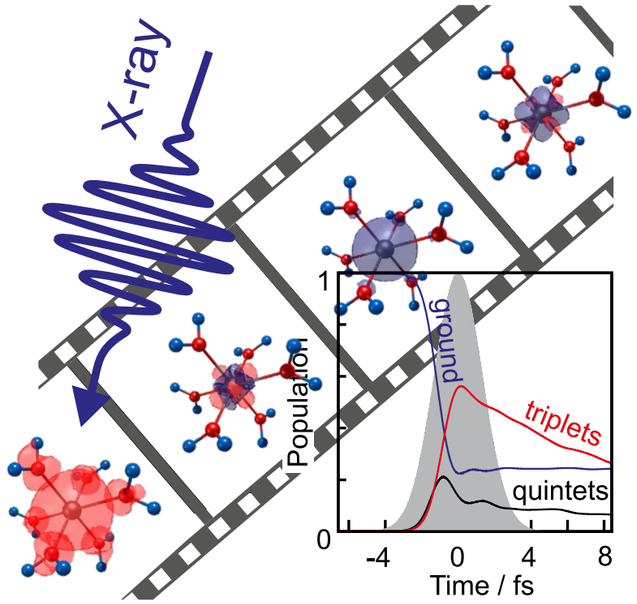
Deciphering the fingerprints of chemical bonds using X-ray spectroscopy

The ongoing developments of technology and improvements in facilities mean that using X-rays to explore the fine details of matter at the atomic level is growing in popularity. But as experiments become more sophisticated, so do results. **Professor Oliver Kühn** from the University of Rostock is working with fellow colleague **Dr Sergey Bokarev** to develop computational methods that will help researchers at the forefront of X-ray spectroscopy, analyse their results.

Whether you have broken an arm or suffered from a toothache, the likelihood is you have probably been X-rayed at some point in your life. As powerful beams of light capable of going through many substances, X-rays are not just useful for looking inside humans; they can be used to study the properties and structure of the molecular world, like the way atoms and molecules change during certain processes such as when a catalyst is used to increase the rate of a reaction.

X-ray science is becoming increasingly important because it is undergoing considerable change



Ultrashort X-ray light pulses (grey shaded area) may trigger an ultrafast (1 fs = 10^{-15}seconds) flip of the electron spin, i.e. of the intrinsic magnetic moment of an electron. It changes the magnetic state of the system from high-spin (quintet) to low-spin (triplet) which can be seen from the results of the simulated population dynamics. Spin-flipping can be used, e.g. for magnetic storage of data.

There are various ways matter can interact with X-rays, and as a result, various ways we can use X-rays. Molecules can diffract X-rays as they pass through, creating patterns typical for their structure. A famous example was the discovery of the DNA structure being a double helix by Watson and Crick. However, molecules can also absorb X-ray photons, promoting electrons to higher energy levels. Since X-ray photons have much shorter wavelengths than visible light, shining X-rays on molecules can be used to excite electrons that are bound close to the nucleus. As this is an unstable situation, the electron will fall back down, possibly emitting a photon at a different wavelength, which gives information complementary to absorption. Each atom has its own specific 'X-ray fingerprint', this means that X-rays can allow researchers to study materials and know exactly which elements they are looking at. This is a vital aspect as the function of enzymes and catalysts, for instance, is associated with changes in the electronic structure of specific atoms. In these examples, the relevant atoms are often metals containing many electrons interacting via Coulombic forces. Therefore, their motion is highly correlated, making the interpretation of X-ray spectra a complicated task.

For years, scientists have used synchrotrons to create high-energy X-ray photons. In recent years, however, there has been a shift towards using Free Electron Lasers (FELs) as a source of intense coherent X-ray light. A prominent example being the XFEL in Hamburg (Germany), which has now been officially opened.

These light sources provide insight into the structure of matter at an unprecedented level of detail. Therefore, the results of X-ray absorption and emission experiments can be rather complex to decipher and require a parallel development of novel computational models. Being part of a worldwide activity of theoretical physicists

and chemists, Professor Kühn together with Dr Bokarev and their colleagues are focusing on developing innovative ways to improve the available methods for interpretation of experimental results obtained by various X-ray spectroscopies.

