# Orbital Magnetization in Condensed Matter: Part 2

Raffaele Resta

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# Outline

1. Single-point formula: Noncrystalline systems & supercells
2. Application: NMR shielding tensor
3. Geometrical observables: local vs. nonlocal
4. **M** and AHC as local properties

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2. Application: NMR shielding tensor
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4. **M** and AHC as local properties

# Single point formula

$$M_\gamma = \frac{\varepsilon_{\gamma\alpha\beta}}{2c(2\pi)^3}\,\mathrm{Im}\sum_n\int_{\mathrm{BZ}} d\mathbf{k}\,\langle\partial_\alpha u_{n\mathbf{k}}|(\,H_{\mathbf{k}}+\epsilon_{n\mathbf{k}}-2\mu\,)\,|\partial_\beta u_{n\mathbf{k}}\rangle$$

- Discretized on a reciprocal-cell mesh for numerical implementation.
- Invariant by cell doubling.
- Large supercell limit: **Single point formula**.

$$M_\gamma \simeq \frac{\varepsilon_{\gamma\alpha\beta}}{2cV}\,\mathrm{Im}\sum_n\langle\partial_\alpha u_{n0}|(\,H_0+\epsilon_{n0}-2\mu\,)\,|\partial_\beta u_{n0}\rangle$$

$$|\partial_\alpha u_{n0}\rangle \;=\; \sum_{m\neq n}|u_{m0}\rangle\frac{\langle u_{m0}|\,v_\alpha\,|u_{n0}\rangle}{\epsilon_{m0}-\epsilon_{n0}}$$

- Good for Car-Parrinello simulations!
- Even the Chern number can be evaluated single-point: Is this an **oxymoron?**

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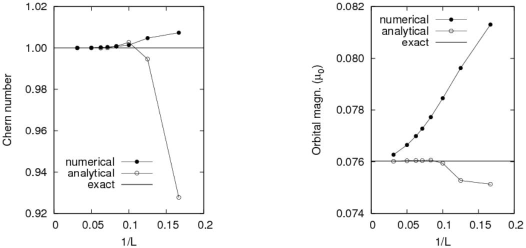
# Convergence with supercell size

(D. Ceresoli & R.R.)



Chern number & orbital magnetization as a function of the supercell size, evaluated using the single-point formulas for the Haldane model Hamiltonian. The largest *L* corresponds to 2048 sites in the supercell.

# Outline

# Definition: The NMR shielding tensor

- An external magnetic field $\mathbf{B}^{\mathrm{ext}}$ is applied to a **finite** sample.
- The field induces an orbital current: the total (shielded) field inside the sample is $\mathbf{B}(\mathbf{r}) = \mathbf{B}^{\mathrm{ext}} + \mathbf{B}^{\mathrm{ind}}(\mathbf{r})$.
  **Notice:** $\mathbf{B}(\mathbf{r})$ depends on sample shape.
- At nuclear site $\mathbf{r} = \mathbf{r}_s$ (to linear order):

$$\mathbf{B}_s^{\mathrm{ind}} = -\overleftrightarrow{\sigma}_s \cdot \mathbf{B}^{\mathrm{ext}}\,, \qquad \mathbf{B}_s = (1 - \overleftrightarrow{\sigma}_s) \cdot \mathbf{B}^{\mathrm{ext}}$$

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# Shape dependence

$$1 - \overleftrightarrow{\sigma}_s = \frac{\partial \mathbf{B}_s}{\partial \mathbf{B}^{\text{ext}}}$$

- Suppose we neglect the **macroscopic** induced field, thus identifying the macroscopic total **B** field inside the material with the external one $\mathbf{B}^{\text{ext}}$. Then

$$1 - \overleftrightarrow{\sigma}_s = \frac{\partial \mathbf{B}_s}{\partial \mathbf{B}}$$

- This is **exact** for a sample in the form of a slab, and $\mathbf{B}^{\text{ext}}$ normal to the slab.
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# Computations: (1) The “direct” approach

(F. Mauri & coworkers)

- The only viable approach so far for crystalline systems.

