Theory of x-ray matter interaction Photoabsorption

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HELMHOLTZ RESEARCH FOR GRAND CHALLENGES

CFEL SCIENCE

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DER FORSCHUNG | DER LEHRE | DER BILDUNG

DESY

Bibliography

R. Santra, **Concepts in X-ray Physics**
J. Phys. B: At. Mol. Opt. Phys. **42** 169801 (2009).

N. Rohringer, **Introduction to the theory of x-ray matter interaction,** https://arxiv.org/abs/1811.12052

1895: Discovery of X-rays by Wilhelm Röntgen

(1st Nobel Prize in Physics 1901)

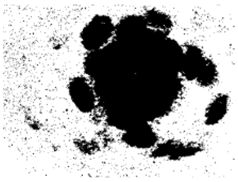
Contrast by absorption

Presentation Speech: C.T. Odhner President of Royal Swedish Academy

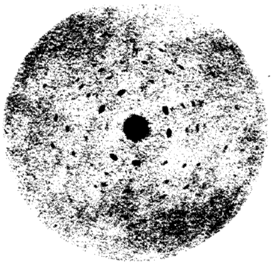
"And there is no doubt that much success will be gained in physical science when this strange energy form is sufficiently investigated and its wide field thoroughly explored."

Diffraction of X-rays by crystals

Max von Laue (Nobel prize in physics 1914)

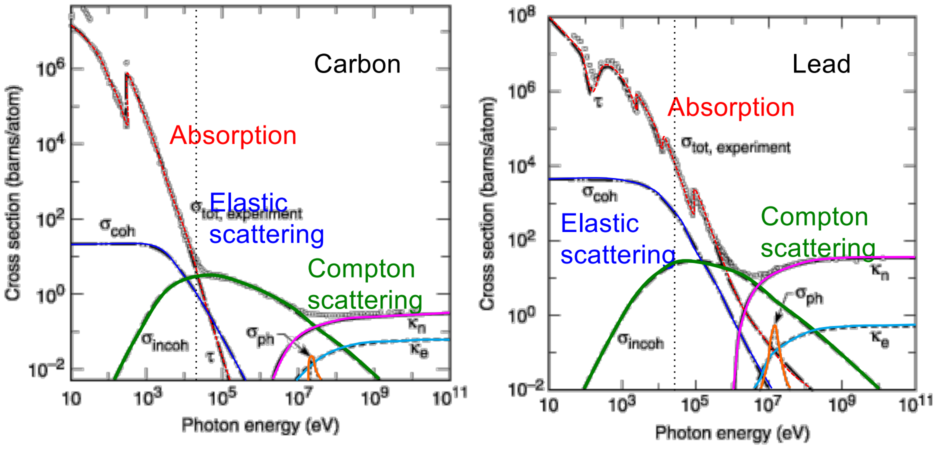


1st ever X-ray diffraction pattern
Copper sulfate
(1912)



Irradiation along
4-fold symmetry axis

Cross-section of x-ray matter interaction processes



Absorption of photons
Coherent elastic scattering
Compton (incoherent) scattering
Nuclear photo absorption
Nuclear-field electron/positron pair production
Electron-postitron pair production

Absorption Cross section: approx. 1 Mbarn = 10^{-22} m^2
Focus size: 1 μm^2
Photons per pulse: 10^{11} in 10 fs
Absorption probability per atom / fs = 1 / fs

 J. H. Hubbell, H. A. Gimm, J. Phys. Chem. Ref. Data 9, 1023 (1980).

Outlook

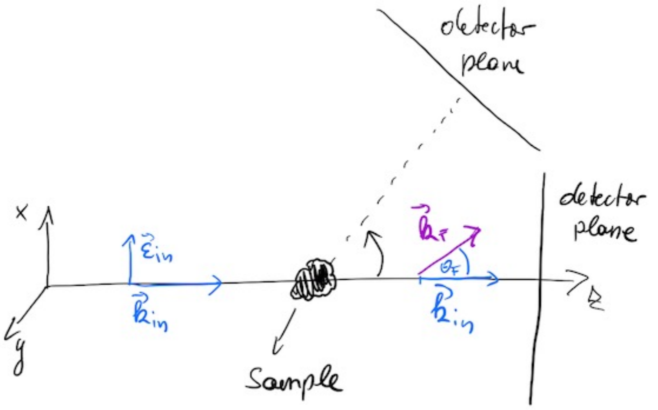
The concept of a cross section
- Quantum electrodynamics + perturbation theory
- Electronic degreed in 2nd quantization
- S-matrix & Transition rates

X-ray photo absorption
- Many-body effects in single-photon absorption

Multi-photon absorption at FELs
- The role of the higher-order coherence
- Rate equation approach
- Role of transient resonances
- From single-atom to solids – methods to describe warm-dense matter

Calculating transition probabilities by scattering approach

Scattering theory – concept of cross section for a specific process



- Treat electromagnetic field quantized
- Treat electronic d.o.f by second quantization ⟶ sing—particle interpretation
- Transition matrix element (S-Matrix) ⟶ transition rate

Quantization of the Electromagnetic field

Quantized Hamiltonian (dropping vacuum fluctuations):

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

Bosonic commutator relations for creation and annihilation operators:

$$[\hat{a}_{\boldsymbol{k},\lambda}, \hat{a}^{\dagger}_{\boldsymbol{k}',\lambda'}] = \delta_{\boldsymbol{k},\boldsymbol{k}'}\delta_{\lambda,\lambda'} \qquad \begin{array}{l} [\hat{a}_{\boldsymbol{k},\lambda}, \hat{a}_{\boldsymbol{k}',\lambda'}] = 0 \\ [\hat{a}^{\dagger}_{\boldsymbol{k},\lambda}, \hat{a}^{\dagger}_{\boldsymbol{k}',\lambda'}] = 0 \end{array}$$

Expansion of vector potential in quantized-field modes:

$$\hat{\boldsymbol{A}}(\boldsymbol{x}) = \sum_{\boldsymbol{k},\lambda} \sqrt{\frac{2\pi}{V\omega_{\boldsymbol{k}}\alpha^2}} \left\{ \hat{a}_{\boldsymbol{k},\lambda}\boldsymbol{\epsilon}_{\boldsymbol{k},\lambda} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}} + \hat{a}^{\dagger}_{\boldsymbol{k},\lambda}\boldsymbol{\epsilon}^{*}_{\boldsymbol{k},\lambda} \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}} \right\}$$

Minimal Coupling Hamiltonian for matter-field interaction

Single-particle Hamiltonian for nuclei and electrons (assuming point charges):

$$\hat{h}_i = \frac{[\boldsymbol{p}_i - \alpha q_i \boldsymbol{A}(\boldsymbol{x}_i)]^2}{2m_i} + q_i \Phi(\boldsymbol{x}_i)$$

Giving rise to dynamic electron-field interaction (neglected for nuclei due to large mass m_i)

Coulomb potential of all the point charges in the system

$$\Phi(\boldsymbol{x}) = \sum_j \frac{q_j}{|\boldsymbol{x} - \boldsymbol{x}_j|}$$

Total Hamiltonian can be split in: $\hat{H} = \hat{H}_{\text{mol}} + \hat{H}_{\text{EM}} + \hat{H}_{\text{int}}$

$$\hat{H}_{\text{mol}} = \hat{T}_{\text{N}} + \hat{V}_{\text{NN}} + \hat{H}_{\text{el}}$$

Includes:
electronic kinetic energy
electron-electron Coulomb interaction
electron-nucleus Coulomb interaction

Nuclear kinetic energy $\hat{T}_{\text{N}} = -\frac{1}{2}\sum_n \frac{\nabla_n^2}{M_n}$

nucleus-nucleus repulsion: $\hat{V}_{\text{NN}} = \sum_{n<n'} \frac{Z_n Z_{n'}}{|\boldsymbol{R}_n - \boldsymbol{R}_{n'}|}$

Second quantization for the electronic degrees of freedom

Introducing electronic field creation and annihilation operators

Electronic field operator (spinor): $\hat{\psi}(\boldsymbol{x}) = \begin{pmatrix} \hat{\psi}_{+1/2}(\boldsymbol{x}) \\ \hat{\psi}_{-1/2}(\boldsymbol{x}) \end{pmatrix}$

Fermionic anticommutation relations:

$$\{\hat{\psi}_\sigma(\boldsymbol{x}), \hat{\psi}_{\sigma'}(\boldsymbol{x}')\} = 0 \qquad \{\hat{\psi}_\sigma(\boldsymbol{x}), \hat{\psi}^\dagger_{\sigma'}(\boldsymbol{x}')\} = \delta_{\sigma,\sigma'}\delta^{(3)}(\boldsymbol{x} - \boldsymbol{x}')$$
$$\{\hat{\psi}^\dagger_\sigma(\boldsymbol{x}), \hat{\psi}^\dagger_{\sigma'}(\boldsymbol{x}')\} = 0$$

