Electronic response to X-ray free-electron laser pulses

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Alster in Hamburg, Germany

Overview

- Introduction to XFEL
- Theory / XATOM toolkit
- Applications to XFEL experiments
- Conclusion

Acknowledgment

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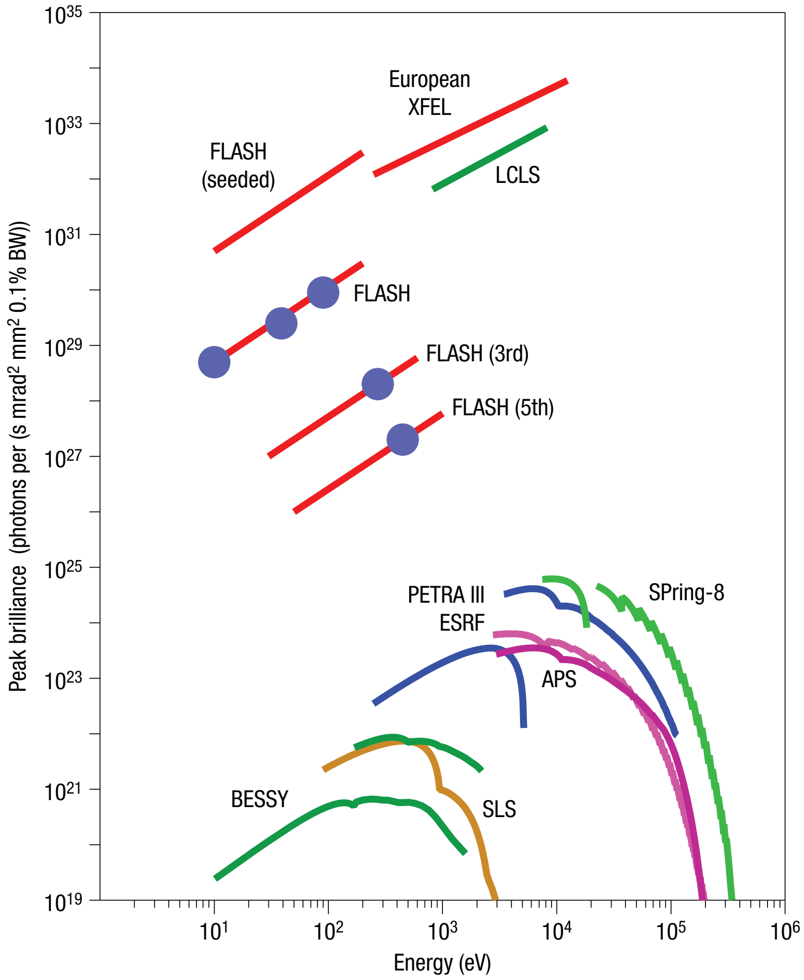
What is XFEL?

- XFEL: X-ray Free-Electron Laser
- Ultraintense
  - synchrotron: at most one photon absorbed per pulse
  - XFEL: many photons absorbed per pulse
  - fluence: ~10^{13} photons per μm^2 per pulse
  - peak intensity: ~10^{18} W/cm^2
- Ultrafast
  - pulse duration: femtoseconds or sub-fs
- Characteristics of X rays
  - large penetration depth: small absorption probability
  - element specific: inner-shell electrons
  - Å wavelength: imaging with atomic resolution



Ackermann *et al.*, *Nature Photon.* **1**, 336 (2007).

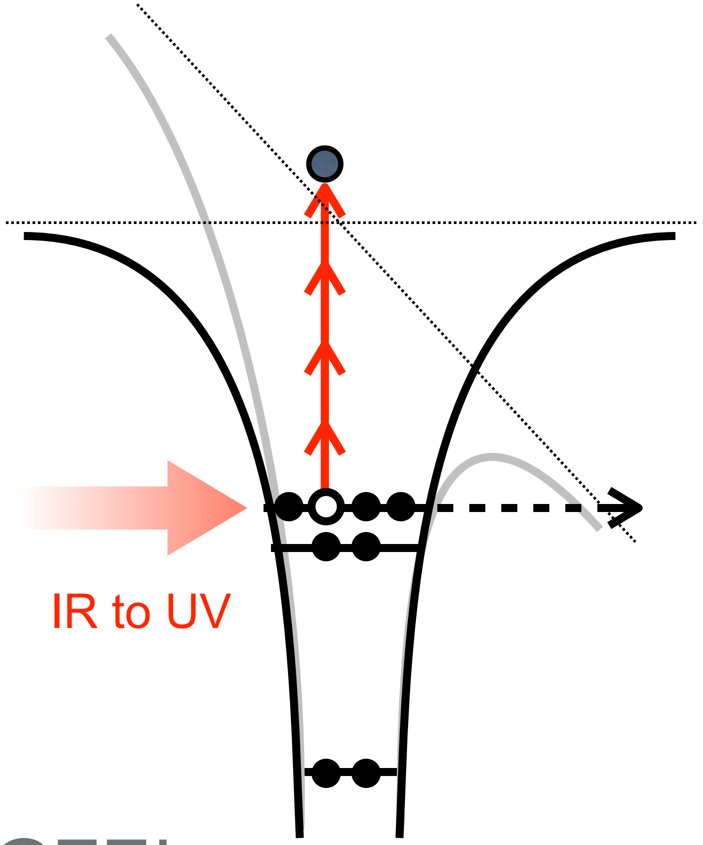
Where are XFELs?

- FLASH at DESY, Germany (2004)
- LCLS at SLAC, USA (2009)
- SACLA at RIKEN Harima, Japan (2011)
- PAL XFEL at Pohang, Korea (2015)
- European XFEL, Germany (2015)

What differences from optical strong-field?

