Angstrom resolution imaging of atom clusters
(PhD thesis)

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BME – SZFKI
2003

Introduction

The development of the experimental techniques and equipments often leads to dramatic changes in a given field or even boosts many areas. It is not unusual, that new fields appear. This is true for the synchrotron radiation. The introduction of synchrotron sources significantly increased the speed of traditional measurements and allowed the collection of much higher quality data. Further a lot of new methods were introduced such as magnetic X-ray scattering, nuclear resonant scattering, etc. Probably the most spectacular impact were in the structure determination of biological systems. In the last decades thousands of protein structures were solved with atomic resolution.

The synchrotrons have already reached the technical limits. Therefore a new tool, the X-ray Free Electron Lasers (X-FEL) have become the center of interest. The X-FEL can produce x-ray pulses with higher power and with shorter pulselength than that was available ever before. These unique properties might lead to as large impact on many fields of science as synchrotron radiation did in previous years.

In 1999 a project called Femtosecond Imaging of Biomolecules with X-Rays was launched. The aim was to review the current limits of structure determination, and examine whether the structure of a single molecule or biological system (e.g. a virus) can be determined with atomic resolution. The X-ray diffraction group of the MTA Research Institute for Solid State Physics and Optics joined the work. The results described in the PhD thesis are parts of this research.

Previous works and objectives

Radiation damage is the fundamental limitation of structure determination of single biological molecules with X-ray diffraction techniques. Applying traditional methods, the sample looses its original structure well before enough information could be collected for the reconstruction. The image formed in an experiment contains the original structure mixed with the whole history of the target through the measurement.

Useful structural information can be obtained from the observation of the elastic X-ray scattering events, while the radiation damage is caused by the energy delivery of inelastic scatterings. The cross sections of the inelastic prosesses are much larger than the elastic ones for elements mostly contained by biomolecules (C,O,N,H), so inelastic scatterings occure more often. The primary inelasic events generate cascades of secondary ionizations. Large avalanches can grow up doing significant deteriorations in the sample. If the system is a cluster of atoms or a molecule, it explodes due to the repulsion between the ionized atoms.

Although much effort was made to find different ways to reduce the impact of the radiation damage (such as crystallizing, cooling down, etc.), the real solution seems to be to enhance the power of the radiation sources, so that enough information could be collected before the damage of the avalanches developes.

The first breakthrough in the X-ray physics of the XXI. century will definitely be the appearance of the X-ray Free Electron Lasers. They will exceed the syncrotrons in the power ($\sim 10^{22}\,\mathrm{W/cm^2}$, $\sim 10^{12}$ photon/pulse) and in the shortness ($\sim$100 fs) of the pulses. These characteristics make the X-FEL a good candidate for single molecule imaging. The first experimental X-FELs are already operating in the UV regime (Tesla Test Facility, DESY, Hamburg). Although these devices cannot be used for atomic structure determinations, preliminary studies of different experimental techniques and the physical processes in the samples can be carried out. Further there is a need of theoretical studies and numerical modelling of the behavior of matter in the extreme condition of the XFEL pulses. One of these studies is related to single molecule imaging.

The idea of single molecule imaging with X-ray Free Electron Lasers comes from R. Neutze et al. [Nature, **406**, 752]. They investigated the radiation damage during the measurement. However they neglected the effect of the stripped electrons. Analyzing the possibility of structure determination they did not take into account the imaging process of the reconstruction method. They based their estimate solely on the actual static deformations. In my work I remedy these shortcomings.

Our previous estimate indicated that the electrons play an important role in forming the dynamics of the cluster. Accordingly, my aim was to study the radiation damage of molecules and atom clusters considering the electrons that have been stripped from the atoms due to the ionization processes. This led to a model, that contains the most important interactions between the electrons and atoms, and between the particles and the electromagnetic field. Further a computer code fast enough to simulate 1000–10000 atom systems had to be developed.

I also study a possibility of structure determination based on the moleculardymanics simulations of the cluster. The first approximation to do this is the analysis of the geometrical displacement of atoms. However, we arrived at a more accurate estimate of the number of photons giving useful structural information by taking into account the properties of the imaging and reconstruction process beside the pure geometrical factors.

Short summary of results

1. I worked out a model to simulate the dynamics of atom clusters in the beam of an intense X-ray Free Electron Laser [2]. The modell contains the most important interactions: the Coulomb interaction, the bonds between atoms, the photoeffect, the Auger and fluorescent relaxations of the ions, and the secondary ionizations caused by the electrons. I made a computer code based on this model, which can be used to simulate the Coulomb explosion of carbon clusters caused by an X-ray pulse.

