Acta Crystallographica Section A
Foundations of Crystallography
ISSN 0108-7673

Received 15 January 2003
Accepted 27 February 2003

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

Vladimir G. Tsirelson,[a,b]* Semen V. Gorfman[a] and Ullrich Pietsch[b]

[a]Department of Quantum Chemistry, Mendeleev University of Chemical Technology, Moscow 125047, Russia, and [b]Universität Potsdam, Institut für Physik, Am Neuen Palais 10, 14469 Potsdam, Germany. Correspondence e-mail: tsirel@muctr.edu.ru

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.

1. Introduction

The response of a crystalline compound to a permanent external electric field can be separated into different contributions: (i) the change of unit-cell parameters (as well as the relative atomic coordinates) accompanied by a break of the symmetry group of the crystal; (ii) the thermal and static displacement parameters are changed and an additional change in atomic coordinates (relative coordinates) due to internal strain arises; (iii) a polarization of the electron density. In the macroscopic scale, it results in the inverse piezoelectric effect (for noncentrosymmetric space group crystals) and dielectric polarization. To explore the response of the many-electron systems on the external field, Stahn *et al.* (2001) performed a density-functional calculation of the electronic response under the external electric field using the 'supercell' approach by Kunc & Resta (1983). The external-field potential was superimposed on the crystalline one and the 'improved' potential was used in the self-consistent procedure. A similar approach was applied by Krijn & Feil (1986) and Velders & Feil (1989) in their study of the molecular polarizability.

X-ray diffraction is a promising tool for revealing the microscopic nature of the behavior of solids in an external electric field (Fujimoto, 1982; Pietsch *et al.*, 1985; Aslanov *et al.*, 1989; Graafsma *et al.*, 1992, 1993, 1998; Stahn *et al.*, 1998, 2001; van Reeuwijk, Vonk, Puig-Molina & Graafsma, 2000; van Reeuwijk, Puig-Molina & Graafsma, 2000; van Reeuwijk *et al.*, 2001; Guillot, 2002). The correct treatment of the X-ray diffraction results demands knowledge of the relative contributions of different nature to the scattering intensity. X-rays are scattered at electrons, thus redistribution of the electron density under the influence of the external field should change the scattering intensity. However, the quantum-mechanical analysis of this phenomenon and the estimation of its significance for X-ray diffraction have not been done before. The exploration of this matter is the aim of this study. We present a quantum-mechanical description of the X-ray diffraction by a motionless N-electron atom in the presence of a permanent external electric field. Our approach is based on the works of Feil (1977), Stewart (1977), Stewart & Feil (1977), Tsirelson (1989, 1993) and Tsirelson & Ozerov (1996), who applied a non-stationary perturbation theory to describe the X-ray scattering on a free atom and on a crystal.

In the first part of the paper, we explicitly describe the interaction of X-radiation with an atom in an external electric field. The first and second orders of the perturbation theory are considered and the physical phenomena associated with them are discussed. Then we consider the approximation that allows the numerical results to be obtained. The latter are discussed in the final part of the paper.

2. Theoretical consideration

The X-ray scattering cross section of electrons is about 10^7 times larger than that of nuclei; therefore, the photon–electron interaction needs to be considered only. The X-ray photon energy, $\hbar\omega \simeq 10^4$ eV is much larger than the electron–nuclei binding energy of ~10–100 eV. Therefore, a photon scattering having a characteristic time of $\tau = \omega^{-1} \simeq 10^{-19}$ s can be considered as an absorption of a photon with the wavevector, $\mathbf{k}_0$, from an incident X-ray beam followed by an emission of a photon in the direction $\mathbf{k}_1$. The scattered X-ray intensity is related to the probability of this process, which has to be determined.

We shall start from the consideration of a single-electron motionless atom. Before interaction, the external electric field is zero and the Hamiltonian of the system 'atom + radiation' is a sum of the atomic, $\hat{H}_{\rm at}$, and radiation, $\hat{H}_{\rm rad}$, parts. The states of such a system are described by the products of the non-perturbed electron wavefunctions, $\varphi_n(\mathbf{x})\exp[-i(E_n/\hbar)t]$, and the radiation wavefunctions, $|\nu_k\rangle\exp[(-iE_{\nu_k}/\hbar)t]$:

$$\Psi_{n\nu_k}(\mathbf{x},t) = \varphi_n(\mathbf{x})|\nu_k\rangle\exp[-i(E_{n\nu_k}/\hbar)t]. \tag{1}$$

$\mathbf{x} = \{\mathbf{r}, s\}$ denotes the position and spin of the electron under consideration, ν_k lists the number of X-ray photons moving along the **k** direction. The energy of a non-interacting system, $E_{n\nu_k}$, consists of the energy of an atom in the electronic state n and the energy of the photons in the radiation state $|\nu_\mathrm{k}\rangle$:

$$E_{n\nu_k} = E_n + \sum_k \nu_k \hbar\omega_k \tag{2}$$

with $\omega_k = c|\mathbf{k}|$ are the X-ray frequencies and c is the light velocity.

