Chapter 1
Basic Principles of the Interaction of X-Rays with Matter: Quantum Electrodynamical Analysis

Microscopic analysis of various processes arising due to the interaction of X-rays with condensed matter was considered in many papers, especially in the fundamental monograph [1], where the basic principles of X-ray optics were described. However, since that time a series of advanced techniques for X-ray structure characterization have been actively developed, such as the diffraction near the absorption edges [2], diffraction in the ferromagnetic materials [3], methods using the high-intensity radiation from the X-ray laser [4], and others.

Traditionally, the anisotropic correlative effects as well as the nonlinear processes due to the interaction of the intensive electromagnetic field with media are more essential in the optical range of wavelengths and there is a huge number of reviews in this field (for example, [5–8] and references therein). For the analysis of these processes, the microscopic equations of quantum electrodynamics have to be used, which imply the quantum properties of both the electromagnetic field and the matter are taken into account.

At the same time, in the basic books on the X-ray scattering by the inhomogeneous structures interaction of the radiation with matter is based on the simplest model where electrons are considered as classical oscillators [9, 10]. However, the progress in experimental and theoretical physics demands to consider this interaction on the basis of the first principles of quantum electrodynamics in order to analyze the limits of the conventional approximations. The main goal of this chapter is the systematic investigation of these problems.

1.1 Equations of X-Ray Optics

X-rays are the unique instrument for investigation of the structure of materials, and it is extremely important for the great number of high-technological processes. The advantages of X-ray applications are conditioned by a series of essential factors: (i) small wavelength providing the resolution compared with the characteristic size

of the electron density distribution in atoms; (ii) a weak interaction of X-ray beams with the matter providing non-destructive characterization of the objects; (iii) simple and universal form of this interaction which is important for the solution of the inverse problem when the electron density distribution in the investigated medium is reconstructed on the basis of the X-ray scattering profiles; (iv) possibility to describe the evolution of X-ray wave field in a medium on the basis of the perturbation theory applied directly to the microscopic equations of quantum electrodynamics.

Let us consider the main approximations used on the way from quantum electrodynamics to the macroscopic Maxwell's equations for electromagnetic field in a medium [8, 11]. The start point is the Schrödinger equation for the total state vector $|\Phi(t)>$ that corresponds to the whole system, the non-relativistic quantum medium and the quantized electromagnetic field:

$$i\hbar \frac{\partial}{\partial t}|\Phi(t)>= \hat{H}|\Phi(t)> \tag{1.1}$$

with the Hamiltonian that has the following form in the Coulomb gauge (see, for example, [7]):

$$\hat{H} = \hat{H}_M + \sum_j^{N_e} \left\{ \frac{1}{2m} \left[-2\frac{e_0}{c}\hat{p}_j \hat{A}(r_j) + \frac{e_0^2}{c^2}(\hat{A}(r_j))^2 \right] \right.$$

$$\left. -\frac{e_0\hbar}{2mc}\sigma_j \hat{H}(r_j) \right\} + \sum_{ks} \hbar\omega_k a_{ks}^+ a_{ks} \equiv \hat{H}_M + \hat{H}_{MR} + \hat{H}_R;$$

$$\hat{H}_M = \sum_j^{N_e} \frac{\hat{p}_j^2}{2m} + \hat{U}(\{r_j\});$$

$$\hat{A}(r) = \sum_{ks} \sqrt{\frac{2\pi\hbar c^2}{\omega_k V}} e_{ks}[a_{ks}e^{ikr} + a_{ks}^+ e^{-ikr}];$$

$$\hat{H}(r) = [\nabla \times \hat{A}]; \quad (ke_{ks}) = 0. \tag{1.2}$$

Here e_0, m are the electron charge and mass, respectively; interaction between X-ray field and atomic nuclei can be neglected; $\hbar$ is the Plank constant; c is the light velocity; $a_{ks}(a_{ks}^+)$ is the operator of annihilation (creation) of the photon with the frequency $\omega_k = ck$, wave vector k and polarization e_{ks}; $\hat{A}(r)$ and $\hat{H}(r)$ are the operators of the transversal vector potential and magnetic field, correspondingly; r_j, $\sigma_j/2$ are the coordinate and spin of jth electron; N_e is the total number of electrons; $\hat{H}_M$ is the Hamiltonian of the medium with the potential energy operator $\hat{U}(\{r_j\})$ which corresponds to the Coulomb interaction between electrons and nuclei and provides the stable state of medium. Operator $\hat{H}_{MR}$ is the Hamiltonian of the electron interaction with the quantum field, the term proportional to the magnetic

field is included in order to consider the anisotropic ferromagnetic materials; $\hat{H}_R$ is the Hamiltonian of a free electromagnetic field.

Conventional approach for description of the interaction between X-rays and medium corresponds to the Maxwell's equations for the classical electromagnetic field coupled with the Schrödinger equation for the electron subsystem. Sometimes the latter one is also considered in a semiclassical way. This system of equations is the theoretical basis for so-called X-ray optics approach [1]. It is possible, however, to deduce these equations directly from the Eq. (1.1) for the state vector of the whole system if the adiabatic perturbation theory [12] is used, and that allows to define the limits of the semiclassical approximation. Figure 1.1 represents schematically the sequence of the transformation that should be done in order to pass from the quantum electrodynamics to the X-ray optics approach.

The canonical transformation of the field operator [13], being applied to the Hamiltonian (1.2), separates the time dependent classical field $A(r, t)$ from the radiation component $\hat{A}_R(r)$ defined by the quantum fluctuations of the electromagnetic field relatively to the selected classical field [8]:

$$\hat{U}_R(t) = \prod_{ks} e^{c_{ks}a_{ks}^+ - c_{ks}^* a_{ks}} = \prod_{ks} e^{c_{ks}a_{ks}^+} e^{-c_{ks}^* a_{ks}} e^{-1/2|u_{ks}(t)|^2};$$

$$c_{ks}(t) = u_{ks}(t)e^{-i\omega_k t}; \quad \hat{U}_R^+ \hat{A}(r)\hat{U}_R = A(r, t) + \hat{A}_R(r);$$

$$A(r, t) = \sum_{ks} \sqrt{\frac{2\pi\hbar c^2}{\omega_k V}} e_{ks}[u_{ks}e^{ikr - i\omega_k t} + u_{ks}^* e^{-ikr + i\omega_k t}];$$

$$\hat{A}_R(r) = \sum_{ks} \sqrt{\frac{2\pi\hbar c^2}{\omega_k V}} e_{ks}[a_{ks}e^{ikr} + a_{ks}^+ e^{-ikr}]. \tag{1.3}$$

Fig. 1.1 Schematic representation of importance of different approximations for light and X-ray optics
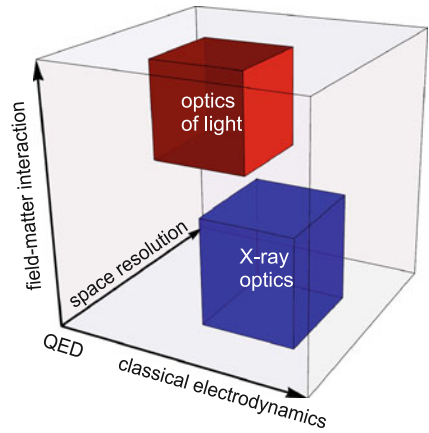
and canonical transformation of other operators in the Eq. (1.1) leads to the following equations:

$$\hat{H}_R(t) = \hat{U}_R^+(t)\hat{H}_R\hat{U}_R(t)$$

$$= \hat{H}_R + \sum_{ks} \hbar\omega_k[a_{ks}^+ c_{ks}(t) + a_{ks}c_{ks}^*(t) + |u_{ks}(t)|^2];$$

$$i\hbar\hat{U}_R^+ \frac{\partial}{\partial t}\hat{U}_R = i\hbar\frac{\partial}{\partial t} + i\hbar\sum_{ks}[(\dot{u}_{ks}(t)a_{ks}^+ e^{-i\omega_k t} - \dot{u}_{ks}^*(t)a_{ks}e^{i\omega_k t})$$

$$-i\omega_k(u_{ks}(t)a_{ks}^+ e^{-i\omega_k t} + u_{ks}^*(t)a_{ks}e^{i\omega_k t}) - i\omega_k|u_{ks}(t)|^2$$

$$+\frac{1}{2}(\dot{u}_{ks}(t)u_{ks}^*(t) - \dot{u}_{ks}^*(t)u_{ks}(t))]; \quad \dot{u}_{ks} \equiv \frac{\partial}{\partial t}u_{ks}. \quad (1.4)$$

The Schrödinger Eq. (1.1) is then transformed to:

$$i\hbar\frac{\partial}{\partial t}|\Psi(t)> = \hat{H}(t)|\Psi(t)>;$$

$$|\Phi(t)> = e^{i\phi(t)}\hat{U}_R^+|\Psi(t)>;$$

$$\phi(t) = \frac{1}{2}\sum_{ks} i\hbar\omega_k[\dot{u}_{ks}(t)u_{ks}^*(t) - \dot{u}_{ks}^*(t)u_{ks}(t)]. \quad (1.5)$$

Here the time-dependent Hamiltonian $\hat{H}(t)$ is a functional of the undefined components $u_{ks}(t)$ of the classical field in the medium and it has the following form:

$$\hat{H}(t) = \hat{H}_M + \hat{H}_{MR}(t) + \hat{H}_R;$$

$$\hat{H}_{MR}(t) = \sum_{j}^{N_e}\left\{\frac{1}{2m}\left[-2\frac{e_0}{c}\hat{p}_j(A(r_j, t) + \hat{A}_R(r_j))\right.\right.$$

$$\left.\left. +\frac{e_0^2}{c^2}(A(r_j, t) + \hat{A}_R(r_j))^2\right] - \frac{e_0\hbar}{2mc}\sigma_j(H(r_j, t) + \hat{H}_R(r_j))\right\}$$

$$-i\hbar\sum_{ks}(\dot{u}_{ks}(t)a_{ks}^+ e^{-i\omega_{ks}t} - \dot{u}_{ks}^*(t)a_{ks}e^{i\omega_k t}). \quad (1.6)$$

In the Hamiltonian of interaction $\hat{H}_{MR}(t)$, the part $\hat{H}_{MR}^c(t)$ defines the adiabatic evolution of the quantum medium under the influence of the classical electromagnetic field with the Fourier components $u_{ks}(t)$. Actually, these values define the displaced equilibrium positions for the quantum oscillators corresponding to the quantized field modes. Semiclassical approximation is defined by the wave function of the system with the radiation field being in the ground (vacuum) state relatively to the new equilibrium positions:

$$\hat{H}^{(0)}(t) = \hat{H}_M + \hat{H}_{MR}^c(t) + \hat{H}_R;$$

$$|\Psi^{(0)}(t)> \equiv |\Psi_c(t)> = |\Psi_M(t)> |0>; \quad \hat{H}_R|0> = 0;$$

$$i\hbar\frac{\partial}{\partial t}|\Psi_M(t)> = [\hat{H}_M + \hat{H}_{MR}^c(t)]|\Psi_M(t)>;$$

$$\hat{H}_{MR}^c(t) = \sum_j^{N_e}\left\{\frac{1}{2m}[-2\frac{e_0}{c}\hat{p}_j A(r_j,t)\right.$$

$$\left. +\frac{e_0^2}{c^2}A^2(r_j,t)] - \frac{e_0\hbar}{2mc}\sigma_j H(r_j,t)\right\}. \tag{1.7}$$

To investigate the stability of this state, the first order approximation relatively to the radiation field operators [12] has to be considered:

$$|\Psi(t)> \approx |\Psi_c(t)> + |\Psi^{(1)}(t)>; \quad <\Psi^{(1)}(t)|\Psi_c(t)> = 0, \tag{1.8}$$

where the first order correction includes the excited states of the quantized electromagnetic field and it is orthogonal to the zeroth-order state vector. As the result, the state vector $|\Psi^{(1)}(t)>$ satisfies to the equation:

$$\left\{i\hbar\frac{\partial}{\partial t} - \hat{H}^{(0)}(t)\right\}|\Psi^{(1)}(t)> = \hat{H}^{(1)}(t)|\Psi^{(0)}(t)>;$$

$$\hat{H}^{(1)}(t) = \sum_j^{N_e}\left\{-\frac{e_0}{mc}\hat{p}_j\hat{A}_R(r_j)\right.$$

$$\left. +\frac{e_0^2}{mc^2}A(r_j,t)\hat{A}_R(r_j) - \frac{e_0\hbar}{2mc}\sigma_j\hat{H}_R(r_j))\right\}$$

$$-i\hbar\sum_{ks}(\dot{u}_{ks}(t)a_{ks}^+e^{-i\omega_k t} - \dot{u}_{ks}^*(t)a_{ks}e^{i\omega_k t}). \tag{1.9}$$

The zeroth order state vector (1.7), being substituted into the Eq. (1.9), make it possible to calculate its projection onto the state vector $<\Psi_M(t)|$ defining the medium evolution in the selected classical field. The quantum radiation processes are neglected in the zeroth approximation, therefore the normalization condition for the corresponding state vector is conserved during the time $<\Psi^{(0)}(t)|\Psi^{(0)}(t)> = const$:

$$<\Psi_M(t)|\hat{H}^{(1)}(t)|\Psi_M(t)>|0> = 0;$$

$$\sum_{ks}\left\{\sqrt{\frac{2\pi\hbar}{\omega_k V}}e_{ks}J_{ks}(t) + i\hbar\dot{u}_{ks}(t)e^{-i\omega_k t}\right\}a_{ks}^+|0> = 0;$$

$$J_{ks}(t) = <\Psi_M(t)|\sum_j^{N_e}J_j(t)e^{-ikr_j}|\Psi_M(t)>;$$

$$\boldsymbol{J}_j(t) = \frac{e_0}{m}\hat{\boldsymbol{p}}_j - \frac{e_0^2}{mc}\boldsymbol{A}(\boldsymbol{r}_j, t) + i\frac{e_0\hbar}{2m}[\boldsymbol{\sigma}_j \times \boldsymbol{k}]. \tag{1.10}$$

The zeroth order solution (1.7) will be stable relatively to the quantum fluctuation of the electromagnetic field if the coefficients at the first power of the creation operator are equal to zero, i.e. when the Eq. (1.10) is satisfied [12]. Thus, the Fourier components of the classical field are expressed through the microscopic current $\boldsymbol{J}_j(t)$ of the electrons in the medium:

$$\dot{u}_{\boldsymbol{k}s}(t) = \frac{i}{\hbar}\sqrt{\frac{2\pi\hbar}{\omega_{\boldsymbol{k}}V}}\boldsymbol{e}_{\boldsymbol{k}s}\boldsymbol{J}_{\boldsymbol{k}s}(t)e^{i\omega_{\boldsymbol{k}s}t}. \tag{1.11}$$

Following to the method described in [8], this approximation results in the conventional form of Maxwell's equations for the transversal classical field. The first derivative of the vector potential holds:

$$-\frac{1}{c}\frac{\partial}{\partial t}\boldsymbol{A}(\boldsymbol{r}, t) = \sum_{\boldsymbol{k}s}\sqrt{\frac{2\pi\hbar}{\omega_{\boldsymbol{k}}V}}\boldsymbol{e}_{\boldsymbol{k}s}\{[\dot{u}_{\boldsymbol{k}s}e^{i\boldsymbol{k}\boldsymbol{r}-i\omega_{\boldsymbol{k}}t} + \dot{u}_{\boldsymbol{k}s}^*e^{-i\boldsymbol{k}\boldsymbol{r}+i\omega_{\boldsymbol{k}}t}]$$
$$+ i\omega_{\boldsymbol{k}}[u_{\boldsymbol{k}s}e^{i\boldsymbol{k}\boldsymbol{r}-i\omega_{\boldsymbol{k}}t} - u_{\boldsymbol{k}s}^*e^{-i\boldsymbol{k}\boldsymbol{r}+i\omega_{\boldsymbol{k}}t}]\}, \tag{1.12}$$

and using the expressions (1.10) and (1.11) along with the relation

$$\sum_s e_{\boldsymbol{k}s}^\mu e_{\boldsymbol{k}s}^\nu = \delta_{\mu,\nu} - \frac{k_\mu k_\nu}{k^2} \equiv t_{\mu\nu},$$

the first term in (1.12) is transformed to:

$$< \Psi_M(t)| \sum_j^{N_e} \sum_{\boldsymbol{k}} \frac{4\pi}{\omega_{\boldsymbol{k}}V}t_{\mu\nu}\left\{\left[\frac{e_0}{m}\hat{\boldsymbol{p}}_j - \frac{e_0^2}{mc}\boldsymbol{A}(\boldsymbol{r}_j, t)\right]\sin(\boldsymbol{k}(\boldsymbol{r} - \boldsymbol{r}_j))\right.$$
$$\left. + \frac{e_0\hbar}{2m}([\boldsymbol{\sigma}_j \times \boldsymbol{k}]\cos(\boldsymbol{k}(\boldsymbol{r} - \boldsymbol{r}_j))\right\}\Psi_M(t)>. \tag{1.13}$$

The expression (1.13) becomes a zero because of the presence of the odd function under the sum over $\boldsymbol{k}$.

