

MO 30 Poster: Quantum Chemistry

Zeit: Dienstag 16:30–18:30

Raum: Labsaal

MO 30.1 Di 16:30 Labsaal

Use of double group theory for analyzing the term splitting in crystal fields — ●KATYA RYKHLINSKAYA and STEPHAN FRITZSCHE — Universität Kassel, Institut für Physik, D-34132 Kassel, Germany

The electron structure and symmetry of crystals can be resolved by investigating the term splitting of atoms in a crystal field. i. e. if the electron density of the atom has to obey the symmetry of the crystal. Then, the presence of the electron spin and the spin-orbit interaction leads to an additional term splitting [1]. In fact, the concept of spin is very important to explain a number of phenomena, such as electron paramagnetic resonance, the Zeeman effect and various others.

The splitting of the electron terms in a crystal field can be treated using the so-called double symmetry groups. To facilitate the use of the double group theory we present the program BETHE [2], which has been extended recently in order to classify the term splitting in crystal fields and to generate approximate wave functions for atomic levels. In addition, our program also provides a simple access to the group theoretical data for 72 most widely applied point and double groups. The interactive design of this program is illustrated by a number of examples which may help the user in following the literature and in daily research work.

[1] B. S. Tsukerblat, *Group Theory in Chemistry and Spectroscopy* (Academic Press, London, 1994).

[2] K. Rykhinskaya, S. Fritzsche, *Comp. Phys. Commun.*, 171 (2005) 119.

MO 30.2 Di 16:30 Labsaal

Berechnung der magnetischen Eigenschaften kleiner Moleküle und Cluster in Rahmen der nicht-kollinearen DFT — ●J. ANTON und B. FRICKE — Institut für Physik, Universität Kassel, 34109 Kassel

Bei der Berechnung spektroskopischer Eigenschaften von kleinen Molekülen und Clustern wird oft die Dichte-Funktional-Theorie verwendet. Die Güte solcher Rechnungen hängt entscheidend von den verwendeten Austausch-Korrelation-Funktionalen ab. Für die offen-schaligen Moleküle ist es zB. notwendig die Spin-Polarisation der Elektronenhülle zu berücksichtigen. In einer nicht-relativistischen Beschreibung werden dann Dichte-Funktionalen verwendet, die nicht von der Ladungsdichte sondern von der Spin-Dichten abhängen. Bekanntlich ist der Spin eines Teilchen in einer relativistischen Beschreibung keine gute Quantenzahl, so daß dieser Konzept in die relativistische Theorie nicht übernommen werden kann. Dieses konzeptionelle Problem läßt sich aber mit Hilfe der Magnetisierungsdichte umgehen. In den letzten Jahren haben wir unseres relativistische DFT-Programm um die Magnetisierungsdichte erweitert [1]. Dies hat nicht nur zu deutlichen Verbesserungen bei der Berechnung der spektroskopischen Eigenschaften geführt, sondern öffnete uns zusätzlich einen Zugang zu den magnetischen Eigenschaften von Molekülen und Clustern.

Es werden die Auswirkungen der Nicht-Kollinearität der Magnetisierungsdichte auf die spektroskopischen und magnetischen Eigenschaften kleiner Moleküle und Cluster diskutiert. Diese Ergebnisse werden auch mit den experimentellen Werten verglichen.

[1] J. Anton, B. Fricke, E. Engel, *Phys. Rev. A* **69**, 012505 (2004)

MO 30.3 Di 16:30 Labsaal

Classical calculation of transient absorption spectra monitoring ultrafast electron transfer processes — ●IGOR USPENSKIY, BIRGIT STRODEL, and GERHARD STOCK — Institut für Physikalische und Theoretische Chemie, J.W. Goethe Universität Marie-Curie-Str. 11, 60439 Frankfurt am Main, Germany

The mapping approach [1] is applied to the classical description of the ultrafast electron transfer processes. Several classical approximations to calculate time- frequency- resolved pump-probe spectra are represented. We generalize various versions of semiclassical Frank-Condon approximation to the case of nonadiabatically coupled potential energy surfaces [2]. Moreover, we employed classical electron analog model to define the classical analog of electron dipole transition operator [3]. We studied foregoing methods for models, which describe (i) the internal conversions in symmetric potential spin-boson model with external ground state, and (ii) electron-transfer model in mixed-valence system of the compound $(\text{NH}_3)_5\text{Ru}^{\text{III}}\text{NCRu}^{\text{II}}(\text{CN})_5^-$ with reduced number of vibrational modes. Exact reference data are compared to approximate calculations of populations, wave-packet motions, as well as time-frequency resolved spectra

for various durations of the pump and probe pulses.

[1] G. Stock and M. Thoss, *Phys. Rev. Lett.* **78**, 578 (1997).

[2] S. Diltthey, S. Hahn, and G. Stock, *J. Chem. Phys.* **112**, 4910 (2000).

[3] G. Stock and W. H. Miller, *J. Chem. Phys.* **99**, 1545 (1993).

MO 30.4 Di 16:30 Labsaal

Quantum-classical calculation of time-resolved infrared spectra of biomolecules — ●ROMAN GORBUNOV, NGUYEN PHUONG, and GERHARD STOCK — Institut für Physikalische und Theoretische Chemie, J.W. Goethe Universität, Marie-Curie-Str. 11, 60439 Frankfurt am Main, Germany

Various approaches for the calculation of vibrational spectra of peptides in aqueous solution are discussed. To describe the amide I vibrations in peptides, we use an ab initio based exciton model combined with a solvent correction of local amide I frequencies. The exciton model of amide I vibrations contains the conformationally dependent force constants of the local vibrations as well as the coupling between them. The solvent correction is based on an empirical relation between frequency of the local vibrations in peptide and the corresponding electric field produced by surrounding water molecules. Conformational dynamics of the peptide and the dynamics of surrounding water molecules were obtained by classical molecular dynamic simulations. In the present work, we have studied the influence of the solvent correction on the vibrational spectra. Different protonation states (reflecting different pH values) were considered and their influence on the vibrational spectra was investigated. The accuracy of the second order cumulant expansion and the Condon approximation were studied for different cases.