Spontaneous polarization in periodic solids and its computation in FHI*aims*

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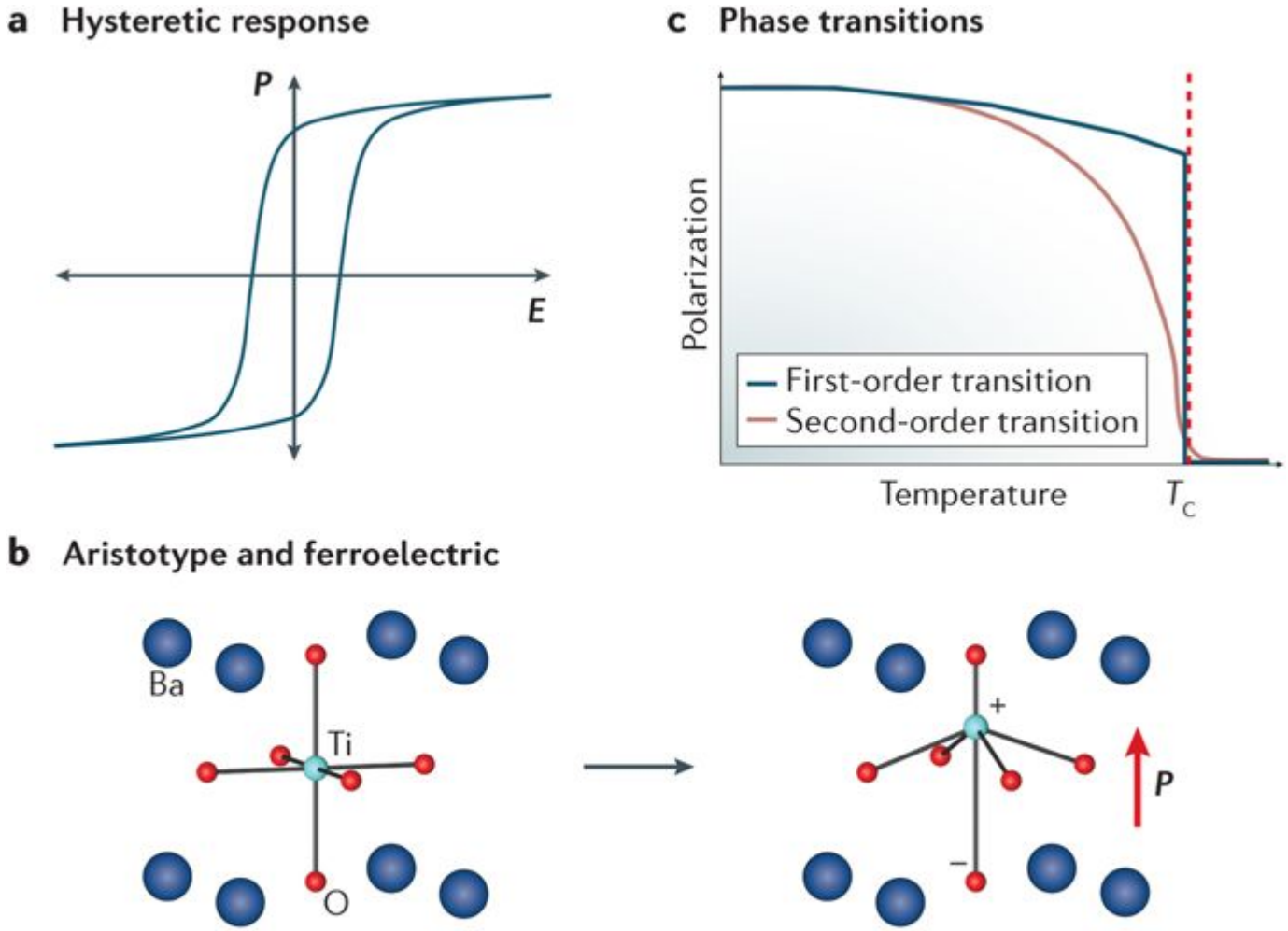
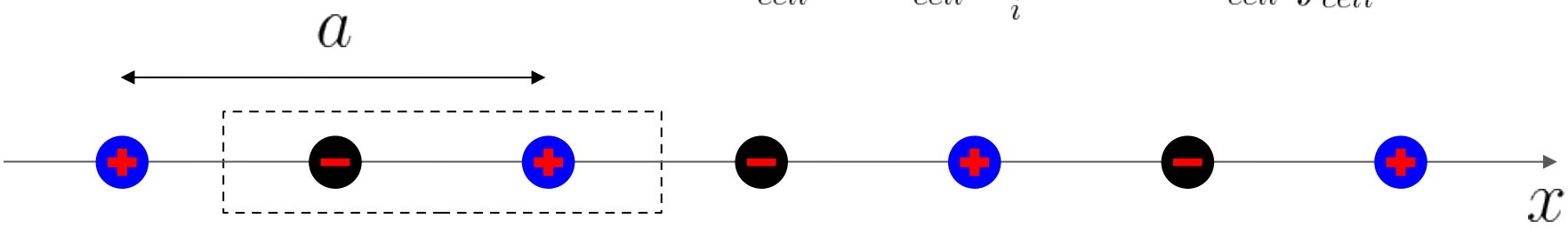
Spontaneous polarization



