Berry phases and the (modern) theory of polarization

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No affiliation

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Outline

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Main tenet of polarization theory

- For a bounded sample **P** is a (trivial) **vector** :

$$\mathbf{P} = \frac{1}{V} \int d\mathbf{r}\, \mathbf{r}\rho(\mathbf{r})$$

- Within Born-von-Kàrmàn PBCs:

- Insofar as PBCs are adopted
  P is a **lattice**: arbitrary by a “quantum”

- For a large bounded sample the vector **P** converges to one of the lattice values: which one? It depends on termination!
- **Caveat:** Even the surfaces must be **insulating**!

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Three manifestations of polarization

1. Polarization linearly induced by some perturbation: $\partial \mathbf{P} / \partial \lambda$
   (problem solved long ago by linear response & DFPT)

2. Polarization difference $\Delta \mathbf{P}$ between two structures
   (as measured since decades in ferroelectric oxides)

3. Polarization “itself” (a.k.a. “formal” polarization)

[1] Linearly induced polarization $\partial \mathbf{P}/\partial\lambda$

- Examples:
  - Permittivity

$$\overleftrightarrow{\epsilon}_{\infty} = \overleftrightarrow{1} + 4\pi \frac{\partial \mathbf{P}}{\partial \mathbf{E}}, \qquad \mathbf{E} \text{ is the internal (screened) field}$$

  - Born effective-charge tensors

$$\overleftrightarrow{Z}^{*}_{s} = \frac{\partial \mathbf{P}}{\partial \mathbf{R}_{s},}, \quad \mathbf{E} = 0$$

- What is **actually** computed (by LRT, DFPT)?

$$\frac{\partial \mathbf{P}}{\partial \lambda} = \frac{\partial \mathbf{P}/\partial t}{\partial \lambda/\partial t} = \frac{\mathbf{j}}{\dot{\lambda}} \quad \text{current density induced by } \dot{\lambda}$$

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Notice:
$\mathbf{E} = 0$ is a boundary condition for integrating Poisson Eq.

- Besides insulating crystals, it applies at it stands to:
  - Charge transport in insulating liquids (Grasselli & Baroni, Nature Phys. 2019)
  - Inertia of the many-electron system in metals (Dreyer, Coh, & Stengel, PRL 2022)

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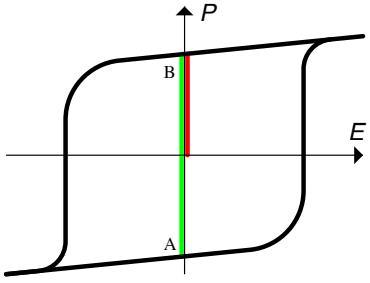
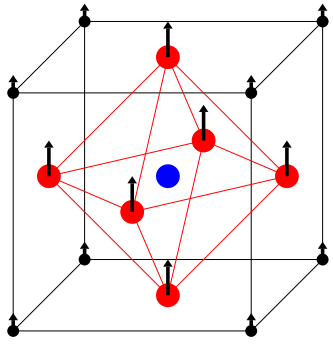
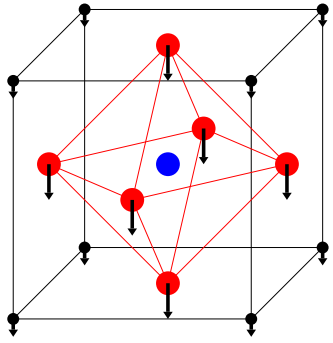
[2] Polarization difference $\Delta\mathbf{P}$

- Experimental definition of "spontaneous" **P** in ferroelectrics:





A



B

The observable is the **integrated transient current**:

$$\mathbf{P} = \frac{1}{2}\int_A^B \mathbf{j}(t)\, dt$$

- Can it be evaluated with a two-point formula?

$$\mathbf{P} = \frac{1}{2}(\mathbf{P}_B - \mathbf{P}_A), \quad \mathbf{E} = 0$$

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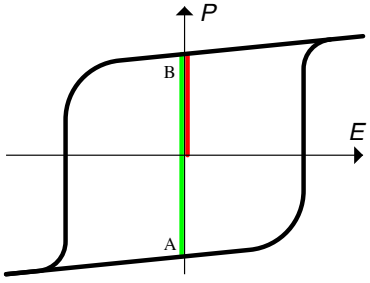

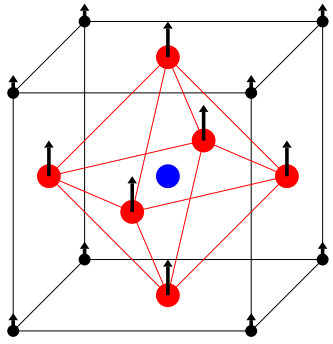

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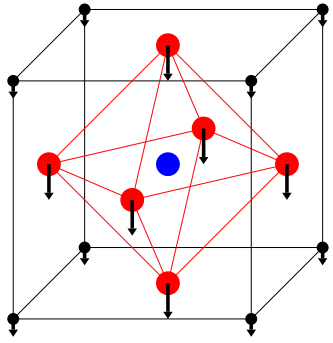

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[3] The Berry-phase theory (formerly called "modern")

King-Smith & Vanderbilt, PRB 1993; Vanderbilt & King-Smith, PRB 1993

- **P** is a Berry phase of the Bloch orbitals
  A phase is arbitrary mod 2π
  P is arbitrary mod 2π (rescaled to dimensionless units)
- The polarization "quantum"
  - In 1D the quantum is e
  - In 2D and 3D the quantum is $e \times \frac{\text{lattice vector}}{\text{cell volume}}$
  - Polarization is **a lattice**
- In inversion-symmetric crystals:
  - $\mathbf{P} \neq 0$
  - The **polarization lattice** is inversion-symmetric
  - In quasi-1D (stereoregular polymers)
    P is a $\mathbb{Z}_2$ topological invariant:
    - either $P = 0 \bmod e$ ($\mathbb{Z}_2$-even)
    - or $P = e/2 \bmod e$ ($\mathbb{Z}_2$-odd)

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The cell-volume pitfall

- **To nonbelievers:**
  The cell volume is somewhat arbitrary.....
  Is **P** a **uniquely defined** multivalued property?

