REHE 2014: 11th International Conference on Relativistic Effects in Heavy-Element Chemistry and Physics

Smolenice Castle, Smolenice

Slovakia


Organizing Institutions:

Institute of Inorganic Chemistry, Slovak Academy of Sciences
Computing Centre, Slovak Academy of Sciences
Comenius University in Bratislava
Slovak University of Technology in Bratislava

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- Martin Kaupp (Berlin, Germany)
- Olga Malkina (Bratislava, Slovakia)
- Vladimir Malkin (Bratislava, Slovakia)
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Programme

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Abstracts of Oral Contributions
Application of a Relativistic Coupled-Cluster Theory to the Effective Electric Field in YbF

M. Abe\textsuperscript{1,2}, G. Gopakumar\textsuperscript{1,2}, M. Hada\textsuperscript{1,2}, B. P. Das\textsuperscript{3}, H. Tatewaki\textsuperscript{4}, D. Mukherjee\textsuperscript{5}

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The electric dipole moment of the electron (eEDM, or namely \(d_e\)) is an important probe of Charge-Conjugation and Parity (CP) symmetry violation. The search for \(d_e\) has gone on for almost a half century, but so far it has not been observed. However, its upper limit has gradually become lower during this time. A recent molecular experiment using ThO\textsuperscript{1} provides the best limit for \(d_e\) as lower than \(0.87 \times 10^{-28} \text{ [e cm]}\) at 90\% confidence level. This is an order of magnitude improvement over the previous best limit which came from YbF.\textsuperscript{2} Attempts are currently under way to improve the limit for YbF, and a new result is expected in the near future. Direct measurement of the value of \(d_e\) in the molecule is not possible but the interaction energy between \(d_e\) and internal electric field \(E_{\text{int}}\) inside the molecule can be measured. This interaction energy is shown in Eq. (1).

\[
\langle \Psi | \vec{H}_{\text{EDM}} | \Psi \rangle = d_e \left( \sum_{\text{elec}}^{N_{\text{elec}}} \beta \sigma \cdot E_{\text{int}} \right) = d_e E_{\text{eff}},
\]

where \(\beta\) is a Dirac matrix and \(\sigma\) are spin matrices. The net electric field acting on an electron inside a molecule is called the effective electric field \(E_{\text{eff}}\). We can obtain the value of \(E_{\text{eff}}\) only from relativistic molecular orbital calculations. It is possible to extract \(d_e\) by combining the measured value of the interaction energy with the calculated value of the effective field. Therefore accurate relativistic calculations of \(E_{\text{eff}}\) are indispensable for the search of eEDM.

In this study, we have developed a rigorous method to calculate \(E_{\text{eff}}\) in polar molecules. We have used the relativistic coupled cluster singles and doubles (RCCSD) method based on the Dirac-Coulomb Hamiltonian. We have modified and combined the UTChem and DIRAC08 codes for this purpose. We have calculated \(E_{\text{eff}}\) for YbF molecule using the Dyall’s triple-zeta (TZ) or quadruple-zeta (QZ) basis in uncontracted form. Table I summarize the obtained data. We obtain the value of \(E_{\text{eff}}\) as \(23.1 \text{ GV/cm}\) in our best CCSD calculation, where we have used 79-active electrons (i.e. no-frozen core calculation). This is calculated using the QZ basis, one of the most accurate relativistic basis sets. Our best permanent dipole moment is 3.60 Debye while the experimental counterpart is 3.91 Debye. The error in \(DM\) from the experiment is 8\%. As a relevant quantity of \(E_{\text{eff}}\), we have also calculated parallel component of hyperfine coupling constant \(A_{//}\). When we use 79-CCSD/QZ level, the calculated \(A_{//}\) reproduce the experimental \(A_{//}\) within 7\% accuracy. From the comparison with experiment in \(DM\) and \(A_{//}\), we assess the error of present \(E_{\text{eff}}\) less than 10\%.


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<th>Method/Basis</th>
<th>(T_1) Diag.</th>
<th>(E_{\text{eff}}) (GV/cm)</th>
<th>(A_{//}) (MHz)</th>
<th>(DM) (D)</th>
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<td>-</td>
<td>17.9</td>
<td>-</td>
<td>3.21</td>
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<td>DF/TZ</td>
<td>-</td>
<td>18.2</td>
<td>-</td>
<td>3.21</td>
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<tr>
<td>DF/QZ</td>
<td>-</td>
<td>18.2</td>
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<td>49e-CCSD/DZ</td>
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<td>22.7</td>
<td>-</td>
<td>3.59</td>
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<td>79e-CCSD/QZ</td>
<td>0.0311</td>
<td>23.1</td>
<td>7913</td>
<td>3.60</td>
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<td>Exp.</td>
<td>-</td>
<td>7424\textsuperscript{[1]}</td>
<td>3.91\textsuperscript{[4]}</td>
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Theoretical study of the relativistic molecular rotational g-tensor

Martín C. Ruiz de Azúa¹, I. Agustín Aucar², Sergio S. Gomez², Claudia G. Giribet¹

¹Physics Department of the Natural and Exact Science Faculty - UBA and IFIBA Institute CONICET
²Physics Department of the Natural and Exact Science Faculty - UNNE and IMIT Institute CONICET

An original formulation of the relativistic molecular rotational g-tensor valid for heavy atom containing compounds is presented. In such formulation the relevant terms of a molecular Hamiltonian for non relativistic nuclei and relativistic electrons in the laboratory system are considered, including electron-nucleus Breit interaction effects. Terms linear and bilinear in the nuclear rotation angular momentum and an external uniform magnetic field are considered within first and second order (relativistic) perturbation theory to obtain the rotational g-tensor. Relativistic effects are further analyzed by carrying out the linear response within the elimination of the small component (LRESC) expansion. Quantitative results for model systems HX (X = F, Cl, Br, I), XF (X = Cl, Br, I) and YH⁺ (Y = Ne, Ar, Kr, Xe, Rn) are obtained both at the RPA and DFT levels of approximation. Relativistic effects are shown to be small for this molecular property. The relation between the rotational g-tensor and susceptibility tensor which is valid in the non relativistic theory does not hold within the relativistic framework, and differences between both molecular parameters are analyzed for the model systems under study. It is found that the non relativistic relation remains valid within 2% even for the heavy IH, IF and XeH⁺ systems. Only for the sixth-row Rn atom a significant deviation of this relation is found.
Relativistic effects on magnetic resonance spectroscopic parameters can be very large. An ongoing project in our research group is focused on the mechanisms responsible for the magnitudes, signs, and trends, of magnetic resonance parameters of f-element, transition metal, and heavy main group element compounds, as observed in NMR and EPR spectroscopy. The project has led to the implementation of relativistic methodology in the open-source NWChem quantum chemistry package, additional developments using other quantum chemistry codes, and the development of chemically intuitive analysis methods for calculated molecular spectroscopic parameters. In this talk we present results from recent computational studies of magnetic resonance parameters utilizing relativistic quantum chemical methods. Results from a collaboration with Helene Bolvin (Toulouse) on magnetic properties of f–element systems, such as the electronic structure and g-factors of actinyl nitrate and carbonate complexes, are highlighted. Ab-initio results are compared with crystal field models. We showcase successes and failures of magnetic property calculations for heavy element compounds using Kohn-Sham density functional theory (DFT) with common approximate functionals.

Selected References

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URL http://dx.doi.org/10.1021/ct2008507

URL http://dx.doi.org/10.1021/ct200623j

URL http://dx.doi.org/10.1063/1.3702628
Modification of the Atomic Mean Field Integrals (AMFI)

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In the last decade, or more, the spin-free two-component relativistic methods for treatments relativistic effects in atoms and molecules has proven to lead to highly accurate results compared both to experiment and four-component calculations. The spin-dependent operators are more difficult to handle. The best way to do it is to use the Breit-Pauli representation of the spin-orbit operator and to calculate first- and second-order corrections to the relativistic scalar energies. The practical use of the two-electron Breit-Pauli spin-orbit integrals are very difficult to handle in the molecular calculations. The two-electron spin-orbit integrals contribute to the spin-orbit matrix element between Slater determinants which are singly or doubly excited relative to one another. The matrix element between singly excited determinants can, just like in the Hartree-Fock equations, be written as a pseudo one-electron integral. The key aspect of a mean-filed theory is to neglect interactions between doubly excited states and to include all two-electron integrals in pseudo one-electron integrals. The theory has been defined and implemented by B. Hess and modified by B. Schimmelpfennig. Hundreds of atomic and molecular applications have been performed with the AMFI integrals. However, the careful look at the atomic results and the splittings between levels with different $j$ quantum numbers shows that the results are far from satisfactory. In my talk I will show how the modification of the atomic mean-field integrals can lead to great accuracy comparable to the experimental results.

References


Relativity and the ion chemistry of tungsten hexacarbonyl

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Tungsten hexacarbonyl, W(CO)$_6$, is frequently used as a precursor for focused electron beam induced deposition, whereby nanoscale tungsten/tungsten carbide structures can be written on silicon wafers and other surfaces [1]. We have studied different aspects of this technologically important process by one-component, two-component and four-component quantum chemical methods in order to identify crucial elementary steps.

In this presentation we will discuss general symmetry aspects, the interplay between spin-orbit coupling and Jahn-Teller effects on the photoelectron spectrum of the title compound as well as subsequent ionic fragmentation pathways which lead to the formation of tungsten and tungsten carbide derivatives.

Relativistic DFT studies of structural and physicochemical properties of Lanthaneide and Actinide complexes

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Tools available at the ZORA/DFT level of theory permit to investigate, with a satisfying accuracy, different physicochemical properties of Lanthaneide (Ln) and Actinide (An) complexes, among them magnetic couplings in binuclear uranium complexes, redox properties of uranium complexes as well as differentiation between homologous Ln(III) and An(III) complexes.

Regarding exchange couplings between uranium atoms in binuclear complexes, several systems have been studied, covering different oxidation states (V, IV and III) of uranium, giving rise to the following cases: 5f²-5f⁴, 5f⁴-5f³ and 5f³-5f⁴ [1]. Theoretical results using the broken symmetry approach and a hybrid functional are in agreement with available experimental data. In the studied complexes, spin polarization is exalted by the effective participation of the 5f metal orbitals in bonding. Regarding redox properties, it is shown that taking into account spin-orbit coupling as well as solvation effects is required to get the best agreement between computed properties and electrochemically measured ones (correlation coefficient r=0.993) [2]. Finally, with regard to Ln(III)/An(III) differentiation, it is shown that computations at the above mentioned level of theory, permit (i) to explain the selectivity of polyazine ligands in relation with the reprocessing of the used nuclear fuel [3], and (ii) to rationalize the observed different cyanide and/or isocyanide coordinations in Cerium and Uranium complexes [4].

Lanthanide(III) and actinide(III) hydration and liquid-liquid extraction using cyanex 301.

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The separation of actinides(III) from lanthanides(III) is a difficult problem occurring in the nuclear fuel cycle and the treatment of nuclear waste. In 1995 Zhu and coworkers found that the liquid-liquid extraction from a slightly acidic (pH ≈ 3-4) aqueous solution using purified Cyanex 301 [bis(2,4,4-trimethyl-pentyl)dithiophosphinic acid, HBTMPDTP; the acid is denoted hereafter as HL and its anion as L−] in kerosene exhibits a high separation factor of > 5000 between AmIII and EuIII [1, 2]. Typically the underlying chemical reasons used to explain this finding are, e.g., the formation of different extraction complexes for lanthanides(III) and actinides(III) or stronger covalent bonding contributions in the extraction complexes of the actinides(III) compared to the lanthanides(III). Quantum chemical calculations using f-in-core pseudopotentials and density functional theory however yielded ML3 extraction complexes for both lanthanides(III) and actinides(III), and found no evidence for a significantly stronger covalent bonding in the latter [3, 4]. The preference of actinides(III) over lanthanides(III) was attributed in this work to the significantly more stable lanthanide(III) hydration complexes [5, 6]. Accurate coupled cluster results for the hydration energies of lanthanides(III) and actinides(III) were recently obtained by using the incremental scheme [7, 8]. In fact it was also shown by a comparison to ab initio results that the treatment of the open EuIII 4f⁶ shell within density functional theory leads to a too high f occupancy when EuIII is complexed by soft ligands, e.g. the sulphur atoms in Cyanex 301 [9]. The conclusion that EuIII -S bonds are significantly less covalent than AmIII -S bonds (only) drawn from their longer bond lengths obtained in such calculations is shown to be invalid.

Atomic CI Calculations with a Linear Scaling Algorithm

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Highly correlated atomic calculations are vital for testing theories against experiment. The traditional methods for atomic calculations, such as CI, MCSCF, and coupled-cluster, use an iterative method such as the Davidson algorithm for finding the energies and wave functions of a few states. This method scales as N^2, where N is the number of determinants or CSF, as the core of the algorithm is a matrix-vector product of the Hamiltonian on a vector.

In this work, an algorithm is presented that scales as N. Although the core of the algorithm is still a matrix-vector product, the factorization of the electron-electron interaction and the use of radial functions tabulated on a grid are exploited to reduce the matrix-vector product to a series of steps involving the generation and contraction of vectors. Some comparisons are made with RI methods, which can also be used to reduce the scaling.

As the electron-electron interaction operator can be factorized into products of one-electron operators for the instantaneous Coulomb interaction, the Gaunt interaction, and the fully retarded interaction (e.g. in the Lorentz gauge), the method is applicable to calculations that include both a high level of electron correlation and a high level of relativity. The linear scaling opens the way for larger and faster calculations than current methods, with the potential to increase the accuracy of atomic calculations.

Preliminary results will be presented for helium-like ions.
Atomic calculations and search for new physics

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Accurate atomic calculations are needed for planning experimental work on search for new physics beyond standard model and for the interpretation of the measurements. We have developed a range of methods which combine some well known techniques and techniques developed in our group. These include configuration interaction method, many-body perturbation theory, coupled cluster and correlation potential methods, etc. The calculations are relativistic and based on solving Dirac equations. Breit and QED corrections are also included.

Search for new physics includes the study of the space and time invariance violation in atoms [1], interaction of atoms with axions and other hypothetical particles constituting dark matter [2], search for variation of the fundamental constants in quasar absorption spectra and atomic clocks [3].

