Electronic response to X-ray free-electron laser pulses

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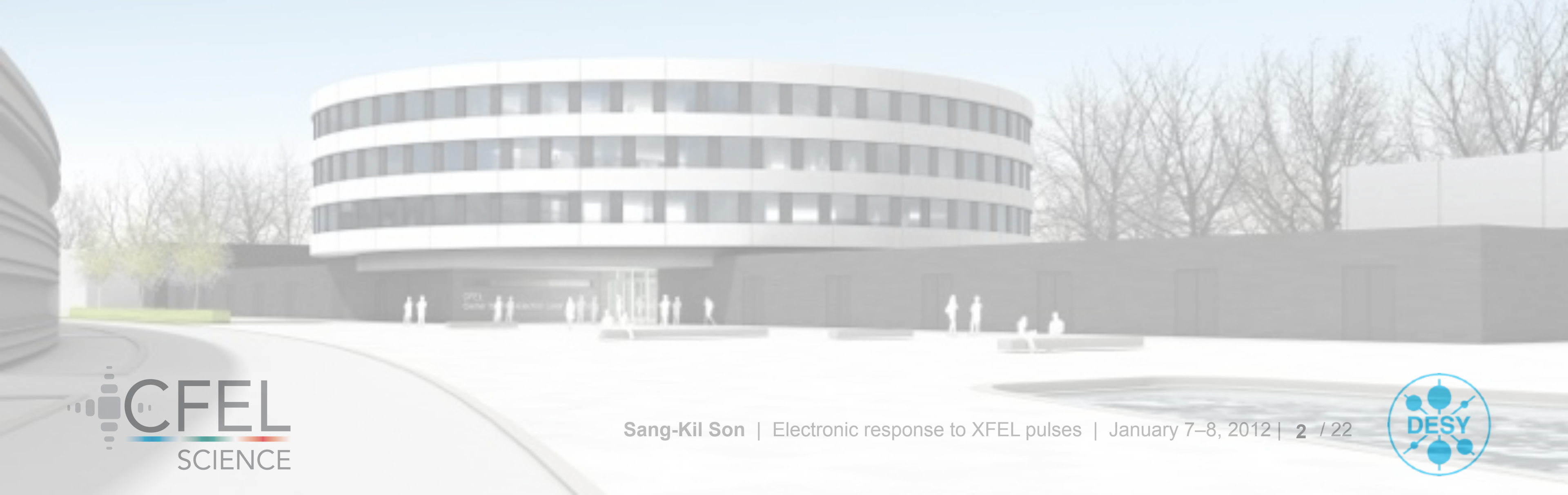
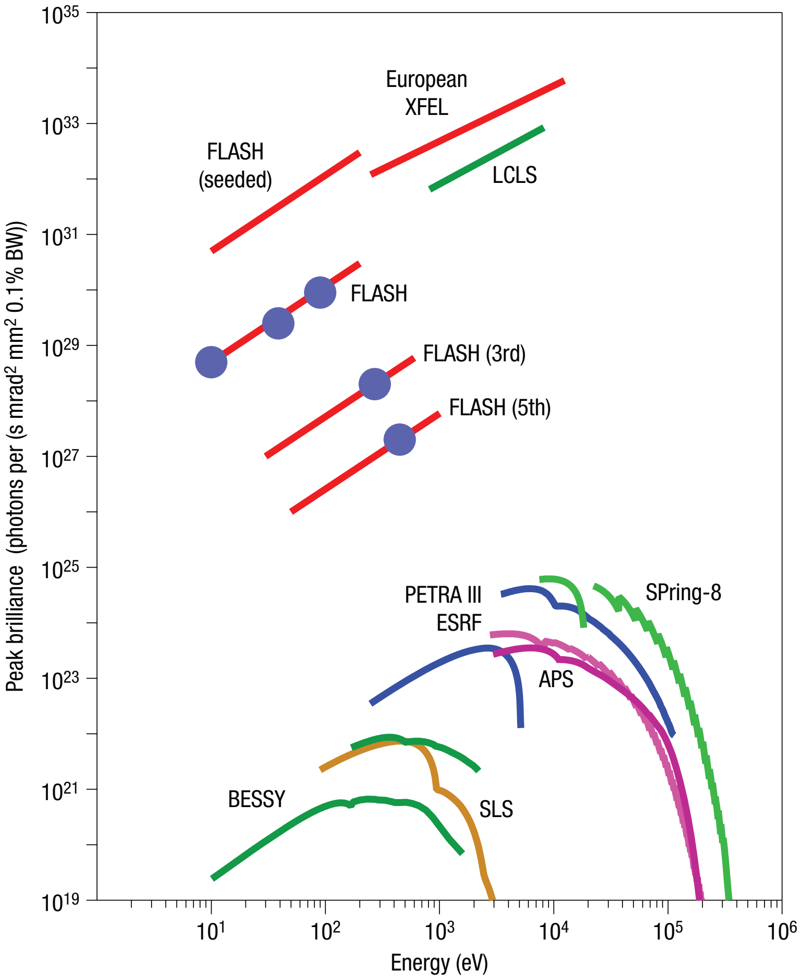
Overview

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



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 Stanford, USA (2009)
- SACLA at RIKEN Harima, Japan (2011)
- European XFEL, Germany (2015)


