

Chapter 3

Potentials and Electronic Structure

Calculations of Non-regular Nanosystems

3.1 Introduction

Any *ab initio* calculations of physical characteristics of condensed materials, associated with the electron and phonon subsystems, require the calculations or construction of potentials (potential functions) that take into account simulated effects. Moreover, this concerns not only the electronic structure of the material sample as a whole but also local or spatially limited structural defects in it. The first step on the way to obtaining potentials is to calculate the electronic spectrum of a sample considering it as a quantum mechanical object. However, some simplifying approximations are necessary. In these cases, one-electron approximation is practically preferable, when the motion of each electron of the system is considered in the averaged field of nuclei and other electrons. The averaged field takes into account both the pure Coulomb interaction of the charged particles of the system and the exchange-correlation effects in the electronic subsystem. In the simplest version of such an approximation, the dynamics of the lattice of a rigid body (*adiabatic approximation*) is neglected, and only the stationary approach is considered. However, even for such an option, the problem of calculating the electronic spectrum of a non-regular condensed system is very problematic.

3.2 Atomic Potential Functions

Consider the methodology of calculations in the case of isolated neutral atoms. There are two classes of problems that can be distinguished in quantum mechanics.

The first class includes eigenvalue problems, when resulting from the solution of the Schrödinger equation $Hu_i = \varepsilon_i u_i$, one-electron wave functions u_i and the corresponding values of the energies of one-electron states ε_i are sought. This is usually a self-consistent procedure, since the exact form of the potential function is

not known and can be obtained in the process of iteration on the basis of some starting *seeding* potential. Boundary conditions of wave functions provide the ‘natural’ property of their vanishing at the infinity. Namely, wave functions go to zero at the infinity or on the sample boundaries (as an approximation). In this case, as is known, a discrete energy spectrum is obtained. Then, based on the wave functions obtained, wave functions of many-electron states and the corresponding basis are formed.

The second class of stationary problems includes scattering problems, when, for example, a plane electron wave is scattered by a potential $V(\mathbf{r})$ and the Schrodinger equation:

$$(\Delta + k^2)\psi_k(\mathbf{r}) = V(\mathbf{r})\psi_k(\mathbf{r}) \quad (3.1)$$

is solved under boundary conditions corresponding to the scattered wave, for example:

$$\psi_{\mathbf{k}} \rightarrow \exp(i\mathbf{k}\mathbf{r}) + f(\theta, \varphi)\exp(ikr)/r, \quad (3.2)$$

where the solution is sought as a superposition of the original plane wave $\exp(i\mathbf{k}\mathbf{r})$ and a spherical scattered wave dependent on scattering θ and azimuth angles φ .

Initially, it was assumed that such a statement of the problem is reasonable only for positive energies $k^2 = \varepsilon > 0$. However, subsequently this approach was successfully used for negative energy states of atoms and molecules and was formed as a cluster multiple scattering method for calculating the electronic structure of complex molecules and impurities in solids (see, e.g. [1]). Later, these principles were used to construct various calculation schemes suitable for disordered solids. More details of the scattering problem concerning the calculation of the electronic properties of disordered semiconductors are considered, for example, in [2].

Knowledge of the right potential $V(\mathbf{r})$ is highly desirable, but not always necessary. It is enough to simulate the so-called pseudopotential. This is due to the fact that in most practical operation cases of electronic devices, the deep electronic states of condensed systems are passive.

3.2.1 Construction of Atomic Potential Functions

It is intuitively clear that the potential function of an isolated atom (or potential) is an element of the potential function of any condensed system. However, the latter cannot be obtained by a simple superposition. Therefore, a detailed analysis of the factors determining the atomic potential is required. There is a group of methods that make it possible to calculate the potential as a result of solving the eigenvalue problem. These methods are based on the Hartree approach, which proposed a one-electron equation for the spin-orbitals u_i of the wave function of the i -th electron in an atom.

The solution of the Schrödinger equation, which should be solved with an electronic spectrum of atoms, molecules and solids (both ordered and disordered), usually uses the non-relativistic approximation and requires the knowledge of the self-consistent potential (self-consistent potential energy) of an electron in the field of nuclei and other electrons to come to the one-electron problem. As a rule, such a potential is unknown or known only for some particular cases. For free (isolated) atoms, one can perform a self-consistent procedure of the Hartree–Fock–Slater type [1] and find the self-consistent potential of the atom, as well as the corresponding wave functions in the one-electron approximation. Such a calculation reduces to the numerical integration of a system of differential equations of the type:

$$[-\nabla_1^2 + V_C(1) + V_{Xi}(1)]u_i(1) = \varepsilon_i i_i(1), \quad (3.3)$$

where $-\nabla_1^2$ is the kinetic energy operator (in **Ry**-Rydberg units) and $V_C(1)$ is the Coulomb potential energy of the electron at point 1 due to its interaction with the nucleus and other electrons of the system. For an atom with a charge number Z :

$$V_C(1) = -\frac{ZZ}{r} + \sum_j n_j \int u_j^*(2)u_j(2)g_{12}dV_2, \quad (3.4)$$

where $u_j^*(2)u_j(2)$ is the density of the electron charge of j -th orbital at the point 2, $g_{12} = 2/r_{12}$, r_{12} is the distance between points 1 and 2 and n_j is the number of the orbital filling (0 or 1). The term $V_{Xi}(1) = -n_i \int u_i^*(2)u_i(2)g_{12}dV_2$ takes into account that the electron on the i -th orbital does not interact with itself. The integration is carried out over the entire volume of the atom. The total charge density by Hartree is $\rho(1) = \sum_i n_i u_i^*(1)u_i(1)$. In this case, the one-electron functions included in the known determinant total wave function [1] $\Psi = \frac{1}{\sqrt{N!}} \det\|\mathbf{u}_{k_1}(1), \mathbf{u}_{k_2}(2), \dots, \mathbf{u}_{k_N}(N)\|$ with $k_i = 1, 2, \dots, N$ are varied and minimize the total energy of the atom. The use of such wave functions in the variational procedure leads to the Hartree–Fock equation:

$$[-\nabla_1^2 + V_C(1)]u_i(1) - \sum_j n_j \int u_j^*(2)u_i(2)g_{12}dV_2 u_j(1) = \varepsilon_i u_i(1). \quad (3.5)$$

However, the set of spin-orbitals in the Hartree–Fock method, which minimizes the total energy, is ambiguous, and the value ε_i in the Hartree method becomes the matrix ε_{ij} . It is possible to choose orbitals which diagonalize ε_{ij} .

Slater rewrote Eq. (3.5) in the following way:

$$[-\nabla_1^2 + V_C(1) + V_{XiHF}(1)]u_i(1) = \varepsilon_i u_i(1), \quad (3.6)$$

where

$$V_{XiHF} = - \frac{\sum_j n_j \int u_i(1) u_j^*(2) u_j(1) u_i(2) g_{12} dV_2}{u_i^*(1) u_i(1)}, \quad (3.7)$$

is the exchange-correlation term.

The charge that creates the potential is called the exchange-correlation charge, or the ‘Fermi hole’. The Fermi hole moves together with the electron and is a metal surrounding electron-like sphere, from which the electron charge is eliminated. The size of the Fermi hole can be estimated, knowing the local density of the electron charge, namely, $r_s = [3\rho/4\pi]^{-1/3}$, which is also called the Wigner radius r_s . Note, that in the electronic theory of metals [3], the parameter r_s uniquely characterizes the state of the electronic subsystem. In the limit case $r_s \rightarrow 0$, the kinetic energy $k^2 \sim 1/r_s^2$ dominates over the energy of the electron–electron Coulomb interaction $\sim 1/r_s$. For $r_s \rightarrow \infty$ the electron gas density is small, and the electrons are localized, forming Wigner lattice. Under the transition to $r_s \neq 0$, quantum effects and the long-range exchange interaction are switched on.

Then, the total energy of the electron subsystems per one electron looks like:

$$\varepsilon = \frac{E}{N} = \left(-\frac{1.792}{r_s} + \frac{2.65}{r_s^{3/2}} - \frac{0.73}{r_s^2} - \dots \right), Ry. \quad (3.8)$$

The Hartree–Fock equation, which is well applicable to atoms, turns out to be of little use for solids because of a rather complicated exchange-correlation term. Slater proposed to replace V_{XiHF} by the weighted average values with weights corresponding to the probability of finding the electron in position 1 of the i -th spin-orbitals:

$$[V_{XiHF}]_{AV} = \frac{\sum_{i\uparrow, j\uparrow} n_i n_j \int u_i^*(1) u_j^*(2) u_j(1) u_i(2) g_{12} dV_2}{\sum_{k\uparrow} n_k u_k^*(1) u_k(1)}, \quad (3.9)$$

where $\uparrow(\downarrow)$ is the position of the spin ‘up’(down). The formula for electrons with the spin $\uparrow$ for a gas of free electrons is as follows:

$$[V_{XiHF}]_{AV} = -6[3\rho \uparrow(1)/4\pi]^{1/3} = V_{XS}(1). \quad (3.10)$$

The formula for electrons with the spin $\downarrow$ looks similar.

As a result, a self-consistent field method based on the equation:

$$[-\nabla_1^2 + V_C(1) + V_{XS}(1)] u_{i\uparrow}(1) = \varepsilon_i u_{i\uparrow}(1) \quad (3.11)$$

has been developed.

It was widely used in various calculations of the electronic structure of atoms. In particular, such calculations were performed by Herman and Skillman [4] for all atoms of the periodic system. An introduction of the statistical exchange-correlation potential (3.9) is convenient for calculations because of its locality. However, the price that has to be paid for this relative simplicity is expressed in a noticeable discrepancy between the total atomic energies calculated by successive Hartree–Fock method and Hartree–Fock–Slater method used. It was also found that if we introduce the statistical exchange-correlation term into the expression for the total energy and then apply the variational principle, then we obtain the exchange-correlation potential as $(2/3)V_{XS}(1)$. Therefore, in the future, the statistical approximation started to be used in the form:

$$V_{X\alpha}(1) = \alpha V_{XS}(1) = -6\alpha(3\rho/8\pi)^{1/3}, \quad (3.12)$$

where α is a certain coefficient, which is usually calculated from the condition that the total Hartree–Fock and Hartree–Fock–Slater energies are identical in the so-called $X\alpha$ -approximation. The physical details of the coefficient can be elucidated by means of a many-electron theory.

Note that α is a function of the Wigner correlation radius r_s . If we take into account the inhomogeneity in the distribution of the electron density and perform the gradient expansion $\rho(\mathbf{r})$ on powers $\nabla\rho$ at the vicinity of the mean electron density ρ_0 , then, up to terms of the second order, one can obtain:

$$V_{XS}^H(1) = \frac{2}{3}V_{XS}(1) + \frac{2\pi}{(3\pi^2)^{4/3}} \left[\frac{4}{3} \left(\frac{\nabla\rho}{\rho} \right)^2 - 2 \frac{\nabla^2\rho}{\rho} \right] \rho^{-1/3}. \quad (3.13)$$

The expediency of such a form of the exchange-correlation potential is discussed below. The analysis, carried out in [5–7], makes it possible to use the analytical potential of Gaspar [8, 9] for potentials modelling:

$$V^G(r) = -\frac{2Z}{r} \cdot \frac{\exp(-\lambda r/\mu)}{(1 + Ar/\mu)}, \quad (3.14)$$

where $\lambda = 0.1837$, $\mu = 0.8853Z^{-1/3}$, $A = 1.05$, which is a successful approximation of the self-consistent potential function $V_C(1) + V_{Xi}(1)$ of the Hartree method in a wide range of numbers Z . Thus, in (3.14), only the electrostatic interaction of electrons with the nucleus and with each other is taken into account, but the exchange-correlation interaction is not taken into consideration in any way. If we separate the electron part of the potential from the nucleon (nuclear) part, then, using the Poisson equation, it is possible to restore the ‘realistic’ density of the electron charge:

$$\rho(r) = \Delta_r V_e / 8\pi, \quad (3.15)$$

where Δ_r is the radial part of Laplace operator, $V_e(r) = \frac{2Z}{r} - V^G(r)$, $V_e(r) = 2Z/r - V^G(r)$. Further, using the exchange-correlation correction in the form (3.12), we obtain the potential of the atom:

$$V_{\text{at}}(r) = V^G(r) + V_{X\alpha}(r). \quad (3.16)$$

A comparison with the self-consistent calculations of Herman–Skillman potentials [4] for $\alpha=1$ gives good results [5–7]. For numerical calculations, it is convenient to introduce the designation $f(r) = \exp(-\lambda r/\mu)/(1 + Ar/\mu)$.

Then, $V^G(r) = -\frac{2Z}{r}f(r)$.

Further, after transformations we obtain:

$$\begin{aligned} f'(r) &= \lambda_\mu f(r) - A_\mu f(r), f''(r) = -(\lambda_\mu + A_\mu)f'(r) + A_\mu^2 f(r), \rho(r) = -\Delta_r V^G(r) \\ &= -Zf''(r)/4\pi r \end{aligned}$$

where

$$\lambda_\mu = \lambda/\mu, A_\mu = (A/\mu)(1 + Ar/\mu)^{-1}.$$

It can also be seen that the total charge of the atom is:

$$Q = \int_0^\infty \rho(r) 4\pi r^2 dr = - \int_0^\infty Z r f''(r) dr = -Z.$$

The exchange-correlation correction in the form (3.12), which contains an implicit dependence on the charge number Z , creates great difficulties in constructing the ‘crystalline’ potentials of complex compounds. These difficulties can be circumvented by introducing a more complicated exchange-correlation correction (3.13) in the form:

$$V_{X\alpha\beta} = [\alpha + \beta G(\rho)] V_{XS}, \quad (3.17)$$

where $\alpha = 0.67$, $\beta \cong 0.003$, $G(\rho) = \frac{4}{3} \left(\frac{\nabla \rho}{\rho} \right)^2 - 2 \frac{\nabla^2 \rho}{\rho}$ and $V_{XS} = -6[3\rho/8\pi]^{1/3}$.

Thus, at the cost of introducing a new adjustable parameter, we can achieve the constancy of α and β . To ensure a better convergence of numerical calculations, we can write:

$$V_{X\alpha\beta} = \alpha \left[1 + th \left(\frac{\beta}{\alpha} G(\rho) \right) \right] V_{XS}, \quad (3.18)$$

where analytic properties of the function $th(x)$ are used.