$$1 - \overleftrightarrow{\sigma}_s = \frac{\partial \mathbf{B}_s}{\partial \mathbf{B}}$$

- Evaluated via linear-response theory.
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# Computations: (2) Our “converse” approach

Thonhauser, Mostofi, Marzari, Resta & Vanderbilt (JCP 2009)

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# The “converse” approach: main concept

$$1 - \overleftrightarrow{\sigma}_s = \frac{\partial \mathbf{B}_s}{\partial \mathbf{B}}$$

- $\mathbf{B}_s$ can be ideally measured via the torque acting on a classical magnetic (point) dipole at site $\mathbf{r}_s$:

$$\mathbf{B}_s = -\frac{\partial \mathcal{E}}{\partial \mathbf{m}_s}$$

- $\mathcal{E}$ is the energy per cell of a periodic lattice of such dipoles (one per cell) in a macroscopic field $\mathbf{B}$.

$$1 - \overleftrightarrow{\sigma}_s = -\frac{\partial}{\partial \mathbf{B}} \frac{\partial \mathcal{E}}{\partial \mathbf{m}_s} = -\frac{\partial}{\partial \mathbf{m}_s} \frac{\partial \mathcal{E}}{\partial \mathbf{B}}$$

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# The “converse” approach, cont’d

$$\mathbf{M} = -\frac{1}{V_{\text{cell}}} \frac{\partial \mathcal{E}}{\partial \mathbf{B}}$$

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- **In words:**
  $1 - \overleftrightarrow{\sigma}_s$ is the macroscopic orbital magnetization linearly induced by a classical point dipole at $\mathbf{r}_s$ and its periodic replicas.
- Computations by finite differences, switching on the $\mathbf{m}_s$ perturbation and evaluating the induced macroscopic magnetization $\mathbf{M}$.
- If we “switch off” the electronic response, then $\partial \mathbf{M}/\partial \mathbf{m}_s = 1/V_{\text{cell}}$, as it must be.

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# The “converse” approach, cont’d

$$\mathbf{M} = -\frac{1}{V_{\text{cell}}}\frac{\partial \mathcal{E}}{\partial \mathbf{B}}$$

$$1 - \overleftrightarrow{\sigma}_s = -\frac{\partial}{\partial \mathbf{m}_s}\frac{\partial \mathcal{E}}{\partial \mathbf{B}} = V_{\text{cell}}\frac{\partial \mathbf{M}}{\partial \mathbf{m}_s}.$$

- **In words:**
  $1 - \overleftrightarrow{\sigma}_s$ is the macroscopic orbital magnetization linearly induced by a classical point dipole at $\mathbf{r}_s$ and its periodic replicas.
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# NMR shielding tensor for H in selected molecules

| | experiment | direct | converse |
|---|---|---|---|
| $H_2$ | 26.26 | 26.2 | 26.2 |
| HF | 28.51 | 28.4 | 28.5 |
| $CH_4$ | 30.61 | 30.8 | 31.0 |
| $C_2H_2$ | 29.26 | 28.8 | 28.9 |
| $C_2H_4$ | 25.43 | 24.7 | 24.8 |
| $C_2H_6$ | 29.86 | 30.2 | 30.4 |

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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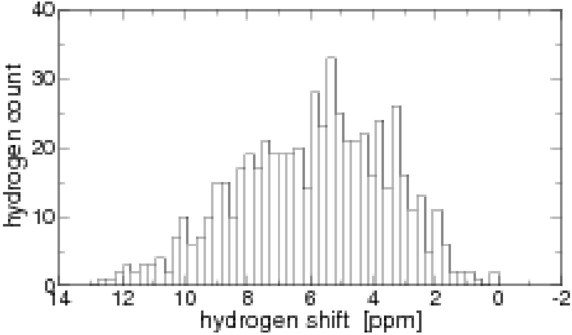

Five snapshots, 64 molecule-supercell:
average over 640 H atoms.

Average and spread very similar to what previously found with the direct method (and smaller supercells).

