REX: A Stepping Stone from Hückel Theory to Relativistic Quantum Chemistry

Proton Spin Relaxation in Paramagnetic Complexes

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Abstract

As a tribute to Prof. Pekka Pyykkö on the occasion of his forthcoming 60th birthday, we review his important contributions to the field of relativistic quantum chemistry beginning with the 1977 development of relativistic extended Hückel Theory, or REX. This semi-empirical method may be viewed as a computational procedure for extrapolating the atomic Dirac-Fock results of Desclaux to molecules containing one or more heavy atoms, thus obtaining estimates of spin-orbit splittings and relativistic bonding effects in molecules. It has also served as a bridge to more rigorous treatments of relativistic effects in quantum chemistry.

As a second topic we summarize our recent work on the theory of proton spin relaxation in paramagnetic complexes with two or more unpaired electrons, that is, with electronic spin $S \geq 1$ quantized with respect to molecular axes by zero-field spin-orbit interactions. For these systems, for which esr investigations are often not feasible, the nmr paramagnetic relaxation enhancement provides a unique spectroscopic probe into the electron spin level structure and relaxation properties.