- Go back to KIttel, Chapter 1 (my emphasis in red)
  - "The set of **mathematical points** to which the basis is attached is called the lattice"
  - "**of course** the lattice points are just **mathematical constructions**"
  - "A primitive cell is a **minimum-volume cell**"
  - "There is always one lattice point for primitive cell"

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What is a crystal?

- Whenever a solid is **crystalline**, its Bravais lattice is unique even when a supercell is needed for computation:
  - Interacting electrons
  - Finite temperature
  - Quantum nuclei
  - Chemical disorder (i.e. solid solutions)
- Lattice defined as the appropriate average (if needed):

Amorphous & liquid systems

- Polarization “itself” is **ill defined**
- Polarization **derivatives** and **differences** are well defined
- Infrared spectra of liquids routinely computed via the **single-point Berry phase** (©Resta1998):
  - Fourier transform of **P** autocorrelation function
  - Car-Parrinello simulations on a supercell
  - The supercell “quantum” is quite small
  - $\Delta\mathbf{P} = \mathbf{P}(t + \Delta t) - \mathbf{P}(t)$ on a CP time step is much smaller!
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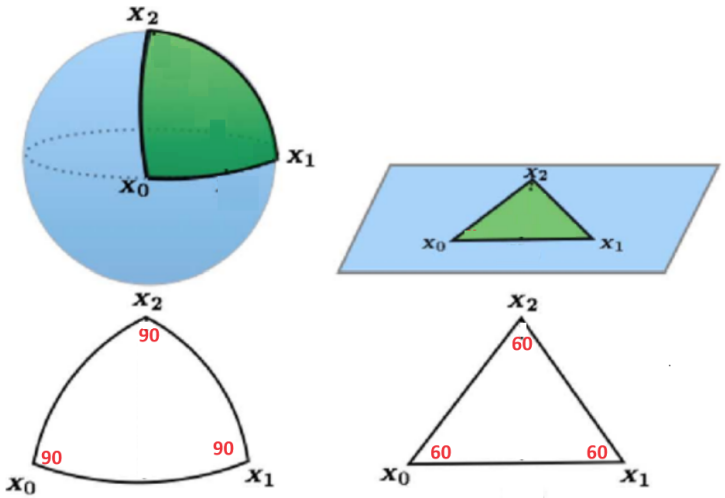
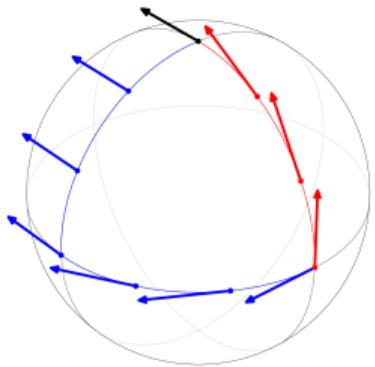
A simple “curved space”



An ant crawling on a 2D surface (space):
How can it discover whether it is flat or curved?

Theorema egregium (Gauss, 1827)

Gaussian curvature
of a spherical surface $K = 1/R^2$



Integrated over an octant:

$$\int_\Sigma d\sigma\ K = \frac{1}{8} \times 4\pi R^2 \times \frac{1}{R^2} = \frac{\pi}{2}$$

- Sum of the three angles:

$$\alpha_1 + \alpha_2 + \alpha_3 = \pi + \gamma = \pi + \int_\Sigma d\sigma\ K$$

- Angular mismatch for parallel transport:

$$\gamma = \int_\Sigma d\sigma\ K$$

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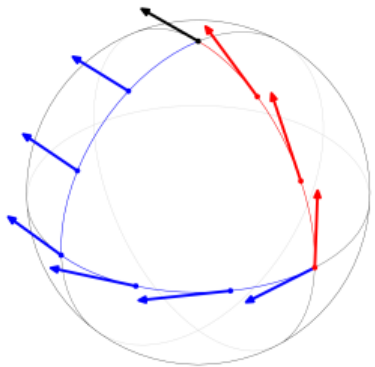

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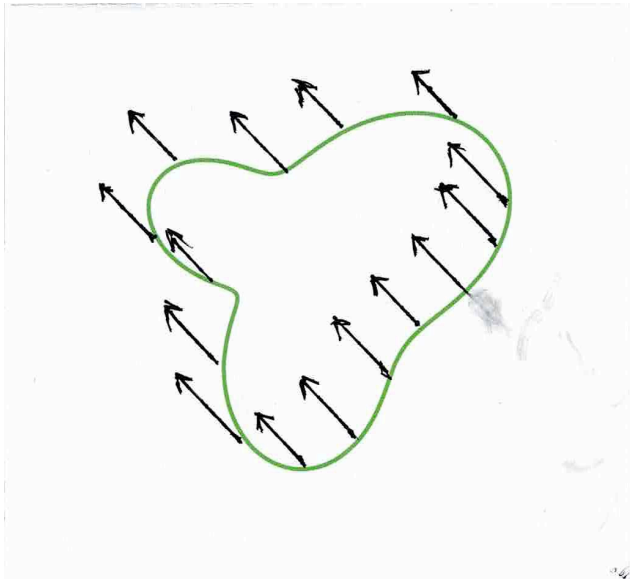

