The influence of a presence of a heavy atom on spin-spin coupling constants between two light atoms in organometallic compounds and halogen derivatives.

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The importance of relativistic effects is getting widely recognized in the scientific community and more and more molecular properties are being calculated using relativistic Hamiltonians. It is known that the presence of a heavy nucleus in the molecule affects not only the Nuclear Magnetic Resonance (NMR) properties of the heavy nucleus in question, but influences also the shielding constants and indirect spin-spin coupling constants of nearby light nuclei (heavy-atom-on-light-atom, or HALA, effect). However, while the relativistic effects on the shielding constants of light nuclei neighbouring heavy atoms are relatively well investigated, the parallel phenomenon occurring for the nuclear spin-spin coupling constants is almost unexplored. There is a handful of papers dealing with the situation when a heavy atom mediates the geminal coupling between two light atoms but there are practically no studies concerning the situation where the heavy atom is not in the coupling path.

As we have shown in our previous study on heavy metal cyanides, the HALA effects on the $^1\mathbf{J}_{CN}$ are sizeable [1]. These findings inspired us to look more closely at the influence of the presence of heavy atom on the one-bond spin-spin coupling constant of the nearby light nuclei.

The systems under study are aliphatic hydrocarbons substituted with I, At, Cd and Hg. This choice allowed us to study substituent effects on $^1J_{CC}$ and $^1J_{CH}$ and to explore the factors, which may influence the HALA effect on these properties: the nature of the heavy atom substituent and carbon hybridization.

The calculations are carried out using density functional theory with the zeroth-order regular approximation Hamiltonian (with the spin-orbit term included) [2] and with the four-component Dirac-Coulomb Hamiltonian [3], since our secondary aim is to compare the performance of ZORA-DFT and Dirac-Kohn-Sham methods for modelling of HALA effects on the spin-spin coupling constants.

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