I-R Theory and Applications of Relativistic Quantum-Chemical Methods to Molecular Properties of Compounds Containing Heavy Elements

Accurate quantum-chemical calculations of molecular properties which are concerned with a magnetic field and/or an electron spin distribution are required well-correlated and relativistic quantum-chemical theories, especially when the molecules contain heavy elements. Paramagnetic NMR chemical shifts of Fe-complexes, heavy-element NMR of halogen compounds, and magnetic circular dichroism (MCD) of halogen compounds are listed below. The 2nd-order Douglas-Kroll quantum-chemical theory including a magnetic field is also presented.

I-R-1 Quantum-Chemical Calculations for Para-Magnetic ^{13}C NMR Chemical Shifts of Iron-Bound Cyanide Ions of Iron Porphyrins in Ground and Low-Lying Excited States Containing Ferric $(d_{xy})^2(d_{xz,yz})^3$ and $(d_{xy})^1(d_{xz,yz})^4$ Configurations

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The objectives of this brief communication are as follows. (i) Using an accurate quantum-chemical method, SAC/SAC-CI, we present accurate energy-levels for ferric $(d_{xy})^2(d_{xz,yz})^3$ and $(d_{xy})^1(d_{xz,yz})^4$ in bis (cyanide) porphyrinato Iron(III) [FeP(CN)$_2$], bis (cyanide)(*meso*-tetraethyl) por-phyrinatoIron(III) [FeTEP(CN)$_2$], and (cyanide) (imidazole) porphyrinato-Iron(III) [FeP(CN-Im)]. (ii) We calculate the paramagnetic ^{13}C NMR chemical shifts of iron-bound ^{13}CN of the above three complexes, both in the ground and low-lying excited states including the ferric $(d_{xy})^2(d_{xz,yz})^3$ and $(d_{xy})^1(d_{xz,yz})^4$ configurations. Then we show the relations between the calculated ^{13}C chemical shifts, the electronic configurations, and the ruffling of the porphyrin rings.

The trans-ligand effect on the paramagnetic ^{13}C NMR chemical shifts of the iron-bound ^{13}CN$^-$ was well reproduced by the present calculations. Further, in [FeP(CN)$_2$], which has a ruffled porphyrin ring, the $(d_{xy})^1(d_{xz,yz})^4$ configuration is included in the ground state, and the alternative $(d_{xy})^2(d_{xz,yz})^3$ configuration is located closely in energy to the ground state. Ruffling of porphyrin rings extremely affects the ^{13}C chemical shift of iron-bound CN in the $(d_{xy})^1(d_{xz,yz})^4$ configuration but not in the $(d_{xy})^2(d_{xz,yz})^3$ configuration.

I-R-2 Nuclear Magnetic Shielding Constants of Halogens in X$^-$ and XO$_4^-$ (X = F, Cl, Br, I) —Relativistic and Electron-Correlation Effects—

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A series of calculations of halogen nuclear magnetic shielding constants and chemical shifts in X$^-$ and XO$_4^-$ (X = F, Cl, Br, I) was carried out to discuss the relativistic and electron-correlation effects and, in special, the non-additivity of both the effects. The second-order Douglas-Kroll-Hess (DKH2) method was used as a relativistic hamiltonian, and the Møller-Plesset method was applied to the generalized UHF wave function. The calculated chemical shifts in ClO$_4^-$ and IO$_4^-$ agree reasonably well with the observed ones, though there are no experimental values in FO$_4^-$ and BrO$_4^-$. The relativistic effect was quite large especially in IO$_4^-$ as reported previously, while the electron-correlation effect is significant in both FO$_4^-$ and IO$_4^-$. The non-additivity of the relativistic and the electron-correlation effects in magnetic shielding constants is unexpectedly large in IO$_4^-$, and therefore a relativistic electron-correlated method is crucial for describing accurate heavy-element nuclear magnetic shielding constants and chemical shifts.

