}}$$

- Therefore 
$$\psi_{n\mathbf{k}}(\mathbf{r}) e^{-i\mathbf{k} \cdot \mathbf{R}'} = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} w_n(\mathbf{R}, \mathbf{r}) e^{i(\mathbf{R} - \mathbf{R}') \cdot \mathbf{k}}$$

- Adding over  $k$  
$$\sum_{\mathbf{k}} \psi_{n\mathbf{k}}(\mathbf{r}) e^{-i\mathbf{k} \cdot \mathbf{R}'} = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} w_n(\mathbf{R}, \mathbf{r}) \sum_{\mathbf{k}} e^{i(\mathbf{R} - \mathbf{R}') \cdot \mathbf{k}} = \sqrt{N} w_n(\mathbf{R}', \mathbf{r})$$

- Therefore

$$w_n(\mathbf{R}, \mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} \psi_{n\mathbf{k}}(\mathbf{r}) e^{-i\mathbf{k} \cdot \mathbf{R}}$$

# Properties I

- If we add a lattice vector

$$\begin{aligned}w_n(\mathbf{R} + \mathbf{R}', \mathbf{r} + \mathbf{R}') &= \frac{1}{\sqrt{N}} \sum_{\mathbf{k}}^{BZ} \psi_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}') e^{-i(\mathbf{R} + \mathbf{R}') \cdot \mathbf{k}} \\&= \frac{1}{\sqrt{N}} \sum_{\mathbf{k}}^{BZ} \psi_{n\mathbf{k}}(\mathbf{r}) e^{i\mathbf{k} \cdot \mathbf{R}'} e^{-i(\mathbf{R} + \mathbf{R}') \cdot \mathbf{k}} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}}^{BZ} \psi_{n\mathbf{k}}(\mathbf{r}) e^{-i\mathbf{R} \cdot \mathbf{k}} \\&= w_n(\mathbf{R}, \mathbf{r})\end{aligned}$$

- Thus

$$w_n(\mathbf{R}, \mathbf{r}) = w_n(\mathbf{r} - \mathbf{R})$$

# Properties II

- Let's compute

$$\begin{aligned} \int_{\text{crystal}} d\mathbf{r} w_n^* (\mathbf{r} - \mathbf{R}) w_n (\mathbf{r} - \mathbf{R}') &= \\ &= \frac{1}{N} \int_{\text{crystal}} d\mathbf{r} \sum_{\mathbf{k}, \mathbf{k}'}^{BZ} \psi_{n\mathbf{k}}^* (\mathbf{r}) e^{i\mathbf{R} \cdot \mathbf{k}} \psi_{n\mathbf{k}'} (\mathbf{r}) e^{-i\mathbf{R}' \cdot \mathbf{k}'} \\ &= \frac{1}{N} \sum_{\mathbf{k}, \mathbf{k}'}^{BZ} e^{i\mathbf{R} \cdot \mathbf{k}} e^{-i\mathbf{R}' \cdot \mathbf{k}'} \int_{\text{crystal}} d\mathbf{r} \psi_{n\mathbf{k}}^* (\mathbf{r}) \psi_{n\mathbf{k}'} (\mathbf{r}) = \frac{1}{N} \sum_{\mathbf{k}, \mathbf{k}'}^{BZ} e^{i\mathbf{R} \cdot \mathbf{k}} e^{-i\mathbf{R}' \cdot \mathbf{k}'} \delta_{\mathbf{k}, \mathbf{k}'} \\ &= \frac{1}{N} \sum_{\mathbf{k}}^{BZ} e^{i(\mathbf{R} - \mathbf{R}') \cdot \mathbf{k}} = \delta_{\mathbf{R}, \mathbf{R}'} \end{aligned}$$

# Continuum version of Wannier functions

- Making the switch to the continuum:

$$w_n(\mathbf{R}, \mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}}^{BZ} \psi_{n\mathbf{k}}(\mathbf{r}) e^{-i\mathbf{k} \cdot \mathbf{R}} \rightarrow \frac{1}{\sqrt{N}} \frac{V}{(2\pi)^3} \int_{BZ} d\mathbf{k} \psi_{n\mathbf{k}}(\mathbf{r}) e^{-i\mathbf{k} \cdot \mathbf{R}}$$

Therefore

$$\Psi(\mathbf{k}) = \frac{1}{\sqrt{N}} \frac{V e^{-i\mathbf{k} \cdot \mathbf{R}}}{(2\pi)^3}$$