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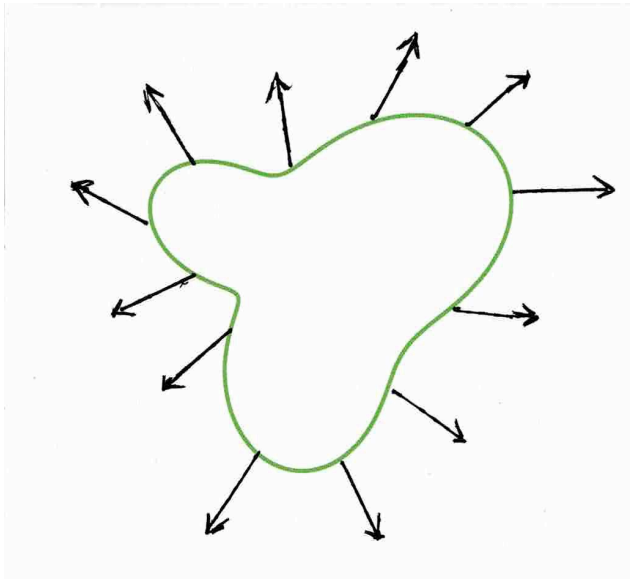

Arbitrary transport

Theorema egregium: $$\gamma = \oint_{\partial\Sigma} d\phi = \int_{\Sigma} d\sigma\, K \mod 2\pi$$

What happens if Σ is a **closed surface** (i.e. no $\partial\Sigma$ to speak of)?

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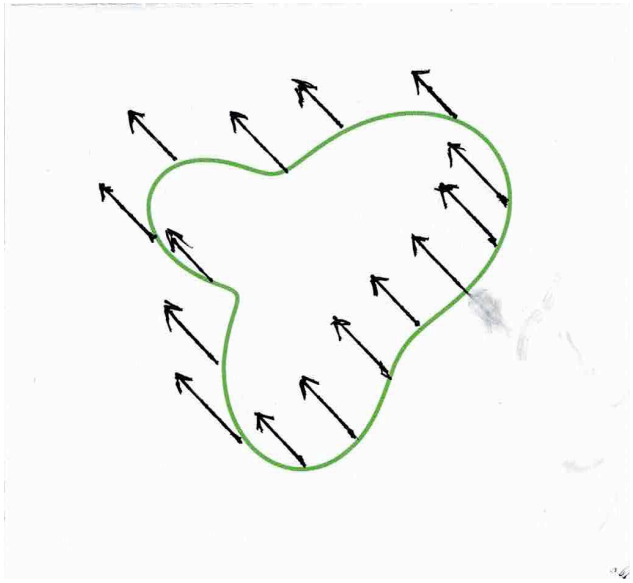

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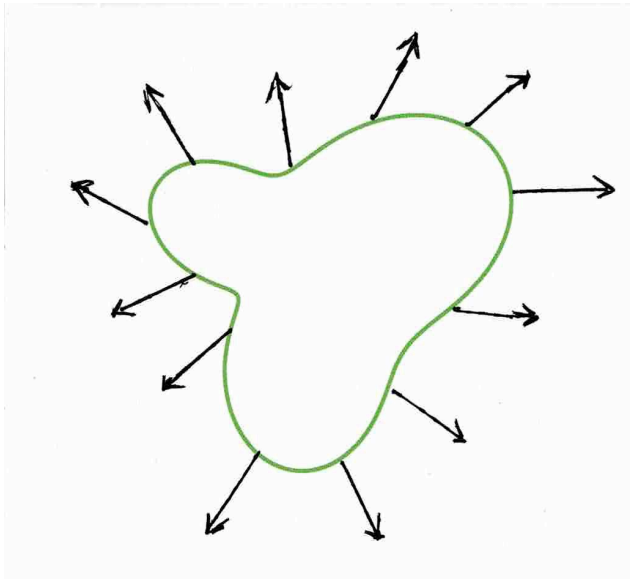

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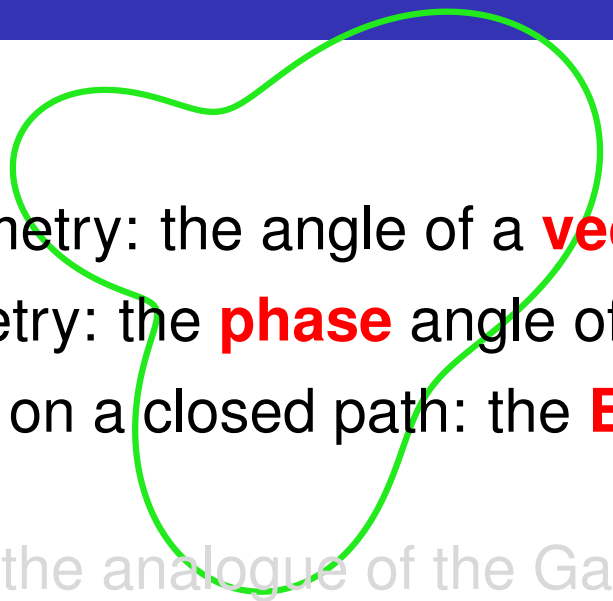

Holonomy:

- In differential geometry: the angle of a **vector**
- In quantum geometry: the **phase** angle of a **state vector**
- Angular mismatch on a closed path: the **Berry phase** γ