Representation of the electronic Hamiltonian (independent of particle number):

$$\hat{H}_{\text{el}} = \int d^3x \hat{\psi}^\dagger(\boldsymbol{x}) \left\{ -\frac{1}{2}\nabla^2 - \sum_n \frac{Z_n}{|\boldsymbol{x} - \boldsymbol{R}_n|} \right\} \hat{\psi}(\boldsymbol{x}) + \frac{1}{2}\int d^3x \int d^3x' \hat{\psi}^\dagger(\boldsymbol{x}) \hat{\psi}^\dagger(\boldsymbol{x}') \frac{1}{|\boldsymbol{x} - \boldsymbol{x}'|} \hat{\psi}(\boldsymbol{x}') \hat{\psi}(\boldsymbol{x})$$

kinetic energy — electron-ion interaction — electron-electron interaction

Representation of the electron-field interaction:

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

Photo absorption (1st order in A)
Elastic or inelastic resonance scattering (2nd order in A)

Elastic scattering (1st order A^2)
Inelastic scattering

Interaction picture, perturbation theory

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

State vector in interaction picture: $|\Psi, t\rangle_{\mathrm{int}} = \mathrm{e}^{\mathrm{i}\hat{H}_0 t}|\Psi, t\rangle$

Adiabatic switching of interaction

Schrödinger equation in interaction picture:

$$\int_{-\infty}^{t} \mathrm{i}\frac{\partial}{\partial t}|\Psi, t\rangle_{\mathrm{int}} = \int_{-\infty}^{t} \mathrm{e}^{\mathrm{i}\hat{H}_0 t}\hat{H}_{\mathrm{int}}\mathrm{e}^{-\epsilon|t|}\mathrm{e}^{-\mathrm{i}\hat{H}_0 t}|\Psi, t\rangle_{\mathrm{int}}$$

Initial condition: $\lim_{t\to-\infty} |\Psi, t\rangle_{\mathrm{int}} = |I\rangle$ State vector contains information of photon field & electrons

Formal integration of Schrödinger Equation gives perturbation expansion:

$$|\Psi, t\rangle_{\mathrm{int}} = |I\rangle - \mathrm{i}\int_{-\infty}^{t} \mathrm{d}t'\mathrm{e}^{\mathrm{i}\hat{H}_0 t'}\hat{H}_{\mathrm{int}}\mathrm{e}^{-\epsilon|t'|}\mathrm{e}^{-\mathrm{i}\hat{H}_0 t'}|\Psi, t'\rangle_{\mathrm{int}}$$

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$$- \int_{-\infty}^{t} \mathrm{d}t'\mathrm{e}^{\mathrm{i}\hat{H}_0 t'}\hat{H}_{\mathrm{int}}\mathrm{e}^{-\epsilon|t'|}\mathrm{e}^{-\mathrm{i}\hat{H}_0 t'}\int_{-\infty}^{t'} \mathrm{d}t''\mathrm{e}^{\mathrm{i}\hat{H}_0 t''}\hat{H}_{\mathrm{int}}\mathrm{e}^{-\epsilon|t''|}\mathrm{e}^{-\mathrm{i}\hat{H}_0 t''}|I\rangle$$
$$+ \ldots$$

Transition (S) Matrix

Transition amplitude from state *I* to *F*:

$$S_{FI} = \lim_{t\to\infty} \langle F|\Psi, t\rangle_{\text{int}}$$

$$\mathrm{e}^{\mathrm{i}E_F t'}\langle F| \qquad |I\rangle \mathrm{e}^{-\mathrm{i}E_I t'}$$

$$\langle F|\Psi,t\rangle_{\text{int}} = \underbrace{\langle F|I\rangle}_{=0} - \mathrm{i}\int_{-\infty}^{t} \mathrm{d}t' \langle F|\mathrm{e}^{\mathrm{i}\hat{H}_0 t'}\hat{H}_{\text{int}}\mathrm{e}^{-\epsilon|t'|}\mathrm{e}^{-\mathrm{i}\hat{H}_0 t'}|I\rangle$$
$$- \sum_M \int_{-\infty}^{t} \mathrm{d}t' \langle F|\mathrm{e}^{\mathrm{i}\hat{H}_0 t'}\hat{H}_{\text{int}}\mathrm{e}^{-\epsilon|t'|}\mathrm{e}^{-\mathrm{i}\hat{H}_0 t'}|M\rangle \int_{-\infty}^{t'} \mathrm{d}t'' \, \mathrm{e}^{\mathrm{i}\hat{H}_0 t''}\langle M|\mathrm{e}^{-\epsilon|t''|}\mathrm{e}^{-\mathrm{i}\hat{H}_0 t''}|I\rangle$$

$$S_{FI} = -\mathrm{i}\int_{-\infty}^{\infty} \mathrm{d}t\,\mathrm{e}^{\mathrm{i}(E_F-E_I)t}\langle F|\hat{H}_{\text{int}}|I\rangle$$
$$- \int_{-\infty}^{\infty} \mathrm{d}t \sum_M \mathrm{e}^{\mathrm{i}(E_F-E_M)t}\langle F|\hat{H}_{\text{int}}|M\rangle \int_{-\infty}^{t} \mathrm{d}t'\,\mathrm{e}^{\mathrm{i}(E_M-E_I-\mathrm{i}\epsilon)t'}\langle M|\hat{H}_{\text{int}}|I\rangle$$

$$S_{FI} = -\mathrm{i}\, 2\pi\,\delta(E_F-E_I)\langle F|\hat{H}_{\text{int}}|I\rangle$$
$$- \sum_M \int_{-\infty}^{\infty} \mathrm{d}t\,\mathrm{e}^{\mathrm{i}(E_F-E_M)t}\langle F|\hat{H}_{\text{int}}|M\rangle\langle M|\hat{H}_{\text{int}}|I\rangle \frac{\mathrm{e}^{\mathrm{i}(E_M-E_I)t}}{\mathrm{i}(E_M-E_I-\mathrm{i}\epsilon)}$$

Transition (S) Matrix

Transition amplitude from state *I* to *F*:

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$$\mathrm{e}^{\mathrm{i}E_F t'}\langle F| \qquad |I\rangle \mathrm{e}^{-\mathrm{i}E_I t'}$$

$$\langle F|\Psi,t\rangle_{\text{int}} = \underbrace{\langle F|I\rangle}_{=0} - \mathrm{i}\int_{-\infty}^{t} \mathrm{d}t' \langle F|\mathrm{e}^{\mathrm{i}\hat{H}_0 t'}\hat{H}_{\text{int}}\mathrm{e}^{-\epsilon|t'|}\mathrm{e}^{-\mathrm{i}\hat{H}_0 t'}|I\rangle$$
$$- \sum_M \int_{-\infty}^{t} \mathrm{d}t' \langle F|\mathrm{e}^{\mathrm{i}\hat{H}_0 t'}\hat{H}_{\text{int}}\mathrm{e}^{-\epsilon|t'|}\mathrm{e}^{-\mathrm{i}\hat{H}_0 t'}|M\rangle \int_{-\infty}^{t'} \mathrm{d}t'' \, \mathrm{e}^{\mathrm{i}\hat{H}_0 t''}\langle M|\mathrm{e}^{-\epsilon|t''|}\mathrm{e}^{-\mathrm{i}\hat{H}_0 t''}|I\rangle$$

$$S_{FI} = -\mathrm{i}\int_{-\infty}^{\infty} \mathrm{d}t\,\mathrm{e}^{\mathrm{i}(E_F-E_I)t}\langle F|\hat{H}_{\text{int}}|I\rangle$$

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

From transition amplitude to transition rate

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

Transition probability: $|S_{FI}|^2$

$$[\delta(E_F - E_I)]^2 = \delta(E_F - E_I)\int_{-T/2}^{T/2}\frac{\mathrm{d}t}{2\pi}\mathrm{e}^{\mathrm{i}(E_F-E_I)t} = \delta(E_F - E_I)\frac{T}{2\pi}$$

Transition rate: $\Gamma_{FI} = \dfrac{|S_{FI}|^2}{T}$

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

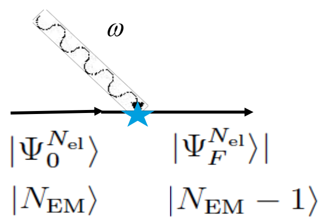
$$\hat{H}_{\text{int}} = \alpha\int \mathrm{d}^3x\hat{\psi}^\dagger(\boldsymbol{x})\left[\hat{\boldsymbol{A}}(\boldsymbol{x})\cdot\frac{\boldsymbol{\nabla}}{\mathrm{i}}\right]\hat{\psi}(\boldsymbol{x}) + \frac{\alpha^2}{2}\int \mathrm{d}^3x\hat{\psi}^\dagger(\boldsymbol{x})\hat{A}^2(\boldsymbol{x})\hat{\psi}(\boldsymbol{x})$$