The calculations are also used to study systems where experimental data poor or absent. This includes highly charged ions [4] and super heavy elements [5].

Recent progress in heavy elements calculations by modified Fock Space coupled cluster method.
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Different modifications of relativistic multiroot multireference coupled cluster method are presented. Novel formulations include several variants of the Intermediate Hamiltonian method, mixed-sector approach, double Fock space procedure and few other modifications of standard multireference coupled cluster approach. The presented modifications have several methodological and computational advantages, substantially elevate precision of computed atomic properties and open the door for calculation of a large number of electronic states not accessible by traditional multireference coupled cluster methods. For instance, in contrast to the standard Fock-space schemes, the starting point in most novel approaches can be extended to certain non closed-shell configurations.

Applications to heavy atomic systems are presented, including calculations of ionization potentials, electron affinities and electronic spectra, as well as some energy derivative properties (e.g. static polarizabilities, nuclear electric quadrupole moments, atomic EDM, etc.). Nature of the ground state and chemical activity of many superheavy elements are discussed. Excellent agreement with available experimental data and significant improvement compared with some other high-level approaches are obtained.
Relativistic and QED effects, space-time variation of the fundamental constants and violation of fundamental symmetries

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Relativistic effects make frequency of atomic transitions to depend on the fine structure constant alpha. This allowed us to suggest several methods to search for the space-time variation of alpha using astrophysical and laboratory measurements [1]. There are new results for the alpha variation based on the quasar absorption spectra data. These results indicate the variation of alpha in space [2]. The spatial variation can explain fine tuning of the fundamental constants which allows humans (and any life) to appear. We appeared in the area of the Universe where the values of the fundamental constants are consistent with our existence. There is an agreement between the results obtained using different telescopes and different redshifts. Also, now there are no contradictions between the results obtained by different groups.

These astrophysical results may be used to predict the variation effects for atomic clocks which are very small and require improvement of the sensitivity by 1-2 orders of magnitude. This improvement may be achieved using 229Th nuclear clocks where the effect of the variation is hugely enhanced. There are also enhanced effects in multiply charged ions [3], and certain atomic and molecular transitions.

The relativistic corrections enhance effects of parity and time reversal violation in heavy atoms and molecules by an order of magnitude. Measurements and calculations of such effects allows one to test unification theories. New results will be presented.

Our group has also performed relativistic many-body calculations of the superheavy elements spectra and QED corrections to energy levels and electromagnetic amplitudes using the radiative potential method [4].

Exploring Fundamental Physics in Diatomic Molecules

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The enormous surplus of matter over antimatter in our universe is a fact that remains unexplained by the Standard Model (SM) of elementary particles [1]. A microscopic violation of the combined symmetries Charge (C) conjugation and spatial Parity (P) has been identified as one of several conditions which can give rise to an appreciable baryon number and explain this asymmetry. It is expected that flavor-diagonal CP violation, absent in the SM, must be sought for and that Electric Dipole Moments (EDMs) constitute a sensitive probe of such New Physics beyond the SM. Given the validity of the CPT theorem, the measurement of an EDM would be the first direct signature of the violation of time-reversal (T) invariance.

I will in this talk in particular address the search for the electric dipole moment of the electron. A relativistic four-component configuration interaction approach [2] extended for the evaluation of scalar-pseudoscalar and vector-pseudovector P- and T-odd interaction constants, as well as magnetic hyperfine interaction constants [3,4] has been used to study properties related to the search for the eEDM in the $^3\Delta_1$ electronic state of candidate diatomic molecules [3,4,5]. For ThO $\Omega = 1$ we obtain [4] a value of

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Figure 1: Model dependency of the electron EDM effective electric field in ThO.

$E_{\text{eff}} = 75.2 \left[ \text{GV/cm} \right]$ with an estimated error bar of 3% and 10% smaller than a previously reported result [J. Chem. Phys., 139:221103, 2013]. A weighted average of the two results, $E_{\text{eff}} = 76 \left[ \text{GV/cm} \right]$ [6], combined with a recent measurement [Science, 343:269, 2014], leads to an eEDM upper bound of $|d_e| < 9.6 \times 10^{-29} e\text{ cm}$ which constrains possible extensions to the Standard Model of particle physics.

References
Perturbative Treatment of Spin-Orbit Coupling on top of Scalar-Relativistic Quantum-Chemical Calculations

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Scalar-relativistic effects are often significantly more pronounced than those due to spin-orbit coupling. A separation of the relativistic Hamiltonian into a scalar and spin-dependent part, as proposed by Dyall, thus opens the possibility for cost-effective relativistic quantum-chemical calculations. Efficiency is achieved by focusing on a rigorous treatment of the spin-free scalar-relativistic part which, if required, afterwards is augmented by perturbative corrections for spin-orbit coupling.

In this contribution, we present schemes for the perturbative treatment of spin-orbit effects on top of scalar-relativistic computations using (a) the spin-free Dirac-Coulomb (SFDC) scheme and (b) the spin-free one-electron variant of exact-two-component (SFX2C-1e) theory. We discuss the appropriate choices for the spin-orbit perturbation and demonstrate the accuracy of the implemented schemes in calculations for the energy and first-order electric properties of selected heavy-element compounds.
During the last few years several attempts to introduce relativistic quantum methods in a QED framework were published\(^1\). One of the main difficulties is related to merging electron correlation and QED effects on the same theoretical framework.

The path integral formalism was developed long time ago as an alternative to the wave function based formalism. Both are completely equivalent, though the first one is mostly applied by the quantum field community of physicist, and the second one is more traditionally applied by quantum chemist and molecular physicist. Scientists working with polarization propagators are in between. Even though calculations of atomic and molecular response properties with polarization propagators at second-order level of approach, SOPPA, are today among the most reliable, they are still not widely applied by quantum chemists, perhaps by historical reasons\(^2\).

The path integral formalism is the natural quantum language that gives solid grounds to derive polarization propagators. I am going to show in this lecture how to do it and what can we learn doing it: there is a rule to write propagators within the path integral formalism as a representation. One can work out generating functionals from which to obtain double-time Green functions or polarization propagators. So the physical insights that are intrinsic to the path integral formulation of quantum mechanics are nicely applied to our propagators. Indeed one is aware now on why polarization propagators are defined with exactly the same formal expressions within both regimes, relativistic and non-relativistic: it is due to its foundations on the path integral formalism\(^3\).

On the other hand, within the relativistic regime new operators shall replace the spin-adapted tensor operators. The most natural generalization are the well-known Kramers operators that span a new basis. When the matrices of the principal propagator are expressed in this last tensor basis, making \(c \to \infty\) they become the NR spin-adapted matrices. This finding gives strong support on what the Kramers operators mean, and also on the physical information that the principal propagator contain at any regime. Working within the relativistic regime one should change the non relativistic way of thinking to get deeper though unusual physical insights\(^3\).

My main concern is to show that from this new theoretical development, it shall be possible to find out new roads for properly including QED and electron correlation effects, on atomic and molecular properties. Why not for going even further?

Calculations in heavy ions for fundamental physics tests

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Bound state quantum electrodynamics (BSQED) is the fundamental theory that describes the properties of normal and exotic atoms and ions. Detailed knowledge and understanding of BSQED is required to improve our knowledge of the standard model, and for applications in low-energy particle physics as well as nuclear physics. It may also have impact on properties concerning quantum chemistry. For example, the “proton size puzzle” \cite{1, 2} which comes from the $7\sigma$ difference between the proton size extracted from normal and muonic hydrogen has been unsolved for 4 years. The distance of the muon to the nucleus in the case of muonic hydrogen is the same as the distance between the electron and the nucleus for the $1s$ electron in Te ($Z = 52$).

We review the present status of BSQED and relativistic calculations, and comparison with experiments, in few-electron heavy ions. We then describe progress and difficulties toward calculations of systems with many electrons. As an illustration we present some new results obtained in the evaluation of ionization energies of elements up to $Z = 110$ using Multiconfiguration Dirac-Fock codes and new needs for very demanding applications like finding candidates for high-accuracy heavy-ions based atomic clocks.

References

Fully relativistic *ab initio* EPR calculations

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In 2013 we published the first paper [1] based on a new, fully ab initio, four-component implementation of EPR calculations in a local development version of the DIRAC program [2]. In this talk I will present our ongoing efforts for better models and for better computational procedures for fully ab initio relativistic calculations of g-tensors, hyperfine couplings, and zero-field splittings.

I will also discuss two special points:

- What is the best choice of basis states for the quasi-degenerate subspace?
- QED effects on g-tensors


Relativistic and quantum electrodynamics effects for frequency dependent polarizability and refractivity of helium

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The pressure dependence of the refractivity of gaseous helium and the present-day frequency metrology can be employed to construct an atomic pressure standard, replacing the current, 350 years old one, based on the height of the mercury column. This can be achieved if the dynamic polarizability of helium at $\lambda=6330\text{Å}$ can be determined ab initio with an error smaller than 0.2 ppm. Such a determination is possible assuming the validity of quantum electrodynamics (QED) and using large, and highly optimized explicitly correlated basis sets to compute the relativistic and QED corrections to the nonrelativistic dynamic polarizability. Methods of computing these corrections, including the relativistic and QED recoil effects will be discussed and the results obtained for helium will be presented with particular emphasis on the error bar estimation. The final values computed by us have uncertainties that are significantly smaller (sometimes by nearly two orders of magnitude) than those of the most accurate measurements and are sufficient to establish the new metrology standard based on properties of low-density helium.

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Large spin-orbit effects on NMR/EPR parameters

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Over the last two decades it has become increasingly clear that NMR chemical shifts can be strongly influenced by the effects of special relativity, leading to various new and interesting phenomena, particularly for compounds of the heavier elements.\(^{1}\) Spin-orbit effects on NMR shifts of nuclei near a heavy atom can be very large when an efficient Fermi-contact-type mechanism for the transfer of spin-orbit-induced spin polarization exists.\(^{1}\) \(^1\)H Shifts are thus particularly susceptible to such spin-orbit effects, but any main-group atom in its maximum oxidation state is affected significantly. Starting from basic considerations and using the full machinery of relativistic quantum chemistry, we will show, how such arguments led us to consider, for example, \(^1\)H and \(^13\)C shifts in uranium(VI) organometallics (and related species), and how unprecedented shift ranges have been discovered.\(^{2,3}\) In particular, it is predicted that diamagnetic U(VI) hydride complexes may feature \(^1\)H shifts up to +200 ppm, completely outside the known range in the proton NMR of diamagnetic compounds.\(^{3}\) Other aspects pertain to EPR parameters\(^{4}\) and to the still more challenging issue of computing NMR shifts for open-shell metal complexes.\(^{5}\)


\(^{5}\) M. Kaupp, F. H. Köhler Combining NMR spectroscopy and quantum chemistry as tools to quantify spin density distributions in molecular magnetic compounds Coord. Chem. Rev. 2009, 253, 2376-2386.
Relativistic Density Matrix Renormalization Group

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In the past decades relativistic quantum chemistry has significantly improved the understanding of structure, bonding characteristics, and reactivity of heavy element compounds. A reliable study of the chemistry of heavy-elements calls in general for a rigorous treatment of relativistic electron correlation – static and dynamic – on an equal footing. For meeting the latter requirement, the density matrix renormalization group (DMRG) method [1,2] and its combination with orbital optimization (DMRG-SCF) has emerged in recent years in non-relativistic quantum chemistry as a valuable alternative [3-6] to conventional multiconfiguration wave function approaches such as, for example, complete-active-space SCF (CASSCF) as well as multireference configuration interaction (MRCI) and coupled cluster (MRCC).

In this contribution we outline the formulation and implementation of the first relativistic two- and four-component DMRG approach [7] which includes spin-orbit coupling variationally from the outset. The performance of our new relativistic DMRG module is discussed in comparison to traditional relativistic multireference wave function methods.

Moreover, we shall discuss our recent developments of a relativistic second-generation DMRG module [8] which takes full advantage of a matrix-product state parametrization for the wave function and of a matrix-product operator representation for the Hamiltonian.

Origin and Cure of the Brown-Ravenhall disease.

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Ruhr-University Bochum Germany

The concept of a Brown -Ravenhall disease (BRD) , also referred to as 'continuum dissolution' , that goes back to J. Sucher, is based on a subtle misunderstanding of the role of 'negative-energy states' in relativistic many electron theory. The BRD can inhibit a variational solution of the Dirac-Coulomb Hamiltonian in configuratuation space. The BRD can be avoided (without the need of a no-pair projection) if one formulates the theory strictly in terms of a Fock-space based on the Dirac vacuum.
Relativistic Molecular Quantum Mechanics (RMQM) as the union of Relativistic Quantum Chemistry (RQC) and Quantum Electrodynamics (QED) consists of three components (i.e., Hamiltonian, wave function, and property), each of which is confronted with some fundamental issues, including, e.g., 'What is the appropriate relativistic many-electron Hamiltonian?'[1-4], 'How to make explicit and/or local representations of relativistic wave functions?'[2,5,6], 'How to formulate relativistic properties?'[7-10], 'How to interface RQC and QED?'[2-4], etc. In this lecture I shall try to address these fundamental issues from both conceptual and methodological standpoints, so as to establish the 'big picture' of RMQM[11].

Zero-Field Splitting and Phosphorescence Rates in Ir$^{III}$ (ppy)$_{3}$

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For a collection of transition metal organic complexes including $f_{ac}$-Ir(ppy)$_{3}$, Yersin and coworkers [1] observed a (non-linear) correspondence between the average emission decay time of the $T_{1}$ state and the magnitude of its zero-field splitting (ZFS). In interpreting the temperature dependence of the emission spectra, the population distribution of the fine-structure levels of the $T$, state was assumed to obey a Boltzmann relation. Based upon this model, Yersin et al. concluded that sublevel III of the $T$, state (i.e., the fine-structure level with highest energy) exhibits the fastest radiative transition to the electronic ground state. The transition from the central sublevel (II) was supposed to be at least one order of magnitude slower while emission from the lowest sublevel (I) was considered to be electronically forbidden. Furthermore, these authors reported a strong dependence of the photophysical properties on the environment.

