siesta On-line School 2024

November 14, 2024

# Polarisation and Born charges

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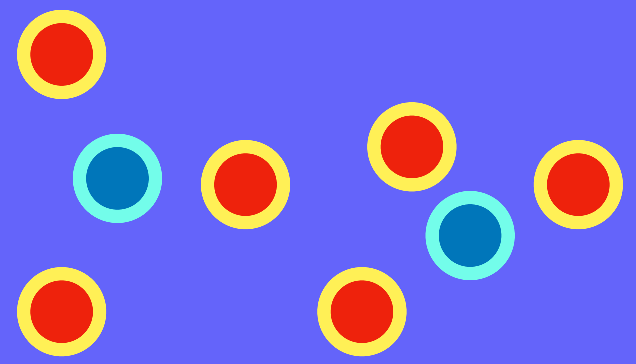
# Introduction to Modern Theory of Polarisation

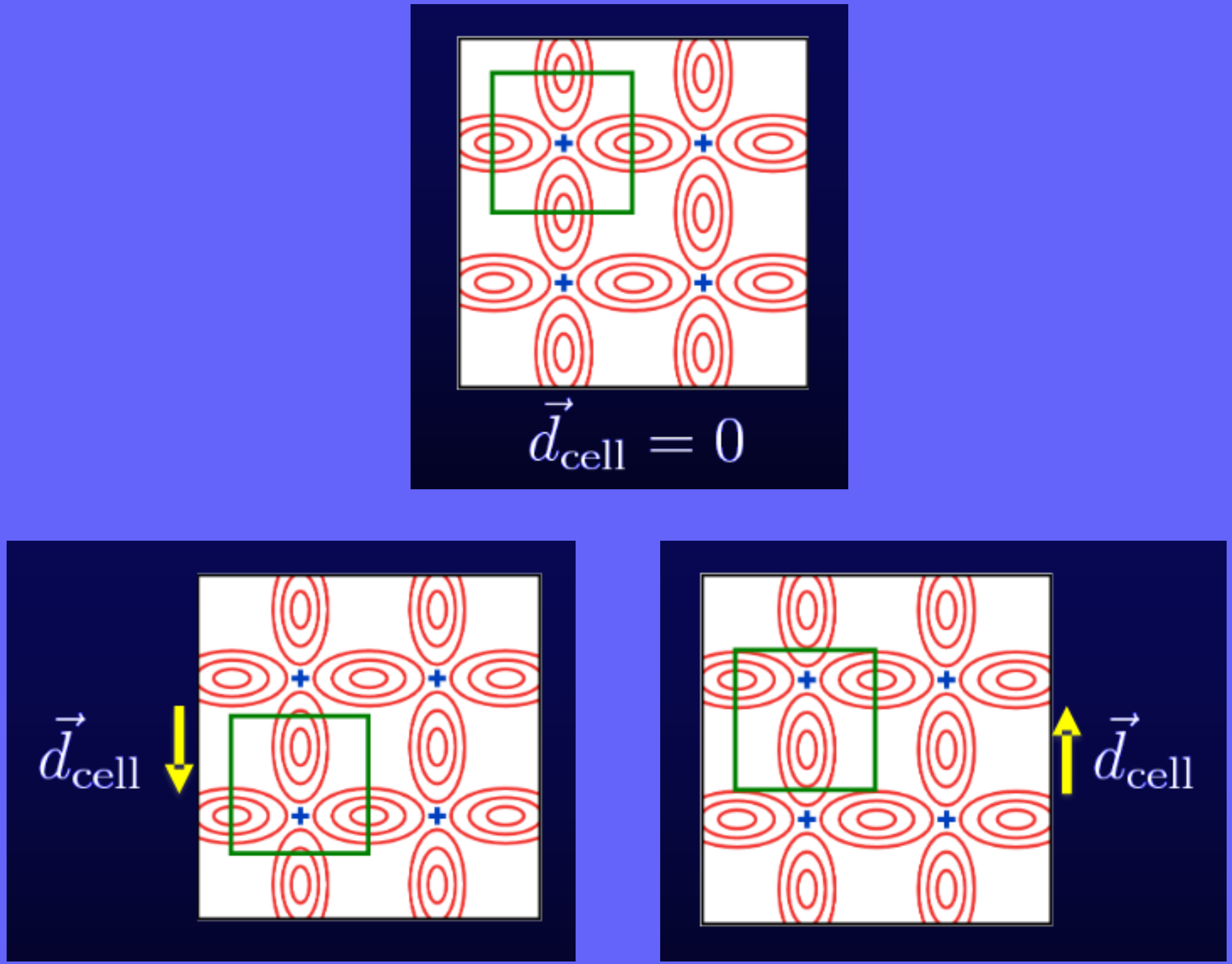
R. Resta, D. Vanderbilt, "Theory of Polarization: A Modern Approach". In: Physics of Ferroelectrics. Topics in Applied Physics, vol 105. Springer, Berlin, Heidelberg (2007). https://doi.org/10.1007/978-3-540-34591-6_2

N.A. Spaldin "A beginner's guide to the modern theory of polarization". Journal of Solid State Chemistry **195**, 2–10 (2012).