The Berry curvature is the analogue of the Gaussian curvature

- In differential geometry $\gamma = \oint_{\partial\Sigma} d\phi = \int_{\Sigma} d\sigma \; K$
- In quantum geometry $\gamma = \oint_{\partial\Sigma} d\phi = \int_{\Sigma} d\kappa d\lambda \; \Omega(\kappa, \lambda)$
- Σ domain included by the closed path $\partial\Sigma$

Berry curvature = Berry phase per unit area

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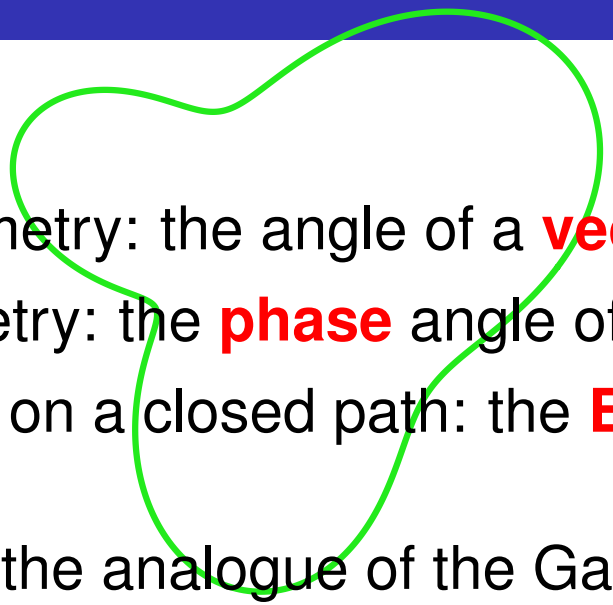

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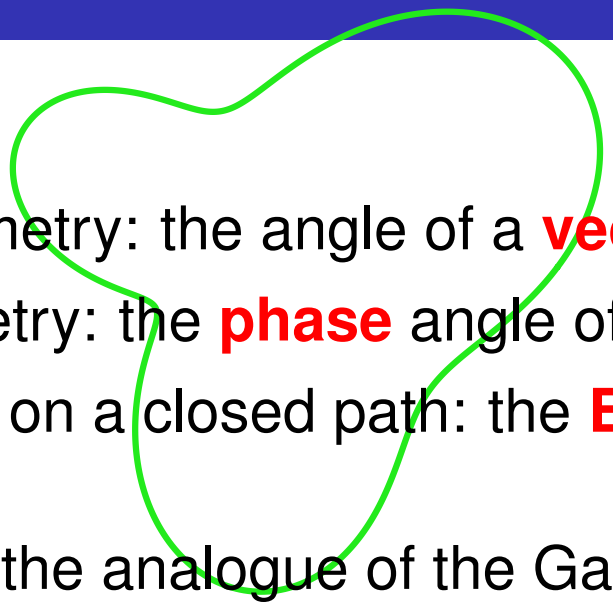

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Berry connection & Berry curvature

- Infinitesimal phase difference:

$$d\phi = -\mathrm{Im}\ \ln \langle \Psi_{0,\kappa\lambda} | \Psi_{0,\kappa+d\kappa\ \lambda+d\lambda} \rangle$$

- Berry connection (gauge dependent)

$$\begin{aligned} d\phi &= i\langle \Psi_0 | \partial_\kappa \Psi_0 \rangle d\kappa + i\langle \Psi_0 | \partial_\lambda \Psi_0 \rangle d\lambda \\ &= \mathcal{A}_\kappa d\kappa + \mathcal{A}_\lambda d\lambda \end{aligned}$$

- Berry curvature (gauge invariant)

$$\Omega(\kappa,\lambda) = \partial_\lambda \mathcal{A}_\kappa - \partial_\kappa \mathcal{A}_\lambda = -2\,\mathrm{Im}\ \langle \partial_\kappa \Psi_0 | \partial_\lambda \Psi_0 \rangle$$

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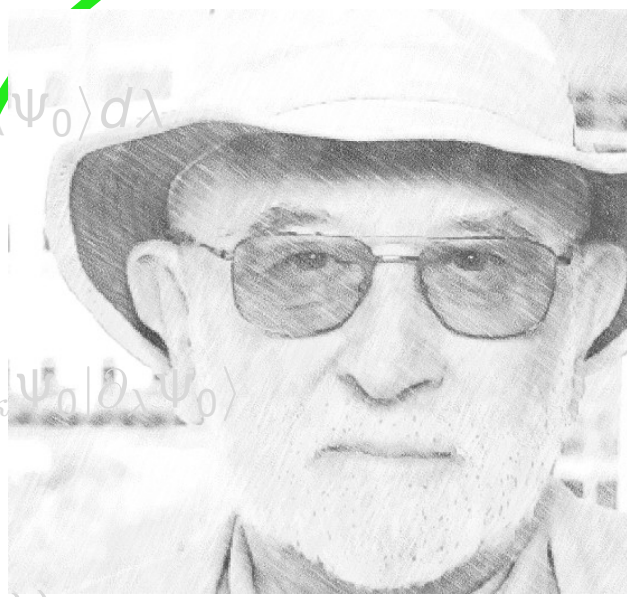

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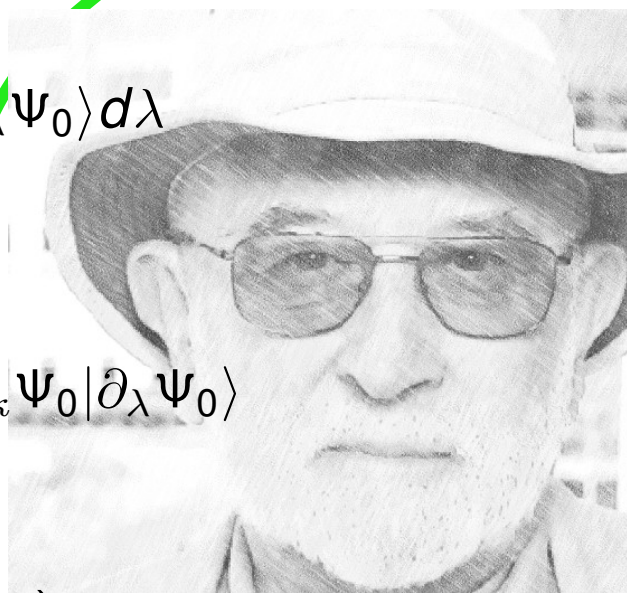


