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# Static Electric Dipole Polarizabilities of Atoms and Molecules

A thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry

> at Massey University, Albany New Zealand.

## Ivan S. Lim

2004

#### **Candidate's Declaration**

This is to certify that research carried out for my Doctoral thesis entitled "*Static Electric Dipole Polarizabilities of Atoms and Molecules*" in the Institute of Fundamental Sciences, Massey University at Albany, New Zealand is my work and that the thesis material has not been used in part or in whole for any other qualification.

Candidate's Name: Ivan S. Lim Signature:

Date: July 20, 2004

#### **Supervisor's Declaration**

This is to certify that research carried out for the Doctoral thesis entitled "*Static Electric Dipole Polarizabilities of Atoms and Molecule*" was done by Mr. Ivan S. Lim in the Institute of Fundamental Sciences, Massey University at Albany, New Zealand. The thesis material has not been used in part or in whole for any other qualification, and I confirm that that the candidate has pursued the course of study in accordance with the requirements of the Massey University regulations.

Supervisor's Name: Prof. Peter Schwerdtfeger

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#### Abstract

The static dipole polarizabilities and ionization potentials of the first and second main group elements, including the charged ions, are obtained from all-electron relativistic coupled-cluster theory using a scalar relativistic Douglas-Kroll Hamiltonian. Spin-orbit coupling effects are investigated using a fully relativistic four-component Dirac-Coulomb-Hartree-Fock scheme followed by a secondorder many-body perturbation treatment to account for electron correlation. Periodic trends in the dipole polarizabilities and the ionization potentials are In each case, a detailed discussion on electron correlation and discussed. relativistic effects are given. A relationship for relativistic and electron correlation effects between the dipole polarizability and the ionization potential is established. Particular attention is paid to the evaluation of a near basis set limit quality of the dipole polarizabilities. This is accomplished by the evaluation of all-electron basis sets used, followed by an extensive study on the convergence behavior of the dipole polarizabilities with respect to a finite basis set expansion. The present all-electron dipole polarizabilities are believed to be very precise, especially for charged ions where the availability of experimental values are Scalar relativistic small-core pseudopotentials are fitted and their limited. performance is tested in terms of static dipole polarizabilities and ionization potentials. It is demonstrated that the small-core definition of the pseudopotential (nine-valence electron for the main group 1 and ten-valence electron for the main group 2 elements) enables us to safely omit core-valence correlation without scarifying accuracy. Following atomic dipole polarizabilities, applications are made to molecules starting with alkali dimers and their singly charged ions. The scalar relativistic pseudopotentials of this study are used to calculate equilibrium bond lengths, dissociation energies, vibrational frequencies and the dipole polarizabilities of these dimers. The change in the molecular dipole polarizabilities from the corresponding atomic dipole polarizabilities are discussed in terms of molecular bonding models. Simple ammonia complexes of the alkali-metals and their singly charged ions are studied. The equilibrium geometries, dissociation energies, harmonic vibrational frequencies as well as the dipole polarizabilities of these complexes are given.

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## 12 Conclusion

### Appendices

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	<b>Core Polarization Potentials</b>

B All-electron Basis Sets

Some of the work described in this thesis has been published already. The relevant references are:

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