

## Chapter 3 Scattering from an Atom

The atomic scattering factor represents how an atom scatters X-ray. It is dominated by the structure factor of an atom, which is sometimes called “atomic form factor” or “atomic structure factor”. Note that the structure factor of an atom is definitely determined by the electron density on the atom. Dispersion effect, which will be described later in this Chapter, is usually included in the atomic scattering factor by addition of dispersion correction terms, but it is not necessary in some cases. Both the electron density and dispersion effect of an isolated atom are unique to the element. The electron density of an isolated atom is evaluated by quantum mechanical calculation.

In Chap. 2, it has been concluded that the observed diffraction (scattering) intensity should be proportional to the squared absolute value of the “Fourier transform of the electron density” (structure factor), when the effect of multiple scattering is neglected (kinematical theory of diffraction). Actually, it is not necessary for ordinary users of crystal structure analysis to calculate the electron density, or even Fourier transform given by an integral formula, because the electron density of all the elements and the Fourier transforms have already been evaluated and tabulated, and the diffraction from a crystal can be treated by the sum of the waves scattered by the atoms, at least as the first approximation. If it is necessary to refer the values of atomic structure factors, we usually use the tabulated values theoretically calculated. The structure factors of all the elements and many ions are listed in “International Tables for Crystallography, Vol. C”, edited by the International Union of Crystallography. Furthermore, standard application software for crystal structure analysis holds the data for atomic structure factor inside. As a result, what the ordinary users should do is just indicating the elements included in a crystal to the application software.

Quiz: which is the case where the diffraction from a crystal can NOT be approximated by the sum of the scattering of atoms ?

- A. when the effect of finite size of a crystal cannot be neglected
- B. when the effects of chemical bonds cannot be neglected
- C. when the dispersion effect cannot be neglected
- D. when the thermal vibration of atoms cannot be neglected

### 3-1 Cartesian and spherical coordinates

It is assumed that the electron density of an atom has spherical symmetry, in other words, the electron density is treated as a function of the distance from the center. How is the structure factor expressed in this case ? **Spherical coordinate system** represented by  $(r, \theta, \phi)$  is generally more

convenient than the **Cartesian (orthogonal) coordinate system**  $(x, y, z)$  to treat an object with spherical symmetry.

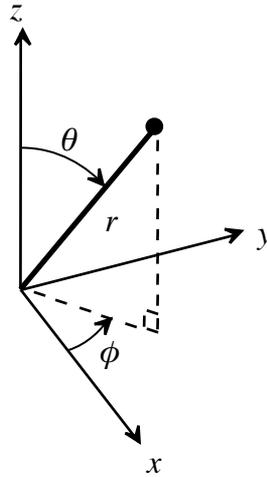


Fig. 3.1 Relations between the Cartesian coordinate  $(x, y, z)$  and spherical coordinate  $(r, \theta, \phi)$ .

The relationship between the Cartesian coordinate and spherical coordinate is given by

$$\begin{aligned} x &= r \sin \theta \cos \phi \\ y &= r \sin \theta \sin \phi \\ z &= r \cos \theta \end{aligned} \quad (3.1)$$

And the following relation :

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(x, y, z) dx dy dz = \int_0^{\infty} \int_0^{\pi} \int_0^{2\pi} f(r \sin \theta \cos \phi, r \sin \theta \sin \phi, r \cos \theta) r^2 \sin \theta d\phi d\theta dr \quad (3.2)$$

generally holds.

### 3-2 Structure factor for electron density with spherical symmetry

When the electron density distribution has spherical symmetry, the function to express the electron density  $\rho(x, y, z)$  can be simplified as a function with one argument,  $r = \sqrt{x^2 + y^2 + z^2}$ , so it can be written as  $\rho(r)$ . Here we consider a case where the diffraction vector is parallel to the  $z$ -axis (or we take a Cartesian coordinate system having  $z$ -axis parallel to the scattering vector). The scattering vector is given by

$$\vec{K} = \begin{pmatrix} 0 \\ 0 \\ K \end{pmatrix}. \quad (3.3)$$

The formula of (three-dimensional) Fourier transform (structure factor)  $f(\vec{K})$  of the spherical electron density  $\rho(r)$  can be transformed as follows,

