1.2 From atomic form factor to anomalous scattering

Scattering Block Course
12.-13.02.2024

University of Zurich[UZH]

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Relativistic dipole radiation

Relativistic energy and mass

- Total relativistic energy of particle of mass m_e travelling at velocity v

$$\mathcal{E} = \frac{m_e c^2}{\sqrt{1-(v/c)^2}} = \frac{m_e c^2}{\sqrt{1-\beta^2}}$$

$$\gamma = \frac{1}{\sqrt{1-\beta^2}}$$

- This is equal to the rest mass energy + kinetic energy

$$\mathcal{E} = m_e c^2 + \mathrm{KE}$$

- Therefore

$$\mathrm{KE} = m_e c^2 \left(\frac{1}{\sqrt{1-\beta^2}} - 1 \right)$$

β and γ

- We know

$$\gamma = \frac{1}{\sqrt{1-\beta^2}}$$

- Therefore

$$\beta = \left(1 - \frac{1}{\gamma^2}\right)^{1/2}$$

- But

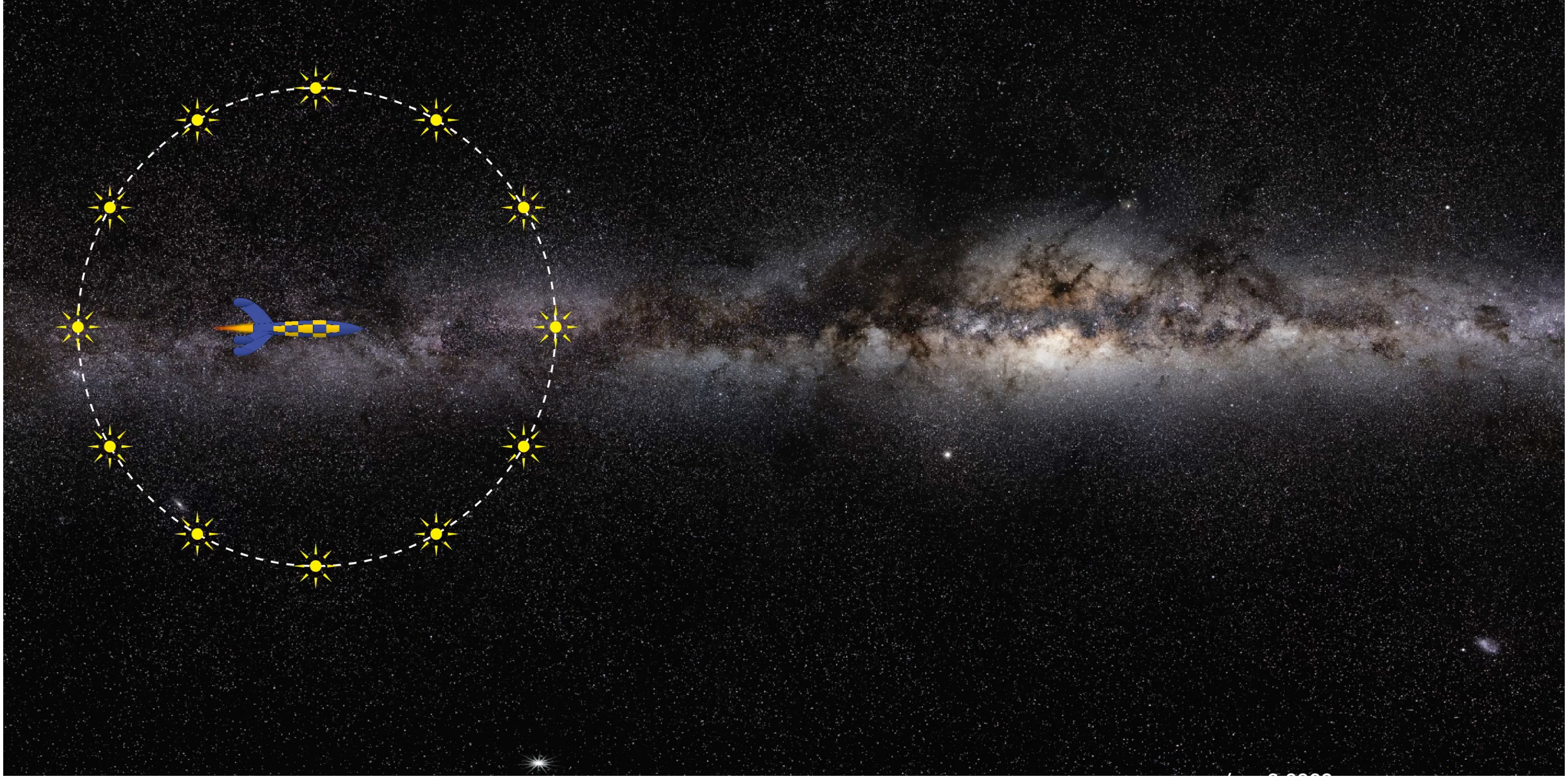
$$\frac{1}{\gamma^2} \ll 1$$

- Therefore

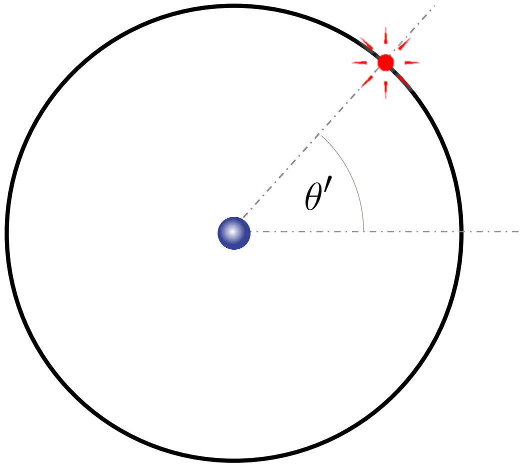
$$\beta \approx \left(1 - \frac{1}{2\gamma^2}\right)$$

N.B. $(1+x)^n \approx 1 + nx; \quad x \ll 1$

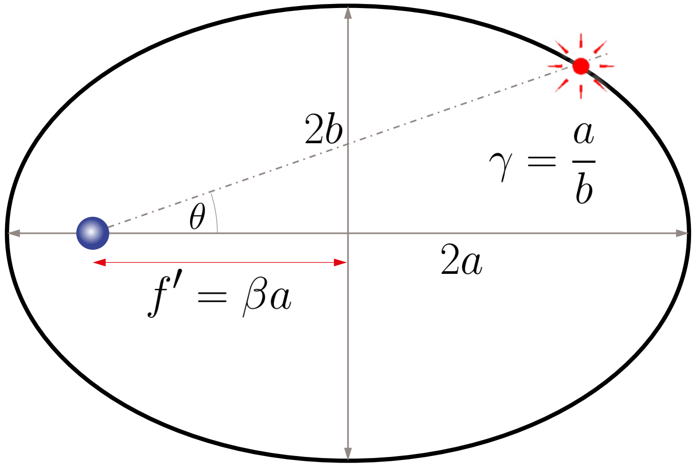
Special relativity in a nutshell



Spatial distortion by special relativity



$v = 0$



$v > 0$

$$\beta = v/c$$

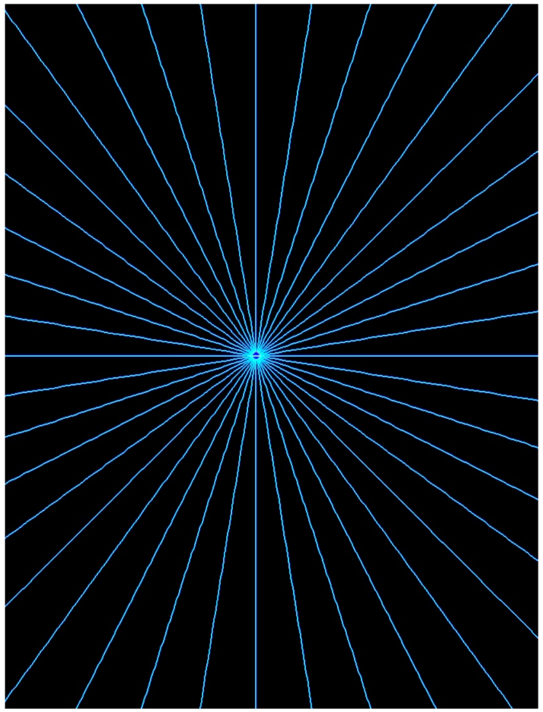
$$\gamma = \frac{1}{\sqrt{1-\beta^2}}$$

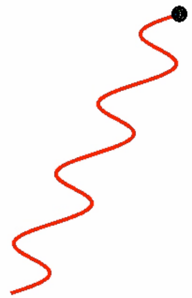
$$\theta = \sin^{-1}\left[\frac{\sin\theta'}{\gamma(1+\beta\cos\theta')}\right]$$

See also “Mr Tompkins in Paperback”, George Gamow (Canto Classics)

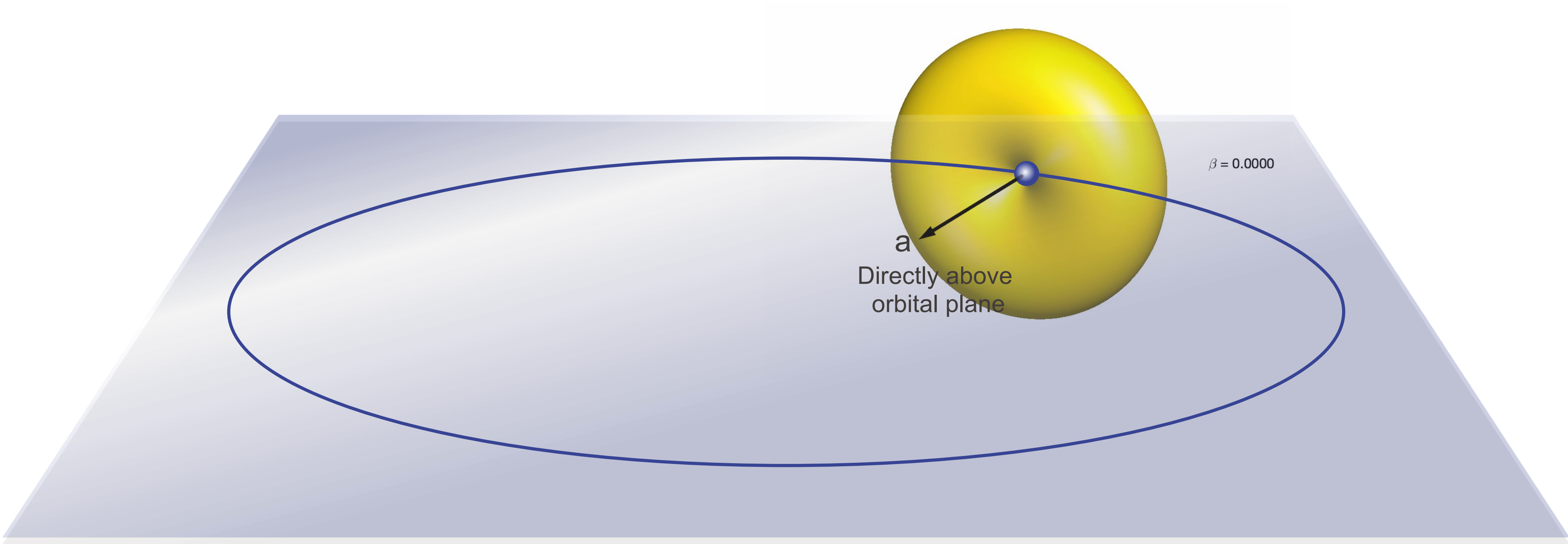
From dipole to synchrotron radiation

Remember dipole radiation:





