Polarization as a Berry phase

Most important reference followed in these notes
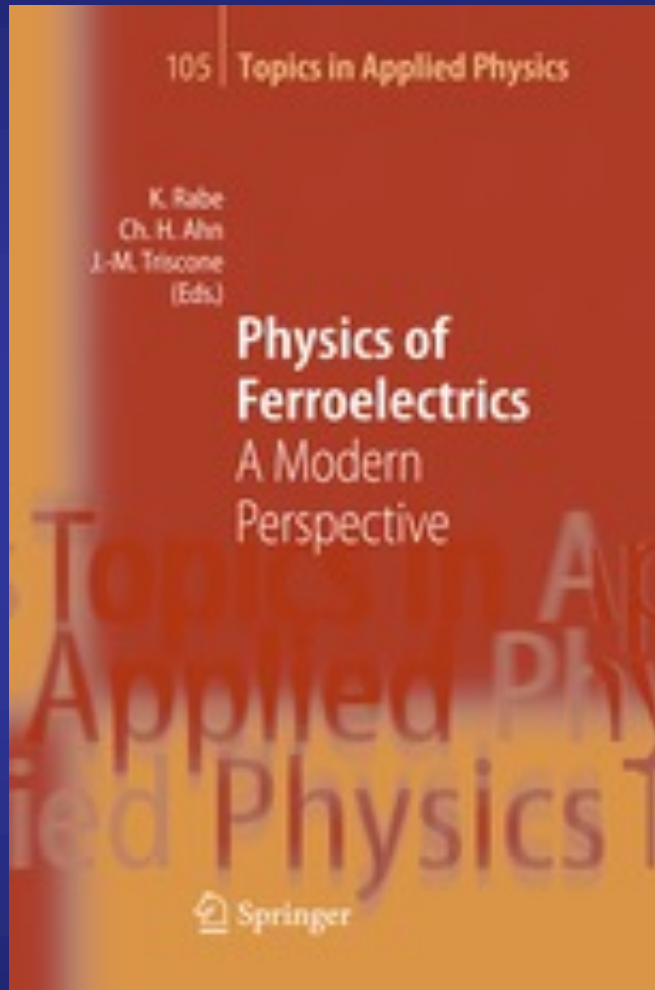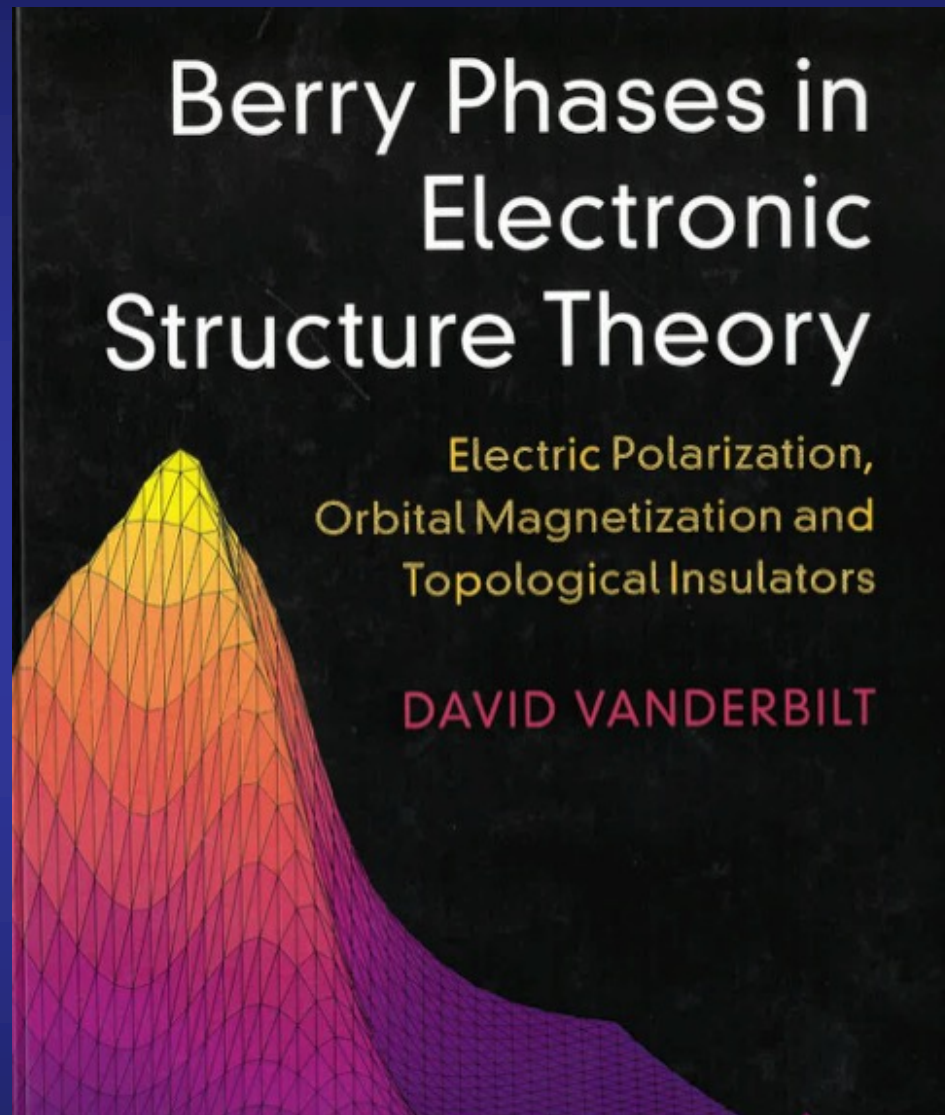

