

ASSIGNMENTS OF ISOTROPIC HYPERFINE COUPLING CONSTANTS OF RADICALS CONTAINING THIRD ROW NUCLEI USING DFT METHODS

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The reliability of density functional theory (DFT) in the determination of the isotropic hyperfine coupling constants (hfccs) of the ground states of radicals containing ^{29}Si , ^{31}P , and ^{33}S nuclei is examined. The lack of theoretical hfccs for the radicals containing those nuclei has encouraged us to carry out a complete study.

The (DFT) methodology is giving accurate values of spin densities and is allowing good assignments of experimental hfcs¹⁻⁴. The use of these DFT methods allow to compute hfccs with a lower time cost, using the same basis respect to other post-HF methods. Recently, we have studied neutral, anions and cations radicals with doublet and quartet electronic states⁴. We have analyzed systems from small diatomic radicals to medium size systems considering three hybrid functional (B3LYP, B3P86 and B3PW91) and four different basis sets: Pople's 6-31G*, Dunning's cc-pVQZ, Ahlrichs's TZVP and Barone's EPR-III.

In the same way, a complete analysis about the predictive power of several hybrid functionals and different basis sets for predicting the isotropic hyperfine coupling constants of radicals containing ^{29}Si ($I = 1/2$), ^{31}P ($I = 1/2$), and ^{33}S ($I = 3/2$) nuclei is carried out. The hfccs for the radicals studied are compared with experimental data obtaining a good correlation. Regression statistical study of the data is used as an appropriate methodology for the correlation analysis.

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