FLASH and European XFEL on DESY campus


LCLS


SACLA

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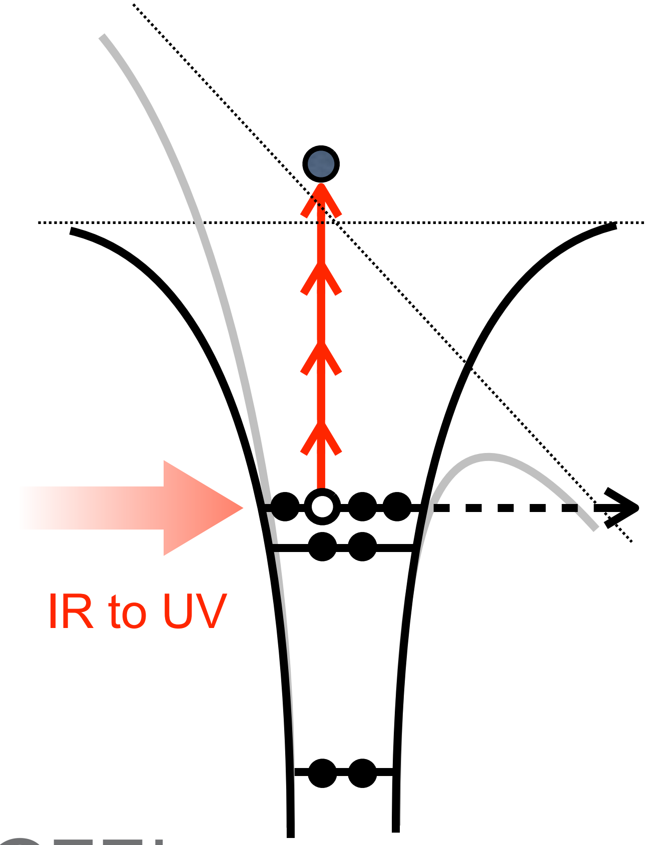
What differences from optical strong-field?