Chapter 2:
Theory of polarization: A modern approach.
R. Resta and D. Vanderbilt

Most important references followed in this lecture

Importance of the electric polarization

The macroscopic polarization is the most essential concept in
any phenomenological description of dielectric media

The macroscopic **polarization** is an **intensive vector quantity**
An intensive property is one whose magnitude is independent of the size of the system

Intuitively, carries the meaning of a electric dipole moment per unit volume

The presence of an spontaneous and switchable macroscopic polarization is the
defining property of a ferroelectric material

The macroscopic polarization is central to the whole physics of ferroelectrics

Despite its primary role in phenomenological theories and its overwhelming importance,
the macroscopic polarization has long evaded microscopic understanding

The standard picture:
the Clausius-Mossotti model
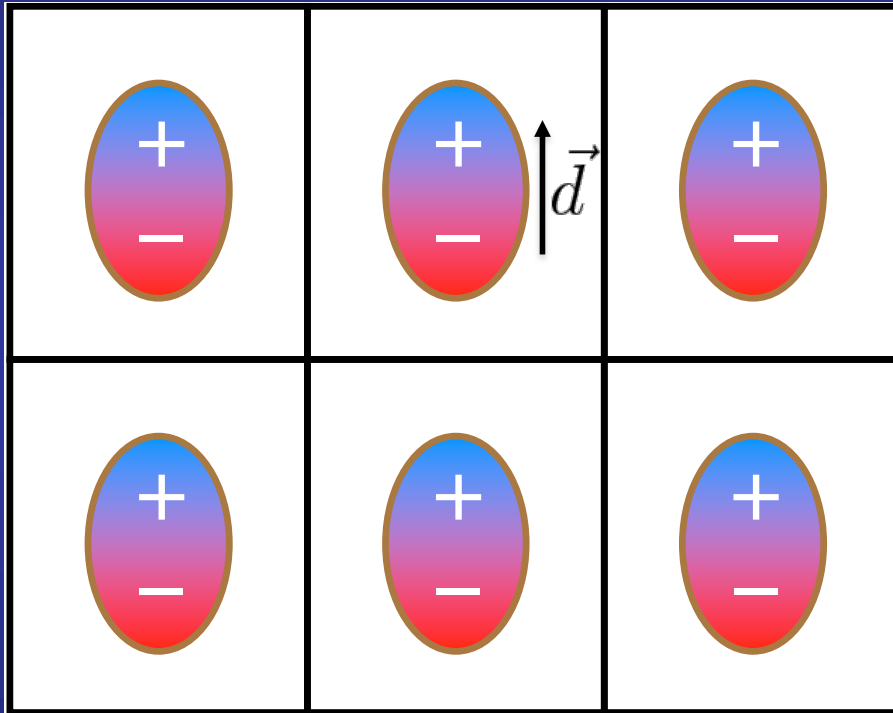
The presence of identifiable polarizable units is assumed

The charge distribution is regarded as the superposition of **localized contributions**, each providing an electric dipole $\vec{d}$
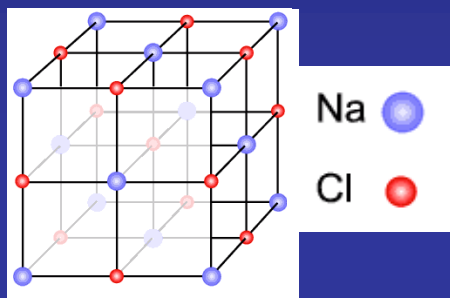
The Clausius-Mossotti macroscopic polarization is **defined** in a crystalline Claussius-Mossotti solid as

