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Subject: **ONR Grant Award N0014-17-1-2803 – Polarization, magnetization and other geometrical properties of the electronic ground state – Final reports**

With reference to the Grant Award N0014-17-1-2803 "Polarization, magnetization and other geometrical properties of the electronic ground state", please find herewith the following reports as required:

- 1 copy of the Final Technical Report
- 1 copy of the model SF 298

We regret to inform you that, due to the covid emergency, the program has been partly disrupted, particularly because of canellation of several conference travels, For this reason a part of the grant money has not been spent.

We remain at your disposal for any further information.

Best regards,

Dott. Stefano Fabris

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Final Report on ONR N00014-17-1-2803
Polarization, magnetization, and other geometrical properties of the electronic ground state
09/01/2017 - 12/31/2021

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Technical objectives

The grant has supported theoretical and computational research work on materials of interest to the ONR Division 332, specifically ferroelectrics, piezoelectrics, flexoelectrics, magnetoelectrics, and multiferroics.

Our research concerns some geometrical observables of the electronic ground state, whose archetype is the macroscopic electric polarization of solids, for which first-principle understanding dates since 1992 onwards. The other geometrical observables investigated recently look quite different among themselves—from a phenomenological and applicative viewpoint—yet they share many common features on the theoretical, algorithmic, and computational sides.

The list of geometrical observables addressed in this research work includes physical properties as diverse as electrical polarization, orbital magnetization, anomalous Hall effect, X-ray circular dichroism, longitudinal conductivity, as well as the general theory of the insulating state.

Technical approach

It is now clear that the geometrical observables come in two very different classes. The observables of class (i) only make sense for insulators, and are defined modulo 2π (in dimensionless units), while the observables of class (ii) are defined for both insulators and metals, and are single-valued.

As for class (i), two observables are known: electrical polarization and the "axion" term in magnetoelectric response; for both observables the modulo 2π ambiguity is fixed only after the termination of the insulating sample is specified. Furthermore in presence of some protecting symmetry only the values zero or π (mod 2π) are allowed: the observable becomes then a topological $\mathbb{Z}_2$ index: a $\mathbb{Z}_2$-odd crystalline insulator cannot be "continuously deformed" into a $\mathbb{Z}_2$-even one without closing the gap.

Owing to their single-valuedness, the geometrical observables in class (ii) can also be defined locally in coordinate space: they admit therefore a "density". We have extended their definitions to the cases of a noncrystalline and/or a macroscopically inhomogeneous sample, and even a bounded sample: in all these cases there is no **k** vector to speak of. The observables in class (i) instead, being multiple valued, do not admit a density. In particular "polarization density" is a nonsensical concept.

The established approach to the geometrical ground-state properties is via reciprocal-space (k-space) integration—over the Brillouin zone for insulators, over the Fermi volume for metals—of the appropriate function of **k**. As said above, we have also successfully pursued a different and innovative path, providing a "dual" formulation of the same class-(ii) observables in coordinate space, thus extending the scope of the theory to noncrystalline and inhomogeneous materials as well.

Accomplishments

Dissemination

We have written an invited Chapter for a new edition of the "Handbook of Materisl Modeling" (Springer, 2020), where the state of the art about the theories of polarization and orbital magnetization is presented [8].

We have written an invited popular presentation of the geometrical ground-state observables in condensed matter, published on "Il Nuovo Saggiatore" (Italian analog of Physics Today) [5].

We have published Lecture Notes for an international school, focussing on the many-body (i.e. beyond band-structure) formulation of the known geometrical observables [7].

We have published a thorough review (invited) about the "theory of the insulating state", originally developed mostly by the PI over more than 20 years [1].

Electrical polarization

The theory of macroscopic electrical polarization has been completed in the 1990s, both at the band-structure level (1993) and in a many-body framework (1998). Even today this outstanding breakthrough is little known beyond the community of electronic structure specialists, owing to the occurrence of somewhat "exotic" concepts (Berry phases and the like), while instead no reference to the familiar dipole of a bounded crystallite is made. We have in a sense reversed the approach, by showing that one can define the dipole of a bounded sample in an alternative way, from which the results of the modern theory follow quite naturally. The paper [12] has been written targeting a readership of chemical physicists, and in fact it has been selected as an "Editor's Pick" by J. Chem. Phys.

We also published a paper [2] addressing the long-standing problem of polarization within DFT, clarifying the reasons for an apparently paradoxical situation. Within DFT, the exact Kohn-Sham potential yields the exact electron density, ergo the exact dipole of a bounded system (e.g. a crystallite). Instead, for an unbounded system DFT does not provide (in principle) the exact polarization of an interacting-electron system.

Anomalous Hall conductivity and orbital magnetization

The anomalous Hall conductivity is by definition the Hall conductivity in absence of an external magnetic field; it manifests itself in ferromagnetic metals and, more generally, when the material spontaneously breaks time-reversal symmetry. Besides extrinsic effects, there is also a geometrical contribution which only depends on the pristine material. We have proved that the phenomenon is local and does not require un unbounded solid with periodic boundary conditions. It can be defined and computed for bounded samples and inhomogeneous systems, as well as for ribbons, polymers, layered materials; a similar formalism applies to orbital magnetization in the same kind of reduced-dimensionality materials [6].

