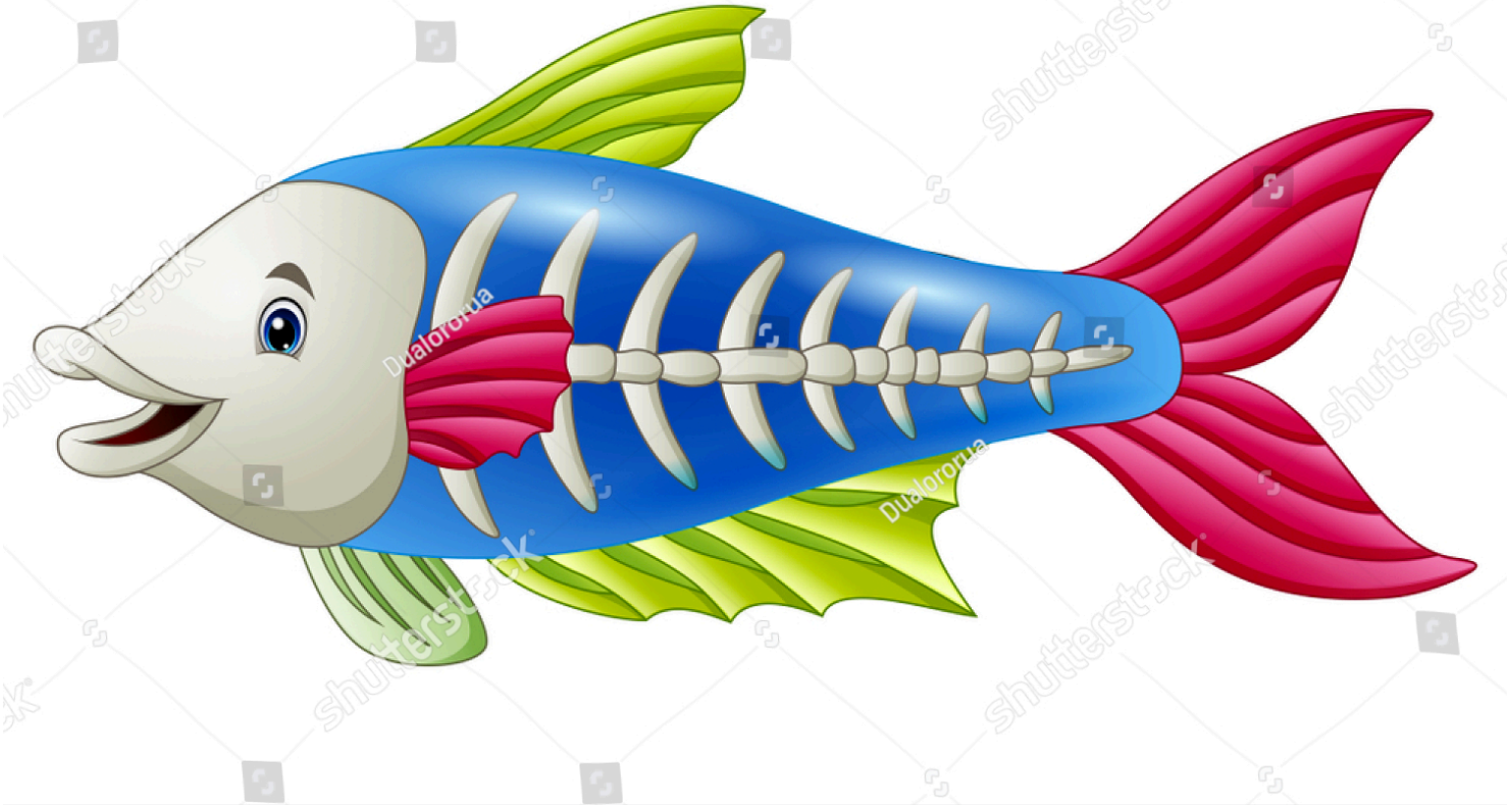
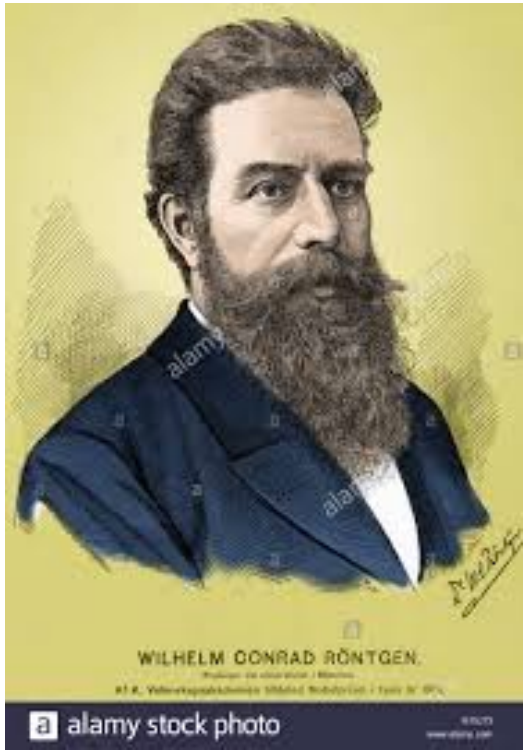
Atomic Physics

Chapter 6 X ray



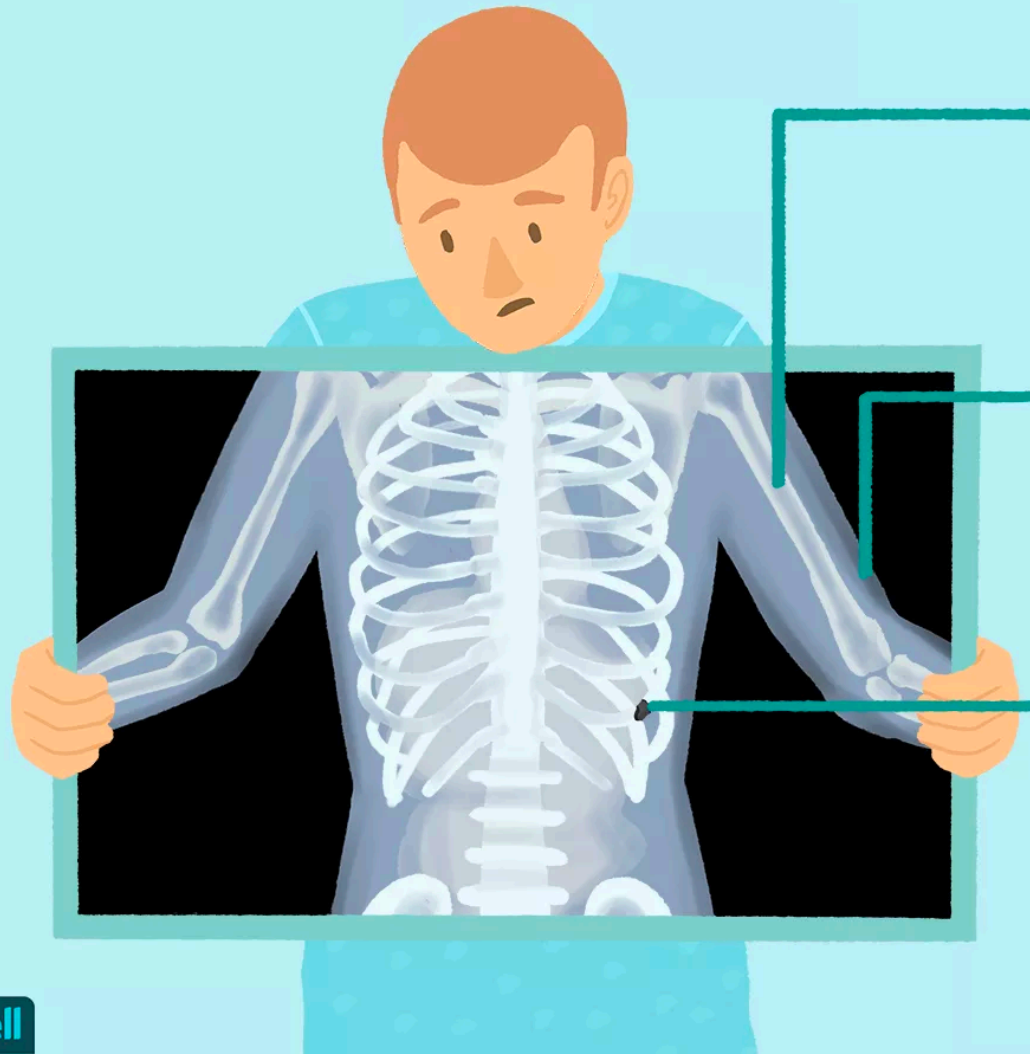
6.1 The discovery of X ray

X-rays were discovered in 1895 by the German physicist Wilhelm Roentgen. He found that a beam of high-speed electrons striking a metal target produced a new and extremely penetrating type of radiation.





How to Read an X-Ray



Bones

Block radiation, appear white

Muscle, Fluid, Fats

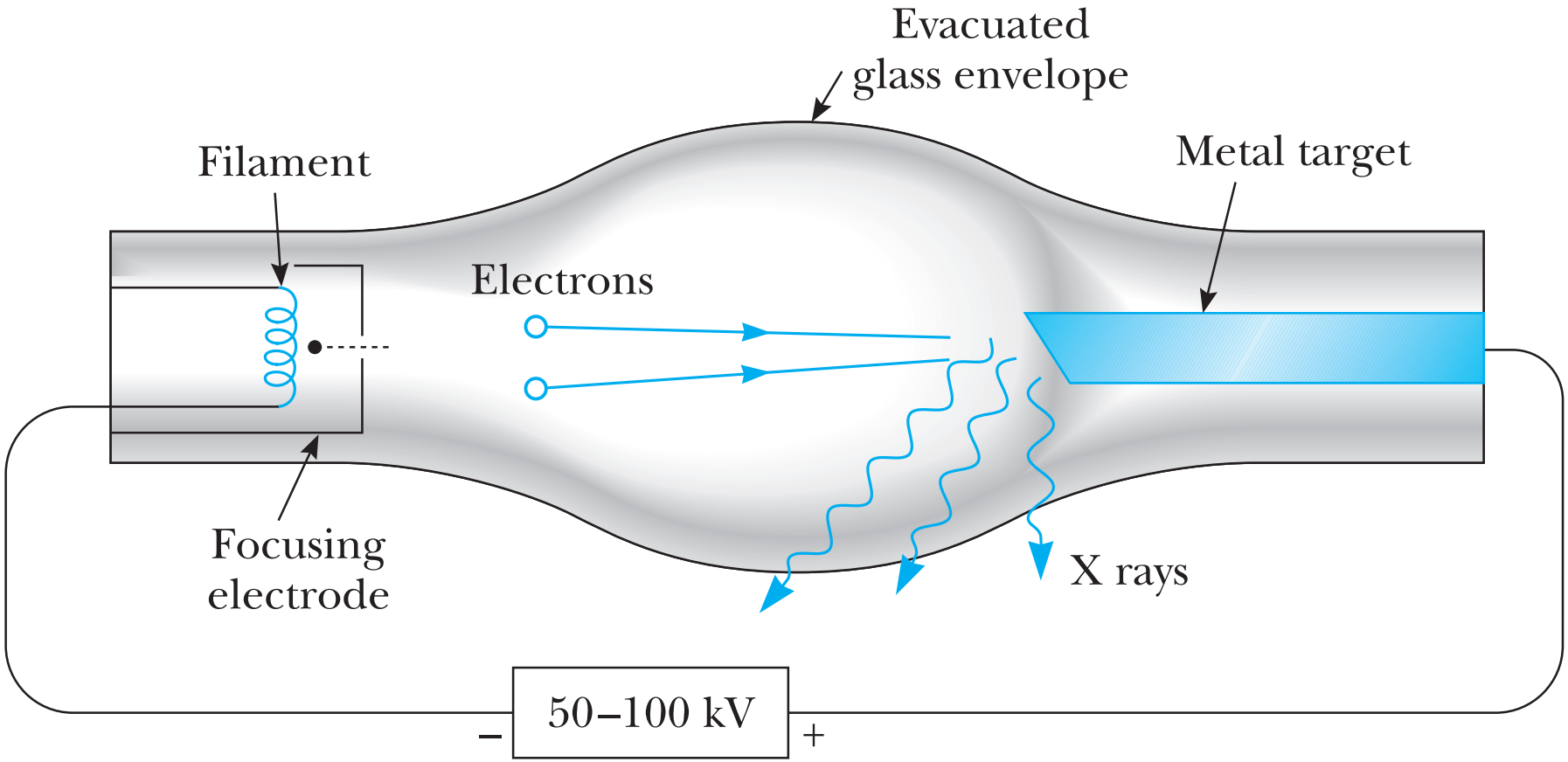
Some radiation passes through, appear grey