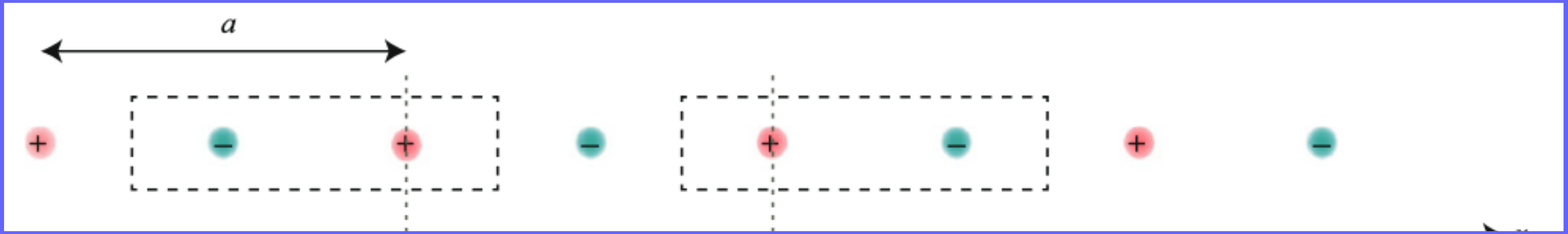
$$dipole \longrightarrow \vec{d} = \sum_i q_i \cdot \vec{r}_i$$



$$\vec{d} = \int \vec{r}\, \rho(\vec{r})\, d\vec{r}$$



# Introduction to Modern Theory of Polarisation




Different choices of the unit cell give different values of the polarization

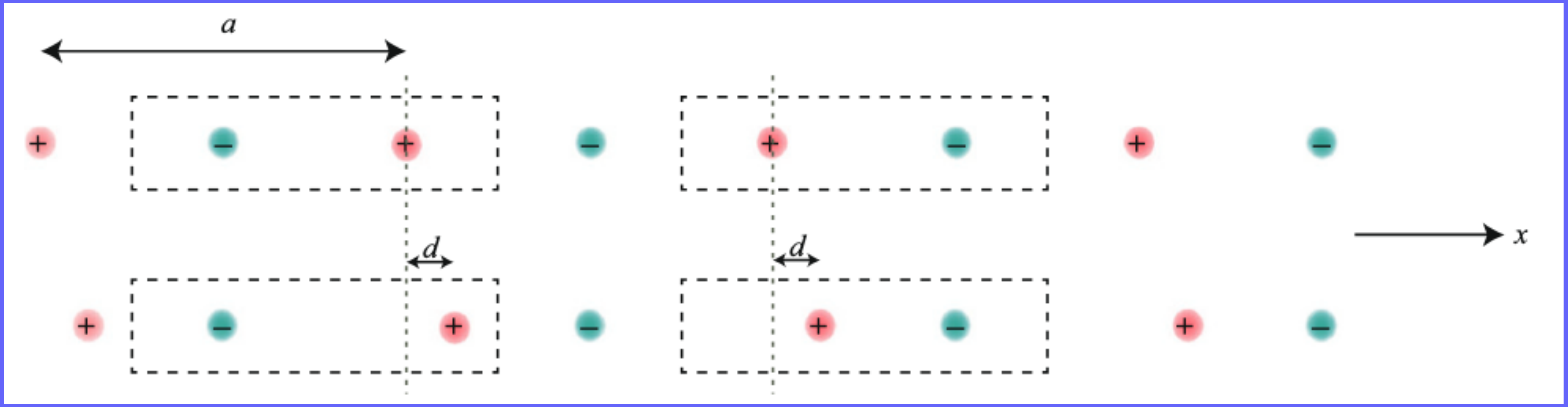
$$p_0 = \frac{d}{a} = \frac{1}{a}\sum_i q_i x_i = \frac{1}{a}\left(-1 \times \frac{a}{4} + 1 \times \frac{3a}{4}\right) = \frac{1}{2}$$

$$p_0' = \frac{1}{a}\left(+1 \times \frac{a}{4} - 1 \times \frac{3a}{4}\right) = -\frac{1}{2}$$

This collection of polarisation values is usually known as "polarisation lattice".
In this case, you'll find ±1/2, ±3/2, ±5/2, etc.

