Orbital Magnetization in Periodic Systems

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Modern theory of electrical polarization

Theory developed since \( \sim 1992 \), nowadays mature.

- The theory is based on a Berry phase.
- Several first-principle calculations have been performed in many nonmetallic materials: spontaneous polarization in ferroelectrics, piezoelectricity, infrared spectra in solids and liquids....
- Most electronic-structure computer codes on the market implement the Berry phase as a standard option: CRYSTAL, PWSCF, ABINIT, VASP, SIESTA, CPMD...
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- Only model-Hamiltonian results published so far.
- The very first ab-initio calculations are in press by now:
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- Only \textit{model}-Hamiltonian results published so far.
- The very first \textit{ab-initio} calculations are in press by now:
  - NMR shielding tensors in several materials:  
  - Spontaneous magnetization in Fe, Co, and Ni:  
    \textit{D. Ceresoli, U. Gertsmann, A.P. Seitsonen, & F. Mauri},  
- These are \textit{pseudopotential} implementations; there are good reasons which make \textit{all-electron} implementations desirable.
Outline

1. Why do we need a kind of “exotic” theory?
   - The dipole of a finite molecule
   - The “dipole” of a solid

2. Role of macroscopic fields

3. Modern theory of polarization: main features

4. Modern theory of orbital magnetization

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Fig. 11–8. A complex crystal lattice can have a permanent intrinsic polarization $\mathbf{P}$. 
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TEXTBOOK DEFINITIONS ARE NONCOMPUTABLE!
MACROSCOPIC POLARIZATION $\mathbf{P}$ HAS NOTHING TO DO WITH THE PERIODIC CHARGE DENSITY OF THE POLARIZED SOLID

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Trivial definitions
(atomic units throughout)

\[ m = \frac{1}{2c} \int dr \, \mathbf{r} \times \mathbf{j}(\mathbf{r}) + m_{\text{spin}} \]

\[ d = -\int dr \, n(\mathbf{r}) + d_{\text{nuclear}} \]

- \( d \) is nonzero only in absence of inversion symmetry.
- \( m \) is nonzero only in absence of time-reversal symmetry.
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Orbital and spin magnetization are well separated, either experimentally or in (nonrelativistic) QM.

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Independent electrons
(either Hartree-Fock or Kohn-Sham, double occupancy)

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\begin{align*}
\mathbf{m} &= 2 \frac{1}{2c} \sum_{n \in \text{occupied}} \langle \varphi_n | \mathbf{r} \times \mathbf{v} | \varphi_n \rangle \\
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Macroscopic magnetization and polarization
(naive textbook view)

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M = \frac{m}{V} = \frac{1}{2cV} \int dr \, r \times j(r)
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- **Common drawback:**
  Surface terms contribute *extensively* to the dipole: so \( M \) and \( P \) are apparently surface properties: *not* bulk ones!

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Any quantity defined or computed within PBC is by definition “bulk”.

However... The position operator $r$ is incompatible with Born-von Kármán PBCs.

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For a molecule, one can speak of the external fields $E_{\text{ext}}$ and $B_{\text{ext}}$.

- By definition, they are the fields in the vacuum region far away from the molecule.
- They can also be regarded as a boundary condition for the integration of Poisson equation.
- If $E_{\text{ext}} = 0$, then $d$ is the spontaneous (equilibrium) electrical dipole.
- If $B_{\text{ext}} = 0$, then $m$ is the spontaneous (equilibrium) magnetic dipole.
- The linear responses to nonvanishing $E_{\text{ext}}$ and $B_{\text{ext}}$ are by definition the linear electric and magnetic polarizability.
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For an infinite periodic solid, one cannot speak of external fields $E_{\text{ext}}$ and $B_{\text{ext}}$.

- The measurable microscopic fields inside the material are $E^{(\text{micro})}(r)$ and $B^{(\text{micro})}(r)$.
- Average over a macroscopic scale $\rightarrow$ $E$ and $B$ (average over a cell in crystalline materials).
- The value of the $E$ and $B$ is not a bulk property; instead, it is an arbitrary boundary condition.
- Electronic-structure codes require a lattice-periodical potential, hence they impose $E = 0$ and $B = 0$ (otherwise Bloch states would not exist!)
- The modern theories address $P$ and $M$ in zero fields only.
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A finite solid as very large cluster

One can again speak of the **external** fields $E_{\text{ext}}$ and $B_{\text{ext}}$ for a finite cluster cut from the bulk.