Breaks, Fractures

Radiation passes completely through, appear black

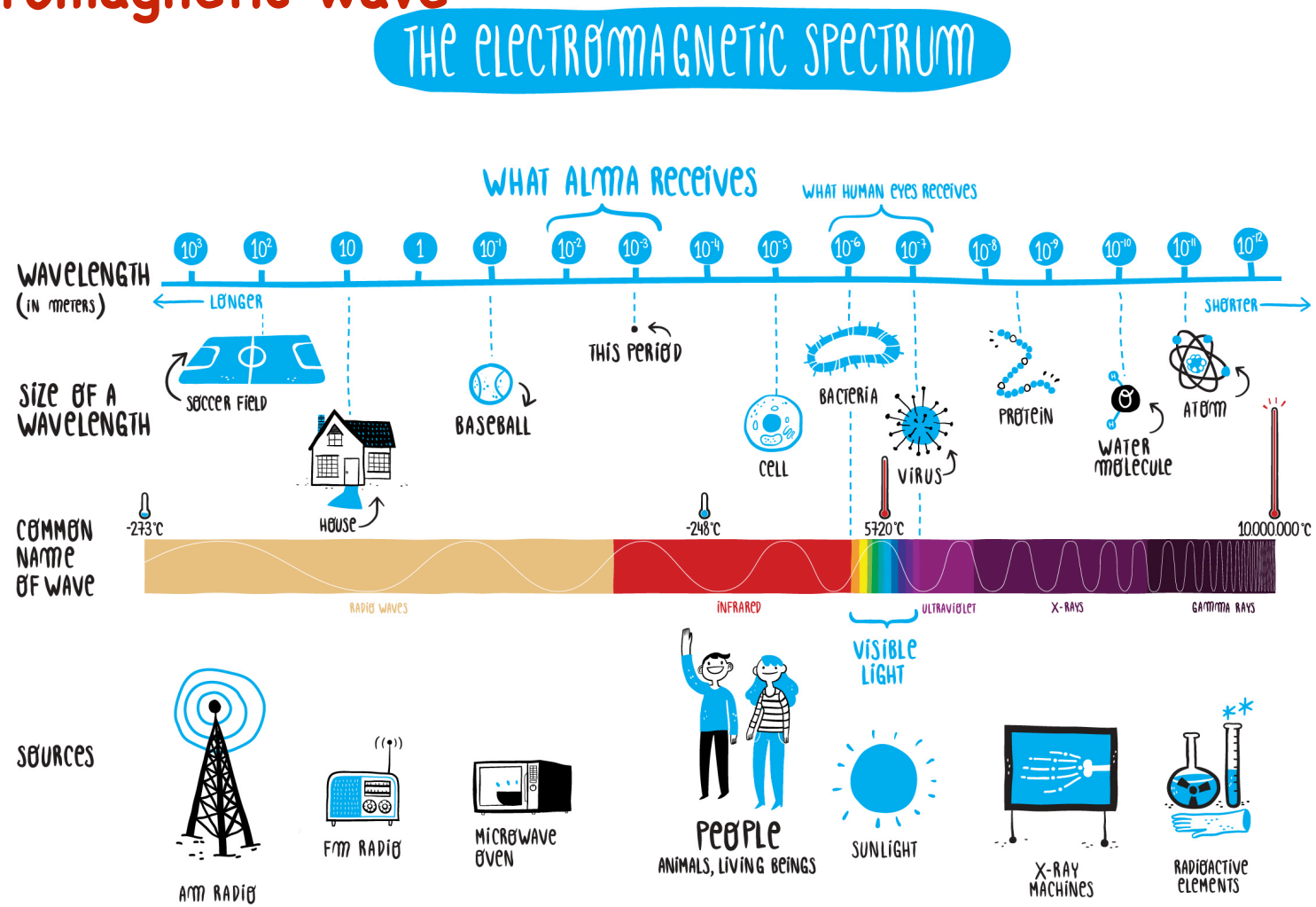
verywell

X-rays Tube

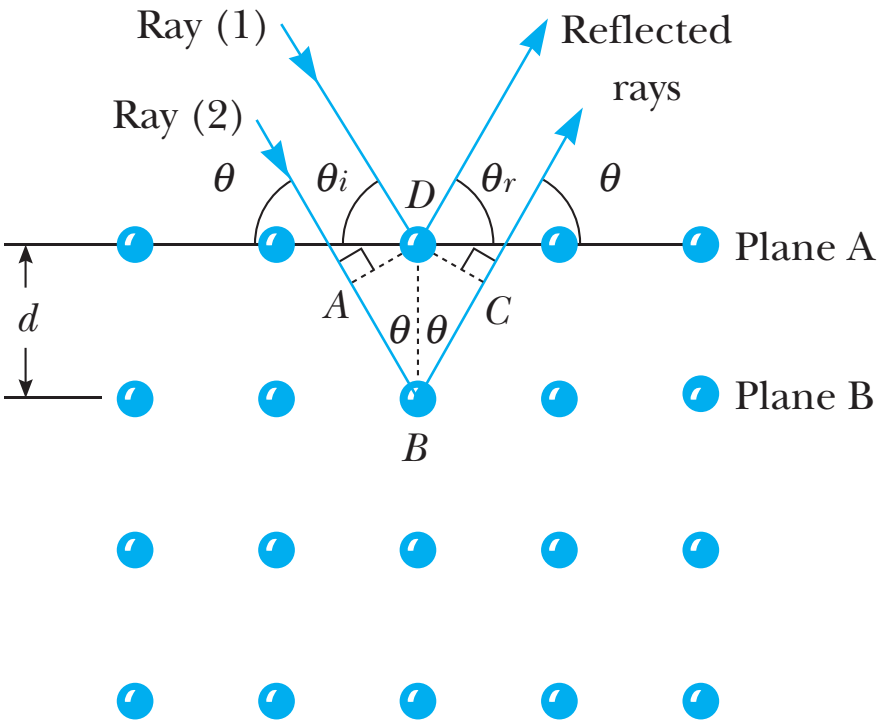

Evacuated
glass envelope
Filament
Metal target
Electrons
Focusing
electrode
X rays
50–100 kV
–
+

6.1 The discovery of X ray

Electromagnetic wave

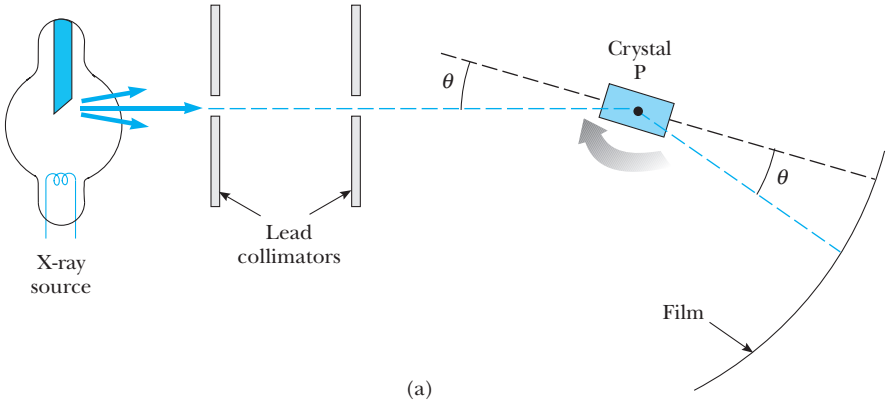


X ray diffraction

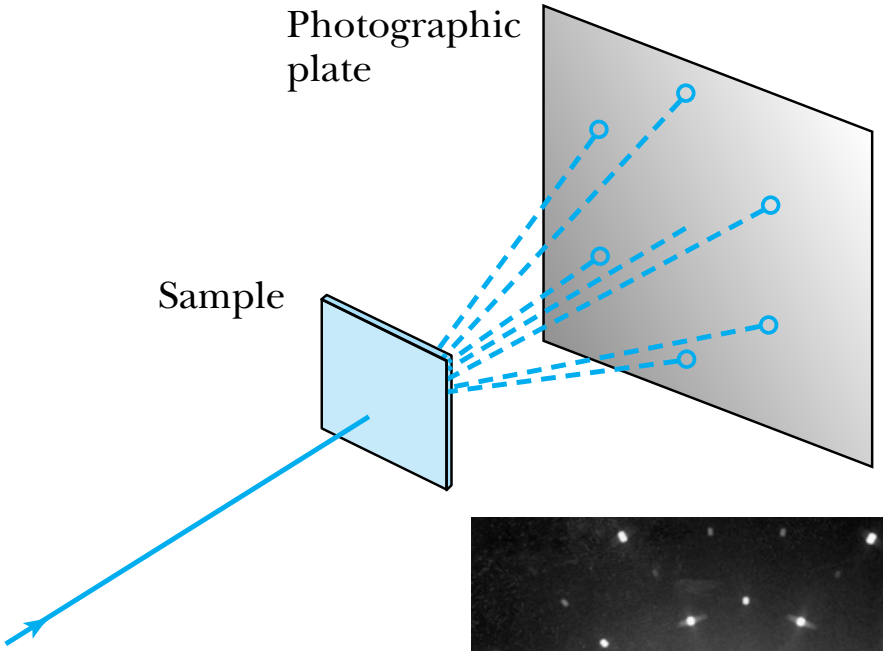


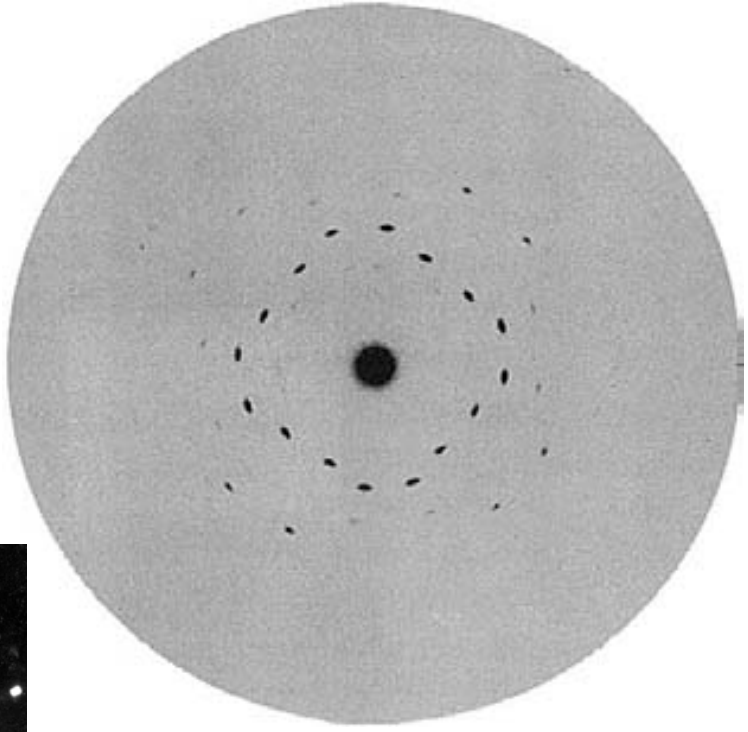
Bragg equation

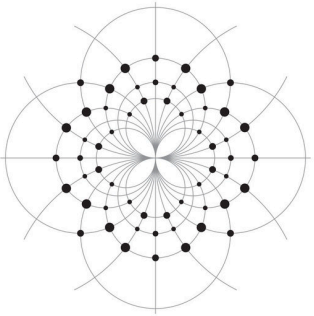
$$n\lambda = 2d \sin\theta \qquad n = 1, 2, 3, \ldots$$