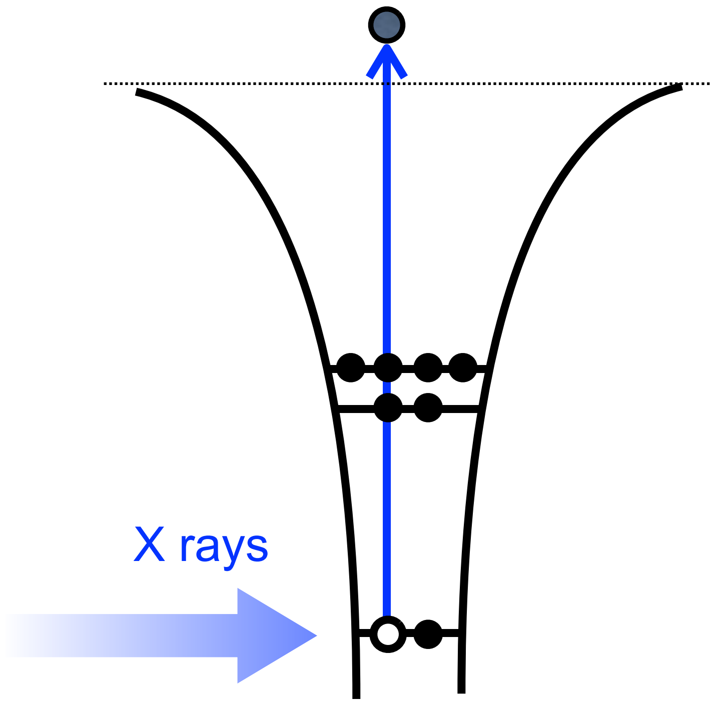
> Optical strong-field regime

- tunneling or multiphoton processes
- valence-electron ionization

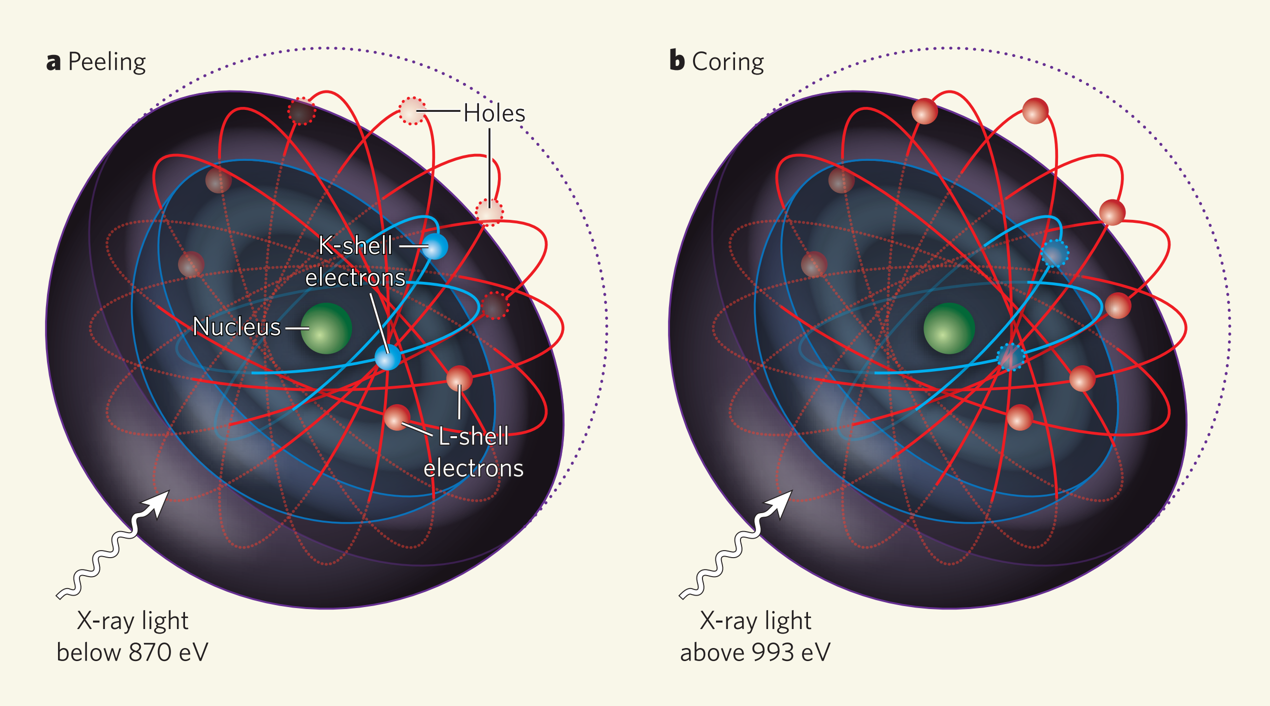


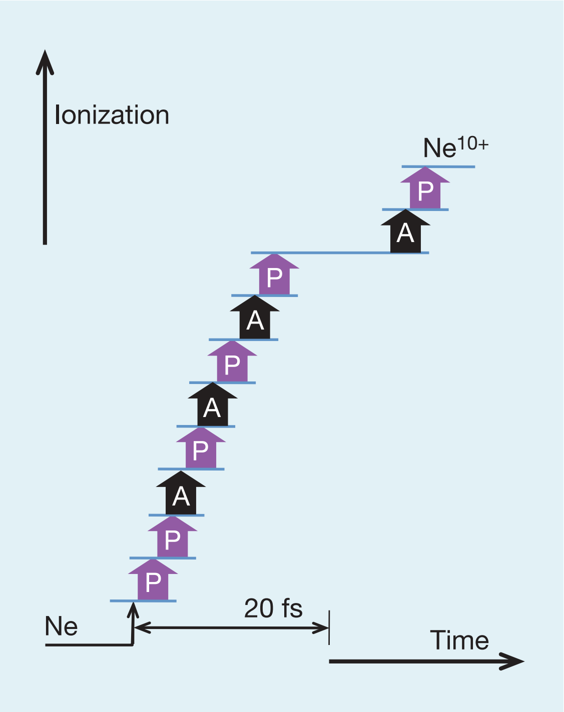
> Intense X-ray regime

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



Multiphoton Multiple Ionization





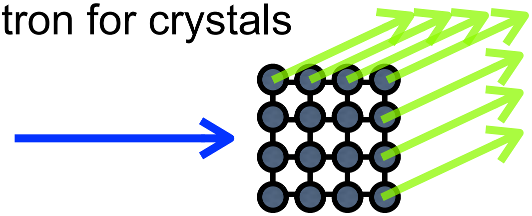
Figures from Wark, *Nature* **466**, 35 (2010).

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

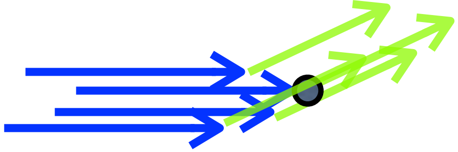
- First LCLS experiment: fundamental atomic physics in XFEL
- Lots of x-ray photons: repeated *K*-shell ionization (P) followed by Auger relaxation (A)
- Good agreement between experiment and theory (Nina Rohringer and Robin Santra)

Ultrafast X-ray scattering

- X-ray scattering
  - synchrotron for crystals

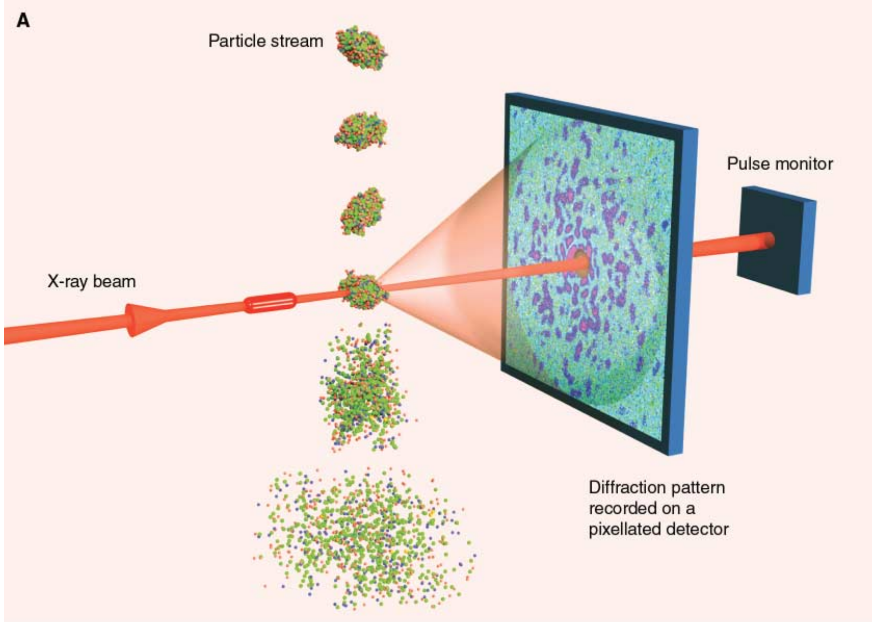


  - XFEL for single molecules or nanocrystals



~10^7 times
more photons

- Single-shot imaging of individual macromolecules
  - Ultrafast (femtosecond) pulse: scattering before Coulomb explosion (nuclear radiation damage)
  - A hottest topic in XFEL science:
    Chapman *et al.*, *Nature Phys.* **2**, 839 (2007).
    Chapman *et al.*, *Nature* **470**, 73 (2011).
    Seibert *et al.*, *Nature* **470**, 78 (2011).
  - Electronic radiation damage is unavoidable.