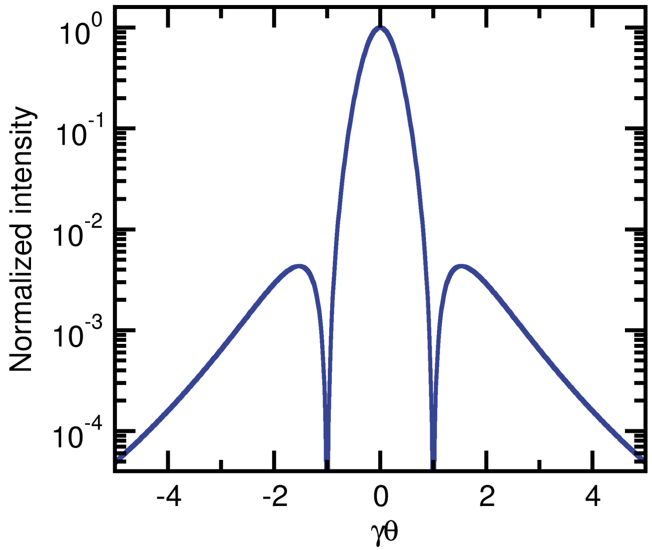
From dipole radiation to synchrotron radiation

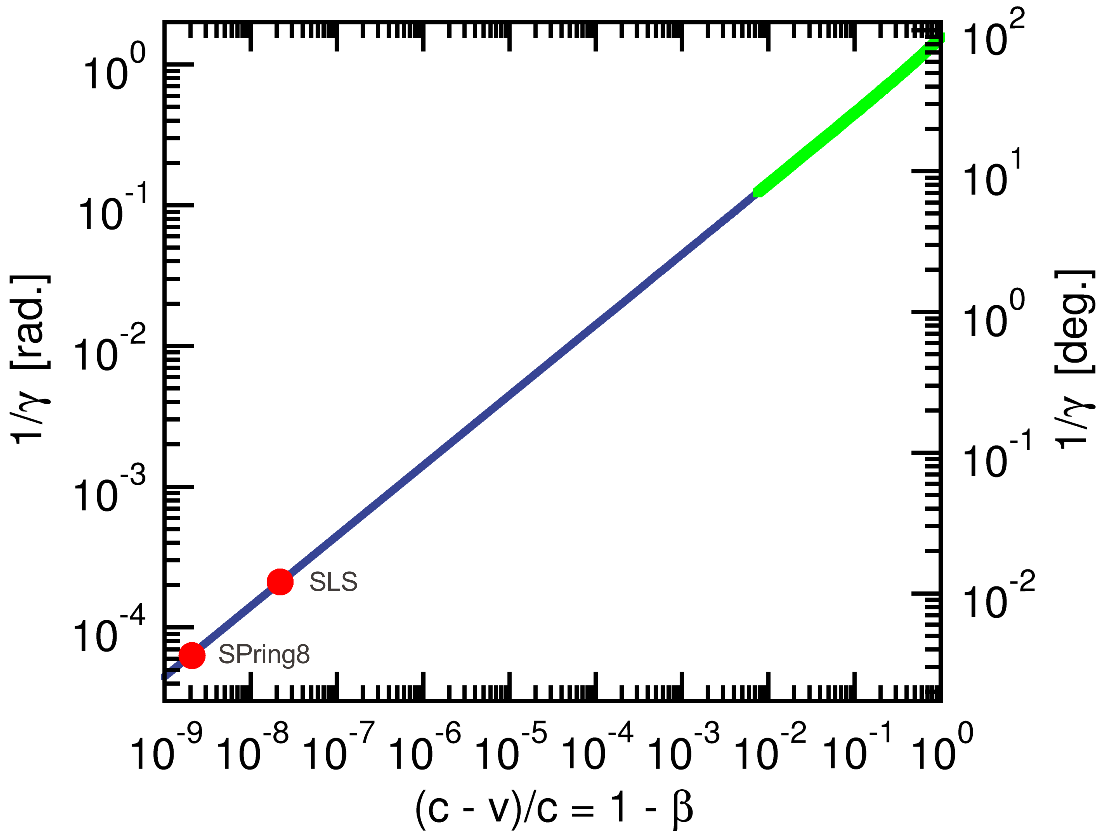


From dipole to synchrotron radiation

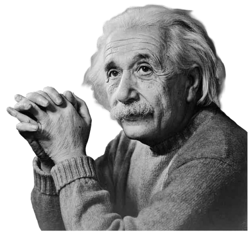
$$\theta = \sin^{-1}\left[\frac{\sin\theta'}{\gamma(1+\beta\cos\theta')}\right]$$

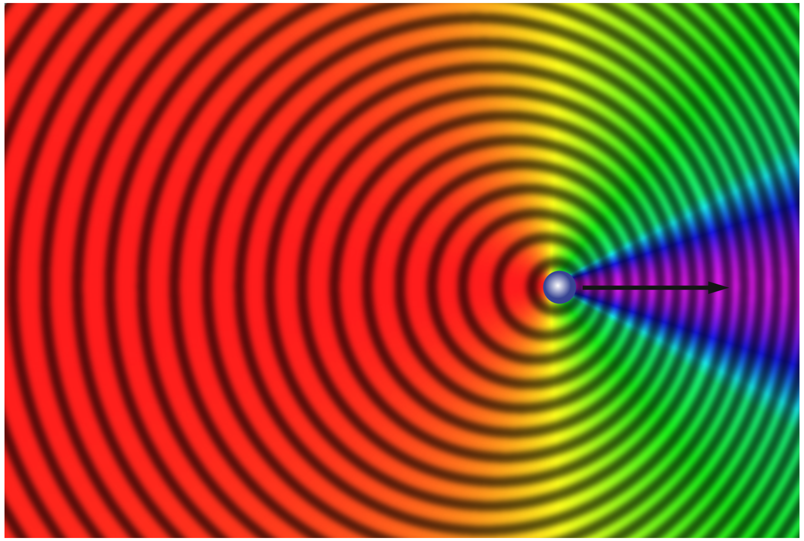
θ' in frame of reference of electron = $\pi/2$
θ in observer's F.o.R. = $1/\gamma$
Opening angle = $\pm\ 1/\gamma$
FWHM $\simeq 1/\gamma$



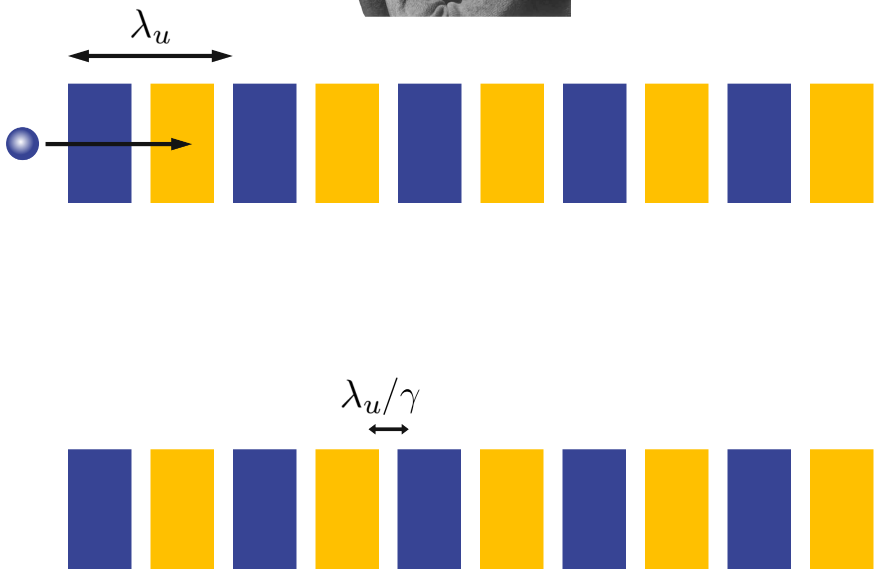


Doppler + Einstein = synchrotron x-rays





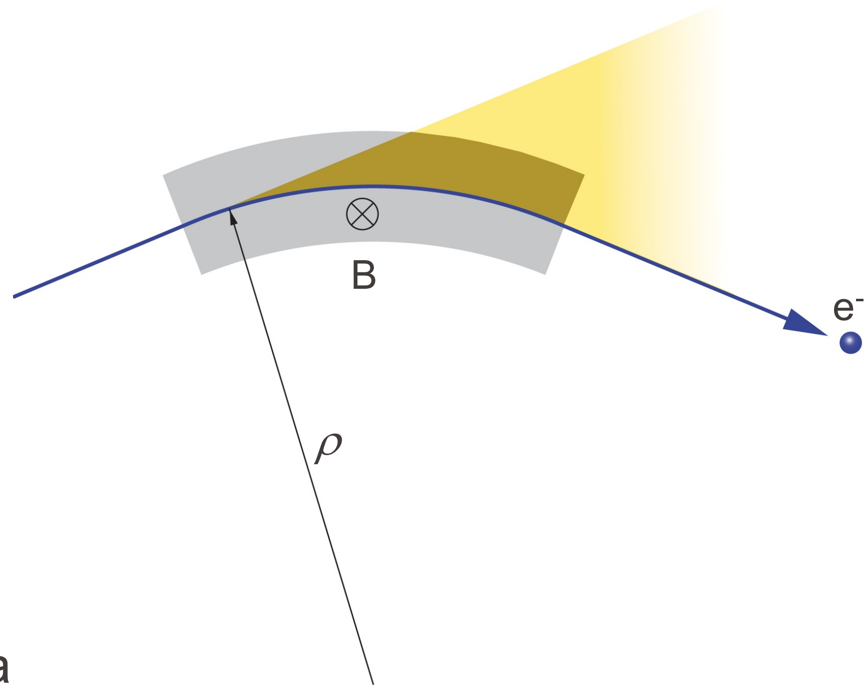
$$\frac{\nu_{\rm obs}}{\nu_{\rm source}} = \sqrt{\frac{1+\beta}{1-\beta}} \approx 2\gamma$$



$$\lambda_u/2\gamma^2 \sim \text{Å}$$

I got the power

$$\frac{dP}{d\Omega}(\theta = 0) \propto \gamma^6$$



- Assumes a constant acceleration a. Also proportional to a^2

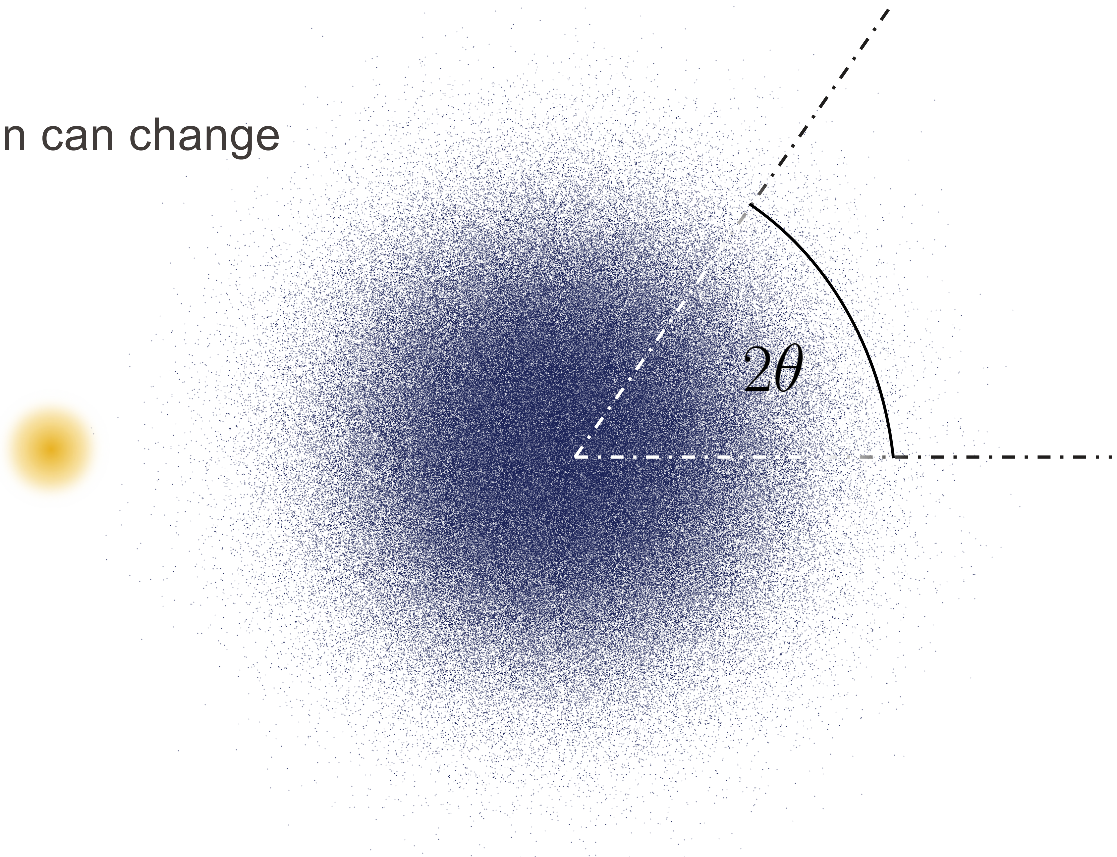
$$a = c^2/\rho = \frac{ceB}{\gamma m_e}$$

