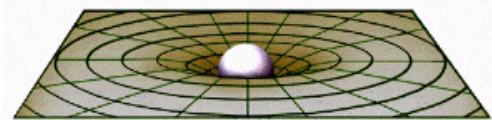


Relativistic effects in molecules

Relativistic Density Functional Theory: Efficient Methods for Molecules and Materials



Relativity is decisive for atomic configurations, bond lengths, binding energies, and many other properties of heavy-element compounds. Relativistic effects can be understood in terms of the relativity-induced contraction of s and p orbitals, the concomitant increased shielding of the nuclear field, and the resulting expansion of d and f manifolds. In addition to these kinematic effects, spin-orbit interaction as the second important relativistic effect is already noticeable in spectra of light elements. For heavy elements, spin-orbit effects become essential for the valence electronic structure; as they compare in magnitude to the Coulomb interaction of valence electrons.

Relativistic density functional studies performed in our group are based on the Douglas-Kroll-Hess (DKH) approach. The scalar relativistic variant of the DKH method of solving the Dirac-Kohn-Sham problem is an efficient procedure for treating compounds of heavy elements including such complex systems as transition metal clusters, adsorption complexes, and solvated actinide compounds. This method allows routine all electron density functional calculations on heavy-element compounds and provides a reliable alternative to the popular approximate strategy based on relativistic effective core potentials. For many application problems where a spin-orbit interaction is of crucial importance two-component DKH variants are applied.

Our implementations of this methodology, at first in the LCGTO-FF-DF program (linear combination of Gaussian-type orbitals fitting functions density functional),^[1,2,3] and later on in the parallel DF software ParaGauss^[4,5] had long been the only ones applied to problems beyond methodological tests on small molecules.^[6]

[1] B.I. Dunlap, N. Rösch:

The Gaussian-Type Orbitals Density-Functional Approach to Finite Systems, in: *Density Functional Theory of Many-Fermion Systems*, S. B. Trickey (Hrsg.), *Adv. Quantum Chem.*, **21**, 317-339 (1990).

[2] O.D. Häberlen, N. Rösch:

A Scalar-Relativistic Extension of the Linear Combination of Gaussian-Type Orbitals Local Density Functional Method: Application to AuH, AuCl, and Au₂ *Chem. Phys. Lett.*, **199**, 491-496 (1992). DOI: [10.1016/0009-2614\(92\)87033](https://doi.org/10.1016/0009-2614(92)87033)

[3] V.A. Nasluzov, N. Rösch:

Density Functional Based Structure Optimization for Molecules Containing Heavy Elements: Analytical Energy Gradients of the Douglas-Kroll-Hess Scalar Relativistic Approach to the LCGTO-DF Method *Chem. Phys.*, **210**, 413-425 (1996). DOI: [10.1016/0301-0104\(96\)00137-1](https://doi.org/10.1016/0301-0104(96)00137-1)

[4] N. Rösch, S. Krüger, M. Mayer, V.A. Nasluzov:

The Douglas-Kroll-Hess Approach to Relativistic Density Functional Theory: Methodological Aspects and Applications to Metal Complexes and Clusters, in: *Recent Developments and Applications of Modern Density Functional Theory*, J. M. Seminario (ed.), Elsevier, Amsterdam, 497 (1996). [Link](#)

[5] T. Belling, T. Gauschopf, S. Krüger, F. Nörtemann, M. Staufer, M. Mayer, V.A. Nasluzov, U. Birkenheuer, N. Rösch: ParaGauss, Version 2.0, Technische Universität München, (1998).

[6] Th. Belling, Th. Gauschopf, S. Krüger, F. Nörtemann, M. Staufer, M. Mayer, V. A. Nasluzov, U. Birkenheuer, N. Rösch:

ParaGauss: A Density Functional Approach to Quantum Chemistry on Parallel Computers, in: *Scientific Computing in Chemical Engineering II*, Vol. 1, F. Keil, M. Mackens, H. Voß und J. Werther (Hrsg.), Springer, Heidelberg, 1999, S. 66-73.

[7] T. Belling, T. Gauschopf, S. Krüger, F. Nörtemann, M. Staufer, M. Mayer, V.A. Nasluzov, U. Birkenheuer, A. Hu, A. Matveev, A.V. Shor, M.S.K. Fuchs-Rohr, K.M. Neyman, D.I. Ganyushin, T. Kerdcharoen, A. Woiterski, N. Rösch: ParaGauss, Version 2.2, Technische Universität München, 2001.

- [8] M. Mayer, S. Krüger, N. Rösch:
A Two-Component Variant of the Douglas-Kroll Relativistic Linear Combination of Gaussian-Type Orbitals Density Functional Method: Spin-Orbit Effects in Atoms and Diatomics, *J. Chem. Phys.* **115**, 4411-4423 (2001). DOI: [10.1063/1.1390509](https://doi.org/10.1063/1.1390509)
- [9] A. V. Matveev, M. Mayer, N. Rösch:
Efficient Symmetry Treatment for the Nonrelativistic and Relativistic Molecular Kohn-Sham Problem. The Symmetry Module of the Program ParaGauss, *Comp. Phys. Comm.* **160**, 91-119 (2004). DOI: [10.1016/j.cpc.2004.02.013](https://doi.org/10.1016/j.cpc.2004.02.013)
- [9] S. Majumder, A. V. Matveev, N. Rösch:
Spin-Orbit Interaction in the Douglas-Kroll Approach to Relativistic Density Functional Theory: The Screened Nuclear Potential Approximation for Molecules, *Chem. Phys. Lett.* **382**, 186-193 (2003). DOI: [10.1016/j.cplett.2003.10.072](https://doi.org/10.1016/j.cplett.2003.10.072)
- [10] A. V. Matveev, V. A. Nasluzov, N. Rösch:
Linear Response Formalism for the Douglas-Kross-Hess Approach to the Dirac-Kohn-Sham Problem: First- and Second-Order Energy Derivatives, *Int. J. Quantum Chem.* **107**, 3236-3249 (2007). DOI: [10.1002/qua.21501](https://doi.org/10.1002/qua.21501)