Because of its prominence as a phosphorescence emitter in organic light-emitting diodes (OLEDs), various theoretical investigations were undertaken on Ir(ppy)$_{3}$ in the last decade, several among them explicitly including spin-orbit coupling. All agree in stating that the lowest excited triplet state exhibits mainly metal-to-ligand charge-transfer (MLCT) character with contributions from ligand-centered (LC) excitations. However, none of these studies can reproduce the large ZFS nor do they offer a conclusive explanation for the fact that sublevel I exhibits the smallest transition rate while sublevel III has the largest one.

In the present study, we strive for finding an efficient but still reliable computational method to determine the spectral properties of such complexes. To this end, we evaluate the influence of various approaches and computational parameters on the photophysical properties of $f_{ac}$-Ir(ppy)$_{3}$. Using multi-reference spin-orbit interaction methods we find, for example, a strong dependence of the ZFS and the phosphorescence rates on the atomic orbital basis while the scalar relativistic excitation energy of the lowest-lying triplet state is very little affected.

Development of Efficient Two-Component Relativistic Method for Large Systems

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This presentation reviews our recent studies on the developments of the relativistic electron correlation calculations for large systems. The first key technique is the local unitary transformation (LUT) scheme \(^{[1,2]}\) with the infinite-order Douglas-Kroll-Hess (IODKH) method \(^{[3,4]}\), which achieve the linear-scaling computational cost for the unitary transformations for one- and two-electron operators. Reiher and coworkers \(^{[5,6]}\) independently proposed a similar local technique for one-electron operator. The second is the combination with the linear-scaling divide-and-conquer (DC)-based electron-correlation theories \(^{[7]}\), which have been developed for the nonrelativistic calculations of the second-order Møller–Plesset (MP2) \(^{[8]}\) and coupled cluster theories with single and double excitations (CCSD) \(^{[9,10]}\) methods in addition to the Hartree-Fock (HF) method \(^{[11,12]}\). Numerical applications (Fig. 1) clarified overall linear-scaling computational costs with small prefactors for the present methods, namely DC-HF, MP2, and CCSD with the LUT-IODKH Hamiltonian.

FIG. 1. System-size dependences of CPU times for (HF)\(n (n = 2, 3, \ldots, 50)\) by the conventional and DC-based HF, MP2, and CCSD methods using IODKH/IODKH Hamiltonians with (w/) and without (w/o) LUT scheme. A single core of a Hexa Core Xeon/3.33 GHz processor was used.

Melting of Mercury: Importance of Relativistic and Many-Body Effects

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Mercury, Hg, is the only elemental metal which is liquid at room temperature. It has long been speculated that relativistic effects play a vital role in the explanation: The valence (6s) electrons are stabilized by direct relativistic effects causing a very weak van-der-Waals bonding in the mercury dimer and in small clusters. Increasing the cluster size, we find covalent and finally metallic bonding. The next-neighbor distance decreases accordingly from about 3.6 Å in the dimer to 3.0 Å in the solid. This already hints at a strong influence of many-body effects in the interaction energy.

In my talk, I will present mercury melting simulation performed in a parallel-tempering Monte-Carlo framework. The accuracy and efficiency of this method for very weakly interacting systems has been proven in the study of rare-gas clusters [1] and in high-pressure melting studies of Argon [2]. Central to all simulations is a highly accurate, while computationally efficient evaluation of the interaction energy. The standard many-body expansion, which works well for rare gases, does not converge for mercury. We therefore resorted to the so-called diatomics-in-molecules (DIM) model [3]: the many-body effects are described effectively by expanding the Hamiltonian in a basis of the ground and 12 lowest-lying excited states of the Hg dimer. A non-relativistic DIM model was developed [4] and both, the relativistic and the non-relativistic model were updated using highly accurate, ab initio ground and excited potential curves of the Hg dimer [5]. Comparison of results obtained with the 'pure' pair potentials gave information about the importance of many-body effects. The results showed that indeed scalar-relativistic effects have a marked influence on the melting behavior combined with complicated many-body effects. The results for the small clusters are not following a well-defined trend with increasing cluster size but the observed behavior can be linked to trends found when comparing the DIM effective pair potentials with the pure ones. For the extended system we get very convincing results - within the relativistic model, the experimental melting temperature as well as the density is very well reproduced. And comparison with the non-relativistic results prove without doubt the impact of relativity: Without relativistic effects mercury would melt more than 100°C higher than observed and would not be liquid at room temperature [7]!

The REHE programme of the ESF and some recent examples in the field

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The REHE programme of the ESF ran 1993-98, after which the REHE conferences continued an autonomous existence, demonstrating the vitality of the field. This is also demonstrated by the volume of the RTAM database rtam.csc.fi, explained in [1]. For a review on the basic theory aspects, see [2], and for some examples on applications, see [3]. The latest result from the author’s group is the theoretical understanding of the observed, unbridged Au(II)-Au(II) covalent bonds [4]. These bonds are attributed to a novel 6s6p5dxy hybridization. The work on the 32-electron principle was ripe for the first review [5].

References
Reduced asymptotic scaling in four-component self-consistent field calculations

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The high computational cost and complexity of relativistic methods, in particular methods based on the four-component Dirac formalism, is due to the need to evaluate four-center, two-electron repulsion integrals (ERIs) over complex 4-spinor basis functions. The need to perform relativistic calculations on larger molecules using more complicated spinor functions drives the search for improved methods for calculating these integrals. In this talk, I will present a method for fast evaluation of electron-repulsion integrals in the four-component domain, which takes advantage of a simultaneous evaluation of ERIs over the large- and the restricted kinetically/magnetically balanced (RKB/RMB) small-component 2-spinors using a recursive Obara-Saika scheme [1, 2]. An atom-centered basis of dimension \( N \) nominally produces \( O(N^4) \) four-center ERIs, but in the range of large-scale calculations, only a quadratic number of four-center ERIs rises to non-negligible two-electron matrix elements. In order to reduce the asymptotic scaling of four-component Dirac-Hartree-Fock and/or Dirac-Kohn-Sham calculations, methods for identifying significant elements in the Coulomb interaction as well as the exact exchange matrix will be discussed. This results in an analytically exact method substantially reducing the number of floating point operations and memory accesses needed for the four-component Fock matrix construction.

All the improvements reduce the computational cost of four-component SCF methods to a level where the calculations can be performed routinely on systems containing more than hundred atoms and/or a few thousand 4-spinor basis functions. In this case, the computational bottleneck is progressively shifted towards matrix diagonalization, particularly in the four-component formalism where the Fock matrix becomes significantly larger compared to the nonrelativistic case. Moreover, as diagonalization is hard to parallelize well, it becomes a bottleneck in large-scale quantum chemistry simulations running on parallel computing platforms. Therefore, a recently developed Thouless-expansion-based diagonalization-free approach for ground-state optimization [3] has been adapted to the four-component relativistic regime [4] and implemented within the program package ReSpect,[5] To demonstrate the robustness and efficiency of the implementation, I will present the results of four-component SCF ground-state optimization of several heavy-metal complexes. The diagonalization-free procedure is about twice as fast as the corresponding diagonalization.

Four-component relativistic calculations in the time domain

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In the talk, I will discuss the implementation and application of a code for propagating four-component relativistic densities in the time domain in the framework of Kohn–Sham density functional theory. [2] The code has been developed in the framework of the ReSpect [1] program for calculating Relativistic Spectroscopic properties. I will in particular discuss the application of the code to a study of the \(L_2\) and \(L_3\) edges of the sulphur atom as well as the fluorine \(K\) edge in \(\text{SF}_6\), demonstrating that accurate results for the energy separation between the \(2p_{1/2}\) and \(2p_{3/2}\) orbitals can be obtained using this approach, [3] and good agreement with experimental spectra. [4]

References

[1] ReSpect, version 3.3.0 (beta), 2013; Relativistic Spectroscopy DFT program. M. Repisky; S. Komorovsky; V. G. Malkin; O. L. Malkina; M. Kaupp; K. Ruud, with contributions from R. Bast; U. Ekström; S. Knecht; O. I. Malkin; E. Malkin (see http://rel-qchem.sav.sk).


Theoretical X-ray spectroscopy of actinide compounds

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X-ray Absorption Near Edge Structure (XANES) spectroscopy is element-specific due to the local nature and large energy spacing of core orbitals, but at the same time chemically interesting because its sensitivity to the chemical environment of the XANES-active nucleus. In actinide chemistry XANES spectroscopy is currently actively pursued to investigate the degree of participation of actinide 5\textit{f} orbitals in bonding\cite{1}.

In the present contribution we discuss to what extent XANES spectroscopy can be used to investigate covalency. We report simulated XANES spectra for the isoelectronic series \textit{UO}\textsubscript{2}\textsuperscript{2+}, \textit{OUN}\textsuperscript{+} and \textit{UN}\textsubscript{2} based on the 4-component Dirac-Coulomb Hamiltonian and using the following methods: restricted excitation window time-dependent-Hartree-Fock or DFT, complex response as well as the Static Exchange approximation (STEX), available in the DIRAC code for relativistic molecular calculations\cite{2}.

References


Model Lamb shift operator for a relativistic many-electron atom

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A model operator approach to calculations of the Lamb shift in relativistic many-electron atoms and ions is considered. The model Lamb shift operator is constructed as a sum of local and nonlocal potentials which are defined using the results of \textit{ab initio} calculations of the diagonal and nondiagonal one-loop QED contributions with H-like wave functions. The proposed operator can be easily included in any calculations based on the Dirac-Coulomb-Breit Hamiltonian. The efficiency of the method is demonstrated by calculations of the Lamb shifts in neutral alkali metals, Cu-like ions, superheavy atoms, and Li-like ions. The detailed description of the method and its applications are presented in Ref. \cite{1}.

Four-component wave function methods for 100-atom systems: Complete active space self-consistent field

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We will present efficient algorithms for computing quasi-degenerate ground states of heavy-element complexes based on the four-component Dirac Hamiltonian and complete active space self-consistent field method. Utilizing parallel software infrastructure developed in our open-source BAGEL package,¹ we have made fully relativistic simulations of 100-atom systems routine,²-⁴ a goal long deemed impractical due the computational complexity of solving the Dirac equation using wave function ansätze. Computation of zero-field splitting of single-molecule magnets⁵ and electronic structure of heavy-element complexes in static magnetic fields⁶ will be discussed.

The accurate relativistic electronic structure treatment of superheavy elements with nuclear charge Z = 111-120 and beyond.

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It is well known that relativistic effects dominate the chemistry of the trans-actinides, and unusual properties are often predicted due to strong scalar relativistic or spin-orbit effects [1]. For example, both Cp (Z=112) and Fl (Z=114) are predicted to be more chemically inert compared to their lighter congeners, the former due to direct relativistic 7s stabilization and the latter due to strong spin-orbit effects, which make Fl a closed-shell atom. Recent solid-state calculations predict Cp to be a semi-conductor, and Fl to be a metal. In order to accurately predict the chemistry of superheavy elements accurate quantum chemical methods are required. In addition, for the accurate prediction of properties with “chemical accuracy” (~1 kJ/mol) quantum electrodynamic effects at lowest order have to be accounted for [2], especially for the s-block elements. This includes the frequency dependent Breit interaction (BI, i.e., retarded photon exchange between two electrons), one-loop electron self-energy (SE), and the vacuum polarization (VP, photon self-energy). To solve the Dirac equation including Breit and QED effects for multi-electron atoms is a formidable task, and currently is not well developed for molecular systems (if at all). It is therefore convenient to include such effects within the pseudopotential approximation [3,4]. There are two different ways of doing this, which will be useful for future applications to molecular systems:

Scheme 1: An effective one-electron Hamiltonian (QED all-electron pseudopotential) of the following form

\[ H_{\text{QED eff}}(\vec{r}_i) = \tilde{H}_{\text{BI}}(\vec{r}_i) + \tilde{H}_{\text{SE}}(\vec{r}_i) + \tilde{H}_{\text{VP}}(\vec{r}_i) \]

with

\[ \tilde{H}(\vec{r}_i) = \tilde{H}_{\text{local}}(\vec{r}_i) + \tilde{H}_{\text{semi-local}}(\vec{r}_i) = \sum_k A_k \phi_k^0 - \alpha_k \phi_k^0 + \sum_{l=0}^{\max} \sum_{j=1/2}^{l+1/2} \sum_{l'} B_{ljaljl'} \phi_{ljl'} - \beta_{ljaljl'} \sum_{m,j=1}^{l-1/2} |jm\rangle \langle jm| \]

is introduced to account for the BI, SE and VP contributions. The freely adjustable parameters \( A_k, B_{ljaljl'}, \alpha_k, \alpha_l \) and \( \beta_{ljaljl'} \) need to be fitted to a well-chosen pre-determined all-electron QED-Dirac-Hartree-Fock (DHF) spectrum of atomic and ionic systems. Work here is in progress.

Scheme 2: If one is only interested in the valence space for chemical studies, a one-electron QED effective core potential (QED-ECP) including BI, SE and VP similar to eq.(1) can be introduced [3,4]. The parameters are then fitted to a well-chosen pre-determined QED-DHF valence spectrum of atomic and ionic systems. Great progress has already been made recently in QED-ECPs, which clearly showed that QED effects can be incorporated with good accuracy into the valence space compared to all-electron calculations. Scheme 1 can be seen as an extension to Pyykkö’s local QED approach [5], and progress in this direction is currently underway in collaboration with the Mark Hoffmann’s group at the University of North Dakota.

Accurate determination of nuclear quadrupole moments and nuclear quadrupole-coupling constants

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Nuclear quadrupole moments provide information about the charge distribution of a given nucleus. Their interaction with the electric-field gradient at that nucleus leads to nuclear-quadrupole couplings that can provide fingerprint information about the local chemical environment of the given nucleus which is observable in various spectroscopic techniques like rotational, NMR or Mössbauer spectroscopy. The reliable determination of nuclear quadrupole moments as well as quadrupole-coupling constants requires the accurate computation of electric-field gradients. The latter requires an accurate description of the electron density in the vicinity of the nucleus and is challenging due to slow basis-set convergence as well as the importance of electron correlation and relativistic effects.

In this talk, we report on a protocol for the highly accurate determination of electric-field gradients based on large-scale coupled-cluster calculations with additional consideration of scalar-relativistic and spin-orbit effects. We apply this protocol

- to revise the values for the bromine and sulfur quadrupole moments[1, 2] based on an analysis of experimental quadrupole couplings for HBr as well as CS and SiS, respectively,
- for the accurate calculation of copper quadrupole-coupling constants[3],
- to determine within a joint experimental and theoretical investigation the hyperfine structure in the rotational spectrum of CH₂FI[4].