- e.g., an increase in storage-ring energy by 25% (2.4 GeV to 3.0 GeV) results in an increase in central-cone power density of a factor 3.8

The atomic form factor

Elastic scattering of photons

- Elastic (Thomson) scattering of photons by electrons
  - $h\nu_{in} = h\nu_{out}$
- Direction (momentum) of photon can change thru' an angle 2θ
  - Wavevector $k = 2\pi/\lambda$
  - $E = hc/\lambda = \hbar ck$
  - Photon momentum = $h/\lambda = \hbar k$
  - $|k_{in}| = |k_{out}|$
  - $\overrightarrow{\Delta k} = \overrightarrow{Q} = \overrightarrow{k_{in}} - \overrightarrow{k_{out}}$
  - Q = "scattering vector"



The scattering vector, Q

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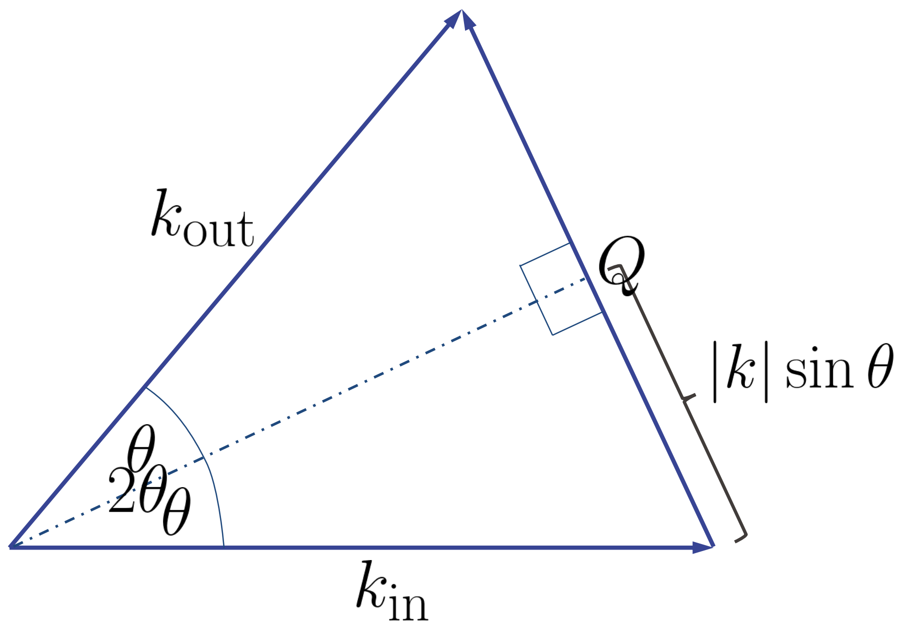
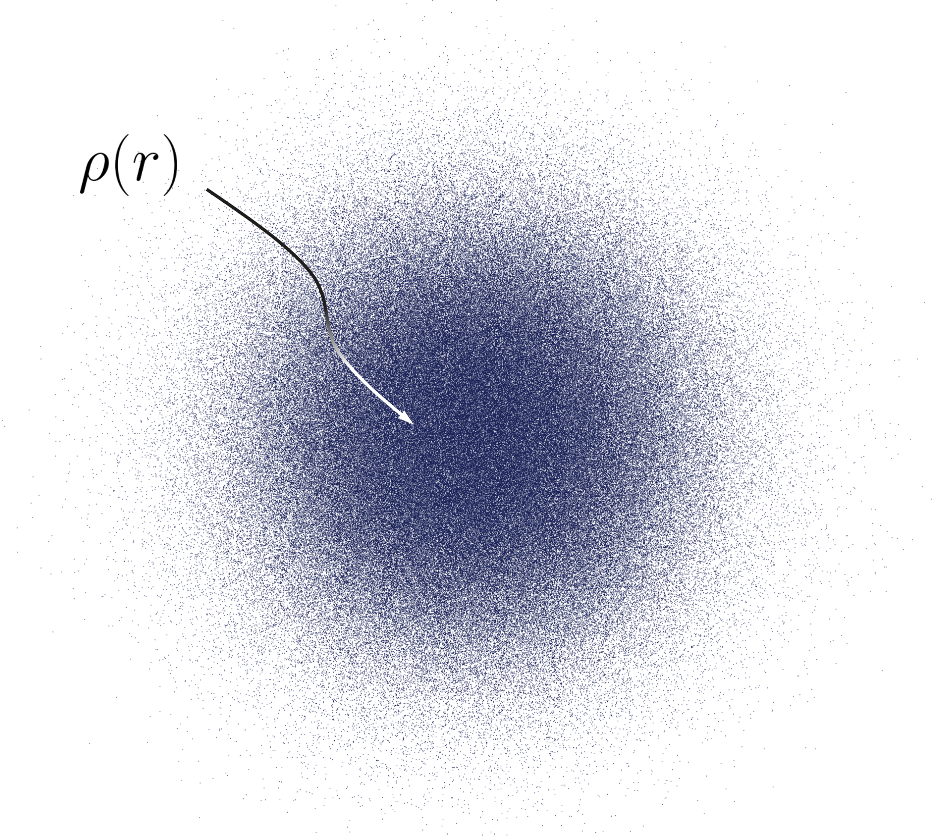
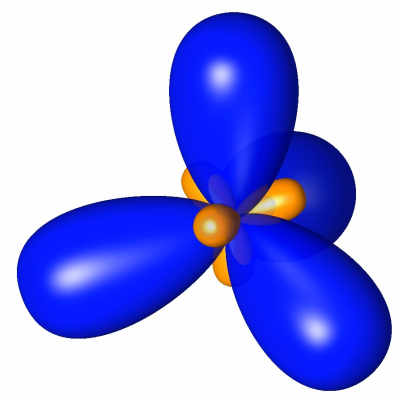


$$Q = 2|k|\sin\theta = (4\pi/\lambda)\sin\theta$$

Scattering off an atom (atomic number Z)



- Neutral atom has Z electrons
- Atom has an electron-density distribution $\rho(r)$
- Assume electrons are quasi unbound
- Normally assumed to be spherically symmetric
  - Poor approximation for low-Z atoms, e.g., carbon in diamond – four of six electrons involved with sp^3-hybridized bonds



The atomic form factor, $f(\mathbf{Q})$, is the far-field scattering amplitude produced by the electron cloud $\rho(r)$

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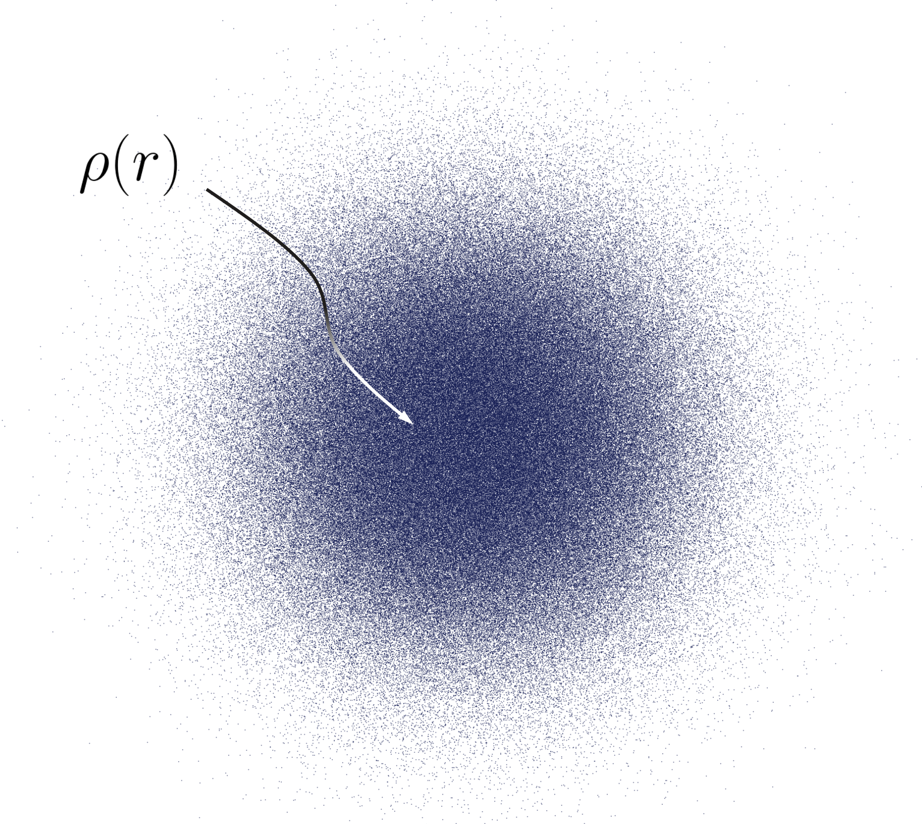

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$$f(\mathbf{Q}) = \int_{\text{atom}} \rho(\mathbf{r}) e^{i\mathbf{Q}\cdot\mathbf{r}} dV$$