# Current I

- Using

We get

$$\Psi(\mathbf{k}) = \frac{1}{\sqrt{N}} \frac{V e^{-i\mathbf{k} \cdot \mathbf{R}}}{(2\pi)^3}$$

$$\begin{aligned} \mathbf{j}_n &= \frac{(2\pi)^3}{V} \sum_{\mathbf{R}} \int_{BZ} d\mathbf{k} \Psi_{n\mathbf{R}}^*(\mathbf{k}) \hat{\mathbf{j}}_{n\mathbf{k}}(t) \Psi_{n\mathbf{R}}(\mathbf{k}) = \\ &= \frac{1}{N(2\pi)^3} \sum_{\mathbf{R}} \int_{BZ} d\mathbf{k} \frac{1}{\hbar} \frac{\partial E_{n\mathbf{k}}(t)}{\partial \mathbf{k}} - \frac{e}{N(2\pi)^3} \sum_{\mathbf{R}} \int_{BZ} d\mathbf{k} \frac{\partial \mathcal{A}_n(\mathbf{k})}{\partial t} \\ &= -\frac{e}{(2\pi)^3} \int_{BZ} d\mathbf{k} \frac{\partial \mathcal{A}_n(\mathbf{k})}{\partial t} \end{aligned}$$

# Polarization change

- The polarization change is then

$$\begin{aligned}\Delta \mathbf{P} &= \sum_v \int_0^{t_f} dt \mathbf{j}_v(t) = \frac{-e}{(2\pi)^3} \sum_v \int_{BZ} d\mathbf{k} \int_0^{t_f} dt \frac{\partial \mathcal{A}_v(\mathbf{k})}{\partial t} \\ &= \frac{-e}{(2\pi)^3} \sum_v \int_{BZ} d\mathbf{k} \left[ \mathcal{A}_v(\mathbf{k}, t_f) - \mathcal{A}_v(\mathbf{k}, 0) \right]\end{aligned}$$

# Definition of polarization

- We thus define the electronic contribution to the polarization as

$$\mathbf{P}_{el} = \frac{-e}{(2\pi)^3} \sum_v \int_{BZ} d\mathbf{k} \mathcal{A}_v(\mathbf{k})$$

- and the total polarization as

$$\mathbf{P} = \frac{e}{V} \sum_{\text{ions}} Z_i \mathbf{r}_i - \frac{e}{(2\pi)^3} \sum_v \int_{BZ} d\mathbf{k} \mathcal{A}_v(\mathbf{k})$$

$$\mathbf{P} = \frac{e}{V} \sum_{\text{ions}} Z_i \mathbf{r}_i - \frac{e}{V} \sum_{v\mathbf{k}} \mathcal{A}_v(\mathbf{k})$$

# Berry connection/Wannier functions

- Because

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} w_n(\mathbf{R}, \mathbf{r}) e^{i\mathbf{R} \cdot \mathbf{k}}$$

- we get

$$u_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} w_n(\mathbf{R}, \mathbf{r}) e^{i(\mathbf{R}-\mathbf{r}) \cdot \mathbf{k}}$$

- Therefore

$$\frac{\partial u_{n\mathbf{k}}(\mathbf{r})}{\partial \mathbf{k}} = \frac{-i}{\sqrt{N}} \sum_{\mathbf{R}} \mathbf{r} w_n(\mathbf{R}, \mathbf{r}) e^{i(\mathbf{R}-\mathbf{r}) \cdot \mathbf{k}}$$

# Berry connection I

- We then have 
$$\mathcal{A}_v(\mathbf{k}) = i \int d\mathbf{r} u_{v\mathbf{k}}^*(\mathbf{r}) \frac{\partial u_{v\mathbf{k}}(\mathbf{r})}{\partial \mathbf{k}}$$
$$= \frac{1}{N} \int d\mathbf{r} \sum_{\mathbf{R}, \mathbf{R}'} w_v^*(\mathbf{R}', \mathbf{r}) \mathbf{r} w_v(\mathbf{R}, \mathbf{r}) e^{i(\mathbf{R}-\mathbf{R}') \cdot \mathbf{k}}$$
- Therefore 
$$\sum_{\mathbf{k}} \mathcal{A}_v(\mathbf{k}) = \sum_{\mathbf{k}} i \int d\mathbf{r} u_{v\mathbf{k}}^*(\mathbf{r}) \frac{\partial u_{v\mathbf{k}}(\mathbf{r})}{\partial \mathbf{k}}$$
$$= \frac{1}{N} \int d\mathbf{r} \sum_{\mathbf{R}, \mathbf{R}'} w_v^*(\mathbf{R}', \mathbf{r}) \mathbf{r} w_v(\mathbf{R}, \mathbf{r}) \sum_{\mathbf{k}} e^{i(\mathbf{R}-\mathbf{R}') \cdot \mathbf{k}}$$
$$= \frac{1}{N} \sum_{\mathbf{R}, \mathbf{R}'} \int d\mathbf{r} w_v^*(\mathbf{R}', \mathbf{r}) \mathbf{r} w_v(\mathbf{R}, \mathbf{r}) N \delta_{\mathbf{R}, \mathbf{R}'}$$
$$= \sum_{\mathbf{R}} \int d\mathbf{r} \left| w_n(\mathbf{R}, \mathbf{r}) \right|^2 \mathbf{r}$$

