Quantum transport & polarization

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Trieste, 2021

Outline

1 Faraday laws of electrolysis

2 Modern view of a liquid

3 A flavor of topology

4 The adiabatic current

5 The “electron-in-broth” formula (one electron)

6 Many electrons in broth: transport and conductivity

7 Infrared spectra

8 Insulators vs. metals

9 Polarization

10 A $\mathbb{Z}_2$ topological invariant

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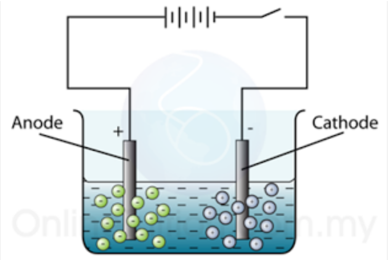
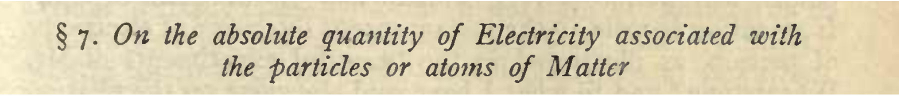
First law of electrolysis, 1832

(Modern formulation, from Wikipedia)

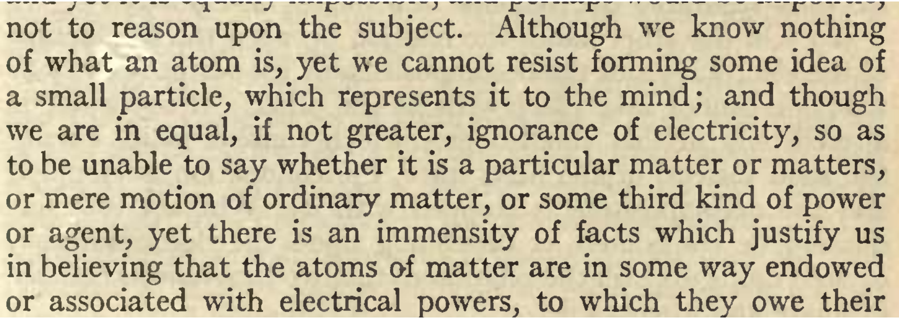


The mass of a substance altered at an electrode during electrolysis is directly proportional to the quantity of electricity transferred at that electrode. Quantity of electricity refers to the quantity of electrical charge.

Faraday verbatim



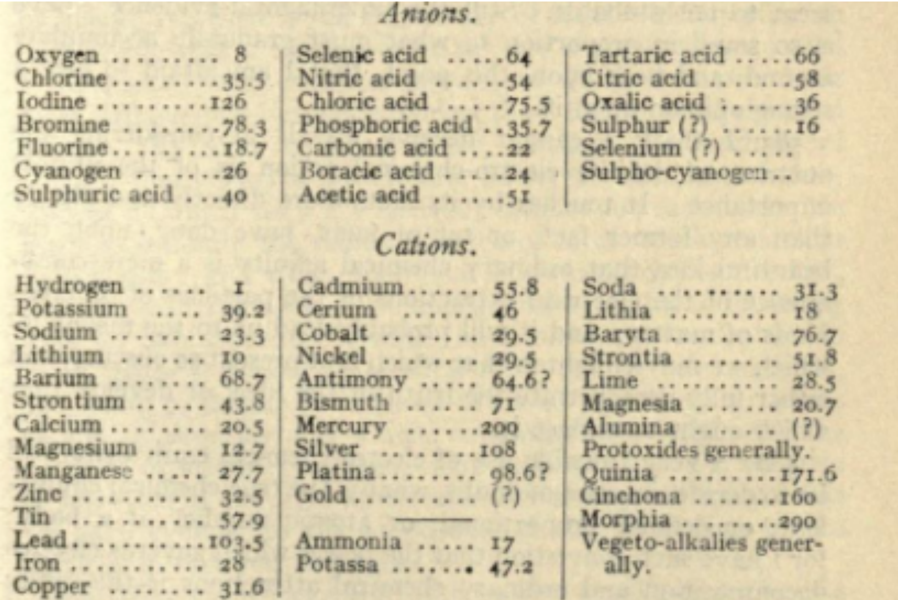
§ 7. *On the absolute quantity of Electricity associated with the particles or atoms of Matter*



not to reason upon the subject. Although we know nothing of what an atom is, yet we cannot resist forming some idea of a small particle, which represents it to the mind; and though we are in equal, if not greater, ignorance of electricity, so as to be unable to say whether it is a particular matter or matters, or mere motion of ordinary matter, or some third kind of power or agent, yet there is an immensity of facts which justify us in believing that the atoms of matter are in some way endowed or associated with electrical powers, to which they owe their

Faraday's "equivalent numbers" (1832)

(Notice: in 1832 Mendeleev was not yet born!



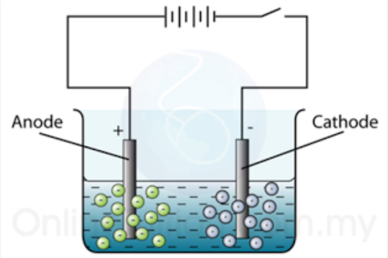
Anions.

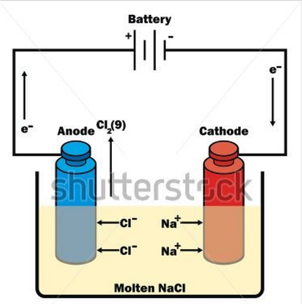
Oxygen	8	Selenic acid	64	Tartaric acid	66
Chlorine	35.5	Nitric acid	54	Citric acid	58
Iodine	126	Chloric acid	75.5	Oxalic acid	36
Bromine	78.3	Phosphoric acid	35.7	Sulphur (?)	16
Fluorine	18.7	Carbonic acid	22	Selenium (?)	
Cyanogen	26	Boracic acid	24	Sulpho-cyanogen	
Sulphuric acid	40	Acetic acid	51		

Cations.

Hydrogen	1	Cadmium	55.8	Soda	31.3
Potassium	39.2	Cerium	46	Lithia	18
Sodium	23.3	Cobalt	29.5	Baryta	76.7
Lithium	10	Nickel	29.5	Strontia	51.8
Barium	68.7	Antimony	64.6?	Lime	28.5
Strontium	43.8	Bismuth	71	Magnesia	20.7
Calcium	20.5	Mercury	200	Alumina	(?)
Magnesium	12.7	Silver	108	Protoxides generally.	
Manganese	27.7	Platina	98.6?	Quinia	171.6
Zinc	32.5	Gold	(?)	Cinchona	160
Tin	57.9			Morphia	290
Lead	103.5	Ammonia	17	Vegeto-alkalies generally.	
Iron	28	Potassa	47.2		
Copper	31.6				

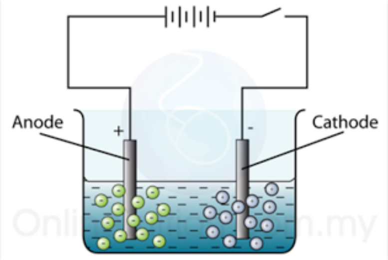
Electrolytic solutions vs. molten salts

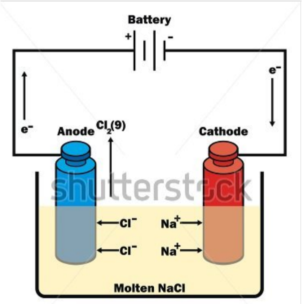




What about molten **metals**?

