Today's Outline - August 24, 2016

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- Scattering from molecules and crystals

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- X-ray absorption

Scattering from molecules

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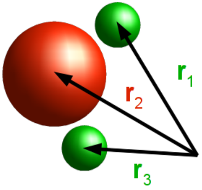

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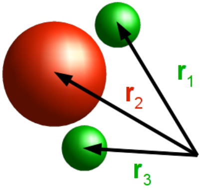

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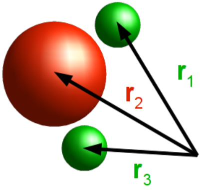

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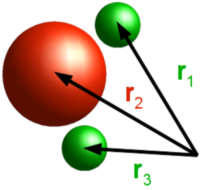

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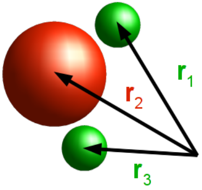

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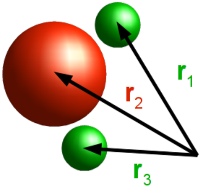

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Scattering from a crystal

and similarly, to a crystal lattice ...

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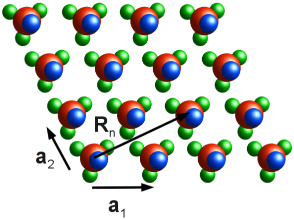

. . . which is simply a periodic array of molecules

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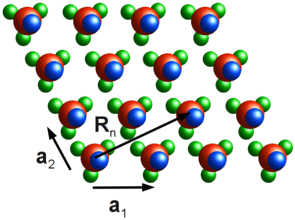

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$$F^{crystal}(\mathbf{Q}) = F^{molecule} F^{lattice}$$

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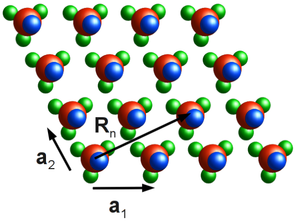

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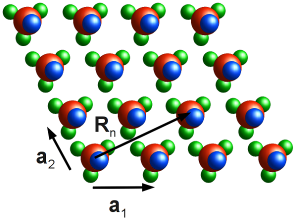

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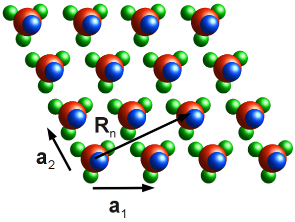

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The lattice term, $\sum e^{i\mathbf{Q}\cdot\mathbf{R}_n}$, is a sum over a large number so it is always small unless $\mathbf{Q}\cdot\mathbf{R}_n = 2\pi m$ where $\mathbf{R}_n = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$ is a real space lattice vector and m is an integer.

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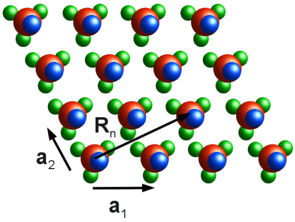

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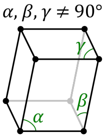
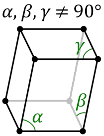
Crystal lattices

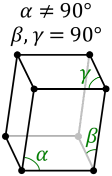
There are 7 possible real space lattices: triclinic,



Crystal lattices

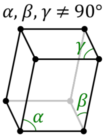
There are 7 possible real space lattices: triclinic, monoclinic,

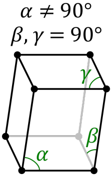


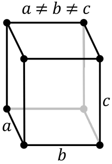


Crystal lattices

There are 7 possible real space lattices: triclinic, monoclinic, orthorhombic,







Crystal lattices

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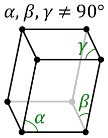

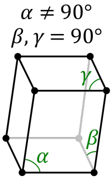

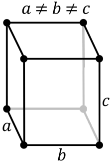

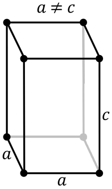

Crystal lattices

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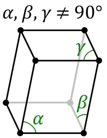

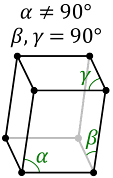

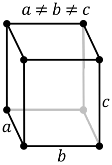

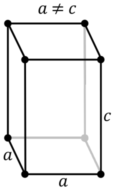

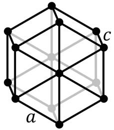

Crystal lattices

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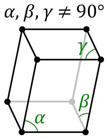
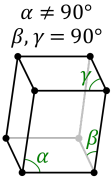
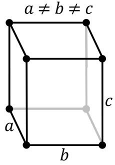
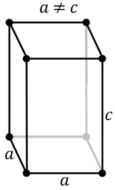
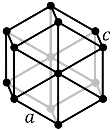
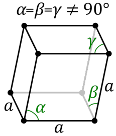






