Fundamentals of X-ray interaction with matter

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DESY Summer Student Lectures 'Photon Science'
August 3 and 7, 2017

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Outline

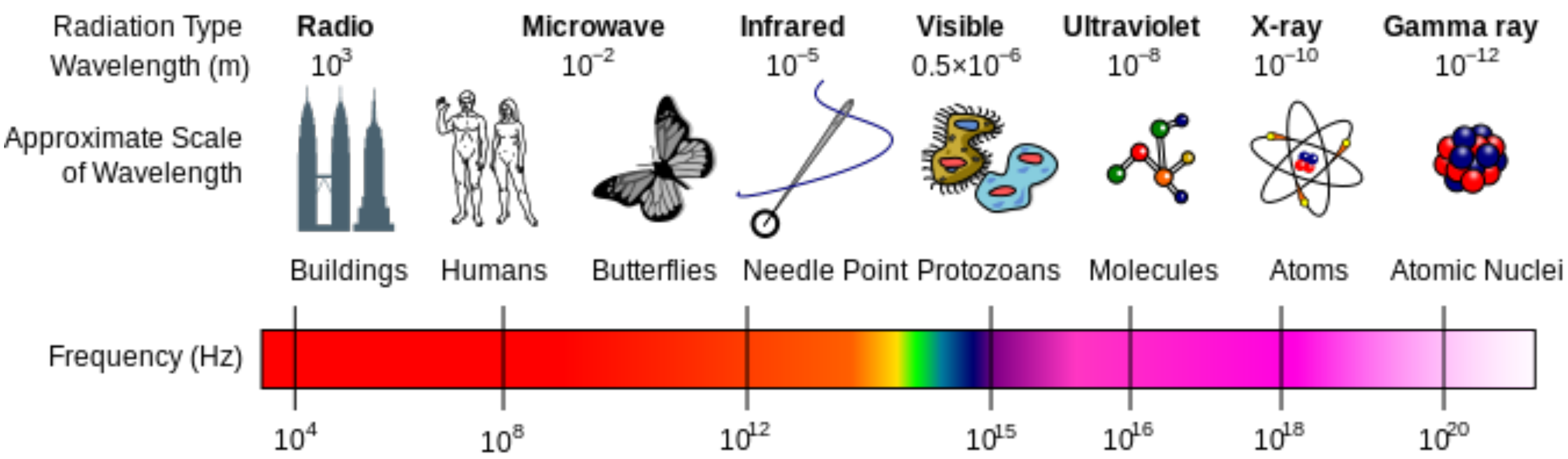
- First day (August 3, 2017)
  - Introduction
  - Theory of X-ray–matter interaction
  - X-ray absorption
- Second day (August 7, 2017)
  - X-ray fluorescence
  - Auger decay
  - X-ray scattering
  - X-ray atomic physics on computer: XATOM

What’s X-ray?

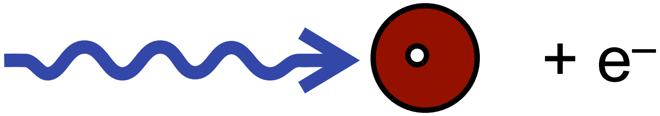
Nick Veasey,
1970 Mini Driver, 2012

X-ray is…

- discovered by Wilhelm Röntgen in 1895
- photon energy: 100 eV ~ 100 keV
- wavelength: 0.01 nm to 10 nm
- penetrability
- element selectivity



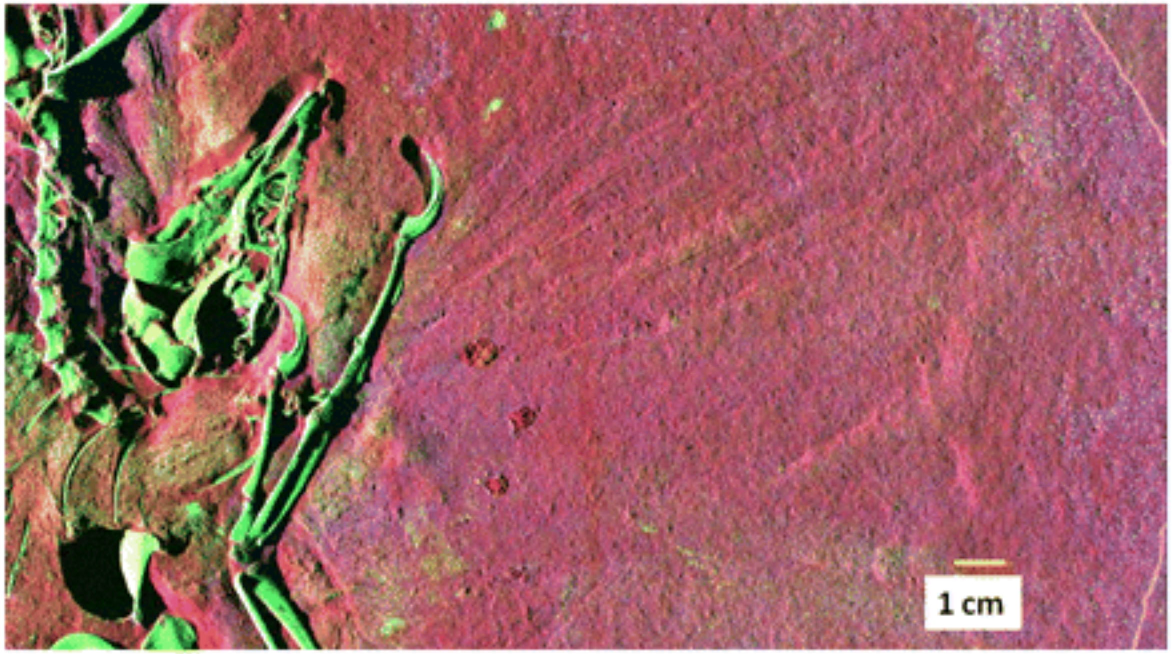
X-ray absorption



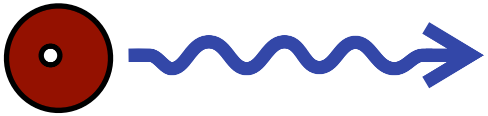
C absorption ≪ Ca absorption

Hand with rings: Röntgen’s first medical X-ray in 1895 (Nobel prize in 1901)

X-ray fluorescence

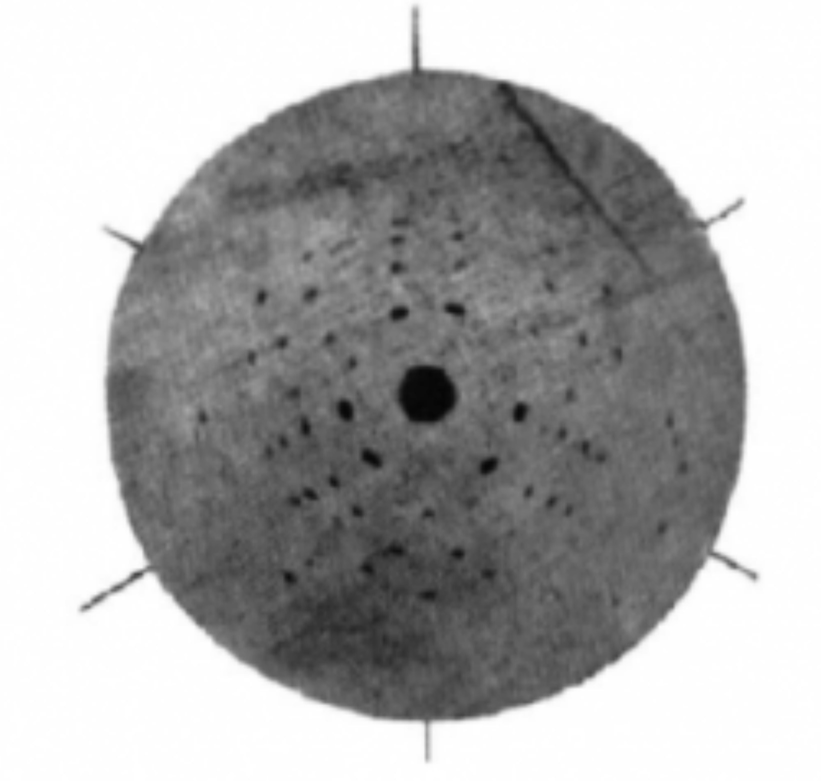


Archaeopteryx: False color SRS-XRF map,
U. Bergmann *et al.*, *PNAS* **107**, 9060 (2010).

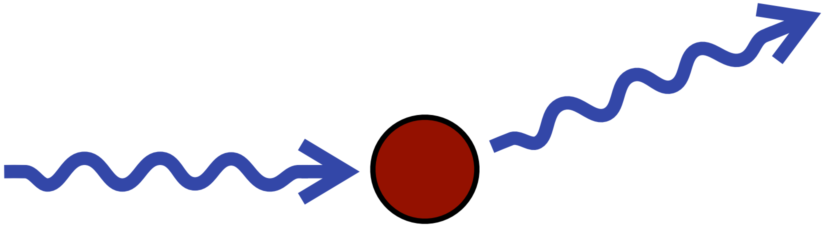


feathers were real; remnant chemical composition revealed by X-ray fluorescence

X-ray scattering

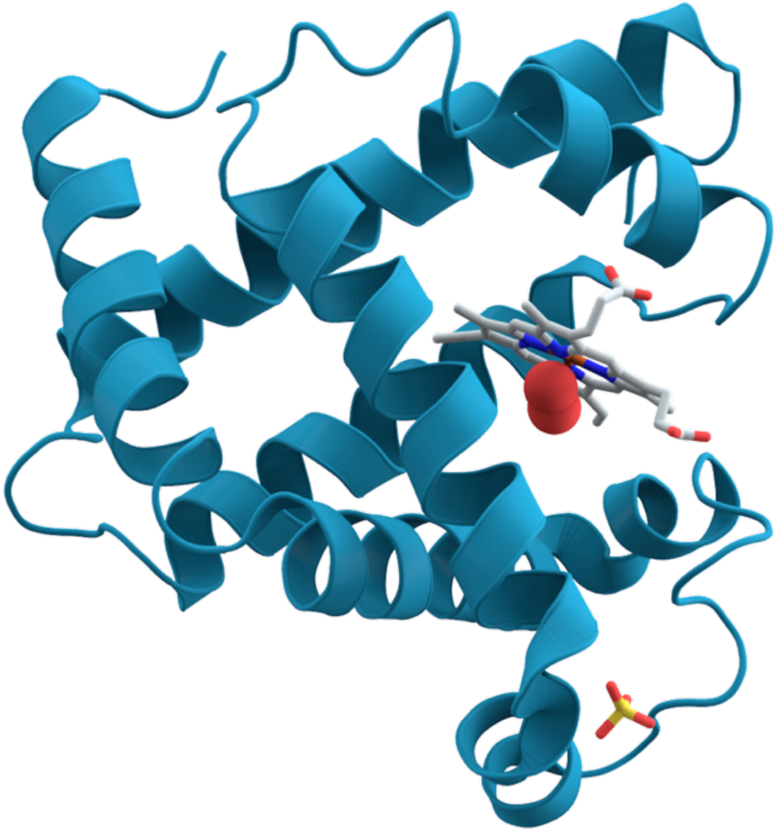


Zinc blend: first published diffraction pattern of a crystal by Max von Laue in 1912 (Nobel prize in 1914)

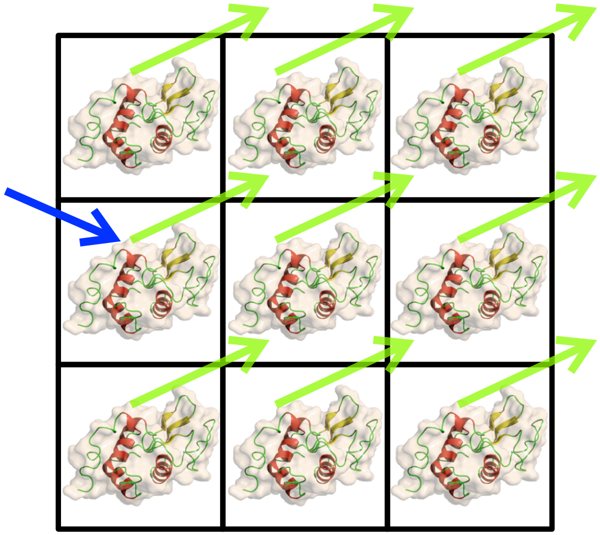


Elastic X-ray scattering from a crystal makes diffraction pattern.

X-ray crystallography



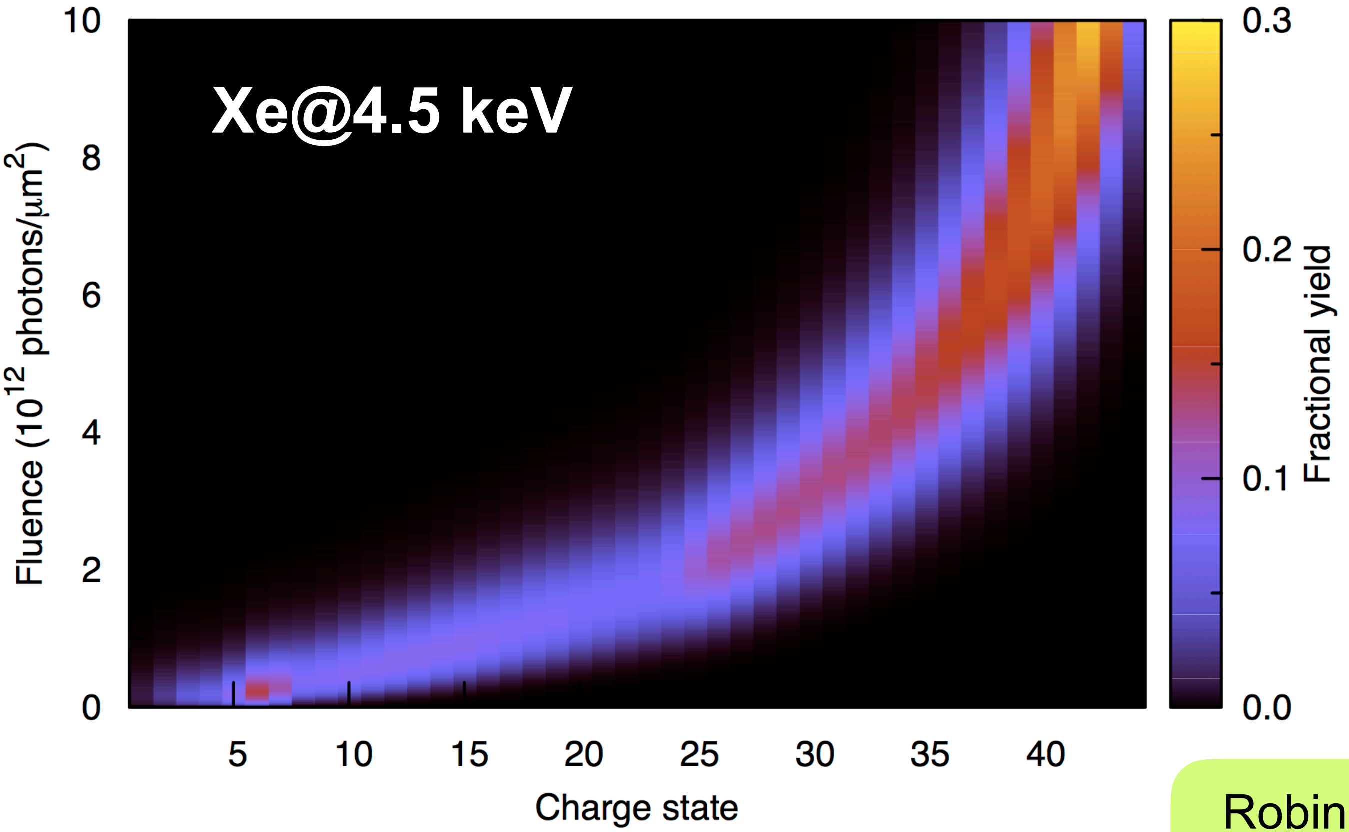
Myoglobin: first protein structure revealed by X-ray crystallography by John Kendrew in 1958 (Nobel prize in 1962 with Max Perutz)



X-ray crystallography can reveal atomic structure of biological macromolecules.

Martin's lectures on August 14/16

High X-ray intensity

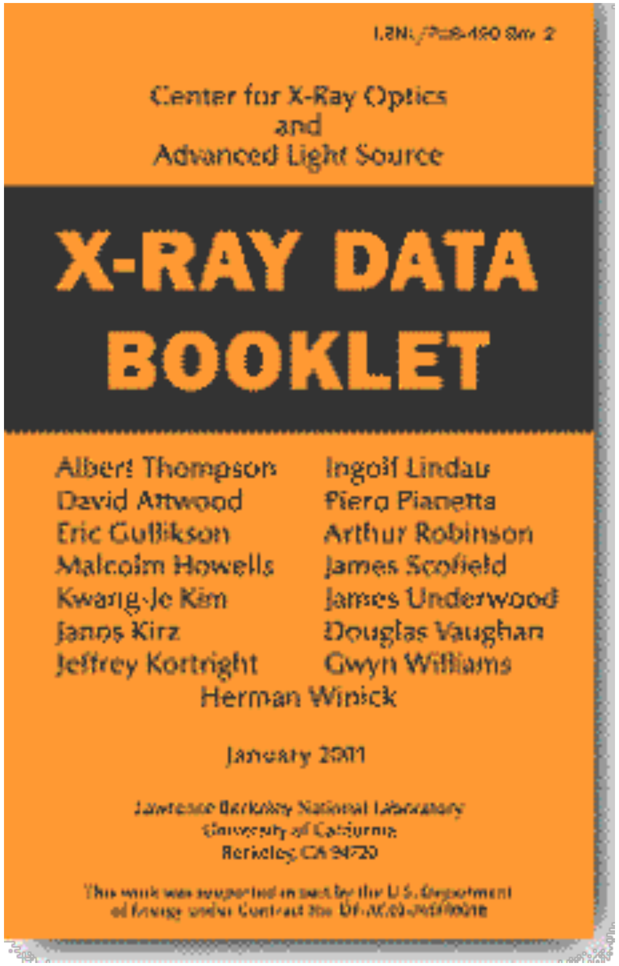


Robin's lectures on August 10

- Here we will discuss only one-photon absorption limit.
- Later you will see more interesting physics with intense x-ray pulses.