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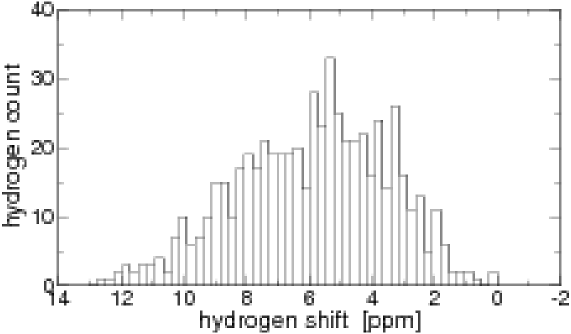

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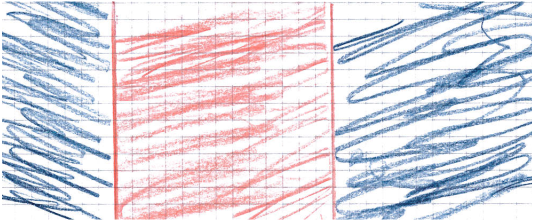
# Outline

1. Single-point formula: Noncrystalline systems & supercells
2. Application: NMR shielding tensor
3. Geometrical observables: local vs. nonlocal
4. **M** and AHC as local properties

# Local vs. nonlocal observables

- Most **nongeometrical** observables are local (e.g. spin magnetization)
- They are meaningful for inhomogeneous systems



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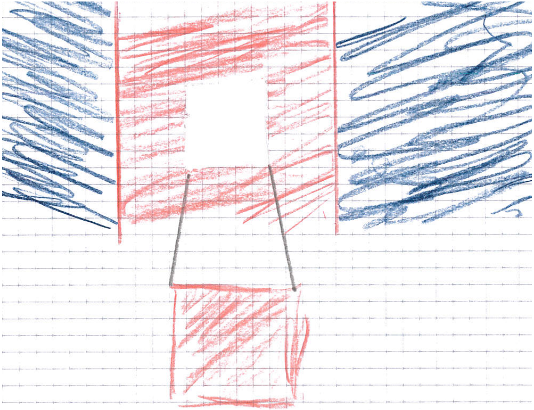

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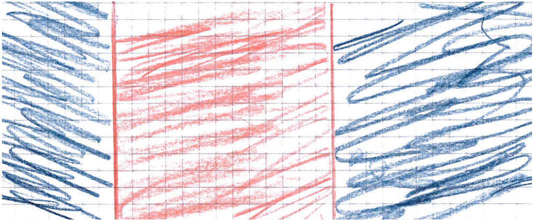
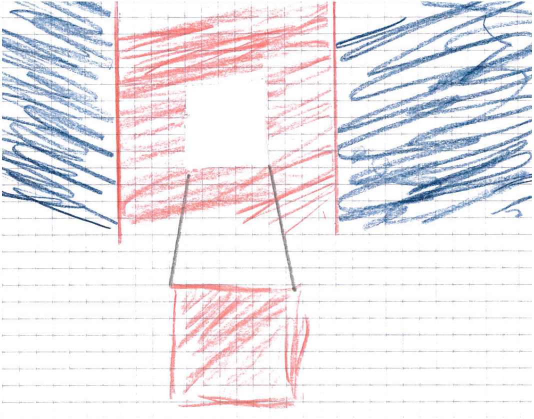


$$\langle \mathcal{O} \rangle = \int_{\mathrm{BZ}} \frac{d\mathbf{k}}{(2\pi)^d} \, \mathfrak{f}(\mathbf{k})$$

- **Implicitly** requires:
  - Crystalline system
  - **Homogenous** noncrystalline system (supercell)
- Useless for macroscopically inhomogeneous systems

# Physical property of a given region



- Any **k**-space approach is **useless!**
- Can we address the geometrical observables in **r-space**?