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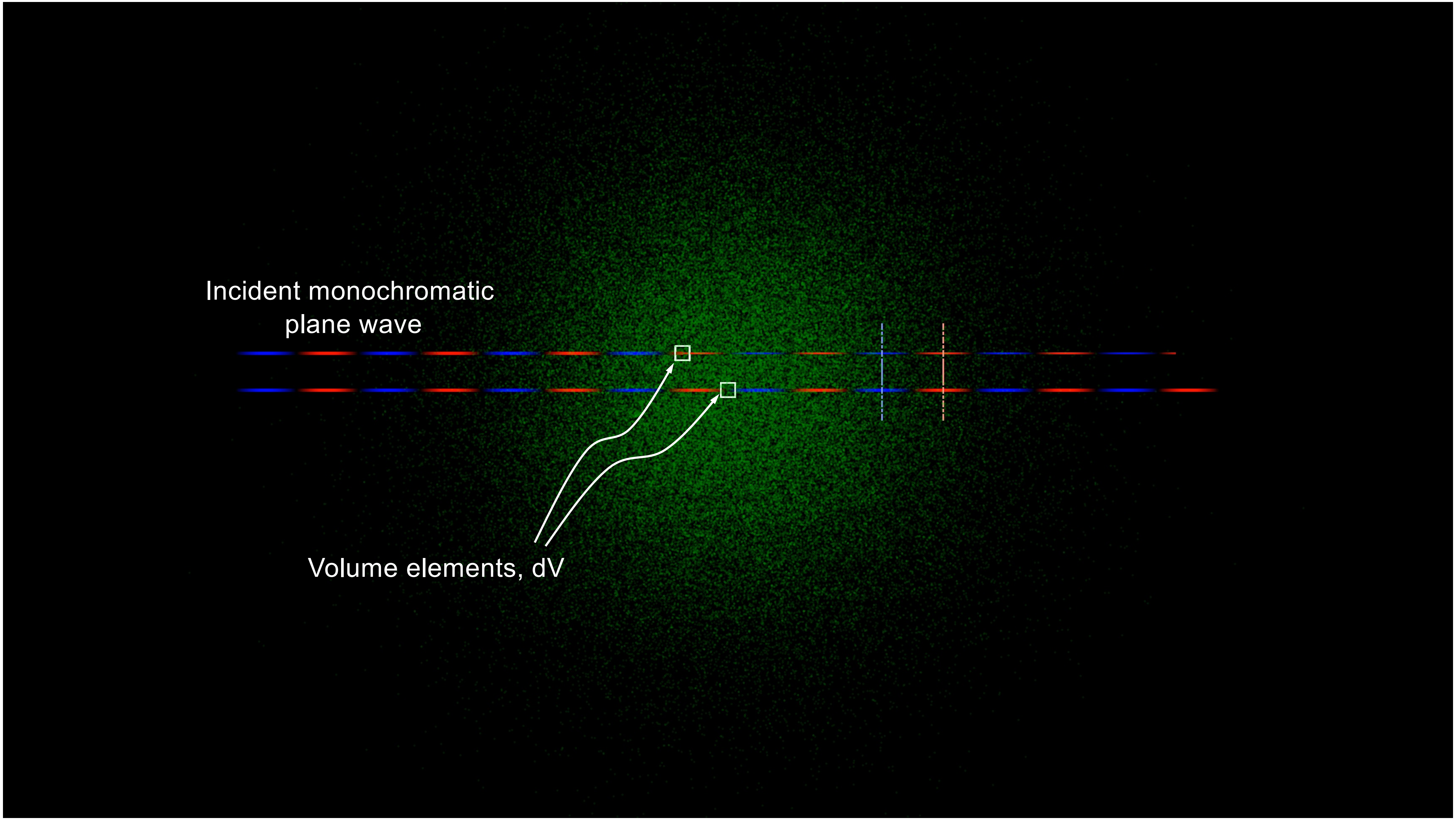
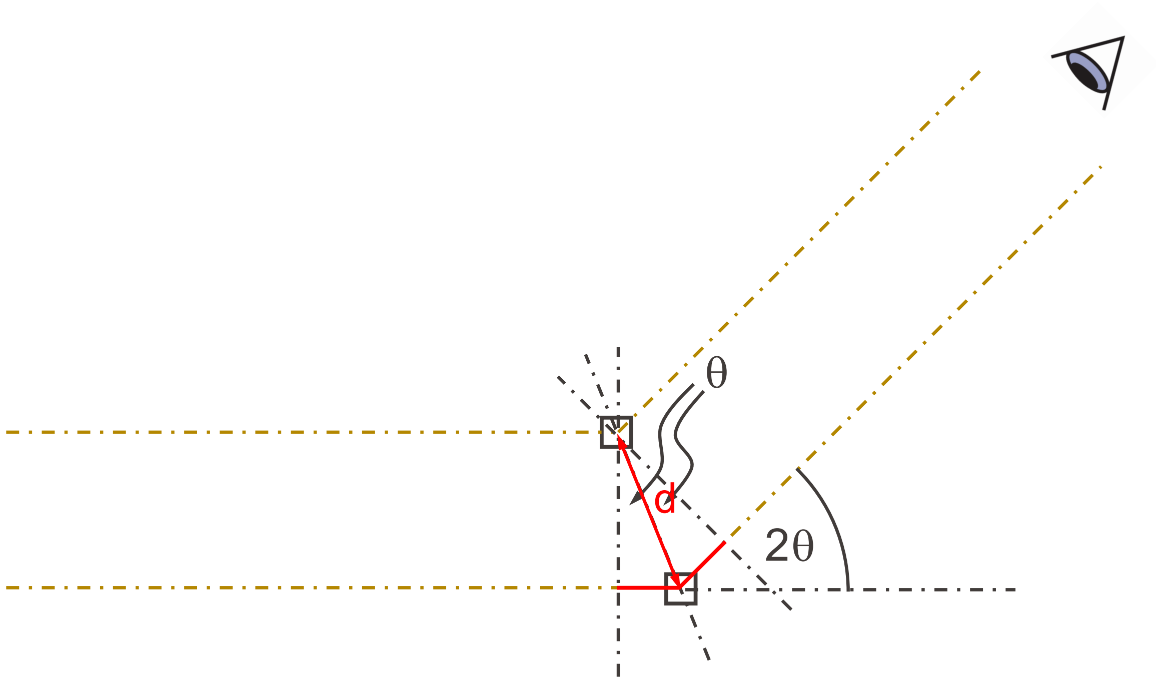


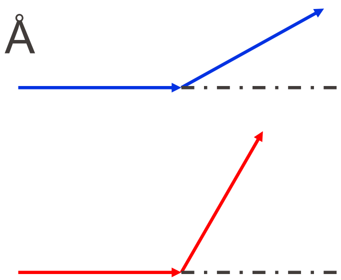
Incident monochromatic plane wave
Volume elements, dV

Scattering between elements dV



Scattering between elements dV

- Example
  - θ = 14.48°, sin θ = 0.25. λ = 1 Å
    sin θ/λ = 0.25 $Å^{-1}$
  - θ = 30°, sin θ = 0.5. λ = 2 Å
    sin θ/λ = 0.25 $Å^{-1}$



  - Interference effect (i.e., amplitude of scattered radiation @ 2θ) the same in both cases because sin θ/λ is the same

Optical path difference (OPD) between two volume elements dV separated by d

$$\mathrm{OPD} = 2d\sin\theta$$

$$\#\,\mathrm{wavelengths} = 2d\,\sin\theta/\lambda$$

$$\phi = 4\pi d \sin\theta/\lambda = Qd = \mathbf{Q}\cdot\mathbf{r}$$

The atomic scattering factor, f

- $f(\mathbf{Q})$ is the FT of $\rho(r)$
  - Spherical approximation: $\rho(r)$ = sum of 3D-Gaussian probability distributions
  - The FT of a Gaussian is also a Gaussian
  - Describe $f(\mathbf{Q})$ as a sum of four Gaussians plus a constant

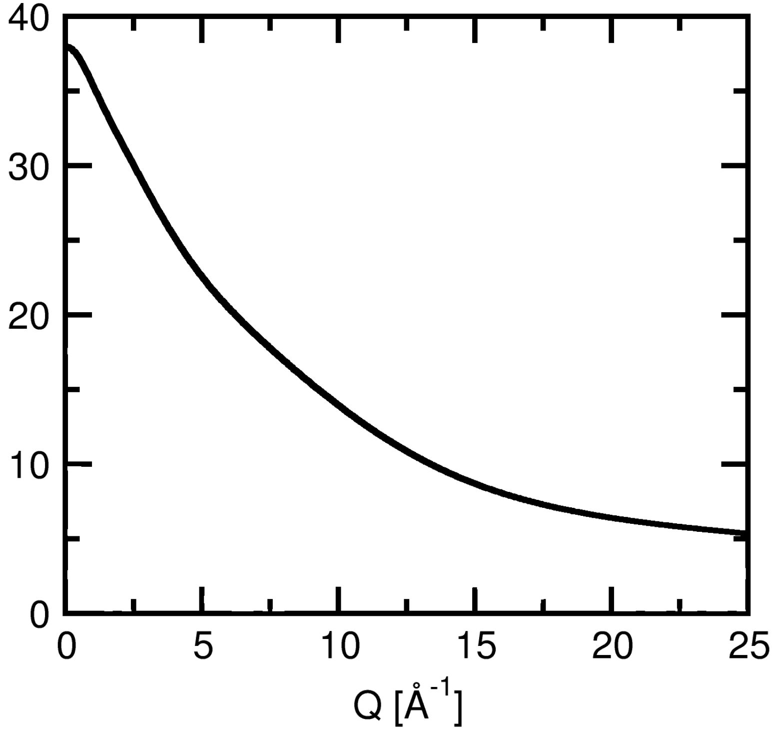
$$f^0(\mathbf{Q}) = \sum_{i=1}^{4} a_i \exp\left[-b_i \left(\frac{Q}{4\pi}\right)^2\right] + c$$

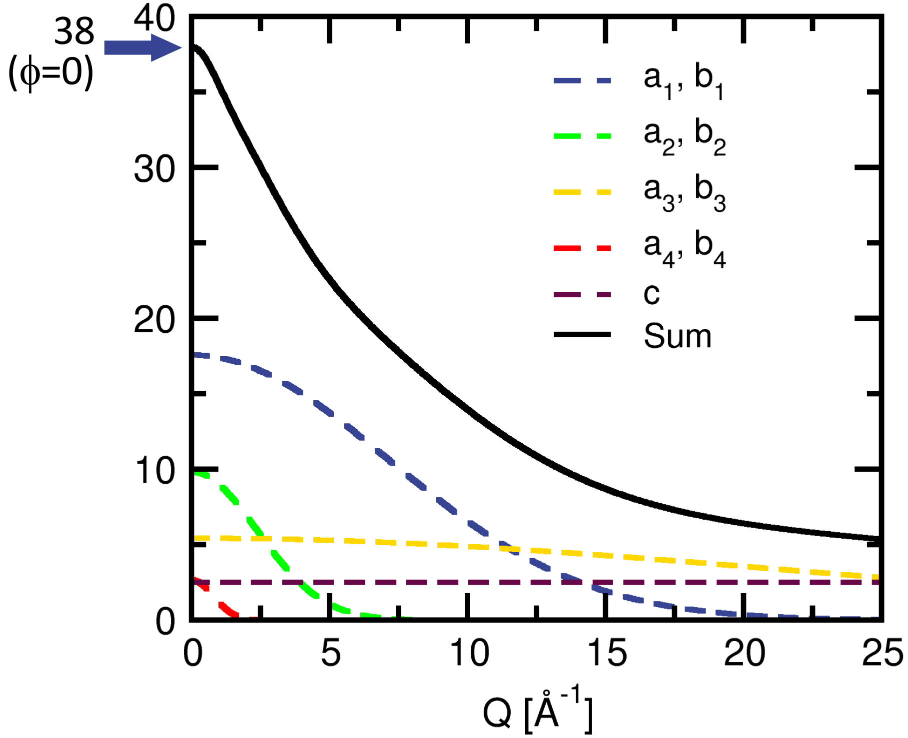
International Tables for Crystallography

See also: http://lampx.tugraz.at/~hadley/ss1/crystaldiffraction/atomicformfactors/formfactors.php

The atomic scattering factor, f

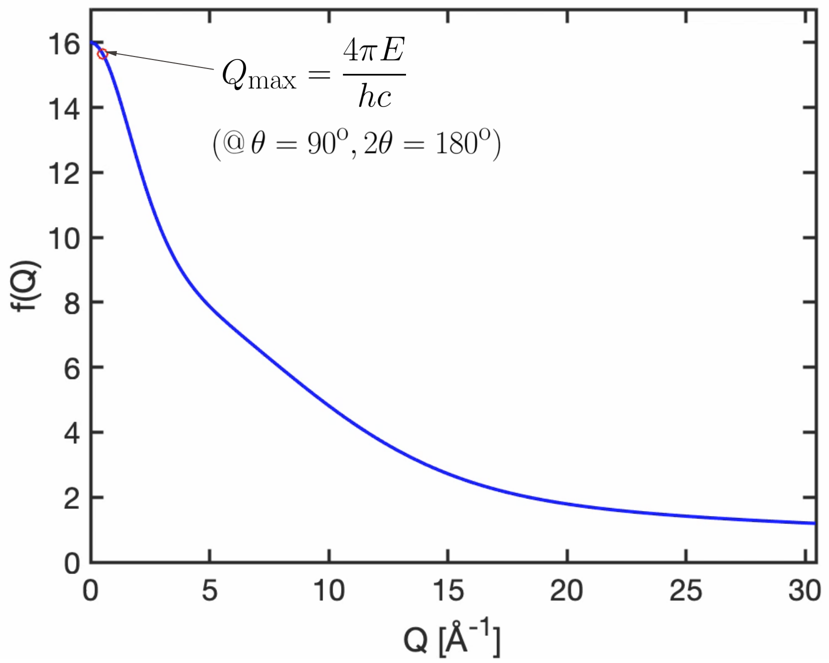
- Example: strontium (Z = 38)

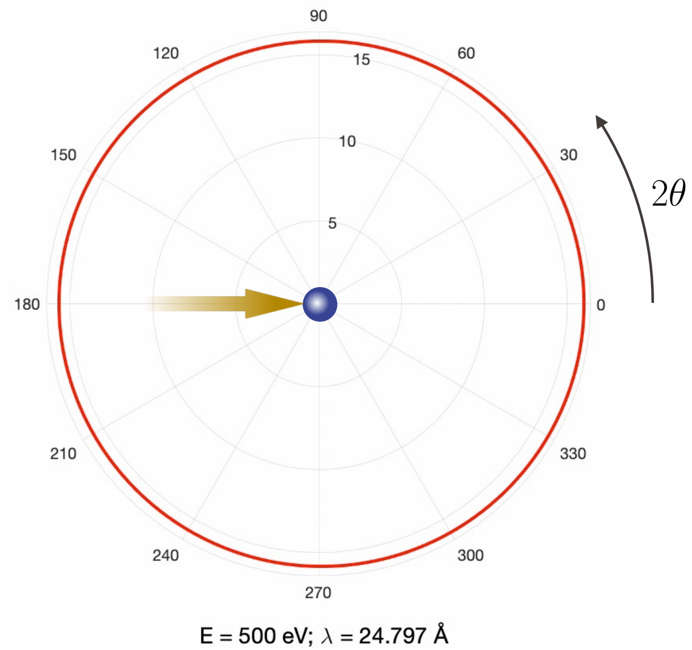




f describes the distribution of elastic scattering by an atom relative to the direction of the incident photon

Scattering from a sulfur atom – The movie!



