

Localization and polarization in the insulating state of matter

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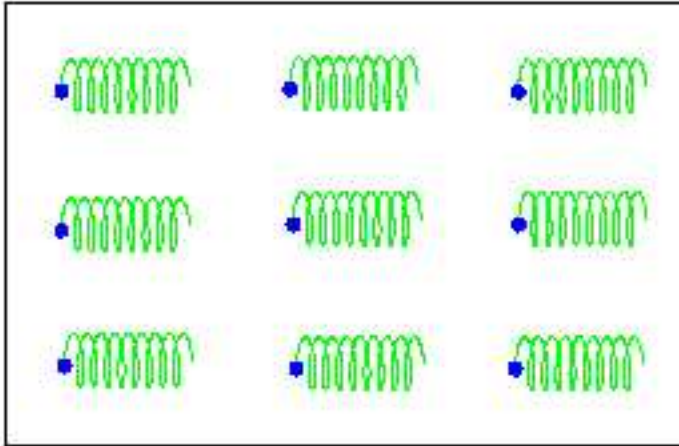
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Benasque, September 2004

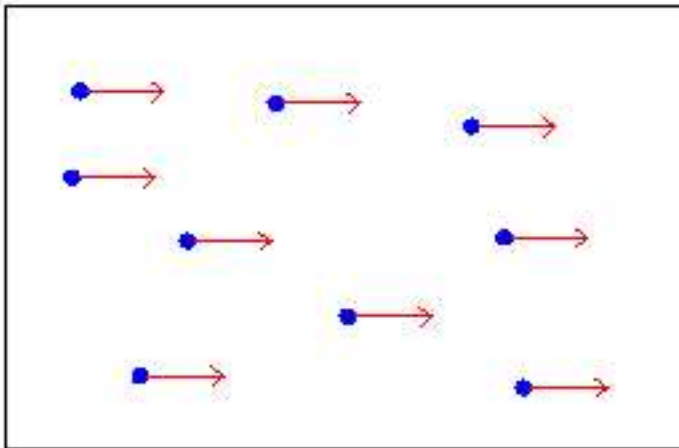
Outline

- Before 1926: Classical insulators and metals.
- Circa 1928: Band theory of insulators vs. metals.
- 1964: W. Kohn, “Theory of the insulating state”.
- 1992 onwards: “Modern theory of polarizazion”
(based on a Berry phase).
- 1999 onwards: Theory of the insulating state revisited.

In classical physics

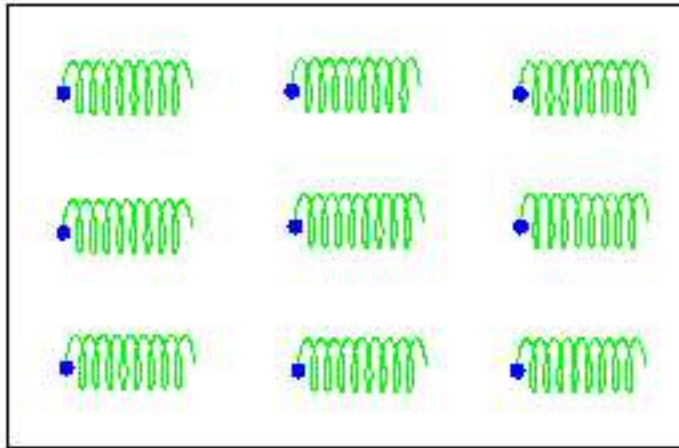


Insulator
(Lorentz, 1909)

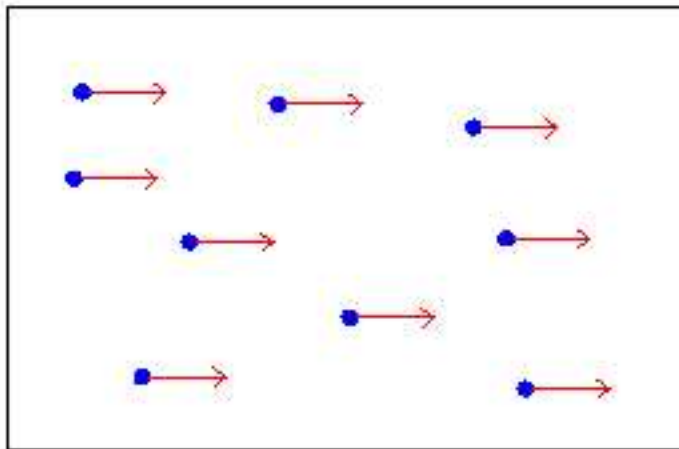


Metal
(Drude, 1900)