$$\begin{aligned}
 f(\vec{K}) &= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \rho(r) \exp(-2\pi i \vec{K} \cdot \vec{r}) dx dy dz \\
 &\stackrel{\text{eq. (3.2)}}{=} \int_0^{\infty} \int_0^{\pi} \int_0^{2\pi} \rho(r) e^{-2\pi i Kr \cos \theta} r^2 \sin \theta d\phi d\theta dr \\
 &\stackrel{\uparrow}{=} 2\pi \int_0^{\infty} \int_0^{\pi} \rho(r) e^{-2\pi i Kr \cos \theta} r^2 \sin \theta d\theta dr, \\
 &\quad \int_0^{2\pi} d\phi = 2\pi \\
 &\stackrel{\uparrow}{=} 2\pi \int_0^{\infty} \int_{-1}^1 \rho(r) e^{2\pi i Kr t} r^2 dt dr \\
 &\quad \begin{array}{l} -\cos \theta = t \\ \sin \theta d\theta = dt \\ \theta : 0 \rightarrow \pi \\ t : -1 \rightarrow 1 \end{array} \\
 &= 2\pi \int_0^{\infty} r^2 \rho(r) \left[ \frac{1}{2\pi i Kr} e^{2\pi i Kr t} \right]_{-1}^1 dr \\
 &= \frac{1}{iK} \int_0^{\infty} r \rho(r) (e^{2\pi i Kr} - e^{-2\pi i Kr}) dr \\
 &= \frac{2}{K} \int_0^{\infty} r \rho(r) \sin(2\pi Kr) dr \tag{3.4}
 \end{aligned}$$

We can calculate the structure factor  $f(\vec{K})$  for any scattering vector  $\vec{K}$  by the above equation, when the spherical electron density distribution  $\rho(r)$  is known. The structure factor is determined solely by the length of the scattering vector  $K = |\vec{K}| = \frac{2 \sin \Theta}{\lambda}$ , when the electron density distribution has spherical symmetry.

### 3-2-1 Case of electron density with spherical normal distribution

What is the structure factor of three-dimensional normal distribution (Gaussian function), for example, given by the following equation ?

$$\rho(r) = \frac{1}{(2\pi)^{3/2} \sigma^3} \exp\left(-\frac{r^2}{2\sigma^2}\right), \tag{3.5}$$

In the above equation,  $\sigma$  is the standard deviation indicating the broadness of the distribution. Application of a Cartesian coordinate system is exceptionally easy in this case.

In the Cartesian coordinate system, the solution should be

$$f(\vec{K}) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{1}{(2\pi)^{3/2} \sigma^3} \exp\left(-\frac{r^2}{2\sigma^2}\right) \exp(-2\pi i \vec{K} \cdot \vec{r}) dx dy dz$$

$$\begin{aligned}
&= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{1}{(2\pi)^{3/2} \sigma^3} \exp\left(-\frac{x^2 + y^2 + z^2}{2\sigma^2}\right) \exp(-2\pi i Kz) dx dy dz \\
&= \int_{-\infty}^{\infty} \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{x^2}{2\sigma^2}\right) dx \int_{-\infty}^{\infty} \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{y^2}{2\sigma^2}\right) dy \\
&\quad \times \int_{-\infty}^{\infty} \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{z^2}{2\sigma^2}\right) \exp(-2\pi i Kz) dz \\
&= \int_{-\infty}^{\infty} \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{z^2}{2\sigma^2}\right) \exp(-2\pi i Kz) dz \\
&= \int_{-\infty}^{\infty} \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{z^2}{2\sigma^2}\right) \cos(2\pi Kz) dz \\
&= \exp(-2\pi^2 K^2 \sigma^2), \tag{3.6}
\end{aligned}$$

where the formula :

$$\int_{-\infty}^{\infty} \frac{1}{\sqrt{\pi}\gamma} \exp\left(-\frac{x^2}{\gamma^2}\right) \cos(2\pi kx) dx = \exp(-\pi^2 k^2 \gamma^2) \tag{3.7}$$

is used on the last equation.

In the spherical coordinate system, the solution will be

$$\begin{aligned}
f(K) &= \frac{2}{(2\pi)^{3/2} \sigma^3 K} \int_0^{\infty} r \exp\left(-\frac{r^2}{2\sigma^2}\right) \sin(2\pi Kr) dr \\
&= \frac{2}{(2\pi)^{3/2} \sigma^3 K} \left\{ \left[ -\sigma^2 \exp\left(-\frac{r^2}{2\sigma^2}\right) \sin(2\pi Kr) \right]_0^{\infty} + 2\pi K \sigma^2 \int_0^{\infty} \exp\left(-\frac{r^2}{2\sigma^2}\right) \cos(2\pi Kr) dr \right\} \\
&= \frac{2}{\sqrt{2\pi}\sigma} \int_0^{\infty} \exp\left(-\frac{r^2}{2\sigma^2}\right) \cos(2\pi Kr) dr \\
&= \exp(-2\pi^2 K^2 \sigma^2). \tag{3.8}
\end{aligned}$$

Note that the structure factor also has the formula of a Gaussian function (normal distribution) with the standard deviation of  $\frac{1}{2\pi\sigma}$ .