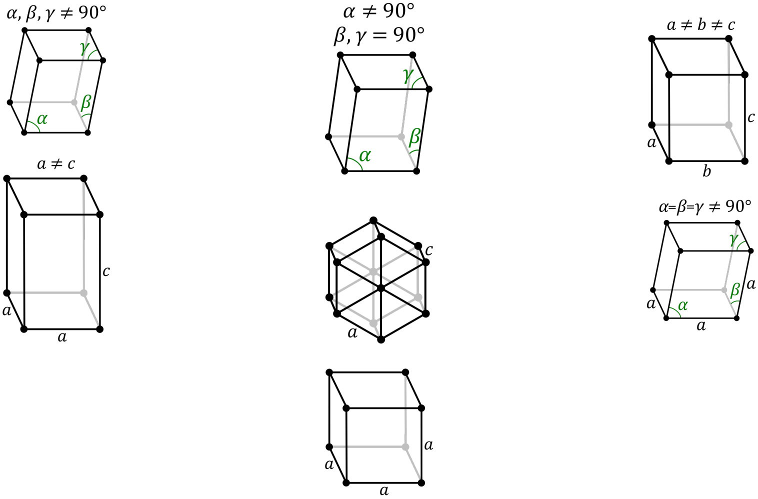






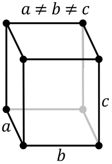
Crystal lattices

There are 7 possible real space lattices: triclinic, monoclinic, orthorhombic, tetragonal, hexagonal, rhombohedral, cubic



Lattice properties

Consider the orthorhombic lattice for simplicity (the others give exactly the same result).



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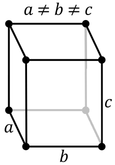

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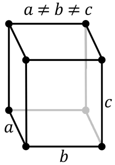

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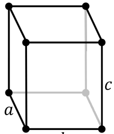

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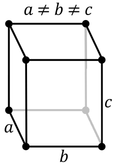

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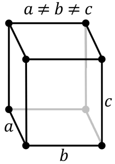

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A simple way of calculating the volume of the unit cell!

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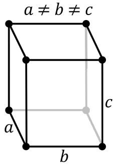

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This unit cell is repeated infintely in 3-dimensions and thus, the location of each lattice point can be calculated relative to any arbitrary lattice point designated as the origin.

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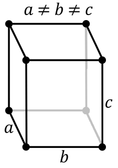

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Each lattice point is at the end of a lattice vector, $\mathbf{R}_n$

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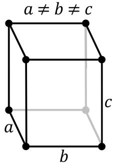

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$$\mathbf{R}_n = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$$

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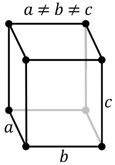
Consider the orthorhombic lattice for simplicity (the others give exactly the same result).



$$\mathbf{a}_1 = a\hat{\mathbf{x}}, \quad \mathbf{a}_2 = b\hat{\mathbf{y}}, \quad \mathbf{a}_3 = c\hat{\mathbf{z}}$$
$$\mathbf{a}_1 \times \mathbf{a}_2 = ab\hat{\mathbf{z}}$$
$$(\mathbf{a}_1 \times \mathbf{a}_2) \cdot \mathbf{a}_3 = ab\hat{\mathbf{z}} \cdot c\hat{\mathbf{z}}$$
$$(\mathbf{a}_1 \times \mathbf{a}_2) \cdot \mathbf{a}_3 = abc = V$$

A simple way of calculating the volume of the unit cell!

This unit cell is repeated infintely in 3-dimensions and thus, the location of each lattice point can be calculated relative to any arbitrary lattice point designated as the origin.

Each lattice point is at the end of a lattice vector, $\mathbf{R}_n$ and a crystal is made by putting a molecule at each lattice point.

$$\mathbf{R}_n = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$$

Reciprocal lattice

For any lattice in real space, it is useful to construct what is called a reciprocal space lattice.