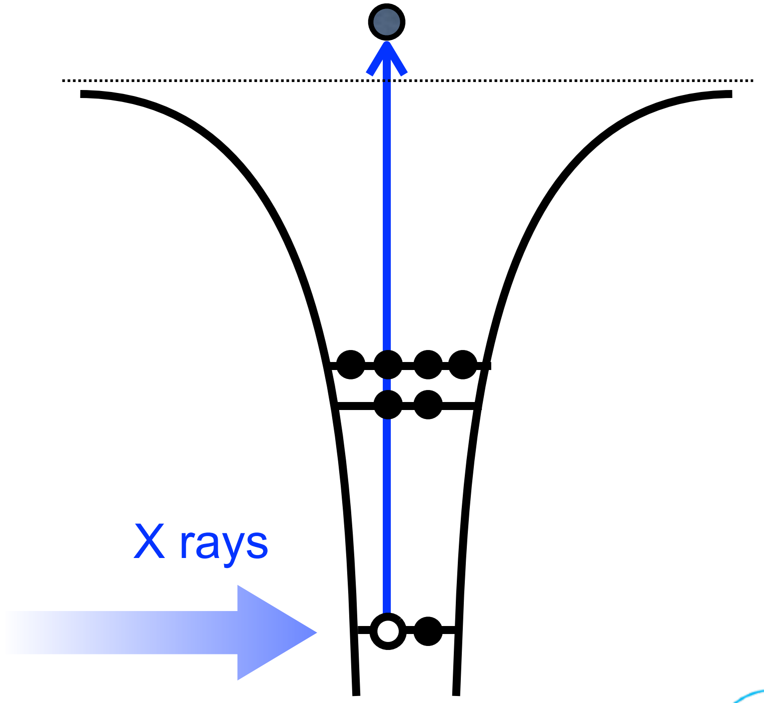
Optical strong-field regime

- tunneling or multiphoton processes
- valence-electron ionization

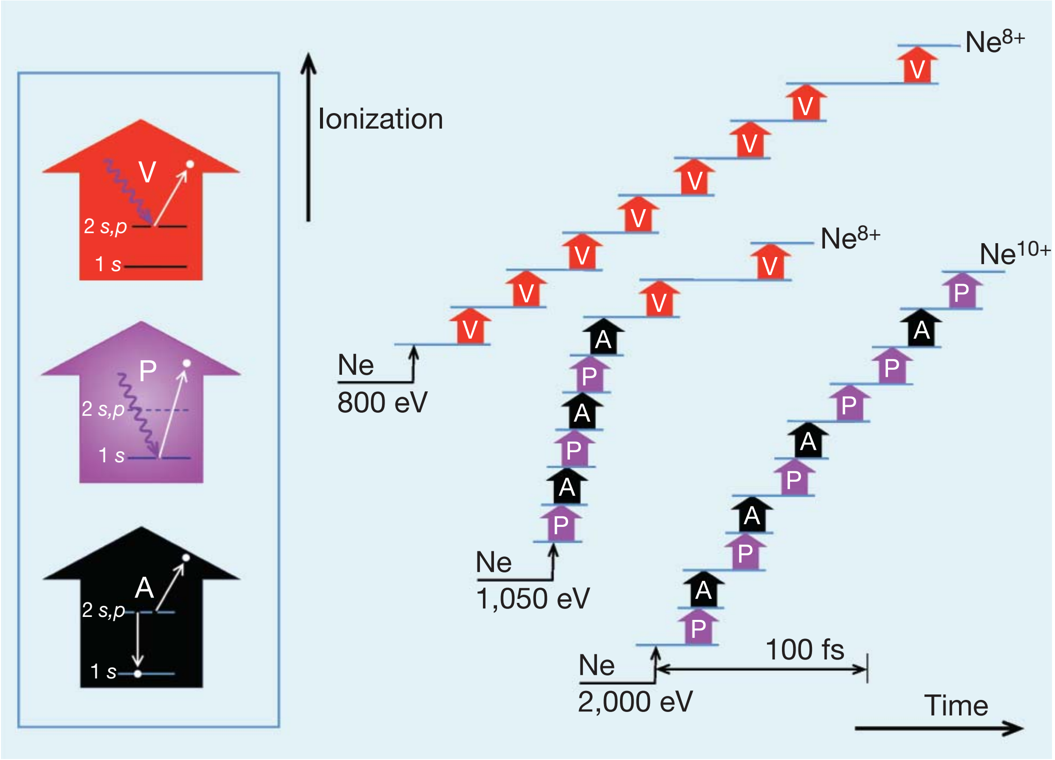


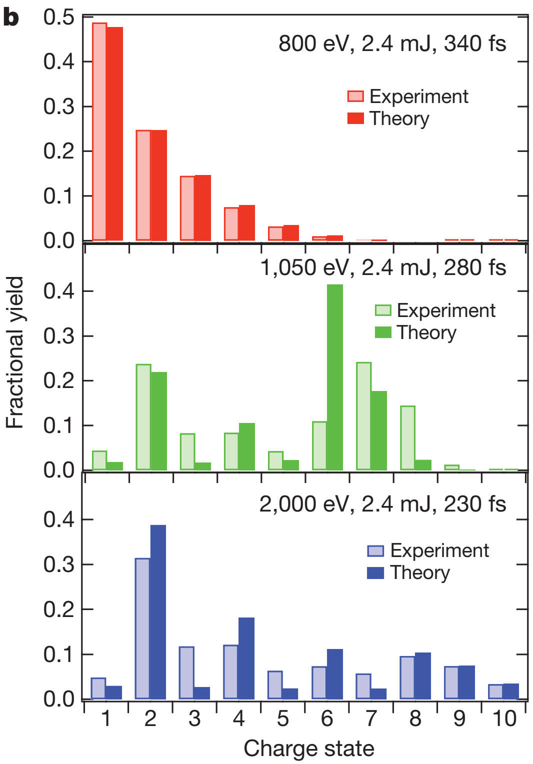
Intense X-ray regime

- mainly one-photon processes
- core-electron ionization and relaxation
- multiphoton multiple ionization via a sequence of one-photon processes



Multiphoton Multiple Ionization

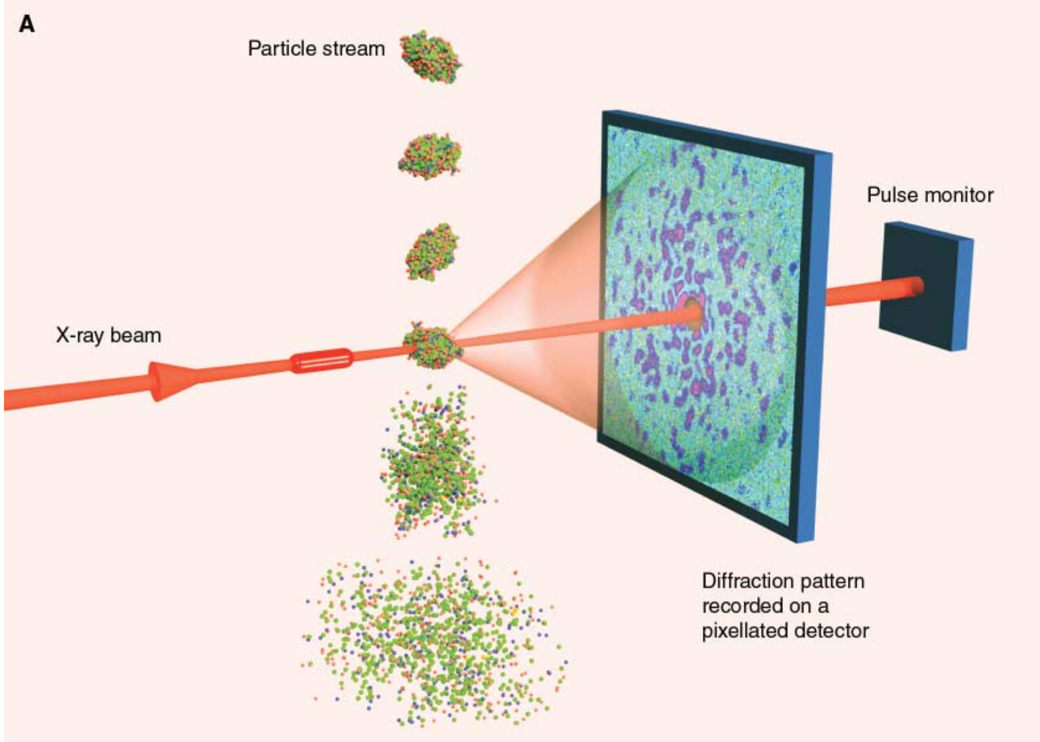




Young *et al.*, *Nature* **466**, 56 (2010).

- First LCLS experiment: fundamental atomic physics in XFEL
- Lots of x-ray photons: repeated *K*-shell ionization (P) followed by Auger relaxation (A)
- Good agreement between experiment and theory (Nina Rohringer and Robin Santra)

Ultrafast X-ray scattering



Gaffney & Chapman, *Science* **316**, 1444 (2007).

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Nature **470**, 73 (2011).

Nature **470**, 78 (2011).

Nature Photon. **6**, 35 (2012).

Science **337**, 362 (2012).

Nature Meth. **9**, 259 (2012).

Nature Meth. **9**, 263 (2012).

⋮

- Single-shot imaging of individual macromolecules or nano-sized crystals
- Ultrafast (femtosecond) pulse: diffraction before Coulomb explosion
- Electronic radiation damage is unavoidable.

X-ray-induced atomic processes

- Based on nonrelativistic QED and perturbation theory
- Hamiltonian

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

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

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

- Perturbation theory

$$\hat{H} = \hat{H}_0 + \hat{H}_{\mathrm{int}}$$

$$|I\rangle\text{: initial state,} \quad |F\rangle\text{: final state}$$

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

Santra, *J. Phys. B* **42**, 023001 (2009).