X-ray Absorption

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

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

$$\hat{\boldsymbol{A}}(\boldsymbol{x}) = \sum_{\boldsymbol{k},\lambda}\sqrt{\frac{2\pi}{V\omega_{\boldsymbol{k}}\alpha^2}}\left\{\hat{a}_{\boldsymbol{k},\lambda}\boldsymbol{\epsilon}_{\boldsymbol{k},\lambda}\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}} + \hat{a}^\dagger_{\boldsymbol{k},\lambda}\boldsymbol{\epsilon}^*_{\boldsymbol{k},\lambda}\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}}\right\}$$



Initial state: $|I\rangle = |\Psi_0^{N_{\text{el}}}\rangle|N_{\text{EM}}\rangle$ → Final state: $|F\rangle = |\Psi_F^{N_{\text{el}}}\rangle|N_{\text{EM}} - 1\rangle$

$$\Gamma_{FI} = 2\pi\delta(E_F^{N_{\text{el}}} - E_0^{N_{\text{el}}} - \omega_{\text{in}})\left|\langle\Psi_F^{N_{\text{el}}}|\langle N_{\text{EM}} - 1|\alpha\int \mathrm{d}^3x\hat{\psi}^\dagger(\boldsymbol{x})\hat{\boldsymbol{A}}(\boldsymbol{x})\cdot\frac{\boldsymbol{\nabla}}{\mathrm{i}}\hat{\psi}(\boldsymbol{x})|\Psi_0^{N_{\text{el}}}\rangle|N_{\text{EM}}\rangle\right|^2$$

$$\hat{a}_{\boldsymbol{k},\lambda}|N_{\text{EM}}\rangle = \delta_{\boldsymbol{k},\boldsymbol{k}_{\text{in}}}\delta_{\lambda,\lambda_{\text{in}}}\sqrt{N_{\text{EM}}}|N_{\text{EM}} - 1\rangle$$

$$\Gamma_{FI} = 2\pi\delta(E_F^{N_{\text{el}}} - E_0^{N_{\text{el}}} - \omega_{\text{in}})\frac{2\pi}{V\omega_{\text{in}}\alpha^2}N_{\text{EM}}\alpha^2\left|\langle\Psi_F^{N_{\text{el}}}|\int \mathrm{d}^3x\hat{\psi}^\dagger(\boldsymbol{x})\mathrm{e}^{\mathrm{i}\boldsymbol{k}_{\text{in}}\cdot\boldsymbol{x}}\boldsymbol{\epsilon}_{\boldsymbol{k}_{\text{in}},\lambda_{\text{in}}}\cdot\frac{\boldsymbol{\nabla}}{\mathrm{i}}\hat{\psi}(\boldsymbol{x})|\Psi_0^{N_{\text{el}}}\rangle\right|^2$$

Photon flux: $J_{\text{EM}} = \dfrac{1}{\alpha}\dfrac{N_{\text{EM}}}{V}$

$$\Gamma_{FI} = \frac{4\pi^2}{\omega_{\text{in}}}\alpha J_{\text{EM}}\delta(E_F^{N_{\text{el}}} - E_0^{N_{\text{el}}} - \omega_{\text{in}})\left|\langle\Psi_F^{N_{\text{el}}}|\int \mathrm{d}^3x\hat{\psi}^\dagger(\boldsymbol{x})\mathrm{e}^{\mathrm{i}\boldsymbol{k}_{\text{in}}\cdot\boldsymbol{x}}\boldsymbol{\epsilon}_{\boldsymbol{k}_{\text{in}},\lambda_{\text{in}}}\cdot\frac{\boldsymbol{\nabla}}{\mathrm{i}}\hat{\psi}(\boldsymbol{x})|\Psi_0^{N_{\text{el}}}\rangle\right|^2$$

Definition of the photoabsorption cross section

$$\underbrace{\Gamma_{FI}/J_{\text{EM}}}_{\sigma_F(\boldsymbol{k}_{\text{in}},\lambda_{\text{in}}) = \Gamma_{FI}/J_{\text{EM}}} = \frac{4\pi^2}{\omega_{\text{in}}}\alpha\delta(E_F^{N_{\text{el}}} - E_0^{N_{\text{el}}} - \omega_{\text{in}}) \left| \langle \Psi_F^{N_{\text{el}}} | \int \mathrm{d}^3x \hat{\psi}^\dagger(\boldsymbol{x}) \mathrm{e}^{\mathrm{i}\boldsymbol{k}_{\text{in}}\cdot\boldsymbol{x}} \boldsymbol{\epsilon}_{\boldsymbol{k}_{\text{in}},\lambda_{\text{in}}} \cdot \frac{\boldsymbol{\nabla}}{\mathrm{i}} \hat{\psi}(\boldsymbol{x}) | \Psi_0^{N_{\text{el}}} \rangle \right|^2$$

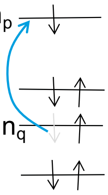
Expansion of field operators in single-particle orbitals $\varphi_p(\boldsymbol{x})$: $\hat{\psi}(\boldsymbol{x}) = \sum_p \varphi_p(\boldsymbol{x}) \hat{c}_p$

$$\sigma_F(\boldsymbol{k}_{\text{in}},\lambda_{\text{in}}) = \frac{4\pi^2}{\omega_{\text{in}}}\alpha\delta(E_F^{N_{\text{el}}} - E_0^{N_{\text{el}}} - \omega_{\text{in}}) \left| \sum_{p,q} \underbrace{\langle \varphi_p | \mathrm{e}^{\mathrm{i}\boldsymbol{k}_{\text{in}}\cdot\boldsymbol{x}} \boldsymbol{\epsilon}_{\boldsymbol{k}_{\text{in}},\lambda_{\text{in}}} \cdot \frac{\boldsymbol{\nabla}}{\mathrm{i}} | \varphi_q \rangle}_{\text{single-particle transition dipole}} \underbrace{\langle \Psi_F^{N_{\text{el}}} | \hat{c}_p^\dagger \hat{c}_q | \Psi_0^{N_{\text{el}}} \rangle}_{\text{Overlap integral, Containing all electron correlations (exact)}} \right|^2$$

single-particle transition dipole

Overlap integral, Containing all electron correlations (exact)

Assumption: Groundstate is a Hartree-Fock single Slater determinant



$$|\Psi_0^{N_{\text{el}}}\rangle \approx \prod_{i=1}^{N_{\text{el}}} \hat{c}_i^\dagger |\text{vacuum}\rangle$$

$\langle \Psi_F^{N_{\text{el}}} | \hat{c}_p^\dagger \hat{c}_q | \Psi_0^{N_{\text{el}}} \rangle$ =1 if *q* initially occupied & appropriately chosen final state

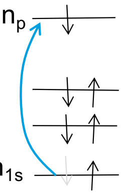
Definition of the sub-shell photoabsorption cross section

$$\sigma(\boldsymbol{k}_{\text{in}},\lambda_{\text{in}}) = \frac{4\pi^2}{\omega_{\text{in}}}\alpha\delta(E_F^{N_{\text{el}}} - E_0^{N_{\text{el}}} - \omega_{\text{in}}) \left| \sum_{p,q} \underbrace{\langle \varphi_p | \mathrm{e}^{\mathrm{i}\boldsymbol{k}_{\text{in}}\cdot\boldsymbol{x}} \boldsymbol{\epsilon}_{\boldsymbol{k}_{\text{in}},\lambda_{\text{in}}} \cdot \frac{\boldsymbol{\nabla}}{\mathrm{i}} | \varphi_q \rangle}_{\text{single-particle transition dipole}} \underbrace{\langle \Psi_F^{N_{\text{el}}} | \hat{c}_p^\dagger \hat{c}_q | \Psi_0^{N_{\text{el}}} \rangle}_{\text{Overlap integral, Containing all electron correlations (exact)}} \right|^2$$

single-particle transition dipole

Overlap integral, Containing all electron correlations (exact)

Assumption: Groundstate is a Hartree-Fcok single Slater determinant

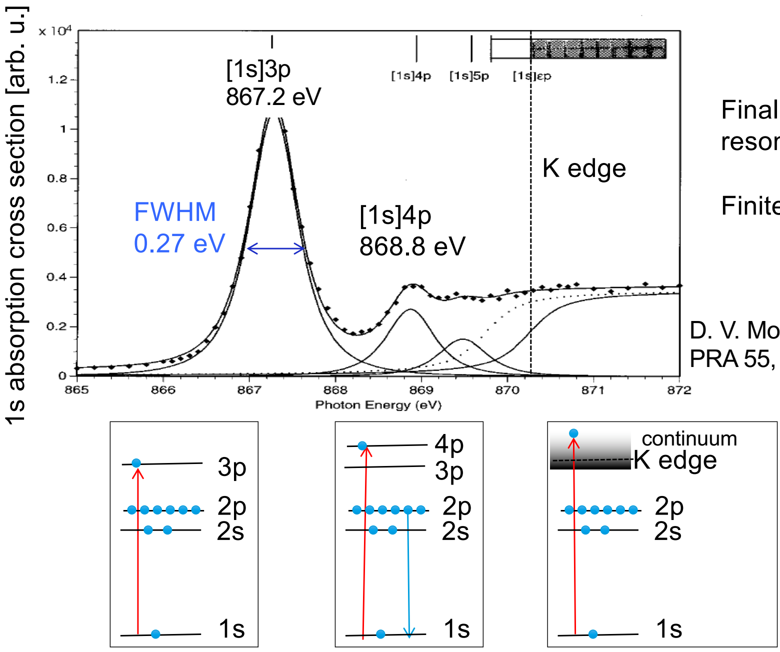


$$|\Psi_0^{N_{\text{el}}}\rangle \approx \prod_{i=1}^{N_{\text{el}}} \hat{c}_i^\dagger |\text{vacuum}\rangle$$

