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X-ray scattering amplitude of an atom in a permanent external electric field

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Abstract

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):

$$\Delta f(\mathbf{H}) = -\frac{4meE}{\hbar^2 k}\left(\sum_i \int \varphi_i^*(\mathbf{x}) z^2 \varphi_i(\mathbf{x}) d\mathbf{x} - \sum_i \sum_{j\neq i} \left| \int d\mathbf{x} \varphi_i^*(\mathbf{x}) z \varphi_j(\mathbf{x}) \right|^2 \right) \times$$
$$\left(\sum_i \int \varphi_i^*(\mathbf{x}) z \exp(-2\pi i \mathbf{H}\mathbf{r}) \varphi_i(\mathbf{x}) d\mathbf{x} - \sum_i \sum_{j\neq i} \int d\mathbf{x} \varphi_i^*(\mathbf{x}) z \varphi_j(\mathbf{x}) \int d\mathbf{x} \varphi_j^*(\mathbf{x}) \exp(-2\pi i \mathbf{H}\mathbf{r}) \varphi_i(\mathbf{x}) \right) \quad \text{(A.1)}$$

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

$$I_1 = \int d\mathbf{r} \varphi_i^*(\mathbf{r}) z \varphi_j(\mathbf{r})$$
$$I_2 = \int d\mathbf{r} \varphi_i^*(\mathbf{r}) z^2 \varphi_i(\mathbf{r}) \quad , \quad \text{(A.2)}$$

$$\begin{aligned} I_3 &= \int d\mathbf{r}\varphi_i^*(\mathbf{r})\exp(-2\pi i\mathbf{H}\mathbf{r})\varphi_j(\mathbf{r}) \\ I_4 &= \int d\mathbf{r}\varphi_i^*(\mathbf{r}) z\exp(-2\pi i\mathbf{H}\mathbf{r})\varphi_i(\mathbf{r}) \end{aligned} \quad . \tag{A.3}$$

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

$$\begin{aligned} \Phi_\mu(r,\theta,\varphi) &= N_\mu R_\mu(r) Y_{lm}(\theta,\varphi) \\ R_\mu(r) &= r^{n_\mu - 1}\exp\{-\xi_\mu r\} \\ N_\mu &= (2\xi_\mu)^{n_\mu + 1/2}[(2n_\mu)!]^{-1/2} \\ Y_{lm}(\theta,\varphi) &= \frac{1}{2}\sqrt{\frac{2l+1}{\pi}\frac{(l-|m|)!}{(l+|m|)!}} P_l^{|m|}(\cos\theta)\exp(im\varphi) \end{aligned} \tag{A.4}$$

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

$$\begin{aligned} I_1 &= \sum_\mu\sum_\nu d_\mu^{(i)} d_\nu^{(j)} \langle \mu | z | \nu \rangle \\ I_2 &= \sum_\mu\sum_\nu d_\mu^{(i)} d_\nu^{(i)} \langle \mu | z^2 | \nu \rangle \end{aligned} \tag{A.5}$$

$$\begin{aligned} I_3 &= \sum_\mu\sum_\nu d_\mu^{(i)} d_\nu^{(j)} \langle \mu | \exp(-2\pi i\mathbf{H}\mathbf{r}) | \nu \rangle \\ I_4 &= \sum_\mu\sum_\nu d_\mu^{(i)} d_\nu^{(i)} \langle \mu | z\exp(-2\pi i\mathbf{H}\mathbf{r}) | \nu \rangle \end{aligned} \tag{A.6}$$

Explicitly, the integrals (A.5) look as

$$\langle \mu | z | \nu \rangle = N_\mu N_\nu \int_0^\infty dr r^3 R_\mu(r) R_\nu(r) \int_0^{2\pi} d\varphi \int_0^\pi d\theta \sin\theta\cos\theta Y_{l_\mu m_\mu}^*(\theta,\varphi) Y_{l_\nu m_\nu}(\theta,\varphi) \tag{A.7}$$

$$\langle \mu | z^2 | \nu \rangle = N_\mu N_\nu \int_0^\infty dr r^4 R_\mu(r) R_\nu(r) \int_0^{2\pi} d\varphi \int_0^\pi d\theta \sin\theta\cos^2\theta Y_{l_\mu m_\mu}^*(\theta,\varphi) Y_{l_\nu m_\nu}(\theta,\varphi) \tag{A.8}$$

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

$$R(n,\xi) = \int_0^\infty r^n \exp(-\xi r) dr = \frac{n!}{\xi^{n+1}} \quad . \tag{A.9}$$

The angular integrals

$$A(n, l_\mu, l_\nu, m_\mu, m_\nu) = \int_0^{2\pi} d\varphi \int_0^\pi d\theta \sin\theta\cos^n\theta Y_{l_\mu m_\mu}^*(\theta,\varphi) Y_{l_\nu m_\nu}(\theta,\varphi) \tag{A.10}$$

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

and the normalization property

$$xP_l^m(x) = \frac{1}{2l+1}\Big((l-m+1)P_{l+1}^m(x) + (l+m)P_{l-1}^m(x)\Big) \quad . \tag{A.11}$$

and the normalization property

$$\int_{-1}^{1} P_j^m(x)P_r^m(x)dx = \frac{2}{2j+1}\frac{(j+m)!}{(j-m)!}\delta_{jr}$$