# Total polarization I

- The total polarization is then

$$\begin{aligned}
 \mathbf{P} &= \frac{e}{V} \sum_{\text{ions}} Z_i \mathbf{r}_i - \frac{e}{V} \sum_{\mathbf{R}} \int d\mathbf{r} \left| w_n(\mathbf{r} - \mathbf{R}) \right|^2 \mathbf{r} \\
 &= \frac{e}{V} \sum_{\text{unit cell } j, \mathbf{R}} Z_j (\mathbf{r}_j + \mathbf{R}) - \frac{e}{V} \sum_{\mathbf{R}} \int d\mathbf{r}' \left| w_n(\mathbf{r}') \right|^2 (\mathbf{r}' + \mathbf{R}) \\
 &= \frac{eN}{V} \sum_j Z_j \mathbf{r}_j + \frac{e}{V} \sum_{\mathbf{R}, j} Z_j \mathbf{R} - \frac{e}{V} \sum_{\mathbf{R}} \mathbf{R} \int d\mathbf{r}' \left| w_n(\mathbf{r}') \right|^2 \\
 &\quad - \frac{e}{V} \sum_{\mathbf{R}} \int d\mathbf{r}' \left| w_n(\mathbf{r}') \right|^2 \mathbf{r}' \\
 &= \frac{eN}{V} \sum_{\text{unit cel}} Z_i \mathbf{r} - \frac{e}{V} \sum_{\mathbf{R}} \int d\mathbf{r} \left| w_n(\mathbf{r}) \right|^2 \mathbf{r} \\
 &= \frac{e}{v_c} \sum_{\text{unit cel}} Z_i \mathbf{r} - \frac{e}{v_c} \int d\mathbf{r} \left| w_n(\mathbf{r}) \right|^2 \mathbf{r}
 \end{aligned}$$

# Properties III

- Let us now consider

$$\mathbf{R}^j w_n(\mathbf{r}) = \frac{V}{\sqrt{N} (2\pi)^3} \int_{BZ} d\mathbf{k} \psi_{n\mathbf{k}}(\mathbf{r}) \mathbf{R}^j e^{-i\mathbf{k}\cdot\mathbf{R}}$$

$$= \frac{V}{\sqrt{N} (2\pi)^3} \left( \frac{1}{-i} \right)^j \int_{BZ} d\mathbf{k} \psi_{n\mathbf{k}}(\mathbf{r}) \nabla^j e^{-i\mathbf{k}\cdot\mathbf{R}}$$

$$= - \frac{V}{\sqrt{N} (2\pi)^3} \left( \frac{1}{-i} \right)^j \int_{BZ} d\mathbf{k} e^{-i\mathbf{k}\cdot\mathbf{R}} \nabla^j \psi_{n\mathbf{k}}(\mathbf{r})$$

- This is proportional to the  $R^j$  coefficient in the Fourier expansion of a periodic function of  $\mathbf{k}$ , and it goes to zero for sufficiently large  $R$ .

# Tight binding comparison

- When we did tight binding, we defined

$$\phi_{aj,k}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot (\mathbf{R} + \mathbf{d}_j)} \phi_{aj,\mathbf{R}}(\mathbf{r})$$

- Compare with definition of Wannier function

$$\psi_{nk}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} w_n(\mathbf{R}, \mathbf{r}) e^{i\mathbf{R} \cdot \mathbf{k}}$$

- So that for a Bravais-lattice TB hamiltonian the Wannier function for position  $\mathbf{R}$  is simply the atomic orbital at atom  $\mathbf{R}$ .

# Localization of Wannier functions

- The above arguments suggest that the Wannier function is strongly localized, so that the integral of  $r$  always converges and the definition of polarization always makes sense.

# Changing the phase of the $u$ 's

- If I change the phase of the  $u$ 's such that

$$u_{n\mathbf{k}}(\mathbf{r}) \rightarrow u_{n\mathbf{k}}(\mathbf{r}) e^{i\varphi_n(\mathbf{k})}$$

$$\mathcal{A}_n(\mathbf{k}) \rightarrow i \int_{BZ} u_{n\mathbf{k}}^*(\mathbf{r}) e^{-i\varphi_n(\mathbf{k})} \frac{\partial}{\partial \mathbf{k}} u_{n\mathbf{k}}(\mathbf{r}) e^{i\varphi_n(\mathbf{k})}$$

$$= i \int_{BZ} u_{n\mathbf{k}}^*(\mathbf{r}) \frac{\partial}{\partial \mathbf{k}} u_{n\mathbf{k}}(\mathbf{r}) - \frac{\partial \varphi_n(\mathbf{k})}{\partial \mathbf{k}} \int_{BZ} u_{n\mathbf{k}}^*(\mathbf{r}) u_{n\mathbf{k}}(\mathbf{r})$$

$$= i \int_{BZ} u_{n\mathbf{k}}^*(\mathbf{r}) \frac{\partial}{\partial \mathbf{k}} u_{n\mathbf{k}}(\mathbf{r}) - \frac{\partial \varphi_n(\mathbf{k})}{\partial \mathbf{k}} = \mathcal{A}_n(\mathbf{k}) - \frac{\partial \varphi_n(\mathbf{k})}{\partial \mathbf{k}}$$