L. Martin, *Nature Reviews Materials* **2**, 16087 (2016)

Modern Theory of Polarization

$$\mathbf{p} = \frac{\mathbf{d}}{V_{cell}} = \frac{1}{V_{cell}} \sum_i q_i \mathbf{r}_i = \frac{1}{V_{cell}} \int_{cell} \mathbf{r}\rho(\mathbf{r}) d\mathbf{r}$$



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

In a bulk periodic system:

- Polarization forms a *lattice*

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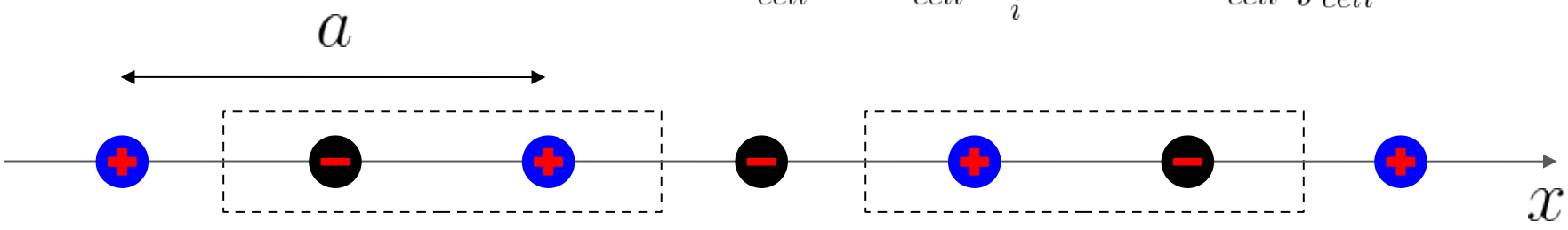

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$$p = \frac{d}{a} = \frac{1}{a}(1 \times \frac{a}{4} - 1 \times \frac{3a}{4}) = -\frac{1}{2}$$

In a bulk periodic system:

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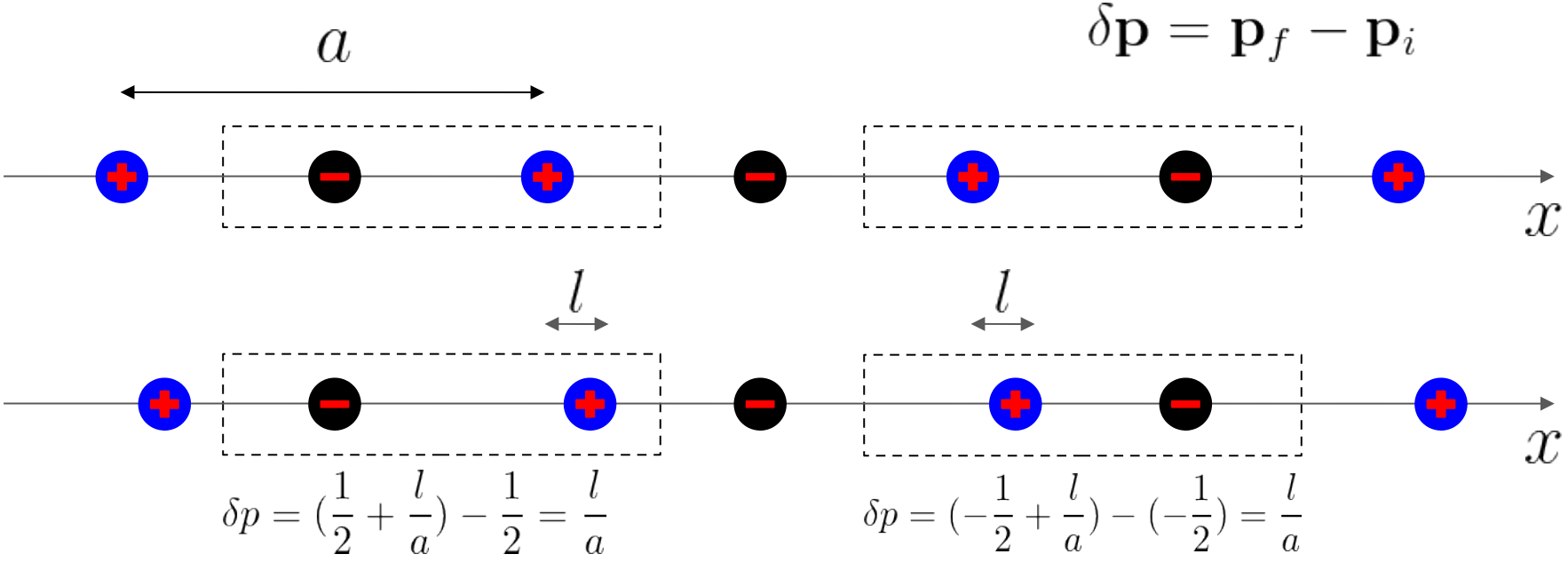
- Polarization is a *multi-valued* function and can only be defined *modulo* a *polarization quantum* $\mathbf{P}_q = e\mathbf{R}/V_{cell}$
- It is impossible to use knowledge of periodic charge distributions to give a unique value of polarization

