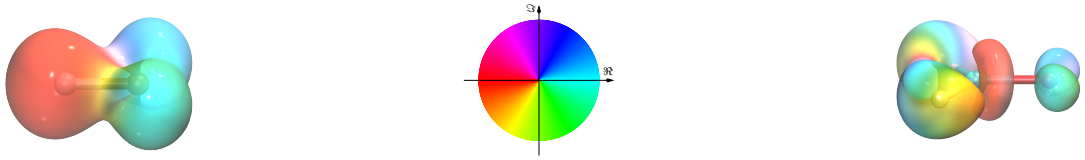
Symmetry and reactivity in magnetic fields: a perspective from conceptual DFT

Bang C. Huynh[1], Meilani Wibowo-Teale[1], Andrew M. Wibowo-Teale[1], Frank De Proft[2], and Paul Geerlings[2]

[1]*School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, United Kingdom*
[2]*Research group of General Chemistry (ALGC), Vrije Universiteit Brussel (VUB), Pleinlaan 2, B-1050 Brussels, Belgium*
bang.huynh@nottingham.ac.uk

ABSTRACT

In many familiar applications of quantum-chemical theories, all underlying mathematical quantities such as molecular orbitals (MOs) and electron densities can be made real to allow for convenient visualisation, analysis, and interpretation. However, such fortuitous reality cannot be guaranteed in general, especially in the presence of external magnetic fields where complex phases inevitably complicate their appearances and obfuscate their interpretation (Figure 1). In this contribution, I will show that a suitable consideration of symmetry via group and representation theories, which has been automated through the general framework of the recently developed program for **Q**uantum **Sym**bolic **Sym**metry, QSym^2 [1], allows chemists to apply almost the same intuition as with real-valued quantities to understand their chemical behaviours and implications. In particular, I will examine the unitary and magnetic symmetries of important DFT quantities such as frontier MOs, electron densities, and Fukui functions for two archetypal σ- and π-systems, hydrogen fluoride (HF) and formaldehyde (H_2CO), in external magnetic fields. The obtained insights lead to the definition of the concepts of *modular* and *phasal symmetry breaking*, which provide a formalisation for the deep connection between the macroscopic constraints on the electric dipole moment due to time reversal and the microscopic symmetry properties of wavefunction- and density-based quantities. Finally, I will explain how this understanding sheds light on some peculiar chemical properties and reactivity under the influence of magnetic fields, such as the orbital-driven reversal of electric dipole moments [1, 3] and the inability of magnetic fields to induce enantioselectivity [2].



(a) HF, $|\mathbf{B}_\perp| = 0.74B_0$ (b) H_2CO, $|\mathbf{B}_\perp| = 1.00B_0$

Figure 1: Examples of complex-valued MOs from current-DFT. Complex-phase colours are shown on the accompanied colour wheel. The highest-occupied MOs are shown in both cases.

References

[1] Huynh, B. C., Wibowo-Teale, M. & Wibowo-Teale, A. M. QSym^2: A Quantum Symbolic Symmetry Analysis Program for Electronic Structure. *J. Chem. Theory Comput.* **2024**, *20*, 114–133.

[2] Wibowo-Teale, M., Huynh, B. C., Wibowo-Teale, A. M., De Proft, F. & Geerlings, P. Symmetry and reactivity of π-systems in electric and magnetic fields: a perspective from conceptual DFT. arXiv: 2402.15595, **2024**. In review.

[3] Irons, T. J. P., Huynh, B. C., Teale, A. M., De Proft, F. & Geerlings, P. Molecular charge distributions in strong magnetic fields: a conceptual and current DFT study. *Mol. Phys.* **2022**, e2145245.