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

Sang-Kil Son[1] and Robin Santra[1,2]

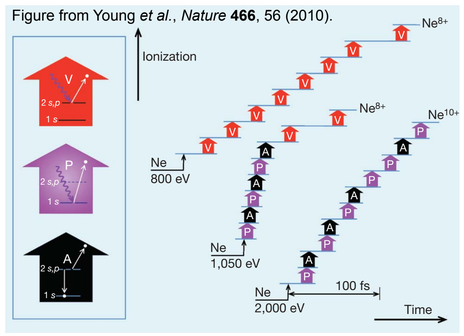
[1]CFEL, DESY, Germany / [2]Department of Physics, University of Hamburg, Germany

Introduction

X-ray free-electron lasers (XFEL) open a new era in science and technology, offering many unique opportunities that have not been conceivable with conventional light sources. Because XFELs produce ultrashort pulses with a very high x-ray photon fluence, materials interacting with XFEL pulses undergo significant radiation damage and possibly become highly ionized. To understand the underlying physics, it is crucial to describe 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 XATOM toolkit can handle all possible electronic configurations of all atom/ion species, and calculate physical observables during/after intense x-ray pulses. By use of XATOM, we can explore many exciting XFEL-related phenomena from multiphoton multiple ionization to molecular imaging.

Diagrams of multiphoton absorption mechanisms in Ne induced by ultraintense X-ray pulses

Figure from Young *et al.*, *Nature* **466**, 56 (2010).



Theoretical and numerical details

Hamiltonian and perturbation theory

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 with the Latter tail correction.

$$\hat{H} = \hat{H}_{\mathrm{mol}} + \hat{H}_{\mathrm{EM}} + \hat{H}_{\mathrm{int}}$$

$$\hat{H}_{\mathrm{EM}} = \sum_{\mathbf{k},\lambda} \omega_{\mathbf{k}} \hat{a}^{\dagger}_{\mathbf{k},\lambda} \hat{a}_{\mathbf{k},\lambda}, \quad \omega_{\mathbf{k}} = |\mathbf{k}|/\alpha$$

$$\hat{H}_{\mathrm{int}} = \alpha \int d^3x\, \hat{\psi}^{\dagger}(\mathbf{x}) \left[\hat{\mathbf{A}}(\mathbf{x}) \cdot \frac{\boldsymbol{\nabla}}{i} \right] \hat{\psi}(\mathbf{x}) + \frac{\alpha^2}{2} \int d^3x\, \hat{\psi}^{\dagger}(\mathbf{x}) \hat{A}^2(\mathbf{x}) \hat{\psi}(\mathbf{x})$$

$|I\rangle$: initial state, $|F\rangle$: final state

$$\Gamma_{FI} = 2\pi\delta(E_F - E_I) \left| \langle F|\hat{H}_{\mathrm{int}}|I\rangle + \sum_M \frac{\langle F|\hat{H}_{\mathrm{int}}|M\rangle\langle M|\hat{H}_{\mathrm{int}}|I\rangle}{E_I - E_M + i\epsilon} + \cdots \right|^2$$

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 *n*-hole configurations, and calculate charge state distribution, electron/fluorescence spectra, scattering signals, etc.

$$\frac{d}{dt} P_I(t) = \sum_{I' \neq I}^{\text{all config.}} \left[\Gamma_{I' \to I} P_{I'}(t) - \Gamma_{I \to I'} P_I(t) \right]$$

P **Photoabsorption** $|I\rangle = |\Psi_0^{N_{\mathrm{el}}}\rangle|N_{\mathrm{EM}}\rangle$, $|F\rangle = |\Psi_F^{N_{\mathrm{el}}}\rangle|N_{\mathrm{EM}}-1\rangle$

$$\sigma_{\mathrm{P}}(i,\omega) = \frac{4}{3}\alpha\pi^2\omega N_i \sum_{l_j=|l_i-1|}^{l_i+1} \frac{l_>}{2l_i+1} \left| \int_0^{\infty} P_{n_i l_i}(r) P_{\varepsilon l_j}(r)\, r\, dr \right|^2$$