Modern Theory of Polarization



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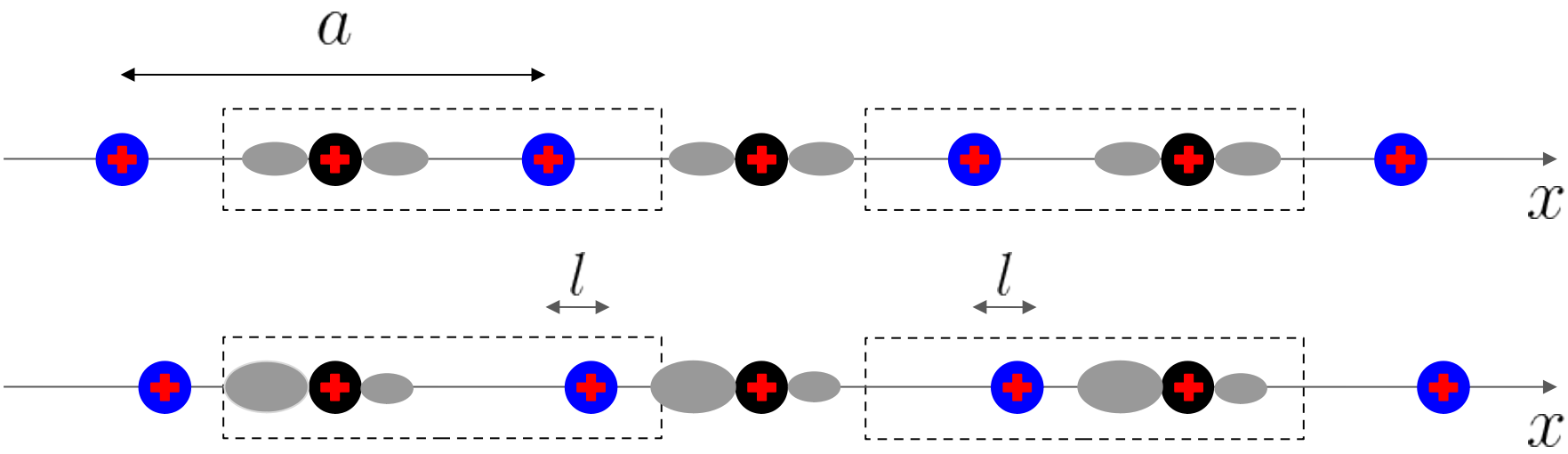
- It is impossible to use knowledge of periodic charge distributions to give a unique value of polarization
- *Change in polarization* is single-valued and well-defined; Experiments measure the change in polarization