# Electrical polarization and orbital magnetization, again

$$\begin{aligned}\mathbf{P} &= \frac{\mathbf{d}}{V} = \frac{1}{V}\int d\mathbf{r}\;\mathbf{r}\;\rho^{(\mathrm{micro})}(\mathbf{r})\\ \mathbf{M} &= \frac{\mathbf{m}}{V} = \frac{1}{2cV}\int d\mathbf{r}\;\mathbf{r}\times\mathbf{j}^{(\mathrm{micro})}(\mathbf{r})\end{aligned}$$

- These **r**-space formulas are definitely **NOT** local!
- The multivalued nature of **P** **rules out** any local description
- Instead, **M** **can** be recast in a local form (similar in spirit to an integration by parts):
  - R. Bianco & R. Resta, PRL 2013 (insulators)
  - A. Marrazzo & R. Resta, PRL 2016 (metals)

# One-body density matrix, a.k.a. ground-state projector

Single-particle orbitals (Hartree-Fock or Kohn-Sham): $\psi_n(\mathbf{r})$

Density matrix (spinless electrons):

$$\mathcal{P}(\mathbf{r}, \mathbf{r}') = \sum_{n = \text{occupied}} \psi_n(\mathbf{r}) \psi_n^*(\mathbf{r}')$$

- $\mathcal{P}(\mathbf{r}, \mathbf{r}')$ uniquely determines all ground state properties (including the independent-electron wave function)
- Embeds the information about **any** g.s. observable
- The dipoles (electric and magnetic) of a **finite** crystallite are trivial functions of $\mathcal{P}(\mathbf{r}, \mathbf{r}')$ **but. . .**

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# Density matrix in a crystal (single band)

$$\mathcal{P}(\mathbf{r},\mathbf{r}') = \sum_{n = \text{occupied}} \varphi_n(\mathbf{r})\varphi_n^*(\mathbf{r}') \quad \rightarrow \quad \frac{V_{\text{cell}}}{(2\pi)^3}\int_{\text{BZ}} d\mathbf{k} \;\; \psi_{\mathbf{k}}(\mathbf{r})\psi_{\mathbf{k}}^*(\mathbf{r}')$$

For a condensed system in the thermodynamic limit:

- In the **bulk of the material** $\mathcal{P}(\mathbf{r},\mathbf{r}')$ is independent of boundary conditions (either periodic or “open”)
- Does the **bulk part** of $\mathcal{P}(\mathbf{r},\mathbf{r}')$ contain the information to evaluate **P** and **M**?

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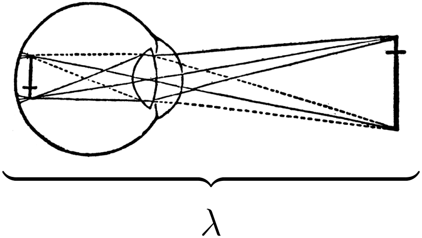
# Nearsightedness (© by W. Kohn)



In the bulk of insulators (either topologically trivial or nontrivial):

$$|\mathcal{P}(\mathbf{r},\mathbf{r}')| \propto \mathrm{e}^{-|\mathbf{r}-\mathbf{r}'|/\lambda} \qquad \text{for } |\mathbf{r}-\mathbf{r}'| \to \infty$$

($\lambda$ related to the valence-conduction energy gap)

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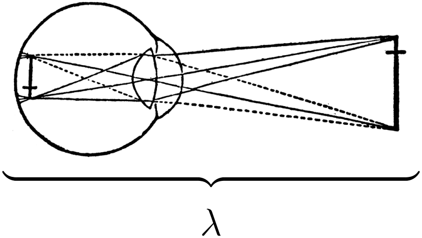

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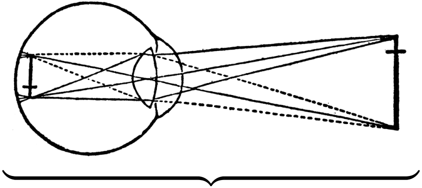

$\lambda$

The poor demon sits well inside the sample:

- Cannot see beyond $\lambda$
- Cannot see the sample boundary
- Cannot distinguish between periodic and “open” BCs
- **Can he measure P and M ?**

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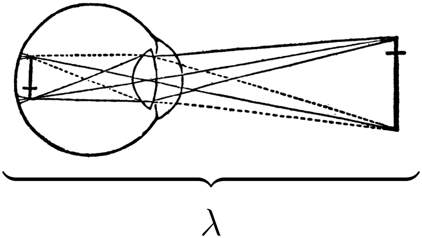