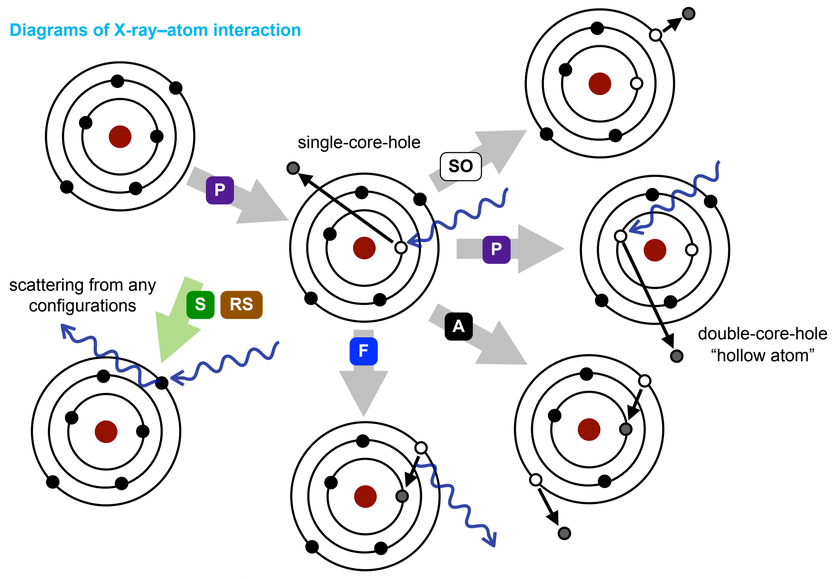
F **Fluorescence** $|I\rangle = \hat{c}_i|\Phi_0^{N_{\mathrm{el}}}\rangle|0\rangle$, $|F\rangle = \hat{c}_{i'}|\Phi_0^{N_{\mathrm{el}}}\rangle\hat{a}^{\dagger}_{\mathbf{k}_F,\lambda_F}|0\rangle$

$$\Gamma_{\mathrm{F}}(i,j) = \frac{4}{3}\alpha^3 (I_i - I_j)^3 \frac{N_i^{\mathrm{H}} N_j}{4l_j+2} \cdot \frac{l_>}{2l_i+1} \left| \int_0^{\infty} P_{n_i l_i}(r) P_{n_j l_j}(r)\, r\, dr \right|^2$$

A **Auger / Coster–Kronig decay** $|I\rangle = \hat{c}_i|\Phi_0^{N_{\mathrm{el}}}\rangle$, $|F\rangle = \hat{c}_a^{\dagger}\hat{c}_j\hat{c}_{j'}|\Phi_0^{N_{\mathrm{el}}}\rangle$

$$\Gamma_{\mathrm{A}}(i,jj') = \pi \frac{N_i^{\mathrm{H}} N_{jj'}}{2l_i+1} \sum_{L=|l_j-l_{j'}|}^{l_j+l_{j'}} \sum_{S=0}^{1} \sum_{l_{i'}} (2L+1)(2S+1) |M_{LS}(j,j',i,i')|^2$$

Diagrams of X-ray–atom interaction



SO **Shake-off process**: sudden approximation

$$p_{\mathrm{SO}}(i;I,I') = 1 - \left| \int_0^{\infty} P_{n_i l_i}(r;I) P_{n_i l_i}(r;I')\, dr \right|^2$$