Electrolytic solutions vs. molten salts





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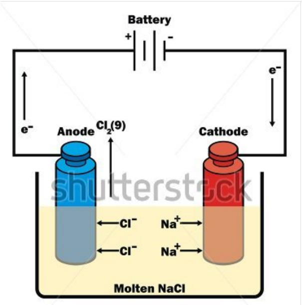
Electrolyte or molten salt

- An assembly of:
  - Point-like nuclei
  - Electronic charge density
- Electron density all over the place
- How much charge “belongs” to each nucleus?
- Ionic charges arbitrary & noninteger



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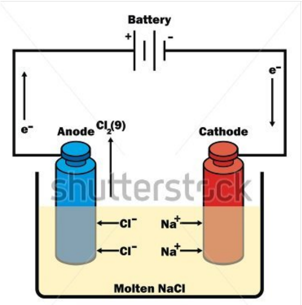

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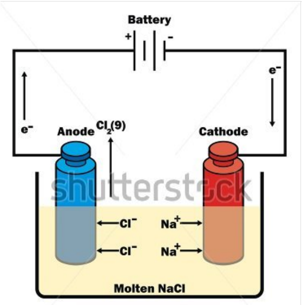
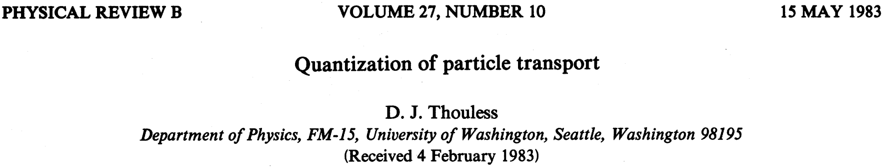


The ultimate solution



PHYSICAL REVIEW B VOLUME 27, NUMBER 10 15 MAY 1983

Quantization of particle transport

D. J. Thouless

Department of Physics, FM-15, University of Washington, Seattle, Washington 98195

(Received 4 February 1983)

- Faraday's law is reconciled with QM owing to topology
- The transported charge is a topological invariant
- Historical perspective:
  Q: Why did this paper appear in 1983?
  A: Topology entered the theory of quantum Hall effect in 1982 (the famous TKNN invariant).

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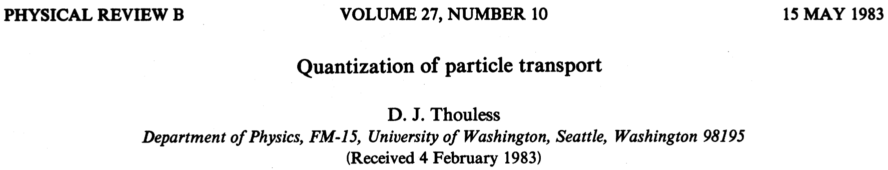

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A few months afterwards

(Pendry & Hodges, J. Phys. C 1984)

Verbatim:

- “. . . in condensed matter there is no way of extracting integer charges for the ions from a charge-density map.”
- “. . . in insulating systems atoms or ions diffusing through the system carry with them charges which are integral multiples of e.”
- “In a **static** configuration no evidence is found for integral charges, the existence of which is manifested by the **transport** properties alone.”

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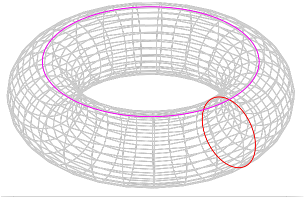
Gauss-Bonnet-Chern theorem

Parametric Hamiltonian
on a closed surface (a torus) :



$$H(\vartheta,\varphi) = H(\vartheta+2\pi,\varphi) = H(\vartheta,\varphi+2\pi)$$

- Ground **nondegenerate** eigenstate $|\psi_0(\vartheta,\varphi)\rangle$
- Berry curvature $\Omega(\vartheta,\varphi) = i\,(\langle\frac{\partial}{\partial\vartheta}\psi_0|\frac{\partial}{\partial\varphi}\psi_0\rangle - \langle\frac{\partial}{\partial\varphi}\psi_0|\frac{\partial}{\partial\vartheta}\psi_0\rangle)$
- Chern number:

$$\frac{1}{2\pi}\int_0^{2\pi} d\vartheta \int_0^{2\pi} d\varphi \;\; \Omega(\vartheta,\varphi) = C \;\in \mathbb{Z}$$

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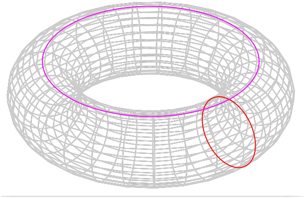

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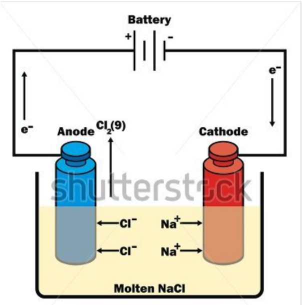
Thouless' "angles"



- $\vartheta \to k$ (inverse length)
- $\varphi \to t$ (time)
- $H(k, t)$ periodic over $(\frac{2\pi}{L}, T)$
- Thouless theorem:

$$Q = \int_0^T dt\ I(t) = e\, C$$

$$C = \frac{1}{2\pi} \int_0^{2\pi/L} dk \int_0^T dt\ \Omega(k, t)$$

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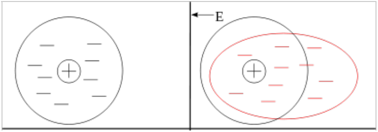
Dipolar polarization of an atom



- Think of polarization in a time-dependent (adiabatic) way: $\mathbf{E} = \mathbf{E}(t)$

- $H(t)$ varies slowly in time
- Adiabatic limit: $\Delta t \gg \hbar/(\varepsilon_1 - \varepsilon_0)$
- $|\psi_0(t)\rangle$ instantaneous ground eigenstate

$$\frac{\partial \rho(\mathbf{r})}{\partial t} = -e\frac{\partial}{\partial t}|\psi_0(\mathbf{r})|^2 = -e\,[\,\dot{\psi}_0^*(\mathbf{r})\psi_0(\mathbf{r}) + \psi_0^*(\mathbf{r})\dot{\psi}_0(\mathbf{r})\,] \neq 0$$

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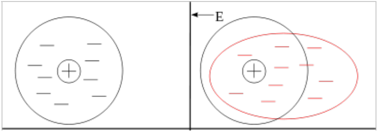

