Impact of hollow-atom formation on coherent x-ray scattering at high intensity

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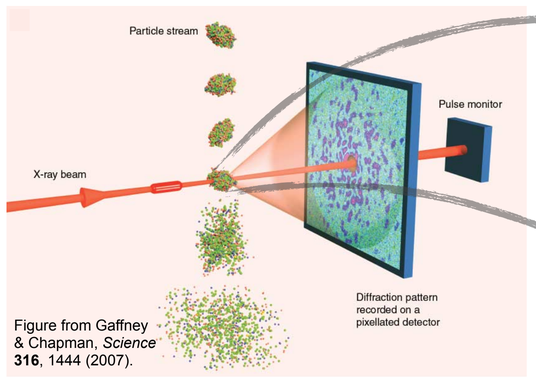
Abstract

X-ray free-electron lasers (FELs) are promising tools for structural determination of macromolecules via **coherent x-ray scattering**. During ultrashort and ultraintense x-ray pulses with an atomic scale wavelength, samples are subject to **radiation damage** and possibly become highly ionized, which may influence the quality of x-ray scattering patterns. We develop a toolkit to treat **detailed ionization, relaxation, and scattering dynamics** for an atom within a consistent theoretical framework. The coherent x-ray scattering problem including radiation damage is investigated as a function of x-ray FEL parameters such as pulse length, fluence, and photon energy. We find that the x-ray scattering intensity saturates at a fluence of ~10^7 photons/Å^2 per pulse, but can be maximized by using a pulse duration much shorter than the time scales involved in the relaxation of the inner-shell vacancy states created. Under these conditions, both inner-shell electrons in a carbon atom are removed, and the resulting **hollow atom** gives rise to a scattering pattern with little loss of quality for a spatial resolution > 1 Å. Our numerical results predict that in order to scatter from a carbon atom 0.1 photons per x-ray pulse, within a spatial resolution of 1.7 Å, a fluence of 1×10^7 photons/Å^2 per pulse is required at a pulse length of 1 fs and a photon energy of 12 keV. By using a pulse length of a few hundred attoseconds, one can suppress even secondary ionization processes in extended systems. The present results suggest that high-brightness **attosecond x-ray FELs** would be ideal for **single-shot imaging of individual macromolecules**.

Introduction

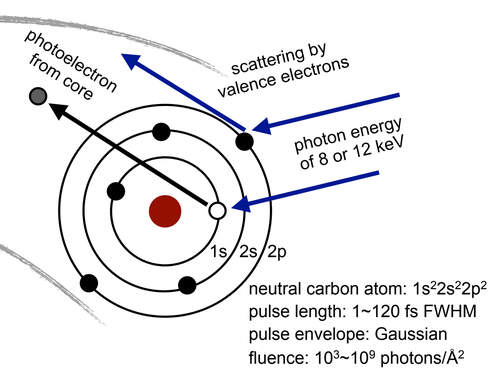
Single-shot imaging of individual macromolecules



Single-shot imaging employs coherent x-ray scattering to determine the atomically resolved structure of non-crystallized biomolecules or other nanoparticles, with the high fluence of a tightly focused x-ray FEL pulse that could produce a significant amount of scattered photons.

Each target molecule undergoes electronic damage, and the positively charged atomic ions formed in this way repel each other, thus leading to Coulomb explosion of the target molecule. These radiation damage effects could degrade the scattering patterns and hinder the determination of the atomic positions in the target molecule. To suppress the impact of the molecular Coulomb explosion on atomically resolved imaging, one must effectively freeze the atomic motion during the x-ray pulse, requiring a pulse duration of no more than ten femtoseconds.

What happens inside the atom?