Magnetic anisotropy through cooperativity in multinuclear transition metal complexes: boosting the anisotropy by heavy-element “spin $\frac{1}{2}$” centers

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To be a candidate for a good single-molecule magnet, a compound should have a reasonably large zero field splitting, a reasonably large total spin, and preferably axial symmetry. We investigate how this can be achieved in multi-heteronuclear $d$-Block transition metal complexes with both $3d$ and $5d$ centers. While spin-orbit coupling is large at the $5d$ center, the $3d$ centers contribute many unpaired electrons. If the heavy-element building block does not have a single-ion anisotropy it might still transfer its spin-orbit effects to the $3d$ center(s) through anisotropic exchange. We present spin-orbit configuration interaction calculations on a bi- and trinuclear compound with one Os$^{III}$ and one or two Mn$^{II}$ centers to demonstrate the mechanism.

The interaction between the metal centers brings about zero-field splitting which is entirely due to anisotropic exchange (none of the centers contributes a sizeable single-ion anisotropy). Because of strong spin-orbit coupling, the Os center behaves as a pseudo-spin with $S = \frac{1}{2}$ which shows antiferromagnetic and anisotropic exchange coupling with the Mn centers. The ground state of the binuclear complex has a pseudo $S = 2$ ground state with an axial zero field splitting parameter $D = +0.59 \text{ cm}^{-1}$, while the trinuclear complex has a pseudo $S = \frac{9}{2}$ ground state with a negative $D = -0.32 \text{ cm}^{-1}$. Coordination of the second Mn center thus increases total spin and magnetic anisotropy, and reverses the sign of $D$. 

\[
\left[\left(\text{H}_3\text{N}\right)_3 \text{MnCl}_3 \text{Os} \left(\text{NH}_3\right)_3\right]^{2+} \quad \text{and} \quad \left[\left(\text{H}_3\text{N}\right)_3 \text{MnCl}_3 \text{OsCl}_3 \text{Mn} \left(\text{NH}_3\right)_3\right]^+ 
\]
The importance of core-valence correlation in simple model systems. Applications to cold atoms and nuclear quadrupole moments.

prof. Lucas Visscher, Department of Chemistry and Pharmaceutical Sciences, Amsterdam Center for Multiscale Modeling, VU University Amsterdam

Thanks to developments in basis sets for all-electron relativistic calculations it becomes feasible to study the importance of core-valence correlation in heavy elements in more detail. In this talk I will focus on simple diatomic molecules and try to assess the importance of correlating the core for both valence properties (dissociation curves for weakly interacting atoms) and properties in which the electron density is probed in the core region (electric field gradients). Besides presenting representative examples I will also discuss the possibilities and the limitations of the currently available implementations of relativistic coupled cluster methods.
Methodologies and Development Towards Quantitative Accuracy for the Heavy Elements: Structural, Energetic, and Spectroscopic Properties

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While significant effort has been invested in accurate computational methodologies for main group species, there has been much less focus upon f-block chemistry. Here, DFT and \textit{ab initio} single reference and multireference methodologies have been considered in conjunction with a variety of basis sets for the prediction of structural, energetic, and spectroscopic properties of several classes of lanthanide species in the common 3+ oxidation state, as well as in lower oxidation states. Routes to address relativistic effects have been considered, and possible composite strategies are addressed. The role of orbitals in bonding and the impact of the correlation of the subvalence upon thermochemical and photophysical properties are considered.
Abstracts of Posters
Molecular properties originated in molecular rotation: 4 component and LRESC analysis

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Abstract

An original formulation of the relativistic molecular rotational $g$-tensor valid for heavy atom containing compounds is presented. In such formulation the relevant terms of a molecular Hamiltonian for non relativistic nuclei and relativistic electrons in the laboratory system are considered, including electron-nucleus Breit interaction effects. Terms linear and bilinear in the nuclear rotation angular momentum and an external uniform magnetic field are considered within first and second order (relativistic) perturbation theory to obtain the rotational $g$-tensor. Relativistic effects are further analyzed by carrying out the linear response within the elimination of the small component (LRESC) expansion. Quantitative results for model systems $HX$ ($X = F, Cl, Br, I$), $XF$ ($X = Cl, Br, I$) and $YH^+$ ($Y = Ne, Ar, Kr, Xe, Rn$) are obtained both at the RPA and DFT levels of approximation. Relativistic effects are shown to be small for this molecular property. The relation between the rotational $g$-tensor and susceptibility tensor which is valid in the non relativistic theory does not hold within the relativistic framework, and differences between both molecular parameters are analyzed for the model systems under study. It is found that the non-relativistic relation remains valid within 2% even for the heavy $IH, IF$ and $XeH^+$ systems. Only for the sixth-row $Rn$ atom a significant deviation of this relation is found.

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The Relativistic Correlation Problem

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Abstract

The correlation energy \( E_c \) is the difference between the exact eigenvalue of the Hamiltonian and its expectation value in the Hartree-Fock approximation. The exact eigenvalue is not available, but in the non-relativistic domain the best solution is a full CI (for a given basis).

In the present work we consider the correlation energy of two-electron atoms. In the non-relativistic case coordinate scaling makes the one-electron problem independent of nuclear charge. The two-electron operator becomes multiplied with the inverse nuclear charge, which can be considered a perturbation strength parameter. Using the complete set of determinants of the one-electron solutions allows the development of a \( 1/Z \) expansion of the correlation energy, showing that it is to lowest order independent of nuclear charge.

In the relativistic domain, as first observed by Brown and Ravenhall, the same procedure leads to continuum dissolution, demonstrating that the relativistic Dirac-Coulomb Hamiltonian has no bound solutions. Relativistic calculations are therefore based on the Dirac-Coulomb Hamiltonian embedded by projection operators that eliminate negative-energy orbitals.

Our main goal will be to show that the best solution of the wave equation for the embedded Dirac-Coulomb Hamiltonian, is not a Full CI, as in the non-relativistic case, but a MCSCF which uses a CI development in positive-energy orbitals only, but which keeps rotations between the positive and negative energy orbitals to optimize the projection operator.

---

Atomic nuclei are not point-like but extended objects. With their diameters of a few femtometer they are about five orders of magnitude smaller than the complete atoms. The main quantities characterizing an atomic nucleus include its proton and neutron numbers, $Z$ and $N$ (their sum being the mass number $A$ of the nucleus), as well as its total magnetic moment, $\mu$, and its half-life $T_{1/2}$. All currently known atomic nuclei have proton numbers in the range $1 \leq Z \leq 118$, and all nuclei with $Z > 82$ (Pb) exhibit radioactive decay ($T_{1/2} < \infty$) [1]. The magnetic moment is linked to the nuclear spin angular momentum through the magnetogyric relation, written in dimension-free terms as $\mu / \mu_N = g I / \hbar$ ($\mu_N$ nuclear magneton, $\hbar$ reduced Planck constant). The sign of the $g$-factor indicates whether the two vectors involved are oriented in parallel ($g > 0$) or anti-parallel ($g < 0$) to each other.

Both the nuclear charge $Ze$ ($e$ elementary charge) and the nuclear magnetic moment $\mu$ are distributed over the volume of the nucleus. The resulting distributions are known as nuclear charge density distribution and nuclear magnetization distribution. A nuclear size effect on some physical or chemical property of interest can now be defined as the difference between two values of that property, evaluated once with extended distributions of charge and/or magnetic moment and once with corresponding point-like distributions.

The importance of the inclusion of extended nuclear charge and magnetic moment distributions in the theory of hyperfine interactions and of electron scattering from nuclei is well known since long [2]. Nowadays, however, the study of nuclear size effects and the inclusion of extended models for the distribution of charge [3, 4] and magnetization [5] are pretty much standard.

This presentation gives an overview of models frequently used to represent the distributions of nuclear charge and magnetization. Some examples for nuclear size effects will be included as well.


Equilibrium constant in isotope exchange reaction of Pb-EDTA using Infinite-Order-Douglas-Kroll-Hess approaches

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Isotope ratio is widely measured in not only analytical chemistry but also geochemistry, cosmochemistry, etc. A general isotopic exchange reaction is described as

\[ A'Y + AX = AY + A'X \quad (A' : \text{light isotope}, A : \text{heavy isotope}) \]  \hspace{1cm} (1)

In this system, equilibrium constant (in other words, isotope fractionation factor) \( \alpha \), \( \frac{[AY]}{[A'Y]} \times \frac{[A'X]}{[AX]} \), is always close to 1. Thus the isotope fractionation coefficient \( \varepsilon \) is conventionally defined as \( \alpha - 1 \). The origin of isotope fractionations was often explained from the differences of vibrational energy levels caused by isotopic nuclear mass differences. However this nuclear mass effect can only explain isotope fractionations of light elements. In 1996, experimental results of Fujii et al. \cite{fujii1996} and a theory of Bigeleisen \cite{bigeleisen1996} explained a new origin of isotope fractionations in heavy elements, so called nuclear volume effect. This effect is caused from electronic state differences due to isotopic difference of nuclear-charge-volume. The corresponding term in \( \varepsilon \), denoted as nuclear volume term \( \ln K_{nv} \), is described as follows with total energies of each compound.

\[ \ln K_{nv} = (\frac{kT}{\hbar^2}) \left[ \frac{E(AX) - E(A'X)}{E(AY) - E(A'Y)} - 1 \right] \]  \hspace{1cm} (2)

This nuclear volume effect is significant in heavy elements and related to electronic state of the nuclear vicinity. Therefore, relativistic effect is very important. Schauble \cite{schauble2007} and Abe et al. \cite{abe2008} proposed 4-component relativistic calculations of \( \ln K_{nv} \). Recently, Nemoto et al. calculated \( \ln K_{nv} \) in uranium isotope exchange system by various 2-component relativistic approximate theories.\cite{nemoto2013} They showed the infinite-order Douglas-Kroll-Hess method with the mean-field spin-orbit interaction (IODKH+MFSO) provided very close results to \( \ln K_{nv} \) with the 4-component method.

Hence in this study, we apply the IODKH+MFSO method for the calculation of \( \ln K_{nv} \) in lead-EDTA (ethylenediaminetetraacetic acid) isotope exchange systems in Eq. (3).

\[ ^{208}\text{Pb}^{2+}(\text{H}_2\text{O})_{6}^{2+}\text{MPb}^{2+}\text{EDTA(2H)}^{2-} = ^{M}\text{Pb}^{2+}(\text{H}_2\text{O})_{6}^{2+}^{208}\text{Pb}^{2+}\text{EDTA(2H)}^{2-} \]  \hspace{1cm} (M=206,207)  \hspace{1cm} (3)

The lead-EDTA compound contains 35 atoms and it is hard to be calculated with 4-component method and better with IODKH in the sense of computational time. We used DIRAC12 program to obtain the total energies. We also obtain the nuclear mass term \( \ln K_{nm} \) from the harmonic frequency calculation using the DFT (B3LYP) method with Gaussian09. Summation of these two terms approximately corresponds to isotope fractionation coefficient \( \varepsilon \), experimentally obtained.

Table 1 summarizes our results in the unit of per mil (\( 10^{-3} \)). The calculated \( \varepsilon \) is about three times larger than the experimental \( \varepsilon \) but the sign, indicating the direction of reaction, and the order of magnitude are same. Since the precision of \( 10^{-7} \sim 10^{-8} \) a.u. in total energy is required to obtain this tiny quantity for \( \ln K_{nm} \), we consider this agreement is reasonable. We confirm nuclear volume term \( \ln K_{nv} \) is dominant and nuclear mass term \( \ln K_{nm} \) is very small in our calculations. Further analysis and discussion will be presented in our poster.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
\textbf{mass term} & \textbf{volume term} & \textbf{fractionation coefficient} & \textbf{Exp.}\cite{nomura2013} \textbf{[\%]} \\
\hline
\textbf{lnK_{nm}} & \textbf{lnK_{nv}} & \textbf{lnK_{m}} & \textbf{\varepsilon} \\
\hline
0.057 & 0.400 & 0.457 & 0.16 \\
0.028 & 0.239 & 0.268 & 0.10 \\
\hline
\end{tabular}
\caption{calculated values of lnK_{nm},lnK_{nv} and \varepsilon with experimental \varepsilon. [\%]}
\end{table}

Visual analysis of relativistic effects in 4-component $g$-tensors

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Visual analysis of 4-component $g$-tensors (calculated using the 3-SCF method) has been made possible by plotting the $g$-tensor as a property density. This can be decomposed into terms corresponding to each operator in the $g$-tensor calculation: Zeeman, Spin-Orbit/Orbital-Zeeman coupling, and other terms that originate from purely relativistic effects (“relativistic terms”). The latter include the effect labelled “relativistic mass correction” at the 1-component level. We present visualisation and analysis of the contributions arising from these relativistic terms for both light and heavy-element systems.

Figure 1. Analysis of relativistic contributions to different components of the $g$-tensor densities in SeO molecule: Left - $g_L$; Right – $g_\parallel$ (presented with cut-off of +/-1 ppm per volume unit in a.u.).

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Mechanisms of spin crossover in Fe(II) complexes

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Spin crossover occurs in metal-organic complexes of d⁴ ... d⁷ transition metal ions coordinated by groups that induce a rather weak ligand field. Such compounds have two low-energy states, one with maximum electron pairing and one with a maximum number of unpaired d electrons. A transition between these low and high spin states can be induced by changing temperature, pressure or by light. The spin crossover mechanism may involve various intersystem crossings and internal conversions and therefore its theoretical study requires analysis of the results of accurate quantum chemical calculations. We studied the mechanisms by combining TDDFT and CASPT2 electronic structure calculations to obtain equilibrium geometries, vibrational frequencies and relative energies with a recently developed time-dependent formalism for calculating intersystem crossing rates within Fermi’s Golden rule approximation [1]. The approach is illustrated for various Fe(II)-based spin crossover compounds.