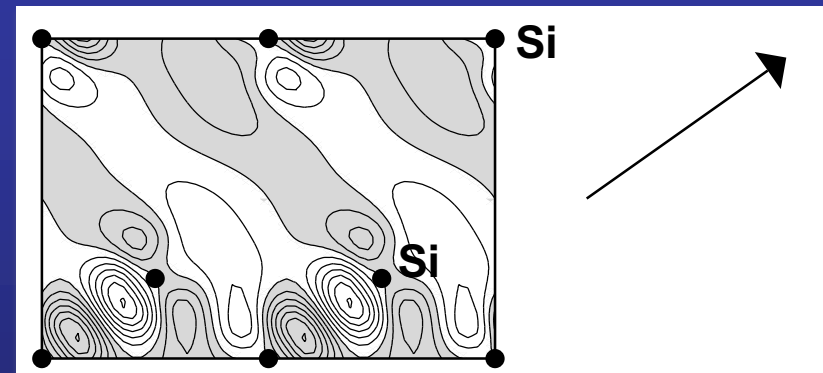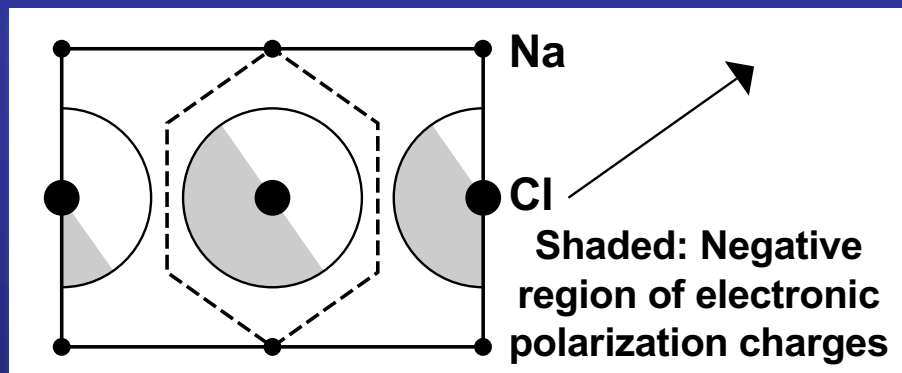$$\vec{P}_{\mathrm{CM}} = \frac{\vec{d}}{V_{\mathrm{cell}}}$$

The Claussius-Mossotti m[odel]
does not correspond to re[ality]

**Induced charge-density in th[e...]
by a constant field** $\mathcal{E}$

Bulk Si
(100) plane

Bulk Si
(111) plane

**Crystalline NaCl
Claussius-Mossotti picture**

Na
Cl

**Crystalline Si
First-principles result**

A

Na

Cl

**Shaded: Negative
region of electronic
polarization charges**

Si

Si
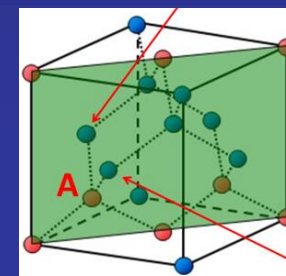
The central point behind the Claussius-Mossotti view is that the distribution of induced charge is resolved into contributions that can be ascribed to identifiable "polarization centers"

The electronic polarization charge in a crystal has a periodic continuous distribution which cannot be unambiguously partitioned into localized contributions

10

Fallacy of defining the polarization via the charge distribution

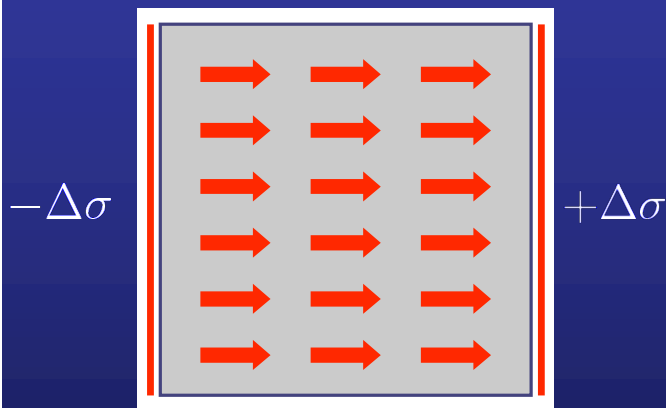**First trial: since** $\vec{P}$ **carries the meaning of dipole moment per unit volume, it is tempting to define it as** the dipole of the macroscopic sample divided by its volume

$$\vec{P}_{\text{sample}} = \frac{\vec{d}_{\text{sample}}}{V_{\text{sample}}} = \frac{1}{V_{\text{sample}}} \int_{\text{sample}} d\vec{r} \ \vec{r} \rho(\vec{r})$$

In order to apply this equation, we need to assume a macroscopic but finite crystal

But then the integral has contributions of both the surface and the bulk regions, that are difficult to disentangle

Imagine a cubic sample of dimensions $L \times L \times L$

$-\Delta\sigma$ $+\Delta\sigma$

The surface preparation changes in such a way that a new surface charge density $+\Delta\sigma$ **appears on the right surface face and** $-\Delta\sigma$ **on the left**