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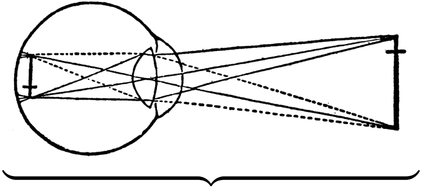

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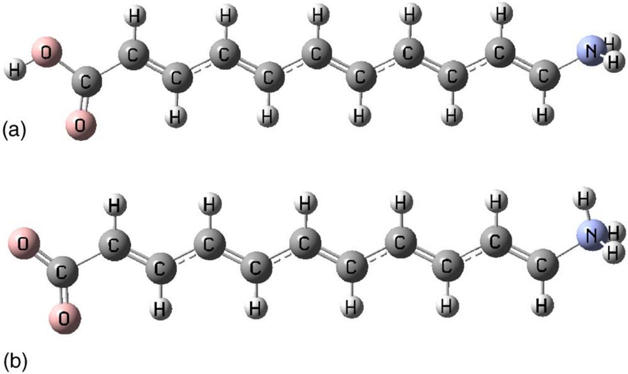
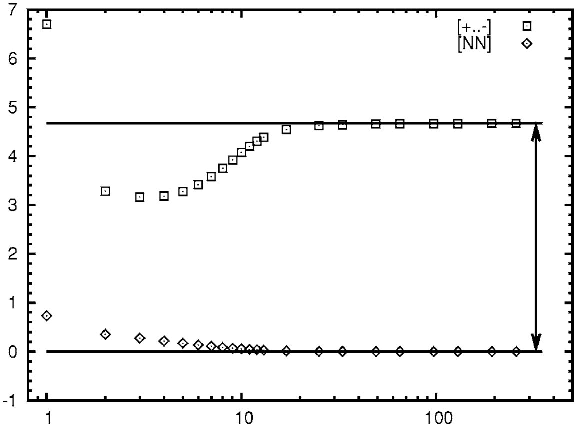
# A 1d insulator (polyacetylene), different terminations



Our demon, sitting in the bulk, would guess $\mathbf{P} = 0$. Is he right?

# Polarization of a centrosymmetric polymer



$\underbrace{\hspace{4cm}}$ nearsightness range

**Right answer:** $P = 0$ modulo $e$

# Outline

1. Single-point formula: Noncrystalline systems & supercells
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3. Geometrical observables: local vs. nonlocal
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# The modern theories: **P** and **M** as BZ integrals

- Single band, spinless electrons, no macroscopic fields

$$\begin{aligned} H|\psi_{\mathbf{k}}\rangle &= \varepsilon_{\mathbf{k}}|\psi_{\mathbf{k}}\rangle \\ H_{\mathbf{k}}|u_{\mathbf{k}}\rangle &= \varepsilon_{\mathbf{k}}|u_{\mathbf{k}}\rangle \qquad |u_{\mathbf{k}}\rangle = e^{-i\mathbf{k}\cdot\mathbf{r}}|\psi_{\mathbf{k}}\rangle \quad H_{\mathbf{k}} = e^{-i\mathbf{k}\cdot\mathbf{r}}He^{i\mathbf{k}\cdot\mathbf{r}} \end{aligned}$$

- **1992-93: Polarization**

$$\mathbf{P} = \mathbf{P}_{\text{nuclei}} + \frac{e}{(2\pi)^3}\operatorname{Im}\int_{\text{BZ}} d\mathbf{k}\ \langle u_{\mathbf{k}}|\nabla_{\mathbf{k}} u_{\mathbf{k}}\rangle$$

- **2005-06: Orbital Magnetization**

$$\mathbf{M} = \frac{e}{\hbar c(2\pi)^3}\operatorname{Im}\int_{\text{BZ}} d\mathbf{k}\ \langle\nabla_{\mathbf{k}} u_{\mathbf{k}}| \times (H_{\mathbf{k}} + \varepsilon_{\mathbf{k}} - 2\mu)\,|\nabla_{\mathbf{k}} u_{\mathbf{k}}\rangle$$

# Modern theory of magnetization

- The **k**-space formula for **M** has **no** “quantum” indeterminacy
- Tinkering with the boundaries does **not** alter the **M** value
- A Maxwell demon sitting deeply in the material is able to measure **M** even without “seeing” the boundaries
- The bulk $\mathcal{P}(\mathbf{r},\mathbf{r}')$ determines **M** unambiguously — even for topological insulators
- May we obtain the **M** value directly from $\mathcal{P}(\mathbf{r},\mathbf{r}')$ in **r** space, **avoiding** the “detour” in **k** space?