The second term in the Eq. (1.12) represents the classical component of the electric field operator after the transformation (1.3). Thus, the Eq. (1.12) defines the conventional relationship between the vectors of the electric field strength and the vector potential for the classical transversal field:

$$-\frac{1}{c}\frac{\partial\boldsymbol{A}(\boldsymbol{r}, t)}{\partial t} = \boldsymbol{E}_t(\boldsymbol{r}, t). \tag{1.14}$$

The differentiation of the expression (1.14) results in the following formula for the derivative of the vector potential:

$$\frac{1}{c^2}\frac{\partial^2 A(r,t)}{\partial t^2} = -\sum_{ks}\sqrt{\frac{2\pi\hbar c^2}{\omega_k V}}e_{ks}\left\{k^2[u_{ks}e^{ikr-i\omega_k t} + u^*_{ks}e^{-ikr+i\omega_k t}]\right.$$

$$\left. +i\frac{\omega_k}{c^2}[\dot{u}_{ks}e^{ikr-i\omega_k t} - \dot{u}^*_{ks}e^{-ikr+i\omega_k t}]\right\}. \quad (1.15)$$

Finally, the inhomogeneous equation for the vector potential of the classical electromagnetic field can be found by taking into account the definitions (1.3) and (1.11):

$$\Delta A(r,t) - \frac{1}{c^2}\frac{\partial^2 A(r,t)}{\partial t^2} = -\frac{4\pi}{c}J_t(r,t);$$

$$J_t(r,t) = \frac{1}{2}[J_1(r,t) + J_1^+(r,t)]; \quad \nabla J_t(r,t) = 0;$$

$$J_1(r,t) = <\Psi_M(t)|\sum_j^{N_e}\sum_k \frac{t_{\mu\nu}}{V}\left\{\left[\frac{e_0}{m}\hat{p}_j - \frac{e_0^2}{mc}A(r_j,t)\right]\cos(k(r-r_j))\right.$$

$$\left. +i\frac{e_0\hbar}{2m}([\sigma_j \times k]\sin(k(r-r_j)))\right\}|\Psi_M(t)>. \quad (1.16)$$

Expression (1.16) for the current density can be symmetrized due to commutativity of the operators under the sum. Equations (1.14) and (1.16) define the propagation of the transversal classical field in the medium. In the framework of Coulomb gauge, the longitudinal part of the electrical field $E_l(r,t)$ is defined as the gradient of the scalar potential $\varphi(r,t)$ which is the sum of Coulomb potentials $\hat{V}(\{r_j\})$ of all charged particles averaged over the vector state $|\Psi_M(t)>$ of the medium. This results in the macroscopic equation [14]:

$$\nabla E_l(r,t) = 4\pi\rho(r,t); \quad \Delta\varphi(r,t) = -4\pi\rho(r,t);$$

$$E_l(r,t) = -\nabla\varphi(r,t); \quad \rho(r,t) = e_0\sum_j <\Psi_M(t)|\delta(r-r_j)|\Psi_M(t)>. \quad (1.17)$$

In the neutral medium the charge density should be represented as a divergence of the vector that is used to denote as $(-P)$. Then the integral charge over the medium volume is reduced to the surface integral and equals to zero [14]:

$$\int \rho(r,t)dV = -\int \nabla P dV = -\oint P dS = 0. \quad (1.18)$$

The physical meaning of the vector P follows from the formulas:

$$\int r\rho(r,t)dV = -\int r\nabla P =$$

$$-\oint \mathbf{r}(\mathbf{P}d\mathbf{S}) + \int (\mathbf{P}\nabla)\mathbf{r}dV = \int \mathbf{P}dV. \tag{1.19}$$

Thus the dipole polarization vector $\mathbf{P}(\mathbf{r}, t)$ for the electron subsystem can be calculated microscopically as follows:

$$\mathbf{P}(\mathbf{r}, t) = e_0 \sum_j^{N_e} < \Psi_M(t)|\mathbf{r}_j \delta(\mathbf{r} - \mathbf{r}_j)|\Psi_M(t)>. \tag{1.20}$$

In general case the polarization vector $\mathbf{P}(\mathbf{r}, t)$ can be expressed through the average electron current by means of the following equation:

$$i\frac{\partial \mathbf{P}(\mathbf{r}, t)}{\partial t} = \frac{e_0}{2\hbar} \sum_j^{N_e} \{< \Psi_M(t)|[\mathbf{r}_j \hat{H}^{(0)}]\delta(\mathbf{r} - \mathbf{r}_j)|\Psi_M(t) >$$
$$+ < \Psi_M(t)|\delta(\mathbf{r} - \mathbf{r}_j)[\mathbf{r}_j \hat{H}^{(0)}]|\Psi_M(t) >\},$$
$$\mathbf{r}_j \hat{H}^{(0)} - \hat{H}^{(0)}\mathbf{r}_j = [\mathbf{r}_j \hat{H}^{(0)}], \tag{1.21}$$

with the Hamiltonian $\hat{H}^{(0)}$ defined by formula (1.7). Calculating the commutator in (1.21), the vector $\mathbf{P}(\mathbf{r}, t)$ and its Fourier transformation $\mathbf{P}(\mathbf{r}, \omega)$ can be expressed in the following way:

$$\frac{\partial \mathbf{P}(\mathbf{r}, t)}{\partial t} = \mathbf{J}(\mathbf{r}, t); \quad \mathbf{P}(\mathbf{r}, \omega) = \frac{i}{\omega}\mathbf{J}(\mathbf{r}, \omega);$$

$$\mathbf{J}(\mathbf{r}, t) = \frac{1}{2} < \Psi_M(t)| \sum_j^{N_e} [\hat{\mathbf{J}}_j \delta(\mathbf{r} - \mathbf{r}_j) + \delta(\mathbf{r} - \mathbf{r}_j)\hat{\mathbf{J}}_j]|\Psi_M(t) >;$$

$$\hat{\mathbf{J}}_j = \frac{e_0}{m}\hat{\mathbf{p}}_j - \frac{e_0^2}{mc}\mathbf{A}(\mathbf{r}_j, t) + \frac{e_0\hbar}{2m}[\boldsymbol{\sigma}_j \times \nabla_\mathbf{r}], \tag{1.22}$$

with $\mathbf{J}(\mathbf{r}, t)$ as the average electron current in the medium. In neutral medium the average current is equal to zero if the external field is absent. Vector potential $\mathbf{A}(\mathbf{r}, t)$ is the only characteristic of the field in the Hamiltonian $\hat{H}^{(0)}$. Therefore in the considered case of linear electrodynamics $\mathbf{J}(\mathbf{r}, \omega)$ should be proportional to $\mathbf{A}(\mathbf{r}, \omega)$ and is represented in the following form (see below Sect. 1.2):

$$\mathbf{J}_\mu(\mathbf{r}, \omega) = \frac{\omega^2}{4\pi c}\hat{\chi}(\omega)\mathbf{A}(\omega), \tag{1.23}$$

with the medium polarizability $\hat{\chi}(\mathbf{r}, \mathbf{r}', \omega)$, which is the integral tensor operator

$$(\hat{\chi}(\omega)\mathbf{A}(\omega))_\mu = \int d\mathbf{r}'\chi_{\mu,\nu}(\mathbf{r}, \mathbf{r}'\omega)A_\nu(\mathbf{r}', \omega). \tag{1.24}$$

This value can also be expressed as a sum of the operators $\hat{\chi}^t$ and $\hat{\chi}^l$ that define the transversal (1.16) and longitudinal parts of the average current, respectively. Finally, all physical fields in the medium are expressed through the vector potential:

$$\boldsymbol{E}(\boldsymbol{r}, \omega) = \frac{i\omega}{c} \boldsymbol{A}(\boldsymbol{r}, \omega) - \nabla\varphi(\boldsymbol{r}, \omega) = \frac{i\omega}{c}[1 - \hat{\chi}^l(\omega)]\boldsymbol{A}(\omega);$$

$$\boldsymbol{D}(\boldsymbol{r}, \omega) = \boldsymbol{E}(\boldsymbol{r}, \omega) + 4\pi \boldsymbol{P}(\boldsymbol{r}, \omega) = \frac{i\omega}{c}[1 + \hat{\chi}^t(\omega)]\boldsymbol{A}(\omega);$$

$$\boldsymbol{H}(\boldsymbol{r}, \omega) = [\nabla \times \boldsymbol{A}(\boldsymbol{r}, \omega)], \qquad (1.25)$$

where $\boldsymbol{D}(\boldsymbol{r}, \omega)$ is the electrical displacement vector. Thus the use of the vector potential $\boldsymbol{A}(\boldsymbol{r}, t)$ is sufficient for the description of X-ray scattering in condensed media. The formulas (1.7) and (1.16) construct the system of the coupled Schrödinger-Maxwell's equations which is the basis for the description of the field-medium interaction in X-ray optics.

In accordance with the analysis above, these equations are applicable when the off-diagonal matrix elements of the operator $\hat{H}^{(1)}(t)$ in (1.9) are negligible for the processes under consideration. These elements correspond to the transitions between quasi-energy levels of the medium in the classical field $\boldsymbol{A}(\boldsymbol{r}, t)$ [8], which lead to the creation of new quanta of the electromagnetic field. The additional shift of the levels of the quasi-energy caused by these transitions can be evaluated by taking into account the second order of the adiabatic perturbation theory on the operator $\hat{H}^{(1)}(t)$ [12]. The diamagnetic term $\sim \boldsymbol{A}(\boldsymbol{r}_j, t)$ in the current density (1.16) is known to define the main contribution to the interaction between X-rays and medium [1]. Therefore, the relative shift of the quasi-energy level ϵ_f caused by the transitions of the quantum electromagnetic field to the excited one-photon states (quantum electrodynamics effects) is defined by the following dimensionless parameter:

$$\xi_{QED} \approx \sum_j^{N_e} \sum_{\boldsymbol{k}} \sum_{f'} \frac{2\pi\hbar}{\omega_{\boldsymbol{k}} V} \left(\frac{e_0^2 \boldsymbol{A}(\boldsymbol{r}_j, t)}{mc}\right)^2 \frac{M_{ff'}^j(\boldsymbol{k})}{|\epsilon_f||\hbar\omega_{\boldsymbol{k}} + \epsilon_{f'} - \epsilon_f|};$$

$$M_{ff'}^j(\boldsymbol{k}) = < \Psi_M^{f'}|e^{i\boldsymbol{k}\boldsymbol{r}_j}|\Psi_M^{f'} >. \qquad (1.26)$$

The characteristic energies of the electrons are essentially less than the energy of photons $|\epsilon_f| \ll \hbar\omega_{\boldsymbol{k}}$ if the wavelengths of X-ray range are considered. In this assumption, the classical field has the amplitude

$$A_0 \approx \frac{c}{\bar{\omega}} E_0,$$

with E_0 as the amplitude of the electric field strength, and $\bar{\omega}$ is the characteristic frequency of the field, and the parameter (1.26) can be estimated as

$$\xi_{QED} \approx \frac{4\pi e_0^2 n_e}{m\bar{\omega}^2} |\bar{M}|^2 \frac{e_0^2 E_0^2}{2m\bar{\omega}^2 |\epsilon_f|}. \qquad (1.27)$$

Here n_e is the electron density in the medium and the following estimation for the matrix elements $M^j_{ff'}(\mathbf{k})$ is used:

$$\sum_{\mathbf{k}} \sum_{f'} \frac{M^j_{ff'}(\mathbf{k})}{\omega_\mathbf{k}^2} \approx \frac{|\bar{M}|^2}{\bar{\omega}^2}.$$

The first factor in (1.27) has the same value as the X-ray susceptibility of the medium in the classical Maxwell's equations [1]. Therefore, the quantum effects for the electromagnetic field might be essential only if the classical field creates the medium ponderomotive [15] energy $U_p = e_0^2 E_0^2 / 2m\bar{\omega}^2$, which is comparable with the electron energy $|\epsilon_f|$. This condition can be fulfilled, for instance, in the ultrashort pulses from the X-ray free-electron laser [4].

1.2 Average Current Density and X-Ray Polarizability

The fundamental principles of the quantum electrodynamic shows that the semiclassical approach based on the solution of the system of coupled Schrödinger-Maxwell's equations describes the interaction of X-rays and medium with an accuracy sufficient for the most of the applications. These equations follow from the formulas (1.7), (1.16):

$$i\hbar \frac{\partial}{\partial t} |\Psi_M(t)> = [\hat{H}_M + \hat{H}^c_{MR}(t)]|\Psi_M(t)>;$$

$$\hat{H}^c_{MR}(t) = \sum_j^{N_e} \left\{ \frac{1}{2m} \left[-2\frac{e_0}{c} \hat{\mathbf{p}}_j \mathbf{A}(\mathbf{r}_j, t) \right. \right.$$
$$\left. \left. + \frac{e_0^2}{c^2} \mathbf{A}^2(\mathbf{r}_j, t) \right] - \frac{e_0\hbar}{2mc} \boldsymbol{\sigma}_j \mathbf{H}(\mathbf{r}_j, t) \right\}. \tag{1.28}$$

$$\Delta \mathbf{A}(\mathbf{r}, t) - \frac{1}{c^2} \frac{\partial^2 \mathbf{A}(\mathbf{r}, t)}{\partial t^2} = -\frac{4\pi}{c} \mathbf{J}_t(\mathbf{r}, t); \quad \nabla \mathbf{A}(\mathbf{r}, t) = 0, \tag{1.29}$$

where $\mathbf{J}_t$ is the transversal component of the average current

$$\mathbf{J}(\mathbf{r}, t) = \frac{1}{2} <\Psi_M(t)| \sum_j^{N_e} [\hat{\mathbf{J}}_j \delta(\mathbf{r} - \mathbf{r}_j) + \delta(\mathbf{r} - \mathbf{r}_j)\hat{\mathbf{J}}_j]|\Psi_M(t)>$$

$$\hat{\mathbf{J}}_j = \frac{e_0}{m} \hat{\mathbf{p}}_j - \frac{e_0^2}{mc} \mathbf{A}(\mathbf{r}_j, t) + \frac{e_0\hbar}{2m} [\boldsymbol{\sigma}_j \times \nabla_\mathbf{r}]. \tag{1.30}$$

Further simplification of this system of nonlinear equations is possible due to the weak interaction of the X-ray wave-field with the medium, which makes possible the usage of the perturbation theory over the operator $\hat{H}^c_{MR}(t)$ for the solution of the Eq. (1.28). In general case, the medium state vector is defined by the series over the full set of the eigenfunctions $|\Psi_f>$ of the Hamiltonian $\hat{H}_M$:

$$|\Psi_M(t)> = \sum_f C_f(t)|\Psi_f> e^{-\frac{i}{\hbar}E_f t}; \quad \hat{H}_M|\Psi_f> = E_f|\Psi_f>;$$

$$\hat{H}_M = \sum_j^{N_e} \frac{\hat{p}_j^2}{2m} + U(\{r_j\}); \quad |\Psi_f> \equiv |\Psi_f(\{r_j\})>. \quad (1.31)$$

Here index f includes the whole set of the quantum numbers of the multi-electron system in the potential field $U(\{r_j\}$ created by the Coulomb interactions between the electrons and the nuclei in the medium.

In the text below, the principal assumptions are briefly discussed, which are used in order to calculate the average current (1.30) on the basis of the solution of Eq. (1.31) [1]. There is no necessity to use any particular form of the potential field $U(\{r_j\}$ and wave functions in (1.31), if the problem is considered in the framework of the linear response theory [16, 17]. The substitution of the expansion (1.31) into the Eq. (1.30) leads to the formula, which defines the evolution of the coefficients $C_f(t)$:

$$i\hbar\frac{\partial C_f(t)}{\partial t} = -\sum_{f'} M_{ff'}(t) C_{f'}(t) e^{\frac{i}{\hbar}(E_f - E_{f'})t};$$

$$M_{ff'}(t) = <\Psi_f|\hat{H}^c_{MR}(t)|\Psi_{f'}>. \quad (1.32)$$

The standard "adiabatic switch-off" condition is used here for the interactions within the limit $t \to -\infty$ [16, 17]:

$$M_{ff'}(t) \to M_{ff'}(t)e^{\nu t}; \quad \nu \to 0,$$

and the system is assumed to be in the ground state when the field is absent:

$$C_f^{(0)} = \delta_{f0}.$$

Using these approximations in the first order of the perturbation theory, the expression for C_f is obtained:

$$C_f(t) \approx \delta_{f0} + \frac{i}{\hbar}\int_{-\infty}^t M_{f0}(t') e^{\frac{i}{\hbar}(E_f - E_0 - i\hbar\nu)t'} dt';$$

$$|\Psi_M(t)> \approx |\Psi_0> e^{-\frac{i}{\hbar}E_0 t}$$

$$+\frac{i}{\hbar}\sum_{f\neq 0}e^{-\frac{i}{\hbar}E_f t}\int_{-\infty}^{t}M_{f0}(t')|\Psi_f > e^{\frac{i}{\hbar}(E_f-E_0-i\hbar\nu)t'}dt'. \qquad (1.33)$$

The formulas (1.33) are then used in the wave function (1.31), and the current (1.30) can be calculated with an accuracy of the first order on the electromagnetic field. The average current is supposed to be zero without field and is caused by the transitions of the system into the excited states:

$$J_{t\mu}(r,t)=\sum_{j,l}^{N_e}\int_{-\infty}^{t}<\Psi_0|\hat{T}_{\mu\lambda}^{jl}(r,r',t-t')A_\lambda(r',t')e^{\nu t'}dt'dr'|\Psi_0>;$$

$$\hat{T}_{\mu\lambda}^{jl}(r,r',t-t')=-\frac{e_0^2}{mc}\{\delta(r-r_j)\delta(r'-r_j)\delta_{jl}\delta(t-t')\delta_{\mu\lambda}$$

$$-\frac{im}{\hbar}\sum_{f\neq 0}e^{\frac{i}{\hbar}(E_f-E_0)(t'-t)}\hat{v}_\mu^j\delta(r-r_j)|\Psi_f><\Psi_f|\hat{v}_\lambda^l\delta(r'-r_l)$$

$$+\frac{im}{\hbar}e^{-\frac{i}{\hbar}(E_f-E_0)(t'-t)}\hat{v}_\lambda^l\delta(r'-r_l)|\Psi_f><\Psi_f|\hat{v}_\mu^j\delta(r-r_j)\};$$

$$\hat{v}_\mu^j=\frac{1}{m}\hat{p}_\mu^j+\frac{\hbar}{2m}([\sigma_j\times\nabla_r])_\mu. \ (1.34)$$

The transversal part of the current is appeared because it is proportional to the transversal vector potential $A_\lambda(r',\omega)$.