Its surface preparation changes might mean:
- Adsorption of some molecules from the ambient
- Oxydation
- Surface reconstruction

Fallacy of defining the polarization via the charge distribution

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$-\Delta\sigma$

Imagine a cubic sample of dimensions $L \times L \times L$

The surface preparation changes in such a way
that a new surface charge density $+\Delta\sigma$ **appears**
on the right surface face and $-\Delta\sigma$ **on the left**

This results in a change in the dipole moment scaling as L^3

$$\Delta\vec{P} = \frac{1}{L^3}\left(\Delta\sigma \times L^2\right) \times L = \Delta\sigma$$
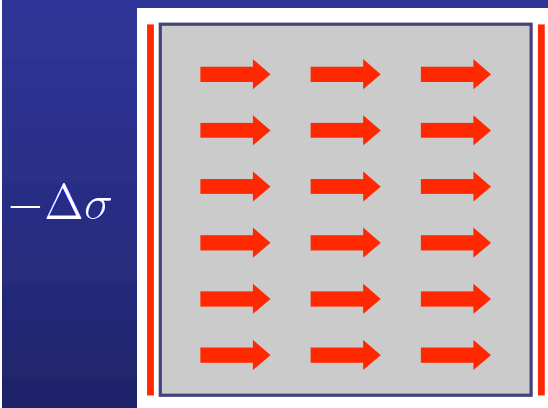
Fallacy of defining the polarization via the charge distribution

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Imagine a cubic sample of dimensions $L \times L \times L$

$-\triangle\sigma$ $+\triangle\sigma$

The surface preparation changes in such a way
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And then in a change in $\vec{P}_{\text{sample}}$ **despite the fact that the conditions in the interior**
have not changed. This is not an useful bulk definition of the polarization
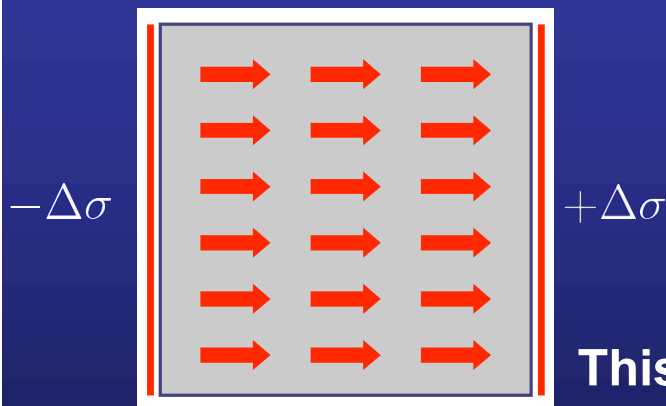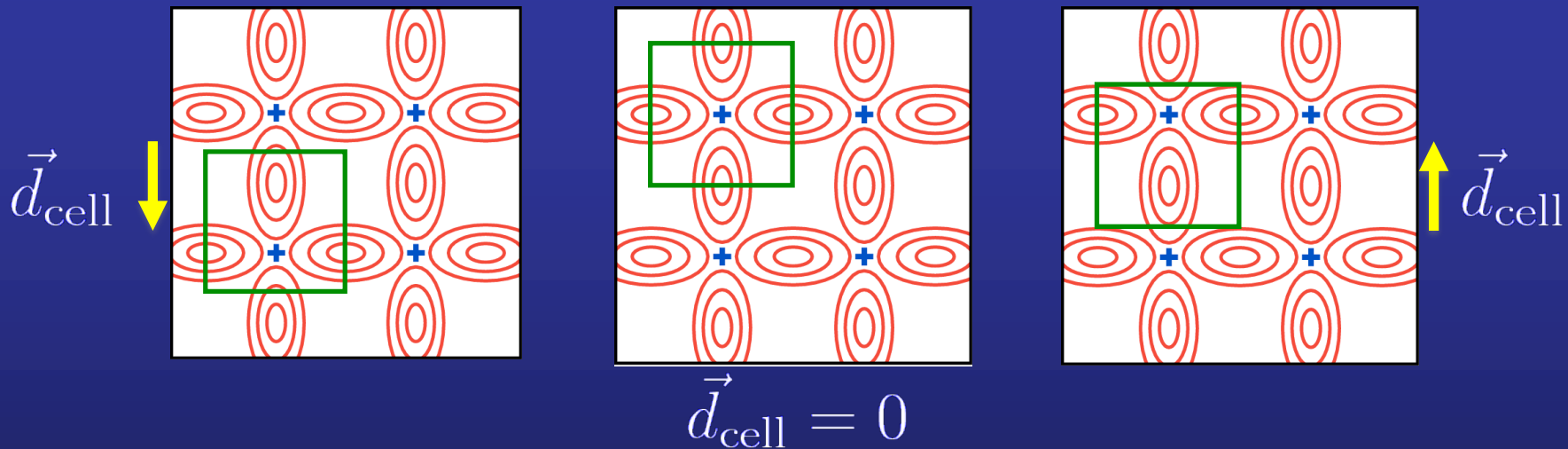
Fallacy of defining the polarization via the charge distribution

