Polarization in band theory

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This article is a reading note of the relevant chapters in Berry Phases in Electronic Structure Theory by David Vanderbilt.

1 Ill-definedness of $\boldsymbol{P}$ using $\rho(\boldsymbol{r})$

A tempting definition of the polarization vector is

$$\boldsymbol{P}_{\text{dip}} = \frac{1}{V_{\text{u.c.}}} \int_{\text{u.c.}} \boldsymbol{r}\rho(\boldsymbol{r})\,\mathrm{d}^d\boldsymbol{r}\,, \tag{1}$$

where $\rho(\boldsymbol{r})$ includes the charge distribution of both electrons and atoms. Despite its clear physical meaning of "total dipole moment", this definition depends on the choice of the primitive unit cell. To see why, note that if we do an infinitesimal change of $\boldsymbol{P}$, then according to the charge conservation equation, which may be seen as a constraint on the variance, we have

$$\begin{aligned}
\delta\boldsymbol{P}_{\text{dip}} &= \frac{1}{V_{\text{u.c.}}} \int_{\text{u.c.}} \boldsymbol{r}\,\delta\rho\,(\boldsymbol{r})\,\mathrm{d}^d\boldsymbol{r} \\
&= \frac{1}{V_{\text{u.c.}}} \int_{\text{u.c.}} \boldsymbol{r}(-\,\delta t\,\boldsymbol{\nabla}\cdot\boldsymbol{j})\,\mathrm{d}^d\boldsymbol{r} \\
&= -\frac{\delta t}{V_{\text{u.c.}}} \int_{\partial(\text{u.c.})} \boldsymbol{r}(\mathrm{d}\boldsymbol{S}\cdot\boldsymbol{j}) + \frac{\delta t}{V_{\text{u.c.}}} \int_{\text{u.c.}} \boldsymbol{j}\,\mathrm{d}^d\boldsymbol{r}\,.
\end{aligned} \tag{2}$$

The last term is the average current, which does have a clear definition:

$$\boldsymbol{J}(t) = \frac{1}{V_{\text{u.c.}}} \int_{\text{u.c.}} \boldsymbol{j}(\boldsymbol{r},t)\,\mathrm{d}^d\boldsymbol{r}\,, \tag{3}$$

which is *not* dependent to the spatial position of the primitive unit cell, since at the ground state, $\rho(\boldsymbol{r})$ is strictly periodic: the atomic part is of course periodic, and the electronic part $-e\sum_{n,\boldsymbol{k}}|\psi_{n\boldsymbol{k}}|^2$, since $|\psi_{n\boldsymbol{k}}|^2 = |u_{n\boldsymbol{k}}|^2$, the latter being periodic, is also periodic. So we find the variance of $\boldsymbol{P}_{\text{dip}}$ equals to one term that is not dependent to the primitive unit cell and another term that is highly dependent to the surface of the primitive unit cell. On the other hand, from physical intuition we expect to see

$$\delta\boldsymbol{P}(t) = \boldsymbol{J}\,\delta t\,. \tag{4}$$

Thus $\boldsymbol{P}_{\text{dip}}$ can't be a good definition of $\boldsymbol{P}$.

One way to make up for the loss is to average $\boldsymbol{P}_{\text{dip}}$ over possible positions of the primitive unit cell. This however gives a constantly vanishing value, since now

$$\bar{\boldsymbol{P}}_{\text{dip}} \propto \int_{\text{u.c.}} \mathrm{d}^d\boldsymbol{r}' \int_{\text{u.c.}} \boldsymbol{r}\rho(\boldsymbol{r}-\boldsymbol{r}')\,\mathrm{d}^d\boldsymbol{r}\,,$$

where instead of moving the primitive unit cell, we equivalently move the charge distribution. But then due to charge neutrality, we find $\int \mathrm{d}^d\boldsymbol{r}'\,\rho(\boldsymbol{r}-\boldsymbol{r}') = 0$, so the whole equation vanishes.

We may also want to try to define $\boldsymbol{P}$ for a supercell, possibly the crystal itself, and if the surface-dependent term vanishes, we now at least have a macroscopic definition of $\boldsymbol{P}$. But then note that $\boldsymbol{r} \sim L$ while $\mathrm{d}\boldsymbol{S} \sim L^2$, and $1/V \sim 1/L^3$, so this doesn't seem to be possible for a generic crystal.

2 A dynamic definition

An alternative way to define $\boldsymbol{P}$ is to integrate (4). That's to say, we first need an expression of $\partial_\lambda\boldsymbol{P}$.