The interaction Hamiltonian responsible for the scattering in an external electric field can be presented as a sum of the scattering, $\hat{W}^{(S)}$, and the electric field, $\hat{W}^{(E)}$, parts:

$$\hat{W} = \hat{W}^{(S)} + \hat{W}^{(E)} \tag{3}$$

$$\hat{W}^{(S)} = (e^2/2mc^2)\hat{\mathbf{A}}^2(\mathbf{r}) \tag{4}$$

$$\hat{W}^{(E)} = e(\mathbf{E}\cdot\mathbf{r}). \tag{5}$$

Here e is the absolute value of the electron charge, m is the electron mass, $\hat{\mathbf{A}}$ is a vector potential operator and **E** is a permanent external electric field (the Coulomb gauge is used and only dipole atomic polarization is considered).[1]

In terms of a non-relativistic perturbation theory (Landau & Lifshitz, 1977), the wavefunction of an atom interacting with an X-ray and an electric external field can be presented as an expansion over the functions (1):

$$\Psi(\mathbf{r}, t) = \sum_n \sum_{\nu_k} c_{n\nu_k}(t)\varphi_n(\mathbf{r})|\nu_k\rangle \exp[-i(E_{n\nu_k}/\hbar)t]. \tag{6}$$

The squared expansion coefficients, $|c_{n\nu_k}|^2$, give the probability of a system to transit from a ground (primary) state to the state $n\nu_\mathrm{k}$. After interaction, there are ν_1 photons moving along the $\mathbf{k}_1$ direction, ν_2 photons moving along the $\mathbf{k}_2$ direction *etc.*, and the electron is in the n electronic state of the atom. The coefficients can be found from the system of equations resulting from the non-stationary Schroedinger equation:

$$i\hbar[\mathrm{d}c_{n\nu_k}(t)/\mathrm{d}t] = \sum_m \sum_{\mu_k} W_{n\nu_k,m\mu_k} c_{m\mu_k}(t) \exp(i\omega_{n\nu_k,m\mu_k}t). \tag{7}$$

Here $\omega_{n\nu_k,m\mu_k} = (E_{n\nu_k} - E_{m\mu_k})/\hbar$ and the matrix elements of the interaction Hamiltonian consist of the sum of the scattering and the electric field terms: $W_{n\nu_k,m\mu_k} = W^{(E)}_{n\nu_k,m\mu_k} + W^{(S)}_{n\nu_k,m\mu_k}$.

The non-perturbed wavefunction of a system consisting of one photon in the primary X-ray beam and one-electron atom in the atomic ground state has the form $\Psi = \varphi_0 \exp(-i\omega_{01_0}t)|1_0, 0_1, 0_2, \ldots\rangle$. The first-order perturbation theory gives the following expression for the expansion coefficients:

$$c^{(1)}_{n\nu_k}(t) = c^{(0)}_{n\nu_k} + (i\hbar)^{-1} \int\limits_{-\infty}^{t} (W^{(S)}_{n\nu_k,01_0} + W^{(E)}_{n\nu_k,01_0}) \exp(i\omega_{n\nu_k,01_0}t')\,\mathrm{d}t',$$

where the zero-order coefficients are given by $c^{(0)}_{n\nu_k} = \delta_{n0}\delta_{\nu_0 1}\delta_{\nu_1 0}\ldots$. This equation describes the scattering associated with the term $\hat{W}^{(S)}$ [equation (4)] and the atom polarization, which is related to the term $\hat{W}^{(E)}$ [equation (5)]. The influence of the electric field on the scattering process we are interested in appears in the second order of the perturbation theory (Landau & Lifshitz, 1977). After the elastic scattering to the $\mathbf{k}_1$ direction, the final state of an atom remains unchanged ($m = 0$) and the final radiation state is $|\nu_k\rangle = |0_0,1_1,\ldots\rangle$. The corresponding equation for the expansion coefficients is

$$\begin{aligned} c^{(2)}_{01_1}(t) = {} & (i\hbar)^{-1} \int\limits_{-\infty}^{t} \mathrm{d}t'\,(W^{(E)}_{01_1,01_0} + W^{(S)}_{01_1,01_0}) \exp(i\omega_{01_1,01_0}t') \\ & + (i\hbar)^{-2} \int\limits_{-\infty}^{t} \mathrm{d}t' \sum_m \sum_{\mu_k} (W^{(E)}_{01_1,m\mu_k} + W^{(S)}_{01_1,m\mu_k}) \\ & \times \exp(i\omega_{01_1,m\mu_k}t') \int\limits_{-\infty}^{t'} \mathrm{d}t''(W^{(E)}_{m\mu_k,01_0} + W^{(S)}_{m\mu_k,01_0}) \\ & \times \exp(i\omega_{m\mu_k,01_0}t''). \end{aligned} \tag{8}$$

