# Abstract

Ph.D. thesis of Jochen Autschbach: ,,Zur Berechnung relativistischer Effekte und zum Verständnis ihrer Trends bei Atomen und Molekülen" ("On the calculation of relativistic effects and how to interpret them in atoms and molecules"), Universität Siegen, Germany, 1999.

After a brief discussion of quantum chemical standard methods (chapter 1) and relativistic quantum chemistry (chapter 2), in chapter 3 the relativistic effects of properties of atomic shells are investigated. A detailed analysis of the fractional relativistic corrections of atomic orbital energies and radii of the atoms no. 1 to 118 shows new relativistic periodic trends. An explanation of several anomalies of relativistic effects, among them the well known "gold-maximum", is given on the basis of the periodic trends and the appearently unsystematic atomic ground state configurations.

Forces in molecules, especially by means of the Hellmann-Feynman theorem, are discussed in chapter 4, where also several formulae are derived, which are used in chapters 5 and 6. Chapter 5 contains a density-functional study of the binding forces in $N_2$ and HCl. By analyzing the spatial origin of the Hellmann-Feynman forces it is concluded that both the topology of the molecular deformation density as well as the sharp core polarizations are approximately equally important to determine the forces.

Relativistic bonding energies and forces of several diatomic gold compounds are analyzed in chapter 6. The relativistic energy corrections are computed with the help of an implementation of the nonsingular relativistic perturbation theory DPT into the Amsterdam density functional program. Several paradox interpretation schemes are applied to explain the spatial origin of relativistic bond energies and binding forces. Different mathematical formulations create different physical pictures. A "chemical" interpretation is preferrable and possible.