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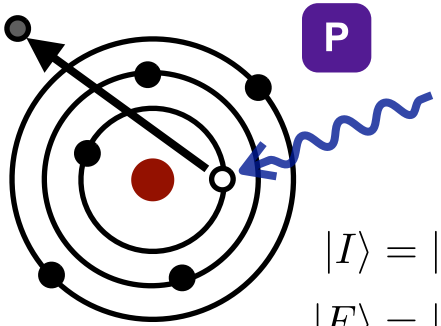
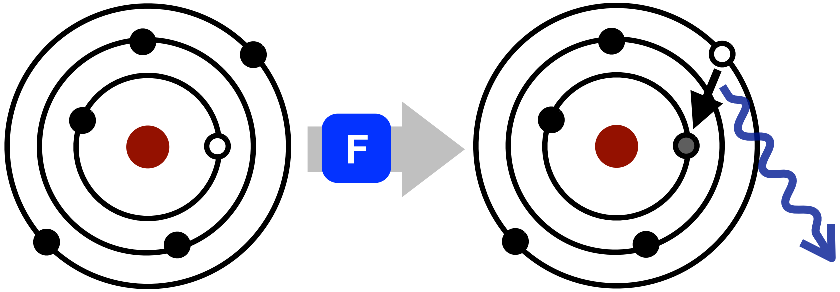
X-ray-induced atomic processes (cont.)

- Photoabsorption



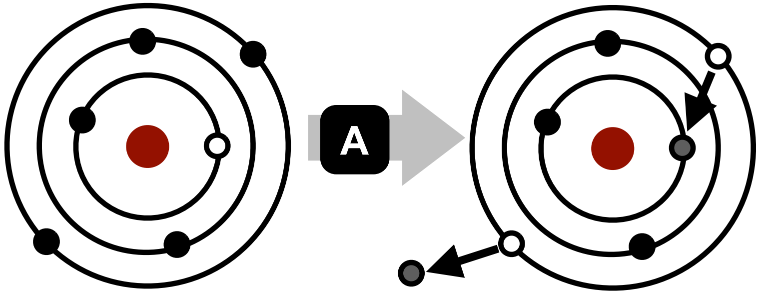
$$|I\rangle = |\Psi_0^{N_\text{el}}\rangle|N_\text{EM}\rangle$$
$$|F\rangle = |\Psi_F^{N_\text{el}}\rangle|N_\text{EM}-1\rangle$$

- Fluorescence



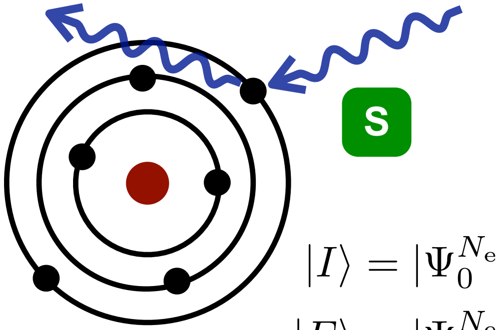
$$|I\rangle = \hat{c}_i|\Phi_0^{N_\text{el}}\rangle|0\rangle, \quad |F\rangle = \hat{c}_{i'}|\Phi_0^{N_\text{el}}\rangle\hat{a}^\dagger_{\mathbf{k}_F,\lambda_F}|0\rangle$$

- Auger and Coster–Kronig decay



$$|I\rangle = \hat{c}_i|\Phi_0^{N_\text{el}}\rangle, \quad |F\rangle = \hat{c}_a^\dagger\hat{c}_j\hat{c}_{j'}|\Phi_0^{N_\text{el}}\rangle$$

- Elastic X-ray scattering



$$|I\rangle = |\Psi_0^{N_\text{el}}\rangle|N_\text{EM}\rangle$$
$$|F\rangle = |\Psi_0^{N_\text{el}}\rangle\hat{a}^\dagger_{\mathbf{k}_F,\lambda_F}|N_\text{EM}-1\rangle$$

Electronic damage dynamics by XFEL

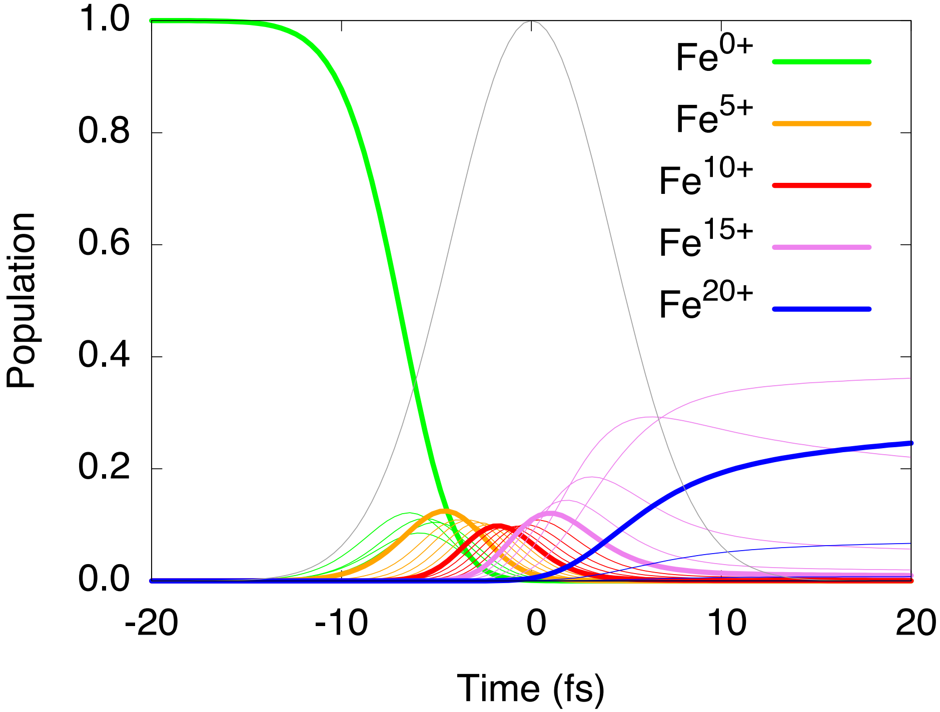
Coupled rate equation

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

Numerical procedure

- construct all possible *n*-hole configurations for +*n* charge state for all possible *n*
- optimize orbital structures for each configuration
- calculate cross sections and rates for each configuration
- solve a set of rate equations with all parameters

Fe @ 8 keV, 5×10^{12} photons/μm^2, 10 fs FWHM



XATOM: toolkit for X-ray atomic physics

- What XATOM can do:
  - Hartree–Fock–Slater method, bound and continuum states
  - photoionization / photoabsorption cross sections
  - Auger and Coster–Kronig rates, and fluorescence rates
  - elastic x-ray scattering form factors including dispersion corrections
  - shake-off branching ratios
  - two-photon ionization / resonant excitation included
  - plasma screening effect included
  - large-scale coupled rate equations: direct solution or Monte–Carlo solution
- Features:
  - versatile and simple
  - captures all relevant basic processes
  - useful for atoms, molecules and clusters
  - becomes an essential tool for XFEL simulations

Applications to XFEL science

Multiphoton multiple ionization

- Ionization dynamics of heavy atoms

Son & Santra, *Phys. Rev. A* **85**, 063415 (2012).

- Xe at LCLS: ultra-efficient ionization

Rudek, Son *et al.*, *Nature Photon.* (DOI: 10.1038/nphoton.2012.261).

- Xe at SACLA: deep inner-shell ionization

Fukuzawa, Son *et al.*, submitted.

Ultrafast X-ray scattering

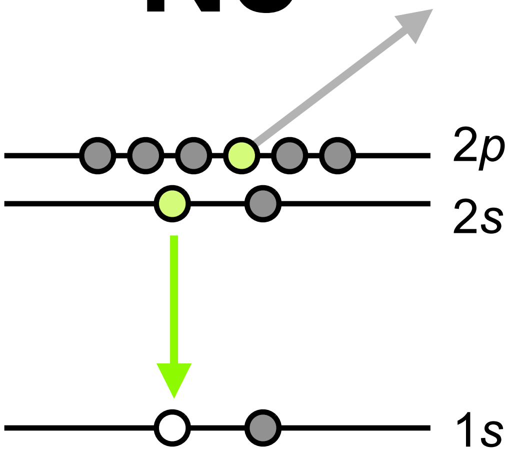
- C: scattering vs. absorption

Son, Young & Santra, *Phys. Rev. A* **83**, 033402 (2011).