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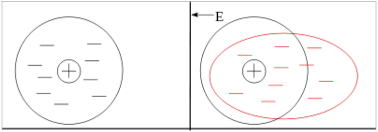

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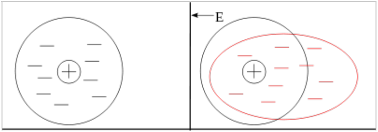
Induced dipole



Continuity equation: $\dfrac{\partial\rho(r)}{\partial t} = -\nabla\cdot\mathbf{j}(\mathbf{r})$

$$\mathbf{d} = \int_0^{\Delta t} dt \int d\mathbf{r}\,\mathbf{r}\frac{\partial\rho(r)}{\partial t} = -\int_0^{\Delta t} dt \int d\mathbf{r}\,\mathbf{r}\,\nabla\cdot\mathbf{j}(\mathbf{r})$$

Improved adiabatic approximation

Continuity equation: $$\frac{\partial \rho(r)}{\partial t} = -\nabla \cdot \mathbf{j}(\mathbf{r})$$

$$\mathbf{j}(\mathbf{r}) = -\frac{e}{2} [\, -i\psi_0^*(\mathbf{r})\nabla\psi_0(\mathbf{r}) + \text{c.c.}\,]$$

- Simple case $H(t)$: time-reversal-invariant
- Instantaneous ground eigenstate $|\psi_0(t)\rangle$ **real**
- $\mathbf{j}(\mathbf{r})$ **vanishes** (any $\mathbf{r}$, any t)
- Need a better formula for the adiabatic current!

- Thouless formula:

$$|\psi\rangle \simeq |\psi_0\rangle + i\hbar \sum_{n\neq 0} |\psi_n\rangle \frac{\langle \psi_n|\dot{\psi}_0\rangle}{\varepsilon_0 - \varepsilon_n}$$

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Infinite system with periodic boundary conditions

Switch to **1d** from now on: $$\frac{\partial \rho(x,t)}{\partial t} = -\frac{\partial j(x,t)}{\partial x}$$

- A macroscopic current $j^{(\mathrm{macro})}(t)$ constant in x is **divergenceless**
- $j(x,t) \to j(x,t) + j^{(\mathrm{macro})}(t)$ does not affect $\rho(x,t)$
- $j^{(\mathrm{macro})}(t)$ is due to a source at $-\infty$ and a drain at $+\infty$.
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Macroscopic polarization of a solid

(Resta 1992, King-Smith & Vanderbilt 1993)

- Polarization is the dipole per unit volume

$$\mathbf{P} = \frac{1}{V}\mathbf{d} = \frac{1}{V_{\text{sample}}}\int_{\text{sample}} d\mathbf{r}\;\mathbf{r}\rho(r) \neq \frac{1}{V_{\text{cell}}}\int_{\text{cell}} d\mathbf{r}\;\mathbf{r}\rho(r)$$

- **Meaningless** for a lattice-periodical $\rho(r)$

- The modern theory:
  - **P** **has nothing to do** with the periodic distribution $\rho(r)$ contrary to what **most textbooks pretend!**
  - $\partial\mathbf{P}/\partial t = \mathbf{j}^{(macro)}(t) \quad \Longrightarrow$

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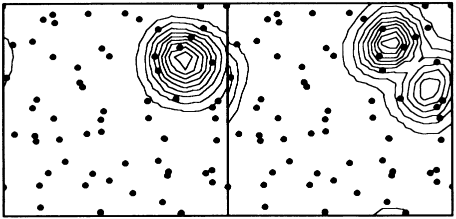
F-center in a molten salt

(Selloni, Carnevali, Car, & Parrinello 1987)



- Mixed quantum-classical simulation
- 31 Cl^- and 32 K^+ ions, plus **one electron**
- Both Newton & Schrödinger eqs. with **PBCs**

- Diffusion: asymptotically $\langle|\mathbf{r}_e(t)|^2\rangle = 6D_e t$
- How to evaluate $\langle\mathbf{r}_e(t)\rangle$ within PBCs?

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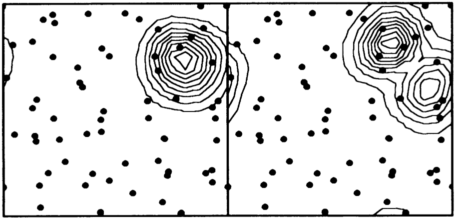

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The position operator: fundamentals

- It is the simple multiplicative operator which maps (1d): $\psi(x) \to x\ \psi(x)$

- Its expectation value is: $\langle x \rangle = \int dx\ x\, |\psi(x)|^2$

- The multiplicative operator x is **not** a legitimate operator when adopting periodic boundary conditions (as we do in condensed matter physics)

- A different definition of the position operator has to be adopted

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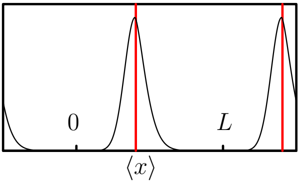
How does one define the electron-distribution center?



- $\langle x\rangle = \int dx\ x\,|\psi_0(x)|^2$ is nonsense
- $\langle x\rangle$ must be defined modulo L
- The electron-in-broth formula:

$$\langle x\rangle = \frac{L}{2\pi}\mathrm{Im}\ \mathrm{ln}\ \int_0^L dx\ e^{i\frac{2\pi}{L}x}\,|\psi_0(x)|^2$$

- Notice the occurrence of a **phase** (“Im ln”)

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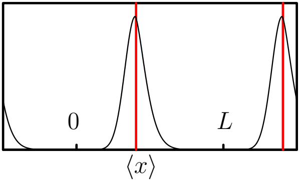

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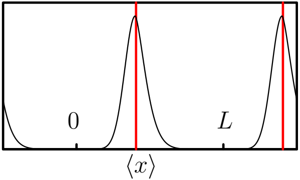
The adiabatic current



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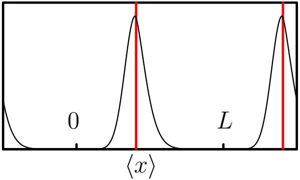
- $\psi_0(x,t)$ adiabatic instantaneous eigenstate
- Macroscopic current:

$$j^{(macro)}(t) = -\frac{e}{L}\frac{d\langle x \rangle}{dt} = -\frac{e}{2\pi}\frac{d}{dt}\mathrm{Im}\,\ln \int_0^L dx\, \mathrm{e}^{i\frac{2\pi}{L}x}\, |\psi_0(x,t)|^2$$

- Coincides with Thouless formula for $L \to \infty$

The adiabatic current



$$\langle x\rangle = \frac{L}{2\pi}\mathrm{Im}\,\ln\int_0^L dx\, \mathrm{e}^{i\frac{2\pi}{L}x}\,|\psi_0(x)|^2$$

