MO 15: Theorie: Quantenchemie

Zeit: Mittwoch 16:45–17:45   Raum: VMP 6 HS-F

MO 15.1   Mi 16:45   VMP 6 HS-F

The d-Hamiltonian: A new approach for evaluating optical spectra of transition metal complexes — •STEFAN LEBERNEGG, GEORG AMTHAUER, and MICHAEL GRODZICKI — FB Materialforschung und Physik, Universität Salzburg, Hellbrunnerstraße 34, A-5020 Salzburg

The full multi-centre molecular Hamiltonian in local density approximation for a mononuclear transition metal complex is transformed into a single-centre Hamiltonian explicitly including overlap, covalency and ligand-field effects. The orbital interactions of the metal d-orbitals with the ligand orbitals appear as a repulsive pseudopotential yielding the dominant contribution to the ligand-field splitting. This repulsive pseudopotential exhibits the same angular dependence as the electrostatic potential from the ligands entering the Hamiltonian of ligand-field theory. For this reason, ligand-field theory very often yields the correct splitting pattern of the d-orbitals. The radial part, however, is considerably different from the simple expression of ligand-field theory. In particular, there is no general theoretical justification for a R^{-5}-dependence of the ligand-field splitting even for complexes of cubic symmetry. The reliability and capability of this new approach is demonstrated by calculating the d-orbital splitting pattern for a number of selected systems. Therefore the d-Hamiltonian is a new and versatile tool for interpreting and evaluating optical spectra (as well as magnetic properties) of transition metal complexes.

MO 15.2   Mi 17:00   VMP 6 HS-F

Relativistic and non-relativistic local density functional, benchmark results and investigation on alkali dimers — •OSSAMA KULLIE[1,3], EBERHARD ENGEL[2], and DIETMAR KOLB[3] — [1]Laboratoire de Chimie Quantique, UMR 7177 CNRS/Universite Louis Pasteur, 4, rue Blaise Pascal, 67000 Strasbourg, France — [2]Center for Scientific Computing, J. W. Goethe University Frankfurt am Main. — [3]Department of Natural Sciences, University of Kassel, Germany

The two spinor minimax method combined with the numerical finite element method used by us has proved to be very accurate, one obtains benchmark values in relativistic density functional calculations for diatomic molecules with respect to the solution, and the relativistic contamination errors in the 4-spinor calculations which is avoided in the 2-spinor minimax formulation by exact projection against the negative continuum. I will show in the present talk investigation on the relat. and nonrelat. local-density functional on alkali dimers (Li_2 through Fr_2), presenting highly accurate results [1]. We give benchmark values for the respective functional thus showing the true behavior of these functionals and their trend with increasing Z the atomic charge. In comparison with experiment the alkali dimers exhibit a different behavior compared to the dimers of the group 11 investgated in our previous work [2] which indicates that the correlation part is more

crucial in the description of alkali dimers. [1] O. Kullie, E. Engel and D. Kolb, submitted to the J. Phys. B. [2] O. Kullie, H. Zhang, and D. Kolb, chem. Phys. **351**, 106 (2008).

MO 15.3   Mi 17:15   VMP 6 HS-F

A first principles scheme to distinguish between Förster and non-Förster excitation energy transfer — •DIRK HOFMANN and STEPHAN KÜMMEL — Department of Theoretical Physics, University of Bayreuth, 95440 Bayreuth, Germany

Excitation energy transfer is a key process in the light-harvesting mechanism initializing the energy-converting machinery of plants and photosynthetic bacteria. The standard method to interpret experimental data of excitation energy transfer between two molecules separated by a distance R is the so-called Förster theory. This theory considers separated donor and acceptor molecules interacting via a Coulomb interaction that is approximated as a dipole-dipole coupling. One of this theory's characteristics is a R^{-6}-dependence of the energy transfer rate. The aim of our work is to describe excitation energy transfer in the framework of Time-Dependent Density Functional Theory with real-time propagation on a real-space grid. This approach allows to go beyond the approximations of the standard (Förster) theory. Therefore, the method can be a valuable tool to distinguish between Förster like and non-Förster like excitation energy transfer.

MO 15.4   Mi 17:30   VMP 6 HS-F

Theoretical investigation of the proton transfer coordinates of 3-hydroxyflavone in the S_0 and S_1 states — •ANDREAS FUNK[1], MIHAJLO ETINSKI[2], KRISTINA BARTL[1], TIMO FLEIG[2], and MARKUS GERHARDS[1] — [1]Physikalische und Theoretische Chemie, TU Kaiserslautern, Erwin Schrödinger-Str. 52, 67663 Kaiserslautern — [2]Institut für Theoretische Chemie, Heinrich-Heine-Universität, Universitätsstr. 1, 40225 Düsseldorf

Proton transfer (PT) reactions in flavonoids play an important role for photoprotection. IR/UV experiments on 3-hydroxyflavone and its cluster with two water molecules yield, in combination with theoretical calculations, direct structural information for the electronic ground and excited state. Different partly unexpected geometries are discussed. According to the experiments a non proton transfer structure is observed for both the S_0 and the S_1 states but in the S_1 state the proton transfer can be induced leading to an additional proton transfer structure. As PT reaction coordinates can be strongly anharmonic, an accurate theoretical description of anharmonicities is of great importance to compare the results with experiments. A strategy to analyze the frequency of the OH stretching mode involved in the PT coordinates of the S_0 and S_1 states is presented. The potential energy surfaces of the PT coordinates have been calculated at the DFT, time-dependent DFT and CC2 level of theory. The results are compared to the IR/UV experiments of our group.