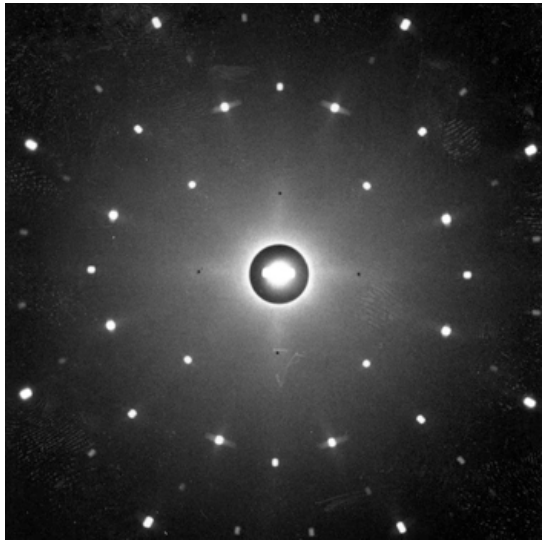


Laue diffraction transmission method

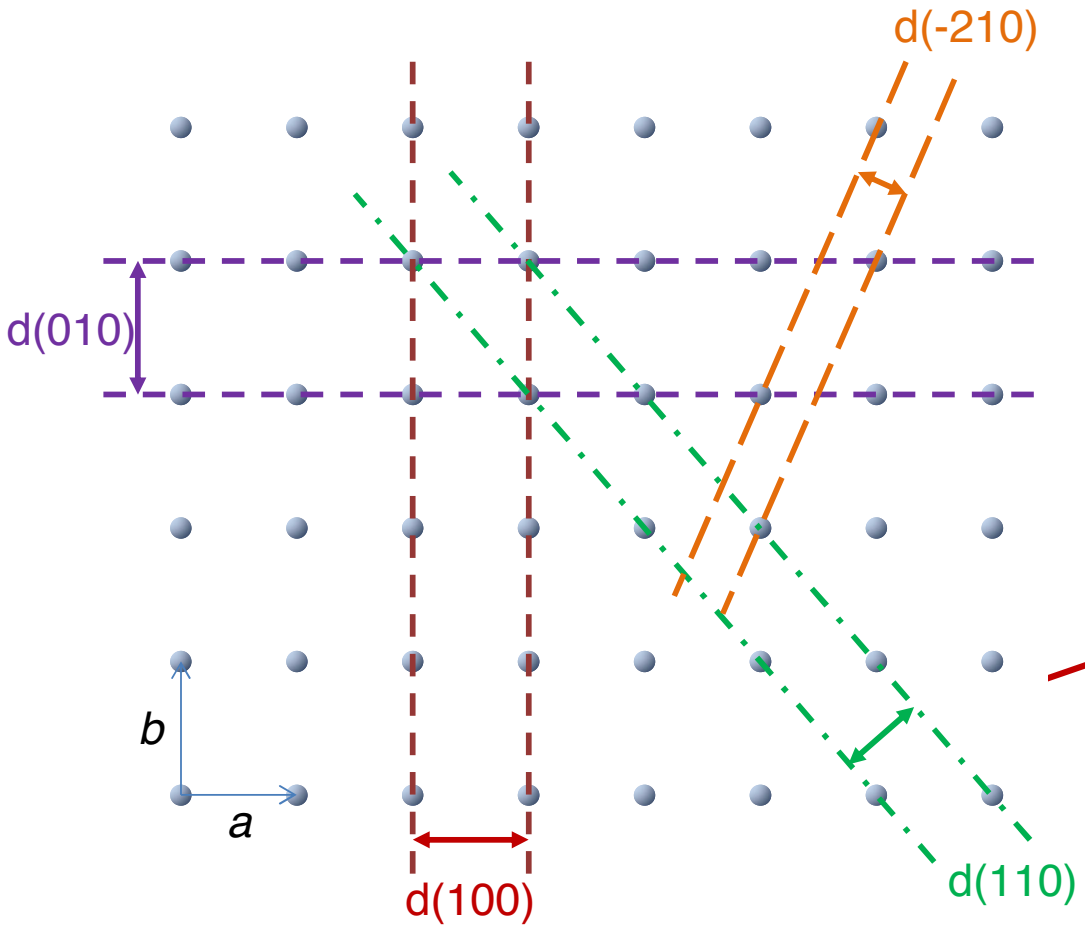


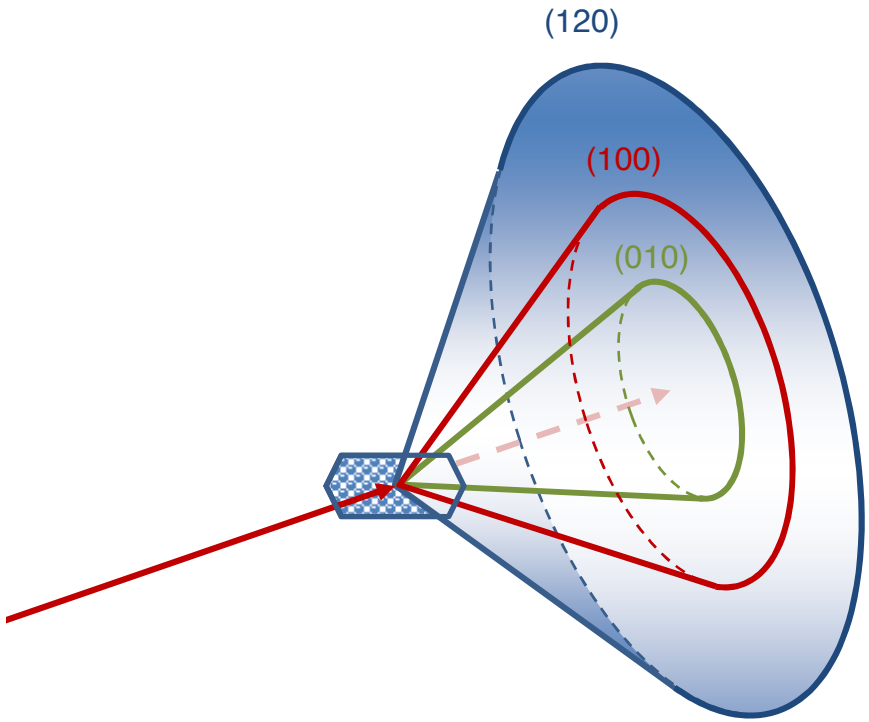






The diffraction of X ray





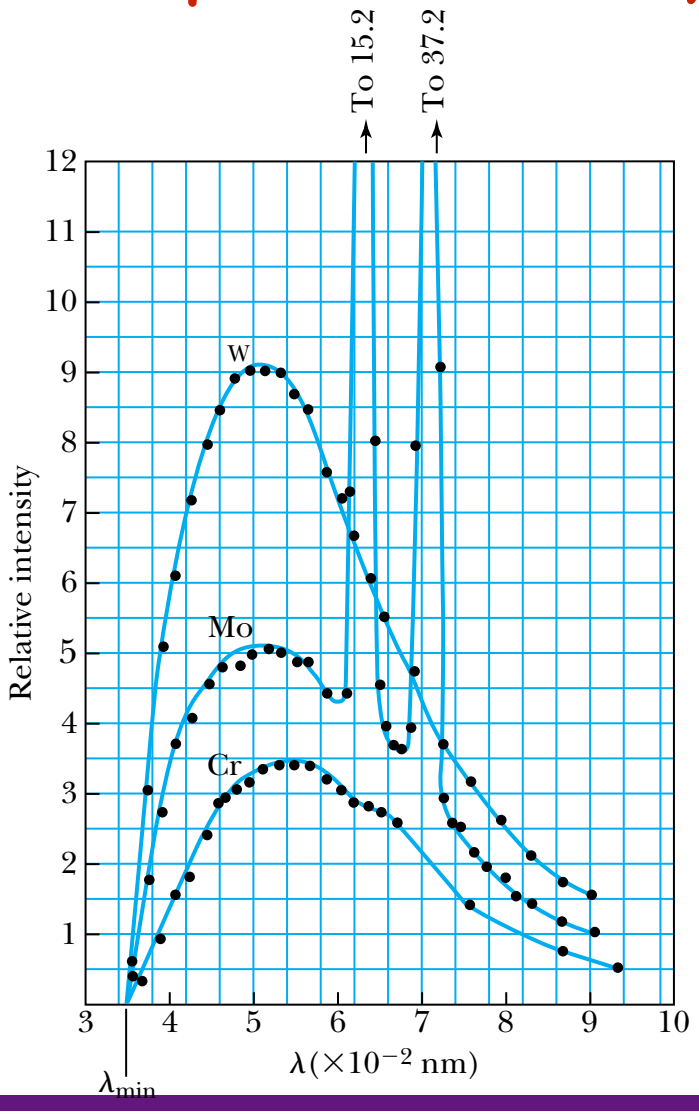
6.1 The discovery of X ray

The polarization of X ray

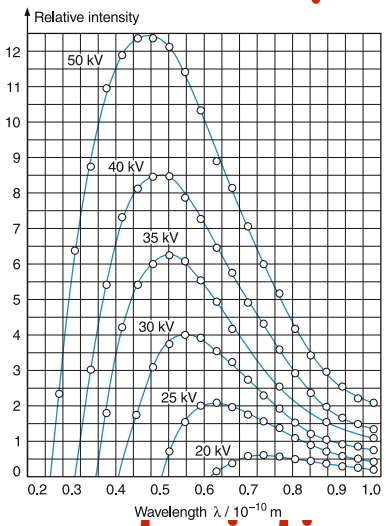


6.2 X ray production

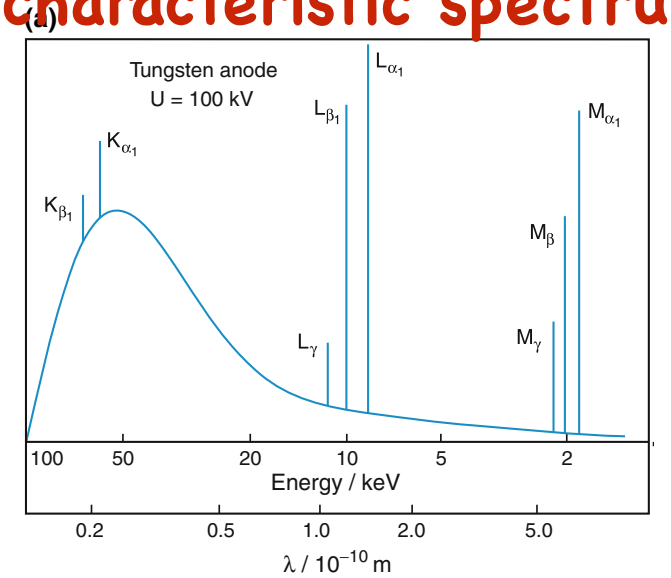
The spectrum of X ray



The continuous spectrum



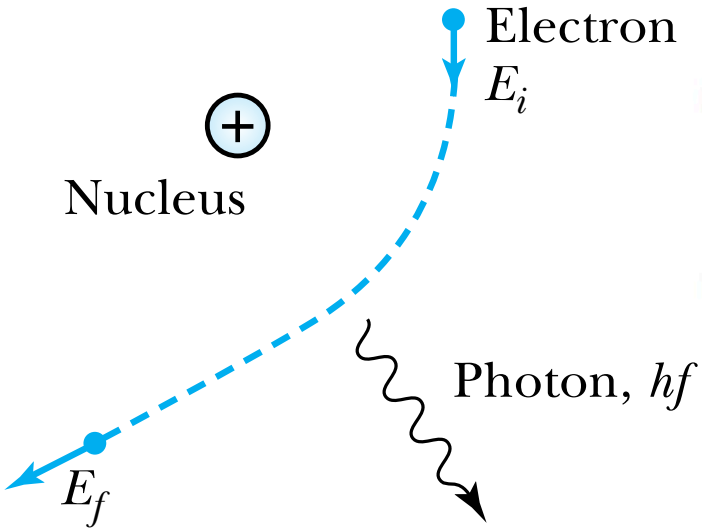
The characteristic spectrum

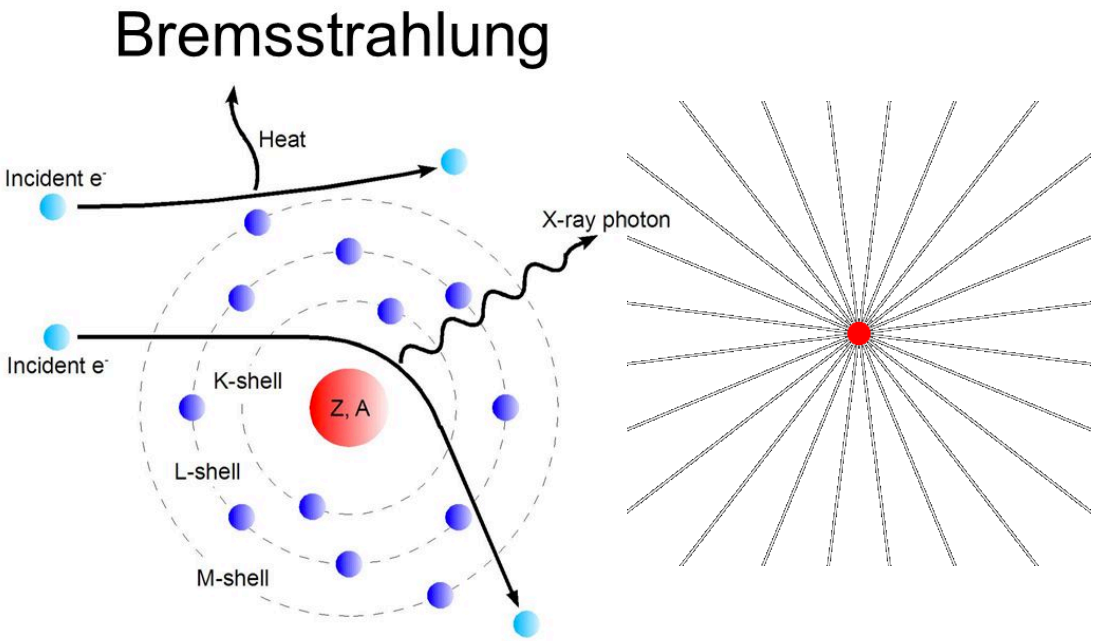


6.2 X ray production

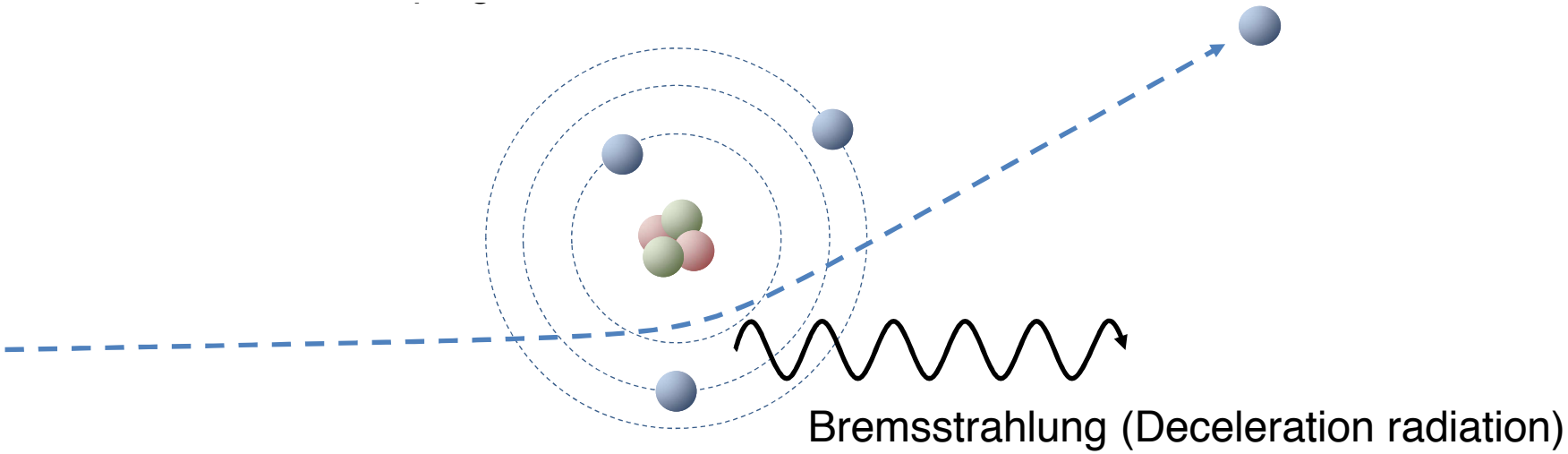
The continuous spectrum:

An energetic electron passing through matter will radiate photons and lose kinetic energy. The process by which photons are emitted by an electron slowing down is called bremsstrahlung, from the German word for "braking radiation."





The continuous spectrum



Electron is deflected and decelerated by the atomic nucleus. (Inelastic scattering).

Deflected electron emits electromagnetic radiation. Wavelength depends on the loss of energy.

The minimum wavelength is due to the inverse photoelectric effect. The conservation of energy requires that the electron kinetic energy equal the maximum photon energy:

$$eV_0 = hf_{\max} = \frac{hc}{\lambda_{\min}}$$

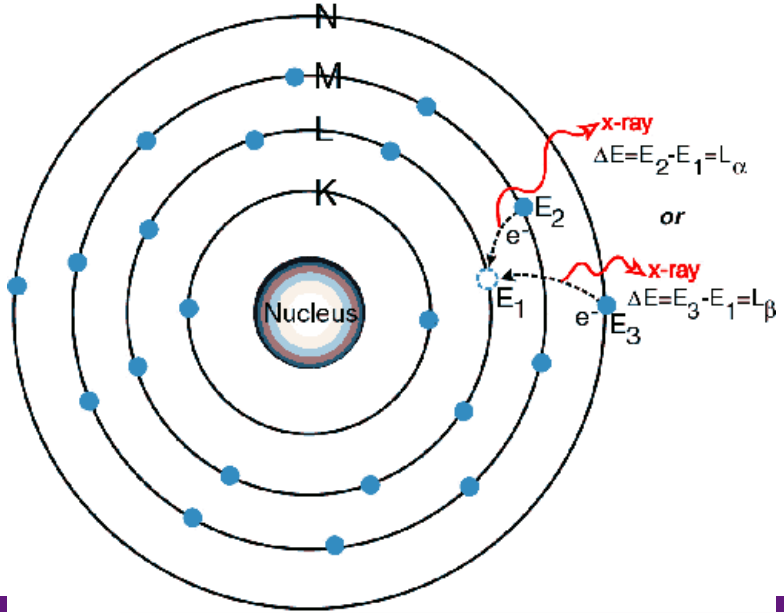
Therefore, the minimum wavelength (Duane-Hunt rule) is

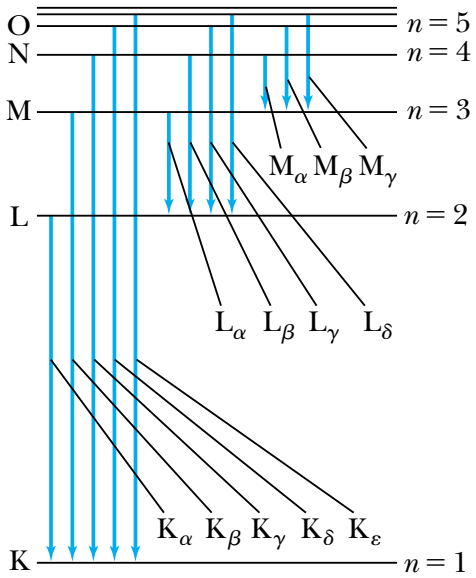
$$\lambda_{\min} = \frac{hc}{e}\frac{1}{V_0} = \frac{1.240 \times 10^{-6}\,\mathrm{V \cdot m}}{V_0}$$

6.2 X ray production

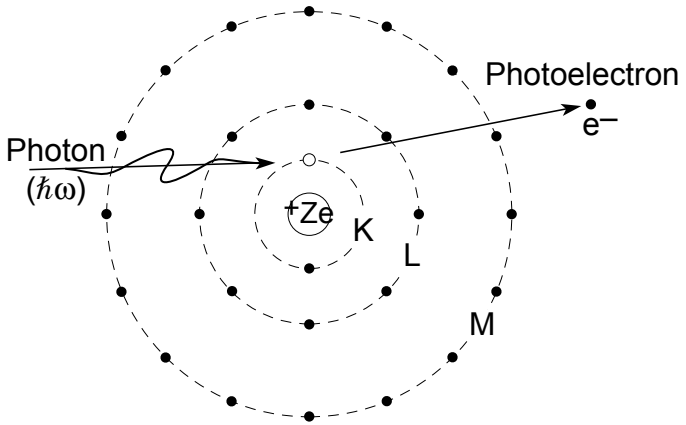
The characteristic spectrum:

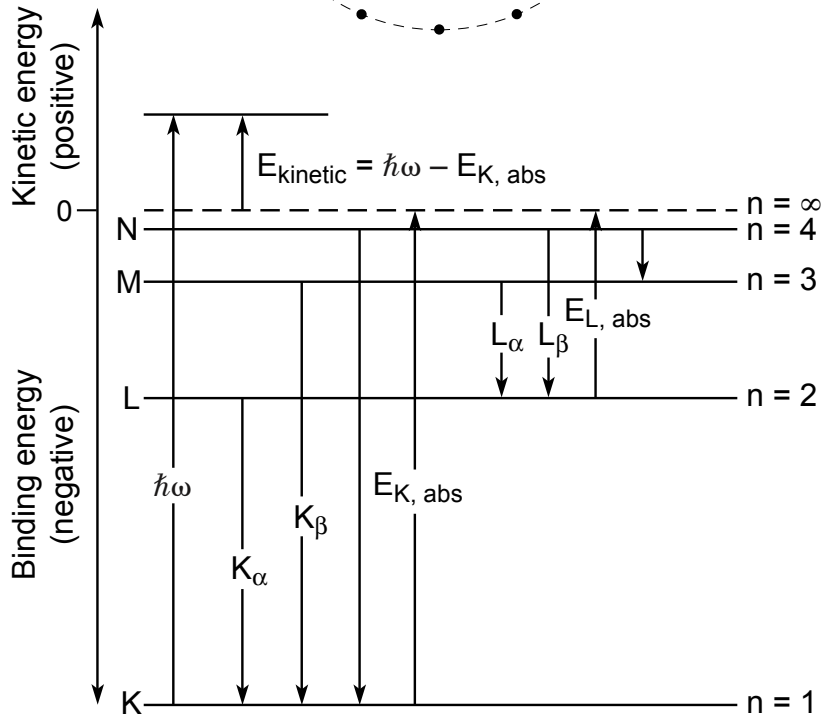
The atom is most stable in its lowest energy state or ground state, so it is likely that an electron from one of the higher shells will change its state and fill the inner-shell vacancy at lower energy, emitting radiation as it changes its state.