Modern Theory of Polarization



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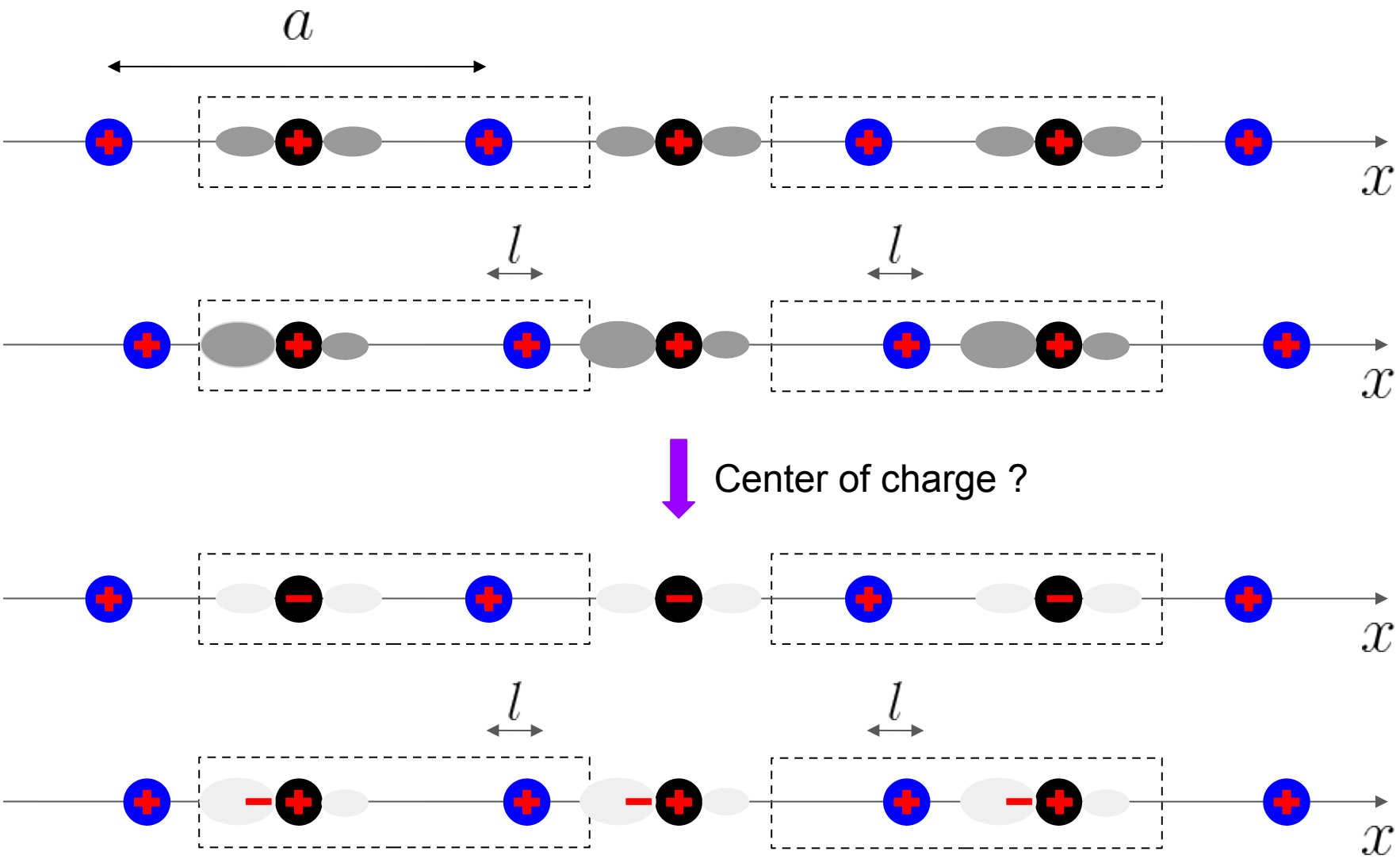
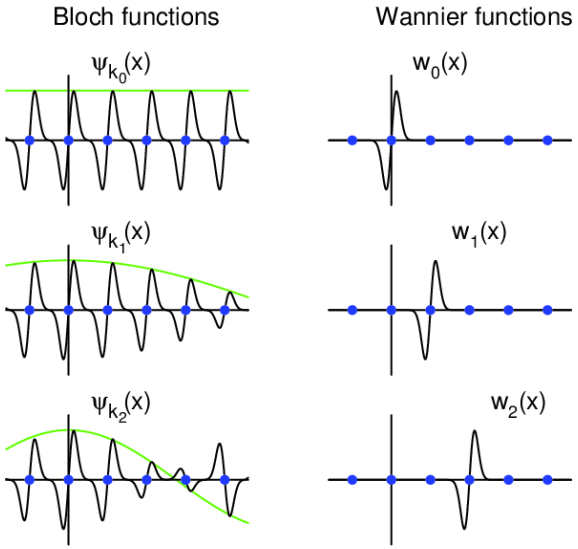


Modern Theory of Polarization



Bloch function: $$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r})$$

Wannier function:

$$w_{n\mathbf{R}}(\mathbf{r}) = w_n(\mathbf{r}-\mathbf{R}) = \frac{V_{cell}}{(2\pi)^3}\int_{BZ} d\mathbf{k} e^{-i\mathbf{k}\cdot\mathbf{R}} \psi_{n\mathbf{k}}(\mathbf{r})$$

Wannier charge center (WCC):

$$\bar{\mathbf{r}}_n = \int w_n^*(\mathbf{r})\mathbf{r}w_n(\mathbf{r})d\mathbf{r} = i\frac{V_{cell}}{(2\pi)^3}\int_{BZ} d\mathbf{k}\langle u_{n\mathbf{k}}|\nabla_{\mathbf{k}} u_{n\mathbf{k}}\rangle$$

