

APPLICATION OF GREEN FUNCTIONS TO THE CALCULATION OF DISORDERED CRYSTALS AND MOLECULES WITH REGARD FOR ELECTRON CORRELATIONS

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UDC 539.2
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We obtain the Green function of a disordered crystal with regard for the electron-electron interaction. The electron states of the system are described in the multiband tight binding model. In the case of the crystal infinite elementary cell, we show that our approach could be applied to a description of molecular energy spectra. The energy spectrum and effective charges on atoms at the ends of a tricyanogenbutadienecarbazole molecule are calculated.

Introduction

The successes in studying the properties of disordered systems (alloys, disordered semiconductors, and amorphous materials) are results of the electron theory development. The alloys are the most studied among these systems.

The traditional ideas of the properties of alloys that are based on the Born approximation cannot be applied in the case of the large potential of impurity scattering that takes place at a description of transition metal alloys. Considerable achievements in the description of these systems are connected with the application of multi-scattering methods involving the coherent potential approach (CPA) [1] that is the best one-site approach to the alloy property description. However, an account of interatomic correlations, that considerably affect the alloy properties, requires to come out of the scope of the one-site approach and take account of the cluster scattering. A lot of papers are devoted to this problem. Among the cluster extensions of the CPA, one could distinguish the augmented space cluster method [2–4] and “traveling cluster” approximation [5]. These methods solve the problem of constructing a self-consistent approximation that takes the scattering on clusters into account and preserves the analyticity and the translation invariance of the system Green’s function averaged over configurations.

In [6, 7], there were developed the method of account of statistical correlations based on the cluster expansion of one- and two-particle Green functions that determine the electron energy spectrum and electric conductivity of alloys. The CPA is a zero approximation of this method. The corrections to the CPA are obtained by summation of the contributions of scattering by clusters of two-, three-, and more atoms. It happens to be that the contributions of these scattering processes decrease with increase in the number of atoms in the clusters according to some small parameter.

However, the above-cited papers neglect the electron correlations that may be important at the description of electron states in the crystals with narrow energy bands [8] and multiatom molecules [9].

In the present paper, we propose the method of cluster expansion of the Green functions and thermodynamic potentials of the electron system of a disordered crystal with regard for the electron correlations. The electron states of the system are described in the multiband tight binding model. The CPA is chosen as the zero approximation in this expansion. In the case of infinite primitive cell of the crystal, we obtained the equation for energy spectrum and electron charge distribution in molecules and clusters. With the help of this equation, the energy spectrum and charge distribution in a tricyanogenbutadienecarbazole (TCBC) molecule have been calculated.

1. The Hamiltonian

The Hamiltonian of the system of electrons in a disordered crystal in the Wannier-representation takes the form

$$H = H_0 + H_{\text{int}}, \quad (1)$$

where the zero-approximation Hamiltonian

$$H_0 = \Phi_0 + H_{e0} \quad (2)$$

consists of the Hamiltonian of the subsystem of non-interacting electrons

$$H_{e0} = \sum_{\substack{n_1 i_1 \gamma_1 \\ n_2 i_2 \gamma_2}} h_{n_1 i_1 \gamma_1, n_2 i_2 \gamma_2}^{(0)} a_{n_1 i_1 \gamma_1}^+ a_{n_2 i_2 \gamma_2},$$

and the energy of electrostatic interactions of ions Φ_0 in the equilibrium positions. The perturbation Hamiltonian in (1)

$$H_{\text{int}} = H_{ei} + H_{ee} \quad (3)$$

consists of the Hamiltonian of the electron-ion (electron-impurity) interaction

$$H_{ei} = \sum_{\substack{n_1 i_1 \gamma_1 \\ n_2 i_2 \gamma_2}} w_{n_1 i_1 \gamma_1, n_2 i_2 \gamma_2} a_{n_1 i_1 \gamma_1}^+ a_{n_2 i_2 \gamma_2}$$

and the Hamiltonian of the pair wise electron-electron interaction

$$H_{ee} = \frac{1}{2} \sum_{n_1, n_2, n_3, n_4} v_{n_3, n_4}^{(2) n_1, n_2} a_{n_1}^+ a_{n_2}^+ a_{n_3} a_{n_4}, \quad (n \equiv ni\gamma).$$

Here, $a_{ni\gamma}^+$, $a_{ni\gamma}$ are the creation and annihilation operators of an electron in the state that is described by the Wannier function $\varphi_{ni\gamma}(\xi) = \langle \xi | ni\gamma \rangle$, $\xi = (\vec{r}, \sigma)$; the index of the state γ is specified by the number of an energy band and spin projection σ on the z axis, n is the number of a primitive cell of the crystal, i is the index of a sublattice, $h_{n_1 i_1 \gamma_1, n_2 i_2 \gamma_2}^{(0)}$ are the matrix elements of the one-electron Hamiltonian of the pure crystal that consists of atoms of kind A.

