MO 24 Theory I

Zeit: Samstag 14:00–16:15 Raum: HU 2097

MO 24.1 Sa 14:00 HU 2097

Effective Hamiltonian for the 1-body Reduced Density Matrix functional theory — •Nektarios Lathiotakis, Nicole Helbig, and E.K.U. Gross — Theoretische Physik, Freie Universitaet Berlin, Arnimallee 14, 14195, Berlin

One-body reduced density matrix (1-RDM) functional theory is an appealing choice to tackle the many-electron problem in atoms, molecules and solids. It has been shown to predict accurately the correlation energy in small molecular systems. 1-RDM functionals are usually expressed in terms of, and minimized with respect to, the natural orbitals and the corresponding occupation numbers.

There exists no non-interacting Kohn-Sham system reproducing the 1-RDM of interacting particles. We will demonstrate, however, that one can define a non-interacting system yielding only the natural orbitals of the interacting system. The effective Hamiltonian of this non-interacting system will be investigated, the meaning of its energy spectrum is discussed and a perturbative scheme to evaluate this Hamiltonian will be presented.

MO 24.2 Sa 14:15 HU 2097

Orbital Functionals in Current-Density Functional Theory — •Stefano Pittalis, Stefan Kurth, and Nicole Helbig — Freie Universität Berlin, Theoretische Physik, Arnimallee 14, D-14195 Berlin

A proper description of many-electron systems in the presence of magnetic fields within a density functional framework requires the current density to be used as basic variable besides the electron density. Unlike in ordinary spin-density functional theory, where only the coupling of the magnetic field to the spin degrees of freedom is taken into account, in current density functional theory (CDFT) one also allows for coupling to the orbital degrees of freedom. We will show how the Optimized Effective Potential formalism is extended to CDFT and present a practical scheme for the calculation of the xc-potential and xc-vector potential within a KLI-type approximation. Numerical results will be presented for open shell atoms.

MO 24.3 Sa 14:30 HU 2097

Different Variational Approaches to the Relativistic two-center Coulomb Problem — •Hui Zhang, Hongjun Luo, and Dietmar Kolb — FB 18, Univ. Kassel

In a recent paper [1] we showed that the minimax approach gives a perfect solution to the relativistic two-centre Coulomb problem for the light H_2^+ and the super-heavy Th_2^{179+}, free of any artefacts. However the non-linear energy dependence makes the calculations very expensive. Now we succeeded in variational linearizations where the well known kinetic balance may be viewed as the simplest approximation: by doubling the space of variational parameters and generating a systematic basis for the small spinor components the minimax values may be reached with high precision however keeping it a linear eigenvalue problem. Detailed comparisons with traditional 4-spinor and kinetic balance LCAO are made and further applications given.

[1] H. Zhang, O.Kullie, D. Kolb, J. Phys. B: At. Mol. Opt. Phys. 37, 905 (2004)

MO 24.4 Sa 14:45 HU 2097

Small molecules in VUV fields — •Björn Zimmermann and Jan-Michael Rost — Max-Planck-Institute for the Physics of Complex Systems, Nöthnitzer Str. 38, 01187 Dresden

In the near future the free electron laser in the VUV regime (XFEL) will become a reality. This will open to door to the short wave length regime in very intense fields, on which hardly anything is known. However, at the TESLA test facility it was already possible to perform with the very first XFEL light pioneering experiments on clusters and small molecules. We will present first results towards the understanding of the effects of those extreme VUV fields on small molecules.

MO 24.5 Sa 15:00 HU 2097

Electronic structure and core-hole dynamics of Ozone — •Karoline Wiesner — Center for Computational Science and Engineering, University of California Davis, One Shields Ave, Davis, CA 95616

The electronic structure of the ozone molecule has been studied with spectroscopic techniques and computations, focusing on core-hole states. The electronic configuration and the nuclear dynamics of O_3 have been found to be highly correlated. Effects of this correlation are found in several experiments. In this presentation a few results of that study will be focused on. Core ionization was studied with electron spectroscopy using synchrotron radiation. The induced nuclear dynamics observed are inherently different for ionization of the two sites. Ab-initio MRCI computations of the electronic configurations for the two core-ionized states explain the nuclear dynamics in terms of changes in the orbitals involved in the dominant configurations.Another effect of this correlatation was found in Resonant Auger Spectroscopy (RAE) experiments. A symmetry break in excitation probability was observed. It is explained with vibronic coupling between two core-excited states that leads to localization of the excitation to one of the two chemical bonds. This result verifies the localized picture of core excitation in large molecular systems, even when symmetry-equivalent sites are involed.

MO 24.6 Sa 15:15 HU 2097

Reaktionsquerschnitte und Geschwindigkeitskonstante der komplexbildenden S_N2–Reaktion $Cl^- + CH_3Cl' \rightarrow ClCH_3 + Cl'^-$ — •Carsten Hennig und Stefan Schmatz — Institut für Physikalische Chemie, Georg-August-Universität Göttingen, Tammanstr. 6, D-37077 Göttingen

Die Aufklärung des S_N2–Mechanismus in der Chemie ist von grundlegendem Interesse. Wir berichten von Berechnungen der Reaktionsquerschnitte und Geschwindigkeitskonstanten der symmetrischen S_N2–Reaktion $Cl^- + CH_3Cl' \rightarrow ClCH_3 + Cl'^-$ in einem dimensionsreduzierten Modell. Dabei werden die beiden C-Cl-Streckschwingungen, die Inversionsschwingung der Methylgruppe sowie die hochfrequente C–H–Streckschwingung in einer zeitunabhängigen quantenmechanischen Streurechnung explizit berücksichtigt.