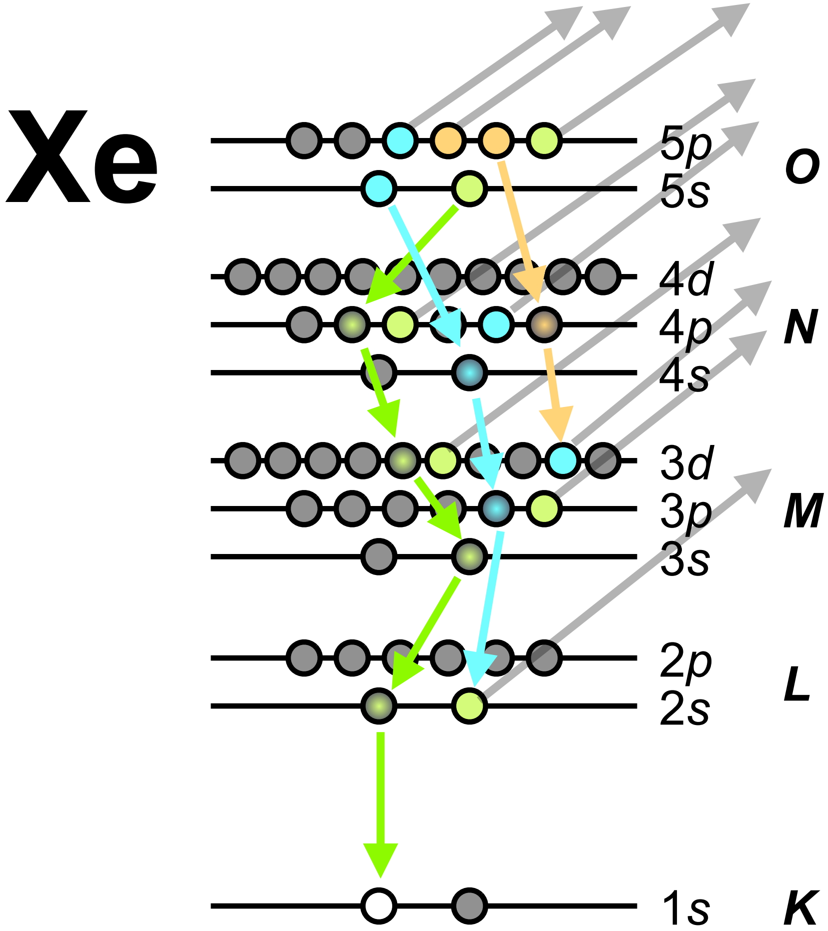
- Fe: MAD at high X-ray intensity

Son, Chapman & Santra, *Phys. Rev. Lett.* **107**, 218102 (2011).

