Comprehensive relativistic *ab initio* and density functional theory studies on PtH, PtF, PtCl, and $Pt(NH_3)_2Cl_2$

Wenjian Liu and Robert Franke

Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany

Abstract

Platinum monohydride is taken as an example to compare the performance of various relativistic and correlation approaches, such as all-electron DPT (direct perturbation theory), ECP (effective core potential); RSPT2, RSPT3 (second and third order multireference Rayleigh-Schrödinger perturbation theory), CCSD(T) (coupled-cluster with singles, doubles and perturbative triples) as well as four-component relativistic density functional theory. It is shown that *first order* DPT performs *significantly* better than the (first order) Breit-Pauli Hamiltonian. The performance of different approaches for the excitation energies of the platinum diatomics is critically discussed. The molecular spectroscopic constants for PtF and PtCl are predicted for the first time. The geometric data for several isomers of cis- and trans-$Pt(NH_3)_2Cl_2$ is reported. The corresponding energetic data is calculated at relativistic all-electron- and ECP-CCSD(T) as well as four-component relativistic density functional levels of theory. Contrary to previous statements, it is found that the two C_{2v} isomers of cis-$Pt(NH_3)_2Cl_2$ are *not* degenerate in energy, which could be ascribed to Cl-H interactions.