I-R-3 Quasi-Relativistic Theory for Magnetic Shielding Constant. I. Formulation of the Douglas-Kroll Transformation with Magnetic Field and Applications to Atomic Systems

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A two-component quasi-relativistic theory based on the Douglas-Kroll-Hess transformation is developed in order to study a magnetic shielding constant. The Hamiltonian that is proposed in this study is considering the relativistic effect on magnetic vector potential with the Douglas-Kroll theory. The present Hamiltonian can be applied to calculation of magnetic shielding constants, without further expansion in powers of c^{-1}. By applying the finite-perturbation theory and generalized-UHF wavefunction to this study, we calculate the magnetic shielding constants of two-electron ions, ten-electron ions, and noble gas atoms. The calculation results with the present theory are compared with the result of the Dirac-Hartree-Fock calculation. The numerical difference of the present theory from the DHF is 3% or less. However, a quasi-relativistic theory that handled the magnetic vector potential at the non-relativistic level largely underestimates the relativistic effect. The picture change effect is quite important for the magnetic shielding constant of heavy elements. The change of orbital picture is significant in the valence orbital magnetic response as well as the core orbital response. The effect of finite distribution of nucleus is also studied with using Gaussian nucleus model. The present theory is able to reproduce the correct behavior of the finite nucleus effect that has been reported in the Dirac theory. However, the non-relativistic theory and quasi-relativistic theory with non-relativistic vector potential underestimate the finite nucleus effect.

I-R-4 Quasi-Relativistic Theory for Magnetic Shielding Constant. II. Gauge Including Atomic Orbital and Applications to Molecules

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We present a relativistic theory of the magnetic shielding constants and the chemical shifts for molecules include heavy elements. The present theory is based on the Douglas-Kroll-Hess quasi-relativistic approximation. The gauge-including atomic orbital method is adapted to the quasi-relativistic Hamiltonian to allow the origin independent calculations. The present theory is applied to the hydrogen and halogen magnetic shielding constants of hydrogen halides and mercury magnetic shielding constants and ^{199}Hg chemical shifts of mercury dihalides and methyl mercury halides. The relativistic correction to the magnetic interaction term little affects the magnetic shielding constant of hydrogen; however, the correction is the dominant origin of the heavy atom shifts of the magnetic shielding constant of the heavy halogens. The basis set dependence of mercury shielding constants is quite large in the relativistic calculation; using the basis function which is optimized by the relativistic method is important to describe the relativistic effect properly. The relativistic correction to the magnetic interaction term is quite important for mercury dihalides in which relativistic effects from mercury and halogen are strongly coupled. Without this correction we obtain quite incorrect results. The origin of the 199Hg chemical shifts in mercury dihalides is the spin-orbit interaction from the heavy halogens. In methyl mercury halides the paramagnetic shielding term as well as the spin-orbit interaction from the heavy halogens dominates the 199Hg chemical shifts.

I-R-5 Theoretical Studies on MCD with Finite Perturbation Method and Relativistic Corrections

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The generalized UHF (GUHF)/SECI method for the MCD Faraday terms with the finite magnetic-field perturbation were presented and compared the results for ethylene, *p*-benzoquinone (BQ), and *o*-BQ with those by the conventional sum-over-states method. Their difference was not negligible, and even the signs were contrary for the lowest π-π^* state of ethylene. Quasi-relativistic treatments in the calculations of the Faraday terms were also discussed. The method was applied to the three n-π^* states ($^3\Pi_{1u}$, $^3\Pi_{0u}$, and $^1\Pi_u$) of I_2, Br_2, Cl_2, and F_2. The relativistic effects become more important as molecule is heavier. The Faraday terms for I_2 and Br_2 were dramatically changed by the relativistic correction from the non-relativistic results, whereas the effects were negligible for Cl_2 and F_2 in contrast. This indicates that the relativistic corrections are essential to the theoretical treatments of MCD for molecules containing heavy atoms.