Main references

http://xdb.lbl.gov



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X-RAY DATA
BOOKLET

Albert Thompson
David Attwood
Eric Gullikson
Malcolm Howells
Kwang-Je Kim
Janos Kirz
Jeffrey Kortright
Ingolf Lindau
Piero Pianetta
Arthur Robinson
James Scofield
James Underwood
Douglas Vaughan
Gwyn Williams
Herman Winick

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Berkeley, CA 94720

R. Santra, *J. Phys. B* **42**, 023001 (2010).

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J. Phys. B: At. Mol. Opt. Phys. **42** (2009) 023001 (16pp) doi:10.1088/0953-4075/42/2/023001

PHD TUTORIAL

Concepts in x-ray physics

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Abstract
A basic introduction to the theory underlying x-ray processes is provided. After general remarks on the practical advantages of using x-rays for probing matter, the derivation of the minimal-coupling Hamiltonian within nonrelativistic quantum electrodynamics is outlined. Perturbation theory is reviewed and applied to describe x-ray-induced processes. In connection with x-ray absorption, inner-shell binding energies and the photon energy dependence of the x-ray absorption cross section are discussed. In the context of x-ray scattering, atomic and molecular scattering factors are introduced, the complex index of refraction is derived, and the nonrelativistic theory of Compton scattering is described. The final topic is x-ray fluorescence and Auger decay of inner-shell-excited systems.

1. Introductory remarks

Since their discovery in the year 1895 by Wilhelm Conrad Röntgen [1], x-rays have become an indispensable tool for studying the structure and electronic properties of matter. Equally important is the role x-rays have come to play in medicine, archaeology, art, security, astronomy and other applications. To date, 19 Nobel prizes have been awarded for x-ray-related research (W C Röntgen 1901, M von Laue 1914, W H Bragg and W L Bragg 1915, C G Barkla 1917, K M G Siegbahn 1924, A H Compton 1927, P J W Debye 1936, H J Muller 1946, M F Perutz and J C Kendrew 1962, F H C Crick, J D Watson, and M H F Wilkins 1962, D Crowfoot Hodgkin 1964, W N Lipscomb 1976, A M Cormack and G N Hounsfield 1979, K M Siegbahn 1981, H A Hauptman and J Karle 1985, J Deisenhofer, R Huber and H Michel 1988, P D Boyer and J E Walker 1997, P Agre and R MacKinnon 2003, R Kornberg 2006).

As a new generation of x-ray sources—so-called x-ray free-electron lasers [2, 3]—is about to come online [4–6], it is timely to familiarize newcomers, experimentalists and theorists alike, with some of the basic properties that make x-rays such a powerful tool. This is attempted in this tutorial. The emphasis is on the development of a consistent theoretical framework that may be employed to describe a variety of x-ray processes. Throughout, the x-rays are assumed to be used as a weak, essentially nonperturbative *probe*. Basic applications of x-rays will be covered. However, since this is a tutorial, there is not a single topic that is discussed in great depth, and some topics, e.g., x-ray sources and x-ray optics [7, 8], are not discussed at all.

This tutorial is structured as follows. In section 2, the derivation of the Hamiltonian underlying nonrelativistic quantum electrodynamics is sketched. This Hamiltonian, in combination with perturbation theory (section 3), allows one to describe all basic x-ray processes. X-ray absorption is the topic of section 4. In section 5, x-ray scattering processes are discussed. Finally, in section 6, relaxation processes following the excitation of an inner-shell electron are treated.

Atomic units are employed, i.e., $m_e = 1$, $|e| = 1$, $\hbar = 1$ and $c = 1/\alpha$, where m_e is the electron mass, e is the electron charge, $\hbar$ is Planck's constant divided by 2π, c is the speed of light in vacuum and $\alpha = \frac{e^2}{\hbar c} \approx 1/137$ is the fine-structure constant. The atomic unit of length is the bohr, $a_0 = \frac{1}{\alpha}\frac{\hbar}{m_e c} \approx 0.529$ Å. The atomic unit of cross section is $a_0^2 \approx 28.0$ Mb, where a *barn* (b) equals 10^{-28} m^2. The atomic unit of energy is the hartree, $E_h = m_e c^2 \alpha^2 \approx 27.2$ eV.

Depending on the photon energy, we typically distinguish between the following two x-ray regimes [7, 8]. Photons with an energy between ~10 E_h (~300 eV) and ~100 E_h (a few keV) are called *soft x-rays*. Soft x-rays cover, roughly, the 1s binding energies for elements ranging from carbon

0953-4075/09/023001+16$30.00

How to treat interaction between X-ray and matter?

Total Hamiltonian

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

- X-rays interact with the electrons only
- Non-relativistic quantum electrodynamics
- Principle of Minimal Coupling
- Time-dependent perturbation theory

Atomic units used:

$$m_e = 1$$

$$|e| = 1$$

$$\hbar = 1$$

$$1/4\pi\epsilon_0 = 1$$

$$(c = 1/\alpha,\ \ a_0 = 1)$$

Hamiltonian for free electromagnetic field

Hamiltonian for the free electromagnetic field (harmonic oscillator)

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

Field operator: creates or annihilates a photon in the mode (***k***,*λ*).

$$\hat{a}_{\boldsymbol{k},\lambda} |n_{\boldsymbol{k},\lambda}\rangle = \sqrt{n_{\boldsymbol{k},\lambda}} |n_{\boldsymbol{k},\lambda} - 1\rangle$$

$$\hat{a}^{\dagger}_{\boldsymbol{k},\lambda} |n_{\boldsymbol{k},\lambda}\rangle = \sqrt{n_{\boldsymbol{k},\lambda} + 1} |n_{\boldsymbol{k},\lambda} + 1\rangle$$

Commutator relations for photon mode operators

$$[\hat{a}_{\boldsymbol{k},\lambda}, \hat{a}_{\boldsymbol{k}',\lambda'}] = 0$$

$$[\hat{a}_{\boldsymbol{k},\lambda}, \hat{a}^{\dagger}_{\boldsymbol{k}',\lambda'}] = \delta_{\boldsymbol{k},\boldsymbol{k}'} \delta_{\lambda,\lambda'}$$

$$[\hat{a}^{\dagger}_{\boldsymbol{k},\lambda}, \hat{a}^{\dagger}_{\boldsymbol{k}',\lambda'}] = 0$$

Molecular Hamiltonian

Molecular Hamiltonian

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

$$\hat{T}_{\mathrm{N}} = -\sum_{a} \frac{\nabla_a^2}{2M_a} \qquad \hat{V}_{\mathrm{NN}} = \sum_{a<a'} \frac{Z_a Z_{a'}}{|\boldsymbol{R}_a - \boldsymbol{R}_{a'}|}$$

Electronic Hamiltonian using the second quantization

$$\hat{H}_{\mathrm{el}} = \int d^3x \, \hat{\psi}^\dagger(\boldsymbol{x}) \left\{ -\frac{\nabla^2}{2} - \sum_a \frac{Z_a}{|\boldsymbol{x} - \boldsymbol{R}_a|} \right\} \hat{\psi}(\boldsymbol{x}) + \frac{1}{2} \int d^3x \int d^3x' \, \hat{\psi}^\dagger(\boldsymbol{x}) \hat{\psi}^\dagger(\boldsymbol{x}') \frac{1}{|\boldsymbol{x} - \boldsymbol{x}'|} \hat{\psi}(\boldsymbol{x}') \hat{\psi}(\boldsymbol{x})$$

Anticommutator relations for electron field operators

$$\{\hat{\psi}_\sigma(\boldsymbol{x}), \hat{\psi}_{\sigma'}(\boldsymbol{x}')\} = 0,$$

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

$$\{\hat{\psi}^\dagger_\sigma(\boldsymbol{x}), \hat{\psi}^\dagger_{\sigma'}(\boldsymbol{x}')\} = 0.$$

Interaction Hamiltonian

Interaction between electrons and photons
(minimal coupling, Coulomb gauge)

p•A and A²

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

Mode expansion of vector potential

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

$$\boldsymbol{k} \cdot \boldsymbol{\epsilon}_{\boldsymbol{k},\lambda} = 0, \quad \boldsymbol{\epsilon}^*_{\boldsymbol{k},1} \cdot \boldsymbol{\epsilon}_{\boldsymbol{k},2} = 0$$

p•A: one-photon absorption in first order; one-photon scattering in second order

A²: one-photon scattering in first order

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Time-dependent perturbation theory

Full Hamiltonian and unperturbed part $$\hat{H} = \underbrace{\hat{H}_{\mathrm{mol}} + \hat{H}_{\mathrm{EM}}}_{\hat{H}_0} + \hat{H}_{\mathrm{int}}$$

Initial state: $|I\rangle = |\Psi_0^{N_{\mathrm{el}}}\rangle|N_{\mathrm{EM}}\rangle$

Interaction-picture state vector to second order in perturbation

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

Transition rate to second order in perturbation

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

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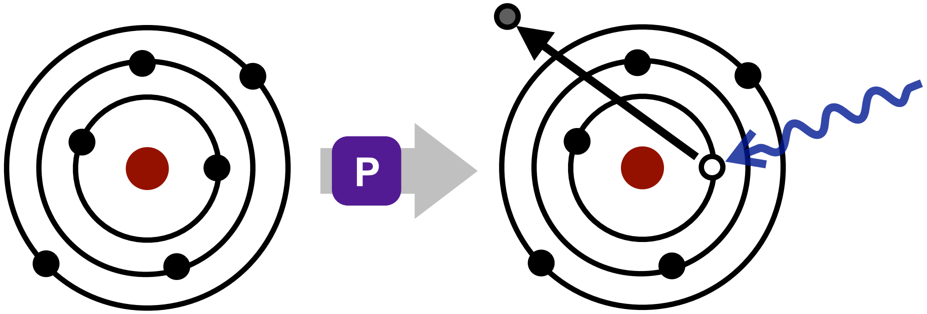
X-ray absorption



Initial state: $|I\rangle = |\Psi_0^{N_{\mathrm{el}}}\rangle |N_{\mathrm{EM}}\rangle$

Final state: $|F\rangle = |\Psi_F^{N_{\mathrm{el}}}\rangle |N_{\mathrm{EM}} - 1\rangle$

Absorption rate: $\Gamma_{FI} = 2\pi\delta(E_F - E_I) \left| \langle F | \hat{H}_{\mathrm{int}} | I \rangle \right|^2$

X-ray absorption

X-ray absorption rate

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

X-ray photon flux

$$J_{\mathrm{EM}} = \frac{1}{\alpha}\frac{N_{\mathrm{EM}}}{V}$$

X-ray absorption cross section

$$\sigma = \Gamma_{FI}/J_{\mathrm{EM}}$$

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

how to treat many-electron systems?

Electronic many-body problem

Introducing a set of orthonormal spin orbitals $\{\varphi_p(\boldsymbol{x})\}$

An electronic one-body Hamiltonian

$$\hat{F} = \sum_p \varepsilon_p \hat{c}_p^\dagger \hat{c}_p$$

$$\hat{F}|\varphi_p\rangle = \varepsilon_p|\varphi_p\rangle$$

Creation and annihilation operators for $|\varphi_p\rangle$: $\hat{c}_p^\dagger$ and $\hat{c}_p$

$$\{\hat{c}_p, \hat{c}_q\} = 0,$$

$$\{\hat{c}_p, \hat{c}_q^\dagger\} = \delta_{p,q},$$

$$\{\hat{c}_p^\dagger, \hat{c}_q^\dagger\} = 0.$$

Connecting with the field operators

$$\hat{\psi}(\boldsymbol{x}) = \sum_p \varphi_p(\boldsymbol{x})\hat{c}_p,$$

$$\hat{\psi}^\dagger(\boldsymbol{x}) = \sum_p \varphi_p^\dagger(\boldsymbol{x})\hat{c}_p^\dagger$$

Mean-field model

Independent-electron model $\hat{H}_{\mathrm{el}} \approx \hat{F}$

Mean-field ground state in terms of a single Slater determinant

$$|\Psi_0^{N_{\mathrm{el}}}\rangle \approx |\Phi_0^{N_{\mathrm{el}}}\rangle \equiv \prod_{i=1}^{N_{\mathrm{el}}} \hat{c}_i^\dagger |\mathrm{vacuum}\rangle$$

Mean-field ground-state energy $E_0^{N_{\mathrm{el}}} \approx \langle \Phi_0^{N_{\mathrm{el}}} | \hat{F} | \Phi_0^{N_{\mathrm{el}}} \rangle = \sum_{i=1}^{N_{\mathrm{el}}} \varepsilon_i$

Hartree-Fock (HF) method: minimizing $\langle \Phi_0^{N_{\mathrm{el}}} | \hat{H}_{\mathrm{el}} | \Phi_0^{N_{\mathrm{el}}} \rangle$

the best choice among the mean-field models

Koopmans' theorem

One-hole state

$$|\Phi_i^{N_{\mathrm{el}}-1}\rangle \equiv \hat{c}_i |\Phi_0^{N_{\mathrm{el}}}\rangle$$

Energy of one-hole state

$$E_i^{N_{\mathrm{el}}-1} \approx \langle \Phi_i^{N_{\mathrm{el}}-1} | \hat{F} | \Phi_i^{N_{\mathrm{el}}-1} \rangle = \left\{ \sum_{j=1}^{N_{\mathrm{el}}} \varepsilon_j \right\} - \varepsilon_i$$

Ionization potential

$$I_i \equiv E_i^{N_{\mathrm{el}}-1} - E_0^{N_{\mathrm{el}}}$$

Koopmans' theorem: valid for HF orbitals

$$\begin{aligned} I_i = & \langle \Phi_i^{N_{\mathrm{el}}-1} | \hat{H}_{\mathrm{el}} | \Phi_i^{N_{\mathrm{el}}-1} \rangle \\ & - \langle \Phi_0^{N_{\mathrm{el}}} | \hat{H}_{\mathrm{el}} | \Phi_0^{N_{\mathrm{el}}} \rangle = -\varepsilon_i \end{aligned}$$

For Neon,

Koopmans	EXP
$-\varepsilon_{2p} = 23.1$ eV	21.6 eV
$-\varepsilon_{2s} = 52.5$ eV	48.5 eV
$-\varepsilon_{1s} = 892$ eV	870 eV

Note: Koopmans received a Nobel prize in Economics in 1975, of course, not because of this theorem.

X-ray absorption within mean-field model

Particle-hole state $|\Phi_i^a\rangle \equiv \hat{c}_a^\dagger |\Phi_i^{N_\mathrm{el}-1}\rangle = \hat{c}_a^\dagger \hat{c}_i |\Phi_0^{N_\mathrm{el}}\rangle$

Initial state $|I\rangle = |\Phi_0^{N_\mathrm{el}}\rangle |N_\mathrm{EM}\rangle$

Final state $|F\rangle = \hat{c}_a^\dagger \hat{c}_i |\Phi_0^{N_\mathrm{el}}\rangle |N_\mathrm{EM}-1\rangle$

Cross section for particle-hole transition

$$\sigma_i^a(\boldsymbol{k}_\mathrm{in}, \lambda_\mathrm{in}) = \frac{4\pi^2}{\omega_\mathrm{in}} \alpha \delta(\varepsilon_a + I_i - \omega_\mathrm{in}) \left| \langle \varphi_a | \mathrm{e}^{\mathrm{i}\boldsymbol{k}_\mathrm{in}\cdot\boldsymbol{x}} \boldsymbol{\epsilon}_{\boldsymbol{k}_\mathrm{in},\lambda_\mathrm{in}} \cdot \frac{\boldsymbol{\nabla}}{\mathrm{i}} | \varphi_i \rangle \right|^2$$

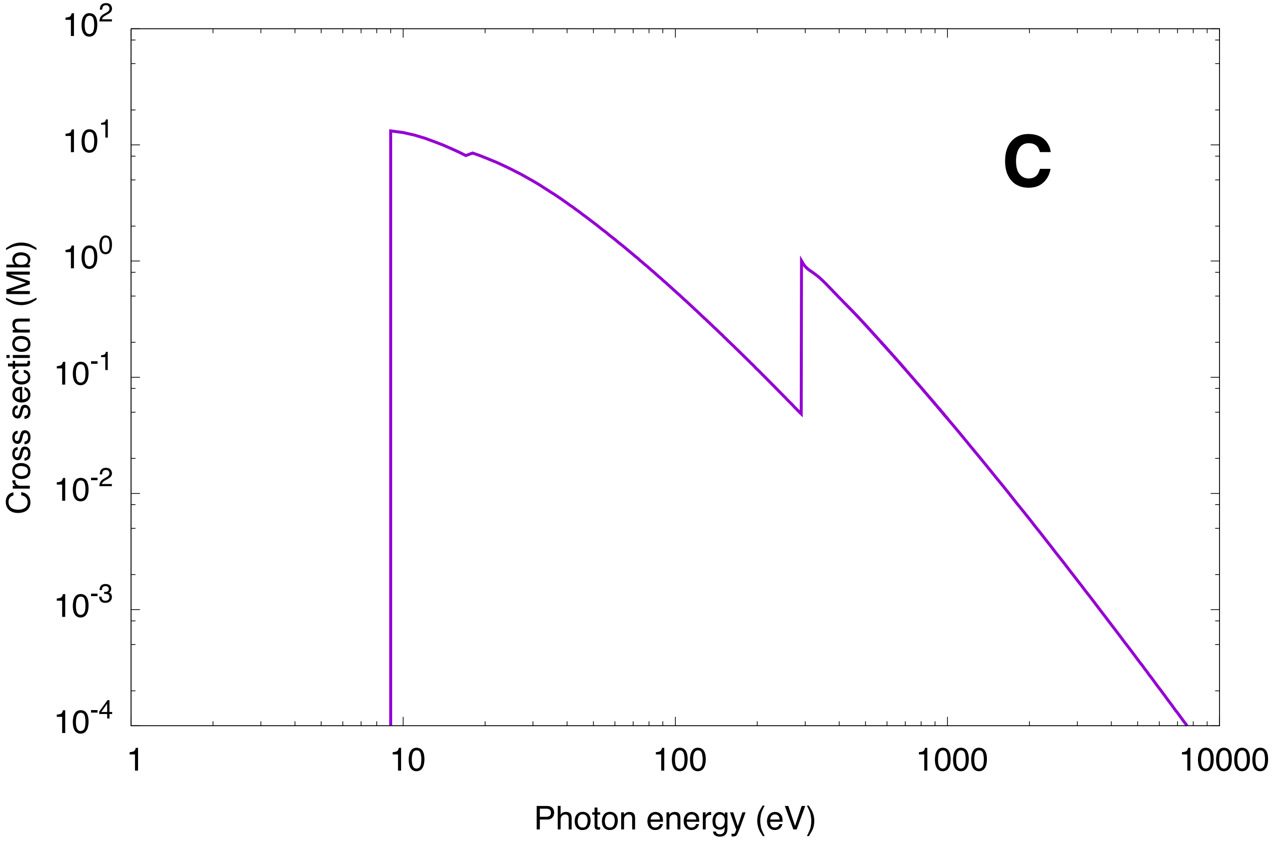
Energy of excited electron $\varepsilon_a = \omega_\mathrm{in} - I_i > 0$ **"Photoelectric effect"**

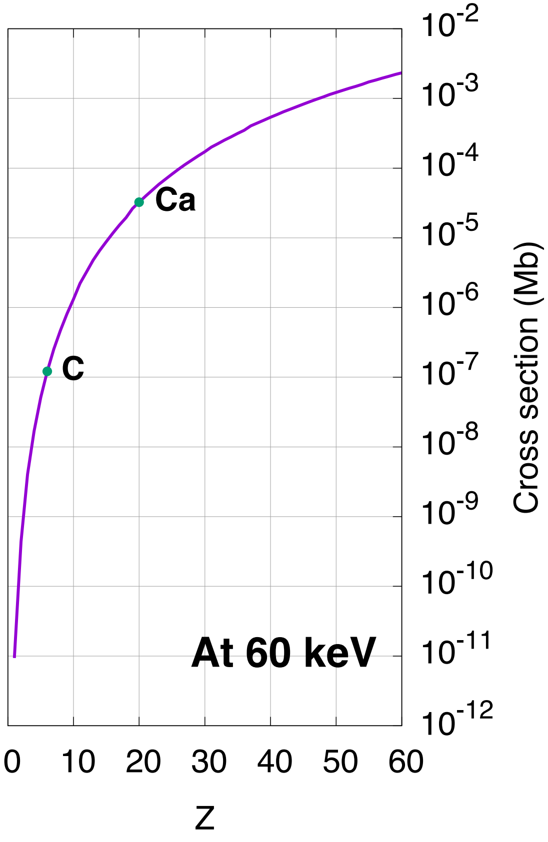
Note: Einstein received a Nobel prize in 1921 for the photoelectric effect, not for theory of relativity.

