

Symmetry of Magnetically Induced Currents

MAGIC 2022 | Peterhouse, Cambridge, UK

Bang C. Huynh[†], Andrew M. Teale[†]

[†]School of Chemistry, University of Nottingham, UK

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 $\mathbf{B} = \nabla \times \mathbf{A}(\mathbf{r})$, consider the **Schrödinger–Pauli Hamiltonian** in atomic units:

$$\hat{\mathcal{H}} = \frac{1}{2} \sum_{k=1}^{N_e} \left| -\hat{\mathbf{p}}_k + \mathbf{A}(\mathbf{r}_k) \right|^2 + \sum_{k=1}^{N_e} v_{\text{ext}}(\mathbf{r}_k) + \frac{1}{2} \sum_{k \neq l}^{N_e} \frac{1}{|\mathbf{r}_k - \mathbf{r}_l|} + \frac{g_s}{2} \sum_{k=1}^{N_e} \mathbf{B} \cdot \hat{\mathbf{s}}_k$$

Weil, J. A. & Bolton, J. R. **Electron Paramagnetic Resonance**. 2nd (John Wiley & Sons, Inc., Hoboken, New Jersey, 2007).

Tellgren, E. I. et al. **J. Chem. Phys.** **148**, 024101 (January 2018).

Irons, T. J. P. et al. **Chemistry (MDPI)**. **3**, 916–934 (August 2021).

The electronic Hamiltonian

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

$$\hat{\mathcal{H}} = \frac{1}{2} \sum_{k=1}^{N_e} \left| -\hat{\mathbf{p}}_k + \mathbf{A}(\mathbf{r}_k) \right|^2 + \sum_{k=1}^{N_e} v_{\text{ext}}(\mathbf{r}_k) + \frac{1}{2} \sum_{k \neq l}^{N_e} \frac{1}{|\mathbf{r}_k - \mathbf{r}_l|} + \frac{g_s}{2} \sum_{k=1}^{N_e} \mathbf{B} \cdot \hat{\mathbf{s}}_k$$

↑
kinetic

Weil, J. A. & Bolton, J. R. **Electron Paramagnetic Resonance**. 2nd (John Wiley & Sons, Inc., Hoboken, New Jersey, 2007).

Tellgren, E. I. et al. **J. Chem. Phys.** **148**, 024101 (January 2018).

Irons, T. J. P. et al. **Chemistry (MDPI)**. **3**, 916–934 (August 2021).

The electronic Hamiltonian

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

$$\hat{\mathcal{H}} = \frac{1}{2} \sum_{k=1}^{N_e} \left| -\hat{\mathbf{p}}_k + \mathbf{A}(\mathbf{r}_k) \right|^2 + \boxed{\sum_{k=1}^{N_e} v_{\text{ext}}(\mathbf{r}_k)} + \frac{1}{2} \sum_{k \neq l}^{N_e} \frac{1}{|\mathbf{r}_k - \mathbf{r}_l|} + \frac{g_s}{2} \sum_{k=1}^{N_e} \mathbf{B} \cdot \hat{\mathbf{s}}_k$$

↑
 external potential

Weil, J. A. & Bolton, J. R. **Electron Paramagnetic Resonance**. 2nd (John Wiley & Sons, Inc., Hoboken, New Jersey, 2007).

Tellgren, E. I. et al. **J. Chem. Phys.** **148**, 024101 (January 2018).

Irons, T. J. P. et al. **Chemistry (MDPI)**. **3**, 916–934 (August 2021).

The electronic Hamiltonian

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

$$\hat{\mathcal{H}} = \frac{1}{2} \sum_{k=1}^{N_e} \left| -\hat{\mathbf{p}}_k + \mathbf{A}(\mathbf{r}_k) \right|^2 + \sum_{k=1}^{N_e} v_{\text{ext}}(\mathbf{r}_k) + \boxed{\frac{1}{2} \sum_{k \neq l}^{N_e} \frac{1}{|\mathbf{r}_k - \mathbf{r}_l|}} + \frac{g_s}{2} \sum_{k=1}^{N_e} \mathbf{B} \cdot \hat{\mathbf{s}}_k$$

↑
electron-electron interaction

Weil, J. A. & Bolton, J. R. **Electron Paramagnetic Resonance**. 2nd (John Wiley & Sons, Inc., Hoboken, New Jersey, 2007).

Tellgren, E. I. et al. **J. Chem. Phys.** **148**, 024101 (January 2018).

Irons, T. J. P. et al. **Chemistry (MDPI)**. **3**, 916–934 (August 2021).

The electronic Hamiltonian

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

$$\hat{\mathcal{H}} = \frac{1}{2} \sum_{k=1}^{N_e} \left| -\hat{\mathbf{p}}_k + \mathbf{A}(\mathbf{r}_k) \right|^2 + \sum_{k=1}^{N_e} V_{\text{ext}}(\mathbf{r}_k) + \frac{1}{2} \sum_{k \neq l}^{N_e} \frac{1}{|\mathbf{r}_k - \mathbf{r}_l|} + \frac{g_s}{2} \sum_{k=1}^{N_e} \mathbf{B} \cdot \hat{\mathbf{s}}_k$$

spin Zeeman interaction

Weil, J. A. & Bolton, J. R. **Electron Paramagnetic Resonance**. 2nd (John Wiley & Sons, Inc., Hoboken, New Jersey, 2007).

Tellgren, E. I. et al. **J. Chem. Phys.** **148**, 024101 (January 2018).

Irons, T. J. P. et al. **Chemistry (MDPI)**. **3**, 916–934 (August 2021).