2.1 Review of some quantum mechanic results

Before doing that let's show some general formalism in quantum mechanics. Suppose we have Hamiltonian $H(\lambda)$, and thus

$$\partial_\lambda \langle O\rangle_n = \langle \partial_\lambda n|O|n\rangle + \langle n|O|\partial_\lambda n\rangle = 2\,\mathrm{Re}\,\langle n|O|\partial_\lambda n\rangle = 2\,\mathrm{Re}\,\langle \partial_\lambda n|O|n\rangle\,, \tag{5}$$

and it can be proved that we have the following Sternheimer equation

$$|\partial_\lambda n\rangle = -\mathrm{i}A_n\,|n\rangle + \sum_{m\neq n}\frac{|m\rangle\langle m|}{E_n - E_m}\partial_\lambda H\,|n\rangle\,, \tag{6}$$

where

$$A_n = \mathrm{i}\,\langle n|\partial_\lambda n\rangle \tag{7}$$

is the Berry connection, the integral of which is the Berry phase. Note that the only $|n\rangle$ component of $|\partial_\lambda n\rangle$ is the $-\mathrm{i}A_n$ term, and therefore from the norm conservation condition, we find that A_n is always real.

We define

$$T_n = \sum_{m\neq n}\frac{|m\rangle\langle m|}{E_n - E_m}. \tag{8}$$

Again, since the only $|n\rangle$ component in $|\partial_\lambda n\rangle$ is the Berry phase term, we have

$$Q_n\,|\partial_\lambda n\rangle = T_n\partial_\lambda H\,|n\rangle\,, \tag{9}$$

where

$$Q_n = \sum_{m\neq n}|m\rangle\langle m|\,, \tag{10}$$

which removes the $|n\rangle$ component from a wave function. (6) then becomes

$$Q_n\,|\partial_\lambda n\rangle = T_n\partial_\lambda H\,|n\rangle\,. \tag{11}$$

Since in

$$\langle n|O|\partial_n n\rangle = -\mathrm{i}A_n\,\langle n|O|n\rangle + \langle n|OQ_n|n\rangle\,,$$

the first term is always imaginary, we have

$$\partial_\lambda \langle O\rangle_n = 2\,\mathrm{Re}\,\langle n|OQ_n|\partial_\lambda n\rangle = 2\,\mathrm{Re}\,\langle \partial_\lambda n|Q_nO|n\rangle\,. \tag{12}$$

Now if we are in a many-body fermionic system with very weak interaction between particles, we have

$$\partial_\lambda \langle O\rangle = \sum_n^{\mathrm{occ}}\partial_\lambda \langle O\rangle_n = 2\,\mathrm{Re}\sum_n^{\mathrm{occ}}\langle n|OQ_n|\partial_\lambda n\rangle = 2\,\mathrm{Re}\sum_n^{\mathrm{occ}}\langle \partial_\lambda n|Q_nO|n\rangle\,. \tag{13}$$

This expression can be further simplified: after defining

$$Q = \sum_n^{\mathrm{unocc}}|n\rangle\langle n| = 1 - \sum_n^{\mathrm{occ}}|n\rangle\langle n|\,, \tag{14}$$

we have

$$\begin{aligned}
2\,\mathrm{Re}\sum_n^{\mathrm{occ}}\langle n|O(Q_n - Q)|\partial_\lambda n\rangle &= 2\,\mathrm{Re}\sum_n^{\mathrm{occ}}\left(\sum_{m\neq n} - \sum_m^{\mathrm{unocc}}\right)\langle n|O|m\rangle\,\langle m|\partial_\lambda n\rangle \\
&= 2\,\mathrm{Re}\sum_n^{\mathrm{occ}}\sum_{m\neq n}^{\mathrm{occ}}\langle n|O|m\rangle\,\langle m|\partial_\lambda n\rangle \\
&= \sum_n^{\mathrm{occ}}\sum_{m\neq n}^{\mathrm{occ}}(\,\langle n|O|m\rangle\,\langle m|\partial_\lambda n\rangle + \langle m|O|n\rangle\,\langle \partial_\lambda n|m\rangle).
\end{aligned}$$

Since $\langle n|m\rangle$ doesn't change no matter how you adjust λ, we have

$$0 = \partial_\lambda \langle n|m\rangle = \langle \partial_\lambda n|m\rangle + \langle n|\partial_\lambda m\rangle , \tag{15}$$

and thus

$$\begin{aligned} 2\,\mathrm{Re}\sum_n^{\mathrm{occ}} \langle n|O(Q_n - Q)|\partial_\lambda n\rangle &= \sum_n^{\mathrm{occ}}\sum_{m\neq n}^{\mathrm{occ}} (\,\langle n|O|m\rangle\,\langle m|\partial_\lambda n\rangle - \langle m|O|n\rangle\,\langle n|\partial_\lambda m\rangle) \\ &= 0, \end{aligned}$$

and thus (13) becomes

$$\partial_\lambda \langle O\rangle = 2\,\mathrm{Re}\sum_n^{\mathrm{occ}} \langle \partial_\lambda n|QO|n\rangle = 2\,\mathrm{Re}\sum_n^{\mathrm{occ}} \langle n|OQ|\partial_\lambda n\rangle . \tag{16}$$

This is the formula that's going to be used to evaluate $\partial_\lambda \boldsymbol{P}$.

