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Relativity and Electron Correlation in Chemistry

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7. Summary and conclusions

7.1. Summary

In this thesis we describe a method for relativistic quantum mechanical calculations on molecules. We obtain relativistic zero order wave functions by the use of the Dirac-Fock method and improve these by relativistic Configuration Interaction. This opens the way for an accurate *ab initio* treatment of both relativity and electron correlation in molecules or clusters that contain one or more heavy nuclei.

In the first chapters we describe the fundamental physical background of the method that is based on the Dirac-Coulomb-(Gaunt) equation. Use of variational methods to obtain the eigenvalues and eigenfunctions that correspond to the lowest electron states is possible, even though the hamiltonian is unbound from below. Collapse into "spurious" or positronlike states of lower energy is on the effective one-electron Dirac-Fock level prevented by the use of kinetic or atomic balance. Use of the no-pair approximation avoids problems with lower-lying states in the many-electron CI-calculations.

The implementation of the method (MOLFDIR) is described in chapter 3. This set of computer programs enables a thorough study of the properties of small molecules. Its performance is dominated by the large numbers of two-electron integrals that arise from the use of four-spinor one-electron functions. The range of possible applications of the Dirac-Fock part is mainly determined by the total number of electrons that need to be included in the calculation. The feasibility of CI calculations depends on the number of active valence spinors and electrons. The limitations of both methods are of a technical nature, we did not encounter any fundamental problems with the use of the Dirac-Coulomb-Gaunt hamiltonian.

In chapter 5 we describe the PtH molecule. If ω - ω coupling is used (Hunds case c), the bonding in this molecule can be clearly understood in a simple single configurational model. Attempts to describe the bond in a non-relativistic Λ - Σ coupling formalism (Hunds case a) give rise to large mixings between the states. Due to the atomic nature of the spin-orbit splitting, such approaches may, however, give good results provided that the spin-orbit parameter that is used in a perturbation treatment is chosen carefully. Accurate calculation of the bond length of this molecule requires a good treatment of both relativity and electron correlation. Neglect or approximate treatment of either one of them may give errors in the order of 0.05 Å. Excitation energies are less sensitive to electron correlation but are strongly influenced by the spin-orbit coupling.

In chapter 6 we study the influence of relativity and electron correlation on the d-d spectrum of CoF_6^{2-} , RhF_6^{2-} and IrF_6^{2-} . The first peaks in the electronic spectrum of these ions arise from interconfigurational transitions from the $t_{2g}^5 {}^2T_{2g}$ ground state to the $t_{2g}^4 e_g^1 {}^4T_{1g}$ and ${}^4T_{2g}$ states. The effect of relativity is largest for the IrF_6^{2-} where the ground state is split by an amount of 0.91 eV. The calculated spin-orbit splittings do not vary much with the level of CI that is used and agree well with experiment. In all ions the LS-coupling scheme may still be used to assign the states since the intermultiplet splittings are larger than the intramultiplet spin-orbit splittings. The inclusion of charge transfer configurations in the wave functions lowers the ${}^2T_{2g}$ ground state relative to the excited states. These charge transfer states are most important in CoF_6^{2-} , where a multiconfigurational description is essential for the calculation of the excitation energies.

7.2. Conclusions

Relativity and electron correlation can now be treated on an equal footing using the method and computer programs that are presented in this thesis. Both are found to be important in the description of heavy transition metal complexes.

In addition to the use of a relativistic one-electron operator, relativistic corrections to the Coulomb two-electron interaction operator may be included. The influence of the largest of such corrections, the magnetic Gaunt interaction, is found to be insignificant for most molecular properties calculated.

The present implementation of the method is suitable for benchmark calculations on relatively small molecules of general shape. Although the computational requirements are still large, calculations may be done in a routine fashion. The modular set-up of the computer program allows for an easy incorporation of new methods and (technical) improvements of the existing algorithms.

In the transition metal compounds that were treated in this thesis, the most important manifestation of relativity found is the large spin-orbit coupling in the 5d shell. The thereby induced splittings in the electronic spectra are well described in both the Dirac-Fock and the Dirac-Fock-CI method.

7.3. Suggestions for further research

The discussions in this thesis have focused on energy differences between electronic states and on energy dependent quantities like bond lengths and harmonic frequencies. The wave functions that are obtained from the calculations may, however, also be used for calculation of electronic properties like dipole moments and transition probabilities. This asks for the derivation of operators that can be used in a

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relativistic formalism and for the implementation of new algorithms to perform the actual calculations.

Besides the use of direct Configuration Interaction one can apply most of the other accurate methods that were developed to solve the Schrödinger equation to the Dirac equation. The development of relativistic versions of methods like the Coupled Cluster method, the Multi Configurational Self Consistent Field method and the Density Functional method can give computer programs that are as accurate for calculations on heavy elements as the present ab initio programs are for the lighter atoms. The new relativistic algorithms may use Kramers' symmetry in order to reach the same computational reductions as are obtained by the separation of spin and space coordinates that is possible in the non-relativistic calculations.

Apart from these further technical developments, more research on the relativistic corrections to the Coulomb interaction is desirable. The effect of the Gaunt interaction can be studied more extensively than is done in this thesis and the effect of the Breit retardation term and of other quantum electrodynamical corrections on molecular properties should be investigated.