Restrict summation over *q* to a specific sub-shell: For example: 1s photoionisation cross section:

$$\sigma_{1s}(\boldsymbol{k}_{\text{in}},\lambda_{\text{in}}) = \frac{4\pi^2}{\omega_{\text{in}}}\alpha\delta(E_F^{N_{\text{el}}} - E_0^{N_{\text{el}}} - \omega_{\text{in}}) \left| \sum_{q=\,1s,\,p} \langle \varphi_p | \mathrm{e}^{\mathrm{i}\boldsymbol{k}_{\text{in}}\cdot\boldsymbol{x}} \boldsymbol{\epsilon}_{\boldsymbol{k}_{\text{in}},\lambda_{\text{in}}} \cdot \frac{\boldsymbol{\nabla}}{\mathrm{i}} | \varphi_q \rangle \langle \Psi_F^{N_{\text{el}}} | \hat{c}_p^\dagger \hat{c}_q | \Psi_0^{N_{\text{el}}} \rangle \right|^2$$

1s photoabsorption-cross section of Neon

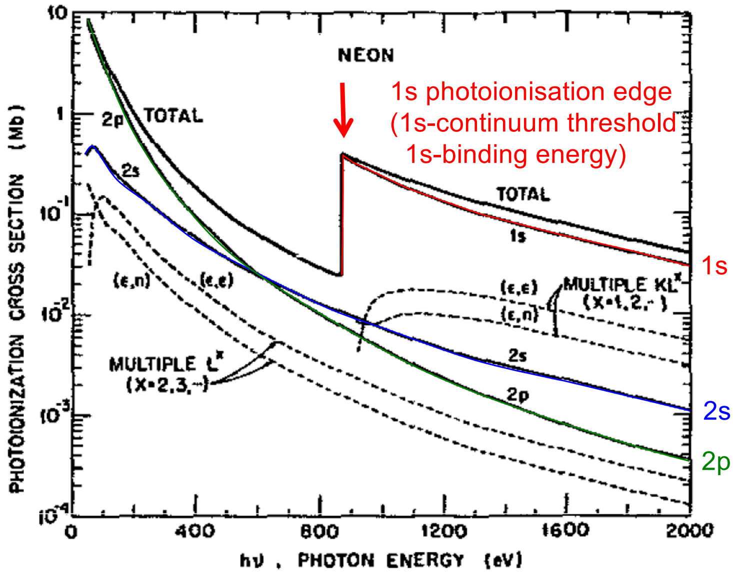


Final width of resonances

Finite lifetime !

D. V. Morgan et al., PRA 55, 1113 (1997)

Neon sub-shell photoionization cross section

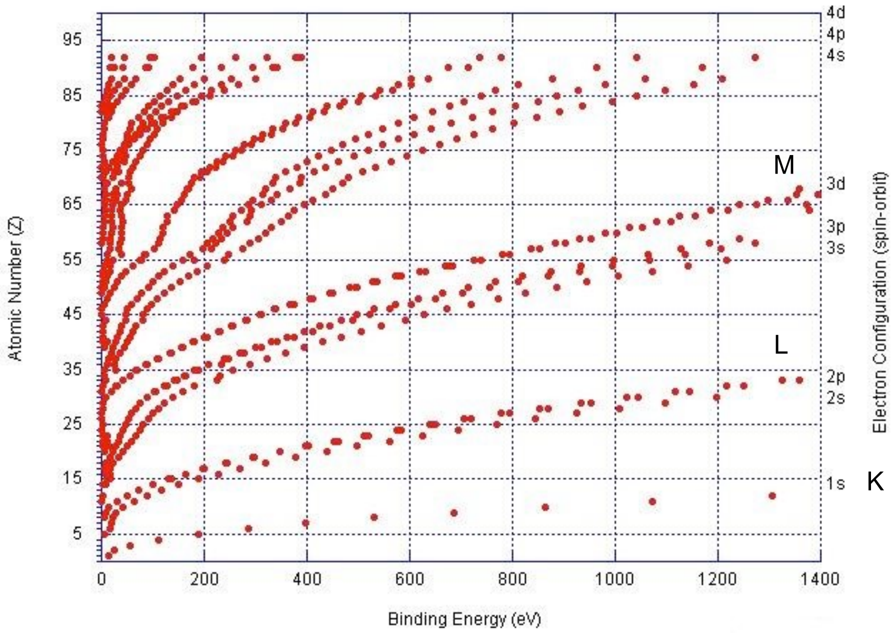


Photoionisation cross section at threshold: ~ 1 Mb (10^{-18} cm^2)

V. Schmidt, Rep. Prog. Phys. 55, 1483 (1992).

Element sensitivity of x-rays

Sub-shell binding energies as a function of nuclear charge



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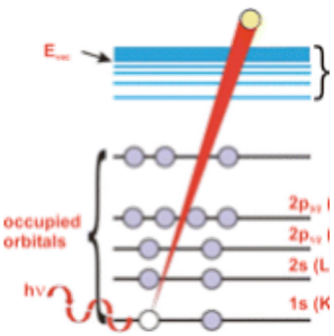
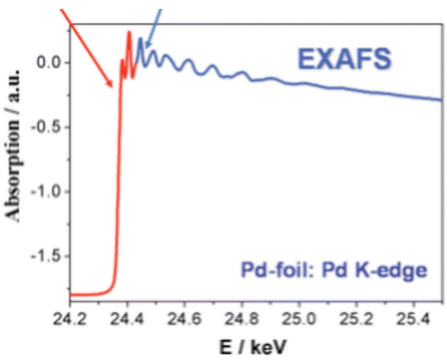
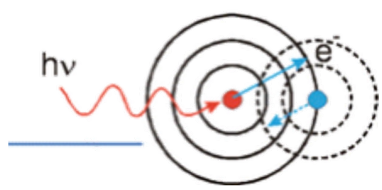
Structural information of photoabsorption

XANES (X-ray Absorption Near Edge Structure) & EXAFS (Extended X-ray Absorption Fine Structure)

$$\sigma_{1s}(\boldsymbol{k}_{\text{in}}, \lambda_{\text{in}}) = \frac{4\pi^2}{\omega_{\text{in}}} \alpha \delta(E_F^{N_{\text{el}}} - E_0^{N_{\text{el}}} - \omega_{\text{in}}) \left| \sum_{q=1s;\, p} \langle \varphi_p | \mathrm{e}^{\mathrm{i}\boldsymbol{k}_{\text{in}} \cdot \boldsymbol{x}} \boldsymbol{\epsilon}_{\boldsymbol{k}_{\text{in}}, \lambda_{\text{in}}} \cdot \frac{\boldsymbol{\nabla}}{\mathrm{i}} | \varphi_q \rangle \langle \Psi_F^{N_{\text{el}}} | \hat{c}_p^\dagger \hat{c}_q | \Psi_0^{N_{\text{el}}} \rangle \right|^2$$







De Broglie wavelength of photo-electron: λ [Å]=12/(E_{el} [eV])$^{1/2}$

For photo-electron energy of 50 eV: λ= 1.7 Å

Interference (scattering of photoelectron) → EXAFS is highly sensitive to changes in bond length

J.-D. Grunwaldt and A. Baiker, Phys. Chem. Chem. Phys. 7, 3526 (2005).

X-ray atom interaction probability

Calculate the ionization rate for Neon at the 1s threshold for typical pulses of 3rd generation synchrotron light source at the 1s threshold, assuming a cross section of 1 Mb.

