

2.7.3 Electronic Spectroscopy of Open-Shell Molecules and Relativistic Effects in Quantum Chemistry and Spectroscopy

Computational Electronic Spectroscopy and Theory Development by Benjamin Helmich-Paris

ABSTRACT: My research focuses on the development and application of electronic structure theory methods for electronic spectroscopy of open-shell molecules. For open-shell molecules in low-spin states only multi-reference (MR) methods can provide at least a qualitatively correct description of the electronic structure. In a recent benchmark study on singlet excitation energies and UV/Vis absorption intensities with the simplest MR method, i.e. CASSCF, I could show that the linear response (LR) approach is most accurate and generally applicable. Nevertheless, the accuracy of all CASSCF methods is fairly poor and dynamic correlation should be included by either MR second-order perturbation theory or a hybrid CASSCF density functional theory (DFT) approach. Furthermore, I have proposed an efficient implementation of LR-CASSCF which is based on modern integral decomposition techniques and is applicable to large open-shell molecules with hundreds of atoms. Improvements of the accuracy by a hybrid CASSCF – DFT approach are currently investigated. In other research projects, I have introduced spin-orbit coupling to describe (circularly polarized) phosphorescence lifetimes of closed-shell molecules with an approximate coupled cluster method (CC2) and inter-molecular interactions of large heavy-element containing molecules with the Dirac Møller-Plesset second-order perturbation theory method. Future research will be devoted to the development of more accurate MR LR electronic structure methods that are based on second-order perturbation theory. I am confident that these approaches will become standard tools for simulating electronic spectra of open-shell low-spin molecules with 100 atoms and more.

The focal point of my research, since I have joined the *Max-Planck-Institut für Kohlenforschung* in 2018, is the development and application of state-of-the-art electronic structure methods for computing electronic spectra of open-shell molecules. Open-shell molecules frequently occur in many fields of chemistry and physics. In organic synthesis and material science, stable radicals are well-known and serve for many purposes, e.g. radical markers and reagents or organic conductors and even superconductors at low temperatures. Most prominent are open-shell transition metal complexes that are used in homogeneous catalysis or form the active center in many enzymes. Despite a vast progress of molecular electronic structure theory (*quantum chemistry* (QC)) in the last decades, state-of-the-art QC methods are still very limited in providing accurate predictions for open-shell molecules of decent size, in particular if they are in a low-spin state.

To describe molecules in an open-shell low-spin state, a linear combination of spin-adapted determinants is inevitable. The most established and most reliable approaches are based on a linear combination of all combinatorially possible determinants (configuration interaction (CI)) generated from a small subset of active orbitals - the so-called active space. The conceptually and also computationally simplest method is the complete active space self-consistent field (CASSCF) method that minimizes the energy with respect to the molecular orbital and CI coefficients. The CASSCF ansatz is not meant for high accuracy but can rather describe the electronic structure of the open-shell complexes qualitatively correct. With CASSCF there several approaches one can pursue to compute excitation energies and transition moments that are required to simulate the UV/Vis absorption and electronic circular

dichroism spectra. The most practical and efficient variants for computing many electronic states are state averaging (SA) and linear response (LR) theory that are from a conceptual point of view very different. To explore the accuracy of SA- and LR-CASSCF for singlet excitation energies and oscillator strengths (UV/Vis intensities), I have recently performed a benchmark study^[1] with a well-established test set originally designed by the former Max-Planck director Prof. Walter Thiel, which contains more than 150 valence transition in prototypical organic chromophores. I could show that LR-CASSCF is more accurate than SA-CASSCF. Furthermore, the study revealed that all CASSCF variants showed the poorest performance of all ab initio QC methods as dynamic electron correlation is not accounted for. A good compromise between accuracy and efficiency can be obtained when combining CASSCF with density functional theory (DFT), i.e. in particular the long-range LR-CASSCF short-range DFT method (srDFT) proved to be fairly accurate (Fig. 1).

The recent findings of the benchmark study were the motivation to work on an efficient computer implementation of the LR-CASSCF method that can be easily applied when simulating many electronic transitions in large open-shell molecules with hundreds of atoms^[2]. The newly developed LR-CASSCF implementation is integrated into the QC package ORCA of the Max-Planck director Prof. Frank Neese and benefits from a well-established infrastructure and efficient algorithms for computing and processing two-electron integrals, which is the major computational bottleneck of CASSCF calculations with decent active space sizes. I have also revised some of the time-critical integral transformations and, therefore, could also contribute to improving the performance of

the conventional CASSCF energy minimization algorithm^[3]. Within the LR-CASSCF project, I have also found a simple and very convenient way to visualize the electronic transitions by employing so-called natural transition orbitals, which are well known and frequently used for simpler excited methods as time-dependent (TD) DFT, but were so far not proposed for the more elaborate LR-CASSCF method.