Subshell x-ray absorption cross section

$$\sigma_i(\boldsymbol{k}_\mathrm{in}, \lambda_\mathrm{in}) = \sum_a \sigma_i^a(\boldsymbol{k}_\mathrm{in}, \lambda_\mathrm{in})$$

Photoionization cross section calculation





- PCS changes by varying ω and Z; edge structures

K-shell photoionization: a simple model

- Simple model of an atomic species of atomic number Z
  - 1*s* orbital ~ H-like 1*s* orbital of Z

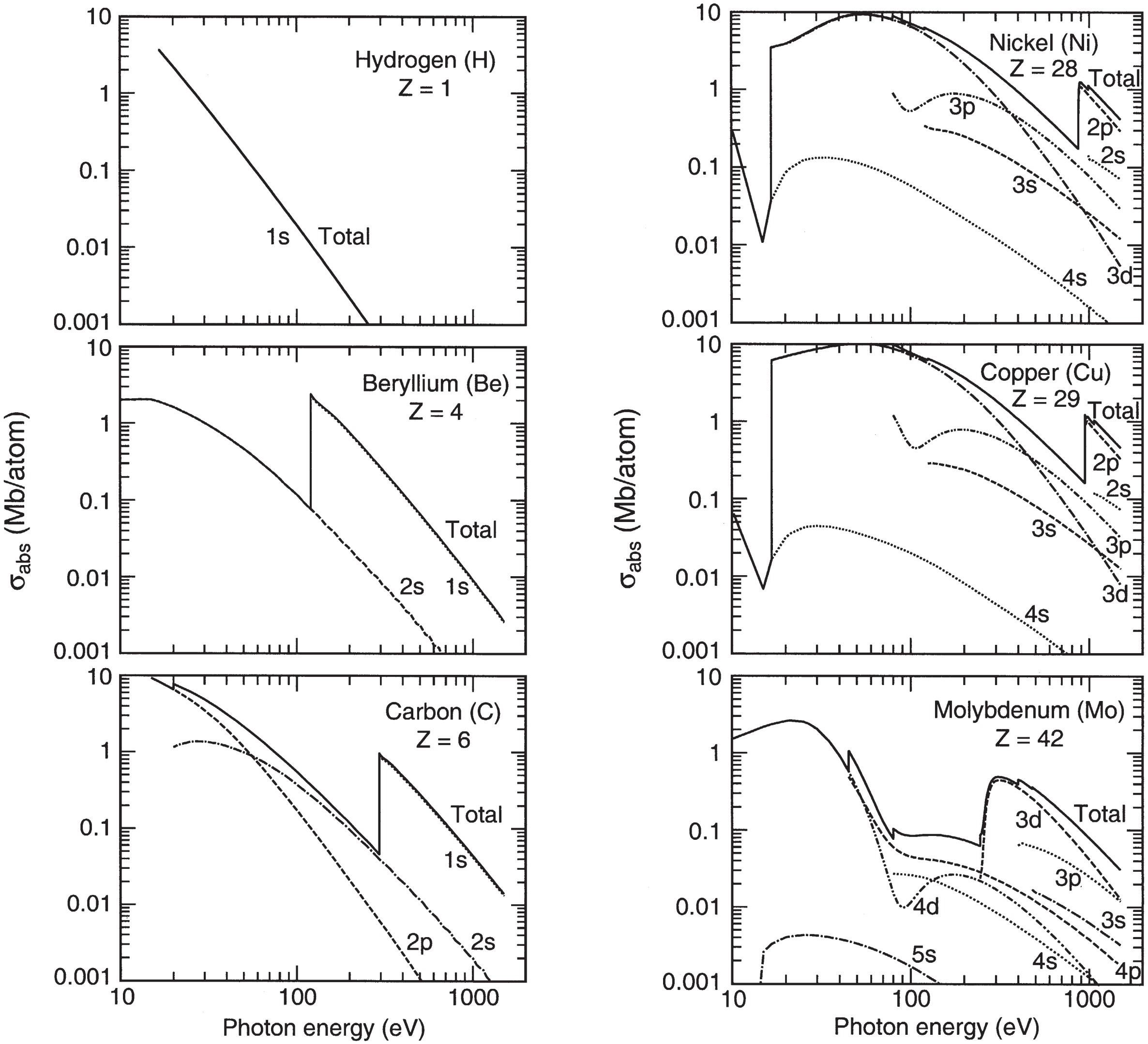
$$u_{1s}(r) \propto Z^{3/2} r e^{-Zr}, \qquad I_{1s} = Z^2/2$$

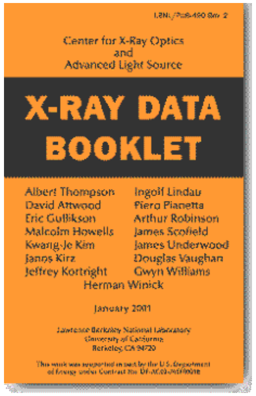
  - photoelectron wave function ~ plane wave (assuming $\omega_{\text{in}} \gg I_{1s}$)
- At fixed photon energy ω, $\sigma_{\text{abs}} \sim Z^5$

  Compare σ_{C} (Z=6) and σ_{Ca} (Z=20): $(20/6)^5 \sim 400$ times
- At fixed Z, $\sigma_{\text{abs}} \sim \omega_{\text{in}}^{-7/2}$

  For a given atom, the x-ray absorption cross section above the 1*s* threshold decreases with increasing photon energy.

Table of photoionization cross sections





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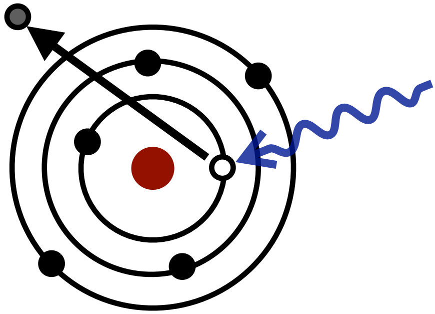
Jeffrey Kortright
Ingolf Lindau
Piero Pianetta
Arthur Robinson
James Scofield
James Underwood
Douglas Vaughan
Gwyn Williams
Herman Winick

January 2001

Lawrence Berkeley National Laboratory
University of California
Berkeley, CA 94720

or



running XATOM

Applications of X-ray absorption

- X-ray photoelectron spectroscopy: measuring *photoelectron energy*
    - XPS (PES)
    - ESCA
- X-ray absorption spectroscopy: measuring *absorption cross section* as a function of *photon energy*
    - XAS
    - XANES (NEXAFS)
    - EXAFS

XPS: X-ray Photoelectron Spectroscopy

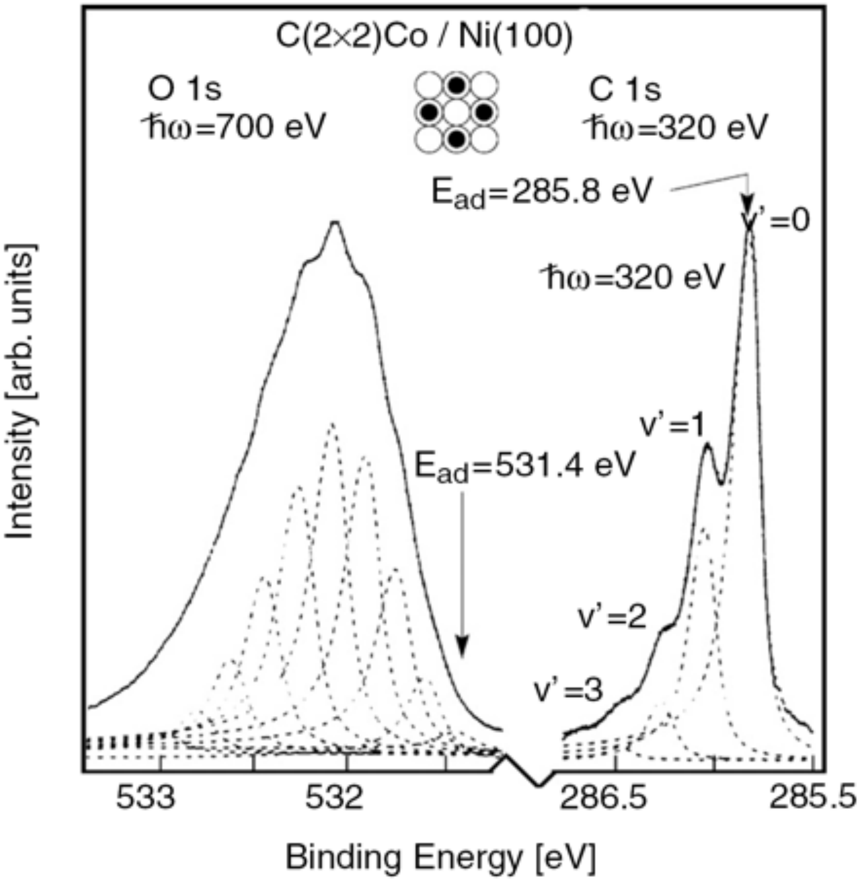


Figure 8. High-resolution XPS spectra of C1s and O1s from a $c(2 \times 2)$ CO/Ni(1 0 0) [38]. The fine structure is due to intramolecular stretch vibrations of the adsorbed CO molecules.

PES: Photo-Emission (or Photo-Electron) Spectroscopy

$$\underset{\text{measured}}{\underset{\uparrow}{\varepsilon_a}} = \underset{\text{fixed}}{\underset{\uparrow}{\omega_{\text{in}}}} - I_i$$

ESCA: Electron Spectroscopy for Chemical Analysis

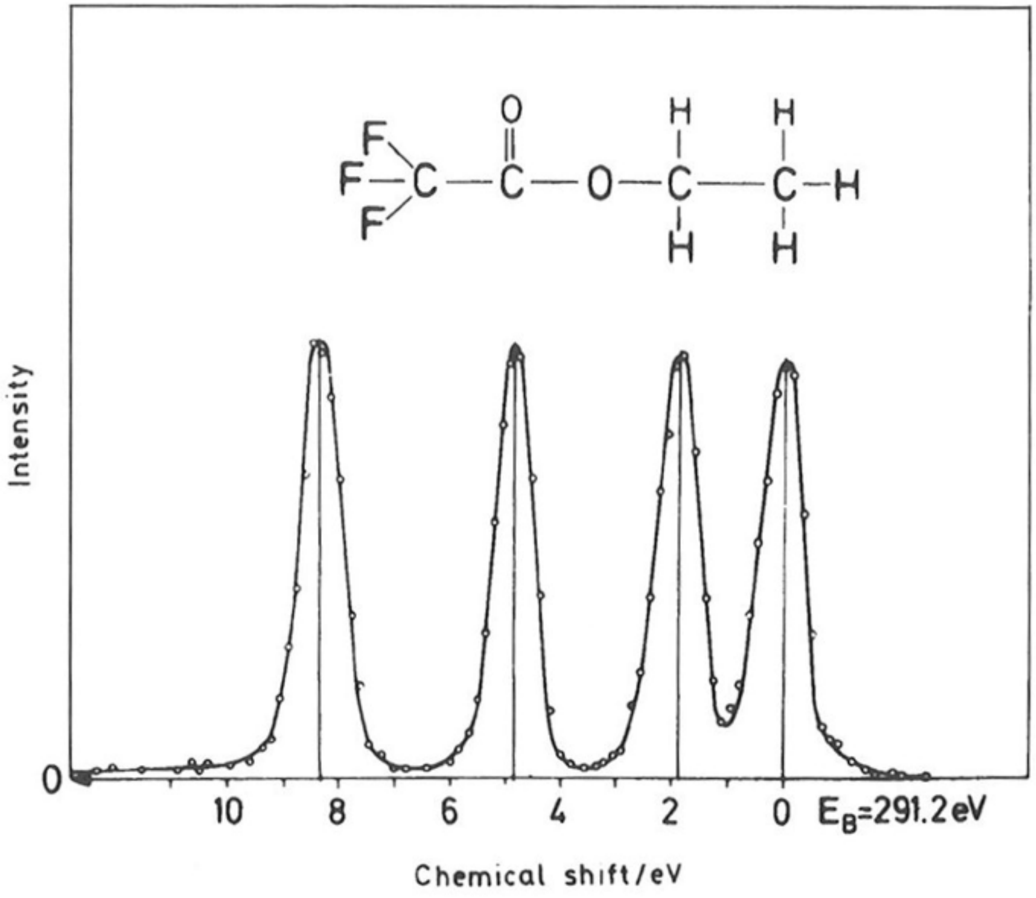


Figure 8.14 The monochromatized Al*K*α carbon 1*s* XPS spectrum of ethyltrifluoroacetate showing the chemical shifts relative to an ionization energy of 291.2 eV. (Reproduced, with permission, from Gelius, U., Basilier, E., Svensson, S., Bergmark, T., and Siegbahn, K., *J. Electron Spectrosc.*, **2**, 405, 1974)

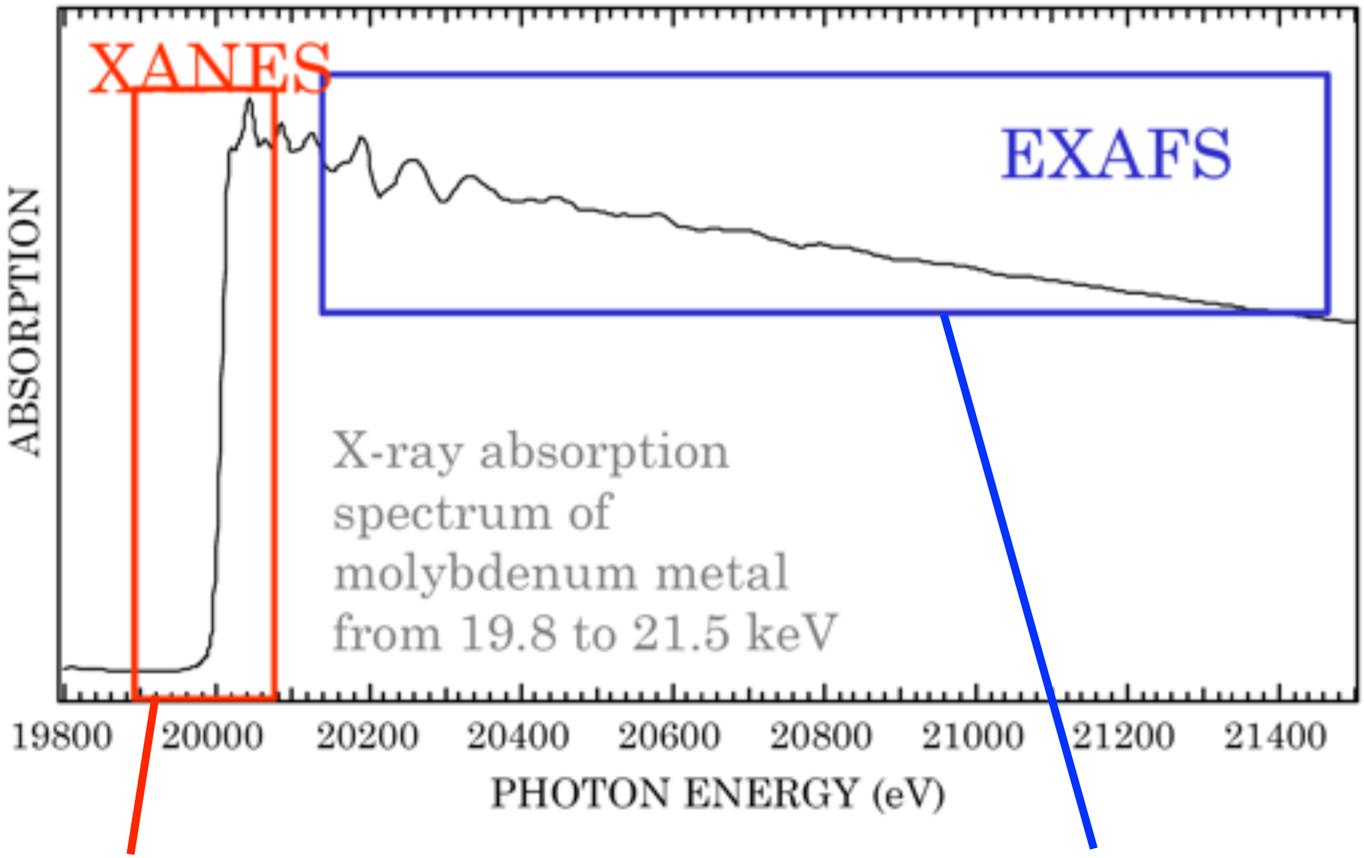
$$\varepsilon_a = \omega_{\text{in}} - I_i$$

fixed

measured

ESCA molecule:
first molecule used for ESCA by Kai Siegbahn (Nobel prize in 1981)