The parameters governing thermal spin crossover are discussed for a series of five spin crossover materials [2]. The different spin crossover behavior of two [Fe(mtz)₆]²⁺ complexes (mtz: methyl-tetrazole) occupying different lattice sites in Fe(mtz)₆(BF₄)² is explained [3]. Our calculations established that the relative energies of the relevant states depend on the orientation of the tetrazole ligands and, moreover, that the two complexes indeed have different ligand orientations. Light-induced spin crossover occurs in the [Fe(2,2'-bipyridine)₃]²⁺ complex. Our results for this complex show that ultrafast deactivation from the initially excited metal-to-ligand charge transfer state to the high spin final state occurs via different channels [4].

Topology of electron density and the Fourier transform of electron density. Impact of picture change error and relativistic effects

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The poster will briefly summarize the importance of picture change error (PCE) correction in the quasirelativistic electron density and the Laplacian of electron density. The relativistic effects will be presented at 1- and 2-component levels of theory, accounting for scalar and also spin-orbit effects, respectively [1].

Furthermore, the Fourier transform of the electron density [2] (i.e. the X-ray structure factors) will be exploited more closely for heavier element compounds. PCE and relativistic effects will be considered for the evaluated structure factors. The 2-component structure factors should be employed in the extension of the X-ray Constrained Wavefunction fitting procedure [3] as well as in the X-ray Wavefunction Refinement including Hirshfeld Atom Refinement [4, 5, 6] at the General Complex Hartree Fock level of theory (GCHF, i.e. unrestricted 2-component). Finally, some of the properties of the unrestricted Kramers pairs symmetry for the GCHF wave function will be presented [7]. All calculations of the quasirelativistic electron densities, Laplacians and structure factors have been performed in the Tonto package [8].

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Calculation of EPR g-tensor in the framework of 2- and 4-component unrestricted HF and DFT approaches

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In two- and four-component approaches the spin-orbit (SO) operator is included into the ground state Hamiltonian variationally, and consequently, the SO contributions to the EPR g-tensor are taken into account up to infinite order. The g-tensor is calculated as an expectation value of the Zeeman operator over the ground state wave function. In a number of publications it has been shown that higher-order spin-orbit effects can be important for accurate calculation of the g-tensor in heavy-element compounds. Yet the discussion of how best to take higher-order spin-orbit contributions into account is far from being over. In particular, there is certain confusion about such approaches.

In one of the cornerstone papers concerning the inclusion of higher-order spin-orbit effects, van Lenthe, Wormer, and van der Avoird presented a method for calculation of g-tensor based on the properties of Kramers pairs. This approach was developed within the two-component restricted framework, and does not account for spin polarization effects. Furthermore, unless extended, it is only applicable to doublet systems. In the present work we extend this method of calculating the g-tensor to the two- and four-component unrestricted frameworks. This extension requires the evaluation of integrals between Kramers pair wavefunctions. In the unrestricted framework the MOs used to construct one of the Kramers pairs are mutually orthogonal to one another, however, they are not orthogonal to those MOs used to construct the other Kramers pair. The problems associated with both approaches are discussed. The accuracy of this approach is evaluated at the HF and DFT levels by applying it to a series of small molecules, and comparing the results which are obtained with similar results obtained using the so-called 3SCF approach.


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Electron Electric Dipole Moment in ThF⁺

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Nowadays, Standard Model incompleteness is largely acknowledged. Indeed, it fails to explain the huge surplus of matter over antimatter in the universe. A $CP$ (Charge conjugation and spatial Parity) violation is assumed to be responsible for this asymmetry and a non-zero electron electric dipole moment ($e$EDM) would be a probe of this New Physics beyond the Standard Model.

Polar diatomic molecules are promising systems in search of the electron EDM, in particular molecules containing actinide. Recently, the most constraining upper bound on the electron EDM have been obtained from measurements on ThO [2].

In our work, we employed a relativistic four-component configuration interaction approach to determine the electron electric dipole moment effective electric field in the $\Omega = 1$ state of the ThF⁺ molecule. We obtained a value of $E_{\text{eff}} = 35.2 \, \text{GV cm}^{-1}$ much smaller than the previous result reported by Meyer et al. [1]. By using the same wavefunction model, we carried out the calculation of the magnetic hyperfine interaction constant $A_{||}$ as an expectation value resulting in $A_{||} = 1833 \, \text{MHz}$ for the $\Omega = 1$ state.


Electronic decay processes of ionized systems are e.g. the Auger decay or the Inte-
ratomically/ Intermolecular Decay (ICD). In both, an energetically low lying vacancy is filled
by an electron of an energetically higher lying orbital and a secondary electron is instan-
taneously emitted to the continuum.

We present a relativistic implementation of the non-relativistically established FanoADC-
Stieltjes method [1] into Dirac [2]. In contrast to atomic codes, it can be used for the
calculation of lifetimes with less than spherical symmetry.

The decay widths of such processes from an initial state $|\Phi\rangle$, including continuum electrons
with the corresponding states $|\chi_{\beta,\varepsilon}\rangle$, can for each decay channel $\beta$ be described by Fano’s
Golden Rule [3]:

$$\Gamma_{\beta}(E_{\Phi}) = 2\pi |\langle \chi_{\beta,\varepsilon} | \hat{H} - E_{\Phi} | \Phi \rangle |^2$$  (1)

In order to mimic the continuum functions in an $L^2$ basis, a large set of Algebraic Dia-
grammatic Construction (ADC) $2h1p$ functions is utilized. After a suitable partitioning
of the ADC matrix into initial and final state subspaces, the above equation is evaluated
for all possible combinations. The resulting pseudo-spectrum is then treated via Stieltjes-
imaging to yield the decay width, which is anti-proportional to the lifetime.

We apply this method to the Auger processes following the Kr3d$^{-1}$ and Xe4d$^{-1}$ ionization
and discuss the influence of relativistic effects on the lifetimes [4].

Micro-solvation of Methyl-Mercury \([\text{CH}_3\text{Hg(H}_2\text{O)}_n]^{+}; \quad n = 1, 2, 3\)

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Mercury has been widely used in medicine as antiseptic and fungicidal (Merthiolate), ophthalmic (mercury oxide II) and diuretic (mercuric chloride), however it is now possible to replace most of these products by others that do not contain mercury. The FDA (Food and Drug Administration of USA) recognizes that some of these mercury-containing drugs are safe for human health \([1]\).

Mercury exists in different chemical forms, each one with different toxicity levels; all of them can induce changes in the human nervous system \([2]\). Studying mercury in aqueous systems is important for two reasons: first, because most of mercury produced by natural sources or by anthropogenic origin could end up in water bodies; in water bodies all these mercury species could transform into methyl-mercury (\(\text{CH}_3\text{Hg}^{+}\)), which is known to bio-accumulate by organisms and to bio-magnify through the food chain \([3]\). The second reason is the fact that all known biochemical processes occur in aqueous media, in addition, water comprises about 70 − 80% by weight of all living organisms \([4]\).

The behavior of methyl-mercury in a biological environments has not been clearly described at the molecular level \([5]\). For this reason, a structural description of the \(\text{CH}_3\text{Hg}^{+} \cdots n\text{H}_2\text{O}\) molecular interactions is necessary as a first approach to understand the biological processes in which they are involved.

We used MP2 and ECPs to account for scalar relativistic effects and to analyze structural stability and molecular interactions among \(\text{CH}_3\text{Hg}^{+} \cdots n\text{H}_2\text{O}\) (Figure 1a, 1c, 1d, 1f - 1k), we also study and describe different reaction mechanisms of \([\text{CH}_3\text{Hg}]^{+}\) in aqueous media (Figure 1b, 1e, 1l, 1m). Also, bonding properties are analyzed within the QTAIM framework \([6]\). QTAIM provides a universal definition of what constitutes bonding; in particular, we gain insight from properties calculated at bond critical points (BCP) and ring critical points (RCP) for all kinds of interactions (Figure 1).

Figure 1: Equilibrium structures for \([\text{CH}_3\text{Hg(H}_2\text{O)}_n]^{+}\), \(a,b) n=1, c-e) n=2 y f-m) n=3\). Carbon atoms are shown in yellow, oxygen atoms in red, hydrogen atoms in white and mercury atoms in blue. BCPs are shown in green and bonding paths in black, RCPs are shown in purple and their paths in blue.

References

Getting to know the enigmatic astatine: towards the theoretical modeling of astatine-containing species in condensed phase

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²¹¹At is considered to be a possible radiotherapeutic agent in nuclear medicine, due to its nature (α-emitter) and relatively short half-life (≃ 7h). This latter aspect, crucial for its successful therapeutical use, combined with the low yields of its production method (bombardment of ²⁰⁹Bi targets with α-particles) makes it difficult for experimentalists to characterize its chemistry under conditions close to the physiological ones (pH 7), an important step to devise linker agents that can effectively mediate the transport of the radioactive species into tumorous cells.

These constraints have motivated the use of theoretical approaches to complement experimental investigations[1], with a focus currently on understanding the electronic structure of the AtO⁺ species in vacuum and in solution, since its complex AtO(OH) is thought to be the most stable At species under physiological conditions. However, these investigations focused exclusively on electronic structure methods of limited accuracy such as MP2 or DFT, and it is therefore important to cross-validate their performance with other, more accurate approaches before tackling more complex situations.

This contribution therefore aims at discussing the performance of selected density functional approximations (DFAs) with respect to that of accurate correlated methods (IHFSCCSD, NEVPT2, MRCI) in describing the ground and low-lying excited electronic structure of AtO⁺ and that of the [AtO-H₂O]⁺ complex. Furthermore, we discuss the performance of two-step approaches to incorporate spin-orbit coupling in the calculations (e.g. spin-orbit CI) with respect to one-step approaches based on four-component calculations employing the Dirac-Coulomb Hamiltonian [2].


Calculations of EPR hyperfine coupling constants of tetragonal elongated [ReF₆]²⁻ and [IrF₆]²⁻ complexes

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We have calculated the EPR hyperfine coupling tensors of the [ReF₆]²⁻ and [IrF₆]²⁻ complexes at the DFT/PBE0 level using the 2-component ZORA method with spin-orbit coupling treated both variationally and via perturbation theory, as implemented in the ADF program [1], and using the 4-component non-collinear spin-density method as implemented, in the ReSpect program [2], with restricted kinetically balanced basis set.

The considered complexes, [ReF₆]²⁻ and [IrF₆]³⁺, have interesting magnetic properties, e.g. they are well suited for building blocks in single molecule magnets [3]. Due to the lattices in which the ions have been studied experimentally, the octahedral ions are tetragonally elongated and the partly filled t₂g level of the d-orbitals splits according to figure 1. The electron configuration of the two ions differs, d⁵ and d⁴ respectively, and as a consequence this splitting of the d-orbitals may affect the calculations differently.

![Diagram](image.png)

Figure 1: Splitting of the t₂g level of d-orbitals due to elongation.

We find that for [IrF₆]³⁺, the results obtained by treating the spin-orbit contribution variationally or via perturbation theory differ significantly - the former being in agreement with the 4-components results. In this context we will also discuss the electronic excitation energies obtained using TD-DFT.


[2] ReSpect, version 3.3.0 (beta), 2013; Relativistic Spectroscopy DFT program of authors Repisky M.; Komorovsky S.; Malkin V. G.; Malkina O. L.; Kaupp M.; Ruud K., with contributions from Bast R.; Ekstrom U.; Knecht S.; Malkin Ondik I.; Malkin E. (see [http://rel-qchem.sav.sk](http://rel-qchem.sav.sk))

Rapid Electron Repulsion Integral Technique for Compounds Including Heavy Elements

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In quantum chemical calculations on systems containing heavy atoms, one computational bottleneck is an evaluation of electron repulsion integrals (ERIs). This situation is more severe than that on systems composed of only light atoms because the basis sets of heavy elements include orbitals with a high angular momentum and/or a long contraction and general-contraction (GC) scheme is often used in their basis sets. For these ERI calculations, accompanying coordinate expansion (ACE)\(^{[1]}\) and recurrence relation (RR) method\(^{[2]}\) and its extended one\(^{[3]}\) to GC scheme, which are efficient for ERIs with those orbitals, are suitable. In this study, we have developed a new algorithm combined ACE-RR with transfer relations (TRs)\(^{[4]}\) (namely, ACE-TRR) and its extended one to GC scheme\(^{[5]}\).

In ACE-TRR scheme, TRs are expressed as

\[
\text{Bra-TR} : \quad (i_A + 1, i_B - 1) = (i_A, i_B) + \Delta r \cdot (i_A, i_B - 1), \quad (1)
\]

\[
\text{Ket-TR} : \quad (i_C + 1, i_D - 1) = (i_C, i_D) + \Delta r \cdot (i_C, i_D - 1). \quad (2)
\]

The relations reduce the explicit ERI evaluation by changing angular momenta in ERIs. Here, \(\Delta r\), \(\Delta C\), and \(\Delta D\) (\(r = x, y, z\)) represent the distances between orbital centers. Using TRs recursively, an ERI is represented as a linear combination of 2-dimensional (2D) integrals:

\[
\text{ERI} = (L_A, L_B \mid L_C, L_D) = \sum_{i_A, i_B} C_{i_A}^{Bra} C_{i_B}^{Ket} (0, i_B \mid 0, i_D). \quad (3)
\]

In ACE-TRR, the 2D-integrals are written as an ACE-RR expression with

\[
(0, i_B \mid 0, i_D) = \sum_{\{N_i\}} C_{\{N_i\}}^{ABCD} (0, i_B, i_D). \quad (4)
\]

Here, \(C_{\{N_i\}}^{ABCD}\) and \(H_{\{N_i\}}^{ABCD}\) are termed as accompanying coordinate parts and core parts. The core parts are constructed using ACE-vertical RRs, which increase angular momenta after contractions.

Figure 1 shows CPU times of ERI calculations for 3D Au clusters performed by ACE-RR, ACE-TRR, and their extended algorithms to GC orbitals. For comparison, SEWARD, GAMESS, and HONDOPPLUS are also used. The basis set size is (27823p15d10f)/[694p3d1f]\(^{[6]}\). ACE-TRR drastically reduces CPU times in comparison with ACE-RR. Moreover, GC-ACE-TRR is the fastest in these algorithms.

Implementation of diagonalization-free algorithm in ReSpect at one- and four-component level.

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Noga and Šimunek [1] recently proposed a Thouless-expansion-based diagonalization-free algorithm (DF algorithm) that can be used in SCF procedures. The method has been thoroughly analyzed, particularly with respect to cases for which it is difficult or computationally expensive to find a good initial guess, and adapted for the four-component relativistic scheme. Several modifications improving the performance of the approach have been suggested [2].