# Choosing the phase I

- If I demand that the wavefunction be periodic in  $\mathbf{k}$ :  $\varphi_n(\mathbf{k} + \mathbf{K}) = \varphi_n(\mathbf{k}) + 2\pi M_n(\mathbf{k}, \mathbf{K})$
- where  $M$  is an integer. Then  $M$  cannot depend on  $\mathbf{k}$  because  $\mathbf{k}$  can change continuously:

$$\varphi_n(\mathbf{k} + \mathbf{K}) = \varphi_n(\mathbf{k}) + 2\pi M_n(\mathbf{K})$$

- Thus  $2\pi M_n(\mathbf{K}) = \mathbf{K} \cdot \mathbf{R}_n$
- So  $\varphi_n(\mathbf{k} + \mathbf{K}) = \varphi_n(\mathbf{k}) + \mathbf{K} \cdot \mathbf{R}_n$
- Define

$$\varphi_n(\mathbf{k}) = \theta_n(\mathbf{k}) + \mathbf{k} \cdot \mathbf{R}_n$$

# Choosing the phase II

- Then

$$\begin{aligned}\varphi_n(\mathbf{k} + \mathbf{K}) &= \theta_n(\mathbf{k} + \mathbf{K}) + (\mathbf{k} + \mathbf{K}) \cdot \mathbf{R}_n \\ &= \varphi_n(\mathbf{k}) + \mathbf{K} \cdot \mathbf{R}_n = \theta_n(\mathbf{k}) + (\mathbf{k} + \mathbf{K}) \cdot \mathbf{R}_n\end{aligned}$$

- or

$$\theta_n(\mathbf{k} + \mathbf{K}) = \theta_n(\mathbf{k})$$

- This means that the most general form for the phase is a periodic function plus  $\mathbf{kR}$

# Back to the connection

- For the change of phase  $u_{n\mathbf{k}}(\mathbf{r}) \rightarrow u_{n\mathbf{k}}(\mathbf{r}) e^{i\varphi_n(\mathbf{k})}$

$$\mathcal{A}_n(\mathbf{k}) \rightarrow \mathcal{A}_n(\mathbf{k}) - \frac{\partial \varphi_n(\mathbf{k})}{\partial \mathbf{k}} = \mathcal{A}_n(\mathbf{k}) - \frac{\partial \theta_n(\mathbf{k})}{\partial \mathbf{k}} - \mathbf{R}_n$$

$$\Delta \mathbf{P} = \frac{-e}{(2\pi)^3} \int_{BZ} d\mathbf{k} \frac{\partial \theta_n(\mathbf{k})}{\partial \mathbf{k}} + \frac{-e}{(2\pi)^3} \int_{BZ} d\mathbf{k} \mathbf{R}_n$$

$$= 0 + \frac{-e}{(2\pi)^3} \mathbf{R}_n \frac{(2\pi)^3}{v_c} = \frac{-e \mathbf{R}_n}{v_c}$$

- So we get the quantum of polarization. It means that polarization is defined modulus a quantum.

# Explicit Calculation of the current

- The following slides show an explicit calculation of the polarization current without using the concept of Berry connection from the very beginning.

# Change in polarization

- From Maxwell's equations

$$\nabla \cdot \mathbf{P} = -\rho_b$$

$$\dot{\mathbf{j}}_b = \frac{\partial \mathbf{P}}{\partial t} + \nabla \times \mathbf{M}$$

- Then in a non-magnetic material one can calculate the change in polarization

$$\Delta \mathbf{P} = \int_0^{t_f} \dot{\mathbf{j}}_b dt$$

- Define dimensionless parameter  $\lambda = t/t_f$

$$\Delta \mathbf{P} = t_f \int_0^1 \frac{d\mathbf{P}}{d\lambda} d\lambda = \frac{1}{\dot{\lambda}} \int_0^1 \frac{d\mathbf{P}}{d\lambda} d\lambda$$

# Adiabatic hamiltonian

- Let's assume that we have a crystal hamiltonian in which the potential has a slow time-dependence but does not change the periodicity:

$$H_t = -\frac{\hbar^2 \nabla^2}{2m} + V(\mathbf{r}, \lambda) \quad \lambda = \lambda(t); \quad \frac{\partial}{\partial t} = \frac{\partial}{\partial \lambda} \frac{d\lambda}{dt} = \dot{\lambda} \frac{\partial}{\partial \lambda}$$

- The corresponding snapshot Schrödinger equation is  $H_t \psi(\lambda) = E(\lambda) \psi(\lambda)$
- whose solutions can be written as Bloch functions  $\psi(\lambda) = \psi_{n\mathbf{k}}(\mathbf{r}, \lambda) = u_{n\mathbf{k}}(\mathbf{r}, \lambda) e^{i\mathbf{k} \cdot \mathbf{r}}$
- where the  $\mathbf{k}$ 's are not functions of time because the periodicity is unchanged. In the adiabatic approximation the snapshot solutions are taken as good approximations to the real solutions.