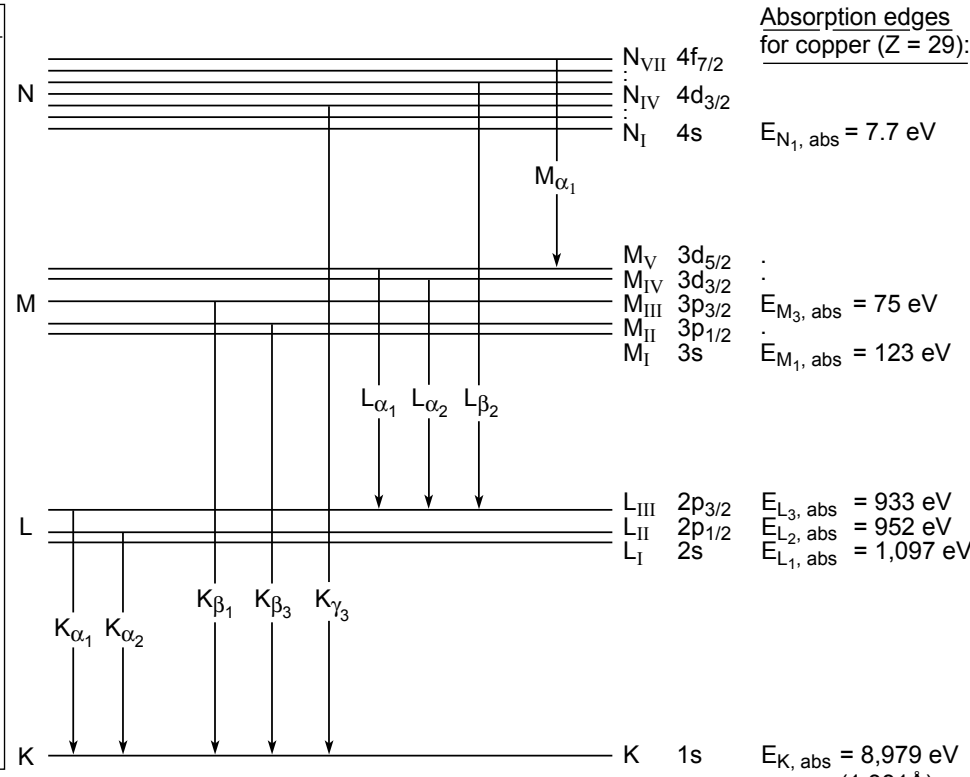


The characteristic spectrum





n	ℓ	j
4	3	7/2
4	3	5/2
⋮	⋮	⋮
4	0	1/2
3	2	5/2
3	2	3/2
3	1	3/2
3	1	1/2
3	0	1/2
2	1	3/2
2	1	1/2
2	0	1/2
1	0	1/2



Absorption edges for copper (Z = 29):

$E_{N_1, abs}$ = 7.7 eV

$E_{M_3, abs}$ = 75 eV

$E_{M_1, abs}$ = 123 eV

$E_{L_3, abs}$ = 933 eV

$E_{L_2, abs}$ = 952 eV

$E_{L_1, abs}$ = 1,097 eV

$E_{K, abs}$ = 8,979 eV (1.381Å)

Cu K_{α_1} = 8,048 eV (1.541Å)
Cu K_{α_2} = 8,028 eV (1.544Å)
Cu K_{β_1} = 8,905 eV

Cu L_{α_1} = 930 eV
Cu L_{α_2} = 930 eV
Cu L_{β_1} = 950 eV

6.2 X ray production

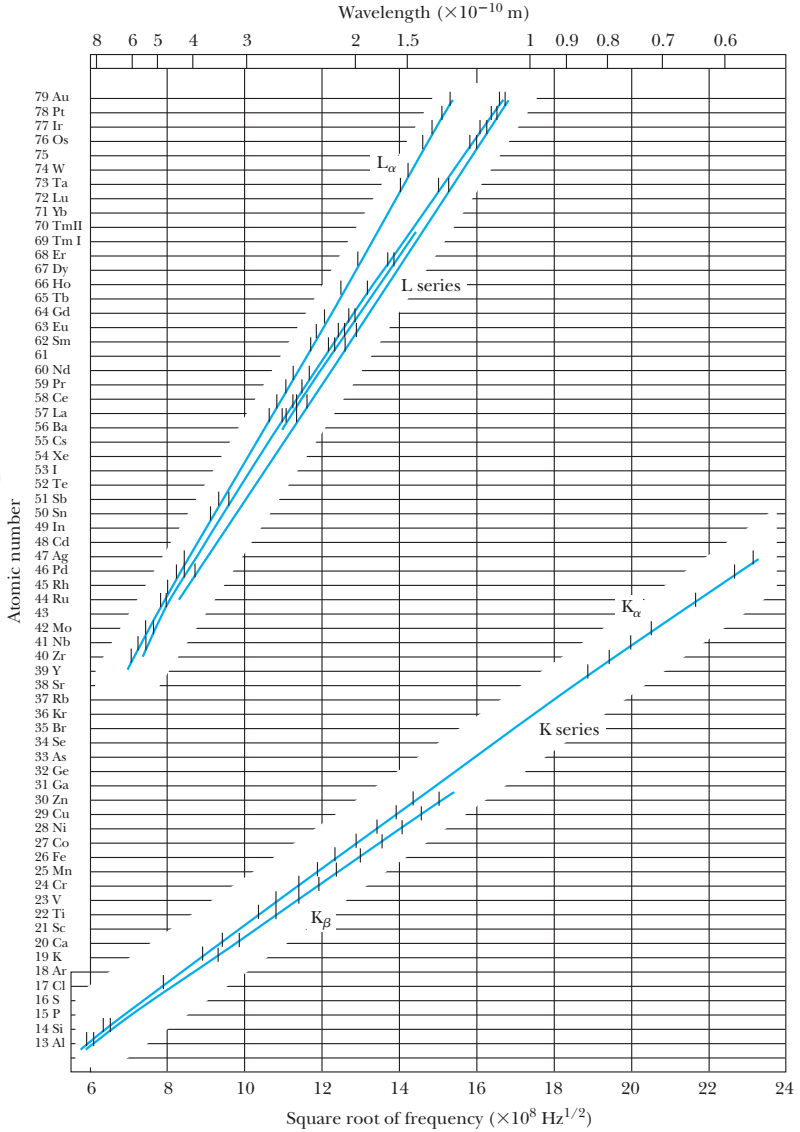
Moseley formula

$$\frac{1}{\lambda_{K_\alpha}} = R(Z-1)^2\left(\frac{1}{1^2}-\frac{1}{2^2}\right) = \frac{3}{4}R(Z-1)^2$$

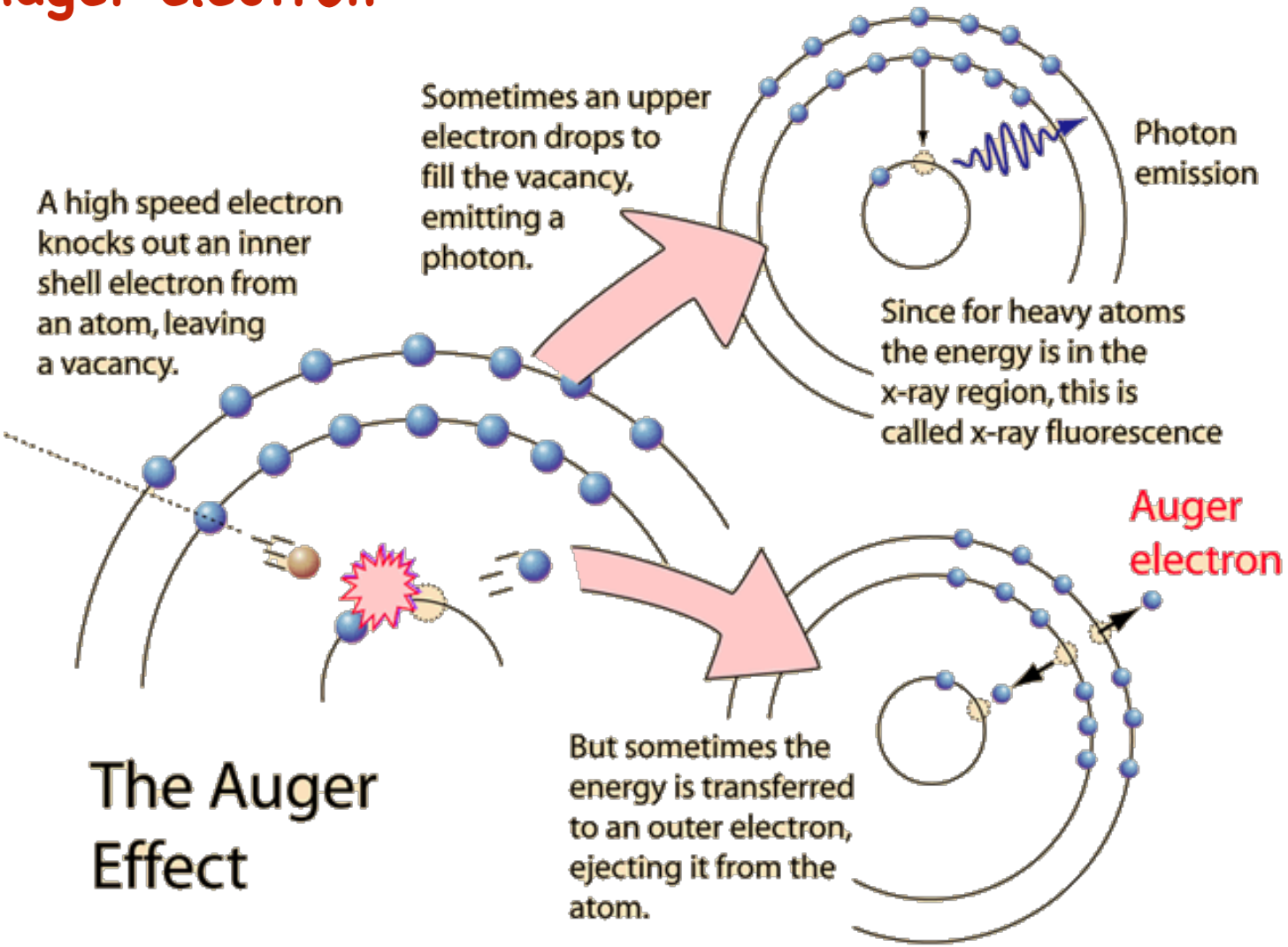
$$f_{K_\alpha} = \frac{c}{\lambda_{K_\alpha}} = \frac{3cR}{4}(Z-1)^2$$

$$\frac{1}{\lambda_K} = R(Z-1)^2\left(\frac{1}{1^2}-\frac{1}{n^2}\right) = R(Z-1)^2\left(1-\frac{1}{n^2}\right)$$

