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Keywords: surface, polypeptide, theory

MS.76.3

Optimization of materials with time dependent density functional theory

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The theory of Quantum Optimal Control (QOCT) aims to the theoretical design of external fields capable of controlling quantum mechanical systems. Nowadays, experimentally, the so-called pulse shaping techniques can be used to design pulses that produce a desired effect on atoms or molecules. These may react in complex manners when they are irradiated with high-intensity electromagnetic pulses: multi-photon, tunneling and over-the-barrier ionization, laser driven photo-induced isomerizations or fragmentations, and high harmonic generation are some of the non-linear effects that are observed.

We wish to investigate the control of these complex phenomena from first principles, by making use of time-dependent density-functional theory (TDDFT) to describe the electrons, a real-space numerical representation, and various optimization techniques.

In this talk, I will present this marriage of the QOCT techniques with TDDFT, along with various application examples.

Keywords: control, laser, theory

MS.76.4

Density functional calculations of electron energy loss data and inelastic mean free paths in elemental and binary materials

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Density functional theory is used to determine joint density of states and optical energy loss data for elemental metals and compounds. A novel transform algorithm is then employed to produce electron energy loss spectra and inelastic mean free paths. These results are compared with recent high profile experimental measurements in the low-energy region of strong plasmon resonances.

We present calculations of electron energy loss spectra and inelastic mean free paths determined using transformed optical loss data from density functional theory. Our novel approach enables investigation of plasmon excitation and electron scattering without the use of empirical fitting parameters or experimental data - common requirements of previous theory [1]. We consider elemental metals copper, molybdenum, zinc and selenium, and the binary semiconductor zinc selenide. The technique is extensible to any non-crystalline or crystalline uniform material.

Results are compared with recent high precision measurements of the inelastic mean free path [2, 3] derived from x-ray absorption experiments [4, 5]. Surprising outcomes of these investigations include accurate dynamic bond lengths [6] and complementary approaches to single crystal structure [7,8]. Broadening mechanisms in the momentum-dependent energy loss function, and the energy evolution of plasmon peaks are investigated as potential sources of error in established theory. We consider the effects of crystal structure on the energy loss spectrum, and critically investigate the correlation between inelastic scattering in polyatomic systems and their corresponding elemental systems. This work focuses on electron energies below 100 eV – the region of strong plasmon resonance – where published data is highly uncertain and incomplete.

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Keywords: density functional theory, IMFP, photoelectron

MS.76.5

Topological analysis of charge densities obtained from experiment and plane-wave calculations

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Accurate electron density distribution functions ($\rho(r)$) for crystals can be obtained from high resolution experiment and calculated by means of density functional (DFT) methods. To recover the experimental electron density one should carry out multipole refiment procedure on the dataset collected with high redundancy at low temperature. Such an "experimental" electron density function usually is suffer from systematic errors caused by thermal motion or/and absorption effects etc. Thus, DFT calculations should be "method of choice" to obtain very accurate $\rho(r)$ function in the case of molecular crystals. Indeed, it does not to carry out long-time experiments and multipole refinement. Unfortunately, the convergence between experimental and optimized atomic coordinates and cell parameters is still not ideal for the most of the modern DFT functionals. Besides, all-electron treatment of molecular crystals can be achieved only for small cells which are not contain heavy atoms.

The most abundant type of DFT calculations of crystals is based on the usage of plane wave basis set and pseudopotentials. Pseudopotentials are usually considered as very bad choice to obtain the $\rho(r)$ function suitable for the topological analysis in terms of R. Bader's "Atoms in molecules" theory. In many cases the critical points (CP) (3,-1) could not be localized. To overcome this problem the pseudopotentials with small radius of core region (r_c) (hard pseudopotentials) should be chosen.

The suitable pseudopotentials can be generated by hand, but they are also can be obtained with quantum chemical programs. Our choice is the VASP code which is supplied with rich library of hard non-local

pseudopotentials (projected augmented waves, PAWs). The calculated ρ(r) function is equidistant 3D grid. The dimension of 3D grid can be easily adjusted by internal keywords of the VASP program and it is limited by the size of the system RAM only.

