(21) # Modern theory of polarization (MTP) David's book

All equations are going to be derived for non-interacting Hamiltonian

$H\psi_q = \varepsilon_q \psi_q$, where $\langle \vec{r} | \psi_q \rangle = \psi_q(\vec{r})$ is wave function for a single particle.

All final equations translate to multy particle system with "trivial" modifications, like $u_q(\vec{r}_1) \Rightarrow u_q(\vec{r}_1, \vec{r}_2, \dots \vec{r}_N)$.

However, the MTP is defined only through the wave function and its phase, i.e., Berry phase. No formulation of polarization in terms of response functions exists. Knowing $G(\vec{r}_1, \vec{r}_2)$ seems not sufficient. Probably $\chi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{r}_4)$ not enough either? Open problem!

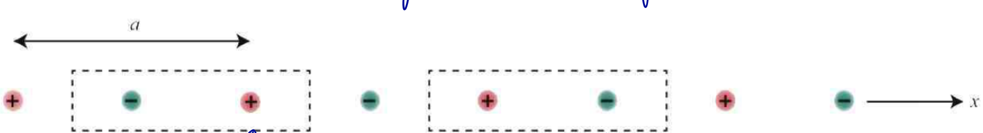
Short intro to problems in defining polarization

Naive expectation: $P_{nr} = \frac{1}{V_{cell}} \int_{cell} d^3r\, \vec{r} \rho(\vec{r})$

Miserably fails:
1) Answer depends on the choice of the unit cell.
2) For solids it is diverging

1) Non-uniqueness of polarization.

Consider NaCl 1D analog but with completely localized charges.
For completely localized charges we can use P_{nr}.



unit cell

$\frac{a}{4}$ $\frac{3a}{4}$ $\frac{a}{4}$ $\frac{3a}{4}$

$P = \frac{e}{V_{cell}}\left(-\frac{a}{4} + \frac{3a}{4}\right) = \frac{e}{V_{cell}} \cdot \frac{a}{2}$ | $P = \frac{e}{V_{cell}}\left(\frac{a}{4} - \frac{3a}{4}\right) = \frac{e}{V_{cell}}\left(-\frac{a}{2}\right)$

Which one is correct? It turns out P is defined up to $P \pm \frac{ea}{V_{cell}}$.
Given a system, we can not define it more precisely than up to $\pm\frac{ea}{V_{cell}}$. David calls such quantity "lattice valued vector", which can take values

$$P = \left(p_0 - \frac{Mea}{V_{cell}}, p_0 - \frac{(M-1)ea}{V_{cell}}, \dots, p_0, p_0 + \frac{Mea}{V_{cell}}, \dots\right)$$

$M \to \infty$

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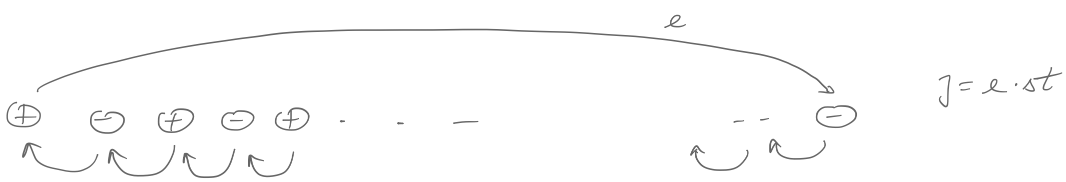
This is not a problem, because in experiment we always care about the change of polarization and not the absolute value.

The change $\frac{dP}{dt} = \vec{J}$ is current that flows through a unit cell

Imagine we take our original system of charges and transport one unit of charge from atom $1 \to 2 \to 3 \to \cdots$



after that operation, the charges of the system are the same, hence the same polarization. But we transported an entire quant of polarization, hence large current. Polarization actually changed from

$$P_1 = \left(p_0 - \frac{Mea}{V_{cell}},\ p_0 - \frac{(M-1)ea}{V_{cell}},\ \cdots,\ p_0,\ p_0 + \frac{Mea}{V_{cell}},\ \cdots\right) \quad M \to \infty$$

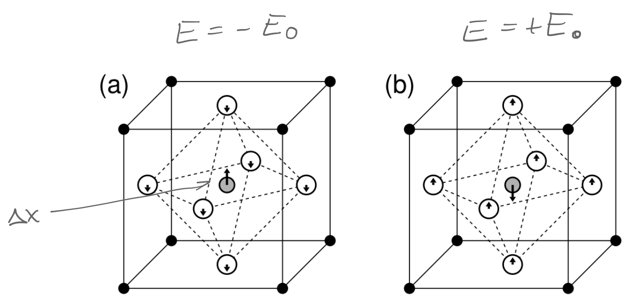
to

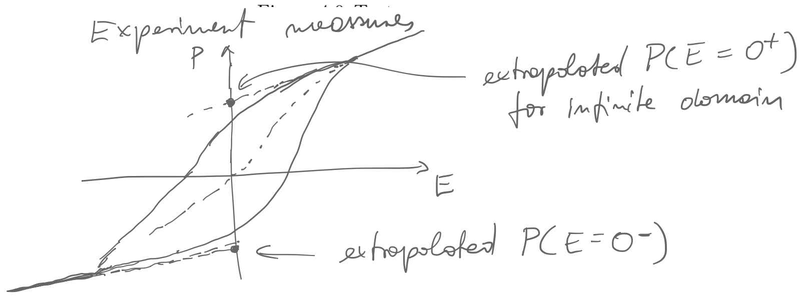
$$P_2 = \left(p_0 + \frac{ea}{V_{cell}} - \frac{Mea}{V_{cell}},\ p_0 + \frac{ea}{V_{cell}} - \frac{(M-1)ea}{V_{cell}},\ \cdots\right) \quad M \to \infty$$

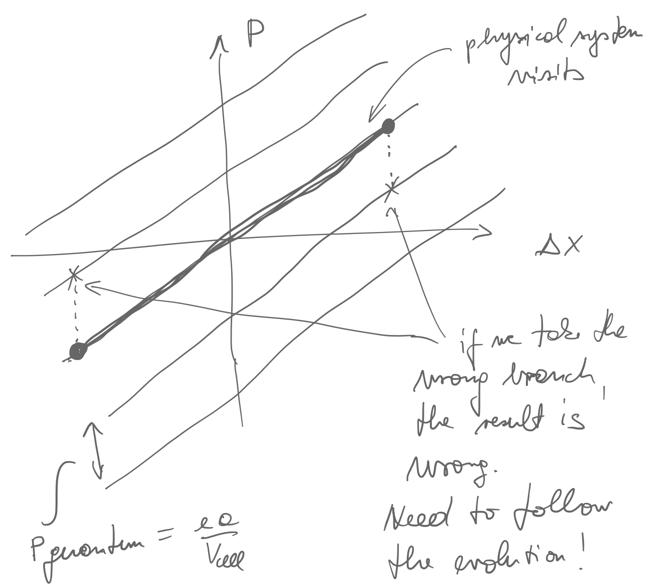
but $P_1 = P_2$ hence we see no change of the system.