The operator of the potential energy of an electron in the field of ion cores of the crystal may be written as

$$V(\vec{r}) = \sum_{ni} v^{ni}(\vec{r} - \vec{r}_{ni}),$$

where \vec{r} is the electron radius vector, $\vec{r}_{ni} = \vec{r}_n + \vec{\rho}_i$ is the radius-vector of the equilibrium position of an atom in the ni -th site of the crystal lattice. A random correction to the one-electron Hamiltonian of a pure crystal associated with an impurity is

$$w_{n_1 i_1 \gamma_1, n_2 i_2 \gamma_2} = \sum_{ni} w_{n_1 i_1 \gamma_1, n_2 i_2 \gamma_2}^{ni}, \quad (4)$$

where

$$w_{n_1 i_1 \gamma_1, n_2 i_2 \gamma_2}^{ni} = \sum_{\lambda} c_{ni}^{\lambda} w_{n_1 i_1 \gamma_1, n_2 i_2 \gamma_2}^{\lambda ni},$$

$$w_{n_1 i_1 \gamma_1, n_2 i_2 \gamma_2}^{\lambda ni} = v_{n_1 i_1 \gamma_1, n_2 i_2 \gamma_2}^{\lambda ni} - v_{n_1 i_1 \gamma_1, n_2 i_2 \gamma_2}^{Ani},$$

$$v_{n_1 i_1 \gamma_1, n_2 i_2 \gamma_2}^{\lambda ni} = \int \varphi_{n_1 i_1 \gamma_1}^*(\xi) v^{\lambda}(\vec{r} - \vec{r}_{ni}) \varphi_{n_2 i_2 \gamma_2}(\xi) d\xi.$$

Random numbers c_{ni}^{λ} take the values 1 or 0 if the λ -kind atom is at the ni -th site or not, respectively.

2. The Green Function

The temperature Green function can be defined for the electron system [10]. By using the Wick theorem [10] for calculation the temperature Green functions of a disordered crystal, we could build the diagram technique analogous to that for a homogeneous system. Performing the Fourier transformation and using the known relations between the spectral presentations of the temperature and time Green functions [10], we obtain the equation for a retarded Green function with the help of analytic continuation on the real axis:

$$G(\varepsilon) = G_0(\varepsilon) + G_0(\varepsilon) (w + \Sigma_{ee}(\varepsilon)) G(\varepsilon), \quad (5)$$

where $G(\varepsilon)$ is the spectral presentation of the electron one-particle Green function, $G_0(\varepsilon)$ is the corresponding Green function of zero order.

A solution of system (5) is

$$G(\varepsilon) = [[G_0(\varepsilon)]^{-1} - (w + \Sigma_{ee}(\varepsilon))]^{-1}, \quad (6)$$

where

$$G_0(\varepsilon) = [\varepsilon - H_0^{(1)}]^{-1}, \quad H_0^{(1)} = \|h_{ni\gamma, n'i'\gamma'}^0\|. \quad (7)$$

The mass operator of the Green function, that describes the electron-electron interaction in the system, may be presented as

$$\Sigma_{eeni\gamma, n'i'\gamma'}(\varepsilon) = \Sigma_{eeni\gamma, n'i'\gamma'}^{(1)} + \Sigma_{eeni\gamma, n'i'\gamma'}^{(2)}(\varepsilon), \quad (8)$$

where

$$\Sigma_{een, n'}^{(1)} = -\frac{1}{4\pi i} \int_{-\infty}^{\infty} d\varepsilon' f(\varepsilon') \tilde{v}_{n_1, n'}^{(2) n, n_2} \times$$

$$\times [G_{n_1, n_2}(\varepsilon') - G_{n_2, n_1}^*(\varepsilon')],$$

$$\Sigma_{ee n, n'}^{(2)}(\varepsilon) = -\left(\frac{1}{2\pi i}\right)^2 \int_{-\infty}^{\infty} d\varepsilon_1 \int_{-\infty}^{\infty} d\varepsilon_2 \tilde{v}_{n_2, n_1}^{(2) n, n_3} \times$$

$$\times \left\{ f(\varepsilon_1) f(\varepsilon_2) [G_{n_5, n_2}^*(\varepsilon - \varepsilon_1 + \varepsilon_2) G_{n_1, n_4}(\varepsilon_1) -$$

$$- G_{n_2, n_5}(\varepsilon - \varepsilon_1 + \varepsilon_2) G_{n_4, n_1}^*(\varepsilon_1)] \right\} \times$$

$$\begin{aligned} & \times \left[G_{n_6, n_3}(\varepsilon_2) - G_{n_3, n_6}^*(\varepsilon_2) \right] + \\ & + f(\varepsilon_1) f(\varepsilon_1 + \varepsilon_2) \left[G_{n_2, n_5}(\varepsilon_2) - G_{n_5, n_2}^*(\varepsilon_2) \right] \times \\ & \times \left[G_{n_1, n_4}(\varepsilon_1) G_{n_6, n_3}(\varepsilon_1 + \varepsilon_2 - \varepsilon) - \right. \\ & \left. - G_{n_4, n_1}^*(\varepsilon_1) G_{n_3, n_6}^*(\varepsilon_1 + \varepsilon_2 - \varepsilon) \right] \} \tilde{v}_{n_6, n'}^{(2)n_4, n_5}, \end{aligned}$$

$\tilde{v}_{n_1, n'}^{(2)n, n_2} = v_{n_1, n'}^{(2)n, n_2} - v_{n', n_1}^{(2)n, n_2}$, ($n \equiv ni\gamma$), $f(\varepsilon)$ is the Fermi function. For simplicity, the vertex terms in (8) were taken in the zero approximation.