Suppose:
- Pulse duration of 100 ps
- 10^6 photon / pulse
- Focal area of 100 μm^2

Calculate the ionisation probability per pulse

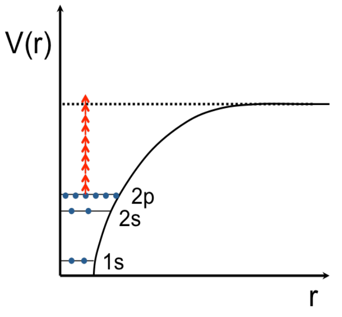
Now the same exercise for a typical, focused FEL pulse:

Suppose:
- Pulse duration of 10 fs
- 10^{12} photon / pulse
- Focal area of 1 μm^2

Within of a single pulse, multiple photo-ionization becomes possible ➡ nonlinear interaction

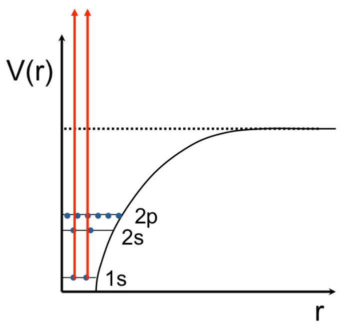
Intense optical versus X-ray field-atom interaction

Short-wavelength,
optical strong-field process



single-electron
multi-photon interactions

Strong-field X-ray interaction

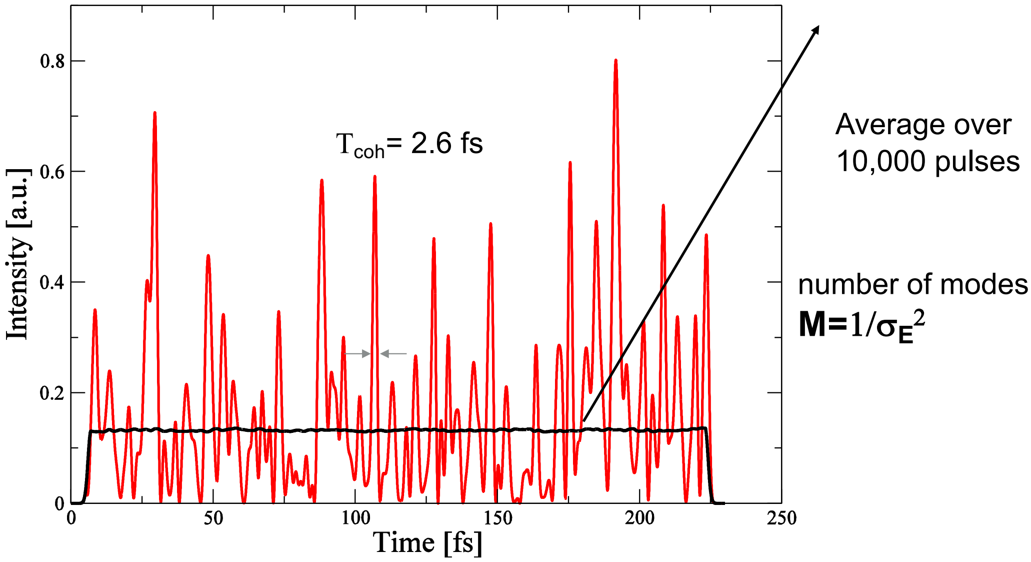


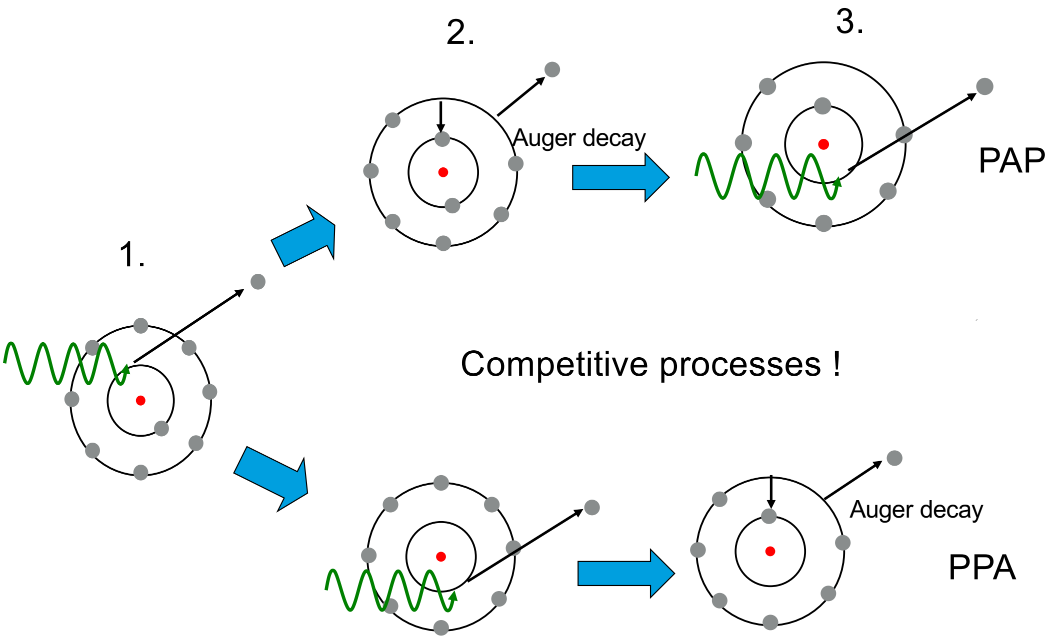
single-electron
single-photon
interactions

Statistical properties of radiation matter in both cases

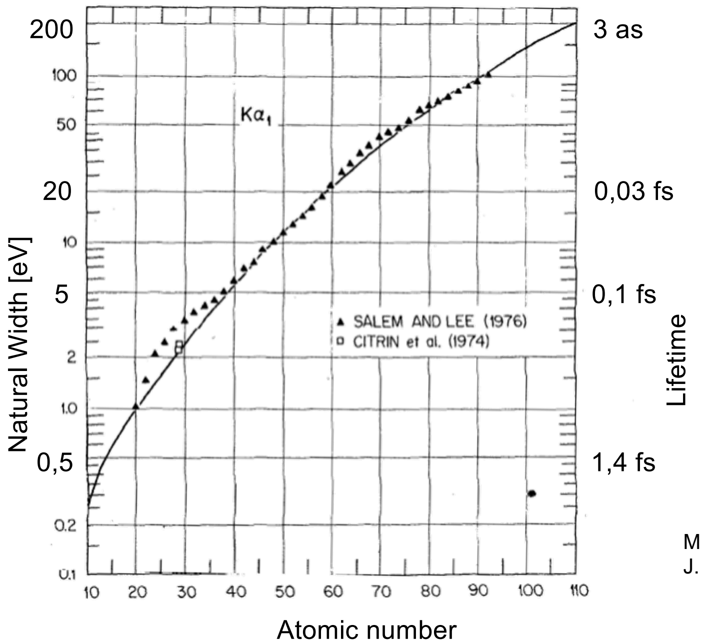
Typical simulated SASE FEL pulse for LCLS parameters

ω=1.05 keV, relative bandwidth 4.3x10^{-4}, pulse duration t_{pulse}=230 fs



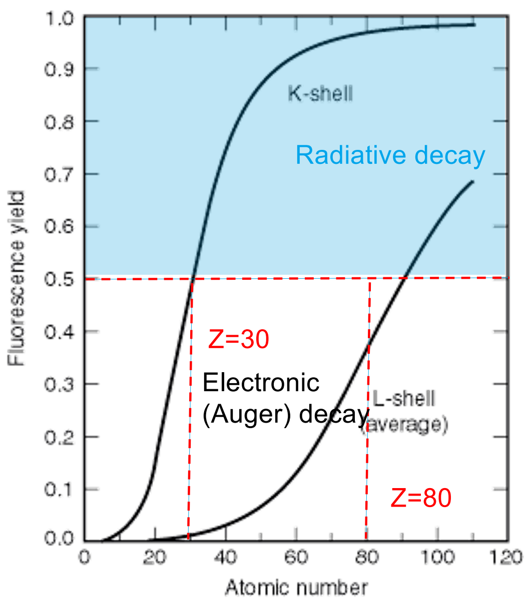


Natural width of $K\alpha_1$ x-ray lines



M. O. Krause and J. H. Oliver,
J. Phys. Chem Ref. Data, 8 329 (1979)

Fluorescence Yield – Radiative versus Auger decay



M. O. Krause, J. Phys. Chem. Ref. Data 8, 307 (1979).
M. O. Krause and J. H. Oliver, *J. Phys. Chem. Ref. Data* **8**, 329 (1979).

Rate equations for Neon

Following the time-dependent occupation/depletion of electronic configurations and charge states

$$\dot{N}(t) = -\overset{P}{\sigma^0_{1s}} N(t) j(t) - \sigma^0_{2s} N(t) j(t) - \sigma^0_{2p} N(t) j(t)$$

$$\dot{N}^+_{1s}(t) = \sigma^0_{1s} N(t) j(t) - (r^+_{1s;2s2s} + r^+_{1s;2s2p} + \overset{A}{r^+_{1s;2p2p}}) N^+_{1s}(t) - (\overset{P}{\sigma^+_{1s;1s}} + \sigma^+_{1s;2s} + \sigma^+_{1s;2p}) N^+_{1s}(t) j(t) - \overset{F}{f^+} N^+_{1s}(t)$$

$$\dot{N}^+_{2s}(t) = \sigma^0_{2s} N(t) j(t) - (\sigma^+_{2s;1s} + \sigma^+_{2s;2s} + \sigma^+_{2s;2p}) N^+_{2s}(t) j(t)$$

$$\dot{N}^+_{2p}(t) = \sigma^0_{2p} N(t) j(t) - (\sigma^+_{2p;1s} + \sigma^+_{2p;2s} + \sigma^+_{2p;2p}) N^+_{2p}(t) j(t)$$

$$\dot{N}^{2+}_{2p^2}(t) = r^+_{1s;2p2p} N^+_{1s}(t) + \sigma^+_{2p;2p} N^+_{2p}(t) j(t) - (\sigma^{2+}_{2p^2;1s} + \sigma^{2+}_{2p^2;2s} + \sigma^{2+}_{2p^2;2p}) N^{2+}_{2p^2}(t) j(t)$$