Hence to calculate polarization, we need to follow the evolution of the system with external field

Theoretical calculation should give



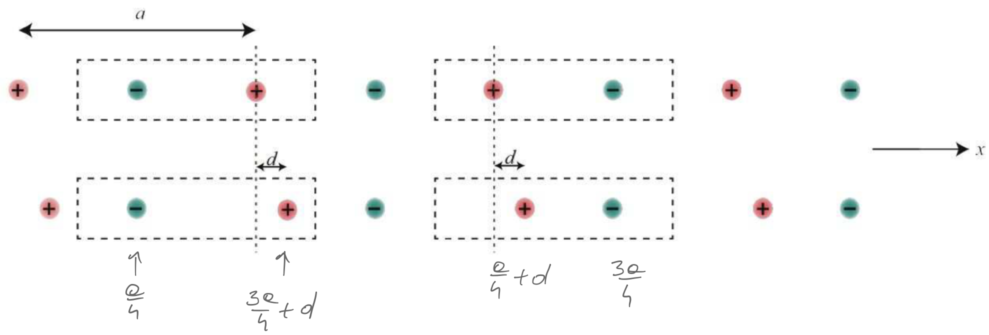




(23)

Now we know that the change with displacement should be measurable.

Let's calculate it



$$P_2 = \frac{e}{V_{cell}}\left(-\frac{a}{4}+\frac{3a}{4}+d\right) \qquad P_2 = \frac{e}{V_{cell}}\left(\frac{a}{4}+d-\frac{3a}{4}\right)$$

$$= P_1 + \frac{e}{V_{cell}}\cdot d \qquad P_2 = P_1 + \frac{e}{V_{cell}}\cdot d$$

$P_2 - P_1 = \frac{e}{V_{cell}}\cdot d$ as expected and is unique.

Why is P not zero when there is no displacement?

If the system has inversion symmetry, then P has to commute with inversion

$$I \cdot P = P$$

If $P = \frac{ea}{V_{cell}}(-M, -M+1, \ldots, -1, 0, 1, \ldots, M-1, M)$ $\quad \lim M \to \infty$

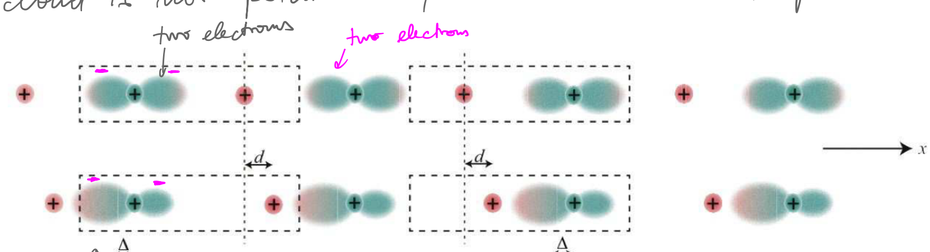
then $I \cdot P = P$

If $P = \frac{ea}{V_{cell}}\left(-M+\frac{1}{2}, -M+\frac{3}{2}, \ldots -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}, \ldots M-\frac{3}{2}, M-\frac{1}{2}\right)$ $\quad \lim M \to \infty$

then $I \cdot P = P$

These are the only two possibilities. Either integer or half-integer quantum.

More realistic system would look like that Fig below, because electronic cloud is not point-like, but it moves and spreads.



Wannier function with center at $\frac{a}{4}-\Delta$.

It turns out that the details of the Wannier function do not matter. Only it's center of mass plays the role of displacement.

If we calculate $\langle r \rangle_W = \int dx\, W^*(x)\, x\, W(x) = \frac{a}{4} - \Delta$

Then: $P_2 = \frac{e}{V_{cell}}\left(\frac{a}{4} - 2\left(\frac{a}{4}-\Delta\right) + \frac{3a}{4} + d\right) = P_1 + \underline{\frac{e}{V_{cell}}(d + 2\Delta)}$

extra change due to movement of Wannier functions.

What if we do not want to construct Wannier functions. Can we compute P?

Yes, there is formula in terms of Bloch states, which can be used:

$$\langle \vec r\rangle = \sum_{m\in \text{band}} \int d^3r\, W_m(\vec r)\cdot \vec r\, W_m(\vec r) = \frac{V_{cell}}{(2\pi)^3}\sum_{m=\text{band}} \int d^3k \left\langle u_{mk}\middle| i\frac{\partial u_{mk}}{\partial \vec k}\right\rangle \qquad (1)$$

$$\underbrace{\psi_{mk}(\vec r)}_{\substack{\text{Bloch w.f.}\\ \text{Solution of S.E.}}} = e^{i\vec k\vec r}\underbrace{u_{mk}(\vec r)}_{\substack{u_{mk}(\vec r+\vec R) = u_{mk}(\vec r)\\ \text{periodic part}}}$$

We will first prove this identity (1), and later introduce more rigorously the polarization operator in Q.M. formulation.

Proof of (1):

Wannier functions for an isolated band $W_m(\vec r-\vec R) = \frac{V_{cell}}{(2\pi)^3}\int_{BZ} d^3k\, e^{-i\vec k\cdot\vec R}\psi_{mk}(\vec r)$

Note also that
$$\int_{BZ} d^3k\, e^{i\vec k(\vec R-\vec R')} = \underbrace{\delta_{\vec R,\vec R'}}_{\text{reciprocal}}\frac{(2\pi)^3}{V_{cell}}$$

$$\underbrace{\sum_{\vec R}}_{\text{reciprocal}} e^{-i(\vec k-\vec k')\vec R} = \delta^3(\vec k-\vec k')\frac{(2\pi)^3}{V_{cell}}$$

Let's check

- $$\langle u_{m\vec k}|u_{m\,\vec k+\vec b}\rangle = \int_{cell} d^3r\, \langle u_{m\vec k}|\vec r\rangle\langle \vec r|u_{m\,\vec k+\vec b}\rangle = \int_{cell} d^3r \left(\psi_{mk}(\vec r)e^{-i\vec k\vec r}\right)^* \left(\psi_{m\,\vec k+\vec b}\, e^{-i(\vec k+\vec b)\vec r}\right)$$
$$= \int_{cell} d^3r\, e^{-i\vec b\cdot\vec r}\psi^*_{mk}(\vec r)\,\psi_{mk}(\vec r)$$

- $$W_m(\vec r-\vec R) = \frac{V_{cell}}{(2\pi)^3}\int_{BZ} d^3k\, e^{-i\vec k\cdot\vec R}\psi_{mk}(\vec r) \Rightarrow \sum_{\vec R} W_m(\vec r-\vec R)\, e^{i\vec k\vec R} = \psi_{mk}(\vec r)$$