2.2 The change of polarization

In band theory, different $\boldsymbol{k}$ points don't influence each other, and therefore $\boldsymbol{k}$ can be thought of as an instance of λ. Suppose $H = T + V$ is the single electron Hamiltonian, which acts on Bloch states

$$\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} u_{n\boldsymbol{k}}(\boldsymbol{r}), \tag{17}$$

and we find the Hamiltonian acting on $u_{n\boldsymbol{k}}$ is

$$H_{\boldsymbol{k}} = \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} H \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}, \tag{18}$$

and we have

$$H_{\boldsymbol{k}} u_{n\boldsymbol{k}} = E_{n\boldsymbol{k}} u_{n\boldsymbol{k}}. \tag{19}$$

Since we are going to work with $u_{n\boldsymbol{k}}$, we need to modify the normalization convention. Usually, the inner product is defined as

$$\int \mathrm{d}^d\boldsymbol{r}\, \psi^*_{n'\boldsymbol{k}'}(\boldsymbol{r})\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = \delta_{nn'}\delta_{\boldsymbol{k}\boldsymbol{k}'}, \tag{20}$$

in which we integrate over the whole sample V. Thus, in empty lattice, we have

$$\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} \underbrace{\frac{1}{\sqrt{V}} \mathrm{e}^{\mathrm{i}\boldsymbol{G}_n\cdot\boldsymbol{r}}}_{u_{n\boldsymbol{k}}} . \tag{21}$$

The main problem of this normalization convention of $u_{n\boldsymbol{k}}$ is it makes the definition of the inner product of $u_{n\boldsymbol{k}}$ hard, since what we want is

$$\langle u_{n\boldsymbol{k}}|u_{n'\boldsymbol{k}}\rangle = \int_{\mathrm{u.c.}} \mathrm{d}^d\boldsymbol{r}\, u_{n\boldsymbol{k}}(\boldsymbol{r})^* u_{n'\boldsymbol{k}'}(\boldsymbol{r}), \tag{22}$$

but under this definition we have $\langle u_{n\boldsymbol{k}}|u_{n\boldsymbol{k}}\rangle = V_{\mathrm{u.c.}}/V = 1/N$, where N is the total number of primitive unit cells. It can be verified that the correct normalization convention should be the follows:

$$\psi_{n\boldsymbol{k}} = \frac{1}{\sqrt{N}} u_{n\boldsymbol{k}} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}, \quad \psi_{n\boldsymbol{k}} \simeq \frac{1}{\sqrt{V}} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}, \quad u_{n\boldsymbol{k}} \simeq \frac{1}{\sqrt{V_{\mathrm{u.c.}}}}, \tag{23}$$

and under this convention, for periodic quantity $Q(\boldsymbol{r})$, we have

$$\langle \psi_{n\boldsymbol{k}}|Q(\boldsymbol{r})|\psi_{n\boldsymbol{k}}\rangle = \langle u_{n\boldsymbol{k}}|Q(\boldsymbol{r})|u_{n\boldsymbol{k}}\rangle . \tag{24}$$

(24) can't be directly used for $-e\boldsymbol{r}$, since $\boldsymbol{r}$ of course is not periodic. However, we have

$$\begin{aligned}\boldsymbol{P} &\coloneqq \frac{1}{V}\sum_{\boldsymbol{k}}\sum_{n}^{\mathrm{occ}}\langle\psi_{n\boldsymbol{k}}|-e\boldsymbol{r}|\psi_{n\boldsymbol{k}}\rangle\\ &= \frac{1}{V}\sum_{\boldsymbol{k}}\sum_{n}^{\mathrm{occ}}\sum_{\boldsymbol{R}}\int_{\text{u.c. at }\boldsymbol{R}}\mathrm{d}^d\boldsymbol{r}\,\frac{1}{N}u^*_{n\boldsymbol{k}}(\boldsymbol{r})(-e\boldsymbol{r})u_{n\boldsymbol{k}}(\boldsymbol{r})\\ &= \frac{1}{V}\sum_{\boldsymbol{k}}\sum_{n}^{\mathrm{occ}}\frac{1}{N}\sum_{\boldsymbol{R}}\int_{\text{one u.c.}}\mathrm{d}^d\boldsymbol{r}\,u^*_{n\boldsymbol{k}}(\boldsymbol{r})(-e\boldsymbol{r}-e\boldsymbol{R})u_{n\boldsymbol{k}}(\boldsymbol{r})\\ &= \frac{1}{V}\sum_{\boldsymbol{k}}\sum_{n}^{\mathrm{occ}}\left(\int_{\text{one u.c.}}\mathrm{d}^d\boldsymbol{r}\,u^*_{n\boldsymbol{k}}(\boldsymbol{r})(-e\boldsymbol{r})u_{n\boldsymbol{k}}(\boldsymbol{r})-e\frac{1}{N}\sum_{\boldsymbol{R}}\boldsymbol{R}\right),\end{aligned}\tag{25}$$