It yields

$$A(1,l_\mu,l_\nu,m_\mu,m_\nu) = \frac{1}{\sqrt{(2l_\mu+1)(2l_\nu+1)}}\sqrt{\frac{(l_\mu+|m_\mu|)!(l_\nu-|m_\nu|)!}{(l_\mu-|m_\mu|)!(l_\nu+|m_\nu|)!}} \times \left\{(l_\nu-|m_\nu|+1)\delta_{l_\nu+1 l_\mu} + (l_\nu+|m_\nu|)\delta_{l_\nu-1 l_\mu}\right\}\delta_{m_\mu m_\nu} \tag{A.12}$$

$$A(2,l_\mu,l_\nu,m_\mu,m_\nu) = \delta_{m_\mu m_\nu}\sqrt{\frac{1}{(2l_\mu+1)(2l_\nu+1)}\frac{(l_\mu-|m_\mu|)!}{(l_\mu+|m_\mu|)!}\frac{(l_\nu-|m_\nu|)!}{(l_\nu+|m_\nu|)!}} \times$$
$$\left(\begin{array}{l}\frac{1}{2l_\mu+3}\frac{(l_\mu+|m_\mu|+1)!}{(l_\mu-|m_\mu|+1)!}\Big[(l_\mu-|m_\mu|+1)(l_\nu-|m_\nu|+1)\delta_{l_\mu l_\nu} + (l_\mu-|m_\mu|+1)(l_\nu+|m_\nu|)\delta_{l_\mu+1 l_\nu-1}\Big] + \\ +\frac{1}{2l_\mu-1}\frac{(l_\mu+|m_\mu|-1)!}{(l_\mu-|m_\mu|-1)!}\Big[(l_\mu+|m_\mu|)(l_\nu-|m_\nu|+1)\delta_{l_\mu-1 l_\nu+1} + (l_\mu+|m_\mu|)(l_\nu+|m_\nu|)\delta_{l_\mu l_\nu}\Big]\end{array}\right) \tag{A.13}$$

To calculate the integrals $\langle\mu|\exp(-2\pi i\mathbf{Hr})|\nu\rangle$ and $\langle\mu|z\exp(-2\pi i\mathbf{Hr})|\nu\rangle = \frac{i}{2\pi}\frac{\partial}{\partial H_z}\langle\mu|\exp(-2\pi i\mathbf{Hr})|\nu\rangle$ in (A.6) we can apply the expansion (Arfken, 1985):

$$\exp(-2\pi i\mathbf{Hr}) = 4\pi\sum_{n=0}^{\infty}(-i)^n j_n(2\pi Hr)\sum_{m=-n}^{m=n} Y_{nm}^*(\theta,\varphi)Y_{nm}(\beta,\gamma) \tag{A.14}$$

$\mathbf{H} = (H\sin\beta\cos\gamma, H\sin\beta\sin\gamma, H\cos\beta)$, $\mathbf{r} = (r\sin\theta\cos\varphi, r\sin\theta\sin\varphi, r\cos\theta)$, $j_n(2\pi Hr)$ is a spherical Bessel function of *n* order. Thus

$$\langle\mu|\exp(-2\pi i\mathbf{Hr})|\nu\rangle = N_\mu N_\nu\sum_n(-i)^n S_n(n_\mu+n_\nu,\xi_\mu+\xi_\nu,H)D_n(l_\mu,l_\nu,m_\mu,m_\nu,m_\nu-m_\mu,\beta,\gamma) \tag{3.25}$$

The radial integrals

$$S_n(N,Z,H) = \int_0^\infty r^N\exp(-Zr)\,j_n(2\pi Hr)dr \tag{A.15}$$

are calculated using formula (Stewart et al, 1965)

$$S_n(N,Z,H) = \frac{2^{n+1/2}(N+n)!}{(2\pi H)^{N+1}(2n+1)!!\beta^{n+1/2}(1+\alpha^2)^{(N+1/2)/2}} \times {}_2F_1(N+1/2,-N+1/2,n+3/2,(1+\beta^2)^{-1}) \tag{A.16}$$

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

The angular integrals

$$D_n(l_\mu, l_\nu, m_\mu, m_\nu, m, \beta, \gamma) = Y_{nm}(\beta, \gamma) \int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin\theta Y^*_{l_\mu m_\mu}(\theta, \varphi) Y_{l_\nu m_\nu}(\theta, \varphi) Y^*_{nm}(\theta, \varphi) \quad \text{(A.17)}$$

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

$$\int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin\theta Y^*_{l_\mu m_\mu}(\theta, \varphi) Y_{l_\nu m_\nu}(\theta, \varphi) Y^*_{nm}(\theta, \varphi) = \sqrt{\frac{2n+1}{4\pi}} g^n(l_\mu, m_\mu, l_\nu, m_\nu) \delta_{m_\nu - m_\mu, m} \quad \text{(A.18)}$$

As a result, we arrive at simple expression

$$D_n(l_\mu, l_\nu, m_\mu, m_\nu, m_\nu - m_\mu, \beta, \gamma) = \sqrt{\frac{2n+1}{4\pi}} g^k(l_\mu, m_\mu, l_\nu, m_\nu) Y_{nm_\nu - m_\mu}(\beta, \gamma) \quad . \quad \text{(A.19)}$$

Literature

Arfken, G. (1985). Mathematical Methods for Physicists. Academic, Orlando.

McWeeny, R.&Sutcliffe, B.T. (1976). Methods of Molecular Quantum Mechanics. 2nd Ed. Academic, New York.

Stewart, R.F., Davidson, E.R.&Simpson, W.T. (1965). J. Chem. Phys., 42, 3175-3187.

Bethe, H.A (1964). Intermediate quantum mechanics. W.A. Benjamin Inc., NewYork - Amsterdam.