



Synchrotron x-rays and condensed matter/Rayonnement X synchrotron et matière condensée

## X-rays and matter – the basic interactions

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### Abstract

In this introductory article we attempt to provide the theoretical basis for developing the interaction between X-rays and matter, so that one can unravel properties of matter by interpretation of X-ray experiments on samples. We emphasize that we are dealing with the *basics*, which means that we shall limit ourselves to a discussion of the interaction of an X-ray photon with an isolated atom, or rather with a single electron in a Hartree–Fock atom. Subsequent articles in this issue deal with more complicated – and interesting – forms of matter encompassing many atoms or molecules. **To cite this article:** *J. Als-Nielsen, C. R. Physique 9 (2008)*. © 2008 Published by Elsevier Masson SAS on behalf of Académie des sciences.

### Résumé

**Rayons X et matière – les interactions fondamentales.** Cet article introductif vise à fournir les bases théoriques pour le développement de l'interaction entre rayons X et matière, de telle sorte qu'il soit possible de révéler les propriétés de la matière par des expériences de rayons X sur des échantillons. Nous soulignons que nous nous intéressons aux fondements, ce qui signifie que nous nous limitons à une discussion de l'interaction entre un photon X et un atome isolé ou plutôt avec un seul électron dans un atome de Hartree–Fock. D'autres articles de ce numéro traitent de formes plus complexes – et plus intéressantes – de la matière, constituées de nombreux atomes ou molécules. **Pour citer cet article :** *J. Als-Nielsen, C. R. Physique 9 (2008)*. © 2008 Published by Elsevier Masson SAS on behalf of Académie des sciences.

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### 1. Cross sections

We shall limit the discussion to two phenomena that can happen when an X-ray photon interacts with an electron in a Hartree–Fock atom: the X-ray photon can be elastically scattered by the electron bound in the atom, or the X-ray photon can be absorbed by the atom, maintaining energy conservation by emission of the electron from the atom. The ability to absorb, or to scatter, is given quantitatively by the corresponding cross sections, to be defined as follows. Consider one atom in an X-ray beam with a flux of  $\Phi_0$  photons/sec/cm<sup>2</sup>. The absorption rate,  $W_{4\pi}$ , will be proportional to  $\Phi_0$ , and that defines the absorption cross section  $\sigma_a$  of the atom:

$$W_{4\pi} = \sigma_a \Phi_0 \tag{1a}$$

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The subscript  $4\pi$  is a reminder that we do not specify the direction of the expelled electron – it may come out anywhere within the total solid angle of  $4\pi$ .

Similarly, the number of photons scattered through the solid angle element  $\Delta\Omega$ , will be proportional to  $\Phi_0$ , as well as to  $\Delta\Omega$ :

$$W_{\Delta\Omega} = \frac{d\sigma}{d\Omega} \Phi_0 \Delta\Omega \quad (1b)$$

Both the absorption cross section  $\sigma_a$  and the scattering cross section,  $d\sigma/d\Omega$ , have the dimension of area, and this is commonly given in units of the barn,  $10^{-24} \text{ cm}^2$ .

The order of magnitude of the scattering cross section can be derived by a simple classical consideration. The incident X-ray beam, considered as an electromagnetic wave, will have an energy density proportional to the square of the electrical field  $E_{\text{in}}$ . Considered as a beam of photons, the photon flux  $\Phi_0$  will be the photon number density times the photon velocity  $c$ ; however, the photon number density is the energy density divided by the photon energy  $\hbar\omega$ , so one can write the flux  $\Phi_0$  [photons/area-unit/sec] =  $\alpha \cdot E_{\text{in}}^2$  where  $\alpha$  is a constant that we do not need to evaluate explicitly. The electric field in the incident beam will drive the electron, bound in the atom, to oscillate with the same frequency which we can, and will, assume to be much higher than any of the ‘eigenfrequencies’ of the bound electron. An oscillating electron radiates. In the far field, at distance  $R$ , the radiation field  $E_{\text{rad}}$  will give an intensity through the area  $R^2\Delta\Omega$  which is  $\alpha \cdot E_{\text{rad}}^2 R^2\Delta\Omega$ , (which is independent of  $R$  because  $E_{\text{rad}}$  decays as  $1/R$ ) so the scattering cross section is simply

$$\frac{d\sigma}{d\Omega} = \left[ \frac{E_{\text{rad}} R}{E_{\text{in}}} \right]^2$$

