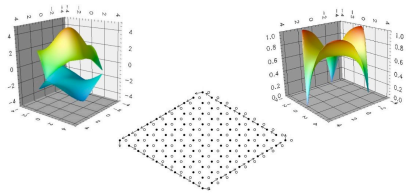
# Orbital Magnetization in Condensed Matter



**Dates :**
***Jun 15, 2009 - Jun 17, 2009***

**Location :**
***CECAM-HQ-EPFL, Lausanne, Switzerland***

**Raffaele Resta**
*CNR-INFM Democritos and University of Trieste*

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# 1 Details

## 1.1 Description

Macroscopic magnetization is a fundamental concept that all undergraduates learn about in elementary courses. In view of this, it is truly extraordinary that before 2005 there was no generally accepted formula for the macroscopic orbital magnetization in condensed matter. Orbital magnetization--as opposed to spin magnetization--occurs whenever time-reversal symmetry is broken in the spatial wavefunction. For instance, in a ferromagnet the spin-orbit interaction transmits the symmetry breaking from the spin degrees of freedom to the spatial (orbital) ones; the two contributions to the total magnetization can be resolved experimentally. Other examples include the induced magnetization in applied magnetic fields, or in any other time-reversal-symmetry breaking perturbations. Whenever the unperturbed system is nonmagnetic, the induced magnetization is 100% of the orbital kind.

Sweeping advances are occurring these days in the field of orbital
magnetization, and a "modern theory" is in development. The key formulas are resemblant of (but more complex than) the Berry-phase formulas of the modern theory of electric polarization, developed in the 1990s. So far, formulas for orbital magnetization have been established for: (1) crystalline solids, either metallic or
insulating, at the mean field level (HF or Kohn-Sham); (2) noncrystalline insulators at a the mean-field level (such as for Car-Parrinello simulations). Some progress has been achieved even in the case of a correlated wavefunction, but the ultimate theory has not yet been developed.

As for implementations, only model Hamiltonians have been addressed so far; a first-principle implementation is under way at the time this proposal is written. Concerning applications of the novel theory, a promising novel scheme for evaluating NMR shielding tensors has been proposed; its first-principle implementation is also under way.

Another open issue relates orbital magnetization (which is a ground state property) to magnetic circular dichroism, by means of magneto-optical sum rules widely used by X-ray spectroscopists at synchrotron facilities. Related sum rules have been used to measure local orbital moments even in antiferromagnets, where the macroscopic magnetization is zero. A precise microscopic definition of local orbital magnetization is still lacking (for both ferromagnets and antiferromagnets).

# 2 Key references

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# 3 Program

## Day 1 - June, 15th 2009

Fundamentals

- 09:20 to 09:30 - Welcome
- 09:30 to 10:00 - **Raffaele Resta**
  Macroscopic magnetization: Analogies to and differences from the case of electrical polarization
- 10:00 to 10:15 - Discussion
- 10:15 to 10:45 - **David Vanderbilt**
  Theory of orbital magnetization in crystalline systems
- 10:45 to 11:00 - Discussion
- 11:00 to 11:30 - Coffee Break
- 11:30 to 12:00 - **Qian Niu**
  Theory of Orbital Magnetization and its Generalization to Interacting Systems
- 12:00 to 12:15 - Discussion
- 12:15 to 14:00 - Lunch Break

Experiment

- 14:00 to 14:30 - **Patrick Bruno**
  Hall Effect, Generalized Einstein Relation, and Berry Phase
- 14:30 to 14:45 - Discussion
- 14:45 to 15:15 - **Gerrit van der Laan**
  Sum rules for E1-E1 x-ray absorption
- 15:15 to 15:30 - Discussion
- 15:30 to 15:55 - **Andrei Rogalev**
  X-ray Magnetic Circular Dichroism Studies of Paramagnetics
- 15:55 to 16:00 - Discussion
- 16:00 to 16:15 - Coffee Break
- 16:15 to 16:45 - **Fabrice Wilhelm**
  Induced orbital magnetism of 5d transition metals studied with XMCD
- 16:45 to 17:00 - Discussion

Calculations

- 17:00 to 17:20 - **Davide Ceresoli**
  First principles theory of the orbital magnetization: ferromagnetic metals and organometallic complexes
- 17:20 to 17:30 - Discussion
- 17:30 to 17:45 - **Yugui Yao**
  First principles calculations of Orbital magnetization-Preliminary Results
- 17:45 to 17:50 - Discussion