Second trial: since $\vec{P}$ carries the meaning of dipole moment per unit volume, it is tempting to define it as the dipole of one unit cell divided by the volume of the unit cell

$$\vec{P}_{\text{cell}} = \frac{\vec{d}_{\text{cell}}}{V_{\text{cell}}} = \frac{1}{V_{\text{cell}}} \int_{\text{cell}} d\vec{r}\ \vec{r} \rho(\vec{r})$$

The integration is carried out on one unit cell well in the interior of the sample

$\vec{d}_{\text{cell}}$ $\vec{d}_{\text{cell}} = 0$ $\vec{d}_{\text{cell}}$

The result depends on the shape and location of the unit cell

The average of $\vec{P}_{\text{cell}}$ over all possible translational shifts vanishes

Fallacy of defining the polarization via the charge distribution

Third trial: define $\vec{P}$ as the cell average of a microscopic polarization

$$\nabla \cdot \vec{P}_{\text{micro}} = -\rho(\vec{r})$$

But this equation does not uniquely define $\vec{P}_{\text{micro}}$.
Any divergence free vector field (for instance, a constant field) can be added to $\vec{P}_{\text{micro}}$ **without affecting the left-hand side**

More over…

$$\vec{P} = \Omega^{-1} \int_{\text{cell}} \vec{P}(\vec{r}) \, d^3r, \qquad \vec{\nabla} \cdot \vec{P}(\vec{r}) = -\rho(\vec{r}), \qquad \vec{P} = \Omega^{-1} \int_{\text{cell}} \vec{r} \rho(\vec{r}) \, d^3r + \Omega^{-1} \int_{\text{surface}} \vec{r} \left[\hat{n} \cdot \vec{P}(\vec{r}) \right] ds,$$

Macroscopic polarization

Bulk term that depends on the charge density

Integral over the surface charge density. Charge transferred across the cell boundary

The two terms depend on the choice of the unit cell. Only the sum is invariant
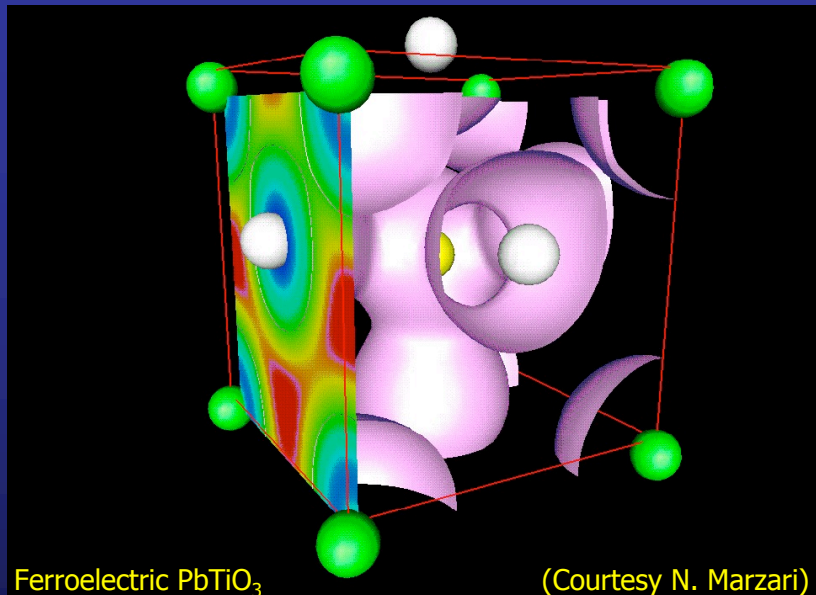
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Third trial: define $\vec{P}$ as the cell average of a microscopic polarization

$$\nabla \cdot \vec{P}_{\mathrm{micro}} = -\rho(\vec{r})$$

$$\vec{P}_{\mathrm{cell}} = \frac{1}{V_{\mathrm{cell}}} \int_{\mathrm{cell}} d\vec{r} \ \vec{r}\rho(\vec{r}) + \frac{1}{V_{\mathrm{cell}}} \int_{\mathrm{surface}} \vec{r}\left[\hat{n} \cdot \vec{P}_{\mathrm{micro}}(\vec{r})\right] dS \qquad \nabla \cdot \vec{P}_{\mathrm{micro}} = -\rho(\vec{r})$$

The integration is carried out on one unit cell well in the interior of the sample

