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

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Zero-field Hamiltonian, $\hat{\mathscr{H}}_0(v_\mathrm{ext})$

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

- 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:

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

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polar time-even

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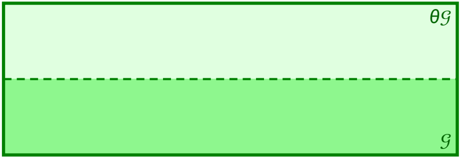
$$\mathcal{G} + \theta\mathcal{G}$$



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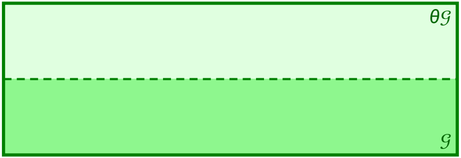
polar time-odd



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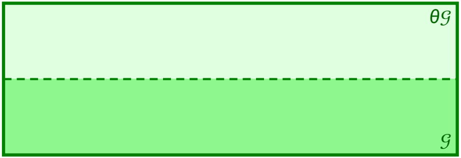

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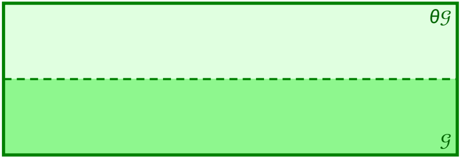
$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0(v_{\mathrm{ext}}) + \underbrace{\boxed{\boldsymbol{A}(\boldsymbol{r}_k)\cdot\hat{\boldsymbol{p}}_k}}_{\mathrm{O}(3)+\theta\mathrm{O}(3)} + \frac{g_s}{2}\sum_{k=1}^{N_e}\boldsymbol{B}\cdot\hat{\boldsymbol{s}}_k + \underbrace{\boxed{\frac{1}{2}A^2(\boldsymbol{r}_k)}}_{\mathrm{O}(3)+\theta\mathrm{O}(3)}.$$



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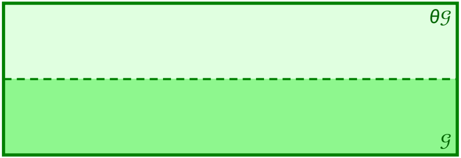
axial time-odd



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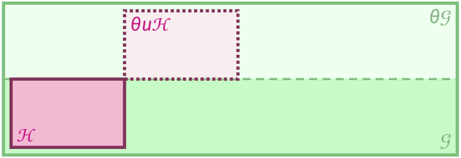
$\mathcal{H} + \theta u \mathcal{H}$
$(u \in \mathcal{G}, \hat{u}\boldsymbol{B} = -\boldsymbol{B})$



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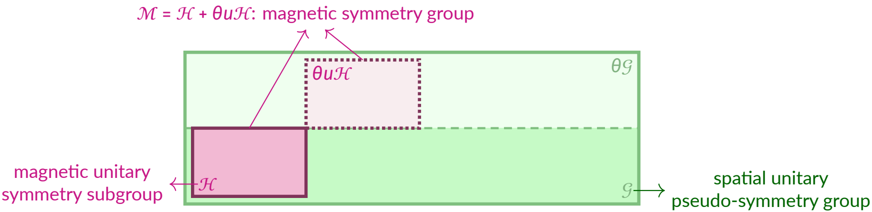

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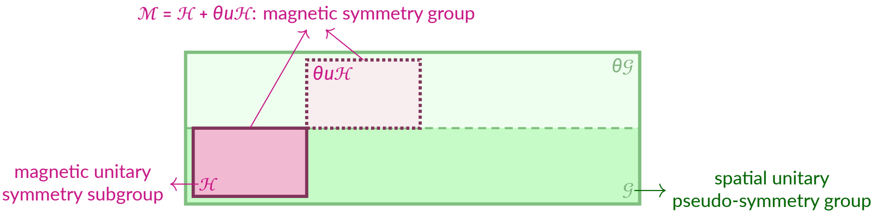
- If $\mathcal{M} = \mathcal{H} + \theta u \mathcal{H}$ is isomorphic to a **unitary group $\mathcal{M}'$**, we write $\mathcal{M} = \mathcal{M}'(\mathcal{H})$.