S **Elastic X-ray scattering** $|I\rangle = |\Psi_0^{N_{\mathrm{el}}}\rangle|N_{\mathrm{EM}}\rangle$, $|F\rangle = |\Psi_0^{N_{\mathrm{el}}}\rangle\hat{a}^{\dagger}_{\mathbf{k}_F,\lambda_F}|N_{\mathrm{EM}}-1\rangle$

$$f^0(\mathbf{Q}) = \int \rho(\mathbf{r})\, e^{i\mathbf{Q}\cdot\mathbf{r}}\, d^3r$$

$$\frac{d\sigma_{\mathrm{S}}}{d\Omega}(t) = \sum_I^{\text{all config.}} P_I(t) \frac{d\sigma_{\mathrm{S}}}{d\Omega}\Big|_I = \left(\frac{d\sigma}{d\Omega}\right)_{\mathrm{T}} \sum_I^{\text{all config.}} P_I(t) |f_I^0(\mathbf{Q})|^2$$

RS **Resonant elastic X-ray scattering (dispersion correction)**: second-order term

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

$$f'(\omega) = -\frac{1}{2\pi^2\alpha} \mathcal{P} \int_0^{\infty} \frac{\omega'^2}{\omega'^2 - \omega^2} \sigma_{\mathrm{P}}(\omega') d\omega'$$

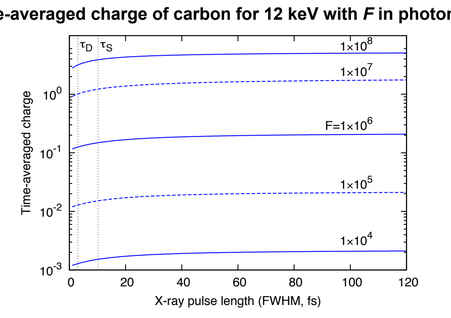
$$f''(\omega) = -\frac{\omega}{4\pi\alpha} \sigma_{\mathrm{P}}(\omega)$$

C
scattering from hollow atom

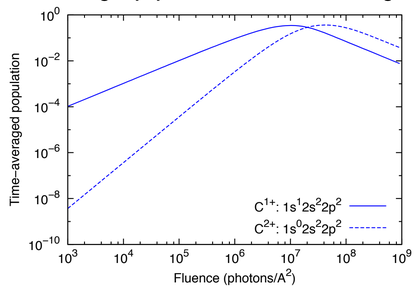
$1s^2 2s^2 2p^2$
***N* of config. = 27**

One of the prospective applications of XFEL is single-shot imaging of individual macromolecules, which employs coherent X-ray scattering to determine the atomically resolved structure of non-crystallized biomolecules or other nanoparticles. During ultrashort and ultraintense X-ray pulses 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 dynamics 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 scattering signals. The present results suggest that high-brightness attosecond XFELs would be ideal for single-shot imaging of individual macromolecules.

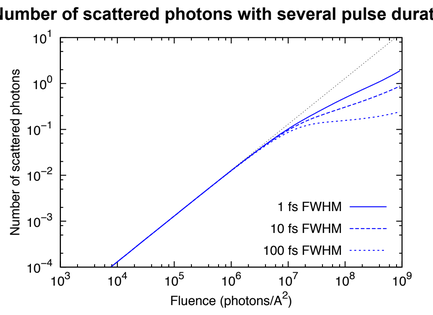
Time-averaged charge of carbon for 12 keV with *F* in photons/Å²



Time-averaged populations of core-hole configurations



Number of scattered photons with several pulse durations



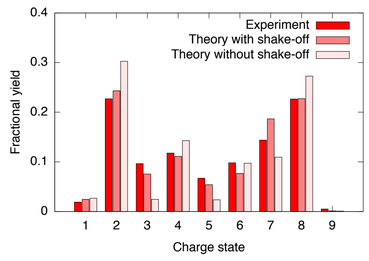
S.-K. Son, L. Young & R. Santra, *Phys. Rev. A* **83**, 033402 (2011).