Decay cascade for heavy atoms

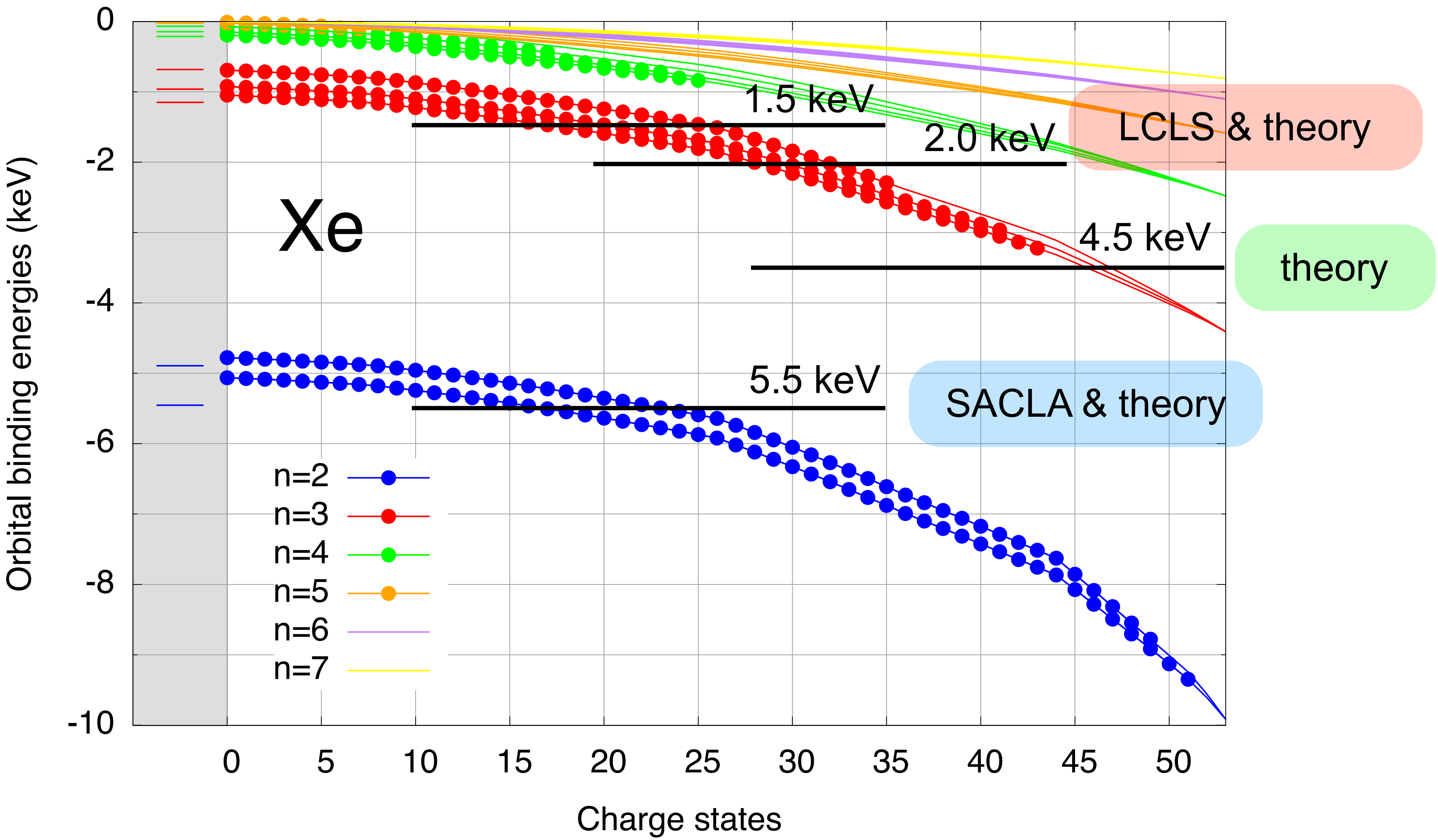


$Ne^{+*} \rightarrow Ne^{2+} + e^-$



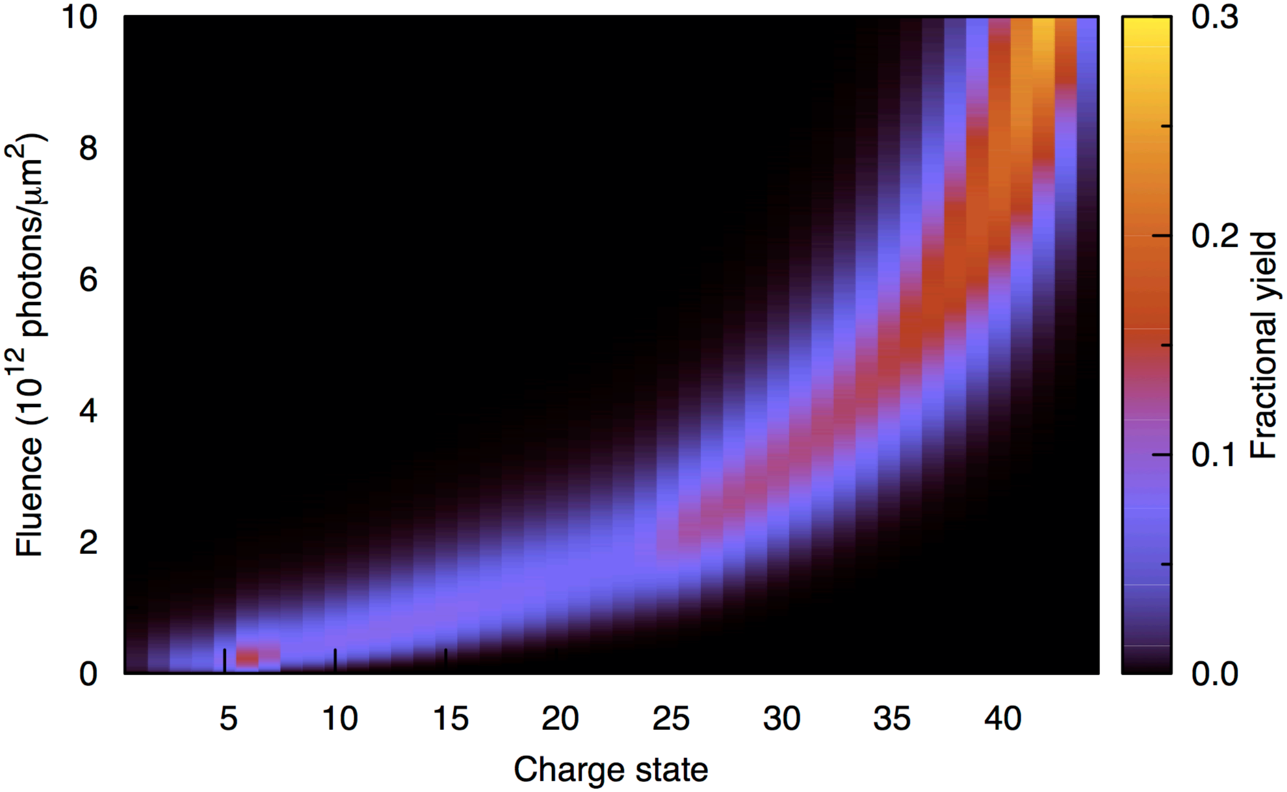
$Xe^{+*} \rightarrow Xe^{(n+1)+} + ne^-$

Xenon atom interacting with hard X rays



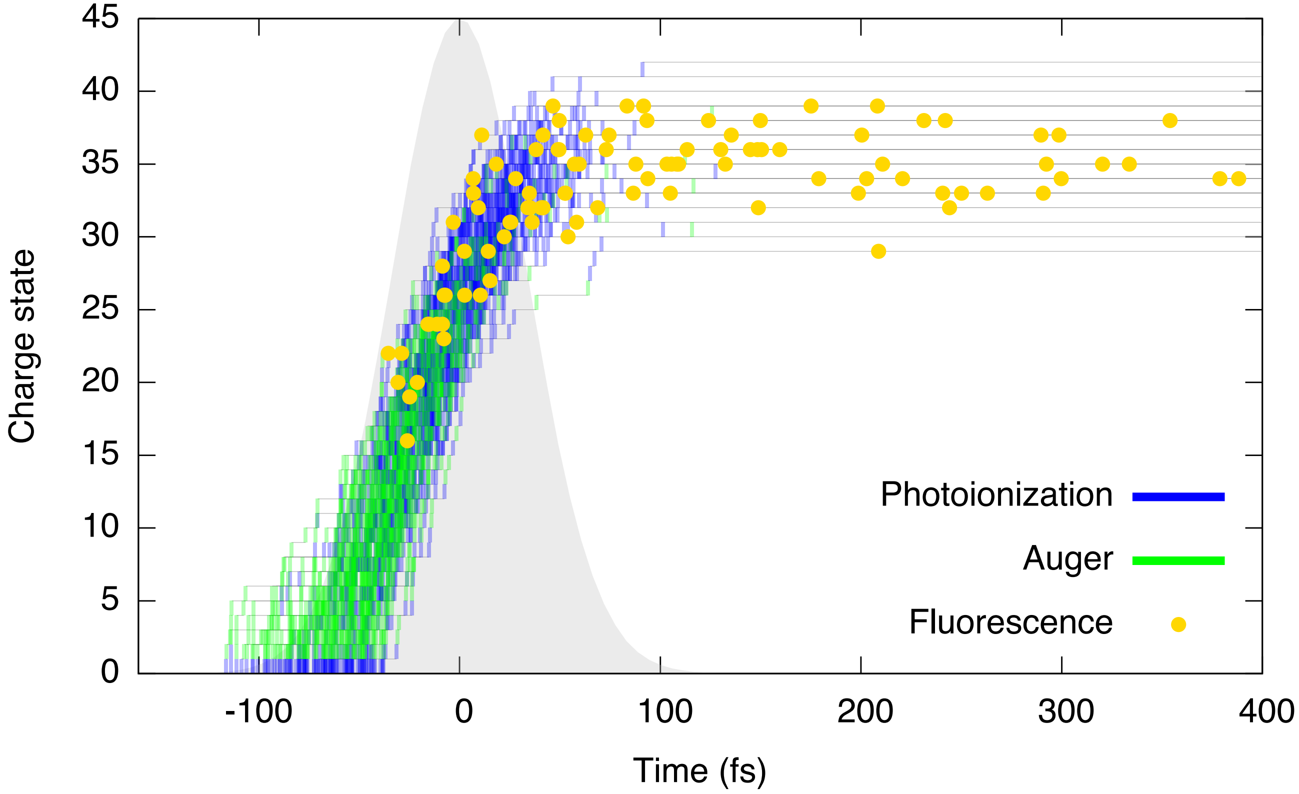
Ionization dynamics of heavy atoms

- Calculation of charge state distributions as a function of fluence
- At 4.5 keV: potentially strip off all 44 electrons (in *M*-, *N*-, and *O*-shell)



Son & Santra, *Phys. Rev. A* **85**, 063415 (2012).

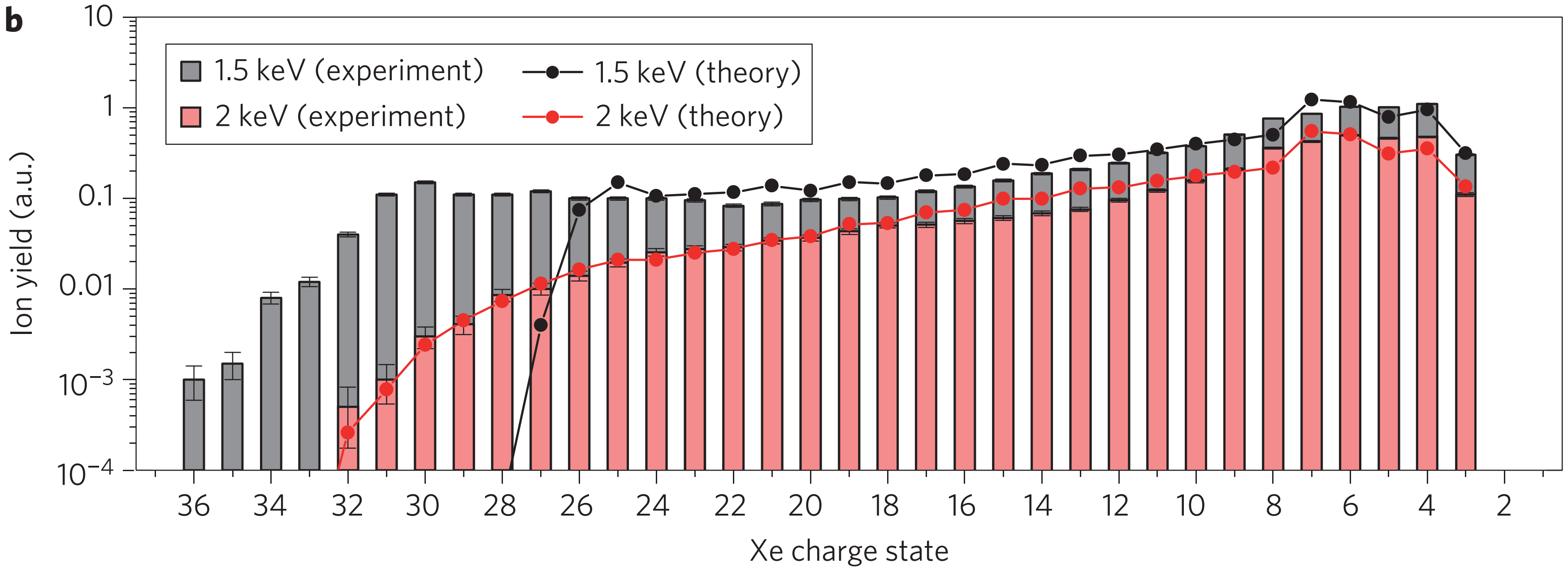
Ionization dynamics of heavy atoms (cont.)