The electronic Hamiltonian

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

$$\begin{aligned}\hat{\mathcal{H}} &= \frac{1}{2} \sum_{k=1}^{N_e} \left| -\hat{\mathbf{p}}_k + \mathbf{A}(\mathbf{r}_k) \right|^2 + \sum_{k=1}^{N_e} v_{\text{ext}}(\mathbf{r}_k) + \frac{1}{2} \sum_{k \neq l}^{N_e} \frac{1}{|\mathbf{r}_k - \mathbf{r}_l|} + \frac{g_s}{2} \sum_{k=1}^{N_e} \mathbf{B} \cdot \hat{\mathbf{s}}_k \\ &= \frac{1}{2} \sum_{k=1}^{N_e} \hat{\mathbf{p}}_k^2 + \sum_{k=1}^{N_e} v_{\text{ext}}(\mathbf{r}_k) + \frac{1}{2} \sum_{k \neq l}^{N_e} \frac{1}{|\mathbf{r}_k - \mathbf{r}_l|} + \mathbf{A}(\mathbf{r}_k) \cdot \hat{\mathbf{p}}_k + \frac{g_s}{2} \sum_{k=1}^{N_e} \mathbf{B} \cdot \hat{\mathbf{s}}_k + \frac{1}{2} A^2(\mathbf{r}_k)\end{aligned}$$

Weil, J. A. & Bolton, J. R. **Electron Paramagnetic Resonance**. 2nd (John Wiley & Sons, Inc., Hoboken, New Jersey, 2007).

Tellgren, E. I. et al. **J. Chem. Phys.** **148**, 024101 (January 2018).

Irons, T. J. P. et al. **Chemistry (MDPI)**. **3**, 916–934 (August 2021).

The electronic Hamiltonian

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

$$\begin{aligned}\hat{\mathcal{H}} &= \frac{1}{2} \sum_{k=1}^{N_e} \left| -\hat{\mathbf{p}}_k + \mathbf{A}(\mathbf{r}_k) \right|^2 + \sum_{k=1}^{N_e} v_{\text{ext}}(\mathbf{r}_k) + \frac{1}{2} \sum_{k \neq l}^{N_e} \frac{1}{|\mathbf{r}_k - \mathbf{r}_l|} + \frac{g_s}{2} \sum_{k=1}^{N_e} \mathbf{B} \cdot \hat{\mathbf{s}}_k \\ &= \boxed{\frac{1}{2} \sum_{k=1}^{N_e} \hat{\mathbf{p}}_k^2 + \sum_{k=1}^{N_e} v_{\text{ext}}(\mathbf{r}_k) + \frac{1}{2} \sum_{k \neq l}^{N_e} \frac{1}{|\mathbf{r}_k - \mathbf{r}_l|}} + \mathbf{A}(\mathbf{r}_k) \cdot \hat{\mathbf{p}}_k + \frac{g_s}{2} \sum_{k=1}^{N_e} \mathbf{B} \cdot \hat{\mathbf{s}}_k + \frac{1}{2} A^2(\mathbf{r}_k)\end{aligned}$$

↑
Zero-field Hamiltonian, $\hat{\mathcal{H}}_0(v_{\text{ext}})$

Weil, J. A. & Bolton, J. R. **Electron Paramagnetic Resonance**. 2nd (John Wiley & Sons, Inc., Hoboken, New Jersey, 2007).

Tellgren, E. I. et al. *J. Chem. Phys.* **148**, 024101 (January 2018).

Irons, T. J. P. et al. *Chemistry (MDPI)*. **3**, 916–934 (August 2021).

The electronic Hamiltonian

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

$$\begin{aligned}\hat{\mathcal{H}} &= \frac{1}{2} \sum_{k=1}^{N_e} \left| -\hat{\mathbf{p}}_k + \mathbf{A}(\mathbf{r}_k) \right|^2 + \sum_{k=1}^{N_e} v_{\text{ext}}(\mathbf{r}_k) + \frac{1}{2} \sum_{k \neq l}^{N_e} \frac{1}{|\mathbf{r}_k - \mathbf{r}_l|} + \frac{g_s}{2} \sum_{k=1}^{N_e} \mathbf{B} \cdot \hat{\mathbf{s}}_k \\ &= \frac{1}{2} \sum_{k=1}^{N_e} \hat{p}_k^2 + \sum_{k=1}^{N_e} v_{\text{ext}}(\mathbf{r}_k) + \frac{1}{2} \sum_{k \neq l}^{N_e} \frac{1}{|\mathbf{r}_k - \mathbf{r}_l|} + \boxed{\mathbf{A}(\mathbf{r}_k) \cdot \hat{\mathbf{p}}_k + \frac{g_s}{2} \sum_{k=1}^{N_e} \mathbf{B} \cdot \hat{\mathbf{s}}_k} + \boxed{\frac{1}{2} A^2(\mathbf{r}_k)}\end{aligned}$$

Weil, J. A. & Bolton, J. R. **Electron Paramagnetic Resonance**. 2nd (John Wiley & Sons, Inc., Hoboken, New Jersey, 2007).

Tellgren, E. I. et al. *J. Chem. Phys.* **148**, 024101 (January 2018).

Irons, T. J. P. et al. *Chemistry (MDPI)*. 3, 916–934 (August 2021).

The electronic Hamiltonian

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

$$\begin{aligned}\hat{\mathcal{H}} &= \frac{1}{2} \sum_{k=1}^{N_e} \left| -\hat{\mathbf{p}}_k + \mathbf{A}(\mathbf{r}_k) \right|^2 + \sum_{k=1}^{N_e} v_{\text{ext}}(\mathbf{r}_k) + \frac{1}{2} \sum_{k \neq l}^{N_e} \frac{1}{|\mathbf{r}_k - \mathbf{r}_l|} + \frac{g_s}{2} \sum_{k=1}^{N_e} \mathbf{B} \cdot \hat{\mathbf{s}}_k \\ &= \frac{1}{2} \sum_{k=1}^{N_e} \hat{\mathbf{p}}_k^2 + \sum_{k=1}^{N_e} v_{\text{ext}}(\mathbf{r}_k) + \frac{1}{2} \sum_{k \neq l}^{N_e} \frac{1}{|\mathbf{r}_k - \mathbf{r}_l|} + \mathbf{A}(\mathbf{r}_k) \cdot \hat{\mathbf{p}}_k + \frac{g_s}{2} \sum_{k=1}^{N_e} \mathbf{B} \cdot \hat{\mathbf{s}}_k + \frac{1}{2} A^2(\mathbf{r}_k) \\ &= \hat{\mathcal{H}}_0(v_{\text{ext}}) + \mathbf{A}(\mathbf{r}_k) \cdot \hat{\mathbf{p}}_k + \frac{g_s}{2} \sum_{k=1}^{N_e} \mathbf{B} \cdot \hat{\mathbf{s}}_k + \frac{1}{2} A^2(\mathbf{r}_k).\end{aligned}$$

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

Weil, J. A. & Bolton, J. R. **Electron Paramagnetic Resonance**. 2nd (John Wiley & Sons, Inc., Hoboken, New Jersey, 2007).