Under the action of a dc field:



**Electron do not flow freely
(they polarize instead)**

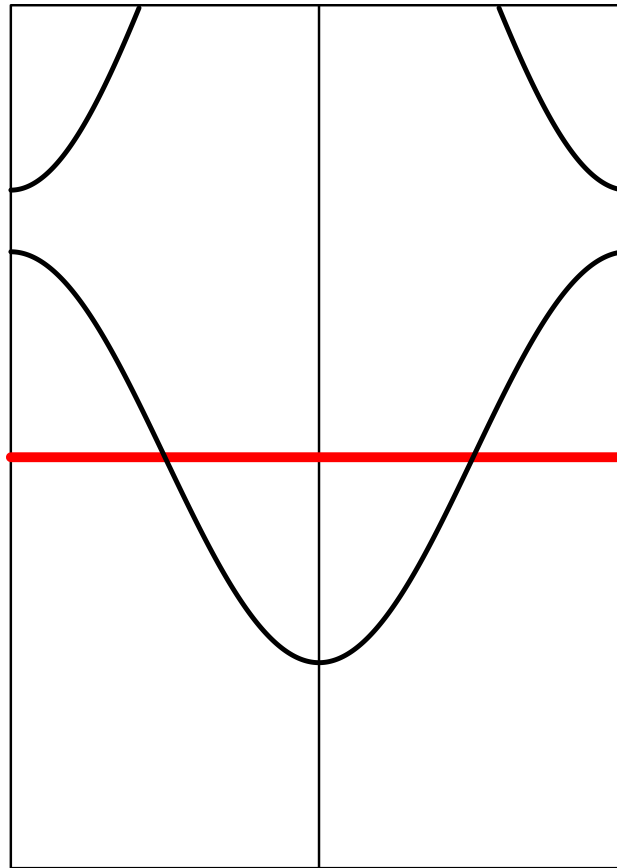
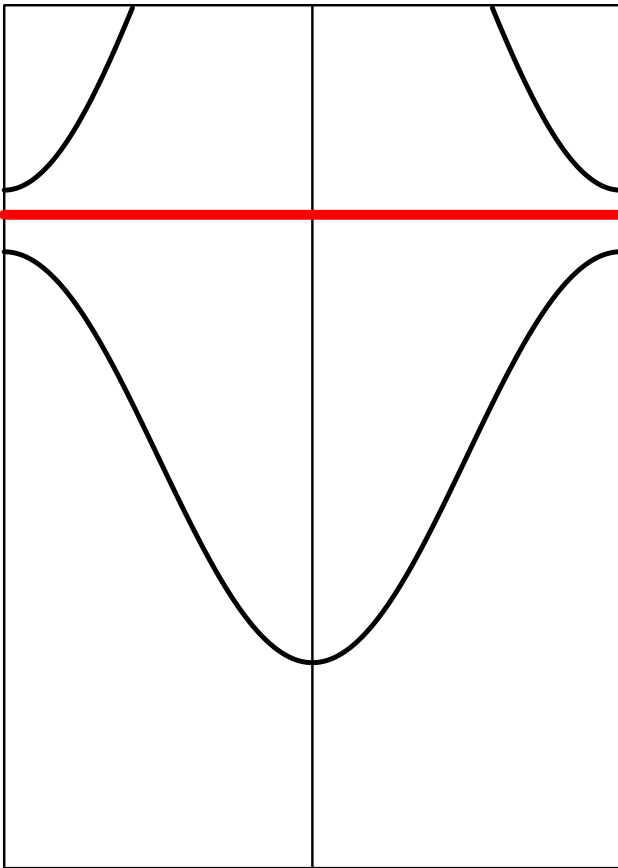


**Electrons flow freely
(hindered by scattering)**

In quantum physics (Bloch, 1928)

Insulator

Metal



Theory of the Insulating State*

WALTER KOHN

University of California, San Diego, La Jolla, California

(Received 30 August 1963)

