University of Groningen

Relativistic quantum chemistry applied

Jong, Wibe Albert de; Nieuwpoort, W.C

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
1998

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):
Jong, W. A. D., & Nieuwpoort, W. C. (1998). *Relativistic quantum chemistry applied*. s.n.

Chapter 8

Summary

Relativity has a significant influence in chemistry. This is not only the case for chemical systems with elements in the lower regions of the periodic system but also for molecules with only elements from the upper regions of the periodic system, as will be shown in this thesis.

In chapter 1 we introduced the reader to the relativistic effects and their influence in chemistry. The main goal of this thesis research was to calculate properties of chemical systems including relativity and to interpret experimental data. We have chosen to study these chemical systems within an *ab initio* relativistic framework with the Dirac Hamiltonian as a starting point. In chapter 2 the many-electron generalization of the Dirac Hamiltonian is introduced and, by gradually allowing more and more well defined standard quantum chemistry approximations, we will arrive at the relativistic quantum chemistry model that was implemented in the MOLFDIR program package. This code was then applied to a variety of molecules.

In chapter 3 we studied the relativistic effects on the so-called ionized and neutral excited states of the copper halide series CuX (with X = Cl, Br, I). The ionized excited states, which are described by states arising from a $Cu^+(3d^94s^1)$ $X^-(ns^2np^6)$ configuration, are found to be strongly affected by mixing of the states due to spin-orbit interaction. These spin-orbit effects arise from the copper atom and are similar throughout the whole copper halide series. On the other hand, the spin-orbit effects in the neutral excited states, arising from the $Cu(3d^{10}4s^1)$ $X(ns^2np^5)$ configuration, are caused by the spin-orbit splitting on the halides and become more important when going to the heavier halides.

MOLFDIR is an ideal tool for relativistic benchmark calculations due to the various correlation methods, available in the program package, and its fully relativistic framework. In chapter 4 we performed benchmark calculations on the spectroscopic properties bond length, harmonic frequency and dissociation energy of the interhalogen series ClF, BrF, BrCl, IF, ICl and IBr. For all molecules studied in this chapter a weakening of the bond was found which was attributed to spin-orbit interaction. We found that for these fairly light systems the

relativistic and correlation effects are largely additive. A huge amount of theoretical work has been done on the calculation of the electric dipole moment of the interhalogens but all with approximate relativistic approaches. We calculated the electric dipole moment and electric quadrupole moment as expectation values. The electric dipole polarizability was studied within the random phase approximation[41]. The relativistic effects were found to have a significant effect on these properties.

The ground, excited and ionized states of the iodine molecule have been studied in chapter 5. Our calculated results for the ground state were found to be in close agreement with experimental data. Core-valence correlation and basis functions with higher angular momenta were found to be important to obtain results in agreement with experiment. The potential energy curves of the excited and low-lying ionized states have been calculated and their respective spectroscopic properties were determined. Relativistic effects, and in particular spin-orbit coupling between states, were found to be extremely important. Our results for the excited states are in close agreement with experiment and with the results of Teichteil and Pelissier[183]. The spectroscopic properties of the low-lying ionized states are in close agreement with experimental data. We have reassigned a recently measured ionized state on the basis of our calculations.

In chapter 6 we studied the uranium hexafluoride (UF_6) molecule. The uranium atom is a heavy element and hence requires a relativistic model in order to understand its properties. We showed that relativity reorders the valence spinors and changes the character of the HOMO which is now in good agreement with experiment. The photoelectron spectrum of UF_6 could be reproduced by our calculations. Calculations on the excited states of the UF_6 cation and the electron affinity also give results that are in agreement with experiment.

The bonding properties of the uranyl ion ($[UO_2]^{2+}$) were studied within a fully relativistic framework and presented in chapter 7. We observed the so-called "U(6p) core-hole" which has a influence on the bonding properties of the molecule. The ordering of the valence spinors differs from previous theoretical predictions but we agree that the HOMO has σ_u character and has a large U(5f) contribution. The electric field gradient (EFG) on the uranium site was evaluated and we showed that the U(6p) core-hole and relativistic effects have a large influence on the size of the EFG. The influence of other effects, in particular that of the environment of the uranyl cluster was found to be significant.

From our fully relativistic *ab initio* quantum chemical calculations on various chemical systems we conclude that relativity often has a significant effect on the calculated properties of the systems studied. For the molecules containing elements from the upper region of the periodic system the most important relativistic effect is the spin-orbit interaction. For the heavier elements also the scalar relativistic effects become important.