Tellgren, E. I. et al. **J. Chem. Phys.** **148**, 024101 (January 2018).

Irons, T. J. P. et al. **Chemistry (MDPI)**. **3**, 916–934 (August 2021).

Tensor transformations

- Let v be a rank- k Cartesian tensor in three dimensions.

Birss, R. R. **Symmetry and Magnetism**. (North-Holland Pub. Co., Amsterdam, 1966).

Bradley, C. J. & Davies, B. L. **Rev. Mod. Phys.** **40**, 359–379 (April 1968).

Lazzeretti, P. et al. **Nucl. Magn. Shield. Mol. Struct.** (ed Tossell, J. A.) 163 (Springer Science+Business Media, B.V., Maryland, 1993).

Tensor transformations

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

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

Birss, R. R. **Symmetry and Magnetism**. (North-Holland Pub. Co., Amsterdam, 1966).

Bradley, C. J. & Davies, B. L. **Rev. Mod. Phys.** **40**, 359–379 (April 1968).

Lazzeretti, P. et al. **Nucl. Magn. Shield. Mol. Struct.** (ed Tossell, J. A.) 163 (Springer Science+Business Media, B.V., Maryland, 1993).

Tensor transformations

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

$$\hat{u}\mathbf{e}_i = \mathbf{e}_j [U_{ji}]$$

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

Birss, R. R. *Symmetry and Magnetism*. (North-Holland Pub. Co., Amsterdam, 1966).

Bradley, C. J. & Davies, B. L. *Rev. Mod. Phys.* **40**, 359–379 (April 1968).

Lazzeretti, P. et al. *Nucl. Magn. Shield. Mol. Struct.* (ed Tossell, J. A.) 163 (Springer Science+Business Media, B.V., Maryland, 1993).

Tensor transformations

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

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

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

- ❖ \mathbf{v} is a **polar** tensor if

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

- ❖ \mathbf{v} is an **axial** tensor if

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

Birss, R. R. *Symmetry and Magnetism*. (North-Holland Pub. Co., Amsterdam, 1966).

Bradley, C. J. & Davies, B. L. *Rev. Mod. Phys.* **40**, 359–379 (April 1968).

Lazzeretti, P. et al. *Nucl. Magn. Shield. Mol. Struct.* (ed Tossell, J. A.) 163 (Springer Science+Business Media, B.V., Maryland, 1993).

Tensor transformations

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

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

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

- \mathbf{v} is a **polar** tensor if

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

- \mathbf{v} is an **axial** tensor if

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

+1 for proper rotations, -1 for improper rotations

Birss, R. R. *Symmetry and Magnetism*. (North-Holland Pub. Co., Amsterdam, 1966).

Bradley, C. J. & Davies, B. L. *Rev. Mod. Phys.* **40**, 359–379 (April 1968).

Lazzeretti, P. et al. *Nucl. Magn. Shield. Mol. Struct.* (ed Tossell, J. A.) 163 (Springer Science+Business Media, B.V., Maryland, 1993).

Tensor transformations

- Let 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

$$\hat{\theta} [\zeta_1 \quad \zeta_2] = [\zeta_2^* \quad -\zeta_1^*].$$

Birss, R. R. **Symmetry and Magnetism**. (North-Holland Pub. Co., Amsterdam, 1966).

Bradley, C. J. & Davies, B. L. **Rev. Mod. Phys.** **40**, 359–379 (April 1968).

Lazzeretti, P. et al. **Nucl. Magn. Shield. Mol. Struct.** (ed Tossell, J. A.) 163 (Springer Science+Business Media, B.V., Maryland, 1993).

Tensor transformations

- Let \mathbf{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

$$\hat{\theta} [\zeta_1 \quad \zeta_2] = [\zeta_2^* \quad -\zeta_1^*].$$

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

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

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

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

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

Birss, R. R. **Symmetry and Magnetism**. (North-Holland Pub. Co., Amsterdam, 1966).

Bradley, C. J. & Davies, B. L. **Rev. Mod. Phys.** **40**, 359–379 (April 1968).

Lazzeretti, P. et al. **Nucl. Magn. Shield. Mol. Struct.** (ed Tossell, J. A.) 163 (Springer Science+Business Media, B.V., Maryland, 1993).

Tensor classifications

There are *four* types of tensors under spatial-temporal transformations.

- **polar time-even** tensors

- position vectors \mathbf{r}

- **polar time-odd** tensors

- linear momentum vectors \mathbf{p}
 - magnetic vector potentials \mathbf{A}
 - current densities \mathbf{j}

- **axial time-even** tensors

- **axial time-odd** tensors

- angular momentum vectors \mathbf{l}
 - magnetic field vectors \mathbf{B}

Birss, R. R. *Symmetry and Magnetism*. (North-Holland Pub. Co., Amsterdam, 1966).

Bradley, C. J. & Davies, B. L. *Rev. Mod. Phys.* **40**, 359–379 (April 1968).

Lazzeretti, P. et al. *Nucl. Magn. Shield. Mol. Struct.* (ed Tossell, J. A.) 163 (Springer Science+Business Media, B.V., Maryland, 1993).

Symmetry and pseudo-symmetry groups

Definition (symmetry group)

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

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

Symmetry and pseudo-symmetry groups

Definition (symmetry group)

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

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

Definition (pseudo-symmetry group)

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

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

Groups in magnetic fields

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

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0(v_{\text{ext}}) + \mathbf{A}(\mathbf{r}_k) \cdot \hat{\mathbf{p}}_k + \frac{g_s}{2} \sum_{k=1}^{N_e} \mathbf{B} \cdot \hat{\mathbf{s}}_k + \frac{1}{2} A^2(\mathbf{r}_k).$$

Wigner, E. *Group Theory and Its Application to the Quantum Mechanics of Atomic Spectra*. 386 (Academic Press, London, 1959).