- $$\langle u_{m\vec k}|u_{m\,\vec k+\vec b}\rangle = \int_{cell} d^3r\, e^{-i\vec b\cdot\vec r}\sum_{\vec R,\vec R'} \underbrace{e^{-i\vec k\vec R}W^*_m(\vec r-\vec R)\, e^{i\vec k\vec R'}W_m(\vec r-\vec R')}_{\text{depends only on } \vec R'-\vec R\text{, hence we can set } \vec R'=0 \text{ and cancel } \frac{1}{N}.}$$

$$= \int_{cell} d^3r\, e^{-i\vec b\cdot\vec r}\sum_{\vec R} e^{-i\vec k\vec R}W^*_m(\vec r-\vec R)\,W_m(\vec r) = \sum_{\vec R} e^{-i\vec k\cdot\vec R}\underbrace{\int_{cell} d^3r\, W^*_m(\vec r-\vec R)\, e^{-i\vec b\cdot\vec r}\, W_m(\vec r)}_{\langle W_m(\vec R)|\, e^{-i\vec b\vec r}\,|W_m(0)\rangle}$$

- expand both sides for small $\vec b$:

$$\left\langle u_{m\vec k}\middle| u_{m\vec k} + \vec b\cdot\frac{\partial}{\partial\vec k}u_{m\vec k} + \frac{1}{2}\left(\vec b\cdot\frac{\partial^2}{\partial\vec k^2}\right)u_{mk} + \ldots\right\rangle = \sum_{\vec R} e^{-i\vec k\cdot\vec R}\langle W_m(\vec R)|\, 1 - i\vec b\cdot\vec r - \tfrac{1}{2}(\vec b\cdot\vec r)^2 + \ldots\,|W_m(0)\rangle$$

25 Previous equation is valid for any $\vec{b}$, hence

$$\langle u_{n\vec{k}} | u_{n\vec{k}} \rangle = \sum_{\vec{R}} e^{-i\vec{k}\cdot\vec{R}} \langle W_n(\vec{R}) | W_n(0) \rangle = 1$$

$$i \langle u_{n\vec{k}} | \frac{\partial}{\partial \vec{k}} u_{n\vec{k}} \rangle = \sum_{\vec{R}} e^{-i\vec{k}\cdot\vec{R}} \langle W_n(\vec{R}) | \vec{r} | W_n(0) \rangle \Rightarrow \frac{V_{cell}}{(2\pi)^3} \int e^{i\vec{k}\cdot\vec{R}} \langle u_{n\vec{k}} | i \frac{\partial}{\partial \vec{k}} u_{n\vec{k}} \rangle d^3k = \langle W_n(\vec{R}) | \vec{r} | W_n(0) \rangle$$

$$-\langle u_{n\vec{k}} | \frac{\partial^2}{\partial \vec{k}^2} | u_{n\vec{k}} \rangle = \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \langle W_n(\vec{R}) | r^2 | W_n(0) \rangle \Rightarrow -\frac{V_{cell}}{(2\pi)^3} \int e^{i\vec{k}\cdot\vec{R}} \langle u_{n\vec{k}} | \frac{\partial^2}{\partial \vec{k}^2} u_{n\vec{k}} \rangle d^3k = \langle W_n(\vec{R}) | r^2 | W_n(0) \rangle$$

Finally for the home cell $\bar{r} = \langle W_n(R=0) | \vec{r} | W_n(R=0) \rangle = \frac{V_{cell}}{(2\pi)^3} \int d^3k \langle u_{n\vec{k}} | i \frac{\partial}{\partial \vec{k}} u_{n\vec{k}} \rangle$ as promised.

This is well defined only for insulators

$$\bar{r^2} = \langle W_n(0) | r^2 | W_n(0) \rangle = \frac{V_{cell}}{(2\pi)^3} \int d^3k \langle u_{nk} | -\frac{\partial^2}{\partial k^2} | u_{nk} \rangle$$

Fluctuations of the Wannier centers.

We have a recipy to compute P, and we know that only ΔP makes sense, which is:

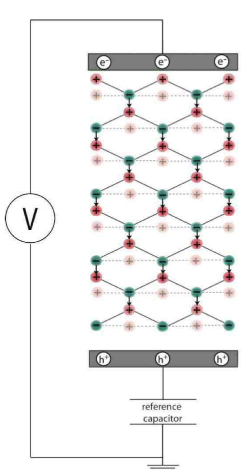
$$\langle r \rangle_{final} - \langle r \rangle_{initial} = \frac{V_{cell}}{(2\pi)^3} \int d^3k \left[\langle u^f_{nk} | i \frac{\partial}{\partial k} u^f_{nk} \rangle - \langle u^i_{nk} | i \frac{\partial}{\partial k} u^i_{nk} \rangle \right]$$

But we do not have real understanding of why P is not uniquely defined and how is this connected to the Berry phase.
How this follows from general laws of Q.M.?

Back to the question of why P is not a simple correlation function.

We expect : $P_W = \frac{1}{V_{cell}} \int_{cell} d^3r \, \vec{r} \rho(\vec{r})$ and for

current we know : $\vec{J}(t) = \frac{1}{V_{cell}} \int_{cell} d^3r \, j(\vec{r}, t)$ where we have in mind slow adiabatic change with time, so that we are always in quasi equilibrium.



When we slowly turn on voltage, the positive ions slowly move to new positions, which allows the current to flow.

Then: $\delta P = J\,\delta t$ should be obeyed

$$\delta P(t) = \frac{1}{V_{cell}}\int d^3r\, \vec{r}\, \frac{\delta \rho}{\delta t}\,\delta t$$

continuity $\frac{\delta \rho}{\delta t} = -\vec{\nabla}\cdot\vec{j}$

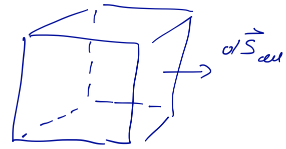
local charge conservation in a unit cell.

$$= -\frac{1}{V_{cell}}\int d^3r\, \vec{r}\,(\vec{\nabla}\cdot\vec{j})\,\delta t$$

$$\vec{\nabla}(\vec{r}\cdot\vec{j}) = \vec{j} + \vec{r}\cdot(\vec{\nabla}\cdot\vec{j})$$

$$\int_{V_{cell}} d^3r\, \vec{\nabla}(\vec{r}\cdot\vec{j}) = \int_{V_{cell}} d^3r\, \vec{j} + \int_{V_{cell}} d^3r\, \vec{r}\cdot(\vec{\nabla}\cdot\vec{j})$$

$$\int_{S_{cell}} \vec{r}\,(\vec{j}\cdot d\vec{S}) = \int_{V_{cell}} d^3r\, \vec{j} + \int_{V_{cell}} d^3r\, \vec{r}\cdot(\vec{\nabla}\cdot\vec{j})$$



$$\int \vec{\nabla} f\, d^3r = \int_{\partial V} f\cdot d\vec{S}$$

$$\delta P(t) = -\frac{1}{V_{cell}}\int_{S_{cell}} \vec{r}\,(\vec{j}\cdot d\vec{S})\,\delta t + \underbrace{\frac{1}{V_{cell}}\int d^3r\, \vec{j}\,\delta t}_{\text{The true current we observe in experiment}}$$

non-zero during adiabatic evolution, because current flows through the sample ($\int_{S_{cell}} \vec{j}\cdot d\vec{S} = 0$ but $\int \vec{r}\,(\vec{j}\cdot d\vec{S})$ is not)

But we need to have $\frac{\delta P}{\delta t} = \frac{1}{V_{cell}}\int d^3r\, \vec{j} = \frac{I}{V_{cell}}$ for E.M. to be valid.
The culprint is the P formula with ill defined $\vec{r}$ in the equation that grows and diverges, is not cell periodic.