To find the state density of the electron subsystem, it is necessary to average the Green function (6) over arrangements of atoms in the crystalline lattice. As a result, the density of electron states per one atom is

$$g(\varepsilon) = -\frac{1}{\pi\nu N} \text{ImSp}\langle G(\varepsilon) \rangle_c. \quad (9)$$

In (9), $\langle \dots \rangle_c$ denotes the configuration average. For brevity, we will omit index c near the bracket $\langle \dots \rangle_c$.

Expression (6) differs from the corresponding expression of the Green function of the one-particle Hamiltonian of a disordered system only by the view of mass operators. In connection with this, we use the well-known methods of the theory of disordered systems [11].

We perform the cluster expansion of the Green function $G(\varepsilon)$ presenting the mass operator as a sum of the one-site operators and choosing the effective medium Green function as the zero one-site approximation. This is just an extension of the cluster expansion of the Green function $G(\varepsilon)$ ignoring the multiparticle interaction [6, 7]. The effective medium Green function is determined by the expression

$$\tilde{G}(\varepsilon) = [[G_0(\varepsilon)]^{-1} - \sigma_{\text{eff}}(\varepsilon)]^{-1}. \quad (10)$$

Here, $\sigma_{\text{eff}}(\varepsilon)$ is the effective medium potential (coherent potential) that will be specified below.

Green function (6) satisfies the equation

$$G(\varepsilon) = \tilde{G}(\varepsilon) + \tilde{G}(\varepsilon) \tilde{\Sigma}(\varepsilon) G(\varepsilon), \quad (11)$$

where

$$\tilde{\Sigma}(\varepsilon) = \Sigma_e(\varepsilon) - \sigma_{\text{eff}}(\varepsilon) = w + \Sigma_{ee}(\varepsilon) - \sigma_{\text{eff}}(\varepsilon).$$

The operator of scattering T -matrix is defined by

$$G(\varepsilon) = \tilde{G}(\varepsilon) + \tilde{G}(\varepsilon) T(\varepsilon) \tilde{G}(\varepsilon). \quad (12)$$

Presenting the mass operators as sums of the one-site operators

$$\tilde{\Sigma}(\varepsilon) = \sum_{(n_1 i_1)} \tilde{\Sigma}^{n_1 i_1}(\varepsilon),$$

we obtain the scattering T -matrix in the form of a series whose terms describe the scattering by clusters with different numbers of sites (see, for example, [6])

$$T = \sum_{(n_1 i_1)} t^{n_1 i_1} + \sum_{(n_1 i_1) \neq (n_2 i_2)} T^{(2)n_1 i_1, n_2 i_2} + \dots, \quad (13)$$

where $t^{n_1 i_1}$ is the scattering operator at one site

$$t^{n_1 i_1} = \left[I - \tilde{\Sigma}^{n_1 i_1} \tilde{G} \right]^{-1} \tilde{\Sigma}^{n_1 i_1}, \quad (14)$$

and the scattering operator at two sites equals

$$\begin{aligned} T^{(2)n_1 i_1, n_2 i_2} = \\ \left[I - t^{n_1 i_1} \tilde{G} t^{n_2 i_2} \tilde{G} \right]^{-1} t^{n_1 i_1} \tilde{G} t^{n_2 i_2} \left(I + \tilde{G} t^{n_1 i_1} \right). \end{aligned} \quad (15)$$

The coherent potential is determined from the condition $\langle t^{0i_1} \rangle = 0$ and satisfies the equation

$$\begin{aligned} \sigma_{\text{eff}}^{0i_1}(\varepsilon) = \left\langle [1 - (\Sigma_e^{0i_1} - \sigma_{\text{eff}}^{0i_1}(\varepsilon)) \tilde{G}]^{-1} \right\rangle^{-1} \times \\ \times \left\langle [1 - (\Sigma_e^{0i_1} - \sigma_{\text{eff}}^{0i_1}(\varepsilon)) \tilde{G}]^{-1} \Sigma_e^{0i_1} \right\rangle. \end{aligned} \quad (16)$$

For the electron number $Z_{\lambda i} = \sum_{\gamma} Z_{\lambda i \gamma}$ and the magnetic moment projection $m_{\lambda i} = \sum_{\gamma} m_{\lambda i \gamma}$ at the atom of kind λ at the ni -th site, we may write down the relation

$$Z_{\lambda i \gamma} = Z_{ni\gamma\sigma}^{m_{\lambda i}} + Z_{ni\gamma-\sigma}^{m_{\lambda i}}, \quad m_{\lambda i \gamma} = Z_{ni\gamma\sigma}^{m_{\lambda i}} - Z_{ni\gamma-\sigma}^{m_{\lambda i}}, \quad (17)$$

that gives

$$Z_{ni\gamma\sigma}^{m_{\lambda i}} = (Z_{\lambda i \gamma} + m_{\lambda i \gamma})/2, \quad Z_{ni\gamma-\sigma}^{m_{\lambda i}} = (Z_{\lambda i \gamma} - m_{\lambda i \gamma})/2.$$