The radiated field will be proportional to the charge ( $-e$ ) and to the acceleration. But since Newton we have known that acceleration is the ratio between force, here  $(-e)E_{\text{in}}$ , and mass  $m$ , so  $E_{\text{rad}}/E_{\text{in}}$  must be proportional to  $e^2/m$ , or to the length (in c.g.s. units)  $r_0 = e^2/mc^2$  – the Thomson length of the electron, which is  $2.82 \times 10^{-5}$  Angstrom. The scattering cross section for one electron is therefore of the order  $r_0^2$ . The discussion can be refined by noting from the classical theory of radiation that the radiated field is proportional to the *observed* acceleration of the charged particle. In other words, if the observer is *at* the direction of the acceleration, that is in the direction of the incident field, i.e. the polarization direction, then he will not observe any acceleration at all, but if he is within the plane perpendicular to the incident field he will see the full acceleration. In general, as seen by inspection, he will see the fraction  $\boldsymbol{\varepsilon} \cdot \boldsymbol{\varepsilon}'$  of the full acceleration, where  $\boldsymbol{\varepsilon}$ , and  $\boldsymbol{\varepsilon}'$ , are unit vectors in the direction of polarization of the incident and scattered wave, respectively. By this heuristic argument we have obtained the result

$$\left( \frac{d\sigma}{d\Omega} \right)_{\text{1 electron}} = (r_0 \boldsymbol{\varepsilon} \cdot \boldsymbol{\varepsilon}')^2 \quad (2)$$

We note that the scattering cross section as derived here does not depend on the X-ray energy, presumably because we *assumed* that it was much higher than any transition energy within the atom. If we consider the entire atom of  $Z$  electrons and assume they all radiate in phase, the scattering cross section would be proportional to  $Z^2$ . Since the dimension of the electron cloud in an atom is of the same order of magnitude as the X-ray wavelength, the electrons do *not* radiate in phase. With the electron cloud density being  $\rho(\mathbf{r})$ , the resulting, effective radiating charge is easily shown to be  $\int \rho(\mathbf{r}) e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}} d\mathbf{r}$ , where  $\mathbf{k}$  and  $\mathbf{k}'$  are the wavevectors of the incident and scattered waves. This integral, or Fourier transform of the charge density, is called the formfactor  $f(\mathbf{Q} = \mathbf{k} - \mathbf{k}')$  of the atom, and it approaches  $Z$  as  $\mathbf{k} \rightarrow \mathbf{k}'$ . The resulting scattering cross section of an atom is thus

$$\left( \frac{d\sigma}{d\Omega} \right)_{\text{1 atom}} = [f(\mathbf{Q}) r_0 (\boldsymbol{\varepsilon} \cdot \boldsymbol{\varepsilon}')]^2 \quad (3)$$

In contrast to this discussion of the elastic scattering of X-rays, there is no semi-classical way to obtain the order of magnitude of the absorption cross section. Phenomenological, the absorption cross section varies roughly with the X-ray energy as  $(\hbar\omega)^{-3}$  and with atomic number as  $Z^4$ .

## 2. Outline of QM scheme

The main purpose of the rest of this article is to lay out the quantum mechanical (QM) evaluation of X-ray cross sections, so that the reader will understand how both the scattering and absorption cross sections are derived from

one and the same scheme of calculation. This scheme was developed about 80 years ago and is therefore described in many text books. It is included here only for completeness of the issue. The difficulty in comprehending the scheme lies mainly in the elaborate nomenclature, and in order not to be lost in that, it may be worthwhile first to describe the overall idea in the development in terms of a series of items.

1. We shall relate cross sections, as defined above, to quantum mechanical transition probabilities  $W$ . Here we remind the reader about Fermi's golden rule, which gives  $W$  in terms of a matrix element  $M_{if} = \langle f | H_{\text{int}} | i \rangle$ , with the nomenclature  $i$  for initial, and  $f$  for final states, and the density of final states.  $H_{\text{int}}$  is the interaction potential which allows the transition from one stationary state of an electron in the isolated atom to another stationary state by interaction with the X-ray photon field. Instead of going into more detail and long formulae at this point, we refer to Table 1, where this step in the scheme is spelled out.
2. Next, we must discuss  $H_{\text{int}}$ . With no ELM field the Hamiltonian for a free electron is simply  $p^2/(2m)$ , and for the electron in the Hartree–Fock potential  $\varphi(\mathbf{r})$  it is  $p^2/(2m) - e\varphi(\mathbf{r})$ . With an electric field the Hamiltonian is  $p^2/(2m) - e\varphi(\mathbf{r}) + H_{\text{int}}$  with

$$H_{\text{int}} = (e/m)\mathbf{p} \cdot \mathbf{A} + e^2/(2m)[\mathbf{A} \cdot \mathbf{A}] \tag{4}$$

