Symmetry of Magnetically Induced Currents

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13th September 2022

Introduction

Overview

- Symmetry and pseudo-symmetry *groups* in magnetic fields
- *Unitary* representation analysis on *linear spaces*
- *Wavefunction* and *current density* symmetries
    - *Relationships* between wavefunction and current density symmetries
    - Symmetry *descent* and symmetry *breaking* in magnetic fields

Groups in magnetic fields

The electronic Hamiltonian

- For an N_e-electron system in a *uniform* magnetic field $\boldsymbol{B} = \boldsymbol{\nabla} \times \boldsymbol{A}(\boldsymbol{r})$, consider the **Schrödinger–Pauli Hamiltonian** in atomic units:

$$\hat{\mathscr{H}} = \frac{1}{2}\sum_{k=1}^{N_\mathrm{e}} \left|-\hat{\boldsymbol{p}}_k + \boldsymbol{A}(\boldsymbol{r}_k)\right|^2 + \sum_{k=1}^{N_\mathrm{e}} v_\mathrm{ext}(\boldsymbol{r}_k) + \frac{1}{2}\sum_{k\neq l}^{N_\mathrm{e}} \frac{1}{|\boldsymbol{r}_k - \boldsymbol{r}_l|} + \frac{g_s}{2}\sum_{k=1}^{N_\mathrm{e}} \boldsymbol{B}\cdot\hat{\boldsymbol{s}}_k$$

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external potential

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electron–electron interaction

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spin Zeeman interaction

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&= \frac{1}{2} \sum_{k=1}^{N_\mathrm{e}} \hat{p}_k^2 + \sum_{k=1}^{N_\mathrm{e}} v_\mathrm{ext}(\boldsymbol{r}_k) + \frac{1}{2} \sum_{k \neq l}^{N_\mathrm{e}} \frac{1}{|\boldsymbol{r}_k - \boldsymbol{r}_l|} + \boldsymbol{A}(\boldsymbol{r}_k) \cdot \hat{\boldsymbol{p}}_k + \frac{g_s}{2} \sum_{k=1}^{N_\mathrm{e}} \boldsymbol{B} \cdot \hat{\boldsymbol{s}}_k + \frac{1}{2} A^2(\boldsymbol{r}_k) \\
&= \hat{\mathscr{H}}_0(v_\mathrm{ext}) + \boldsymbol{A}(\boldsymbol{r}_k) \cdot \hat{\boldsymbol{p}}_k + \frac{g_s}{2} \sum_{k=1}^{N_\mathrm{e}} \boldsymbol{B} \cdot \hat{\boldsymbol{s}}_k + \frac{1}{2} A^2(\boldsymbol{r}_k).
\end{aligned}$$

- How does each term transform *spatially* and *temporally*?

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Tensor transformations

- Let $\boldsymbol{v}$ be a rank-k Cartesian tensor in three dimensions.

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Tensor transformations

- Let $\boldsymbol{v}$ be a rank-k Cartesian tensor in three dimensions.
- *Spatially*, let $u \in \mathrm{O}(3)$ be any **proper** or **improper rotation** that acts on an orthogonal basis $\{\boldsymbol{e}_i\}$ spanning $\mathbb{R}^3$ according to

$$\hat{u}\boldsymbol{e}_i = \boldsymbol{e}_j\, U_{ji}.$$

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$\boldsymbol{U}$: representation matrix for u in $\{\boldsymbol{e}_i\}$

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To consider the *linear* action of u on $\boldsymbol{v}$, let $\boldsymbol{v}' = \hat{u}\boldsymbol{v}$.

