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$$
\frac{dI(\mathbf{Q},\omega)}{d\Omega} = C(\Omega) \int_{-\infty}^{\infty} dt J(t) \sum_{I} P_{I}(t) \left| F_{P}^{0}(\mathbf{Q}) + \sum_{j=1}^{N_{H}} f_{j,I_{j}}(\mathbf{Q},\omega) e^{i\mathbf{Q} \cdot \mathbf{R}_{j}} \right|
$$

$$
f_{j,I_{j}}(\mathbf{Q},\omega) = f_{j,I_{j}}^{0}(\mathbf{Q}) + f'_{j,I_{j}}(\omega) + if''_{j,I_{j}}(\omega)
$$

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Sang-Kil Son¹ and Robin Santra^{1,2} 1CFEL, DESY / 2Department of Physics, University of Hamburg

C scattering from hollow atom consequent Auger decay the 1s-shell vacancy is filled by a 2s,p-shell electron and another 2s, p electron is emitted (A, black arrow). These V, P and P valiening from nonow atom

Figure 1 \sim 1 \sim

Introduction Theoretical and numerical details

XATOM: an integrated toolkit for X-ray and atomic physics

X-ray free-electron lasers (XFEL) open a new era in science and technology, offering many possibilities that have not been conceivable with conventional light sources. Because of their very high fluence within very short pulse duration, materials interacting with XFEL undergo significant radiation damage and possibly become highly ionized. To comprehend underlying physics, it is crucial to understand detailed ionization and relaxation dynamics in individual atoms during XFEL pulses. Here we present an integrated toolkit to investigate X-ray–induced atomic processes and to simulate electronic damage dynamics. This toolkit can easily handle all possible electronic configurations of all atom/ion species, and calculate physical observables during/after intense X-ray pulses. It has been successfully applied to study many XFEL-related phenomena from multiphoton ionization to molecular imaging.

Hartree-Fock-Slater model

To treat X-ray–atom interactions, we employ a consistent *ab initio* framework based on nonrelativistic quantum electrodynamics and perturbation theory. For implementation, we use the Hartree-Fock-Slater model, which employs a local density approximation to the exact exchange interaction, with the Latter tail correction.

Ne nonlinear X-ray response 1*s***22***s***22***p***⁶** *N* **of config. = 63**

Fe MAD at high intensity 1*s***22***s***22***p***63***s***23***p***63***d***64***s***²** *N* **of config. = 194,481**

Xe role of high-*E* **fluorescence 1***s***22***s***22***p***63***s***23***p***63***d***¹⁰ 4***s***24***p***64***d***105***s***25***p***⁶** *N* **of config. = 1,120,581**

 $1s²2s²2p²$ *N* of config. = 27 target; the actual pulse energy on target is reduced by five reflections an ionization step, V, P or A. Horizontal steps are approximately to scale time between photoionization events or Auger decay.

Charge state distribution produced by 1110 eV (1.27 mJ)

 $f^{\prime} (\omega) = - \frac{1}{2 \pi^2 \alpha} {\cal P}$ \int_0^∞ 0 ω'^2 $\frac{\partial}{\partial \omega^{\prime 2} - \omega^2} \sigma_{\rm P}(\omega^{\prime}) d\omega^{\prime}$ $f''(\omega) = -\frac{\omega}{4\pi\alpha}$ $\sigma_{\rm P}(\omega)$

> $\begin{array}{c} \hline \end{array}$ $\Big\}$ $\Big\}$ $\Big\}$ $\Big\}$ \vert

followed by simultaneous multiphoton absorption, as energetically required to reach the next higher charge state17, is one proposed mechanism, although the excitation of spectralfeatures such as a giant atomic resonance may modify this simple picture18. Studies of high-intensity photoabsorption mechanisms in this wavelength regime have also been conducted on more complex targets3,19. For argon clusters, it was found that ionization is best described by sequential single-photon absorption19 and that plasma effects such as inverse bremsstrahlung,important at longer wavelengths (.100 nm; refs 20, 21), no longer contribute. For solid aluminium targets, researchers recently observed the phenomenon of saturated absorption (that is, a fluence-dependent absorption cross-section) using 15-fs, 13.5-nm pulses and intensities up to

In the short-wavelength regime accessible with the LCLS, single

photons ionize deep inner-shell electrons and the atomic response to

, ,1 nm)

One of the prospective applications of XFEL is single-shot imaging of the proopoothe upphoduono of African formaging-size meaging of individual macromolecules, which employs coherent X-ray scattering to determine the atomically resolved structure of noncrystallized biomolecules or other nanoparticles. During ultrashort ergenming in term center of energy marring managements. cess with a well-known cross-section of the calibration of the calibra samples are subject to radiation damage, which may influence the quality of X-ray scattering patterns. Our numerical simulations of coherent X-ray scattering signals including electronic damage dynamics show that hollow-atom formation and the associated Narmos show that honow atom formation and the associated-state values of V ray fractional charge-state phases chomenon of λ -ray transparency of frastrated absorption play a crucial role in optimizing the strength and quality of single-shot X-ray scattering signals. The present results suggest that high-brightness attosecond XFELs would be ideal for single-shot imaging of individual macromolecules. phenomenon of X-ray transparency or frustrated absorption play a

can be examined experimentally. In contrast to the studies at longer wavelengths, all ionization steps are energetically allowed via singlephoton absorption, a fact that makes theoretical modelling considerably simpler. We exploit the remarkable flexibility of the LCLS (photon energy, pulse duration, pulse energy) combined with high resolution electron and ion time-of-flight spectrometers, to monitor and quantify photoabsorption pathways in the prototypical neon