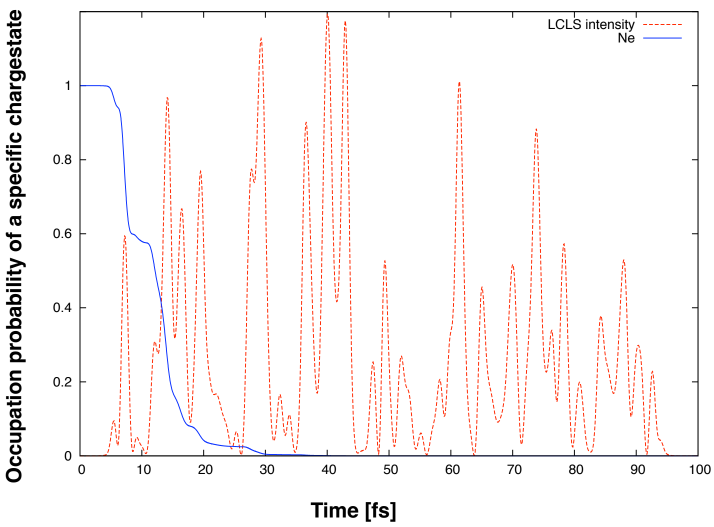
$$\dot{N}^{2+}_{1s^2}(t) = \sigma^+_{1s;1s} N^+_{1s}(t) j(t) - (r^{2+}_{1s^2;2s2s} + r^{2+}_{1s^2;2s2p} + r^{2+}_{1s^2;2p2p}) N^{2+}_{1s^2}(t) - (\sigma^{2+}_{1s^2;2s} + \sigma^{2+}_{1s^2;2p}) N^{2+}_{1s^2}(t) j(t) - f^{2+} N^{2+}_{1s^2}(t)$$

......

Fluorescence yield in Neon: 1.8%
Most probable sequence of events: PAPAPA.....

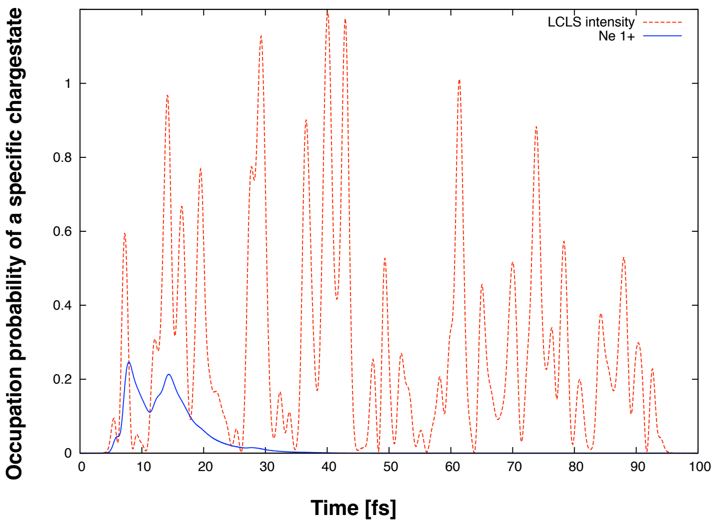
N. Rohringer, R. Santra, Phys. Rev. A 76, 033416 (2007)
S.-K. Son, R. Santra, Phys. Rev. A 85, 063415 (2012)

Charge-state evolution as a function of time in Neon



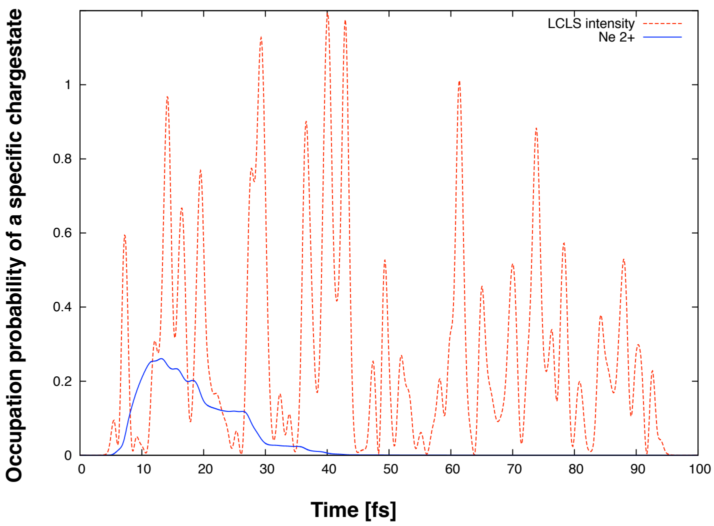
Parameters: pulse of 100 fs, 10^{12} photons, ω=1.4 keV, focused to 2 μm

Charge-state evolution as a function of time in Neon



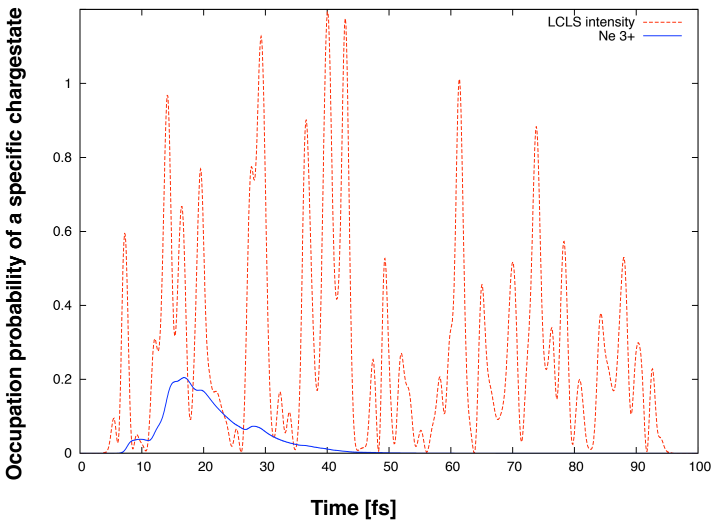
Parameters: pulse of 100 fs, 10^{12} photons, ω=1.4 keV, focused to 2 μm

Charge-state evolution as a function of time in Neon



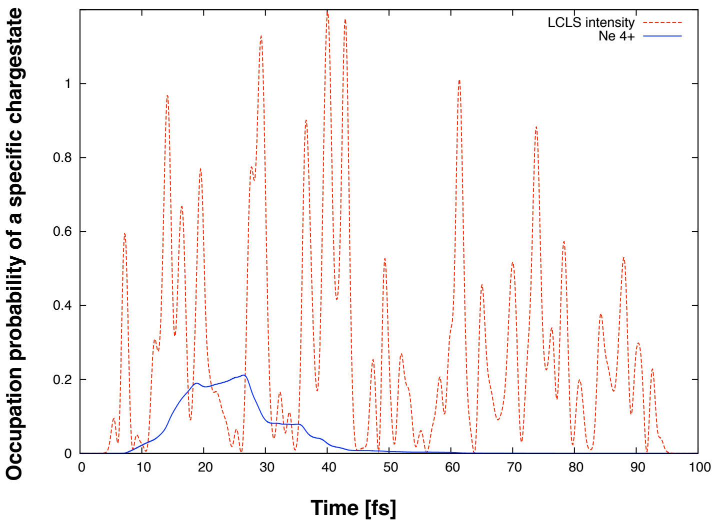
Parameters: pulse of 100 fs, 10^{12} photons, ω=1.4 keV, focused to 2 μm

Charge-state evolution as a function of time in Neon



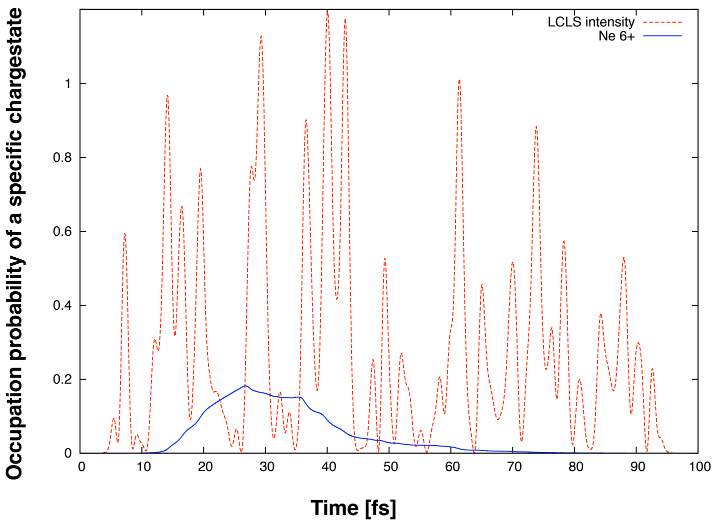
Parameters: pulse of 100 fs, 10^{12} photons, ω=1.4 keV, focused to 2 μm