It might contain 0 (or not), but it must be centrosymmetric around zero

# Introduction to Modern Theory of Polarisation




$$p_0 = \frac{d}{a} = \frac{1}{a}\sum_i q_i x_i = \frac{1}{a}\left(-1\times\frac{a}{4} + 1\times\frac{3a}{4}\right) = \frac{1}{2}$$

$$p_0' = \frac{1}{a}\left(+1\times\frac{a}{4} - 1\times\frac{3a}{4}\right) = -\frac{1}{2}$$

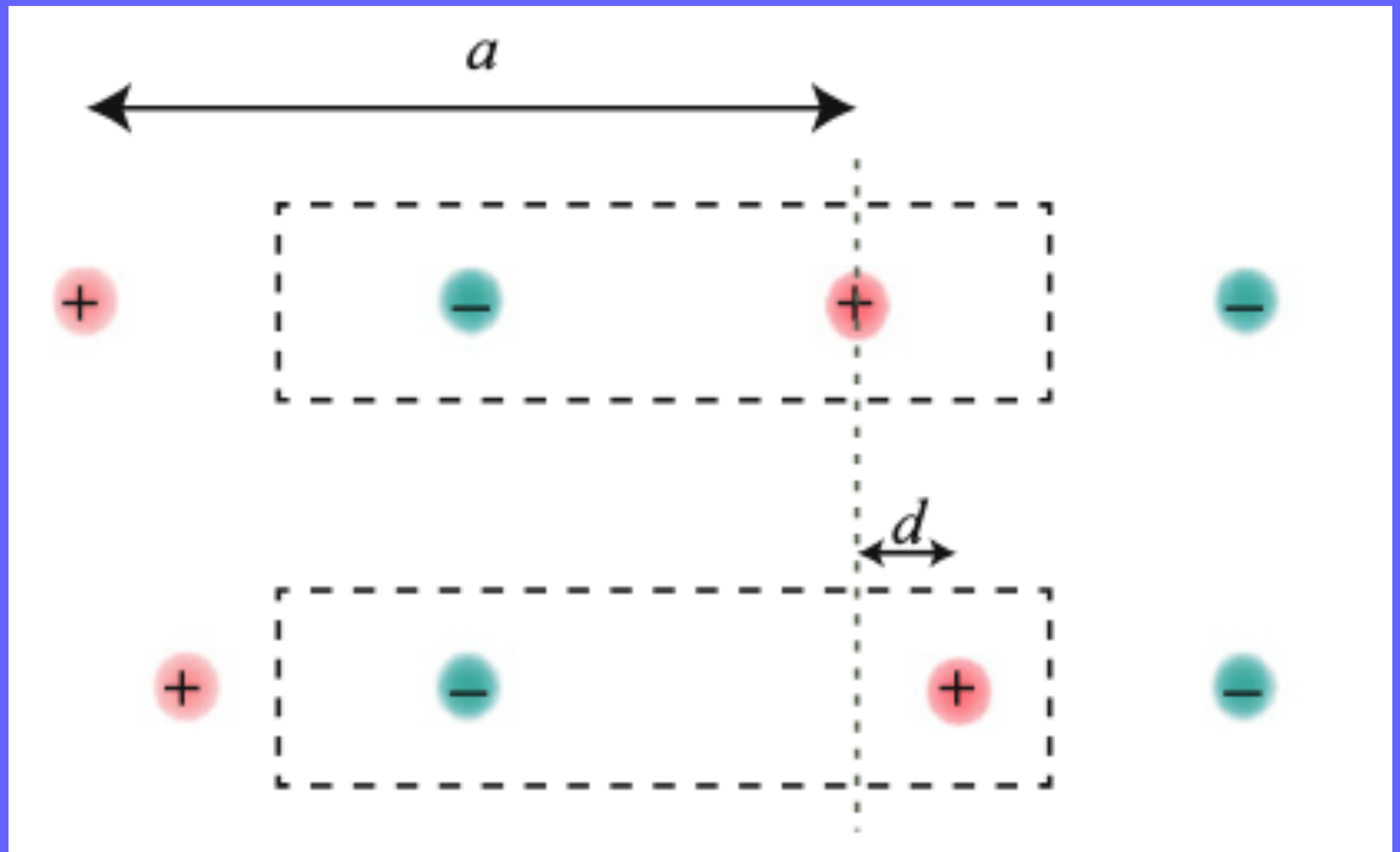
$$p_1 = \frac{1}{a}\left(-1\times\frac{a}{4} + 1\times\left(\frac{3a}{4}+d\right)\right) = \frac{1}{2}+\frac{d}{a}$$