In treating isolated molecules, where boundary is insulating, we can use $P = \int d^3r\, \vec{r}\,\rho(\vec{r})$ because the surface term vanishes. But in solids it would have the form $P = \sum_{i\in \text{occupied}} \int d^3r\, \vec{r}\, |\psi_{ik}(\vec{r})|^2 = \sum_{i\in \text{occupied}} \langle \psi_{ik} | \vec{r} | \psi_{ik} \rangle$ which is ill defined for infinite solid.

Conclusion: We need to start from observable we know how to handle, the current $\vec{j}$ and derive $\vec{P}$ to satisfy $I = \frac{dP}{dt}$

$$\vec{j} = \frac{d\vec{P}}{dt} = \frac{d\vec{P}}{d\lambda}\frac{d\lambda}{dt} = \dot{\lambda}\frac{d\vec{P}}{d\lambda} = \dot{\lambda}\frac{e}{V_{cell}}\frac{d\langle\vec{r}\rangle}{d\lambda}$$

Need $\frac{d\langle\vec{r}\rangle}{d\lambda}$!

$$\hat{\vec{v}} = \frac{d}{dt}\, e^{iHt}\,\hat{\vec{r}}\, e^{-iHt} = i\,[H,\hat{\vec{r}}]$$

Heisenberg operators

$$\langle\psi_{n\vec{k}}|\vec{v}|\psi_{m\vec{k}}\rangle = i\left(\langle\psi_{n\vec{k}}|H\vec{r}|\psi_{m\vec{k}}\rangle - \langle\psi_{n\vec{k}}|\vec{r}H|\psi_{m\vec{k}}\rangle\right)$$
$$= i\,(E_n - E_m)\,\langle\psi_{n\vec{k}}|\vec{r}|\psi_{m\vec{k}}\rangle$$

(note $E_n = E_n(\vec{k})$)

Hence: $\underline{\langle\psi_{n\vec{k}}|\vec{r}|\psi_{m\vec{k}}\rangle} = -i\,\underbrace{\frac{\langle\psi_{n\vec{k}}|\vec{v}|\psi_{m\vec{k}}\rangle}{E_n - E_m}}$ valid for $m \neq n$

well defined object because $\vec{v} = \frac{\vec{P}}{m} = \frac{-i}{m}\frac{\partial}{\partial\vec{r}}$

Use Bloch's theorem $\psi_{n\vec{k}}(\vec{r}) = e^{i\vec{k}\vec{r}}u_{n\vec{k}}(\vec{r})$ where $u_{n\vec{k}}$ is cell periodic. Then

$$\langle\psi_{n\vec{k}}|\vec{v}|\psi_{m\vec{k}}\rangle = \int d^3r\, u^*_{n\vec{k}}(\vec{r})\,\underbrace{e^{-i\vec{k}\vec{r}}\,\vec{v}\,e^{i\vec{k}\vec{r}}}_{\equiv\,\vec{v}_{\vec{k}}}\,u_{m\vec{k}}(\vec{r})$$

because it is now cell periodic

also cell periodic

Idea: Replace $\vec{v}_{\vec{k}}$ by $\frac{\partial H_{\vec{k}}}{\partial\vec{k}}$.

Check: $\frac{\partial}{\partial\vec{k}}\left(e^{-i\vec{k}\vec{r}}He^{i\vec{k}\vec{r}}\right) = -i\,e^{-i\vec{k}\cdot\vec{r}}(\vec{r}H - H\vec{r})e^{i\vec{k}\cdot\vec{r}} = i\,e^{-i\vec{k}\vec{r}}[H,\vec{r}]e^{i\vec{k}\vec{r}} = e^{-i\vec{k}\cdot\vec{r}}\,\vec{v}\,e^{i\vec{k}\vec{r}}$

There is no term $\frac{\partial H}{\partial\vec{k}}$ because in this representation $H = \sum_i\frac{(i\nabla_i)^2}{2m} + \sum_i V_{ext}(\vec{r}_i) + \sum_j V_c(\vec{r}_i - \vec{r}_j)$

Note that $e^{-i\vec{k}\vec{r}}He^{i\vec{k}\vec{r}}$ is cell periodic, because

therefore: $\langle\psi_{n\vec{k}}|\vec{v}|\psi_{m\vec{k}}\rangle = \int d^3r\, u^*_{n\vec{k}}(\vec{r})\,\frac{\partial}{\partial\vec{k}}\left(e^{-i\vec{k}\vec{r}}He^{i\vec{k}\vec{r}}\right)u_{m\vec{k}}(\vec{r}) = \langle u_{n\vec{k}}|\frac{\partial}{\partial\vec{k}}\left(e^{-i\vec{k}\vec{r}}He^{i\vec{k}\vec{r}}\right)|u_{m\vec{k}}\rangle$

$$\langle\psi_{n\vec{k}}|\vec{r}|\psi_{m\vec{k}}\rangle = -i\,\frac{1}{E_n - E_m}\langle u_{n\vec{k}}|\frac{\partial}{\partial\vec{k}}\Big(\underbrace{e^{-i\vec{k}\vec{r}}He^{i\vec{k}\vec{r}}}_{H_{\vec{k}}}\Big)|u_{m\vec{k}}\rangle \qquad m \neq n$$

Note $\underline{H_{\vec{k}}|u_{n\vec{k}}\rangle = \varepsilon_{\vec{k}}|u_{n\vec{k}}\rangle}$

For polarization $P = \frac{e}{V_{cell}}\langle\vec{r}\rangle$ we would need $\langle\psi_{n\vec{k}}|\vec{r}|\psi_{n\vec{k}}\rangle$ which we do not have. However, for the change of P ($\frac{dP}{d\lambda}$) only off-diagonal matrix elements contribute, and we can definitely compute $\frac{dP}{d\lambda}$ due to movement of atoms. To do that, we need to repeat perturbation theory, i.e., how to compute the change of the W.F. under adiabatic change: $\frac{\partial}{\partial\lambda}|n(\lambda)\rangle$

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Linear response through ordinary perturbation theory

We have a variable λ, which changes the system adiabatically (like electric field moves atoms in the unit cell, or momentum changes $u_{n\vec{k}}$)

How do eigenstates change as a function of λ?