Alternative expression

- Berry curvature:

$$\begin{aligned}\Omega(\kappa,\lambda) &= i(\langle\partial_\kappa\Psi_0|\partial_\lambda\Psi_0\rangle - \langle\partial_\lambda\Psi_0|\partial_\kappa\Psi_0\rangle)\\ &= -2\,\mathrm{Im}\,\langle\partial_\kappa\Psi_0|\partial_\lambda\Psi_0\rangle;\end{aligned}$$

- Also expressed as a Kubo formula:

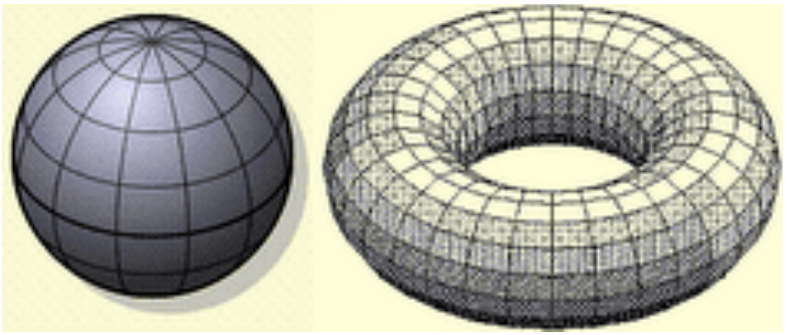
$$\Omega(\kappa,\lambda) = -2\,\mathrm{Im}\sum_{n\neq 0}\frac{\langle\Psi_0|\partial_\kappa\hat{H}|\Psi_n\rangle\langle\Psi_n|\partial_\lambda\hat{H}|\Psi_0\rangle}{(E_0-E_n)^2}.$$

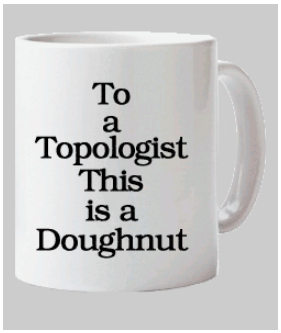
A flavor of topology

Integrating the **Gaussian curvature** over a closed surface:

- Gauss-Bonnet theorem (1848)

$$\frac{1}{2\pi}\int_{\Sigma} d\sigma\, K = 2(1-g)$$





$g = 0$ $g = 1$ $g = 1$ $g = 2$

- Genus g integer: counts the number of “handles”

From quantum geometry to quantum topology

Integrating the **Berry curvature** over a closed surface (in our case a torus):

- Gauss-Bonnet-Chern theorem (1944)

$$\frac{1}{2\pi}\int_{\Sigma} d\kappa d\lambda\, \Omega(\kappa.\lambda) = C_1 \in \mathbb{Z}$$

- C_1 first Chern number, a.k.a. $\mathbb{Z}$ topological invariant

- **Topological observable:**
  - Intensive ground-state property, expressed as: **a universal constant** $\times$ **an integer number**
  - **Robust** under change of the experimental conditions
  - Measurable in principle with **infinite precision** (the limit being set by the constant's accuracy)

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Connection and curvature

- Bloch orbitals $|\psi_{j\mathbf{k}}\rangle$ belong to different Hilbert spaces:

$$\langle \psi_{j\mathbf{k}} | \psi_{j\mathbf{k}+d\mathbf{k}} \rangle \equiv 0$$

- Geometry of **periodic** Bloch orbitals $|u_{j\mathbf{k}}\rangle = \mathrm{e}^{-i\mathbf{k}\cdot\mathbf{r}} |\psi_{j\mathbf{k}}\rangle$:

$$\langle u_{j\mathbf{k}} | u_{j\mathbf{k}+d\mathbf{k}} \rangle \neq 0 \quad \text{i.e. same Hilbert space}$$

- **Berry connection** of band j:

$$d\phi - \mathrm{Im}\,\mathrm{ln}\,\langle u_{j\mathbf{k}} | u_{j\mathbf{k}+d\mathbf{k}} \rangle = i \langle u_{j\mathbf{k}} | \partial_{\mathbf{k}} u_{j\mathbf{k}} \rangle \cdot d\mathbf{k}$$

- **Berry curvature** of band j

$$\Omega_{\mathbf{k}\lambda} = -2\,\mathrm{Im}\,\langle \partial_{\mathbf{k}} u_{j\mathbf{k}} | \partial_{\lambda} u_{j\mathbf{k}} \rangle \quad \text{in linearly induced } \mathbf{P}$$

$$\Omega_{\alpha\beta}(\mathbf{k}) = -2\,\mathrm{Im}\,\langle \partial_{k_\alpha} u_{j\mathbf{k}} | \partial_{k_\beta} u_{j\mathbf{k}} \rangle \quad \text{in conductivity theory}$$

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- **Berry connection** of band j:

$$d\phi - \mathrm{Im}\,\ln \langle u_{j\mathbf{k}} | u_{j\mathbf{k}+d\mathbf{k}} \rangle = i \langle u_{j\mathbf{k}} | \partial_{\mathbf{k}} u_{j\mathbf{k}} \rangle \cdot d\mathbf{k}$$