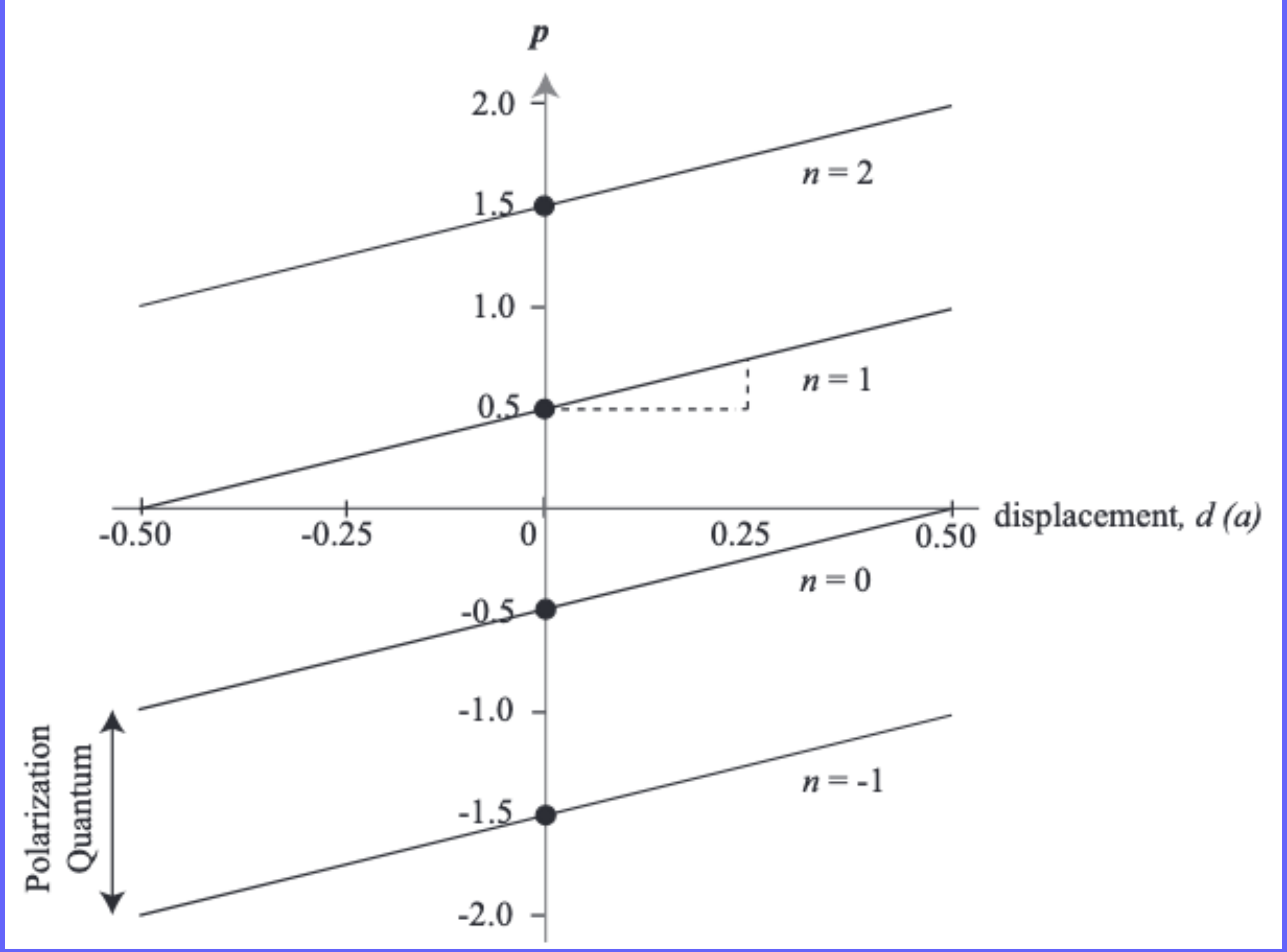
$$p_1' = \frac{1}{a}\left(+1\times\left(\frac{a}{4}+d\right) - 1\times\frac{3a}{4}\right) = -\frac{1}{2}+\frac{d}{a}$$

$$\Delta p = p_1 - p_0 = \frac{d}{a} \longleftrightarrow \Delta p' = p_1' - p_0' = \frac{d}{a}$$

Changes in polarisation are well defined!

# Introduction to Modern Theory of Polarisation




Quantum of polarisation: $\vec{P}_q = \frac{1}{\Omega} e \vec{R}$

Changes in polarisation are well defined!

# Introduction to Modern Theory of Polarisation

$$\Psi_{n\mathbf{k}}(\mathbf{r})$$

- cell-periodic function $\Psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r})$
- Wannier Functions $w_n(\mathbf{r}-\mathbf{R}) = \sqrt{N}\frac{\Omega}{(2\pi)^3}\int_{BZ} d^3\mathbf{k}\; e^{-i\mathbf{k}\cdot\mathbf{R}}\,\Psi_{n\mathbf{k}}(\mathbf{r})$