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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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- 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.
  $\hookrightarrow$ 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

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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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$$\boldsymbol{D}^\Gamma(u_k) = \boldsymbol{S}^{-1}\boldsymbol{T}(u_k),$$

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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

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

↪ Enables projection-based unitary representation analysis on V_J

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(pseudo-)symmetry-transformed current density

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:

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

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

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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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- We employ the **ipsocentric *DZ*** method which makes use of a continuous set of gauge transformations:

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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:

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second derivatives of four-centre overlap integrals

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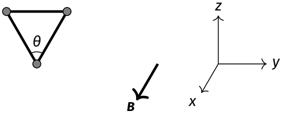
(pseudo-)symmetry-transformed London orbitals

Current density symmetry

The electronic structure of H_3 radical

- Consider a triangular H_3 radical in a *perpendicular magnetic field*.



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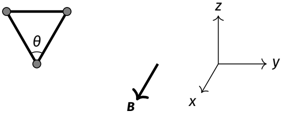

- Back-of-the-envelope properties for $\theta = 60^\circ$:

Zero field

- Spatial sym. group: $\mathcal{G} = \mathcal{D}_{3h}$

Finite fields

- Magnetic sym. group: $\mathcal{M} = \mathcal{D}_{3h}(\mathcal{C}_{3h})$
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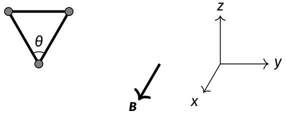

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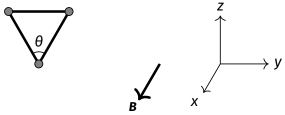

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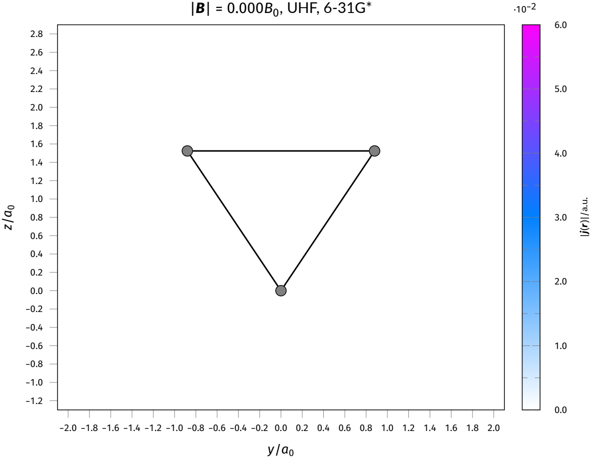
Ground UHF current density in H_3 radical

- UHF, 6-31G*, $M_S = -1/2$



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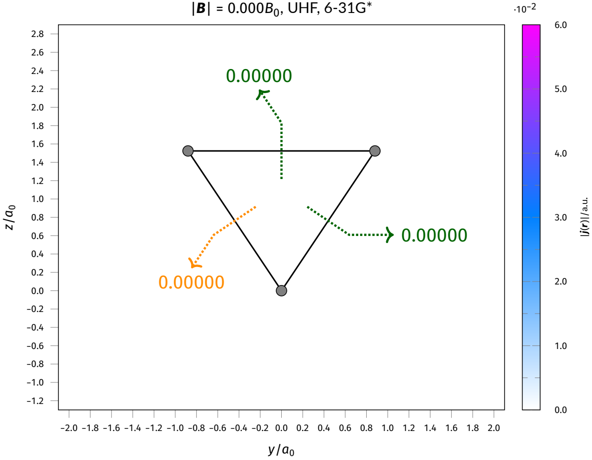

Current density symmetry breaking

- The ground UHF current density in equilateral H_3 radical displays *symmetry breaking* at all $|\boldsymbol{B}|/B_0 \in (0, 1]$.

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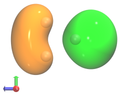
$$A' \oplus \Gamma' \oplus \bar{\Gamma}'(\mathcal{C}_{3h}) \leftarrow A_2' \oplus E'(\mathcal{D}_{3h}).$$

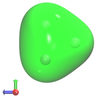
- This suggests that the underlying UHF density and wavefunction are also symmetry-broken.

Current density symmetry breaking

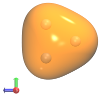
- Consider the UHF wavefunction at $|\boldsymbol{B}| = 0$:
  - Overall symmetry: $A'_1 \oplus E'(\mathcal{D}_{3h}) \Rightarrow$ *symmetry-broken*
  - Occupied molecular-orbital isosurfaces at isovalues ±0.1:



$\beta_2, A'_1 \oplus E'(\mathcal{D}_{3h})$



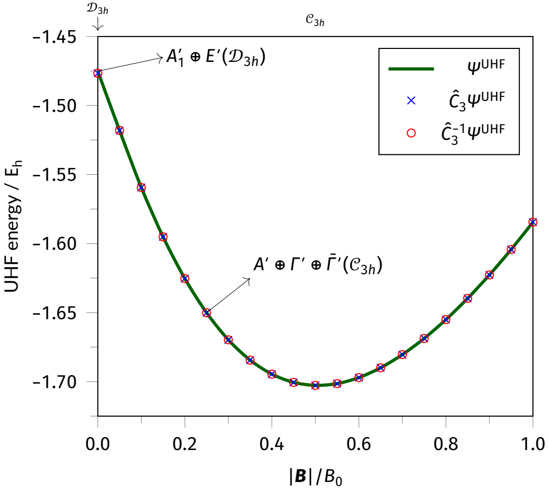
$\alpha_1, A'_1 \oplus E'(\mathcal{D}_{3h})$



$\beta_1, A'_1 \oplus E'(\mathcal{D}_{3h})$

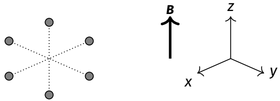
Current density symmetry breaking

- This UHF symmetry breaking *persists* at finite field strengths:



Degenerate current density symmetry

- Consider an octahedral H_6 cluster.



- Back-of-the-envelope properties for $\boldsymbol{B}$ along z:

Zero field

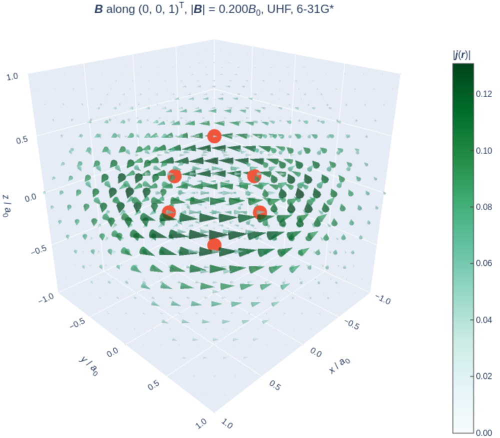
- Spatial sym. group: $\mathcal{G} = \mathcal{O}_h$

Finite fields

- Magnetic sym. group: $\mathcal{M} = \mathcal{D}_{4h}(\mathcal{C}_{4h})$
  - Mag. unitary sym. subgroup: $\mathcal{H} = \mathcal{C}_{4h}$
  - Spatial pseudo-sym. group: $\mathcal{G} = \mathcal{O}_h$
- Ground current: $A_g(\mathcal{C}_{4h}) \leftarrow T_{1g}(\mathcal{O}_h)$

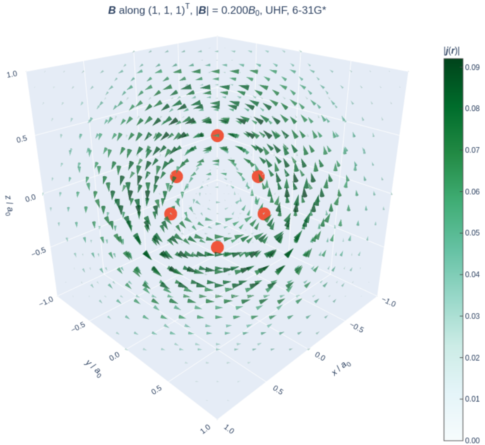
Principal-field current density in H_6 cluster

- UHF, 6-31G*, $M_S = 0$
- $\boldsymbol{B}$ along z-direction
- $\boldsymbol{j}(\boldsymbol{r})$ symmetry: $A_g(\mathcal{C}_{4h}) \leftarrow T_{1g}(\mathcal{O}_h)$
- UHF symmetry: $B_g(\mathcal{C}_{4h})$



Non-principal-field current density in H_6 cluster

- UHF, 6-31G*, $M_S = 0$
- $\boldsymbol{B}$ along $(1, 1, 1)^{\mathsf{T}}$ direction
- $\boldsymbol{j}(\boldsymbol{r})$ symmetry:
  $A_g(\mathcal{S}_6) \leftarrow \underline{T_{1g}} \oplus A_{2g}(\mathcal{O}_h)$
- UHF symmetry: $\bar{\Gamma}_g(\mathcal{S}_6)$



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Conclusion and Outlook

- Completed:
  - Developed a *unitary*-symmetry-based framework to characterise the *spatial* properties of magnetically induced current densities
  - Tested the framework on simple, high-symmetry systems
- To do:
  - Relate the unitary symmetry of current densities to other magnetic properties calculated from them
  - Extend the framework to **corepresentations** to take into account *antiunitary* symmetry
  - Consider also **double-valued** representations and corepresentations to handle odd-electron systems correctly

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