Applying the previously introduced notation, we can obtain:

$$\begin{aligned}
\nabla_r \rho &= Z(f''' - f''/r)/4\pi r, \\
\rho'' &= Z(f^{iv} - 2f'''/r + 2f''/r^2)/4\pi r, \\
\nabla^2 \rho &= Zf^{iv}/4\pi r, \\
f''' &= -2A_\mu^3 f(r) + 2A_\mu^2 f'(r) - (\lambda_\mu + A_\mu)f''(r), \\
f^{iv} &= 6A_\mu^4 f(r) - 6A_\mu^3 f'(r) + 3A_\mu^2 f''(r) - (\lambda_\mu + A_\mu)f'''(r).
\end{aligned}$$

Thus, $G(\rho)$ and, consequently, $V_{X\alpha\beta}$ can be expressed in the analytical form, which is very important for numerical simulations.

A comparison of the analytical potentials (3.16) with the self-consistent calculations of Herman–Skillman potentials [4] for $\alpha = 1$ provides good results in a wide range of charge numbers [5–7] and is shown in Fig. 3.1.

The exchange-correlation corrections of the form $V_{X\alpha}$ (3.12) and $V_{X\alpha\beta}$ (3.18), which yielded close values throughout the entire range of the α parameter variations, have also been thoroughly investigated. In addition, the inclusion of analytical potentials of the type (3.16) in the scheme of self-consistent calculations of atoms ensures fast convergence. The calculation efficiency is widely confirmed [2].

3.3 ‘Crystalline’ Potentials

Using the procedure for constructing the potentials of atoms and the superposition principle, we can develop a technique for calculating crystalline potentials. Moreover, for slightly correlated systems such as liquids, this procedure is as follows:

$$V_C(r) = V^G(r) + V^G(a - r), \quad (3.19)$$

$$\rho_{cr}(r) = \rho(r) + \rho(a - r), \quad (3.20)$$

$$V_{exch}(r) = -6\alpha[3\rho_{cr}(r)/8\pi]^{1/3}, \quad (3.21)$$

$$V_{cr}(r) = V_C(r) + V_{exch}(r), \quad (3.22)$$

where a is the distance to the nearest neighbouring atom smeared in the vicinity of the selected ‘central’ one. Following this logic, it is also possible to construct crystalline potentials which are necessary for the realization of the scattering problem in the cluster approach. Then, the Coulomb part of the potential and the electron density are obtained, as above, based on the principle of superposition of the corresponding factors of individual atoms, namely:

$$V_C(\mathbf{r}) = V^G(\mathbf{r}) + \sum_{\gamma, n_\gamma} V_\gamma^G(\mathbf{r} - \mathbf{R}_{n_\gamma}^\gamma), \quad (3.23)$$

$$\rho_{cr}(\mathbf{r}) = \rho(\mathbf{r}) + \sum_{\gamma, n_\gamma} \rho_\gamma(\mathbf{r} - \mathbf{R}_{n_\gamma}^\gamma), \quad (3.24)$$

where γ is the type of atom and n_γ is the number of atoms neighbours.

Then the crystalline potential is calculated:

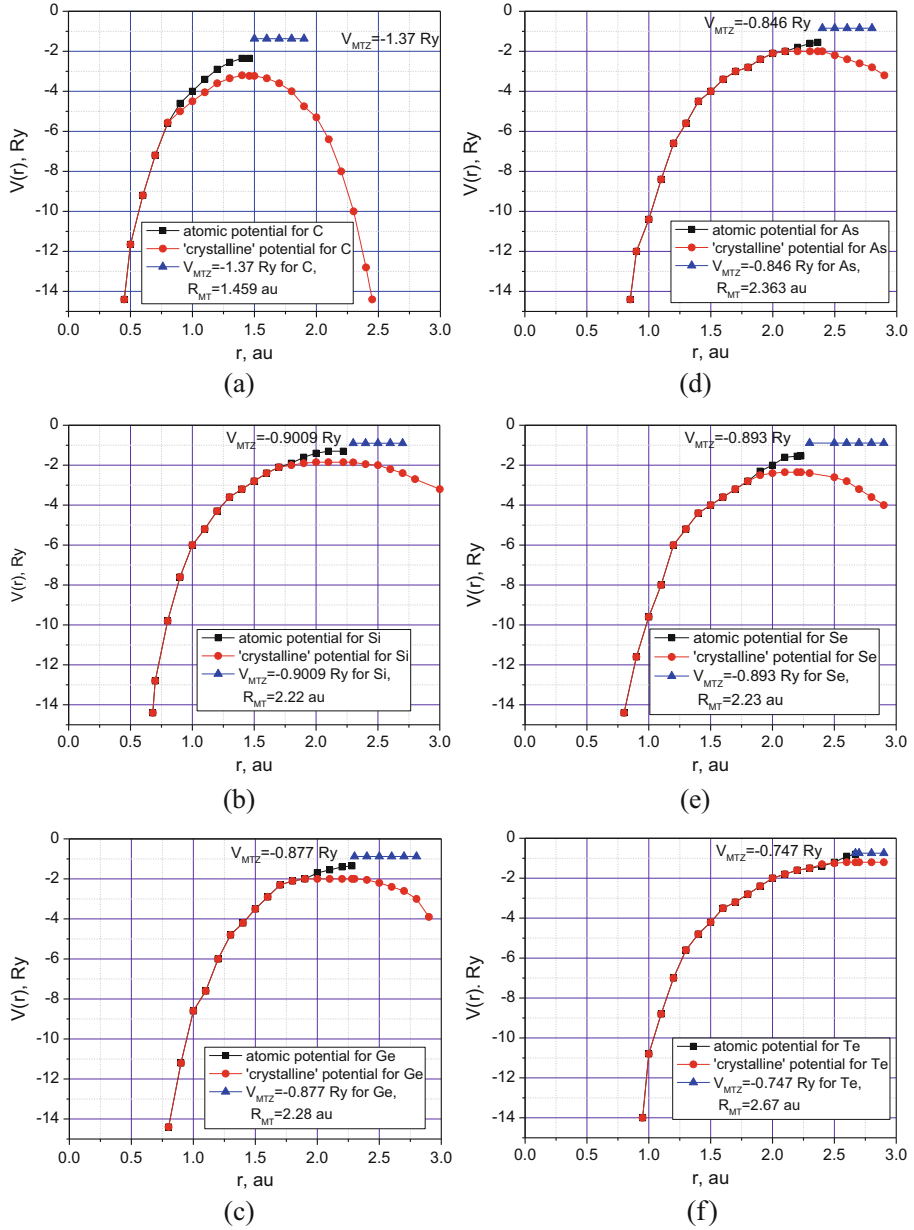


Fig. 3.1 Potentials (a, b, c, d, e, f): atomic potentials, crystalline potentials, MT-zero levels

$$V_{\text{cr}}(\mathbf{r}) = V_C(\mathbf{r}) + V_{\text{exch}}(\mathbf{r}), \quad (3.25)$$

where

$$V_{\text{exch}}(\mathbf{r}) = -6\alpha[3\rho_{\text{cr}}(\mathbf{r})/8\pi]^{1/3}. \quad (3.26)$$

For binary and more complex compounds, the exchange-correlation correction $V_{X\alpha\beta}$ (3.18) should be used. Applying the known MT-approximation of the potentials V_{cr} and ρ_{cr} , these functions are averaged over the surface of the MT-sphere, and then the spherically symmetric MT-potential of a single scatterer is constructed:

$$V_{\text{MT}}(r) = V_{\text{cr}}(r) - V_{\text{MTZ}}, \quad (3.27)$$

where $V_{\text{MTZ}} = -2/R_{\text{MT}}$, e.g. for monoelemental covalent materials, R_{MT} is the MT-radius and $V_{\text{MTZ}} = -2(x1/R_{\text{MT}}^A + (1-x)1/R_{\text{MT}}^B)$ for binary materials A_xB_{1-x} , where R_{MT}^A and R_{MT}^B are radii of the corresponding MT-spheres [2, 11, 12].

3.4 Potentials of Charged Defects

An important direction in the calculation of the electronic structure of non-regular nanosystems is the modelling of defects of various natures. However, since any defect formation is ultimately associated with a local transfer of the electron charge, the simulation itself is reduced to constructing a local defect potential which takes this transfer into account. Such a procedure is considered using the example of modelling of bonds switching in chalcogenides in the processes of photo- and radiation-stimulated transformations in the atomic structure (see Fig. 3.2). Typical applications of photoinduced structural transformations in chalcogenide glasses are presented in Table 3.1.

Chalcogenide glasses and corresponding nanosystems include group XVI chalcogen elements of the periodic table: {O}, S, Se, Te, {Po}. Chalcogenides are considered to be alloys of chalcogens and elements of groups III, IV, V, VI, e.g. As_2S_3 , GeSe_2 , $\text{Ge}_2\text{Sb}_2\text{Te}_5$, etc., but glass-forming materials are characterized by wide composition ranges. Atomic coordination of chalcogenide glasses is

Fig. 3.2 Typical transformations of chalcogenide charged defects

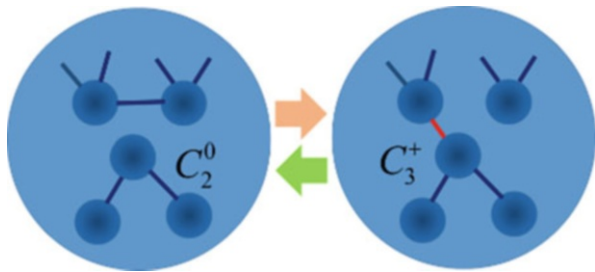


Table 3.1 Photoinduced structural transformations in chalcogenide glasses

Materials	Devices	Process
Photoresists	Vidicons	Holography
Photonic crystals	Diffraction elements DVD RW discs	Thermoplastic recording
Integral optics		Xerography

described by the ‘8- N rule’ (N = no. of valence electrons): *chalcogens* ($\{O\}$, S, Se) = 2 ($N = 6$) (Te) = 2 (3 dative), *pnictogens* (P, As, Sb) = 3 ($N = 5$), *tetragens* (Si, Ge) = 4 ($N = 4$) and *halogens* (Cl, Br, I) = 1 ($N = 7$).

In the framework of *Phillips–Thorpe constraint theory*, we can assume that a glass structure is a *continuous network* (CN) with r_i of constituent elements i , and for the average coordination number of CN $\langle r \rangle = \sum_i x_i r_i$, where x_i and r_i are the

mole fraction and the coordination number, respectively, referring to each species i in the glass. The *bond-stretching constraint* is $\langle r \rangle / 2$, and the *bond-bending constraint* is $2\langle r \rangle - 3$. The average number of atomic constraints in a system can be expressed as $n = \frac{\langle r \rangle}{2} + (2\langle r \rangle - 3)$, where $\langle r \rangle$ is the average coordination number of atoms in the system. The total number of constraints is $n_{\text{tot}} = \frac{5\langle r \rangle}{2} - 3$. For 3D this critical value $\langle r_{\text{cr}} \rangle = 12/5 = 2.4$ is called the rigidity percolation threshold, because, at this composition, rigid structures percolate throughout the glass, leading to an isostatic network [13].

Fundamental reasons of photo-transformations in chalcogenides and, as a result, their high photosensitivity are as follows:

- Bandgap photons excite electrons from the top of the VB – i.e. *lone-pair* electrons.
- Optical excitation can cause changes in weak van der Waals ‘intermolecular’ interactions.
- Low atomic coordination number of chalcogens favours local structural rearrangements – without necessarily breaking covalent bonds.
- Similar (~octahedral 3/4-fold) coordination geometry of a-/c-phases in *telluride* glasses $\rightarrow$ ps/ns changes.

Photo- and radiation-induced changes are responsible for local structural changes in chalcogenide systems and can be explained by local nanosized defect transformations [14–16].

Street and Mott [48] proposed a model of dangling bonds, with the combination of positively and negatively charged dangling bonds D^+ and D^- having, respectively, no and two spin-paired electrons, energetically favoured over the neutral dangling bond D^0 with one unpaired electron. This defect-based version of the negative-U model was developed by Kastner et al. [49] for the case of a-Se, with a singly coordinated, negatively charged selenium (C_1^-) and a threefold coordinated, positively charged site (C_3^+) emerging as the most likely equilibrium defect configurations. Moreover, for the study of dangling bonds, the general negative-U model was developed by Anderson [50] and later by Karpov et al. [51] based on the

self-localization of electron (and hole) pairs (SLEP). Charged defects analysis is primary for the explanation of photo- and radiation-induced local nanosized transformations in chalcogenide systems [17–19] including corresponding nanomemory materials [20].

The idea of modelling is to correct the outer part of the non-defect electronic cloud [21]. For this purpose, s - and p -like orbitals are used:

$$\varphi_s(\mathbf{r}) = C_s \exp(-r/r_0) Y_{00}(\mathbf{r}), \quad (3.28)$$

$$\varphi_p(\mathbf{r}) = C_p \exp(-r/r_0) Y_{1m}(\mathbf{r}), \quad (3.29)$$

where C_s and C_p are the normalization coefficients, r_0 is the characteristic covalent radius and $m = -1, 0, 1$. Then, the radial densities of the electron charge are represented as:

$$\rho_s(r) = C'_s \exp\left(\frac{-2r}{r_0}\right), \quad (3.30)$$

$$\rho_p(r) = C'_p r^2 \exp\left(\frac{-2r}{r_0}\right), \quad (3.31)$$

where $C'_s = 4/r_0^3$ and $C'_p = 4/3r_0^5$ are calculated using the normalization condition

$$\int_0^\infty \rho(r) 4\pi r^2 dr = 1.$$

The corresponding contributions to the potentials are calculated as:

$$V(r) = \frac{2}{r} \int_0^r \rho(r') 4\pi r'^2 dr', \quad (3.32)$$

i.e.

$$V_s(r) = -\frac{2}{r} \left\{ 1 - \exp\left(\frac{-2r}{r_0}\right) \left[\frac{1}{2!} \left(\frac{2r}{r_0}\right)^2 + \frac{1}{1!} \left(\frac{2r}{r_0}\right)^1 + \frac{1}{0!} \left(\frac{2r}{r_0}\right)^0 \right] \right\}, \quad (3.33)$$

$$V_p(r) = -\frac{2}{r} \left\{ 1 - \exp\left(\frac{-2r}{r_0}\right) \times \left[\frac{1}{4!} \left(\frac{2r}{r_0}\right)^4 + \frac{1}{3!} \left(\frac{2r}{r_0}\right)^3 + \frac{1}{2!} \left(\frac{2r}{r_0}\right)^2 + \frac{1}{1!} \left(\frac{2r}{r_0}\right)^1 + \frac{1}{0!} \left(\frac{2r}{r_0}\right)^0 \right] \right\}. \quad (3.34)$$

Then, finally, the Coulomb part of the defect potential can be presented in the form:

$$V_C(r) = V^G(r) - n_s V_s(r) - n_p V_p(r), \quad (3.35)$$

where n_s and n_p ($(\geq, \leq 0)$) are numbers of added or removed s - and p -electrons. Further, the potential (3.35) is included into the general scheme for building potentials. A more general approach related to the potentials that do not possess spherical symmetry is considered in [21, 22], where some aspects of the generalization of the MT-approximation are studied.