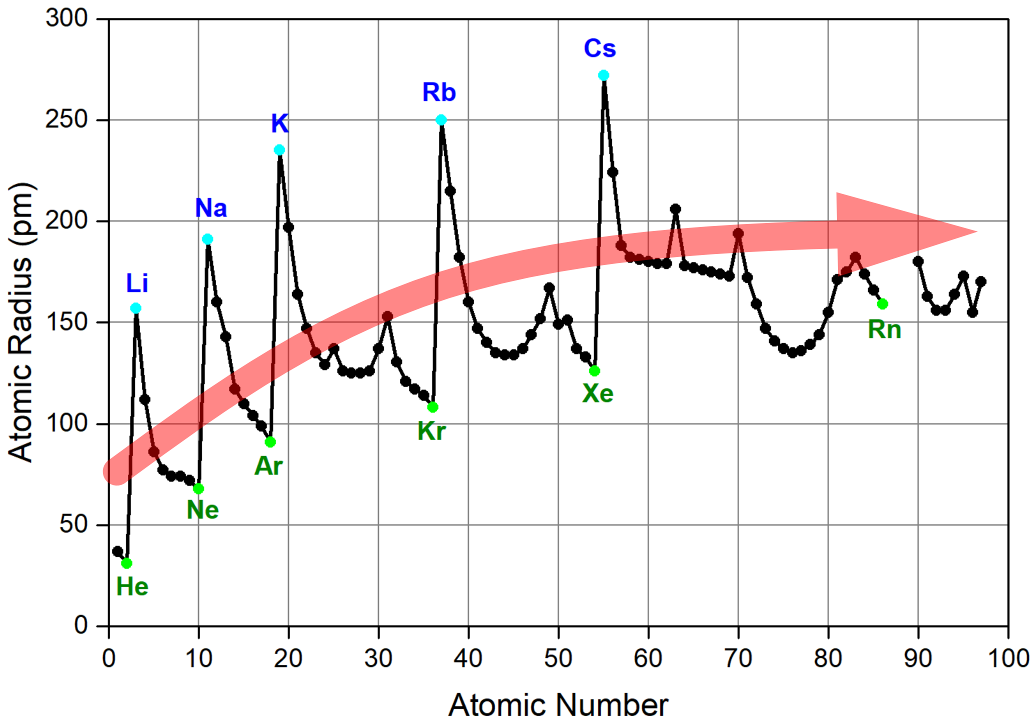


f as a function of 2θ ($-\pi$ to $-\pi$)
and photon energy E (500 eV to 30 keV)

$$Q = \frac{4\pi}{\lambda}\sin\theta = \frac{4\pi E}{hc}\sin\theta$$

Big atom = small atomic form factor? No!

- Rules in Fourier transforms
  - Big features in real space have narrow Fourier transforms
  - Atomic radii of the elements:



- But larger atoms have larger atomic form factors! Why??
  - Note that neighbouring noble gases and alkaline elements in atomic number (e.g. Kr & Rb) have very large differences in atomic radius
  - This is due to the valence electrons!
    - Valence electrons determine chemistry
  - But for x-rays, valence electrons are no better (often worse) scatterers than any of the other electrons

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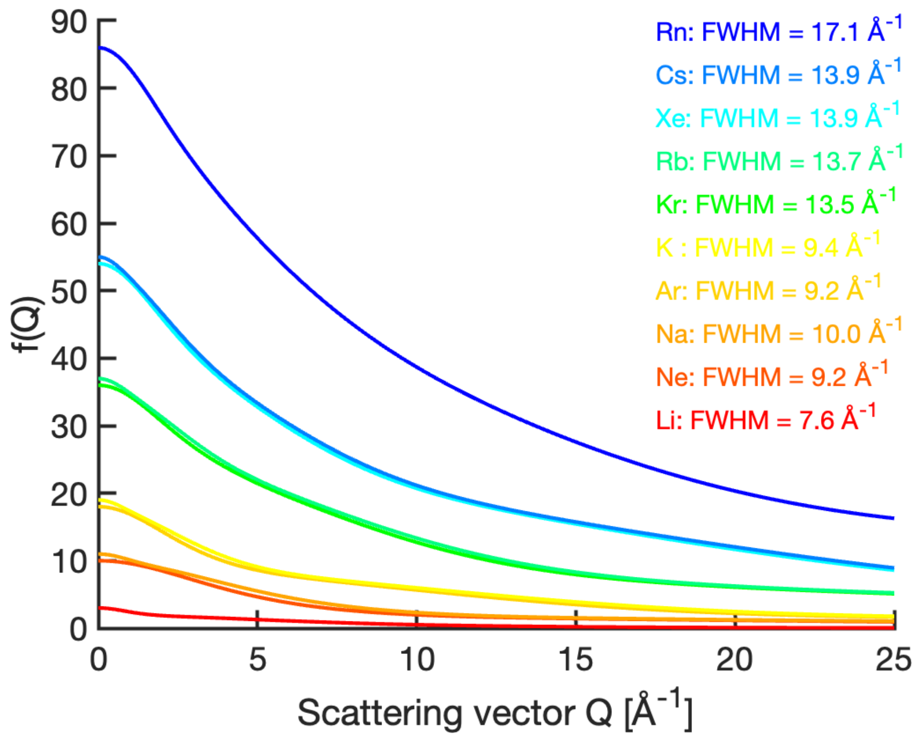

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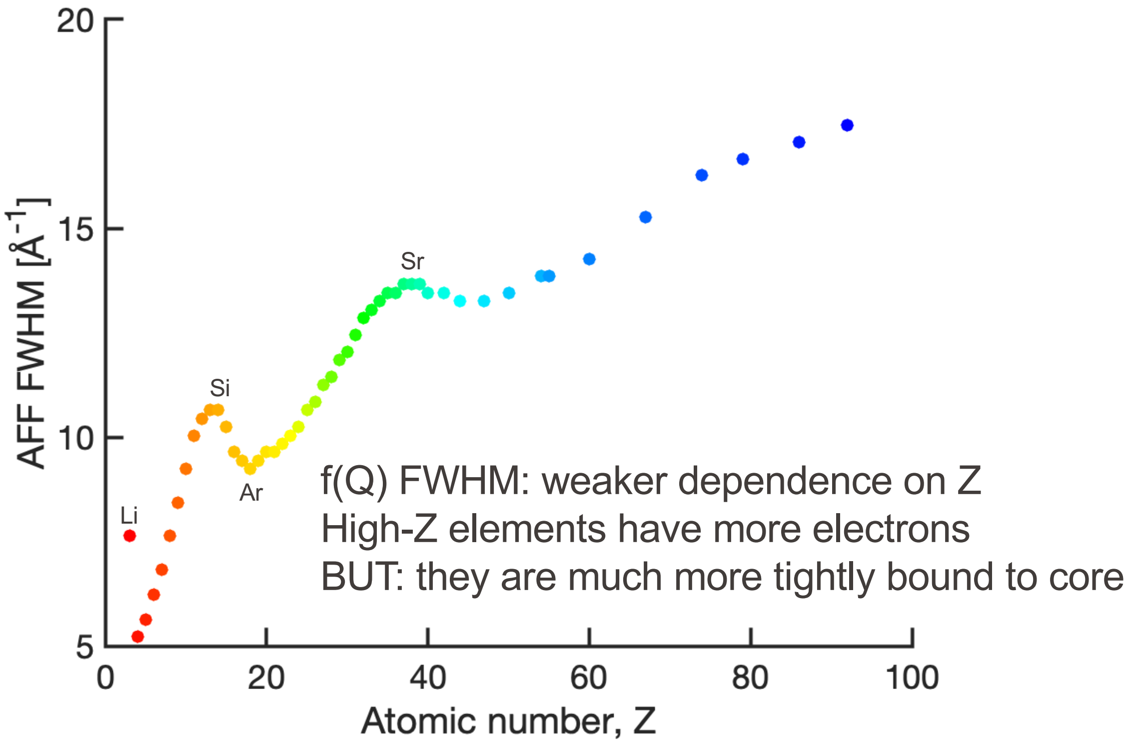

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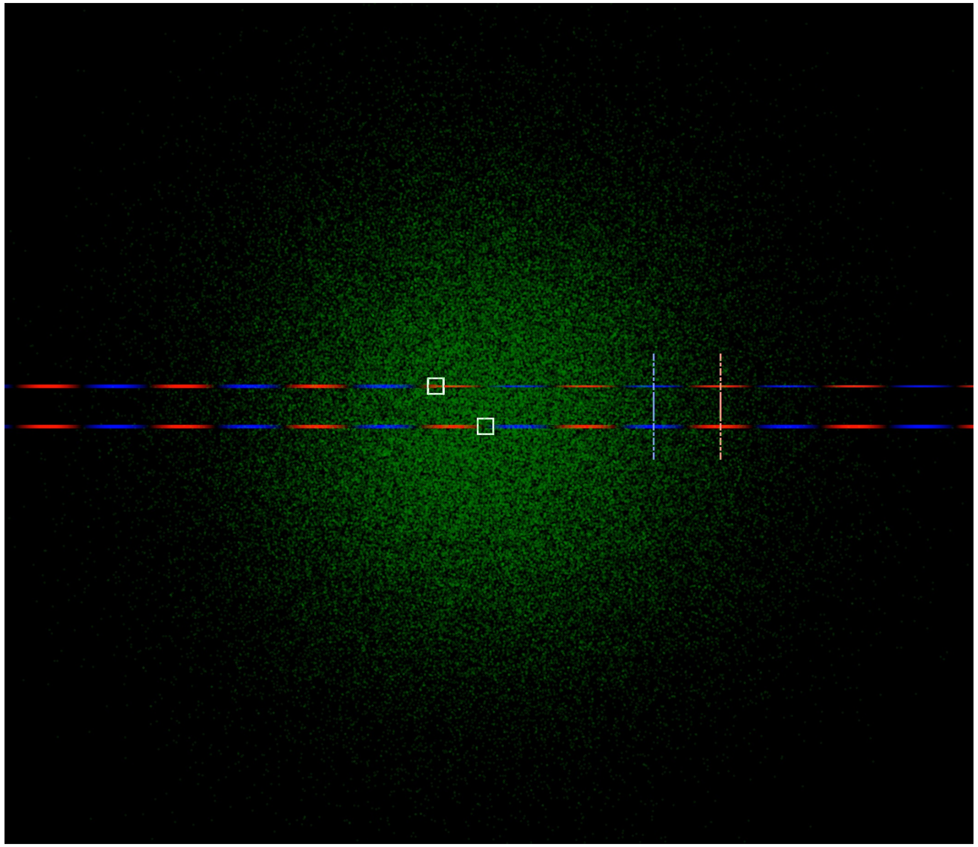
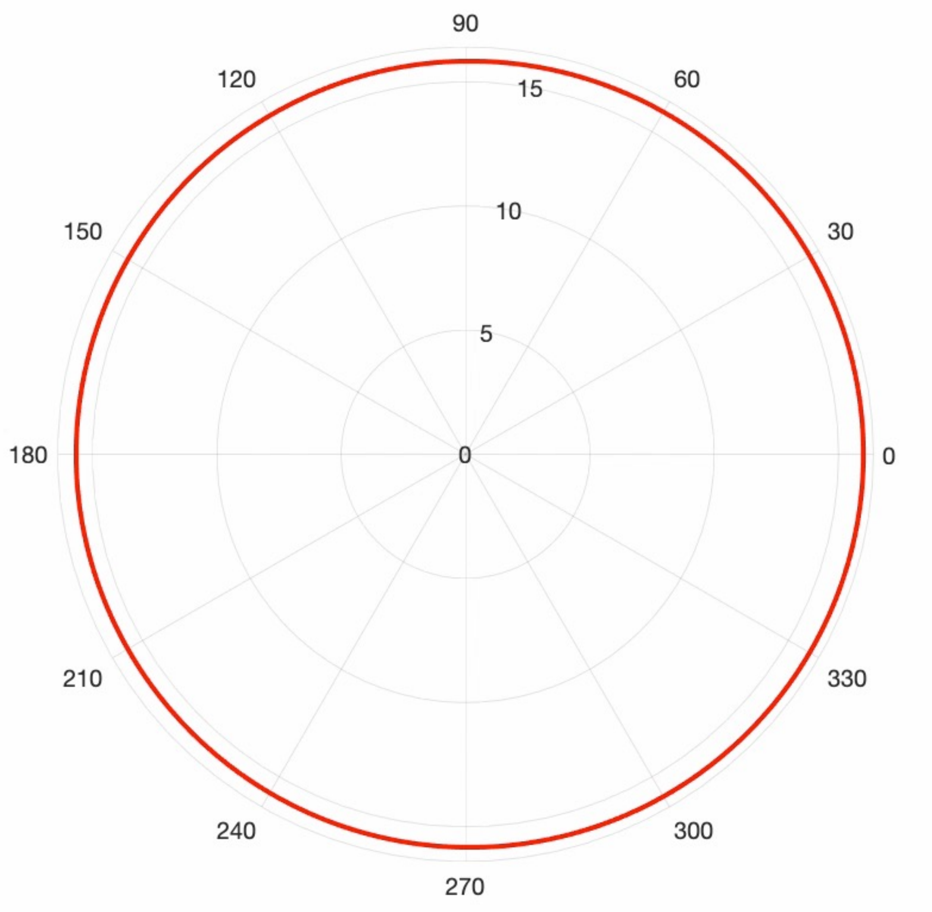
Summary – elastic scattering… so far