where in the third line, we use the periodic condition of $u_{n\boldsymbol{k}}$, and since the first term in the third line contains no dependence on $\boldsymbol{R}$, the $1/N$ factor cancels with the summation over $\boldsymbol{R}$, while in the second term, the dependence on $u_{n\boldsymbol{k}}$ is just the normalization condition. Now the physical meaning of the second term is clear: it's important when the system we are working with is a part of an electric dipole together with another system. Thus, formally, we have reconfirmed that the polarization is

$$\boldsymbol{P}=\frac{1}{V}\sum_{\boldsymbol{k}}\sum_{n}^{\mathrm{occ}}\langle u_{n\boldsymbol{k}}|-e\boldsymbol{r}|u_{n\boldsymbol{k}}\rangle=\int_{1\mathrm{BZ}}\frac{\mathrm{d}^d\boldsymbol{k}}{(2\pi)^d}\underbrace{\sum_{n}^{\mathrm{occ}}\langle u_{n\boldsymbol{k}}|-e\boldsymbol{r}|u_{n\boldsymbol{k}}\rangle}_{-e\langle\boldsymbol{r}\rangle_{\boldsymbol{k}}}.\tag{26}$$

We have already shown that (26) can't be taken literally, and to proceed we evaluate its time derivative, and get

$$\begin{aligned}\partial_\lambda\langle\boldsymbol{P}\rangle &= -e\int_{1\mathrm{BZ}}\frac{\mathrm{d}^d\boldsymbol{k}}{(2\pi)^d}\partial_\lambda\langle\boldsymbol{r}\rangle_{\boldsymbol{k}}\\ &= -e\int_{1\mathrm{BZ}}\frac{\mathrm{d}^d\boldsymbol{k}}{(2\pi)^d}\cdot 2\,\mathrm{Re}\sum_{n}^{\mathrm{occ}}\langle\partial_\lambda u_{n\boldsymbol{k}}|Q_{\boldsymbol{k}}\boldsymbol{r}|u_{n\boldsymbol{k}}\rangle.\end{aligned}\tag{27}$$

Note that here $Q_{\boldsymbol{k}}$ is not Q_n in (13), but Q in (16): here $\boldsymbol{k}$ is considered an "external" parameter. What we want to do is to eliminate any $\boldsymbol{r}$ in the expression to avoid ambiguity mentioned above. We define

$$\boldsymbol{v}_{\boldsymbol{k}}=\frac{1}{\mathrm{i}\hbar}[\boldsymbol{r},H_{\boldsymbol{k}}]=\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}v\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}},\tag{28}$$

which is the counterpart of $\boldsymbol{v}$ in the quantum mechanics about $\{u_{n\boldsymbol{k}}\}$, and we can then find

$$\boldsymbol{v}_{\boldsymbol{k}}=\frac{1}{\hbar}\frac{\partial H_{\boldsymbol{k}}}{\partial\boldsymbol{k}},\tag{29}$$

since

$$\frac{\partial H_{\boldsymbol{k}}}{\partial\boldsymbol{k}}=(-\mathrm{i}\boldsymbol{r})\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}H\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}+\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}H\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}\cdot\mathrm{i}\boldsymbol{r}=-\mathrm{i}[\boldsymbol{r},H_{\boldsymbol{k}}].$$

Then from (28), we find

$$\langle u_{m\boldsymbol{k}}|\boldsymbol{v}_{\boldsymbol{k}}|u_{n\boldsymbol{k}}\rangle=\frac{1}{\mathrm{i}\hbar}\langle u_{m\boldsymbol{k}}|\boldsymbol{r}H_{\boldsymbol{k}}-H_{\boldsymbol{k}}\boldsymbol{r}|u_{n\boldsymbol{k}}\rangle=\frac{1}{\mathrm{i}\hbar}(E_{n\boldsymbol{k}}-E_{m\boldsymbol{k}})\langle u_{m\boldsymbol{k}}|\boldsymbol{r}|u_{n\boldsymbol{k}}\rangle,$$

$$\langle u_{m\boldsymbol{k}}|\boldsymbol{r}|u_{n\boldsymbol{k}}\rangle=\frac{\mathrm{i}\hbar}{E_{n\boldsymbol{k}}-E_{m\boldsymbol{k}}}\langle u_{m\boldsymbol{k}}|\boldsymbol{v}_{\boldsymbol{k}}|u_{n\boldsymbol{k}}\rangle,$$