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where h, k, and l are integers called Miller indices

Laue condition

Because of the construction of the reciprocal lattice

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$\mathbf{G}_{hkl} \cdot \mathbf{R}_n$

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$$\mathbf{G}_{hkl} \cdot \mathbf{R}_n = (n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3) \cdot (h\mathbf{a}_1^* + k\mathbf{a}_2^* + l\mathbf{a}_3^*)$$

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As we shall see later, this Laue condition, is equivalent to the more typically used Bragg condition for diffraction: $2d\sin\theta = n\lambda$

Multiple slit interference

A crystal is, therefore, a diffraction grating with $\sim 10^{20}$ slits!

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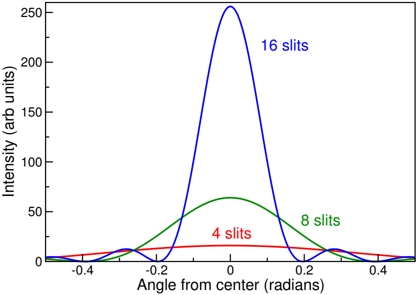

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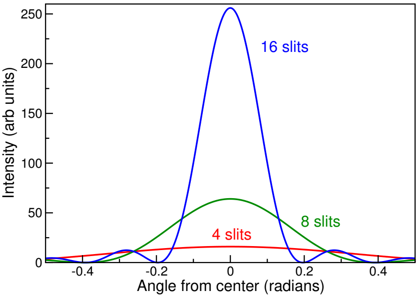

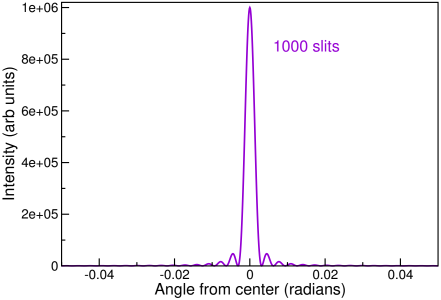

Compton scattering

A photon-electron collision

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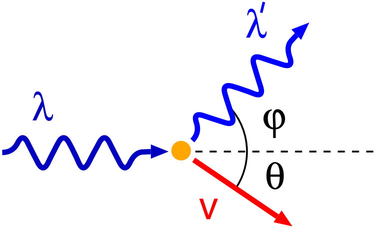

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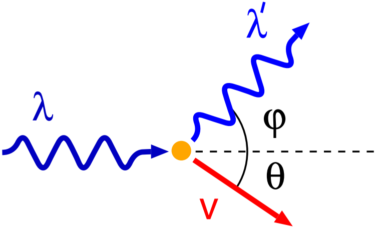

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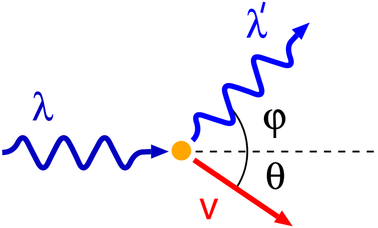

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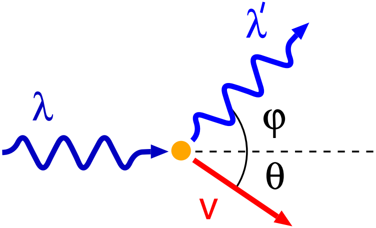

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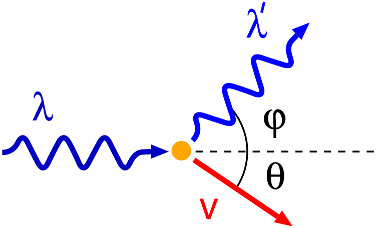

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Treat the electron relativistically and conserve energy and momentum

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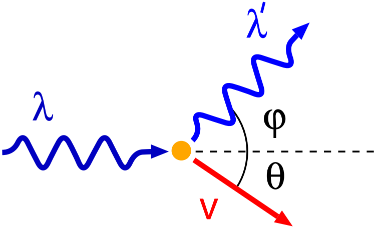

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$$mc^2 + \frac{hc}{\lambda} = \frac{hc}{\lambda'} + \gamma mc^2 \quad \text{(energy)}$$

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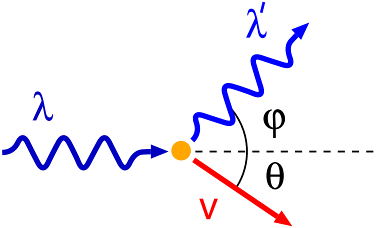