The quantity $Z_{ni\gamma\sigma}^{m_{\lambda i}}$ in (17) is expressed in terms of the conditional density of electron states $g_{ni\gamma\sigma}^{m_{\lambda i}}(\varepsilon)$ of the energy band γ and the spin projection σ as

$$Z_{ni\gamma\sigma}^{m_{\lambda i}} = \int_{-\infty}^{\infty} f(\varepsilon, \mu_e, \Theta) g_{ni\gamma\sigma}^{m_{\lambda i}}(\varepsilon) d\varepsilon, \quad (18)$$

where

$$g_{ni\gamma\sigma}^{m_{\lambda i}}(\varepsilon) = -\frac{1}{\pi} \text{Im} \langle G_{ni\gamma\sigma, ni\gamma\sigma}(\varepsilon) \rangle_{(ni) \in m_{\lambda i}}. \quad (19)$$

Averaging in (19) is performed provided that the atom of kind λ is located at the ni -th site and the localized moment projection equals to $m_{\lambda i}$.

We set that the magnetic moment projection at the atom of kind λ takes two values $m_{\lambda i} = \pm \mu_{\lambda i}$. It is also

assumed that the probability $P_{ni}^{m_{\lambda i}}$ to find the moment projection $m_{\lambda i}$ at the ni -th site depends only on the moment projection sign and does not depend on the atom kind. Keeping this in mind, we can write

$$P_{ni}^{\lambda m_{\lambda i}} = P_{ni}^{\lambda} P_{ni}^{m_{\lambda i}},$$

$$P_{ni, n' i'}^{\lambda m_{\lambda i}, \lambda' m_{\lambda' i'}} = P_{ni, n' i'}^{\lambda, \lambda'} P_{ni, n' i'}^{m_{\lambda i}, m_{\lambda' i'}}, \quad (20)$$

where $P_{ni}^{\lambda m_{\lambda i}} = \langle c_{ni}^{\lambda m_{\lambda i}} \rangle$ and $P_{ni, n' i'}^{\lambda m_{\lambda i}, \lambda' m_{\lambda' i'}} = \langle c_{ni}^{\lambda m_{\lambda i}} c_{n' i'}^{\lambda' m_{\lambda' i'}} \rangle$ are the one- and two-particle probability distribution functions of atoms and magnetic moments in the crystal.

For binary alloys with lattices of the cubic symmetry, we define the parameter of long order η_a as

$$P_{ni}^A = c^A - \eta_a \nu_2 / \nu$$

for ν_1 subsattices of the first type,

$$P_{ni}^A = c^A + \eta_a \nu_1 / \nu$$

for ν_2 subsattices of the second type,

$$P_{ni}^B = 1 - P_{ni}^A, \quad (21)$$

where $\nu = \nu_1 + \nu_2$, c^A and $c^B = 1 - c^A$ are the alloy component (A and B) concentrations.

The relations analogous to (21) may be written for the magnetic long order:

$$P_{ni}^{\mp \mu \lambda i} = c^{\mp \mu} \mp \eta_m \nu_2 / \nu$$

for ν_1 subsattices of the first type,

$$P_{ni}^{\mp \mu \lambda i} = c^{\mp \mu} \pm \eta_m \nu_1 / \nu$$

for ν_2 subsattices of the second type,

where $c^{+\mu} = c^{-\mu} = 0.5$ if there is no an external magnetic field.

The conditional probabilities $P_{n' i', 0i}^{\lambda' / \lambda}$ and $P_{n' i', 0i}^{m_{\lambda' i'} / m_{\lambda i}}$ are related to the parameters of interatomic correlations $\varepsilon_{0i, n' i'}^{A}$ and pair correlations in orientation of the localized moments $\varepsilon_{0i, n' i'}^{-\mu \lambda i, -\mu \lambda' i'}$ by the relations

$$P_{0i, n' i'}^{\lambda \lambda'} = P_{0i}^{\lambda} P_{n' i', 0i}^{\lambda' / \lambda} =$$

$$= P_{0i}^{\lambda} P_{n' i'}^{\lambda'} + \varepsilon_{0i, n' i'}^{A A} (\delta_{\lambda A} - \delta_{\lambda B}) (\delta_{\lambda' A} - \delta_{\lambda' B}),$$

$$P_{0i, n' i'}^{m_{\lambda i}, m_{\lambda' i'}} = P_{0i}^{m_{\lambda i}} P_{n' i', 0i}^{m_{\lambda' i'} / m_{\lambda i}} = P_{0i}^{m_{\lambda i}} P_{n' i'}^{m_{\lambda' i'}} +$$

$$+ \varepsilon_{0i, n' i'}^{-\mu \lambda i, -\mu \lambda' i'} (\delta_{m_{\lambda i}, -\mu \lambda i} - \delta_{m_{\lambda i}, \mu \lambda i}) \times$$

$$\times (\delta_{m_{\lambda' i'}, -\mu \lambda' i'} - \delta_{m_{\lambda' i'}, \mu \lambda' i'}), \quad (22)$$

where δ is the Kronecker symbol.