In this paper a new and more comprehensive characterization of the insulating state of matter is developed. This characterization includes the conventional insulators with energy gap as well as systems discussed by Mott which, in band theory, would be metals. The essential property is this: Every low-lying wave function Φ of an insulating ring breaks up into a sum of functions, $\Phi = \sum_{\alpha} c_{\alpha} \Phi_{\alpha}$, which are localized in disconnected regions of the many particle configuration space and have essentially vanishing overlap. This property is the analog of localization for a single particle and leads directly to the electrical properties characteristic of insulators. An Appendix deals with a soluble model exhibiting a transition between an insulating and a conducting state.

Two key messages:

- the insulating behavior reflects a certain type of organization of the electrons in the ground state
- insulating characteristics are a strict consequence of electronic localization (in an appropriate sense) and do not require an energy gap

Phenomenologically:

Metal:

Has a finite dc conductivity.

Insulator:

Has a vanishing dc conductivity
(at zero temperature!).

....but also:

Metal:

Macroscopic polarization is trivial:

It is **not** a bulk effect.

Insulator:

Has a nontrivial macroscopic polarization:

bulk effect, material dependent.

Modern theory of polarization

A genuine **revolution** since 1992.

Previously, the phenomenon was **not** understood: most textbooks contain incorrect statements.

Macroscopic polarization obtains from the electronic wavefunction as a **Berry phase**.

Simple case: one-dimensional spinless electrons

Condensed system in 1d: N electrons in a segment of length L :

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

where L is large with respect to atomic dimensions.

Thermodynamic limit:

$$N \rightarrow \infty, L \rightarrow \infty, N/L = n_0 \text{ constant.}$$

Using only the **ground-state** Ψ , we are going to build a dimensionless complex number \mathfrak{Z}_N .

Periodic boundary conditions (BvK)

The wavefunction is **periodic** (with period L) over each electronic variable x_j separately:

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

Equivalently, one imagines the electrons confined to a circular rail, where the coordinates are actually the angles $2\pi x_j/L$, defined modulo 2π .

Key quantity

(for both polarization & localization)

The dimensionless complex number \mathfrak{z}_N , defined as the expectation value of the “many-body phase operator” (or “twist operator”) U :

$$\mathfrak{z}_N = \langle \Psi | U | \Psi \rangle = \int_0^L dx_1 \dots \int_0^L dx_N |\Psi(x_1, \dots, x_N)|^2 U(x_1, \dots, x_N);$$

$$U(x_1, \dots, x_N) = \exp \left(i \frac{2\pi}{L} \sum_{j=1}^N x_j \right).$$

Notice: (i) U is unitary; (ii) it obeys periodic BvK boundary conditions; (iii) it is genuinely many-body.

Modern theory of polarization (bottom line thereof)

The electronic contribution to the macroscopic electric polarization of the system can be cast in the very compact form:

$$P_{\text{el}} = \frac{e}{2\pi} \lim_{N \rightarrow \infty} \text{Im} \log \mathfrak{z}_N.$$

The key quantity of the modern theory of polarization is the **Berry phase**:

$$\gamma = \lim_{N \rightarrow \infty} \text{Im} \log \mathfrak{z}_N.$$

Notice: Such phase is ill defined if \mathfrak{z}_N goes to zero!

First moment of the electron distribution
(from polarization theory):

$$P_{\text{el}} = \frac{eN}{L} \langle x \rangle$$

$$\langle x \rangle = \frac{L}{eN} P_{\text{el}} = \frac{1}{N} \frac{L}{2\pi} \text{Im log } \mathfrak{z}_N.$$

For a molecule (**no** BvK, N **fixed**, $L \rightarrow \infty$):

$$U(x_1, \dots, x_N) = \exp \left(i \frac{2\pi}{L} \sum_{j=1}^N x_j \right) \simeq 1 + i \frac{2\pi}{L} \sum_{j=1}^N x_j$$

$$\mathfrak{z}_N = \langle \Psi | U | \Psi \rangle \simeq 1 + i \frac{2\pi}{L} \langle \Psi | \sum_{j=1}^N x_j | \Psi \rangle$$

$$\text{Im log } \mathfrak{z}_N \simeq \frac{2\pi}{L} \langle \Psi | \sum_{j=1}^N x_j | \Psi \rangle$$