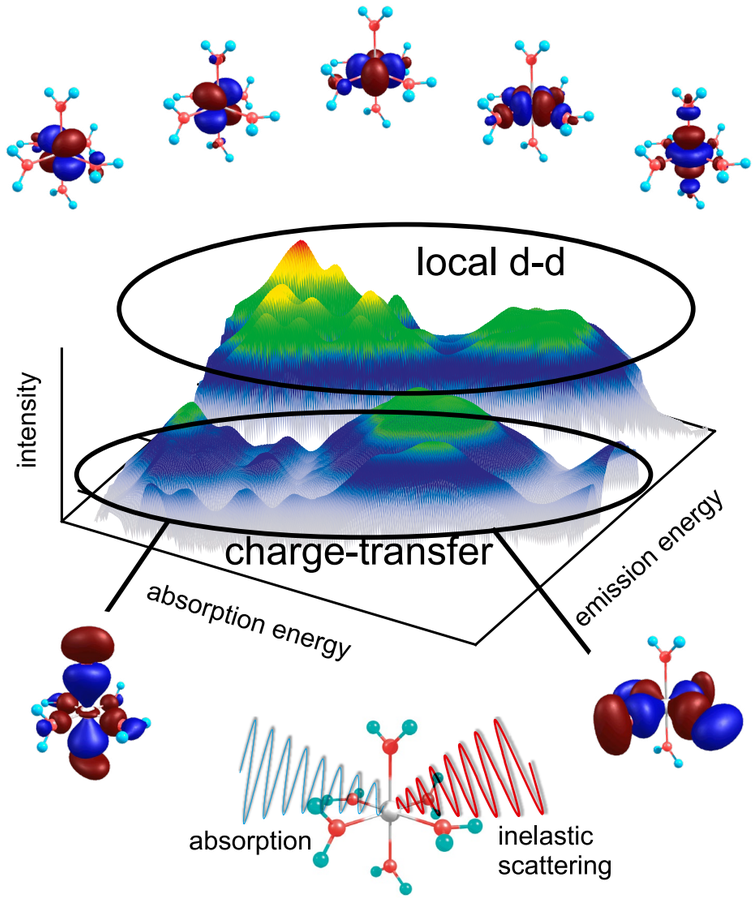
WHAT ARE THE CHALLENGES?

The motion of electrons in molecules is governed by the laws of quantum mechanics. Recalling the famous quote by Nobel laureate P.A.M. Dirac "The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are thus completely known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved. Therefore, any progress is necessarily connected to make meaningful approximations. Prof Kühn and his team adapted an approximate method to the requirements of X-ray spectroscopy, which is not only capable of describing the correlated electronic motion but is also systematically improvable towards the exact results. Attaining these is just hampered by the lack of currently available computational power of even supercomputer facilities.

In the traditional chemists' picture, chemical bonds are associated with the electrons occupying so-called molecular orbitals. For instance, the binding of ligands like carbon monoxide to a metal like iron, is explained by an exchange of electrons between their orbitals. In 2013, Kühn and Bokarev together with their experimental partners at the Helmholtz Center in Berlin, were able to validate this decades-old picture by unravelling the X-ray fingerprints of the flow of electrons between metal and ligands in a model catalyst called iron pentacarbonyl.

In another example, manganese compounds have been studied, which are used as catalysts for water oxidation, inspired by natural photosynthesis. During the catalytic reaction, the manganese atoms exchange electrons with the reaction partners. To understand mechanistic details and follow the process, it is vital to be able to identify the associated characteristic changes in X-ray spectra. This has been achieved by a joint experimental and theoretical study in 2015, which will aid the design of future improved catalysts.

While these examples used X-rays from a synchrotron source, in a more recent development, Kühn and Bokarev gave



An example of the Resonant Inelastic X-ray Scattering (RIXS) spectrum of a manganese-based catalyst $[Mn(H_2O)_6]^{2+}$. The spectrum contains multiple features at different incoming and outgoing photon energies in the soft X-ray range (about 660 eV). These are fingerprints of the electronic structure, containing information about the interaction between metal and ligands; the molecular orbitals corresponding to local (between manganese orbitals, termed d-d) and non-local or charge-transfer (between the metal centre and the ligands) transitions of electrons are also depicted. Understanding the origin of these features with the help of theoretical modelling assists rational design of improved catalysts.

a new twist to spin dynamics, which will become experimentally available with the advanced coherent X-ray sources such as FELs. Electron spin can be understood as giving the electron the properties of a tiny magnet. The details of the interaction between the spins of its many electrons can make a material magnetic, enabling it to be used for storing information, like on a hard disc. For developing novel storage technologies, the time it takes to turn these tiny magnets upside down is of utmost importance. In a recent study, the Rostock group demonstrated that by using extremely short flashes of X-rays, this process can be controlled despite competing decay channels, and the flipping time substantially reduced.