- $\psi_0(x,t)$ adiabatic instantaneous eigenstate
- Macroscopic current:

$$j^{(macro)}(t) = -\frac{e}{L}\frac{d\langle x\rangle}{dt} = -\frac{e}{2\pi}\frac{d}{dt}\mathrm{Im}\,\ln\int_0^L dx\, \mathrm{e}^{i\frac{2\pi}{L}x}\,|\psi_0(x,t)|^2$$

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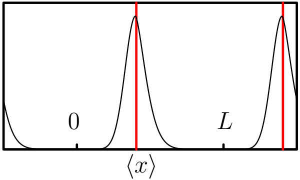
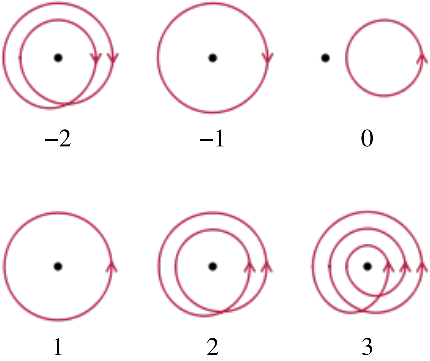
Quantization of transport



$$\langle x \rangle = \frac{L}{2\pi} \operatorname{Im} \ln \mathfrak{z}, \qquad \mathfrak{z} = \int_0^L dx\, e^{i\frac{2\pi}{L}x} |\psi_0(x)|^2 = \langle \psi_0 | e^{i\frac{2\pi}{L}x} | \psi_0 \rangle$$

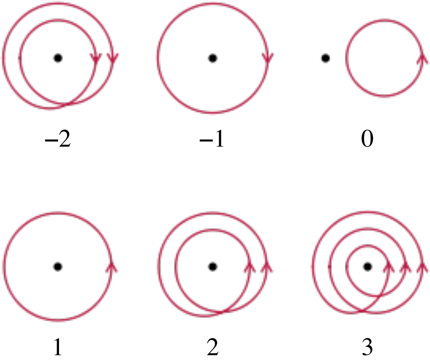
- $\mathfrak{z}$ a complex number, with $|\mathfrak{z}| \leq 1$
- $\mathfrak{z}(t)$ traces a path in the complex plane
- Suppose that $H(T) = H(0)$ for some T, then $\mathfrak{z}(T) = \mathfrak{z}(0)$
- How much charge has been transported?

Winding number



- The transported charge is the winding number (times $-e$) plus the charge transported by the classical ions
- Winding number ill defined if $\mathfrak{z}(t) = 0$ along the path!

Winding number



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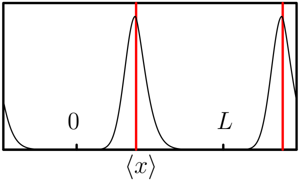
Localization vs. delocalization



$$\mathfrak{z} = \int_0^L dx\, \mathrm{e}^{i\frac{2\pi}{L}x} |\psi_0(x)|^2$$

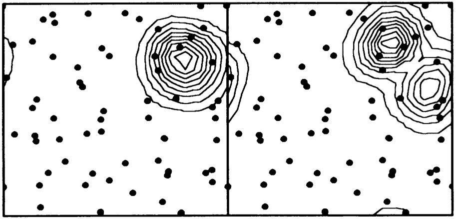
- Extremely localized distribution:

$$|\psi_0(x)|^2 = \sum_{m=-\infty}^{\infty} \delta(x - x_0 - mL) \quad \Rightarrow \quad \mathfrak{z} = \mathrm{e}^{i\frac{2\pi}{L}x_0}$$

- Extremely delocalized distribution:

$$|\psi_0(x)|^2 = \frac{1}{L} \quad \Rightarrow \quad \mathfrak{z} = 0$$

Current of the classical charges (1d)



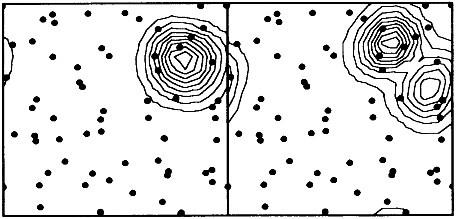
- Charges $Q_\ell = \pm e$ at sites X_ℓ:

  Dipole $d = \sum_\ell Q_\ell X_\ell$ **ill-defined** within PBCs

- Dipole defined modulo L:

$$d = \frac{eL}{2\pi} \mathrm{Im} \ln \mathrm{e}^{i \frac{2\pi}{eL} \sum_\ell Q_\ell X_\ell}$$

Total current: one electron + classical charges



$$\begin{aligned} j_x^{(macro)} &= \frac{e}{2\pi}\frac{d}{dt}\left(-\mathrm{Im}\ln\langle\psi_0|\mathrm{e}^{i\frac{2\pi}{L}x}|\psi_0\rangle + \mathrm{Im}\ln \mathrm{e}^{i\frac{2\pi}{eL}\sum_\ell Q_\ell X_\ell}\right) \\ &= \frac{e}{2\pi}\frac{d}{dt}\mathrm{Im}\ln\langle\psi_0|\mathrm{e}^{i\frac{2\pi}{L}\left(-x+\sum_\ell \frac{Q_\ell}{e}X_\ell\right)}|\psi_0\rangle \end{aligned}$$

- For a periodic evolution:
  Transported charge = winding number of $\mathfrak{z}(t)$ (times e)

$$\mathfrak{z}_x(t) = \langle\psi_0|\mathrm{e}^{i\frac{2\pi}{L}\left(-x+\sum_\ell \frac{Q_\ell}{e}X_\ell\right)}|\psi_0\rangle$$

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N electrons within PBCs

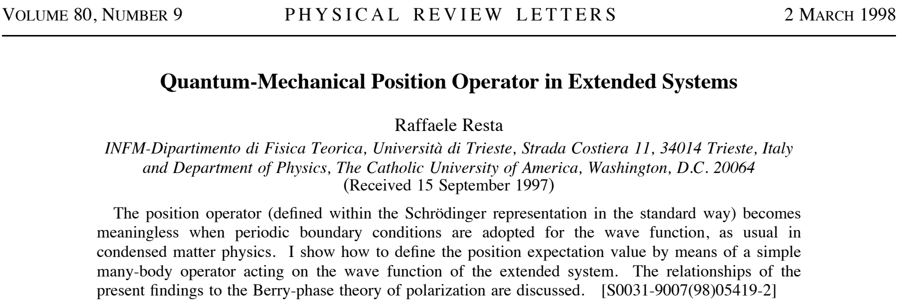
- Condensed system in 1d: N spinless electrons in a segment of lenght L:

$$\Psi_0 = \Psi_0(x_1, x_2, \dots x_j, \dots x_N),$$

- L large with respect to atomic dimensions.
- Thermodynamic limit:
  $N \to \infty$, $L \to \infty$, $N/L = n_0$ constant.
- Ψ_0 periodic over each electronic variable x_j separately:

$$\Psi_0 = \Psi_0(x_1, x_2, \dots x_j, \dots x_N) = \Psi_0(x_1, x_2, \dots x_j + L, \dots x_N)$$