Charge-state evolution as a function of time in Neon



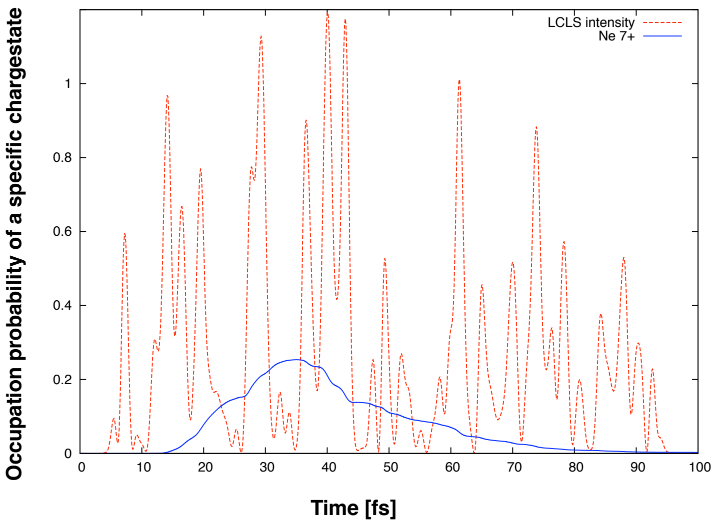
Parameters: pulse of 100 fs, 10^{12} photons, ω=1.4 keV, focused to 2 μm

Charge-state evolution as a function of time in Neon



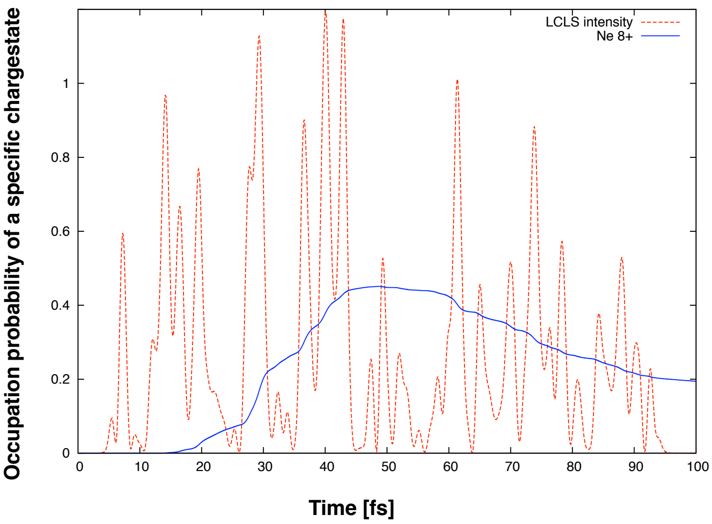
Parameters: pulse of 100 fs, 10^{12} photons, ω=1.4 keV, focused to 2 μm

Charge-state evolution as a function of time in Neon



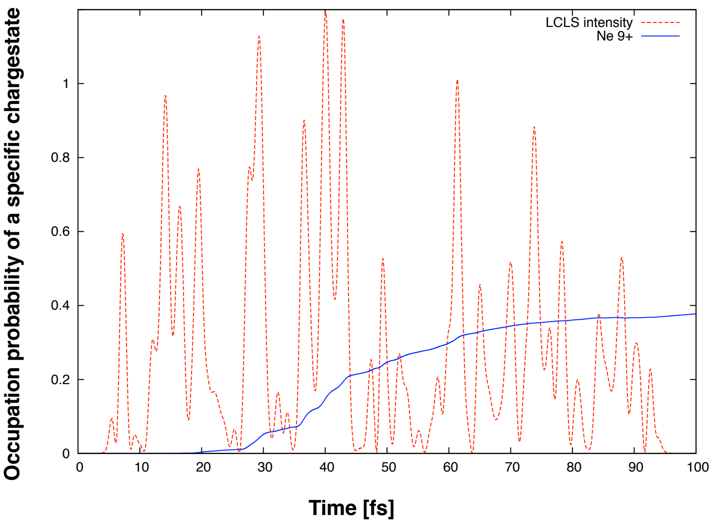
Parameters: pulse of 100 fs, 10^{12} photons, ω=1.4 keV, focused to 2 μm

Charge-state evolution as a function of time in Neon



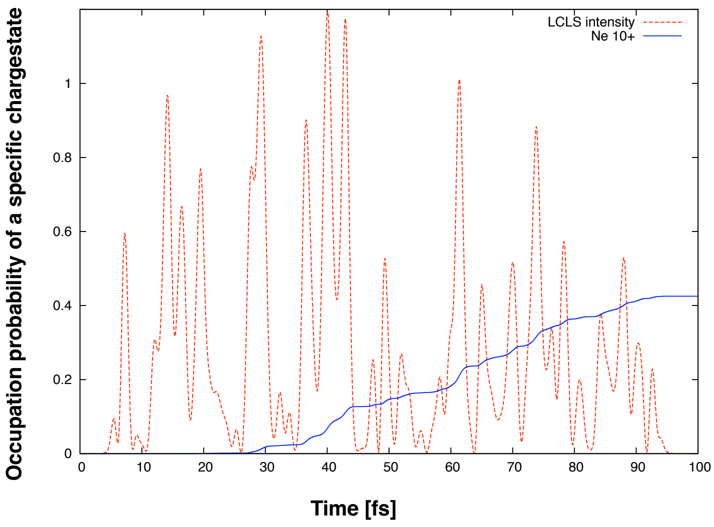
Parameters: pulse of 100 fs, 10^{12} photons, ω=1.4 keV, focused to 2 μm

Charge-state evolution as a function of time in Neon



Parameters: pulse of 100 fs, 10^{12} photons, ω=1.4 keV, focused to 2 μm

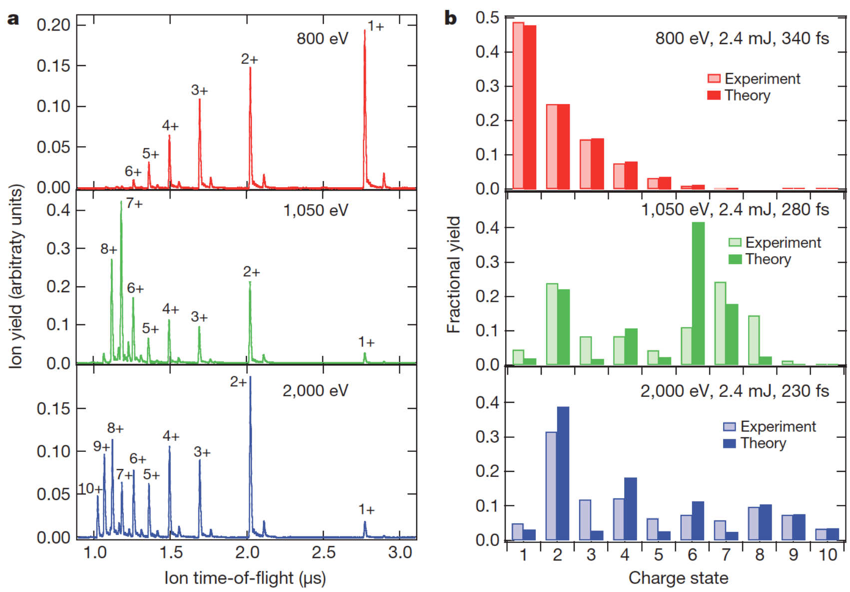
Charge-state evolution as a function of time in Neon



Parameters: pulse of 100 fs, 10^{12} photons, ω=1.4 keV, focused to 2 μm

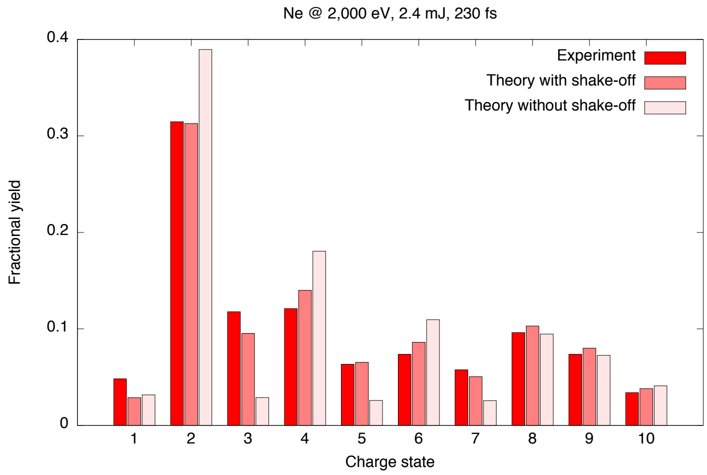
Experimental Results of 1st user experiment @ LCLS

Ion charge spectrum of atomic neon at different LCLS photon frequencies and pulse durations