3.5 Electronic Structure and Total Energy: Atoms, Molecules and Nanoclusters

The problem of calculating the total energy of a large condensed system (crystal, disordered material) is one of the oldest in theory. Usually, this problem is reduced to the calculation of the binding energy of a large condensed system, namely, the *cohesive energy* $E_{\text{coh}} = E_{\text{tot}}^{\text{at}} - E_{\text{tot}}^{\text{sys}}/N$, where $E_{\text{tot}}^{\text{at}}$ is the total energy of its atoms and $E_{\text{tot}}^{\text{sys}}$ is the total energy of the system under consideration. In this connection, it is possible to single out problems of calculation of the total energy of atoms, molecules, macromolecules, nanoclusters, nanocrystals, large non-regular disordered condensed systems and, finally, crystals. Each of these problems has its own peculiarities.

Note that the total energy of atoms arises as a natural result of self-consistent calculations of their electronic spectra [1]. It is practically impossible to realize this calculation self-consistently of the total energy for large quantum systems. At the same time, the calculation of the total energy is very important, because any change of states in the electron and phonon subsystems of a large quantum system (crystal, disordered solid) leads to a change in the value of its total energy. Local and total phase transitions, in particular, are also accompanied by a change in the total energy, and its estimates are of fundamental importance for understanding the features of structural and other transformations under the influence of radiation and electromagnetic radiation on functional materials. Local phase transitions, for example, take place in the processes of optical recording of information in nanocrystalline and amorphous semiconductor films [2, 23, 24].

The total energy, as a fundamental characteristic, comprehensively characterizes the functional material as a physical object with all possible elementary excitations in it, including, as a rule, many problems of exciting the electronic and phonon subsystems, as well as their interaction [3, 25, 26]. The most natural way to estimate the total energy of large quantum system is apparently based on the formalism of the functional electron charge density $\rho(\mathbf{r})$ [27, 28]. The total energy as a density functional for the ground state of a multielectron system in the presence of an external potential can be presented in the form:

$$E_{\text{tot}}[V_{\text{EXT}}, \rho] = E_{\text{ee}}[V_{\text{EXT}}, \rho] = T[\rho] + \int d\mathbf{r} V_{\text{EXT}}(\mathbf{r})\rho(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{\text{XC}}[\rho], \quad (3.36)$$

where the kinetic energy, the energy of interaction of the electron gas with the external potential, the energy of the electron–electron interaction and the exchange–correlation energy are summed up. There are three main problems of this general formula (3.36) using:

1. The finding of $\rho(\mathbf{r})$ that minimizes the functional $E_{\text{tot}}[V_{\text{EXT}}, \rho]$
2. The estimation of the kinetic energy functional $T[\rho(\mathbf{r})]$
3. The estimation of the exchange–correlation energy functional

A consistent but very laborious way of calculation was proposed by Kohn and Sham [27, 28]. On the basis of the solution of a system of one-electron equations for varying wave functions of fictitious noninteracting electrons:

$$\{-\nabla^2 + V_{\text{KS}}[\rho(\mathbf{r})]\}\varphi_j(\mathbf{r}) = \varepsilon_j\varphi_j(\mathbf{r}), \quad (3.37)$$

where φ_j and ε_j are one-particle eigenfunctions and eigenvalues and $V_{\text{KS}}[\rho(\mathbf{r})]$ is the integrally differential of potential:

$$V_{\text{KS}}[\rho(\mathbf{r})] = V_{\text{EXT}}(\mathbf{r}) + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \frac{\partial E_{\text{XC}}[\rho(\mathbf{r})]}{\partial \rho(\mathbf{r})} = V_{\text{EXT}}(\mathbf{r}) + V_{\text{C}}[\rho(\mathbf{r})] + V_{\text{XC}}[\rho(\mathbf{r})], \quad (3.38)$$

where V_{C} is the Coulomb potential and V_{XC} is the exchange–correlation potential. Then, $\rho(\mathbf{r})$ is determined in a self-consistent manner similar to the procedure in the Hartree–Fock–Slater method. The kinetic energy of the many-electron system is calculated as:

$$T[\rho] = \sum_j \langle \varphi_j | \varepsilon_j - V_{\text{KS}}[\rho] | \varphi_j \rangle. \quad (3.39)$$

Further, the local density approximation is usually used, consisting of a slowly varying $\rho(\mathbf{r})$; hence, we can assume:

$$E_{\text{XC}}[\rho] \cong \int d\mathbf{r} \rho(\mathbf{r}) \varepsilon_{\text{XC}}[\rho(\mathbf{r})], \quad (3.40)$$

where $\varepsilon_{\text{XC}}[\rho(\mathbf{r})]$ is the exchange–correlation energy per electron of density $\rho(\mathbf{r})$ of a homogeneous electron gas. The corresponding exchange–correlation potential is then represented in the form of $V_{\text{XC}} = \partial E_{\text{XC}} / \partial \rho$.

We can meet various representations for E_{XC} . In this case, we only note the way of finding in the form:

$$\varepsilon_{\text{XC}} = \varepsilon_{\text{X}} + \varepsilon_{\text{C}}, \quad (3.41)$$

taking into account:

$$\epsilon_X = -0.9164/r_S, \quad (3.42)$$

$$\epsilon_C = \begin{cases} -0.2846/(1 + 1.9529r_S^{1/2} + 0.3334r_S, & \text{if } r_S \geq I, \\ -0.0960 + 0.0622 \ln r_S - 0.0232r_S + 0.004r_S \ln r_S, & \text{if } r_S < I, \end{cases} \quad (3.43)$$

where r_S is Wigner radius. Then, the exchange-correlation potential is obtained in the form:

$$V_{XC} = \epsilon_{XC} - \frac{r_S}{3} \frac{d\epsilon_{XC}}{dr_S}. \quad (3.44)$$

The Eqs. (3.41, 3.42 and 3.43) make it possible to distinguish ‘pure’ exchange and correlation and can be included in the simulation design scheme. However, if we use Slater’s statistical approximation, we will get:

$$\epsilon_{XC} = \frac{3}{4} \rho(\mathbf{r}) V_{XC}(\mathbf{r}), \quad (3.45)$$

where:

$$V_{XC} = \alpha V_{XS} = V_{X\alpha} = -6\alpha(3\rho(\mathbf{r})/8\pi)^{1/3}, \quad (2/3 \leq \alpha \leq 1).$$

Consequently, in (3.45), the exchange and correlation are not distinguishable. This feature, in a certain sense, is the lack of statistical approximation.

The model of the atom in the statistical approximation of the distribution of the electron charge is based on the fact that the electron subsystem of an atom is considered in the field of its nucleus as an ‘electron liquid’, i.e. as an electron gas with the ‘included’ exchange-correlation interaction.

The approximation, however, is that the electronic subsystem is considered locally free. This means that at each point in space $\mathbf{r}$ the electron of the subsystem is regarded as a plane electron wave. Then the total energy of the atom can be presented as a function of the electron charge density $\rho(\mathbf{r})$:

$$E[\rho(\mathbf{r})] = \int \frac{3}{5} (3\pi^2)^{2/3} \rho^{5/3}(\mathbf{r}) d\mathbf{r} + \int \rho(\mathbf{r}) v_n(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \rho(\mathbf{r}) v_e(\mathbf{r}) d\mathbf{r} + \int \rho(\mathbf{r}) v_x[\rho(\mathbf{r})] d\mathbf{r}, \quad (3.46)$$

where v_n , v_e and v_x are the corresponding electron–nucleon, electron–electron and exchange-correlation interaction potentials. Assuming that, on the average, the charge of an electron of an atom is distributed in a spherically symmetric manner with respect to the nucleus is possible to represent (3.46) in the form:

Table 3.2 Total energies of the ground states of atoms

Atom	$E_{\text{tot}}, \text{Ry}$	$E_{\text{tot}}^{\text{XF}}, \text{Ry}$ [1, 29]
Ne	−264.904	−257.067
Si	−571.258	−577.638
P	−679.411	−681.297
S	−786.024	−794.923
Ar	−1036.516	−1053.635
Ge	−4188.585	−4150.718
As	−4712.566	−4468.256
Se	−5019.476	−4799.731
Xe	−5563.094	−5504.111

$$E[\rho(r)] = \int \left[\frac{3}{5}(3\pi^2)^{2/3} \rho^{5/3}(r) + \frac{1}{2} \rho(r) V_e(r) - \rho(r) \frac{2Z}{r} - \frac{9}{2} \alpha \left(\frac{3}{8\pi} \right)^{1/3} \rho^{4/3}(r) \right] 4\pi r^2 dr. \quad (3.47)$$

Table 3.2 shows the energies of the ground states of atoms calculated according to formula (3.47) (see [22, 23]) in comparison with the results of self-consistent calculations [1, 29]. In [22], the detailed numerical studies of various contributions to the total energy are given, $E_{\text{tot}} = T_e + U_{\text{en}} + U_{\text{ee}} + U_{\text{xc}}$, where T_e is the total kinetic energy of the electron charge, U_{en} is the energy of interaction of the electron gas with the nucleus, U_{ee} is the energy of the interelectronic interaction and U_{xc} is the energy of the exchange-correlation interaction.

Note that the discrepancy of evaluations by the analytical relationship (3.47) of E_{tot} with self-consistent calculations does not exceed 5%. This procedure can also be used to calculate the total energy of more complex systems (e.g. molecules, nanoclusters, etc.). The necessary condition in this case is the construction of realistic electron charge density functions $\rho(\mathbf{r})$ and one-electron potentials of the above-mentioned systems $V(\mathbf{r})$ based on the superposition principle. The ability to calculate the total energy of nanoclusters is fundamental. For disordered systems, this is extremely important, since such systems are represented by a set of nanoclusters which are close in their properties, geometry and morphology. The size of such a nanocluster is estimated by the characteristic order parameter L . In fact, this is a quasi-translational ‘symmetry’ with a ‘period’.

As for complex composite systems (e.g. binary compounds $A_x B_{1-x}$), such large clusters are formed of basic structural units or small (basic) clusters characterizing the system at the level of short-range order.

This approach in consideration of the atomic structure was used in calculations of the density of electronic states $\text{As}_x\text{Se}_{1-x}$, $\text{Sb}_x\text{Se}_{1-x}$ and $\text{As}_x\text{S}_{1-x}$ [14, 30–32]. The calculations of the total energy are performed in different ways of computing the electronic structure of polyatomic complexes, since the total energy is a self-consistent parameter [1]. However, in most cases the calculation approaches use the concept of the density functional [33]. The difference is only

in the value of the electronic charge, which is included in the core part, and the remainder of it, which is responsible for the interatomic interaction.

To calculate the total energy of the cluster:

$$E^{\text{CL}} = E_{\text{ion}} + E_{\text{ee}}[V_{\text{ext}}, \rho], \quad (3.48)$$

where E_{ion} and E_{ee} are the internuclear and electronic parts of the total energy; it is necessary to use cluster sums for the electron density:

$$\rho^{\text{CL}}(\mathbf{r}, \mathbf{R}_1, \dots, \mathbf{R}_N) = \sum_i \rho^i(\mathbf{r} - \mathbf{R}_i), \quad (3.49)$$

and potentials:

$$V_{\text{EXT}}^{\text{CL}}(\mathbf{r}, \mathbf{R}_1, \dots, \mathbf{R}_N) = 2 \sum_i \frac{Z_i}{|\mathbf{r} - \mathbf{R}_i|}, \quad (3.50)$$

$$V_{\text{ee}}^{\text{CL}}(\mathbf{r}, \mathbf{R}_1, \dots, \mathbf{R}_N) = \sum_i V_e^i(\mathbf{r} - \mathbf{R}_i). \quad (3.51)$$

Taking into account that all significant changes in the system are related to the outer ('core') part of the electron cloud, it is advisable to introduce a certain version of the MT-approximation into the calculation scheme. Cutting out the 'core parts' of ρ^{CL} , $V_{\text{EXT}}^{\text{CL}}$ and $V_{\text{ee}}^{\text{CL}}$ by the 'MT-spheres', and considering them spherically symmetric inside the 'MT-spheres', we get:

$$E^{\text{CL}} = \sum_i E_i^{\text{MT}} + \sum_{i \neq j} \frac{Z_i' Z_j'}{|\mathbf{R}_i - \mathbf{R}_j|} + T_e' + U_{\text{en}}' + U_{\text{ee}}' + U_{\text{xc}}', \quad (3.52)$$

where T_e' , U_{en}' , U_{ee}' and U_{xc}' are analogues of corresponding quantities $T_e, U_{\text{en}}, U_{\text{ee}}$ and U_{xc} .

However, it must be taken into account that in this case the integration of functions without spherical symmetry over the interstitial space is performed, i.e. triple integrals of the type $\Omega^{-1} \int F(\vec{r}) d\vec{r}$ are computed. $E[\rho(\mathbf{r})]$ is found according to the procedure (3.47) when integrating over the volume of the 'MT-sphere'.

The excess charge of the core $Z' = Z - \int_0^{R_{\text{MT}}} \overline{\rho^{\text{CL}}(\mathbf{r})} 4\pi r^2 dr$, where $\overline{\rho^{\text{CL}}(\mathbf{r})}$ is the density of the electron charge, averaged over the spherical layers. In this case, the radius R_{MT} may not coincide with the analogous one for the potentials [2.5–7] because Z should be equal to the number of valence electrons of a given atom.

