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Overcoming Challenges in Density Functional Theory-Based Calculations of Hyperfine Coupling Constants for Heavy Heteroatom Radicals

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Streszczenie

This study assesses density functional theory (DFT) methods for their accuracy in calculating hyperfine coupling constants (HFCCs) of heavy heteroatom radicals with heteroatoms including Sb, Bi, In, Tl, and Sn. Given the essential role of electron paramagnetic resonance spectroscopy in characterization of these species, it is crucial that theoretical models can predict HFCCs accurately for heavy elements. This work presents a computational approach that addresses crucial factors: selection of basis set, hybrid exchange-correlation functional, higher Hartree–Fock (HF) exchange, and the Gaussian description of nuclear charge. The relativistic effects are introduced using one-component linear response theory with the second-order Douglas–Kroll–Hess formalism and the fully relativistic four-component Dirac–Kohn–Sham method. The findings show that, while one-component DFT is accurate for the 4th-row elements, the four-component method is more precise for the 5th-row radicals and the one-component approach fails for the 6th-row congeners. Increasing HF exchange significantly improves HFCC predictions. The developed framework for accurate HFCC calculations will enhance the understanding of electronic and magnetic properties of heavy element radicals and can be used by computational chemists and experimentalists alike.

Słowa kluczowe

density functional calculations, electron paramagnetic resonance spectroscopy, heavy heteroatom radicals, hyperfine coupling constants, relativistic effects

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