MO 42: Quantum Chemistry (Theory)

Zeit: Mittwoch 11:30–12:15 Raum: 6D

MO 42.1 Mi 11:30 6D

Relativistic density functional calculations based on the 2-spinor minimax principle for diatomic molecules — •Ossama Kullie and Dietmar Kolb — FB18, Uni Kassel, Heinrich-Plett Str. 40, 341132 Kassel, Germany

The two spinor minimax method, utilizing the finite element methods (FEM), gives highly accurate values in relativistic density density functional calculations for two atomic molecules, especially considering systems with up to super heavy atoms like Rg_2. One obtain benchmark values for bond length, vibrational frequency, and dissociation energy. In our previous work we demonstrated this for Dirac-Fock-Slater (DFS) functional [1]. In present talk we show density functional calculations for different type of functionals including Non- and relativistic LDA,and eventual GGAs, functionals for the dimers of the group 11 (IB) of the periodic table Cu_2, Ag_2, Au_2, Rg_2. We compare our result with values from the literature and with the experimental values so far are available. We hope that we can, like in the case of DFS, show in a systematic way the behaviors of these functionals and shed new light on this behaviors.

[1] O. Kullie, H. Zhang, J. Kolb and D. Kolb, Relativistic density functional calculations using two-spinor minimax Finite-Element method and linear combination of atomic orbitals for $ZnO, CdO, HgO, UubO$ and Cu_2, Ag_2, Au_2, Rg_2. J. Chem. Phys. **126**, 1 (2007).

MO 42.2 Mi 11:45 6D

On the matrix singularity problem in the variational Gaussian wave packet method — •Tomaž Fabčič, Jörg Main, and Günter Wunner — 1. Institut für Theoretische Physik, Universität Stuttgart, 70550 Stuttgart

Variational solutions of the time-dependent Schrödinger equation are often based on Gaussian wave packets (GWP) as trial functions. The equations of motion for the time-dependent Gaussian parameters become ill-conditioned from time to time during the propagation, and this problem increases with the number of propagated GWP, leading to extremely small step sizes of the integration routines. On the other hand a sufficiently large number of GWP is necessary to obtain accurate results. The instabilities of the equations of motion are due to a temporary overcrowding of the set of GWP, making the set of linear equations that has to be solved after each time step of integration nearly singular. We present a novel method to overcome these numerical problems by subjecting the GWP to adequate inequality constraints, rendering the integration process orders of magnitude faster. The power of the method is demonstrated for a two dimensional non-integrable model potential.

MO 42.3 Mi 12:00 6D

Vanadium Oxide Compounds with Quantum Monte Carlo — •Annika Bande and Arne Lüchow — Institut für Physikalische Chemie, RWTH Aachen University, Landoltweg 2, 52056 Aachen, Germany

Transition metals and their compounds display an astonishing variety of all kinds of chemical systems which exhibit very different types of bonding and excitation spectra. These systems are at the forefront of electronic structure research, most appealing methods in this context are correlated ones such as configuaration interaction, coupled-cluster or quantum Monte Carlo (QMC).

In this study the QMC method has been used to calculate several vanadium oxide molecules and ions as well as the vanadium atom in the ground and different excited states. The guide functions, which consist of one or only few Slater determinants, were obtained from Hartree-Fock, density functional or multi configuration self consistent field calculations and supplemented with a Jastrow correlation factor. Different pseudopotentials were applied in order to optimize the QMC procedure in terms of efficiency to aim at extending the calculations to much larger systems and reaction pathways.