and therefore

$$\underbrace{\sum_{m\neq n}|u_{m\boldsymbol{k}}\rangle\langle u_{m\boldsymbol{k}}|\,\boldsymbol{r}\,|u_{n\boldsymbol{k}}\rangle}_{Q_{n\boldsymbol{k}}}=\mathrm{i}\hbar\underbrace{\sum_{m\neq n}\frac{|u_{m\boldsymbol{k}}\rangle\langle u_{m\boldsymbol{k}}|}{E_{n\boldsymbol{k}}-E_{m\boldsymbol{k}}}\boldsymbol{v}_{\boldsymbol{k}}}_{T_{n\boldsymbol{k}}}|u_{n\boldsymbol{k}}\rangle,$$

and the RHS of (27) becomes (note that according to (13) and (16), $Q_{n\boldsymbol{k}}$ and $Q_{\boldsymbol{k}}$ can be used in place of each other in the expression)

$$\begin{aligned}\partial_\lambda \langle \boldsymbol{P} \rangle &= -e \int_{1\mathrm{BZ}} \frac{\mathrm{d}^d \boldsymbol{k}}{(2\pi)^d} \cdot 2\,\mathrm{Re} \sum_n^{\mathrm{occ}} \langle \partial_\lambda u_{n\boldsymbol{k}} | \mathrm{i}\hbar T_{n\boldsymbol{k}} \boldsymbol{v}_{\boldsymbol{k}} | u_{n\boldsymbol{k}} \rangle \\ &= e\hbar \int_{1\mathrm{BZ}} \frac{\mathrm{d}^d \boldsymbol{k}}{(2\pi)^d} \cdot 2\,\mathrm{Im} \sum_n^{\mathrm{occ}} \langle \partial_\lambda u_{n\boldsymbol{k}} | T_{n\boldsymbol{k}} \boldsymbol{v}_{\boldsymbol{k}} | u_{n\boldsymbol{k}} \rangle \,.\end{aligned} \tag{30}$$

Further, using (29) and (9), we have

$$T_{n\boldsymbol{k}} \boldsymbol{v}_{\boldsymbol{k}} \, |u_{n\boldsymbol{k}}\rangle = \frac{1}{\hbar} T_{n\boldsymbol{k}} \frac{\partial H_{\boldsymbol{k}}}{\partial \boldsymbol{k}} \, |u_{n\boldsymbol{k}}\rangle = \frac{1}{\hbar} Q_{n\boldsymbol{k}} \, |\partial_{\boldsymbol{k}} u_{n\boldsymbol{k}}\rangle \,,$$

and thus

$$\begin{aligned}\partial_\lambda \langle \boldsymbol{P} \rangle &= e \int_{1\mathrm{BZ}} \frac{\mathrm{d}^d \boldsymbol{k}}{(2\pi)^d} \cdot 2\,\mathrm{Im} \sum_n^{\mathrm{occ}} \langle \partial_\lambda u_{n\boldsymbol{k}} | Q_{n\boldsymbol{k}} | \partial_{\boldsymbol{k}} u_{n\boldsymbol{k}} \rangle \\ &= e \int_{1\mathrm{BZ}} \frac{\mathrm{d}^d \boldsymbol{k}}{(2\pi)^d} \cdot 2\,\mathrm{Im} \sum_n^{\mathrm{occ}} \langle \partial_\lambda u_{n\boldsymbol{k}} | Q_{\boldsymbol{k}} | \partial_{\boldsymbol{k}} u_{n\boldsymbol{k}} \rangle \,.\end{aligned} \tag{31}$$

The derivation from (27) to (31) can be heuristically done by replacing $\boldsymbol{r}$ by $\mathrm{i}\partial_{\boldsymbol{k}}$, where we identify $\boldsymbol{k}$ and real momentum $\boldsymbol{p}$; this however is not always true, since the commutation relation between $\boldsymbol{r}$ and the operator corresponding to $\boldsymbol{k}$ is not clear. The last step is to get rid of $Q_{\boldsymbol{k}}$. To see why, note that

$$\sum_n^{\mathrm{occ}} \langle \partial_\lambda u_{n\boldsymbol{k}} | Q_{\boldsymbol{k}} | u_{n\boldsymbol{k}} \rangle = \sum_n^{\mathrm{occ}} \langle \partial_\lambda u_{n\boldsymbol{k}} | u_{n\boldsymbol{k}} \rangle - \sum_n^{\mathrm{occ}} \sum_m^{\mathrm{occ}} \langle \partial_\lambda u_{n\boldsymbol{k}} | u_{m\boldsymbol{k}} \rangle \langle u_{m\boldsymbol{k}} | \partial_{\boldsymbol{k}} u_{n\boldsymbol{k}} \rangle \,,$$