### 3-2-2 Case of electron density of spherical exponential distribution

What is the structure factor of three-dimensional exponential electron density distribution as another example given by the following equation ?

$$\rho(r) = \frac{1}{8\pi\sigma^3} e^{-r/\sigma} \tag{3.9}$$

Note that the exact solution of the 1s electron density of a “hydrogen-like atom” has this formula.

This function is normalized, which can be examined by integrating over the whole three dimensional space, as follows,

$$\begin{aligned}
\int_0^{\infty} \int_0^{\pi} \int_0^{2\pi} \rho(r) r^2 \sin\theta d\varphi d\theta dr &= 4\pi \int_0^{\infty} \rho(r) r^2 dr = \frac{1}{2\sigma^3} \int_0^{\infty} r^2 e^{-r/\sigma} dr \\
&= \frac{1}{2\sigma^3} \left\{ \left[ -\sigma r^2 e^{-r/\sigma} \right]_0^{\infty} + 2\sigma \int_0^{\infty} r e^{-r/\sigma} dr \right\} = \frac{1}{\sigma^2} \left\{ \left[ -\sigma r e^{-r/\sigma} \right]_0^{\infty} + \sigma \int_0^{\infty} e^{-r/\sigma} dr \right\} \\
&= \frac{1}{\sigma} \left[ -\sigma e^{-r/\sigma} \right]_0^{\infty} = 1.
\end{aligned} \tag{3.10}$$

The structure factor will be given by

$$\begin{aligned}
f(K) &= \frac{1}{4\pi K \sigma^3} \int_0^{\infty} r e^{-r/\sigma} \sin(2\pi K r) dr \\
&= \frac{1}{4\pi K \sigma^3} \left\{ \left[ -\sigma r e^{-r/\sigma} \sin(2\pi K r) \right]_0^{\infty} + \sigma \int_0^{\infty} e^{-r/\sigma} \sin(2\pi K r) dr + 2\pi K \sigma \int_0^{\infty} r e^{-r/\sigma} \cos(2\pi K r) dr \right\} \\
&= \frac{1}{4\pi K \sigma^2} \left[ \int_0^{\infty} e^{-r/\sigma} \sin(2\pi K r) dr + 2\pi K \int_0^{\infty} r e^{-r/\sigma} \cos(2\pi K r) dr \right] \\
&= \frac{1}{4\pi K \sigma^2} \left\{ \left[ -\sigma e^{-r/\sigma} \sin(2\pi K r) \right]_0^{\infty} + 2\pi K \sigma \int_0^{\infty} e^{-r/\sigma} \cos(2\pi K r) dr \right. \\
&\quad \left. + 2\pi K \left[ -\sigma r e^{-r/\sigma} \cos(2\pi K r) \right]_0^{\infty} + 2\pi K \sigma \int_0^{\infty} e^{-r/\sigma} \cos(2\pi K r) dr \right. \\
&\quad \left. - 4\pi^2 K^2 \sigma \int_0^{\infty} r e^{-r/\sigma} \sin(2\pi K r) dr \right\} \\
&= \frac{1}{\sigma} \int_0^{\infty} e^{-r/\sigma} \cos(2\pi K r) dr - 4\pi^2 K^2 \sigma^2 f(K),
\end{aligned} \tag{3.11}$$

and the solution about  $f(K)$  should be

$$f(K) = \frac{1}{\sigma(1 + 4\pi^2 K^2 \sigma^2)} \int_0^{\infty} e^{-r/\sigma} \cos(2\pi K r) dr. \tag{3.12}$$