- **Berry curvature** of band j

$$\Omega_{\mathbf{k}\lambda} = -2\,\mathrm{Im}\,\langle \partial_{\mathbf{k}} u_{j\mathbf{k}} | \partial_{\lambda} u_{j\mathbf{k}} \rangle \quad \text{in linearly induced } \mathbf{P}$$

$$\Omega_{\alpha\beta}(\mathbf{k}) = -2\,\mathrm{Im}\,\langle \partial_{k_\alpha} u_{j\mathbf{k}} | \partial_{k_\beta} u_{j\mathbf{k}} \rangle \quad \text{in conductivity theory}$$

Connection and curvature

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The famous formula (King-Smith and Vanderbilt, 1993)

- Polarization in zero **E** field:

$$\mathbf{P} = -2e \int_{\mathrm{BZ}} \frac{d\mathrm{k}}{(2\pi)^d} \, \mathcal{A}(\mathbf{k}) + \mathbf{P}^{(\mathrm{nuclear})}, \qquad \mathcal{A}(\mathbf{k}) = i \sum_{j=1}^{n_\mathrm{b}} \langle u_{j\mathbf{k}} | \partial_{\mathbf{k}} u_{j\mathbf{k}} \rangle$$

- Periodic gauge mandatory:

$$|\psi_{\mathbf{k}+\mathbf{G}}\rangle \equiv |\psi_{\mathbf{k}}\rangle \quad \Rightarrow \quad |u_{\mathbf{k}+\mathbf{G}}\rangle \equiv \mathrm{e}^{-i\mathbf{G}\cdot\mathbf{r}} |u_{\mathbf{k}}\rangle$$

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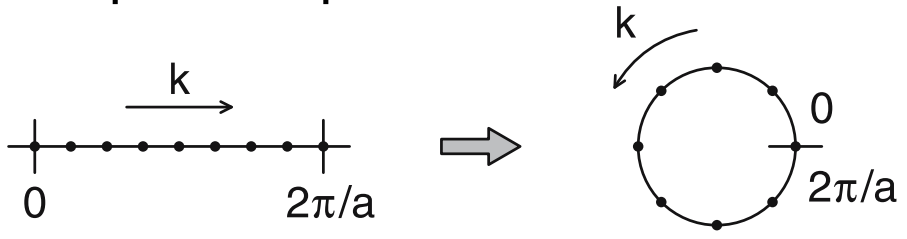

Key features

$$\mathbf{P} = -2i\,e \sum_{j=1}^{n_\mathrm{b}} \int_{\mathrm{BZ}} \frac{d\mathrm{k}}{(2\pi)^d}\; i\langle u_{j\mathbf{k}} | \partial_{\mathbf{k}} u_{j\mathbf{k}} \rangle \;+\; \mathbf{P}^{(\mathrm{nuclear})}$$

- Invariant by translation of the coordinate origin
- Gauge-invariant modulo the "quantum" $\frac{e\mathbf{R}}{V_{\mathrm{cell}}}$
- Gauge-invariant by Marzari-Vanderbilt Bloch-orbital mixing
- Choice of the branch obvious when evaluating **polarization derivatives** by finite differentiation: Born effective charges, piezoelectricity...
- Cannot be used as such to evaluate dielectric constants
- Choice of the branch simple even when evaluating **spontaneous polarization**

Cubic lattice in 3D, single band

- Integral on the reciprocal cell:

$$P_x^{(\text{electronic})} = -\frac{2i\,e}{(2\pi)^3}\int_0^{\frac{2\pi}{a}} dk_y \int_0^{\frac{2\pi}{a}} dk_z \int_0^{\frac{2\pi}{a}} dk_x \,\langle u_{\mathbf{k}} | \partial_{k_x} u_{\mathbf{k}} \rangle$$

- The inner integral is a Berry phase:

$$\begin{aligned} P_x^{(\text{electronic})} &= -\frac{2e}{(2\pi)^3}\int_0^{\frac{2\pi}{a}} dk_y \int_0^{\frac{2\pi}{a}} dk_z \,\gamma_x(k_y, k_z) \\ \gamma_x(k_y, k_z) &= i\int_0^{\frac{2\pi}{a}} dk_x \,\langle u_{\mathbf{k}} | \partial_{k_x} u_{\mathbf{k}} \rangle \end{aligned}$$

Discretization of the single-band Berry phase

- Integral of the Berry connection on a closed loop:

$$\gamma_x(k_x, k_y) = i \int_0^{\frac{2\pi}{a}} dk_x \, \langle u_{\mathbf{k}} | \partial_{k_x} u_{\mathbf{k}} \rangle = \int_0^{\frac{2\pi}{a}} dk_x \, \mathcal{A}_x \mathbf{k})$$

- The Berry connection is the infinitesimal phase difference:

$$\mathcal{A}_x(\mathbf{k}) \, \Delta k_x \simeq -\mathrm{Im} \log \langle u_{\mathbf{k}} | u_{\mathbf{k}+\Delta\mathbf{k}} \rangle, \quad \Delta\mathbf{k} \text{ along } x$$

- Discretizing with n points at constant (k_y, k_z):

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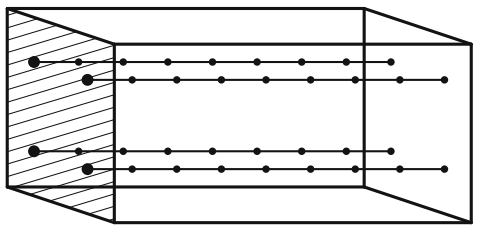
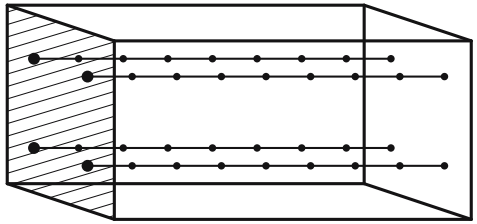