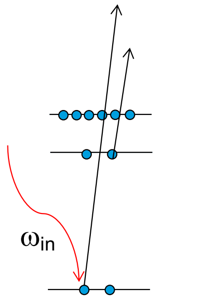


L. Young et al., ***Nature*** **466**, 56 **(2010)**.

The effect of shake-off in multiple ionisation of Ne



Shake-off effects



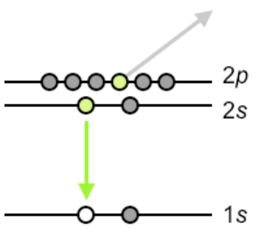
$$\sigma(\boldsymbol{k}_{\rm in},\lambda_{\rm in}) = \frac{4\pi^2}{\omega_{\rm in}}\alpha\delta(E_F^{N_{\rm el}} - E_0^{N_{\rm el}} - \omega_{\rm in})\left|\sum_{p,q}\langle\varphi_p|e^{i\boldsymbol{k}_{\rm in}\cdot\boldsymbol{x}}\boldsymbol{\epsilon}_{\boldsymbol{k}_{\rm in},\lambda_{\rm in}}\cdot\frac{\boldsymbol{\nabla}}{i}|\varphi_q\rangle\langle\Psi_F^{N_{\rm el}}|\hat{c}_p^\dagger\hat{c}_q|\Psi_0^{N_{\rm el}}\rangle\right|^2$$

 Calculation & Figure with courtesy to Sang Kil Son

Configuration space explored in nonlinear x-ray interaction

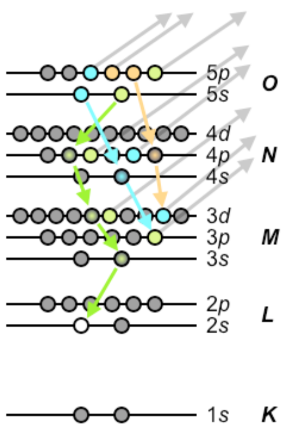
Number of involved electronic configurations grows drastically for heavier elements

Ne



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

Xe



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

Auger (Coster-Kronig) decay cascade

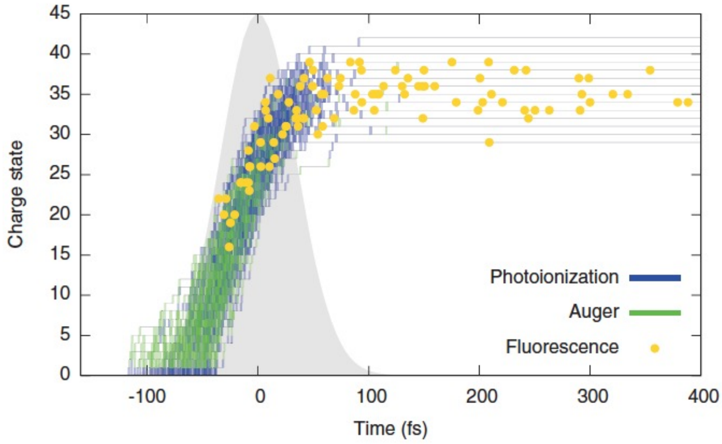
Neon @ 1,5 keV: ~ 50 Configurations

Xenon @ 1,5 keV: > 10^6 Configurations

 Add source of picture

Solving rate equations for multiple ionization in Xe

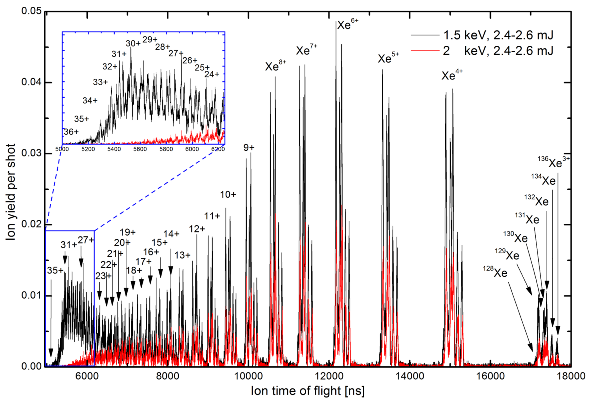
100 sample trajectories, Xe @ 4,5 keV, 80fs, 5 x 10^{12} photons/μm^2



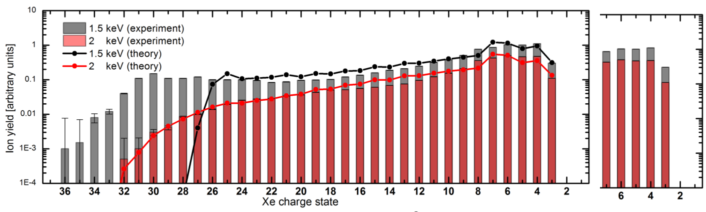
Supposing energy of 4,5 keV (above threshold for M, N and O-shell ionisation)
More than 1 Million configurations of Xe and Xe ions

Theory: Xatom Code – Monte Carlo approach to rate equations
San Kil Son & Santra, Phys. Rev. A 85 ,063415(2012)

Resonances can play subsantial role in efficient multi ionization



Why is maximum charge state at 2 keV (Xe^{32+}) lower than at 1.5 keV (Xe^{36+})?

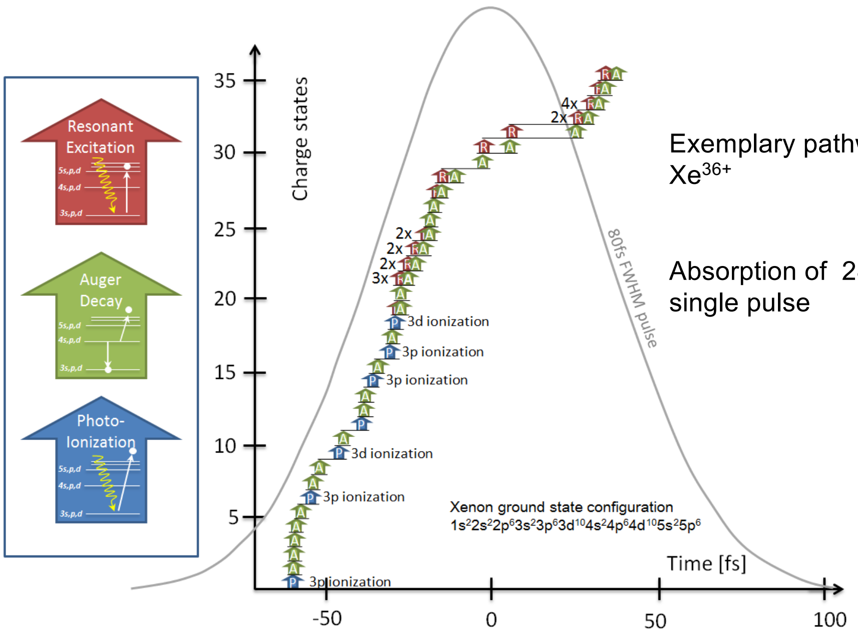


Calculations by
Sang-Kil Son and Robin Santra

Something must be happening at 1.5 keV that goes beyond the sequential $P(A)^nP(A)^n$ scheme modelled by the calculations...

B. Rudek *et al.*, Nature Photonics **6**, 858 (2012)

The effect of resonances in multiple ionization of Xenon



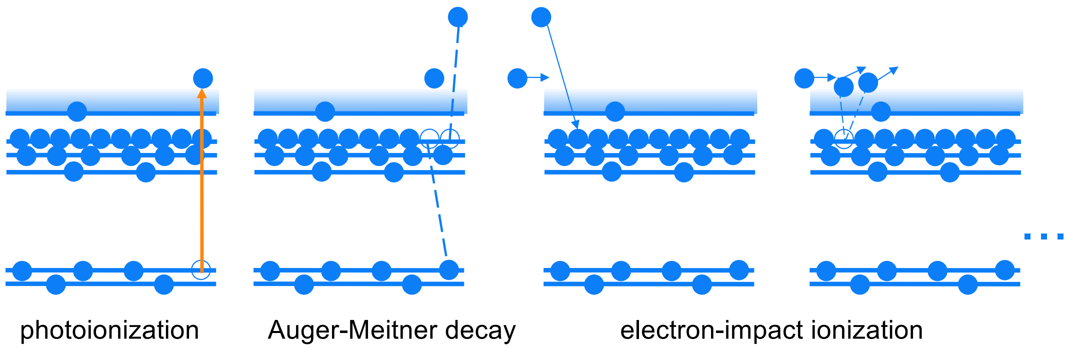
Exemplary pathway leading to Xe^{36+}

Absorption of 28 photons in a single pulse

B. Rudek *et al.*, Nature Photonics **6**, 858 (2012)

Transition from warm-dense matter to plasma

What secondary processes happen at solid-state density?



- elastic and inelastic collisions of electrons and ions,
- recombination processes,
- short range electron–electron scattering.

Summary

The concept of a cross section

- Quantum electrodynamics + perturbation theory
- Electronic degreed in 2nd quantization
- S-matrix & Transition rates

X-ray photo absorption

- Many-body effects in single-photon absorption

Multi-photon absorption at FELs

- The role of the higher-order coherence
- Rate equation approach
- Role of transient resonances