Bradley, C. J. & Davies, B. L. *Rev. Mod. Phys.* **40**, 359–379 (April 1968).

Lazzeretti, P. et al. *Nucl. Magn. Shield. Mol. Struct.* (ed Tossell, J. A.) 163 (Springer Science+Business Media, B.V., Maryland, 1993).

Keith, T. A. & Bader, R. F. *J. Chem. Phys.* **99**, 3669–3682 (1993).

Groups in magnetic fields

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

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0(v_{\text{ext}}) + \mathbf{A}(\mathbf{r}_k) \cdot \hat{\mathbf{p}}_k + \frac{g_s}{2} \sum_{k=1}^{N_e} \mathbf{B} \cdot \hat{\mathbf{s}}_k + \frac{1}{2} A^2(\mathbf{r}_k).$$

polar time-even

Wigner, E. *Group Theory and Its Application to the Quantum Mechanics of Atomic Spectra*. 386 (Academic Press, London, 1959).

Bradley, C. J. & Davies, B. L. *Rev. Mod. Phys.* **40**, 359–379 (April 1968).

Lazzeretti, P. et al. *Nucl. Magn. Shield. Mol. Struct.* (ed Tossell, J. A.) 163 (Springer Science+Business Media, B.V., Maryland, 1993).

Keith, T. A. & Bader, R. F. *J. Chem. Phys.* **99**, 3669–3682 (1993).

Groups in magnetic fields

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

$$\hat{\mathcal{H}} = \boxed{\hat{\mathcal{H}}_0(v_{\text{ext}})} + \mathbf{A}(\mathbf{r}_k) \cdot \hat{\mathbf{p}}_k + \frac{g_s}{2} \sum_{k=1}^{N_e} \mathbf{B} \cdot \hat{\mathbf{s}}_k + \frac{1}{2} A^2(\mathbf{r}_k).$$

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



Wigner, E. *Group Theory and Its Application to the Quantum Mechanics of Atomic Spectra*. 386 (Academic Press, London, 1959).

Bradley, C. J. & Davies, B. L. *Rev. Mod. Phys.* **40**, 359–379 (April 1968).

Lazzeretti, P. et al. *Nucl. Magn. Shield. Mol. Struct.* (ed Tossell, J. A.) 163 (Springer Science+Business Media, B.V., Maryland, 1993).

Keith, T. A. & Bader, R. F. *J. Chem. Phys.* **99**, 3669–3682 (1993).

Groups in magnetic fields

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

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0(v_{\text{ext}}) + \boxed{\mathbf{A}(\mathbf{r}_k)} \cdot \hat{\mathbf{p}}_k + \frac{g_s}{2} \sum_{k=1}^{N_e} \mathbf{B} \cdot \hat{\mathbf{s}}_k + \frac{1}{2} A^2(\mathbf{r}_k).$$

↑
polar time-odd



Wigner, E. *Group Theory and Its Application to the Quantum Mechanics of Atomic Spectra*. 386 (Academic Press, London, 1959).

Bradley, C. J. & Davies, B. L. *Rev. Mod. Phys.* **40**, 359–379 (April 1968).

Lazzeretti, P. et al. *Nucl. Magn. Shield. Mol. Struct.* (ed Tossell, J. A.) 163 (Springer Science+Business Media, B.V., Maryland, 1993).

Keith, T. A. & Bader, R. F. *J. Chem. Phys.* **99**, 3669–3682 (1993).

Groups in magnetic fields

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

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0(v_{\text{ext}}) + \mathbf{A}(\mathbf{r}_k) \cdot \hat{\mathbf{p}}_k + \frac{g_s}{2} \sum_{k=1}^{N_e} \mathbf{B} \cdot \hat{\mathbf{s}}_k + \frac{1}{2} A^2(\mathbf{r}_k).$$

↑
polar time-odd



Wigner, E. *Group Theory and Its Application to the Quantum Mechanics of Atomic Spectra*. 386 (Academic Press, London, 1959).

Bradley, C. J. & Davies, B. L. *Rev. Mod. Phys.* **40**, 359–379 (April 1968).

Lazzeretti, P. et al. *Nucl. Magn. Shield. Mol. Struct.* (ed Tossell, J. A.) 163 (Springer Science+Business Media, B.V., Maryland, 1993).

Keith, T. A. & Bader, R. F. *J. Chem. Phys.* **99**, 3669–3682 (1993).

Groups in magnetic fields

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

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0(v_{\text{ext}}) + \boxed{\mathbf{A}(\mathbf{r}_k) \cdot \hat{\mathbf{p}}_k} + \frac{g_s}{2} \sum_{k=1}^{N_e} \mathbf{B} \cdot \hat{\mathbf{s}}_k + \boxed{\frac{1}{2} A^2(\mathbf{r}_k)}.$$

$\uparrow \quad \quad \quad \uparrow$

$O(3) + \theta O(3) \quad \quad \quad O(3) + \theta O(3)$



Wigner, E. *Group Theory and Its Application to the Quantum Mechanics of Atomic Spectra*. 386 (Academic Press, London, 1959).

Bradley, C. J. & Davies, B. L. *Rev. Mod. Phys.* **40**, 359–379 (April 1968).

Lazzeretti, P. et al. *Nucl. Magn. Shield. Mol. Struct.* (ed Tossell, J. A.) 163 (Springer Science+Business Media, B.V., Maryland, 1993).

Keith, T. A. & Bader, R. F. *J. Chem. Phys.* **99**, 3669–3682 (1993).

Groups in magnetic fields

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

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0(v_{\text{ext}}) + \mathbf{A}(\mathbf{r}_k) \cdot \hat{\mathbf{p}}_k + \frac{g_s}{2} \sum_{k=1}^{N_e} \mathbf{B} \cdot \hat{\mathbf{s}}_k + \frac{1}{2} A^2(\mathbf{r}_k).$$

↑
axial time-odd



Wigner, E. *Group Theory and Its Application to the Quantum Mechanics of Atomic Spectra*. 386 (Academic Press, London, 1959).