Ne
nonlinear X-ray response

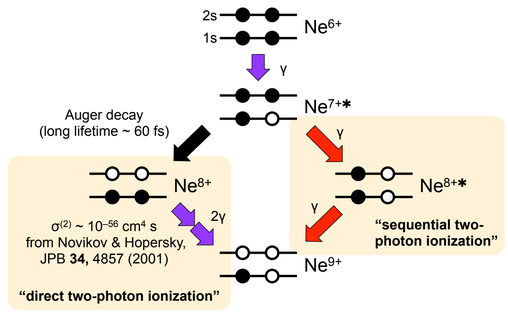
$1s^2 2s^2 2p^6$
***N* of config. = 63**

The study and applications of nonlinear processes from the micro-wave 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 Ne^{9+} production on intensity when the photon energy is below the K-shell threshold of Ne^{8+}. 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.

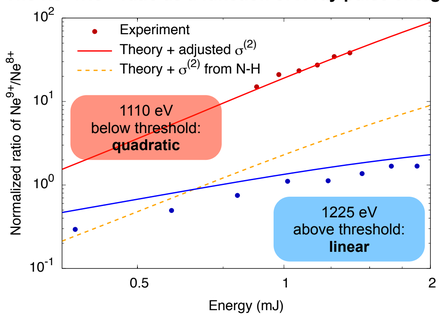
Charge state distribution of neon produced at 1110 eV



Two-photon ionization mechanisms at 1110 eV



The Ne^{9+}/Ne^{8+} ratio as a function of X-ray pulse energy



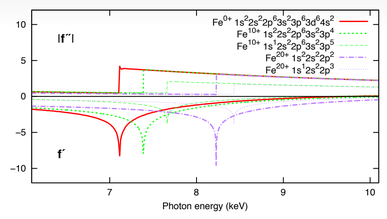
G. Doumy *et al.*, *Phys. Rev. Lett.* **106**, 083002 (2011).

Fe
MAD at high intensity

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$
***N* of config. = 27,783**

The MAD (multiwavelength anomalous diffraction) method is used to determine phase information in X-ray crystallography by employing anomalous scattering from heavy atoms. Because of the ultra-brightness of XFEL, samples experience severe and unavoidable electronic radiation damage, especially to heavy atoms, which hinders direct implementation of MAD with XFEL. We propose a generalized version of the MAD phasing method at high x-ray intensity. We demonstrate the existence of a Karle–Hendrickson-type equation for the MAD method in the high-intensity regime and calculate relevant coefficients with electronic damage dynamics and accompanying changes of the dispersion correction. Our work provides an important conceptual extension of the recent development of femtosecond nanocrystallography using XFELs.

Dispersion corrections of several selected charge states of iron



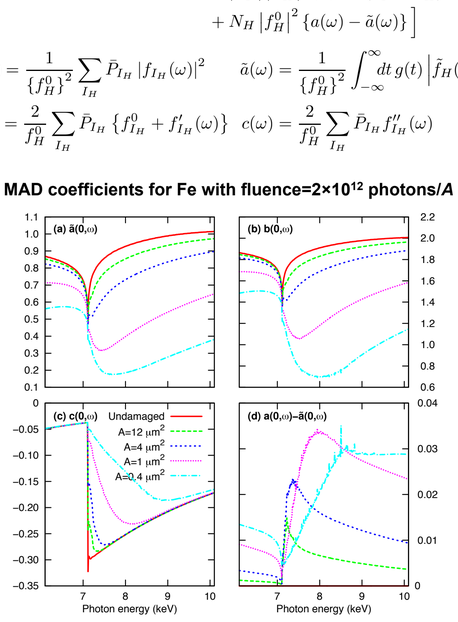
Generalized Karle–Hendrickson equation

$$\frac{dI(\omega)}{d\Omega} = \mathcal{F}C(\Omega) \Big[|F_P^0|^2 + |F_H^0|^2\, \tilde{a}(\omega) + |F_P^0||F_H^0|\, b(\omega)\cos\left(\phi_P^0 - \phi_H^0\right) + |F_P^0||F_H^0|\, c(\omega)\sin\left(\phi_P^0 - \phi_H^0\right) + N_H |f_H^0|^2 \{a(\omega) - \tilde{a}(\omega)\} \Big]$$