- Xe: $1s^2\, 2s^2 2p^6\, \underline{3s^2 3p^6 3d^{10}\, 4s^2 4p^6 4d^{10}\, 5s^2 5p^6}$
- Computational challenge: # of coupled rate eqs. ~1M → Monte-Carlo

Son & Santra, *Phys. Rev. A* **85**, 063415 (2012).

Ultra-efficient ionization by XFEL

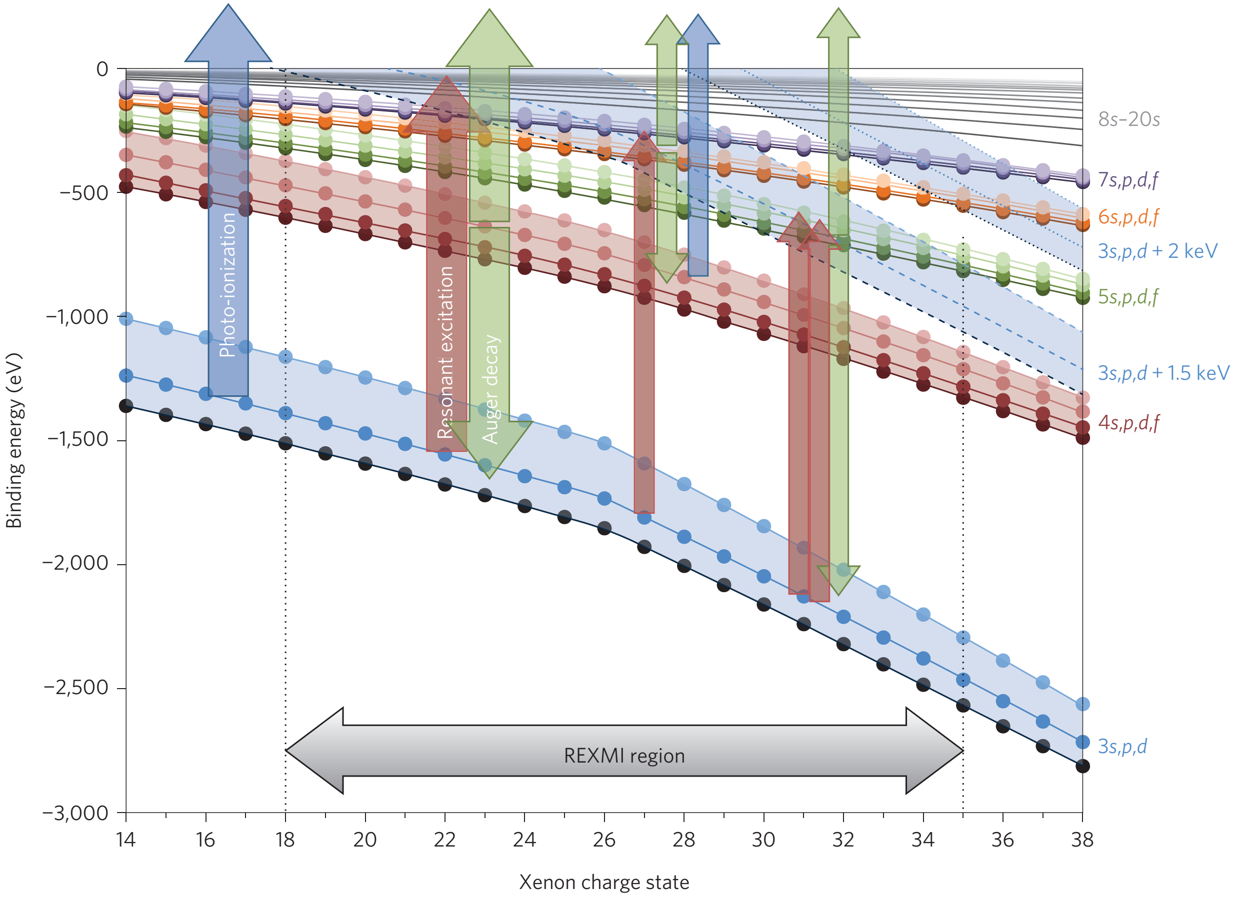


- Charge state distribution of Xe measured at LCLS
- At 2 keV: good agreement between experiment and theory
- At 1.5 keV: unprecedented high charge states (up to Xe^{36+}) in experiment

Rudek, Son *et al.*, *Nature Photon.* (DOI: 10.1038/nphoton.2012.261).

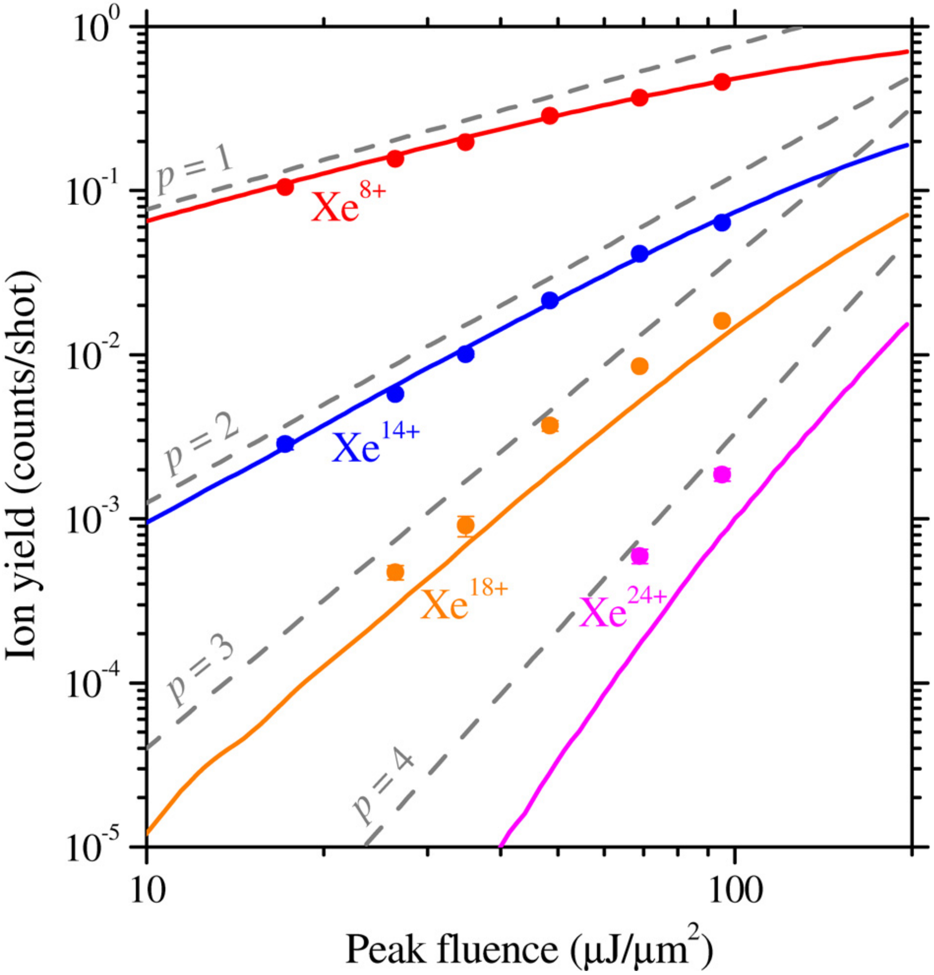
Ultra-efficient ionization by XFEL (cont.)