Ferroelectric PbTiO₃   (Courtesy N. Marzari)

$\vec{P}_{\mathrm{cell}}$ **is well defined only within a extreme Claussius-Mossotti model, where the periodic charge can be decomposed with no ambiguity by chosing the cell boundary to lie in an interstitial region of vanishing charge density**

In many materials, a Claussius-Mossotti model is completely inappropriate

Fallacy of defining the polarization via the charge distribution

It is impossible to obtain the value of $\vec{P}$ from the induced charge density alone

A knowledge of the periodic electronic charge distribution in a polarized crystalline solid cannot, even in principle, be used to construct a meaningful definition of the polarization

This message has not reached the most popular textbooks

Ch. Kittel
Introduction to Solid State Physics
John Wiley and Sons

Polarization

The polarization P is defined as the **dipole moment per unit volume**, averaged over the volume of a cell. The total dipole moment is defined as

$$p = \Sigma q_n r_n \,, \tag{1}$$

where r_n is the position vector of the charge q_n. The value of the sum will be independent of the origin chosen for the position vectors, provided that the system is neutral. The dipole moment of a water molecule is shown in Fig. 1.

Counterintuitive and disturbing conclusion:
The macroscopic polarization in the bulk region of a solid should be determined by what "happens" in the bulk

Solution: focus on the CHANGE in $\vec{P}_{\mathrm{sample}}$ that occurs during some process

$$\Delta \vec{P} = \int dt \frac{1}{V_{\mathrm{cell}}} \int_{\mathrm{cell}} d\vec{r}\, \vec{j}(\vec{r}, t)$$

Polarization as an adiabatic flow of current

Most measurements of bulk macroscopic polarization of materials do not access its absolute value, but only its derivatives

Electrical permittivity

$$\chi_{\alpha\beta} = \frac{\partial P_\alpha}{\partial \mathcal{E}_\beta}$$

Pyroelectric coefficients

$$\Pi_\alpha = \frac{dP_\alpha}{dT}$$

Piezoelectric tensors

$$\gamma_{\alpha\beta\delta} = \frac{\partial P_\alpha}{\partial \epsilon_{\beta\delta}}$$

Born effective charges

$$Z^*_{s,\alpha\beta} = \frac{V_{\text{cell}}}{e} \frac{\partial P_\alpha}{\partial u_{s,\beta}}$$

Fundamental equation of the modern theory of polarization

$$\frac{d\vec{P}}{dt} = \vec{j}$$

$\vec{j}$ **is the macroscopic (cell averaged) current density**

$$\Downarrow$$

$$\Delta\vec{P} = \vec{P}(\Delta t) - \vec{P}(0) = \int_0^{\Delta t} dt\, \vec{j}(t)$$

In the adiabatic limit:

$\vec{j}$ **goes to zero**

Δt **goes to infinity**

So the integral stays finite

The induced macroscopic polarization in condensed matter can be defined in terms of adiabatic flows of currents within the materials

The value of the macroscopic polarization is determined by what happens in the bulk of the solid, being insensitive to the surface

Basic prescriptions for a theory of polarization

Let us introduce a parameter λ having the meaning of a dimensionless adiabatic time

λ varies continously between:
- An "initial state" ($\lambda = 0$), i.e. the state of the system before the application of some perturbation (sublattice displacement, strain, electric field, etc).
- A "final state" ($\lambda = 1$), i.e. the state of the system after the application of the perturbation

$$\Delta \vec{P} = \int_0^1 d\lambda \frac{d\vec{P}}{d\lambda}$$

This is a well defined bulk vector property.
It directly corresponds with the response properties

Important: the transient current has to be due only to the change in the polarization.
The system has to remain insulating for all the intermediate values of λ.
If not, an extra contribution to the current not uniquely defined will contribute

Basic prescriptions for a theory of polarization:
Case of the spontaneous polarization of a ferroelectric

λ **scale the sublattice displacements**

λ **varies continously between:**
- **An "initial state" (** $\lambda = 0$ **), i.e. the state of the system in a centrosymmetric reference structure**
- **A "final state" (** $\lambda = 1$ **), i.e. the state of the system in the spontaneously polarized structure**

$$\vec{P}_{\text{eff}} = \int_0^1 d\lambda \frac{d\vec{P}}{d\lambda} \qquad (\lambda = 0 : \text{centrosymmetric reference})$$

For the case of pyroelectricity, piezoelectricity (measured in a shorted capacitor), dynamical charges, and spontaneous polarization, the derivative is taken at zero electric field

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$$\vec{P}_{\text{eff}} = \int_0^1 d\lambda \frac{d\vec{P}}{d\lambda} \qquad (\lambda = 0 : \text{centrosymmetric reference})$$

This is related with a current.