The substitution of the expression (1.34) into the Maxwell's Eq. (1.29) demonstrates that the linear response of the medium is defined by the integral operator $\hat{T}_{\mu\lambda}^{jl}(r,t-t')$ which has a cumbersome functional dependence on the multi-electron wave functions:

$$\Psi_f(\{r_j\})\equiv<\{r_j\}|\Psi_f>.$$

Hereinafter, we change to the Fourier representation over the time variable in the Eq. (1.29):

$$\Delta A(r,\omega)+\frac{\omega^2}{c^2}A(r,\omega)=-\frac{4\pi}{c}J_t(r,\omega);$$

$$A(r,t)=\int d\omega A(r,\omega)e^{-i\omega t}. \qquad (1.35)$$

The Fourier image of the current holds:

$$J_{t\mu}(r,\omega)=c\sum_{j}^{N_e}\sum_{l}^{N_e}\int dr'<\Psi_0|\hat{T}_{\mu\lambda}^{jl}(r,r',\omega)A_\lambda(r',\omega)|\Psi_0>;$$

$$\hat{T}_{\mu\lambda}^{jl}(r,r',\omega)=-r_0\{\delta(r-r_j)\delta(r'-r_l)\delta_{jl}\delta_{\mu\lambda}$$

$$-\sum_{f \neq 0} \frac{2(E_f - E_0)}{(E_f - E_0)^2 - (\hbar\omega + i\nu)^2}$$

$$\times \hat{v}^j_\mu \delta(\mathbf{r} - \mathbf{r}_j)|\Psi_f> < \Psi_f|\hat{v}^l_\lambda \delta(\mathbf{r}' - \mathbf{r}_l)\}, \qquad (1.36)$$

where $r_0 = e_0^2/mc^2$ is the classical electron radius. The first term in the operator $\hat{T}^{jl}_{\mu\lambda}(\mathbf{r}, \mathbf{r}'\omega)$ is not related to the transitions of the atoms in the medium to the excited states, however, it corresponds to the coherent scattering of the electromagnetic field from the electrons with coordinates $\{\mathbf{r}_j\}$. This process is defined by the amplitude of the elastic Compton scattering $(-r_0)$ of the photon on the free electron at zero angle [18]. The second term is also defined by the coherent scattering of the electromagnetic field but this time through the virtual transitions of the electrons to the intermediate states with the energy E_f. In the optical wavelength range, this term solely defines the contribution to the system linear response. For the X-rays, it becomes essential near the resonance, when the photon energy almost coincides with the transition energy $E_f - E_0 \approx \hbar\omega$ [1], which makes possible the following substitution:

$$\frac{2(E_f - E_0)}{(E_f - E_0)^2 - (\hbar\omega + i\nu)^2} \approx \frac{1}{E_f - E_0 - \hbar\omega - i\nu}.$$

After the solution of the Eq. (1.35), the dependence of the vector potential $A_\lambda(\mathbf{r}', \{\mathbf{r}_j\}, \omega)$ on the electron coordinates averaged over the state vector $|\Psi_0>$ has to be taken into account. In order to separate the calculation of the electromagnetic field from the procedure of the averaging over the electron coordinates, the relationship below is used. This relationship has been proved in details in the theory of wave scattering from an arbitrary system with the large number of the scattering centers [19, 20]:

$$< \Psi_0|\hat{T}^{jl}_{\mu\lambda}(\mathbf{r}, \mathbf{r}', \{\mathbf{r}_j\}, \omega)A_\lambda(\mathbf{r}', \{\mathbf{r}_j\}, \omega)|\Psi_0 >=$$

$$=< \Psi_0|\hat{F}^{jl}_{\mu\lambda}(\mathbf{r}, \mathbf{r}', \{\mathbf{r}_j\}, \omega)|\Psi_0 > A_\lambda(\mathbf{r}', \omega). \qquad (1.37)$$

Here the renormalized scattering operator $\hat{F}^{jl}_{\mu\lambda}(\mathbf{r}, \mathbf{r}', \omega)$ includes all non-coherent and inelastic processes at a single scattering center. In particular, such renormalization of the amplitude for the scattering of the electromagnetic wave by free electron leads to the complex scattering amplitude with imaginary part defined by the total scattering cross-section accordingly to the optical theorem:

$$(-r_0) \Rightarrow f(0); \quad f'(0) = -r_0; \quad f''(0) = \frac{\omega}{4\pi c}\sigma_t(\omega), \qquad (1.38)$$

where σ_t is the total cross-section of the Compton scattering of photon by free electron (Klein-Nishina formula) [21]:

$$\sigma_t(\omega) = 2\pi r_0^2 \left\{ \frac{1+\beta}{\beta^3} \left[\frac{2\beta(1+\beta)}{1+2\beta} - \ln(1+2\beta) \right] \right.$$

$$\left. + \frac{\ln(1+2\beta)}{2\beta} - \frac{1+3\beta}{(1+2\beta)^3} \right\}; \quad \beta = \frac{\hbar\omega}{mc^2}. \tag{1.39}$$

The renormalization procedure for the part of the scattering operator related to the intermediate transitions to the excited states is defined by the substitution [20]:

$$\frac{1}{E_f - E_0 - \hbar\omega - i\nu} \Rightarrow \frac{1}{E_f - E_0 - \hbar\omega - i\Gamma_f/2}, \tag{1.40}$$

where Γ_f is the total width of the excited state of the system with the energy E_f. Actually, this value includes transitions from the level to all possible states and is connected with the total cross-section of the inelastic photon scattering at the bound electrons.

Hereinafter, the medium is considered as an unlimited continuum, which does not restrict the generality of the further analysis. The most interesting for the applications, the macroscopic non-homogeneities of real medium (layered structures, defects, deformed crystals and others), can be described within the framework of the conventional scattering theory [19]. In this approach, each macroscopic element of the investigated object is considered as unrestricted and variation of the medium properties at different parts are considered either as small perturbations (for example, [22–24]) or by means of the boundary conditions sewing together the solutions of the Maxwell's equations for different parts of the medium (for example, [9, 25]). In the case of the continuous medium, the Fourier representation over the space variables can be used for the Eqs. (1.35)–(1.37):

$$k^2 A(\boldsymbol{k}, \omega) - \frac{\omega^2}{c^2} A(\boldsymbol{k}, \omega) = \frac{4\pi}{c} J_t(\boldsymbol{k}, \omega);$$

$$\boldsymbol{k} A(\boldsymbol{k}, \omega) = 0. \quad A(\boldsymbol{r}, t) = \int d\boldsymbol{k} d\omega A(\boldsymbol{k}, \omega) e^{i(\boldsymbol{k}\boldsymbol{r} - \omega t)}, \tag{1.41}$$

and the linear response function can be written in the form:

$$J_{t\mu}(\boldsymbol{k}, \omega) = c \frac{1}{(2\pi)^3} \int d\boldsymbol{k}' \sum_{j}^{N_e} \sum_{l}^{N_e} F_{\mu\lambda}^{jl}(\boldsymbol{k}, \boldsymbol{k}'\omega) A_\lambda(\boldsymbol{k}', \omega);$$

$$F_{\mu\lambda}^{jl}(\boldsymbol{k}, \boldsymbol{k}'\omega) = f(0) \left\{ <\Psi_0| e^{i(\boldsymbol{k}'-\boldsymbol{k})\boldsymbol{r}_j} |\Psi_0> \delta_{jl}\delta_{\mu\lambda} \right.$$

$$- \sum_{f \neq 0} \frac{m}{E_f - E_0 - \hbar\omega - i\Gamma_f/2}$$

$$\left. \times <\Psi_0| \hat{v}_\mu^j e^{-i\boldsymbol{k}\boldsymbol{r}_j} |\Psi_f> <\Psi_f| \hat{v}_\lambda^l e^{i\boldsymbol{k}'\boldsymbol{r}_l} |\Psi_0> \right\} \tag{1.42}$$

For further calculation of the average current (1.42), the state vectors $|\Psi_f>$ should be defined as the solutions of the Schrödinger Eq. (1.31) for multi-electron system. The adiabatic and one-electron approximations are used here, which are explained in many text books (for example, [26, 27]). The one-electron states are described by the wave functions which satisfy to the Schrödinger equation with self-consistent periodic potential and the Bloch theorem:

$$\psi_{\alpha,\kappa}(\boldsymbol{r}+\boldsymbol{n}) = e^{i\kappa\boldsymbol{n}}\psi_{\alpha,\kappa}(\boldsymbol{r}), \tag{1.43}$$

where $\boldsymbol{n} = l_1\boldsymbol{a} + l_2\boldsymbol{b} + l_3\boldsymbol{c}$; $l_i = 0, \pm1, \pm2, \ldots$ is the vector of translation decomposed over the vectors $\boldsymbol{a}$, $\boldsymbol{b}$, $\boldsymbol{c}$ of the basic crystal cell. These wave functions correspond to the zone energy spectrum $\epsilon_\alpha(\boldsymbol{\kappa})$, where index α is the number of zone and κ is the quasi-momentum vector restricted by the first Brillouin zone [26]. The total number of different quasi-momentum vectors is equal to the number of the basic cells N due to boundary conditions [27]. All the formulas below can also be applied to the homogeneous medium in the limits $\boldsymbol{a}, \boldsymbol{b}, \boldsymbol{c} \to \infty$.

Due to the translational symmetry the wave functions can be normalized as follows:

$$\psi_{\alpha,\kappa}(\boldsymbol{r}) = \frac{1}{\sqrt{N}}\tilde{\psi}_{\alpha,\kappa}(\boldsymbol{r});$$

$$\int |\psi_{\alpha,\kappa}(\boldsymbol{r})|^2 d\boldsymbol{r} = \int_\Omega |\tilde{\psi}_{\alpha,\kappa}(\boldsymbol{r})|^2 d\boldsymbol{r} = 1, \tag{1.44}$$

where Ω is the volume of the basic cell ($V = N\Omega$).

In the considered representation, the sum over electron coordinates in the expression (1.42) in the ground state of a crystal is reduced to the summation over the filled zones taking into account the normalization condition on the total number of electrons. As for example, for the one-particle operators it means:

$$I(\boldsymbol{Q}) = \sum_j <\Psi_0|e^{i\boldsymbol{Q}\boldsymbol{r}_j}|\Psi_0> \Rightarrow \sum_{\alpha,\kappa}^{occ} g_{\alpha,\kappa} \int \psi_{\alpha,\kappa}^*(\boldsymbol{r})e^{i\boldsymbol{Q}\boldsymbol{r}}\psi_{\alpha,\kappa}(\boldsymbol{r})d\boldsymbol{r}$$

$$= \frac{1}{N}\sum_{\boldsymbol{n}} e^{i\boldsymbol{Q}\boldsymbol{n}} \sum_{\alpha,\kappa}^{occ} g_{\alpha,\kappa} \int e^{i\boldsymbol{Q}\boldsymbol{r}}|\tilde{\psi}_{\alpha,\kappa}(\boldsymbol{r})|^2 d\boldsymbol{r};$$

$$\sum_{\alpha,\kappa}^{occ} \int g_{\alpha,\kappa}|\psi_{\alpha,\kappa}(\boldsymbol{r})|^2 d\boldsymbol{r} = \sum_{\alpha,\kappa}^{occ} \int_\Omega g_{\alpha,\kappa}|\tilde{\psi}_{\alpha,\kappa}(\boldsymbol{r})|^2 d\boldsymbol{r} = N_e, \tag{1.45}$$

where $g_{\alpha,\kappa}$ are the numbers of the filling up (multiplicity of degeneracy) of the energy levels in zones, $g_{\alpha,\kappa} = 2$ in the case of the ideal non-polarized crystal and it varies within the limits $0 < g_{\alpha,\kappa} < 2$ in solid solutions or crystals with defects, N_e is the total number of electrons in the crystal.

The integrations in the matrix elements (1.45) are based on the following relationships [26]:

$$\sum_n e^{i\boldsymbol{Q}\boldsymbol{n}} = N\frac{(2\pi)^3}{V}\sum_H \delta(\boldsymbol{Q}-\boldsymbol{H});$$

$$I(\boldsymbol{Q}) = \frac{(2\pi)^3}{V}\sum_H \delta(\boldsymbol{Q}-\boldsymbol{H})\sum_{\alpha,\kappa}^{occ}\int_\Omega g_{\alpha,\kappa}\tilde{\psi}_{\alpha,\kappa}^*(\boldsymbol{r})e^{i\boldsymbol{H}\boldsymbol{r}}\tilde{\psi}_{\alpha,\kappa}(\boldsymbol{r})d\boldsymbol{r}, \quad (1.46)$$

where $\boldsymbol{H}$ are the crystal reciprocal lattice vectors.

Let us consider in details the main contribution to the average current which is defined by the non-resonant scattering from electrons and is described by the first term in the Eq. (1.42). By taking into account the relation (1.46), the current is:

$$J_{t\mu}^{(e)}(\boldsymbol{k},\omega) = c\frac{1}{\Omega}f(0)\sum_H F(\boldsymbol{H})A_\mu(\boldsymbol{k}+\boldsymbol{H},\omega);$$

$$F(\boldsymbol{H}) = \frac{1}{N}\sum_{\alpha,\kappa}^{occ}\int_\Omega g_{\alpha,\kappa}e^{i\boldsymbol{H}\boldsymbol{r}}|\tilde{\psi}_{\alpha,\kappa}(\boldsymbol{r})|^2 d\boldsymbol{r}. \quad (1.47)$$

Here $F(\boldsymbol{H})$ stands for the cell scattering factor of the crystal basic cell, normalized by the total number N_c of the electrons in the elementary cell:

$$F(0) = \frac{1}{N}\sum_{\alpha,\kappa}^{occ}\int_\Omega g_{\alpha,\kappa} = \frac{N_e}{N} = N_c. \quad (1.48)$$

By the definition, the function

$$\rho_e(\boldsymbol{r}) = \frac{1}{N}\sum_{\alpha,\kappa}^{occ}\int_\Omega g_{\alpha,\kappa}|\tilde{\psi}_{\alpha,\kappa}(\boldsymbol{r})|^2 = \sum_H F(\boldsymbol{H})e^{-i\boldsymbol{H}\boldsymbol{r}} \quad (1.49)$$

describes the space distribution of the electron density in the cell. The transition to the constant electron density $N=1$, $\Omega \to \infty$, $N_e \to \infty$, $N_e/\Omega \to n_e$ corresponds to the homogeneous medium:

$$J_{t\mu}^{(e)}(\boldsymbol{k},\omega) = cn_e f(0)A_\mu(\boldsymbol{k},\omega). \quad (1.50)$$

Substituting the average current into the Maxwell's Eq (1.41), the above equations are reduced to the commonly used form:

$$k^2 A(\boldsymbol{k},\omega) - \frac{\omega^2}{c^2}\sum_H \varepsilon^{(e)}(\boldsymbol{H},\omega)A(\boldsymbol{k}+\boldsymbol{H},\omega) = 0;$$

$$\varepsilon^{(e)}(\boldsymbol{H}, \omega) = \delta_{\boldsymbol{H},0} + \chi^{(e)}(\boldsymbol{H}, \omega); \ \chi^{(e)}(\boldsymbol{H}, \omega) = \frac{4\pi c^2}{\omega^2 \Omega} f(0) F(\boldsymbol{H}), \quad (1.51)$$

where $\varepsilon^{(e)}(\boldsymbol{H}, \omega)$ and $\chi^{(e)}(\boldsymbol{H}, \omega)$ are the Fourier components of the non-resonant part of the X-ray dielectric constant and susceptibility, respectively. To calculate the resonant part of the scattering operator in (1.41), the sum over the electron coordinates is separated into two parts:

$$\sum_{j}^{N_e} \sum_{l}^{N_e} e^{i(k'r_l - kr_j)} \Rightarrow \sum_{\boldsymbol{n}} e^{i(k'-k)\boldsymbol{n}} \sum_{j}^{\tilde{N}_e} \sum_{l}^{\tilde{N}_e} e^{i(k'r_l - kr_j)}$$

$$+ \sum_{\boldsymbol{n}} \sum_{\boldsymbol{n}' \neq \boldsymbol{n}} \sum_{j}^{\tilde{N}_e} \sum_{l}^{\tilde{N}_e} e^{i(k'(r_l + \boldsymbol{n}') - k(r_j + \boldsymbol{n}))}, \quad (1.52)$$

where $\tilde{N}_e$ includes summation over the electron coordinates in a single basic cell and the summation over the translation vectors $\boldsymbol{n}, \boldsymbol{n}'$ transfers it to the whole crystal.

In the framework of the Hartree approximation, the state vector of the system is defined by the simple product of the one-electron wave functions. In this case, the nonzero probabilities for the transitions to the excited states (f) present only for the terms with $\boldsymbol{n} = \boldsymbol{n}'$. The terms with $\boldsymbol{n} \neq \boldsymbol{n}'$ are accounted due to the correlation and exchange effects which are rather small for the non-relativistic atoms. They may play an important role, for example, in the resonant X-ray spectroscopy [2], however, in the majority of applications this contribution to the X-ray susceptibility is neglected [1].