First moment:

$$\langle x \rangle = \frac{1}{N} \frac{L}{2\pi} \text{Im} \log \mathfrak{z}_N.$$

Second cumulant moment:

$$\langle x^2 \rangle_c = \langle x^2 \rangle - \langle x \rangle^2 = -\frac{1}{N} \left(\frac{L}{2\pi} \right)^2 \log |\mathfrak{z}_N|^2.$$

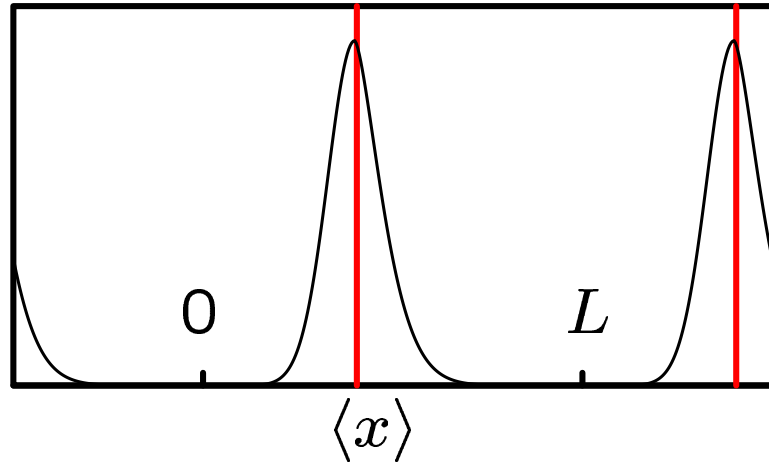
Properties:

- (i) The moments are global properties of the many-electron wavefunction as a whole (e.g. **not** of the one-electron orbitals);
- (ii) The moments are intensive quantities.
- (iii) If \mathfrak{z}_N goes to zero, the first moment is ill defined and the second moment **diverges** !

In 3d: Localization tensor $\langle r_\alpha r_\beta \rangle_c$

- $\langle r_\alpha r_\beta \rangle_c$ is an intensive quantity which measures the **global** localization of the many-body wavefunction as a whole.
- Very general:
Crystalline or disordered;
independent–electrons or correlated.
- $\langle r_\alpha r_\beta \rangle_c$ finite in insulators, divergent in metals:
It is a **ground-state property** which discriminates very sharply between insulators and metals.
- In the **special** case of a crystalline system of independent electrons, the trace of $\langle r_\alpha r_\beta \rangle_c$ coincides with the quadratic spread of the optimally localized Wannier orbitals (Marzari & Vanderbilt, 1997).

A flavor of how the algebra works (lone electron in a periodic box)



First moment:

$$\langle x \rangle \neq \int_{-\infty}^{\infty} dx x |\psi(x)|^2 \quad (\text{nonsense!})$$

$$\mathfrak{z} = \int_0^L dx e^{i\frac{2\pi}{L}x} |\psi(x)|^2, \quad \langle x \rangle = \frac{L}{2\pi} \text{Im} \log \mathfrak{z}.$$

(Selloni, Carnevali, Car, Parrinello, PRL 1987)

Second cumulant moment

Complete localization:

$$|\psi(x)|^2 = \sum_{m=-\infty}^{\infty} \delta(x - x_0 - mL) \longrightarrow z = e^{i\frac{2\pi}{L}x_0}$$

Complete delocalization:

$$|\psi(x)|^2 = \frac{1}{L} \longrightarrow z = 0$$

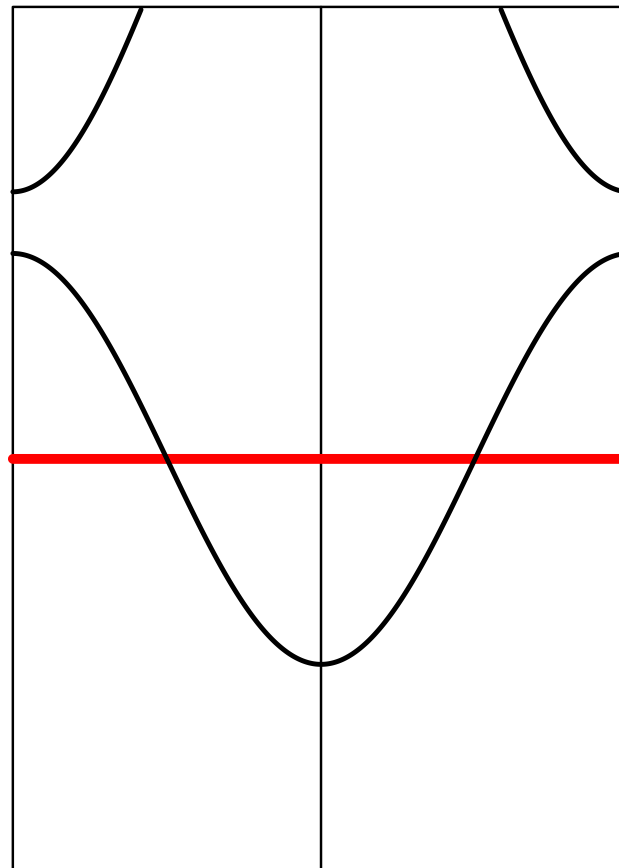
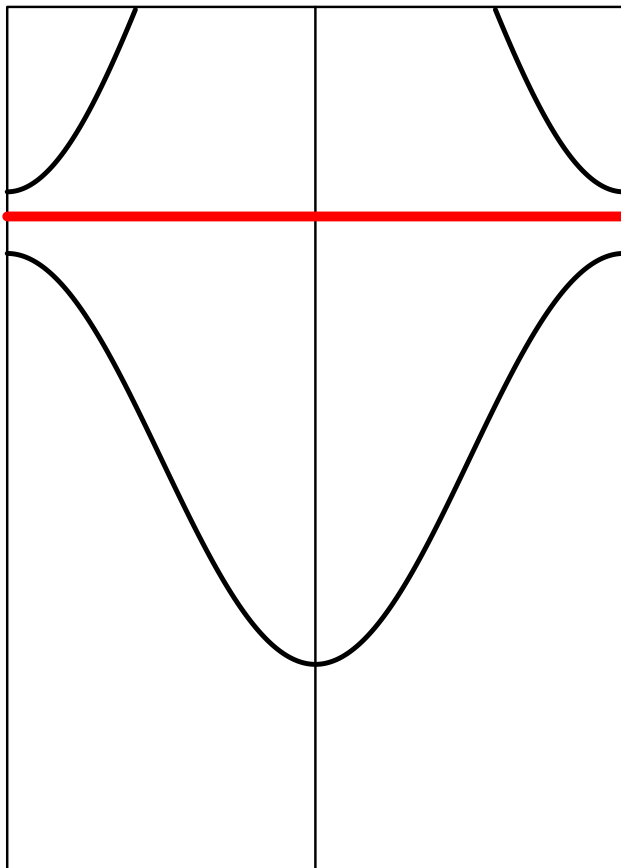
$$\langle x \rangle = \frac{L}{2\pi} \text{Im} \log z$$

$$\langle x^2 \rangle_c = \langle x^2 \rangle - \langle x \rangle^2 = - \left(\frac{L}{2\pi} \right)^2 \log |z|^2$$

Crystal of independent electrons (infinite)