The current carrying particles are:
- **Nuclei: can be safely dealt with as classical point charges whose contributions are trivial**
- **Electrons: quantum nature is essential**

Formal description of the Berry-phase approach: Formulation in continuous k-space

R. D. King-Smith and David Vanderbilt

Department of Physics and Astronomy, Rutgers University, P. O. Box 849, Piscataway, New Jersey 08855-0849

(Received 10 June 1992)

$$\frac{d\vec{P}_{el}(\lambda)}{d\lambda} = \frac{ife\hbar}{mV_{\text{sample}}} \sum_{\vec{k}} \sum_{n=1}^{M} \sum_{m=M+1}^{\infty} \left(\frac{\langle \psi_{\vec{k},n}^{(\lambda)}|\vec{p}|\psi_{\vec{k},m}^{(\lambda)}\rangle \langle \psi_{\vec{k},m}^{(\lambda)}|\frac{\partial V_{KS}^{(\lambda)}}{\partial \lambda}|\psi_{\vec{k},n}^{(\lambda)}\rangle}{\left(\varepsilon_{\vec{k},n}^{(\lambda)} - \varepsilon_{\vec{k},m}^{(\lambda)}\right)^2} + \text{c.c.} \right)$$

This derivative is a well defined bulk-vector property

The total change in polarization can be computed as a the integral as a function of the parameter λ that changes continuously and adiabatically betweeen an initial state $(\lambda = 0)$ and a final state $(\lambda = 1)$

$$\Delta \vec{P} = \int_0^1 \frac{\partial \vec{P}}{\partial \lambda} d\lambda$$

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$$\Delta \vec{P} = \int_0^1 \frac{\partial \vec{P}}{\partial \lambda} d\lambda$$

But who is

$$\vec{P}_{\text{el}}(\lambda)$$

The central result of the modern theory of polarization

$$\vec{P}_{\text{eff}} = \Delta \vec{P}_{\text{ion}} + \left[\vec{P}_{\text{el}}(1) - \vec{P}_{\text{el}}(0) \right]$$

The trivial nuclear contribution $\Delta \vec{P}_{\text{ion}}$ has been restored

Formal description of the Berry-phase approach: Formulation in continuous k-space

$$\vec{P}_{\text{eff}} = \Delta\vec{P}_{\text{ion}} + \left[\vec{P}_{\text{el}}(1) - \vec{P}_{\text{el}}(0)\right]$$

Central result of the modern theory of polarization

$$\vec{P}_{\text{el}}(\lambda) = \frac{fe}{(2\pi)^3}\,\Im\sum_{n=1}^{M}\int_{\text{BZ}} d\vec{k}\,\langle u_{\vec{k}n}^{(\lambda)}|\nabla_{\vec{k}}|u_{\vec{k}n}^{(\lambda)}\rangle$$

$$\vec{A}(\vec{k}) = i\langle u_{\vec{k}n}^{(\lambda)}|\nabla_{\vec{k}}|u_{\vec{k}n}^{(\lambda)}\rangle$$ **"Berry connection" or "gauge potential"**

Its integral over a close manifold (here the Brillouin zone) is known as a "Berry phase"

The result is independent of the path traversed through parameter space. It depends only on the end-points.
Implicitly, we assume that the system must remain insulating everywhere along the path (we remain in the adiabatic approximation)

Electronic polarization as a Berry phase.
Discretize equation (in 1D)

$$P_{\text{el}}(\lambda) = \frac{fe}{2\pi} \sum_{n=1}^{M} \Im \left[\ln \prod_{j=0}^{N_k-1} \langle u_{k_j n}^{(\lambda)} | u_{k_{j+1} n}^{(\lambda)} \rangle \right]$$

In this equation we have to compute the global product of wavefunctions across the Brillouin zone

$$\ldots \langle u_{k_1 n}^{(\lambda)} | u_{k_2 n}^{(\lambda)} \rangle \langle u_{k_2 n}^{(\lambda)} | u_{k_3 n}^{(\lambda)} \rangle \langle u_{k_3 n}^{(\lambda)} | u_{k_4 n}^{(\lambda)} \rangle \ldots$$

In general, this is a complex number
**The operation $\Im \ln$ takes the phase of this number**

This phase is insensitive to a change of any of the wavefunctions $|u_{k_j n}^{(\lambda)}\rangle$ since each $|u_{k_j n}^{(\lambda)}\rangle$ appears once in bra and once in a ket.