A permanent electric field does not change the radiation state. Therefore the matrix elements of the electric field part, $W^{(E)}_{m\nu_k,n\mu_k}$, are zero if the condition $|\mathrm{Rad}(\nu_k)\rangle \neq |\mathrm{Rad}(\mu_k)\rangle$ holds. For a single-photon scattering, the terms containing a second power of $W^{(S)}_{m\nu_k,n\mu_k}$ are neglected. As a result, the following terms remain on the right-hand side of (8):

$$(i\hbar)^{-1} \int\limits_{-\infty}^{t} \mathrm{d}t' W^{(S)}_{01_1,01_0} \exp(i\omega_{01_1,01_0}t'), \tag{9}$$

$$\begin{aligned} & (i\hbar)^{-2} \int\limits_{-\infty}^{t} \mathrm{d}t' \sum_m W^{(S)}_{01_1,m1_0} \exp(i\omega_{01_1,m1_0}t') \\ & \times \int\limits_{-\infty}^{t'} \mathrm{d}t''\, W^{(E)}_{m1_0,01_0} \exp(i\omega_{m1_0,01_0}t''), \end{aligned} \tag{10}$$

$$\begin{aligned} & (i\hbar)^{-2} \int\limits_{-\infty}^{t} \mathrm{d}t' \sum_m W^{(E)}_{01_1,m1_1} \exp(i\omega_{01_1,m1_1}t') \\ & \times \int\limits_{-\infty}^{t'} \mathrm{d}t'' W^{(S)}_{m1_1,01_0} \exp(i\omega_{m1_1,01_0}t''). \end{aligned} \tag{11}$$

The integral (9) accounts for a scattering with a single-step transition of a system from the state 01_0 to the state 01_1, *i.e.* the scattering on the atomic ground-state electron density. The term (10) describes the scattering accompanied by the electron transition through the intermediate state $m1_0$ ($01_0 \rightarrow m1_0 \rightarrow 01_1$), *i.e.* it accounts for electric field influence on the X-ray

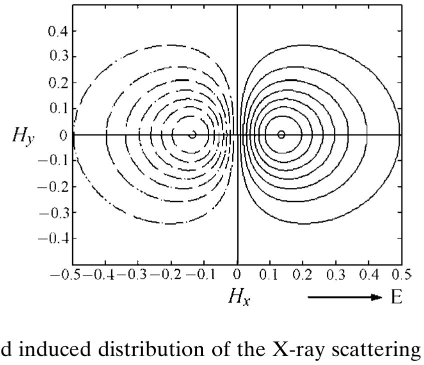

Figure 1
Electric field induced distribution of the X-ray scattering for a hydrogen atom in the reciprocal-space plane defined by the H_x and H_y Cartesian coordinates.

---

[1] We ignore the photon absorption or emission; to account for these effects, the interaction Hamiltonian (3) should be complemented with the term $(e/mc)(\hat{\mathbf{A}}\cdot\hat{\mathbf{p}})$ containing the electron momentum operator $\hat{\mathbf{p}} = -i\hbar\nabla$.

photon scattering. In contrast, the term (11) is related to the influence of the incident photon on the electron polarization of an atom.

If the electric field is directed along the Z axis of the local atomic Cartesian coordinate system, the electric field related matrix elements have the form

$$\hat{W}^{(E)}_{m1_0,n1_0} = eEz_{mn} \tag{12}$$

with $z_{mn} = \langle m|z|n\rangle$. The expansion of the vector potential operator, $\hat{\mathbf{A}}$, in Fourier series (Loudon, 1973; Cohen-Tannoudji *et al.*, 1992) allows us to write the matrix elements connected with a single scattering $\mathbf{k}_0 \rightarrow \mathbf{k}_1$ as

$$W^{(S)}_{m1_1,n1_0}(\alpha, \beta) = (2\pi\hbar/\Omega) r_0 c^2 (\omega_0\omega_1)^{-1/2} f_{mn}(\mathbf{H})(\mathbf{e}_{\mathbf{k}_0\alpha} \cdot \mathbf{e}_{\mathbf{k}_1\beta}). \tag{13}$$

Ω is a normalization volume for the vector potential, the unit vectors $\mathbf{e}_{\mathbf{k}\alpha}$ describe the states of the X-ray photon polarization, $r_0 = e^2/mc^2$ is the classic electron radius, $\mathbf{H} = (\mathbf{k}_1 - \mathbf{k}_0)/2\pi$, $f_{nm}(\mathbf{H}) = \langle n|\exp(-2\pi i\mathbf{H}\cdot\mathbf{r})|m\rangle$ is the X-ray scattering-factor matrix element ($\mathbf{H} = \boldsymbol{\Delta}\mathbf{k}/2\pi$ is a scattering vector).

Inserting the matrix elements (12) and (13) into (9)–(11), we can rewrite (8) as

$$c^{(2)}_{01_1} = -i(r_0c^2/\Omega)(\omega_0\omega_1)^{-1/2} f_E(\mathbf{H})\delta(\omega_1 - \omega_0)(\mathbf{e}_{\mathbf{k}_0,\alpha} \cdot \mathbf{e}_{\mathbf{k}_1,\beta}). \tag{14}$$

The quantity $f_E(\mathbf{H})$ is the X-ray atomic scattering factor in the presence of a permanent external electric field. It can be expressed as

$$f_E(\mathbf{H}) = f_{00}(\mathbf{H}) + \Delta f(\mathbf{H}) \tag{15}$$

and differs from the standard one, $f_{00} = \int \mathrm{d}\mathbf{r}\, \varphi_0^*(\mathbf{r}) \exp(-2\pi i\mathbf{H}\cdot\mathbf{r})\varphi_0(\mathbf{r})$ (Tsirelson & Ozerov, 1996) by the electric field induced contribution

$$\Delta f(\mathbf{H}) = -eE\left(\sum_m \frac{f_{0m}(\mathbf{H})z_{m0} + z_{0m}f_{m0}(\mathbf{H})}{\hbar\omega_{m0}}\right). \tag{16}$$