and since we have (15), the complex conjugate of the second term is

$$\sum_n^{\mathrm{occ}} \sum_m^{\mathrm{occ}} \langle u_{m\boldsymbol{k}} | \partial_\lambda u_{n\boldsymbol{k}} \rangle \langle \partial_{\boldsymbol{k}} u_{n\boldsymbol{k}} | u_{m\boldsymbol{k}} \rangle = \sum_n^{\mathrm{occ}} \sum_m^{\mathrm{occ}} (-\langle \partial_\lambda u_{n\boldsymbol{k}} | u_{m\boldsymbol{k}} \rangle)(-\langle u_{m\boldsymbol{k}} | \partial_{\boldsymbol{k}} u_{n\boldsymbol{k}} \rangle)$$

and is the same as the original form, and thus we find that the second term is always real, and thus

$$\partial_\lambda \langle \boldsymbol{P} \rangle = e \int_{1\mathrm{BZ}} \frac{\mathrm{d}^d \boldsymbol{k}}{(2\pi)^d} \cdot 2\,\mathrm{Im} \sum_n^{\mathrm{occ}} \langle \partial_\lambda u_{n\boldsymbol{k}} | \partial_{\boldsymbol{k}} u_{n\boldsymbol{k}} \rangle \,. \tag{32}$$

Thus, the change of the polarization vector is rewritten into a rather elegant form.

2.3 Berry phase and polarization

The next problem is what's the RHS of (32). We will find it's Berry curvature. Here again we first review the general formalism of Berry phase in quantum mechanics. Recall that we have (6) and (7), and from the equations we find in adiabatic evolution, we have

$$|n(\lambda)\rangle = \mathrm{e}^{\text{some other dynamic factor}} \mathrm{e}^{-\mathrm{i}\int_0^\lambda A_n \mathrm{d}\lambda} \, |n(\lambda = 0)\rangle \,. \tag{33}$$

The notation $A_n \, \mathrm{d}\lambda$ actually is $A_{n,\mu} \, \mathrm{d}\lambda^\mu$, since there may be more than one turning parameter in the Hamiltonian. So A_n is just a *connection* in differential geometry, where the underlying manifold is the range of λ, and at each point in the manifold we have a vector space, the index of which is n, and the parallel transport is adiabatic evolution. Thus, the status of A_n is comparable to the vector potential in electromagnetism, or Christoffel symbols in general relativity. Then we may ask whether the Berry connection is "inherently curved", i.e. whether if we slowly change λ and ultimately turn it back, we get a non-zero phase factor before $|n\rangle$. In electromagnetism this means we need to calculate $\boldsymbol{B} = \boldsymbol{\nabla} \times \boldsymbol{A}$; in general relativity this means we need to calculate the Riemann curvature tensor. In the general formalism of quantum mechanics this means we need to calculate *Berry curvature*; note that in an experimental setting where particles are confined in a very small range compared with the length scale of the variance of the magnetic field, we

can change λ to $\boldsymbol{r}$, and the Berry phase is just the phase factor induced by the vector potential. The Berry curvature is then

$$\Omega_{n,\mu\nu} = \partial_\mu A_{n,\nu} - \partial_\nu A_{n,\mu}. \tag{34}$$

Here μ, ν, etc. are indices of λ. Since

$$A_{n,\mu} = \mathrm{i} \langle n | \partial_\mu n \rangle , \tag{35}$$

we have

$$\begin{aligned} \Omega_{n,\mu\nu} &= \partial_\mu A_{n,\nu} - \partial_\nu A_{n,\mu} \\ &= \mathrm{i} \langle \partial_\mu n | \partial_\nu n \rangle + \mathrm{i} \langle n | \partial_\mu \partial_\nu n \rangle - \mathrm{i} \langle \partial_\nu n | \partial_\mu n \rangle - \mathrm{i} \langle n | \partial_\nu \partial_\mu n \rangle \\ &= -2 \operatorname{Im} \langle \partial_\mu n | \partial_\nu n \rangle = \mathrm{i} \langle \partial_\mu n | \partial_\nu n \rangle - \mathrm{i} \langle \partial_\nu n | \partial_\mu n \rangle . \end{aligned} \tag{36}$$

Suppose C is a closed routine in the space of possible λ, and the Berry phase accumulated by moving λ around this routine is equal to

$$\mathrm{e}^{-\mathrm{i} \oint_C A_{n,\mu} \mathrm{d}\lambda^\mu} = \mathrm{e}^{-\mathrm{i} \int_S \Omega_{n,\mu\nu} \mathrm{d}x^\mu \mathrm{d}x^\nu}, \tag{37}$$

where S is a surface in the parameter space whose boundary is C. $A_{n,\mu}$ changes when we add an arbitrary phase factor before wave functions; but $\Omega_{n,\mu\nu}$ is invariant under such a gauge transformation. There, of course, is a subtlety about whether Ω is well-defined within S: it's possible that Ω has some kind of spikes within C, which may be due to gauge choice in the wave function phase and is reflected by the $2\pi n$ degree of freedom on the LHS.