As the integral part of the above equation has the relation:

$$\begin{aligned}
\int_0^{\infty} e^{-r/\sigma} \cos(2\pi K r) dr &= \left[ -\sigma e^{-r/\sigma} \cos(2\pi K r) \right]_0^{\infty} - 2\pi K \sigma \int_0^{\infty} e^{-r/\sigma} \sin(2\pi K r) dr \\
&= \sigma - 2\pi K \sigma \left\{ \left[ -\sigma e^{-r/\sigma} \sin(2\pi K r) \right]_0^{\infty} + 2\pi K \sigma \int_0^{\infty} e^{-r/\sigma} \cos(2\pi K r) dr \right\} \\
&= \sigma - 4\pi^2 K^2 \sigma^2 \int_0^{\infty} e^{-r/\sigma} \cos(2\pi K r) dr,
\end{aligned} \tag{3.13}$$

the following equation is derived,

$$\int_0^{\infty} e^{-r/\sigma} \cos(2\pi Kr) dr = \frac{\sigma}{1 + 4\pi^2 K^2 \sigma^2}. \quad (3.14)$$

We can derive solution from Eqs. (3.11) and (3.13) for the structure factor of exponential distribution given by

$$f(K) = \frac{1}{(1 + 4\pi^2 K^2 \sigma^2)^2} \quad (3.15)$$

### 3-3 Tables of atomic scattering factor

As shown in the section 3-2, the atomic structure factor for a spherical electron density distribution is a function of the length of the scattering vector  $K = 2(\sin\Theta)/\lambda$  or  $(\sin\Theta)/\lambda$ . “International Tables for Crystallography Vol. C” lists the atomic structure factors for elements and ions varying on the value  $(\sin\theta)/\lambda$ . The table below shows a part of the table listed in the “international Tables”.

Table 3.1 Atomic structure factors (part of “International Tables”)

Element	H	He	Li	Be	B	C	N	O	F	Ne
Z	1	2	3	4	5	6	7	8	9	10
Method	HF	RHF								
$(\sin\theta)/\lambda$ (Å <sup>-1</sup> )										
0.00	1.000	2.000	3.000	4.000	5.000	6.000	7.000	8.000	9.000	10.000
0.01	0.998	1.998	2.986	3.987	4.988	5.990	6.991	7.992	8.993	9.993
0.02	0.991	1.993	2.947	3.950	4.954	5.958	6.963	7.967	8.970	9.973
0.03	0.980	1.984	2.884	3.889	4.897	5.907	6.918	7.926	8.933	9.938
0.04	0.966	1.972	2.802	3.807	4.820	5.837	6.855	7.869	8.881	9.891
0.05	0.947	1.957	2.708	3.707	4.724	5.749	6.776	7.798	8.815	9.830
0.06	0.925	1.939	2.606	3.592	4.613	5.645	6.682	7.712	8.736	9.757
0.07	0.900	1.917	2.502	3.468	4.488	5.526	6.574	7.612	8.645	9.672
0.08	0.872	1.893	2.400	3.336	4.352	5.396	6.453	7.501	8.541	9.576
.	.	.	.	.	.	.	.	.	.	.
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.	.	.	.	.	.	.	.	.	.	.

An approximate formula given by

$$f\left(\frac{\sin\theta}{\lambda}\right) = \sum_{i=1}^4 a_i \exp\left(-\frac{b_i \sin^2\theta}{\lambda^2}\right) + c \quad (3.15)$$

is often applied to evaluate the atomic structure factor. It is known that this formula is a good approximation in the range  $0 < (\sin\theta)/\lambda < 2.0 \text{ \AA}^{-1}$ . It is also known that the formula given by Eq. (3.15) is NOT a good approximation in the range  $(\sin\theta)/\lambda > 2.0 \text{ \AA}^{-1}$ , and considerably deviated from the exact value. But the formula is still useful, because the value of  $(\sin\theta)/\lambda$  should always be less than  $2.0 \text{ \AA}^{-1}$  for the X-ray having the wavelength longer than  $0.5 \text{ \AA}$ , practically used for the measurement. The values of the 9 parameters  $a_1, b_1, a_2, b_2, a_3, b_3, a_4, b_4, c$  for some elements and ions are listed in Table 3.2.