The expansion of the exponent in (16) in the Taylor series $\exp(-2\pi i\mathbf{H}\cdot\mathbf{r}) \approx \langle 0|1 - 2\pi i\mathbf{H}\cdot\mathbf{r}|m\rangle$ for small $\mathbf{H}$ values yields

$$\Delta f(H) = 4\pi ieE \sum_m (|z_{0m}|^2/\hbar\omega_{0m})H. \tag{17}$$

Here we suppose that the scattering vector is directed along the Z axis and takes into account the identity $|z_{0m}|^2 = z_{0m}z_{m0}$. Recalling that polarizability is expressed as $\alpha = (2e^2/\hbar)\sum_m |z_{0m}|^2/\hbar\omega_{0m}$ (Slater, 1960), we can present (17) as

$$\Delta f(H) = i2\pi e\alpha EH. \tag{18}$$

This expression exhibits the linear dependence of the field-induced contribution to the scattering amplitude in the range of small scattering angles. Buckingham (1994) and Matthew & Yosif (1984) have derived the same expression from semi-classical arguments.

3. Computational details

An explicit calculation of expression (16) requires knowledge of the accurate wavefunctions for electronic excited states: their calculation is a difficult problem. However, there is an important approximation (Kirkwood, 1932; Slater, 1960)

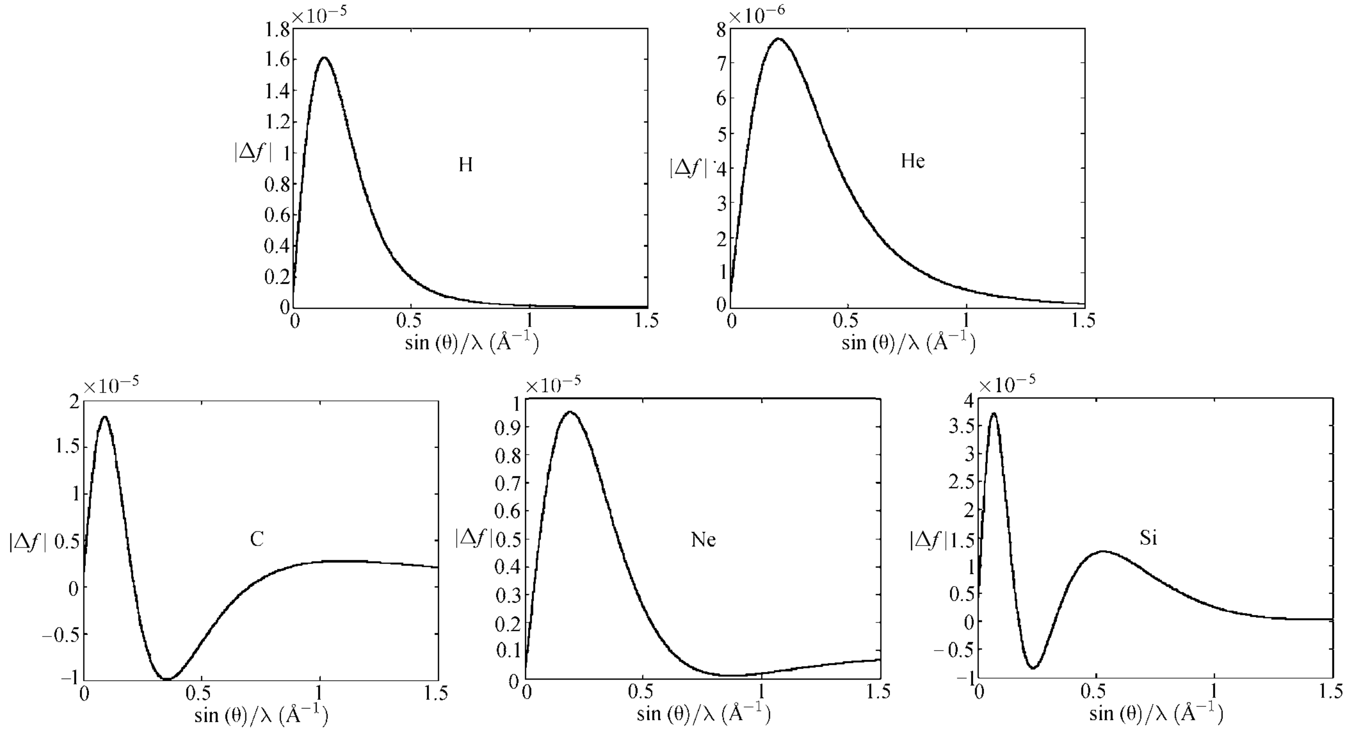

Figure 2
Electric field induced contributions to the X-ray scattering for some atoms (field $\mathbf{E}$ = 4 kV mm^{-1} is directed along the scattering vector).

allowing a calculation to be performed using the ground-state wavefunctions only.

