Going into the forbidden: Magnetic circular dichroism calculations for spin/dipolar forbidden transitions

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Magnetic circular dichroism spectroscopy (MCD) is a valuable tool for interpreting electronic transitions that are difficult to discern using other techniques, particularly for molecules without inherent optical activity or for samples that cannot be conveniently oriented in a polarized light beam. MCD combines the differential one-photon absorption of left- and right-circularly polarized light used in circular dichroism spectroscopy with a longitudinal static magnetic field that induces optical activity through the Faraday effect.

In this talk, I will present our latest developments in the Orca code for computing Magnetic Circular Dichroism spectra. Our formulation, based on quasi-degenerate perturbation theory, allows us to take into account spin-orbit coupling effects after the TD-DFT step and external magnetic field perturbations responsible for the magnetic circular dichroism intensity through the Faraday effect.

The methodology has been extended to the use of the full semi-classical field-matter interaction operator to model the complete light perturbation over the electrons, and to the framework of excited state dynamics over a path integral approach that computes nuclear dynamics under the harmonic oscillator approximation to account for nuclear vibrational effects.

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