- Transient resonant excitation from 3*p* even after 3*p* ionization is closed (Xe^{26+}), bringing up to Xe^{36+}
  → *REXMI* mechanism
- Electron shuffling: more than one electron resonantly excited
- Densely-spaced Rydberg states and large bandwidth of X-rays



Rudek, Son *et al.*, *Nature Photon.* (DOI: 10.1038/nphoton.2012.261).

Deep inner-shell ionization by XFEL



- Charge state distribution of Xe measured at SACLA
- At 5.5 keV, *L*-shell ionization can be initiated:
  ~27M coupled rate eqs.
  → Monte-Carlo on the fly
- 4-photon absorption induces 26-electron ejection (Xe^{26+}) via intraatomic electron-electron interaction.

Fukuzawa, Son *et al.*, (submitted).

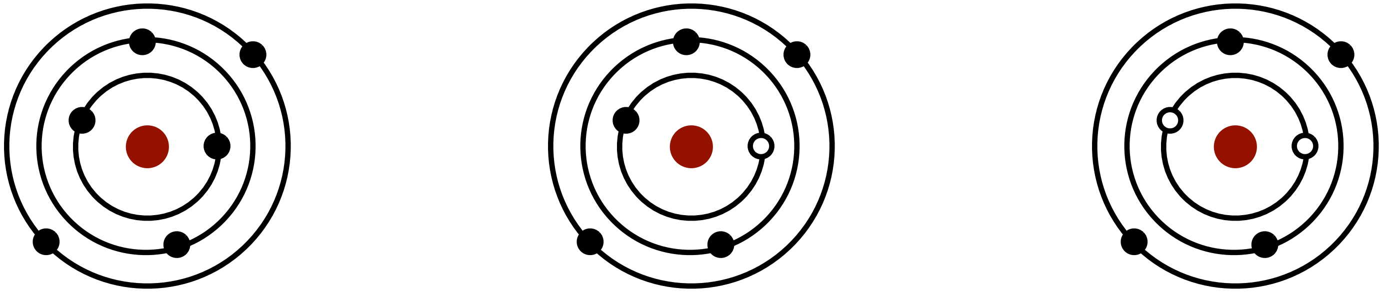
Scattering from hollow atoms

- Elastic X-ray scattering form factor

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

- Scattering affected by hollow-atom formation

For C @12 keV and resolution=1.7 Å

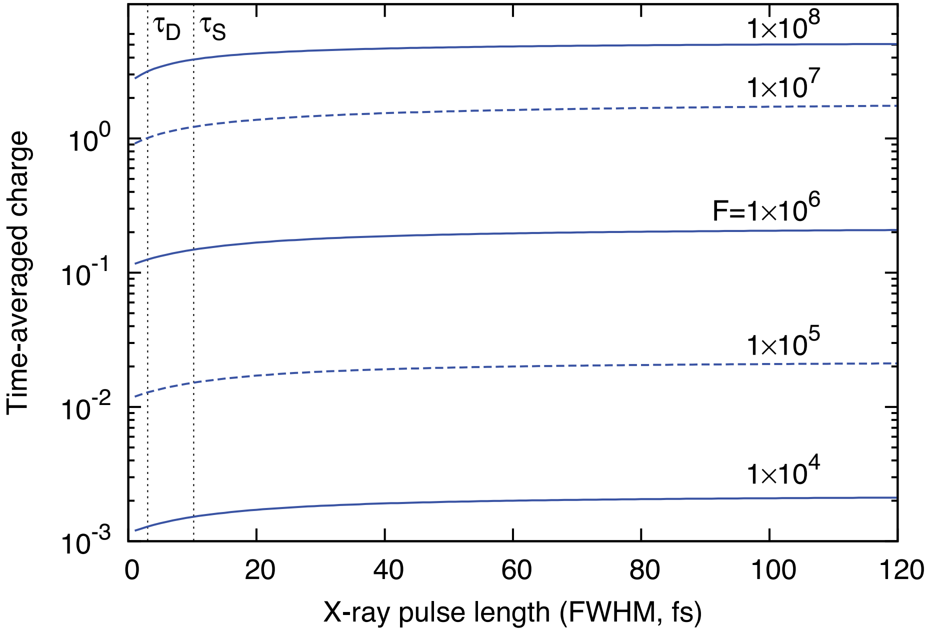


	neutral	single-core-hole	double-core-hole
σ_{sc}/σ_{abs} =	0.057	0.075	0.305

intensity-induced X-ray transparency for Ne: Young *et al.*, *Nature* **466**, 56 (2010).
frustrated absorption for N_2: Hoener *et al.*, *Phys. Rev. Lett.* **104**, 253002 (2010).

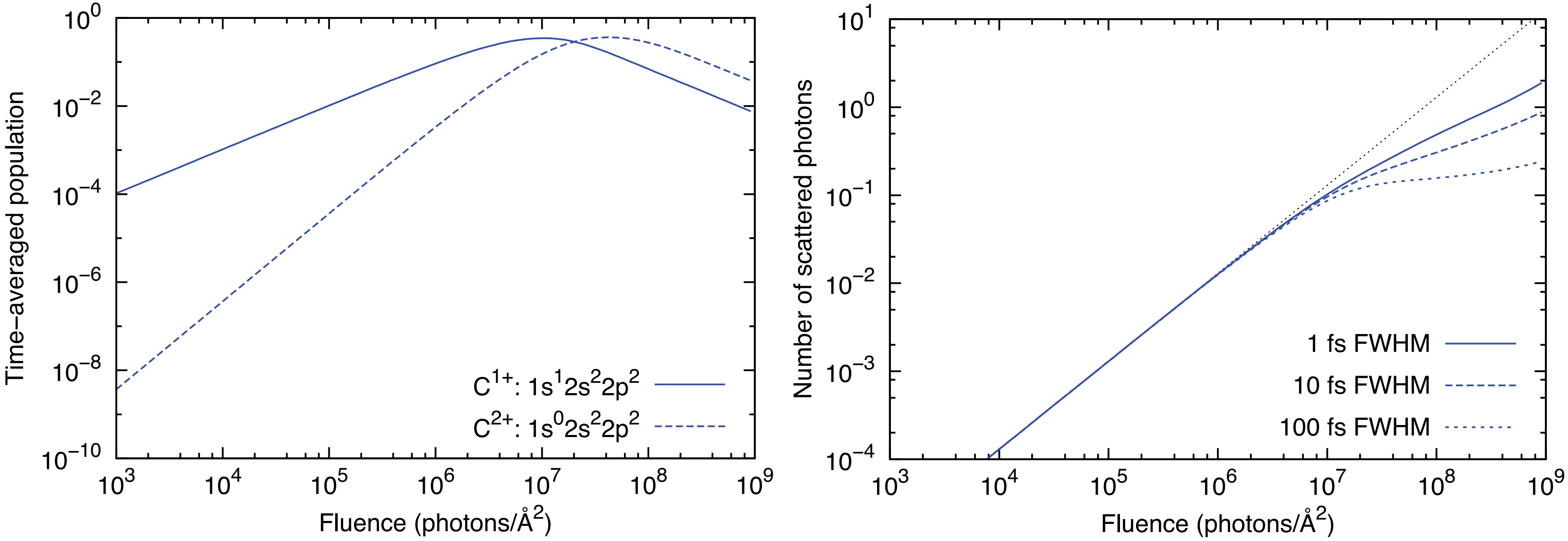
Scattering from hollow atoms (cont.)

- Carbon: time-averaged charge as a function of the pulse duration
- Less time-averaged charge when the pulse duration is short enough to compete with core-hole lifetimes (Auger lifetime).
- *Higher intensity* of XFEL pulses induces *less ionization* due to hollow-atom formation.



Son, Young & Santra, *Phys. Rev. A* **83**, 033402 (2011).

Scattering from hollow atoms (cont.)