The matrix elements z_{0m} in (16) decay rapidly with increase of the energy level m (Slater, 1960). The transition frequencies are not changed as rapidly as z_{0m} and can be replaced by some average value. Taking into account the closure property of the total set of the wavefunctions and the sum rule for matrix elements, we arrive at the following approximate expression for the electric field induced contribution to the atomic scattering factor:

$$\Delta f(\mathbf{H}) \approx -\frac{2eE}{\hbar}\frac{1}{\langle\omega_{m0}\rangle}\langle 0|zf(\mathbf{H})|0\rangle. \qquad (19)$$

The Thomas–Reiche–Kuhn sum rule for a one-electron system (Loudon, 1973; Bethe, 1964),

$$(2m/\hbar)\sum_n \omega_{n0}|z_{n0}|^2 = 1, \qquad (20)$$

can be transformed in the same manner:

$$\langle\omega_{n0}\rangle \approx \frac{\hbar}{2m\langle 0|z^2|0\rangle}. \qquad (21)$$

Inserting the average transition frequency (21) in (19), we arrive at

$$\Delta f(\mathbf{H}) \approx -\frac{4meE}{\hbar^2}\langle 0|z^2|0\rangle\langle 0|z\exp(-2\pi i\mathbf{H}\cdot\mathbf{r})|0\rangle. \qquad (22)$$

This approximate expression is suitable for calculations: it contains the ground-state electronic wavefunctions only, which are known quite accurately for free atoms (Clementi & Roetti, 1974).

For the many-electron atom, the one-electron interaction Hamiltonian (3) should be replaced by the sum $\sum_i \hat{W}_i$ (Feil, 1977, 1992): the sums over electrons, $\sum_i z_i$ and $\sum_i \exp(-2\pi i\mathbf{H}\cdot\mathbf{r}_i)$, will appear in (23) instead of respective single-electron operators, and the many-electron wavefunction $\psi(\mathbf{x})$ ($\mathbf{x} = \{\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N\}$) will appear instead of a single-electron wavefunction φ_0. The total number of electrons, k, must also be used in the right-hand side of the Thomas–Reiche–Kuhn sum rule (20). As a result, expression (22) is generalized in the following way:

$$\Delta f(\mathbf{H}) \approx -\frac{4meE}{\hbar^2}\frac{\left\langle 0\left|\left(\sum_i z_i\right)^2\right|0\right\rangle}{k}\left\langle 0\left|\sum_{ij} z_i\exp(-2\pi i\mathbf{H}\cdot\mathbf{r}_j)\right|0\right\rangle. \qquad (23)$$

To get an explicit expression for the electric field induced addition to scattering amplitude for the many-electron atom, let us rewrite z^2 and $z\exp\{-2\pi i\mathbf{H}\cdot\mathbf{r}\}$ separating the diagonal and off-diagonal terms:

$$\begin{aligned}\left(\sum_i z_i\right)^2 &= \sum_i z_i^2 + \sum_i\sum_{j\neq i} z_i z_j,\\ \sum_i z_i \sum_j \exp(-2\pi i\mathbf{H}\cdot\mathbf{r}_j) &= \sum_i z_i\exp(-2\pi i\mathbf{H}\cdot\mathbf{r}_i) \qquad (24)\\ &\quad + \sum_i\sum_{j\neq i} z_i\exp(-2\pi i\mathbf{H}\cdot\mathbf{r}_j).\end{aligned}$$

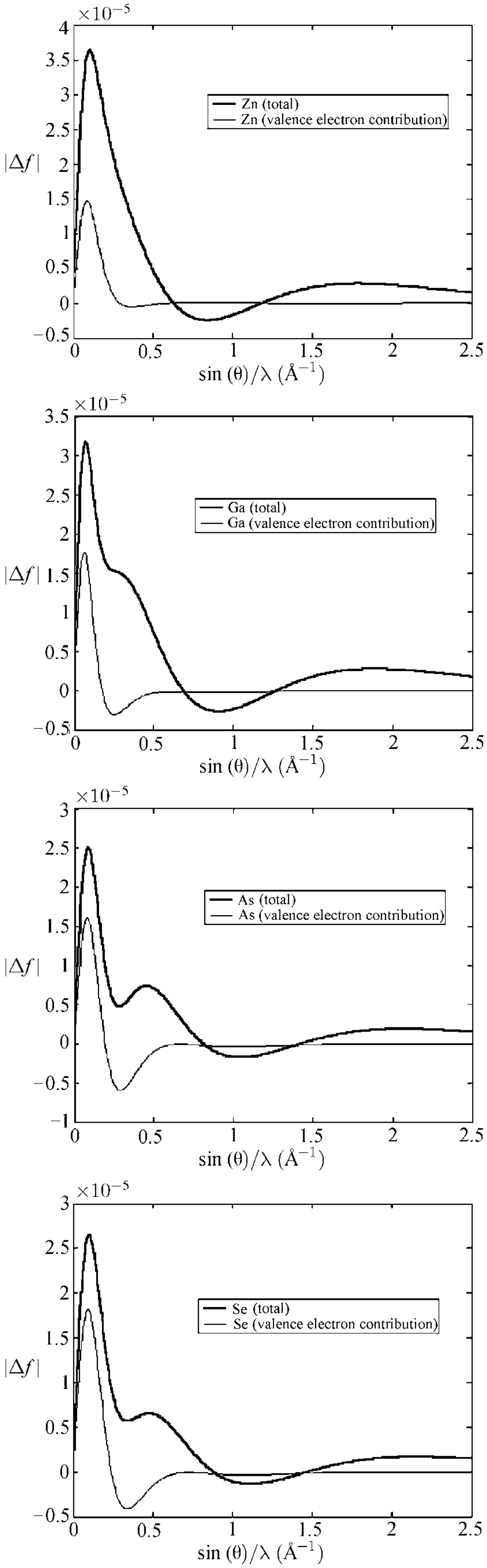

Figure 3
Electric field induced contributions to the X -ray scattering for Zn, Ga, As and Se atoms; total and valence-electron contributions are shown.

