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 $f''(\omega) = -\frac{\omega}{4\pi\alpha}$

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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 with ejection of electrons, leading to the creation of warm dense matter or plasma. To comprehend the 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. The

toolkit enables us to connect details of electronic dynamics in atoms and the evolution of atomic processes in plasmas generated by XFEL.

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. = 27,783**

Xe role of resonances 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**

Charge state distribution produced at 1110 eV (1.27 mJ)

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)

 $1s²2s²2p²$ and indicate the mean $1s²$ *N* of config. = 27 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 target; the actual pulse energy on target is reduced by five reflections on the actual pulse reduced by five r time between photoionization events or Auger decay.

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

NATURE | VOL 466|1 JULY 2010 ARTICLES | VOL 466|1 JULY 2010 ARTICLES | VOL 466|1 JULY 2010 ARTICLES | VOL 466| **Diagrams of multiphoton absorption mechanisms in Ne induced by ultraintense X-ray pulses**

response occur over the initial operating photon energy range of

C scattering from hollow atom 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 rise to photoemission from the 1s shell (P, purple arrow), and in the consequent Auger decay the 1s-shell vacancy is filled by a 2s, p-shell electron is filled by a 2s, p-shell ele and another 2s,p electron is emitted (A, black arrow). These V, P and A processes are shown in more detail in the inset; they all increase the charge of rattering trom hollow a multiphoton absorption stripping the neon atom. The horizontal direction

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

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 Figure 1 [|] Diagram of the multiphoton absorption mechanisms in neon

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

ejected, creating 1s vacancies that are refilled by rapid Auger decay, a parameter above 993 σ $\overline{}$ if the photoionization rate exceeds that of $\mathcal{L}_{\mathcal{A}}$ above 1.36 keV, it is possible to fully strip neon, as \mathbf{S} Figure 2a shows experimental ion charge-state \mathbf{a} ferent photon energies, $\frac{1}{2}$ energies represent the different ionization mechanisms—valence ionization, inner-shell ionization in the regime far \vert above all charge stages of c large for the dosage at $\frac{1}{\sqrt{2}}$ neon (dosage 5 cross-section 3 fluence) is comparable to that proposed for the biomolecule imaging experiment where a 0.1-mm focal $\overline{}$, we observe all processes that are energetically all processes that are energies that are energy \sim single-photon absorption. Thus, at 2,000 eV, we observe Neumann absorpti at 800 eV we find charge states as \parallel as $\overline{}$ indicating a fully-stripped valence shell. We note that valence shell. We note that valence shell. We note stripping up to Ne7¹ was previously observed in neon for 90.5-eV, One of the prospective applications of XFEL is single-shot imaging of individual macromolecules, which employs coherent X-ray both at 800 eV, where it 800 eV, where is dependent only of the state of the state of the state of the state o scattering to determine the atomically resolved structure of noncrystallized biomolecules or other nanoparticles. During ultrashort and ultraintense X-ray pulses with an atomic scale wavelength, untaintense x-ray puises with an atomic scale wavelength, 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 Nent X ray scallering signals including electronic damage- $\frac{1}{2}$ show that hollow-atom formation and the associated phenomenon of X-ray transparency or frustrated absorption play a crucial role in optimizing the strength and quality of single-shot X-ray $\frac{1}{2}$ order to $\frac{1}{2}$ much more proposed in the propos tering signals. The present results suggest that ingri-brighting attosecond XFELs would be ideal for single-shot imaging of individual macromolecules. **Example states up to the example states up to the example states up to the example of the example states up to the exam** dynamics show that hollow-atom formation and the associated scattering signals. The present results suggest that high-brightness

Charge state distribution of xenon (80 fs, 2.5 mJ, 3×3 µm²)

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Fluorescence spectrum of xenon as a function of fluence

In recent experiments, the CFEL-MPG-ASG team has measured charge state distribution and fluorescence spectra of Xe atoms at LCLS XFEL. 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, which can be explained by the multiple-core-hole states of 3*p* and 3*d* subshells in the intermediate charge states and resonantly enhanced absorption processes in the high charge states.

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 essential equation for the MAD method is reformulated and relevant coefficients are calculated with detailed electronic damage dynamics of heavy atoms and accompanying changes of the dispersion correction. Our study opens up a new opportunity of resolving the phase problem in femtosecond nanocrystallography with XFELs.

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 conducted at LCLS XFEL. 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. This observation will boost the emergence of nonlinear X-ray physics.

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Dispersion corrections of several selected charge states of iron

Rate equation model

To simulate electronic dynamics during intense X-ray pulses, we employ the rate equation approach with all computed cross sections and rates for all possible configurations, and calculate charge state distribution, electron and fluorescence spectra, scattering signals, and so on.

Towards plasmas

This toolkit is extendable to implement various plasma screening models that may cause atomic structural changes, and to include electron energy distributions and collisional ionization processes.