The scattering operator is defined by the transitions to the levels of unfilled energy bands $E_0 \to \epsilon_\alpha(\boldsymbol{\kappa}); \ E_f \to \epsilon_{\alpha_1}(\boldsymbol{\kappa}_1)$ with the energy width $\gamma_{\alpha_1}(\boldsymbol{\kappa}_1)$ that takes into account various processes of atom decay from the excited state:

$$F_{\mu\lambda}^{jl(2)}(\boldsymbol{k}, \boldsymbol{k}'\omega) \approx -\frac{1}{N^2} \sum_{\boldsymbol{n}} e^{i(k'-k)\boldsymbol{n}} \sum_{\alpha, \boldsymbol{\kappa}}^{occ} g_{\alpha, \boldsymbol{\kappa}}$$

$$\times \sum_{\alpha_1, \boldsymbol{\kappa}_1} \frac{m f(0) M_{\alpha, \boldsymbol{\kappa}, \mu}^{\alpha_1, \boldsymbol{\kappa}_1}(-\boldsymbol{k}) M_{\alpha_1, \boldsymbol{\kappa}_1, \lambda}^{\alpha, \boldsymbol{\kappa}}(\boldsymbol{k}')}{\epsilon_{\alpha_1}(\boldsymbol{\kappa}_1) - \epsilon_\alpha(\boldsymbol{\kappa}) - \hbar\omega - i\gamma_{\alpha_1}(\boldsymbol{\kappa}_1)}. \quad (1.53)$$

The matrix elements from the operator of the current $M_{\alpha, \boldsymbol{\kappa}, \mu}^{\alpha_1, \boldsymbol{\kappa}_1}(-\boldsymbol{k})$ are also reduced to the integrals over the single basic cell:

$$M_{\alpha, \boldsymbol{\kappa}, mu}^{\alpha_1, \boldsymbol{\kappa}_1}(-\boldsymbol{k}) = \int_\Omega \tilde{\psi}_{\alpha_1, \boldsymbol{\kappa}_1}^*(\boldsymbol{r}) \hat{v}_\mu e^{-i\boldsymbol{k}\boldsymbol{r}} \tilde{\psi}_{\alpha, \boldsymbol{\kappa}}(\boldsymbol{r}) d\boldsymbol{r}. \quad (1.54)$$

Using the expression (1.46), the resonant contribution to the average current can be found:

$$J_{t\nu}^{(2)}(\boldsymbol{k}, \omega) = c \frac{1}{\Omega} f(0) \sum_{\boldsymbol{H}} t_{\nu\mu} F_{\mu,\lambda}(\boldsymbol{k}, \boldsymbol{H}) A_\lambda(\boldsymbol{k} + \boldsymbol{H}, \omega);$$

$$F_{\mu,\lambda}(\boldsymbol{k}, \boldsymbol{H}) = -\frac{1}{N^2} \sum_{\alpha,\boldsymbol{\kappa}}^{occ} g_{\alpha,\boldsymbol{\kappa}} \sum_{\alpha_1,\boldsymbol{\kappa}_1} \frac{m M_{\alpha,\boldsymbol{\kappa},\mu}^{\alpha_1,\boldsymbol{\kappa}_1}(-\boldsymbol{k}) M_{\alpha_1,\boldsymbol{\kappa}_1,\lambda}^{\alpha,\boldsymbol{\kappa}}(\boldsymbol{k} + \boldsymbol{H})}{\epsilon_{\alpha_1}(\boldsymbol{\kappa}_1) - \epsilon_\alpha(\boldsymbol{\kappa}) - \hbar\omega - i\gamma_{\alpha_1}(\boldsymbol{\kappa}_1)}, \quad (1.55)$$

which represents the anomalous contribution to the X-ray susceptibility of the crystal [28]:

$$k^2 A_\mu(\boldsymbol{k}, \omega) - \frac{\omega^2}{c^2} \sum_{\boldsymbol{H}} \varepsilon_{\mu,\lambda}^t(\boldsymbol{k}, \boldsymbol{H}, \omega) A_\lambda(\boldsymbol{k} + \boldsymbol{H}, \omega) = 0;$$

$$(\boldsymbol{k} A(\boldsymbol{k}, \omega)) = 0;$$

$$\varepsilon_{\mu,\lambda}^t(\boldsymbol{k}, \boldsymbol{H}, \omega) = \varepsilon^{(e)}(\boldsymbol{H}, \omega)\delta_{\mu,\lambda} + \chi_{\mu,\lambda}^{(a)}(\boldsymbol{k}, \boldsymbol{H}, \omega);$$

$$\chi_{\mu,\lambda}^{(a)}(\boldsymbol{k}, \boldsymbol{H}, \omega) = \frac{4\pi c^2}{\omega^2 \Omega} f(0) F_{\mu,\lambda}(\boldsymbol{k}, \boldsymbol{H}). \quad (1.56)$$

1.3 Scattering Factors

The elastic scattering of X-ray radiation from the electrons of a crystal contributes mainly to the X-ray susceptibility, which is determined from the scattering amplitude in the formula (1.47):

$$F(\boldsymbol{H}) = \frac{1}{N} \sum_{\alpha,\boldsymbol{\kappa}}^{occ} \int_\Omega g_{\alpha,\boldsymbol{\kappa}} e^{i\boldsymbol{H}\boldsymbol{r}} |\tilde{\psi}_{\alpha,\boldsymbol{\kappa}}(\boldsymbol{r})|^2 d\boldsymbol{r}. \quad (1.57)$$

If the direct experimental measurement of the scattering amplitude could be possible, the expansion (1.47) would permit to unambiguously calculate the function $\rho_e(\boldsymbol{r}) = \sum_{\alpha,\boldsymbol{\kappa}}^{occ} g_{\alpha,\boldsymbol{\kappa}} |\tilde{\psi}_{\alpha,\boldsymbol{\kappa}}(\boldsymbol{r})|^2$, which is the main goal of X-ray structure analysis [29]. However, the measurement of the intensity of the scattered radiation allows to find the modulus $|F(\boldsymbol{H})|$ only. The values $F(\boldsymbol{H})$ are complex in general case, therefore the theoretical calculation of the scattering amplitude is necessary on the basis of preliminary model of the electron density which is defined more exactly by fitting the experimental data by means of iterative retrieval procedure [30].

In the considered here quantum description of the system, the electron density modeling is based on the choice of some approximation for the wave functions $\tilde{\psi}_{\alpha,\boldsymbol{\kappa}}(\boldsymbol{r})$ corresponding to the zone spectrum of the electron in a crystal. In the practical crystallography [29], the commonly used approach is based on the strong coupling approximation [31], which neglects the overlapping of the wave functions of electrons from different atoms. This approximation takes into account the fact that the main contribution to the amplitude is defined by the scattering from the electrons of the internal shells, the characteristic sizes of which are essentially less than the

distance between the atoms. Thus, the overlapping of the electron wave functions from different atoms is exponentially small and the electron density does not depend on the quasi-wave vector $\boldsymbol{\kappa}$:

$$|\tilde{\psi}_{\alpha,\kappa}(\boldsymbol{r})|^2 \rightarrow |\tilde{\psi}_\alpha(\boldsymbol{r})|^2; \quad \frac{1}{N}\sum_\kappa g_{\alpha,\kappa} = g_\alpha, \tag{1.58}$$

where the values g_α define the populations of the electron states in the isolated atoms of the basic cell.

Introducing the variables $\boldsymbol{R}_a$ and ξ_a for the coordinates of the atom nucleus in the basic cell and the set of quantum numbers for the filled electron states in this atom, respectively, and the sum over the index α includes the summation over both $\boldsymbol{R}_a$ and ξ_a, the scattering factor can be represented as follows:

$$F(\boldsymbol{H}) = \sum_{\boldsymbol{R}_a,\xi_a}^{occ} g_{\boldsymbol{R}_a,\xi_a} \int_\Omega e^{i\boldsymbol{H}\boldsymbol{r}} |\varphi_{\xi_a}(\boldsymbol{r} - \boldsymbol{R}_a)|^2 d\boldsymbol{r}, \tag{1.59}$$

where $\varphi_{\xi_a}(\boldsymbol{r} - \boldsymbol{R}_a)$ are the normalized one-electron wave functions corresponding to the isolated atom. Within the considered in this chapter accuracy, the limits of integration in (1.59) can be expanded to the infinite volume. We also introduce the atomic scattering factors (ASF) $F_a(\boldsymbol{H})$:

$$F(\boldsymbol{H}) = \sum_a F_a(\boldsymbol{H})e^{i\boldsymbol{H}\boldsymbol{R}_a}; \quad F_a(\boldsymbol{H}) = \int e^{i\boldsymbol{H}\boldsymbol{r}} \rho_a(\boldsymbol{r})d\boldsymbol{r};$$

$$\rho_a(\boldsymbol{r}) = \sum_{\xi_a}^{occ} g_{\xi_a} |\varphi_{\xi_a}(\boldsymbol{r})|^2. \tag{1.60}$$

which are directly connected with the electron density $\rho_a(\boldsymbol{r})$ of the atom situated in the point $\boldsymbol{R}_a$. They are expressed through the one-electron wave functions $\varphi_{\xi_a}(\boldsymbol{r})$ of the isolated atom and normalized by number of electrons N_a in this atom:

$$F_a(0) = N_a; \quad \sum_a N_a = N_c. \tag{1.61}$$

The accuracy of this approximation is defined by the overlapping integrals I_{ab} for the wave functions of electrons from different atoms, and the correction to the scattering factor (1.59) is defined by the parameter:

$$\Delta F(\boldsymbol{H}) \sim |I_{ab}|; \quad I_{ab} = \int \varphi_{\xi_a}^*(\boldsymbol{r})\varphi_{\xi_b}(\boldsymbol{r} - \boldsymbol{R}_b + \boldsymbol{R}_a)d\boldsymbol{r}, \ b \neq a, \tag{1.62}$$

which is connected with the characteristic width of the one-electron zones [31].

Another important renormalization of the coherent scattering factors is stipulated by the oscillations of the atomic nuclei:

$$\boldsymbol{R}_a = \boldsymbol{R}_a^{(0)} + \boldsymbol{\zeta}_a, \tag{1.63}$$

where the value $\boldsymbol{\zeta}_a$ describes the deviation of nucleus from the equilibrium positions $\boldsymbol{R}_a^{(0)}$. In the quantum solid state theory the parameter $\boldsymbol{\zeta}_a$ is expressed in terms of operators of the phonon creation and annihilation [32].

The observed value of the scattering factor, being the function of the crystal temperature T, is defined by the average on the phonon statistical distribution:

$$\bar{F}(\boldsymbol{H}, T) = Sp \left\{ \hat{\rho}_{ph}(T, \boldsymbol{\zeta}_a) \sum_a F_a(\boldsymbol{H}) e^{i\boldsymbol{H}(\boldsymbol{R}_a^{(0)} + \boldsymbol{\zeta}_a)} \right\}. \tag{1.64}$$

When the phonon spectrum $\omega_p(\boldsymbol{\kappa})$ (p stands for the various branches of the spectrum) is known, the averaging gives an additional factor, called Debye-Waller, in the scattering amplitude of each atom [31]:

$$e^{-W_a(\boldsymbol{H}, T)}.$$

This factor takes into account the decrease of the elastic scattering amplitude due to the probability of the inelastic processes of the phonon excitation in a crystal. If the Boze-Einstein statistics for the phonon distribution is used, this factor can be represented in the form [32]:

$$\bar{F}(\boldsymbol{H}, T) = \sum_a F_a(\boldsymbol{H}) e^{i\boldsymbol{H}\boldsymbol{R}_a^{(0)}} e^{-W_a(\boldsymbol{H}, T)};$$

$$W_a(\boldsymbol{H}, T) = -\frac{\hbar}{M_a} \sum_{\mu, \nu} B_{\mu, \nu} H_\mu H_\nu, \tag{1.65}$$

where M_a is the atomic mass, H_μ, ($\mu = 1, 2, 3$) are the projections of the reciprocal lattice vector on the basic vectors of the elementary cell; the tensor $B_{\mu, \nu}$ does not depend on the atom but does on the integral characteristics of the crystal:

$$B_{\mu, \nu} = \frac{\Omega}{(2\pi)^3} \sum_p \int e_\mu^p e_\nu^p \frac{\coth \beta_p(\boldsymbol{\kappa})}{\omega_p(\boldsymbol{\kappa})} d\boldsymbol{\kappa}; \quad \beta_p = \frac{\hbar \omega_p(\boldsymbol{\kappa})}{k_B T}. \tag{1.66}$$

The values $e_\mu^p(\boldsymbol{\kappa})$ are the projections of the polarization vector for the phonon branch p on the basic vectors of the elementary cell; k_B is the Boltzmann constant.

Another approximation for the scattering factors used in (1.60) is the calculation of ASF for isolated atoms [29]. In this approximation, the expansion of the plane wave [33] is used in formula (1.60):

$$e^{i\boldsymbol{H}\boldsymbol{r}} = \sum_{l'=0}^{\infty}(i)^{l'}(2l'+1)\,j_{l'}(Hr)\,P_{l'}(\cos\widehat{\boldsymbol{H}\boldsymbol{r}}). \qquad (1.67)$$

The expansion is performed over the spherical Bessel functions $j_{l'}(Hr)$ and the Legendre polynomials $P_{l'}(\cos\widehat{\boldsymbol{H}\boldsymbol{r}})$ depending on the angle between the vectors $\boldsymbol{H}$ and $\boldsymbol{r}$. Using this model, the ASF is represented in the following form:

$$F_a(\boldsymbol{H}) = F_{is}(H) + \Delta F_{an}(\boldsymbol{H});$$
$$F_{is}(H) = 4\pi\int\rho(r)\frac{\sin Hr}{H}r\,dr;$$
$$\Delta F_{an}(\boldsymbol{H}) = \int\sum_{\xi_a}^{unoccupied}\sum_{l'=1}^{\infty}g_{\xi_a}|\varphi_{\xi_a}(r,\theta_a,\phi_a)|^2$$
$$\times (i)^{l'}(2l'+1)\,j_{l'}(Hr)\,P_{l'}(\cos\widehat{\boldsymbol{H}\boldsymbol{r}})d\boldsymbol{r}. \qquad (1.68)$$

The completely occupied (closed) electron shells in any atom contributes only to the spherically symmetric part of the electron density $\rho(r)$, and therefore the isotropic part $F_{is}(H)$ of ASF is defined by the scattering from all atomic electrons. In general case, it exceeds essentially the anisotropic contribution ΔF_{an} to ASF which includes the summation over unfilled shells only. Overlapping of the wave functions from different atoms in a basic cell is important only for these electrons [29] and the contribution ΔF_{an} should be taken into account together with the correction $\Delta F(\boldsymbol{H})$ from the expression (1.62).

Thus, the basic part of the X-ray susceptibility consists of the scattering factor which is the sum of ASF for the individual atoms. Each ASF is the Fourier image of the spherically symmetric part of the atomic electron density. Unlike to the expression (1.68), in the standard X-ray applications, the ASF is usually considered as the function of the parameter s related to the transmitted scattering wave vector $\boldsymbol{Q}$ as:

$$\boldsymbol{Q} = \boldsymbol{k}' - \boldsymbol{k}; \quad Q = 4\pi s; \quad s = \frac{\sin\theta}{\lambda}, \qquad (1.69)$$

where λ is the radiation wavelength, and 2θ is the scattering angle. The parameter s is more useful for the practical applications because of with a rather good accuracy it has a variation range in the limited interval for any atom $0 \le s \le 6 \ \mathring{A}^{-1}$. Using these notations, the ASF is written as:

$$F_{is}(H) \rightarrow F_0(s) = \int_0^{\infty}\rho(r)\frac{\sin 4\pi sr}{s}r\,dr. \qquad (1.70)$$

In order to calculate ASF from (1.70), it is necessary to choose the approximation for the electron density $\rho(r)$ in multi-electron atoms (ions). The most fundamental one is the Hartree-Fock approximation for the one-electron wave functions [34], when the wave functions are taken in the form of tables [35]. These tables are not very

convenient for the practical usage, and it is very difficult to use this approach for account of various corrections to ASF as well as for the atomic excited states and variation of the electron configurations for atoms or ions in the external field.

In certain applications, the Thomas-Fermi model for ASF calculation, which implements the electron density as a universal function in the whole range of the nucleus charge Z_a and number of electrons N_a [36, 37], is satisfactory [29]. However, this model does not take into account the shell oscillations of the electron density and its behavior at small and large distances, and as a result does not provide a sufficient accuracy for ASF calculation. Therefore, the analytical interpolation of the Hartree-Fock data directly for the function $F_0(s)$ is mostly used. The typical form of the interpolation is:

$$F_0(s) = \sum_{j=1}^{4} a_j e^{-b_j s^2} + c, \ 0 \leq s \leq 2,$$

with a set of the parameters a_j, b_j, c which are individual for every atom or ion and are chosen by numerical fitting of the Hartree-Fock data in the interval $0 \leq s \leq 2$ [38]. By means of several additional parameters, this interpolation was generalized in work [39] for the interval $2 \leq s \leq 6$. The results of interpolation are represented as the tables for the parameters corresponding to all atoms and some ions [29].

This approach is used in various software packages for calculation of the X-ray susceptibility (for example, [40, 41]). Unfortunately this interpolation does not refer to the wave functions and hence limits the ability of the physical interpretations. Moreover, this method does not allow to calculate the above mentioned corrections to ASF.

Recently a new model for ASF approximation was suggested in the works [42, 43] based on the analytical interpolation of one-electron wave functions by means of the parameter set, which is interpreted as the effective charges of the electron shells. This approach makes possible to calculate numerous characteristics of the isolated atoms (ions) by using the universal analytical formulas, in a similar way as in Thomas-Fermi model. The accuracy of this approach is comparable with the one by the Hartree-Fock approximation. Analytical wave functions of the model describe correctly the shell oscillations and the asymptotic behavior of the electron density and therefore can be used for the calculation of various corrections to ASF.

As mentioned above, the main approximation for quantitative description of multi-electron atoms is based on the Hartree-Fock model. All the electrons move in the field of the self-consistent potential, which is calculated together with the wave functions from the system of integro-differential equations [34]. There exist also other numerical approaches for calculation of the electron structure of atoms, for example, the method of effective potential [44] or suggested recently algorithm for the direct numerical solution of the Schrödinger equation [45]. However, the analytical approximations for the atomic wave functions are still of big interest for many applications [46, 47]. This approximation may be obtained by applying the interpolation for the numerical results with a number of fitting parameters for each orbital [48].

There exist effective analytical models for the atoms, which implement the wave function of each electron as the Coulomb orbital [49] with phenomenological values of effective charges or quantum defects (for example, [50]). These parameter [42] are calculated in the framework of the operator method for solution of the Schrödinger equation and an accurate analytical approximation for ASF is found. However, the parameters of this approximation are individual for each atom or ion and the additional pre-calculated tables have to be used. In the paper [43], the generalization of the shell model was suggested which allows a calculation of the effective charges for any atom or ion by means of the universal formula. This approach results in the effective analytical approximation for ASF and gives the possibility to calculate the above mentioned corrections.

   Here we consider briefly the microscopic basis for this model. The one-electron Hamiltonian of the atom can be written in the following form (the Coulomb system of units with $e = \hbar = m = 1$ [49] is used in this paragraph):

$$\hat{H}_\sigma = \sum_i \left(\frac{\hat{p}_i^2}{2} - \frac{Z - \sigma_i}{r_i} \right). \tag{1.71}$$

   The eigenfunctions and the eigenvalues correspond to the solutions of the Schrödinger equation for the hydrogen-like atom with different screening constants σ_i for every electron. This model was used successfully in the very first papers on the quantum mechanical description of the atom (for example, [51, 52]). The accurate Hartree-Fock functions are shown to be very close to the Coulomb functions [48], however, the model is not widely used as a Thomas-Fermi one for calculation of the atomic characteristics. The reason is the operator (1.71), which is derived not from the initial Hamiltonian of atom and thus no method exists to calculate the empiric parameters σ_i for the atoms or ions. Different solutions for these problems were suggested, for example, in the paper [53] the operator (1.71) was obtained by means of virial theorem and in the paper [42] the effective charges were calculated on the basis of the operator method. However, in both cases the parameters σ_i were calculated for each atom and shell by individual numerical algorithm.

