Periodic Trends of Spin-Orbit Heavy Atom on the Light Atom Effect to NMR Chemical Shifts Rationalized

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The importance of relativistic effects on the NMR parameters in heavy-atom (HA) compounds, particularly the SO-HALA (Spin-Orbit Heavy Atom on the Light Atom) effect on NMR chemical shifts, has been known for about 40 years. However, generally valid correlation between the electronic-structure of heavy element complexes and SO-HALA effect have been missing. By analyzing $^1$H NMR chemical shifts of the 6th-period hydrides (Cs-At) we uncovered the basic electronic-structure principles and mechanisms that dictate the size and sign of the SO-HALA NMR chemical shifts. In brief, partially occupied HA valence shells induce relativistic shielding at the light atom (LA) nuclei, while empty HA valence shells induce relativistic deshielding. The LA nucleus thus became relativistically shielded in 5d$^2$-5d$^8$ and 6p$^4$ HA hydrides and deshielded in 4f$^0$, 5d$^0$, 6s$^0$, 6p$^0$ HA hydrides. The introduced principles have a general validity across the periodic table and can be extended to non-hydride LAs as well. Moreover, the connection between the SO-HALA NMR chemical shifts and Spin-Orbit-induced Electron Deformation Density (SO-EDD) is derived. SO-EDD provides an intuitive understanding of the SO-HALA effect in terms of the depletion/concentration of the electron density at LA nuclei caused by spin-orbit coupling due to HA in the presence of magnetic field. Using an analogy between SO-EDD concept and arguments from classic NMR theory, the complex question of the SO-HALA NMR chemical shifts becomes easily understandable for a wide chemical audience.

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