The Berry phase φ_n gives the contribution to the polarization arising from band n, as a global phase property of the manifold of occupied one-electron states

Electronic polarization: formulation in 3D

To compute $\varphi_{n,j} = \dfrac{1}{\Omega_{\mathrm{BZ}}} \Im \displaystyle\int_{\mathrm{BZ}} d^3k \langle u_{\vec{k},n} | \vec{G}_j \cdot \nabla_{\vec{k}} | u_{\vec{k},n} \rangle$

The sampling of the Brillouin zone is arranged as
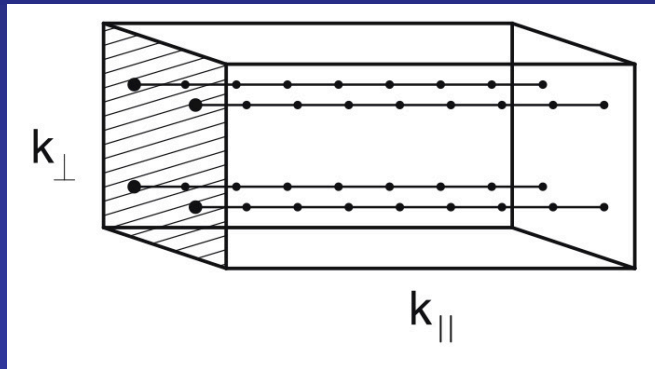
$k_\parallel$ is the direction along $\vec{G}_j$

$\vec{k}_\perp$ refers to the 2D space of wavevectors spanning the other two primitive reciprocal lattice vectors

For a given $\vec{k}_\perp$ **the Berry phase is computed along the string of M k-points extending along** $k_\parallel$ **as in the one-dimensional case**

```
%block PolarizationGrids
  20  4   4  yes
   4 20   4  yes
   4  4  20  yes
%endblock PolarizationGrids
```

Formal polarization as a multivalued vector quantity

The question, what is $\vec{P}$ is answered not by giving a single-vector, but a lattice of vectors related by translations $\dfrac{e\vec{R}}{\Omega}$
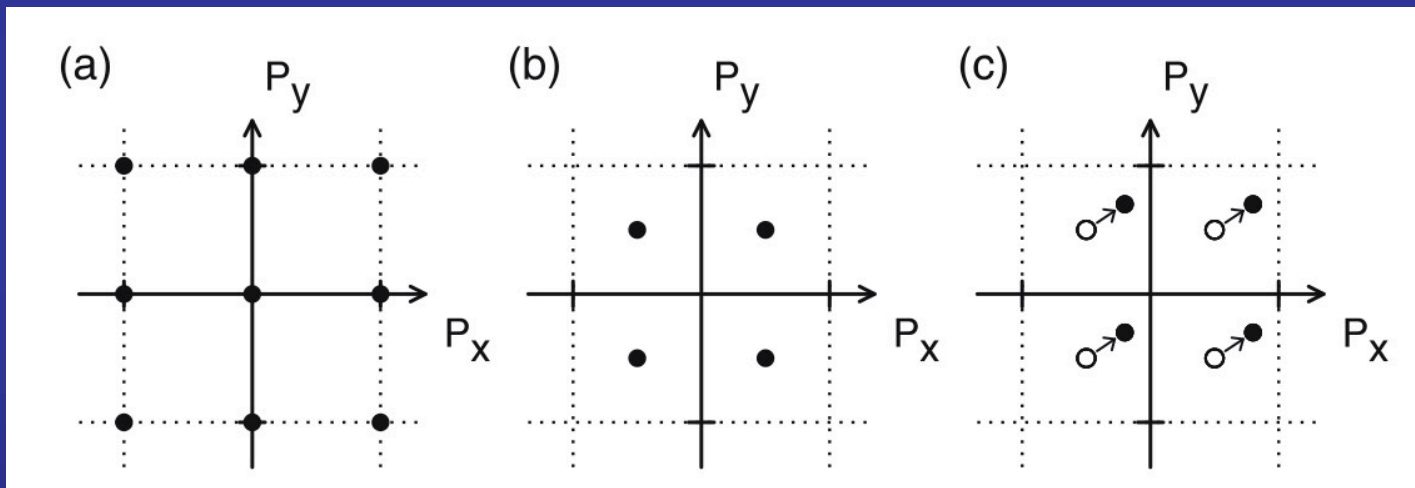
Central result of the modern theory of polarization

The formal polarization

$$\vec{P} = \vec{P}_{\text{el}} + \vec{P}_{\text{ion}} = \frac{fe}{(2\pi)^3} \Im \sum_{n=1}^{M} \int_{\text{BZ}} d\vec{k} \, \langle u_{\vec{k}n}^{(\lambda)} | \nabla_{\vec{k}} | u_{\vec{k}n}^{(\lambda)} \rangle + \frac{e}{V_{\text{cell}}} \sum_{s} Z_s^{\text{ion}} \vec{r}_s$$

is only well-defined $\mod \dfrac{e\vec{R}}{\Omega}$

where:

$\vec{R}$ **is a any lattice vector**

Ω **is the primitive-cell volume**