## Day 2 - June, 16th 2009

Molecules and ions

- 09:00 to 09:30 - **E.K.U. Gross**
  Exact Born-Oppenheimer decomposition of the complete electron-nuclear wave function
- 09:30 to 09:45 - Discussion
- 09:45 to 10:15 - **Paolo Lazzeretti**
  Induced orbital paramagnetism in BH, CH+, C4H4, and C8H8 systems
- 10:15 to 10:30 - Discussion
- 10:30 to 10:50 - **Uwe Gerstmann**
  Ab initio calculation of the electronic g-tensor beyond perturbation theory: diatomic molecules and defects in semiconductors
- 10:50 to 11:00 - Discussion
- 11:00 to 11:15 - Coffee Break
- 11:15 to 11:40 - **Philippe Sainctavit**
  Is there a relation between the magnetic anisotropy of a single molecule magnet and the orbital magnetic moments of its ions ?
- 11:40 to 11:45 - Discussion
- 11:45 to 12:15 - **Guang-Yu Guo**
  Orbital magnetization, XMCD and magnetic hyperfine field
- 12:15 to 12:30 - Discussion
- 12:30 to 14:00 - Lunch Break

Theory developments (1)

- 14:00 to 14:30 - **Ivo Souza**
  What is the most physical way of dividing up the orbital magnetization into two gauge-invariant parts?
- 14:30 to 14:45 - Discussion
- 14:45 to 15:05 - **Raffaele Resta**
  Single k-point formulas for the electrical and magnetic cases
- 15:05 to 15:15 - Discussion
- 15:15 to 15:45 - **Sergej Savrasov**
  Calculations of Magnetic Exchange Interactions in d- and f- Electron Systems
- 15:45 to 16:00 - Discussion
- 16:00 to 16:15 - Coffee Break

Topological insulators

- 16:15 to 16:45 - **David Vanderbilt**
  Orbital magnetoelectric effects and topological insulators
- 16:45 to 17:00 - Discussion
- 17:00 to 17:20 - **Ming-Che Chang**
  Optical properties of topological insulator
- 17:20 to 17:30 - Discussion
- 19:30 to 21:30 - Dinner

## Day 3 - June, 17th 2009

Theory developments (2)

- 09:00 to 09:30 - **Jonathan Yates**
  Spin-spin coupling in the solid state
- 09:30 to 09:45 - Discussion
- 09:45 to 11:05 - **Anne-Christine Uldry**
  Spin and orbital moments in the Fe-Cr alloy
- 10:05 to 10:15 - Discussion
- 10:15 to 10:45 - **Timo Thonhauser**
  Orbital Magnetization and its Connection to NMR Chemical Shifts
- 10:45 to 11:00 - Discussion
- 11:00 to 11:30 - Coffee Break
- 12:00 to 12:15 - Discussion
- 11:30 to 12:00 - **Junren Shi**
  Polarization Induced by Inhomogeneity
- 12:00 to 12:15 - Discussion
- 12:15 to 14:00 - Lunch Break

- 14:00 to 16:00 - Discussion

# 4 Participant List

**Organizers**

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# 5 Abstract list

### *Calculations of Magnetic Exchange Interactions in d- and f- Electron Systems*

**Sergej Savrasov**
Univeristy of California

## Abstract

The use of linear response based magnetic force theorem for calculating exchange interactions in magnetic materials is well established. In this talk several recent applications of this method to extract exchange couplings in systems such as Mott insulators, high temperature superconductors and novel iron based superconductors will be given together with its shortcomings when applying the method to 4f systems (such, e.g., as Gd) and to systems exhibiting orbital moments such, e.g, as Ce and Ce compounds. Possible ways to improve the approach will be discussed.

### *Ab initio calculation of the electronic g-tensor beyond perturbation theory: diatomic molecules and defects in semiconductors*

**Uwe Gerstmann**
University of Paderborn

## Abstract

We show how a recently developed formula for the orbital magnetization can be used to calculate the elements of the electronic g-tensor in an ab-initio pseudopotential scheme whereby the spin-orbit coupling enters explicitly the self-consistent cycle [*].

In comparison with linear response approachs, the new method allows an improved calculation of the $g$-tensor of paramagnetic systems containing heavy elements (e.g. the XeF molecule) or systems with large deviations of the g-tensor from the free electron value. The latter situation is encountered in paramagnetic centers in solids, such as those exhibiting a moderate Jahn-Teller distortion.

[*] work done in collaboration with D. Ceresoli, A.P. Seitsonen, F. Mauri

### *X-ray Magnetic Circular Dichroism Studies of Paramagnetics*

**Andrei Rogalev**
ESRF-Grenoble
**Coauthor(s) :** F. Wilhelm, J. Goulon, N. Jaouen, J.P. Kappler

## Abstract

X-ray Magnetic Circular Dichroism (XMCD) spectroscopy is a well-established experimental tool to study the microscopic origin of magnetism allowing one to determine separately spin and orbital magnetic moments. So far, XMCD has been extensively used to investigate mainly ferro- or

ferrimagnetic materials and only very few studies have been performed on paramagnetic compounds.

