Relativity: Relatively Uninteresting for Chemists?

The periodic table of elements is among the corner stones of chemistry. In the given order, in both the periods (rows) and groups (columns), elements show some specific properties. However, when going around the bottom of the periodic table (transitions metals) few elements show unusual properties due to relativistic effects. For instance, gold is not silvery like most of the other metals in the same group. Mercury is a liquid unlike its immediate neighbours, cadmium and gold. These differences can be explained by the concepts of quantum chemistry.

Initially, the concepts of quantum chemistry were developed without considering the theory of relativity (the Schrödinger equation, 1925). Latter, Paul Dirac (1928) formulated a relativistic wave equation to account for relativistic effects. They are treated depending on the electron speed relative to the speed of light. Hence, they are more pronounced for heavy elements where electrons attain relativistic speeds. As such, if we calculate the properties of gold without considering relativistic effects, then we get silvery colour, which is not in line with the reality. However, if relativistic corrections are included, the calculated values become more close to the reality. This is mainly due to the contraction of 6s orbital and expansion of 5d orbital of gold making it to absorb in a different region of the electromagnetic radiation compared to silver.

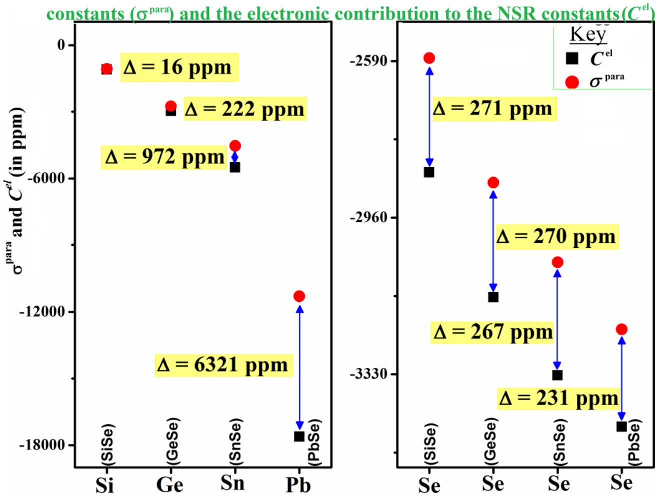
Nuclear magnetic resonance (NMR) properties are among the molecular properties affected by relativistic effects. NMR spectroscopy is a powerful spectroscopic technique used to get detailed information about the chemical environment, dynamics and structure of molecules. Chemists use it to determine molecular structures by analysing for example the chemical shielding (σ_K, the difference between the applied external magnetic field and the field at the nucleus, caused by the surrounding shells of electrons) in parts per million (ppm), chemical shift (δ_K, the difference between the chemical shielding of a certain nucleus K and the same nucleus in a reference molecule) in ppm, and spin-spin coupling constant (*J*, a measure of the interaction between neighbouring nuclei of a molecule) in Hertz. Medical practitioners use the multidimensional NMR imaging technique, magnetic resonance imaging (MRI), for diagnostic purposes.

In some cases, determination of NMR properties using experiments may need additional input from quantum chemistry. For instance, until recently, the chemical shielding of a certain nucleus was estimated after getting half information (the paramagnetic contribution to the chemical shielding, σ^{para}) from the electronic contribution to the experimental nuclear spin-rotation (NSR) constant and the other half (the diamagnetic contribution to the chemical shielding, σ^{dia}) from calculations using quantum chemistry (see the following equation). This approach may give reasonable results for very light atoms. However, it fails when considering heavy atoms if relativistic corrections are not taken into account.

$$\sigma_K = \boxed{\sigma_K^{dia} + \sigma_K^{para}} \approx \boxed{\underset{\text{From calc.}}{\sigma_K^{dia}}} + \boxed{\underset{\text{From exp.}}{\left(\frac{10^9 m_p}{2 m_e g_K B_r}\right) C_K^{el}}}$$

In this study, the diatomic molecules of silicon selenide (SiSe), silicon telluride (SiTe), germanium selenide (GeSe), germanium telluride (GeTe), tin selenide (SnSe), tin telluride (SnTe), lead selenide (PbSe) and lead telluride (PbTe) were considered to show the importance of relativistic corrections to the nuclear absolute shielding constants. Details of the contributions of the NSR constants and NMR shielding constants are presented in the paper. The σ^{para} contributions obtained from direct shielding calculations are compared with electronic contributions to the NSR constants (C^{el} in the above equation). I presented the sources of the errors of the previously reported values of all the nuclei in the above molecules. For instance, the difference between C^{el} and σ^{para} of Si in SiSe is 16 ppm, however, it increases to 6321 ppm for Pb in PbSe (see the figure below). Note that lead is very heavy compared to silicon. The error for the selenium nucleus in most of the molecules is ≈270 ppm, whereas it is ≈1125 ppm for the tellurium nucleus. The difference increases as the atoms become heavier showing the importance of relativistic corrections.

Comparison of the paramagnetic contribution to the absolute shielding constants (σ^{para}) and the electronic contribution to the NSR constants(C^{el})



To sum up, relativistic corrections to σ^{para} of the absolute shielding constants are very significant compared to σ^{dia} . This shows that determining σ^{para} from C^{el} causes unrecoverable error on the total absolute shielding constant. The results also show the shortcomings of the old assumption of getting the absolute shielding constants indirectly from C^{el} using the above equation. By taking care of the relativistic corrections, I presented new accurate absolute shielding scales of all nuclei aiming that the results will be used for future benchmarking of similar theoretical as well as related experimental studies. The approach I followed in this study can be used as an immediate remedy for such kind of magnetic property determinations.

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