The ultimate solution



VOLUME 80, NUMBER 9 PHYSICAL REVIEW LETTERS 2 MARCH 1998

Quantum-Mechanical Position Operator in Extended Systems

Raffaele Resta
INFM-Dipartimento di Fisica Teorica, Università di Trieste, Strada Costiera 11, 34014 Trieste, Italy
and Department of Physics, The Catholic University of America, Washington, D.C. 20064
(Received 15 September 1997)

The position operator (defined within the Schrödinger representation in the standard way) becomes meaningless when periodic boundary conditions are adopted for the wave function, as usual in condensed matter physics. I show how to define the position expectation value by means of a simple many-body operator acting on the wave function of the extended system. The relationships of the present findings to the Berry-phase theory of polarization are discussed. [S0031-9007(98)05419-2]

- Nuclei (charge eZ_ℓ) & electrons (charge $-e$) altogether:

$$\mathfrak{z} = \langle \Psi_0 | e^{i\frac{2\pi}{L}\left(-\sum_j x_j + \sum_\ell Z_\ell X_\ell\right)} | \Psi_0 \rangle$$

- Adiabatic current & macroscopic polarization $(1d)$:

$$j^{(macro)} = \frac{e}{2\pi}\frac{d}{dt}\text{Im}\ln\mathfrak{z} \qquad P = \frac{e}{2\pi}\text{Im}\ln\mathfrak{z} = \frac{e}{2\pi}\gamma$$

A molten salt

- Electrons and nuclei in a cubic periodic cell of side L

$$\mathfrak{z}_x(t) = \langle \Psi_0 | \mathrm{e}^{i\frac{2\pi}{L}\left(\sum_j x_j - \sum_\ell Z_\ell X_\ell\right)} | \Psi_0 \rangle \qquad \gamma_x(t) = \operatorname{Im} \ln \mathfrak{z}_x(t)$$

- Polarization and charge flux across the cell:

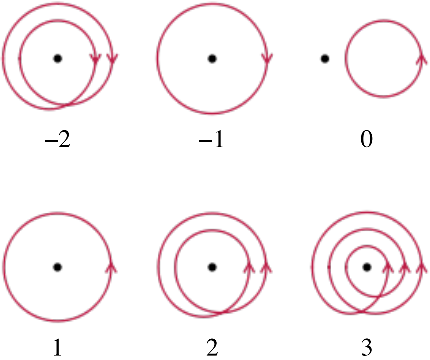
$$P_x(t) = -\frac{e}{2\pi L^2}\gamma_x(t) \qquad I_x(t) = -\frac{e}{2\pi}\frac{d}{dt}\gamma_x(t)$$

- Transported charge in time T:

$$Q = \int_0^T dt\; I_x(t) = -\frac{e}{2\pi}\int_0^T dt\; \frac{d}{dt}\gamma_x(t) = -\frac{e}{2\pi}[\gamma_x(T) - \gamma_x(0)]$$

- Suppose that $H(T) = H(0)$ for some T, then $\mathfrak{z}_x(T) = \mathfrak{z}_x(0)$
  How much charge has been transported?

Thouless quantization of charge transport



- $\mathfrak{z}_x(t)$ traces a path in the complex plane, with $|\mathfrak{z}_x(t)| \leq 1$
- The transported charge is the winding number (times $-e$)
- Topological nature of Faraday's law!
- Winding number ill defined if $\mathfrak{z}_x(t) = 0$ along the path!

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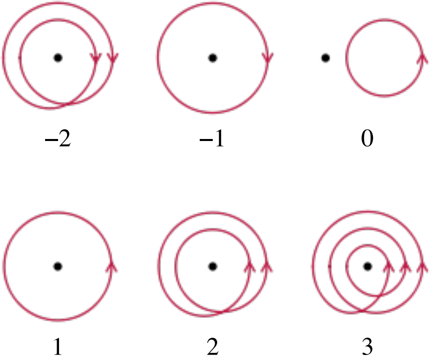

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- The transported charge is the winding number (times $-e$)
- Topological nature of Faraday's law!
- Winding number ill defined if $\mathfrak{z}_x(t) = 0$ along the path!

Alternative formulations of the current density

CP simulations yield adiabatic wavefunctions & trajectories

- **Numerical derivative:** single-point Berry phase

$$\begin{aligned} j_x(t) &= -\frac{e}{2\pi L^2}\frac{d}{dt}\gamma_x(t) \\ &\simeq -\frac{e}{2\pi L^2}\frac{\gamma_x(t+\Delta t)-\gamma_x(t)}{\Delta t} \end{aligned}$$

- **Analytical derivative:** linear response

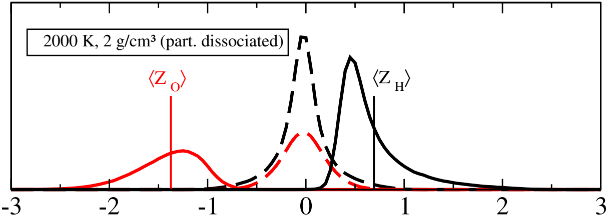
$$j_\alpha(t) = \frac{e}{L^3}\sum_{\ell=1}^{N} Z^*_{\ell,\alpha\beta}(t)\; v_{\ell,\beta}(t)$$

- Born effective charge tensors $\overset{\leftrightarrow}{Z}{}^*_\ell$ from DFPT

Z^* tensors in partially dissociated water

54 O atoms and 108 H atoms in a PBCs simulation cell in zero **E** field

Distribution of the $\overset{\leftrightarrow}{Z}{}^*_\ell$ tensors: diagonal (solid) & off-diagonal (dashed)

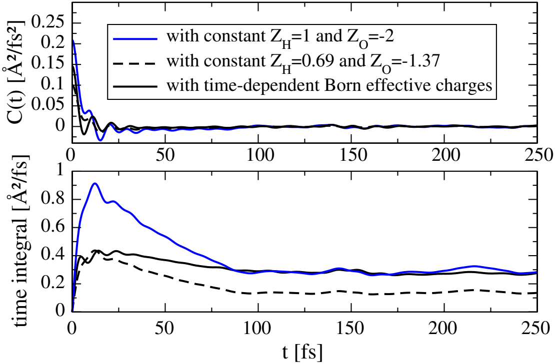


French, Hamel, & Redmer, Phys. Rev. Lett. **107**, 185901 (2011)

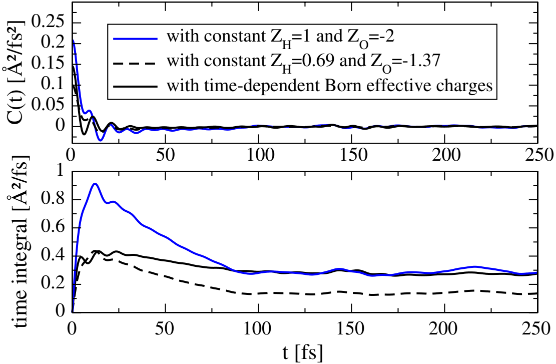
Ionic conductivity

Fluctuation-dissipation theorem (Green-Kubo) for ionic conductivity:

$$\sigma = \frac{L^3}{3k_\mathrm{B}T}\int_0^\infty dt \, \langle \, \mathbf{j}(t) \cdot \mathbf{j}(0) \, \rangle$$