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

$$\bar{\mathbf{r}}_n = \int w_n^*(\mathbf{r})\;\mathbf{r}\; w_n(\mathbf{r}) d^3\mathbf{r}$$

$$\bar{\mathbf{r}}_n = i\frac{\Omega}{(2\pi)^3}\int_{BZ} e^{-i\mathbf{k}\cdot\mathbf{R}}\,\langle u_{n\mathbf{k}}|\frac{\partial u_{n\mathbf{k}}}{\partial\mathbf{k}}\rangle\; d^3\mathbf{k}$$

$$\Delta\mathbf{P} = \mathbf{P}^{(1)} - \mathbf{P}^{(0)} = \Delta\mathbf{P}_{ion} + \sum_n^{occ} q_n \bar{\mathbf{r}}_n$$

$$\mathbf{A}(\mathbf{k}) = i\langle u_{n\mathbf{k}}|\nabla_{\mathbf{k}}|u_{n\mathbf{k}}\rangle$$

"Berry connection"

# Introduction to Modern Theory of Polarisation

$$P_n = (\frac{e}{2\pi})\ \phi_n$$ "Berry phase"

$$\phi_n = \mathrm{Im} \int dk\ \langle u_{n\mathbf{k}} | \partial_k | u_{n\mathbf{k}} \rangle = \mathrm{Im} \ln \prod_{j=0}^{M-1} \langle u_{n,k_j} | u_{n,k_{j+1}} \rangle$$


$$\cdots \langle u_{n,k_1} | u_{n,k_2} \rangle \langle u_{n,k_2} | u_{n,k_3} \rangle \langle u_{n,k_3} | u_{n,k_4} \rangle \cdots$$

Insensitive to individual phases

In 3D:

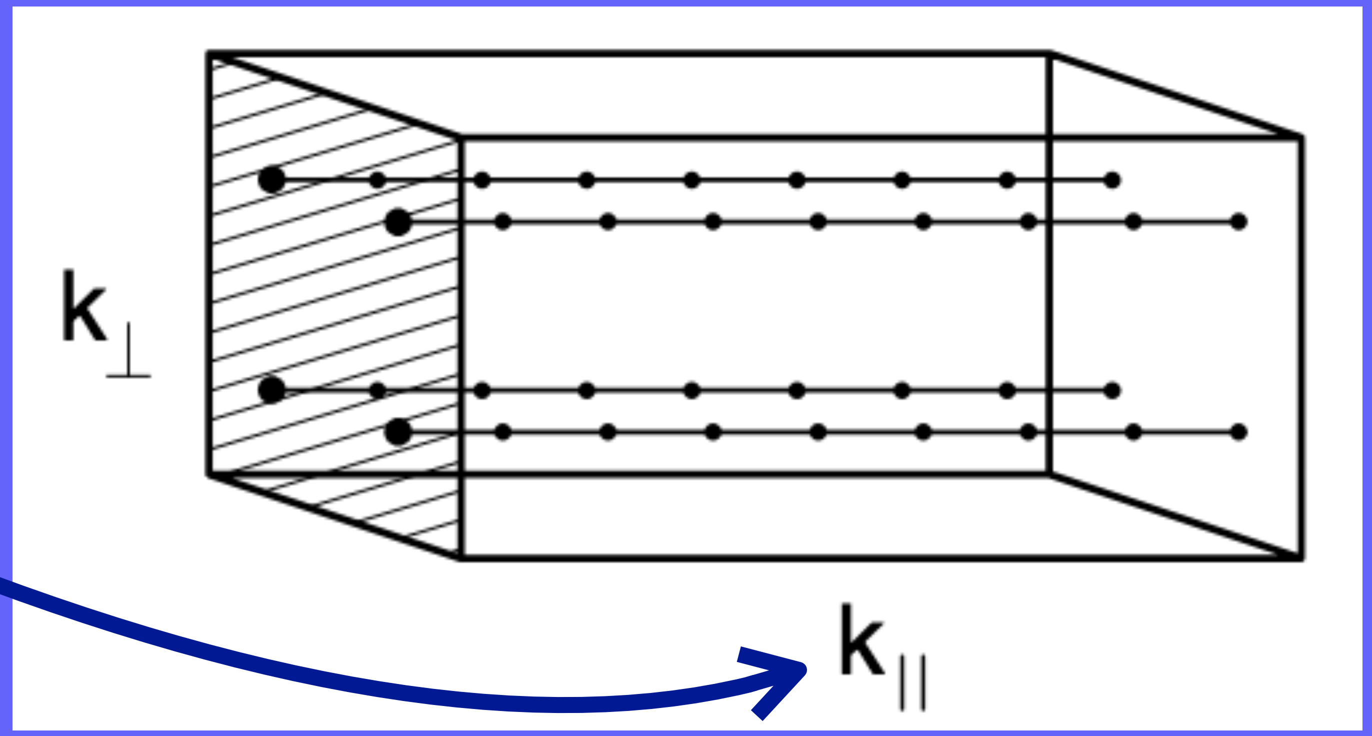
$$\phi_{n,j} = (\Omega / e)\ \mathbf{G}_j \cdot \mathbf{P_n} = \Omega^{-1}\, \mathrm{Im} \int_{BZ} d^3k\ \langle u_{n\mathbf{k}} | \mathbf{G}_j \cdot \nabla_{\mathbf{k}} | u_{n\mathbf{k}} \rangle$$