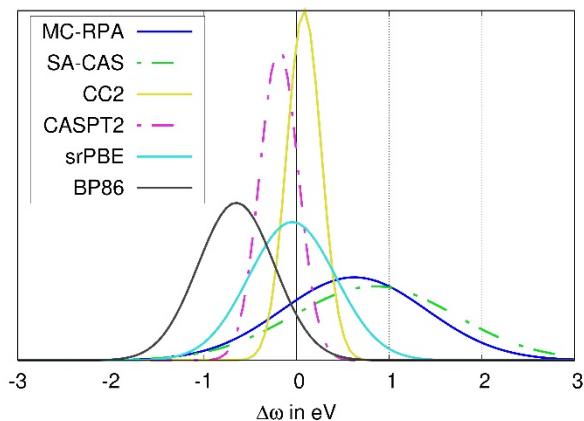


Figure 1. Normal distribution of deviation from the CC3 reference singlet excitation energies computed with various methods.

Based on experience gained from the previous benchmark study and several other applications it is clear that the LR-CASSCF absorption spectra can only be sufficiently accurate (even almost as accurate as second-order multi-reference perturbation theory) if all spectroscopically relevant orbitals can be included in the active space. This is not feasible for most chromophores and a more effective way of including dynamic electron into LR-CASSCF is the addition of a DFT exchange-correlation functional, e.g. as done by the range separation-based srDFT variant. I am currently pursuing an efficient LR-srDFT implementation in ORCA together with an external collaboration, Prof. Hans Jørgen Aa. Jensen (SDU Odense, DK).

In a side project, I have also contributed to the computation of circularly polarized phosphorescence (CPP) rates with the approximate coupled cluster method CC2^[4]. CPP can only be described by the theory of relativity, in particular, spin-orbit coupling, as it involves an electronic transition from a triplet excited state back to the singlet ground state, which is spin-forbidden (zero probability) in non-relativistic quantum mechanics. Moreover, CPP can be detected only for chiral molecules that absorb linearly polarized light, which might be exploited to distinguish between different enantiomers. In that work, we reported for the first time calculations of CPP at the coupled cluster level with different levels of sophistication when treating relativistic effects.

In another project, me and my collaborators have explored how to make Dirac wave function (second-order Møller-Plesset perturbation theory (MP2)) calculations feasible for large molecules^[5]. This is particularly relevant when computing inter-molecular interaction energies of molecules with heavy elements that cannot be described properly by standard DFT methods as the dispersion interaction is either missing or accounted for by an additional empirical correction term. In this work, we have generalized a low-scaling non-relativistic MP2 approach for the Dirac two-

component formalism, which employs the Laplace transformation (LT) of the orbital-energy denominator and sparse-matrix operations. With our efficient implementation we were able to perform the largest Dirac two-component wave function calculation that has been ever performed (nearly 10'000 orbital basis functions). Unfortunately, screening of negligible intermediates only worked effectively for nearly linear molecules. A re-design of the algorithm together with a new implementation in ORCA is currently pursued which will facilitate large calculations with so-called second-order wave function methods. This is a collaboration with Dr. Róbert Izsák and Dr. Bernardo de Souza (Universidade Federal de Santa Catarina, BRA).

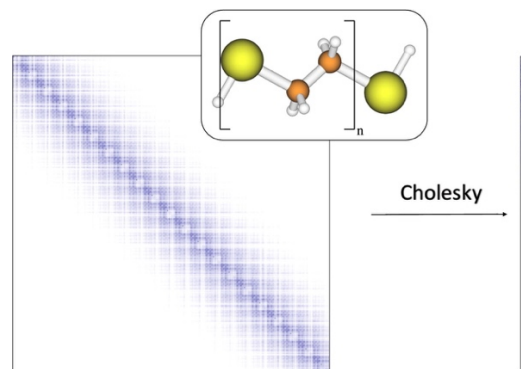


Figure 2. Sparse intermediates of LT-based MP2 implementation.

Future research will be devoted primarily to develop more accurate LR MR methods that have at least the same accuracy and scope of application as standard MR second-order perturbation theory methods, but are also capable of providing many electronic states without exceedingly large active spaces. Also, extending the applicability of the LR-srDFT method for fluorescence and resonance Raman spectra will be of high priority.

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