The total energy of the whole system can be considered as $E_{\text{tot}}^{\text{sys}} \cong \sum_i E_{\text{tot},i}^{\text{CL}} + E_{\text{rest}}$. Especially when it comes to local (intra-cluster) changes

$\Delta E_{\text{tot}}^{\text{sys}} \cong \Delta \sum_i E_{\text{tot},i}^{\text{CL}}$ in the total energy of the non-perturbing 'rest medium'.

3.6 Interatomic Interaction Potentials and Force Calculations

The calculation of the dynamic properties of solids is based on the knowledge of the forces $\mathbf{F}_i$ acting on the corresponding ions with coordinates $\mathbf{R}_i$.

Then, for the cluster we have:

$$\mathbf{F}_i = -\nabla_{\mathbf{R}_i} E^{\text{CL}} = 2 \sum_{i \neq j} \frac{Z'_i Z'_j (\mathbf{R}_i - \mathbf{R}_j)}{|\mathbf{R}_i - \mathbf{R}_j|^3} - \nabla_{\mathbf{R}_i} E_{\text{ee}} = \mathbf{F}_i^{\text{ion}} + \mathbf{F}_i^{\text{el}}. \quad (3.54)$$

Significant problems arise with the evaluation of the second term, which has a complex structure, since according to (3.49, 3.50 and 3.51) ρ^{CL} , $V_{\text{EXT}}^{\text{CL}}$ and $V_{\text{ee}}^{\text{CL}}$ are functions of the positions of the ions $\mathbf{R}_j$. Consequently, each value of the number T_e' , U'_{en} , U'_{ee} and U'_{xc} will contain their gradients $\nabla_{\mathbf{R}_i}(\dots)$. Then it is possible to write:

$$\begin{aligned} \mathbf{F}_i^{\text{el}} = & - \int d\mathbf{r} \frac{\partial V_{\text{EXT}}(\mathbf{r}, \mathbf{R})}{\partial \mathbf{R}_i} \rho(\mathbf{r}, \mathbf{R}) - \int d\mathbf{r} V_{\text{EXT}}(\mathbf{r}, \mathbf{R}) \frac{\partial \rho(\mathbf{r}, \mathbf{R})}{\partial \mathbf{R}_i} = \\ & - \int d\mathbf{r} \frac{\partial V_{\text{EXT}}(\mathbf{r}, \mathbf{R})}{\partial \mathbf{R}_i} \rho(\mathbf{r}, \mathbf{R}) - \int d\mathbf{r} \frac{\delta E_{\text{ee}}}{\delta \rho} \frac{\partial \rho(\mathbf{r}, \mathbf{R})}{\partial \mathbf{R}_i} = \mathbf{F}_i^{\text{el}(1)} + \mathbf{F}_i^{\text{el}(2)}, \end{aligned} \quad (3.55)$$

where $V_{\text{EXT}}(\mathbf{r}, \mathbf{R})$ is the ‘external’ ‘crystalline’ potential and $\mathbf{R} = \{\mathbf{R}_j\}$ is a set of coordinates of atoms.

Forces in the electron-ion system, which do not contain density gradients of the type $\nabla_{\mathbf{R}_i} \rho$, together represent the so-called Hellmann–Feynman force $\mathbf{F}_i^{\text{HF}} = \mathbf{F}_i^{\text{ion}} + \mathbf{F}_i^{\text{el}(1)}$, which takes into account the classical electrostatic interaction and is determined only by the potential gradients. In our case:

$$\begin{aligned} \mathbf{F}_i^{\text{el}(1)} = & - \int \frac{\partial}{\partial \mathbf{R}_i} \sum_{i \neq j} \frac{2Z_i}{|\mathbf{R}_i - \mathbf{R}_j|} \rho^{\text{CL}}(\mathbf{r}, \mathbf{R}_1, \dots, \mathbf{R}_N) d\mathbf{r} \\ & + \frac{1}{2} \int \frac{\partial}{\partial \mathbf{R}_i} V_{\text{ee}}^{\text{CL}}(\mathbf{r}, \mathbf{R}_1, \dots, \mathbf{R}_N) d\mathbf{r}, \end{aligned} \quad (3.56)$$

where analytical functions are used. The force $\mathbf{F}_i^{\text{el}(2)}$ that is usually found from the Schrödinger equation by the variation Kohn–Sham procedure [27, 28] can also be obtained directly using analytical functions. In a simpler version of the evaluation of force characteristics, and following the general rules of potential modelling, we can write down the potential of the pair interaction:

$$\Phi(R) = \int \rho_1(r) V_2(R-r) 4\pi r^2 dr, \quad (3.57)$$

and the interaction force:

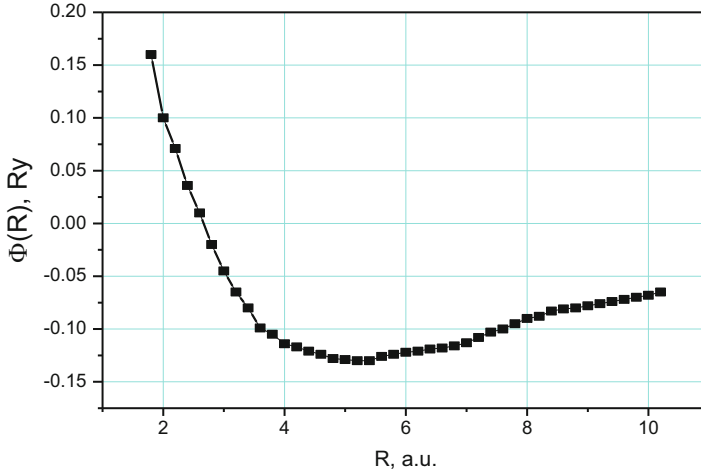


Fig. 3.3 Model potential of pair interaction of Se atoms

$$F(R) = -d\Phi/dR = \int \rho_1(r)[dV_2(R-r)/dR]4\pi r^2 dr, \quad (3.58)$$

where $\rho_1(r)$ is the density of the electron charge of atom 1 (central) and $V_2(R-r)$ is the potential of atom 2 or ‘quasi-atom’ 2, which, in fact, expresses the potential of the ‘rest medium’ (i.e. crystalline potential) [15]. Figure 3.3 shows the model potential of the pair interaction for Se calculated on the basis of (3.57).

3.7 Multiple Scattering Theory and Effective Media Approach

The absence of a structural periodicity of disordered materials makes it difficult to describe their electronic structure in general. The main difficulty is to set the boundary conditions that would be adequate for physical conditions with a limited fragment of the structure, namely, a cluster. In fact, the only reasonable possibility in this case is to use various modifications of boundary conditions of the ‘effective medium’ type, which is the carrier of the disorder property of matter in the far field. The features of the near and middle orders, as a rule, are taken into account in detail.

The experience of numerical calculations shows that a significant increase in the size of the considered fragment of the structure, at which boundary conditions can be neglected in general, is not effective and requires a lot of computer time. In addition, macroscopic physical quantities in disordered materials do not depend on the detailed configurations of atoms and are obtained by averaging over the set of possible configurations. The averaged information about the structure is contained in paired and many-particle distribution functions. This fact is a formal basis for

statistical averaging of other physical quantities, and the calculation of large structural fragments has no practical meaning.

Another aspect of the problem is the formal (i.e. mathematical) implementation of the cluster approach using any version of the concept of an effective medium.

In this sense, there are two basic possibilities: (1) the *tight-binding approximation* using one or another standard basic set of wave functions and (2) the *nearly free electron approximation*, which is usually based on the scattering theory and uses the Bessel functions as a key set.

3.7.1 Methods of Electronic Structure Calculation of Non-regular Condensed Materials

As it has already been mentioned, the problem of effectively calculating the electronic properties of structurally disordered substances can be solved in different ways of approximation of the effective medium, which differ from each other by the method of approximate averaging of the total perturbation series for one-electron Green's functions (see, e.g. [34]). Thus, for example, in the stationary case, when the system is characterized by a Hamiltonian:

$$H = H_0 + H_1, \quad (3.59)$$

where H_0 is the Hamiltonian of non-perturbed system, H_1 is the perturbation and the corresponding Green's functions are given by the resolvents:

$$G_0(z) = (z - H_0)^{-1}, \quad (3.60)$$

$$G(z) = (z - H)^{-1}, \quad (3.61)$$

and the perturbation series for $G(z)$ is as follows:

$$G = G_0 + G_0 H_1 G_0 + G_0 H_1 G_0 H_1 G_0 + \dots = G_0 + G_0 H_1 G. \quad (3.62)$$

Next, we introduce the transition T -matrix $T(z)$, in which all perturbation effects H_1 are automatically taken into account, that is:

$$H_1 G = T G_0, \quad (3.63)$$

which yields from (3.62):

$$G = G_0 + G_0 T G_0. \quad (3.64)$$

Naturally, the introduction of $T(z)$ itself does not solve the problem of the spectrum of the perturbed system but only shifts the emphasis in this problem and allows us to rewrite a number of perturbations (3.62) in the form:

$$T = H_1 + H_1 G T. \quad (3.65)$$

Further, taking into account a specific nature of the disordered system, the configurational averaging of the Green's function in (3.64) is performed. Details of the averaging procedure are determined by the properties of the disordered system itself. In accordance with (3.62) and (3.64), the following averaging possibilities arise:

$$\langle G \rangle = G_0 + G_0 \langle H_1 G \rangle \quad (3.66)$$

and

$$\langle G \rangle = G_0 + G_0 \langle T \rangle G_0. \quad (3.67)$$

The assumption $\langle H_1 G \rangle \cong \langle H_1 \rangle \langle G \rangle$ in (3.66) leads to the so-called virtual crystal approximation.

In the case of $\langle H_1 \rangle = \varepsilon$, we obtain:

$$\langle G(E) \rangle = (E - H_0 - \varepsilon)^{-1} = (E - \langle H \rangle)^{-1}. \quad (3.68)$$

Actually, $\langle G(H) \rangle$ is calculated as $\langle G(\langle H \rangle) \rangle$ and only leads to a shift of the energy scale by ε . This shift can be eliminated by selecting $H_0 = \langle H \rangle$ and $H_1 = H - \langle H \rangle$. Then, we obtain $\langle G \rangle = G_0$.

The possibility associated with averaging, according to (3.67), considers $T = f(\{t_m\})$ as a function of the individual T -matrices of the individual nodes $\mathbf{m}$. Then, if we assume:

$$\langle T \rangle = f(\langle t_m \rangle), \quad (3.69)$$

we get the *average T-matrix approximation*. In this case, the shift of the spectrum occurs on a complex energy-dependent quantity, i.e. similarly to (3.68), we have:

$$\langle G(E) \rangle = (E - H_0 - \Sigma(E))^{-1}, \quad (3.70)$$

where, for example, in the case of a *single-site approximation*, we obtain:

$$\Sigma = \frac{\langle t_m \rangle}{1 + \langle t_m \rangle G_0(\mathbf{m}, \mathbf{m})}, \quad (3.71)$$

More consistently, the concept of an effective medium is carried out in the coherent potential approximation (CPA), where an unknown effective Hamiltonian H_e of some effective medium with unknown complex energy-dependent eigenvalues Σ is immediately introduced. Then, in the expansion (3.64), instead, we use the effective Green's function $G_e = (E - H_e)^{-1}$. Then

$$G = G_e + G_e T' G_e, \quad (3.72)$$

where

$$T' = H'_1 + H'_1 G_e T', \quad (3.73)$$

$$H'_1 \equiv H - H_e. \quad (3.74)$$

Following the well-known definitions, the Green's function averaged over the configuration is calculated as:

$$\langle G(z) \rangle = \langle (z - H)^{-1} \rangle = \left(z - H_0 - \sum \langle z \rangle \right)^{-1}. \quad (3.75)$$

Specify further the definition of the Hamiltonian of the system in the following way:

$$H = (H_0 + V_e(z)) + (V - V_e(z)) = H_e + H'_1, \quad (3.76)$$

where V is the potential of the then studied material and $V_e(z)$ is the energy-dependent effective potential. By averaging in (3.72), we obtain:

$$\langle G(z) \rangle = G_e + G_e \langle T' \rangle G_e, \quad (3.77)$$

$$\sum \langle z \rangle = z - H_0 - [\langle G(z) \rangle]^{-1} = V_e + \langle T' \rangle (1 + G_e \langle T' \rangle)^{-1}, \quad (3.78)$$

provided:

$$\langle T(z) \rangle = 0, \quad (3.79)$$

allows finding $\Sigma(z)$. The condition (3.79) implies the *coherent potential approximation* (CPA), which under the given conditions is the simplest and is equivalent to the choice $\langle G \rangle = G_e$.

Table 3.3 [22] presents the main calculation methods associated with the concept of an effective medium.

Moreover, a virtual crystal approximation might not be totally reliable, because in this case the role of the effective medium is fulfilled simply by the real averaged potential. The moment and the recursive methods are reduced to the calculation of $G(z)$ and the partial densities of different groups of atoms in the system, which is equivalent to the $G(z)$ moment expansion in the form of the density of states of different orders or continued fractions.

The problem of these methods is the convergence of the expansions. The unreasonable breakdown of such expansions leads to unphysical results. An effective medium is not explicitly present here too. As a rule, these approximations are considered in the tight-binding formalism. Here, the long-standing tradition in the band calculations of crystals is affected. Another direction, based on the concept of nearly free electrons, is usually based on the previously mentioned MT-model of scattering potentials. The spherical symmetry of such potentials is a strong simplification of reality, which gives quite good results in many cases.

Table 3.3 Methods of electronic structure calculations using effective medium concepts

Approximation	Contributors
Quasi-crystalline approximation – QCA	M Lax (1951, 1952) J M Ziman (1966) F Cyrot-Lackmann (1966)
Self-consistent quasi-crystalline approximation – SQCA	B L Gyorffy (1970) M Watabe (1971) J Korringa, R L Mills (1972)
Self-consistent single-site approximation – SSSA	L Schwartz, N Ehrenreich (1917) Y Ishida, F Yonezawa (1973) B Movaghar et al. (1974)
Coherent potential approximation – CPA	P Soven (1967) F Yonezawa (1968)
Effective medium approximation – EMA	L Roth (1974)

However, there are also approaches that generalize the MT-model and correct the spherical symmetry of the potentials by taking into account the effects of asymmetry [22–24]. Table 3.4 presents some methods for calculating the electronic structure using the MT-approximation of potentials. These methods are based on the well-known formalism of the KKR method (Korringa–Kohn–Rostoker) [35]. There is also a synthetic direction that combines the advantages of the strong-coupling approximation and MT-model representations (the MTO method of localized MT-orbitals – LMTO) [36].