The robustness and efficiency of the improved algorithm are demonstrated on the results of four-component diagonalization-free SCF calculations of several heavy-metal complexes, the largest of which contains more than 80 atoms (about 6000 4-spinor basis functions). The diagonalization-free procedure is about twice as fast as the corresponding diagonalization.


Electronic structure calculations in quantum chemistry are generally based on the Born-Oppenheimer approximation (BOA). The error generated by the BOA is negligibly small in most cases such as thermo-dynamical discussions in chemical reactions or molecular geometries. However, the BOA breaking effects are non-negligible in the sense of spectroscopic accuracy. Spectroscopic accuracy in experiments has been drastically improved during a few decades. The BOA breaking effects are possible to be observed in the current experimental techniques.

The first-order correction to the BOA in perturbation theory is so-called diagonal Born-Oppenheimer correction (DBOC) \[^1\]. The DBOC is the expectation value of the nuclear kinetic-energy operators over the electronic wave function shown in Eq. (1).

\[
E_{DBOC} = \sum_{A=1}^{N} \frac{1}{2M_A} \left\langle \Psi (\mathbf{r}; \mathbf{R}) \right| \nabla_{R_A}^2 \left| \Psi (\mathbf{r}; \mathbf{R}) \right\rangle .
\]  

Here, the summation runs over all nuclei in a molecule. \(N\) is the total number of nuclei. \(M_A\) is the corresponding nuclear mass and \(\nabla_{R_A}^2\) is the second-derivative with respect to nuclear coordinate \(R_A\). \(\Psi (\mathbf{r}; \mathbf{R})\) is the normalized electronic wave function depending on the electronic coordinates \(\mathbf{r}\) and nuclear coordinates \(\mathbf{R}\).

In this study, we have developed a program to evaluate the DBOC based on relativistic Hamiltonians at the restricted HF level. We have adopted the 2nd-order and infinite-order Douglas-Kroll-Hess (IODKH) methods at their spin-free levels.

We discuss the relativistic effect on the DBOC using as benchmarks the alkaline earth metal (Be, Mg, Ca, Sr), group 12 (Zn, Cd, Hg) and noble gas (He, Ne, Ar, Kr, Xe, Rn) atoms. Fig. 1 shows the \(E_{DBOC}\) of these atoms at the non-relativistic and IODKH levels. We used the primitive Gaussian functions from ANO-RCC basis set except for polarization functions for all atoms. The two DBOC energies calculated non-relativistic and IODKH are similar in lighter atoms (until around \(Z=20\)) but their difference increases significantly for heavier atoms. For Rn, the relativistic correction to \(E_{DBOC}\) is around 27%. The DBOC itself apparently larger in heavier atoms. Therefore, the DBOC might be important for heavier atoms. In my poster, we will also discuss the molecular systems, \(\text{H}_2\text{X}(\text{X}=\text{O}, \text{S}, \text{Se}, \text{Te})\)\[^2\].

Real-time solution of the time-dependent Dirac-Coulomb equation

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In this poster I will outline an approach to solve the time-dependent Hartree-Fock and Kohn-Sham equations with the relativistic four-component Dirac-Coulomb Hamiltonian and demonstrate an application to X-ray spectroscopy. The approach is based on the direct propagation of a one-electron reduced density matrix in the time domain, thus obtaining a non-perturbative solution of the time-dependent equations [1]. We have implemented this method in the ReSpect [2] code (Relativistic Spectroscopy) and performed one-component benchmark calculations. Results on this poster will include the sulfur L₂ and L₃ edges of the SF₆ molecule, where a properly captured splitting of the sulfur p-orbitals due to the spin-orbit interaction will be shown, and the shifts of the fluorine K-edge excitations caused by the relativistic effects [3]. Our results agree well with available experimental data [4].

A relativistic four-component method for calculations of indirect nuclear spin-spin coupling tensors at the non-collinear density functional level of theory is reported. The present implementation differs from the previously published one [1, 2] in two main points. 1) no approximations to the four-center integrals and the exchange-correlation functional were made and 2) the contribution from the exact exchange is included thus allowing the use of hybrid DFT functionals. All calculations employ a state-of-the-art four-component approach using a restricted magnetically balanced basis set (mDKS-RMB). Benchmark calculations are presented for the set of small systems as well as chemically relevant systems with more than 50 atoms. Importance of proper treatment of relativistic effects in calculation of indirect nuclear spin-spin coupling constants between one heavy and one light nucleus or between two heavy nuclei is emphasized. For this purpose the results obtained with the new approach are compared with the results of more approximate methods as well as with available experimental data.

Electronic absorption spectra from 4-component real-time
time-dependent DFT

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A fully relativistic four-component approach for solving the time-dependent Dirac equation is presented and implemented. The method is based on the numerical solution of the time-dependent Dirac equation in real time in the framework of Hartree-Fock and DFT approaches. The time-dependent Dirac equation is solved by a second order mid-point Magnus method [1].

This poster demonstrates an application of the method for calculations of electronic absorption spectra. As in more traditional non-relativistic calculations [1], the absorption energies are obtained by using a Fourier analysis of the time evolution of the dipole moments after exiting a system in its ground state by an external impulse. The method also allows one to obtain the relative intensities of the excitations.

The developed method was implemented in the ReSpect code [2] and applied to a number of model systems [3]. Calculations for hydrogen-like atoms where an analytical solution of the Dirac equation is available show a very good match with the analytical solution. The results for the ns → np excitations in group 12 atoms demonstrate that the method is able to reproduce experimental excitation energies including formally spin-forbidden transitions and in agreement with other calculations [4, 5].

References

Extensive relativistic modeling of NMR and NSOR parameters

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The relativistic effects are important for relatively light elements in the context of nuclear spin spectroscopies, such as nuclear magnetic resonance (NMR) as well as novel nuclear spin-induced optical rotation (NSOR) spectroscopy [1]. In this presentation, I will discuss several cases where the proper treatment of relativity as well as basis set and electron correlation effects provides predictive, and even quantitative, quality NMR and NSOR parameters that can be used in conjunction with highly accurate rovibrational treatment or in extended, nano-sized, systems in order to, e.g., reach the bulk limit.

In addition to a heavy nucleus itself, the NMR shielding of light element in close vicinity of it is affected by the well known relativistic heavy-atom to light-atom (HALA) effect. In order to model NMR chemical shift in novel Xe-molecules, it is imperative to combine high-level correlation treatment with relativistic modeling [2]. In addition to decisive HALA effects on rovibrationally averaged light atom NMR shieldings [3], we also discuss the fully quantum mechanical treatment of thermal rovibrational effects on relativistic light and heavy atom NMR shieldings and their isotopic shifts [4,5].

Since the Knight shift due to the relativistic Dirac fermions plays only a minor role, we have been able to provide reasonable estimates for NMR parameters of pure graphene [6,7] and its derivatives [7] by extrapolation to large system limit. By switching the focus on, perhaps more interesting, finitesized graphene quantum dots (GQD), we have shown how they can be characterized in detail by NMR spectroscopy [8].

The optical detection of nuclear magnetic polarization effects, such as NSOR [1], combines the molecular antisymmetric polarizability with the hyperfine interactions. Therefore, the NSOR is shown to be very sensitive to the electron correlation and basis set [1], rovibrational and environmental [9] as well as relativistic effects [9]. While being computationally very demanding third-order property, the novel completeness optimized (CO) -basis sets enable DFT modeling of Faraday optical rotation (FOR) and NSOR in GQDs [10].

Electric multipole polarizabilities of the ground state of the relativistic hydrogen-like atom: application of the Sturmian expansion of the generalized Dirac–Coulomb Green function

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For many physical problems, the knowledge of the Dirac–Coulomb Green function is required. Among several well-known representations of that function, a particularly convenient one is that in the form of the Sturmian expansion constructed in [1]. It was already used to derive closed-form expressions for various electromagnetic properties of the relativistic hydrogen-like atoms in electric or magnetic dipole fields.

Using the Sturmian expansion of the generalized Dirac–Coulomb Green function [1], we derive a closed-form expression for the multipole electric polarizabilities of the ground state of the Dirac one-electron atom placed in a weak, static, multipole electric field. The result is of the form:

\[ \alpha_L = \alpha_{L,L} + \alpha_{L,L-1}, \]  
(1)

where

\[ \alpha_{L,L} = \frac{a_0^{2L+1}}{2^{2L} Z^{2L+2}} \frac{L \gamma_1 (\gamma_1 + 2) \Gamma(2 \gamma_1 + 2L + 2)}{(2L + 1)^2 \Gamma(2L + 1)} \left[ 1 - \frac{(\gamma_1 + 1)^2 (\gamma_1 + 1)^2 (\gamma_1 + 1)^2}{\gamma_1 (\gamma_1 + 2) \Gamma(2 \gamma_1 + 2L + 2) \Gamma(2 \gamma_1 + 2L + 1)} \right] \]  
(2)

and

\[ \alpha_{L,L-1} = -\frac{a_0^{2L+1}}{2^{2L} Z^{2L+2}} \frac{\gamma_1 (L \gamma_1 - 2L - 2) \Gamma(2 \gamma_1 + 2L + 2)}{(2L + 1)^2 \Gamma(2 \gamma_1 + 1)} \left[ 1 - \frac{(L \gamma_1 - L - 1)^2 (L \gamma_1 + 1)^2 (\gamma_1 + 1)^2}{L \gamma_1 (L \gamma_1 - 2L - 2) \Gamma(2 \gamma_1 + 2L + 2) \Gamma(2 \gamma_1 + 1)} \right] \]  
(3)

Here \( \Gamma(z) \) is the Euler’s gamma function, \( \gamma_\kappa = \sqrt{\kappa^2 - (\alpha Z)^2} \) (\( \alpha \) is the Sommerfeld’s fine structure constant), while \( \_3F_2 \) is the generalized hypergeometric function.

We show that analogous formulas and numerical result in [2] contained mistakes. For \( L = 1 \) (dipole field), our expression agrees with earlier calculations [1,3]. In the nonrelativistic limit our formula reduces to the expression for the multipole polarizability of the Schrödinger one-electron atom in the ground state [4].

Molecular dynamics of $[\text{Cu(H}_2\text{O)}_{36}]^{2+}$ clusters including calculations of hyperfine coupling constants/Fermi contact terms

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Molecular dynamics (MD) of Cu(II) in water environment is presented. The 300 and 350 K MD simulations are carried out in NWChem package [1]. The studied system is composed of one copper dication solvated with thirty molecules of water. MD simulation of the aforementioned bulk at 300 K prefers more the sixfold coordination of Cu(II) dication, while at 350 K the coordination number is dynamically changing between five and six.

The non-relativistic (NR) B3LYP/6-31G** calculations of Fermi contact terms are carried in NWChem package [1]. The four-component relativistic (REL) calculations of B3LYP/unc-cc-pVDZ hyperfine coupling constants (HFCC) of Cu(II) are performed in ReSpect program [2]. It is found, that the first solvation sphere (coordination polyhedron) has a dominant influence in the case of the NR calculations of Fermi contact terms. The inclusion of molecules from second solvation sphere and/or COSMO solvation model has been found of small importance in such calculations. The relativistic effects (especially spin-orbit contribution) as well as a proper evaluation of HFCC [3-5] are found essential, i.e. there is significant shift between the NR Fermi contact terms and the 4-component REL hyperfine coupling constants of copper dication.

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RELATIVISTIC EFFECTS ON MAGNETIC SHIELDINGS
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Recent theoretical and computational developments of full relativistic formalisms give now the opportunity to calculate and analyse the electronic origin of magnetic molecular properties of heavy-atom containing molecules, and improve the understanding of such properties.

DFT is usually the method of choice for calculation of NMR properties in medium-size heavy-atom containing molecules because it includes electron correlation at an affordable computational cost. Only in non relativistic regime it gives reliable results compared with experimental ones but it is not good enough in relativistic calculations of NMR magnetic properties. This is because the functional used were developed in order to assess the study of medium-size heavy-atom containing molecules or to analyse NR-like electronic mechanisms that may explain tendencies or absolute values of magnetic shieldings. It is, therefore, of interest to assess whether DFT is a valuable tool in quantitative predictions of Sn and Pb NMR properties.

In this work we present calculations of NMR shieldings of Sn and Pb atoms in XY4nZn (X = Sn, Pb; Y, Z = H, F, Cl, Br, I) and PbH4−nIn (n = 0, 1, 2, 3, 4) family of compounds with four-component functionals. We found that results of calculations with Relativistic Polarization Propagator Approach at Random Phase Approximation level (RelPPA-RPA) are more reliable than the DFT ones. We carried out calculations of nuclear magnetic shieldings with different functionals (KT2, KT3, PBE0, B3LYP, BLYP and BP86) and we argue on why those DFT functionals must be modified in order to obtain better results of such parameter within the relativistic regime. There is a dependence among both, electron correlation and relativistic effects that should be introduced in the functionals. They were parameterized only within a nonrelativistic regime and so they are not able to introduce properly the relativistic effects.

We also applied the linear response elimination of small components (LRESC) formalism to calculate those shieldings and learn whether including only few leading relativistic correcting terms is enough for getting quantitative reproduction of the full relativistic value. It was observed that the nuclear magnetic shieldings change when the number and weight of the substituent heavy-halogen atoms varies. We analysed also each relativistic correction given by the LRESC method and splitted them in two: core-dependent and ligand-dependent, looking for the electronic mechanisms involved in the different relativistic effects and in the total relativistic value. From this analysis we were able to study in more detail the electronic mechanism involved in the new relativistic effect proposed recently and named as heavy atom effect on vicinal heavy atom (HAVHA). We found that the main electronic mechanism is the Spin-orbit or \( \sigma_p^{(1)} \) correction, though \( \sigma_p^{(1)} \) and \( \sigma_p^{(3)} \) corrections are also important.