XAS: X-ray Absorption Spectroscopy



X-ray absorption spectrum of molybdenum metal from 19.8 to 21.5 keV

$$\varepsilon_a = \underset{\substack{\big\uparrow \\ \text{varied}}}{\omega_{\text{in}}} - I_i$$

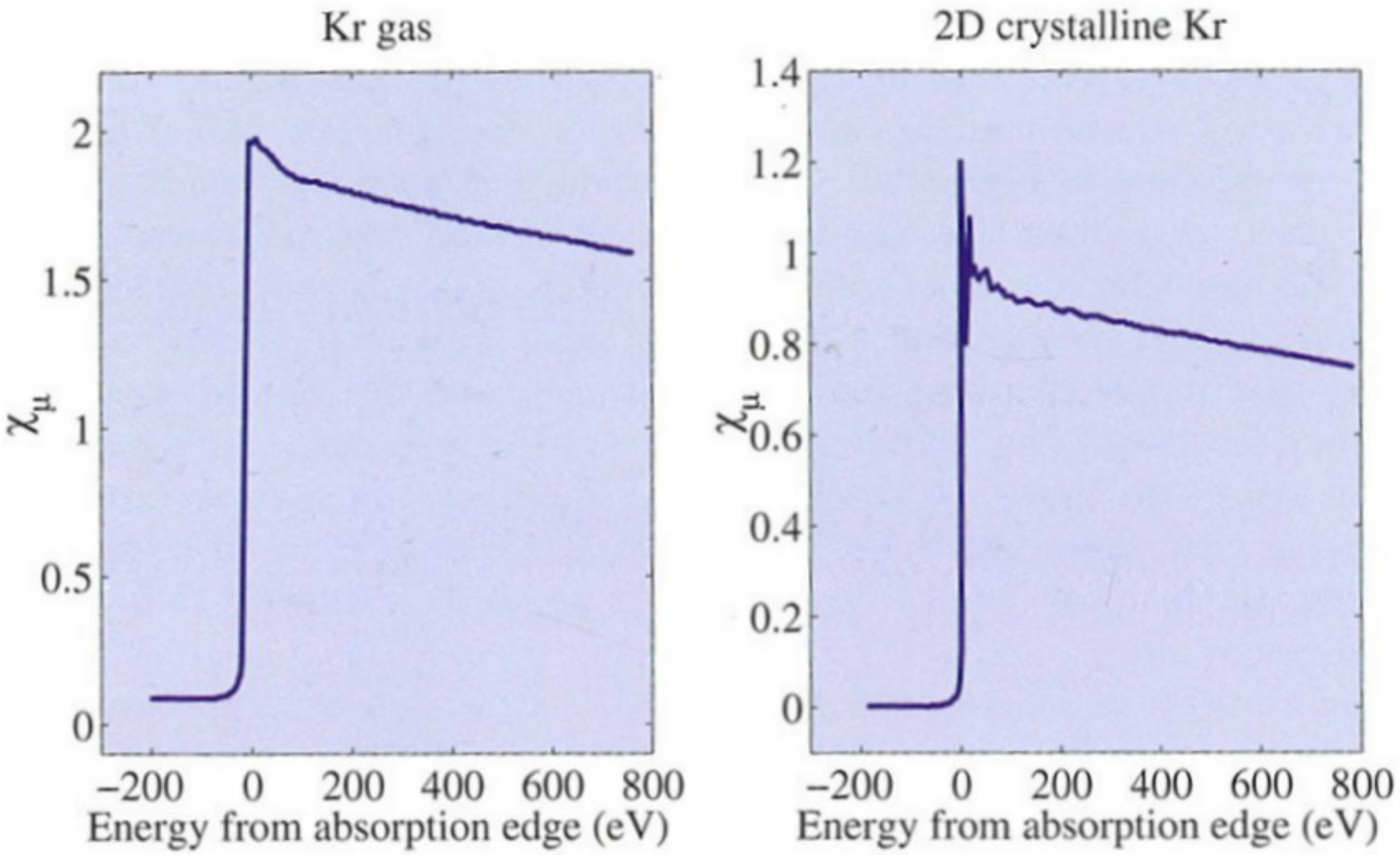
solid target: transmission

gas phase or very dilute target: fluorescence

NE: depends on local coordination environment and oxidation state

E: depends on nearest-neighbor geometry

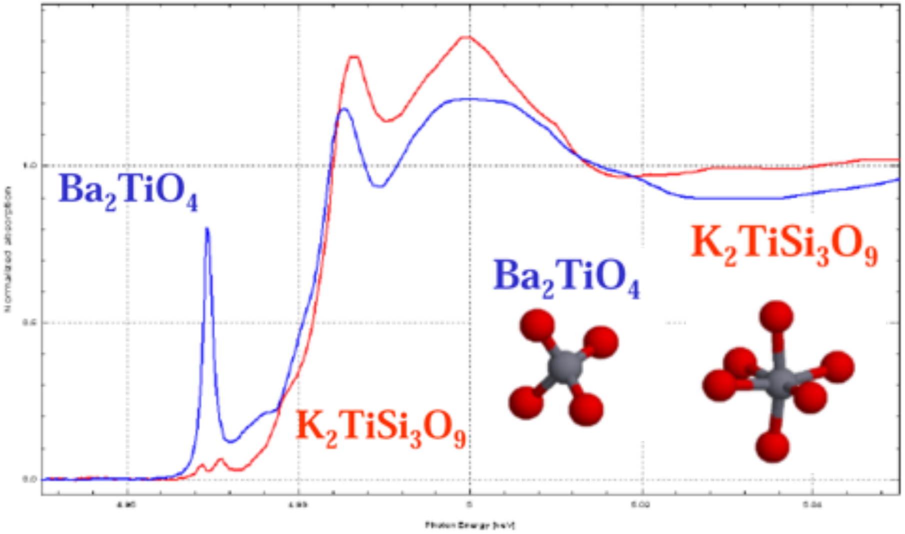
EXAFS: Extended X-ray Absorption Fine Structure



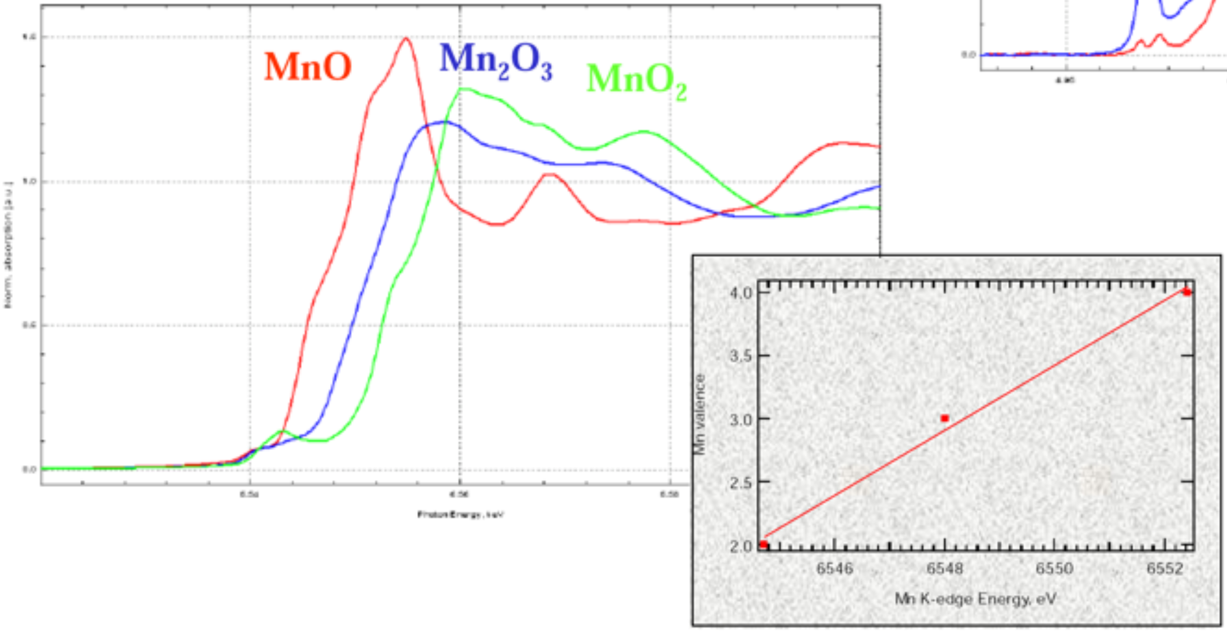
EXAFS reflects nearest-neighbor geometry and
it is highly sensitive to changes in bond lengths.

XANES: X-ray Absorption Near-Edge Structure

Also called **NEXAFS**: Near-Edge X-ray Absorption Fine Structure



different coordination environments



different oxidation states

Summary

- X-rays can probe atomic structure and electronic structure of matter.
- X-rays interact with the electrons only.
- Hamiltonians for EM, molecule, and interaction between them

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

- The mean-field theory for electronic many-body problem
- Transition rate calculated within the time-dependent perturbation theory

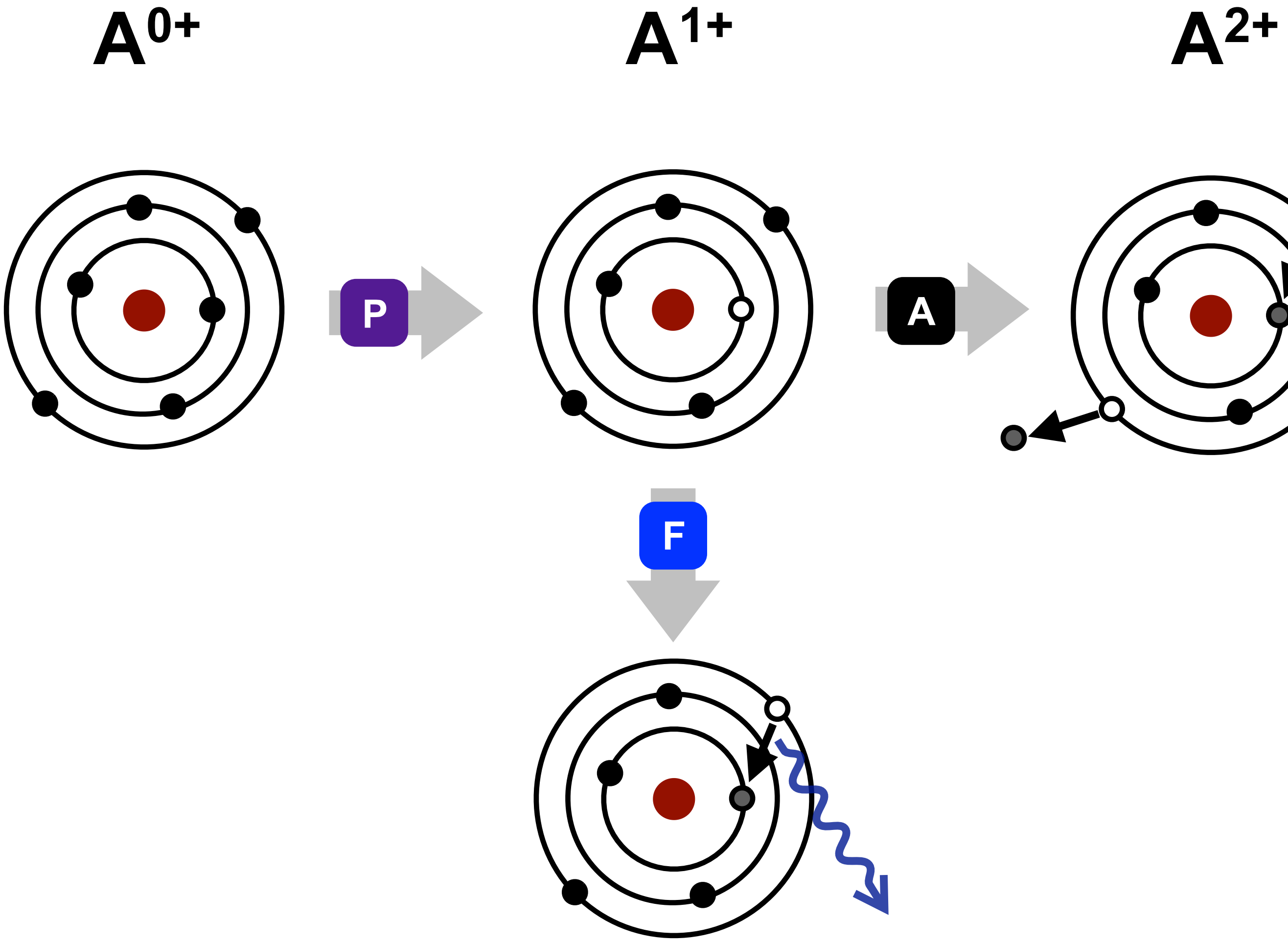
$$\Gamma_{FI} = 2\pi\delta(E_F - E_I)\left|\langle F|\hat{H}_{\mathrm{int}}|I\rangle\right|^2$$

- The theoretical framework applied for calculating a photoabsorption cross section
- X-ray absorption applications: XPS, ESCA, XAS, XANES, EXAFS, …

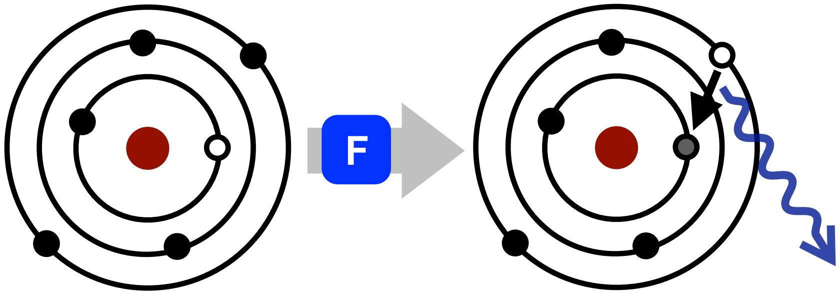
Outline

- First day (August 3, 2017)
  - Introduction
  - Theory of X-ray–matter interaction
  - X-ray absorption
- Second day (August 7, 2017)
  - X-ray fluorescence
  - Auger decay
  - X-ray scattering
  - X-ray atomic physics on computer: XATOM

Decay of inner-shell-excited systems



X-ray fluorescence within mean-field model



Initial state: $|I\rangle = \hat{c}_i |\Phi_0^{N_\mathrm{el}}\rangle |0\rangle$

Final state: $|F\rangle = \hat{c}_{i'} |\Phi_0^{N_\mathrm{el}}\rangle \hat{a}^\dagger_{\boldsymbol{k}_F,\lambda_F} |0\rangle$

Partial X-ray fluorescence rate

$$\Gamma_{FI} = 2\pi\delta\left(E_F - E_I\right) \left| \langle F | \hat{H}_\mathrm{int} | I \rangle \right|^2$$

$$= \frac{4\pi^2}{V\omega_F} \delta(I_{i'} + \omega_F - I_i) \left| \langle \varphi_i | \mathrm{e}^{-\mathrm{i}\boldsymbol{k}_F\cdot\boldsymbol{x}} \boldsymbol{\epsilon}^*_{\boldsymbol{k}_F,\lambda_F} \cdot \frac{\boldsymbol{\nabla}}{\mathrm{i}} | \varphi_{i'} \rangle \right|^2$$

$$\Gamma_{i,i'} = \sum_{\boldsymbol{k}_F,\lambda_F} \Gamma_{FI} = \sum_{\lambda_F} \frac{V}{(2\pi)^3} \int \mathrm{d}\Omega_F \int_0^\infty \mathrm{d}k_F \, k_F^2 \Gamma_{FI}$$