Here  $\mathbf{A}$  is the vector potential of the ELM field from which the magnetic field  $\mathbf{B}$  is given by  $\mathbf{B} = \nabla \times \mathbf{A}$ , and  $\mathbf{p}$  is the electron momentum, because that Hamiltonian will produce the correct Lorentz force  $-e(\mathbf{E} + \mathbf{v} \times \mathbf{B})$ . We refer the reader to the Appendix for the details.

3. How does one evaluate the matrix element  $M_{if} = \langle f | H_{\text{int}} | i \rangle$ ? Here there are two points to consider. First, how do we explicitly write down the initial and final states and second, how do we derive the operator  $H_{\text{int}}$  in a form that is consistent with the notation of these states? The states have two components, one for the ELM field and one for the electron in the Hartree–Fock atom. For the electron we shall use  $|0\rangle_e$  for the initial state, which is the electron in the ground state. The final electron state is denoted  ${}_e\langle 1|$  if the electron is expelled from the atom as a photo-electron. For elastic Thomson scattering the final state is identical to the initial state, i.e.  ${}_e\langle 0|$ . The initial state of the ELM field is a plane wave with wavevector  $\mathbf{k}$  and linear polarization  $\boldsymbol{\varepsilon}$ . The minimal intensity is *one* photon in this state. For elastic Thomson scattering the wavevector and polarization are changed to  $\mathbf{k}'$  and  $\boldsymbol{\varepsilon}'$ , respectively, whereas for photo-absorption the one photon in the initial state is changed to *zero* photon occupation. Consequently, we write the initial and final ELM state for Thomson scattering as

$$\begin{aligned} |i\rangle_X &= |0\rangle|0\rangle \cdots |1\rangle \cdots |0\rangle|0\rangle \cdots \\ {}_X\langle f| &= \langle 0|\langle 0| \cdots \langle 0| \cdots \langle 1| \langle 0| \cdots \end{aligned} \tag{5}$$

where the different place of the occupation number '1' in the final state indicates that the wavevector, polarization changed from  $(\mathbf{k}, \boldsymbol{\varepsilon})$  to  $(\mathbf{k}', \boldsymbol{\varepsilon}')$ . For photoabsorption the initial state is still  $|i\rangle_X$ , and the final state has zeros on all occupation numbers. The full initial (final) state to be inserted into the matrix element is

$$|i\rangle = |i\rangle_X |0\rangle_e \quad \text{and} \quad \langle f| = {}_X\langle f| {}_e\langle 0| \quad \text{for scattering or} \quad \langle f| = {}_X\langle f| {}_e\langle 1| \quad \text{for absorption}$$

We are now ready to discuss the operator form of  $H_{\text{int}}$ .

### 2.1. The operator form of $H_{\text{int}}$

The initial ELM state is one standing wave with wavevector  $\mathbf{k}$ , polarization  $\boldsymbol{\varepsilon}$ , confined in a box of volume  $V$ , cf. the drawing in Table 1. With one photon in this state, the energy will be  $\hbar\omega_{\mathbf{k}}$ , and the energy density  $\hbar\omega_{\mathbf{k}}/V$ . The classical vector potential will be of the form

$$\mathbf{A}(\mathbf{r}, t) = \boldsymbol{\varepsilon} A_0 [e^{i(\mathbf{k}\cdot\mathbf{r} - \omega t)} + \text{c.c.}] = \boldsymbol{\varepsilon} A_0 2 \cos(\mathbf{k} \cdot \mathbf{r} - \omega t) \tag{6}$$