In this presentation, we wish to report the results of thorough XMCD studies of orbital magnetization in a variety of paramagnetic systems:
- Paramagnetic Curie insulators (salts of rare earth elements and of 5d transition metals) give rise to an intense XMCD signal in the hard X-ray range under high magnetic field and at low temperature;
- Spin and orbital moments in Pauli paramagnets has been investigated on a pure Pd single crystal with enhanced temperature-independent paramagnetic susceptibility. Using magneto-optical sum rules we were able to determine the spin moment (0.012$\mu$B) and the orbital moment (0.003 $\mu$B) induced in the Pd 4d shell by a magnetic field of 7 Tesla. The latter was decomposed into two contributions: the Kubo-Obata term and the one arising from the spin-orbit interaction
- Very weak XMCD signals due to a field induced orbital magnetization have been detected at the L-edges of Eu3+ Van Vleck Paramagnetic compounds.

## *Sum rules for E1-E1 x-ray absorption*

**Gerrit van der Laan**
Diamond Light Source

## Abstract

Sum rules relating the integrated intensity of the spin-orbit split manifolds of the core to valence shell transitions in x-ray absorption spectroscopy have been well established [1]. The sum rules for XMCD have become powerful tools to obtain the element-specific spin and orbital part of the magnetic moments in materials. The sum rule for XMLD relates the integrated intensity to the anisotropic part of the spin-orbit interaction, which is proportional to the magnetocrystalline anisotropy energy of the material [2]. The spin-orbit sum rule for the isotropic XAS (or EELS) gives us the type of angular moment coupling in e.g. actinide metals [3].
However, the derivation of the sum rules contains many assumptions and the most important ones will be discussed here. There is a large discrepancy in the angular dependence of the orbital moment as assessed by the XMCD sum rule compared to experimental results obtained by macroscopic techniques [4], which is so far not well understood.

## Key References

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Angular momentum sum rules for x-ray absorption
Phys. Rev. B 57, 112 - 115 (1998).

[2] G. van der Laan
Magnetic linear x-ray dichroism as a probe of the magnetocrystalline anisotropy
Phys. Rev. Lett. 82, 640 - 643 (1999).

[3] K.T. Moore and G. van der Laan
Nature of the 5f states in actinide metals
Rev. Mod. Phys. 81, 235 - 298 (2009).

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Microscopic origin of magnetocrystalline anisotropy in transition metal thin films
J. Phys.: Condens. Matter 10, 3239 - 3253 (1998).

### *Hall Effect, Generalized Einstein Relation, and Berry Phase*

**Patrick Bruno**
ESRF Grenoble

### *Optical properties of topological insulator*

**Ming-Che Chang**
National Taiwan Normal University

## Abstract

The axion coupling in topological insulator couples electric polarization with magnetic field, and magnetization with electric field. As a result, the usual laws of electromagnetic (EM) wave propagation are modified. We report on some preliminary, classical results regarding the reflection and refraction of EM wave at the surface of a topological insulator. Based on these results, possible ways to determine the axion coupling by optical measurement are suggested.

### *Orbital magnetization, XMCD and magnetic hyperfine field*

**Guang-Yu Guo**
National Taiwan University, Department of Physics, Taipei 106

## Abstract

X-ray magnetic circular dichroism (XMCD) is measured as the difference in the absorption rate between left and right circularly polarized x rays. In the early 1990's, Thole et al. discovered that the integrated XMCD signals for a given spin-orbit split absorption edge are related to the local spin and orbital magnetic moments (XMCD sum rules) [1,2]. This discovery initiated an exciting period for the synchrotron radiation-based x-ray spectroscopy because XMCD became a powerful probe of magnetism in solids. [3] Nevertheless, these XMCD sum rules were derived based on a single-ion model. Thus, the validity of these sum rules was subsequently analyzed by a number of research groups worldwide by both using the results of explicit ab initio band-structure calculations and rederiving the sum rules within the framework of itinerant electron theory. In this talk, I will report my own attempts to verify the XMCD sum rules through both numerical [4,5] and analytical [6,7] calculations.
The magnetic hyperfine field of an ion in a solid is the magnetic field at the site of the atomic nucleus produced by the electrons in the solid and may be measured by the nuclear methods such as the Moesbauer effect and the nuclear magnetic resonance (NMR). It is another useful probe of the local magnetization in, e.g., magnetic multilayers and thin films. In this talk, I will present our ab initio studies of the hyperfine

field in various magnetic metals [8,9,10] which demonstrated that the hyperfine
field contains not only the main Fermi contact (spin) contribution but also the significant contribution from the orbital magnetization. Furthermore,
the orbital hyperfine field is shown to be linearly related to the local orbital magnetic moment of the ion concerned.