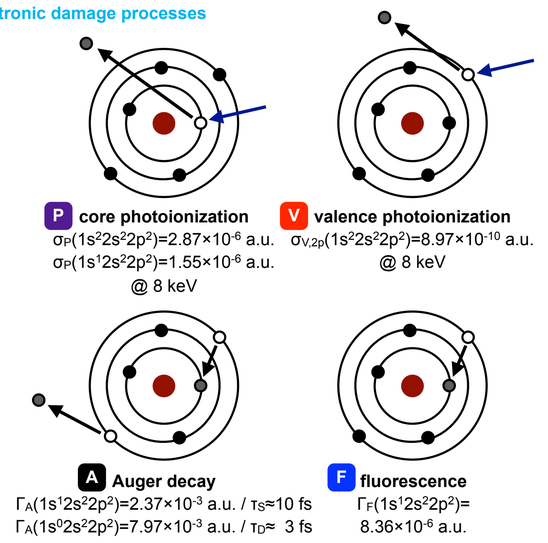
neutral carbon atom: $1s^2 2s^2 2p^2$
pulse length: 1~120 fs FWHM
pulse envelope: Gaussian
fluence: 10^3~10^9 photons/Å^2

Since the electronic damage processes are mainly atom-specific in the x-ray regime, one may concentrate on the interaction of the x rays with individual atoms.

Even if the atomic motion during an x-ray pulse is negligible, electronic damage (photoionization and relaxation) dynamics during the x-ray pulse may directly influence x-ray scattering patterns by altering the electronic density in the target.

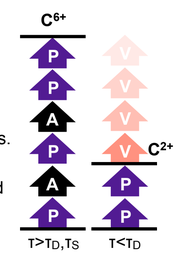
Thus it is crucial to understand detailed ionization and relaxation dynamics in individual atoms under ultrashort and ultraintense x-ray pulses.

Electronic damage processes



Electronic damage cascade

In the x-ray regime, photoionization predominantly affects inner-shell (core) electrons. If the pulse length is long enough, many electrons can be stripped off in a sequence of **P** and **A**. If the pulse length is short enough, all core electrons in a given atom may be removed before **A** occurs. The resulting hollow atom retains its core vacancies and suppresses further electronic damage. This effect is called x-ray transparency or frustrated absorption, and might be beneficial for single-shot imaging of individual molecules.



XATOM toolkit

Theory

We implement an integrated toolkit, XATOM, to treat x-ray-induced processes based on nonrelativistic quantum electrodynamics and perturbation theory within the Hartree–Fock–Slater model.

Physical processes

> Photoionization
> Auger (Coster–Kronig) decay
> Fluorescence
> Shake-off
> Elastic x-ray scattering
> Resonant elastic x-ray scattering (dispersive correction)

The toolkit can compute photoionization cross sections, Auger / fluorescence rates, shake-off branching ratios, and atomic form factors for a given electronic configuration of any atomic species.

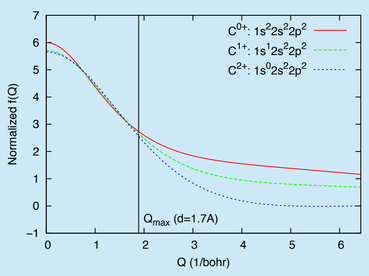
Damage dynamics

To simulate electronic damage dynamics in intense x-ray pulses, we use the rate equation approach with photoionization cross sections, Auger rates, and fluorescence rates, for all possible electronic configurations.

Applications

> Ionization, relaxation, and scattering dynamics at high intensity
> Nonlinear x-ray absorption processes
> Charge distribution analysis of noble gases in FELs
> Photoelectron / Auger / fluorescence spectra
> Multi-wavelength anomalous diffraction at high intensity

Atomic form factor



Normalized atomic form factor of carbon

To examine variations of x-ray scattering patterns for different electronic configurations, especially for core-hole configurations created via photoabsorption, we calculate atomic form factors for the filled core (neutral: $1s^2 2s^2 2p^2$), the single-core-hole ($1s^1 2s^2 2p^2$), and the double-core-hole ($1s^0 2s^2 2p^2$) configurations.