Professor Kühn and his team are focusing on X-ray-matter interaction, developing innovative ways to improve the characterisation of compounds using X-ray spectroscopy

This research is opening new doors when it comes to X-ray science, allowing researchers across the world to probe increasingly complex processes. As the technology to produce X-rays continues to improve, the methods developed by Prof Kühn and his team will enable researchers across different disciplines, to further our understanding of how functional materials work on the atomic scale. Progress on the simulation side is expected to come with the emerging quantum computers, which will further push the limits to an extent not foreseen by the founding fathers of quantum mechanics.

Q&A

What are X-rays biggest 'rivals' when it comes to studying the electronic structures of matter?

Traditional spectroscopy in the visible or ultraviolet regime has been developed to a high sophistication. Its focus is on valence electrons, whose density is usually smeared out over the whole molecule. In contrast, X-rays are unique for probing local changes in electron density e.g. during a chemical reaction. In terms of the X-ray sources, large-scale facilities like XFELs are competing with tabletop so-called 'high-harmonic generation' setups in the soft X-ray regime.

Why is it important to know how electrons behave in atoms and compounds?

Electrons are the glue that holds molecules together. Hence analysing the electron density distribution is key to understanding chemical bonding as well as bond breaking and formation during chemical reactions. On the other hand, the transfer of electrons between molecules is at the heart of many processes, ranging from corrosion and catalysis to photosynthesis.

Why are you personally interested in the subject?

Clearly, X-ray spectroscopy provides extremely detailed insight into fundamental processes across the disciplines of natural sciences. The combination with high time resolution is likely to reshape our way of thinking of these processes and the underlying concepts in the near future. From the theory side, studying the intricate many-body dynamics of electrons and nuclei is simply just a fascinating endeavour.

The future of X-ray science is in time-resolution

Do you think synchrotrons or free electron lasers will be the future of X-ray spectroscopy?

Synchrotron sources are well-established and have a prominent place in scientific investigations. Free electron lasers open up a new direction, with a strong focus on time-resolution. In a way, these are complementary experiments, which will coexist for a mutual benefit.

What are the big questions you're hoping to answer through your research in the next couple of years?

The interaction of matter with X-rays also leads to the ejection of electrons leaving the molecules ionised. The characteristics of these electrons yield information which is complementary to photon emission. The power of simultaneous analysis of these emission events has yet to be explored. Furthermore, understanding the interplay between different electron-out channels is one of the key challenges that will be tackled by our group.

Detail

RESEARCH OBJECTIVES

Professor Oliver Kühn and Dr Sergey Bokarev are developing computational methods that will help researchers at the forefront of X-ray spectroscopy, analyse their results and design new experiments.

FUNDING

- Deutsche Forschungsgemeinschaft (KU 952/10-1, BO 4915/1-1)
- Deanship of Scientific Research (DSR), King Abdulaziz University, Jeddah (D-003-435)

COLLABORATORS

- Prof Emad F. Aziz, Helmholtz Center Berlin, Germany
- Prof Saadullah G. Aziz, Chemistry Department, King Abdulaziz University, Jeddah, Saudi Arabia

BIO

Prof Kühn studied Physics at the Humboldt University of Berlin. After receiving his PhD in 1995, he worked as a postdoc at the universities of Rochester and Lund. From 1997-2007, he has been a senior researcher at the Free University of Berlin. He became a Professor of Theoretical Physics at the University of Rostock in 2008.

Dr Bokarev studied Chemistry at the Lomonosov Moscow State University where he received his PhD degree in 2009. Since 2010, he has been working in the group with Prof Kühn at the University of Rostock, where he is heading the junior research group '' Theoretical X-ray Spectroscopy''.

CONTACT

Prof Dr Oliver Kühn
Institute of Physics
University of Rostock
Albert Einstein Straße 23-24
18059 Rostock
Germany

E: oliver.kuehn@uni-rostock.de
T: +49 381 498 6950
W: http://web.physik.uni-rostock.de/quantendynamik/