Von besonderer Bedeutung ist der Einfluss der häufig als Beobachtermoden behandelten Inversionsschwingung und der C–H–Steckschwingung. In den Reaktionsquerschnitten zeigt sich – im Gegensatz zu diesem Konzept – noch deutlicher als in den zuvor berechneten Reaktionswahrscheinlichkeiten ein starker kooperativer Effekt der C-Cl-Streckschwingung mit der Inversionsschwingung sowie die Möglichkeit des Energietransfers aus der C–H–Streckschwingung.

Die Geschwindigkeitskonstante weist eine klare Abweichung vom experimentell bekannten Wert auf. Zur Erklärung wird auf mögliche neue Modelle zur Behandlung der Drehimpulse sowie der Abweichung von der Kollinearität eingegangen.

MO 24.7 Sa 15:30 HU 2097

Internal dynamics in $(CH_3)_3SnCl$: FT-MW and Permutation-Inversion (PI) group theoretical investigations — •Melanie Schnell[1,2], Jens-Uwe Grabow[1], and Jon Hougen[2] — [1]Universität Hannover, Institut für Physikalische Chemie, D-30167 Hannover — [2]National Institute of Standards and Technology, Optical Technology Division, Gaithersburg, MD 20899, USA

The rotational spectrum of the C_{3v}-symmetric trimethyl tin chloride $(CH_3)_3SnCl$, a molecule with three methyl tops connected to a tin atom, has been studied using a pulsed supersonic jet FT microwave spectrometer. The internal rotations of the methyl tops are hindered by barriers of about 150 cm^{-1} leading to a complex splitting pattern of the rotational levels. Consequently, one single rotational transition of $(CH_3)_3SnCl$ splits into more than 1000 lines due to internal rotation, quadrupole coupling of the chlorine nucleus, and the large amount of Sn and Cl isotopomers. The high barrier group theoretical tunneling-rotational formalism appropriate for the PI group G_{162} is used to support the spectroscopic analysis by deriving splitting patterns of the rotational levels as well as statistical weights. A combination of group theory and Stark effect measurements have been used to determine the dipole moment of $(CH_3)_3SnCl$ to be 4.0925(41) D and to distinguish between levels of the different rotational-torsional species of G_{162}, since only the A_1, A_2, I_4 and I_5 levels will have solely a second order Stark effect. It can be shown that the A_1 and A_2 species in G_{162} can be fitted to a rigid rotor Hamiltonian enabling the determination of the Sn–Cl bond length to 2.5448 Å.

MO 24.8 Sa 15:45 HU 2097

Chrysazine, a possible molecular optical switch? — •A. G. Zacarias and E. K. U. Gross — Institut fuer Theoretische Physik, Freie Universitaet Berlin, Arnimallee 14, D-14195 Berlin, Germany

The basic idea of molecular electronics is to use single molecules as the basic elements (transistors, wires, etc.) of electronic devices. The leads can be combined with a huge variety of molecules allowing one to custom-build a virtually infinite number of distinct possible molecular electronic devices. The approach used here to calculate the current-voltage characteristics of single molecules is based on time-independent density functional theory and Green's function techniques. We have investigated the transport properties of the Chrysazine molecule and some of its derivates. These molecules are known to be biologically active due to a proton transfer from the marginal to the central oxygen. We have calculated the current-voltage characteristics for different isomers in order to clarify how the position of the proton influences the transport properties of these molecules. The possibility of using these molecules as optical switches will be explored.

MO 24.9 Sa 16:00 HU 2097

How to measure the electron mass with two protons? — •Valenzuela Salazar Tristán, Senem Kilic, Jean-Philippe Karr, Remy Battesti, and Laurent Hilico — D'epartement de physique et modélisation, Université d'Evry, rue du père André Jarlan, 91025 Evry cedex, France

The vibrational energy levels of the H_+^2 molecular ion mainly depends on the very well known Rydberg constant and on the electron to proton mass ratio m/M. It is thus possible to measure directly this mass ratio from a spectroscopy experiment between to vibrational levels. Because H_+^2 is an homonuclear ion, one must use two photon spectroscopy. We have shown [Hil01] that one of the most favourable transition is the J=0, v=0 to v=1 infra red transition at 9.13 microns.

We have built a RF Paul trap for H_+^2 ion trapping. The v = 0 ions can be selected by UV photodissociation of the v>0 levels. The transition to the v=1 level will be excited using laser light at 9.13 microns and detected by UV photodissociation.

We are currently developping the 9.13 microns laser source. It is a quantum cascade laser (QCL) frequency locked to a stabilised C02 laser.

[Hil01] L. Hilico, N. Billy, B. Grémaud, and D. Delande Polarisabilities, light shifts and two-photon transition probabilities between J=0 states of the H_+^2 and D_+^2 molecular ions J. Phys. B 34, 491 (2001).