Neglecting the scattering processes by clusters of three and more atoms, we may obtain the conditional density of electron states as

$$g_{ni\gamma\sigma}^{m_{\lambda i}} = -\frac{1}{\pi} \text{Im} \left\{ \left[\tilde{G} + \tilde{G} t^{m_{\lambda i} ni} \tilde{G} \right]_{ni\gamma\sigma, ni\gamma\sigma} + \right.$$

$$+ \sum_{\substack{(n' i') \neq (ni) \\ \lambda', m_{\lambda' i'}}} P_{n' i', ni}^{\lambda' m_{\lambda' i'} / \lambda m_{\lambda i}} \left[\tilde{G} (t^{m_{\lambda' i'} n' i'} + \right.$$

$$\left. \left. T^{(2)m_{\lambda i} ni, m_{\lambda' i'} n' i'} + T^{(2)m_{\lambda' i'} n' i', m_{\lambda i} ni} \right) \tilde{G} \right]_{ni\gamma\sigma, ni\gamma\sigma} \left. \right\}. \quad (23)$$

The total density of electron states equals

$$g(\varepsilon) = \frac{1}{v} \sum_{i, \gamma, \sigma, \lambda, m_{\lambda i}} P_{0i}^{\lambda m_{\lambda i}} g_{0i\gamma\sigma}^{m_{\lambda i}}(\varepsilon). \quad (24)$$

3. Thermodynamic Potential

To calculate the thermodynamic potential, we develop a diagram technique [11] analogous to the diagram technique of temperature Green functions. The thermodynamic potential of the system can be presented as

$$\Omega = \Omega_0 + \Omega', \quad (25)$$

where

$$\Omega' = -\frac{1}{\pi} \text{Im} \int_0^1 \frac{d\lambda}{\lambda} \int_{-\infty}^{\infty} d\varepsilon f(\varepsilon) \times$$

$$\times \text{Sp} \langle (w(\lambda) + \Sigma_{ee}(\varepsilon, \lambda)) G(\varepsilon, \lambda) \rangle. \quad (26)$$

While obtaining formula (25), we renamed the interaction Hamiltonian H_{int} (3) multiplying it by a parameter λ and setting $H_{\text{int}}(\lambda) = \lambda H_{\text{int}}$.

The thermodynamic potential Ω_0 in (25) provided that there is no interaction may be written in the form

$$\Omega_0 = \Omega_c + \Omega_{0e}, \quad (27)$$

where Ω_{0e} is the thermodynamic potential of the electron subsystem

$$\Omega_{0e} = -\nu N \Theta \int_{-\infty}^{\infty} \ln \left(1 + e^{(\mu_e - \varepsilon) / \Theta} \right) g_0(\varepsilon) d\varepsilon.$$

The state density $g_0(\varepsilon)$ is given by (9), where $G(\varepsilon)$ is substituted by the zero-order Green function $G_0(\varepsilon)$.

The configuration component of the thermodynamic potential Ω_c in (27), that depends on the distribution atoms of different kinds over sites of the crystalline lattices, is

$$\Omega_c = \langle \Phi_0 \rangle - \Theta S_c, \quad (28)$$

where $S_c = -\langle \ln P_c \rangle$ is the configuration entropy, $P_c(\{c_{ni}^{\lambda m \lambda_i}\})$ is the distribution function of atoms and magnetic moments over the lattice sites.

Neglecting small terms $O(\lambda^2)$ in integral (26), we obtain the approximate expression of the thermodynamic potential of the electron subsystem Ω_e that was obtained in [12]. Neglecting the electron-electron interaction or setting $\Sigma_{ee}(\varepsilon) = 0$, we get the thermodynamic potential of a disordered crystal obtained earlier in [13].

The free energy F , related to the thermodynamic potential Ω by $F = \Omega + \mu_e \langle N_e \rangle$, as a function of the system volume V , temperature Θ , number of electrons N_e , and inter-atomic correlation parameters $(\varepsilon_{n_1 i_1, n_2 i_2}, \eta)$ is

$$F = \langle \Phi_0 \rangle - \Theta S_c + \Omega_{0e} + \Omega' + \mu_e \langle N_e \rangle. \quad (29)$$

The configuration part of the alloy entropy S_c in (29) is connected with the distribution probabilities of atoms and localized moments over the crystalline lattice sites $P_{n_1 i_1 \dots n_\nu i_\nu}^{\lambda_1 m \lambda_1 i_1 \dots \lambda_\nu m \lambda_\nu i_\nu}$ by the relation

$$S_c = - \left[\sum_{\substack{(n_1 i_1) \\ \lambda_1, m \lambda_1 i_1}} P_{n_1 i_1}^{\lambda_1 m \lambda_1 i_1} \ln P_{n_1 i_1}^{\lambda_1 m \lambda_1 i_1} + \frac{1}{2} \sum_{\substack{(n_1 i_1) \neq (n_2 i_2) \\ \lambda_1, m \lambda_1 i_1, \lambda_2, m \lambda_2 i_2}} P_{n_1 i_1, n_2 i_2}^{\lambda_1 m \lambda_1 i_1, \lambda_2 m \lambda_2 i_2} \times \right. \\ \left. \times \ln \frac{P_{n_1 i_1, n_2 i_2}^{\lambda_1 m \lambda_1 i_1, \lambda_2 m \lambda_2 i_2}}{P_{n_1 i_1}^{\lambda_1 m \lambda_1 i_1} P_{n_2 i_2}^{\lambda_2 m \lambda_2 i_2}} + \dots \right]. \quad (30)$$