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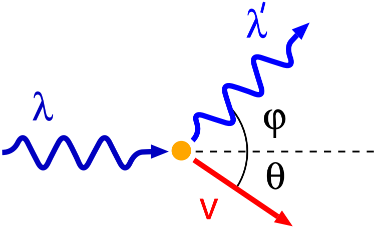

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Compton scattering derivation

squaring the momentum equations

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$$\left(\frac{h}{\lambda} - \frac{h}{\lambda'}\cos\phi\right)^2 = \gamma^2 m^2 v^2 \cos^2\theta$$

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now add them together,

$$\gamma^2 m^2 v^2 \left(\sin^2\theta + \cos^2\theta\right) = \left(\frac{h}{\lambda} - \frac{h}{\lambda'}\cos\phi\right)^2 + \left(-\frac{h}{\lambda'}\sin\phi\right)^2$$

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now add them together, substitute $\sin^2\theta + \cos^2\theta = 1$, expand the squares,

$$\gamma^2 m^2 v^2 \left(\sin^2\theta + \cos^2\theta\right) = \left(\frac{h}{\lambda} - \frac{h}{\lambda'}\cos\phi\right)^2 + \left(-\frac{h}{\lambda'}\sin\phi\right)^2$$

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$$\frac{m^2 v^2}{1-\beta^2} = \frac{h^2}{\lambda^2} - \frac{2h^2}{\lambda\lambda'}\cos\phi + \frac{h^2}{\lambda'^2}$$

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now add them together, substitute $\sin^2\theta + \cos^2\theta = 1$, expand the squares, and $\sin^2\phi + \cos^2\phi = 1$, then rearrange and substitute $v = \beta c$

$$\gamma^2 m^2 v^2 \left(\sin^2\theta + \cos^2\theta\right) = \left(\frac{h}{\lambda} - \frac{h}{\lambda'}\cos\phi\right)^2 + \left(-\frac{h}{\lambda'}\sin\phi\right)^2$$

$$\gamma^2 m^2 v^2 = \frac{h^2}{\lambda^2} - \frac{2h^2}{\lambda\lambda'}\cos\phi + \frac{h^2}{\lambda'^2}\sin^2\phi + \frac{h^2}{\lambda'^2}\cos^2\phi$$

$$\frac{m^2 c^2 \beta^2}{1-\beta^2} = \frac{m^2 v^2}{1-\beta^2} = \frac{h^2}{\lambda^2} - \frac{2h^2}{\lambda\lambda'}\cos\phi + \frac{h^2}{\lambda'^2}$$

Compton scattering derivation (cont.)

Now take the energy equation and square it,

$$\left(mc^2 + \frac{hc}{\lambda} - \frac{hc}{\lambda'}\right)^2 = \gamma^2 m^2 c^4 = \frac{m^2 c^4}{1-\beta^2}$$

Compton scattering derivation (cont.)

Now take the energy equation and square it, then solve it for β^2

$$\left(mc^2 + \frac{hc}{\lambda} - \frac{hc}{\lambda'}\right)^2 = \gamma^2 m^2 c^4 = \frac{m^2 c^4}{1-\beta^2}$$

$$\beta^2 = 1 - \frac{m^2 c^4}{\left(mc^2 + \frac{hc}{\lambda} - \frac{hc}{\lambda'}\right)^2}$$

Compton scattering derivation (cont.)

Now take the energy equation and square it, then solve it for β^2 which is substituted into the equation from the momentum.

$$\left(mc^2 + \frac{hc}{\lambda} - \frac{hc}{\lambda'}\right)^2 = \gamma^2 m^2 c^4 = \frac{m^2 c^4}{1-\beta^2}$$

$$\beta^2 = 1 - \frac{m^2 c^4}{\left(mc^2 + \frac{hc}{\lambda} - \frac{hc}{\lambda'}\right)^2}$$

$$\frac{h^2}{\lambda^2} + \frac{h^2}{\lambda'^2} - \frac{2h^2}{\lambda\lambda'}\cos\phi = \frac{m^2 c^2 \beta^2}{1-\beta^2}$$

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Compton scattering derivation (cont.)

$$\frac{h^2}{\lambda^2} + \frac{h^2}{\lambda'^2} - \frac{2h^2}{\lambda\lambda'}\cos\phi = \left(mc + \frac{h}{\lambda} - \frac{h}{\lambda'}\right)^2 - m^2c^2$$

Compton scattering derivation (cont.)