X-ray fluorescence energy $\omega_F = I_i - I_{i'}$

X-ray fluorescence transition lines

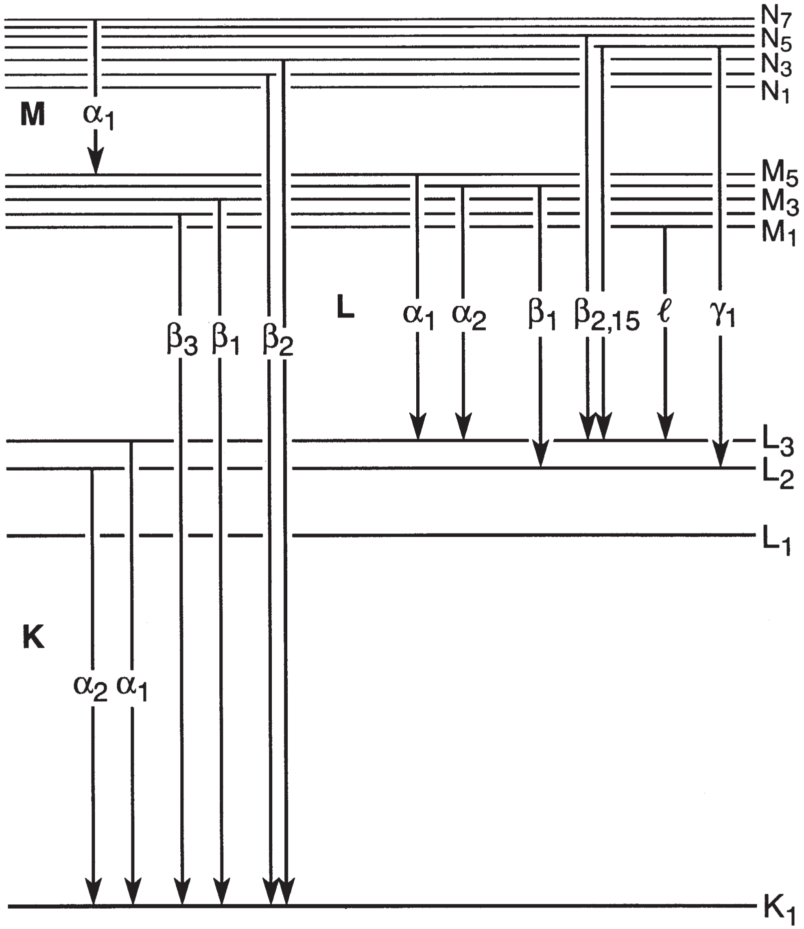


Fig. 1-1. *Transitions that give rise to the emission lines in Table 1-3.*

Characteristic transition energies
➔ fingerprint of elements

Energy (eV)	Element	Line	Relative intensity
54.3	3 Li	$K\alpha_{1,2}$	150
108.5	4 Be	$K\alpha_{1,2}$	150
183.3	5 B	$K\alpha_{1,2}$	151
277	6 C	$K\alpha_{1,2}$	147
348.3	21 Sc	Ll	21
392.4	7 N	$K\alpha_{1,2}$	150
395.3	22 Ti	Ll	46
395.4	21 Sc	$L\alpha_{1,2}$	111
399.6	21 Sc	$L\beta_1$	77
446.5	23 V	Ll	28
452.2	22 Ti	$L\alpha_{1,2}$	111
458.4	22 Ti	$L\beta_1$	79
500.3	24 Cr	Ll	17
511.3	23 V	$L\alpha_{1,2}$	111
519.2	23 V	$L\beta_1$	80
524.9	8 O	$K\alpha_{1,2}$	151
556.3	25 Mn	Ll	15
572.8	24 Cr	$L\alpha_{1,2}$	111
582.8	24 Cr	$L\beta_1$	79
615.2	26 Fe	Ll	10
637.4	25 Mn	$L\alpha_{1,2}$	111
648.8	25 Mn	$L\beta_1$	77
676.8	9 F	$K\alpha_{1,2}$	148
677.8	27 Co	Ll	10
705.0	26 Fe	$L\alpha_{1,2}$	111
718.5	26 Fe	$L\beta_1$	66
742.7	28 Ni	Ll	9
776.2	27 Co	$L\alpha_{1,2}$	111
791.4	27 Co	$L\beta_1$	76
811.1	29 Cu	Ll	8
833	57 La	$M\alpha_1$	100
848.6	10 Ne	$K\alpha_{1,2}$	150

⋮

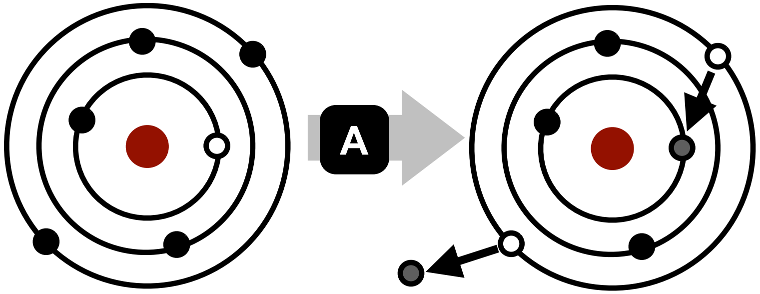
Kα fluorescence: a simple model

- Simple model of an atomic species of atomic number *Z*
  - 1*s* orbital ~ H-like 1*s* orbital of *Z*
  - 2*p* orbital ~ H-like 2*p* orbital of *Z*

- Kα photon energy: $\omega_{K\alpha} \sim Z^2$

- Kα fluorescence rate: $\Gamma_{K\alpha} \sim Z^4$

Auger decay within mean-field model



Initial state: $|I\rangle = \hat{c}_i |\Phi_0^{N_\text{el}}\rangle$

Final state: $|F\rangle = \hat{c}_a^\dagger \hat{c}_j \hat{c}_{j'} |\Phi_0^{N_\text{el}}\rangle,$

$$j, j' \neq i$$

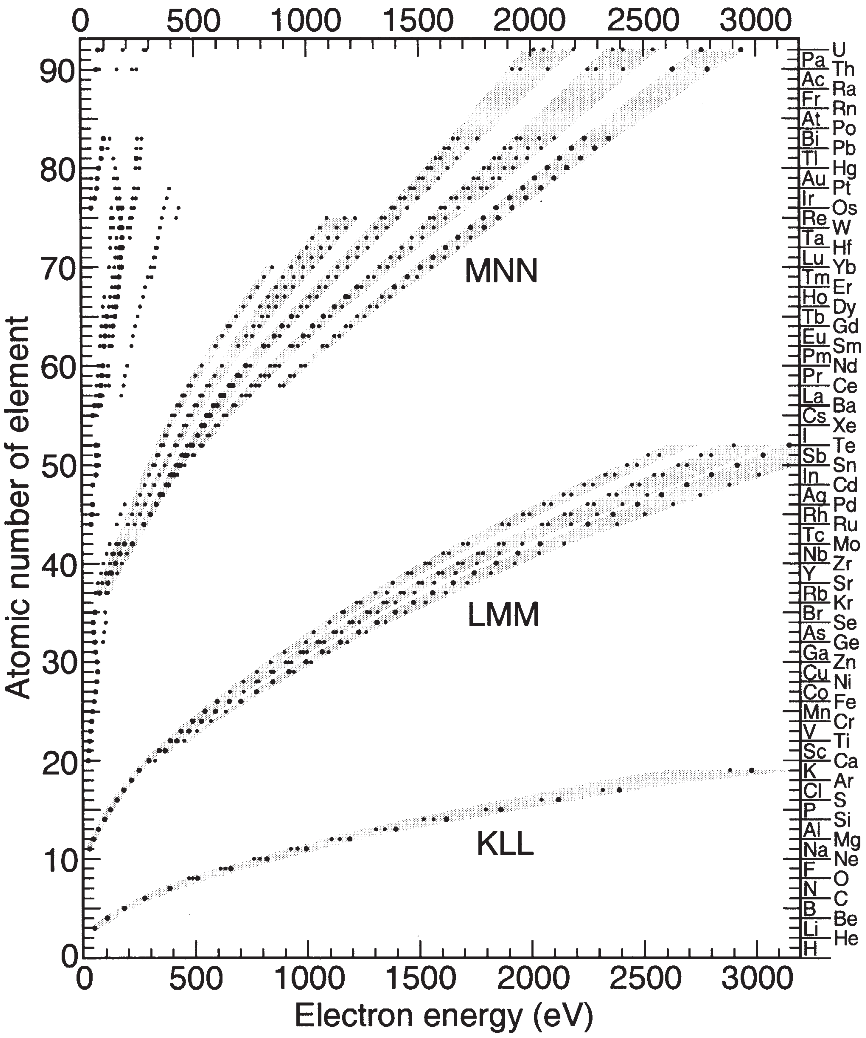
Perturbation theory $\hat{H}_0 = \hat{F},\ \hat{H}_\text{int} = \frac{1}{2} \sum_{pqrs} v_{pqrs} \hat{c}_p^\dagger \hat{c}_q^\dagger \hat{c}_s \hat{c}_r - \sum_{pq} \sum_i \{v_{piqi} - v_{piiq}\} \hat{c}_p^\dagger \hat{c}_q$

Coulomb matrix element $v_{pqrs} = \int d^3x \int d^3x' \varphi_p^\dagger(\boldsymbol{x}) \varphi_q^\dagger(\boldsymbol{x}') \frac{1}{|\boldsymbol{x} - \boldsymbol{x}'|} \varphi_r(\boldsymbol{x}) \varphi_s(\boldsymbol{x}')$

Partial Auger rate $\Gamma_{i,jj'} = 2\pi \sum_a |v_{aijj'} - v_{aij'j}|^2 \delta(\varepsilon_a + I_j + I_{j'} - I_i)$

Auger electron energy $\varepsilon_a = I_i - I_j - I_{j'}$

Auger electron energies



Auger electron energies for the elements. Points indicate the electron energies of the principal Auger peaks for each element. The larger points represent the most intense peaks. (Reproduced by permission of Physical Electronics, Inc.)

KLL Auger decay: a simple model

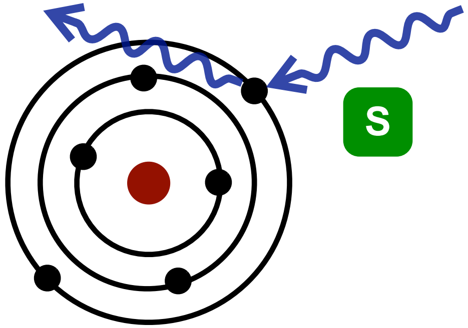
- Simple model of an atomic species of atomic number *Z*
  - 1*s* orbital ~ H-like 1*s* orbital of *Z*
  - 2*p* orbital ~ H-like 2*p* orbital of *Z*
  - Auger electron wave function ~ plane wave

- Focus on the channel with two 2*p* holes in the final state

- *KLL* Auger electron energy: $\varepsilon_{KLL} \sim Z^2$

- *KLL* Auger decay rate: $\Gamma_{KLL} \sim Z^0$

Elastic X-ray scattering



Initial state: $|I\rangle = |\Psi_0^{N_{\mathrm{el}}}\rangle |N_{\mathrm{EM}}\rangle$

Final state: $|F\rangle = |\Psi_0^{N_{\mathrm{el}}}\rangle \hat{a}^\dagger_{\boldsymbol{k}_F,\lambda_F} |N_{\mathrm{EM}} - 1\rangle$

$$\Gamma_{FI} = \frac{(2\pi)^3}{V} \frac{N_{\mathrm{EM}}}{V} \frac{1}{\omega_F \omega_{\mathrm{in}}} \left| \boldsymbol{\epsilon}^*_{\boldsymbol{k}_F,\lambda_F} \cdot \boldsymbol{\epsilon}_{\boldsymbol{k}_{\mathrm{in}},\lambda_{\mathrm{in}}} \right|^2 \left| f^0(\boldsymbol{k}_{\mathrm{in}} - \boldsymbol{k}_F) \right|^2 \delta(\omega_F - \omega_{\mathrm{in}})$$

Scattering (or form) factor $f^0(\boldsymbol{Q}) = \int \mathrm{d}^3x\, \rho^{(\mathrm{el})}(\boldsymbol{x}) \mathrm{e}^{\mathrm{i}\boldsymbol{Q}\cdot\boldsymbol{x}}$

Scattering vector
(or momentum transfer) $\boldsymbol{Q} = \boldsymbol{k}_{\mathrm{in}} - \boldsymbol{k}_F$

Electron density $\rho^{(\mathrm{el})}(\boldsymbol{x}) = \langle \Psi_0^{N_{\mathrm{el}}} | \hat{\psi}^\dagger(\boldsymbol{x}) \hat{\psi}(\boldsymbol{x}) | \Psi_0^{N_{\mathrm{el}}} \rangle$

Elastic x-ray scattering cross section

Differential cross section

$$d\sigma = \sum_{\boldsymbol{k}_F,\lambda_F} \frac{\Gamma_{FI}}{J_{\mathrm{EM}}} = \frac{V}{(2\pi)^3}\alpha^3 d\Omega \sum_{\lambda_F} \int_0^\infty d\omega_F\, \omega_F^2 \frac{\Gamma_{FI}}{J_{\mathrm{EM}}}$$

$$\frac{d\sigma(\boldsymbol{Q})}{d\Omega} = \alpha^4 \left|f^0(\boldsymbol{Q})\right|^2 \sum_{\lambda_F} \left|\boldsymbol{\epsilon}^*_{\boldsymbol{k}_F,\lambda_F} \cdot \boldsymbol{\epsilon}_{\boldsymbol{k}_{\mathrm{in}},\lambda_{\mathrm{in}}}\right|^2 = \left(\frac{d\sigma}{d\Omega}\right)_T \left|f^0(\boldsymbol{Q})\right|^2$$

Total form factor decomposed in terms of atomic contributions

$$f^0(\boldsymbol{Q}) \approx \int d^3x \sum_n \rho_n^{(\mathrm{el})}(\boldsymbol{x} - \boldsymbol{R}_n) e^{i\boldsymbol{Q}\cdot\boldsymbol{x}}$$

$$= \sum_n \left\{ \int d^3x' \rho_n^{(\mathrm{el})}(\boldsymbol{x}') e^{i\boldsymbol{Q}\cdot\boldsymbol{x}'} \right\} e^{i\boldsymbol{Q}\cdot\boldsymbol{R}_n}$$

$$\equiv \sum_n f_n^0(\boldsymbol{Q}) e^{i\boldsymbol{Q}\cdot\boldsymbol{R}_n}$$

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Atomic form factor

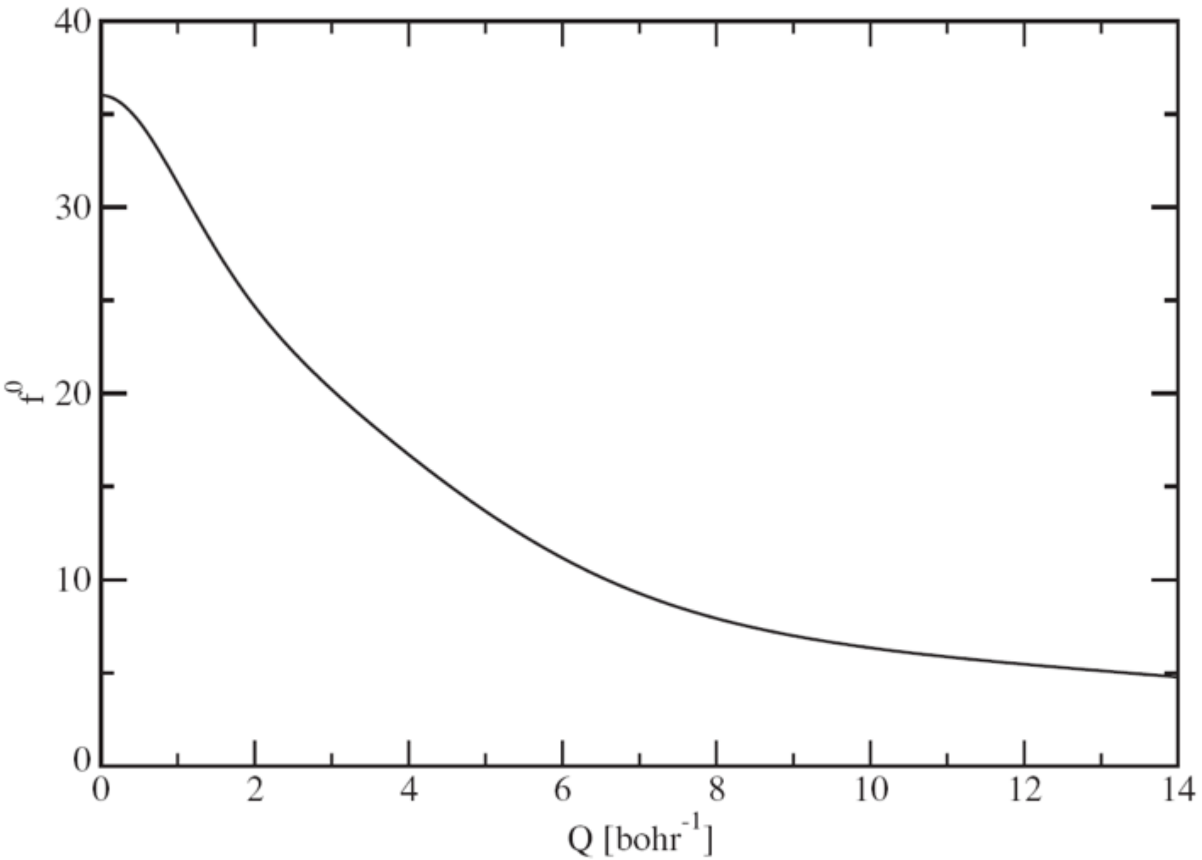
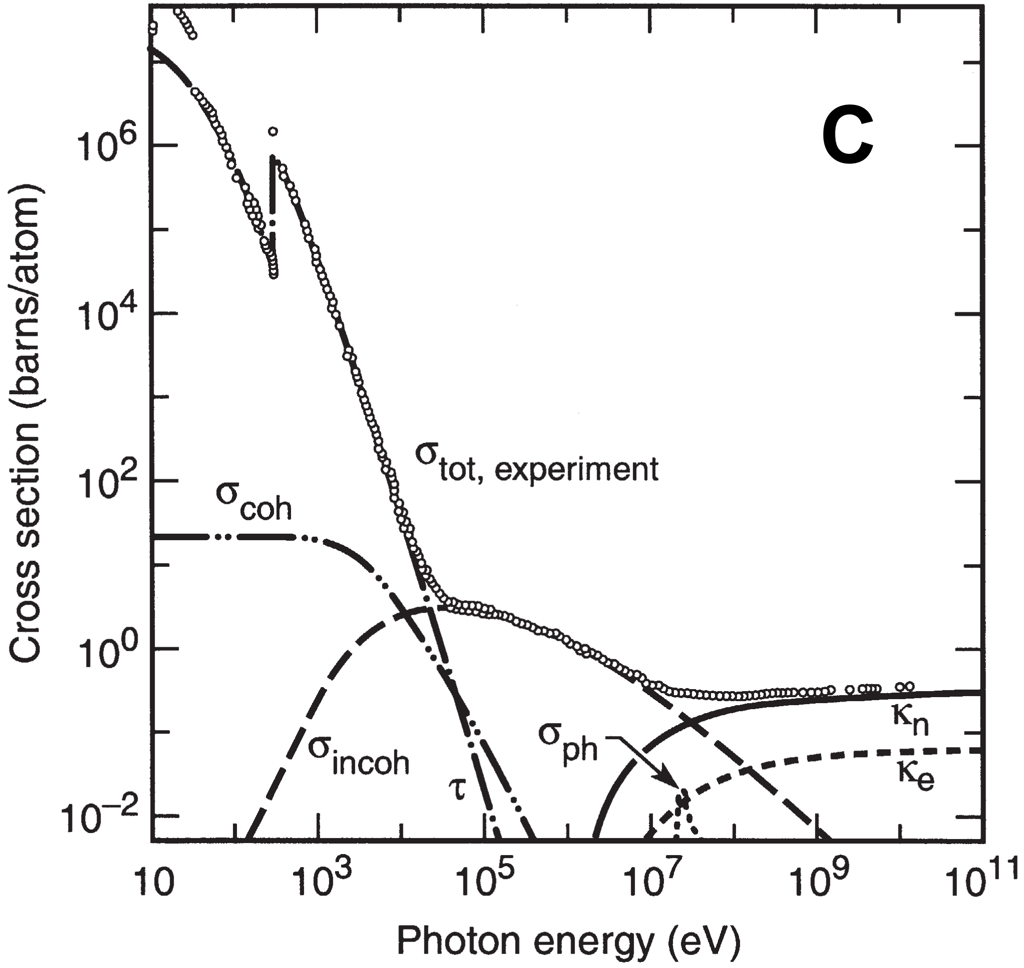


Figure 2. Calculated elastic scattering factor f^0 of atomic krypton, as a function of the momentum transfer $Q \equiv |\mathbf{Q}|$.