To facilitate a direct comparison between the three different charge states, the form factors are normalized with the following normalization factor:

$$\int_{Q<Q_{\max}(d)} \sqrt{N_{\text{neutral}}(\Omega)}\, d\Omega \Big/ \int_{Q<Q_{\max}(d)} \sqrt{N_I(\Omega)}\, d\Omega,$$

The shapes of the three normalized form factors are quite similar to each other, indicating that core-hole formation causes little degradation of the quality of the x-ray scattering pattern.

Hollow-atom formation

The time-averaged population of the *I*th configuration is given by

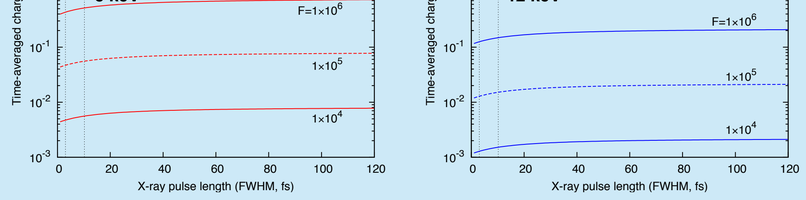
$$\bar{P}_I = \int_{-\infty}^{\infty} P_I(t) f(t)\, dt,$$

where *f*(*t*) is the normalized x-ray pulse envelope. Then the time-averaged charge is given by

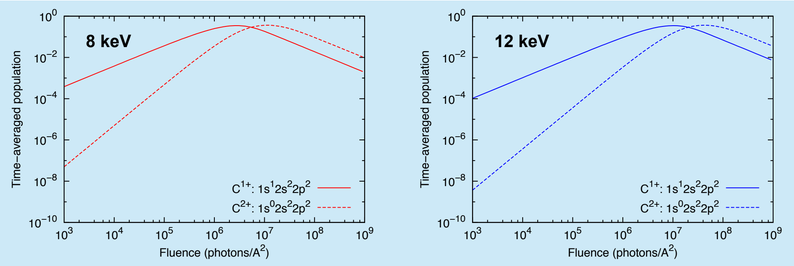
$$\bar{Z} = \sum_I^{\text{all config.}} Z_I \bar{P}_I.$$

When the pulse length is short enough to compete with core-hole lifetimes, it suppresses the sequence of core photoionization and Auger decay steps. By decreasing the pulse duration (increasing the peak intensity), the time-averaged charge can be minimized due to this x-ray transparency or frustrated absorption. Productions of single-core-hole and double-core-hole configurations are saturated around 10^6~10^8 photons/Å^2 for 1 fs FWHM.

Time-averaged charge vs. pulse length

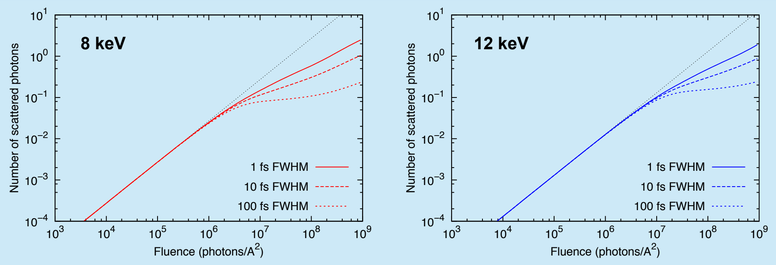


Time-averaged population vs. fluence (1 fs FWHM)



Influence on x-ray scattering

Number of scattered photons vs. fluence (resolution=1.7 Å)