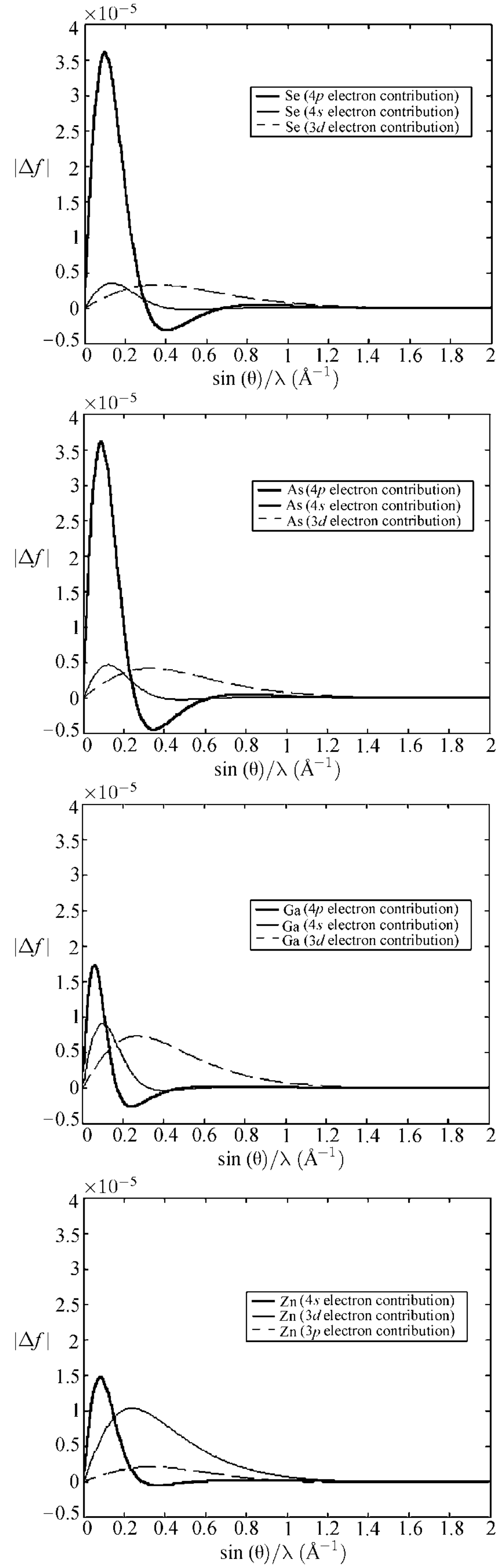

Figure 4
Contributions of outer *s*, *p* and *d* electrons to the electric field induced addition to the X-ray scattering for Zn, Ga, As and Se atoms.

In a single-determinant approximation (McWeeny & Sutcliffe, 1976), when the ground-state electronic wavefunction consists of the atomic spin orbitals $\varphi(\mathbf{x})$, the matrix elements of (24) take the form

$$\left\langle 0\left|\left(\sum_i z_i\right)^2\right|0\right\rangle = \sum_i \int \varphi_i^*(\mathbf{x}) z^2 \varphi_i(\mathbf{x})\,\mathrm{d}\mathbf{x} - \sum_i \sum_{j\neq i} \left|\int \mathrm{d}\mathbf{x}\,\varphi_i^*(\mathbf{x}) z \varphi_j(\mathbf{x})\right|^2 \qquad (25)$$

$$\begin{aligned}\sum_{ij}\langle 0|z_i \exp(-2\pi i\mathbf{H}\cdot\mathbf{r}_j)|0\rangle &= \sum_i \int \mathrm{d}\mathbf{x}\,\varphi_i^*(\mathbf{x}) z \exp(-2\pi i \mathbf{H}\cdot\mathbf{r})\varphi_i(\mathbf{x}) \\ &\quad - \sum_i\sum_{j\neq i}\int \mathrm{d}\mathbf{x}\,\varphi_i^*(\mathbf{x}) z\varphi_j(\mathbf{x}) \\ &\quad \times \int \mathrm{d}\mathbf{x}\varphi_j^*(\mathbf{x})\exp(-2\pi i\mathbf{H}\cdot\mathbf{r})\varphi_i(\mathbf{x})\end{aligned} \qquad (26)$$

Here we suppose that the condition $\int \mathrm{d}\mathbf{x}\,\varphi_i^*(\mathbf{x}) z \varphi_i(\mathbf{x}) = 0$ holds, *i.e.* atomic orbitals possess a center of symmetry. Now $\Delta f(\mathbf{H})$ is easily calculated for free atoms using an expansion of the atomic orbitals over the Slater-type functions. The derivation of the corresponding expressions is deposited.[2]

4. Discussion

Contribution to an atomic scattering factor, $\Delta f(\mathbf{H})$, induced by a permanent external electric field is a purely imaginary antisymmetric $[\Delta f(\mathbf{H}) = -\Delta f(-\mathbf{H})]$ function, which is linearly proportional to the field applied. Fig. 1 shows the graphical dependence of $|\Delta f\ (\mathbf{H})|$ in the reciprocal-space plane. The value of $|\Delta f(\mathbf{H})|$ is zero if the field E is perpendicular to scattering vector $\mathbf{H}$ (Fig. 1) and maximal if $\mathbf{E}\uparrow\uparrow\mathbf{H}$.