## Key References


[1] B. T. Thole et al., Phys. Rev. Lett. 68, 1943 (1992).
[2] P. Carra et al., Phys. Rev. Lett. 70, 694 (1993).
[3] C. T. Chen et al., Phys. Rev. Lett. 75, 152 (1995).
[4] G. Y. Guo et al., Phys. Rev. B 50, 3861 (1994).
[5] G. Y. Guo et al., J. Magn. Magn. Mater. 148, 66 (1995).
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### *What is the most physical way of dividing up the orbital magnetization into two gauge-invariant parts?*


**Ivo Souza**
University of California, Berkeley
**Coauthor(s) :** David Vanderbilt


## Abstract


An intriguing feature of the modern theory of orbital magnetization in crystals is that it identifies two separately gauge-invariant - and hence potentially separately measurable - contributions to M_orb[1,2,3]. Intuitively, one is associated with the "self-rotation", and the other with the "itinerant circulation" part of the electron motion. Unfortunately this appealing physical picture becomes blurry upon closer inspection. Already in the simplest case of an insulator with a single valence band subtly different partitions of M_orb were obtained in the two original derivations of the bulk orbital magnetization formula[1,2]. Matters are complicated further when it comes to multiband insulators, Chern insulators, and metals. For example, it is not clear how to extend the semiclassical derivation of the two terms in Ref. 1 to a multiband gauge-invariant framework. A multiband gauge-invariant partition of M_orb was proposed in Ref. 3, but it remained unclear how to separate experimentally the two resulting terms.

I will discuss how the f-sum rule for the magnetic circular dichroism spectrum provides a natural way of dividing up M_orb into two parts[4]. The sum rule yields a contribution to M_orb whose relation to the various terms defined in Refs. [1-3] is as follows: in the

single-band case it reduces to the self-rotation term of Ref. 1. In the multiband case it equals the difference between the gauge-invariant local and itinerant circulations defined in Ref. 3 (which for a single band reduce to the ones in Ref. 2). In the case of ordinary band insulators it can be thought of as the gauge-invariant part of the self-rotation of the Wannier functions, in complete analogy with the gauge-invariant part of the Wannier spread[5]. Like M_orb itself, the sum rule remains well-defined in metals and Chern insulators, even though the simple Wannier-based interpretation is lost.

## Key References

[1] D. Xiao, J. Shi, and Q. Niu, Phys. Rev. Lett. 95, 137204 (2005).
[2] T. Thonhauser, D. Ceresoli, D. Vanderbilt, and R. Resta, Phys. Rev. Lett. 95, 137205 (2005).
[3] D. Ceresoli, T. Thonhauser, D. Vanderbilt, and R. Resta, Phys. Rev. B 74, 024408 (2006).
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### *Spin-spin coupling in the solid state*

**Jonathan Yates**
Oxford University

## Abstract

Sin-spin (or J) coupling is an indirect interaction of the nuclear magnetic moments mediated by bonding electrons, and provides a direct map of the atomic connectivities in a material. In solution-state NMR, J-coupling measurements can often be obtained from one dimensional spectra where the multiplet splitting in the peaks is clearly resolved. However, in the solid-state, this is often not the case as these splittings are typically obscured by the broadenings from anisotropic interactions. In recent years, bond correlation experiments, in particular, those employing spin-echo magic angle spinning techniques, have resulted in accurate measurements of J-coupling in both inorganic and organic systems.

To complement and support these advances in experimental technique we have developed a first principles method to calculate J-coupling in solid-state systems. We have applied this technique, in combination with experimental work undertaken by several groups, to a range of solid-state systems. Examples include both organic and inorganic crystals (ordered and disordered), and couplings which involve a range of nuclei and bond types (regular, hydrogen bonds, and also non-bonding interactions).

### *Orbital magnetoelectric effects and topological insulators*

**David Vanderbilt**
Rutgers University

## Abstract

I will first briefly review the theory of the intrinsic (Karplus-Luttinger) contribution to the anomalous Hall conductivity of a metal, which essentially involves integrating the Berry curvature over the occupied Fermi sea. If one looks at the limit as a band is filled and the Fermi surfaces disappear, the integrated Berry curvature takes an integer value ("Chern number") that is normally zero. By definition, a "Chern insulator" is one in which this integer is non-zero. Strangely, the orbital magnetization is linear in the Fermi energy in this case, because of contributions from chiral edge states at the surface of the crystal. Such a system is also known as a "quantum Hall insulator" because it would exhibit a quantum Hall effect in the absence of a magnetic field. While no examples are known to exist in nature, theoretical models of Chern insulators are readily constructed (Haldane first did so two decades ago [1]), and there is no known reason why they should not exist. I shall briefly discuss some of our theoretical work on the properties of such prospective Chern insulators [2-3], and speculate about prospects for discovering experimental realizations.