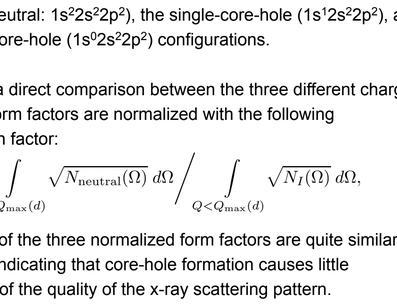
To describe the strength of the x-ray scattering signals, the number of scattered photons limited to the desired spatial resolution length *d* is given by

$$N_{\text{S}}(d) = \int_{Q<Q_{\max}(d)} \left[\int_{-\infty}^{\infty} J(t) \frac{d\sigma_{\text{S}}}{d\Omega}(t)\, dt \right] d\Omega,$$

where *J*(*t*) is the incident photon flux and $d\sigma_S(t)/d\Omega$ is the time-dependent differential scattering cross section. To measure the quality of the x-ray scattering patterns, we employ a modified *R*-factor,

$$R(d) = \int_{Q<Q_{\max}(d)} \left| \frac{\sqrt{N_{\text{real}}(\Omega)}}{\int_{Q'<Q_{\max}(d)} \sqrt{N_{\text{real}}(\Omega')}\, d\Omega'} - \frac{\sqrt{N_{\text{ideal}}(\Omega)}}{\int_{Q'<Q_{\max}(d)} \sqrt{N_{\text{ideal}}(\Omega')}\, d\Omega'} \right| d\Omega.$$

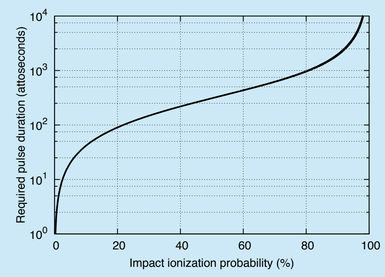
R-factor vs. resolution (10^7 photons/Å^2, 1 fs FWHM)



For low fluences, the number of scattered photons depends linearly on the fluence of incident photons, but is independent of the pulse length. To scatter at least 0.1 photons, the fluence must be in the regime above 10^6 photons/Å^2. At high fluence, after saturation of core ionization, the number of scattered photons is no longer a linear function of the fluence and, particularly, depends sensitively on the pulse length.

We examine the correlation between the *R*-factor and the desired spatial resolution for the pulse length of 1 fs FWHM and the fluence of 10^7 photons/Å^2. Because of the reduction of electronic damage at higher photon energies, the *R*-factor at 12 keV is less than that at 8 keV. For *d* > 1 Å, the spatially localized reduction of electron density in the 1s shell in the single-core-hole and double-core-hole configurations is difficult to resolve, rendering the *R*-factor rather low.

Impact ionization



Pulse duration required for a given impact ion. probability

Another important damage mechanism characteristic of extended molecular systems is impact ionization by (quasi-)free electrons. For an x-ray pulse much shorter than inner-shell decay lifetimes, impact ionization by Auger electrons is irrelevant, but impact ionization by photoelectrons is not negligible. By using short pulses, one can suppress photoelectron impact ionization.

Using the mean-free-path definition, we consider the pulse-weighted, time-averaged impact ionization probability for a 12 keV photoelectron in a carbon-based medium (mean-free-path: ~13 nm) during the x-ray pulse and find the pulse duration required for a given impact ionization probability. For a time-averaged impact ionization probability of 20%, the pulse duration required is about 100 attoseconds, corresponding to a Fourier-limited bandwidth of the order of 10 eV.

Conclusions

> Electronic damage and coherent x-ray scattering using ultrashort and ultraintense x-ray pulses attainable with current and future x-ray FELs are investigated.

> X-ray-induced damage processes including photoionization, Auger decay, and fluorescence, and coherent x-ray scattering processes are treated by the XATOM toolkit.

> Hollow-atom formation and the associated phenomenon of x-ray transparency and frustrated absorption play a crucial role in optimizing the strength and quality of single-shot x-ray scattering signals.

> In order to scatter from a carbon atom 0.1 photons per x-ray pulse, within a spatial resolution of 1.7 Å, a fluence of 1×10^7 photons/Å^2 per pulse is required at a pulse length of 1 fs and a photon energy of 12 keV.

> Attosecond x-ray FELs with a pulse length of ~100 as, ~10^{13} photons per pulse, and a photon energy of ~12 keV are ideal for single-shot imaging of individual macromolecules at atomic resolution.

References

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