Quantum-mechanical description of the X-ray scattering by the many-electron atom in a permanent external electric field is developed in terms of the perturbation theory. Explicit expression for the electric field-induced addition to the atomic scattering factor is derived and calculations for some atoms are performed. It was found that the change of the X-ray structure factor due to an electric field is too small to be detected with existing experimental techniques.

The general expression for the electric-field induced contribution to the X-ray atomic structure factor in a single-determinant approximation has the form (2.5),(2.9):

\[
\Delta f (H) = - \frac{4 m e E}{\hbar^2 k} \left( \sum_i \int \phi_i^* (x) z^2 \phi_i (x) dx - \sum_i \sum_{j \neq i} \left| \int dx \phi_i^* (x) z \phi_j (x) \right|^2 \right) \times \\
\left( \sum_i \int \phi_i^* (x) z \exp (-2 \pi i H r) \phi_i (x) dx - \sum_i \sum_{j \neq i} \int dx \phi_i^* (x) z \phi_j (x) \int dx \phi_j^* (x) \exp (-2 \pi i H r) \phi_i (x) \right) 
\]

(A.1)

Owing the orthogonality of the spin functions \( \eta (s) \) in the atomic spin-orbitals \( \phi (x) = \phi (r) \eta (s) \), the calculation of (A.1) is reduced to the computation of the following integrals over the position-space variable \( r \):

\[
I_1 = \int d r \phi_i^* (r) z \phi_j (r) \\
I_2 = \int d r \phi_i^* (r) z^2 \phi_i (r) 
\]

(A.2)
$$I_3 = \int dr \Phi^*_i(r) \exp(-2\pi i \mathbf{Hr}) \Phi_i(r)$$
$$I_4 = \int dr \Phi^*_i(r) z \exp(-2\pi i \mathbf{Hr}) \Phi_i(r) .$$

(A.3)

Present the atomic orbitals as an expansion over the Slater-type functions $\Phi_i(r) = \sum \mu d^{(i)}_\mu \Phi_\mu(r)$ (McWeeny & Sutcliffe, 1976), which are determined as

$$\Phi_\mu(r, \theta, \varphi) = N_\mu R_\mu(r) Y_{lm}(\theta, \varphi)$$
$$R_\mu(r) = r^{n_\mu} \exp\{-\xi_\mu r\}$$
$$N_\mu = (2\xi_\mu)^{n_\mu+1/2} [(2n_\mu)!]^{-1/2}$$

(A.4)

$$Y_{lm}(\theta, \varphi) = \frac{1}{2 \sqrt{\pi}} \int \frac{(2l+1)(l-|m|)!}{(l+|m|)!} P_l^m(\cos \theta) \exp(im\varphi)$$

The expansion coefficients $d^{(i)}_\mu$ and exponential factors $\xi_\mu$ for atoms from H till Xe are given by Clementi & Roetti (1974). The integrals (A.2)-(A.3) are now transformed to expressions

$$I_1 = \sum \mu \sum \nu d^{(i)}_\mu d^{(j)}_\nu \langle \mu | z | \nu \rangle$$
$$I_2 = \sum \mu \sum \nu d^{(i)}_\mu d^{(j)}_\nu \langle \mu | z^2 | \nu \rangle$$

(A.5)

$$I_3 = \sum \mu \sum \nu d^{(i)}_\mu d^{(j)}_\nu \langle \mu | \exp(-2\pi i \mathbf{Hr}) | \nu \rangle$$
$$I_4 = \sum \mu \sum \nu d^{(i)}_\mu d^{(j)}_\nu \langle \mu | z \exp(-2\pi i \mathbf{Hr}) | \nu \rangle$$

(A.6)

Explicitly, the integrals (A.5) look as

$$\langle \mu | z | \nu \rangle = N_\mu N_\nu \int_0^\infty dr r^3 R_\mu(r) R_\nu(r) \int_0^{2\pi} d\varphi \int_0^\pi d\theta \sin \theta \cos \theta Y^*_l m_\mu(\theta, \varphi) Y_{l_\nu m_\nu}(\theta, \varphi)$$

(A.7)

$$\langle \mu | z^2 | \nu \rangle = N_\mu N_\nu \int_0^\infty dr r^4 R_\mu(r) R_\nu(r) \int_0^{2\pi} d\varphi \int_0^\pi d\theta \sin \theta \cos^2 \theta Y^*_l m_\mu(\theta, \varphi) Y_{l_\nu m_\nu}(\theta, \varphi)$$

(A.8)

The radial parts of (A.7) and (A.8) are calculated using the formula

$$R(n, \xi) = \int_0^\infty r^n \exp(-\xi r) dr = \frac{n!}{\xi^{n+1}} .$$

(A.9)

The angular integrals

$$A(n, l_\mu, l_\nu, m_\mu, m_\nu) = \int_0^{2\pi} d\varphi \int_0^\pi d\theta \sin \theta \cos^n \theta Y^*_l m_\mu(\theta, \varphi) Y_{l_\nu m_\nu}(\theta, \varphi)$$

(A.10)

are calculated using the recurrent relationship (Arfken, 1985):
and the normalization property

\[ xP_n^m(x) = \frac{1}{2l+1} ((l-m+1)P_n^m(x) + (l+m)P_n^m(x)) \]  

(A.11)

and the normalization property

\[ \int_{-1}^{1} P_n^m(x)P_n^m(x)dx = \frac{2}{2j+1} \frac{(j+m)!}{(j-m)!} \delta_{\mu_1}\delta_{\mu_2} \]