$|m(\lambda)\rangle$ eigenstates for current value of λ

$$H(\lambda)\,|m(\lambda)\rangle = E_m(\lambda)\,|m(\lambda)\rangle$$

depend on λ smoothly

Examples: • $H_{\vec{k}}\,|u_{n\vec{k}}\rangle = \varepsilon_{\vec{k}}\,|u_{n\vec{k}}\rangle$ smooth dependence on $\vec{k}$ required!

• $H(\lambda)\,|u_{n\vec{k}}(\lambda)\rangle = \varepsilon_{\vec{k}}(\lambda)\,|u_{n\vec{k}}(\lambda)\rangle$ smooth dependence on λ.

First order derivative:

$$\frac{\partial H}{\partial \lambda}|m\rangle + H\left|\frac{\partial m}{\partial \lambda}\right\rangle = \frac{\partial E_m}{\partial \lambda}|m\rangle + E_m\left|\frac{\partial m}{\partial \lambda}\right\rangle$$

$$\frac{\partial E_m}{\partial \lambda} = \frac{\partial}{\partial \lambda}\langle m|H|m\rangle = \langle m|\frac{\partial H}{\partial \lambda}|m\rangle + \underbrace{\langle \tfrac{\partial m}{\partial \lambda}|H|m\rangle + \langle m|H|\tfrac{\partial m}{\partial \lambda}\rangle}$$

$E_m \frac{\partial}{\partial \lambda}\langle m|m\rangle = 0$ because states are kept normalized!

$$(E_m - H)\left|\frac{\partial m}{\partial \lambda}\right\rangle = \underbrace{\left(\frac{\partial H}{\partial \lambda} - \langle m|\frac{\partial H}{\partial \lambda}|m\rangle\right)|m\rangle}$$

$$\underbrace{\sum_n \underbrace{|n\rangle\langle n|}_{=I}\frac{\partial H}{\partial \lambda}|m\rangle - |m\rangle\langle m|\frac{\partial H}{\partial \lambda}|m\rangle}$$

$$\boxed{(E_m - H)\left|\frac{\partial m}{\partial \lambda}\right\rangle = \sum_{n\neq m} |n\rangle\langle n|\frac{\partial H}{\partial \lambda}|m\rangle} \qquad (1)$$

if $n \neq m$ then:

$$\left|\frac{\partial m}{\partial \lambda}\right\rangle = (E_m - H)^{-1}\sum_{n\neq m}|n\rangle\langle n|\frac{\partial H}{\partial \lambda}|m\rangle = \sum_{n\neq m}\frac{1}{E_m - E_n}|n\rangle\langle n|\frac{\partial H}{\partial \lambda}|m\rangle$$

covers Hilbert space orthogonal to $|m\rangle$

but there must be a term also in the direction of $|m\rangle$.
It is an arbitrary value, here designated by iA_m

$$\boxed{\left|\frac{\partial m}{\partial \lambda}\right\rangle = -iA_m|m\rangle + \sum_{n\neq m}\frac{1}{E_m - E_n}|n\rangle\langle n|\frac{\partial H}{\partial \lambda}|m\rangle} \qquad (2)$$

We can check the correctness by plugging it back to Eq (1).

29 check: $(E_m - H)\left[-iA_m|m\rangle + \sum_{m\neq M} \frac{1}{E_M - E_m} |m\rangle\langle m|\frac{\partial H}{\partial \lambda}|M\rangle\right] \stackrel{?}{=} \sum_{m\neq M} |m\rangle\langle m|\frac{\partial H}{\partial \lambda}|M\rangle$

$$-i(E_M - E_M)A_M|M\rangle + \sum_{m\neq M} \frac{E_M - E_m}{E_M - E_m} |m\rangle\langle m|\frac{\partial H}{\partial \lambda}|M\rangle$$

$$\underbrace{-i(E_M-E_M)A_M|M\rangle}_{=0} \qquad \sum_{m\neq M} |m\rangle\langle m|\frac{\partial H}{\partial \lambda}|M\rangle = \checkmark$$

Recall: $$\boxed{\left|\frac{\partial M}{\partial \lambda}\right\rangle = -iA_M|M\rangle + \sum_{m\neq M} \frac{1}{E_M - E_m} |m\rangle\langle m|\frac{\partial H}{\partial \lambda}|M\rangle} \quad (2)$$

check that if H does not depend on λ we get:

$$\left|\frac{\partial M}{\partial \lambda}\right\rangle = -iA_M|M\rangle \Rightarrow |M(\lambda)\rangle = e^{-iA_M\lambda}|M(0)\rangle$$

When H does not depend on λ, we do not expect eigenfunctions to change, hence $A_M \in$ Real, change of "irrelevant" phase. Most often this term is dropped because of "irrelevant phase".

But note that this is a Berry phase, because multiplying by $\langle M|$ we get:

$$\left\langle M\middle|\frac{\partial M}{\partial \lambda}\right\rangle = -iA_M$$

For now we will avoid this term, and write:

$$\boxed{\hat{Q}_M\left|\frac{\partial M}{\partial \lambda}\right\rangle = \sum_{m\neq M} \frac{1}{E_M - E_m} |m\rangle\langle m|\frac{\partial H}{\partial \lambda}|M\rangle} \quad (3)$$

where $\hat{Q}_M = 1 - |M\rangle\langle M|$ is projector to the rest of the Hilbert space.

How do observables change with λ? $\langle M|O|M\rangle$?

We have in mind an operator O that does not depend on λ explicitely: (like $\vec{r}, \vec{p}, \cdots$)

The positions of nuclei change $R_i(t)$, but $\vec{p} = -i\vec{\nabla}$ does not change it's form.

H is changing because it depends on nuclei $R(t)$.

$$\frac{\partial}{\partial \lambda}\langle M|O|M\rangle = \left\langle\frac{\partial M}{\partial \lambda}\middle|O\middle|M\right\rangle + \left\langle M\middle|O\middle|\frac{\partial M}{\partial \lambda}\right\rangle$$

$\hat{O}$ hermitian, then $\left\langle\frac{\partial M}{\partial \lambda}\middle|O\middle|M\right\rangle^* = \left\langle M\middle|O^\dagger\middle|\frac{\partial M}{\partial \lambda}\right\rangle = \left\langle M\middle|O\middle|\frac{\partial M}{\partial \lambda}\right\rangle$

and $$\frac{\partial}{\partial \lambda}\langle M|O|M\rangle = 2\,\mathrm{Re}\left(\left\langle\frac{\partial M}{\partial \lambda}\middle|O\middle|M\right\rangle\right)$$

(30)