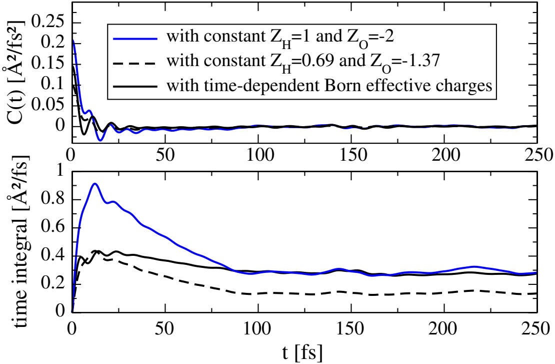
Topological quantization



The integer values $Z^*_{\mathrm{O}} = -2$ and $Z^*_{\mathrm{H}} = 1$ work **much better** than the actual $\langle Z^*_{\mathrm{O}} \rangle$ and $\langle Z^*_{\mathrm{H}} \rangle$ values!

Topological explanation:
F. Grasselli & S. Baroni, Nature Phys. **15**, 967 (2019)

Topological quantization



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Classical fluctuation-dissipation formula

- Imaginary part (absorptive) of the dielectric constant:

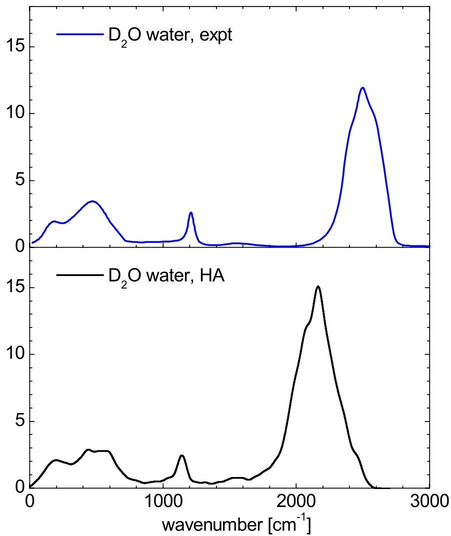
$$\varepsilon''(\omega) = 4\pi\chi(\omega) = \frac{2\pi\,\omega}{3k_{\mathrm{B}}T\,L^3}\int_{-\infty}^{\infty} dt\,\mathrm{e}^{i\omega t}\langle \mathbf{d}(t)\cdot\mathbf{d}(0)\rangle$$

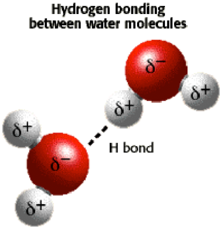
- $\mathbf{d}(t) = L^3\mathbf{P}(t)$ extensive dipole of the simulation cell

$$\begin{aligned}\varepsilon''(\omega) &= \frac{2\pi L^3\omega}{k_{\mathrm{B}}T}\int_{-\infty}^{\infty} dt\,\mathrm{e}^{i\omega t}\,\langle P_x(t)\,P_x(0)\rangle \\ &= \frac{2\pi L^3\omega}{k_{\mathrm{B}}T}\left(\frac{1}{2\pi L^2}\right)^2\int_{-\infty}^{\infty} dt\,\mathrm{e}^{i\omega t}\,\langle \gamma_x(t)\,\gamma_x(0)\rangle\end{aligned}$$

Car-Parrinello (ab-initio MD) simulation for water

(W. Chen, M. Sharma, R. Resta, G. Galli,& R. Car, PRB 2008)





Peaks:

- translations
- librations
- bond bending
- bond stretching

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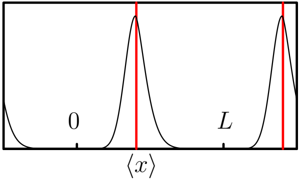
Phase, distance, localization (one electron in 1d)



$$\mathfrak{z} = \int_0^L dx\, \mathrm{e}^{i\frac{2\pi}{L}x}\, |\psi_0(x)|^2 = \langle\psi_0|\mathrm{e}^{i\frac{2\pi}{L}x}|\psi_0\rangle$$

- $\gamma = \mathrm{Im}\ln\mathfrak{z} \quad\longrightarrow\quad \langle x_0\rangle$ center of the electron distribution
- The center is ill-defined when $\mathfrak{z} = 0$
- Extremely localized vs. extremely delocalized
  $|\psi_0(x)|^2 = \delta(x - x_0) \longrightarrow \mathfrak{z} = \mathrm{e}^{i\frac{2\pi}{L}x_0}, \quad |\psi_0(x)|^2 = \frac{1}{L} \longrightarrow \mathfrak{z} = 0$
- Quadratic spread: $-\left(\frac{L}{2\pi}\right)^2 \ln|\mathfrak{z}|^2$,
- Quantum pseudodistance: $D_{12}^2 = -\ln|\langle\psi_1|\psi_2\rangle|^2$

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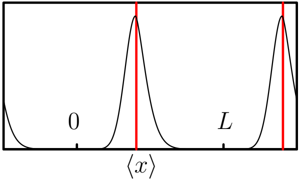

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Theory of the insulating state

$$\mathfrak{z}_N = \langle \Psi_0 | \mathrm{e}^{-i \frac{2\pi}{L} \sum_j x_j} | \Psi_0 \rangle$$

- Electronic term in polarization

$$P^{(\mathrm{el})} = \frac{e}{2\pi} \operatorname{Im} \log \lim_{N \to \infty} \mathfrak{z}_N$$

- It is impossible to **define** polarization whenever

$$\lim_{N \to \infty} \mathfrak{z}_N = 0$$

all insulators: $\lim_{N \to \infty} |\mathfrak{z}_N| = 1$ **all metals:** $\lim_{N \to \infty} \mathfrak{z}_N = 0$

Resta-Sorella localization length

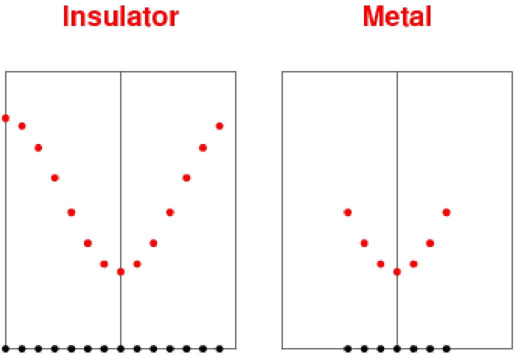
R. Resta & S. Sorella, Phys. Rev. Lett. **82**, 370 (1999)

$$\lambda^2 = -\lim_{N\to\infty} \frac{1}{N} \left(\frac{L}{2\pi}\right)^2 \ln |\mathfrak{z}_N|^2$$

- Intensive quantity (tensor in 3*d*)
- λ is finite in all insulators
- λ diverges in all metals

- Very general: **all kinds** of insulators:
  - Correlated insulator
  - Independent electrons, crystalline a.k.a. “band insulator”
  - Independent electrons, disordered
  - Quantum Hall insulator

Band insulators vs. band metals



PBCs over 14 cells: $L = Ma$, $M = 14$ in this drawing:
14 Bloch vectors in the Brillouin zone.