- $\boldsymbol{v}$ is a **polar** tensor if

$$v'_{ab\ldots k} = U_{ap}U_{bq}\ldots U_{kz}\, v_{pq\ldots z}.$$

- $\boldsymbol{v}$ is an **axial** tensor if

$$v'_{ab\ldots k} = |\boldsymbol{U}|U_{ap}U_{bq}\ldots U_{kz}\, v_{pq\ldots z}.$$

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+1 for proper rotations, −1 for improper rotations

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Tensor transformations

- Let $\boldsymbol{v}$ be a rank-k Cartesian tensor in three dimensions.
- *Temporally*, let θ be the **time reversal** that acts on an orthogonal basis $\{\zeta_1, \zeta_2\}$ of a two-component spinor according to

$$\hat{\theta}\begin{bmatrix}\zeta_1 & \zeta_2\end{bmatrix} = \begin{bmatrix}\zeta_2^* & -\zeta_1^*\end{bmatrix}.$$

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To consider the *antilinear* action of θ on $\boldsymbol{v}$, let $\boldsymbol{v}'' = \hat{\theta}\boldsymbol{v}$.

- $\boldsymbol{v}$ is a **time-even** tensor ($\boldsymbol{i}$-tensor) if

$$\boldsymbol{v}'' = \boldsymbol{v}.$$

- $\boldsymbol{v}$ is a **time-odd** tensor ($\boldsymbol{c}$-tensor) if

$$\boldsymbol{v}'' = -\boldsymbol{v}.$$

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Tensor classifications

- There are *four* types of tensors under spatial-temporal transformations.
  - **polar time-even** tensors
    - position vectors $\boldsymbol{r}$
  - **axial time-even** tensors
  - **polar time-odd** tensors
    - linear momentum vectors $\boldsymbol{p}$
    - magnetic vector potentials $\boldsymbol{A}$
    - current densities $\boldsymbol{j}$
  - **axial time-odd** tensors
    - angular momentum vectors $\boldsymbol{l}$
    - magnetic field vectors $\boldsymbol{B}$

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Symmetry and pseudo-symmetry groups

Definition (symmetry group)

All transformations $\hat{T}$ that leave the electronic Hamiltonian $\hat{\mathscr{H}}$ invariant, *i.e.* $\hat{T}\hat{\mathscr{H}}\hat{T}^{-1} = \hat{\mathscr{H}}$, form the **symmetry group** of $\hat{\mathscr{H}}$. Such transformations are called **symmetry transformations**.

- Symmetry transformations impose *constraints* on the eigenfunctions of $\hat{\mathscr{H}}$ and properties calculated from them.

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Definition (pseudo-symmetry group)

Consider a term $\hat{\mathscr{H}}' \subset \hat{\mathscr{H}}$. All transformations $\hat{T}$ that leave $\hat{\mathscr{H}}'$ invariant but not the full $\hat{\mathscr{H}}$ form a **pseudo-symmetry group** of $\hat{\mathscr{H}}$. Such transformations are called **pseudo-symmetry transformations**.

- Pseudo-symmetry transformations provide ways to understand eigenfunctions of $\hat{\mathscr{H}}$ *(complicated)* from the perspective of $\hat{\mathscr{H}}'$ *(simpler)*.

Groups in magnetic fields

- Let us revisit the electronic Hamiltonian in a uniform magnetic field:

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polar time-even

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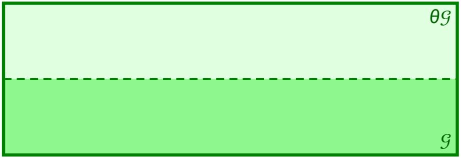
$\mathcal{G} + \theta\mathcal{G}$



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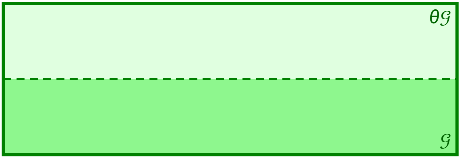
polar time-odd



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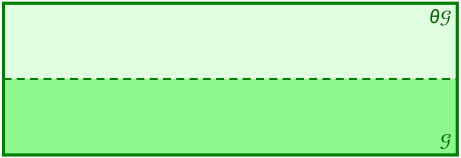