There has been a great deal of interest recently in another kind of topological insulator, the "Z2" or "quantum spin Hall" insulator. Such a system can be conceptualized by imagining that a spin-up system of electrons having Chern number +1 coexists with a spin-down system having Chern number -1 in such a way that the system as a whole has total Chern number zero and obeys time-reversal (T) symmetry. Even when the spin-orbit interaction is turned on, the system carries a topological "even-odd" (Z2) label that distinguishes it from a normal insulator. Again, chiral edge states are required, provided that T symmetry also remains unbroken at the surfaces. Some of the recent excitement about this subject is due to the discovery of experimental realizations in the Bi[x]Sb[1-x] [4], Bi[2]Te[3] [5], and related systems.

Third, I will try to give a flavor of our recent theory of the orbital contribution to the linear magnetoelectric effect (or equivalently, to the surface Hall conductivity) in magnetoelectric insulators [6]. The theory exhibits many attractive analogies to the theory of polarization, and involves a higher-order kind of Chern index than was introduced above. Interestingly, our theory predicts that the surface of a Z2 topological insulator, if it is gapped by a T-breaking perturbation, will exhibit a half-integer quantum Hall effect.

## Key References


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[3] S. Coh and D. Vanderbilt, Phys. Rev. Lett. 102, 107603 (2009).
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[6] A.M. Essin, J.E. Moore, and D. Vanderbilt, Phys. Rev. Lett. 102, 146805 (2009).


### *Theory of orbital magnetization in crystalline systems*


**David Vanderbilt**
Rutgers University


## Abstract


There are subtleties associated with the proper definition of orbital magnetization in a crystalline solid that are similar to those that arise in the theory of electrical polarization, related to the fact that matrix elements of the position operator are ill-defined in the Bloch representation. Standard methods for computing the orbital magnetization have been based on integrating orbital currents

inside muffin-tin spheres, and while this may be a very good approximation in some contexts, it fails to capture a possible "interstitial" or "itinerant" contribution to the orbital magnetization.

In 2005, two groups independently solved this long-standing problem, using quite different methods: a semiclassical wavepacket approach in one case [1], and a derivation based on the Wannier representation in the other [2-3]. More recently, a third independent derivation of the same formula has been given based on the long-wave limit [4]. In this talk I will review our Wannier-based derivation [2-3]. The orbital magnetization of a periodic insulator was shown to be comprised of two contributions, an obvious one associated with the internal circulation of bulk-like Wannier functions in the interior and an itinerant one arising from net currents carried by Wannier functions near the surface. Our final expression for the orbital magnetization can be rewritten as a bulk property in terms of Bloch functions, making it simple to implement in modern code packages. The correctness of the expression was tested by evaluating it for model two-dimensional tight-binding systems. Recently, Ceresoli et al. have computed the orbital magnetization for Fe, Ni, and Co using the new approach [5].

An interesting aspect of the theory is that the orbital magnetization can be decomposed into two contributions, corresponding roughly to the internal-circulation and itinerant pieces, each of which is independently gauge-invariant (i.e., invariant with respect to k-dependent unitary rotations among the occupied Bloch states). The physical meaning of these terms and their connections with the static limits of dynamical phenomena are discussed in Ref. [6].

## Key References

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### *Theory of Orbital Magnetization and its Generalization to Interacting Systems*

**Qian Niu**
University of Texas at Austin

## Abstract

Recently, a new formula for the orbital magnetization was proposed. In this talk, I will review the original derivation of the formula based on the semi-classical wave-packet dynamics, as well as a general derivation based on the standard perturbation theory of quantum mechanics. The quantum derivation clarifies the origin of the novel aspects of the semi-classical derivation, such as the Berry phase correction to the density of states. It is valid for general systems including insulators with or without a Chern number, metals at zero or finite temperatures. More importantly, we are able to combine the quantum derivation with the exact current and spin density functional theory (SCDFT), proving the validity of the formula for interacting systems. With this development, the new magnetization formula, in combination with the recent advances in the construction of optimized

effective potential for SCDFT, will turn out to be a powerful practical tool for the study of systems that have long defied traditional ab-initio methods.

## Key References

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### *Polarization Induced by Inhomogeneity*

**Junren Shi**
Institue of Physics, Chinese Academy of Sciences

## Abstract

We develop a new formula for calculating the electric polarization of an inhomogeneous system. It is shown that the electric polarization induced by the inhomogeneity can be expressed as a difference of a Chern-Simons field between the final and initial state. This is a generalization to the geometric formula of King-Smith and Vanderbilt, which is only applicable for the homogeneous system. The new formula demonstrates a new application of the semi-classical approach, besides that on the orbital magnetization.

## Key References

Di Xiao, Junren Shi, Dennis P. Clougherty and Qian Niu, Phys. Rev. Lett. 102, 087602 (2009)

### *Macroscopic magnetization: Analogies to and differences from the case of electrical polarization*

**Raffaele Resta**
CNR-INFM Democritos and University of Trieste

## Abstract

In this introductory talk, I will start with some basic considerations of macroscopics electrostatics and magnetostatics, including the relationship between macroscopic polarization/magnetization and macroscopic fields as a function of the shape of a finite sample. The limiting cases of purely either longitudinal or transverse polarization/magnetization will be illustrated.