We chose to study neon because notable changes in the electronic response occur over the initial operating photon energy range of LCLS, 800–2,000 eV (l 5 1.5–0.6 nm), as shown schematically in Fig. 1. There and in the following, V, P and A refer to the ejection of valence, inner-shell and Auger electrons, respectively. In all cases, sequential single-photon ionization dominates, although the differing electron ejection mechanisms lead to vastly different electronic configurations within each ionization stage. The binding energy of a 1s electron in neutral neon is 870 eV. For photon energies below this, the valence shell is stripped, as shown at the top of Fig. 1 in a VV… sequence. Above 870 eV, inner-shell electrons are preferentially ejected, creating 1s vacancies that are refilled by rapid Auger decay, a PA sequence. For energies above 993 eV, it is possible to create 'hollow' neon, that is, a completely empty 1s shell, in a PP sequence if the photoionization rate exceeds that of Auger decay. For energies above 1.36 keV, it is possible to fully strip neon, as shown at the

Figure 2a shows experimental ion charge-state yields at three dif-

ferent photon energies, 800 eV, 1,050 eV and 2,000 eV. These photon energies represent the different ionization mechanisms—valence ionization, inner-shell ionization and ionization in the regime far above all edges of all charge stages of neon. Despite the relatively large focal spot for these studies, ,1 mm, the dosage at 2,000 eV for neon (dosage 5 cross-section 3 fluence) is comparable to that proposed for the biomolecule imaging experiment where a 0.1-mm focal

. At the maximum fluence of ,105X-ray photons

, we observe all processes that are energetically allowed via

single-photon absorption. Thus, at 2,000 eV, we observe Ne10¹ and at 800 eV we find charge states as high as Ne8¹ (a fractional yield of

0.3%), indicating a fully-stripped valence shell. We note that valence stripping up to Ne7¹ was previously observed in neon for 90.5-eV, 1.8 3 10¹⁵ W cm2² irradiation18,22. At this intermediate photon

energy, 90.5 eV, the highest charge state can not be reached by a

Figure 2b compares the experimental ion charge-state yields with

theoretical calculations based on a rate equation model that includes only sequential single-photon absorption and Auger decay processes12. For simulations, two parameters are required, the X-ray fluence and pulse duration. The fluence (pulse energy/area) on target may be calculated from measured parameters for pulse energy and focal spot size. The X-ray pulse energies quoted throughout this rise to photoemission from the 1s shell (P, purple arrow), and in the

ionize 2s, p-shell valence electrons (V, red arrow). Higher energy X-rays given arrow (V, red arrow). Higher e

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Coefficients for the extended Karle-Hendrickson equation

In recent experiments, the CFEL-MPG-ASG team has measured charge state distribution and fluorescence spectra of Xe in coincidence. From theoretical point of view, this Xe problem is challenging because it has more than 1 million configurations and enormous numbers of processes are involved in electronic damage cascade. We have employed a Monte-Carlo approach to effectively solve the rate equation to attack this formidable task. Our numerical simulations show that charge state distribution of Xe is higher than expected from core-shell thresholds consideration. Also we have found an unusual nonlinear increase of high-energy fluorescence lines from 3*p* and 3*d* transitions as the fluence increases. From time-averaged population analysis of core-hole states, it can be shown that multiple-core-hole states of 3*p* and 3*d* subshells are responsible for these phenomena.

MAD (multi-wavelength anomalous diffraction) is used to determine phase information in X-ray crystallography by employing resonant elastic X-ray scattering from heavy atoms. We have recently proposed that the MAD phasing method can be extended to structural determination of molecules under intense X-ray pulses. The scattering intensity (per unit solid angle) including electronic

damage dynamics at high intensity (only heavy atoms scatter anomalously and undergo electronic damage) can be written as

If we assume that there is only one kind of heavy atoms and changes of their configurations happen independently, the above equation can be reduced to a generalized Karle-Hendrickson equation,

The study and applications of nonlinear processes from the microwave to the ultraviolet frequencies are extensive, but not realized for X-ray until now. We present the first experimental evidence of nonlinear response in the X-ray regime. In theory, we have extended our model to include shake-off processes and to adapt the two-photon ionization cross section for the rate equation model. We have measured and analyzed quadratic dependence of Ne⁹⁺ production on intensity when the photon energy is below the K-shell threshold of Ne⁸⁺. Nonlinear response comes from two channels: direct two-photon ionization and sequential two-photon ionization with transient excited states competing with the Auger decay clock.