   Unlike the other approaches, the considered here model defines the values Z_{eff} for any electron and any atom (ion) by the universal analytical formula, which depends on the nucleus charge and occupations of the one-electron quantum levels. To prove this statement, we start from the Schrödinger equation for the non-relativistic atom with N-electrons and nucleus charge Z:

$$\hat{H}_A \Psi_\Lambda(X) = E_\Lambda \Psi_\Lambda(X);$$
$$\hat{H}_A = \sum_{i=1}^{N} (\frac{\hat{p}_i^2}{2} - \frac{Z}{r_i}) + \sum_{j>i}^{N} \sum_{i=1}^{N-1} \frac{Z}{|\boldsymbol{r}_j - \boldsymbol{r}_i|}. \tag{1.72}$$

Here the state vector depends on $4N$ variables, which are the electron coordinates and spins $X = (x_1, x_2, \ldots x_N)$; $x_i = (\boldsymbol{r}_i, \boldsymbol{s}_i)$, and the quantum numbers $\Lambda = (\lambda_1, \lambda_2, \ldots \lambda_N)$; $\lambda_i = (n_i, l_i, m_i, s_i)$.

The general scheme of the operator method [54, 55] is used for the solution of the Eq. (1.72), i.e. as a first step the orthonormalized set of the model functions $\psi_\Lambda(X, \Omega_\Lambda)$ depending on the variational parameters Ω_Λ has to be chosen. The different sets $\psi_\Lambda(X, \Omega_\Lambda)$ should be used for the different quantum numbers Λ [54, 55]. The corresponding to Λ wave function to be found is expanded over the model functions $\psi_\Lambda(X, \Omega_\Lambda)$:

$$\Psi_\Lambda(X) = \psi_\Lambda(X, \Omega_\Lambda) + \sum_{\Lambda' \neq \Lambda} C_{\Lambda', \Lambda} \psi_{\Lambda'}(X, \Omega_\Lambda). \tag{1.73}$$

The energy of this state and the coefficients of the expansion (1.73) are derived from the system of nonlinear algebraic equations including matrix elements of the initial Hamiltonian:

$$E_\Lambda = H_{\Lambda\Lambda} + \sum_{\Lambda' \neq \Lambda} H_{\Lambda\Lambda'} C_{\Lambda', \Lambda};$$

$$H_{\Lambda'\Lambda_1} = < \psi_{\Lambda'}(X, \Omega_\Lambda) | \hat{H}_\Lambda | \psi_{\Lambda_1}(X, \Omega_\Lambda) >;$$

$$C_{\Lambda', \Lambda} = -[H_{\Lambda'\Lambda'} - H_{\Lambda\Lambda}]^{-1} [H_{\Lambda'\Lambda} + \sum_{\Lambda_1 \neq \Lambda' \neq \Lambda} H_{\Lambda'\Lambda_1} C_{\Lambda_1, \Lambda}]. \tag{1.74}$$

In according with the reference [54, 55], the successive iterations of the Eq. (1.74) are converged even for the arbitrary choice of the zero approximation functions $\psi_\Lambda(X)$. Therefore, these functions are chosen here in the form of a simple product of the one-particle Coulomb orbitals [48]:

$$\psi_\Lambda(X, \Omega_\Lambda) = \prod_{\lambda_i}^{\lambda_{max}} \phi_{\lambda_i}(Z_{\lambda_i}, x_i);$$

$$\phi_{\lambda_i}(Z_{\lambda_i}, x_i) = C_{n,l,m} R_{nl}(r_i, Z_{n,l}) Y_{lm}(\theta_i, \varphi_i) \chi_s;$$

$$\lambda_i = (n, l, m, s); \quad \sum_{\lambda_i}^{\lambda_{max}} 1 = N, \tag{1.75}$$

where $R_{nl}(r_i, Z_{n,l})$ are the hydrogen-like radial wave functions corresponding to the charge $Z_{n,l}$; $Y_{lm}(\theta_i, \varphi_i)$ are the spherical harmonics and χ_s are the spin functions of the electron, $C_{n,l,m}$ is normalization coefficient.

Similarly to the Thomas-Fermi model, such a choice of the function means that the exchange interaction is neglected but the Pauli principle is taken into account because of the quantum numbers of all electrons are different. Parameter λ_{max} is defined by the number N of the electrons and $N \neq Z$ for ions. In accordance

with [56], this choice of the zeroth order wave functions leads to a good accuracy for calculation of the atomic characteristics and permits to take analytically into a account the correlation and exchange corrections.

We choose the quantum numbers λ_i in accordance with an order of occupations of one-electron states, and the increasing sequence of the integral numbers ($\lambda_i \rightarrow i$; $\lambda_{max} \rightarrow i_{max}$) is associated with this sequence. Then the zeroth approximation for energy depends on the set of variational parameters $\hat{O}\{Z_i\}$ and is defined by the formula:

$$E_\Lambda^{(0)}(\{Z_i\}) = \sum_{i=1}^{i_{max}} < \phi_{\lambda_i}(Z_i, x)|[\frac{\hat{p}^2}{2} - \frac{Z}{r}]|\phi_{\lambda_i}(Z_i, x) >$$

$$+ \sum_{i=1}^{i_{max}} \sum_{j>i}^{i_{max}} < \phi_{\lambda_i}(Z_i, x_1), \phi_{\lambda_j}(Z_j, x_2)|\frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}|\phi_{\lambda_i}(Z_i, x_1), \phi_{\lambda_j}(Z_j, x_2)>.$$

$$(1.76)$$

This expression was used in the paper [54, 55] for the numerical calculation of the effective charges in the zeroth approximation of the operator method. It is possible to find analytically the approximate variational solution for these values, too. The problem only is a right choice of a sufficiently good approximation for the matrix elements of two-particle operator. Here, the following fact is used: for the hydrogen-like orbits their average radius is defined mainly by the principal quantum number and depends weakly on other quantum numbers, and thus the following estimation gives a very good accuracy:

$$< \phi_{n_1,l_1,m_1,s_1}|r|\phi_{n_1,l_1,m_1,s_1} >\ll< \phi_{n_2,l_2,m_2,s_2}|r|\phi_{n_2,l_2,m_2,s_2} >, \text{ if } n_1 < n_2;$$
$$< \phi_{n_1,l_1,m_1,s_1}|r|\phi_{n_1,l_1,m_1,s_1} >\approx< \phi_{n_2,l_2,m_2,s_2}|r|\phi_{n_2,l_2,m_2,s_2} >, \text{ if } n_1 = n_2. \quad (1.77)$$

This estimate introduces the following one-particle approximation for the matrix elements of two-particle operator:

$$V_{\lambda_i,\lambda_j} \equiv< \phi_{\lambda_i}, \phi_{\lambda_j}|\frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}|\phi_{\lambda_i}, \phi_{\lambda_j} >\approx< \phi_{\lambda_j}|\frac{1}{r_2}|\phi_{\lambda_j} >, \text{ if } n_i < n_j; \quad (1.78)$$

$$V_{\lambda_i,\lambda_j} \approx \frac{1}{4}[< \phi_{\lambda_i}|\frac{1}{r_1}|\phi_{\lambda_i} > + < \phi_{\lambda_j}|\frac{1}{r_2}|\phi_{\lambda_j} >], \text{ if } n_i = n_j. \quad (1.79)$$

Formula (1.79) has a simple physical interpretation: for each electron in the atomic layer with the principal number n_j all the electrons from internal layers with $n_j > n_i$ give the identical (equal to unity) contributions to the nucleus charge screening that corresponds to the result of the classical electrodynamics for spherically symmetric charge distribution. At the same time, each additional electron in the same layer (with $n_i = n_j$) contributes to the screening with the value equals to 1/2. After the symmetrization on the coordinates of the electrons in the layer, the coefficient

in (1.79) becomes equal to $1/4$. In this electrostatic approximation, the Hamiltonian of the zeroth order takes one-particle form. The approximation (1.78)–(1.79) for the matrix elements can be essentially improved if the dependence of the screening charge of every electron on its orbital momentum is also taken into account. This dependence is found in a general form with some undefined numerical coefficients if the symmetry of the group $SO(4, 2)$ for atomic Hamiltonian is used [57]. Then the following approximation for the diagonal matrix elements of the two-particle operator can be used:

$$V^A_{\lambda_i,\lambda_j} = \left(1 - \frac{\alpha}{2(2l_i+1)} - \beta\frac{l_i(l_i+1)}{n_j^2}\right) < \phi_{\lambda_j}|\frac{1}{r_2}|\phi_{\lambda_j} >, \; n_i < n_j; \quad (1.80)$$

$$V^A_{\lambda_i,\lambda_j} = \frac{5}{16}\left[\left(1 + \frac{1}{6} + \beta\frac{l_i(l_i+1)}{n_i^2}\right) < \phi_{\lambda_i}|\frac{1}{r_1}|\phi_{\lambda_i} > \right.$$
$$\left. + \left(1 + \frac{1}{6} + \beta\frac{l_j(l_j+1)}{n_j^2}\right) < \phi_{\lambda_j}|\frac{1}{r_2}|\phi_{\lambda_j} >\right], \; n_i = n_j, \quad (1.81)$$

with still undefined parameters α and β, which will be discussed below.

Besides, a small modification of the screening coefficient $1/4 \to 5/16$ for the electrons in the same layer corresponds to well known variational solution for the effective charge in two-electron atom [49]. In the result, the following expression defines the energy of the state with the given set of the quantum numbers in zeroth approximation of the operator method:

$$E^{(0)}(Z, N)_\Lambda \approx \sum_\lambda g_{nlms} < R_{n,l}(Z_{n,l}, r)|\left[\frac{\hat{p}^2}{2} - \frac{Z_{n,l}}{r}\right]|R_{n,l}(Z_{n,l}, r) >=$$

$$-\sum_\lambda g_{nlms}\frac{Z_{n,l}^2}{2n^2};$$

$$Z_{n,l} = Z - \sum_{n_1=1}^{n-1}\sum_{l_1=0}^{n_1-1}\sum_{m_1=-l}^{l}\sum_{s_1=\pm1} g_{n_1l_1m_1s_1}\varkappa_{n,l_1}$$

$$-\frac{5}{16}\left[\sum_{l_1=0}^{n-1}\sum_{m_1=-l}^{l}\sum_{s_1=\pm1} g_{nl_1m_1s_1}\varkappa'_{n,l_1} - \varkappa'_{n,l}\right];$$

$$\varkappa_{n,l} = 1 - \frac{\alpha}{2(2l+1)} - \beta\frac{l(l+1)}{n^2}; \; \varkappa'_{n,l} = 1 + \frac{1}{6} + \beta\frac{l(l+1)}{n^2},$$

$$\sum_\lambda \equiv \sum_{n=1}^{n_{max}}\sum_{l=0}^{n-1}\sum_{m=-l}^{l}\sum_{s=\pm1} \quad (1.82)$$

where the occupation numbers $g_{nlms} = 1$ for the filled and $g_{nlms} = 0$ for empty one-electron states. These numbers are normalized by the condition:

$$\sum_{n=1}^{n_{max}} \sum_{l=0}^{l_{max}} \sum_{m=-l}^{l} \sum_{s=\pm 1} g_{nlms} = N. \tag{1.83}$$

In general case, the nonzero values g_{nlms} are defined by the occupations of one-electron states for the considered atom or ion. Parameter β is calculated uniquely by satisfying the formula (1.82) to the asymptotic expression for the energy of neutral atom in the limit $Z \to \infty$ (for example, [58, 59]):

$$E = -0,768745 Z^{7/3}. \tag{1.84}$$

In order to find this asymptotic expression, the sums over n, l in formulas (1.82) and (1.83) have to be replaced by the integrals and the terms with the maximal degree of Z have to be extracted:

$$n_{max} \approx \left(\frac{3}{2}Z\right)^{1/3}; \ E^{(0)}(Z, Z) \approx \frac{9}{28} 12^{2/3} Z^{7/3} \left(1 + \frac{1}{10}\beta + \frac{1}{50}\beta^2\right). \tag{1.85}$$

By comparing the formula (1.85) with the expression (1.84) the value $\beta \approx 0,417472$ is calculated. Thus, the only undefined parameter not depending on Z in the Hamiltonian (1.73) is the value α, which makes the correction of the screening value due to the presence of equivalent electrons. The mean squared radius of atoms $r_A = \sqrt{<r^2>}$, being an important for many applications [34], proves to be most sensitive to the value α parameter. In the considered model the parameter α was chosen provided the function $r_A(Z)$ is the best approximation for the same function calculated on the basis of Hartree-Fock model [60]. Finally, the value found is $\alpha \approx 0,576$.

Thus, the wave functions (1.75) with the effective charges calculated from the analytical formulas (1.82) make it possible to estimate in a simple way and with a good accuracy the numerous characteristics of atoms and ions with arbitrary Z and N. Below the comparison is given for some physical values calculated using the analytical formulas with the numerical results of the Hartree-Fock [60] and Thomas-Fermi [58, 59] models.

Figure 1.2 shows the dependence of the total energy of the neutral atoms on the nucleus charge and Fig. 1.3 shows the functions $r_A(Z)$ for all mentioned above models. The relative deviation of the analytical results from the Hartree-Fock model is not exceeding 3 %.

Figures 1.4 and 1.5 show the radial distributions of the electron density for several atoms. The analytical approach interpolates well the Hartree-Fock numerical data in the entire range of the radial coordinate and shows the correct asymptotic behavior of the density at small and large distances.

Fig. 1.2 The total energy of neutral atoms as the function of nucleus charge *solid line* corresponds to operator method and *dashed line* to Hartree-Fock results

$E_{tot}/Z^{(7/3)}$
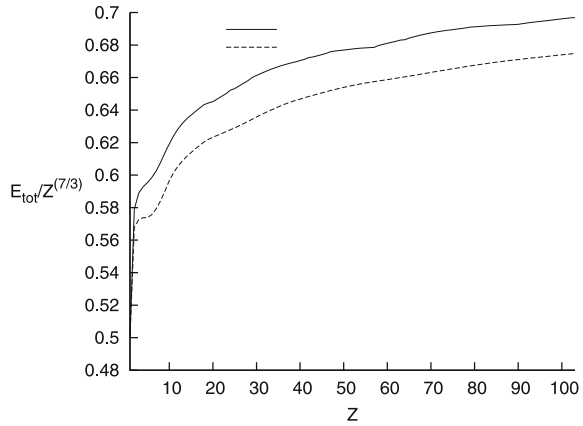
Fig. 1.3 Mean squared radius of neutral atoms as the function of nucleus charge: *solid line* correspond to operator method and *dashed line* to Hartree-Fock results
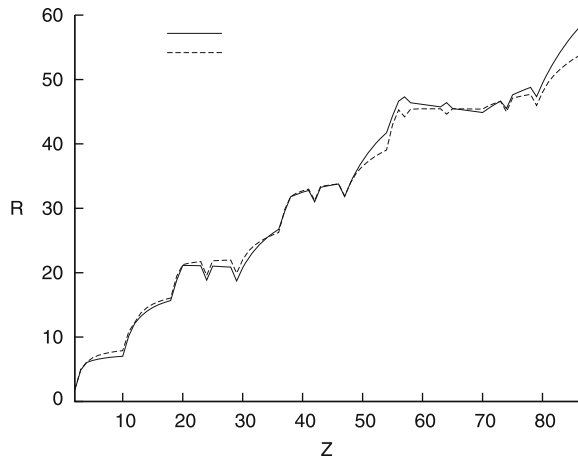
Figures 1.6 and 1.7 refer to ions of He and Li series, respectively, and demonstrate the high precision of the ionization potentials $IP(Z, N) = E_{tot}(Z, N) - E_{tot}(Z, (N - 1))$ calculated in the framework of the considered model.