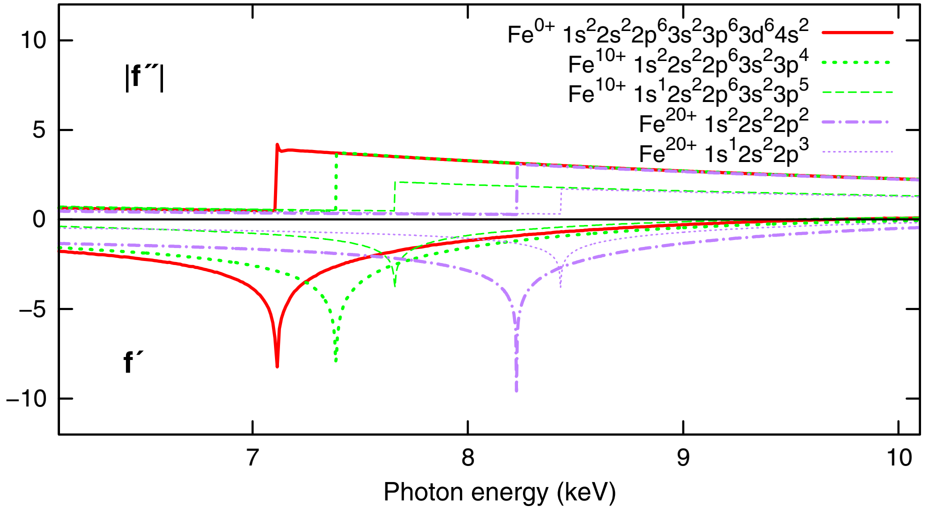


- Hollow-atom formation saturates around 10^{15} photons/μm^2.
- Nonlinear effect on scattering intensity after this saturation
- Theoretical results suggest a shorter pulse (i.e., attosecond XFEL) would be ideal for single-shot imaging.

Son, Young & Santra, *Phys. Rev. A* **83**, 033402 (2011).

MAD at high X-ray intensity

- Phase problem: $F(\mathbf{Q}) = \int d^3r \; \rho(\mathbf{r}) \; e^{i\mathbf{Q}\cdot\mathbf{r}} = \; |F(\mathbf{Q})| \; e^{i\phi(\mathbf{Q})}$
- MAD: <u>M</u>ultiwavelength <u>A</u>nomalous <u>D</u>iffraction
- With dispersion correction: $f(\mathbf{Q},\omega) = f^0(\mathbf{Q}) + f'(\omega) + i f''(\omega)$
- Phase obtained from interferences b/w normal and anomalous terms
- Remarkable changes of *f*′ and *f*″ for different configurations and charges



Anomalous scattering of Fe near *K* edge

Son, Chapman & Santra, *Phys. Rev. Lett.* **107**, 218102 (2011).

MAD at high X-ray intensity (cont.)

- Generalized Karle–Hendrickson equation at high x-ray intensity

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

3 unknowns at every single **Q**: $\left|F_P^0\right|,\ \left|F_H^0\right|, \Delta\phi^0 (= \phi_P^0 - \phi_H^0)$

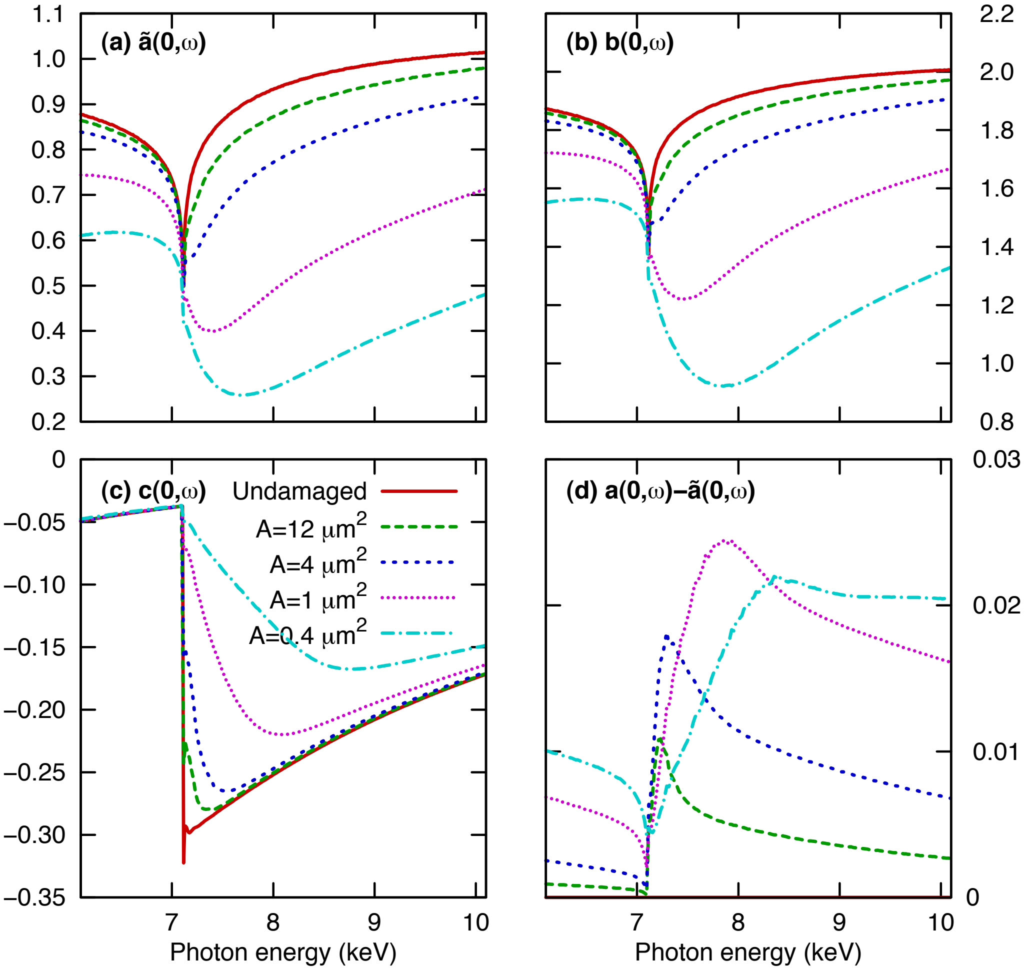
$$a(\omega) = \frac{1}{\{f_H^0\}^2}\sum_{I_H} \bar{P}_{I_H} \left|f_{I_H}(\omega)\right|^2 \qquad \tilde{a}(\omega) = \frac{1}{\{f_H^0\}^2}\int_{-\infty}^{\infty} dt\, g(t) \left|\tilde{f}_H(\omega, t)\right|^2$$

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

Son, Chapman & Santra, *Phys. Rev. Lett.* **107**, 218102 (2011).

MAD at high X-ray intensity (cont.)

- MAD coefficients calculated by XATOM
- First demonstration of MAD phasing method in extreme conditions of ionizing radiations
- Bleaching effect becomes beneficial to phasing.
- Theoretical study opens up a new potential for *ab initio* structural determination in femtosecond x-ray nanocrystallography.



Son, Chapman & Santra, *Phys. Rev. Lett.* **107**, 218102 (2011).

Conclusion

- Recent advent of XFEL opens up many unique opportunities in physics, chemistry, biology, and material science.
- It is crucial to understand interaction of ultraintense and ultrafast X-ray pulses with atoms and molecules.
- XATOM is an integrated toolkit to investigate X-ray–induced atomic processes and to simulate electronic damage dynamics.
- We explore ultra-efficient multiple ionization and deep inner-shell ionization of heavy atoms, scattering from hollow atoms, and novel diffraction method with heavy atoms.
- Theoretical studies with XATOM explain recent LCLS and SACLA experiments and lead to new XFEL experiments.
- XATOM becomes an essential tool for XFEL simulations.

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Zheng Li
Pankaj Kumar Mishra

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Prof. Dr. Beata Ziaja-Motyka
Dr. Zoltan Jurek
Dr. Nikita Medvedev
Dr. Robert Thiele

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Thank you for your attention!