Bradley, C. J. & Davies, B. L. *Rev. Mod. Phys.* **40**, 359–379 (April 1968).

Lazzeretti, P. et al. *Nucl. Magn. Shield. Mol. Struct.* (ed Tossell, J. A.) 163 (Springer Science+Business Media, B.V., Maryland, 1993).

Keith, T. A. & Bader, R. F. *J. Chem. Phys.* **99**, 3669–3682 (1993).

Groups in magnetic fields

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

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0(v_{\text{ext}}) + \mathbf{A}(\mathbf{r}_k) \cdot \hat{\mathbf{p}}_k + \frac{g_s}{2} \sum_{k=1}^{N_e} \mathbf{B} \cdot \hat{\mathbf{s}}_k + \frac{1}{2} A^2(\mathbf{r}_k).$$

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



Wigner, E. *Group Theory and Its Application to the Quantum Mechanics of Atomic Spectra*. 386 (Academic Press, London, 1959).

Bradley, C. J. & Davies, B. L. *Rev. Mod. Phys.* **40**, 359–379 (April 1968).

Lazzeretti, P. et al. *Nucl. Magn. Shield. Mol. Struct.* (ed Tossell, J. A.) 163 (Springer Science+Business Media, B.V., Maryland, 1993).

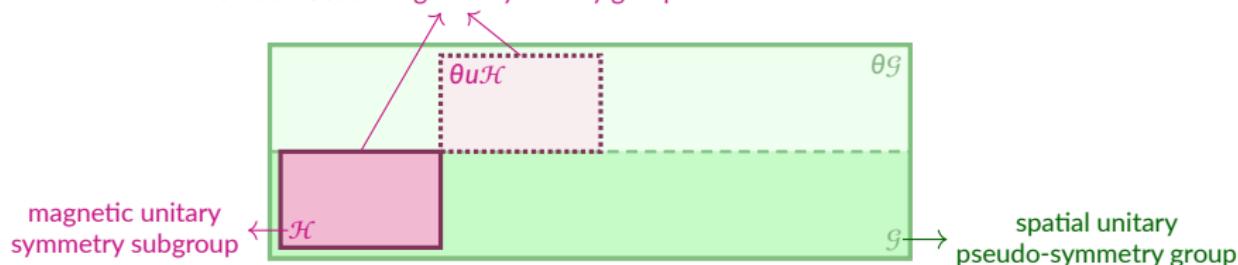
Keith, T. A. & Bader, R. F. *J. Chem. Phys.* **99**, 3669–3682 (1993).

Groups in magnetic fields

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

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0(v_{\text{ext}}) + \mathbf{A}(\mathbf{r}_k) \cdot \hat{\mathbf{p}}_k + \frac{g_s}{2} \sum_{k=1}^{N_e} \mathbf{B} \cdot \hat{\mathbf{s}}_k + \frac{1}{2} A^2(\mathbf{r}_k).$$

$\mathcal{M} = \mathcal{H} + \theta u \mathcal{H}$: magnetic symmetry group



Wigner, E. *Group Theory and Its Application to the Quantum Mechanics of Atomic Spectra*. 386 (Academic Press, London, 1959).

Bradley, C. J. & Davies, B. L. *Rev. Mod. Phys.* **40**, 359–379 (April 1968).

Lazzeretti, P. et al. *Nucl. Magn. Shield. Mol. Struct.* (ed Tossell, J. A.) 163 (Springer Science+Business Media, B.V., Maryland, 1993).

Keith, T. A. & Bader, R. F. *J. Chem. Phys.* **99**, 3669–3682 (1993).

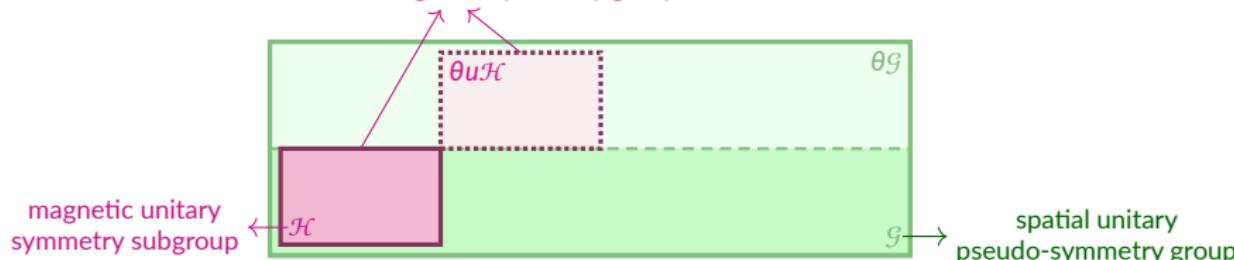
Groups in magnetic fields

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

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0(v_{\text{ext}}) + \mathbf{A}(\mathbf{r}_k) \cdot \hat{\mathbf{p}}_k + \frac{g_s}{2} \sum_{k=1}^{N_e} \mathbf{B} \cdot \hat{\mathbf{s}}_k + \frac{1}{2} A^2(\mathbf{r}_k).$$

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

$\mathcal{M} = \mathcal{H} + \theta u \mathcal{H}$: magnetic symmetry group



Wigner, E. *Group Theory and Its Application to the Quantum Mechanics of Atomic Spectra*. 386 (Academic Press, London, 1959).

Bradley, C. J. & Davies, B. L. *Rev. Mod. Phys.* **40**, 359–379 (April 1968).

Lazzeretti, P. et al. *Nucl. Magn. Shield. Mol. Struct.* (ed Tossell, J. A.) 163 (Springer Science+Business Media, B.V., Maryland, 1993).

Keith, T. A. & Bader, R. F. *J. Chem. Phys.* **99**, 3669–3682 (1993).