The considered interpolation for the wave functions delivers the analytical expressions for the isotropic part of ASF (1.70) for any ion or atom. In the one-electron approximation the isotropic electron density is defined by the population numbers g_{nl} of the atom or ion shells and the normalized radial wave functions $R_{nl}(Z_{nl}, r/a_B)$ corresponding to the Coulomb orbitals with the effective charges $Z_{nl}, a_B = 0.529177A$ is the Bohr radius:

$$\rho(r) = \frac{1}{4\pi} \sum_{nl} g_{nl} |R_{nl}(Z_{nl}, r/a_B)|^2. \tag{1.86}$$

The integral (1.70) from this equation can be calculated analytically in the following form [61]:

Fig. 1.4 Radial distributions
of the electron densities for
Bi atom: *solid line* is oper-
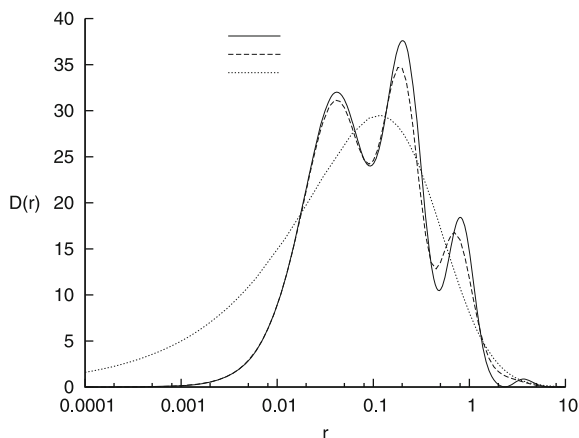ator method; *dashed line*
is Hartree-Fock model and
dotted line is Thomas-Fermi
model
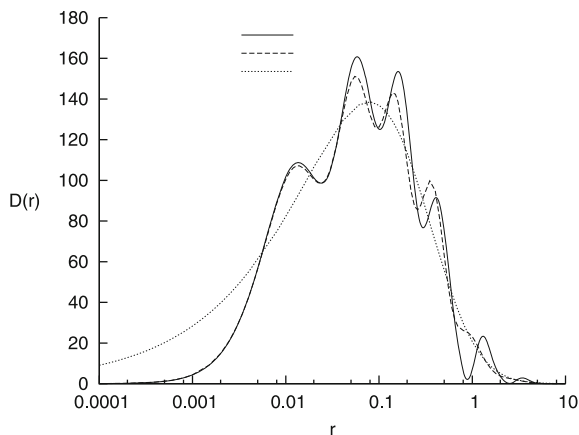
Fig. 1.5 Radial distributions
of the electron densities for
Fe atom: *solid line* is oper-
ator method, *dashed line*
is Hartree-Fock model and
dotted line is Thomas-Fermi
model

$$F_0(s) = \sum_{nl} g_{nl} F_{nl}(\xi_{nl}, q); \quad \xi_{nl} = \frac{2Z_{nl}}{n}, \ q = 4\pi s a_B, \qquad (1.87)$$

where the partial ASF values $F_{nl}(\xi_{nl}, q)$ are defined by the formula:

$$F_{nl}(\xi_{nl}, q) = -\xi_{nl}^{2l+3} \frac{(n-l-1)!(n+l)!}{2n}$$

$$\times \sum_{k=0}^{n-l-1} \sum_{k=0}^{n-l-1} \frac{\xi_{nl}^{k+m}}{(2l+k+1)!(2l+m+1)!k!m!} \frac{d^{2l+1+k+m}}{d\xi^{2l+1+k+m}} \frac{1}{\xi_{nl}^2 + q^2}. \quad (1.88)$$

The explicit formulas for ASF of atoms from the periodical system is listed in the
paper [42], for example, for atoms of Ne and Ca:

Fig. 1.6 Absolute values
of the ionization potentials
for He series: *solid line* is
operator method; *stars* are
Hartree-Fock results
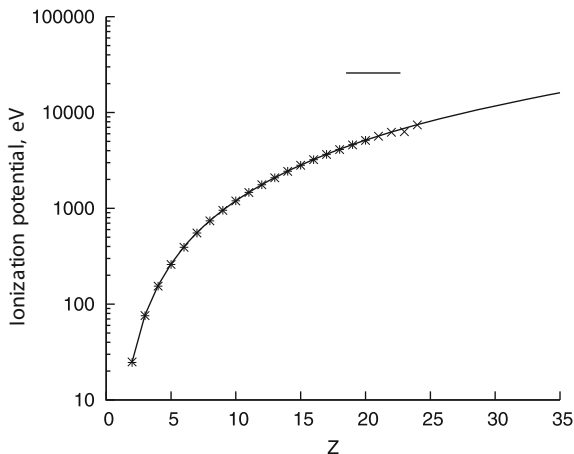
Fig. 1.7 Absolute values
of the ionization potentials
for Li series: *solid line* is
operator method; *stars* are
Hartree-Fock results
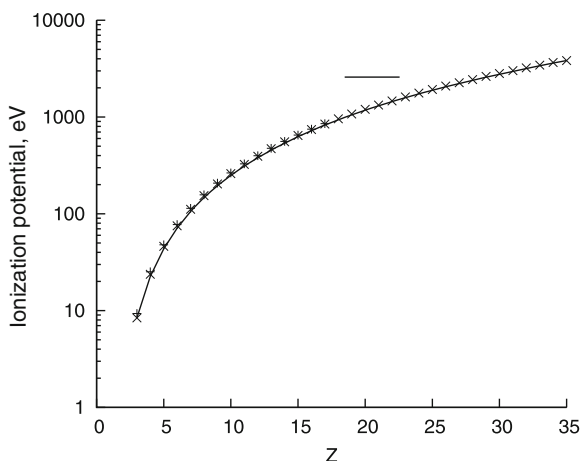
$$F_{10}(\xi_{10}, q) = \frac{16Z_{10}^4}{(4Z_{10}^2 + q^2)^2};$$

$$F_{20}(\xi_{20}, q) = \frac{Z_{20}^4(Z_{20}^4 - 3q^2 Z_{20}^2 + 2q^2)}{(Z_{20}^2 + q^2)^4}. \tag{1.89}$$

The graphical dependence of ASF calculated from formula (1.87) *vs* parameter
$s = \sin\theta/\lambda$ is shown in Fig. 1.8 for the atoms of Si, Ba, Cu and Mn^{3+} ion. These
simulations approximate the Hartree-Fock numerical values with high accuracy [29].
The formulas above can also be applied for the ions with core in the internal shell,
which is important in the case of the interaction of the femto-second pulses from
X-ray free electron laser (XFEL) with the matter [4]. Figure 1.9 demonstrates a good
coincidence of the analytical results with the numerical ones [62].

Fig. 1.8 Comparison of analytical (*lines*) and numerical (*dots*) results for ASF of Si, Ba, Cu atoms and Mn^{3+} ion
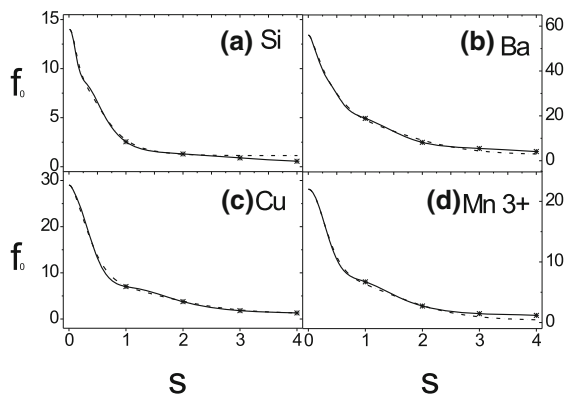
Fig. 1.9 Comparison of analytical (*solid line*) and numerical (*dotted line*) results for calculation of ASF for internal shells of ions C with core hole
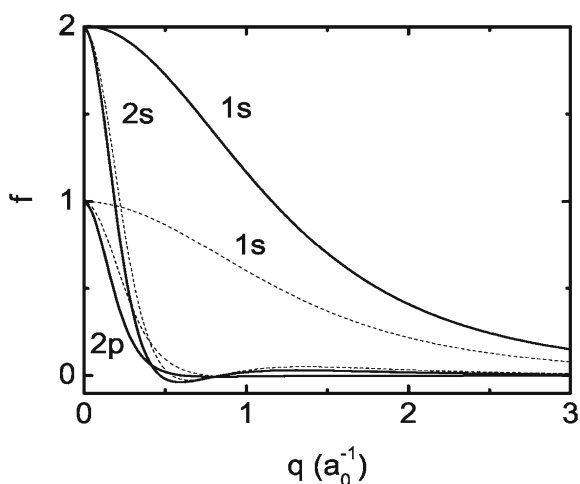
The one-electron functions (1.75) accounts for the corrections (1.62) to the scattering factor of the basic cell because of the overlap of the wave functions of electrons in the external shells from the different atoms. The following procedure for the calculation of this correction in the crystals with the diamond-type basic cell (C; Si; Ge) can be considered [42]. In order to take into account the influence of the neighboring atoms, the states with the lowest energies should be found using the linear combinations of the wave functions of 4 electrons from the external shell ($n0$; $n1$) from each atom. As a result, the lowest levels are found to correspond to the collective states, where all electrons have parallel spins and are described by the following set of the functions [29]:

$$\psi_1 = \frac{1}{2}[R_{n0}Y_{00} + R_{n1}(-\sqrt{2}Y_{11} + Y_{10})];$$

$$\psi_2 = \frac{1}{2}[R_{n0}Y_{00} + Y_{11}(\sqrt{2}Y_{11} - Y_{10})];$$

$$\psi_3 = \frac{1}{2}[R_{n0}Y_{00} + R_{n1}(-\sqrt{2}Y_{11} - Y_{10})];$$

$$\psi_4 = \frac{1}{2}[R_{n0}Y_{00} + R_{n1}(\sqrt{2}Y_{11} + Y_{10})], \tag{1.90}$$

where Y_{lm} are the spherical harmonics and R_{nl} are the radial wave functions of the external electrons corresponding to the isolated atoms. Thus, the external layer gives the following contribution to the electron density:

$$\rho_n(r) = \sum_{j=1}^{4} |\psi_j|^2 = \frac{1}{4\pi}[R_{n0}^2 + 3|R_{n1}|^2],$$

that differs from the analogous value in the isolated atom:

$$\rho_n^{(0)} = \frac{1}{2\pi}[R_{n0}^2 + R_{n1}^2].$$

Figure 1.10 shows the change of ASF of each atom due to the influence of other atoms in the elementary cell:

$$\Delta F_0(s) = F_{n1}(\xi_{n1}, q) - F_{n0}(\xi_{n0}, q), \tag{1.91}$$

with $n = 2$ for C, $n = 3$ for Si, $n = 4$ for Ge. In spite of rather small correction to the absolute value of ASF, it could be essential for the analysis of the forbidden reflections [63].

The direct approximation for the wave function can also be important for the analysis of the changes in the electron density due to the effect of external or inter-crystal fields [42]. For instance, the additional Hamiltonian of the spin-orbit interaction for atoms (C; Si; Ge) in the ground state under the action of the magnetic field Ξ directed along z axis is defined as [49]:

Fig. 1.10 Correction to ASF due to the influence of the neighboring atoms (C - *solid line*, Si - *dashed line*, Ge - *dotted line*)
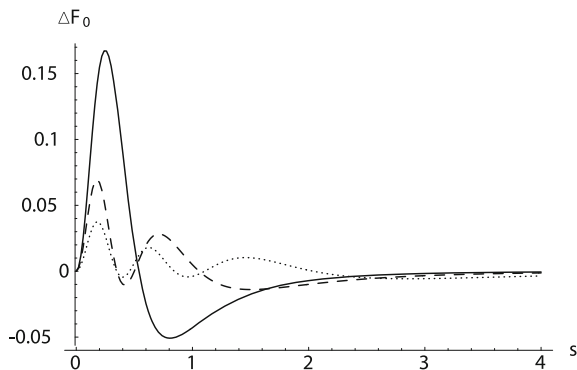
$$\delta\hat{H} = A(\hat{\boldsymbol{L}}\hat{\boldsymbol{S}}) + \mu_B(\hat{L}_z + 2\hat{S}_z)\mathcal{E}, \tag{1.92}$$

where $A > 0$ is the constant of the spin-orbit interaction for two external p-electrons with the total orbital $\hat{\boldsymbol{L}}$ and spin $\hat{\boldsymbol{S}}$ momenta, μ_B is the Bohr magneton. This operator does not change the effective charges of the radial wave functions but effects on the angular distribution of the electron density. Eigenfunctions of the operator (1.92) are defined by its diagonalization with the eigenfunctions of the operators $\hat{\boldsymbol{L}}, \hat{\boldsymbol{S}}$ - $|M_L, M_S>$. Then the ground state follows from the following linear combination:

$$|\varPhi_0>= c_1|1, -1> +c_2|0, 0> +c_3|-1, 1>;$$
$$c_1 = \frac{1}{\sqrt{3}}\left(1 + \xi - \frac{2}{9}\xi^2\right), \ c_2 = \frac{1}{\sqrt{3}}\left(1 - \frac{5}{9}\xi^2\right),$$
$$c_3 = -\frac{1}{\sqrt{3}}\left(1 - \xi - \frac{2}{9}\xi^2\right); \quad \xi = \frac{\mu_B\mathcal{E}}{A}. \tag{1.93}$$

These wave functions account for the anisotropic part in the electron density and for the anisotropic contribution (1.68) to ASF which is proportional to the second Legendre polynomial considered as the function of the angle θ between z axis and vector $\boldsymbol{H}$:

$$\Delta F_{an}(\boldsymbol{H}) = -\frac{10}{9}\xi^2 P_2(\cos\theta) f_m(s);$$
$$f_m(s) = \int_0^\infty r^2 R_{nl}^2(r)\left(\frac{\pi}{2qr}\right)^{1/2} J_{5/2}(qr)dr; \ q = 4\pi a_B s, \tag{1.94}$$

where $J_{5/2}(qr)$ is the Bessel function.

Figure 1.11 shows the functions $f_m(s)$ for atoms Si and Ge. When the external magnetic field is strong, the anisotropic part of ASF is comparable with the anomalous dispersion corrections and may bring the important information on the inter-crystalline fields.

Fig. 1.11 ASF correction in the external magnetic field
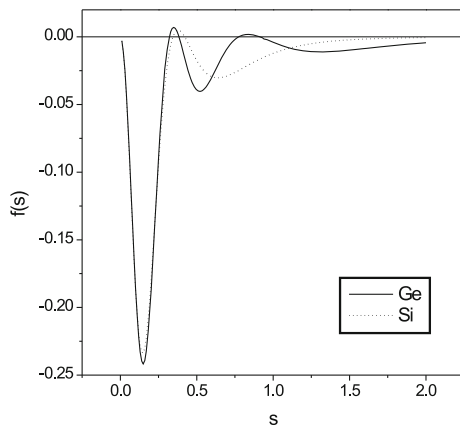
1.4 Numerical Calculation of Debye-Waller Factor

Debye-Waller factor (DWF), see Eq. (1.66), gives an essential contribution to the
X-ray susceptibility. Most of software packages [40, 41] calculate DWF on the basis
of the Debye model for the phonon spectrum [31] and the phenomenological values
of the Debye temperature Θ_D of the crystals. However, the experimental value of
Θ_D is known for relatively few crystals [29]. When the experimental value of Θ_D
is unknown, the average value of the Debye temperatures of the crystals for all
atoms in the basic cell is used without a sufficient theoretical argumentation. Thus,
the development of a method for the evaluation of Θ_D for arbitrary crystals is an
actual problem. Moreover, some diffraction experiments require calculations of the
DWF taking into account the anisotropy factors and different branches of the phonon
spectrum. The experimental density of the phonon states [64] are known for only a
few materials; the situation for most crystalline structures however is unclear. Here
we consider the method for simulation of the force matrix for an arbitrary crystal,
which realizes both the evaluation of Θ_D and the microscopic calculation of DWF
with good accuracy [42].

In the case, when DWF is characterized by a single parameter Θ_D, the harmonic
oscillations of atoms in a crystal cell result in attenuation of the elastic scattering
amplitudes by the value of DWF. In the isotropic approximation, this factor for the
atom with the index p in the crystallographic unit cell is defined by the formula:

$$e^{-2W_p} = e^{-B_p(T)s^2}. \tag{1.95}$$

Here $s = \frac{\sin\theta_B}{\lambda}$ and the main contribution to the temperature coefficient $B(T)$ is
supposed to be introduced by the acoustic branch of the phonon spectrum, so the
result can be presented in the following way [32]:

$$W_p(T) = \frac{3h^2}{2M_p\kappa_B\Theta} \int_0^1 x \coth\left(\frac{x\Theta}{2T}\right) dx, \tag{1.96}$$

where κ_B is the Boltzmann constant and the Debye temperature is defined by the
expression:

$$\Theta_D = \frac{\hbar u k_D}{\kappa_B}; \qquad k_D = \left(\frac{6\pi^2}{\Omega_0}\right)^{1/3}. \tag{1.97}$$

This is a result of linear interpolation of the dispersion law for acoustic phonons
$\omega(k) \simeq uk$ within the Debye sphere with the radius k_D, which depends on the
volume of the unit cell of the crystal Ω_0. Thus, in the considered approximation, the
value Θ_D or its related sound velocity u is the only parameter influencing DWF.

From the microscopical point of view, the parameter u should be found from the
dispersion equation for the phonon frequencies defined by the harmonic force matrix
of the crystal. Because the approximation of pairwise interactions is satisfactory for
the real density of atoms in crystals [27], a realistic two-particle potential [65] can be

used for the construction of the force matrix. The distance between two neighboring atoms in the crystal cell is different from the equilibrium distance in the molecule consisting of the same atoms. However, according to the researches in chemical crystallography, this difference is small due to the fact that the atomic binding in the crystals is mainly defined by the same external electron shells as in the molecules [66]. Thus, since a model potential approximates the electron term of two bound atoms in some neighborhood of the equilibrium distance R_0, it can also be used for finding the force matrix elements at distances corresponding to the atomic positions within the unit cell of a real crystal. In the approximation of pairwise interaction, the element of the force matrix is defined by the following formula [27]:

$$D_{ij}^{pq} = \kappa_{pq} \left[\frac{(R_{pq} - R_{0pq})}{R_{pq}} \delta_{ij} + \frac{R_{0pq}}{R_{pq}} n_i^{pq} n_j^{pq} \right]; \qquad \boldsymbol{n}^{pq} = \frac{\boldsymbol{R}_{pq}}{R_{pq}}. \qquad (1.98)$$

Here upper indices in the force matrix enumerate the different atoms in the cell and lower ones correspond to the atomic shifts from their equilibrium positions in Cartesian coordinates; κ_{pq} and R_{0pq} are the harmonic force constants and the equilibrium distance in the molecule corresponding to the atom pair with indexes (pq), respectively; vector $\boldsymbol{R}_{pq}$ is the real distance between these atoms in the crystal cell.