X-ray circular dichroism

An incorrect belief widespread among experimentalists holds that synchrotron radiation can measure orbital magnetization **M**. The belief owes to a "celebrity" paper bearing the misleading title "X-ray circular dichroism as a probe of orbital magnetization" (Thole et al., Phys. Rev. Lett. 1992). Contrary to the claim, such probe measures a quite interesting and useful geometrical property of the electronic ground state, yet different from **M** . I have thoroughly clarified the issue and discussed the properties of this observable in comparison to **M**. Both observables are a measure of spontaneous time-reversal (T) breaking in the given material: by definition, **M** is the derivative of the free-energy density with respect to the magnetic field (orbital term thereof, with a minus sign). Synchrotron radiation accesses the free-energy derivative with respect to a different T-breaking probe; the said probe has the virtue of coupling to orbitals degrees of freedom only.

We have presented and discussed the issue in [5], [7]. and [9]. Since, as said above, our result is regarded as "revolutionary" in the synchrotron-physics community, our paper [9] has received a Comment from a knowledgeable synchrotron theorist (Masssimo Altarelli); our answer, providing further clarification, is published as [11]. But despite our best efforts, the wrong idea that synchrotron radiation can access orbital magnetization remains strongly entrenched in the minds of all synchrotron physicists.

Drude weight and dc conductivity

The Drude weight measures the inverse inertia of a many-electron system, when probed by a dc electric field: it is therefore the key entry in the theory of dc longitudinal conductivity. We have proved its–hitherto unnoticed–geometrical nature, and we have shown that, geometry-wise, the Drude weight has a remarkable affinity to orbital magnetization [3].

A bounded sample does not support a dc current, therefore one could guess that the Drude weight is ill-define therein. We have shown instead that by probing the many-electron system with low-frequency fields the actual value of the Drude weight can be retrieved. Simulations on a very simple model system validate our theory [10].

Theory of the insulating state

In our previous work—also reviewed in [1]—we have shown that the insulating character of a material is a geometrical property of the electronic ground state and does not require an energy gap. The theory so far was only capable of addressing macroscopically homogeneous systems; more recently, we have addressed, geometry-wise the insulating/metallic character of a region in an inhomogeneous system. We have defined a geometrical "marker" which probes the insulating state locally, and we have validated it by means of computer simulations; the paper appeared on Phys. Rev. Lett. [4].

Signature

Signed: Raffaele Resta, Principal Investigator

Summary of publications supported by ONR Grant 14-17-1-2803

1. R. Resta,
   Theory of the insulating state,
   Riv. Nuovo Cimento **41**, 463 (2018).

2. R. Resta,
   Polarization in Kohn-Sham density-functional theory,
   Eur. Phys J. B **91**, 100 (2018).

3. R. Resta,
   Drude weight and superconducting weight,
   J. Phys.: Condens. Matter **30**, 414001 (2018).

4. A. Marrazzo and R. Resta,
   Local theory of the insulating state,
   Phys. Rev. Lett. **122**, 166602 (2019).

5. R. Resta,
   Geometrical observables in condensed matter: Electrical polarization, orbital magnetization, and more,
   Il Nuovo Saggiatore **35** (5/6), 7 (2019).

6. E. Drigo and R. Resta,
   Chern number and orbital magnetization in ribbons, polymers, and single-layer materials,
   Phys. Rev. B **101**, 165120 (2020).

7. R. Resta,
   Geometry and Topology in Many-Body Physics,
   in: *Topology, Entanglement, and Strong Correlations Modeling and Simulation* Vol. **10**, E. Pavarini and E. Koch, eds. (Forschungszentrum Juelich, 2020), Ch. 10.
   `https://https://www.cond-mat.de/events/correl20/manuscripts/resta.pdf`

8. R. Resta,
   Electrical polarization and orbital magnetization: The position operator tamed,
   in: *Handbook of Materials Modeling,* W. Andreoni and S. Yip, eds. (Springer, 2020), p. 151.

9. R. Resta,
   Magnetic circular dichroism versus orbital magnetization,
   Phys. Rev. Research **2**, 023139 (2020).

10. G. Bellomia and R. Resta,
    Drude weight in systems with open boundary conditions,
    Phys. Rev. B **102**, 205123 (2020).

11. R. Resta,
Magnetic circular dichroism versus orbital magnetization: Reply to a Comment,
Phys. Rev. Research **2**, 048002 (2020).

12. R. Resta,
From the dipole of a crystallite to the polarization of a crystal,
J. Chem. Phys. **154**, 050901 (2021); selected as an Editor's Pick.

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The program has been partly disrupted by the covid emergency, particularly because of cancellation of several conference travels. For this reason a part of the grant money has not been spent.

14. ABSTRACT
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