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

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

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

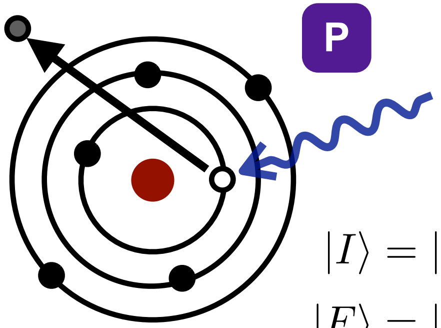
$$|I\rangle\text{: initial state,} \quad |F\rangle\text{: final state}$$

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

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

X-ray-induced atomic processes (cont.)

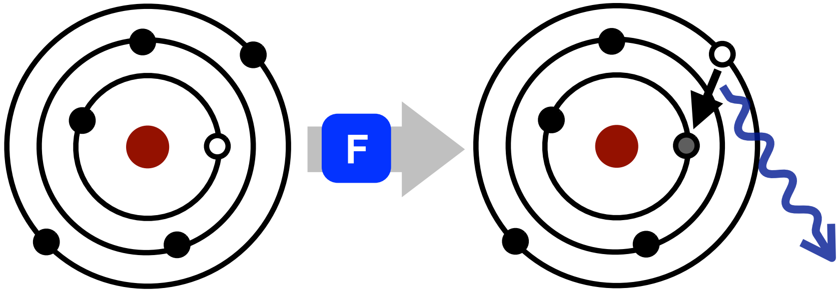
Photoionization



$$|I\rangle = |\Psi_0^{N_{\rm el}}\rangle |N_{\rm EM}\rangle$$

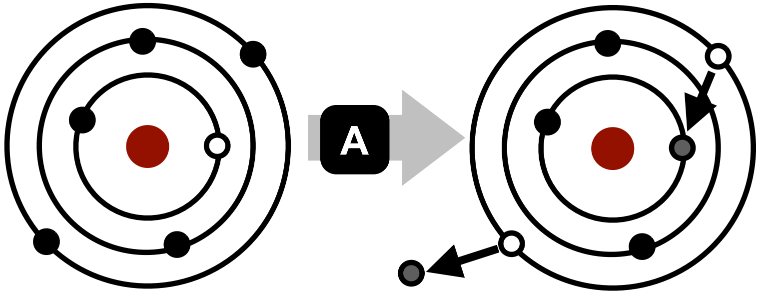
$$|F\rangle = |\Psi_F^{N_{\rm el}}\rangle |N_{\rm EM}-1\rangle$$

Fluorescence



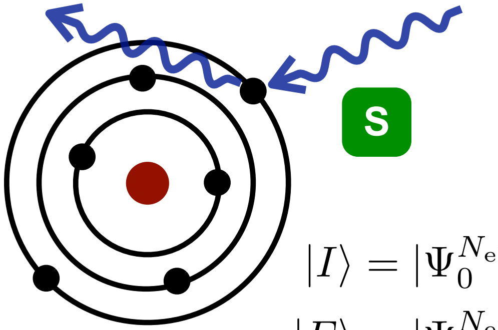
$$|I\rangle = \hat{c}_i |\Phi_0^{N_{\rm el}}\rangle |0\rangle, \;\; |F\rangle = \hat{c}_{i'} |\Phi_0^{N_{\rm el}}\rangle \hat{a}^\dagger_{\mathbf{k}_F,\lambda_F} |0\rangle$$

Auger and Coster–Kronig decay



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

Elastic X-ray scattering



$$|I\rangle = |\Psi_0^{N_{\rm el}}\rangle |N_{\rm EM}\rangle$$

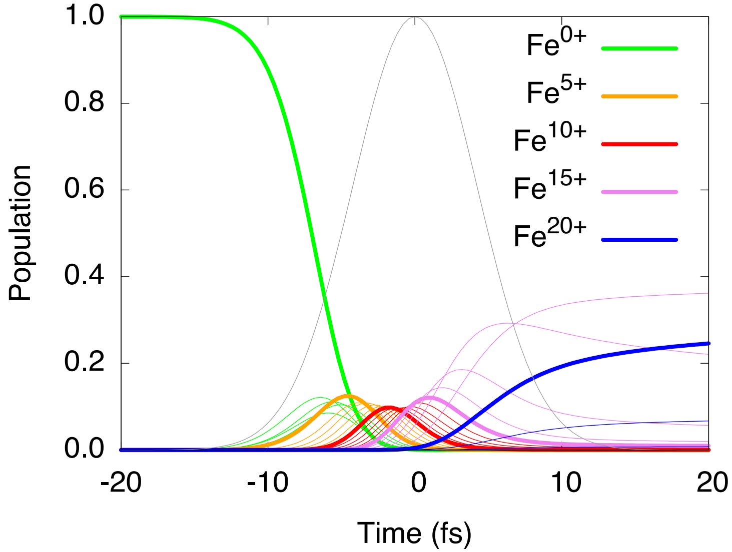
$$|F\rangle = |\Psi_0^{N_{\rm el}}\rangle \hat{a}^\dagger_{\mathbf{k}_F,\lambda_F} |N_{\rm EM}-1\rangle$$

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
- Each atomic process is treated in the perturbative regime, but ionization and relaxation dynamics are non-perturbative.



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 with a proper long-range correction
  - bound and continuum states, transition dipole matrix elements
  - photoionization / photoabsorption cross sections
  - Auger and Coster–Kronig rates
  - fluorescence rates
  - elastic x-ray scattering form factors including dispersion corrections
  - shake-off branching ratios
  - large-scale coupled rate equations: direct solution or Monte–Carlo solution
- Features:
  - versatile and simple
  - captures all relevant basic processes
  - useful to atoms, molecules and clusters
  - becomes an essential tool for XFEL simulations

See the XATOM poster

Applications of XATOM

Multiphoton multiple ionization

- Ne: nonlinear response

Doumy *et al.*, *PRL* **106**, 083002 (2011).
Sytcheva, Pabst, Son & Santra, submitted.