- Scattering amplitude from the entire electron cloud $\rho(r)$ as function of scattering vector Q
  = atomic scattering factor f
  - Integrate scattering over atom volume
  - Take into account relative phases of scattering from all volume elements dV
- Note
  - Also called "atomic form factor"
  - Normally expressed as f(sin θ/λ) or f(Q)

Summary – elastic scattering… so far



E = 500 eV; λ = 24.797 Å

- Forward scattering
  - $\theta = 0$; $Q = 0$
  - All volume elements dV scatter in phase: $\phi = 0$
  - Integral of $\rho(r)$ is therefore simply Z, the number of electrons in the atom (assuming no ionicity)
  - $f(Q = 0) = f(0) = Z$
- As θ increases
  - Increasing "scrambling" and destructive interference between scattering from different volume elements dV
  - $f(\sin\theta/\lambda)$ [or f(Q)] decreases quasi-monotonically (sum of four Gaussians + constant)
  - Maximum accessible Q-value increases with photon energy

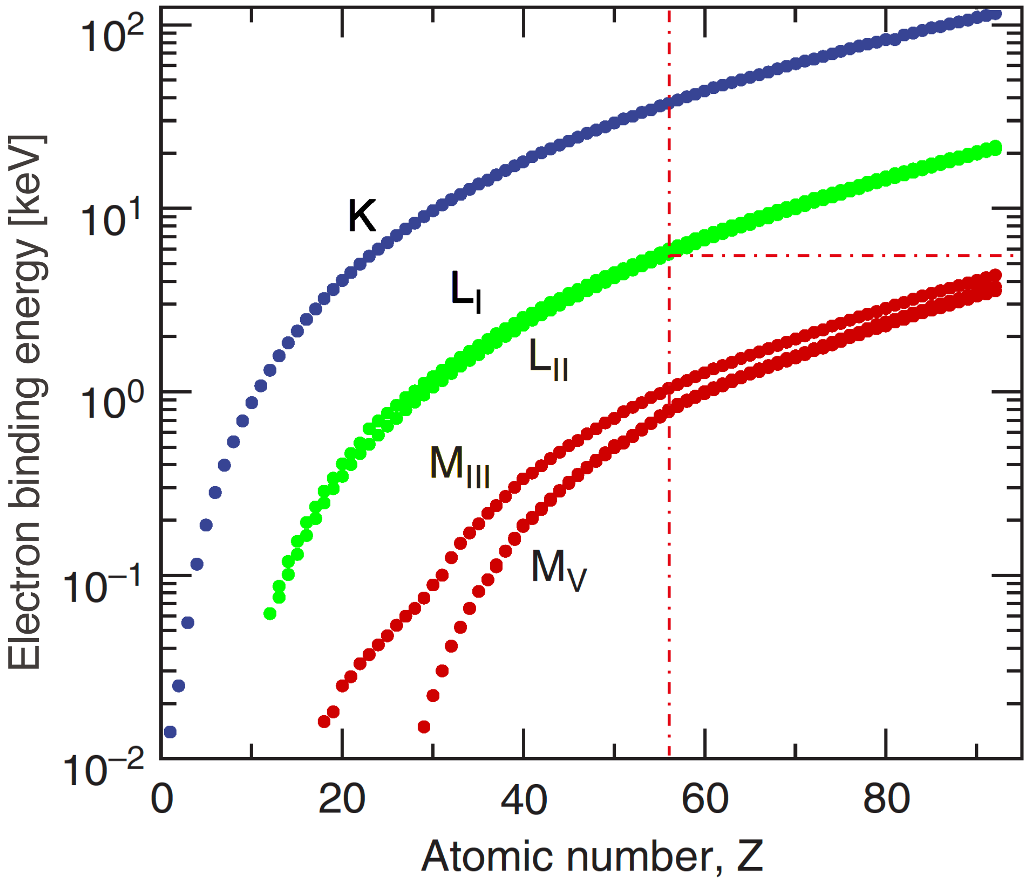
Anomalous scattering

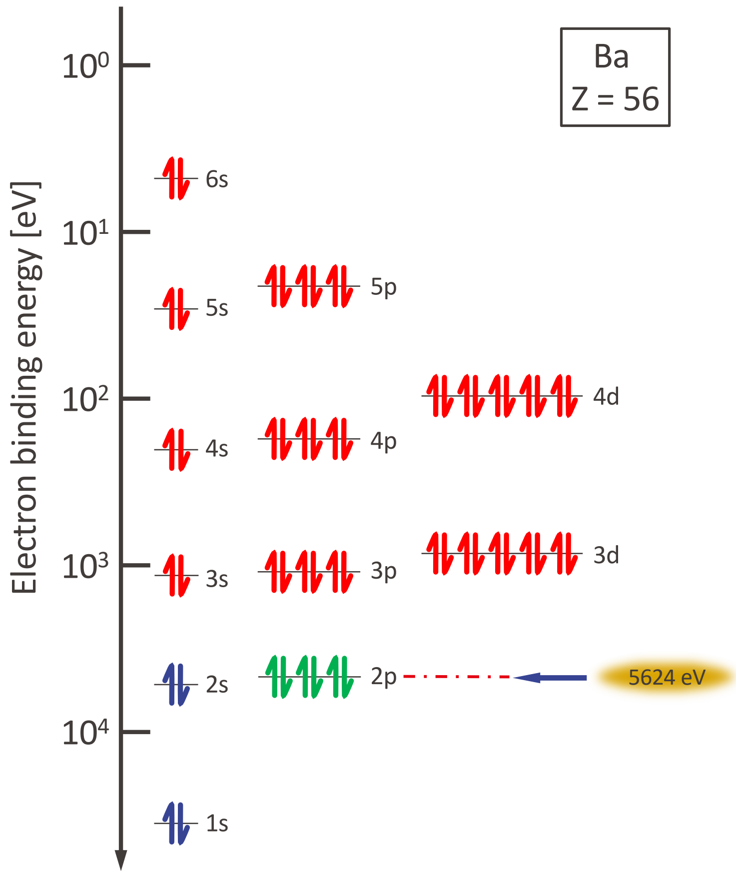
f^0 and beyond

$$f^0(\mathbf{Q}) = \sum_{i=1}^{4} a_i \exp\left[-b_i\left(\frac{Q}{4\pi}\right)^2\right] + c$$

Based on the assumption that all electrons in the atom are essentially unbound
Response is instantaneous
No coupled oscillator

Electron binding energies of the elements





Bound electrons' response to x-rays

- Damped-oscillator model

$$\frac{d^2z}{dt^2} + \Gamma\frac{dz}{dt} + \omega_0^2 z = \frac{-E_0 q}{m_e}\, e^{i\omega t}$$

Driving force of incident EM-radiation

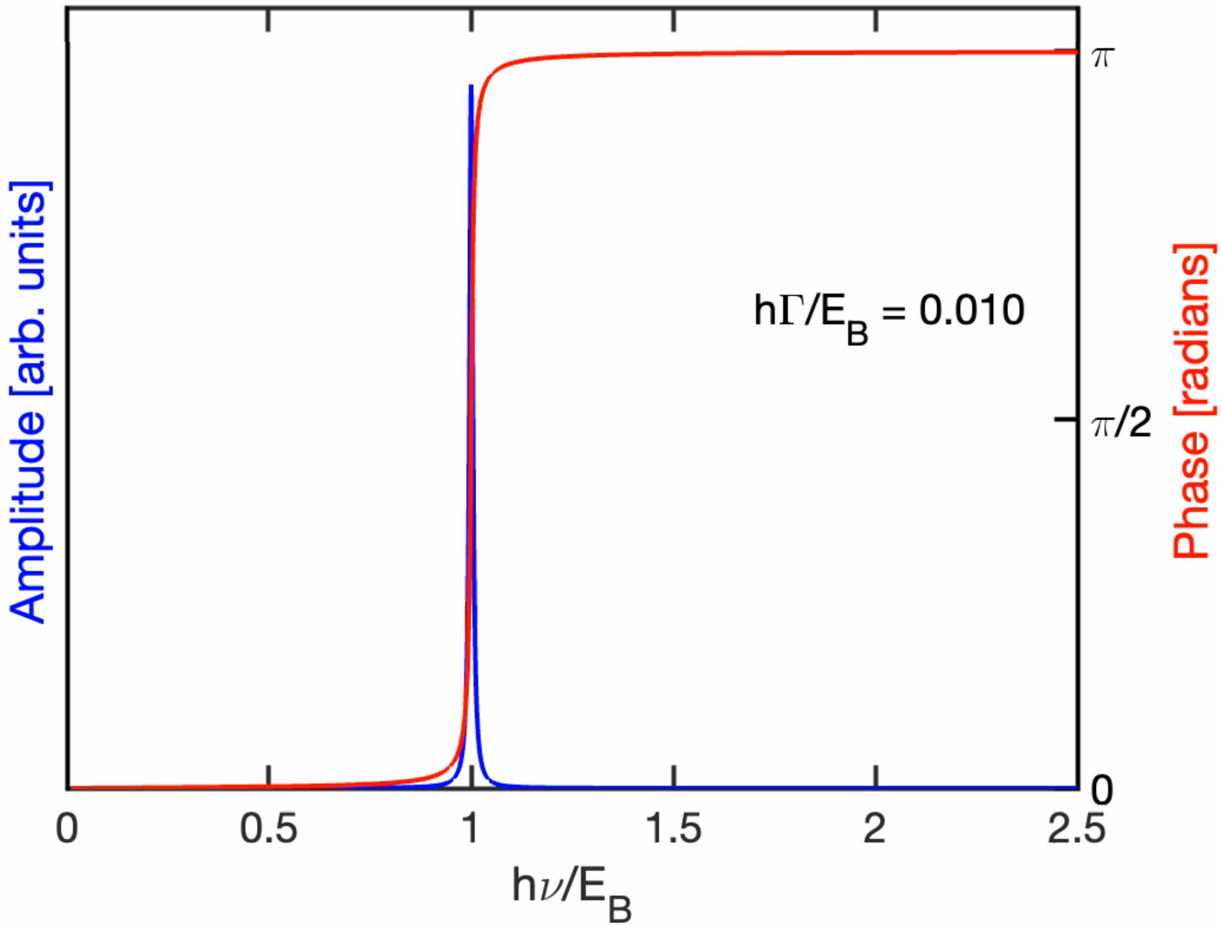
- Damping term $\Gamma\frac{dz}{dt}$: normally $\Gamma \ll \omega_0 \;(= E_B/\hbar)$