Insulator

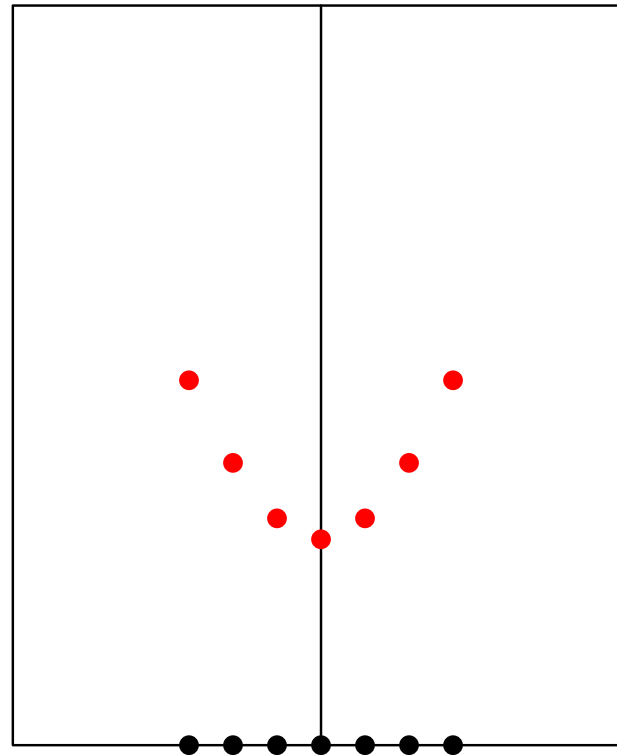
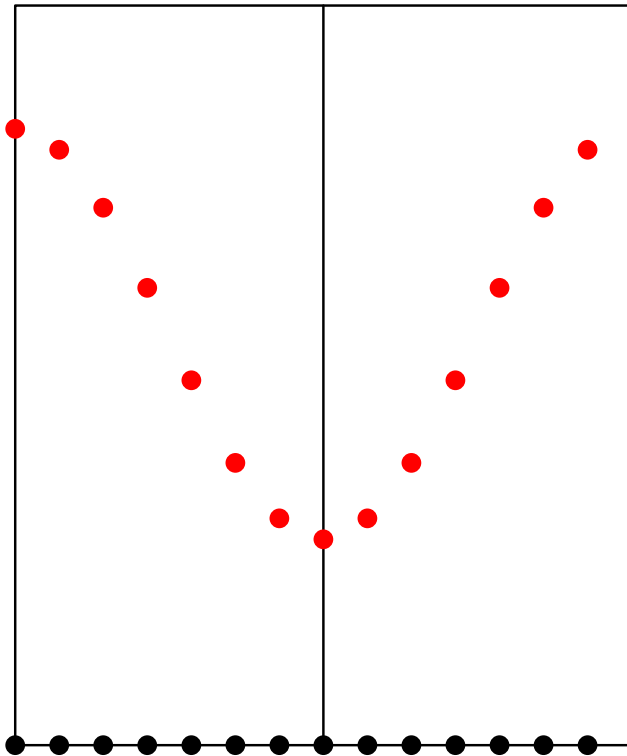
Metal



Crystal of independent electrons (finite)

Insulator

Metal



(In this figure, $L = 14$ times the lattice constant)

$|\Psi\rangle$ is an N -particle Slater determinant.

- BvK imposed over $L = Ma$:
 M allowed Bloch vectors in the reciprocal cell.
- $|\Psi\rangle$ **can** be written as a determinant of (occupied) Bloch orbitals, **both** in the insulating and in the metallic case.
- **Key difference:** The whole band is used to build the insulating $|\Psi\rangle$, while only one half of the band is used for the metallic $|\Psi\rangle$.

$$\mathfrak{z}_N = \langle \Psi | e^{i\frac{2\pi}{L}\hat{X}} | \Psi \rangle = \langle \Psi | \tilde{\Psi} \rangle$$

Theorem: $\langle \Psi | \tilde{\Psi} \rangle = \det S$

$$S_{s,s'} = \langle \varphi_s | \tilde{\varphi}_{s'} \rangle = \int_0^L dx \psi_{q_s}^*(x) e^{i\frac{2\pi}{L}x} \psi_{q_{s'}}(x).$$

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

The matrix element vanishes unless $q_{s'} = q_s - 2\pi/L$,
 that is $s' = s - 1$: the determinant **factors**.

$$\mathfrak{z}_N = \det S = \prod_s S_{s,s-1}$$

Phase of \mathfrak{z}_N :

Berry phase, macroscopic polarization.

Modulus of \mathfrak{z}_N :