Unitary representation analysis

Group unitary representations on linear spaces

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

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

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

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

Group unitary representations on linear spaces

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

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

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

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

- We seek to decompose Γ into known *irreducible* representations of \mathcal{G} on V .
 - ↪ This *quantifies* the *symmetry* of \mathbf{v} under the action of \mathcal{G} .
- To this end, we pick a reference element $\mathbf{v}_i = \hat{u}_i \mathbf{v}$ in $\mathcal{G} \cdot \mathbf{v}$ and define the **representation matrices** $D^\Gamma(u_k)$ for all $u_k \in \mathcal{G}$:

$$\hat{u}_k \mathbf{v}_i = \sum_j \mathbf{v}_j D^\Gamma_{ji}(u_k).$$

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** $\langle \cdot | \cdot \rangle$.

Representation matrix determination

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

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

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

Representation matrix determination

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

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

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

- Application of $\hat{\mathcal{P}}$ on the defining equation for $\mathbf{D}^T(u_k)$ yields

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

where

$$T_{ij}(u_k) = \langle \mathbf{v}_i | \hat{u}_k \mathbf{v}_j \rangle.$$

Representation matrix determination

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

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

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

- Application of $\hat{\mathcal{P}}$ on the defining equation for $\mathbf{D}^T(u_k)$ yields

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

where

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

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

Current density linear space

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

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

↪ Enables projection-based unitary representation analysis on V_J

Current density linear space

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

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

- ↪ Enables projection-based unitary representation analysis on V_J
- Given a current density $\mathbf{j}(\mathbf{r})$ and a symmetry or pseudo-symmetry *unitary* group \mathcal{G} , the required overlap matrix elements for the symmetry analysis of $\mathbf{j}(\mathbf{r})$ are of the form

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

Current density linear space

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

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

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

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

(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**:

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

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

$$\mathbf{j}(\mathbf{r}) = \mathbf{j}_d(\mathbf{r}) + \mathbf{j}_p(\mathbf{r})$$

$$\mathbf{j}_d(\mathbf{r}) = -\mathbf{A}(\mathbf{r}) \sum_{\sigma} \omega_{\mu}^*(\mathbf{r}) \omega_{\nu}(\mathbf{r}) P_{\sigma}^{\nu\mu}, \quad \mathbf{j}_p(\mathbf{r}) = \frac{i}{2} \sum_{\sigma} \nabla \omega_{\mu}^*(\mathbf{r}) \omega_{\nu}(\mathbf{r}) P_{\sigma}^{\nu\mu} + \text{c.c.}$$

Soncini, A. & Fowler, P. W. *Chem. Phys. Lett.* **396**, 174–181 (2004).

Tellgren, E. I. et al. *J. Chem. Phys.* **129**, 154114 (October 2008), Tellgren, E. I. et al. *J. Chem. Phys.* **140**, 034101 (January 2014).

Irons, T. J. P. et al. *Chemistry (MDPI)*. **3**, 916–934 (August 2021).

Non-perturbative current densities

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

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

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

$$\mathbf{j}(\mathbf{r}) = \mathbf{j}_d(\mathbf{r}) + \mathbf{j}_p(\mathbf{r})$$

$$\mathbf{j}_d(\mathbf{r}) = -\mathbf{A}(\mathbf{r}) \sum_{\sigma} \omega_{\mu}^*(\mathbf{r}) \omega_{\nu}(\mathbf{r}) P_{\sigma}^{\nu\mu}, \quad \mathbf{j}_p(\mathbf{r}) = \frac{i}{2} \sum_{\sigma} \nabla \omega_{\mu}^*(\mathbf{r}) \omega_{\nu}(\mathbf{r}) P_{\sigma}^{\nu\mu} + \text{c.c.}$$

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

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

Soncini, A. & Fowler, P. W. *Chem. Phys. Lett.* **396**, 174–181 (2004).

Tellgren, E. I. et al. *J. Chem. Phys.* **129**, 154114 (October 2008), Tellgren, E. I. et al. *J. Chem. Phys.* **140**, 034101 (January 2014).

Irons, T. J. P. et al. *Chemistry (MDPI)* **3**, 916–934 (August 2021).

Ipsocentric DZ

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

$$\mathbf{G} \equiv \mathbf{G}(\mathbf{r}) = \mathbf{r},$$

so that $\mathbf{j}_d(\mathbf{r})$ vanishes and $\mathbf{j}(\mathbf{r}) = \mathbf{j}_p(\mathbf{r})$ formally.

Ipsocentric DZ

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

$$\mathbf{G} \equiv \mathbf{G}(\mathbf{r}) = \mathbf{r},$$

so that $\mathbf{j}_d(\mathbf{r})$ vanishes and $\mathbf{j}(\mathbf{r}) = \mathbf{j}_p(\mathbf{r})$ formally.

- In addition,

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

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

Integrals

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

$$\begin{aligned}
 T_{m1}(e) &= \int (\hat{u}_m \mathbf{j}_p)(\mathbf{r})^\dagger \mathbf{j}_p(\mathbf{r}) d\mathbf{r} \\
 &= \frac{1}{4} \sum_{\sigma\sigma'} (P_\sigma^{v\mu})^* P_{\sigma'}^{v'\mu'} \\
 &\quad \int (\hat{u}_m \omega_v^*)(\mathbf{r}) \nabla (\hat{u}_m \omega_\mu)(\mathbf{r})^\top [\nabla \omega_{\mu'}^*(\mathbf{r}) \omega_{v'}(\mathbf{r}) - \nabla \omega_{\mu'}(\mathbf{r}) \omega_{v'}^*(\mathbf{r})] d\mathbf{r} + \text{c.c.}
 \end{aligned}$$