- The microscopic fields $E^{(\text{micro})}(r)$ and $B^{(\text{micro})}(r)$ tend to $E_{\text{ext}}$ and $B_{\text{ext}}$ in the vacuum region far away from the cluster.
- Inside the material, the macroscopic averages of $E^{(\text{micro})}(r)$ and $B^{(\text{micro})}(r)$ are **different** from $E_{\text{ext}}$ and $B_{\text{ext}}$ because of **screening**.
- The relationship between unscreened (a.k.a. external) and screened (a.k.a. internal) fields depends on **shape**.
- Hence, a given choice of the screened fields $E$ and $B$ closely corresponds to a choice of a sample shape.
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**P in a crystalline solid**

\[ \mathbf{P} = \mathbf{P}_{\text{ionic}} + \mathbf{P}_{\text{electronic}} \]

\[ \psi_{nk}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u_{nk}(\mathbf{r}) \]

- The—by now famous—Berry-phase formula (King-Smith & Vanderbilt, 1993):

\[ \mathbf{P}_{\text{electronic}} = \frac{-2ie}{(2\pi)^3} \sum_{n \in \text{occupied}} \int_{\text{BZ}} d\mathbf{k} \langle u_{nk} | \partial_k u_{nk} \rangle \]

- Equivalently, and perhaps more intuitively, in terms of Wannier functions:

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\[ P_{\text{electronic}} = -\frac{2e}{V_{\text{cell}}} \sum_{n \in \text{occupied}} \langle w_n | r | w_n \rangle \]
The theory is formulated in terms of either Bloch orbitals or Wannier functions.

This requires a lattice-periodical potential, i.e. $E = 0$.

The modern theory addresses the macroscopic polarization induced by something other than a macroscopic field: ferroelectricity, piezoelectricity, lattice dynamics in polar crystals (Born effective charges).

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1. Why do we need a kind of “exotic” theory?
   - The dipole of a finite molecule
   - The “dipole” of a solid

2. Role of macroscopic fields

3. Modern theory of polarization: main features

4. Modern theory of orbital magnetization

5. Application: NMR shielding tensor

6. Results
Heuristically, by analogy with the electrical case

- For an insulator, in absence of inversion symmetry, in zero $E$ field, we have

  \[ P_{\text{electronic}} = -\frac{2}{V_{\text{cell}}} \sum_{n \in \text{occupied}} \langle w_n | r | w_n \rangle \]

- By analogy, in absence of time-reversal symmetry, in zero $B$ field, it is tempting to write:

  \[ M = -\frac{2}{2cV_{\text{cell}}} \sum_{n \in \text{occupied}} \langle w_n | r \times v | w_n \rangle \]

**Question:** Is this the correct formula for the bulk magnetization?

**Answer:** No!
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\[ v = \frac{i}{\hbar} [H, r] ; \quad \psi_{nk}(r) = e^{i k \cdot r} u_{nk}(r) ; \quad H(k) = e^{-i k \cdot r} H e^{i k \cdot r} \]

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It breaks time-reversal symmetry.

Two nonequivalent sites per cell. Insulator at half-filling (only the lowest band occupied).

Zero flux through the unit cell:
The macroscopic $B$ field is zero;
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Model Hückel-like Hamiltonian in 2d
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Formula assessed via computer experiments
(2d, single occupancy, single band, atomic units)

- **(A)** Periodic “bulk” system:
  \[ M = -\frac{i}{2c(2\pi)^2} \int_{BZ} dk \langle \partial_k u_k | \times H(k) | \partial_k u_k \rangle \]

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Local circulation & itinerant circulation (2d)

- Magnetization that originates from the circulation of the Boys/Wannier orbitals (same formula as before):

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- The final magnetization formula:

\[ M = -\frac{i}{2c(2\pi)^2} \int_{\text{BZ}} dk \langle \partial_k u_k | \times [H(k) + \varepsilon(k)] | \partial_k u_k \rangle. \]

- Proof: both numerical and analytical
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If we change the energy zero by \( \Delta \varepsilon \), the magnetization apparently changes by

\[ \Delta M = -\frac{i2\Delta \varepsilon}{2c(2\pi)^2} \int_{BZ} d\mathbf{k} \langle \partial_k u_k \rangle \times |\partial_k u_k\rangle. \]

But

\[ C_1 = \frac{i}{(2\pi)^2} \int_{BZ} d\mathbf{k} \langle \partial_k u_k \rangle \times |\partial_k u_k\rangle \]

is the **Chern number**, a topological integer.

\[ C_1 = 0 \] for “normal” insulators. \( C_1 \neq 0 \) only in rather exotic cases (such as the quantum Hall regime).
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The final magnetization formula:

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is the **Chern number**, a topological integer.