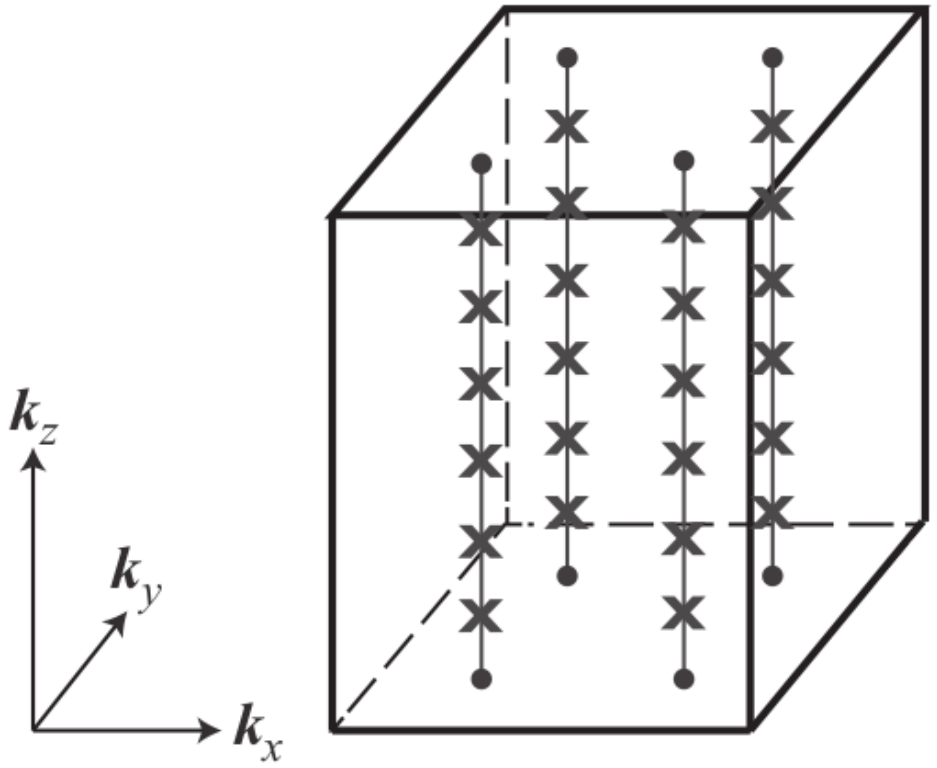
Berry phase $\frac{\varphi_n}{2\pi}$

Electronic polarization:

$$\mathbf{P}_e = \frac{-e}{V_{cell}}\sum_n^{occ} \bar{\mathbf{r}}_n$$

Formulation in discrete ***k***-space

$$\varphi_n = i \int d\mathbf{k} \langle u_{n\mathbf{k}} | \nabla_{\mathbf{k}} u_{n\mathbf{k}} \rangle = i \ln \prod_{j=0}^{N-1} \langle u_{n\mathbf{k}_j} | u_{n\mathbf{k}_{j+1}} \rangle$$



$$k_{||} = \frac{2\pi}{Na} j, \;\; j = 0, 1, ..., N-1$$

$$\varphi_n(k_{||}) = -\Im \ln \prod_{j=0}^{N-1} \langle u_{nk_j} | u_{nk_{j+1}} \rangle$$

$$\varphi_n = \frac{1}{N_{k_\perp}} \sum_{k_\perp} \varphi_n(k_{||})$$

$$\varphi_{nuc} = \sum_I Z_I^{nuc} s_I \quad \textit{(real space)}$$

$$P = (\sum_n \frac{\varphi_n}{2\pi} + \varphi_{nuc}) \times P_q$$

$$= \widetilde{P} + m \times P_q$$

Implementation in FHIaims

FHIaims use NAOs as basis functions

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mu} C_{n\mu}(\mathbf{k}) \sum_{p} e^{i\mathbf{k}\cdot\mathbf{R}_p} \phi^a_\mu(\mathbf{r}-\mathbf{R}_p)$$

$$\psi_{n\mathbf{k}}(\mathbf{r}+\mathbf{R}_q) = e^{i\mathbf{k}\cdot\mathbf{R}_q} \psi_{n\mathbf{k}}(\mathbf{r})$$

where $\boldsymbol{R}_p$ and $\boldsymbol{R}_q$ are lattice vectors.

