Light-matter interaction in a relativistic perspective

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A semi-classical treatment invoking the electric-dipole approximation is a common starting point for a theoretical description of light–matter interactions. The latter approximation amounts to assuming that the wavelength of the electromagnetic field is long compared to the spatial extension of the molecular system such that the molecule effectively sees a uniform electric field. Formally it corresponds to retaining only the zeroth-order term of an expansion of the interaction operator in orders of the length of the wave vector. While this is often justifiable at low intensities in the optical range, the availability of high-energy X-ray photons and intense laser pulses motivates investigations into the effects of going beyond this simplification.

In general, methods for going beyond the electric-dipole approximation have been based on multipole expansions of the minimal coupling light-matter interaction operator which, in truncated form, may introduce unphysical gauge-origin dependence into the molecular properties.[1] This is particularly problematic for molecular systems where no natural choice of gauge origin exists. In a seminal paper, Bernadotte *et al.* presented an approach for the calculation of origin-independent intensities within the non-relativistic framework, beyond the electric-dipole approximation, by truncating the oscillator strength, rather than the interaction operator, in orders of the wave vector.[2]. However, Lestrange *et al.* [3] found that inclusion of the second-order oscillator strength of the electric-dipole allowed ligand K-edge transition of $TiCl_4$ made the total oscillator strength negative. Negative oscillator strengths to second-order were also reported by Sørensen *et al.*[4] in metal K-edge transitions of $[FeCl_4]^-$, but only for certain basis sets, which led them to conclude that they were due to incomplete basis sets rather than missing higher-order contributions to the oscillator strength. In a second paper [5], where $[FeCl_4]^-$ is revisited, Sørensen *et al.* speculate that the fourth-order electric-octupole-electric-octupole contribution may reverse the sign "provided that no other higher terms also grows disproportionately large".

To avoid the above issues, we recently proposed using the *full* semi-classical light–matter interaction operator in the context of linear absorption spectroscopy in the non-relativistic regime.[6] In a second paper[7] we presented a mixed analytical-numerical approach to isotropically average oscillator strengths computed with the full light-matter interaction operator.[7] This novel approach has been followed up by Sørensen *et al.*[8]

We have now extended our approach to the relativistic regime [9]. Our implementation in DIRAC[10] features the full light-matter interaction, but also the multipole expansion to arbitrary order, including rotational averaging. This places us in the unique position of being able to investigate the convergence of the latter expansion.

References

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