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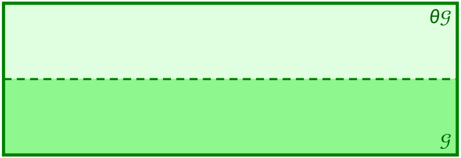
$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0(v_{\text{ext}}) + \underbrace{\boxed{\boldsymbol{A}(\boldsymbol{r}_k)\cdot\hat{\boldsymbol{p}}_k}}_{\mathrm{O}(3)+\theta\mathrm{O}(3)} + \frac{g_s}{2}\sum_{k=1}^{N_\mathrm{e}} \boldsymbol{B}\cdot\hat{\boldsymbol{s}}_k + \underbrace{\boxed{\frac{1}{2}A^2(\boldsymbol{r}_k).}}_{\mathrm{O}(3)+\theta\mathrm{O}(3)}$$



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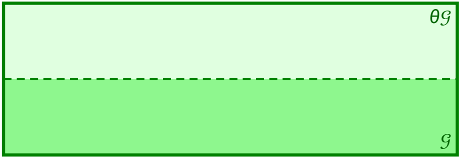

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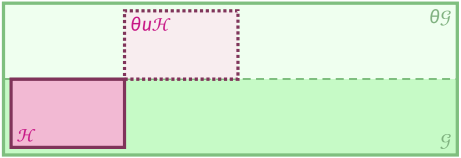
$\mathcal{H} + \theta u\mathcal{H}$

$(u \in \mathcal{G}, \hat{u}\boldsymbol{B} = -\boldsymbol{B})$



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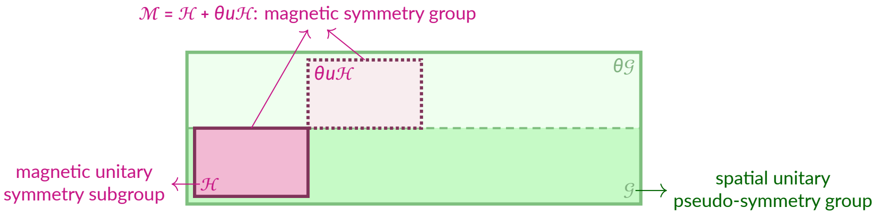

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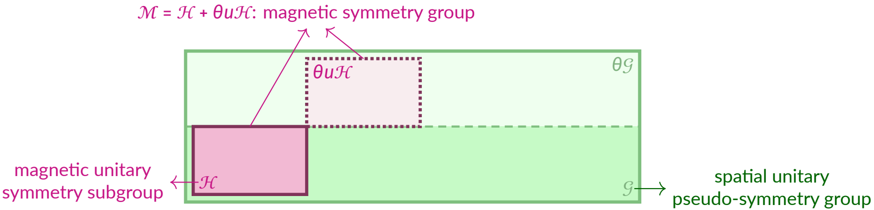
- If $\mathcal{M} = \mathcal{H} + \theta u\mathcal{H}$ is isomorphic to a **unitary group $\mathcal{M}'$**, we write $\mathcal{M} = \mathcal{M}'(\mathcal{H})$.



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Unitary representation analysis

Group unitary representations on linear spaces

- Consider a **group** $\mathcal{G}$ that acts *unitarily* on a **linear space** V.
- Let $\boldsymbol{v}$ be an element in V. The unitary action of $\mathcal{G}$ on $\boldsymbol{v}$ generates an **orbit**

$$\mathcal{G} \cdot \boldsymbol{v} = \{\hat{u}_i \boldsymbol{v} \mid u_i \in \mathcal{G}\}$$

which spans a **representation subspace** $\Gamma \subseteq V$.

For simplicity, we will assume that $\mathcal{G} \cdot \boldsymbol{v}$ is a linearly independent basis.

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  For simplicity, we will assume that $\mathcal{G} \cdot \boldsymbol{v}$ is a linearly independent basis.
- We seek to decompose Γ into known *irreducible* representations of $\mathcal{G}$ on V.

