Relativistic and correlation effects on heavy molecules containing Sn and Pb atoms

Alejandro F. Maldonado[1], Gustavo A. Aucar[1]

[1] Physics Department, Natural and Exact Science Faculty, Northeastern University of Argentina and Institute of Modelling and Innovation on Technology, IMIT, Corrientes, Argentina

e-mail: aleoml@yahoo.com.ar

A new procedure that was recently published[1], which mix together accurate experimental chemical shifts (δ) and theoretical magnetic shieldings (σ) of heavy atom containing molecules, was applied on a family of heavy-halogen containing molecules to calculate the absolute value of σ(Sn) and σ(Pb). We found out that the absolute magnetic shielding σ(Sn; $SnMe_4$) in gas phase shall be close to 3852.38 ppm $\pm$ 20,33 ppm. In the case of Pb, σ(Pb; $PbMe_4$) shall be close to 14067.10 ppm $\pm$ 501.90. Such values correspond to the RPA level of approach within relativistic polarization propagators, that seems to be the more accurate as compared with DFT calculated values.

We also studied the dependence of such shieldings with 4-component functionals as implemented in the DIRAC code. To our knowledge there are no previous studies on these matters. We show that RPA results are more reliable than the DFT ones. We argue that DFT functionals should be modified to give better results of NMR magnetic shieldings within the relativistic regime. There is a dependence between electron correlation and relativistic effects that should be introduced in one way or another in the functionals. They were parameterized in a nonrelativistic context and so cannot be used properly within the relativistic regime.

In the $XY_{4-n}Z_n$ (X = Sn, Pb; Y, Z = H, F, Cl, Br, I; n = 0, 1, 2) family of compounds there should appear the newest heavy-atom effect on vicinal heavy atoms, HAVHA[2, 3]. We found that such effects are among the most important relativistic effects in compounds were the central atom is surrounded by three or four halogen atoms belonging to the fourth or fifth row of the Periodic Table.

[1] Maldonado A. F., Giménez C. A. and Aucar G. A., (2012) *Chem. Phys.* **395**, 755 - 81.

[2] Maldonado A. F. and Aucar G. A., (2009) *Phys. Chem. Chem. Phys.* **11**, 5615 - 5627.

[3] Melo J. I., Maldonado A. F. and Aucar G. A. (2011) *Theor. Chem. Account*, **129**, 483 - 494.