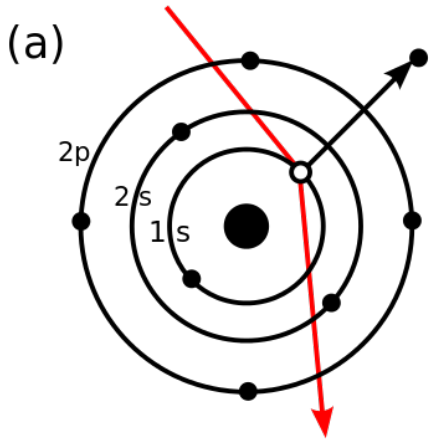




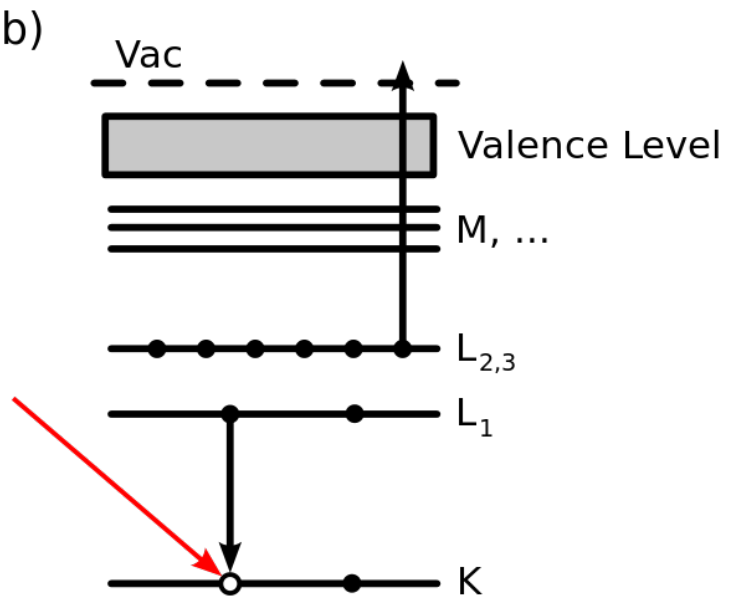
Auger electron

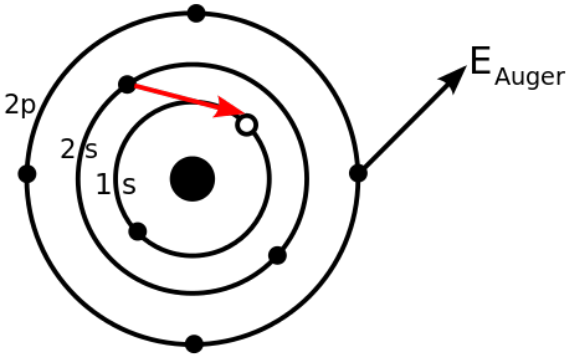


Auger electron



Electron collision





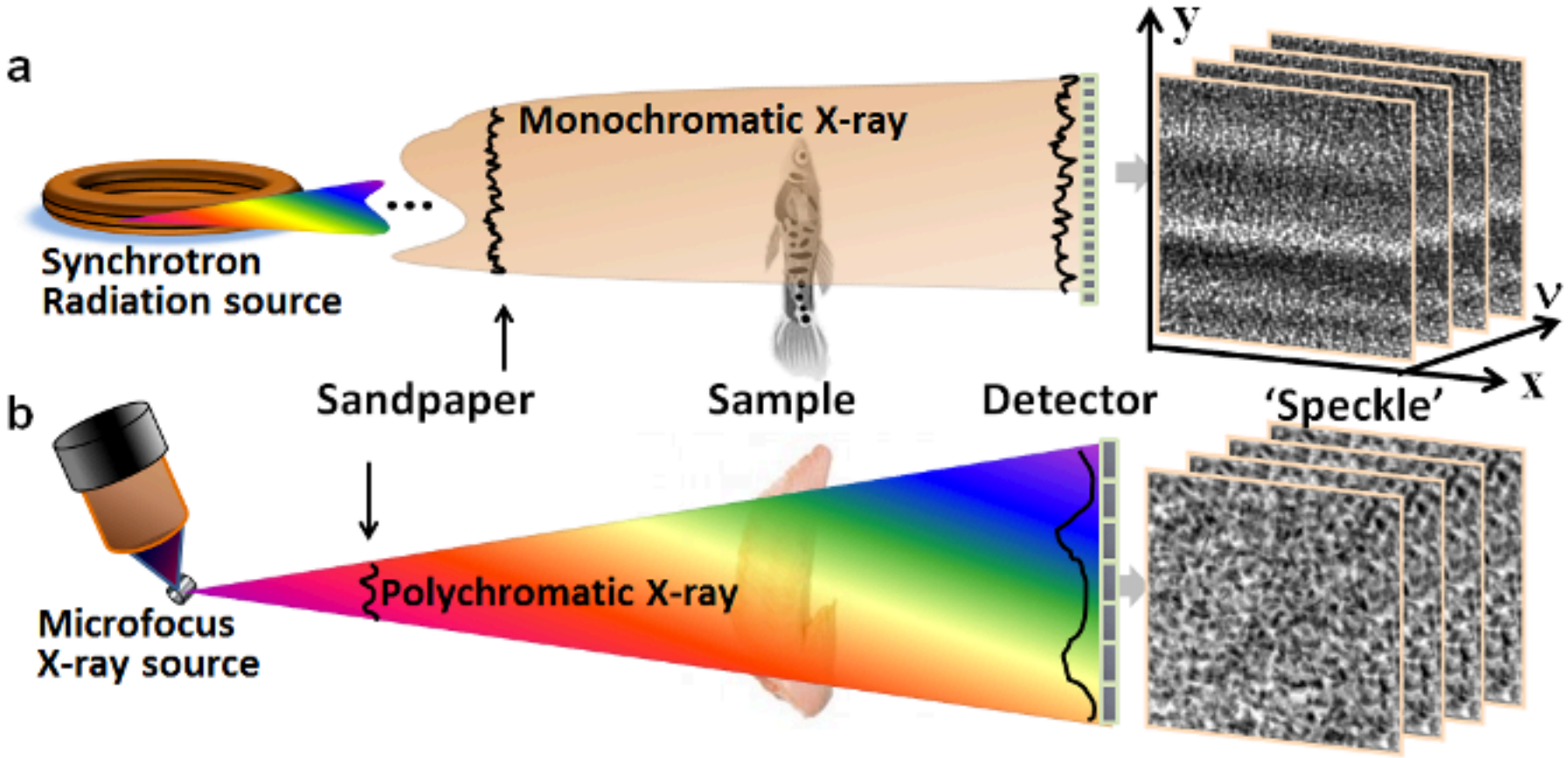
Auger electron emission

The kinetic energy of Auger electron

$$E_{ae} = E_K - E_{L_1} - E_{L_{2,3}}$$

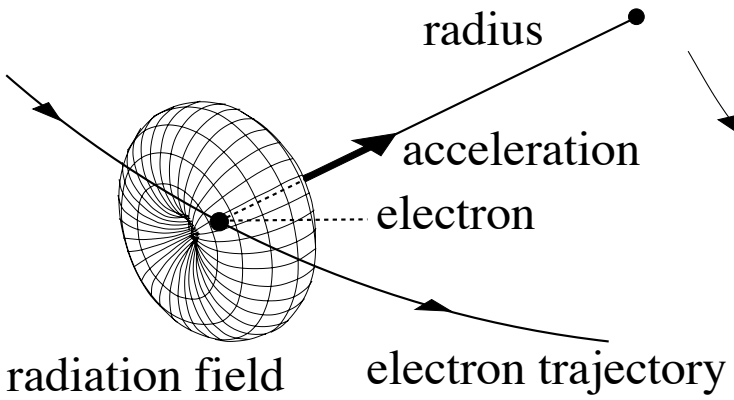
6.2 X ray production

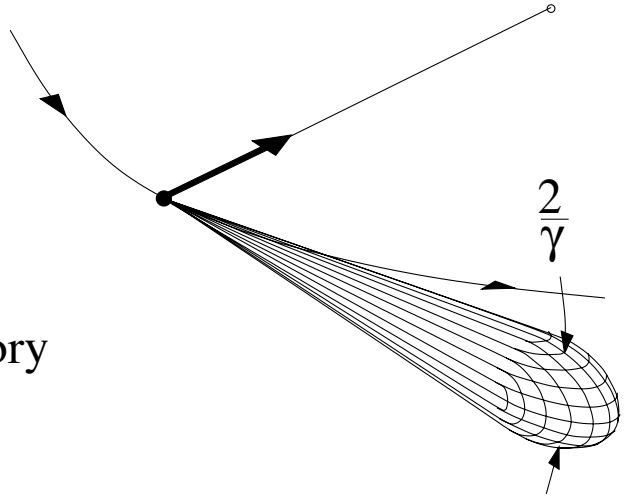
Synchrotron Radiation: In cyclic accelerators, when charged particles are accelerated, they radiate electromagnetic energy called synchrotron radiation.



Synchrotron Radiation

Rest frame → Lorentz transformation → Laboratory frame





$$\gamma = \frac{1}{\sqrt{1-\left(\frac{v}{c}\right)^2}} = \frac{E}{m_0 c^2}$$

Opening angle

Synchrotron Radiation

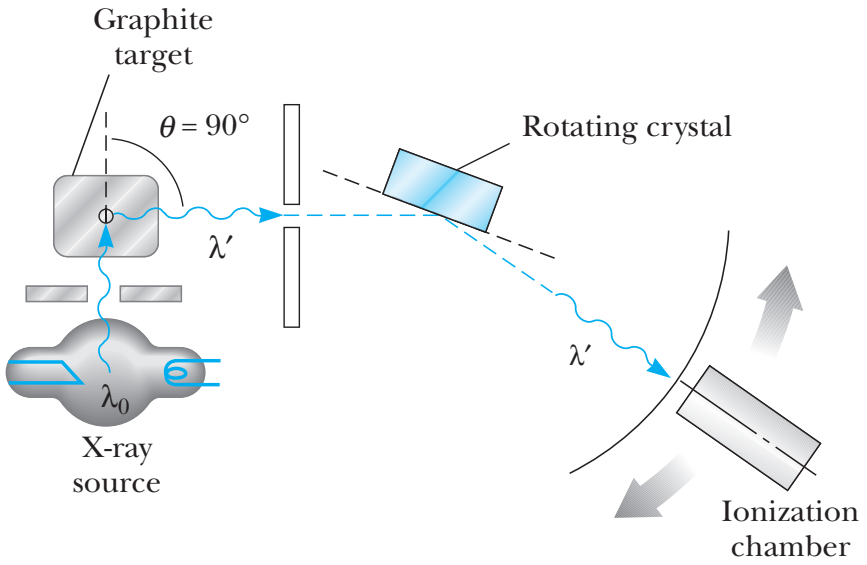
The very high intensity of the source yields images with a high signal-to-noise ratio on short time-scales, which enables fast radiographic investigations.

The beam can be easily monochromated. This allows correlations between attenuation values and the chemical constituents of the sample

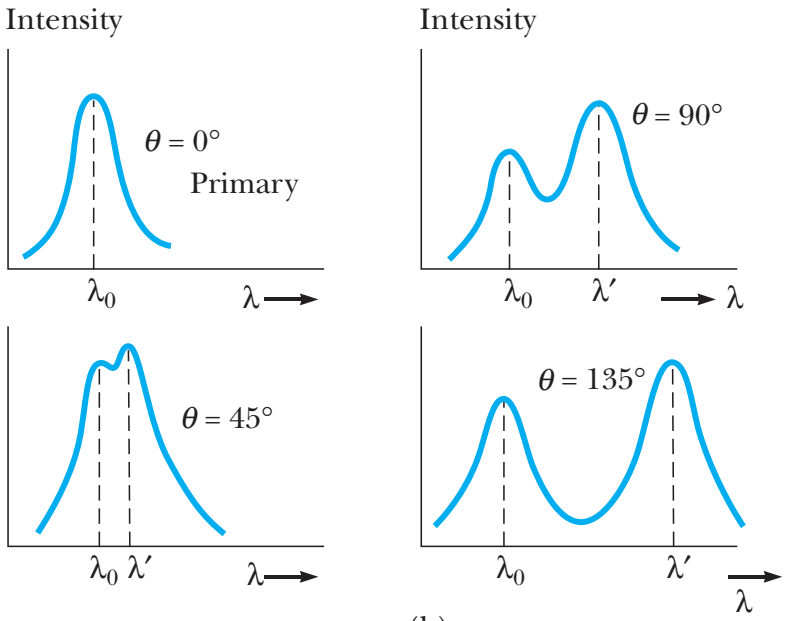
The option to vary the energy of the radiation enables the investigation of objects with very different absorption coefficients within the same measuring environment.

6.3 Compton scattering

At backward-scattering angles, there appeared to be a component of the emitted radiation (called a modified wave) that had a longer wavelength than the original primary (unmodified) wave.



(a)



(b)

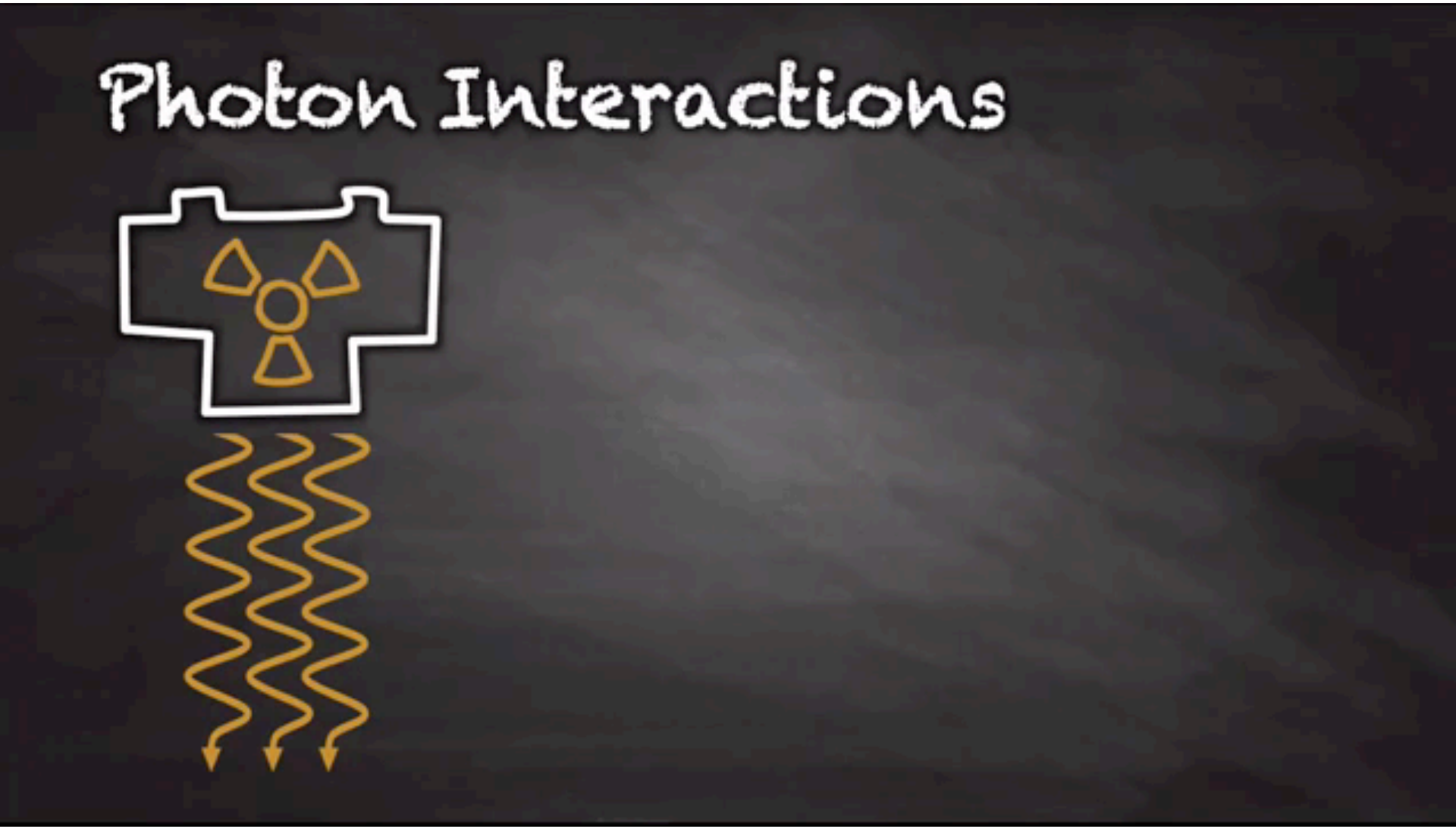
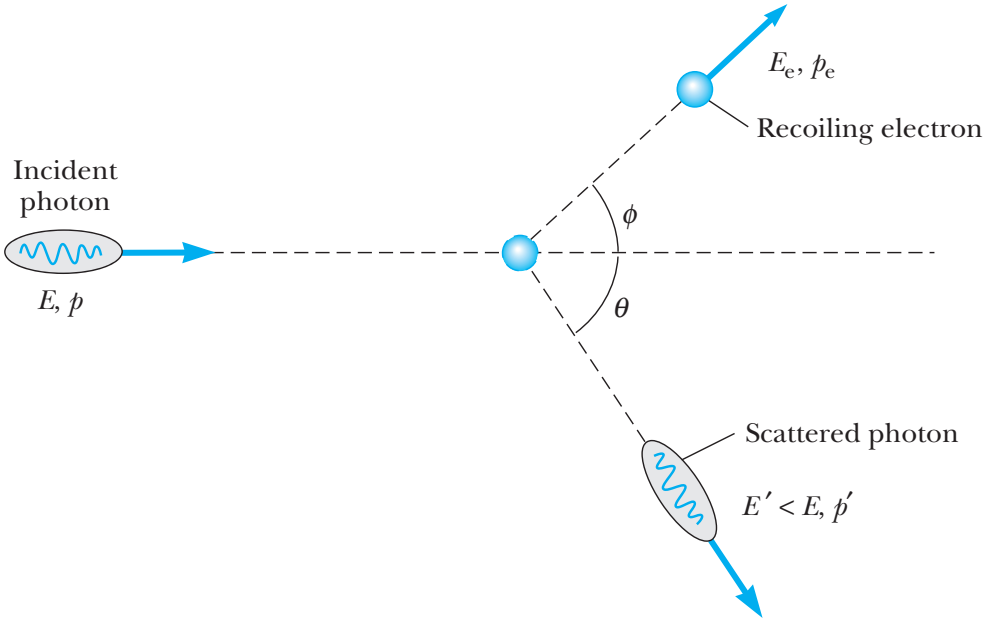

Photon Interactions

Diagram representing Compton scattering of a photon by an electron.