Numerical gauge-invariance



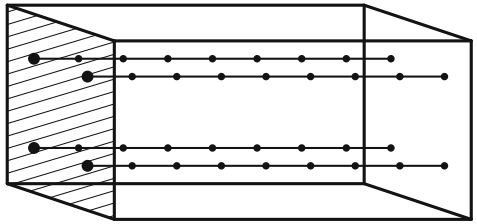
$$\gamma_x(k_y,k_z) = \int_0^{\frac{2\pi}{a}} dk_x\, \mathcal{A}_x(\mathbf{k}) \quad \rightarrow \quad -\mathrm{Im} \sum_{s=0}^{n-1} \log \langle u_{\mathbf{k}_s} | u_{\mathbf{k}_{s+1}} \rangle$$

$$= \quad -\mathrm{Im}\, \log \prod_{s=0}^{n-1} \langle u_{\mathbf{k}_s} | u_{\mathbf{k}_{s+1}} \rangle$$

- Erratic phase factors irrelevant:

$$\gamma_x(k_y,k_z) = -\mathrm{Im}\, \log \langle u_{\mathbf{k}_0} | u_{\mathbf{k}_1} \rangle \langle u_{\mathbf{k}_1} | u_{\mathbf{k}_2} \rangle \ldots \langle u_{\mathbf{k}_{n-1}} | u_{\mathbf{k}_n} \rangle$$

Numerical gauge-invariance



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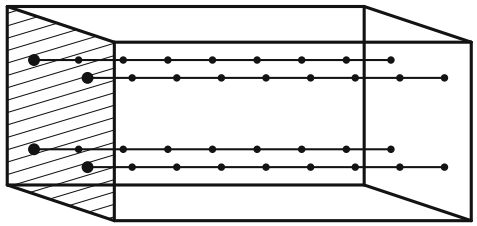
Many-band discretization



- $n_\mathrm{b} \times n_\mathrm{b}$ connection matrix:

$$\langle u_{\mathbf{k}_s} | u_{\mathbf{k}_{s+1}} \rangle \;\rightarrow\; S_{jj'}(\mathbf{k}_s, \mathbf{k}_{s+1}) = \langle u_{j\mathbf{k}_s} | u_{j'\mathbf{k}_{s+1}} \rangle$$

$$\gamma_x(k_y, k_z) = -\mathrm{Im}\,\log\det \prod_{s=0}^{n-1} S_{jj'}(\mathbf{k}_s, \mathbf{k}_{s+1})$$

- Invariant by Marzari-Vanderbilt unitary transform
- Implemented as such in many DFT codes

Electronic term, Wannier formulation

- $|w_j\rangle$ Wannier function of band j in a given cell
- Wannier centers:

$$\tilde{\mathbf{r}}_j = \langle w_j | \mathbf{r} | w_j \rangle$$

- Electronic term:

$$\mathbf{P}^{(\text{electronic})} = -\frac{2\,e}{V_{\text{cell}}} \sum_{j=1}^{n_{\text{b}}} \tilde{\mathbf{r}}_j$$

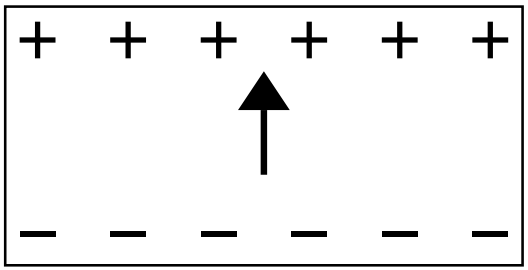
- Same key features as for the Berry-phase theory (multivaluednes, generalized gauge invariance...)
- Algebra of the transformation known since the 1960s

Outline

Why different quanta are never observed? (in 3D materials)

The bulk material has polarization $\mathbf{P}_0$ in zero $\mathbf{E}$ field

- A slab cleaved normal to $\mathbf{P}_0$:



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  - Energy **cost:** $E^2/(8\pi)\times$ volume
  - Very likely the surface is **metallic**

- A slab cleaved parallel to $\mathbf{P}_0$:

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  - When polarization is switchable (ferroelectrics)
    Spontaneous $\mathbf{P}$ is parallel

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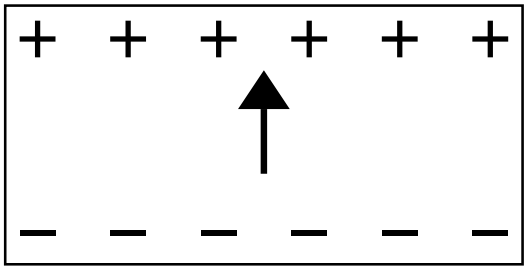

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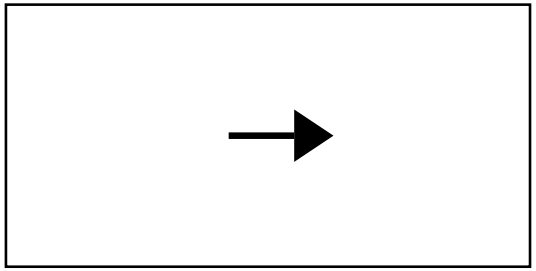