The electric field is derived from  $\mathbf{E} = -\partial\mathbf{A}/\partial t$ , and the time-averaged energy density is  $\varepsilon_0\langle \mathbf{E} \cdot \mathbf{E} \rangle = \varepsilon_0 A_0^2 2\omega^2$ , using that the time average of  $\sin^2 \omega t$  is  $\frac{1}{2}$ . To determine  $A_0$  the classical expression for the energy density is equated with the quantum form of  $\hbar\omega_{\mathbf{k}}/V$ , resulting in

$$A_0 = \sqrt{\frac{\hbar}{2\varepsilon_0 V \omega_{\mathbf{k}}}} \tag{7}$$

Table 1

Comment	Elastic scattering	Absorption
Figure	(a) Scattering	(b) Absorption
Definition of cross sections	$\frac{d\sigma}{d\Omega} = \frac{W_{\Delta\Omega}}{\Phi_0 \Delta\Omega}$	$\sigma_a = \frac{W_{4\pi}}{\Phi_0}$
Fermi's Golden rule	$W_{\Delta\Omega} = \frac{2\pi}{\hbar} \int  M_{if} ^2 \rho(\varepsilon_f) \delta(\varepsilon_f - \varepsilon_i) d\varepsilon_f$	$W_{4\pi} = \frac{2\pi}{\hbar} \int  M_{if} ^2 \rho(\varepsilon_{pe}) \delta(\varepsilon_{pe} - (\varepsilon_i - \varepsilon_B)) d\varepsilon_{pe}$
Density of states	$\rho(\varepsilon_f) = \frac{V}{(2\pi)^3} k_f^2 \frac{dk_f}{d\varepsilon_f} \Delta\Omega$	$\rho(\varepsilon_{pe}) = 2 \cdot \frac{V}{(2\pi)^3} \frac{d\mathbf{q}}{d\varepsilon_{pe}}$
Wavevector vs. energy	$k_f^2 \frac{dk_f}{d\varepsilon_f} = \frac{1}{(\hbar c)^3} \varepsilon_f^2$	$d\mathbf{q} = q^2 (\sin\theta d\theta d\varphi) dq$
Cross section vs. $M_{if}$	$\frac{d\sigma}{d\Omega} = \left(\frac{V}{2\pi}\right)^2 \frac{1}{(\hbar c)^4} \int  M_{if} ^2 \varepsilon_f^2 \delta(\varepsilon_f - \varepsilon_i) d\varepsilon_f$	$\sigma_a = 2 \left(\frac{V}{2\pi}\right)^2 \frac{1}{\hbar c} \int  M_{if} ^2 \delta(\varepsilon_{pe} - (\varepsilon_i - \varepsilon_B)) q^2 (\sin\theta d\theta d\varphi) dq$

The operator form of  $\mathbf{A}$  must contain creation,  $a^\dagger$ , and annihilation,  $a$ , operators of photon-states with wavevector  $\mathbf{k}$  obeying relations such as

$$a^\dagger|0\rangle = 1|1\rangle; \quad a|1\rangle = 1|0\rangle; \quad a^\dagger a|1\rangle = 1 \cdot |1\rangle \quad (8)$$

We are thus led to the time-independent operator form of  $\mathbf{A}$  from expressions (6)–(8):

$$\hat{\mathbf{A}} = \sum_{\mathbf{k}, \varepsilon} \hat{\mathbf{A}}_{\mathbf{k}, \varepsilon} \quad \text{where } \hat{\mathbf{A}}_{\mathbf{k}, \varepsilon} = \varepsilon [\hbar / (2\varepsilon_0 V \omega_{\mathbf{k}})]^{1/2} [a_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{r}} + a_{\mathbf{k}}^\dagger e^{-i\mathbf{k} \cdot \mathbf{r}}]$$

Returning to the operator form of the interaction as given in Eq. (4), one must examine whether  $\hat{\mathbf{A}}$  and the operator form  $\hat{\mathbf{p}}$  of the electron momentum  $\mathbf{p}$  commute. Since  $\hat{\mathbf{p}}$  is proportional to  $\nabla$ , the differential operator, we get  $\hat{\mathbf{p}}(\hat{\mathbf{A}}\psi) = \hat{\mathbf{A}}(\hat{\mathbf{p}}\psi) + cst \cdot \psi(\nabla \cdot \mathbf{A})_{\text{op}}$ , and if the gauge is chosen so that  $\nabla \cdot \mathbf{A} = 0$ , then, indeed, the two operators do commute. With this gauge we can therefore assert the operator form of  $H_{\text{int}}$  from (4) by just imagining an operator ‘hat’ over the vectors  $\mathbf{p}$  and  $\mathbf{A}$ .