# Current I

For the current, I calculate the velocity for each electron and add over all electrons. This velocity is

$$\mathbf{v}_{n\mathbf{k}}(\lambda) = \frac{1}{m} \langle \psi_{n\mathbf{k}}(\lambda) | \mathbf{p} | \psi_{n\mathbf{k}}(\lambda) \rangle = \frac{\hbar}{m} \langle \psi_{n\mathbf{k}}(\lambda) | -i\mathbf{\nabla} | \psi_{n\mathbf{k}}(\lambda) \rangle$$

- In term of the u's

$$\begin{aligned} \mathbf{v}_{n\mathbf{k}}(\lambda) &= \frac{\hbar}{m} \int d\mathbf{r} u_{n\mathbf{k}}^*(\mathbf{r}, \lambda) e^{-i\mathbf{k}\cdot\mathbf{r}} [-i\mathbf{\nabla}] u_{n\mathbf{k}}(\mathbf{r}, \lambda) e^{i\mathbf{k}\cdot\mathbf{r}} \\ &= \frac{\hbar}{m} \int d\mathbf{r} u_{n\mathbf{k}}^*(\mathbf{r}, \lambda) [-i\mathbf{\nabla} + \mathbf{k}] u_{n\mathbf{k}}(\mathbf{r}, \lambda) \\ &= \frac{1}{\hbar} \int d\mathbf{r} u_{n\mathbf{k}}^*(\mathbf{r}, \lambda) \frac{\partial H_{\mathbf{k}}}{\partial \mathbf{k}} u_{n\mathbf{k}}(\mathbf{r}, \lambda) = \frac{1}{\hbar} \int d\mathbf{r} u_{n\mathbf{k}}^*(\mathbf{r}, \lambda) \left[ \frac{\partial}{\partial \mathbf{k}}, H_{\mathbf{k}} \right] u_{n\mathbf{k}}(\mathbf{r}, \lambda) \end{aligned}$$

# Current II

where  $H_k = \frac{\hbar^2}{2m} (-i\nabla + \mathbf{k})^2 + V(\mathbf{r}, \lambda)$

- is the well-known hamiltonian for the u's.

Therefore, within the adiabatic approximation we get

$$\mathbf{v}_{nk}(\lambda) = \frac{1}{\hbar} \frac{\partial E_{nk}(\lambda)}{\partial \mathbf{k}}$$

- But the integral of this over the BZ is zero (integral of the gradient of a periodic function), and therefore we conclude that for a filled band we have no current within the adiabatic approx. We must incorporate non-adiabatic corrections to get something different from zero.

# Non-adiabatic correction

- Let's assume that  $|u(0)\rangle = |n\mathbf{k}, 0\rangle$
- Then according to Rev. Mod Phys 82 1959 the lowest order relevant correction to adiabaticity is

$$|n\mathbf{k}, \lambda\rangle = |n\mathbf{k}, \lambda\rangle - i\hbar\dot{\lambda} \sum_{n' \neq n} \frac{|n'\mathbf{k}, \lambda\rangle \langle n'\mathbf{k}, \lambda| \frac{\partial}{\partial \lambda} n\mathbf{k}, \lambda\rangle}{E_{n\mathbf{k}}(\lambda) - E_{n'\mathbf{k}}(\lambda)}$$

- Therefore, the average velocity is

$$v_{n\mathbf{k}}(\lambda) = \frac{1}{\hbar} \times \left[ \langle n\mathbf{k}, \lambda | + i\hbar\dot{\lambda} \sum_{n' \neq n} \frac{\langle n'\mathbf{k}, \lambda | \langle \frac{\partial}{\partial t} n\mathbf{k}, \lambda | n'\mathbf{k}, \lambda \rangle}{E_{n\mathbf{k}}(\lambda) - E_{n'\mathbf{k}}(\lambda)} \right] \frac{\partial H}{\partial \mathbf{k}} \left[ |n\mathbf{k}, \lambda\rangle - i\hbar\dot{\lambda} \sum_{n' \neq n} \frac{|n'\mathbf{k}, \lambda\rangle \langle n'\mathbf{k}, \lambda | \frac{\partial}{\partial t} n\mathbf{k}, \lambda\rangle}{E_{n\mathbf{k}}(\lambda) - E_{n'\mathbf{k}}(\lambda)} \right]$$