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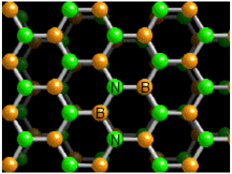
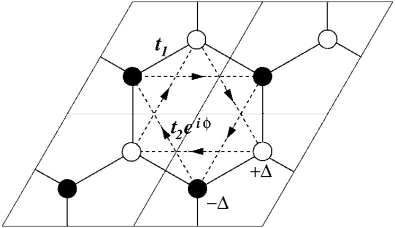
# The “Haldanium” workhorse in our simulations



**+ “some magnetism”**

Tight-binding parameters:

- 1st-neighbor hopping $t_1$
- staggered onsite $\pm\Delta$
- complex 2nd-neighbor $t_2 e^{i\phi}$



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- Insulating (either trivial or **topological**) at half filling
- **Metallic** at any other filling

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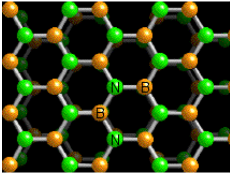

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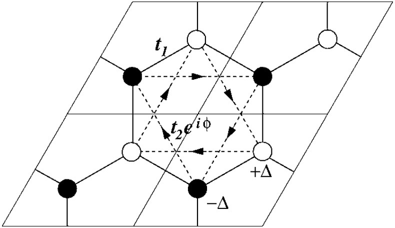

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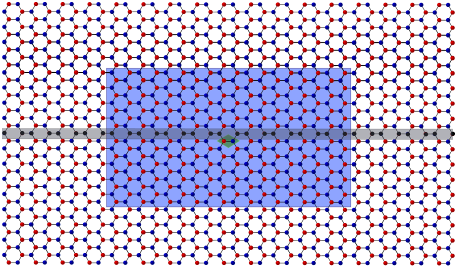
# A flake of Haldanium (OBC)



Sample of 2550 sites, line with 50 sites

Can our demon (nearsighted, sitting in the bulk of the sample) measure the $M$ value?

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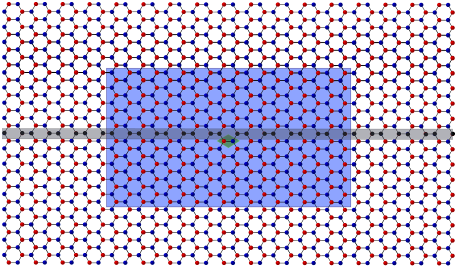

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**Can our demon (nearsighted, sitting in the bulk of the sample) measure the *M* value?**

# Anomalous Hall conductivity and orbital magnetization

- One-body density matrix, a.k.a. ground-state projector:

$$\mathcal{P} = \sum_{\epsilon_j < \mu} |\varphi_j\rangle\langle\varphi_j| \quad \text{(spinless)}$$

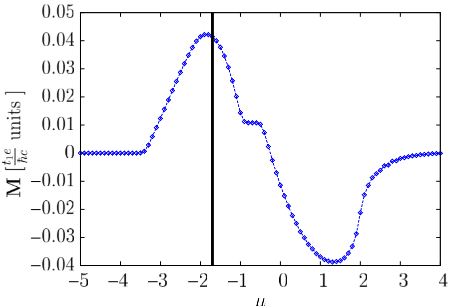
- Tensor fields in **r**-space:

$$\begin{aligned} \mathfrak{F}_{\alpha\beta}(\mathbf{r}) &= \text{Im}\,\langle\mathbf{r}|\,\mathcal{P}\,[r_\alpha,\mathcal{P}]\,[r_\beta,\mathcal{P}]\,|\mathbf{r}\rangle \\ \mathfrak{M}_{\alpha\beta}(\mathbf{r}) &= \text{Im}\,\langle\mathbf{r}|\,|\mathcal{H}-\mu|\,[r_\alpha,\mathcal{P}]\,[r_\beta,\mathcal{P}]\,|\mathbf{r}\rangle. \end{aligned}$$