## 2.2. QM evaluation of the Thomson cross section

It is clear that the term in  $H_{\text{int}}$  linear in  $\mathbf{A}$  leads to absorption because the operator  $a_{\mathbf{k}}$  operating to the right will annihilate the incident photon, and by closure  ${}_X\langle 0|0\rangle_X = 1$ . The term quadratic in  $\mathbf{A}$ , containing two sums, can lead to elastic scattering because the term  $a_{\mathbf{k}}$  in the first summation over  $\mathbf{k}$ , will annihilate the incident photon by operating to the right, but  $a_{\mathbf{k}'}^\dagger$  from the other summation will create an outgoing photon with wavevector  $\mathbf{k}'$  in operating to the right. The resulting matrix element is then

$$\begin{aligned} M_{if}^{\text{Thomson}} &= \frac{e^2}{2m} \boldsymbol{\varepsilon} \left[ \frac{\hbar}{2\varepsilon_0 V \omega} \right]^{1/2} \cdot \boldsymbol{\varepsilon}' \left[ \frac{\hbar}{2\varepsilon_0 V \omega'} \right]^{1/2} e \langle 0 | e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}} | 0 \rangle_e \\ &= \frac{e^2 \hbar}{2m\varepsilon_0 V} \frac{\boldsymbol{\varepsilon} \cdot \boldsymbol{\varepsilon}'}{[\omega\omega']^{1/2}} e \langle 0 | e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}} | 0 \rangle_e \end{aligned}$$

The last factor is indeed the Fourier transform of the charge density of the electron in ground state, or, considering all the electrons in the atom, it translates into the atomic formfactor  $f(\mathbf{Q})$  (with  $\mathbf{Q} = \mathbf{k} - \mathbf{k}'$ ) as anticipated already in Eq. (3). Also the polarization term  $\boldsymbol{\varepsilon} \cdot \boldsymbol{\varepsilon}'$  is recognized. From Table 1 we have

$$\frac{d\sigma}{d\Omega} = \left(\frac{V}{2\pi}\right)^2 \frac{1}{(\hbar c)^4} \int |M_{if}|^2 \varepsilon_f^2 \delta(\varepsilon_f - \varepsilon_i) d\varepsilon_f$$

which, together with  $\varepsilon_f = \varepsilon_i = \hbar\omega$ , indeed leads to expression (3) for the Thomson cross section.

### 2.3. QM evaluation of the absorption cross section

With the comfortable assurance that the QM scheme outlined above leads to the correct scattering cross section, we shall now proceed to discuss the absorption cross section as evaluated by the same scheme. Again we have to evaluate the matrix element  $M_{if}$ , and to this end we first consider the ‘bra’  ${}_e\langle 1|_X\langle 0|$  operated upon by  $(\hat{\mathbf{p}} \cdot \boldsymbol{\varepsilon})a_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}}$ . The occupation number operator  $a$  is annihilating when operating on a ‘ket’, but in operating on a ‘bra’ it acts as a creation operator, so  ${}_X\langle 0|a_{\mathbf{k}} = {}_X\langle 1|$ . If we take  ${}_e\langle 1|$  as a free-electron state with wavevector  $\mathbf{q}$ , then  ${}_e\langle 1|\hat{\mathbf{p}} = \hbar\mathbf{q}{}_e\langle 1|$ . Unfortunately this simple result is not the correct answer, because the photo-electron is *not* a free electron, since it is moving in the Coulomb field of the ion left behind after the electron is expelled from the atom. Nevertheless, for the sake of simplicity we shall first pretend that a free electron wavefunction is accurate enough, and proceed to obtain

$$\begin{aligned} M_{if}^{\text{absorbion}} &= \frac{e}{m} (\hbar\mathbf{q} \cdot \boldsymbol{\varepsilon}) \left[ \frac{\hbar}{2\varepsilon_0 V \omega} \right]^{1/2} {}_e\langle 1|e^{i\mathbf{k}\cdot\mathbf{r}}|0\rangle_e \\ &= \frac{e\hbar}{m} (\mathbf{q} \cdot \boldsymbol{\varepsilon}) \left[ \frac{\hbar}{2\varepsilon_0 V \omega} \right]^{1/2} \int \psi_{e,f}^* e^{i\mathbf{k}\cdot\mathbf{r}} \psi_{e,i} d\mathbf{r} \\ &= \frac{e\hbar}{m} (\mathbf{q} \cdot \boldsymbol{\varepsilon}) \left[ \frac{\hbar}{2\varepsilon_0 V \omega} \right]^{1/2} \frac{1}{\sqrt{V}} \int e^{-i\mathbf{q}\cdot\mathbf{r}} e^{i\mathbf{k}\cdot\mathbf{r}} \psi_{1s} d\mathbf{r} \end{aligned} \quad (9)$$

