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Atomic and molecular response properties within a relativistic framework

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Abstract:
The relativistic quantum chemistry, RQC, is at the moment the best theoretical framework that one have at hands when wants to describe the atomic and molecular quantum world. Even though it is not usually necessary to consider the influence of relativistic effects on the description of the chemistry world, when accuracy is involved or heavy-atoms (belonging to the 4^{th} or lower rows of the periodic table) are part of such a world, there is no option, one should work within a relativistic framework.

Almost 40 years ago few authors (being Pekka Pyykkö the central figure) started to highlight the fact that relativistic effects can strongly influence many chemical properties of the heavier elements. [1, 2] It was in the early 1990s that an small community of theoretical chemist started to do some fundamental contributions to the RQC which so grew faster than previously by the development of new theories and its implementations in computational codes. Several specific books appeared since then. [3 - 8] Today RQC is a mature field lead by european research teams, though there are also some experts spread out in all continents. In South America there are only few consolidated teams working in this quickly evolving field.

The importance of including relativistic effects on the studies of response atomic and molecular properties compelled the theoretical chemists to develop new specific relativistic theories and models. It is not only the accuracy but also the physics behind those properties which must be considered. Few examples: i) the four well known non relativistic, NR, mechanisms of the NMR indirect J-coupling are unified in one; ii) diamagnetic and paramagnetic terms of the NMR magnetic shielding are also unified and iii) some NR relationships among molecular properties, like the Flygare relation between spin-rotation constants and NMR magnetic shieldings must be modified.[9] New mechanisms and so, new physics is behind all this.[3, 8, 10, 11]

In this presentation I will briefly describe the state of the art of one of the most active areas of the RQC, that of response properties. In this area one can apply methods that are wave-function-based, DFT-based or based on polarization propagators. I will focus in the relativistic polarization propagator formalism, which is the one I was engaged in during the last 25 years.[10] I will also briefly expose another two-component model, known as linear response elimination of small component [11] from which one can grasp new insights about the electronic mechanisms that underlies molecular properties.

Examples will be given. I shall show in them when relativistic corrections should be included, how can we do it, and what new effects and understandings appear when working within a relativistic framework.

Key-words: Relativistic effects; polarization propagator; LRESC; magnetic properties

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