Table 3.2 Parameters for calculating the atomic structure factors

		$a_1$	$b_1$	$a_2$	$b_2$	$a_3$	$b_3$	$a_4$	$b_4$	$c$	Maximum error	$\sin\theta/\lambda$ ( $\text{\AA}^{-1}$ )	Mean error
H	SDS	0.493	10.5109	0.322912	26.1257	0.140191	3.14236	0.040810	57.8	0.003038	0.000	0.00	0.000
H	HF	0.48992	20.6593	0.262003	7.74039	0.196767	49.5519	0.049879	2.2016	0.001305	0.000	0.17	0.000
H <sup>1-</sup>	HF	0.89766	53.1368	0.565616	15.1870	0.415815	186.576	0.116973	3.5671	0.002389	0.002	0.09	0.001
He	RHF	1.12820	...	...	...	...	...	...	...	...	...	...	...
Li	...	...	...	...	...	...	...	...	...	...	...	...	...
Li <sup>1+</sup>	...	...	...	...	...	...	...	...	...	...	...	...	...
Be	...	...	...	...	...	...	...	...	...	...	...	...	...
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### 3-4 Atomic scattering factors of light elements

The atomic structure factors for the atoms from the atomic number “1: hydrogen” to “10: neon” are shown in the figure below. The values are calculated by the approximate formula given in the former section.

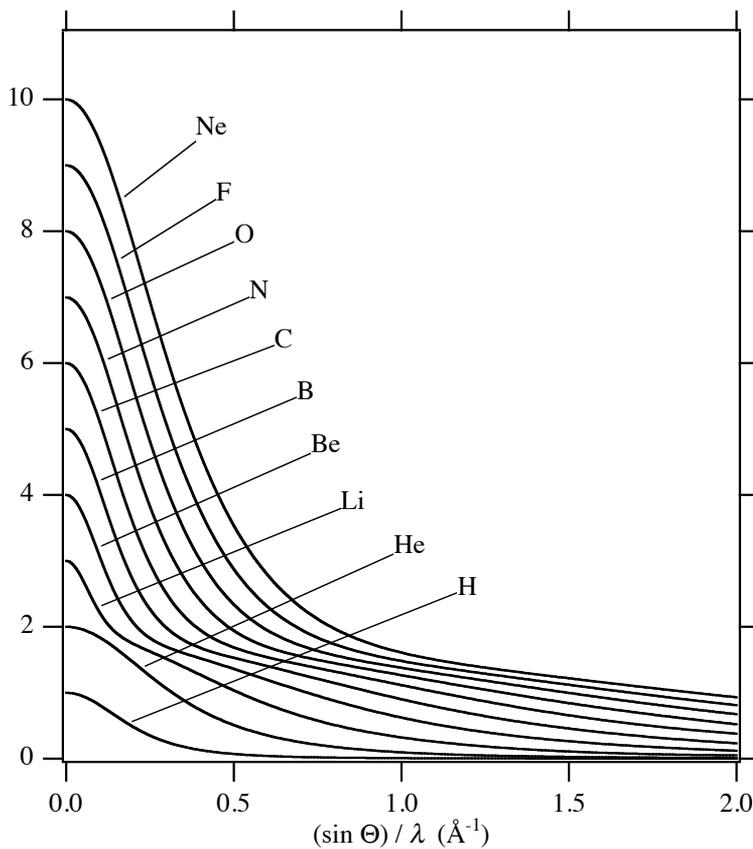


Fig. 3.2 Atomic structure factors of light elements

The abscissa  $(\sin \Theta) / \lambda$  is half the length of the scattering vector  $K = 2(\sin \Theta) / \lambda$ . The value of the scattering factor at  $(\sin \Theta) / \lambda = 0$  is exactly equal to the atomic number. Note that the **longer tail** of the atomic scattering factor for the atoms of **larger atomic number** corresponds to the **smaller orbital size of inner shell electrons** caused by larger charge of the nucleus.

### 3-5 Dispersion effect

So far, we have assumed that all the electrons can be treated as free electrons. However, stronger scattering can be caused by **resonance effect**, when the photon energy of the X-ray is close to the energy of absorption edge, in other words, the frequency of the X-ray is close to the natural frequency of bound electrons. This phenomenon was previously called “**anomalous dispersion**” in the field of X-ray crystallography, but currently called just “**dispersion**” or “**dispersion effect**”.

When the dispersion effect is taken into account, the atomic scattering factor is approximated by

$$f(K) = f_0(K) + \Delta f' + i\Delta f'' \quad (3.16)$$

where  $f_0(K)$  is the real structure factor, and the complex  $\Delta f' + i\Delta f''$  is the dispersion correction terms (previously called anomalous dispersion terms). The value of the dispersion correction terms depends on the element and the wavelength of the X-ray. In principle, the dispersion terms should also depend on the length of the scattering vector (or the scattering angle)  $K = |\vec{K}| = 2(\sin \Theta) / \lambda$ , but the values of the dispersion correction terms are usually treated as constant values against  $K$ .