$$P_n = (\frac{e\Omega}{2\pi}) \sum_j \phi_{n,j}\ \mathbf{R}_j$$

$$\phi_{n,j} = \frac{1}{N_{k_\perp}} \sum_{k_\perp} \phi_n(k_\perp)$$

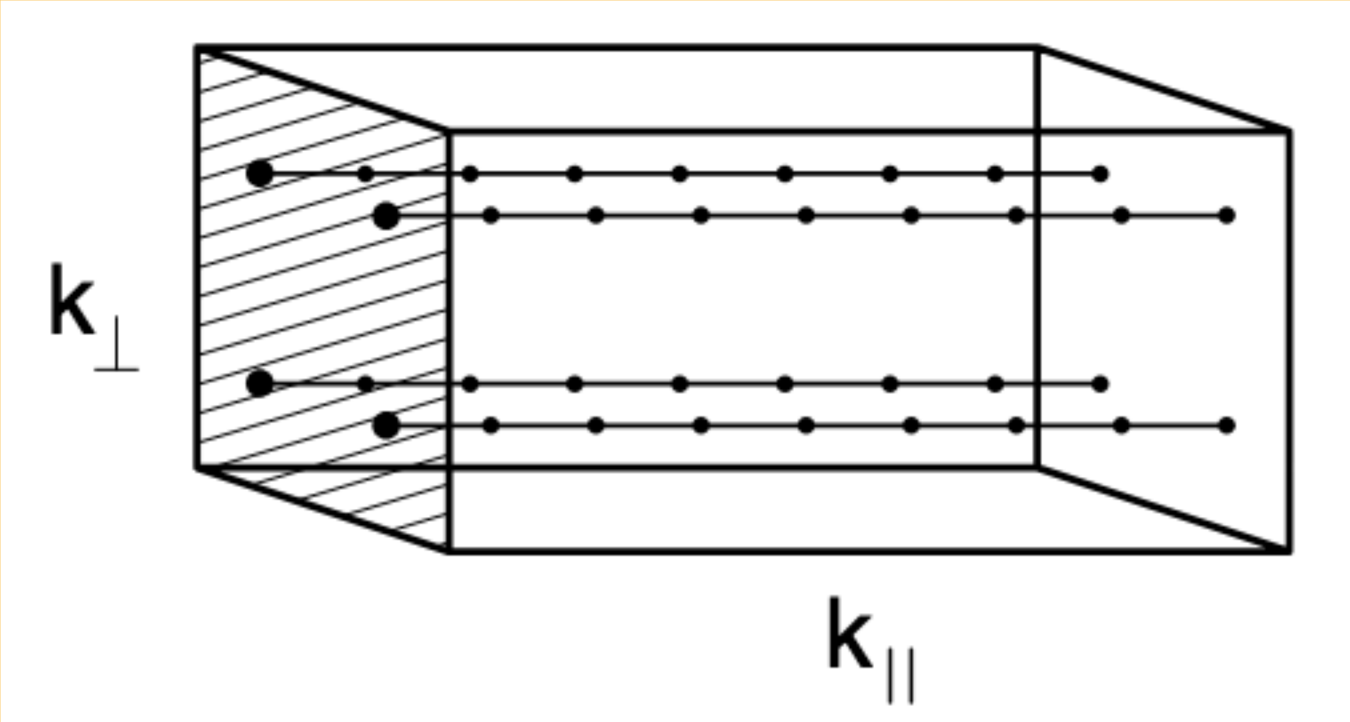
Averaging within the same "branch"

$k_{||}$ is the direction along $G_j$



# What do you need to compute P?

```
%block PolarizationGrids
10.    4.    4.    yes
 4.   10.    4.     No
 4.    4.   10.
%endblock PolarizationGrids
```




```
siesta: Macroscopic polarization per unit cell (a.u.):
siesta: Along the lattice vectors       18.927592     18.927592     75.548548
siesta: Along cartesian directions      32.783594      0.000000     75.548548

siesta: Macroscopic polarization per unit cell (Debye):
siesta: Along the lattice vectors       48.109140     48.109140    192.025256
siesta: Along cartesian directions      83.327585      0.000000    192.025256
```