Switching then to microscopics, I will focus on the position operator r, which is unbound and "forbidden" in the Hilbert space of the wavefunctions obeying periodic Born-von-Karman boundary conditions (PBC), while it is trivial within "open" boundary conditions (OBC). This feature has hampered a microscopic theory of macroscopic polarization until the early 1990s (see Ref. [1] for a review), and of macroscopic orbital magnetization until 2005 (see next talk).

Notice that the r operator enters the textbook definition of both electrical polarization and orbital magnetization, while it is harmless about spin magnetization. It also enters the definition of (spin) toroidic moment [2]. For crystalline systems within an independent-electron scheme (e.g. Kohn-Sham), our macroscopic observables are expressed as Brillouin-zone (BZ) integrals, where the key ingredients are k-derivatives of (the periodic part of) the Bloch orbitals.

In the case of electrical polarization, the BZ integral can be equivalently expressed--perhaps more intuitively--in terms of the electrical dipoles of the Wannier charge distributions in the unit cell. The analogous tempting assumption--namely, that orbital magnetization can be expressed in terms of the magnetic dipoles of the Wannier orbitals in the unit cell--turns out to be incorrect.

To understand the reason for the difference, one has to consider a finite sample within OBC, where the counterpart of the Wannier orbitals are still well defined localized orbitals. In a finite sample, due to the unbound nature of the r operator, surface charges/currents give a nonvanishing contribution to macroscopic polarization/magnetization. The charge of Wannier orbitals, even in the surface region, is quantized (equal to one) and neutralized by the classical nuclear charge: ergo, there cannot be any surface contribution to electrical polarization. Instead, in the magnetic case, the current carried by the Wannier orbitals is not quantized, and the surface region contributes nontrivially to orbital magnetization. However, as shown in the next talk, even this contribution can be expressed in terms of bulk quantities within PBC.

## Key References

[1] D. Vanderbilt and R. Resta, in: "Conceptual foundations of materials: A standard model for ground- and excited-state properties", S.G. Louie and M.L. Cohen, eds. (Elsevier, 2006), p. 139.
[2] C.D. Batista, G. Ortiz, and A.A. Aligia, Phys. Rev. Lett. 101, 077203 (2008).

### *Exact Born-Oppenheimer decomposition of the complete electron-nuclear wave function*

**E.K.U. Gross**
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### *Induced orbital paramagnetism in BH, CH+, C4H4, and C8H8 systems*

**Paolo Lazzeretti**
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## Abstract

Concise information on the general features of
the quantum-mechanical current density induced in the electrons
of a molecule by a spatially uniform, time-independent
magnetic field is obtained via a stagnation graph that shows
the isolated singularities and the lines
at which the current density vector field vanishes.
Stagnation graphs provide a compact description
of current density vector fields and help
the interpretation of molecular magnetic response, e.g.,
magnetic susceptibility and nuclear magnetic shielding.
A few noticeable examples are discussed.
The stagnation graph of cyclopropane, obtained at the Hartree-Fock level
via a procedure based on continuous transformation of the origin of the
current density formally annihilating the diamagnetic contribution, shows
that the current interpretation of this molecule
as an archetypal sigma-aromatic system should be revised.
The stagnation graphs of lithium hydride, acetylene, carbon dioxide, and
azulene
provide the first evidence of the existence of electronic toroidal
currents inducing orbital
anapole moments.
The induced orbital paramagnetism of boron monohydride, cyclobutadiene and
clamped
cyclooctatetraene are explained via stagnation graphs showing that
vortical lines occur
at the intersection of nodal surfaces of real and imaginary components of
the the electronic
wave function.

### *Single k-point formulas for the electrical and magnetic cases*

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## Abstract

For crystalline systems within an independent-electron scheme (e.g. Kohn-Sham), both electrical polarization [1] and orbital magnetization [2] are expressed as a Brillouin-zone integral. For disordered systems most Car-Parrinello simulations are performed in a large supercell within a single k-point framework.

The single-point polarization formula exists since a long time [3], and has been widely used, e.g. in the computation of infrared spectra. It is worth stressing that the single-point polarization formula can be regarded as the special case of a more general many-body formula, expressed in terms of an explicitly correlated wavefunction, well beyond independent-electron schemes.

The analogous single-point orbital magnetization formula has been

established in 2007 [4]; as a corollary, even the Chern number can be evaluated--somewhat counterintuitively--from a single Hamiltonian diagonalization. However, at variance with the electrical case, the single-point formula does not seem to lead towards a many-body theory, allowing the computation of orbital magnetization in terms of an explicitly correlated wavefunction.

