First-Principles Calculations of Spectroscopic Signatures III

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Project Term
2024 - 2025

Clusters
Lichtenberg II Cluster Darmstadt

Software
VASP, Quantum ESPRESSO

Additional Software
Yambo

Institute
Institute of Theoretical Physics

University
Justus Liebig University Giessen

Introduction

Linking experimental and theoretical observations on a physical system is one of the key objectives of modern science. The task of our group is to calculate spectroscopic signatures of solids and molecules from first principles, i.e. solely using the basic laws of physics and without employing empirical parameters. The calculated electronic and optical properties give direct access to observable spectra, which can be compared with experimental measurements. This allows us to explain the microscopic physical mechanisms in the considered systems and to verify proposed physical models. Yet, modelling the macroscopic properties of a given material on the basis of its atomic structure is a challenging task, which is carried out in two steps. Firstly, the electronic ground state of the system is modelled in the framework of the density functional theory (DFT). Structural and electronic excitations can be calculated in a second step. We calculate spectroscopic signatures of different systems, ranging from 0D clusters to 3D bulk materials. The strong connection with experimental counterparts allows us to develop a combined approach which goes beyond state-of-the-art investigations. Thus, we establish novel and powerful tools, which support the knowledge gain in materials science.

Methods

The density functional theory (DFT) permits the computation of the electronic ground-state energy and the ground-state charge density of a given atomic configuration (solids and molecules). These quantities result from the Kohn-Sham (KS) eigenvalue equations, which are solved within a self-consistent scheme using efficient and established numerical algorithms. The periodic unit cell approach discretises the differential operators into matrices acting on the Fourier coefficients of the wavefunctions (plane waves). The infinite sums are truncated according to the convergence of macroscopic quantities (usually the total energy). The continuous Brillouin zone is integrated on a grid of k-point samples. The number of k-points is reduced by symmetry relations and typically amounts to~100 for bulk systems, and~10 for surfaces. Similarly to the number of plane waves, the optimal number of k-points is determined by the convergence of macroscopic quantities. The matrices are diagonalised within efficient iteration schemes, most importantly the well established Davidson block diagonalisation and a residual minimization scheme (direct inversion in the iterative subspace, RMM-DIIS).

Results

Subproject A: Subproject A is devoted to the investigation of $LiNbO_3$, $LiTaO_3$, and their $LiNbO_3$-$LiTaO_3$ solid solutions as investigated in the research group FOR5044. The latter are mostly simulated by DFT as implemented in the VASP and QuantumEspresso codes within the special quasirandom structures (SQS) model, which allows to simulate disordered alloys within the supercell approach. The approach to the calculation of the nonlinear optical response based on the calculation of the polarization in the time-domain, which we implemented during the previous project runtime, has been applied to strained $LiNbO_3$ and $LiTaO_3$ materials, revealing how the optical response can be 2manipulated by external stimuli. Ground and exited state properties of the solid soultions have been calculated from first principles. Ferroelectric domain walls in $LiNbO_3$ and $LiTaO_3$ have been modeled atomistically, the domain form has been modeled by an Ising approach on the basis of the coupling coefficients calculated within DFT.

Subproject 2: Subproject 2 is dedicated to the investigation of the adamantane-based molecular clusters and their unique nonlinear optical properties as investigated in the research group FOR2824. Prototypical model systems are the adamantane shaped $[(RT)_4E_6]$ clusters (with R = organic group; T = C, Si, Ge, Sn; E = O, S, Se, CH_2). After calculating the ground state atomic and electronic structure of different molecules, we have furthed explored the effect of chemical modifications (ligand field) and habitus (single molecular cluster, molecular crystals) on the optical response. This was the continuation of the investigation started in the previous compute time grant.

Discussion

Subproject 1: With the compute time provided by the NHR4CES at the Lichtenberg 2 cluster a row of novel and relevant results could be produced that led to the publication of not less than 12 peer reviewed publication related to subproject 1. The investigation of ferroelectric solid solutions in cooperation with our experimental partners yield insight concerning atomic and electronic structure, optical spectroscopy signatures, lattice dynamics, heat capacity, and defect structures. The calculated properties have been compared with corresponding experimental results from the groups of Profs. H. Fritze and H. Schmidt (TU Clausthal), S. Ganschow (IKZ Berlin) M. Imlau (TU Osnabrück), and C. Sil- berhorn (Uni Paderborn) showing an excellent agreement and providing further insight towards the materials properties. Most remarkable is the investigation of ferrolectric domain walls (DWs) performed in the framework of a cooperation with Prof. Lukas Eng (TU Dresden), in which we were able to explain the origin of the conductivity of DWs in otherwise insulating materials.

Subproject 2: Within that last year we could elevate the insight achieved by the atomistic models by developing analytical tools that allow to relate optical nonlinearties with particularly relevant electronic transitions. We could demonstrate that the optical nonlinearities have their origin in the ligand field, in particular in the delocalized π-orbitals of the phenyl-substituents. The molecular core is not directly involved in the transitions leading to the generation of the optical nonlinerities, however it influences the intensity of the optical response by symmetry breaking. Our calculations explain the results of the experimental investigation of this class of molecules, synthetized by our experimental colleagues (Prof. S. Dehnen at the KIT and Prof. P. W. Schreiner at the Justus-Liebig- Universität Gießen) and characterized by optical measurements within the group of Prof. K. Volz at the Philipps Universität Marburg. Moreover, they provide a path toward the design of molecules with optimized optical response.

Publications

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