   In this section, we use the Debye interpolation for the phonon spectrum and neglect the anisotropy effects. This means that the standard dispersion equation for the acoustical phonon branch [27] should be averaged over all directions in the space of phonon wave vectors as well as over different directions in the unit cell of the direct space. If the approximation of the nearest neighbors is used for the force matrix of the crystal, the average sound velocity can be estimated by the following simple formula:

$$u = \frac{2\pi c a_0 \bar{\nu}}{3\sqrt{2}}; \qquad a_0 = (\Omega_0)^{1/3}; \qquad \bar{\nu} = \frac{1}{\sigma} \sum_{p=1}^{\sigma} \nu_{A_p B_p}. \qquad (1.99)$$

Here a_0 represents the average size of the unit cell; the summation is over all different pairs of nearest neighbor atoms in the cell, where σ is a number of such a pair; $\nu_{A_p B_p}$ is the oscillation frequency in cm^{-1} for a pair of atoms with the index p; the numerical coefficient $1/3$ in the formula (1.99) is due to averaging over all the directions. Substituting the expression (1.99) into the definition of Debye temperature (1.97), a universal correlation between Θ_D and $\bar{\nu}$ can be found:

$$\Theta_D = \frac{hc}{3\sqrt{2}\kappa_B} (6\pi^2)^{1/3} \bar{\nu}. \qquad (1.100)$$

The formula (1.100) corresponds to the known interpretation of the Debye temperature of the crystal; its value is proportional to the characteristic phonon frequency. In a standard unit system the numerical coefficient in the formula (1.100) is close to unity:

$$\Theta_D[K] \simeq \bar{\nu}[\text{cm}^{-1}]. \tag{1.101}$$

If a recipe for the calculation of the harmonic frequency for any given pair of atoms is known, then this formula can be used for a simple evaluation of the Debye temperature of an arbitrary crystal. The elastic constant κ_A describing the interaction between the identical atoms in two-atomic homo-nuclear molecules and the harmonic approximation for interatomic potential $V(R)$ are expressed as [67]:

$$\kappa_A = (2\pi\nu_A c)^2 M_A,$$
$$V_A(R) \simeq -E_0 + \frac{1}{2}\kappa_A(R - R_0)^2. \tag{1.102}$$

Here the interatomic potential $V(R)$ corresponds to the ground electron term with the binding energy E_0 at equilibrium distance R_0; ν_A is the principal oscillation frequency of the homo-nuclear molecule in cm^{-1} composed from two identical atoms with the mass M_A; c is the velocity of light. Theoretical calculations of the constant κ_A ab initio with a spectroscopic accuracy for homo- and hetero-nuclear molecules requires some complicated quantum-mechanical calculations of electron terms [68]. However, so-called realistic potentials for atom-atom interaction like the Lennard-Jones potential, can provide a sufficient accuracy for statistically averaged macroscopic characteristics of molecular gases [65]:

$$V_A(R) = \frac{\beta_A}{R^{12}} - \frac{\alpha_A}{R^6}. \tag{1.103}$$

The parameter β_A corresponds to the repulsive part of the potential at small distances, and the constant α_A is proportional to the product of squared dipole moments of interacting atoms and simulates the Van der Waals attraction at large distances [49]. The Lennard-Jones potential does not provide the detailed description of electron terms in the entire range of the interatomic distance [68], and therefore it can not be used for precise evaluation of the dissociation energy of the molecule. Nevertheless, it describes quite well the behavior of real potentials near their minima [65], which are of special interest for us in the scope of the harmonic approximation. The above mentioned characteristics of the harmonic potential are expressed through the constants α_A and β_A as

$$R_{0A} = \left[\frac{2\beta_A}{\alpha_A}\right]^{1/6}; \qquad E_{0A} = -\frac{\alpha_A^2}{4\beta_A}; \qquad \kappa_A = 36\alpha_A\left[\frac{\alpha_A}{2\beta_A}\right]^{4/3}. \tag{1.104}$$

Actually, the temperature factor in structure amplitudes is the result of statistic averaging and therefore the fine details of the potential are not essential. With analogous accuracy the values α_A and β_A can be used for a two-atom potential in order to evaluate the Debye temperature. However, the experimental data received both from the cross-sections and from the oscillation spectra are known for a relatively small set of different atomic pairs. Therefore the general recipe for the estimation of α_{AB} and

β_{AB} for arbitrary interacting atoms A and B must be provided. Such a general recipe can be derived from the scaling dependence of the interaction potential established in the framework of statistic theory of atom [69]. A repulsive part of the potential for two different atoms (ions) has been calculated as a geometric average of interaction potentials $V_A^{(rep)}(R)$ and $V_B^{(rep)}(R)$ taken from the independent pairs AA and BB of identical atoms:

$$V_{AB}^{(rep)}(R) = \sqrt{V_A^{(rep)}(R)V_B^{(rep)}(R)}. \qquad (1.105)$$

These correlations fitted well the experimental data in a large range of interatomic distances [69].

Considering the Eq. (1.105) independently for large and small interatomic distances, the values α_{AB}, β_{AB} for interactions between different atoms can be evaluated by means of the simple formulas based on the same averages:

$$\beta_{AB} \simeq \sqrt{\beta_A \beta_B}; \quad \alpha_{AB} \simeq \sqrt{\alpha_A \alpha_B}. \qquad (1.106)$$

Substituting the Eqs. (1.106) into the formulas (1.103) and (1.104), we deduce the combinative rules for the evaluation of potential parameters for hetero-nuclear diatomic molecules:

$$R_{0AB} = \sqrt{R_{0A}R_{0B}}; \qquad \nu_{AB} = \left[\nu_A \nu_B \frac{M_A + M_B}{2\sqrt{M_A M_B}} \right]^{1/2};$$

$$E_{0AB} = \sqrt{E_{0A}E_{0B}}; \qquad \kappa_{AB} = (2\pi c \nu_{AB})^2 \mu_{AB}; \quad \mu_{AB} = \frac{M_A M_B}{M_A + M_B}, \quad (1.107)$$

using the experimental data for the homo-nuclear molecules. Here ν_A and ν_B are the principal oscillation frequencies of the molecules A_2 and B_2; ν_{AB} corresponds to the molecule AB and the difference in the reduced masses for homo- and hetero-nuclear molecules is taken into account.

Certainly, these combinative rules are semi-phenomenological due to the choice of the model potential and the lack of a sufficient theoretical ground for the expression (1.105). The effectiveness and accuracy of these relations can be investigated by applying them to diatomic molecules with known parameters. Table 1.1 lists all the necessary parameters for diatomic homo-nuclear molecules from the reference book [67].

The comparison of the calculated binding energy E_0 presented in the table with the energy of dissociation [67] is rather formal in our context. This is because the Lennard-Jones potential is not a good model for the electron term for all interatomic distances. In fact only the parameters ν and R_0 are important for the presented model since they exactly define the behavior of the potential in the harmonic approximation. The parameters for molecules, marked by the symbol (*), are absent in [67] and we calculated these values by means of the combinative rules (1.105) based on experimental data for materials containing these atoms along with other ones.

Table 1.1 Parameters of diatomic homo-nuclear molecules [67]

Atom	ν, cm^{-1}	E_0, eV	R_0, Å
H	4401	4.48	0.74
He	1861	2.36	1.04
Be*	1343	13.32	1.39
B	1051	3.02	1.59
C	1854	6.21	1.24
N	2358	9.76	1.10
O	1580	5.12	1.21
F	916	1.60	1.41
Ne	14	0.00	3.10
Na	159	0.72	3.08
Mg	190	0.05	3.89
Al	350	1.55	2.47
Si	510	3.21	2.25
P	780	5.03	1.89
S	726	4.37	1.89
Cl	560	2.48	1.99
Ar	26	0.01	3.76
K	92	0.51	3.90
Ca	241	0.13	4.28
Sc	42	1.65	2.40
Ti*	489	1.30	2.17
V*	552	2.48	2.09
Cr	475	1.56	2.17
Mn	110	0.23	2.59
Fe	218	1.06	2.04
Co	365	1.69	3.20
Ni	286	2.36	2.96
Cu	264	2.03	2.22
Zn*	329	1.78	3.41
Ga*	219	1.40	2.43
Ge*	336	2.82	2.16
As	429	3.96	2.10
Se	430	3.16	2.17
Br	325	1.97	2.28
Kr	24	0.02	4.03
Rb	57	0.49	3.79
Sr*	202	5.82	3.05
Y*	282	1.62	–
Zr*	423	12.05	8.41
Nb	280	11.89	2.36
Mo	370	4.89	–
Tc	–	–	–
Ru*	338	3.41	2.17
Rh*	363	2.92	2.09
Pd*	91	0.73	3.16

(continued)

Table 1.1 (continued)

Atom	ν, cm^{-1}	E_0, eV	R_0, Å
Ag	192	1.66	2.59
Cd*	164	0.08	4.28
In	142	1.01	2.86
Sn*	315	1.99	2.78
Sb	272	3.09	2.34
Te	251	2.68	2.56
I	214	1.54	2.66
Xe	30	0.02	4.36
Cs	29	0.39	4.47
Ba*	150	11.26	3.25
La*	257	2.50	2.83
Ce*	886	2.50	2.74
Pr*	240	11.59	–
Nd	–	16.02	–
Pm	–	–	–
Sm	–	7.20	–
Eu*	166	11.43	–
Gd*	216	16.84	–
Tb	248	1.32	–
Dy	–	13.13	–
Ho	251	0.82	3.11
Er	–	14.50	–
Tm	–	6.49	–
Yb	162	0.17	2.89
Lu	246	10.11	2.63
Hf	330	13.11	2.44
Ta	365	13.15	2.36
W	385	9.04	–
Re	290	–	–
Os	260	–	–
Ir	279	6.16	2.36
Pt	218	6.35	2.28
Au	191	2.30	2.47
Hg	36	0.07	3.30
Tl	102	0.90	3.07
Pb	161	0.82	3.03
Bi	156	3.09	3.07
Po	155	1.90	–
Th	249	–	–
U	207	7.61	–

Figures 1.12 and 1.13 show the comparison of experimental [67] parameters of heteronuclear molecules with their theoretical values, calculated according to the combinative rules of (1.105). X-axis at these pictures represents the experimen-

tal values and y-axis defines the theoretical values. Thus, ideal correspondence of experiment and theory should result in situation of all the points on a single straight line.

To prove the described above theory, about two hundred different molecules described in [67] have been examined. Despite the large variation in the range of absolute values for real molecule parameters, the evaluation of these values using the combinative rules is rather effective: the mean square error is 3 % when estimating R_0 and 8 % for ν. The largest deviation reaches 30 % and are related to a few molecules with the hydrogen atom, for which the statistical evaluations are not a good approximation. The formula derived can also be used for a rough estimation of the dissociation energy; the mean square error for this parameter is about 25 % because of the above mentioned reasons. The corrections to the parameters considered for interacting ions can be estimated in the framework of Thomas-Fermi model [69].

Fig. 1.12 Comparison of the calculated with (1.105) and experimental values of the equilibrium distances R_{AB} for diatomic molecules
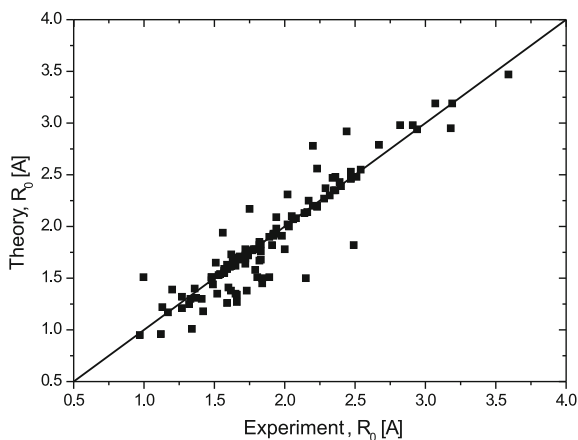
Fig. 1.13 Comparison of the calculated with (1.105) and experimental values of the principal frequencies ν_{AB} for diatomic molecules
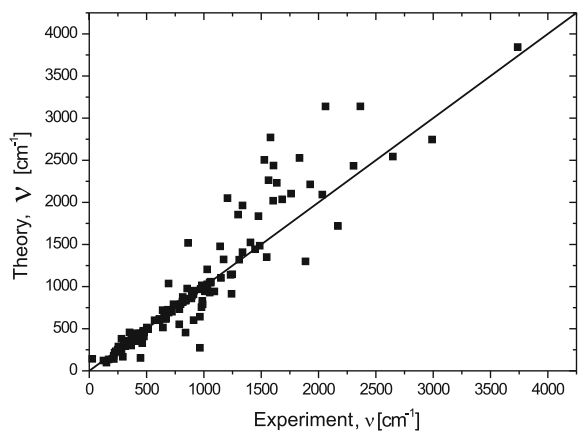
Table 1.2 Comparison of the theoretical Θ_{th} and experimental Θ_{exp} Debye temperatures

Crystal	Cell	Θ_D^{exp}, K		Θ_D^{th}, K	ε
		min	max		
Cu	f.c.c.	304	342	264	0.101
Ag		212	220	192	0.059
Au		155	190	191	0.051
Ca		220	230	241	0.034
Sr		148	171	202	0.118
Al		375	428	350	0.069
Th		145	170	249	0.225
Pb		68	105	161	0.301
V		300	413	552	0.215
Nb		252	301	280	0.006
Ta		230	245	365	0.212
Ni		375	476	286	0.196
Rh		315	370	363	0.029
Pd		263	280	91	0.498
Ir		285	–	279	0.011
Pt		225	248	218	0.041
Li	b.c.c.	277	430	351	0.004
Na		146	180	159	0.012
K		100	163	92	0.177
Rb		58	85	57	0.113
Cs		42	54	29	0.247
Ba		115	–	150	0.132
Cr		405	485	475	0.033
Mo		360	388	370	0.005
W		270	384	385	0.081
Fe		355	467	218	0.307
C	Diamond	1800	2242	1854	0.043
Si		505	685	510	0.077
Ge		211	400	336	0.048
Sn		260	–	315	0.096
Be	h.c.p.	1000	1376	1343	0.061
Mg		290	342	190	0.249
Zn		200	305	329	0.132
Cd		120	172	164	0.058
La		132	152	257	0.288
Gd		152	–	216	0.174
Tl		96	100	102	0.020
Ti		342	430	489	0.118
Zr		250	288	423	0.223
Hf		213	–	330	0.215
Re		275	310	290	0.004
Co		385	–	365	0.027
Ru		400	426	338	0.100

Table 1.2 (continued)

Crystal	Cell	Θ_D^{exp}, K min	max	Θ_D^{th}, K	ε
Os		250	256	260	0.014
B	Tetragonal	1250	–	1051	0.086
In		78	129	142	0.157
Sn		163	258	315	0.199
Hg	Rhombohedral	37	100	36	0.311
As		224	285	429	0.255
Sb		140	200	272	0.231
Bi		62	120	156	0.263
U	Orthorhombic	200	–	207	0.017
Ga		125	240	219	0.091
Br		110	–	325	0.494
I		106	–	214	0.338
LiH	B1	815	–	1525	0.303
LiF		650	685	602	0.052
LiCl		463	–	515	0.053
LiBr		387	–	458	0.084
LiI		331	–	411	0.108
NaF		439	–	382	0.069
NaCl		270	300	301	0.027
NaBr		200	243	249	0.058
NaI		151	198	217	0.109
KF		321	333	299	0.058
KCl		218	–	227	0.020
KBr		152	–	178	0.079
KI		115	200	152	0.018
RbF		238	–	260	0.044
RbCl		176	–	187	0.030
RbBr		128	–	136	0.030
RbI		108	–	111	0.014
CsF		184	–	200	0.042
AgCl		130	143	352	0.441
PbS		230	–	414	0.286
PbSe		168	–	278	0.247
PbTe		139	–	203	0.187
MgO		750	890	553	0.194
CsCl	B2	166	–	141	0.081
CsBr		119	–	98	0.097
CsI		93.6	–	78	0.091
TlCl		125	–	283	0.387
TlBr		114	–	192	0.255
AgI	B3	120	183	203	0.145
GaAs		314	–	306	0.013
GaSb		233	–	248	0.031
ZnS		300	–	504	0.254
					$\varepsilon_{aver} = 0.135$

The Table 1.2 gives a comparison between experimental Debye temperatures Θ_D^{exp} and values calculated with the formula (1.101). Practically all calculated values of Θ_D^{th} are within $\pm 10\%$ of experimentally reported Debye temperatures determined by different methods [29]. Figure 1.14 is a graphical representation of the Table 1.2 in the coordinates $(\Theta_D^{exp}; \Theta_D^{th})$.

The presented method for microscopic simulation of the harmonic potential for arbitrary pair of atoms gives a recipe for an accurate calculation of DWF. The accuracy is provided by the optical branches of the phonon spectrum and anisotropy of DWF in the crystals with the polyatomic unit cell. The anharmonic effects are neglected in this case and the interaction between atoms in neighboring cells are only taken into account when calculating DWF.

In general, every force matrix element includes four components (Γ, X, Y, Z), which are described as follows:

(Γ): Contribution of the atoms situated in the same unit cell. These elements of the force matrix are denoted by $\Gamma_{i,j}^{\alpha,\beta}$. Here lower indices correspond to usual Cartesian components ($i, j = 1, 2, 3$) and upper ones enumerate s atoms in the same cell ($\alpha, \beta = 1, \ldots, s$). The unit cell is assumed to consist of s_1 atoms of one type, s_2 atoms of other type etc., where $s_1 + s_2 + \cdots = s$. The distance between some atom with number α_1 and all the atoms of the same type in the cell is expressed as:

$$R_{\alpha_1,\beta_1}^{11} = \sqrt{\sum_{i=1}^{3}(x_i^{\alpha_1} - x_i^{\beta_1})^2 a_i^2},$$

where the dimensionless atom coordinates x_i are measured in fractions of the corresponding basic vectors a_i of the crystal. In the framework of the considered approximation, the only least distances are kept and the number of them defines the coordination number for this type of atoms [27]:

Fig. 1.14 Comparison of the experimental Θ_D^{exp} and calculated Θ_D^{th} values of the Debye temperatures for crystals
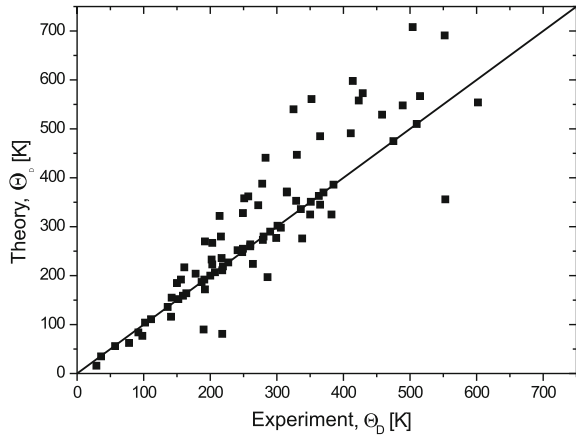
$$l_1, \quad 1 \leq l_1 \leq s_1; \quad 1 \leq \alpha_1 \leq s_1; \quad 1 \leq \beta_1 \leq l_1.$$

The analogous procedure delivers the distances and the coordination numbers for atoms of different types:

$$R^{pq}_{\alpha_p, \beta_q}, \quad 1 \leq \alpha_p \leq s_p; 1 \leq \beta_q \leq l_{pq},$$

where l_{pq} is the number of atoms of the type q closest to the atom of the type p. A one-cell contribution to elements of the force matrix is calculated by the Eq.(1.98):

$$\Gamma^{\alpha, \beta}_{i,j} \to \Gamma^{\alpha_p, \beta_q}_{i,j} = \kappa_{pq}(x_i^{\alpha_p} - x_i^{\alpha_q})(x_j^{\alpha_p} - x_j^{\alpha_q})a_i a_j [R^{pq}_{\alpha_p, \beta_q}]^{-2}. \qquad (1.108)$$

Here κ_{pq} are the harmonic constants for the interaction between atoms of type p and q, calculated by means of the Eq. (1.107).