The Absolute Shielding Constants of Heavy Nuclei: Resolving the Enigma of the $^{119}$Sn Absolute Shielding

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Despite careful experimental work, the tin absolute shielding constants show large differences between experimental results and four-component relativistic calculations. We demonstrate that this apparent disagreement is due to the breakdown of the commonly assumed relation between the electronic contribution to the nuclear spin-rotation constants and the paramagnetic contribution to the NMR shielding constants. We further show that this breakdown has significant consequences for determination of absolute shielding constants of nuclei, leading i.e. to differences of about a 1000 ppm for $^{119}$Sn.[1]

Calculation of the binding energies of berylliumlike ions

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In this work the calculations of the binding energies of four-electron (berylliumlike) ions are performed for the wide range of the nuclear charge values $Z = 18 - 96$. To formulate the QED perturbation theory the two-time Green function method is employed [1]. Instead of the usual Furry picture, where only the nucleus is considered as a source of the external field, here we add to the zeroth-order Hamiltonian also some screening potential. The perturbation theory is constructed in powers of the difference between the full QED interaction Hamiltonian and the screening potential. This approach accelerates the convergence of the perturbative series. As the main screening potential the local Dirac-Fock potential is used [2]. The calculations with other potentials (Kohn-Sham, Perdew-Zunger) allow to estimate the uncertainty of our results.

The calculations incorporate the first two orders of the rigorous QED perturbation theory. The third and higher orders of the interelectronic interaction are calculated within the Breit approximation by means of the configuration-interaction Dirac-Fock-Sturm method [3, 4]. In addition, the effects of nuclear recoil and nuclear polarization are taken into account.

Investigations of highly charged berylliumlike ions (along with investigations of H-, He- and Li-like systems) may serve for tests of QED at strong fields. Furthermore, such precise calculations might be useful for the tasks of mass spectrometry [5].

Mechanism of spin-orbit effects on the ligand NMR chemical shift in transition-metal complexes

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The relativistic effects of heavy atom (HA) can contribute significantly to the nuclear magnetic shielding on neighboring light atom (LA), via so called HALA effects.[1] A part of the relativistic nuclear shielding on the light atom related to the spin-orbit coupling is called spin-orbit shielding, $\sigma^{SO}$. The spin-orbit effects are propagated from the HA to the LA typically via dominating Spin-orbit/Fermi-contact mechanism (SO/FC).[2] This propagation has been shown to be affected by s-character of the light atom in the bond and energy differences between $\sigma^{SO}$-active occupied and vacant molecular orbitals.[2],[3] In our study of octahedral iridium(III) complexes, we indicated another factor influencing magnitude of the $\sigma^{SO}$, the d-character of the transition-metal atom (amount of d orbitals) involved in the HA-LA bonding.[4] The correlation between the d-character and the $\sigma^{SO}$ was tested on a series of Ir(III), Pt(II), Pt(IV), and Au(III) complexes and was found to be applicable in a set of compounds with the same central atom.[4]

The $\sigma^{SO}$ on the light atom in Ir(III) or Pt(II) complexes can easily amount $+40$ ppm, while in gold compounds one may observe negative $\sigma^{SO}$ contributions ($-20$ ppm, see Figure). Based on the analysis of molecular orbitals in d⁸ square-planar complexes we try to rationalize this difference in terms of different orbital compositions for the gold and platinum complexes.

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Simulation of a COLTRIMS Experiment for Direct Determination of Absolute Configuration

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In a conceptual study [1] we could show that Cold Target Recoil Ion Momentum Spectroscopy (COLTRIMS) can be used for the direct determination of the absolute configuration in the gas phase on a per molecule basis. For this purpose, the time of flight of ionic fragments and their impact data on a position sensitive detector are employed. We implemented a molecular dynamics simulation to calculate the trajectories of ionic fragments and thereby mimic the Coulomb explosion imaging (CEI) experiment after initial five-fold ionization of the methane derivatives R- and S-CHBrClF. Trajectories computed for random orientations and varying enantiomeric ratios were employed to generate artificial event sets that were used to test the analysis routines for the experimental data. The computational setup and simulation results are presented on this poster and compared to experimental data. It is possible to extend the simulation to more realistic potentials and fragment distributions.

Relativistic calculations of critical distances for homonuclear quasi-molecules

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Homonuclear one-electron quasi-molecules in molecular physics are analogous to hydrogen-like ions in atomic physics. It is known that the ground-state level reaches the upper border of the negative-energy continuum spectrum when the internuclear distance $R$ becomes equal to the critical distance $R_{cr}$. For distances $R < R_{cr}$, the ground-state level dives into the negative-energy Dirac continuum. In the present work, the critical distances for homonuclear quasi-molecules are calculated for a range of point-like and extended nuclei with $85 \leq Z \leq 100$. In addition, high-precision relativistic calculations of the ground-state energies of molecular ions with charges $Z=1, 2, 10, 20, 30, 40, 50, 60, 70, 80, 90, 92, 100$ at “chemical distances” $R = 2/Z$ (in a.u.) are performed. To solve the two-center Dirac equation the Dirac-Fock-Sturm method [1] is used. According to this method the wave functions represent a set of the Dirac-Sturm basic functions, which are central-field four-component Dirac bispinors centered at the ions. The radial parts of these orbitals are obtained by solving numerically the finite-difference radial one-center Dirac and Dirac-Sturm equations.

The results for the ground-states energies of the molecular ions are compared with the corresponding data obtained in [2]. As to the critical distances, they are compared with the related calculations performed in [3, 4, 5, 6, 7, 8].

The relevance of 4f-orbitals in the electronic structure of Ce(C₈H₈)₂, Ce(C₈H₆)₂ and Cp₂CeZ (Z = O, NH, CH-, CH₂)

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The electronic structure of bis(η⁸-cyclooctatetraene), bis(η⁸-pentalene) and bis(cyclopentadienyl) cerium systems of the type Cp₂CeZ (Z = O, NH, CH-, CH₂) is analyzed. CASSCF calculations were performed using unitary rotations in the orbital space. It can be shown that bis(η⁸-cyclooctatetraene) and bis(η⁸-pentalene) cerium have an open-shell singlet ground state for orbitals with maximum cerium 4f and ligand π character. This corresponds to a Ce(III)-based molecular Kondo system. Electronic structure calculations on bis(cyclopentadienyl) cerium systems also indicate an open-shell singlet ground state. In case of Z = CH-, CH₂ the singlet ground state consists to more than 90% of the 4fπ configuration when using nearly pure cerium 4f and carbon π orbitals of the Z-group. In contrast, the systems with Z = O, NH have a contribution of about 58% a₁p₁ for the singlet ground state where a is an orbital with a mixed cerium 4f and 5d character. In this case the π character of the Z-group (oxygen or nitrogen) was maximized.

Figure 1: Orbital mixing (top) and configuration mixing (bottom) in Cerocene at the CASSCF level. Vertical lines indicate situations with a leading a₄ (-4.5°) and a₃b₁ (+25.0°) configuration, exhibiting strong and weak Ce 4f-ring π orbital mixing, respectively.

Potential Energy Surfaces of $\text{Au}_n\text{Pt}_m$ ($n+m=4$) at Scalar and Two-Component Relativistic Levels

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Clusters of gold\textsuperscript{[1]}, platinum\textsuperscript{[2]} and their mixtures are relevant in many fields of research due to potential applications in medicine, catalysis, nanomaterials, among others. For $\text{Au}_4$, a structure of $D_{2h}$ symmetry is reported as the global minimum\textsuperscript{[3]}, whereas for $\text{Pt}_4$, if the spin-orbit (SO) coupling is considered, a structure of $D_{2d}$ symmetry is found, while a structure of $C_{3v}$ symmetry is the global minimum without SO effects\textsuperscript{[2]}. Non-relativistic calculations on the bimetallic clusters suggest planar structures for the global minimum\textsuperscript{[4]}. Although for the monometallic clusters studies considering the SO coupling have been reported, it should be noted that it is possible to complement such information exploring other structural motifs and different spin states.

In view of the above, we performed a computational study at DFT scalar and two-component relativistic levels for $\text{Au}_n\text{Pt}_m$ ($n+m=4$) starting from eight different structural motifs in the three lowest spin states of each system. We present an analysis of the effects of SO coupling on the geometries and the relative energies.

When SO coupling is considered during the optimization, the structures become closer in energy. For $\text{Au}_4$ one structure of $D_{3h}$ symmetry is reported for the first time here, whose relative energy does not change when the SO effects are considered (see Figure 1).

Finally, for the scalar relativistic calculations we present the relative energetic ordering of structures in different spin states, and evidence of overlapping among such potential energy surfaces.

Analytical gradient for spin-dependent infinite-order Douglas-Kroll-Hess method with local unitary transformation

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Relativistic effect is essential for reliable prediction of molecular property in heavy-element system. We have developed the local unitary transformation (LUT) scheme [1-3] with the spin-free infinite-order Douglas-Kroll-Hess (IODKH) method [4,5] to achieve the accurate and efficient two-component relativistic energy and geometry calculations at the HF, MP2, and DFT levels. In this study, the analytical energy gradient of the spin-dependent (SD) IODKH method with/without the LUT scheme was developed.

In the IODKH method, the Dirac Hamiltonian is completely block-diagonalized by unitary transformation. This transformation in the LUT scheme is approximated by the block-diagonal form of the subsystem contributions adopted as atomic partitioning. This simplifies the derivative expression of the IODKH method as follows:

\[
\frac{\partial}{\partial R_{ij}} \langle \psi | H^{NR} | \psi \rangle = \begin{cases} 
\frac{\partial}{\partial R_{ij}} \langle \psi | \sum_{\alpha} V_{\alpha} | \psi \rangle & (A = B) \\
\frac{\partial}{\partial R_{ij}} \langle \psi | \sum_{\alpha} V_{\alpha} + V_{\alpha}^{A,B} | \psi \rangle + \frac{\partial}{\partial R_{ij}} \langle \psi | V_{\alpha}^{A,B} | \sum_{\alpha} V_{\alpha}^{A,B} | \psi \rangle & (A \neq B, R_{ij} \leq \tau) \\
\frac{\partial}{\partial R_{ij}} \langle \psi | V_{\alpha}^{A,B} | \sum_{\alpha} V_{\alpha}^{A,B} | \psi \rangle & (A \neq B, R_{ij} > \tau)
\end{cases}
\]  

where A, B, and C are the subsystems, \(R_A\) is the coordinate of the nucleus A, \(H^{NR}\) is the kinetic operator, \(V^{NR}\) is the nuclear-attraction operator, \(V^\alpha\) is the relativistic nuclear-attraction operator, \(R_{AB}\) is the distance between atoms A and B, and \(\tau\) is the cutoff radius of the relativistic interaction. Table 1 shows the bond length of diatomic molecules obtained by the non-relativistic Table 1: Bond length (Å) of diatomic molecules.

| (NR), (LUT-)SF-IODKH, (LUT-)SD-IODKH, and four-component (4c) methods at the HF level. We confirmed that SD-IODKH is highly accurate: the largest difference from 4c in SD-IODKH is 0.005 Å. LUT-SF-IODKH also reproduced the bond length of 4c within 0.005 Å. Figure 1 shows the system-size dependence of the CPU time in the SF-IODKH and LUT-SF-IODKH transformation of one- and three-dimensional silver clusters. The results indicate that the LUT scheme drastically reduces the computational costs of conventional IODKH transformation. The scalings are liner even in three-dimensional clusters. |

Theoretical studies of P & T violations in heavy polar diatomic molecules

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Abstract

It is widely recognized that heavy atoms and heavy-polar diatomic molecules are the potential candidates for the experimental search for the permanent electric dipole moments (EDMs) arising from the violations of space inversion symmetry (P) and time reversal symmetry (T). The observations of non-zero P,T-odd effects in these systems at the presently accessible (expected) level of experimental sensitivity would signal new physics beyond the Standard Model (SM) of electroweak and strong interactions [1]. This is undoubtedly of fundamental importance in physics. Despite the well known limitations of the SM, there is very little experimental data available which would be in direct contradiction with this theory [2]. Some popular extensions of the SM, which overcome its disadvantages are yet to be confirmed experimentally.

In this presentation, the evaluations of the \( P,T \)-odd interaction strengths \( W_d \) and \( W_s \), using the relativistic many-body theory will be discussed. The former arises from the interaction of electron EDM \( d_e \) with the molecular electric field, and the latter arises due to the electron-nucleus scalar-pseudoscalar (S-PS) interaction. The knowledge of \( W_d \) is essential in obtaining a reliable limit on the electron EDM \( d_e \), while that of \( W_s \) is necessary to extract the information related to the electron-nucleus (S-PS) coupling constant \( k_s \), and the two together, to test the SM of particle physics. The most recent results of \( W_d \) and \( W_s \), for the ground state of YbF obtained using a state-of-the-art coupled cluster (CC) approach will be presented and compared with those estimated earlier [3].

References


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Calculation of nuclear magnetic resonance shielding tensor using frozen density embedding in the relativistic framework

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The modelling of nuclear magnetic resonance (NMR) parameters (such as the NMR shielding tensor) of compounds containing heavy metal nuclei in the condensed phase still poses many challenges for modern quantum chemistry. One difficulty arises from the nature of compounds containing heavy nuclei, which calls for the accurate treatment of both electron correlation and relativistic effects, the latter being essential for calculating the shielding tensor of both heavy and light nuclei connected to the first, due to the so-called “heavy-atom effect on the light-atom shielding” (HALA)¹ effect. Another difficulty is that the shielding tensor is very sensitive to changes in electronic structure caused, for instance, by interactions of a compound with its immediate surroundings (e.g. solvent molecules)², thus requiring an accurate description of the interaction between the two.

While nowadays calculations of the NMR shielding tensor of compounds with heavy centres can be routinely performed with a wide range of relativistic Hamiltonians and post-Hartree-Fock², ³ methods, most of them are performed on isolated species or with embedding models based on continuum solvation models or combined quantum mechanics/molecular mechanics (QM/MM) schemes. While the latter may represent an improvement over calculation on the isolated species, it remains the case that they cannot properly treat specific interactions (such as hydrogen bonding) which can be of great importance for NMR spectra.

An interesting but relatively unexplored alternative⁶ is the use of purely quantum mechanical embedding methods such as frozen-density embedding (FDE)⁴ which, apart from being capable of describing such specific interactions, allow for a seamless combination of density functional theory (DFT) and wave-function theory (WFT) methods⁵ in a cost-effective framework for obtaining molecular properties. In this contribution we therefore discuss the generalisation of the FDE formalism for obtaining NMR properties⁶ in a relativistic framework, outlining its implementation and applications to heavy-element compounds in an aqueous environment.