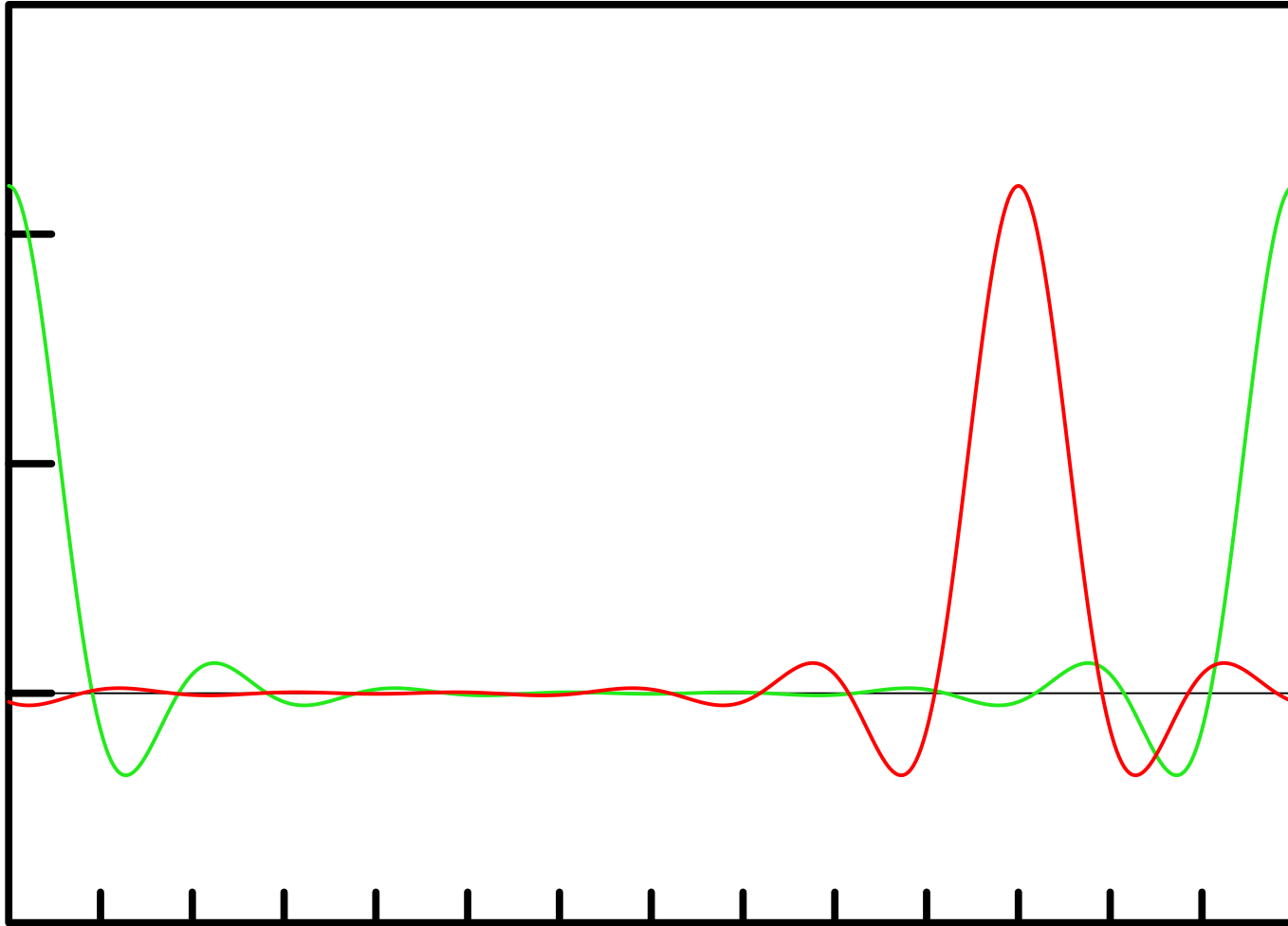
Second cumulant moment, alias localization tensor.

in a metal:

The determinant is zero, the phase (ergo macroscopic polarization) is ill defined.

The second cumulant moment $\propto -\log |\mathfrak{z}_N|$ is **infinite** (even for finite N).

Transformation to Wannier orbitals



MAIN MESSAGE:

**One discriminates
between insulators and metals
scrutinizing the ground state only
(no excitations!)**

$\langle x^2 \rangle_c$ measures the localization of the many-body wavefunction as a whole,
for **any** insulator (band, Mott, Anderson....).

Is $\langle x^2 \rangle_c$ an experimentally measurable quantity?

In a real three-dimensional system:

Is $\langle r_\alpha r_\beta \rangle_c$ an experimentally measurable quantity?