Conservation of energy

$$E + m_e c^2 = E' + E_e$$

Conservation of momentum

$$p = p' \cos\theta + p_e \cos\phi$$

$$p' \sin\theta = p_e \sin\phi$$

Therefore

$$p_e^2 = (p')^2 + p^2 - 2pp' \cos\theta$$

With De Broglie relation

$$p_{\text{photon}} = \frac{E}{c} = \frac{hf}{c} = \frac{h}{\lambda}$$

We have

$$E_e = hf - hf' + m_e c^2 \qquad E_e^2 = p_e^2 c^2 + m_e^2 c^4$$

$$p_e^2 = \left(\frac{hf'}{c}\right)^2 + \left(\frac{hf}{c}\right)^2 - \frac{2h^2 ff'}{c^2}\cos\theta$$

Finally

$$\lambda' - \lambda_0 = \boxed{\frac{h}{m_e c}}(1 - \cos\theta)$$

Compton wavelength

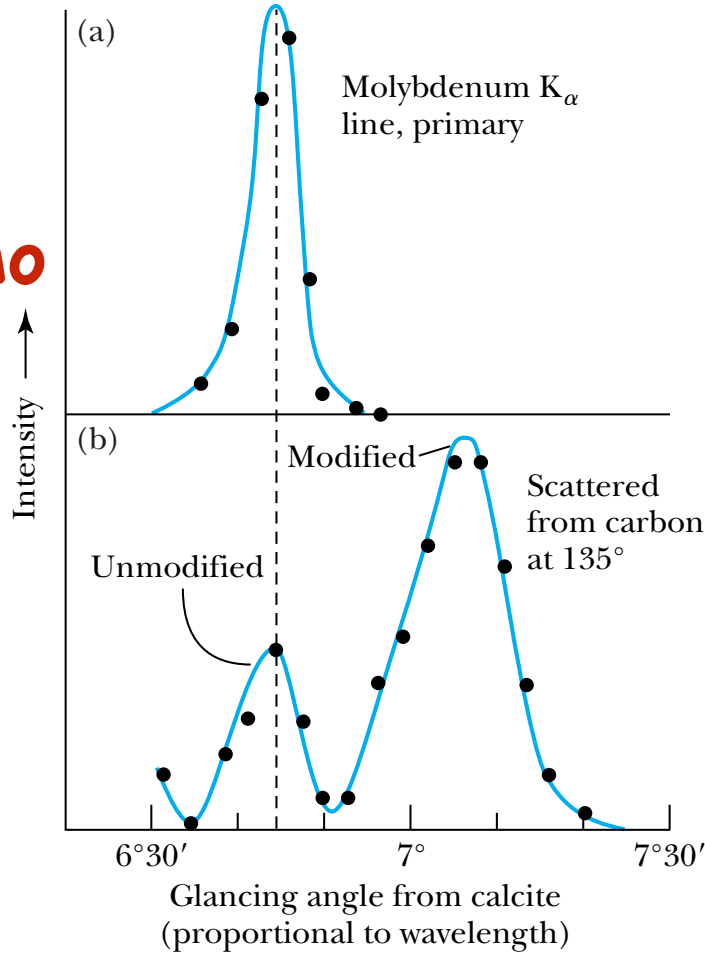
$\lambda_C = 2.426 \times 10^{-3}$ nm

6.3 Compton scattering

Compton's original data showing

1.the primary x-ray beam from Mo unscattered

2. the scattered spectrum from carbon at 135° showing both the modified and unmodified wave.



Pair Production

In the photoelectric effect, bremsstrahlung, and the Compton effect, we have studied exchanges of energy between photons and electrons. Have we covered all possible mechanisms?

For example, can the kinetic energy of a photon be converted into particle mass and vice versa?

It would appear that if none of the conservation laws are violated, then such a process should be possible.

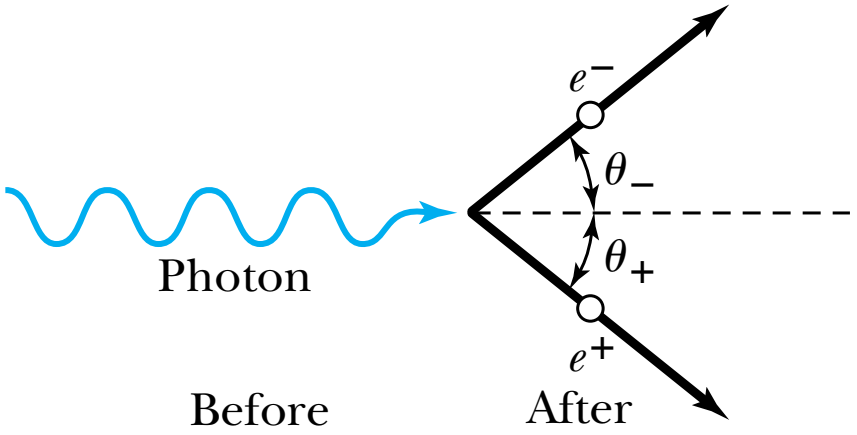
Pair Production

Experiments show that a photon's energy can be converted entirely into an electron and a positron in a process called pair production. The reaction is

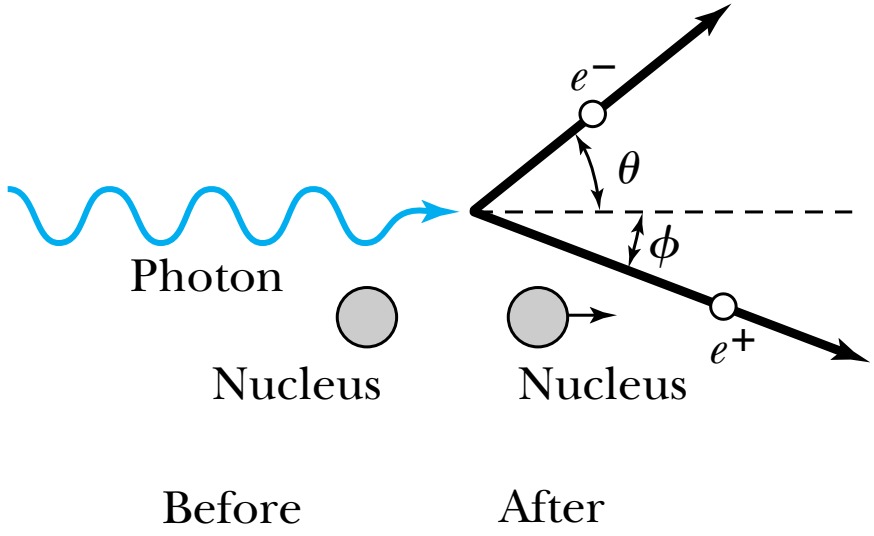
$$\gamma \rightarrow e^{+} + e^{-}$$

However, this process occurs only when the photon passes through matter, because energy and momentum would not be conserved if the reaction took place in isolation. The missing momentum must be supplied by interaction with a nearby massive object such as a nucleus.

Pair Production



(a) Free space (**cannot occur**)



(b) Beside nucleus

Pair Production

Consider the conversion of a photon into an electron and a positron that takes place inside an atom where the electric field of a nucleus is large. The nucleus recoils and takes away a negligible amount of energy but a considerable amount of momentum. The conservation of energy will now be

$$hf = E_+ + E_- + \text{K.E. (nucleus)}$$

The photon energy must be at least equal to $2m_ec^2$ in order to create the masses of the electron and positron.

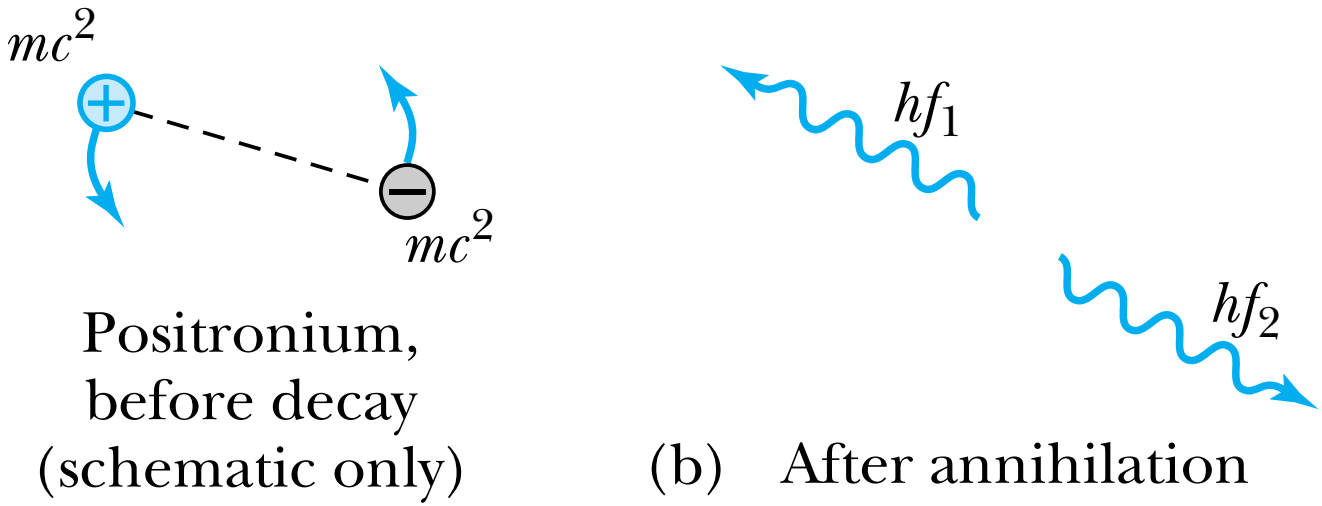
$$hf > 2m_ec^2 = 1.022\ \text{MeV} \qquad \text{(for pair production)}$$

Pair Annihilation

Eventually the electron and positron annihilate each other (typically in 10^{-10} s), producing electromagnetic radiation (photons). The process

$$e^+ + e^- \rightarrow \gamma + \gamma$$

is called **pair annihilation.**



(a) Positronium, before decay (schematic only)

(b) After annihilation

Pair Annihilation

The conservation laws for the process will be

$$2m_e c^2 \approx hf_1 + hf_2$$

$$0 = \frac{hf_1}{c} - \frac{hf_2}{c}$$

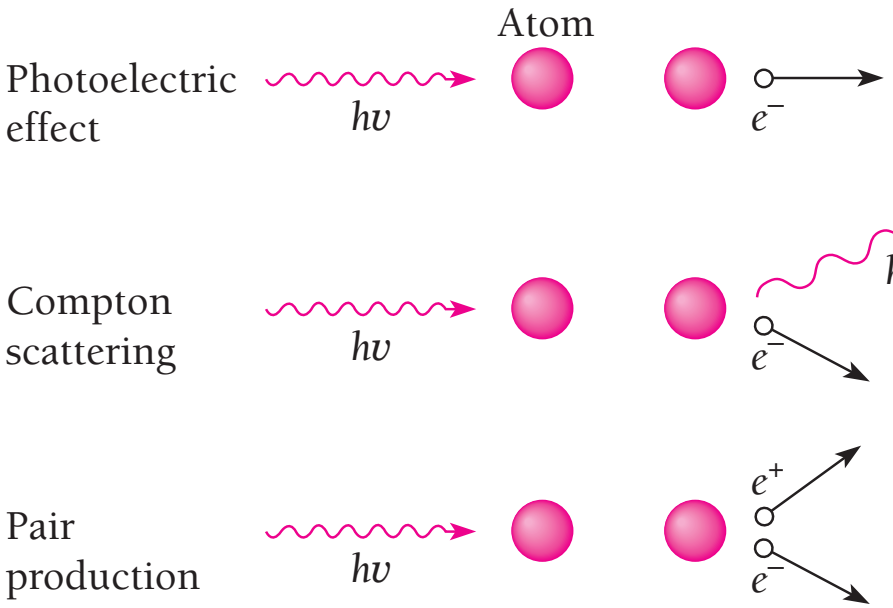
The frequencies are identical

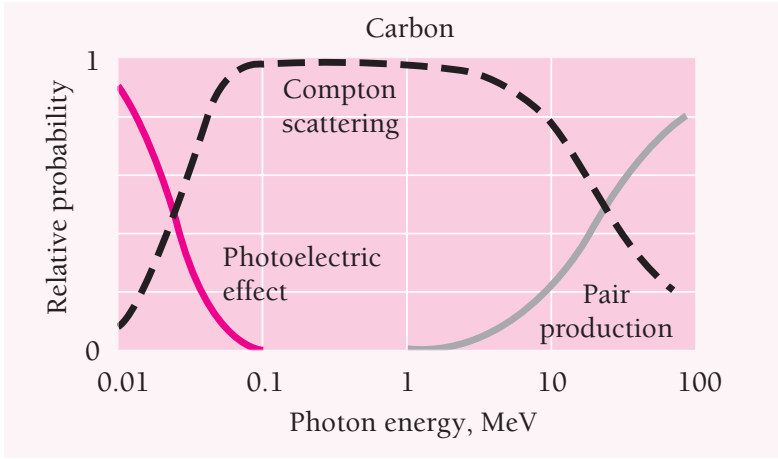
$$hf = m_e c^2 = 0.511\ \text{MeV}$$

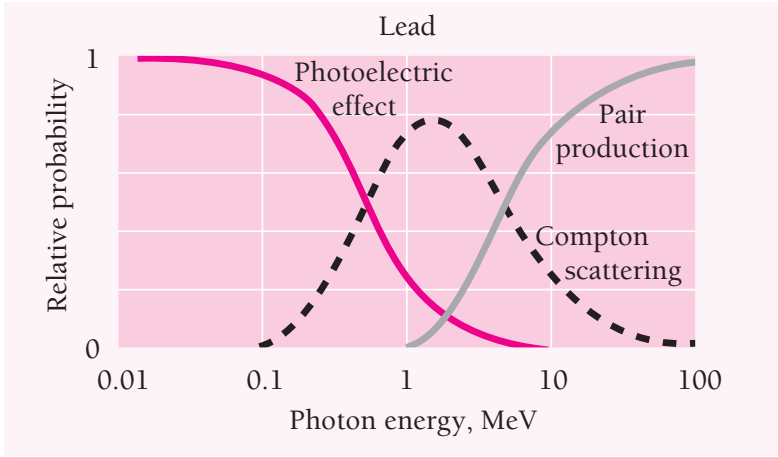
In other words, the two photons from positronium annihilation will move in opposite directions, each with energy 0.511 MeV. This is exactly what is observed experimentally.