3.7.2 *Non-regular Condensed Medium: ‘Liquid Metal’ Model*

The simplest idea about a disordered solid is to treat the latter as an ensemble of non-regularly located atomic spheres. It is clear that such a system will be characterized mainly by a pair function of the distribution of atoms. Correlation functions of a higher order have not a decisive significance. Such a model treats a non-regular disordered solid as a liquid [2, 5–7]. It can be a good model for metal and semiconductor metals and, in some cases, glasses of high homogeneity. The developed cluster approach [2, 6, 7] in the case of considering the electronic properties of the aforementioned type of condensed matter, leads to a study of the behaviour of the trial electron wave in the system ‘monatomic cluster + rest medium’ (Fig. 3.4a). In this case, the potential of a single scatterer, enclosed in a cluster volume, takes into account the averaging of the nearest environment from the first coordination sphere. Within the framework of this model, the influence of the nearest neighbour located at the distance a is taken into account. Thus, the potential of a single bond is constructed. This potential plays the role of the crystalline potential of the material being modelled.

Table 3.4 Methods of electronic structure calculations using MT-approximation

Approximation	Objects	Contributors
Quasi-crystalline approximation	Liquid metals	J M Ziman (1966) J Lloyd (1967)
Quasi-crystalline approximation	Transition metals	P W Andersen, W L McMillan (1967)
Self-consistent single-site approximation	Disordered alloys Cu-Ni	L Schwartz, H Ehrenreich (1971)
Concept of finite clusters	Amorphous C, Si, Ge	J Keller (1971) T C McGill, J Klima (1972)
Modified quasi-crystalline approximation	Disordered metal substitutional alloys, liquid metals	L Schwartz et al., (1975)
Self-consistent single-site approximation	Liquid metals	J Bethel, J L Beeby (1977)
Single-site approximation of effective medium	Liquid metals	W John, W Keller (1977)
Coherent potential approximation on the basis of the concept of finite clusters	Amorphous Si	S Yoshino, M Inoue, M Okazaki (1975)
Coherent potential approximation on the basis of the concept of finite clusters	Amorphous semiconductors, Si, Ge, As, Te, Se, Sb, binary chalcogenides, nanocarbon, nano-Si, nano-Se	Yu Shunin (1981–2014)

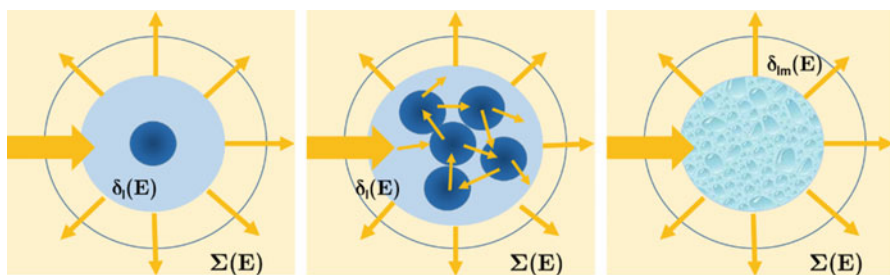


Fig. 3.4 The general scheme of the calculation method for the electronic structure based on the theory of multiple scattering and the coherent potential approximation of an atomic cluster as a group of MT-potentials embedded into effective medium; (a) ‘liquid metal’ model; (b) a polyatomic cluster of predefined atomic structure; (c) a polyatomic cluster with a potential function of a general form. $\Sigma(E)$ is the coherent potential of an effective medium

The next step is based on the crystalline potential of the MT-approximation, according to (3.27); also see Fig. 3.5a–f. The radius of the MT-sphere is chosen equal to a half of the distance to the nearest neighbour [1–3, 5].

The potential (3.27) should be used for the numerical integration of the radial Schrödinger equation (see, e.g. [37]):

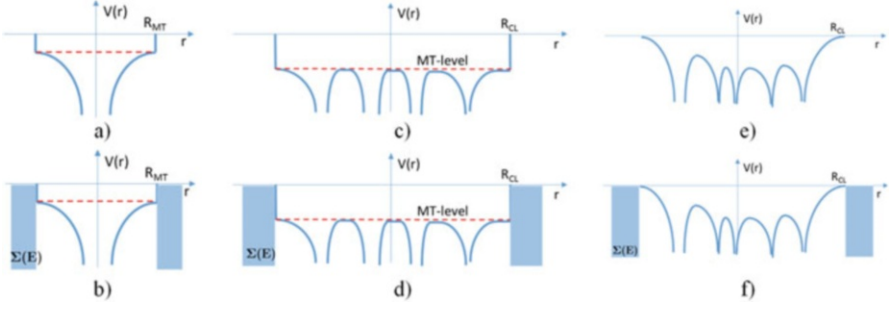


Fig. 3.5 Potential models in the scattering problem for electronic structure calculations of various non-regular disordered materials: (a) MT-potential in vacuum; (b) a group of MT-potentials in vacuum; (c) a general potential in vacuum; (d) a cluster with MT-potential in the effective medium; (e) a cluster of MT-potentials in the efficient medium; (f) a cluster with potential of general form in the effective medium. R_{MT} is the radius of the MT-potential; R_{CL} is the radius of the cluster

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR_l}{dr} \right) + \left[\kappa^2 - \frac{l(l+1)}{r^2} - V(r) \right] R_l = 0 \quad (3.80)$$

and the calculation of logarithmic derivatives $\gamma_l = \frac{R_l'(r)}{R_l(r)} \Big|_{R_{MT}}$, where $R_l(r)$ are the radial wave functions. Then, based on the known relationship, phase shifts δ_l are calculated [37]:

$$\text{tg } \delta_l = \frac{\kappa j_l'(\kappa R_{MT}) - \gamma_l j_l(\kappa R_{MT})}{\kappa n_l'(\kappa R_{MT}) - \gamma_l n_l(\kappa R_{MT})},$$

where $j_l(\kappa r)$ and $n_l(\kappa r)$ are the Bessel and Neumann functions, $\kappa = \sqrt{E}$.

The numerical integration of the Schrödinger Eq. (3.80) was carried out by the Runge–Kutta method. The peculiarity of the algorithm is the fact that the integration interval $(0, R_{MT})$ is divided into two parts. For the small r in the neighbourhood of the singularity of the atomic potential, the solution of (3.80) is sought in the form $R_l = r^l f(r)$, and the equation of the function $f(r)$ has the form:

$$f'' + \frac{2}{r} (l+1) f' + [\kappa^2 - V(r)] f = 0. \quad (3.81)$$

The solution of (3.81) must be regular near the singularity of the potentials. For large r , regions of a weak potential change, the Eq. (3.80) itself is integrated. The solutions in these two regions are sewn together for a small r . The text of the numerical integration programme for the Schrödinger equation, as well as the entire software package for calculation of logarithmic derivatives γ_l and phase shifts δ_l (see, also, Fig. 3.6), is presented in [38–40].

Further, taking into account the spherical symmetry of the potentials (3.27), the radial part of the Green's function is represented in the form:

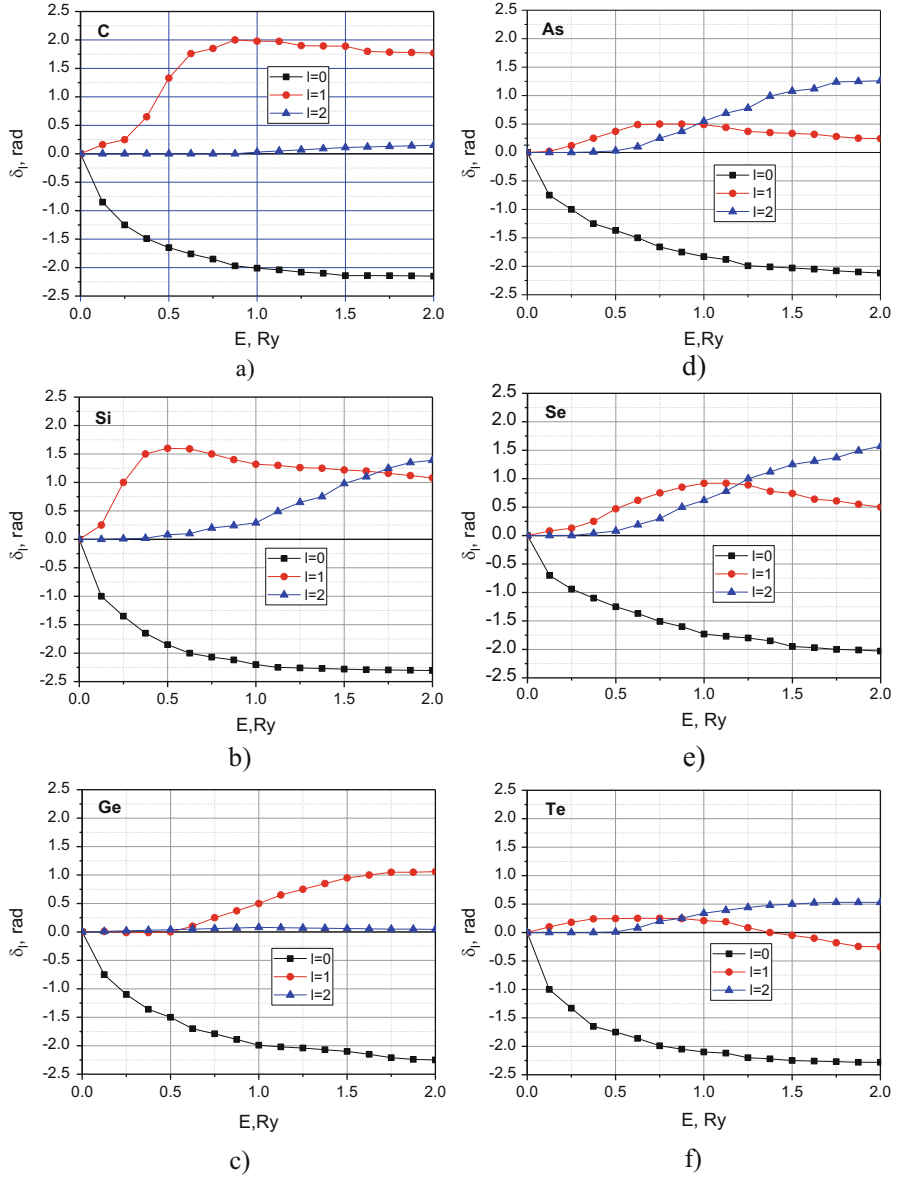


Fig. 3.6 Calculated phase shifts for C, Si, Ge, As, Se and Te scatterers

$$G_l(r, r') = kF_l(kr_>)J_l(kr_<), \quad (3.82)$$

where $r_>$ and $r_<$ are the larger and smaller of $\{r, r'\}$.

The function $J_l(kr) = \cos \delta_{jl}(kr) - \sin \delta_{nl}(kr)$ corresponds to a free electron wave, satisfying the radial Schrödinger equation for $r > R_{MT}$. In order to take into

account the effect of the damping of the electron wave in the far field and the dispersion properties of the effective medium, we must look for $F_l = N_l + A_l J_l$, where $N_l = \cos \delta_l n_l(kr) + \sin \delta_l j_l(kr)$ also satisfies the Schrodinger equation, and A_l is the complex self-consistent coefficient.

As it can be seen, when $A_l = i$, $F_l = \exp(i\delta_l) h_l^{(+)}(kr)$, where $h_l^{(+)}(kr)$ is the Hankel function describing the outgoing wave with asymptotic behaviour $\sim \exp(ikr)/r$ at $r \rightarrow \infty$. Further, based on the constructed Green's function, the density of electronic states is calculated:

$$\rho(E) = \frac{2}{\pi} \text{ImSp} G(\mathbf{r}, \mathbf{r}'; E), \quad (3.83)$$

which, for the monatomic cluster embedded into the effective medium, gives the following expression [2, 6, 7]:

$$\rho(E) = \frac{2}{\pi} \sum_l (2l+1) \left[\frac{d\delta_l}{dE} - R_C^2 J_l^2 \sqrt{E} \frac{\partial \gamma_l(E, R_C)}{\partial E} \right] \text{Im} A_l, \quad (3.84)$$

where R_C is the radius of the cluster sphere and $\gamma_l(E, R_C)$ is the logarithmic derivative at the cluster boundary. Using the self-consistency condition for the coherent potential approximation:

$$\int \langle \mathbf{k} | \tilde{t} | \mathbf{k}' \rangle d\Omega_{\mathbf{k}} = 0; \quad (3.85)$$

within the framework of this model, we obtain the dispersion equation:

$$\sum_l (2l+1) \tilde{t}(K) = \frac{1}{K} \sum_l (2l+1) \exp(i\delta_l) \sin \delta_l(K, R_C) = 0, \quad (3.86)$$

where $\tilde{t}(K)$ is the t -matrix of the effective medium and K is the radial part of the complex wave vector $\mathbf{K}$ of the scattered electron wave $\Psi_E = A \exp(i\mathbf{K}\mathbf{r})$, the damping of which simulates the absence of long-range order in the system. Complex phase shifts $\delta_l(K, R_C)$ and logarithmic derivatives $\gamma_l(K, R_C)$ on the boundary of the cluster are determined in the same way as it was done for the MT-sphere:

$$\text{tg } \delta_l(K, R_C) = \frac{K j_l'(KR_C) - \gamma_l j_l(KR_C)}{K n_l'(KR_C) - n_l j_l(KR_C)}, \quad (3.87)$$

and

$$\gamma_l(k, R_C) = \frac{k [\cos \delta_l j_l'(kR_C) - \sin \delta_l n_l'(kR_C)]}{\cos \delta_l j_l(kR_C) - \sin \delta_l n_l(kR_C)}. \quad (3.88)$$

The self-consistent parameter A_l is then determined from the equation:

$$k \left[\frac{N'_l(kR_c) + A_l J'_l(kR_c)}{N_l + A_l J_l} \right] = K \frac{h_l^{(+)}(KR_c)}{h_l^{(+)}(KR_c)}. \quad (3.89)$$

Numerous calculations for amorphous and nanocrystalline C, Si, Ge, As, Se and Te were carried out based on this model [2, 6, 7].