In the last equation we have substituted the normalized free-electron wave function for  $\psi_{e,f}$  and, just for illustration, assumed that the electron being expelled is a K-electron with wavefunction  $\psi_{1s}$ . The integral is then simply the Fourier transform of the initial, bound state electron wavefunction, and denoting the Fourier transform by  $\phi(\mathbf{Q})$ ,  $\mathbf{Q}$  being  $\mathbf{Q} = \mathbf{k} - \mathbf{q}$ , we find the squared matrix element for the *particular* process where the photo electron has a definite wavevector  $\mathbf{q}$  (rather than any wavevector consistent with energy conservation) to be

$$|M_{if}^{\text{absorbion}}|^2 = \left(\frac{e\hbar}{m}\right)^2 \frac{\hbar}{2\varepsilon_0 V^2 \omega} [(\mathbf{q} \cdot \boldsymbol{\varepsilon})\phi(\mathbf{Q} = \mathbf{k} - \mathbf{q})]^2$$

By integrating over all directions of  $\mathbf{q}$  we recall the result from Table 1

$$\sigma_a = 2 \left(\frac{V}{2\pi}\right)^2 \frac{1}{\hbar c} \int |M_{if}^{\text{absorbion}}|^2 \delta(\varepsilon_{pe} - (\varepsilon_i - \varepsilon_B)) q^2 (\sin\theta d\theta d\varphi) dq \quad (10)$$

We note (with satisfaction) that the volume  $V$  disappears in the expression for the absorption cross section.

From now on the evaluation is mostly a matter of dry, mathematical manipulation that we shall skip and in stead refer the reader to the book ‘Elements of Modern X-ray Physics’ [1, Chapter 6, pp. 208–213]. The notation in this reference is the same as used here. We state the intermediate result

$$\sigma_a = 32\lambda r_0 \frac{4}{3} \left[ \frac{\omega_A^2}{\omega\omega_c} \right]^{5/2} \quad \text{for } \hbar\omega_K \ll \hbar\omega \ll \hbar\omega_c \quad (11)$$

The result has the virtue that it is in closed mathematical form in the stated limit, namely that the incoming photon energy is much larger than the binding energy  $\hbar\omega_K$  of the electron, considered to be a K-electron, but still small compared to the electron rest mass energy  $\hbar\omega_c = 2mc^2$ . The remaining undefined parameter in Eq. (11) is  $\hbar\omega_A$ . It has to do with the initial wavefunction  $\psi_{1s}$  of the electron, here assumed to be a K-electron. This wavefunction is like the ground state wavefunction of the electron in a hydrogen atom, characterized by the Bohr radius  $a_0 = 0.53 \text{ \AA}$ , but since in our case the electron is in the Coulomb field of charge  $Z$  rather than 1, the Bohr radius is  $Z$  times smaller and thus

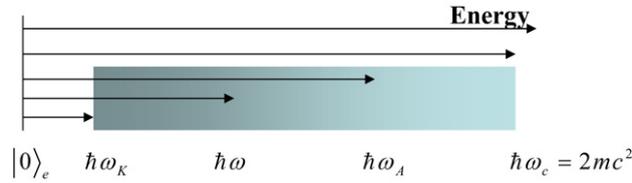


Fig. 1. The various energies (from [1]).

considerably smaller than the X-ray wavelength. The inverse length,  $\kappa = Z/a_0$ , is a wavenumber, and the parameter  $\omega_A$  is defined in terms of this wavenumber by  $\hbar\omega_A = \hbar c\kappa$ , so  $\omega_A$  is proportional to  $Z$  and  $\hbar\omega_A \gg \hbar\omega$ . Fig. 1, taken from the reference [1] may be the easiest way to grasp the definitions of  $\hbar\omega_{\text{various}}$ .

It is interesting to note from (11) that the absorption cross section presumably is much larger than the scattering cross section since  $\lambda r_0 \gg r_0^2$ , tacitly guessing that the  $\omega_A^2/(\omega\omega_c)$  is of order unity.