6.4 Photon absorption

The three chief ways in which photons of light, x-rays, and gamma rays interact with matter







6.4 Photon absorption

The intensity I of an x- or gamma-ray beam is equal to the rate at which it transports energy per unit cross-sectional area of the beam.

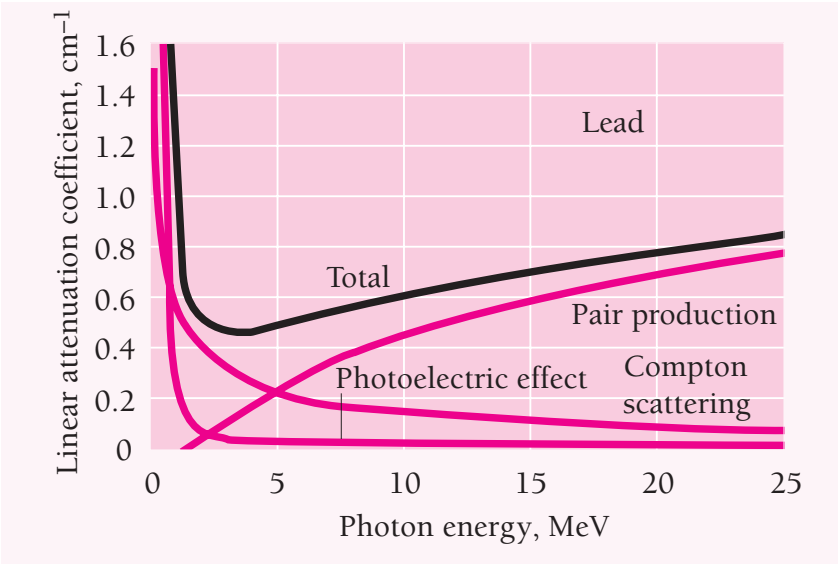
$$-\frac{dI}{I} = \mu\, dx$$

Radiation intensity I

$$I = I_0 e^{-\mu x}$$

Absorber thickness

$$x = \frac{\ln\,(I_0/I)}{\mu}$$

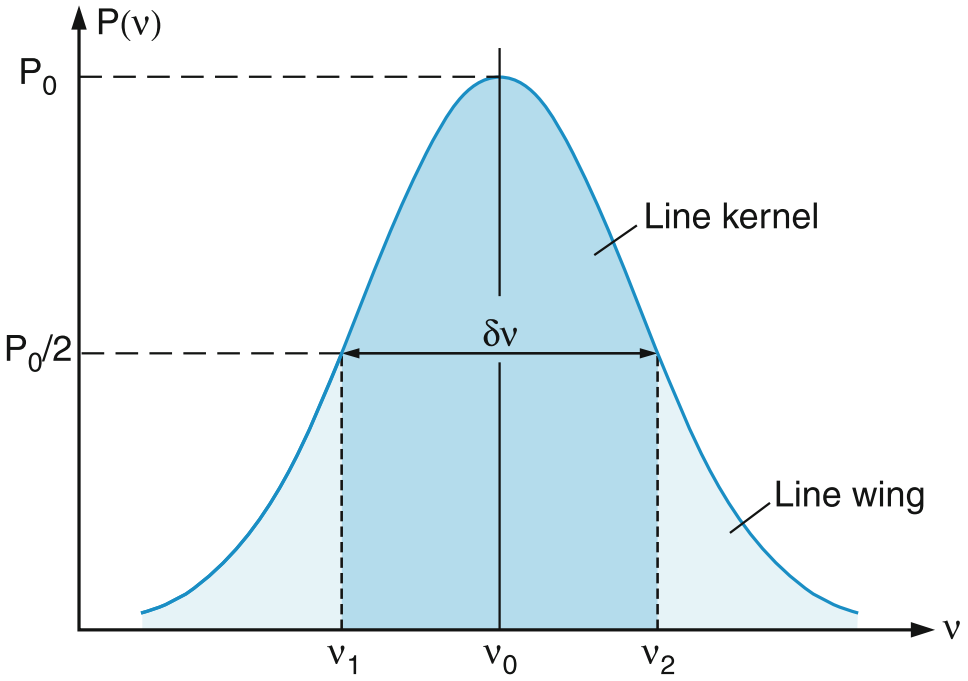


6.4 linear absorption coefficient

Linear Absorption Coefficient (cm^{-1})					
λ (pm)	**Air**	**Water**	**Aluminum**	**Copper**	**Lead**
10		0.16	0.43	3.2	43
20		0.18	0.76	13	55
30		0.29	1.3	38	158
40		0.44	3.0	87	350
50	8.6×10^{-4}	0.66	5.4	170	610
60	1.3×10^{-3}	1.0	9.2	286	1000
70	1.95×10^{-3}	1.5	14	430	1600
80	2.73×10^{-3}	2.1	20	625	
90	3.64×10^{-3}	2.8	30	875	
100	4.94×10^{-3}	3.8	41	1200	
150	1.56×10^{-2}	12	124		
200	3.64×10^{-2}	28	275		
250	6.63×10^{-2}	51	524		

6.5 Line Profiles of Spectral Lines

The absorption or emission of radiation on an atomic transition does not result in a strictly monochromatic spectral line, but rather in a frequency distribution around the central frequency υ_0



This gives aline profile I ($\upsilon-\upsilon_0$) with a full-width at half-maximum $\delta\upsilon$, which not only depends on the spectral resolution of the measuring apparatus but also on basic physical properties, such as the lifetimes of the atomic states involved in the transition, the velocity distribution of the moving atoms and the pressure of the gaseous sample.

The intensity I (υ_1)= I (υ_2)=1/2 I (υ_0) of the spectral line profile has dropped to half its maximum value at the line center (full width half maximum FWHM).

6.6 Natural Linewidth

The spectral interval inside the full half-width is called the line kernel, the ranges outside the line wings.

An excited atom can deliver its excitation energy in the form of spontaneous emission. We will describe the excited electron by the classical model of a damped harmonic oscillator with mass m, spring constant D and eigenfrequency ω_0

The time dependent amplitude of its oscillation can be obtained from the equation of motion

$$\ddot{x} + \gamma \dot{x} + \omega_0^2 x = 0,$$

Its real solution is

$$x(t) = x_0 e^{-(\gamma/2)t}\left[\cos\omega t + (\gamma/2\omega)\sin\omega t\right].$$

with the initial conditions

$$x_{(0)} = x_0, \dot{x}_{(0)} = -x_0 \cdot \delta/2$$

The frequency of the damped oscillator

$$\omega = \sqrt{\omega_0^2 - (\gamma/2)^2}$$

is slightly lower than ω_0 of the undamped oscillator.

We can neglect the second term and approximate ω by ω_0.

$$x(t) \approx x_0 e^{-(\gamma/2)t}\cos\omega_0 t.$$

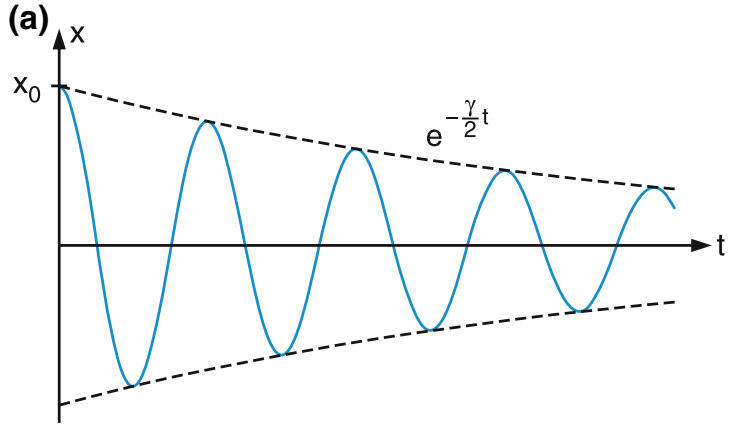
6.6 Natural Linewidth

The Fourier transformation of x(t) yields the frequency distribution of the amplitudes

$$A(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} x(t) e^{-i\omega t}\, dt$$

$$= \frac{1}{\sqrt{2\pi}} \int_{0}^{+\infty} x_0 e^{-(\gamma/2)t} \cos\omega_0 t\, e^{-i\omega t}\, dt,$$

where we have assumed that the excitation of the atom occurs at t = 0, which means that the oscillation starts at t = 0, giving x(t < 0)= 0



The elementary integration yields the complex amplitudes

$$A(\omega) = \frac{x_0}{\sqrt{8\pi}} \left[\frac{1}{\mathrm{i}(\omega_0 - \omega) + \gamma/2} + \frac{1}{\mathrm{i}(\omega_0 + \omega) + \gamma/2} \right].$$

The second term can be neglected. Therefore the spectral radiation power density $P_\omega(\omega)$ is

$$P_\omega(\omega) \propto A(\omega) A^*(\omega).$$

and

$$P_\omega(\omega) = \frac{C}{(\omega - \omega_0)^2 + (\gamma/2)^2}.$$

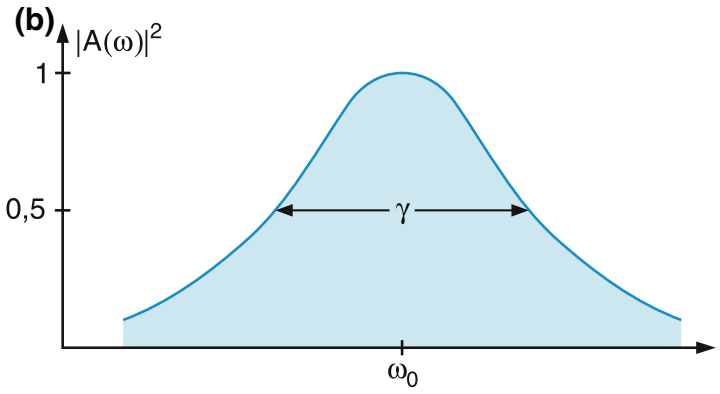
The constant C is chosen in such a way that the total power becomes

$$\int_0^\infty P_\omega(\omega)\, \mathrm{d}\omega = P_0.$$

6.7 Natural Linewidth

The integration of this integral yields

$$C = P_0 \gamma / 2\pi .$$



The normalized line profile

$$P_\omega(\omega) = P_0 \frac{\gamma/2\pi}{(\omega - \omega_0)^2 + (\gamma/2)^2}$$

is called the Lorentzian profile. The full-width at half-maximum (FWHM) is

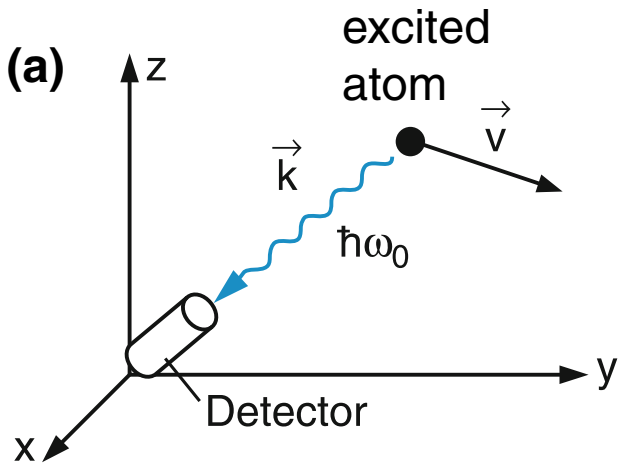
$$\delta\omega_n = \gamma \Rightarrow \delta\nu_n = \gamma/2\pi .$$

It is called the natural linewidth, because it is caused by the spontaneous emission of the atom, without any external influences.

6.8 Doppler Broadening

If an excited atom moves with the velocity v= {v_x ,v_y,v_z}, the center frequency of the radiation, emitted into the direction of the wave vector k of the wave appears for an observer at rest Doppler-shifted to

$$\omega_e = \omega_0 + \boldsymbol{k} \cdot v \quad \text{with} \quad |\boldsymbol{k}| = 2\pi/\lambda$$



$$\omega_e = \omega_0 + \vec{k} \cdot \vec{v}$$

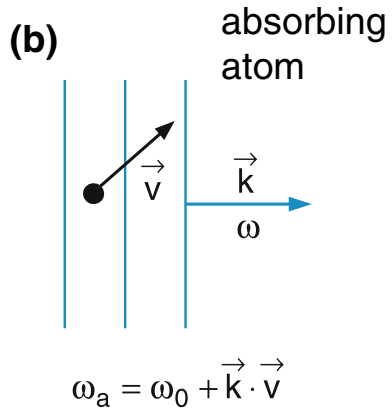
6.8 Doppler Broadening

For an absorption atom, it is also very similar. The frequency of the incident wave therefore has to be

$$\omega = \omega_a = \omega_0 + \boldsymbol{k} \cdot v$$

FIf the wave travels in the z direction its wave vector is $k = \{0,0,v_z\} \Rightarrow k \cdot v = k_z v_z$ and the absorption frequency becomes

$$\omega_a = \omega_0 + k_z v_z = \omega_0 (1 + v_z / c)$$



6.8 Doppler Broadening

At thermal equilibrium, the velocities of the atom follow a Maxwell-Boltzmann distribution,

$$n_i(v_z)\,\mathrm{d}v_z = \frac{N_i}{v_\mathrm{w}\sqrt{\pi}}\mathrm{e}^{-(v_z/v_\mathrm{w})^2}\,\mathrm{d}v_z,$$

The total number of all atoms in level E_i per unit volume is

$$N_i = \int_{-\infty}^{+\infty} n_i(v_z)\,\mathrm{d}v_z$$

When the frequency shift is considered,

$$n_i(\omega)\,\mathrm{d}\omega = \frac{cN_i}{\omega_0 v_\mathrm{w}\sqrt{\pi}}\mathrm{e}^{-[c(\omega-\omega_0)/(\omega_0 v_\mathrm{w})]^2}\,\mathrm{d}\omega$$

The intensity profile of a Doppler-broadened absorption or emission line becomes

$$P_\omega(\omega) = P_\omega(\omega_0)\mathrm{e}^{-[c(\omega-\omega_0)/(\omega_0 v_\mathrm{w})]^2}.$$

This a Gaussian function that is symmetric to the center frequency ω_0. The full half-width is

$$\delta\omega_D = |\omega_1 - \omega_2|$$

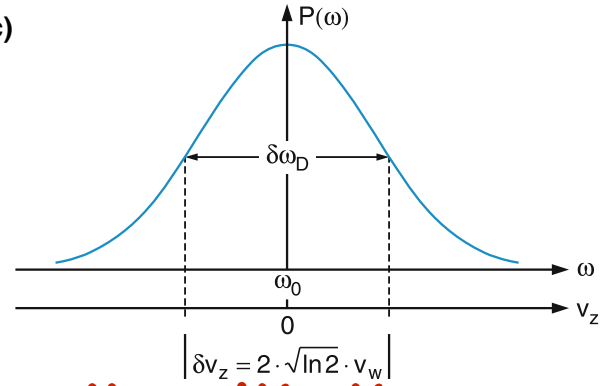
$$\text{with} \quad P(\omega_1) = P(\omega_2) = \frac{1}{2}P(\omega_0).$$

Using the most probable velocity component

$$v_w = (2k_B T/m)^{1/2}$$

we can obtain

$$\omega_0 \cdot v_w/c = \delta\omega_D \cdot (4\ln 2)^{-1/2}$$

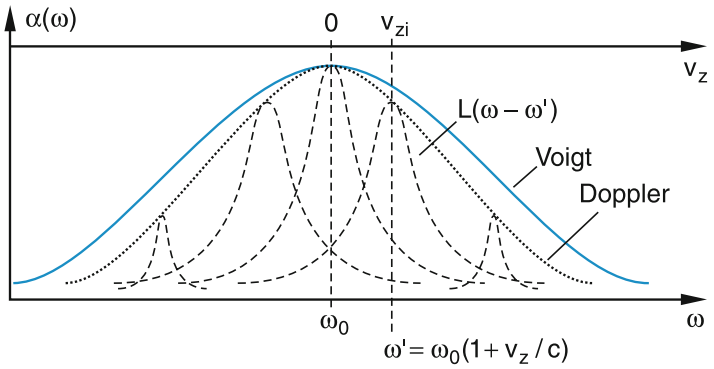


The Doppler-width $\delta\omega_D$ increases proportionally with the frequency ω_0 but decreases with increasing mass m of the atom.