Souza, Wilkens & Martin, PRB 2000

Yes, related to conductivity:

$$\langle r_\alpha r_\beta \rangle_c = \frac{\hbar V}{\pi e^2 N} \int_0^\infty \frac{d\omega}{\omega} \operatorname{Re} \sigma_{\alpha\beta}(\omega).$$

inequality (diagonal elements):

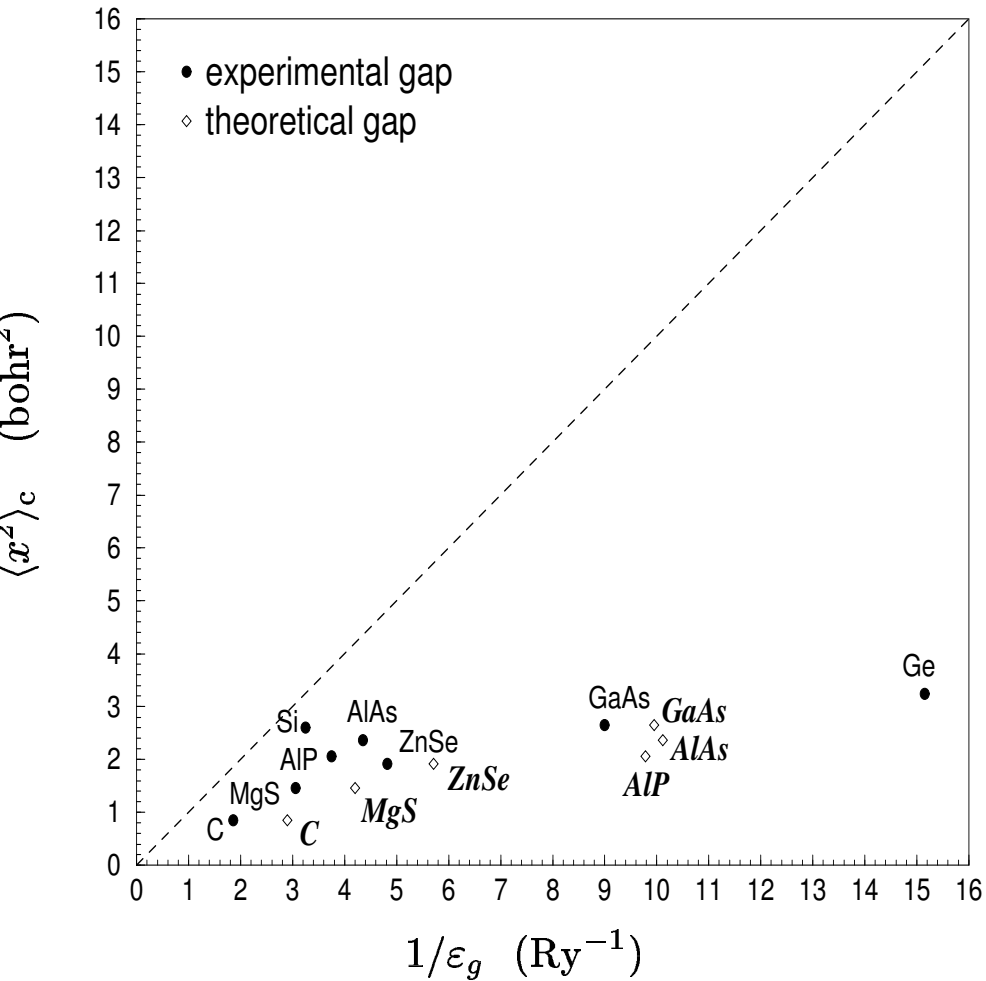
$$\langle r_\alpha r_\alpha \rangle_c \leq \frac{\hbar^2}{2m_e E_g}.$$

Notice:

A **ground-state** property is experimentally accessed via **excitation** measurements. This basic result owes to a **fluctuation-dissipation** sum rule.

Calculations for cubic semiconductors

(Sgiarovello, Peressi, and Resta PRB 2001)



$$\langle r_\alpha r_\alpha \rangle_c \leq \frac{\hbar^2}{2m_e E_g}$$

Conclusions

Localization (as defined here) **discriminates between insulators and metals.**

The key ingredient is \mathfrak{z}_N :

Expectation value of the “twist” operator.

Its **phase** yields polarization, its **modulus** yields localization.

\mathfrak{z}_N is a ground state property; it doesn't need any spectral information.

The localization tensor is an observable related to conductivity.

Electrons in cubic semiconductors are very localized.