$$a(\omega) = \frac{1}{\{f_H^0\}^2} \sum_{I_H} \bar{P}_{I_H} |f_{I_H}(\omega)|^2 \qquad \tilde{a}(\omega) = \frac{1}{\{f_H^0\}^2} \int_{-\infty}^{\infty} dt\, g(t) \left| \tilde{f}_H(\omega,t) \right|^2$$

$$b(\omega) = \frac{2}{f_H^0} \sum_{I_H} \bar{P}_{I_H} \{ f_{I_H}^0 + f'_{I_H}(\omega) \} \qquad c(\omega) = \frac{2}{f_H^0} \sum_{I_H} \bar{P}_{I_H} f''_{I_H}(\omega)$$

MAD coefficients for Fe with fluence=2×10¹² photons/*A*



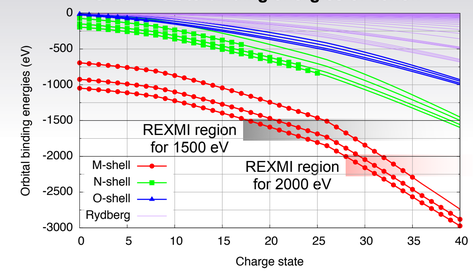
S.-K. Son, H. N. Chapman & R. Santra, *Phys. Rev. Lett.* **107**, 218102 (2011).

Xe
ultra-efficient ionization

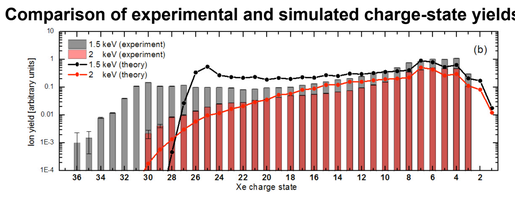
$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$
***N* of config. = 1,120,581**

The CFEL-MPG-ASG team has measured charge state distributions and fluorescence spectra of Xe atoms at LCLS XFEL. From a theoretical point of view, this Xe problem is quite challenging because it requires more than 1 million coupled rate equations and enormous numbers of processes are involved in electronic damage cascade. We employ a Monte-Carlo approach to effectively solve the rate equation to attack this formidable task. We observe surprisingly high charge states of Xe at 1500 eV up to Xe^{36+}, far beyond the straightforward sequential one-photon ionization limit at Xe^{26+}. We find that transient resonant excitations in the highly charged ions open new ionization channels and enhance the ionization process. Our study provides fundamental insight into the interaction of intense X-ray pulses with heavy atoms.

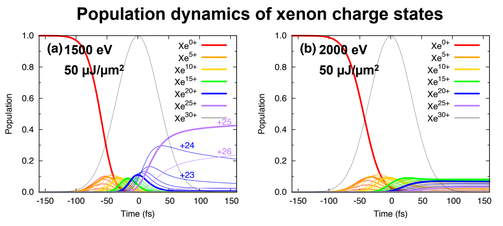
Ground-state binding energies of xenon



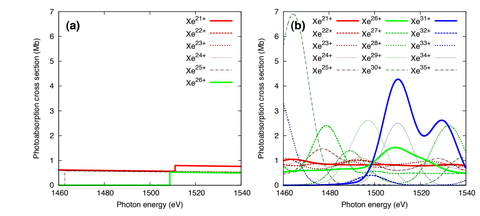
Comparison of experimental and simulated charge-state yields



Population dynamics of xenon charge states



Photoabsorption cross sections calculated (a) without and (b) with resonances only for the ground-state configurations



B. Rudek *et al.*, submitted.
Collaboration with CFEL–MPG–ASG

Center for Free-Electron Laser Science
CFEL is a scientific cooperation of the three organizations:
DESY – Max Planck Society – University of Hamburg