Absorption vs. scattering



C@12 keV

$$\frac{\sigma_{\text{sc}}}{\sigma_{\text{abs}}} \sim \frac{1}{18}$$

Dispersive correction to elastic X-ray scattering

- Resonant elastic x-ray scattering: When the photon energy approaches to the ionization potential, the second order of p•A becomes important.

Elastic X-ray scattering tensor: second-order correction with p•A

$$
\begin{aligned}
f_{i,j}(\boldsymbol{Q},\boldsymbol{k}_{\text{in}}) = {} & f^0(\boldsymbol{Q})\delta_{i,j} \\
& + \sum_r \langle \Psi_0^{N_{\text{el}}} | \int \mathrm{d}^3x \hat{\psi}^\dagger(\boldsymbol{x}) \mathrm{e}^{-\mathrm{i}\boldsymbol{k}_F\cdot\boldsymbol{x}} \frac{(\boldsymbol{\nabla})_i}{\mathrm{i}} \hat{\psi}(\boldsymbol{x}) | \Psi_r^{N_{\text{el}}} \rangle \\
& \times \frac{1}{E_0^{N_{\text{el}}} + \omega_{\text{in}} - E_r^{N_{\text{el}}} + \mathrm{i}\epsilon} \\
& \times \langle \Psi_r^{N_{\text{el}}} | \int \mathrm{d}^3x \hat{\psi}^\dagger(\boldsymbol{x}) \mathrm{e}^{\mathrm{i}\boldsymbol{k}_{\text{in}}\cdot\boldsymbol{x}} \frac{(\boldsymbol{\nabla})_j}{\mathrm{i}} \hat{\psi}(\boldsymbol{x}) | \Psi_0^{N_{\text{el}}} \rangle .
\end{aligned}
$$

Dispersive correction to elastic X-ray scattering

Elastic X-ray scattering in the forward direction

Scalar scattering factor $f(\omega_{\text{in}}, \boldsymbol{\epsilon}_{\text{in}}) = f^0(\mathbf{0}) + f'(\omega_{\text{in}}, \boldsymbol{\epsilon}_{\text{in}}) + \mathrm{i} f''(\omega_{\text{in}}, \boldsymbol{\epsilon}_{\text{in}})$

Total number of electrons

$$f^0(\mathbf{0}) = N_{\text{el}}$$

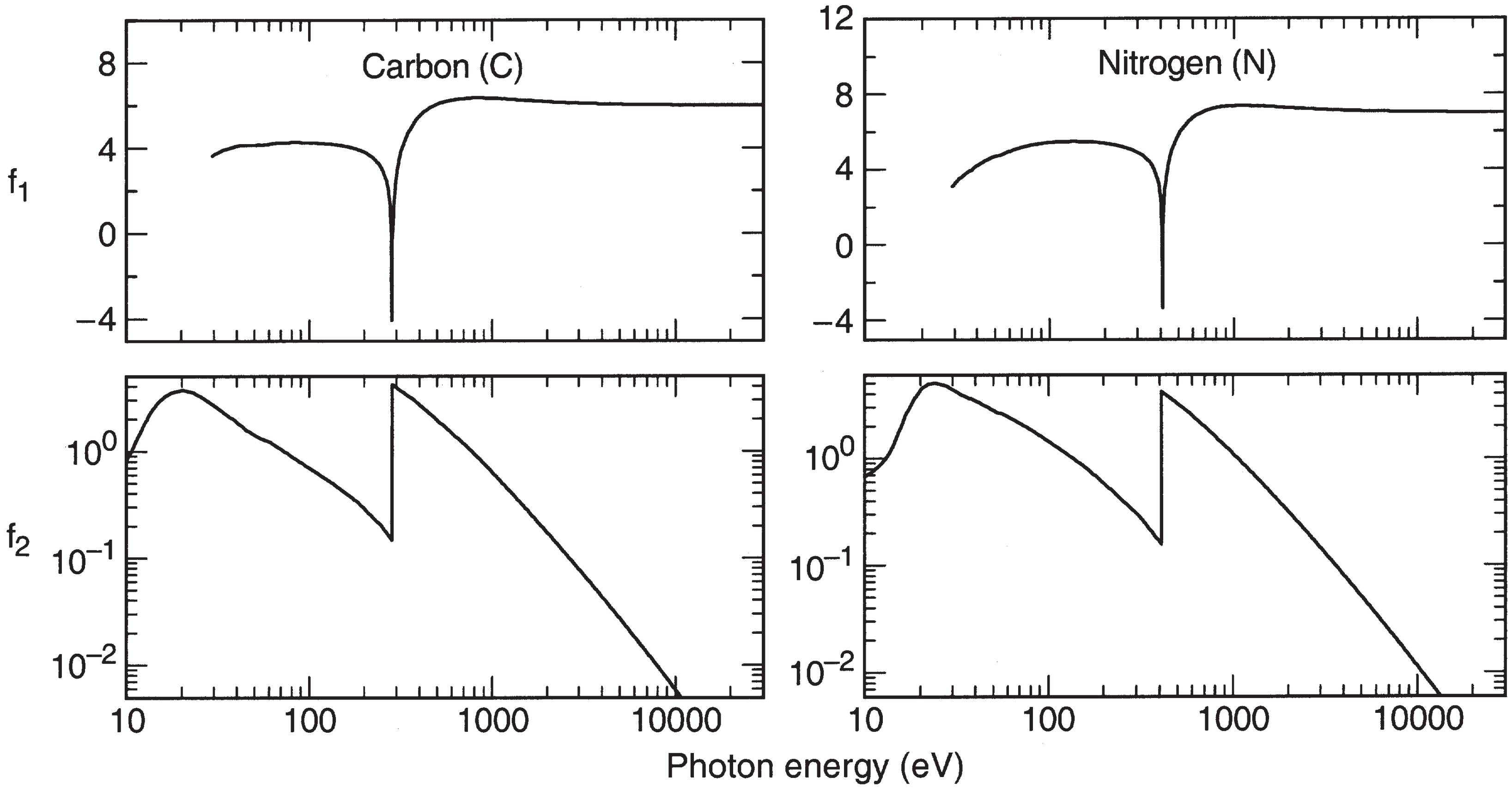
Relationship between imaginary part of scattering factor and absorption cross section

$$f''(\omega_{\text{in}}, \boldsymbol{\epsilon}_{\text{in}}) = -\frac{\omega_{\text{in}}}{4\pi\alpha} \sum_F \sigma_F(\omega_{\text{in}}, \boldsymbol{\epsilon}_{\text{in}})$$

Kramers-Kronig relation

$$f'(\omega_{\text{in}}, \boldsymbol{\epsilon}_{\text{in}}) = \frac{1}{\pi} \mathrm{Pr} \int_{-\infty}^{\infty} \mathrm{d}\omega'_{\text{in}} \frac{f''(\omega'_{\text{in}}, \boldsymbol{\epsilon}_{\text{in}})}{\omega'_{\text{in}} - \omega_{\text{in}}}$$

Dispersive correction (anomalous scattering)



$$f_1 \equiv f^0 + f' \qquad f_2 \equiv -f''$$

X-ray scattering

elastic vs. inelastic **without *M* vs. with *M***

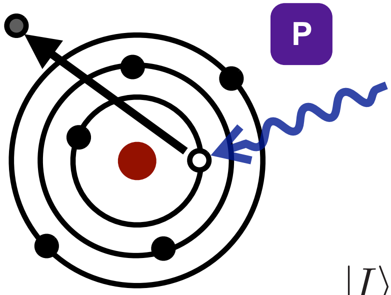
$|\Psi_I^{\mathrm{el}}\rangle = |\Psi_F^{\mathrm{el}}\rangle$ $|\Psi_I^{\mathrm{el}}\rangle \neq |\Psi_F^{\mathrm{el}}\rangle$ **(A^2)** **(p•A)**

- Elastic X-ray scattering
  - Non-resonant elastic X-ray scattering via A^2
  - Resonant elastic X-ray scattering via p•A (Dispersion correction)
- Inelastic X-ray scattering
  - Non-resonant inelastic X-ray scattering via A^2 (Compton scattering)
  - Resonant inelastic X-ray scattering via p•A (RIXS or resonant X-ray Raman)

Summary

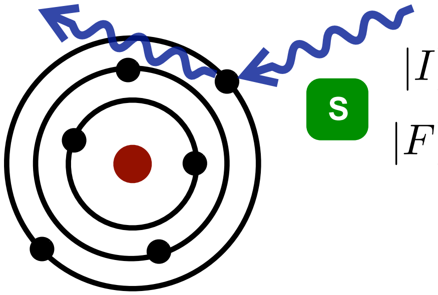
- Photoabsorption

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



- Elastic X-ray scattering

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

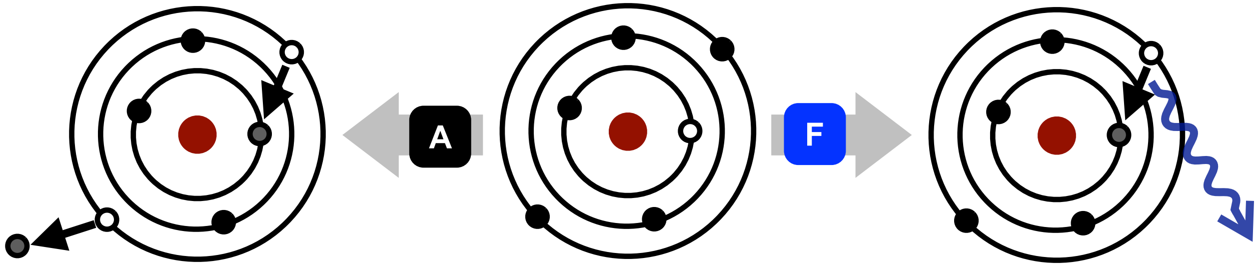


- Auger decay

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

- X-ray fluorescence

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



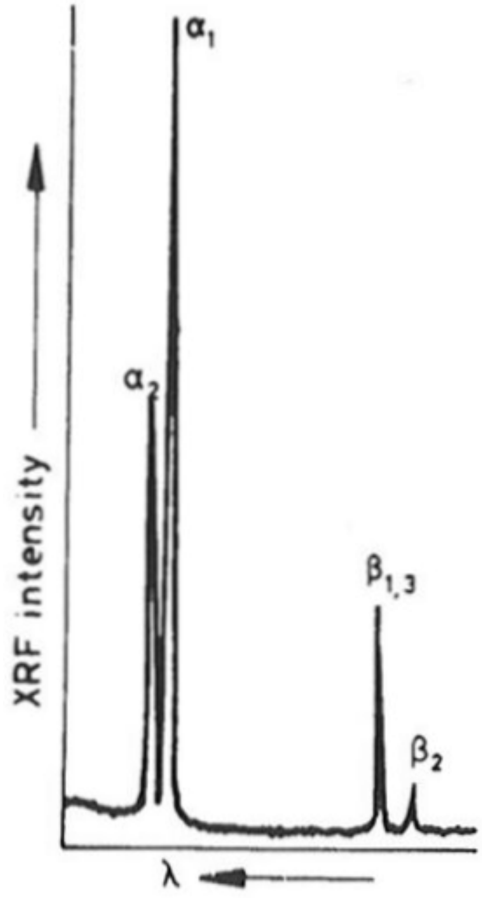
- TD perturbation theory

$$\Gamma_{FI} = 2\pi\delta\left(E_F - E_I\right)\left|\langle F|\hat{H}_\mathrm{int}|I\rangle\right|^2$$

  - Calculates photoabsorption cross section, fluorescence rate, Auger rate, scattering form factor and its dispersion correction (with second order)

Applications

XRF: X-Ray Fluorescence



Transition lines

$K\alpha_1 : K_1 - L_3,\ 1s - 2p_{3/2}$

$K\alpha_2 : K_1 - L_2,\ 1s - 2p_{1/2}$

$K\beta_1 : K_1 - M_2,\ 1s - 3p_{1/2}$

$K\beta_2 : K_1 - N_{2,3},\ 1s - 4p_{1/2,3/2}$

$K\beta_3 : K_1 - M_3,\ 1s - 3p_{3/2}$

position: transition energy

intensity: transition rate

Figure 8.30 *K* emission spectrum of tin. The α_1 and β_2 lines are at 0.491 and 0.426 Å, respectively. (Reproduced, with permission, from Jenkins, R., *An Introduction to X-ray Spectrometry*, p. 22, Heyden, London, 1976)

Hidden painting by Van Gogh made visible

AES: Auger Electron Spectrum

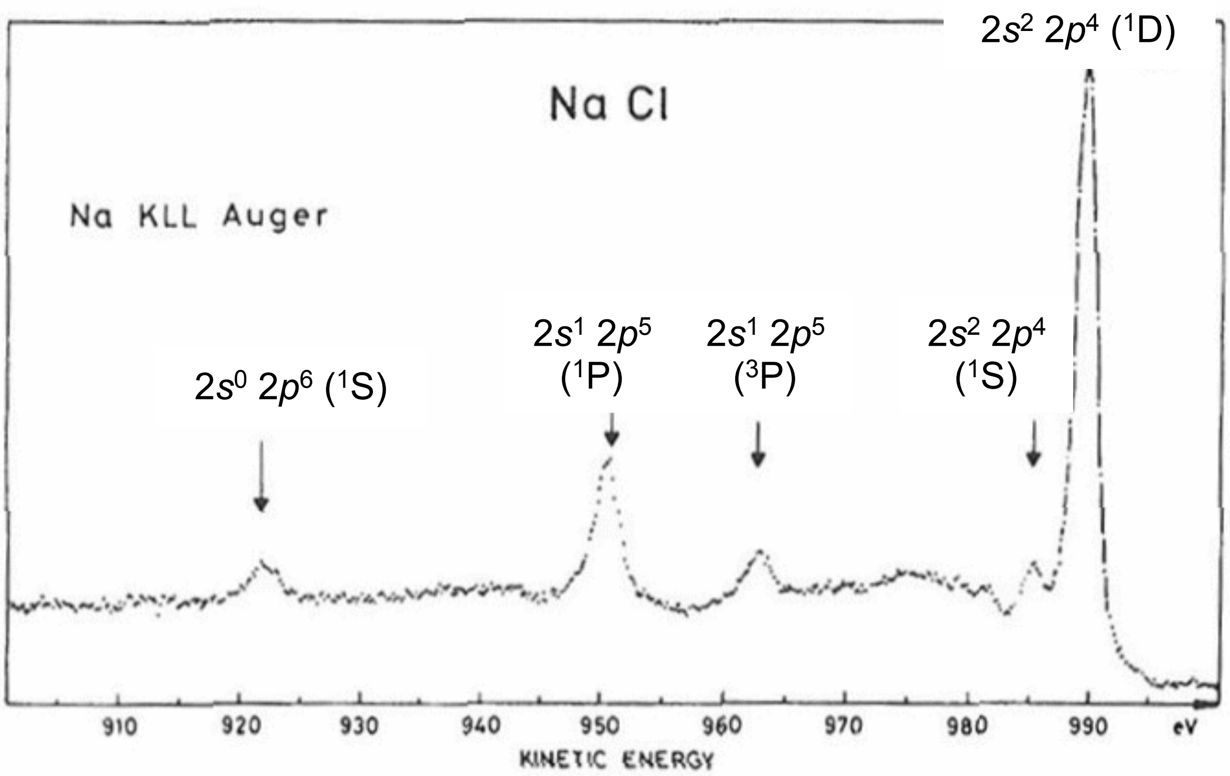


Figure 8.26 The $KL_{\mathrm{II,III}}L_{\mathrm{II,III}}$ ($^1D_2$ and $^1S_0$) Auger spectrum of sodium in solid NaCl. (Reproduced, with permission, from Siegbahn, K. (June 1976), *Publication No. UUIP-940*, p. 81, Uppsala University Institute of Physics)