# Non-adiabatic velocity I

$$\mathbf{v}_{n\mathbf{k}}(\lambda) = \frac{1}{\hbar} \left\langle n\mathbf{k}, \lambda \left| \frac{\partial H_0}{\partial \mathbf{k}} \right| n\mathbf{k}, \lambda \right\rangle - i\dot{\lambda} \sum_{n' \neq n} \frac{\left\langle n\mathbf{k}, \lambda \left| \frac{\partial H}{\partial \mathbf{k}} \right| n'\mathbf{k}, \lambda \right\rangle \left\langle n'\mathbf{k}, \lambda \left| \frac{\partial}{\partial t} n\mathbf{k}, \lambda \right\rangle}{E_{n\mathbf{k}}(\lambda) - E_{n'\mathbf{k}}(\lambda)} +$$

$$\mathbf{v}_{n\mathbf{k}}(\lambda) = \frac{1}{\hbar} \frac{\partial E_n(\mathbf{k}, \lambda)}{\partial \mathbf{k}} - i\dot{\lambda} \sum_{n' \neq n} \frac{\left\langle n\mathbf{k}, \lambda \left| \frac{\partial H}{\partial \mathbf{k}} \right| n'\mathbf{k}, \lambda \right\rangle \left\langle n'\mathbf{k}, \lambda \left| \frac{\partial}{\partial t} n\mathbf{k}, \lambda \right\rangle}{E_{n\mathbf{k}}(\lambda) - E_{n'\mathbf{k}}(\lambda)} + c.c.$$

$$\mathbf{v}_{n\mathbf{k}}(\lambda) = \frac{1}{\hbar} \frac{\partial E_n(\mathbf{k}, \lambda)}{\partial \mathbf{k}} - i\dot{\lambda} \sum_{n' \neq n} \frac{\left\langle n\mathbf{k}, \lambda \left| \frac{\partial H}{\partial \mathbf{k}} \right| n'\mathbf{k}, \lambda \right\rangle \left\langle n'\mathbf{k}, \lambda \left| \frac{\partial}{\partial \lambda} n\mathbf{k}, \lambda \right\rangle}{E_{n\mathbf{k}}(\lambda) - E_{n'\mathbf{k}}(\lambda)} + c.c.$$

- But we showed in Week 12

$$\begin{aligned} E_{n'} \left\langle n\mathbf{k} \left| \frac{\partial}{\partial \mathbf{k}} \right| n'\mathbf{k} \right\rangle &= \left\langle n\mathbf{k} \left| \frac{\partial}{\partial \mathbf{k}} H \right| n'\mathbf{k} \right\rangle = \left\langle n\mathbf{k} \left| \frac{\partial H}{\partial \mathbf{k}} \right| n'\mathbf{k} \right\rangle + \left\langle n\mathbf{k} \left| H \frac{\partial}{\partial \mathbf{k}} \right| n'\mathbf{k} \right\rangle \\ &= \left\langle n\mathbf{k} \left| \frac{\partial H}{\partial \mathbf{k}} \right| n'\mathbf{k} \right\rangle + E_n \left\langle n\mathbf{k} \left| \frac{\partial}{\partial \mathbf{k}} \right| n'\mathbf{k} \right\rangle \end{aligned}$$

- Then

$$(E_{n'} - E_n) \left\langle n\mathbf{k} \left| \frac{\partial}{\partial \mathbf{k}} \right| n'\mathbf{k} \right\rangle = \left\langle n\mathbf{k} \left| \frac{\partial H}{\partial \mathbf{k}} \right| n'\mathbf{k} \right\rangle$$

# Non-adiabatic velocity II

$$\mathbf{v}_{n\mathbf{k}}(\lambda) = \frac{1}{\hbar} \frac{\partial E_n(\mathbf{k})}{\partial \mathbf{k}} + i\dot{\lambda} \sum_{n' \neq n} \langle n\mathbf{k}\lambda | \frac{\partial}{\partial \mathbf{k}} | n'\mathbf{k}\lambda \rangle \langle n'\mathbf{k}, \lambda | \frac{\partial}{\partial \lambda} | n\mathbf{k}, \lambda \rangle + c.c.$$

$$\mathbf{v}_{n\mathbf{k}}(\lambda) = \frac{1}{\hbar} \frac{\partial E_n(\mathbf{k})}{\partial \mathbf{k}} + i\dot{\lambda} \sum_{n'} \langle n\mathbf{k}\lambda | \frac{\partial}{\partial \mathbf{k}} | n'\mathbf{k}\lambda \rangle \langle n'\mathbf{k}, \lambda | \frac{\partial}{\partial \lambda} | n\mathbf{k}, \lambda \rangle + c.c.$$

$$-i\dot{\lambda} \langle n\mathbf{k}\lambda | \frac{\partial}{\partial \mathbf{k}} | n\mathbf{k}\lambda \rangle \langle n\mathbf{k}, \lambda | \frac{\partial}{\partial \lambda} | n\mathbf{k}, \lambda \rangle + c.c.$$