We can also insert identity I

$$2\,\mathrm{Re}\left(\left\langle\frac{\partial m}{\partial\lambda}\right| I\, O \left| m\right\rangle\right) = 2\,\mathrm{Re}\Big(\sum_{m\neq m}\left\langle\frac{\partial m}{\partial\lambda}\right|m\rangle\langle m|O|m\rangle + \underbrace{\underbrace{\underbrace{\left\langle\frac{\partial m}{\partial\lambda}\right|m\rangle}_{i A_m}\underbrace{\langle m|O|m\rangle}_{\in \text{Real}}}_{\in Ym}}_{Ym \text{ can be dropped}}\Big)$$

We got:

$$\boxed{\frac{\partial}{\partial\lambda}\langle m|O|m\rangle = 2\,\mathrm{Re}\left(\left\langle\frac{\partial m}{\partial\lambda}\right| Q_m\, O\left|m\right\rangle\right)} \quad (4)$$

Next if $|m\rangle$ is an occupied state, we want to replace Q_m by more convenient

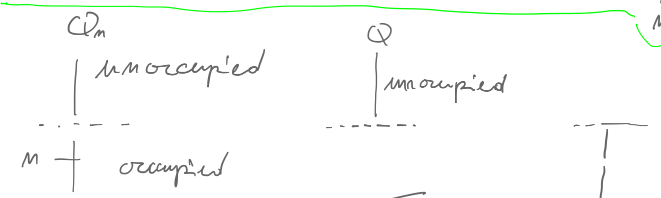
$$Q = \sum_{m\in\text{unoccupied}} |m\rangle\langle m| = 1 - \sum_{m\in\text{occupied}} |m\rangle\langle m|$$

which is independent of m.

$$\boxed{\sum_{m\in occ}\frac{\partial}{\partial\lambda}\langle m|O|m\rangle = \sum_{m\in occ} 2\,\mathrm{Re}\left(\left\langle\frac{\partial m}{\partial\lambda}\right| Q\, O\left|m\right\rangle\right)} \quad (5)$$

We will prove that the difference $(4)-(5)$ vanishes when summing over all occupied states.

$$X_m = \mathrm{Re}\left(\left\langle\frac{\partial m}{\partial\lambda}\right|(Q_m - Q)\,O\left|m\right\rangle\right) = \mathrm{Re}\Big(\sum_{\substack{m\neq m\\ m\in occ}}\left\langle\frac{\partial m}{\partial\lambda}\right|m\rangle\langle m|O|m\rangle\Big) = \sum_{\substack{m\neq m\\ m\in occ}}\Big\{\left\langle\frac{\partial m}{\partial\lambda}\right|m\rangle\langle m|O|m\rangle + \left\langle m\left|\frac{\partial m}{\partial\lambda}\right.\right\rangle\langle m|O|m\rangle\Big\}$$



$$Q_m - Q = \sum_{\substack{m'\neq m\\ m'\in\text{occupied}}} |m\rangle\langle m|$$

$Q_m - Q$

Then $\frac{\partial}{\partial\lambda}\langle m|m\rangle = 0$ therefore

$$\left\langle\frac{\partial m}{\partial\lambda}\right|m\rangle + \left\langle m\left|\frac{\partial m}{\partial\lambda}\right.\right\rangle = 0$$

$$X_m = \sum_{\substack{m\neq m\\ m\in occ}} -\left\langle m\left|\frac{\partial m}{\partial\lambda}\right.\right\rangle\langle m|O|m\rangle + \left\langle m\left|\frac{\partial m}{\partial\lambda}\right.\right\rangle\langle m|O|m\rangle$$

$$\text{If}\quad \sum_{m\in occ} X_m = \sum_{\substack{m,m\in occ\\ m\neq m}} \langle m|O|m\rangle\left\langle m\left|\frac{\partial m}{\partial\lambda}\right.\right\rangle - \langle m|O|m\rangle\left\langle m\left|\frac{\partial m}{\partial\lambda}\right.\right\rangle = 0$$

$m \leftrightarrow m$ dummy variables

(31) Polarization derivation (continuation)

We derived before:

$$\langle \psi_{n\vec k}|\vec r|\psi_{m\vec k}\rangle = -i\,\frac{1}{E_n-E_m}\langle u_{n\vec k}|\frac{\partial}{\partial \vec k}\big(\underbrace{e^{-i\vec k\vec r}\,H\,e^{i\vec k\vec r}}_{H_{\vec k}}\big)|u_{m\vec k}\rangle \qquad n\neq m$$

Note $H_k|u_{nk}\rangle = \varepsilon_k|u_{nk}\rangle$

Multiply by $|u_{n\vec k}\rangle$ and sum over n:

$$\sum_{n\neq m}|u_{n\vec k}\rangle\langle u_{n\vec k}|\underbrace{e^{-i\vec k\vec r}\,\vec r\,e^{i\vec k\vec r}}_{\vec r}|u_{m\vec k}\rangle = -i\sum_{n\neq m}\frac{1}{E_n-E_m}|u_{n\vec k}\rangle\langle u_{n\vec k}|\frac{\partial}{\partial\vec k}H_{\vec k}|u_{m\vec k}\rangle$$

$$\|$$

We derived by perturbation theory

$$\boxed{\hat Q_m|\frac{\partial m}{\partial\lambda}\rangle = \sum_{n,\,n\neq m}\frac{1}{E_m-E_n}|n\rangle\langle n|\frac{\partial H}{\partial\lambda}|m\rangle} \qquad (3)$$

identify $|n\rangle = |u_{n\vec k}\rangle$
$\lambda = \vec k$

Then:

$$\langle u_{n\vec k}|\ \Big/\ \sum_{n\neq m}|u_{nk}\rangle\langle u_{n\vec k}|\vec r|u_{m\vec k}\rangle = +i\,\hat Q_m|\frac{\partial u_{m\vec k}}{\partial\vec k}\rangle$$

$$\langle u_{n\vec k}|\vec r|u_{m\vec k}\rangle = +i\langle u_{n\vec k}|\hat Q_m|\frac{\partial u_{m\vec k}}{\partial\vec k}\rangle$$ valid for any $u_{n\vec k}\neq u_{m\vec k}$

Then: $\hat Q_m\,\vec r\,|u_{m\vec k}\rangle = +i\,\hat Q_m|\frac{\partial u_{m\vec k}}{\partial\vec k}\rangle$

hence it looks like we can replace $\vec r \to i\frac{\partial}{\partial\vec k}$ in matrix element of $|u_{\vec k}\rangle$

Just like $\vec k = -i\frac{\partial}{\partial\vec r}$.

Matrix elements of $\vec r$ operator are: $\langle u_{n\vec k}|\vec r|u_{m\vec k}\rangle = \langle u_{n\vec k}|(i\frac{\partial}{\partial\vec k})|u_{m\vec k}\rangle$ as long as $n\neq m$!