- Xe: ultra-efficient ionization

Rudek, *et al.*, submitted.

Ultrafast X-ray scattering

- C: scattering vs. absorption

Son, Young & Santra, *PRA* **83**, 033402 (2011).

- Fe: MAD at high X-ray intensity

Son, Chapman & Santra, *PRL* **107**, 218102 (2011).

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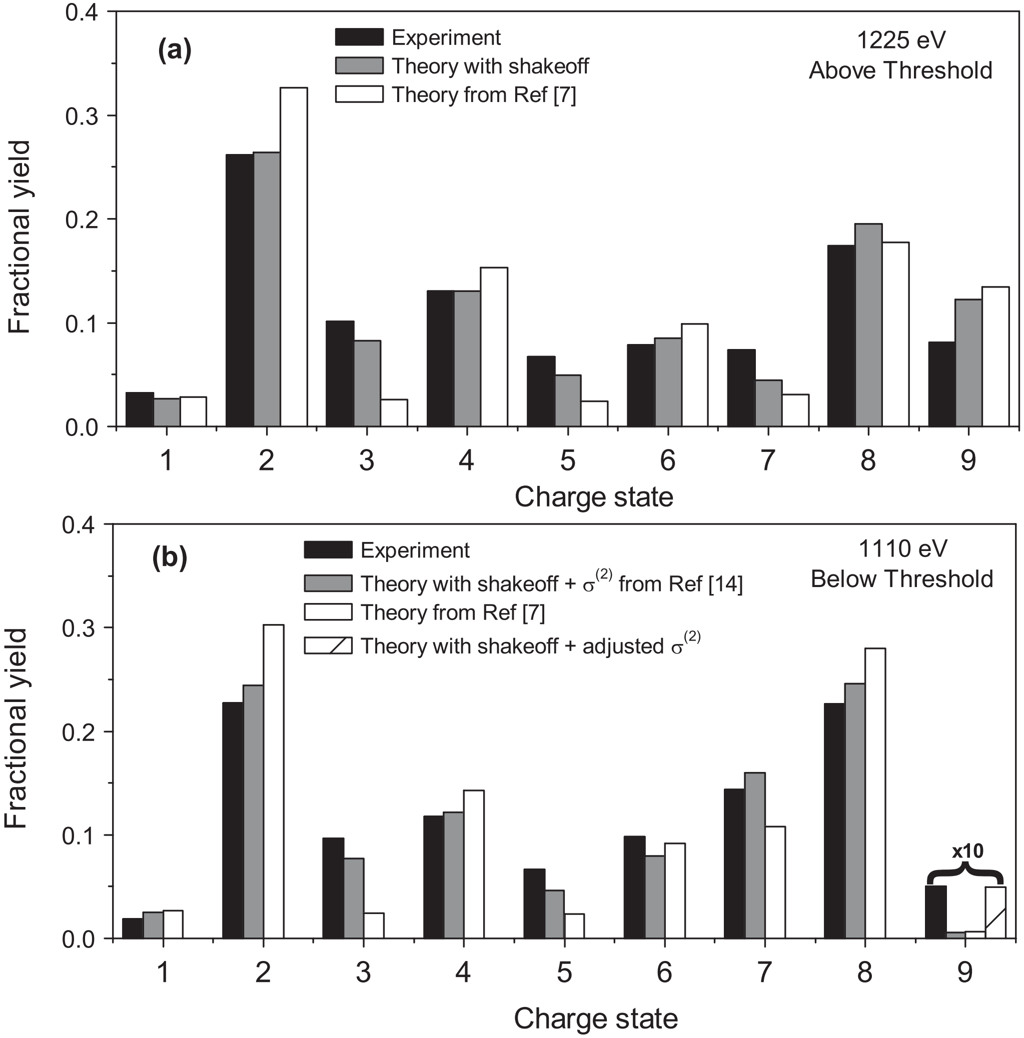
Nonlinear response to XFEL

- Charge state distribution of Ne: good agreement between experiment and theory
  Young *et al.*, *Nature* **466**, 56 (2010).
- Even better if shake-off processes are included
- Study of Ne^{9+} production from Ne^{8+} measured at LCLS
- Photon energy above / below *K*-shell threshold of Ne^{8+} to observe nonlinear response

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



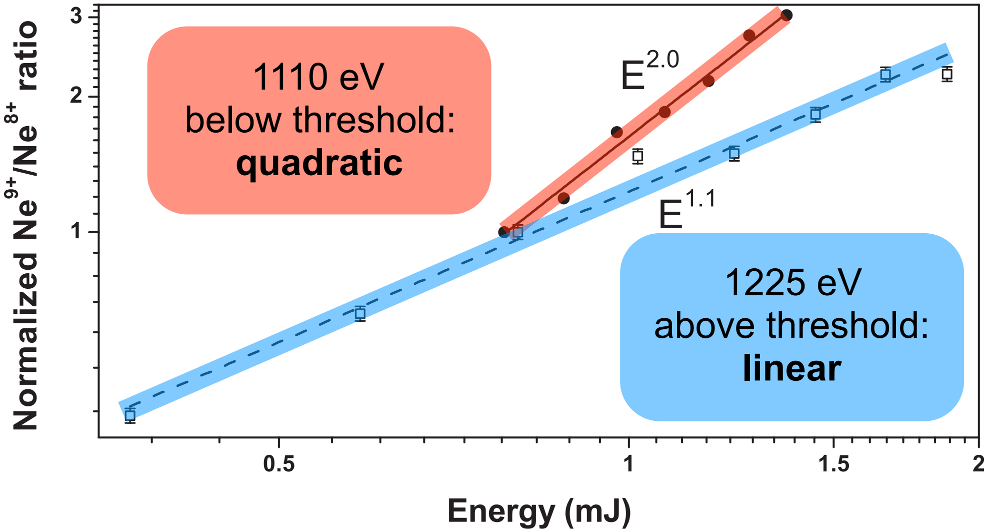
Nonlinear response to XFEL (cont.)