  due to re-radiation via dipole radiation

- Solutions: amplitude: $A(\omega) = \dfrac{-E_0 q/m}{\left[(\omega_0^2 - \omega^2)^2 + (\Gamma\omega)^2\right]^{1/2}}$

  phase: $\tan(\delta) = \dfrac{\Gamma\omega}{(\omega_0^2 - \omega^2)}$

Bound electrons' response to x-rays



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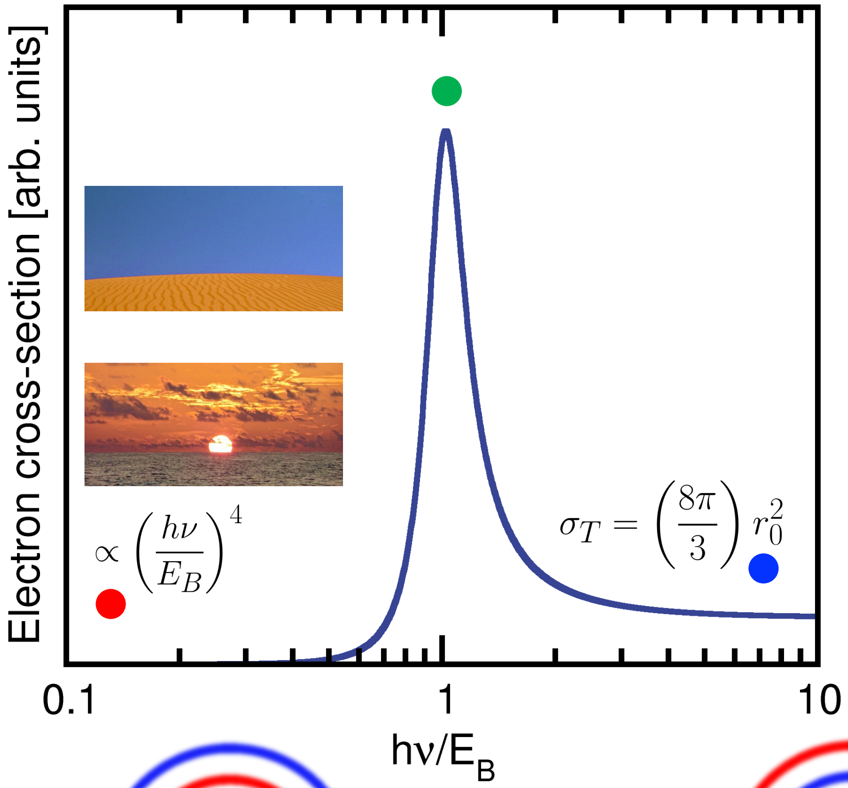
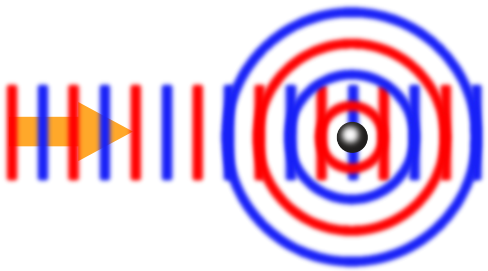
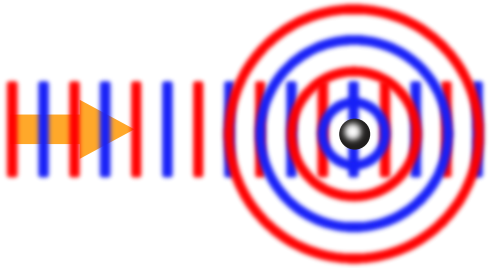
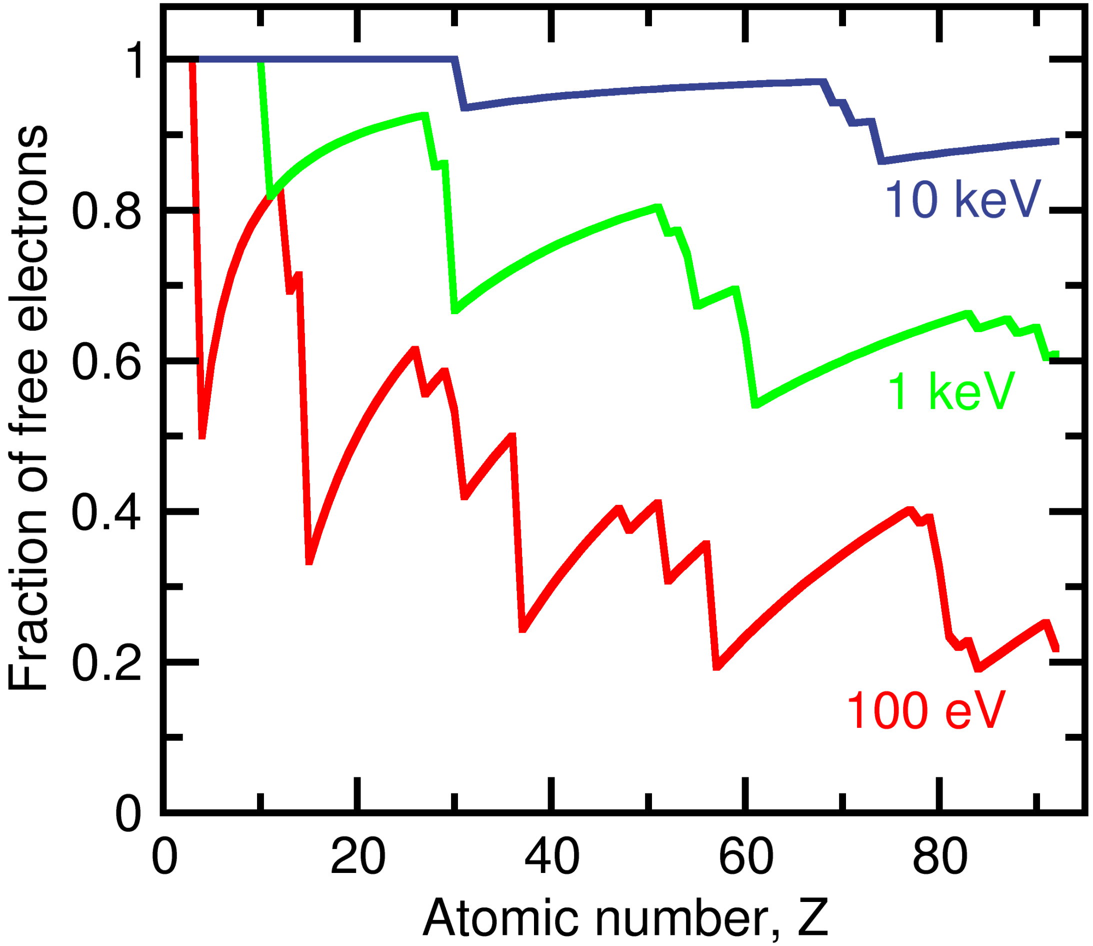






- $h\nu \ll E_B$
  - Response strongly suppressed ~ 0
  - "Rayleigh scattering" $\propto h\nu^4$
  - $\phi = 0$
  - $n > 1$
- $h\nu \gg E_B$
  - Thomson scattering, electron quasi "free"
  - $\phi = \pi$ – scattered radiation out of phase with incident beam
  - $n < 1$
- $h\nu \simeq E_B$
  - Resonance
  - Enhanced response
  - $\phi = \pi/2$: dissipation (absorption)

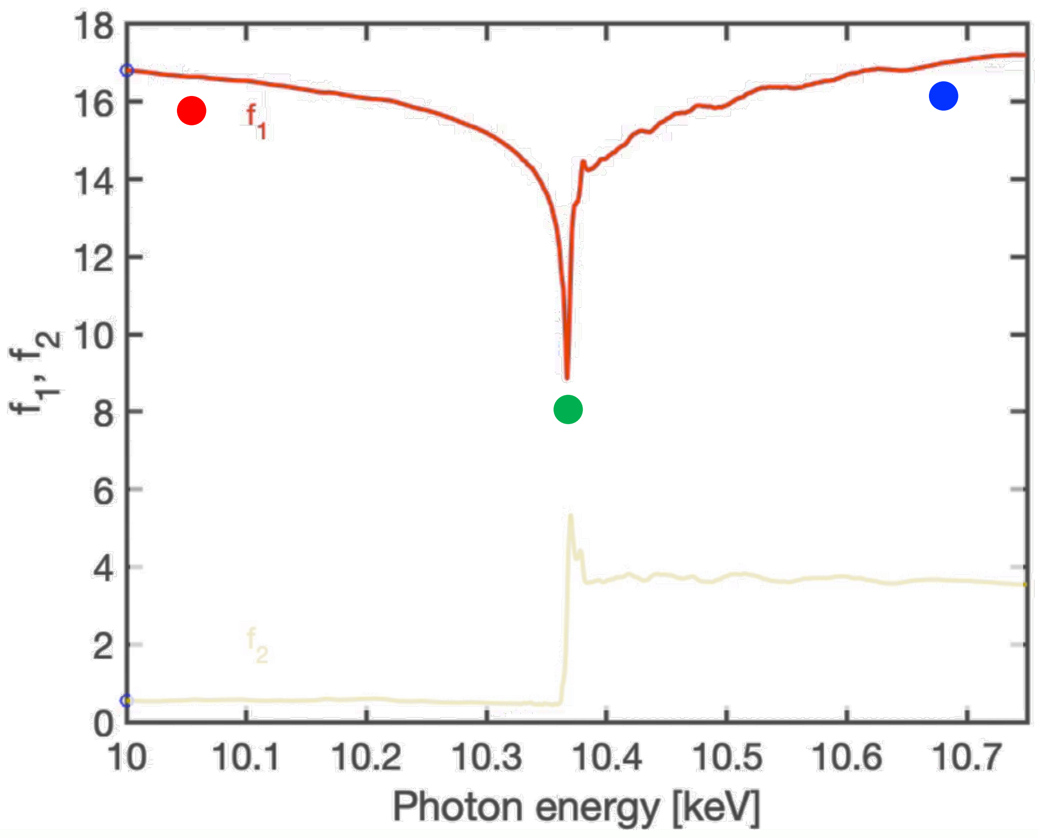
Atomic response to x-rays



Take-home message:

Most electrons in atoms can be considered to be quasi “free” for $h\nu$ > keV

Correction terms to f: f’