We previously derived:

$$\boxed{\sum_{m\in occ}\frac{\partial}{\partial\lambda}\langle m|O|m\rangle = \sum_{m\in occ}2\,\mathrm{Re}\left(\langle\frac{\partial m}{\partial\lambda}|Q_m O|m\rangle\right)} \qquad (5)$$

$m\in$ occup — unoccupied — occupied

To calculate the change of $\frac{\partial\langle O\rangle}{\partial\lambda}$ for occupied states we need matrix elements of O only between occupied and unoccupied states, i.e.,

$\frac{\partial\langle\vec r\rangle}{\partial\lambda}$ needs only matrix elements: $\langle u_{n\vec k}|\vec r|u_{m\vec k}\rangle$ hence $n\neq m$!

unoccupied — occupied

which is simply given by: $\underline{\vec r = (i\frac{\partial}{\partial\vec k})}$

(32)

Repeat: $$\boxed{\sum_{\underbrace{m}_{m\in\text{occup}}\in occ}\frac{\partial}{\partial\lambda}\langle m|O|m\rangle=\sum_{m\in occ}2\,\mathrm{Re}\left(\langle\frac{\partial m}{\partial\lambda}|\underbrace{Q}_{\text{unoccupied}}\,\underbrace{O}_{\text{occupied}}|m\rangle\right)} \quad (5)$$

Next:
$$\boxed{\begin{aligned}&\text{Insert}\quad |m\rangle\to|u_{m\vec{k}}\rangle \qquad \text{and } O=-i\frac{\partial}{\partial\vec{k}}\\ &\sum_m \to \frac{V_{cell}}{(2\pi)^3}\int d^3k\sum_m\end{aligned}}$$

$$\frac{\partial}{\partial\lambda}\langle\vec{r}\rangle\equiv\underbrace{\frac{V_{cell}}{(2\pi)^3}\int d^3k\sum_{m\in occ}}_{\text{sum over all states in the crystal}}\frac{\partial}{\partial\lambda}\langle u_{m\vec{k}}|\vec{r}|u_{m\vec{k}}\rangle=\underbrace{\frac{V_{cell}}{(2\pi)^3}\int d^3k\sum_{m\in occup}}_{\text{all states of e crystal}}2\,\mathrm{Re}\left(\langle\frac{\partial u_{m\vec{k}}}{\partial\lambda}|Q\,(i)\frac{\partial}{\partial\vec{k}}|u_{m\vec{k}}\rangle\right)$$

Finally:

$$\frac{d}{d\lambda}P=\frac{e}{V_{cell}}\frac{\partial}{\partial\lambda}\langle\vec{r}\rangle=\frac{e}{(2\pi)^3}\sum_{m\in occ}\int_{BZ}d^3k\;2\,\mathrm{Im}\langle\frac{\partial u_{m\vec{k}}}{\partial\lambda}|Q\frac{\partial}{\partial\vec{k}}|u_{m\vec{k}}\rangle$$

We want to drop $Q=1-P$. We will show that $\langle\ldots|P|\ldots\rangle$ is purely real, hence Q can be dropped.

$$\sum_{m\in occ}\langle\frac{\partial u_{m\vec{k}}}{\partial\lambda}|P\frac{\partial}{\partial\vec{k}}|u_{m\vec{k}}\rangle=\sum_{\substack{m\in occ\\ n\in occ}}\underbrace{\underbrace{\langle\frac{\partial u_{m\vec{k}}}{\partial\lambda}|u_{n\vec{k}}\rangle}_{a}\underbrace{\langle u_{n\vec{k}}|\frac{\partial u_{m\vec{k}}}{\partial\vec{k}}\rangle}_{a^*}}_{|a|^2}\in\text{Real}.$$

Finally:

$$\frac{dP}{d\lambda}=\frac{e}{(2\pi)^3}\sum_{m\in occ}\int_{BZ}d^3k\;2\,\mathrm{Im}\langle\frac{\partial u_{m\vec{k}}}{\partial\lambda}|\frac{\partial u_{m\vec{k}}}{\partial\vec{k}}\rangle$$

Next we want to compute P for each state of the crystal, i.e., we need a two point formula for change of $\Delta P=P_{final}-P_{initial}$. Formally we just write $\Delta P=\int_i^f\frac{dP}{d\lambda}d\lambda=\int_0^1\frac{dP}{d\lambda}d\lambda$ hence:

$$\Delta P=\int_0^1\frac{dP}{d\lambda}d\lambda=\frac{2e}{(2\pi)^3}\sum_{m\in occ}\int_0^1 d\lambda\int_{BZ}d^3k\;\mathrm{Im}\langle\frac{\partial u_{m\vec{k}}}{\partial\lambda}|\frac{\partial u_{m\vec{k}}}{\partial\vec{k}}\rangle$$

(33) Lets see what this means for 1D crystal like we discussed in the intro:

$$\Delta P = \frac{2e}{2\pi} \sum_{m \in occ} \underbrace{\int_0^1 d\lambda \int_0^{2\pi/a} dz}_{\text{2D space}} \, \mathrm{Im} \left\langle \frac{\partial u_{mz}}{\partial \lambda} \middle| \frac{\partial u_{mz}}{\partial z} \right\rangle$$

Define a vector quantity
$$\vec{A} \equiv \begin{pmatrix} A_m^{(\lambda)} \\ A_m^{(z)} \\ 0 \end{pmatrix} = \begin{pmatrix} i \left\langle u_{mz} \middle| \frac{\partial u_{mz}}{\partial \lambda} \right\rangle \\ i \left\langle u_{mz} \middle| \frac{\partial u_{mz}}{\partial z} \right\rangle \\ 0 \end{pmatrix}$$

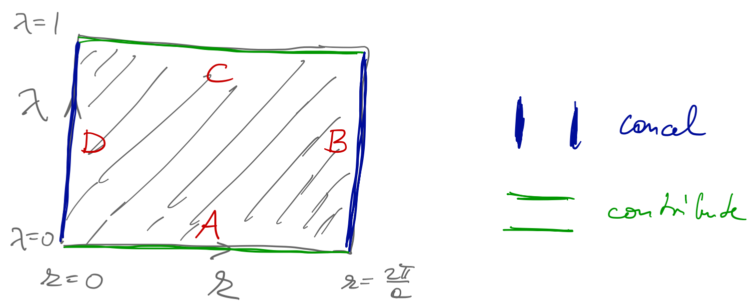
Then

$$\left(\vec{\nabla} \times \vec{A}\right)_3 = \frac{\partial}{\partial \lambda} A_m^{(z)} - \frac{\partial}{\partial z} A_m^{(\lambda)} = i \left\langle \frac{\partial u_{mz}}{\partial \lambda} \middle| \frac{\partial u_{mz}}{\partial z} \right\rangle + \cancel{i \left\langle u_{mz} \middle| \frac{\partial^2}{\partial \lambda \partial z} u_{mz} \right\rangle}$$
$$- i \left\langle \frac{\partial}{\partial z} u_{mz} \middle| \frac{\partial u_{mz}}{\partial \lambda} \right\rangle - \cancel{i \left\langle u_{mz} \middle| \frac{\partial^2}{\partial z \partial \lambda} u_{mz} \right\rangle}$$
$$= i \left(\left\langle \frac{\partial u_{mz}}{\partial \lambda} \middle| \frac{\partial u_{mz}}{\partial z} \right\rangle - \left\langle \frac{\partial u_{mz}}{\partial \lambda} \middle| \frac{\partial}{\partial z} u_{mz} \right\rangle^* \right)$$
$$= -2 \, \mathrm{Im} \left(\left\langle \frac{\partial u_{mz}}{\partial \lambda} \middle| \frac{\partial u_{mz}}{\partial z} \right\rangle \right)$$