Practical session: Polarisation calculations with the Berry-phase approach

# Born effective charges

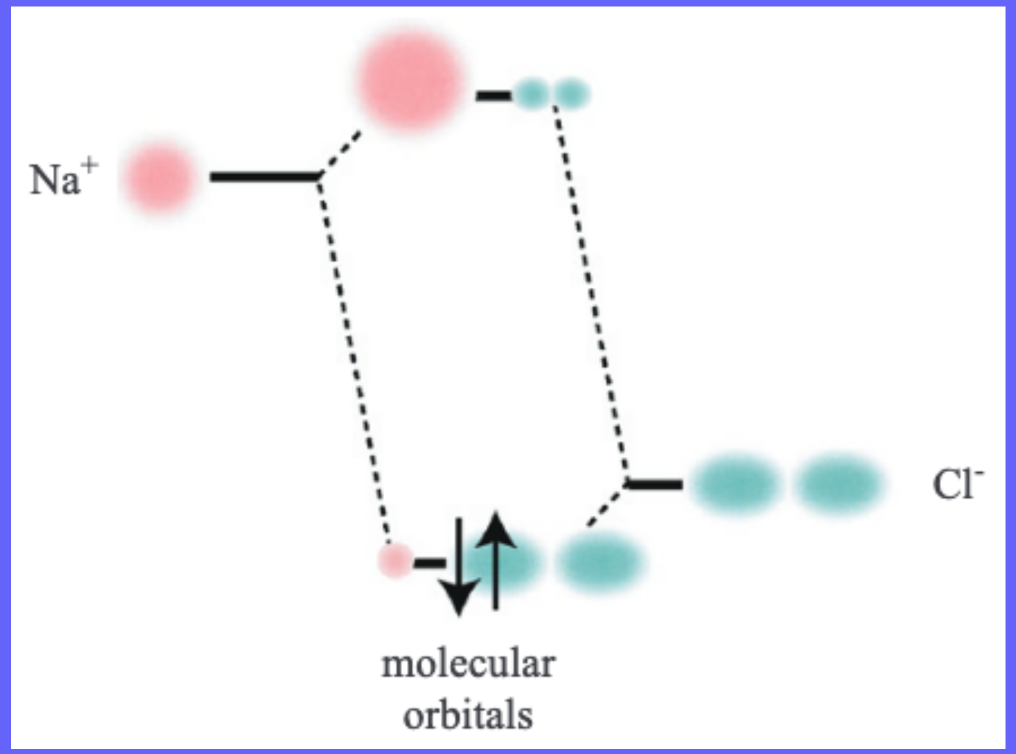
$$Z^*_{i,\alpha\beta} = \frac{\Omega}{e}\frac{\partial P_\alpha}{\partial \tau_{i,\beta}}$$

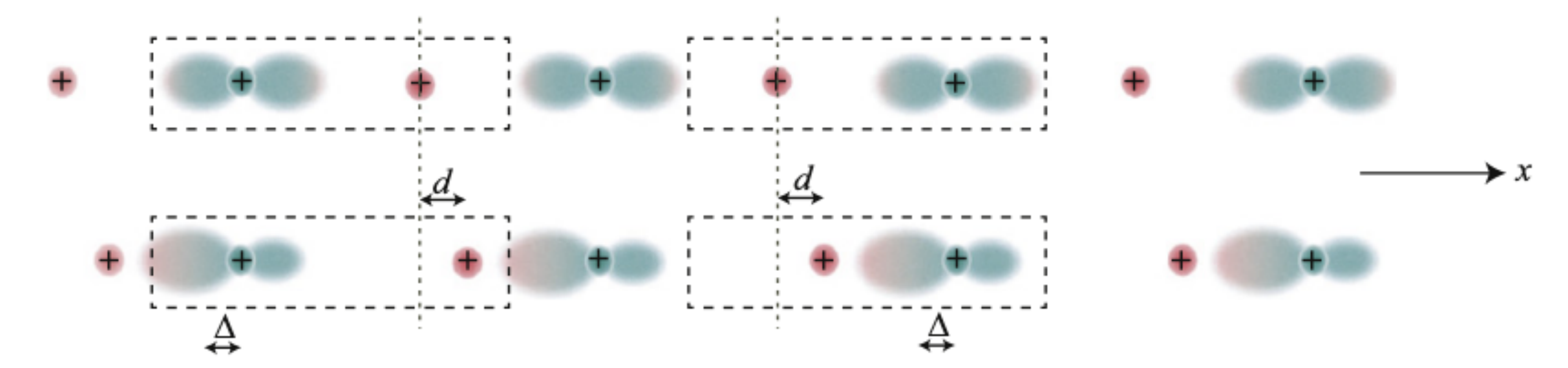
"Change in polarisation in direction $\alpha$ linearly induced by a sublattice displacement $\tau_i$ in direction $\beta$ in zero macroscopic electric field"

$$F_{i,\alpha} = -e\sum_\beta Z^*_{i,\beta\alpha}\mathscr{E}_\beta$$

"Measures the force F linearly induced in the $\alpha$ direction on the i-th nucleus by a uniform macroscopic field $\mathscr{E}$ in the $\beta$ direction (at zero displacement)"

$$p_0 = \frac{1}{a}\left(+1\cdot\frac{a}{4} + 1\cdot\frac{3a}{4} + (-2)\cdot\frac{a}{4}\right) = \frac{1}{2}$$