## Key References

[1] D. Vanderbilt and R. Resta, in: "Conceptual foundations of materials: A standard model for ground- and excited-state properties", S.G. Louie and M.L. Cohen, eds. (Elsevier, 2006), p. 139.
[2] D. Ceresoli, T. Thonhauser, D. Vanderbilt, and R. Resta, Phys. Rev. B 74, 024408 (2006).
[3] R. Resta, Phys. Rev. Lett. 80, 1800 (1998).
[4] D. Ceresoli and R. Resta, Phys. Rev. B 76, 012405 (2007).

### *First principles calculations of Orbital magnetization-Preliminary Results*

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## Abstract

The recent discovered formula about the orbital magnetization for periodic solid can include contribution from the interstitial regions, which are usually ignored in the past calculations. Using this formula, we calculate the orbital magnetizations in the ferromagnetic transition metals Fe, Co, Ni by FLAPW method. However, we have not obtained improved results compared with experimental ones.

### *First principles theory of the orbital magnetization: ferromagnetic metals and organometallic complexes*

**Davide Ceresoli**
MIT

## Abstract

We present first principles calculations of the orbital magnetization in real materials by evaluating a recently discovered formula for periodic systems, within density functional theory. We obtain improved values of the orbital magnetization in the ferromagnetic metals Fe, Co, and Ni, by taking into account the contribution of the interstitial regions neglected so far in literature. [*]

We also use the orbital magnetization to compute the EPR $g$-tensor in transition metal complexes. In these systems, the main issue is spurious self-interaction in most exchange-correlation functionals, often leading to the electrons being over-delocalized, and even resulting

in unphysical fractional occupation numbers. I will show that the DFT + Hubbard U approach improves the agreement with respect to experiment, of the EPR g-tensor and hyperfine couplings in high-spin Mn-oxo complexes. [**]

[*] work done in collaboration with: U. Gerstmann, A. P. Seitsonen and F. Mauri
[**] work done in collaboration with: E. Li and N. Marzari

### *Is there a relation between the magnetic anisotropy of a single molecule magnet and the orbital magnetic moments of its ions ?*

**Philippe Sainctavit**
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**Coauthor(s) :** Matteo Mannini, Francesco Pineider, Marie-Anne Arrio, Ricardo Moroni, Christophe Cartier dit Moulin, Andrea Cornia, Dante Gatteschi and Roberta Sessoli.

## Abstract

Single Molecule Magnets (SMM) are new molecules developed by coordination chemistry that present at low temperature magnetic properties similar to those of nanomagnets: blocking temperature, opening of the magnetic cycle, magnetic anisotropy. In order to understand the parameters governing these properties we have applied X-ray Magnetic Circular Dichroism (XMCD). The technique is well suited to give information on the magnetic structure of the individual ions present in one molecule and it gives direct information on the orbital magnetic moment. The molecules for which the opening of the magnetic cycle is the largest are Mn12 and Fe4 SMM. For both molecules we measured 3d ions L2,3 edges and we obtained that the orbital magnetic moments on the ions of the molecules (Mn(IV) and Mn(III) in Mn12 SMM and Fe(III) in Fe4 SMM) are very close to zero (always below 0.05 Bohr magneton with $|/|$ below 0.02) [1,2,3]. On the contrary we measured on another molecule, Cr[(CN)Ni]6 an orbital magnetic moment on Ni(II) ions as large as 0,15 mB (with $|/| = 0.07$) but for which no opening of the magnetic cycle could be detected down to temperatures as low as 20 mK [4]. These findings tend to show that the orbital magnetic moment of the individual ions is not governing the SMM hysteresis.

## Key References

[1] Matteo Mannini, Francesco Pineider, Philippe Sainctavit, Chiara Danieli, Edwige Otero, Corrado Sciancalepore, Anna Maria Talarico, Marie-Anne Arrio, Andrea Cornia, Dante Gatteschi and Roberta Sessoli. Magnetic memory of a single-molecule quantum magnet wired to a gold surface. Nature Materials 8, 194-197 (2009)

[2] Matteo Mannini, Francesco Pineider, Philippe Sainctavit, Loic Joly, Arantxa Fraile-Rodri Ì□guez, Marie-Anne Arrio, Christophe Cartier dit Moulin, Wolfgang Wernsdorfer, Andrea Cornia, Dante Gatteschi, and Roberta Sessoli. X-Ray Magnetic Circular Dichroism Picks out Single-Molecule Magnets Suitable for Nanodevices. Advanced Materials, 21, 167-171 (2009)

[3] Matteo Mannini, Philippe Sainctavit,[ Roberta Sessoli, Christophe Cartier dit Moulin, Francesco Pineider, Marie-Anne Arrio, Andrea Cornia, and Dante Gatteschi. XAS and XMCD Investigation of MnMonolayers on Gold. Chemistry : a European Journal, 14, 7530-7535 (2008)