14 occupied orbitals in the insulating state ($N = M$),
7 occupied orbitals in the metallic state ($N = M/2$).

Crystalline system of independent electrons

Before the thermodynamic limit: N and L **finite**

- $|\Psi_0\rangle$ is written as a determinant of occupied Bloch orbitals, in **both** the insulating and the metallic case.
- **Key difference:**
  The whole band is used to build the insulating $|\Psi_0\rangle$, while only one half of the band is used for the metallic $|\Psi_0\rangle$.

Insulators vs. metal

$$S = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & {\color{red}\blacksquare} \\ \blacksquare & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \blacksquare & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \blacksquare & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \blacksquare & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \blacksquare & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \blacksquare & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \blacksquare & 0 \end{pmatrix}$$

- **Zero determinant** in the metallic case!
- In a band metal $\lambda^2 = \infty$ **even at finite N**
- In a band insulator $\lambda^2 \propto I^{(\mathrm{SWM})} \propto$ WFs quadratic spread

Wannier functions, one dimension, single band

- $L \to \infty,$ k continuous:

$$X_\ell = \ell a \qquad |w_\ell\rangle = \frac{a}{2\pi} \int_{\mathrm{BZ}} dk \; \mathrm{e}^{ikX_\ell} \, |\psi_k\rangle$$

- $L = Ma$ finite, k_j discrete:

$$|w_\ell\rangle = \frac{1}{M} \sum_{j=1}^{M} \mathrm{e}^{ik_jX_\ell} \, |\psi_{k_j}\rangle$$

- **Caveat:** Gauge arbitrariness in $|\psi_{k_j}\rangle$

Invariance of the many-body ground state

- So far, we have written $|\Psi_0\rangle$ an N-particle Slater determinant of Bloch orbitals.
- Any determinant is invariant for unitary transformation of the vectors (orbitals) within the occupied manifold.
- We transform the **Bloch** (delocalized) orbitals into **Wannier** (localized) orbitals.
- In the **insulating case**:
    - The occupied manifold is the whole band: $|\Psi_0\rangle$ is invariant by such unitary transformation.
    - $|\Psi_0\rangle$ can be **equivalently** written as an N-particle Slater determinant of **Wannier** orbitals.
- What about the **metallic** case?

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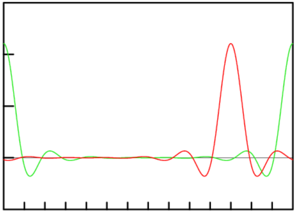
Invariance of the many-body ground state (cont'd)



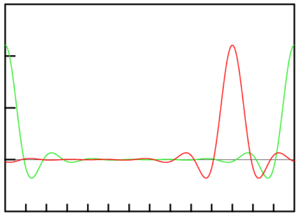
- Finite L
  - In this drawing, again $L = Ma$, with $M = 14$:
  - Slater determinant built with M occupied Wannier orbitals $w_n(x)$.

- Infinite L $\quad (M \to \infty)$

$$|w_\ell\rangle = \frac{a}{2\pi} \int_{\mathrm{BZ}} dk \; \mathrm{e}^{ikX_\ell} \, |\psi_k\rangle$$

$$\int_{-\infty}^{\infty} dx \, |\langle x | w_\ell \rangle|^2 = 1 \qquad \textbf{finite!}$$

Invariance of the many-body ground state (cont'd)



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$$\int_{-\infty}^{\infty} dx \; |\langle x | w_\ell \rangle|^2 = 1$$ **finite!**

Maximally localized Wannier functions

- With the **optimal** choice of the gauge:

$$|\langle x|w_\ell\rangle| \to 0 \qquad \textbf{exponentially} \text{ for } x \to \pm\infty$$

$$\langle w_n|x^2|w_n\rangle - |\langle w_n|x|w_n\rangle|^2 \qquad \textbf{minimum}$$

- The minimum “quadratic spread” is equal to the RS λ^2
- The spread diverges in the metallic case.
- **Caveat:** In 3*d* there are some complications: Marzari-Vanderbilt MLWFs (1997).

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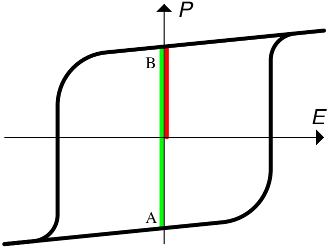
8. Insulators vs. metals
9. **Polarization**
10. A $\mathbb{Z}_2$ topological invariant

Spontaneous polarization of a ferroelectric

R. Resta, Ferroelectrics **136**, 51 (1992)



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

$$\mathbf{P}_s = \int_0^{\Delta t} \mathbf{j}(t)\, dt \qquad = \int_0^1 d\lambda\, \frac{d}{d\lambda}\mathbf{P}_{\text{electronic}} + \Delta\mathbf{P}_{\text{nuclear}}$$

Any current is mostly related to the **phase** of the wavefunction (not to the square modulus!)

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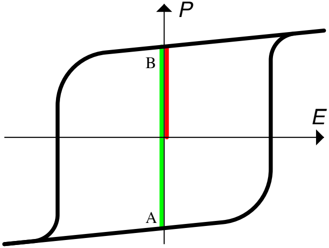

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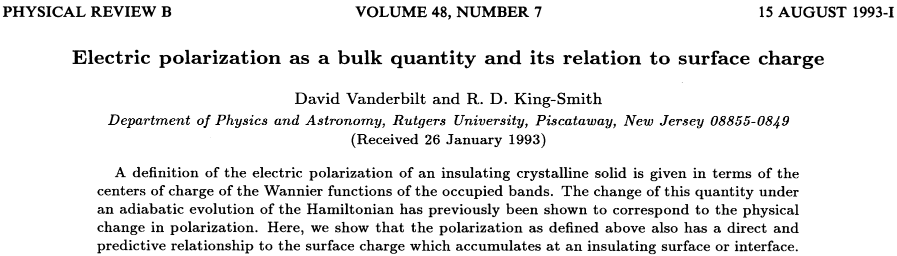


PHYSICAL REVIEW B VOLUME 48, NUMBER 7 15 AUGUST 1993-I

Electric polarization as a bulk quantity and its relation to surface charge

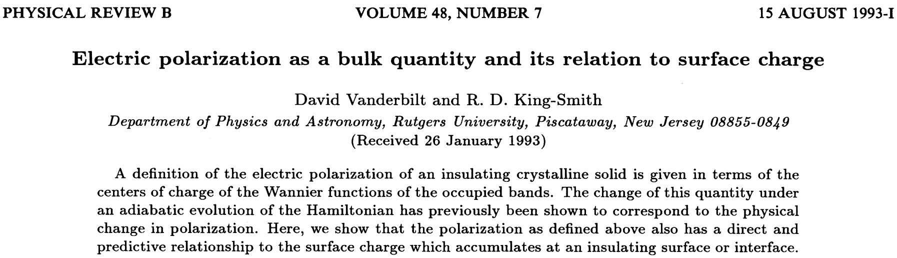
David Vanderbilt and R. D. King-Smith
Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08855-0849

(Received 26 January 1993)

A definition of the electric polarization of an insulating crystalline solid is given in terms of the centers of charge of the Wannier functions of the occupied bands. The change of this quantity under an adiabatic evolution of the Hamiltonian has previously been shown to correspond to the physical change in polarization. Here, we show that the polarization as defined above also has a direct and predictive relationship to the surface charge which accumulates at an insulating surface or interface.