After expansion,

$$\frac{h^2}{\lambda^2} + \frac{h^2}{\lambda'^2} - \frac{2h^2}{\lambda\lambda'}\cos\phi = \left(mc + \frac{h}{\lambda} - \frac{h}{\lambda'}\right)^2 - m^2c^2$$

$$= m^2c^2 + \frac{h^2}{\lambda^2} + \frac{h^2}{\lambda'^2} - \frac{2mch}{\lambda} - \frac{2mch}{\lambda'} + \frac{2h^2}{\lambda\lambda'} - m^2c^2$$

Compton scattering derivation (cont.)

After expansion, cancellation,

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Compton scattering derivation (cont.)

After expansion, cancellation, and rearrangement, we obtain

$$\frac{h^2}{\lambda^2} + \frac{h^2}{\lambda'^2} - \frac{2h^2}{\lambda\lambda'}\cos\phi = \left(mc + \frac{h}{\lambda} - \frac{h}{\lambda'}\right)^2 - m^2c^2$$

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Compton scattering derivation (cont.)

After expansion, cancellation,

$$\frac{h^2}{\lambda^2} + \frac{h^2}{\lambda'^2} - \frac{2h^2}{\lambda\lambda'}\cos\phi = \left(mc + \frac{h}{\lambda} - \frac{h}{\lambda'}\right)^2 - m^2c^2$$

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$$\frac{2h^2}{\cancel{\lambda\lambda'}}(1-\cos\phi) = 2m\left(\frac{hc}{\lambda} - \frac{hc}{\lambda'}\right) = 2mhc\left(\frac{\lambda'-\lambda}{\lambda\lambda'}\right) = \frac{2mhc\Delta\lambda}{\cancel{\lambda\lambda'}}$$

$$\Delta\lambda = \frac{h}{mc}(1-\cos\phi)$$

Compton scattering results

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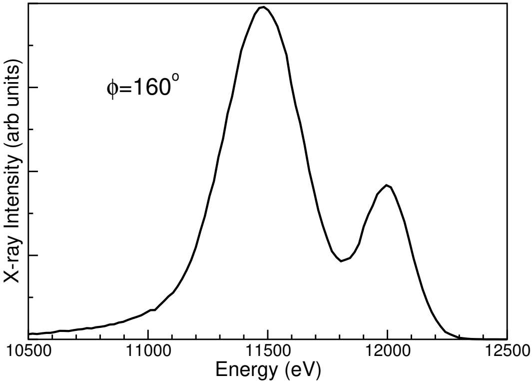
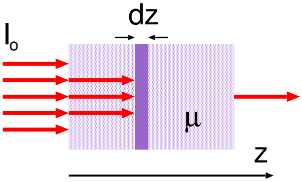


X-ray absorption



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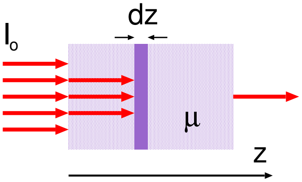

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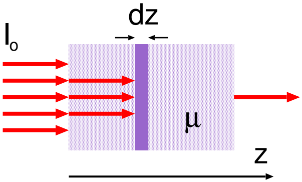

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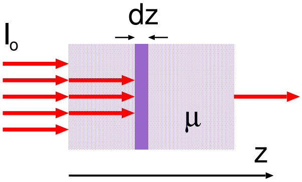

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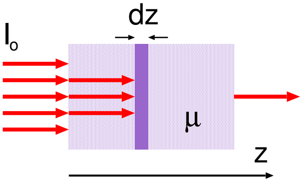

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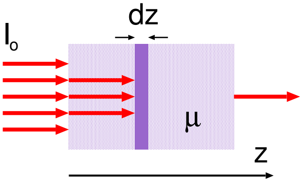

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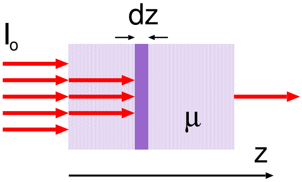

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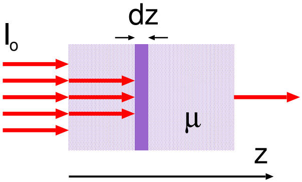

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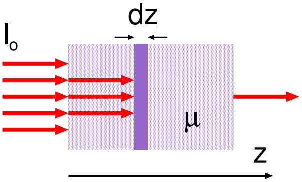