[4] M.-A. Arrio, A. Scuiller, Ph. Sainctavit, Ch. Cartier dit Moulin, T. Mallah, and M. Verdaguer. Soft X-ray Magnetic Circular Dichroism in Paramagnetic Systems: Element-Specific Magnetization of

Two Heptanuclear CrIII MII6 High-Spin Molecules.Journal of the American Chemical Society 121, 6414-6420 (1999)

### *Orbital Magnetization and its Connection to NMR Chemical Shifts*

**Timo Thonhauser**
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## Abstract

We propose an alternative approach for computing the NMR response in periodic solids that is based on the recently developed theory of orbital magnetization [1-4]. Instead of obtaining the shielding tensor from the response to an external magnetic field, we derive it directly from the orbital magnetization appearing in response to a microscopic magnetic dipole [5]. Our new approach is very general, and it can be applied to either isolated or periodic systems. The converse procedure has an established parallel in the case of electric fields, where Born effective charges are often obtained from the polarization induced by a sublattice displacement instead of the force induced by an electric field. Our novel approach is simple and straightforward to implement since all complexities concerning the choice of the gauge origin are avoided and the need for a linear-response implementation is circumvented. We have demonstrated its correctness and viability by calculating chemical shieldings in simple molecules, crystalline diamond, and liquid water, finding excellent agreement with previous theoretical and experimental results. Applications to more complex systems are currently in progress.

## Key References

[1] D. Xiao, J. Shi, and Q. Niu, Phys. Rev. Lett. 95, 137204 (2005).
[2] T. Thonhauser, D. Ceresoli, D. Vanderbilt, and R. Resta, Phys. Rev. Lett. 95, 137205 (2005).
[3] D. Ceresoli, T. Thonhauser, D. Vanderbilt, and R. Resta, Phys. Rev. B 74, 024408 (2006).
[4] J. Shi, G. Vignale, D. Xiao, and Q. Niu, Phys. Rev. Lett. 99, 197202 (2007).
[5] T. Thonhauser, D. Ceresoli, A. Mostofi, N. Marzari, R. Resta, D. Vanderbilt, arxiv: 0709.4429.

### *Spin and orbital moments in the Fe-Cr alloy*

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## Abstract

The Fe-Cr system exhibits an interesting phase diagram where short-range order and frustration are suspected to play a key role in the formation of microstructures. The Fe-Cr alloys have recently come under scrutiny for their potential role as structural materials for the next generation of nuclear reactors. A crucial issue in this context is the behaviour of the material over a long period of time and intense irradiation, which has to be tackled by both experiments and modelling. As the modelling of ferritic alloys beyond the quantum mechanical scale is often validated against the results obtained from DFT, it seems important to establish as well a one-to-one experimental validation of the DFT predictions. Spectroscopic measurements obtained at synchrotron irradiation facilities present such a possibility. In particular, the orbital-to-spin moment ratios of Fe can be both calculated and measured by X-ray Magnetic Circular Dichroism (XMCD). A series of calculations

with Wien2k through a range of Cr concentration is under way. While the orbital moments in these compounds are weak, they are nonetheless sensitive to changes of the local atomic environment and their role as probe for different microstructures are being investigated.

### *Induced orbital magnetism of 5d transition metals studied with XMCD*

**Fabrice Wilhelm**
ESRF

## Abstract

Many current and anticipated applications for magnetic materials involve heterostructures or alloys containing magnetic and “non-magnetic” components. The experimental technique that allows one to study the induced magnetism in “non magnetic” elements is the X-Ray Magnetic Circular Dichroism (XMCD). It provides quantitative information on spin and orbital magnetic moments of atoms in both amplitude and direction. Since X-ray absorption spectra are related to the density of unoccupied states at the absorbing atom for a given angular momentum, the XMCD is an appropriate tool to study hybridization effects and magnetic interactions.
In the first part of the talk, I will present XMCD studies performed at the L3,2-edges of the 5d TM element in 3d-5d magnetic systems which reveal a strong polarization of the 5d band induced by a large 3d/5d hybridisation. I will show that in certain materials such as Fe/W multilayers and VAu4 compounds, the induced orbital moment of W and Au is breaking the Hund’s third rules.
In the second part of the talk, I will present XMCD studies preformed at the L3,2-edges of the 5d TM element in 4f-5d and even 5f-5d magnetic systems. I will show that in RE-5d compounds, such as NdPt2, GdPt2 and HoPt2, despite the strongly localized character of the 4f shells, the shape of the XMCD signal at the L-edges of 5d elements are directly related to the nature of 4f elements and that the sizeable orbital magnetic polarization at the Pt atom is found to depend strongly on the spin-orbit coupling of the RE elements.