The equilibrium parameters of interatomic correlation $(\varepsilon_{0i_1, n_2 i_2}, \eta)$ are defined from the alloy free energy minimum [11]:

$$\frac{\partial F}{\partial \varepsilon_{0i_1, n_2 i_2}} = 0, \quad \frac{\partial F}{\partial \eta} = 0. \quad (31)$$

The Fermi level μ_e is determined from the equation

$$\langle Z \rangle = \int_{-\infty}^{\infty} f(\varepsilon, \mu_e, \Theta) g(\varepsilon) d\varepsilon, \quad (32)$$

where $g(\varepsilon)$ is given by (9), $\langle Z \rangle = \langle N_e \rangle / \nu N$ is the average number of electrons per atom, $\langle Z \rangle = c^A Z_A + c^B Z_B$.

The method proposed above allows one to study the electron structure, free energy, and parameters of inter-atomic correlation of disordered crystals. The results obtained allow one to take into account the influence of strong electron correlations on the electron energy spectrum and properties of the transient metal alloys with narrow energy bands.

The determination of the equilibrium distribution of electrons over the sites of crystalline lattices $Z_{\lambda_i \gamma}$ (the electron density), localized magnetic moments $m_{\lambda_i \gamma}$, correlation parameters of atom distributions $(\eta_a, \varepsilon_{0i, lj}^{AA})$, and orientations of momenta $(\eta_m, \varepsilon_{0i, lj}^{-\mu \lambda_i, -\mu \lambda' j})$ are reduced to obtaining the minimum of the free energy F (28). If there are no localized magnetic moments ($m_{\lambda_i \gamma} = 0$), $Z_{\lambda_i \gamma}$ and $(\eta_a, \varepsilon_{0i, lj}^{AA})$ serve as variation parameters.

The energy of electrons in the crystal corresponds to the poles of Green function (6). For the ideal (completely ordered) crystal, the energies are defined by the equation

$$\det \left\| \varepsilon \delta_{i\gamma, i'\gamma'} - h_{i\gamma, i'\gamma'}(\vec{k}) - \Sigma_{ee i\gamma, i'\gamma'}(\vec{k}, \varepsilon) \right\| = 0, \quad (33)$$

where $h_{i\gamma, i'\gamma'}(\vec{k})$, $\Sigma_{ee i\gamma, i'\gamma'}(\vec{k}, \varepsilon)$ are the Fourier transforms of the jumping integral $h_{n_1 i_1 \gamma_1, n_2 i_2 \gamma_2} = h_{n_1 i_1 \gamma_1, n_2 i_2 \gamma_2}^{(0)} + w_{n_1 i_1 \gamma_1, n_2 i_2 \gamma_2}$ and mass-operator $\Sigma_{ee n_1 i_1 \gamma_1, n_2 i_2 \gamma_2}(\varepsilon)$.

The results of this work point out the possible ways of generalization of the one-band Hubbard model known in magnetism theory for the description of influence of strong electron correlations on the electron structure and properties of the disordered alloys of transient metals with narrow energy bands.

4. The Molecule Energy Spectrum

The proposed method of account of the electron correlation may be applied in studying the electron structure of clusters and molecules. All one has to do is to nullify the temperature Θ and matrix elements of Hamiltonian (6)–(8) with different numbers of the primitive cells. The point is that the transition to free molecules corresponds to the transition to infinite volume of the crystal primitive cell. In this case, the matrix of Green operator (6) becomes block-diagonal. Setting $h_{i\gamma, i'\gamma'}(\vec{k}) = h_{n_i \gamma, n_{i'} \gamma'} = h_{i\gamma, i'\gamma'}$ and

$\Sigma_{eei\gamma,i'\gamma'}(\vec{k}, \varepsilon) = \Sigma_{eeni\gamma,ni'\gamma'}(\varepsilon) = \Sigma_{eei\gamma,i'\gamma'}(\varepsilon)$ in (32), we obtain the equation for the electron energy in a molecule

$$\det \|\varepsilon \delta_{i\gamma,i'\gamma'} - h_{i\gamma,i'\gamma'} - \Sigma_{eei\gamma,i'\gamma'}(\varepsilon)\| = 0. \quad (34)$$

In this equation, $h_{i\gamma,i'\gamma'} = h_{ni\gamma,ni'\gamma'}$ are matrix elements of the one-electron Hamiltonian of the molecule that presented in the basis of site wave functions. The most common choice of the basis functions is the wave functions of electron states of free atoms that make up the cluster or molecule under study. In this case, the index $i\gamma$ of the basis function denotes the number of an atom i and the orbital on this atom or the set of corresponding quantum numbers γ that includes the electron spin σ . In this approach, the basis is supposed to be orthogonal. Equation (34) is the existence condition of the solution of the system

$$\sum_{i'\gamma'} (\varepsilon \delta_{i\gamma,i'\gamma'} - h_{i\gamma,i'\gamma'} - \Sigma_{eei\gamma,i'\gamma'}(\varepsilon)) C_{i'\gamma'} = 0, \quad (35)$$

where $C_{i'\gamma'}$ are the expansion coefficients of the wave function of a molecule in the basis orthonormal wave functions

$$\psi(\xi) = \sum_{i\gamma} C_{i\gamma} \varphi_{i\gamma}(\xi). \quad (36)$$

Equations (6)–(8) and (35) present the closed system of equations for the eigenvalues of energy and wave functions of the molecule.