- $\mathfrak{F}_{\alpha\beta}(\mathbf{r})$ and $\mathfrak{M}_{\alpha\beta}(\mathbf{r})$ are **“densities”** well defined even for disordered and/or inhomogeneous bounded samples

# Orbital magnetization a a function of the Fermi level

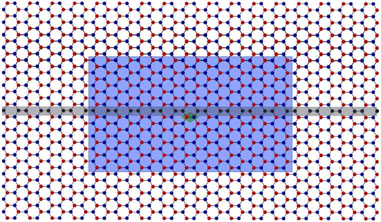
A. Marrazzo and R. Resta, Phys. Rev. Lett. **116**, 137201 (2016)



**At convergence all formulas coincide:**

- **Textbook formula:** $\frac{1}{2cV}\int d\mathbf{r}\;\mathbf{r}\times\mathbf{j}^{(\mathrm{micro})}(\mathbf{r})$
- $M_\gamma = -\frac{ie}{2\hbar c}\varepsilon_{\gamma\alpha\beta}\int_{\mathrm{FV}} d\mathbf{k}\,\langle\partial_\alpha u_{j\mathbf{k}}|\,(H_{\mathbf{k}}+\epsilon_{j\mathbf{k}}-2\mu)\,|\partial_\beta u_{j\mathbf{k}}\rangle$
- **Our novel formula:** $\frac{e}{2\hbar c}\varepsilon_{\gamma\alpha\beta}\mathrm{Tr}_V\left\{\mathfrak{M}_{\alpha\beta}\right\}$

# Why is our formula for **M** better than the trivial one?



$$\mathbf{m} = \frac{1}{2c}\int d\mathbf{r}\;\mathbf{r}\times\mathbf{j}(\mathbf{r}) = -\frac{e}{2c}\int d\mathbf{r}\;\langle\mathbf{r}|\,P\,\mathbf{r}\times\mathbf{v}\,|\mathbf{r}\rangle$$

$$\mathbf{m} = -\frac{ie}{2\hbar c}\int d\mathbf{r}\;\langle\mathbf{r}|\,|H-\mu|\,[\mathbf{r},P]\times[\mathbf{r},P]\,|\mathbf{r}\rangle$$

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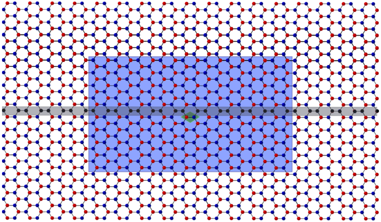

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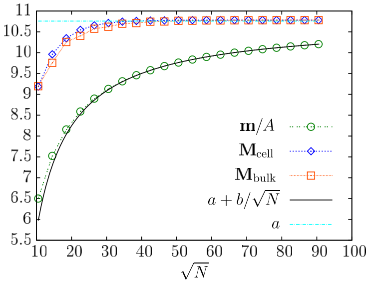
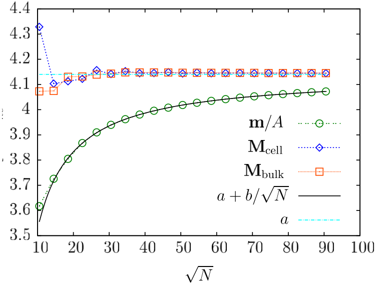
(similar in spirit to an integration by parts)

# Fast convergence in both insulator and metal



Insulator



Metal

- **$1/L$ convergence with size:** $\frac{1}{2cV}\int d\mathbf{r}\,\mathbf{r}\times\mathbf{j}^{(\mathrm{micro})}(\mathbf{r})$
- **Much better convergence:** $\frac{e}{2\hbar c}\varepsilon_{\gamma\alpha\beta}\mathrm{Tr}_V\left\{\mathfrak{M}_{\alpha\beta}\right\}$