Now we find the RHS of (32) is just the Berry curvature: we then have

$$\partial_\lambda \langle \boldsymbol{P} \rangle = -e \int_{1\mathrm{BZ}} \frac{\mathrm{d}^d \boldsymbol{k}}{(2\pi)^d} \sum_n^{\mathrm{occ}} \Omega_{n,\lambda\boldsymbol{k}}. \tag{38}$$

From this equation, we can do partial integral over the variable λ, and then we find

$$\Delta \langle \boldsymbol{P} \rangle = -e \sum_n^{\mathrm{occ}} \int_{1\mathrm{BZ}} \frac{\mathrm{d}^d \boldsymbol{k}}{(2\pi)^d} \int_{\lambda_\mathrm{i}}^{\lambda_\mathrm{f}} (\partial_\lambda A_{n\boldsymbol{k}} - \partial_{\boldsymbol{k}} A_{n\lambda}). \tag{39}$$

The integrant in the first term becomes $\Delta A_{n\boldsymbol{k}}$; the second term vanishes because of the periodic boundary condition of the first Brillouin zone – the $d = 1$ case illustrates this clearly, since $k = 0$ is equivalent to $k = 2\pi/a$. Thus we find

$$\Delta \langle \boldsymbol{P} \rangle = -e \sum_n^{\mathrm{occ}} \int_{1\mathrm{BZ}} \frac{\mathrm{d}^d \boldsymbol{k}}{(2\pi)^d} (\boldsymbol{A}_{n\boldsymbol{k}}(\lambda = \lambda_\mathrm{f}) - \boldsymbol{A}_{n\boldsymbol{k}}(\lambda = \lambda_\mathrm{i})). \tag{40}$$

Here we have changed the symbol of the Berry connection to the bold $\boldsymbol{A}$ to remind ourself that due to the vector nature of $\boldsymbol{k}$, this quantity is a vector, namely

$$\boldsymbol{A}_{n\boldsymbol{k}} = \mathrm{i} \langle u_{n\boldsymbol{k}} | \partial_{\boldsymbol{k}} u_{n\boldsymbol{k}} \rangle . \tag{41}$$

A natural definition of $\langle \boldsymbol{P} \rangle$, then, seems to be

$$\langle \boldsymbol{P} \rangle = -e \sum_n^{\mathrm{occ}} \int_{1\mathrm{BZ}} \frac{\mathrm{d}^d \boldsymbol{k}}{(2\pi)^d} \boldsymbol{A}_{n\boldsymbol{k}}, \tag{42}$$

since λ in principle contains all information about the band structure, and $\langle \boldsymbol{P} \rangle$ should be a function of λ; now if we add a constant at $\lambda = \lambda_\mathrm{i}$ to $\langle \boldsymbol{P} \rangle$, it can't change when λ changes, leading to the question about its origin.

3 Wannier function and charge center

Although (42) looks elegant, its derivation doesn't have a clear physical meaning. In this section we assign an interpretation of this equation using Wannier charge centers.

Recall that the main problem for the naive spatial averaging definition (26) is that $\boldsymbol{r}$ is an unbounded operator, and summing over the whole space creates ambiguity (2). An alternative

way to evaluate (26) is to first recast the expression in Wannier representation, and then average over the expectation of $\boldsymbol{r}$ in each Wannier function.

The first step is to find what is the charge center of a Wannier function. At the current state, we define Wannier functions for a given band, although it's possible that to reach maximally localized Wannier functions, we need to remix several bands. The Wannier function for a given band is therefore

$$\phi_{n\boldsymbol{R}}(\boldsymbol{r}) = \frac{1}{\sqrt{N}} \sum_{\boldsymbol{k}} \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}} \psi_{n\boldsymbol{k}}(\boldsymbol{r}) = \frac{1}{N} \sum_{\boldsymbol{k}} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{R})} u_{n\boldsymbol{k}}(\boldsymbol{r}), \tag{43}$$

and therefore

$$u_{n\boldsymbol{k}}(\boldsymbol{r}) = \sum_{\boldsymbol{R}} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{R}-\boldsymbol{r})} \phi_{n\boldsymbol{R}}, \tag{44}$$