Unfortunately, the energy dependence as well as the dependence on  $Z$  is not quite right in Eq. (11). The experimental facts are  $\sigma_a \propto (\hbar\omega)^{-3} Z^4$  whereas Eq. (11) predicts  $\propto (\hbar\omega)^{-2.5} Z^5$ . The reason is the simplifying but crude approximation that the photoelectron is a free electron, rather than moving in the Coulomb potential of the positive ion left behind when the photoelectron escaped from the neutral atom. But that approximation was only introduced for mathematical convenience, so if one does it rigorously with the correct photoelectron wavefunction, it turns out that one gets a result quite similar to Eq. (11), but with a correction factor that indeed repairs the wrong energy and  $Z$  dependence of Eq. (11):

$$\sigma_{a,K} = 2 \cdot 32\lambda r_0 \frac{4}{3} \left[ \frac{\omega_A^2}{\omega\omega_c} \right]^{5/2} f(\xi) \tag{12}$$

$$\xi = \sqrt{\frac{\omega_K}{\omega - \omega_K}}; \quad f(\xi) = 2\pi \sqrt{\frac{\omega_K}{\omega}} \frac{e^{-4\xi \arccot \xi}}{1 - e^{-2\pi\xi}}$$

The factor 2 is due to the fact that there are 2 K electrons in the absorbing atom. The formula does *not* include other absorption processes than those corresponding to the emission of a K-electron, and it is tacitly assumed that the X-ray photon energy is sufficient, i.e.  $\hbar\omega \geq \hbar\omega_K$ . At the threshold  $\hbar\omega \rightarrow \hbar\omega_K +$  the discontinuity is easily evaluated to be

$$\sigma_a(\hbar\omega = \hbar\omega_K) = 2 \cdot 32\lambda r_0 \frac{4}{3} \left[ \frac{\omega_A^2}{\omega_K\omega_c} \right]^{5/2} \frac{2\pi}{e^4} \tag{13}$$

In Fig. 2 we show the calculated absorption cross section vs. photon energy for three different atoms.

### 3. Perturbation theory to second order and resonant scattering

The Fermi Golden Rule referred to so far is derived by perturbation theory only to first order. For completeness we include the transition probability  $W$  to second order:

$$W = \frac{2\pi}{\hbar} \left| \langle f | H_{\text{int}} | i \rangle + \sum_{n=1}^{\infty} \frac{\langle f | H_{\text{int}} | n \rangle \langle n | H_{\text{int}} | i \rangle}{E_i - E_n} \right|^2 \rho(E_f) \tag{14}$$

where the sum is over all possible states  $|n\rangle$  with energy  $E_n$ . It can now be seen that the  $\mathbf{A} \cdot \mathbf{p}$  term, which is linear in creation and annihilation operators, via the second term in (14), can produce scattering via an intermediate state  $|n\rangle$ : the incident photon is first destroyed while the electron makes a transition from the ground state,  $|0\rangle_e$ , to an intermediate state  $|n\rangle$ . The electron then makes a transition from  $|n\rangle$  to  $|0\rangle_e$  while a photon with the same energy as the incident photon energy is created, i.e. an elastically scattered photon. The second term will be particularly important when the photon energy  $E_i$  is near the energy difference between the intermediate and ground state of the electron, leading to what is termed *resonant* scattering.