The *overlap integral* between the *lattice-periodic* part of the Bloch function,

$$\begin{aligned}
\langle u_{nk_j} | u_{nk_{j+1}} \rangle &= \langle \psi_{nk_j} | e^{i(\mathbf{k}_{j+1}-\mathbf{k}_j)\cdot\mathbf{r}} | \psi_{nk_{j+1}} \rangle \\
&= \sum_{\nu\mu} C^*_{\nu,m}(\mathbf{k}_j) C_{\mu,n}(\mathbf{k}_{j+1}) \sum_{p,q} e^{i(\mathbf{k}_{j+1}\cdot\mathbf{R}_p - \mathbf{k}_j\cdot\mathbf{R}_q)} \langle \phi^b_\nu(\mathbf{r}-\mathbf{R}_q) | e^{i(\mathbf{k}_{j+1}-\mathbf{k}_j)\cdot\mathbf{r}} | \phi^a_\mu(\mathbf{r}-\mathbf{R}_p) \rangle \\
&\overset{\mathbf{k}_{j+1}-\mathbf{k}_j \approx \mathbf{0}}{=} \sum_{\nu\mu} C^*_{\nu,m}(\mathbf{k}_j) C_{\mu,n}(\mathbf{k}_{j+1}) \sum_{p,q} e^{i\mathbf{k}_j\cdot(\mathbf{R}_p-\mathbf{R}_q)} \langle \phi^b_\nu(\mathbf{r}-\mathbf{R}_q) | \phi^a_\mu(\mathbf{r}-\mathbf{R}_p) \rangle \\
&= \sum_{\nu\mu} C^*_{\nu,m}(\mathbf{k}_j) C_{\mu,n}(\mathbf{k}_{j+1}) S_{\nu\mu}(\mathbf{k}_j) \\
&\overset{\text{or}}{\neq} \sum_{\nu\mu} C^*_{\nu,m}(\mathbf{k}_j) C_{\mu,n}(\mathbf{k}_{j+1}) S_{\nu\mu}(\mathbf{k}_{j+1})
\end{aligned}$$

Good or *not* ?

Spontaneous polarization in BaTiO3

```
lattice_vector 3.994000  0.000000  0.000000
lattice_vector 0.000000  3.994000  0.000000
lattice_vector 0.000000  0.000000  4.036000
atom_frac   0.000000 0.000000 0.000000  Ba
atom_frac   0.500000 0.500000 0.500000  Ti
atom_frac   0.500000 0.500000 0.000000   O
atom_frac   0.500000 0.000000 0.500000   O
atom_frac   0.000000 0.500000 0.500000   O
```

Ref.: centrosymmetric

```
lattice_vector 3.994000  0.000000  0.000000
lattice_vector 0.000000  3.994000  0.000000
lattice_vector 0.000000  0.000000  4.036000
atom_frac   0.00000000 0.00000000 0.00000000  Ba
atom_frac   0.50000000 0.50000000 0.51517436  Ti
atom_frac   0.50000000 0.50000000 0.97356131   O
atom_frac   0.50000000 0.00000000 0.48343742   O
atom_frac   0.00000000 0.50000000 0.48343742   O
```