3.7.3 A Model of a Non-regular Material in the Cluster Approach

The cluster approximation developed in [2, 6, 7, 30–32] consists in considering the structure of the investigated material as a finite cluster embedded into the effective medium (effective energy-dependent potential (see Fig. 3.5)). At first, the atomic structure at the level of the near order and, if required, medium order (e.g. for binary, ternary and more complicated nanocompounds) is postulated.

Then, the construction of crystalline potentials with respect to a given atomic structure is carried out. Various models of crystalline potentials are presented in Fig. 3.6b–e. Further, the MT-approximation of the crystalline potentials is introduced. The MT-approximation symmetrizes crystalline potentials. The scattering problem for individual MT-potentials is solved, and the corresponding phase shifts are found. The cluster of MT-potentials is embedded into the effective complex potential, which is calculated self-consistently. The procedure for constructing MT-potentials is based on the relations (3.23, 3.24, 3.25, 3.26 and 3.27).

Passing to the system of MT-potentials, from the point of view of scattering theory, it becomes inconvenient and cumbersome to use realistic potentials with a complex relief. Therefore, this approach uses a non-local shell energy-dependent pseudopotential:

$$\langle \mathbf{r}_\alpha | V_\alpha | \mathbf{r}'_\alpha \rangle = \sum_{lm} A_{lm}^\alpha(E) \frac{\delta(|\mathbf{r}'_\alpha| - R_{MT}^\alpha)}{(R_{MT}^\alpha)^2} \frac{\delta(|\mathbf{r}_\alpha| - R_{MT}^\alpha)}{(R_{MT}^\alpha)^2} Y_{lm}(\mathbf{r}'_\alpha) Y_{lm}(\mathbf{r}_\alpha), \quad (3.90)$$

where $\mathbf{r}_\alpha$ is the radius vector of the position of the atom. The coefficients A_{lm}^α are selected in such a way as to provide the same scattering properties as for a realistic potential. The calculation of the density of electronic states is based on the Lloyd formula [41–43] for the integral density of states:

$$N(E) = -\frac{2}{\pi} \ln \det \|G(E)\|, \quad (3.91)$$

where $G = G_e + G_e t_e G_e$ and G_e is the unperturbed Green's function and t is the matrix of the effective medium. The density of electronic states of a cluster in an effective medium is calculated by the formula:

$$\rho(E) = \frac{2}{\pi} \Delta [\text{Im} \ln \det \|Z(E) - H'(K)/H(K)\|] / \Delta E, \quad (3.92)$$

where $Z(E)$ are the structural energy-dependent cluster constants, $H(K) = \delta_{ll'} \delta_{mm'} h_l^{(1)}(kR_c)$, $h_l^{(1)}$ is the Hankel function of the 1st kind and R_c is the radius of the cluster. The self-consistency condition in the framework of the coherent potential approximation in this case is as follows:

$$\mathbf{Spt}_e(K, E) = 0, \quad (3.93)$$

where:

$$t_e(K, E) = \frac{Z(E)J(K) - J'(K)}{Z(E)H(K) - H'(K)} - \frac{1}{iK}, \quad (3.94)$$

and

$$J(K) = \delta_{ll'} \delta_{mm'} j_l(KR_c). \quad (3.95)$$

3.7.4 Scattering on the General Type Potential

The problem of electron scattering in a field of the general form potential $V(\mathbf{r})$ leads to finding a solution of Eq. (3.1) that satisfies the boundary condition of the scattered wave. The wave function expansion in terms of partial waves $\Psi(\mathbf{r}) = \sum_L (g_L(r)/r) Y_L(\mathbf{r})$ gives a system of coupled ordinary differential equations in relation to radial wave functions g_L [44, 45]:

$$-\frac{d^2}{dr^2} g_L + \frac{l(l+1)}{r^2} g_L + \sum_L W_{LL'}(r) g_{L'}(r) = E g_L(r), \quad (3.96)$$

where $W_{LL'}(r) = \int Y_L^*(\mathbf{r}) V(\mathbf{r}) Y_{L'}(\mathbf{r}) d\Omega_r$ are the potential moments. The analysis carried out in [21, 22] demonstrates the decoupling of the system of Eq. (3.96), which is reduced to the uncoupled equation set:

$$-\frac{d^2}{dr^2} g_L + \frac{l(l+1)}{r^2} g_L + W_{LL}(r) g_L = E g_L. \quad (3.97)$$

The potential of a general form used as a scatterer can be considered either as a nonspherically symmetric potential of the atom or as a potential of a cluster region with a complex topography of the potential function (see, Fig. 3.6c, f). Numerical simulation was performed for Si nanoclusters embedded in ‘vacuum’ (1, 5, 17-atomic clusters [22]). To construct the potential, it is necessary to take into

account a number of features that distinguish Si, as a semiconductor with a covalent bond, from well-studied ionic compounds. If in ionic compounds the valence electrons are localized near the atomic cores, then in covalent ones valence electrons are distributed in the interstitial space with a high degree of heterogeneity. The maximum density of the electron charge is observed along the bond line of the neighbouring atoms. Such a charge distribution can be interpreted as a homopolar covalent bond. Simulation of this bond is possible in two ways, namely, by (1) cutting off the core part of the electron charge and redistribution of the valence charge along the bond direction and (2) introducing into the Hamiltonian a term that describes the covalent interaction in explicit direct form. In this case, the spatial inhomogeneity of the electron charge density in the cluster volume was due to the superposition of the electron charge densities of the nearest atoms. The described procedure for reproducing the electron charge density of a cluster region with the subsequent construction of its potential based on the principles allows one to estimate the MT-approximation of potentials, where the complex form of the potential function in the interatomic region is replaced by its mean value-MT-zero.

In this sense, the model under consideration can be considered a generalized MT-approximation, since the MT-boundary here is moved on a considerable distance from the centre of the cluster.

Numerical integration of equations of the type (3.97) makes it possible to obtain T -matrix elements, then phase shifts δ_L , which are related to the elements T_L by the known relation $T_L = \exp(2i\delta_L) - 1$. EDOS for the potentials under consideration can be written [12, 13]:

$$\rho(E) = \frac{k}{\pi} R_c^2 \sum_L [\cos \delta_L j_L(kR_c) - \sin \delta_L n_L(kR_c)]^2 \frac{d\gamma_L(k, R_c)}{\Omega dE}, \quad (3.98)$$

where Ω is the cluster volume.

Another way to calculate EDOS is related to direct computations of phase functions T_L , logarithmic derivatives and matrix elements of the T -matrix without direct calculations of wave functions $g_L(r)$. Using the well-known relations, we can obtain the equation for the phase transition function:

$$dT_L(r)/dr = -2ikr^2 W_{LL}(r) \left[j_L(kr) + \frac{1}{2} T_L(r) h_L^{(1)}(kr) \right]^2, \quad (3.99)$$

The initial condition for Eq. (3.99) corresponds to the situation when scattering does not occur. It means that the radius of action of the perturbing potential is zero and $T_L(k, 0) = 0$. Taking into account the relations connecting scattering matrices definitions: $T_L = S_L - 1 = \exp[2i\delta_L] - 1 = 2i \exp[i\delta_L] \sin \delta_L$, we obtain equations for the phase functions $S_L(r)$ of scattering or phase shifts $\delta_L(r)$:

$$dS_L(r)/dr = -\frac{1}{2}ikr^2W_{LL}\left[h_l^{(2)}(kr) + S_L(r)h_l^{(1)}(kr)\right]^2, \quad (3.100)$$

and

$$d\delta_L(r)/dr = -kr^2W_{LL}[j_l(kr)\cos\delta_L(r) - n_l(kr)\sin\delta_L(r)]^2. \quad (3.101)$$

The initial conditions for the Eqs. (3.100) and (3.101) are, respectively, $S_L(k, 0) = 1$ and $\delta_L(k, 0) = 0$. A work with the Eqs. (3.99, 3.100 and 3.101) and, in particular, with the Eq. (3.101) presents notable advantages: (1) phase shifts δ_L are obtained directly from the integration (3.101), which are then used to calculate the EDOS by the formula of type (3.98); (2) during the calculation it is easy to investigate the influence of the form of the potential function on the scattering properties of the potential region; and (3) Eq. (3.101) is a differential equation of the first order, and the computer time expenses are less than in the case of the radial Schrödinger equation integration. However, a serious obstacle in calculating software implementation by the method of phase functions is encountered due to nonlinearity of the differential equations for phase functions. For them, the convergence of various difference schemes and the optimal methods of their construction are poorly studied.

3.8 Monoatomic Nanosystems: Nano-Si, Nano-Se

The successful application of the multiple scattering theory concept in the coherent potential approximation for monoelement nanomaterials with pronounced covalence C, Si, Ge, As, Se, Sb, Te is presented in [2, 6–8, 12, 24]. These materials represent, on the one hand, a wide range of elements of the periodic system, and, on the other hand, they have different coordination at the level of short-range order (the number of nearest neighbours for Se and Te-2, As and Sb-3, C, Si and Ge-4). The main task of modelling is the parametric study of the electronic structure of nanoparticles through the effect of the number of atoms in a nanocluster.

3.8.1 Production of Nanosilicon

There are various ways of nanosilicon production which were developed mainly in the 2000s. Usually the method of plasma-chemical synthesis is used. The technology is as follows: silicon is introduced into argon plasma at the temperature about 6000 °C. It is evaporated, decomposing into separate atoms, and supersaturated vapour is formed. Then, the vapour is condensed and forms silicon nanoparticles of a spherical shape. In fact, nanostructures of 8–200 nm are assembled. Nanopowders of silicon are of undoubted interest for various fields of technology and industry, which begin to experience a great need for these materials because of their unique properties.

3.8.1.1 Nanosilicon Applications

The change of condensation conditions allows, in certain limits, to control the properties of synthesized nanoparticles. The plasma flow is gradually cooled, the silicon atoms are captured and actually re-formed and the 'sought-for' nanostructures are 'assembled'. So, changing the synthesis modes (temperature, cooling rate, etc.), it is possible to control the process of growth of nanosilicon particles.

In particular, it is possible to obtain particles of nanocrystalline silicon of the necessary size (2–50 nm) and the most suitable spherical form. It is also possible to obtain hollow silicon nanospheres from 5 to 60 nm in diameter. Such materials are of great interest for applications in nanophotonics and catalysis. They can be used to create the so-called biological nanocapsules, placing the necessary substances in the internal volume. They can be in demand for the storage of various gases, including hydrogen. Varying the size of such nanospheres, it is possible to control their optical and electronic properties. Obtaining and researching silicon-containing nanoparticles, new properties with the different morphology and structural organization are very relevant.

The possibilities of applying nanosilicon are far from being limited. If, for example, a layer of particles of this chemical element with a thickness no more than 10 nm is applied to the surface of the solar battery, then the battery efficiency will increase by 5% (the main role is played by the effect of re-emission of ultraviolet light quanta). Plasma-chemical nanosilicon can be used in the development of a fundamentally new technology for cancer combating. Its essence lies in the fact that on the surface of spherical particles, oxygen is available. Its usual triplet state is biologically inert. But, if we bring it into an excited, singlet state, 'highlighting' the nanosilicon with a laser, it turns into the strongest oxidizer and literally burns cancer-infected cells, if, of course, the drug is delivered to the right place. Nanodispersed silicon powders have the ability to absorb ultraviolet radiation and are widely used for making sunscreen cosmetics.

3.8.1.2 Other Nanosilicon Applications

In agricultural production, the use of nanosilicon improves the absorption of nitrogen, phosphorus and potassium by crops. Nano-transformed silicon stimulates growth processes and stress resistance of agricultural crops and accelerates the maturation process. The main function of silicon in plants can be called the increasing of the resistance level to any stresses and unfavourable conditions and the ability to withstand toxins.

In medical practice, nanosilicon:

- Creates electrical colloidal systems that have the property of 'sticking' to themselves viruses and pathogens that are dangerous to humans. Organic compounds of silicon are able to form bioelectric charged systems that adhere to pathogens (influenza, fungi, herpes, hepatitis, etc.) and neutralize them

- Plays a major role in the connective tissue components and bonds individual fibres of elastin and collagen
- Together with protein structures promotes the formation of enzymes, amino acids and hormones
- Affects the work of the nervous system and brains (improves the conductivity of nerve fibres and the function of certain structures of the brain and energizes the cerebellum, which is responsible for controlling and coordinating our movements and balance)
- Stimulates the activity of the immune system (increases resistance to viral and bacterial infections) and influences metabolic processes in erythrocytes, monocytes and lymphocytes
- Is an antioxidant that blocks the processes of peroxide and enzymatic oxidation of lipids, which in turn increases the protective functions of the epidermis and increases the resistance of nails and hair to the oxidative effects of free radicals
- Ensures the elasticity of the walls of the vessels and the ability to respond to brain commands to widen and narrow the vessels
- Prevents the penetration of cholesterol into the blood plasma and the deposition of lipids on the vessels walls

In the scientific community, nanosilicon evokes the keenest interest, including the actual creation of new morphological structures such as Si-fullerenes. In this case, nanosilicon becomes economically competitive in comparison with nanocarbon. To obtain nanosilicon is cheaper than nanocarbon, since silicon is presented in nature much wider. Silicon processing technologies are also well developed and very effective. Nanosilicon has many reasons to occupy an important niche in the knowledge-intensive industry and market in the nearest time.

3.8.2 Nanosilicon: Calculations of Electronic Structure

Figure 3.7 shows cluster models of nanosilicon in the effective medium. Figure 3.8 shows EDOS curves and corresponding coherent potentials for 1-, 2- and 5-atomic silicon clusters.