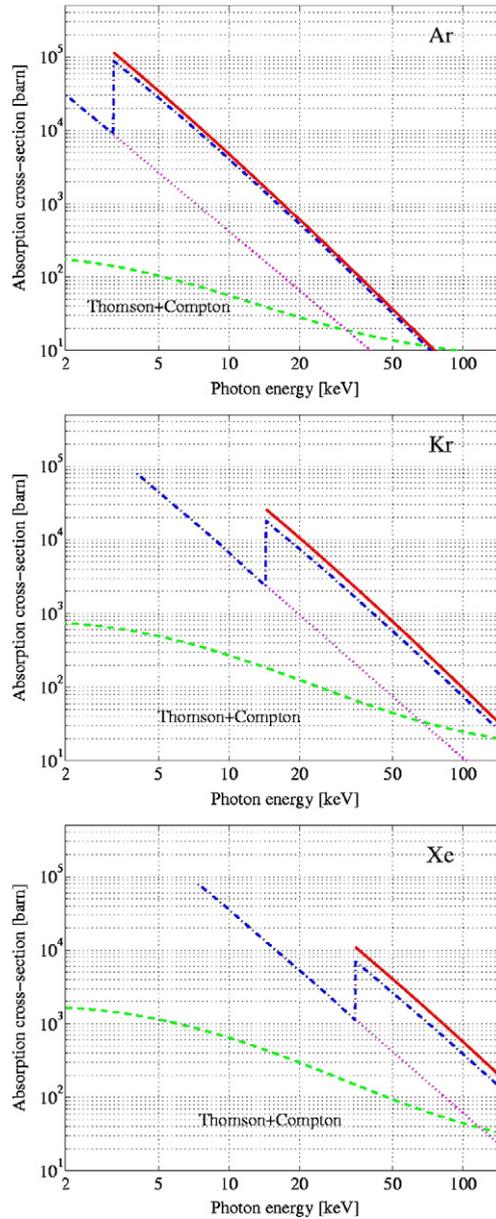


Fig. 2. The photoelectric absorption cross sections of Ar, Kr and Xe plotted on a double logarithmic scale for energies in the vicinity of the K-edges. The dot-dashed lines represent the results of calculations within the self-consistent Dirac–Hartree–Fock framework. The solid lines are calculated from Eq. (13) with  $\hbar\omega_K$  equal to the experimentally observed values. The extrapolated contribution from the L electrons (dotted lines) was added to produce the final result. For completeness the cross sections for Thomson and Compton scattering are plotted as the dashed lines. The L edges of Kr (around 2 keV) and Xe (around 5 keV) have been omitted for clarity.

### Appendix A. The Lorentz force

The Hamiltonian  $H = (\mathbf{p} + e\mathbf{A})^2/2m - e\varphi(\mathbf{r})$ , giving the interacting Hamiltonian of Eq. (4), will produce the correct Lorentz force, as we shall now see.

We shall use the Lagrangian method  $\dot{x} = \partial H/\partial p_x$  and  $\dot{p}_x = -\partial H/\partial x$ :

$$\text{Hamiltonian } H = \frac{1}{2m} [(p_x + eA_x)^2 + (p_y + eA_y)^2 + (p_z + eA_z)^2] - e\varphi \tag{A.1}$$

$$x\text{-component of Lagrangian } \dot{x} = \partial H / \partial p_x = 2\{p_x + e \cdot A_x(\mathbf{r})\} / (2m) \quad (\text{A.2})$$

$$\dot{p}_x = -\partial H / \partial x \quad \text{or}$$

$$\begin{aligned} \dot{p}_x &= e \frac{\partial \varphi}{\partial x} - \frac{1}{2m} \left[ (p_x + eA_x)e \frac{\partial A_x}{\partial x} + (p_y + eA_y)e \frac{\partial A_y}{\partial x} + (p_z + eA_z)e \frac{\partial A_z}{\partial x} \right] 2 \\ &= e \frac{\partial \varphi}{\partial x} - e \left[ \dot{x} \frac{\partial A_x}{\partial x} + \dot{y} \frac{\partial A_y}{\partial x} + \dot{z} \frac{\partial A_z}{\partial x} \right] \end{aligned} \quad (\text{A.3})$$

In the last equation we have inserted  $\dot{x}$  from the first equation (A.2). From (A.2) we derive the Lorentz force component in the  $x$ -direction:

$$F_{x, \text{Lorentz}} = m\ddot{x} = (\dot{p}_x + e\dot{A}_x)$$

We evaluate  $\dot{A}_x$  as follows and insert  $\dot{p}_x$  from (A.3),

$$e\dot{A}_x(\mathbf{r}, t) = e \left[ \frac{\partial A_x}{\partial t} + \dot{x} \frac{\partial A_x}{\partial x} + \dot{y} \frac{\partial A_x}{\partial y} + \dot{z} \frac{\partial A_x}{\partial z} \right]$$

to get

$$\dot{p}_x + e\dot{A}_x(\mathbf{r}, t) = e \frac{\partial \varphi}{\partial x} + e \frac{\partial A_x}{\partial t} - e \left[ \dot{y} \left( \frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y} \right) + \dot{z} \left( \frac{\partial A_z}{\partial x} - \frac{\partial A_x}{\partial z} \right) \right]$$

On the right-hand side, the first two terms are precisely the Lorentz force  $x$ -component due to the electric field. In the squared parenthesis  $(\frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y}) = (\nabla \times \mathbf{A})_z$  and  $(\frac{\partial A_z}{\partial x} - \frac{\partial A_x}{\partial z}) = -(\nabla \times \mathbf{A})_y$ , so the squared parenthesis times the charge  $(-e)$  is indeed  $(\mathbf{v} \times \mathbf{B})_x$ , the Lorentz force  $x$ -component due to the magnetic field. The  $y$  and  $z$  components are derived in the same way, so indeed the stated Hamiltonian produces the correct Lorentz force.

## References

- [1] J. Als-Nielsen, D. McMorrow, Elements of Modern X-Ray Physics, J. Wiley, 2002.