(X,Y,Z): 3 contributions from atoms in neighboring cells. The distance to these atoms can be found by coordinate translations by one of the basis lattice vectors:

$$(XR)^{pq}_{\alpha_p, \beta_q} = \sqrt{(x_1^{\alpha_p} - x_1^{\beta_q} - 1)^2 a_1^2 + (x_2^{\alpha_p} - x_2^{\beta_q})^2 a_2^2 + (x_3^{\alpha_p} - x_3^{\beta_q})^2 a_3^2};$$

$$(YR)^{pq}_{\alpha_p, \beta_q} = \sqrt{(x_1^{\alpha_p} - x_1^{\beta_q})^2 a_1^2 + (x_2^{\alpha_p} - x_2^{\beta_q} - 1)^2 a_2^2 + (x_3^{\alpha_p} - x_3^{\beta_q})^2 a_3^2};$$

$$(ZR)^{pq}_{\alpha_p, \beta_q} = \sqrt{(x_1^{\alpha_p} - x_1^{\beta_q})^2 a_1^2 + (x_2^{\alpha_p} - x_2^{\beta_q})^2 a_2^2 + (x_3^{\alpha_p} - x_3^{\beta_q} - 1)^2 a_3^2},$$

here the same approximation of the nearest neighbors has been used. If the pair of atoms of selected type has been already encountered in the group Γ of the initial cell, then the same pairs in the groups (XR), (YR), (ZR) are taken into account only when the inequalities $(\{S\}R)^{pq}_{\alpha_p, \beta_q} \leq R^{pq}_{\alpha_p, \beta_q}, \{S\} = X, Y, Z$ are fulfilled. After such a selection procedure, the additional contributions to the force matrix are calculated as follows:

$$X^{\alpha_p, \beta_q}_{i,j} = \kappa_{pq}(x_i^{\alpha_p} - x_i^{\alpha_q} - \delta_{i1})(x_j^{\alpha_p} - x_j^{\alpha_q} - \delta_{j1})a_i a_j [(XR)^{pq}_{\alpha_p, \beta_q}]^{-2};$$
$$Y^{\alpha_p, \beta_q}_{i,j} = \kappa_{pq}(x_i^{\alpha_p} - x_i^{\alpha_q} - \delta_{i2})(x_j^{\alpha_p} - x_j^{\alpha_q} - \delta_{j2})a_i a_j [(YR)^{pq}_{\alpha_p, \beta_q}]^{-2};$$
$$Z^{\alpha_p, \beta_q}_{i,j} = \kappa_{pq}(x_i^{\alpha_p} - x_i^{\alpha_q} - \delta_{i3})(x_j^{\alpha_p} - x_j^{\alpha_q} - \delta_{j3})a_i a_j [(ZR)^{pq}_{\alpha_p, \beta_q}]^{-2},$$

$$(1.109)$$

with δ_{ij} as the Kronecker symbol.

The next step is the calculation of the phonon eigenfrequencies. Taking into account a translational symmetry of the crystal in the equations for small atomic oscillations in the conventional way [27], the equations of motion for the phonon variables $\xi_i^{\alpha_p}(\boldsymbol{k})$ and frequencies are:

$$M_p \omega^2 \xi_i^{\alpha_p} = \sum_{\beta_q, j} \Gamma_{i,j}^{\alpha_p, \beta_q} (\xi_i^{\alpha_p} - \xi_j^{\beta_q}) +$$

$$\frac{1}{2} \sum_{\beta_q, j} X_{i,j}^{\alpha_p, \beta_q} (\xi_i^{\alpha_p} - \xi_j^{\beta_q} e^{ik_1 a_1}) +$$

$$\frac{1}{2} \sum_{\alpha_q, j} X_{i,j}^{\alpha_q, \beta_p} (\xi_i^{\alpha_p} - \xi_j^{\beta_q} e^{-ik_1 a_1}) + Tr\{\}. \tag{1.110}$$

here the symbol $Tr\{\}$ means that the analogous terms with matrices Y, Z should be also included, and k_i are the projections of the wave vector on the corresponding basis vectors of the unit cell. We should also note that in general the force matrices in the equations are not symmetrical on all indices. For example, the element X^{α_1, β_q} defines the interaction between atom of the type 1 in selected cell and atoms of the type q in the displaced cell. Vice versa, only that atoms of the type q from the basis cell, which are interacting with atom of the type 1 in the displaced cell, contribute to the element X^{α_q, β_1}.

The approximate solution for the Eq. (1.110) is built taking into account the fact, that the main contribution in the integrals over the phonon energy in the DWF is defined by the range of small values of k in the vicinity of the extremum of each phonon zone. The principal character of this contribution can be explained by the maximum value of the state density because of the phonon group velocity becomes zero in this range [27], and the exponentials in the Eq. (1.110) can be expanded into the series by k. Besides, the acoustic branches of the phonon spectrum can be extracted by using new variables, namely the coordinate of the center of mass of the cell:

$$R_i = \frac{1}{M} \sum_p M_p \sum_{\alpha_p} \xi_i^{\alpha_p};$$

where M is the total mass of the cell; M_p is the mass of the atom of the type p, and the relative coordinates are:

$$\rho_i^{\alpha_p} = \xi_i^{\alpha_p} - R_i; \quad \sum_p M_p \sum_{\alpha_p} \rho_i^{\alpha_p} = 0.$$

The last relation means that the number of independent equations is equal to 3(s-1) but three other components of the variable (for example, with index $\alpha_p = 1$) depend on the rest and thus can be found from the equation

$$\rho_i^1 = -\frac{1}{M_1} \sum_p M_p \sum_{\alpha_p \neq 1} \rho_i^{\alpha_p}. \tag{1.111}$$

In order to find the motion equation for the center of mass, all the Eq. (1.110) are summarized by justifying to accuracy $O(k^2)$:

$$M\omega^2 R_i = \frac{k_1^2 a_1^2}{2} \sum_p \sum_{\alpha_p} \sum_{\beta_q,j} \left[X_{i,j}^{\alpha_p,\beta_q} + X_{i,j}^{\alpha_q,\beta_p} \right] R_j$$

$$+ \frac{ik_1 a_1}{2} \sum_p \sum_{\alpha_p} \sum_{\beta_q,j} [X_{i,j}^{\alpha_p,\beta_q} - X_{i,j}^{\alpha_q,\beta_p}]\rho_j^{\beta_q} + Tr\{\}. \qquad (1.112)$$

The equations for the relative variables can be solved in the approximation of the independent oscillations which is also used in the theory of small vibrations of molecules [68]. In this case, the coupling of various oscillations is taken into account only through the coordinate of the mass center. Then the average deviation of each atom from its equilibrium position is equal to zero relative to the center of mass of the unit cell. Using this fact, the equations of motion for relative coordinates are as follows:

$$M_p\omega^2 \rho_i^{\alpha_p} = -M_p\omega^2 R_i + \sum_{\beta_q,j} \left[\Gamma_{i,j}^{\alpha_p,\beta_q} + \frac{1}{2}(X_{i,j}^{\alpha_p,\beta_q} + X_{i,j}^{\alpha_q,\beta_p}) \right]\rho_j^{\alpha_p}$$

$$- \frac{ik_1 a_1}{2} \sum_{\beta_q,j} [X_{i,j}^{\alpha_p,\beta_q} - X_{i,j}^{\alpha_q,\beta_p}]R_j + Tr\{\}. \ (1.113)$$

Physically the approximation used means that only the average force acting to selected atom from the side of all neighbors is taken into account. For the case of small k, the optical frequencies $\omega_p^{(\nu)}$; $\nu = 1, 2, 3$ can be found from the Eq. (1.113). The number of such optical branches is $3(s - 1)$ and for atoms of the type p they degenerate with the multiplicity $3s_p$ (for the first one the multiplicity is $3(s_1 - 1)$). These branches of the phonon spectrum are defined by diagonalization of p matrices of dimension (3×3), which result in the following equations for the eigenfrequencies and orthonormalized polarization vectors $e_i^\nu(p)$:

$$\omega_p^{(\nu)} = \sqrt{\frac{\lambda_p^\nu}{M_p}}; \qquad \lambda_p^\nu e_i^\nu = \sum_j D_{ij}^p e_j^\nu;$$

$$D_{ij}^p = \sum_{\beta_q,j} \left[\Gamma_{i,j}^{\alpha_p,\beta_q} + \frac{1}{2}(X_{i,j}^{\alpha_p,\beta_q} + X_{i,j}^{\alpha_q,\beta_p}) + Tr\{\} \right]. \qquad (1.114)$$

The acoustic branches then can be found from the Eq. (1.110) by substitution of the relative coordinates by the center of mass. Then the spectrum of the acoustic eigenfrequencies is defined by the acoustic 4-rank tensor depending on the force matrix and the vector $\boldsymbol{k}$ [49]. As a result, there exists an anisotropy of the sound velocity in different directions of propagation even in cubic crystals. However, by the definition, the DWF depends on the constant 2-rank tensor which is determined by the symmetry of the crystal only and does not depend on the vector $\boldsymbol{k}$ [49] because of the averaging over the $\boldsymbol{k}$ during the integration on the phonon variables. This fact

allows the use of an averaging procedure over all the directions of $\boldsymbol{k}$ in the dispersion equation. Mathematically this corresponds to the following substitution:

$$\int f[\omega(\boldsymbol{k})]k^2 dk d\Omega \simeq \int f[<\omega(k)>]k^2 dk d\Omega,$$

$$<\omega(k)>=\sqrt{I}; \qquad I = \frac{1}{4\pi}\int \omega^2(\boldsymbol{k})d\Omega.$$

Then the Eq. (1.110) transform to:

$$
M\omega^2 R_i = \frac{k^2 a_1^2}{6} \sum_p \sum_{\alpha_p} \sum_{\beta_q,j} [X_{i,j}^{\alpha_p,\beta_q} + X_{i,j}^{\alpha_q,\beta_p}]R_j
$$

$$
+ \frac{k^2 a_1^2}{12 M_1} \sum_q M_q \sum_{\alpha_p} \sum_{\beta_q \neq 1,m} [X_{i,m}^{\alpha_p,1} - X_{i,m}^{1,\beta_p}]
$$

$$
\times \sum_{\gamma_r,l} [D_{ml}^q]^{-1} \sum_j [X_{l,j}^{\beta_q,\gamma_r} - X_{l,j}^{\beta_r,\gamma_q}]R_j
$$

$$
- \frac{k^2 a_1^2}{12} \sum_p \sum_{\alpha_p \neq 1} \sum_{\beta_q,m} [X_{i,m}^{\alpha_p,\beta_q} - X_{i,m}^{\alpha_q,\beta_p}]
$$

$$
\times \sum_{\gamma_r,l} [D_{ml}^q]^{-1} \sum_j [X_{l,j}^{\beta_q,\gamma_r} - X_{l,j}^{\beta_r,\gamma_q}]R_j + Tr\{\}. \qquad (1.115)
$$

and the problem is again reduced to the diagonalization of the symmetrical (3×3) matrix. The solution for the optical frequencies is then found in the form

$$
\omega_a^\nu(k) = \frac{ka_0}{\sqrt{M}}c_\nu; \quad \nu = 1, 2, 3; a_0 = (\Omega_0)^{1/3}
$$

and defines three acoustical phonon branches. In this parametrization, the normalized vectors of polarization e_{ia}^ν and eigenvalues c_ν no longer depend on k:

$$
c_\nu^2 e_{ia}^\nu = \sum_j A_{ij} e_{ja}^\nu;
$$

$$
A_{ij} = \frac{b_1^2}{6} \sum_p \sum_{\alpha_p} \sum_{\beta_q,j} [X_{i,j}^{\alpha_p,\beta_q} + X_{i,j}^{\alpha_q,\beta_p}]
$$

$$
+ \frac{b_1^2}{12} \sum_q M_q \sum_{\alpha_p} \sum_{\beta_q \neq 1,m} [X_{i,m}^{\alpha_p,1} - X_{i,m}^{1,\beta_p}]
$$

$$
\times \sum_{\gamma_r,l} [D_{ml}^q]^{-1} \sum_j [X_{l,j}^{\beta_q,\gamma_r} - X_{l,j}^{\beta_r,\gamma_q}]R_j
$$

$$-\frac{k^2 b_1^2}{12} \sum_{p} \sum_{\alpha_p \neq 1} \sum_{\beta_q, m} [X_{i,m}^{\alpha_p, \beta_q} - X_{i,m}^{\alpha_q, \beta_p}]$$

$$\times \sum_{\gamma_r, l} [D_{ml}^q]^{-1} \sum_{j} [X_{l,j}^{\beta_q, \gamma_r} - X_{l,j}^{\beta_r, \gamma_q}] + Tr\{\};$$

$$b_i = \frac{a_i}{a_0}. \qquad (1.116)$$

To derive a final formula for DWF, the general definition of the Debye-Waller factor is used for the atom with number t in the unit cell [29]:

$$DWF_t = e^{-\sum_{i,j} B_{ij}^t q_i q_j}; \quad B_{i,j}^t = 2\frac{\hbar^2}{M_t} W_{i,j}. \qquad (1.117)$$

Here the projections of the transmitted wave vector q_i should be calculated in the coordinate system connected with unit cell

$$q_i = \frac{2\pi}{d} l_i; \qquad d = \left[\sqrt{l_1^2 g_1^2 + l_2^2 g_2^2 + l_3^2 g_3^2} \right]^{-1},$$

where d is the interplane distance for the given reflection defined by Miller indices l_i; n_i are the minimal integers for this reflection; g_i are the standard basis vectors of the reciprocal lattice. In this definition, tensor W_{ij} does not depend on the atom number and is the characteristics of the crystal as a whole [32]:

$$W_{ij} = \frac{\Omega_0}{2\hbar} \sum_{(p)} \sum_{\nu} e_i^\nu e_j^\nu \int \frac{d\mathbf{k}}{(2\pi)^3} f(\omega_p^\nu), \qquad (1.118)$$

where the summation is performed on all optical and acoustic branches and f is the function of the Bose-Einstein distribution:

$$f(\omega) = \frac{1}{\omega} \left[1 + \frac{2}{\exp \hbar\omega/k_B T - 1} \right].$$

Below we split the general expression for W into two parts related to optical W^o and to acoustic W^a oscillations. The above-mentioned expansion on small k corresponds to the Einstein approximation when the optical frequencies are considered as constants in the Brillouin zone [27]. Then taking into account the multiplicity of the optical branches, W^o is calculated as:

$$W_{ij}^o = \frac{1}{2\hbar} \sum_{p} s_p' \sum_{\nu} e_i^{\nu p} e_j^{\nu p} f(\omega_p^\nu). \qquad (1.119)$$

The frequencies and vectors of polarization for optical branches have been defined in the Eq. (1.114). Index s'_p means that the value $(s_1 - 1)$ should be substituted instead of s_1 for the atoms of the type 1.

The acoustic contribution to the DWF can be found in the following form

$$W_{ij}^a = \frac{1}{2\hbar} \sum_{\nu} e_{ia}^{\nu} e_{ja}^{\nu} \frac{\Omega_0}{2\pi^2} \int_0^{k_D} dk \frac{k\sqrt{M}}{a_0 c_{\nu}}$$

$$\times \left[\frac{\exp\left(\hbar k a_0 c_{\nu}/k_B T \sqrt{M}\right)}{\exp\left(\hbar k a_0 c_{\nu}/k_B T \sqrt{M}\right) - 1} \right]; \quad k_D = \left(\frac{6\pi^2}{\Omega_0}\right)^{1/3}. \tag{1.120}$$

By analogy with Debye temperature, three different parameters are introduced for each polarization of the acoustic phonons:

$$\Theta_{\nu} = \frac{\hbar a_0 k_D c_{\nu}}{k_B \sqrt{M}},$$

and finally the acoustic part of DWF is:

Fig. 1.15 The value $B^t(T)$ in the Debye-Waller factor for the atom of (**a**) As and (**b**) Ge in the crystal GaAs $(\Theta_D = 210K)$ as a function of the temperature. The *dashed line* presents the results of [64], obtained on the basis of the experimental phonon spectrum; the *solid line* is a calculation by the present algorithm; the *dash-dotted curve* represent the optical phonon spectrum
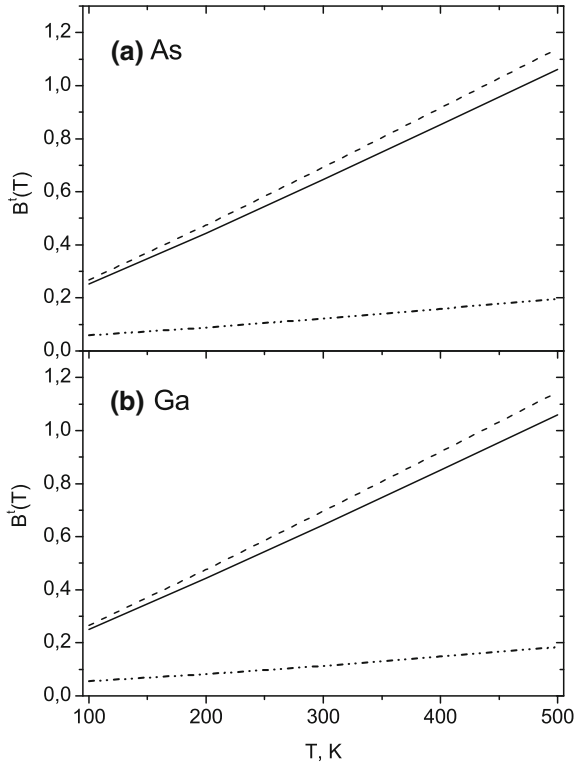
$$W_{ij}^a = \frac{3}{2k_B} \sum_\nu e_{ia}^\nu e_{ja}^\nu \frac{1}{\Theta_\nu} \int_0^1 x \, dx \coth\left(\frac{x\Theta_\nu}{2T}\right). \qquad (1.121)$$

The formulas (1.118)–(1.121) establish the algorithm for calculation of the Debye-Waller factor for X-ray susceptibilities. By this algorithm, the Fourier components of the susceptibility for crystals are calculated by using the symmetrical tensor W, which includes only 6 components in the most general case. To illustrate this result, the Debye-Wallers factors for the atoms of As and Ga in the crystal GaAs have been calculated. Figure 1.15 demonstrates a good agreement between the DWF temperature dependence calculated by proposed method and the phenomenological dependence found on the basis of the experimental density of the phonon states [64]. The optical part of the DWF, usually not taken into account in the standard program packages [40, 41], seems to be an important part of the total DWF value, as Fig. 1.15 illustrates, too.

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