Fig. 2 depicts the electric field induced contribution to an atomic scattering factor for the set of light atoms when the angle between the electric field direction and the scattering vector is taken as zero. The same dependence for more heavy many-electron atoms As, Ga, Zn, Se is shown in Fig. 3; in this case, both the total and valence-electron contributions are given. We can conclude that the valence electrons define the $\Delta f(\mathbf{H})$ function behavior in the low-angle region of the reciprocal space, while the $\Delta f(\mathbf{H})$ character in the range of high-angle scattering is determined by the internal shells.

Fig. 4 shows the separate contributions of different electronic shells to the function $|\Delta f(\mathbf{H})|$. Analyzing these figures, we can make a conclusion that each turning point in the total electron contribution in Fig. 4 is related to a separate atomic shell.

The $\Delta f(\mathbf{H})$ value is positive everywhere for closed-shell atoms, like He and Ne, while $\Delta f(\mathbf{H})$ is negative for some $\mathbf{H}$ values for the open-shell atoms (the electric field is directed along the scattering vector). As Fig. 5 demonstrates, the last feature results from the cross-over integrals (26), which have appeared owing to the antisymmetric properties of the atomic wavefunction: the atomic amplitude in the absence of the

---

[2] These data are accessible in electronic format and are available from the IUCr electronic archives (Reference: AV0062). Services for accessing these data are described at the back of the journal.

external field consists of the sum of the single-electron terms only. Note that only those cross-over terms are not zero for which the difference of orbital quantum number of the corresponding shells is equal to unity. A contribution of these terms to the field-induced atomic scattering amplitude is of the same order of magnitude as the contribution of the separate electron shells (Fig. 4). The total non-diagonal contribution is mainly defined by the outermost electrons.

Thus, the external field distorts mainly the valence-electronic shells. The $\Delta f(\mathbf{H})$ value is small for all atoms: $\Delta f(\mathbf{H}) \sim 10^{-5}$–$10^{-4}$ when the electric field $\mathbf{E} \sim 1$–10 kV mm^{-1} (a typical electric field magnitude in modern X-ray experiments). Therefore, the electric field induced changes in the atomic form factors can nowadays be neglected in the X-ray diffraction studies of solids in an external electric field.

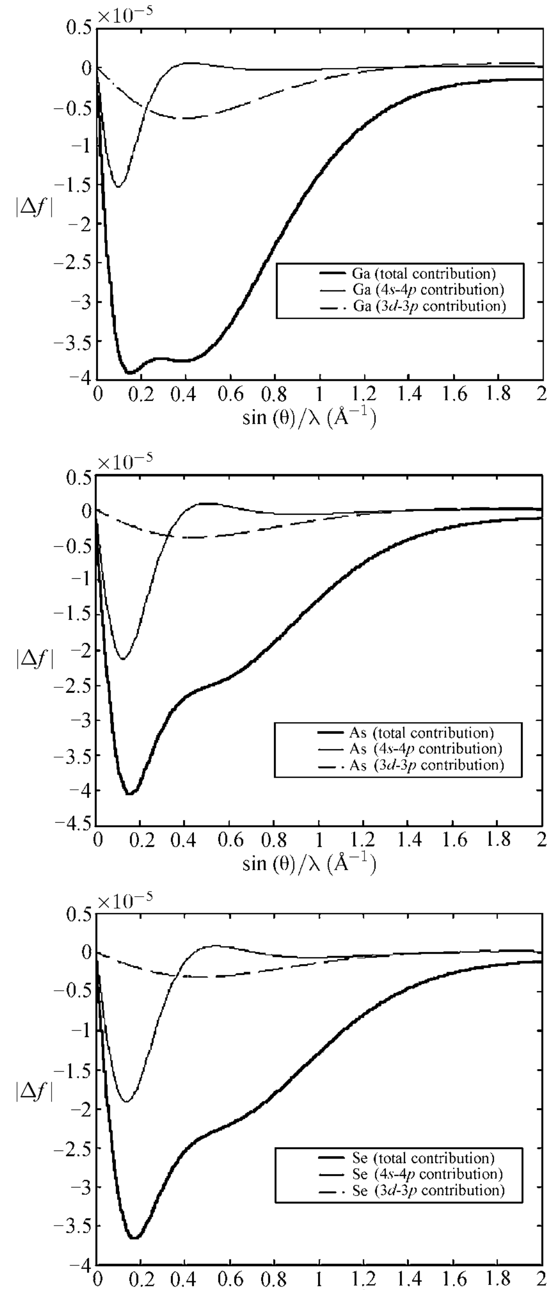

Figure 5
Cross-over contributions to the electric field induced addition to the X-ray scattering for atoms As, Ga and Se atoms (see text).