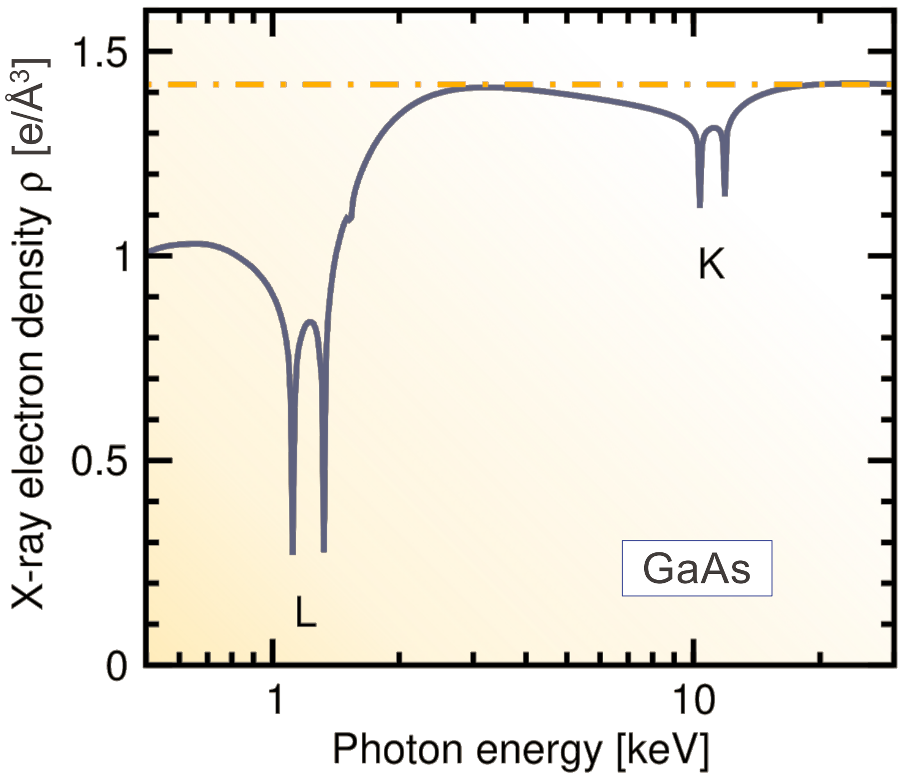
- $h\nu < E_B$
  - Reduced response from those electrons that are bound ⇒ small reduction in scattering factor
  - Add a negative component f’
  - f’ is a function of hν
- $h\nu \gg E_B$
  - Electron quasi “free”
  - f’ ⇒ 0
- $h\nu \simeq E_B$
  - Resonance
  - Enhanced response ⇒ maximal |f’|

$$f_1(Q, \hbar\omega) = f^0(Q) + f'(\hbar\omega)$$

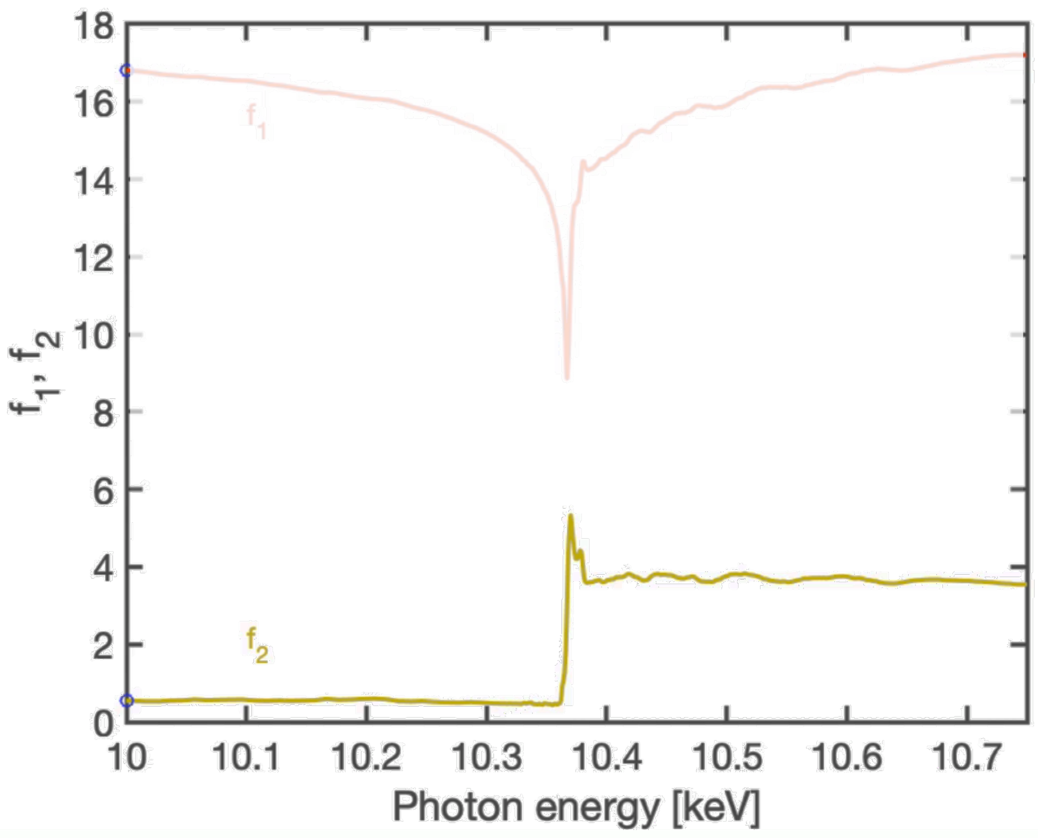
$$f'(\hbar\omega) < 0$$

f' accounts for damped oscillation amplitude

- Effect of f' is to make the atom "appear" from the perspective of the x-rays to have fewer electrons (< Z) than far above an absorption edge
  - ρ as "seen" by x-rays decreases
  - Scattering strength decreases near absorption edges



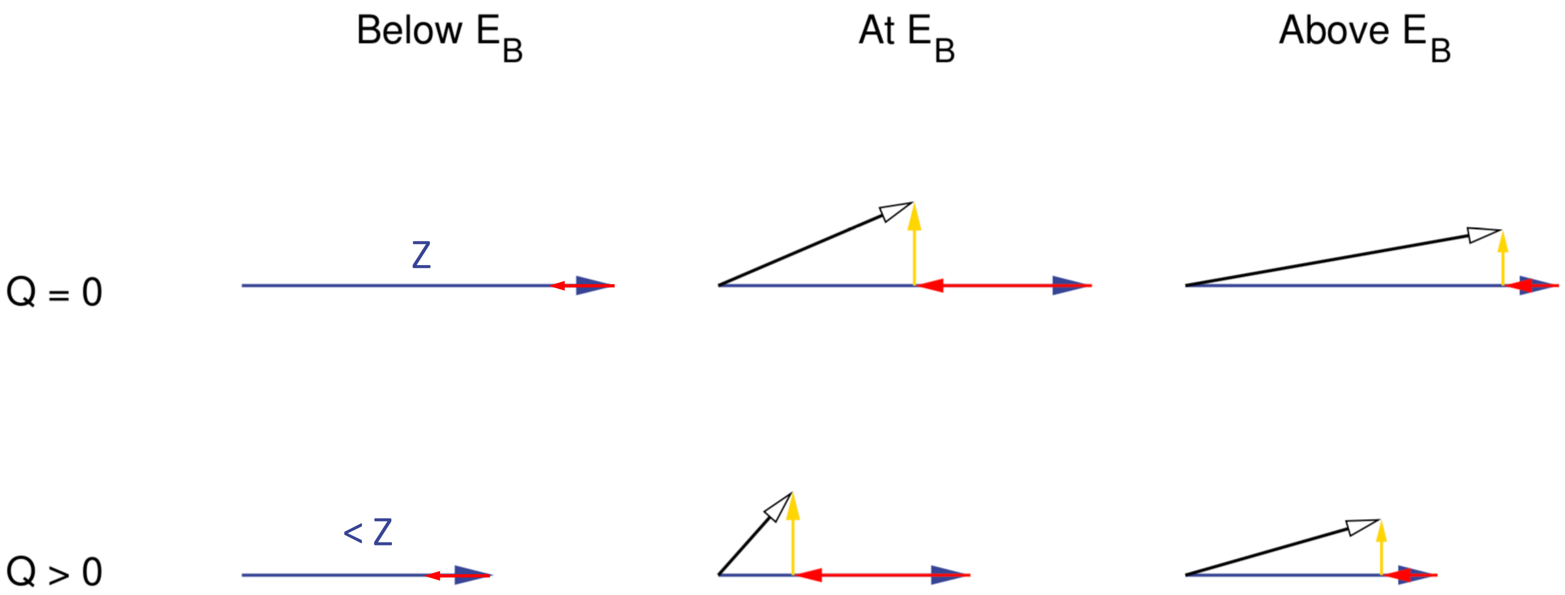
Correction terms to f: f''



- $h\nu \simeq E_B$
  - Resonance
  - Enhanced response ⇒ maximal |f'|
  - Phase shift @ resonance = $\pi/2$
    - Express as imaginary component if''
    - f' a function of $h\nu$
    - Results in energy dissipation (absorption)

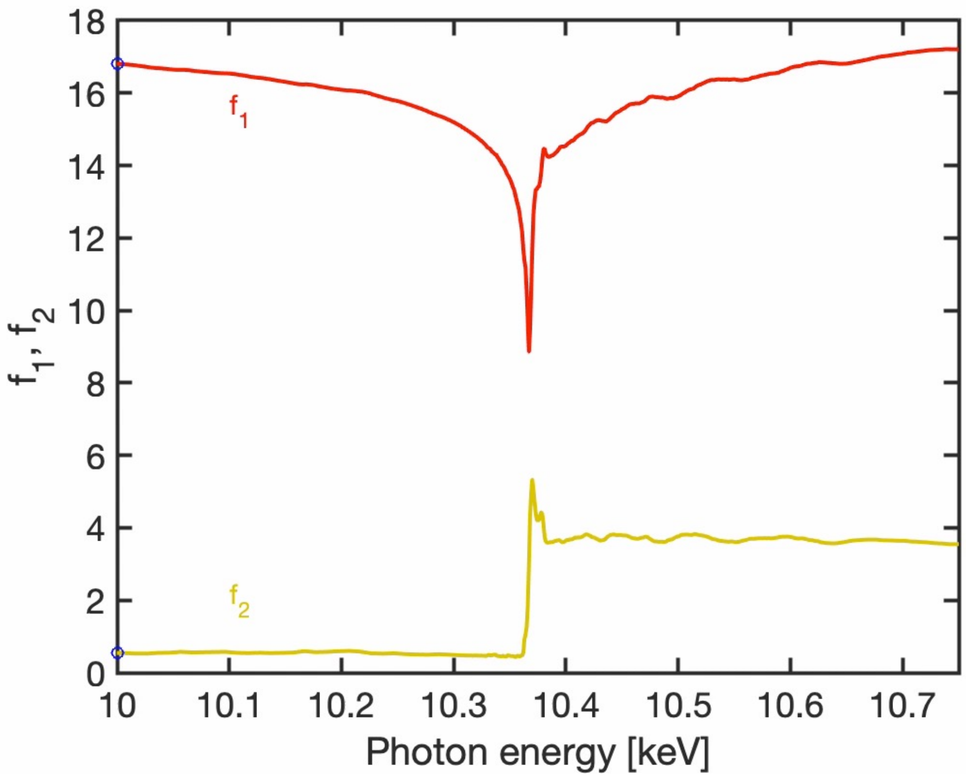
$$f_2 = f'' = \frac{\sigma_a}{2\lambda r_0}$$

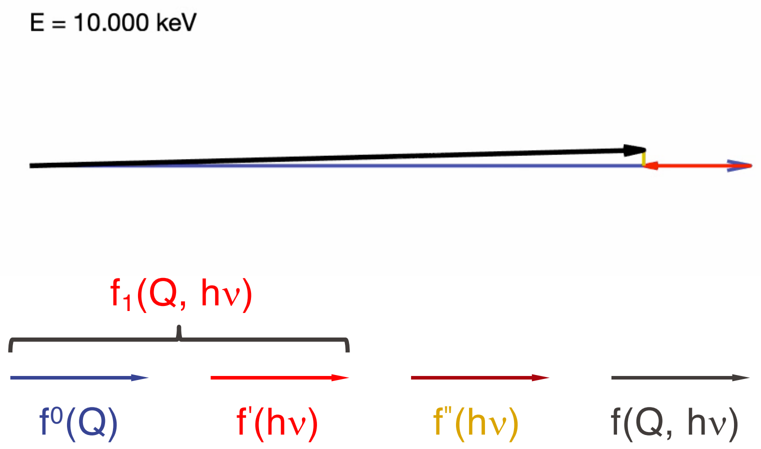
Summary of correction terms f’ and f”



$$f(Q, \hbar\omega) = \underbrace{f^0(Q) + f'(\hbar\omega)}_{f_1(Q,\, \hbar\omega)} + \underbrace{if''(\hbar\omega)}_{if_2(\hbar\omega)}$$

Change in f for Ga @ K-edge and Q = 4.45 Å^{-1}





Coming up…