The integrals of the matrix elements of the Green function that appear in the expression of mass operator (8) can be written in the form

$$Z_{i\gamma,i'\gamma'} = -\frac{1}{\pi} \int_{-\infty}^{\mu_0} \text{Im} G_{i\gamma,i'\gamma'}(\varepsilon) d\varepsilon = \sum_k n_k C_{i\gamma}^{(k)} C_{i'\gamma'}^{(k)*}, \quad (37)$$

where μ_0 is the upper filled level of energy, k is the molecular orbital number, n_k is the population number of the orbital. The number of valence electrons in the state γ , related to the atom i , is equal to $Z_{i\gamma} = Z_{i\gamma,i\gamma}$. The total number of electrons, related to the atom i , is equal to $Z_i = \sum_{\gamma} Z_{i\gamma}$. The effective charge on the atom is

$$\Delta Z_i = Z_i^{(0)} - Z_i, \quad (38)$$

where $Z_i^{(0)}$ is the number of valence electrons in the free atom i that are included into the calculation.

Equation (34) jointly with the equation of density matrix $Z_{i\gamma,i'\gamma'}$ is the closed system of equations for

calculation of the energy and charge distribution in the molecule. This system can be solved self-consistently by setting $Z_i = Z_i^{(0)}$ at the first step of the iteration procedure.

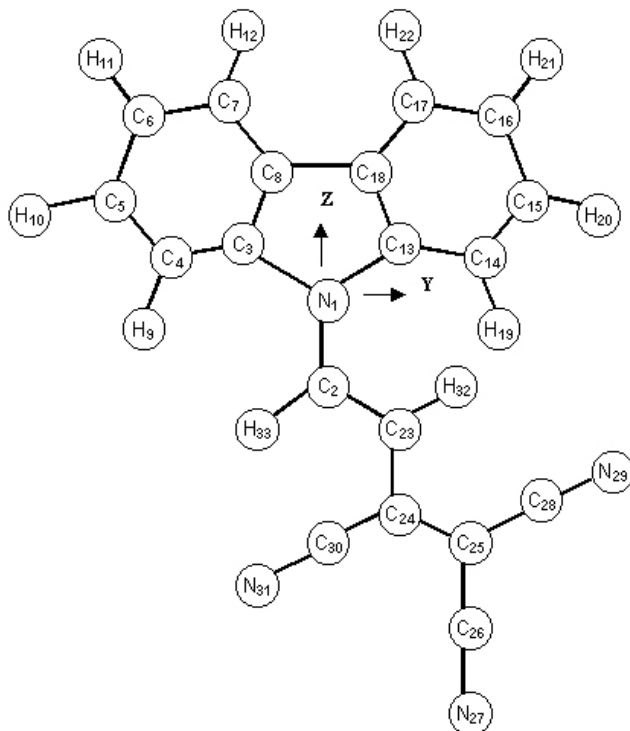
Equations (35), (37) are a generalization of equations of the molecular orbital method that is the linear combination of atomic orbitals (MO LKAO) with account of the electron correlation. Neglecting $\Sigma_{eei\gamma,i'\gamma'}^{(2)}(\varepsilon)$ in the mass operator of Green functions (8), we obtain the known system of the MO LKAO that is based on the Hartree–Fock mean field [14–16].

As an example, we present here the results of calculation of the energy spectrum and effective charges on atoms of a tricyanogebutadienecarbazole (TCBC) molecule. The TCBC crystals are very promising materials for the registration and transformation of infrared laser radiation into visible radiation. When excited, these organic crystals can transport the inner charge. They also possess a considerable optical nonlinearity. Interpretation of the results of experimental study of the absorption spectra and luminescence of these substances requires calculations of the energy spectrum and charge distribution in the TCBC molecules. However, there are no such calculations in the literature.

We have calculated the matrix elements of Hamiltonian (1) by using of the wave functions and potentials of individual atoms obtained with the help of the Slater–Koster method [17, 18]. The basis orthogonalization is performed by the Löwdin method [19]. In the process of calculations, we ignore the three- and four-center two-electron integrals $\tilde{v}_{i_2\gamma_2,i_3\gamma_3}^{(2)i_1\gamma_1,i_2\gamma_2}$ and $\tilde{v}_{i_3\gamma_3,i_4\gamma_4}^{(2)i_1\gamma_1,i_2\gamma_2}$ in expression (8).

The structure of a TCBC molecule and numbers of atoms are presented in Fig.1. The distances between atoms used in the calculation are taken from [20]. The results of calculation of the energy of the ground and excited levels of the molecule are given in the table. For each orbital with the number k , we indicate a number of atom i , its kind λ , and the set of quantum numbers $\gamma = nl$ of the atomic orbital that has the largest expansion coefficient $C_{i\gamma}^{(k)}$. The part of the molecule energy spectrum that is associated with the long wave edge of absorption spectra is presented as well.