Stokes theorem:
$$\int_{\text{shape}} dS \left(\vec{\nabla} \times \vec{A}\right) = \int_{\partial \text{shape}} d\vec{l} \cdot \vec{A}$$

Here $dS = d\lambda \cdot dz$

Define 2D space



$$-\Delta P \cdot \left(\frac{2\pi}{e}\right) = \int \vec{\nabla} \times \vec{A} \, d\lambda \, dz = \underbrace{\int_0^{2\pi/a} \left[\vec{A}(\lambda=0, z)\right]_z dz}_{A} + \underbrace{\int_0^1 d\lambda \left[\vec{A}(\lambda, z=\tfrac{2\pi}{a})\right]_\lambda}_{B} + \underbrace{\int_{2\pi/a}^0 \left[\vec{A}(\lambda=1, z)\right]_z dz}_{C} + \underbrace{\int_1^0 d\lambda \left[\vec{A}(\lambda, z=0)\right]_\lambda}_{D}$$

$\Delta P = -\frac{e}{2\pi} \cdot X$

$\Delta P \left(\frac{2\pi}{e}\right)$

$$\int_0^{2\pi/a} \left[\underbrace{A^{(z)}(\lambda=0)}_{A} - \underbrace{A^{(z)}(\lambda=1)}_{C}\right] dz + \int_0^1 \left[\underbrace{A^{(\lambda)}(z=\tfrac{2\pi}{a})}_{B} - \underbrace{A^{(\lambda)}(z=0)}_{D}\right] d\lambda$$

Crucial point $u_{mz}\big|_{z=0} = u_{mz}\big|_{z=\frac{2\pi}{a}}$ because this is the same point.

Hence B and D segments cancel
$$\int_0^1 \left(\left\langle u_m(z=\tfrac{2\pi}{a}) \middle| \tfrac{\partial}{\partial \lambda} u_m(z=\tfrac{2\pi}{a}) \right\rangle - \left\langle u_m(z=0) \middle| \tfrac{\partial}{\partial \lambda} u_m(z=0) \right\rangle \right) d\lambda = 0$$

(33) Then $\Delta P = -\frac{e}{2\pi}\sum_{n \in occ}\int_0^{2\pi/a} dk\,[A^{(k)}(\lambda=1) - A^{(k)}(\lambda=0)] = -\frac{ei}{2\pi}\sum_{n\in occ}\int_0^{2\pi/a} dk\left[\langle u_{nk}|\frac{\partial u_{nk}}{\partial k}\rangle\Big|_{\lambda=1} - \langle u_{nk}|\frac{\partial u_{nk}}{\partial k}\rangle\Big|_{\lambda=0}\right]$

Important: We need to substract value at $\lambda=1$ and $\lambda=0$. Hence P is a property of the state (up to a quantum).

Finally we can generalized this to 3D (straighforward) to get:

$$\Delta P^\alpha = -\frac{e}{(2\pi)^3}\sum_{n\in occ}\int_{BZ} d^3k\,(i)\left[\langle u_{n\vec k}|\frac{\partial u_{n\vec k}}{\partial k_\alpha}\rangle\Big|_{\lambda=1} - \langle u_{n\vec k}|\frac{\partial u_{n\vec k}}{\partial k_\alpha}\rangle\Big|_{\lambda=0}\right] = -\frac{e}{(2\pi)^3}\int d^2k_\beta \underbrace{\sum_{n\in occ}\Phi_n^\alpha(1,k_\beta) - \Phi_n^\alpha(0,k_\beta)}_{\boxed{P \propto \text{Berry phase}}}$$

Here we introduce Berry connection: $\vec A_{n\vec k} = i\langle u_{n\vec k}|\frac{\partial u_{n\vec k}}{\partial \vec k}\rangle$

Berry phase: $\Phi_n^\alpha(\lambda, k_\beta) = \oint A^\alpha_{n\vec k}\, dk_\alpha$

Berry curvature: $\Omega_n^{(\lambda,\alpha)} = -2\,\mathrm{Im}\langle \frac{\partial u_{n\vec k}}{\partial \lambda}|\frac{\partial u_{n\vec k}}{\partial k_\alpha}\rangle$

Some of these quantities are not gauge invariant $\Rightarrow$ P is lattice vector quantity (defined up to quantum of $P = \frac{e \cdot a}{V_{cell}}$)

Let's redefine $\tilde u_{n\vec k}(\vec r) = e^{-i\beta(\vec k)} u_{n\vec k}(\vec r)$

$e^{-i\beta(\vec k)}$ periodic function of $\vec k$ in BZ, hence $\beta(\vec k=0) - \beta(\vec k=(\pi,\pi,\pi)) = 2\pi m$

$$\tilde A^\alpha_{n\vec k} = i\langle u_{n\vec k}\, e^{i\beta(\vec k)}\left[\frac{\partial}{\partial k_\alpha}\right] e^{-i\beta(\vec k)}|u_{n\vec k}\rangle$$

$$= i\langle u_{n\vec k}\, e^{i\beta(\vec k)}\, e^{-i\beta(\vec k)}\left[-i\frac{d\beta}{dk_\alpha} + \frac{\partial}{\partial k_\alpha}\right]|u_{n\vec k}\rangle = \frac{d\beta}{dk_\alpha} + A^\alpha_{n\vec k}$$

Conclusion: $\vec A_{nk}$ is not gauge invariant (like vector potential $\vec A$ for B field ($\vec B = \vec\nabla\times\vec A$))

What about Berry phase?

$$\tilde\Phi_n^\alpha = \int_0^{2\pi/a} dk_\alpha\left(\frac{d\beta}{dk_\alpha} + A^\alpha_{n\vec k}\right) = \Phi_n^\alpha + \underbrace{[\beta(\tfrac{2\pi}{a}) - \beta(0)]}_{2\pi m \text{ with } m \text{ integer}}$$

Conclusion: Berry phase unique up to $2\pi m$ quantum.

If $\Phi_n^\alpha \Rightarrow \Phi_n^\alpha + 2\pi m$ then $\Delta P^\alpha \Rightarrow \Delta P^\alpha - \frac{e}{(2\pi)^3}\left(\frac{2\pi}{a_\beta}\frac{2\pi}{a_\gamma}\right)2\pi m = \Delta P^\alpha - \underbrace{\boxed{\frac{e\, a_\alpha}{V_{cell}}}}_{P \text{ quantum}} \cdot m$