Topology of electron density and the Fourier transform of electron density of heavy atom compounds. Diphenylmercury and triphenylbismuth

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This theoretical study is focused on the electron density and the Laplacian of the electron density of diphenylmercury and triphenylbismuth. A comparison of electron correlation and relativistic effects will be presented. BLYP functional and Hartree-Fock approaches are employed and the quasirelativistic Infinite Order Two-Component (IOTC) Hamiltonian [1] is used to include relativity. Besides that, several additional effects in the electron density and the Laplacian are considered such as the picture change error (PCE) of the IOTC wave function and/or basis set significance. Scalar and 1-electron spin-orbit relativistic effects are split into separate contributions and the extent of 2-electron spin-orbit effects is critically investigated.

Furthermore, the Fourier transform of the electron density [2] (i.e. the X-ray structure factors) is exploited more closely for the studied heavy element compounds, including PCE, relativistic effects and electron correlation.

The relativistic 1-component and 2-component structure factors are employed in an extension of the X-ray Wavefunction Refinement procedure [3] including X-ray Constrained Wavefunction fitting [4] as well as Hirshfeld Atom Refinement [5, 6]. All calculations have been performed in the Tonto package [7].

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