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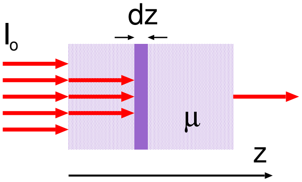

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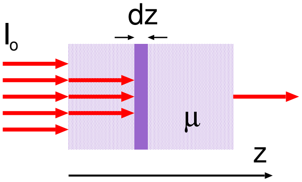

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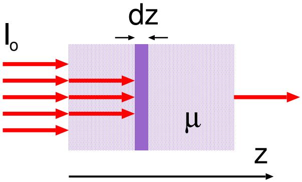

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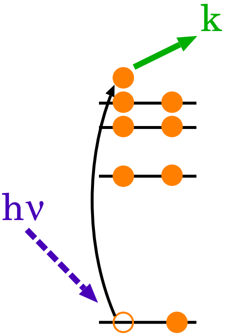
This is just Beer's law with an absorption coefficient which depends on x-ray parameters.

Absorption event



- X-ray is absorbed by an atom

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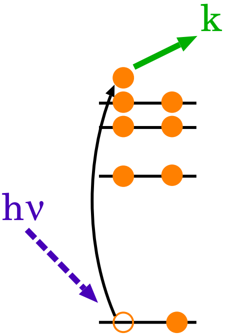

- X-ray is absorbed by an atom
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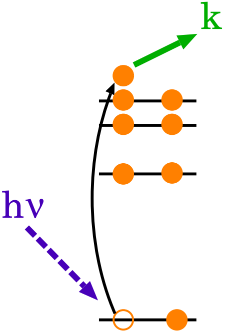

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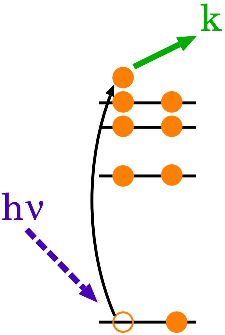
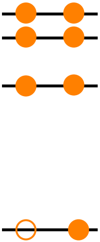


- X-ray is absorbed by an atom
- Energy is transferred to a core electron
- Electron escapes atomic potential into the continuum
- Ion remains with a core-hole

Fluorescence emission

An ion with a core-hole is quite unstable ($\approx 10^{-15}$s)



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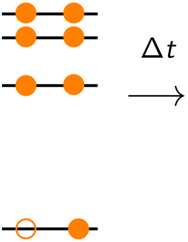
- After a short time a higher level electron will drop down in energy to fill the core hole



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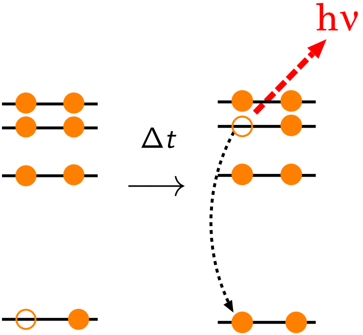

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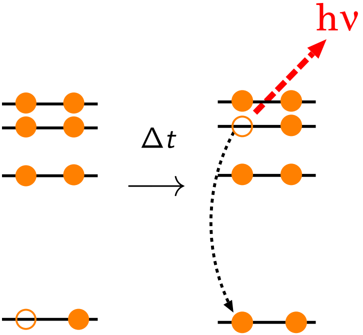

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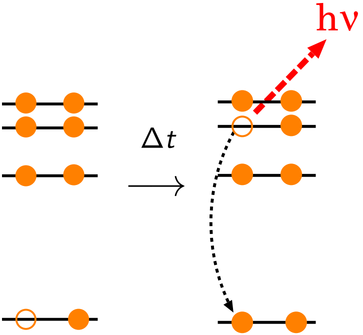

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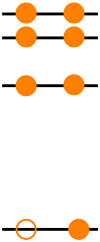
- The result is a cascade of fluorescence photons which are characteristic of the absorbing atom

Auger emission

While fluorescence is the most probable method of core-hole relaxation there are other possible mechanisms



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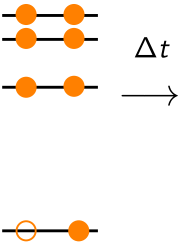