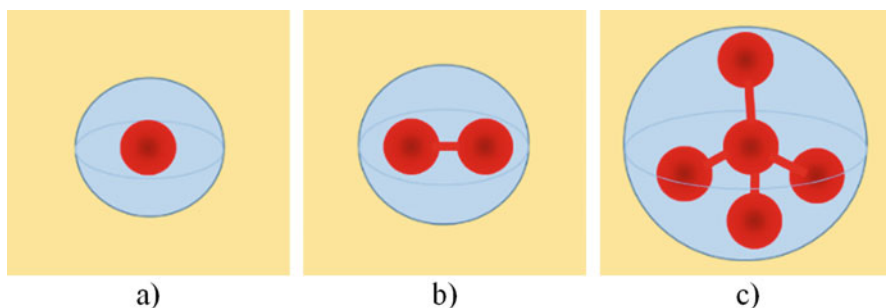


Fig. 3.7 Nanosilicon models: (a) 1-atomic cluster; (b) 2-atomic cluster; (c) 5-atomic cluster. Interatomic distance is 2.22 au

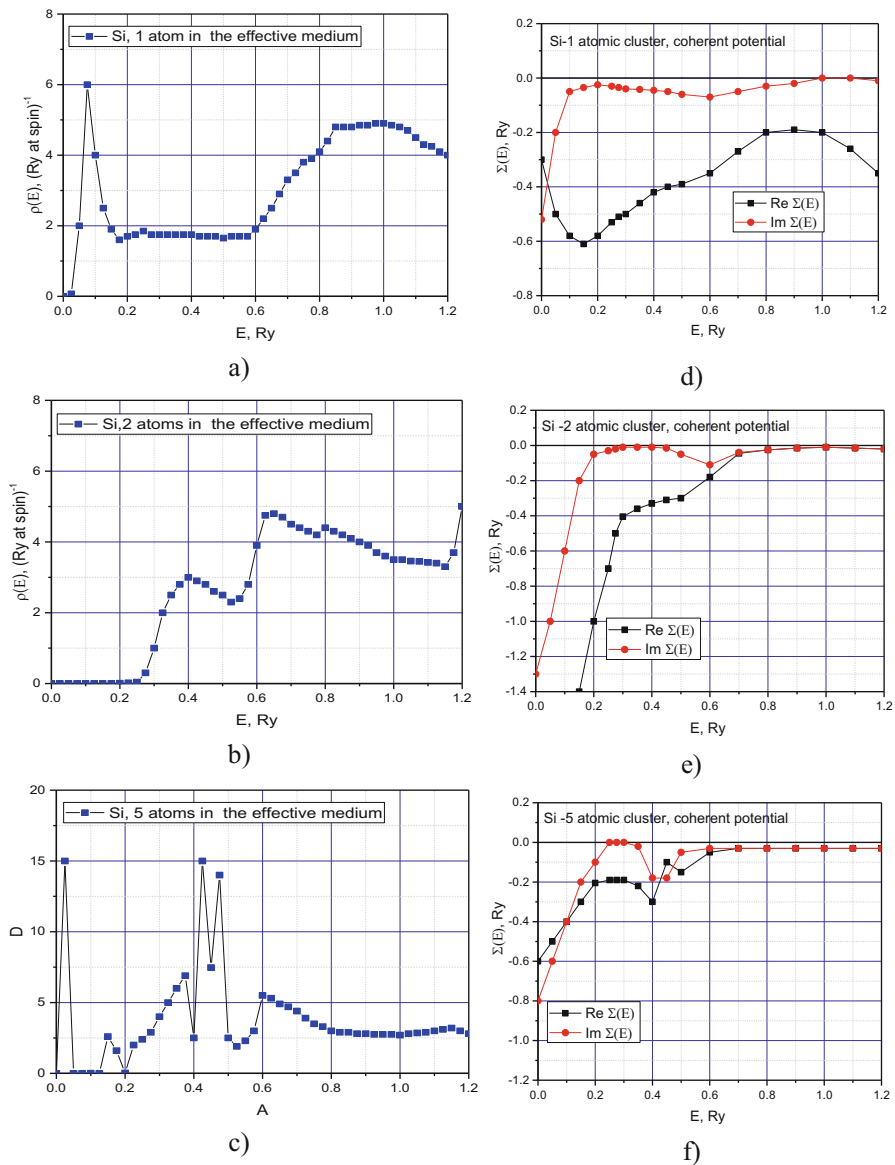


Fig. 3.8 Modelling of nanocrystalline silicon: (a, b, c) – density of electronic states for 1-, 2- and 5-atomic clusters; (d, e, f) – corresponding coherent potentials

Figures 3.9 and 3.10 represent the model and EDOS calculation results for PES 18-atomic cluster as a spherical nanoparticle of 15 nm in diameter, embedded into a ‘vacuum’. Although a solid-state maximum exists in the vicinity $E \sim 0.3\text{Ry}$, the degeneracy of the EDOS curve profile is generally observed. This fact can be

Fig. 3.9 Model of nanoparticle in 'vacuum', 18-atomic cluster, nanoparticle diameter is about 15 nm

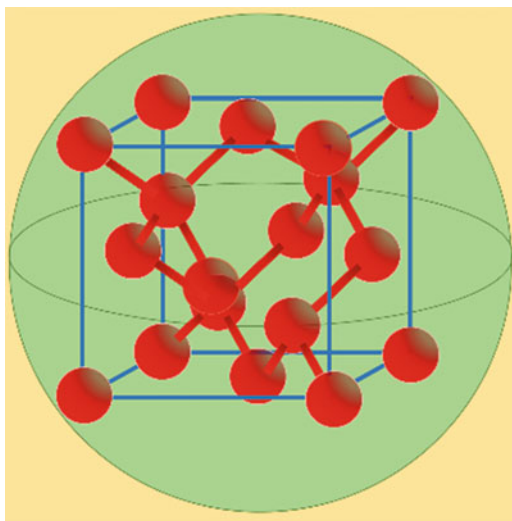
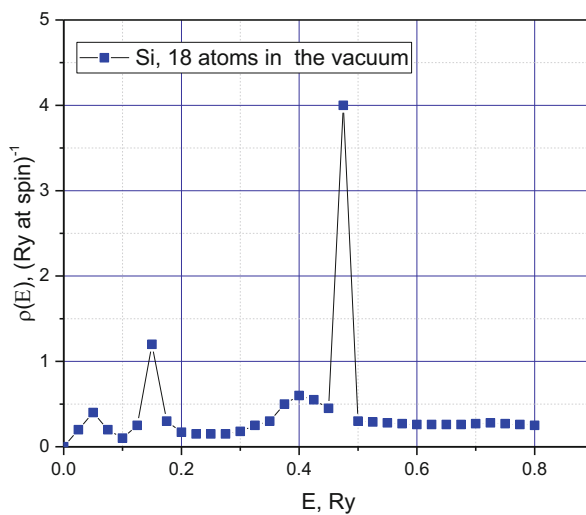


Fig. 3.10 Typical density of electronic density of states of nanosilicon particle



attributed to a decrease in the symmetry of the atomic configuration (in comparison with the symmetry of the 5-atomic cluster).

3.8.3 Selenium Versus Nano-selenium

Selenium (Se) was discovered by the outstanding Swedish chemist Jons Berzelius in 1817. Se is a fairly common microelement. Se is a non-metallic chemical

element, the element of the XVI group of the periodic table. In chemical activity and physical properties, it resembles *sulphur* and *tellurium*. Se appears in a number of allotropic forms: the most popular are *a red amorphous powder*, a red crystalline material and *a grey crystalline metal-like form called metallic selenium*. This last form conducts electricity better in the light than in the dark and is used in photocells. Se burns in air and is unaffected by water but dissolves in concentrated nitric acid and alkalis.

3.8.3.1 General Se Applications

- Se has good photovoltaic and photoconductive properties, and it is used extensively in electronics, such as photocells, light meters and solar cells.
- The second largest use of selenium is in the glass industry: selenium is used to remove colour from glass, to give a red colour to glasses and enamels.
- The third main use, taking about 15%, is sodium selenite for animal feeds and food supplements.
- Se can also find applications in photocopying, in the toning of photographs. Its artistic use is to intensify and extend the tonal range of black and white photographic images.
- Other uses of selenium are in metal alloys such as lead plates used in storage batteries and in rectifiers to convert AC current in DC current. Selenium is used to improve the abrasion resistance in vulcanized rubbers. Some selenium compounds are added to antidandruff shampoos.

3.8.3.2 Nano-selenium in the Environment

- Se is among the rarer elements on the surface of this planet and is rarer than silver. Selenium is present in the atmosphere as methyl derivatives. Non-combined Se is occasionally found, and there are around 40 known selenium-containing minerals, some of which can have as much as 30% selenium – but all are rare and generally they occur together with sulphides of metals such as copper, zinc and lead.
- The main producing countries are Russia, the USA, Bolivia and Canada. Global industrial production of selenium is around 1500 tonnes a year, and about 150 tonnes of Se are recycled from industrial waste and reclaimed from old photocopiers.
- Se occurs naturally in the environment. It is released through both natural processes and human activities. Well-fertilized agricultural soil generally has about 400 mg/ton since the element is naturally present in phosphate fertilizers and is often added as a trace nutrient. In its natural form as an element, selenium cannot be created or destroyed, but Se does have the ability to change form.

- The behaviour of Se in the environment strongly depends upon its interactions with other compounds and the environmental conditions at a certain location at a certain time.
- Se can accumulate in the body tissues of organisms and can then be passed up through the food chain.

3.8.3.3 Health Effects of Nano-selenium

Humans may be exposed to selenium in several different ways:

- Se exposure takes place either through food or water or when we come in contact with soil or air that contains high concentrations of selenium. This is not very surprising, because selenium occurs naturally in the environment extensively and it is very widespread. The exposure to selenium mainly takes place through food, because selenium is naturally present in grains, cereals and meat.
- Humans need to absorb certain amounts of Se daily, in order to maintain good health. Food usually contains enough selenium to prevent disease caused by shortages.
- Se uptake through food may be higher than usual in many cases, because in the past many selenium-rich fertilizers have been applied on farmland.
- Se poisoning may become so severe in some cases that it can even cause death.
- Overexposure of selenium fumes may produce accumulation of fluid in the lungs, garlic breath, bronchitis, pneumonitis, bronchial asthma, nausea, chills, fever, headache, sore throat, shortness of breath, conjunctivitis, vomiting, abdominal pain, diarrhoea and enlarged liver. Se is an eye and upper respiratory irritant and a sensitizer. Overexposure may result in red staining of the nails, teeth and hair. Selenium dioxide reacts with moisture to form selenious acid, which is corrosive to the skin and eyes.

Se demonstrates:

- Three antigenic functions on hepatitis B
- Three antigenic functions on hepatitis C
- A magical liver protection ability being the natural killer of liver diseases

3.8.4 Nano-selenium: Calculations of Electronic Structure

Cluster models of the nano-selenium are presented in Fig. 3.11.

The results of the EDOS modelling and the corresponding coherent potentials of nanocrystalline models (Fig. 3.11) are presented in Fig. 3.12. It is shown that the 3-atomic cluster reflects the electronic properties of amorphous selenium, and the 7-atomic cluster gives the main features of its nanocrystalline modification [6–8, 12]. The structural data used in the calculations corresponds to trigonal selenium.

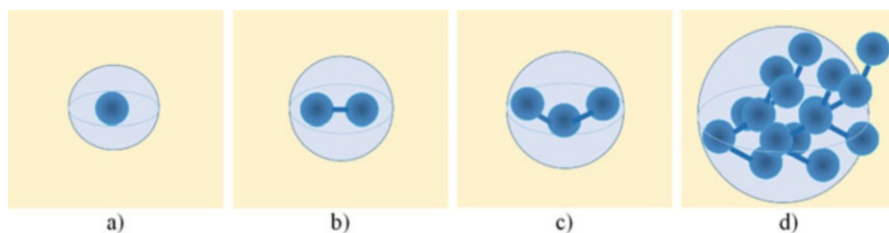


Fig. 3.11 Nano-selenium models: (a) 1-atomic cluster; (b) 2-atomic cluster; (c) 3-atomic cluster; (d) 7-atomic cluster. Interatomic distance is 2239 a.u

The purpose of this numerical study is to find out at which level of a short-range order the crystalline properties begin to appear. The obtained data indicate that the second coordination sphere already sufficiently well determines the nanocrystalline properties. This is consistent, in particular, with the Ioffe–Regel hypothesis, about the decisive role of a short-range order in determining the electronic properties of non-regular disordered semiconductor materials.

3.9 Nanocompounds: *Nanochalcogenides*

A fundamental difficulty in modelling electronic properties of the binary chalcogenide-type compounds is the reproduction of the composition characteristic x . Calculations have demonstrated that the short-range order at the level of the first coordination sphere of the atomic structure under consideration makes it possible to obtain the correct EDOS of monoelement amorphous and nanocrystalline semiconductors. In fact, this means the essential role of nanoscale factors. This circumstance made it possible to apply a similar calculation scheme for binary chalcogenides. However, in this case, it is necessary to solve the problem of constructing ‘crystalline’ potentials of a binary compound for any x , which is for monoelemental materials looks relatively simple [2, 34]. However, if the problem of potentials can be considered technical, then the concept of the structure of a binary compound is nontrivial and cannot be based only on the level of a short-range order.

The atomic structure of the system for arbitrary x is a system with a medium order.

Namely, this level of the structural configuration can provide the reproduction of the atomic structure characteristic of a given ‘ x ’. It should be taken into account that this is not a substitutional alloy with a regular matrix but a system with explicit topological disorder.