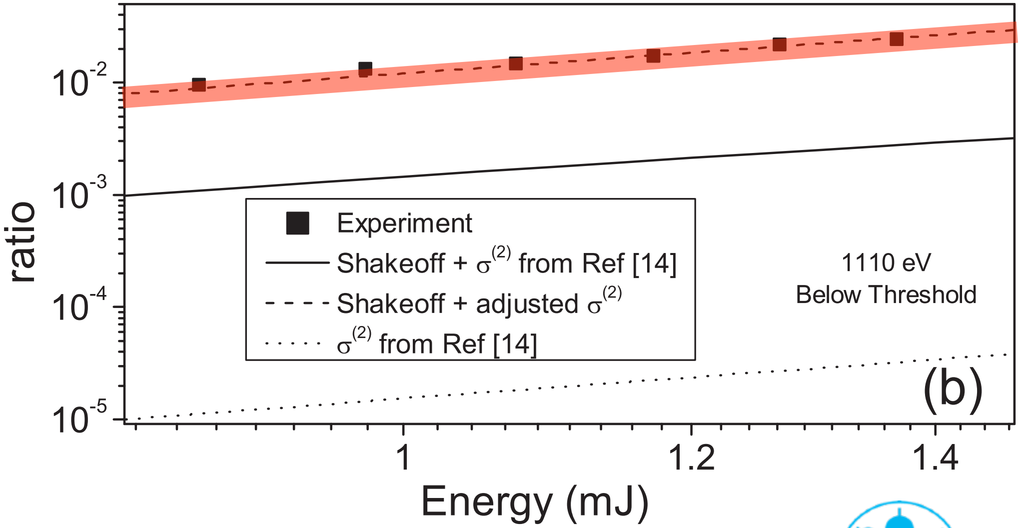
- First exp. evidence of nonlinear absorption in the x-ray regime
- Two mechanisms of nonlinear response: direct and sequential two-photon ionizations
- Direct $\sigma^{(2)}$ estimated from measurement, which is ~700 times larger than expected from previous calculation

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

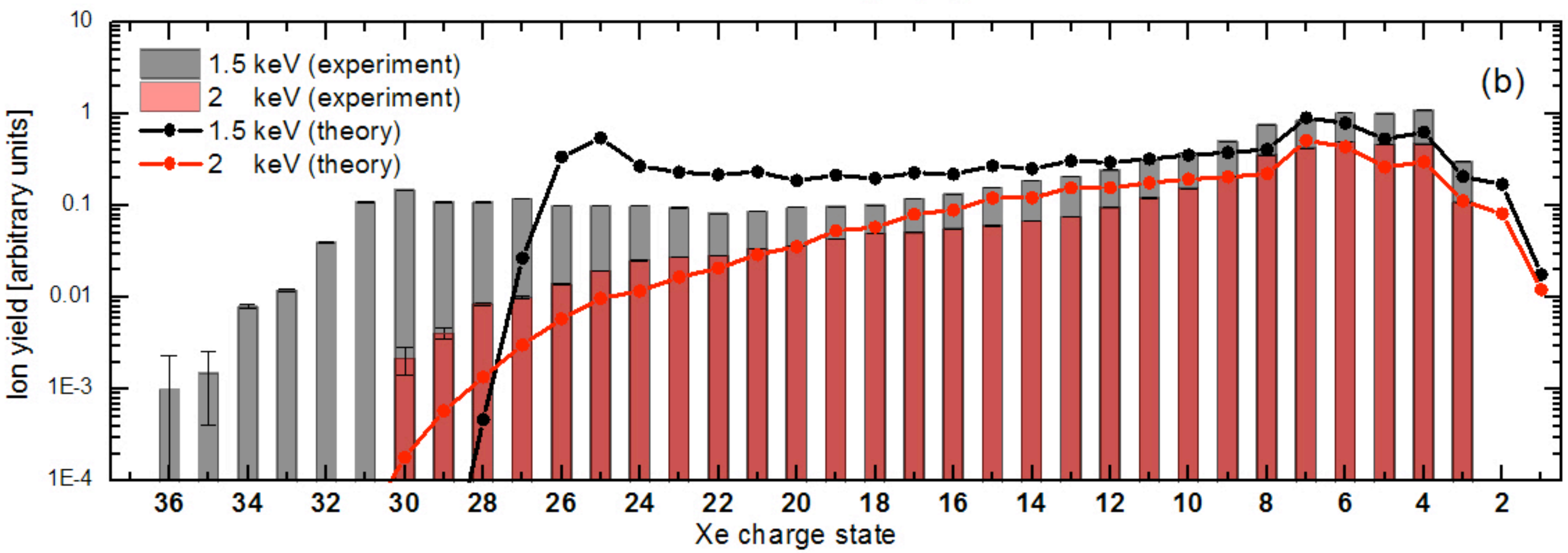
- Enhanced by 1*s*4*p* resonance and finite bandwidth of XFEL

  Sytcheva, Pabst, Son & Santra, submitted.