Integrals

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

$$\begin{aligned} T_{m1}(e) &= \int (\hat{u}_m \mathbf{j}_p)(\mathbf{r})^\dagger \mathbf{j}_p(\mathbf{r}) d\mathbf{r} \\ &= \frac{1}{4} \sum_{\sigma\sigma'} (P_\sigma^{v\mu})^* P_{\sigma'}^{v'\mu'} \\ &\quad \boxed{\int (\hat{u}_m \omega_v^*)(\mathbf{r}) \nabla (\hat{u}_m \omega_\mu)(\mathbf{r})^\top [\nabla \omega_{\mu'}^*(\mathbf{r}) \omega_{v'}(\mathbf{r}) - \nabla \omega_{\mu'}(\mathbf{r}) \omega_{v'}^*(\mathbf{r})] d\mathbf{r} + \text{c.c.}} \end{aligned}$$



second derivatives of four-centre overlap integrals

Integrals

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

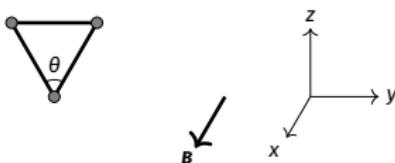
$$\begin{aligned} T_{m1}(e) &= \int (\hat{u}_m \mathbf{j}_p)(\mathbf{r})^\dagger \mathbf{j}_p(\mathbf{r}) d\mathbf{r} \\ &= \frac{1}{4} \sum_{\sigma\sigma'} (P_\sigma^{v\mu})^* P_{\sigma'}^{v'\mu'} \\ &\quad \int (\hat{u}_m \omega_v^*)(\mathbf{r}) \nabla (\hat{u}_m \omega_\mu)(\mathbf{r})^\top [\nabla \omega_{\mu'}^*(\mathbf{r}) \omega_{v'}(\mathbf{r}) - \nabla \omega_{\mu'}(\mathbf{r}) \omega_{v'}^*(\mathbf{r})] d\mathbf{r} + \text{c.c.} \end{aligned}$$

(pseudo-)symmetry-transformed London orbitals

Current density symmetry

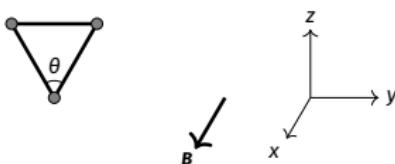
The electronic structure of H₃ radical

- Consider a triangular H₃ radical in a *perpendicular magnetic field*.



The electronic structure of H₃ radical

- Consider a triangular H₃ radical in a *perpendicular magnetic field*.



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

Zero field

Finite fields

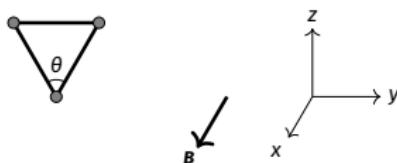
- Spatial sym. group: $\mathcal{G} = \mathcal{D}_{3h}$

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

- Mag. unitary sym. subgroup: $\mathcal{H} = \mathcal{C}_{3h}$
- Spatial pseudo-sym. group: $\mathcal{G} = \mathcal{D}_{3h}$

The electronic structure of H₃ radical

- Consider a triangular H₃ radical in a *perpendicular magnetic field*.



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

Zero field

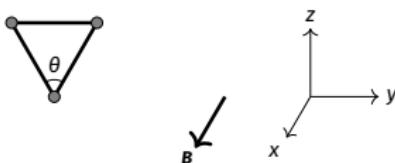
Finite fields

- Spatial sym. group: $\mathcal{G} = \mathcal{D}_{3h}$
- Magnetic sym. group: $\mathcal{M} = \mathcal{D}_{3h}(\mathcal{C}_{3h})$
 - Mag. unitary sym. subgroup: $\mathcal{H} = \mathcal{C}_{3h}$
 - Spatial pseudo-sym. group: $\mathcal{G} = \mathcal{D}_{3h}$
- Ground term: $E'(\mathcal{D}_{3h})$
- Ground term: $\Gamma'(\mathcal{C}_{3h})$ where

$$E'(\mathcal{D}_{3h}) \rightarrow \Gamma'(\mathcal{C}_{3h}) \oplus \bar{\Gamma}'(\mathcal{C}_{3h})$$

The electronic structure of H₃ radical

- Consider a triangular H₃ radical in a *perpendicular magnetic field*.



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

Zero field

Finite fields

- Spatial sym. group: $\mathcal{G} = \mathcal{D}_{3h}$
- Magnetic sym. group: $\mathcal{M} = \mathcal{D}_{3h}(\mathcal{C}_{3h})$
 - Mag. unitary sym. subgroup: $\mathcal{H} = \mathcal{C}_{3h}$
 - Spatial pseudo-sym. group: $\mathcal{G} = \mathcal{D}_{3h}$
- Ground term: $E'(\mathcal{D}_{3h})$
- Ground term: $\Gamma'(\mathcal{C}_{3h})$ where

$$E'(\mathcal{D}_{3h}) \rightarrow \Gamma'(\mathcal{C}_{3h}) \oplus \bar{\Gamma}'(\mathcal{C}_{3h})$$
- Ground current: $A'(\mathcal{C}_{3h}) \leftarrow A'_2(\mathcal{D}_{3h})$

Ground UHF current density in H₃ radical

- ❖ UHF, 6-31G*, $M_S = -1/2$

Ground UHF current density in H₃ radical

- ❖ UHF, 6-31G*, $M_S = -1/2$

Current density symmetry breaking

- The ground UHF current density in equilateral H₃ radical displays *symmetry breaking* at all $|\mathbf{B}|/B_0 \in (0, 1]$.

Current density symmetry analysis gives

$$A' \oplus \Gamma' \oplus \bar{\Gamma}'(\mathcal{C}_{3h}) \leftarrow A'_2 \oplus E'(\mathcal{D}_{3h}).$$

Current density symmetry breaking

- The ground UHF current density in equilateral H₃ radical displays *symmetry breaking* at all $|\mathbf{B}|/B_0 \in (0, 1]$.