From the point of view of the cluster model developed in [2, 22, 23], the structure of a non-regular binary compound can be considered as a set of different basic clusters represented in a structural matrix with different statistical weights

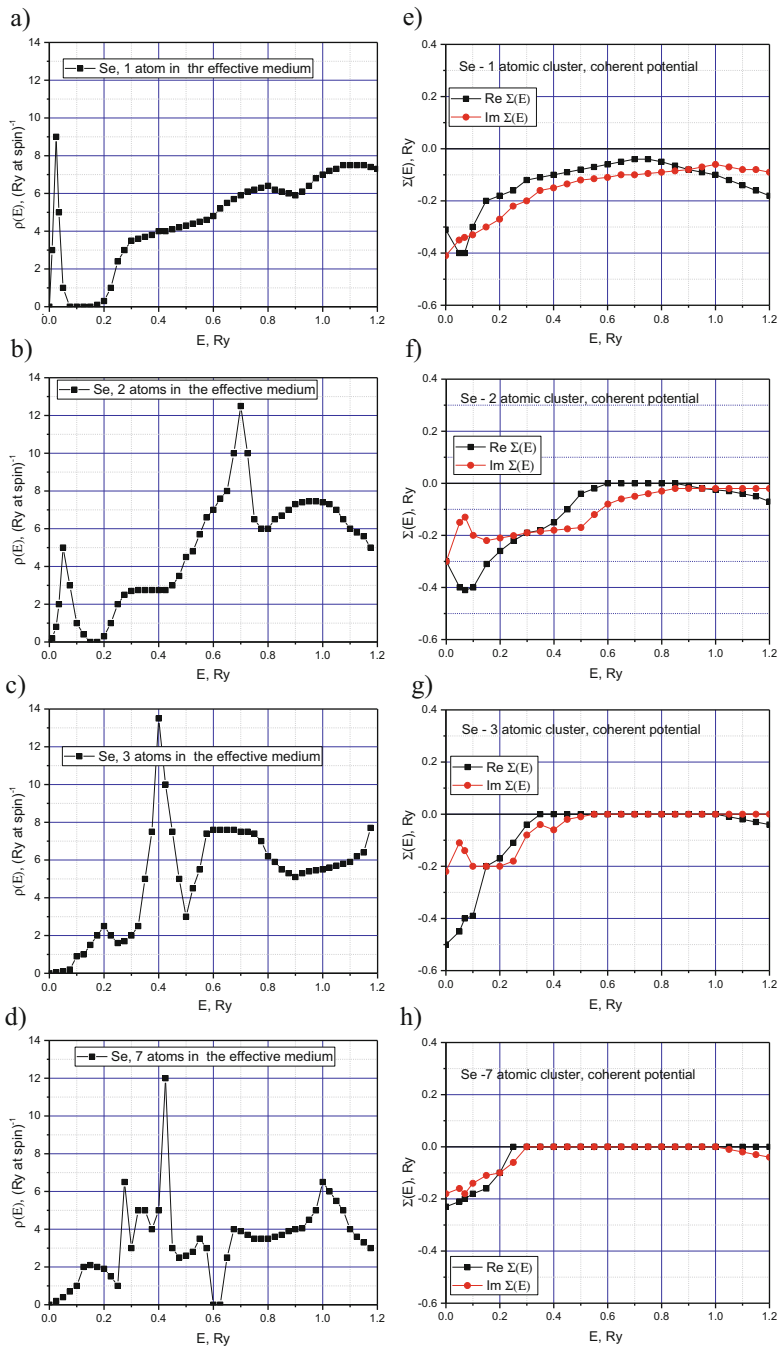


Fig. 3.12 Modelling of nanocrystalline selenium: (a, b, c, d) – density of electronic states for 1-, 2-, 3- and 7-atomic clusters; (e, f, g, h) – corresponding coherent potentials

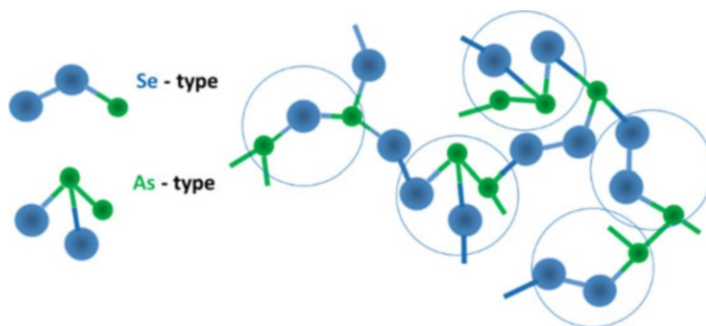


Fig. 3.13 Model of chalcogenide nanocrystalline material based on the concept of structural units: binary compound with As-type and Se-type structural units

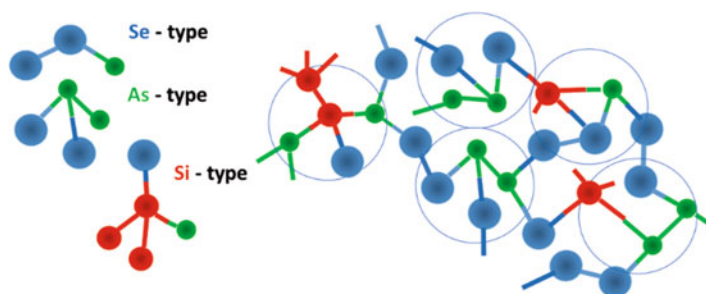


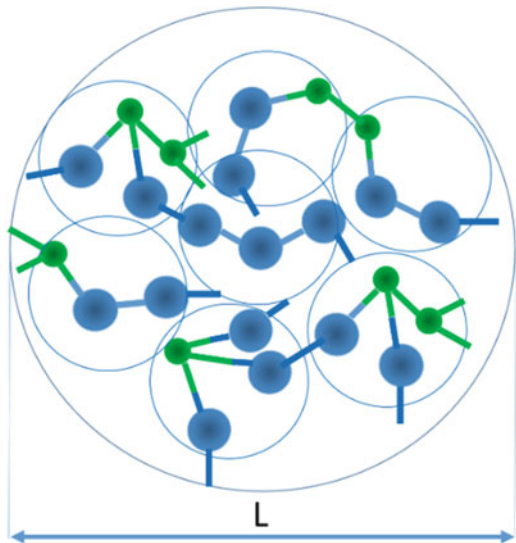
Fig. 3.14 Model of chalcogenide nanocrystalline material based on the concept of structural units: ternary compound with As-type, Se-type and Si-type structural units

(see Figs. 3.13 and 3.14) [23, 46] in an effective medium. It might seem, that it is possible to calculate simply a large cluster that takes into account the features of the atomic structure of the investigated composition A_xB_{1-x} . However, it is a very time-consuming calculation. Moreover, this calculation is not reasonable for essential contribution of a short-range order into EDOS. But, since the short-range order in the binary compound can vary significantly from node to node of the structural matrix of the nanocrystalline material, there is the statistics of the basic clusters that determines the final EDOS [23, 31, 32, 46] (Fig. 3.15).

3.9.1 Binary and Ternary Chalcogenide Glassy Systems

The bandgap estimation in numerical modelling is based on the cluster model including the group of basic clusters (Se_3 , As_4 , AsSe_3 , As_2Se_2 , As_2Se , etc.) embedded into the effective medium with a complex potential in accordance with the CPA.

Fig. 3.15 The model of the characteristic cluster structure of the non-regular chalcogenide system A_xB_{1-x} , L is the characteristic size (scale) of the system



The selection of a composition of clusters for the reproduction of a necessary predefined x is performed according to the relation:

$$As_xSe_{1-x} \sim \sum_i^N [As_{k_i}Se_{l_i}] \alpha_i, \quad (3.102)$$

where $[As_{k_i}Se_{l_i}]$ is the symbolic designation of the i -th basic cluster, k_i and l_i are the number of As- and Se-type atoms, α_i is the weight coefficient of the i -th basic cluster and N is the number of basic clusters.

The averaging of physical characteristics, for example, $\bar{E}_g$, is performed by the formula:

$$\bar{E}_g = \left(\sum_{i=1}^N \alpha_i E_g^i \right) / \left(\sum_{i=1}^N \alpha_i \right). \quad (3.103)$$

The values E_g^i are obtained in the EDOS calculations for each basic i -th cluster, taking into account the mass density ρ_i determining the radius of the cluster R_{CL}^i . When selecting the composition of basic clusters, it is also necessary to take into consideration the chemical ordering in the system, that is, take into account the characteristic binding energies of As–As, Se–Se and As–Se (2.07, 2.14, 2, 26 eV, respectively).

This circumstance has a noticeable effect in the ‘rare’ composition at $0.45 < x < 0.66$, where stronger As–Se bonds are more likely to occur. Combining the composition of basic clusters pursues the goal of reproducing the characteristic space topological invariant of the system As_xSe_{1-x} . Figure 3.16 and Table 3.5 illustrate the results of bandgap estimations for various cluster compositions.

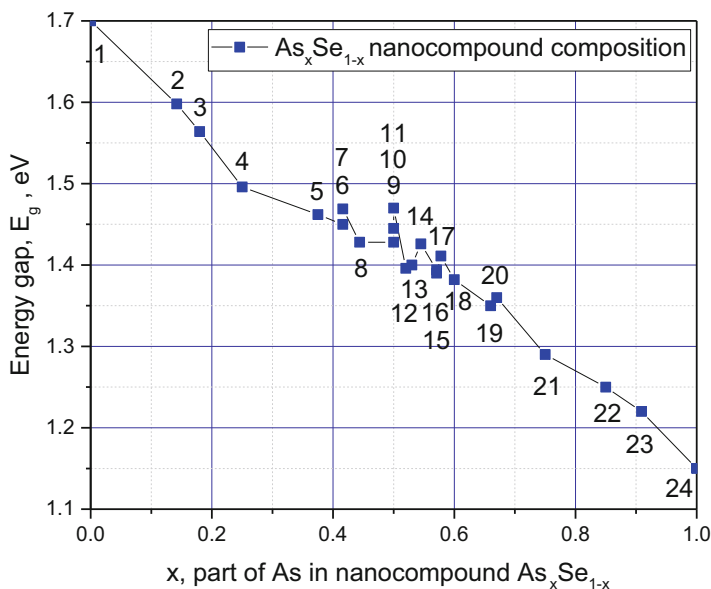


Fig. 3.16 Energy gap of nanocrystalline $\text{As}_x\text{Se}_{1-x}$ via the composition number x

The ambiguity of structural ordering in complex non-regular solids and nanocrystalline materials A_xB_{1-x} can be considered as their common property. The features of the short-range order in the neighbourhood of each node are, first of all, due to the physical conditions for the system preparation and, secondly, the principle of chemical ordering taking into account the 8-N rule and the values of the neighbouring atoms binding energies.

Reproduction of a given composition is possible in many ways. For example, at $x = 0.50$, the increase in the cluster fraction of the As_4 and Se_3 type in the system leads to the increase in the bandgap (Fig. 3.16, point 11, = 1.47 eV) in comparison with the more equilibrium structure, where there are clusters of the As_2Se_2 type (Point 9, $E_g^i = 1.428$ eV). Moreover, the first atomic configuration can be associated with freshly evaporated film and the second one with the annealed film. Then an estimation of the energy gap changes under the photoinduced transformation and gives the value of $\Delta E_g \approx 0.04$ eV.

At subsequent light effects, we find $\Delta E_g \approx 0.02$ eV (structural transitions: state '11' $\Leftrightarrow$ state '9'). These estimations are generally in satisfactory agreement with data on photoinduced changes ($\Delta E_g \approx 0.015$ eV for amorphous As_2Se_3 [47]).

The developed cluster multicomponent model [24] using the cluster calculation method [10, 21–23, 30, 32, 46] allows performing energy estimations of the change in optical properties under induced structural changes. It should also be noted that the calculation data satisfactorily describe the general nature of the experimental dependence (see Fig. 3.16). The cluster approach to binary and more complex

Table 3.5 Nanocrystalline $\text{As}_x\text{Se}_{1-x}$ energy gap via the cluster composition

	Cluster type	x	E_g^i , eV
1	Se_3	0.0	1.700
2	$(\text{Se}_3)(\text{AsSe}_3)$	0.142	1.598
3	$(\text{Se}_3)(\text{AsSe}_3)_2$	0.180	1.564
4	AsSe_3	0.250	1.496
5	$(\text{AsSe}_3)(\text{As}_2\text{Se}_2)$	0.375	1.462
6	$(\text{AsSe}_3)(\text{As}_2\text{Se}_2)_2$	0.416	1.450
7	$(\text{AsSe}_3)_3(\text{As}_2\text{Se}_2)_3(\text{As}_2\text{Se})_3 (\text{Se}_3)$	0.416	1.469
8	$(\text{AsSe}_3)_2(\text{As}_2\text{Se}_2)(\text{As}_2\text{Se})_2$	0.444	1.428
9	As_2Se_2	0.500	1.428
10	$(\text{As}_4)(\text{Se}_3) (\text{As}_2\text{Se}_2)$	0.500	1.445
11	$(\text{As}_4)_3(\text{Se}_3)_4$	0.500	1.470
12	$(\text{As}_2\text{Se}_2)(\text{As}_2\text{Se})_2 (\text{Se}_3)(\text{As}_4)(\text{AsSe}_3)$	0.520	1.396
13	$(\text{As}_4)_3 (\text{Se}_3)_4 (\text{As}_2\text{Se}_2)(\text{As}_2\text{Se})_{12} (\text{AsSe}_3)_{12}$	0.530	1.400
14	$(\text{As}_4)(\text{Se}_3) (\text{As}_2\text{Se}_2)$	0.545	1.426
15	$(\text{As}_2\text{Se}_2)(\text{As}_2\text{Se})$	0.571	1.394
16	$(\text{As}_4)_3(\text{Se}_3)_4 (\text{As}_2\text{Se}_2)_{12}$	0.571	1.390
17	$(\text{AsSe}_3)(\text{As}_2\text{Se}_2)(\text{As}_2\text{Se})_2$	0.578	1.411
18	$(\text{As}_2\text{Se}_2)(\text{As}_2\text{Se})$	0.600	1.382
19	$(\text{As}_4)(\text{Se}_3) (\text{As}_2\text{Se}_2)_3$	0.660	1.350
20	As_2Se	0.670	1.360
21	$(\text{As}_4)(\text{As}_2\text{Se})_2$	0.750	1.290
22	$(\text{As}_4)(\text{As}_2\text{Se})$	0.850	1.250
23	$(\text{As}_4)_2(\text{As}_2\text{Se})$	0.909	1.220
24	As_4	1.0	1.150

amorphous systems based on the proposed multiconfiguration model is rather general. It allows making E_g reasonable estimations for materials of the $A_x^{\text{V}}B_{1-x}^{\text{VI}}C_y^{\text{IV}}$ -type. The more accurate are these estimations, the more carefully the calculations of electronic properties of the basic clusters occurring in these materials will be performed. It is worth noting that the cluster multicomponent model is indirectly confirmed by the results of photoemission measurements for As_2Se_3 , As_2S_3 and As_2Te_3 , which indicate that electronic spectra, for example, nanocrystalline As_2Se_3 can be obtained by statistical mixing of electronic spectra of monoelements As and Se.

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