Ultra-efficient ionization by XFEL

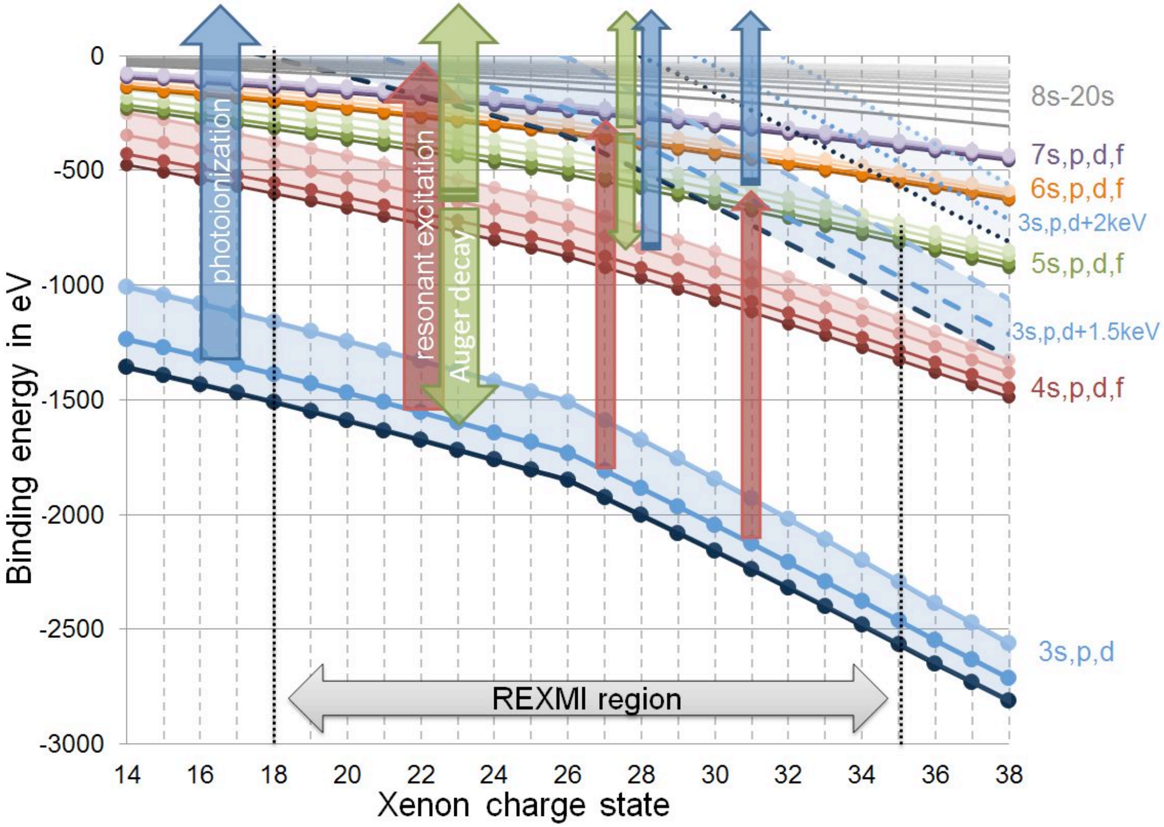


- Charge state distribution of Xe measured at LCLS
- At 2000 eV: good agreement between experiment and theory
- At 1500 eV: unprecedented high charge states (up to Xe^{36+}) in experiment
- Computational challenge: # of coupled rate equations = 1,120,581

Rudek, Son *et al.*, submitted.

Ultra-efficient ionization by XFEL (cont.)

- Sequential one-photon ionization at 1500 eV would be up to Xe^{26+}.
- REXMI (Resonance-Enhanced X-ray Multiple Ionization): resonant excitation from 3*p* after 3*p* ionization is closed
- Current modeling does not include resonant excitations.



Rudek, Son *et al.*, submitted.

