A Relativistic Treatment of Atoms and Molecules

From Relativity to Electroweak Interaction

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Abstract

Relativistic quantum chemistry is the relativistic formulation of quantum mechanics applied to many-electron systems, that is to atoms, molecules and solids. It combines the principles of special relativity, which are obeyed by any fundamental physical theory, with the basic rules of quantum mechanics. By construction, it represents the most fundamental theory of all molecular sciences, which describes matter by the action, interaction and motion of the elementary particles. This science is of vital importance to physicists, chemists, material scientists, and biologists with a molecular view of the world.

A full relativistic treatment of atoms and molecules which includes the quantization of the electromagnetic field is currently one of the most challenging tasks in electronic structure theory. Therefore, relativistic effects in atoms and molecules were studied computationally. A combination of wave function and density functional based methods within a correct relativistic framework proved necessary to achieve accurate results of various atomic and molecular properties. The first part of this thesis deals with investigations in atomic systems including quantum electrodynamic effects in the ionization potentials of a large number of elements. K-shell and L-shell ionizations potentials for ^{268}Mt were calculated and static dipole polarizabilities of the neutral group 14 elements were investigated. The second part concentrates on molecular systems including superheavy element monohydrides up to 120H^{+}). In particular, the chemical bonding of the superheavy elements 119 and 120 are investigated for the first time. Electric field gradients of a number of gold and copper compounds were also calculated and the nuclear quadrupole moment of gold and copper determined in good agreement with experiment. Finally, the parity violation energy difference in the chiral molecule bromochlorofluoromethane (CHFClBr) was investigated by relativistic coupled-cluster theory to provide benchmark results for all future investigations in this field.

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Abbreviations

BI	Breit interaction
BSSE	basis set superposition error
CC	coupled-cluster
CCSD	coupled-cluster singles and doubles
CI	configuration interaction
CIS	configuration interaction singles
CISD	configuration interaction singles and doubles
DFT	density functional theory
DHF	Dirac-Hartree-Fock
DK	Douglas-Kroll
DKS	Dirac-Kohn-Sham
EFG	electric field gradient
FCI	full configuration interaction
FSCC	Fock-space coupled-cluster
GGA	generalized gradient approximation
GTO	Gaussian-type orbitals
HF	Hartree-Fock
LDA	local density approximation
MCSCF	multi-configurational Hartree-Fock
MP2	second-order Møller-Plesset perturbation theory
NR	non-relativistic
NQM	nuclear quadrupole moment
NQCC	nuclear quadrupole coupling constant
PNC	parity non-conservation
PV	parity violation
PVED	parity violation energy difference
QED	quantum electrodynamics

RKB	restricted kinetic balance
SE	self-energy
SHE	superheavy element
TDDFT	time-dependent density functional theory
UKB	unrestricted kinetic balance
VP	vacuum polarization
XC	exchange-correlation