Current density symmetry analysis gives

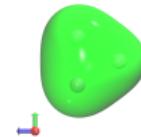
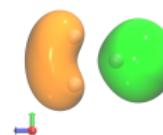
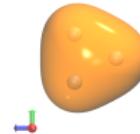
$$A' \oplus \Gamma' \oplus \bar{\Gamma}'(\mathcal{C}_{3h}) \leftarrow A'_2 \oplus E'(\mathcal{D}_{3h}).$$

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

Current density symmetry breaking

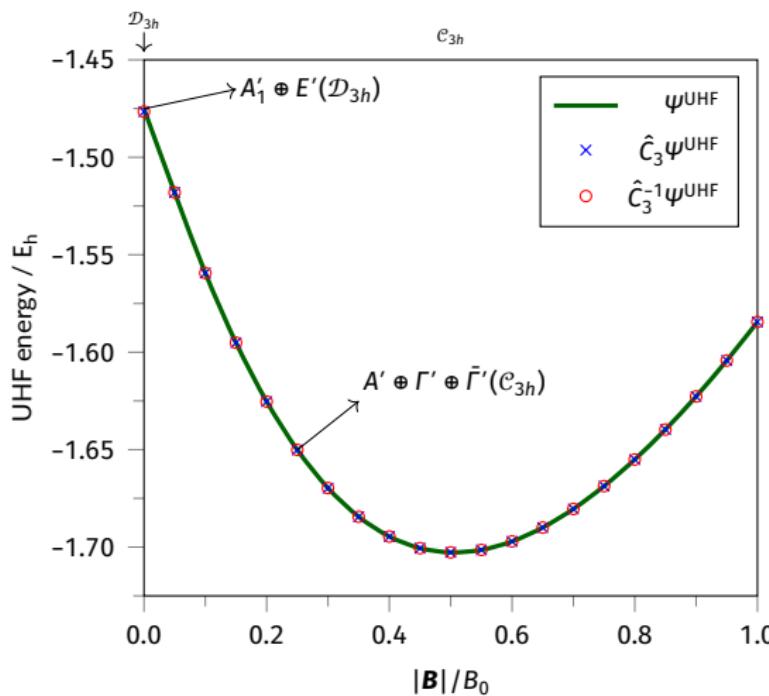
- Consider the UHF wavefunction at $|\mathbf{B}| = 0$:

- Overall symmetry: $A'_1 \oplus E'(\mathcal{D}_{3h}) \Rightarrow$ **symmetry-broken**
- Occupied molecular-orbital isosurfaces at isovalues ± 0.1 :

 $\alpha_1, A'_1 \oplus E'(\mathcal{D}_{3h})$  $\beta_1, A'_1 \oplus E'(\mathcal{D}_{3h})$  $\beta_2, A'_1 \oplus E'(\mathcal{D}_{3h})$

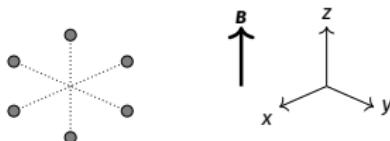
Current density symmetry breaking

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



Degenerate current density symmetry

- Consider an octahedral H₆ cluster.



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

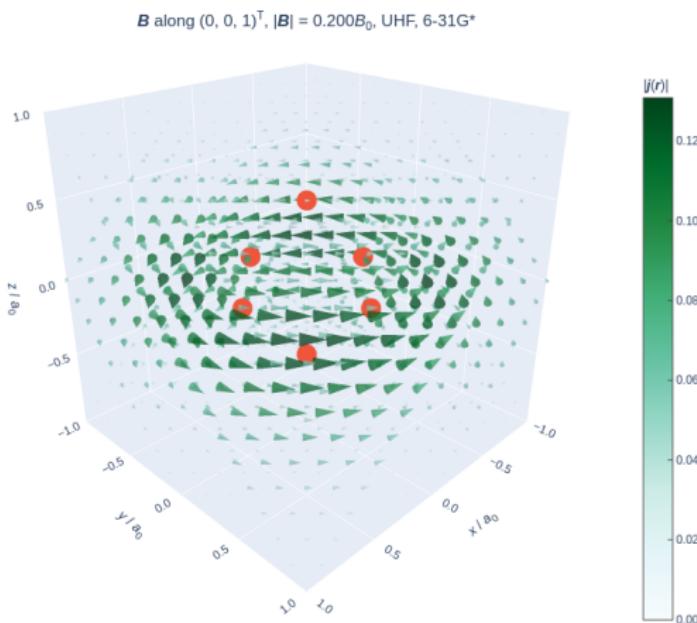
Zero field

Finite fields

- Spatial sym. group: $\mathcal{G} = \mathcal{O}_h$
- 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: $A_g(\mathcal{C}_{4h}) \leftarrow T_{1g}(\mathcal{O}_h)$

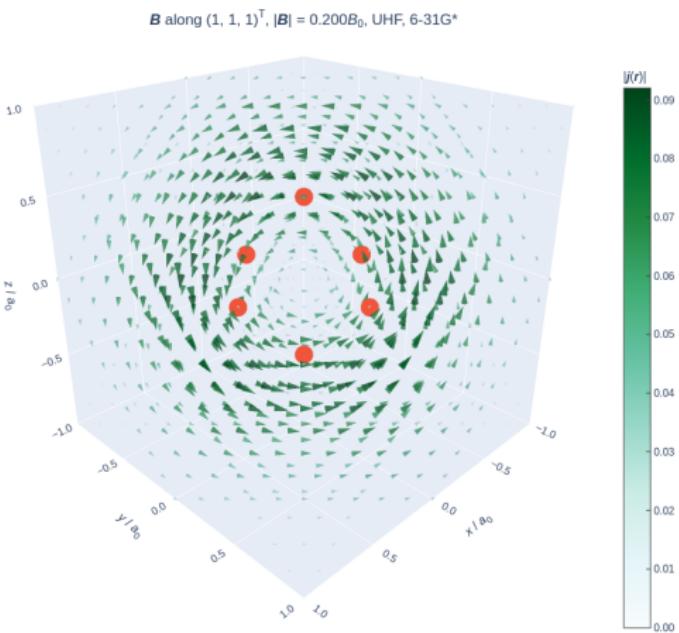
Principal-field current density in H₆ cluster

- ❖ UHF, 6-31G*, $M_S = 0$
- ❖ \mathbf{B} along z-direction
- ❖ $j(\mathbf{r})$ 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 H₆ cluster

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



Conclusion

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

Acknowledgements

Acknowledgements

- ❖ Prof. Andy Teale for magnetism and current discussions
- ❖ Dr Tom Irons for symmetry and integral discussions
- ❖ The rest of Teale group for general support



University of
Nottingham
UK | CHINA | MALAYSIA