The wavelength of the maximum intensity of one-photon luminescence, which is obtained from the table, corresponds to transitions between the states with molecular orbitals 103 and 102 and equals $\lambda_1 = 621$ nm. The study of reflection spectra and excitation of



Energy levels of a tricyanogenbutadienecarbazole molecule

photoconductivity of TCBC crystals showed that the intermolecular interaction is one-dimensional in these crystals [21]. It is known that the two-photon absorption and photoluminescence are described by the nonlinear cubic susceptibility associated with the two-photon absorption by the three-level method proposed in [22]. According to our calculations this susceptibility is connected with the transitions between molecular orbitals 102, 103, and 111. The long-wave limit of the two-photon absorption spectrum, as follows from the results given in the table, equals $\lambda_2 = 1142$ nm. The experimental data [22] give $\lambda_1^{\text{ex}} \approx 640$ nm that is in good agreement with our calculation. The wavelength of excitation of the two-photon luminescence according to [22] is $\lambda_{\text{ex}} = 1064$ nm that is close to λ_2 .

Appearance of the charges ΔZ_i (38) on hydrogen atoms $\Delta Z_{\text{H}} \approx -0.05$, carbon atoms $\Delta Z_{\text{C}_3} = \Delta Z_{\text{C}_8} \approx 0.1$, $\Delta Z_{\text{C}_4} = \Delta Z_{\text{C}_7} \approx -0.1$, $\Delta Z_{\text{C}_5} = \Delta Z_{\text{C}_6} \approx -0.05$ and nitrogen atoms $\Delta Z_{\text{N}_1} \approx 0.1$, $\Delta Z_{\text{N}_{27}} = \Delta Z_{\text{N}_{29}} = \Delta Z_{\text{N}_{31}} \approx 0.15$ results in the emerge of the dipole moment of the TCBC molecule in the ground state with the components $P_{0,x} = 0$, $P_{0,y} = 2.52 \cdot 10^{-29}$ C · m, $P_{0,z} = -8.15 \cdot 10^{-29}$ C · m.

The results of analogous calculations, which have been performed with the help of our method for a

Tricyanogenbutadienecarbazole molecule

k	$i \lambda(\gamma)$	E, eV
Virtual orbitals		
120	33 H (2p)	-2.275587
119	20 H (2p)	-2.302358
118	10 H (2p)	-2.302358
117	32 H (2p)	-2.366030
116	9 H (2p)	-2.405866
115	12 H (2p)	-2.409065
114	22 H (2p)	-2.409065
113	21 H (2s)	-2.457967
112	11 H (2s)	-2.457967
111	19 H (2p)	-2.462389
110	33 H (2s)	-2.504307
109	32 H (2s)	-2.513860
108	20 H (2s)	-2.518661
107	10 H (2s)	-2.518661
106	9 H (2s)	-2.609248
105	22 H (2s)	-2.613740
104	12 H (2s)	-2.613740
103	19 H (2s)	-2.636588
Occupied orbitals		
102	29 N (2p)	-4.636450
101	31 N (2p)	-4.636450
100	27 N (2p)	-4.740308
99	31 N (2p)	-4.740308
98	27 N (2p)	-4.740308
97	29 N (2p)	-4.740308
96	28 C (2p)	-4.890593
95	30 C (2p)	-4.890593
94	26 C (2p)	-4.959070
93	30 C (2p)	-4.959113
92	28 C (2p)	-4.959113
91	26 C (2p)	-4.959113
90	18 C (2p)	-5.173234
89	8 C (2p)	-5.173234
88	24 C (2p)	-5.210267
87	25 C (2p)	-5.210268
86	1 N (2p)	-5.215135
85	13 C (2p)	-5.253330
84	3 C (2p)	-5.253330

carbazole molecule, are in good agreement with the experimental data on absorption spectra [23]. By comparison, we note that calculations of the energy spectrum of the carbazole molecule performed in [20] with the help of the CNDO/S method result in the positions of energy levels considerably different (≈ 2 eV) from the experimental data on ionization potentials and absorption spectra [23].

Thus, the proposed method of calculation of the electron structure of molecules, which takes the electron correlation and basis orthogonalization into account, allows one to describe correctly the energy spectrum and charge distribution in molecules.

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Received 28.03.03.

Translated from Ukrainian by V.N. Mal'nev

ЗАСТОСУВАННЯ ФУНКЦІЙ ГРІНА ДО РОЗРАХУНКУ НЕВПОРЯДКОВАНИХ КРИСТАЛІВ ТА МОЛЕКУЛ З ВРАХУВАННЯМ ЕЛЕКТРОННИХ КОРЕЛЯЦІЙ

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Резюме

З урахуванням електрон-електронної взаємодії отримано вираз для функції Гріна неупорядкованого кристала. Електронні стани системи описано в багатозонній моделі сильного зв'язку. У наближенні нескінченно великого розміру примітивної комірки кристала показано можливість застосування зазначеного підходу для опису енергетичного спектра молекул. Виконано розрахунок енергетичного спектра й ефективних зарядів на атомах молекули триціанобутадіенкарбазолу.