To compare the experimental and theoretical ρ(r) functions we carried out the high-resolution X-ray studies and DFT calculations of crystal structures of coordination compounds containing group 14 elements. The present work covers the results obtained for two complexes with formally divalent Ge and Sn and six formally tetravalent Si, Ge and Sn. We used the ρ(r) function calculated for the corresponding isolated molecules as reference points to evaluate the influence of crystal packing and possible systematic errors. The topological parameters (the values of ρ(r), its Laplacian (∇^2ρ(r)), kinetic and potential energy densities) in CP(3,-1) were compared. The most prominent differences are revealed for the ∇^2ρ(r) values. The latter are defined by dimension of 3D grid. On the other hand, the values of atomic volumes and charges are in good agreement. In our opinion the usage of our methodology is allowed to investigate the chemical bonding in any crystal with volume of the unit cell to be up to 4000-5000 $Å^3$.

Keywords: DFT calculations, charge density, topological analysis

MS.77.1

Advances in instrumentation, automation and validation of fast XAFS experiments
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Time resolved X-ray absorption spectroscopy can be performed in the so-called Quick-EXAFS (QEXAFS) mode, where the spectrum is collected "on-the-fly" using fast monochromators at synchrotron radiation facilities [1]. Such experiments yield e.g. structural information during fast chemical decomposition reactions, thin film deposition, solid-state reactions and phase transformations. Currently, most scientific applications focus on catalyst research [2], [3]. A dedicated facility is available at the Swiss Light Source (SLS) [4], several other are currently under development worldwide.

Depending on photon flux and sample quality, repetition rates of about 100 Hz can be realized for the XANES range. A new optimized monochromator enables the acquisition of full high quality EXAFS spectra with a scan range of typically 1 keV - up to about 2.5 keV - in only 50 ms per spectrum. This setup employs a channel cut crystal, a cam driven tilt table for rapid angular oscillations and a novel fast readout system for the Bragg angle. Latest developments also allow a user friendly variation of the scanned energy range within experiments by remote control [5]. Since a fast sequential energy scanning technique is used, the detection of fluorescence radiation or surface sensitive techniques like X-ray reflection measurements can be applied. A reference sample can be monitored simultaneously with each measurement to detect minor edge shifts reliably. Even XANES microtomography becomes feasible, using the fast scanning monochromator with refractive X-ray lenses for beam focusing. Using cryogenic cooling, the monochromator crystal can cope with the full heat load from third generation undulator sources, and excellent data quality can be obtained. Currently, a new dedicated setup using an insertion device at the PETRA III storage ring (DESY, Hamburg, Germany) is under development.

However, such measurements require very fast high precision detection systems with low noise level, and the photon energy at each instant must be known with high accuracy. Special care is necessary to avoid dynamic distortions of the measured absorption spectra.

In addition, the high data acquisition rates make special software developments necessary for fast continuous measurements [6].

The most recent technical developments of fast XAFS measurements, the current states and different experimental realizations of hard- and software are discussed. Experimental factors which are influencing the data quality like the homogeneity of real samples, photon flux and beam stability are evaluated.

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Keywords: XAS, synchrotron_radiation, in-situ_measurement

MS.77.2

Standardizing Data Formats for X-ray Absorption Spectra and Libraries
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As the number of high-quality facilities for collecting x-ray absorption spectra (XAS) and the size of the community using XAS grow, there is an increasing need for transferring measured XAS data between different beamlines and different analysis applications. This is particularly true for spectra measured on "model compounds" which are often used as reference spectra for XANES analysis or for calibrating analysis procedures. Unfortunately, there is no standardized file format to exchanging data. We present the efforts of a working group to define and implement a standardized file format for XAS format that can be used to exchange XAS data between researchers and analysis programs. The XAS Data Interchange (XDI) format defines a structured plain-text column data file. A header contains meta-data as keyword, value pairs with pre-defined keywords describing the spectra and experimental conditions. Numerical data is represented in white-space delimited text, with each row of data corresponding to an energy value at which the measurement was taken. Any of several pre-defined column data types can be stored for the most common types of XAS scans. For example, either energies or monochromator angles can be stored as the primary dependent variable. Sampled intensities or calculated absorption values (or both) can be stored. Normalized absorption spectra and isolated χ(k) spectra can also be stored. The format and a programming interface to it will be shown. With this format for a plain-text file which represents a single spectrum, we also show efforts to build libraries of spectra using the free and portable SQLite relational database engine. A prototype application to build and manage spectral libraries which can be either used for individual storage or easily shared between researchers will be shown.

Keywords: XAS, XANES, database