It yields

\[
A(1, l_\mu, l_\nu, m_\mu, m_\nu) = \frac{1}{\sqrt{(2l_\mu+1)(2l_\nu+1)}} \frac{\sqrt{(l_\mu+m_\mu)! (l_\nu-m_\nu)!}}{(l_\mu+m_\mu)! (l_\nu+m_\nu)!} \times \{(l_\nu-m_\nu+1)\delta_{\nu_\mu} + (l_\mu+m_\mu)\delta_{\nu_{\mu+1}}\}\delta_{m_\mu m_\nu} 
\]  

(A.12)

\[
A(2, l_\mu, l_\nu, m_\mu, m_\nu) = \delta_{m_\mu m_\nu} \sqrt{\frac{1}{(2l_\mu+1)(2l_\nu+1)}} \frac{\sqrt{(l_\mu-m_\mu)! (l_\nu-m_\nu)!}}{(l_\mu+m_\mu)! (l_\nu+m_\nu)!} \times 
\left[ \frac{1}{2l_\mu+3(l_\mu-m_\mu+1)!} \left( \begin{array}{c} l_\mu+m_\mu \vspace{1mm} \\
\vspace{1mm} l_\nu \end{array} \right) (l_\nu-m_\nu+1)\delta_{\nu_{\mu}} + \left( \begin{array}{c} l_\mu+m_\mu \vspace{1mm} \\
\vspace{1mm} l_\nu \end{array} \right) (l_\mu+m_\mu)\delta_{\nu_{\mu+1}} \right] + 
\left[ \frac{1}{2l_\nu-1(l_\nu-m_\nu-1)!} \left( \begin{array}{c} l_\mu+m_\mu \vspace{1mm} \\
\vspace{1mm} l_\nu \end{array} \right) (l_\nu-m_\nu+1)\delta_{\nu_{\mu-1}} + \left( \begin{array}{c} l_\mu+m_\mu \vspace{1mm} \\
\vspace{1mm} l_\nu \end{array} \right) (l_\mu+m_\mu)\delta_{\nu_{\mu}} \right] 
\right] \]

(A.13)

To calculate the integrals \( \langle \mu | \exp(-2\pi i H_r) | \nu \rangle \) and \( \langle \mu | \exp(-2\pi i H_r) | \nu \rangle = \frac{i}{2\pi} \frac{\partial}{\partial H_z} \langle \mu | \exp(-2\pi i H_r) | \nu \rangle \) in (A.6) we can apply the expansion

(Arfken, 1985):

\[
\exp(-2\pi i H_r) = 4\pi \sum_{n=0}^{\infty} (-i)^n j_n(2\pi H_r) \sum_{m=-n}^{n} Y^*_{nm}(\theta, \phi) Y_{nm}(\beta, \gamma) 
\]  

(A.14)

**H** = (H sin \( \beta \) cos \( \gamma \), H sin \( \beta \) sin \( \gamma \), H cos \( \beta \)), \( r = (r \sin \theta \cos \phi, r \sin \theta \sin \phi, r \cos \theta) \), \( j_n(2\pi H_r) \) is a spherical Bessel function of \( n \) order. Thus

\[
\langle \mu | \exp(-2\pi i H_r) | \nu \rangle = N_{\mu} N_{\nu} \sum_{n} (-i)^n S_{n}(n_{\mu} + n_{\nu}, \xi_{\mu} + \xi_{\nu}, H) D_{n}(l_{\mu}, l_{\nu}, m_{\mu}, m_{\nu} - m_{\mu}, \beta, \gamma) 
\]  

(3.25)

The radial integrals

\[
S_{n}(N, Z, H) = \int_{0}^{\infty} r^N \exp(-Zr) j_n(2\pi H r) dr 
\]  

(A.15)

are calculated using formula (Stewart et al, 1965)

\[
S_{n}(N, Z, H) = \frac{2^{n+1/2}(N+n)!}{(2\pi H)^{N+1}(2n+1)!!(1+\alpha^2)^{N+1/2}z} \times E_{1/2}(N+1/2, -N+1/2, n+3/2, (1+\beta^2)^{-1}) 
\]  

(A.16)
where \( _2F_1 \) is hyper-geometrical function (Arfken, 1985), \( \alpha = Z / 2\pi H, \beta = \alpha + (1 + \alpha^2)^{1/2} \)

The angular integrals

\[
D_n(l_\mu, l_\gamma, m_\mu, m_\gamma, m, \beta, \gamma) = Y_{nm}(\beta, \gamma) \int_0^{2\pi} d\varphi \int_0^\pi d\theta \sin \theta Y_{l_\mu m_\mu}^* (\theta, \varphi) Y_{l_\gamma m_\gamma} (\theta, \varphi) Y_{nm}^* (\theta, \varphi) \tag{A.17}
\]

are reduced to the Gaunt coefficients \( g^n(l_\mu, m_\mu, l_\gamma, m_\gamma) \) (Bethe, 1964) defined by

\[
\int_0^{2\pi} d\varphi \int_0^\pi d\theta \sin \theta Y_{l_\mu m_\mu}^* (\theta, \varphi) Y_{l_\gamma m_\gamma} (\theta, \varphi) Y_{nm}^* (\theta, \varphi) = \sqrt{\frac{2n+1}{4\pi}} g^n(l_\mu, m_\mu, l_\gamma, m_\gamma) \delta_{n-m_{\mu,-m}} \tag{A.18}
\]

As a result, we arrive at simple expression

\[
D_n(l_\mu, l_\gamma, m_\mu, m_\gamma, m, \beta, \gamma) = \sqrt{\frac{2n+1}{4\pi}} g^n(l_\mu, m_\mu, l_\gamma, m_\gamma) Y_{nm} (\beta, \gamma) \tag{A.19}
\]

Literature