$$\varepsilon_a = I_i - I_j - I_{j'}$$

Auger channels

$1s - 2s\,2s : 2s^0 2p^6$ ^{1}S

$1s - 2s\,2p : 2s^1 2p^5$ ^{1}P

^{3}P

$1s - 2p\,2p : 2s^2 2p^4$ ^{1}S

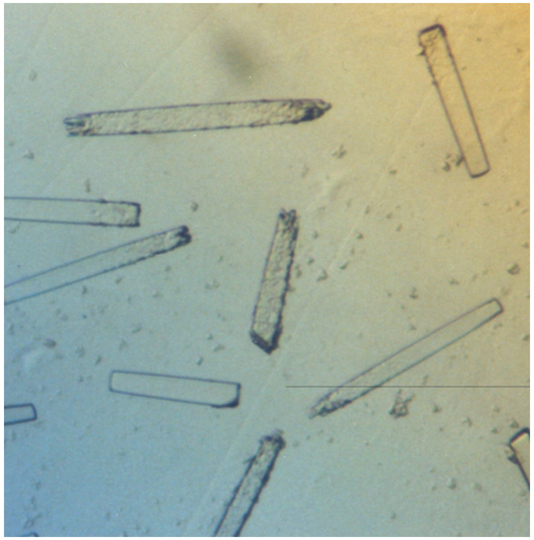
$\cancel{^3\mathrm{P}}$

^{1}D

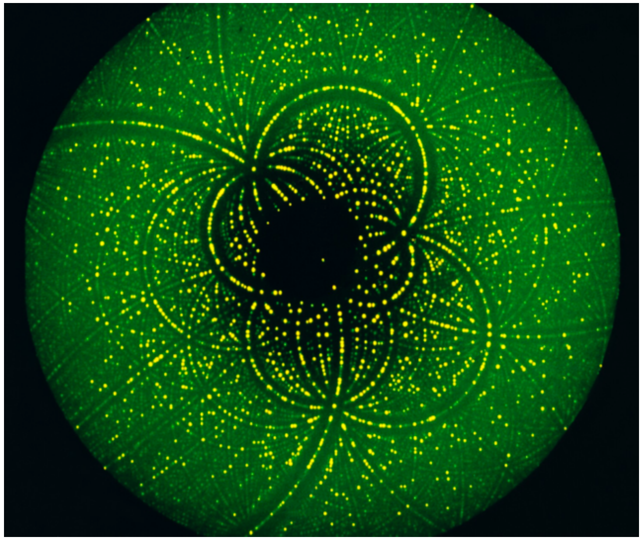
position: Auger energy

intensity: Auger rate

X-ray crystallography

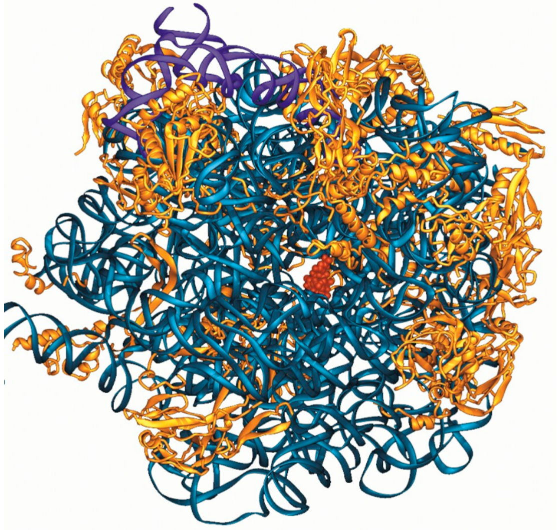


Protein crystal



X-ray diffraction pattern

$$I \sim \left| f^0(\boldsymbol{Q}) \right|^2$$

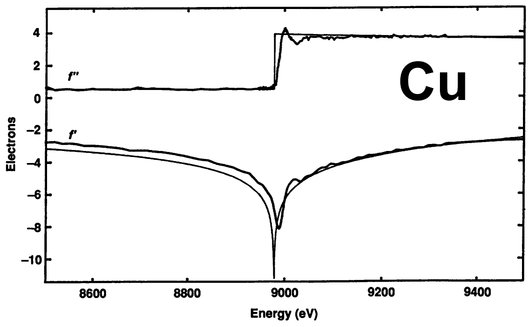


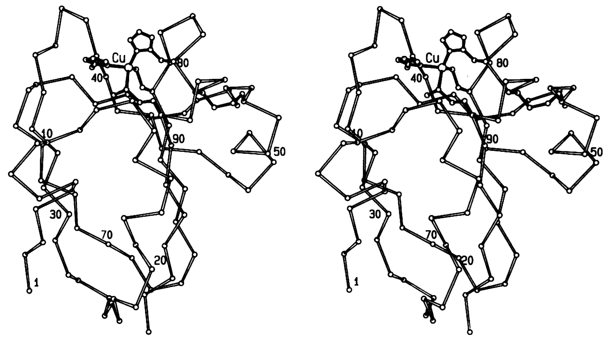
Molecular structure of a protein

$$f^0(\boldsymbol{Q}) \underset{\mathrm{FT}}{\overset{\mathrm{IFT}}{\rightleftarrows}} \rho^{(\mathrm{el})}(\boldsymbol{x})$$

Phase problem and MAD

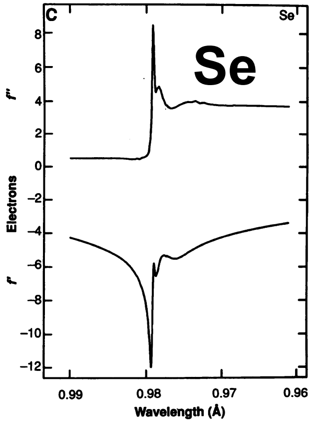
- Phase problem: only $|f(Q)|$ measured, hindering IFT to obtain $\rho^{(el)}$
- MAD (multiwavelength anomalous diffraction): a well-established phasing method with synchrotron radiation since late 80’s.

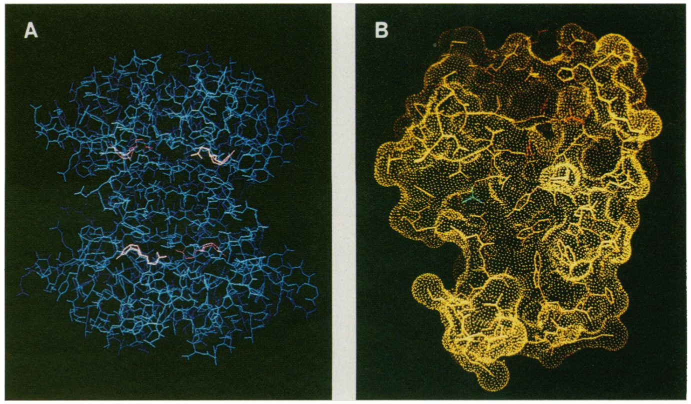




Cucumber basic blue protein

Guss *et al.*, *Science* **241**, 806 (1988).





A) Streptavidin

Hendrickson *et al.*, *PNAS* **86**, 2190 (1989).

B) Ribonuclease H

Yang *et al.*, *Science* **249**, 1398 (1990).

Picture taken from Hendrickson, *Science* **254**, 51 (1991).

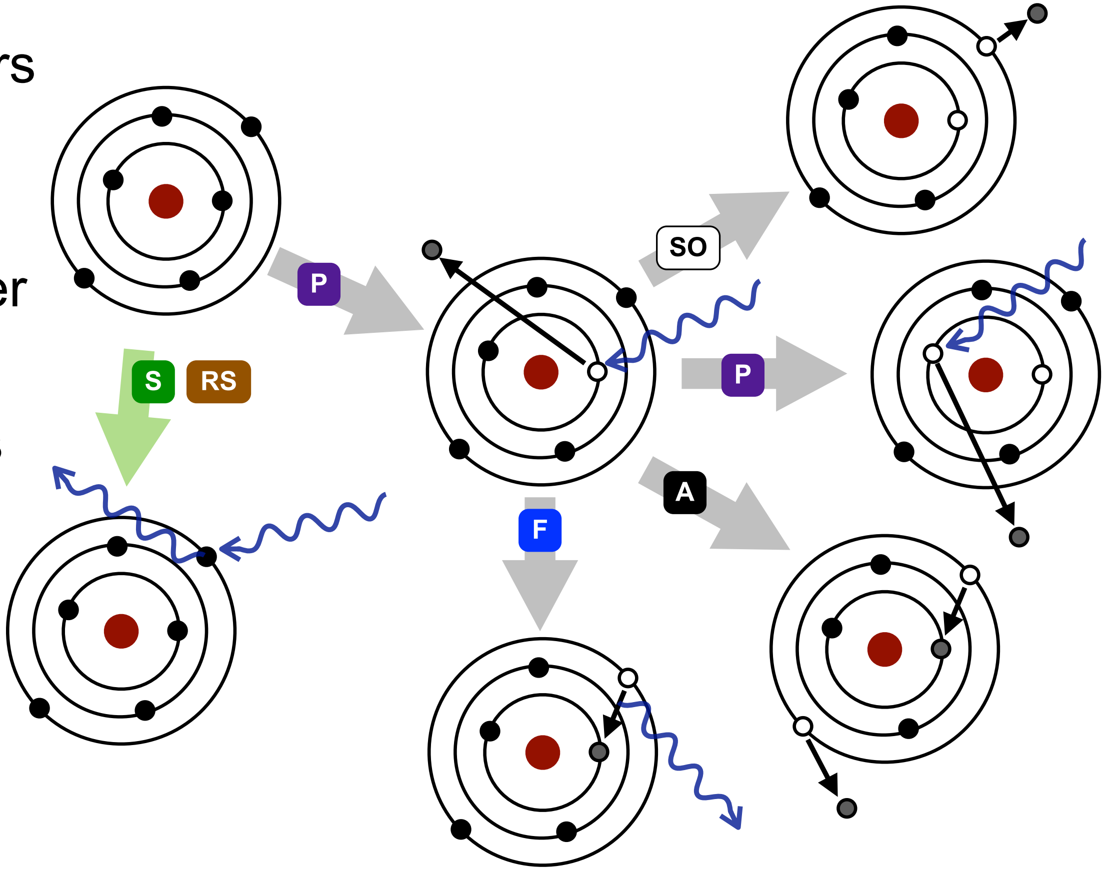
Computer simulations with XATOM

XATOM: all about x-ray atomic physics

- Computer program suite to describe dynamical behaviors of atoms interacting with XFEL pulses
- Uses the Hartree-Fock-Slater model
- Calculates all cross sections and rates of x-ray-induced processes for any given element

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

Jurek, Son, Ziaja & Santra,
J. Appl. Cryst. **49**, 1048–1056 (2016).

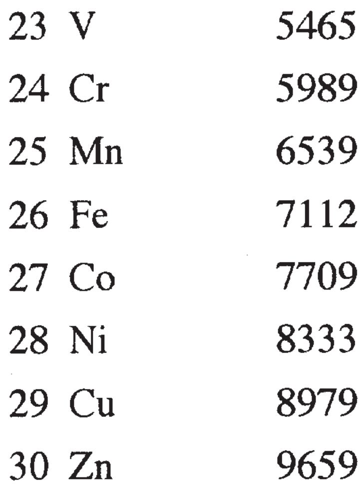


Calculations online

- Orbital binding energy and orbital shape
- Photoionization cross section
- Fluorescence spectrum
- Auger spectrum
- Atomic form factor
- Dispersion correction of atomic form factor

Q & A

- Why does the cross section decrease as the photon energy increases?
- Why does x-ray interact with core electrons more than valence electrons?
- What is the double-core-hole (DCH) state?
- What x-ray parameters do we need to create DCH?
- Why does MAD need metals (heavy atoms) in proteins?



		IE(1*s*)
23	V	5465
24	Cr	5989
25	Mn	6539
26	Fe	7112
27	Co	7709
28	Ni	8333
29	Cu	8979
30	Zn	9659

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Backup slides

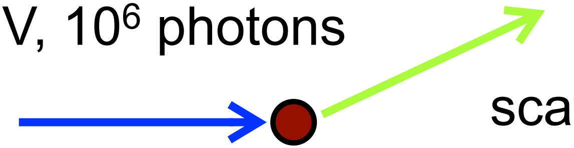
Cross section in mega-barn?

- What is the cross section?
  - An effective area to measure the probability of interaction between particles
- How small is Mb (megabarn)?
  - 1 Mb ~ 10^{-22} m^2
  - 1 barn ~ 10^{-28} m^2 ~ cross-sectional area of a Uranium nucleus
  - probability = $\sigma \times F$
  - C at 12 keV: σ_P ~ 20 barn
    typical fluence: F ~ 10^4 ph/μm^2
    ➔ absorption prob. ~ 2×10^{-11}
    ➔ scattering prob. ~ 1×10^{-12}

"He couldn't hit the broad side of a barn."

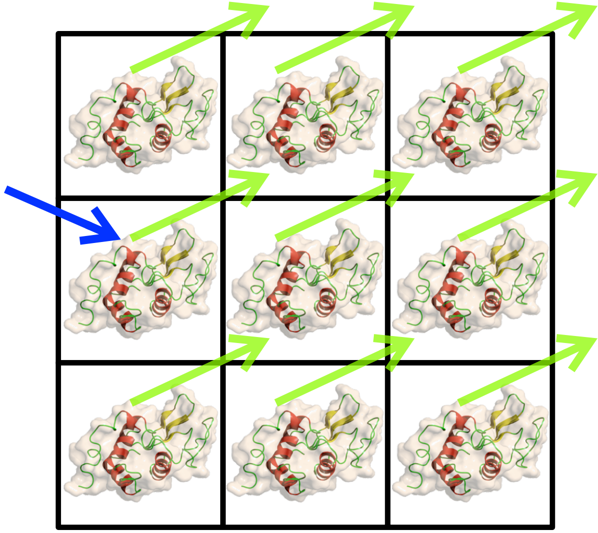
Why X-ray free-electron laser

- Carbon at synchrotron radiation: 12 keV, 10^6 photons on 10μm × 10μm

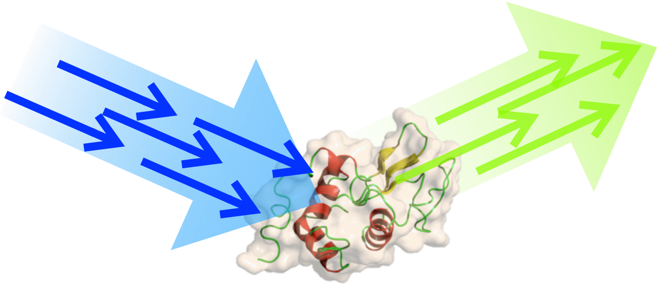


scattering probability ~ 10^{-12}

- Signal amplification



~10^8 molecules in a μm-sized crystal



high x-ray fluence from XFEL (×10^8~10^{10} more than synchrotron radiation)

Minimal coupling Hamiltonian

Minimal coupling: reproducing Newton's eq. for a particle (q_i, m_i, $\boldsymbol{x}_i$) in an EM field

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

The vector potential ***A*** and the scalar potential Φ are related to ***E*** and ***B***

$$\boldsymbol{E} = -\boldsymbol{\nabla}\Phi - \alpha \frac{\partial \boldsymbol{A}}{\partial t},$$
$$\boldsymbol{B} = \boldsymbol{\nabla} \times \boldsymbol{A}.$$

By adopting the *Coulomb gauge*: $\boldsymbol{\nabla} \cdot \boldsymbol{A} = 0$ and transverse magnetic field: $\boldsymbol{\nabla} \cdot \boldsymbol{B} = 0$

$$\begin{aligned} \boldsymbol{E} &= \boldsymbol{E}^{\parallel} + \boldsymbol{E}^{\perp}, \\ \boldsymbol{E}^{\parallel} &= -\boldsymbol{\nabla}\Phi \qquad (\boldsymbol{\nabla} \times \boldsymbol{E}^{\parallel} = \boldsymbol{0}), \\ \boldsymbol{E}^{\perp} &= -\alpha \frac{\partial \boldsymbol{A}}{\partial t} \qquad (\boldsymbol{\nabla} \cdot \boldsymbol{E}^{\perp} = 0). \end{aligned}$$

$$\begin{aligned} \boldsymbol{\nabla} \cdot \boldsymbol{E} &= \boldsymbol{\nabla} \cdot \boldsymbol{E}^{\parallel} \\ &= -\nabla^2 \Phi \\ &= 4\pi \sum_j q_j \delta^{(3)}(\boldsymbol{x} - \boldsymbol{x}_j) \end{aligned}$$

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

⬇

Coulomb potential

Minimal coupling gives the interaction Hamiltonian, p·A and A^2 terms.

Second quantization in a nutshell

- Quantizing a single particle ➔ wavefunction, *first quantization*
- Quantizing a wavefunction ➔ Fock states, *second quantization*

$$|\{n_\alpha\}\rangle \equiv |n_1, n_2, \cdots, n_\alpha, \cdots\rangle$$

- Electrons are interpreted as excitations of quantum field
- Field operator is a two-component spinor $\hat{\psi}(\boldsymbol{x}) = \begin{pmatrix} \hat{\psi}_{+1/2}(\boldsymbol{x}) \\ \hat{\psi}_{-1/2}(\boldsymbol{x}) \end{pmatrix}$
- Creation and annihilation operators: an electron at position ***x*** with spin *σ*

$$\hat{\psi}^\dagger_\sigma(\boldsymbol{x}) \text{ and } \hat{\psi}_\sigma(\boldsymbol{x})$$

- Fermion: satisfying the anticommutation relations
- *H* does not include *N* of electrons ➔ a property of the quantum state
- Easy for the particle-hole formalism
  combined with orbital picture, e.g., $|\Phi^a_i\rangle = \hat{c}^\dagger_a \hat{c}_i |\Phi^{N_\mathrm{el}}_0\rangle$

Harmonic oscillator

$$\hat{H}_{\mathrm{osc}} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{q}^2, \qquad [\hat{q}, \hat{p}] = i\hbar.$$

Let's define an operator

$$\hat{a} = \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{q} + i\frac{\hat{p}}{2m}\right), \qquad \hat{a}^\dagger = \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{q} - i\frac{\hat{p}}{2m}\right),$$

Then, we have $[\hat{a}, \hat{a}^\dagger] = 1$

$$\hat{H}_{\mathrm{osc}} = \hbar\omega\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right)$$

Interaction picture & TDPT

Schrödinger picture: time-dependence on the state vector

Heisenberg picture: time-dependence on the operator

Interaction-picture state vector: $|\Psi, t\rangle_{\mathrm{int}} = \mathrm{e}^{\mathrm{i}\hat{H}_0 t}|\Psi, t\rangle$

Perturbation theory with adiabatic switching $\hat{H} = \hat{H}_0 + \hat{H}_{\mathrm{int}}\mathrm{e}^{-\epsilon|t|}, \ \epsilon \to 0^+$

Schwinger–Tomonaga eq. $\mathrm{i}\frac{\partial}{\partial t}|\Psi, t\rangle_{\mathrm{int}} = \mathrm{e}^{\mathrm{i}\hat{H}_0 t}\hat{H}_{\mathrm{int}}\mathrm{e}^{-\epsilon|t|}\mathrm{e}^{-\mathrm{i}\hat{H}_0 t}|\Psi, t\rangle_{\mathrm{int}}$

Initial condition: $\lim_{t\to-\infty}|\Psi, t\rangle_{\mathrm{int}} = |I\rangle$

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

Transition amplitude:

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

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

XPS: X-ray Photoelectron Spectroscopy

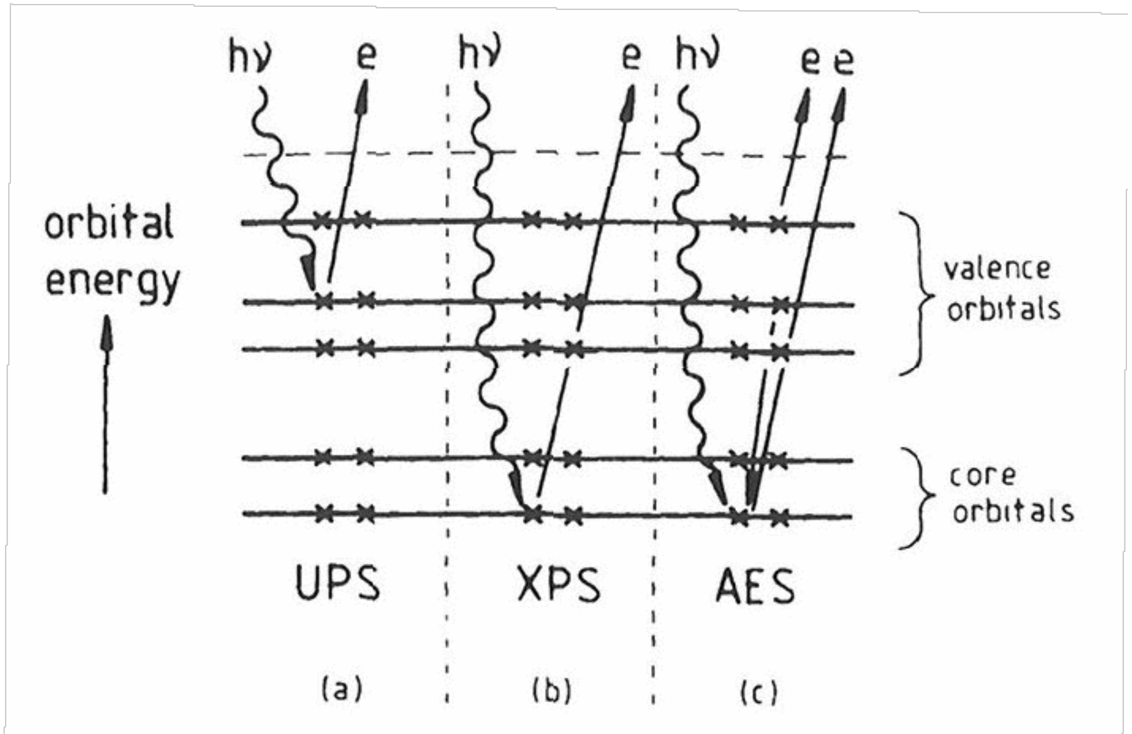
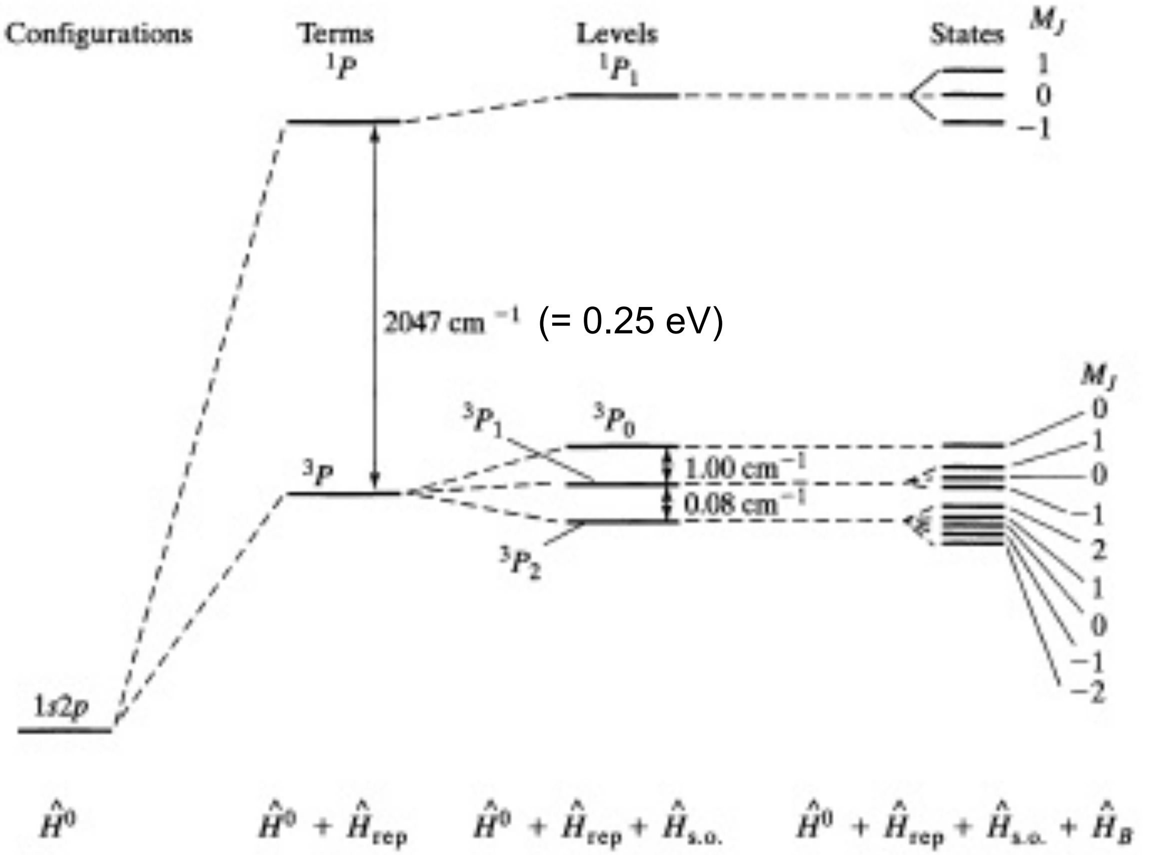


Figure 8.1 Processes occurring in (a) ultraviolet photoelectron spectroscopy (UPS), (b) X-ray photoelectron spectroscopy (XPS), (c) Auger electron spectroscopy (AES)

$$\varepsilon_a = \omega_{\text{in}} - I_i$$

Configuration, term, level, and states

Ira N. Levine,
Quantum Chemistry
(Prentice Hall)



(= 0.25 eV)

FIGURE 11.6 Effect of inclusion of successive terms in the atomic Hamiltonian for the 1s2p helium configuration. $\hat{H}_B$ is not part of the atomic Hamiltonian but is due to an applied magnetic field.

Energy span for ground and excited states

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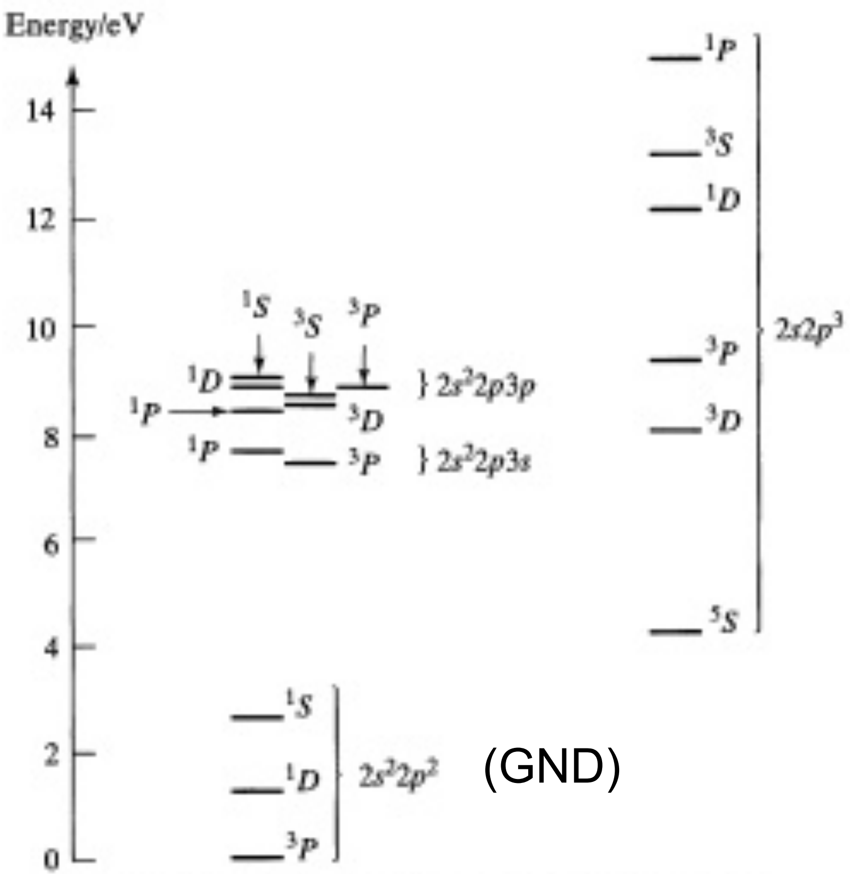
Quantum Chemistry
(Prentice Hall)



(EXT)

(GND)

FIGURE 11.4 Some term energies of the carbon atom.

Macroscopic x-ray refractive index

Complex index of refraction

$$n = 1 - \delta + \mathrm{i}\beta$$

Relationship between electric susceptibility and scalar scattering factor (forward direction)

$$\chi(\omega_{\mathrm{in}}, \boldsymbol{\epsilon}_{\mathrm{in}}) = \frac{\alpha_{\mathrm{P}}(\omega_{\mathrm{in}}, \boldsymbol{\epsilon}_{\mathrm{in}})}{V} = -\frac{f(\omega_{\mathrm{in}}, \boldsymbol{\epsilon}_{\mathrm{in}})}{V\omega_{\mathrm{in}}^2}$$

Refractive index expressed in terms of atomic number densities and atomic scattering factors (forward direction)

$$\begin{aligned} n &= \sqrt{1 + 4\pi\chi} \\ &\approx 1 - \frac{2\pi}{\omega_{\mathrm{in}}^2} \sum_i n_i f_i \end{aligned}$$

$$f_i(\omega_{\mathrm{in}}, \boldsymbol{\epsilon}_{\mathrm{in}}) = f_i^0(\mathbf{0}) + f_i'(\omega_{\mathrm{in}}, \boldsymbol{\epsilon}_{\mathrm{in}}) + \mathrm{i} f_i''(\omega_{\mathrm{in}}, \boldsymbol{\epsilon}_{\mathrm{in}})$$

Attenuation coefficient

Attenuation coefficient

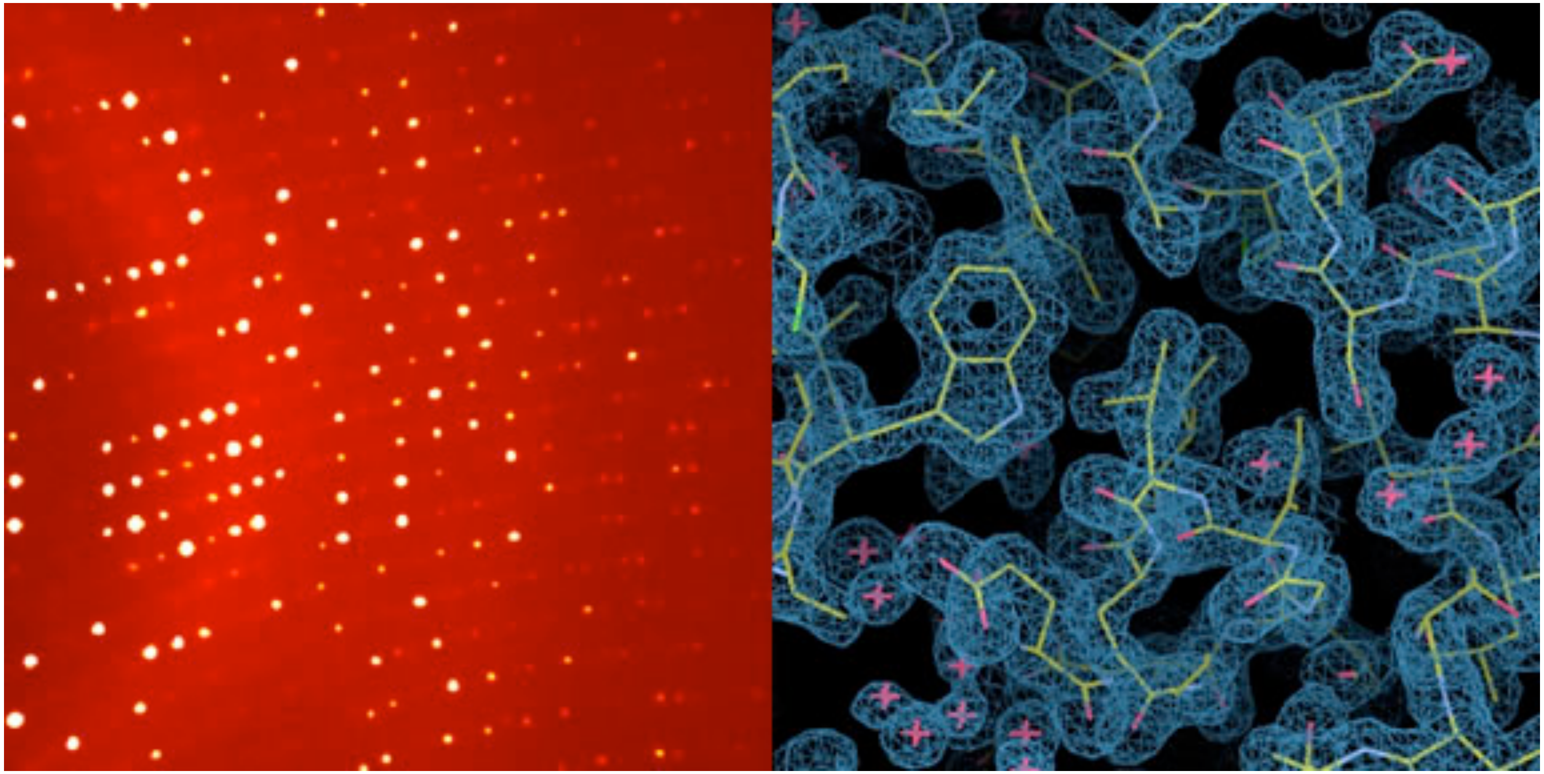
$$\begin{aligned}\mu &= \mu_{\text{abs}} + \mu_{\text{sc}} \\ &= (\sigma_{\text{abs}} + \sigma_{\text{sc}})\, n\end{aligned}$$

σ: cross section, *n*: number density

Transmittance (uniform attenuation): Beer–Lambert law

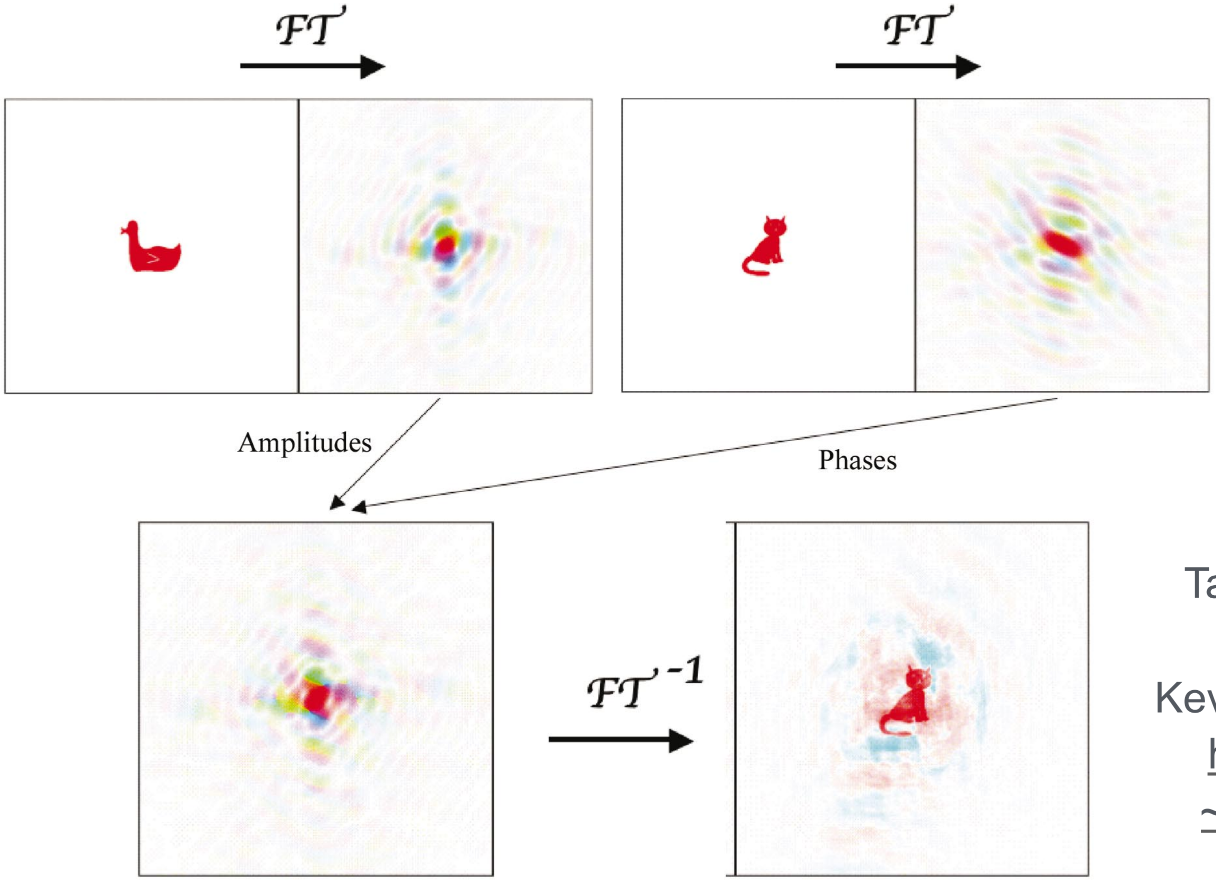
$$T = \mathrm{e}^{-\mu l}$$

Structural determination of macromolecules



Picture taken from http://www.sandiego.edu/cas/chemistry/newsletter/

Why are phases important?



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cat's phases + duck's amplitudes → reconstruction of the cat