Charge displacement analysis on four-component relativistic electron densities: a characterization study of Cn (E112), Fl (E114) and E118 interacting with gold clusters

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We have recently devised a simple yet instructive scheme for analysing a chemical bond in terms of the charge rearrangement taking place upon formation of an adduct from two fragments. Our approach is based on the so called Charge Displacement (CD) function [1]

\[
\Delta q(z) = \int_{-\infty}^{z} dz' \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \Delta \rho(x, y, z') \, dx \, dy
\] (1)

defined as a progressive partial integration along a suitable z axis of the difference \( \Delta \rho \) between the electron density of the adduct and that of its non-interacting fragments. A careful analysis of the CD function (quantifying the charge flow, upon formation of a bond, along the interaction axis) proved to point out on a quantitative ground interesting bonding features such as, for example, donation and back-donation components in transition metal-alkenes and -alkynes interaction [2].

We carried out a computational campaign on Super Heavy Elements (SHEs) Cn (E112), Fl (E114) and E118 interacting with Auₙ (\( n = 1, 7, 20 \)) gold clusters using an efficient parallel implementation [3] of the all-electron four-component Dirac-Kohn-Sham (DKS) program BERTHA [4]. A comparative CD analysis on the Auₙ-SHE bond provides insights into the chemical properties of the considered SHEs, contributing to the still open debate about to what extent relativistic effects break group trends in the Periodic Table [5].

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Probing Ro-Vibrational and X-ray Absorption Spectroscopic Data for Very Heavy Rare-Gas Species with Relativistic Coupled Cluster Theory

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Rare gas dimers are dispersion bound molecules and their proper description therefore requires very high level of correlation theory. There are plenty of available experimental and theoretical data for spectroscopic constant up-to the dimer of Xenon but for the heavier rare gases (Z=86, 118) there are no reliable data so far [1]. Relativistic effects are also expected to be very strong for both the dimers. In the present contribution, we will first report CCSD(T)-sr-DFT results with relativistic Hamiltonian.

Core-hole spectroscopy is crucial test for relativistic methodologies. In the present study, we have investigated cases where spin-orbit coupling is expected to be high. Several physical effects such as core-relaxation, core-core correlation and the Auger shift need to be accurately described [2]. We report $\Delta CCSD$ calculations of core-ionisation energies with various physically motivated approximation to the CC amplitudes.


Chemical Aspects of the Actinide Series  
(also Correcting some Textbook Stories)

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It is well known in principle that the heavy f-block elements have a particularly rich set of valence orbitals, comprising s, p, d and f atomic orbitals of competitive importance. Direct-energy & self-consistent orbital effects of scalar relativity & spin-orbit coupling as well as the common core shielding & angular-momentum centrifugal effects all play a role, in addition to Coulomb correlation & angular momenta coupling. The demands of reliable computational approaches are challenging. Density functionals sometimes work, sometimes behave catastrophically like in the first-row transition metal series. - Compounds of the first actinoid octet (Ac, Th, Pa, U, Np, Pu, Am, Cm) exhibit many astonishing bonding properties. Carbon may be more convincingly called tetravalent than in C2; instead of a pi-bond, the spin-uncoupled di-radical may be more stable; actinoid oxide molecules show exciting patterns of electronic-geometric structures; heavy noble gas atoms may change the electronic state of a matrix encapsulated molecule; remarkable self-organizing patterns are obtained; etc. The textbook rules of atomic orbital occupation, of f-orbital relevance, of preferred oxidation states must be applied with some reservation.

The M1-to-E2 and E1-to-M2 cross-susceptibilities of the Dirac one-electron atom

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We consider a Dirac one-electron atom placed in a weak, static, uniform magnetic \( B \) [or electric \( F \)] field. We show that, to the first order in the strength of the perturbing field, the only electric \( Q^{(1)} \) [or magnetic \( \mathcal{M}^{(1)} \)] multipole moment induced by the field in the ground state of the atom is the quadrupole one. The coordinate-free form of these tensors are respectively

\[
Q^{(1)}_{2\mu} = (4\pi\epsilon_0) c \alpha_{M1\rightarrow E2} \left[ \frac{3}{4} (\nu_\mu B + B\nu_\mu) - \frac{1}{2} (\nu_\mu \cdot B) I \right] , \\
\mathcal{M}^{(1)}_{2\mu} = (4\pi\epsilon_0) c \alpha_{E1\rightarrow M2} \left[ \frac{3}{4} (\nu F + F\nu) - \frac{1}{2} (\nu \cdot F) I \right] ,
\]

where \( I \) is the unit dyad, \( \nu_\mu \) is the unit vector parallel (when \( \mu = +1/2 \)) or antiparallel (when \( \mu = -1/2 \)) to the field vector \( B \), while \( \nu \) is the unit vector antiparallel to the permanent magnetic dipole moment of the atom. The coefficients \( \alpha_{M1\rightarrow E2} \) and \( \alpha_{E1\rightarrow M2} \) appearing above are the magnetic-dipole-to-electric-quadrupole and the electric-dipole-to-magnetic-quadrupole cross-susceptibilities of the atom, respectively. Using the Sturmian expansion of the generalized Dirac–Coulomb Green function [1], we derive closed-form expressions for these two quantities [2, 3]. The results are of the form

\[
\alpha_{M1\rightarrow E2} = \frac{\alpha Z^4}{\Gamma^2 (2\gamma_1 + 5)} \left[ (\gamma_1 + 1) R - 1 \right], \\
\alpha_{E1\rightarrow M2} = -\frac{\alpha Z^4}{\Gamma^2 (2\gamma_1 + 5)} \left[ (\gamma_1 - 2) R - 1 \right],
\]

where \( \Gamma(z) \) is the Euler’s gamma function, \( \gamma_\kappa = \sqrt{\kappa^2 - (\alpha Z)^2} \), while

\[
R = \frac{\gamma_1 + \gamma_2}{\gamma_1 (\gamma_1 + 2)} \frac{\Gamma(\gamma_1 + 2) \Gamma(\gamma_1 + \gamma_2 + 3)}{\Gamma(\gamma_1 + \gamma_2 + 1)} \left( \begin{array}{c}
\gamma_2 - \gamma_1 - 2, \gamma_2 - \gamma_1 - 1, \gamma_2 - \gamma_1 \\
\gamma_2 - \gamma_1 + 1, 2\gamma_2 + 1
\end{array} \right) \cdot
\]

with \( {}_3F_2 \) being the generalized hypergeometric function. In the nonrelativistic limit, \( \alpha_{M1\rightarrow E2} \) tends to zero. This agrees with earlier calculations [4–6] of that quantity, based on the Schrödinger or Pauli equation for the electron, which predicted the quadratic dependence of the induced electric quadrupole moment on the magnetic induction \( B \).

The first of the authors very recently received a more general result for \( \alpha_{M1\rightarrow E2} \), which describes this quantity for an arbitrary excited state of the atom. [7]

BERTHA: Distributed Memory approach to all-electron Dirac-Kohn-Sham calculation

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We propose a full memory-distributed algorithm, which significantly improves the overall performances of the all-electron four-component Dirac-Kohn-Sham (DKS) module of the program BERTHA [1]. We developed an original procedure for mapping the DKS matrix between an efficient integral-driven distribution, guided by the structure of specific G-spinor basis sets [2] and by density fitting algorithms [3], and the two-dimensional block-cyclic distribution scheme required by the ScaLAPACK library employed for the linear algebra operations. This implementation, because of the efficiency in the memory distribution, represents a leap forward in the applicability of the DKS procedure to arbitrarily large molecular systems and its porting on last-generation massively parallel systems [4]. The performance of the code is illustrated by some test calculations on several molecular systems of increasing size performed on different architectures including the FERMI BlueGene/Q system at CINECA.

Figure 1: Memory usage per process as a function of the execution time using a number of processors increasing in doubling steps from 4 to 256.

U₂@C₈₀: Endohedral Fullerene with Unwilling U-U Bonding

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Abstract: The nature of bonding in U₂C₈₀ molecule found experimentally¹ is studied here. DFT pseudopotential calculations predict endohedral C₁ U₂@C₈₀ with a septet ⁷A_u ground state and r_U-U ~ 3.9 Å. Recent studies have shown that in small U₆@C₆₀ cage² multiple U-U bonding is forced sterically with a short r_U-U of ~ 2.5 Å while in large U₄@C₉₀ cage³ the U₂ unit dissociates to r_U-U ~ 6.5 Å. The U₂@C₈₀ system presents an interesting case. At the minimum distance r_U-U ~ 3.9 Å the MO analysis reveals presence of two one-electron-two-center bonds. The relevant MOs are formed of U(5f) orbitals. Quantum theory of atoms in molecules (QTAIM) also reveals U-U bonding. QTAIM delocalization index⁴ (DI = 1.01) points to a single U-U bond (or two one-electron two-center bonds) as compared to the reference free U₂ molecule (DI = 5.98) with multiple U-U bonding. The enclosed U atoms use their 5f electron shells to prevent unfavorable nuclear repulsion of charged U³⁺. Therefore, we coined the term “unwilling bonding” for this unique bonding pattern.

Figure 1. The U₂@C₈₀ and examples of U-U 5f-5f bonding orbitals.

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Prediction of structure and NMR chemical shifts in square-planar transition-metal complexes (Pt, Ir, Rh, Au, Pd)

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Prediction of NMR chemical shifts in heavy-atom compounds is still a demanding task for theoretical chemistry, mostly due to the relativistic effects originating at heavy atoms. The relativistic contributions of the heavy atom(s) can easily represent about one third (30%) of the total NMR shielding constant of the light atom.[1] To predict the NMR chemical shifts correctly, two basic things are required: relevant geometry and reliable method for calculation of NMR chemical shifts. Significant effects of geometry on the relativistic NMR shielding have been demonstrated[2] calling for the careful calibration of methods for optimizing the geometry.

To calculate the NMR shielding constants, one may use either four-component relativistic methods (demanding, but without any additional approximations within Dirac-Coulomb framework), or one- or two-component relativistic approximations like two-component ZORA approach (approximated, with some missing important terms, e.g., kernel contribution missing completely).[3]

We present a DFT calibration study, which is dealing with performance of various DFT functionals for geometry optimization as well as with the calculation of relativistic NMR shielding constants in square-planar Pt, Ir, Rh, Au and Pd complexes using two-(SO-ZORA in ADF) and four-component (as implemented in ReSpect) [4] methods. The geometry performance was evaluated using cluster models based on the X-ray topologies for a series of DFT functionals. Subsequently, the NMR chemical shifts were calculated for molecules optimized by the selected DFT approach. The influence of method (two- vs. four-component calculations), functional, and exact-exchange admixture in functional on the NMR chemical shifts of both light atoms (13C, 15N, 31P) and heavy atom (195Pt) will be discussed.

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The calculations of the carbon-carbon coupling constants mediated by a heavy atom

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The $^2J_{CC}$ spin-spin coupling constants in the systems with heavy atom (Cd, In, Sn, Sb, Te, Hg, Tl, Pb, Bi and Po) in the coupling path have been calculated by means of density functional theory. The main goal was to estimate HALA (heavy-atom-on-light-atom) effects on spin-spin coupling constants and to explore the factors which may influence the HALA effect on these properties, including the nature of the heavy atom substituent and carbon hybridization. The methods applied range, in order of reduced complexity, from Dirac-Kohn-Sham method (density functional theory with four-component Dirac-Coulomb Hamiltonian), through DFT with two- and one-component Zeroth Order Regular Approximation Hamiltonians, to scalar effective core potentials (ECPs) with the non-relativistic Hamiltonian. Thus, we are able to compare the performance of ZORA-DFT and Dirac-Kohn-Sham, ECP methods for modelling of the HALA effects on the spin-spin coupling constants.

The value of $^2J_{CC}$ depends strongly on electron configuration. Generally the $^2J_{CC}$ couplings are the biggest for compounds containing 12th group elements and the smallest for compounds containing 15/16th group elements. For the 5th row of periodic table the relativistic contribution to $^2J_{CC}$ does not exceed 26% of full spin-spin coupling constant, whereas for 6th row elements it is even about 83%.

The ratio between the spin-orbit coupling term and the scalar term depends on electron configuration of heavy atom and carbon type. For molecules containing 12-15th group elements scalar term is a leading term in the relativistic correction, whereas for 16th group of periodic table the spin-orbit coupling term becomes sizeable or even dominates the relativistic correction.

A comparison of the results obtained by means of different methods of including the relativistic effects indicates that ZORA-DFT (with the spin-orbit coupling term included) reproduces the DKS results very well.

The performance of scalar ECPs depends, obviously, on the relative weight of the scalar and the spin-orbit coupling terms, but when the former are dominant, ECPs reproduce correctly the results obtained with more elaborate relativistic method, provided the outer core electrons on the heavy atom are accounted for explicitly (‘small core’ types of ECPs).
Relativistic mapping between NMR and NSR

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We highlight three aspects of NMR (nuclear magnetic resonance) and NSR (nuclear spin-rotation):

(1) **Relativistic theory of NMR.** The nonrelativistic theory [1] of NMR was established in 1950 by Ramsey, but the corresponding relativistic counterpart was long plagued by the ‘missing’ diamagnetism. This was fully resolved only in 2007 [2] (for a recent review see Ref. [3]).

(2) **Relativistic theory of NSR.** The nonrelativistic theory [1] of NSR was also established in 1950 by Ramsey. Because of the involvement of nuclear degrees of freedom, the proper formulation must invoke the body-fixed relativistic molecular Hamiltonians [4,5] that are transformed rigorously from the space-fixed ones. Electrons are here treated fully relativistically, whereas nuclei are treated quasi-relativistically.

(3) **Relativistic mapping between NMR and NSR.** The nonrelativistic relation between NMR shielding and NSR constant was again established in 1950 by Ramsey [1] and was later popularized by Flygare [6]. According to this relation, a fully relativistic measurement (NSR constant) is translated into a nonrelativistic value, “experimental NMR shielding”. This is problematic even for F in HF: The relativistic effect is here ca. 5 ppm and larger by one order of magnitude than the error bar propagated from the uncertainty in the experimental measurement of NSR. It turns out [4,5] that a direct relativistic mapping between NMR and NSR is possible, which allows to establish true experimental NMR shielding scales[7].

For a comprehensive review, see Ref. [8].

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