Practically, the values of  $\Delta f'$  and  $\Delta f''$  do not significantly depend on the scattering angle, because the electrons that can be resonated by the X-ray are the inner shell (K shell or L shell) electrons. Note that the oscillation of point charge will make non-directive emission expressed by “dipole radiation” and it should be independent of  $K$ . The dispersion correction terms can sometimes be neglected at all, because the values become small when the photon energy of the X-ray is not close the absorption edge.

The table below lists some of the values of dispersion correction terms.

Table 3.3 Examples of dispersion correction

	CuK $\alpha$ (~ 1.54 Å)		MoK $\alpha$ (~ 0.71 Å)		
	$\Delta f'$	$\Delta f''$	$\Delta f'$	$\Delta f''$	
C	0.0181	0.0091	0.0033	0.0016	N, O, F have similar values
Si	0.2541	0.3302	0.0704	0.1023	Al, P, S, Cl have similar values
Ge	-1.0885	0.8855	0.1547	1.8001	Fe, Cu, Ni, Br have similar values
Sn	0.0259	5.4591	-0.6537	1.4216	

The “K $\alpha$ ” line means the radiation caused by the emission of excess energy on filling the K-shell vacancy induced by irradiation of electron, with a L-shell electron. The wavelength of CuK $\alpha$  X-ray is about 1.54 Å. We should be careful, when we analyze the diffraction data of materials including transition metal elements having an absorption edge close to the emission of the source X-ray, for example, the X-ray wavelength for the K-absorption edges of Co (cobalt) and Ni (nickel) are 1.49 Å and 1.61 Å, respectively, the L<sub>I</sub>-absorption edge of Eu (europium) is 1.54 Å, the L<sub>II</sub>-absorption edge of Gd (gadolinium) is 1.56 Å, and L<sub>III</sub>-absorption edge of Ho (holmium) is 1.54 Å. Resonance effect usually enhance the scattering, but as can be seen in the above table, the real part of the dispersion correction term of Ge (germanium) has a negative value, because the K-absorption edge of Ge is located at slightly shorter wavelength (higher frequency) than 1.54 Å.

The term “dispersion” has been originally used for the dependence of the refractive index on the wavelength. White light like sun light is dispersed to red, orange, yellow, green, blue, violet lights, when it goes through a prism, as shown in Fig. 3.3.



Fig. 3.3 Triangular prism dispersing light (normal dispersion).

The refractive index of a transparent material usually becomes higher for shorter wavelength of light. This is why the light of shorter wavelength (blue or violet light) changes the direction more steeply than the light of longer wavelength (red light), and this tendency is called “**normal dispersion**”. But, lower refractive index for shorter wavelength is sometimes observed, particularly in case of materials that has a resonant absorption peak in near infrared or visible region, and this case was used to be called “**anomalous dispersion**” in the field of electronic (UV-VIS-NIR; ultraviolet-visible-near infrared) spectroscopy.

The (anomalous) dispersion for X-ray can also be considered to be the effect of resonant absorption, similarly to the electronic spectroscopy. In an atom, electrons move along orbits around a nucleus, and there is a kind of natural frequency about the motion of the electrons. If the frequency of the X-ray is accidentally close to the natural frequency of an orbital electron, larger amplitude of oscillating motion can be induced, and thus stronger scattered wave may be caused. In general, an object having a natural frequency forced to oscillate by external oscillating field, shows small phase shift of oscillation from the field at the frequency lower than the natural frequency, but will be delayed about  $90^\circ$  at the natural frequency, and shows larger shift of phase up to  $180^\circ$  at the external field frequency higher than the natural frequency of the oscillator. The  $90^\circ$  delay of the phase is expressed by a purely imaginary number, and the dispersion effect is generally expressed by a complex number to include phase delay of the oscillator.

Note that the amplitude of the X-ray scattering cannot strictly be proportional to the Fourier transform of the electron density, when we take the dispersion effect into account.

[ Exercise ]

Assume two different electron density distributions,

$$\rho(r) = \frac{1}{8\pi\sigma^3} e^{-r/\sigma},$$

$$\sigma = 0.1 \text{ \AA}, 1 \text{ \AA},$$

and evaluate the structure factors for the wavelength  $\lambda = 1.5 \text{ \AA}$  of the X-ray at the scattering (diffraction) angles:

$$2\theta = 0, 30, 60, 90, 120, 150^\circ$$

Then, discuss the difference in the dependence of a structure factor between the inner shell electrons and valence electrons, based on the results of calculation.