- Instead of addressing Δ**P**, it is possible to define **P “itself”**
- However....
  P is not a vector, **it is a lattice!**
- **P** is only defined modulo a “quantum”

The second Vanderbilt & King-Smith paper



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Center of charge (1d & quasi-1d systems)

According e.g. to **Kittel textbook** **P** is nonzero when "....the **center** of positive charge does not coincide with the **center** of negative charge"

- N spinless electrons in a segment of lenght L:

$$\Psi_0 = \Psi_0(x_1, x_2, \ldots x_j, \ldots x_N),$$

- Periodic boundary conditions:

$$\Psi_0 = \Psi_0(x_1, x_2, \ldots x_j, \ldots x_N) = \Psi_0(x_1, x_2, \ldots x_j + L, \ldots x_N)$$

- Nuclei of charge eZ_ℓ at sites X_ℓ
- **Centers of charge:**

$$\sum_\ell Z_\ell X_\ell - \langle \Psi_0 | \sum_j x_j | \Psi_0 \rangle$$

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Center of charge, better

- Within PBCs coordinates are actually **angles**
- The two “centers” must be defined **modulo L**
- Their **difference** must be origin-invariant

$$\sum_{\ell} Z_\ell X_\ell - \langle \Psi_0 | \sum_j x_j | \Psi_0 \rangle$$

$$\longrightarrow \frac{L}{2\pi} \text{Im ln } \mathrm{e}^{i \frac{2\pi}{L} \sum_\ell Z_\ell X_\ell} + \frac{L}{2\pi} \text{Im ln } \langle \Psi_0 | \mathrm{e}^{-i \frac{2\pi}{L} \sum_j x_j} | \Psi_0 \rangle$$

- Polarization in 1d (R. Resta, PRL 1998):

$$P = \frac{e}{2\pi} \text{Im ln } \langle \Psi_0 | \mathrm{e}^{i \frac{2\pi}{L} \left(\sum_\ell Z_\ell X_\ell - \sum_j x_j \right)} | \Psi_0 \rangle$$

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Berry phase & the "quantum"

$$\gamma = \text{Im}\ln\ \langle\Psi_0|\mathrm{e}^{i\frac{2\pi}{L}\left(\sum_\ell Z_\ell X_\ell - \sum_j x_j\right)}|\Psi_0\rangle$$

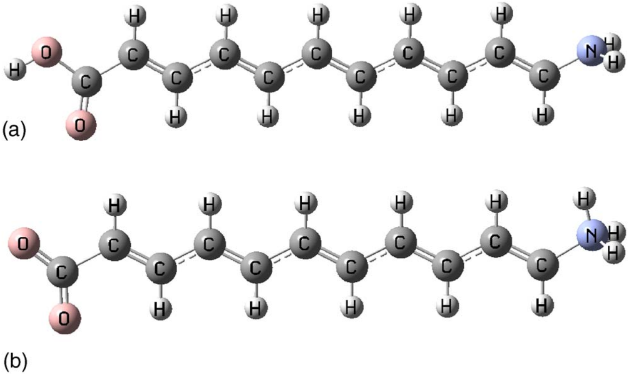
$$P_x = e\frac{\gamma}{2\pi} \quad \text{defined modulo } e$$

- γ is the Berry phase in disguise
- γ includes the nuclear contribution

Outline

1 Faraday laws of electrolysis
2 Modern view of a liquid
3 A flavor of topology
4 The adiabatic current
5 The “electron-in-broth” formula (one electron)
6 Many electrons in broth: transport and conductivity
7 Infrared spectra
8 Insulators vs. metals
9 Polarization
10 A $\mathbb{Z}_2$ topological invariant

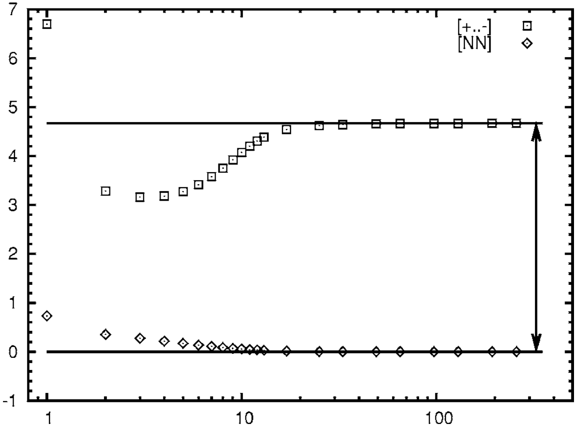
A 1d insulator (polyacetylene), different terminations



Guess for a centrosymmetric polymer: $\mathbf{P} = 0$. Is this right?

Dipole per monomer

(Kudin, Car, & Resta, JCP 2007)



$\mathbb{Z}_2$ classification of centrosymmetric polymers

$\mathbb{Z}_2$-even: $P = 0 \mod e$

Alternant polyacetylene, model molecular crystal.....

$\mathbb{Z}_2$-odd: $P = e/2 \mod e$

Model ionic crystal.....

- $\mathbb{Z}_2$ invariant **topological**:
  - Independent e.g. of ionicity difference
  - Independent of the theory level (tight-binding, first-principle...)
  - Robust by continuous deformation of the wavefunction

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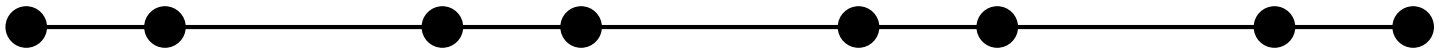

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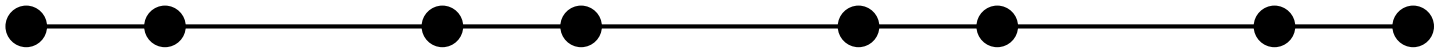
Simple tight-binding Hamiltonians



$\mathbb{Z}_2$-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 **centrosymmetry**
- When joining the two with a continuous & centrosymmetric deformation of the Hamiltonian **the gap closes!**