At the same time, the polarization contribution to the scattering factor might be measurable if the accuracy of measurement is about 0.1% and an external field strength is up to 100 kV mm^{-1}. In addition, the effective crystal field is strongly inhomogeneous, the distribution of the inner-crystal electrostatic potential, $\varphi(\mathbf{r})$, is relatively flat in the valence shells of the bonded atoms (Tsirelson *et al.* 2001). The actual inner-crystal field strength $\mathbf{E} = -\mathrm{grad}\,\varphi(\mathbf{r})$ in this region is much smaller than the average field strength (~10^4–10^5 V m^{-1}). Moreover, the effective inner-crystal field differs from the external one. For example, in cubic crystals, the Lorentz internal field is $[(\varepsilon + 2)/3]\mathbf{E}$, where ε is the static dielectric constant, which normally ranges between 2 and 10 in dielectrics and semiconductors. Therefore, the effective field can reach much larger values in ferroelectrics and the influence of the atomic polarization on the X-ray structure factor in these compounds deserves special consideration.

The authors acknowledge the financial support by the Deutsche Forschungsgemeinschaft (grants Pi 217/19–1 and 436 RUS 113/247/1). We also thank Professor D. Feil for useful comments.

References

Aslanov, L. A., Trunov, V. A., Fetisov, G. V., Priemychev, V. A., Rybakov, V. B., Kasman, Ya. A. & Bulkin, A. P. (1989). *J. Appl. Cryst.* **22**, 42–45.

Bethe, H. A. (1964). *Intermediate Quantum Chemistry*. New York: Amsterdam.

Buckingham, A. D. (1964). *Acta Cryst.* **17**, 960–962.

Clementi, E. & Roetti, C. (1974). *At. Data Nucl. Data Tables*, **14**, 177–478.

Cohen-Tannoudji, C., Dupont-Roc, J. & Grynberg, C. (1992). *Atom–Photon Interactions. Basic Processes and Interactions.* New York: John Wiley.

Feil, D. (1977). *Isr. J. Chem.* **16**, 103–110.

Feil, D. (1992). *Lecture Notes on Light and Matter.* Twente University, Enschede, The Netherlands.

Fujimoto, I. (1982). *Acta Cryst.* A**38**, 337–345.

Graafsma, H., Heunen, G. W. J. C. & Schulze, C. (1998). *J. Appl. Cryst.* **31**, 414–422.

Graafsma, H., Majewski, J., Coppens, P. & Cahen, D. (1993). *J. Solid State Chem.* **105**, 520–527.

Graafsma, H., Paturle, A., Wu, L., Sheu, H.-S., Majewski, J., Poorthuis, G. & Coppens, P. (1992). *Acta Cryst.* A**48**, 113–120.

Guillot, R., Alle, P., Fertey, P., Hansen, N. K. & Elkaïm, E. (2002). *J. Appl. Cryst.* **35**, 360–363.

Kirkwood, J. G. (1932). *Phys. Z.* **33**, 57–60.

Krijn, M. P. C. M. & Feil, D. (1986). *J. Chem. Phys.* **85**(1), 319–323.

Kunc, K. & Resta, R. (1983). *Phys. Rev. Lett.* **51**, 686–689.

Landau, L. D. & Lifshitz, E. M. (1977). *Quantum Mechanics.* Oxford: Pergamon.

Loudon, R. (1973). *The Quantum Theory of Light.* Oxford: Clarendon.

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

Matthew, J. A. D. & Yosif, S. Y. (1984). *Acta Cryst.* A**40**, 716–721.

Pietsch, U., Mahlberg, J. & Unger, K. (1985). *Phys. Status Solidi B*, **131**, 67–72.

Reeuwijk, S. J. van, Puig-Molina, A. & Graafsma, H. (2000). *Phys. Rev.* **62**, 6192–6197.

Reeuwijk, S. J. van, Puig-Molina, A. & Graafsma, H. (2001). *Phys. Rev. B*, **64**, 134105–1–134105–6.

Reeuwijk, S. J. van, Vonk, V., Puig-Molina, A. & Graafsma, H. (2000). *J. Appl. Cryst.* **33**, 1422–1429.

Slater, J. C. (1960). *Quantum Theory of Atomic Structure*, Vols. I and II. New York: McGraw-Hill.

Stahn, J., Pietsch, U., Blaha, P. & Schwarz, K. (2001). *Phys. Rev. B*, **63**, 165205–1–10.

Stahn, J., Pucher, A., Geue, T., Daniel, A. & Pietsch, U. (1998). *Europhys. Lett.* **44**, 714–720.

Stewart, R. F. (1977). *Isr. J. Chem.* **16**, 137–143.

Stewart, R. F. & Feil, D. (1977). *Acta Cryst.* A**36**, 503–506.

Tsirelson, V. G. (1989). *Methods of Structure Analysis*, Vol. 1, edited by B. K. Vainshtein, pp. 37–52. Moscow: Nauka.

Tsirelson, V. G. (1993). *Chemical Bond and Thermal Atomic Motion in Crystals.* Moscow: VINITI Publ.

Tsirelson, V., Avilov, A., Lepeshov, G., Kulygin, A., Stahn, J., Pietsch, U. & Spence, J. C. H. (2001). *J. Phys. Chem.* B**105**, 5068–5074.

Tsirelson, V. G. & Ozerov, R. P. (1996). *Electron Density and Bonding in Crystals.* Bristol, England/Philadelphia, USA: Institute of Physics Publishing.

Velders, G. J. M. & Feil, D. (1989). *Acta Cryst.* B**45**, 359–364.