2. I made a comparison between my model (III.) and two other models (I. and II.) which were successive steps in the creation of our final model [2]. The first includes the bonds between atoms, the photoeffect and the atomic relaxations; this is equvivalent to the picture used by R. Neutze et al. [Nature, **406**, 752] earlier. The second takes into account the charge of the electrons and their Coulomb interactions, but still neglects the secondary ionizations. I pointed out, that in the case of the I. and II. models, the total number of the stripped electrons is underestimated, whereas the charge of the cluster and the speed of the spatial expansion is overestimated.

3. I examined various properties of the Coulomb explosion based on the most realistic model (III.) as a function of the number of the atoms and the length of the X-ray pulse [2]. I showed, that the average charge of the cluster per atom is less for larger systems since the relative number of the slower electrons among the atoms is higher. As a consequence of this there is a difference in the speed of the expansion for various clusters. I showed, that for a given number of atoms, the average charge per atom grows with the pulselength. This effect is more emphasised in smaller clusters.

4. I examined the kinetic energy spectrum of the photoelectrons and the electrons inside the cluster at different times [2]. The electrons in the neighborhood of the cluster are cooling down due to the Coulomb explosion. The spectum of the photoelectrons gets wider in time, and reaches the final form at the end of the pulse.

5. I pointed out, that due to charge rearrangement, the cluster can be divided into an almost neutral center and a positive shell around it [2]. I examined the time dependence of the position of the border. I found, that the speed of the border in a 1500 atom cluster is 1.1 Å/fs. I showed that there is a connection between the charge separation and the energy spectrum of the ions.

6. Based on the simulations of the Coulomb explosion I estimated the number of the scattered photons which give useful structural information on the original molecule. Taking into account the actual static deformations I got that the first 3% and 10% of the pulses can be efficiently used for 50 fs or 10 fs pulses, respectively [1,2]. Based on reconstructions of an exploding 200 atom cluster, I found the better estimate 25% for the number of photons giving useful structural information by taking into account the properties of the imaging and reconstruction process beside the pure geometrical factors in the case of a 10 fs pulse [3]. Further improvement is expected by introducing holographic methods for imaging [4]. These investigations will be part of my future work.

Publications

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[2] Z. Jurek, G. Faigel, M. Tegze. Dynamics in a cluster under the influence of intense femtosecond hard x-ray pulses (submitted *The Eur. Phys. J. B*; arXiv:physics/0306102) .

[3] Z. Jurek, G. Oszlányi, G. Faigel. Imaging atom-clusters by hard x-ray free electron lasers (submitted *Europhys. Lett.*; arXiv:cond-mat/0309083).

[4] G. Faigel, M Tegze, G. Bortel, Z. Jurek, S. Marchesini, M. Belakhovskyo, A. Simionovici. Holographic Methods as Local Probes of the Atomic Order in Solids, (accepted *Spectrochimica Acta Part B*; arXiv:cond-mat/0308375)

Publications — posters and talks

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[6] G. Faigel, Z. Jurek, G. Oszlányi, M. Tegze. Atom cluster imaging by free electron x-ray lasers, From Solid State To BioPhysics International Conference, Croatia, 2002. Invited talk.

[7] Z. Jurek, G. Faigel, M. Tegze. The possibility of atom cluster imaging by free electron X-ray lasers, EPS-12: General Conference "Trends in Physics", Budapest, 2002. Poster.

[8] Z. Jurek, G. Faigel, M. Tegze. Dynamics of atom clusters in a short and intense hard x-ray pulse, Ultrafast X-Ray Science Corsica, France, 2003. Short talk.

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Acknowledgement

I would like to thank my supervisor Gyula Faigel for his help in all areas related to the PhD work. Among many things I learned from him how to solve problems in a deliberate, but still simple way and the importance of critical thinking.

I would like to thank Miklós Tegze for his help in building my model and the helpful discussions about the results of the simulations.

I would like to thank Gábor Oszlányi for his great help in understanding and implementing the reconstuction algoritms.

I would like to thank László Gránásy for making his computer cluster available for my moleculardynamics simulations.

I would like to thank Gábor Bortel and Tamás Pusztai for their help both in computer and in research related topics.

I would like to thank my in-house referees György Szabó and Sándor Varró for their careful review of my thesis which helped me to make it more accurate.

Last, but not least I would like to thank my wife Ágnes and my daughter Rebeka for providing a calm background to my PhD work.