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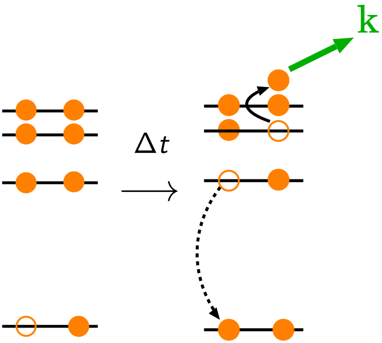

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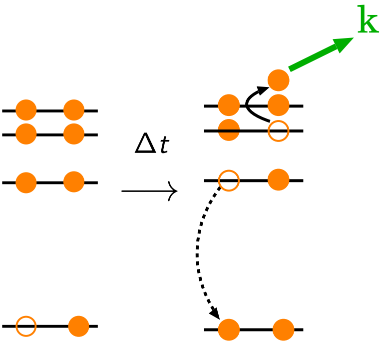

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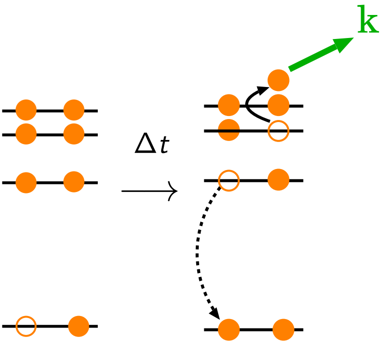

- In the Auger process, a higher level electron will drop down in energy to fill the core hole
- The energy liberated causes the secondary emission of an electron
- This leaves two holes which then filled from higher shells
- So that the secondary electron is accompanied by fluorescence emissions at lower energies

Absorption coefficient

The absorption coefficient μ, depends strongly on the x-ray energy E, the atomic number of the absorbing atoms Z, as well as the density ρ, and atomic mass A:

$$\mu \sim \frac{\quad}{\quad}$$

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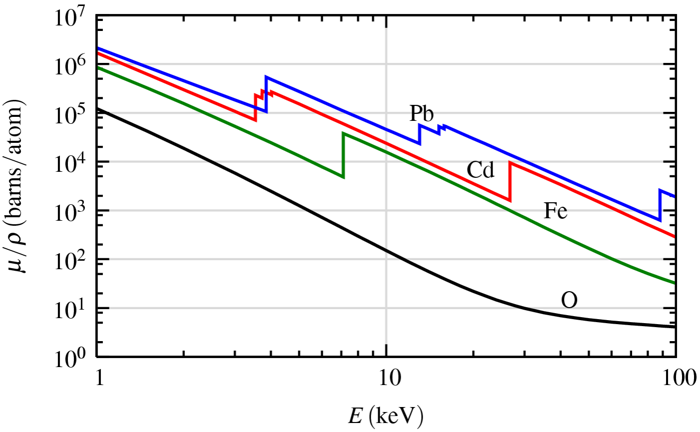
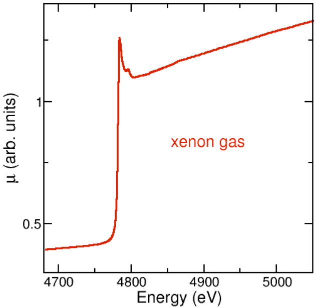


Absorption coefficient

Isolated gas atoms show a sharp jump and a smooth curve



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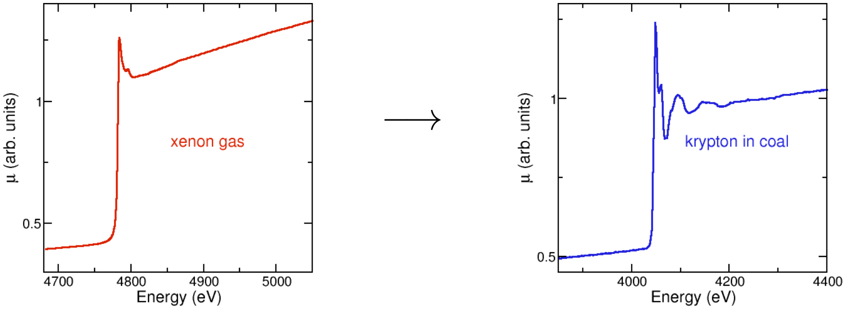
Absorption coefficient

Isolated gas atoms show a sharp jump and a smooth curve
Atoms in a solid or liquid show fine structure after the absorption edge called XANES and EXAFS



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For an elemental material, the absorption coefficient, μ, is simply the product of the atomic density, ρ_a, times the atomic absorption cross-section, σ_a.

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