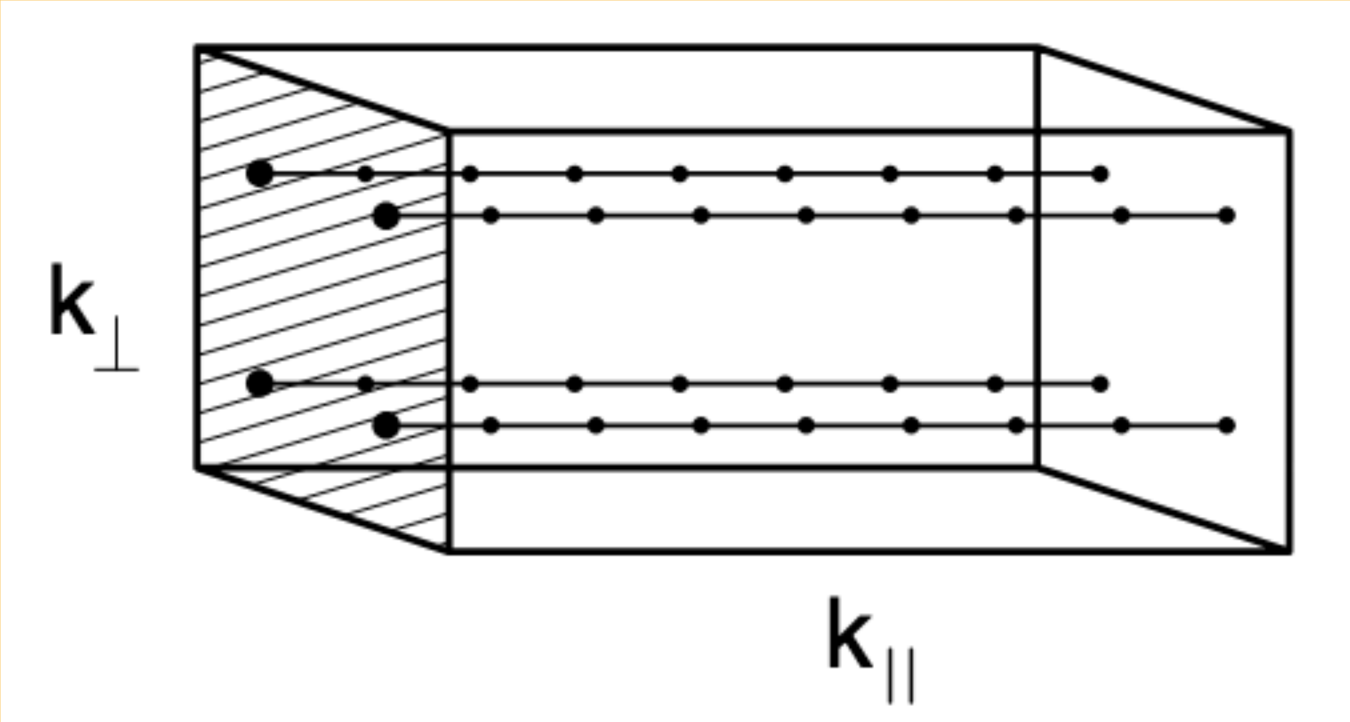




$$p_0 = \frac{1}{a}\left(+1\cdot\frac{a}{4} + 1\cdot\left(\frac{3a}{4}+d\right) + (-2)\cdot\left(\frac{a}{4}-\Delta\right)\right) = \frac{1}{2} + \frac{d}{a} + 2\frac{\Delta}{a}$$

"Acoustic sum rule" $\sum_i Z^*_{i,\alpha\beta} = 0$

# What do you need to compute Z?

```
%block PolarizationGrids
10.    4.    4.    yes
 4.   10.    4.     No
 4.    4.   10.
%endblock PolarizationGrids
```




```
MD.TypeOfRun   FC

BornCharge    True
```

SystemLabel.BC

BC matrix

| | | x | y | z | |
|---|---|---|---|---|---|
| | | 2.7855536 | 0.0009500 | -0.0000000 | Atom 1 |
| | | -0.0169876 | 2.7606635 | 0.0000000 | |
| | | 0.0019465 | 0.0010203 | 0.7221404 | |
| x | | -2.7345884 | 0.0009285 | 0.0000000 | Atom 2 |
| y | | -0.0171787 | -2.7591363 | -0.0000000 | |
| z | | 0.0018542 | 0.0010203 | -0.7242291 | |

Practical session: Polarisation calculations with the Berry-phase approach

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Questions?

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