But the sum over  $n'$  gives the identity, so

$$\begin{aligned} \mathbf{v}_{n\mathbf{k}}(\lambda) = & \frac{1}{\hbar} \frac{\partial \varepsilon_n(\mathbf{k})}{\partial \mathbf{k}} + i\dot{\lambda} \left[ \langle n\mathbf{k}\lambda | \frac{\partial}{\partial \mathbf{k}} \frac{\partial}{\partial \lambda} | n\mathbf{k}\lambda \rangle - c.c. \right] \\ & - i\dot{\lambda} \left[ \langle n\mathbf{k}\lambda | \frac{\partial}{\partial \mathbf{k}} | n\mathbf{k}\lambda \rangle \langle n\mathbf{k}, \lambda | \frac{\partial}{\partial \lambda} | n\mathbf{k}, \lambda \rangle - c.c. \right] \end{aligned}$$

In the third term each of the  $\langle \rangle$  is purely imaginary, so their product is real, and it cancels out when we subtract the c.c

# Non-adiabatic velocity III

Then

$$\mathbf{v}_{n\mathbf{k}}(\lambda) = \frac{1}{\hbar} \frac{\partial \varepsilon_n(\mathbf{k})}{\partial \mathbf{k}} + i\dot{\lambda} \left[ \left\langle n\mathbf{k}\lambda \left| \frac{\partial}{\partial \mathbf{k}} \frac{\partial}{\partial \lambda} \right| n\mathbf{k}\lambda \right\rangle - c.c. \right]$$

But

$$\begin{aligned} \frac{\partial}{\partial \lambda} \left( \Psi^* \frac{\partial \Psi}{\partial \mathbf{k}} \right) &= \frac{\partial \Psi^*}{\partial \lambda} \frac{\partial \Psi}{\partial \mathbf{k}} + \Psi^* \frac{\partial^2 \Psi}{\partial \lambda \partial \mathbf{k}} \\ \frac{\partial}{\partial \mathbf{k}} \left( \frac{\partial \Psi^*}{\partial \lambda} \Psi \right) &= \frac{\partial^2 \Psi^*}{\partial \mathbf{k} \partial \lambda} \Psi + \frac{\partial \Psi^*}{\partial \lambda} \frac{\partial \Psi}{\partial \mathbf{k}} \end{aligned}$$

Therefore

$$\Psi^* \frac{\partial^2 \Psi}{\partial \lambda \partial \mathbf{k}} - \frac{\partial^2 \Psi^*}{\partial \mathbf{k} \partial \lambda} \Psi = \frac{\partial}{\partial \lambda} \left( \Psi^* \frac{\partial \Psi}{\partial \mathbf{k}} \right) - \frac{\partial}{\partial \mathbf{k}} \left( \frac{\partial \Psi^*}{\partial \lambda} \Psi \right)$$

$$\left[ \left\langle n\mathbf{k}\lambda \left| \frac{\partial}{\partial \mathbf{k}} \frac{\partial}{\partial \lambda} \right| n\mathbf{k}\lambda \right\rangle - c.c. \right] = \frac{\partial}{\partial \lambda} \left\langle n\mathbf{k}\lambda \left| \frac{\partial}{\partial \mathbf{k}} \right| n\mathbf{k}\lambda \right\rangle - \frac{\partial}{\partial \mathbf{k}} \frac{\partial \left\langle n\mathbf{k}\lambda \right|}{\partial \lambda} \left| n\mathbf{k}\lambda \right\rangle$$

# Total current I

The total current density is an integral of the velocity over the BZ times  $-e$  divided by the volume. The first term then cancels out as in the adiabatic case, and the third term is also the gradient of a periodic function, so that its integral vanishes. Accordingly, only the second term survives, giving

$$\mathbf{j}_n(\lambda) = \frac{1}{V} \frac{V}{(2\pi)^3} (-e) \int_{BZ} d\mathbf{k} \mathbf{v}_{n\mathbf{k}}(\lambda)$$

$$\mathbf{j}_n(\lambda) = -\frac{i\dot{\lambda}e}{(2\pi)^3} \int_{BZ} d\mathbf{k} \frac{\partial}{\partial \lambda} \left\langle n\mathbf{k}\lambda \left| \frac{\partial}{\partial \mathbf{k}} \right| n\mathbf{k}\lambda \right\rangle$$

# Change in polarization

- The change in polarization is then

$$\Delta \mathbf{P} = \frac{1}{\dot{\lambda}} \int_0^1 j(\lambda) d\lambda = -\frac{ie}{(2\pi)^3} \int_{BZ} d\mathbf{k} \left[ \left\langle n\mathbf{k}\lambda \left| \frac{\partial}{\partial \mathbf{k}} \right| n\mathbf{k}\lambda \right\rangle \right]_0^1$$