  ↪ This *quantifies* the *symmetry* of $\boldsymbol{v}$ under the action of $\mathcal{G}$.
- To this end, we pick a reference element $\boldsymbol{v}_i = \hat{u}_i \boldsymbol{v}$ in $\mathcal{G} \cdot \boldsymbol{v}$ and define the **representation matrices** $\boldsymbol{D}^{\Gamma}(u_k)$ for all $u_k \in \mathcal{G}$:

$$\hat{u}_k \boldsymbol{v}_i = \sum_j \boldsymbol{v}_j D^{\Gamma}_{ji}(u_k).$$

  Their traces, $\chi^{\Gamma}(u_k)$, give the **characters** required for the decomposition of Γ.

Representation matrix determination

- We opt for a projection method.
  ↪ This requires V to be *endowed* with an **inner product** $\langle\cdot|\cdot\rangle$.

Soriano, M. & Palacios, J. J. Phys. Rev. B **90**, 075128 (August 2014).

Representation matrix determination

- We opt for a projection method.
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- Define a non-orthogonal projection operator

$$\hat{\mathscr{P}}_i = \sum_j |\boldsymbol{v}_i\rangle (\boldsymbol{S}^{-1})_{ij} \langle \boldsymbol{v}_j|$$

where $S_{ij} = \langle \boldsymbol{v}_i | \boldsymbol{v}_j \rangle$ such that $\hat{\mathscr{P}}_i |\boldsymbol{v}_j\rangle = \delta_{ij} |\boldsymbol{v}_i\rangle$.

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$$|\mathcal{G}|^3 \text{ elements} \rightarrow \boxed{T_{ij}(u_k)} = \langle \boldsymbol{v}_i | \hat{u}_k \boldsymbol{v}_j \rangle .$$

- *Closure* of $\mathcal{G} \implies T_{ij}(u_k)$ can be *mapped to $T_{m1}(e)$* for some $m = 1, \ldots, |\mathcal{G}|$.
  ↪ $\boldsymbol{T}(u_k)$ can be computed with $\mathcal{O}(|\mathcal{G}|)$ time complexity.

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Current density linear space

- The current densities $\boldsymbol{j}(\boldsymbol{r})$ with $\boldsymbol{r} \in \mathbb{R}^3$ form a linear space V_J.
- Define an inner product $\langle \cdot | \cdot \rangle$ on V_J as

$$\langle \boldsymbol{j}_m | \boldsymbol{j}_n \rangle = \int \boldsymbol{j}_m(\boldsymbol{r})^\dagger \, \boldsymbol{j}_n(\boldsymbol{r}) \, \mathrm{d}\boldsymbol{r}.$$

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- Given a current density $\boldsymbol{j}(\boldsymbol{r})$ and a symmetry or pseudo-symmetry *unitary* group $\mathcal{G}$, the required overlap matrix elements for the symmetry analysis of $\boldsymbol{j}(\boldsymbol{r})$ are of the form

$$T_{m1}(e) = \langle \hat{u}_m \boldsymbol{j} | \boldsymbol{j} \rangle = \int (\hat{u}_m \boldsymbol{j})(\boldsymbol{r})^\dagger \, \boldsymbol{j}(\boldsymbol{r}) \, \mathrm{d}\boldsymbol{r}, \quad u_m \in \mathcal{G}.$$

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Non-perturbative current densities

- Non-perturbative calculations in arbitrarily strong magnetic fields are performed in a basis of **London atomic orbitals**:

$$\omega_\mu(\boldsymbol{r};\boldsymbol{R}_\mu) = \varphi_\mu(\boldsymbol{r};\boldsymbol{R}_\mu)\exp\left[-i\boldsymbol{A}(\boldsymbol{R}_\mu)\cdot\boldsymbol{r}\right].$$