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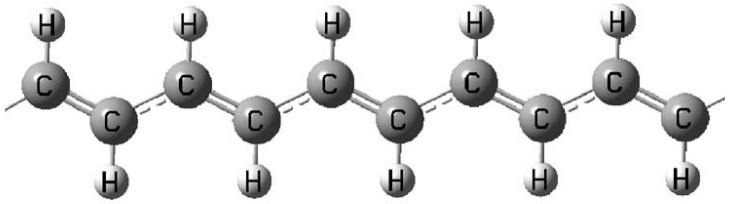
What happens in quasi-1D? Example: Polyacetylene



- Focus on π electrons only:
  they contribute by a single (doubly occupied) band
- Insulating whenever alternating
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- The corresponding WF sits at the double-bond center

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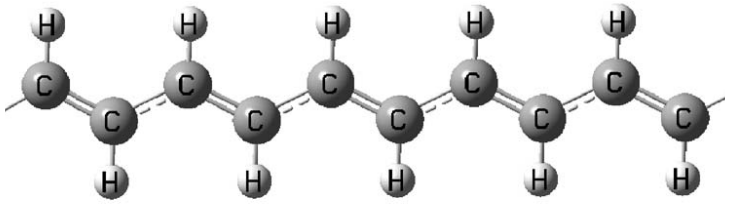

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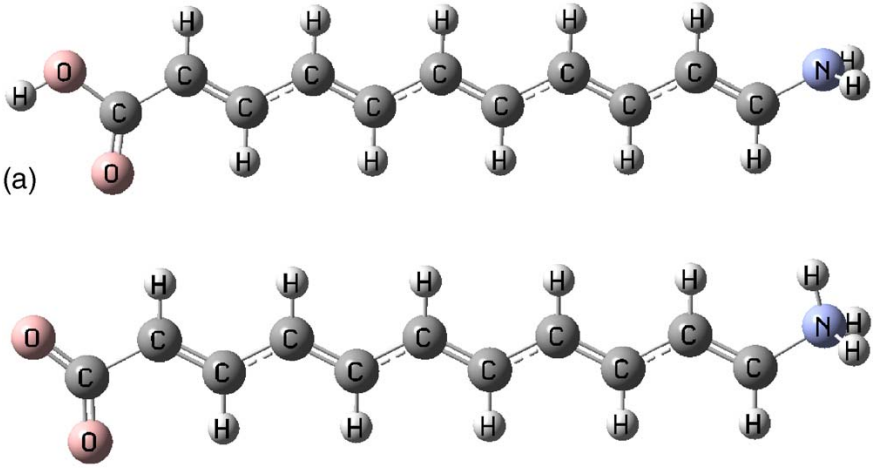
Bounded samples: A computer experiment

K. Kudin, R. Car, & R. Resta, J. Chem Phys. 2007

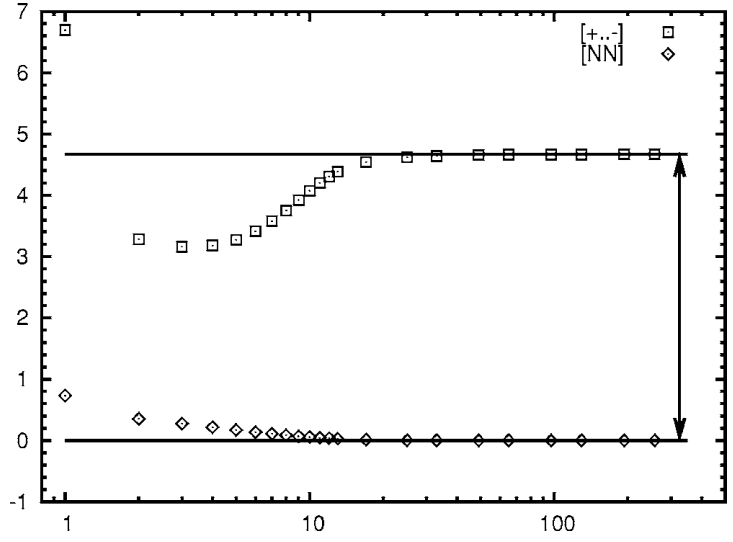


Centrosymmetric bulk:

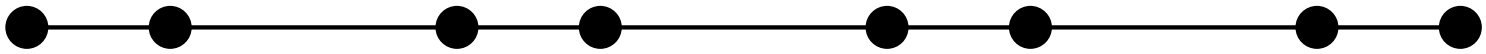
Two different asymmetric terminations

Shown here:
Dipole per monomer

Q.E.D.
either $P = 0$ or $P = e$



Simple I-symmetric tight-binding Hamiltonians



Onsite ϵ_i constant, alternating hoppings t and t'

Constant hopping t, alternating ϵ_i

- Two-band model, insulating at half filling (except when nonalternating)
- Neutralizing nuclear charges: $+e$ on each site

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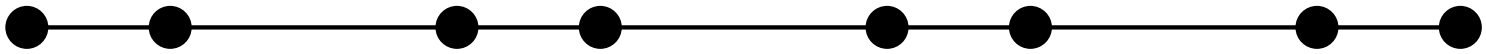

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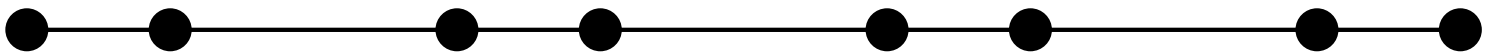
$\mathbb{Z}_2$ topological classification



$\mathbb{Z}_2$-even: Onsite ϵ_i constant, alternating hoppings t and t'

$\mathbb{Z}_2$-odd: Constant hopping t, alternating ϵ_i

- $\mathbb{Z}_2$ invariant protected by **I-symmetry**
- When joining the two with a continuous & I-symmetric deformation of the Hamiltonian **the gap closes!**

Bibliography

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