- This is identical to Eq. 7 in the famous King-Smith/Vanderbilt paper PRB 47 1652

# Berry connection

- But we defined the Berry connection as

$$\mathcal{A}_n(\mathbf{k}) = i \int d\mathbf{r} u_{n\mathbf{k}}^*(\mathbf{r}) \frac{\partial}{\partial \mathbf{k}} u_{n\mathbf{k}}(\mathbf{r})$$

- Therefore

$$\Delta \mathbf{P} = \frac{1}{\dot{\lambda}} \int_0^1 \mathbf{j}(\lambda) d\lambda = -\frac{e}{(2\pi)^3} [\mathcal{A}(\mathbf{k}, 1) - \mathcal{A}(\mathbf{k}, 0)]$$

# Adiabatic correction

- The following slides show a calculation of the lowest-order adiabatic corrections. It was performed to verify that the formulas given in the literature were correct. They appear to be so, but notice that there is a

# Adiabatic perturbation theory I

- Let's start with  $H(t)|\psi(t)\rangle = i\hbar \frac{\partial \psi}{\partial t}$
- Propose an expansion in instantaneous solutions

$$|\psi(t)\rangle = \sum_n e^{-\frac{i}{\hbar} \int_0^t dt' E_n(t')} a_n(t) |n(t)\rangle$$

- Then

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \sum_n e^{-\frac{i}{\hbar} \int_0^t dt' E_n(t')} \times$$

$$\times \left[ E_n(t) a_n(t) |n(t)\rangle + (i\hbar) \dot{a}_n(t) |n(t)\rangle + (i\hbar) a_n(t) |\dot{n}(t)\rangle \right]$$

# Adiabatic perturbation theory II

- Also  $H(t)|\psi(t)\rangle = \sum_n e^{-\frac{i}{\hbar} \int_0^t dt' E_n(t')} a_n(t) E_n(t) |n(t)\rangle$
- Equating both sides:

$$\sum_n \left[ \dot{a}_n(t) |n(t)\rangle + a_n(t) |\dot{n}(t)\rangle \right] e^{-\frac{i}{\hbar} \int_0^t dt' E_n(t')} = 0$$

- Mult. times  $n'$  conj and use orthogonality

$$\dot{a}_{n'}(t) = - \sum_n a_n(t) \langle n'(t) | \dot{n}(t) \rangle e^{-\frac{i}{\hbar} \int_0^t dt' [E_n(t') - E_{n'}(t')]}$$

$$\dot{a}_{n'}(t) \simeq - \langle n'(t) | \dot{n}(t) \rangle e^{-\frac{i}{\hbar} \int_0^t dt' [E_n(t') - E_{n'}(t')]}$$

# Adiabatic perturbation theory II

- We write this as  $\dot{a}_{n'}(t) = g(t) \frac{dF}{dt}$
- with 
$$g(t) = -\langle n'(t) | \dot{n}(t) \rangle; \quad \frac{dF}{dt} = e^{-\frac{i}{\hbar} \int_0^t dt' [E_n(t') - E_{n'}(t')]}$$
- Then 
$$F = i\hbar \frac{e^{-\frac{i}{\hbar} \int_0^t dt' [E_n(t') - E_{n'}(t')]}{E_n(t) - E_{n'}(t)}$$
- I then integrate by parts neglecting small  $dg/dt$ :

$$a_{n'}(t) = -i\hbar \frac{\langle n'(t) | \dot{n}(t) \rangle}{E_n(t) - E_{n'}(t)} e^{-\frac{i}{\hbar} \int_0^t dt' [E_n(t') - E_{n'}(t')]}$$

# Adiabatic perturbation theory III

- So that, to first order

$$\begin{aligned}
 |\psi(t)\rangle &\simeq e^{-\frac{i}{\hbar} \int_0^t dt' E_n(t')} |n(t)\rangle + \sum_{n'} e^{-\frac{i}{\hbar} \int_0^t dt' E_{n'}(t')} a_{n'}(t) |n'(t)\rangle \\
 &= e^{-\frac{i}{\hbar} \int_0^t dt' E_n(t')} |n(t)\rangle \\
 &\quad - i\hbar \sum_{n'} e^{-\frac{i}{\hbar} \int_0^t dt' E_{n'}(t')} \frac{\langle n'(t) | \dot{n}(t) \rangle}{E_n(t) - E_{n'}(t)} e^{-\frac{i}{\hbar} \int_0^t dt' [E_n(t') - E_{n'}(t')]} |n'(t)\rangle \\
 &= e^{-\frac{i}{\hbar} \int_0^t dt' E_n(t')} \left\{ |n(t)\rangle - i\hbar \sum_{n'} \frac{\langle n'(t) | \dot{n}(t) \rangle}{E_n(t) - E_{n'}(t)} |n'(t)\rangle \right\}
 \end{aligned}$$