- In this basis, the current density can be partitioned into the **diamagnetic** and **paramagnetic** contributions with the *non-perturbative* forms:

$$\boldsymbol{j}(\boldsymbol{r}) = \boldsymbol{j}_\mathrm{d}(\boldsymbol{r}) + \boldsymbol{j}_\mathrm{p}(\boldsymbol{r})$$

$$\boldsymbol{j}_\mathrm{d}(\boldsymbol{r}) = -\boldsymbol{A}(\boldsymbol{r})\sum_\sigma \omega_\mu^*(\boldsymbol{r})\omega_\nu(\boldsymbol{r})P_\sigma^{\nu\mu}, \qquad \boldsymbol{j}_\mathrm{p}(\boldsymbol{r}) = \frac{i}{2}\sum_\sigma \boldsymbol{\nabla}\omega_\mu^*(\boldsymbol{r})\omega_\nu(\boldsymbol{r})P_\sigma^{\nu\mu} + \mathrm{c.c.}$$

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- This partition depends on the gauge origin $\boldsymbol{G}$ which manifests itself in

$$\boldsymbol{A}(\boldsymbol{r}) = \frac{1}{2}\boldsymbol{B}\times(\boldsymbol{r}-\boldsymbol{G}).$$

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so that $\boldsymbol{j}_{\mathrm{d}}(\boldsymbol{r})$ vanishes and $\boldsymbol{j}(\boldsymbol{r}) = \boldsymbol{j}_{\mathrm{p}}(\boldsymbol{r})$ formally.

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- In addition,

$$\begin{aligned}\omega_\mu(\boldsymbol{r};\boldsymbol{R}_\mu) &= \varphi_\mu(\boldsymbol{r};\boldsymbol{R}_\mu)\exp\left[-\frac{i}{2}(\boldsymbol{B}\times(\boldsymbol{R}_\mu-\boldsymbol{r}))\cdot\boldsymbol{r}\right]\\ &= \varphi_\mu(\boldsymbol{r};\boldsymbol{R}_\mu)\exp\left[-\frac{i}{2}(\boldsymbol{B}\times\boldsymbol{R}_\mu)\cdot\boldsymbol{r}\right],\end{aligned}$$

which is the same as keeping $\boldsymbol{G}$ at the space-fixed origin.

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Integrals

- The required overlap matrix elements for the symmetry analysis of $\boldsymbol{j}(\boldsymbol{r})$ may now be cast in a computable form:

$$T_{m1}(e) = \int (\hat{u}_m \boldsymbol{j}_\mathrm{p})(\boldsymbol{r})^\dagger \, \boldsymbol{j}_\mathrm{p}(\boldsymbol{r}) \, \mathrm{d}\boldsymbol{r}$$

$$= \frac{1}{4} \sum_{\sigma\sigma'} (P^{\nu\mu}_{\sigma})^* P^{\nu'\mu'}_{\sigma'} \int (\hat{u}_m \omega^*_\nu)(\boldsymbol{r}) \, \boldsymbol{\nabla}(\hat{u}_m \omega_\mu)(\boldsymbol{r})^\mathsf{T} \left[\boldsymbol{\nabla}\omega^*_{\mu'}(\boldsymbol{r}) \, \omega_{\nu'}(\boldsymbol{r}) - \boldsymbol{\nabla}\omega_{\mu'}(\boldsymbol{r}) \, \omega^*_{\nu'}(\boldsymbol{r}) \right] \mathrm{d}\boldsymbol{r} + \text{c.c.}$$

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$\uparrow$

second derivatives of four-centre overlap integrals

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$$\int (\hat{u}_m \omega_{\nu}^{*})(\boldsymbol{r})\, \boldsymbol{\nabla} \boxed{(\hat{u}_m \omega_{\mu})}(\boldsymbol{r})^{\mathrm{T}} \left[\boldsymbol{\nabla}\omega_{\mu'}^{*}(\boldsymbol{r})\, \omega_{\nu'}(\boldsymbol{r}) - \boldsymbol{\nabla}\omega_{\mu'}(\boldsymbol{r})\, \omega_{\nu'}^{*}(\boldsymbol{r}) \right] \mathrm{d}\boldsymbol{r} + \text{c.c.}$$

(pseudo-)symmetry-transformed London orbitals

Current density symmetry

UHF electronic structure