Exp.: non-centrosymmetric

$$P_q = \frac{eR_3}{V_{cell}} = 1.00437\ C/m^2$$

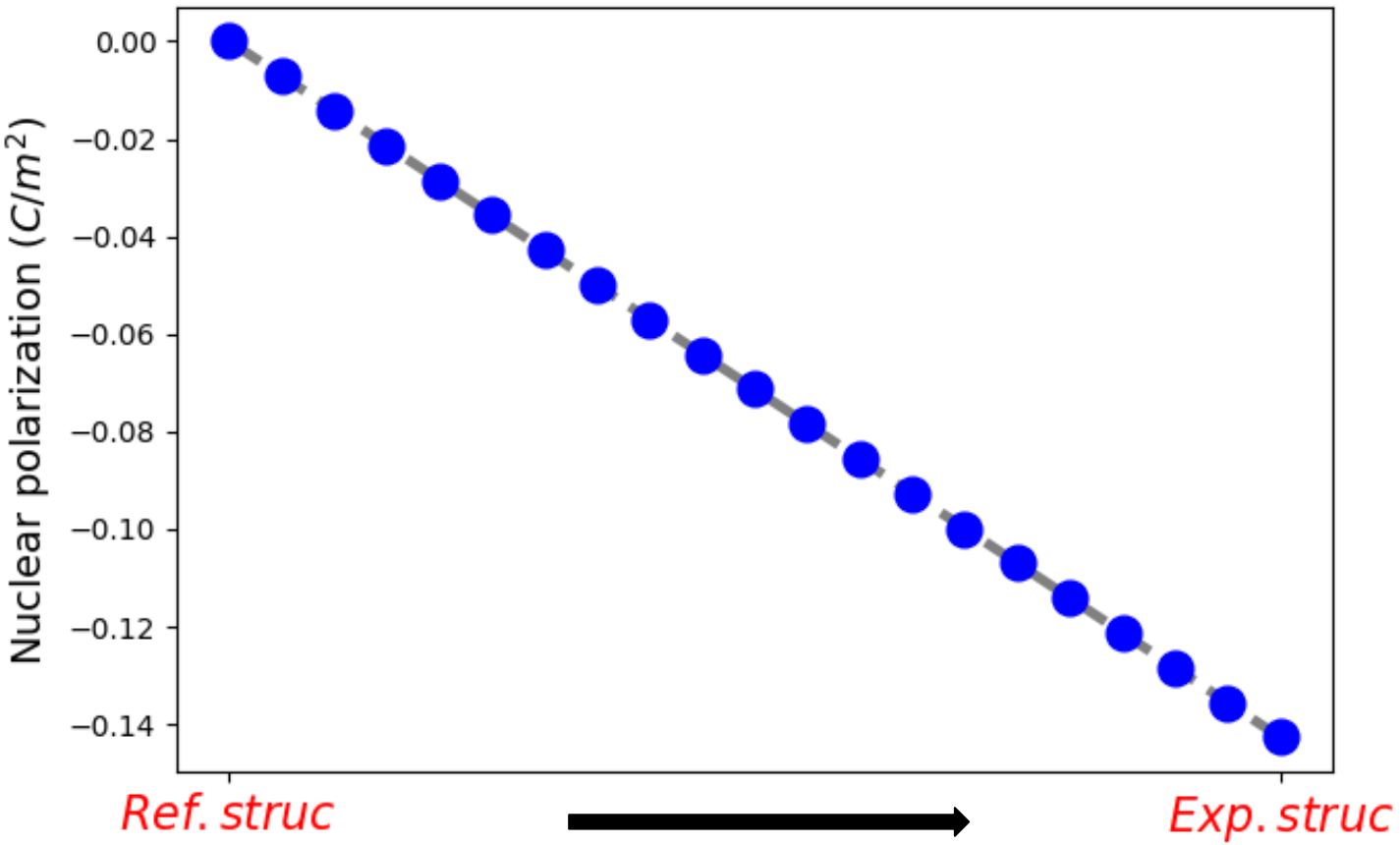
	φ_{nuc}	φ_e	φ
Ref. struc	0.0	0.314	0.314
Exp. struc	-0.143	0.023	-0.12

Spontaneous polarization (C/m^2) for perovskite compounds.

Compound	BerryPI	ABINIT	Experimental	Other calculations
$BaTiO_3$	0.31	0.28	0.26[a]	0.22[b], 0.29[c]

S. J. Ahmed, *Comp. Phys. Comm.* **184**, 647 (2013)

Spontaneous polarization in BaTiO3



Spontaneous polarization in BaTiO3