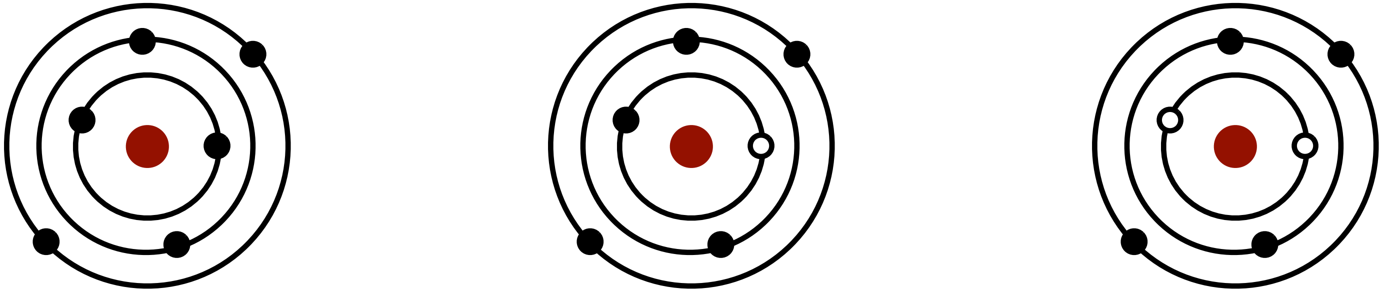
Scattering from hollow atoms

- 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

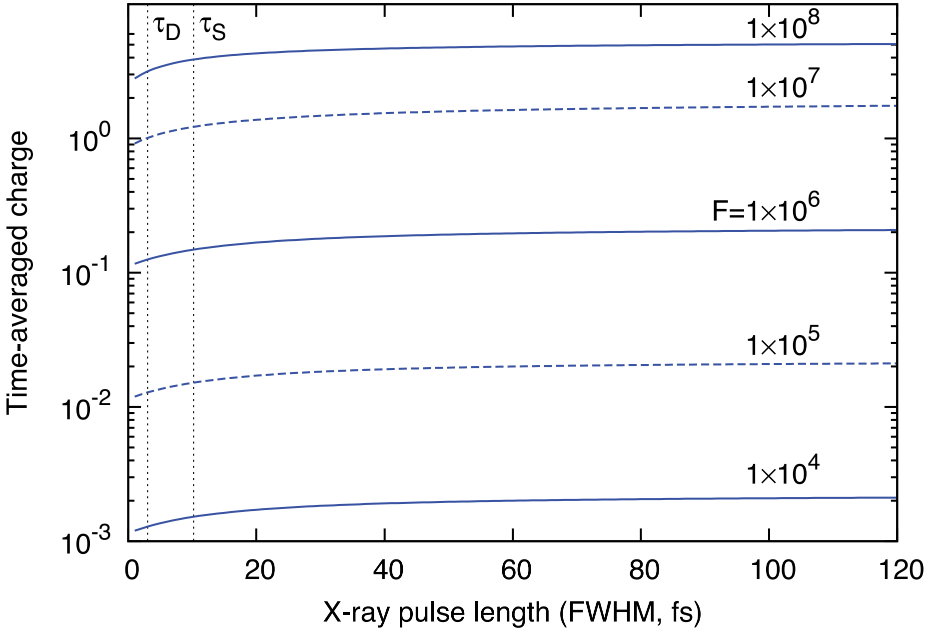


neutral	single-core-hole	double-core-hole
σ_{sc}/σ_{abs} = 0.057	0.075	0.305

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).

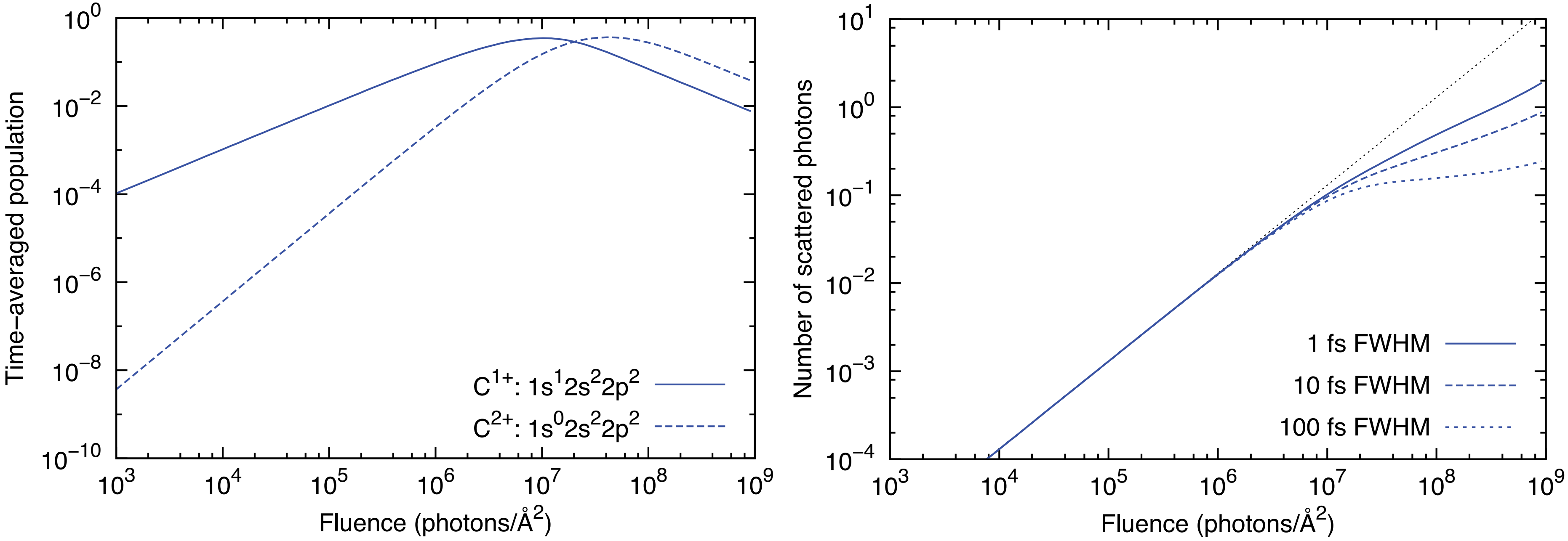
Scattering from hollow atoms (cont.)

- 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 pulse 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 10^7 photons/Å^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).

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 nonlinear X-ray absorption processes, ultra-efficient multiple ionization of heavy atoms, scattering from hollow atoms, and novel diffraction method with heavy atoms.
- Theoretical studies with XATOM explain recent LCLS experiments and lead to new XFEL experiments.
- XATOM becomes an essential tool for XFEL simulations.

Acknowledgment

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Robin Santra


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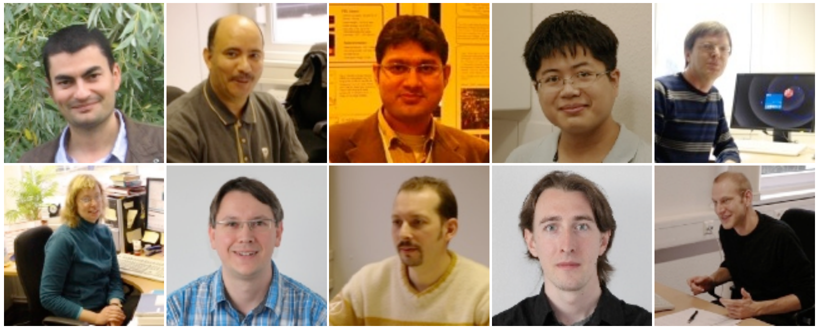
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Thank you for your attention!