\( C_1 = 0 \) for “normal” insulators. \( C_1 \neq 0 \) only in rather exotic cases (such as the quantum Hall regime).
An apparent drawback

The final magnetization formula:

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2. Role of macroscopic fields

3. Modern theory of polarization: main features

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An external magnetic field $B^{\text{ext}}$ is applied to a finite sample. The field induces an orbital current: the total (shielded) field inside the sample is $B(r) = B^{\text{ext}} + B^{\text{ind}}(r)$. Notice: $B(r)$ depends on sample shape.

At nuclear site $r = r_s$ (to linear order):

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The tensor $\sigma_s$ is the quantity actually measured.
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This is \textit{exact} for a sample in the form of a slab, and $B^{\text{ext}}$ normal to the slab.

For other sample shapes, there is a (small) correction.

For a spherical sample \( \overrightarrow{\sigma}_s^\text{sphere} \approx \overrightarrow{\sigma}_s - \frac{8\pi}{3} \chi \).
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The “converse” approach: main concept

\[ 1 - \sigma_s = \frac{\partial B_s}{\partial B} \]

- \( B_s \) can be ideally measured via the torque acting on a classical magnetic (point) dipole at site \( r_s \):

\[ B_s = -\frac{\partial \mathcal{E}}{\partial m_s} \]

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The “converse” approach, cont’d

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NMR shielding tensor for H in selected molecules

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Hydrogen NMR chemical shielding $\sigma$, in ppm, for several different molecules.

Pseudopotential PW calculations in a large supercell.

Core contribution added according to the theory of Pickard & Mauri (2003).
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</tr>
<tr>
<td>CH$_4$</td>
<td>30.61</td>
<td>30.8</td>
<td>31.0</td>
</tr>
<tr>
<td>C$_2$H$_2$</td>
<td>29.26</td>
<td>28.8</td>
<td>28.9</td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>25.43</td>
<td>24.7</td>
<td>24.8</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>29.86</td>
<td>30.2</td>
<td>30.4</td>
</tr>
</tbody>
</table>

Hydrogen NMR chemical shielding $\sigma$, in ppm, for several different molecules.

Pseudopotential PW calculations in a large supercell.

Core contribution added according to the theory of Pickard & Mauri (2003).
NMR shielding tensor for H in liquid water

Five snapshots, 64 molecule-supercell: average over 640 H atoms.

Average and spread very similar to what previously found with the direct method (and smaller supercells).
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Last but not least:

Orbital Magnetization in Ferromagnetic Metals
D. Ceresoli, U. Gertsmann, A.P. Seitsonen, & F. Mauri


<table>
<thead>
<tr>
<th>Metal</th>
<th>e</th>
<th>Expt.</th>
<th>FLAPW LDA</th>
<th>FLAPW PBE</th>
<th>This method LDA</th>
<th>This method PBE</th>
</tr>
</thead>
<tbody>
<tr>
<td>bcc-Fe</td>
<td>[001]</td>
<td>0.081</td>
<td>0.053</td>
<td>0.051</td>
<td>0.0640</td>
<td>0.0658</td>
</tr>
<tr>
<td>bcc-Fe</td>
<td>[111]</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.0633</td>
<td>0.0660</td>
</tr>
<tr>
<td>hcp-Co</td>
<td>[001]</td>
<td>0.133</td>
<td>0.069</td>
<td>0.073</td>
<td>0.0924</td>
<td>0.0957</td>
</tr>
<tr>
<td>hcp-Co</td>
<td>[100]</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.0837</td>
<td>0.0867</td>
</tr>
<tr>
<td>fcc-Ni</td>
<td>[111]</td>
<td>0.053</td>
<td>0.038</td>
<td>0.037</td>
<td>0.0315</td>
<td>0.0519</td>
</tr>
<tr>
<td>fcc-Ni</td>
<td>[001]</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.0308</td>
<td>0.0556</td>
</tr>
</tbody>
</table>

TABLE III: Orbital magnetization $M(e)$ in $\mu_B$ per atom of ferromagnetic metals parallel to the spin, for different spin orientations $e$. The easy axis for Fe, Co and Ni are, respectively, [001], [001] and [111]. Experimental results from Ref. 24; FLAPW results from Ref. 5.
Conclusions

- We have a formula for the macroscopic magnetization $M$ in a crystalline solid (either insulating or metallic).
- It is the magnetic analogue of the well established Berry-phase formula for the electric polarization $P$ (in insulators).
- Both formulæ apply to the case where the macroscopic field ($E$ or $B$) is zero.
- The very first ab-initio implementations are appearing these days.
- I’m not satisfied with the existing analytical proof for the metallic case (but computer simulations on model Hamiltonians are a robust numerical proof).
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