6.8 Doppler Broadening

More detailed consideration shows that a Doppler-broadened spectral line cannot be strictly represented by a pure Gaussian profile as has been assumed in the foregoing discussion. They can overlap as

$$I(\omega) = C \int_0^{\infty} \frac{e^{-[(c/v_p)(\omega_0-\omega')/\omega_0]^2}}{(\omega-\omega')^2 + (\gamma/2)^2} d\omega'$$



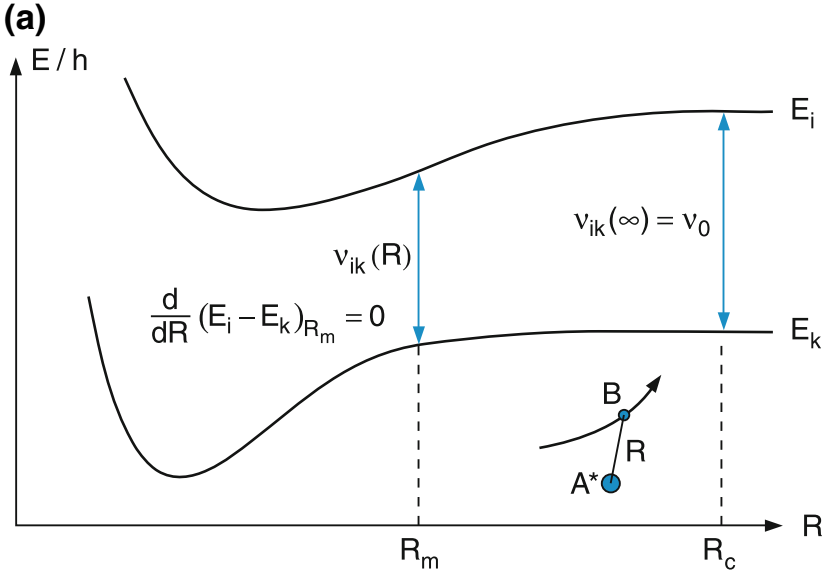
with

$$C = \frac{\gamma N_i c}{2 v_p \pi^{3/2} \omega_0}.$$

This intensity profile, which represents a convolution of Lorentzian and Gaussian profiles is called a Voigt profile.

6.9 Collision Broadening

If an atom A, with energy levels E_i and E_k, approaches another atom or molecule B, the interaction between A and B shifts the energies of both levels. This energy shift depends on the structure of the electron shell of both partners A and B, on the specific energy levels and on the mutual distance R

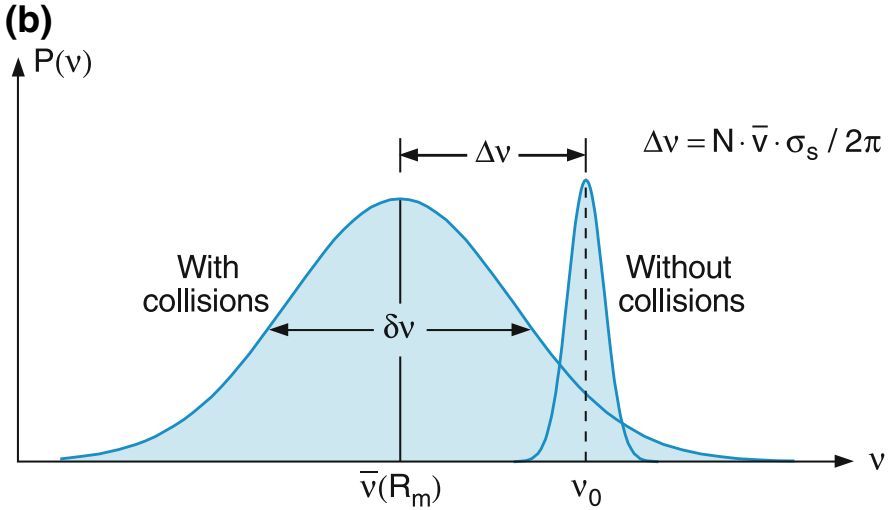


6.9 Collision Broadening

The intensity profile I (ω) of the collision broadened emission line can be described by

$$I(\omega) \propto \int A_{ik}(R) P_{\text{coll}}(R) [E_i(R) - E_k(R)] \, \mathrm{d}R,$$

where $A_{ik}(R)$ is the spontaneous transition probability, which depends on R because the electronic wave functions of the collision pair (AB) depend on R.



6.9 Collision Broadening

The line profile caused by elastic and inelastic collisions is obtained

$$I(\omega) = \frac{\left(\frac{\gamma_n + \gamma_{\text{inel}}}{2} + N\bar{v}\sigma_{\text{b}}\right)^2}{(\omega - \omega_0 - N\bar{v}\sigma_{\text{s}})^2 + \left(\frac{\gamma_n + \gamma_{\text{inel}}}{2} + N\bar{v}\sigma_{\text{b}}\right)^2}.$$

The cross sections

$$\sigma_{\text{b}} = 2\pi \int_0^\infty (1 - \cos\varphi(R))\, R\, \mathrm{d}R$$

$$\sigma_{\text{s}} = 2\pi \int_0^\infty \sin\varphi(R))\, R\, \mathrm{d}R$$

are a measure for the line broadening ($\delta\nu_{\text{b}}$) and the line shift ($\Delta\nu_{\text{s}}$) by elastic collisions.

Induced and Spontaneous Transitions

If an atom in the state $|k\rangle$ with energy E_k is brought into an electromagnetic radiation field with spectral energy density $w_\nu(\nu)$, it can absorb a photon $h\nu$.

The probability per second for such an absorbing transition

$$\frac{\mathrm{d}\mathcal{P}_{ki}^{\mathrm{abs}}}{\mathrm{d}t} = B_{ki}\, w_\nu(\nu)$$

is proportional to the spectral energy density $w_\nu(\nu) = n(\nu)h\nu$ of the radiation field. The proportionality factor B_{ki} is the Einstein coefficient for absorption.

Induced and Spontaneous Transitions

The radiation field can also induce atoms in an excited state with energy E_i to emit a photon with energy $h\nu = E_i - E_k$ into a specific mode of the radiation field and to go into the lower state E_k. This process is called induced (or stimulated) emission. The probability per second for the induced emission is given by

$$\frac{\mathrm{d}\mathcal{P}_{ik}^{\mathrm{ind.\,em}}}{\mathrm{d}t} = B_{ik} w_\nu(\nu).$$

The factor B_{ik} is the Einstein coefficient for induced emission.

Induced and Spontaneous Transitions



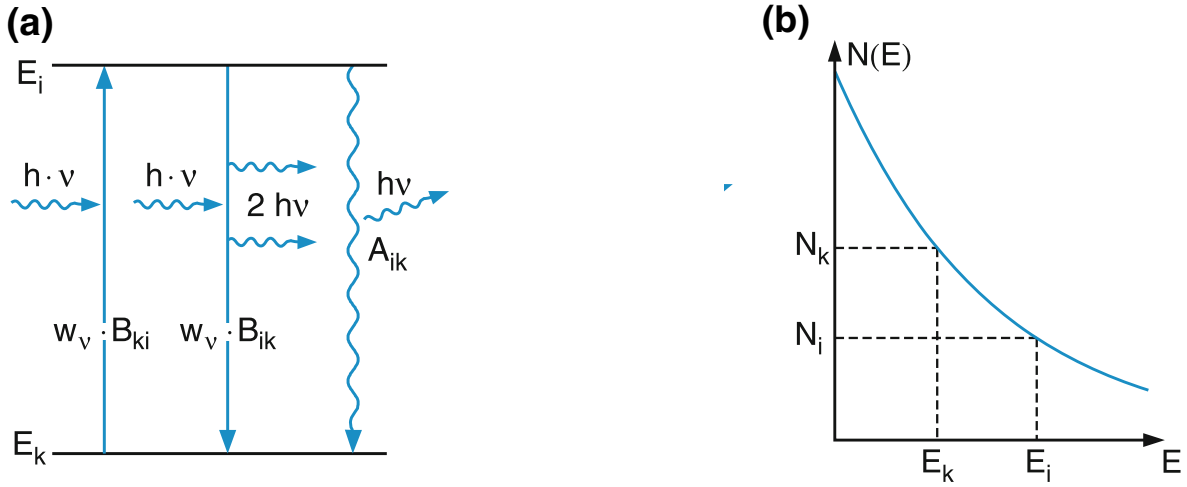
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An excited atom can also give away its excitation energy spontaneously without an external radiation field. This process is called spontaneous emission. Different from the induced emission, the spontaneous photon can be emitted into an arbitrary direction, i.e., into any one of the modes of the radiation field.

$$\frac{\mathrm{d}\mathcal{P}_{ik}^{\mathrm{sp.\,em.}}}{\mathrm{d}t} = A_{ik}.$$

The factor A_{ik} is the Einstein coefficient for spontaneous emission. It is solely dependent on the wave functions of the states $|i\rangle$ and $|k\rangle$ but independent of the radiation field.

Induced and Spontaneous Transitions



Consider N_i atoms in state E_i and N_k atoms in state E_k within the unit volume inside a radiation field with spectral energy density $w(\upsilon)$. Under stationary conditions the number densities N_i and N_k do not vary with time, i.e., they are constant. This means that the absorption rate must be equal to the total emission rate:

$$B_{ki}\, w_\nu(\nu) N_k = (B_{ik}\, w_\nu(\nu) + A_{ik})\, N_i .$$

At thermal equilibrium, the ratio N_i/N_k follows the Boltzmann distribution

$$\frac{N_i}{N_k} = \frac{g_i}{g_k} e^{-(E_i - E_k)/kT} = \frac{g_i}{g_k} e^{-h\nu/kT}$$

where g= 2J + 1 is the statistical weight of a state with energy E and total angular momentum quantum number J. Therefore,

$$w_\nu(\nu) = \frac{A_{ik}/B_{ik}}{(g_k/g_i)(B_{ki}/B_{ik})e^{h\nu/kT} - 1}.$$

The spectral energy density of the thermal radiation field is, on the other side, given by Planck's formula

$$w_\nu = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{h\nu/kT} - 1}.$$

We get for the nominator

$$A_{ik}/B_{ik} = \frac{8\pi h\nu^3}{c^3}$$

and

$$g_k B_{ki}/(g_i B_{ik}) = 1.$$

Therefore

$$B_{ik} = \frac{g_k}{g_i} B_{ki}$$

$$A_{ik} = \frac{8\pi h\nu^3}{c^3} B_{ik}.$$

If both states have equal statistical weights ($g_i = g_k$) the Einstein coefficients for induced absorption and emission are equal.

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The Physics of Atoms and Quanta

18.1 18.2 18.3 18.4 18.8

Exercise

1. Which element has a K_α x-ray line whose wavelength is 0.180 nm?

Exercise

1. Which element has a K_α x-ray line whose wavelength is 0.180 nm?

Solution:

The frequency corresponding to a wavelength of 0.180 nm is

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m/s}}{1.80 \times 10^{-10} \text{ m}} = 1.67 \times 10^{18} \text{ Hz}$$

Therefore

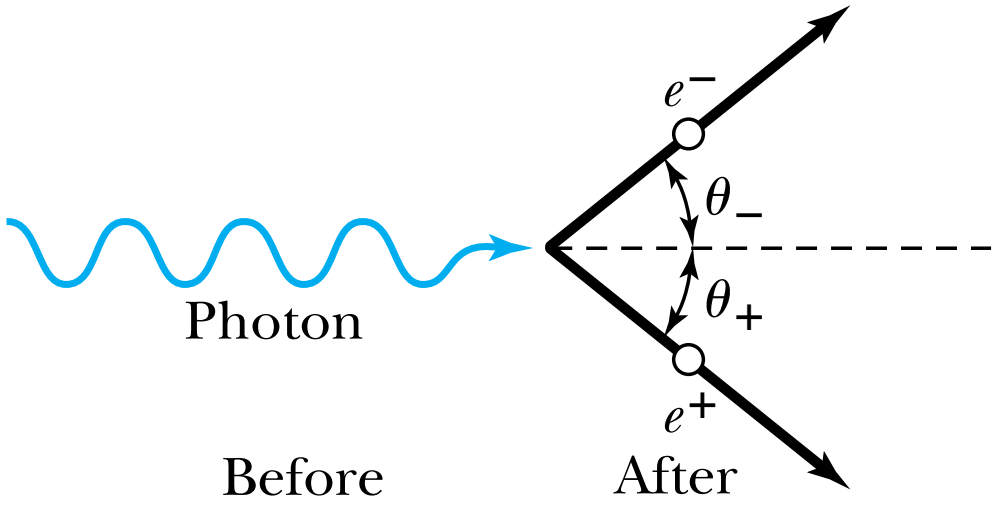
$$Z - 1 = \sqrt{\frac{4}{3cR}} = \sqrt{\frac{(4)(1.67 \times 10^{18} \text{ Hz})}{(3)(3.00 \times 10^8 \text{ m/s})(1.097 \times 10^7 \text{ m}^{-1})}} = 26$$

$$Z = 27$$

The element with atomic number 27 is cobalt.

Exercise

2. Show that a photon cannot produce an electron-positron pair in free space as following figure



Exercise

2. Show that a photon cannot produce an electron-positron pair in free space as following figure

Solution:

Let the total energy and momentum of the electron and the positron be E_-, p_-, and E_+,p_+, respectively. The conservation laws are then

$$hf = E_+ + E_-$$

$$\frac{hf}{c} = p_- \cos\theta_- + p_+ \cos\theta_+$$

$$0 = p_- \sin\theta_- - p_+ \sin\theta_+$$

From the second equation, we have

$$hf_{\max} = p_- c + p_+ c$$

When we inserted the mass-energy relation to first equation

$$hf = \sqrt{{p_+}^2 c^2 + m^2 c^4} + \sqrt{{p_-}^2 c^2 + m^2 c^4}$$

Therefore

$$hf > p_- c + p_+ c$$

The two frequency equations are inconsistent and cannot simultaneously be valid.