and the Berry connection is given by

$$\begin{aligned}
\boldsymbol{A}_{n\boldsymbol{k}} &= \mathrm{i} \langle u_{n\boldsymbol{k}} | \partial_{\boldsymbol{k}} u_{n\boldsymbol{k}} \rangle \\
&= \mathrm{i} \int_{\mathrm{u.c.}} \mathrm{d}^d \boldsymbol{r} \sum_{\boldsymbol{R},\boldsymbol{R}'} \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{R}-\boldsymbol{r})} \phi^*_{n\boldsymbol{R}}(\boldsymbol{r}) \cdot \mathrm{i}(\boldsymbol{R}-\boldsymbol{r}) \cdot \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{R}'-\boldsymbol{r})} \phi_{n\boldsymbol{R}'}(\boldsymbol{r}) \\
&= \sum_{\boldsymbol{R},\boldsymbol{R}'} \int_{\mathrm{u.c.}} \mathrm{d}^d \boldsymbol{r}\, \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{R}'-\boldsymbol{R})} \cdot (\boldsymbol{r}-\boldsymbol{R}) \cdot \phi^*_{n\boldsymbol{R}}(\boldsymbol{r}) \phi_{n\boldsymbol{R}'}(\boldsymbol{r}).
\end{aligned} \tag{45}$$

This equation looks highly complicated, but note that we can set $\boldsymbol{R}$ to $\boldsymbol{R}'$ by integrating over $\boldsymbol{k}$: we have

$$\begin{aligned}
\int_{1\mathrm{BZ}} \frac{\mathrm{d}^d \boldsymbol{k}}{(2\pi)^d} A_{n\boldsymbol{k}} &= \sum_{\boldsymbol{R},\boldsymbol{R}'} \int_{\mathrm{u.c.}} \mathrm{d}^d \boldsymbol{r} \int_{1\mathrm{BZ}} \frac{\mathrm{d}^d \boldsymbol{k}}{(2\pi)^d} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{R}-\boldsymbol{R}')} \cdot (\boldsymbol{r}-\boldsymbol{R}) \cdot \phi^*_{n\boldsymbol{R}}(\boldsymbol{r}) \phi_{n\boldsymbol{R}'}(\boldsymbol{r}) \\
&= \sum_{\boldsymbol{R},\boldsymbol{R}'} \int_{\mathrm{u.c.}} \mathrm{d}^d \boldsymbol{r}\, \frac{1}{V_{\mathrm{u.c.}}} \delta_{\boldsymbol{R}\boldsymbol{R}'} \cdot (\boldsymbol{r}-\boldsymbol{R}) \cdot \phi^*_{n\boldsymbol{R}}(\boldsymbol{r}) \phi_{n\boldsymbol{R}'}(\boldsymbol{r}) \\
&= \frac{1}{V_{\mathrm{u.c.}}} \sum_{\boldsymbol{R}} \int_{\mathrm{u.c.}} \mathrm{d}^d \boldsymbol{r}\, |\phi_{n\boldsymbol{R}}(\boldsymbol{r})|^2 (\boldsymbol{r}-\boldsymbol{R}) \\
&= \frac{1}{V_{\mathrm{u.c.}}} \sum_{\boldsymbol{R}} \int_{\mathrm{u.c.}} \mathrm{d}^d \boldsymbol{r}\, |\phi_{n,\boldsymbol{R}=0}(\boldsymbol{r}-\boldsymbol{R})|^2 (\boldsymbol{r}-\boldsymbol{R}) \\
&= \frac{1}{V_{\mathrm{u.c.}}} \int \mathrm{d}^d \boldsymbol{r}\, |\phi_{n,\boldsymbol{R}=0}(\boldsymbol{r})|^2 \cdot \boldsymbol{r} = \frac{1}{V_{\mathrm{u.c.}}} \langle \boldsymbol{r} \rangle_{\phi_{n,\boldsymbol{R}=0}},
\end{aligned} \tag{46}$$

and it can be seen that the expectation of the position operator under a Wannier state (which is well-defined, since Wannier functions are localized) is related to the Berry phase via the following elegant equation:

$$\langle \boldsymbol{r} \rangle_{\phi_{n,\boldsymbol{R}=0}} = V_{\mathrm{u.c.}} \int_{1\mathrm{BZ}} \frac{\mathrm{d}^d \boldsymbol{k}}{(2\pi)^d} A_{n\boldsymbol{k}}. \tag{47}$$

Inserting this equation to (42), we find

$$\langle \boldsymbol{P} \rangle = \frac{1}{V_{\mathrm{u.c.}}} \sum_{n}^{\mathrm{occ}} \langle -e\boldsymbol{r} \rangle_{\phi_{n,\boldsymbol{R}=0}}. \tag{48}$$

So now we can make sense of (42): if we first find Wannier functions and then find the charge centers (i.e. $\langle \boldsymbol{r} \rangle$, since charge density is just $-e$ times $|\phi_{n\boldsymbol{R}=0}|^2$), and then define the polarization vector according to the charge centers, we just get (42).